SYNTHESIS OF NEW AROMATIC POLYESTERS FROM A BIORENEWABLE FEEDSTOCK: LIGNIN

By

LAURENT MIALON

A THESIS PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

UNIVERSITY OF FLORIDA
2010

ACKNOWLEDGMENTS

I thank the members of my committee for their mentoring and more specifically my adviser Dr. Miller for his ideas and interesting chemistry. I would also like to thank all the members of the Butler Polymer Laboratories for their help and valuable insight. I acknowledge the Miller group for their encouragements and ideas through this project. Not forgetting the University of Florida for all the facilities and high quality lectures that I had the chance to attend to. As well as my former institution CPE Lyon in France that gave me the opportunity to complete my formation in organic chemist by joining the University of Florida

TABLE OF CONTENTS

page

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

C	concentration (mol/L)
Cat	catalyst
CL	ε-caprolactone
DP	degree of polymerization
DSC	differential Scanning Calorimetry
g	grams
GPC	gel Permeation Chromatography
HDPE	high density polyethylene
Hz	hertz
L	liter
mL	milliLiter
M_n	number average Molecular Weight (Da)
M_w	weight average Molecular Weight (Da)
N_2	nitrogen
NMR	nuclear magnetic resonance
[η]	intrinsic viscosity in mL/g
[O]	oxidation
p	conversion
PBT	polybutylene terephthalate
PCL	polycaprolactone
PDI	polydispersity Index
PE	polyethylene
PET	polyethylene terephthalate
PLA	polylactic acid

ppm	parts per Million
PTT	polytrimethylene terephthalate
PVC	poly(vinyl chloride)
PS	polystyrene
ROP	ring opening polymerization
RU	molecular of the repeat unit
S_N2	bimolecular substitution reaction
t	time
t_0	reference time of solvent in viscosity measurements (s)
TFA	trifluoroacetic acid
T_g	glass transition temperature (°C)
TGA	thermogravimetric Analysis
T_m	melting point (°C)
TPA	terephthalic acid
T_{peak}	temperature of TGA for 50% of weight loss under N_2
VA	vanillic acid
VA'	vanillic acid derivative **2.2**
X	% of feed

Abstract of Thesis Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Master of Science

SYNTHESIS OF NEW AROMATIC POLYESTERS FROM A BIORENEWABLE FEEDSTOCK: LIGNIN

By

Laurent Mialon

May 2010

Chair: Stephen A. Miller
Major: Chemistry

Polymer chemistry has taken a very important part in our society. Plastics are everywhere and have diverse applications. The production of polymers is in constant evolution and their feedstock, crude oil, becomes scarcer. Some concerns regarding the recycling of those non biodegradable wastes emerged lately.

A new biorenewable feedstock - lignin - is being investigated giving vanillin and syringaldehyde by oxidation. After functionalizations these two molecules could be perfect candidates for new aromatic polyesters which might be green alternatives to a very common plastic: polyethylene terephthalate. Several polyesters were synthesized from derivatives of vanillic acid and vanillin by step-growth polymerizations in the bulk. The effects of the chemical structure on the thermal properties were studied.

New copolymers between polycaprolactone and aromatic comonomers were also synthesized in order to modify the properties of the aliphatic polyester. This study could widen the application range of polycaprolactone, a biocompatible and biodegradable polymer.

CHAPTER 1
POLYMERS A GENERAL CONCERN

1.1 Importance of Polymers

Polymers are generally large chain-like molecules that are built up with a repetition of structural units called monomers. Those macromolecules have been first discovered in 1811 by Henry Braconnot[1] who was working on derivatives of cellulose. At first, they were mainly derived from nature. In the early 20th century, Baekeland synthesized the first commercial synthetic thermoset: Bakelite[2]. The major production of this new material in the US during World War II started according to R. Seymour, the "polymer age".

Since then, a constant effort has been made to discovered new macromolecules with various chemical, thermal and physical properties. Today, polymers are everywhere from plastic bags to microprocessors and represent a major player in the worldwide economy. In 2006, the production was about 240 million tons and this number should increase to 400 million tons by 2016[3].

Table 1-1. Worldwide polymer consumption in 2006- estimation in 2016[3]

Market Sector	*Consumption 1000 Tons* 2006	2016	*2006-2016 Growth % year*
Food	42,025	71,734	5.5
Textiles	32,176	51,630	4.8
Furniture	13,687	22,993	5.3
Printing	780	1,220	4.6
Plastics products	43,500	78,361	6.1
Fabricated metals	1,519	2,259	4.0
Machinery	2,397	3,658	4.3
Electrical, Electronic	13,810	25,499	6.3
Other transportation	9,330	16,181	5.7
Vehicles, parts	10,746	15,625	3.8
Other equipment	3,852	6,334	5.1
Other manufacturing	21,238	33,569	4.7
Construction	45,886	72,919	4.7
Total	240,947	402,022	5.3

A 1985 U.S. Department of labor study reported that about 60% of the chemical industry workforce was involved in polymers. The production is still in constant progress with the emergence of new industrial powers.

1.2 Problems of Polymers' Massive Production

1.2.1 Feedstock Concerns

Today, 90% of the polymer production concerns six major plastics: polyethylene (high and low densities), polypropylene, polyethylene terephthalate, polystyrene, and polyvinyl chloride. Those organic thermoplastics are produced in major scale and mainly derived from ethylene. Ethylene production is a highly energetic and expensive process that involves steam cracking of saturated hydrocarbons associated to several distillations[4]. This massive production uses huge volumes of crude oil. As a consequence, thermoplastics' manufacture is highly dependent on the oil market- a market that has been unstable over the past decades and oil extraction is subject to geopolitical crisis. Petroleum reserves are finite and will become scarcer and costly over time[5]. As the petroleum resources decrease and the plastic demand increases, finding new organic feedstock becomes a necessity[6].

1.2.2 Recycling Concerns

Since their common use in daily consumption products, plastics' recycling has been a major concern. They generate an enormous amount of waste, the result is a so-called "trash crisis". In fact, polymers packaging is the fastest growing component of common waste in the U.S. with 12.1% in 2007[7].

Recycling polymers is a challenge mainly because, unlike glass or metal, a plastic container is hardly recycled and reused for the same applications. It is generally "downcycled". For example, being recycled, a plastic bottle can be used as fibers for

textile but not for food packaging anymore. In 2007, only 6.8% of plastic were recycled[7] -meaning that most of them are just stored in a landfill, burned or, even worse, thrown away in nature; any of those procedures are environmentally unfriendly and ecologically destructive.

In addtion, polyolefins have a very slow landfill decomposition process, estimated at 500 to 1000 years[8]. Even though this time is not very precise and difficult to study, some research on landfill shows that plastics degradation is considerably slower than any other material[9].

As a polymer chemist, one way to contribute to this problem would be to find new polymers that should ensure their functions but also could easily degrade by a chemical process or even better in the environment, under mild conditions.

In conclusion, in order to have a high economical and ecological impact the new thermoplastics should fulfill the following points: derive from biomass, be biodegradable under a simple chemical process or in the environment, be resistant enough to ensure its functions, and have a relatively cheap, simple production.

CHAPTER 2
NEW POLYESTERS FROM A BIORENEWABLE FEEDSTOCK FOR POLYETHYLENE TEREPHTHALATE MIMICS

2.1 Polyethylene Terephthalate, a Unique Polymer

2.1.1 Importance of Polyethylene Terephthalate

As presented above, our main concerns about thermoplastics are their non-biodegrability, their feedstock: crude oil, and of course their complex recycling. One of the most common plastics is polyethylene terephthalate (PET), aromatic polyester used for food packaging (plastic bottles) or as a fiber. PET is the third most produced polymer in the world after polyethylene and polypropylene. It represents about 18% of the worldwide polymer market.

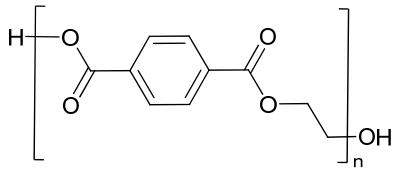


Figure 2-1. Polyethylene terephthalate formula

The backbone of the polymer chain is made of aromatic units, 80% of the carbons are sp^2 hybridized, and those carbons give stiffness to the polymer chain. The two linking sp^3 carbons give some flexibility to the main chain, and are responsible for the relatively low glass transition temperature. It has excellent mechanical properties such as tensile and impact strength, chemical resistance, clarity when amorphous, and is reasonably thermally stable[10, 11].

Those specific thermal and mechanical properties coupled with a cheap cost of production make PET the perfect candidate for large scale production and use as a daily consumption product.

Table 2-1. Thermal and mechanical properties of PET[10, 12]

Property	Test Method	Value (unit)
Molecular weight (repeat unit)	-	192 ($g.mol^{-1}$)
General weight-average M_W	-	30000-80000 ($g.mol^{-1}$)
Density	-	1.41
Glass transition temperature	DSC	69-115(°C)
Melting temperature	DSC	265(°C)
Heat of fusion	DSC	166 (J/g)
Breaking strength	Tensile	50 (MPa)
Tensile strength (Young's modulus)	Tensile	1700 (Mpa)
Yield strain	Tensile	4%
Impact strength	ASTM D256-86	90($J.m^{-1}$)
Linear expansion coefficient α	-	7.10^{-5}(K^{-1})
Water absorption after 24h	-	0.5%
Price	-	0.5-1.25(€.kg^{-1})/ 0.7-2($.$kg^{-1}$)

2.1.2 PET's Production/Synthesis

PET is produced in very large scale; the process has been studied in detail. The macromolecule is obtained by reaction of terephthalic acid (TPA) or its dimethyl ester equivalent dimethylterephthalate (DMT) with ethylene glycol in a step growth polymerization mechanism. The first step of the synthesis is the esterification of terephthalic acid or DMT with ethylene glycol into bis(hydroxyethyl) terephthalate (BHET) under high temperature and by use of transesterification catalysts[13]. The BHET diol is then melt-polymerized under vacuum with an antimony trioxide catalyst[14, 15, 16] to give the polyester with a degree of polymerization near 150[13].

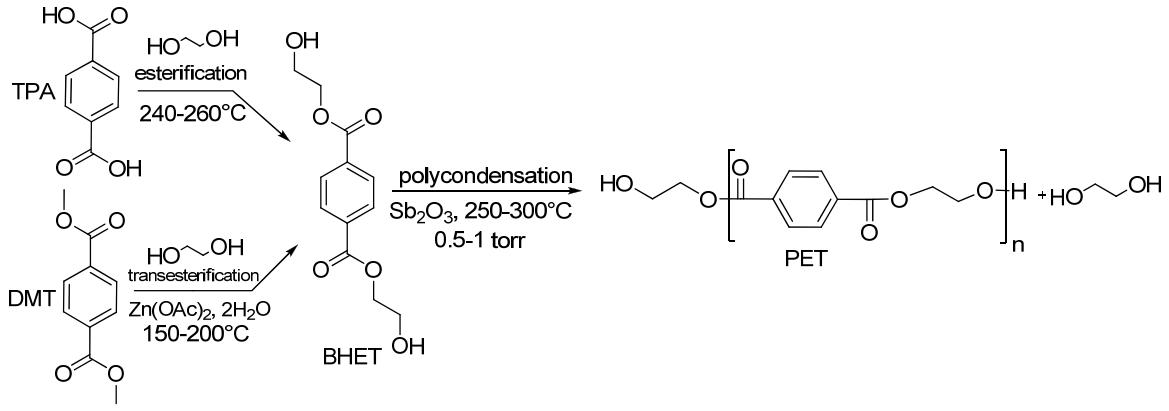


Figure 2-2. Industrial synthesis of PET

Monomer synthesis. Monomers preparation and origin are important, because they will influence the price of the final polymer and also its availability. Terephthalic acid is an aromatic molecule that is industrially produced by oxidation of *para*-xylene[15]. The oxidant here is oxygen and the high yielding reaction is catalyzed by a manganese-cobalt species. Xylene is obtained from a fraction of crude oil: naphtha. Catalytic reforming of octane results in a mixture of xylenes and ethylbenzene[16], *p*-xylene is extracted from the mixture by low temperature crystallization[17].

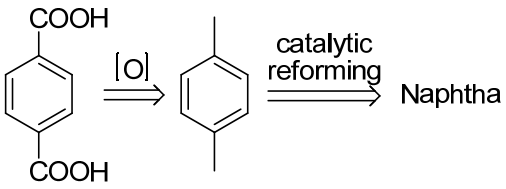


Figure 2-3. Retrosynthesis of TPA

The second element needed is ethylene glycol, this diol can be synthesized by hydrolysis of toxic ethylene oxide, which is derived from ethylene by oxidation over a silver catalyst[18]. A thermal cracking of ethane, an element of crude oil, gives the desired ethylene[19-20].

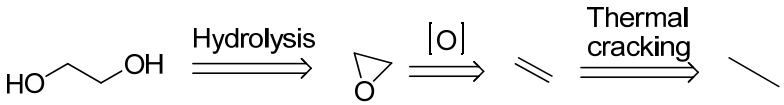


Figure 2-4. Retrosynthesis of ethylene glycol

The two main components of PET's synthesis come from crude oil or natural gas. As presented before, this energy source is not desired for economical and environmental reasons.

2.1.3 PET's Recycling Cycle

One major drawback of PET's recycling is the waste collection process; even though plastic bottles are one of the most collected thermoplastics, 27% of collection in

2005[21], more than 70% of PET production is not reprocessed at all or left in the environment. The main issue is the generated volume- together with a slow degradation process. Eventually, some bottles will be burned giving a good amount of thermal energy and less waste volumes but this procedure is environmentally non-friendly. Due to its massive production, PET has its own recycling code- number one- placed on the bottom of each bottles.

Plastic bottles' recycling process is complicated; they need to be suitable for food consumption and therefore follow strict rules and regulations. As a consequence, it is challenging to recycle a used plastic bottle into another clean one.

Depolymerizations processes such as hydrolysis[22] and methanolysis[23] regenerate monomers/oligomers that can be purified and polymerized again. These processes are not common at all and it is much cheaper and easier to thermally process the bottles into fibers or flakes used for non-food applications.

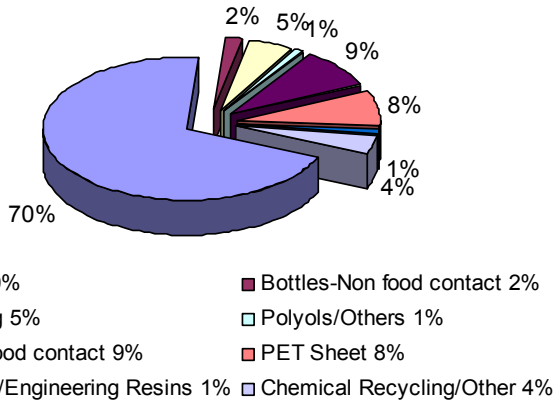


Figure 2-5. Worldwide post consumer PET utilization in 2005[21]

2.2 Natural Molecules Giving New Polymers

The properties of the polymer are the most important features for its applications. The targeted new material should have similar or better properties than the existing PET. The thermal and mechanical specificities of a macromolecule mainly depend on

the chemical structure and especially on the stiffness of the polymer chain[24]. Polyethylene terephthalate has 80% of sp^2 hybridized carbons and 20% of sp^3 hybridized carbons. They provide flexibility to a highly rigid aromatic polymer chain.

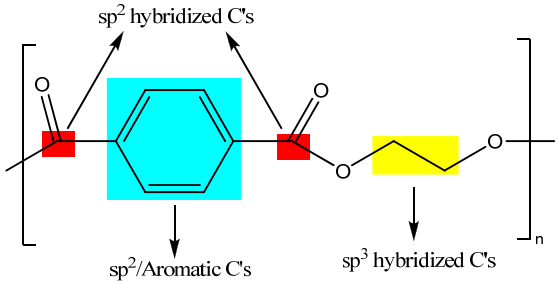


Figure 2-6. Chemical structure of the PET main chain

These aromatic units in the main chain give stiffness to the polymer, which can therefore be used as a food packaging such as plastic bottles without deformation or perforation. This segment also influences the thermal properties ensuring a fairly high glass transition[10] even though the sp^3 hybridized carbons tend to give some flexibility to the chain lowering the T_g. The targeted glass transition should be in a range above room temperature to ensure stability at a minimum of 50-60°C in order to avoid thermal deformation during utilization.

2.2.1 Lignin as a Biorenewable Feedstock

Vanillin is a potential candidate for the synthesis of aromatic polyesters. It can be obtained from lignin, a biopolymer that constitutes about 30% of the carbon in the biosphere[25]. After cellulose, it is the second most abundant biopolymer on earth. The structure analysis is fairly complex because lignin is a highly branched molecule that is believed to be cross-linked and does not have a simple primary structure[26]. Industrially, lignin is a side product of the Kraft process in pulping industry, the production is less than 100,000 tons a year[27]. It is often burned before extraction, and can be a main source of energy to operate pulping factories[28].

The extraction process is known[29] but not often used; it affords the biopolymer that can be oxidized into the expected molecules: vanillin, and syringaldehyde. Those two aromatic molecules have fairly reactive functionalities in *para* positions.

The oxidation process has been studied with various catalysts and the recovery of vanillin is low, about 4-5%[30]. Some new processes are under investigation, especially a promising ion-exchange media that gives the expected aldehydes[31].

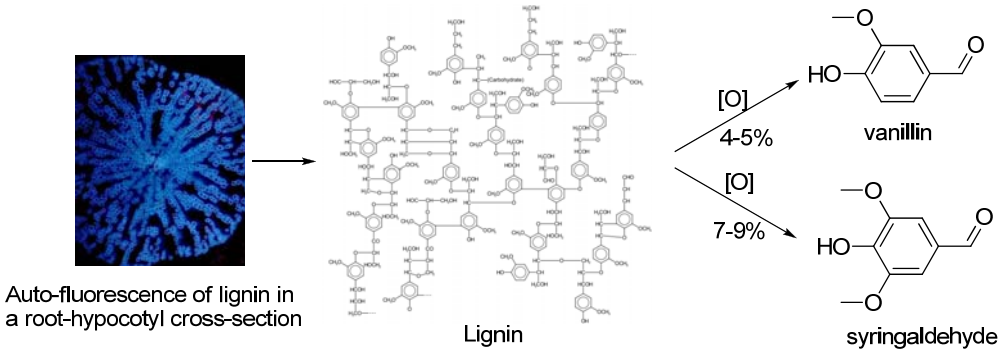


Figure 2-7. From wood, a biorenewable feedstock, to aromatic aldehydes

2.2.2 Types of Monomers Targeted

The polymerization process generally used for polyester formation is a step-growth mechanism. For polycondensations, monomers reacts together forming a polymer releasing small molecules. This reaction can be performed between two monomers with different functionalities, generally called A-A and B-B or a single monomer with both functionalities, called A-B monomer.

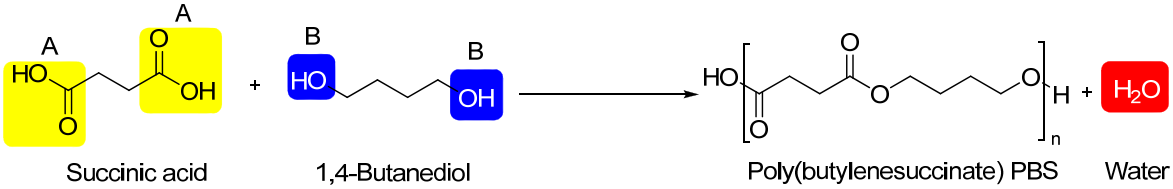


Figure 2-8. Formation of PBS by an A-A/B-B step-growth polymerization[32]

The monomer used for this type of polymerization should be symmetrical to control the repeat unit of the polymer. Otherwise, a random copolymer would be synthesized.

For example, vanillyl alcohol will not be used as an A-A' monomer because it would certainly encounter difficulty controlling the structure of the resulting polymer.

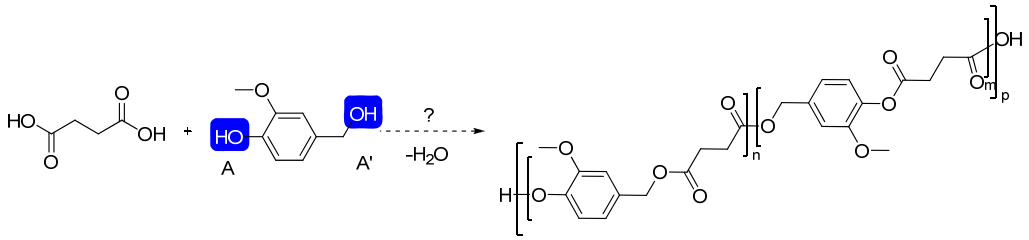


Figure 2-9. Unsymmetrical vanillyl alcohol results in a random copolymer

It is necessary to perform sufficient modification to the starting materials to have a symmetrical di-acid or diol as A-A or B-B monomers.

The second type of reaction involves a so called A-B monomer. The two reactive functionalities are present in a single monomer.

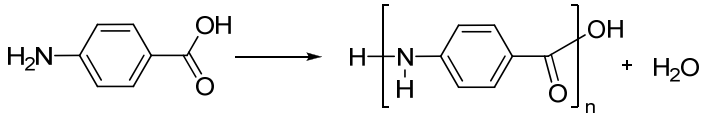


Figure 2-10. Formation of polybenzamide by step-growth polymerization[33]

Those condensation reactions are usually performed in concentrated solutions or under high temperature in the bulk to increase the concentration of monomers, and the kinetics of the polymerization. Dynamic vacuum is also applied to remove the side molecules, generally water or alcohols. This- according to LeChatelier principle- thermodynamically favors the chemical equilibrium towards the product: here the polymer.

Looking at the proposed starting materials, it seems that A-B monomers would be easier to synthesize in few steps. Vanillin is unsymmetrical, this due to its aromatic methoxy functionality. The other drawback for the use of an A-A/B-B system is the necessity of an exact equimolar measurement. If any monomer is present in excess, the

formation of high molecular weight polymer will be prevented by the termination of growing chains by the excess functionality[34].

In summary, a good PET mimic candidate needs to have similar properties, a simple synthesis scheme, and a few simple steps to obtain the A-B monomer. The properties depend on the primary structure of the polymer chain- here, the chemical structure of the macromolecule. PET analogues will be synthesized with macromolecules chemically similar but derived from vanillin, a biorenewable feedstock.

2.3 Previous Studies

2.3.1 PET Mimics Based on Furan Derivatives

Most of the work on PET analogues from biorenewable feedstock is relatively recent and has been done with furan derivatives polymer[35]. A furan 2,5 dicarboxylic acid- one of the 12 priority chemicals for establishing a “green” chemistry industry- is reacted with ethylene glycol through an esterification process. The monomer was reacted in the melt under high vacuum in order to remove, ethylene glycol.

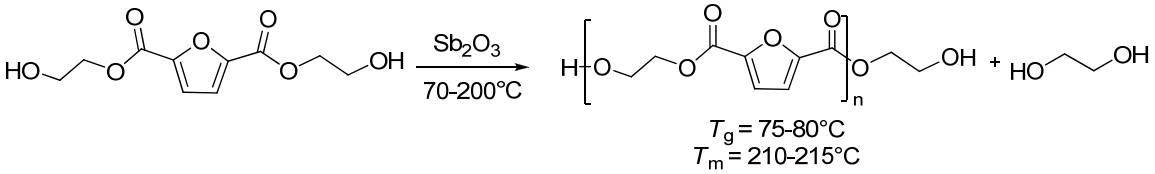


Figure 2-11. Furan dicarboxylic acid a precursor for PET mimic

This moelcule gives thermal properties similar to PET but does not improve them. The glass transition is fairly similar to the one of PET but the melting temperature is lower. Furan polymerizations are acid sensitive and degrade under high temperatures leaving brown products[36]. An alternative to furan chemistry is the use of vanillic acid as a monomeric precursor.

2.3.2 Studies on Vanillic Acid/ Syringic Acid Derivatives

2.3.2.1 Formation of Bifunctional Monomers

A simple oxidation of the aldehyde functionality of vanillin into a carboxylic acid[37] gives vanillic acid. It is a benzoic acid derivative currently used as a flavoring agent.

Some studies have been performed on the reactivity of the hydroxyl group of the molecule and the formation of bifunctional or A-B type monomers[38].

This synthesis can also be applied to syringic acid to give a wider range of possible polyester. The thermoplastics synthesizing by a melt step-growth polymerizations show some interesting thermal and physical properties.

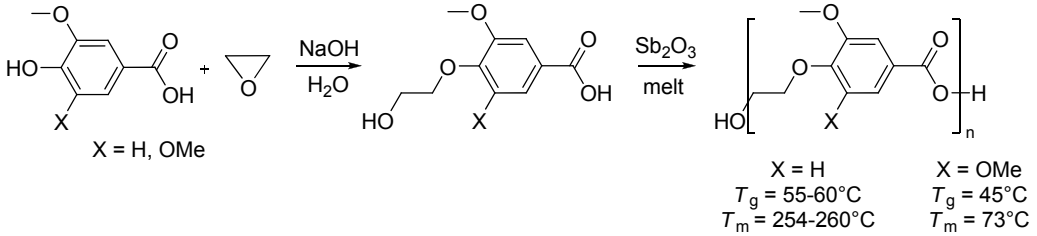


Figure 2-12. Formation of polyester from vanillic acid and syringic acid[38]

2.3.2.2 Bicoupling of Vanillic Acid

Another known synthesis is the coupling of two vanillic acid derivatives with a bifunctional reagent giving a dicarboxylic acid that can be further reacted with a diol[38, 39]. The resulting polyester has some interesting properties and has been pulled into fibers with interesting properties.

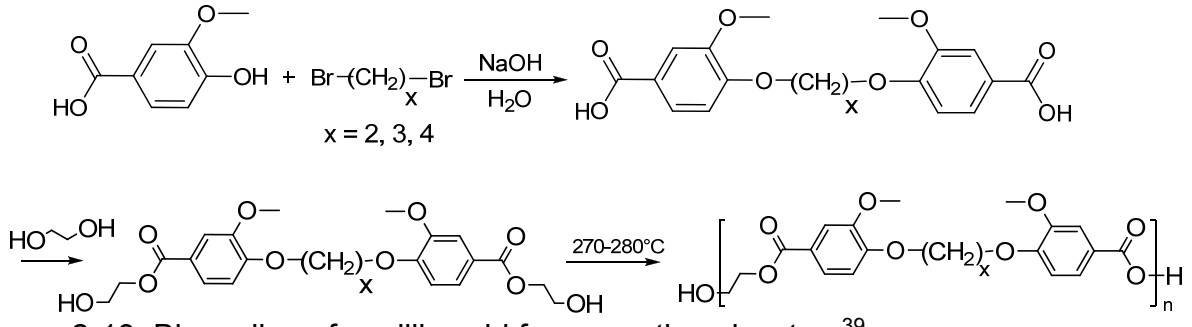


Figure 2-13. Bicoupling of vanillic acid for aromatic polyesters[39]

2.4 Synthesis and Characterization of New Aromatic Polyesters from Vanillic Acid/Syringic Acid

Vanillic acid has been synthesized into monomers in the past. None of those studies showed the influence of the methoxy group(s) on the polymer backbone and more specifically on the thermal properties of the polymer. A study of the nature of the vanillic acid linker-in other words the nature of the carbon oxygen arrangement between the ester linkages-would be useful to understand the thermal behavior of the macromolecule.

2.4.1 Effects of the Methoxy Substituent(s) on the Polymer Chain

Chain-chain interactions and rigidity will have a great influence on the general properties of a polymer chain. We propose a study on the effect of the bulky methoxy group(s) on chain packing and thermal behavior on several polyesters. The work projected here focuses on the synthesis of *p*-hydroxybenzoic acid, vanillic acid, and syringic acid similar derivatives that will be polymerized and thermally studied.

The phenolic alcohol is a reactive functionality common to the three molecules. It can be easily deprotonated due to a resonance stabilized conjugated base[40] becoming a decent nucleophile for an S_N2 reaction.

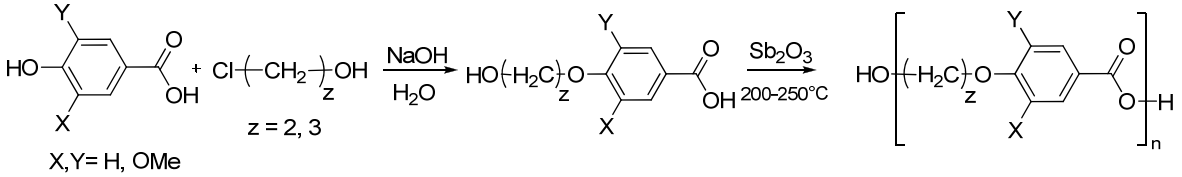
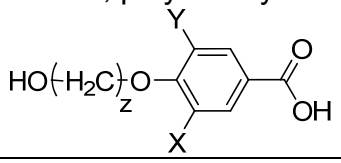


Figure 2-14. Polyester synthesis scheme

The thermal stabilities of our polymers under a nitrogen atmosphere were studied using thermogravimetric analysis (TGA) and thermal characteristics that included melting points and glass transition temperatures were measured by differential scanning calorimetry (DSC).

Table 2-2. Study of the methoxy effects, polymer synthesis



Entry	Monomer	X	Y	Z	% yield (%)	Polymer
a	2.1	H	H	2	70	2.7
b	2.2	OMe	H	2	79	2.8
c	2.3	OMe	OMe	2	71	2.9
d	2.4	H	H	3	50	2.10
e	2.5	OMe	H	3	57	2.11
f	2.6	OMe	OMe	3	82	2.12

Several bimolecular substitution reactions (S_N2) give the A-B monomers with 2 or 3 carbon spacers and different substitutions on the aromatic ring. A series of polymers were synthesized in the melt, water was removed by dynamic vacuum. The moderate yields are probably due to the work-up procedure in the sense that the melted polymer was cooled down under nitrogen leaving a hard solid that was dissolved in an appropriate solvent such as trifluoroacetic acid or *m*-cresol and then crashed out in methanol leaving the low molecular weight material in solution.

Table 2-3. Study of the methoxy effects, thermal properties

Polymer	T_g (°C)	T_m (°C)	T_{peak} (°C)	Z
2.7	80	203	478	
2.8	71	239	433	2
2.9	66	-	450	
2.10	67	179	435	
2.11	65	191	435	3
2.12	51	170	433	

The thermal properties are directly related to the chemical structure. The spatial disposition and folding of the macromolecular chain directly influences the glass

transition for the amorphous part of the chain, the melting point corresponding to the crystalline part of the polymer.

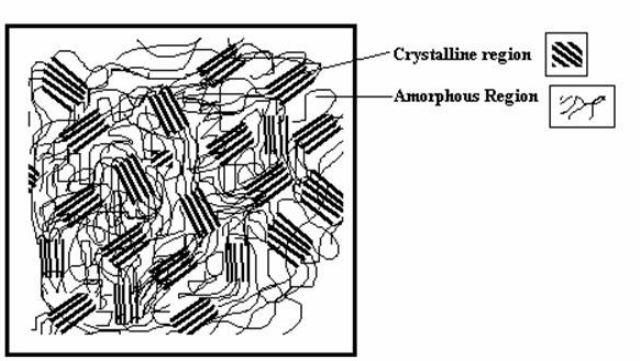


Figure 2-15. Sketch of a polymer chain spatial arrangement[41]

As reported in Table 2-3 it is quite clear that the glass transition decreases by increasing the substitution on the aromatic group[42, 43]. The glass transition is directly correlated to the amorphous phase of the polymer. This phase is not ordered, the space filling is important, and the more space a macromolecule will have to move, in other word the more free volume, the lower the T_g will be.

A bulky substitution on the aromatic group gives more free volume to the molecules creating steric hindrance on the chain that can be found on each repeat unit, so along the entire polymer. A double substitution creates even more space and further lowers the T_g. We can also notice that as the length of the methylene spacer increases the difference in glass transitions decreases due to the fact that the aromatic groups are now further apart from one to another.

In term of chain packing or crystallinity- so the ordered part of the polymer chain - shown by the melting point, the double substitution does not allowed ordering of the chain, polymer **2.9** does not show any melting temperature. The steric hindrance is too high and therefore slows down the crystallization process. This effect is not observed for sample **2.12**, since it shows a melting point of 170°C. In that specific case it seems the

key is the space between the aromatic groups which is not enough in polymer **2.9** to allow crystallinity.

The thermal stability under nitrogen is fairly consistent for all the polymers.

2.4.2 Effects of the Methylene Spacers

Another possible study is to change the number of carbons between the ester bonds and so between the aromatic rings within the polymer chain. The addition of sp^3 carbon spacers should have an effect on the flexibility of the polymer chain. This implies several changes in the chain-chain interactions and crystallization of the polymer.

Our study has been focusing on the vanillic acid derivatives since it comes from a biorenewable feedstock and is readily available on a large scale, unlike syringic acid a much more expensive commercial chemical.

A synthesis of a series of polymers has been performed. The one step nucleophilic substitution under mild condition presented above will be kept as main reaction for the monomer synthesis. The only difference will be for the synthesis of the no carbon spacer molecule.

Oligomers of vanillic acid, no carbon spacer. Several studies have been done on the oligomers of p-hydroxybenzoic acid[44]. But none dealt with the direct polycondensation of vanillic acid. The polycondensation under vacuum has been attempted on vanillic acid without any success. An activation of the carboxylic acid into an ester should give a more volatile byproduct and as a consequence should be easier to remove by vacuum.

The methanoate ester **2.13** has been synthesized and a melt polymerization with a transesterificaiton catalyst during 24h was attempted. An NMR study shows no reaction.

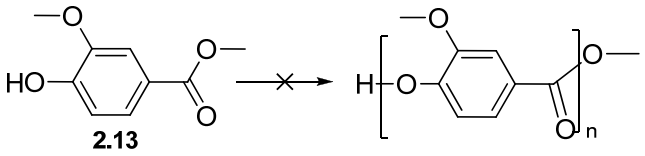


Figure 2-16. Attempt of polymerization of vanillic ester

The phenolic hydroxyl group must be activated to efficiently polymerize vanillic acid[45]. This activation was accomplished by converting the phenolic hydroxyl group to an acetyl group[46].

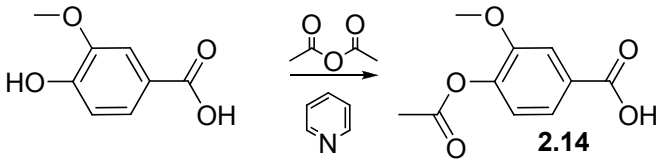


Figure 2-17. Phenolic group activation

Acetic acid was distilled off as a byproduct and collection of this acid allowed the determination of the degree of polymerization (DP) using the Carother's equation[47]:

$DP = \frac{1}{1-p}$ Where p is the conversion of monomer $0 < p < 1$

The conversion, p, can be calculated from the amount of acetic acid released during the polymerization.

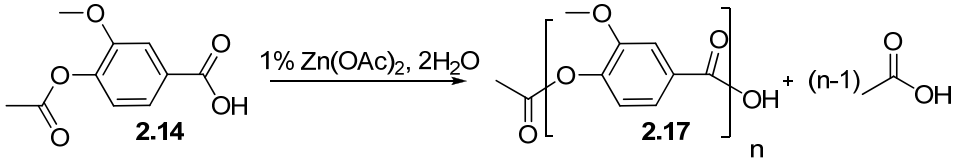


Figure 2-18. Acetyl vanillic acid oligomerization

After a short time, the melt became heterogeneous and solidified in the flask. The oligomers of vanillic acid have a DP between 5 and 6, as calculated using the amount of acetic acid collected during the polymerization. The product was hard and brittle; it could not be melted or dissolved in common solvents.

Study of vanillic acid derivatives. Our first study showed the effect of the methoxy pendant group on the polymer chain. Another important factor is the type and

the length of spacers between the aromatic groups. A possibility is to modify the number of carbon spacers.

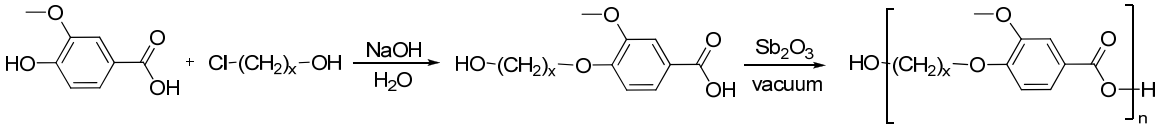


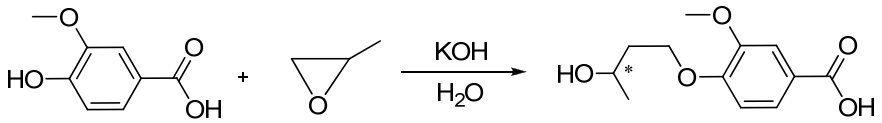
Figure 2-19. Synthesis scheme of vanillic acid derivatives

Table 2-4. Polymerization of vanillic acid derivatives

Entry	Monomer	X	Yield %	Polymer
G	2.14	0	100	2.17
H	2.2	2	79	2.8
I	2.5	3	57	2.11
J	2.15	6	71	2.18
K	2.16	2*	40	2.19

* 1 pendant methyl group

Monomer **2.16** is slightly different since a methyl pendant group was introduced by reacting vanillic acid with a racemic mixture of propylene oxide to give a chiral center on the monomer.



2.16

Figure 2-20. Synthesis of **2.16**

Table 2-5. Thermal properties of the vanillic acid derivative polymers

Polymer	T_g (°C)	T_m (°C)	T_{peak} (°C)
2.17	-	-	-
2.8	70	241	433
2.11	65	191	435
2.18	32	-	445
2.19	71	-	407

The sp^3 hybridized carbons have more degrees of rotational freedom in their conformations than the sp^2 aromatic or carbonyl carbons, which are largely locked in a

planar fashion. So increasing the amount of carbon spacers gives much more flexibility and mobility to the polymer chain. This can be seen with **2.17** and **2.18,** the two extremes polymers where **2.17** is poly(vanillic acid) without any carbon spacers and where **2.18** has 6 carbon spacers. **2.17** is a very stiff infusible and insoluble oligomer without any glass transition and **2.18** has a low glass transition and appears to be much more flexible. This general trend is confirmed with **2.8** and **2.11** as the glass transition tends to decrease with the increment of carbon spacers. The thermal stability is still reasonable under nitrogen.

Polymer **2.19** is a special case in our study since it has a chiral center. As mentioned earlier, monomer **2.16** is a racemic mixture, the propylene oxide used for the synthesis was optically inactive. The polymerization is longer than any other ones and gives lower yield as well. DSC shows without any surprise that **2.19** is an amorphous polymer. The polymer has stereocenters and is atactic. As a consequence the chain packing into crystals is very unlikely. Such behavior can be seen for several kind of atactic polymers such as polystyrene[48].

The glass transition is similar to **2.8**. The chain movement seems to be more difficult with an extra methyl group but it also gives more free volume to the polymer chain in the amorphous phase. The amorphous phase has more free volume in that case and more energy is necessary to have chain motion due to chain-methyl interactions.

Doing a comparison with the thermal properties of polyethylene(T_g = -130°C)[49] and polypropylene (T_g = -10°C)[50] an increase of glass transition was expected from **2.8** and **2.19** but our structure is different , the methyl group is not, in terms of atomic mass, very

important in the repeat unit, so the effect on the interaction is not as important as the one seen in polypropylene.

2.5 Synthesis of Aromatic Polyesters Starting with Vanillin

Vanillin and syringaldehyde are two molecules of choice for that study since they have an aromatic unit and two reactive functionalities: a phenolic alcohol and an aldehyde. The phenolic part of the molecule has been studied previously. Another option is to functionalize these two molecules into A-B monomers by reaction on the aldehyde group.

2.5.1 Perkin Reaction: Formation of a Reactive A-B Monomer

An aldehyde functional group is fairly reactive; and hence several reactions are possible. Our goal is to obtain an A-B monomer in order so an acid functionality needs to be synthesized to give a polyester. Our study focuses on a few step syntheses with relatively good yield and atom economy. These factors have been taken into account during the research for aldehyde reaction.

Condensations are a good way to obtain α-β unsaturated acid groups. A Wittig reaction is an option[51] but is quite complicated and wasteful for our synthesis. A much simpler way is to do a Knoevenagel reaction[52]; these condensation reactions are generally a fairly simple, high yielding and fast[53].

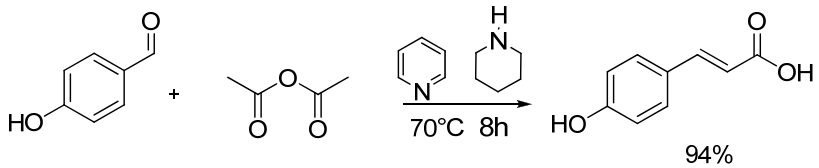


Figure 2-21. Knoevenagel condensation with an aromatic adehyde[54]

This reaction would give us an A-B monomer that could be hydrogenated and then polymerized in the bulk.

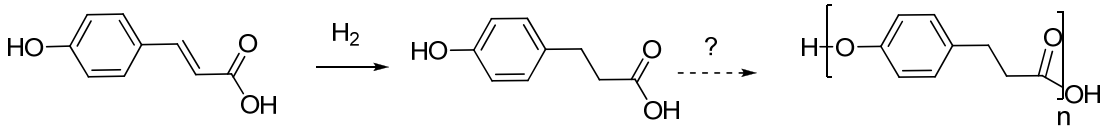


Figure 2-22. Polymerization limited by the aromatic hydroxyl group reactivity

According to our previous study on vanillic acid, the phenolic hydroxyl group is not particularly reactive even under harsh polymerization conditions. Activation of the alcohol functionality could make it react with the acid and give the desired polyester. For poly(hydroxybenzoic acid) the reaction does not occur with the simple alcohol, an activation with an acetyl group is necessary for the polymer formation[45]. Functionalization of the alcohol group is an option[55] but would increase our synthesis by an extra step. Further research led us to the Perkin reaction[56]. Acetic anhydride reacts with an aromatic aldehyde, condensation of the aldehyde as well as the functionalization of the hydroxyl group are obtained in a one step high yielding reaction.

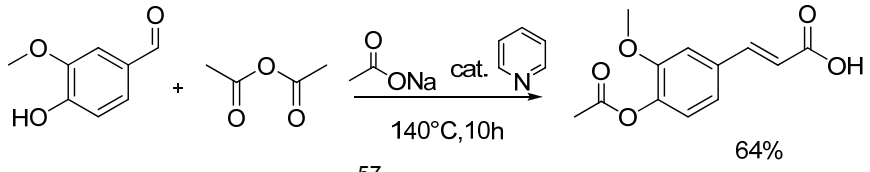


Figure 2-23. Perkin reaction on vanillin[57]

The Perkin reaction is relatively fast and conditions are mild. The work up as well is fairly easy and does not involve any complicated purification step; a simple recrystallization gives the pure yellow solid.

2.5.2 Previous Studies

The Perkin reaction has been mainly used in natural product syntheses[57]. Biodegradable liquid crystals have been attempted by copolymerizing 3-(4-acetoxyphenyl) propanoic acid and 4-acetoxybenzoic acid[58].

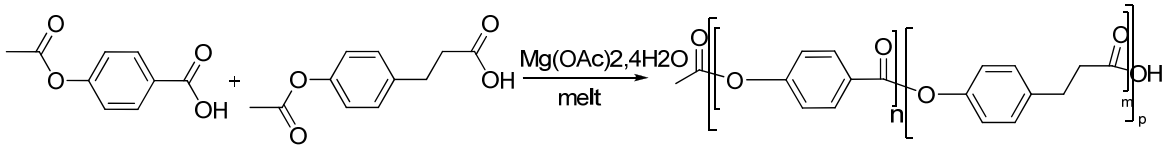


Figure 2-24. Copolymer synthesis with 3-(4-acetoxyphenyl)propanoic acid

The resulting molecule is a random copolyester, a liquid crystal that shows nematic behavior above 220°C and biodegrades in vitro.

Polymerization of acetyl ferulic acid has been patented[59]; the polymerization is done in the bulk and under 5-6 hours of vacuum to remove acetic acid.

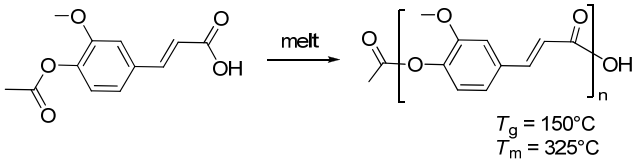


Figure 2-25. Homopolymerization of ferulic acetate

2.5.3 Synthesis of New Polyesters through a Perkin Reaction

Polycondensations have been attempted on the ferulic acid derivatives and most of the polymers reported are colored and will not be good substitutes for polyethylene terephthalate (PET). Ferulic acid is an α-β unsaturated carboxylic acid, the alkene double bond can be hydrogenated to give an A-B monomer that is polymerizable under the same set of conditions. This hydrogenation gives more flexibility to the polymer chain leading to other thermal and mechanical properties than those patented for the ferulic polyester.

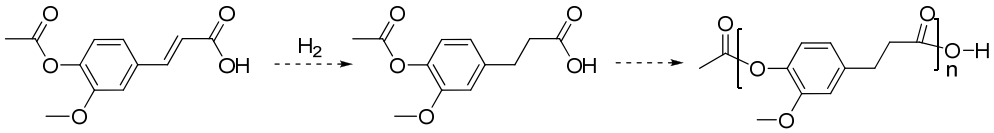


Figure 2-26. Proposed studies on hydrogenated acetyl ferulic acid

2.5.3.1 Monomer Synthesis

The monomer was obtained after a 2 step synthesis composed of the Perkin reaction followed by the saturation of the alkene bond by reaction of hydrogen gas over

palladium on charcoal 10%. Compound **2.20** is a colored compound (brownish yellow) but the hydrogenation gives a beige monomer much more suitable for our study.

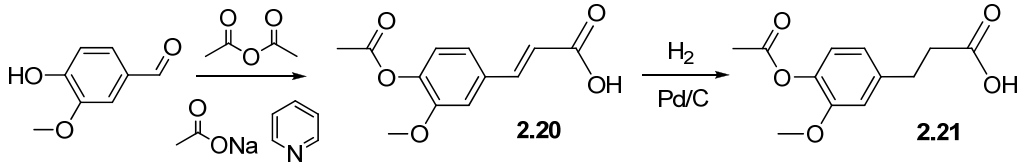


Figure 2-27. Monomer synthesis starting with vanillin

This 2 step synthesis is relatively fast with fairly good yield. The work up for each reaction involves a simple recrystallization, no purification by column chromatography is necessary.

2.5.3.2 Polymers Syntheses

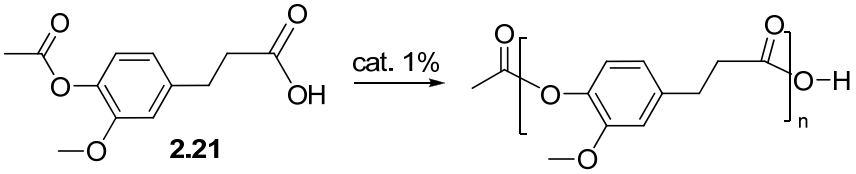


Table 2-6. Poymerization of activated dihydroferulic acid

Entry	Polymer	Temperature (°C)	Catalyst[a]	Melt time (h)/stirring stops(h)	Vacuum time (min)	yield %	Intr. Visco[b] (mL/g)	Mv[c]	DP[d]	Mn
a	2.22	200-220	-	2/1.5	120	83	31	12940	27	4811
b	2.23	200-220	Sb_2O_3	2/0.5	120	67	29	11950	23	4099
c	2.24	200-220	$Zn(OAc)_2$	2/0.5	120	82	27	10980	38	6772
d	2.25	200-220	$Zn(OAc)_2$	2/0.5	360	91	36	15500	50	8910
e	2.26	220-250	$Zn(OAc)_2$	2/0.5	360	68	35	14800	100	17820
f	2.27	200-220	$Zn(OAc)_2$	2h/-	10	43	17	6330	17	3029

a) Catalyst loading at 1mol%
b) Intrinsic viscosity measured with an Ubbelhode in a mixture phenol/1,1,2,2-tetrachloroethane (1/2) at 35°C
c) Calculated with $[\eta]= 1.09\times10^{-2}\ Mv^{0.84}$ with [η] in mL/g
d) Measured by end group analysis

First step of the polymerization was a melt under nitrogen to form oligomers. This was done in order to avoid sublimation of the unreacted monomers. Once vacuum was applied the polymerizations were surprisingly fast, and we can clearly see the distillation of acetic acid.

After a few minutes, the melt became more viscous until stirring was not possible anymore giving a brown viscous melt at the end of the polymerization. The polymers were obtained by dissolution of the melt in a 1-to-5 mixture of trifluoroacetic acid and dichloromethane. The solution was then crashed out with methanol-a solvent in which the monomer is soluble-leaving a beige powder that was filtered and dried in vacuo.

Different conditions were tested and grouped in Table 2-6. The effect of the catalyst is not tremendous, although to our knowledge the reactions seemed to be faster in presence of either antimony trioxide and zinc diacetate dihydrate since the acetic acid removal appeared to be more efficient when vacuum is applied and the stirring stops sooner than with the other catalysts. The end group analysis also shows that the zinc catalyst gives better polymerization degree under similar conditions.

The intrinsic viscosities, measured with an Ubbelhode viscometer, give more information about the molecular weight of those polymers. Polymers **2.22**-**2.28** have similar chain structure and can be compared in term of chain length with their intrinsic viscosities.

The intrinsic viscosities increase slightly with increasing vacuum time. For polymers **2.26** and **2.27-** where the vacuum was 6h- the viscosity was slightly higher than for the 2 hour vacuum polymers. More acetic acid was removed and the reaction was toward the polymer formation and chain length increase. For polymer **2.27** the reaction was stopped during the polymerization and we can clearly see the difference in intrinsic viscosity the yield was still fairly good so even lower molecular weight polymers are insoluble in methanol.

The intrinsic viscosity [η] allows us to estimate the molecular weight of our polymers by comparing them with PET, this will give a relative value, the actual

molecular will be compared to a PET standard. Polyethylene terephthalate has a similar structure to our aromatic polyester. The values obtained with the Mark-Houwink parameters give us an estimation of the molecular weight of our polymers. By comparison with the end group analyses, which are absolute values, we can see that the values are in the same order of magnitude but slightly off. It seems that the Mark-Houwink parameters are more valid for high molecular weight materials, as we can see for polymer **2.26**.

A DSC measurement has been performed for **2.26**-the highest molecular weight material-showing a T_g of 66°C and a melt of 205-210°C. Those values are in the range of PET's thermal properties.

5.3.3 Activation of the Phenoxy Group

As presented previously for the oligomerization of vanillic acid, the activation of the phenoxy group is a necessity for the reaction to occur.

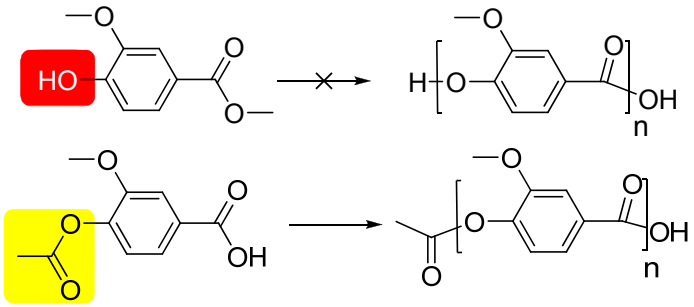


Figure 2-28. Activation of the phenoxy group for vanillic acid oligomers

In our case, the acid group is slightly different since it is bonded to the aromatic unit by 2 sp^3 hybridized carbons that makes it more accessible. A simple study would be to attempt polymerization after removal of the acetoxy group.

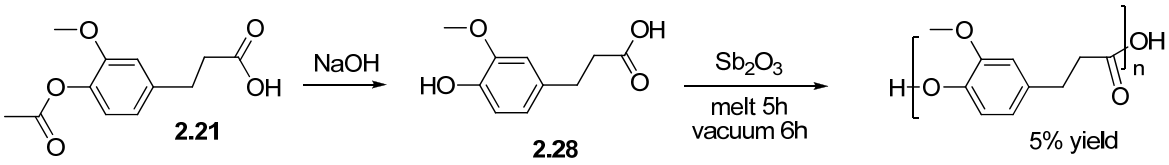


Figure 2-29. Attempt of polymerization without the activation of the phenoxy group

The polymerization was left for a long time (5-6h) under vacuum and neither distillation of acetic acid or viscosity changes were apparent. The reaction was finally stopped after 6h, and only to give 5% of insoluble “polymer” in methanol. The methanol fraction was collected and solvent removed under vacuum leaving a brown solid in the flask. A GPC analysis of the methanol fraction **2.29**- soluble in THF- showed low molecular weight material.

2.6 Conclusions

Polyethylene terephthalate is an important thermoplastic that comes from crude oil. A possible greener feedstock for PET mimics is lignin. Lignin is a biopolymer that can be oxidized into a variety of possible monomers that include syringaldehyde and vanillin. Monomers of vanillic acid and syringic acid derivatives were synthesized and polymerized in the melt giving information about the effect of the aromatic methoxy substituent(s) on the thermal properties. The carbon spacing is also an important structural component that influences the thermal properties. Functionalization of the aldehyde group of vanillin through a Perkin reaction gives a polyester with thermal properties similar to PET in a very fast polymerization reaction.

CHAPTER 3
COPOLYESTERS OF CAPROLACTONE AND VANILLIC ACID DERIVATIVES

3.1 Polycaprolactone an Introduction

Polycaprolactone is an aliphatic polyester that can be obtained from a lactone: ε-caprolactone by Ring Opening Polymerization (ROP). This reaction gives a polyester with a flexible sp^3 hybridized carbon chain.

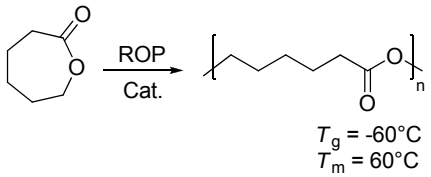


Figure 3-1. Polycaprolactone synthesis

ε-Caprolactone is synthesized with the Baeyer-Villiger oxidation of cyclohexanone[60] that can be obtained by oxidation of cyclohexane[61].

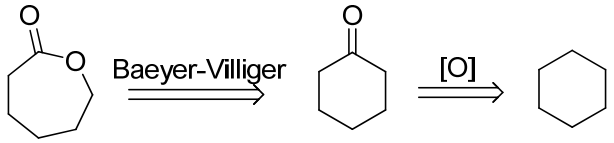


Figure 3-2. Retrosynthesis of ε-caprolactone

Polycaprolactone has a fairly low glass transition and melting point[62] giving a limited range of applications to the polyester. It is a semicrystalline polymer biodegradable and biocompatible. Its principal applications are in biomedical research for implants or even drug delivery systems[63].

Some copolymerizations have been studied in order to improve those properties and widen its range of applications.

3.1.1 Copolymerizations of ε-Caprolactone by ROP

Polycaprolactone is a biocompatible polymer that has many applications in biomedical devices. As a result it's been copolymerized with other biocompatible monomers: lactide[64] and glycolide[65].

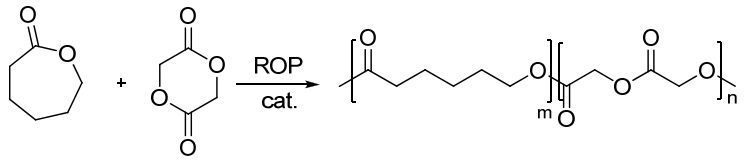


Figure 3-3. Copolymerization of ε-CL and glycolide by ROP

The ring opening reaction is one way to obtain long chain of polycaprolactone. Some copolymers can be synthesized by polycondensation but in general only block copolymers are achieved by formation of a block of prepolymer that can be used as an initiator for the fast ROP reaction[66].

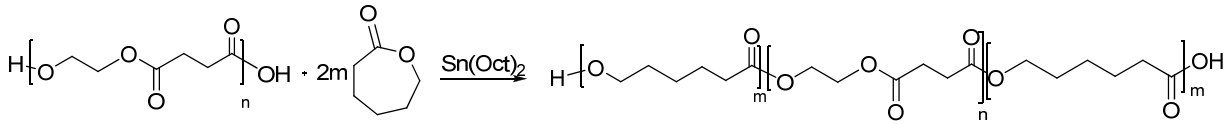


Figure 3-4. Tri-block copolymer of polycaprolactone and poly(ethylene succinate)[64]

Thermal and mechanical properties can be tuned by adjusting the ratio of the comonomers in order to selectively modify the properties of the macromolecule[67].The biodegradation of polycaprolactone could also be changed by copolymerization[68].

3.1.2 Copolymerizations between Aromatic Monomers and Caprolactone

A copolymerization between caprolactone and an aromatic monomer could drastically change the lifetime of the chain with a higher resistivity to hydrolysis. Biodegradation is highly dependent on crystallinity and type of copolymers (random or block) as well as ratios of aromatic/aliphatic chains[69].

By incorporation of an aromatic repeat unit into the polycaprolactone chain, we could be able to tune the thermal and mechanical properties as well as the biodegradation.

In term of synthesis, this polymerization is kind of unusual as it is based on a ring opening polymerization mechanism for the ε-caprolactone coupled with a step-growth polymerization for the aromatic unit. These copolymerizations are usually performed in

the melt with a good transesterification catalyst to have good incorporation of both monomers. Some studies have been reported on the polymerization of ε-caprolactone and terephthalic acid[70] and with a derivative of poly(hydroxybenzoic acid)[71].

A good comonomer for that reaction would be 4-(2-hydroxyethoxy)-3-methoxybenzoic acid, monomer **2.2**. Not only is monomer **2.2** is fairly easy to synthesize in the lab on a decent scale, it also has the most interesting thermal properties since its homopolymer has a relatively high glass transition and melting point. This should give interesting copolymers with ε-caprolactone due to the different structures of both homopolymers.

3.2 Synthesis of the Copolyesters

The polymerization is going to be a combination of ring opening polymerization and step-growth polymerization-both reactions catalyzed by the good transesterification catalyst: titanium isopropoxide[72].

Titanium catalysts have been extensively studied for PET polymerization and the mechanism shows the incorporation of random repeat units within the polymer chain[73]. The catalyst is a Lewis acid and a transesterification catalyst that allows the formation of oligomers of VA' by polycondensation reaction and the ring opening polymerization of CL. Then a 4 centered mechanism with the ester and a coordinated oxygen allows transesterification to occur. This important step happens with caprolactone or the vanillic acid oligomers giving randomness to the chain. Moreover, chains can be randomly transesterified in any repeat unit; this gives even more disorganized chains. The catalyst can be released by ligand exchange.

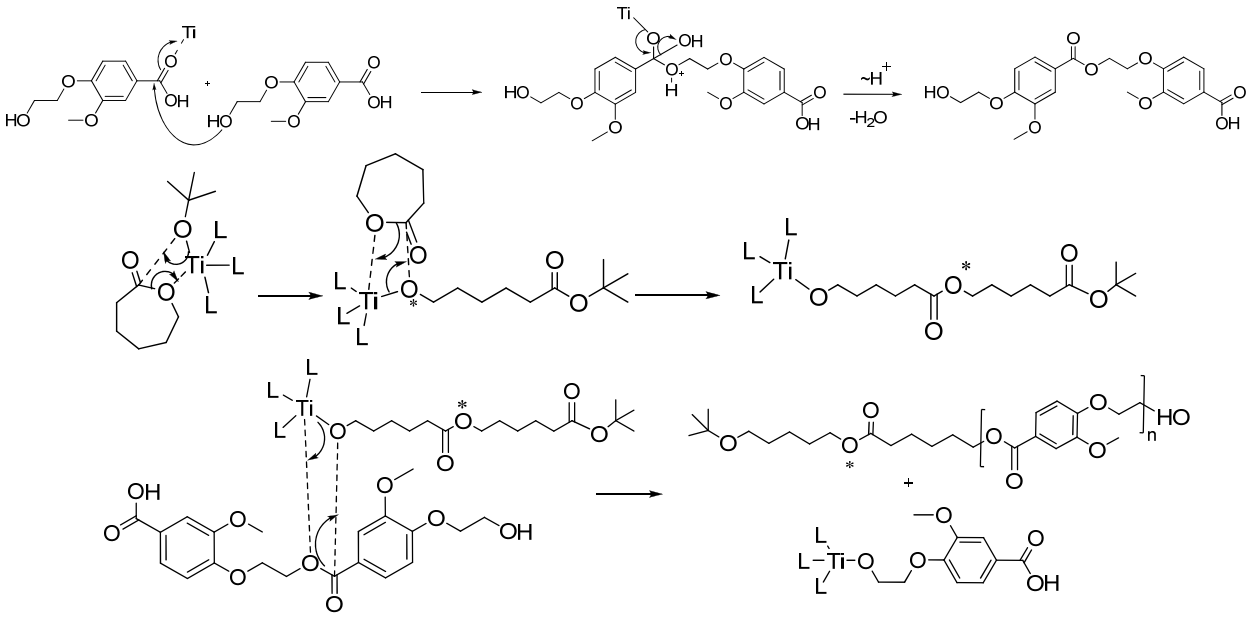


Figure 3-5. Key steps in the mechanism for copolymerization of CL/VA'

The polymerization will be performed in the melt to favor the step-growth polymerization of the vanillic acid derivative and under vacuum for water removal. Distillation of the ε-caprolactone must be avoided in order conserve consistent incorporation in comonomer. The melt will be held under nitrogen for 1h in order to have formation of oligomers and avoid lost of the liquid caprolactone. Higher molecular weight polymer is obtained by applying vacuum and removing water as a byproduct. The reaction is considered complete when the magnetic stirring is not effective which may be anywhere between 2-8h depending on the feed.

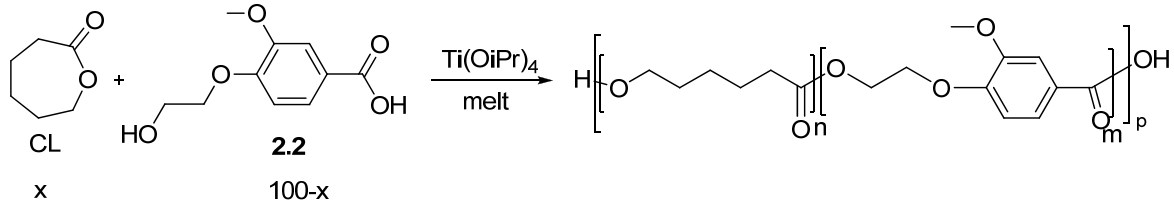


Figure 3-6. Copolymerization of vanillic acid derivative and ε-caprolactone

The copolymerizations are reproducible and give - in relatively high yield - macromolecules with diverse repeat units. The NMR shows that the resulting chain is randomly distributed with diverse integration peaks due to several possibilities in the

repeat unit arrangement. We could have imagined that the ring opening polymerization would have been faster but it seems that the transesterification catalyst does not favor the addition mechanism.

Table 3-1. Series of copolyesters

Entry	Polymer	Feed CL x %	NMR in CL %	Weight % in CL	% Yield
k	3.1	100	100	100	79
l	3.2	90	89.3	83	80
m	3.3	80	79	69	67
n	3.4	70	63.1	50	68
o	3.5	60	53.4	40	65
p	3.6	50	38	27	67
q	3.7	40	34	23	82
r	3.8	30	29.8	20	77
s	3.9	20	16.7	11	69
t	3.10	10	9.2	6	76

As shown in the table 3-1 the vanillic acid derivative **2.2** insertion is close to its feed. Thermal analyses by DSC have conducted to determine the glass transitions and melting point of each polymer sample.

Table 3-2. Thermal properties of the copolyesters.

Polymer	Feed CL/VA'	NMR in CL %	Weight % in CL	T_g (°C)	T_m (°C)	T_g Fox (°C)
3.1	100	100	100	-64	53	-60.0
3.2	90	89.3	83	-40.9	41.5	-45.4
3.3	80	79	69	-26.8	112	-31.6
3.4	70	63.1	50	-4.6	139.5	-10.4
3.5	60	53.4	40	6.2	172.4	2.4
3.6	50	38	27	29.7	198.3	22.5
3.7	40	34	23	41.4	222.7	27.7
3.8	30	29.8	20	46.3	204.3	33.1
3.9	20	16.7	11	59.8	206.7	49.9
3.10	10	9.2	6	66.2	231.1	59.4

The T_g is related to the primary structure of the chain; the more flexible units in the chain such as sp^3 hybridized carbons the more flexible and lower the T_g will be. For high

feed in ε-caprolactone a low T_g is observed. This can be easily seen in figure 3-8 the T_g decreases almost linearly with increase in the flexible repeat unit.

The melting point values do not follow a regular trend but we can confirm that, generally, the melting point decreases when the feed of ε-caprolactone increases. According to the Fox equation[74] for an A-B copolymer:

$$\frac{1}{Tg} = \frac{w_a}{Tg_a} + \frac{(1-w_a)}{Tg_b}$$

Figure 3-7. Fox equation for random copolymers

So knowing the composition of the copolymer by NMR and the T_g of both homopolymers we can predict and compare the measured glass transition to a calculated value. Thermal analyses are somewhat dependent on the molecular weight of the polymers but are pretty comparable to the one calculated with the Fox equation.

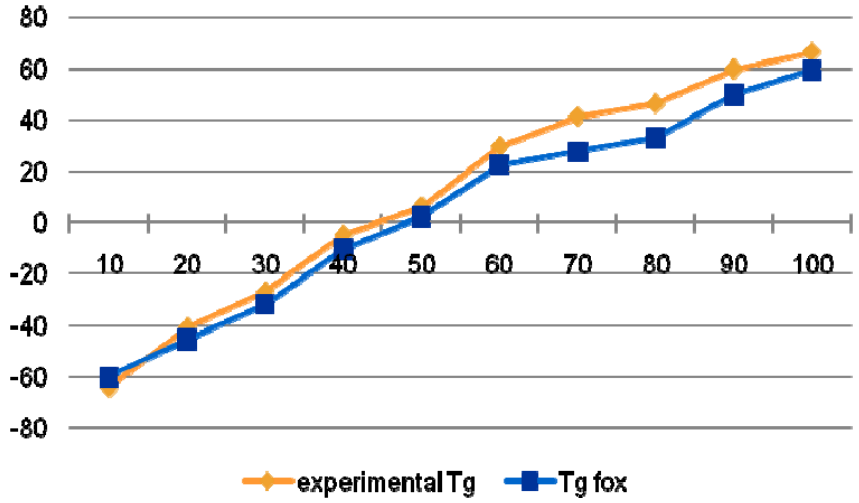


Figure 3-8. Evolution of the glass transition with the feed of ε-caprolactone

The glass transition values are close to the calculated values given by the Fox equation.

3.3 NMR Study and Type of Copolymer Determination

An NMR study of the copolyesters can give us more information about the structure of the macromolecules. A first look at the spectra for diverse feed shows us extra peaks compared to the homopolymers spectrum.

3.3.1 Incorporation Determination

The incorporationof vanillic acid has been the main concern in those polymerizations. Since ring opening polymerizations are supposed to be faster than step- growth polymerization mechanisms.

By NMR VA' shows peaks between 7.5-8ppm corresponding to 2 aromatic hydrogens. Polycaprolactone has a specific peak in the 2-2.5ppm region that matches the 2 α-hydrogens to the carbonyl. Both peaks are supposed to have-in the case of homopolymers- an integration value of 2. By measuring the intensity of both peaks and calculating a ratio, we get the incorporation in VA'.

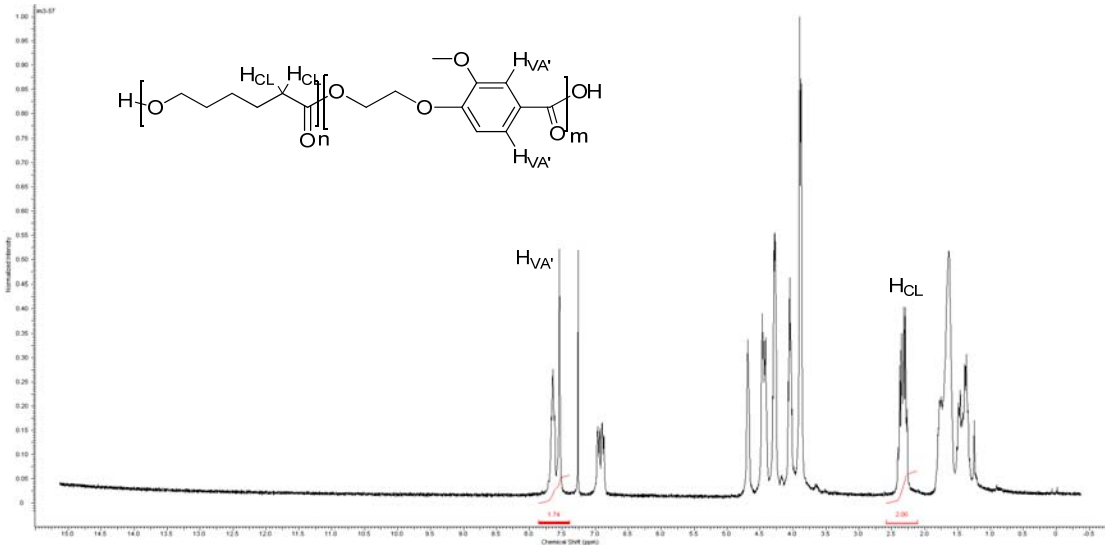


Figure 3-9. Determination of VA' incorporation (polymer **3.5)**

3.3.2 Peak Assignment and Type of Copolymer Synthesized

The NMR of all the copolymers shows some extra peaks in the 3-6ppm region compared to what would be expected according to the homopolymers' spectra.

In a copolymerization 3 cases are possible:

- Random copolymer showing randomly incorporation of both monomers
  VA'VA'CLCLCLCLCLCLVA'CLCLVA'
- Alternating Copolymer : regular alternation of both repeat units
  VA'CL VA'CL VA'CL VA'CL VA'CL
- Copolymer block: 2 blocks of polymers with the same repeat unit
  - VA'VA'VA'VA'VA'VA'VA'CLCLCLCLCLCLCLCL

A first look at the spectra for diverse feed shows us extra peaks than the homopolymers. A first assumption is that the chemical environment is not the same for the hydrogen of a similar repeat unit but with other neighboring molecules.

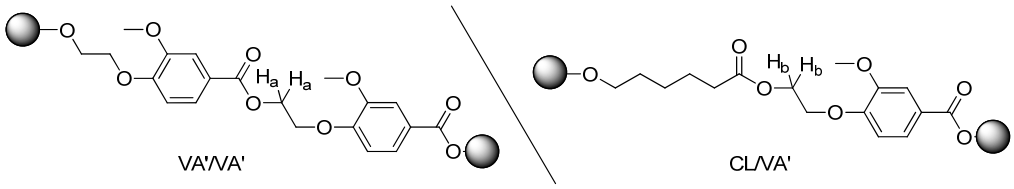


Figure 3-10. Difference of chemical environment within the polymer chain

A study of the integration of the NMR peak can give us more information about the peak assignment.

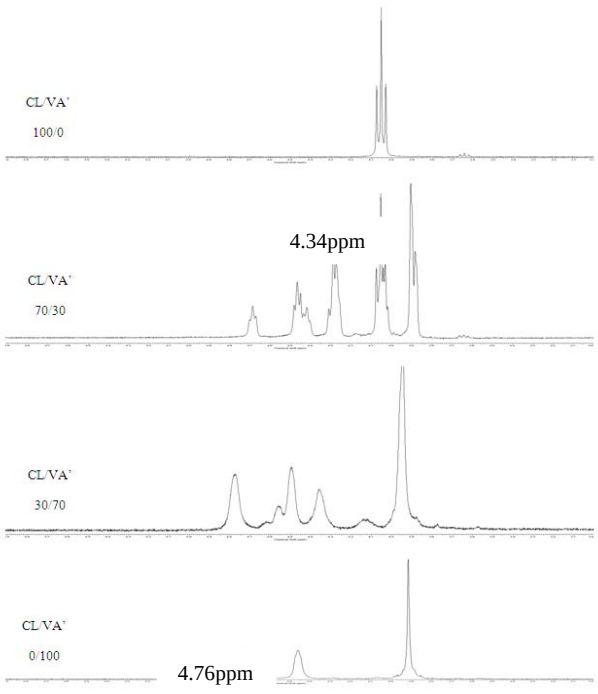


Figure 3-11. NMR peak from 3-5.9 ppm for different copolymers

This NMR study shows the difference in the NMR spectra with the increment of VA' in the melt. We can see a peak at 4.8 ppm appearing and some extra peaks in the 4-4.8 ppm range comparing to the homopolymers

Table 3-3. Relative intensities of the ^1H NMR peaks of H_a and H_b

Polymer	%CL	Intensity I_1 4.76ppm	Intensity I_2 4.34ppm	Intensity 4.1ppm	ratio I_2/I_1
3.2	90	0.35	2.49	12.1	7.1
3.3	80	0.48	2.09	4.82	4.4
3.4	70	0.77	2.13	2.67	2.8
3.5	60	0.9	1.72	1.34	1.9
3.6	50	1.04	1.31	0.65	1.3
3.7	40	1.28	1.2	0.53	0.9
3.8	30	1.35	1	0.37	0.7
3.9	20	1.42	0.57	0.74	0.4
3.10	10	1.49	0.4	0.3	0.3

Peaks at 4.76 ppm and 4.34 ppm are both respectively coupled with another adjacent peak but are the clearest on the NMR spectra. The reference peak will be at 7.0 ppm it correspond to 2 aromatic hydrogens of VA'. This study is more qualitative and helps to assign the peaks in our spectra. According to table 3-3 the intensity of peak I_1 increases with the feed in VA' and peak and inverse for I_2. In that copolymer the ratio of I_2/I_1 is inconsistent so no alternating copolymer has been formed.

A block copolymer would show very little intensity in one of the peak since only one of VA'-CL repeat unit would be possible. Here the variation with the feed is for both intensities.

We can conclude that the copolymer formed in the bulk is a random copolymer. According to intensities I_1 and I_2, the peaks can be assigned in the following NMR spectra.

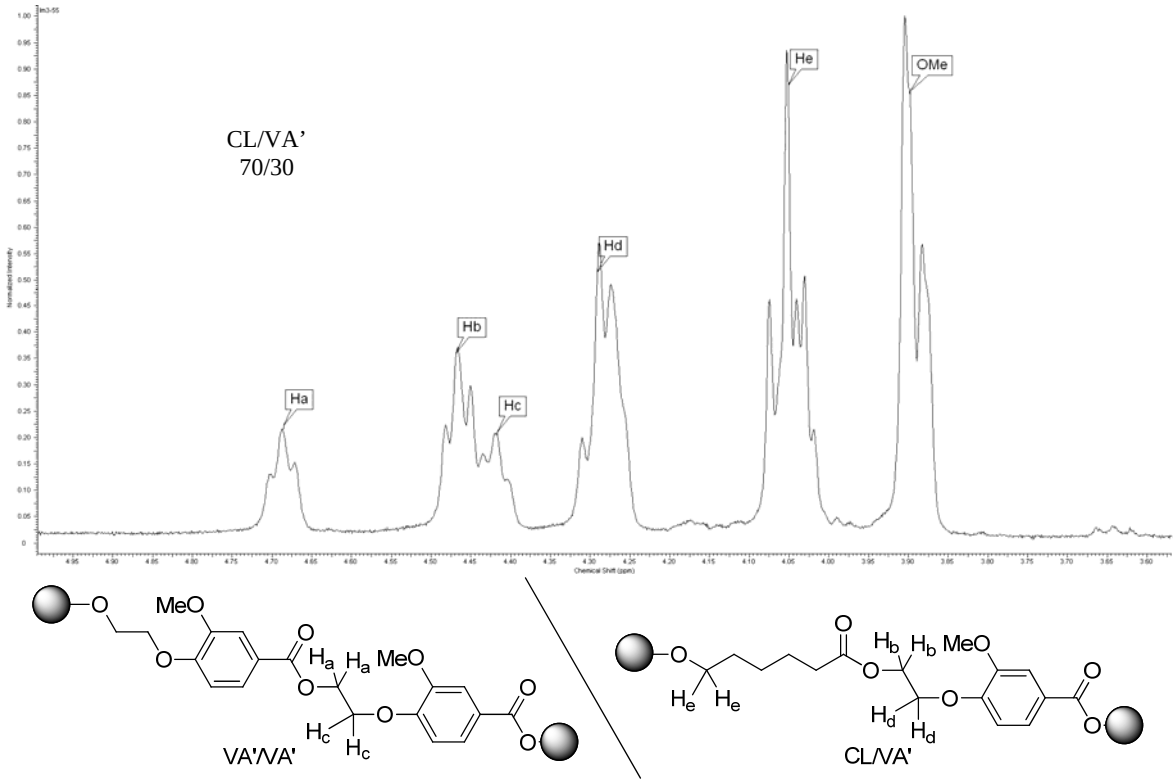


Figure 3-12. Peak assignments in the 3-5 ppm range

An NMR study shows the randomness of the polymer chain. Notably in the 3-6 ppm region where peaks for the VA'/CL repeat unit appears in addition to the known peak of the 2 homopolymers. A study of the ratio gives the composition of the copolyesters that is fairly close to the feed in each monomer.

3.4 New Ideas

3.4.1 Copolymers with Isosorbide Derivatives

Another set of copolymers could be studied starting with a different natural molecule: isosorbide. Isosorbide is a heterocyclic compound derived from glucose[75, 76]. It is a diol that has been used in the past as an initiator for ring opening polymerization of ε-caprolactone[77]. A functionalization of isosorbide into an A-B monomer, alcohol/ acid type could give an interesting comonomer for ε-caprolactone.

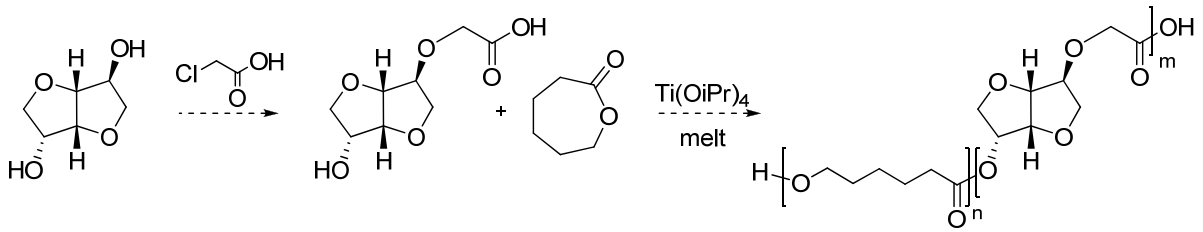


Figure 3-13. Proposed copolymerization isosorbide derivatives with ε-caprolactone

3.4.2 Copolymers of PLA

Poly(lactic acid) has been one of the most developed and studied organic green polymer. It is a biodegradable aliphatic polyester that can be obtained from ring opening polymerization of lactide[78]. Lactide that can be obtained by transformation of lactic acid, extracted from sugar cane or corn starch[79]. PLA is also biocompatible and has been used extensively for biomedical applications[80].

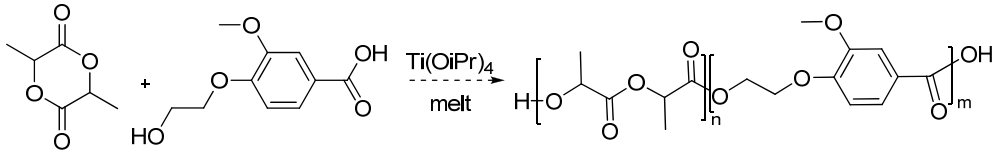


Figure 3-14. Proposed copolymerization of vanillic acid derivatives with lactide.

Similar to polycaprolactone the biodegradation could be tuned by insertion of aromatic repeat units in the aliphatic polyester backbone[81]. The properties and biodegradation could be selected and adapted, depending on the applications, with the feed in vanillic acid derivative into the polymer. It should be noted that the thermal properties of PLA, specifically the T_g,could not be changed much since the glass transitions of both polymers are similar. The T_g of PLA is around 60°C[82] and the homopolymer of vanillic acid derivatives is about 70°C, so no big change is expected in the glass transition for a random copolymer.

3.5 Conclusions

Polycaprolactone is an aliphatic polymer that is biocompatible and biodegradable. Unfortunately its applications are limited by its thermal properties. Copolymers of vanillic

acid derivatives and caprolactone have been successfully synthesized by a step-growth/chain-growth copolymerization giving good incorporation of vanillic acid derivatives into the chain. The glass transition increased with the feed in vanillic acid derivatives and was compared to the calculated values obtained from the Flory equation. An NMR study showed that the monomers insertion was random and gave incorporation ratios similar to the feed ratios. Finally some new ideas emerged from those results with notably the use of isosorbide and lactide for new biodegradable copolymers.

CHAPTER 4
EXPERIMENTAL PROCEDURES

4.1 Molecular Characterizations

Nuclear magnetic resonance (NMR) spectra were recorded using a Varian Mercury 300 MHz spectrometer. Chemical shift is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.0 ppm) or specified solvent. Coupling constants (*J*) are reported in Hertz (Hz). Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintuplet; m, multiplet; br, broad.

Differential scanning chromatographies were measured with DSC Q1000 from TA instruments. About 5-10 mg of samples were weighed in a sealed pan that went through a heat/cool/heat cycle at 10°C/min. The temperature range depends on the experiment but was limited to 300°C by the instrument.

Thermogravimetric analyses were measured with TGA Q5000 from TA Instruments. 5-10 mg of sample were heated at 50° C/min from 25-600°C.

Gel permeation chromatographies were measured at 40°C in THF with a flow rate of 1 mL/min with Polystyrene standard in a GPCV 2000 from WATERS.

Viscosity measurements were done at 35°C in a 1:2 mixture of phenol: 1,1,2,2 tetrachloroethane with a CANNON- Ubbelohde type 150.

4.2 Polymerizations Procedures

Syntheses. All the polymerizations were carried out in a closed flask connected to the Schlenk line with a 180° glass connector. The flask- loaded with monomer and the catalyst- was purged with nitrogen and evacuated 3 times before melting the solid monomer with a heating mantel. The temperature was regulated with a variac transformer. Agitation was effected with a magnetic stir bar. The melt was kept under

nitrogen to allow the formation of oligomers and limit the sublimation during vacuum is applied. Dynamic vacuum was applied on the molten polymer to remove water or acetic acid. At the end of the polymerization the product was cooled under nitrogen leaving a solid that was dissolved in a mixture of trifluoroacetic acid and dichloromethane and then crashed in cold methanol. The solid polymer was obtained by filtration and dried on the Schlenk line overnight.

For the polymerization with the air sensitive titanium catalyst, the vanillic acid derivatives were weighed in the flask; caprolactone and the catalyst were added in the box and the flask was sealed before being opened under nitrogen on the Schlenk line. Caprolactone was distilled over calcium hydride and stored in the glove box.

Viscosity measurements. Intrinsic viscosity measurements were performed with a Ubbelohde viscometer. 15 mL of clean 1: 2 mixture of phenol: 1, 1, 2, 2-tetrachloroethane were poured in the viscometer and allowed to thermally equilibrate for 2h. Exactly 1 mL of about 8 g/L solution of polymer was added for each measurement until the final volume is 20 mL in the viscometer giving a final concentration of about 2 g/L.

$$[\eta] = \lim_{c \longrightarrow 0} \frac{\eta_{sp}}{c} \qquad with \qquad \eta_{sp} = \frac{t - to}{to}$$

$$\frac{\eta_{sp}}{c} = f(c)$$

By doing the Kramer plot, and extrapolating to infinitely dilute solution (c->0) we obtain the intrinsic viscosity. The value is then related to the Mark-Houwink constant for PET in the same solvent and temperature[83]. $[\eta] = 1.09 \times 10^{-2} M_v^{0.84}$

End group analysis. End group analysis is one way to determine molecular weight of a polymer by NMR study. The chemical environment for the end group is different than the one for a repeat unit in the middle of the polymer chain. For example, in a polyester all the ester linkage have the same chemical environment and the end group will be an acid so a different type of structural bond. This implies a difference in chemical shift by NMR and can be noticed for relatively low polymerization degree polymers.

For polymers **2.22**-**2.27** the end group will be an acid and the acetyl group- group that as a specific chemical shift at about 2.4 ppm.

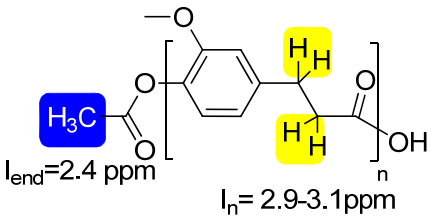


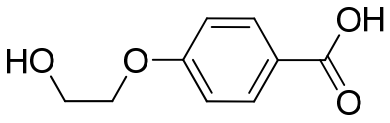
Figure 4-1. End group analysis for molecular weight determination.

Knowing the integration of the methyl group I_{end} by NMR and the 4 hydrogens we can get the number of repeat unit in the polymer chain with the following equation.

$$DP = \frac{3}{4} \times \frac{I_n}{I_{end}} \qquad and\ M_n = \quad RU \times DP$$

4.3 Synthesis Procedures

2.1 *4-(2-hydroxyethoxy)benzoic acid*



2.1

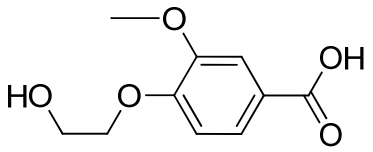
20.0 g (0.145 mol) of *p*-Hydroxybenzoic acid were dissolved in a mixture of 17.1 g (0.428 mol) of sodium hydroxide and 5.3 g (0.035 mol) of sodium iodide in 80 mL of water. The mixture was refluxed and 17.1 g (0.212 mol) of 2-chloroethanol were slowly

added to the reaction flask under nitrogen. After 24h, the reaction flask was cooled down, and acidified with dilute hydrochloric acid solution until the product crashed out. The white crystals were filtered and recrystallized twice from a 5/1 solution of ethanol/water. 15.1 g of white product were obtained in a 57% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 12.61 (br. s, 1H, COOH), 7.87 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.01 (d, *J* = 8.9 Hz, 2H, Ar-H), 4.91 (t, *J* = 4.9 Hz, 1H, OH), 4.05 (t, *J* = 4.5 Hz, 2H, OCH_2), 3.72 (q, *J* = 4.9 Hz, 2H, C**H**$_2$OH).

^{13}C NMR (DMSO, 75 MHz): δ (ppm) = 167.0, 162.3, 131.4(2), 122.9, 114.3(2) 69.8, 59.4.

2.2 *4-(2-hydroxyethoxy)-3-methoxybenzoic acid*



2.2

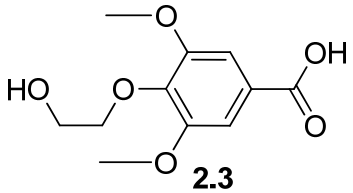
To a solution of 80.0 g (0.48 mol) of vanillic acid, 80.9 g (2.0 mol) of sodium hydroxide and 14.9 g (0.10 mol) of sodium iodide in 100 mL of water. 59.2 g of 2-chloroethanol (0.74 mol) were added dropwise at 100°C under nitrogen diluted in 200 mL of ethanol. After 24h of reflux, the mixture was cooled at room temperature, concentrated under vacuo, and the remaining solid dissolved in water and washed with diethyl ether. The aqueous solution was acidified with hydrochloric acid (3M) and gave a beige solid that after recrystallization in ethanol was white. Filtration gave 72.9 g of **2.2**, in 72% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 12.5 (br. s, 1H, COOH), 7.48 (dd, *J* = 8.4 Hz, 1.9 Hz, 1H, Ar-H), 7.39 (d, *J* = 1.9 Hz, 1H, Ar-H), 6.99 (d, *J* = 8.5 Hz, 1H, Ar-H),

4.84 (t, *J* = 5.0 Hz, 1H, OH), 3.99 (t, *J* = 5.0 Hz, 2H, OCH_2), 3.75 (s, 3H, OCH_3), 3.68 (q, *J* = 5.0 Hz, 2H, C**H**$_2$OH).

^{13}C NMR (DMSO, 75 MHz): δ (ppm) = 167.4, 152.4, 148.7, 123.5, 123.2, 112.3, 112.2, 70.5, 59.7, 55.7.

2.3 *4-(2-hydroxyethoxy)-3,5-dimethoxybenzoic acid*



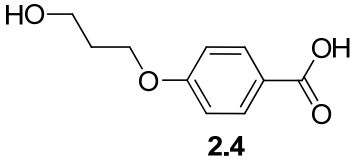
2.3

7.1 g (0.036 mol) of syringic acid, 3.3 g (0.083 mol) of sodium hydroxide and 0.9 g (0.006 mol) of sodium iodide were dissolved in 75 mL of water. 4.2 g (0.052 mol) of 2-chloroethanol were added dropwise to the hot mixture. After 24h, of reaction under reflux, the aqueous solution was acidified with hydrochloric acid and extracted with ethyl acetate. The organic solvent was removed and 5.4 g of crude product were left, it was recrystallized in a mixture of ethanol and water leaving 3.5 g of white pure powder in a 41% yield.

^{1}H NMR (CD_3CO, 300 MHz): δ (ppm) = 12.84 (br. s, 1H, COOH), 7.23 (s, 2H, Ar-H), 4.61 (t, *J* = 5.7 Hz, 1H, OH), 3.94 (t, *J* = 5.6Hz, 2H, OCH_2), 3.82 (s, 6H), 3.62 (q, *J* = 5.6Hz, 2H, CH_2OH).

^{13}C NMR (DMSO, 75 MHz): δ (ppm) = 170.7, 153.0(2), 140.9, 125.0, 107.3(2), 75.4, 61.4, 56.2(2).

2.4 *4-(3-hydroxypropoxy)benzoic acid*



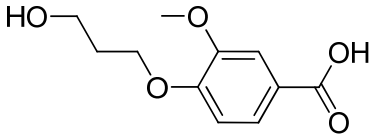
2.4

20.0 g (0.145 mol) of vanillic acid, 17.6 g (0.314 mol) of potassium hydroxide and 2.7 g (0.018 mol) were dissolved in 100 mL of water. 16.5 g (0.175 mol) of 3-chloropropan-1-ol were added to the hot mixture slowly. After 24h of reaction, the aqueous solution was acidified with chlorhydric acid and a white solid crashed out. The crude product was recrystallized in a mix of ethanol and water to give 13.4 g of white powder in a 48% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 12.58 (br. s, 1H, COOH), 7.86 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.99 (d, *J* = 8.8Hz, 2H, Ar-H), 4.56 (t, *J* = 5.0 Hz, 1H, OH), 4.09 (t, *J* = 6.4 Hz, 2H, OCH_2), 3.54 (m, 2H, C**H**$_2$OH), 1.86 (quin, *J* = 6.2 Hz, 2H, CH_2C**H**$_2CH_2$).

^{13}C NMR (DMSO, 75 MHz): δ (ppm) = 167.0, 162.3, 131.4(2), 122.8, 114.2(2), 64.9, 67.2, 32.0.

2.5 *4-(3-hydroxypropoxy)-3-methoxybenzoic acid*



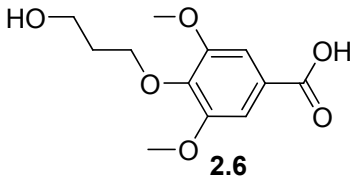
2.5

Same procedure as **2.4** 46% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm)= 12.63 (br. s, 1H, COOH), 7.54 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H, Ar-H), 7.43 (d, *J* = 2.0 Hz, 1H, Ar-H), 7.04 (d, *J* = 8.5 Hz, 1H, Ar-H), 4.56 (t, *J* = 5.3Hz, 1H, OH), 4.09 (t, *J* = 6.4 Hz, 2H, OCH_2), 3.8 (s, 3H, OCH_3), 3.55 (q, *J* = 5.3 Hz, 2H, CH_2OH), 1.88 (quin, *J* = 6.4 Hz, 2H, CH_2C**H**$_2CH_2$)

^{13}C NMR (DMSO, 75 MHz): δ (ppm) = 167.1, 152.0, 148.4, 123.2, 122.8, 112.0, 111.7, 65.3, 57.2, 55.5, 32.0.

2.6 *4-(3-hydroxypropoxy)-3,5-dimethoxybenzoic acid*



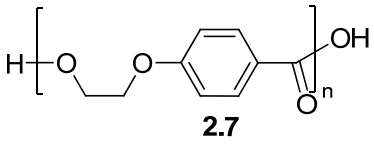
2.6

10.0 g (0.05 mol) of syringic acid, 4.6 g (0.12 mol) of sodium hydroxide and 0.95 g (0.0063 mol) of sodium iodide were dissolved in 80 mL of water. 5.1 g (0.054 mol) of 3-chloropropan-1-ol were added dropwise to the hot mixture. After 48h, the reaction was cooled to room temperature and acidified with hydrochloric acid. 8.0 g of crude product crashed out of solution. The product was dissolved in ethyl acetate and crashed with excess of hexanes giving 6.7 g of pure product in a 52% yield.

^{1}H NMR (CD_3CO, 300 MHz): δ (ppm) = 7.29 (s, 2H, Ar-H), 4.1 (t, *J* = 6.1 Hz, 2H, OCH_2), 3.86 (s, 6H, OCH_3), 3.73 (t, *J* = 6.1Hz, 2H, CH_2OH), 1.86 (quin, *J* = 6.1 Hz, 2H, $CH_2C\mathbf{H}_2CH_2$).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 170.7, 152.8(2), 141.5, 124.7, 107.2(2), 72.4, 61.3, 56.2(2), 32.1.

2.7 *poly(4-(2-hydroxyethoxy)benzoic acid)*



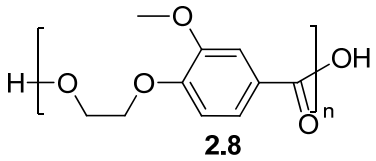
2.7

1.5 g (8.2 mmol) of **2.1** and 0.018 g (0.062 mmol) of antimony trioxide were heated at 200-250°C under nitrogen for 1h. Vacuum was applied for 16h until no more stirring was possible. The procedure described above gave 0.95 g of **2.7** in a 70% yield

^{1}H NMR ($CF_3COOD/CDCl_3$, 300 MHz): δ (ppm) = 8.03 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.01 (d, *J* = 8.5Hz, 2H, Ar-H), 4.75 (br s, 2H, $COOC\mathbf{H}_2$), 4.42 (br. s, 2H, OCH_2).

^{13}C NMR ($CF_3COOD/CDCl_3$, 75 MHz): δ (ppm) = 169.5, 163.4, 132.5(2), 121.6, 114.8(2), 66.2, 64.4.

2.8 *poly(4-(2-hydroxyethoxy)-3-methoxybenzoic acid)*



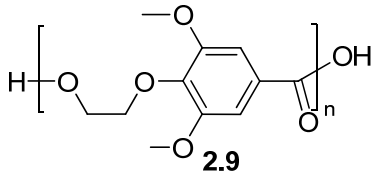
2.8

1.5 g (7.2 mmol) of **2.2** and 0.02 g (0.069 mmol) of antimony trioxide were melted at 200-250°C under nitrogen for 1h. Vacuum was applied for 6h until no more stirring was possible. After work up, 1.1 g of beige powder were obtained in 79% yield.

^{1}H NMR ($CF_3COOD/CDCl_3$, 300 MHz): δ (ppm) = 7.71 (d, *J* = 8.5Hz, 1H, Ar-H), 7.5 (d, *J* = 1.7Hz, 1H, Ar-H), 6.98 (d, *J* = 8.8Hz, 1H, Ar. H), 4.74 (m, 2H, $COOCH_2$), 4.46 (br. s, 2H, OCH_2), 3.92 (s, 3H, OCH_3)

^{13}C NMR ($CF_3COOD/CDCl_3$, 75 MHz): δ (ppm) = 168.4, 152.1, 148.6, 125.0, 122.3, 112.7, 112.4, 67.2, 63.9, 56.3.

2.9 *poly (4-(2-hydroxyethoxy)-3,5-dimethoxybenzoic acid)*



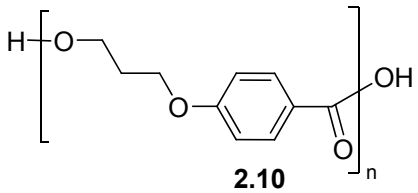
2.9

2.0 g (8.13 mmol) of **2.3** and 0.02 g (0.069 mmol) of antimony trioxide were melted under nitrogen at 150-200°C for 1h. Vacuum was applied for 30h. Work up gave 1.3 g of powder in 71% yield.

^{1}H NMR ($CF_3COOD/CDCl_3$, 300 MHz): δ (ppm) = 7.37 (s, 2H, Ar-H), 4.68 (br, 2H, $COOCH_2$), 4.54 (br., 2H, OCH_2), 3.84 (s, 6H, OCH_3).

^{13}C NMR ($CF_3COOD/CDCl_3$, 75 MHz): δ (ppm) = 168.4, 152.7(2), 140.2, 125.2, 107.5(2), 71.3, 65.2, 56.3(2).

2.10 *poly (4-(3-hydroxypropoxy)benzoic acid)*



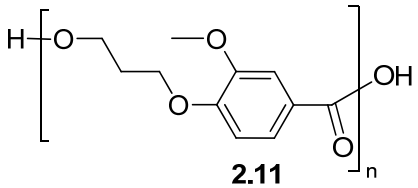
2.10

1.5 g (7.85 mmol) of **2.4** and 0.022 g (0.075 mmol) of antimony trioxide were melted under nitrogen at 150-200°C for 1h. Vacuum was applied for 5h. Work up gave 0.7 g of powder in 50% yield.

^{1}H NMR ($CF_3COOD/CDCl_3$, 300 MHz): δ (ppm) = 8.05 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.03 (d, *J* = 8.5 Hz, 2H, Ar-H), 4.59 (br. s, 2H, $COOCH_2$), 4.25 (br. s, 2H, OCH_2), 2.34 (m, 2H, $CH_2C\mathbf{H}_2CH_2$).

^{13}C NMR ($CF_3COOD/CDCl_3$, 75 MHz): δ (ppm) = 170.2, 163.7, 132.4(2), 121.5, 114.8(2), 113.3, 64.9, 63.3.

2.11 *poly(4-(3-hydroxypropoxy)-3-methoxybenzoic acid)*



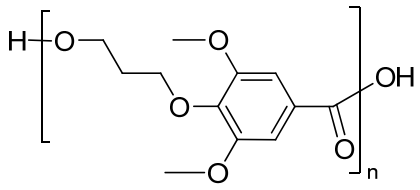
2.11

2.1 g (9.3 mmol) of **2.5** and 0.036 g (0.12 mmol) of antimony trioxide were melted under nitrogen at 200-250°C for 1h. Vacuum was applied for 5h. Work up gave 1.1 g of powder in 57% yield.

^{1}H NMR ($CF_3COOD/CDCl_3$, 300 MHz): δ (ppm) = 7.71 (br s, 1H, Ar-H), 7.57 (m, 1H, Ar. H), 6.96 (d, *J* = 8.5Hz, 1H, Ar-H), 4.56 (t, *J* = 6.1 Hz, 2H, $COOCH_2$), 4.27 (t, *J* = 6.1 Hz, 2H, OCH_2), 3.94 (s, 3H, OCH_3), 2.34 (m, 2H, $CH_2C\mathbf{H}_2CH_2$).

^{13}C NMR ($CF_3COOD/CDCl_3$, 75 MHz): δ (ppm) = 168.6, 152.6, 148.2, 124.8, 121.9, 112.5, 111.7, 65.6, 62.8, 56.2, 28.2.

2.12 *poly(4-(3-hydroxypropoxy)-3,5-dimethoxybenzoic acid*



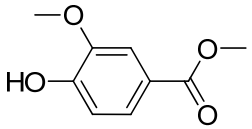
2.12

1.7 g (6.63 mmol) of **2.6** and 0.017 g (0.058 mmol) of antimony trioxide were melted under nitrogen at 200-250°C for 1h. Vacuum was applied for 5h before the magnetic stirring stops. Work up gave 1.3 g of powder in 82% yield.

^{1}H NMR ($CF_3COOD/CDCl_3$, 300 MHz): δ (ppm) = 7.35 (s, 2H, Ar-H), 4.63 (t, *J* = 6.4 Hz, 2H, $COOCH_2$), 4.33 (t, *J* = 5.9 Hz, 2H, OCH_2), 3.89 (s, 3H), 2.26 (quin, *J* = 6.2 Hz, 2H, $CH_2C\mathbf{H}_2CH_2$).

^{13}C NMR ($CF_3COOD/CDCl_3$, 75 MHz): δ (ppm) = 169.5, 153.1(2), 140.7, 125.7, 107.9(2), 71.1, 64.2, 56.4(2), 29.0.

2.13 *methyl 4-hydroxy-3-methoxybenzoate*



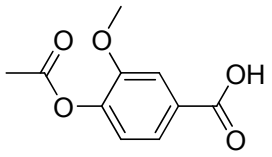
2.13

30.0 g (0.18 mol) of vanillic acid were dissolved in 150 mL of hot methanol. 6 mL of sulfuric acid were added as a catalyst and the reaction mixture is left for 48h at reflux under nitrogen. The solvent was removed and the solid was dissolved in ethyl acetate and then washed with sodium bicarbonate. The organic layer was washed with brine and magnesium sulfate before being removed under vacuum giving 25.0 g of product in 80% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.63 (dd, *J* = 8.2 Hz, 2.0 Hz, 1H, Ar-H), 7.54 (d, *J* = 2.0 Hz, 1H, Ar-H), 6.93 (d, *J* = 8.2 Hz, 1H, Ar-H), 6.12 (br. s, OH), 3.92 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 167.3, 150.4, 146.6, 124.6, 122.6, 114.5, 112.2, 56.5, 52.4.

2.14 *4-acetoxy-3-methoxybenzoic acid*



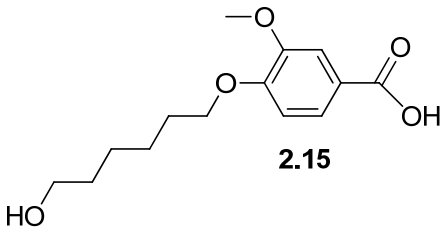
2.14

20.6 g (0.12 mol) of vanillic acid were dissolved in 50 mL of acetic anhydride (0.53 mol) and 50 mL (0.62 mol) of pyridine. The mixture was stirred at room temperature overnight poured on 500 mL of water and acidified with hydrochloric acid. The aqueous solution was extracted with ethyl acetate and rotovaped. A recrystallization from ethyl acetate gave 17.3 g of a beige powder in 67% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.73 (dd, *J* = 8.2 Hz, 1.7 Hz, 1H, Ar-H), 7.68(d, *J* = 1.7 Hz, 1H, Ar-H), 7.11(d, *J* = 8.2 Hz, 1H, Ar-H), 3.88 (s, 3H, OCH_3), 2.32 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 171.1, 168.5, 151.1, 144.2, 123.4, 122.9, 113.8(2), 56.0, 20.6.

2.15 *4-(6-hydroxyhexyloxy)-3-methoxybenzoic acid*



2.15

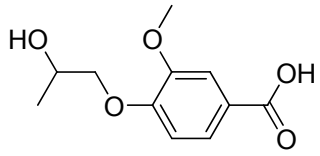
To a solution of 15.0 g (0.089 mol) of vanillic acid, 15.5 g (0.26 mol) of potassium hydroxide, 2.14 g (0.014 mol) of sodium iodide in a mixture of 30 mL of water, and 100 mL of ethanol. 6-chlorohexanol was added dropwise to the hot solution under nitrogen. After 24h of reflux, the mixture was cooled at room temperature, concentrated under

vacuo and the remaining solid dissolved in water. The aqueous solution was acidified with hydrochloric acid (3M) and gave a beige solid that after recrystallization in ethanol/water mixture was white. Filtration gave 18.3 g of **2.14**, in 76% yield.

^{1}H NMR (DMSO, 300 MHz): δ (ppm) = 12.65 (br. s, 1H, COOH), 7.54 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H, Ar-H), 7.44 (d, *J* = 2.0 Hz, 1H, Ar-H), 7.03 (d, *J* = 8.4 Hz, 1H, Ar-H), 4.36 (t, *J* = 5.4 Hz, 1H, OH), 4.02 (t, *J* = 6.7 Hz, 2H, OCH_2), 3.8 (s, 3H, OCH_3), 3.36 (br. s, 2H, CH_2OH), 1.72 (quin, *J* = 6.7 Hz, 2H, CH_2), 1.42 (m, 6H, $OCH_2(CH_2)_3CH_2OH$).

^{13}C NMR (DMSO, 75 MHz): δ (ppm) = 167.2, 152.1, 148.4, 123.2, 122.8, 112.1, 111.8, 68.2, 60.7, 55.5, 32.5, 28.7, 25.4, 25.3.

2.16 *4-(2-hydroxypropoxy)-3-methoxybenzoic acid*



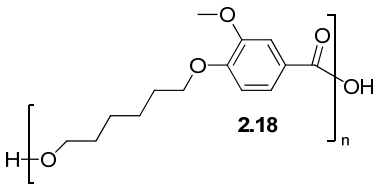
2.16

15.0 g (0.089 mol) of vanillic acid and 10.6 g of potassium hydroxide were dissolved in 50 mL of water. 10.4 g of propylene oxide were added to the solution at room temperature. The mixture was left to stir at room temperature for 72h, then acidified and extracted with ethyl acetate. The organic layer was washed over brine and magnesium sulfate before being removed under vacuum leaving a beige-yellow solid. The solid was dissolved in acetone and crashed with cold hexane leaving 9.5 g of beige powder in 57% yield.

^{1}H NMR (DMSO, 300 MHz): δ (ppm) = 12.66 (br. s, 1H, COOH), 7.54 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H, Ar-H), 7.44 (d, *J* = 1.8 Hz, 1H, Ar. H), 7.04 (d, *J* = 8.4 Hz, 1H, Ar-H), 4.89 (d, *J* = 4.4 Hz, 1H, OH), 3.94 (m, 3H, CH and CH_2), 3.81 (s, 3H, OCH_3), 1.16 (d, *J* = 6.1 Hz, 3H, CH_3).

^{13}C NMR (DMSO, 75 MHz): δ (ppm) = 167.0, 152.0, 148.4, 123.1, 122.9, 112.1, 112.0, 73.8, 64.4, 55.5, 20.3.

2.18 *Poly (4-(6-hydroxyhexyloxy)-3-methoxybenzoic acid)*



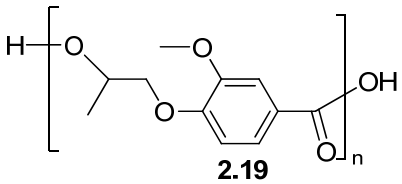
2.18

3.0 g (11.3 mmol) of **2.14** and 0.027 g (0.093 mmol) of antimony trioxide were melted under nitrogen at 200-250°C for 1h. Vacuum was applied for 4h before the magnetic stirring stops. Work up gave 1.95 g of product in 71% yield.

^{1}H NMR ($CF_3COOD/CDCl_3$, 300 MHz): δ (ppm) = 7.73 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H, Ar-H), 7.58 (d, *J* = 2.0 Hz, 1H, Ar-H), 6.94 (d, *J* = 8.8 Hz, 1H, Ar-H), 4.38 (t, *J* = 6.7 Hz, 2H, $COOCH_2$), 4.13 (t, *J* = 6.7 Hz, 2H, OCH_2), 3.97 (s, 3H, OCH_3), 1.85 (m, 4H, $COOCH_2CH_2$ and OCH_2CH_2), 1.53 (m, 4H, $COOCH_2CH_2CH_2$ and $OCH_2CH_2CH_2$).

^{13}C NMR ($CF_3COOD/CDCl_3$, 75 MHz): δ (ppm) = 170.1, 153.5, 148.3, 125.9, 122.2, 113.6, 112.2, 69.8, 67.2, 56.7, 29.1, 28.8, 26.1, 26.0.

2.19 *Poly (4-(2-hydroxypropoxy)-3-methoxybenzoic acid)*



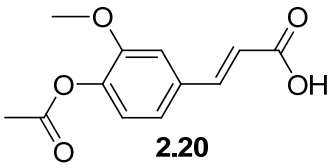
2.19

2.0 g (8.7 mmol) of **2.15** and 0.024 g (0.082 mmol) of antimony trioxide were melted under nitrogen at 150-200°C for 4h. Vacuum was applied for 5h before the magnetic stirring stopped. Work up gave 0.72 g of product in 40% yield.

^{1}H NMR ($CF_3COOD/CDCl_3$, 300 MHz): δ (ppm) = 7.70 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.56 (d, *J* = 2.0 Hz, 1H, Ar-H), 6.98 (d, *J* = 8.5 Hz, 1H, Ar-H), 5.56 (m, 1H, CH), 4.29 (m, 2H, CH_2), 3.87 (s, 3H, OCH_3), 1.5 (d, *J* = 6.5 Hz, 3H, CH_3).

^{13}C NMR ($CF_3COOD/CDCl_3$, 75 MHz): δ (ppm) =168.7, 152.8, 148.3, 125.5, 122.6, 114.1, 112.7, 71.3, 71.1, 56.5, 16.2.

2.20 *3-(4-acetoxy-3-methoxyphenyl)acrylic acid*



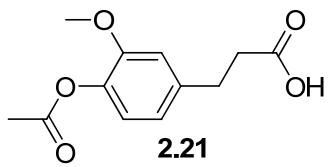
2.20

30.0 g of vanillin (0.197 mol) and 26.0 g of sodium acetate (0.317 mol) were dissolved in 200 mL of acetic anhydride (2.12 mol). About 1 mL of pyridine was added to the flask and the mixture was heating up until reflux. After 24h, the brown solution was poured over about 500 g of crushed ice and the solution was stirred until apparition of a yellow-brown solid. The flask was left overnight in the freezer and the dark yellow solid filter. The crude solid was recrystallized in a mix of acetic acid and water to give 32.3 g of yellow beige solid in a 69% yield.

^{1}H NMR (DMSO, 300 MHz): δ (ppm) = 12.35 (br. s, 1H, COOH), 7.56 (d, *J* = 15.9 Hz, 1H, Ar-CH) , 7.46 (d, *J* = 1.7 Hz, 1H, Ar-H), 7.24 (dd, *J* = 8.2 Hz, 1.7 Hz, 1H, Ar-H), 7.09 (d, *J* = 8.2 Hz, 1H, Ar-H), 6.56 (d, *J* = 15.9 Hz, 1H, C**H**COOH), 3.8 (s, 3H, OCH_3), 2.24 (s, 3H, CH_3).

^{13}C NMR (DMSO, 300MHz): δ (ppm) = 168.4, 167.6, 151.1, 143.4, 140.8, 138.3, 123.2, 121.3, 119.5, 111.8, 56.0, 20.4.

2.21 *3-(4-acetoxy-3-methoxyphenyl)propanoic acid*



2.21

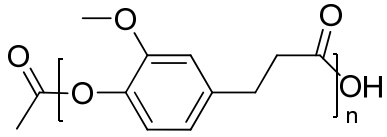
15.0 g (0.064 mol) of **2.20** were dissolved in a mixture of 150: 80 mL of tetrahydrofuran: methanol. The solution was placed in a Parr pressure reactor and 1.5 g

of palladium over charcoal 10% was added. The reaction was stirred under room temperature and under 60 psi of hydrogen for 5h. The black solution was filtered through Celite®545 to remove the palladium. The resulting clear brown solution was dried over magnenisum sulfate and condensed under vacuo. It was then dissolved in tetrahydrofuran and crashed with hexanes giving 12.8 g of beige product in 85% yield.

^{1}H NMR (DMSO, 300 MHz): δ (ppm) = 12.15 (br. s, 1H, COOH), 6.98 (s, 1H, Ar-H), 6.93 (d, *J* = 7.9Hz, 1H, Ar- H), 6.76(d, *J* = 7.9 Hz, 1H, Ar-H), 3.72 (s, 3H, OCH_3), 2.79 (t, *J* = 8.0 Hz, 2H, Ar-CH_2), 2.53 (t, *J* = 8.0 Hz, 2H, C**H**$_2$COOH), 2.20 (s, 3H, CH_3).

^{13}C NMR (DMSO, 300MHz): δ (ppm) = 174.1, 168.9, 150.8, 140.1, 137.8, 122.7, 120.3, 113.1, 55.9, 35.5, 30.5, 20.7.

2.22 *poly(3-(4-hydroxy-3-methoxyphenyl)propanoic acid)*



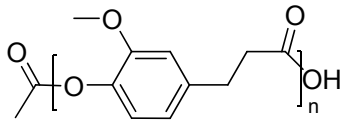
2.22

1.6 g (6.8 mmol) of **2.21** were melted under nitrogen for 2h and vacuum was applied for 2h leaving a brown solid that was dissolved in a mixture of trifluoroacetic acid and dichloromethane and crashed in methanol. 1.0 g of beige product was obtained by filtration in 83% yield.

^{1}H NMR ($CDCl_3$/CF_3COOD, 300 MHz): δ (ppm) = 6.92 (m, 3H, Ar-H), 3.84 (s, 3H, OCH_3), 3.11 (m, 2H, CH_2), 3.0 (m, 2H, CH_2).

^{13}C NMR (DMSO, 300MHz): δ (ppm) = 176.1, 150.9, 140.6, 138.3, 123.2, 121.8, 113.9, 56.6, 36.2, 31.2.

2.23 *poly(3-(4-hydroxy-3-methoxyphenyl)propanoic acid)*



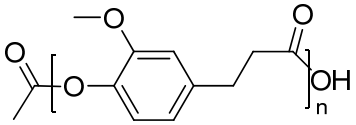
2.23

1.6 g (6.8 mmol) of **2.21** and 0.021 g (0.072 mmol) of antimony trioxide were melted under nitrogen for 2h and 2h of vacuum was applied for 2h leaving a brown solid that was dissolved in a mixture of trifluoroacetic acid and dichloromethane and crashed with methanol. 0.8 g of beige product was obtained by filtration in 67%yield.

^{1}H NMR ($CF_3COOD/CDCl_3$, 300 MHz): δ (ppm) = 6.88 (m, 3H, Ar-H), 3.80 (s, 3H, OCH_3), 3.07 (m, 2H, CH_2), 2.96 (m, 2H, CH_2).

^{13}C NMR ($CF_3COOD/CDCl_3$, 75 MHz): δ (ppm) = 175.5, 150.4, 140.1, 137.8, 122.6, 120.0, 113.4, 56.1, 35.8, 30.7.

2.24 *poly(3-(4-hydroxy-3-methoxyphenyl)propanoic acid)*



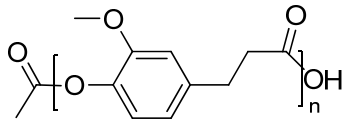
2.24

1.6 g (6.8 mmol) of **2.21** and 0.018 g (0.082 mmol) of zinc diacetate dihydrate were melted under nitrogen for 2h and vacuum was applied for 2h leaving a brown solid that was dissolved in a mixture of trifluoroacetic acid and dichloromethane and crashed with methanol. 1.0 g of beige product was obtained by filtration in 82%yield.

^{1}H NMR ($CF_3COOD/CDCl_3$, 300 MHz): δ (ppm) = 6.92 (m, 3H, Ar-H), 3.84 (s, 3H, OCH3), 3.11 (m, 2H, CH_2), 3.00 (m, 2H, CH_2).

^{13}C NMR ($CF_3COOD/CDCl_3$, 75 MHz): δ (ppm) = 175.4, 150.4, 140.0, 137.8, 122.6, 121.7, 113.3, 56.0, 35.7, 30.7.

2.25 *poly(3-(4-hydroxy-3-methoxyphenyl)propanoic acid)*



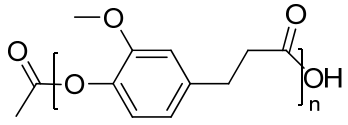
2.25

1.6 g (6.8 mmol) of **2.21** and 0.018 g (0.082 mmol) of zinc diacetate dihydrate were melted under nitrogen for 2h and vacuum was applied for 6h leaving a brown solid that was dissolved in a mixture of trifluoroacetic acid and dichloromethane and crashed with methanol. 1.1 g of beige product was obtained by filtration in 91%yield.

^{1}H NMR ($CF_3COOD/CDCl_3$, 300 MHz): δ (ppm) = 6.9 (m, 3H, Ar-H), 3.83 (s, 3H, OCH_3), 3.10 (m, 2H, CH_2), 2.99 (m, 2H, CH_2).

^{13}C NMR ($CF_3COOD/CDCl_3$, 75 MHz): δ (ppm) = 175.5, 150.4, 140.0, 137.7, 122.6, 121.1, 113.3, 56.0, 35.7, 30.7.

2.26 *poly(3-(4-hydroxy-3-methoxyphenyl)propanoic acid)*



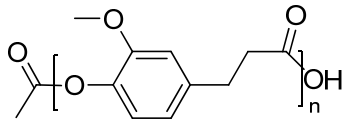
2.26

1.6 g (6.8 mmol) of **2.21** and 0.017 g (0.077 mmol) of zinc diacetate dihydrate were melted under nitrogen at 220-250°C for 2h and vacuum was applied for 6h leaving a brown solid that was dissolved in a mixture of trifluoroacetic acid and dichloromethane and crashed with methanol. 0.82 g of beige product was obtained by filtration in 68%yield.

^{1}H NMR ($CF_3COOD/CDCl_3$, 300 MHz): δ (ppm) = 6.88 (m, 3H, Ar-H), 3.8 (s, 3H, OCH_3), 3.07 (m, 2H, CH_2), 2.96 (m, 2H, CH_2).

^{13}C NMR ($CF_3COOD/CDCl_3$, 75 MHz): δ (ppm) = 175.0, 150.4, 139.8, 137.7, 122.5, 121.0, 113.1, 56.0, 35.7, 30.7.

2.27 *poly(3-(4-hydroxy-3-methoxyphenyl)propanoic acid)*



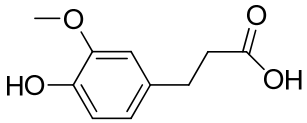
2.27

1.6 g (6.8 mmol) of **2.21** and 0.017 g (0.077 mmol) of zinc diacetate dihydrate were melted under nitrogen for 2h and vacuum was applied for 10min leaving a brown solid that was dissolved in a mixture of trifluoroacetic acid and dichloromethane and crashed with methanol. 0.9 g of beige product was obtained by filtration in 75%yield.

^{1}H NMR ($CF_3COOD/CDCl_3$, 300 MHz): δ (ppm) = 6.88 (m, 3H, Ar-H), 3.8 (s, 3H, OCH_3), 3.07 (m, 2H, CH_2), 2.96 (m, 2H, CH_2).

^{13}C NMR ($CF_3COOD/CDCl_3$, 75 MHz): δ (ppm) = 176.0, 150.5, 140.4, 138.0, 122.8, 121.6, 113.7, 56.2, 35.9, 30.9.

2.28 *3-(4-hydroxy-3-methoxyphenyl)propanoic acid*



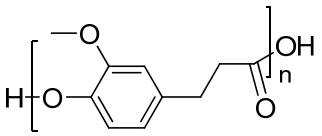
2.28

8.0 g (0.034 mol) of **3.5** and 4.7 g (0.118 mol) of sodium hydroxide were dissolved in 100 mL of water. The solution was refluxed for 5h. After cooling to room temperature the aqueous solution was acidified with hydrochloric acid and extracted with dichloromethane. The organic layer was washed with brine and dried over magnesium sulfate. The evaporation of the solvent left a yellow crude product that was dissolved in dichloromethane and crashed with excess of hexanes. The work up gave 5.5 g of a beige powder in 83% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 6.97 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.73 (br. s, 1H, Ar. H), 6.71 (d, *J* = 1.9 Hz, 1H, Ar-H), 3.88 (s, 3H, OCH_3), 2.90 (t, *J* = 7.8 Hz, 2H, Ar-CH_2), 2.70 (t, *J* = 7.8 Hz, 2H, CH_2COOH).

^{13}C NMR ($CDCl_3$, 75MHz): δ (ppm) = 179.2, 146.4, 144.1, 132.0, 120.8, 114.4, 110.9, 55.8, 36.0, 30.3.

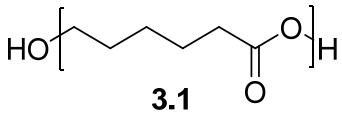
2.29 *Poly(3-(4-hydroxy-3-methoxyphenyl)propanoic acid)*



2.29

1.6 g (8.2 mmol) and 0.0195g (0.067 mmol) of antimony trioxide were heated under nitrogen for 5h and vacuum was applied for 6h. At the end of the 6h the product was still a brown melt in the flask. The product was dissolved in dichloromethane and trifluoroacetic acid and only 0.07 g of product crashed out of methanol in a 5% yield. The methanol was rotovaped leaving 1.5 g of brown solid that was analyzed by GPC showing low molecular weight material.

3.1 *polycaprolactone*

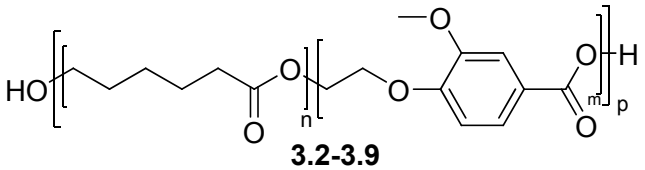


3.1

3.0 g (26 mmol) of caprolactone and 0.083 g (0.29 mmol) of $Ti(OiPr)_4$ were heated at 80°C for 1h under nitrogen and then the temperature was slowly raised to 150°C. The reaction was left 18h until stirring stopped. The orange solid was dissolved in chloroform and crashed in methanol giving 2.2 g, yield of 79%.

^{1}H NMR (300MHz, $CDCl_3$) in ppm: δ (ppm) = 4.05 (t, *J* = 6.7Hz, 2H, $COOCH_2$), 2.3 (t, *J* = 7.5 Hz, 2H, CH_2COO), 1.64 (m, 4H, $COOCH_2C\mathbf{H}_2$, $C\mathbf{H}_2CH_2COO$), 1.38 (m, 2H, $C\mathbf{H}_2CH_2CH_2O$).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 173.5, 64.1, 34.1, 28.3, 25.5, 24.5.



3.2-3.9

3.2 *Copoly [caprolactone-4-(2-hydroxyethoxy)-3-methoxybenzoic acid] 90/10*

To 0.62 g (2.9 mmol) of 4-(2-hydroxyethoxy)-3-methoxybenzoic acid were added 3.02g (26 mmol) of caprolactone and 0.08 g(0.28 mmol) of $Ti(OiPr)_4$. The mixture was melted at about 150°C under nitrogen and left to stir for 1h. Vacuum was applied for 2h until stirring stopped. The solid/gel was dissolved in chloroform and crashed out with methanol giving 2.7 g of polymer in 80% yield.

3.3 *Copoly[caprolactone-4-(2-hydroxyethoxy)-3-methoxybenzoic acid] 80/20*

To 1.0 g (4.8 mmol) of 4-(2-hydroxyethoxy)-3-methoxybenzoic acid were added 2.18 g (19 mmol) of caprolactone and 0.08 g (0.28 mmol) of $Ti(OiPr)_4$. The mixture was melted at about 150°C under nitrogen and left to stir for 1h. Vacuum was applied for 6h until stirring stopped. The solid/gel was dissolved in chloroform and was crashed with methanol giving 2.1 g of polymer in 67% yield.

3.4 *Copoly[caprolactone-4-(2-hydroxyethoxy)-3-methoxybenzoic acid] 70/30*

To 1.5 g (7.1 mmol) of 4-(2-hydroxyethoxy)-3-methoxybenzoic acid were added 1.9 g (16.7 mmol) of caprolactone and 0.07 g (0.24 mmol) of $Ti(OiPr)_4$. The mixture was melted at about 150°C under nitrogen and left to stir for 1h. Vacuum was applied for 6h until stirring stopped. The solid/gel was dissolved in chloroform and crashed out with methanol giving 2.2 g of powder in 68% yield.

3.5 *Copoly[caprolactone-4-(2-hydroxyethoxy)-3-methoxybenzoic acid] 60/40*

To 1.5 g (7.1 mmol) of 4-(2-hydroxyethoxy)-3-methoxybenzoic acid were added 1.2 g (10.5 mmol) of caprolactone and 0.05 g (0.18 mmol) of $Ti(OiPr)_4$. The mixture was

melted at about 150°C under nitrogen and left to stir for 1h. Vacuum was applied for 6h until stirring stopped. The solid/gel was dissolved in chloroform and crashed out with methanol giving 1.74 g of powder in 67% yield.

3.6 *Copoly[caprolactone-4-(2-hydroxyethoxy)-3-methoxybenzoic acid] 40/60*

To 1.5 g (7.1 mmol) of 4-(2-hydroxyethoxy)-3-methoxybenzoic acid were added 0.81 g (7.1 mmol) of caprolactone and 0.05 g (0.18 mmol) of $Ti(OiPr)_4$. The mixture was melted at about 150°C under nitrogen and left to stir for 1h. Temperature was raised to 200°C and Vacuum was applied for 3h until stirring stopped. The solid/gel was dissolved in a mixture of chloroform and trifluoroacetic acid and crashed out with methanol giving 1.54 g of powder in 67% yield.

3.7 *Copoly[caprolactone-4-(2-hydroxyethoxy)-3-methoxybenzoic acid] 30/70*

To 2.5 g (11.8 mmol) of 4-(2-hydroxyethoxy)-3-methoxybenzoic acid were added 0.59 g (5.2 mmol) of caprolactone and 0.05 g (0.18 mmol) of $Ti(OiPr)_4$. The mixture was melted at about 150°C under nitrogen and left to stir for 1h. Temperature was raised to 200°C and vacuum was applied for 3h until stirring stopped. The solid/gel was dissolved in a mixture of chloroform and trifluoroacetic acid and crashed out with methanol giving 2.2 g of powder in 77% yield.

3.8 *Copoly[caprolactone-4-(2-hydroxyethoxy)-3-methoxybenzoic acid] 20/80*

To 3.0 g (14.2 mmol) of 4-(2-hydroxyethoxy)-3-methoxybenzoic acid were added 0.45 g (3.9 mmol) of caprolactone and 0.064 g (0.23 mmol) of $Ti(OiPr)_4$. The mixture was melted at about 200°C under nitrogen and left to stir for 1h. Temperature was raised to 250°C and vacuum was applied for 3h until stirring stopped. The solid/gel was dissolved in a mixture of chloroform and trifluoroacetic acid and crashed out with methanol giving 2.2 g of beige powder in 69% yield.

3.9 *Copoly[caprolactone-4-(2-hydroxyethoxy)-3-methoxybenzoic acid] 10/90*

To 2.5 g (11.8 mmol) of 4-(2-hydroxyethoxy)-3-methoxybenzoic acid were added 0.16 g (1.4 mmol) of caprolactone and 0.05 g (0.18 mmol) of $Ti(OiPr)_4$. The mixture was melted at about 200°C under nitrogen and left to stir for 1h. Temperature was raised to 250°C and vacuum was applied for 2h until stirring stopped. The solid/gel was dissolved in a mixture of chloroform and trifluoroacetic acid and crashed out with methanol giving 1.85 g of beige powder in 76% yield.

APPENDIX A
PROTON AND CARBON NMR

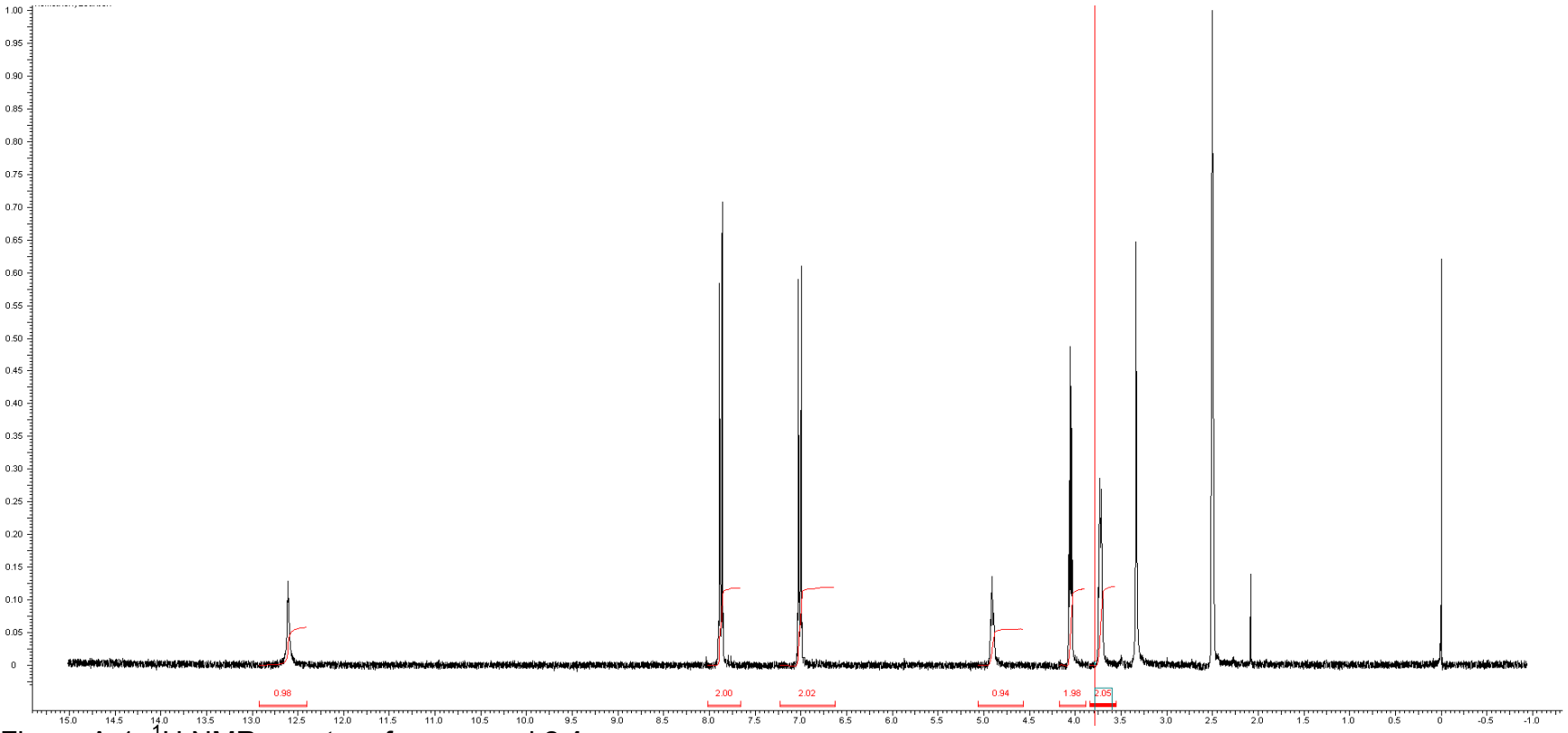


Figure A-1. ^{1}H NMR spectra of compound **2.1**

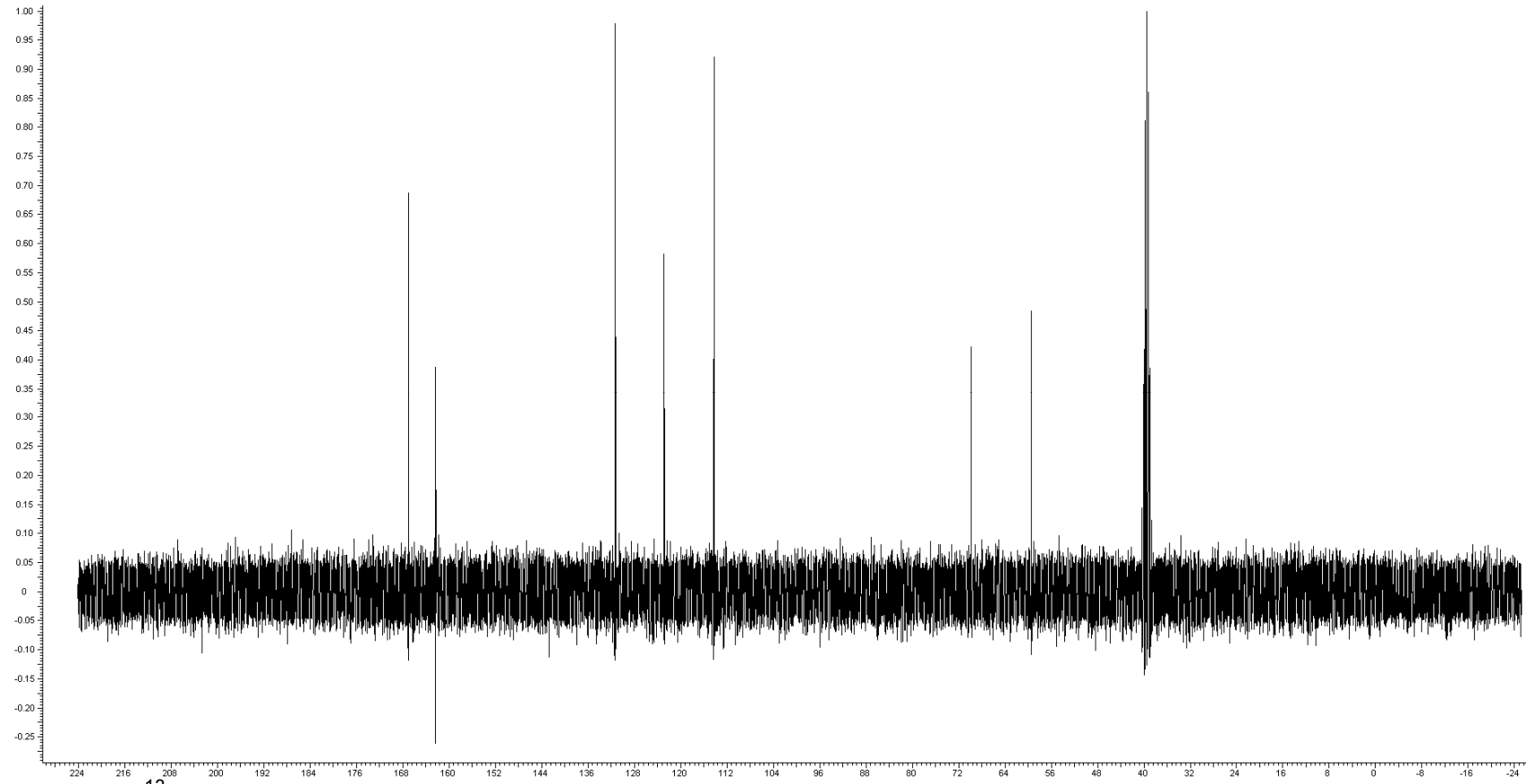


Figure A-2. ^{13}C NMR spectra of compound **2.1**

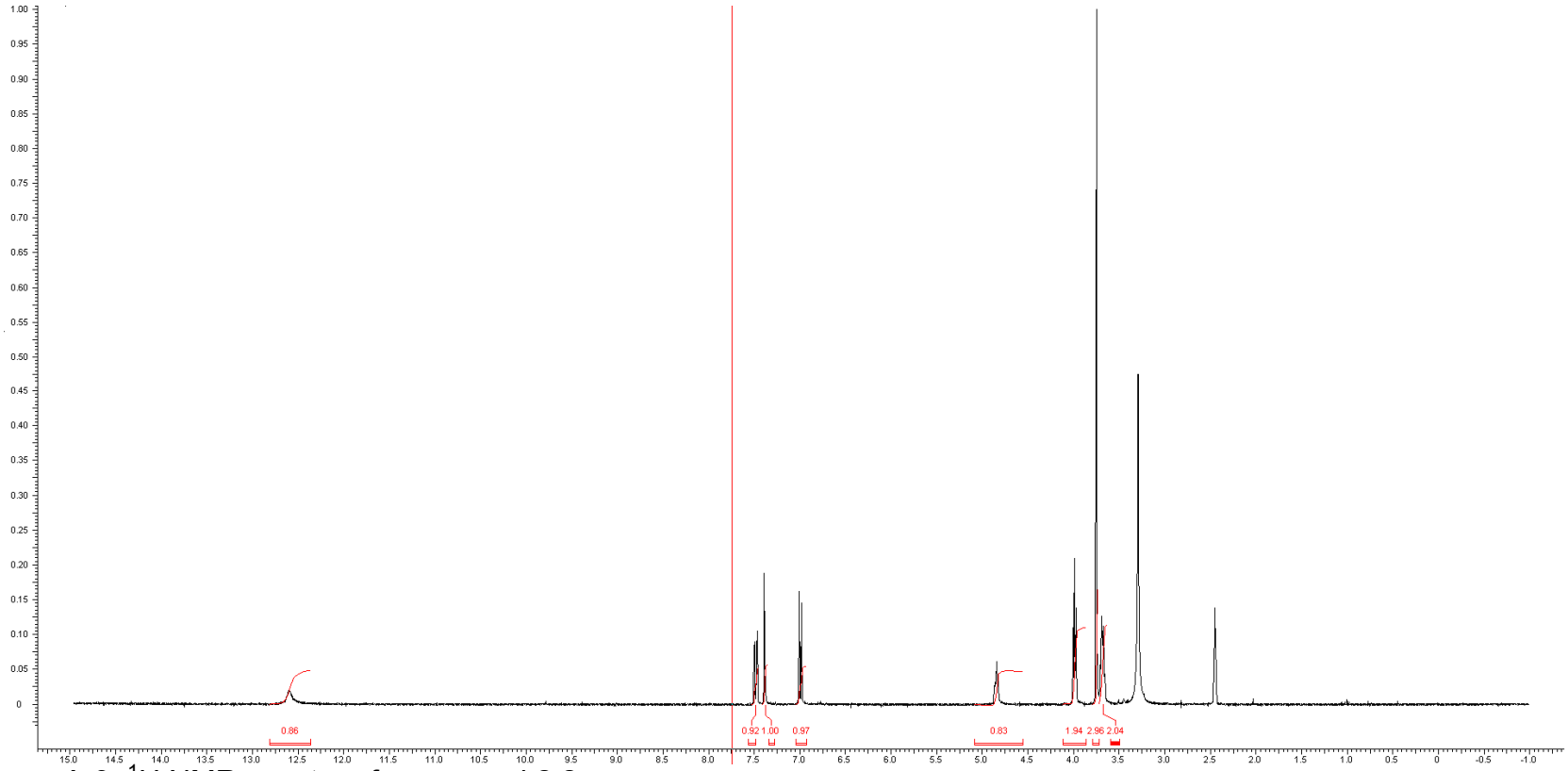


Figure A-3. ^{1}H NMR spectra of compound **2.2**

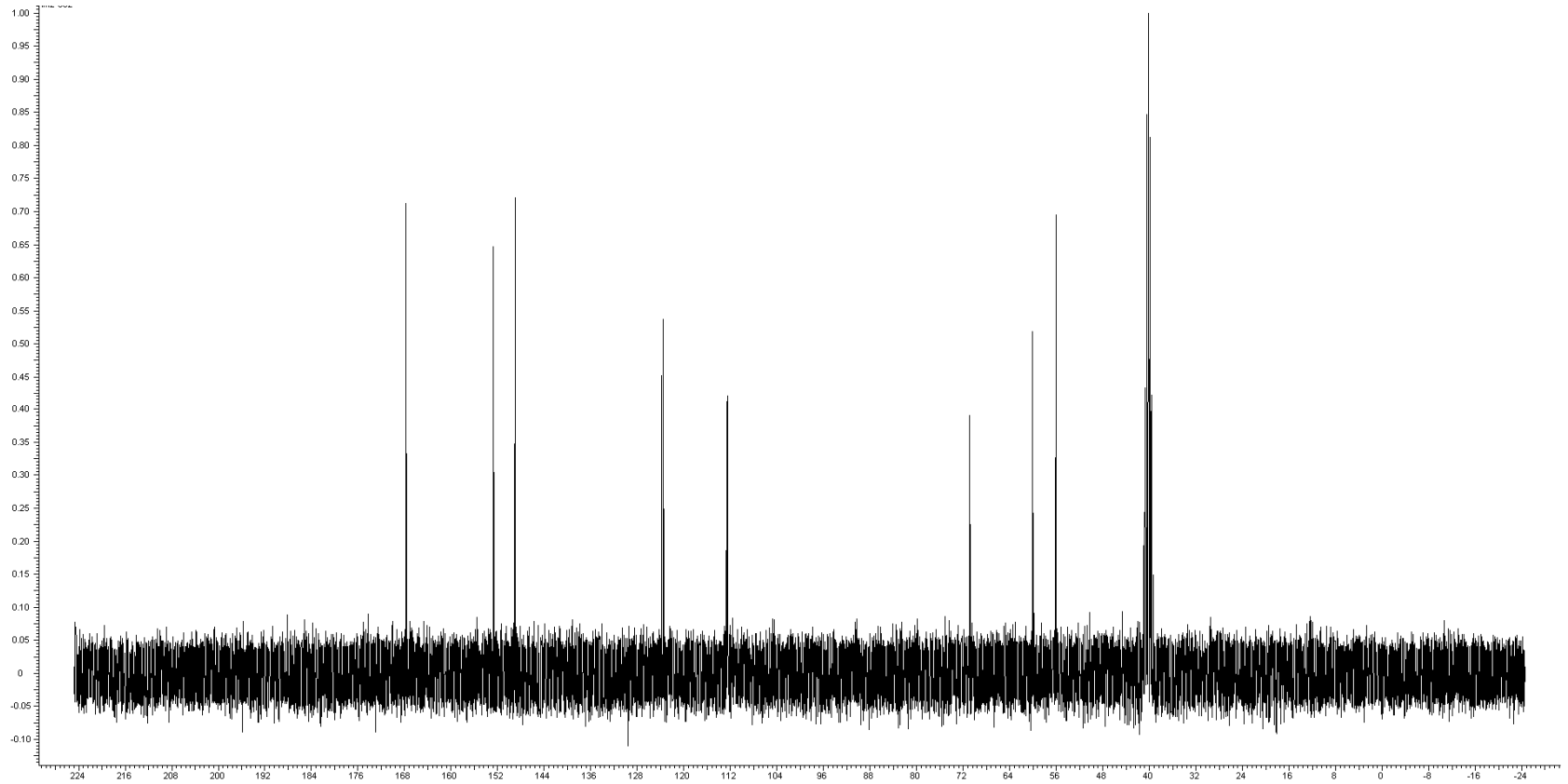


Figure A-4. ^{13}C NMR spectra of compound **2.2**

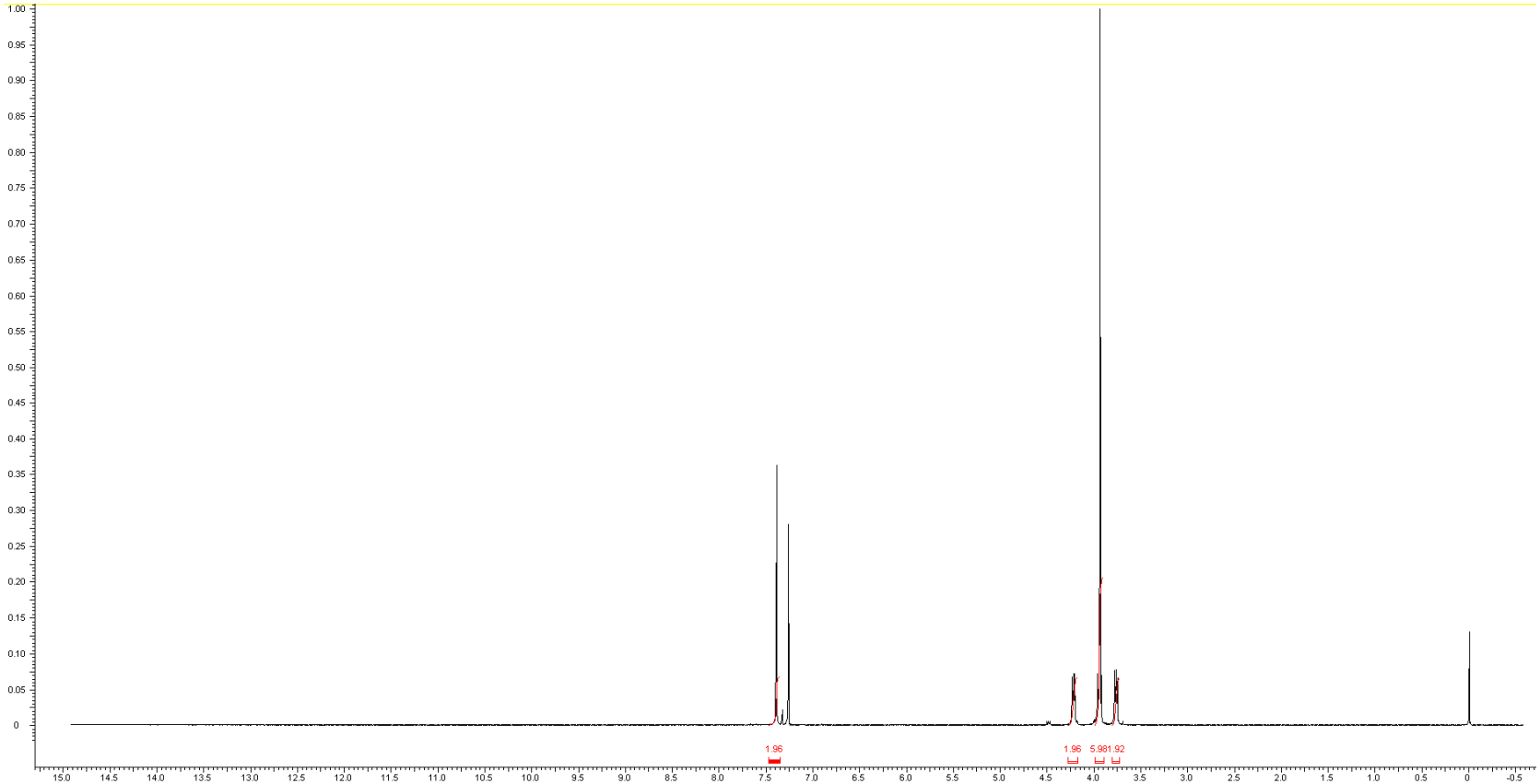


Figure A-5. ^{1}H NMR spectra of compound **2.3**

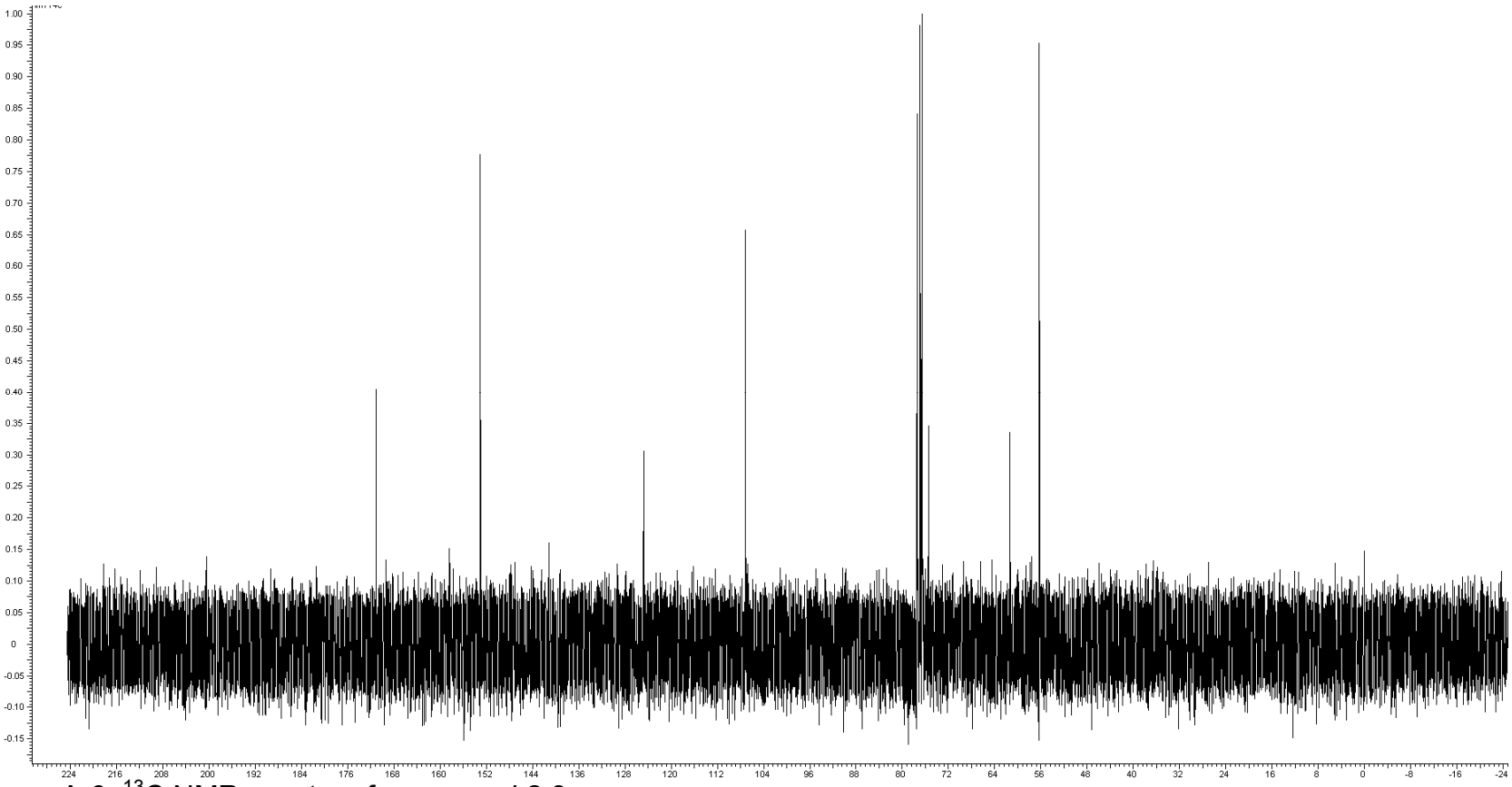


Figure A-6. ^{13}C NMR spectra of compound **2.3**

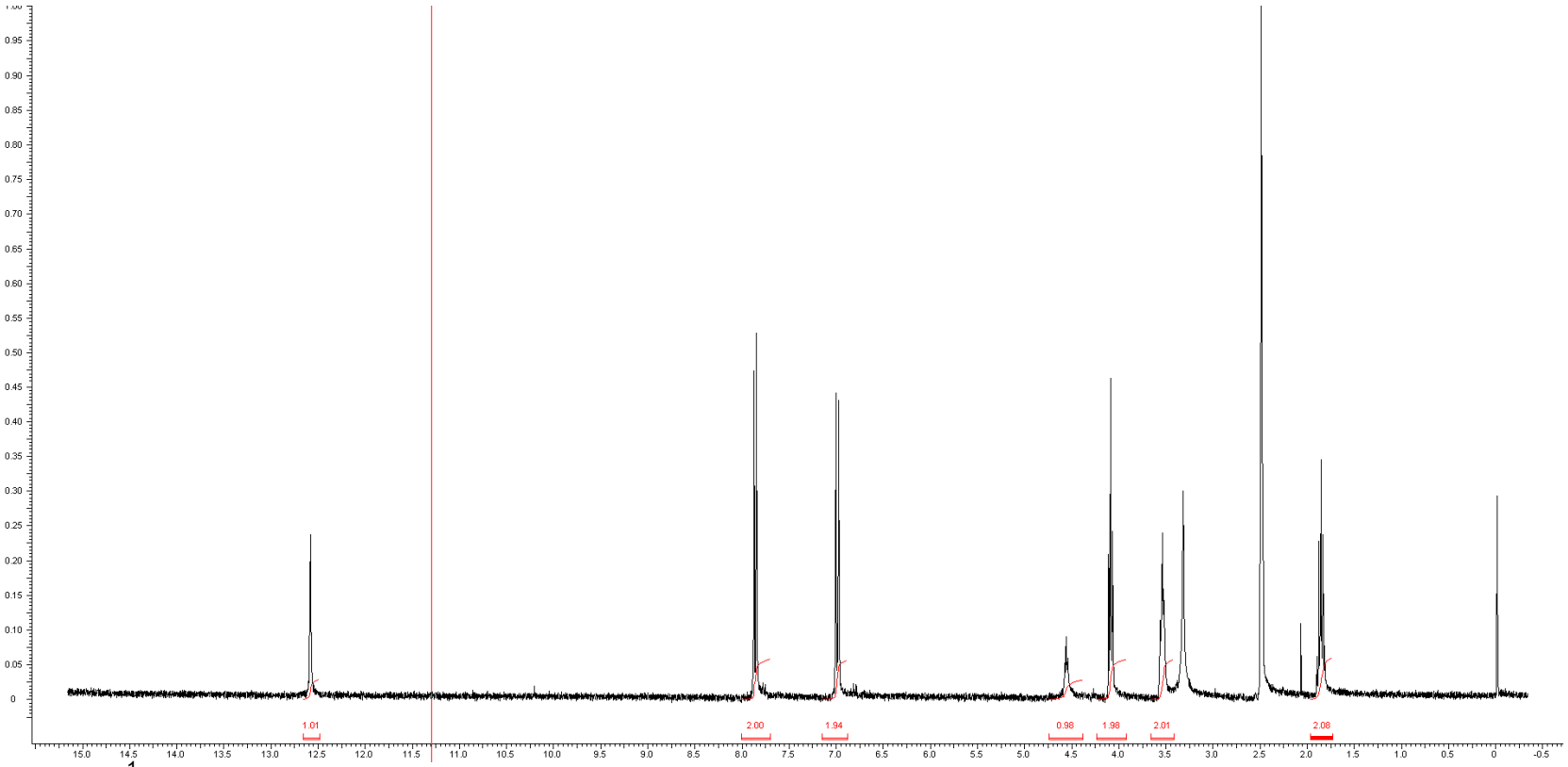


Figure A-7. ^{1}H NMR spectra of compound **2.4**

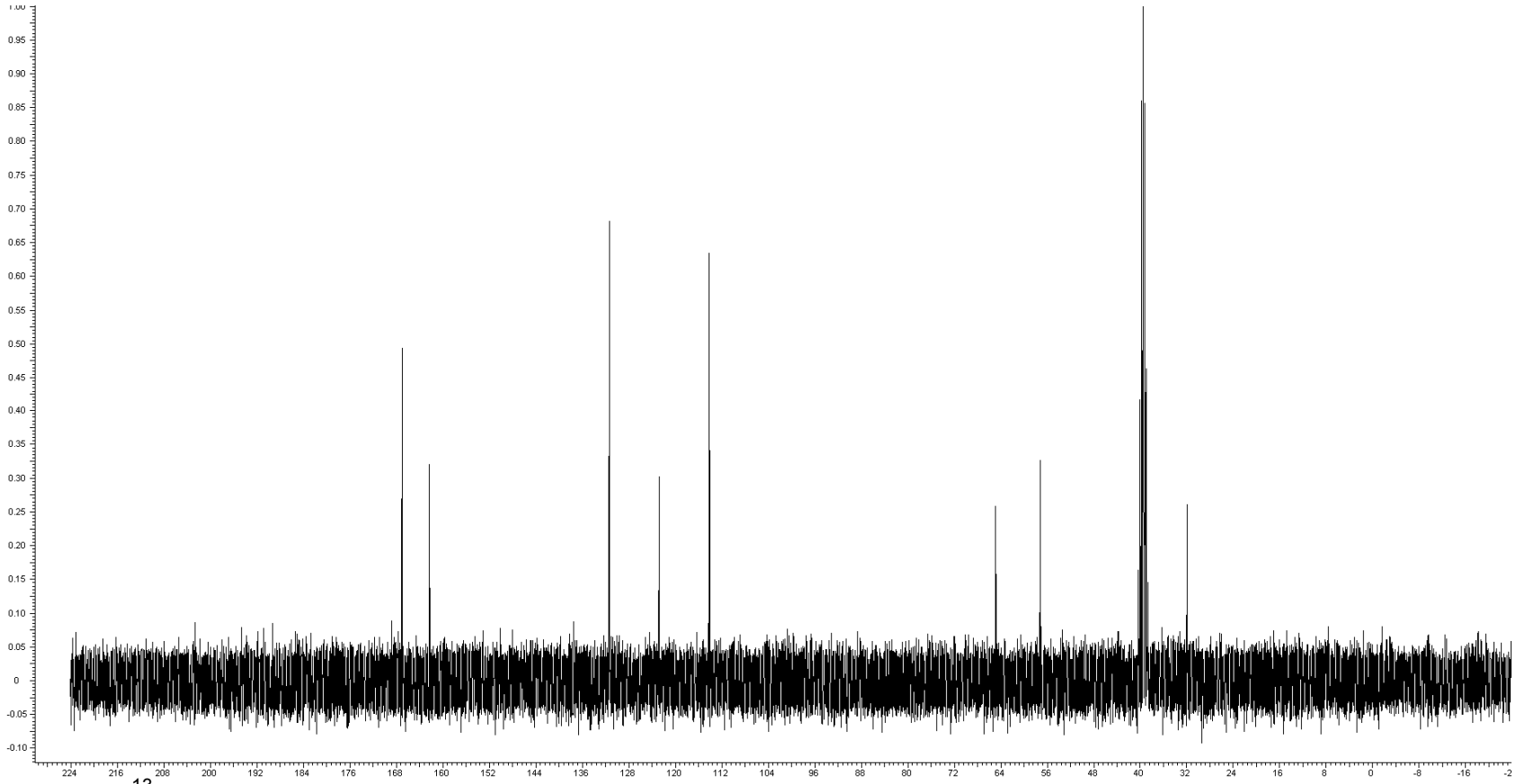


Figure A-8. ^{13}C NMR spectra of compound **2.4**

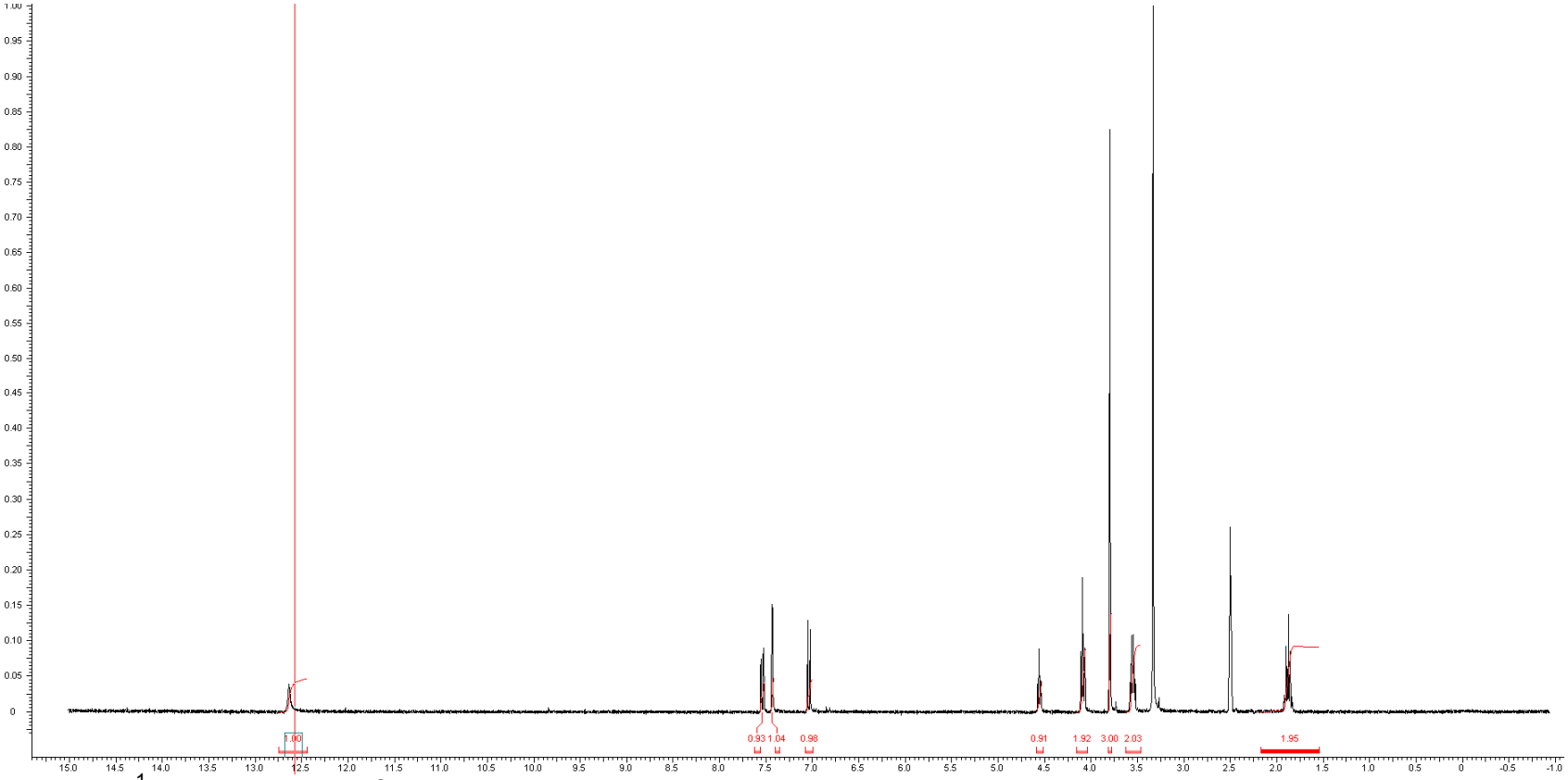


Figure A-9. ^{1}H NMR spectra of compound **2.5**

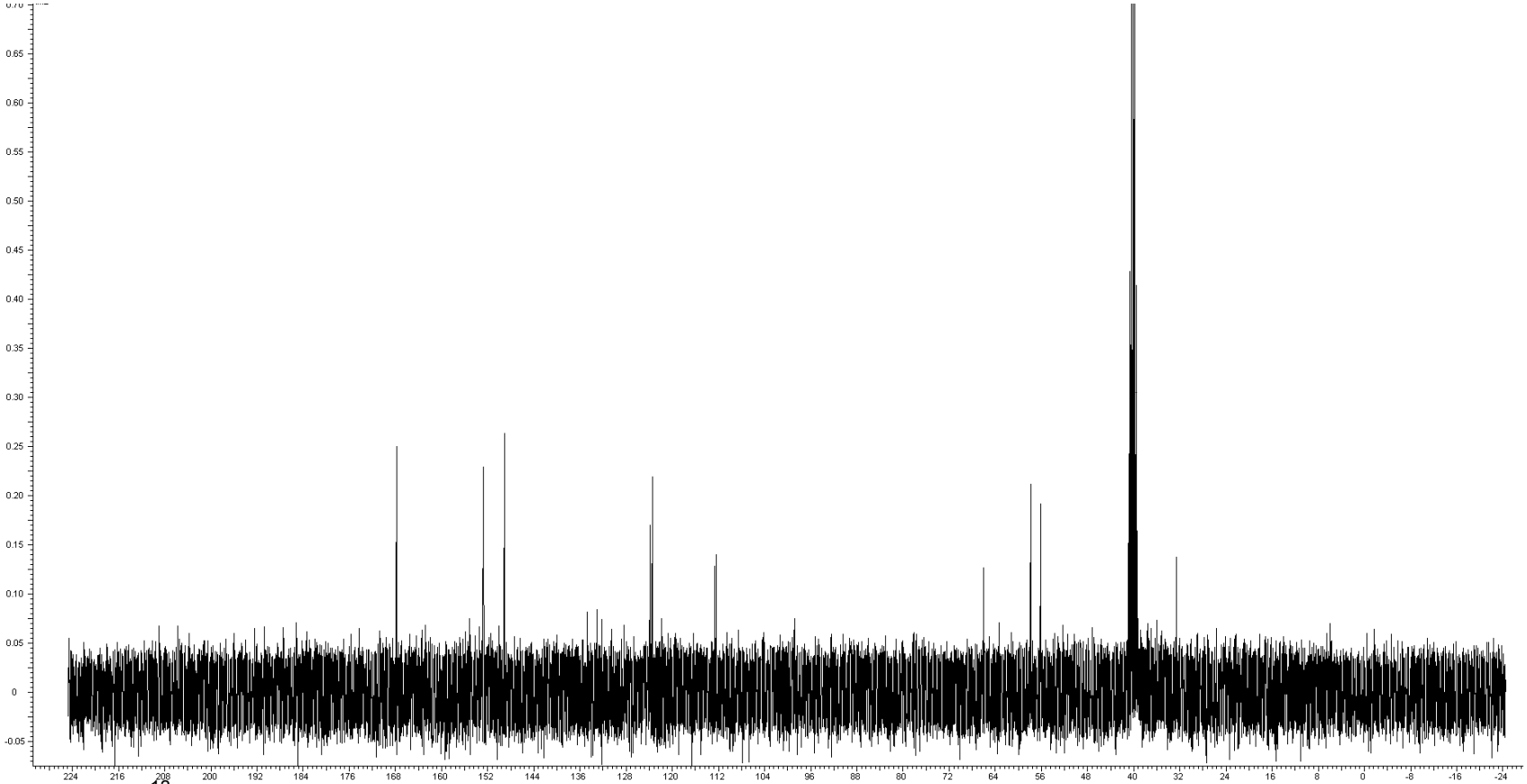


Figure A-10. ^{13}C NMR spectra of compound **2.5**

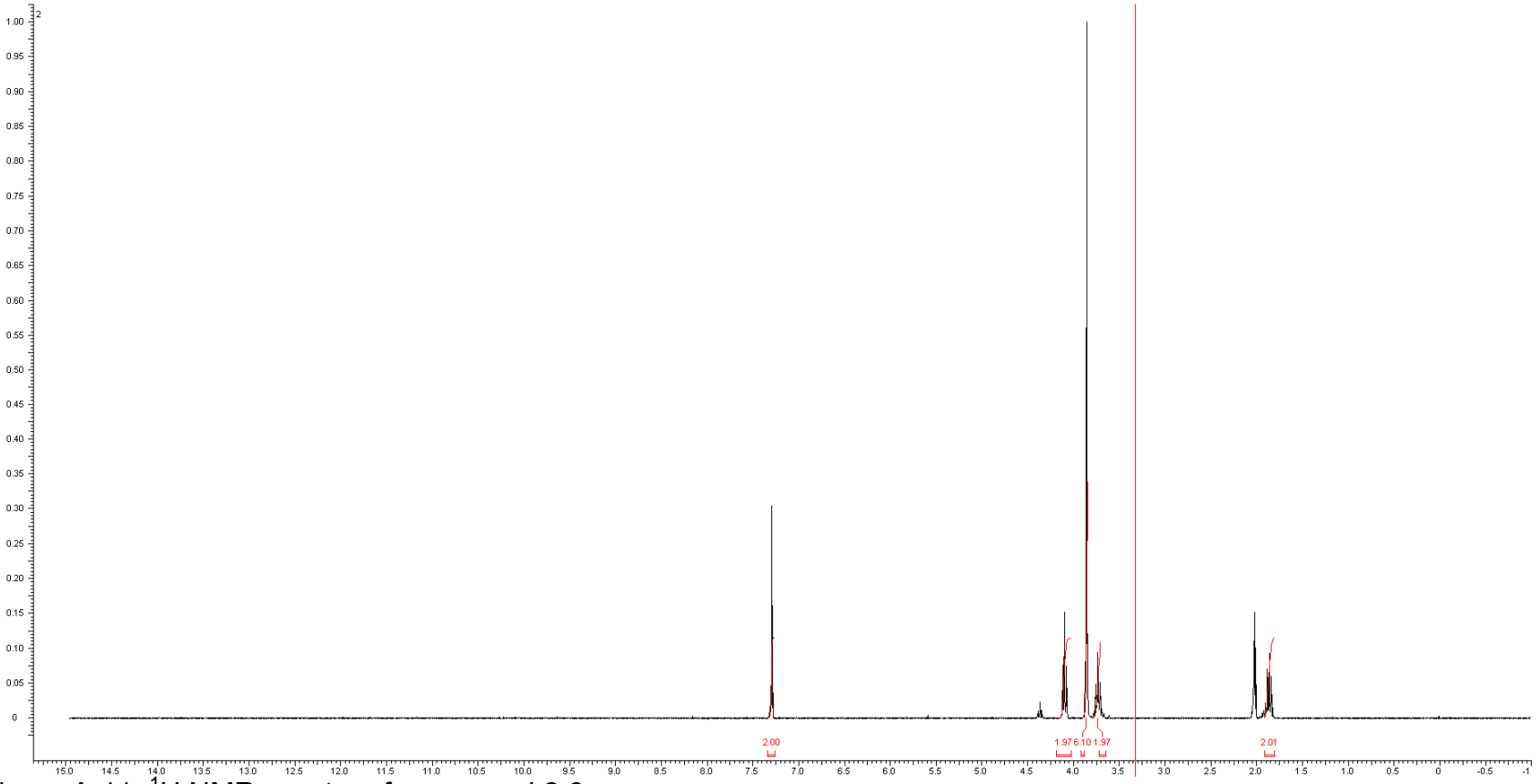


Figure A-11. ^{1}H NMR spectra of compound **2.6**

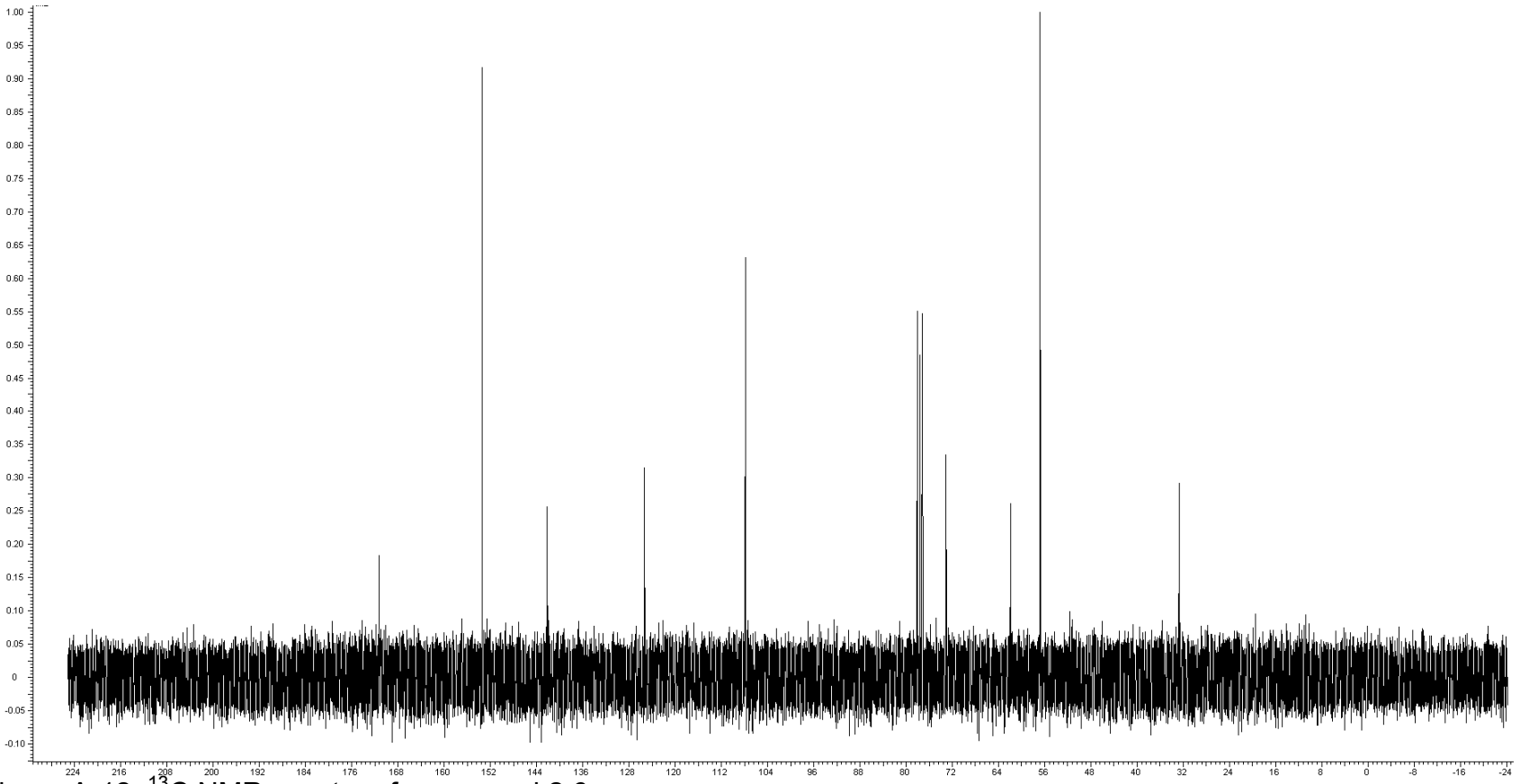


Figure A-12. ^{13}C NMR spectra of compound **2.6**

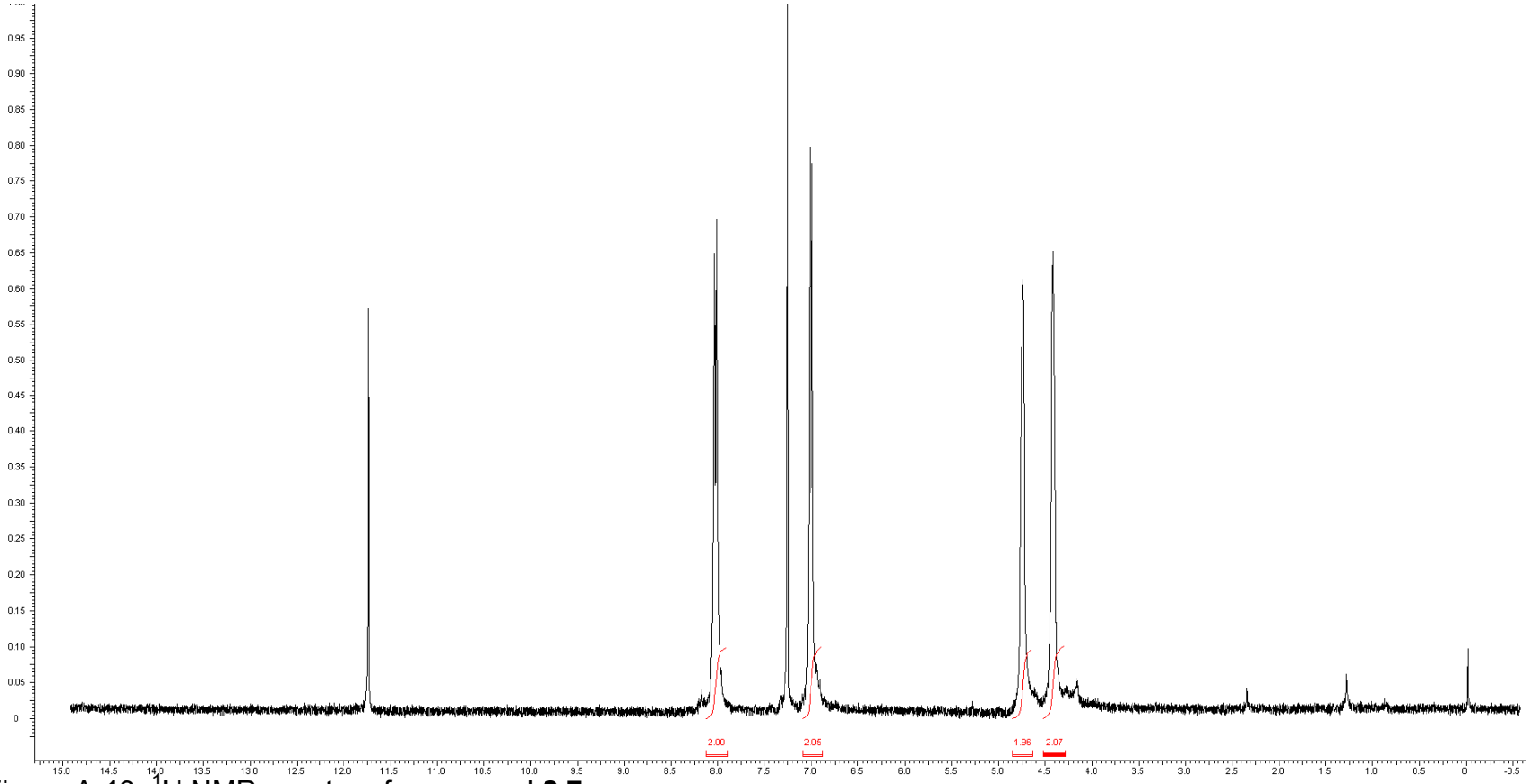


Figure A-13. ^{1}H NMR spectra of compound **2.7**

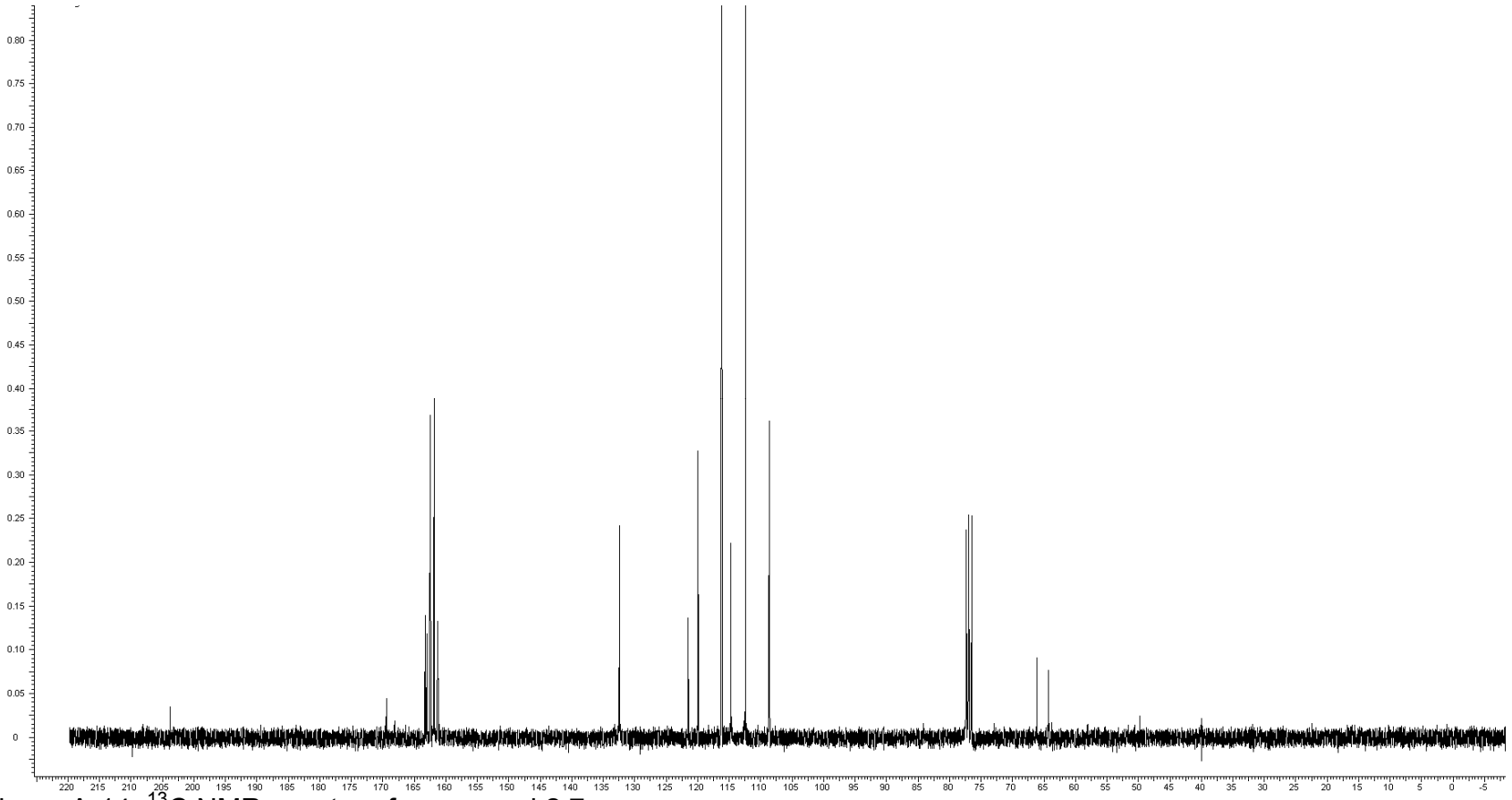


Figure A-14. ^{13}C NMR spectra of compound **2.7**

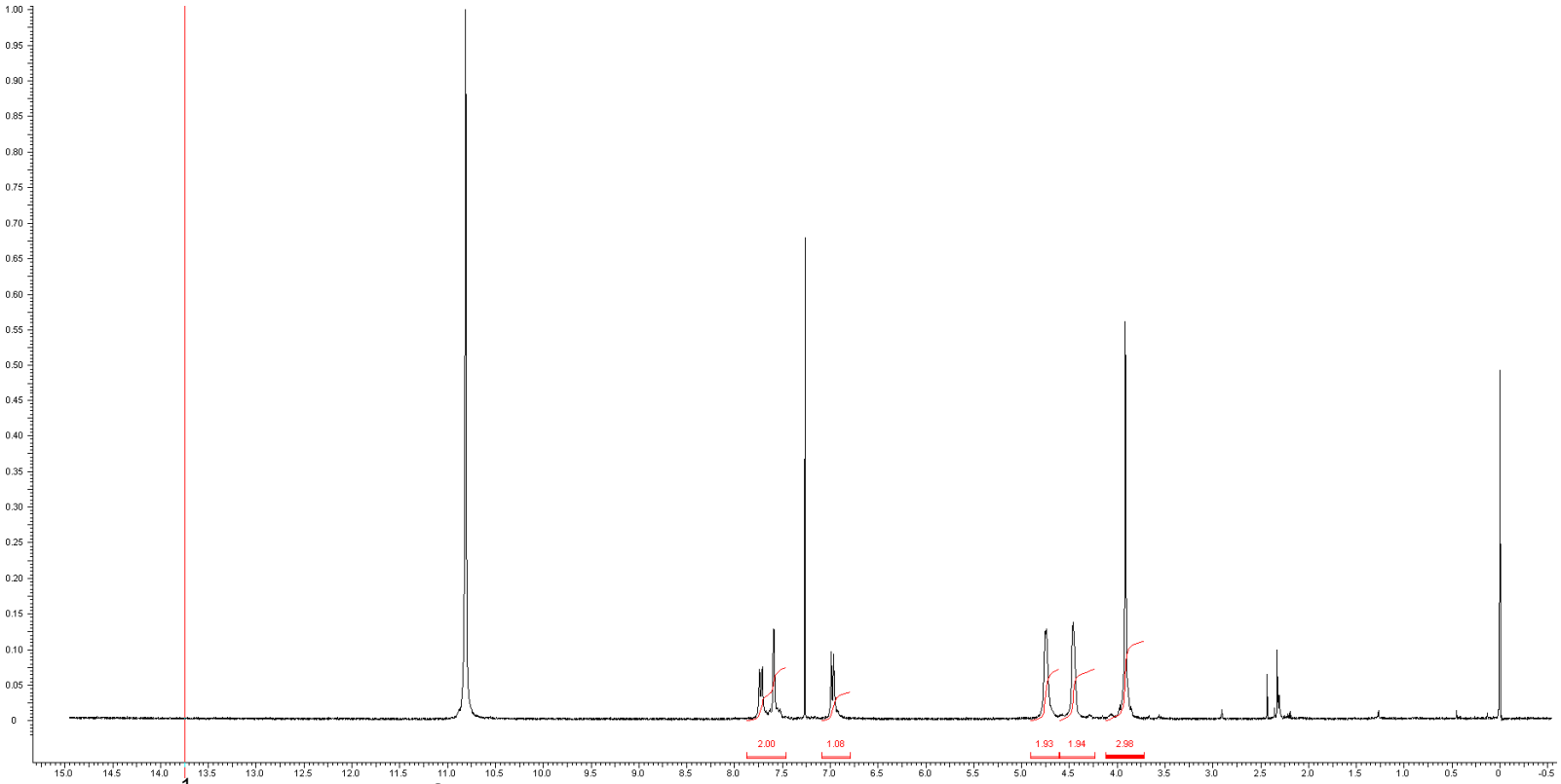


Figure A-15. ^{1}H NMR spectra of compound **2.8**

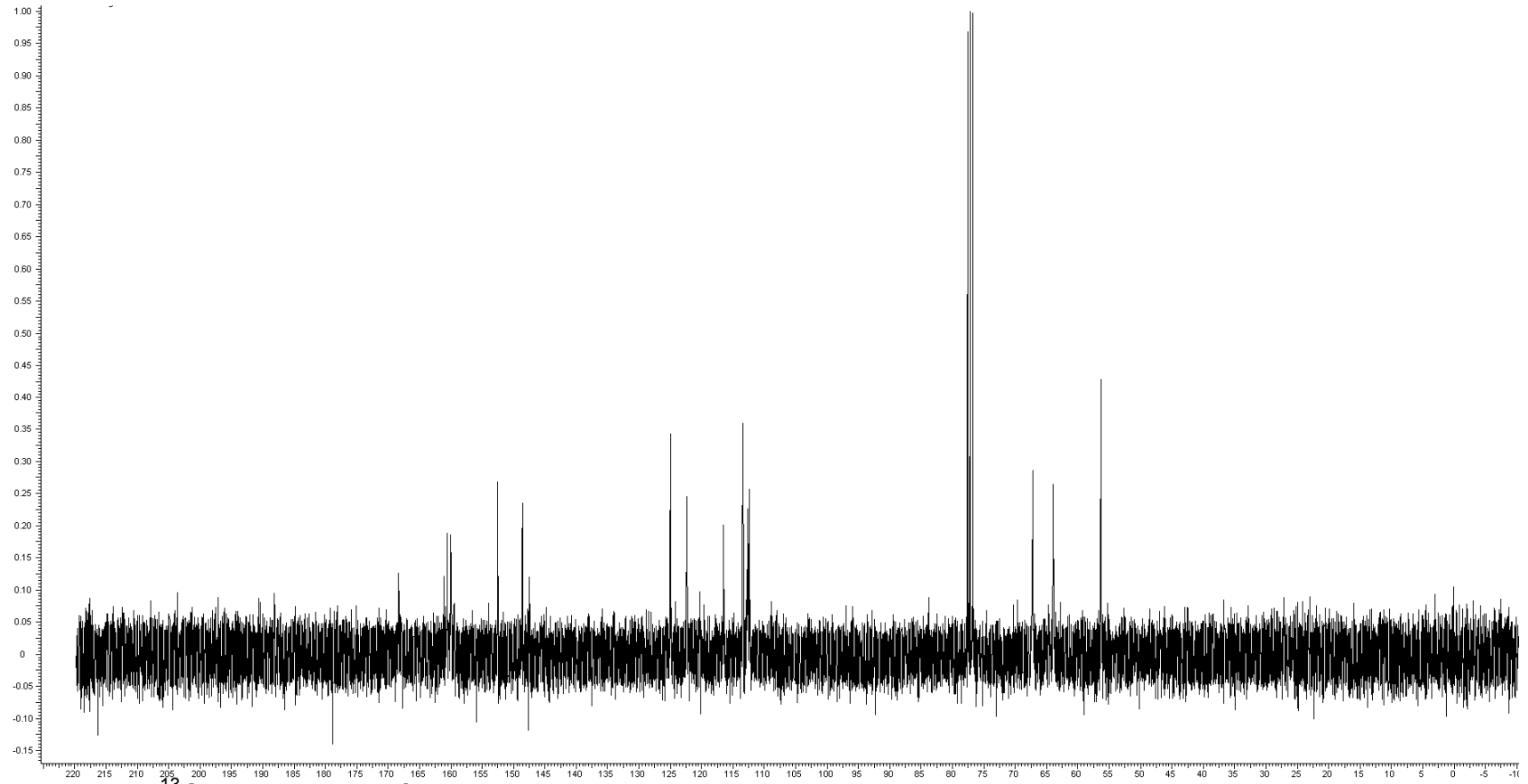


Figure A-16. ^{13}C NMR spectra of compound **2.8**

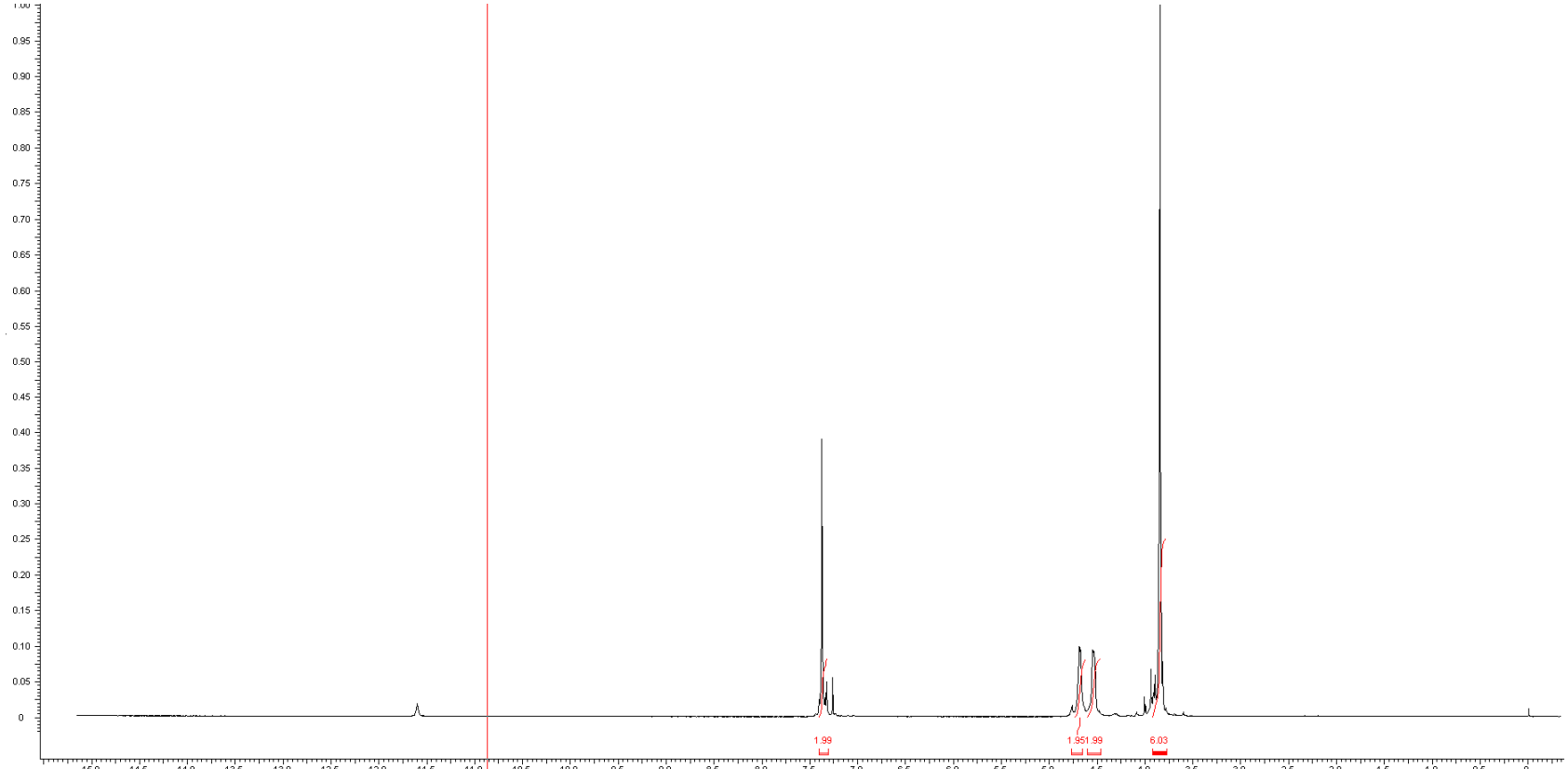


Figure A-17. ^{1}H NMR spectra of compound **2.9**

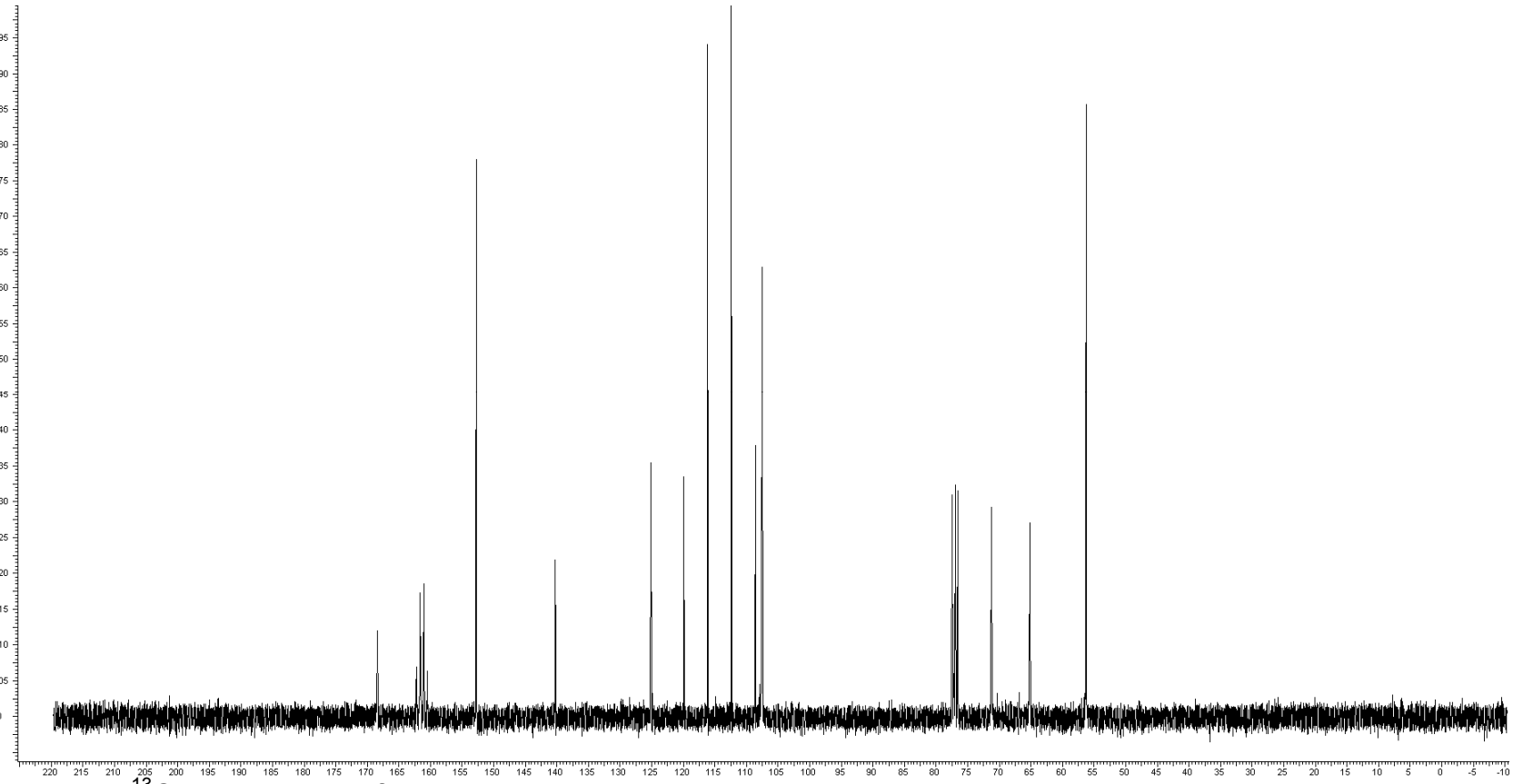


Figure A-18. ^{13}C NMR spectra of compound **2.9**

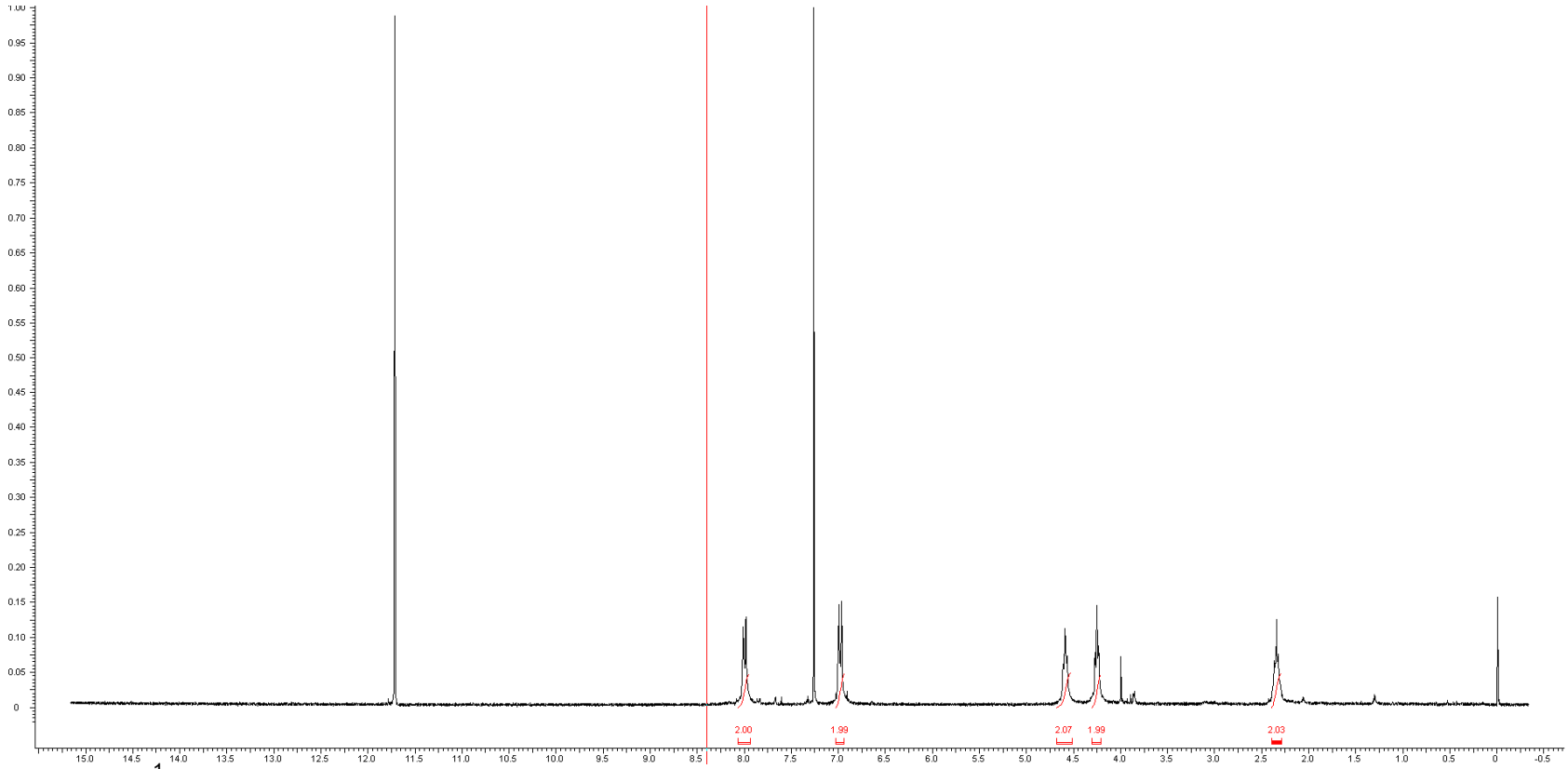


Figure A-19. ^{1}H NMR spectra of compound **2.10**

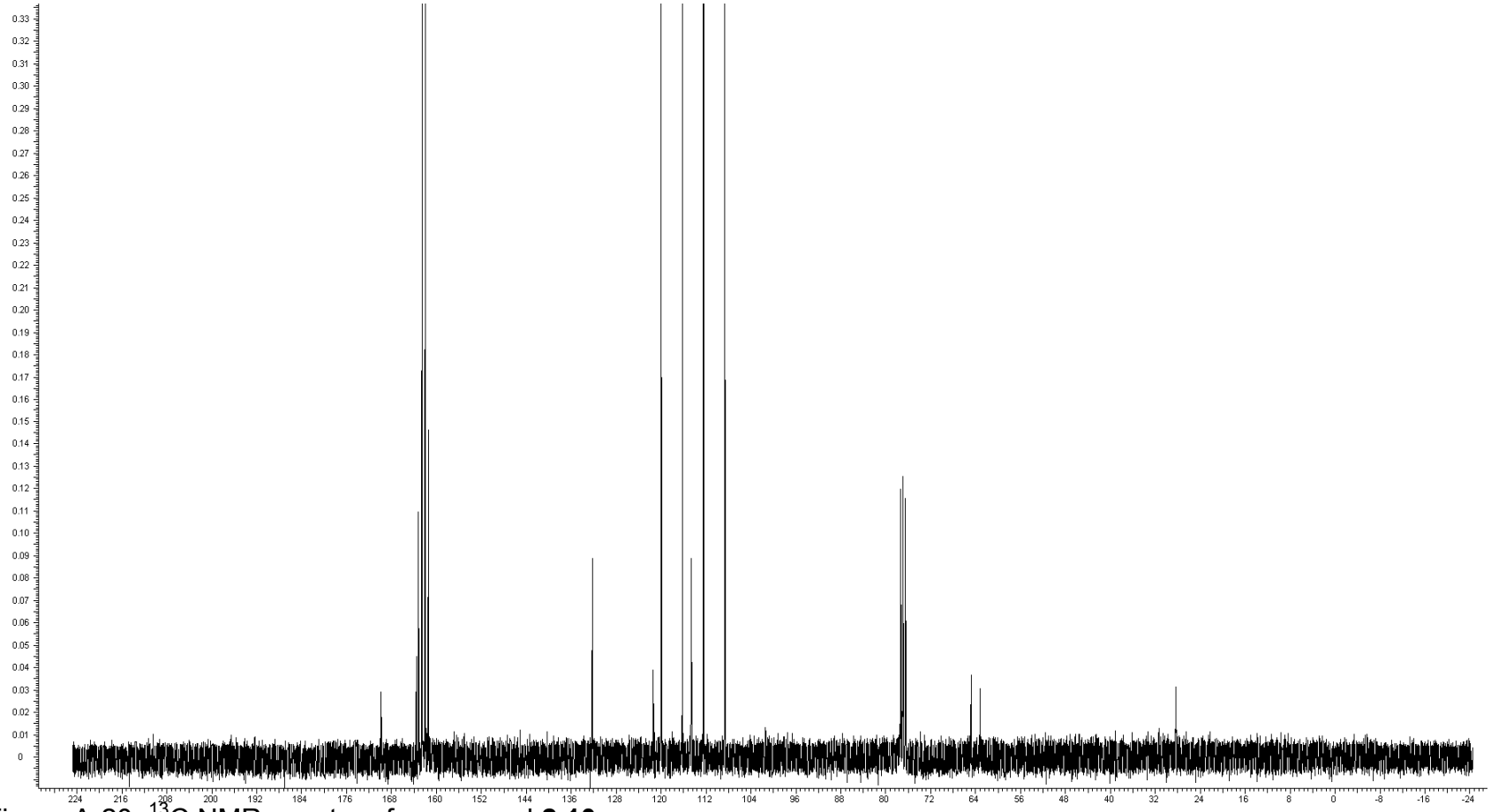


Figure A-20. ^{13}C NMR spectra of compound **2.10**

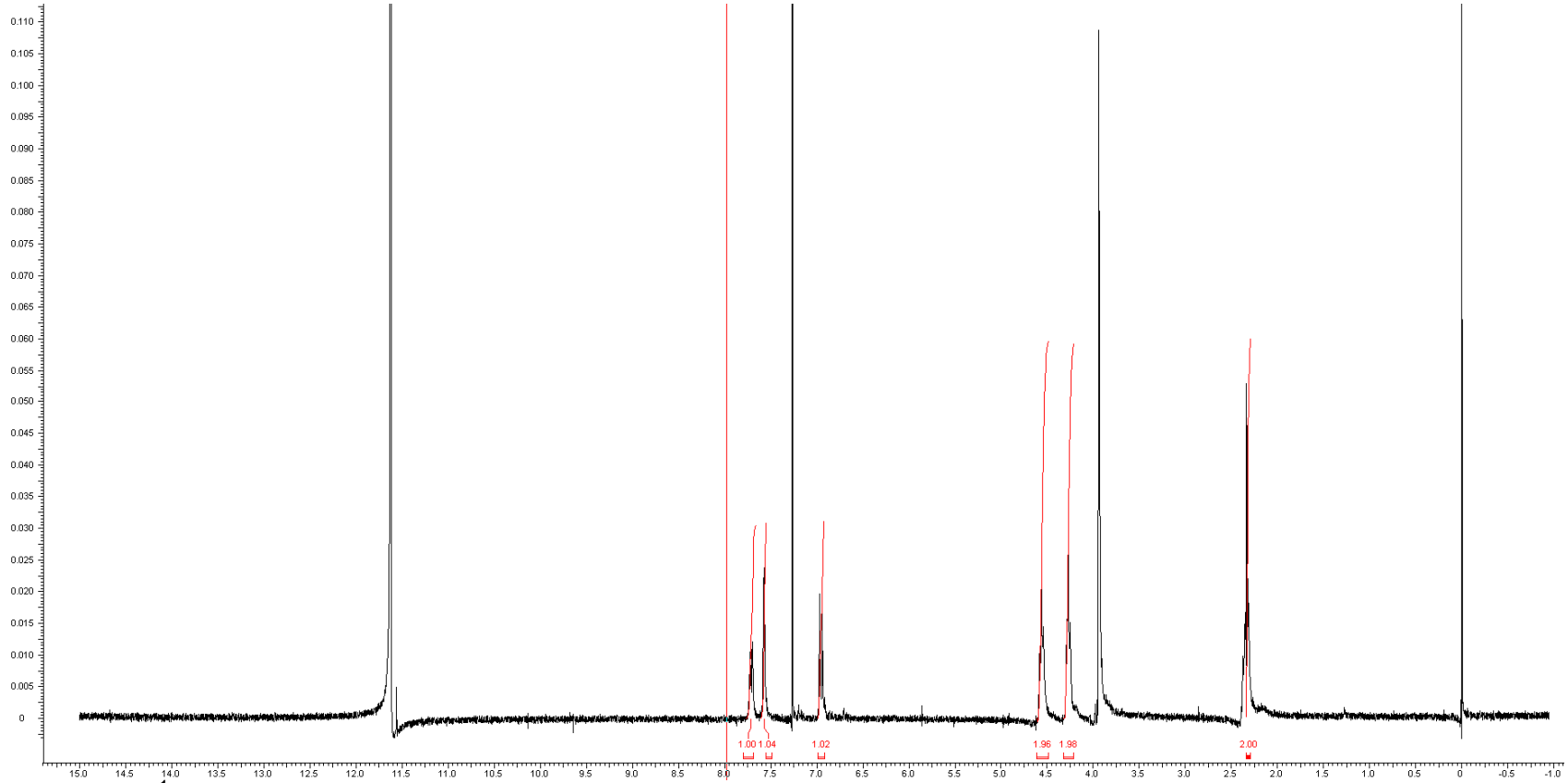


Figure A-21. ^{1}H NMR spectra of compound **2.11**

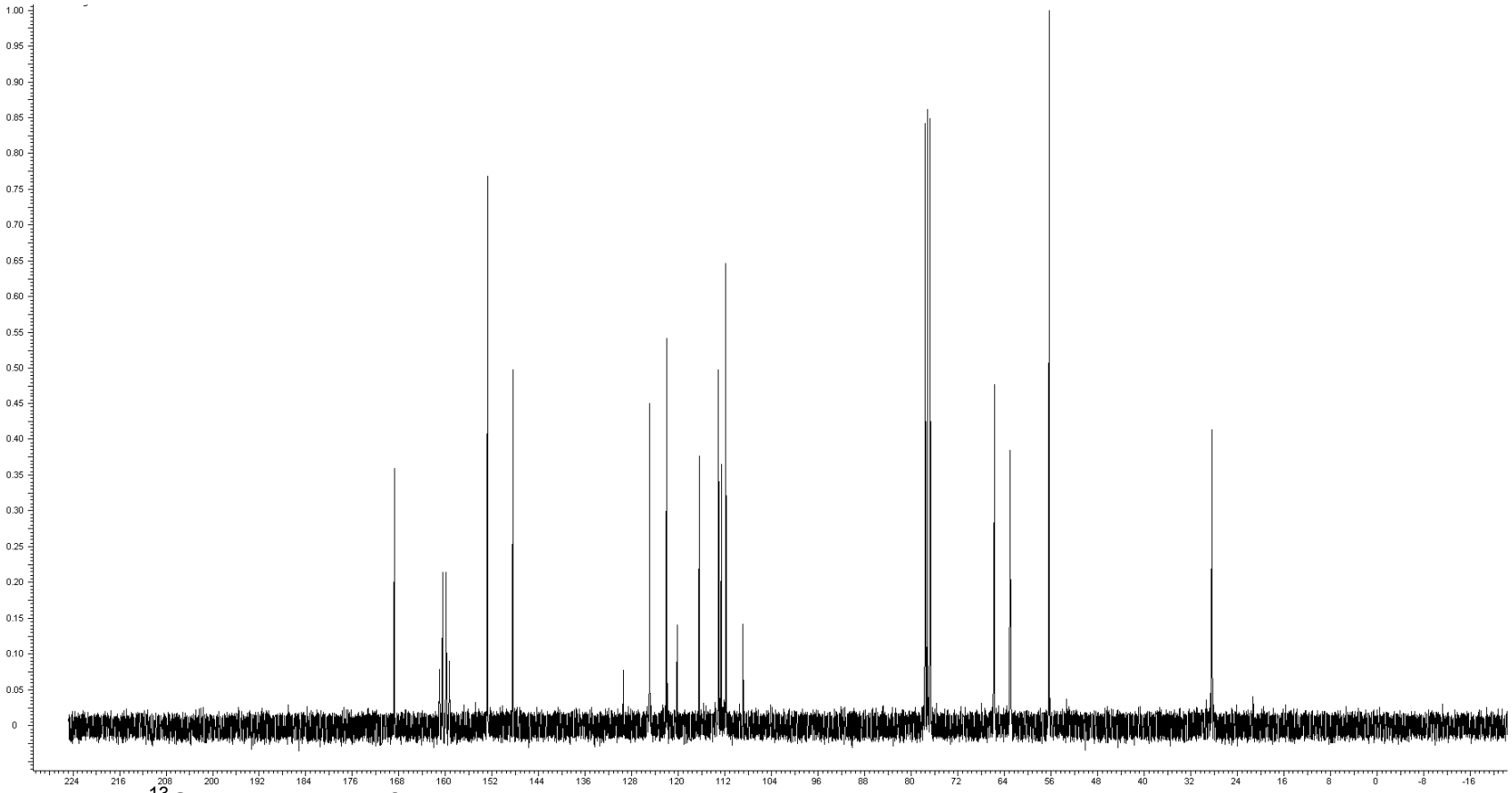


Figure A-22. ^{13}C NMR spectra of compound **2.11**

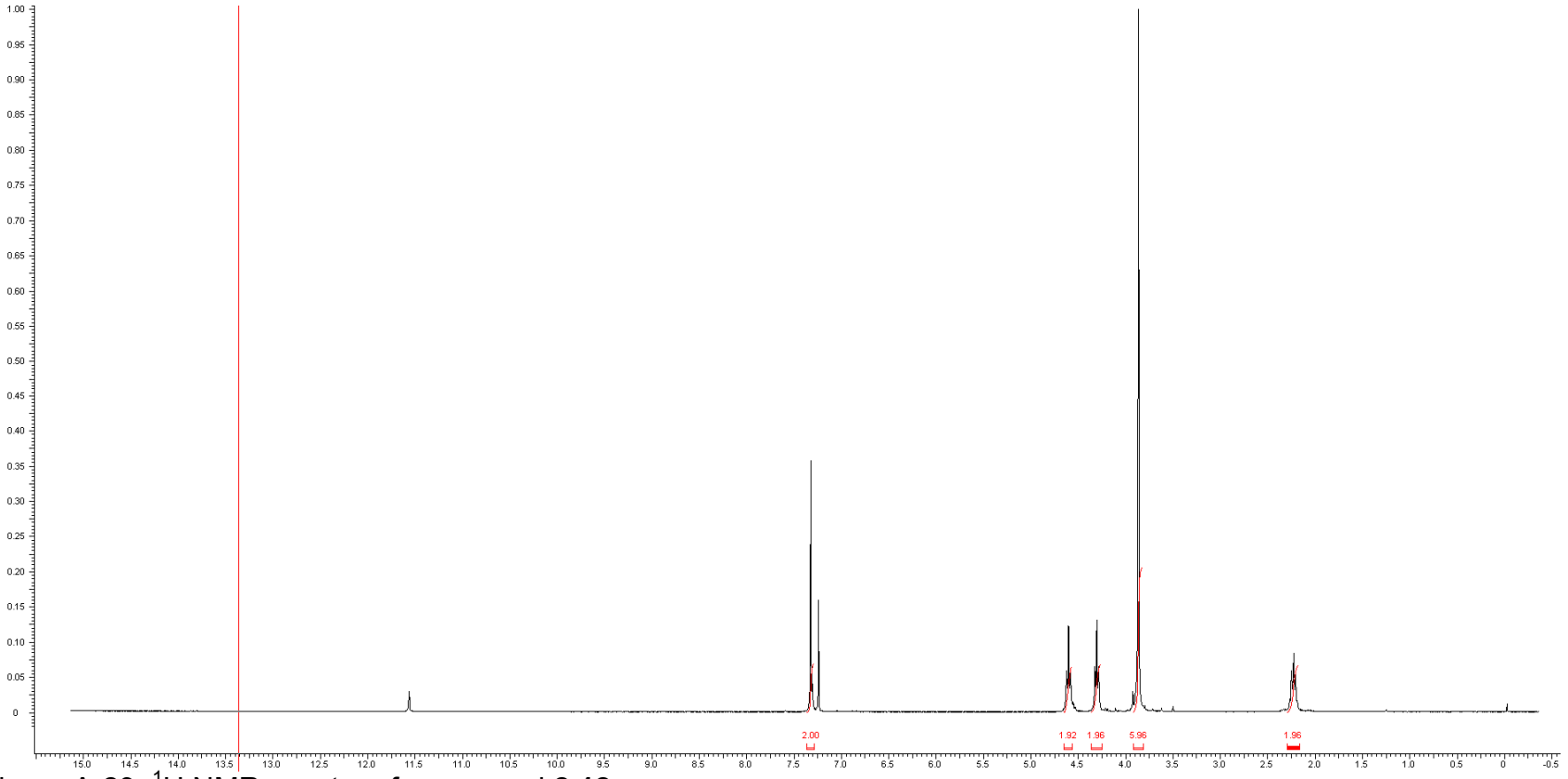


Figure A-23. ^{1}H NMR spectra of compound **2.12**

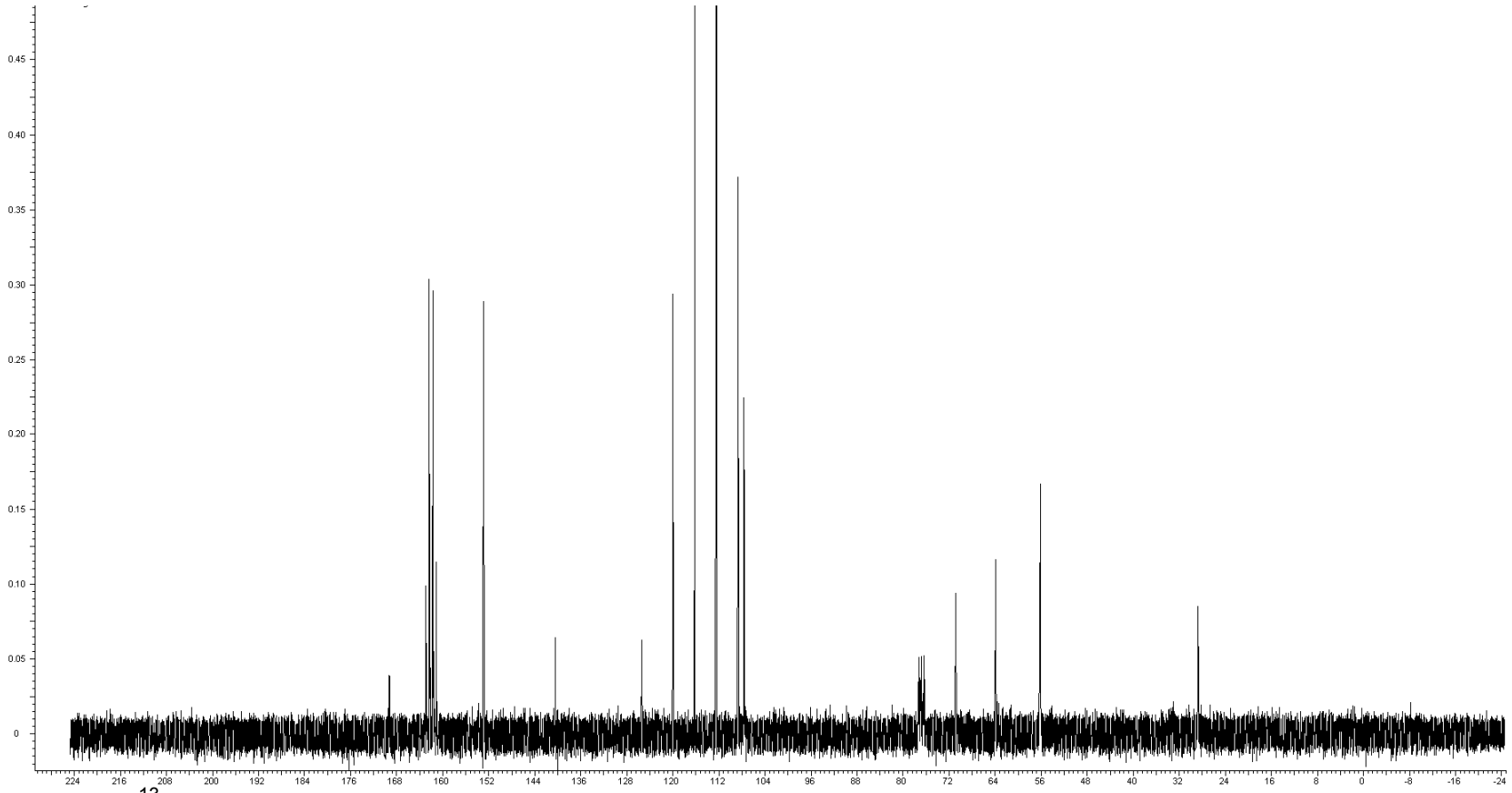


Figure A-24. ^{13}C NMR spectra of compound **2.12**

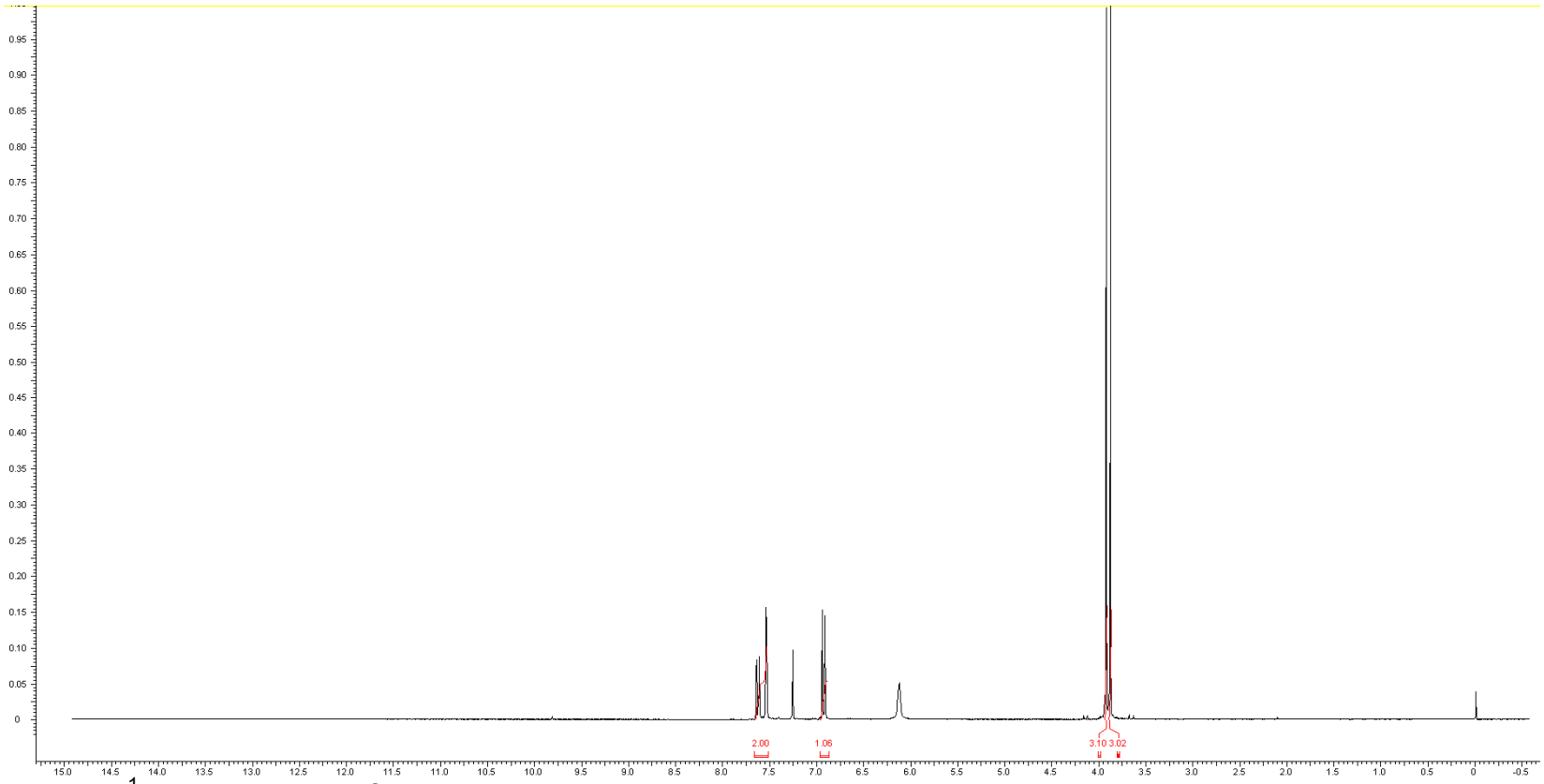


Figure A-25.^{1}H NMR spectra of compound **2.13**

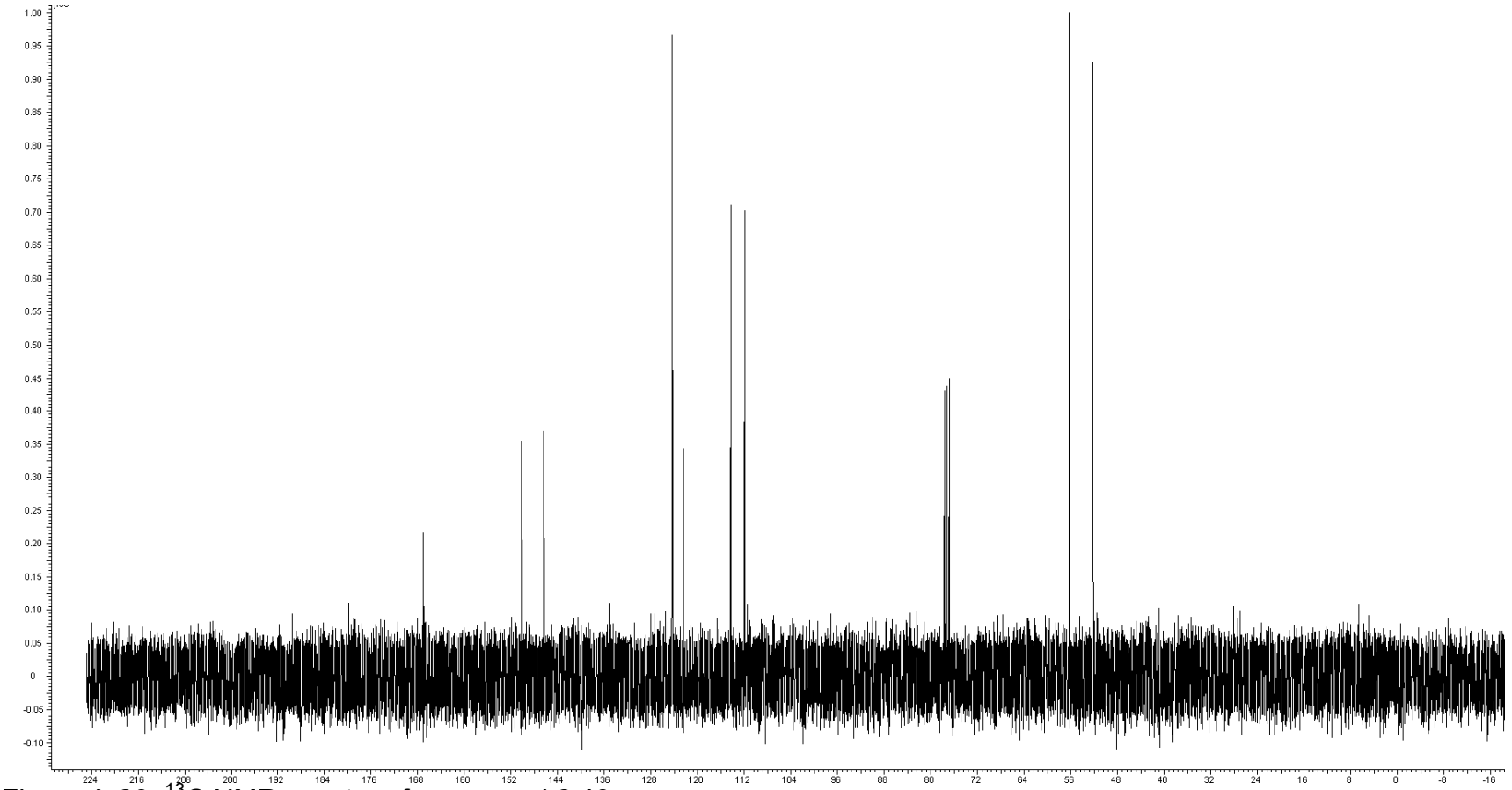


Figure A-26. ^{13}C NMR spectra of compound **2.13**

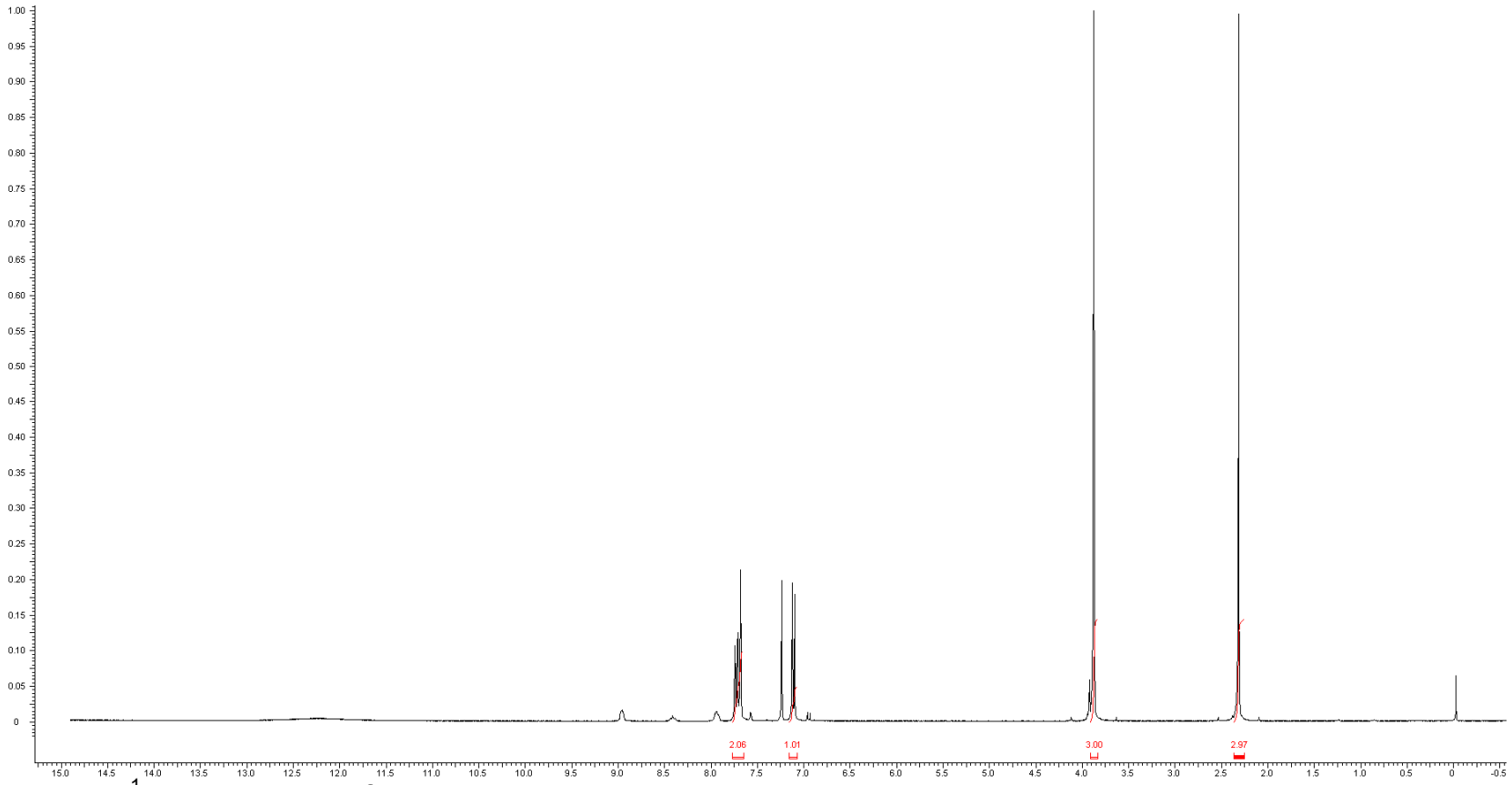


Figure A-27.^{1}H NMR spectra of compound **2.14**

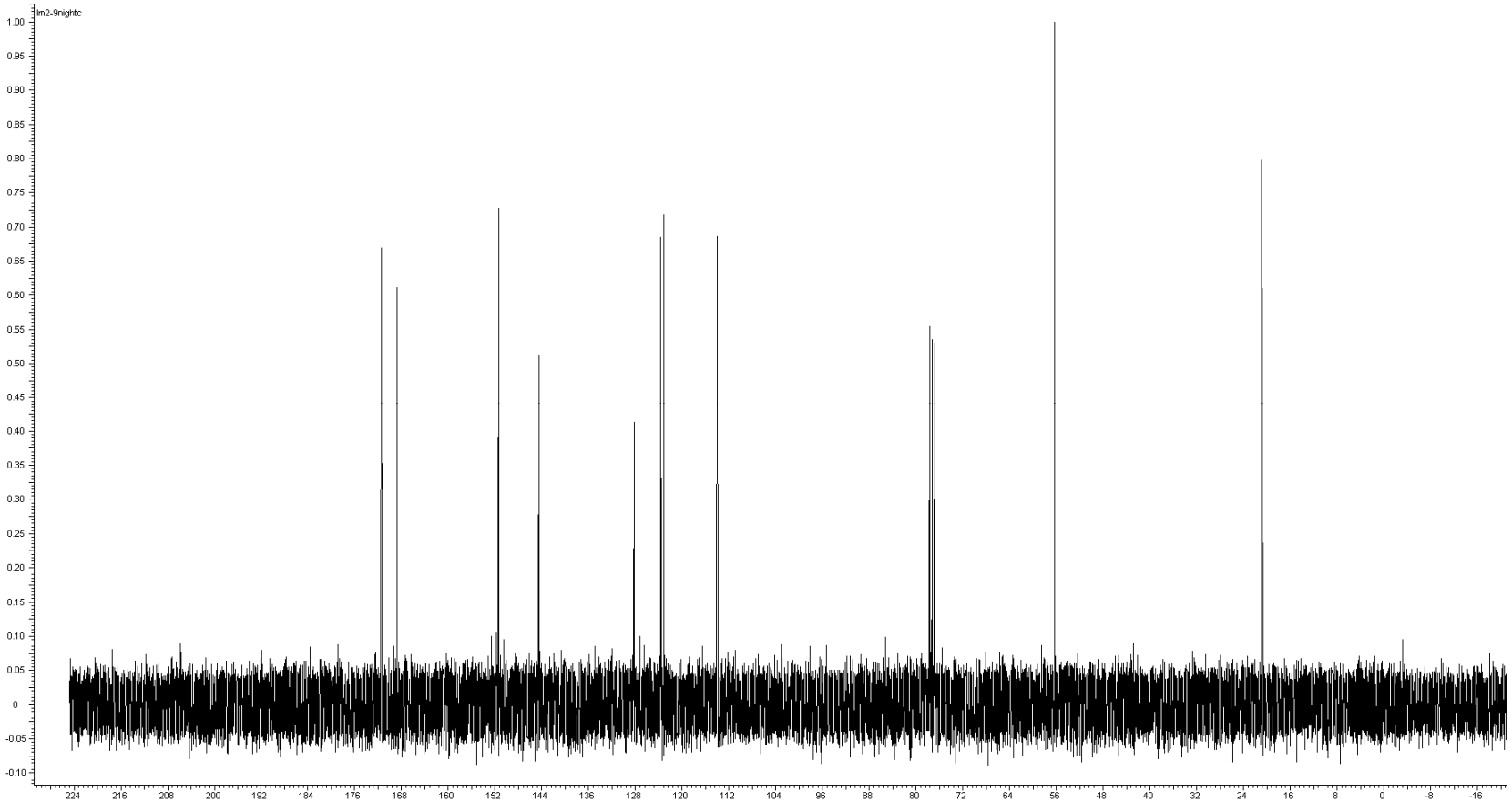


Figure A-28. ^{13}C NMR spectra of compound **2.14**

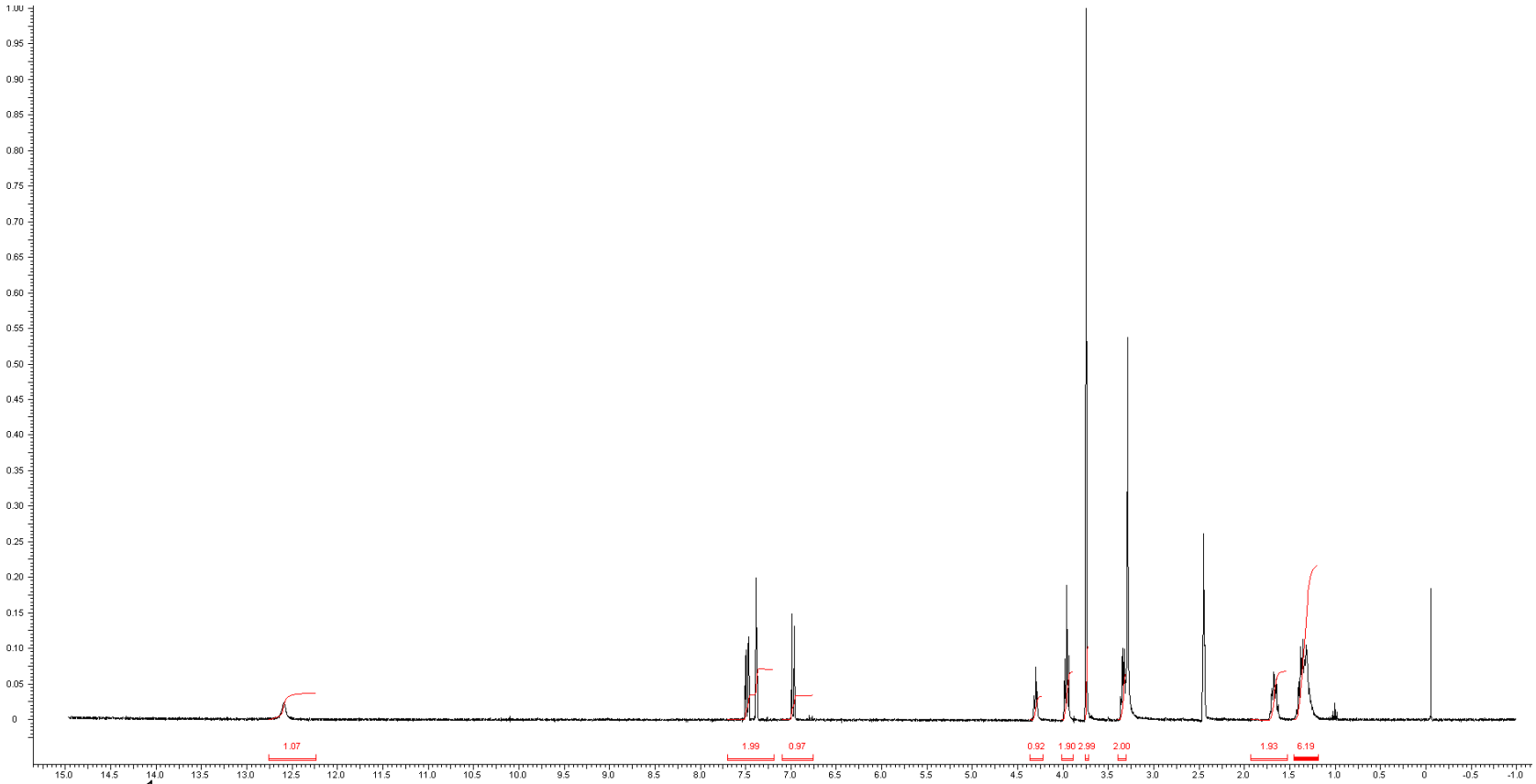


Figure A-29. ^{1}H NMR spectra of compound **2.15**

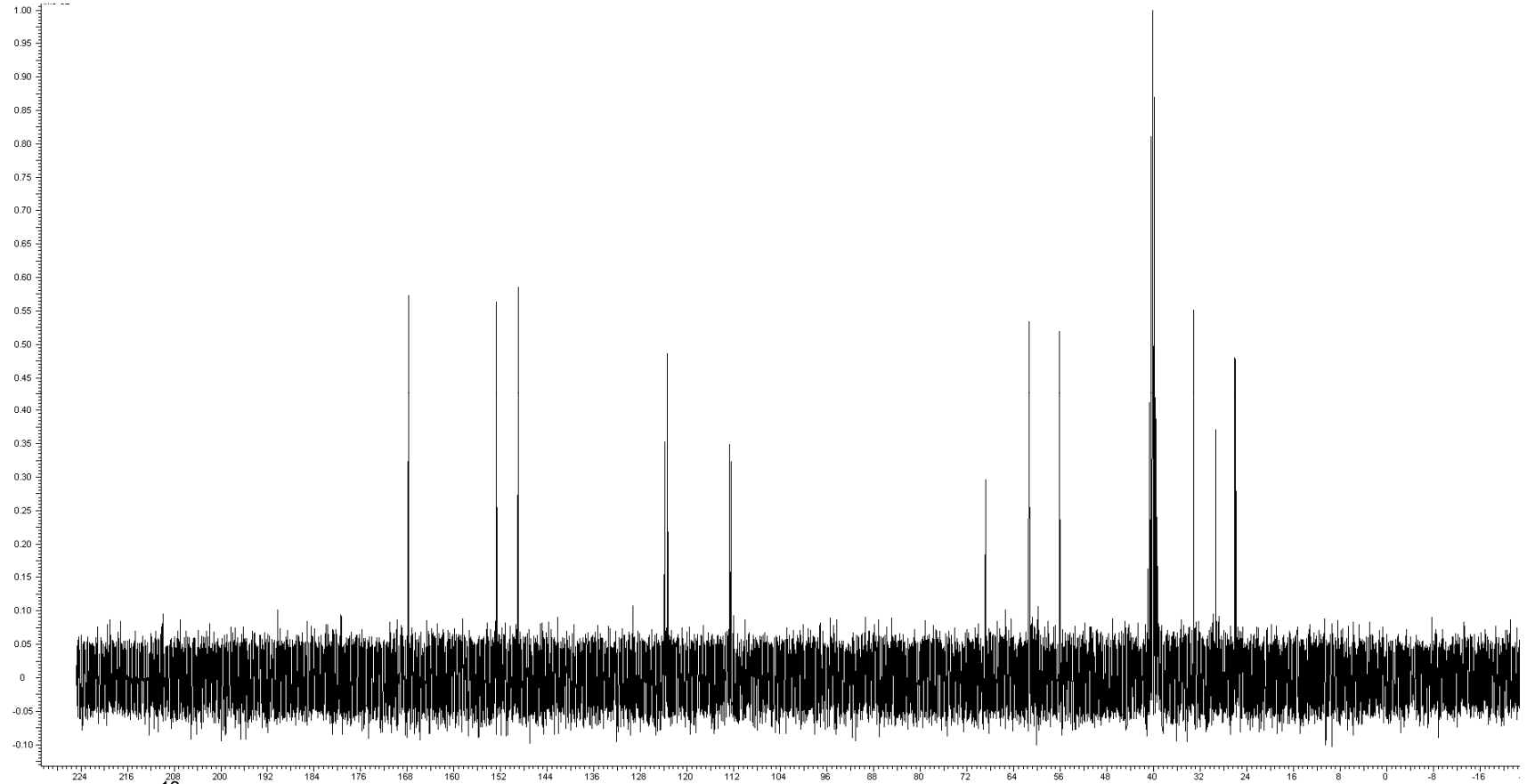


Figure A-30. ^{13}C NMR spectra of compound **2.15**

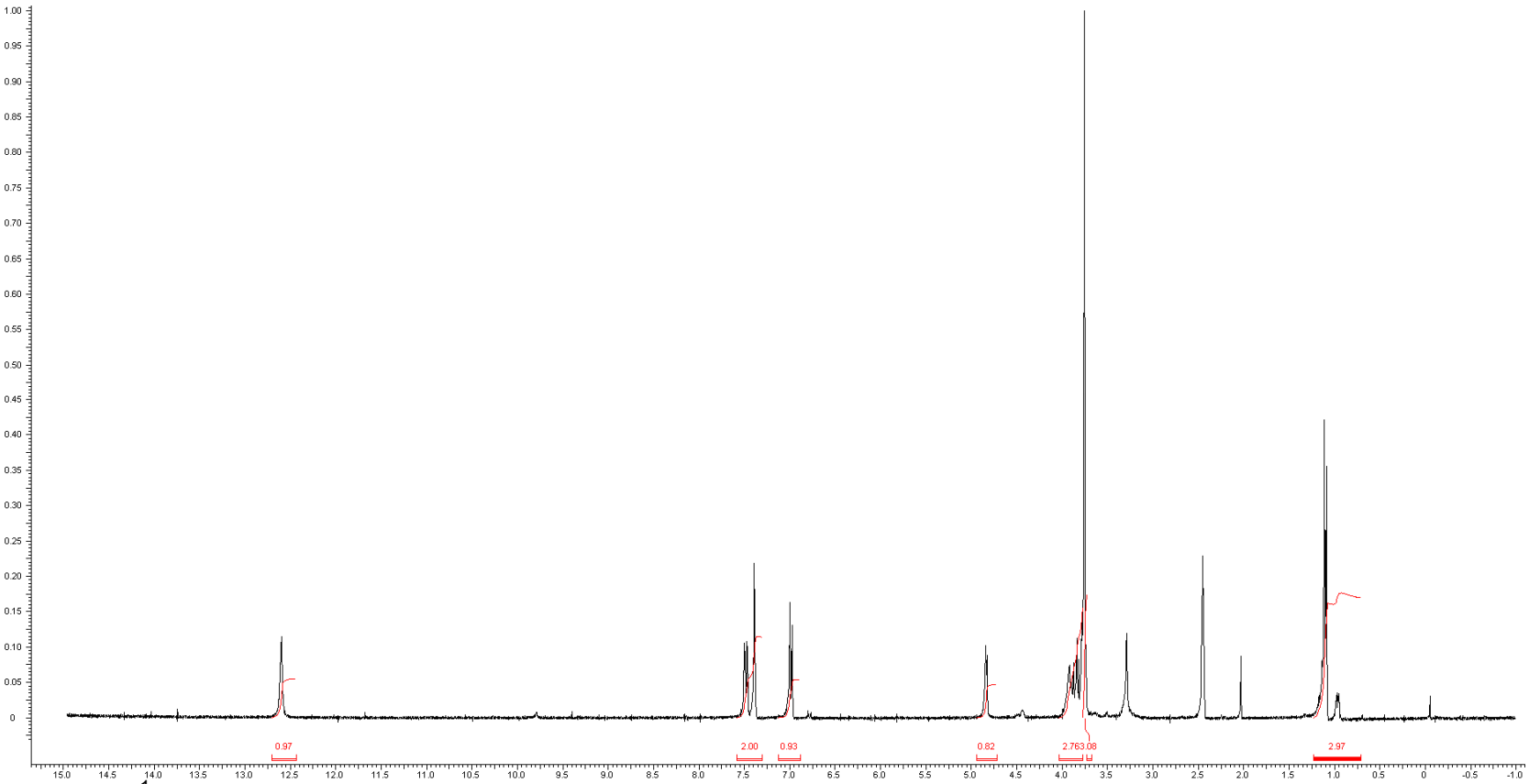


Figure A-31. ^{1}H NMR spectra of compound **2.16**

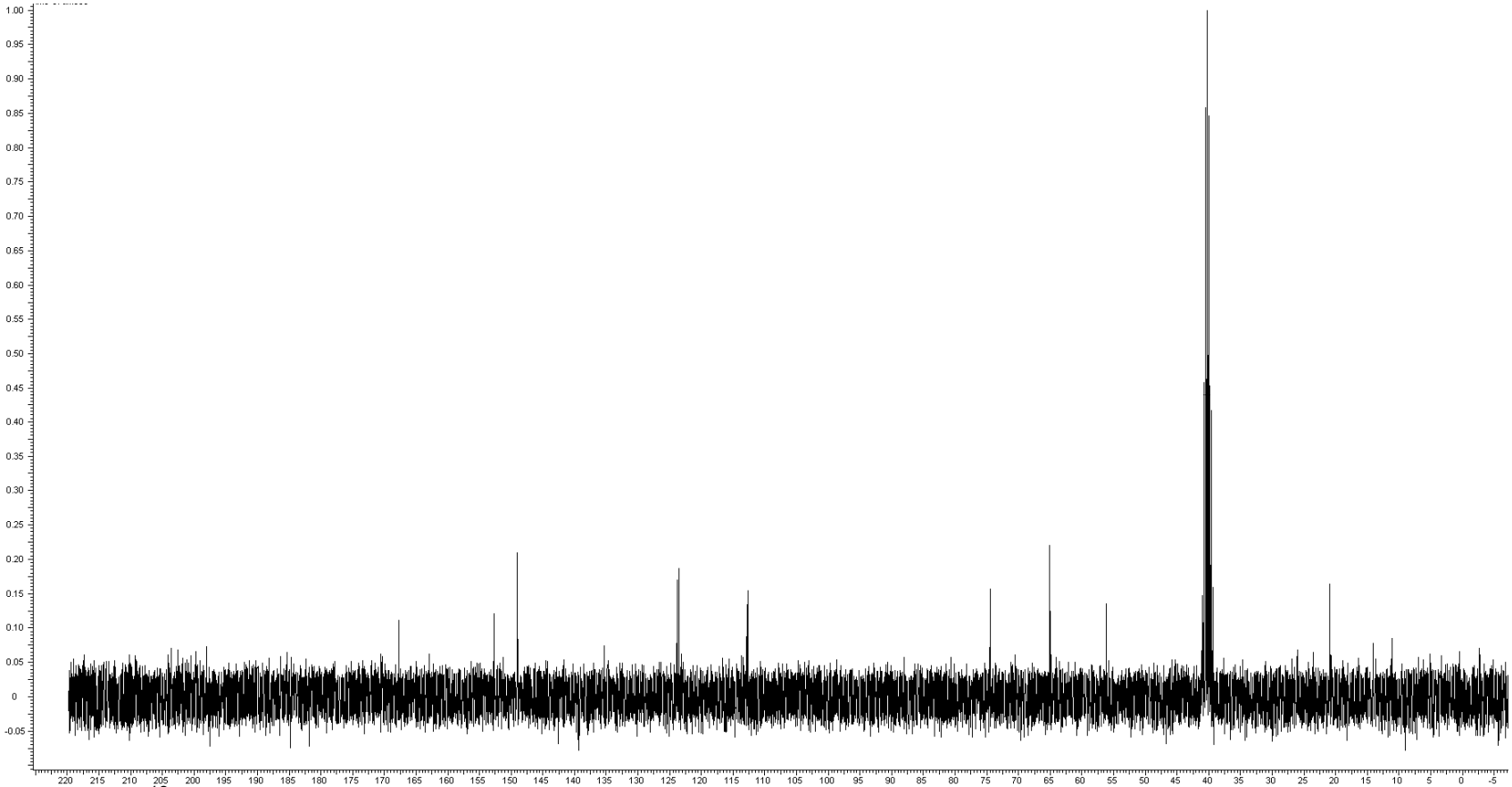


Figure A-32. ^{13}C NMR spectra of compound **2.16**

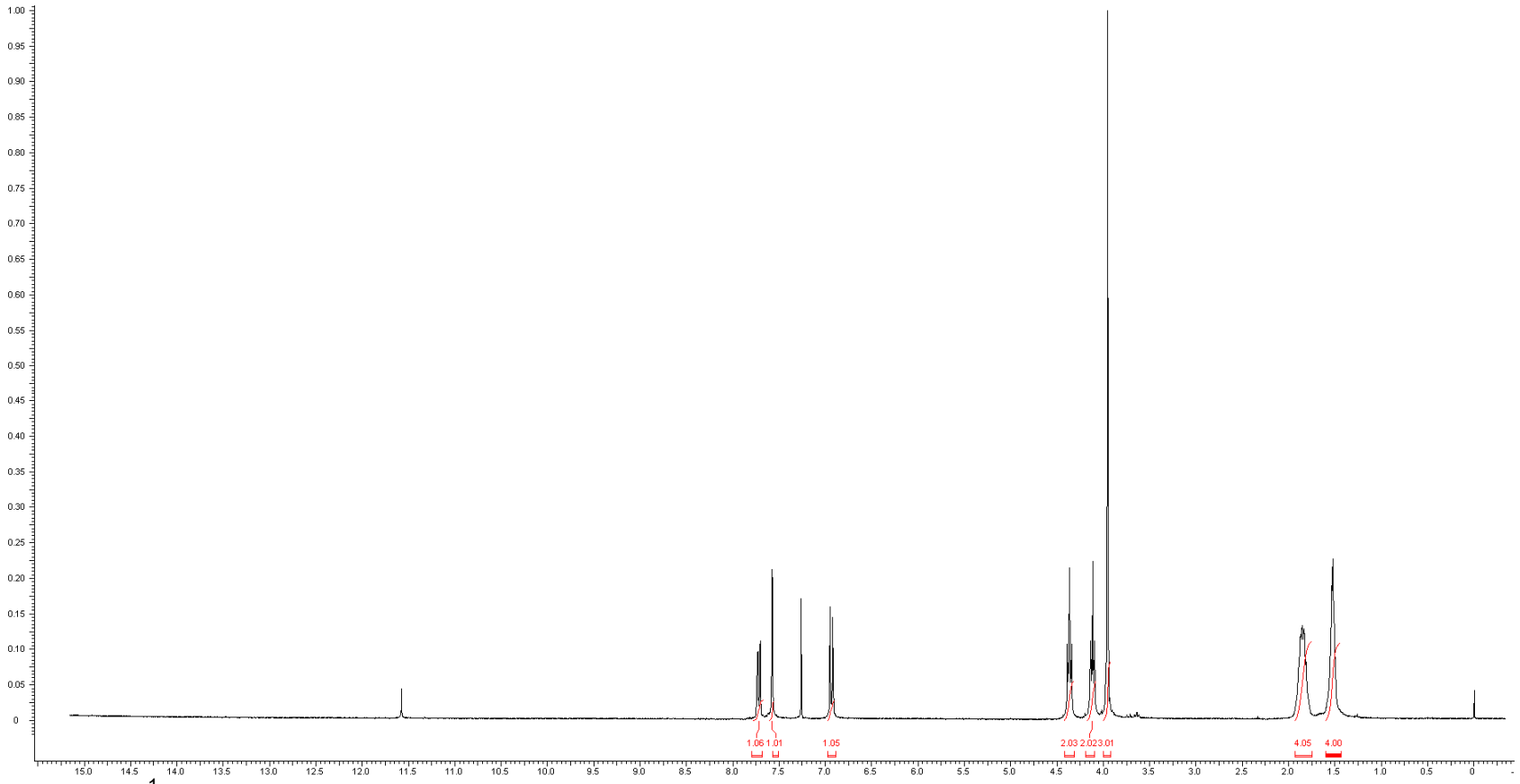


Figure A-33. ^{1}H NMR spectra of compound **2.18**

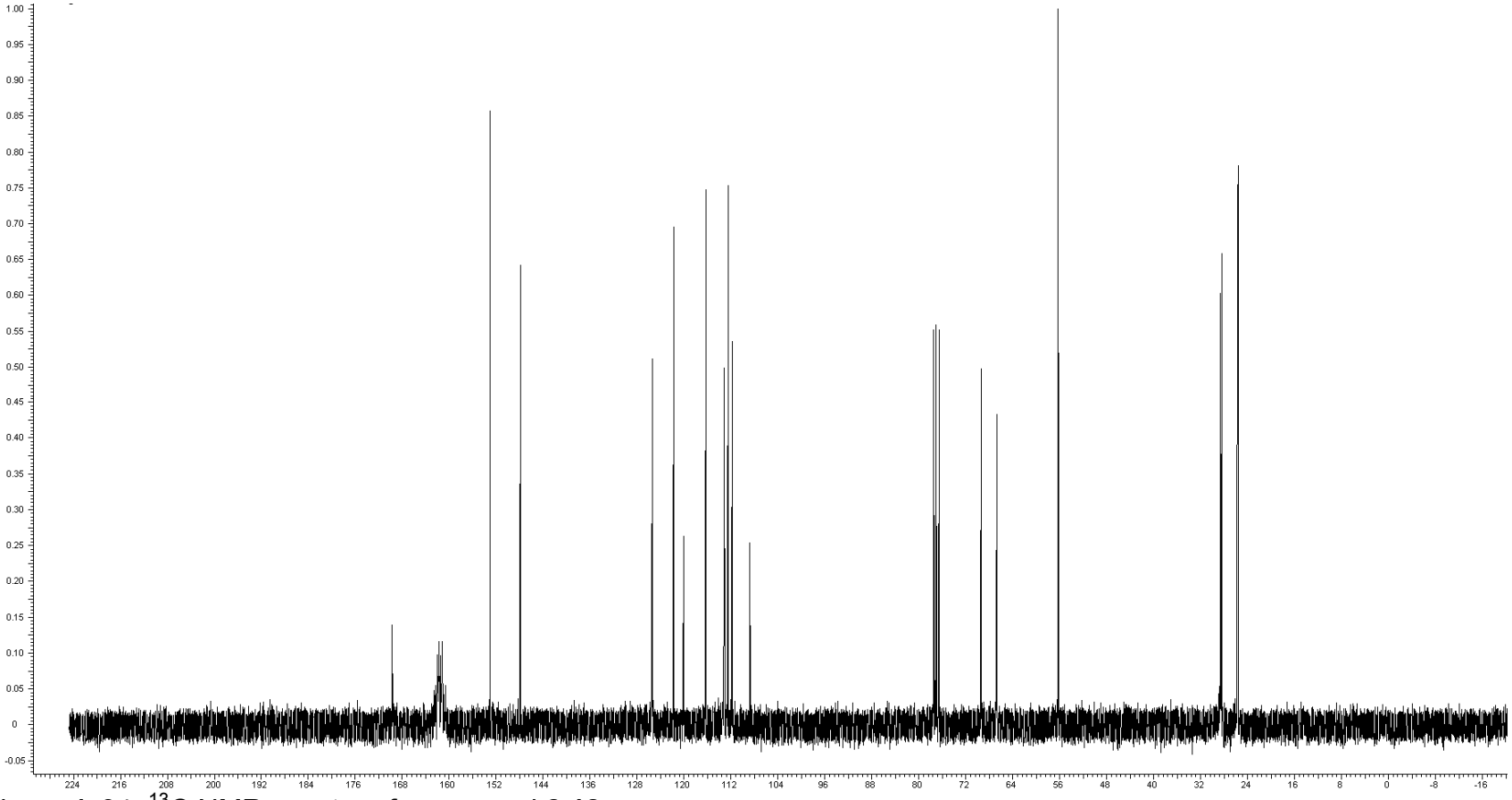


Figure A-34. ^{13}C NMR spectra of compound **2.18**

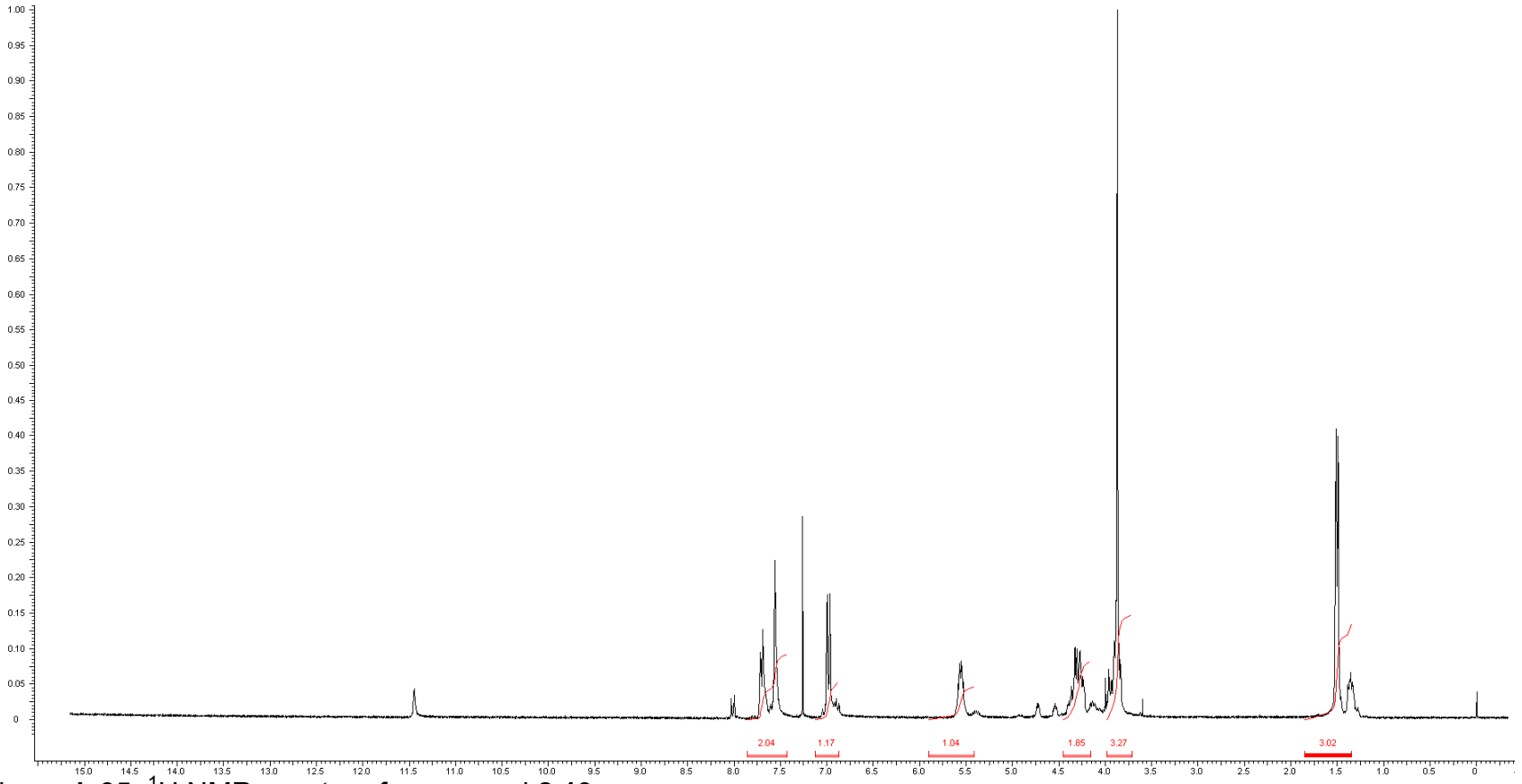


Figure A-35. ^{1}H NMR spectra of compound **2.19**

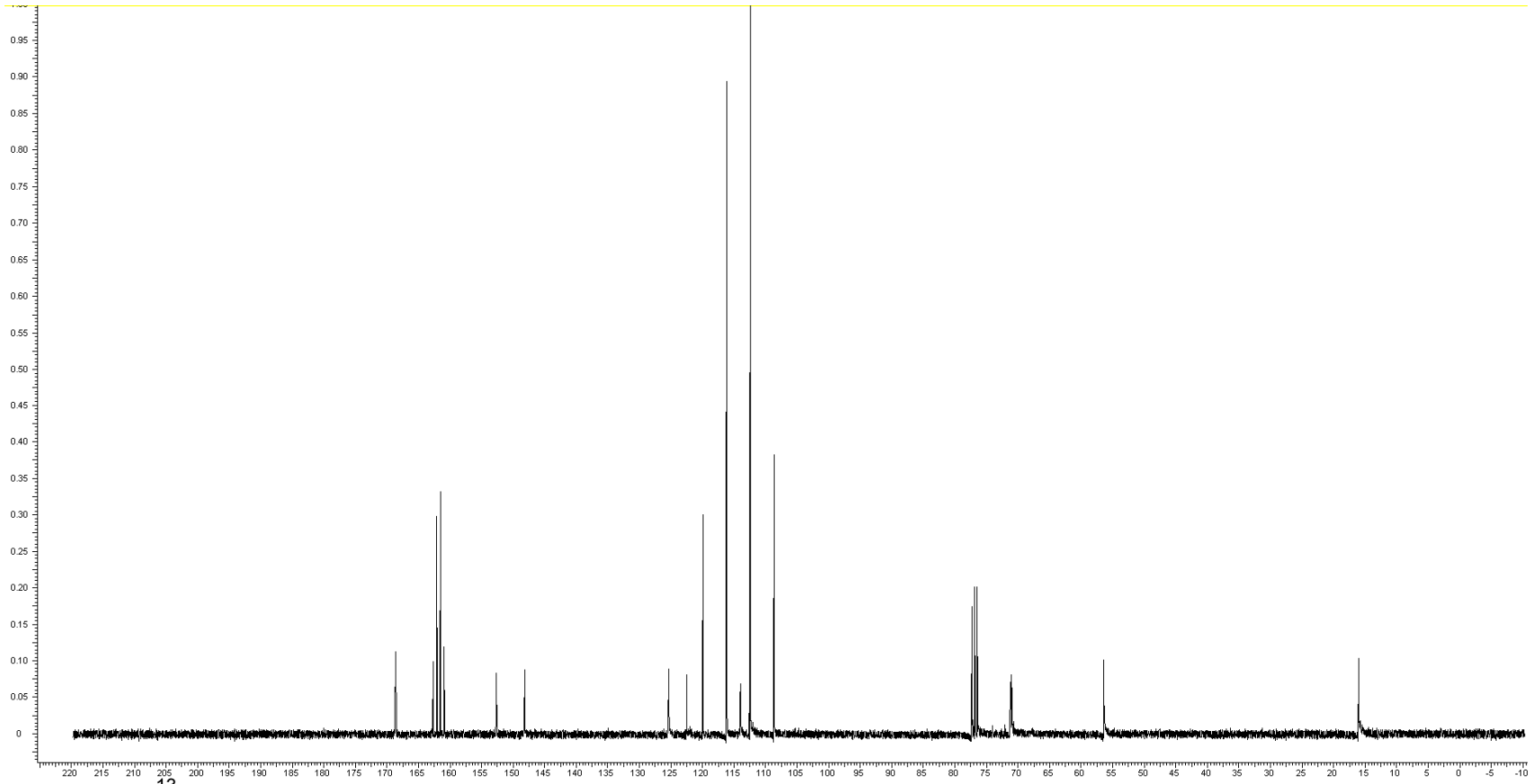


Figure A-36. ^{13}C NMR spectra of compound **2.19**

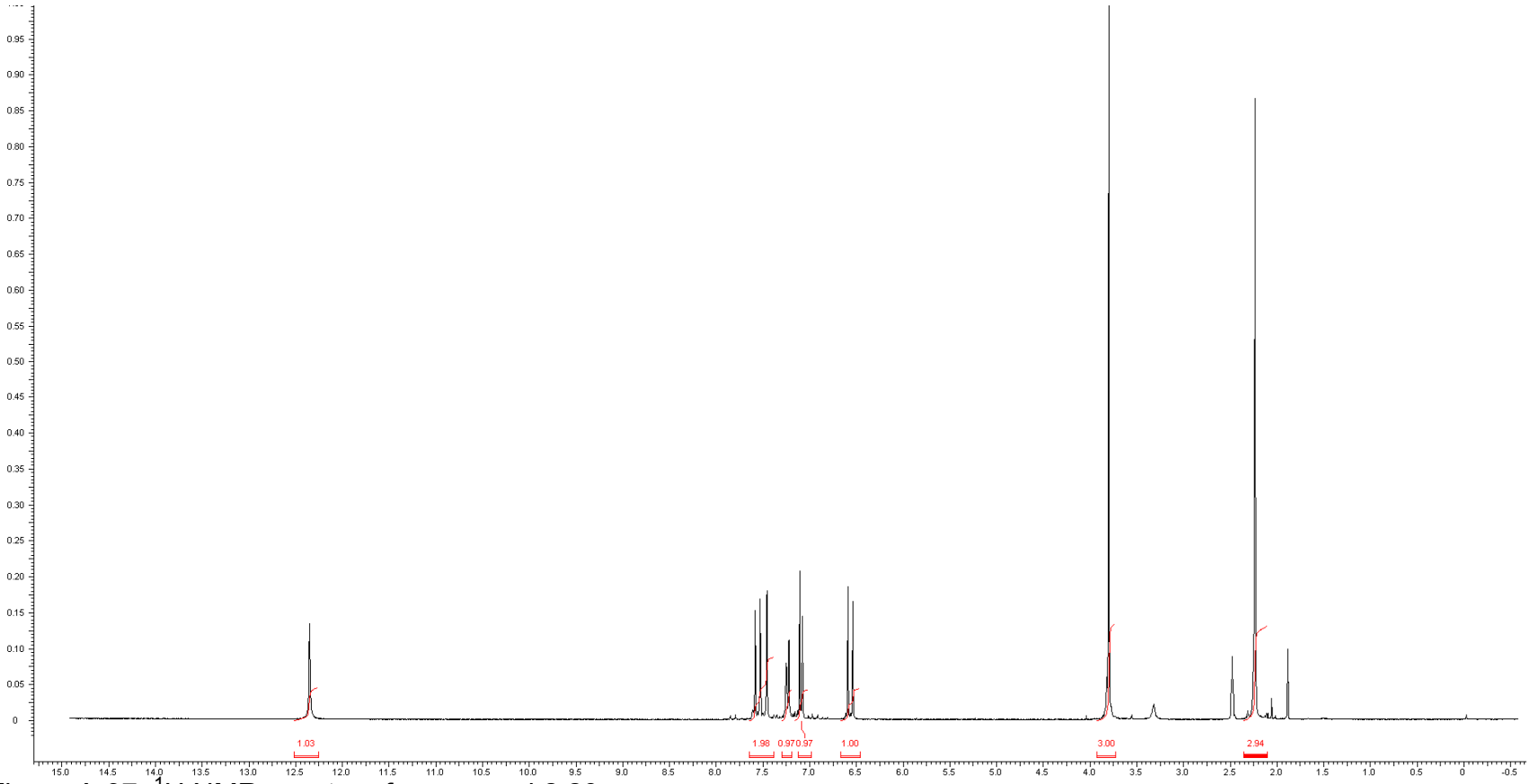


Figure A-37. ^{1}H NMR spectra of compound **2.20**

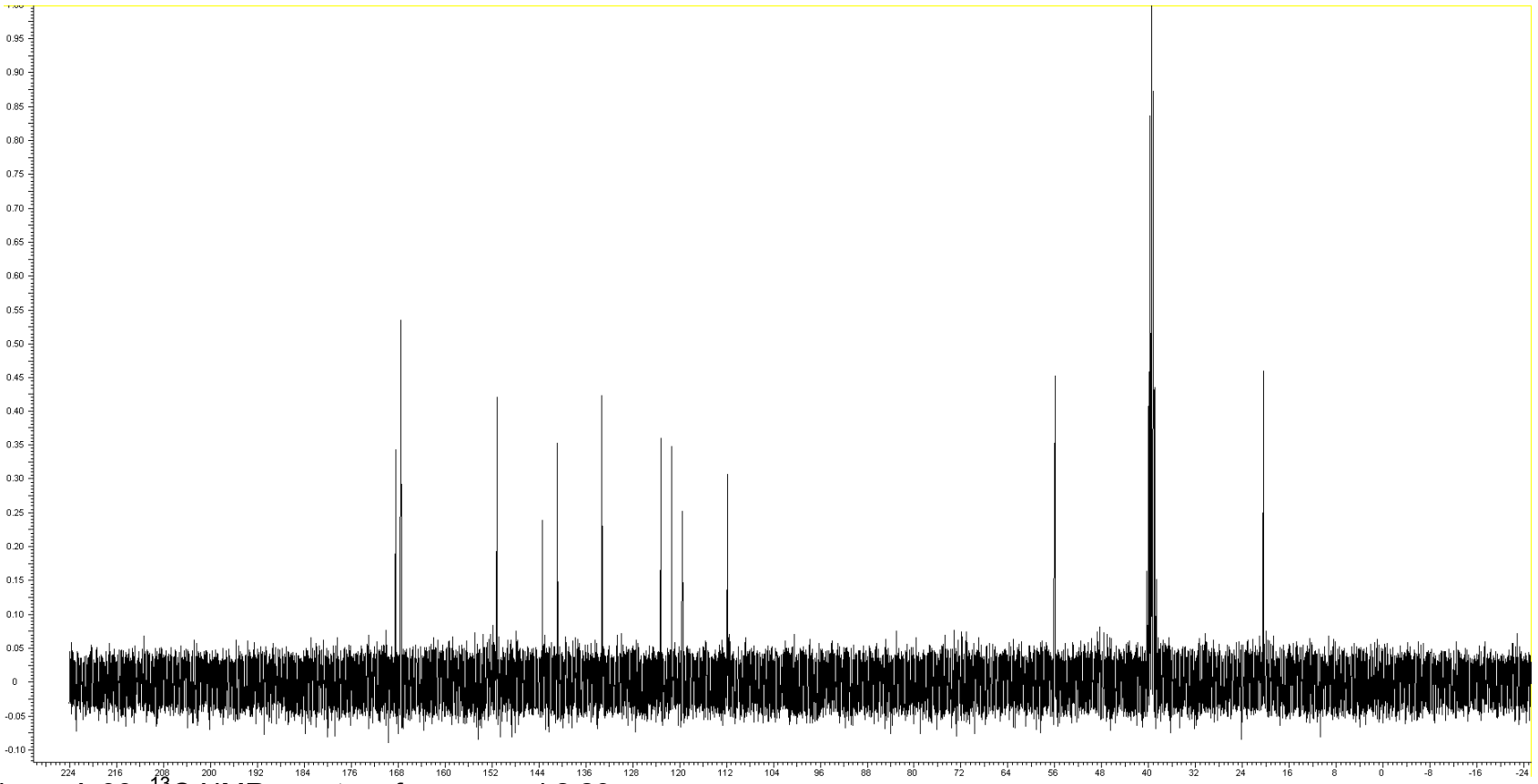


Figure A-38. ^{13}C NMR spectra of compound **2.20**

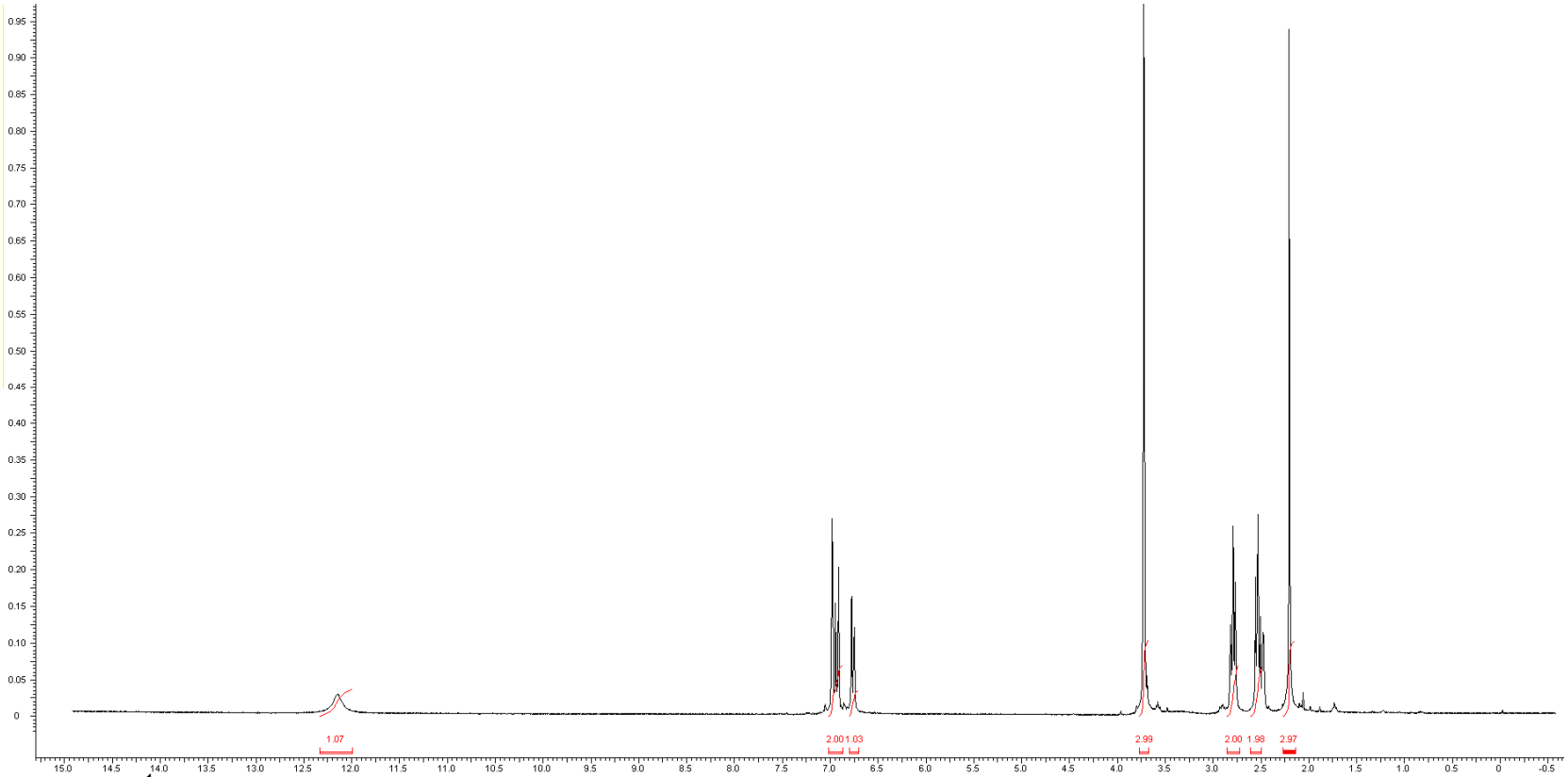


Figure A-39. ^{1}H NMR spectra of compound **2.21**

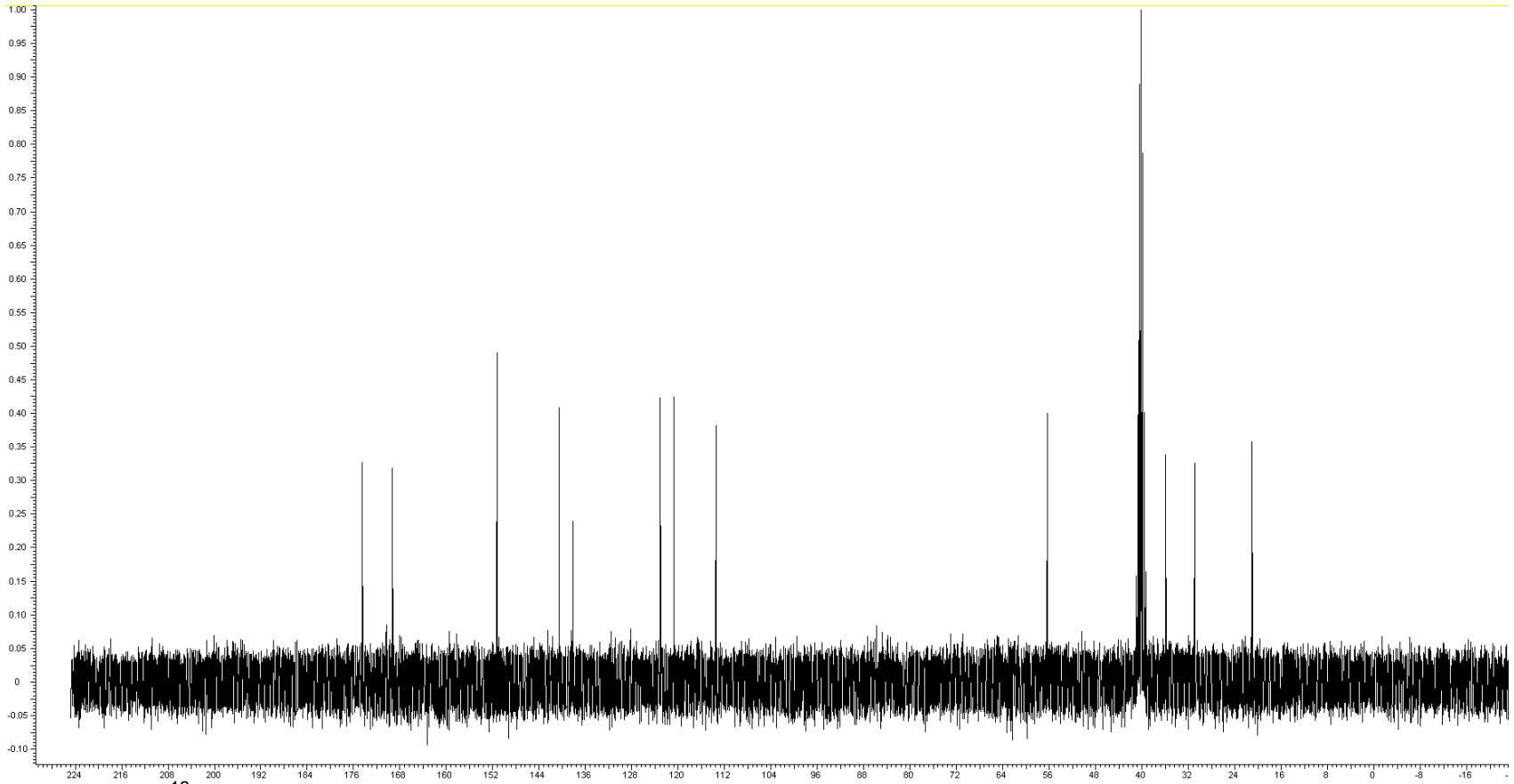


Figure A-40. ^{13}C NMR spectra of compound **2.21**

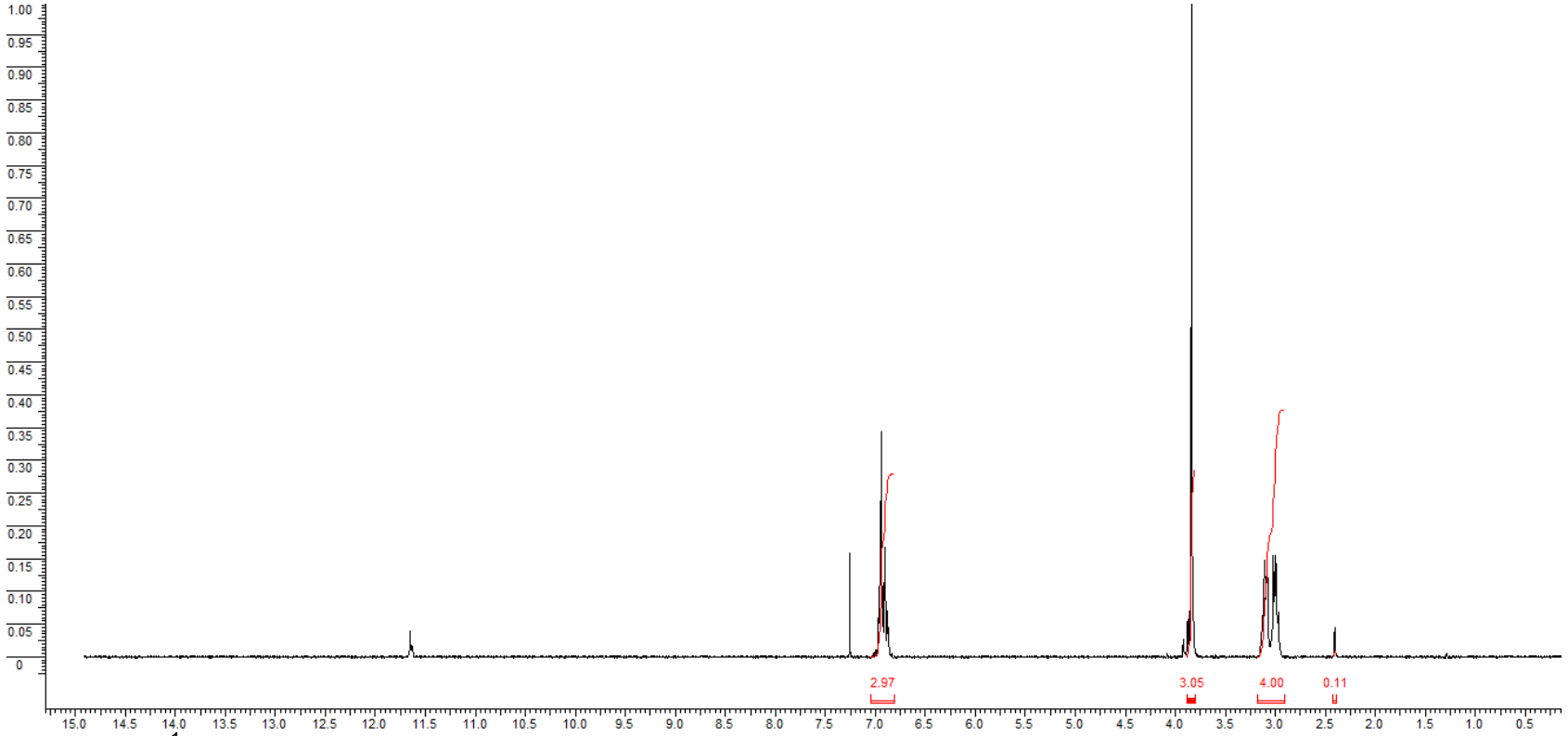


Figure A-41. ^{1}H NMR spectra of compound **2.22**

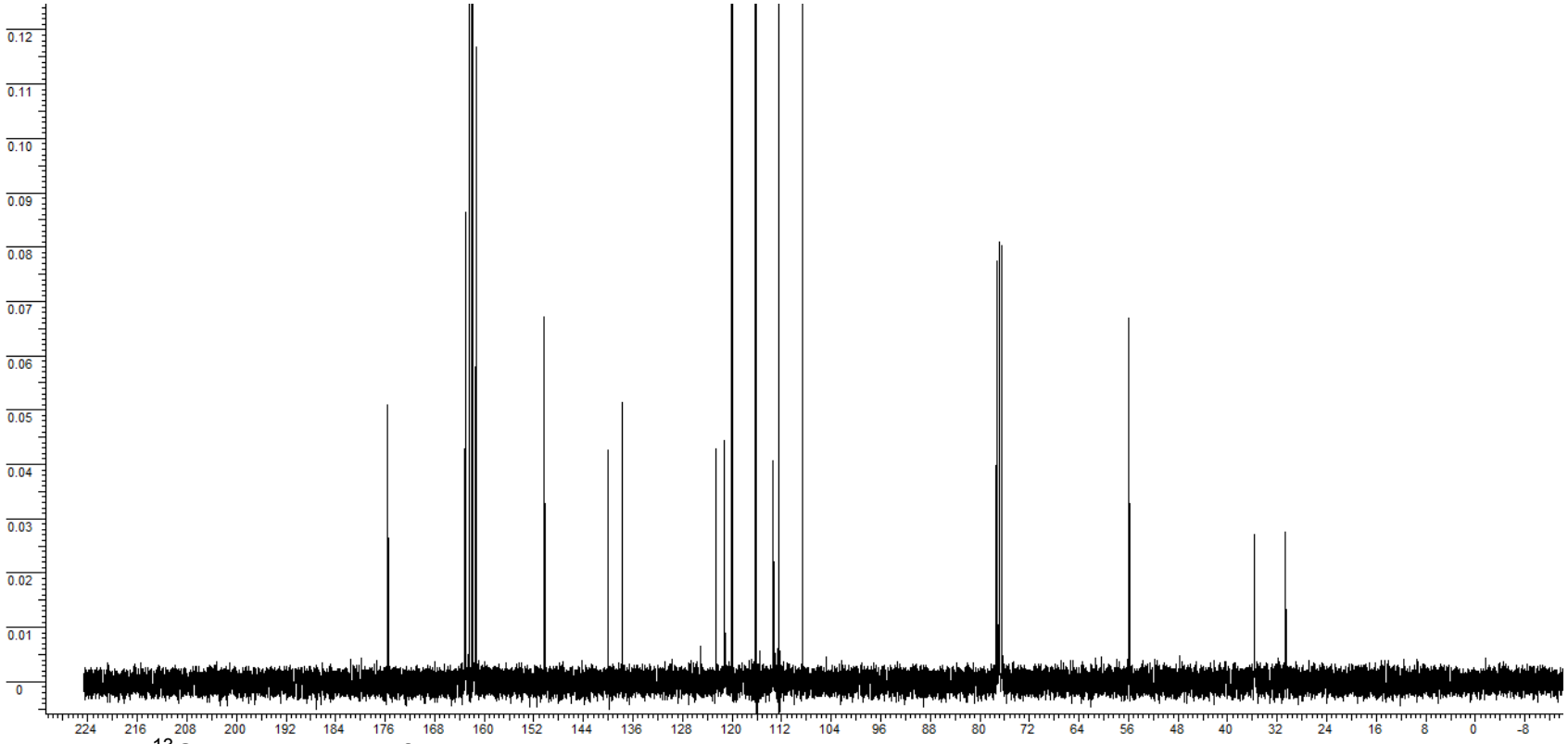


Figure A-42. ^{13}C NMR spectra of compound **2.22**

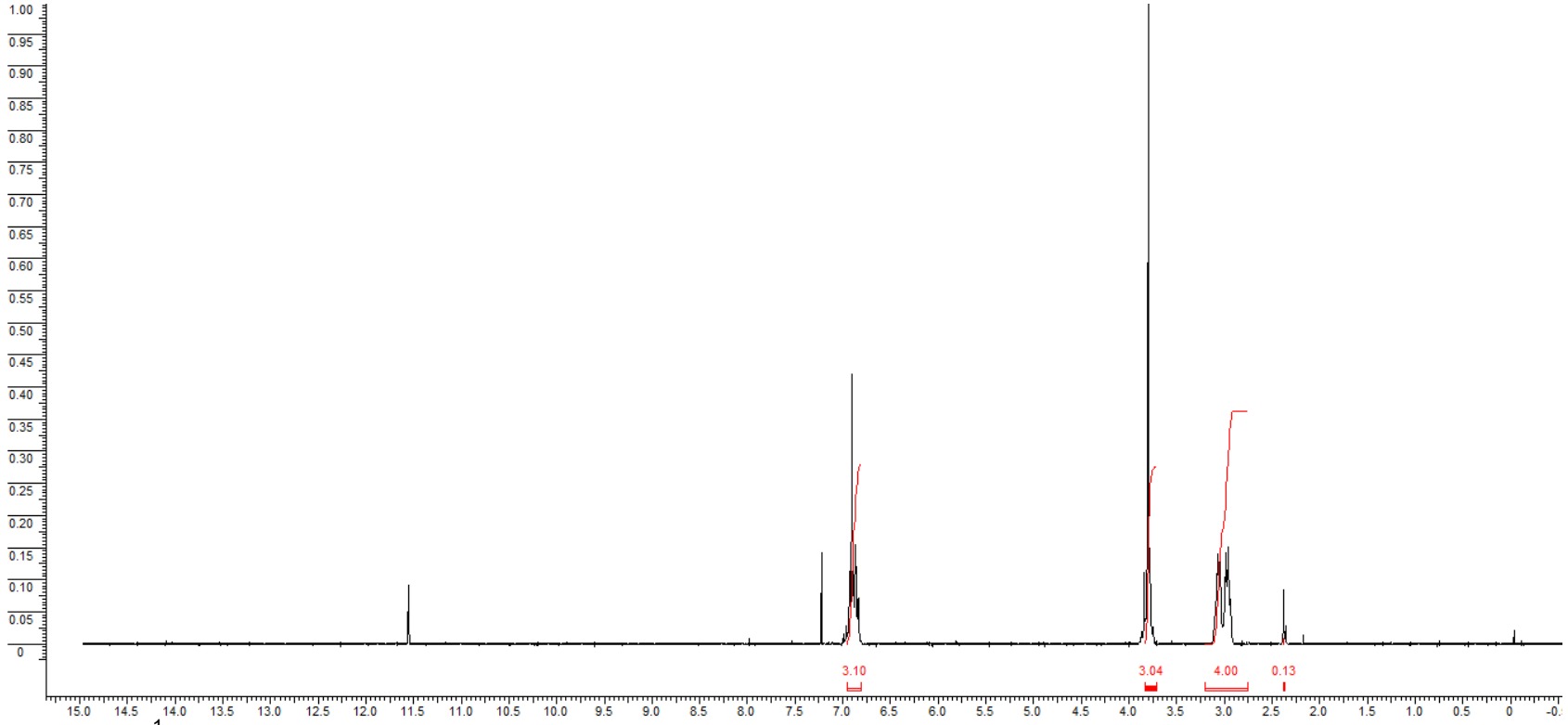


Figure A-43. ^{1}H NMR spectra of compound **2.23**

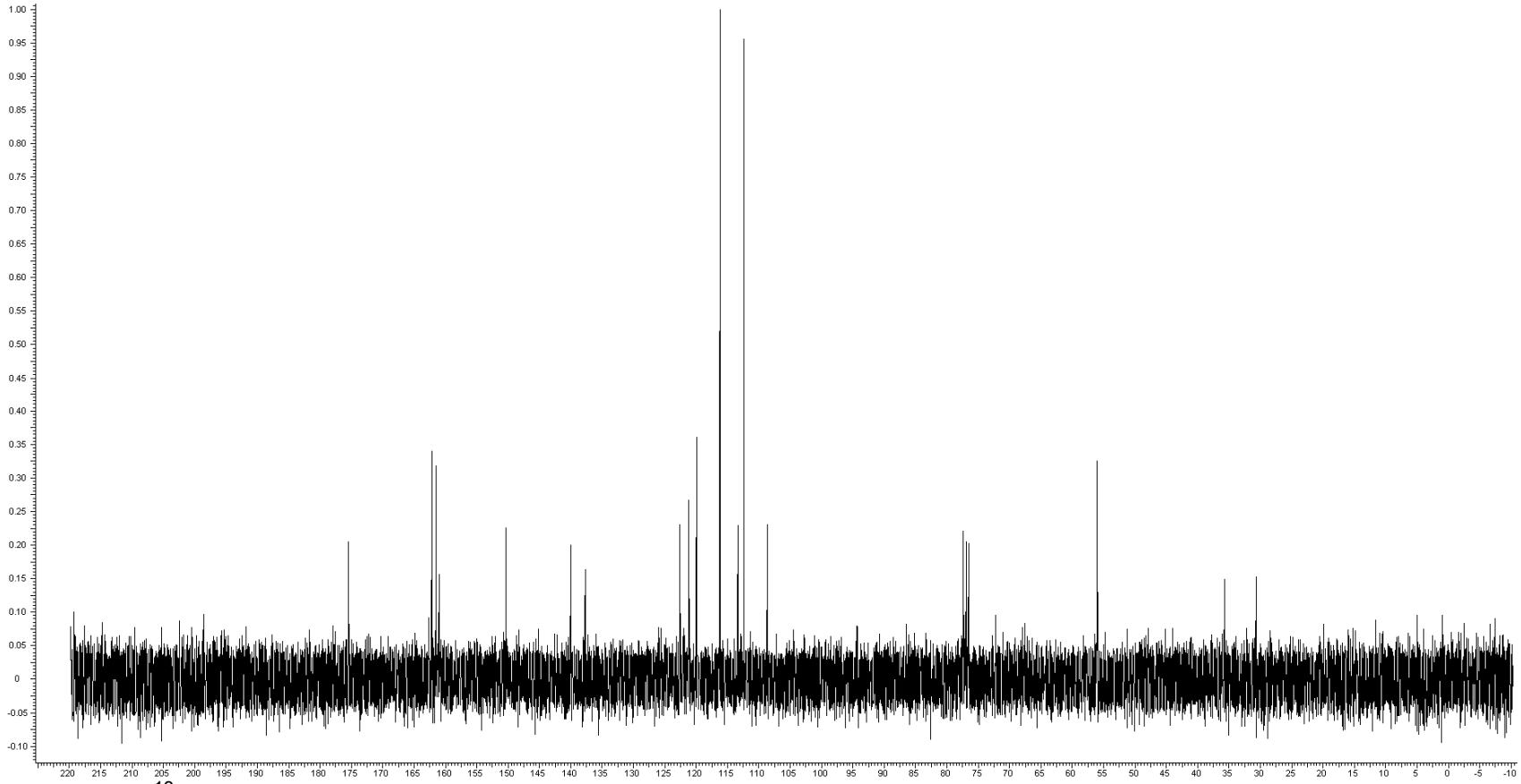


Figure A-44. ^{13}C NMR spectra of compound **2.23**

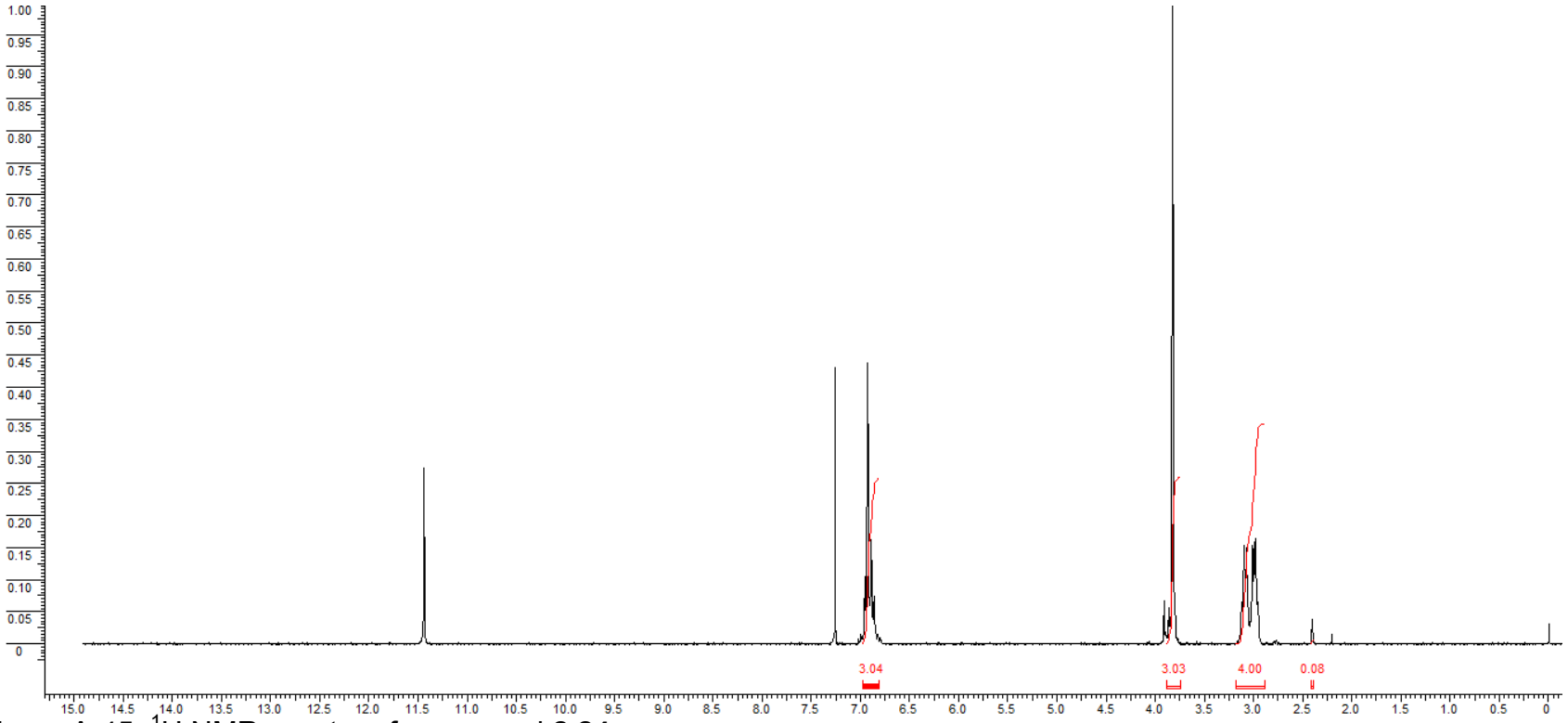


Figure A-45. ^{1}H NMR spectra of compound **2.24**

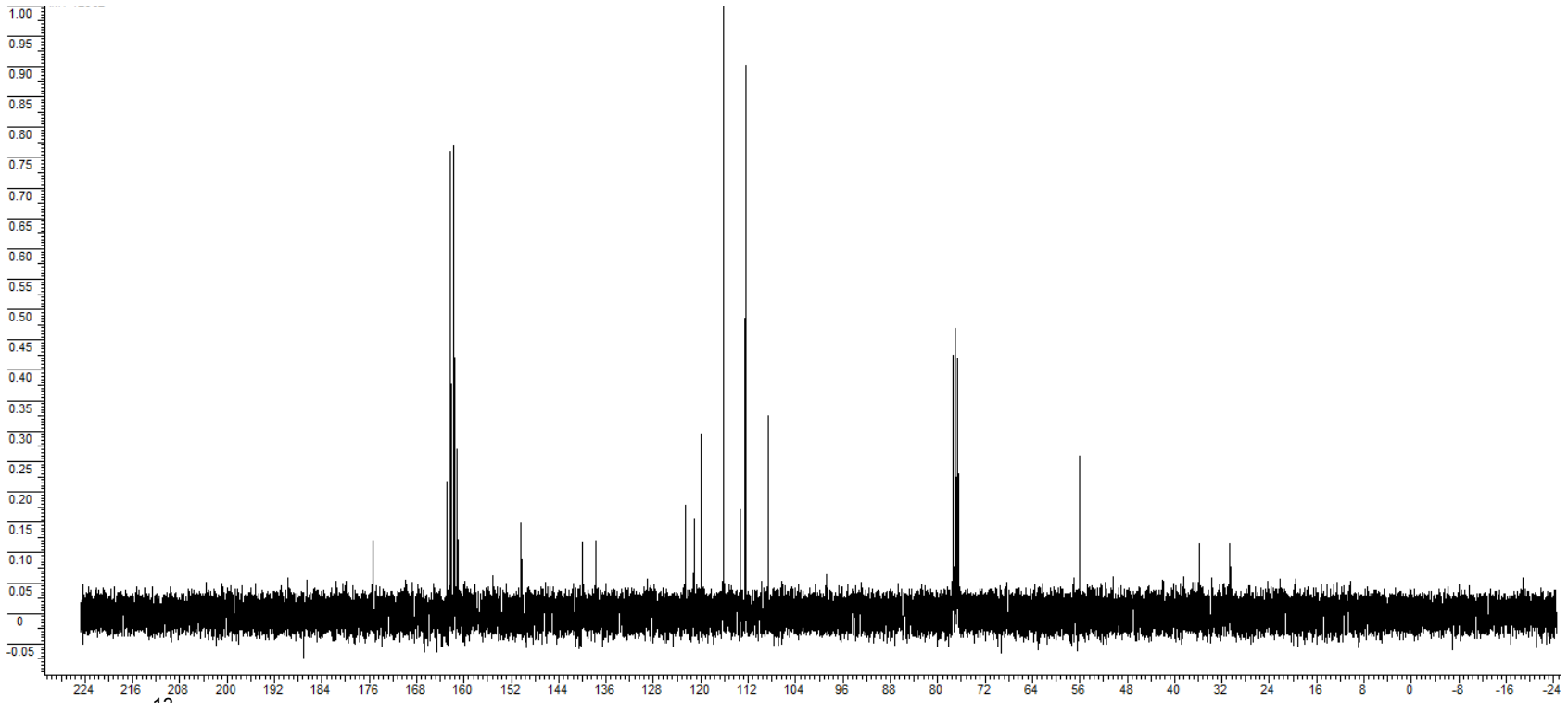


Figure A-46. ^{13}C NMR of compound **2.24**

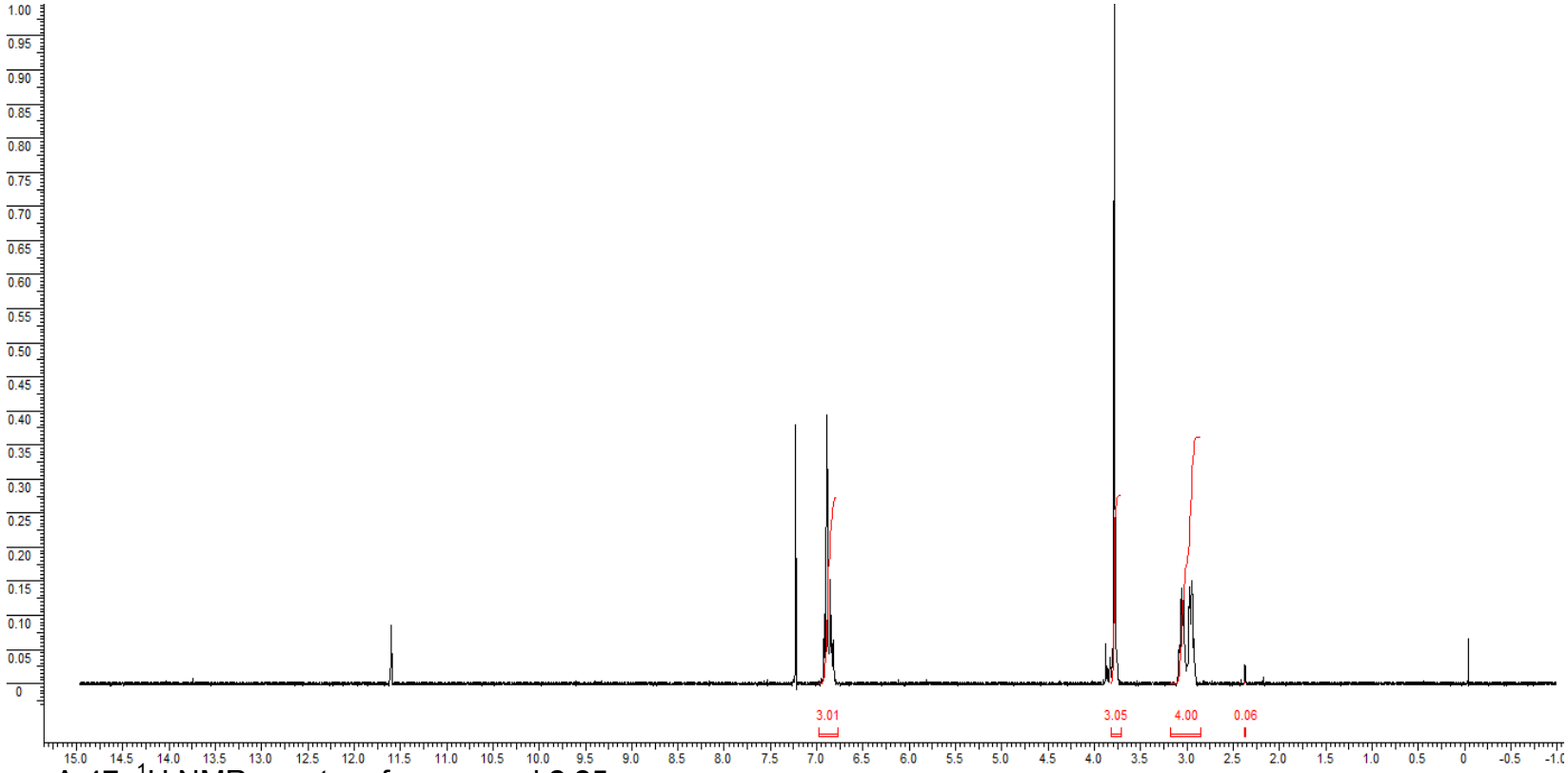


Figure A-47. ^{1}H NMR spectra of compound **2.25**

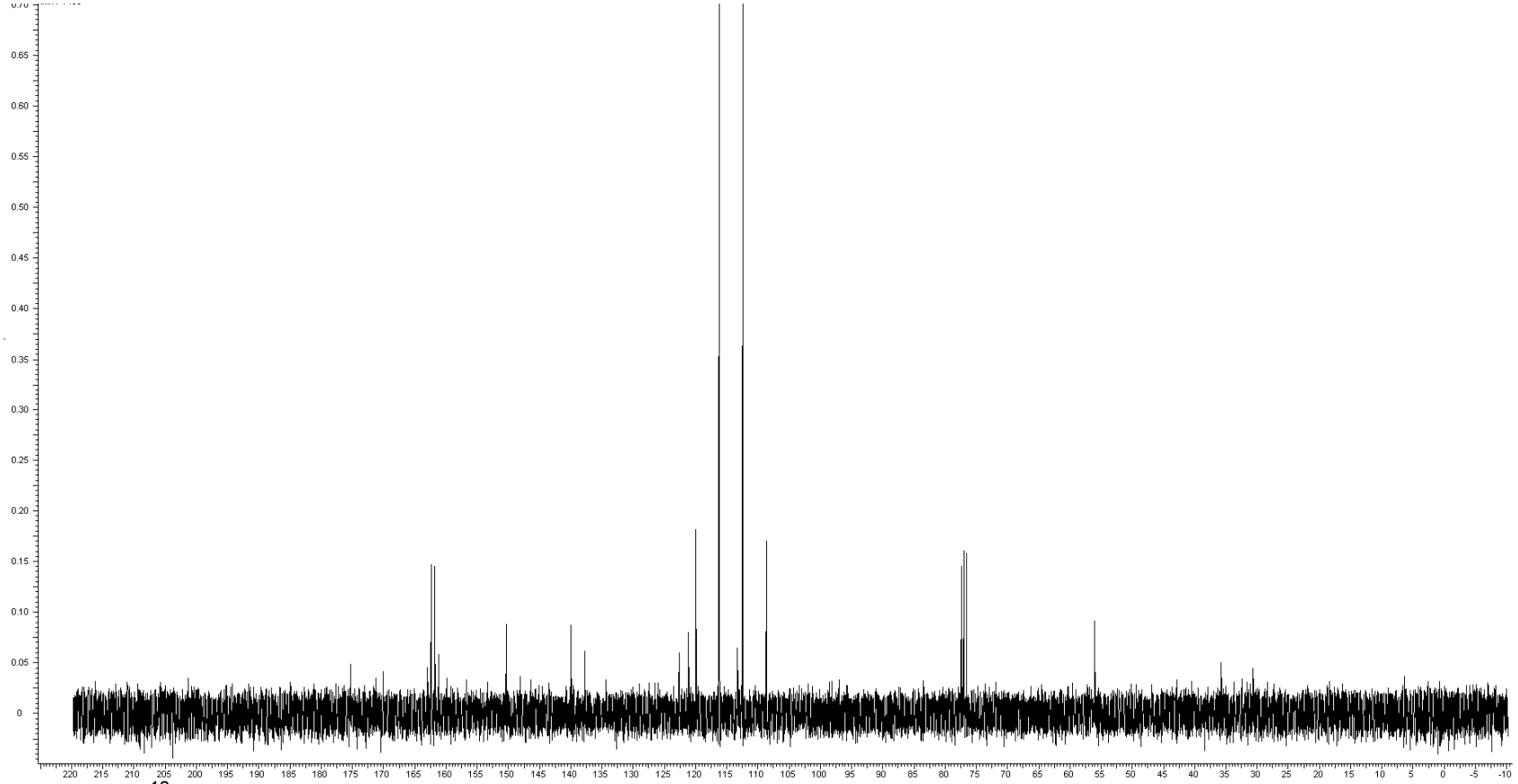


Figure A-48. ^{13}C NMR spectra of compound **2.25**

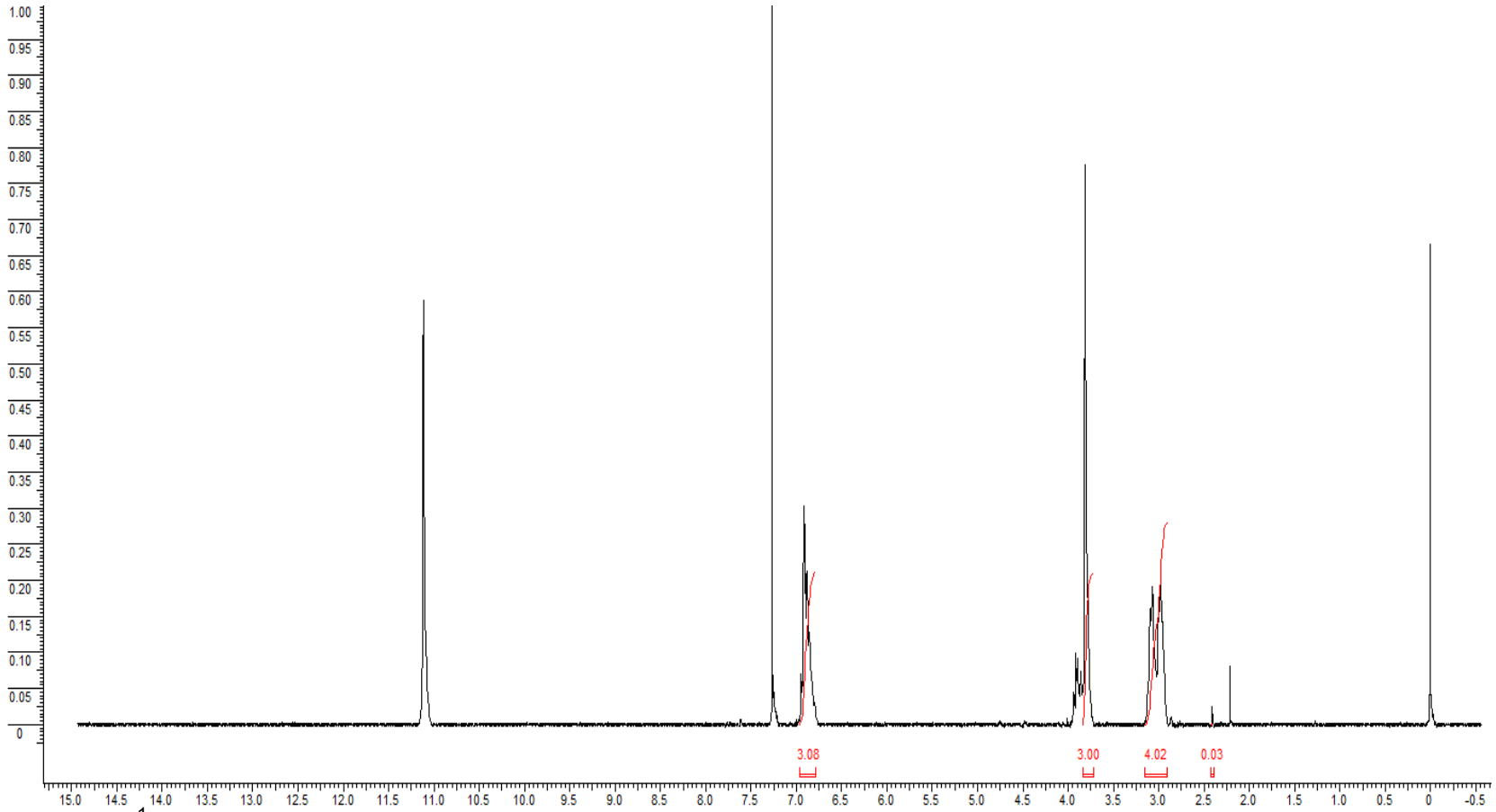


Figure A-49. ^{1}H NMR spectra of compound **2.26**

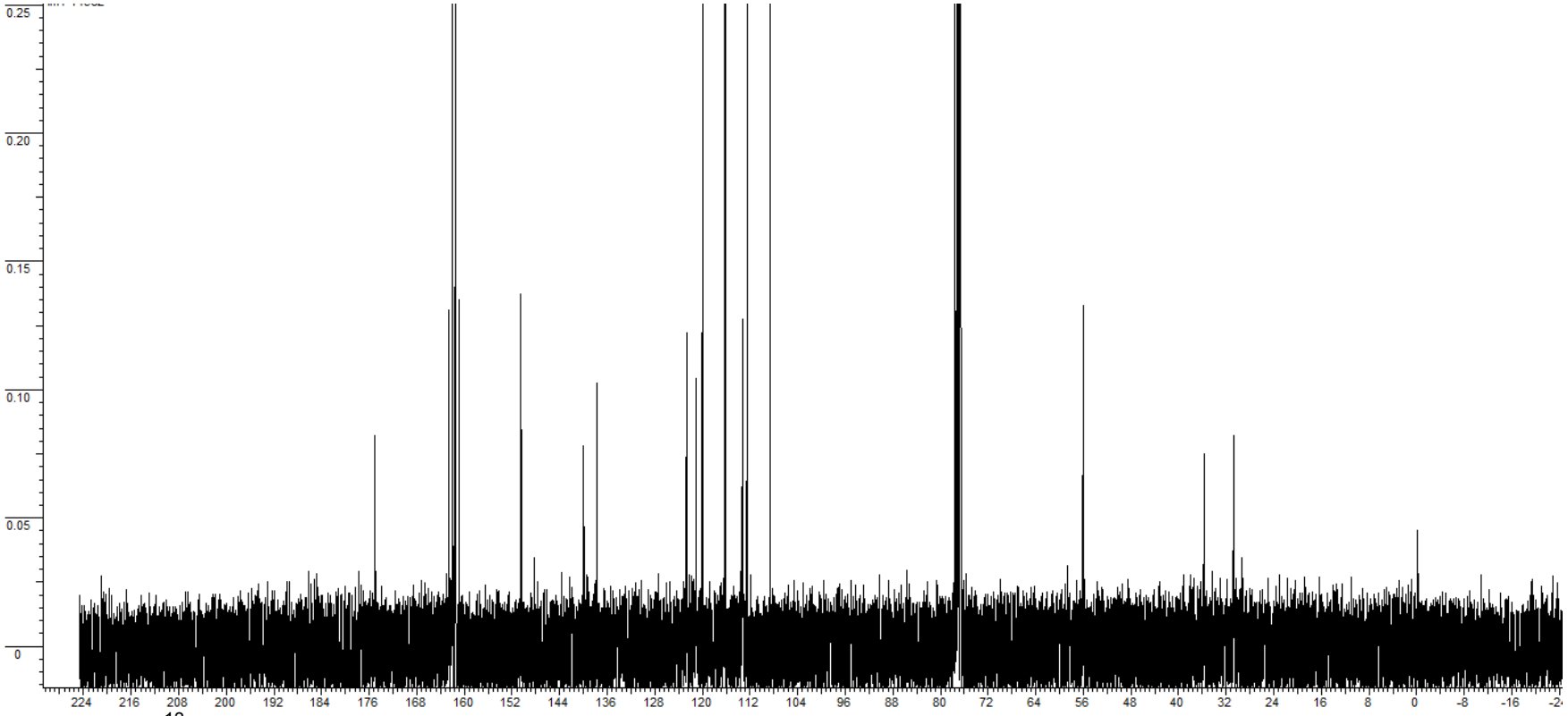


Figure A-50. ^{13}C NMR spectra of compound **2.26**

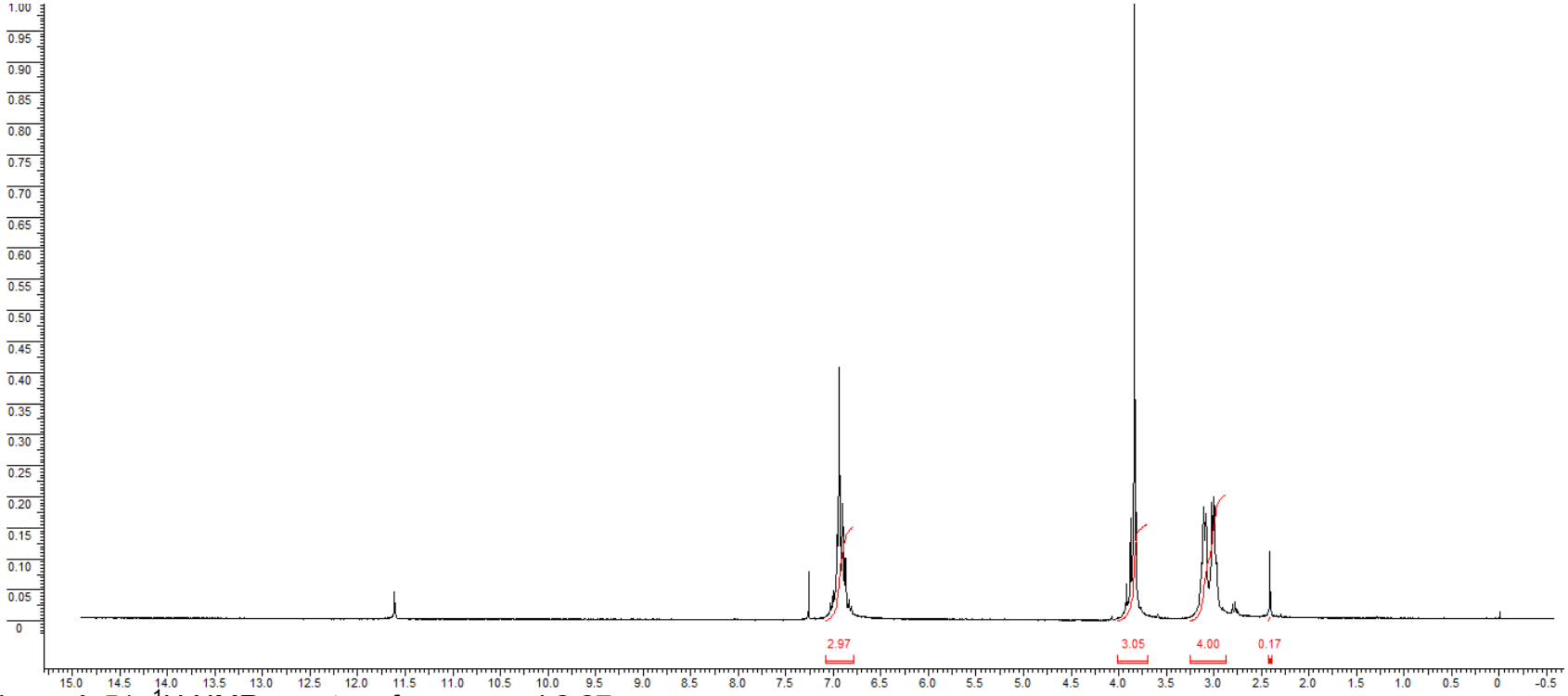


Figure A-51. ^{1}H NMR spectra of compound **2.27**

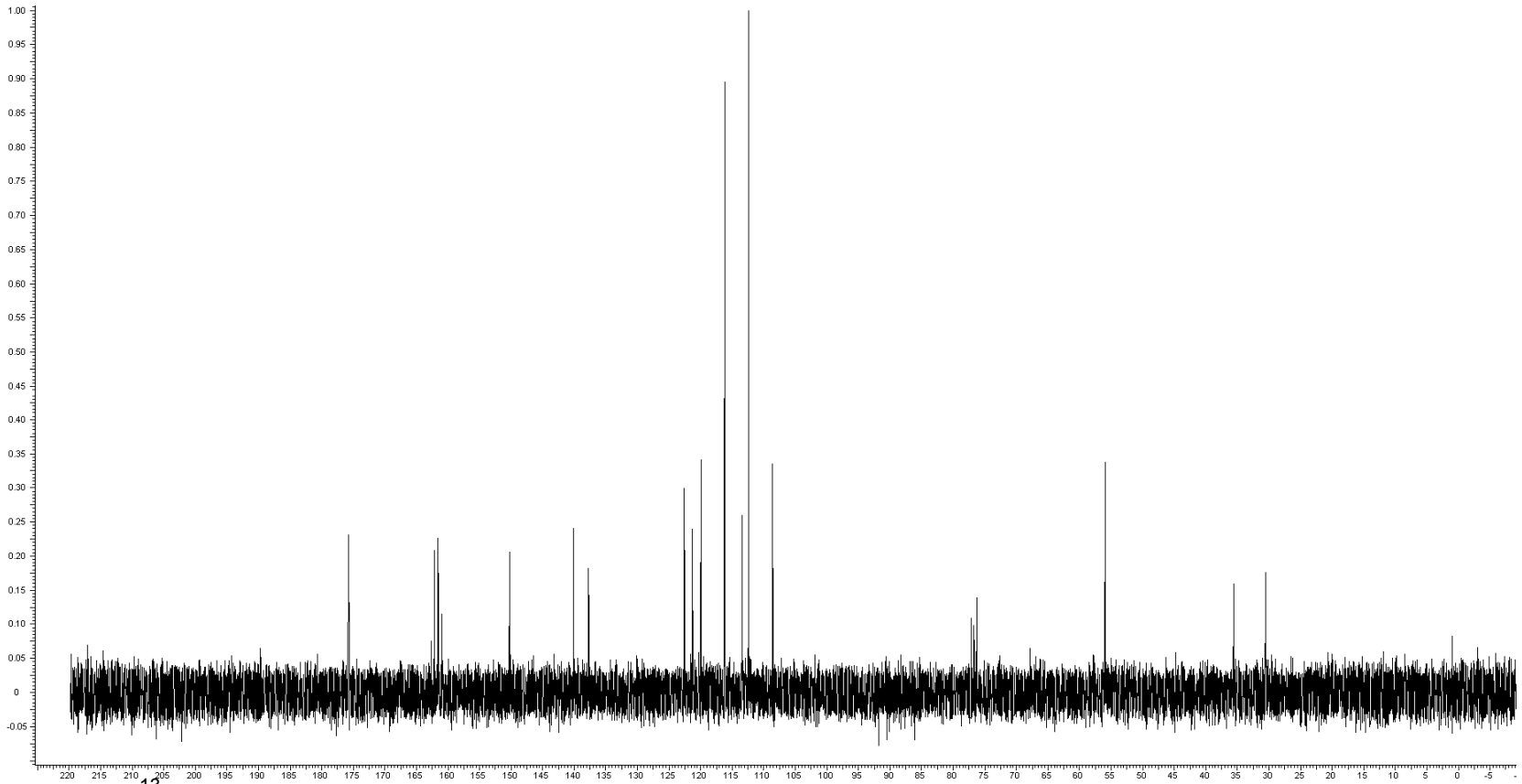


Figure A-52. ^{13}C NMR spectra of compound **2.27**

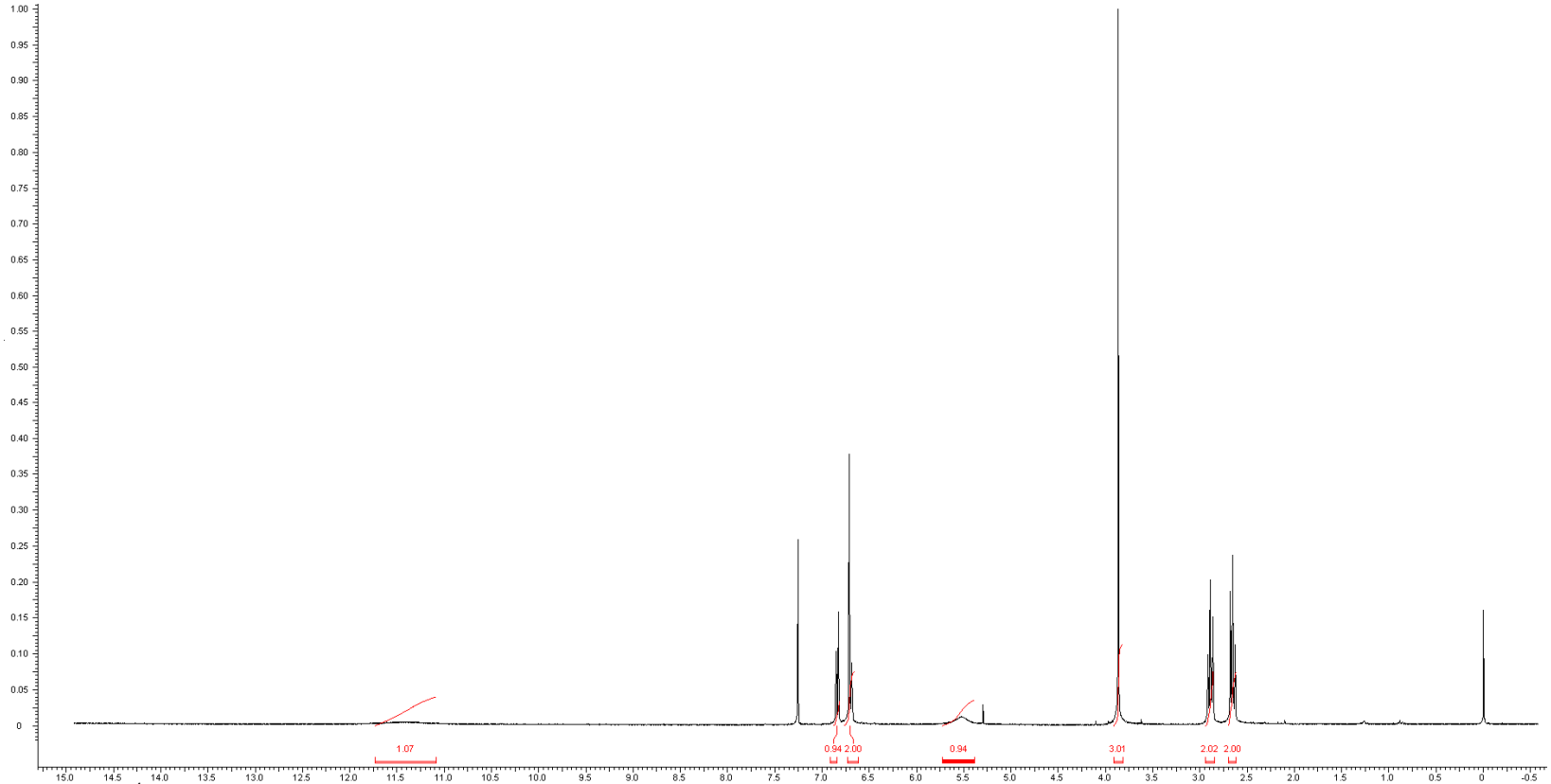


Figure A-53. ^{1}H NMR spectra of compound **2.28**

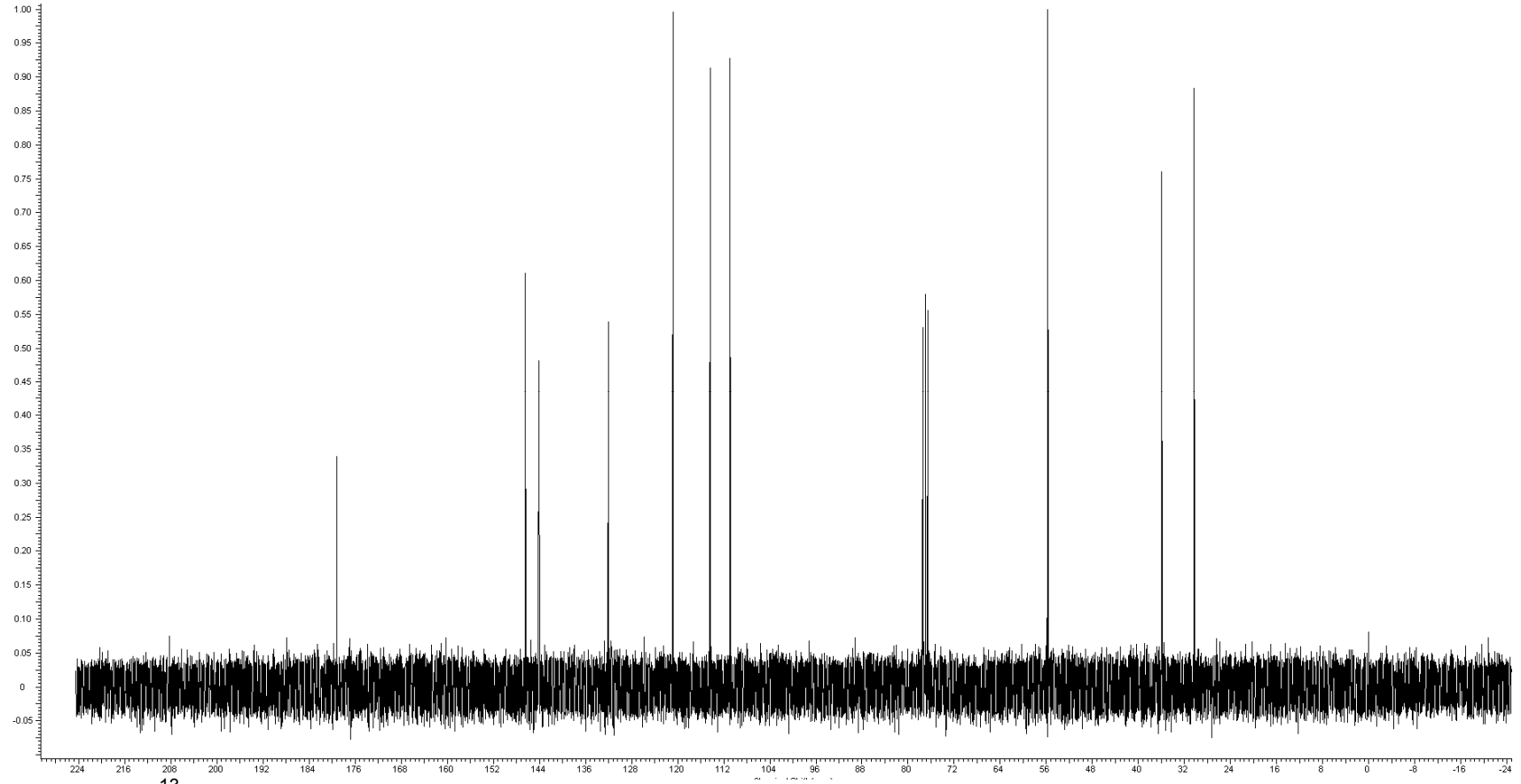


Figure A-54. ^{13}C NMR spectra of compound **2.28**

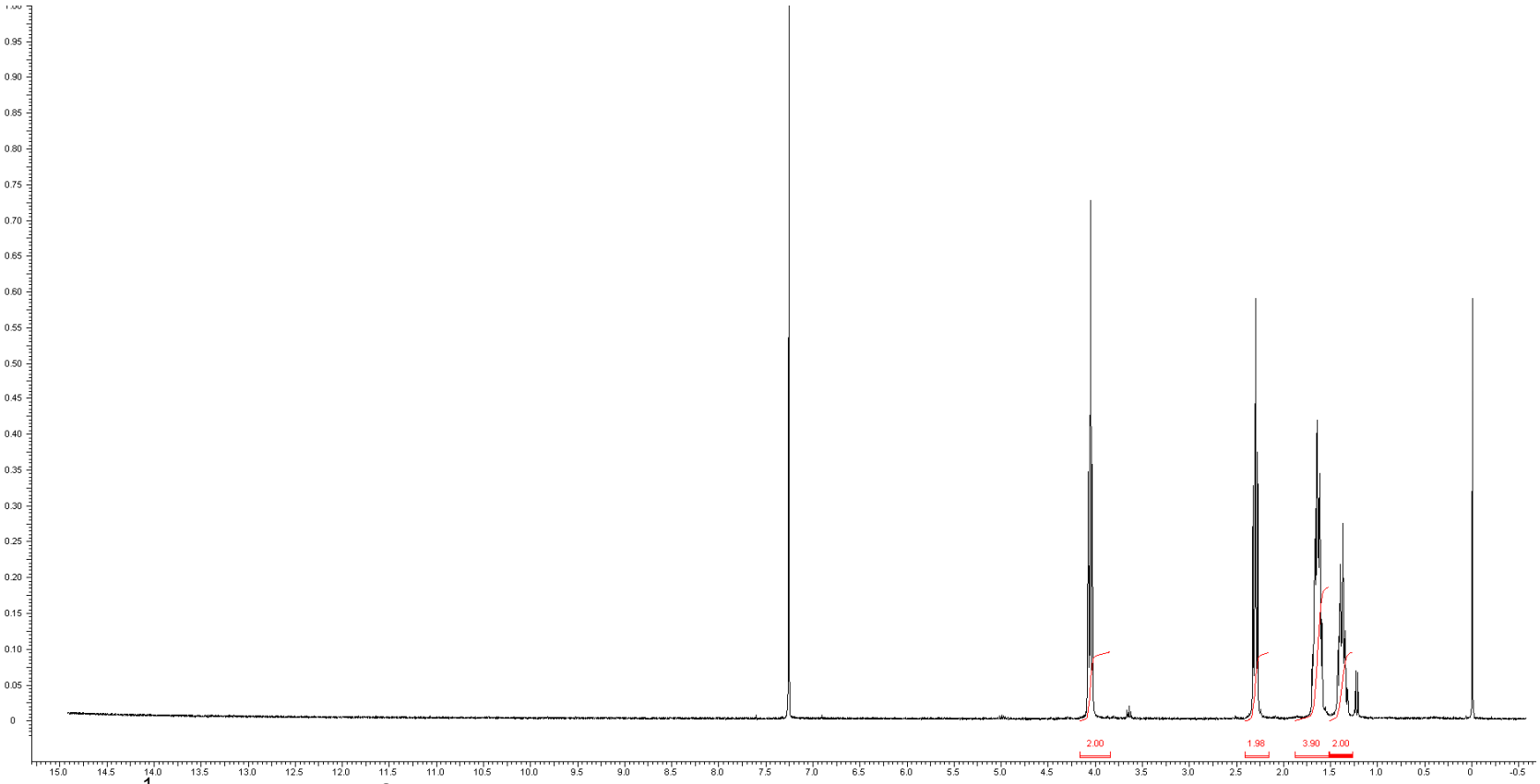


Figure A-55. ^{1}H NMR spectra of compound **3.1**

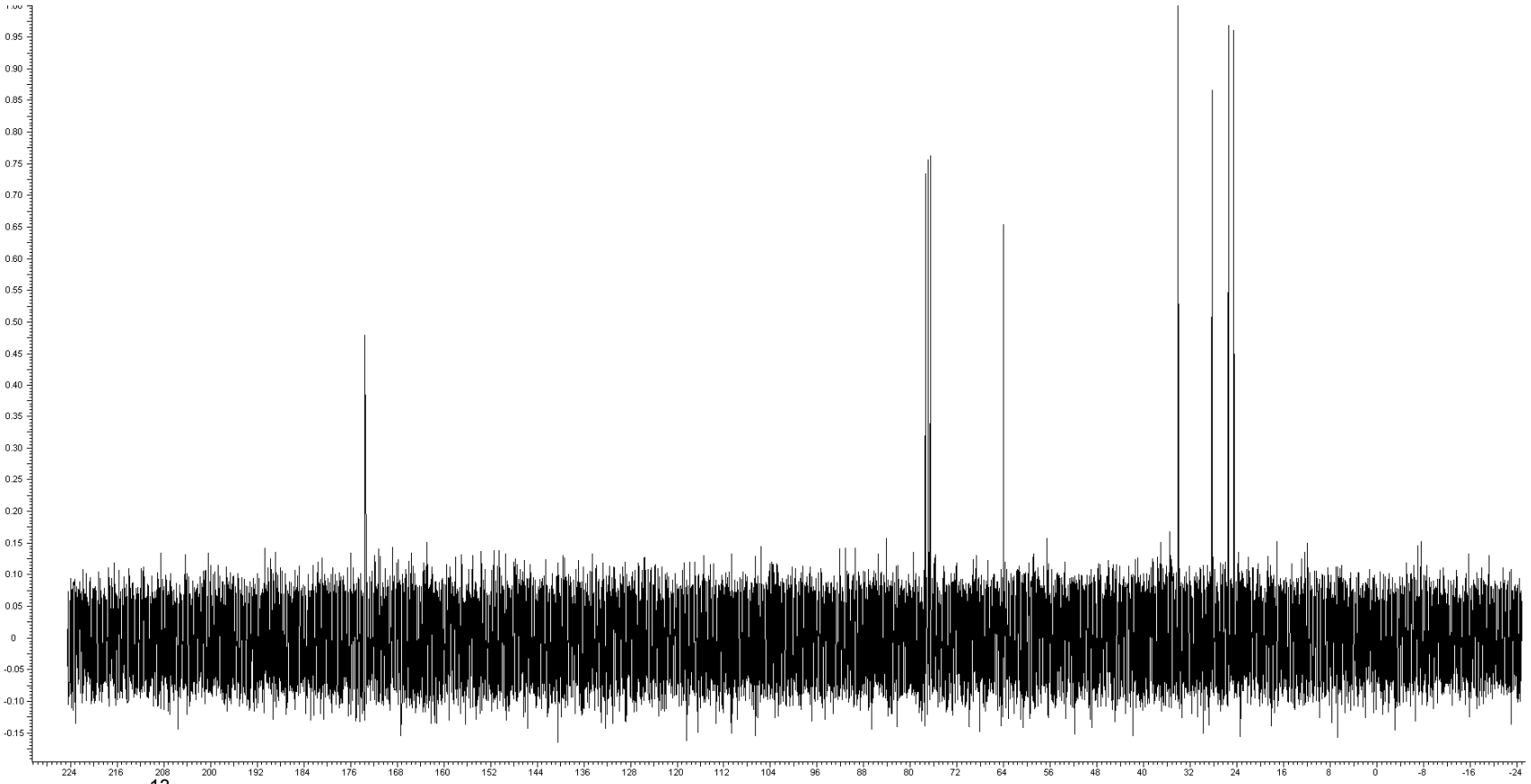


Figure A-56. ^{13}C NMR spectra of compound **3.1**

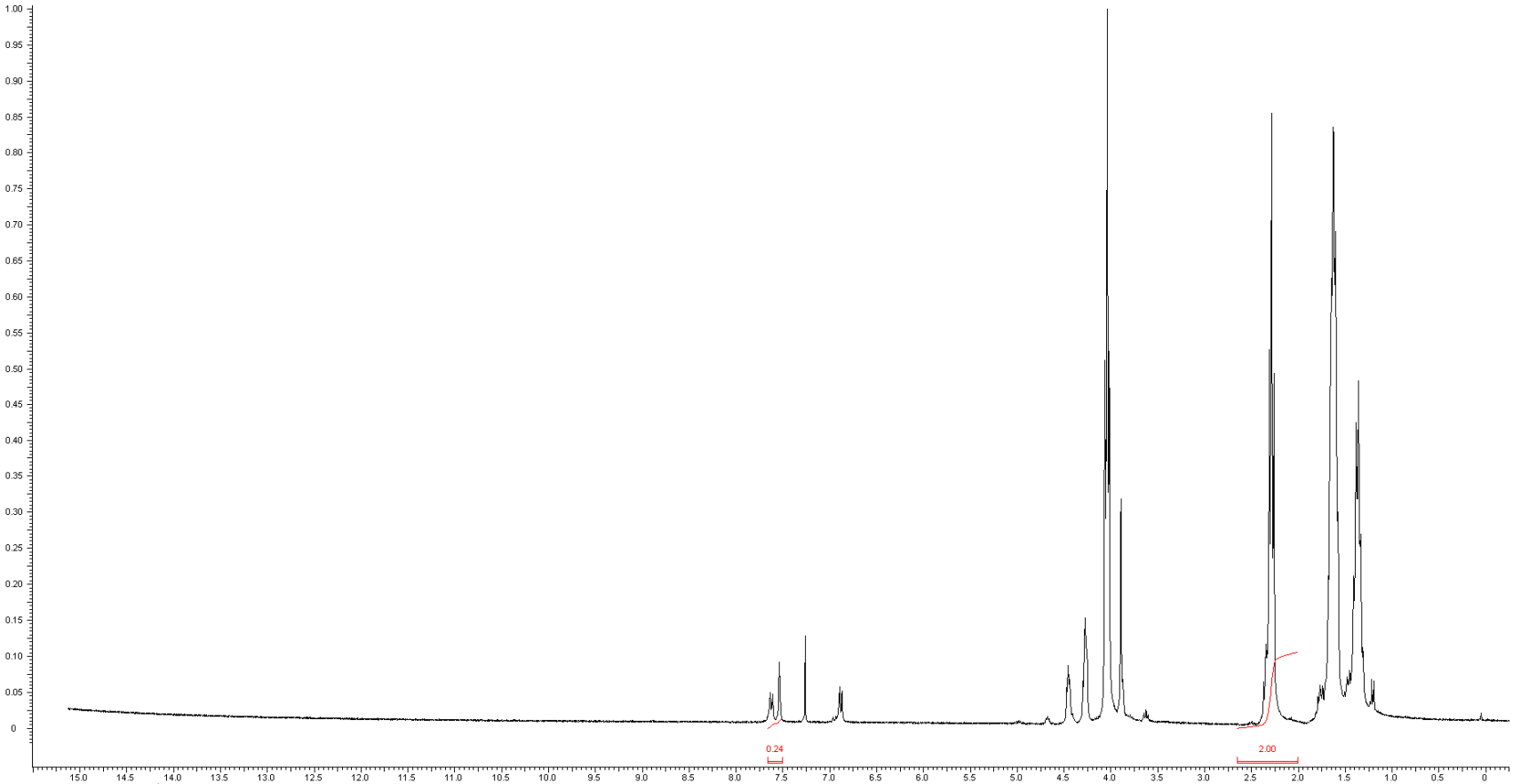


Figure A-57. ^{1}H NMR spectra of compound **3.2**

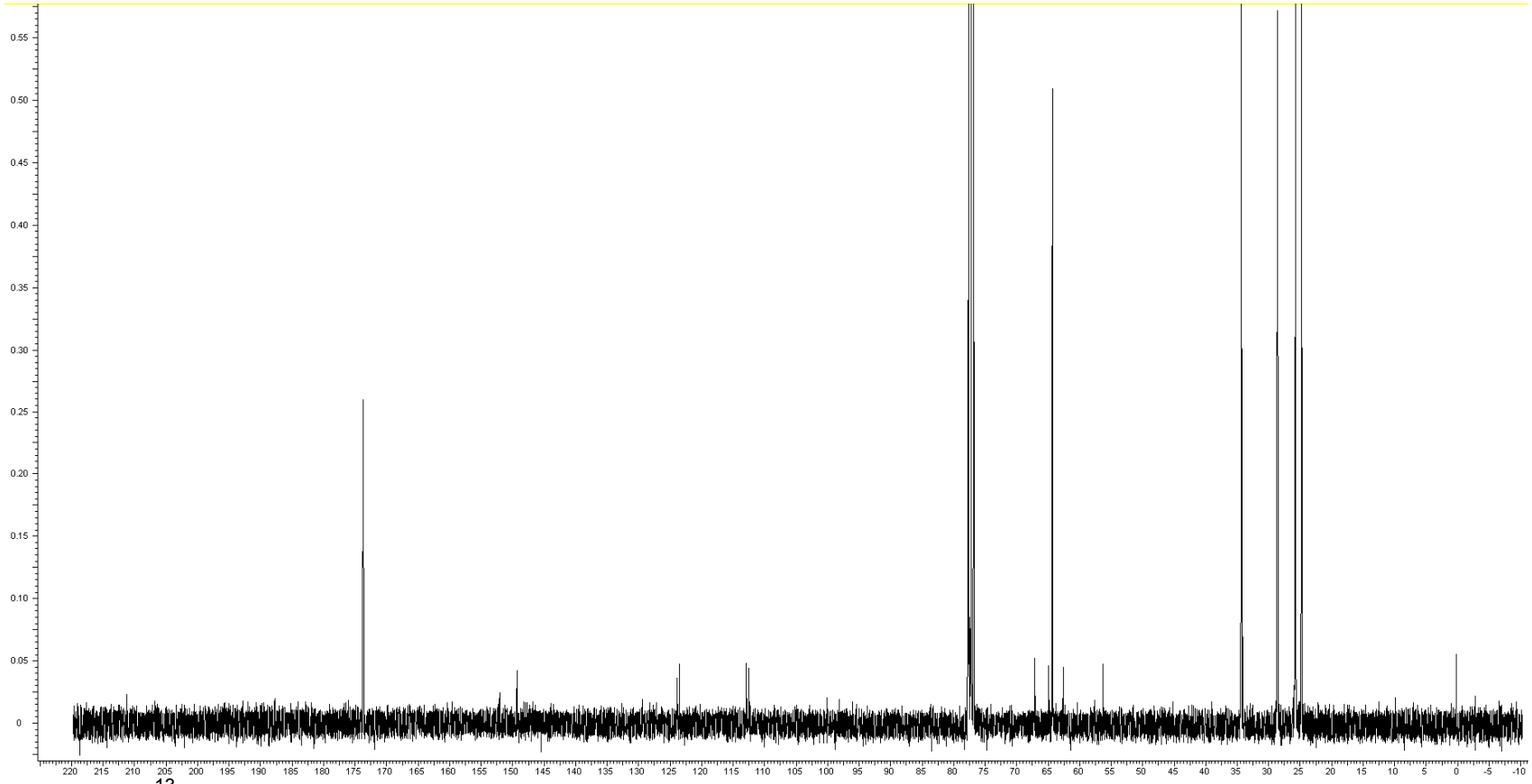


Figure A-58. ^{13}C NMR spectra of compound **3.2**

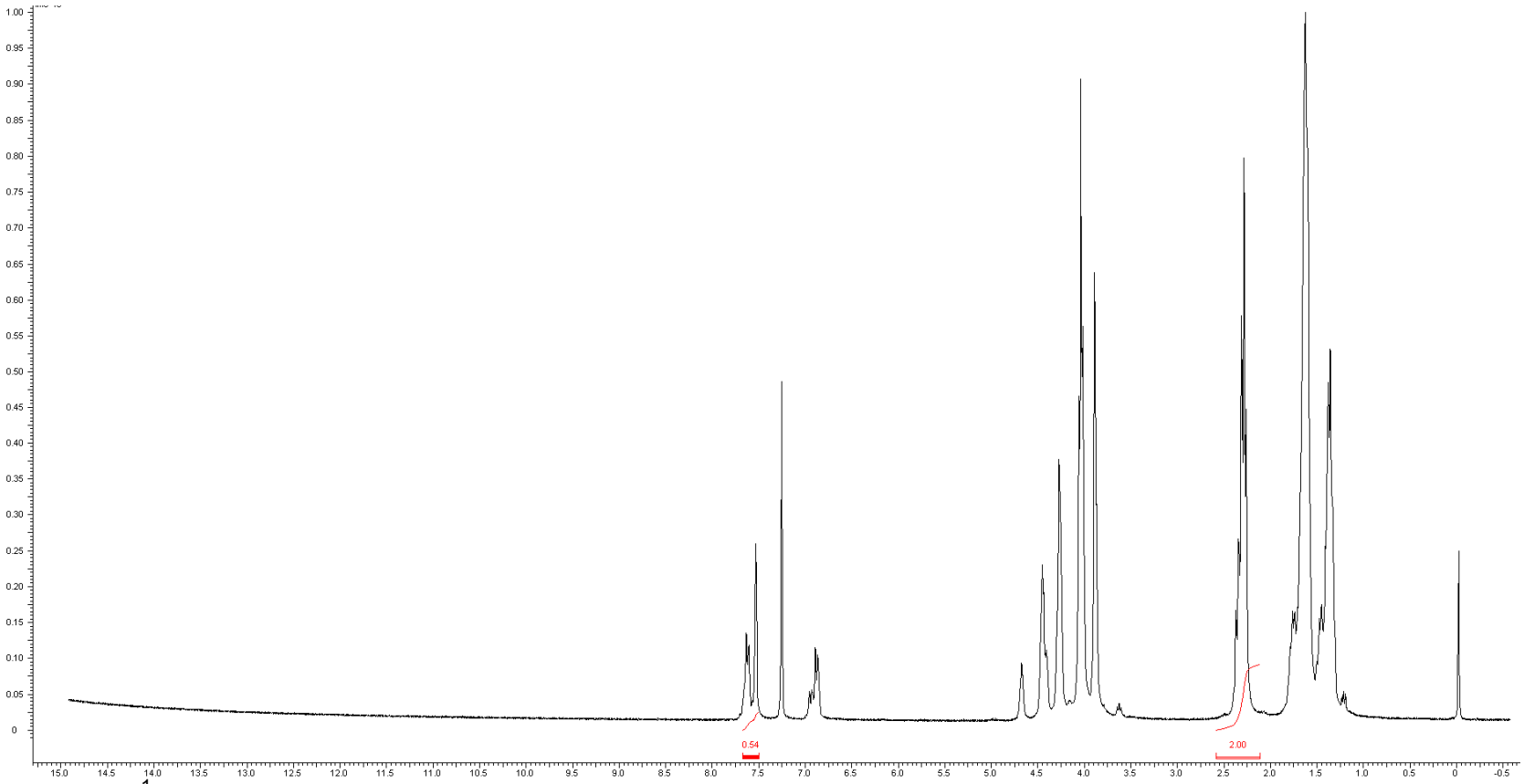


Figure A-59. ^{1}H NMR spectra of compound **3.3**

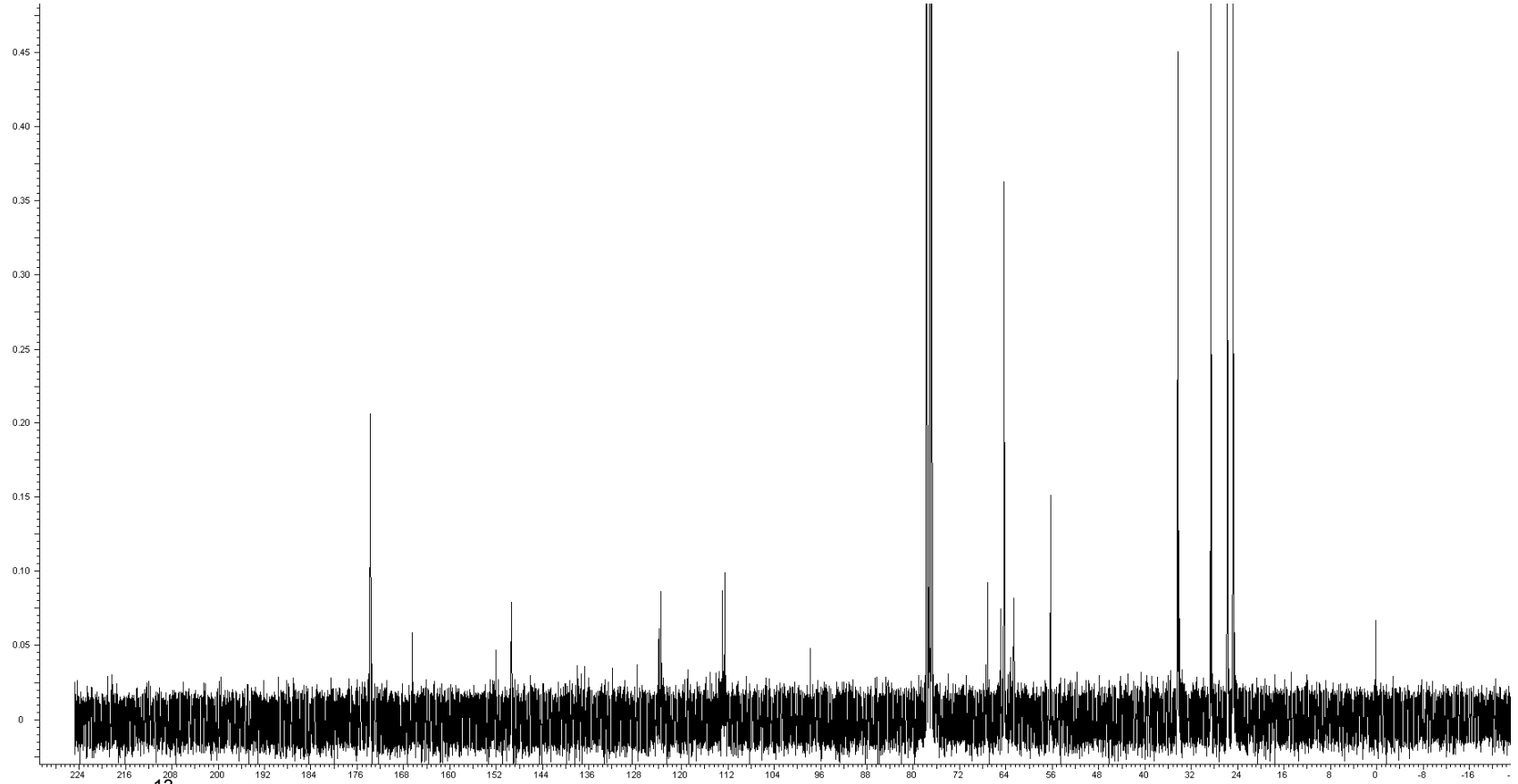


Figure A-60. ^{13}C NMR spectra of compound **3.3**

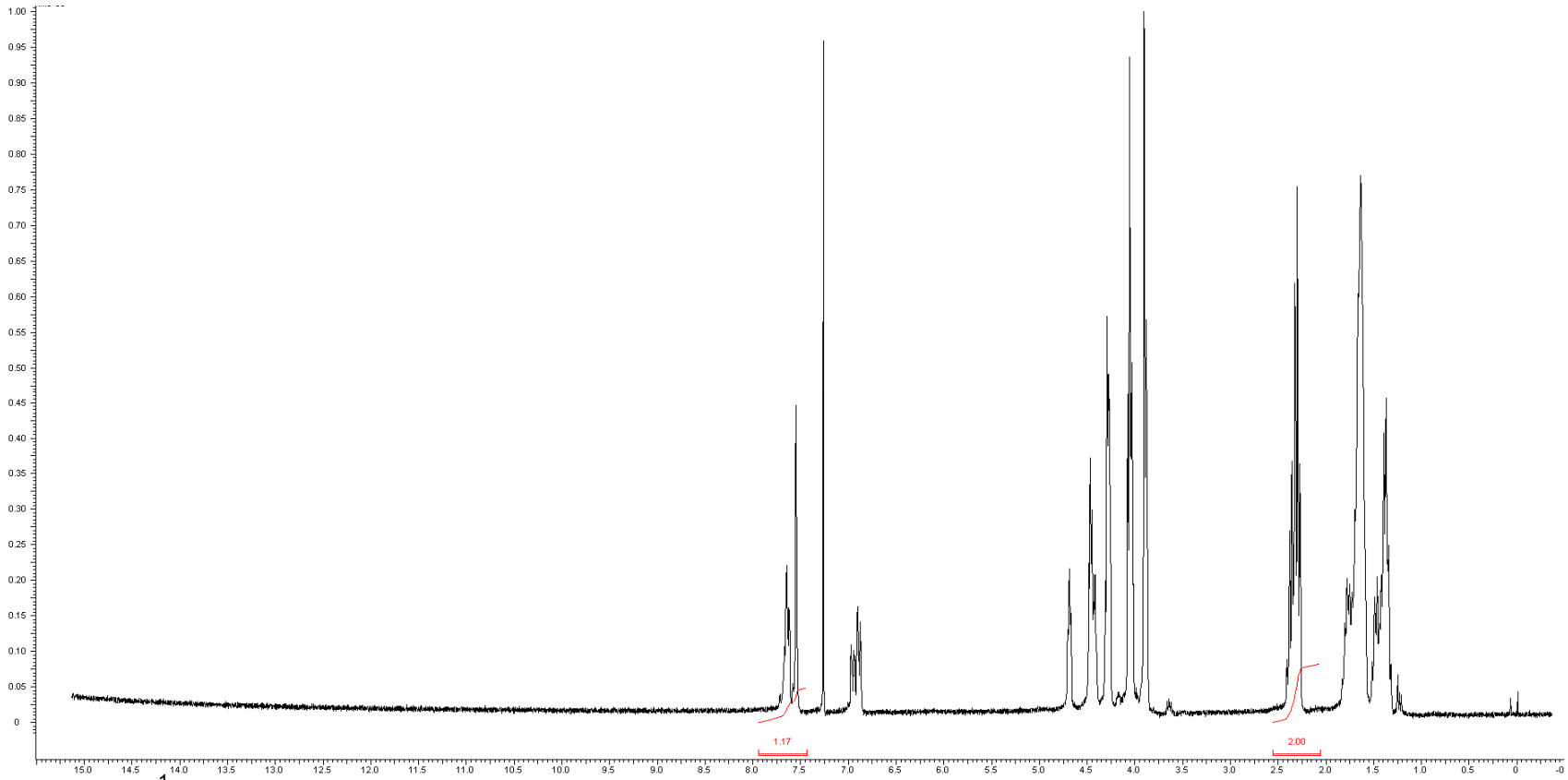


Figure A-61. ^{1}H NMR spectra of compound **3.4**

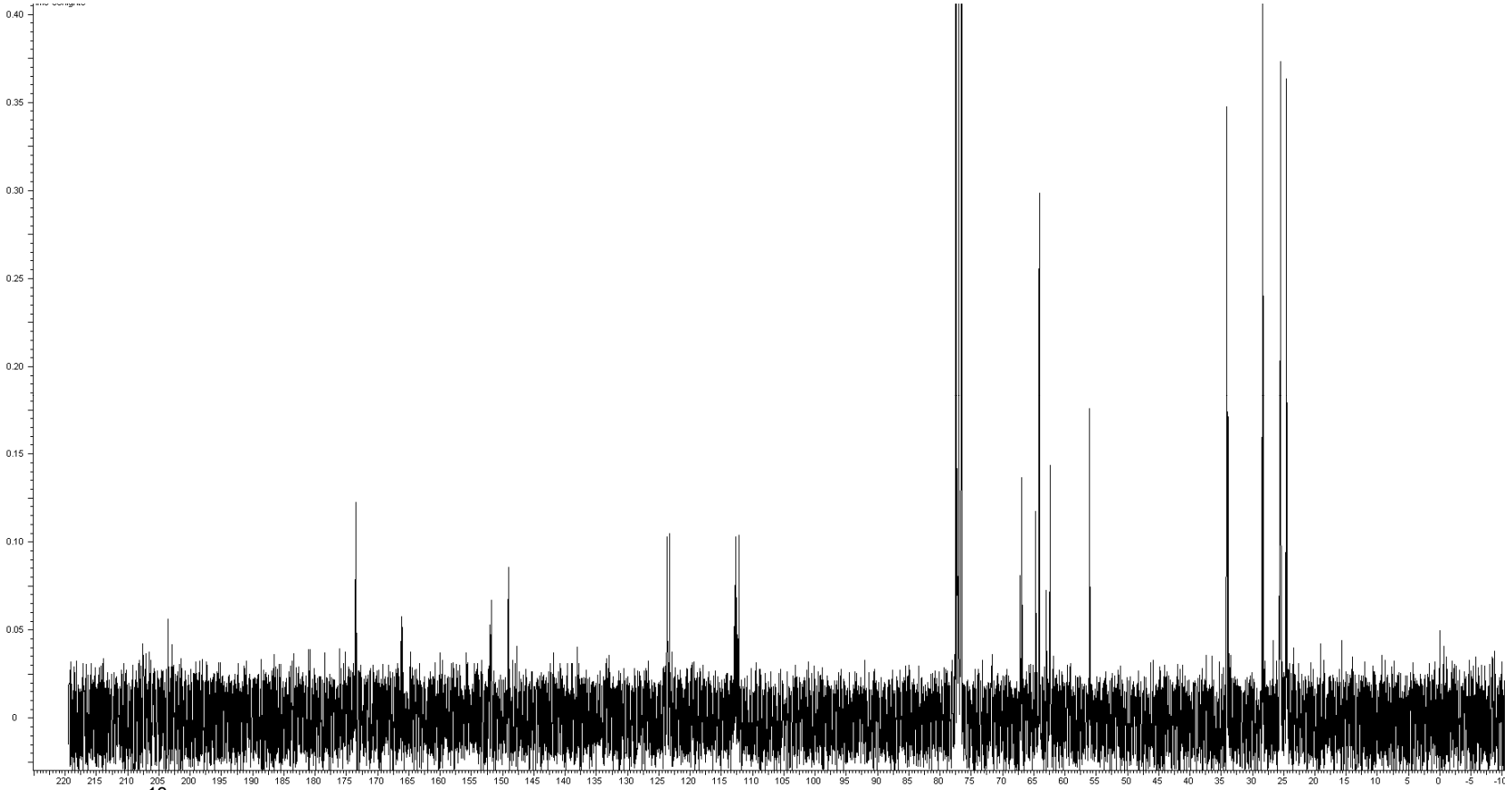


Figure A-62. ^{13}C NMR spectra of compound **3.4**

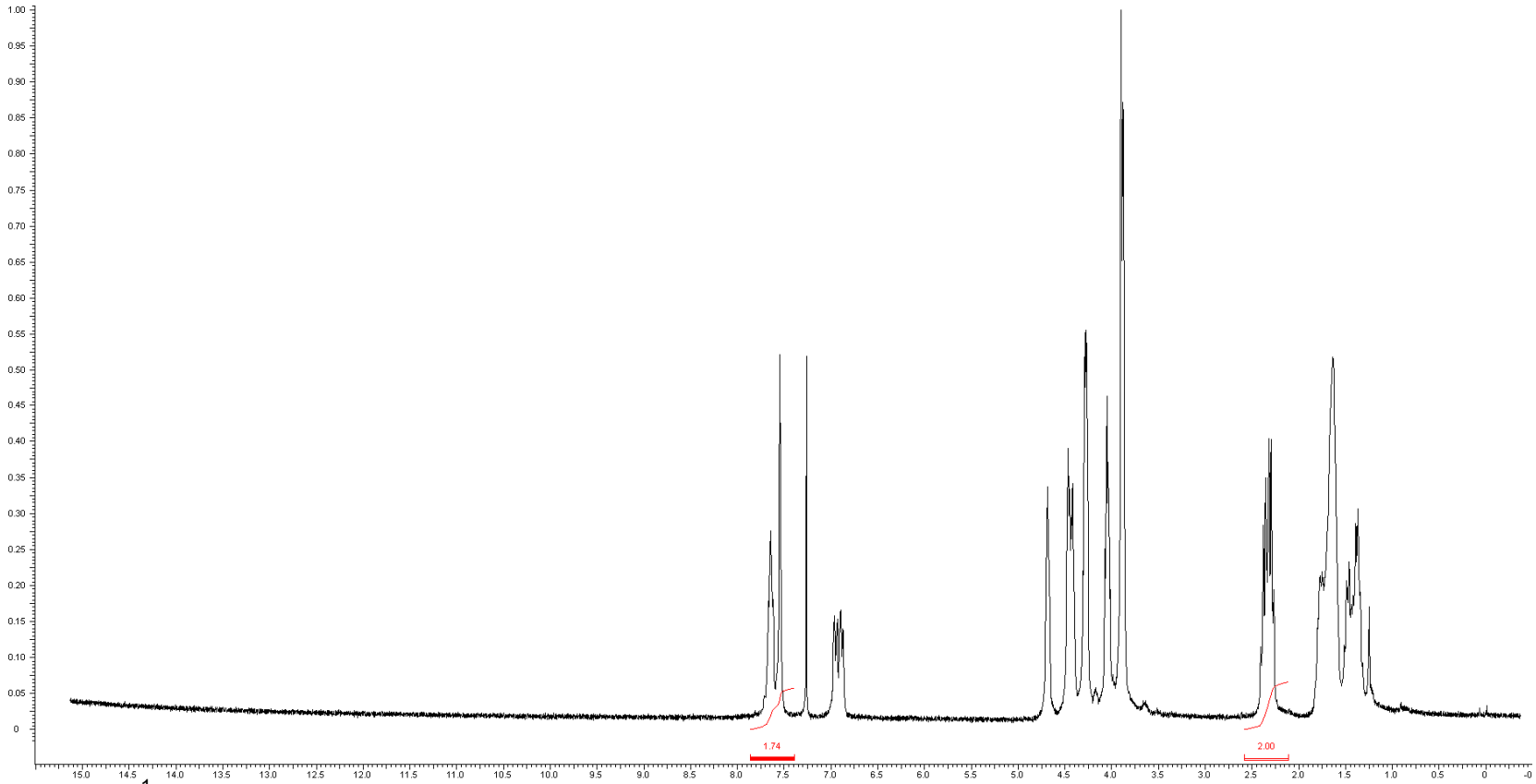


Figure A-63. ^{1}H NMR spectra of compound **3.5**

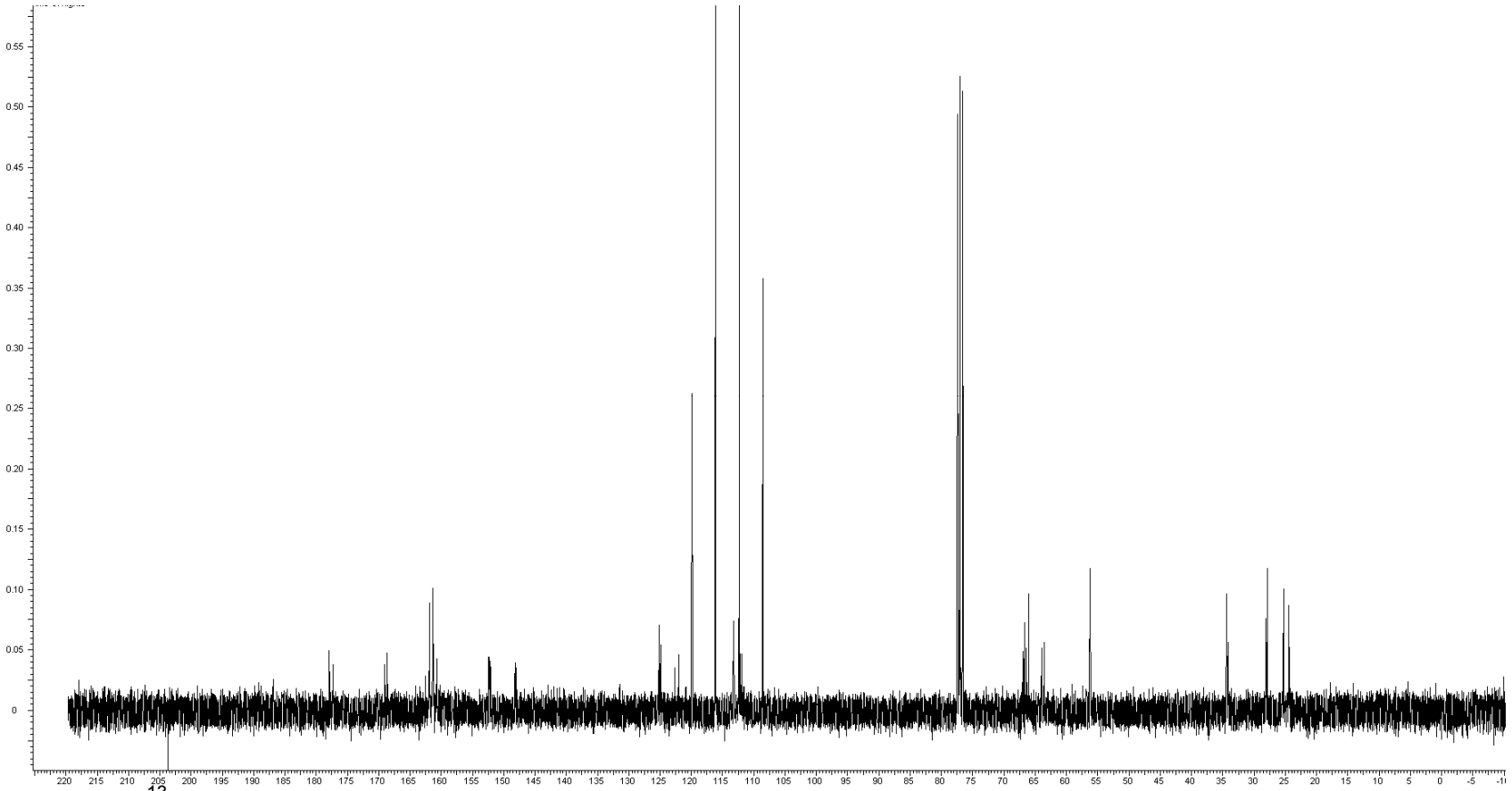


Figure A-64. ^{13}C NMR spectra of compound **3.5**

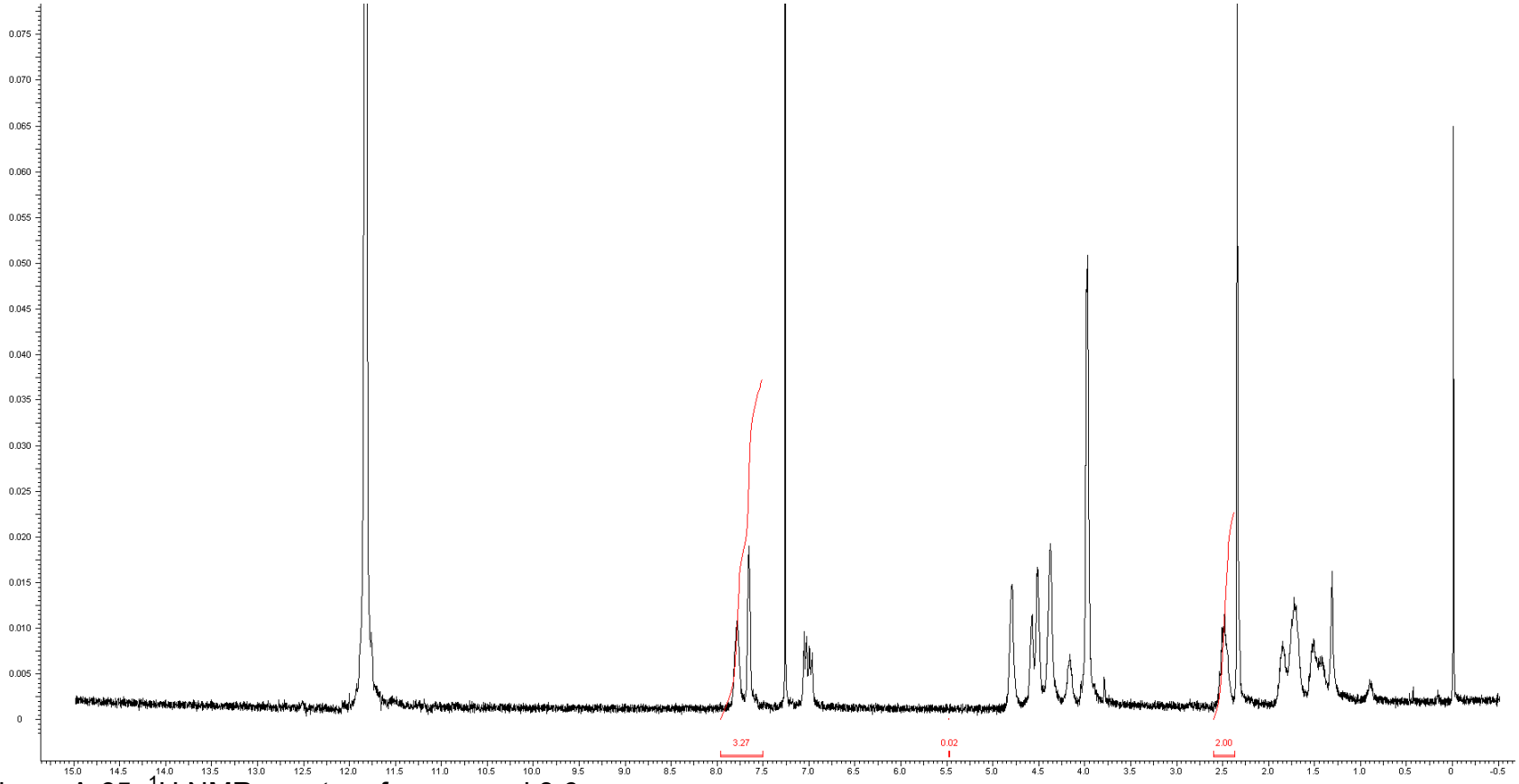


Figure A-65. ^{1}H NMR spectra of compound **3.6**

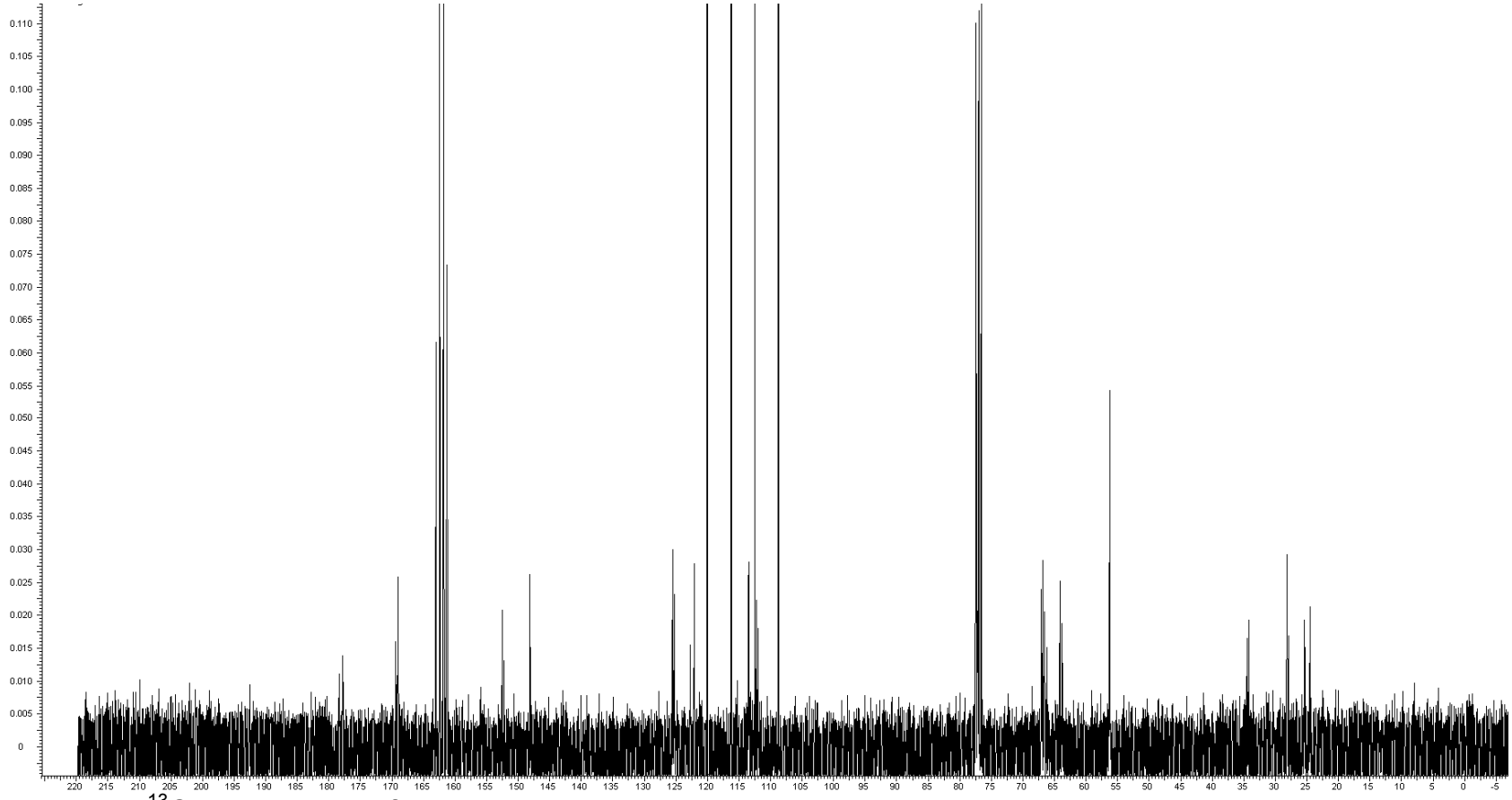


Figure A-66. ^{13}C NMR spectra of compound **3.6**

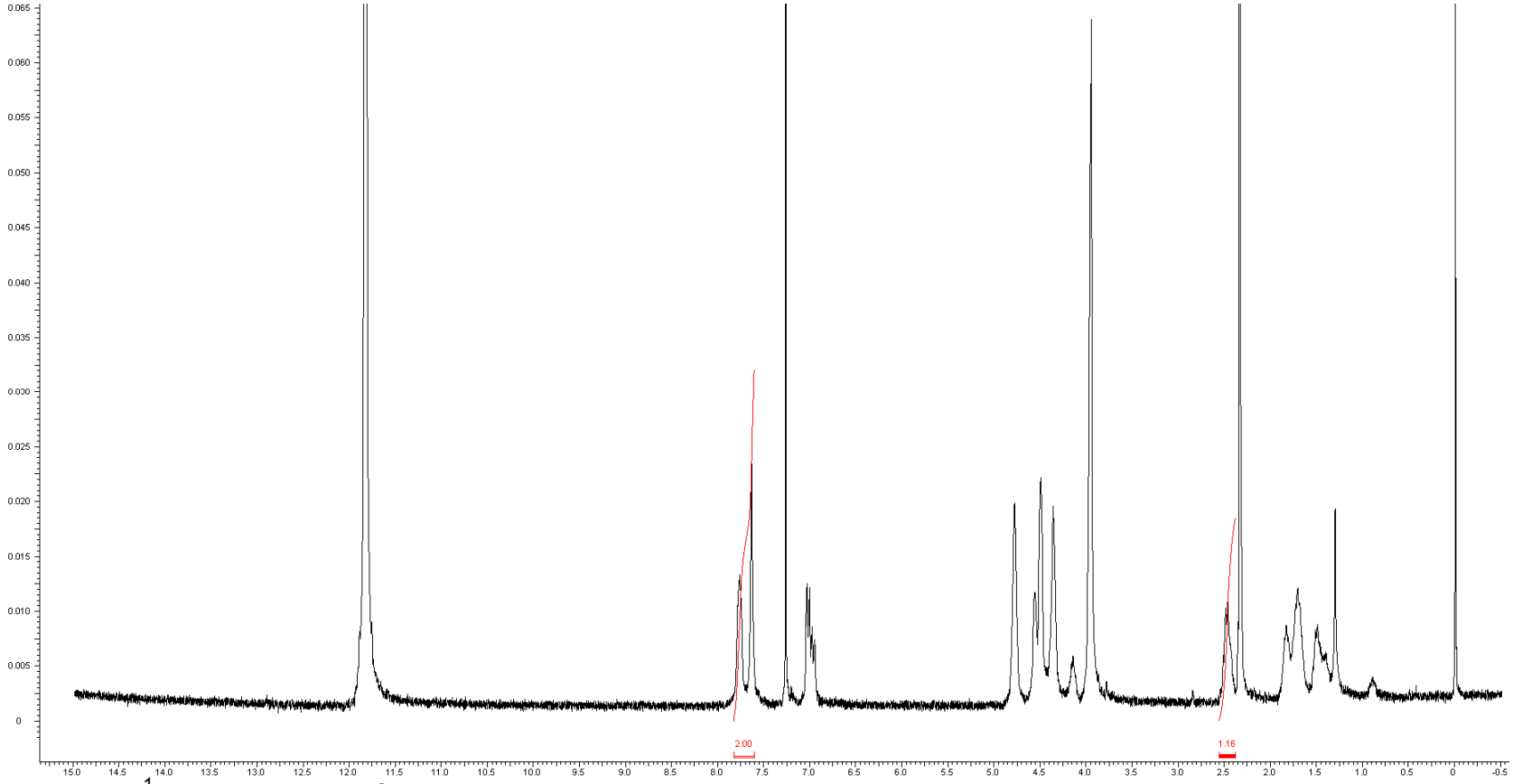


Figure A-67. ^{1}H NMR spectra of compound **3.7**

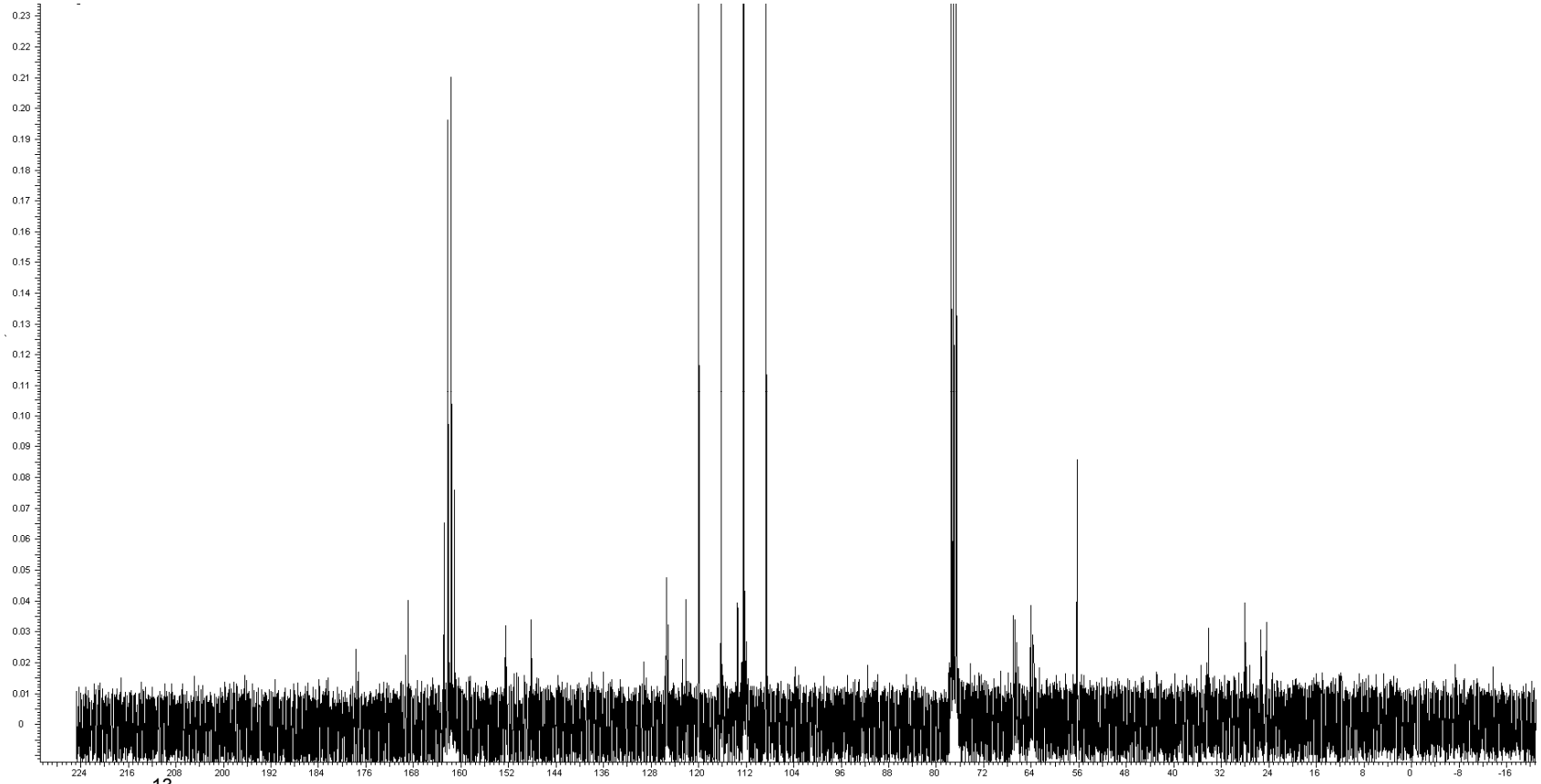


Figure A-68. ^{13}C NMR spectra of compound **3.7**

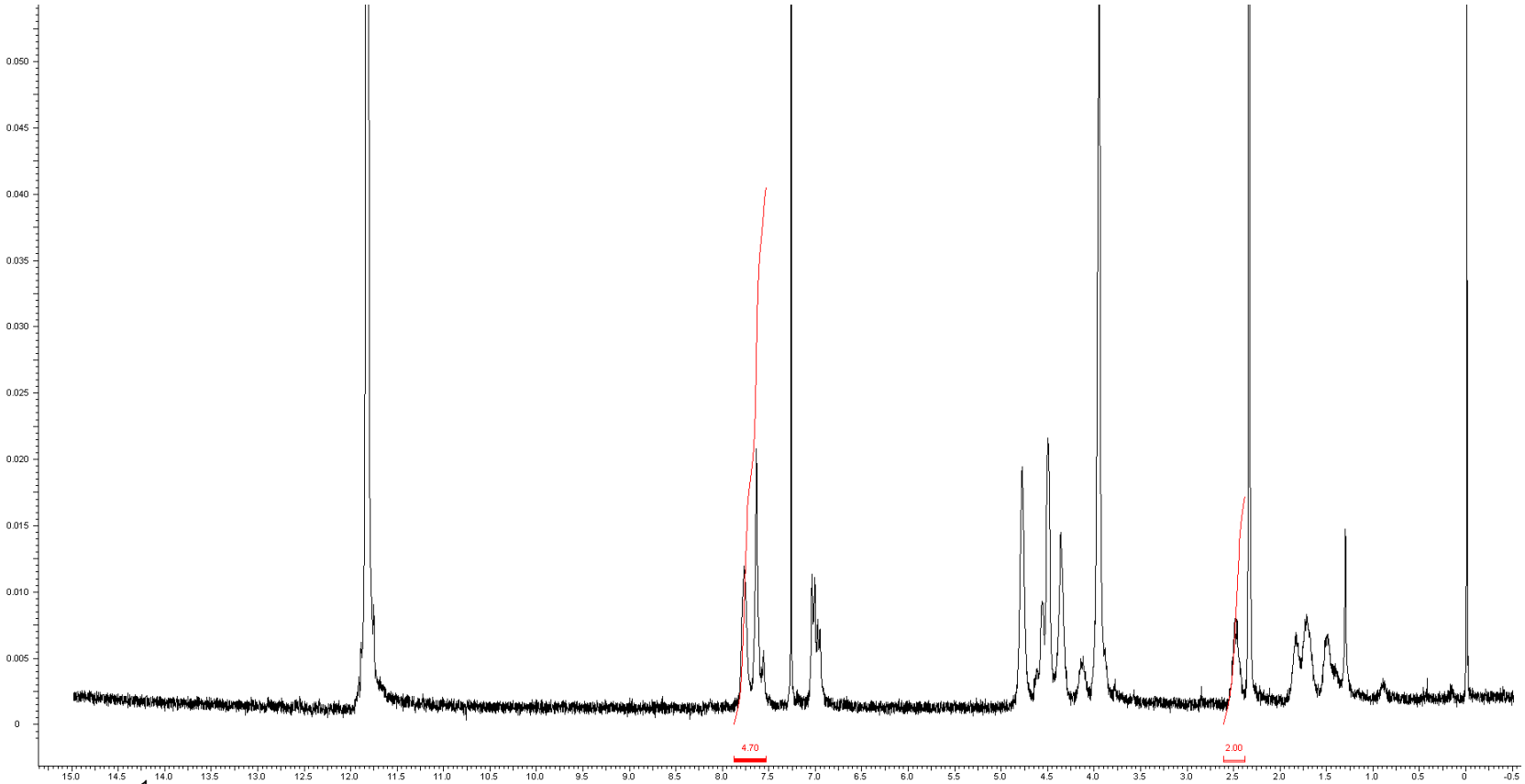


Figure A-69. ^{1}H NMR spectra of compound **3.8**

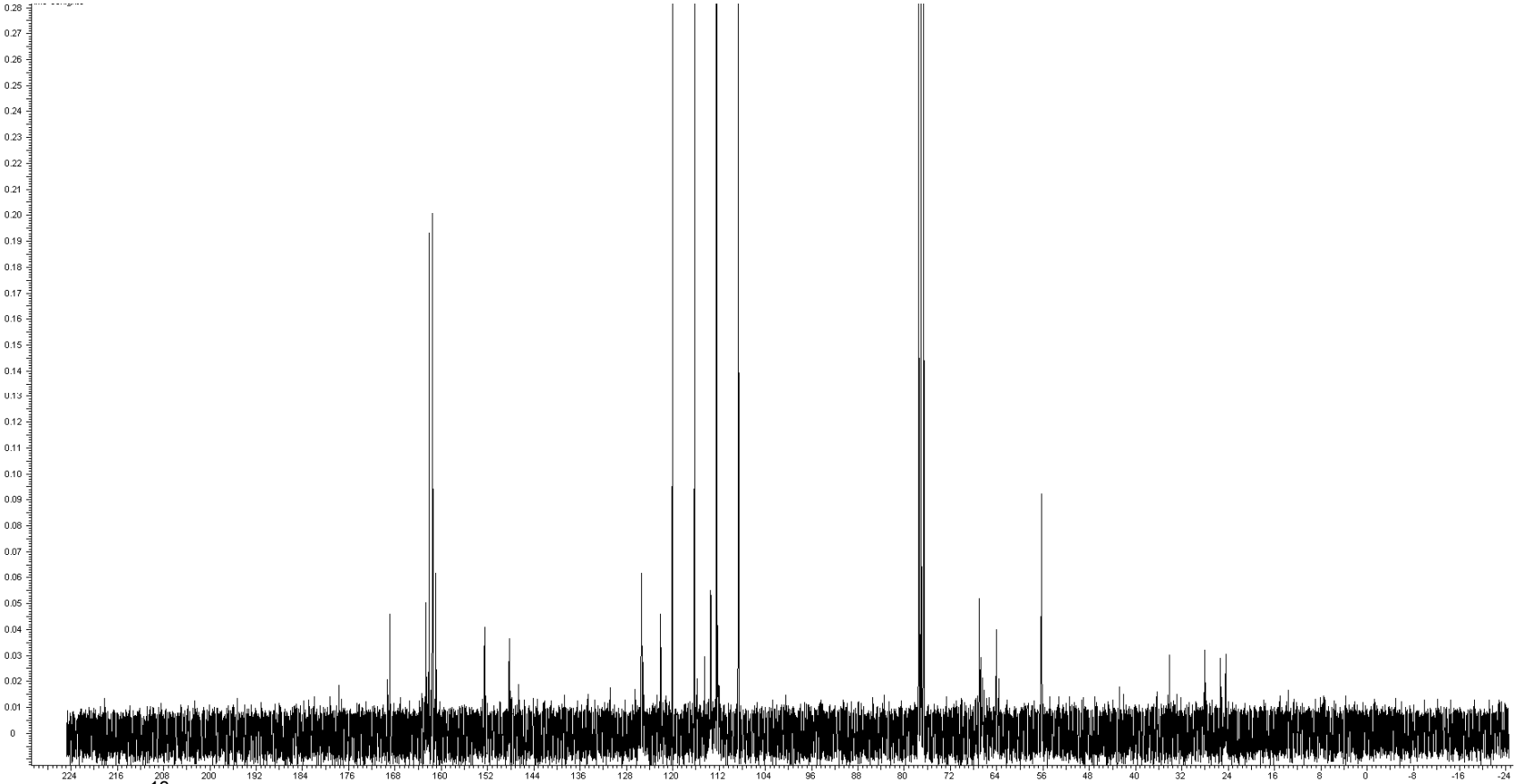


Figure A-70. ^{13}C NMR spectra of compound **3.8**

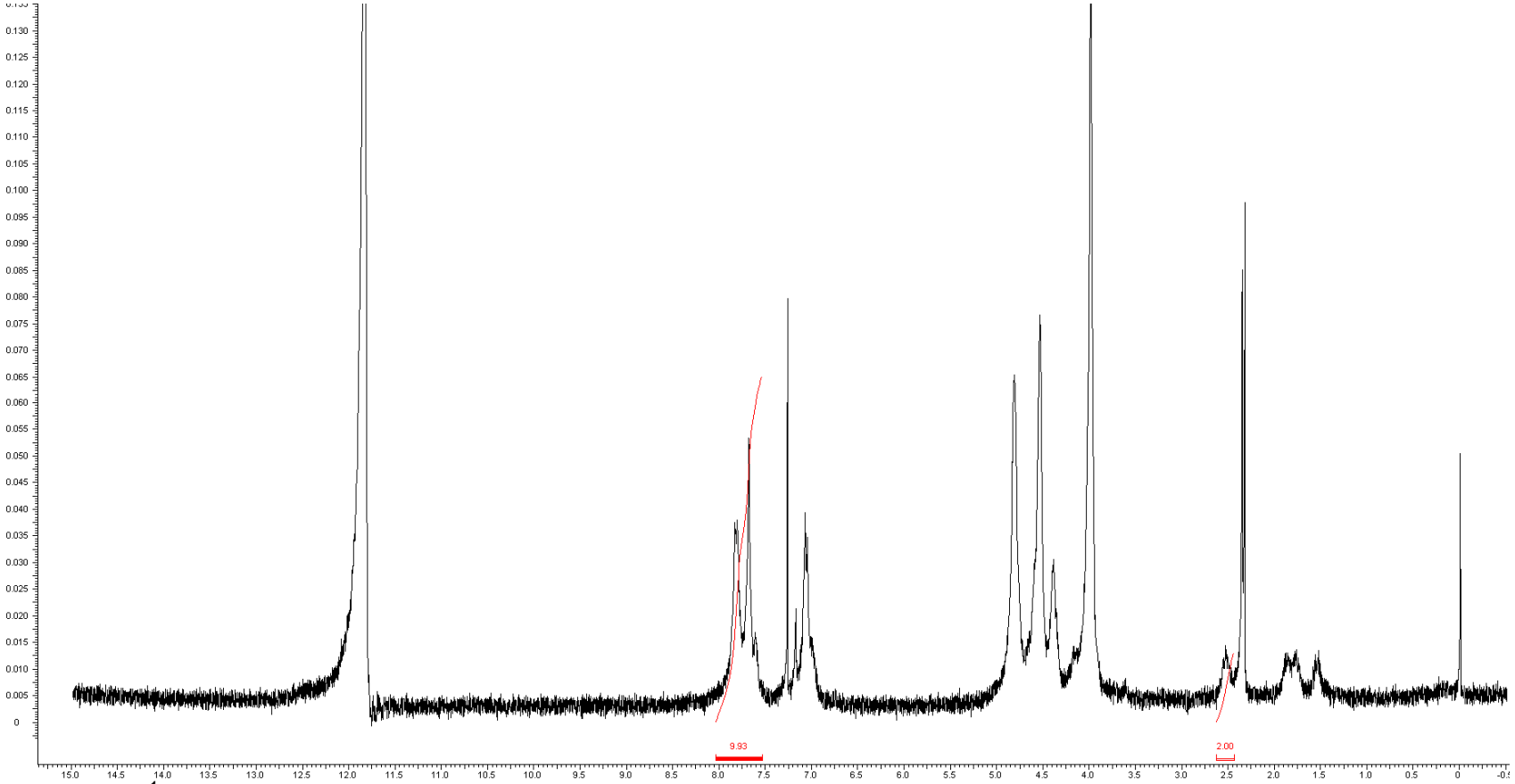


Figure A-71. ^{1}H NMR spectra of compound **3.9**

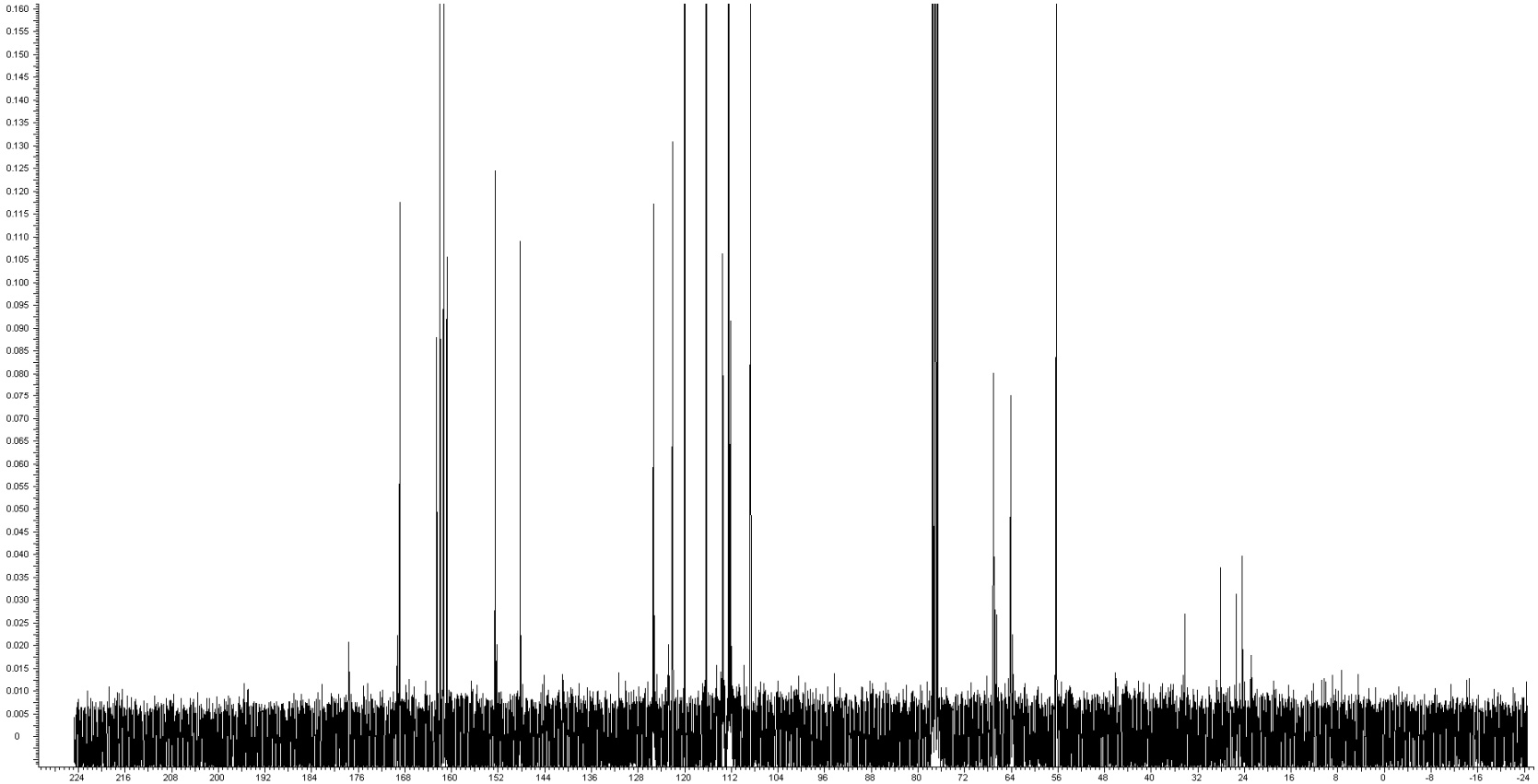


Figure A-72. ^{13}C NMR spectra of compound **3.9**

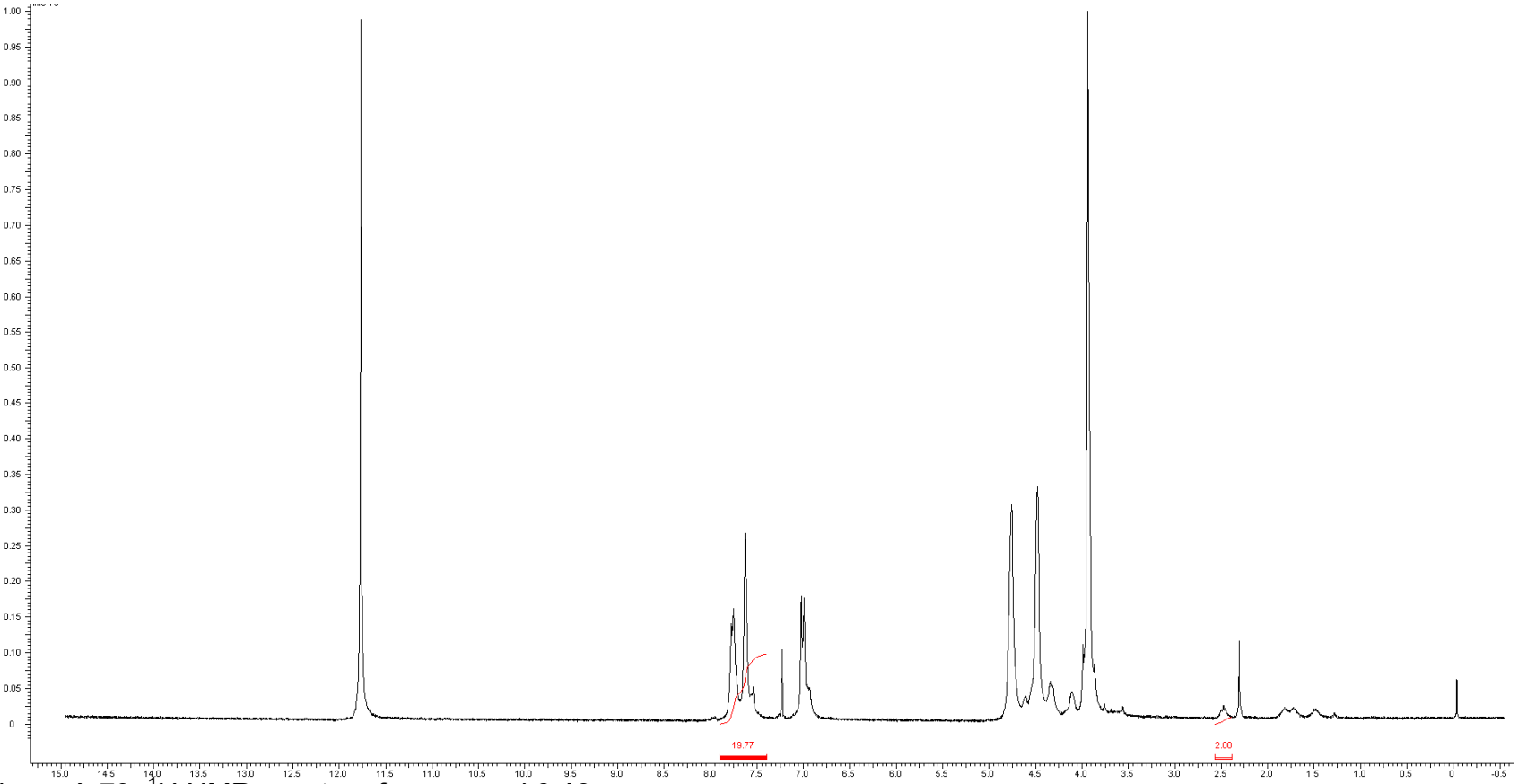


Figure A-73. ^{1}H NMR spectra of compound **3.10**

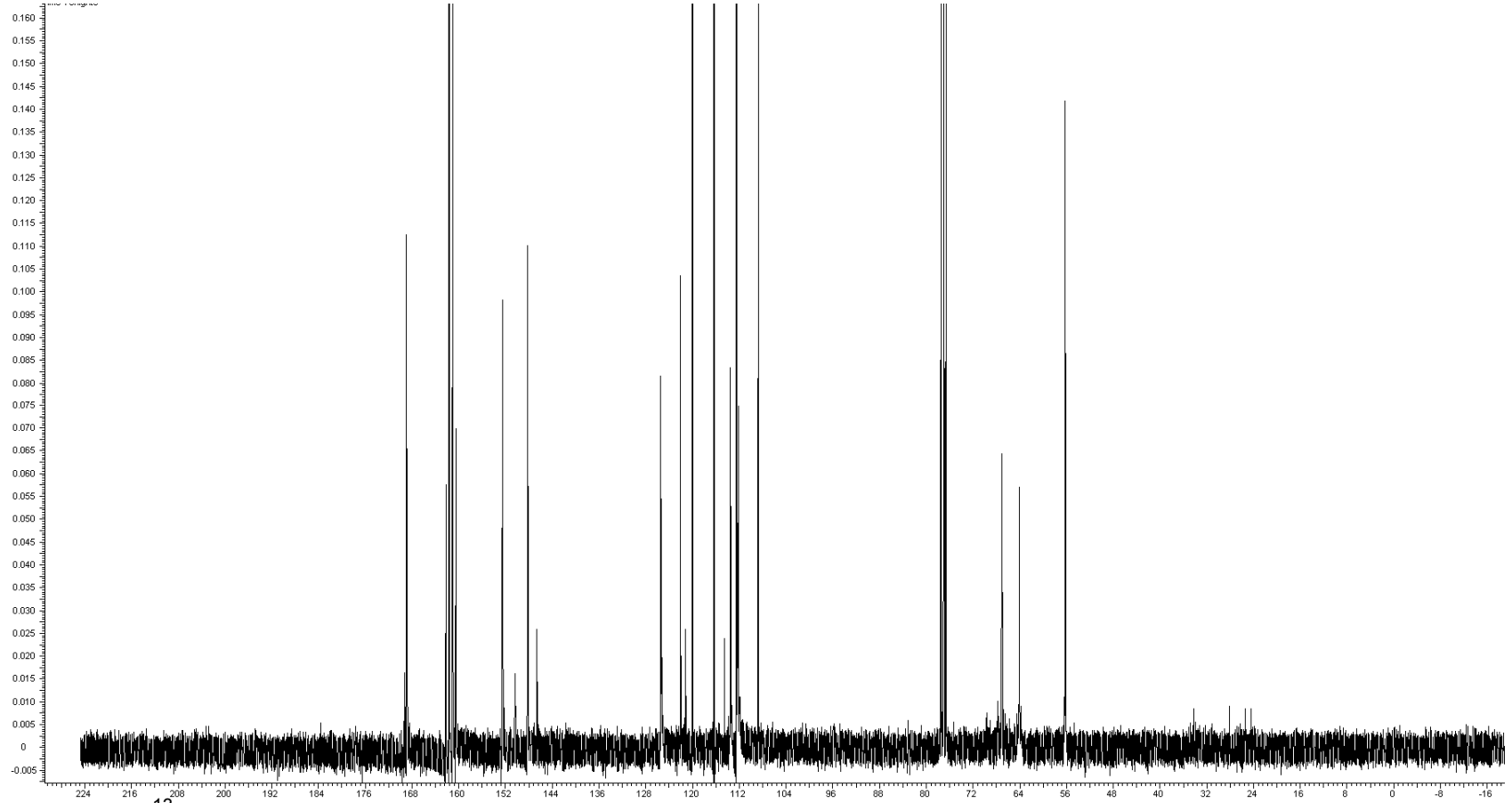


Figure A-74. ^{13}C NMR spectra of compound **3.10**

APPENDIX B
POLYMER DATA

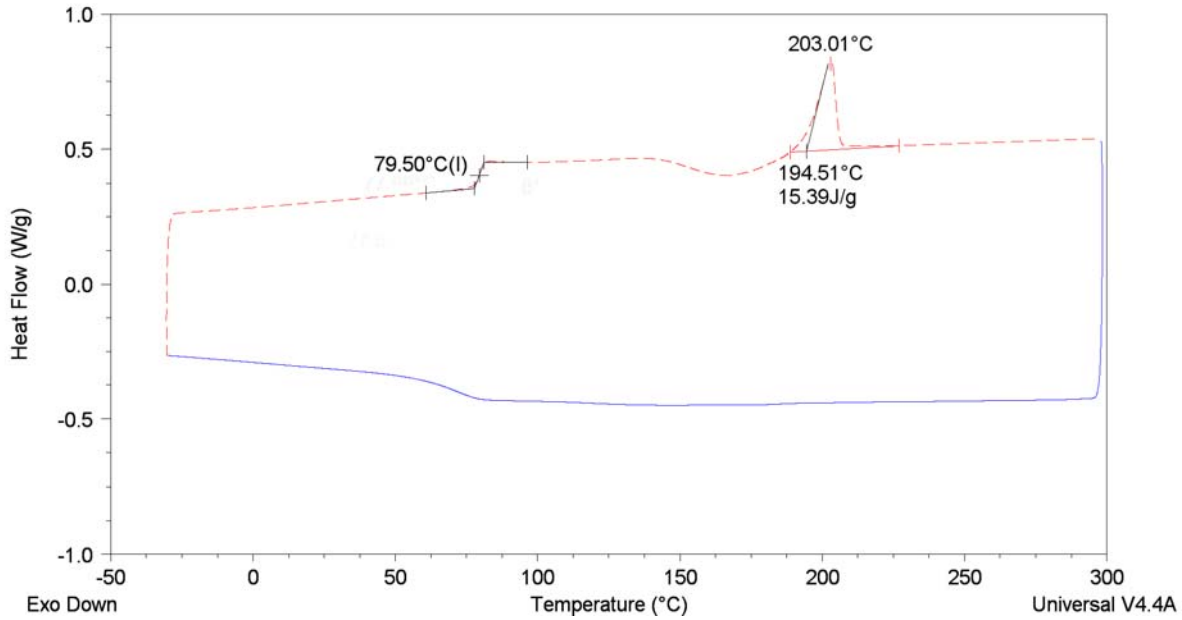


Figure B-1. DSC of polymer **2.7**

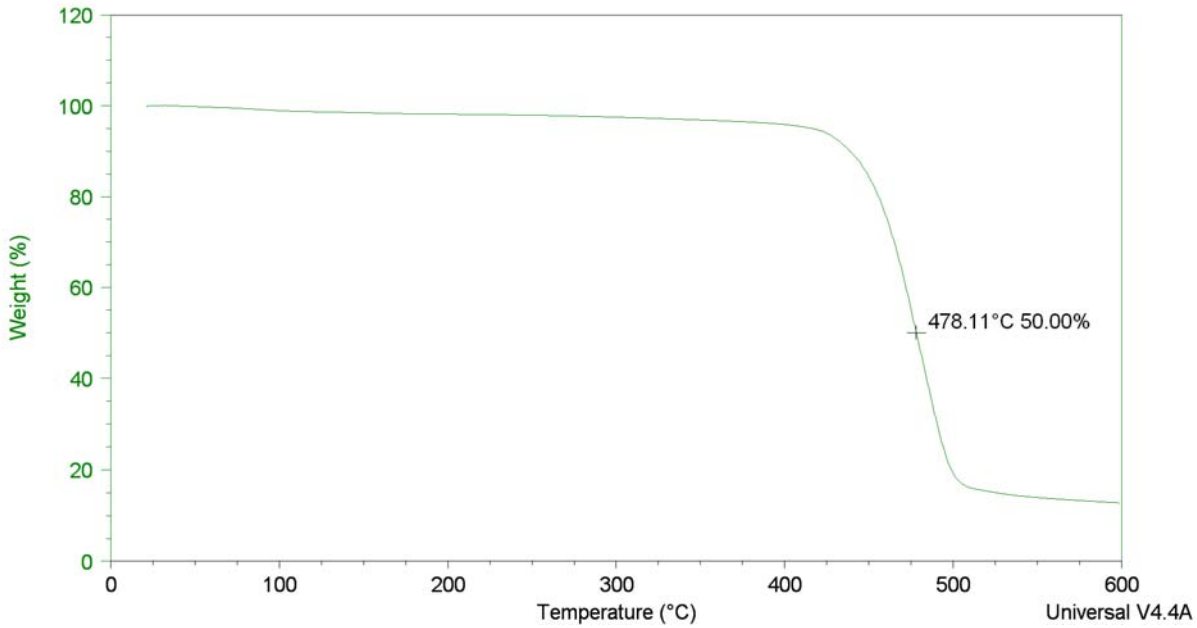


Figure B-2. TGA of polymer **2.7**

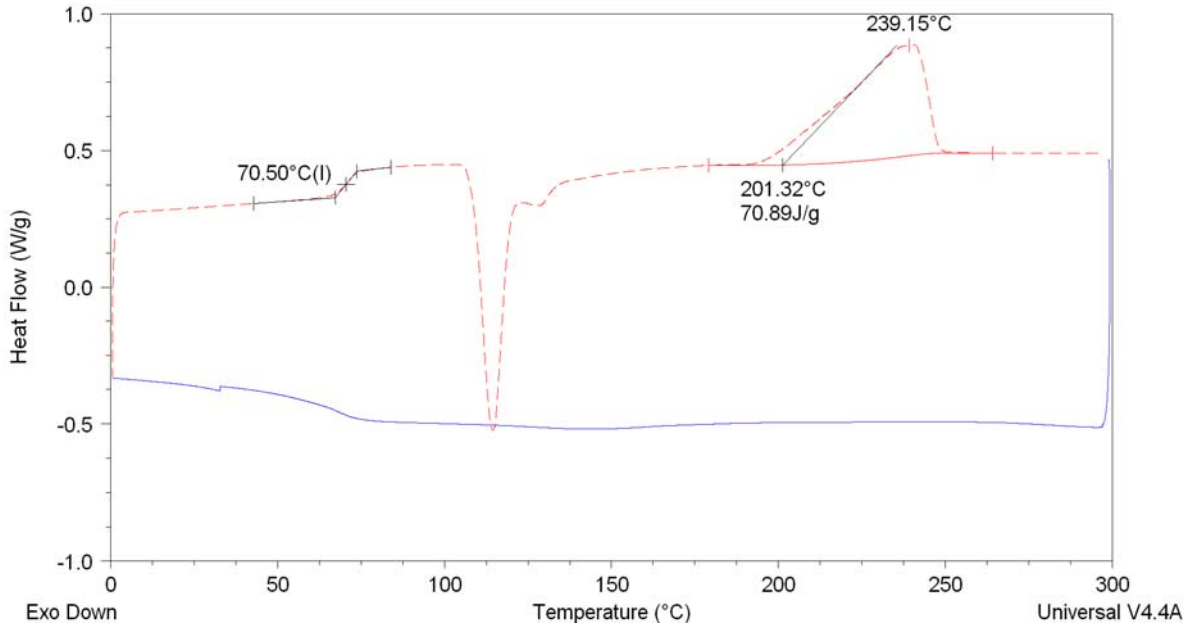


Figure B-3. DSC of polymer **2.8**

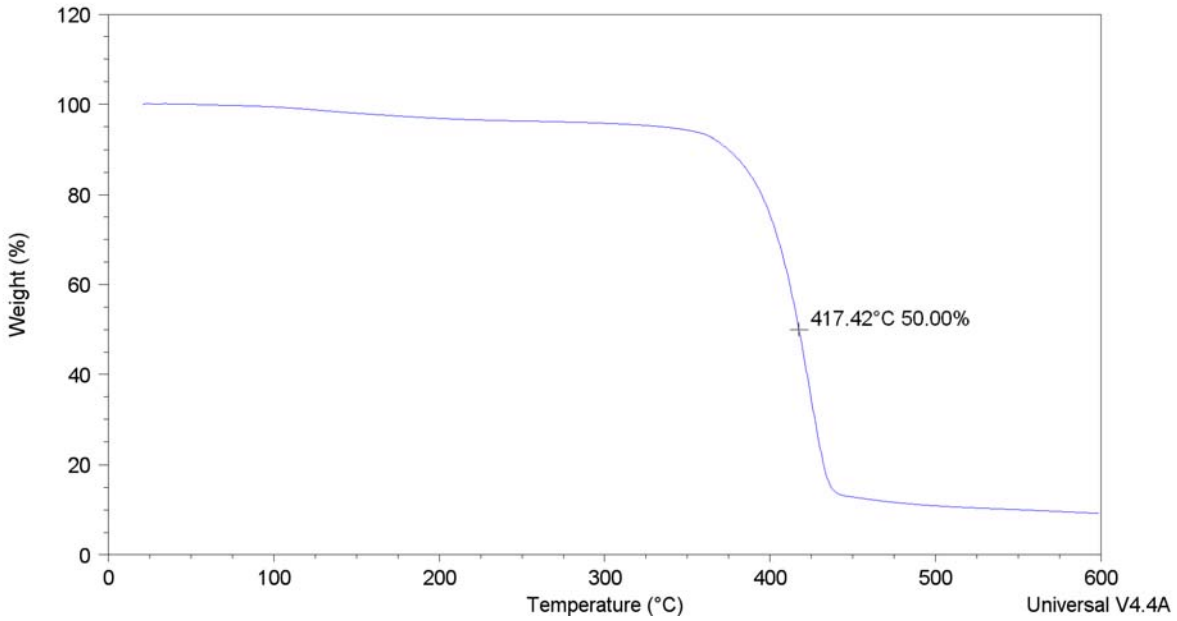


Figure B-4. TGA of polymer **2.8**

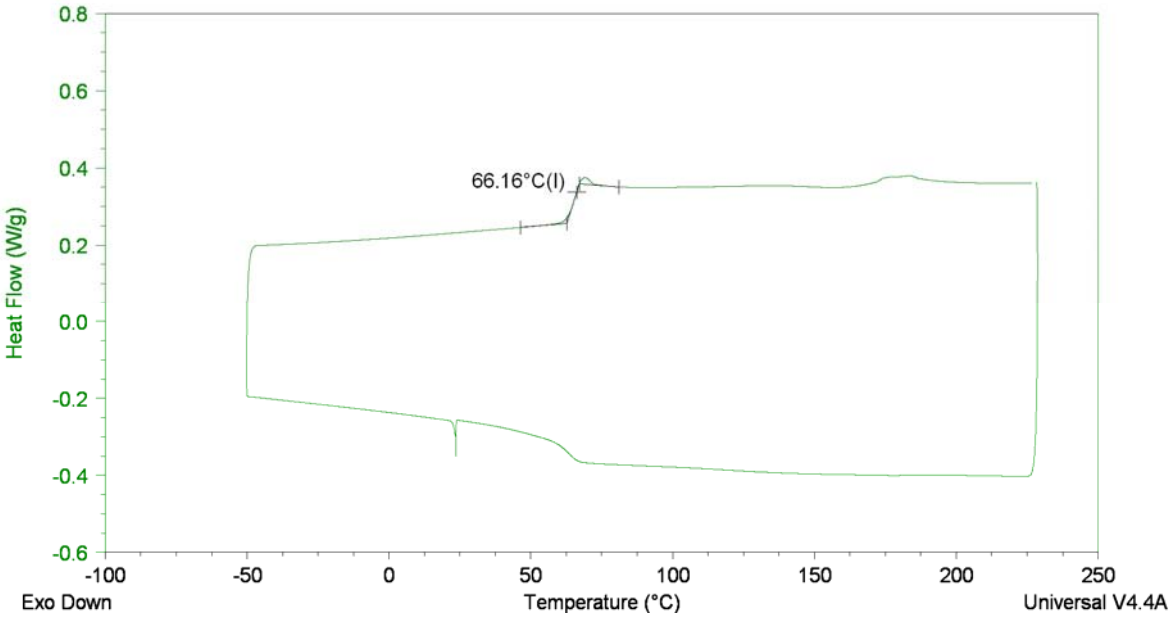


Figure B-5. DSC of polymer **2.9**

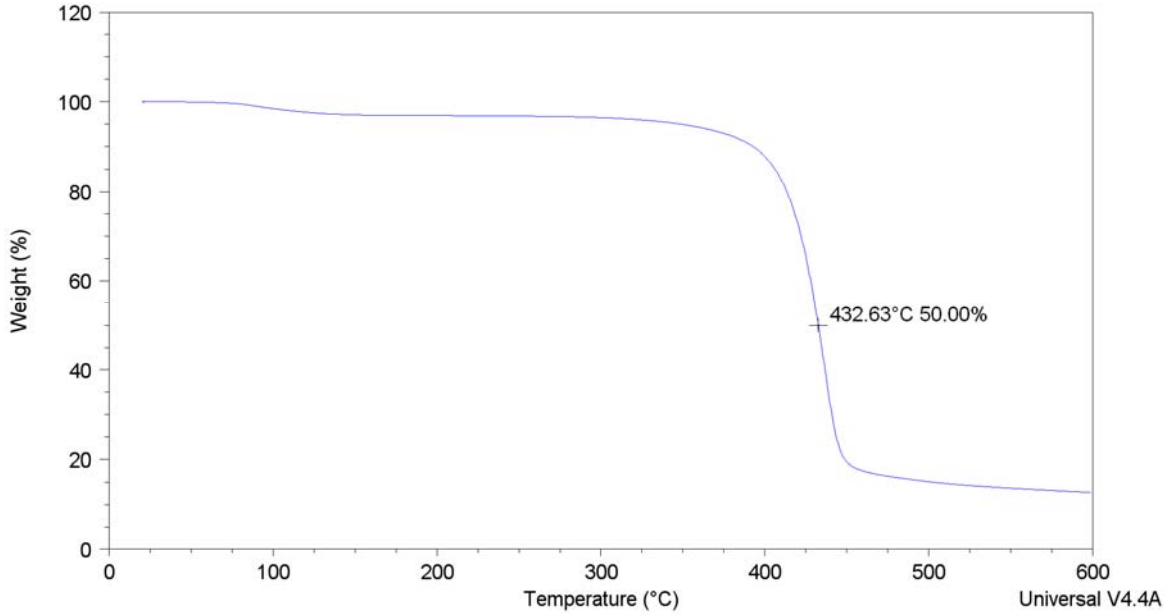


Figure B-6. TGA of polymer **2.9**

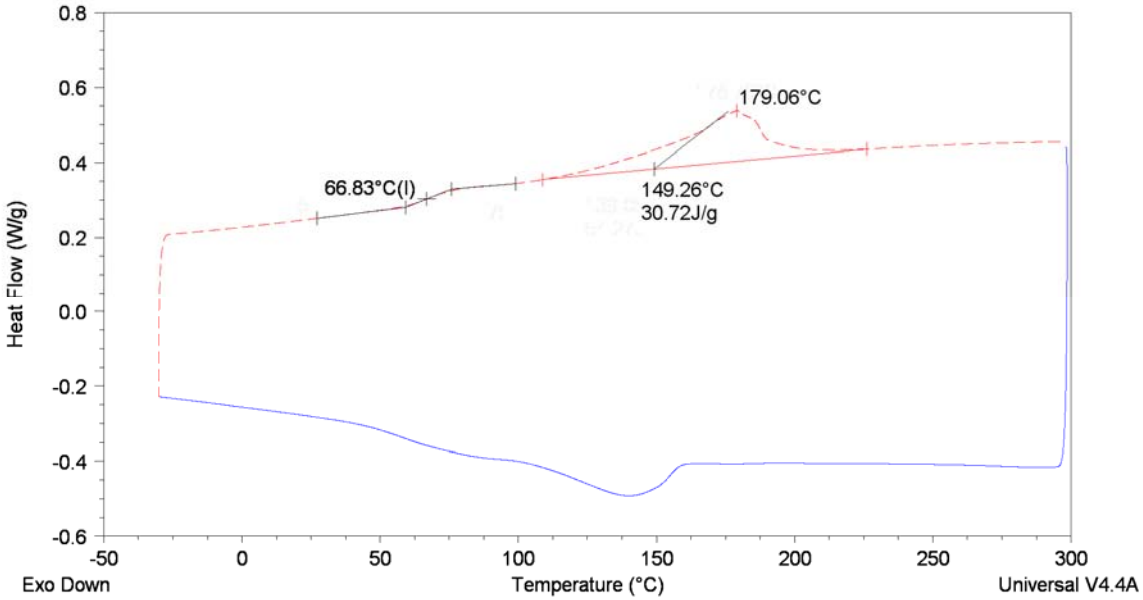


Figure B-7. DSC of polymer **2.10**

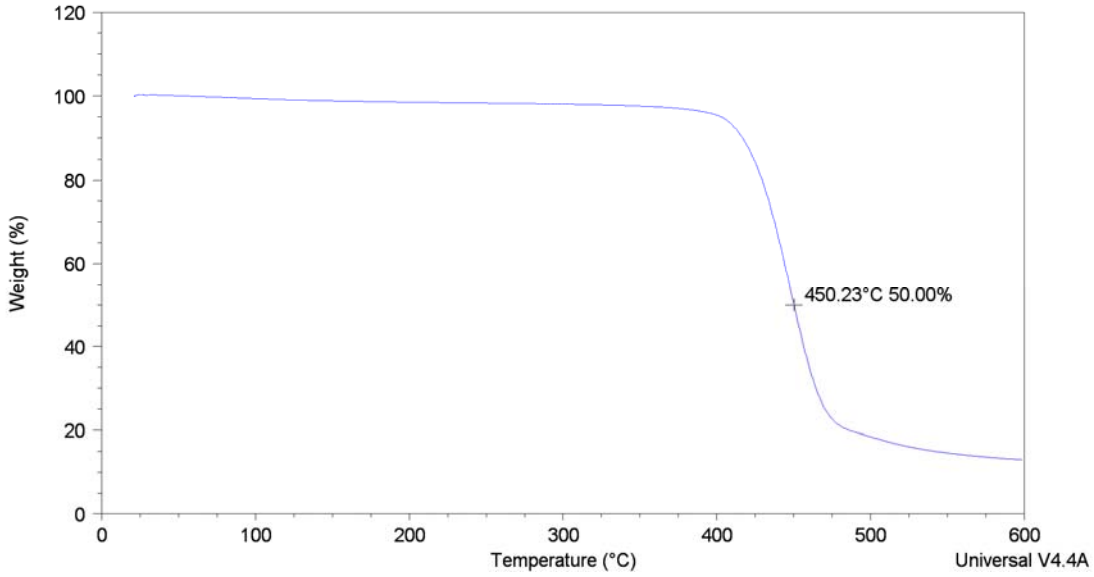


Figure B-8. DSC of polymer **2.10**

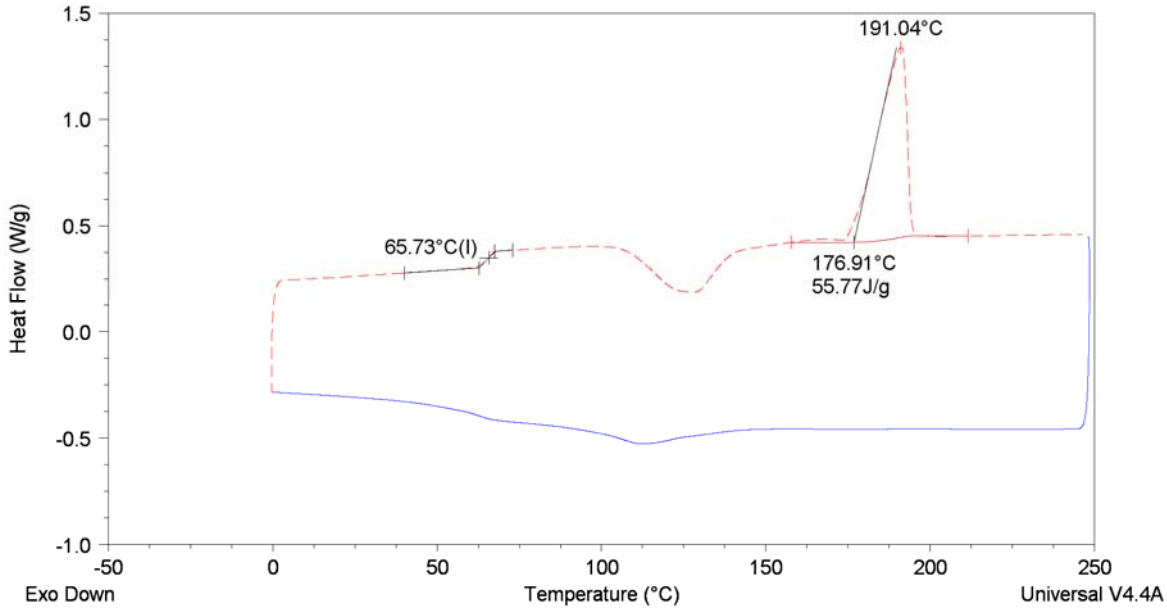


Figure B-9. DSC of polymer **2.11**

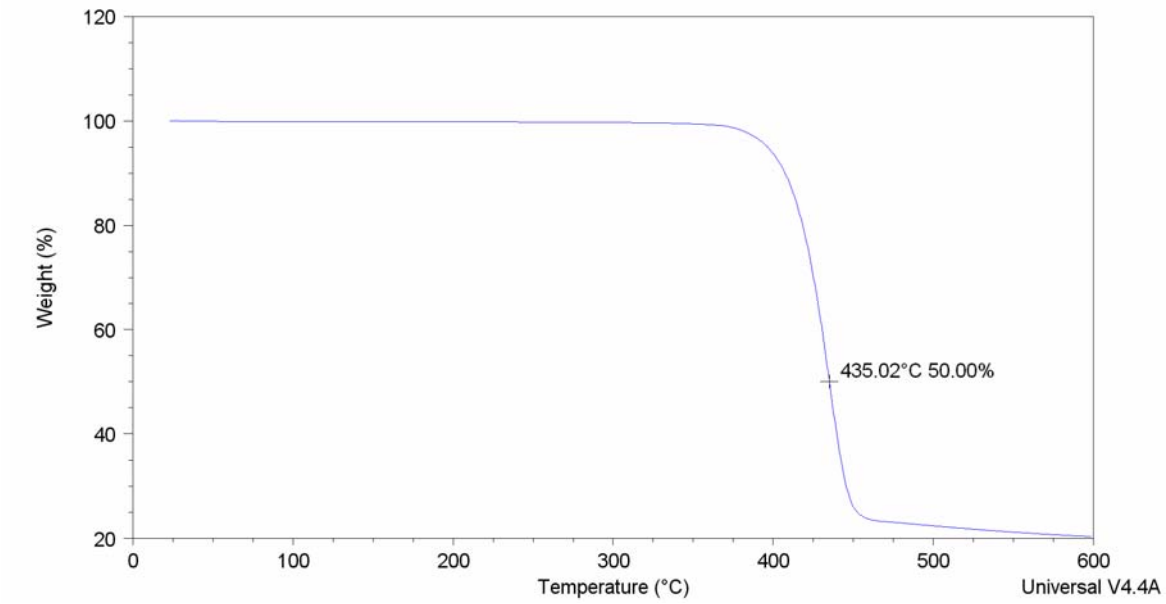


Figure B-10. TGA of polymer **2.11**

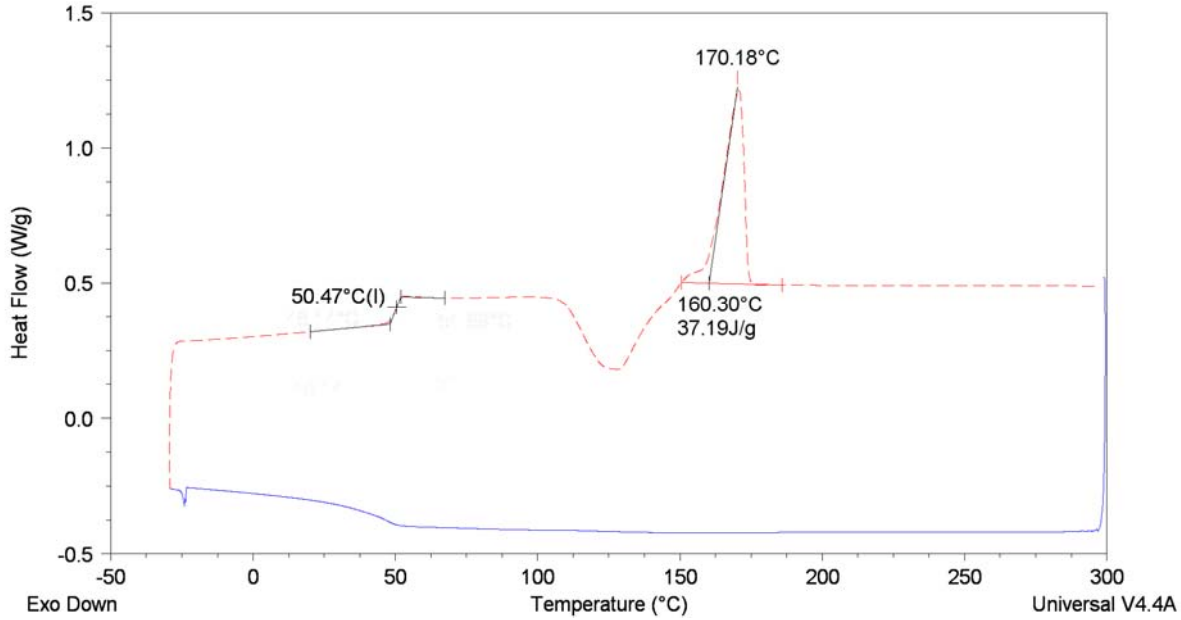


Figure B-11. DSC of polymer **2.12**

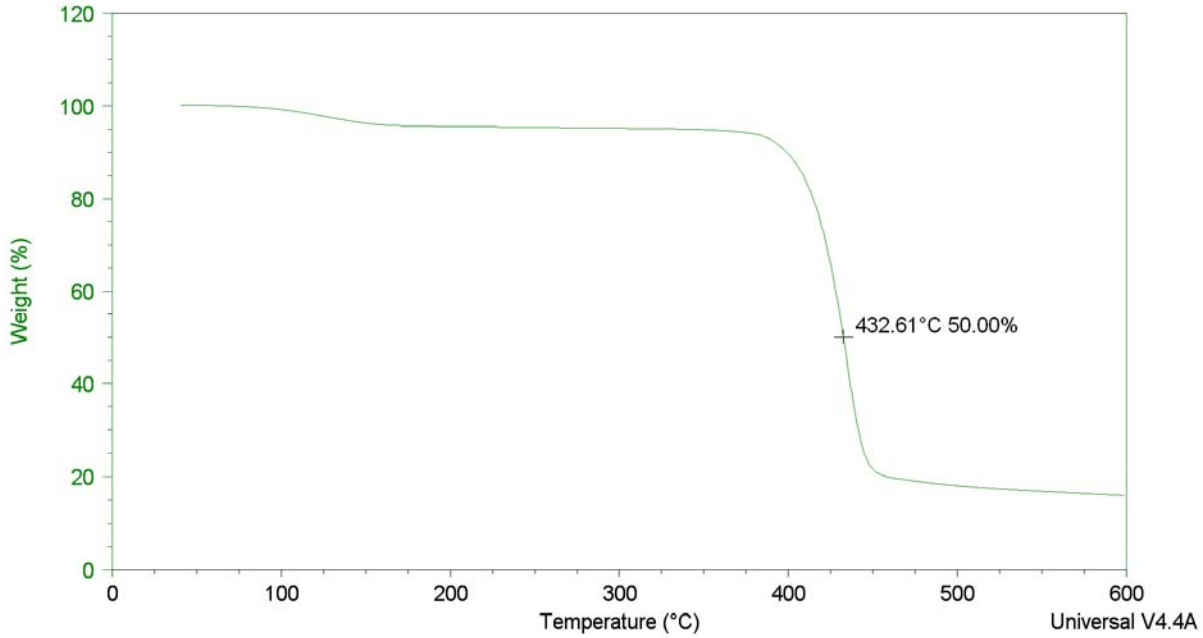


Figure B-12. TGA of polymer **2.12**

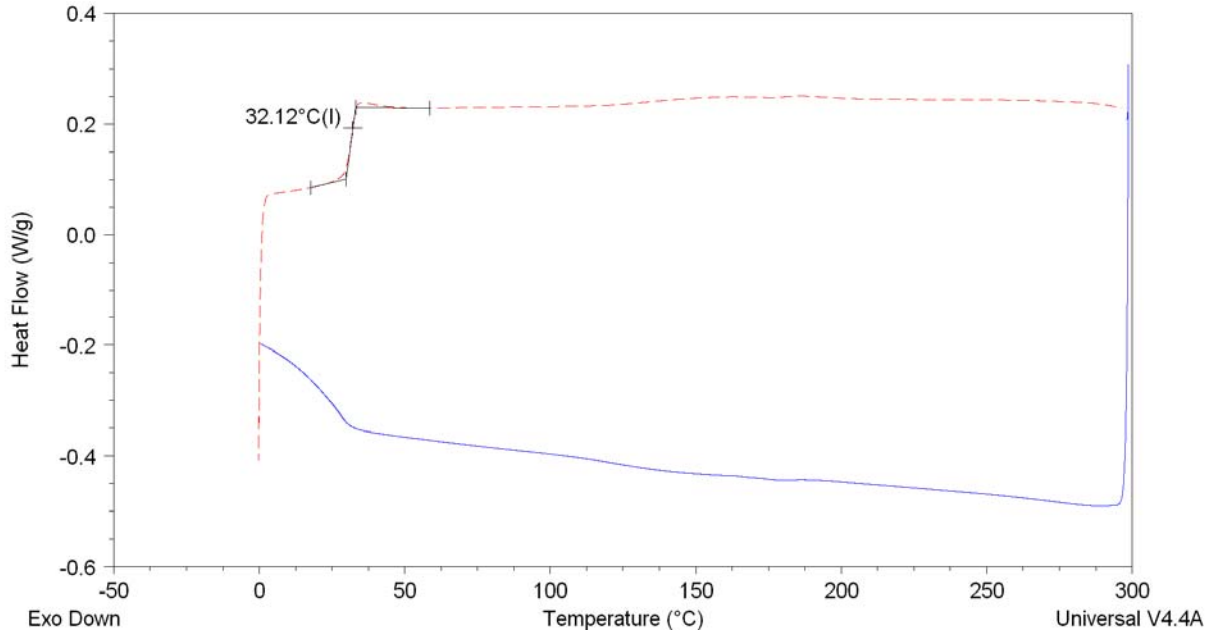


Figure B-13. DSC of polymer **2.18**

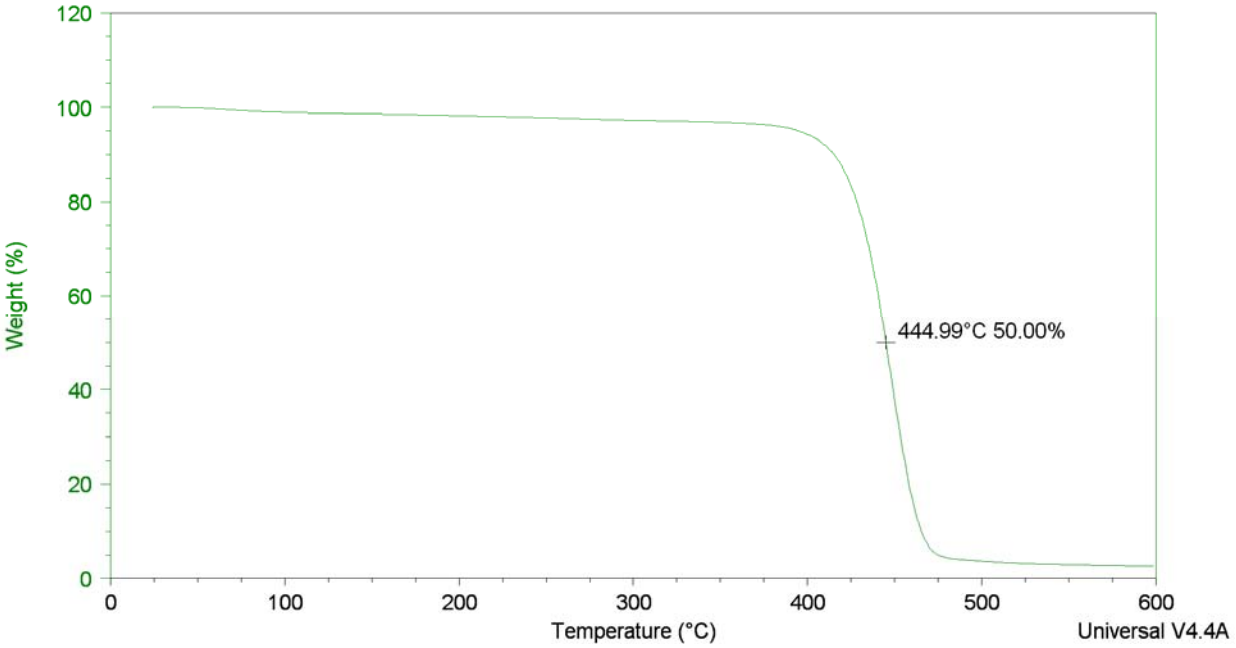


Figure B-14. TGA of polymer **2.18**

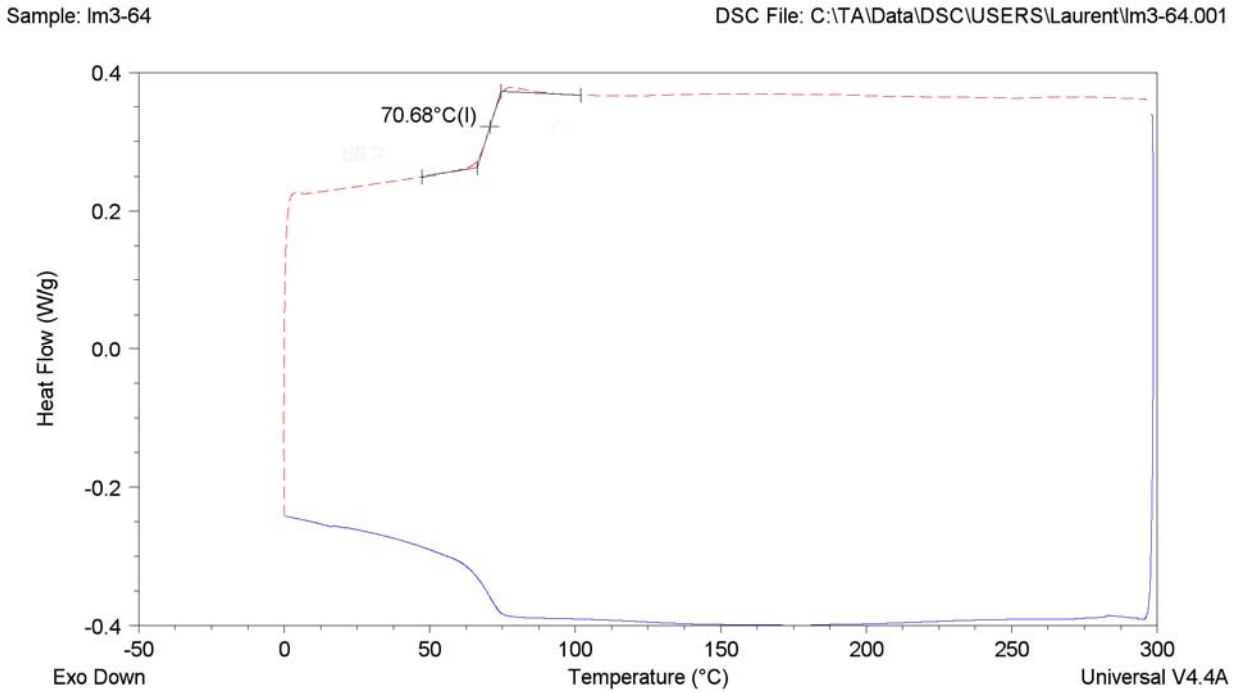


Figure B-15. DSC of polymer **2.19**

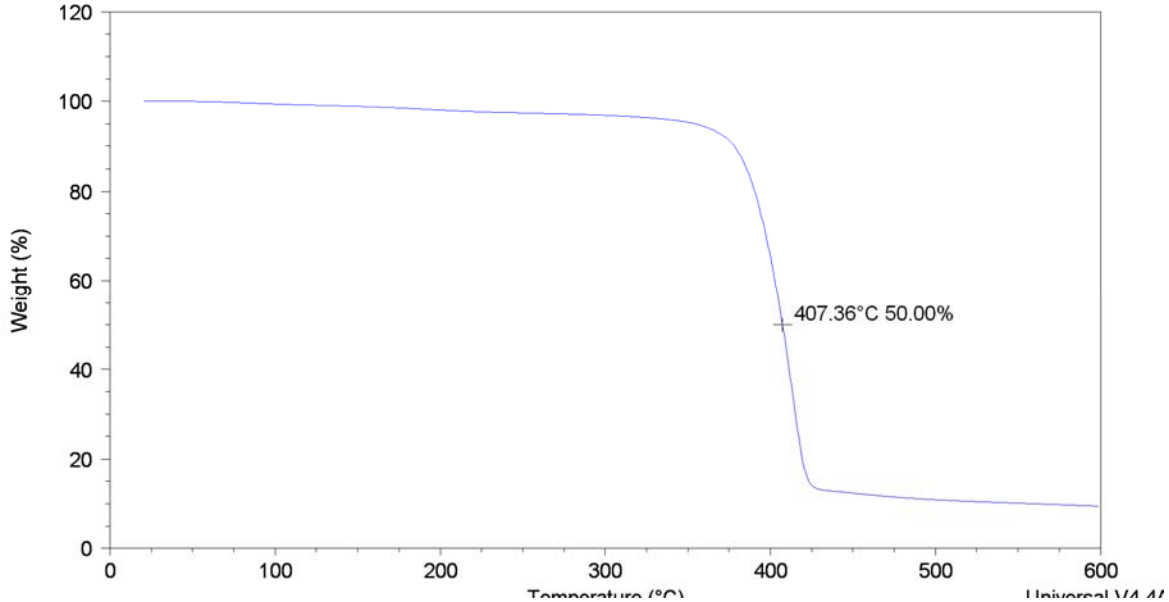


Figure B-16. TGA of polymer **2.19**

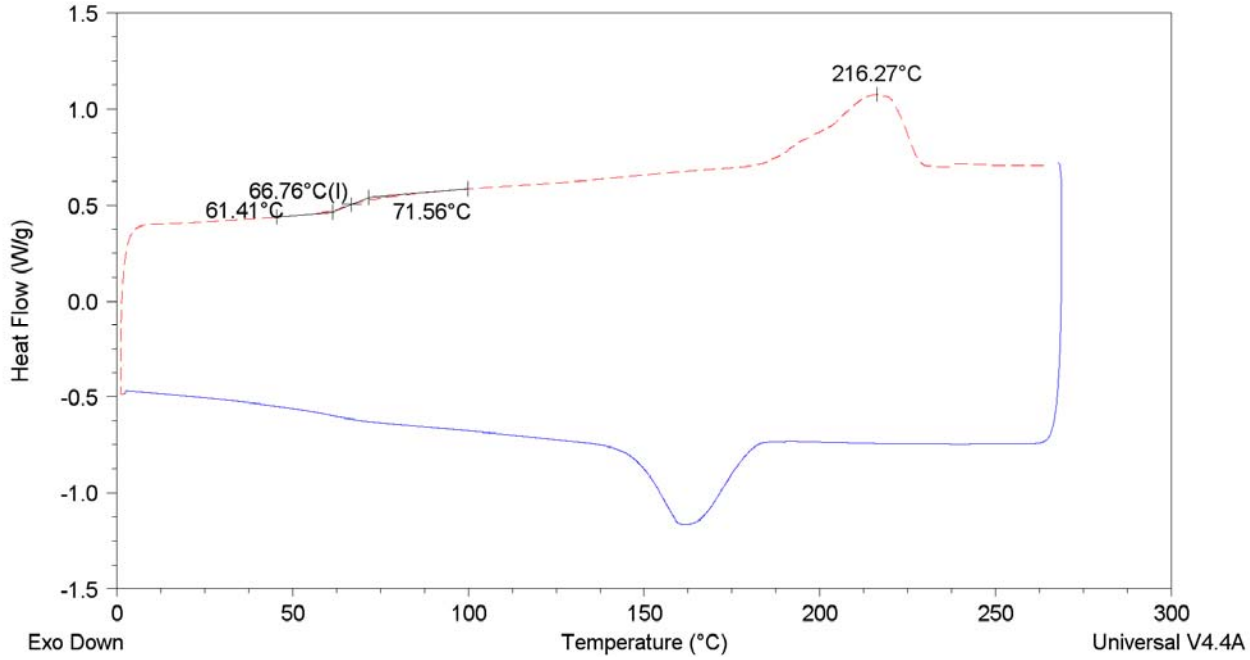


Figure B-17. DSC of polymer **2.26**

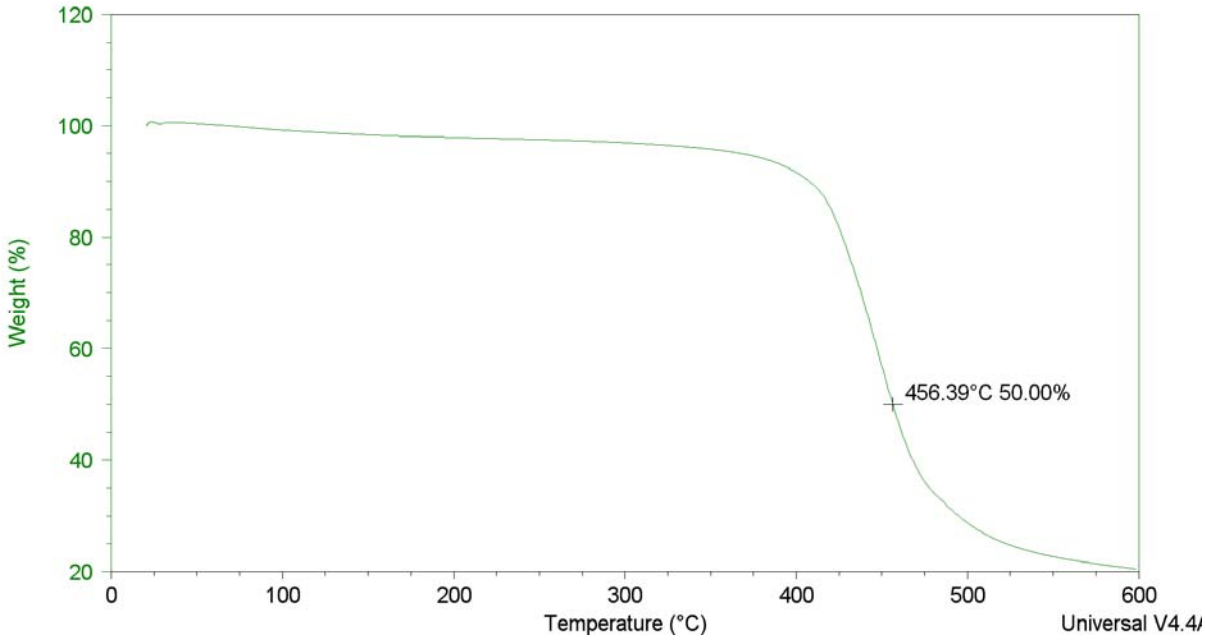
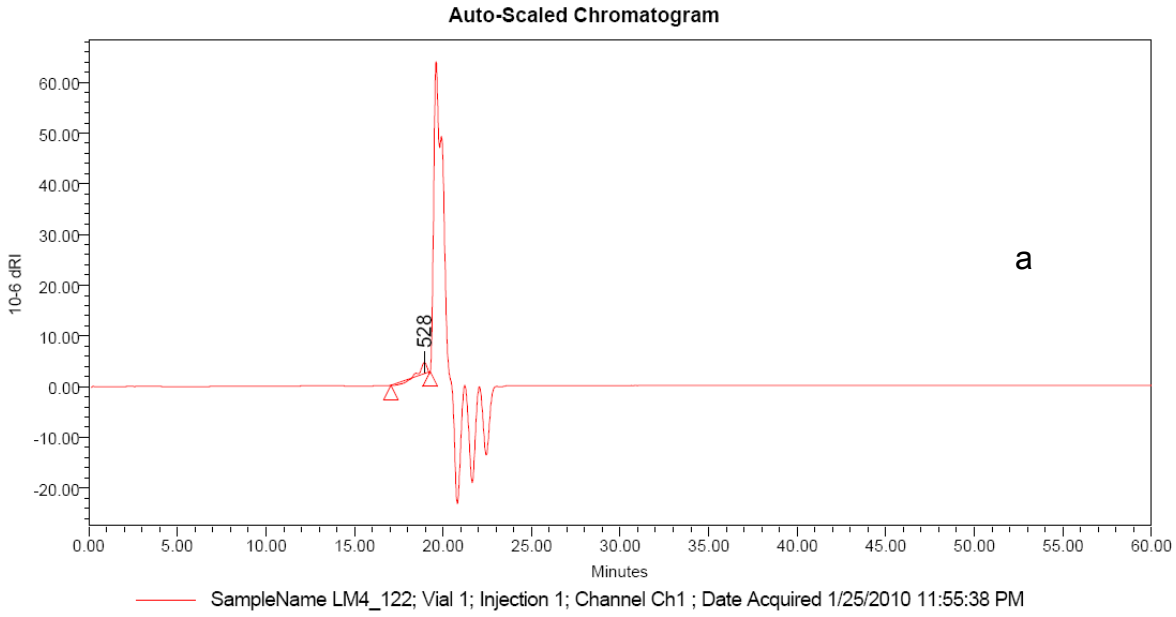


Figure B-18. TGA of polymer **2.26**



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		628	653	528	683	717		1.040214		

b

Figure B-19. GPC analysis of the methanol fraction of **2.29**

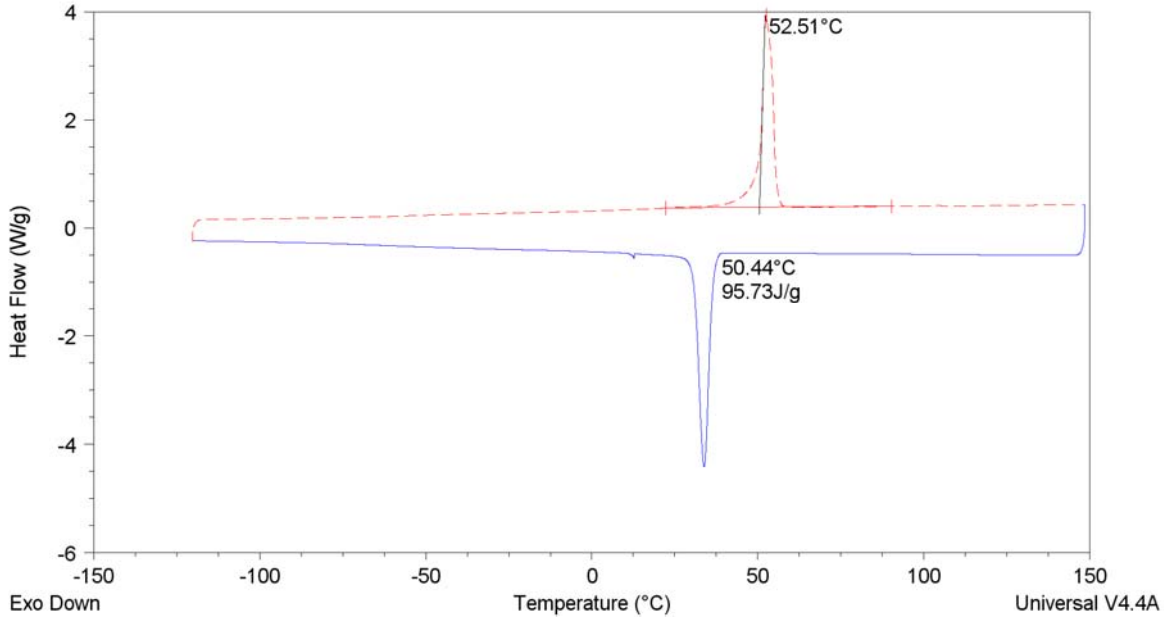


Figure B-20. DSC of polymer **3.1**

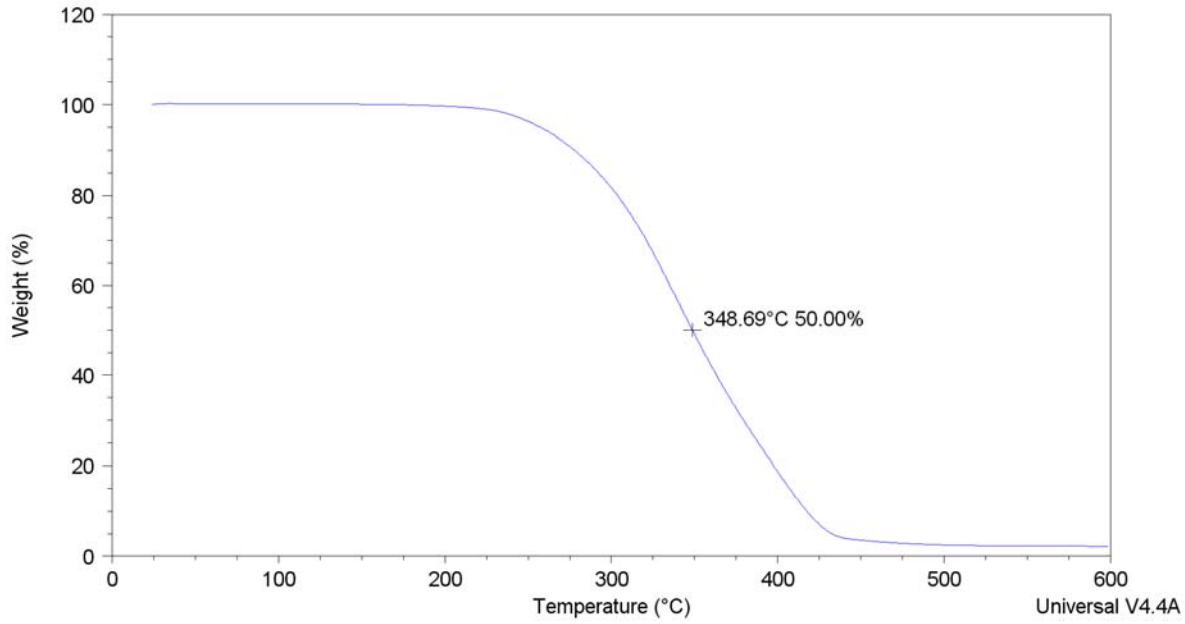


Figure B-21. TGA of polymer **3.1**

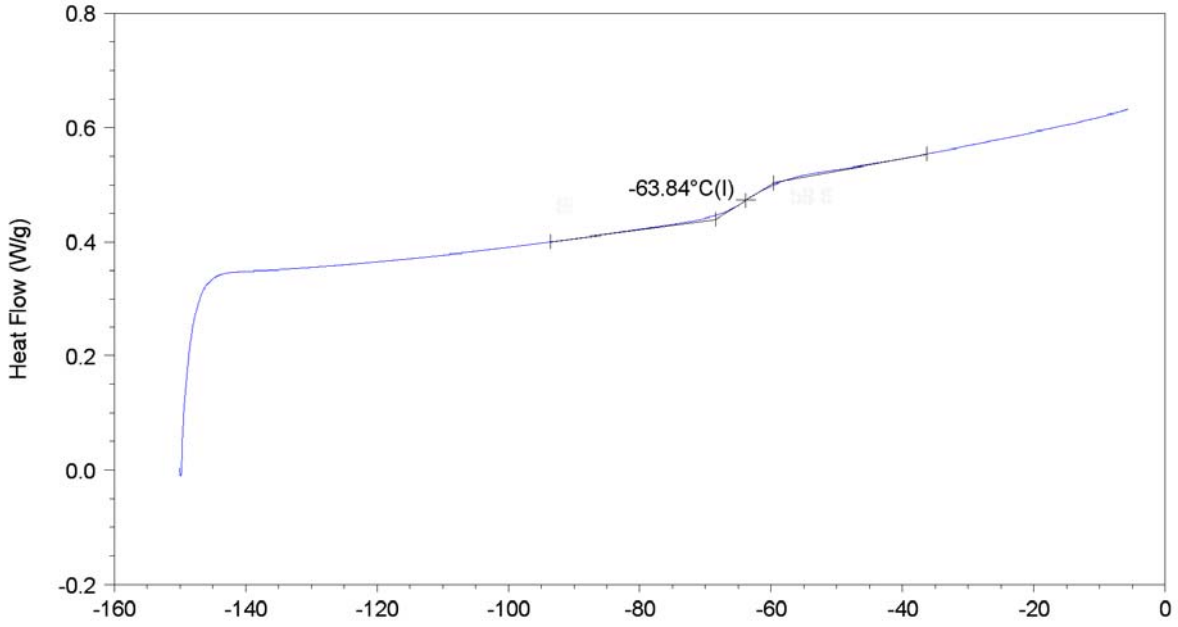
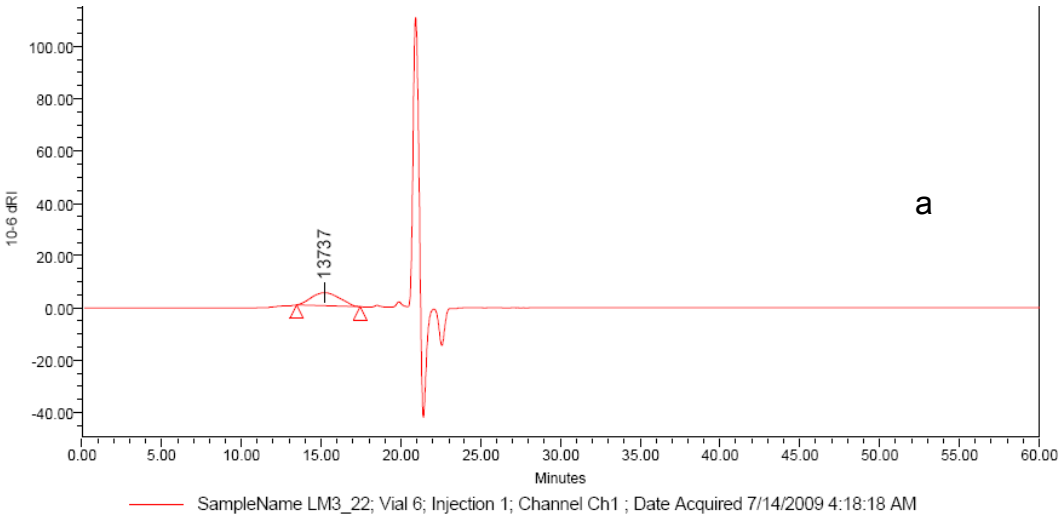


Figure B-22. DSC of polymer **3.1** (T_g at 30°C/min)



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		10342	14694	13737	19983	25283		1.420786		

b

Figure B-23. GPC of polymer **3.1** in THF

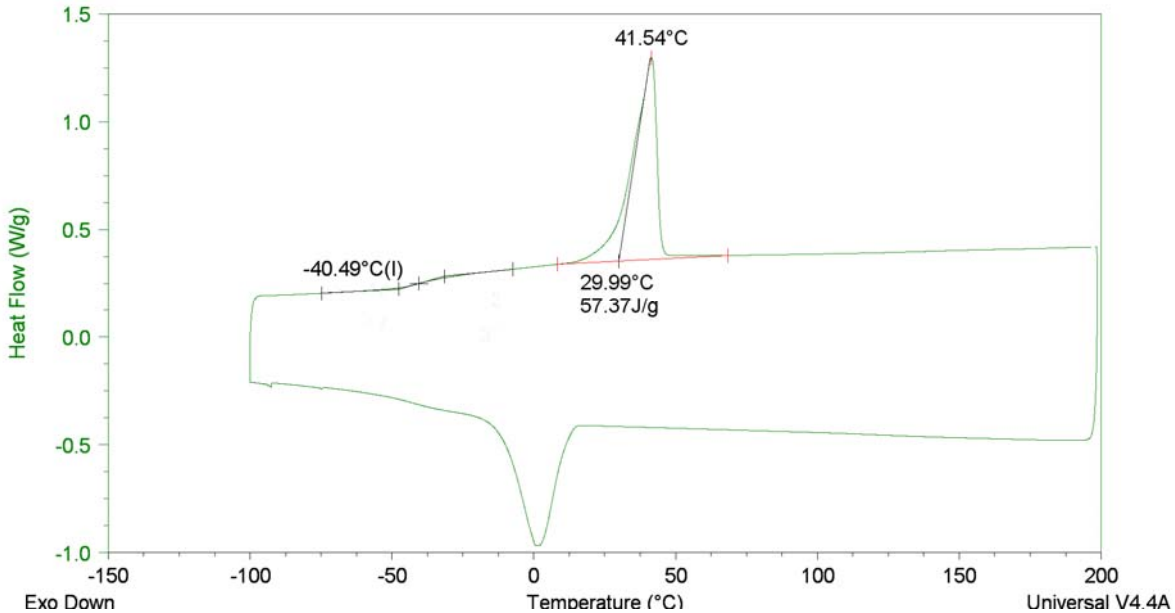


Figure B-24. DSC of polymer **3.2**

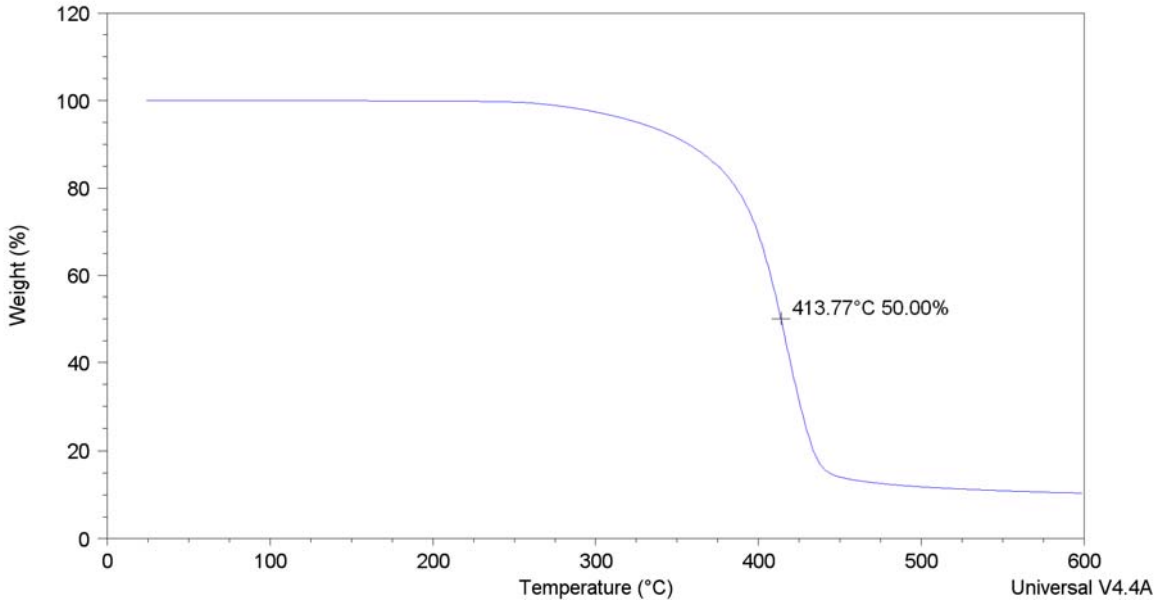


Figure B-25. TGA of polymer **3.2**

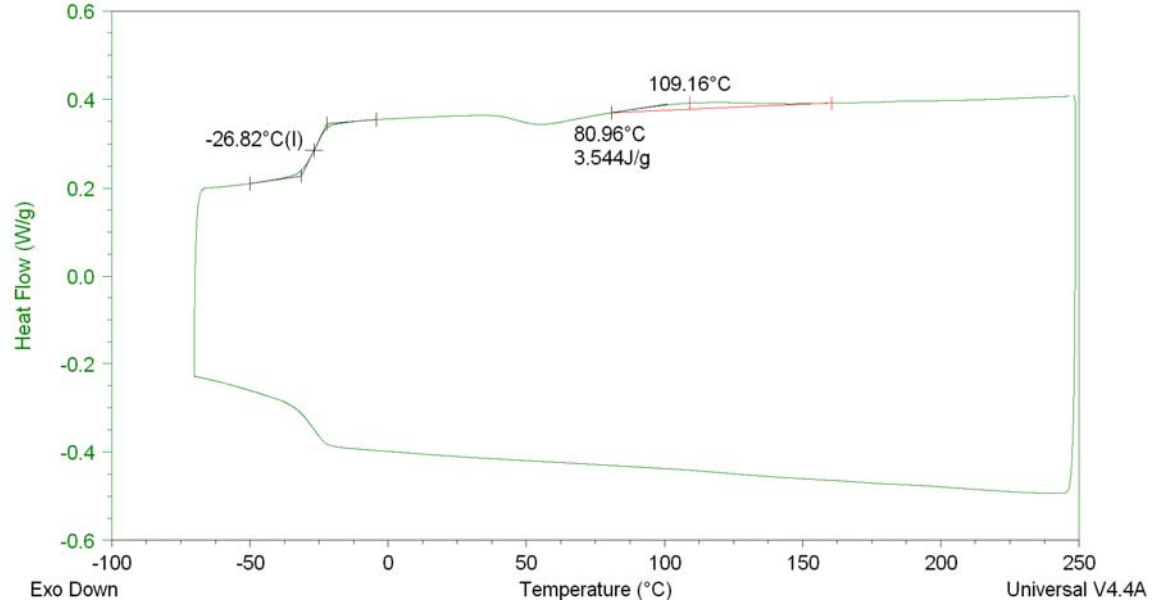


Figure B-26. DSC of polymer **3.3**

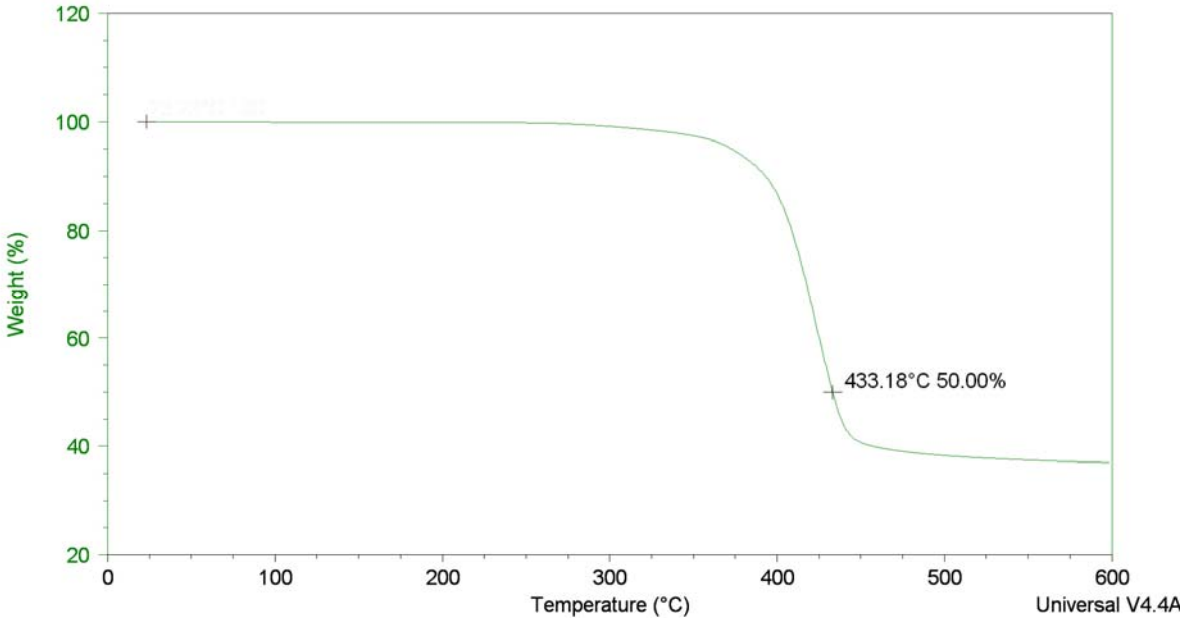


Figure B-27. TGA of polymer **3.3**

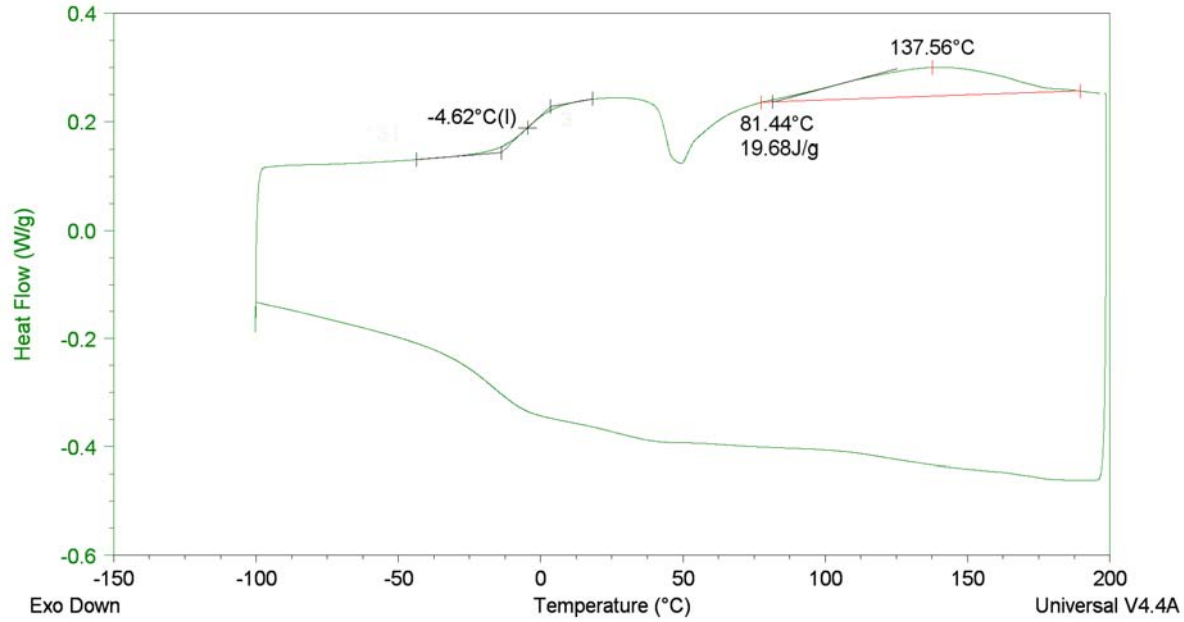


Figure B-28. DSC of polymer **3.4**

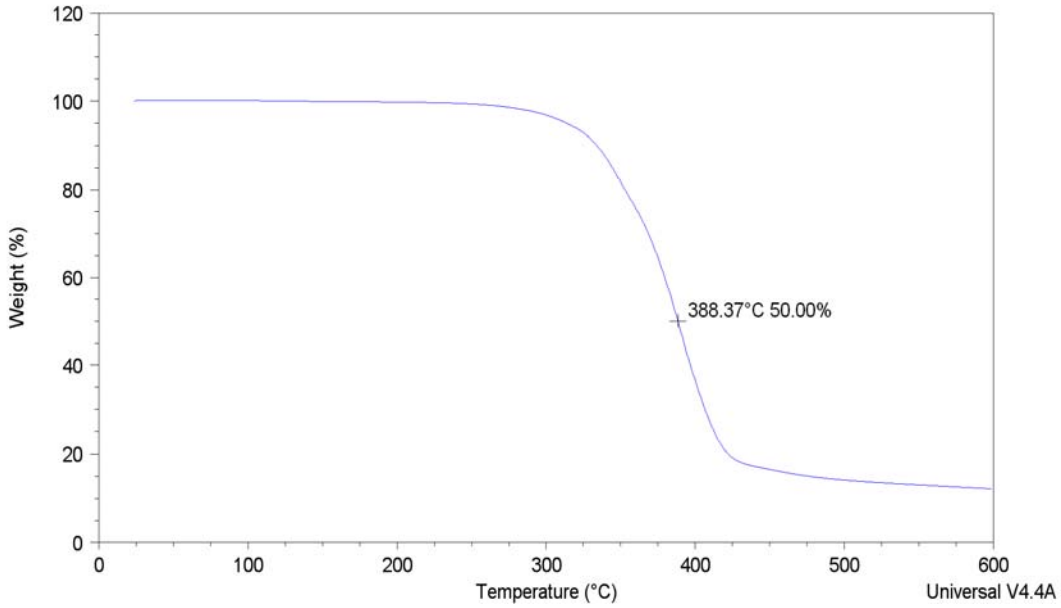


Figure B-29. TGA of polymer **3.4**

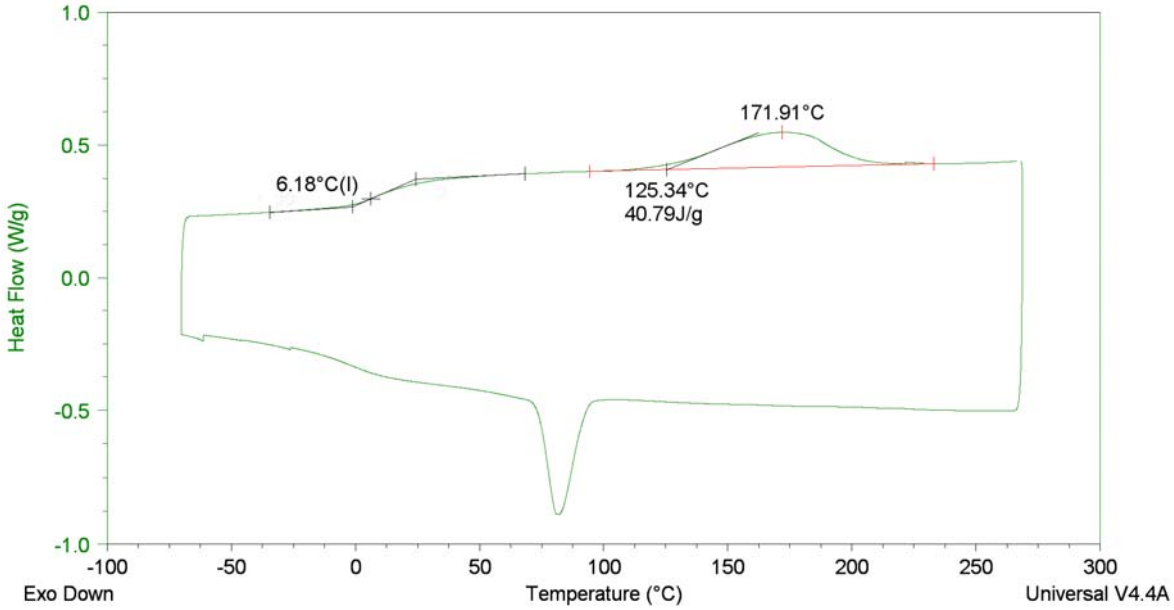


Figure B-30. DSC of polymer **3.5**

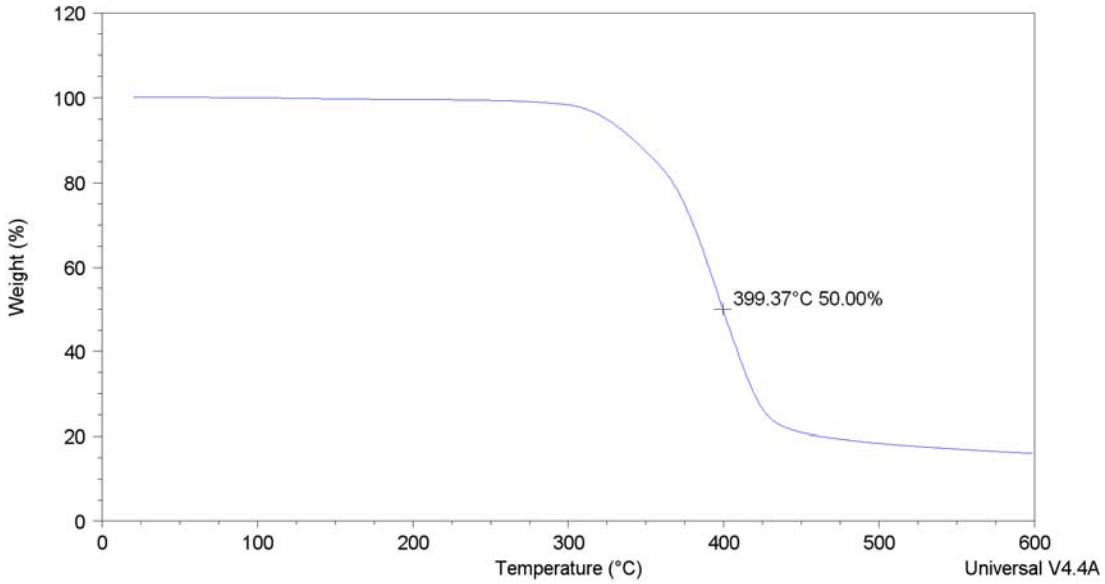


Figure B-31. TGA of polymer **3.5**

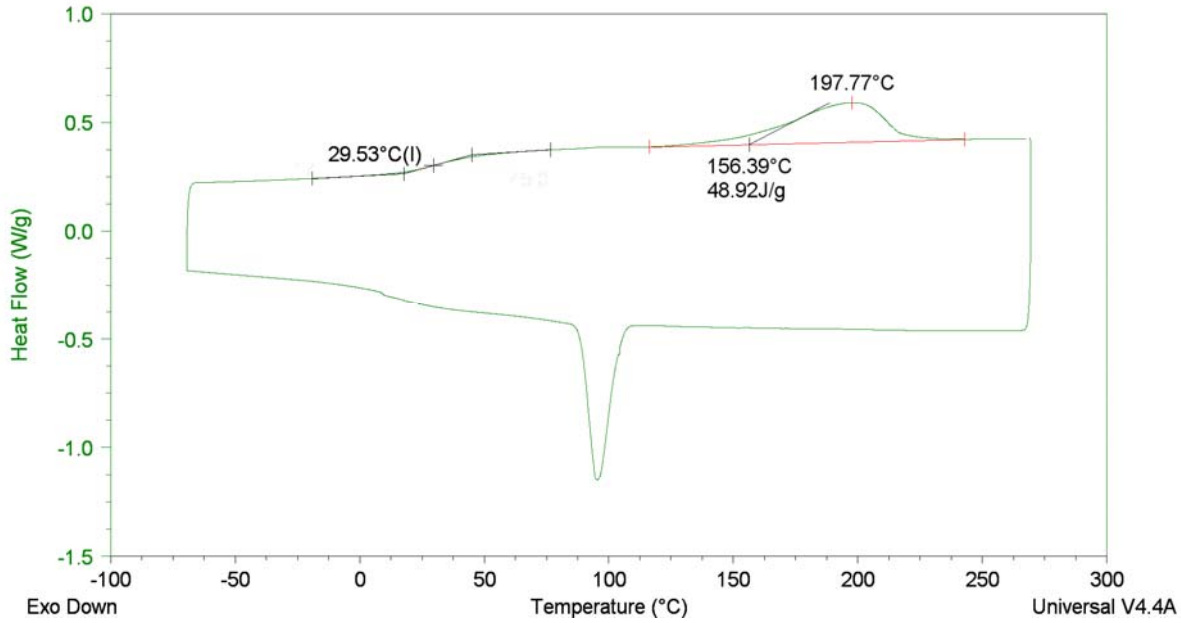


Figure B-32. DSC of polymer **3.6**

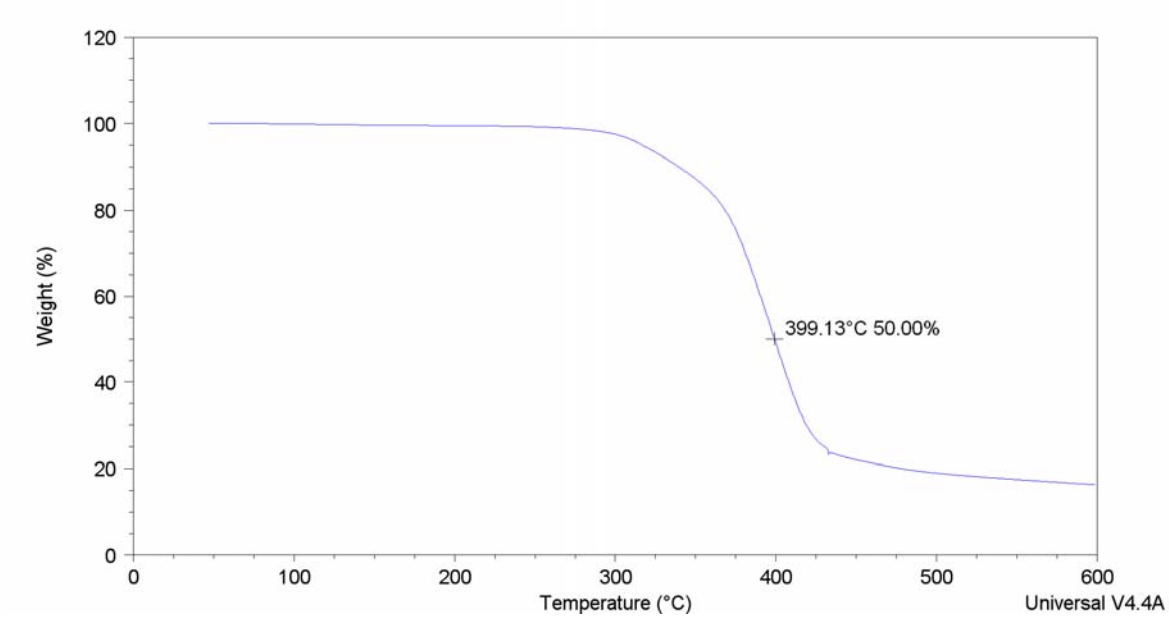


Figure B-33. TGA of polymer **3.6**

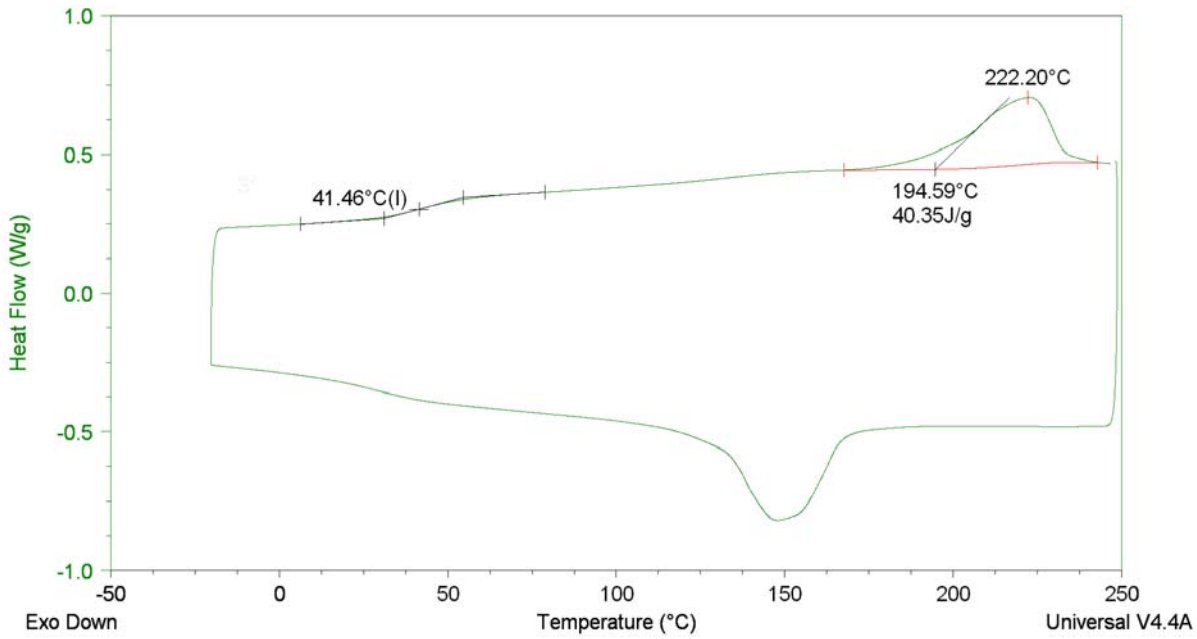


Figure B-34. DSC of polymer **3.7**

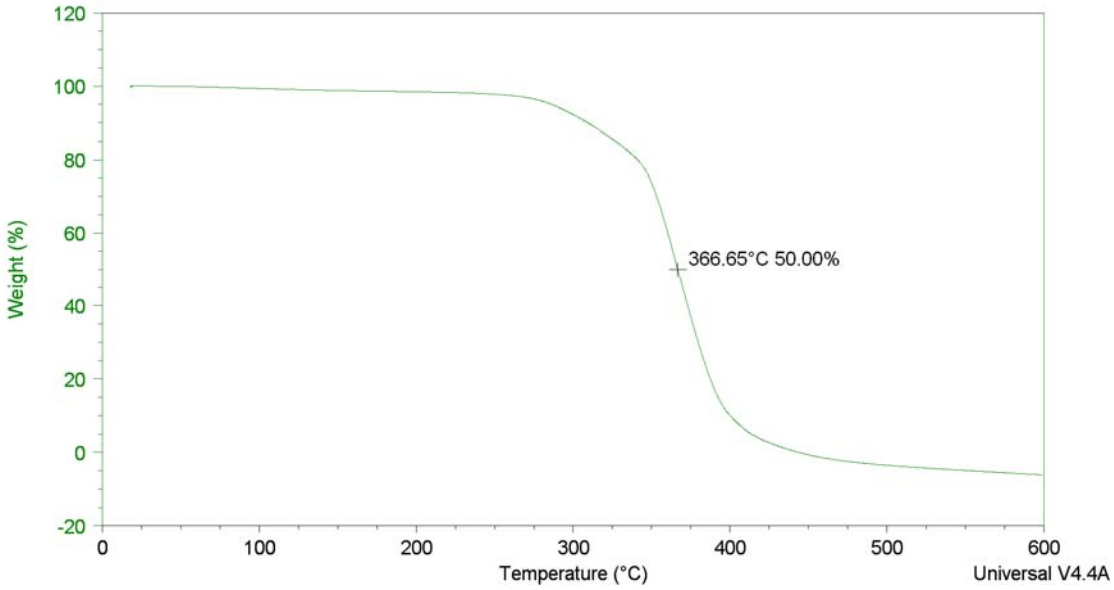


Figure B-35. TGA of polymer **3.7**

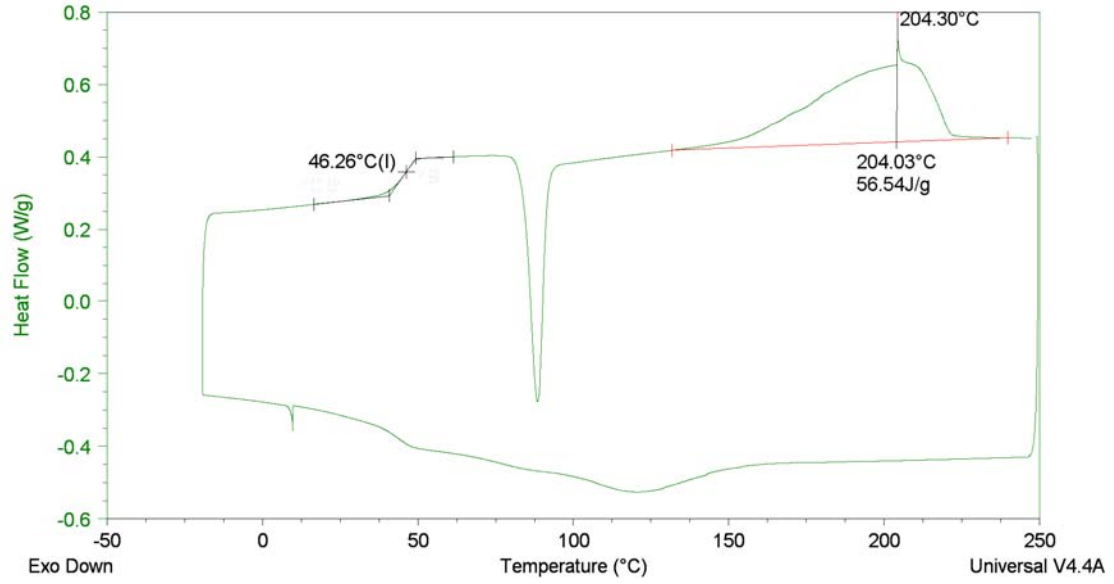


Figure B-36. DSC of polymer **3.8**

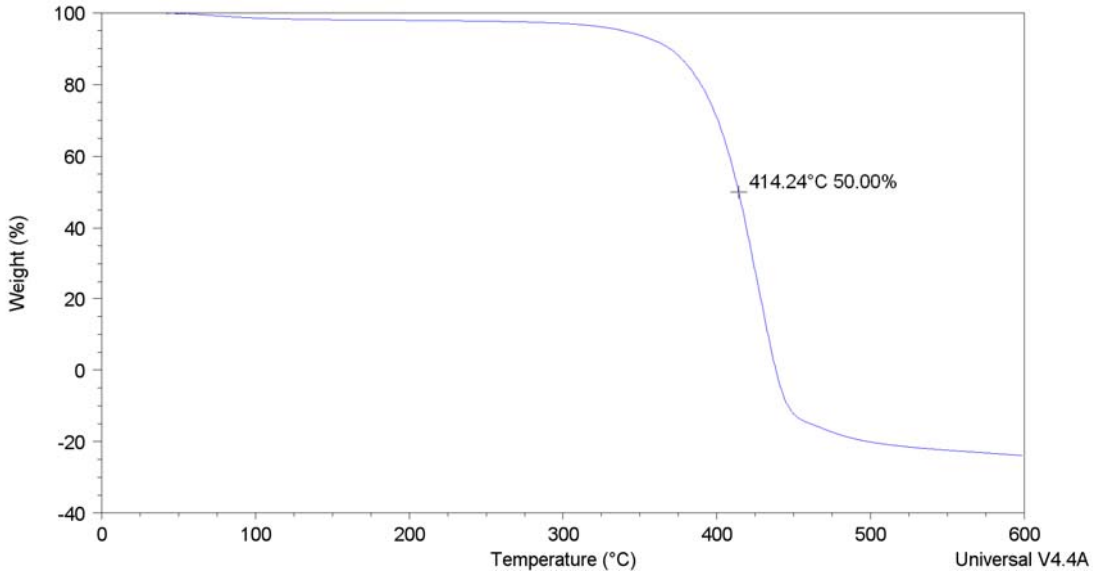


Figure B-37. TGA of polymer **3.8**

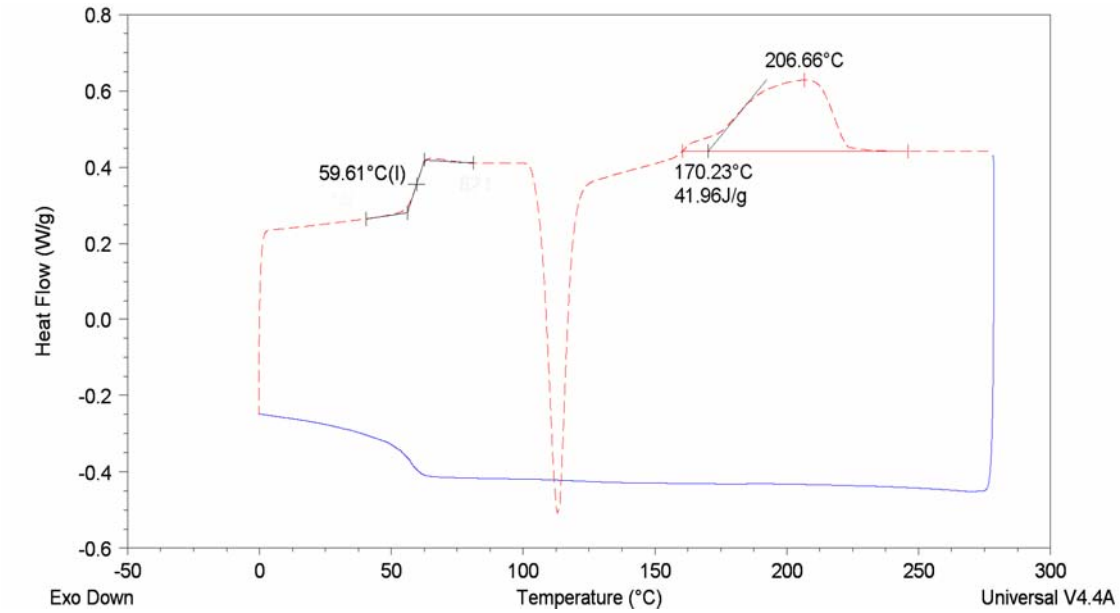


Figure B-38. DSC of polymer 3.9

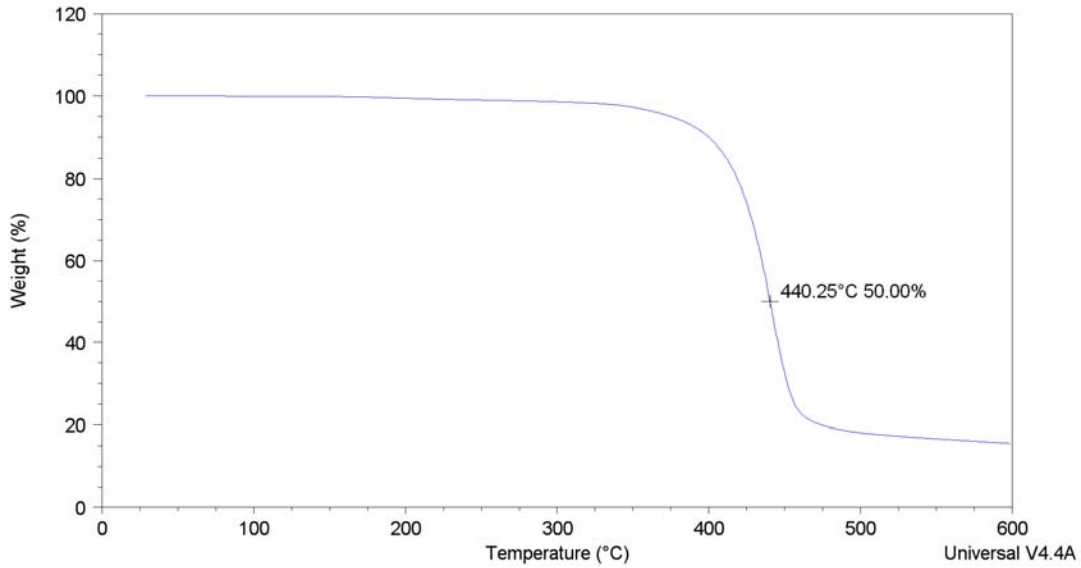


Figure B-39. TGA of polymer **3.9**

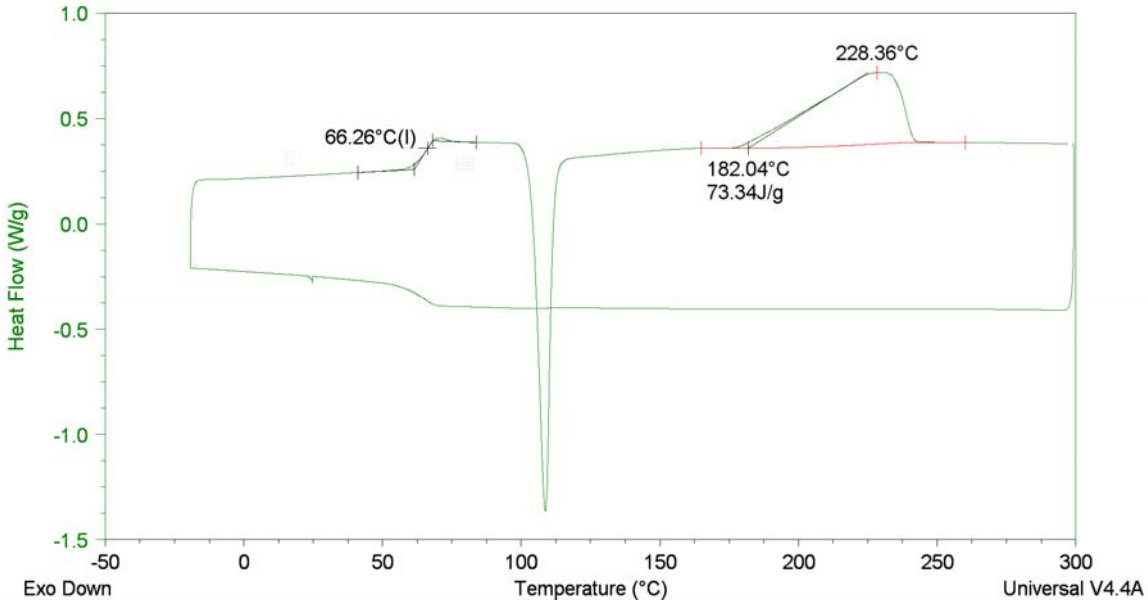


Figure B-40. DSC of polymer **3.10**

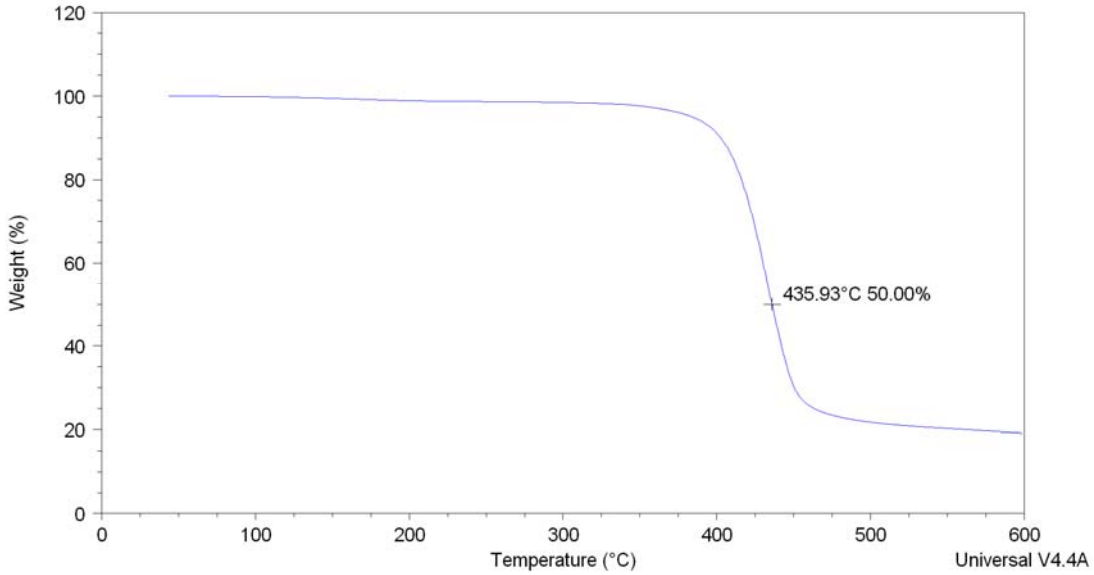


Figure B-41. TGA of polymer **3.10**

LIST OF REFERENCES

(1) *Polymer modification: principles, techniques, and applications*; J., M. J., Ed., 2000.

(2) Baekland, L. *J. Ind. Eng. Chem* **1912**, 3932.

(3) a) *http://www.ogj.com/articles/save_screen.cfm?ARTICLE_ID=329666*.

b) http://plasticsnews.com/fyi-charts/materials.html?id=1199483786 **2008** Plastic europe.

(4) *"Ethylene, keystone to the petrochemical industry."*; Kniel, L.; Winter, O.; Stork, K., Eds., 1980; Vol. 2.

(5) MacKenzie, J. *Nonrenewable resources* **1998**, 97.

(6) Office, U. S. g. A. *"Crude oil: Uncertainly about Future Oil Supply Makes It Important to Develop a Strategy for Addressing a Peak and Decline in Oil Production"*, February 2007.

(7) agency, U. S. E. p. *"Municipal Solid Waste in the United States 2007 Facts and Figures"*, 2007.

(8) Sinclair, R. *J. Macromol. Sci. Part A: Pure Appl. Chem.* **1996**, *A33*, 585.

(9) Swift, G.; Wiles, D. In *Encyclopedia of Polymer Science and Technology* 2004.

(10) Awaja, F.; Pavel, D. *Euro. Polym. J.* **2005**, 1453.

(11) Caldicott, R. *Plast. Eng.* **1999**, 35.

(12) *Polymeren, van keten tot kunstof*; vamdervegt, A. K.; Govaert, L. E., Eds.; VSSD, 2006.

(13) Ravindranath, K.; Mashelkar, R. A. *Developments in Plastics Technology* **1985**, *2*, 1.

(14) El-Toufaili, F.; Feix, G.; Reichert, K.-H. *Journal of Polymer Science: Part A: Polymer Chemistry* **2006**, *44*, 1049.

(15) Industry, O. C. P.

(16) *Industrial organic chemicals*; Witcoff, H. A.; Reuben, B. G., Eds.; John Wyley & Sons: New-York, 1996; Vol. page 321.

(17) *J.S. Industrial organic chemicals*; Witcoff, H. A.; Reuben, B. G., Eds.; Plotkin.

(18) Serafin, J. G.; Liu, A. C.; Seyedmonir, S. R. *Journal of Molecular Catalysis A: Chemical* **1998**, 157.

(19) *"ethylene"* Zimmerman, H.; Walzl, L., Eds.

(20) *Introduction to General, Organic and Biochemistry*; 9e ed.; Bettelheim, F. A.; Brown, W. H.; Campbell, M. K.; Farell, S. O., Eds., 2010.

(21) Bertoli, C. In *Polyester 2005 10th World Congress* Amsterdam, The Netherlands, 2005.

(22) Chen, J.; Chen, L. *Journal of Applied Polymer Science* **1999**, *73*, 35.

(23) Kurokawa, H.; Ohshima, M.; Sugiyama, K.; Miura, H. *Polymer Degradation and Stability* **2003**, *79* 529.

(24) *"The principles of polymerization"* 4th edition pages ed.; Odian, G., Ed.; Wyley Interscience, 2004 *p. 28-36*

(25) Boerjan, W.; Ralph, J.; Baucher, M. *Annu. Rev. Plant Biol.* **2003**, *54*, 519.

(26) Davin, B. L.; Lewis, N. G. *Current Opinion in Biotechnology* **2005**, *16*, 407.

(27) *http://www.ili-lignin.com/aboutlignin.php* International Lignin Institute.

(28) *Lignin, properties and materials*; Glasser, W., G.; Sarkenen, S., Eds., 1989.

(29) Burkart, L. United States, 1999; Vol. Patent 5859236

(30) Wu, G.; Heitz, M.; Chornet, E. *Ind. Eng. Chem. Res.* **1994**, *33*, 718.

(31) Zabkova, M.; Borges da Silva, E.; Rodrigues, A. *Separation and Purification Technology* **2007**, *55*, 56.

(32) Hagfield, A.; Scweitzer, H.; Trova, P.; Green, K. *Syn. Com.* **1994**, *24*, 1025.

(33) Jones, R. S. *Ger. Offen.* **1973**.

(34) Wang, M.; Weinberg, J. M.; Wooley, K. L. *Macromolecules* **2000**, *33*, 734.

(35) Gandini, A.; Silvestre, A. J. D.; Neto, C. P.; Sousa, A. F.; Gomes, M. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 295.

(36) *The behaviour of furan derivatives in polymerization reactions*; Gandini, A., Ed.; Spinger Berlin, 1977; Vol. 25.

(37) Lim, M.; Yoon, M. C.; Rhee, M. *Tetrahedron Letters* **2007**, *48*, 3835.

(38) Lange, W.; Kordsachia, O. *Holz als Rohr- und Werkstoff* **1981**, *39*, 107.

(39) Bock, L. H.; Anderson, J. K. *J. Polym. Sci. Part A: Polym. Chem.* **1955**, *27*, 553.

(40) *"Instant notes organic chemistry second edition"* Patrick, G. L., Ed.; Garland Science, 2000.

(41) *"Polymer Science"*; Gowariker, V. R.; Viswanathan, N. V.; Sreedhar, J., Eds., 1986.

(42) Run, M.; Song, A.; Wang, Y.; Yao, C. *Journal of Applied Polymer Science* **2007**, *104*, 3459.

(43) Muthusamy, A.; Murugavel , S. C. *High Performance Polymers* **2006**, *18*, 227.

(44) Storm, R. S.; Matkovich, V. I.; Cottis, S. G. *Journal of Polymer Science: Polymer Chemistry Edition* **1976**, *14*, 2207.

(45) Gilkey, R.; Caldwell, J. R. *Journal of Applied Polymer Science* **1959**, *2*, 198.

(46) Li, X.-G.; Huang, M.-R.; Guan, G.-H.; Sun, T. *Journal of Applied Polymer Science* **1997**, *66*, 2129.

(47) Carothers, W. H. *Transaction of the Faraday Society* **1935**, *32*, 39.

(48) *"Organic Polymer Characterization"*, NMAB Committee on Organic Polymer, 1977.

(49) Beatly, C. L.; Karasz, F. E. *Polymer reviews* **1979**, *17*, 37.

(50) *"Polypropylene- The definitive User's Guide and Databook"*; Maier, C.; Calafut, T., Eds., 1998; Vol. 123.

(51) Sascha K.; Schweizer, B. W. A., K-H. *Synlett* **2009**, *11*, 1769.

(52) Hagiwara, H.; Sekifuji, M.; M., T.; Hoshi, T.; Suzuki, T. *Chemistry Letters* **2009**, *38*, 926.

(53) Rodrigues-Santos, C. E.; Echevarria, A. *Tetrahedron Letters* **2007**, *48*, 4505.

(54) Ji, R.; Chen, Z.; Corvini, P. F.-X.; Klapper, A.; Brune, A.; Haider, K.; Schaffer, A. *Chemosphere* **2005**, *60*, 1169.

(55) Hatfield, R. D.; Helm, R. F.; Ralph, J. *Analytical and Biochemistry* **1991**, *194*, 25.

(56) Perkin, W. H. *J. of the Chem. Soc* **1877**, *31*.

(57) Fosdick, L. S.; Starke, A. C. *J. Am. Chem. Soc.* **1940**, *62*, 3352.

(58) Prasad, V. S.; Pillai, K. S.; Kricheldorf, H. R. *Journal of Macromolecular Science, Part A* **2001**, *A38*, 641.

(59) Charbonneau USA; Vol. US4230817.

(60) Corma, A.; Navarro, M. T.; Nemeth, L.; Renz, M. *Chem. Commun.* **2001**, 2190.

(61) *"Cyclohexanol and cyclohexanone"* Musser, M. T., Ed.; Ullmann, 2002.

(62) Nava, D.; Salom, C.; Prolongo, M. G.; Masegosa, R. M. *Journal of Materials Processing Technology* **2003**, 143.

(63) Sinha, V. R.; Bansal, K.; Kaushik, R.; Kumria, R.; Trehan, A. *International Journal of Pharmaceutics* **2004**, *278*, 1.

(64) Hiljanen-Vainio, M. P.; Orava, P. A.; Seppala, J. V. *Journal of Biomedical Materials Research* **1997**, *34*, 39.

(65) Dobrzynsky, P.; Li, S.; Kasperczyk, J.; Bero, M.; Gasc, F.; Vert, M. *Biomacromolecules* **2005**, *6*, 483.

(66) Seretoudi, G.; Bikiaris, D.; Panayiotou, C. *Polymer Degradation and Stability* **2002**, *43*, 5405.

(67) Zhu, G.; Li, Y.; Ling, J.; Shen, Z. *Journal of Thermal Analysis and Calorimetry* **2004**, *77*, 833.

(68) Bei, J.-Z.; Li, J.-M.; Wang, Z.-F.; Le, J. C.; Wang, S.-G. *Polymers for Advanced Technologies* **1997**, *8*, 693.

(69) Marten, E.; Muller, R.-J.; Deckwer, W.-D. *Polymer Degradation and Stability* **2005**, *88*, 371.

(70) Wang, S.-G.; Tang, K. *Chinese Journal of Polymer Science* **1999**, *17*, 231.

(71) Lotti, N.; Finelli, L.; Munari, A.; Manaresi, P. *Journal of Thermal Analysis and Calorimetry* **2001**, *66*, 827.

(72) Siling, M. I.; Laricheva, T. N. *Russian Chemicals Reviews* **1996**, *65* 279.

(73) *Modern Polyesters*; Sheirs, J.; Long, T. E., Eds.; Wiley, 2003.

(74) Brostow, V.; Chiu, R.; I.M., K.; Dova-Vassilijou, A. *Materials Letters* **2008**, *62*, 2152.

(75) Noller, C. R. *Chemistry of Organic Compounds*, W.B. Saunders Company, 1965.

(76) Jasinski, W.; Ropuszynski, S. *Prace Naukowe Instytutu Technologii Organicznej I Tworzyw Sztucznych Politechniki Wroclawskiej* **1973**, *12*, 3.

(77) Barrera-Rivera, K. A.; Martinez-Richa, A. *Macromol. Symp.* **2009**, *283-284*, 144.

(78) Chen, H.-Y.; Zhang, J.; Lin, C.; Reibenspies, J. H.; Miller, S. A. *Green Chem.* **2007**, *9*.

(79) Calabia, B. P.; Tokiwa, Y. *Biotechnol. Lett.* **2007**, *29*, 1329.

(80) Gilding, D. K.; Reed, A. M. *Polymer Degradation and Stability* **1979**, *20*, 1459.

(81) Hakkarainen, M.; Albertsson, A.-C. *Adv. Polym. Sci.* **2008**, *211*, 85.

(82) Cao, X.; Mohamed, A.; Gordon, S. H.; Willett, J. L.; Sessa, D. J. *Thermochimica Acta* **2003**, 115.

(83) Kamide, K.; Miyazaki, Y.; Kobayashi, H. *Polymer Journal* **1977**, *9*, 317.

BIOGRAPHICAL SKETCH

Laurent Mialon was born in 1984 in France. He attended the lycée polyvalent de St-Romain en Gal and obtained the scientific Baccalauréat with honors in 2002. Growing a general interest for science, he entered in fall 2002, the preparatory classes to CPE Lyon with a specialization in physics and chemistry. He was admitted to the engineering school Chimie Physique Electronic Lyon (CPE Lyon) in 2005, obtaining his diplôme d'ingénieur in spring 2009. After 2 years of engineering school he enrolled the chemistry department at the University of Florida, specializing in organic chemistry and polymer science. His research on biorenewable polymers was directed by Dr. Stephen A. Miller. He started working as a polymer chemist in R&D for AkzoNobel in February 2010 in Newcastle, UK.