Magnesium and Zinc Complexes of Naphthenic Acid Model Compounds

By:
Matthew Laprade

A00377428

A Thesis Submitted to
Saint Mary's University, Halifax, Nova Scotia
in Partial Fulfillment of the Requirements for
the Degree of Bachelor of Science
with Honours in Chemistry

March 21, 2016

Dr. Jason A.C. Clyburne
Supervisor
Department of Chemistry &
Environmental Science

Dr. Robert D. Singer
Chairperson
Department of Chemistry

Abstract

Bitumen is a key Canadian petroleum resource making up 33% of the world's demand. Bitumen contains naphthenic acids, an undesired component, both environmentally and industrially, due to their toxicity and acidity. Many methods have been proposed for lowering the toxic effects of these acids, to reduce their harmful environmental impacts and to increase the value of the bitumen. In this work, esterification and metal coordination, to zinc and magnesium, were chosen to derivatize several model naphthenic acid compounds, in an attempt to reduce toxicity, bitumen viscosity and corrosion to metal infrastructure.

The RP-HPLC partition coefficient determination showed that esterification is a better method for reducing the polarity of naphthenic acids compared to metal coordination complexes. This is due to the metal complexes also coordinating to water, which is confirmed by the crystal structure data. This water coordination raises the water affinity and polarity of the metal complexes to a higher level than expected. Both the esterification method and the metal coordination method demonstrate the ability to reduce the polarity of model naphthenic acids.

Acknowledgements

Firstly, I would like to thank my supervisor, Dr. Jason A.C. Clyburne. I did not feel that I was worthwhile when he allowed me to join his research group in the summer last year, but I have been ever grateful since then. Since joining Jason's group I have had incredible opportunities towards research and furthering my understanding of the field both inside and outside the lab. I am incredibly grateful and I cannot thank him enough for the opportunity that he has granted me.

I would also like to thank, and congratulate, my fellow Honours students for what we have been able to achieve in the past year while also juggling classes and our own personal lives. I would also like to thank my friend, Andrew Carter for using his personal time to help me review and edit this thesis. Furthermore, I would like to thank Michael A. Land for his depth of knowledge that he was willing to share and willingness to help when it was needed. He is the one whom helped and taught me when I was struggling in the lab, and also provided ideas that I never would have known or considered without him. I would also like to thank the all current and past members of Dr. Clyburne's research group.

Dr. Katherine N. Robertson is someone whom I do not think I will be able to thank enough for everything that she has helped me with. Her expertise with X-ray crystallography and advice has been invaluable during my time within the research group. The amount of her own time that she had sacrificed to finish analyzing some samples, only for me to present her with more, has been numerous and I cannot thank her enough for it.

Dr. Bitu Hurisso has been one of the main people helping with my research. From help with synthesis, to advice on devising the next step to take, he has been vastly important to reach this point. Bitu was always the first one I would seek for a second opinion in regards to an idea to try, a step to take, or what he believed was necessary to complete the picture. For this, he has my extreme gratitude.

The Saint Mary's technicians, Elizabeth McLeod, Darlene Goucher, and Alyssa Doue, have been a great help while working in the chemistry department. Every time I have been in need of something, or unable to location a material, even if it was hidden within the Clyburne lab, they have always been incredibly kind in helping to located it. Furthermore, I would like to thank Dr. Robert Singer and his research group for being incredibly helping and willing to lend out different reagents form their lab.

Finally, I would like to thank Dr. Patricia Granados for all the time that she had put in not only to run and analyze sample, but also to teach me to better understand and use the HPLC. Her guidance from devising the method to operating the HPLC has a highly important part of this research. Without her to help, an important part of this research would not have been possible.

Table of contents

List of figures

List of schemes

List of symbols and abbreviations

°	degrees
°C	degrees Celsius
Å	Angstrom (10-10 m)
ab initio	from Latin, meaning “from the beginning”
ACN	acetonitrile
AIM	atoms in molecules
Ar	aryl
ATR	attenuated total reflection
AN9CA	anthracene-9-carboxylic acid
br	broad
C6D6	deuterated benzene
ca.	*circa* (from Latin, meaning “about, approximately”)
CCHA	*cyclo*-hexaneacetic acid
CCPA	*cyclo*-pentylacetic acid
et al.	*et alii* (from Latin, meaning “and others”)
cm-1	wavenumber
CO_2	Carbon Dioxide
COOH	Carboxylic acid group
CPHA	2-*cyclo*-pentylhexanoic acid
cyhex	*cyclo*-hexane
cypen	*cyclo*-pentane
D2O	deuterium oxide
DCM	dichloromethane
DMSO-D6	deuterated dimethylsulfoxide
EA	elemental analysis
EDG	electron donating group
Et_2O	diethyl ether
Et2Zn	diethylzinc
g	gram
in situ	from Latin, meaning “in the reaction mixture”
in vacuo	from Latin, meaning “in a vacuum”
IR	infrared
J	coupling constant
K	kelvin
K_{OW}	Octanol water partition coefficient
M	molar (moles per liter)
m	multiplet/medium
MeOH	methanol
mg	milligram
$MgCl_2$	magnesium chloride
MHz	megahertz

mL	milliliter
mmol	millimole
MOPCA	3-methyl-octahydro-pentalene-1-carboxylic acid
NaCl	Sodium Chloride
NH_4Cl	Ammonium Chloride
NMR	nuclear magnetic resonance
ohpn	octahydro-pentalene
OSPW	oil sands process water
Ph	phenyl
pm	picometer
ppm	parts per million
q	quartet
RP-HPLC	Reverse phase high performance liquid chromatography
s	singlet/strong
t	triplet
TAN	Total acid number
THF	tetrahydrofuran
vs	very strong
w	weak
XRD	X-ray powder diffraction
$ZnCl_2$	zinc chloride

Chapter 1 - Introduction

1.1 Overview of Athabasca Bitumen

Bitumen is the product of sedimentary organic matter that has been buried and decomposed over the course of millions of years. This breaks down cellular walls and proteins into basic organic compounds. More than 1.2 trillion barrels of bitumen are estimated to reside within the Earth[1] and this meets about 33% of the world's oil demands[2]. Bitumen is a class of heavy oil that is particularly viscous and contains toxic compounds; these compounds result from the interactions between the decomposing organic materials. Part of what makes bitumen toxic is the presence of naphthenic acids that are produced during the formation of bitumen. In Canada, bitumen is primarily extracted from northern Alberta, in the Athabasca and Cold Lake regions.

The presence of these acids within bitumen is a serious problem both environmentally and industrially due to their chemical properties. Naphthenic acids are naturally occurring carboxylic acids and have relatively high polarities compared to other organic molecules. This polarity makes the acids soluble in aqueous systems, where they lower the pH. As well, toxic organic molecules are introduced to the environment, where the acids act as surfactants. This property of naphthenic acids is the initial reason why oil spills are environmentally devastating.

Industrially, naphthenic acids are financially detrimental. Naphthenic acids cause corrosion to metal infrastructure as it promotes oxidation on the metal surfaces. The cost to maintain or replace infrastructure within the oil industry is expensive due to the specialization of the equipment. The TAN of bitumen directly influences the price at

which a barrel of oil can be sold; a relatively high Total Acid Number can reduce the price of a barrel of oil by up to 40%[3]. The presence of naphthenic acids directly influences the Total Acid Number (TAN) of the bitumen and also creates a source of hydrogen bonding within the bitumen. The TAN is defined as the amount of potassium hydroxide (in milligrams) needed to neutralize one gram of oil. The TAN is an industrial term to denote the amount of acidic material that is present within petroleum products. It is these acids that also create a source of hydrogen bonding within bitumen as the majority of bitumen is a collection of nonpolar hydrocarbons. The acidic protons of the naphthenic acids are able to cross link with the polar heads of other naphthenic acids to increase the intermolecular forces present within bitumen through this hydrogen bonding.

The primary intermolecular forces that are present within bitumen are van der Waal's forces; bitumen has a high viscosity as a result. The presence of naphthenic acids introduces a source of hydrogen bonding, which results in the formation of intermolecular cross linking. This cross linking is able to act as a type of net and further prevent movement of bitumen particles; this is another contributing factor to the high viscosity of bitumen.

1.2 Overview of Naphthenic acid structure

Naphthenic acids are defined by the International Union of Pure and Applied Chemistry as "acids, chiefly monocarboxylic, derived from naphthenes."[4] [5] Naphthenes are "*cyclo*-alkanes especially *cyclo*-pentane, *cyclo*-hexane and their alkyl derivatives."[6]

It is worth noting that both of the defined terms are antiquated and no longer used, except within the petroleum and petrochemical industries. There is no single form of naphthenic acid in bitumen, instead there is a mixture of hundreds of different *cyclo*-pentyl and *cyclo*-hexyl carboxylic acids with molecular weights of 120 to well over 700 atomic mass units. The main fraction consists of carboxylic acids with a carbon backbone of 9 to 20 carbon atoms. Molecular structures of naphthenic acids tend to follow the general formula of $C_nH_{2n+z}O_2$. McKee et al. claim that "naphthenic acids are primarily *cyclo*--aliphatic carboxylic acids with 10 to 16 carbons."[7]

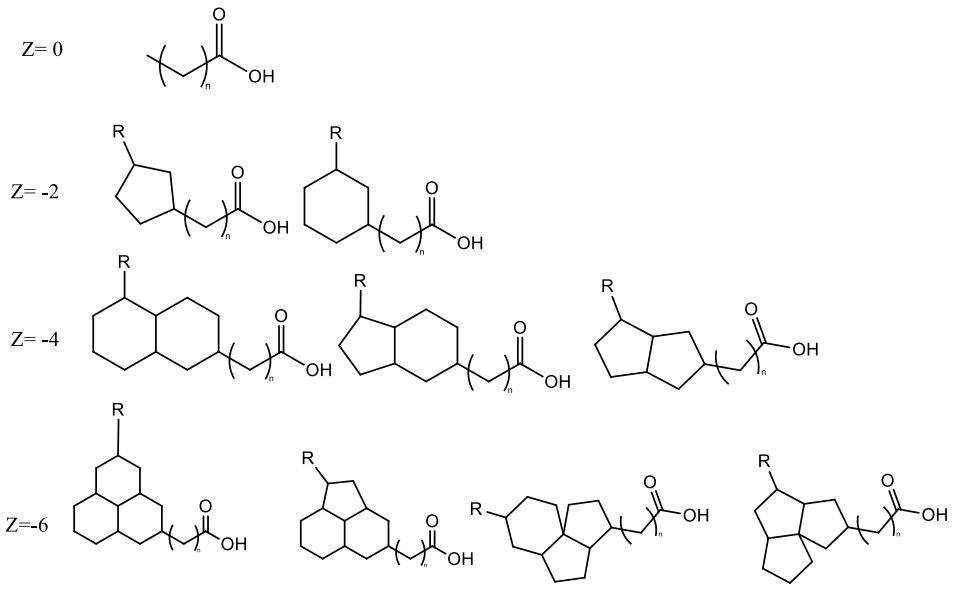


Figure 1: General molecular structures of naphthenic acids for the Z = 0, −2, −4 and −6 series with both five and six carbon rings present and n ≥ 5 following the generalized formula of $C_nH_2n+zO_2$.[8]

The toxicity of the chemicals is dependent upon their physical and/or chemical properties, but also upon the amount of exposure and the frequency of exposure[9]. In Northeastern Alberta, oil sand mining involves the removal of water from the Athabasca

River basin. Water produced from the extraction of bitumen from oil sands is referred to as oil sands process water (OSPW)[10]. Naphthenic acids and other organic compounds are dissolved and concentrated in oil sands process water[11].

Briefly, it is important to eliminate naphthenic acids due to the polar head group (COOH) that they possess. This polar head group allows naphthenic acids to undergo hydrogen bonding and to act as a surfactant within the bitumen. The elimination of the polar head group will reduce the bitumen's acidic nature, which is a disruption to industry, and highly toxic to other organisms. As well, it will reduce the hydrogen bonding forces within the bitumen, which will also reduce the overall viscosity.

1.3 Toxicity of Naphthenic acids

The naphthenic acids in bitumen are dangerous as they can disperse into the environment through waterways. This is possible as they are soluble in the aqueous phase and act as a surfactant to other harmful components of bitumen. A majority of these naphthenic acids will dissociate and diffuse throughout the water column. They can be easily distributed by bulk transportation or leaching processes[12].

Aquatic organisms are more sensitive to naphthenic acids than mammals; the lowest chronic (60-days) LC_{50} for fish was 1.4 mg/L for juvenile chum salmon (*Oncorhynchus keta*), while the lowest acute (96-hours) LC_{50} was 20 mg/L for the same species. Mammals required an oral LD_{50} of 1.75-3.55 g/kg body weight[13]. Both groups, however, presented significant non-lethal effects from exposure to naphthenic acids,

ranging from glycogen accumulation in muscle tissue, to central nervous system depression and convulsions.

1.4 Reduction of polarity in Naphthenic acids

There are various methods that can be used to neutralize the harmful effects of naphthenic acids: (i) the addition of a base to neutralize the acid, (ii) esterification through the use of an alcohol, an organic reaction to convert the acid to an aldehyde or a primary alcohol, or (iii) coordination of the acid to a metal center via the activation of the nucleophile[14]. The coordination method was chosen to be the focus of this research as it provides an inexpensive way to neutralize the naphthenic acids without highly reactive or toxic additives.

All of these methods result in deprotonation of the naphthenic acids. This deprotonation not only reduces the toxic impact of the molecules but also diminishes the intermolecular forces present due to a reduction in the hydrogen bonding. The reduction of these forces, in turn, diminishes the viscosity of the bitumen, as the molecules flow past one another more easily.

Several factors were considered when selecting the method to be used, namely the overall scale and the cost. In terms of scale, the chosen method had to be able to eliminate the naphthenic acids at a high rate in order to meet a production speed of 3 million barrels of bitumen daily, a volume expected to increase to over 4 million barrels a day in a decade in Canada alone. In terms of cost, the method had to be cost effective

and not produce harmful impurities that are either expensive to remove or damaging to metal infrastructure.

1.4.1 Acid base neutralization

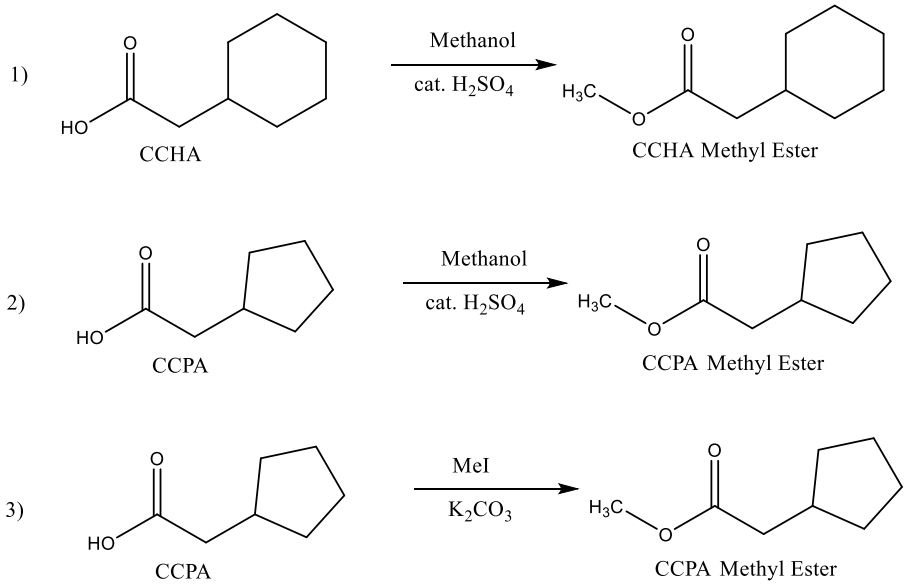
The addition of a base is the simplest method to neutralize an acid, but this introduces the necessity of having to be exact. Otherwise, the toxic effects caused by the acids will instead be replaced by the toxic effects caused by the base. A perfect 1:1 molar ratio will have to be obtained; otherwise excess acid or base will be present. This amount of precision is unlikely to be achieved since over 100 naphthenic acids exist within bitumen in varying concentrations; reaching an exact 1:1 molar ratio is unrealistic. Another issue for this method is that acid-base reactions are reversible under aqueous conditions. The deprotonation of an acid will proceed, but the resulting conjugate base will be protonated in the presence of water which will reform the acid. This method does not offer a permanent solution to the removal of naphthenic acids.

1.4.2 Esterification of carboxylic acids

A second possible method for the elimination of naphthenic acids is esterification; this is done through the addition of simple alcohols using an acid catalyst. However, this method gives rise to challenges in the esterification of bitumen. Fischer esterification is the standard process for this type of reaction, but the addition of a strong acid, to act as a catalyst, into bitumen pipelines is undesirable. Without an acid catalyst, a Fischer

reaction is unable to proceed in high enough yield to be cost-manageable for oil companies.

It is worth noting that the issue of an acid catalyst might potentially be over come through the use of an ionic liquid medium instead of an acid catalyst[15,16]. The ionic liquid in this case would be the bitumen itself, since bitumen contains numerous inorganic and organic compounds that interact together within an inherently acidic environment to create ionic species. An issue in using the bitumen itself as a reaction medium is that it will have a low conversion yield. By using the ionic properties of bitumen to catalyze Fischer esterification of naphthenic acids, the reaction will proceed only until there are not enough ions left to continue promoting the reaction. As naphthenic acids are weak organic acids, there will be a significant percent of unreacted naphthenic acids remaining.



Scheme 1: Proposed syntheses of naphthenic acid esters through Fischer and methyl iodine esterification. 1) CCHA Fischer esterification. 2) CCPA Fischer esterification. 3) CCPA methyl iodine esterification.

1.4.3 Chemical reduction of carboxylic acids to aldehydes

In another method, carboxylic acids can be reduced to aldehydes or primary alcohols; the primary alcohol is more desirable as it has a lower toxicity. This requires a strong reducing agent, such as lithium aluminium hydride, which will induce the conversion of the acid. An issue with this method is that the bitumen must then undergo additional processing in order to remove the excess lithium aluminium hydride. Without removal, the lithium aluminium hydride would be more harmful than the naphthenic acids. There are issues with this method other than just the removal of excess material. Lithium aluminium hydride is highly reactive, making it dangerous to work with. It is self-igniting in the presence of oxygen and a self-igniting material it is undesirable at bitumen extraction sites.

The high reactivity of lithium aluminium hydride also makes it non-selective with what it reacts with. In bitumen, only the naphthenic acids are the targets, anything else that could react within bitumen has the potential to cause degradation within the final petroleum product or create harmful compounds to the purification process. Finally, lithium aluminium hydride is expensive and unreasonable to be of use on a large enough scale to produce 3 million barrels of bitumen daily.

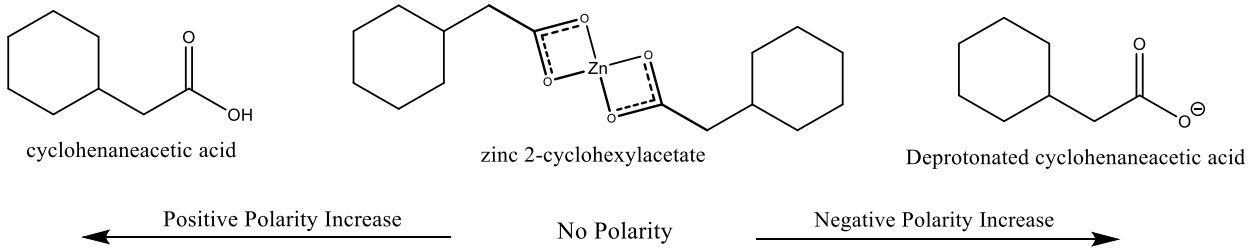
1.4.4 Synthesis of bis-carboxylate metal complexes as a method to lower naphthenic acid polarity

The method chosen for this research is metal center coordination[17,18,19] of the naphthenic acids; it provides the least amount of risk in comparison to the previously

stated methods. Coordination of the acids to a metal center, such as zinc (II) or magnesium (II), will eliminate two molecules of acid at once, while the added metal is inherently non-toxic for its addition into bitumen. A 2:1 molar ratio of acid to metal is necessary, meaning that less reactant will be required when compared to the other methods discussed above. The coordination method also has the same benefits as the Fischer esterification method. These include a reduction of the partition coefficient[20,21] of bitumen as it converts the polar acids into non-polar complexes. The partition coefficient is the concentration measurement of a solute in a mixture of two immiscible solvents[22]. This is then able to determine the solubility difference of the compound across the two phases[23]. A reduction of the partition coefficient of naphthenic acids directly reduces their solubility in water. Reducing naphthenic acid solubility in water will prevent them from acting as surfactants for bitumen, further lessening toxic effects. A method to measure the partition coefficient was adapted from the literature to compare a complex's partition coefficients to the respective unreacted naphthenic acid using reverse phase high performance liquid chromatography. [24] [25]

This coordination to the metal center reduces the overall polarity of the complex relative to the free acids. Decreasing the polarity of the naphthenic acids will reduce their affinity for water. This will cause them to favour remaining within the non-polar bitumen as well as reducing their ability to act as a surfactant. This synthesis will also remove a source of hydrogen bonding within the bitumen, reducing its intermolecular forces and its viscosity. A reduction in bitumen viscosity may not be viewed as immediately important, but in doing so it will be providing a reduction to the amount of bitumen diluent required to reduce the viscosity to meet the standard flow allowed within

an oil pipeline, ~350 cSt[26]. A reduction in the amount of diluent, which is a mixture of *cyclo*-hexane, toluene, and heptane[27], directly correlates to savings for companies as these solvents are expensive and difficult to recover.



Scheme 2: Diagram of non-polarity within zinc 2-cyclohexylacetate complex compared to respective naphthenic acid

Another benefit of this method, one that is not immediately visible, involves the oil pipelines. The naphthenic acids, over time, will corrode the structural integrity of the pipelines used to carry them. They react differently depending upon the transportation method[28] of the bitumen but overall they increase the risk of failure and an oil spill. Though a risk is present, different transportation methods, such as Extra Heavy Crude Oil Pipelines, lessen the risk of corrosion to pipelines to the point where the role of naphthenic acids is almost negligible[29]. Other methods, such as Steam Assisted Gravity Drainage, suffer corrosion not only from the acids present but also from localized corrosion, corrosion for flow-acceleration, and a few other sources[30]. Though corrosion through various means is present within pipelines, it must be noted that, when compared to transportation by rail, pipelines are found to be over 4.5 times less likely to experience a catastrophic occurrence[31]. In the event of an occurrence, 70% of spills are

of ≤1 m^3. Of the occurrences, 17% are present within the actual pipeline; the remaining 83% happen at the facility with secondary containment measures[32]. It is reported that between the years of 2011-2014, about 1084 barrels of oil were spilt from Canadian pipelines[33].

To prevent and reduce corrosion within the pipeline, we propose the use of the metal coordination method (as described earlier) with the metal centers zinc and magnesium being utilized. Zinc will interact with steel in the pipeline to undergo the chemical process of galvanization, in which a protective coating of zinc is applied onto the steel. This galvanization will strengthen the steel pipeline and even repair any pre-existing naphthenic acid corrosion. The other metal, magnesium, can chemically interact with steel to form an alloy that possesses better non-oxidizing properties when compared to steel alone.

1.5 Objectives of this thesis

For this research, several issues involving the relationship between bitumen and naphthenic acids have been identified. These can be related to the objectives of this investigation:

1. How to easily prevent further corrosion within pipelines: The prevention of pipeline corrosion can be accomplished through the elimination of the acidic protons within the naphthenic acids. The coordination of the acid to the chosen metal centers will do this. The interaction of the metal centre with steel will also prevent corrosion of the pipelines.

2. How to easily and cheaply reduce the viscosity of bitumen: The loss of the naphthenic acid protons will reduce the internal forces acting within bitumen; losing a source of hydrogen bonding will lessen the overall attraction forces and reduce the viscosity of the bitumen.
3. How to reduce the toxicity of naphthenic acids: The coordination of naphthenic acids to metal centers will reduce the molecules' dipole moments via coordination to an electrophile. This will also create symmetry in the complex which will further reduce the polar aspects of the naphthenic acids. This will reduce the acids' solubility in aqueous systems, which will be measured through the determination of the samples' partition coefficients.

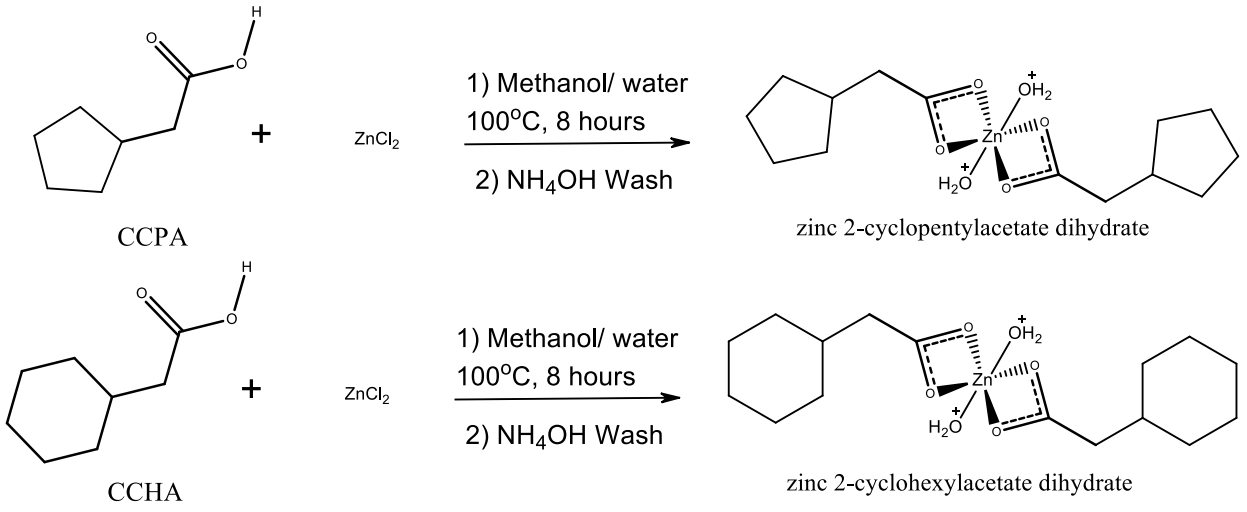
The metal coordinated acids will be compared to the respective esterified acid counterparts in order to determine which of the previously described methods is more effective at completing the goals of this experiment.

Chapter 2 - Results and discussion

2.1 Zinc metal center complexes

2.1.1 Preparation of the zinc 2-cyclohexylacetate dihydrate complex

500 mg of the required naphthenic acid was weighed and dissolved in 10 mL of methanol. 293 mg of zinc chloride was mixed into the solution with 10 mL methanol and the solution heated to 80°C under reflux for 8 hours. After reaction, 20 mL 6M ammonium hydroxide was added and the sample was stirred for 30 minutes. A white precipitate formed in the flask. Spectroscopic analysis was performed on the sample, including ^{1}HNMR, ^{13}CNMR, COSY, HSQC, and IR. The NMR sample was prepared from 30 mg of the complex dissolved in DMSO-D6. A crystal was grown from the sample via evaporation using methanol as the solvent.



Scheme 3: Synthesis methods for the CCPA (top) and CCHA (bottom) zinc complexes.

2.1.2 Analysis of the zinc 2-cyclohexylacetate dihydrate complex

The sample CMJL027 Zn showed a disappearance of the acidic proton peak (when compared to the spectrum of the starting material) in the ^{1}H NMR spectrum, indicating that the CCHA had been deprotonated. Upon review of the CMJL027 Zn ^{13}C {1H} (75 MHz, DMSO-D6, ppm) spectrum, it was found that the large carbonyl peak at 173.7 ppm (s, -COOH) had been replaced with a significantly smaller peak at 175.7 ppm (s, -COOZn). This shift up-field in the spectrum indicates that additional electron density has been introduced to the complex to shield the carbon electrons. This is good supporting evidence for the formation of a zinc complex, since zinc has a large electron shell to create this shielding effect.

The carbonyl peak of the sample is significantly smaller in comparison to the other detected carbon signals and with respect to those of the CCHA control. This may be due to a sensitivity issue of the sample, or some unexpected product being formed to eliminate the carbonyl group, such as would occur with carbon dioxide production. The ^{1}H NMR of the sample also shows a broad peak located at 6.03 ppm that corresponds to the presence of ammonium protons.

The elemental analyses (EA) confirms the presence of nitrogen within the bulk samples, as can been seen for CMJL027 Zn in the experimental section. However, nitrogen does not appear to be adversely interacting with the coordination of the sample; it is instead a matter of purity. The metal coordinated sample was crystallized from slow evaporation in methanol. The crystallization also developed an oily layer that the crystals were resting within. Crystal structures of both samples were obtained using XRD.

2.1.3 Partition coefficient of the zinc 2-cyclohexylacetate dihydrate complex

When comparing the partition coefficient of the samples to CCHA, the acid control was retained for 3.1 minutes, while CMJL027 Zn was retained for 3.8 minutes. The increase of the retention time for CMJL027 Zn supports the hypothesis that metal coordination is a viable method to reduce the polarity of the naphthenic acids. The increase in retention time is not as significant when compared to the methyl ester trials; this may be due to water coordination to the zinc metal center as observed within the crystal structure. This coordination would increase the polarity and the affinity that the complex has towards water, allowing it to be more soluble in the aqueous phase than theorized.

2.1.4 Solid state crystal data of the Zinc metal center complexes

The selected naphthenic acid was reacted with 293 mg of zinc chloride in methanol and heated to 80°C under reflux for 8 hours. After reaction, 20 mL 6M ammonium hydroxide was added and the sample was stirred for 30 minutes. A white precipitate formed within the flask. Crystals were grown from the samples through slow evaporation using methanol as the solvent. X-ray crystallographic analyses were performed by Dr. Katherine Robertson.

The structures of the zinc crystals demonstrate two initially unpredicted phenomena. The first is the bidentate (dual) coordination to the oxygen atoms of the

naphthenic acid. It was initially theorized that the zinc complex would coordinate to a single oxygen atom from each acid molecule and retain a double bond on the other oxygen of the carboxyl group. It seems instead, that the oxygen is undergoing resonance to dissociate the double bond across both atoms, forming a carboxylate salt. This is most likely due to the abundance of electrons that zinc has in its valence shell and the electron negativity of oxygen. The second unpredicted result is that the zinc center is also coordinating with water to form an octahedral structure. This structure allows for more stabilization of the metal atoms compared to the tetrahedral complex. This coordination of water also represents an increase in polarity over what was previously theorized. This increase is likely responsible for the lower than expected results of the partition coefficient comparison.

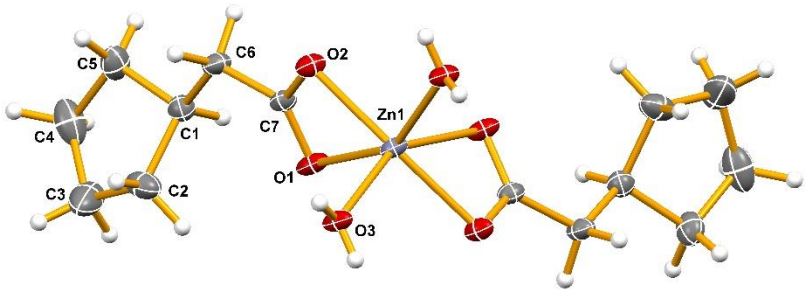


Figure 2: Solid state crystal structure of the CCPA zinc complex. Thermal ellipsoids are drawn at the 50% probability level. (Synthesis performed by Dr. Bitu Hurisso)

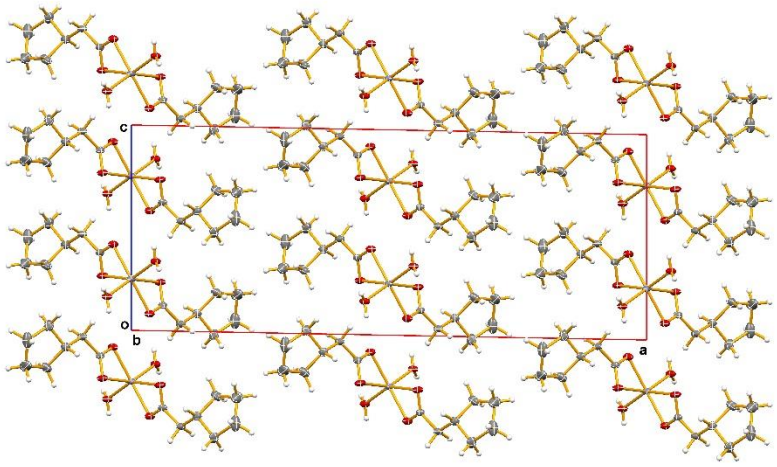


Figure 3: Packing diagram of theCCPA zinc complex viewed down the Y-axis. (Synthesis performed by Dr. Bitu Hurisso)

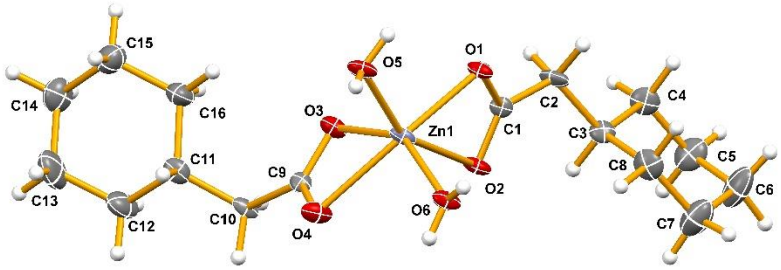


Figure 4: Solid state crystal structure of the CCHA zinc complex. Thermal ellipsoids are drawn at the 50% probability level.

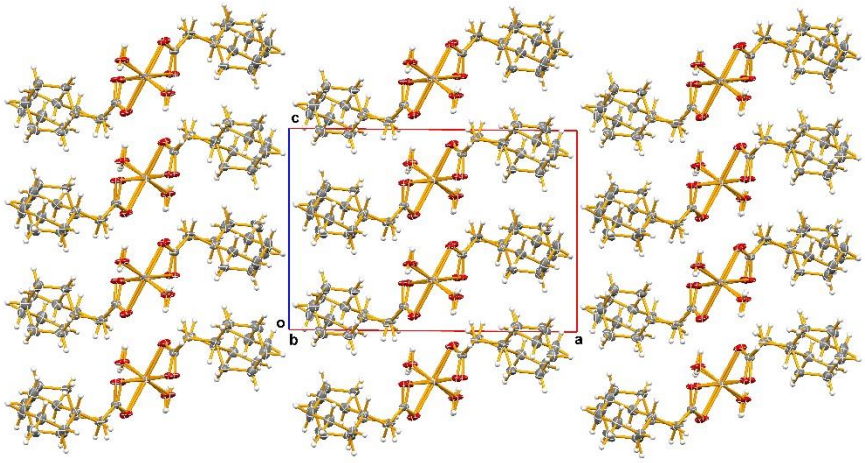
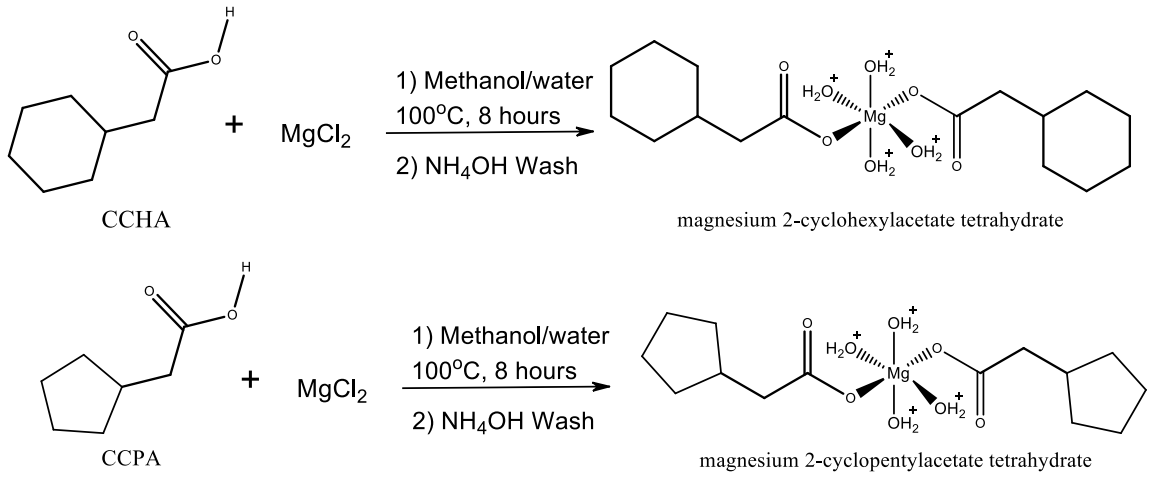


Figure 5: Packing diagram of the CCHA zinc complex viewed down the Y-axis.

2.2 Magnesium metal center complexes

2.2.1 Preparation of the magnesium 2-cyclohexylacetate tetrahydrate complex

500 mg of the required naphthenic acid was weighed and dissolved in 10 mL of methanol. 403 mg of magnesium chloride was mixed into the solution with 10 mL methanol and the solution heated at 80°C under reflux for 8 hours. After reaction, 20 mL of 6M ammonium hydroxide was added and the sample was stirred for 30 minutes. A white precipitate formed within the flask. Spectroscopic analysis was performed on the sample, including ^{1}HNMR, ^{13}CNMR, COSY, HSQC, and IR. The NMR sample was made from 30 mg of the complex dissolved in DMSO-D6. A crystal was grown from the sample with slow evaporation using methanol as the solvent.



Scheme 4: Synthesis methods of the CCPA and CCHA magnesium complexes,

2.2.2 Analysis of the magnesium 2-cyclohexylacetate tetrahydrate complex

CMJL027 Mg showed a disappearance of the acidic proton peak in the ^{1}H NMR spectrum, indicating that the CCHA had been deprotonated. Upon review of the CMJL027 Mg $^{13}C\{1H\}$ (75 MHz, DMSO-D6, ppm) spectrum, two peaks are present, 173.6 (s, -COOH) and 176.1 (s, -COOMg) compared to the CCHA control, which has a large carbonyl peak at 173.7 (s, -COOH). The peak at 173.6 for CMJL027 Mg is presumed to be uncoordinated acid present within the sample. This shift down-field in the spectrum indicates that electron density has been taken from the carbonyl carbon to cause its deshielding. This is good supporting evidence for the formation of a magnesium complex, which does not have a large electron shell. The Mg^{2+} ion would want to pull electron density away from the acid when it reacts, causing a reduction of electron density in the oxygen atoms and thus a deshielding effect on the carbon.

The carbonyl peaks in the sample are significantly smaller in comparison to the other detected carbons within the sample and with respect to the CCHA control. This may be due to a sensitivity issue of the sample, or some unexpected product being formed to eliminate the carbonyl, such as could occur with carbon dioxide production. The ^{1}H NMR spectra of both of these samples show a broad peak located at 6.03 ppm that corresponds to ammonium protons.

The EA of the samples confirms the presence of nitrogen within them, as can been seen for CMJL027 Mg in the experimental section. However, nitrogen does not appear to be adversely interacting during the coordination of the sample; it is instead a matter of purity. The metal coordinated sample was crystallized from slow evaporation in methanol. The crystallization also developed an oily layer that the crystals were resting within. Crystal structures of both samples were obtained from XRD.

2.2.3 Partition coefficient comparison of the magnesium 2-cyclohexylacetate tetrahydrate complex

When comparing the partition coefficient of the samples to CCHA, the acid control was retained for 3.1 minutes, and the CMJL027 Mg peak was not observed down field of the unretained peaks at 247 nm. A small spike occurred at 0.7 minutes when compared to the blank, but as this is directly in the middle of the HPLC grade methanol unretained peaks, it is difficult to assign this to the sample instead of the solvent.

This decrease of retention time for CMJL027 Mg does not support the hypothesis that metal coordination is a viable method to reduce polarity of the naphthenic acids.

This decrease, however, may be due to water coordination to the magnesium metal center, as observed within the crystal structure. This coordination would increase the polarity and the affinity that the complex has towards water, allowing it to be more soluble than theorized. This idea would explain why CMJL027 Mg is less retained than the control acid. The crystal data shows that twice as much water is coordinated in the magnesium complexes compared to the zinc complexes, which would further increase the water solubility of the latter. In case the magnesium complex is not absorbing at the chosen wavelength, the experiment should be redone at a different wavelength where CMJL027 Mg absorbs better.

2.2.4 Solid state crystal data of the Magnesium metal center complexes

The selected naphthenic acid was reacted with 403 mg of magnesium chloride in methanol and heated at 80°C under reflux for 8 hours. After reaction, 20 mL of 6M ammonium hydroxide was added and the sample was stirred for 30 minutes. A white precipitate formed within the flask. Crystals were grown from the samples through slow evaporation using methanol as the solvent. X-ray crystallographic analyses was performed by Dr. Katherine Robertson.

The structures of the magnesium crystals demonstrate an initially unpredicted phenomenon. The unpredicted result is that the magnesium complex is also coordinating with water to form an octahedral structure. This structure allows for more stabilization of the metal atoms compared to the tetrahedral complex. This coordination of water also represents an increase in polarity over what had been previously

theorized. This increase is likely responsible for the lower than expected results of the partition coefficient comparison.

It is also interesting to note that the magnesium structure does not form a bidentate carboxylate structure, where the magnesium is coordinated to both oxygen atoms in the naphthenic acid ligands like the zinc structure does. Instead, each acid molecule coordinates to the magnesium metal center in a monodentate fashion. This may be due to magnesium not having a large valence electron shell thusly preventing the oxygens from withdrawing them. It is unlikely that the size of the atomic radius is influencing the coordination of the complexes with water as magnesium has a larger atomic radius, 145 pm, than zinc, 142 pm.

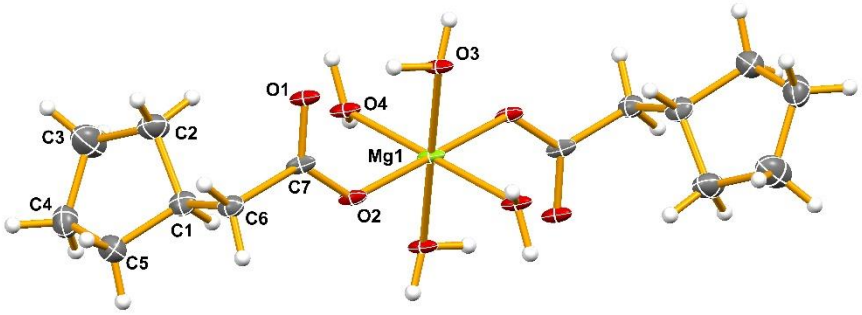


Figure 6: Solid state crystal structure of the CCPA magnesium complex. Thermal ellipsoids are drawn at the 50% probability level. (Synthesis performed by Dr. Bitu Hurisso)

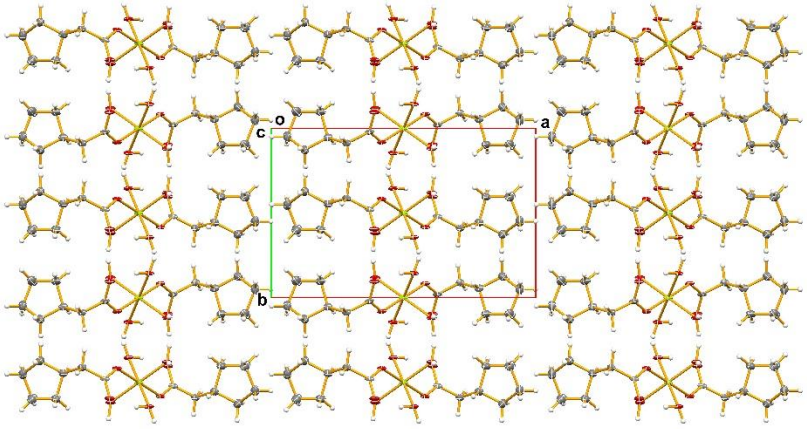


Figure 7: Packing diagram of the CCPA magnesium complex viewed down the Z-axis. (Synthesis performed by Dr. Bitu Hurisso)

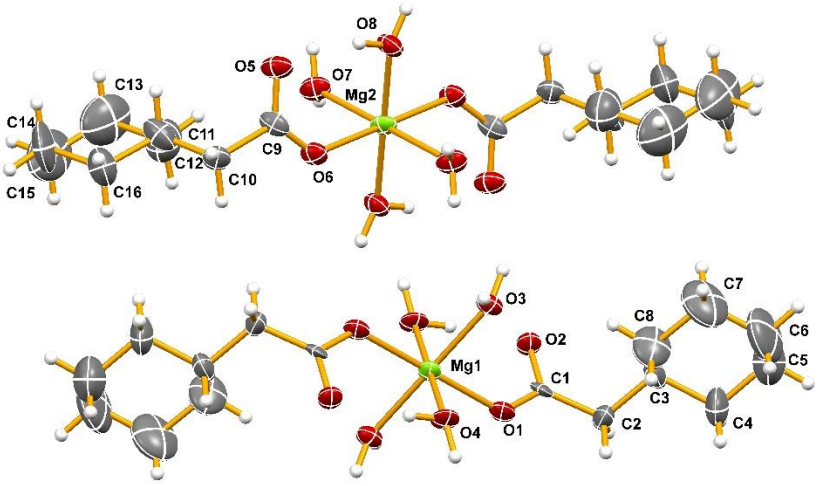


Figure 8: Solid state crystal structure of the CCHA magnesium complex. Thermal ellipsoids are drawn at the 50% probability level.

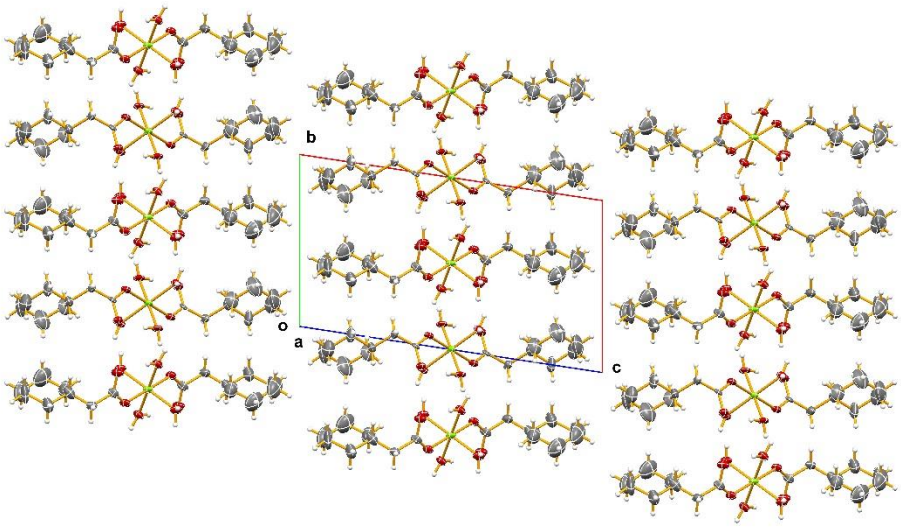


Figure 9: Packing diagram of the CCHA magnesium complex viewed down the X-axis.

2.3 Ammonium hydroxide free metal center complexes

2.3.1 Na_2CO_3 as a base for L_2M complex formation, L= naphthenic acid, M=metal center.

Elemental analyses detected the presence of nitrogen within the previous samples, so the synthesis of the metal coordination complexes was changed from ammonium hydroxide base promoted to sodium carbonate base mediated; further details of the method can be viewed in experimental section. The new coordination method was tested with zinc and CCHA to compare against the pre-existing samples for the viability of the coordination. The new sample did not show the ammonium peak present within the ^1H NMR spectrum that was present within the CMJL027 Zn and Mg samples.

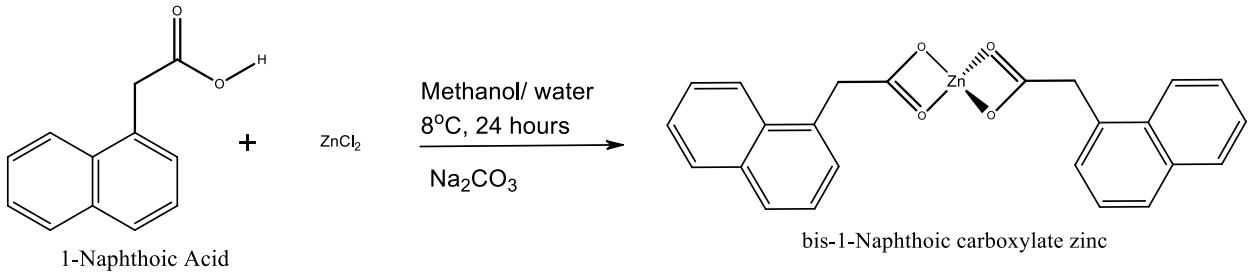
When compared to the spectroscopic data of CMJL027 Zn, the peaks present matched almost exactly. EA was used to confirm that nitrogen was not present within the sample either. The presence of nitrogen was a concern, firstly as a purity issue, and secondly because of the crystal quality being obtained. It was not clear whether the ammonium ions interacted during the crystal growth process, but the crystals that were produced were very hydroscopic, difficult to mount, dissolved in ionic liquids, and became a brown colour when exposed to air for an extended period of time (1-2 weeks).

With this data, the new method was approved for synthesis of other naphthenic acid complexes. CMJL035 was crystallized through slow evaporation in methanol, but crystals of suitable quality were not obtained.

2.3.2 Synthesis of an Na_2CO_3 base mediated L_2M complex

CMJL036 was the first sample obtained after the new method was tried on the selection of naphthenic acids available; it came from the reaction with 1-naphthoic acid to zinc chloride. The product of the reaction showed a disappearance of the acidic proton peak in the ^{1}H NMR spectrum, indicating that the 1-naphthoic acid had been deprotonated. Upon review of the CMJL036 $^{13}C\{1H\}$ (75 MHz, DMSO-D6, ppm) spectrum, the large carbonyl peak at 168.7 (s, -COOH) has been replaced with a significantly smaller peak at 172.4 (s, -COOZn). This shift up-field in the spectrum indicates that additional electron density has been introduced to the complex to shield the carbon electrons. This is good supporting evidence for the formation of a zinc complex, which has a large electron shell to create this shielding effect.

It is also worth noting that all of the aryl signals in the zinc coordinated 1-naphthoic acid have become less resolved. Doublet and triplets have appeared within the spectrum that were not present in that of the control acid. Some of the peaks have also shifted within the field by up to ±0.55 ppm with respect to the acid control. These chemical shifts may be due to the reaction forming undesired side products instead of the intended naphthenic acid zinc complex.



Scheme 5: Synthesis of the zinc coordinated 1-naphthoic acid complex.

2.3.3 Analysis of the Na_2CO_3 base mediated L_2M complex

The sample was sent for EA which confirmed that nitrogen was not present within the sample, as can be seen for CMJL036 in the experimental section. The risk of crystal damage by ammonium was thus minimal. The sample was crystallized via slow evaporation in methanol using an anti-solvent system of ACN and Et_2O. The slow evaporation method did not yield any useful crystals, as instead a highly oily layer remained, but the anti-solvent crystallization produced small needle crystals.

The samples were given the Dr. Robertson for analysis. The XRD spectrum of the 1-naphthoic acid sample was totally unexpected. The structure was helical in shape, wth 1-naphthoic acid ligands spiralling on the outside of the structure with internal cross-linking metal centers forming the backbone of the structure. These metal centers were not the expected zinc atoms, but instead sodium atoms from the sodium carbonate.

This is an interesting result as it emphasizes the coordination diversity of the ligands. It was not expected that sodium would coordinate to the acid, but it shows that the ligand can coordinate to both electron-rich and electron-deficient metal centers. The precise metal center is not fully relevant for the purpose of this experiment. The metals zinc and magnesium were chosen for their availability and the anti-corrosion chemical reactions that they undergo with steel. Sodium does not have this property, but coordination with sodium still allows the sample to reduce the viscosity of bitumen and to lessen the toxic effects of the acid.

A number of naphthenic acids were reacted using this method and had crystals grown. Upon examination of the crystal structures, it was determined that most were small inorganic salts of NaCl, $MgCl_x$, $ZnCl_x$ and NH_4Cl. Only 1-naphthoic and 9-anthracenecarboxylic acid coordinated to form sodium centered complexes. It is presumed that this is because these naphthenic acids are flat and aromatic, which allow for crystal packing in this specific way; the other acids studied would have steric effects causing interference.

2.3.4 Partition coefficient of the Na_2CO_3 base mediated L_2M complex

The comparison of the retention times in the RP-HPLC for CMJL036 compared to the 1-naphthoic acid control is not as straightforward as the previous samples. These samples were more concentrated compared to CMJL027 Zn and Mg samples. This higher concentration is further intensified by the high absorbance the complexes have for light at wavelength 247 nm. This causes a dramatic increase in signal intensity compared to the previous samples, which is unfavourable. This increased signal intensity makes it difficult to determine the exact retention time of the samples as the peaks are broader, and could be shifted due to overloading the column. Regardless, the control 1-naphthoic acid had a retention time of 3.0 minutes at its peak, spread out over about 1.0 minute.

CMJL036 does not have as well defined a peak as the control, instead multiple peaks are present and these fall within the area of the methanol blank. These peaks are significantly larger than those of the blank, so it is thought that the sample eluted in this area and thusly dramatically increased peak height. The next issue is the presence of multiple peaks within the sample, all at the same retention time. This could be contributed to by contamination within the sample caused by the reaction forming undesired side products instead of the intended naphthenic acid zinc complex.

If these peaks do include those of the sample, then CJL036 elutes at its slowest point at 1.0 minute. This implies that the sample is more hydroscopic than the respective acid control. This affinity for water may be due to a resonance structure of the sample creating a dipole moment. This dipole moment could allow for the sample to be more readily soluble in water than previous samples and result in it being more polar

than expected. A polar structure would explain the rapid elution within the polar mobile phase. Alternately, if these peaks are not the sample, then the experiment would have to be run longer to test for longer retention times, as no other peaks were eluted within the 20 minutes the experiment was run for.

2.3.5 Solid state crystal data of Na_2CO_3 base mediated L_2M complexes

The selected naphthenic acid was reacted with 231 mg of zinc chloride and 1 eq of sodium carbonate in methanol and heated at 80°C under reflux for 24 hours. The sample was evaporated and crystals were grown from the samples through anti-solvent crystallization using ACN and Et_2O as solvents. X-ray crystallographic analyses were performed by Dr. Katherine Robertson.

The structures of the sodium=containing crystals are the product of an initially unpredicted phenomenon. It was thought that this synthesis method would cause coordination with the desired metal centers (Zn or Mg), but instead a cross reaction happened with the sodium carbonate. It is not expected that sodium would coordinate to multiple atoms like this due to its small electron shell.

In the 1-naphthoic acid structure, the sodium atoms form a polymeric helical backbone, with the 1-naphthoic acid coordinating to the outside of the structure. The sodium atom is coordinated to multiple atoms; this must be to increase its stability. Acetonitrile is present within the crystal coordinated to sodium atoms. The presence of acetonitrile acts as a void filler for the sodium complex as it is small enough to fit within the voids that are present in the crystal structure. Each unit cell of the crystal structure is

composed of a 1-naphthoic acid molecule, three sodium atoms, and an acetonitrile molecule.

In the 9-anthracenecarboxylic acid structure, the sodium atoms form a polymeric helical backbone, with the 9-anthracenecarboxylic acid ligands coordinating to the outside of the structure. This is similar to the 1-naphthoic acid structure, but instead the sodium atoms are coordinating to water molecules to form the helical backbone while 9-anthracenecarboxylic acids are hydrogen bonding to the water on the outside of the structure. This may be due to 9-anthracenecarboxylic acid being bulkier than the 1-naphthoic acid, causing an increase of steric effects and thus preventing direct bonding to the metal centers. Each unit cell of the crystal structure is composed of a 9-anthracenecarboxylic acid molecule, three sodium atoms, and six water molecules.

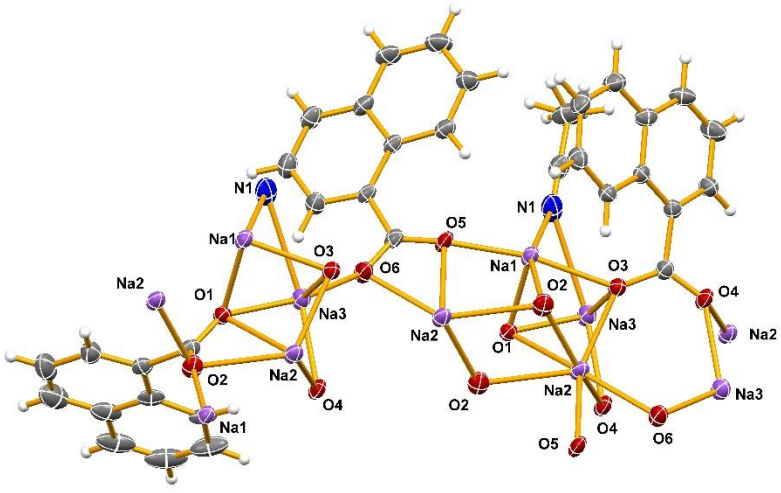


Figure 10: Solid state crystal structure of the 1-naphthoic acid sodium complex. Thermal ellipsoids are drawn at the 50% probability level.(Acetonitrile is present in the crystal acting as a void filler and providing extra stabilization).

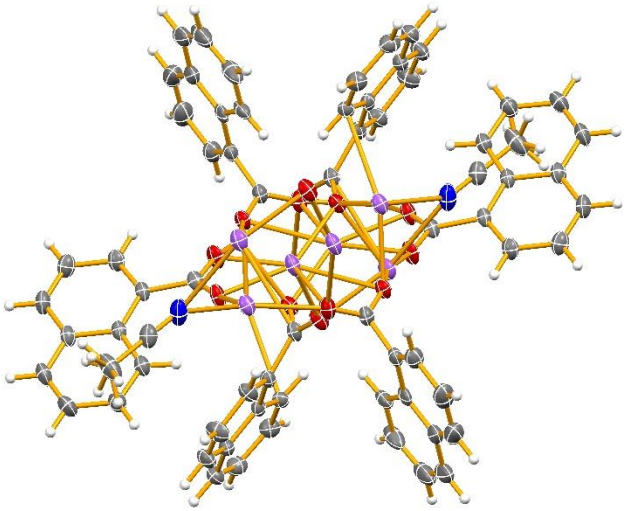


Figure 11: Solid state crystal structure of the 1-naphthoic acid sodium complex packing system. Thermal ellipsoids are drawn at the 50% probability level. (Acetonitrile is present in the crystal acting as a void filler and providing extra stabilization).

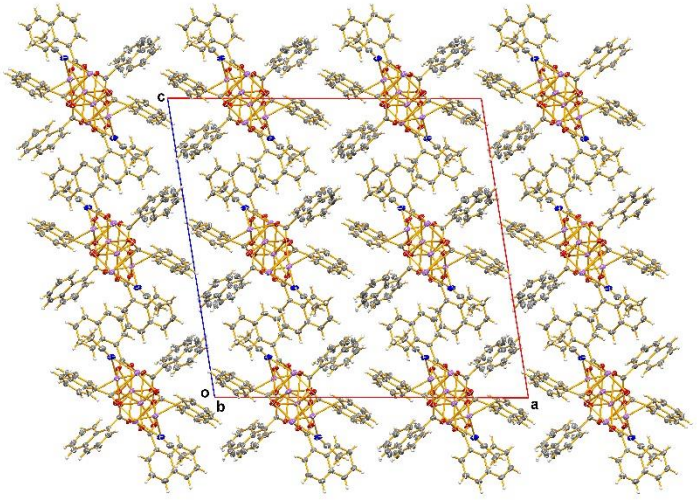


Figure 12: Packing diagram of the1-naphthoic acid sodium complex viewed down the Y-axis. (Acetonitrile is present in the crystal acting as a void filler and providing extra stabilization).

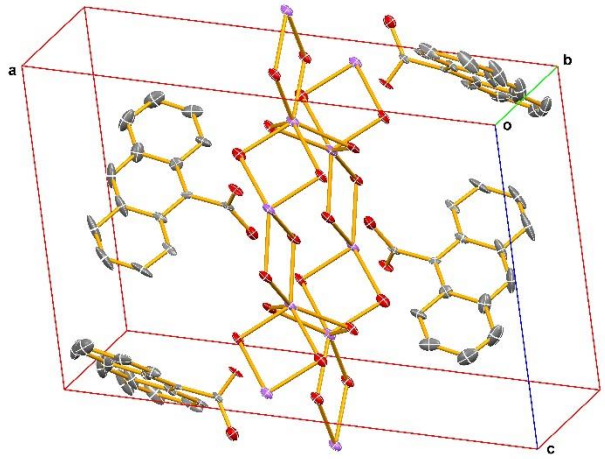


Figure 13: Packing diagram of the 9-anthracenecarboxylic acid sodium complex. Thermal ellipsoids are drawn at the 50% probability level. Gray atoms are carbon, red atoms are oxygen, purple atoms are sodium, Hydrogens have been omitted for clarity

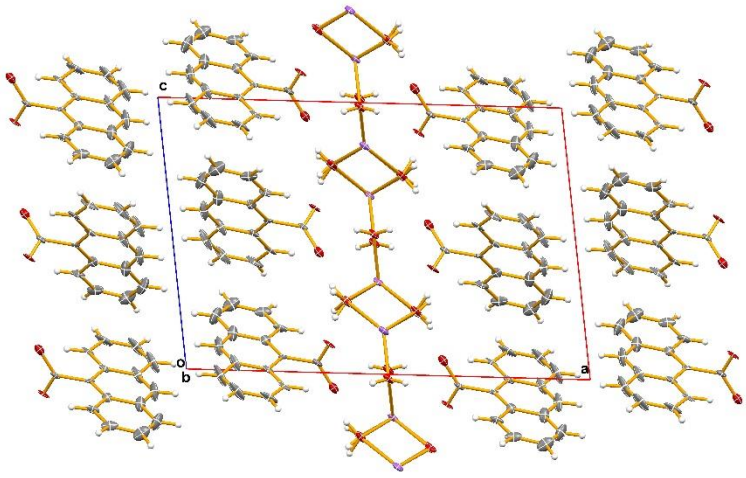
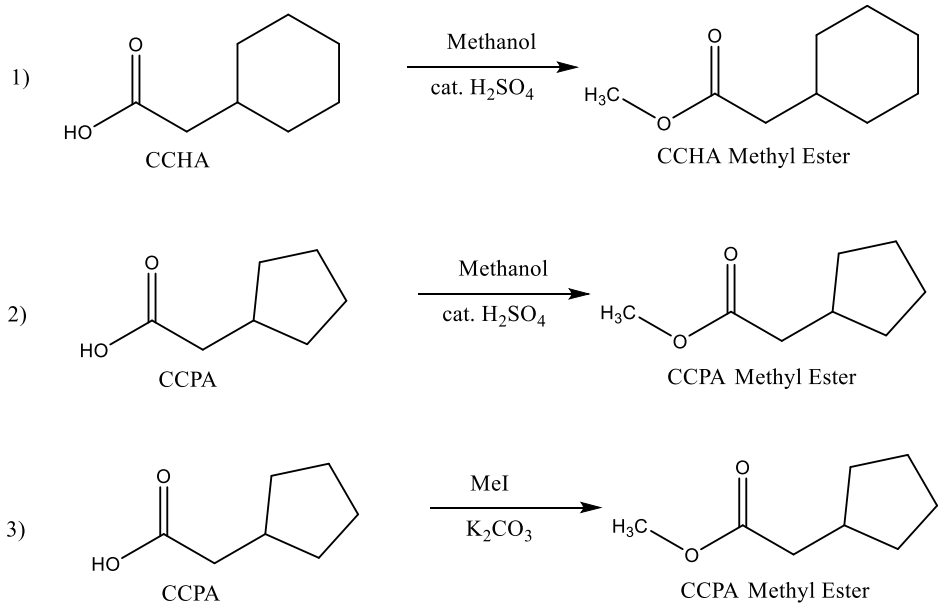


Figure 14: Packing diagram of the 9-anthracenecarboxylic acid sodium complex viewed down the Y-axis.

2.4 Naphthenic acid methyl ester comparison

2.4.1 Naphthenic acid methyl ester preparation

Three methyl esters were chosen from a previous experiment to use as a comparison for the metal coordinated samples. CCPA and CCHA methyl esters were synthesized through Fischer esterification with methanol and catalytic sulfuric acid. The third, a CCPA methyl ester, was synthesized with 1.2 eq methyl iodide in methanol. All three reactions produced liquid esters that smelt strongly of bubble gum and bananas. Spectroscopic analyses were performed on the samples, including ^{1}HNMR, ^{13}CNMR, COSY, HSQC, and IR. NMR samples were made from 30 mg of the complexes dissolved in CD_2Cl_2. Crystals were grown from the samples via the slow evaporation method using methanol as the solvent.



Scheme 6: Proposed syntheses of naphthenic acid esters through Fischer and methyl iodine esterification. 1) CCHA Fischer esterification. 2) CCPA Fischer esterification. 3) CCPA methyl iodine esterification.

2.4.2 Analysis of naphthenic acid methyl esters

The ester formed through methyl iodide esterification does not show full conversion, as judged from the NMR spectra. The ^{1}H NMR spectrum of the methyl iodide ester shows that the acidic proton in not present when compared to the spectrum of the CCPA control. The ^{13}C NMR spectrum, however, shows more carbonyl peaks than one would expect from an ester, which indicates that another form of carbonyl has been synthesized. For this reason, the methyl iodide esterification sample was not used in the comparison of the methods due to the uncertainty of the sample's purity.

In the CCPA methyl ester sample, the ^{1}H (300 MHz, CD_2Cl_2, ppm) spectrum shows that the acidic proton has disappeared compared to the CCPA control. The $^{13}C\{1H\}$ (75 MHz, CD_2Cl_2, ppm) spectrum also helps to confirm esterification, as two carbonyl peaks are present: 174.1 (s, -COO<u>C</u>H_3), and 178.1 (s, -<u>C</u>OOCH_3), in comparison to the CCPA single carbonyl peak of 180.2 ppm (s, -<u>C</u>OOH).

In the CCHA methyl ester sample, the ^{1}H (300 MHz, CD_2Cl_2, ppm) spectrum shows that the acidic proton present has disappeared compared to the CCHA control. The $^{13}C\{1H\}$ (75 MHz, DMSO-D6, ppm) also helps to confirm esterification as two carbonyl peaks are present: 173.8 (s, -<u>C</u>OOCH_3), and 178.8 (s, -COO<u>C</u>H_3), in comparison to the CCHA single carbonyl peak of 173.7 ppm (s, -<u>C</u>OOH).

The esters did not crystallize so their physical structures could not be confirmed. This inability to crystallize is important data to note, as this confirms that the samples were too oily to be able to crystallize. The solid pure naphthenic acids, upon undergoing esterification, became oily liquid esters which supports the loss of polarity of the

samples. This loss of polarity is highly desired as it reduces hydrogen bonding and lowers the water solubility of the complexes.

2.4.3 Partition coefficient comparison of the naphthenic acid methyl esters

A method was adapted from the literature in order to compare a sample's partition coefficients to their respective unreacted naphthenic acids, see CMJL056 as described in the experimental section. For the CCPA acid and ester, the compounds were retained for 2.2 min and 8.7 min, respectively. This shows a significant increase in the hydrophobicity of the sample. For the CCHA acid and ester, the compounds were retained for 3.1 min and 11.2 min, respectively. This once again shows the increase of hydrophobicity between the ester and its respective acid.

This increase in hydrophobicity is presumed to be due to the loss of the hydrogen bonding proton and a loss of polarity in the compounds. These esters, therefore, show initial positive results in reduction of the toxicity of the naphthenic acids. Being less water soluble limits potential marine toxicity while also causing them to favour remaining within the bitumen phase when exposed to water.

2.5 Results and discussion afterword

2.5.1 Notes regarding results and discussion

A large volume of naphthenic acid simulants were selected in order to test the viability of metal coordination across many realistic ligands that would be present in the naphthenic acids within bitumen. Of these, CMJL027-CMJL53 as described in the experimental section, ^{1}HNMR, ^{13}CNMR, COSY, HSQC, and IR spectra appear to collaborate of the presence of the formed coordinated compounds.

With that being said, only a handful of samples were able to provide useable results for X-ray crystallography. Crystals had formed for all compounds, but most were determined to be small inorganic salts of NaCl, $ZnCl_X$, $MgCl_X$, and NH_4Cl, which demonstrates an issue in the purity of the compounds after synthesis. Due to this problem, only samples that provided useful XRD crystallography data were focused on within this section (reactions CMJL027 Zn, CMJL027 Mg and CMJL036); the other reactions are reported on in the experimental section, but were discounted from the discussion in regards to the focus of this thesis.

2.5.2 Crystal structures of larger inorganic salts caused by impurities

This inorganic salt from the impurities of the synthesis of zinc 2-cyclohexylacetate dehydrate. The crystals were grown from the sample (CMJL027 Zn) through slow evaporation using acetonitrile as the solvent. X-ray crystallographic analysis was performed by Dr. Katherine Robertson.

The inorganic salt that is shown is zinc tetrachloride with hydronium cations ($ZnCl_4[H_3O^+]$) as stabilizers. Further inorganic salt contaminations were also isolated from other crystal samples, zinc hexahydrate dinitrate, ($Zn(H_2O)_6(NO_3)_2$). These contaminates were present for all failed crystallization attempts.

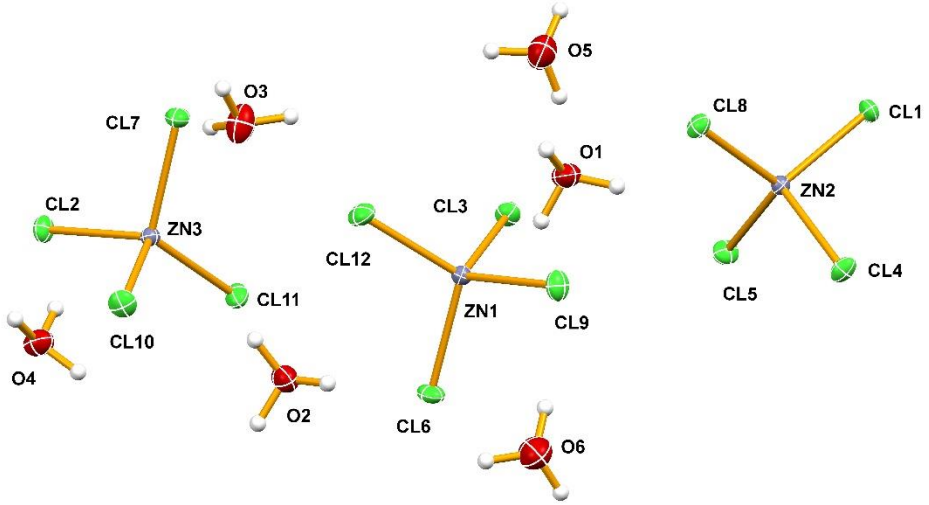


Figure 15: Solid state crystal of one of the larger inorganic salts caused by impurities. Thermal ellipsoids are drawn at the 50% probability level.

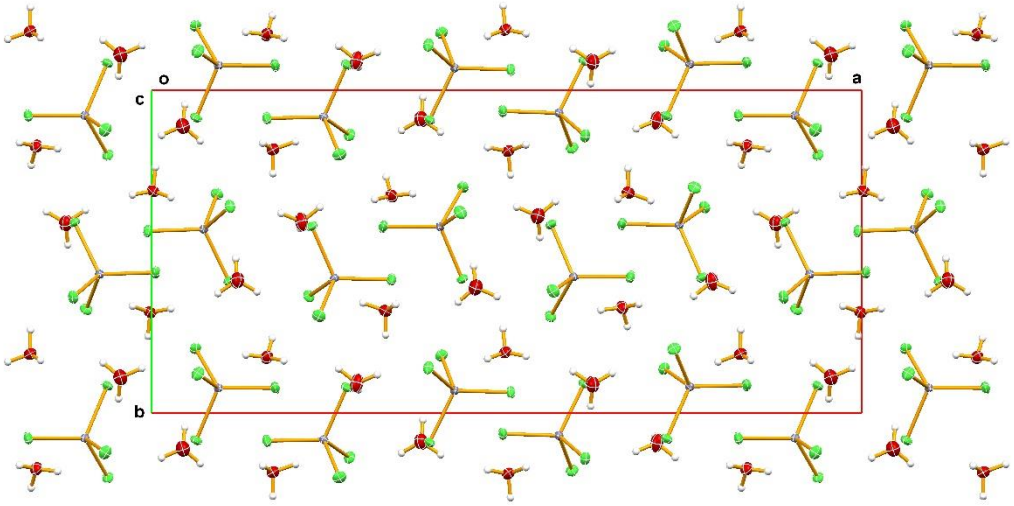


Figure 16: Packing diagram of one of the larger inorganic salts caused by impurities viewed down the Z-axis.

Chapter 3 – Summary and Conclusions

3.1 L_2M complexes conclusions

The metal coordinated complexes, zinc 2-cyclopentylacetate dehydrate, zinc 2-cyclohexylacetate dehydrate, magnesium 2-cyclopentylacetate tetrahydrate, and magnesium 2-cyclohexylacetate tetrahydrate, have been prepared and characterized. These complexes have been shown to be more polar than initially theorized due to the coordination of water to the metal centers which in the process forms octahedral complexes. This coordination of water causes the complexes to be more of a surfactant than desired.

The coordination does convert the polar head group of the acid to a non-polar coordination site. The polarity that is present within the final molecule seems to only be due to the water that is coordinating in the complex. This can be shown with the elution times between zinc 2-cyclohexylacetate dihydrate and magnesium 2-cyclohexylacetate tetrahydrate in the RP-HPLC partition coefficient comparison. These complexes do eliminate the acidic proton from the naphthenic acids which will decrease their toxicity, as well as eliminate a source of hydrogen bonding. This causes an overall drop in the intermolecular forces within bitumen, which allows for a decrease in its viscosity.

3.2 Naphthenic acid methyl ester conclusions

The CCPA and CCHA methyl esters have been shown to eliminate the acidic proton from their respective naphthenic acids. The esters are not symmetrical and

therefore will still possess some polarity, but from the RP-HPLC partition coefficient comparison they show an exceedingly high hydrophobicity. This hydrophobicity causes the esters to have a lower affinity for water when compared to their respective naphthenic acids, causing them to be bad surfactants. This will reduce the toxic effects if acids are spilled in aqueous systems, but also prevent other toxic chemicals in the bitumen from leeching into the environment.

Chapter 4 - Future work

Future work of this research entails purification of the naphthenic acid – metal complexes described in this thesis. This is a priority as the elemental analysis of the compounds synthesized with ammonium hydroxide show nitrogen within the samples, despite previous purification attempts. It has also been noticed that crystal growth of the compounds often yields unusable inorganic salts, in the form of NaCl or NH_4Cl, instead of the crystals of the desired product; A method of purification would help eliminate the time wasted waiting for the growth of crystals.

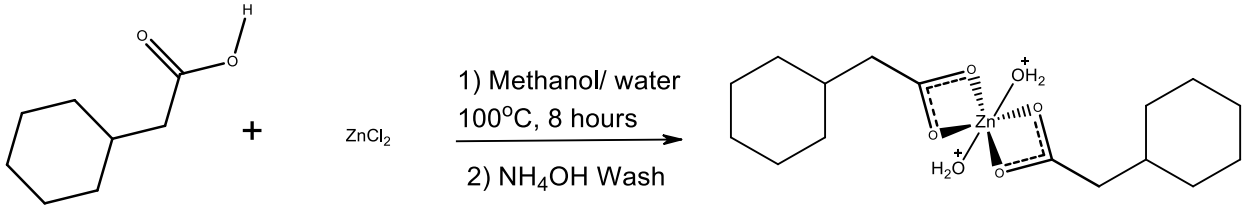
Time will be devoted to replicating the experiments with the use of purer solvents. It is suspected that the solvents used may have been contaminated with unknown materials, causing unforeseen problems with the syntheses. Replication is also important, not only to try and increase purity but to also reproduce the XRD crystallographic data. Since many model naphthenic acids did not appear to be adequate ligands for coordination to the chosen metal centers, it is important to demonstrate that these complexes can (or cannot) be remade.

Furthermore, more experiments will have to be undertaken in order to more precisely determine the complexes' interactions for the determination of the partition coefficient through RP-HPLC. Samples will all be dissolved to the same concentration and then each one will be checked for its precise absorbance range using UV-Vis spectroscopy. A set of standards of known partition coefficients will be prepared to the same concentration as the samples. All samples will be spiked with a substance having an unretainable peak, t_0, in order to properly calibrate the retention times of peaks within

the mobile phase; thiourea or formamide will be used to generate the unretainable peak. Once all samples have been measured, the standards will be used to construct a calibration curve and then the equation of that line will be used to calculate the log of the partition coefficient, $\log K_{OW}$, of the desired methyl ester and metal coordinated samples.

Chapter 5 - Experimental

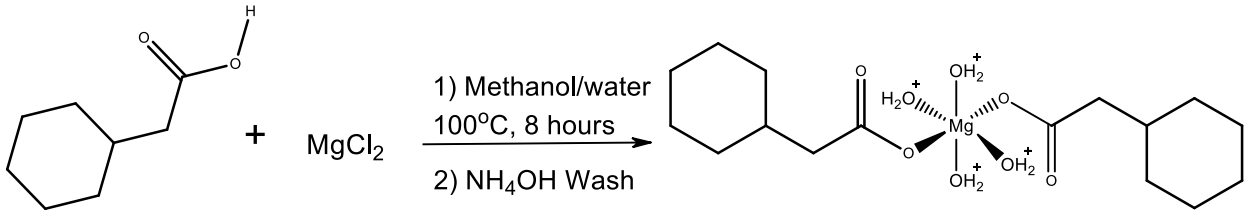
CMJL027 Zn: Synthesis of the Zinc coordinated complex of *cyclo*-hexaneacetic acid (method 1)



499.47 mg of *cyclo*-hexaneacetic acid was weighed into a 100 mL round bottom flask and dissolved in 10 mL of methanol. Zinc chloride was measured out in a 2:1, acid: metal salt molar ratio. 293 mg of the salt was transferred to the flask with a wash of 10 mL of methanol. The sample was placed in a heating mantle and heated at 80°C under reflux for 8 hours. After the 8 hours, the sample had 20 mL of ammonium hydroxide added and was stirred for 30 minutes. A white precipitate formed within the flask. The precipitate was vacuum filtered and was dried in a desiccator. The filtrate was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography were run on the products. Crystals were grown via slow evaporation using methanol as a solvent. ^{1}H NMR (300 MHz, DMSO-D6, ppm): 1.98 (d, 2H, $^{3}J_{CH}$ = 6.80 Hz, cyhex-C$\underline{H}_2$CO$_2$H), 1.65 (m, 6H, $^{3}J_{CH}$ = 33.46 Hz, -cyhex), 1.14 (m, 3H, $^{3}J_{CH}$ = 55.49 Hz, -cyhex), 0.85 (m, 2H, $^{3}J_{CH}$ = 34.27 Hz, -cyhex). ^{13}C{1H} NMR (75 MHz, DMSO-D6, ppm): 25.64 (d, $^{3}J_{CH}$ = 11.41 Hz, -cyhex), 30.59 (s, -cyhex), 32.58 (s, -cyhex), 34.60 (s, -cyhex), 43.38 (s, cyhex-$\underline{C}$H$_2$CO$_2$H), 175.71 (s, cyhex-CH$_2\underline{C}$O$_2$H). IR (ATR, cm-1): 3186 (w, br), 3043 (w, br), 2919 (m), 2849 (m), 1627 (m), 1555 (m), 1535

(s), 1439 (s), 1402 (s, br), 1326 (w), 1246 (w), 1199 (w). EA calculated. [%]: C, 55.24; H, 7.54; N, 0.00; found [%]: C, 34.69; H, 7.44; N, 8.52.

CMJL027 Mg: Synthesis of the Magnesium coordination complex of *cyclo*-hexaneacetic acid (method 1)



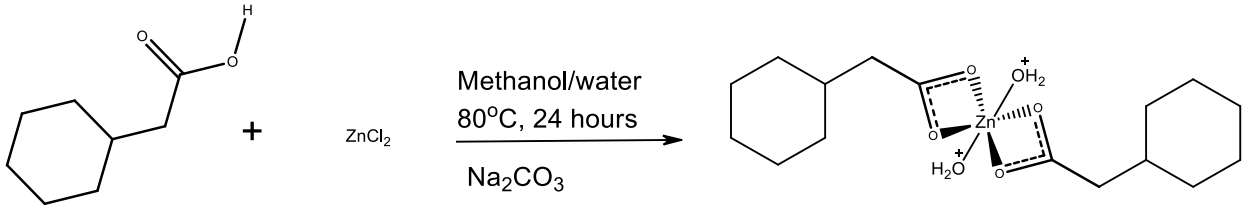
CCHA

magnesium 2-cyclohexylacetate tetrahydrate

544.05 mg of *cyclo*-hexaneacetic acid was weighed into a 20 mL vial. The vial of acid was transferred into a 100 mL round bottom flask and dissolved in 10 mL of methanol. Magnesium chloride, was measured out in a 2:1, acid: metal salt molar ratio. 403 mg of the salt was transferred to the flask with a wash of 10 mL of methanol. The sample was placed in a heating mantle and heated at 80°C under reflux for 8 hours. After the 8 hours, the sample had 20 mL of ammonium hydroxide added and was stirred for 30 minutes. A white precipitate formed within the flask. The precipitate was vacuum filtered and was dried in a desiccator. The filtrate was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography were run on the sample. Crystals were grown via slow evaporation using methanol as the solvent. ^{1}H NMR (300 MHz, DMSO-D6, ppm): 1.95 (d, 2H, $^{3}J_{CH}$ = 6.77 Hz, cyhex-C$\underline{H}_2$CO$_2$H), 1.61 (m, 6H, $^{3}J_{CH}$ = 34.48 Hz, -cyhex), 1.17 (m, 3H, $^{3}J_{CH}$ = 57.17 Hz, -cyhex), 0.88 (m, 2H, $^{3}J_{CH}$ = 33.24 Hz, -cyhex). ^{13}C{1H} (75 MHz, DMSO-D6, ppm): 25.82 (d, $^{3}J_{CH}$ = 11.81 Hz, -cyhex), 30.61 (s, -cyhex), 32.59 (s, -cyhex), 34.53 (s, -cyhex), 43.5 (s, cyhex-$\underline{C}$H$_2$CO$_2$H), 176.18(s, cyhex-CH$_2\underline{C}$O$_2$H). IR (ATR, cm-1): 3117

(m, br), 3025 (m, br), 2919 (vs), 2849 (s), 2803 (m), 1749 (w, br), 1689 (w), 1623 (m), 1586 (s), 1547 (m), 1443 (s), 1392 (vs, br), 1361 (m), 1196 (m), 1123 (w). EA calculated. [%]: C, 62.71; H, 8.56; N, 0.00; found [%]: C, 33.17; H, 7.41; N, 9.03.

CMJL035: Synthesis of the Zinc coordination complex of *cyclo*-hexaneacetic acid (method 2)



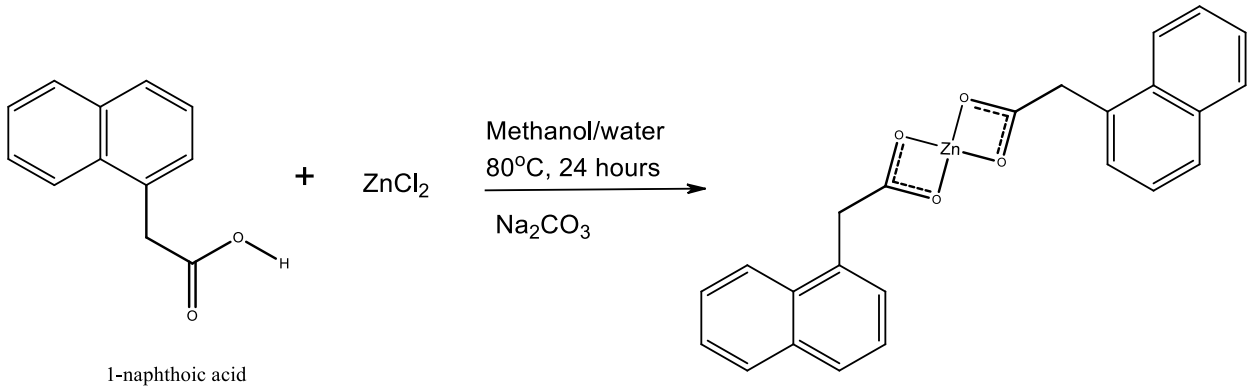
CCHA

zinc 2-cyclohexylacetate dihydrate

501.0 mg of *cyclo*-hexaneacetic acid was weighed into a 100 mL round bottom flask. 375 mg of sodium carbonate was added to the flask. 228 mg of zinc chloride was dissolved in a 15 mL solution of 2:1 methanol : ultrapure water and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was placed under reflux for 24 hours at 80°C. After reacting, the sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography were run for each of the samples. Attempts were made to grow crystals via slow evaporation using methanol as the solvent. ^{1}H NMR (300 MHz, DMSO-D6, ppm): 1.80 (d, 2H, $^{3}J_{CH}$ = 6.87 Hz, cyhex-C$\underline{H}_2$CO$_2$H), 1.65 (m, 6H, ^{3}JCH = 36.98 Hz, -cyhex), 1.16 (m, 3H, $^{3}J_{CH}$ = 55.76 Hz, -cyhex), 0.80 (m, 2H, $^{3}J_{CH}$ = 37.43 Hz, -cyhex). ^{13}C{1H} NMR (75 MHz, DMSO-D6, ppm): 26.15 (d, $^{3}J_{CH}$ = 13.15 Hz, -cyhex), 33.21 (s, -cyhex), 35.31 (s, -cyhex), 46.38 (s, cyhex-$\underline{C}$H$_2$CO$_2$H), 176.85 (s, cyhex-CH$_2\underline{C}$O$_2$H). IR (ATR, cm-1): 2920 (s), 2850 (m), 1578 (vs),

1441 (m), 1418 (s), 1262 (w), 1141 (w), 1119 (w). EA calculated [%]: C, 55.24; H, 7.54; N, 0.00; found [%]: C, 42.50; H, 5.72; N, 0.04.

CMJL036: Synthesis of the Zinc coordination complex of 1-Naphthoic acid (method 2)



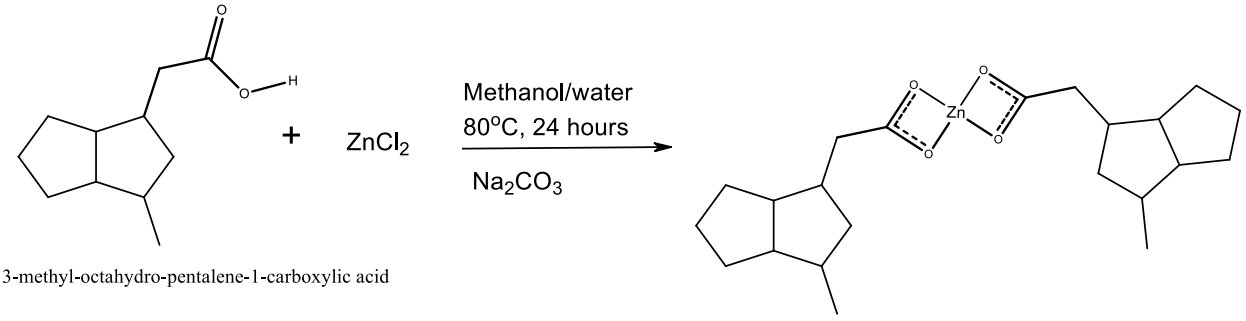
1-naphthoic acid

zinc 2-(naphthalen-1-yl)acetate

552.3 mg of 1-naphthoic acid was weighed into a 100 mL round bottom flask. 342 mg of sodium carbonate was added to the flask. 231 mg of zinc chloride was dissolved in a 15 mL solution of 2:1 methanol : ultrapure water and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was placed under reflux for 24 hours at 80°C. After reacting, the sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent. 1H (300 MHz, DMSO-D6, ppm): 9.00 (m, 1H, $^{3}J_{CH}$ = 16.38 Hz, Ar), 7.82 (m, 3H, $^{3}J_{CH}$ = 23.83 Hz, Ar), 7.41 (m, 3H, $^{3}J_{CH}$ = 19.16 Hz, Ar). ^{13}C{1H} (75 MHz, DMSO-D6, ppm): 124.93 (d, ^{3}JCH = 2.16 Hz, Ar), 125.05 (s, Ar), 126.12 (s, Ar), 127.69 (t, ^{3}JCH = 16.80 Hz, Ar), 130.97 (s, Ar), 133.30 (s, Ar), 139.66 (s, Ar), 172.41 (s, Ar-

$\underline{C}O_2H$). IR (ATR, cm-1): 3048 (w), 1598 (m), 1550 (s, br), 1507 (m), 1411 (s), 1374 (s), 1338 (m), 1255 (m), 1214 (w), 1150 (w), 870 (m), 776 (vs). EA calculated [%]: C, 64.79; H, 3.46; N, 0.00; found [%]: C, 46.84; H, 2.48; N, 0.02.

CMJL037: Synthesis of the Zinc coordination complex of 3-methyl-octahydro-pentalene-1-carboxylic acid (method 2)



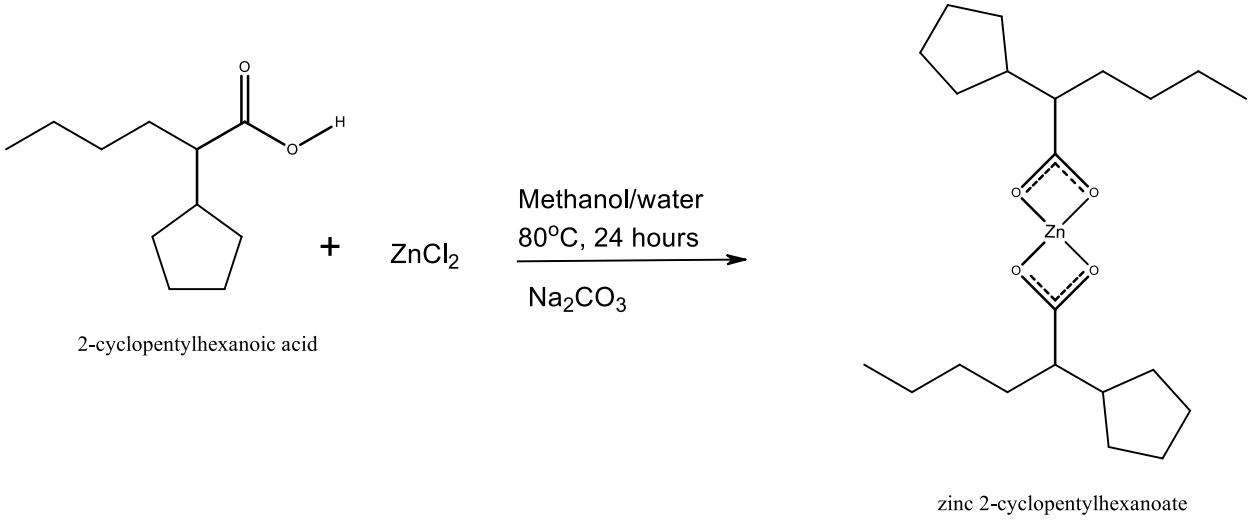
3-methyl-octahydro-pentalene-1-carboxylic acid

zinc 2-(3-methyloctahydropentalen-1-yl)acetate

200.8 mg of 3-methyl-octahydro-pentalene-1-carboxylic acid was weighed into a 100 mL round bottom flask. 131 mg of sodium carbonate was added to the flask. 85 mg of zinc chloride was dissolved in a 15 mL solution of 2:1 methanol : ultrapure water and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was placed under reflux for 24 hours at 80°C. After reacting, the sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent. 1H (300 MHz, DMSO-D6, ppm): 0.93 (d, 3H, $^{3}J_{CH}$ = 6.22 Hz, CHC$\underline{H}_3$), 1.22 (q, 2H, $^{3}J_{CH}$ = 34.79 Hz, -ohpn), 1.41 (m, 6H, ^{3}JCH = 55.40 Hz, -ohpn), 1.85 (m, 3H, $^{3}J_{CH}$ = 78.49 Hz, -ohpn), 2.55 (q, 1H, ^{3}JCH = 23.47 Hz, -ohpn). ^{13}C{1H} (75 MHz, DMSO-D6, ppm): 19.52 (s, -ohpn), 24.58 (s, -ohpn), 31.62 (s, -

ohpn), 33.06 (s, -ohpn), 41.34 (s, -ohpn), 41.63(s, -ohpn), 47.75 (s, -ohpn), 51.32 (s, -ohpn), 55.52 (s, -ohpn), 179.84 (s, ohpn-$\underline{C}O_2H$). IR (ATR, cm-1): processing error, peak wave numbers could not be obtained.

CMJL038: Synthesis of the Zinc coordination complex of 2-*cyclo*-pentylhexanoic acid (method 2)



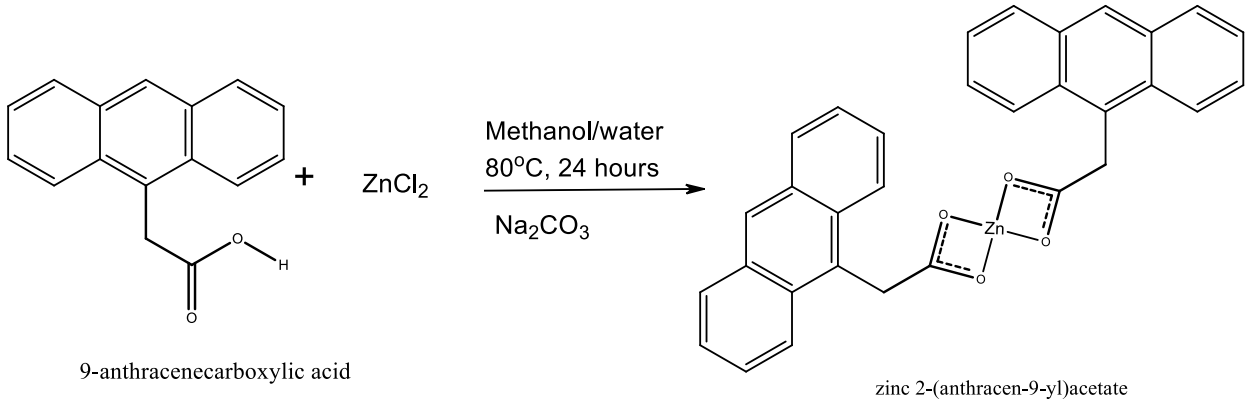
2-cyclopentylhexanoic acid

zinc 2-cyclopentylhexanoate

112.6 mg of 2-*cyclo*-pentylhexanoic acid was weighed into a 100 mL round bottom flask. 72 mg of sodium carbonate was added to the flask. 44 mg of zinc chloride was dissolved in a 15 mL solution of 2:1 methanol : ultrapure water and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was placed under reflux for 24 hours at 80°C. After reacting, the sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent. 1H (300 MHz, DMSO-D6, ppm): 0.82 (t, 3H, $^{3}J_{CH}$ = 13.25 Hz, -C$\underline{H}$CO$_2$H), 1.23 (m, 6H, $^{3}J_{CH}$ = 86.13 Hz, cypen), 1.43 (m, 8H, $^{3}J_{CH}$ = 106.98 Hz,

$CH_3C\underline{H}_2C\underline{H}_2C\underline{H}_2CH(cypen)CO_2H$), 1.78 (t, 8H, ^3JCH = 16.61 Hz, $C\underline{H}_3CH_2CH_2CH_2CH(cypen)CO_2H$). $^{13}C\{1H\}$ (75 MHz, DMSO-D6, ppm): 14.09 (s, $\underline{C}H_3CH_2CH_2CH_2CH(cypen)CO_2H$), 22.59 (s, $CH_3\underline{C}H_2CH_2CH_2CH(cypen)CO_2H$), 24.70 (d, ^3JCH = 22.61 Hz cypen), 30.16 (d, ^3JCH = 11.08 Hz, cypen), 30.90 (s, $CH_3CH_2\underline{C}H_2CH_2CH(cypen)CO_2H$), 31.92 (s, $CH_3CH_2CH_2\underline{C}H_2CH(cypen)CO_2H$), 43.23 (s, $CH_3CH_2CH_2CH_2\underline{C}H(cypen)CO_2H$), 54.43 (s, $CH_3CH_2CH_2CH_2CH(\underline{C}HC_4H_8)CO_2H$), 179.80 (s, $CH_3CH_2CH_2CH_2CH(cypen)\underline{C}O_2H$). IR (ATR, cm^{-1}): 2922 (s), 2852 (m), 1683 (m, br), 1557 (vs), 1447 (m), 1409 (s), 1324 (m), 1298 (m), 1194 (w), 1117 (w).

CMJL040: Synthesis of the Zinc coordination complex of anthracene-9-carboxylic acid (method 2)



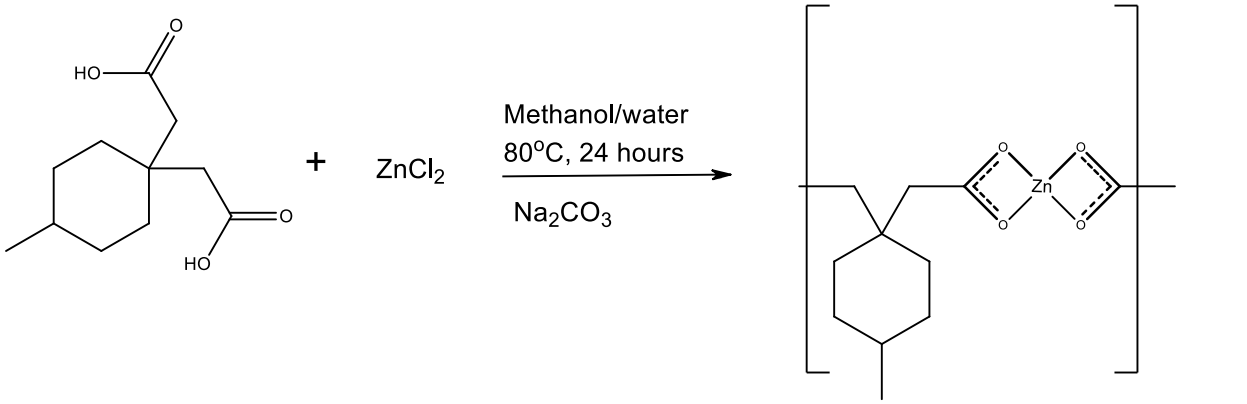
9-anthracenecarboxylic acid

zinc 2-(anthracen-9-yl)acetate

539.0 mg of Anthracene-9-carboxylic acid was weighed into a 100 mL round bottom flask. 300 mg of sodium carbonate was added to the flask. 203 mg of zinc chloride was dissolved in a 15 mL solution of 2:1 methanol : ultrapure water and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was placed under reflux for 24 hours at 80°C. After reacting, the sample was dried through rotary evaporation and transferred to a 20 mL

vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent. 1H (300 MHz, DMSO-D6, ppm): 7.39 (m, 4H, $^{3}J_{CH}$ = 30.11 Hz, Ar), 8.07 (m, 4H, $^{3}J_{CH}$ = 72.50 Hz, Ar), 8.29 (s, 1H, Ar). ^{13}C{1H} (75 MHz, DMSO-D6, ppm): 122.63 (s, Ar), 123.96 (s, Ar), 124.91 (s, Ar), 125.84 (s, Ar), 127.70 (s, Ar), 127.95 (s, Ar), 131.17 (s, Ar), 172.05 (s, Ar-$\underline{C}O_2H$). IR (ATR, cm-1): 3046 (w), 3034 (w), 1556 (vs), 1486 (w), 1434 (s), 1392 (s), 1319 (s), 1274 (m), 1155 (w), 1013 (w), 958 (w), 731 (vs).

CMJL041: Synthesis of the Zinc coordination complex of 3-methyl-1,1-*cyclo*-pentanediacetic acid (method 2)

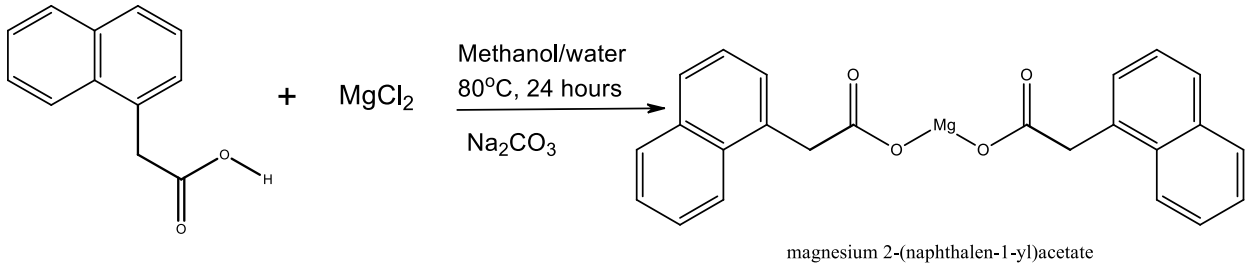


zinc bis-4-methyl-1,1-cyclohexanediacetate

267.7 mg of 3-methyl-1,1-*cyclo*-pentanediacetic acid was weighed into a 100 mL round bottom flask. 206 mg of sodium carbonate was added to the flask. 222 mg of zinc chloride was dissolved in a 15 mL solution of 2:1 methanol : ultrapure water and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was placed under reflux for 24

hours at 80°C. After reacting, the sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent.

CMJL042: Synthesis of the Magnesium coordination complex of 1-Naphthoic acid (method 2)



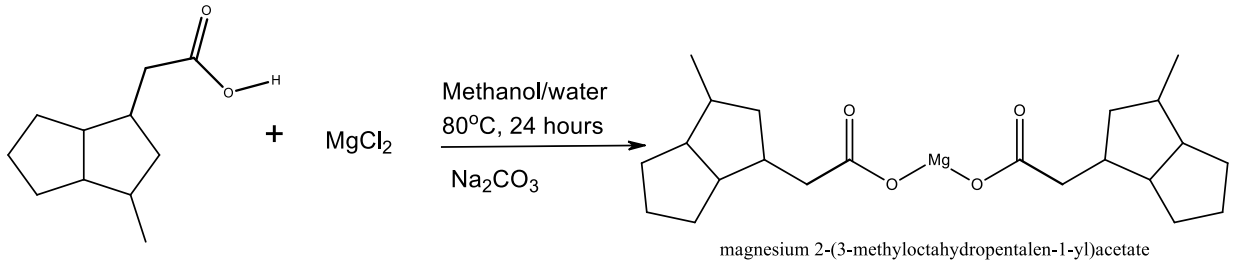
1-naphthoic acid

magnesium 2-(naphthalen-1-yl)acetate

548.7 mg of 1-naphthoic acid was weighed into a 100 mL round bottom flask. 353 mg of sodium carbonate was added to the flask. 339 mg of magnesium chloride hexahydrate was dissolved in a 15 mL solution of 2:1 methanol : ultrapure water and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was placed under reflux for 24 hours at 80°C. After reacting, the sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent. 1H (300 MHz, DMSO-D6, ppm): 9.00 (d, 1H, $^{3}J_{CH}$ = 9.02 Hz, Ar), 7.91 (d, 1H, $^{3}J_{CH}$ = 8.03 Hz, Ar), 7.85 (m, 2H, $^{3}J_{CH}$ = 13.58 Hz, Ar), 7.42 (m, 2H, $^{3}J_{CH}$ = 15.44 Hz, Ar). ^{13}C{1H} (75 MHz, DMSO-D6, ppm): 124.90 (d, ^{3}JCH = 17.51 Hz,

Ar), 125.37 (s, Ar), 127.72 (t, $^{3}J_{CH}$ = 122.54 Hz, Ar), 131.04(s, Ar), 133.34 (s, Ar), 173.17 (s, Ar-$\underline{C}O_2H$). IR (ATR, cm-1): 3047 (w), 2358 (w), 1598 (m), 1542 (s), 1508 (m), 1412 (s), 1375 (s), 1257 (m), 1214 (w), 1151 (w), 869 (w), 776 (vs).

CMJL043: Synthesis of the Magnesium coordination complex of 3-methyl-octahydro-pentalene-1-carboxylic acid (method 2)



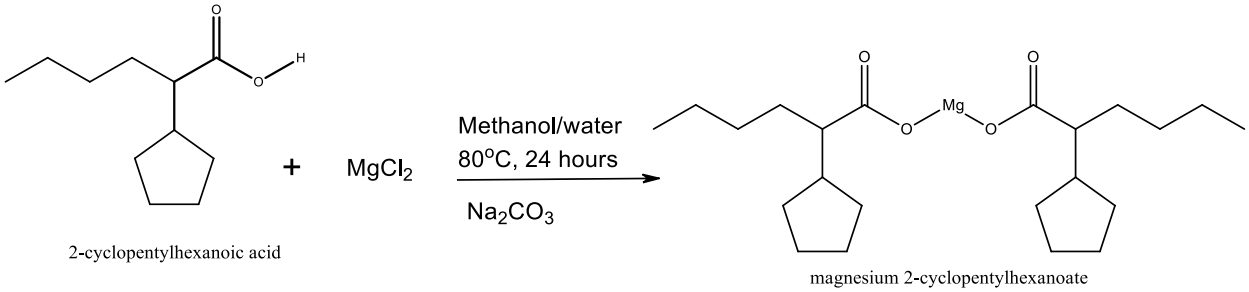
3-methyl-octahydro-pentalene-1-carboxylic acid

magnesium 2-(3-methyloctahydropentalen-1-yl)acetate

214.6 mg of 3-methyl-octahydro-pentalene-1-carboxylic acid was weighed into a 100 mL round bottom flask. 150 mg of sodium carbonate was added to the flask. 140 mg of magnesium chloride hexahydrate was dissolved in a 15 mL solution of 2:1 methanol : ultrapure water and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was placed under reflux for 24 hours at 80°C. After reacting, the sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent. 1H (300 MHz, DMSO-D6, ppm): 0.93 (d, 3H, $^{3}J_{CH}$ = 6.19 Hz, CHC$\underline{H}_3$), 1.22 (q, 2H, $^{3}J_{CH}$ = 34.37 Hz, -ohpn), 1.39 (m, 6H, $^{3}J_{CH}$ = 50.63 Hz, -ohpn), 1.82 (m, 3H, $^{3}J_{CH}$ = 79.09 Hz, -ohpn), 2.54 (q, 1H, $^{3}J_{CH}$ = 22.92 Hz, -ohpn). ^{13}C{1H} (75 MHz, DMSO-D6, ppm): 19.53 (s, -ohpn), 24.60 (s, -ohpn), 31.63 (s, -ohpn), 33.06 (s, -ohpn), 41.31 (s, -ohpn), 41.64 (s, -ohpn), 47.75 (s, -ohpn), 51.33 (s, -ohpn), 55.41 (s, -ohpn), 180.00 (s, ohpn-$\underline{C}O_2H$). IR (ATR, cm-1): 2944

(m), 2929 (m), 2860 (m), 2361 (w), 1711 (w), 1559 (vs), 1415 (vs), 1314 (m), 1272 (w), 1229 (w), 790 (m), 692 (w).

CMJL044: Synthesis of the Magnesium coordination complex of 2-*cyclo*-pentylhexanoic acid (method 2)



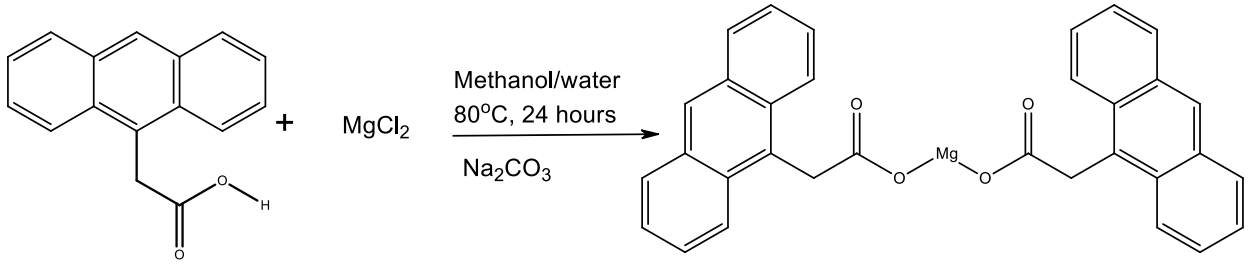
2-cyclopentylhexanoic acid

magnesium 2-cyclopentylhexanoate

141.9 mg of 2-*cyclo*-pentylhexanoic acid was weighed into a 100 mL round bottom flask. 92 mg of sodium carbonate was added to the flask. 78 mg of magnesium chloride hexahydrate was dissolved in a 15 mL solution of 2:1 methanol : ultrapure water and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was placed under reflux for 24 hours at 80°C. After reacting, the sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent. 1H (300 MHz, DMSO-D6, ppm): 0.82 (t, 3H, $^{3}J_{CH}$ = 13.08 Hz, -C<u>H</u>CO$_2$H), 1.24 (m, 6H, $^{3}J_{CH}$ = 84.53 Hz, cypen), 1.43 (m, 8H, $^{3}J_{CH}$ = 112.95 Hz, CH$_3$C<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$CH(cypen)CO$_2$H), 1.78 (t, 8H, $^{3}J_{CH}$ = 15.30 Hz, C<u>H</u>$_3$CH$_2$CH$_2$CH$_2$CH(cypen)CO$_2$H). ^{13}C{1H} (75 MHz, DMSO-D6, ppm): 14.12 (s, <u>C</u>H$_3$CH$_2$CH$_2$CH$_2$CH(cypen)CO$_2$H), 22.62 (s, CH$_3$<u>C</u>H$_2$CH$_2$CH$_2$CH(cypen)CO$_2$H), 24.73 (d, ^{3}JCH = 18.26 Hz cypen), 30.18 (d, ^{3}JCH = 10.61 Hz, cypen), 30.92 (s,

$CH_3CH_2\underline{C}H_2CH_2CH(cypen)CO_2H$), 31.94 (s, $CH_3CH_2CH_2\underline{C}H_2CH(cypen)CO_2H$), 43.24 (s, $CH_3CH_2CH_2CH_2\underline{C}H(cypen)CO_2H$), 54.43 (s, $CH_3CH_2CH_2CH_2CH(\underline{C}HC_4H_8)CO_2H$), 179.92 (s, $CH_3CH_2CH_2CH_2CH(cypen)\underline{C}O_2H$). IR (ATR, cm^{-1}): 2952 (m), 2928 (m), 2859 (m), 2360 (w), 1554 (vs), 1443 (m), 1410 (s), 1312 (w), 1198 (w), 1114 (w).

CMJL045: Synthesis of the Magnesium coordination complex of anthracene-9-carboxylic acid (method 2)

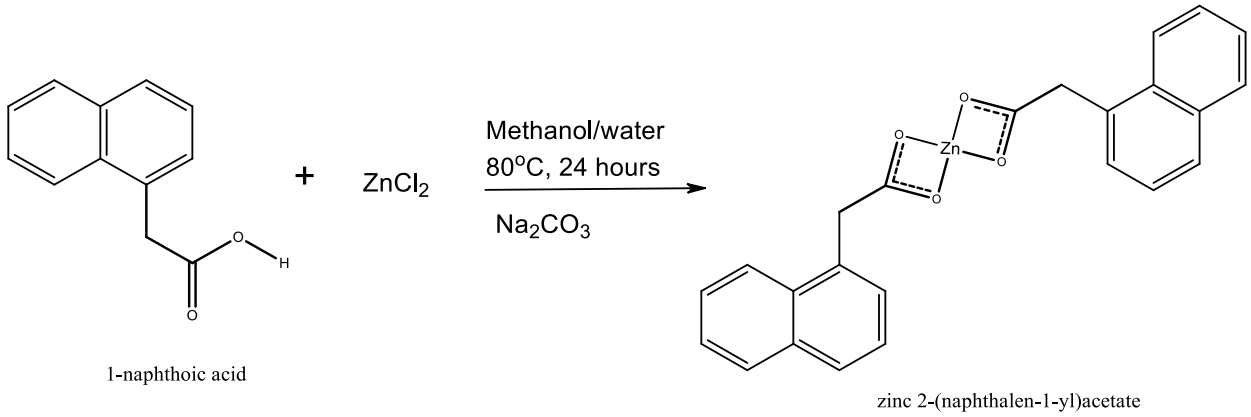


9-anthracenecarboxylic acid

magnesium 2-(anthracen-9-yl)acetate

709.5 mg of Anthracene-9-carboxylic acid was weighed into a 100 mL round bottom flask. 379 mg of sodium carbonate was added to the flask. 355 mg of magnesium chloride hexahydrate was dissolved in a 15 mL solution of 2:1 methanol : ultrapure water and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was placed under reflux for 24 hours at 80°C. After reacting, the sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent.

CMJL046: Synthesis of the Zinc coordination complex of 1-naphthoic acid (method 1)

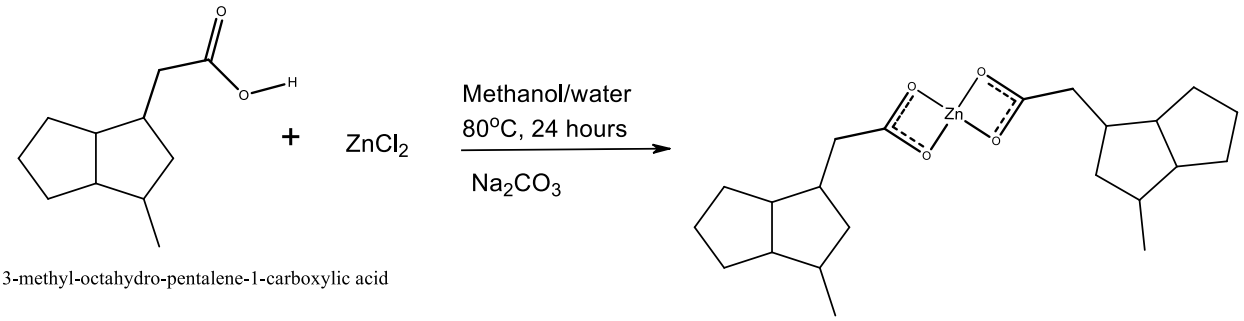


1-naphthoic acid

zinc 2-(naphthalen-1-yl)acetate

583.22 mg of 1-naphthoic acid was weighed into a 100 mL round bottom flask. 323 mg of zinc chloride was dissolved in a 15 mL solution of 2:1 methanol : ultrapure water and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was left to reflux for 6 hours at 100°C. Once the reaction was complete, 40 mL of ammonium hydroxide was added to the flask and the sample was allowed to stir for 30 minutes. No precipitate formed like in CMJL027. The filtrate sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent. 1H (300 MHz, DMSO-D6, ppm): 9.00 (t, 1H, $^{3}J_{CH}$ = 9.77 Hz, Ar), 7.88 (m, 3H, $^{3}J_{CH}$ = 11.32 Hz, Ar), 7.47 (m, 3H, $^{3}J_{CH}$ = 21.32 Hz, Ar). ^{13}C{1H} (75 MHz, DMSO-D6, ppm): 124.95 (s, Ar), 125.36 (s, Ar), 125.79 (s, Ar), 127.01 (d, ^{3}JCH = 14.80 Hz Ar), 127.91 (s, Ar), 129.13 (s, Ar), 130.81 (s, Ar), 133.38 (s, Ar), 136.59 (s, Ar), 171.79 (s, Ar-$\underline{C}O_2H$). IR (ATR, cm-1): 3130 (m, br), 3041 (m, br), 2804 (m, br), 1599 (m), 1542 (m, br), 1508 (m), 1400 (s), 1354 (s), 1253 (m), 1205 (m), 1146 (m), 870 (w), 778 (vs).

CMJL047: Synthesis of the Zinc coordination complex of 3-methyl-octahydro-pentalene-1-carboxylic acid (method 1)

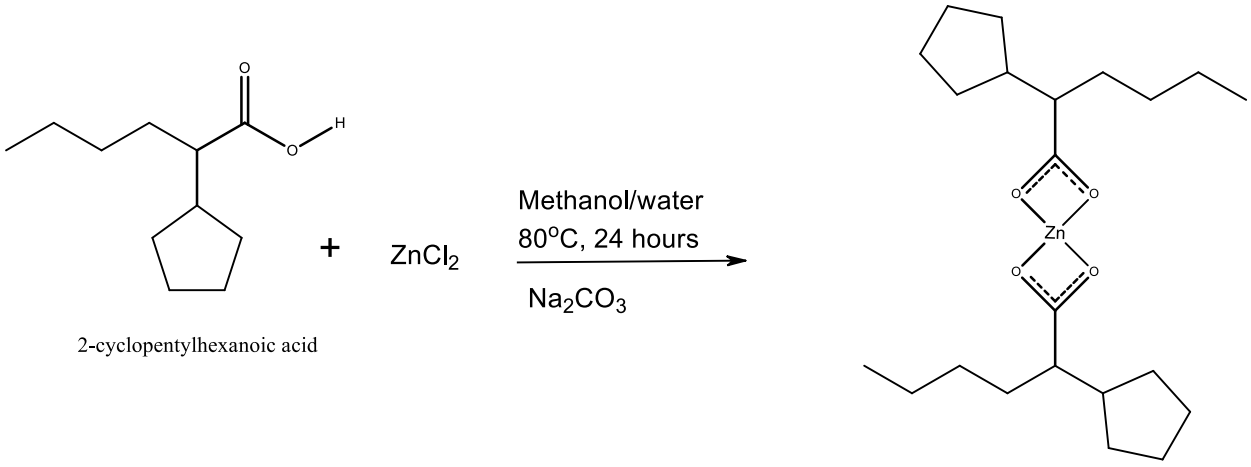


3-methyl-octahydro-pentalene-1-carboxylic acid

zinc 2-(3-methyloctahydropentalen-1-yl)acetate

237.50 mg of 3-methyl-octahydro-pentalene-1-carboxylic acid was weighed into a 100 mL round bottom flask. 151 mg of zinc chloride was dissolved in a 15 mL solution of 2:1 methanol : ultrapure water and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was left to reflux for 6 hours at 100°C. Once the reaction was complete, 40 mL of ammonium hydroxide was added to the flask and the sample was allowed to stir for 30 minutes. No precipitate formed like in CMJL027. The sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent. 1H (300 MHz, DMSO-D6, ppm): 0.95 (d, 3H, $^{3}J_{CH}$ = 6.06 Hz, CHC$\underline{H}_3$), 1.26 (q, 2H, $^{3}J_{CH}$ = 36.14 Hz, -ohpn), 1.44 (m, 6H, $^{3}J_{CH}$ = 52.66 Hz, -ohpn), 1.84 (m, 2H, $^{3}J_{CH}$ = 40.27 Hz, -ohpn), 2.09 (m, 1H, $^{3}J_{CH}$ = 26.85 Hz, -ohpn), 2.58 (q, 1H, $^{3}J_{CH}$ = 18.83 Hz, -ohpn). ^{13}C{1H} (75 MHz, DMSO-D6, ppm): 19.24 (s, -ohpn), 24.51 (s, -ohpn), 31.40 (s, -ohpn), 32.84 (s, -ohpn), 41.38 (s, -ohpn), 47.59 (s, -ohpn), 51.19 (s, -ohpn), 52.77 (s, -ohpn), 179.30 (s, ohpn-$\underline{C}O_2H$). IR (ATR, cm-1): 3161 (w, br), 2946 (s, br), 2863 (s, br), 2361 (w), 1703 (m), 1621 (s), 1536 (vs), 1429 (vs), 1315 (m), 1270 (m), 1139 (w), 787 (m).

CMJL048: Synthesis of the Zinc coordination complex of 2-*cyclo*-pentylhexanoic acid (method 1)



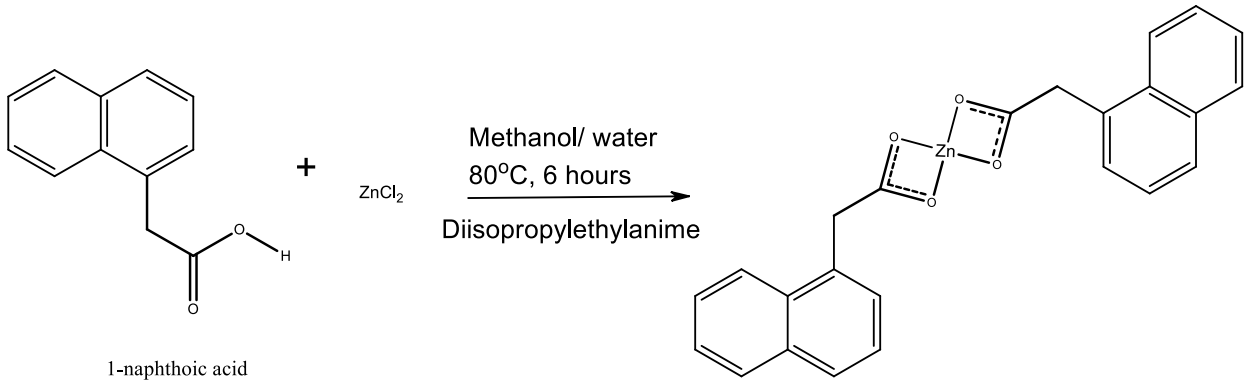
2-cyclopentylhexanoic acid

zinc 2-cyclopentylhexanoate

156.4 mg of 2-*cyclo*-pentylhexanoic acid was weighed into a 100 mL round bottom flask. 110 mg of zinc chloride was dissolved in a 15 mL solution of 2:1 methanol : ultrapure water and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was left to reflux for 6 hours at 100°C. Once the reaction was complete, 40 mL of ammonium hydroxide was added to the flask and the sample was allowed to stir for 30 minutes. No precipitate formed like in CMJL027. The sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent. 1H (300 MHz, DMSO-D6, ppm): 0.83 (t, 3H, $^{3}J_{CH}$ = 13.83 Hz, -C<u>H</u>CO$_2$H), 1.21 (m, 6H, $^{3}J_{CH}$ = 84.80 Hz, cypen), 1.42 (m, 8H, $^{3}J_{CH}$ = 128.12 Hz, CH$_3$C<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$CH(cypen)CO$_2$H), 1.84 (m, 2H, $^{3}J_{CH}$ = 50.70 Hz, C<u>H</u>$_3$CH$_2$CH$_2$CH$_2$CH(cypen)CO$_2$H). ^{13}C{1H} (75 MHz, DMSO-D6, ppm): 13.92 (s, <u>C</u>H$_3$CH$_2$CH$_2$CH$_2$CH(cypen)CO$_2$H), 22.29 (s,

$CH_3\underline{C}H_2CH_2CH_2CH(cypen)CO_2H$), 24.71 (d, $^3J_{CH}$ = 9.55 Hz cypen), 29.62 (s, $CH_3CH_2\underline{C}H_2CH_2CH(cypen)CO_2H$), 30.18 (d, $^3J_{CH}$ = 31.98 Hz, cypen), 31.22 (s, $CH_3CH_2CH_2\underline{C}H_2CH(cypen)CO_2H$), 42.69 (s, $CH_3CH_2CH_2CH_2\underline{C}H(cypen)CO_2H$), 52.07 (s, $CH_3CH_2CH_2CH_2CH(\underline{C}HC_4H_8)CO_2H$), 178.69 (s, $CH_3CH_2CH_2CH_2CH(cypen)\underline{C}O_2H$). IR (ATR, cm^{-1}): 3131 (w, br), 3034 (w, br), 2952 (m), 2859 (m), 2359 (w), 1599 (vs), 1546 (m), 1445 (s), 1423 (vs), 1316 (m), 1118 (w), 941 (w), 897 (w), 734 (w), 691 (w), 524 (s).

CMJL049: Synthesis of the Zinc coordination complex of 1-naphthoic acid using diisopropylethylamine



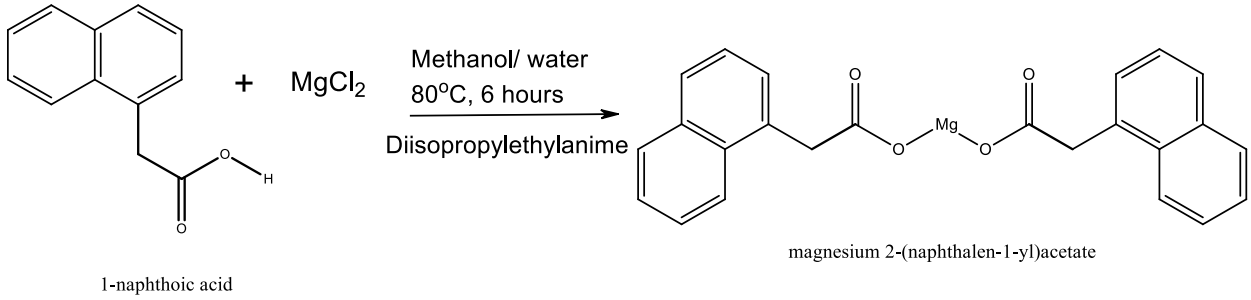
1-naphthoic acid

zinc 2-(naphthalen-1-yl)acetate

621.00 mg of 1-naphthoic acid was weighed into a 100 mL round bottom flask. 466 mg of diisopropylethylamine was added to the flask. 308 mg of zinc chloride was dissolved in 15 mL anhydrous methanol and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was left to reflux for 6 hours at 100°C. After reacting, the sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent. 1H

(300 MHz, DMSO-D6, ppm): 8.98 (t, 1H, $^{3}J_{CH}$ = 9.38 Hz, Ar), 7.95 (m, 3H, $^{3}J_{CH}$ = 28.72 Hz, Ar), 7.51 (m, 3H, $^{3}J_{CH}$ = 26.65 Hz, Ar). ^{13}C{1H} (75 MHz, DMSO-D6, ppm): 124.85 (s, Ar), 125.53 (s, Ar), 126.21 (s, Ar), 126.81 (s, Ar), 128.04 (s, Ar), 130.20 (s, Ar), 130.84 (s, Ar), 133.37 (s, Ar), 170.98 (s, Ar-$\underline{C}O_2$). IR (ATR, cm-1): 2988 (m, br), 2814 (w, br), 2706 (w, br), 2495 (w, br), 1600 (s), 1567 (s), 1507 (m), 1460 (s), 1403 (s), 1357 (vs), 1257 (m), 1131 (s), 788 (vs).

CMJL050: Synthesis of the Magnesium coordination complex of 1-naphthoic acid using diisopropylethylamine



1-naphthoic acid

magnesium 2-(naphthalen-1-yl)acetate

555.50 mg of 1-naphthoic acid was weighed into a 100 mL round bottom flask. 417 mg of diisopropylethylamine was added to the flask. 410 mg of magnesium chloride was dissolved in 15 mL anhydrous methanol and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was left to reflux for 6 hours at 100°C. After reacting, the sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent. 1H (300 MHz, DMSO-D6, ppm): 9.05 (q, 1H, $^{3}J_{CH}$ = 9.80 Hz, Ar), 8.05 (q, 2H, $^{3}J_{CH}$ = 38.97 Hz, Ar), 7.94 (q, 1H, $^{3}J_{CH}$ = 9.56 Hz, Ar) 7.50 (m, 3H, $^{3}J_{CH}$ = 20.32 Hz, Ar).

$^{13}C\{1H\}$ (75 MHz, DMSO-D6, ppm): 124.86 (s, Ar), 125.64 (s, Ar), 126.30 (s, Ar), 126.81 (s, Ar), 128.12 (s, Ar), 128.49 (s, Ar), 130.89 (s, Ar), 133.38 (s, Ar), [(s, Ar-$\underline{C}O_2$) not present]. IR (ATR, cm-1): 2984 (m, br), 2802 (w, br), 2666 (w, br), 2493 (w, br), 1626 (m), 1606 (s), 1572 (s), 1508 (m), 1416 (s), 1378 (vs), 1258 (w), 1132 (m), 788 (vs).

CMJL051: Solubility tests of specific samples for purification

~25 mg of each sample was placed into a 1 dram vial. About 2 mL of the respective solvent was added to each vial. The samples were mixed using a vortex mixer for one minute each. Initial observations of solubility are recorded in the following table. The samples were left to sit sealed on the bench top undisturbed for a week. After a week, observations of solubility were updated in the table. This test was to determine which solvents would be appropriate to further purify the samples of their respective contaminations, NH_4Cl and NaCl, which regularly crystallized instead of the desired product. This solubility test was also to determine the appropriate mobile phase for the RP-HPLC partition coefficient experiments.

Solution	**CMJL027 Zn**	**CMJL027 Mg**	**CMJL036**	**CMJL042**
Acetone	Not Soluble *	Not Soluble	Not Soluble	Partly Soluble
Ultrapure water	Not Soluble	Soluble	Soluble	Soluble
Toluene	Not Soluble **	Not Soluble	Not Soluble	Not Soluble
***Cyclo*-hexane**	Not Soluble	Not Soluble	Not Soluble	Not Soluble
Acetonitrile	Not Soluble *	Not Soluble *	Not Soluble ◊	Not Soluble **

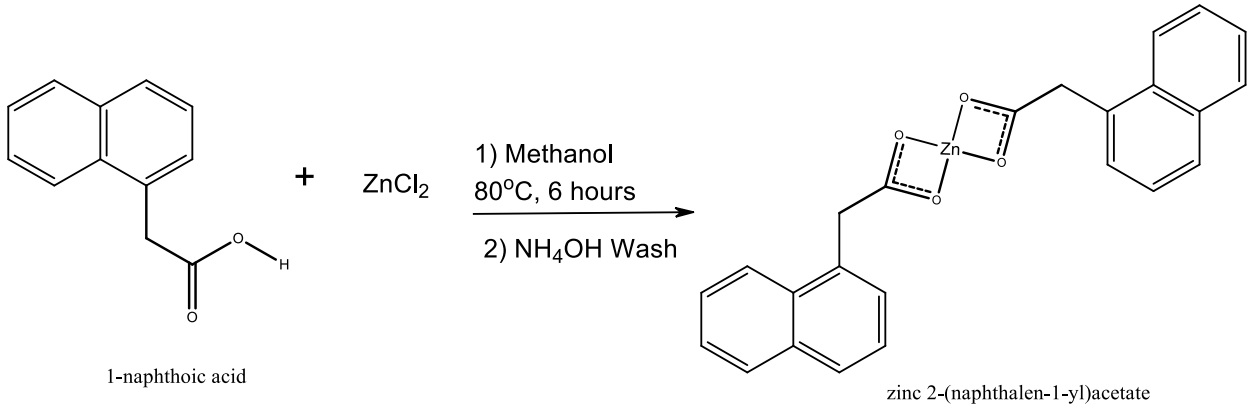
Chloroform	Not Soluble *	Not Soluble *	Slightly Soluble	Slightly Soluble
Dichloromethene	Partly Soluble *	Slightly Soluble *	Slightly Soluble	Not Soluble
Hexanes	Not Soluble	Not Soluble	Not Soluble	Not Soluble
Tetrahydrofuran	Not Soluble *	Not Soluble *	Partly Soluble *	Partly Soluble *

* Sample dissolved fully into solution when left undisturbed for one week

** Sample partially dissolved when left undisturbed for one week

◊ Sample formed needle crystals when left undisturbed for one week

CMJL052: Zinc coordination complex of 1-naphthoic under anhydrous conditions (method 2)



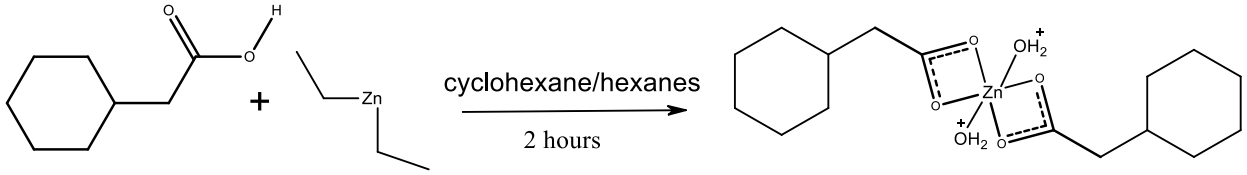
1-naphthoic acid

zinc 2-(naphthalen-1-yl)acetate

887.1 mg of 1-naphthoic acid was weighed into a 100 mL round bottom flask. 363 mg of zinc chloride was dissolved in a 10 mL solution of anhydrous methanol and transferred into the flask. The salt solution was washed with another 10 mL of methanol to ensure complete transfer of the solution. The sample was left to reflux for 6 hours at 100°C. Once the reaction was complete, 40 mL of ammonium hydroxide was added to the flask and the sample was allowed to stir for 30 minutes. No precipitate formed like in CMJL027. The sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}, ^{13}CNMR, COSY, HSQC, IR, and crystallography sample was run for each of the

sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent. 1H (300 MHz, DMSO-D6, ppm): 8.95 (t, 1H, $^{3}J_{CH}$ = 10.01 Hz, Ar), 7.89 (t, 3H, $^{3}J_{CH}$ = 12.39 Hz, Ar), 7.47 (m, 3H, $^{3}J_{CH}$ = 20.26 Hz, Ar). ^{13}C{1H} (75 MHz, DMSO-D6, ppm): 124.92 (s, Ar), 125.39 (s, Ar), 125.87 (s, Ar), 127.33 (d, ^{3}JCH = 15.45 Hz Ar), 127.94 (s, Ar), 129.39 (s, Ar), 130.85 (s, Ar), 133.38 (s, Ar), 171.66 (s, Ar-$\underline{C}O_2$H), 206.53 (s, aldehyde formation?) . IR (ATR, cm-1): 3326 (w, br), 3130 (m, br), 3044 (m, br), 2805 (m), 1549 (s, br), 1401 (s), 1355 (s), 1255 (m), 1213 (m), 1149 (m), 871 (w), 778 (vs).

CMJL053: Diethyl Zinc coordination complex of *cyclo*-hexaneacetic acid



CCHA

zinc 2-cyclohexylacetate dihydrate

321.8 mg of *cyclo*-hexaneacetic acid was weighed into a 100 mL schlenk flask. The acid was roughly ground within the flask using a scoopula and a stir bar was added. The acid was dissolved/suspended in 15 mL of *cyclo*-hexane. The flask was evacuated of air and placed under an argon atmosphere using an argon filled balloon. With a needle, ~2 mL 1 M in hexanes diethyl zinc was added to the flask. The reaction was allowed to stir for two hours. White gas/vapour formed upon the diethyl zinc contacting with the argon atmosphere. As the reaction proceeded, the vapour dissipated. No colour changes was observed in the sample. The sample was dried through rotary evaporation and transferred to a 20 mL vial. ^{1}HNMR, ^{13}CNMR, COSY, HSQC, IR, and crystallography

sample was run for each of the sample. The crystals was attempted to be formed from slow evaporation using methanol as a solvent. 1H (300 MHz, DMSO-D6, ppm): 1.99 (d, 2H, $^{3}J_{CH}$ = 6.88 Hz, cyhex-C$\underline{H}_2CO_2H$), 1.65 (m, 6H, $^{3}J_{CH}$ = 27.50 Hz, -cyhex), 1.14 (m, 3H, $^{3}J_{CH}$ = 67.38 Hz, -cyhex), 0.88 (q, 2H, $^{3}J_{CH}$ = 33.00 Hz, -cyhex). ^{13}C{1H} (75 MHz, DMSO-D6, ppm): 25.81 (d, $^{3}J_{CH}$ = 7.18 Hz, -cyhex), 32.65 (s, -cyhex), 35.02 (s, -cyhex), 206.45 (s, cyhex-$CH_2\underline{C}O_2H$). IR (ATR, cm-1): 2919 (s), 2849 (m), 2665 (w), 1628 (s), 1536 (vs), 1440 (vs), 1419 (vs), 1325 (m), 1267 (m), 1199 (w), 1171 (w), 1125 (w).

CMJL056: Partition coefficient comparison using RP- HPLC, concentrated samples

A method was adapted from the literature to compare a sample's partition coefficients to the respective unreacted naphthenic acid.[34] [35] The samples: CMJL027 Zn, CMJL027 Mg, CMJL036, CMJL042, CMJL052, CMJL053, CCPA, CCHA, 1-napthanoic acid, CCPA methyl ester, and CCHA methyl ester were all dissolved in HPLC grade methanol. The concentration was not controlled as this experiment was only to identify noticeable differences between the samples and the respective acid controls. The RP-HPLC was configured with a ZDRBAX Eclipse XDB-C18 column, a mobile phase of 40:60 ACN : H_2O at a flow rate of 1 mL/min and a DAD set to a wavelength of 247 nm. Samples were allowed to run for 20 minutes and were run in duplicate. The retention times of the samples directly correlate to the partition coefficient of the sample; the longer they are retained within the column, the more hydrophobic the sample is. It is important to note for this experiment, that it is nothing more than for an initial

comparison, a precise measurement of the partition coefficient cannot be determined without a calibration curve of compounds with known partition coefficients.

Spectroscopic & Characterization Techniques

The infrared spectra of all samples were obtained using an attenuated total reflection (ATR) adapter on a Bruker Alpha Spectrometer. Data processing was completed using the OPUS 6.0 software suite.

The NMR experiments were carried out on a Bruker Ultrashield 300 MHz NMR spectrometer with a 7.05 Tesla magnet. The samples were prepared by dissolving a small amount of the compound into an aliquot of the deuterated solvent open to the atmosphere. ^{1}H and $^{13}C\{1H\}$ spectra were referenced to residual solvent downfield of trimethylsilane. Peaks were assigned by considering results from COSY, HSQC and DEPTQ experiments, as well as by relative integration in the ^{1}H spectra. The data was processed using Bruker TOPSIN 3.5pl5.

Elemental analyses (EA) were performed on a Perkin Elmer CHN Analyzer 2400 Series II. Prior to data acquisition standard calibration was conducted with acetanilide supplied by Perkin Elmer. All EA data acquisition was obtained by Patricia Granados of the Centre for Environmental Analysis and Remediation at Saint Mary's University.

HPLC details

The HPLC experiments were carried out on a Agilent 1100 LC-DAD equipped with an autosampler, binary pump, vacuum degasser, thermostatted column, and diode array detector. The column used was a ZDRBAX Eclipse XDB-C18 column, Rapid resolution 4.6x75 mm, 3.5 microns. All data was collected and processed using the software HP Chem Station.

X-ray crystallography details

All X-ray crystallographic analyses were performed by Dr. Katherine Robertson at Saint Mary's University, and all crystallographic diagrams presented within were prepared using Mercury CSD 3.6[36].

The crystal chosen for each determination was attached to the tip of a 400 μm MicroLoop with paratone-N oil. Measurements were made on a Bruker APEXII CCD equipped diffractometer (30 mA, 50 kV) using monochromated Mo Kα radiation (λ = 0.71073 Å) at 125 K, except for the room temperature data collection which was carried out at 26 C[37]. The initial orientation and unit cell were indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° ω-scans, 15 seconds per frame and 12 frames per series, that were well distributed in reciprocal space. For data collection, four ω-scan frame series were collected with 0.5° wide scans, 30 second frames and 366 frames per series at varying φ angles (φ = 0°, 90°, 180°, 270°). The crystal to detector distance was set to 6 cm and a complete sphere of data was collected. Cell refinement and data reduction were performed with the Bruker SAINT software[38], which corrects for beam inhomogeneity, possible crystal decay,

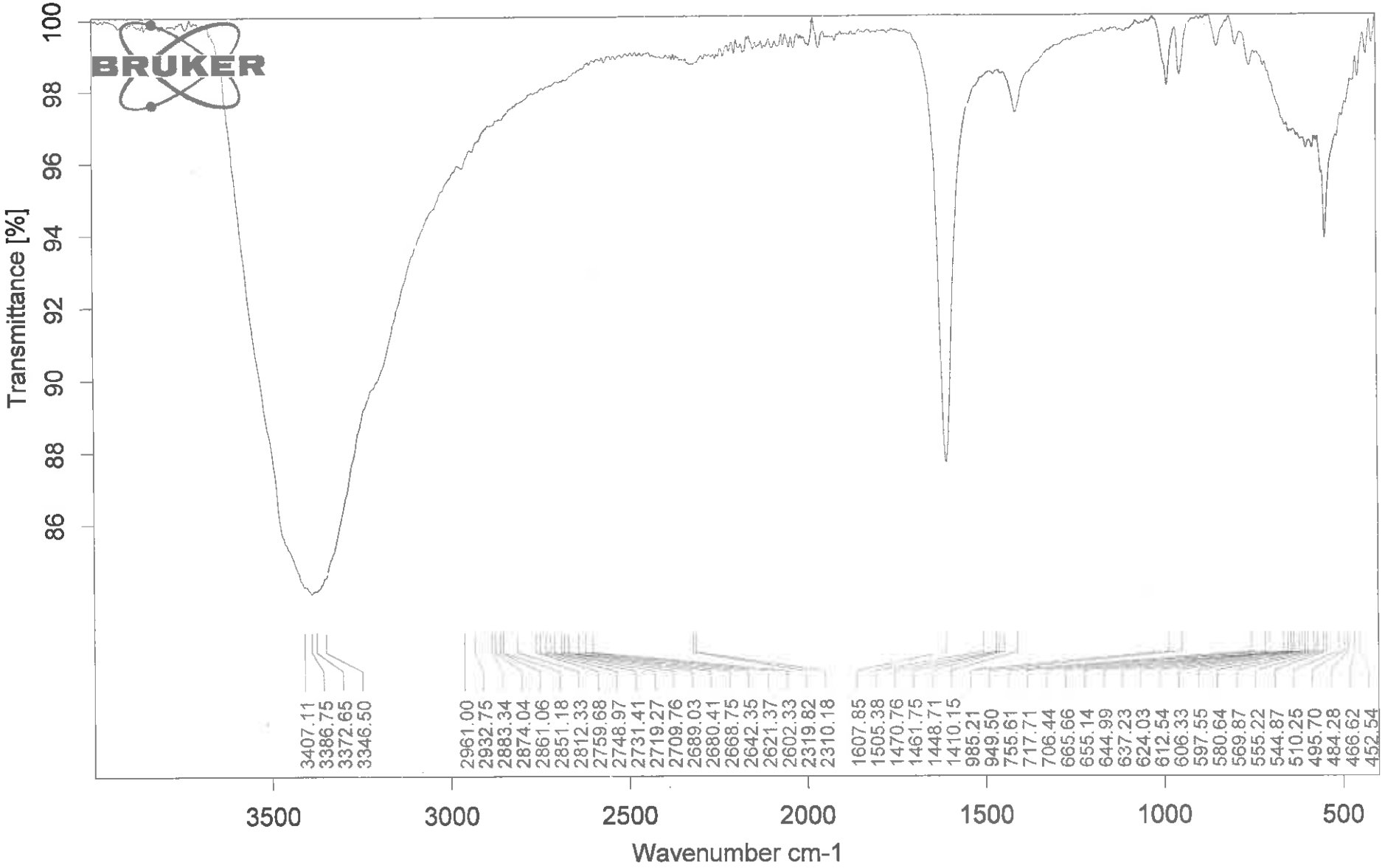
Lorentz and polarisation effects. A multi-scan absorption correction was applied (SADABS)[39]. The structures were solved using either SHELXT-2014[40] or SHELXS-2014[40] and were refined using a full-matrix least-squares method on F^2 with SHELXL-2014[40]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2*U*eq of the parent carbon atom or 1.5*U*eq for methyl hydrogens.

References

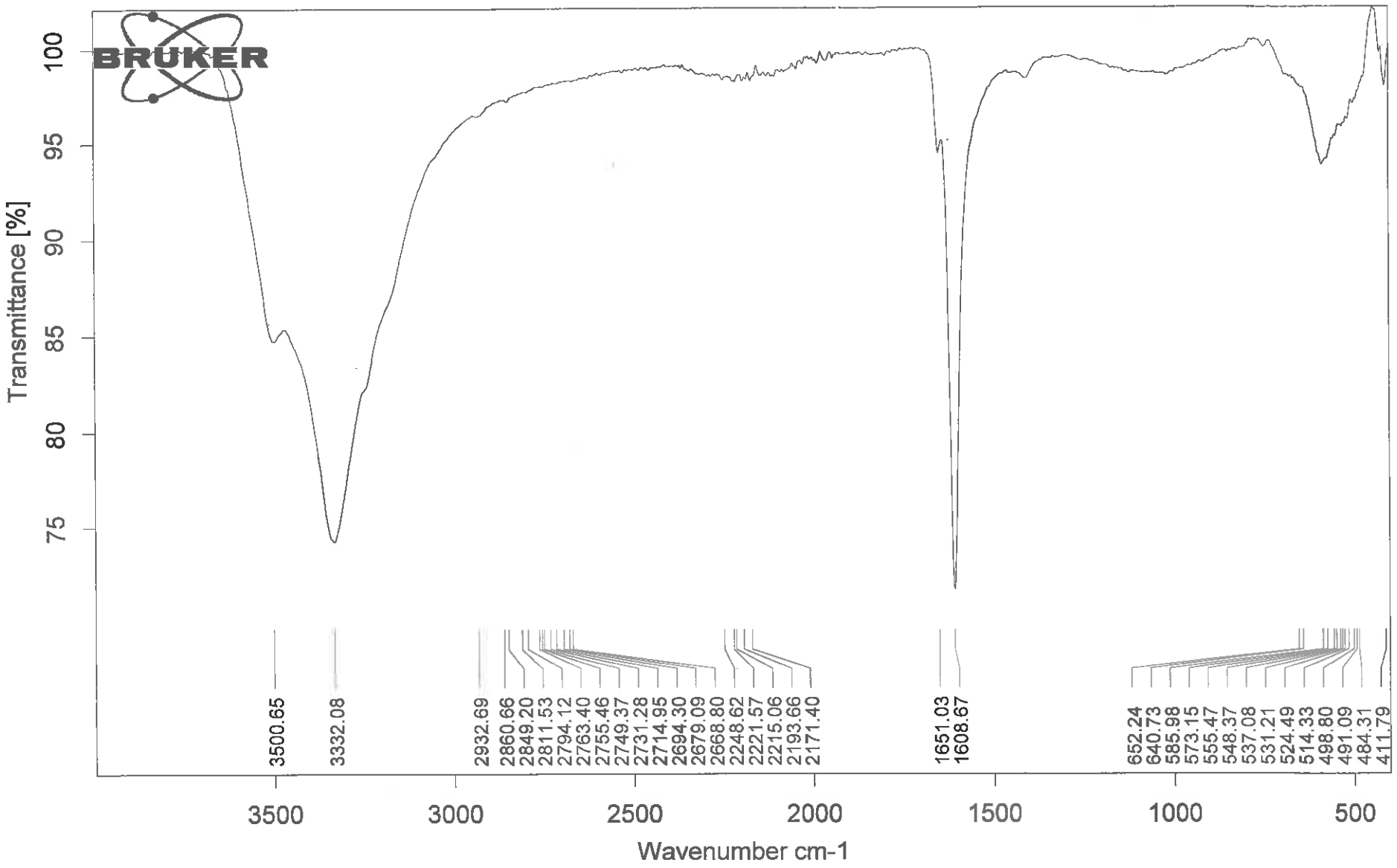
[1] U.S. Department of the Interior,. *Heavy Oil and Natural Bitumen Resources in Geological Basins of the World*; U.S. Geological Survey: Reston, Virginia, 2007.
[2] Fractal Systems, Inc.,. *Understanding the Value Proposition of the JetShear™ Technology Platform*; Fractal Systems, Inc.: Sherbrooke, Quebec, 2016.
[3] Alberta Department of Energy,. *Markets and Prices for Alberta Bitumen Production*; Oil Sands Economics and Royalty Series; Alberta Department of Energy: Edmonton, Alberta, 2007.
[4] Grewer, D.; Young, R.; Whittal, R.; Fedorak, P. *Science of The Total Environment* 2010, *408*, 5997-6010.

[5] McNaught AD, Wilkinson A. IUPAC compendium of chemical terminology. 2nd edn. Chichester, Oxford: Wiley-Blackwell; 1997
[6] Grewer, D.; Young, R.; Whittal, R.; Fedorak, P. *Science of The Total Environment* 2010, *408*, 5997-6010.
[7] McKee, R.; North, C.; Podhasky, P.; Charlap, J.; Kuhl, A. *International Journal of Toxicology* 2013, *33*, 168S-180S.
[8] Mohamed, M.; Wilson, L.; Headley, J.; Peru, K. *Phys. Chem. Chem. Phys.* 2011, *13*, 1112-1122.
[9] Oil Sands Research and Information Network,. *Review of Health Effects of Naphthenic Acids: Data Gaps and Implications for Understanding Human Health Risk*; University of Alberta: Edmonton, Alberta, 2012.
[10] Oil Sands Research and Information Network,. *Review of Health Effects of Naphthenic Acids: Data Gaps and Implications for Understanding Human Health Risk*; University of Alberta: Edmonton, Alberta, 2012.
[11] Grewer, D.; Young, R.; Whittal, R.; Fedorak, P. *Science of The Total Environment* 2010, *408*, 5997-6010
[12] Rogers, V.V., 2003. Mammalian toxicity of naphthenic acids derived from the Athabasca oil sands. PhD Thesis. University of Saskatchewan, Saskatoon, SK, Canada.
[13] Rogers, V.V., 2003. Mammalian toxicity of naphthenic acids derived from the Athabasca oil sands. PhD Thesis. University of Saskatchewan, Saskatoon, SK, Canada.
[14] Cozzi, P. *Chem. Soc. Rev.* 2004, *33*, 410-421.
[15] Gui, J.; Cong, X.; Liu, D.; Zhang, X.; Hu, Z.; Sun, Z. *Catalysis Communications* 2004, *5*, 473-477.
[16] Deng, Y.; Shi, F.; Beng, J.; Qiao, K. *Journal of Molecular Catalysis A: Chemical* 2001, *165*, 33-36.
[17] Gryz, M.; Starosta, W.; Ptasiewicz-bąk, H.; Leciejewicz, J. *Journal of Coordination Chemistry* 2003, *56*, 1505-1511.
[18] Ślepokura, K.; Piątkowska, A.; Lis, T. *Zeitschrift für Kristallographie - Crystalline Materials* 2002, *217*.
[19] Chen, S.; Cheng, M.; Ren, Y.; Tang, L.; Liu, X.; Zai, C.; Liu, Q. *Zeitschrift für anorganische und allgemeine Chemie* 2014, *641*, 610-616.
[20] Finizio, A.; Vighi, M.; Sandroni, D. *Chemosphere* 1997, *34*, 131-161.
[21] Organisation for Economic Co-operation and Development,. *Partition Coefficient (n-octanol/water), High Performance Liquid Chromatography (HPLC) Method*; OECD GUIDELINE FOR TESTING OF CHEMICALS; Paris, France, 1989.
[22] Baka, E.; Comer, J.; Takács-Novák, K. Journal of Pharmaceutical and Biomedical Analysis 2008, 46, 335-341.
[23] OECD (1995), *Test No. 107: Partition Coefficient (n-octanol/water): Shake Flask Method*, OECD Publishing, Paris.
[24] Finizio, A.; Vighi, M.; Sandroni, D. *Chemosphere* 1997, *34*, 131-161.
[25] Organisation for Economic Co-operation and Development,. *Partition Coefficient (n-octanol/water), High Performance Liquid Chromatography (HPLC) Method*; OECD GUIDELINE FOR TESTING OF CHEMICALS; Paris, France, 1989.
[26] Canada's Oil Sands Overview and Bitumen Blending Primer, 2012.
[27] Soper, R. 2016, 107-203.
[28] Natural Resources Canada,. *Corrosion Conditions in the Path of Bitumen from Well to Wheel*; Government of Canada: Toronto, Canada, 2012.

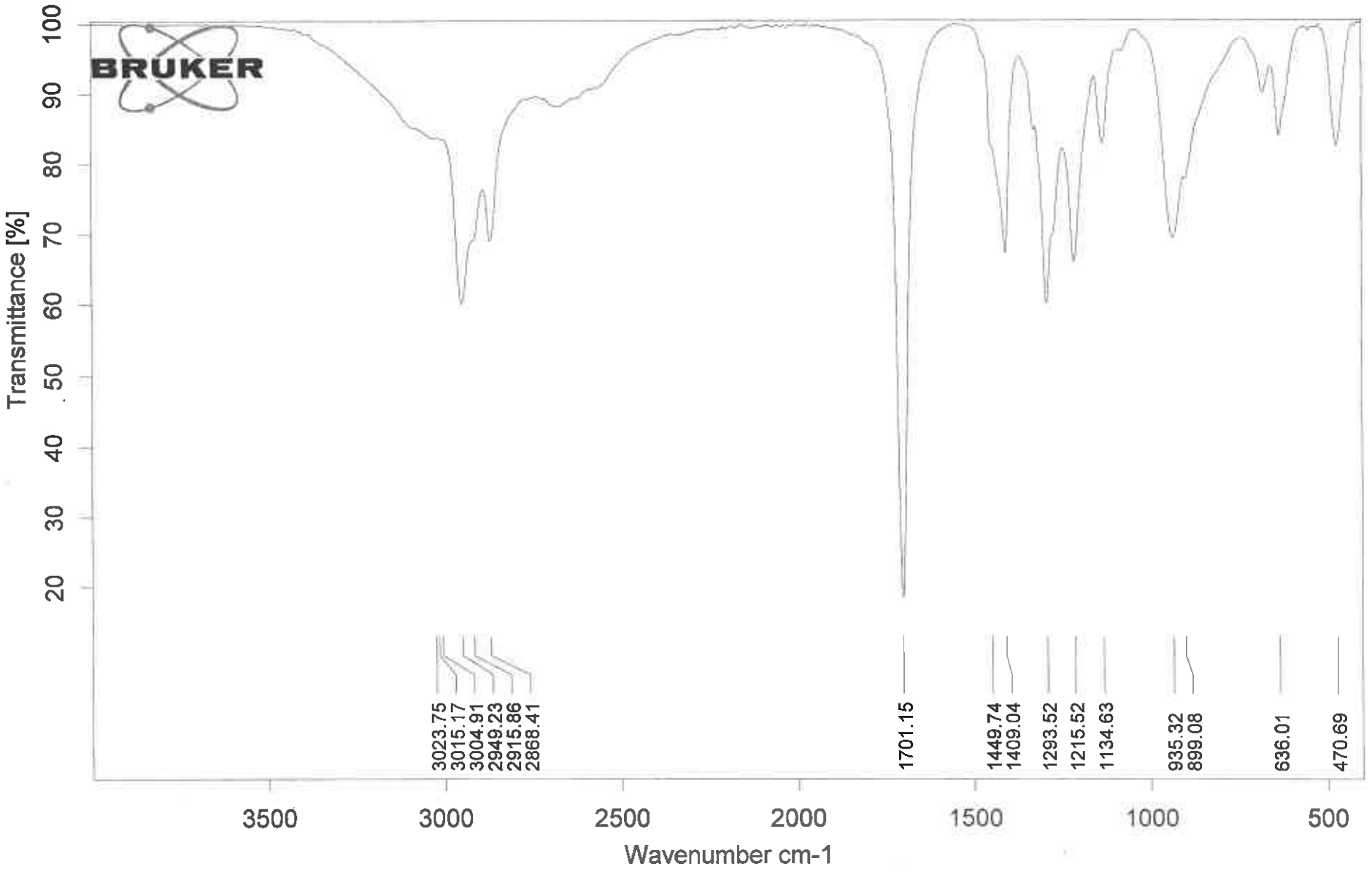
[29] Natural Resources Canada,. *Corrosion Conditions in the Path of Bitumen from Well to Wheel*; Government of Canada: Toronto, Canada, 2012.
[30] Natural Resources Canada,. *Corrosion Conditions in the Path of Bitumen from Well to Wheel*; Government of Canada: Toronto, Canada, 2012.
[31] Green, K.Jackson, T. *Safety in the Transportation of Oil and Gas: Pipelines or Rail?*; FRASER RESEARCH BULLETIN; Fraser Institute, 2015.
[32] Green, K.Jackson, T. *Safety in the Transportation of Oil and Gas: Pipelines or Rail?*; FRASER RESEARCH BULLETIN; Fraser Institute, 2015.
[33] Frequently Asked Questions (FAQs) Concerning Federally-Regulated Petroleum Pipelines in Canada | Natural Resources Canada http://www.nrcan.gc.ca/energy/infrastructure/5893#h-3-1 (accessed Nov 20, 2016).
[34] Finizio, A.; Vighi, M.; Sandroni, D. *Chemosphere* 1997, *34*, 131-161.
[35] Organisation for Economic Co-operation and Development,. *Partition Coefficient (n-octanol/water), High Performance Liquid Chromatography (HPLC) Method*; OECD GUIDELINE FOR TESTING OF CHEMICALS; Paris, France, 1989.
[36] Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Crystallogr.* 2008*, 41*, 466-470.
[37] *APEX II,* Bruker AXS Inc.: Madison, Wisconsin, USA, 2008.
[38] *SAINT,* Bruker AXS Inc.: Madison, Wisconsin, USA, 2008.
[39] *SADABS,* Bruker AXS Inc.: Madison, Wisconsin, USA, 2009.
[40] Sheldrick, G. M. *Acta Cryst.* 2008, *A64*, 112-122; *Acta Cryst.* 2015, *A71*, 3-8; *Acta Cryst.* 2015, *C71*, 3-8.



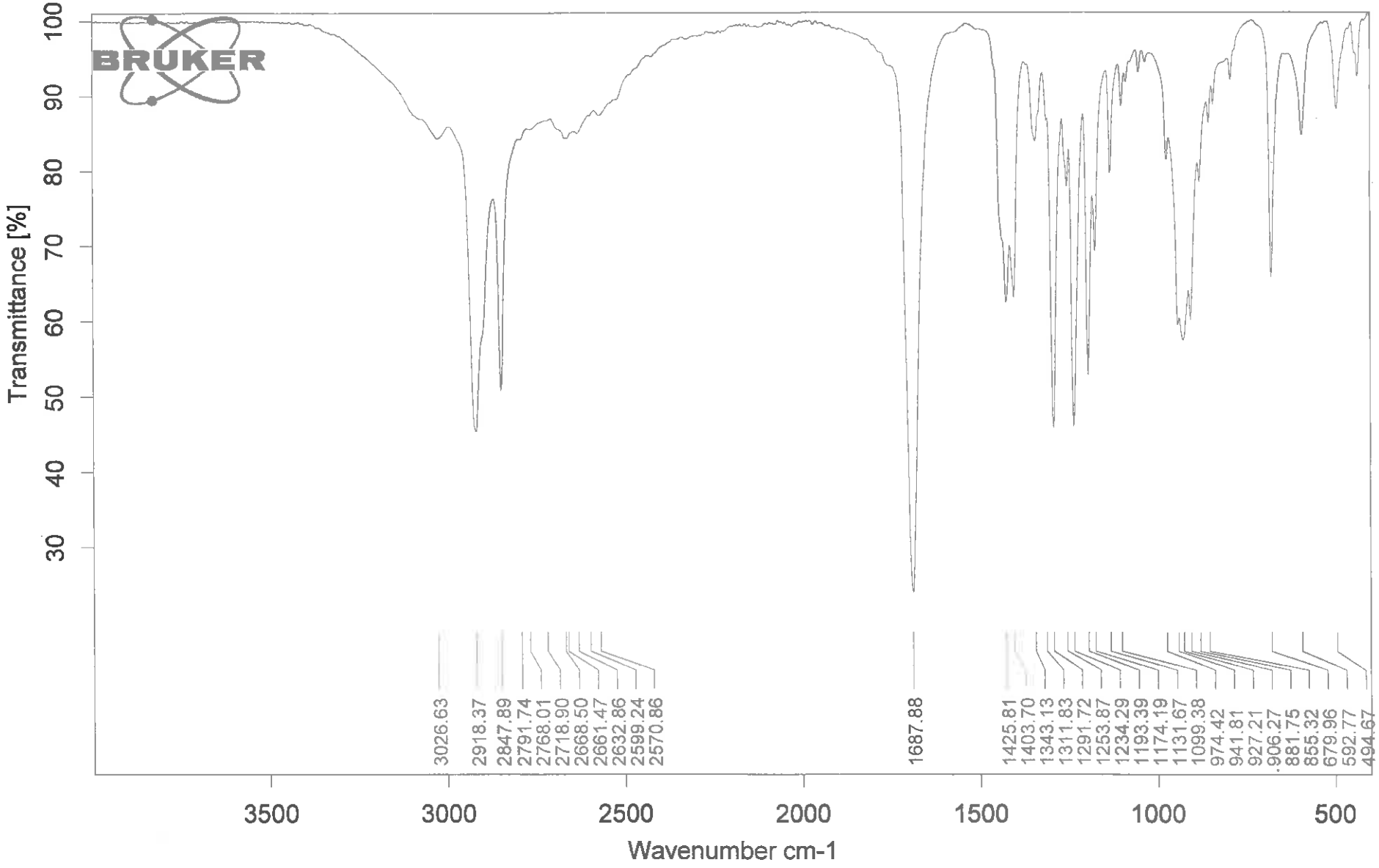
C:\Users\SMUCHEM\Documents\Bruker\OPUS_7.5.18\DATA\MEAS\ZnCl2 Control.0	ZnCl2 Control	Instrument type and / or accessory	25/08/2016



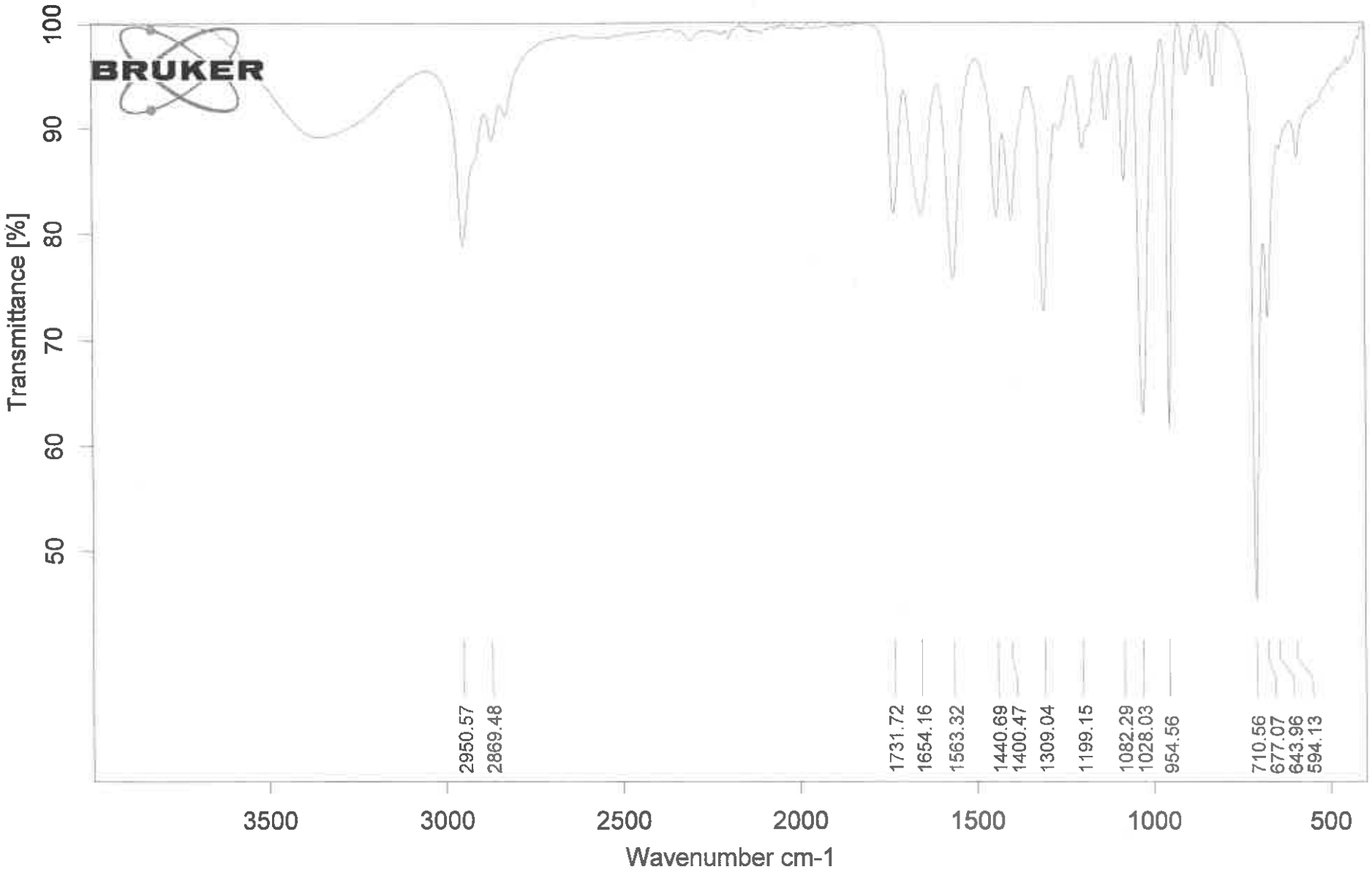
C:\Users\SMUCHEM\Documents\Bruker\OPUS_7.5.18\DATA\MEAS\MgCl2 Control.0	MgCl2 Control	Instrument type and / or accessory	25/08/2016



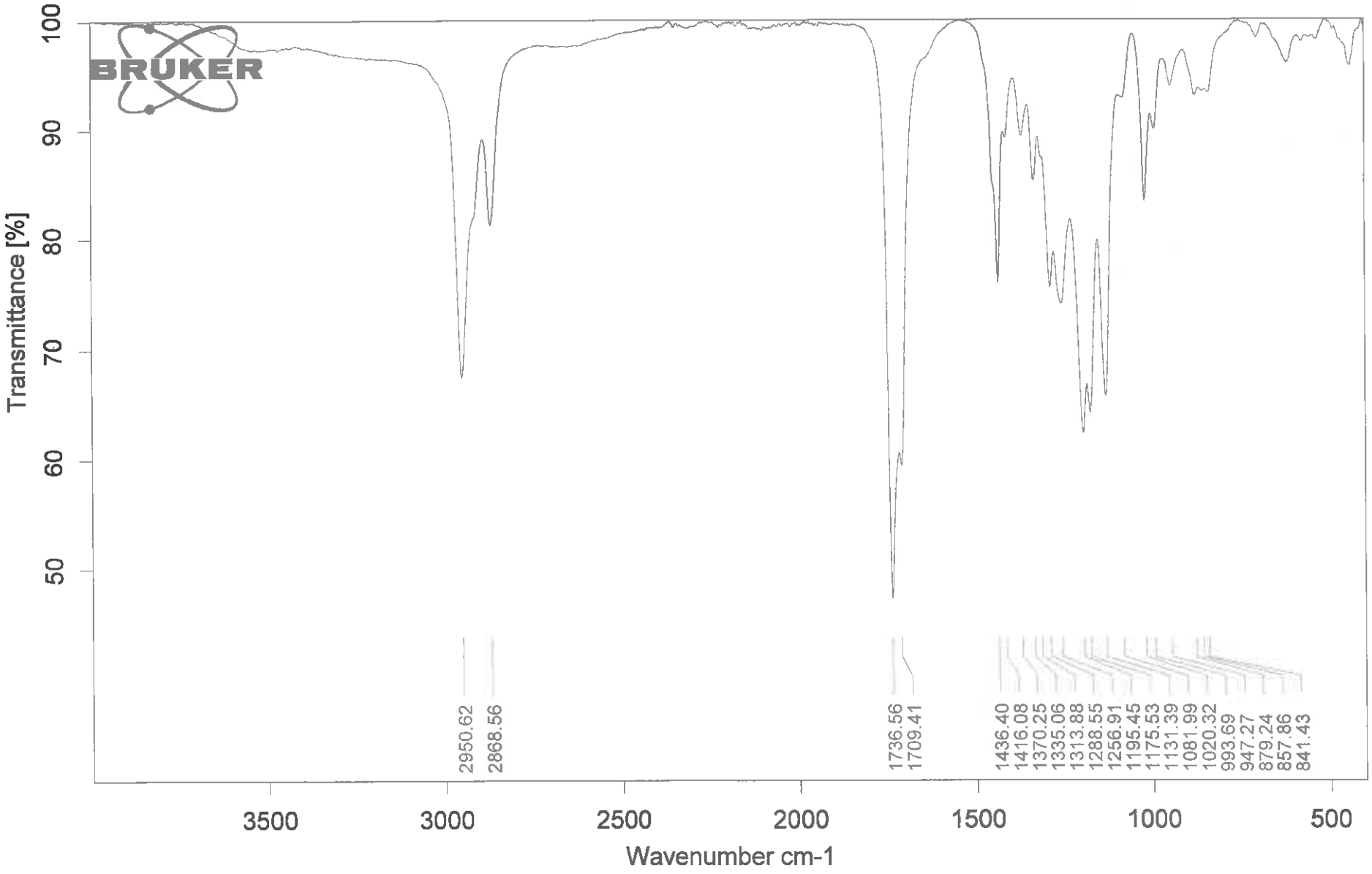
C:\Users\SMUCHEM\Documents\Bruker\OPUS_7.5.18\DATA\MEAS\Cyclopentylacetic acid.0	Cyclopentylacetic acid	Instrument type and	14/06/2016



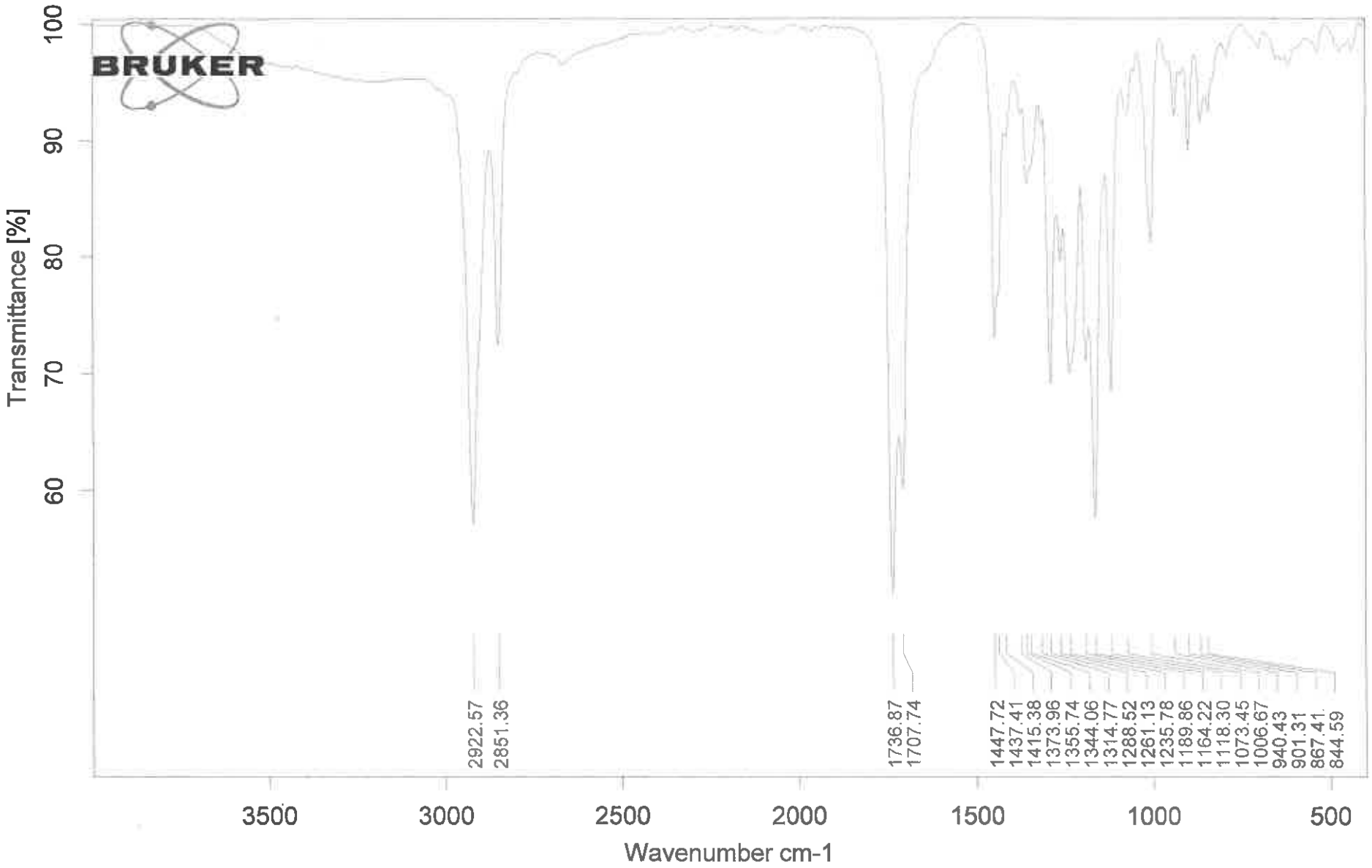
C:\Users\SMUCHEM\Documents\Bruker\OPUS_7.5.18\DATA\MEAS\CCHA Control.0	CCHA Control	Instrument type and / or accessory	19/07/2016



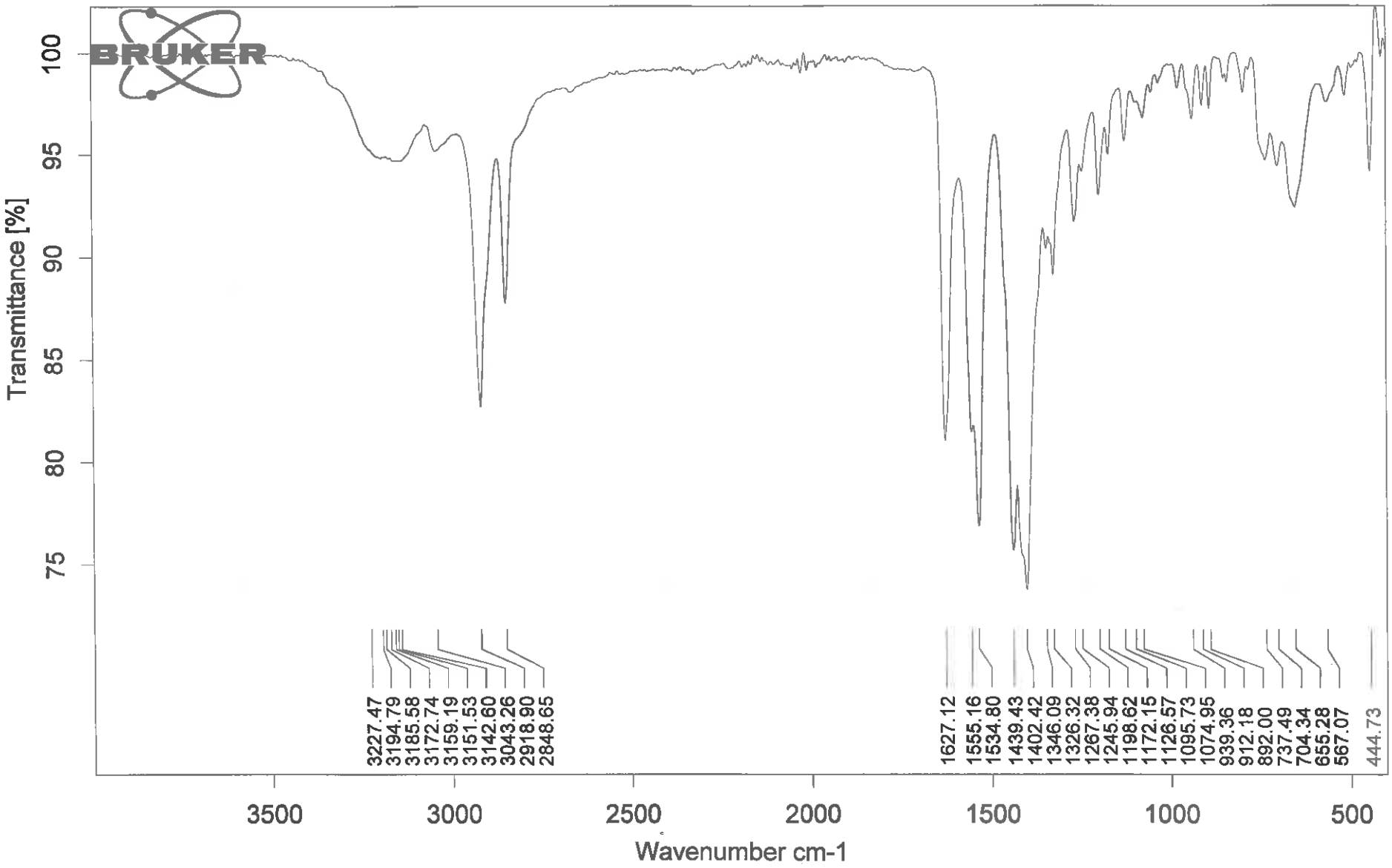
C:\Users\SMUCHEM\Documents\Bruker\OPUS_7.5.18\DATA\MEAS\CMJL014 F with D-DCM and TMS.0	CMJL014 F with D-DCM and TMS	23/06/2016



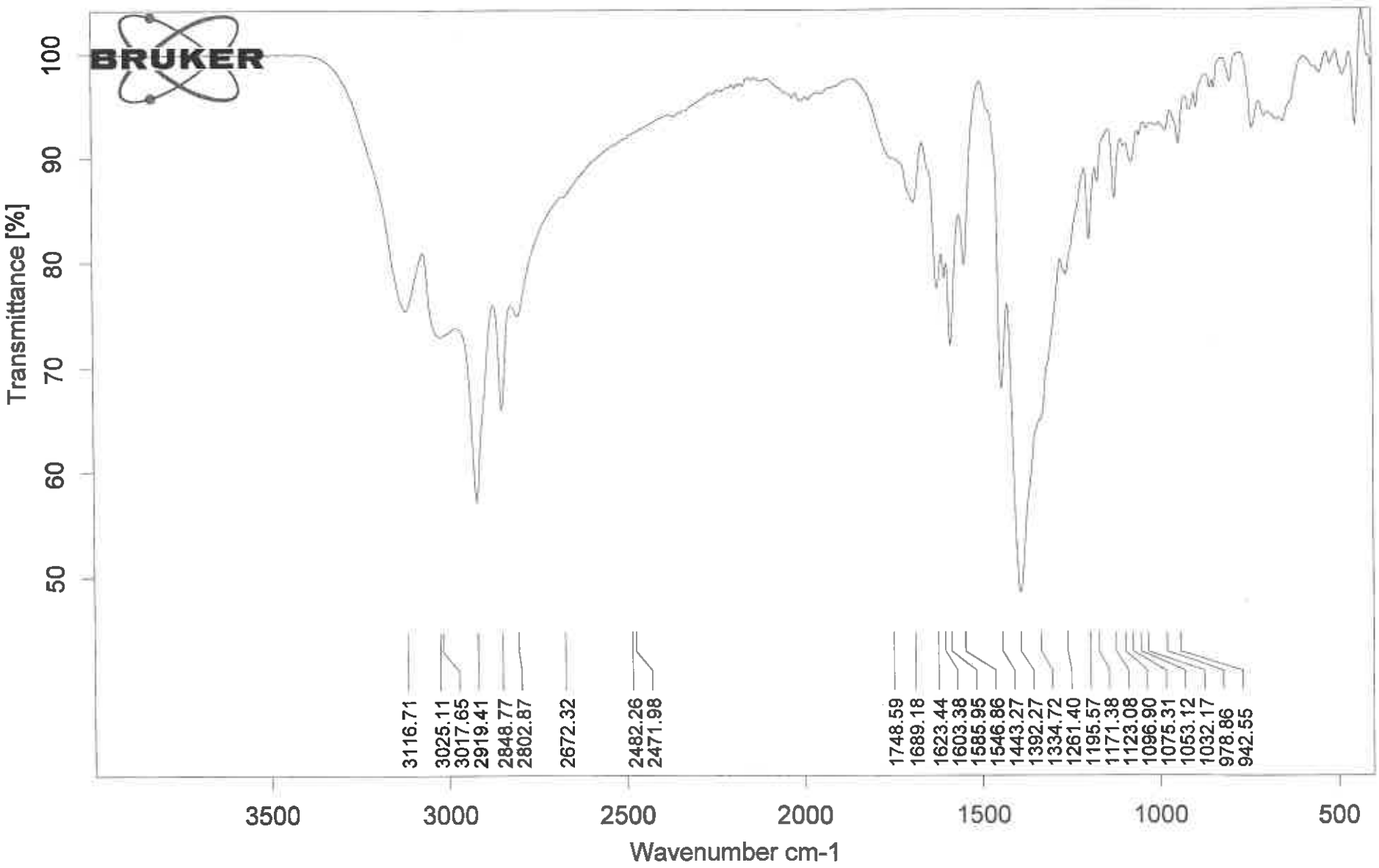
C:\Users\SMUCHEM\Documents\Bruker\OPUS_7.5.18\DATA\MEAS\CMJL015.0	CMJL015	Instrument type and / or accessory	28/06/2016



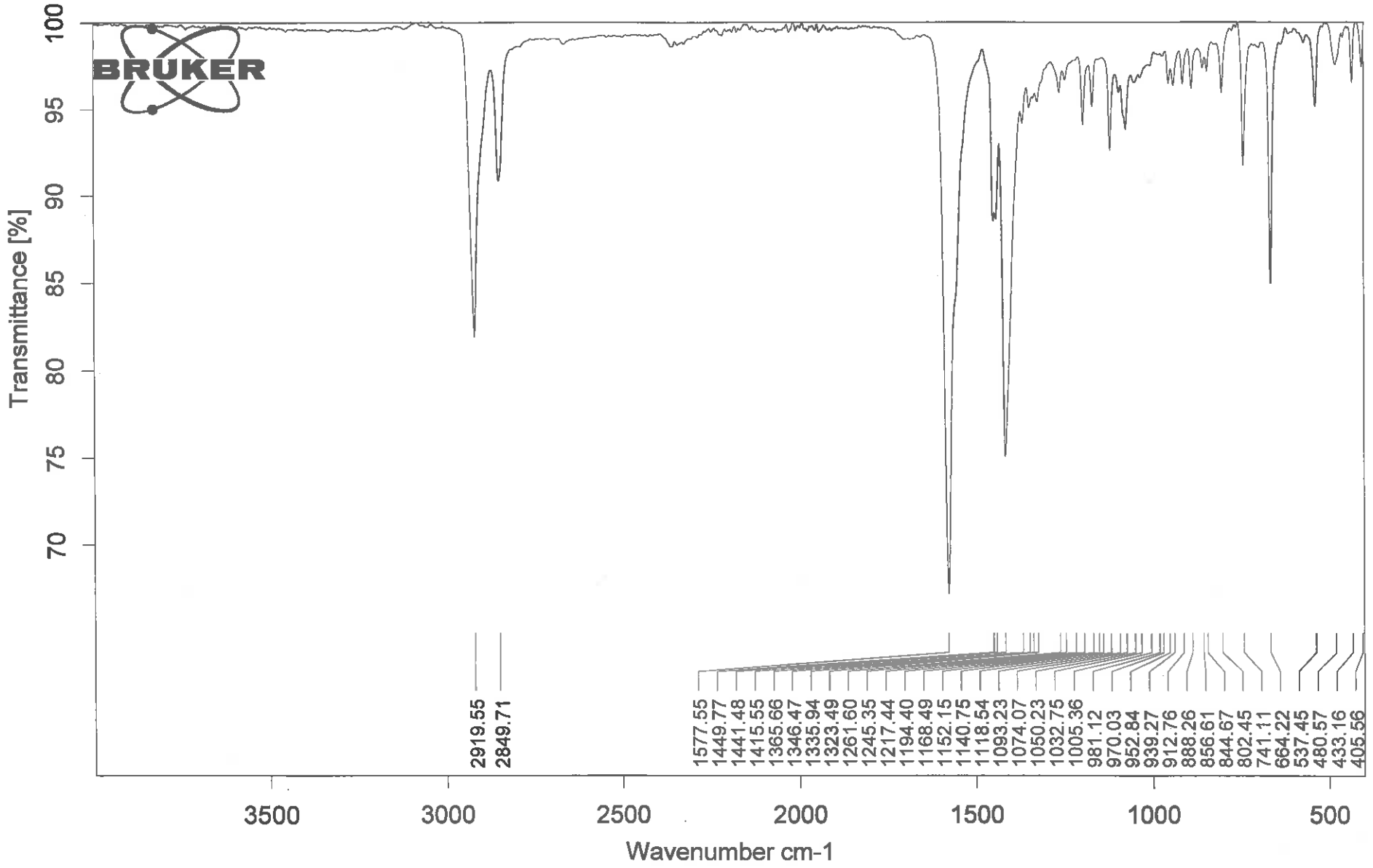
C:\Users\SMUCHEM\Documents\Bruker\OPUS_7.5.18\DATA\MEAS\CMJL020.0	CMJL020	Instrument type and / or accessory	19/07/2016



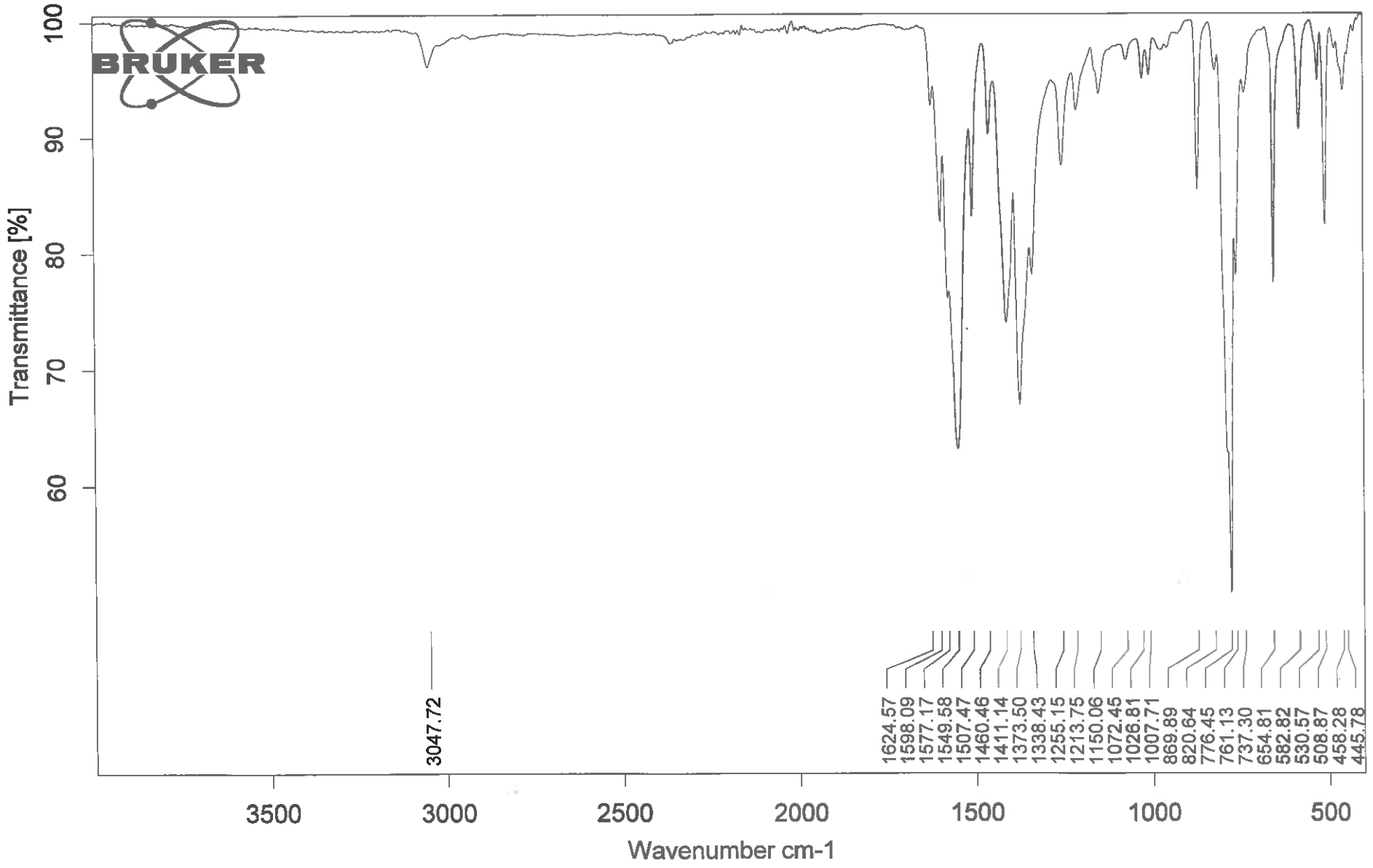
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL027 Zn.0	CMJL027 Zn	Instrument type and / or accessory	03/02/2017



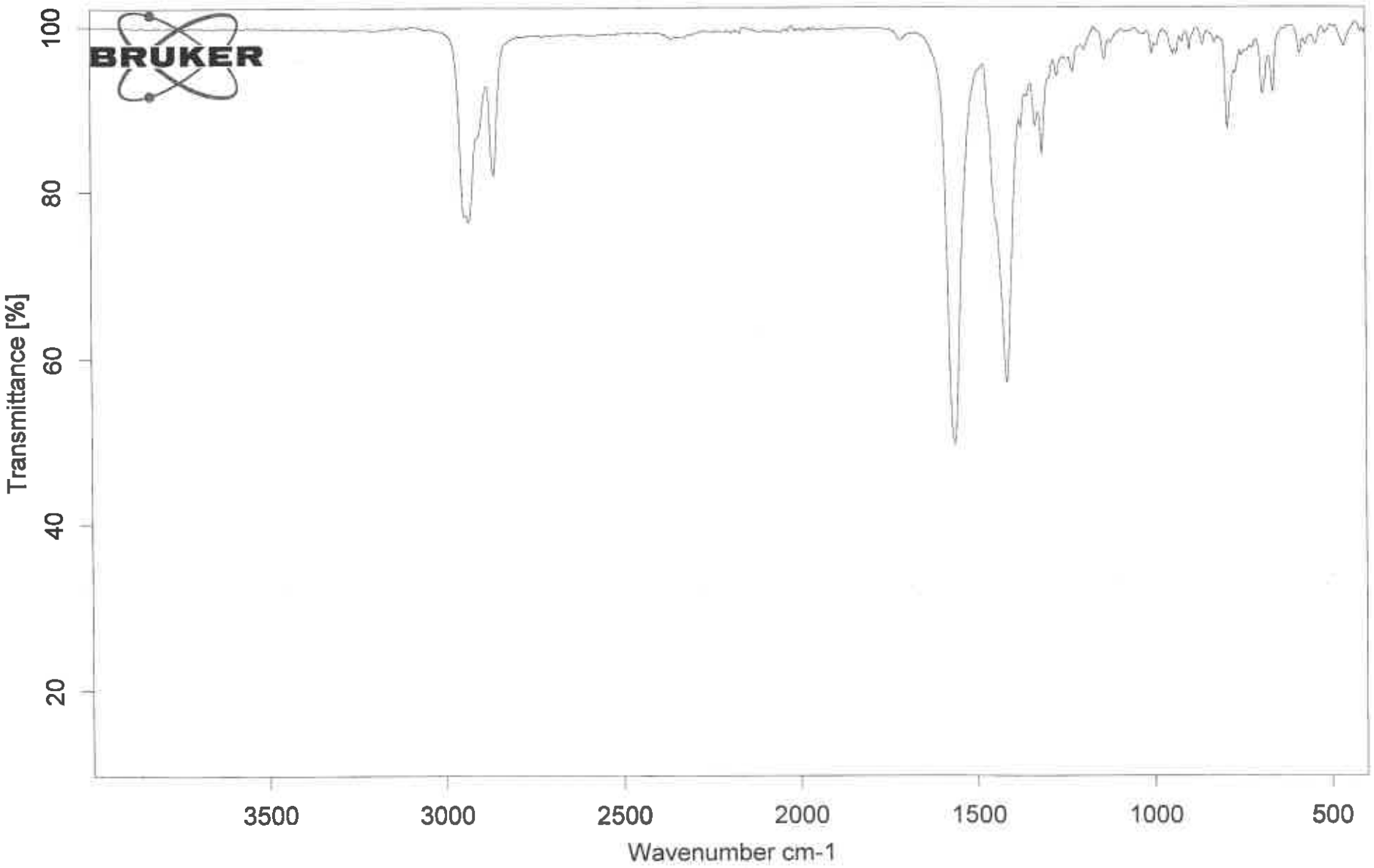
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL027 Mg 0	CMJL027 Mg	Instrument type and / or accessory	03/02/2017



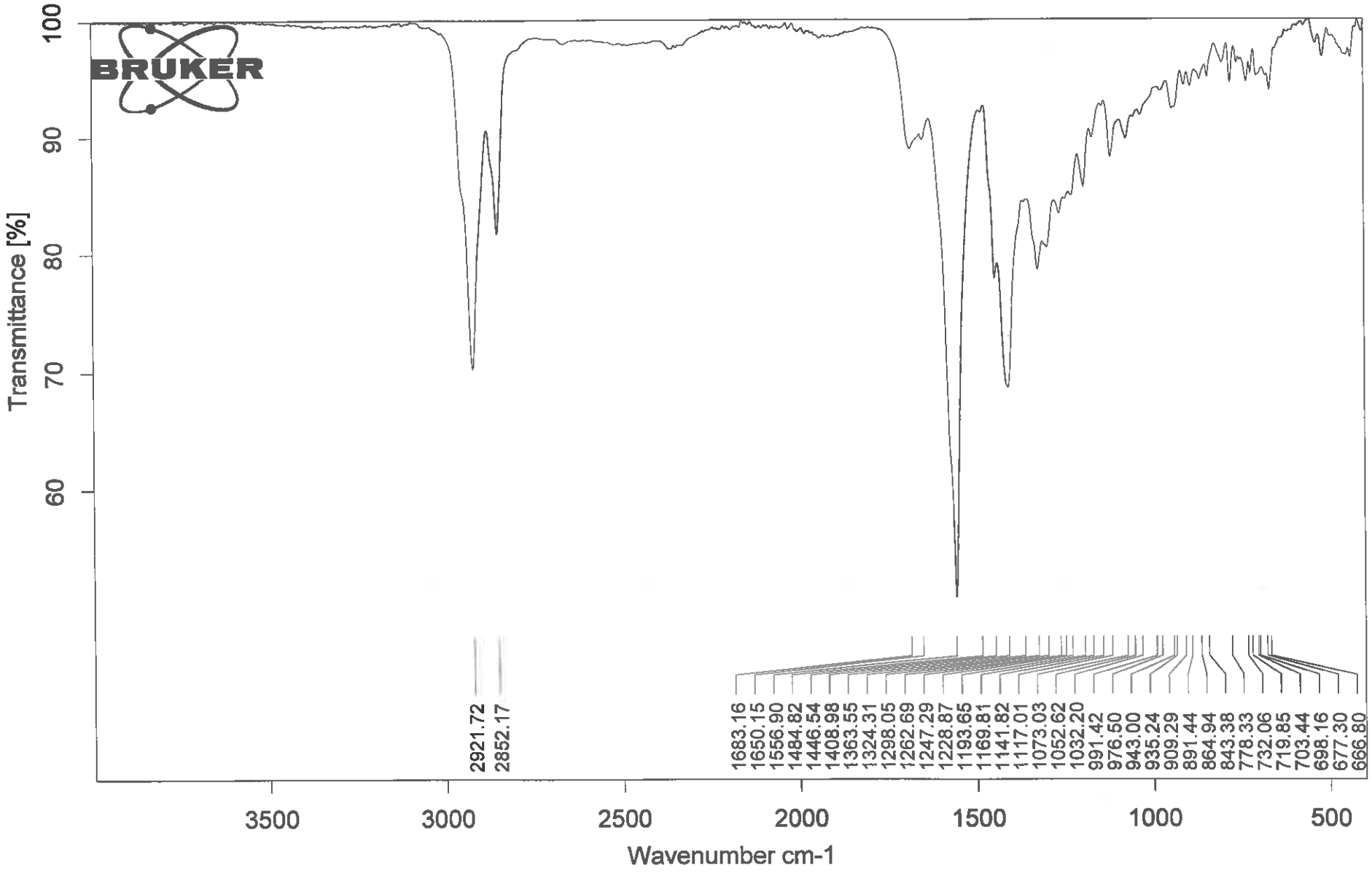
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL035.0	CMJL035	Instrument type and / or accessory	03/02/2017



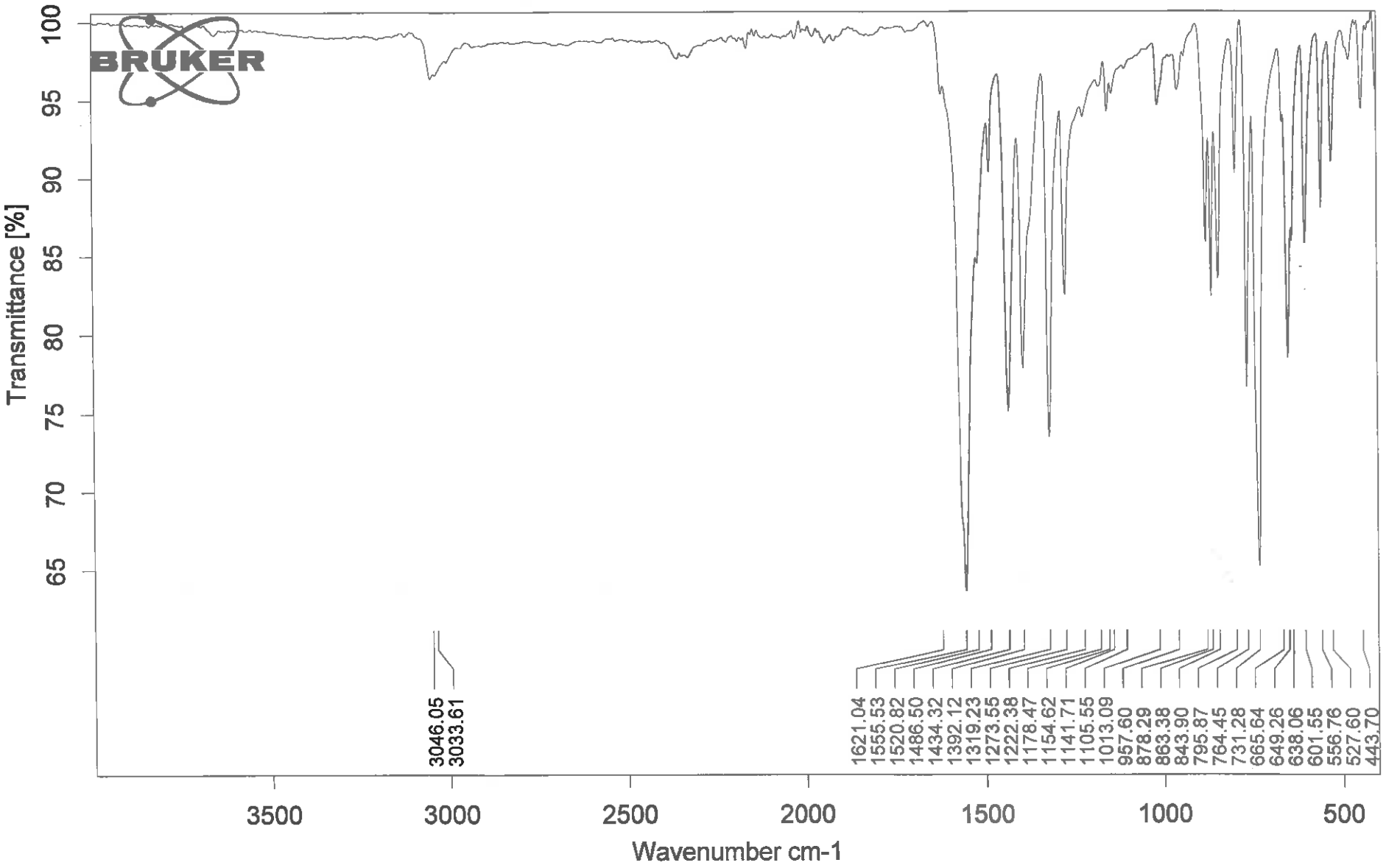
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL036.0	CMJL036	Instrument type and / or accessory	03/02/2017



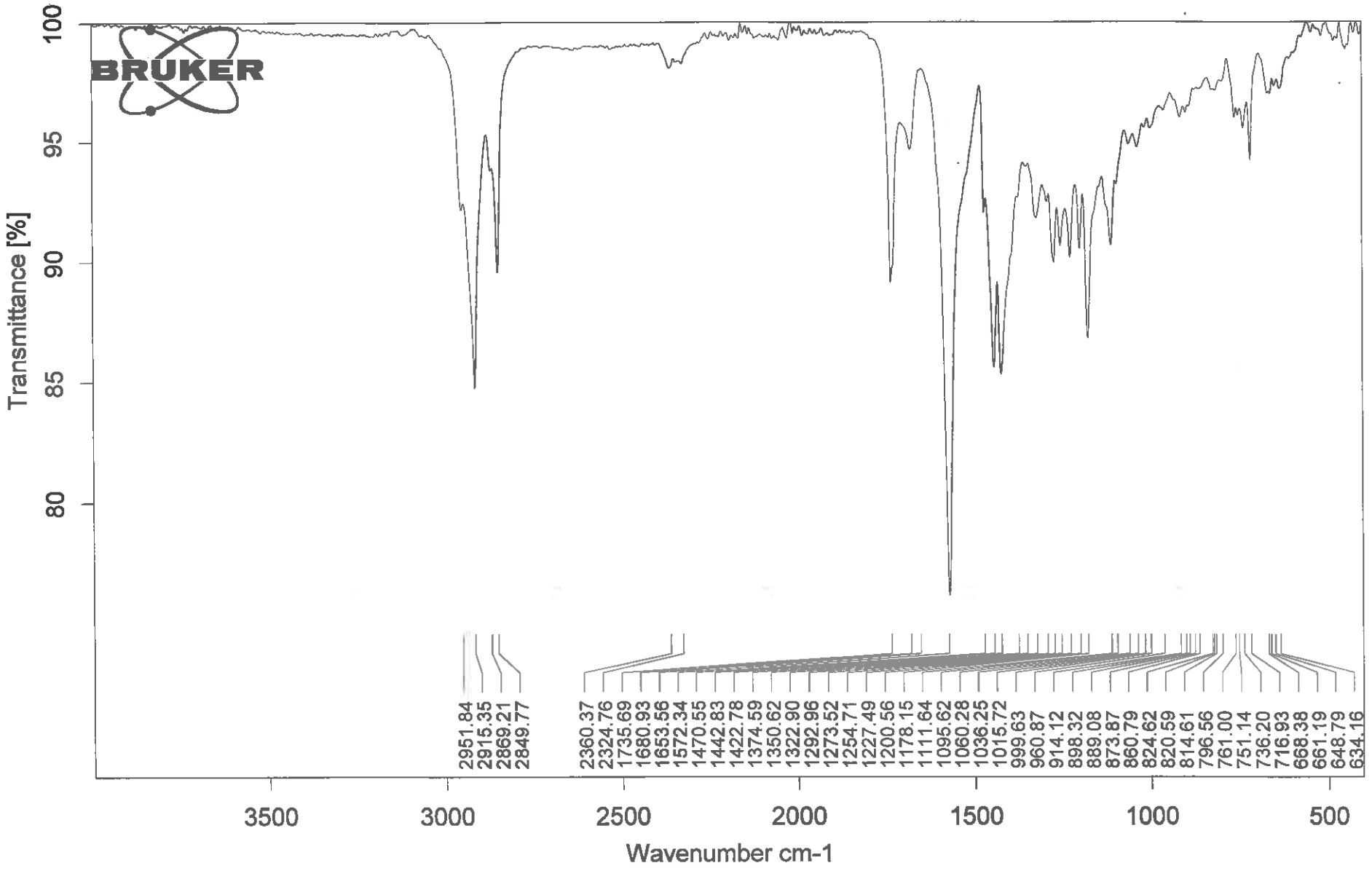
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL037.0	CMJL037	Instrument type and / or accessory	03/02/2017



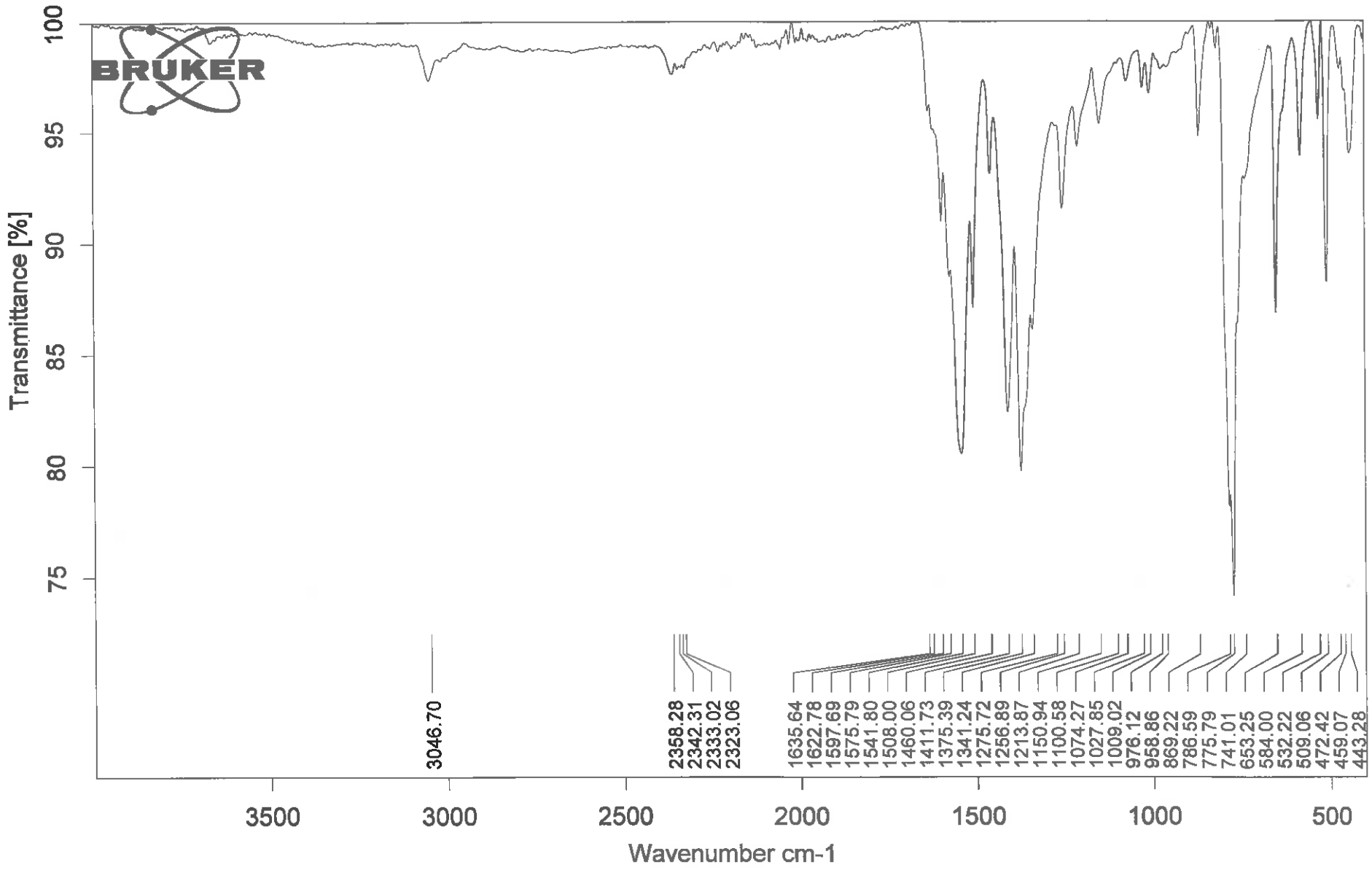
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL038.0	CMJL038	Instrument type and / or accessory	03/02/2017



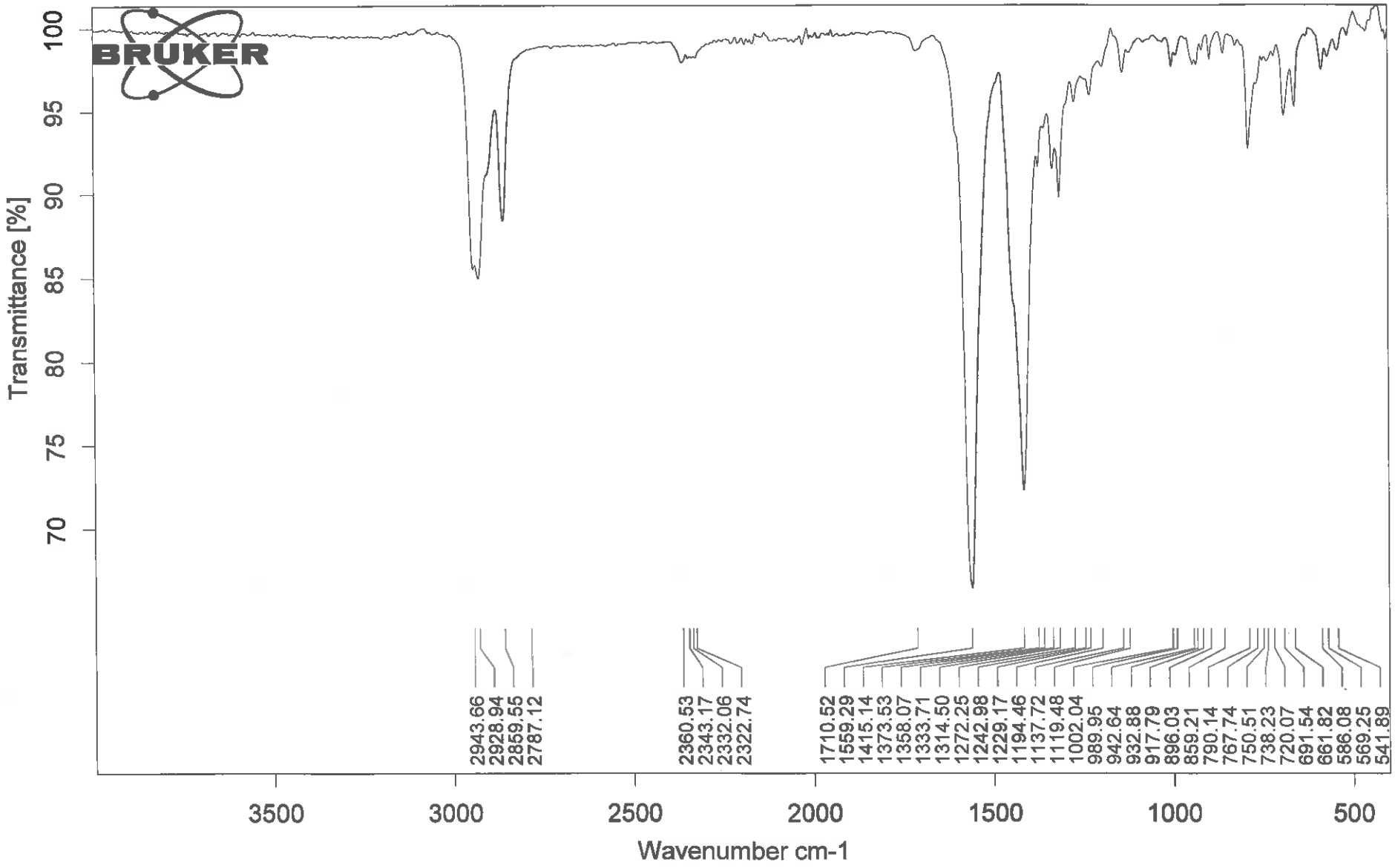
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL040.0	CMJL040	Instrument type and / or accessory	03/02/2017



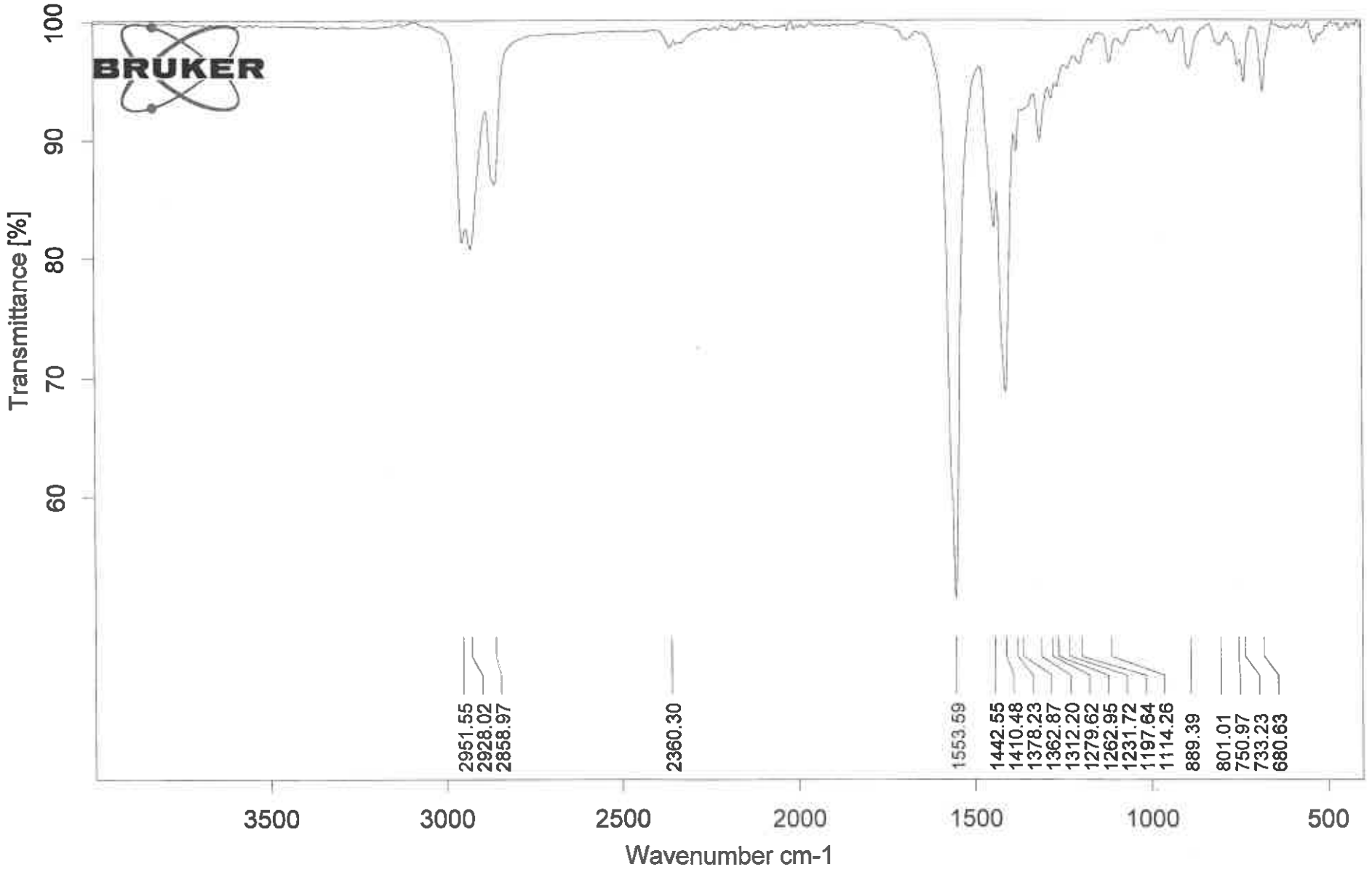
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL041.0	CMJL041	Instrument type and / or accessory	03/02/2017



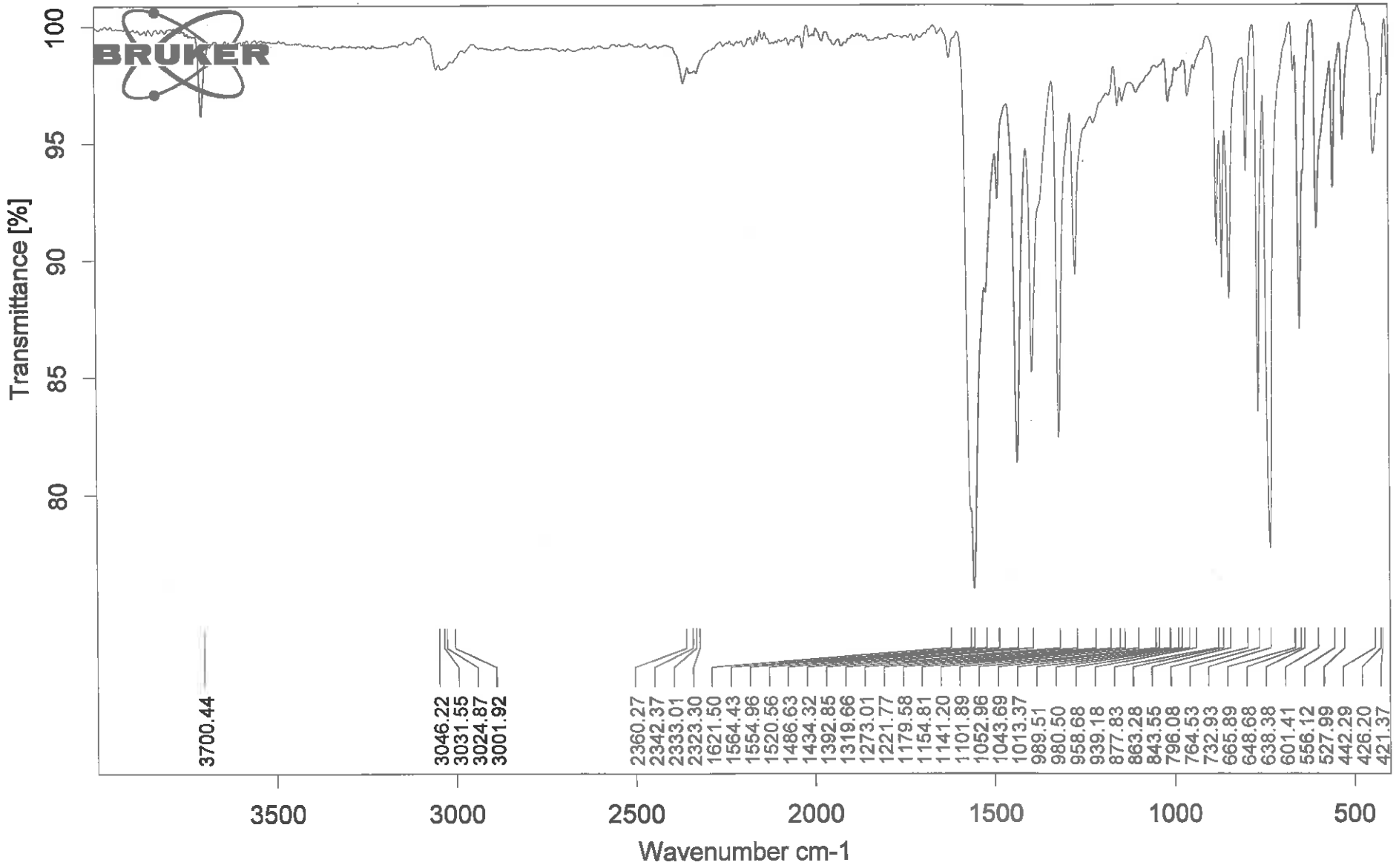
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL042.0	CMJL042	Instrument type and / or accessory	03/02/2017



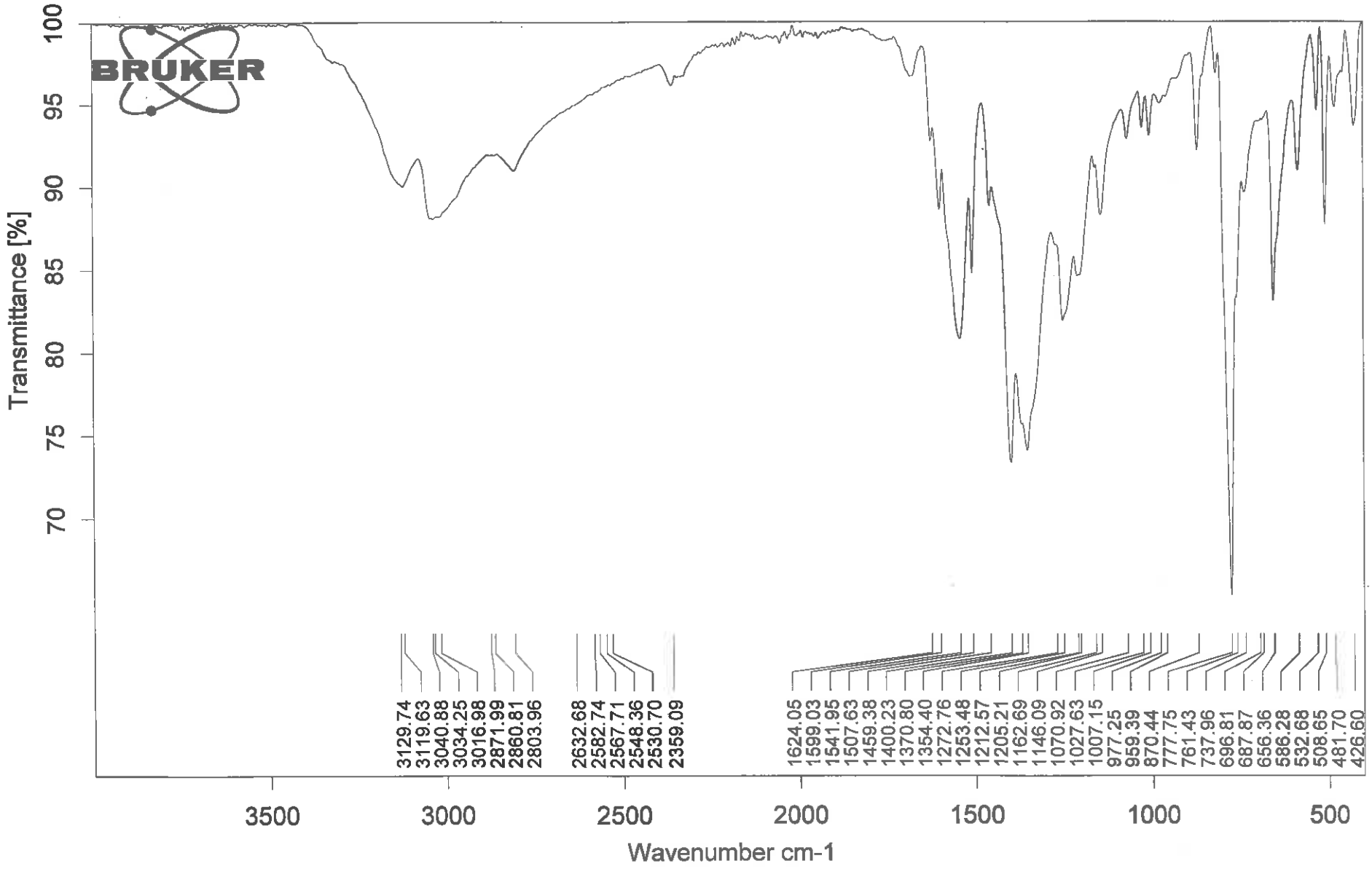
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL043.0	CMJL043	Instrument type and / or accessory	03/02/2017



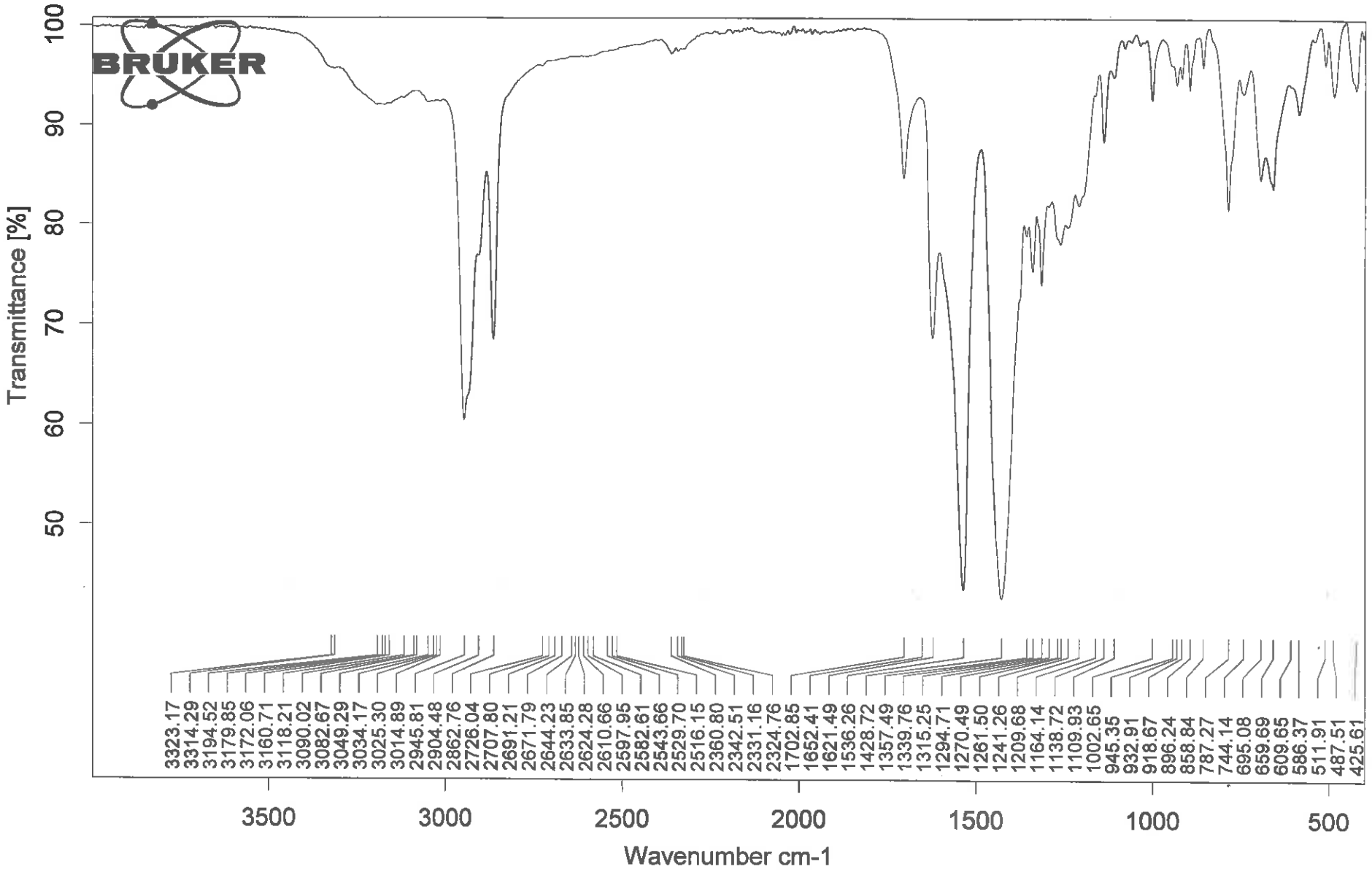
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL044.0	CMJL044	Instrument type and / or accessory	03/02/2017



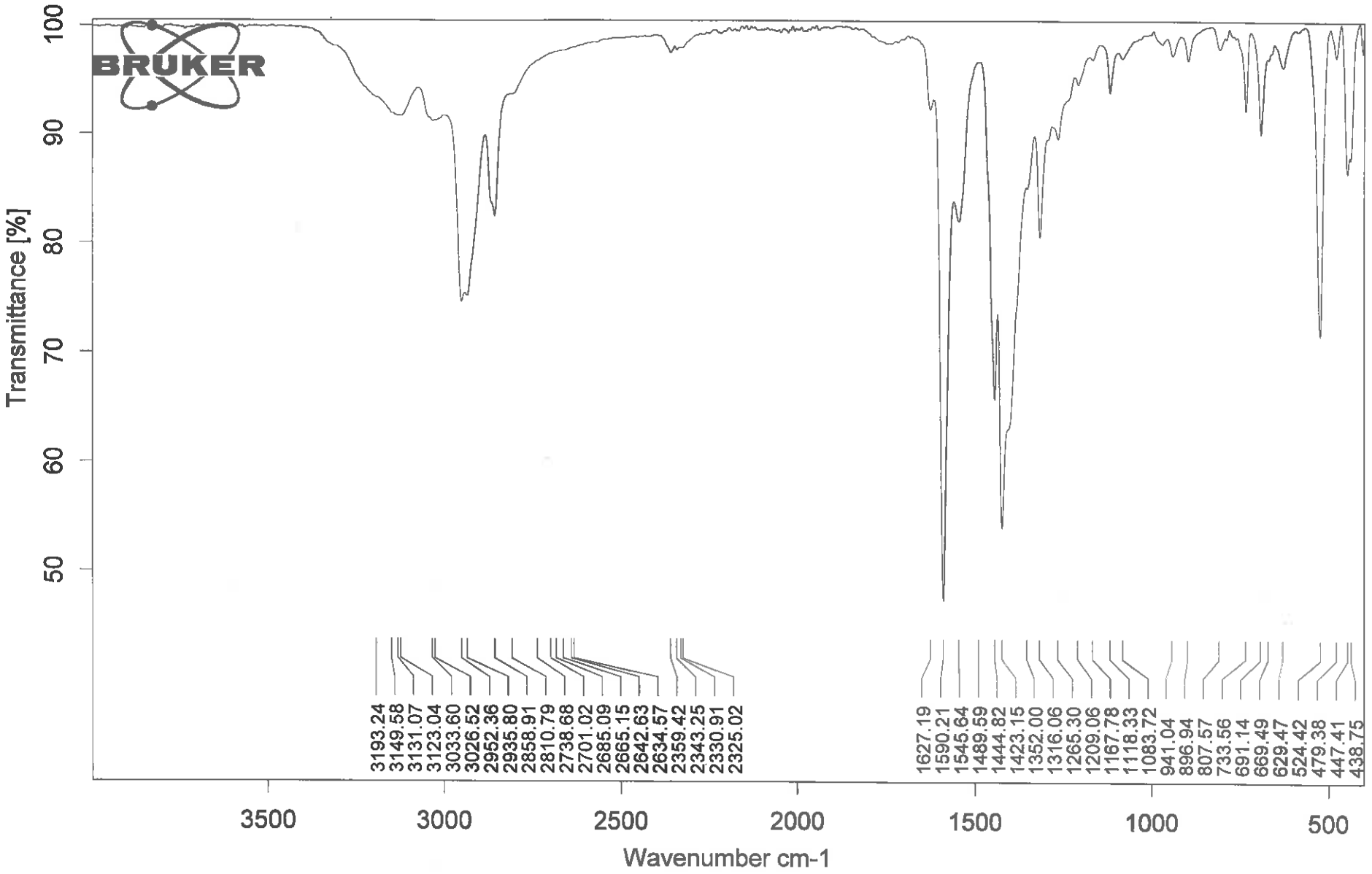
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL045.0	CMJL045	Instrument type and / or accessory	03/02/2017



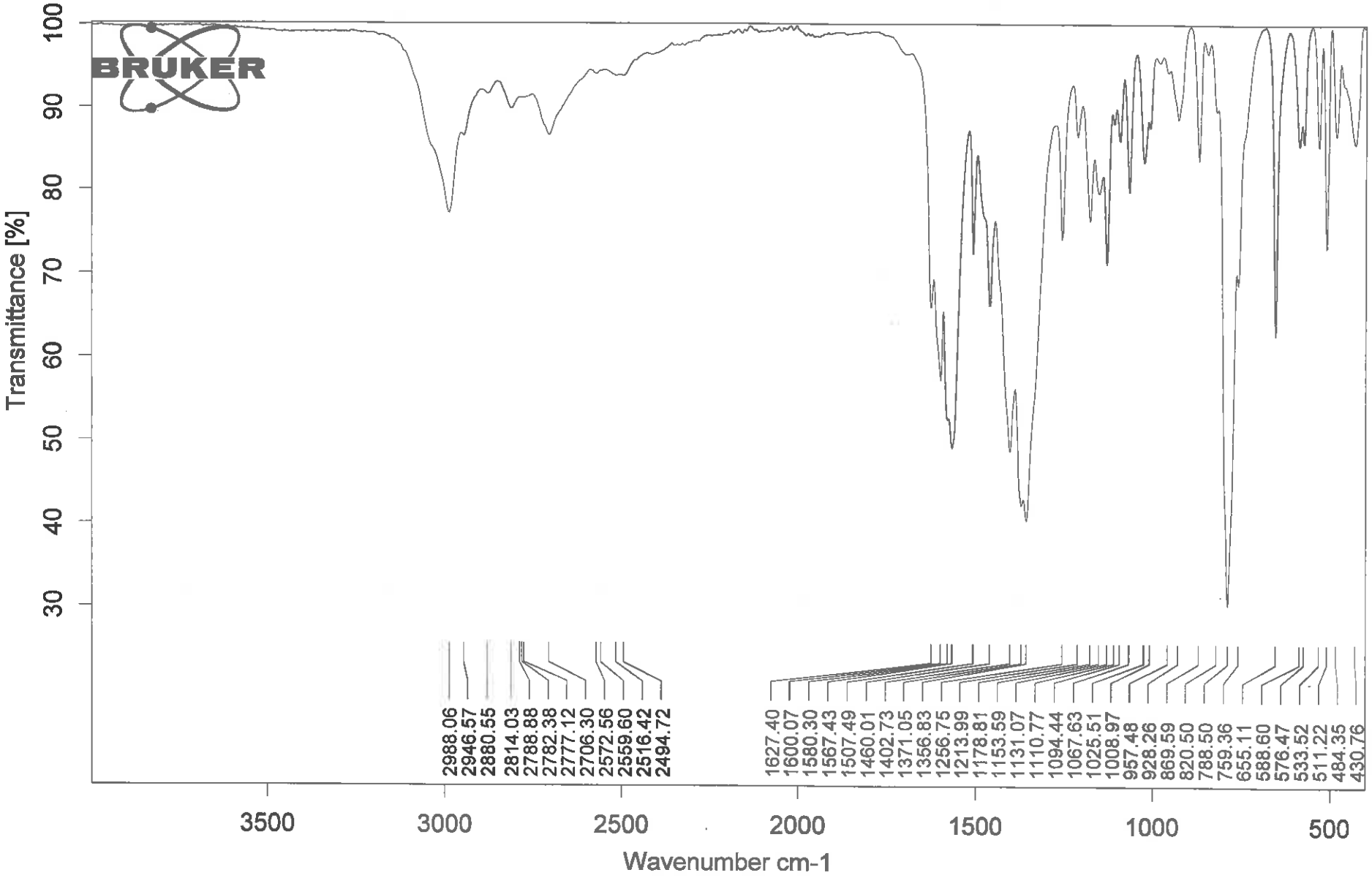
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL046 yellow.0	CMJL046 yellow	Instrument type and / or accessory	03/02/2017



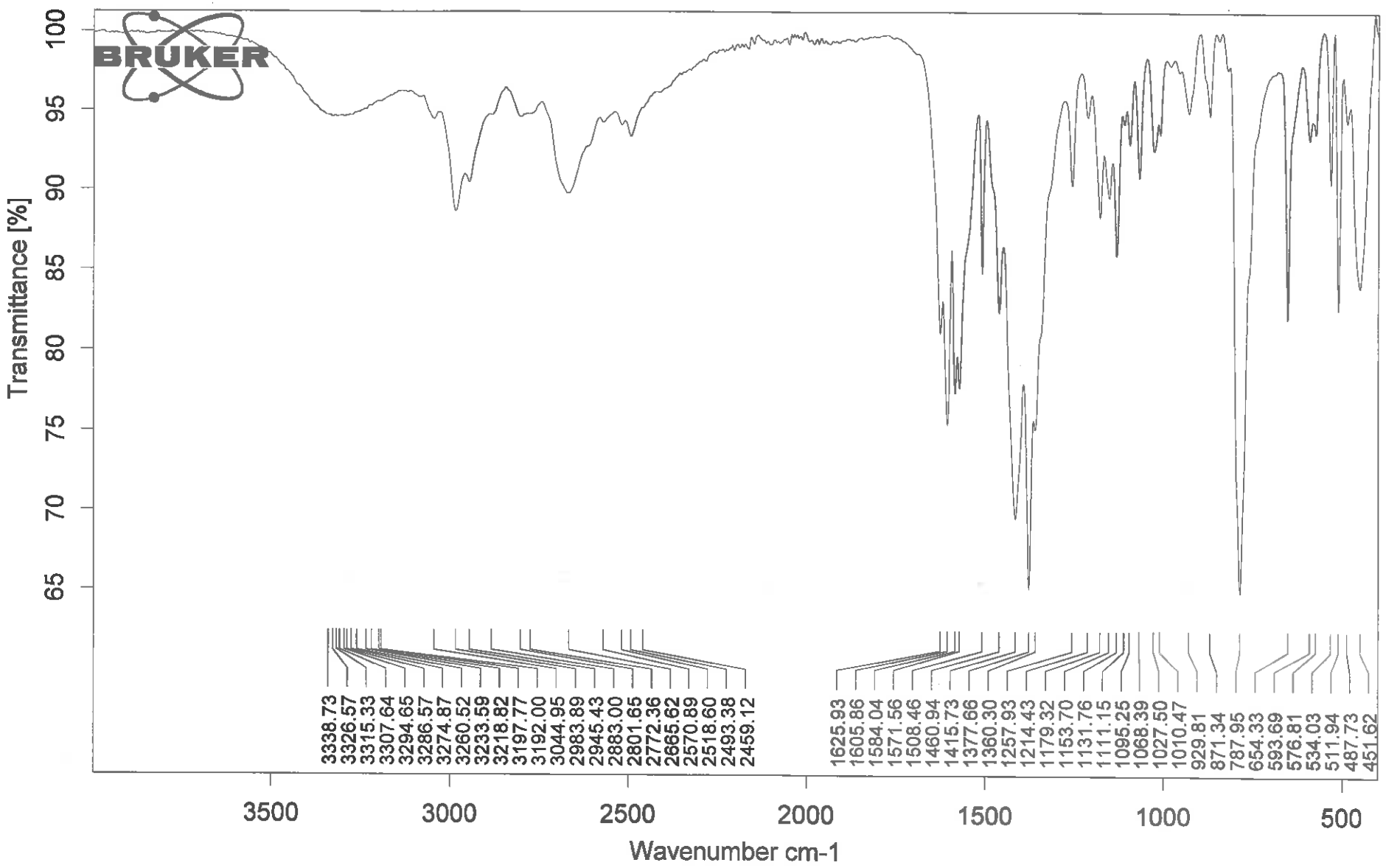
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL047.0	CMJL047	Instrument type and / or accessory	03/02/2017



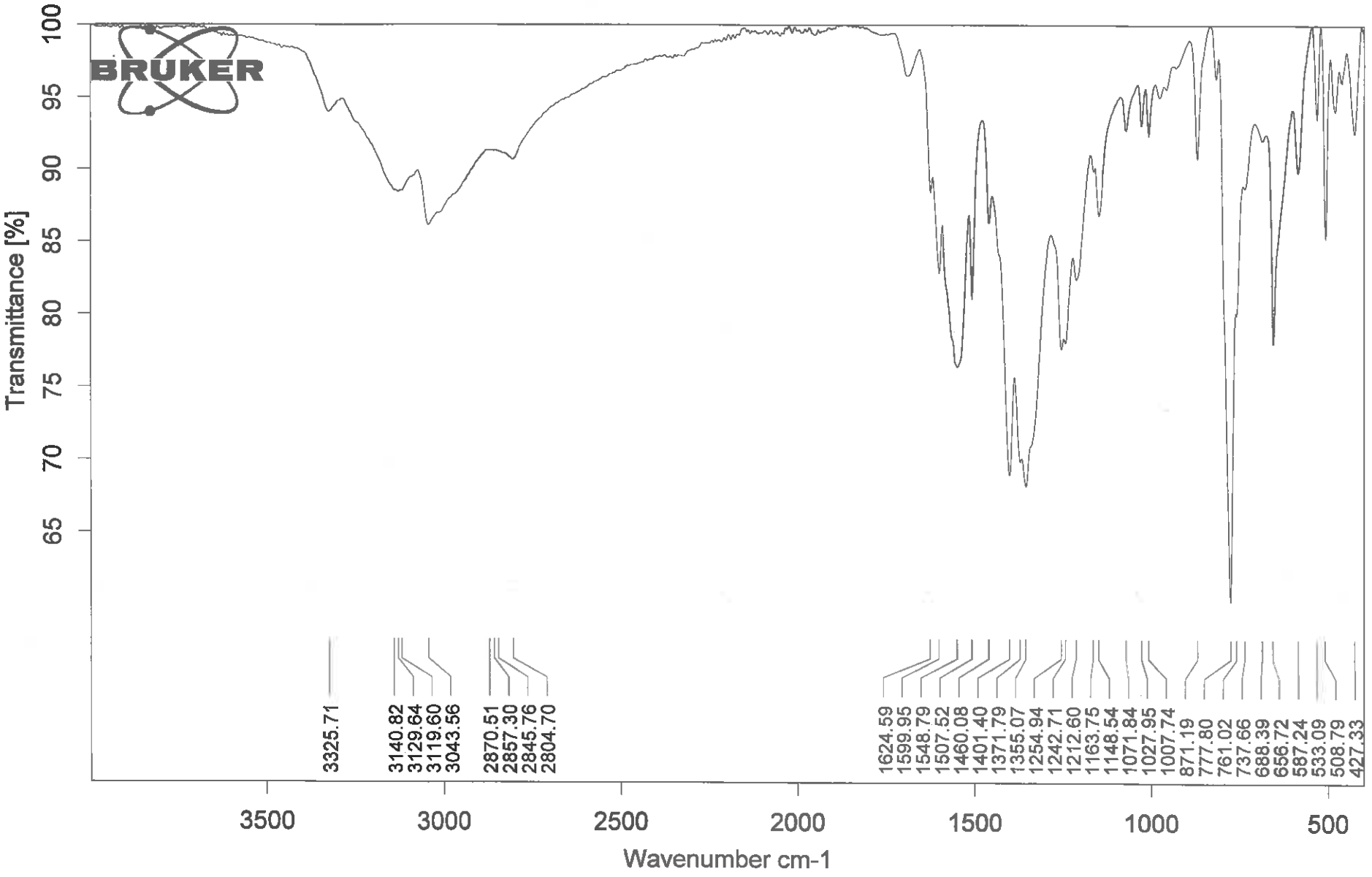
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL048.0	CMJL048	Instrument type and / or accessory	03/02/2017



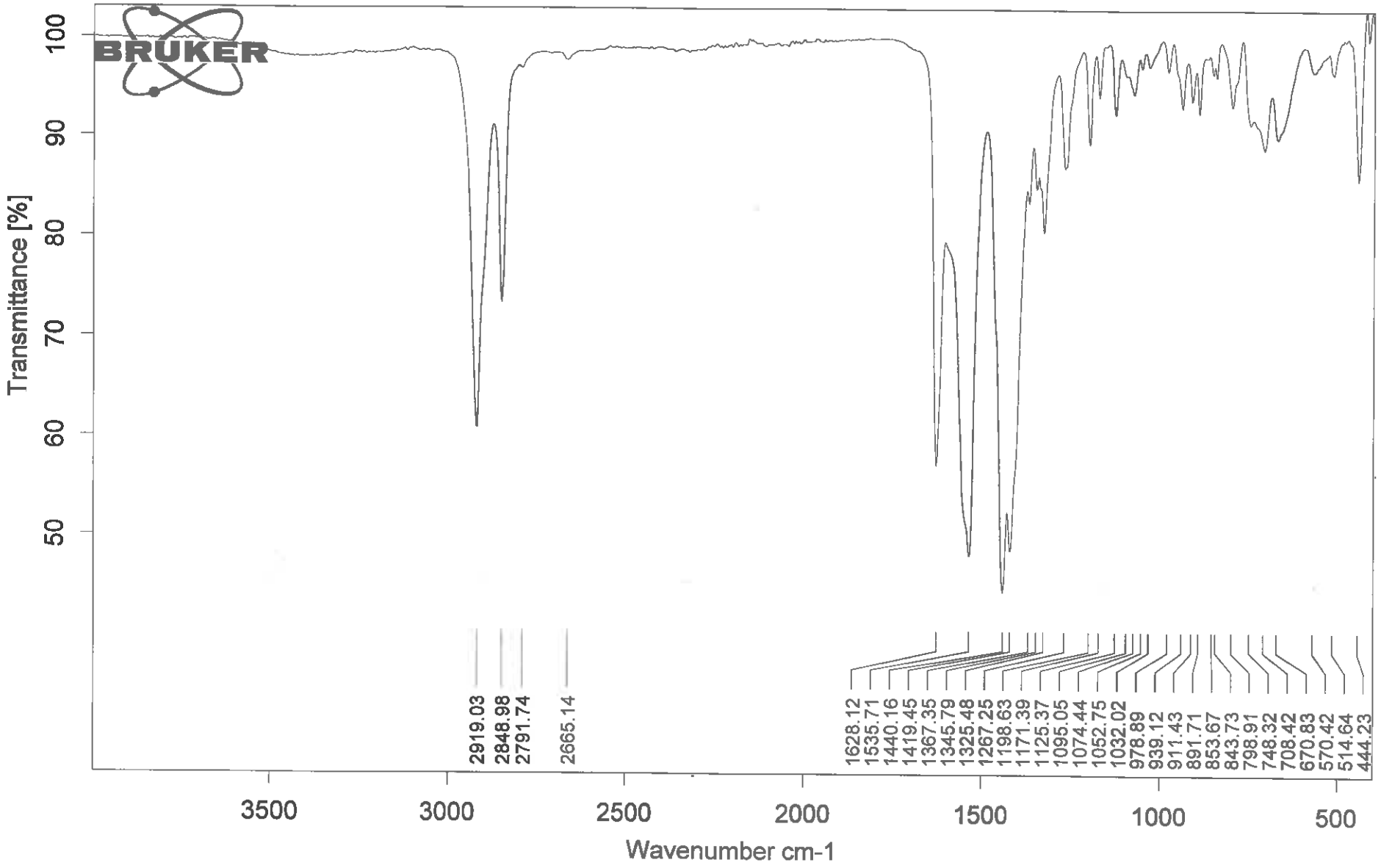
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL049.0	CMJL049	Instrument type and / or accessory	09/02/2017



C:\Users\SMUCHEM\Desktop\Matthew L\CMJL050.0	CMJL050	Instrument type and / or accessory	09/02/2017



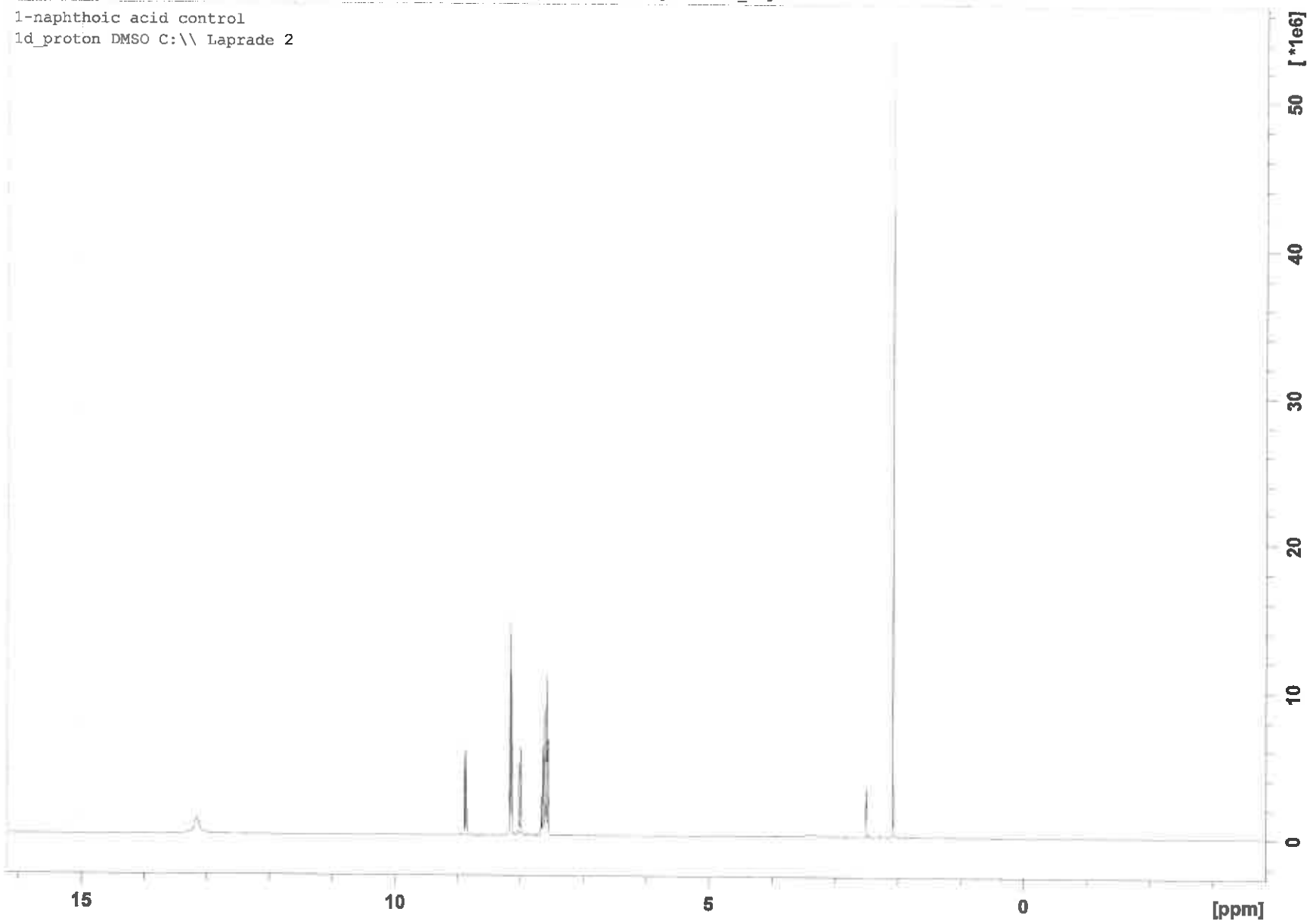
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL052.0	CMJL052	Instrument type and / or accessory	02/03/2017

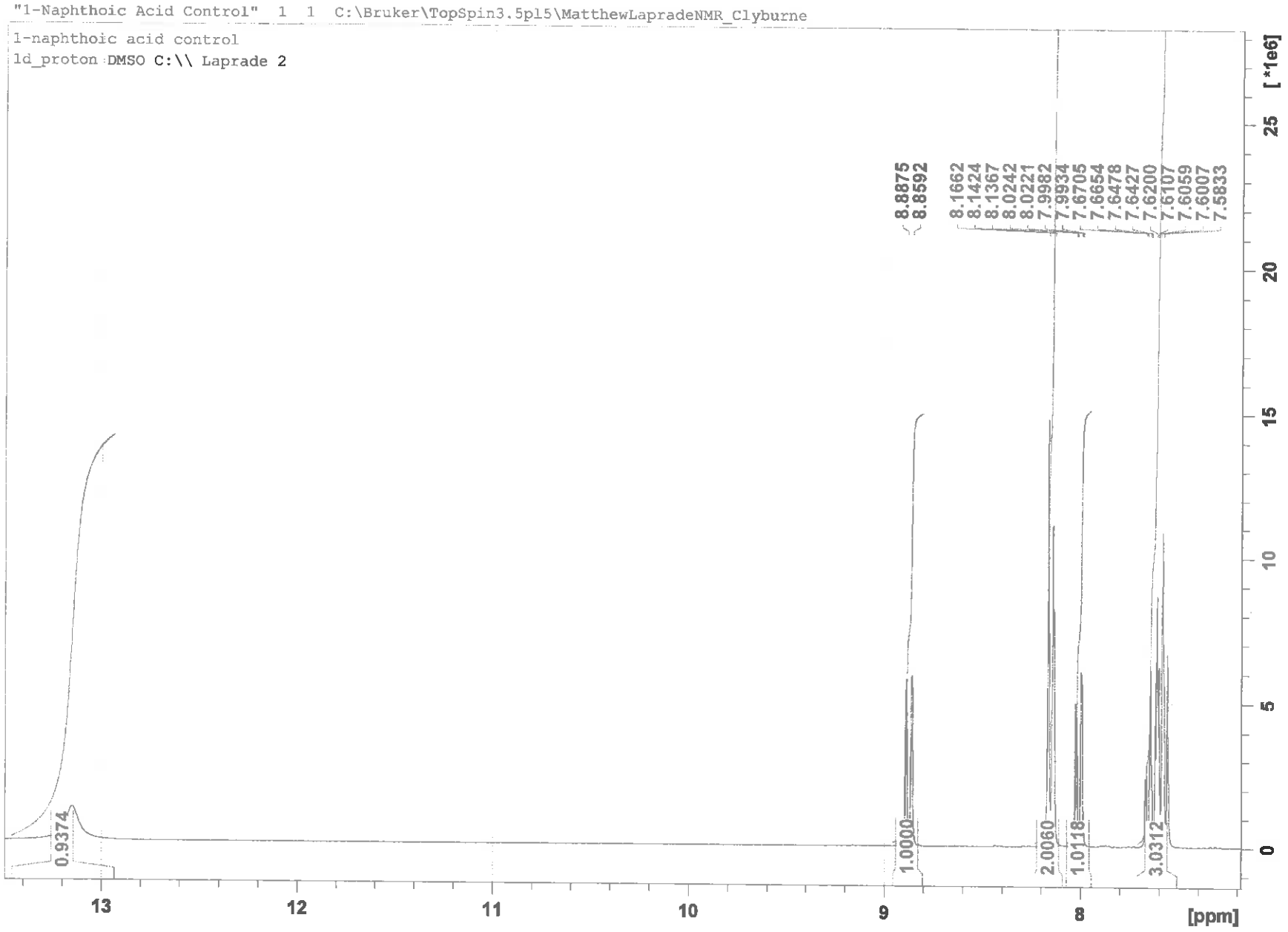


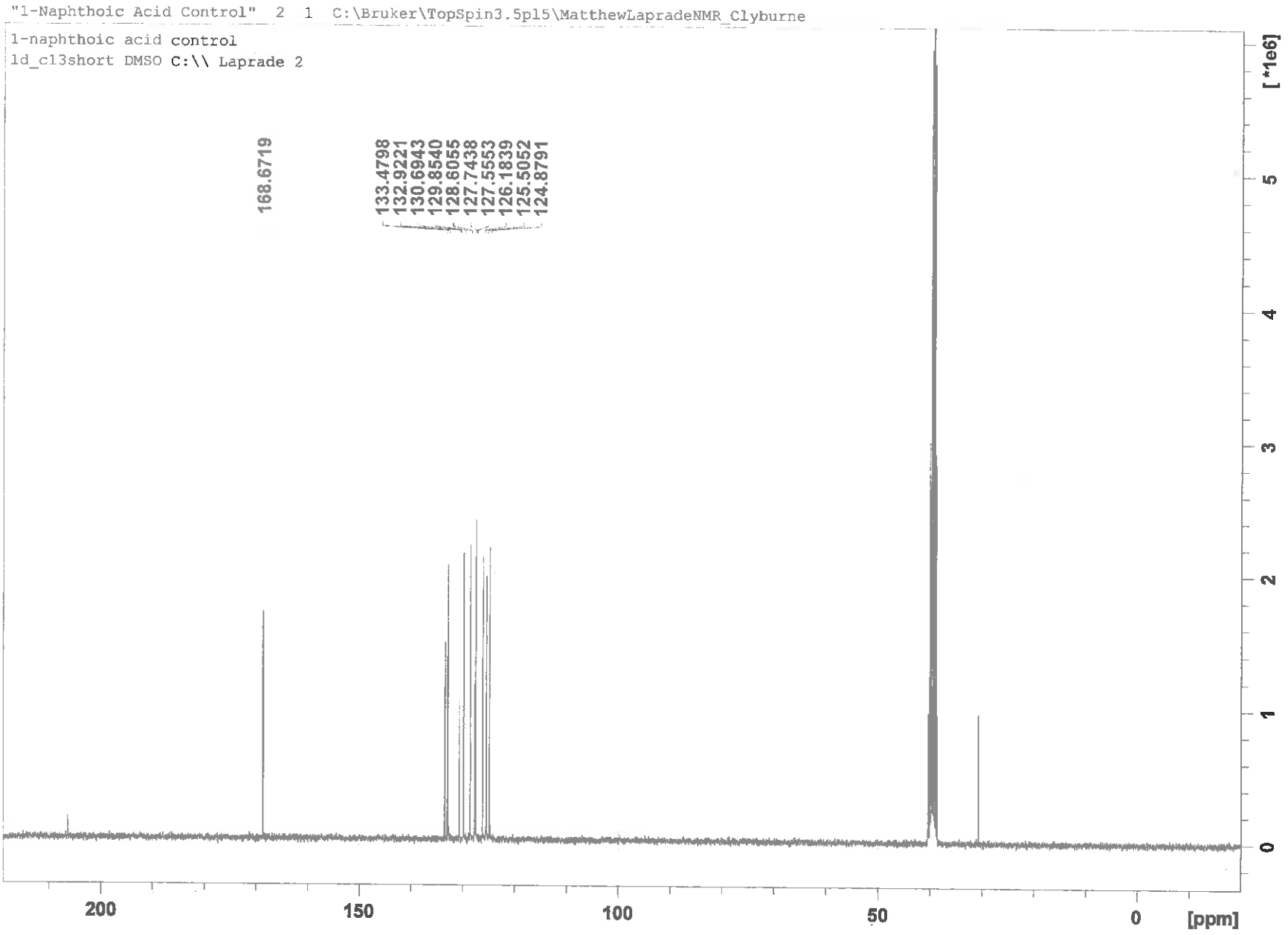
C:\Users\SMUCHEM\Desktop\Matthew L\CMJL053.0	CMJL053	Instrument type and / or accessory	02/03/2017

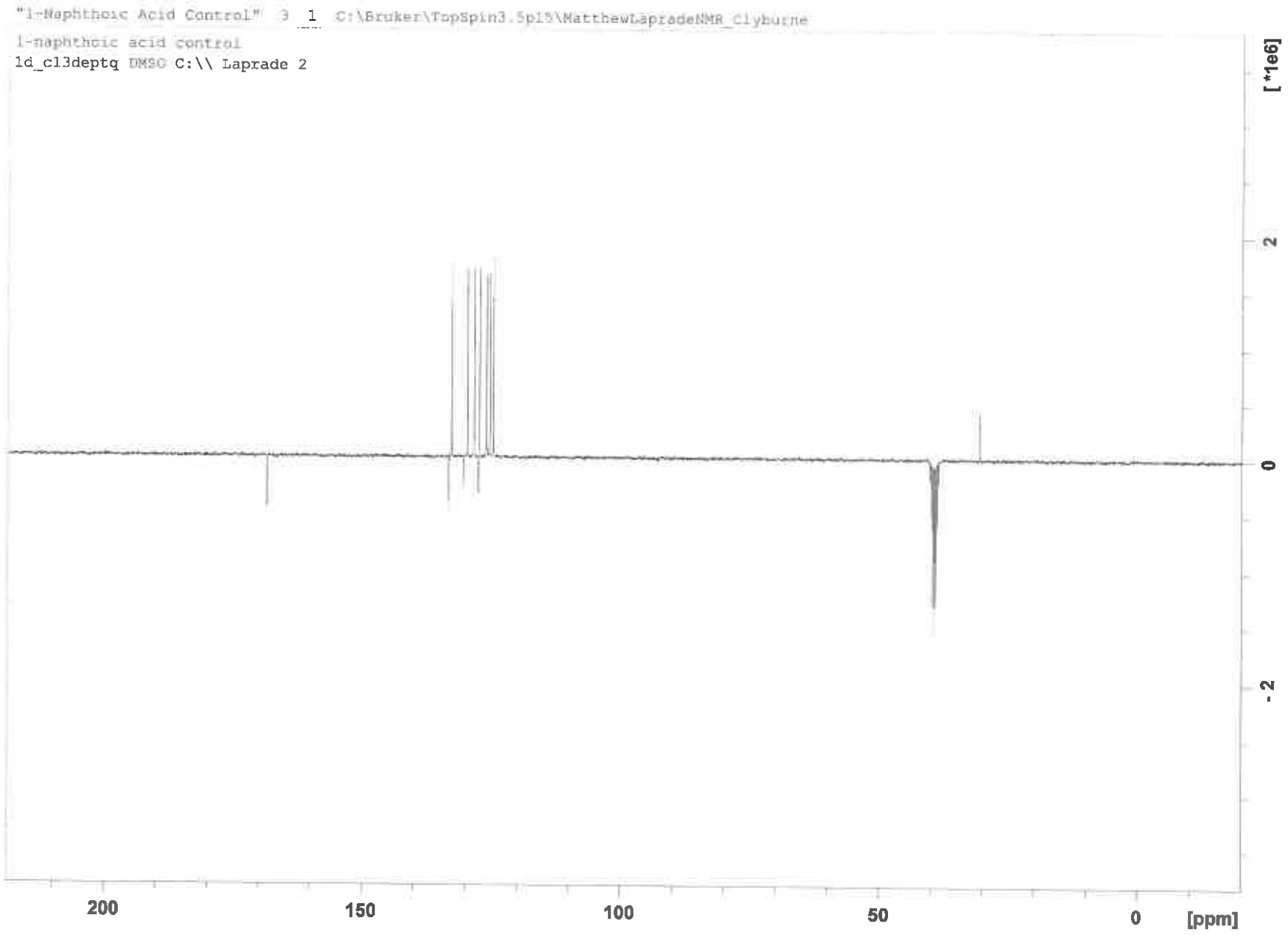
"1-Naphthoic Acid Control" 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne

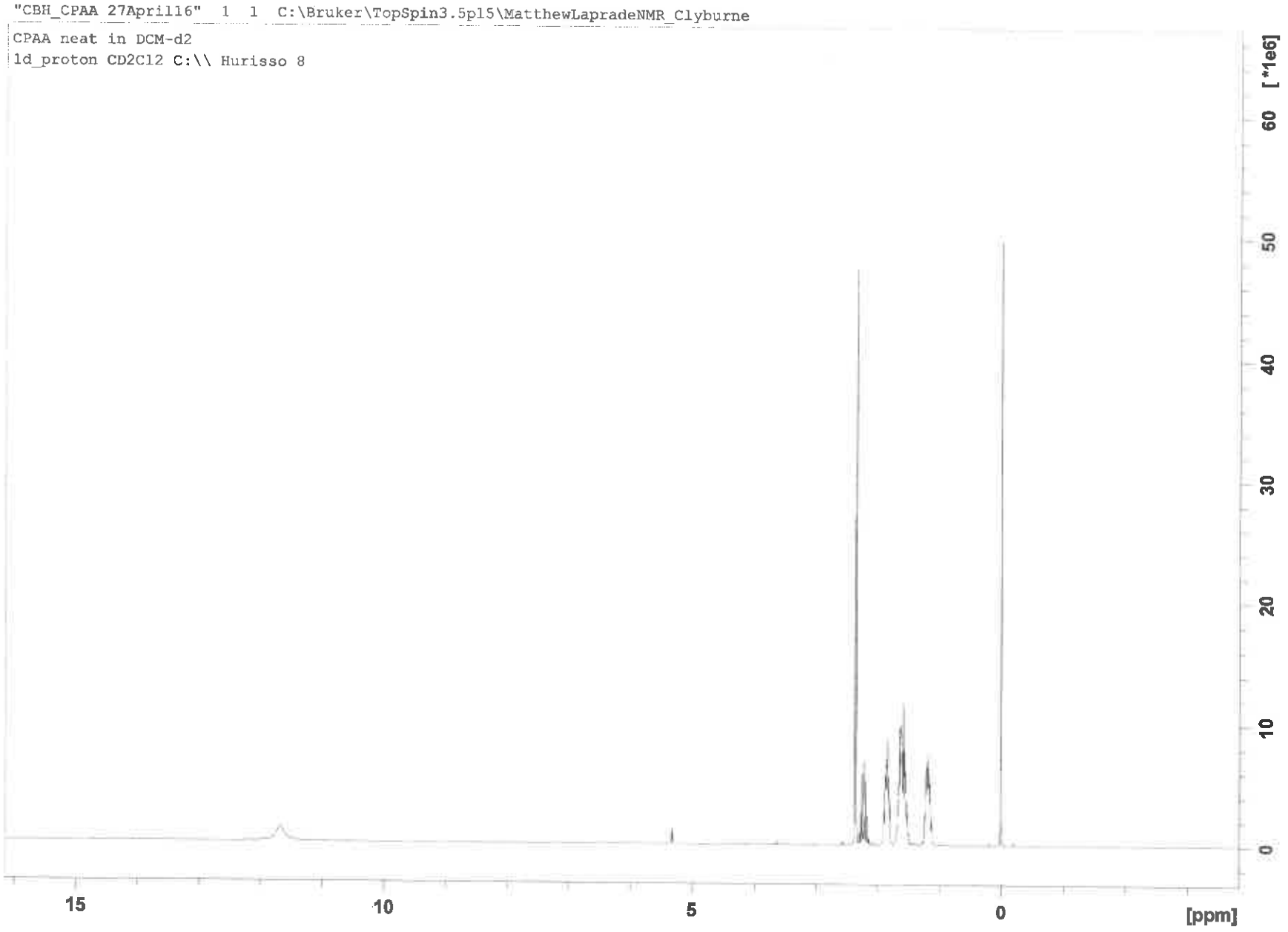
1-naphthoic acid control
1d_proton DMSO C:\\ Laprade 2

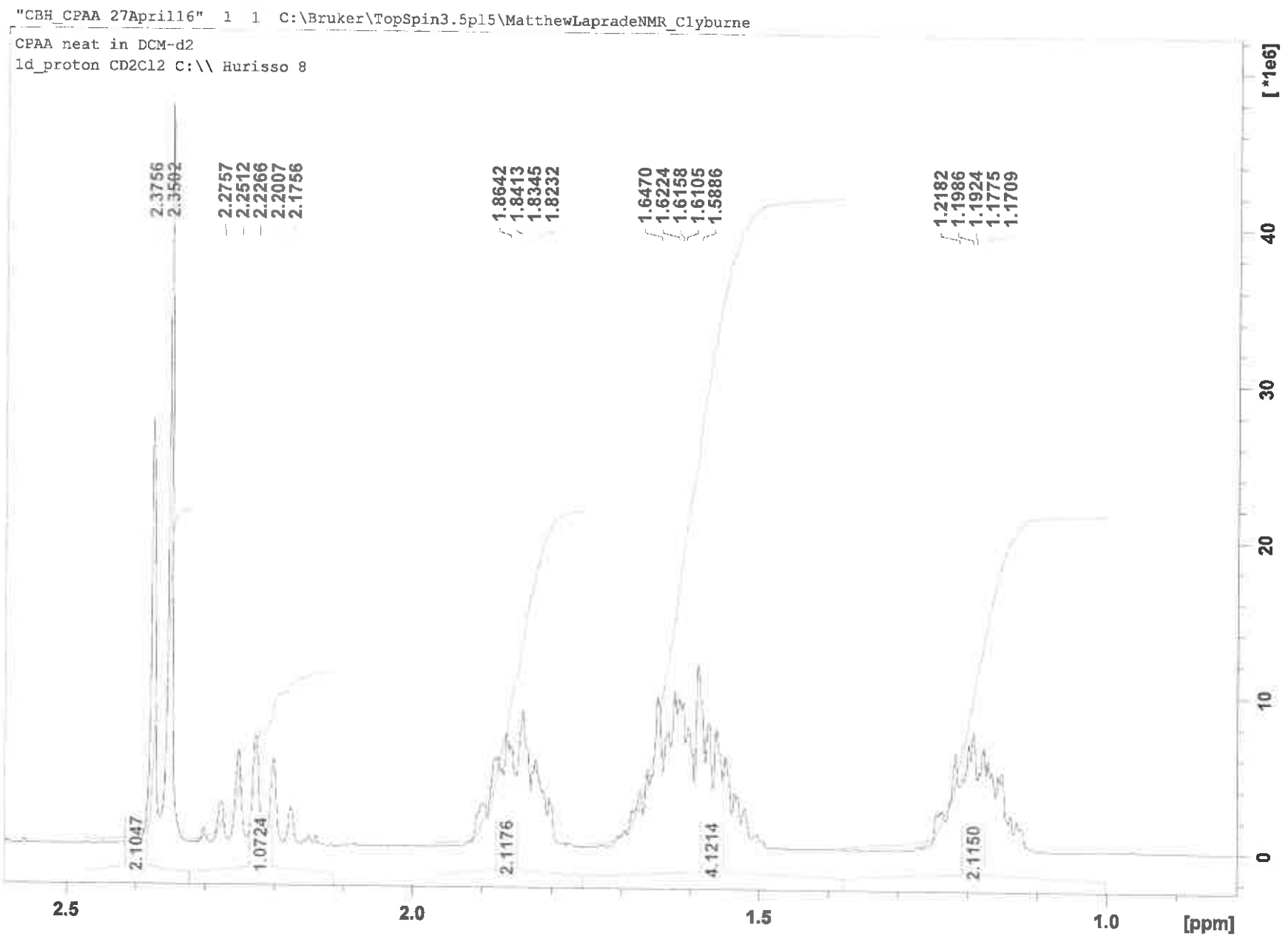


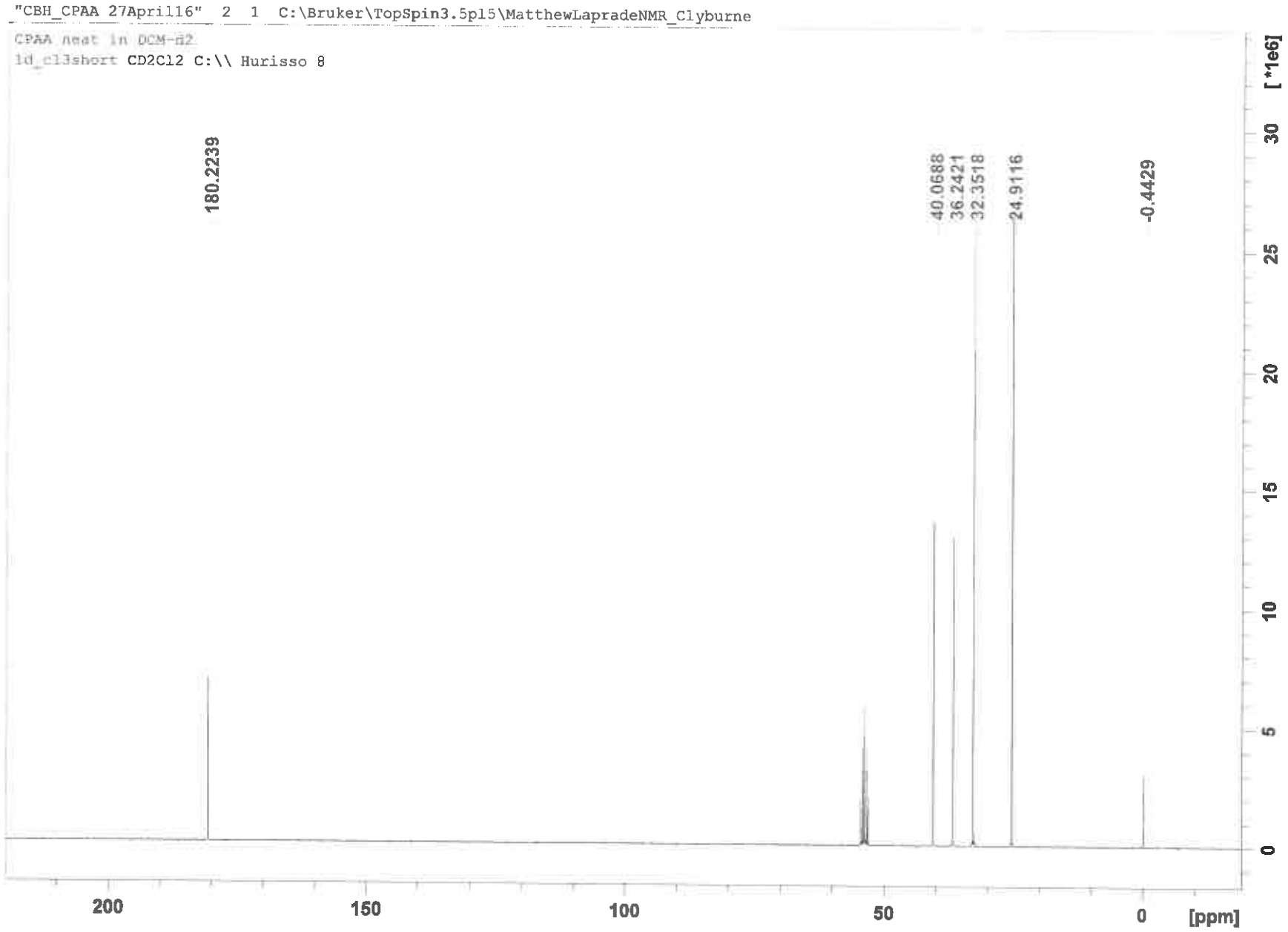

"1-Naphthoic Acid Control" 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-naphthoic acid control
1d_proton DMSO C:\\ Laprade 2
8.8875
8.8592
8.1662
8.1424
8.1367
8.0242
8.0221
7.9982
7.9934
7.6705
7.6654
7.6478
7.6427
7.6200
7.6107
7.6059
7.6007
7.5833
0.9374
1.0000
2.0060
1.0118
3.0312
13
12
11
10
9
8
[ppm]
[*1e6]
25
20
15
10
5
0


"1-Naphthoic Acid Control" 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-naphthoic acid control
1d_c13short DMSO C:\\ Laprade 2
168.6719
133.4798
132.9221
130.6943
129.8540
128.6055
127.7438
127.5553
126.1839
125.5052
124.8791
[*1e6]
0
1
2
3
4
5
200
150
100
50
0
[ppm]


"1-Naphthoic Acid Control" 3 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-naphthoic acid control
1d_c13deptq DMSO C:\\ Laprade 2
[*1e6]
2
0
-2
200
150
100
50
0
[ppm]


"CBH_CPAA 27April16" 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CPAA neat in DCM-d2
1d_proton CD2Cl2 C:\\ Hurisso 8
[*1e6]
60
50
40
30
20
10
0
15
10
5
0
[ppm]

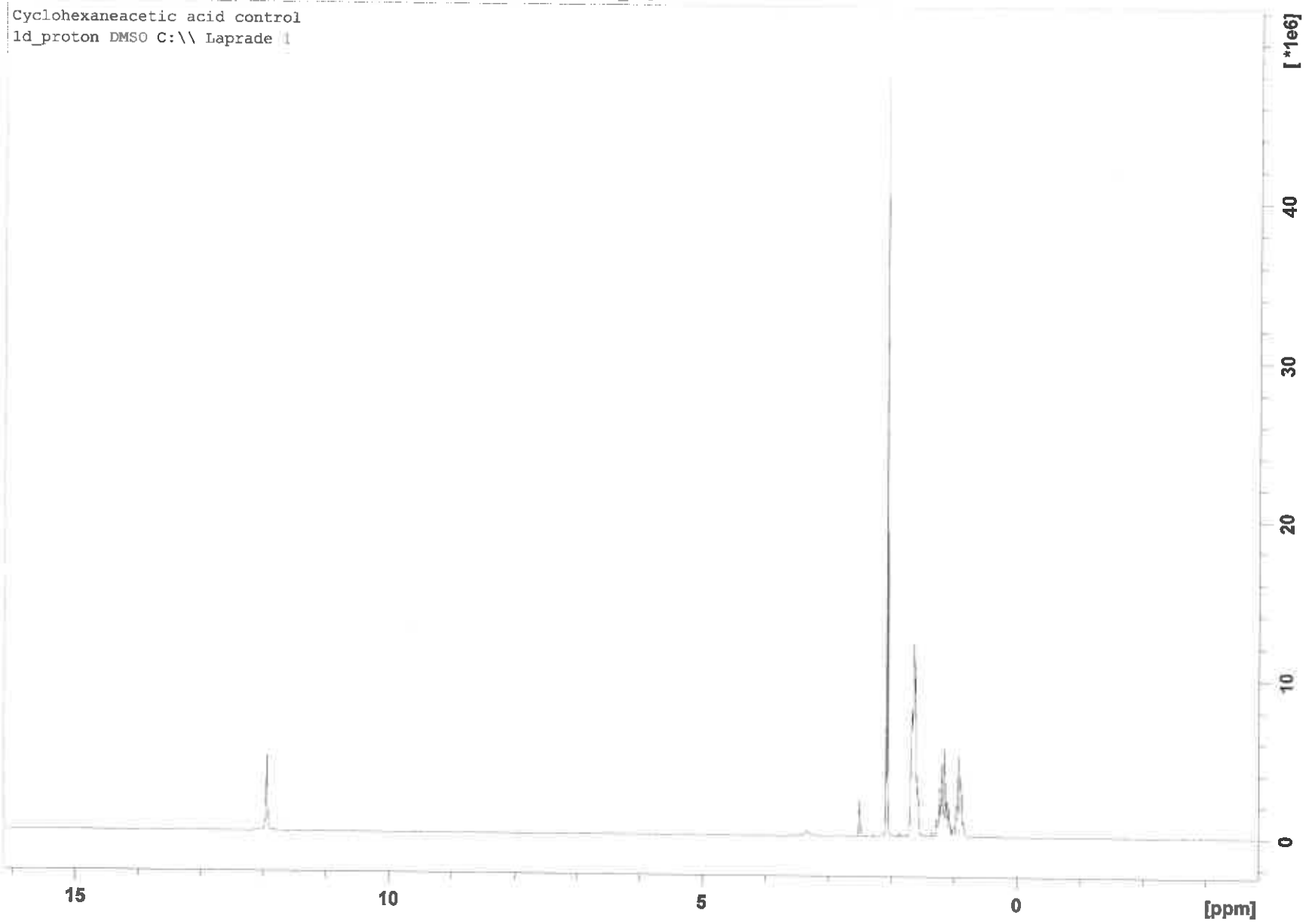

"CBH_CPAA 27April16" 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CPAA neat in DCM-d2
1d_proton CD2Cl2 C:\\ Hurisso 8
2.3756
2.3502
2.2757
2.2512
2.2266
2.2007
2.1756
1.8642
1.8413
1.8345
1.8232
1.6470
1.6224
1.6158
1.6105
1.5886
1.2182
1.1986
1.1924
1.1775
1.1709
2.1047
1.0724
2.1176
4.1214
2.1150
[*1e6]
0
10
20
30
40
2.5
2.0
1.5
1.0
[ppm]

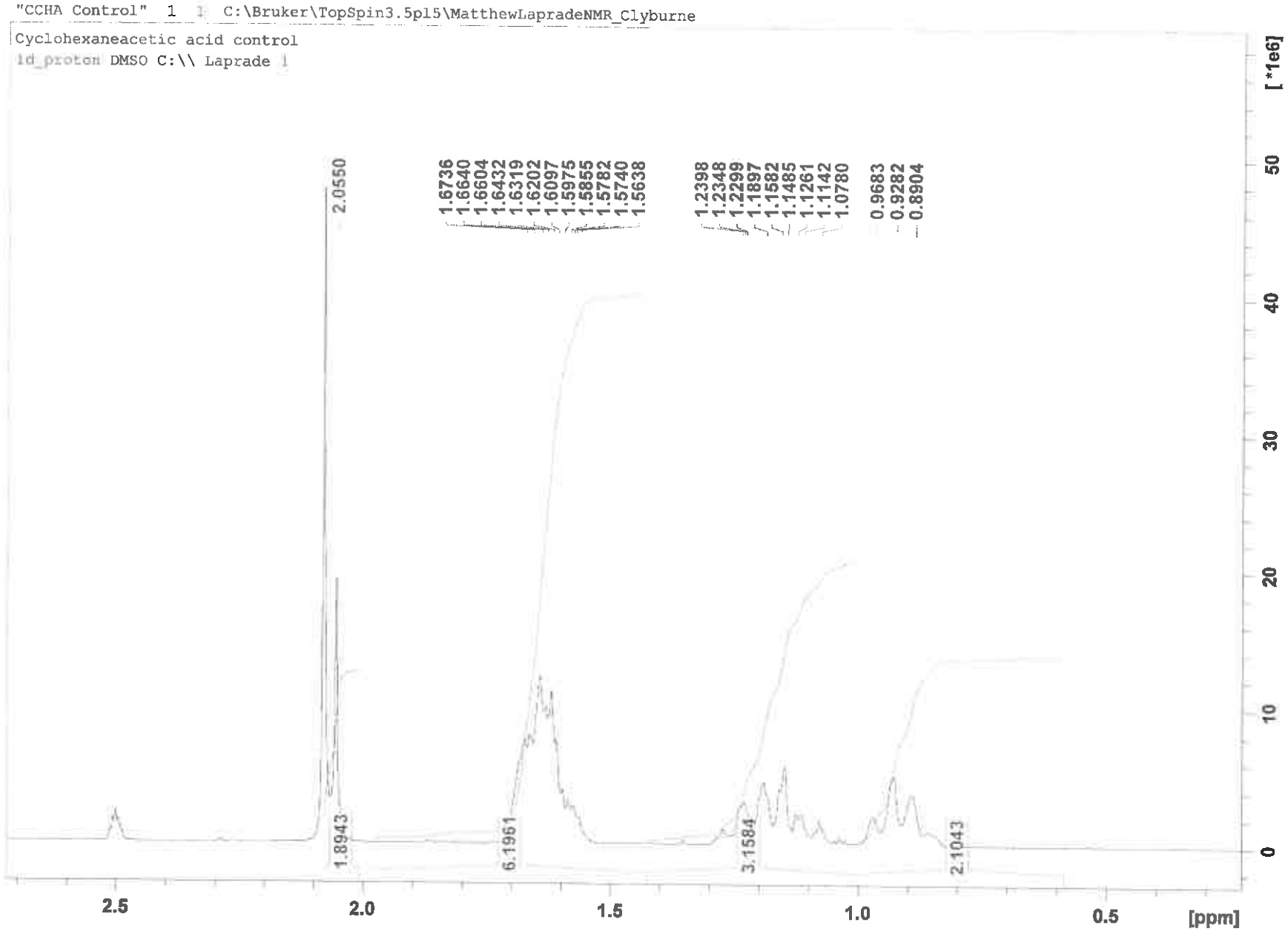

"CBH_CPAA 27April16" 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CPAA neat in DCM-d2
1d_c13short CD2Cl2 C:\\ Hurisso 8
180.2239
40.0688
36.2421
32.3518
24.9116
-0.4429
[*1e6]
30
25
20
15
10
5
0
200
150
100
50
0
[ppm]

"CCHA Control" 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne

Cyclohexaneacetic acid control

1d_proton DMSO C:\\ Laprade 1

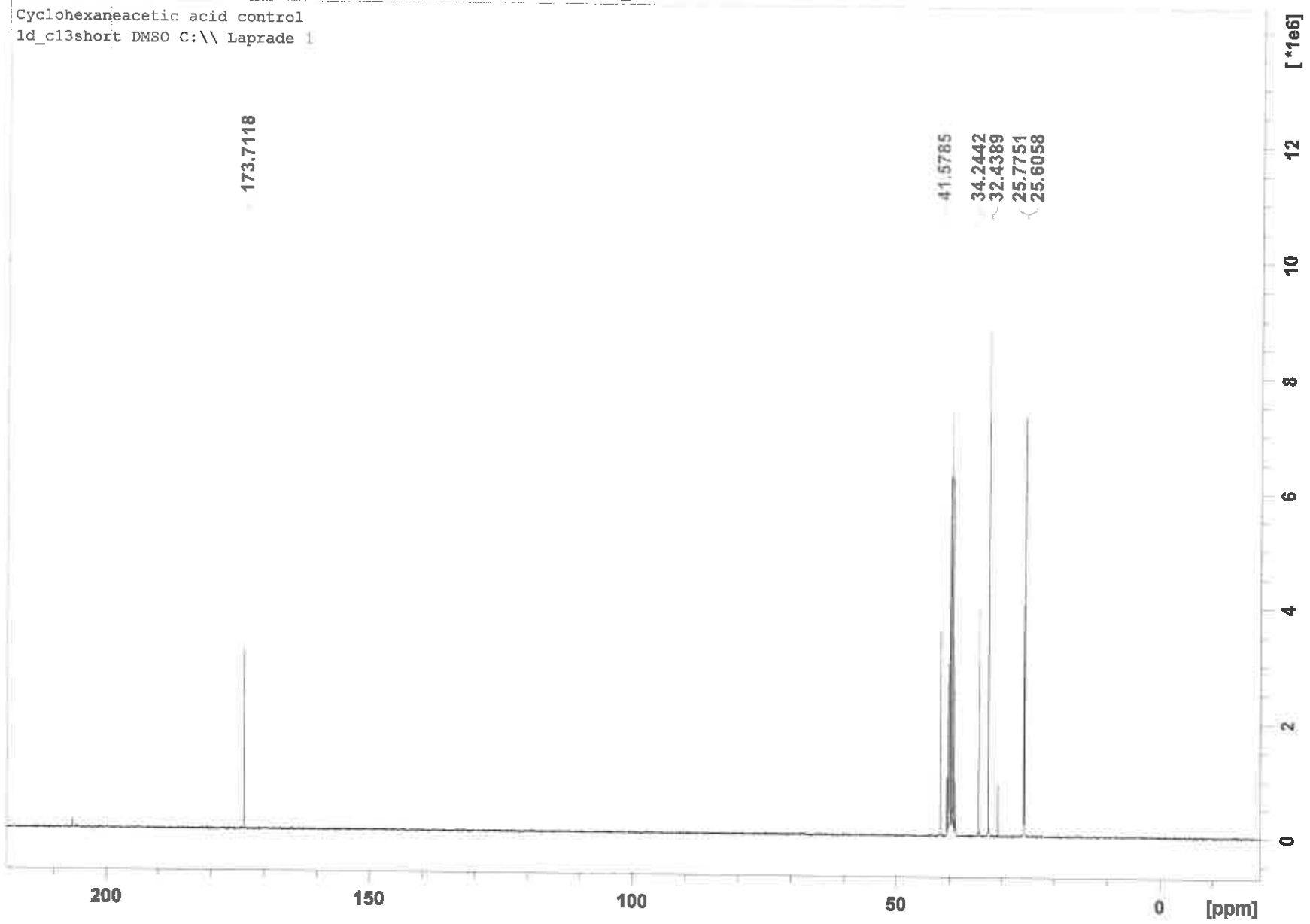


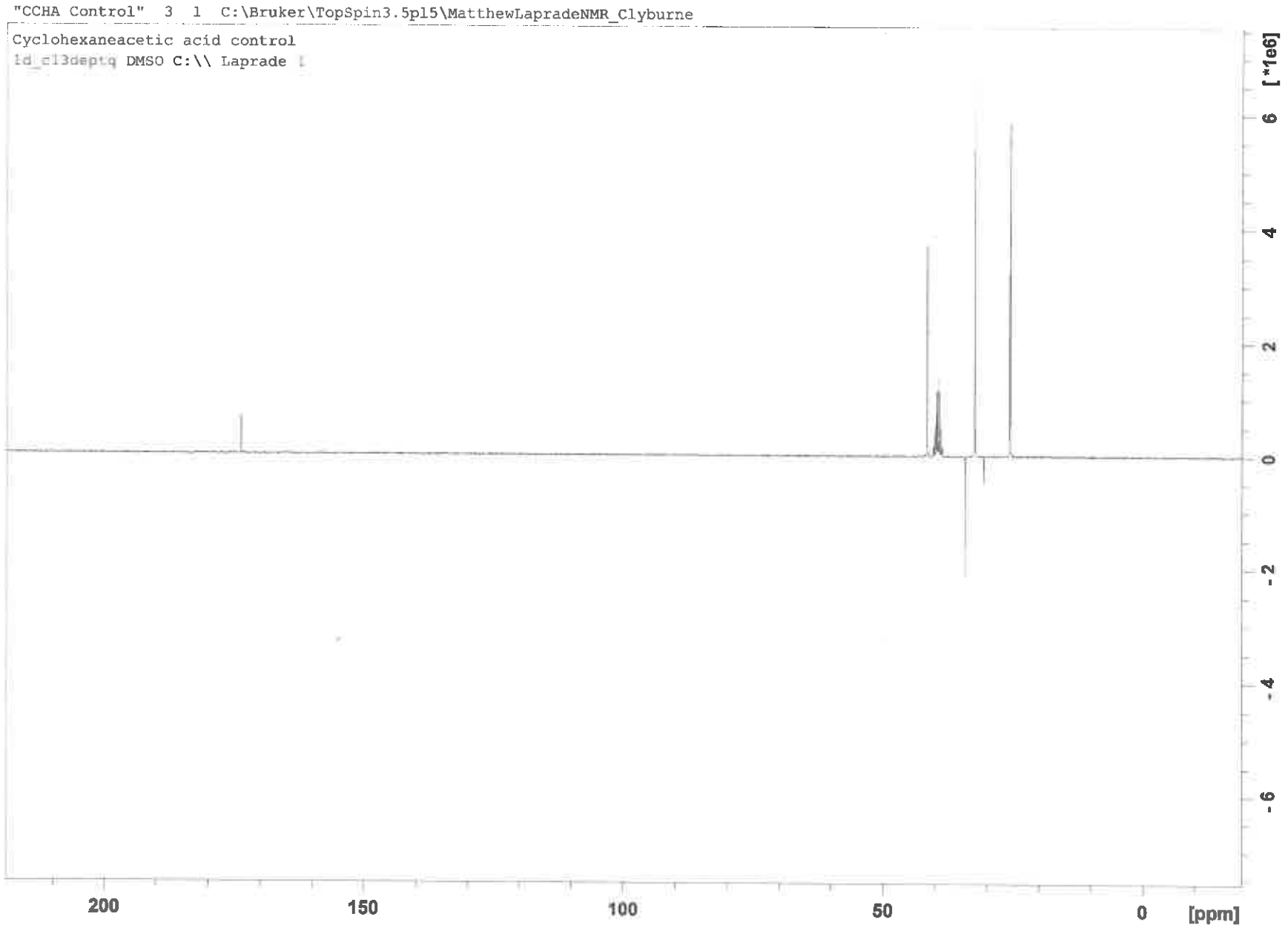

"CCHA Control" 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
Cyclohexaneacetic acid control
1d_proton DMSO C:\\ Laprade 1
2.0550
1.6736
1.6640
1.6604
1.6432
1.6319
1.6202
1.6097
1.5975
1.5855
1.5782
1.5740
1.5638
1.2398
1.2348
1.2299
1.1897
1.1582
1.1485
1.1261
1.1142
1.0780
0.9683
0.9282
0.8904
1.8943
6.1961
3.1584
2.1043
2.5
2.0
1.5
1.0
0.5
[ppm]
0
10
20
30
40
50
[*1e6]

"CCHA Control" 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne

Cyclohexaneacetic acid control

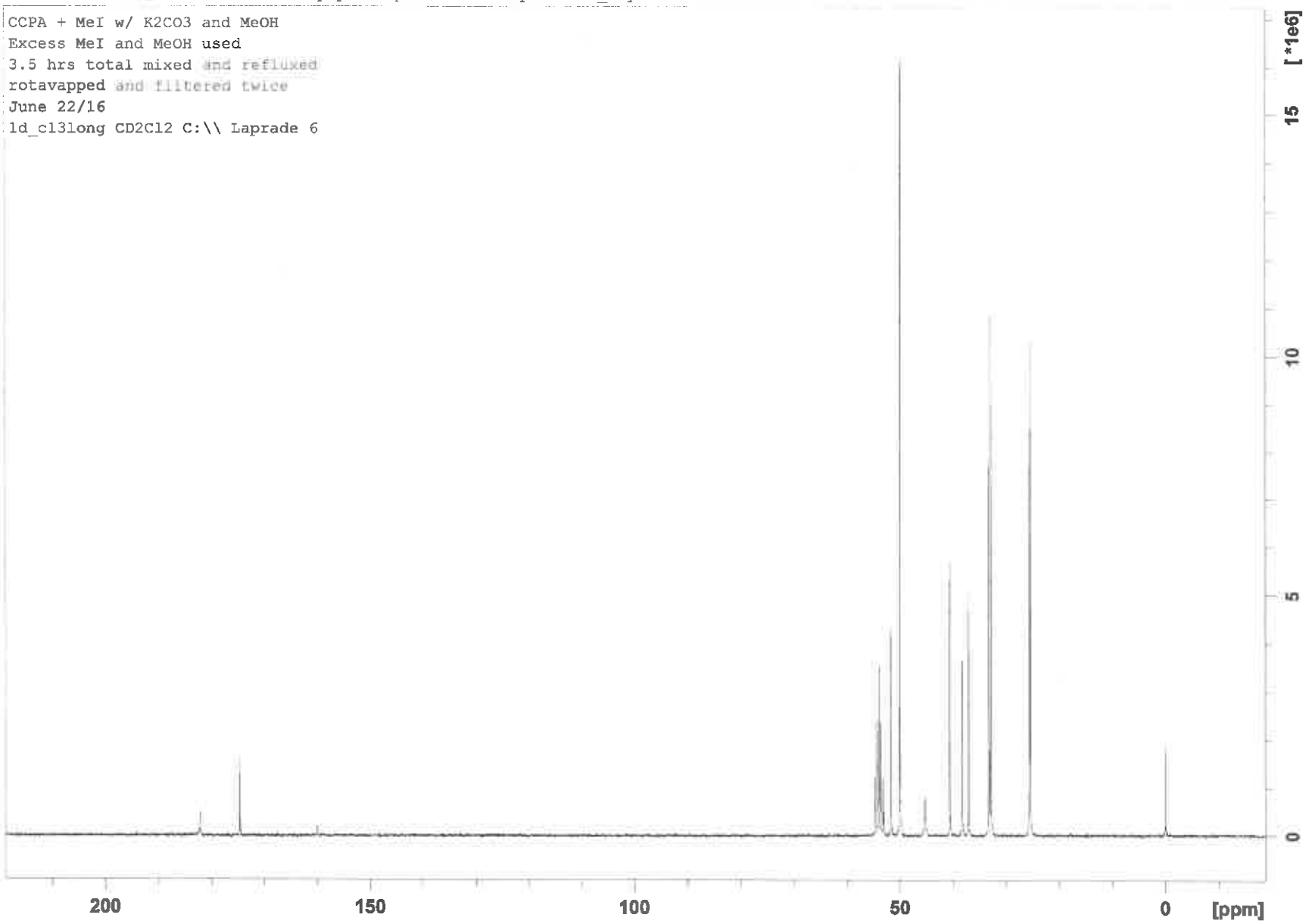
1d_c13short DMSO C:\\ Laprade 1




"CCHA Control" 3 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
Cyclohexaneacetic acid control
id_c13deptq DMSO C:\\ Laprade
[*1e6]
6
4
2
0
-2
-4
-6
200
150
100
50
0
[ppm]

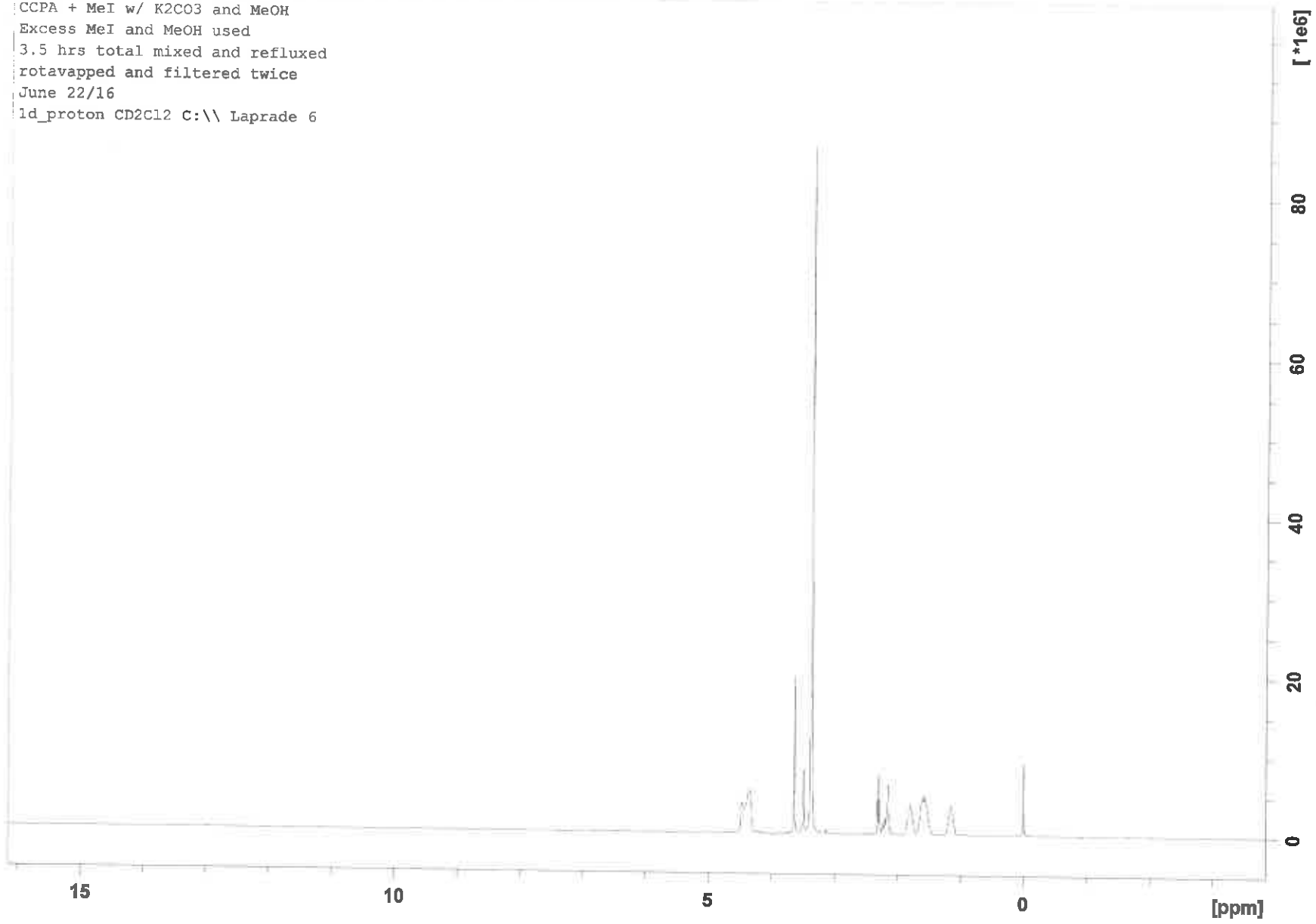
"CMJL014 F" 11 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne

CCPA + MeI w/ K2CO3 and MeOH
Excess MeI and MeOH used
3.5 hrs total mixed and refluxed
rotavapped and filtered twice
June 22/16
1d_c13long CD2Cl2 C:\\ Laprade 6



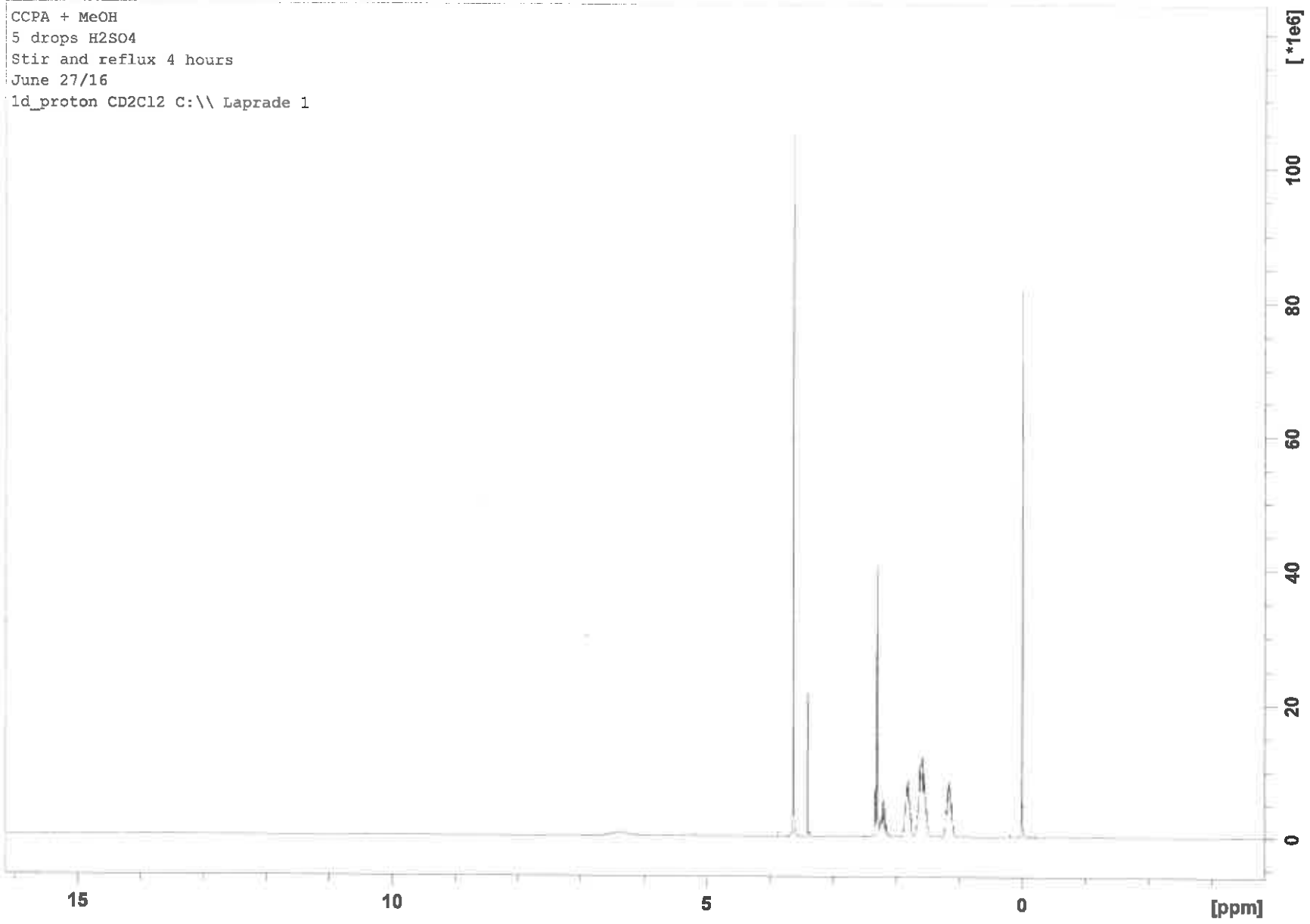
"CMJL014 F" 10 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne

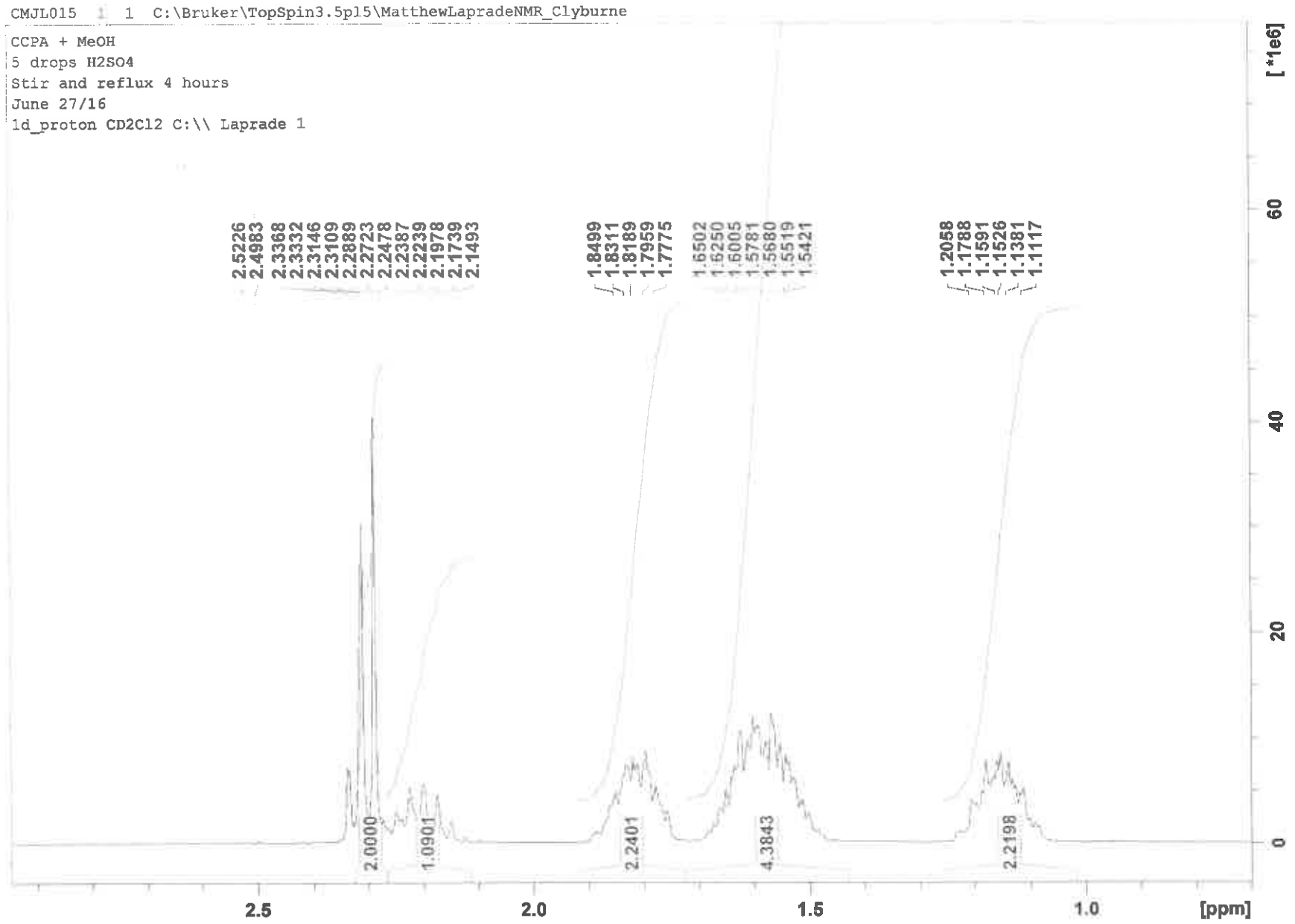
CCPA + MeI w/ K2CO3 and MeOH
Excess MeI and MeOH used
3.5 hrs total mixed and refluxed
rotavapped and filtered twice
June 22/16
1d_proton CD2Cl2 C:\\ Laprade 6

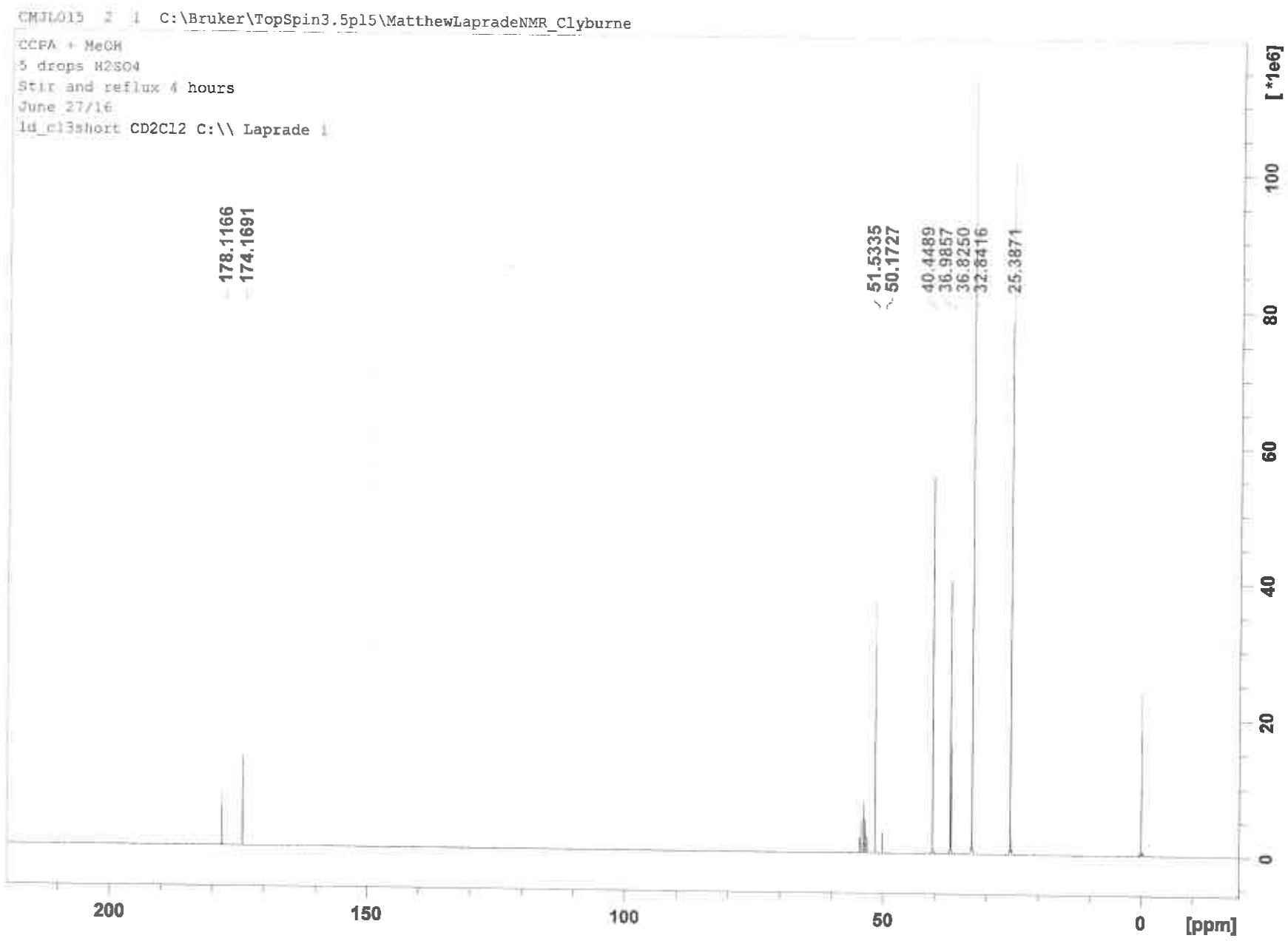


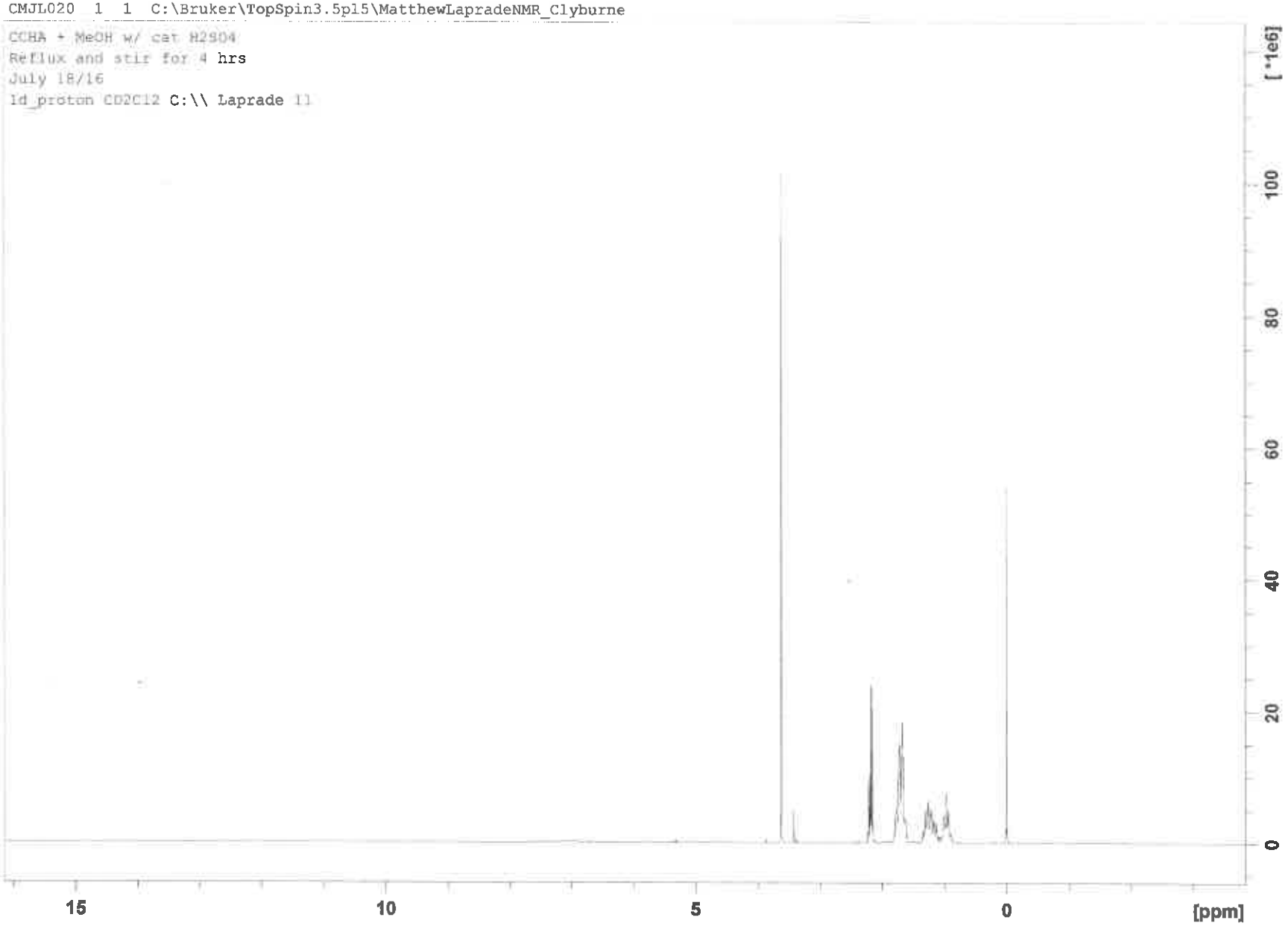
CMJL015 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne

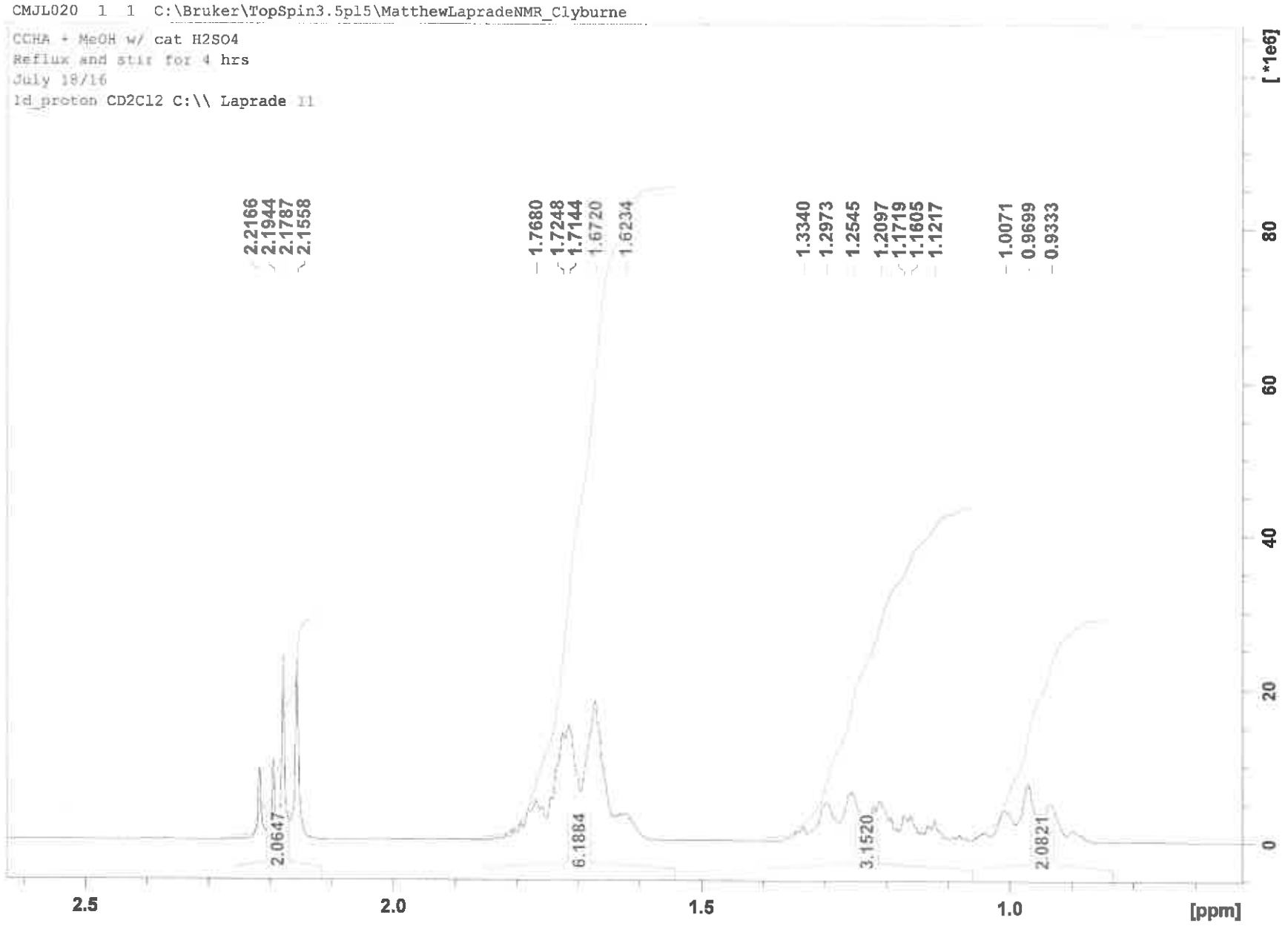
CCPA + MeOH
5 drops H2SO4
Stir and reflux 4 hours
June 27/16
1d_proton CD2Cl2 C:\\ Laprade 1

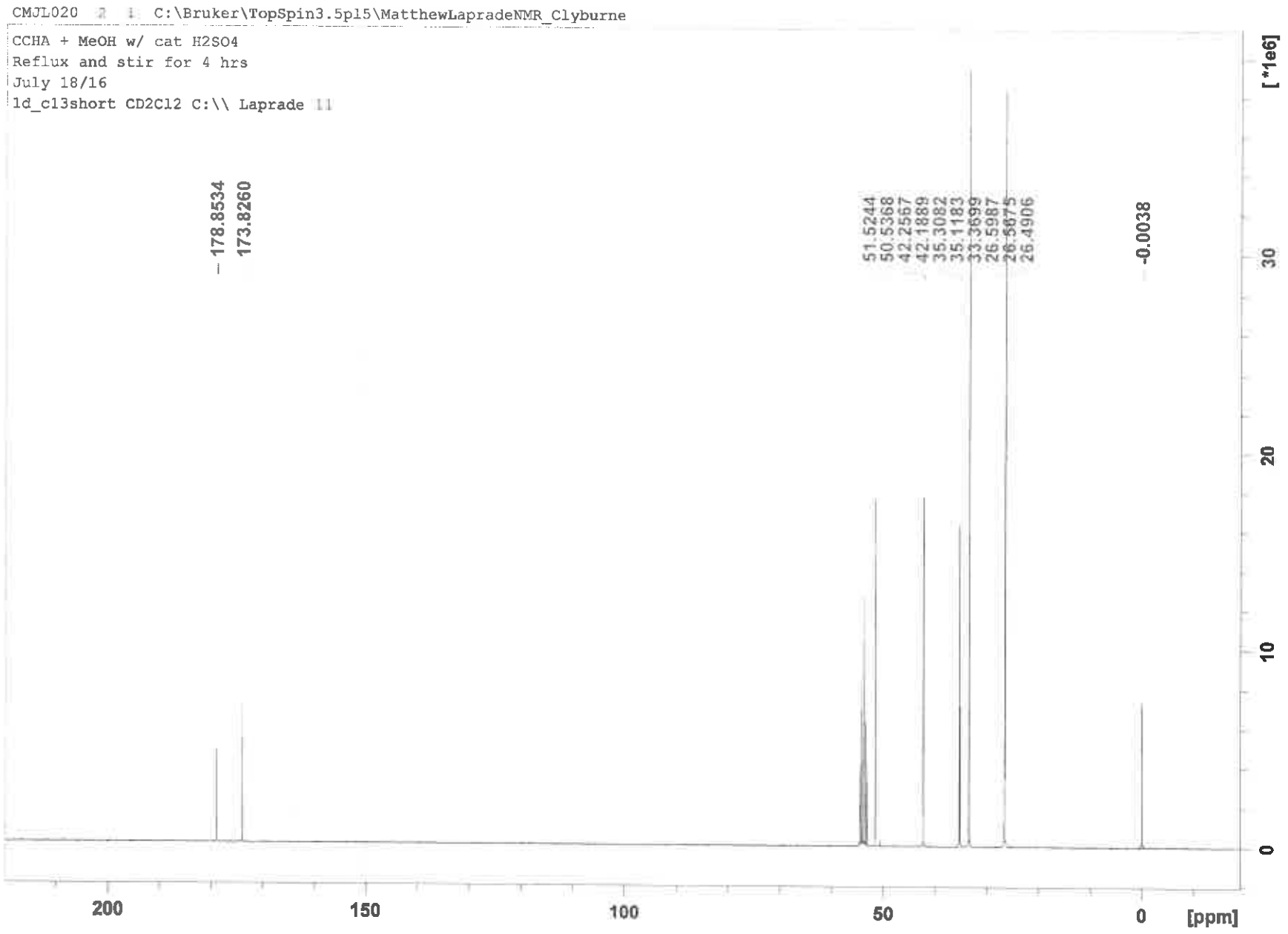


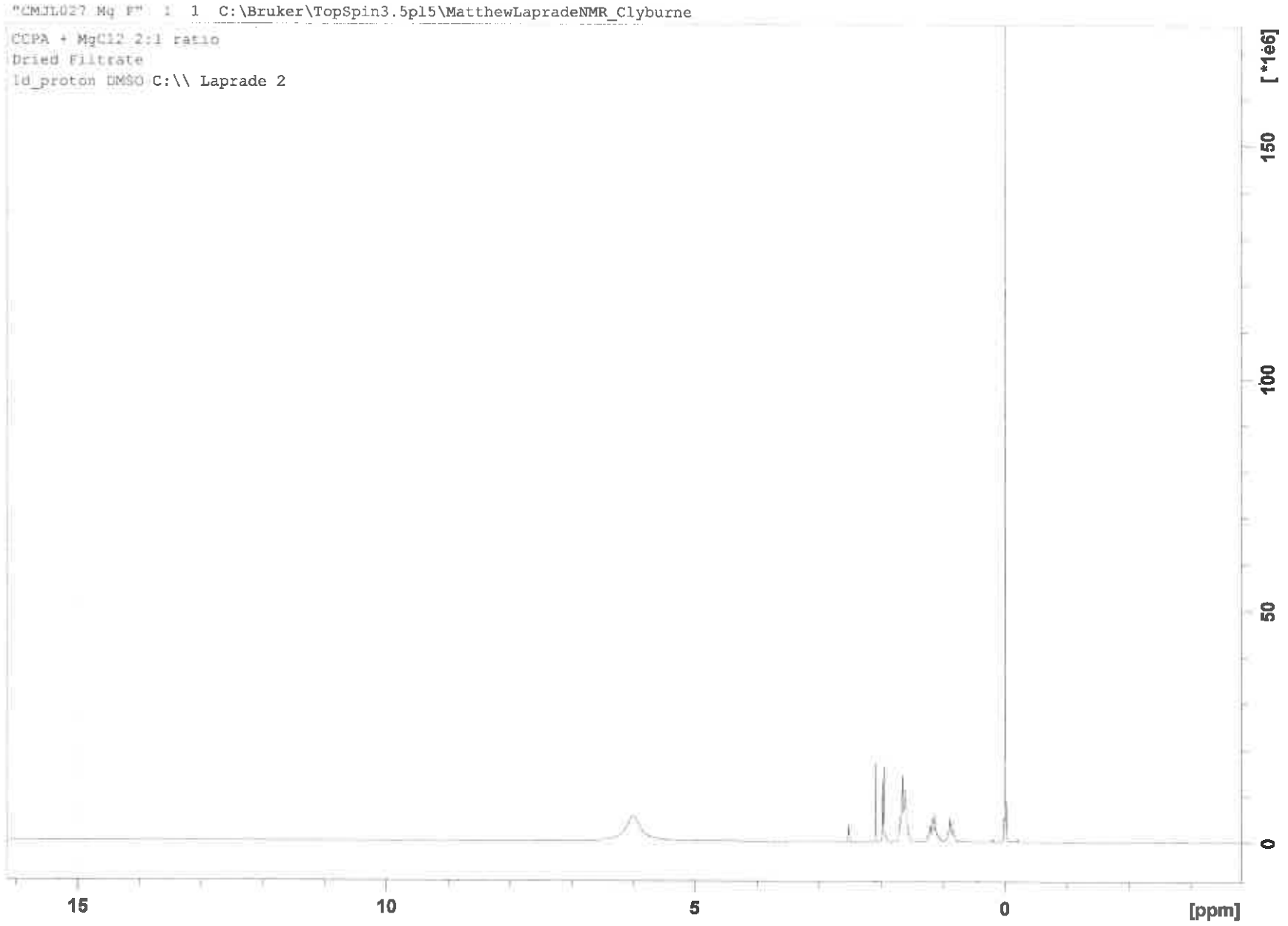

CMJL015 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CCPA + MeOH
5 drops H2SO4
Stir and reflux 4 hours
June 27/16
1d_proton CD2Cl2 C:\\ Laprade 1
2.5226
2.4983
2.3368
2.3332
2.3146
2.3109
2.2889
2.2723
2.2478
2.2387
2.2239
2.1978
2.1739
2.1493
1.8499
1.8311
1.8189
1.7959
1.7775
1.6502
1.6250
1.6005
1.5781
1.5680
1.5519
1.5421
1.2058
1.1788
1.1591
1.1526
1.1381
1.1117
2.0000
1.0901
2.2401
4.3843
2.2198
[*1e6]
60
40
20
0
2.5
2.0
1.5
1.0
[ppm]

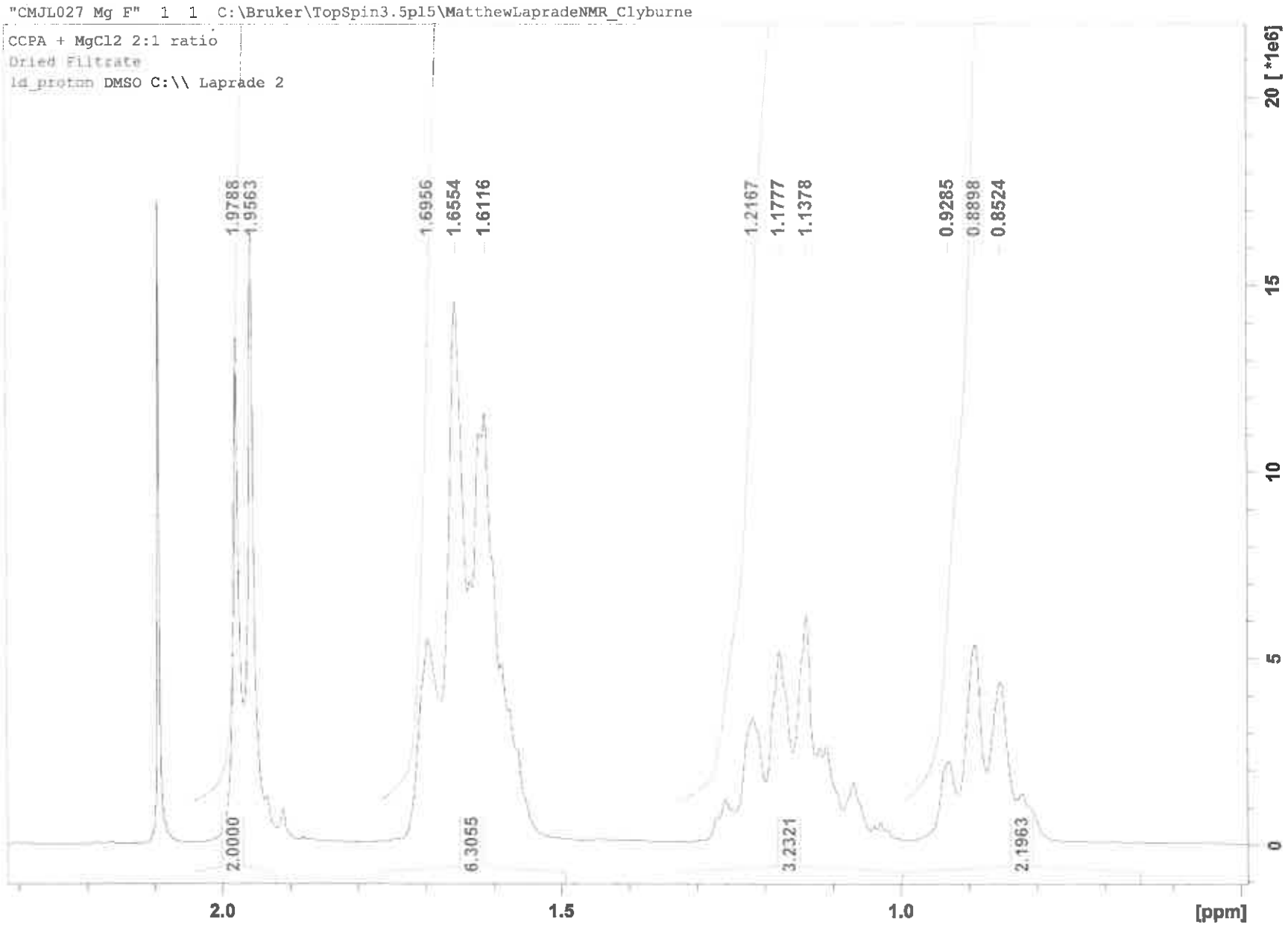

CMJL015 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CCPA + MeOH
5 drops H2SO4
Stir and reflux 4 hours
June 27/16
1d_c13short CD2Cl2 C:\\ Laprade 1
178.1166
174.1691
51.5335
50.1727
40.4489
36.9857
36.8250
32.8416
25.3871
[*1e6]
100
80
60
40
20
0
200
150
100
50
0
[ppm]

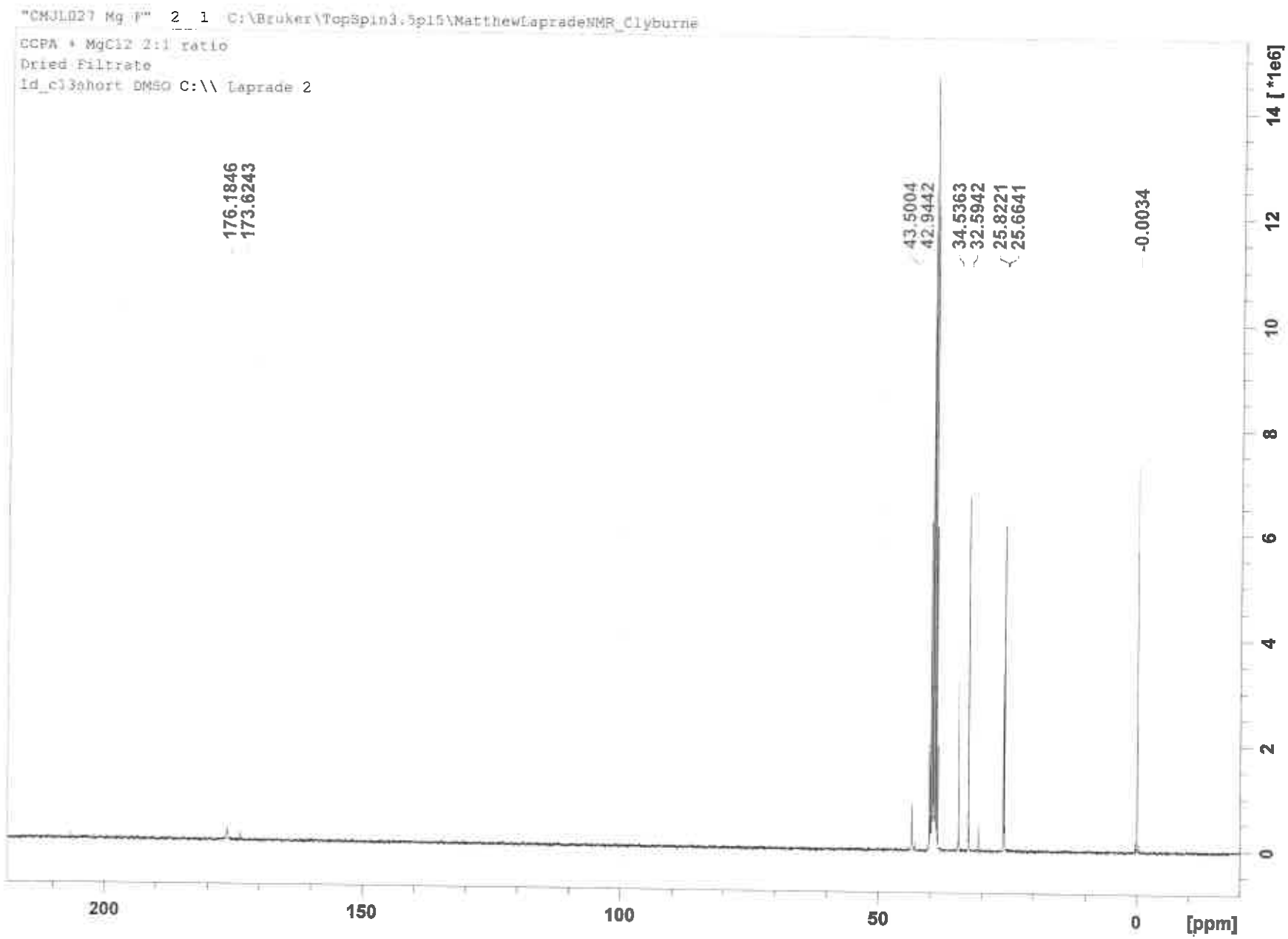

CMJL020 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CCHA + MeOH w/ cat H2SO4
Reflux and stir for 4 hrs
July 18/16
1d_proton CD2Cl2 C:\\ Laprade 11
[*1e6]
100
80
60
40
20
0
15
10
5
0
[ppm]

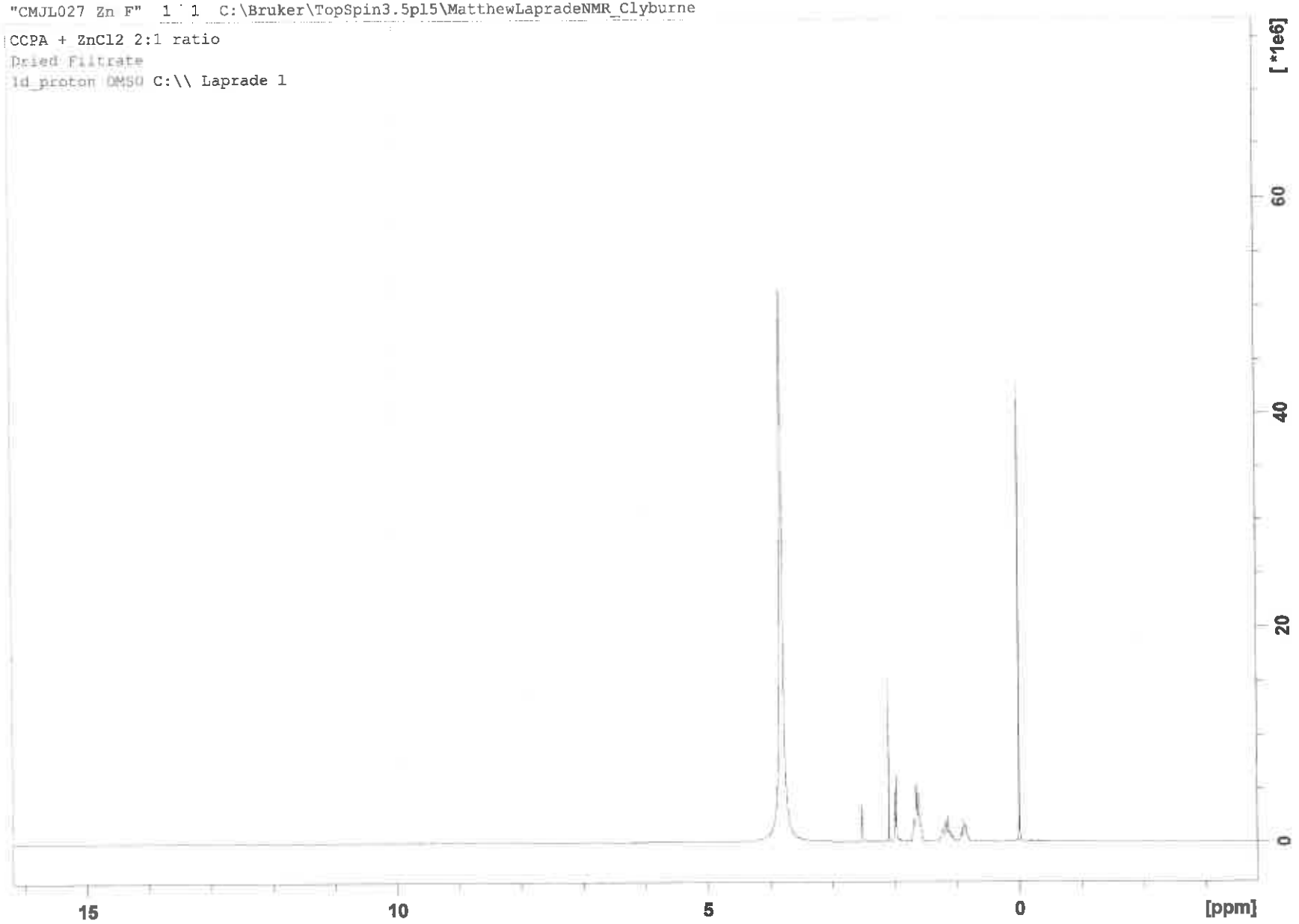

CMJL020 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CCHA + MeOH w/ cat H2SO4
Reflux and stir for 4 hrs
July 18/16
1d_proton CD2Cl2 C:\\ Laprade 11
2.2166
2.1944
2.1787
2.1558
1.7680
1.7248
1.7144
1.6720
1.6234
1.3340
1.2973
1.2545
1.2097
1.1719
1.1605
1.1217
1.0071
0.9699
0.9333
2.0647
6.1884
3.1520
2.0821
[*1e6]
0
20
40
60
80
2.5
2.0
1.5
1.0
[ppm]

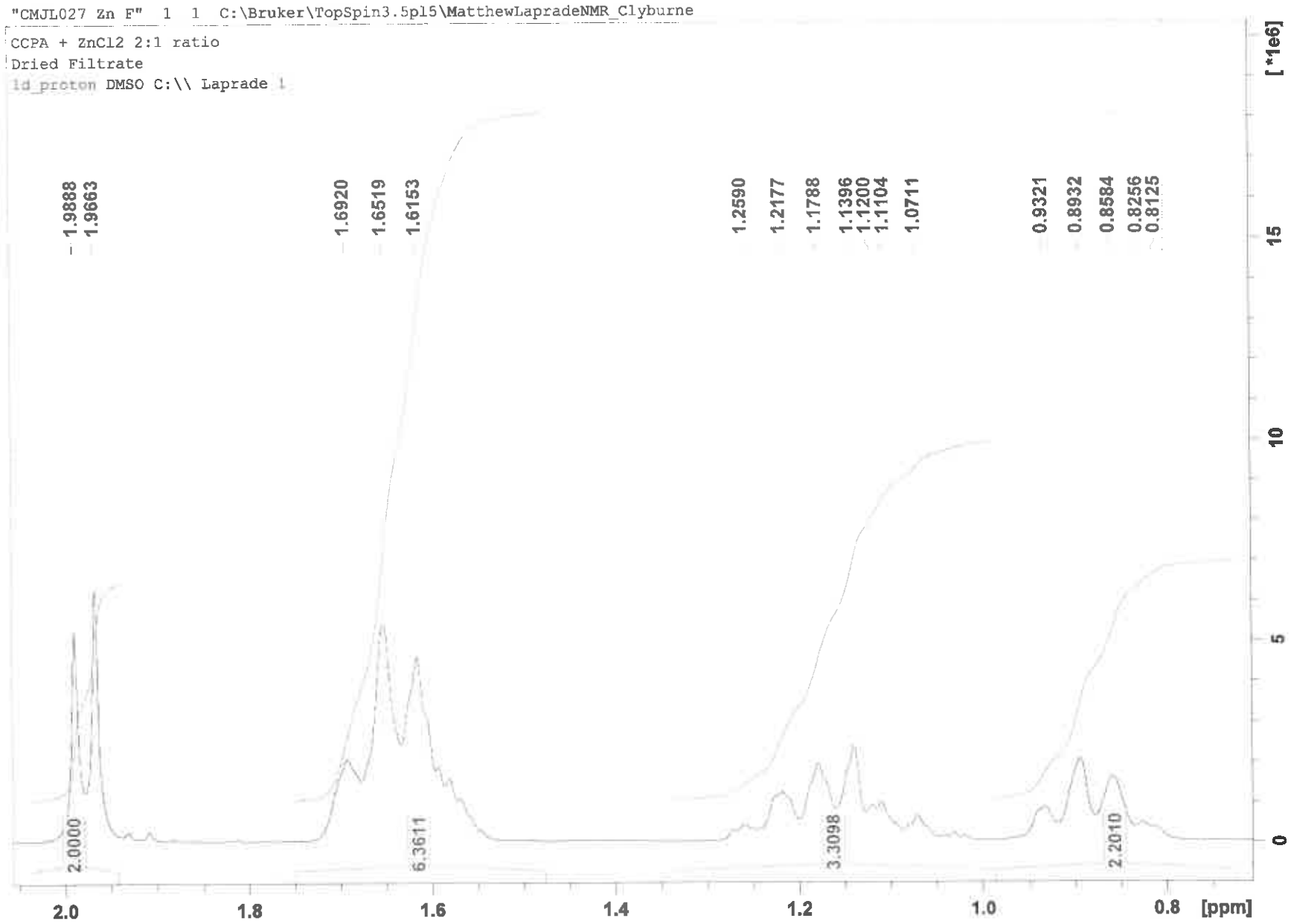

CMJL020 7 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CCHA + MeOH w/ cat H2SO4
Reflux and stir for 4 hrs
July 18/16
1d_c13short CD2Cl2 C:\\ Laprade 11
178.8534
173.8260
51.5244
50.5368
42.2567
42.1889
35.3082
35.1183
33.3699
26.5987
26.5675
26.4906
-0.0038
[*1e6]
30
20
10
0
200
150
100
50
0
[ppm]

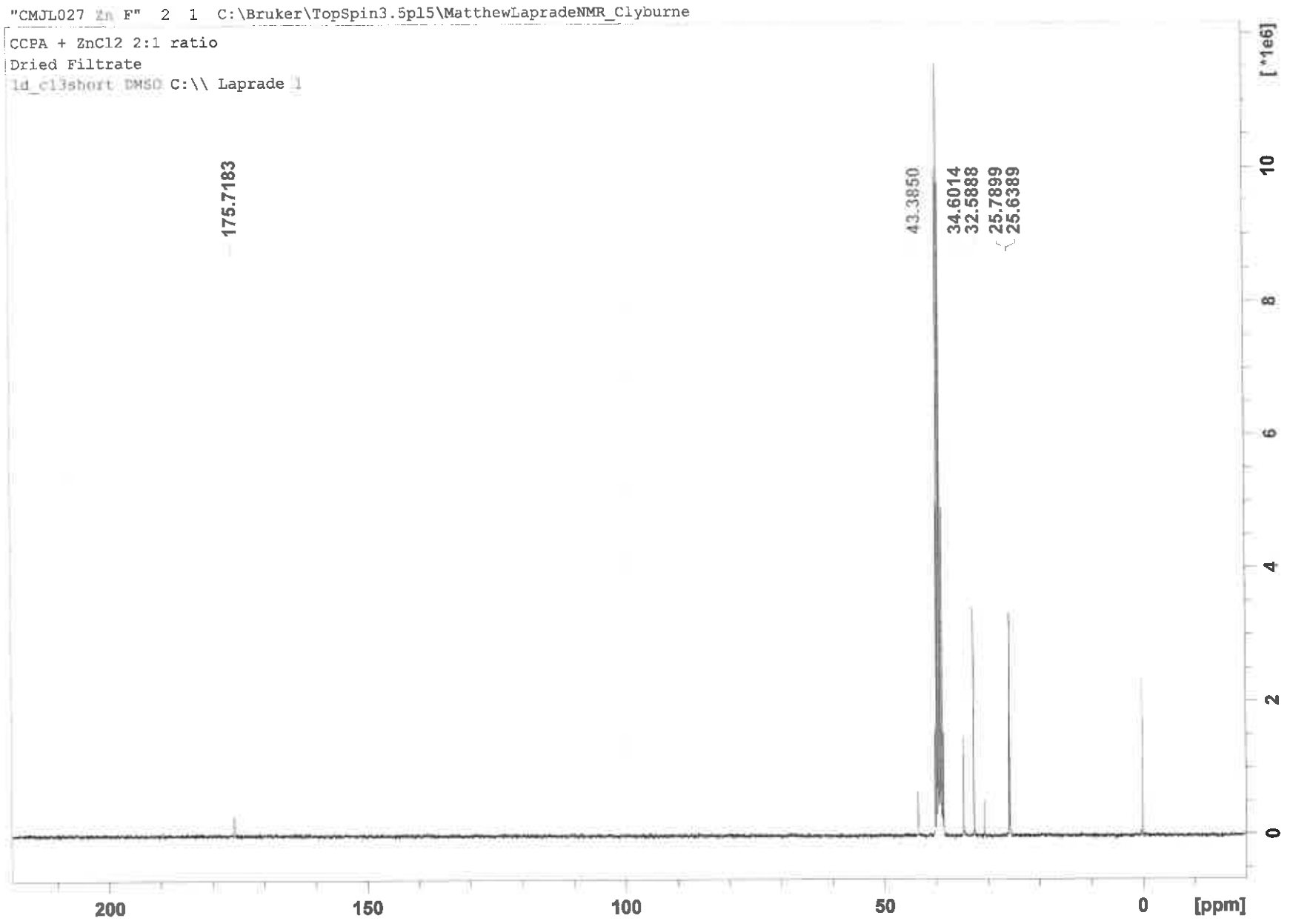

"CMJL027 Mq F" 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CCPA + MgCl2 2:1 ratio
Dried Filtrate
1d_proton DMSO C:\\ Laprade 2
[*1e6]
150
100
50
0
15
10
5
0
[ppm]

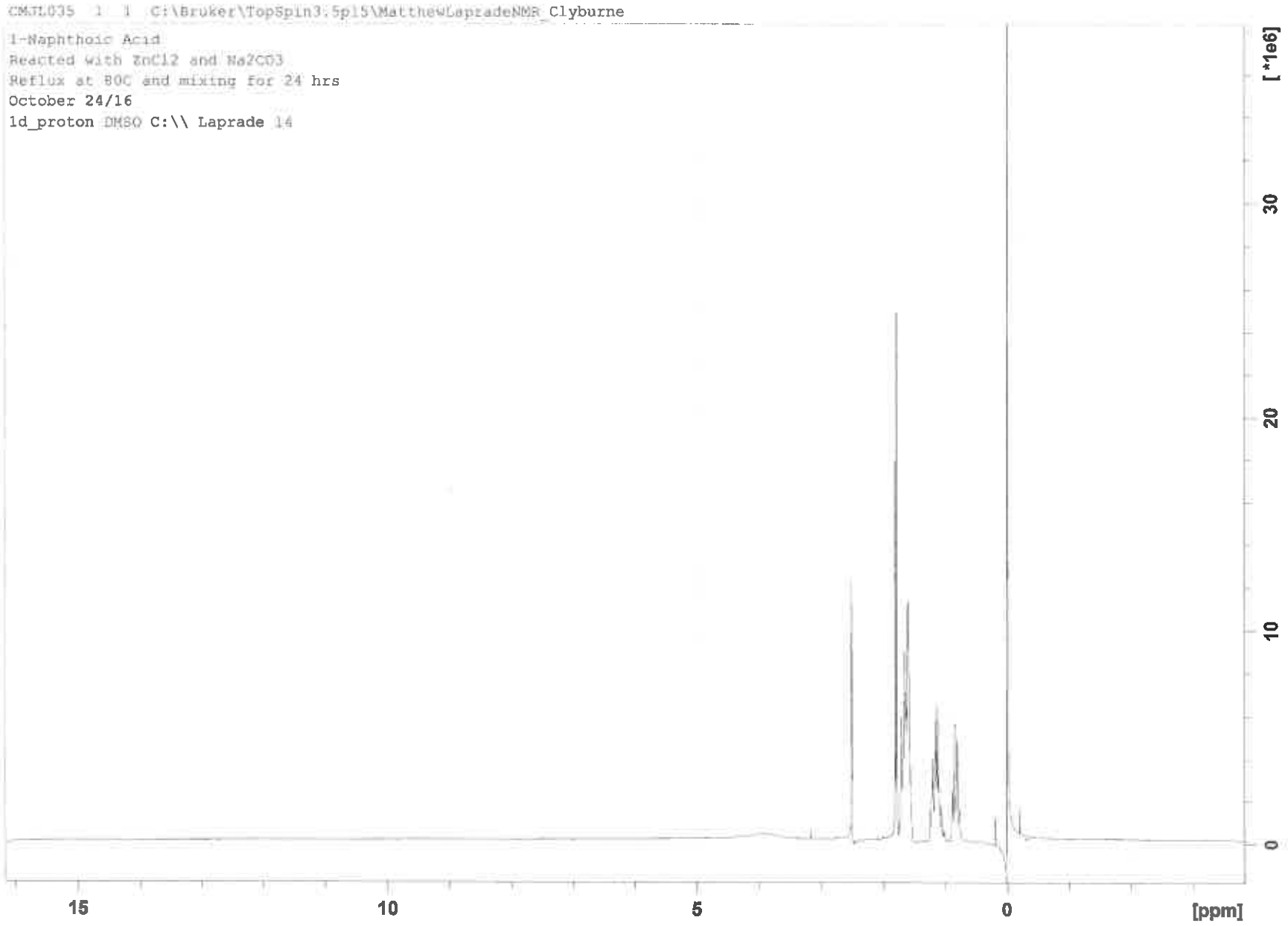

"CMJL027 Mg F" 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CCPA + MgCl2 2:1 ratio
Dried Filtrate
1d_proton DMSO C:\\ Laprade 2
1.9788
1.9563
1.6956
1.6554
1.6116
1.2167
1.1777
1.1378
0.9285
0.8898
0.8524
2.0000
6.3055
3.2321
2.1963
2.0
1.5
1.0
[ppm]
0
5
10
15
20 [*1e6]

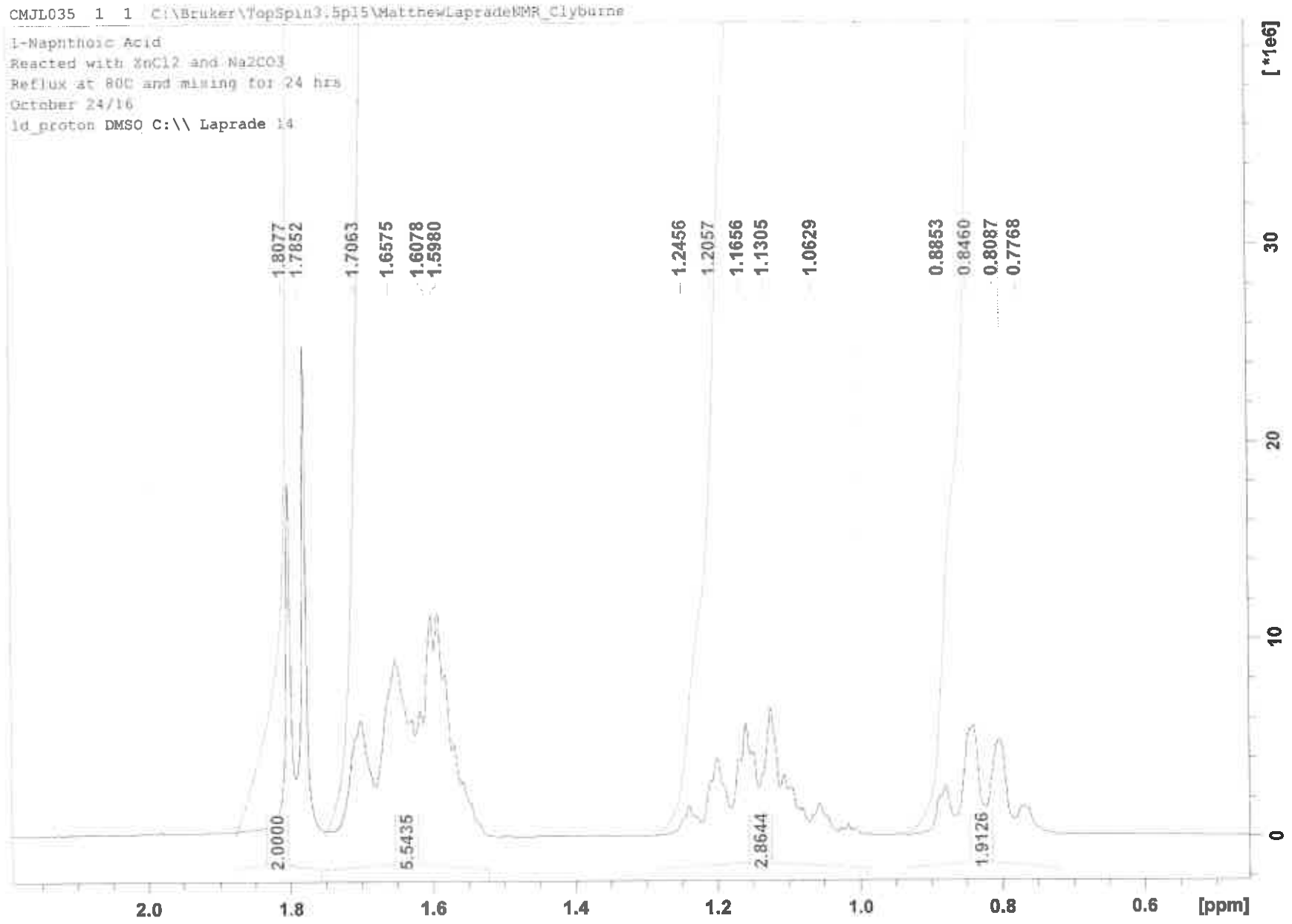

"CMJL027 Mg F" 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CCPA + MgCl2 2:1 ratio
Dried Filtrate
Id_c13short DMSO C:\\ Laprade 2
176.1846
173.6243
43.5004
42.9442
34.5363
32.5942
25.8221
25.6641
-0.0034
14 [*1e6]
12
10
8
6
4
2
0
200
150
100
50
0
[ppm]

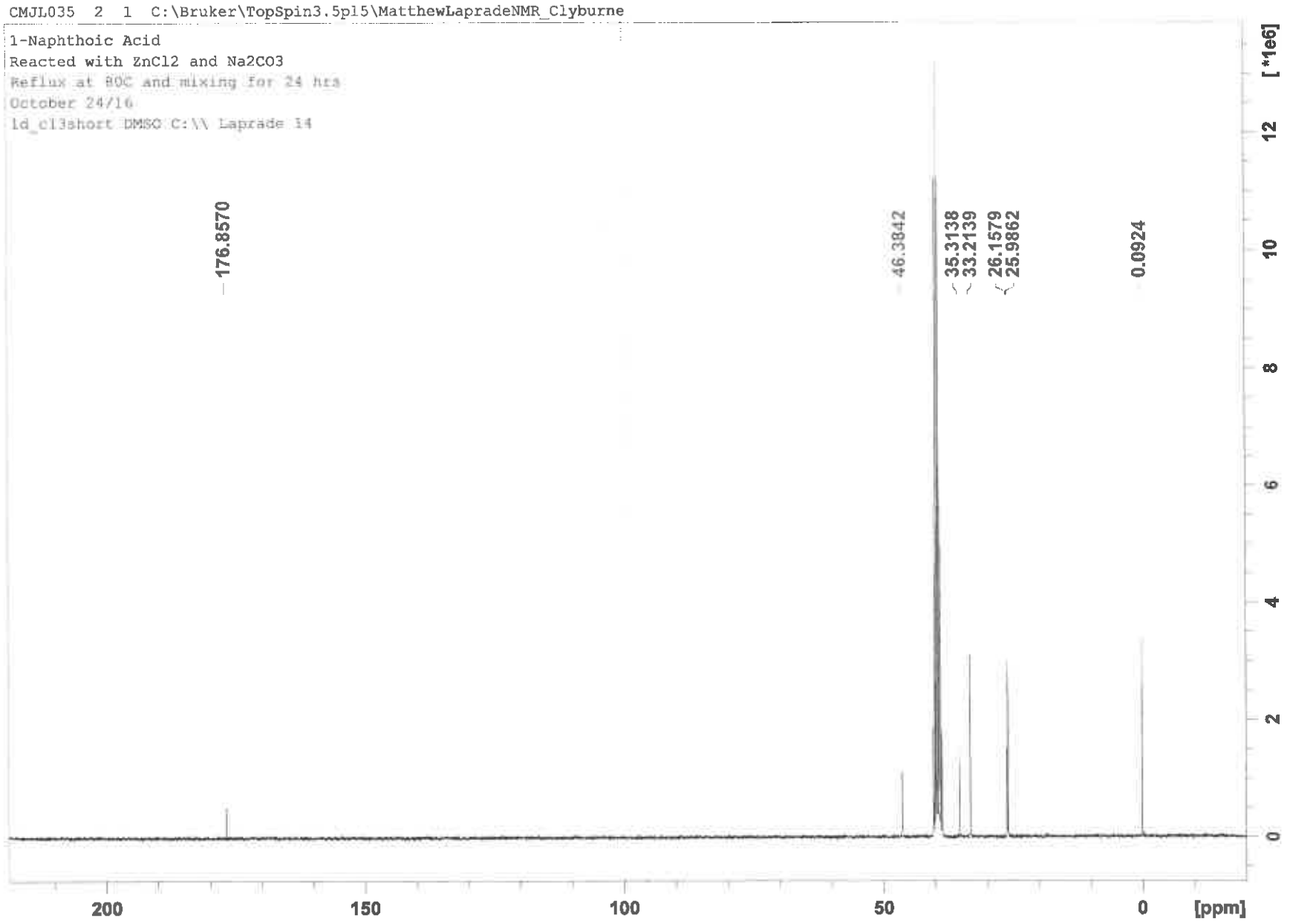

"CMJL027 Zn F" 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CCPA + ZnCl2 2:1 ratio
Dried Filtrate
1d_proton DMSO C:\\ Laprade 1
[*1e6]
60
40
20
0
15
10
5
0
[ppm]

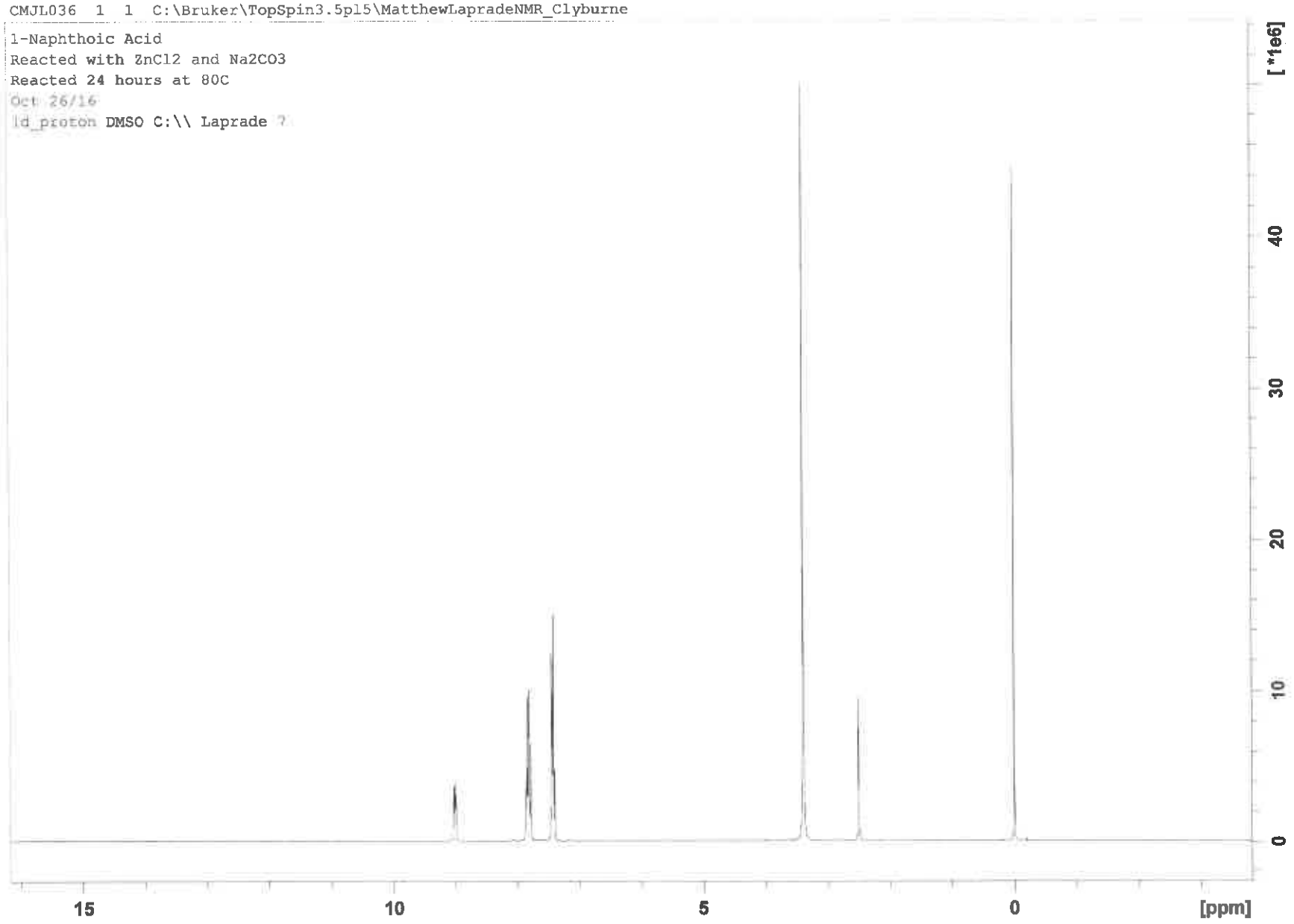

"CMJL027 Zn F" 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CCPA + ZnCl2 2:1 ratio
Dried Filtrate
1d_proton DMSO C:\\ Laprade 1
1.9888
1.9663
1.6920
1.6519
1.6153
1.2590
1.2177
1.1788
1.1396
1.1200
1.1104
1.0711
0.9321
0.8932
0.8584
0.8256
0.8125
2.0000
6.3611
3.3098
2.2010
[*1e6]
15
10
5
0
2.0
1.8
1.6
1.4
1.2
1.0
0.8
[ppm]

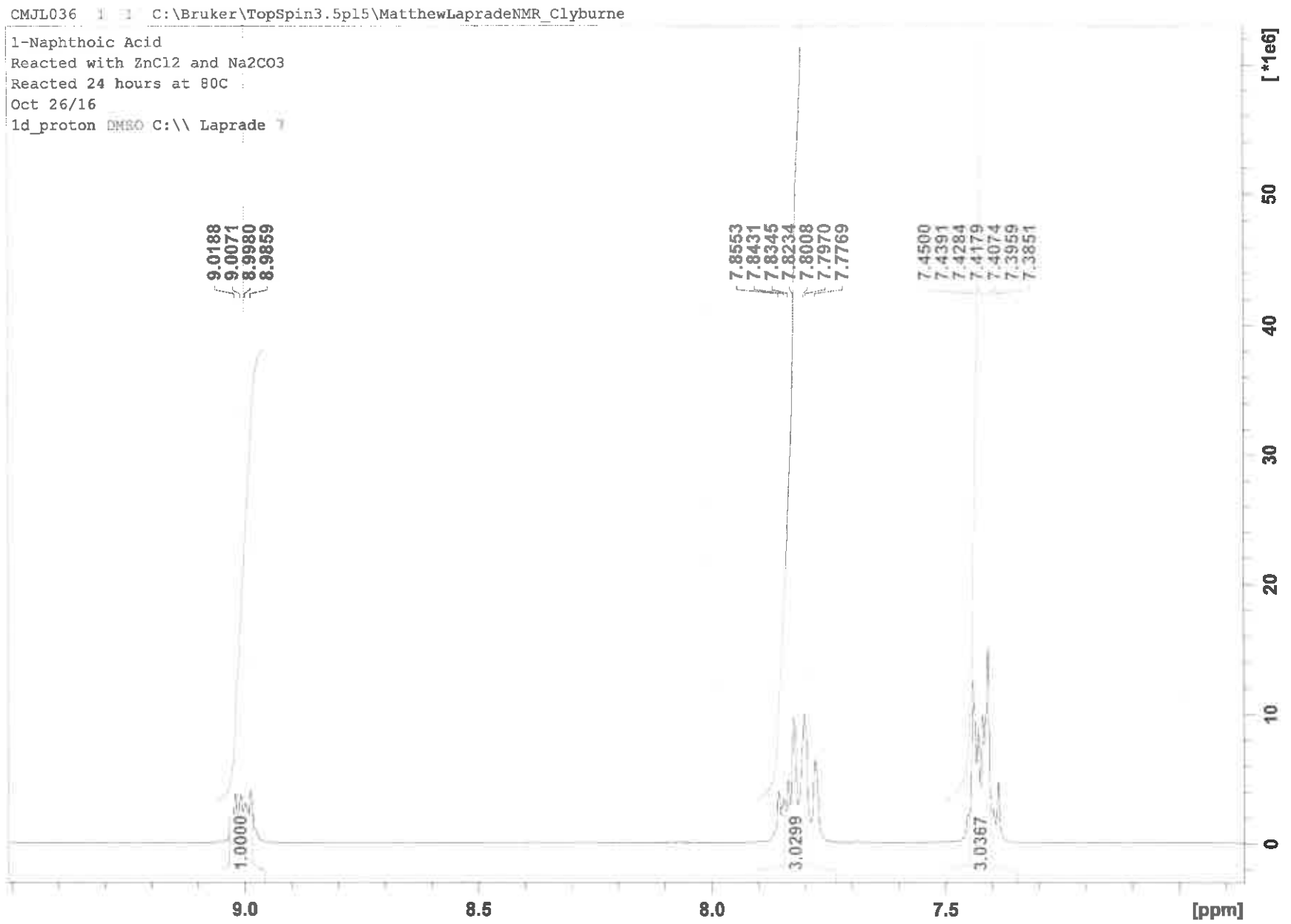

"CMJL027 Zn F" 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CCPA + ZnCl2 2:1 ratio
Dried Filtrate
1d_c13short DMSO C:\\ Laprade 1
175.7183
43.3850
34.6014
32.5888
25.7899
25.6389
[*1e6]
10
8
6
4
2
0
200
150
100
50
0
[ppm]

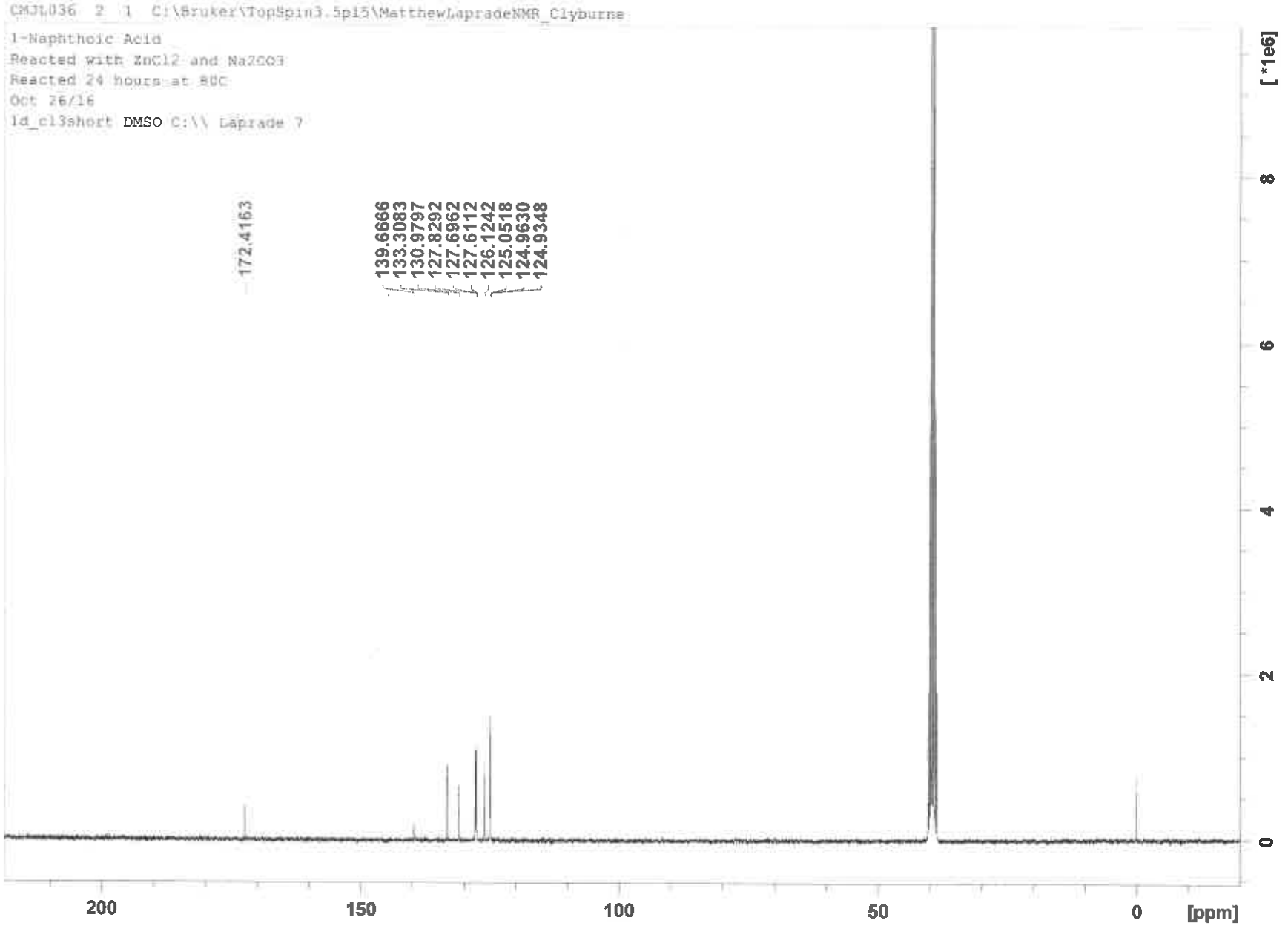

CMJL035 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR Clyburne
1-Naphthoic Acid
Reacted with ZnCl2 and Na2CO3
Reflux at 80C and mixing for 24 hrs
October 24/16
1d_proton DMSO C:\\ Laprade 14
[*1e6]
30
20
10
0
15
10
5
0
[ppm]

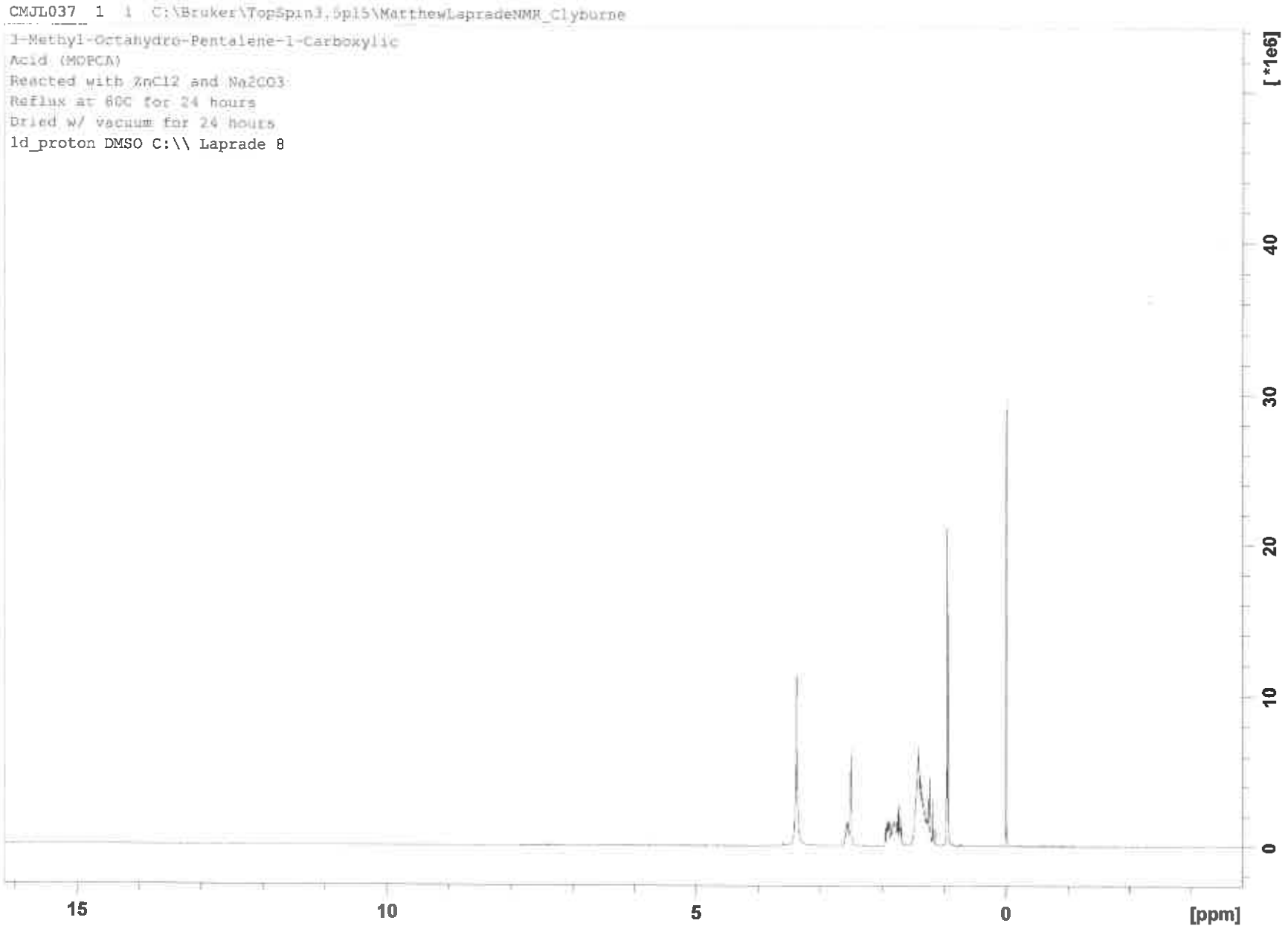

CMJL035 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Napnthoic Acid
Reacted with ZnCl2 and Na2CO3
Reflux at 80C and mixing for 24 hrs
October 24/16
1d_proton DMSO C:\\ Laprade 14
1.8077
1.7852
1.7063
1.6575
1.6078
1.5980
1.2456
1.2057
1.1656
1.1305
1.0629
0.8853
0.8460
0.8087
0.7768
2.0000
5.5435
2.8644
1.9126
[*1e6]
30
20
10
0
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
[ppm]

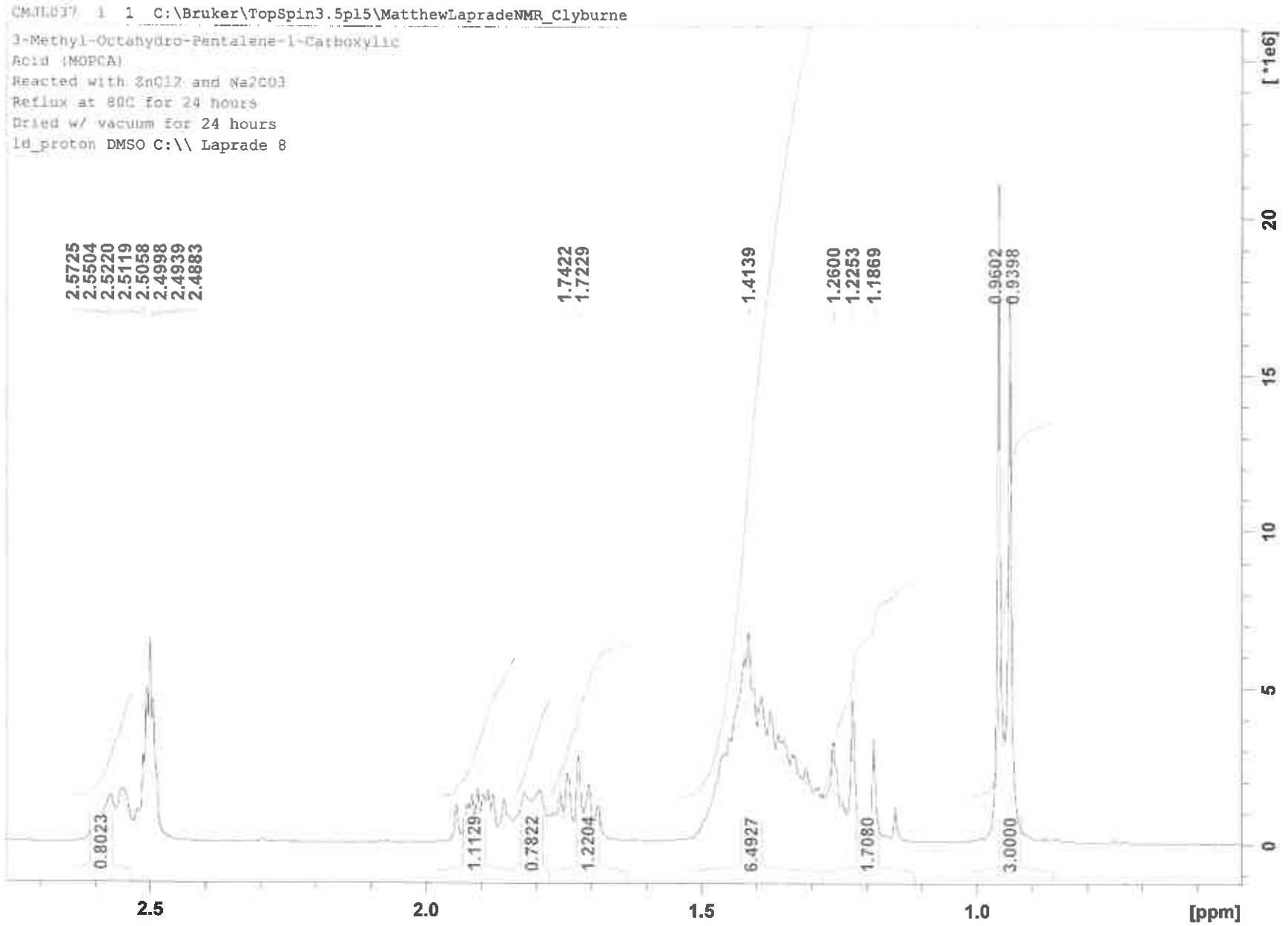

CMJL035 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Naphthoic Acid
Reacted with ZnCl2 and Na2CO3
Reflux at 80C and mixing for 24 hrs
October 24/16
1d_c13short DMSO C:\\ Laprade 14
176.8570
46.3842
35.3138
33.2139
26.1579
25.9862
0.0924
[*1e6]
0
2
4
6
8
10
12
200
150
100
50
0
[ppm]

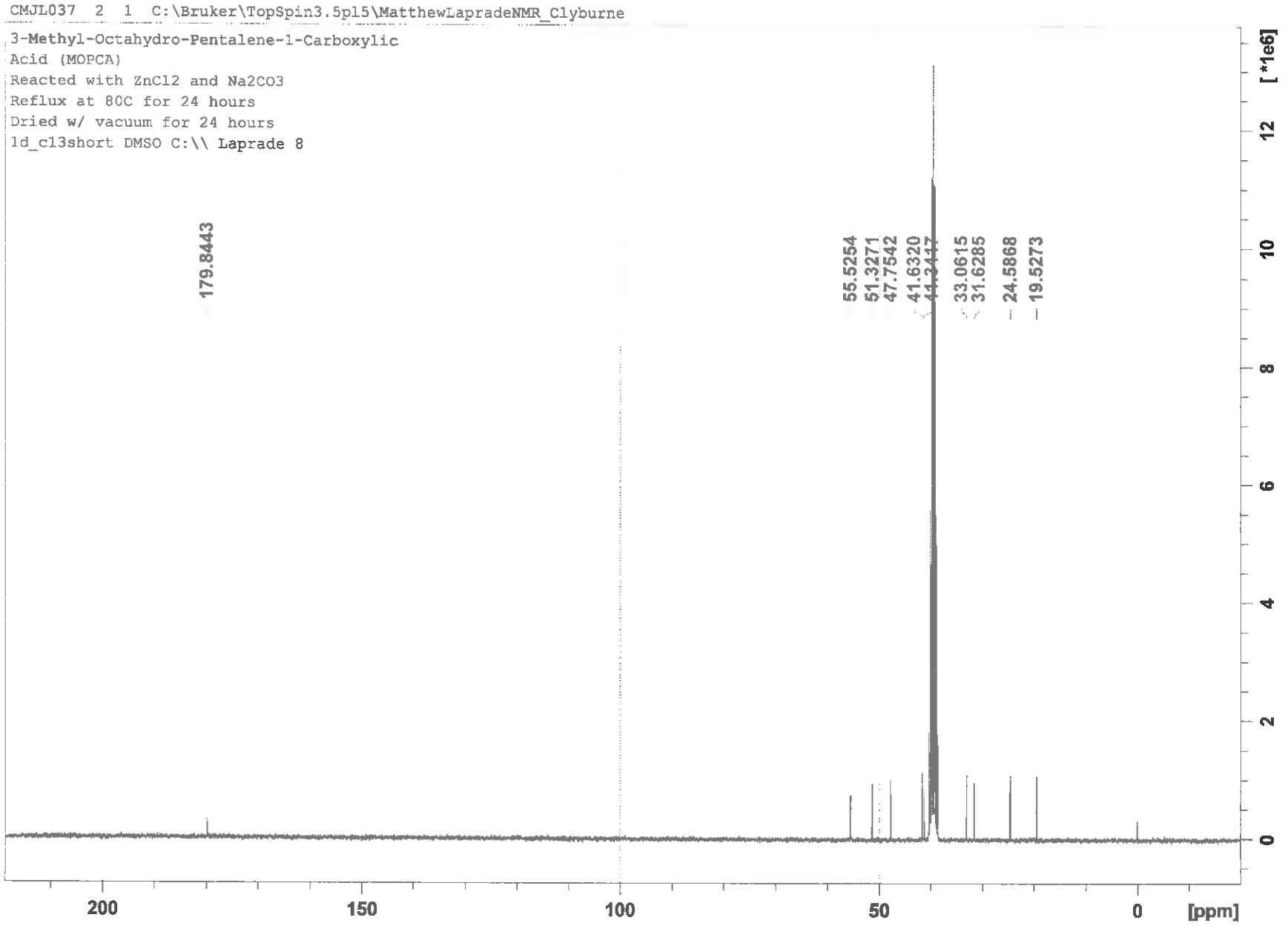

CMJL036 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Naphthoic Acid
Reacted with ZnCl2 and Na2CO3
Reacted 24 hours at 80C
Oct 26/16
1d_proton DMSO C:\\ Laprade 7
[*1e6]
40
30
20
10
0
15
10
5
0
[ppm]

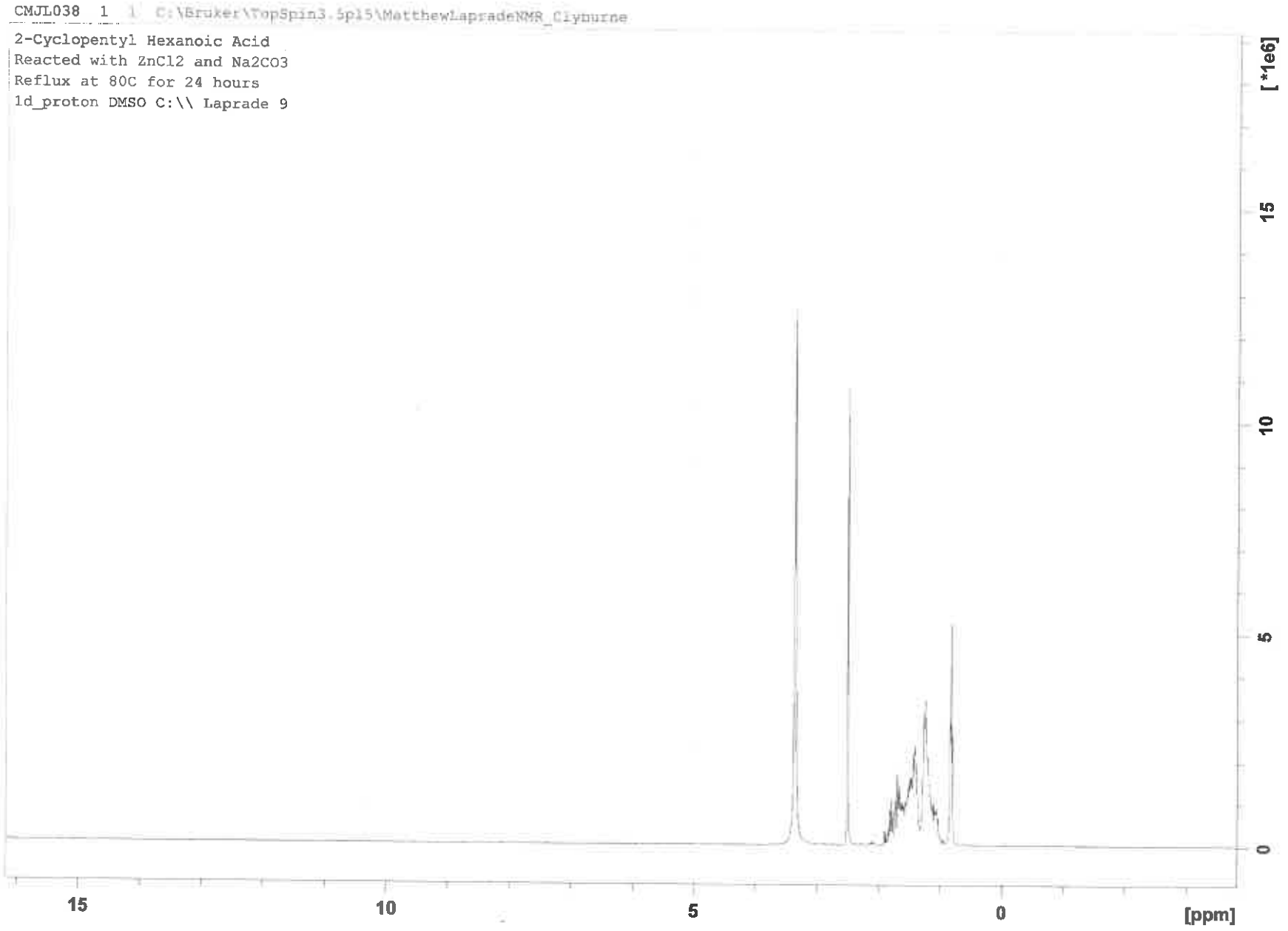

CMJL036 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Naphthoic Acid
Reacted with ZnCl2 and Na2CO3
Reacted 24 hours at 80C
Oct 26/16
1d_proton DMSO C:\\ Laprade 7
9.0188
9.0071
8.9980
8.9859
7.8553
7.8431
7.8345
7.8234
7.8008
7.7970
7.7769
7.4500
7.4391
7.4284
7.4179
7.4074
7.3959
7.3851
1.0000
3.0299
3.0367
9.0
8.5
8.0
7.5
[ppm]
[*1e6]
0
10
20
30
40
50

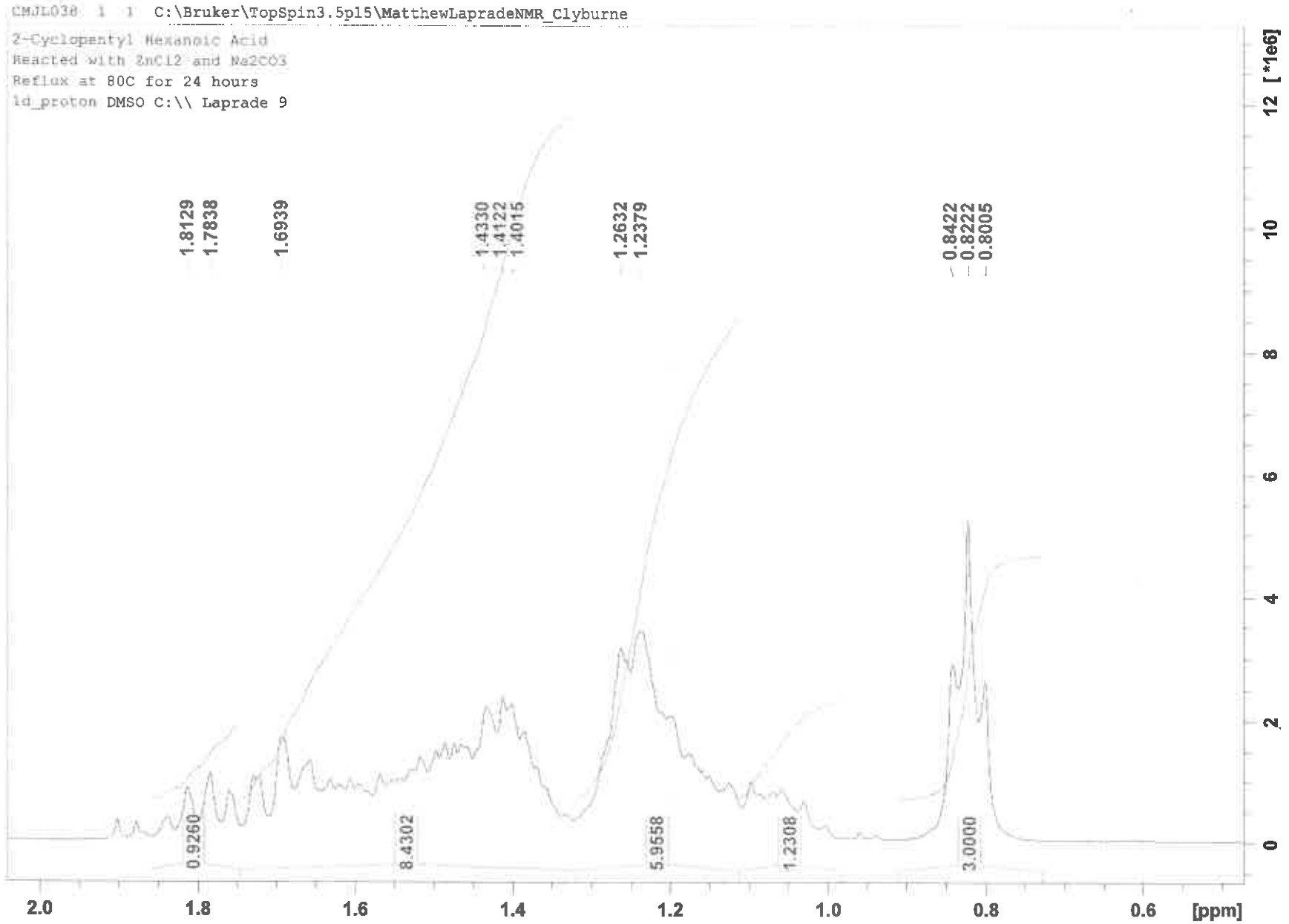

CMJL036 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Naphthoic Acid
Reacted with ZnCl2 and Na2CO3
Reacted 24 hours at 80C
Oct 26/16
1d_cl3short DMSO C:\\ Laprade 7
172.4163
139.6666
133.3083
130.9797
127.8292
127.6962
127.6112
126.1242
125.0518
124.9630
124.9348
[*1e6]
8
6
4
2
0
200
150
100
50
0
[ppm]

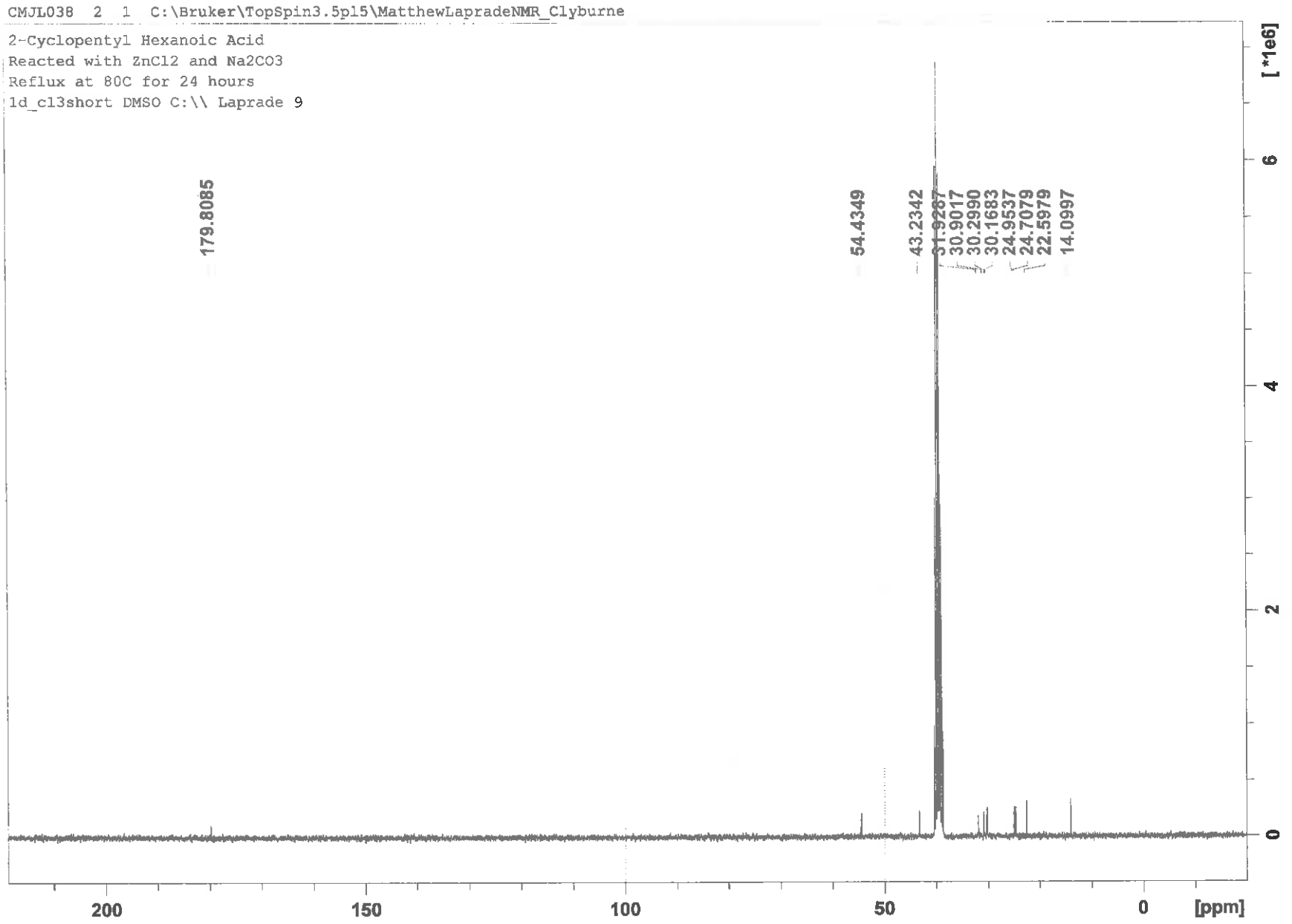

CMJL037 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
3-Methyl-Octahydro-Pentalene-1-Carboxylic
Acid (MOPCA)
Reacted with ZnCl2 and Na2CO3
Reflux at 60C for 24 hours
Dried w/ vacuum for 24 hours
1d_proton DMSO C:\\ Laprade 8
[*1e6]
40
30
20
10
0
15
10
5
0
[ppm]

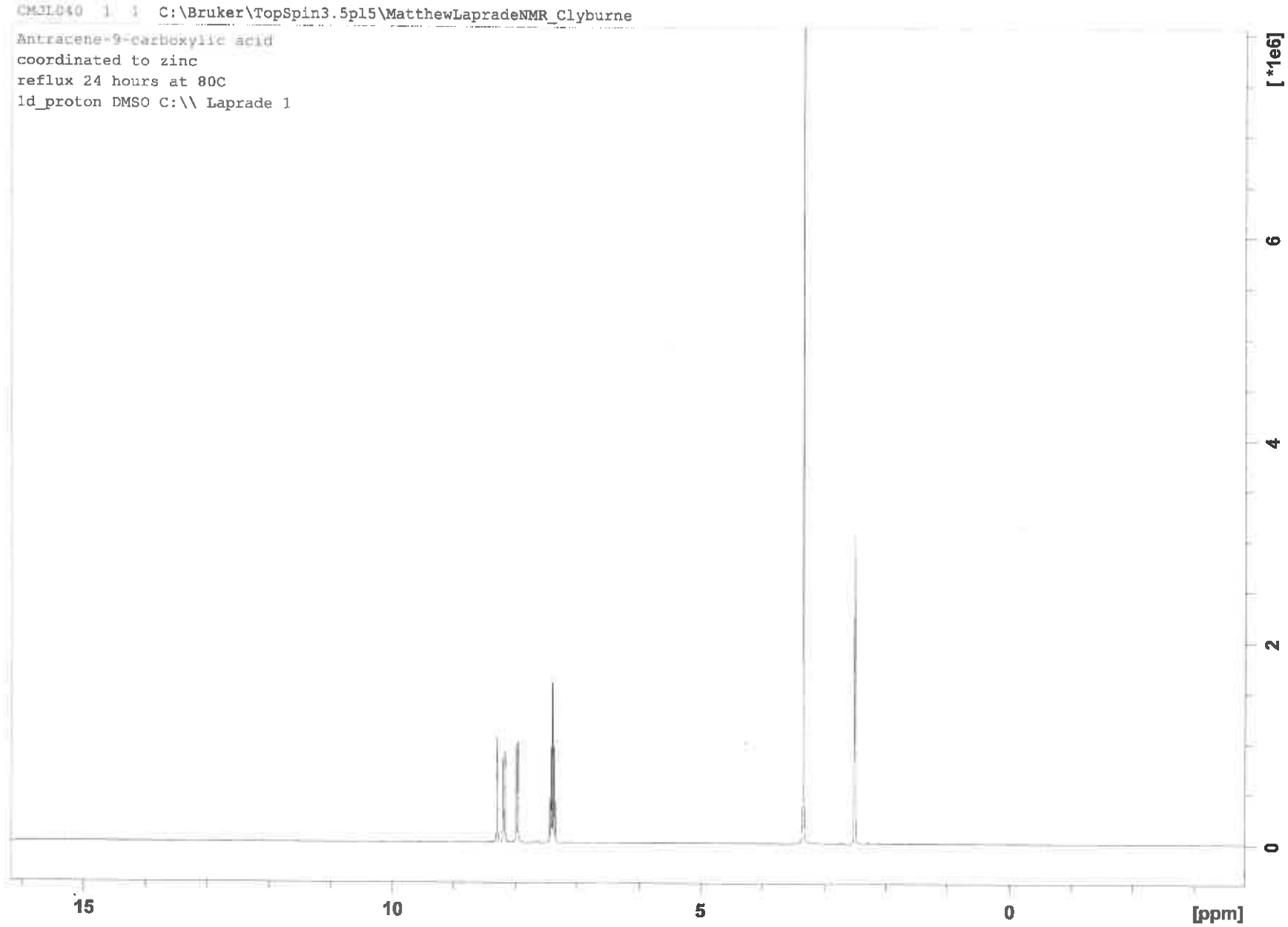

CMJL037 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
3-Methyl-Octahydro-Pentalene-1-Carboxylic
Acid (MOPCA)
Reacted with ZnCl2 and Na2CO3
Reflux at 80C for 24 hours
Dried w/ vacuum for 24 hours
1d_proton DMSO C:\\ Laprade 8
2.5725
2.5504
2.5220
2.5119
2.5058
2.4998
2.4939
2.4883
1.7422
1.7229
1.4139
1.2600
1.2253
1.1869
0.9602
0.9398
0.8023
1.1129
0.7822
1.2204
6.4927
1.7080
3.0000
[*1e6]
20
15
10
5
0
2.5
2.0
1.5
1.0
[ppm]

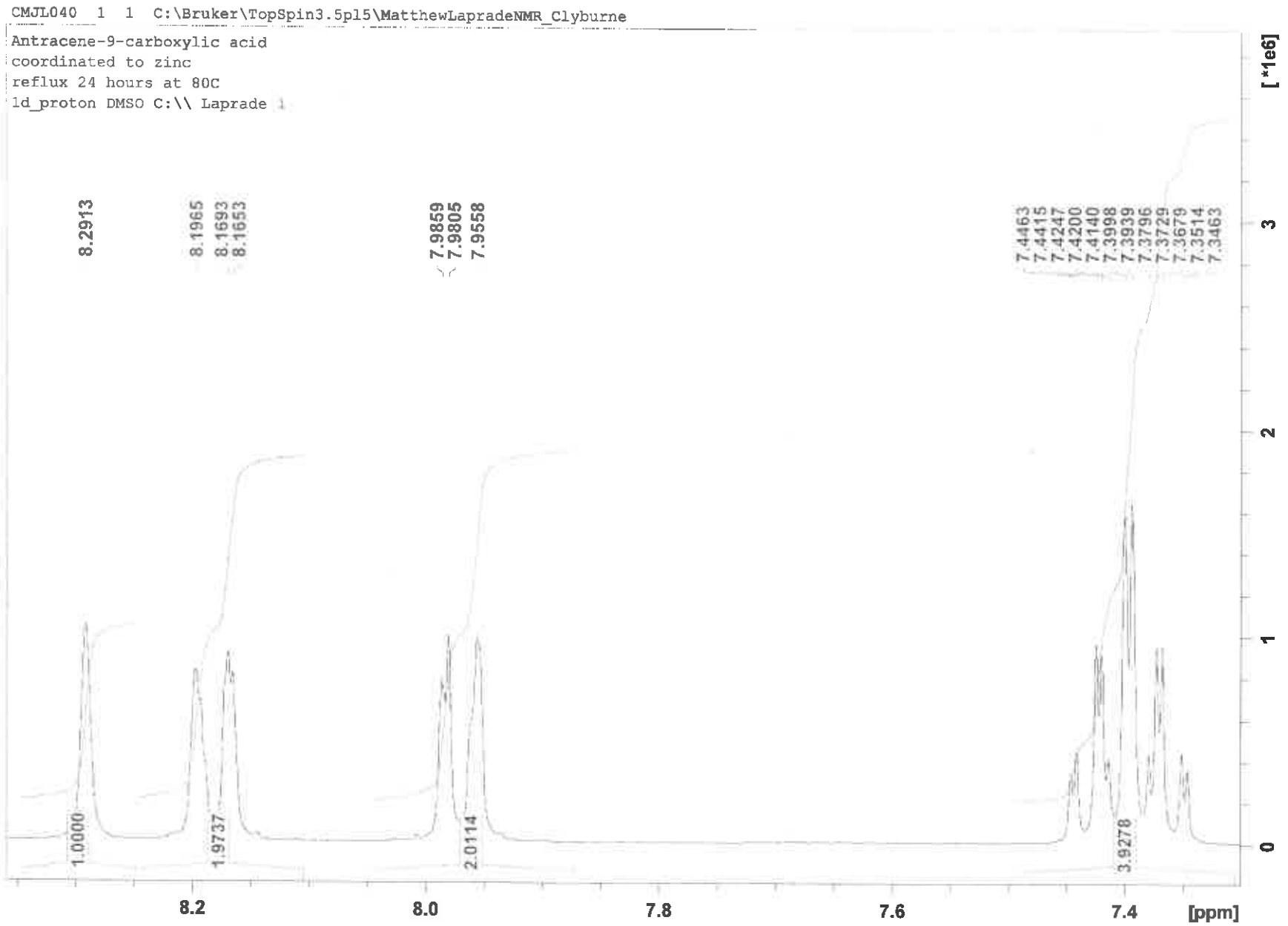

CMJL037 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
3-Methyl-Octahydro-Pentalene-1-Carboxylic
Acid (MOPCA)
Reacted with ZnCl2 and Na2CO3
Reflux at 80C for 24 hours
Dried w/ vacuum for 24 hours
1d_c13short DMSO C:\\ Laprade 8
179.8443
55.5254
51.3271
47.7542
41.6320
33.0615
31.6285
24.5868
19.5273
[*1e6]
0
2
4
6
8
10
12
200
150
100
50
0
[ppm]

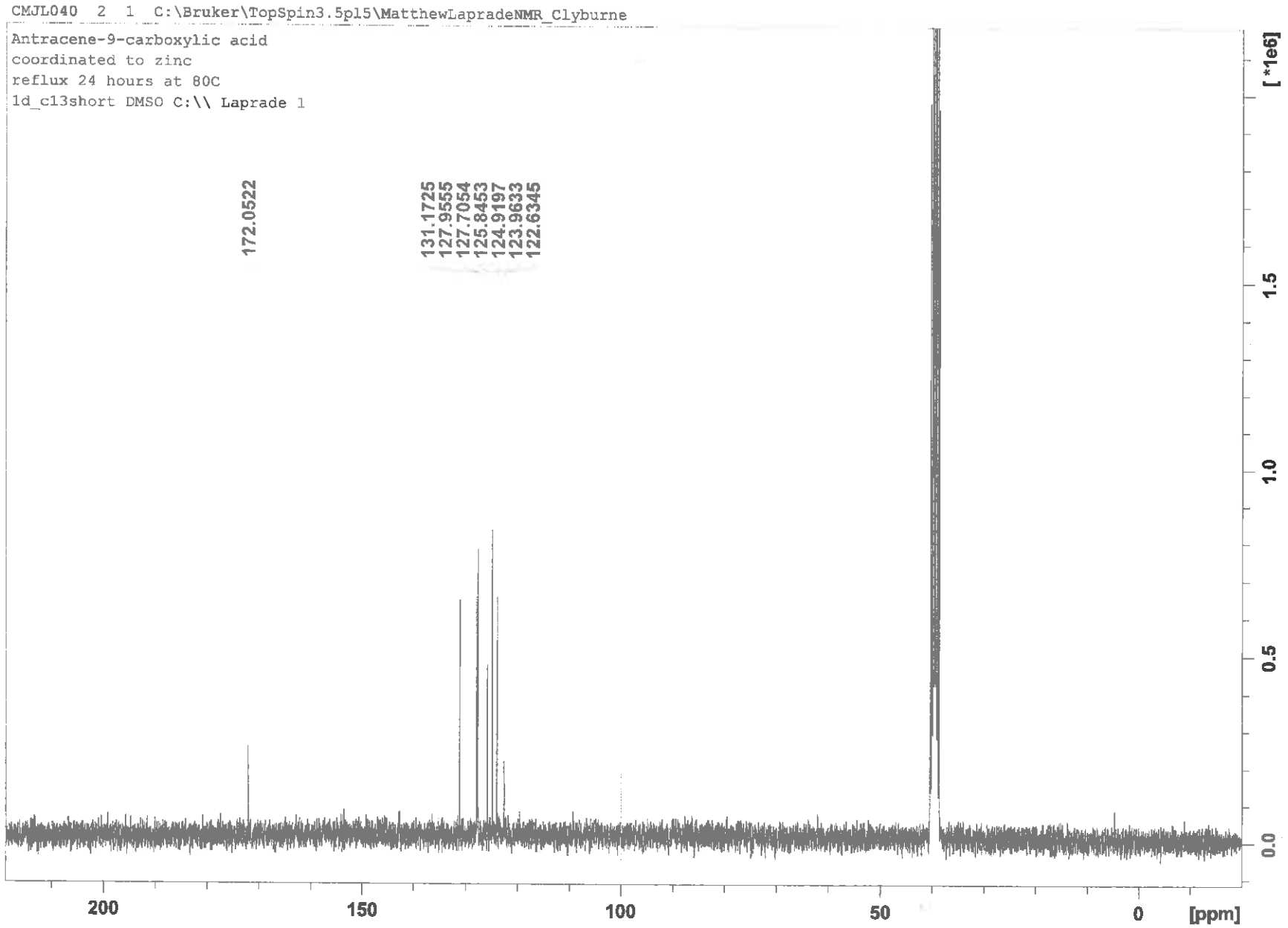

CMJL038 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clynurne
2-Cyclopentyl Hexanoic Acid
Reacted with ZnCl2 and Na2CO3
Reflux at 80C for 24 hours
1d_proton DMSO C:\\ Laprade 9
[*1e6]
15
10
5
0
15
10
5
0
[ppm]

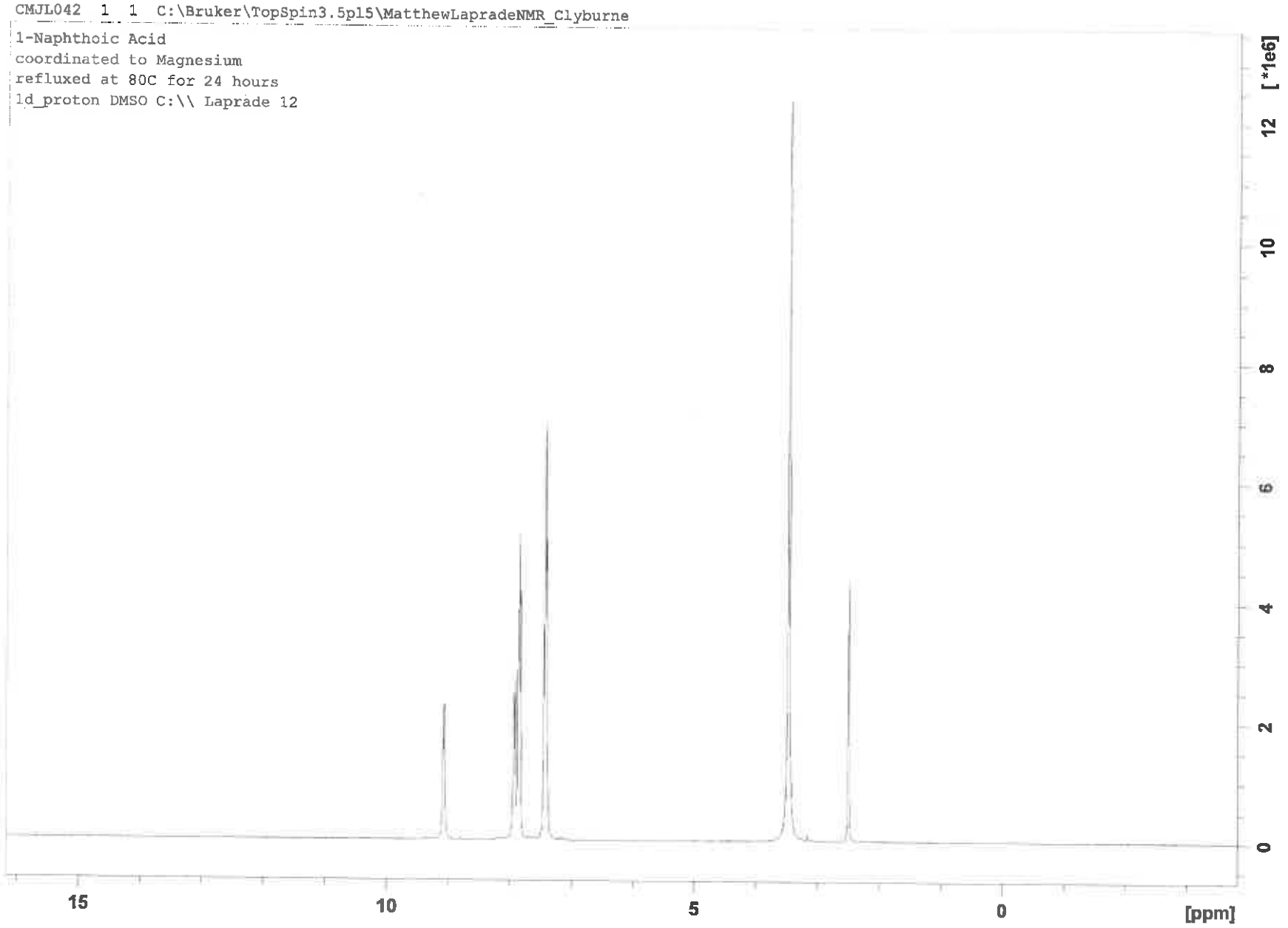

CMJL038 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
2-Cyclopentyl Hexanoic Acid
Reacted with ZnCl2 and Na2CO3
Reflux at 80C for 24 hours
1d_proton DMSO C:\\ Laprade 9
1.8129
1.7838
1.6939
1.4330
1.4122
1.4015
1.2632
1.2379
0.8422
0.8222
0.8005
0.9260
8.4302
5.9558
1.2308
3.0000
12 [*1e6]
10
8
6
4
2
0
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
[ppm]

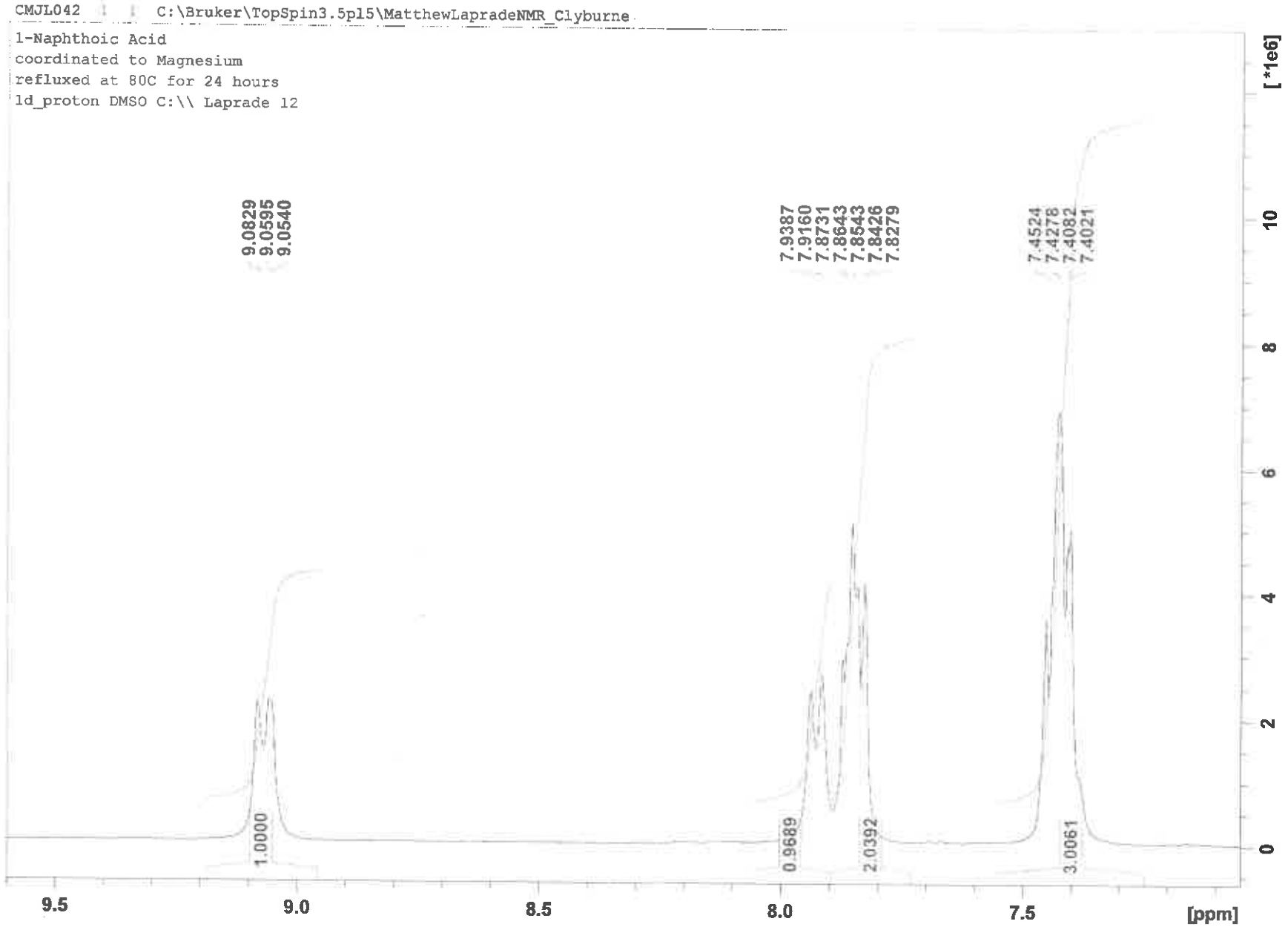

CMJL038 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
2-Cyclopentyl Hexanoic Acid
Reacted with ZnCl2 and Na2CO3
Reflux at 80C for 24 hours
1d_c13short DMSO C:\\ Laprade 9
179.8085
54.4349
43.2342
31.9267
30.9017
30.2990
30.1683
24.9537
24.7079
22.5979
14.0997
[*1e6]
6
4
2
0
200
150
100
50
0
[ppm]

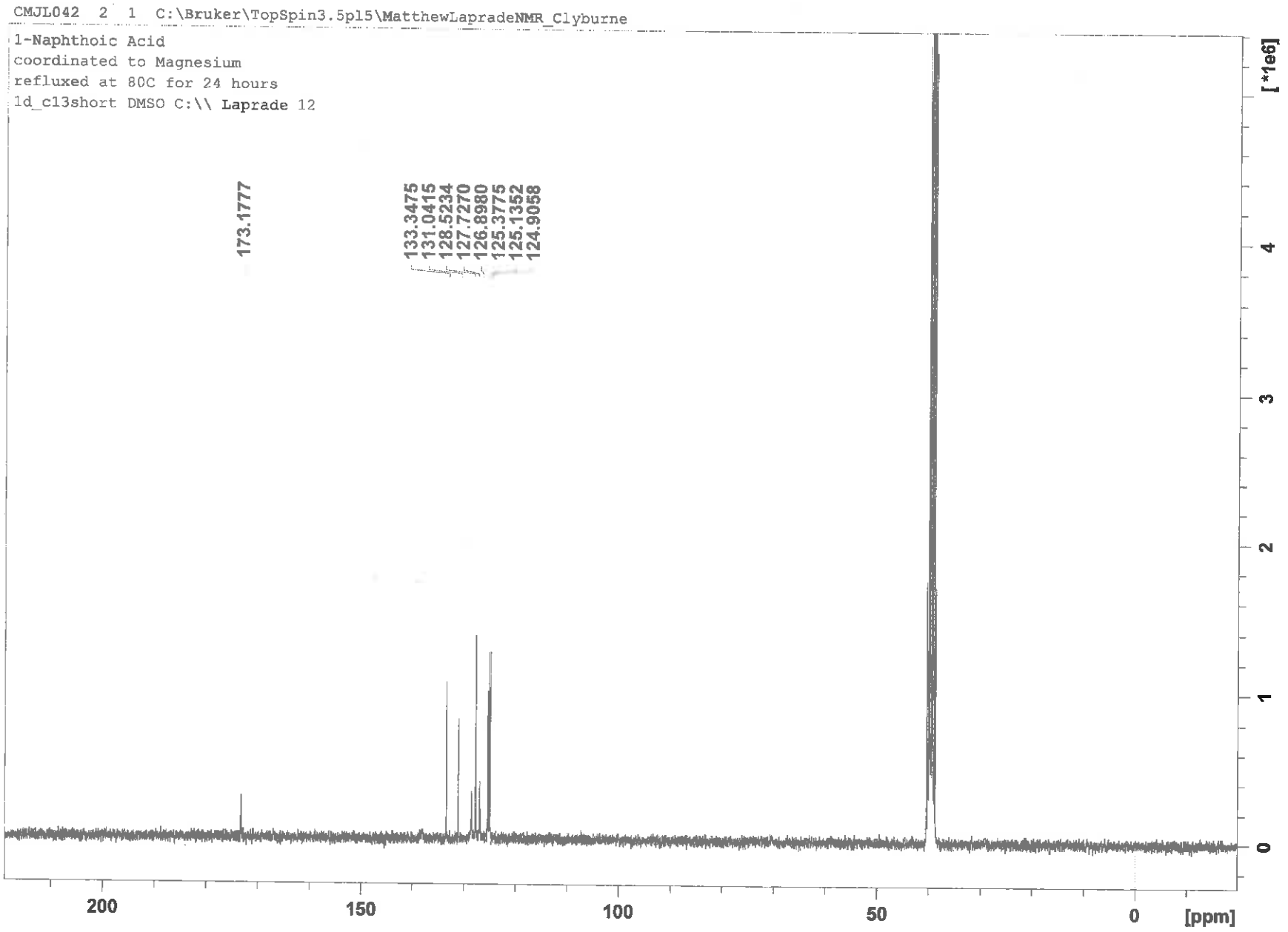

CMJL040 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
Antracene-9-carboxylic acid
coordinated to zinc
reflux 24 hours at 80C
1d_proton DMSO C:\\ Laprade 1
[*1e6]
6
4
2
0
15
10
5
0
[ppm]


CMJL040 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
Antracene-9-carboxylic acid
coordinated to zinc
reflux 24 hours at 80C
1d_proton DMSO C:\\ Laprade 1
8.2913
8.1965
8.1693
8.1653
7.9859
7.9805
7.9558
7.4463
7.4415
7.4247
7.4200
7.4140
7.3998
7.3939
7.3796
7.3729
7.3679
7.3514
7.3463
1.0000
1.9737
2.0114
3.9278
8.2
8.0
7.8
7.6
7.4
[ppm]
[*1e6]
0
1
2
3


CMJL040 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
Antracene-9-carboxylic acid
coordinated to zinc
reflux 24 hours at 80C
1d_c13short DMSO C:\\ Laprade 1
172.0522
131.1725
127.9555
127.7054
125.8453
124.9197
123.9633
122.6345
[*1e6]
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]

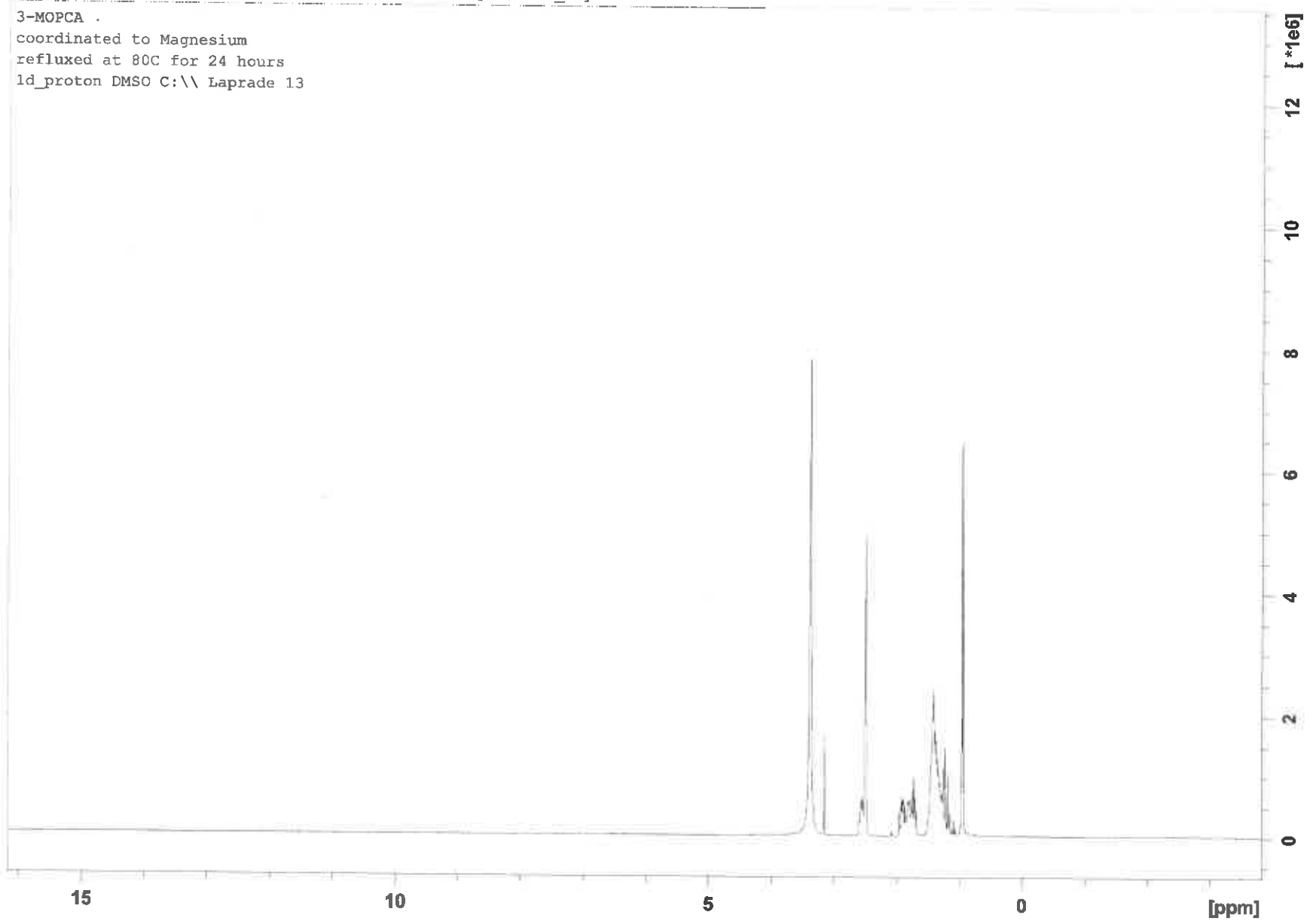

CMJL042 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Naphthoic Acid
coordinated to Magnesium
refluxed at 80C for 24 hours
1d_proton DMSO C:\\ Laprade 12
[*1e6]
12
10
8
6
4
2
0
15
10
5
0
[ppm]


CMJL042 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Naphthoic Acid
coordinated to Magnesium
refluxed at 80C for 24 hours
1d_proton DMSO C:\\ Laprade 12
9.0829
9.0595
9.0540
7.9387
7.9160
7.8731
7.8643
7.8543
7.8426
7.8279
7.4524
7.4278
7.4082
7.4021
1.0000
0.9689
2.0392
3.0061
9.5
9.0
8.5
8.0
7.5
[ppm]
[*1e6]
0
2
4
6
8
10


CMJL042 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Naphthoic Acid
coordinated to Magnesium
refluxed at 80C for 24 hours
1d_c13short DMSO C:\\ Laprade 12
173.1777
133.3475
131.0415
128.5234
127.7270
126.8980
125.3775
125.1352
124.9058
[*1e6]
0
1
2
3
4
200
150
100
50
0
[ppm]

CMJL043 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne

3-MOPCA .
coordinated to Magnesium
refluxed at 80C for 24 hours
1d_proton DMSO C:\\ Laprade 13



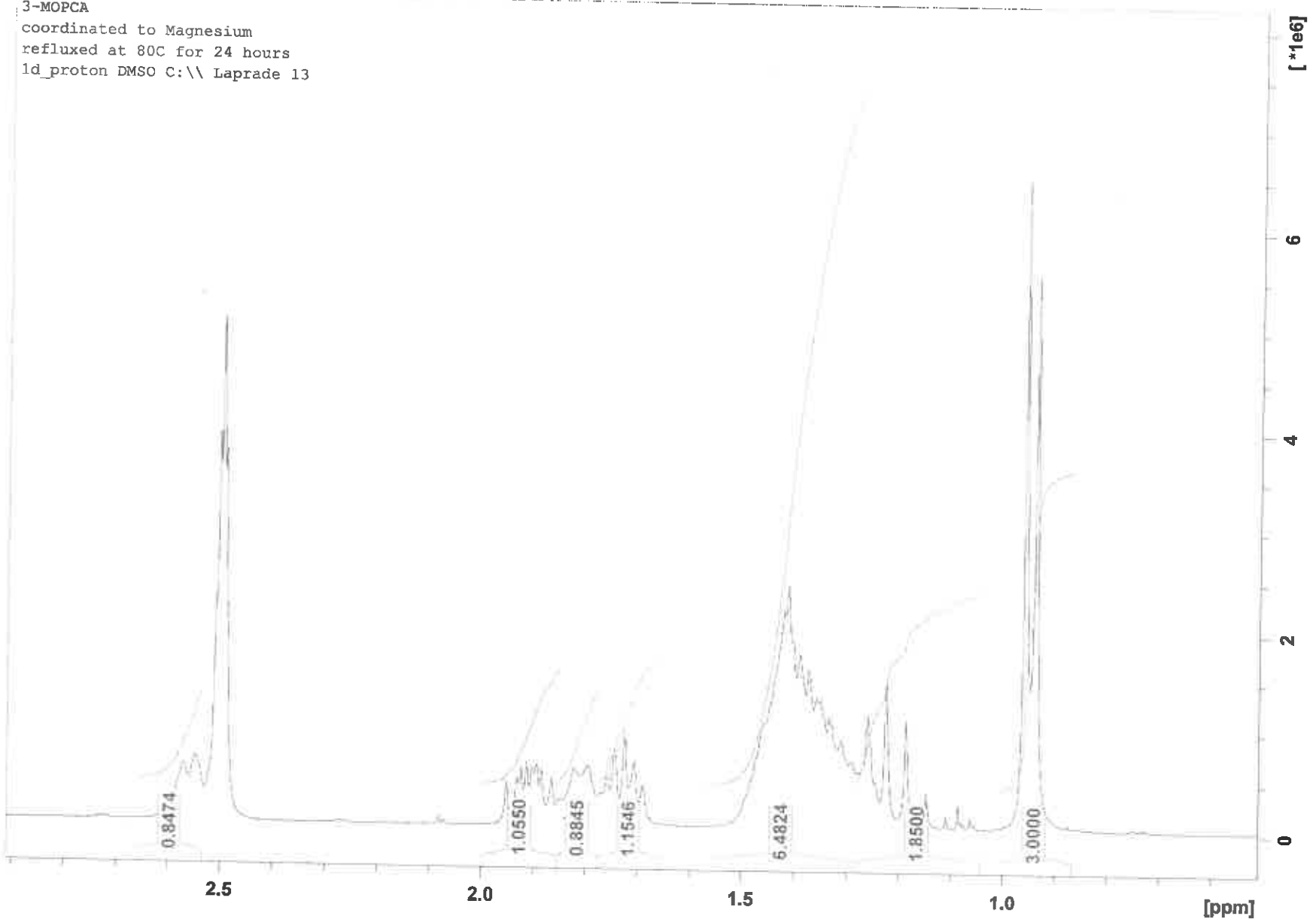
CMJL043 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne

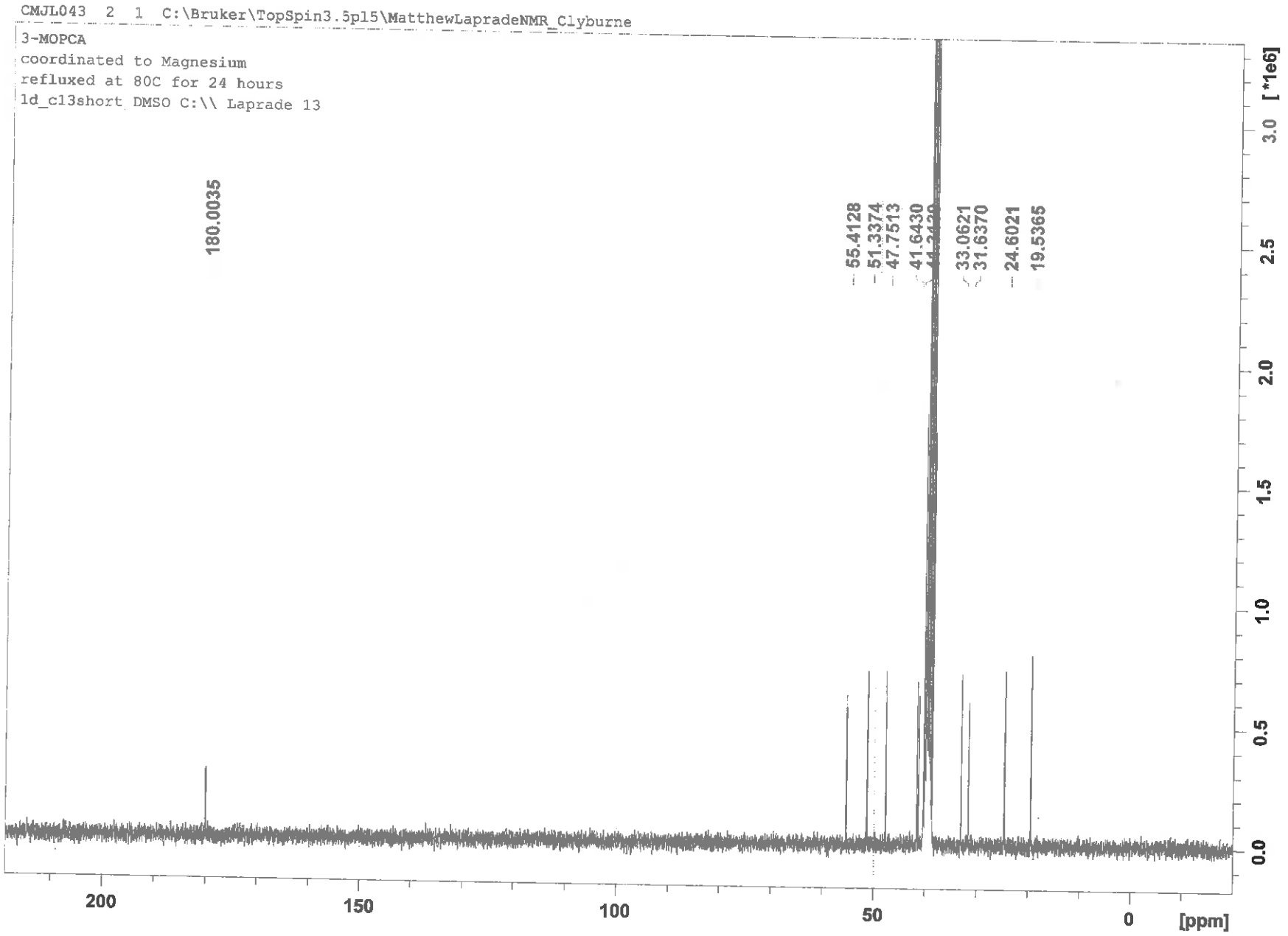
3-MOPCA

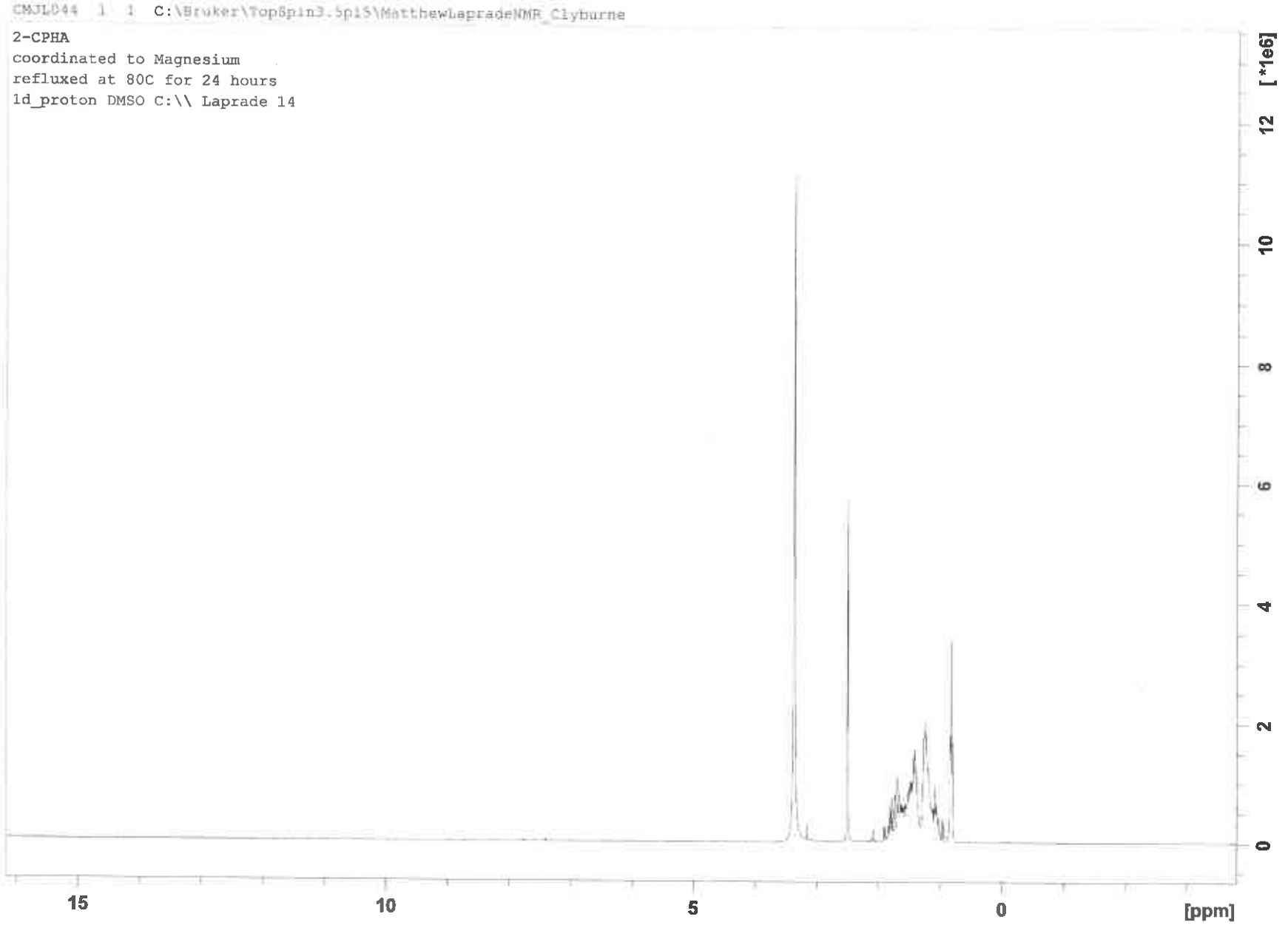
coordinated to Magnesium

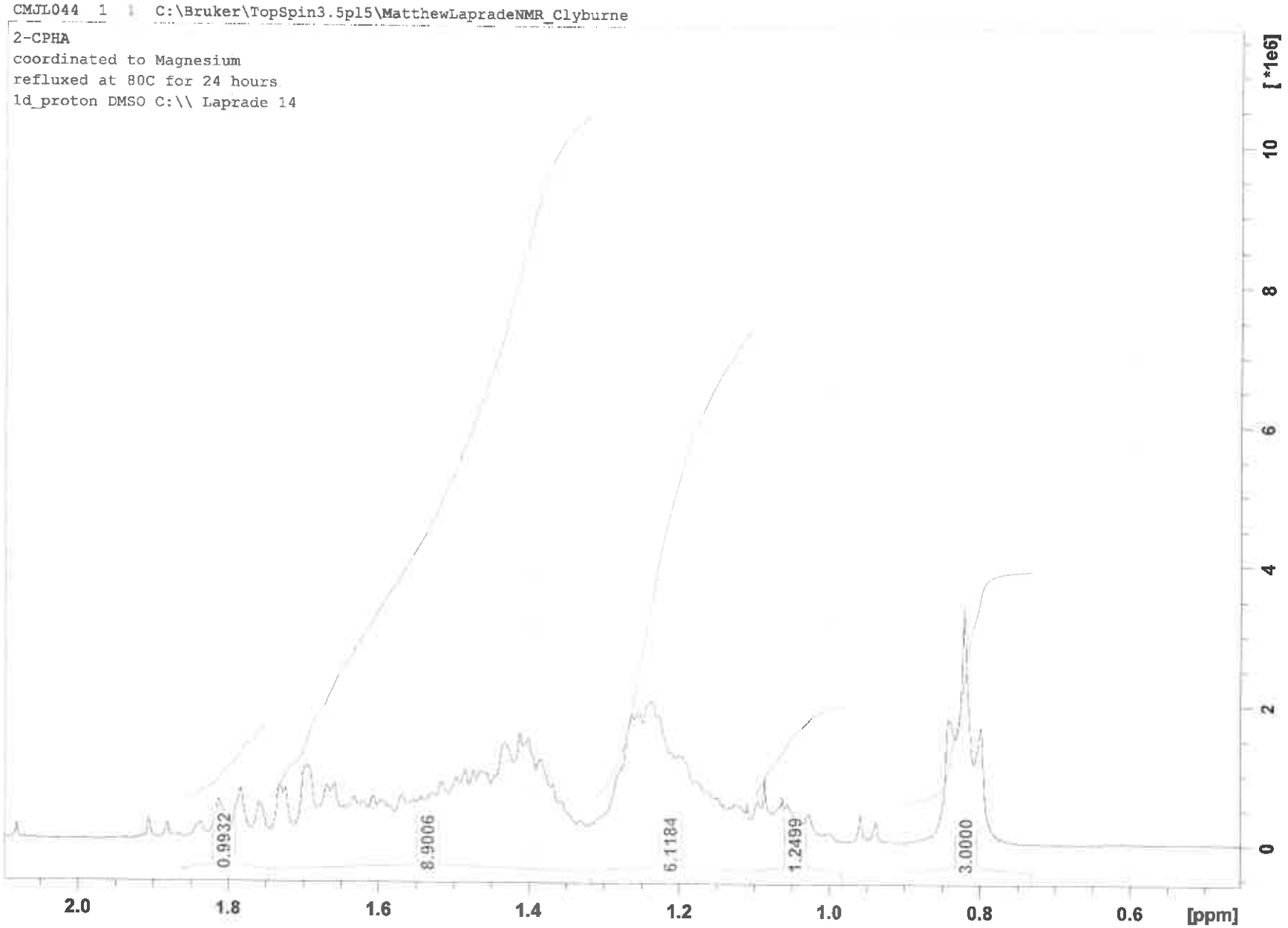
refluxed at 80C for 24 hours

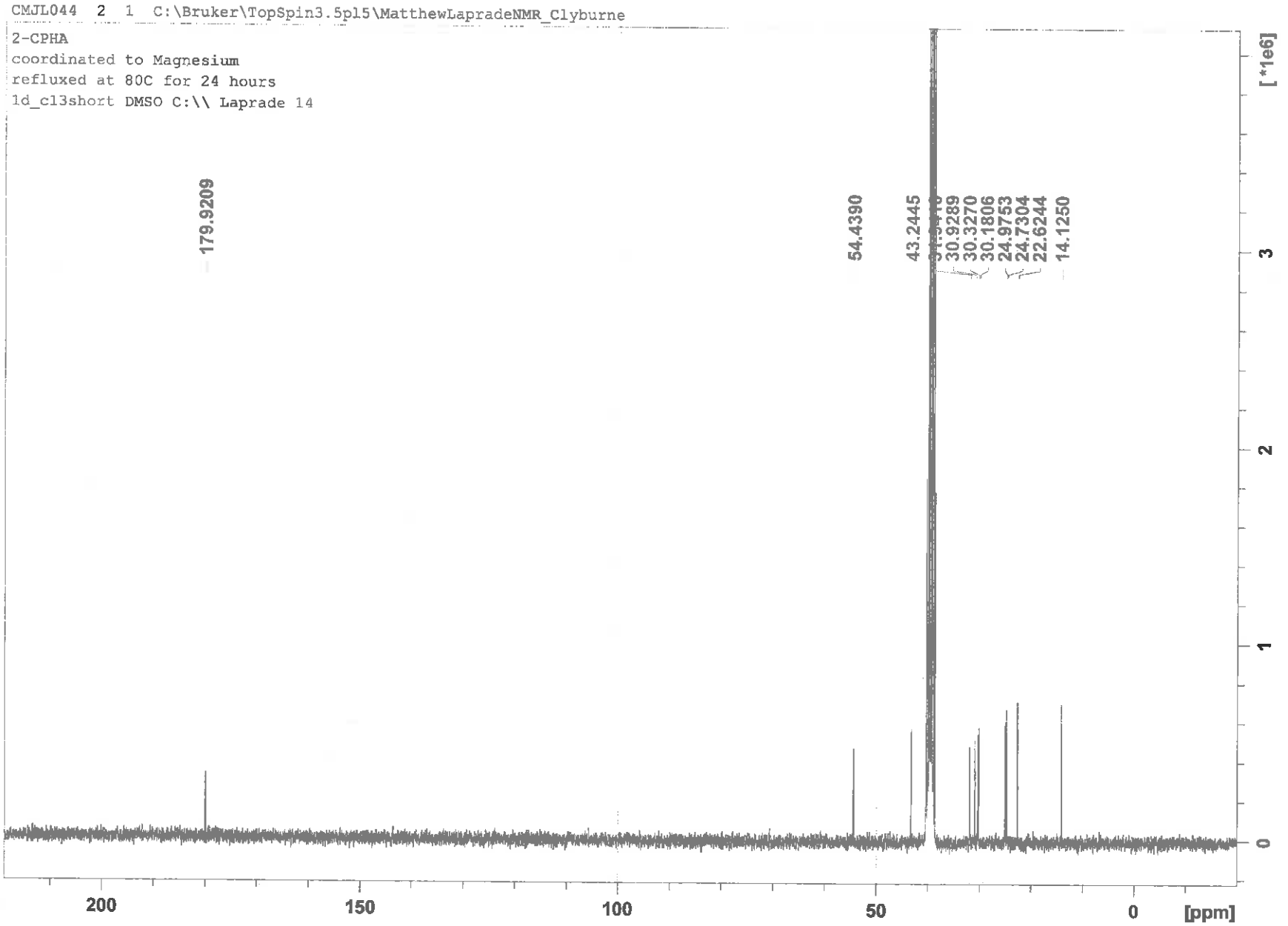
1d_proton DMSO C:\\ Laprade 13

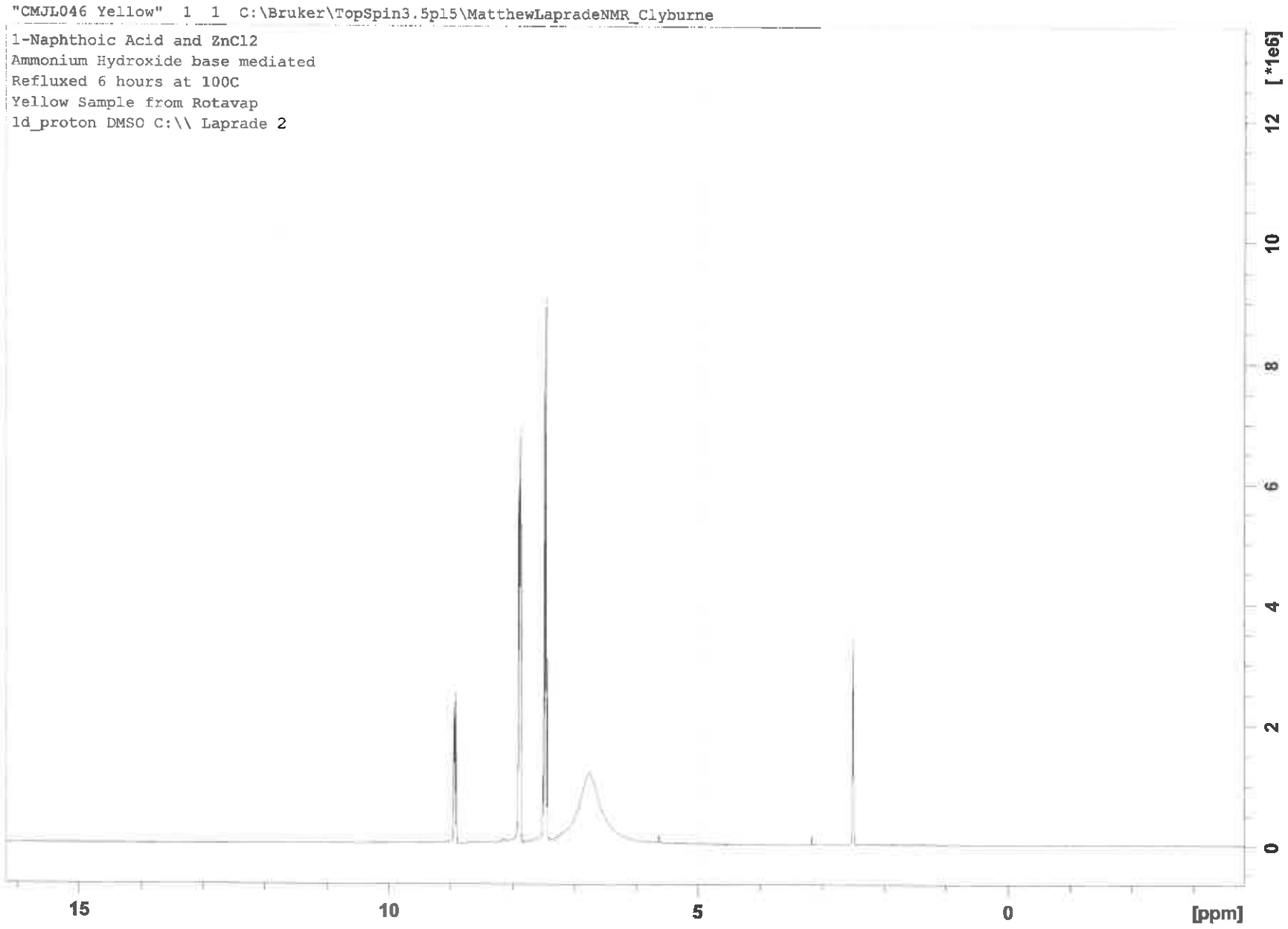


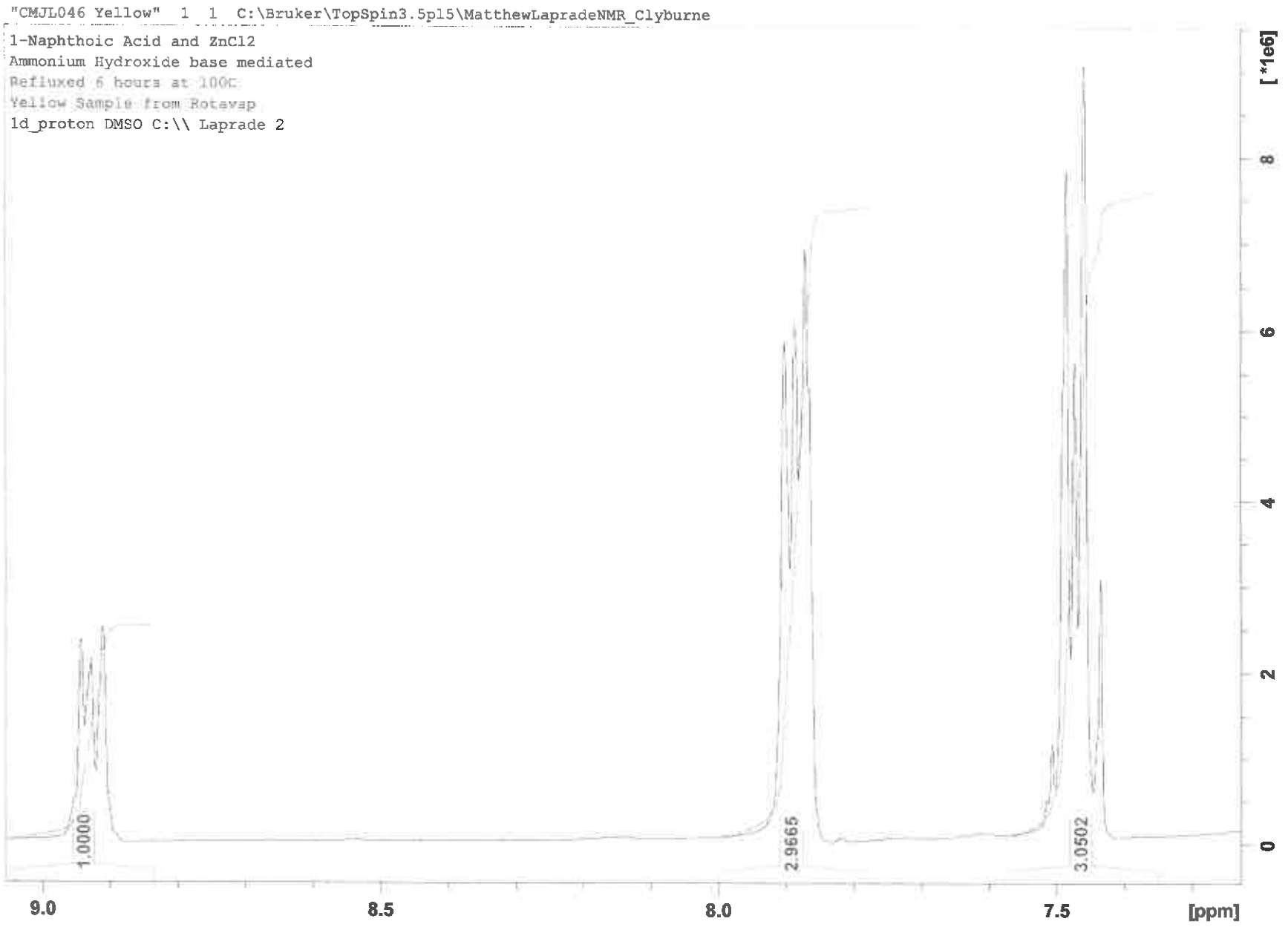

CMJL043 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
3-MOPCA
coordinated to Magnesium
refluxed at 80C for 24 hours
1d_c13short DMSO C:\\ Laprade 13
180.0035
55.4128
51.3374
47.7513
41.6430
33.0621
31.6370
24.6021
19.5365
200
150
100
50
0
[ppm]
0.0
0.5
1.0
1.5
2.0
2.5
3.0
[*1e6]

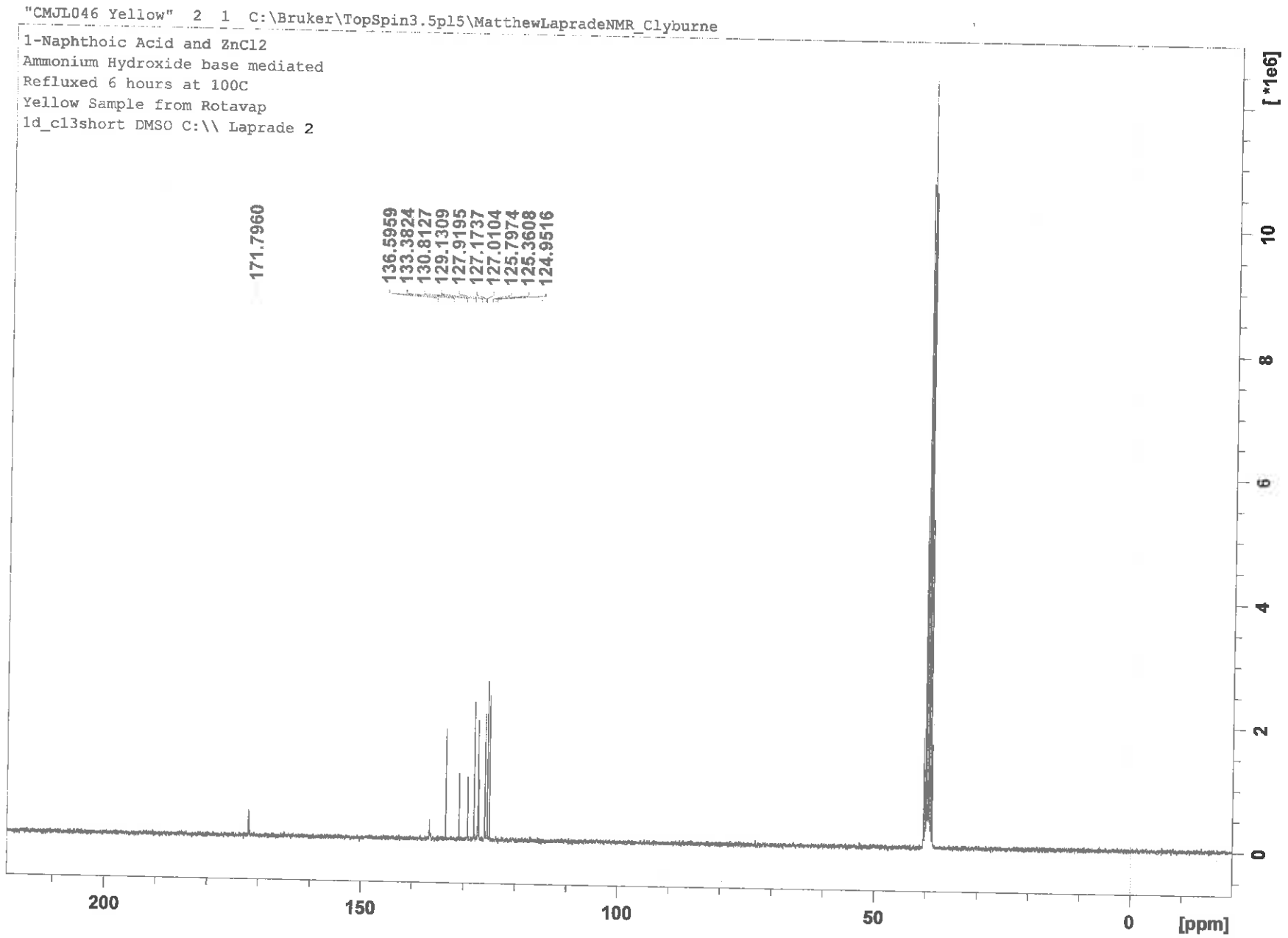

CMJL044 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLaprade\NMR_Clyburne
2-CPHA
coordinated to Magnesium
refluxed at 80C for 24 hours
1d_proton DMSO C:\\ Laprade 14
[*1e6]
12
10
8
6
4
2
0
15
10
5
0
[ppm]

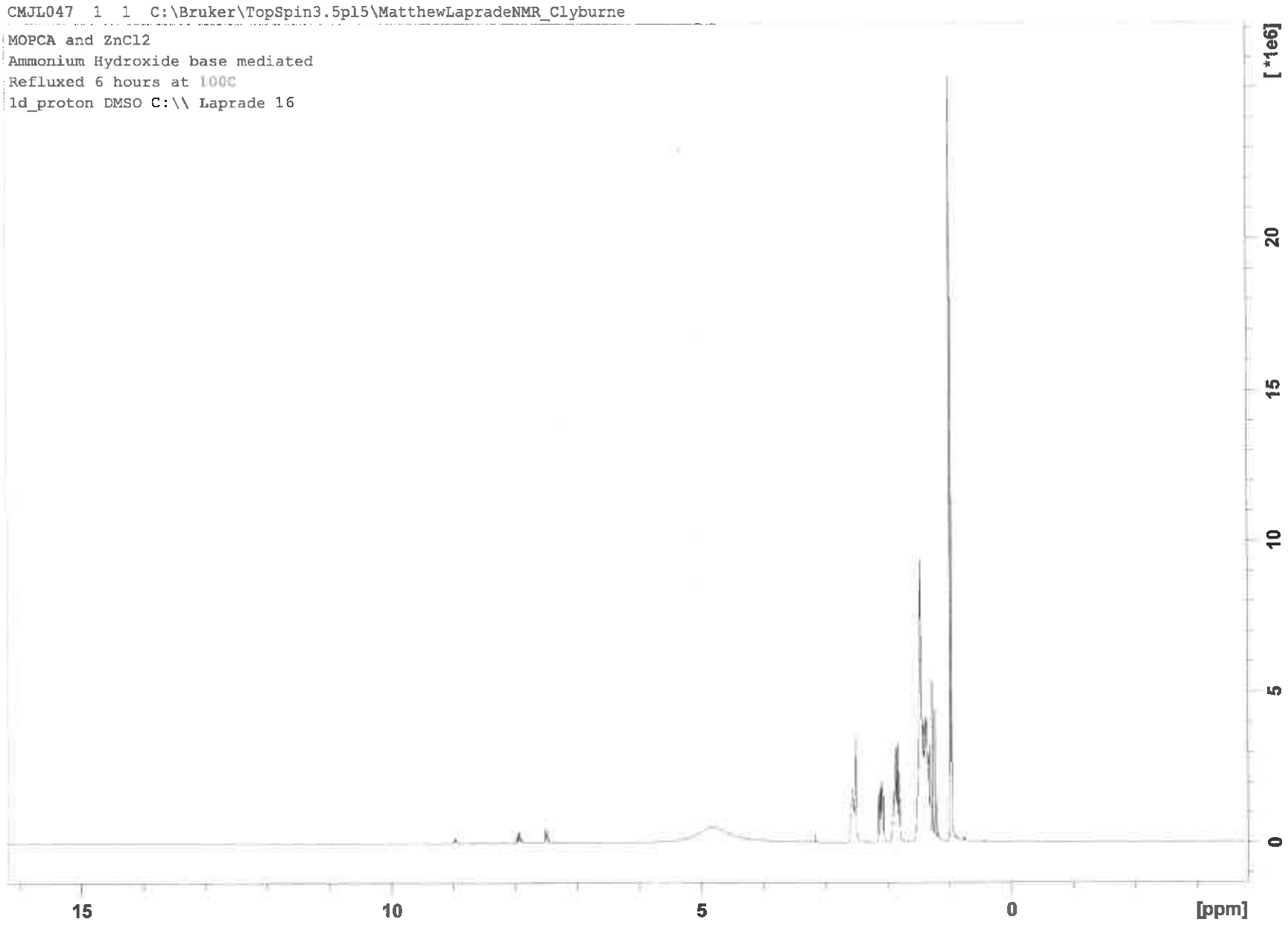

CMJL044 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
2-CPHA
coordinated to Magnesium
refluxed at 80C for 24 hours
1d_proton DMSO C:\\ Laprade 14
0.9932
8.9006
6.1184
1.2499
3.0000
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
[ppm]
0
2
4
6
8
10
[*1e6]

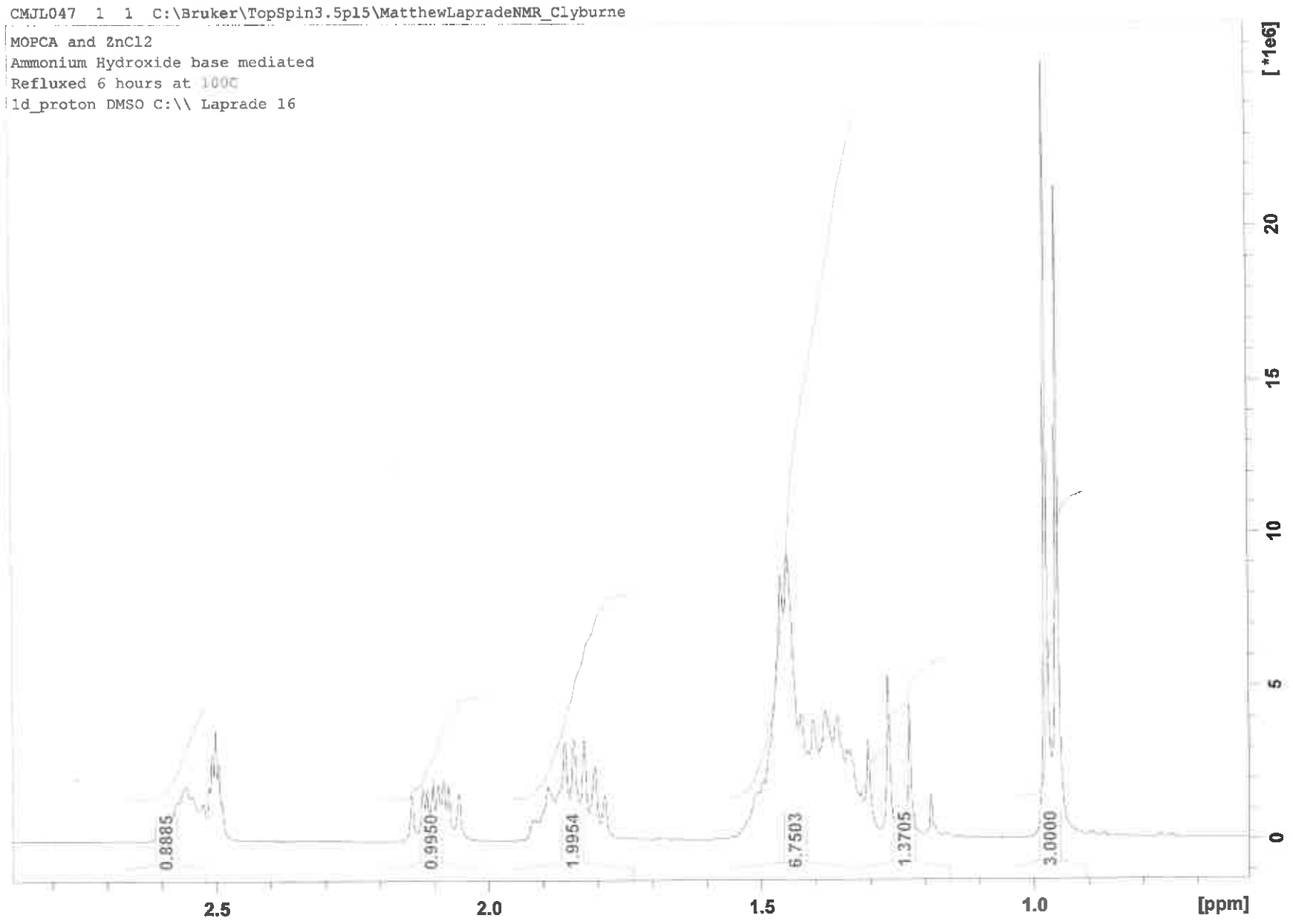

CMJL044 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
2-CPHA
coordinated to Magnesium
refluxed at 80C for 24 hours
1d_c13short DMSO C:\\ Laprade 14
179.9209
54.4390
43.2445
30.9289
30.3270
30.1806
24.9753
24.7304
22.6244
14.1250
[*1e6]
0
1
2
3
200
150
100
50
0
[ppm]

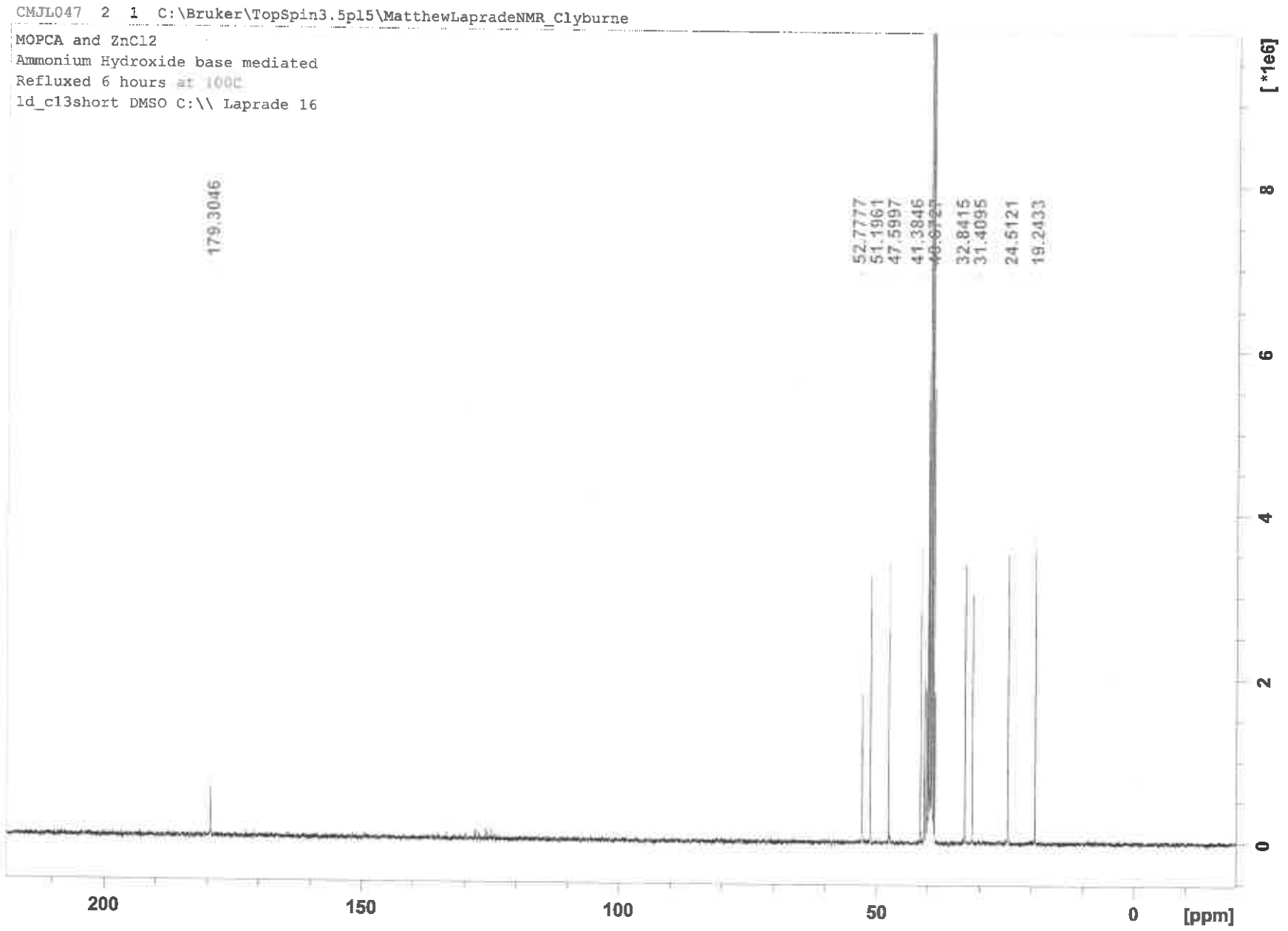

"CMJL046 Yellow" 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Naphthoic Acid and ZnCl2
Ammonium Hydroxide base mediated
Refluxed 6 hours at 100C
Yellow Sample from Rotavap
1d_proton DMSO C:\\ Laprade 2
[*1e6]
12
10
8
6
4
2
0
15
10
5
0
[ppm]

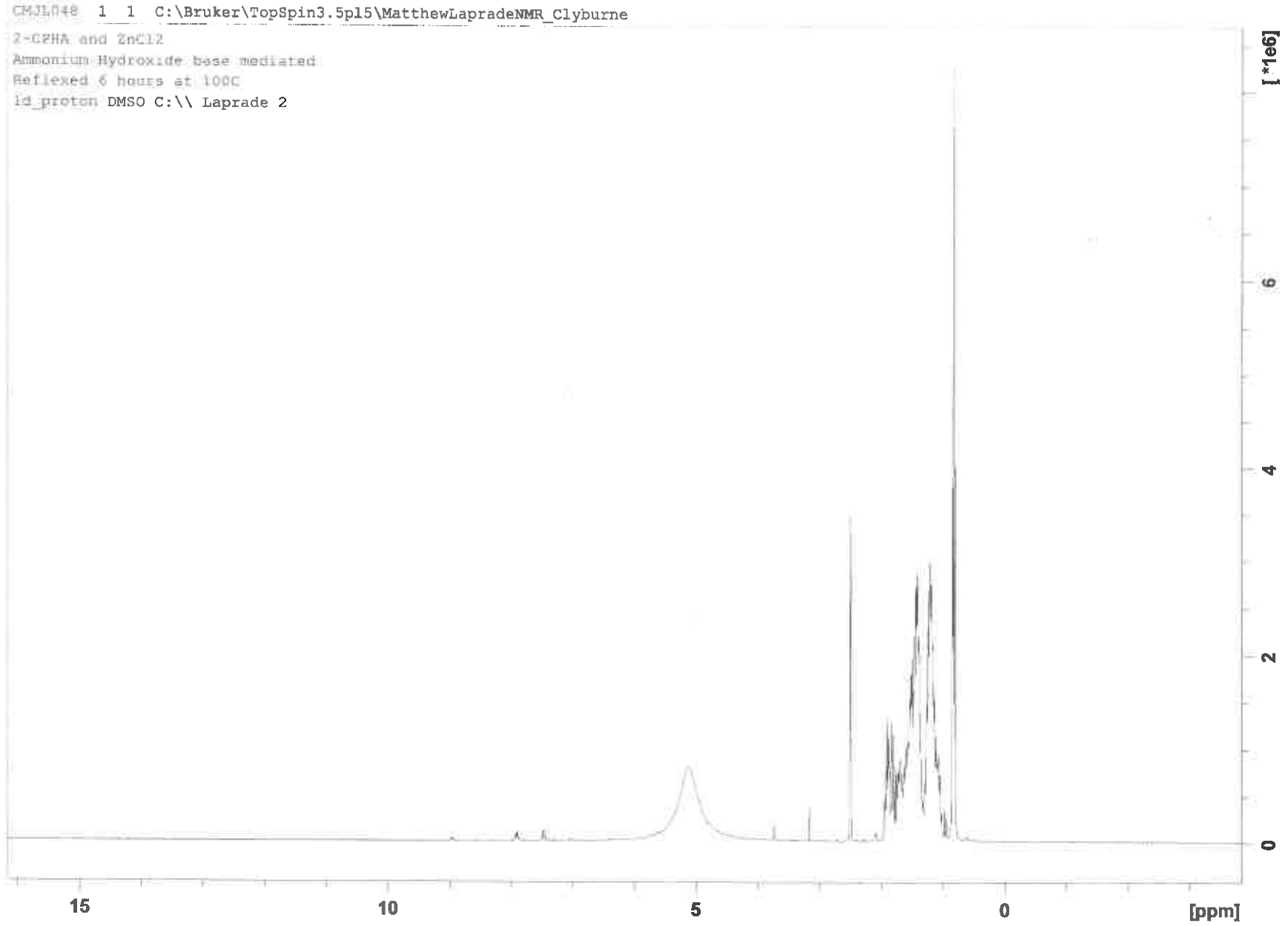

"CMJL046 Yellow" 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Naphthoic Acid and ZnCl2
Ammonium Hydroxide base mediated
Refluxed 6 hours at 100C
Yellow Sample from Rotavap
1d_proton DMSO C:\\ Laprade 2
[*1e6]
8
6
4
2
0
1.0000
2.9665
3.0502
9.0
8.5
8.0
7.5
[ppm]

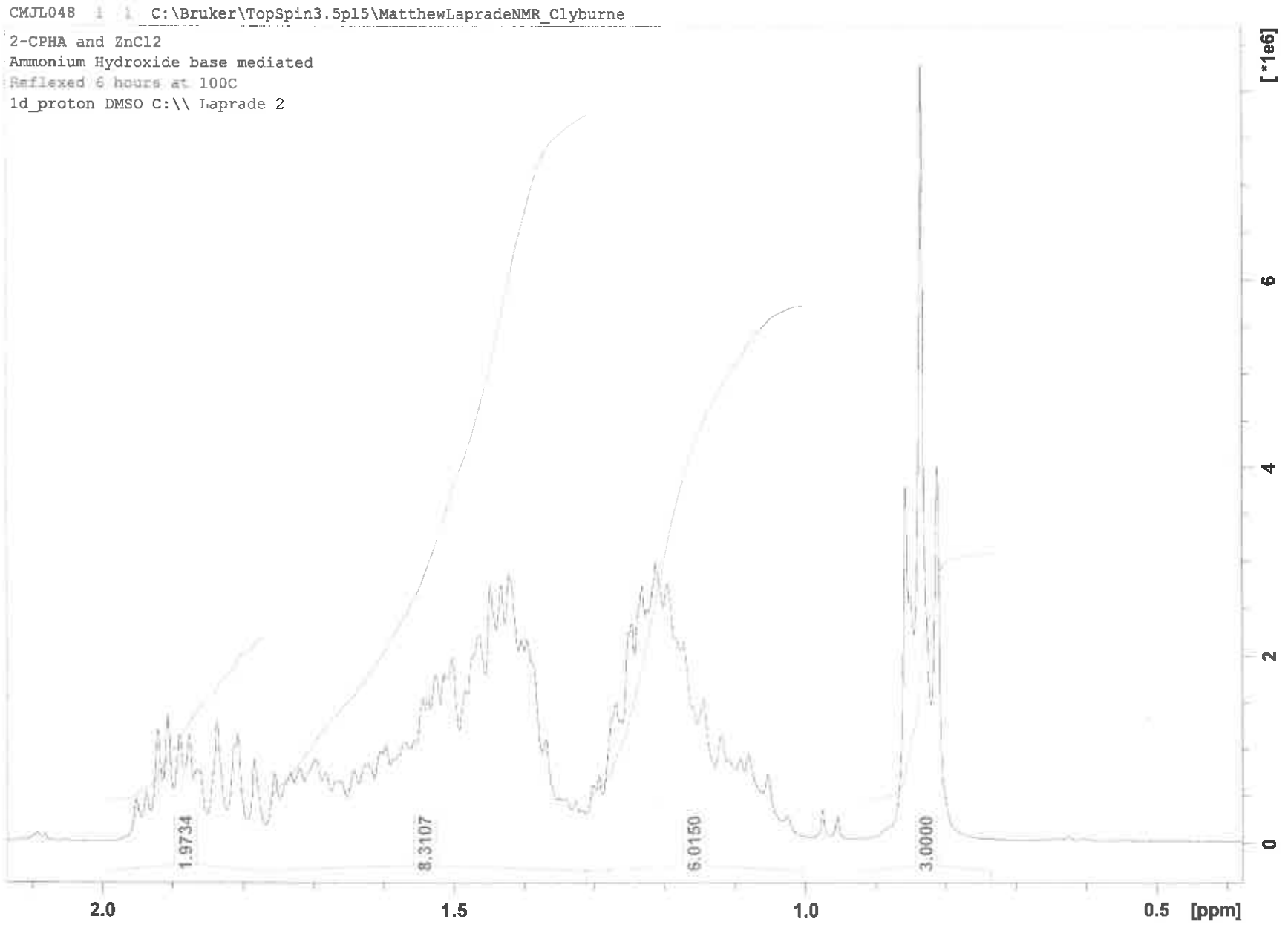

"CMJL046 Yellow" 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Naphthoic Acid and ZnCl2
Ammonium Hydroxide base mediated
Refluxed 6 hours at 100C
Yellow Sample from Rotavap
1d_c13short DMSO C:\\ Laprade 2
171.7960
136.5959
133.3824
130.8127
129.1309
127.9195
127.1737
127.0104
125.7974
125.3608
124.9516
[*1e6]
0
2
4
6
8
10
200
150
100
50
0
[ppm]

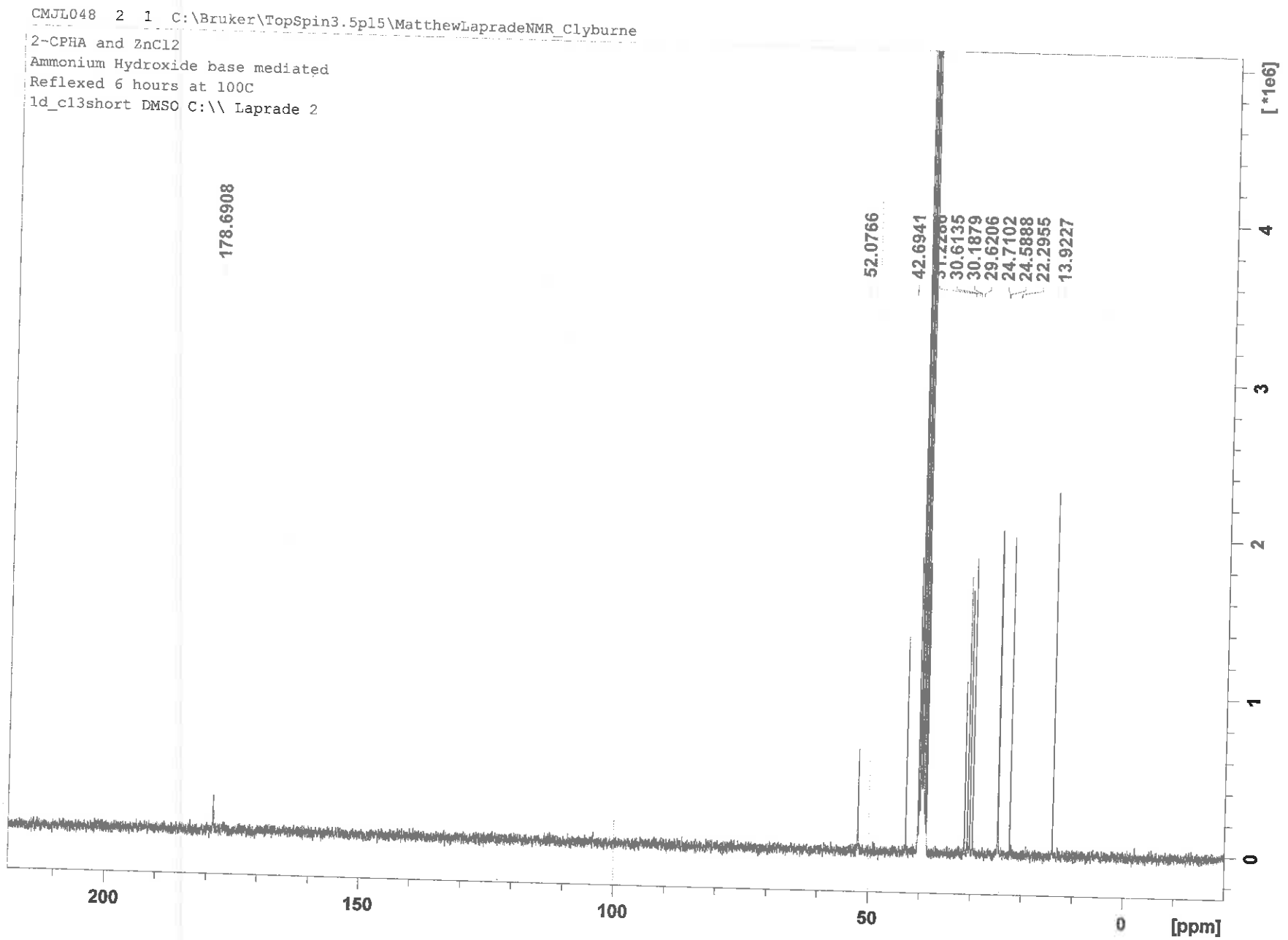

CMJL047 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
MOPCA and ZnCl2
Ammonium Hydroxide base mediated
Refluxed 6 hours at 100C
1d_proton DMSO C:\\ Laprade 16
[*1e6]
20
15
10
5
0
15
10
5
0
[ppm]

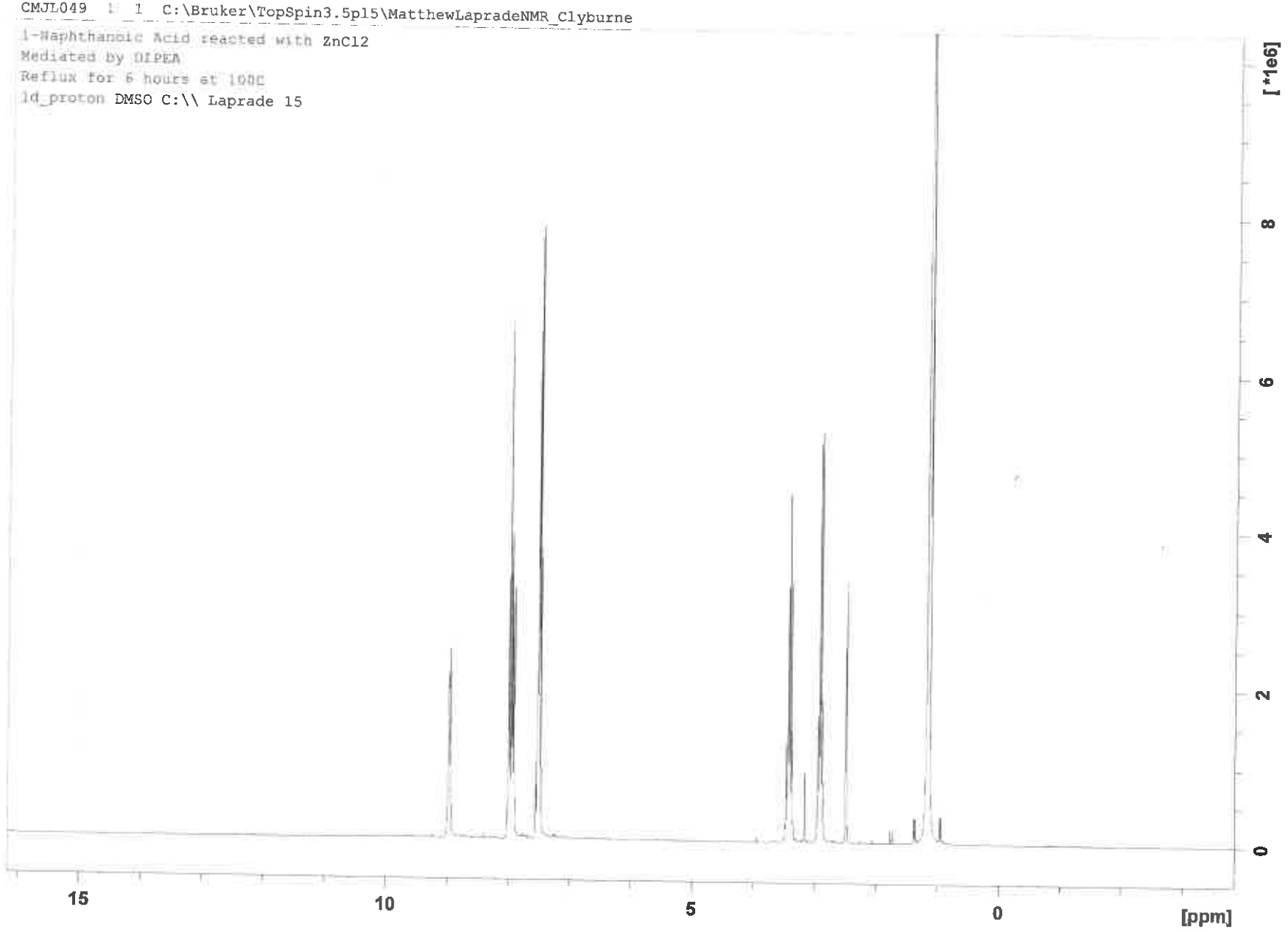

CMJL047 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
MOPCA and ZnCl2
Ammonium Hydroxide base mediated
Refluxed 6 hours at 100C
1d_proton DMSO C:\\ Laprade 16
[*1e6]
20
15
10
5
0
0.8885
0.9950
1.9954
6.7503
1.3705
3.0000
2.5
2.0
1.5
1.0
[ppm]


CMJL047 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
MOPCA and ZnCl2
Ammonium Hydroxide base mediated
Refluxed 6 hours at 100C
1d_c13short DMSO C:\\ Laprade 16
179.3046
52.7777
51.1961
47.5997
41.3846
32.8415
31.4095
24.5121
19.2433
[*1e6]
8
6
4
2
0
200
150
100
50
0
[ppm]


CMJL048 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
2-CPHA and ZnCl2
Ammonium Hydroxide base mediated
Refluxed 6 hours at 100C
1d_proton DMSO C:\\ Laprade 2
[*1e6]
6
4
2
0
15
10
5
0
[ppm]

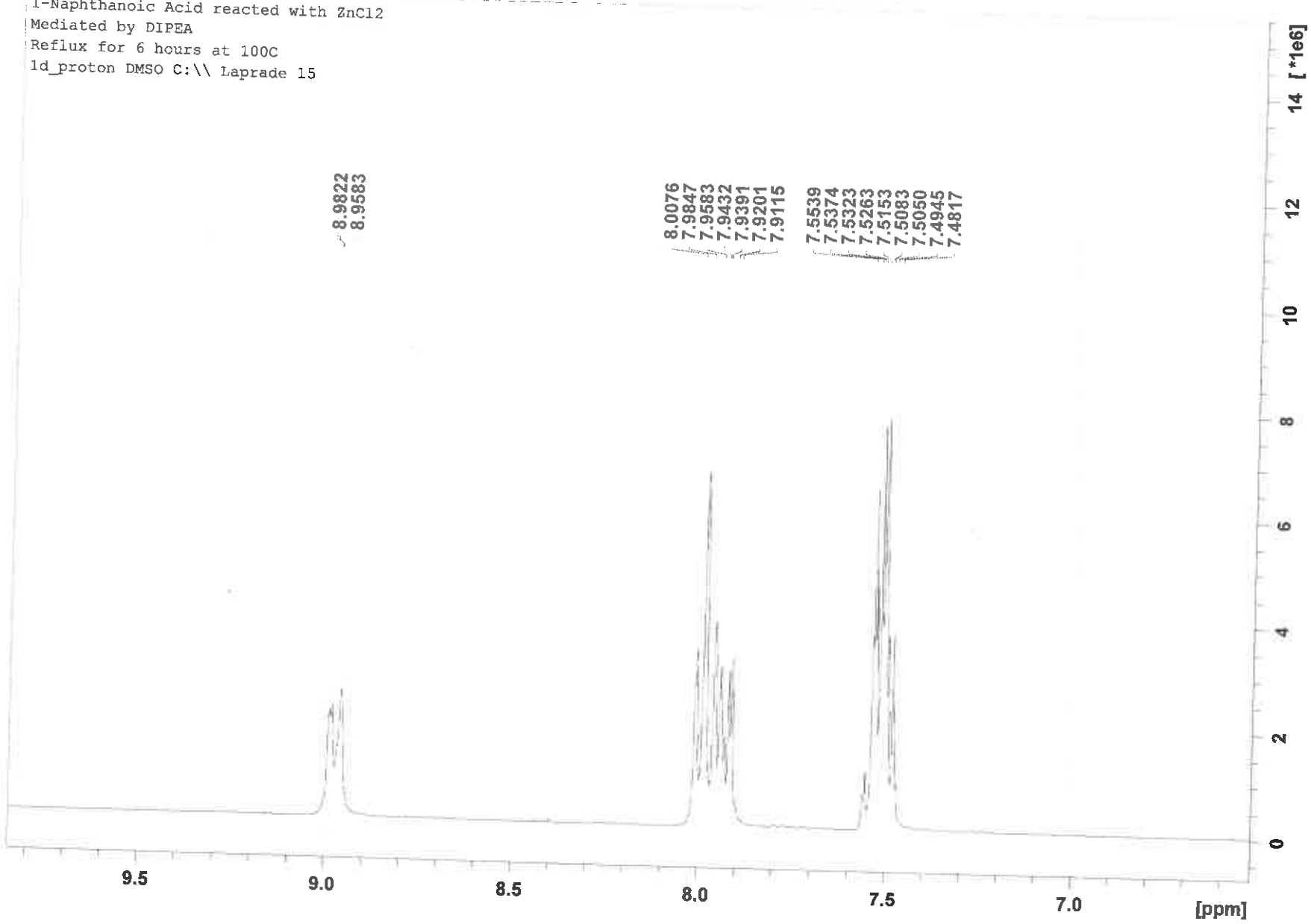

CMJL048 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
2-CPHA and ZnCl2
Ammonium Hydroxide base mediated
Refluxed 6 hours at 100C
1d_proton DMSO C:\\ Laprade 2
1.9734
8.3107
6.0150
3.0000
2.0
1.5
1.0
0.5
[ppm]
[*1e6]
0
2
4
6

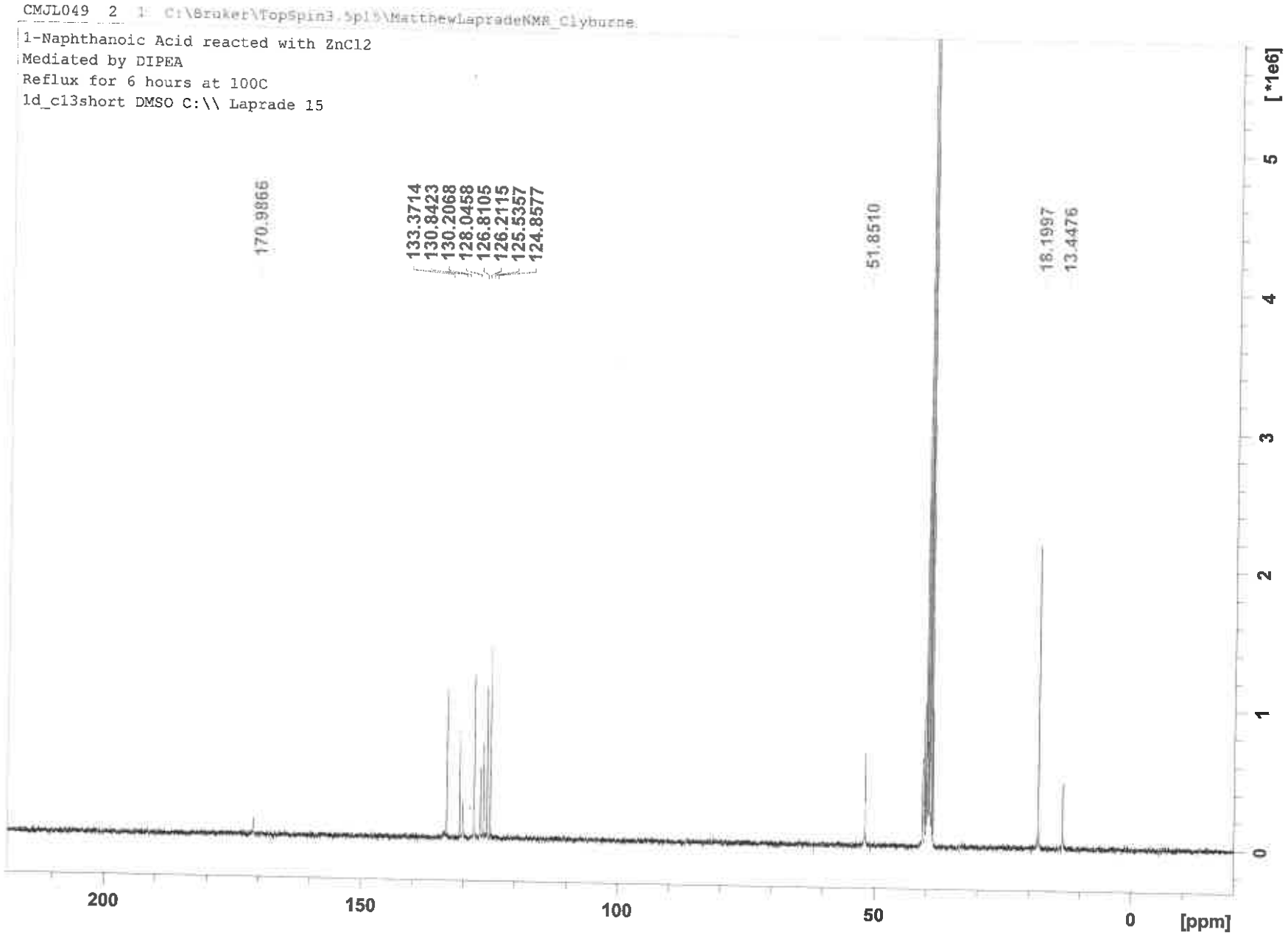

CMJL048 2 1 C:\Bruker\TopSpin3.5p15\MatthewLapradeNMR_Clyburne
2-CPHA and ZnCl2
Ammonium Hydroxide base mediated
Reflexed 6 hours at 100C
1d_c13short DMSO C:\\ Laprade 2
178.6908
52.0766
42.6941
31.4260
30.6135
30.1879
29.6206
24.7102
24.5888
22.2955
13.9227
[*1e6]
4
3
2
1
0
200
150
100
50
0
[ppm]


CMJL049 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Naphthanoic Acid reacted with ZnCl2
Mediated by DIPEA
Reflux for 6 hours at 100C
1d_proton DMSO C:\\ Laprade 15
[*1e6]
8
6
4
2
0
15
10
5
0
[ppm]

CMJL049 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne

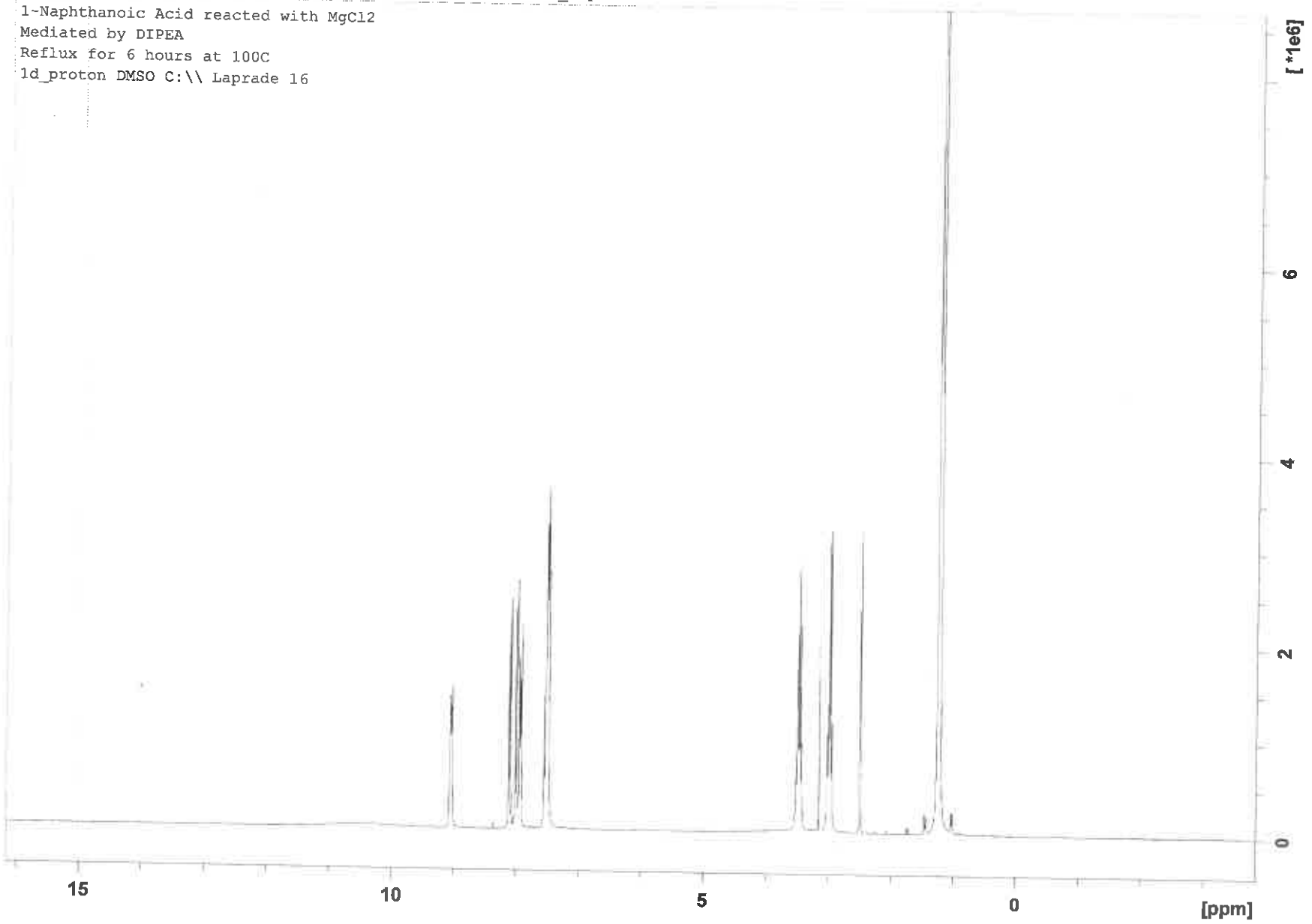
1-Naphthanoic Acid reacted with ZnCl2
Mediated by DIPEA
Reflux for 6 hours at 100C
1d_proton DMSO C:\\ Laprade 15

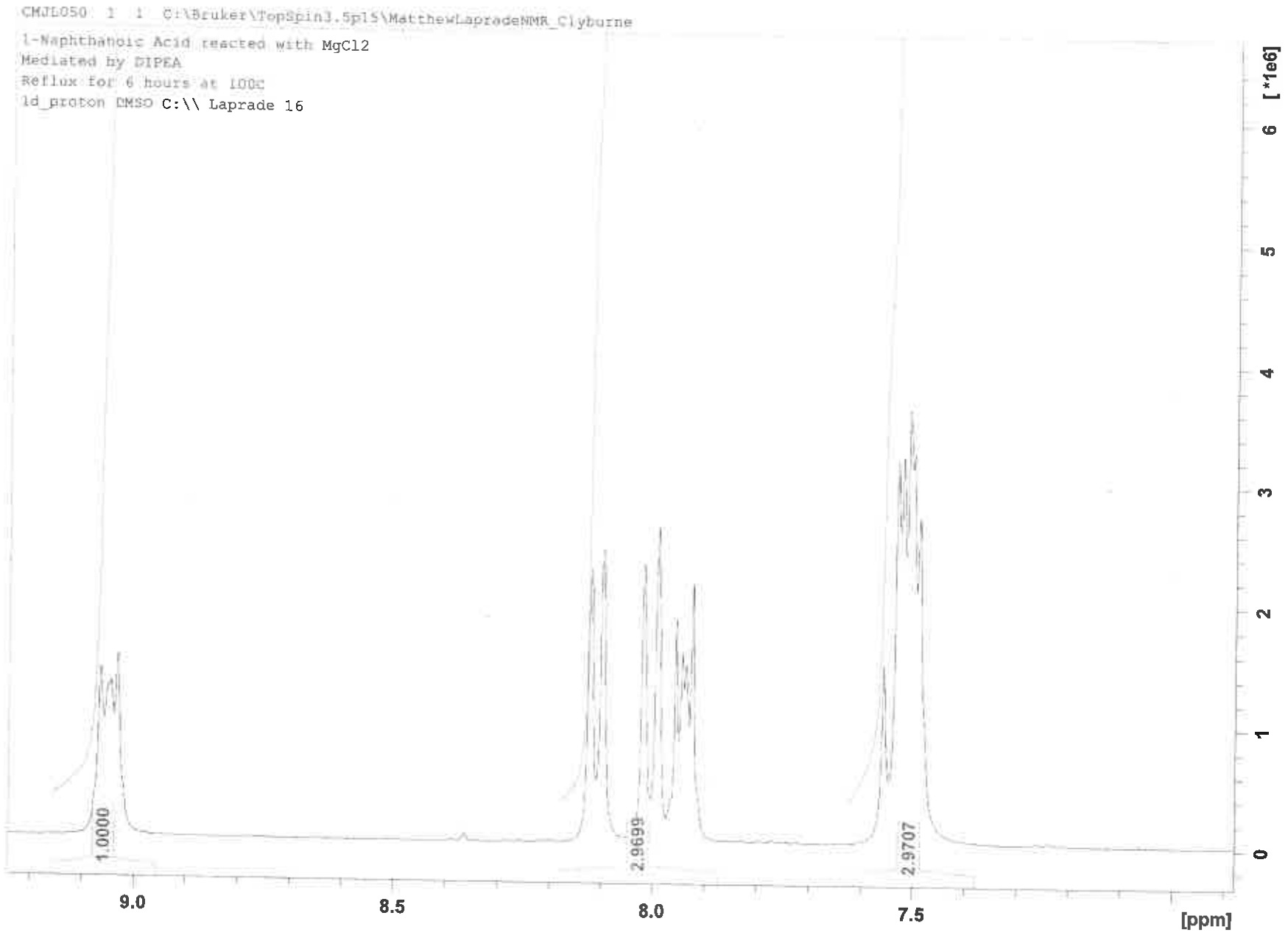


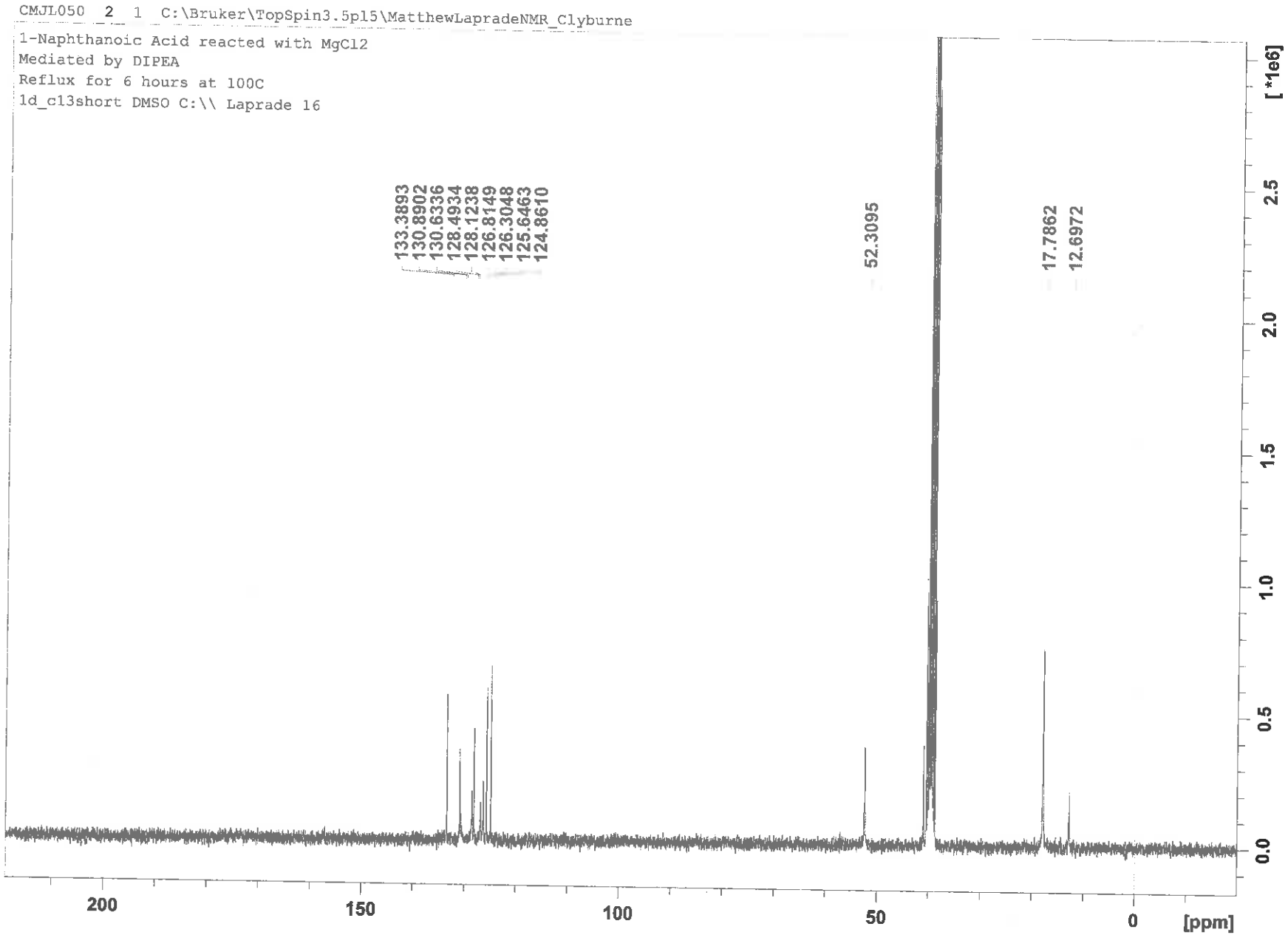

CMJL049 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Naphthanoic Acid reacted with ZnCl2
Mediated by DIPEA
Reflux for 6 hours at 100C
1d_c13short DMSO C:\\ Laprade 15
170.9866
133.3714
130.8423
130.2068
128.0458
126.8105
126.2115
125.5357
124.8577
51.8510
18.1997
13.4476
[*1e6]
[ppm]

CMJL050 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne

1-Naphthanoic Acid reacted with MgCl2
Mediated by DIPEA
Reflux for 6 hours at 100C
1d_proton DMSO C:\\ Laprade 16

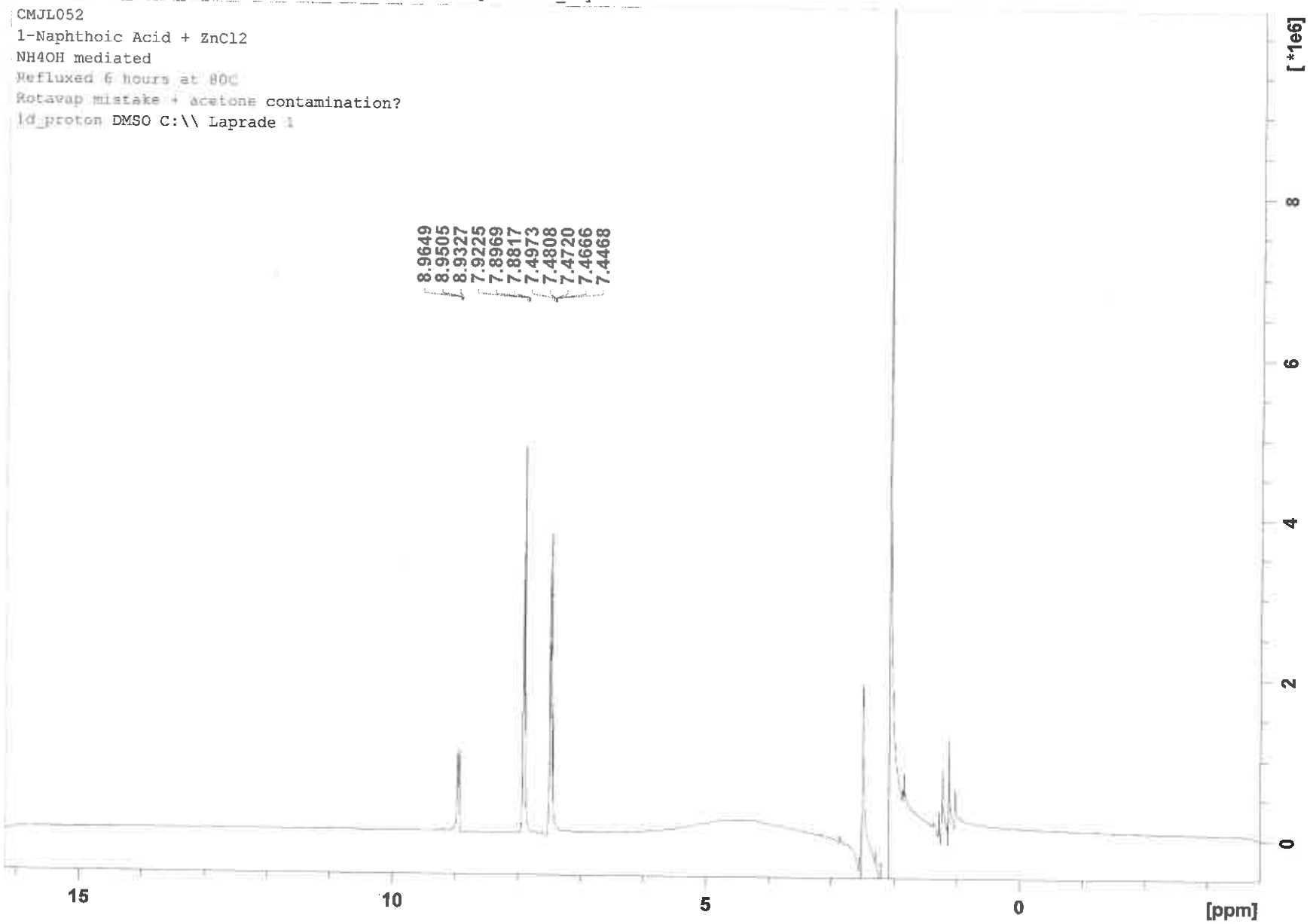


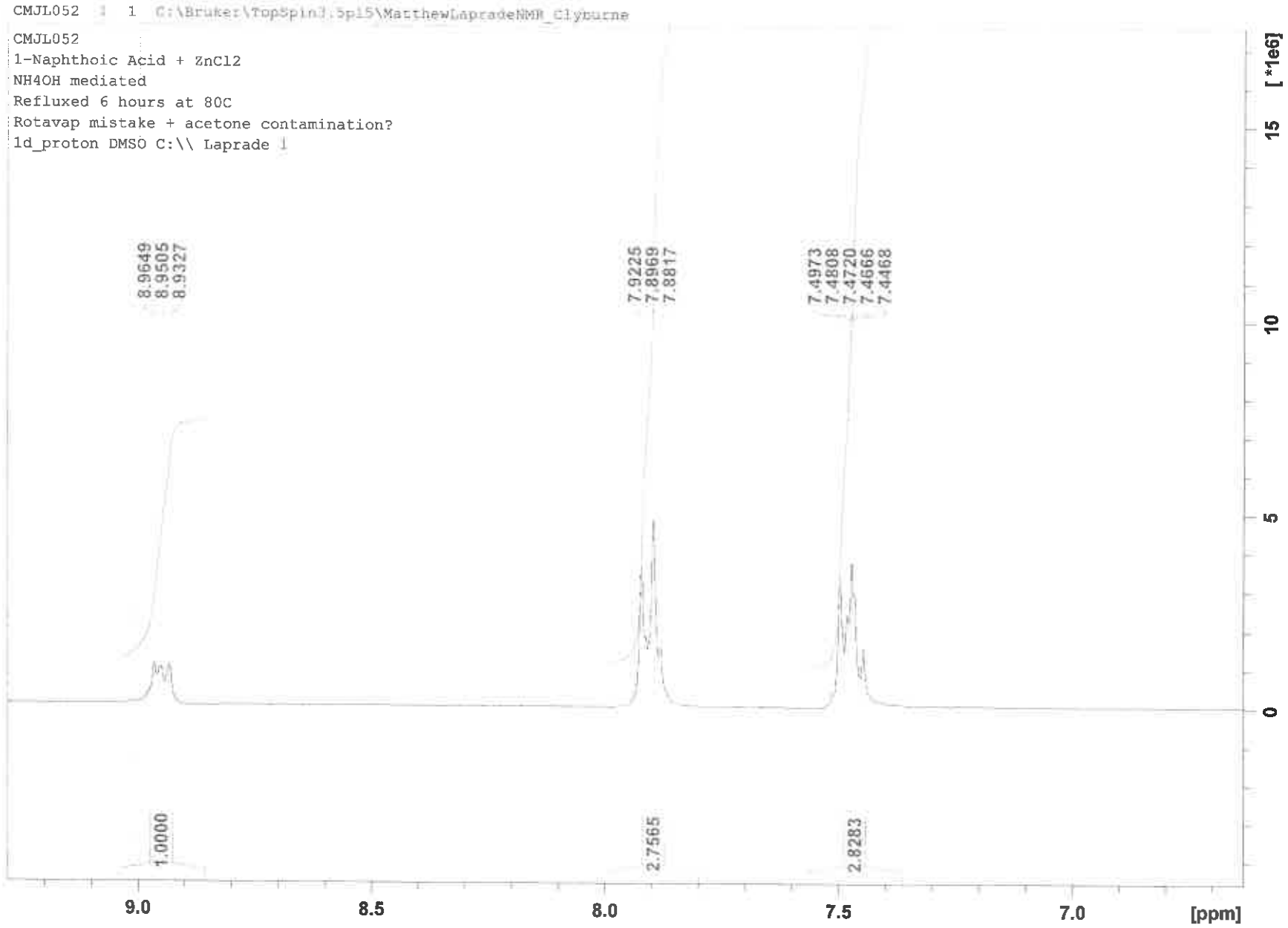

CMJL050 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Naphthanoic Acid reacted with MgCl2
Mediated by DIPEA
Reflux for 6 hours at 100C
1d_proton DMSO C:\\ Laprade 16
1.0000
2.9699
2.9707
9.0
8.5
8.0
7.5
[ppm]
[*1e6]
0
1
2
3
4
5
6

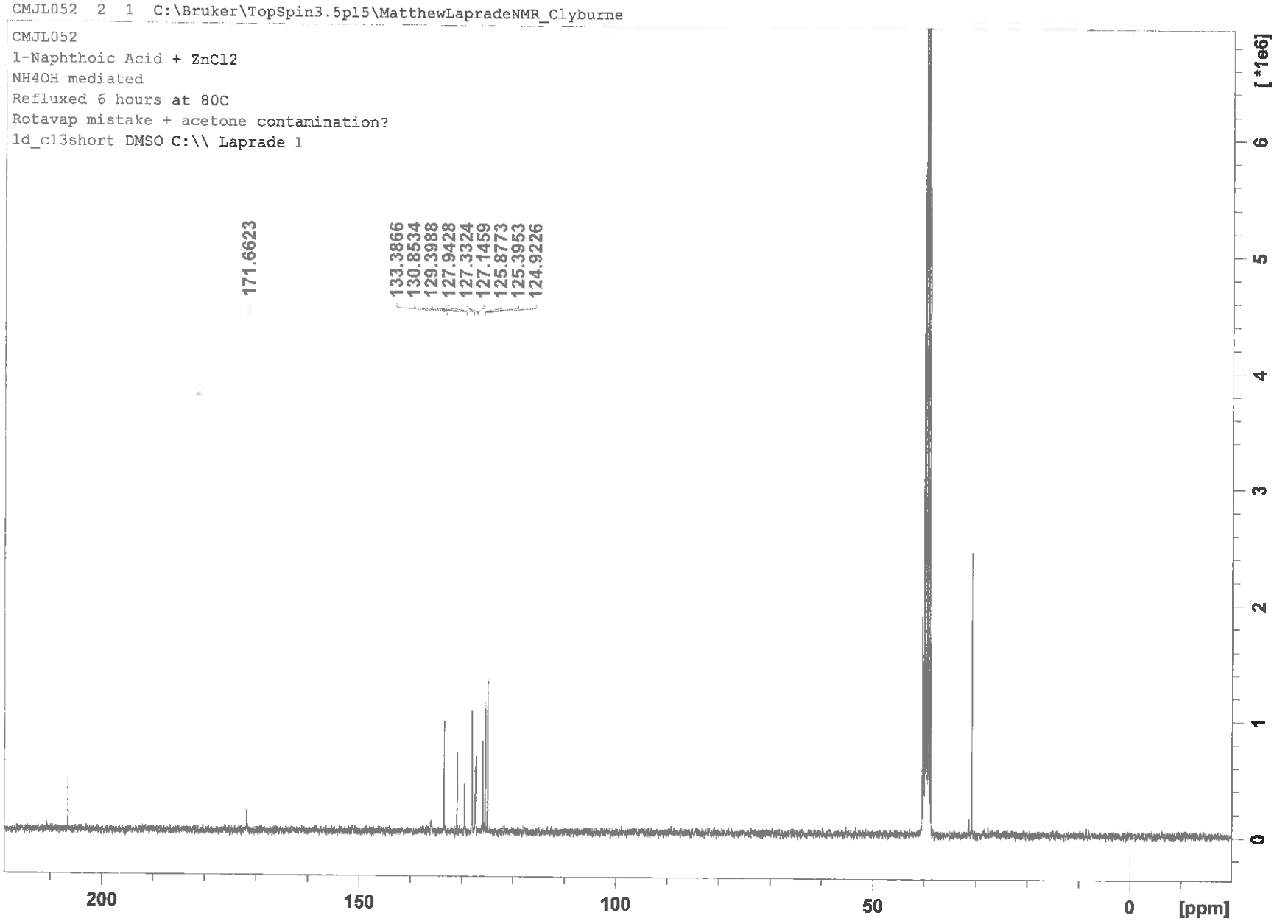

CMJL050 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
1-Naphthanoic Acid reacted with MgCl2
Mediated by DIPEA
Reflux for 6 hours at 100C
1d_c13short DMSO C:\\ Laprade 16
133.3893
130.8902
130.6336
128.4934
128.1238
126.8149
126.3048
125.6463
124.8610
52.3095
17.7862
12.6972
[*1e6]
2.5
2.0
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]

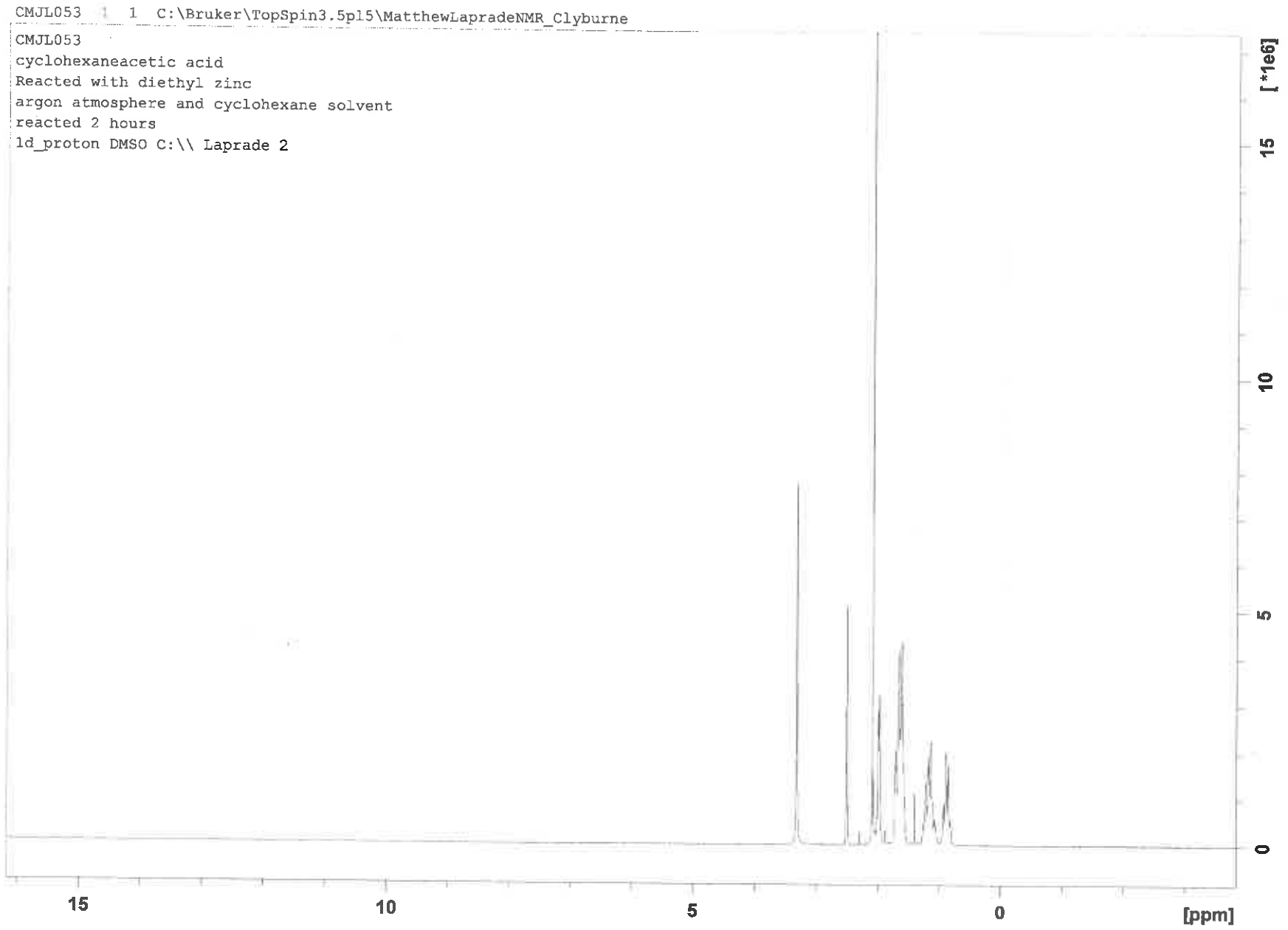
CMJL052 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne

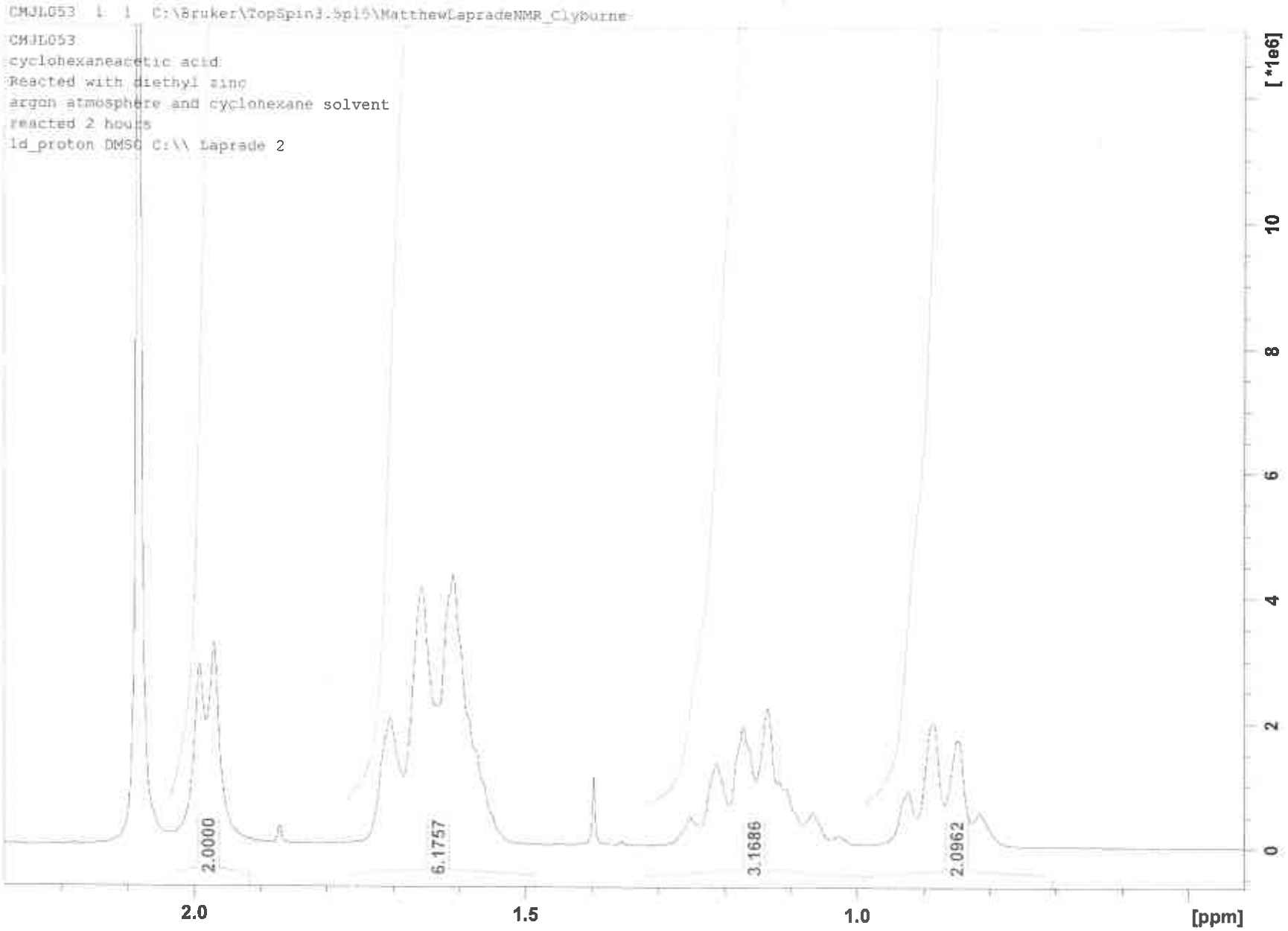
CMJL052
1-Naphthoic Acid + ZnCl2
NH4OH mediated
Refluxed 6 hours at 80C
Rotavap mistake + acetone contamination?
1d_proton DMSO C:\\ Laprade 1




CMJL052 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CMJL052
1-Naphthoic Acid + ZnCl2
NH4OH mediated
Refluxed 6 hours at 80C
Rotavap mistake + acetone contamination?
1d_proton DMSO C:\\ Laprade 1
8.9649
8.9505
8.9327
7.9225
7.8969
7.8817
7.4973
7.4808
7.4720
7.4666
7.4468
1.0000
2.7565
2.8283
9.0
8.5
8.0
7.5
7.0
[ppm]
0
5
10
15
[*1e6]

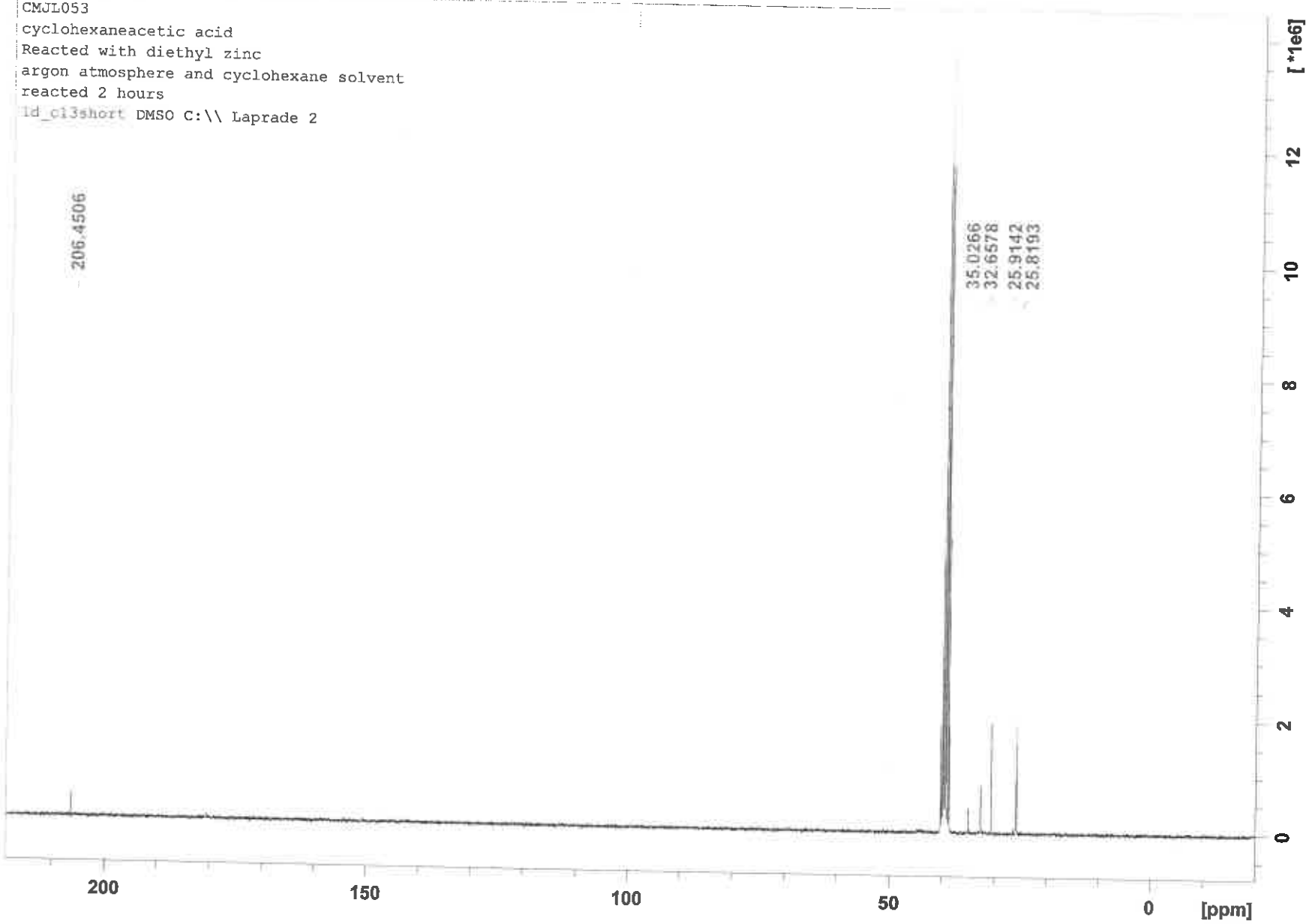

CMJL052 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CMJL052
1-Naphthoic Acid + ZnCl2
NH4OH mediated
Refluxed 6 hours at 80C
Rotavap mistake + acetone contamination?
1d_c13short DMSO C:\\ Laprade 1
171.6623
133.3866
130.8534
129.3988
127.9428
127.3324
127.1459
125.8773
125.3953
124.9226
[*1e6]
0
1
2
3
4
5
6
200
150
100
50
0
[ppm]


CMJL053 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CMJL053
cyclohexaneacetic acid
Reacted with diethyl zinc
argon atmosphere and cyclohexane solvent
reacted 2 hours
1d_proton DMSO C:\\ Laprade 2
[*1e6]
15
10
5
0
15
10
5
0
[ppm]


CMJL053 1 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne
CMJL053
cyclohexaneacetic acid
Reacted with diethyl zinc
argon atmosphere and cyclohexane solvent
reacted 2 hours
1d_proton DMSO C:\\ Laprade 2
2.0000
6.1757
3.1686
2.0962
2.0
1.5
1.0
[ppm]
[*1e6]
0
2
4
6
8
10

CMJL053 2 1 C:\Bruker\TopSpin3.5pl5\MatthewLapradeNMR_Clyburne

CMJL053
cyclohexaneacetic acid
Reacted with diethyl zinc
argon atmosphere and cyclohexane solvent
reacted 2 hours
1d_c13short DMSO C:\\ Laprade 2



SAINT MARY'S UNIVERSITY
One University. One World. Yours.
FACULTY OF SCIENCE

CENTRE FOR ENVIRONMENTAL ANALYSIS AND REMEDIATION
Saint Marys University, Halifax NS B3H 3C3. Science Building Room 501
Phone (902)496-8798 Email: Patricia.Granados@smu.ca

CHN Analyzer, Perkin Elmer 2400 Series II

User's Name Bitu Hurriso
Analyzed by: Patricia Granados
Date: 10-Nov-16

Standard Acetanilide
Supplier Perkin Elmer

Theoretical		Carbon %	Hydrogen %	Nitrogen %
K factor: Acetanilide		71.09	6.71	10.36
QC: Cystine		29.99	5.03	11.66
0		0.00	0.00	0.00
0		0.00	0.00	0.00
0		0.00	0.00	0.00
0		0.00	0.00	0.00
0		0.00	0.00	0.00

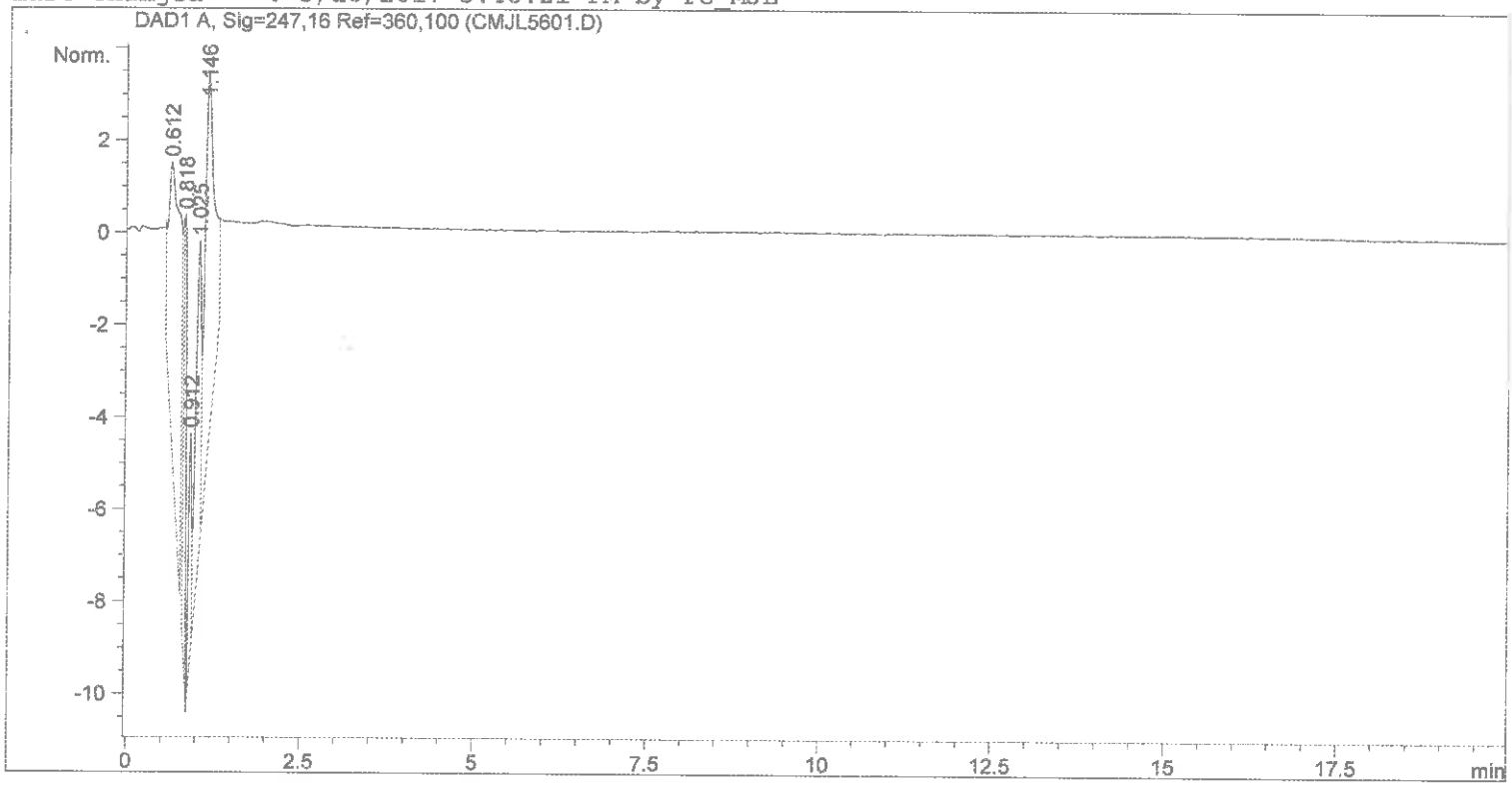
Experimental

Sample Name	Weight mg	Carbon %	Hydrogen %	Nitrogen %
QC Cystine CYS03	3.219	29.98	5.15	11.58
QC Cystine CYS02	3.169	30.02	5.15	11.58
QC Cystine CYS01	3.272	29.97	5.00	11.64

Sample results

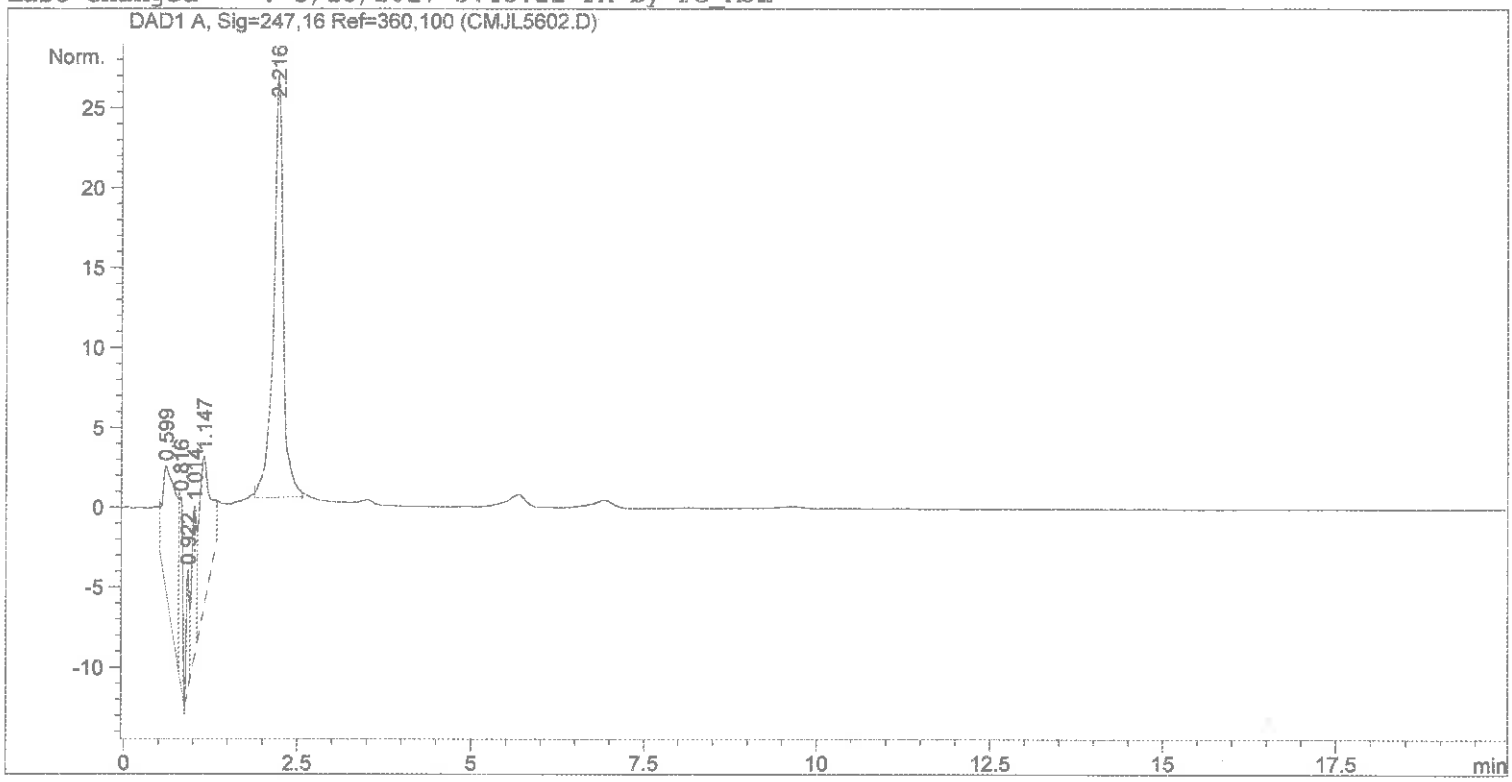
CMJL0332	Sample 2	4.965	34.69	7.44	8.52
CMJL036	Sample 5	6.853	46.84	2.48	0.02
(MJL0334	Sample 1	4.888	33.17	7.41	9.03
CMJL035	Sample 4	3.562	42.50	5.72	0.04
CMJL035	Sample 3	4.786	42.51	5.81	0.01

```
==========================================================================
Injection Date  : 3/16/2017 4:40:44 PM          Seq. Line :   1
Sample Name     : Methanol Blank                Location : Vial 1
Acq. Operator   : PG_MJL                            Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.m
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



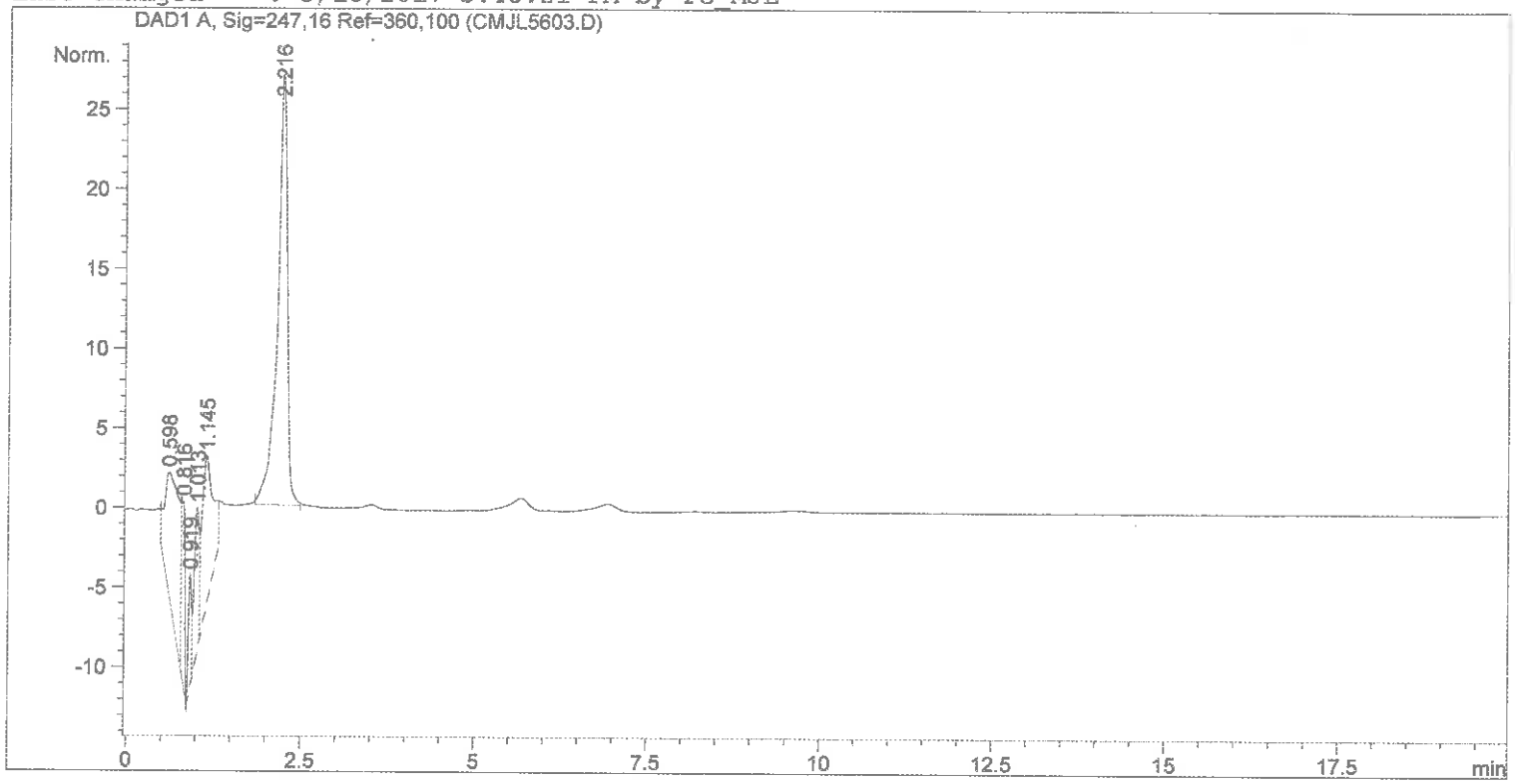

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.612 BB   0.1905   82.41295    5.63851  34.9565
   2   0.818 BP   0.0455   26.87808    9.35964  11.4007
   3   0.912 VV   0.0447   14.38326    5.13329   6.1008
   4   1.025 VV   0.0846   36.97245    7.11985  15.6823
   5   1.146 VB   0.1261   75.11195    8.41961  31.8597

Totals :                  235.75868   35.67091

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

```
==========================================================================
Injection Date  : 3/16/2017 5:03:01 PM          Seq. Line :   2
Sample Name     : CCPA Control                   Location : Vial 2
Acq. Operator   : PG_MJL                            Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.m
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



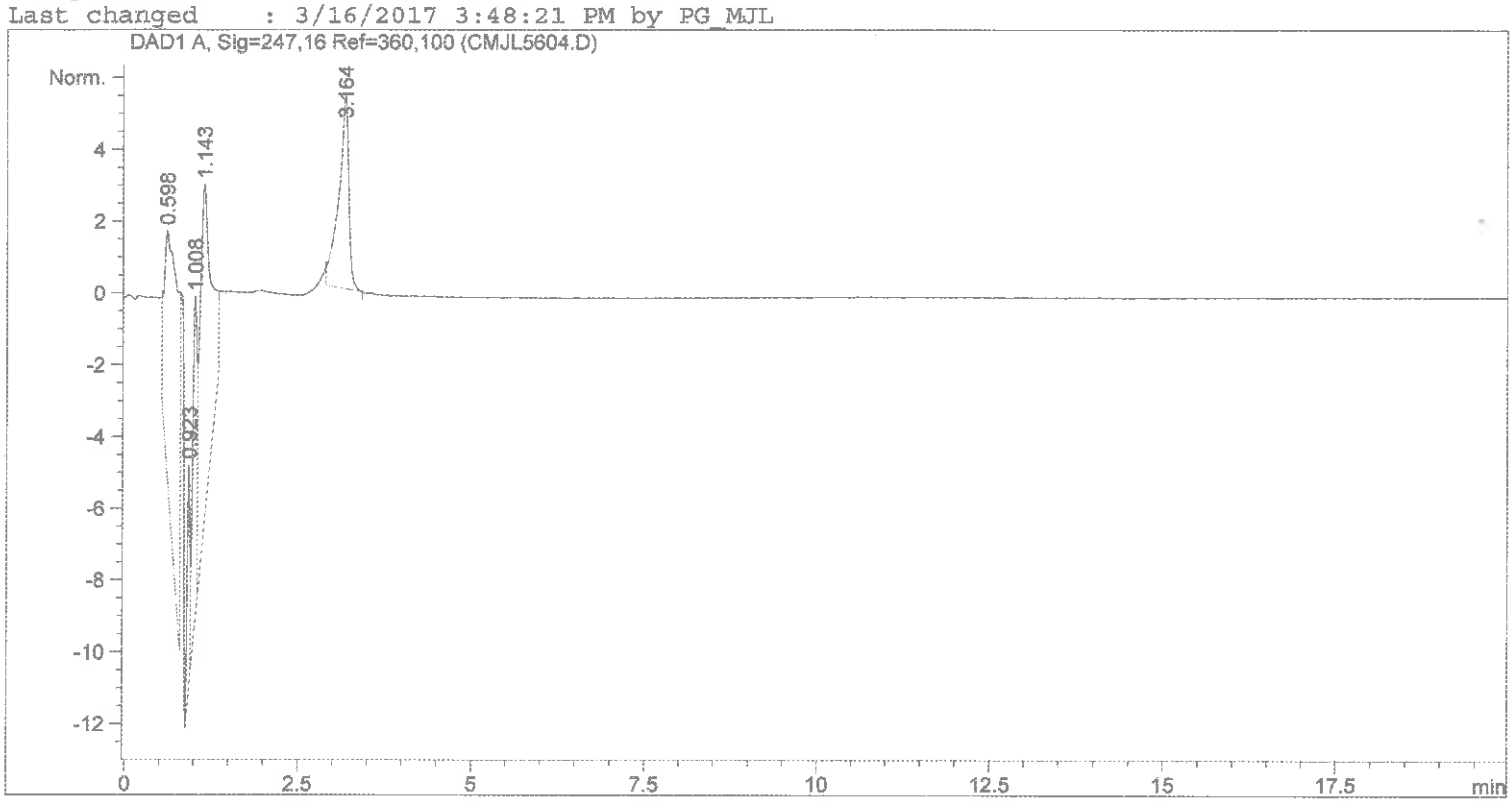

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.599 BV   0.2166  130.62781    7.59867  21.5969
   2   0.816 VP   0.0556   40.93581   11.46708   6.7680
   3   0.922 VV   0.0461   21.87763    7.48425   3.6171
   4   1.014 VV   0.0718   45.24467    9.46689   7.4804
   5   1.147 VB   0.1594  108.10223    9.59985  17.8728
   6   2.216 BB   0.1441  258.05566   26.39330  42.6648

Totals :                  604.84381   72.01005

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

```
==========================================================================
Injection Date  : 3/16/2017 5:25:22 PM          Seq. Line :   2
Sample Name     : CCPA Control                   Location : Vial 2
Acq. Operator   : PG_MJL                            Inj :   2
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.m
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



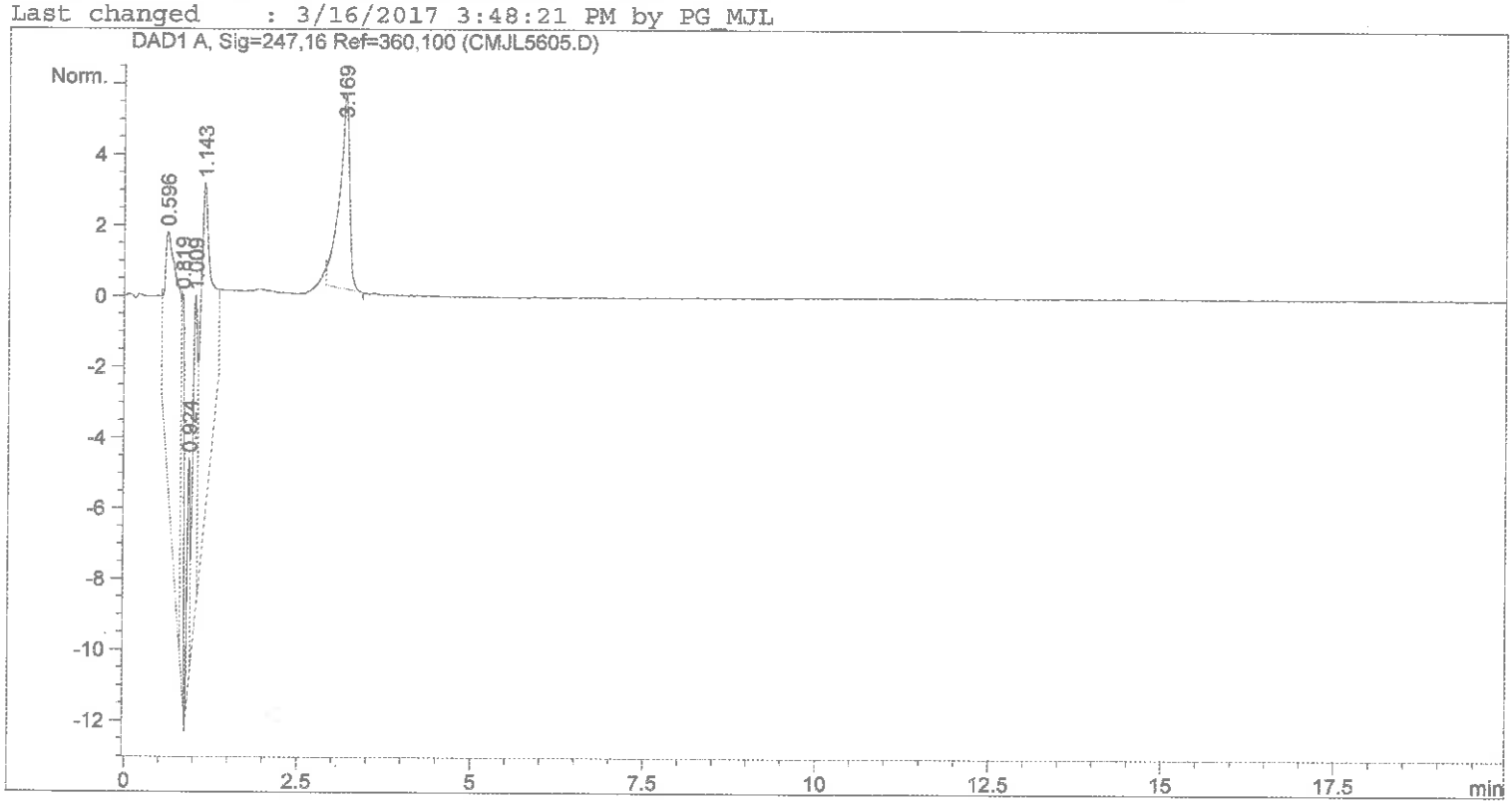

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.598 BV    0.2330  132.96220    7.42127  22.0734
   2   0.816 VP    0.0568   40.98285   11.16848   6.8037
   3   0.919 VV    0.0457   20.49306    7.10146   3.4021
   4   1.013 VV    0.0733   44.95828    9.15758   7.4636
   5   1.145 VB    0.1500  100.73116    9.48032  16.7226
   6   2.216 BB    0.1473  262.23630   27.01409  43.5345

Totals :                   602.36384   71.34321

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

```
==================================================================
Injection Date  : 3/16/2017 5:47:38 PM          Seq. Line :   3
Sample Name     : CCHA Control                   Location : Vial 3
Acq. Operator   : PG_MJL                            Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.m
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



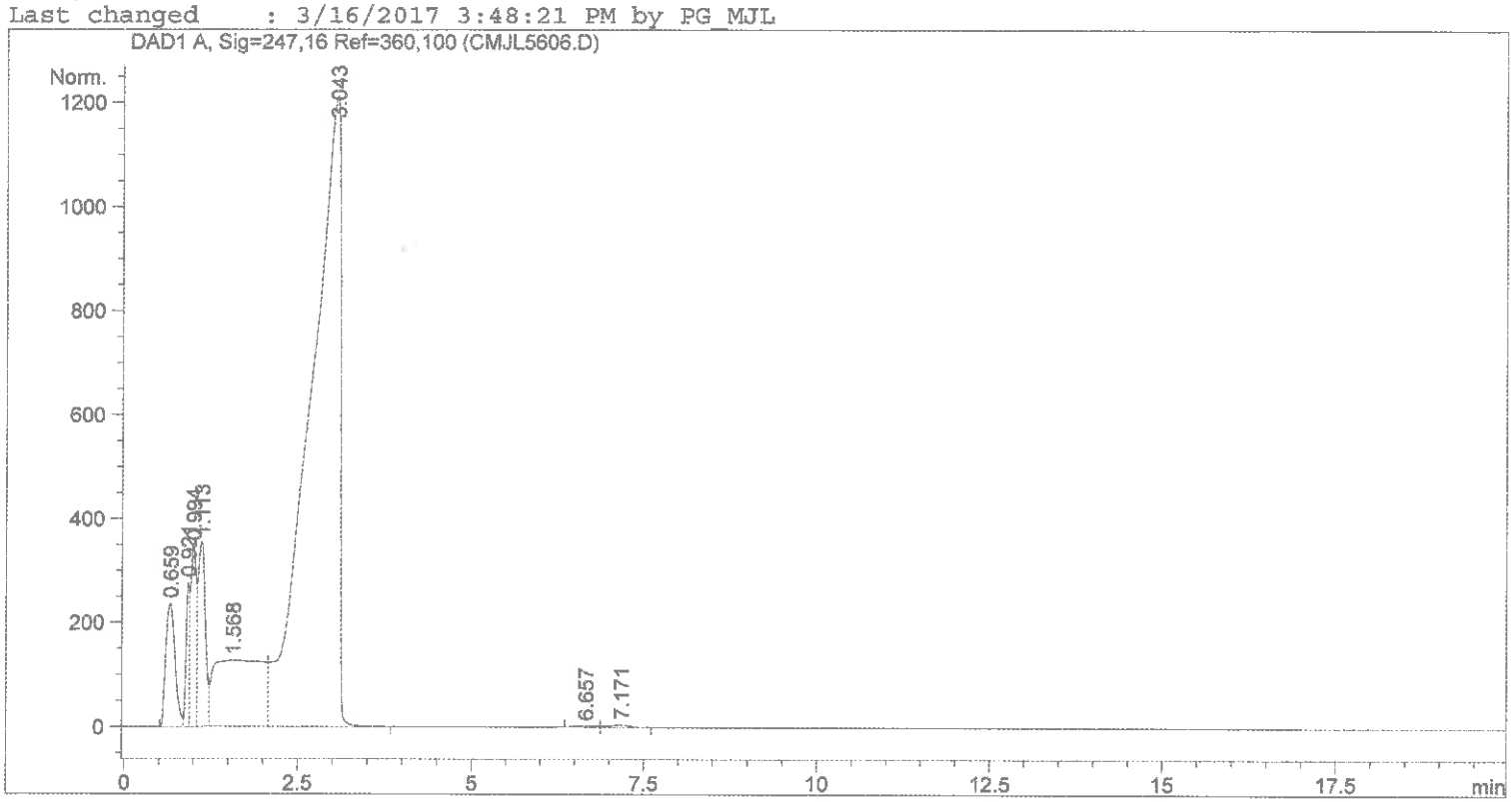

```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.598 BB    0.2197  116.54372    6.61112  34.4283
   2   0.923 PV    0.0436   17.16837    6.34614   5.0717
   3   1.008 VV    0.0646   40.04332    9.23497  11.8292
   4   1.143 VB    0.1635  109.13609    9.53708  32.2400
   5   3.164 BB    0.1431   55.62000    5.35994  16.4308

Totals :                   338.51151   37.08924

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

```
==========================================================================
Injection Date  : 3/16/2017 6:09:52 PM          Seq. Line :   3
Sample Name     : CCHA Control                   Location : Vial 3
Acq. Operator   : PG_MJL                            Inj :   2
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.m
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



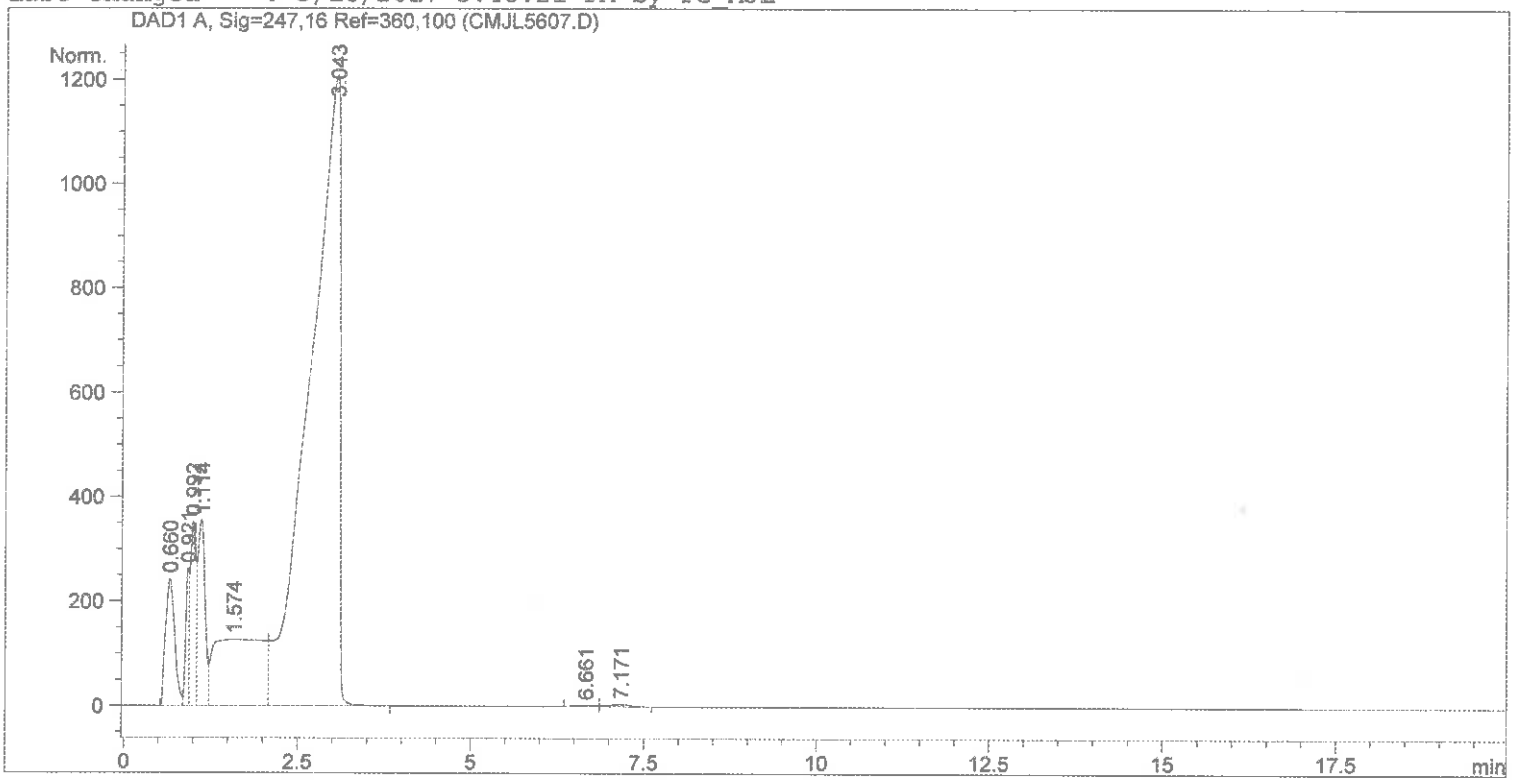

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.596 BV    0.2334  122.70204    6.64597  32.0131
   2   0.819 VP    0.0531   33.79575   10.60294   8.8173
   3   0.924 VV    0.0435   17.78820    6.59855   4.6410
   4   1.009 VV    0.0647   40.79145    9.39058  10.6425
   5   1.143 VB    0.1648  112.19342    9.71357  29.2713
   6   3.169 BP    0.1418   56.01666    5.45509  14.6148

Totals :                  383.28753   48.40671

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

```
==========================================================================
Injection Date  : 3/16/2017 6:32:11 PM          Seq. Line :   4
Sample Name     : Naphthanoic Acid               Location : Vial 4
Acq. Operator   : PG_MJL                            Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.m
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



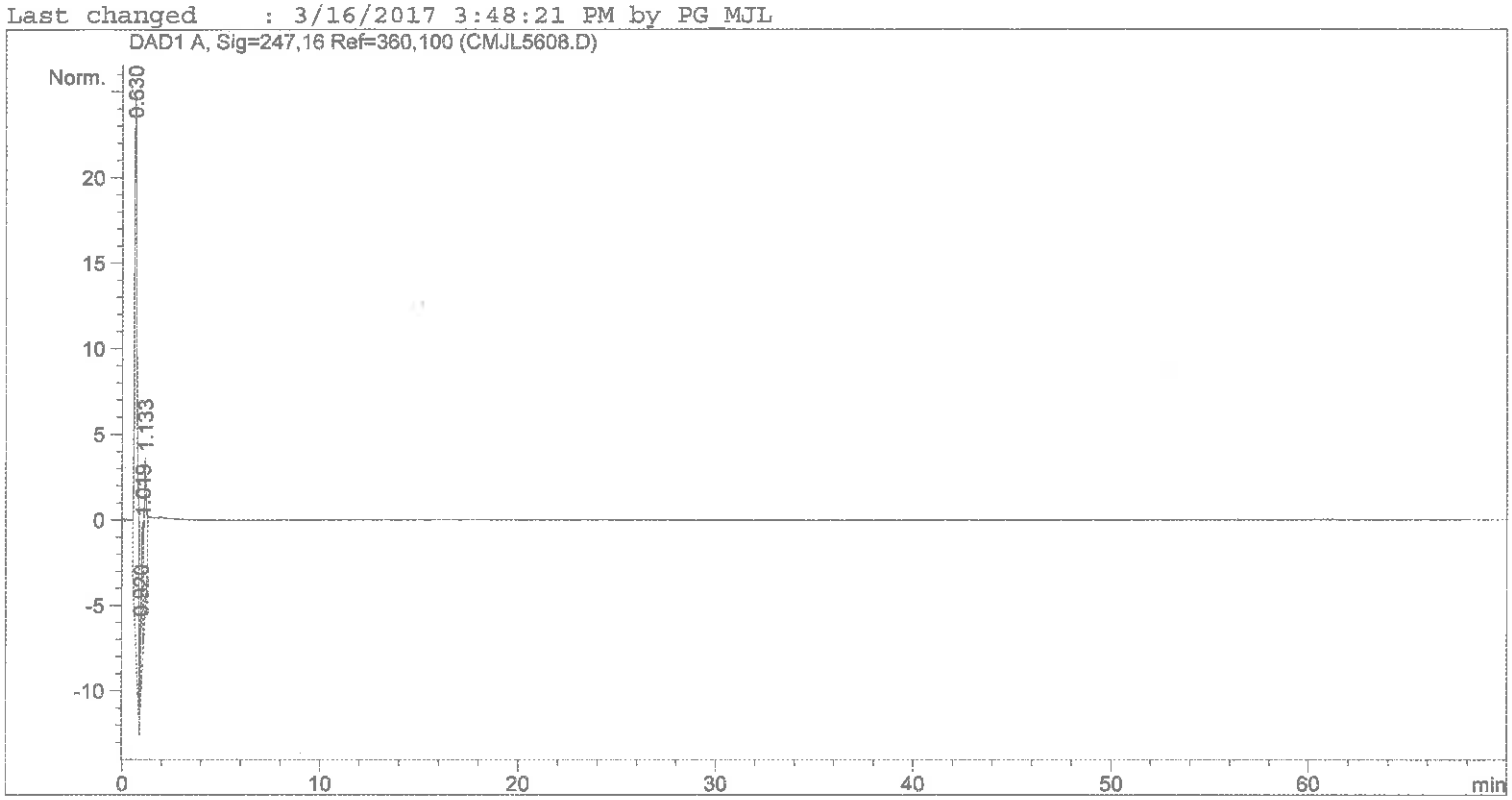

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.659 BV   0.1541 2230.30688  236.27150   4.4806
   2   0.921 VV   0.0511  926.17719  276.46771   1.8606
   3   0.994 VV   0.0836 1950.22168  347.07312   3.9179
   4   1.113 VV   0.1101 2618.65405  354.83505   5.2607
   5   1.568 VV   0.6203 6269.60010  126.92654  12.5953
   6   3.043 VB   0.3954 3.56525e4  1211.37390  71.6238
   7   6.657 BV   0.2741   44.68878    2.34739   0.0898
   8   7.171 VP   0.2959   85.28625    4.21827   0.1713

Totals :                  4.97774e4  2559.51348

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

```
==========================================================================
Injection Date  : 3/16/2017 6:54:37 PM          Seq. Line :   4
Sample Name     : Naphthanoic Acid               Location : Vial 4
Acq. Operator   : PG_MJL                            Inj :   2
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.m
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



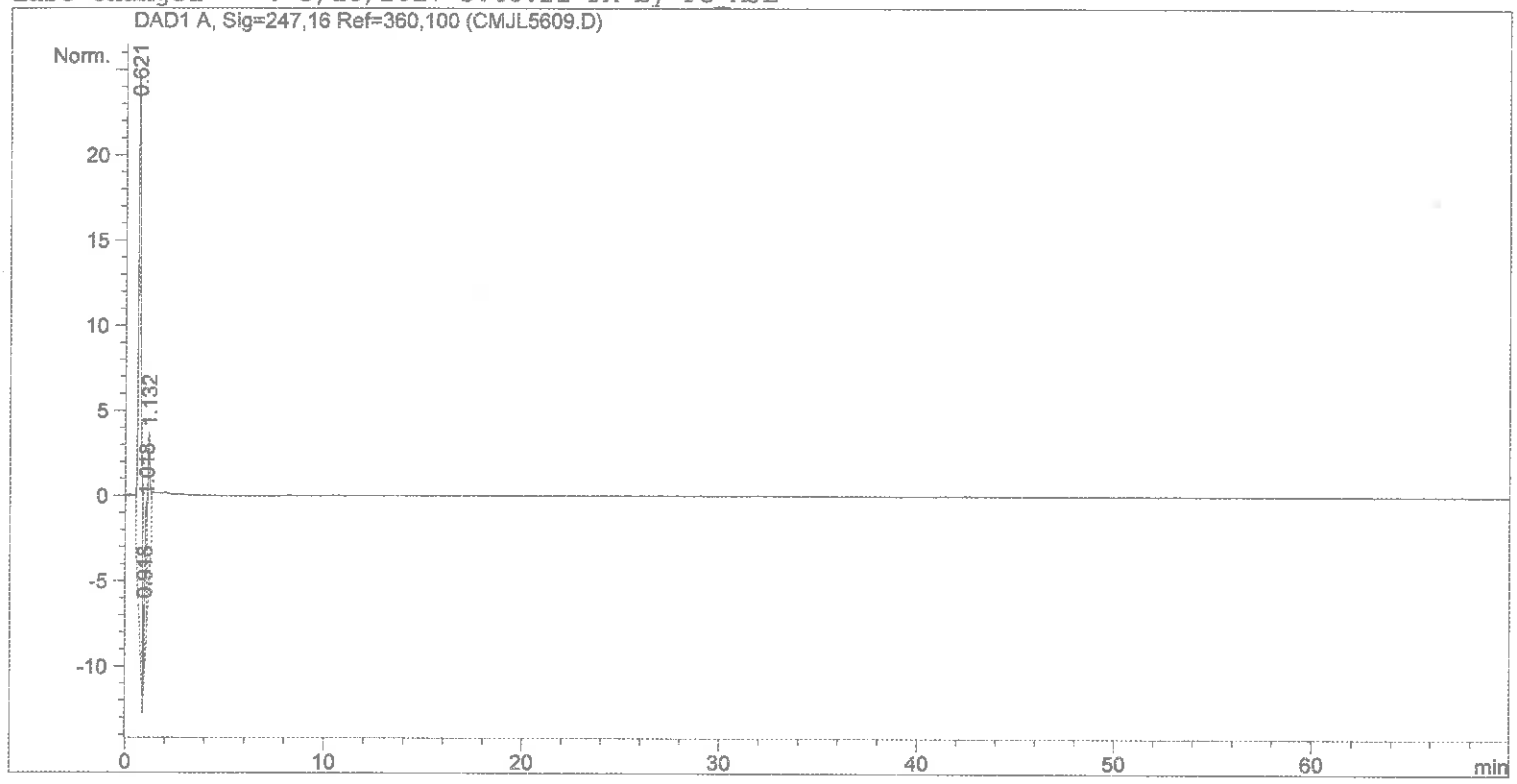

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.660 BV   0.1408 2222.73218  242.74452   4.4614
   2   0.921 VV   0.0525  864.52740  261.65131   1.7353
   3   0.992 VV   0.0816 1985.14148  352.91934   3.9845
   4   1.114 VV   0.1119 2613.78271  354.93335   5.2463
   5   1.574 VV   0.6282 6300.92334  126.70793  12.6471
   6   3.043 VB   0.3969 3.57064e4  1207.85083  71.6693
   7   6.661 BV   0.2715   42.93427    2.30308   0.0862
   8   7.171 VP   0.3001   84.59962    4.14511   0.1698

Totals :                 4.98210e4  2553.25548

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

```
==============================================================================
Injection Date  : 3/16/2017 7:16:55 PM          Seq. Line :   5
Sample Name     : CMJL014F                      Location : Vial 5
Acq. Operator   : PG_MJL                            Inj :   1
Acq. Instrument : Instrument 1                Inj Volume : 20 µl
Method          : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```




```
==============================================================================
                          Area Percent Report
==============================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.630 BP    0.1547  331.76044   30.54276  69.9776
   2   0.920 VV    0.0385   12.48168    5.11288   2.6327
   3   1.019 VV    0.0893   49.30780    8.55161  10.4004
   4   1.133 VB    0.1165   80.54527    9.53758  16.9893

Totals :                   474.09520   53.74483

 Results obtained with enhanced integrator!
==============================================================================
                          *** End of Report ***
```

Injection Date	: 3/16/2017 8:29:07 PM	Seq. Line	: 5
Sample Name	: CMJL014F	Location	: Vial 5
Acq. Operator	: PG_MJL	Inj	: 2
Acq. Instrument	: Instrument 1	Inj Volume	: 20 µl
Method	: D:\Methods\JASONC~1\PARTIT~1.M		
Last changed	: 3/16/2017 3:48:21 PM by PG_MJL		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

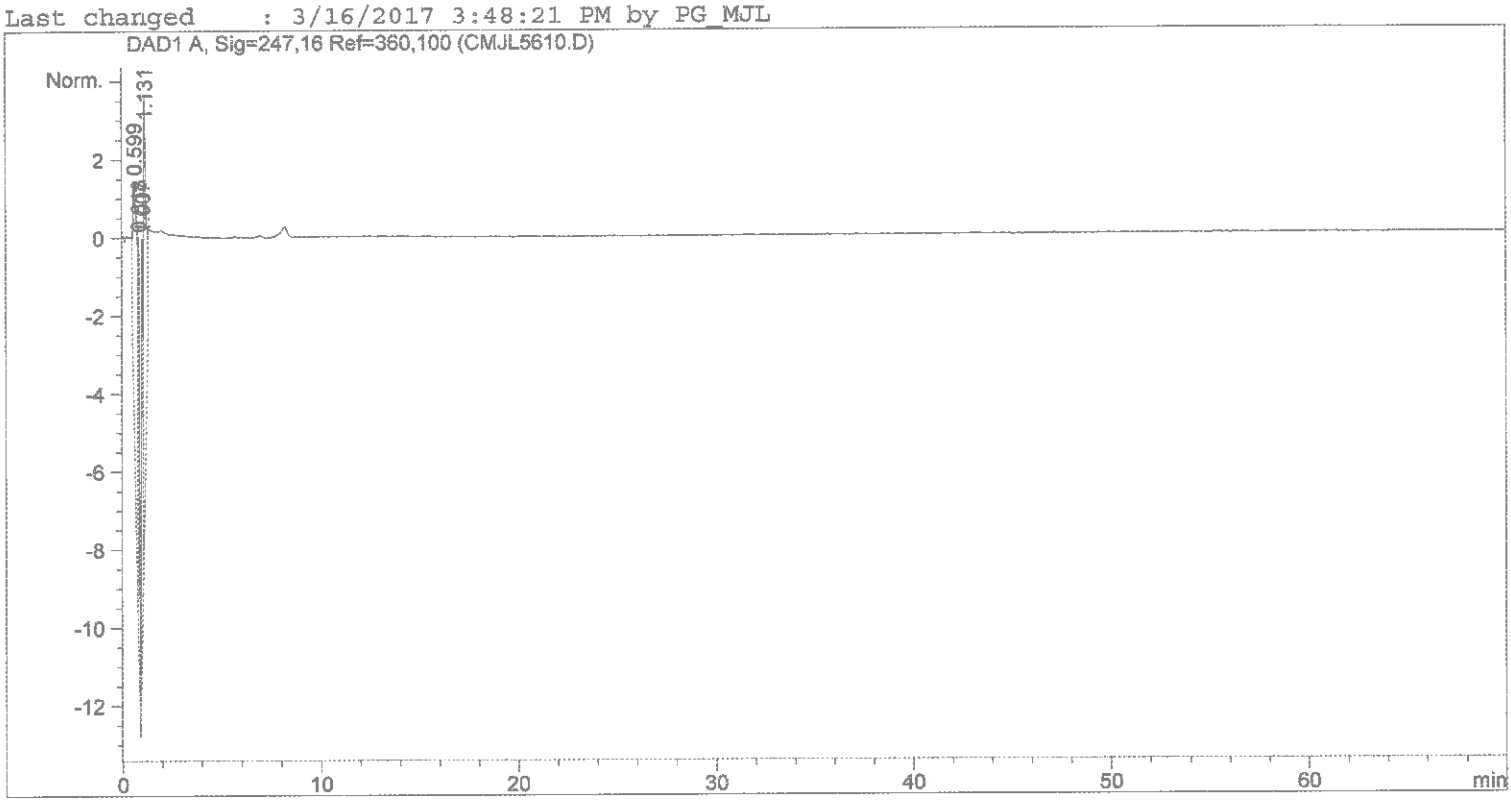
Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	0.621	BP	0.1580	338.41690	30.36167	69.9850
2	0.918	VV	0.0395	11.70176	4.97120	2.4199
3	1.018	VV	0.0892	49.08807	8.52591	10.1515
4	1.132	VB	0.1190	84.34989	9.74020	17.4436
Totals :				483.55662	53.59898	

Results obtained with enhanced integrator!

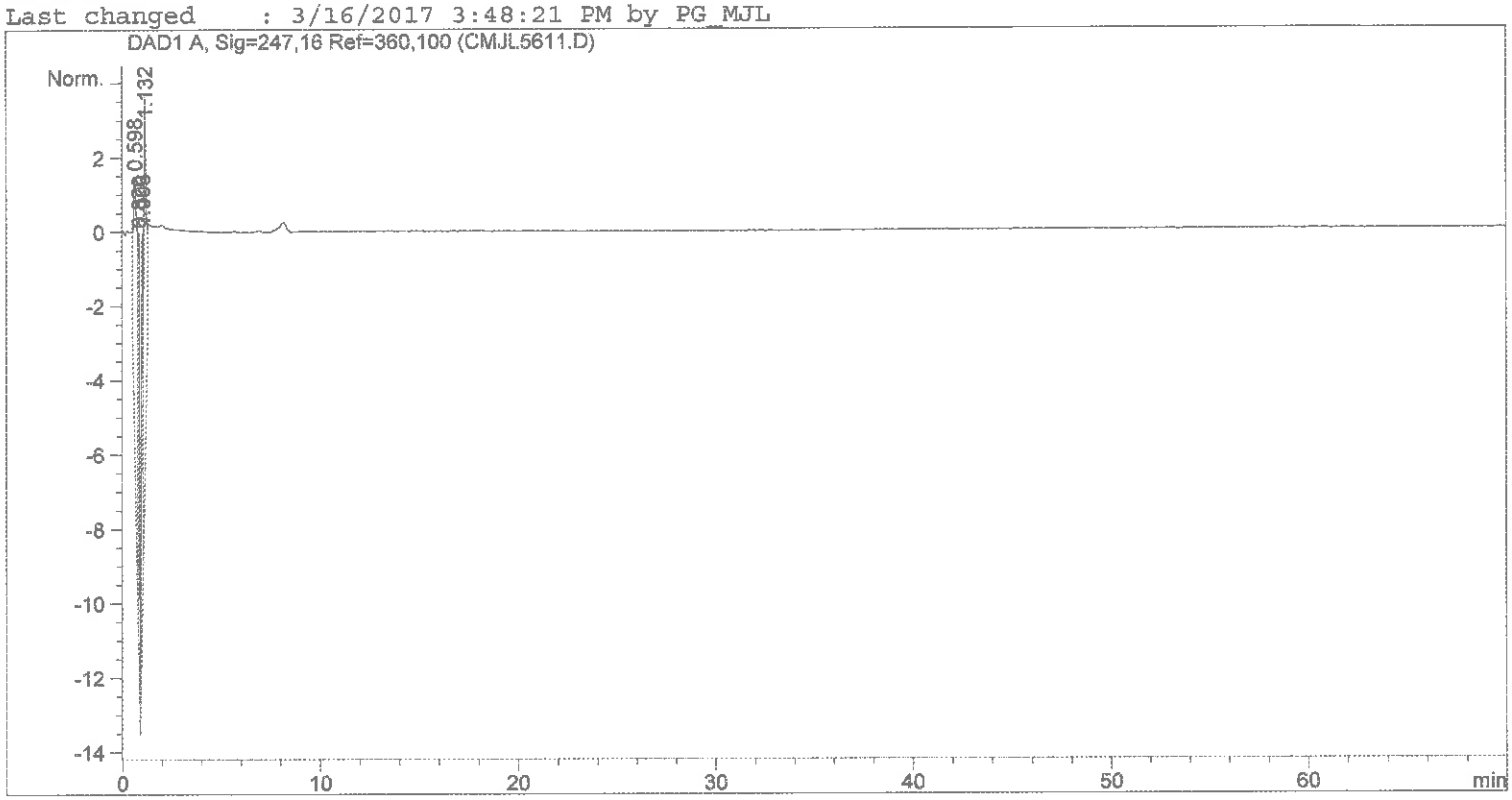
*** End of Report ***

```
==============================================================================
Injection Date  : 3/16/2017 9:41:22 PM          Seq. Line :   6
Sample Name     : CMJL015                        Location : Vial 6
Acq. Operator   : PG_MJL                             Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 20 µl
Method          : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



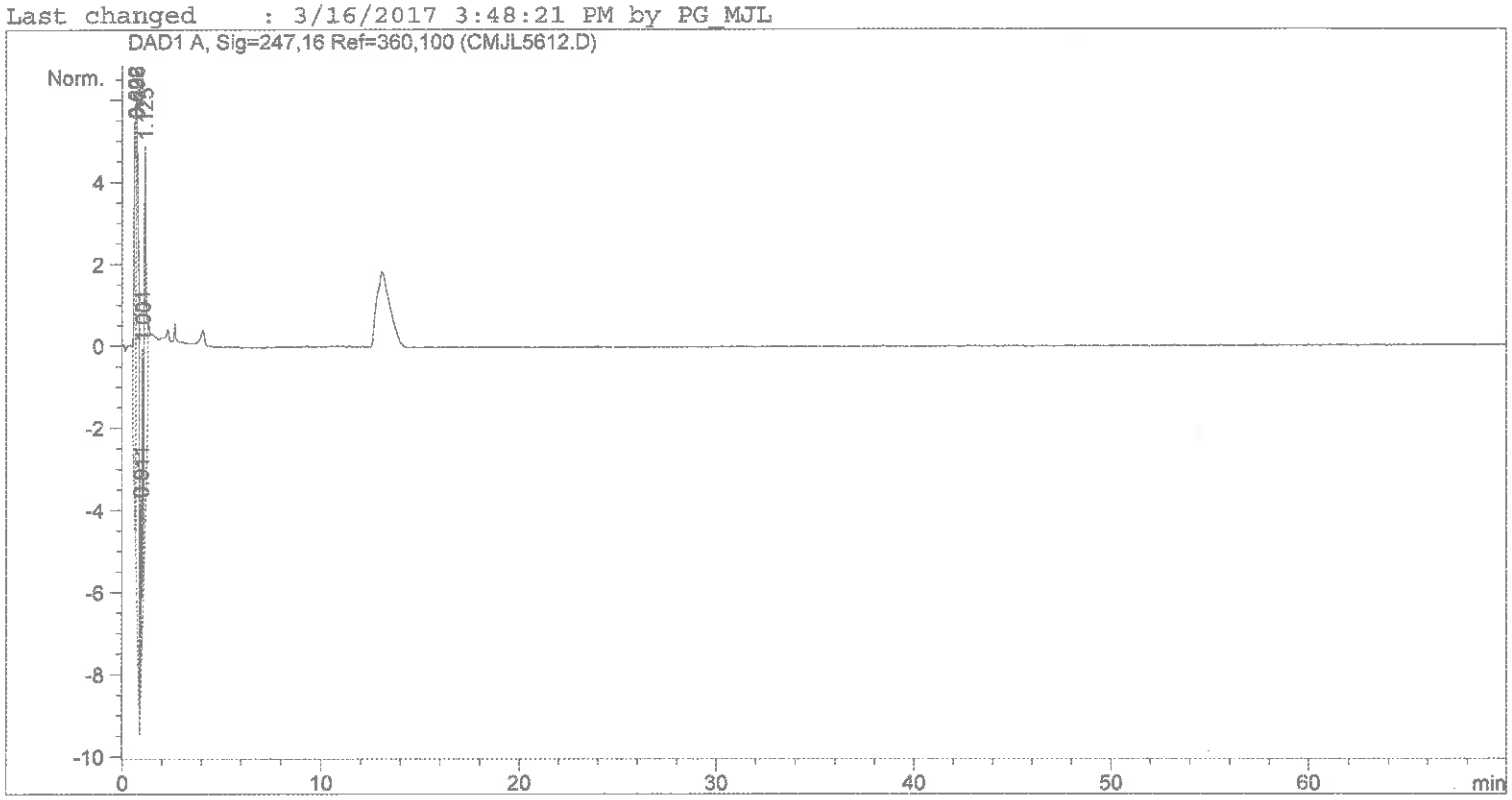

```
==============================================================================
                          Area Percent Report
==============================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.599 BV    0.2369  118.46564    6.61747  37.6374
   2   0.818 VP    0.0638   46.22255   10.83544  14.6853
   3   1.007 VV    0.0849   56.08404    9.49209  17.8183
   4   1.131 VB    0.1262   93.98267    9.94637  29.8590

Totals :                   314.75490   36.89138

 Results obtained with enhanced integrator!
==============================================================================
                          *** End of Report ***
```

```
==========================================================================
Injection Date  : 3/16/2017 10:53:36 PM          Seq. Line :   6
Sample Name     : CMJL015                         Location : Vial 6
Acq. Operator   : PG_MJL                             Inj :   2
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Method          : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



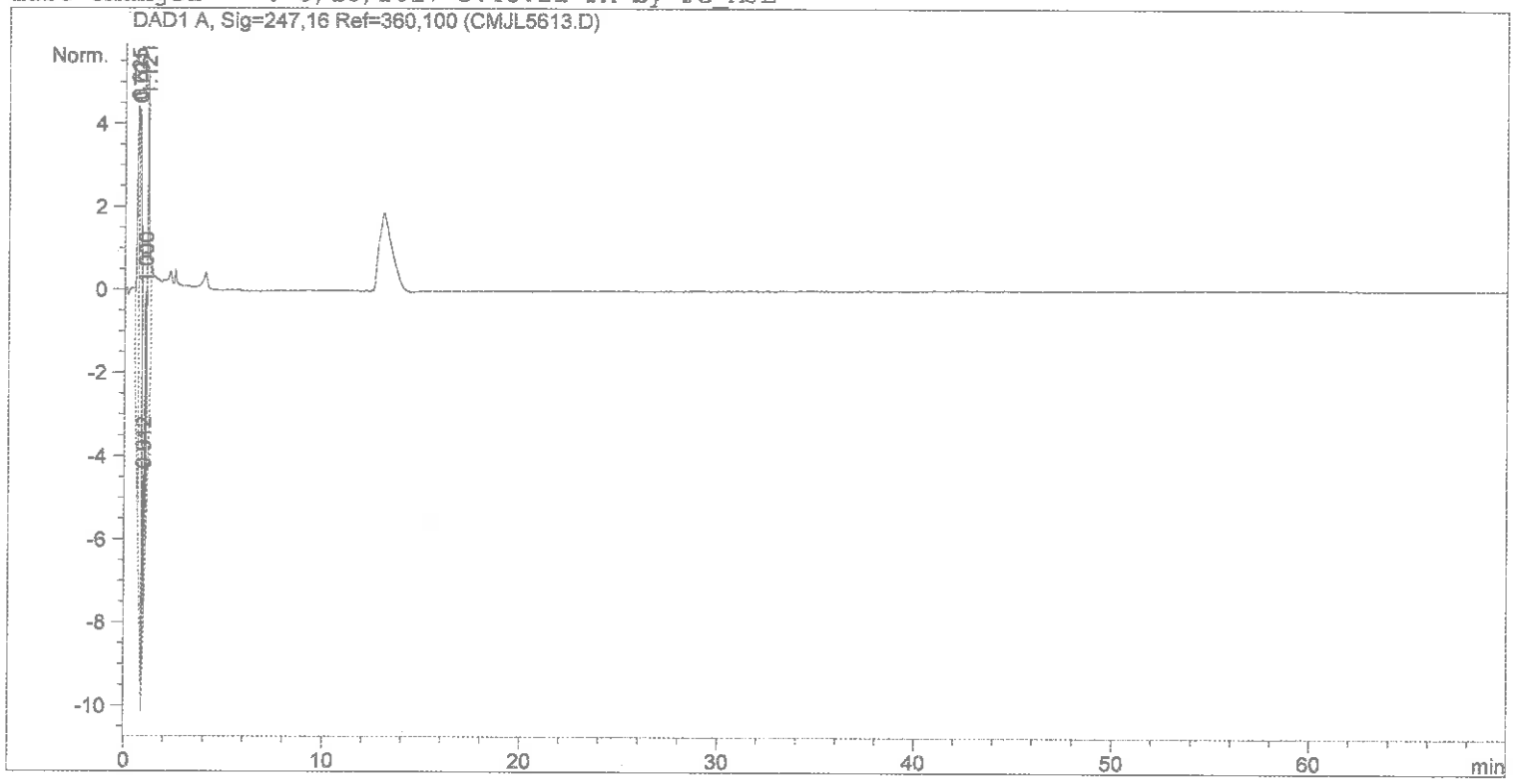

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.598 BB    0.2062  107.62676    6.67226  33.6559
   2   0.820 BP    0.0639   50.90166   11.43439  15.9174
   3   1.006 VV    0.0875   62.02194   10.11998  19.3948
   4   1.132 VB    0.1250   99.23544   10.42651  31.0318

Totals :                   319.78580   38.65313

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

```
==========================================================================
Injection Date  : 3/17/2017 12:05:43 AM          Seq. Line :   7
Sample Name     : CMJL020                         Location : Vial 7
Acq. Operator   : PG_MJL                             Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Method          : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



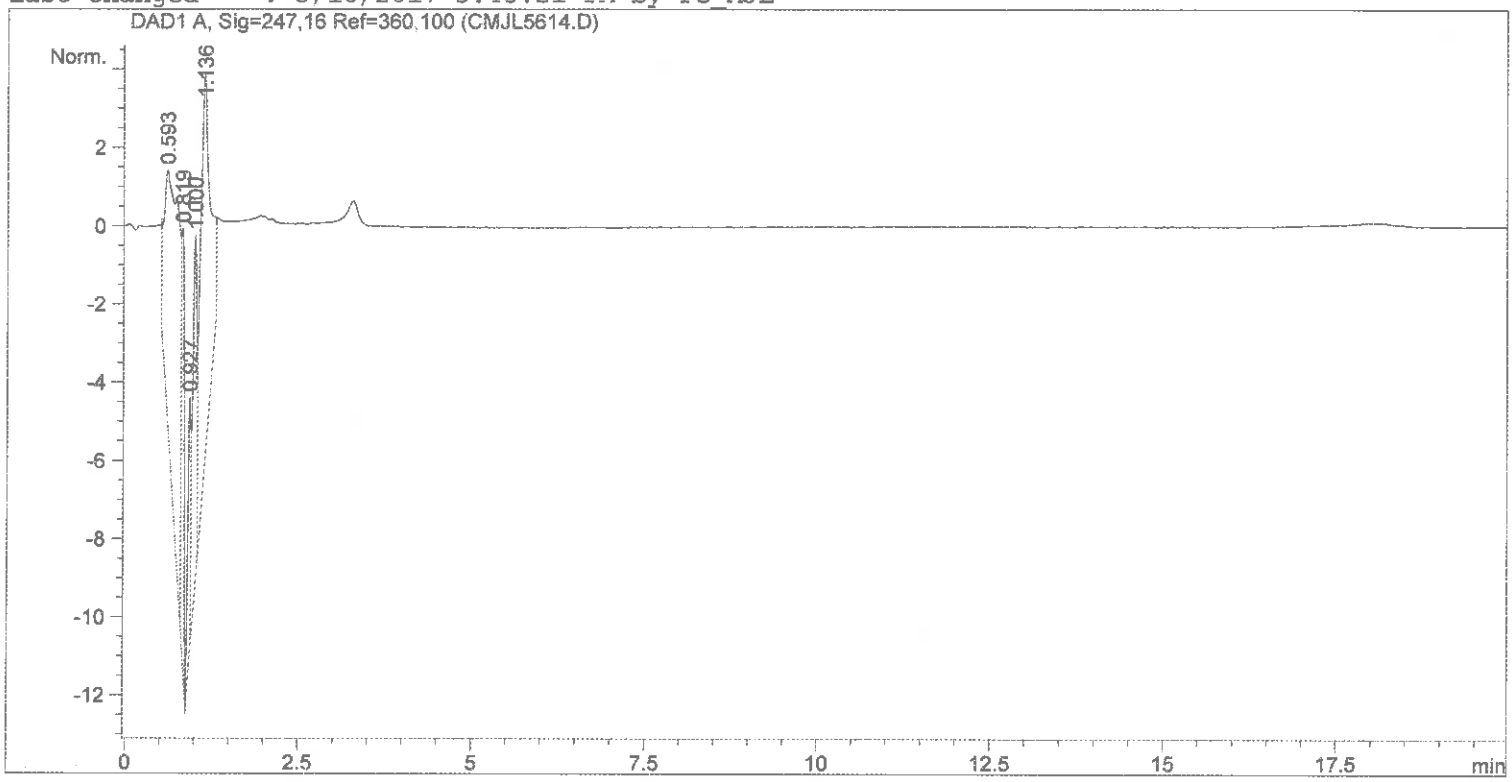

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.622 BV    0.0907   61.86731   10.21307  21.1758
   2   0.696 VP    0.1378  123.82810   11.86514  42.3836
   3   0.911 VV    0.0440   12.14577    4.73040   4.1572
   4   1.001 VV    0.0513   21.87015    6.84411   7.4857
   5   1.125 VB    0.1036   72.44883    9.43030  24.7976

Totals :                   292.16016   43.08303

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

```
==========================================================================
Injection Date  : 3/17/2017 1:17:53 AM          Seq. Line :   7
Sample Name     : CMJL020                        Location : Vial 7
Acq. Operator   : PG_MJL                            Inj :   2
Acq. Instrument : Instrument 1                Inj Volume : 20 µl
Method          : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



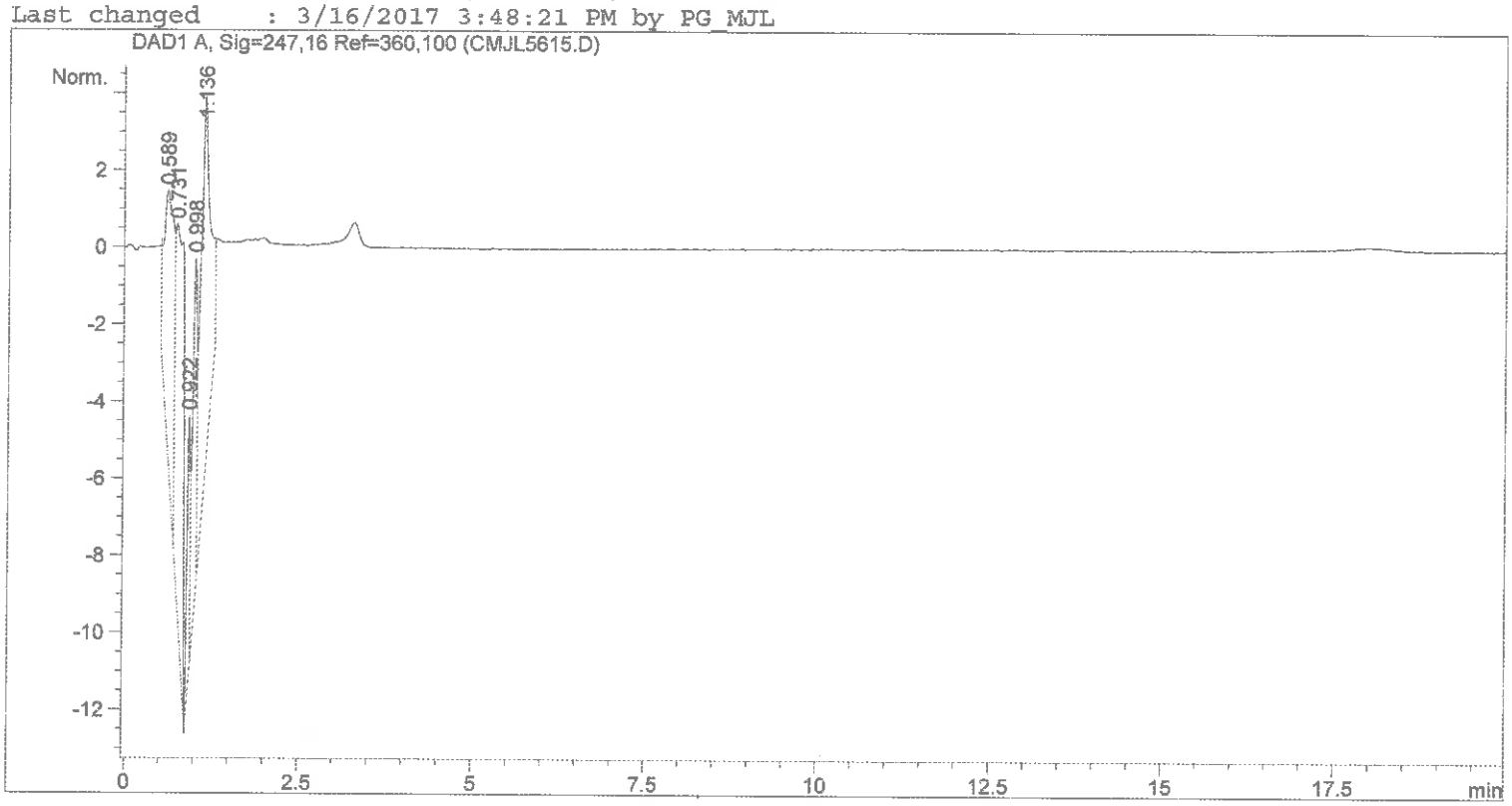

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.625 BV    0.0990   65.90158    9.26219  22.8986
   2   0.701 VP    0.1369  113.30771   10.76000  39.3706
   3   0.912 VV    0.0443   12.21179    4.70196   4.2432
   4   1.000 VV    0.0498   22.51504    7.33545   7.8232
   5   1.121 VB    0.0979   73.86186   10.03365  25.6645

Totals :                   287.79798   42.09324

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

```
==========================================================================
Injection Date  : 3/17/2017 2:30:15 AM          Seq. Line :   8
Sample Name     : CMJL027 Zn                    Location : Vial 8
Acq. Operator   : PG_MJL                           Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.M
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.593 BV    0.2444  122.47483    6.25467  39.0799
   2   0.819 VP    0.0492   34.07801   10.67428  10.8738
   3   0.927 VV    0.0438   18.43044    6.76360   5.8809
   4   1.000 VV    0.0632   38.65796    9.17276  12.3352
   5   1.136 VB    0.1318   99.75485   10.05266  31.8303

Totals :                   313.39608   42.91797

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Injection Date	: 3/17/2017 2:52:38 AM	Seq. Line	: 8
Sample Name	: CMJL027 Zn	Location	: Vial 8
Acq. Operator	: PG_MJL	Inj	: 2
Acq. Instrument	: Instrument 1	Inj Volume	: 20 µl
Acq. Method	: D:\Methods\JASONC~1\2PART.M		
Last changed	: 3/16/2017 4:38:41 PM by PG_MJL		
Analysis Method	: D:\Methods\JASONC~1\PARTIT~1.M		
Last changed	: 3/16/2017 3:48:21 PM by PG_MJL		



Area Percent Report

Sorted By	:	Signal
Multiplier	:	1.0000
Dilution	:	1.0000

Use Multiplier & Dilution Factor with ISTDs

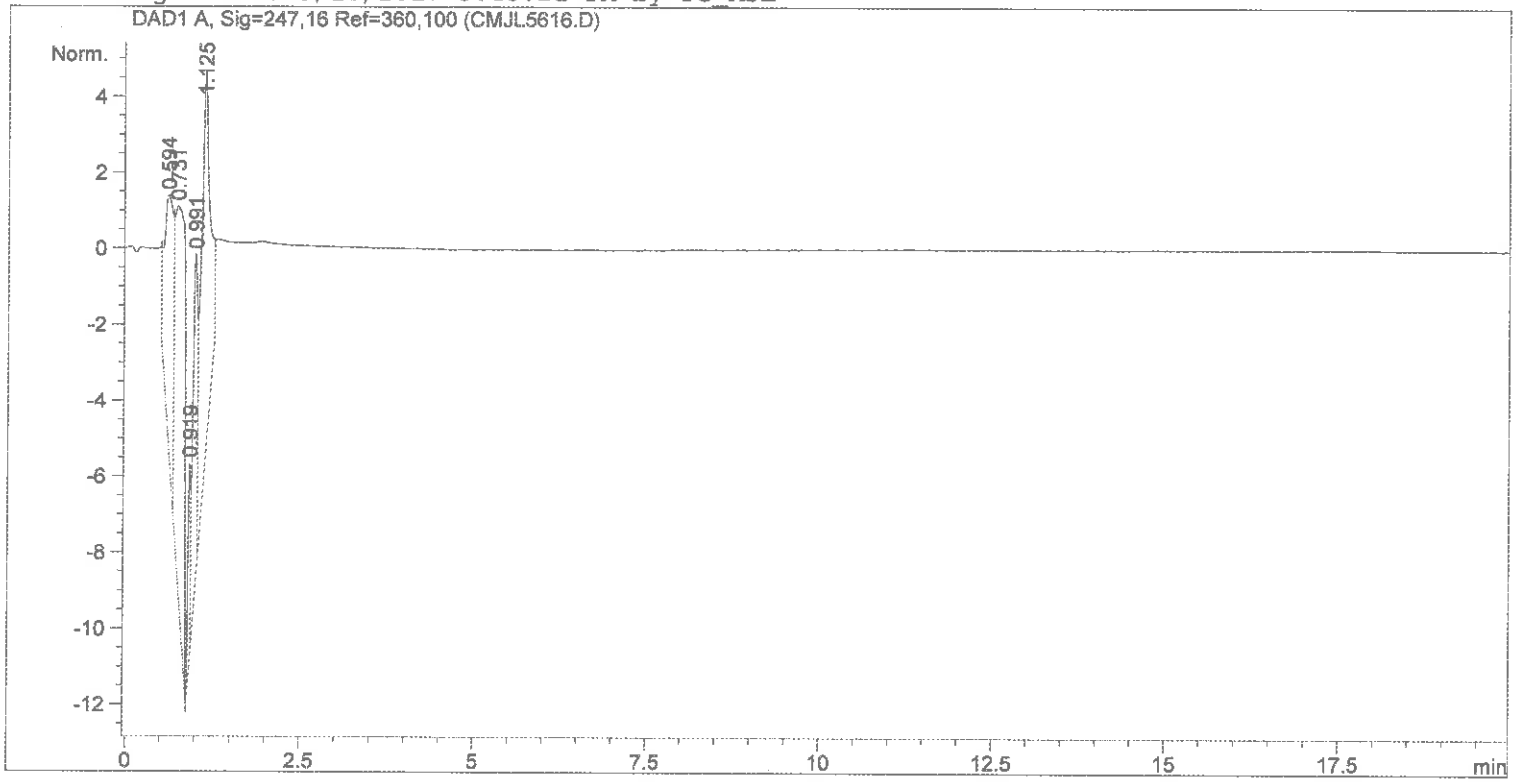
Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	0.589	BV	0.1470	69.80171	6.31348	21.9567
2	0.731	VP	0.1244	91.40769	9.16356	28.7531
3	0.922	VV	0.0431	18.66943	6.99343	5.8726
4	0.998	VV	0.0611	38.86995	9.24241	12.2269
5	1.136	VB	0.1282	99.15720	10.12557	31.1907
Totals :				317.90598	41.83845	

Results obtained with enhanced integrator!

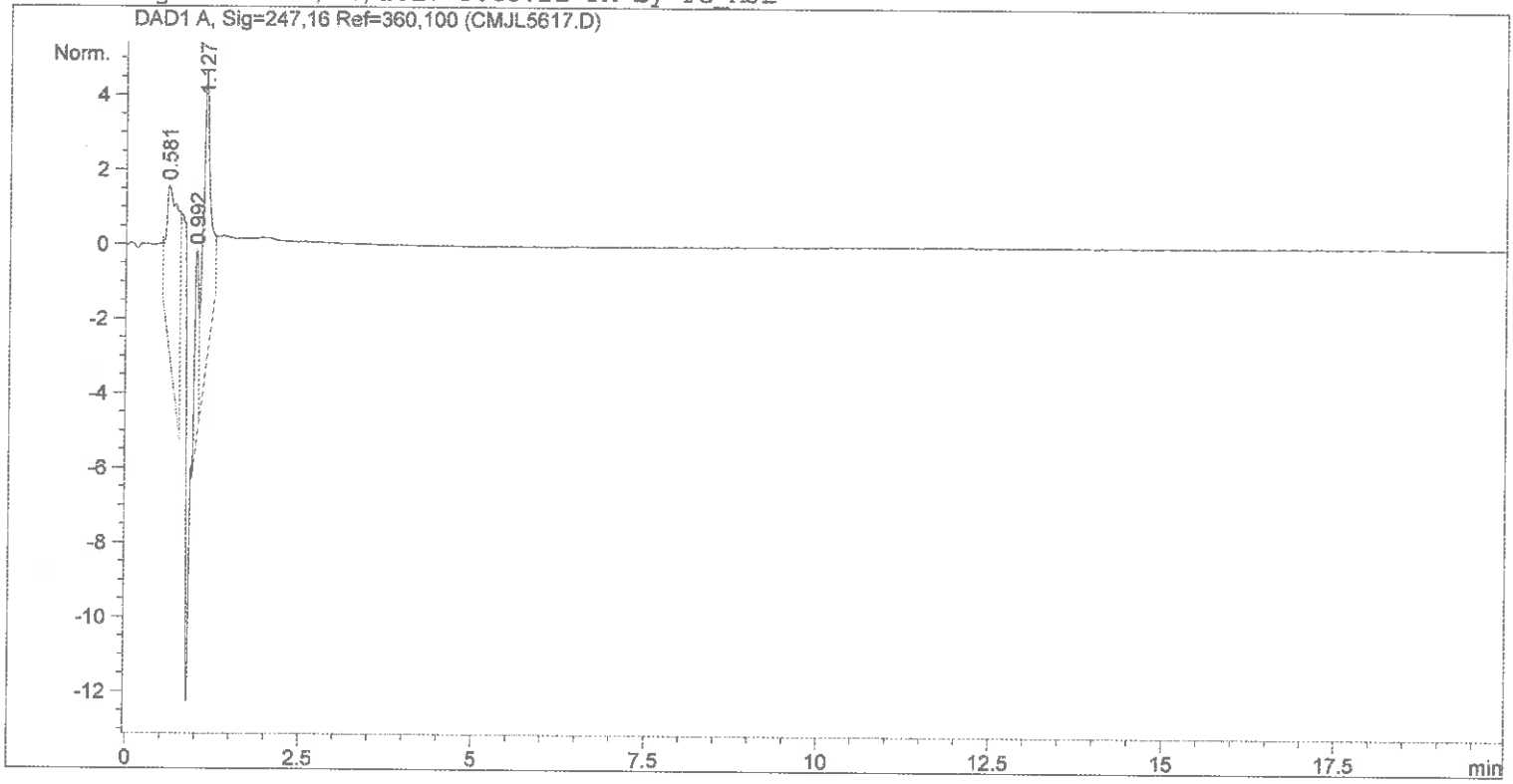
*** End of Report ***

```
==========================================================================
Injection Date  : 3/17/2017 3:15:00 AM          Seq. Line :   9
Sample Name     : CMJL027 Mg                    Location : Vial 9
Acq. Operator   : PG_MJL                        Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.M
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



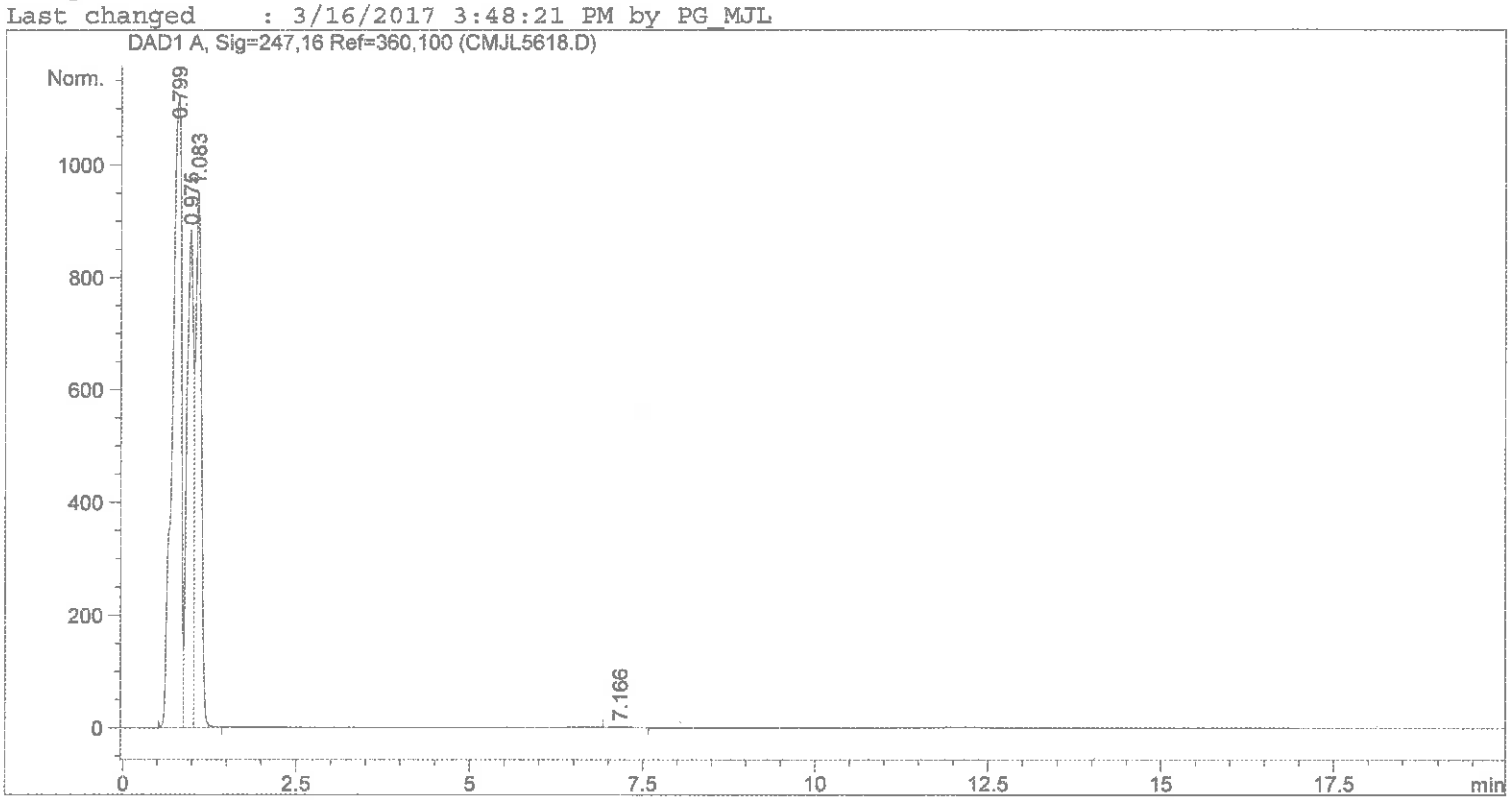

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height      Area
  #   [min]      [min]    [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   0.594 BV    0.1298   60.55944    6.21049  19.6859
   2   0.731 VP    0.1401  103.09990    9.39156  33.5144
   3   0.919 VV    0.0371   12.39966    5.33523   4.0307
   4   0.991 VV    0.0668   39.29121    9.02175  12.7723
   5   1.125 VB    0.1191   92.27840   10.44363  29.9967

Totals :                   307.62862   40.40267

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

```
==============================================================================
Injection Date  : 3/17/2017 3:37:24 AM          Seq. Line :   9
Sample Name     : CMJL027 Mg                     Location : Vial 9
Acq. Operator   : PG_MJL                            Inj :   2
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.M
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



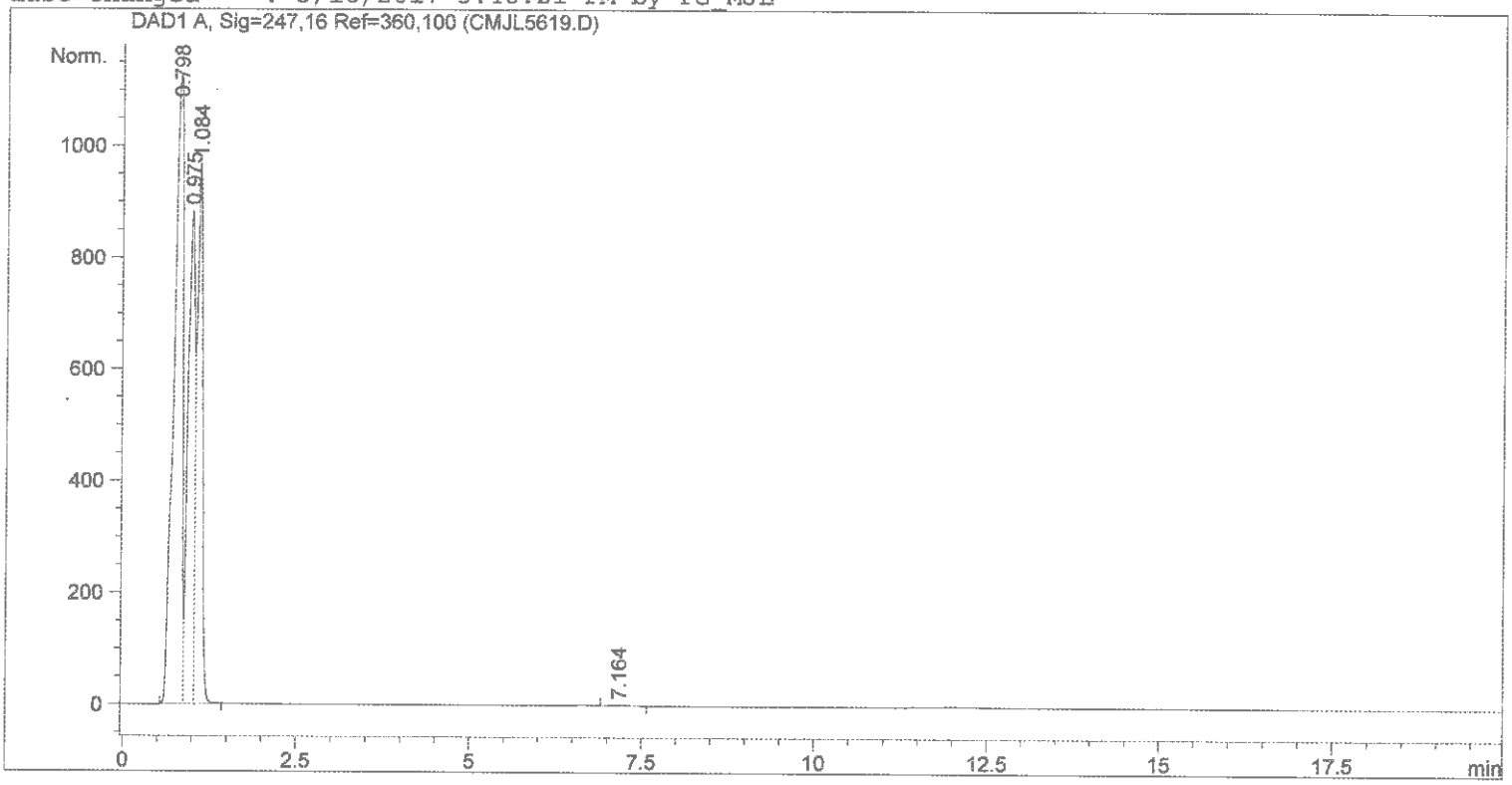

```
==============================================================================
                          Area Percent Report
==============================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]    [mAU*s]    [mAU]        %
----|-------|----|-------|----------|----------|--------
   1   0.581 BB    0.1989   65.49551    4.27076  45.0956
   2   0.992 VV    0.0582   18.98309    5.24606  13.0704
   3   1.127 VB    0.1046   60.75853    7.99703  41.8340

Totals :                    145.23713   17.51384

 Results obtained with enhanced integrator!
==============================================================================
                          *** End of Report ***
```

```
==========================================================================
Injection Date  : 3/17/2017 3:59:56 AM          Seq. Line :  10
Sample Name     : CMJL036                        Location : Vial 10
Acq. Operator   : PG_MJL                            Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.M
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



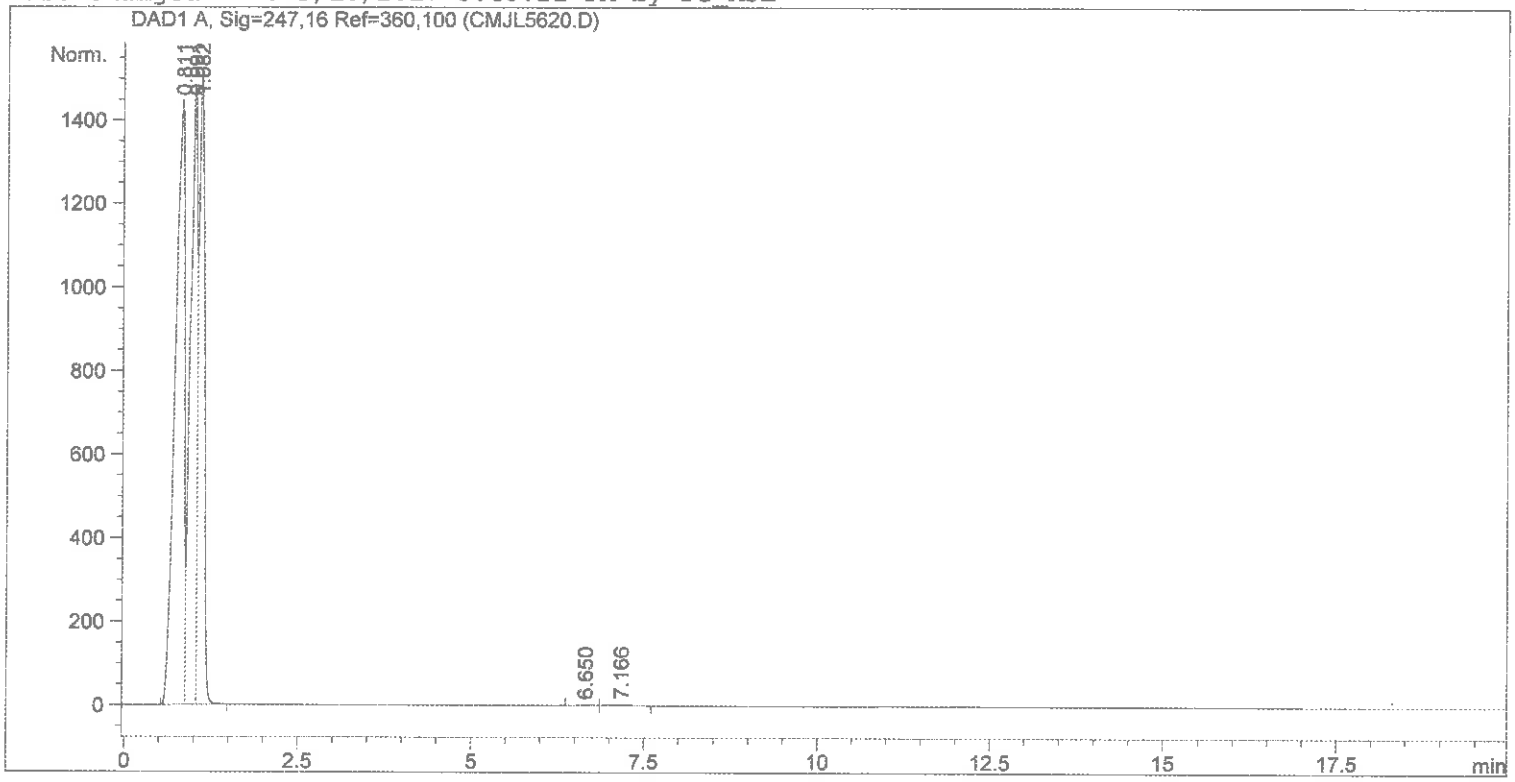

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.799 PV    0.1425 1.02334e4  1120.62366  46.8411
   2   0.975 VV    0.0912 5842.58545  883.35596  26.7431
   3   1.083 VB    0.0884 5751.33594  952.80408  26.3254
   4   7.166 BP    0.2316   19.75206    1.35871   0.0904

Totals :                  2.18471e4  2958.14240

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

```
==============================================================================
Injection Date  : 3/17/2017 4:22:23 AM          Seq. Line :  10
Sample Name     : CMJL036                       Location : Vial 10
Acq. Operator   : PG_MJL                           Inj :   2
Acq. Instrument : Instrument 1                 Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.M
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



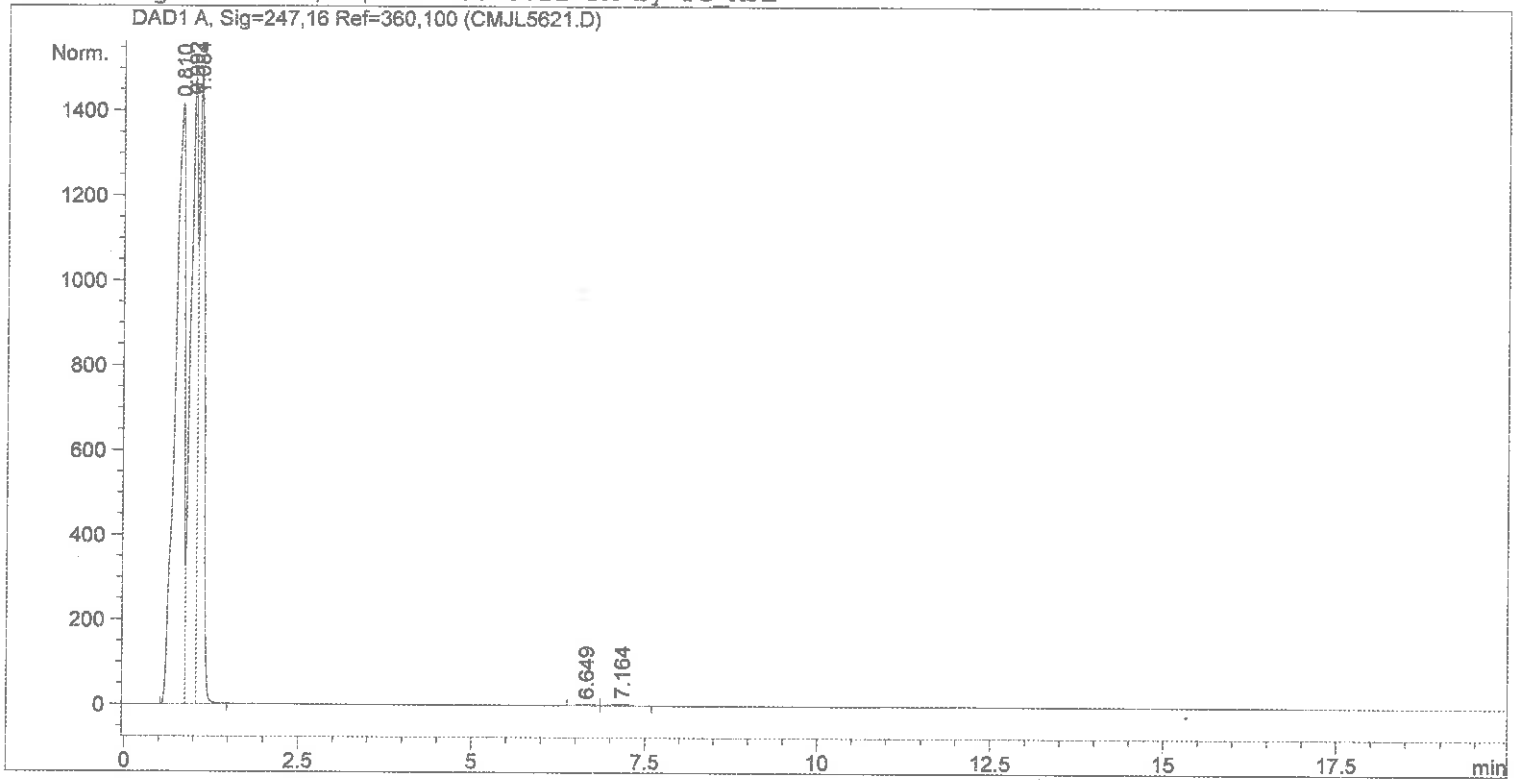

```
==============================================================================
                          Area Percent Report
==============================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|--------|----|-------|----------|----------|--------|
   1   0.798 PV    0.1410 1.01297e4  1125.28711  46.4490
   2   0.975 VV    0.0906 5957.56885  883.84265  27.3181
   3   1.084 VB    0.0867 5699.98584  968.35205  26.1369
   4   7.164 BP    0.2315   20.93538    1.39153   0.0960

Totals :                  2.18082e4  2978.87334

 Results obtained with enhanced integrator!
==============================================================================
                          *** End of Report ***
```

```
==========================================================================
Injection Date  : 3/17/2017 4:44:36 AM          Seq. Line :  11
Sample Name     : CMJL042                       Location : Vial 11
Acq. Operator   : PG_MJL                            Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.M
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



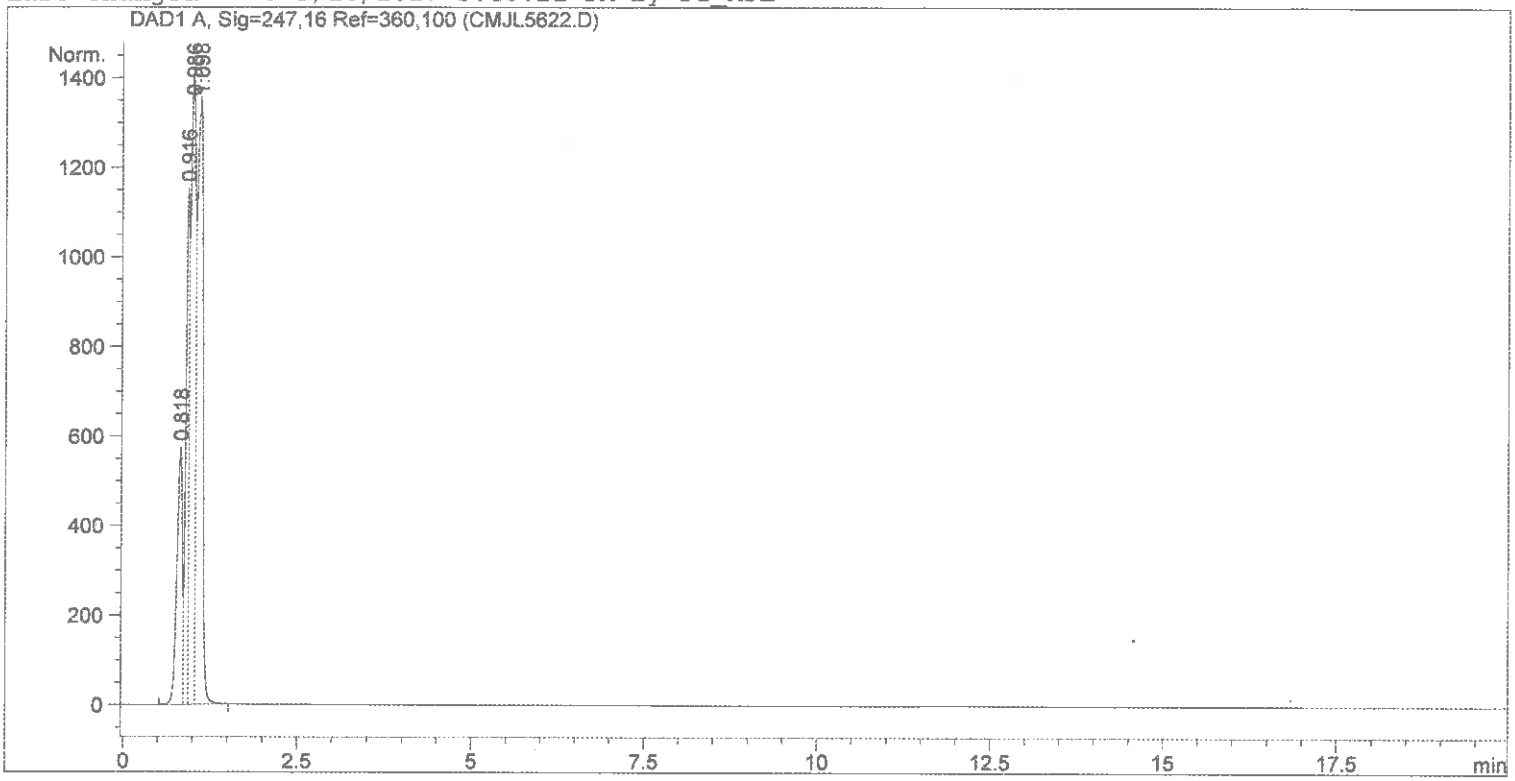

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|--------|----|-------|----------|----------|--------|
   1   0.811 PV    0.1251 1.35450e4  1448.87073  41.3260
   2   0.991 VV    0.0975 1.01166e4  1484.13403  30.8656
   3   1.082 VB    0.0977 9024.73242 1511.00879  27.5345
   4   6.650 BV    0.2647   31.19247    1.74341   0.0952
   5   7.166 VP    0.2921   58.58164    3.02338   0.1787

Totals :                  3.27761e4  4448.78033

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

```
==========================================================================
Injection Date   : 3/17/2017 5:06:58 AM          Seq. Line :  11
Sample Name      : CMJL042                       Location : Vial 11
Acq. Operator    : PG_MJL                            Inj :   2
Acq. Instrument  : Instrument 1                 Inj Volume : 20 µl
Acq. Method      : D:\Methods\JASONC~1\2PART.M
Last changed     : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method  : D:\Methods\JASONC~1\PARTIT~1.M
Last changed     : 3/16/2017 3:48:21 PM by PG_MJL
```



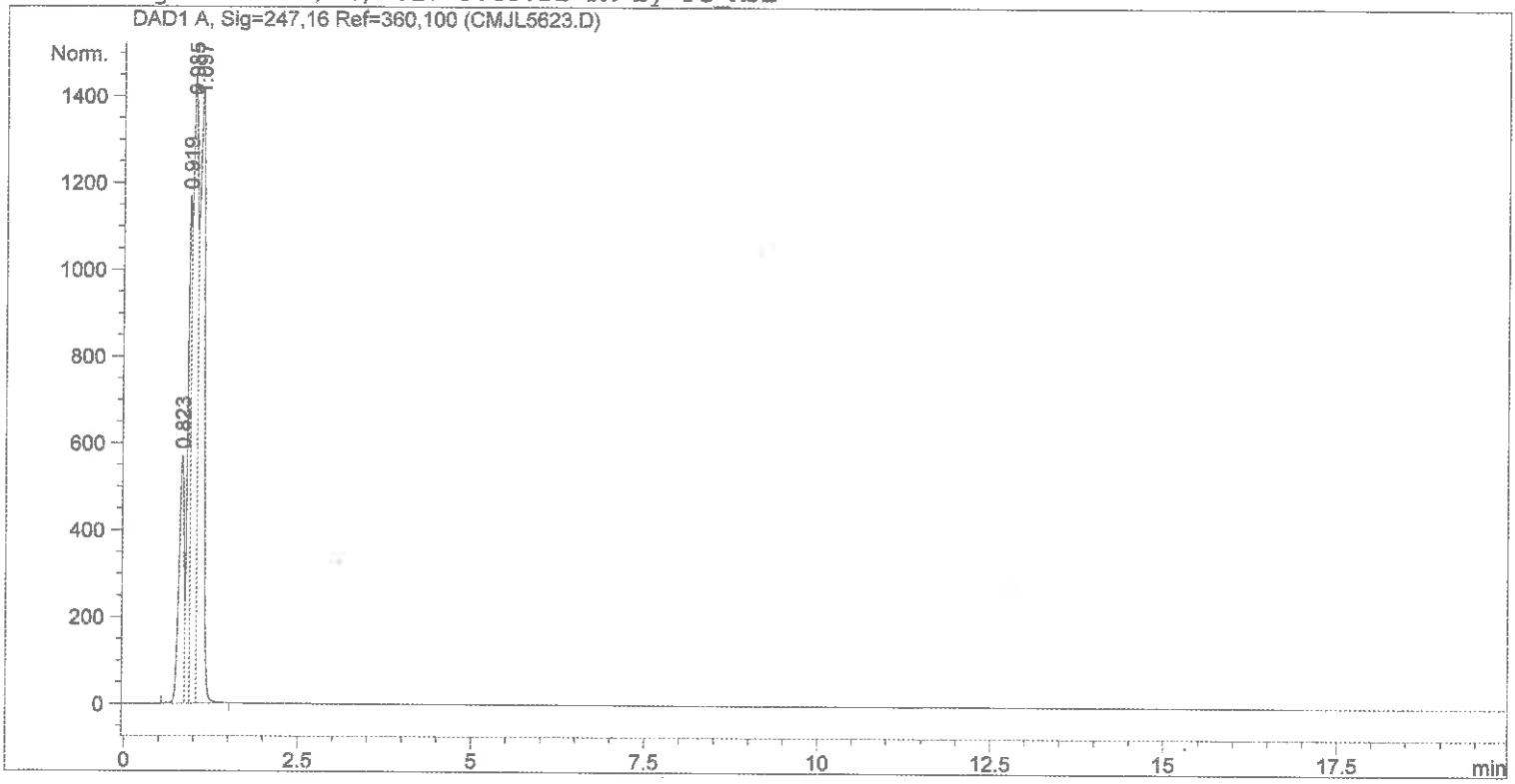

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.810 PV    0.1297 1.35796e4  1418.16919  41.4642
   2   0.992 VV    0.0964 1.01881e4  1477.91528  31.1084
   3   1.084 VB    0.0957 8894.26562 1489.57849  27.1579
   4   6.649 BV    0.2541   29.92941    1.71086   0.0914
   5   7.164 VP    0.2873   58.33497    2.99475   0.1781

Totals :                  3.27502e4  4390.36858

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

```
==========================================================================
Injection Date  : 3/17/2017 5:29:23 AM          Seq. Line :  12
Sample Name     : CMJL052                       Location : Vial 12
Acq. Operator   : PG_MJL                            Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.M
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



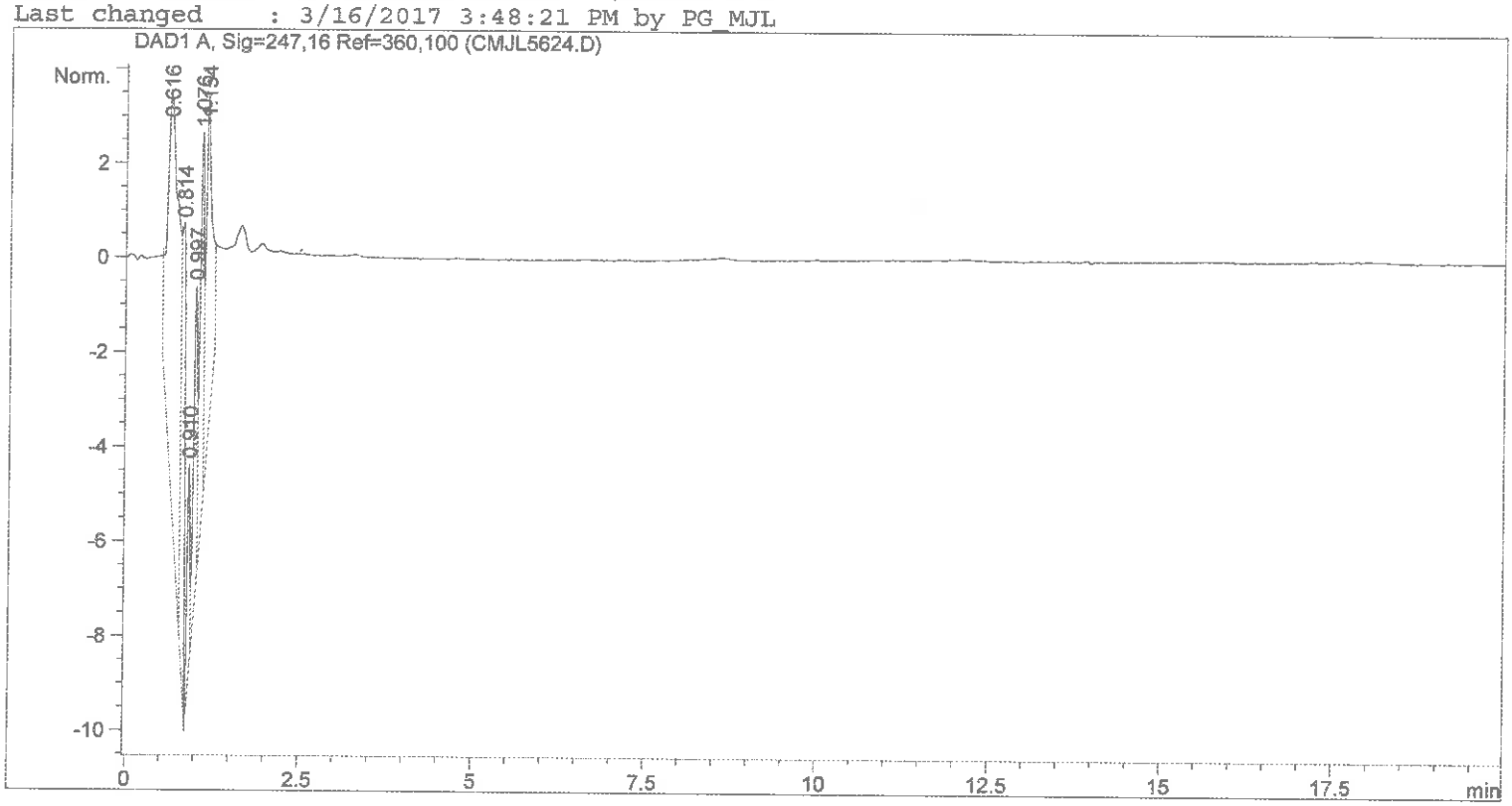

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.818 PV    0.0853 3025.80591  575.95770  13.5568
   2   0.916 VV    0.0484 3603.10352 1154.67090  16.1433
   3   0.986 VV    0.0751 7148.65234 1410.51135  32.0287
   4   1.098 VB    0.0876 8541.93262 1353.73352  38.2712

Totals :                  2.23195e4  4494.87347

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

```
==============================================================================
Injection Date  : 3/17/2017 5:51:43 AM          Seq. Line :  12
Sample Name     : CMJL052                       Location : Vial 12
Acq. Operator   : PG_MJL                            Inj :   2
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.M
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```



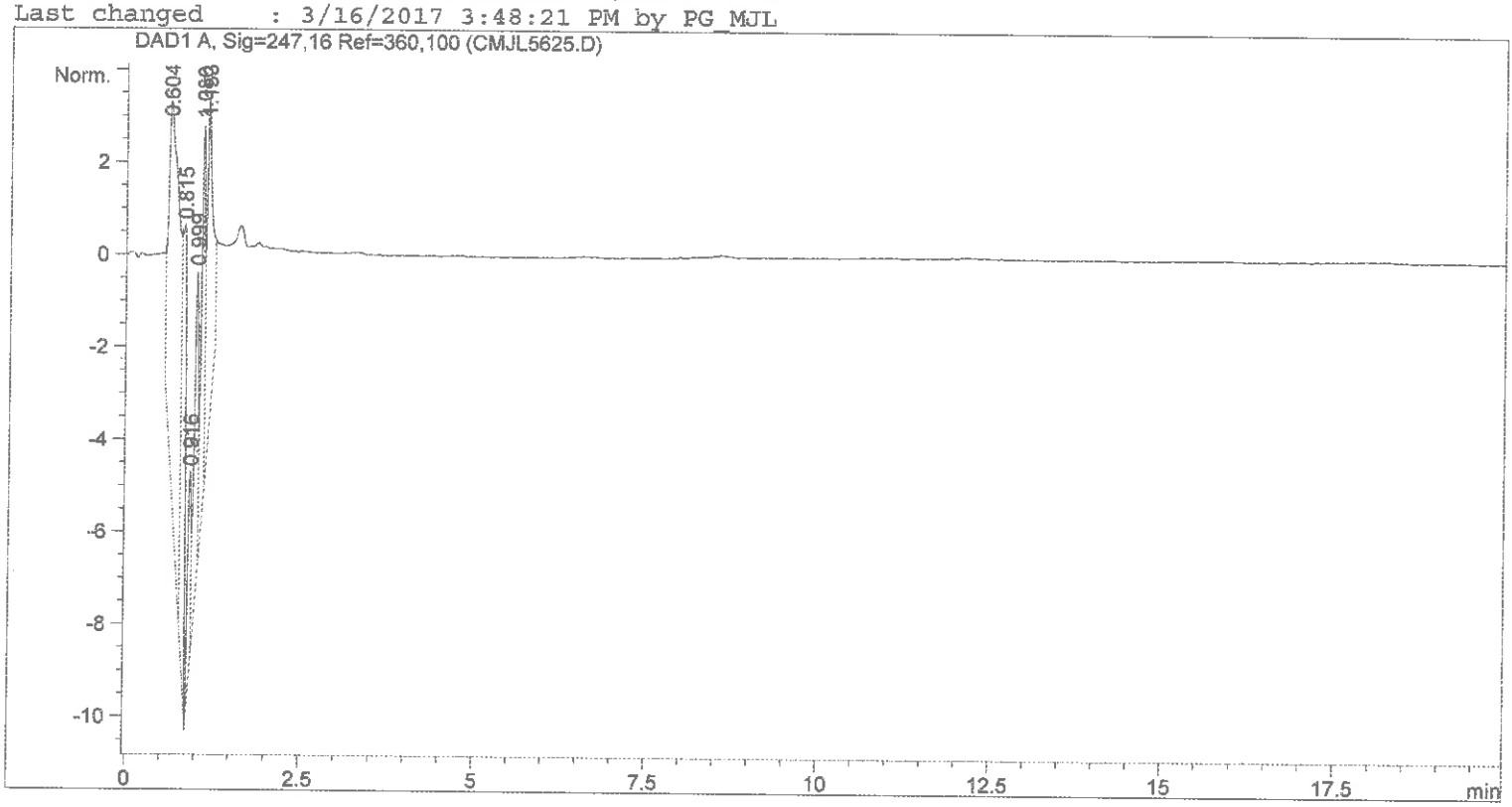

```
==============================================================================
                          Area Percent Report
==============================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.823 PV    0.0800 2846.42090  572.38147  12.8690
   2   0.919 VV    0.0465 3464.93481 1171.00745  15.6653
   3   0.985 VV    0.0766 7295.20850 1452.26624  32.9824
   4   1.097 VB    0.0838 8511.93555 1422.48352  38.4833

Totals :                  2.21185e4  4618.13867

 Results obtained with enhanced integrator!
==============================================================================
                          *** End of Report ***
```

```
==============================================================================
Injection Date   : 3/17/2017 6:13:56 AM          Seq. Line :  13
Sample Name      : CMJL053                       Location : Vial 13
Acq. Operator    : PG_MJL                            Inj :  1
Acq. Instrument  : Instrument 1                  Inj Volume : 20 µl
Acq. Method      : D:\Methods\JASONC~1\2PART.M
Last changed     : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method  : D:\Methods\JASONC~1\PARTIT~1.M
Last changed     : 3/16/2017 3:48:21 PM by PG_MJL
```




```
==============================================================================
                          Area Percent Report
==============================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1   0.616 BV    0.1861  106.71604    7.87445  41.8827
   2   0.814 VP    0.0582   37.23595    9.39629  14.6139
   3   0.910 VV    0.0432   12.54304    4.69606   4.9228
   4   0.997 VV    0.0525   23.29193    6.71635   9.1414
   5   1.076 VV    0.0550   30.98964    8.39847  12.1625
   6   1.154 VB    0.0793   44.02073    7.63358  17.2768

Totals :                   254.79732   44.71520

 Results obtained with enhanced integrator!
==============================================================================
                          *** End of Report ***
```

```
==============================================================================
Injection Date  : 3/17/2017 6:36:08 AM          Seq. Line :  13
Sample Name     : CMJL053                       Location : Vial 13
Acq. Operator   : PG_MJL                            Inj :  2
Acq. Instrument : Instrument 1                  Inj Volume : 20 µl
Acq. Method     : D:\Methods\JASONC~1\2PART.M
Last changed    : 3/16/2017 4:38:41 PM by PG_MJL
Analysis Method : D:\Methods\JASONC~1\PARTIT~1.M
Last changed    : 3/16/2017 3:48:21 PM by PG_MJL
```




```
==============================================================================
                          Area Percent Report
==============================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=247,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.604 BV    0.1719   99.98832    7.48020  39.4567
   2   0.815 VP    0.0611   40.04407    9.51545  15.8019
   3   0.916 VV    0.0479   13.15313    4.52066   5.1904
   4   0.999 VV    0.0586   27.21941    7.11366  10.7411
   5   1.080 VV    0.0495   29.14397    8.59988  11.5006
   6   1.153 VB    0.0763   43.86366    7.72400  17.3092

Totals :                   253.41255   44.95385

 Results obtained with enhanced integrator!
==============================================================================
                          *** End of Report ***
```