Furanic Solvents for Degreasing

SERDP Exploratory Development (SEED) Project WP-2523

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14. ABSTRACT

This limited scope research effort attempted to demonstrate the feasibility of converting building block chemicals readily available from biomass sources into sustainable degreasing solvents for cold cleaning operations. These liquid, oxygenated hydrocarbons all contained a furan ring with additional functionality including carboxylic ester, ether, acetal, alkane/alkene and ketone. The bulk of the solvents had adequate non-polar characteristics to dissolve hydrocarbon substances at the 10 centiStokes level. However, many of the furanic solvents could dissolve 150 centiStokes polyalphaolefin. Furanic solvent with proper non-polar character could degrease bearings coated with the greases MIL-PRF-81322 and MIL-PRF-23823. The solvents were largely of the combustible category with flash points greater than 80 °C. Evaporation rates of the furanic solvents were lower than MIL-PRF-680II.

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Preface

In this report, the term 'furanic' was liberally applied to all the structures shown which incorporate either a furan or tetrahydrofuran heterocyclic ring. Although chemically speaking these are very distinct species, it was believed to better capture the idea of the project and make for easier reading by lay persons not trained in the chemical sciences. Apologies are given to those readers versed in organic chemical nomenclature who may find this greatly annoying. A computer issue at the office caused the loss of virtually all of the detailed experimental procedures and electronic correspondence made during this project. The laboratory notebook, the chemical substances, the NMR data and the project lead survived this traumatic event and so the report was written as best as possible given the situation. The original proposal dealt with making derivatives with furfural but it became apparent early on that both furan and 2-methylfuran should be included, themselves borne from furfural, as they might yield useful materials in this endeavor. It was decided not to pursue the proposed derivatives made from 5-hydroxymethylfurfural, although this compound has been receiving a great deal of attention lately, since its process of manufacture (1Kg/$6000 Sigma-Aldrich) had not reached maturity when work began. The identification of the furanic solvents and intermediates was nothing more than the page numbers corresponding to the laboratory notebook, as this numbering system would help to minimize errors in the preparation of the report. The compound identification numbers do not in any way reflect a hierarchy or valuation of the compounds

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List of Acronyms

DoD	Department of Defense
NMR	Nuclear magnetic resonance
psi	Pounds per square inch
EPA	Environmental Protection Agency
Wt%	Weight percent
°C	Degree Celsius
ppm	Parts per million
pTSA	*Para* toluenesulfonic acid
Kg	kilogram
US	United States
M	molar
Ph. D.	*Philosophiae Doctor*
NAWCWD	Naval Air Warfare Center Weapons Division
MIBK	Methyl isobutyl ketone
DIBK	Diisobutyl ketone
TLC	Thin layer chromatography
g	gram
bp	Boiling point
mm	millimeter
mp	Melting point
Dr.	Doctor
PAO	polyalphaolefin
dl	Dextrorotary/levorotary
^{1}H	Protium isotope
^{13}C	Carbon-13 isotope
EC_{50}	Effective concentration at 50%
Fp	Flash point
mmol	millimole
SERDP	Strategic and Environmental Development Program
SEED	Strategic and Environmental Development Program Exploratory Development
FY	Fiscal year
USAEHR	United States Army Environmental Health Research
cSt	centiStokes
DOT3	Department of transportation specific brake fluid
MIL-PRF	Military performance specification
mg	milligram
mm^3	Cubic millimeter
VOC	Volatile organic compound
OSHA	Occupational Safety and Health Administration

Keywords

Lubricants

Green Chemistry

Degreasing

Solvents

Furfural

Carboxylic acids

Furan

Hydrogenation

Organic Synthesis

Grease

Evaporation

Flash point

Solubility

Cleaning

Bearings

Natural products

Ketones

Esters

Ethers

Toxicity

Hydrocarbon

Condensation

Maintenance

Reduction

Abstract

Objectives. It was proposed in a limited scope research effort to demonstrate the feasibility of converting building block chemicals readily available from biomass sources into sustainable degreasing solvents for cold cleaning operations. Solvents developed through this approach will be compliant with future air quality standards (low levels of volatile organic compounds or VOC), biodegradable, non-toxic and will have low global warming potential (carbon neutral).

Technical Approach. High volume, platform chemicals derived from carbohydrates will be converted by chemical synthesis into a variety of furanic solvents. These solvents will be tested for physical properties important to any new degreasing technology including evaporation rate, flashpoint, boiling point, etc. The solvents will be further evaluated based on their ability to degrease standard metal cartridge bearings. The collected data will allow for conclusions to be drawn about structure property relationships. In addition, a preliminary toxicity study of the solvents against *V. fischeri* will be conducted.

Results. The platform chemical furfuraldehyde and its family of secondary products furan, 2-methylfuran, tetrahydrofurfuryl alcohol, furfuryl alcohol and 2-furoic acid were converted into a series furanic solvents. These liquid, oxygenated hydrocarbons all contained a furan ring with additional functionality including carboxylic ester, ether, acetal, alkane/alkene and ketone. The reactions to create these furanic solvents were not complex with just one or two steps and multi-gram samples of solvents could be prepared. Conditions and catalyst were identified for the reduction of those furan containing substances. The solvents appeared to have low viscosities since they could be pipetted (1 mm inside diameter) without difficulty. The bulk of the solvents had adequate non-polar characteristics to dissolve hydrocarbon substances at the 10 centiStokes level. However, many of the furanic solvents could dissolve 150 centiStokes polyalphaolefin. Understandings of structure-solubility relationships among oxygenated hydrocarbons, which are the most common natural products, led to solvents useful for cleaning non-polar substances. The functional groups of the furanic solvents with the best hydrocarbon solubility were ethers and alkane/alkene. The furanic esters and furanic ketones typically required more aliphatic content to dissolve high viscosity base oil. Furanic solvent with proper non-polar character could degrease bearings coated with the greases MIL-PRF-81322 and MIL-PRF-23823. The furanic solvents could dissolve other lubricants such as metal working fluid, automotive fluids and vegetable oils. The solvents were largely of the combustible category with flash points greater than 80 °C. Those furanic solvents most prone to flammability were the alkane/alkene and ethers of lower molecular weight. The evaporation rates of the solvents were almost all less than one-half that of the current degreasing solvent MIL-PRF-680II, with alkane/alkene and ether being the most volatile. The furanic solvents showed good cold storage stability and only about 25%

of the solvents solidified at -30 °C. Presently, several of the furanic ketone solvents were delivered to collaborators at USAEHR Fort Detrick where Microtox™ analyses are underway.

Benefits. Collecting this data on these furanic solvents has helped to further our understanding of structure function relationships in materials research. Using chemicals obtained from biomass will result in a reduced net carbon footprint for the DoD. Futhermore, it may be possible to produce these solvents cheaper than the current technologies, thus lowering costs associated with degreasing operations at DoD facilities. Using chemicals derived from domestic biomass also reduces the nation's dependence on foreign sources of petroleum and related products. Finding alternate uses for agricultural waste products may lead to new domestic industries and job creation. Tapping into sustainable plant-based resources will result in reduced net carbon emissions while solvent design has the potential to result in solvents that readily biodegrade to innocuous by-products. Use of less toxic compounds will help the DoD maintain compliance with environmental standards set by the EPA, as well as state and local laws.

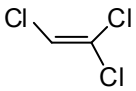
Objective

The technical objective of the proposed work is to demonstrate risk reduction sufficient to enable a full SERDP program aimed at studying the production of sustainable and effective degreasing solvents from feedstock chemicals generated from non-food biomass. By modest chemical transformation, a series of furanic liquids will be synthesized with an array of structural features. These new solvents will be characterized to evaluate pertinent physical properties (flash point, boiling/freezing points, materials compatibility, solvency, stability, water solubility and evaporation rate). The solvents will be further evaluated based on their ability to efficiently degrease typical metal cartridge bearings. From the data, it will be possible to develop a correlation between molecular structure of the solvent molecules and degreasing efficiency as well as other structure property relationships.

Background

Metal-metal contact requires lubrication in order to decrease friction and dissipate heat. Lubricants for these types of contacts vary widely but typically use some form of hydrocarbon based fluid. The fluid can be a light blend of low molecular weight hydrocarbons for machine cutting, or the lubricant can be greases composed of thick, emulsified mixtures of long chain, fatty acid metal salts mixed with hydrocarbon oligomers along with additives such as clay, graphite, PTFE or molybdenum disulfide. An example of a system with metal-metal contacts is a bearing constructed of metal spheres that roll on metal races to reduce rotational friction and support radial and axial loads. Bearings are made in a variety of types and sizes and are common and indispensable to virtually all aircraft, ships and transportation vehicles as well as tools, weaponry, machinery, generators, and heavy equipment (construction, earthwork). Over time and through use, the lubricant used with these moving metal parts will become ineffective through contamination, water absorption, oxidation, thermal breakdown and evaporation. Over the course of the lifetime of the machinery, and to achieve the greatest level of performance and longevity from equipment and vehicles, these metal parts require cleaning periodically to allow for inspection and re-greasing or replacement when necessary. This process of removing a lubrication fluid, grease or other contaminant from a part is referred to as degreasing.

One method for cleaning used at certain sites in the DoD it vapor cleaning. [1] As the name implies, vapor degreasing is accomplished by placing soiled parts in a chamber above a pool of solvent that can be heated to create vapors of the solvent which fill the chamber and condense on the parts. The condensed liquid dissolves the lubricant and drips back into the pool of solvent below. In this way, the part is continually bathed in fresh solvent and is cleaned from the soil after a period of time. The cleaned part is then taken out of the chamber and the residual cleaning fluid on the part is allowed to evaporate. The current solvents used by the DoD for vapor degreasing are halogenated organic compounds such as perchloroethylene (PCE), trichloroethylene (TCE) and *n*-propylbromide (nPB). These compounds have high solvent power and dissolve a variety of substances including non-polar oils, greases and waxes to more polar soils such as tars and coolants. They have high vapor pressures and low boiling points so that after cleaning, they evaporate rapidly and completely. In addition, because they are halogenated, these compounds are not flammable making them safe to use (TCE has no measureable flashpoint).[2] TCE is also cheap, as it is manufactured from chlorine gas and ethylene (obtained from cracking petroleum distillates). To give a sense of scale of TCE use, the Anniston Army Ammunition Depot reported that over 100,000 pounds of TCE were disposed of as hazardous waste in 2007.[3]



TCE

In the process of cold cleaning, soiled parts are submerged in an unheated bath of solvent (dip tank or parts washer) and/or manually scrubbed by a technician to remove soil. This process is known as cold cleaning and is more prevalent than vapor degreasing today. Degreasing

operations are performed throughout the DoD, not only at logistics and engineering depots such as Norfolk Naval Shipyard, Corpus Christie Army Depot or Warner-Robins Air Logistics Center but at virtually all installations. There are some 30 major sites and some 120 smaller sites that make up the DoD facilities network and at each and every site some form or another of degreasing operations going carried out. A thorough report on solvent usage was made in the mid-1980's when it was estimated that large DoD sites use about five hundred 55 gallon drums of solvent per year whereas smaller sites used around one hundred and fifty 55 gallon drums of solvent per year.[4] The Bee and Kawaoka report was concerned with the use of Stoddard solvent in cold cleaning operations.

For cold cleaning, particular blends of petroleum distillate are used such as MIL-PRF-680II which has safer flash point (~ 60 °C). These current degreasing solvents have major ecosystem and workplace environmental drawbacks. Owing to their high vapor pressure (TCE = 72 mm Hg at 20 °C), both cleaning processes, and particularly for vapor degreasing, result in significant vapor emissions. Such vapors are referred to as volatile organic compounds (VOCs) hazards. Personnel can be exposed to these volatile components by epidermal contact and/or inhalation. VOCs can cause adverse biological responses (toxicity) in humans and other organisms by various modes of physiological action. Both TCE and nPB are also federally regulated as VOCs and will likely result in severe restrictions in their use in the future. The equipment used by the DoD to carry out degreasing operations oftentimes do not have the best controls for containing VOCs at the present time.

Hazardous working conditions and damage to air quality due to degreasing operations has not gone unnoticed. Recent legislation in California (SCAQMD Rule 1122) has called for strict monitoring of degreasing operations (cold cleaning) with a low threshold for VOC emissions. Historically, California has set environmental protection precedents that trickle down to the rest of the country. Following this trend, it is likely that the DoD would be required to refit all its facilities with new hardware and emission-containment equipment in compliance with stringent VOC limitations, which would be a very expensive proposition. Biodegradation of degreasing solvents is also a major concern for the DoD and the EPA as TCE/PCE/nPB solvents used since the 1950's have been accidentally released to the environment at many installations such as NAS Moffett Field, Air Force Plant #44 Tucson, Twin Cities Army Ammunition Plant and Marine Corps Base Camp Lejeune.[5] These halogenated solvents are not readily metabolized[6] by microorganisms in the soil and have contaminated soil and drinking water in these areas. Cleanup of these affected areas is extremely difficult and expensive and work continues to this day.

Considering all of the drawbacks to current degreasing solvents, it is clear that replacements are urgently needed at DoD facilities. One replacement technology currently in use by the Anniston Army Depot is Dupont's Vertrel SDG product. This solvent is a mixture of *trans* 1,2-dichloroethylene and hydrofluorocarbons (HFC) and appears to be as effective as TCE but is

much more expensive (Vertrel SDG $7000/55 gal; TCE $620 /55 gal).[7] Obviously, the financial stakes are very high for the DoD.

If one were to propose new solvents technologies for cleaning operations in the DoD such solvents should ideally possess several characteristics: the ability to dissolve and remove both polar and non-polar soils as efficiently as TCE or MIL-PRF-680II; low vapor pressures so that they will fall below threshold levels of VOC set by air quality governing districts; low toxicity to personnel; high flashpoint (temperature at which the solvent can vaporize to form an ignitable mixture in air) to reduce fire/explosion hazards; low global warming potential (GWP) values to limit anthropogenic climate change; and lastly, rapid and complete biodegradation should they be released into the air, water or soil.

It appeared that a truly sustainable solution to degreasing solvents that could fulfill the above requirements and that could be produced on sufficient scale could be derived from non-food biomass and derivative molecules. The United States is fortunate to contain large areas of fertile land on which a variety of crops and forestry products are generated. A significant amount of non-food, waste biomass is generated in the US, with DOE estimates suggesting that hundreds of millions of tons of this material could be sustainably produced. This crude organic material can be viewed as a chemical-feedstock alternative to petroleum sources.[8] Although primary, biobased feedstock chemicals may not have optimal properties for degreasing (high VOC, high flash point, too polar), they can be readily modified through simple chemical transformations into new products with tailored characteristics. Oxygen-containing organic compounds including alcohols, ethers, esters, aldehydes, ketones and carboxylic acids can be readily derived from biomass feedstocks and are well suited for chemical modification. The project took advantage of the convenient reactions that these molecules undergo among one another, and even with carbon dioxide, to create, in a modest combinatorial manner, new organic solvents suitable for environmentally responsible degreasing applications.

Given the plethora of available feedstock chemicals from nature and the short duration of a SEED program, this effort focused primarily on chemical products derived from pentoses. These simple carbohydrates can undergo a thermal dehydration reaction to yield furanic chemicals containing a 5-membered heterocyclic ring. The product of the cyclization of pentose sugars is furfuraldehyde, Figure 1. This dehydration reaction is performed on an annual volume of hundreds of thousands of tons around the world by the Quaker Oats process.[9,10] Non-food hemicellulose from basically any plant (cane bagasse, corn husk, oat hulls, *et cetera*) can be transformed into furfuraldehyde. Furthermore, furfuraldehyde is converted on industrial scale to secondary products that are also useful in this endeavour such as furan, 2-methylfuran and tetrahydrofurfuryl alcohol, Figure 1. This project will use these compounds as platform chemicals from which to build new sustainable solvents that may be drop-in replacements for cold cleaning operations within the DoD.

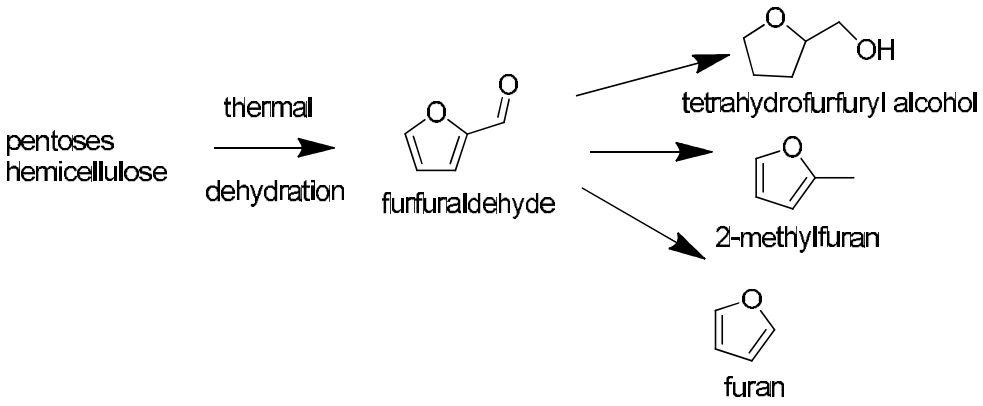


Figure 1 Cyclodehydration of carbohydrate to furanic chemicals

The chemical literature revealed little information correlating the chemical structure of solvents and their effectiveness at soil removal. As mentioned previously, grease is a mixture of both polar and non-polar components and designing a new liquid to be effective at dissolving both kinds of molecules was challenging. During the research project, the structure-degreasing relationship among the furanic solvents will be understood after incorporating a variety of different structural features and functional groups. Evaluating the new solvents in degreasing tests should elucidate which chemical features are most effective for soil removal. Another important consideration in the synthesis of these furanic solvents was ease of synthesis, ideally by a single step, Figure 2. In particular, compounds that could be prepared with high atom economy and maintaining the principles of green chemistry were most desireable. Some of the furanic solvents have been synthesized in the past, but many are new, and in no instance have they been used for the purposes of degreasing.

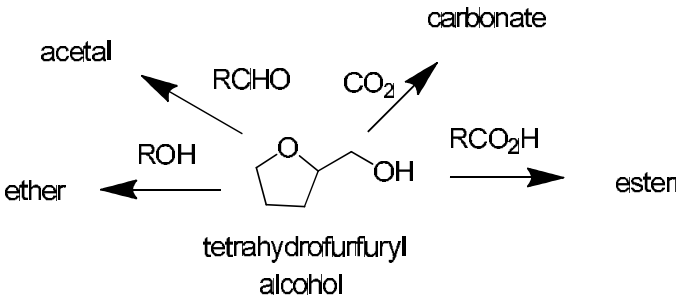


Figure 2 Sample derivitization of tetrahydrofurfuryl alcohol into various products

By collecting a range of data on the furanic solvents including flashpoint, boiling/freezing points, solvency, water solubility, evaporation rate, cleaning efficiency, and materials compatibility, relationship diagrams such as in Figure 3 can be created. The ideal properties in these three modes will be an intersection or 'Goldilocks zone' where certain furanic solvents have high flashpoint (fire safety), low evaporation rate (low VOC) and high degreasing ability (time and energy efficiency).

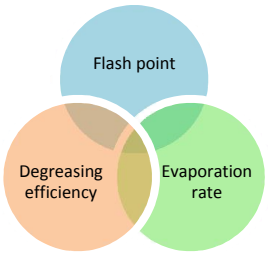


Figure 3 Venn diagram combining multiple data sets

For the most part, chemicals derived from plant based feedstock tend to be completely biodegradable, oftentimes having low toxicities (generally regarded as safe or GRAS) and, by definition, are biorenewable and biobased. Although some of the compounds in this study may not be present in nature, it is hypothesized that they may have low toxicities. The structures have been purposely designed to be simple derivatives of oxidized hydrocarbon with common place functional groups found in the natural world. Therefore, enzymes (e.g. esterases, oxidases, dehydrogenases) will likely hydrolyze, oxidize or otherwise react with them as they would normal substrates. What's more, it has been shown that tetrahydrofuran is a low ecotoxicity hazard to aquatic organisms and that the compound is fully metabolized and thus does not bioaccumulate.[11] The furanic ketones were tested in a typical toxicity screen known as the Microtox® assay.

Materials and Methods

Deuteriochloroform ($CDCl_3$) was the solvent used for all NMR experiments carried out on a Bruker Avance II 300 MHz spectrometer (^1H at 300 MHz, ^{13}C at 75 MHz), Figure 4. NMR data (free induction decay signals) were processed using NUTS software from Acorn NMR (Livermore, CA). All ^1H spectra are referenced to tetramethylsilane ($SiMe_4$) and all ^{13}C spectra are referenced to $CDCl_3$.

Figure 4 Bruker Avance 300 MHz instrument

Tetrahydrofuran, palladium on carbon (5 wt%), acetic anhydride, various carboxylic acids and all of the ketones were obtained from Sigma-Aldrich (Milwaukee) and used as received. The aliphatic alcohols were obtained from Sigma-Aldrich in 99% purity and used as received. Food grade furfural was obtained commercially and distilled at reduced pressure prior to use. Polyalphaoelfin (PAO) with kinematic viscosities of 2, 5, 10, 65 and 150 cSt (Spectrasyn™ and Spectrasyn Elite™ product lines) were obtained from the ExxonMobil Chemical Company, Figure 5.[12] Navsolve and NavHFC cleaning products were obtained from Ecolink, Figure 6. The ester based lubricant Priolube™ 1936 was obtained from Croda. The Ucon™ OSP-18 fluid

was obtained from Dow Chemical Co. Generic mineral oil USP grade was obtained from a local retail pharmacy, Figure 7. The Nyco Mil-PRF-81322G grease was obtained from Fleet Readiness Center China Lake Detachment. MobilGrease33 was purchased from a local Napa Auto Parts.

Figure 5 The generous gift of polyalphaolefin from ExxonMobile Chem. Co.

Figure 6 Navsolve and NavHFC cleaning technologies provided by Ecolink and tetrahydrofurfuryl alcohol from Pennakem

Figure 7 Dow Chemical oil-soluble polyalkyleneglycol, Croda Priolube 1936 and the generic mineral oil

The effect of cold storage on the furanic solvents was carried out as follows. In small screw cap vials were place ~0.5 gram samples of each of the furanic solvents. The samples were collected together in a plastic organizer box and placed in a refrigerator. Two refrigerators were used, one set for -30 °C and the other set at -74 °C. In the first test, the samples were stored in the -30 °C freezer for four days and then visually checked for physical state (solid or liquid). The samples were then removed from the -30 °C freezer and allowed to reach ambient temperature. Afterwards, the samples were stored in the -74 °C freezer for eighteen hours and visually checked for their physical state. Finally, the samples were stored once again in the -30 °C freezer for five days and visually checked for their physical state.

The flash point data for the furanic solvents were collected with a Grabner Instruments MiniFlash FLP by the ASTM D7094 method, Figure 8. Each solvent was tested in triplicate and the median value reported.

Figure 8 Grabner flash point tester

The solubility experiments were all conducted at room temperature. A disposable, borosilicate culture tube (12 mm X 75 mm) was charged with hexanes, mineral oil or PAO (50 mg) and then furanic or other solvent (250 mg) was added. A 10X magnification hand loupe was helpful in noting changes. Upon gentle mixing, Schlieren texture was observed when hydrocarbon dissolved in solvent, owing to changes in density and the refraction of light during dissolution. Soluble mixtures of solvent/hydrocarbon were a single phase upon complete dissolution. Insoluble mixtures, however, appeared as an opaque emulsion during mixing returning to two phases shortly afterwards.

For the evaporation studies, glass shell vials (12 mm x 35 mm) were tared on a balance and then filled with two grams of solvent along with a control vial filled with two grams of *n*-butyl acetate. The vials were stored in an undisturbed area of the climate controlled laboratory (room temperature = 21 °C). The solvent evaporation experiments were done in three batches as furanic and other solvents became available. The three evaporation batches were multi-day affairs with durations of 328, 352 and 213 hours. At the end of the experiment, the mass of solvent remaining in the vials was measured. This raw data is included in the Appendix. The formula to calculate the rate of solvent evaporation was as follows:

Equation 1 [2 grams - (Solvent mass remaining in grams)] / number of hours = rate of solvent evaporation (grams per hour)

The rates of evaporation of the solvents were then normalized to the rate of evaporation of *n*-butyl acetate as follows:

Equation 2 [rate of solvent evaporation (gram/hr)] / [rate of *n*-butyl acetate (gram/hr)] X 100 = rate of evaporation

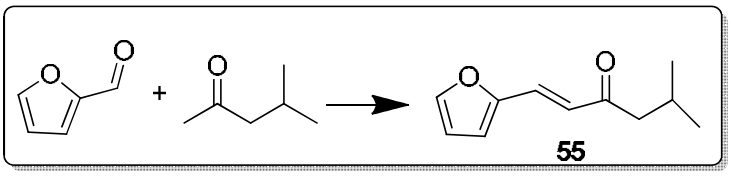
Total immersion corrosion testing was carried out in the following manner. Small glass vials were charged with stainless steel #10 flat washers which were purchased from Home Depot™. Then furanic solvent was added to completely submerge the washer. After nine days, the washers were removed and patted dry with a tissue and visually inspected and compared with untreated washers for pitting or other surface blemishes.

Synthesis of furanic solvents

Figure 9 Some of the furanic solvents and intermediates made during the project

Synthesis of furanic ketone (**82**):

Step 1:

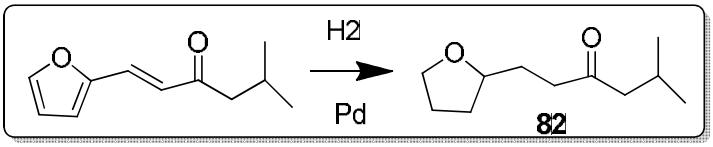


Synthesis of furfurylidenone (**55**)

A 5 L round-bottomed flask equipped with magnetic stirring bar was charged with furfural (560 mL, 672 g, 7 mol), H_2O (1 L) and 4-methyl-2-pentanone (900 mL, 720 g, 7.2 mol, 1.02 equiv). The mixture was vigorously stirred by mechanical agitation at room temperature while a solution of NaOH (29.7 g, 740 mmol) in H_2O (100 mL) was added in a gentle stream over 1 h. The mixture gradually became dark red-brown in color. After 18 h, an aliquot of the reaction mixture was acidified with 1 M HCl and analyzed by NMR which showed the reaction was essentilly complete as only a trace of the aldehyde was remaining. The mixture was quenched by the addition of a solution of conc. H_2SO_4 (20 mL, 370 mmol) in H_2O. After stirring for 2h, the mixture was extracted several times with Et_2O. The extracts were collected and washed with H_2O followed by brine. After drying over anhydrous $MgSO_4$, the solvent was rotary evaporated leaving a thick, brown oil. The oil was distilled under reduced pressure (60 torr). The bulk of the product came over at ~140-155 °C. This was the desired product which had a yellow color (1016 g, 81% yield). NMR was consistent with the drawn structure.

Step 2:

Synthesis of tetrahydrofuranic ketone (**82**), Figure 9.



A Parr™ reactor bottle was charged with furfurylidenone (**55**) (80 g, 449 mmol), 5wt% palladium on carbon (5.6 g, 7 wt% loading) and tetrahydrofuran (100 mL). The reduction was conducted with hydrogen pressure of 40 psi. After 24 h, uptake of hydrogen had ceased. The mixture was removed from the apparatus and carefully filtered under an atmosphere of nitrogen. The solvent was rotary evaporated. The remaining oil was distilled at reduced pressure (1 torr) to give the desired compound as a colorless, mobile liquid (77.8 g, 94%). ^{1}H NMR: δ 3.9-3.6 (m, 3H), 2.6-1.7 (m, 9H), 1.5 (m, 1H), 0.8 (d, 6H); ^{13}C NMR: δ 210.88, 78.62, 67.85, 52.15, 40.21, 31.55, 29.64, 25.90, 24.82, 22.81, 22.79.

Figure 10 400 gram batch of furanic ketone (**82**) for large bearing degreasing experiments

Results & Discussion

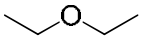
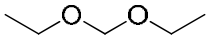
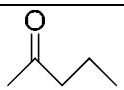
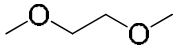
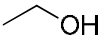
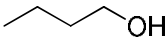
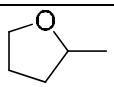
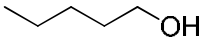
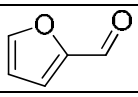
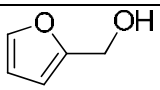
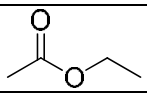
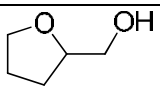
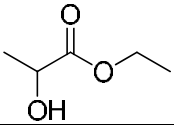
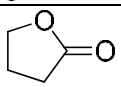
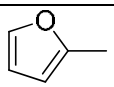
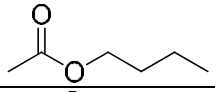
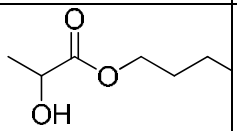
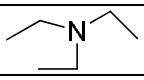
General Solubility Trends of Organic Functional Group with PAO65

Very early in the project some empirical solubility tests were conducted with some organic compounds that were available from the stockroom. The purpose was simply to get familiar with the common organic chemical functional groups and solubility in hydrocarbon substances. The base oil studied at this time was PAO65, polyalphaolefin which has a viscosity of 65 cSt at 100 °C, Table 1. In hindsight, this base oil was too high of viscosity since grease and motor oils are manufactured from 20 cSt or less base oils. Nevertheless, there was knowledge that was gained from this very preliminary study that would prove useful in deciding which target furanic solvents to make during the project.

As anyone with basic organic chemistry knowledge would aniticipate, the small alcohols are too polar to dissolve PAO. But there was more to the story about the solubility of alcohols and hydrocarbons which became the subject of a manuscript, see Appendix V. Also, simple ketones were unable to dissolve the PAO even though they are less polar than alcohol. Finally a hit was found with the carboxylic ester *n*-butyl acetate which had enough non-polar character to dissolve the oil. But removal of two methylene groups from *n*-butyl acetate and ethyl acetate was no longer useful. Not surprisingly, ethyl lactate with an alcohol group was a poor solvent. Even the cyclic ester butyrolactone was too polar for this oil. Another example of how alcohols can greatly influence polarity was that butyl lactate was unable to dissolve the base oil unlike *n*-butyl acetate. Ethers appeared to be excellent solvents since even diethyl ether could dissolve the PAO. Acetal also was useful since diethoxymethane could dissolve the oil. Interestingly, 1,2-dimethoxyethane which is very similar in structure to diethoxymethane was unable to dissolve the oil. The 1,2-dimethoxyethane is a typical structural fragment of polyalkylene glycols lubricants. Also, amines appear to be good non-polar solvents since even the simple triethylamine was able to dissolve the base oil.

Some furanic solvents were also tested. Furfuraldehyde was too polar to be useful and neither were its alcohol derivatives regardless of the oxidation state of the furan ring. However, once the aldehyde functionality was removed then excellent solvents were obtained: tetrahydrofuran, 2-methyltetrahydrofuran, furan and 2-methylfuran. So from this preliminary study it appeared that ether was best functional group for hydrocarbon solubility among the oxygen containing hydrocarbon solvents. Also, it appeared that ketone and ester might be useful with appropriate substitution. It seemed likely that hydroxyl groups would cause deleterious effects on hydrocarbon solubility of furanic solvents and should be avoided.

Table 1 PAO65 Solubility of Furfuraldehyde Products and Various Organic Liquids

Ketone		PAO65 Solubility	**Ether**		PAO65 Solubility
acetone		NO	Diethyl ether		YES
2-butanone (MEK)		NO	Diethoxymethane		YES
2-pentanone		NO	1,2-dimethoxyethane		NO
Alcohol			**Furanic Solvents**		
Ethanol		NO	tetrahydrofuran		YES
1-butanol		NO	2-methyl-tetrahydrofruan		YES
1-pentanol		NO	furfuraldehyde		NO
Ester			Furfuryl alcohol		NO
Ethyl acetate		NO	Tetrahydrofurfuryl alcohol		NO
Ethyl lactate		NO	furan		YES
butyrolactone		NO	2-methylfuran		YES
n-butyl acetate		YES			
n-butyl lactate		NO	**Amines**		
			Triethylamine		YES

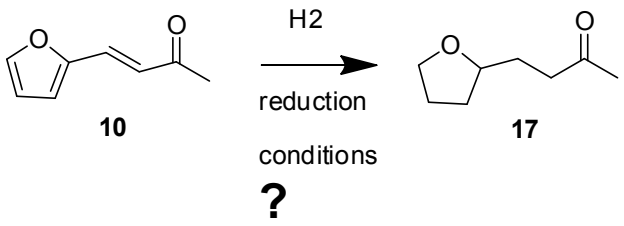
Hydrogenation to Prepare Furanic Solvents

The NMR spectra discussed in this section can be found in Appendix A.

The flash points of the heterocycles furan and tetrahydrofuran are shown below. As one can see, the reduction of furan, or the addition of two molecules of hydrogen, into its tetrahydro derivative, tetrahydrofuran, significantly raises the flash point. The flash point of solvents is a very important safety factor which will be discussed further in a later section. Another reason for reduction of furans is that the aromatic nucleus is reactive and would likely lead to undesired by-products (e.g. oxidation) over time resulting in solvents with poor stability. Furthermore, as will be shown later, the presence of the furan in the structure of a solvent tended to decrease its solubility in hydrocarbons.

	furan	tetrahydrofuran
flash point (°C)	-36	-14

Since the bulk of the chemistry in this project dealt with derivatization of compounds containing the furan heterocycle (furfuraldehyde, furan and 2-methylfuran), the subsequent reduction of substances derived from them was an ever present theme, a kind of background music, to the project. Typically the reduction step was the final sequence in the synthesis of a furanic solvent. In spite of this, it was decided to begin chemistry discussions with the important findings in furan hydrogenation chemistry because of its constant use and technical significance to the project. In addition, the furan reductions were anticipated to be capricious, which turned out to be the case but eventually conditions were developed that worked adequately for the most part as decribed below. Studies in hydrogenation, or reduction, of unsaturated furanic solvents began with the acetone adduct of furfuraldehyde, the furfurylidenone (**10**). This was mainly due to the large quantity available, ease of synthesis and the many previous reports of its successful hydrogenation to reduced derivatives. When one examines potential reduction reactions that could take place with this molecule (**10**) there are many. For example, there are three sites of unsaturation, the two double bonds in the furan heterocycle and the double bond of the enone. These two types of double bonds are of course different based on their chemical structure. Neither type would be expected to behave as a simple alkene since the double bonds in the ring are tied into a thermodynamically stable aromatic system and the ketone is conjugated with and influencing the alkene. But selective reduction to the tetrahydrofuranyl ketone (**17**) was the sought after, selective reduction. Another concern was that ketones can also react with hydrogen to generate alcohols. Likewise, the tetrahydrofuran ring of the desired product (**17**) can undergo further, and unwanted, reduction (e.g. ring cleavage) to alcohols and/or diols. Alcohols are typically polar molecules less likely to be soluble with non-polar soils, however that is not always the case as some cursory data as shown and will be discussed in a later section.



The simplest method to carry out hydrogenation is through heterogeneous catalysis, a process called catalytic hydrogenation commonly used in the chemical industry. Essentially, one dissolves the material to be reduced in a suitable solvent, adds a metal catalyst and exposes the mixture to an atmosphere of hydrogen gas, Figure 10.

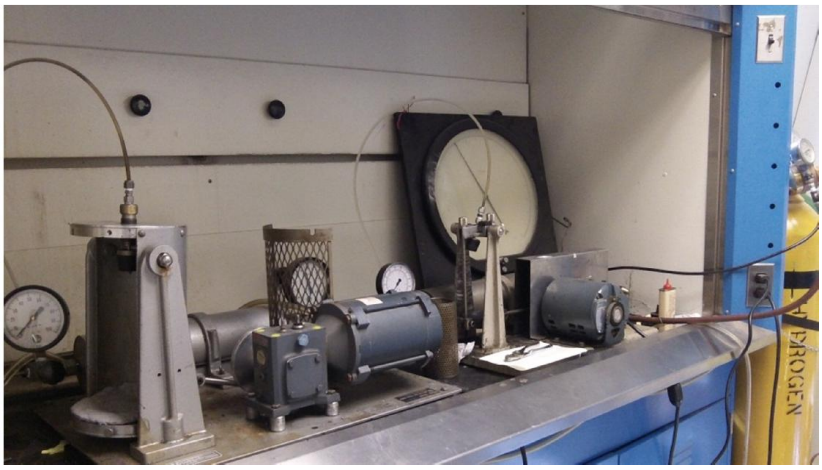
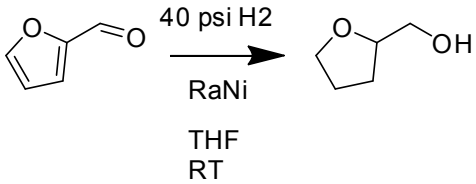


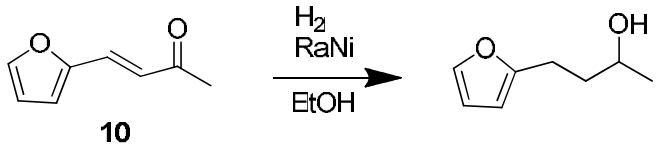
Figure 11 The Parr hydrogenation equipment of the Chemistry Department at China Lake

Some experiences with the reduction of furfural appeared to be useful. Reports of the reduction of furfural by Raney Nickel catalyst used elevated temperature and pressure to obtain tetrahydrofurfuryl alcohol. But it was found that this reduction would take place with only forty psi hydrogen pressure at room temperature. However, under these conditions, a twenty-five gram scale required about six days to reach completion. In any case, the method was useful since it could be carried out on simple, low-pressure hydrogenation equipment that was available.

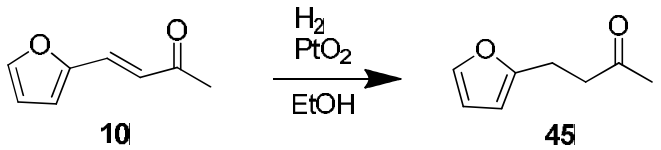


The Raney Nickel conditions [13] were used with furfurylideneacetone (**17**) and after three days the enone double bond had disappeared from the proton NMR. But even after such a long

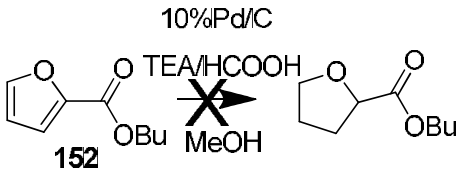
reaction period, the furan resonances were still present in the proton NMR. This indicated that reduction of the furan ring had not taken place, at least not completely. However, the more worrisome peak found in the spectrum was a sharp doublet at 1.2 ppm. This doublet had the characteristic appearance of an isopropyl group which could only become present if the ketone had been reduced to alcohol. Although ketone can be reduced by this catalyst, this result was a little surprising since the temperature of the reaction was not elevated.



Next, reduction with platinum oxide catalyst was attempted. In this case, the product obtained was the dihydro derivative (**45**) where hydrogenation only occurred at the double bond of the enone. The proton NMR spectra clearly showed the disappearance of the enone double bond, but the furan signals were still intact. Although this did not give the desired complete reduction, it represented selective reduction of the enone without disturbing the furan ring, a tool that could be useful at a later stage.

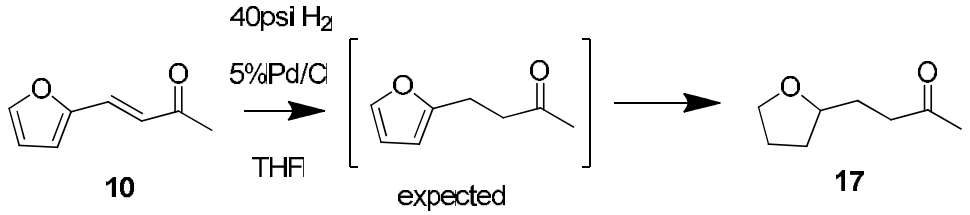


Catalytic transfer hydrogenation was attempted on a furanic ester (**152**) using triethylammonium formate in refluxing methanol with the strong catalyst 10wt% palladium on carbon. These conditions failed to reduce the furan ring of this compound and only the starting material was recovered.



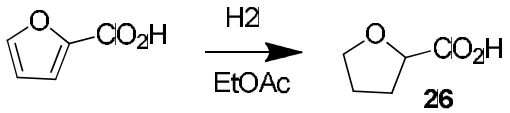
A significant break-through came during other experiments with palladium on carbon. This catalyst is available in a variety of loadings but one of its most inexpensive forms is 5% palladium on carbon. A reaction was set up on the Parr™ apparatus using the following reagents: ten grams furfurylideneacetone (**10**), 0.5 g 5% palladium on carbon and fifty milliliters tetrahydrofuran solvent. The starting hydrogen pressure was forty psi. It was a surprise to see the rate of hydrogen uptake was very fast, commencing immediately upon agitation, so much so that it was believed that there was a leak from improper setup. The reaction was even stopped and the glass vessel was changed to a different one and the mixture placed back on the Parr™. The hydrogen uptake continued as before until after one hour it had stabilized. It was anticipated

that such a weak catalyst might only be capable of reducing the alkene of enone much like the platinum oxide case. However, the product obtained from this reaction was not the expected dihydro derivative (**45**) but in fact was the hexahydro derivative, tetrahydrofuranyl ketone (**17**), where both the alkene and the furan ring became fully saturated. The proton NMR clearly showed the desired connectivity, there was no doublet that would indicated ketone reduction. This unexpected but welcome result showed that mild conditions (room temperature and low pressure) and a relatively inexpensive catalyst could reduce the furan ring system.



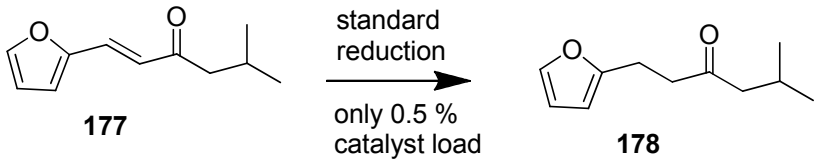
Since all of the proposed target compounds had similar structures, it was anticipated that they all might behave similarly. These conditions were employed throughout this work, referred to henceforth as the 'standard reduction conditions', where the reduction of alkene and/or furan rings was necessary. Though in certain instances the solvent was changed or the hydrogen pressure was made even lower (twenty psi). There were several occasions when reduction of a compound did not work well, or go to completion, and this was likely due to additional factors of the reduction that were not fully understood at that time. And so in these final stages of the project during the writing of this report, there wasn't time enough to go back and correct those issues.

It was also discovered that solvent can play a role in the reduction chemistry, which added another level of complexity. When using tetrahydrofuran as solvent in the reduction of 2-furoic acid by the standard conditions, the reduction to 2-tetrahydrofuroic acid (**26**) was incomplete even after twenty-four hours at forty psi. However, changing the solvent to ethyl acetate and this reduction went to completion after eighteen hours with only twenty psi.



In general, noble metals catalysts are expensive but 5% palladium on carbon[14] is probably one of the cheapest. So during the project, care was taken to use as small amount of this material as possible to maximize effect, although there was a one hundred gram bottle available. When running small reductions (~ten grams) it wasn't considered too extravagant to use one gram of catalyst for these reactions, which represented a ten weight% catalyst loading. It was during scale-up of certain furanic solvents that some new details about the reduction were learned. For example, when a two hundred gram sample of furfurylidenone (**177**) was reduced by the

'standard reduction conditions' with only 1.2 grams of catalyst, the product was not the desired tetrahydrofuranyl ketone (**82**) but was only the dihydro compound (**178**).



It turned out that being frugal with the expensive catalyst would lead to inconsistent results. In this large reaction there was only 0.5 weight% catalyst loading which was the root of the problem. Trying to minimize catalyst will hinder reduction rate, and it was shown that large reactions still require from at least five weight% to ten weight% catalyst loading in order to operate consistently. Thus, a two hundred gram scale reduction, really required at least ten to twenty grams of catalyst, which was cause for some hesitation with many reductions to be run and dwindling catalyst. It should be mentioned that the 'spent' catalyst was recovered and collected since it could possibly be reused. The catalyst's continued activity was confirmed but it was noted that, in otherwise identical reduction reactions, the one employing fresh catalyst absorbed hydrogen faster than that employing 'spent' catalyst. The failed large-scale reduction inadvertently demonstrated that selective reduction of the alkene of a furanic alkene can be accomplished under appropriate conditions, whose usefulness will be described later. It also confirmed the hypothesis that the alkene is the first to undergo reduction and that the furan is more difficult.

An alternative reduction apparatus was also assembled which proved to be useful, Figure 11. A specialized pressure bottle with a polytetrafluoroethylene screw-top fitting for tubing was purchased from Ace Glass.[15] This vessel was adapted to a hydrogen gas cylinder by appropriate valves. These bottles are rated for sixty psi and can also be heated (80 °C maximum). Although the above low-temperature reduction conditions were identified, such that heating reductions was unnecessary, the additional apparatus was useful on several occasions when the Parr™ equipment was in use by department colleagues. However, there were two major differences to this apparatus versus the Parr™: 1) setup could only achieve a maximum hydrogen pressure of twenty psi based on the gas regulator used, and 2) mixing was done with a magnetic stirbar and stir plate. But these changes did not appear to be an issue since several successful reductions of furanic solvents were performed using the apparatus. The additional benefit of the Ace Glass system was than it made very little noise in comparison to the Parr™ equipment.

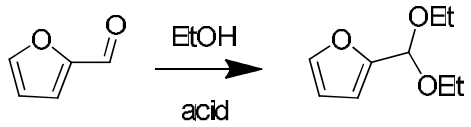
Figure 12 Ace Glass low pressure hydrogenation set up with magnetic stirring

Synthesis of Furanic Acetal Solvents

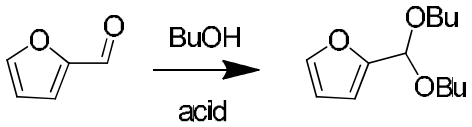
The NMR spectra of reactions and/or products discussed below can be found in Appendix B.

The aldehyde of furfural can undergo reaction with alcohols to form the functional group known as acetals. Of course alcohols are widely available from natural sources and so attempts were made to prepare acetals from furfural. These reactions typically require an acid to catalyze the reaction. But it was found that the when acids were used in a reaction with furfural, the reaction mixtures invariably became dark. The dark color signified that unwanted reaction was taking place with the furan ring, most likely polymerization.

In one reaction, a large excess of ethanol was treated with acetyl chloride to form hydrogen chloride and ethyl acetate *in situ*. To this mixture was added furfural and the mixture was heated to ~ 50 °C. After a short time, the reaction became brown colored and analysis by NMR showed the characteristic proton signal of acetal at ~ 5.5 ppm. However, the furfural never completely reacted and the mixture simply became darker and darker with continued heating. And so not to waste time trying to separate a small quantity of product that formed, the reaction was abandoned.

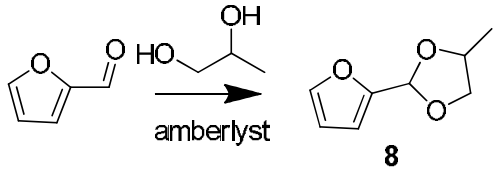


Several attempts to make the dibutyl acetal of furfural from 1-butanol were made. In this case, benzene was used as a solvent to try to minimize unwanted polymerization. Also, this solvent could help remove the by-product water through azeotropic distillation. In this reaction, furfural, 1-butanol and p-toluenesulfonic acid were heated to reflux with a Dean-Stark trap. After one hour, there was some water collected in the trap which showed that perhaps the desired reaction had taken place. Checking the reaction by NMR showed that the reaction appeared to contain a 1:1 mixture of the dibutyl acetal and furfural. So, another portion of butanol was added and the reaction was continued. After two more hours heating, NMR then showed that the mixture had become a 1:2 mixture of dibutyl acetal to furfural. This meant that the acetal had broken down after more alcohol was added. This reaction was also abandoned owing to the expected difficulties in trying to separate the small amount of product formed in the reaction.

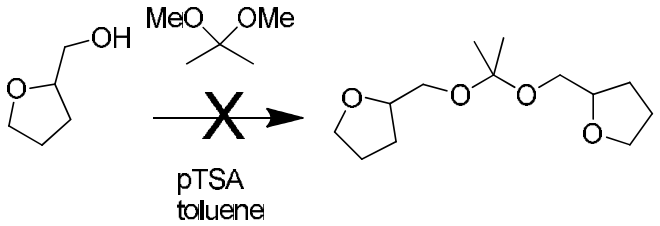


Better luck was had when using a diol in this reaction, which yields a cyclic acetal or 1,3-dioxolane. Using benzene as solvent and Amberlyst 15 resin (a solid, sulfonic acid catalyst), the 1,2-propanediol acetal of furfural (**8**) could be made. In this reaction, the furfural was almost

completely reacted. Careful distillation under reduced pressure gave the product in modest yield that contained just a trace of furfural. The proton NMR of this product is a bit complicated owing to the cis and trans diastereomers about the dioxolane ring.



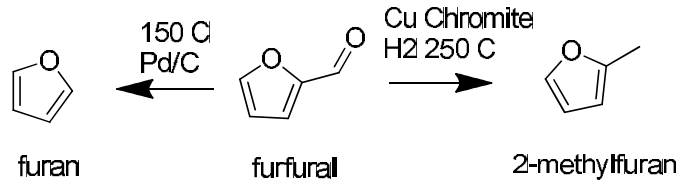
An attempt was made to make the ketal of acetone from tetrahydrofurfuryl alcohol using similar conditions. However, only starting material was recovered from this reaction.



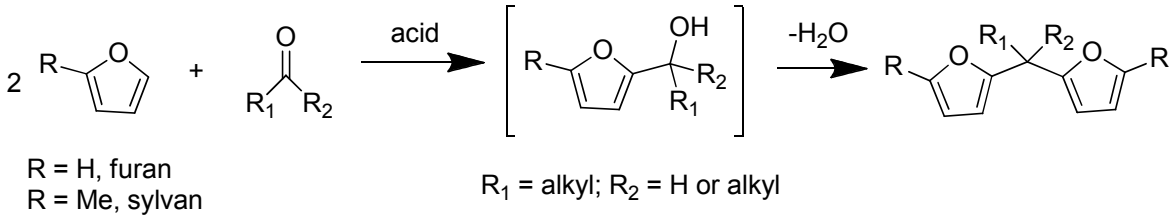
Synthesis of Geminal Difuranic Alkane Solvents

The NMR spectra of reactions and/or products discussed below can be found in Appendix D.

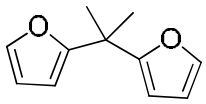
Two other closely related products from furfuraldehyde were employed for this portion of chemical transformation. Furfuraldehyde is converted into 2-methylfuran, or sylvan, on industrial scale using a similar process to that used in the copper chromite reduction of furfural to furfuryl alcohol, only requiring a higher temperature (250 °C). Another industrial scale product from furfuraldehyde is furan, made by the catalytic decarbonylation of the aldehyde. Both of these products are widely available and inexpensive[16] and, since they were so closely related, were included in the present study as platform chemicals.



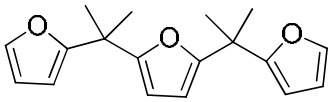
Both furan and 2-methylfuran have unsubstituted 2-position, or *alpha*-carbons, of the aromatic rings and so are ripe for reaction with electrophilic species. Carbonyl compounds can serve as excellent electrophiles as shown in another section dealing with the condensation of furfuraldehyde with ketones. Here those same simple aliphatic ketones as well as aliphatic aldehydes can be used in an alternate condensation manifold. The products obtained from these condensations are geminally[17] substituted difuranic species after elimination of water. The abundance of structurally diverse ketones and aldehydes might lead to useful products.



Reaction of furan with acetone in ethanol with concentrated hydrochloric acid as catalyst was one method for condensation. These conditions gave a mixture of 2:1 dimer (**30dimer**) and trimer (**30trimer**) which could be separated and purified by distillation. Evidently, when furan is exposed to electrophiles there is the possibility of formation of oligomeric species since the furan ring has two reactive and available *alpha*-carbon positions.

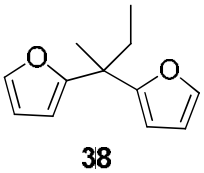


30dimer



30trimer

In another method found in a recent patent[18], two molar equivalents of the furan and one molar equivalent of the carbonyl compound were stirred in seven molar aqueous hydrochloric acid. This method gave a better yield (59%) of the difuran (**30dimer**) and very little of the trimer. Also 2-Butanone was condensed with furan in ethanol with hydrochloric acid which gave difuran (**38**) with very little trimer in this instance. Condensation of furan with acetaldehyde by this method was attempted. The difuran (**43**) was made but in low yield. The low yield likely resulted from the fact that the acetaldehyde sample used was contaminated with significant trioxane. Even while stored at -30 °C, the acetaldehyde will slowly undergo trimerization to form this impurity. Apparently, even while the condensation reaction conditions had water and acid present, the trioxane did not fully hydrolyze. Furan could also be condensed with propionaldehyde and gave difuran (**57**) in modest unoptimized yield. These products were all liquids with pleasant odor reminiscent of flowers.[19]



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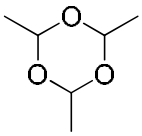
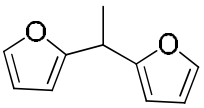


acetaldehyde trimer



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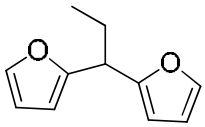
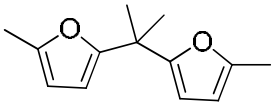


57

These conditions failed, however, when attempting to condense carbonyls with 2-methylfuran. It was later learned that 2-methylfuran undergoes facile hydrolysis in the presence of hydrochloric acid. However, 2-methylfuran gave the desired reaction when the acid was replaced with *p*-toluenesulfonic acid. Heating a mixture of 2-methylfuran, acetone and *p*-toluenesulfonic acid hydrate at 65 °C for eighteen hours gave a 73% yield of the difuran (**145**). An interesting self condensation reaction takes place with 2-methylfuran when heated in a mixture of sulfuric acid and water. This reaction gave a modest yield of the difuranyl ketone (**155**) which was a thick oil. In this reaction, a portion of the 2-methylfuran apparently undergoes hydrolysis to levulinaldehyde ($CH_3COCH_2CH_2CHO$) which then condenses with the remaining 2-methylfuran.



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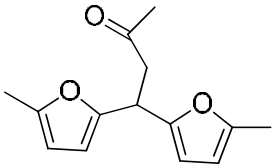
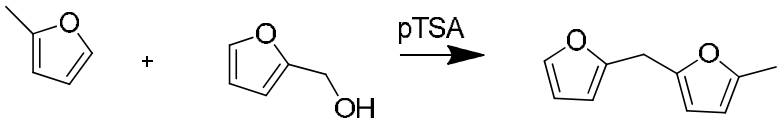


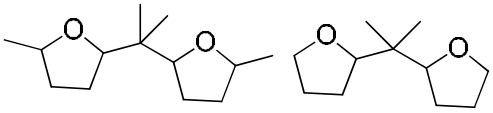
155

Furfuryl alcohol, which has a 'benzylic' alcohol, was anticipated to participate in condensation reactions such as those with 2-methylfuran. A mixture of these two reagents and *para*-toluenesulfonic acid was stirred at room temperature. Although the yield was low, a substance was distilled from this reaction which had NMR that was consistent with the proposed structure.



183

The reduction of the gem difuranic alkanes by the standard conditions (hydrogen and 5% Palladium on carbon catalyst) went without difficulty to give the corresponding octahydro derivatives such as **83B** and **146**. These latter compounds were mixtures of stereoisomers and no attempt was made at their separation. These substances were both pleasant smelling, colorless, mobile liquids.

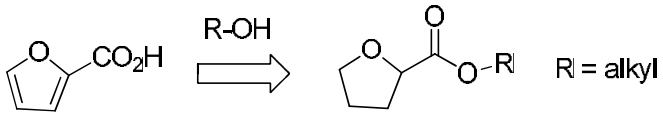


146 **83B**

Synthesis of Furanic Ester Solvents

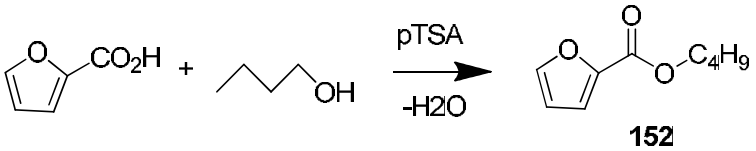
The NMR spectra of reactions and/or products discussed below can be found in Appendix C.

Aldehydes are easily oxidized to carboxylic acids and furfural is no exception. So derivatives of cheap and widely available 2-furoic acid were considered. Of course, carboxylic acids themselves are not interesting for this project, as they are well known to react with metals, but their liquid derivatives might have usefulness. Carboxylic acid esters, or simply esters, were believed to be the best candidates as they are easily made from the acid and an alcohol by many methods. The availability of a wide range of structurally diverse alcohols made it appear likely that esters with degreasing capabilities could be identified.

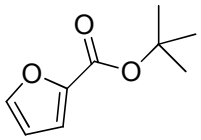


General Method to Make Furanic Esters

The typical conditions for esterification of an acid such as refluxing with alcohol in toluene with *p*-toluenesulfonic acid under Dean-Stark conditions did work well with 2-furoic acid. These reactions typically had a dark color which seemed to increase directly with reaction time. This was the same phenomenon observed during the reactions to create acetals of furfural. The dark impurities of this method were likely due to the reactive 5-position of this acid and/or product undergoing unwanted chemistry (e.g. polymerization). Nevertheless, a sample of butyl 2-furoate (**152**) was made in this manner and isolated in low yield.



Better results in ester synthesis were had using 2-furoyl chloride which was prepared in good yield by reaction of 2-furoic acid with thionyl chloride. Reaction of 2-furoyl chloride and 1-butanol in tetrahydrofuran and triethylamine as base gave an excellent yield of butyl 2-furoate (**152**). The *tert*-butyl furoate (**6**) was made in the same manner from 2-furoyl chloride and *tert*-butanol, but in that case potassium *tert*-butoxide served as base/reactant. Both of these products could be distilled at reduced pressure to pure materials. Also, esterification of glycerol with 2-furyl chloride gave the triglyceride tri(2-furoyl)glycerol (**7**) unfortunately this unreported compound was solid at room temperature.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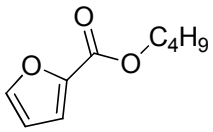
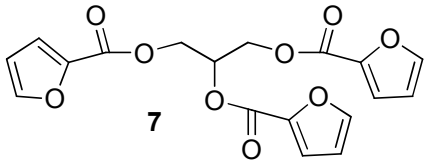
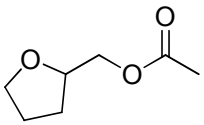

152


7

Further esters were made using readily available tetrahydrofurfuryl alcohol, made by hydrogenation of furfural. In these esters, the furan ring has already been reduced which helped to eliminate the sometimes tricky reduction chemistry. The first preparation of the acetate ester (**35**) was made by reaction of the alcohol with acetic anhydride and pyridine base. The reaction was worked up with water since the excess base and salts had to be removed. Only a low yield of product was obtained although the reaction appeared to be very clean by thin-layer chromatography. Evidently some of the product was lost to the water layer. An improved procedure was found in simply heating the alcohol and 1.5 equivalents of acetic anhydride with a little p-toluenesulfonic acid as catalyst. Afterwards, the product could be distilled at reduced pressure directly from the reaction mixture in 75% yield. In the same way, the butyrate ester (**37**) was made using butyric anhydride. The laurate ester (**159**) was made in 93% yield by reaction of tetrahydrofurfuryl alcohol and lauroyl chloride in tetrahydrofuran solvent with triethylamine base.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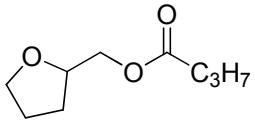
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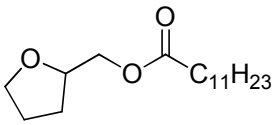
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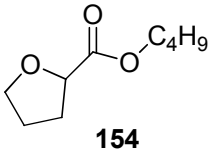
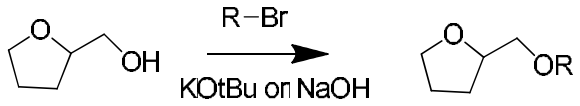

154

During early stages of the research project, there was trouble in reduction of the above butyl ester (**152**) to its tetrahydroderivative. Eventually, 2-furoic acid was reduced to 2-tetrahydrofuroic acid (**153**) in 88% yield by the standard conditions (hydogen and 5% palladium on carbon) with ethyl acetate as solvent. The butyl ester of 2-tetrahydrofuroic acid (**154**) was made by typical azeotropic removal of water by distillation of the toluene solution of the acid and alcohol. In this case, since the furan ring had already been reduced, the color of the reaction remained clear and the ester was obtained in high yield.

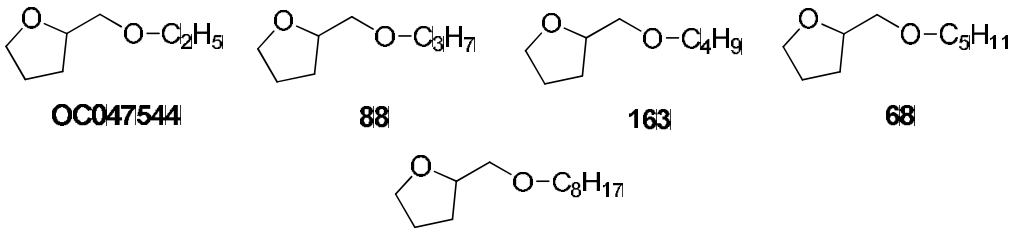
Synthesis of Furanic Ether Solvents

The NMR spectra of reactions and/or products discussed below can be found in Appendix E.

The compounds in this category were primarily derivatives of tetrahydrofurfuryl alcohol. The latter already has the furan ring reduced and so starting with this substance the later hydrogenation reactions could be avoided. These compounds were easily prepared by reacting the tetrahydrofurfuryl alcohol with an alkyl halide and a base.



In one method, the tetrahydrofurfuryl alcohol was deprotonated in tetrahydrofuran using potassium *tert*-butoxide. Afterwards, 1-bromopentane was added and the mixture was refluxed to complete the reaction. In this case, the by-product *tert*-butanol is too sterically hindered to form any ether product and so did not require removal which made for easy reactions. The pentyl ether (**68**) was obtained in high yield and easily purified by distillation. Similar reaction of tetrahydrofurfuryl alcohol with 1-bromooctane gave the octyl ether (**84**) in 60% yield. In this case, the final distillation was a little more complicated in that the excess 1-bromooctane distilled close to the ether product. In similar fashion, the propyl and butyl ethers (**88** and **163**) were made in yields of 55% and 58%, respectively. The ethyl ether (**OC047544**) was a product commercially available from Oakwood Chemicals and included in the study.[20] These ether compounds with short chains all had a pleasant, floral odor. Since the potential odor of a degreaser could be an issue later on, the long chain octyl ether was made. This compound had very little odor, an indication of a higher vapor pressure.

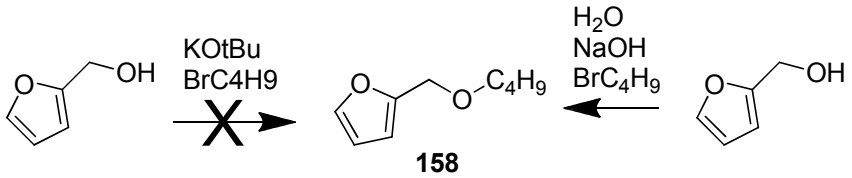


OC047544 **88** **163** **68**

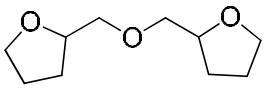
84

The butyl ether of furfuryl alcohol (**158**) was also made to have an example where the furan ring was intact. In this case, when using the potassium *tert*-butoxide method the thin-layer chromatography analysis of the reaction showed two new spots present in the reaction mixture, when there should have been only one. Both spots were less polar and different from the furfuryl

alcohol starting material. Instead of spending time in attempting to explain this observation, heating a mixture of furfuryl alcohol, sodium hydroxide and 1-bromobutane without any solvent gave a good yield of the desired product. A cursory attempt at reducing this compound by the standard reduction conditions failed. This result may be on account of using the alternate reduction apparatus (magnetic stirring bottle) which does not give efficient mixing. Attempts at reduction using the Parr apparatus were not carried out since the reduced product (**163**) had already been made from tetrahydrofurfuryl alcohol.



Also included in this group of ethers is di(tetrahydrofurfurylmethyl)ether (**1932-89**) which was a target structure in the original proposal to this project. This compound was synthesized here at China Lake by a colleague John Stenger-Smith, Ph.D who kindly provided a small quantity for this study. The compound was prepared by nucleophilic substitution reaction of tetrahydrofurfuryl alcohol upon tetrahydrofurfuryl mesylate in the presence of base.

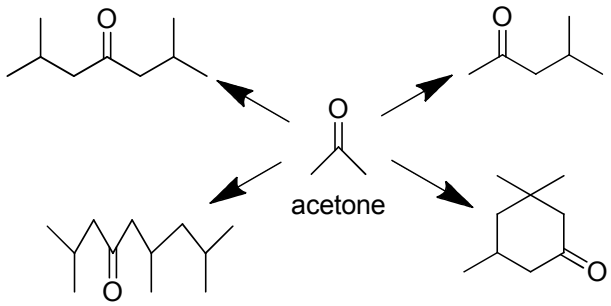


1932-89

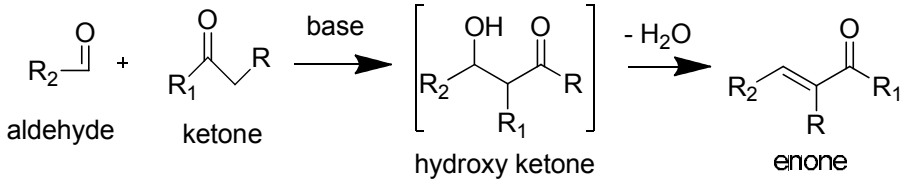
Synthesis of Furanic Ketone Solvents

The NMR spectra of reactions and/or products discussed below can be found in Appendix F.

Simple ketones are manufactured on very large scale[21] and so are inexpensive and commonplace, often employed as solvents in the chemical industry. The ketones can be reacted among themselves to make value added solvents with different solubilities and different applications. For example, Dow® has commercialized several oligomers of acetone including 4-methyl-2-pentanone (MIBK), isophorone, 4,6-dimethyl-2-heptanone, 2,6-dimethyl-4-heptanone (DIBK) and 2,6,8-trimethyl-4-nonanone (Ecosoft™ solvent IK).

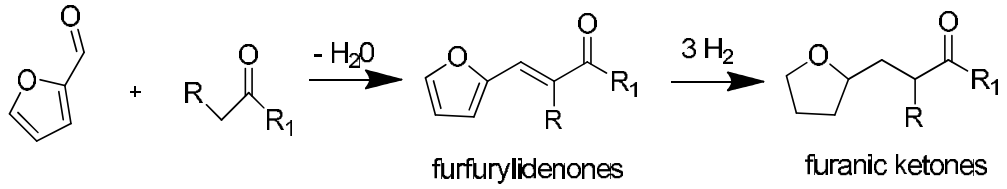


Ketones and aldehydes are ideal partners in the ubiquitous carbon to carbon bond forming reaction known as the Claisen-Schmidt reaction, named for its discoverers.[22] In this form of condensation or aldol reaction, the ketone with an *alpha*-methylene attacks the more electrophilic aldehyde group to give an intermediate hydroxyketone. The reaction can be catalyzed by acid or base, the latter most often used. The hydroxy ketones intermediates can be isolated but, since alcohols tend to increase polarity anyway, under appropriate reaction conditions can spontaneously eliminate water to give a thermodynamically favored *alpha-beta* unsaturated ketone, or enone.



The net result is an addition product between the two partners and loss of water. The enones themselves were not of interest here, mainly due to the likelihood they would be solid at room temperature. Subsequently these could be reacted with hydrogen, or reduced, to rid away the unsaturation and make stable fluids. By running a series of simple ketone solvents through this methodology with furfuraldehyde as a platform, a family of structures that will be referred to as furanic ketones could be prepared. Since this concept is not necessarily new, many of these products have been made previously but without application to cleaning processes. Perhaps,

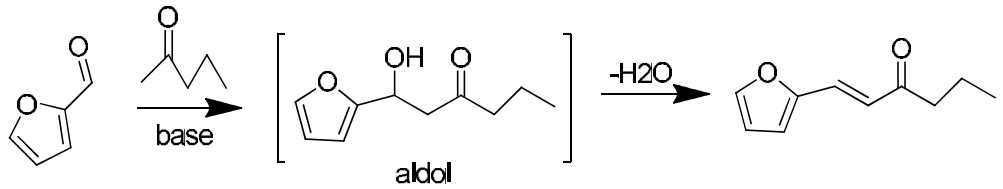
among this group could be found some that would have the sufficient non-polar qualities necessary for degreasing.



The chemical structures and numerical codes discussed in the following section are collected below in the Table 2. Condensation reaction of one mole of furfural with acetone in water with 33% sodium hydroxide base was carried out according to a literature procedure. This gave the corresponding furfurylidenone (**10**) in 66% yield after distillation. Trituration of the still pot residue with heptane gave a small quantity of the dimeric product (**33**). Both of these substances were solid at room temperature. Reduction of these products by the standard conditions gave the corresponding hexahydro- (**17**) and dodecahydro-derivatives (**151**) in modest yield. The furfurylidenone (**10**) could be selectively reduced with magnesium in methanol to give the dihydro product (**45**), however the yield was only ~ 50%.

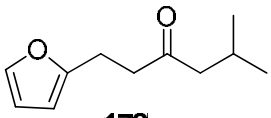
Reaction of furfural with three equivalents of 2-butanone in water with sodium hydroxide base gave the furfurylidenone (**23**) in 96% yield. In this case, reaction had ocurred on both side of the ketone resulting in a 1:1 mixture of geometric isomers. No attempt was made to separate them, however. They were reduced by the standard reduction conditions to the tetrahydrofuryl ketone mixture (**79**).

Reaction of furfural with 2-pentanone was carried out in the manner described above. Here, the observation of a second product along with furfurylidenone (**53**) was noted in the thin-layer chromatography of the reaction mixture. The second spot was very polar and was eventually understood to be the aldol reaction intermediate. These aldol by-product seemded to become more prevalent as the molecular weigh of the ketone increased (*vide infra*). Even when the reaction had not gone to completion, the aldol intermediates were easily removed during the purification of the furfurylidenone by distillation.



The condensation of furfural with the other methyl ketones (pinacolone, 3-methyl-2-butanone, 4-methyl-2-pentanone, 2-hexanone and 2-octanone) all behaved in a manner similar to the pentanone reaction. All of these furfurylidenones were distillable liquids, except for the one made from 2-hexanone (**60**) which was solid at room temperature. All of these compound were

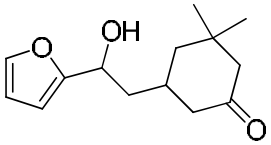
reduced to the tetrahydrofuranyl ketones (**80**, **82**, **149**, **77B**, **143**) by the standard reduction conditions. In a large scale preparation of tetrahydrofuranyl ketone (**82**), the inadvertent synthesis of the dihydro compound (**178**) was made on account of using only 0.5wt% catalyst loading in that reduction (require at least ten times more catalyst). This demonstated that the alkene is first to undergo reduction and that selectivity in the reduction could be accomplished if required later on.



178

The condensation with furfural could also be effected with internal ketones such as 5-nonanone but using sodium methoxide in methanol was best. In this way, a 50% yield of the furfurylidenone (**73B**) was obtained after distillation. The latter was reduced by the standard procedure to give the tetrahydrofuranyl ketone (**91**) in 94% yield. The NMR spectra of this compound was complex owing to the existence of diastereoisomers.

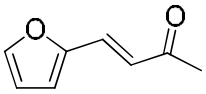
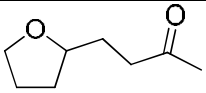
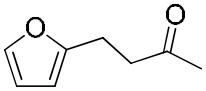
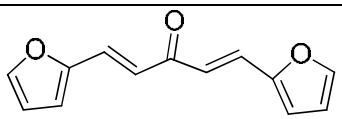
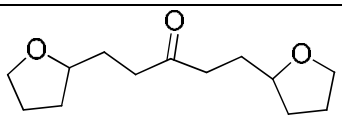
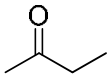
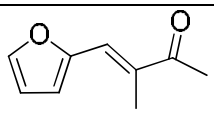
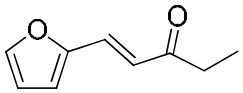
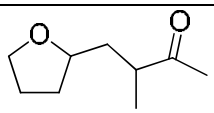
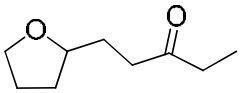
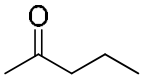
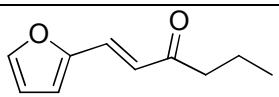
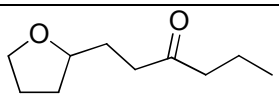
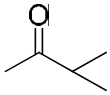
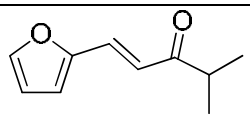
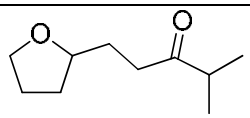
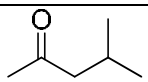
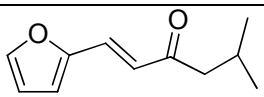
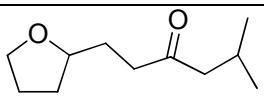
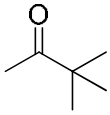
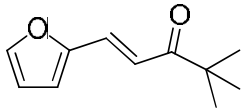
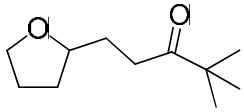
Condensation with isophorone gave interesting results. Much like in the case with 2-pentanone, a second more polar component was observed by thin-layer chromatographic analysis. To determine exactly what these two products of the reaction were, the product was carefully separated by chromatography on silica gel. The upper spot, the less polar component, was indeed the desired furfurylidenone (**44**). The more polar component turned out to be the aldol intermediate with a characteristic triplet at 4.9 ppm which was the C<u>H</u>OH signal split by the adjacent methylene group. In a second preparation, the product mixture was distilled at reduced pressure to try to separate the furfurylidenone (**44**) quickly. The latter was obtained in an early fraction, but continued distillation gave the aldol product in pure form. This was rather remarkable since the distillation temperature at which the aldol product came over was from 150–180 °C, a temperature at which one would expect immediate dehydration to ocurr. Later it was discovered that when this condensation was carried out in ethanol solvent and a small amount of 45% sodium hydroxide as base, the aldol by-product was not observed. In any case, reduction of the furfurylidenone (**44**) by the standard conditions gave the tetrahydrofuranyl ketone (**49**) as a thick oil. This was the only derivative that contained a ring stucture which may be the reason for its greater viscosity.

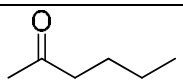
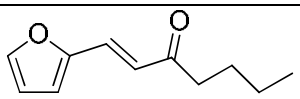
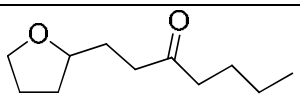
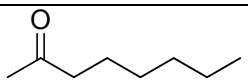
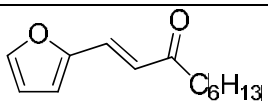
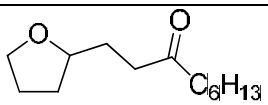
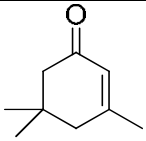
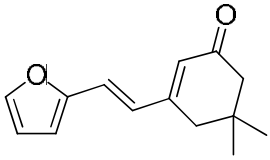
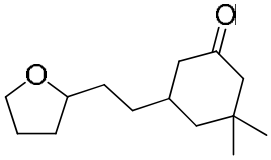
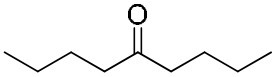
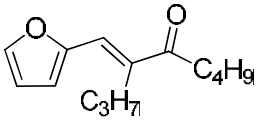
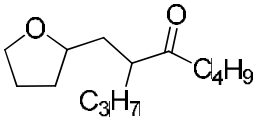


isophorone aldol product

These tetrahydrofuranyl ketones all had an odor that was somewhat flower like and that seemed to decrease in strength with molecular weight.

Table 2 Structure of furanic ketones and intermediate furfurylidenones

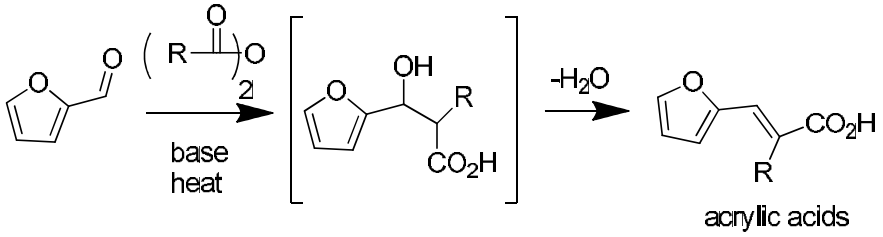
Ketone	Structure		
acetone		 **10**	 **17**
			 **45**
		 **33**	 **151**
Methyl ethyl ketone		  1:1 mixture **23**	  1:1 mixture **79**
2-pentanone		 **53**	 **147**
Methyl isobutyl ketone		 **52B**	 **80**
4-methyl-2-pentanone		 **55**	 **82**
Methyl *t*-butyl ketone (pinacalone)		 **51**	 **149**

2-hexanone		 **60**	 **143**
2-octanone		 **77A**	 **77B**
isophorone		 **44**	 **49**
5-nonanone		 **73B**	 **91**

Synthesis of Alkyl- and Alkenylfuran Solvents and the Behaviour of Furfuraldehyde in the Perkin Condensation

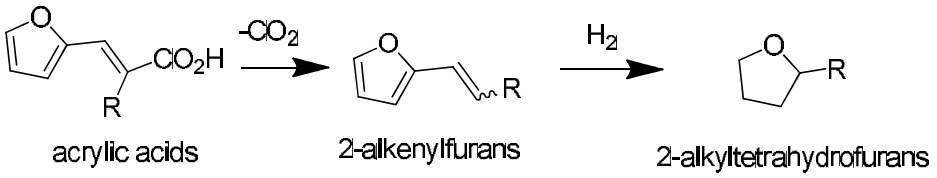
The NMR spectra of reactions and/or products discussed below can be found in Appendix G.

Another method for transformation of furfuraldehyde was examined, a condensation reaction known as the Perkin reaction. In this reaction, furfuraldehyde is reacted with a carboxylic acid anhydride in the presence of a base, usually the alkali carboxylate salt, to produce 2,3-disubstituted acrylic acids.



Anhydrides are an activated form of carbonyl and therefore its methylene group adjacent (*alpha*-CH_2) can serve as nucleophile and attack the aldehyde. There is an intermediate hydroxy acid which under normal conditions is not isolated, since it is unstable to the themal conditions, but eliminates water to give the acrylic acid product. This reaction was first reported in 1868 and since then has become an common synthetic methodology,[23] although most often used in the derivatization of benzaldehydes (C_6H_5CHO).

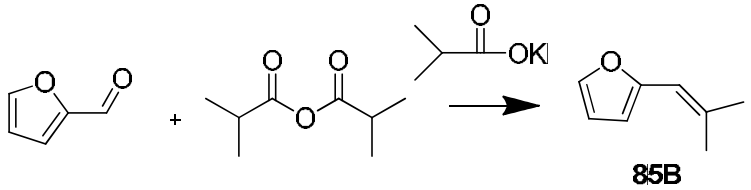
The acrylic acids products made by Perkin reaction of furfuraldehyde were themselves not interesting for the purposes of the present project, since the acids are typically solids and, like most carboxylic acids, would likely cause corrosion issues when exposed to metal surfaces, particularly those composed of iron. However, such acrylic acids can be readily decarboxylated by simple methods leading to 2-alkenylfurans. The latter might be useful products for cleaning or could, in turn, be hydrogenated to 2-alkyltetrahydrofurans expected to have excellent solubility for non-polar soils. For example, the simplest member of this series, 2-methyltetrahydrofuran, is an excellent solvent that is gaining widespread interest in the chemical industry as a 'green' replacement for tetrahydrofuran.[24,25] Although, 2-methyltetrahydrofuran has wonderful solubility characteristics for a variety of soils, its low flash point (-11 °C) makes it too flammable for typical cold cleaning applications.



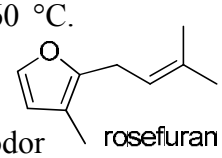
A variety of derivatives in this category could be made corresponding to all the saturated linear carboxylic acids available, many from oilseed crops. For example, those acrylic acids made from short chain fatty acids (C1–C5) would be expected to give 2-alkyltetrahydrofurans with low

boiling points and high flash points. Compounds with high values for these important physical properties could simply be tailored by using the appropriate length fatty acids.

In a review of the chemical literature, there were two instances of Perkin reaction upon furfuraldehyde that were interesting with regard to the project goals. With either isobutyric or isovaleric acid anhydrides, the expected acrylic acid derivatives were not obtained but instead the decarboxylated 2-alkenylfurans were isolated, in relatively good yield.[26] So at least for these two cases, the Perkin condensation and the decarboxylation steps occurred simultaneously.

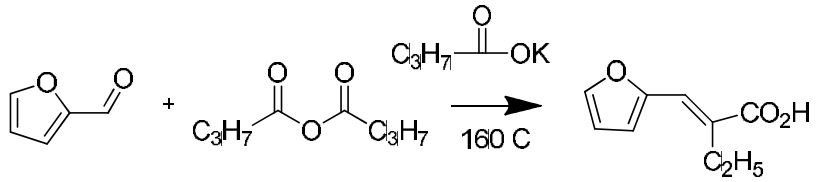


An attempt was made to repeat the synthesis of 2-isobutenylfuran (**85B**). The base, potassium isobutyrate (**21B**), had to be prepared since many of the alkaline carboxylates greater than propionate are not commercially available. Simply reacting a mixture of isobutyric acid with a molar equivalent of potassium *tert*-butoxide in tetrahydrofuran, neutralized the acid. Evaporation of the solvent and by-product *tert*-butanol, left the potassium isobutyrate as a white powder in 95% yield. Briefly, a mixture of furfuraldehyde, isobutyric anhydride and potassium isobutyrate (**21B**) in a 1:1:1 molar ratio was heated in an oil bath set at 160 °C. Even when the internal temperature was only ~ 80 °C, there was evidence of gas generation. This temperature is quite low as a typical temperature for conducting the Perkin reaction is 160 °C. After purification by atmospheric pressure distillation, the product 2-isobutenylfuran (**85B**) was a colorless, low boiling liquid in 81% yield. The isobutenylfuran (**85B**) had a pungent but not unpleasant odor. This odor characteristic may be explained from its similarities to the natural product rosefuran, a component found in the extract of roses. However, 2-isobutenylfuran (**85B**) quickly became yellow in color when stored at room temperature, a phenomenon that could be slowed, but not completely prevented, by storage in the cold. The color development might be caused by oligomerization as shown in the articles of Gandini concerning cationic polymerization of 2-alkenylfurans.[27] This possibility should be studied further as it could be another avenue to create liquid products useful for cleaning.



The reason why these two particular acrylic acids from isobutyric and isovaleric undergo spontaneous decarboxylation under typical Perkin reaction conditions is not understood. Several other groups have confirmed these results but no further light has been shed on the mechanism. It may be that decarboxylation is facilitated by the geminal dimethyl group which facilitates creation of a stable trisubstituted alkene in conjugation with the furan heterocycle. However such a hypothesis can not also explain the isovaleric acid case.

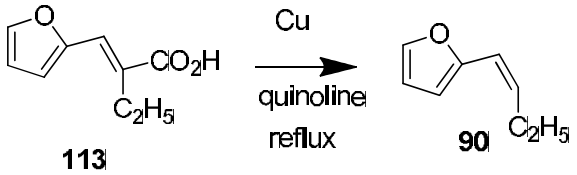
Next, the Perkin reaction with butyric anhydride was carried out in much the same way as the above case (160 °C). This reaction has been reported several times previously.[28] The potassium butyrate (**101A**) salt was prepared analogously to that described above. As with all chemical reactions, organic or otherwise, it is important to have a method with which progress can be determined. Two different methods were used to analyze this reaction and the many others that will be described below. One method is simply taking a drop of the molten reaction mixture and dissolving in an organic solvent for thin layer chromatography (TLC). The other method was to take the reaction aliquot and dissolve it in deuteriochloroform and perform nuclear magnetic resonance spectroscopy. In any case, watching for the disappearance of the aldehyde (singlet ~10 ppm) of furfuraldehyde was an adequate indicator for reaction progress. The TLC method is complicated by the fact that the excess carboxylic acid/anhydride would co-elute with the acrylic acid. The NMR method was far easier to analyze as the resonances of interest in the aromatic region are not complicated (e.g. overlapping) by any aliphatic peaks associated with the carboxylic acid/anhydride. During TLC analysis there was always a small quantity of a fast moving, non-polar substance moving with the solvent front which at the time was not given further thought (*vide infra*). Anyway, the 2-ethyl-3-(2-furanyl)acrylic acid (**113**) could be purified easily owing to the fact that, in this case, the residual butyric acid is soluble in hexanes yet the acrylic acid (**113**) will crystallize form this solvent. Otherwise, this could lead to a two solid acids that would be harder to separate, which will be discussed later.



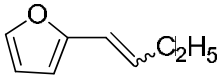
113

Attempts were made to decarboxylate the 2-ethyl-3-(2-furanyl)acrylic acid (**113**) using a standard method (refluxing in quinoline (bp 237 °C) with copper shot). It was found that there must be an adequate quantity of copper to achieve fast, efficient decarboxylation. If sufficient copper was present at reaction start, then decarboxylation was typically complete in less than one hour with nearly quantitative yield. The product was shown to be cis 1-(2-furanyl)butene (**90**) because the alkene proton signals were coupled with an 11.8 Hertz coupling constant, a value consistent with cis alkenes. Even though the reaction temperature was very high, the duration of the reaction was short and the solvent was basic which apparently minimized isomerization of the double bond. These results proved then that the starting acrylic acid (**113**) had trans configuration (as drawn), the furan and ethyl groups occupying the same side of the alkene. In other reactions that did not have enough copper, the reaction was heated much longer and eventually trans alkene began to grow in quantity. The cis 1-(2-furanyl)butene (**90**) could be separated from the quinoline by fractional distillation and was also a colorless oil but soon developed color as in the case 1-(2-furanyl)isobutylene (**85B**). So this result pointed to the possibility that any such 2-alkyl-3-(2-furanyl)acrylic acid would react in similar fashion to give

the decarboxylated alkenylfuran products. It is unclear why nearly an equivalent of copper was required for efficient decarboxylation. The reaction is of course biphasic and perhaps the active copper surface became coated in a short time by organic material. The copper was filtered and recovered from these decarboxylation reactions, however, there was no obvious change in its outward appearance.



The Perkin reaction with butyric anhydride was repeated several times to collect enough acrylic acid (**113**) for subsequent decarboxylation work. Each time there was always an unknown, non-polar product by thin-layer chromatography that had been ignored. And so in one run the reaction mixture was extracted with hexanes in an attempt to isolate the unknown material. The hexanes extract was carefully fractionally distilled at atmospheric pressure which eventually gave the unknown material as a liquid. NMR analysis of the unknown substance showed that it was in fact the decarboxylated product, 1-(2-furanyl)butene (**101B**). So evidently the furanacrylic acids will undergo some decarboxylation under these conditions. The product in this case was a mixture of both the cis and trans diastereomers which makes sense since hot and acidic conditions promote isomerization of cis alkenes. In the previous reported syntheses (*ibid*) of this 2-ethyl-3-(2-furanyl)acrylic acid (**113**), no mention was made of such a by-product likely because those worker were not looking for such. The quantity of the decarboxylated product (**101B**) was low however. But this result suggested that, considering the examples above described, decarboxylation to and isolation of 1-(2-furanyl)alkenes directly from the Perkin reaction could be made to operate as a general process.

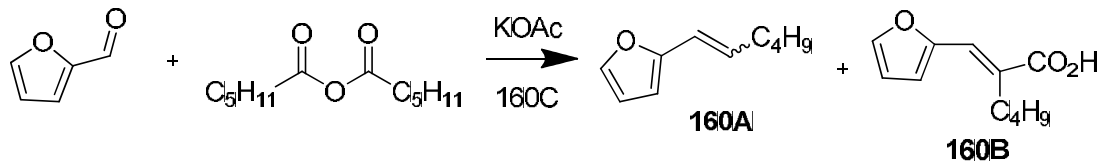


101B

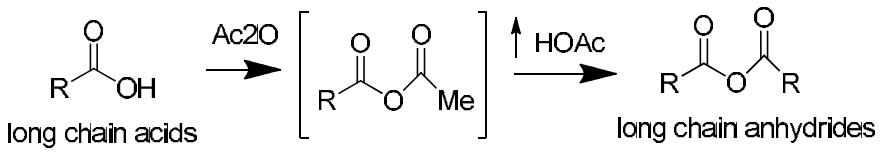
A modest scale-up of this Perkin reaction of furfuraldehyde (48 grams, 1/2 mole), butyric anhydride (1.5 molar equivalents) and potassium butyrate (1 equiv) was carried out. The reaction was run in the oil bath at 160 °C and worked up after four hours. The reaction mixture was basified with sodium hydroxide to move the acids into the water phase and then the neutrals were extracted into hexanes. The hexanes extracts were concentrated and finally distilled to give 13.5 grams of 1-(2-furanyl)butene (**101B**) which represented a 22% yield based on the furfuraldehyde input. The aqueous layer was then acidified from which the 2-ethyl-3-(2-furanyl)acrylic acid (**113**) precipitated. After charcoal treatment and recrystallization from hexanes, 28 grams of the acrylic acid (**113**) were obtained which represented a 33% yield.

It was decided to test the Perkin methodology on higher carboxylic acid anhydride homologs, which might eventually lead to solvents with greater mass and, consequently, higher flash points. Unfortunately, commercial availability of anhydride of higher fatty acid ceases with hexanoic

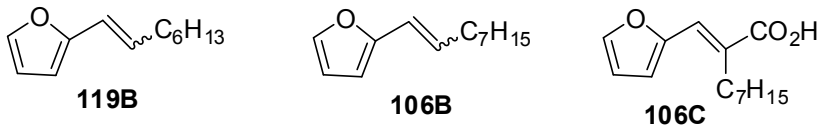
anhydride. The latter was used in the Perkin reaction using the specific conditions of: 1 equiv hexanoic anhydride, 1 equiv furfural, 1 equiv potassium acetate, 160 °C, four hours. Owing to the good results obtained thus far, all subsequent Perkin experiments were run at this temperature. The reaction duration was selected based on NMR analysis of other reactions which showed that at this time virtually all the aldehyde was consumed. The specific conditions are mentioned here because it is not clear those responsible for *in situ* decarboxylation. But indeed, this reaction also gave the desired 1-(2-furanyl)hexene (**160A**) in about 25% yield. The reaction mixture could simply be washed with water to remove the potassium acetate base and then fractionally distilled under reduced pressure to obtain the alkene (**160A**) and later the hexanoic acid. The residue in the distillation pot was the 2-butyl-3-(2-furanyl)acrylic acid (**160B**) in about 35% yield. What this style workup illustrated was that although the yield was low, all the products and starting material could be easily separated by distillation methods, which is made facile since the carboxylic acid is liquid at ambient temperature. The fate of the mass balance of furfuraldehyde is an issue requiring further study.



In order to use still higher anhydride homologs, they required synthesis which turned out to be straight forward using the method of Albitzky.[29] In this procedure the long chain fatty acid was refluxed with a 2.5 molar excess of acetic anhydride and then distilled to remove the by-product acetic acid. This method was found to be quite general and several fatty acids were converted in their anhydride: oleic (**108A**), palmitic (**116A**), pelargonic or nonanoic acid (**106A**), octanoic (**119A**), stearic (**107A**) and 2-ethylhexanoic (**131**). The yield on these reactions was essentially quantitative and after all the acetic acid had been eliminated by distillation (atmospheric then 60 torr), the crude anhydrides were sufficiently pure to use straight away. This avoided reduced pressure distillation of heavy compounds which would likely require a lot of heat, perhaps causing decompositions. Although there was an absence of an acid peak, the proton NMR spectrum of anhydride was not sufficient to prove the structure of anhydride. The carbon NMR spectroscopy was essential in that it clearly showed the characteristic upfield shift in the carbonyl resonance. For example, the carbonyl signal of pelargonic acid is 180.65 ppm, however the carbonyl resonance of pelargonic anhydride is at 169.87 (no other peaks present in this region).



The Perkin reaction of furfural (48 grams, ½ mole), octanoic anhydride (207 grams, 0.7 mole) and sodium propionate (64 grams, 0.66 mole) gave after workup 20.9 grams of 1-(2-furanyl)octene (**119B**) which represented a 23% yield. In this case, the acrylic acid was not isolated. During workup of the octanoic acid reaction, and long chain carboxylic acids in general, it was found that the anhydride and/or acid must be fully hydrolyzed/neutralized or else they contaminate the alkenylfuran extraction. The solution to this problem was to stir the hexanes extract with strong sodium or potassium hydroxide to ensure complete movement of the acid into the water layer. With pelargonic anhydride, the alkene (**106B**) and the acrylic acid (**106C**) were both isolated from the reaction in yields of 28% and 17%, respectively.



Since a furanacrylic acid (**106C**) is a new molecule, further characterization of this solid was performed. Eventually crystals suitable for X-ray analysis were obtained by recrystallization from hexanes. A crystal structure of acid (**106C**) was solved by Dr. Thomas J. Groshen, a collaborator here in the Chemistry Department at China Lake. As can be seen in Figure 12, the furan and alkyl chain occupy the same side of the alkene and the acid was trans to the furan ring.

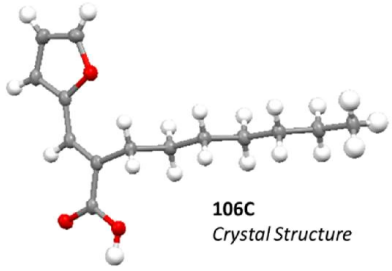
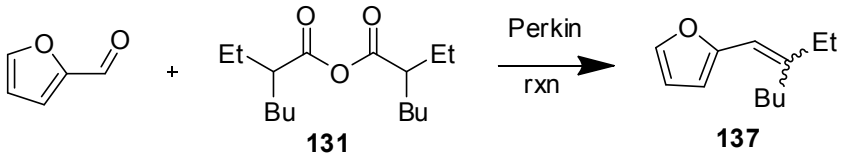


Figure 13 X-ray crystal structure of furanacrylic acid (**106C**)

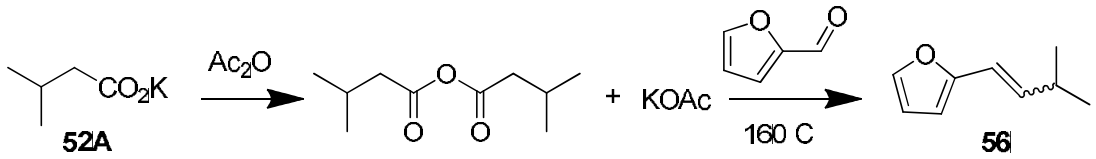
There is a very mature industry in Guebert products from 1-butanol such as 2-ethylhexanoic acid. Such products are widely used as plasticizers. The anhydride from the latter acid (**131**) underwent the Perkin reaction with furfural as expected. The resulting alkenylfuran (**137**) was a mixture of isomers about the double bond. In this work up of this reaction, the anhydride was found to be very resistant to hydrolysis.



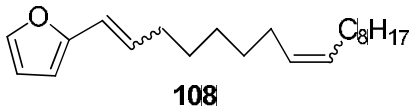
The Perkin reaction was performed many times with many different anhydrides and it was generally found that the yield of the alkenylfuran was about 25% while that of the acrylic acid

was around 50%. The alkene was easier to purify as it was soluble in hexanes and could be freed from acid simply by washing with base. It should be pointed out that an anhydride hydrolyzes to two equivalents of carboxylic acid, which means that there was a great deal of this acid left to remove when the reaction was complete. Since these acrylic acids and the higher carboxylic acids themselves were both solid at room temperature, and the great quantity of acid present, made for a difficult separation since in acid/base washes the two components would behave similarly. Occasionally, the acrylic acid could be made to crystallize away from the carboxylic acid by a solubility difference in hexanes, for example.

An interesting modification of the Perkin reaction was attempted, to try to decrease the amount of higher acid going into the reaction. During early studies of the Perkin reaction, Michael[30] and others had shown that an alkaline higher carboxylate salt will undergo an exchange reaction acetic anhydride to generate the higher anhydride. It was decided to try this with isovaleric acid since this was available and should give the alkenylfuran product as discussed above. The potassium valerate (**52A**) was made by the potassium *tert*-butoxide method. The issue with this method is that there must be two equivalents of salt per equivalent of acetic anhydride, which meant that stirring might be an issue. In the event, the reaction was run as best as possible and then worked up. Indeed, a small amount of the 2-isobutenylfuran (**56**) was isolated which was the typical mixture of cis and trans configuration.

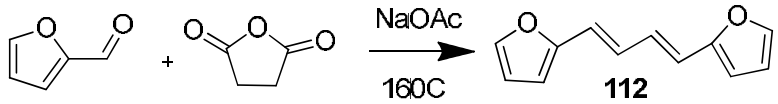


Even unsaturated fatty acids such as oleic acid (18:1), one of the most prevalent long chain mono-unsaturated fats in the plant kingdom, would undergo the Perkin reaction with furfuraldehyde. Although the reaction was run at small scale, a sample of the long chain alkenyl furan (**108**) was isolated as a thick oil. The proton NMR of this substance clearly showed that the newly created alkene was a mixture of cis and trans. Since the natural product oleic acid has a cis double bond, it became of interest to determine any configurational changes at this site after the reaction. The carbon NMR of this compound showed six peaks in the alkenyl region at ~130 ppm, implying that there may be isomers of the internal alkene.

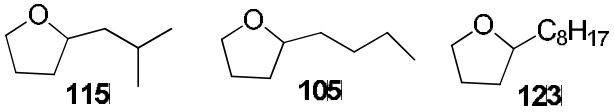


An attempt at a double Perkin of furfural was also made using succinic anhydride. In this reaction that had been reported long ago[31] there were several product among which was difurfurylbutadiene (**112**). The work up of this reaction was more complicated, however a neutral hexane fraction was isolated. Evaporation gave a yellow colored solid, the proton NMR

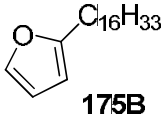
of which was complicated but only showed signals in the aromatic region, which was expected. Further analysis of this product or this reaction were not made.

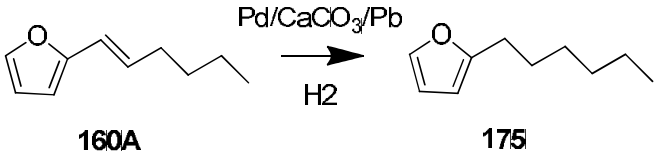


Those 2-alkenylfurans made and purified in sufficient quantity were subjected to the standard reduction conditions. In all of these reductions the corresponding 2-alkyltetrahydrofurans (**115**, **105** and **123**) were obtained in good yield. These substances were all colorless liquids with a pleasant floral odor.



During the research efforts in this area, the interesting work with avocadofurans reported by Rodriguez-Soana *et al.*[32]was discovered. Briefly, by Perkin reaction between furfural and palmitic acid and selective reduction, an antifeedant avococadofuran (**175B**) was prepared. A draft of a manuscript describing this work can be found in the Appendix U. A critical step enabling that synthesis was the selective reduction of the alkene of alkenylfuran. This chemistry was developed using the previously made alkenylfuran (**160A**). A cursory attempt at reduction with platinum oxide catalyst (20% loading) appeared to hydrogenate the alkene first but the reduction was incomplete even after two hours, and when continued another eight hours the mixture no longer had a clean NMR spectrum. Using the 'poisoned' catalyst developed by Lindlar, an excellent yield of the alkylfuran (**175**) was obtained without any disturbance to the furan ring. This could be useful tool to allow further derivitization chemistry of such alkylfurans owing to the rich chemistry the available *alpha* position can undergo.



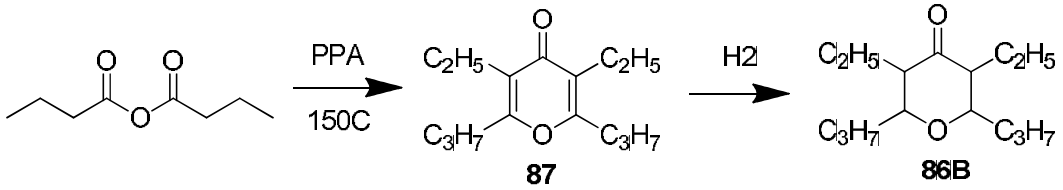


Synthesis of 4-Pyranone Solvent

The NMR spectra of reactions and/or products discussed below can be found in Appendix H.

An interesting transformation of carboxylic anhydrides was found in the literature during the course of work on the Perkin reaction. Mullock and Suschitzky[33] reported that carboxylic anhydrides up to hexanoic when treated with hot polyphosphoric acid will undergo a decarboxylative cyclization to 2,3,5,6-tetraalkyl-4-pyrones. The pyrone made from propionic acid was a solid melting at 36 °C but the other compounds were all reported to be liquids. The hypothesis was that they might have sufficient aliphatic content, with or without reduction, to be suitable degreasing compounds.

Since there was an available supply of anhydride, the reaction was carried out with butyric anhydride. Although, they reported running the reaction at 200 °C, it was found that even in a 150 °C oil bath, obvious carbon dioxide formation would ocurr. The desired pyrone (**87**) was obtained from this reaction in 40% yield and was a mobile liquid.

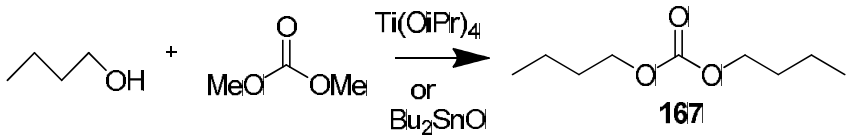


An attempt at reduction of the pyrone (**87**) under the standard conditions failed to bring about any significant reduction, only starting material was isolated. This may be due to the fact that the alkenes in this molecule are tetrasubstituted which are known to be resistant to hydrogenation. More aggressive hydrogenation conditions (high heat and pressure) were not studied, however. It was later discovered that reduction of a similar compound was achieved[34] with fifteen psi hydrogen pressure, acetic acid solvent and 60 °C reaction temperature, but there wasn't enough time to continue work with this substance.

Synthesis of Furanic Carbonate, Dialkyl Carbonates and *N*,*O*-Dialkylcarbamate Solvents
The NMR spectra of reactions and/or products discussed below can be found in Appendix I.

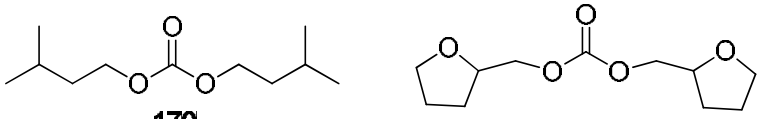
There are concerns about the rising level of carbon dioxide in the atmosphere and the downstream effects it may cause, or is causing, to the environment. Carbon dioxide can be used in organic synthesis reactions not as simply a solvent (supercritical CO_2) but also as a reactant. For example, carbon dioxide can be made to react with alcohols to generate dialkyl carbonates ($ROCO_2R$) with special catalyst. Although, the industrial process to make dimethyl carbonate involves reaction of methanol, carbon monoxide, oxygen and a copper catalyst, among several other methods. This process is carried out on large scale industrially to make dimethyl carbonate, the simplest and cheapest in this class, on a scale of ~300 kilotons *per annum*.[35] The dimethyl and diethyl carbonate are used as solvents but they have high vapor pressures and flash points (14 °C and 33 °C, respectively) which will greatly decrease the chances they could be used in degreasing from a safety standpoint. More importantly, in light of the purposes of this study, both dimethyl and diethyl carbonate were unable to dissolve non-polar soils such as polyalphaolefin (PAO), which will be discussed in more detail later. But the idea came about to use higher alcohols and make carbonates that might be useful for degreasing purposes. It is known that dialkyl carbonates can undergo a form of transesterification reaction with another alcohol to make alternate dialkyl carbonates. This is possible by using dimethyl carbonate, a higher boiling alcohol along with a catalyst and then heating and removing the by-product methanol as it is formed, which draws the reaction equilibrium in the desired direction.

The first target for synthesis was dibutyl carbonate (**167**) since it would have twice as much aliphatic content as diethyl carbonate and presumably more non-polar character. In addition, 1-butanol is a natural product which can be obtained by microbial fermentation (*Clostridium*) processes on large scale. Dibutyl carbonate was first prepared by reaction of silver carbonate with 1-butyl iodide[36] and later reaction of phosgene and 1-butanol.[37] There were two reports involving transesterification reaction with dimethyl carbonate with either dibutyltin oxide[38] or titanium IV tetraisopropoxide ($Ti(iOPr)_4$).[39] Both reactions were carried out and in each case the desired product was isolated. In the dibutyltin oxide route, this catalyst appeared to have volatility as it would co-distill to a certain degree with the dibutyl carbonate. The result being that a white haze remained on the distillation glassware which was difficult to clean. The titanium route did not have this issue and all subsequent chemistry in this area was done by this method.



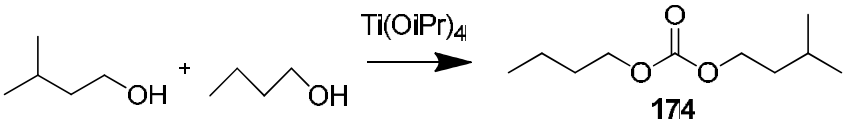
Next, the dialkyl carbonate of isoamyl alcohol (**170**) was made and this reaction ocurred uneventfully. Also, it was decided to try to make a furan derivative. To avoid a later reduction

step, tetrahydrofurfuryl alcohol was used. The reaction ocurred as described above and difurfuryl carbonate (**166**) was found to be a very thick oil that required high vacuum for distillation. Since tetrahydrofurfuryl alcohol was a racemate its dialkylcarbonate (**166**) was expected to be a mixture of *dl* and meso diastereomers. Although the characteristic signal of carbonate at 155 ppm was present in the carbon NMR spectrum, even ten thousand scans did not show the expected 'doubling' of all the carbon signals from these diastereomers.



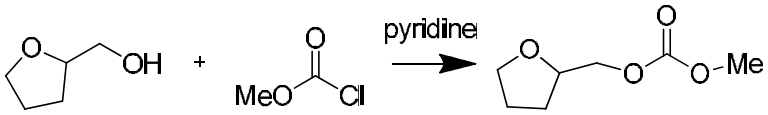
170 **166**

In another experiment, an attempt to make a mixed carbonate by the transesterification method was carried out. Here, two different alcohols were used in the reaction that might form a dialkylcarbonate where the two alkyl groups are not identical. The reaction of 1-butanol : isoamyl alcohol : dimethyl carbonate in an equimolar ratio was set up. During distillation of the product, no attempt was made to fractionate the distillate. NMR evaluation of the product showed that it could be a mixture of carbonates including the mixed carbonate (**174**) since there were several overlapping peaks in the carbonyl area (~155 ppm) of the ^{13}C spectrum.



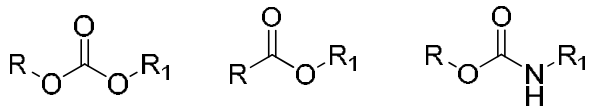
174

The methyl tetrahydrofurfuryl carbonate (**36**) was made by an expedient method in 40% yield. Tetrahydrofurfuryl alcohol was dissolved in tetrahydrofuran solvent and was simply acylated with methyl chloroformate in the presence of base. It was found that triethylamine did not work well and better results were obtained with pyridine as base.

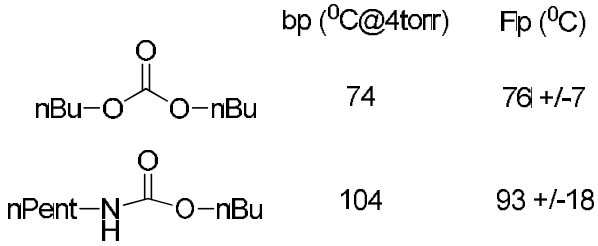


36

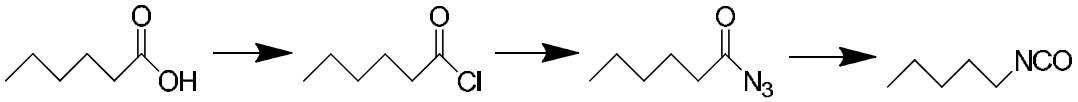
It is important to ensure the new degreasing fluids, that might be drop in replacements of existing technology, have a high flash point to decrease the risk of fire and increase the safety window for technicians performing this work. All of the solvents of the furanic series were composed of just the elements carbon, hydrogen and oxygen and so new ideas were conceived whereby further increases in flash point could be attained. One such concept was to make *N*,*O*-dialkylcarbamates which are structurally very similar to both carboxylic and carbonic acid esters. The carbamate is the replacement of a carbonate oxygen with NH or insertion of NH into an ester.



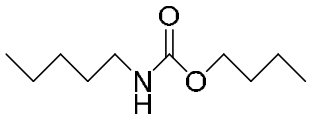
The literature suggests that those reported *N*,*O*-dialkylcarbamates are indeed liquid under ambient conditions which of course is vital for the purposes of a solvent degreaser. Furthermore, predicted boiling and flash points for these compounds were always higher than those of dialkycarbonate of similar structure. As an illustration, the predicted data for dibutyl carbonate and *N*-pentyl-*O*-butylcarbamate are shown below, both had flash points > 60 °C.



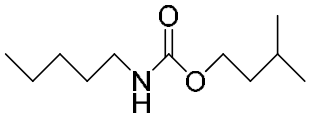
Carbamates can be made by a variety of methods but the simplest way and the one used here was by condensation reaction of isocyanate with alcohol. The requisite isocyanates were generated by the Curtius reaction of carboxylic acid azides which in turn are easily made by reaction of carboxylic acid chloride with sodium azide. This three-step process is very fast and simple to carry out.



Caproic acid, hexanoic acid, a natural product which is a component of palm oils was converted into its acid chloride by reaction with thionyl chloride. In a one pot procedure, this acid chloride was reacted with sodium azide in benzene to generate the acyl azide. After removal of the aqueous layer and drying, the benzene layer containing the acyl azide was heated to reflux for about one hour to cause the rearrangement to isocyanate. Acyl azides can be safety hazards but in this instance were not isolated but kept in solution throughout the sequence. Each step of the sequence was easily monitored by proton NMR noting the shifts in the signal for the *alpha*-methylene group. This signal appeared at 2.85 ppm for the acid chloride, then moved upfield to 2.31 ppm for acyl azide and finally moved downfield to 3.25 ppm for isocyanate. Lastly, an alcohol was added and the heating was continued to complete to synthesis of the carbamates. In this way, two *N*,*O*-dialkylcarbamates were made for testing, *N*-pentyl-*O*-butylcarbamate (**171**) and *N*-pentyl-*O*-isoamylcarbamate (**176**). These substances were both liquids that were distilled to high purity but appeared to have higher viscosity than the dialkylcarbonates.



171



176

Solubility of Furanic Solvents

Introduction to Solubility of Furanic Solvents

This portion of the project could be considered the 'heart and soul' of the research endeavour since the ability of the furanic solvents to dissolve common soils of the DoD was paramount. Although estimations of such properties as boiling and flash points can be made with a fair degree of accuracy *in silico*, predicting solubility is not nearly so straight forward. Solubility refers to the ability of one substance to dissolve in another substance. In this work, solubility refers to one liquid dissolving in a different liquid. More specifically, the goal was to find furanic solvents that were soluble with lubricants used by the DoD. The DoD has all sorts of vehicles and equipment each requiring their own fit-for-purpose lubricants. Trying to cover solubility of all DoD lubricants would be a daunting task. However, since mineral oils and polyalphaolefins make up the vast majority of base oils used in the manufacture lubricants, the solubility data of furanic solvents in these materials would presumably have general applicability. Another working hypothesis was that solubility of base oils in furanic solvent would be the best indicator that the furanic solvent would clean the actual lubricant manufactured from that base oil. This was an important change in tactics since trying to observe the dissolution of a grease into the solvent was difficult. The reason this is so is that the thickening agents of the grease, such as clay or worse still lithium complex soap as shown later, make it nearly impossible to visually determine whether or not there are too phases present as will be shown in later experiments.

Some definition of terms used in this report should be made clear. These experiments in solubility were wholly empirical in nature which anyone could do by the naked eye. The solubility tests employed the furanic solvent in excess over the hydrocarbon base oil, in approximately a 5:1 ratio, respectively. This is the typical strategy of cold cleaning operations anyway, where a soiled part is more or less submerged in a bath of solvent, where the mass of the soil on the part is very low since it is just a thin film. So these solubility experiments are looking at the ability of the hydrocarbon to dissolve into the furanic solvent. When this is the case, the furanic solvent is said to be soluble with the hydrocarbon base oil. However, this does not mean that the furanic solvent and the hydrocarbon base oil are necessarily miscible. In order for that to be determined, the two liquids must be soluble in one another in any proportion. Although this may be the case in certain instances, these additional solubility experiments were not performed and would likely be a little harder to conduct since the base oils, which would be used in excess, have much greater viscosity than the furanic solvents. This can be illustrated by a simple kitchen demonstration: compare the dissolution of a tablespoon of honey into a glass of water with the dissolution of a tablespoon of water into a glass of honey. Which might be easier?

Another important point to clarify is that the base oils are composed of mixtures of primarily hydrocarbon substances, both linear and branched, of various sizes. Of course base oils derived

from petroleum can also contain aromatic substances and sulfur containing compounds as well. Such impurities are absent in PAO, but PAO also contains a distribution of oligomeric species (Figure 13) that make up a manufacturer's particular viscosity, Table 3.[40] So when a furanic solvent can not form a homogenous solution with the hydrocarbon it was deemed insoluble but in fact the solvent may have dissolved/extracted some of the lighter weight components from that base oil. In an ideal world, one would like to have the complete series of each pure oligomer of PAO (e.g. dimer, trimer, tetramer, pentamer, *et cetera*) to determine precisely where solubility of a solvent ends, but this is not possible yet.

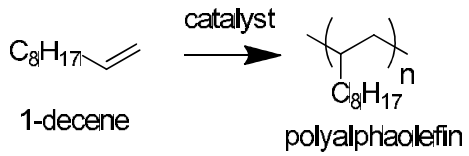


Figure 14 Polyalphaolefin structure and method of manufacture

Table 3 Correlation of polydecene viscosity wth oligomer composition

Viscosity (cSt @ 100 °C)	Dimer (C_{20})	Trimer (C_{30})	Tetramer (C_{40})	Pentamer (C_{50})
2	90	9.0		
4	0.6	84.4	14.5	
6	0.1	33.9	43.5	17.4
8	–	6.0	55.7	27.2
10	–	1.1	42.5	32.3

Experimental Procedure to Determine Solubility of Hydrocarbon in Furanic Solvent

The solubility experiments were all conducted at room temperature. A clear glass test tube was charged with PAO or mineral oil (50 mg) and then furanic solvent (250 mg) was added. A 10X magnification hand loupe was helpful in noting changes. Upon gentle mixing, Schlieren flow[41] was observed for hydrocarbon that dissolved in furanic solvent, owing to changes in density and the refraction of light during dissolution (see Figure 15). Soluble mixtures were a single phase upon complete dissolution. Insoluble mixtures, however, appeared as an opaque emulsion during mixture eventually separating and returning to two phases shortly afterwards.

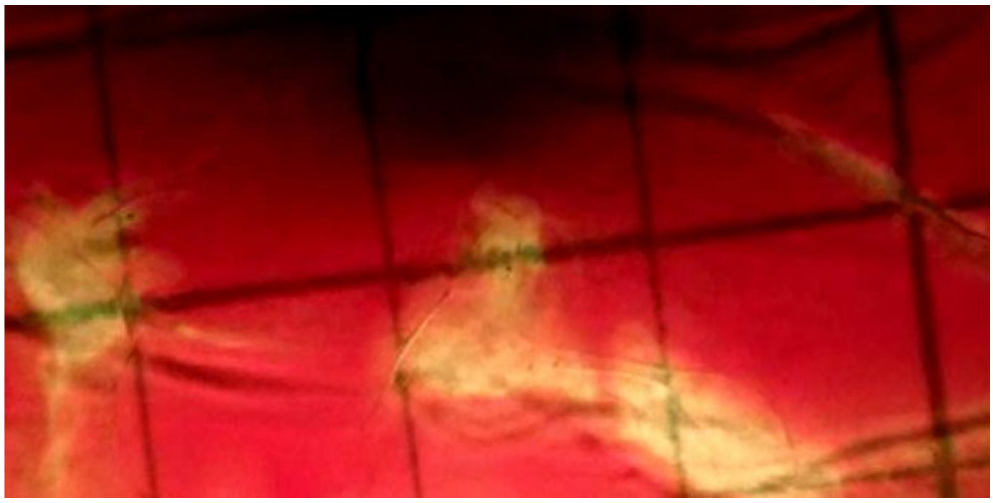
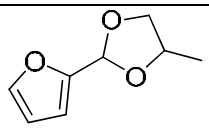


Figure 15 Schleiren texture. Photograph of Schlieren lines observed during the dissolution of red ATF oil with a colorless furanic ketone at 30X magnification. The changes in density as the two fluids dissolve in one another is more easily observed but the same phenomenon occurrs in colorless fluids (e.g. adding vodka to water). The Schlieren texture is constantingly changing, and hence difficult for most cameras to focus on properly, and rapidly dissipates to an equilibrium mixture.

Solubility of Furanic Acetals

The single furanic acetal (**8**) that could be prepared showed poor solubility in hydrocarbon base oil. Although the compound showed solubility in hexanes, that was the end of its solvency for the hydrocarbons tested here, Table 4.

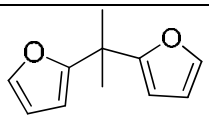
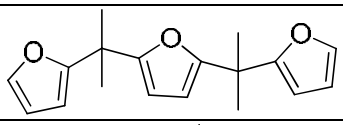
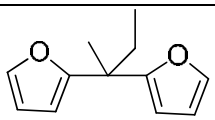
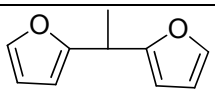
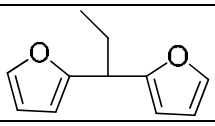
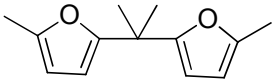
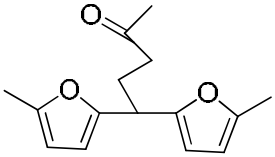
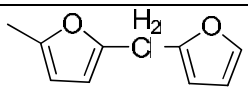
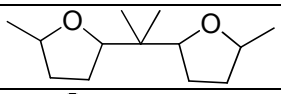
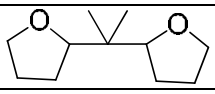
Table 4 Solubility Table of Furanic Acetal

				PAO				
Solvent	Structure	Hexanes	Min. oil	2	5	10	65	150
8		S	i	i			i	

Solubility of Geminal Difuranic Alkanes

Without reduction, the difuranic solvents showed modest solubility to the hydrocarbon base oils, Table 5. But solubility could be improved dramatically with appropriate substitution. For example, the difuran (**30dimer**) made from acetone had modest solubility to 10 cSt PAO. Structural analogs of (**30dimer**), either removal of a methyl group (**43**) or change in the position of a methyl group (**57**), did not change the ability to dissolve mineral oil. But with the addition of a single methylene group, the homologous difuran (**38**) displayed a remarkable jump to become soluble with 65 and even 150 cSt PAO. The addition of another furan ring such as in difuran (**30trimer**) did not improve hydrocarbon solubility. The difuran solvent (**145**) with two additional methyl groups over difuran (**30dimer**) showed improved solubility up to 65 cSt PAO. The difuran (**183**) had poor hydrocarbon solubility which may have resulted from its less aliphatic content. However, reduction of the difuran solvents, for example (**146**) and (**83B**), created excellent solvents at the 150 cSt PAO level.

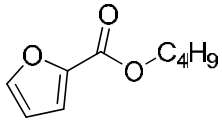
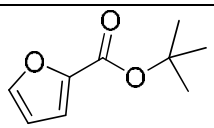
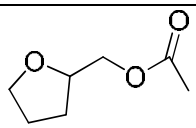
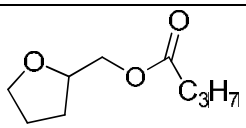
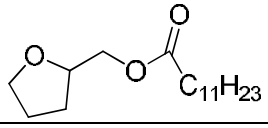
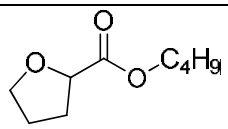
Table 5 Solubility Table of Gem Difuranyl Alkanes

				PAO				
Solvent	Structure	Hexanes	Min. oil	2	5	10	65	150
30dimer			S			S	i	
30trimer			S				i	
38							S	S
43			S				i	
57			S		S		i	
145							S	i
155								
183					i	i		
146			S				S	S
83B			S				S	S

Solubility of Furanic Esters

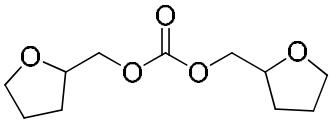
The furanic esters solvent tended to have low hydrocarbon solubility, Table 6. Both butyl ester isomers (**152**) and (**6**) could not dissolve mineral oil. However, reduction of the furan ring (**154**) resulted in improved solubility to include mineral oil and 5cSt PAO. Interestingly, the furanic ester (**37**) which is a sort of reversed ester of, and isomeric with, furanic ester (**154**) lost the ability to dissolve mineral oil and was only soluble up to 2 cSt PAO. Unrelated to solubility but still of importance was the fact that no matter how pure was the furanic ester (**37**), it always had a trace but pungent odor of butyric acid (rancid butter). Since 2-tetrahydrofuroic acid does not have a powerful odor, esters from it (e.g. **154**) had less odor in addition to better hydrocarbon solubility. Solubility of furanic esters could be adjusted from poor (**35** and **37**) to excellent (**159**) by using the appropriate fatty acid. The laurate ester of tetrahydrofurfuryl alcohol (**159**) was soluble up to 150 cSt PAO.

Table 6 Solubility Table of Furanic Ester

				PAO				
Solvent	Structure	Hexanes	Min. oil	2	5	10	65	150
152			i		i		i	
6			i				i	
35		S	i	i	i		i	
37		S	i	S	i	i	i	
159							S	S
154		S	S		S	i	i	

Solubility of Furanic Ethers

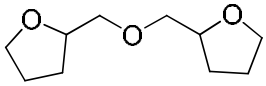
The furanic ethers had excellent solubility for all the hydrocarbons tested, Table 7. Regardless of the oxidation state of the furan ring the furanic ethers showed across the board solubility. Since even smallest furanic ether (**OC047544**) was soluble at the 150 cSt PAO level, the other members of this class with still greater aliphatic content were not tested past 65 cSt PAO level. The smallest furanic ether (**OC047544**) was not soluble in water. The furanic ether (**1932-89**) had modest non-polar character and was soluble over a useful range of hydrocarbons including hexanes, mineral oil and 2–10 cSt PAO. Also, as furanic ether (**1932-89**) was synthesized using dimethylformamide (DMF) solvent, and to eliminate the question of contamination, it was confirmed that DMF was insoluble in both 5 and 10 cSt PAO. Curiously though, furanic solvent (**1932-89**) showed solubility in water much like its structural analog the difuranic carbonate (**166**), which had no hydrocarbon solubility whatever.



166

water soluble

zero hydrocarbon soluble

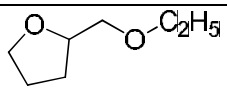
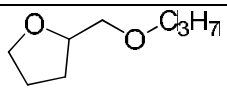
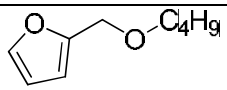
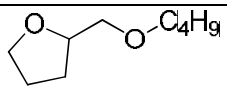
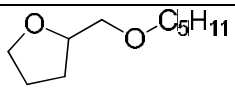
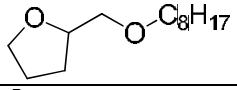
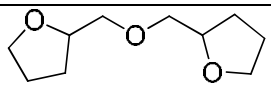


1932-89

water soluble

10 cSt PAO soluble

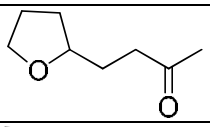
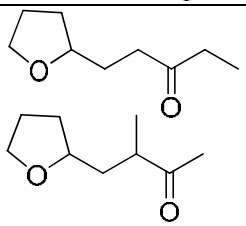
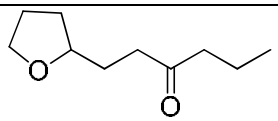
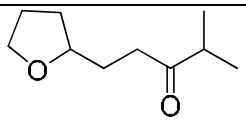
Table 7 Solubility Table of Furanic Ether

				PAO					
Solvent	Structure	Hexanes	Min. oil	2	5	10	65	150	water
OC047544								S	i
88							S		
158							S	S	
163							S		
68							S		
84		S	S				S		
1932-89		S	S	S	S	S	i		S

Solubility of Furanic Ketones

The solubility of the furanic ketones tended to have a direct relationship to the size of the ketone used in their creation, Table 8. For example, the simplest furanic ketone (**17**) made from acetone could dissolve 2 cSt PAO and its next higher homolog, furanic ketone (**79**) could also dissolve 5 cSt PAO. Adding another methylene group, the furanic ketone (**147**) reached both mineral oil and 10 cSt PAO solubility. Interestingly, the furanic ketone (**80**) which is isomeric with (**147**) had a remarkable jump in solubility to include high viscosity 65 cSt PAO. This effect must be due to the branching of the alkyl chain in furanic ketone (**80**). A similar phenomenon was observed in the furanic ketone isomers (**143**), (**82**) and (**149**). These furanic ketones had minimum hydrocarbon solubility at the 65 cSt PAO level, but the additional branching in the structure of solvent (**149**) must be the explanation for its across the board solubility. Here can be seen other examples of the effect of furan ring reduction since solvent (**82**) had solubility up to 65 cSt PAO yet its aromatic analog (**178**) could only dissolve up to 5 cSt PAO, and likewise the solvent pair (**17** and **45**). The furanic ketones (**77B**) and (**91**) made from ketones with high aliphatic content gave excellent hydrocarbon solubilities. However, the use of cyclic ketone resulted in furanic ketone (**10**) solvent with very poor hydrocarbon solubility. The furanic ketone (**151**) containing two tetrahydrofuran rings was a poor solvent only useful up 2 cSt PAO which nevertheless was an improvement solubility over its carbonate analog (**166**).

Table 8 Solubility Table of Furanic Ketones

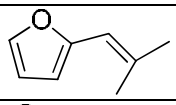
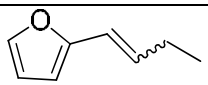
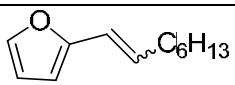
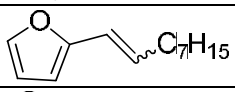
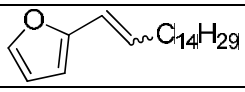
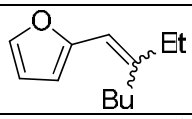
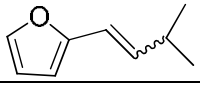
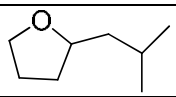
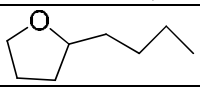
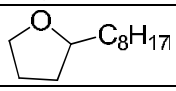
				PAO					
Solvent	Structure	Hexanes	Min. oil	2	5	10	65	150	water
17		S	i	S	i	i	i	i	S
79		S	i	S	S	i	i	i	S
147		S	S	S	S	S	i	i	
80		S	S	S	S	S	S	i	

143		S	S	S	S	S	S	i	
82		S	S	S	S	S	S	i	
149		S	S	S	S	S	S	S	
77B		S	S	S	S	S	S	S	
91		S	S	S	S	S	S	S	
49			i	i	i	i	i	i	
45			i	i	i		i		
151			i	S	i		i		
178			S		S	i	i	i	
51			i				i		

Solubility of Alkyl- and Alkenylfurans

The solubility of the products from the Perkin reaction with furfural was excellent, Table 9. The solubility data collected below may appear scarce but in fact was targeted. Since the compounds were soluble at the 150 cSt PAO level, it wasn't necessary test at less viscous PAO. The data for alkenylfuran (**116**), proved this hypothesis. For solubility in this group, it did not matter the size of the alkene group (**85B** and **116**), nor whether the furan was reduced or not (**85B** and **115**), all of these solvents demonstrated across the board solubility with the hydrocarbon base oils.

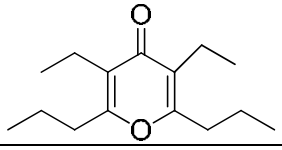
Table 9 Solubility Table For Alkyl- and AlkenylFuran Solvents

				PAO				
Solvent	Structure	Hexanes	Min. oil	2	5	10	65	150
85B							S	S
101B								
160A								S
119B							S	
106B							S	
116		S	S	S	S	S	S	S
137								S
56							S	
115							S	S
105							S	
123							S	

Solubility of 4-Pyrone Solvent

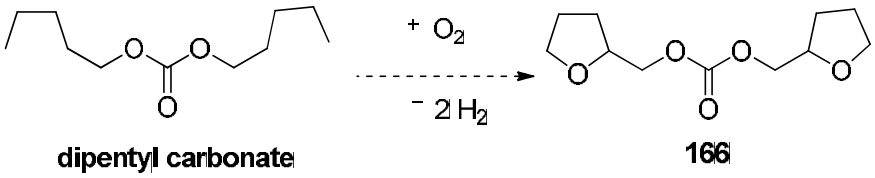
The one member from the family of 4-pyrones (**87**) turned out to be an excellent solvent with across the board solubility of all the hydrocarbons tested, Table 10.

Table 10 Solubility Table for 4-Pyrone Solvent

				PAO				
Solvent	Structure	Hexanes	Min. oil	2	5	10	65	150
87		S	S	S	S	S	S	S

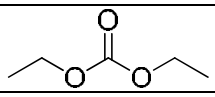
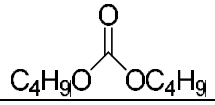
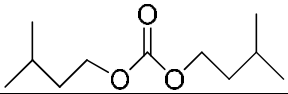
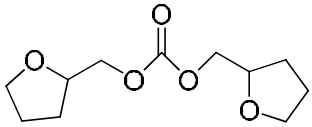
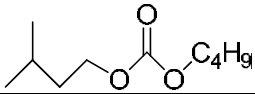
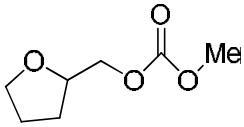
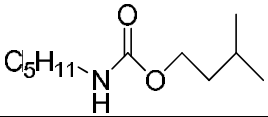
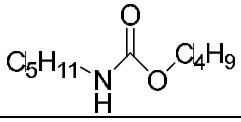
Solubility of Furanic Carbonate, Dialkyl Carbonate and N,O-Dialkylcarbamate

Dialkyl carbonate proved to have excellent non-polar solvency characteristics given sufficient length of aliphatic chain, Table 11. Diethyl carbonate (**DEC**) could dissolve only 5 cSt PAO and mineral oil. However, dibutyl carbonate (**167**) had across the board solubility from hexanes on up to 150 cSt PAO. Both diisoamyl carbonate (**170**) and the mixed carbonate (**174**) were soluble in 65 cSt PAO and likely soluble in 150 cSt PAO since they have more aliphatic content than dibutyl carbonate (**167**). Unfortunately, the two carbonates made from tetrahydrofurfuryl alcohol (**166** and **36**) had no solubility for any of the hydrocarbons tested. These two solvents were tested for water solubility and the ditetrahydrofurfuryl carbonate (**166**) was so polar to be soluble. Since dibutyl carbonate (**167**) was such an excellent solvent, it is very likely that **dipentyl carbonate**, although not made/studied here, would also have across the board solubility with these hydrocarbons. A comparison of the structures of **dipentyl carbonate** and ditetrahydrofurfuryl carbonate (**166**) shows the enormous impact the addition of oxygen and cyclization into furan rings had on solubility of the two compounds.



There was modest success found in the hydrocarbon solvency of the carbamates (**176** and **171**). These compounds could dissolve hexanes, mineral oil and up to 10 cSt PAO. Even though the carbamates had long chain aliphatic structure similar to the dialkyl carbonates, they were unable to dissolve the high viscosity PAO like the latter. The addition of the nitrogen created solvents with slightly higher polarity which would require greater aliphatic content to improve their hydrocarbon solubility.

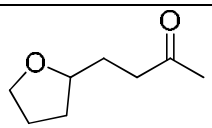
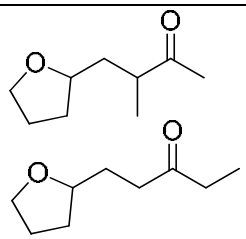
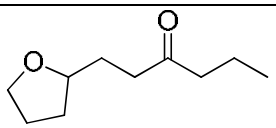
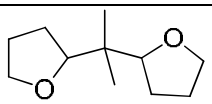
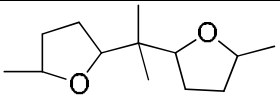
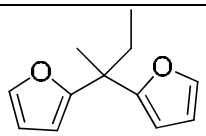
Table 11 Solubility Table for Furanic Carbonate, Dialkyl Carbonate and N,O-Dialky Carbamate

				PAO					
Solvent	Structure	Hexanes	Min. oil	2	5	10	65	150	water
DEC			S		S	i			
167		S	S				S	S	
170							S	S	
166		i	i				i		S
174							S		
36		i	i				i		i
176		S	S	S	S	S	i		
171		S	S	S	S	S	i		

Solubility of Furanic Ketone and Geminal Difuranic Alkanes with Metal Working Fluids

Machine shops are another area where degreasing operations can take place. In this environment, metal working fluids (MWF) are used in the various metal cutting and shaping (drill press, lathe, CNC) and are also used as lubricants for the equipment including machine tool slides, tables and feed mechanisms. These fluids are less highly refined products from petroleum and so contain both naphthenic and paraffinic components and sulfur containing aromatics. Such fluids are usually not suitable for high performance applications such as internal combustion engine lubricant or even multi-purpose grease. In any case, the solubility of three furanic ketones (**17**, **79** and **147**) and two of the gem difurans (**83B** and **146**) were checked against an array of MWF available from the Prototype Assembly Department here at NAWCWDCL, Table 12.

Table 12 Solubility of Furanic Ketone and Gem Difuranyl Alkane with MWF

Solvent	Structure	Extra-virgin Olive Oil	Tellus S2 V68*	Turbo T32*	Tonna 220*	Rotella T 10W*	Valvata J680*
17		S	i	i	i	i	i
79		S	S	S	S	S	i
147		S	S	S	S	S	S
83B		S	S	S	S	S	S
146		S	S	S	S	S	S
38		S	S	S	S	S	S

*Products of Royal Dutch Shell

As can be seen in Table 12, the furanic ketones follow a similar solubility pattern in that more aliphatic content is necessary to achieve across the board solubility of MWF. The published viscosities of the MWF are collected in Table 13 below. Interestingly, the furanic ketone (**79**) was able to dissolve an 18.5 cSt Tonna base oil, but as shown previously this ketone could not completely dissolve a 10 cSt PAO. This may be due to the fact that the Tonna oil is only modestly refined. The furanic ketone (**147**) was able to dissolve the 35 cSt Valvata oil which corresponds with the PAO data where its solubility falls off somewhere between 10 and 65 cSt

PAO. The two gem difuranic solvents (**83B** and **146**) had no trouble dissolving all the MWF. In addition, the aromatic difuran solvent (**38**) that was not reduced could dissolve all the MWF as well. These furanic solvents could also dissolve olive oil which of course is composed of carboxylic esters (triglycerides) high in oleic acid.

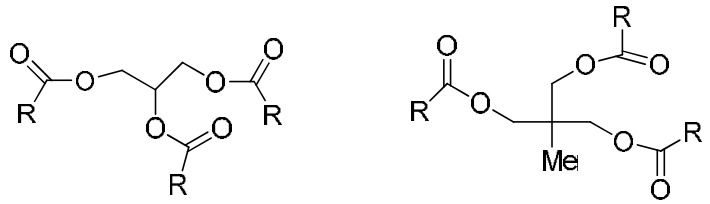
Table 13 Viscosities of the Metal Working Fluids

Lubricant	Kinematic Viscosity at 100 °C
Extra virgin olive oil	15
Shell Tellus S2 V68	10.5
Shell Turbo T32	5.45
Shell Tonna S220	18.5
Shell Valvata J680	35.3
Shell Rotella T 10W	6.5

Solubility of furanic ketones with common automotive lubricants and olive oil

This was a quick check for the solubility of five examples from the furanic ketone family of solvents (**17**, **79**, **147**, **91** and **82**) with some common lubricants in general automotive technology and elsewhere, Figure 16. These solvents were selected because they had already shown a progression in hydrocarbon solvency. As can be seen in the Table 14, the furanic ketones would dissolve 10W-30 motor oil once there was sufficient aliphatic content of the third member of the series solvent (**147**). And from the previous studies with PAO (Table 8), this 10W-30 motor oil probably is manufactured from a 10 cSt base oil, since neither furanic ketones (**17**) or (**79**) could dissolve this viscosity. The automatic transmission fluid must be a lower viscosity probably around 5 cSt since this was the highest viscosity that solvent (**79**) was able to dissolve in the PAO studies. The furanic ketones had solubility with generic DOT3 brake fluid with the simplest member of the series (**17**). Since glycol brake fluids are very polar substances, the solubility with a much more hydrophobic ketone (**91**), one that could dissolve 150 cSt PAO, was tested. But even this solvent would dissolve the brake fluid so that it was not necessary to test all members. A product similar to glycol based brake fluid was tested, Dow's Ucon OSP-18 (20 cSt @ 40 °C). This product is composed of polybutyleneoxide which is a glycol ether polymer that has good hydrocarbon solubility. Indeed, the furanic ketones were soluble in this lubricant even from the simplest member (**17**). To prove generality, a furanic ketone (**82**) with sufficient hydrocarbon solubility could dissolve all of these fluids. The issue of density hasn't been discussed but it was found during these tests with solvent (**82**) that the latter had higher density than the Castrol transmission fluid, Figure 17.

In addition, the furanic ketones all had solubility with generic olive oil and increasing their aliphatic content was unnecessary for this base oil class. Since vegetable oils are composed of esters of glycerol (triglycerides), this demonstrates that the furanic ketones will likely have good solubility for ester base oils. Two more example of an ester based lubricants were Croda's Priolube 1936 (5 cSt @ 100 °C) and Priolube 1445 (12.5 cSt @ 100 °C) and these were soluble with the furanic ketones the same way as the olive oil. The Priolube 1445 is, according to product information, a polyol ester. This is important since another class of lubricants used by the DoD are synthetic esters. The General Electric F404 turbofan engines of in Navy F18 and Air Force F117 use MIL-L-23699 lubricant which is a 5 cSt synthetic neopentyl polyol ester base stock. These five furanic solvents are also a good guage of the likelihood the many other furanic solvents would be able to dissolve all of these common lubricants.



natural triglycerides synthetic polyol ester

Table 14 Solubility of Furanic Ketone with Common Lubricants

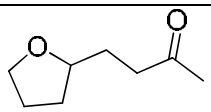
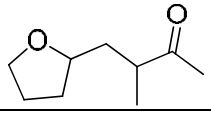
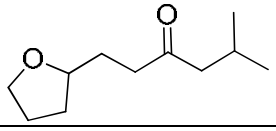
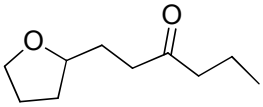
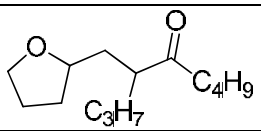
Solvent	Structure	Quaker State™ 10W-30	Castrol® Dexron® ATF	Ucon OSP-18	Priolube 1936	Priolube 1445	DOT3 Brake Fluid	Olive Oil
17		i	i	S	S	S	S	S
79		i	S					S
82		S	S	S	S		S	S
147		S	S	S	S			S
91							S	S

Figure 16 More general lubricants studied: Quaker State 10W-30 motor oil, Dow Ucon OSP-18, Priolube 1936 from Croda and Castrol Dexron automatic transmission fluid

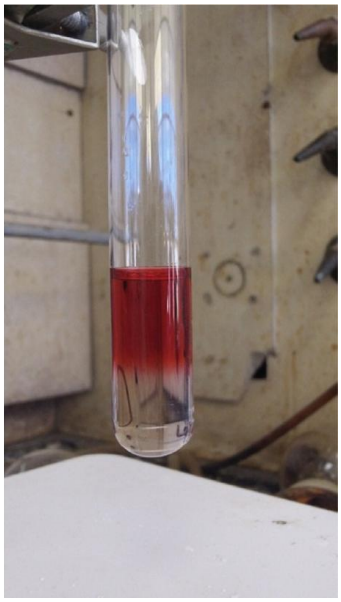


Figure 17 Test tube containing Castrol Dexron ATF (red liquid layer) and furanic ketone (**82**), the solvent has greater density and thus was the lower layer prior to mixing

Flash Point and Evaporation Rate of Furanic Solvents

The evaporation most commonly refers to a liquid substance moving from the liquid phase into the gas phase. This happens naturally of course with water but also where ever sources of liquid organic compounds are produced. For example, natural sources of voliatile organic compounds (VOC) are from the plant kingdom such as pine forests or citrus orchards and this is the same phenomenon that allows one to smell flowers. Manmade sources of volatile organic compounds can be deleterious to the environment by causing bad air quality. Major players in bad air quality are fossil fuel combustion engines, coal fired power plants, but also industrial processes which employ large quantities of organic solvents with high vapor pressure. Of course the VOC can be inhaled by living organism which can lead to health issues. Health risks are much greater for technicians who work with VOC materials since they are in a confined space and the concentration of VOC is much greater. Vapor pressure and evaporation rate are in direct relationship, so a liquid with a greater rate of evaporation will have a vapor pressure higher than another liquid which evaporates more slowly.[42] This of course is a simplistic view of this very complicated and somewhat subjective phenomenon.[43]

The rate of evaporation of the furanic solvents was compared with solvents the volatility properties of which have already been determined. These control liquids were *n*-butyl acetate which has been used as the standard solvent against which the evaporation of other solvents is compared. The current DoD degreasing solvent MIL-PRF-680II was included along with two other solvents: Navsolve®, a MIL-PRF-32295A Type II degreasing solvent and NAVHFC, a hydraulic fluid cleaner. Navsolve is a recent material created specifically as a degreasing material to address the tighter air quality restrictions in states such as California. Navsolve is primarily composed of the cyclosiloxanes D4 and D5 which have documented environmental persistence.[44] NAVHFC is another commercial product composed of petroleum distillates and limonene according to MIL-PRF-680 Type IV and is very similar to MIL-PRF-680 Type II. Information and product specifications for MIL-PRF-680II, Navsolve and NavHFC can be found in Appendices L, N and O. The raw data for the evaporation experiments with furanic solvents and controls is included as Appendix K.

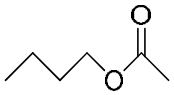
The flash point of a solvent is the temperature at which sufficient vapor is present to be ignited in an air atmosphere. This is a very important physical property of organic liquids that is taken into great consideration in down-selection of degreasing solvents. Degreasing facilities typically have large quantities of these solvents in active use and the work areas are indoors so the the risk of fire must be minimized as far as possible. Currently, DoD employs degreasing solvents that have flash points greater than 61 °C, such as MIL-PRF-680II. This temperature is also the cutoff between classifications as flammable (flash point < 60 °C) or combustible liquids (flash point > 60 °C) according to guidelines set for the transportation of hazardous materials by Occupational Safety and Health Administration (OSHA). In the original proposal, the flash points of several compounds were estimated using the computer program Advanced Chemistry Development

(ACD/LABS) Software V11.2. After collecting the flash point data on several of those planned compounds, those predictions were remarkably close to experimental values.

Evaporation Rate and Flash Point of n-*Butyl Acetate versus Degreasing Solvents*

n-Butyl acetate is the typical standard against which the evaporation rate of solvents are compared. The evaporation studies showed that MIL-PRF-680II had about 1/5 the rate of evaporation of *n*-butyl acetate, Table 15. The other solvents Navsolve and NavHFC had about ½ the rate of evaporation of MIL-PRF-680II and so both of those solvents are less volatile than MIL-PRF-680II. These degreasing solvents were manufactured to have flash points around 61 °C to place them in the combustible rather than flammable category.

Table 15 Evaporation rate and flash point of current degreasing solvents versus n-butyl acetate

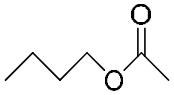
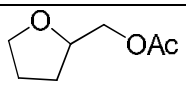
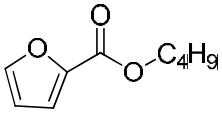
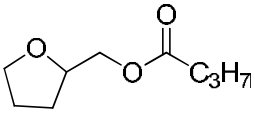
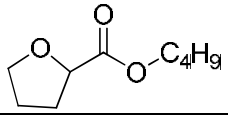
Solvent	Structure	MW	Evaporation Rate	Flash Point (°C)
nBuOAc		116	100	22*
MIL-PRF-680II	Petroleum distillate	-	20.5	62*
NAVSOLVE	Cyclosiloxanes (D4, D5)	-	11	61*
NAVHFC	Petroleum distillate	-	15	61*

*Data from Safety Data Sheets

Evaporation Rate and Flash Point of Furanic Esters

The furanic esters had evaporation rates approximately ten times less than the current MIL-PRF-680II degreasing solvent, Table 16. The flash points of some of the solvents (**35** and **37**) were in the desirable combustible range. The flash point of solvent **37** was higher than solvent **35** owing to greater molecular weight, which is the general pattern. At least in the flash point of the esters, it did not appear important whether the heterocycle was aromatic or hydrogenated (**152** and **154**).

Table 16 Evaporation and flash point of Furanic Ester versus current degreasing solvents

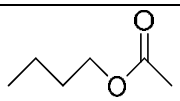
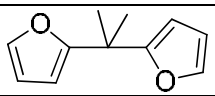
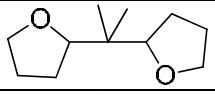
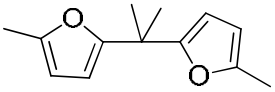
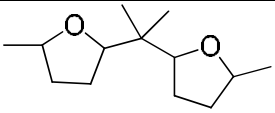
Solvent	Structure	MW	Evaporation Rate	Flash Point (°C)
nBuOAc		116	100	22*
MIL-PRF-680II	Petroleum distillate	-	20.5	62*
NAVSOLVE	Cyclosiloxanes (D4, D5)	-	11	61*
NAVHFC	Petroleum distillate	-	15	61*
35		144	2	84
152		168	2.3	101
37		172	2	97
154		172	0	99

*Data from Safety Data Sheets

Evaporation Rate and Flash Point of Gem Difuranic Alkanes

The evaporation rates of the gem difuranic solvents were less than MIL-PRF-680II with solvent **30dimer** the highest of those tested, Table 17. The flash points were in the combustible range only. Here one can see the effect of reduction of the furan nucleus, as solvent **83B** had only ¼ the rate of evaporation of solvent **30dimer**. Also, the reduction resulted in a higher flash point for solvent **83B** compared with solvent **30dimer**. When more aliphatic content was added making for high molecular weight, a less volatile solvent (**145**) was created from one with higher volatility (**30dimer**).

Table 17 Evaporation rate and flash point of gem difuranyl alkanes versus degreasing solvents

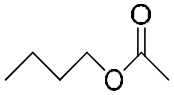
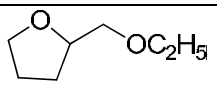
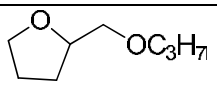
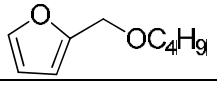
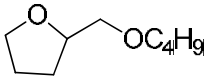
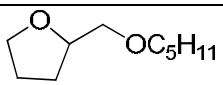
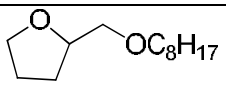
Solvent	Structure	MW	Evaporation Rate	Flash Point (°C)
nBuOAc		116	100	22*
MIL-PRF-680II	Petroleum distillate	-	20.5	62*
NAVSOLVE	Cyclosiloxanes (D4, D5)	-	11	61*
NAVHFC	Petroleum distillate	-	15	61*
30dimer		176	4.1	76
83B		184	1.2	98
145		204	0.4	98
146		212	-	96

*Data from Safety Data Sheets

Evaporation Rate and Flash Point of Furanic Ethers

The furanic ethers tended to have greater volatility among the furanic solvents. Both the low molecular weight furanic ethers (**OC047544** and **88**) had evaporation rates equal or greater than MIL-PRF-680II, Navsolve or NavHFC, Table 18. These two also had low flash points in the flammable range. But increasing their molecular weight brought about a decrease in their evaporation rate. Thus, furanic ether with pentyl ether (**68**) had only 1/5 the rate of evaporation as MIL-PRF-680II and octyl chain (**84**) had only 1/10. The pentyl ether (**68**) at least was in the combustible solvent category. With furanic ethers there was a slightly lower flash point for the aromatic or hydrogenated heterocycle (**158** and **163**).

Table 18 Evaporation rate and flash point of furanic ethers versus degreasing solvents

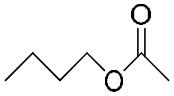
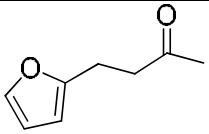
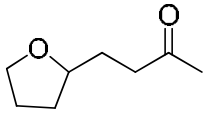
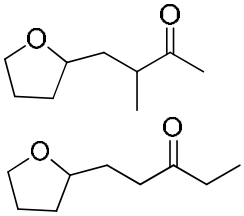
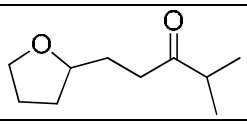
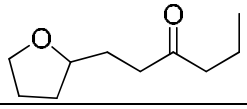
Solvent	Structure	MW	Evaporation Rate	Flash Point (°C)
nBuOAc		116	100	22*
MIL-PRF-680II	Petroleum distillate	-	20.5	62*
NAVSOLVE	Cyclosiloxanes (D4, D5)	-	11	61*
NAVHFC	Petroleum distillate	-	15	61*
OC047544		130	35.5	-
88		144	18.7	55
158		154	8.9	65
163		158	9.6	71
68		172	4	84
84		214	1.2	120

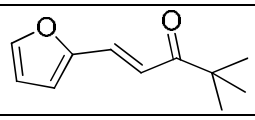
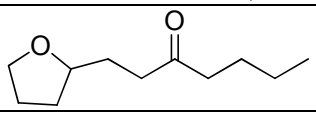
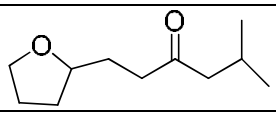
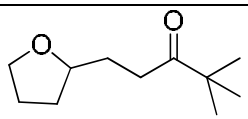
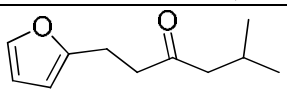
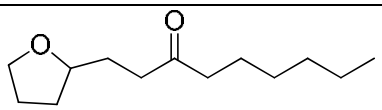
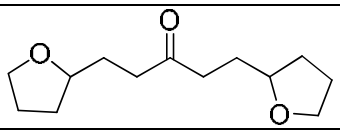
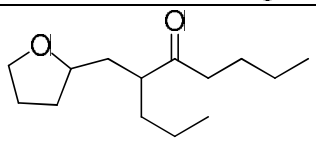
*Data from Safety Data Sheets

Evaporation Rate and Flash Point of Furanic Ketones

The furanic ketones all had flash point equal to or greater that 80 °C placing them in the desirable combustible range, Table 19. Here can be seen the effect of branching in the structure which tends to increase the flash point for example the isomeric furanic ketones (**80** vs. **147**) and (**143** vs. **149**). The evaporation rates of the furanic ketones were very low at the most just 1/5 the rate of MIL-PRF-680II. The flash point of furanic solvents with an aromatic furan ring were slightly higher than the reduced counterpart (**82** and **178** or **17** and **45**).

Table 19 Evaporation rate and flash point of furanic ketones versus degreasing solvents

Solvent	Structure	MW	Evaporation Rate	Flash Point (°C)
nBuOAc		116	100	22*
MIL-PRF-680II	Petroleum distillate	-	20.5	62*
NAVSOLVE	Cyclosiloxanes (D4, D5)	-	11	61*
NAVHFC	Petroleum distillate	-	15	61*
45		138	2	80
17		142	-	83
79	 mixture	156	4	82
80		170	2	90
147		170	2	98

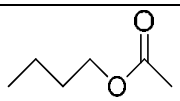
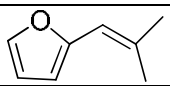
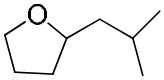
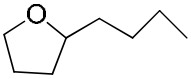
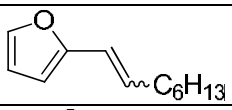
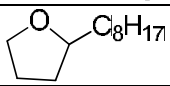
51		178	-	110
143		184	0	112
82		184	0	106
149		184	2	97
178		180	-	102
77B		212	2	130
151		226	0	152
91		226	1.2	122

*values taken from Safety Data Sheets

Evaporation Rate and Flash Point of Alkyl- and AlkenylFurans

Like the furanic ethers, the alkylfuran solvents were among the most volatile solvents, Table 20. The two butylfuran isomers (**115** and **105**) had evaporation rates more than double the rate of MIL-PRF-680II. The alkenylfuran (**85B**) had only 1/10 the evaporation rate of its hydrogenated analog solvent (**115**). But the flash point of these two solvent was nearly the same and they were in the flammable range. One can see that increasing aliphatic content, and hence molecular weight, would decrease evaporation rate and increase flash point (**105** versus **123**).

Table 20 Evaporation rate and flash point of alkyl- and alkenylfuran versus degreasing solvents

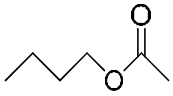
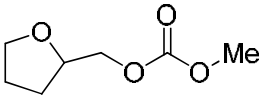
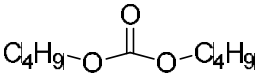
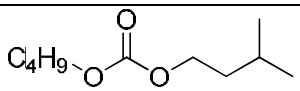
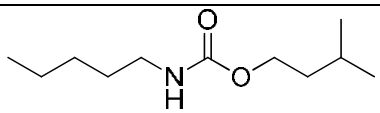
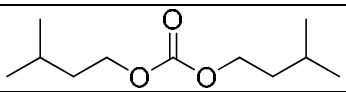
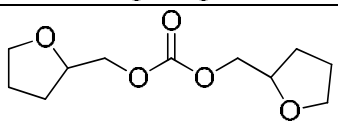
Solvent	Structure	MW	Evaporation Rate	Flash Point (°C)
nBuOAc		116	100	22*
MIL-PRF-680II	Petroleum distillate	-	20.5	62*
NAVSOLVE	Cyclosiloxanes (D4, D5)	-	11	61*
NAVHFC	Petroleum distillate	-	15	61*
85B		122	3.8	35
115		128	46	32
105		128	48	< 20
119		178	-	84
123		184	3.8	81

*Data from Safety Data Sheets

Evaporation Rate and Flash Point of Furanic Carbonates, Dialkyl carbonates and N,O-*Dialkyl Carbamates*

The evaporation rates of the carbonates and carbamates had evaporation rates less than half that of MIL-PRF-680II, Table 21. The carbonates tested here had sufficiently high flash point to put them in the combustible category.

Table 21 Evaporation rate and flash points of furanic carbonate, dialky carbonates and N,O-dialkycarbamates versus degreasing solvents

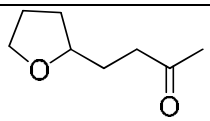
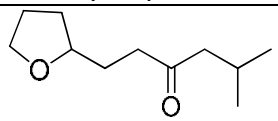
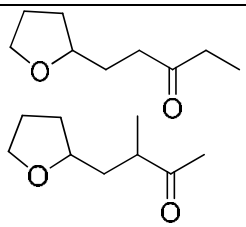
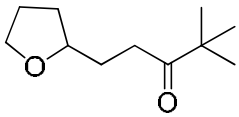
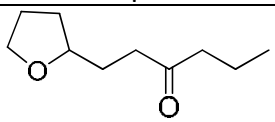
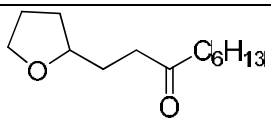
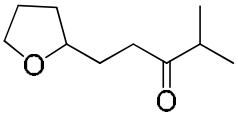
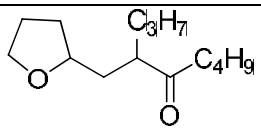
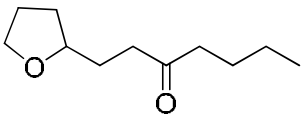
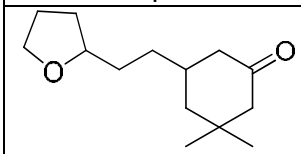
Solvent	Structure	MW	Evaporation Rate	Flash Point (°C)
nBuOAc		116	100	22*
MIL-PRF-680II	Petroleum distillate	-	20.5	62*
NAVSOLVE	Cyclosiloxanes (D4, D5)	-	11	61*
NAVHFC	Petroleum distillate	-	15	61*
36		160	1.2	102
167		174	6.6	78
174		188	3.6	80
176		201	4.7	103
170		202	1	93
166		230	0.4	138

* Value taken from Safety Data Sheets

Comparison of Flash Points of Furanic Ketones and Their Parent Ketone

A comparison of the flash points of the furanic ketones and their parent ketone are shown in the Table 22. One can see that most of the parent ketones are highly flammable with flash points less than 60 °C. But after the derivitization with furfural and reduction, the furanic solvents all had much higher flash points and so are potentially safer solvents.

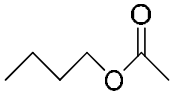
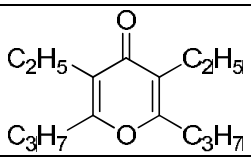
Table 22 Flash point comparison of furanic ketone with parent ketone

Ketone	***Flash Point (℃)***	***Ketone***	***Flash Point (℃)***
Acetone	-20*	4-methyl-2-pentanone	14*
 (**17**)	82	 (**82**)	106
2-butanone	-9*	pinacalone	5*
 (**79**)	81	 (**149**)	97
2-pentanone	10*	2-octanone	62*
 (**147**)	98	 (**77B**)	129
3-methyl-2-butanone	5*	5-nonanone	65*
 (**80**)	90	 (**91**)	122
2-hexanone	25*	isophorone	96*
 (**143**)	112	 (**10**)	na

Evaporation Rate and Flash Point of gamma Pyrone solvent

The evaporation rate for the pyrone solvent (**87**) was not collected but it would likely have a very low rate from such a high molecular weight. However, the flash point for this solvent was collected and was found to be one of the highest of all the solvents made.

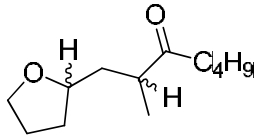
Table 23 Flash point for gamma pyrone solvent

Solvent	Structure	MW	Evaporation Rate	Flash Point (°C)
nBuOAc		116	100	22*
MIL-PRF-680II	Petroleum distillate	-	20.5	62*
NAVSOLVE	Cyclosiloxanes (D4, D5)	-	11	61*
NAVHFC	Petroleum distillate	-	15	61*
87		236	-	143

Stability of Furanic Solvents to Cold Temperature Storage

There are many DoD facilities that are located in areas with cold climates such as those in Alaska, the Northeast and similar geographies around the globe. For safety reasons, hazardous materials such as degreasing solvents are typically stored outside or in warehouses without climate control and so are exposed to fluctuations in temperature. This simple test was carried out to determine the physical state of the furanic solvents to storage at cold temperatures. The results of this test are collected in the Table 23. It can be seen that from the initial -30 °C storage only three furanic solvents (**77B**, **159** and **107**) solidified. This was somewhat surprising as many of the compounds had molecular weights that were high. When the furanic solvents were cooled down further to -74 °C, twelve compounds became solid at this temperature, the three peviously mentioned and nine others. The last test of the compounds at low temperature showed a curious phenomena. After the -74 °C treatment, the furanic solvents were again stored at -30 °C but for a longer period of time. What was found was that several furanic solvents, the yellow highlighted entries in the Table, were solid only after a temperature sequence of -30 °C → -78 °C → -30 °C. So that after the second -30 °C treatment, there were a total of twelve furanic solvents that were solid at this temperature rather than the three found in the first experiment. Possible explanations for this behavior may have something to do with spontaneous crystallization since these samples were not in any way physically disturbed while at low temperature preventing formation of 'seeds'. Liquids may also cool to form glasses which might have indefinite stablility. The -74 °C treatment had 'forced' the sample to crystallize which might henceforth make crystallization easier. But remarkably, of the forty-three solvents tested, thirty of them were at least stable down to -30 °C and the bulk of these were stable fluids down to -78 °C.

One furanic solvent clearly demonstrated the impact that chirality can have on physical properties of organic compounds. The furanic ketone (**91**), which is heavier than two other furanic ketones (**77B** and **143**) both solid at -30 °C, remained liquid even at -78 °C. This is likely due to the fact that furanic solvent (**91**) is composed of a mixture of diastereomers (a total of four compounds) from its two chiral centers. In general, the melting point of an organic substance tends to be depressed by dilution with a different organic substance (e.g. melting point depression).

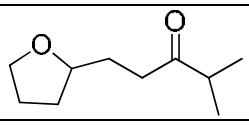
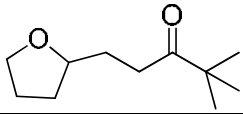
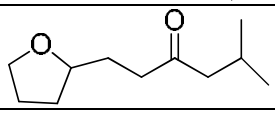
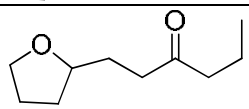
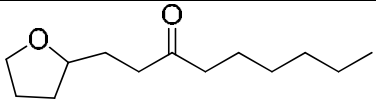
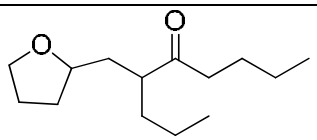
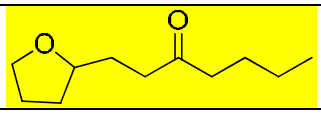
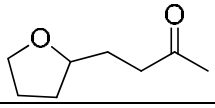
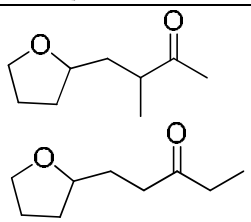
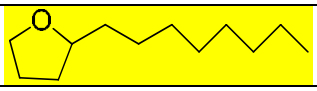


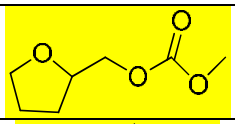
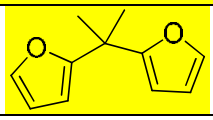
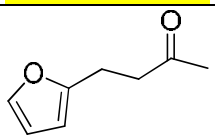
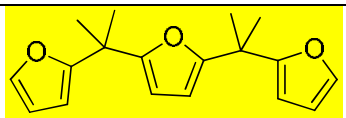
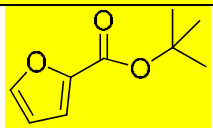
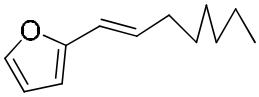
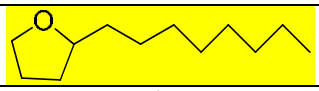
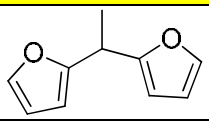
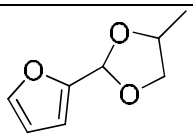
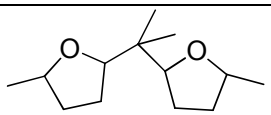
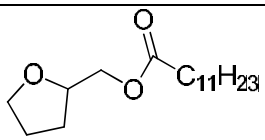
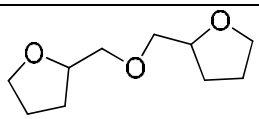
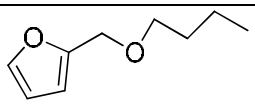
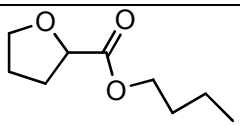
91 (*RR*, *SS*, *RS* and *SR*)

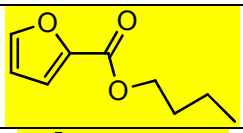
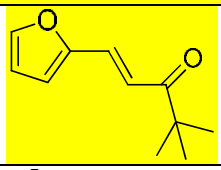
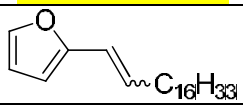
Reduction of the furan ring also helped to decrease the melting temperature of the furanic solvents as the furanic ester (**154**) was stable down to -78 °C and its aromatic counterpart (**152**)

solidified at -30 °C. Lengthening of aliphatic chains in a furanic solvents tended to increase freezing temperature for example the pentyl ether (**68**) remained liquid and the octyl ether (**89**) froze somewhere less that -30 °C. The same was true in the furanic ester series, for example between laurate ester (**159**) and butyl ester (**37**).

Table 24 Stability of Furanic Solvents to Cold Storage

Solvent	Chemical Structure	Formula	-30 °C	-74 °C	-30 °C after -78 °C
80		C10H18O2	L	L	L
149		C11H20O2	L	L	L
82		C11H20O2	L	L	L
147		C10H18O2	L	L	L
77B		C13H24O2	S	S	S
91		C14H26O2	L	L	L
143		C11H20O2	L	S	S
17		C8H14O2	L	L	L
79	 mixture	C9H16O2	L	L	L
123		C12H24O	L	S	S

36		C7H12O4	L	S	S
30 dimer		C11H12O2	L	S	S
45		C8H10O2	L	L	L
30 trimer		C18H20O3	L	L	S
6		C9H12O3	L	L	S
119		C12H18O	L	L	L
123		C12H24O	L	S	S
43		C10H10O2	L	L	L
8		C8H10O3	L	L	L
146		C13H24O2	L	L	L
159		C17H32O3	S	S	S
1932-89		C10H18O3	L	L	L
158		C9H14O2	L	L	L
154		C9H16O3	L	L	L

152		C9H12O3	L	S	S
51		C11H14O2	L	L	S
107		C22H38O	S	S	S

Total Immersion Corrosion

A test for corrosion of metals was carried out using stainless steel washers obtained commercially from HomeDepot™, the exact materials of construction of which were not known but likely Type 316, Figure 18. These washers were small enough to fit into small sample vials which then allowed for very small volumes of furanic solvent to be used in order to fully submerge the washer. Even after nine days in the solvent at room temperature, there appeared to be no staining on any of the washers by the furanic solvents on either the front, back nor edge.

Figure 18 Stainless steel washers used in corrosion analysis

Preliminary Degreasing experiments with Furanic Solvent

At this point of the project authentic samples of military specification bearings or grease had not been acquired. In addition only small quantities of furanic solvent were available. Nevertheless, it was of interested to get some preliminary degreasing data and observations on the degreasing capabilities of the furanic solvents. Several wheel bearings from a motocycle were experimented with because they were small and in a condition requiring replacement. An example of the bearings (69052RS; 25X42X9 mm) is shown in Figure 19, they were soiled with a multipurpose grease that can be found at most autoparts stores.

Figure 19 Used motorcycle bearing 69052RS, shields removed, covered with used grease

The bearing was place in a glass beaker. The solvent selected with test was furanic ketone (**82**) which had good non-polar characteristics. Approximately 15 mL of the solvent was poured into the beaker containing the dirty bearing. The beaker was then swirled by hand for a while but this was taking too long. In order to expedite the test, the beaker was placed on a vibratory plate. After ~ 15 min, the mixture was no longer clear but was full of grey-black debris signifying cleaning of the part, Figure 20.

Figure 20 Mixture formed after vibratory treatment of soiled bearing and furanic solvent (**82**)

The bearing was removed from the solvent bath and was observed to be completely free from the original black soil that had covered it, Figure 21. The bearing of course still had some residual dirty solvent as it was only allowed to drip dry briefly.

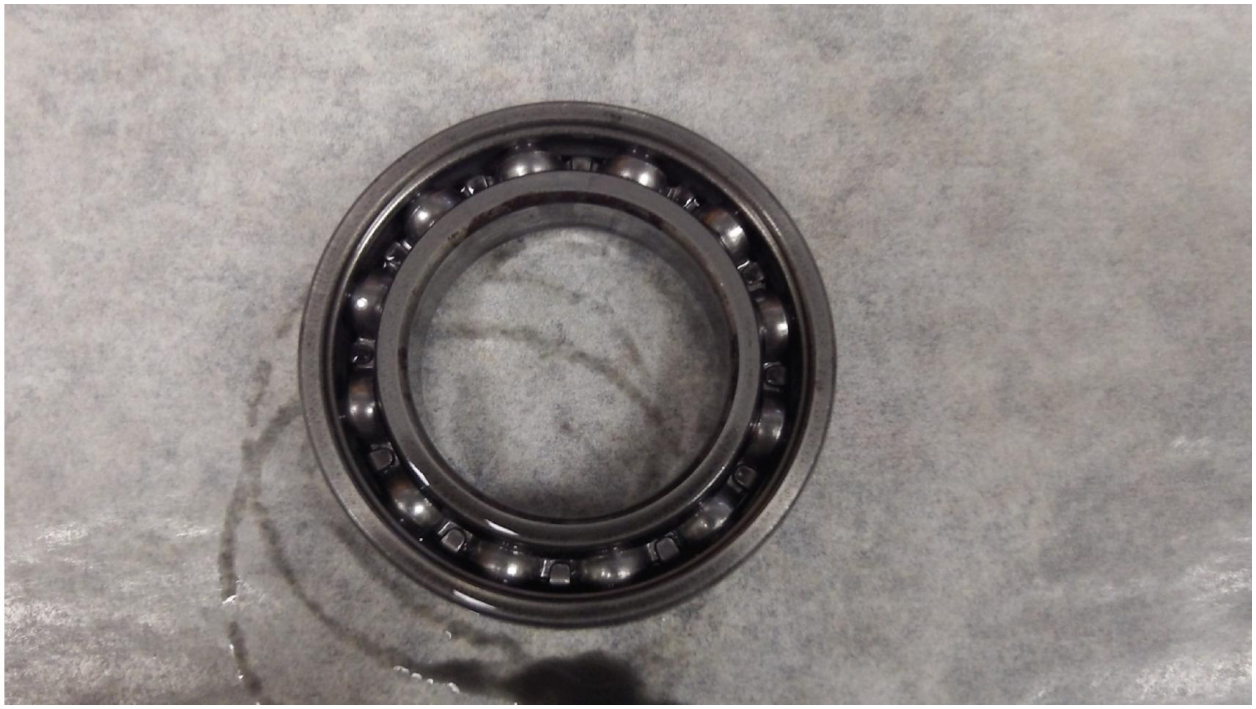


Figure 21 Bearing immediately after pulling from furanic solvent (**82**) bath

Taking some clean rags, the wet bearing was tapped (not brushed) and dried showing that the bearing had become remarkably clean compared to its original condition, Figure 22. Clearly this solvent was able to clean the part sufficient for its visual inspection.

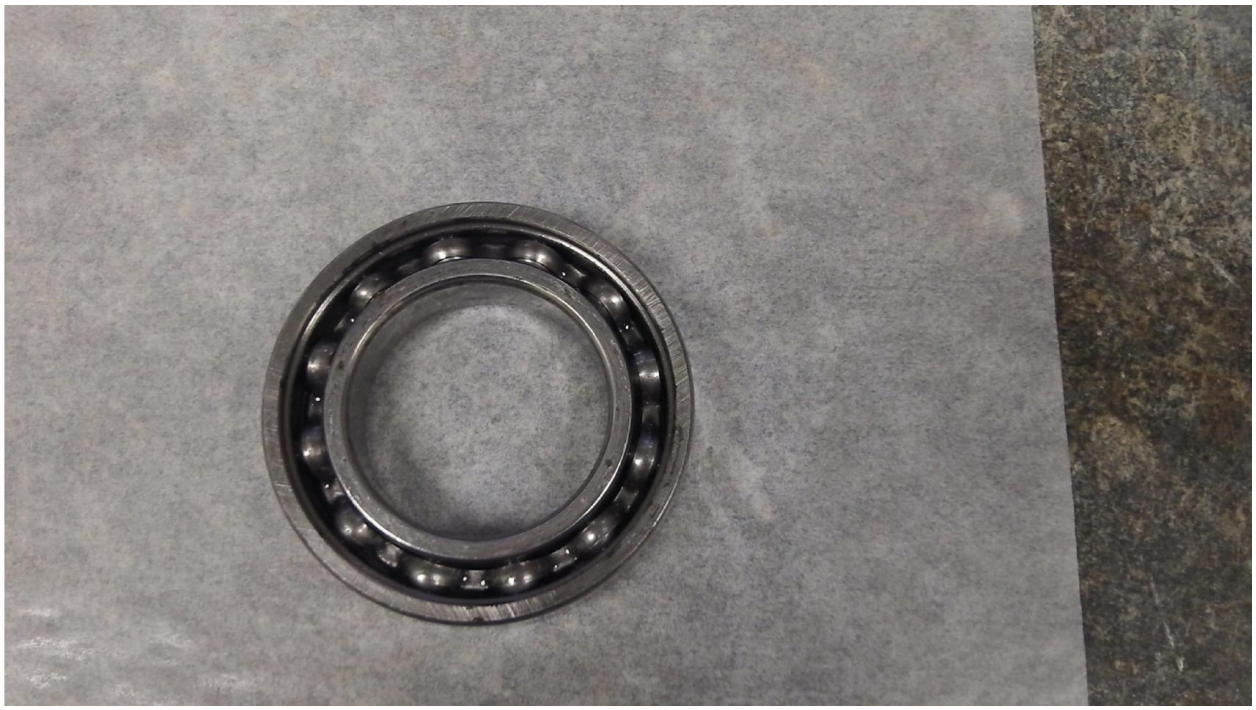


Figure 22 Motorcycle bearing after solvent treatment, spun freely

Because the solvent (**82**) took a significant amount of time and energy to make, some attempts to purify the sample of solvent (**82**) after the degreasing experiement were made. The black colored matter of the old bearing was likely due to very fine metal particles of the bearing itself that had formed and collected in the grease over the lifetime of its use. Filtering this material through silica gel did a poor job of separation, the liquid that came off the column had its original black color, although some presumably larger black particles had been trapped at the top of the column. This makes sense since the metal particles would be composed of a wide spectrum of sizes, the large sizes were effectively trapped by the silica gel. In the next experiment, the soiled furanic solvent was centrifuged in a Labnet Hermle Z200A centrifuge device. The soiled solvent was carefully balanced into two plastic centrifuge tubes and spun at 3500 rpm for 15 minutes. This treatment was sufficient to precipitate most of the fine black particulate matter (Figure 23) which left the supernatant as a clear but brown colored liquid (Figure 24).

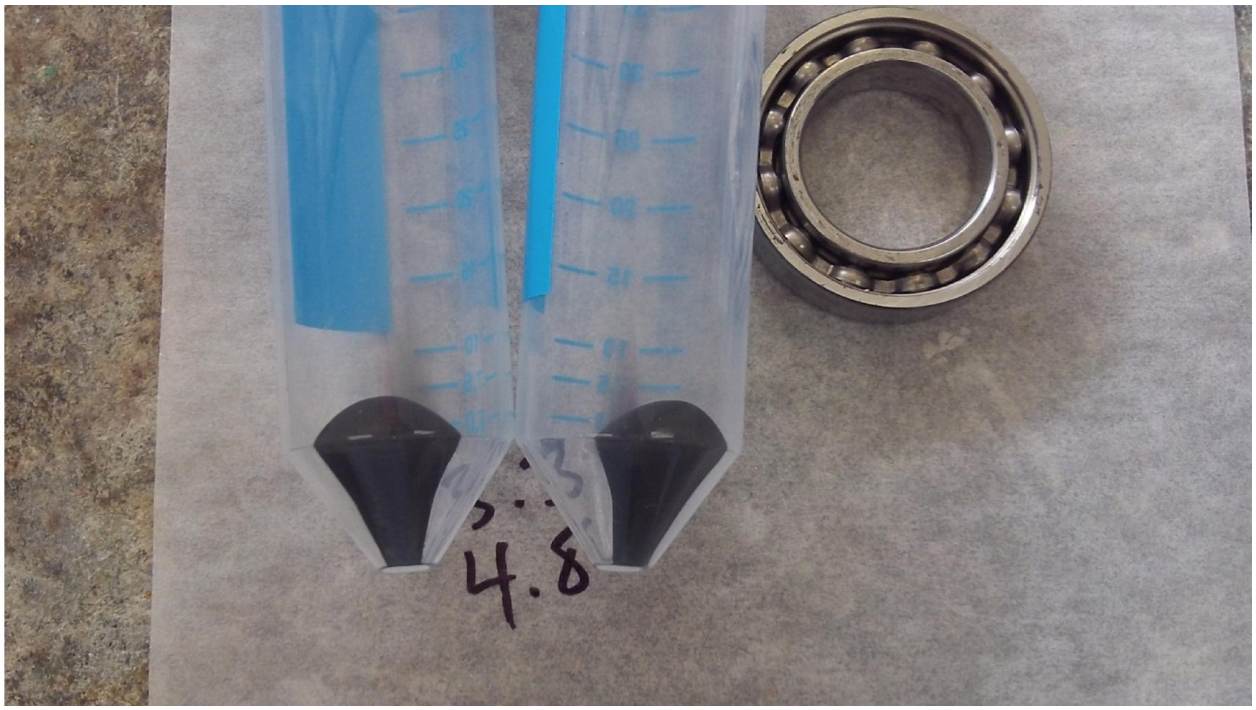


Figure 23 Black particulate matter pelleted from the soiled solvent after centrifugation treatment

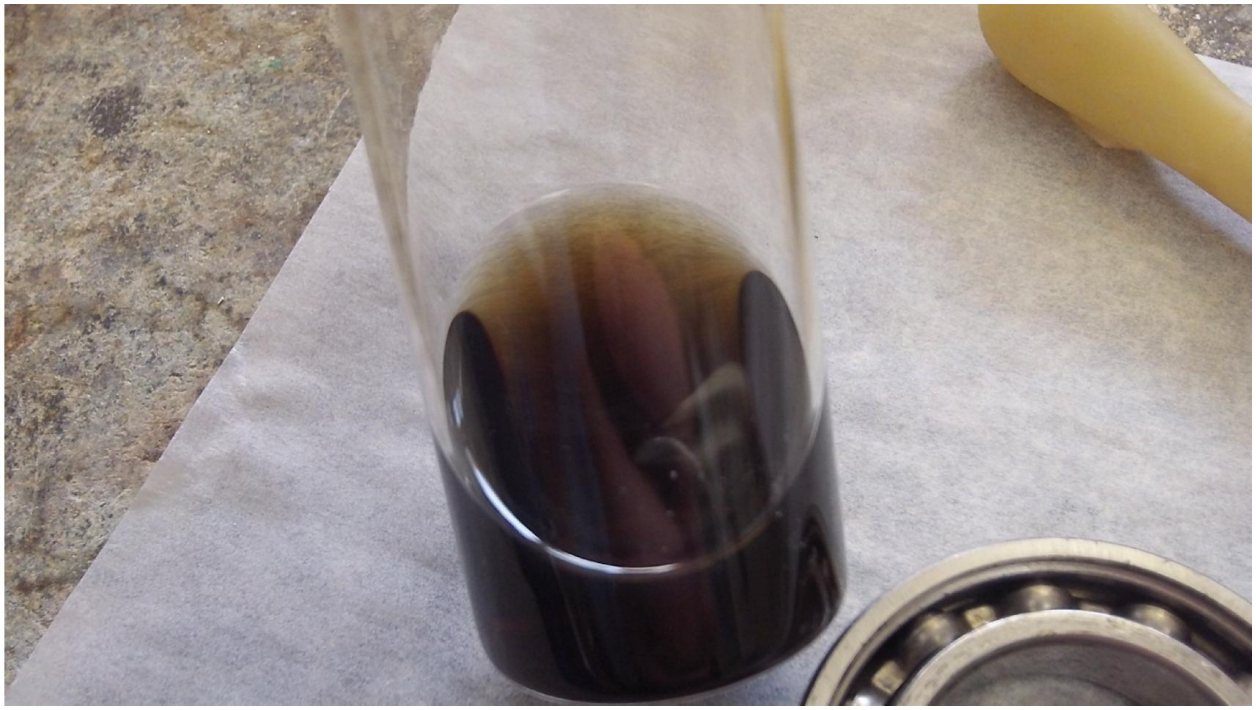


Figure 24 The supernatant after centrifugation treatment of soiled solvent

Degreasing Studies of MIL-PRF-81322 and Mobilgrease33 (MIL-PRF-23827) Greases with Furanic Solvent

Typically grease is manufactured from a base oil and additives package into which a thickening agent is added to create a moldable, semisolid lubricant. A typical multi-purpose grease used by the DoD is MIL-PRF-81322, a wheel bearing grease, and a cleaning solvent used in its removal is MIL-PRF680II, Figure 25. The cleaning of grease with solvents presents special challenges. This is due to the fact that the 'kinetics' of dissolution are not favorable. A simple illustration of this point is shown below.

Figure 25 left) MIL-PRF-680II degreasing solvent; and right) MIL-PRF-81322 wide temperature grease, product manufactured by Nyco

A small vial was filled with some MIL-PRF-680II degreasing solvent (240 mg), the vials neck was packed with a bit of MIL-PRF-81322 grease (100 mg) and then the vial was inverted. In this way, the solvent would also have gravity assistance in dissolving and eventually breaking through and emptying into the test tube, Figure 26. Even after one week incubation, the solvent did not break through the grease although the solvent did take on some yellow color. Grease, although pliable and pumpable, has the tendency to behave as a solid, the result of which means that there must be a mechanical force or component to solvent cleaning of grease particularly. From a chemist's point of view this is very frustrating when one knows that the particular base oil of a grease is soluble in a furanic or other solvent.

Figure 26 MIL-PRF-680II solvent doesn't dissolve MIL-PRF-81322 grease in 'realtime'

In the above experiment one might say that there is a surface area to volume factor affecting the dissolution. So in another experiment, a small amount of grease was swabbed onto the inside of a vial. To this vial was added MIL-PRF680II solvent to a level above that of the grease, so that the grease was fully submerged. This experiment had a much greater mass ratio of solvent the grease as well. The sample was left undisturbed for a period of time. Even with much greater surface area exposed to the solvent, after eighteen hours the grease had not been freed from the sidewall, however the color of the solvent had become yellower indicating some dissolution, Figure 27.

Figure 27 Small sample of grease placed on vial sidewall that did not 'break free' after 18 hours in MIL-PRF-680II

The degreasing experiments with bearings 69052RS (25X42X9 mm^3) were set up using four solvents selected from solubility Table 8. The four furanic solvents selected were furanic ketones (**80**, **79**, **17**) and furanic carbonate (**37**) which had varying degrees of hydrocarbon solubility as previously shown. These solvents would presumably demonstrate examples of both effective and ineffective degreasing solvents. A control degreasing experiment with MIL-PRF-680II was carried out in parallel. Each of the bearings was coated with approximately one gram of MIL-PRF-81322 grease and then placed in separate beakers Figure 28.

Figure 28 Bearing greased with MIL-PRF-81322

The beakers were filled with ~ 15 mL of each solvent which submerged the bearing. In order to facilitate the effect of the solvent to remove grease, a vibratory machine was used to speed up the process of degreasing and eliminate user error found in a manual brushing approach, Figure 29. The bearing/solvent baths were then placed on the vibratory plate for ~ 20 minutes.

Figure 29 Vibratory machine for degreasing experiments

The observations and results from the control experiment with MIL-PRF-680II are shown in the Figure 30 below. The characteristic hazy appearance after degreasing is caused by the suspended particles of thickener (in this case clay) suspended in the solvent.

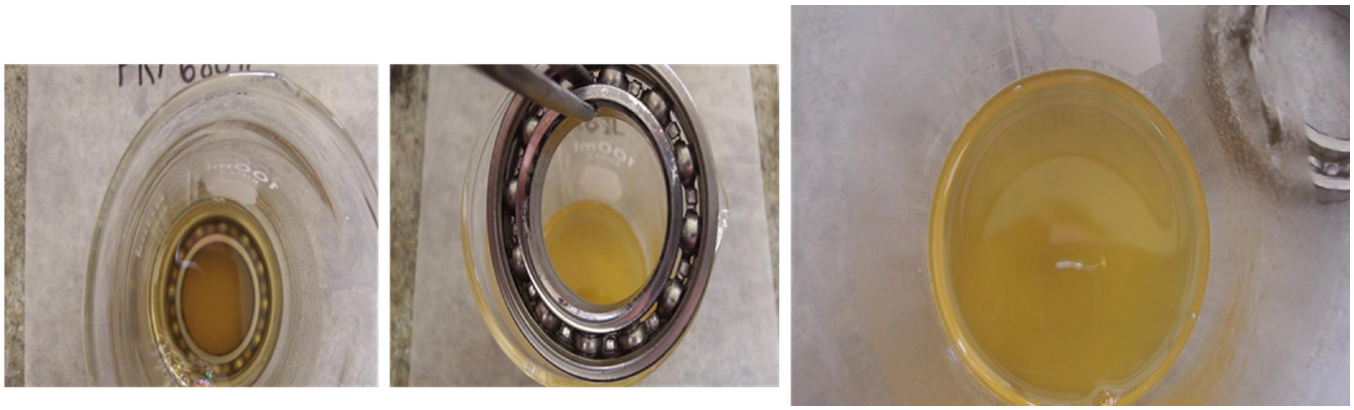


Figure 30 Control experiment of degreasing MIL-PRF-81322 with MIL-PRF-680II; left) after vibration treatment; center) bearing removed from bath showing grease all removed; and right) resulting condition of the MIL-PRF-680II solvent after degreasing

The observations and results with furanic ketone (**80**) are shown in the Figure 31. This solvent was showed solvent behaviour similar to the control MIL-PRF-680II. This result makes correlates well with the solubility data in the Table 8 since this solvent can dissolve high viscosity PAO.

Figure 31 Degreasing MIL-PRF-81322 with furanic solvent (**80**); left) midway through vibratory treatment; center) bearing condition after degreasing experiment; and right) condition of solvent bath after cleaning the grease

The observations and results with furanic ketone (**79**) are shown in the Figure 32. This solvent was showed solvent behaviour similar to the control MIL-PRF-680II. This result was an unexpected result because the specifications for this MIL-PRF-81322 grease made by Nyco (see Appendix) lists the base oil as a 7.5 cSt 'synthetic hydrocarbon', which presumably refers to polyalphaolefin.[45] As previously shown in the solubility Table 8 of the furanic ketones,

solvent (**79**) was only soluble up to 5 cSt PAO. The likely explanation here is that the PAO base oil of this grease is a blend of say a 5 and 10 cSt PAO. If that were the case, then one would expect some breakdown of the grease with this solvent even though it is not a perfect match.

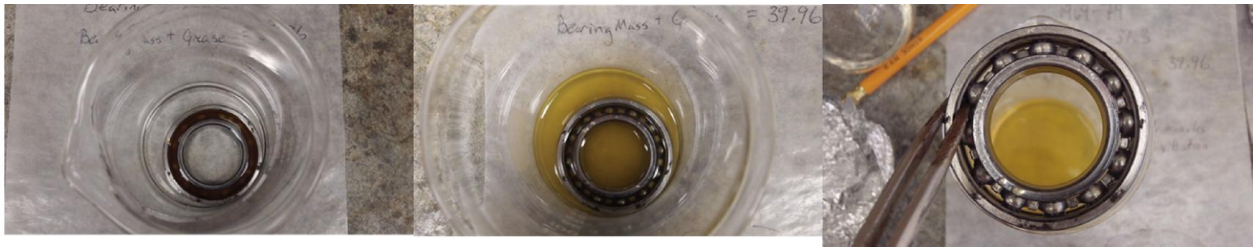


Figure 32 Degreasing MIL-PRF-81322 with furanic solvent (**79**); left) greased bearing in solvent bath prior to vibratory treatment; center) bearing and solvent after degreasing experiment; and right) condition of bearing after cleaning

The observations and results with furanic ketone (**17**) are shown in the Figure 33. In this example one observes the limits of furanic ketone to clean the MIL-PRF-81322 grease. This corresponds well with the solubility data and specifications for this grease. Since this solvent (**17**) could only dissolve hexanes and a 2 cSt PAO (e.g. decene dimer), there was a bit of color taken up by the solvent after the experiement and some grease had at least been broken off of the surface of the bearing. However, it is no surprise that the solvent showed such poor results in breaking down a grease composed of 7.5 cSt PAO.

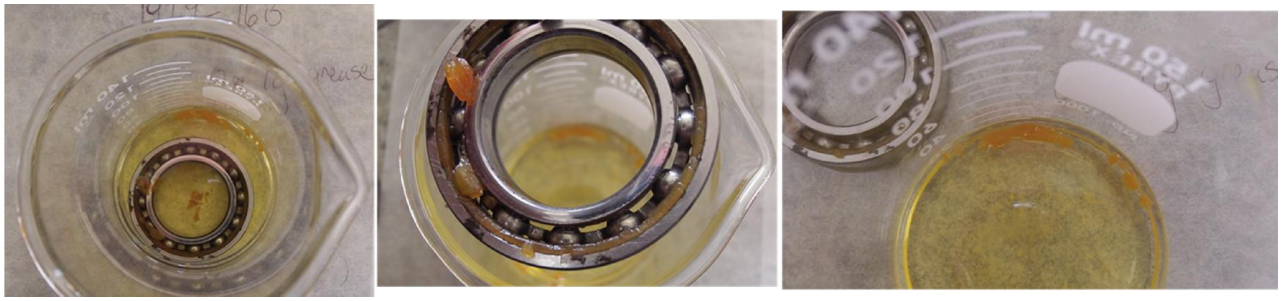


Figure 33 Degreasing MIL-PRF-81322 with furanic solvent (**17**); left) greased bearing in solvent bath after vibratory treatment; center) appearance of the bearing after degreasing experiment, plenty of grease not removed; and right) chunks grease present

The observations and results with furanic carbonate (**36**) are shown in the Figure 34. Here was shown an example of a furanic solvent that had virtually no effect on the grease whatsoever. This result also corresponds with the solubility data since this solvent was unable to dissolve any

hydrocarbon tested.

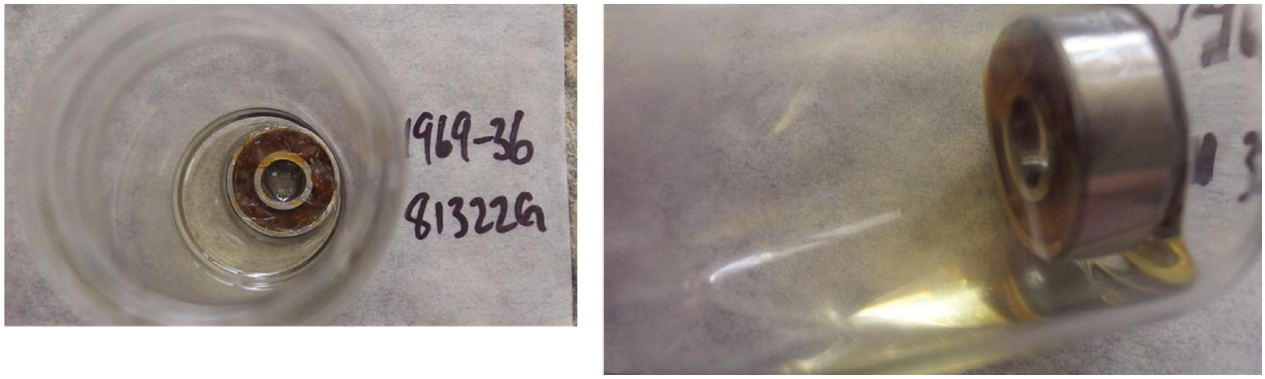


Figure 34 Degreasing MIL-PRF-81322 with furanic solvent (**36**); left) greased bearing in solvent bath after vibratory treatment; right) bearing and solvent after degreasing experiment

To show further applicability of the furanic solvents, degreasing experiments with Mobilgrease33™ which is a MIL-PRF-23827 grease were made, Figure 35. This specification of grease is used in US Army helicoptors in instument bearings.[46] According to the manufacturer, this grease is composed of a lithium complex thickener suspended in PAO and has a blue green color (Appendix M). The base oil of this grease is lighter (3.2 cSt) than the one found in MIL-PRF-81322 (7.5 cSt). This grease is thickened with lithium complex soap.

Figure 35 Appearance of commercial Mobilgrease33 a MIL-PRF-23827 grease

The degreasing experiments with bearings 69052RS (25X42X9 mm^3) were set up using two solvents selected from solubility Table 8. The two furanic solvents selected were furanic ketones which had good (**82**) or marginal (**17**) hydrocarbon solubility as previously shown. These solvents would presumably demonstrate examples of both effective and ineffective degreasing solvents. A control degreasing experiment with MIL-PRF-680II was carried out in parallel. Each of the bearings was coated with approximately one gram of Mobilgrease33 grease and then placed in separate beakers.

The observations and results from the control experiment with MIL-PRF-680II are shown in the Figure 36 below. The characteristic gelatinous appearance and color change after degreasing

Mobilegrease33 is caused by the suspended particles of thickener (in this case lithium complex soap) suspended in the solvent.

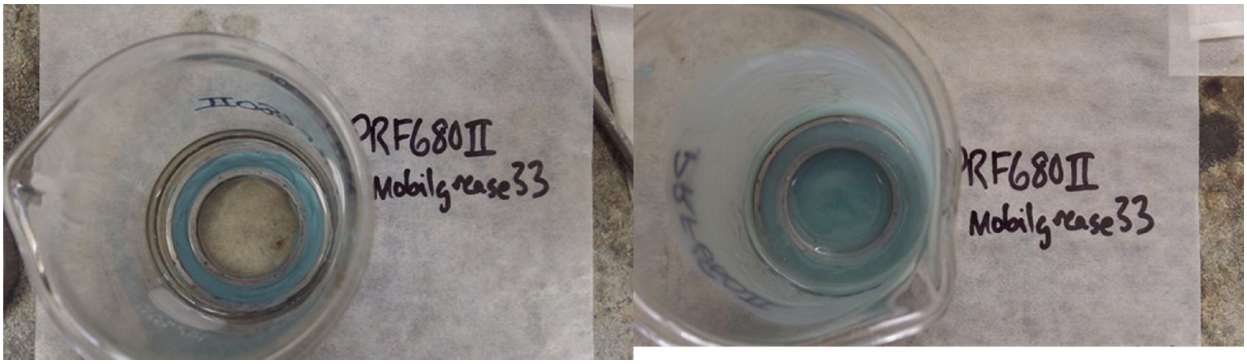


Figure 36 Degreasing MIL-PRF-23827 with control MIL-PRF-680II; left) prior to vibratory treatment; right) after degreasing and remarkably voluminous precipitate from the thickening agent

The observations and results from the furanic solvent (**17** and **82**) are shown in the Figure 37 below. Both of these solvent removed this grease in much the same way that MIL-PRF-680II did. The furanic ketone (**82**) as previously shown can dissolve high viscosity PAO and so has no trouble in cleaning this grease. But even the weakly non-polar furanic ketone (**17**), which was only able to dissolve up to 2 cSt PAO, could remove this grease. Again, perhaps the base oil of Mobilegrease33 is made by mixing a 2 cSt and 5 cSt PAO, in which case one would expect solvent (**17**) to have some cleaning effect.

Figure 37 Results from degreasing MIL-PRF-23827; left) with furanic ketone (**82**); and right) with furanic ketone (**17**)

The experiments with Mobilegrease33 were illustrative of the challenges in determining solubility of a solvent in grease. Some of the very first experiments in determining the solubility of furanic solvents in another material were done with this grease, as a kind of home run approach. But as can be seen in Figure 38, such mixtures become so full of particulate matter from this grease to make it essentially impossible to make adequate observations. One can

understand why those early exploits with Mobilgrease33 in part led to the solubility studies with neat hydrocarbon base oils.

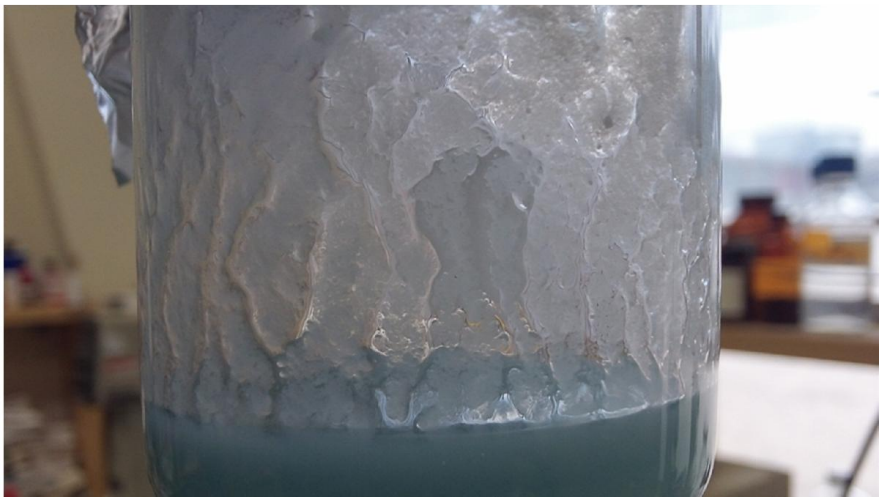


Figure 38 Resulting mixture after degreasing experiment with 15 mL of solvent and only 1 gram of Mobilegrease33

The post-cleaning mixtures from the Mobilegrease33 experiments were spun down on a centrifuge, which pelleted nearly all the white particulate matter. The solvents were decanted away as best as possible from the pelleted material, Figure 39. Although each of these solvents began as colorless liquids, they had become blue green in color resulting from the dissolution of the dye incorporated into the grease during its manufacturing process. Interestingly, the supernatant from solvent (**17**) was just a homogenous, single phase. What one might have expected to observe would be a second phase from an insoluble higher weight oligomer in the 3.5 cSt PAO base oil. So whatever the base oil visosity of this grease, it is dissolved in the furanic ketone (**17**).

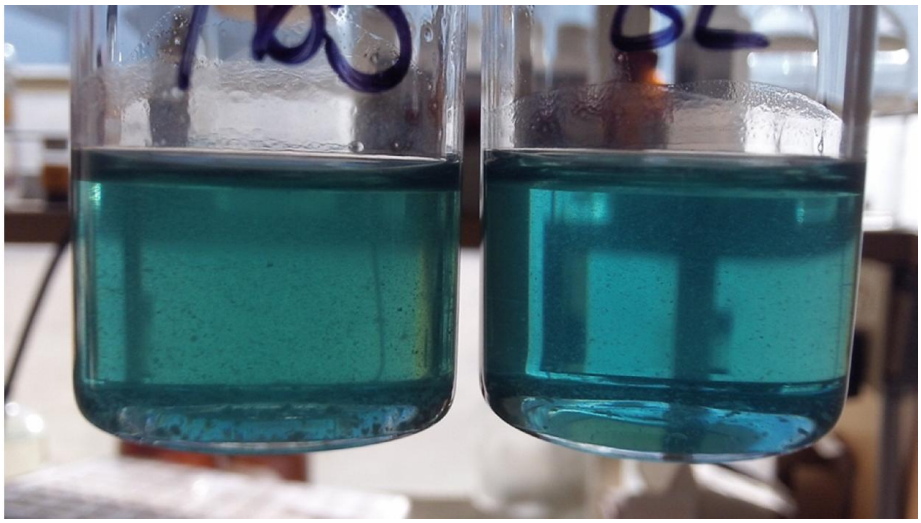


Figure 39 Color change of furanic solvents after cleaning Mobilgrease33, flocculent thickener removed by centrifugation (left, (**17**) and right (**82**))

The white solid material that was pelleted from the centrifugation process was rinsed with acetone, filtered and weighed 170 mg, Figure 40. Since ~ 1 g of grease was used on the bearings, the white thickener material composed 17% of the grease mass. Thus, the remaining mass (~ 800 mg) was made up of the base oil which was dissolved in each of the three solvents tested. What is remarkable is that such a small amount of this thickening agent could cause such a voluminous and gelatinous mixture as shown above.

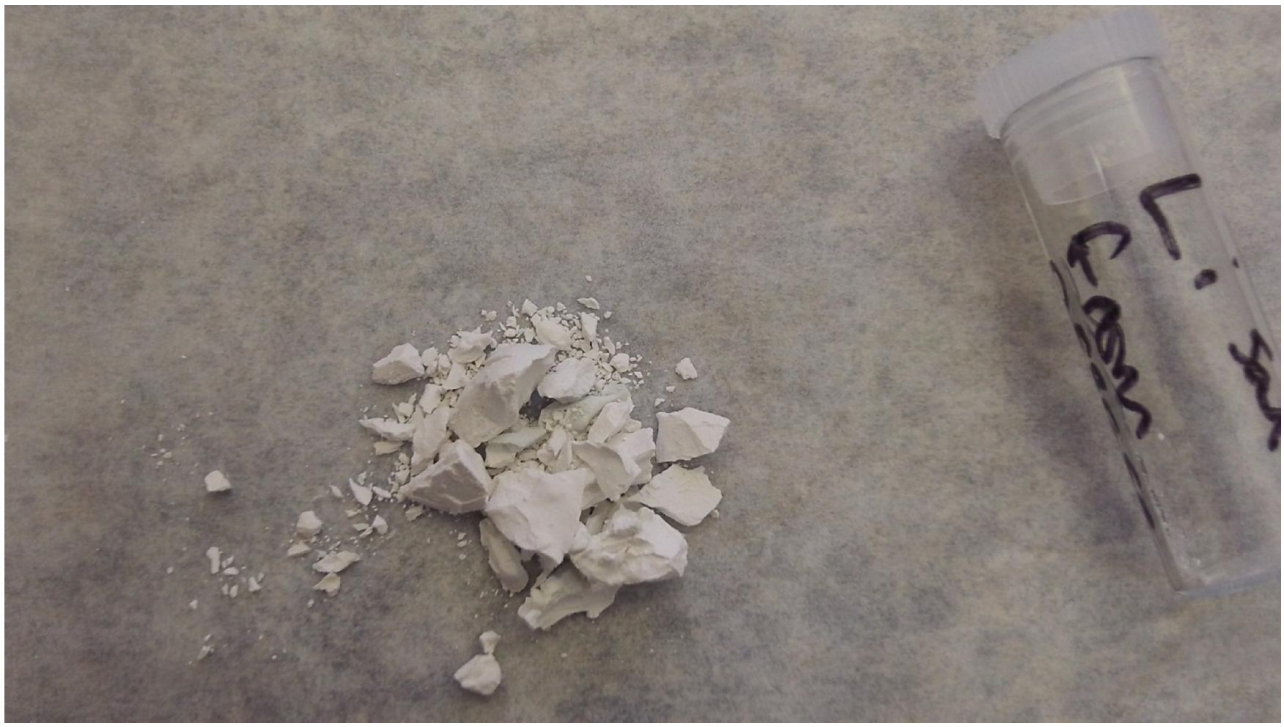


Figure 40 White precipitate after centrifugation from the degreasing experiemtns with Mobilgrease33, a lithium complex thickened grease

Degreasing an F18 Wheel Bearing with Furanic Ketone (82)

Maintenance technicians from Fleet Readiness Center West (FRC WEST) China Lake graciously supplied a soiled bearing (Timken® LL71304-20629) from the nose wheel of an F18 aircraft (VX-9 squadron NAWCWD China Lake). This bearing is slightly smaller (91 mm outside diameter X 15 mm height) than the rear wheel bearings of this aircraft so that the volume of furanic solvent necessary for complete submersion could be minimized (~ 100 mL). These bearings are packed with MIL-PRF-81322 grease and inserted into the wheel hubs by FRC West so the lubricant identity is known. The MIL-PRF-81322 grease was used at FRC WEST China Lake is a product of the French company Nyco and the product specifications are included in Appendix P. This grease is manufactured from 'synthetic hydrocarbon' which is presumably polyalphaolefin with a reported viscosity of 7 cSt at 100 °C. As shown in the photo, the bearing was soiled with significant grease, Figure 41.

Figure 41 Three views of F18 nose wheel bearing taken out of wheel in typical soiled condition

From the solubility data collected, the furanic ketone (**82**) was selected for this experiment since it could be made in sufficient quantity and it demonstrated good solubility including 65 cSt PAO, well beyond the base oil of this particular grease. The bearing was placed in a one liter borosilicate beaker and submerged in the furanic ketone (**82**). The beaker was then gently swirled by hand for approximately 25 minutes. After this time, it appeared that the majority of the 'external' grease had been removed from the bearing. On cursory examination the bearing appeared to be clean and the furanic solvent (**82**) bath had clearly become dirty from dissolving the soil. But as can be seen in the photo, there was significant grease remaining after this initial solvent wash, Figure 42.

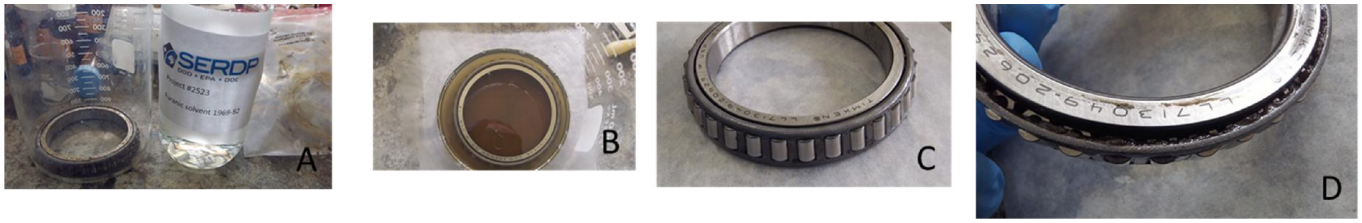


Figure 42 A) soiled bearing, beaker and furanic ketone (**82**); B) results from swirling by hand 25 minutes; C) external appearance of bearing with minimal soil remaining; D) residual grease trapped in concavities of retaining ring

The residual grease remaining was primarily on the backside where there are concavities, particularly under the lip of the retaining ring. At this point, a standard plastic toothbrush was used for about one minute to break up these remaining grease deposits and the bearing was placed back in the furanic solvent bath. After swirling another five minutes, all of the grease appeared to have been removed by visual inspection, Figure 43. The bearing was degreased enough so that a technician could judge whether the bearing had any defects or could be repacked with grease and reinstalled.

Figure 43 Clean bearing after minor scrub with toothbrush directed at remaining grease deposits and condition of the furanic solvent (**82**) after the cleaning process

The furanic ketone solvent (**82**) was able to remove the widely used grease MIL-PRF-81322 from a soiled wheel bearing of a Navy F18 Hornet. The application of mechanical force was necessary to remove some of the grease that was trapped in difficult to access areas of the bearing. This mechanical input is not out of the ordinary in the removal of grease soils. In fact, the standard procedure of the FRC WEST China Lake Detachment is to first scrub the soiled bearing by hand in a parts washer (Inland Technology) with a stiff plastic brush with MIL-PRF-680II solvent. This first step removes the bulk of the grease deposits in the 'nooks and crannies' of the bearings. In a second step, the bearings are loaded into a second automated parts washer (Clarus APW-35) which cycles the bearings held in a wire mesh basket through a 35 gallon bath of MIL-PRF-680II solvent serving as a 'polishing' cleanse. The FRC WEST technicians indicated that dirty bearings freshly removed from a wheel, such as the one used here, would not be cleaned efficiently by the automated Clarus washer alone, that mechanical brushing at the Inland Technology washer to remove the majority of the grease is mandatory. Some product literature describing these two articles of degreasing equipment can be found in Appendix T.

Solubility of Organophosphorus Compounds with Hydrocarbon Base oil and MIL-PRF-81322 Grease

This section describes a slight departure from the furan chemistry to explore the solubility of some organophosphorus liquids. Organic compounds containing phosphorus oftentimes have antiwear properties but also low flammability. Navy and Air Force sponsored research in the 1940's led to low flammability phosphate esters hydraulic fluids. Literature concerning whether or not phosphate ester was soluble in hydrocarbon could not be found. Phosphate ester can be prepared from phenols or from alcohols but it seemed, from the solubility data already collected with the furanic solvents, that trialkyl phosphate would be most likely to dissolve hydrocarbon. A small sample of tributyl phosphate was purchased for experiments. Samples of two other commecial organophosphorus products that appeared interesting to study were generously provided by Cytec Industries. These products were a trialkylphosphine oxide, Cyanex 923, and a phosphinate/phosphonium ionic liquid, Cyphos IL 104 (Figure 44).

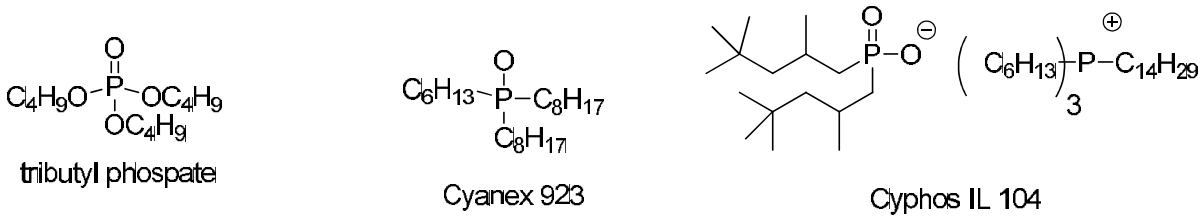


Table 25 Hydrocarbon solubility of organophosphorus liquids and their flash points

Solvent	Min. oil	PAO10	PAO65	PAO150	Flash Point (°C)*
Tributyl phosphate	S	S	i	i	146–165
Cyanex 923	S	S	i	i	182
Cyphos IL 104	S	S	S	S	175

*from Material Safety Data Sheets

As can be seen from the data collected in Table 25, all of these phosphorus containing liquids could dissolve mineral oil as well as 10 cSt PAO. The ionic liquid Cyphos IL 104 could dissolve all the hydrocarbons tested, however it has a very high viscosity and could not be pipetted. The flash point of each of these materials is also collected in Table 25, which shows that they are all stable well above 100 °C.

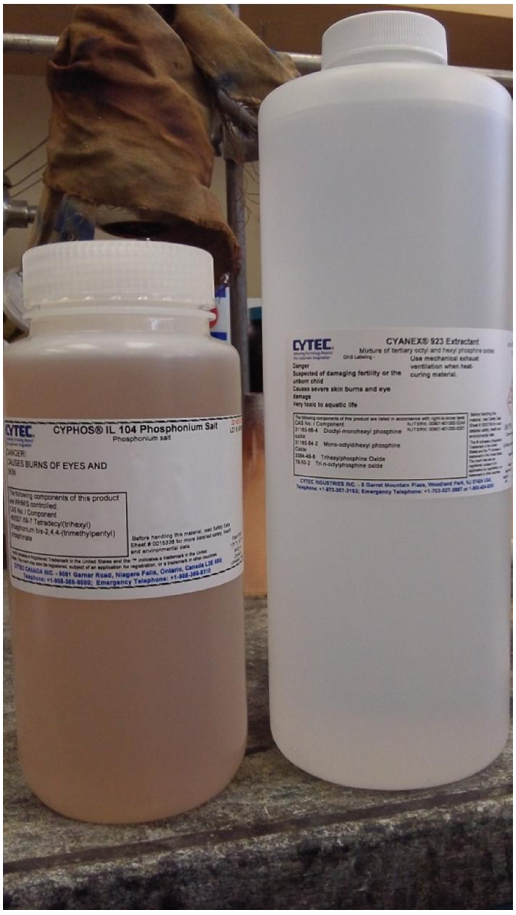


Figure 44 Cytec Industries Cyphos IL 104 and Cyanex 923

A preliminary study of the ability of tributyl phosphate to break down grease was made using the Nyco MIL-PRF-81322 grease. The results of this simple experiment are shown in Figure 45 below. Since MIL-PRF-81322 is made from a 7 cSt base oil, and based on the solubility in Table 25, it is no surprise that tributyl phosphate could dissolve this material. There was a curious purple color to the mixture after dissolving the grease, which may have to do with certain additives of the grease interacting with the solvent.

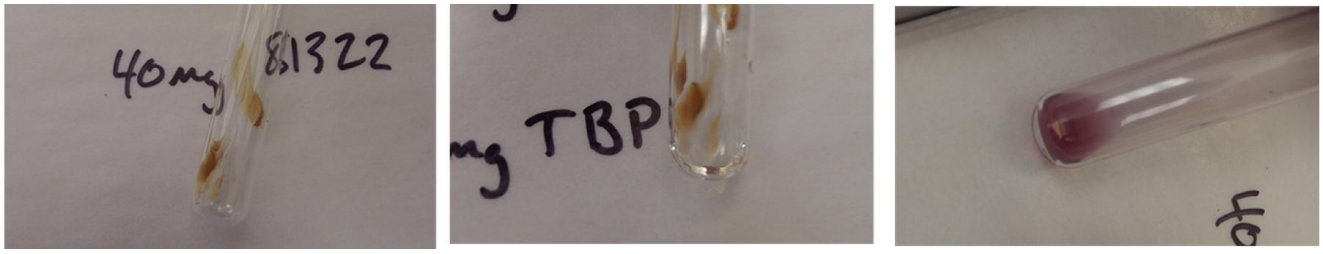


Figure 45 left) MIL-PRF-81322 grease in test tube; center) tributyl phosphate added to tube; right) after 15 min shaking mixture

Microtox® and ECIS Studies with Furanic Solvents

In an attempt to guage and quantify the toxicity of furanic solvents, the rapid and inexpensive method known as the Microtox® assay was selected. In addition, owing to expertise and availability, data from electric cell-substrate impedance sensing (ECIS) was also collected. These tests were carried out by colleagues David Trader, MS and Dr. Valerie Trabosh at the USAEHC Fort Detrick. The Microtox test measures the effect of a substance on the bioluminescence of the bacteria *Vibrio fischeri*, Figure 46. Fluorescence is measured over a period of time and those substances which give a decrease in the magnitude of the light are said to have a negative impact on the organism's normal respiration and metabolism. Hence, such compounds may be toxic to other species as well. Results of this test are typically reported as EC_{50} or the concentration of test substance that causes a 50% reduction in fluorescent activity. The lower the EC_{50} value, the more toxic a test substance is considered to be. This organism lives in a marine environment and so the experiments must be conducted in a 2% saline solution. This presents special challenges in the testing of these furanic solvents. This is due to the fact that these furanic solvents were designed for thier ability to remove hydrocarbon soil and thus might have limited solubility in water, and even less in brine.

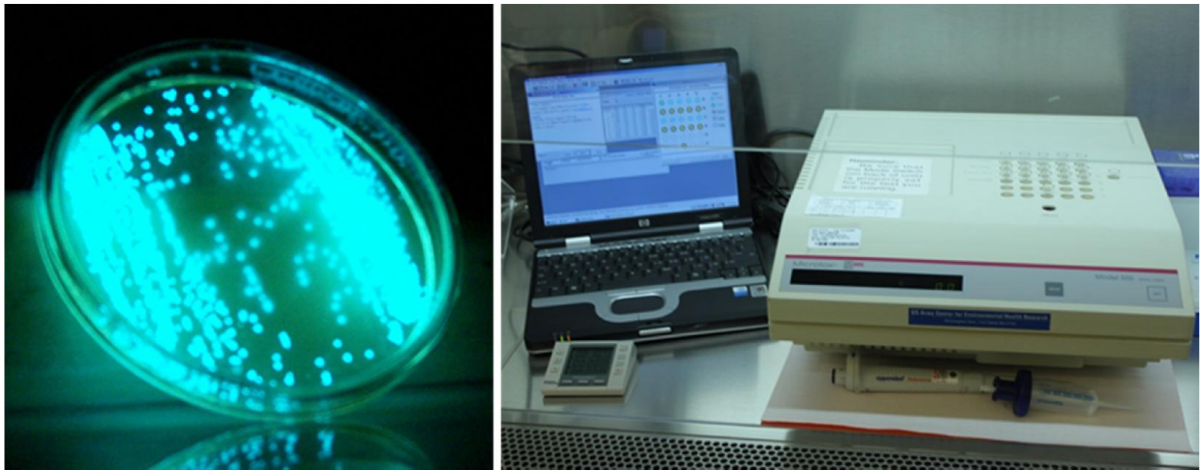


Figure 46 Bioluminescent marine bacteria *Vibrio fischeri* which is studied in the Microtox Assay, along with the Azur Environmental Microtox® Model 500 photometer (right).

The ECIS test was recently developed by Giaever and Keese which employs the rainbow trout gill cells to test for cell morphological changes under various chemical treatments.[47] In the assay, the cells are in an electrical apparatus, a microchip, and the change in impedance is measured. Unaffected cells will continue to show near baseline impedance (ohms Ω) while cells that undergo deleterious changes with exposure to test substance will show a change in the impedance signal owing to changes in cell shape and metabolism. An example of what this data looks like is shown by the plots of the ECIS response to 10% methanol which was used as a training set, Figure 47. The data from eight ECIS chips is shown: 4 tested with control (water, blue lines) and 4 tested with 10% methanol (red lines). As one can see, all four of the 10% methanol treated chips showed a change in impedance, an increase in this case, as compared to

control, representing a 4 for 4 hit rate for this analyte at this concentration. The exact nature of what is physically ocurring to the rainbow trout gill cells is not clear, but what can be said is that there is definitely an impact of this analyte on the cells (shape changes for instance).

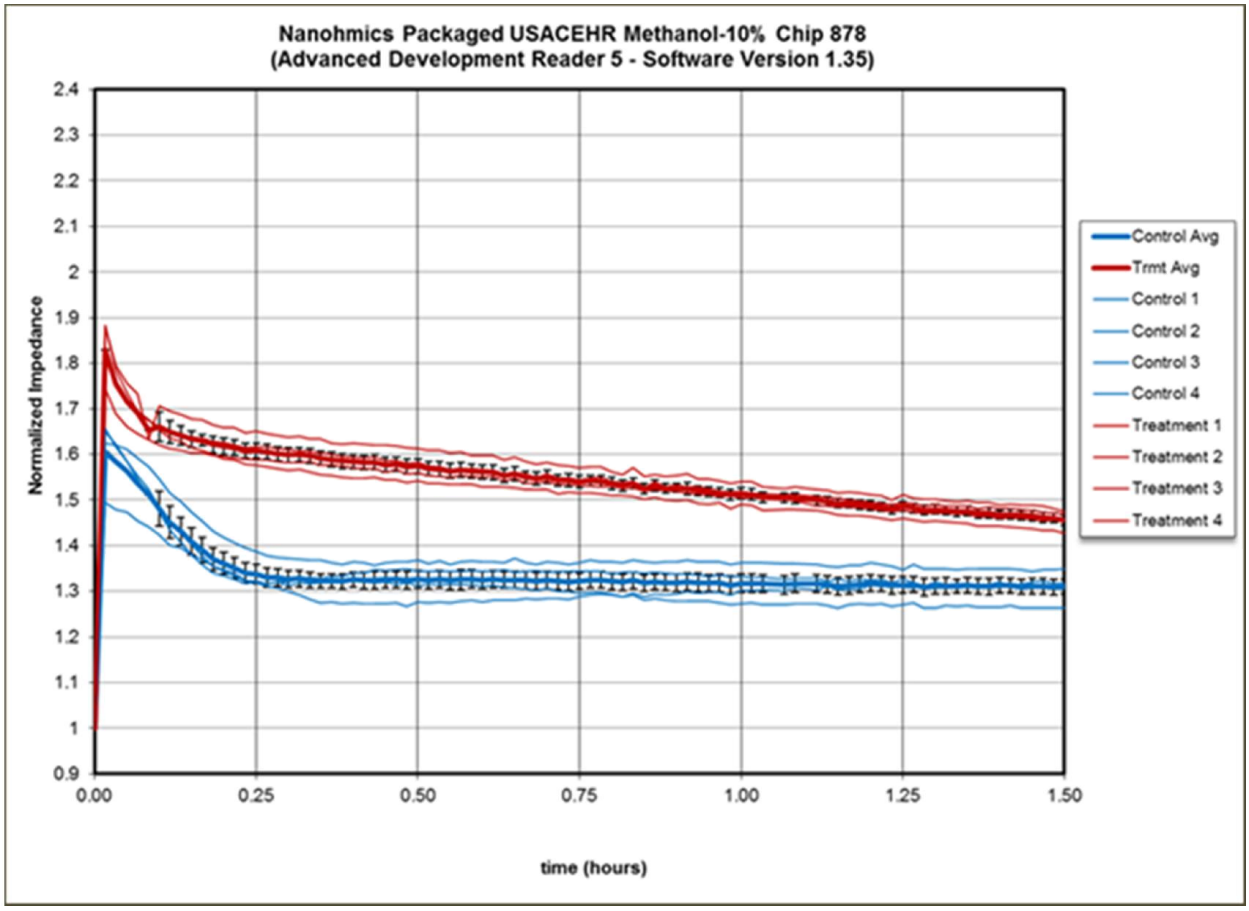


Figure 47 ECIS response to 10% methanol versus control.

A comparison of data between ECIS and Microtox for several important ground water toxins that are checked for on a routine basis by the DoD are collected in Table 26. As one can see, neither test can effectively determine all of the toxins, but when used in conjunction can help to identify a wider range of these important toxins. For example, Microtox is very efficient at detecting cyanide (1.6 mg/L) which is below the military exposure guidelines (MEG), while ECIS can only detect this toxin at 14 mg/L, the human lethal concentration (HLC). Yet, for detecting arsenic, the ECIS assay can do so at four fold lower concentration than Microtox.

Table 26 Microtox/ECIS comparison

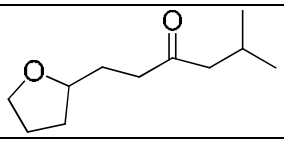
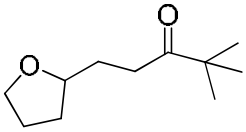
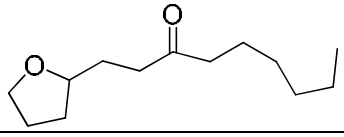
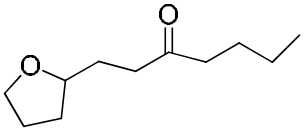
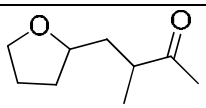
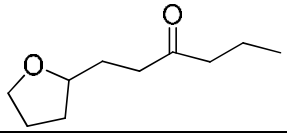
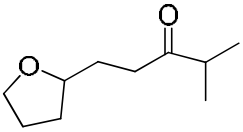
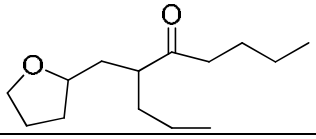
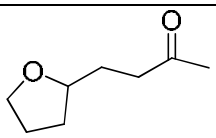
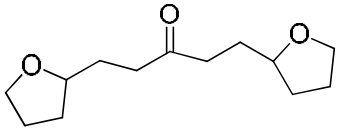
17 Test Chemicals	MEG (mg/L)	Microtox EC50 (mg/L)	ECIS Detection (mg/L)	HLC (mg/L)
Fluoroacetate (sodium)	0.0009	>1989	510	3.9
Mercuric chloride	0.001	0.14	0.25	24.7
Methamidophos	0.002	>239	6,605	1.4
Thallium (sulfate)	0.003	>500	27	13.5
Fenamiphos	0.004	24.2	5.6	0.56
Aldicarb	0.005	32.1	663	0.17
Arsenic (sodium arsenite)	0.02	15.2	4.5	4.5
Paraquat dichloride (cation)	0.05	1136	460	4.6
Nicotine	0.13	69	1000	16.8
Acrylonitrile	0.14	>600	405	600
Pentachlorophenate (sodium)	0.14	1.2	2.5	71.9
Copper sulfate	0.14	0.21	1	103
Methyl parathion	0.15	0.85	21.4	33.6
Toluene	1	14.8	100	840
Cyanide (sodium)	2	1.6	14	14
Phenol	3	29.6	368	91.5
Ammonia	30	>352	100	924
Total between MEG - HLC		6 (10 below 10x HLC)	9 (13 below 10x HLC)	

	Chemical detected in MEG-human lethal concentration range (HLC)
	Chemical detected below MEG value
	Chemical detected between HLC and 10x HLC
	Chemical detected above 10X (HLC)

HLC = human lethal concentration; MEG = military exposure guidelines

Owing to the large number of furanic solvents prepared during the project, it appeared prudent to examine only a group of them to get up to speed in the Microtox/ECIS assay with organic analytes. Thus, it was decided that the family of furanic ketones, if successful, would give data that could provide a useful structure-activity correlation. To empirically determine the solubility of some of the furanic ketones in water, a very simple experiment was carried out. In this experiment, a one liter flask was charged with 100 mg of a furanic ketone solvent, and then 500 mL of water was added. The solvents and data collected are shown in the Table 27. Surprisingly, many of the furanic ketones were soluble at this concentration which was evidenced by a single phase. Even solvents which could dissolve high viscosity PAO such as (**82** and **149**) were soluble in water. Of the samples tested, only two furanic ketones (**77B** and **91**) were not soluble in water which resulted in the compound forming a layer of droplets on the surface of the water since all the furanic ketones have density less than water. These solvents also had the highest molecular weights (>200). Interestingly, furanic solvent (**151**) which was also high molecular weight (226) was soluble in water and this may be due to the fact it has one additional oxygen atom in a second furan ring. Hydrophilic solvent (**151**) is an oxygen analog of hydrophobic solvent (**77B**), which illustrates how heteroatoms can greatly affect solubility.

Table 27 Water solubility of Furanic Ketone

Solvent	Structure	MW	Water Soluble (S) or insoluble (I)
82		184	S
149		184	S
77B		212	I
143		184	S
79		156	S
147		170	S
80		170	S
91		226	I
17		142	S
151		226	S

The required reagent and solutions for the Microtox® assay (freeze-dried *V. fischeri*, osmotic adjusting solution, diluent, and reconstitution solution) were obtained from ModernWater (New Castle, DE). Previous to running the Microtox on the furanic ketones, it was anticipated that a cosolvent might be necessary in order that the compound could be dissolved in the osmotic solution. Typical cosolvents are methanol or dimethylsulfoxide and so the former was chosen and studied in the Microtox assay along with pure water (Millipore), tetrahydrofuran and 2-methyltetrahydrofuran. In accordance with the procedure, analysis of the test solutions is performed at time intervals of 5 and 15 minutes, with the 50% inhibitory concentration (IC50) reported. Each time measurement is done in triplicate for a total of six measurements from which an overall average IC50 value can be obtained by the equation: (average IC50 (5min)) + (average IC50 (15 min)) / 2. It was found that the procedure for running the Microtox sample did not work well with the tetrahydrofuran and 2-methyltetrahydrofuran. In the latter cases, the solvent caused an obvious salt precipitation in the cuvettes which could not be redissolved with vortexing. The preliminary Microtox data for these four liquids is shown in Figure 48.

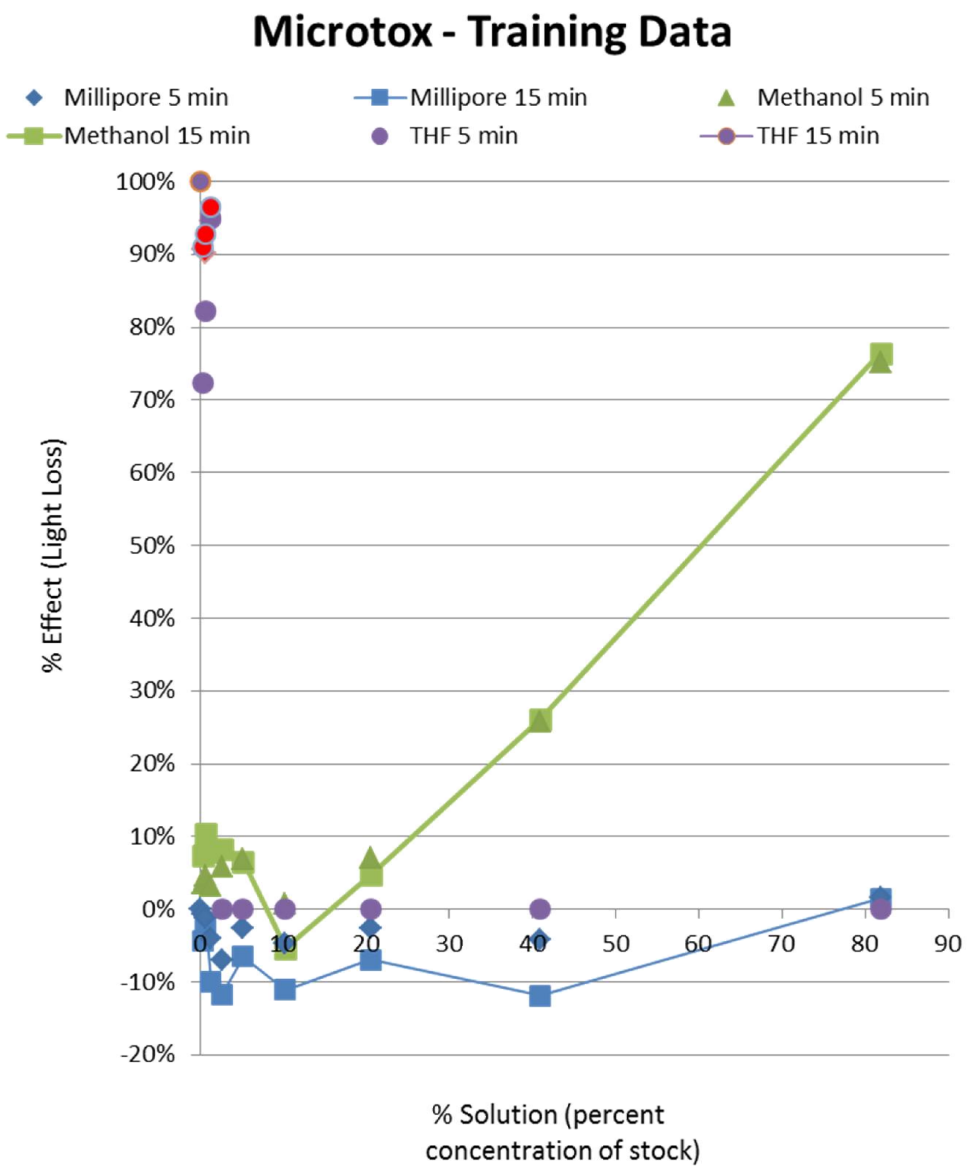


Figure 48 Preliminary Microtox data using Millipore water, methanol, tetrahydrofuran and 2-methyltetrahydrofuran.

As one might expect, the pure water had no effect in the assay and was baseline for all of its measurements, Table 28. The methanol showed a good dose response curve, at low concentration little effect on light production but at higher concentration up to a 70% loss in light activity. From the methanol data the average IC50 at 5 min was found to be 388 g/L and the IC50 15 min was 245 g/L. Thus the overall average IC50 for methanol was 316,000 mg/L, which is considered to be very low toxicity. Unfortunately, the experiments with tetrahydrofuran and 2-methyltetrahydrofuran were carried out using a similar concentration as methanol and

these compounds were too toxic at this concentration and caused immediate loss of light production. This may have also been caused because these solvent caused immediate salt precipitation to occur in making up the sample dilutions.

Table 28 Microtox training data with water, methanol, tetrahydrofuran and 2-methyltetrahydrofuran.

Sample	IC50 (5 min)	IC50 (15 min)
Millipore	Not calculated (neg control)	Not calculated (neg control)
Methanol	388 g/L	245 g/L
THF	Too High, requires dilution	Too High, requires dilution
2-methyl THF	Too High, requires dilution	Too High, requires dilution

Eventually it was discovered that the solvents tetrahydrofuran and 2-methyltetrahydrofuran could be made into usable solution for the Microtox by pre-diluting into 40 mL Millipore water and then making up the sample specimen from these mixtures. And in this manner, the other furanic ketone sample specimens were made and these gave the Microtox data shown in Table 29. Each solvent was run through Microtox in triplicate. These organic solvents gave wide dose response curves unlike metals which have very steep curves.

Table 29 Microtox and ECIS data for furanic ketone solvents

Sample	Structure	IC50 (5 min)	IC50 (15 min)	Microtox AVG IC50 (mg/L)	ECIS response @ Mtox IC50 (mg/L)
Methanol		388 g/L	245 g/L	316,000	100,000 (4/4) 10,000 (2/4) 1,000 (0/4)
THF		1.12, 0.712, 0.753 g/L: AVG: **862 mg/L**	1.135, 0.933, 0.934 g/L **AVG: 893 mg/L**	**878**	**26,340 (3/3)** 8,780 (2/3) 1,000 (0/3)
2-methyl THF		110, 106, 134 mg/L: **AVG: 117 mg/L**	129, 118, 163 mg/L **AVG 137 mg/L**	127	127 (0/3) 1,360 (1/3) 13,600 (1/3) **136,000 (3/3)**

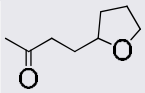
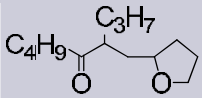
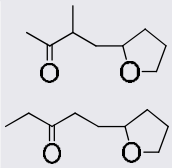
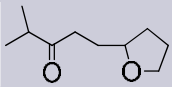
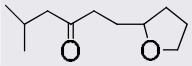
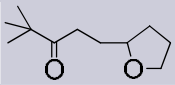
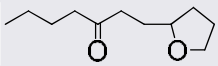
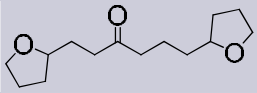
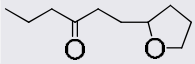
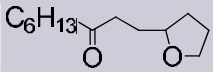
#17		305, 286, 292 mg/L **AVG: 294 mg/L**	354, 339, 346 mg/L **AVG: 346 mg/L**	320	320 (1/3) 978 (0/3)
#91		204, 124, 135 mg/L **AVG: 154 mg/L**	257, 163, 193 mg/L **AVG: 204 mg/L**	179	3/3
#79		142, 167, 138 mg/L **AVG: 149 mg/L**	192, 195, 178 **AVG: 188 mg/L**	169	0/3
#80		142, 133, 135 mg/L **AVG: 137 mg/L**	179, 147, 128 mg/L **AVG: 151 mg/L**	144	0/3
#82		91.7, 77.9, 95.1 mg/L **AVG: 88.2 mg/L**	108.9, 89, 112.9 mg/L **AVG: 103 mg/L**	95.6	0/3
#149		61.4, 66.1, 62.2 mg/L **AVG: 63.2 mg/L**	66.3, 75.6, 76.6 mg/L **AVG: 72.8 mg/L**	68	0/3
#143		57.0, 52.1, 53.8 mg/L **AVG: 54.3 mg/L**	62.3, 57.8, 63.5 mg/L **AVG: 61.6 mg/L**	58	0/3
#151		23.6, 22.3, 24.2 mg/L **AVG: 23.4 mg/L**	28.4, 25.8, 24.2 mg/L **AVG: 26.1 mg/L**	24.8	1/3 248 (0/3)
#147		15.6, 28.0, 16.7 mg/L **AVG: 20.1 mg/L**	18.0, 19.9, 19.7 mg/L **AVG: 19.2 mg/L**	19.7	0/3
#77B		2.25, 1.98, 1.75 mg/L **AVG: 1.99 mg/L**	2.56, 2.40, 1.94 mg/L **AVG: 2.33 mg/L**	2.11	0/3 169 m/L: 3/3

Table color legend:

Ecotoxicity to Aquatic Organisms

Very Highly toxic
(< 0.1 mg/L)

Highly toxic
(0.1 – 1.0 mg/L)

Moderately toxic
(1.0 – 10 mg/L)

Slightly toxic
(10 – 100 mg/L)

Practically non-toxic
> 100 mg/L

https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/technical-overview-ecological-risk-assessment-0

In general, for all of the solvents tested, the toxic effect occurs immediately as both the 5 and 15 minute EC_{50} data are very similar. Addition of a methyl group to tetrahydrofuran increases its toxicity slightly. The EC_{50} data for the furanic ketones appeared reasonable indicating that the solvents were sufficiently soluble in the bioassay medium. All the furanic ketones solvents were more toxic than the parent tetrahydrofuran with an EC_{50} range from ~2–300 mg/L. In general the toxicity of the solvents tended to increase directly with molecular weight, compare **17** and **91**. There appears to be significant correlation of Microtox test data with other bioassays such as fathead minnow (*Pimephales promelas*) acute toxicity. The latter bioassay is used by the EPA to determine ecotoxicity categories for terrestrial and aquatic organisms, the LC_{50} or concentration at which one half of the tested species expire. By this assay, pesticides and other chemicals are classified as 'slightly toxic' (10–100 mg/L), 'practically nontoxic' (>100 mg/L) and 'moderately toxic' (>1–10 mg/L). If the Microtox assay results of the tetrahydrofuranic ketones were to be directly correlated with the fathead minow acute toxicity test, a relationship shown to be statistically significant among hundreds of organic compounds,[48] then the solvents can be categorized by the coloring scheme shown in the Table 29. Solvents **17**, **91**, **79** and **80** were all non-toxic; solvents **82**, **149**, **143**, **151** and **147** were only slightly toxic; and only the long chain **77B** was moderately toxic. Although all the furanic solvents made in the project were not tested

in the Microtox, it would appear from the results of these furanic ketones that the others would likely be non-toxic or only slightly toxic since they are not far removed structurally speaking.

The ECIS response rate of these solvents is also collected in Table 29. The test was used to determine 'hit' or 'non-hit', meaning that there was effect or no effect with exposure to solvent using the previously determined Microtox EC50 concentration. For example, in the case of methanol (Microtox EC50 = 316,000mg/L), a concentration of 100,000 mg/L brought about a 4 for 4 hit rate in the ECIS, while diluting to 10,000 mg/L only 2 out of 4 hits and further to 1,000 mg/L zero hits out of 4. With this data one could say that because the ECIS is getting a 50% hit rate at 10,000 mg/L, the ECIS is more sensitive to methanol than is the Microtox assay. With tetrahydrofuran, the ECIS result was different, 1000 mg/L produced zero hits out of three chips, while high concentrations began to produce hits: 2 out of 3 at 8780 mg/L and 3 out of 3 at 26340 mg/L. Thus, ECIS was less sensitive with tetrahydrofuran than the Microtox assay. And the same was true with the structurally similar 2-methyltetrahydrofuran. Only the furanic ketones **91** gave a 3 for 3 response rate in ECIS for the same concentration as Microtox EC50. Solvent **17** and **151** had a one for 3 response rate in ECIS. For solvents **79**, **80**, **82**, **149**, **143**, **147** and **77B** there was a zero for 3 ECIS response at Microtox EC50 concentration. Of this latter group, typically going up in concentration (100X) caused unity in response, **77B**. Solvents **17** and **151** which had a hit at Microtox concentration, showed no hits in ECIS when diluted 10 fold, as one would expect to observe. Because the bulk of the furanic ketones solvents were poorly responsive in the ECIS assay, this might indicate that rainbow trout cells, more closely related to humans than *V. fisherii*, might indicate these compounds are not particularly toxic.

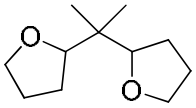
Conclusions and Implications for Future Research

Over three dozen furanic solvents were prepared during this one-year, SERDP Exploratory Development project. Many of these oxygenated hydrocarbon solvents were shown to have sufficient hydrocarbon solubility over a wide viscosity range of base oils, both mineral and synthetic, typical in the manufacture lubricants used by the DoD. The concept that simple chemical derivatization of furfuraldehyde, and its allied species furan and 2-methylfuran, into solvents with non-polar character, and hence degreasing potential, proved to be a viable strategy. Using authentic lubricant base oils was an easy and accurate method for empirical determination of the solubility of test solvent. The useful furanic solvents covered a range of easily prepared functional groups including ether, ester, alkene/alkane and ketone. The furanic esters required longer chain alcohol or carboxylic acid to achieve hydrocarbon solubility at the 10 cSt base oil level. But such a length carboxylic acid could be esterified just as well with simple alcohols to be effective (e.g. methyl caproate dissolves 65 cSt PAO). The hydrocarbon solubility of furanic ketones was based primarily on the ketone used in the derivatization of furfural. The furanic ketones had much higher flash points compared to the parent ketones which were generally highly flammable. The furanic ethers were excellent solvents regardless of the aliphatic content. The flash point of the furanic ethers could be modified by increasing molecular weight. The furanic carbonates were not found to be useful as hydrocarbon solvent, it would appear that they require a medium chain fatty alcohol to offset their polarity. However, the dialkyl carbonates made from alcohols of chain length ≥ C4 were excellent solvents that could be made easily from biobutanol and similar natural alcohols. The introduction of nitrogen tended to make a solvent more polar, nevertheless the *N*,*O*-dialkylcarbamates could dissolve up to 10 cSt PAO. Some caution should be taken as carbamate with similar structure has been shown to have biological activity in insects.[49] Although only one member was made, it appears that gamma-pyrone is another class from which excellent hydrocarbon solvents can be made.

Given base oil specifications of a lubricant it was easy to match furanic solvent for optimal solubility and cleaning. Furanic solvent downselected from solubility screening were shown to dissolve and remove two standard military specification greases from roller bearings. The series of furanic ketones and their solubility gradient was an effective tool by which to measure viscosity of polyalphaolefin. Most of the solvents had freezing points less than -30 °C which could make the solvents useful in cold climates. The flash points of the solvents were generally above the 60 °C cutoff point similar to current technologies. Except in two instances, all of the furanic solvents had evaporation rates less than MIL-PRF-680II degreasing solvent.

The toxicity screening by the Microtox assay appeared to be superior to the ECIS assay for testing organic solvents. The EC50 data collected on the furanic ketones showed that they are generally in the non-toxic concentration range. Although only a small subset of the total solvents were tested in this manner, it would appear that all of the furanic solvents would have similar toxicity profiles owing to their structural similarities.

Near the end of the project some product brochures from the US company Pennakem LLC became available. In their portfolio, it was discovered that Pennakem LLC manufactures/sells one of the furanic solvents made and shown to be an excellent solvent, the gem difuranic alkane (**83B**) which they sell as DTHFP (ditetrahydrofurylpropane). This compound is a polymerization modifier in the manufacture of high performance tires.[50] This information was not known at project start. This solvent was shown to have excellent solubility for all of the soils tested in this project and its flash point (98 °C) is in the safe range for Type II and III degreasing solvents. So the project has inadvertently found a new use for this material. In one of several phone conversations with Mr. Barry Roberts, the North American sales manager for Pennakem LLC, a price quote of $9/pound for this material was given. By unit conversion (density ≅ 1 g/mL) this comes out to about ~$4000 per 55 gallon drum which already isn't too far removed from the price for the same amount of the current degreasing technology MIL-PRF-680II ($1000)[2] or a new degreaser on the block, Navsolve ($2414).[51] Anyway prices are always subject to change and the point here being that the material is on their shelf, ready to ship, and likely available large quantities. Furthermore, Mr. Roberts expressed interest in the idea of working together under the umbrella of a Cooperative Research and Development Agreement (CRDA) which might allow for access to large quanitities of furanic solvent (**83B**) and perhaps other furfural derivatives Pennakem has available that were not studied here. Having 35 gallons of material available with which to fill a parts washer could allow for a pilot scale demonstration evaluation at a DoD depot site.



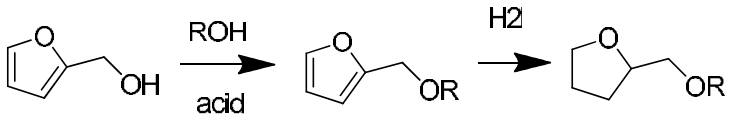
DTHFP

To take the next step for trying to qualify a solvent such as (**83B**) as a degreasing fluid, and/or other furanic solvents made during this project, more engineering based testing needs to be done. Such test must include further materials compatibility such as: total immersion corrosion of aircraft materials, stress corrosion of titanium, and sandwich corrosion. There are private laboratories which do this type of research exclusively such as SMI Incorporated (Miami) who have tested many solvents for government organizations. Testing for toxicity might not have been the best tact, but testing for biodegradation would make more sense. There are common less expensive varieties out there such as the 28 day biodegradation test. It must be emphasized that large quantities of solvent (multi-gallon) must be available for these test which is essentially destroyed in the process.

The research carried out with the Perkin reaction may have appeared to be a bit self-indulgent. However, the potential of this new technology discovered during this project could be tremendous. The Perkin reaction, at least in the form shown here, is a very 'green' process as there is no solvent used and no exotic transition metal catalyst is necessary either. Just a cursory glance at the oleochemical industry (175 million metric tons 2013) shows the magnitude at which fatty acids are produced annually, where the unit of measure is railroad cars. The US is a major producer of both vegetable and animal fats so domestic sources are plentiful. The Perkin reaction with furfuraldehyde causes decarboxylation of the fatty acid under relatively mild

conditions which otherwise requires high temperature, high pressure and most often an expensive catalyst. Further study of this process, whose mechansim is not clear even today, will be necessary to increase yield of alkenylfuran. The products from this reaction have been shown to be excellent degreasing solvents but these products could have many other uses such as combustion fuels, lubricants, polymers, healthcare products, paints, *et cetera*.

Only a few members of the furanic solvent classes were prepared after it became apparent of their utility. Furanic ethers were very easy to prepare and likely this could be scaled up without issue here at China Lake. It could be possible to make the furanic ethers using furfuryl alcohol as shown below based on some literature precedent which could eliminate the use of halogenated intermediates.



Admittedly, the furanic solvents need to be tested against a wider array of lubricants which might be accessable by partnering with one of the large DoD depot sites (Robins AFB, Cherry Point or Jacksonville) who deal in cleaning processes as one of their primary functions. These large sites generally have experience in SEDRP/ESTCP programs.

Other degreasing ideas that came about from this project would be to use solvents that had a wider flash point safety margin so that they could be used at elevated temperature, such as the alkyl phosphorus liquids shown, low viscosity PAO (normal alpha olefin dimer/trimer mixes) or vegetable oils. Such solvents that could be used at higher temperatures where it is anticipated that substances such as grease, which are difficult to clean without some mechanical input, might simply 'melt off' for a hands free cleaning solution. Phosphorus containing substances are known to have lower fire potential.

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[17] Geminally or gem substituted indicates the two substituents are bonded to the same atom.

[18] GW Huffman et al US Patent 4,577,035, 18 March 1986.

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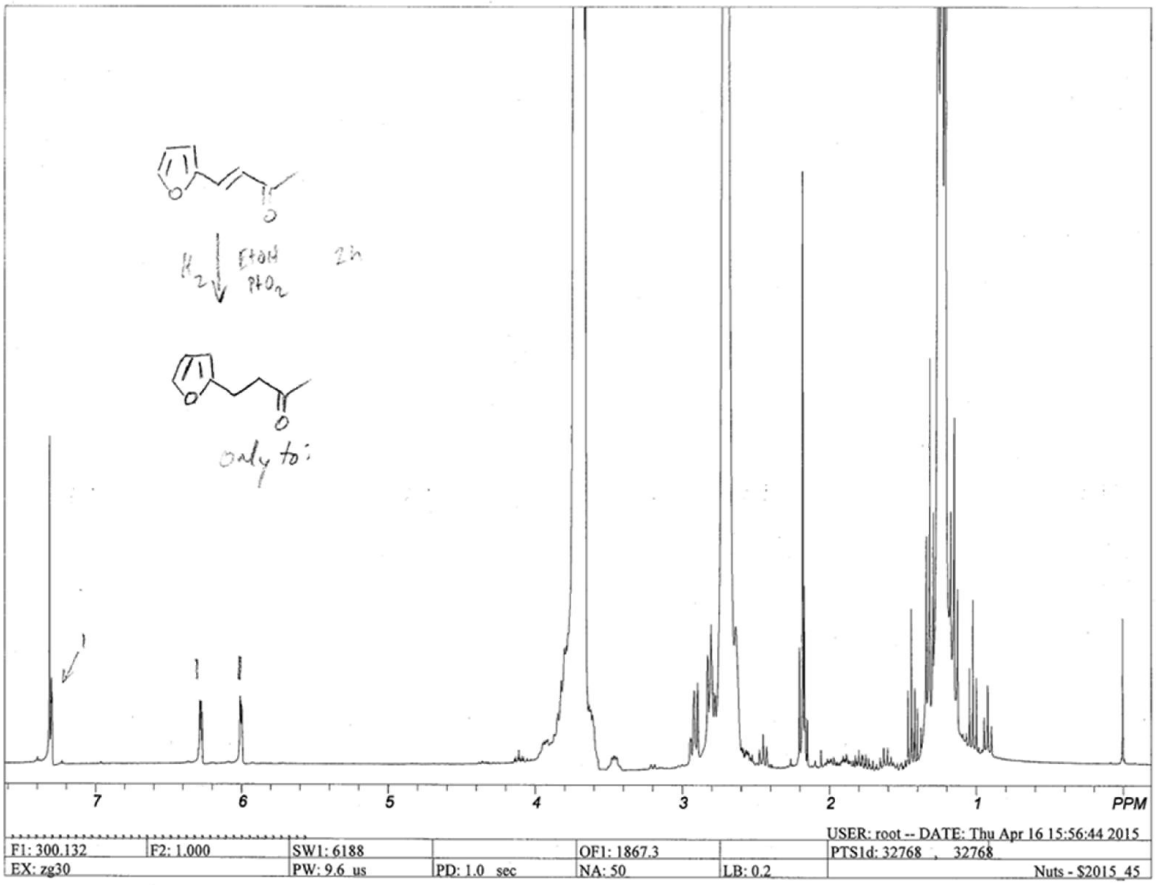
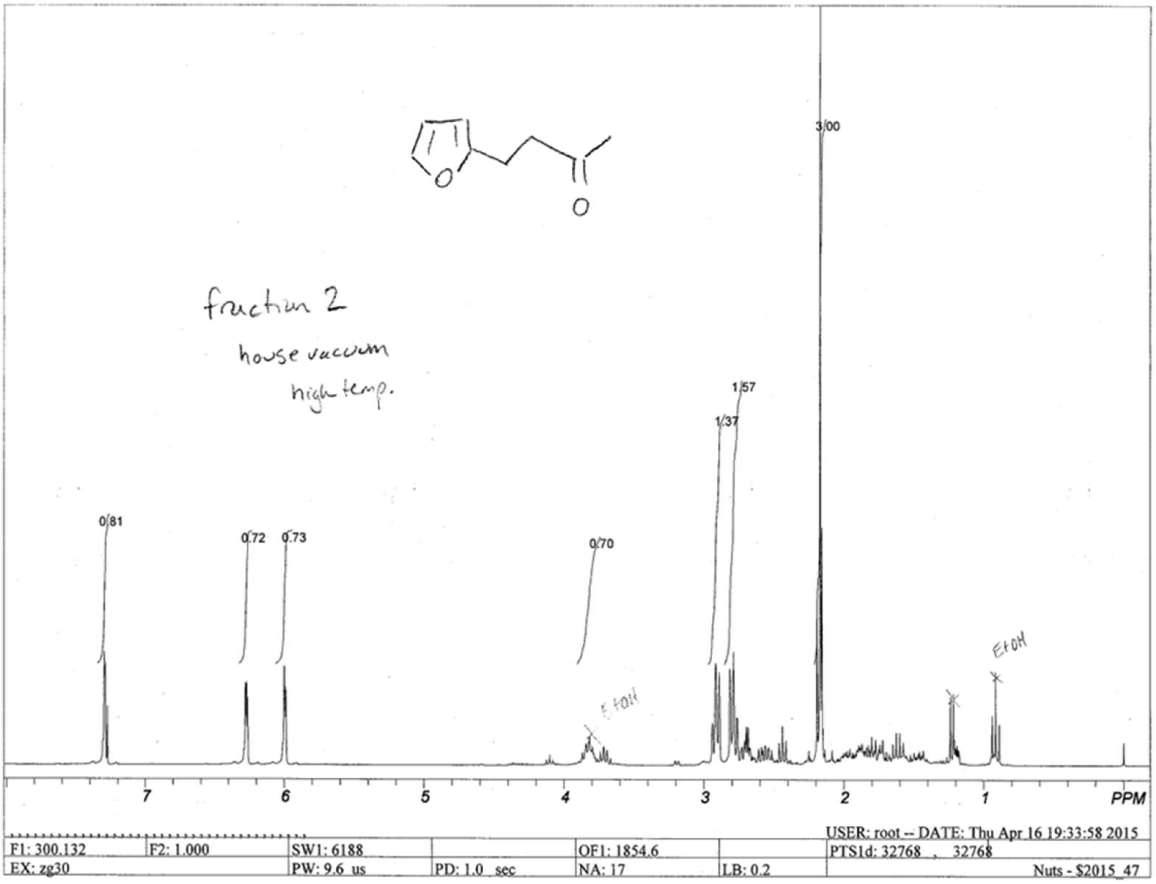
Appendices

Appendix A NMR Data from Hydrogenation Research

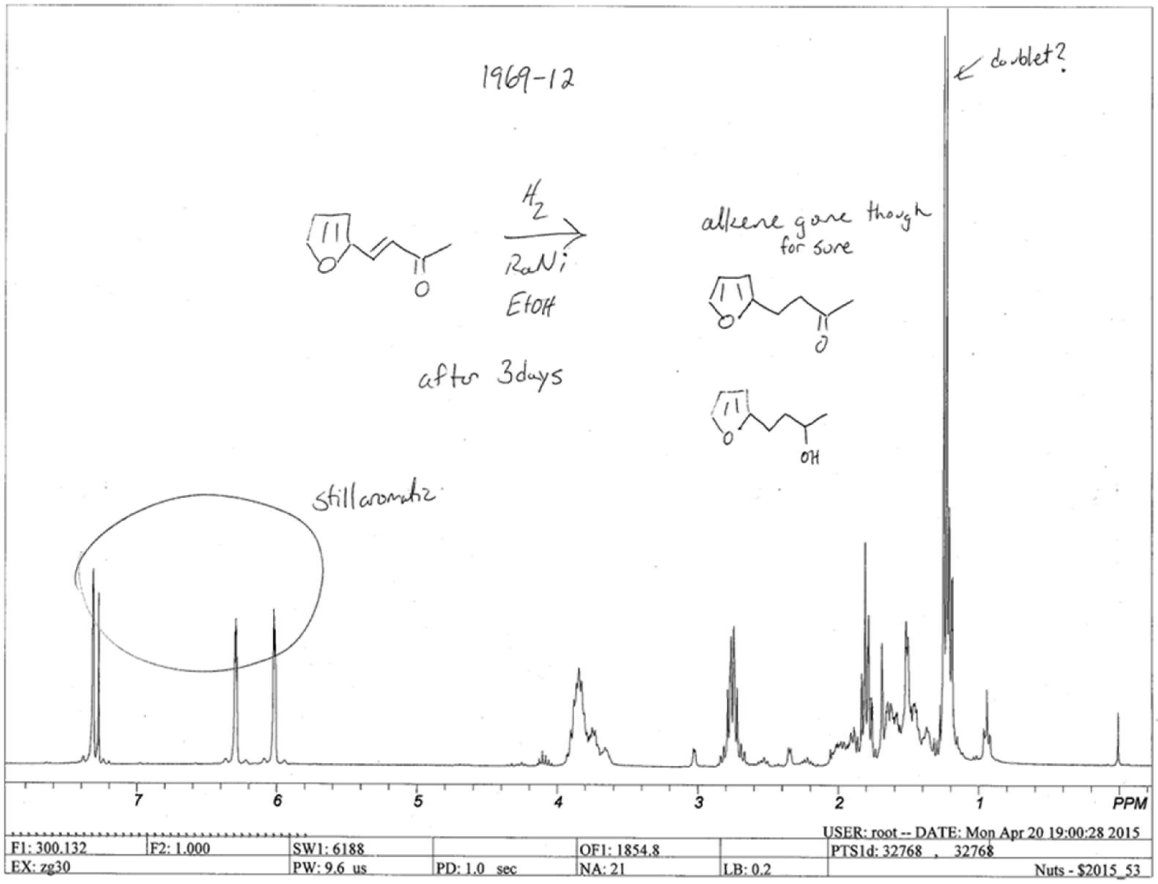
Incomplete reduction of **10** with platinum oxide



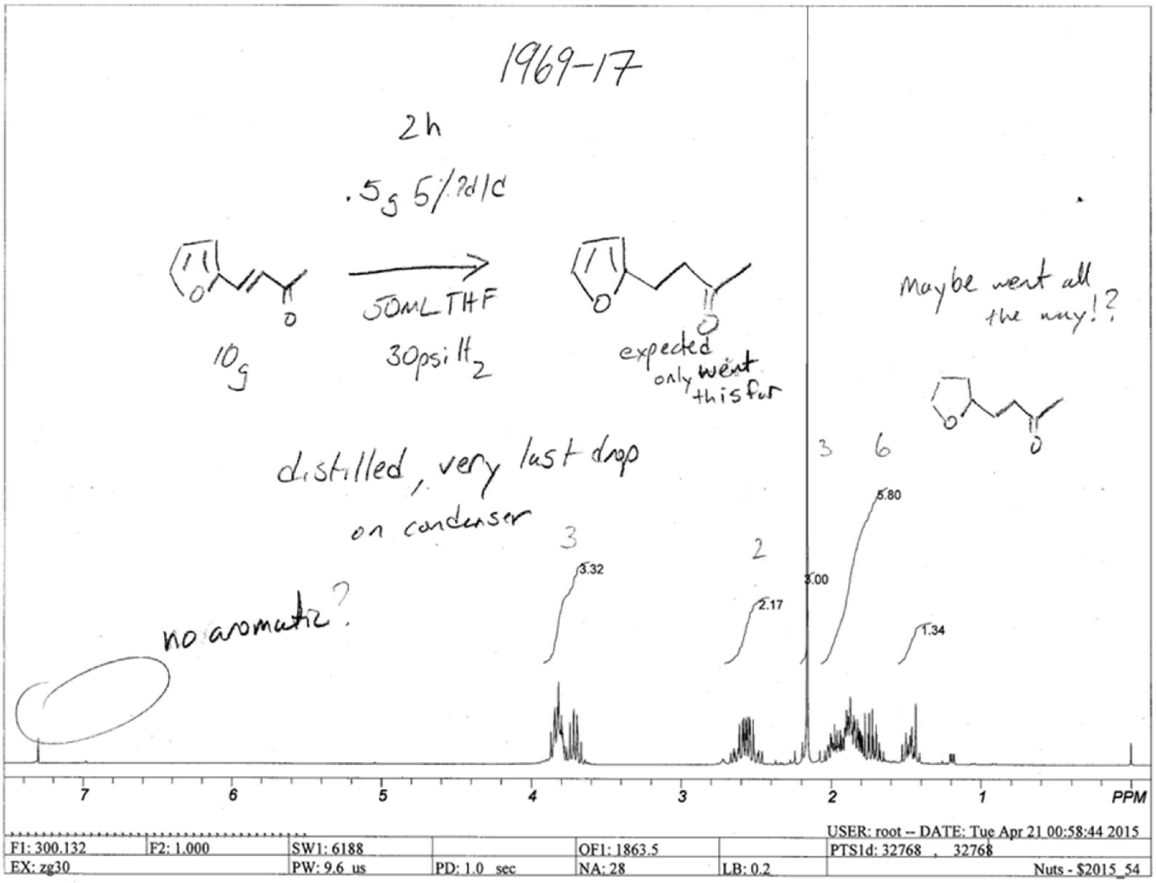
Isolation of furanyl ketone (**45**) from incomplete platinum oxide reduction of furfurylidenone (**10**)



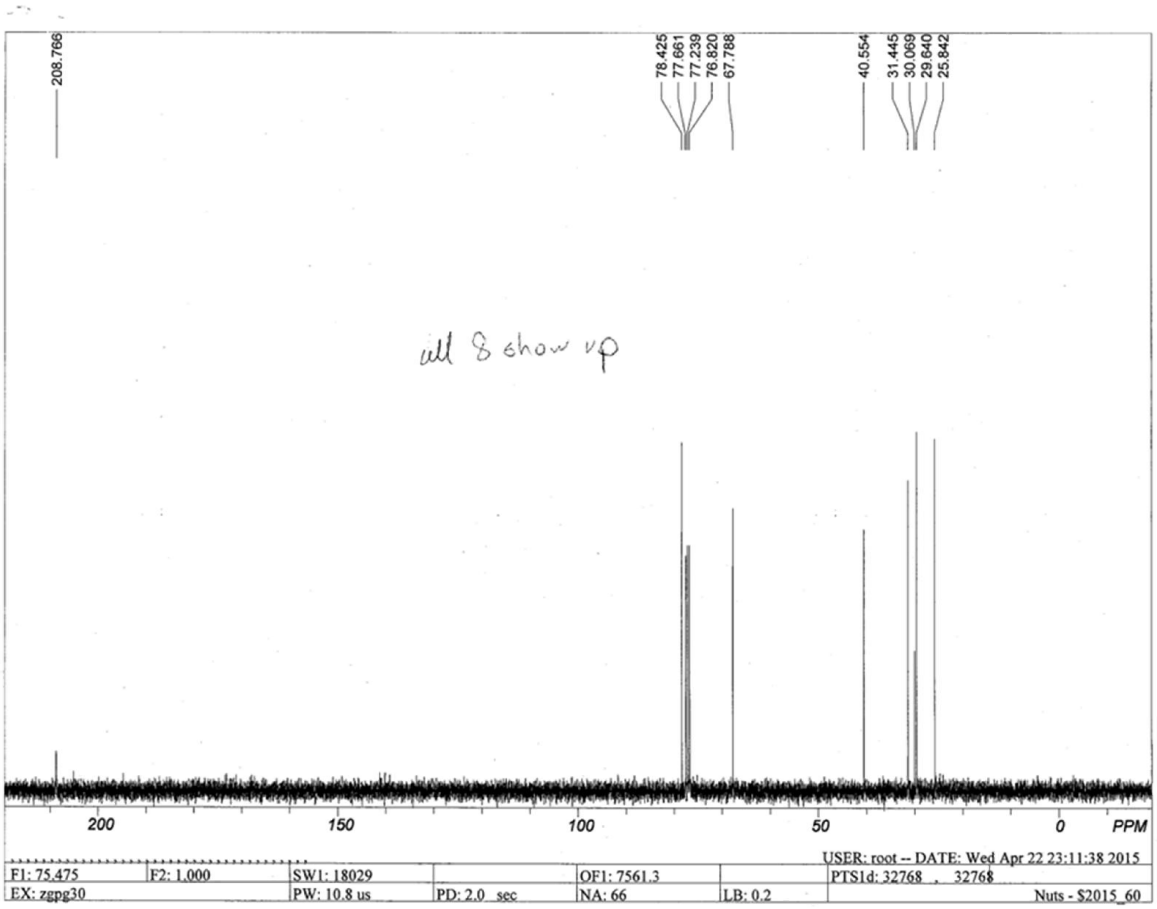
Mixture of product with possible ketone reduction from Raney Nickel hydrogenation of **10**



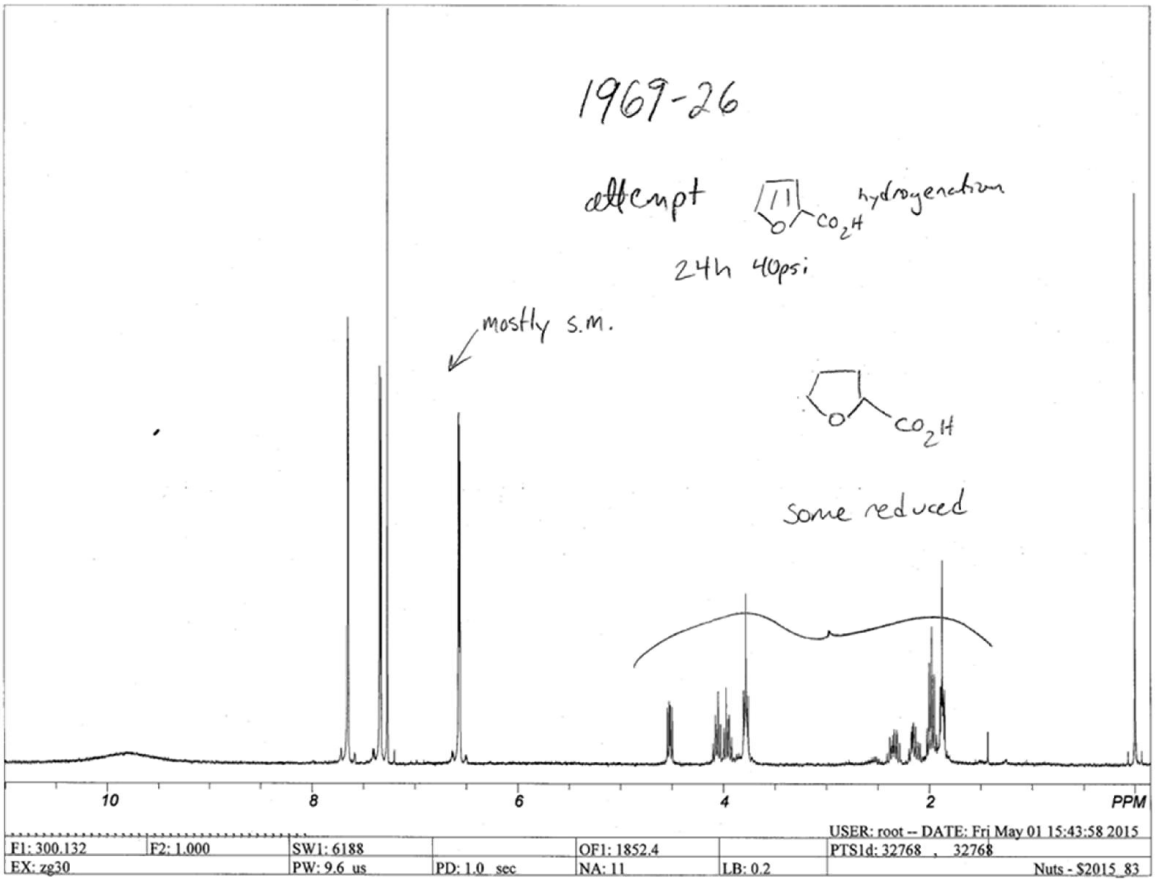
Complete reduction of **10** to **17** by the standard reduction conditions; Proton NMR of **17**



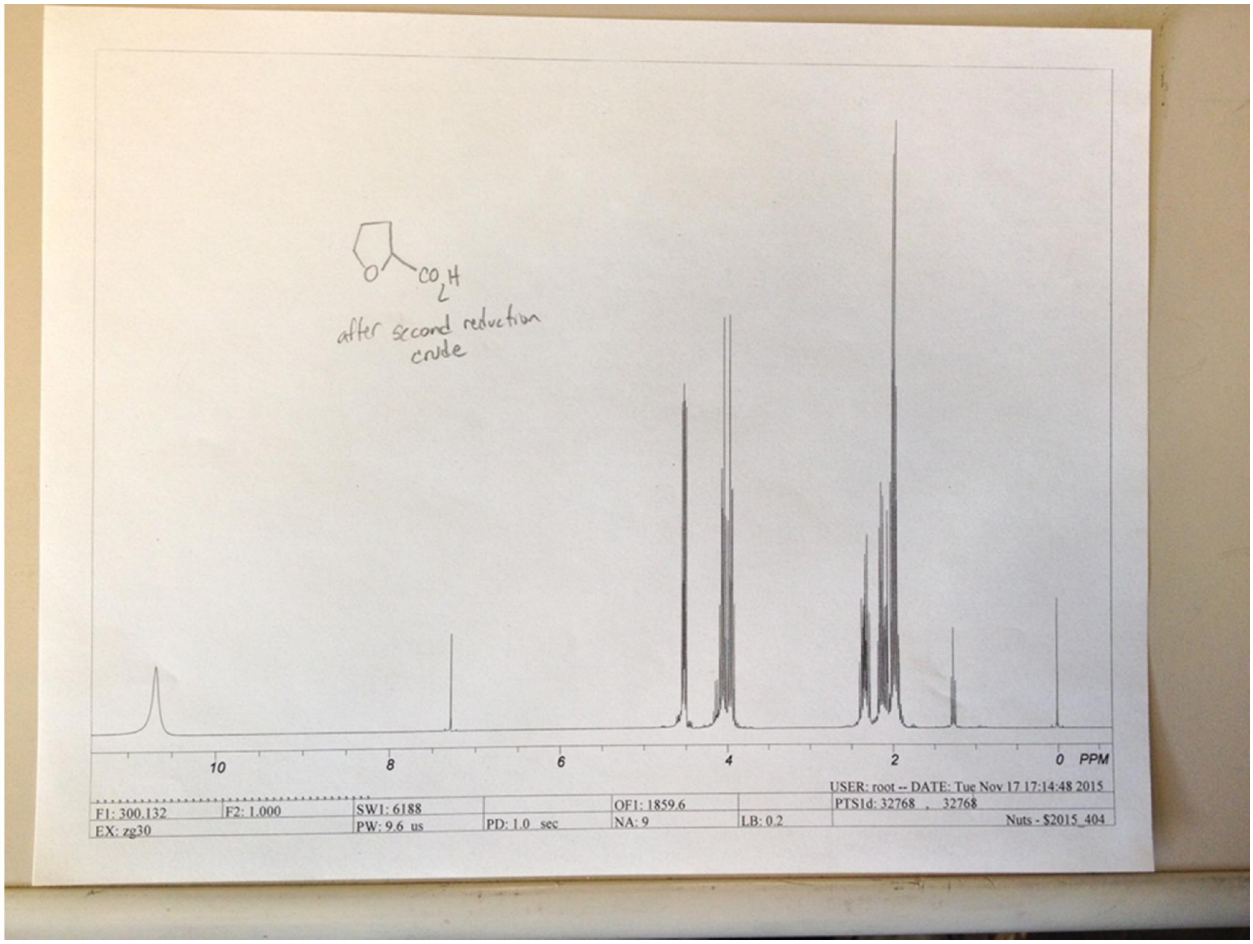
Carbon NMR of **17**



Attempted reduction of 2-furoic acid in tetrahydrofuran solvent, incomplete reduction.

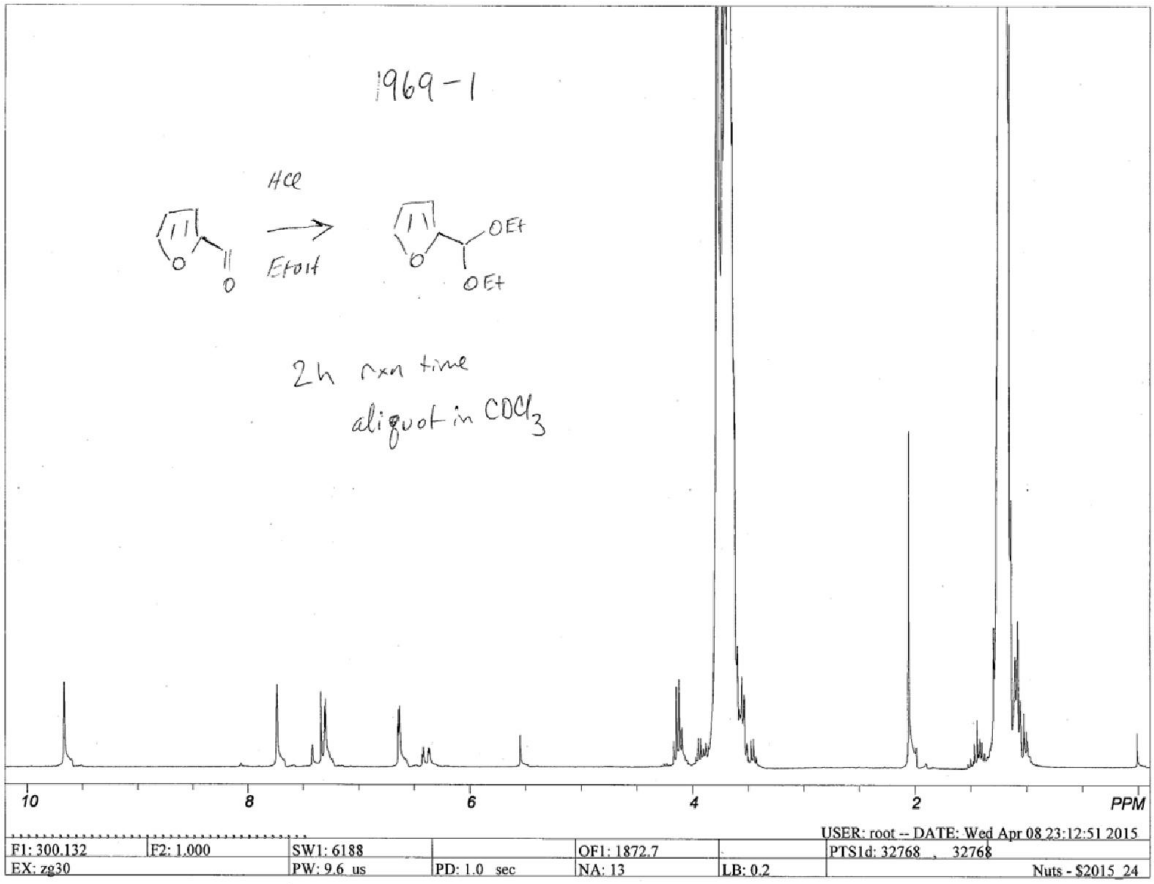


Reduction of 2-furoic acid to 2-tetrahydrofuroic acid (**26**) when ethyl acetate used as solvent, complete reduction.

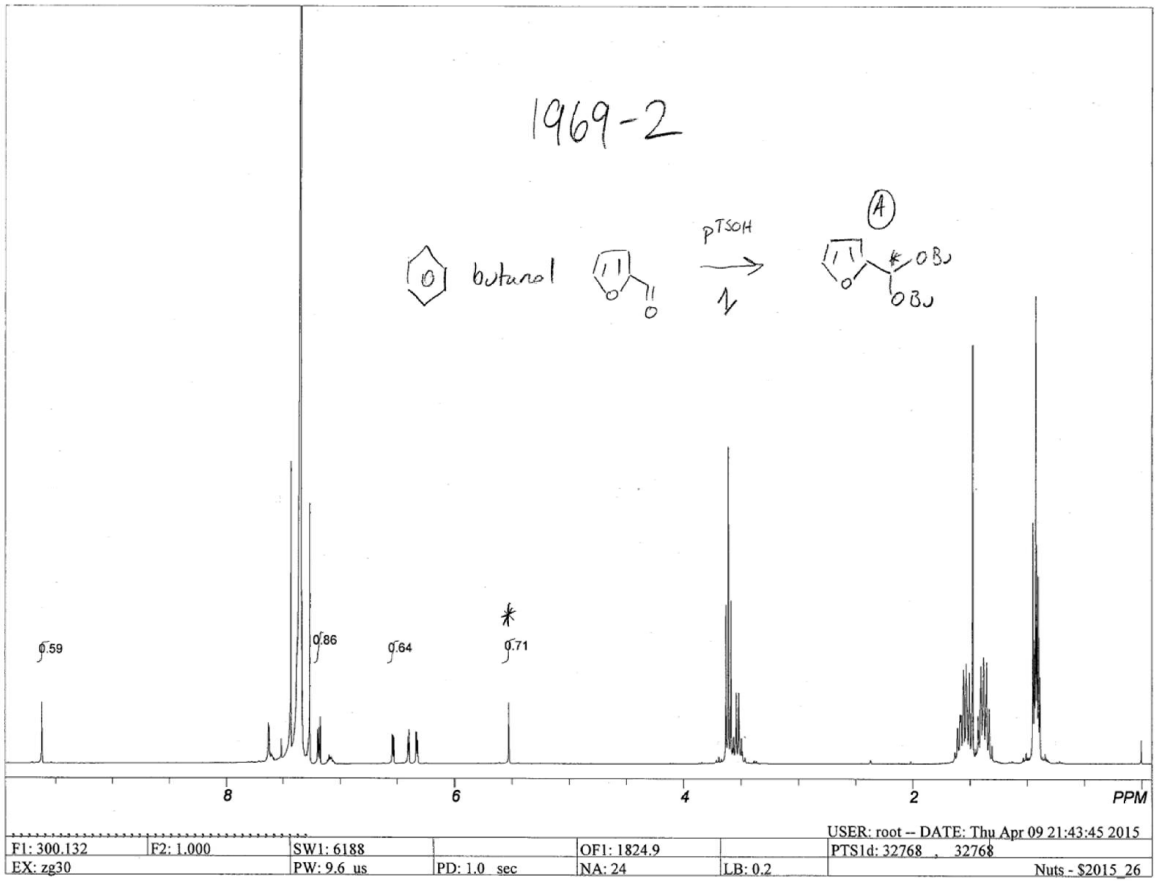


Appendix B NMR Data of the Furanic Acetals

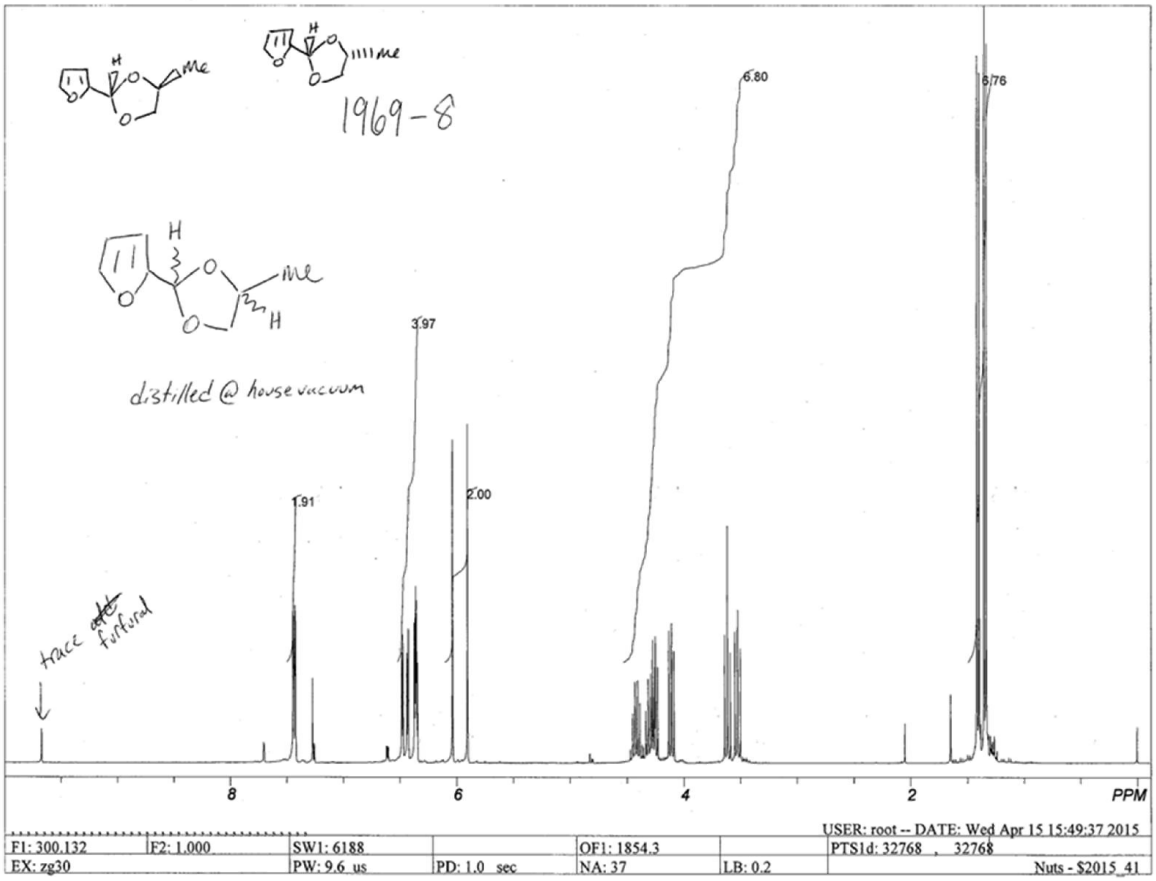
Incomplete acetalization of furfural with ethanol



Incomplete acetalization of furfural with butanol with azeotropic distillation

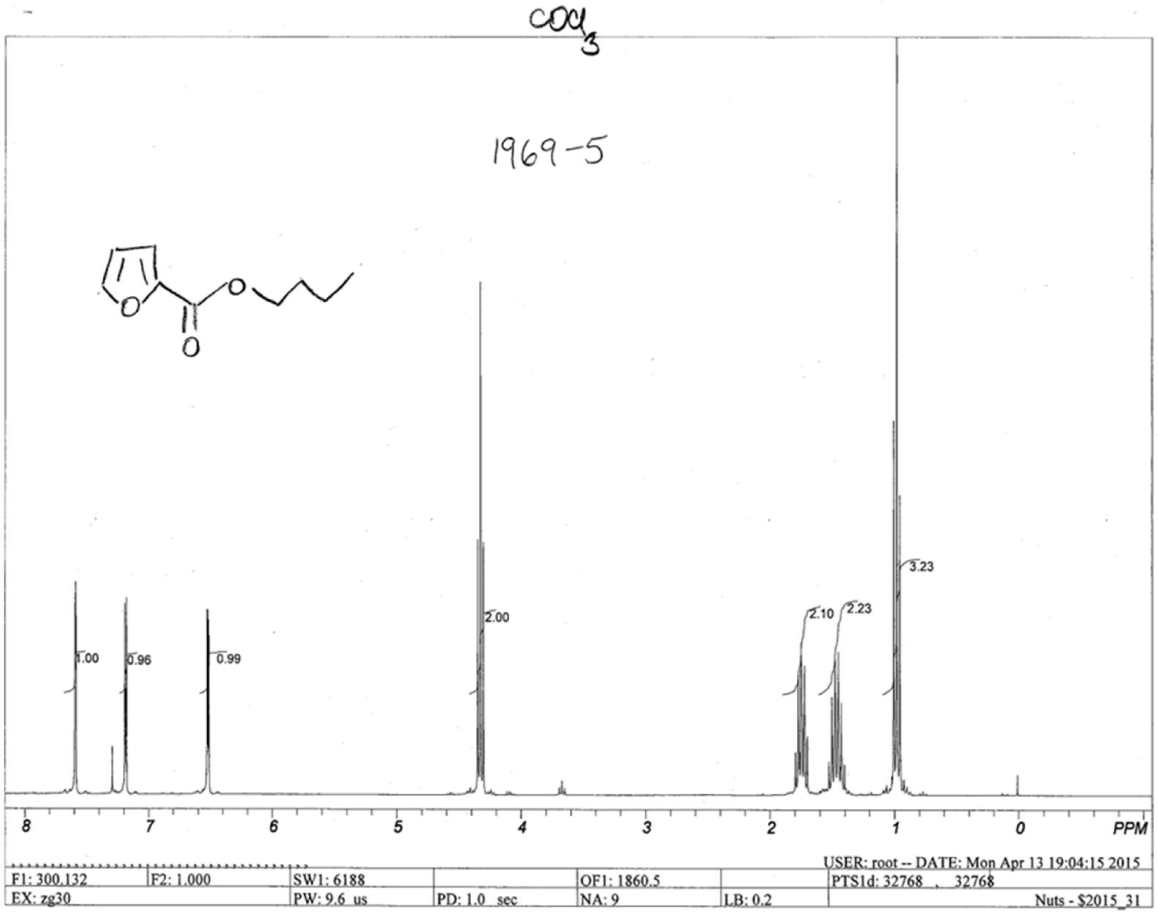


Successful acetalization of furfural with 1,2-propanediol to make furanyl acetal (**8**)

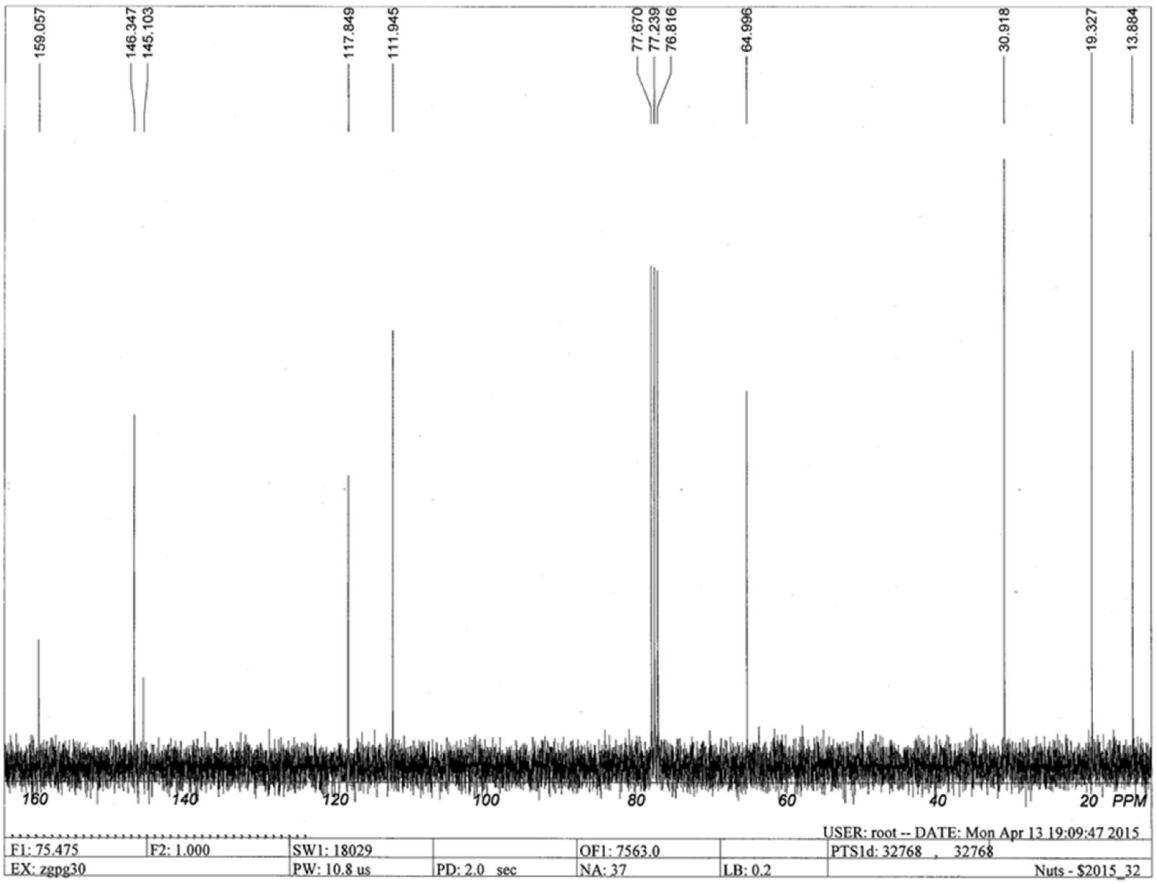


Appendix C NMR Data for Furanic Esters

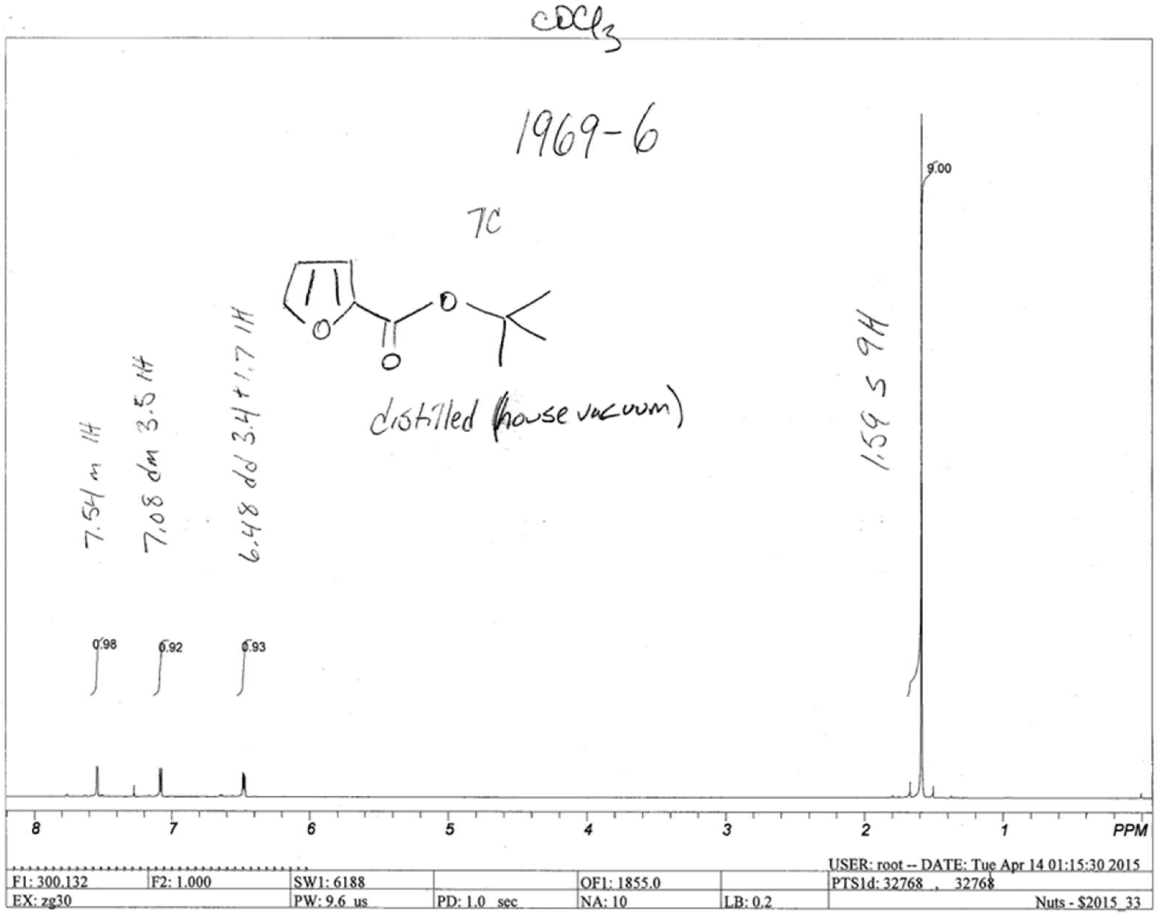
Proton NMR of butyl 2-furoate (**152**)



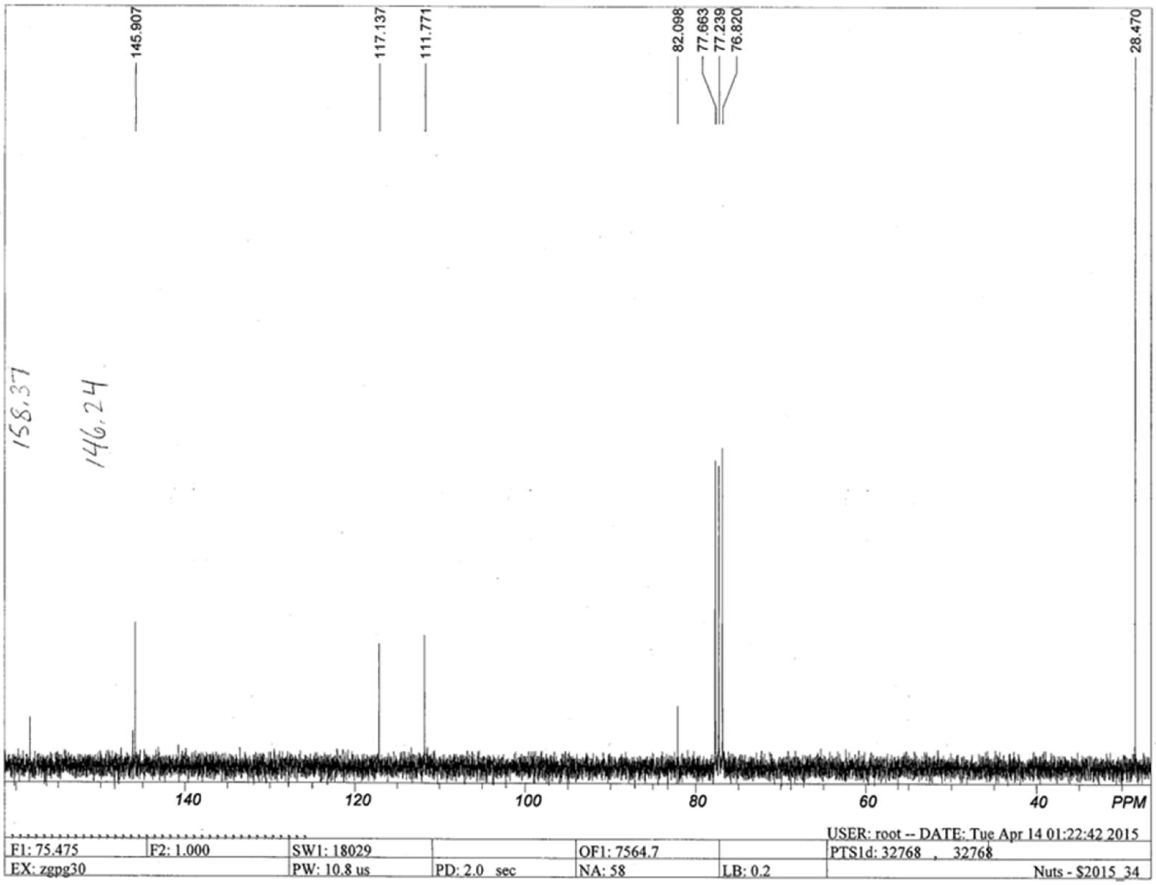
Carbon NMR of butyl 2-furoate (**152**)



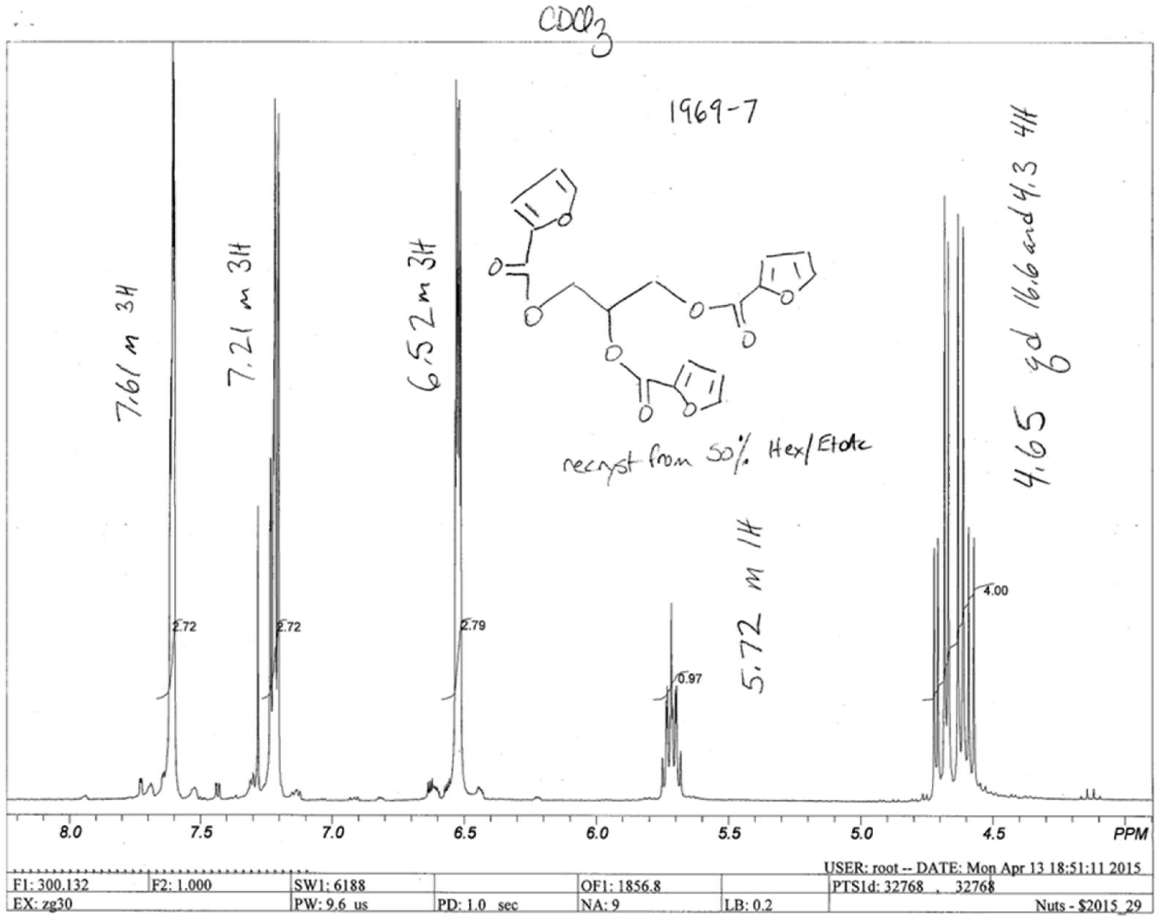
Proton NMR of *tert*-butyl 2-furoate (**6**)



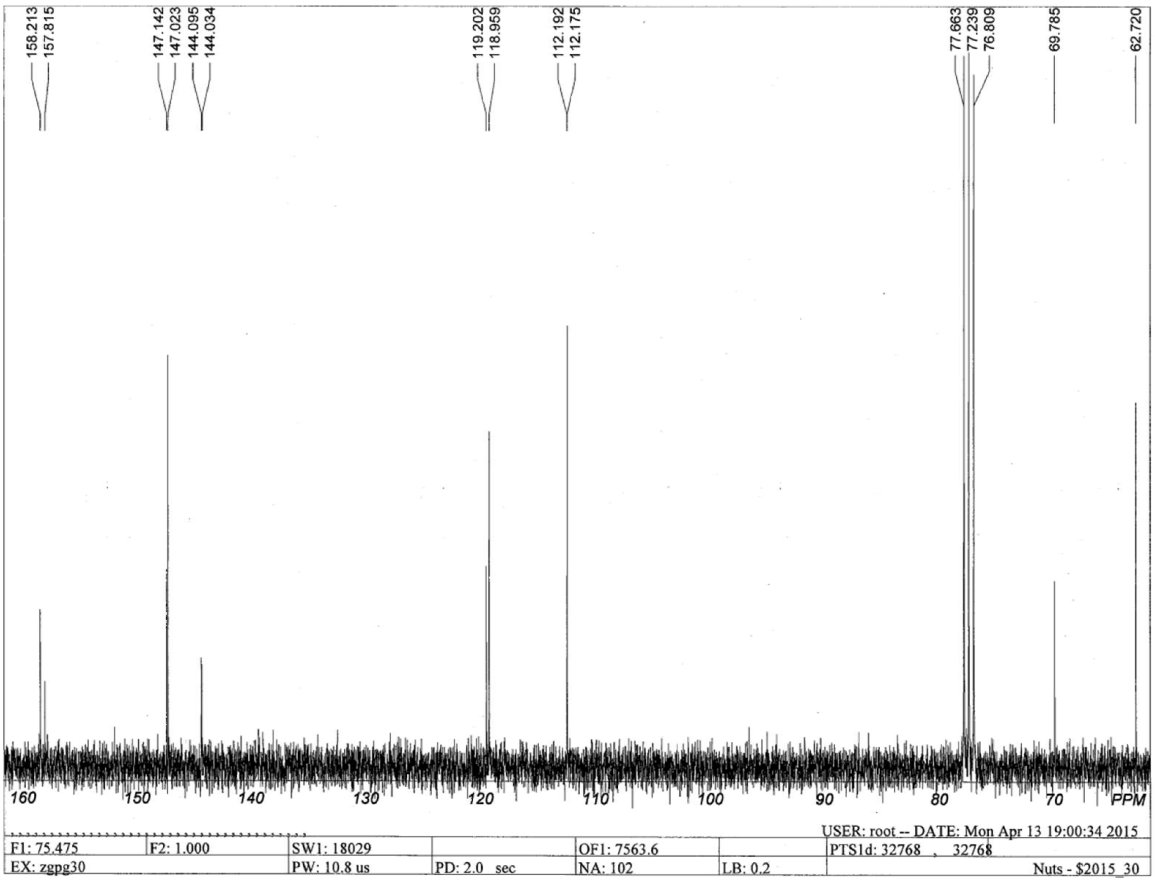
Carbon NMR of *tert*-butyl 2-furoate (**6**)



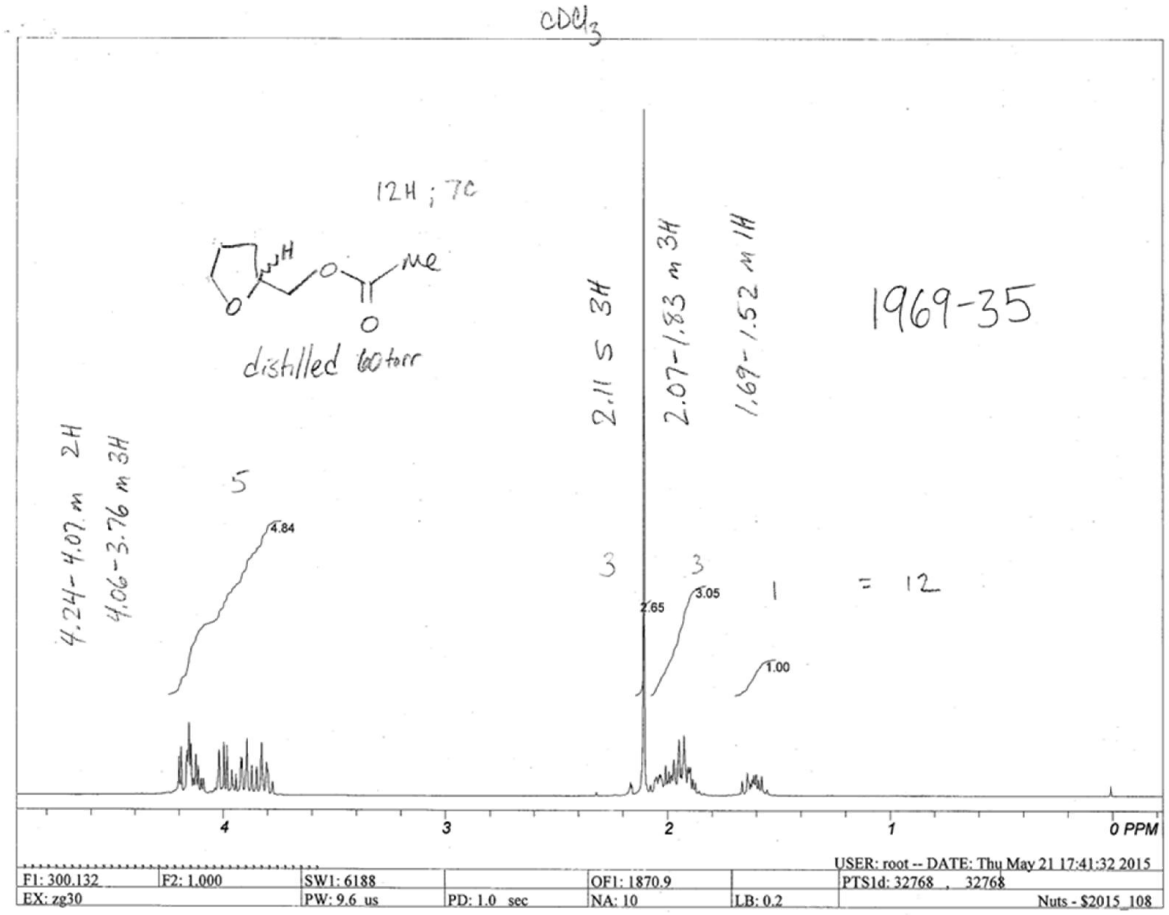
Proton NMR of triglyceride of 2-furoic acid (**7**)



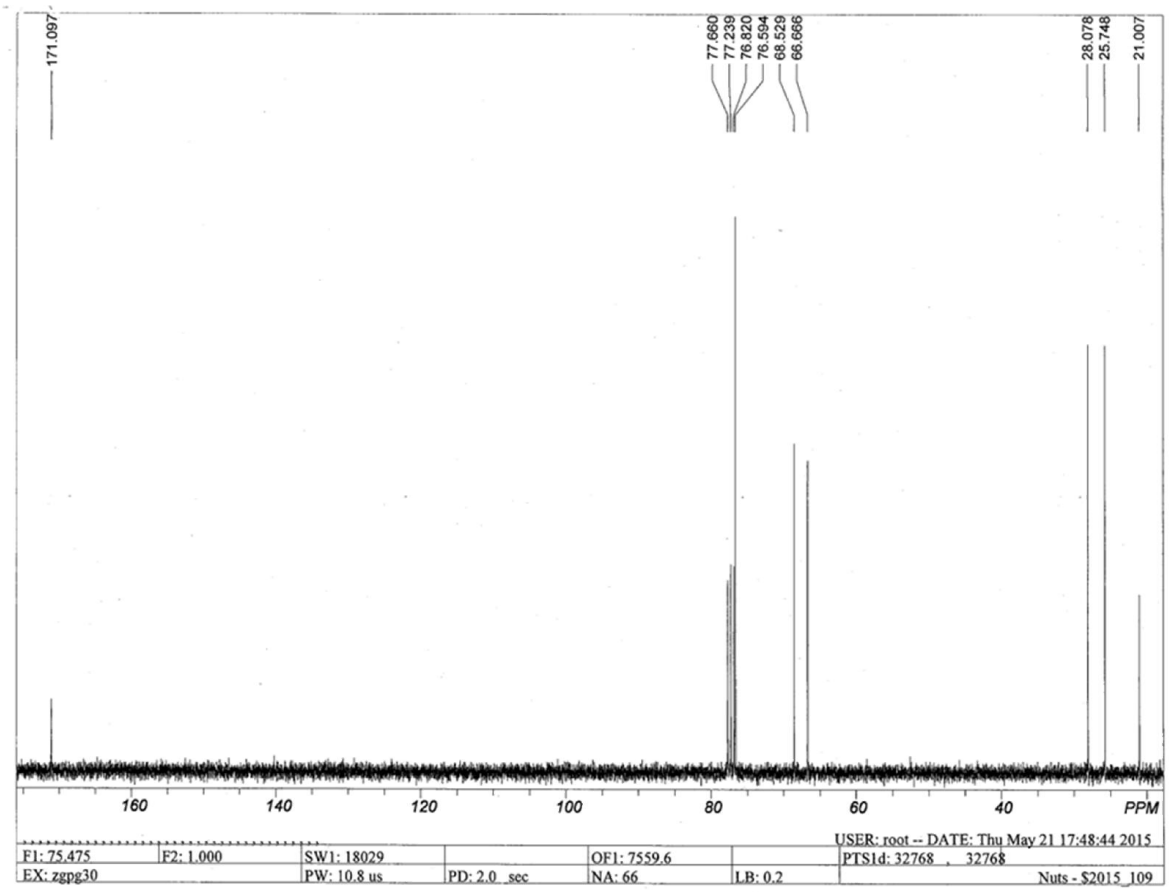
Carbon NMR of triglyceride of 2-furoic acid (**7**)



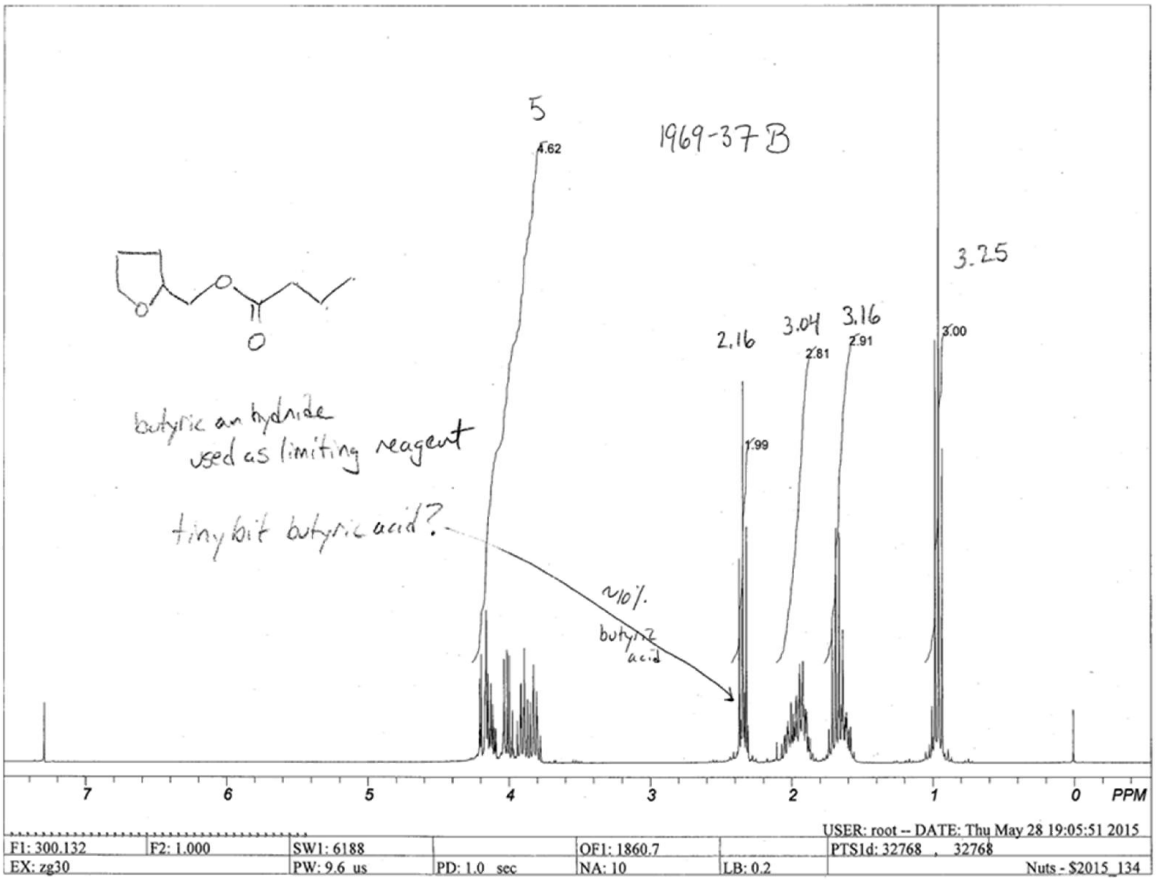
Proton NMR of acetate ester of tetrahydrofurfuryl alcohol (**35**)



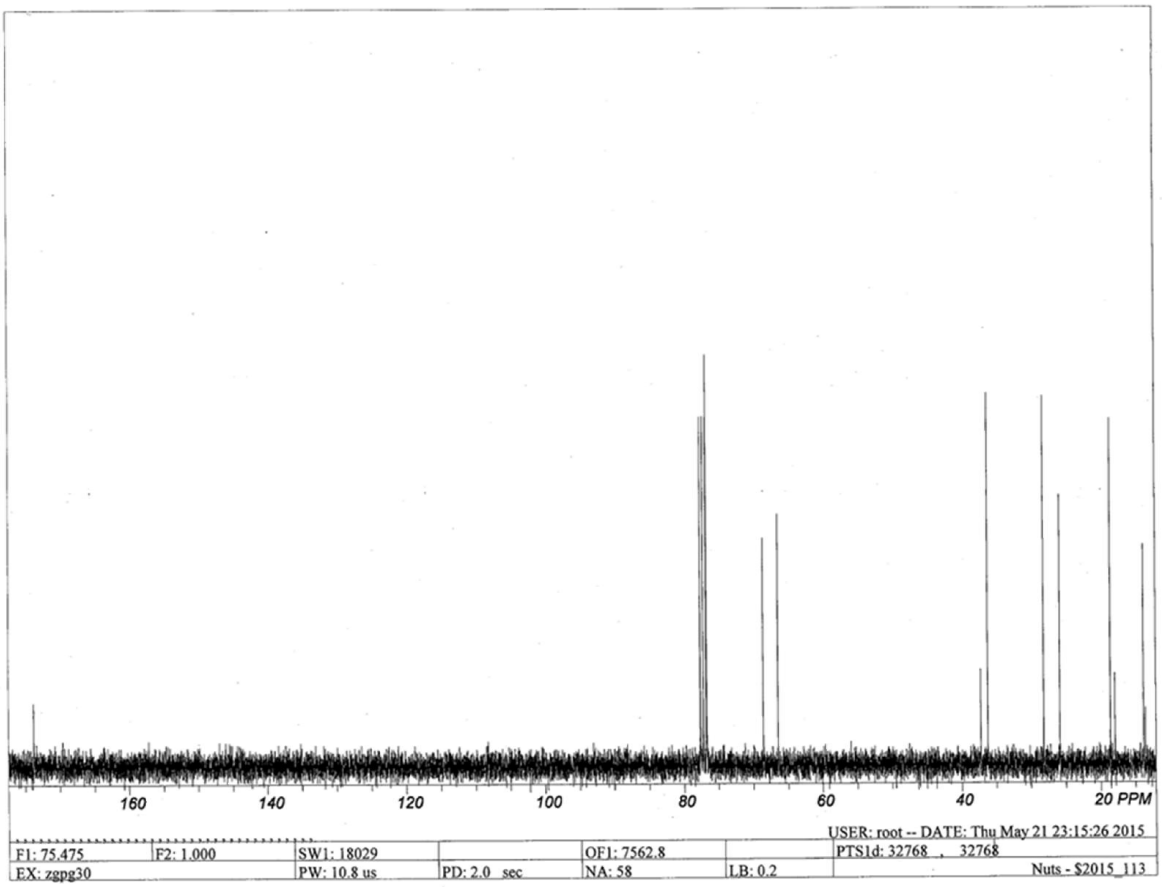
Carbon NMR of acetate ester of tetrahydrofurfuryl alcohol (**35**)



Proton NMR of tetrahydrofurfuryl butyrate (**37**)

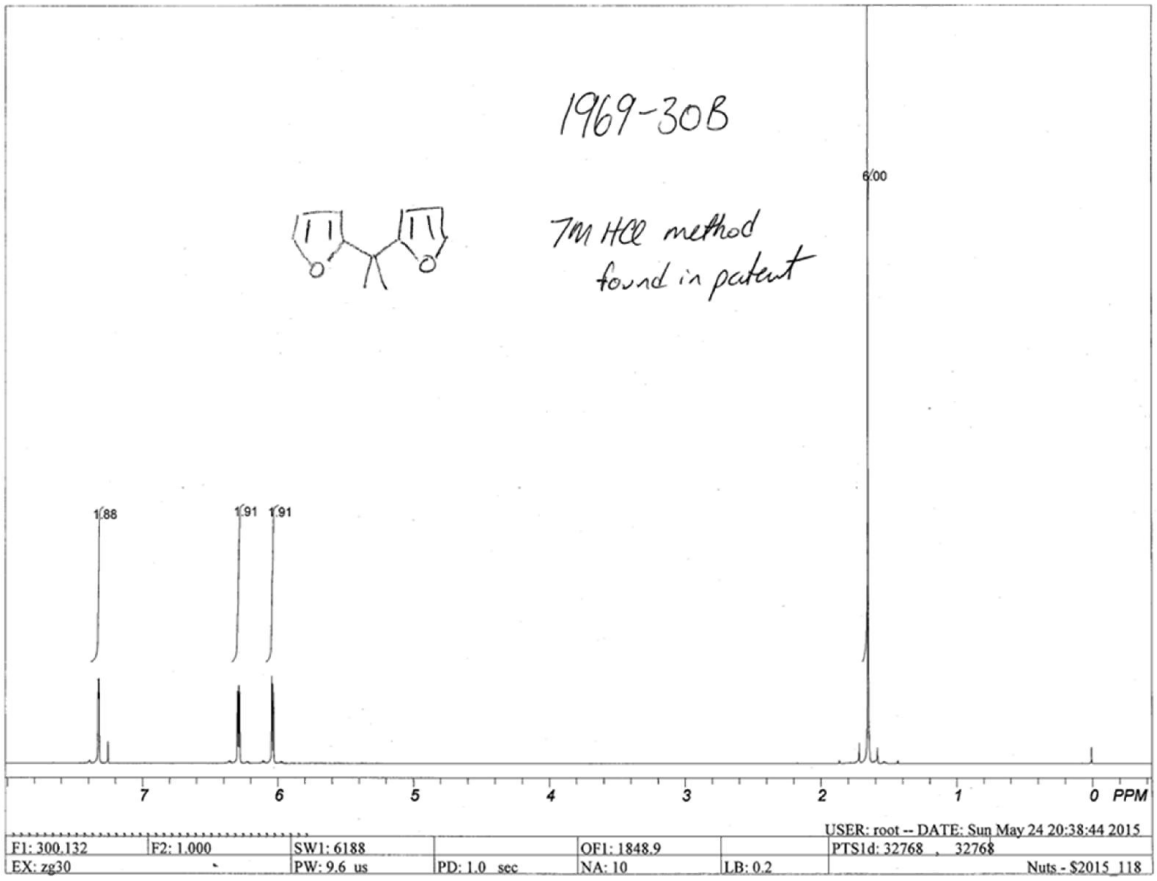


Carbon NMR of tetrahydrofurfuryl butyrate (**37**)

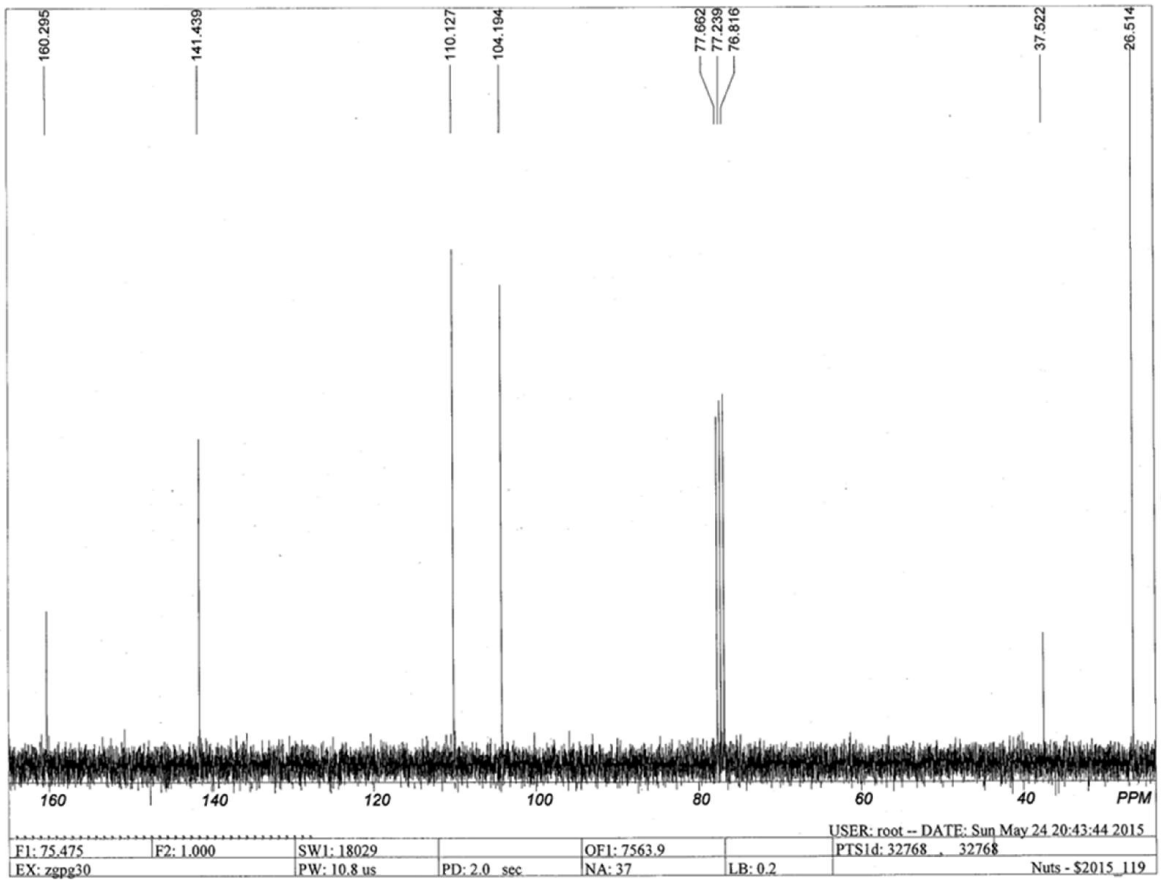


Appendix D NMR Data for Difuranic Solvents

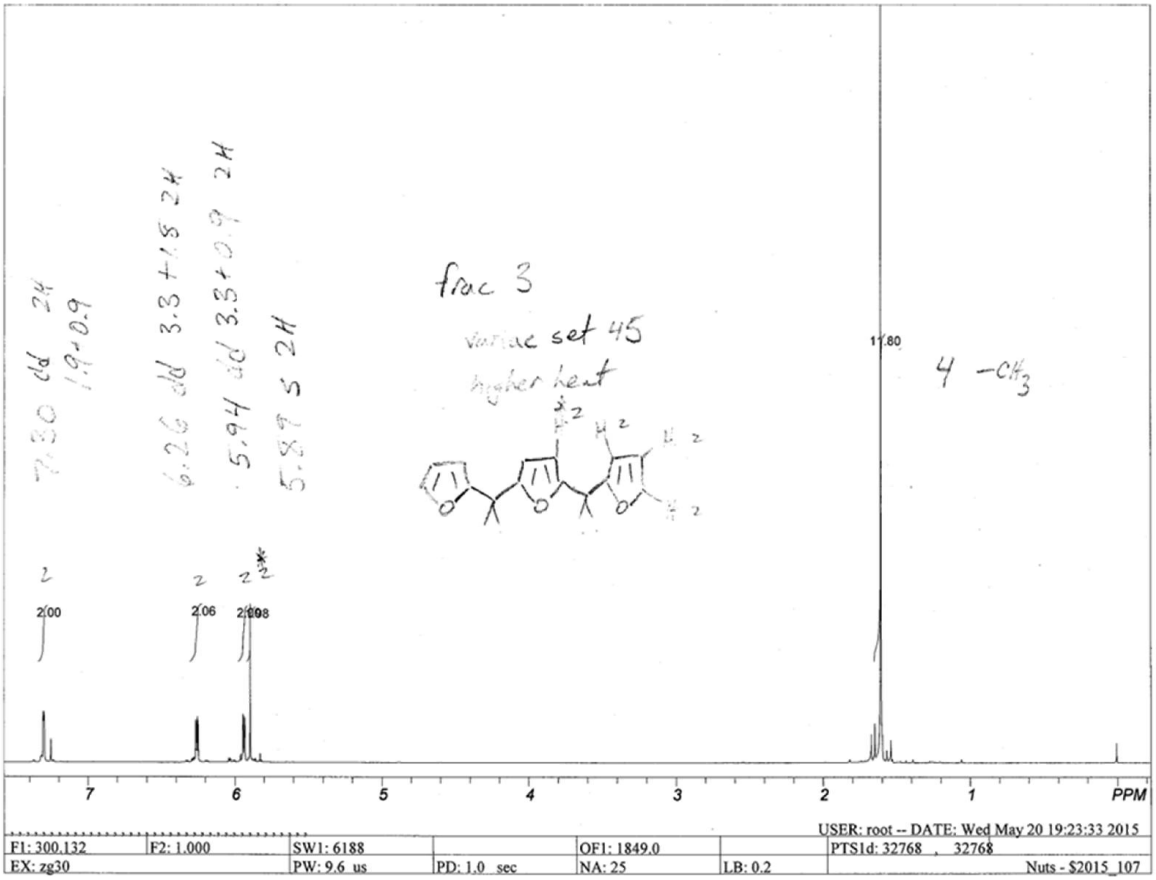
Proton NMR of difuran (**30dimer**)



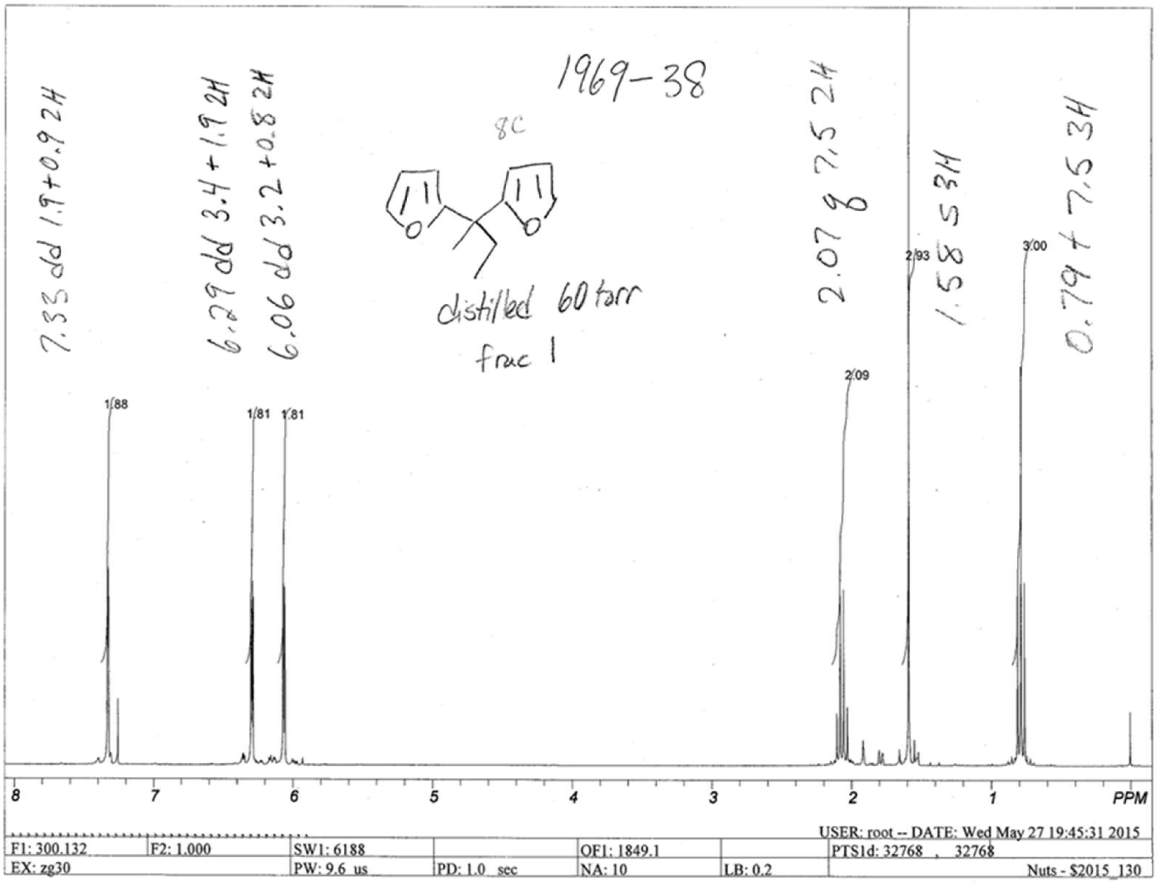
Carbon NMR of difuran (**30dimer**)



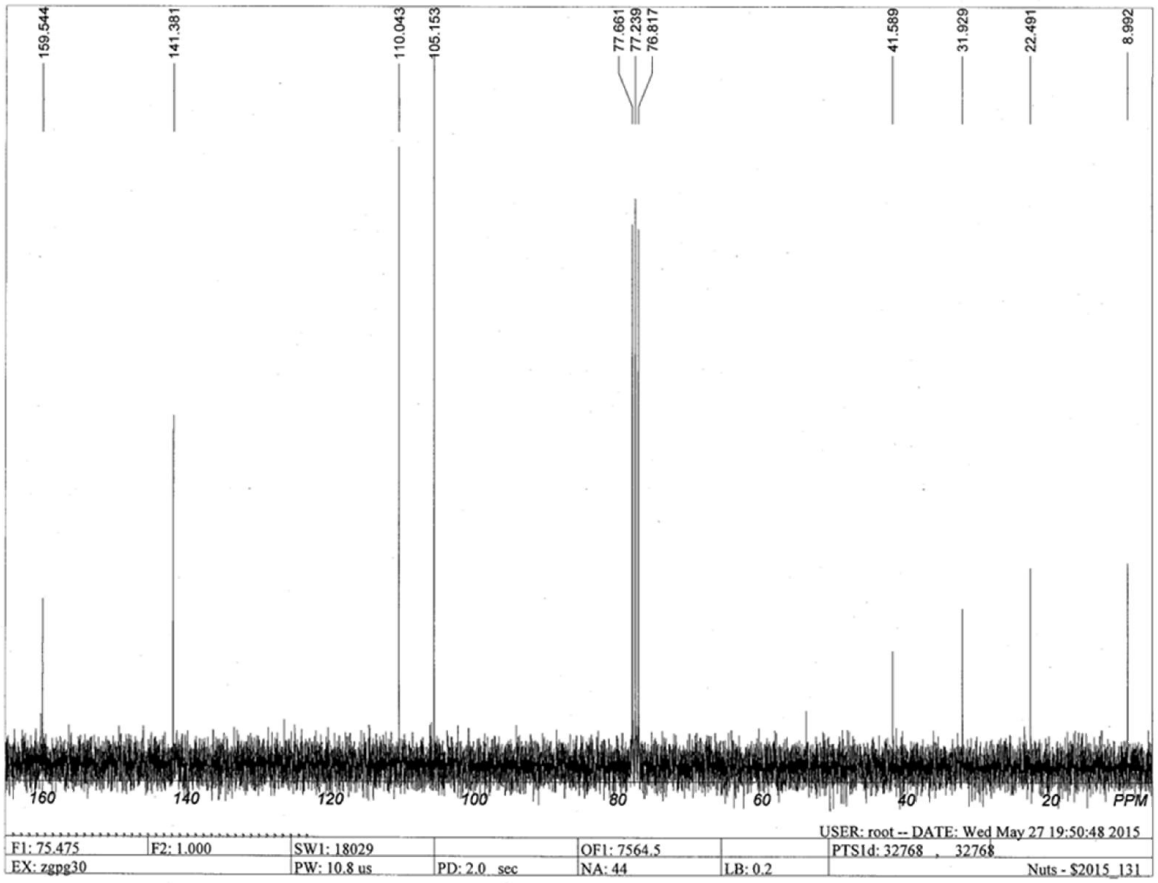
Proton NMR of difuran (**30trimer**)



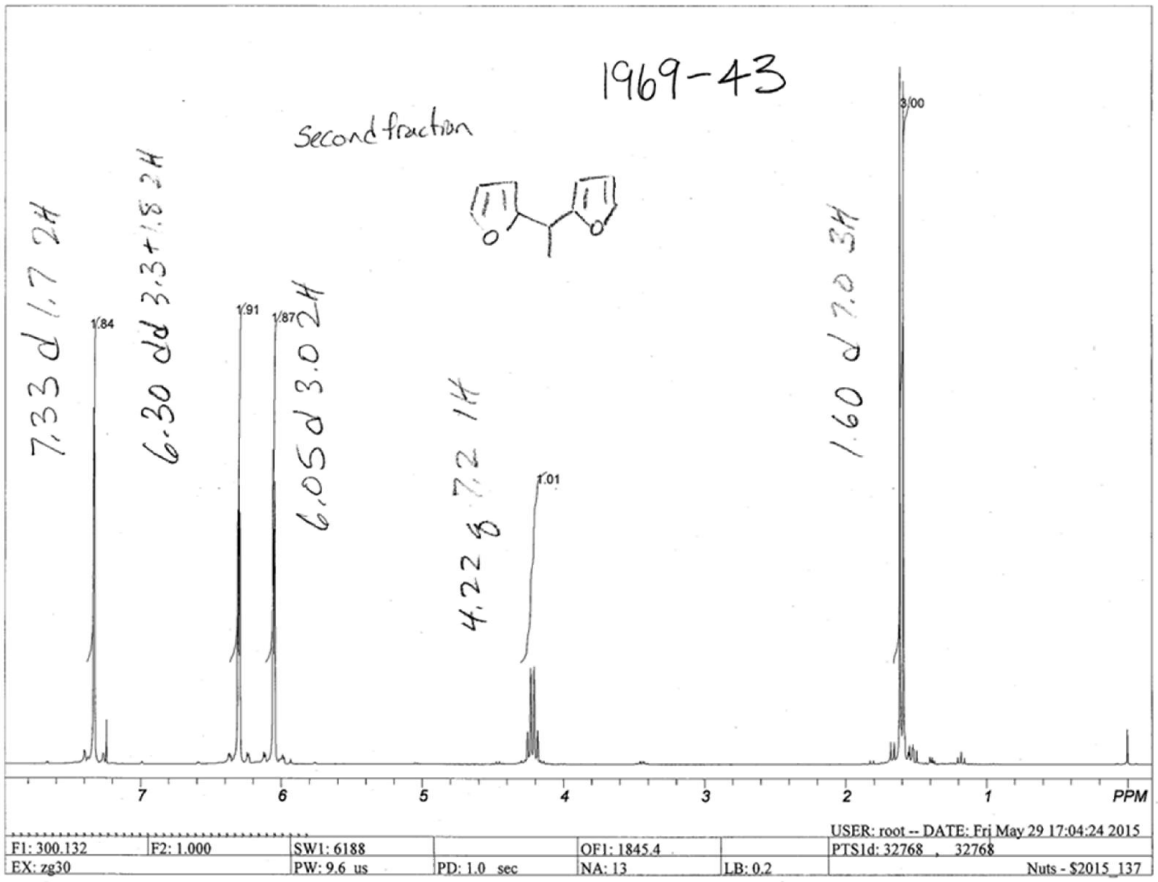
Proton NMR of difuran (**38**)



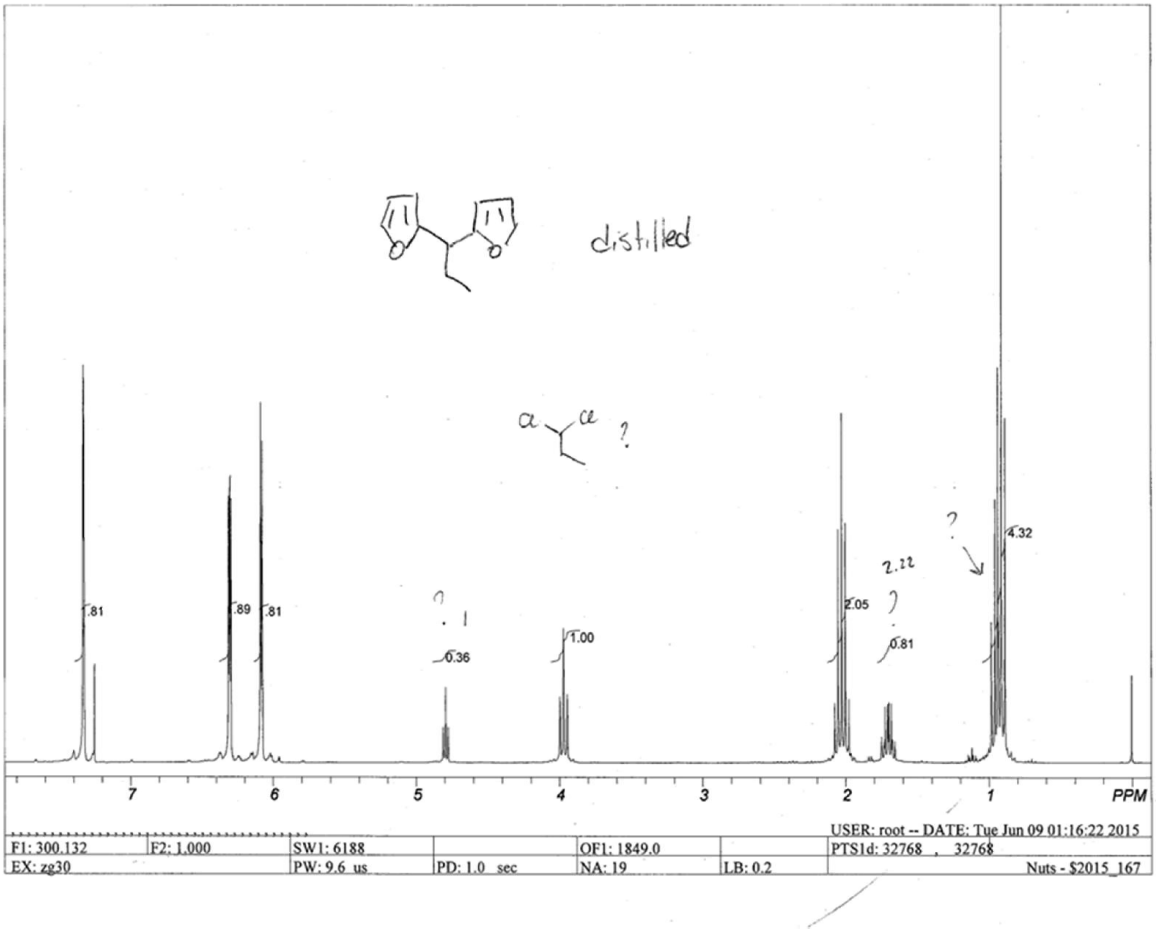
Carbon NMR of difuran (**38**)



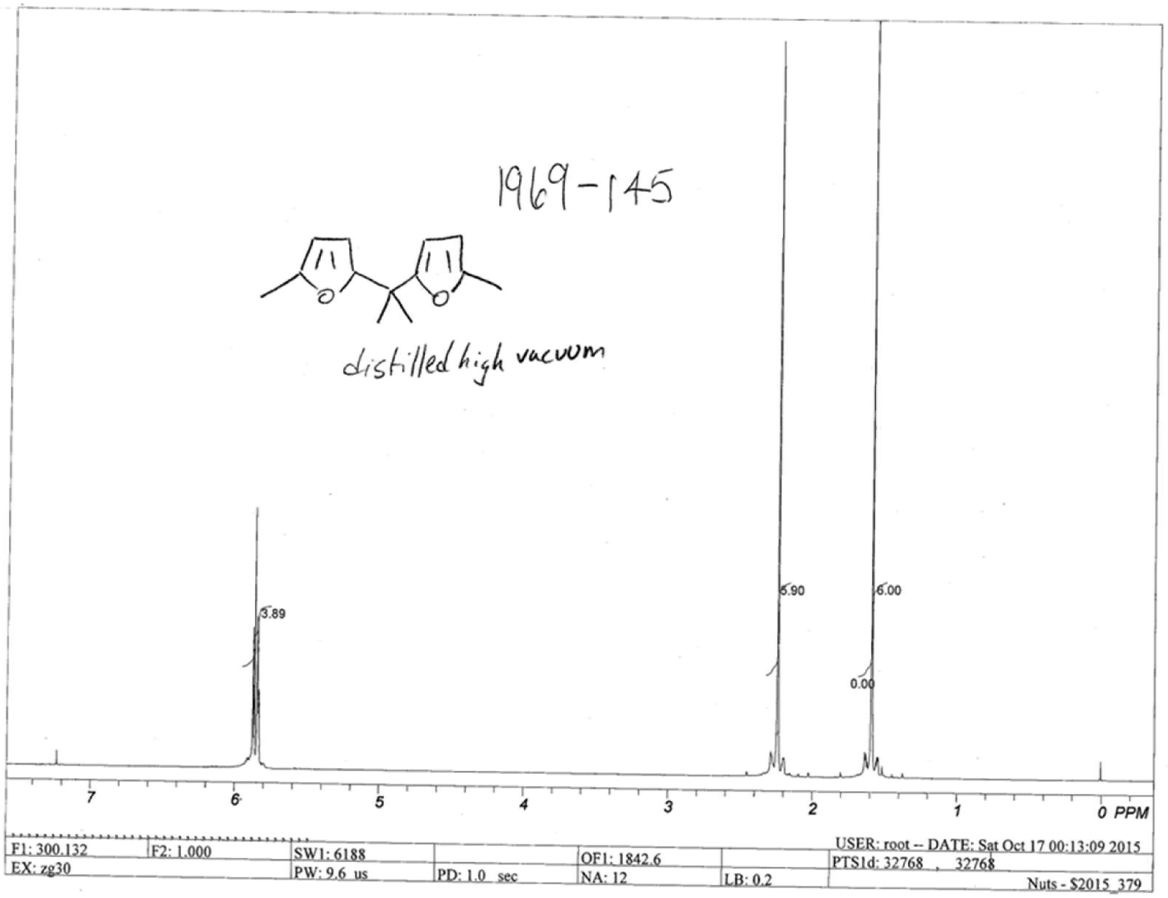
Proton NMR of difuran (**43**)



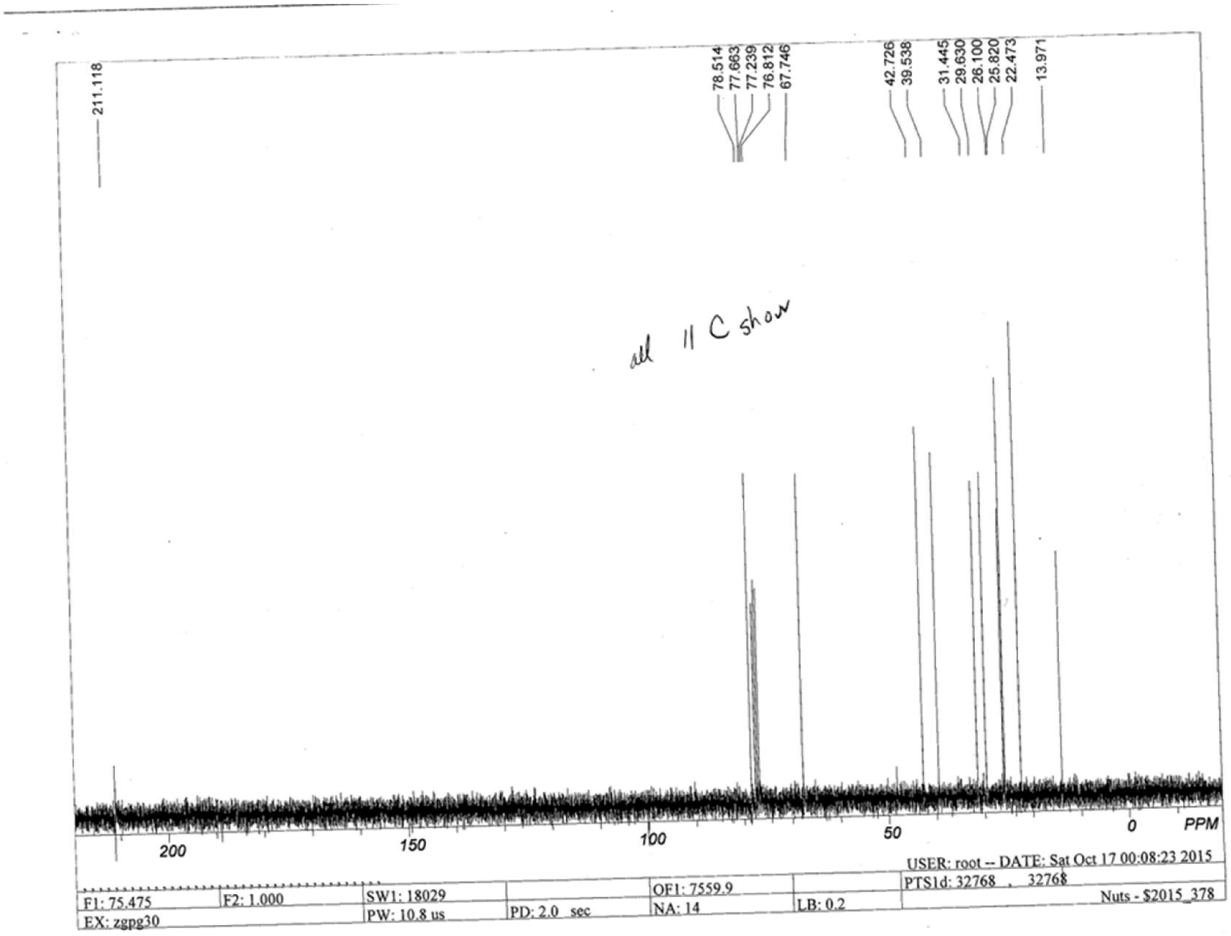
Proton NMR of difuran (**57**)



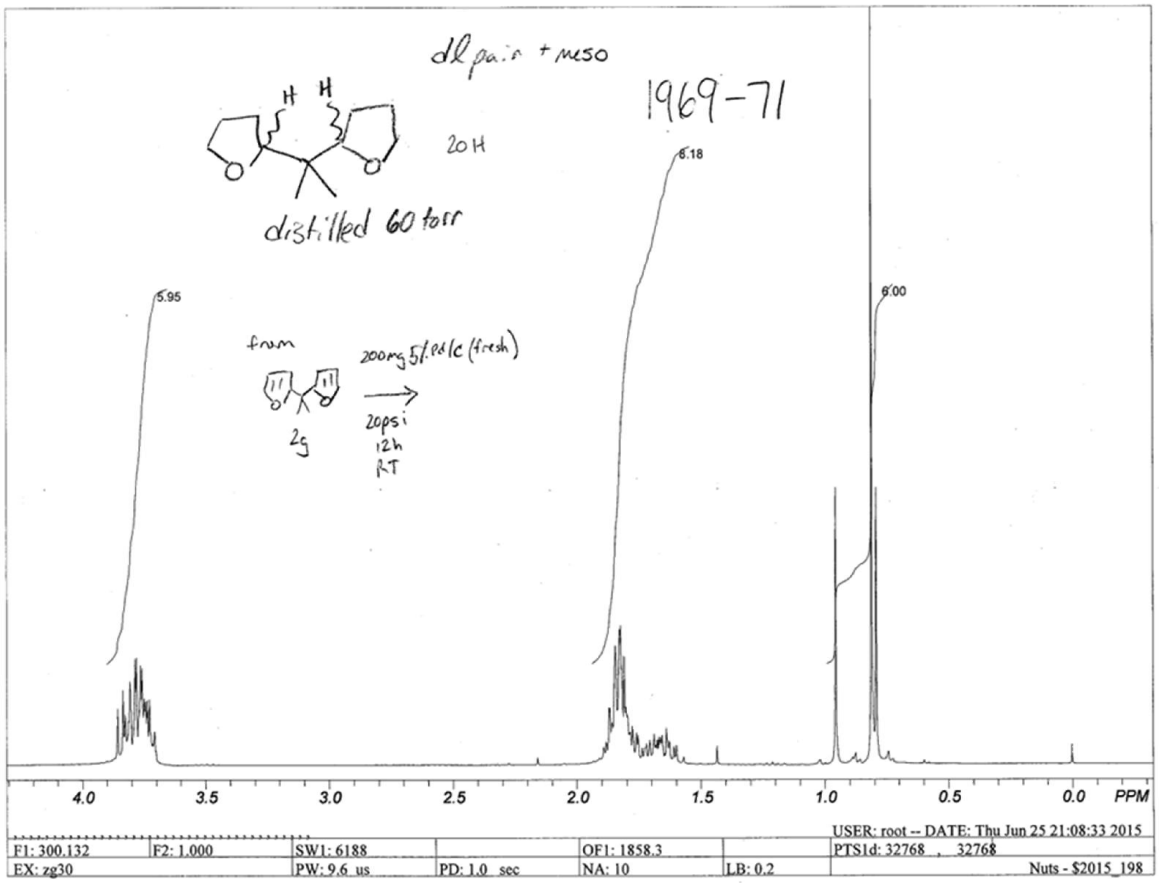
Proton NMR of difuran (**145**)



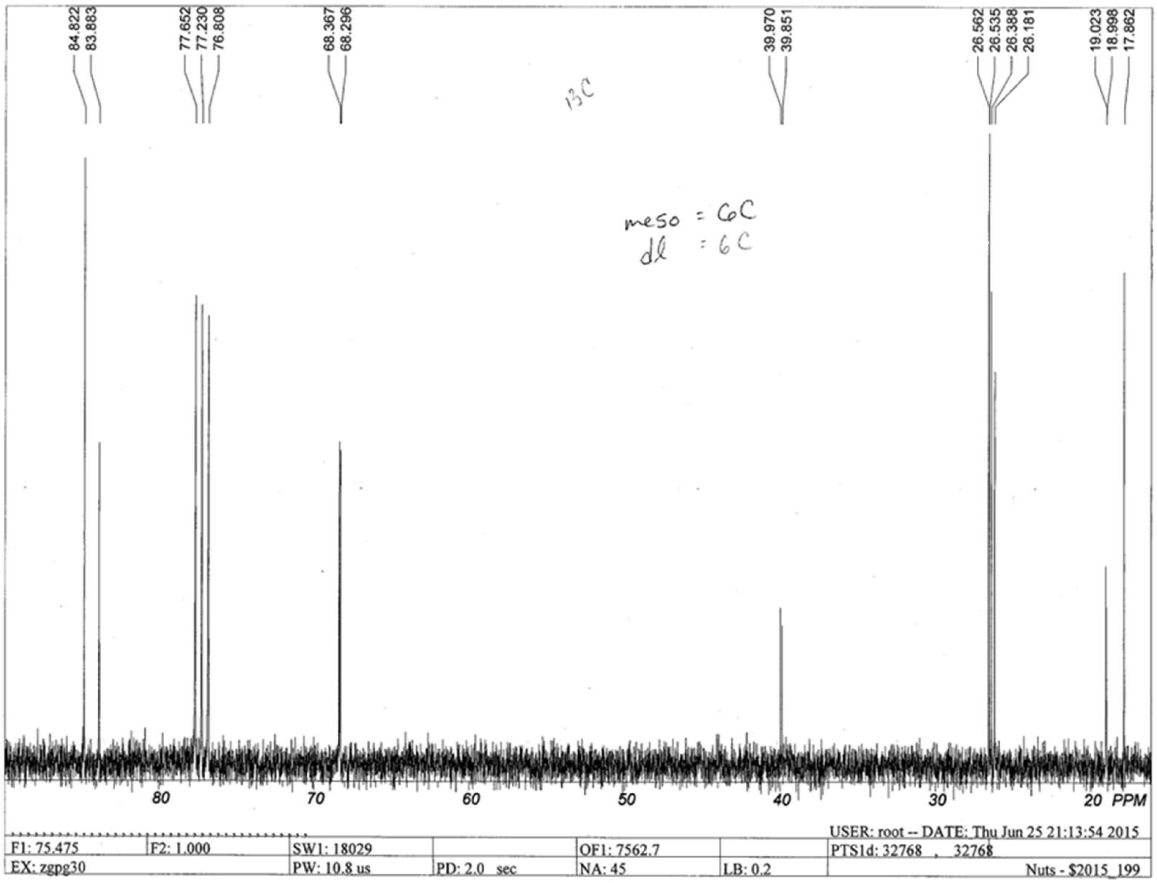
Carbon NMR of difuran (**145**)



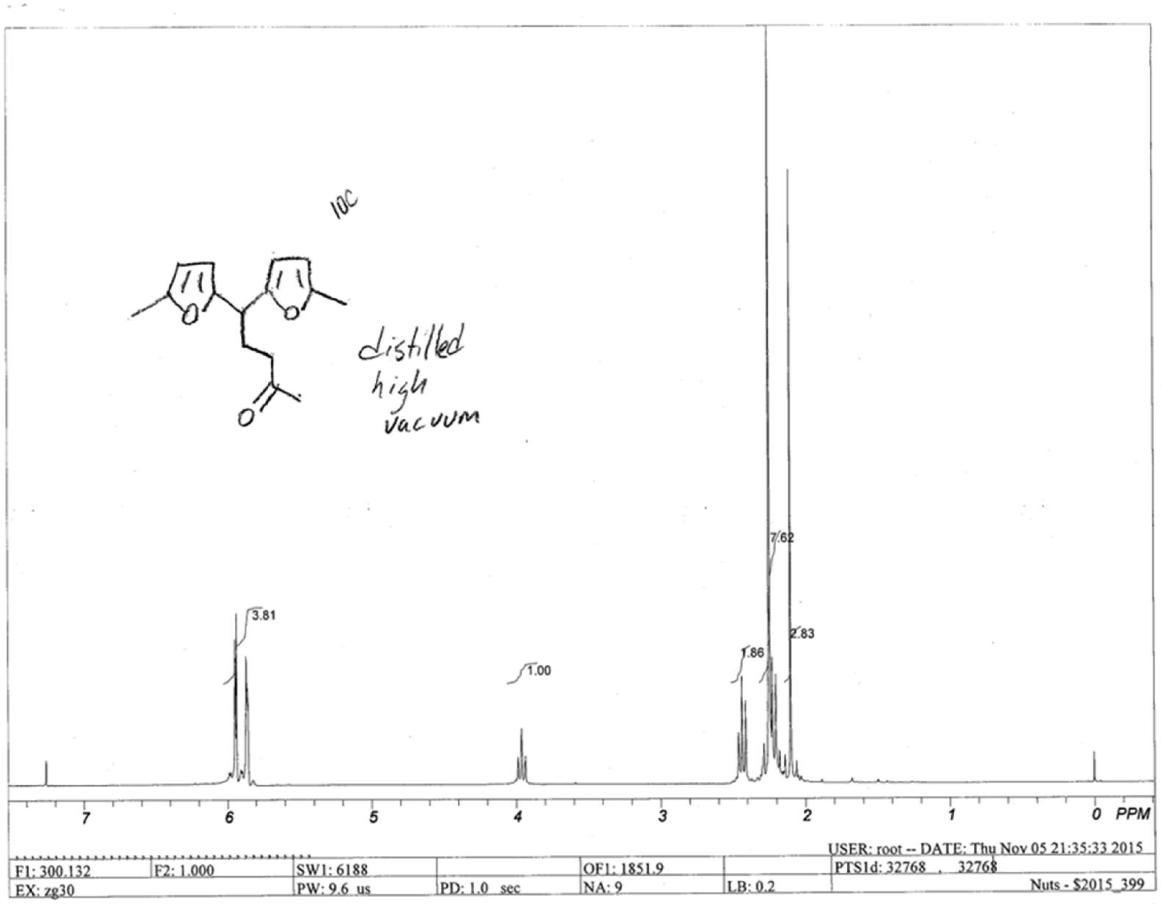
Proton NMR of ditetrahydrofuran (**83B**)



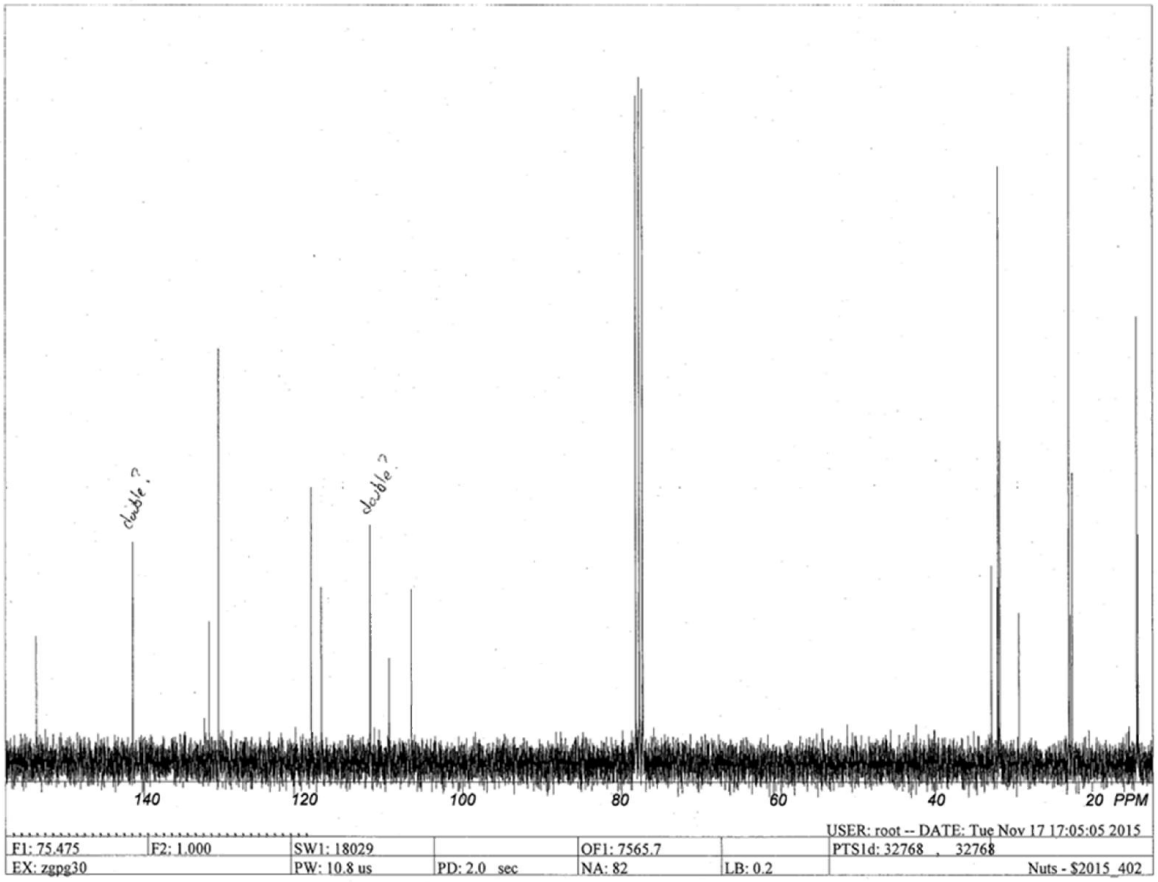
Carbon NMR of ditetrahydrofuran (**83B**)



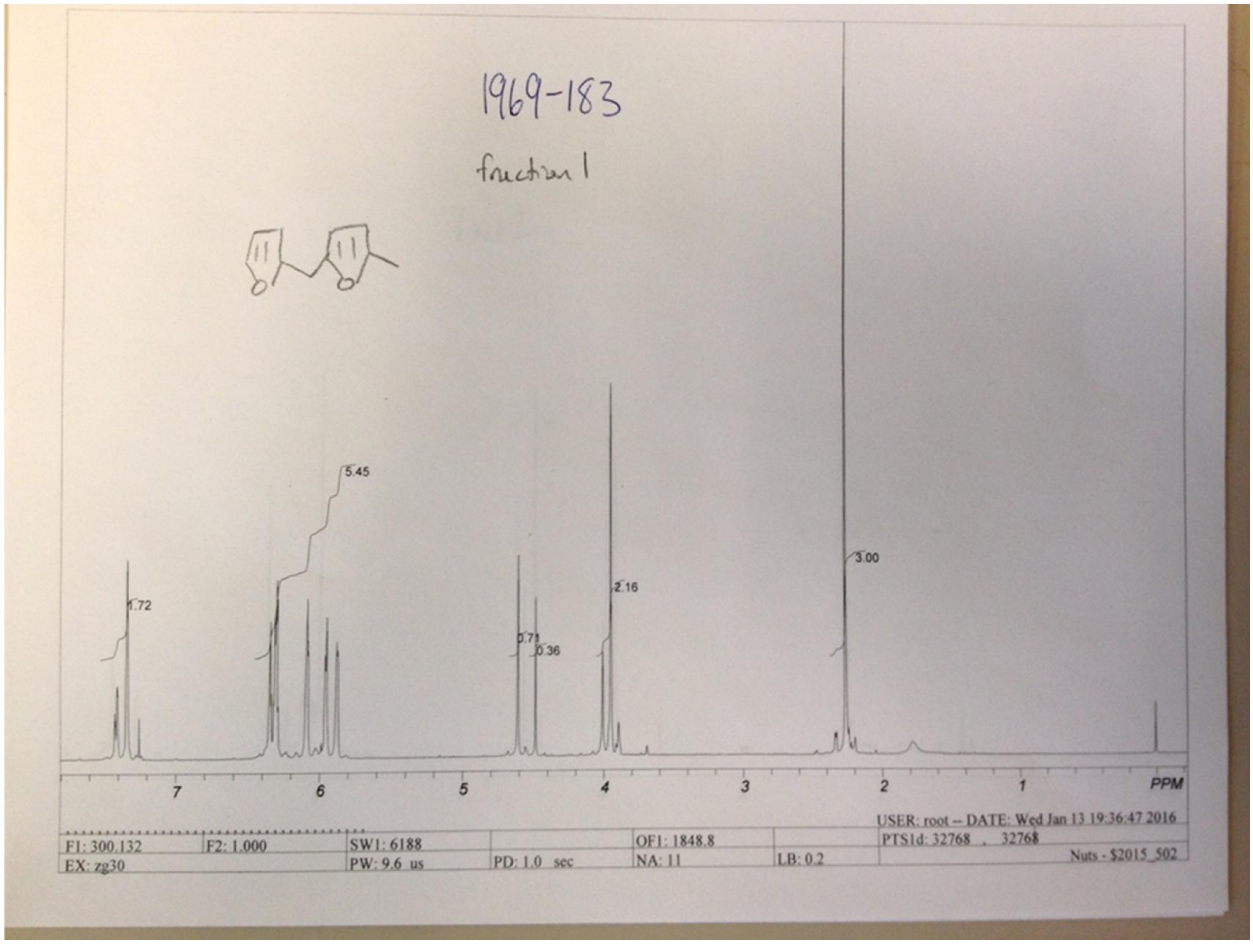
Proton NMR of difuranyl ketone (**155**)



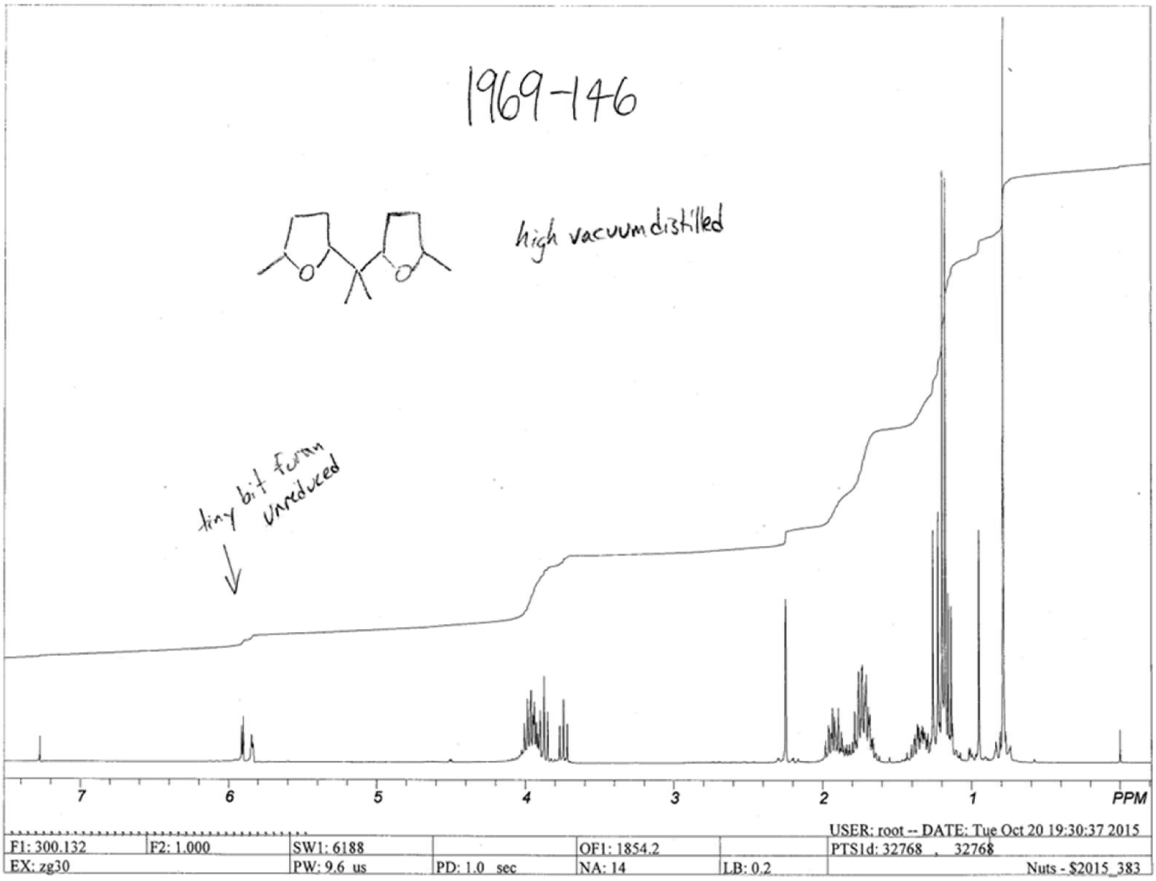
Carbon NMR of difuranyl ketone (**155**)



Proton NMR of difuran (**183**)

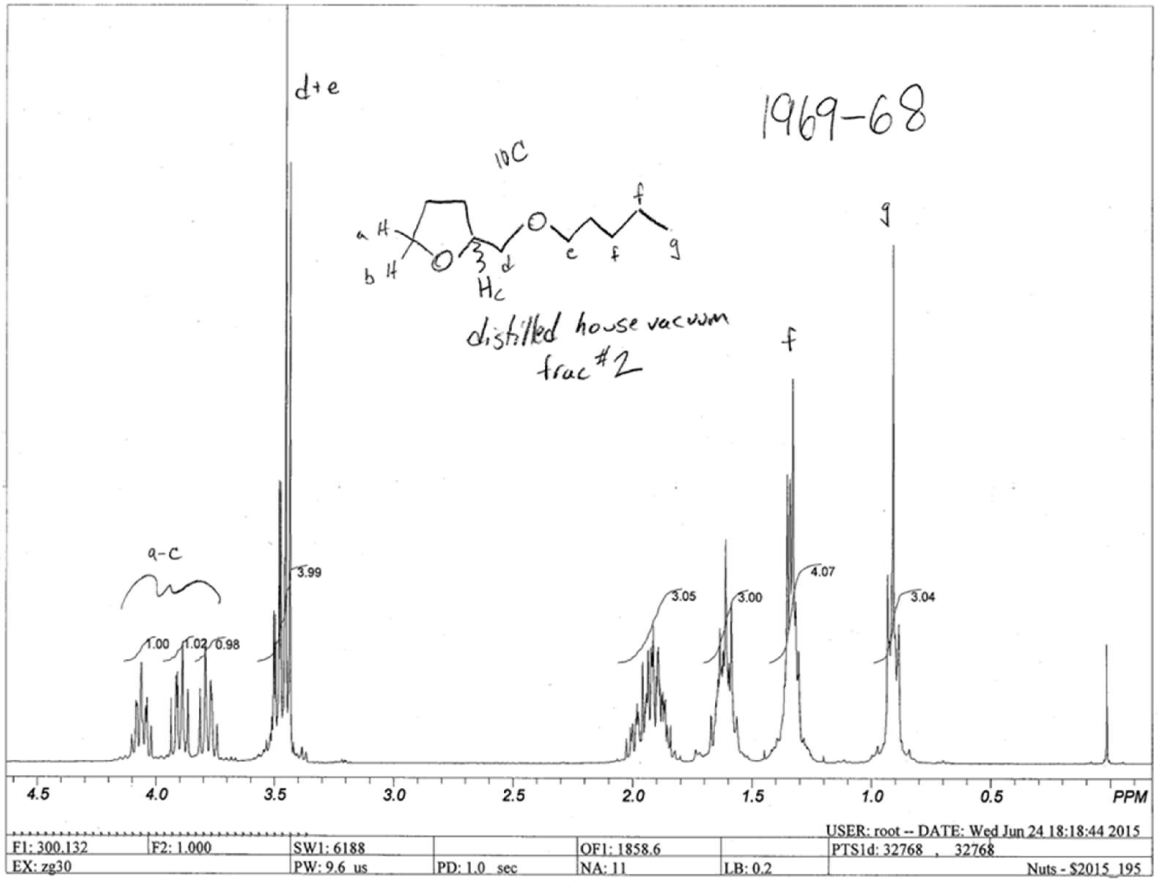


Proton NMR of difuran (**146**)

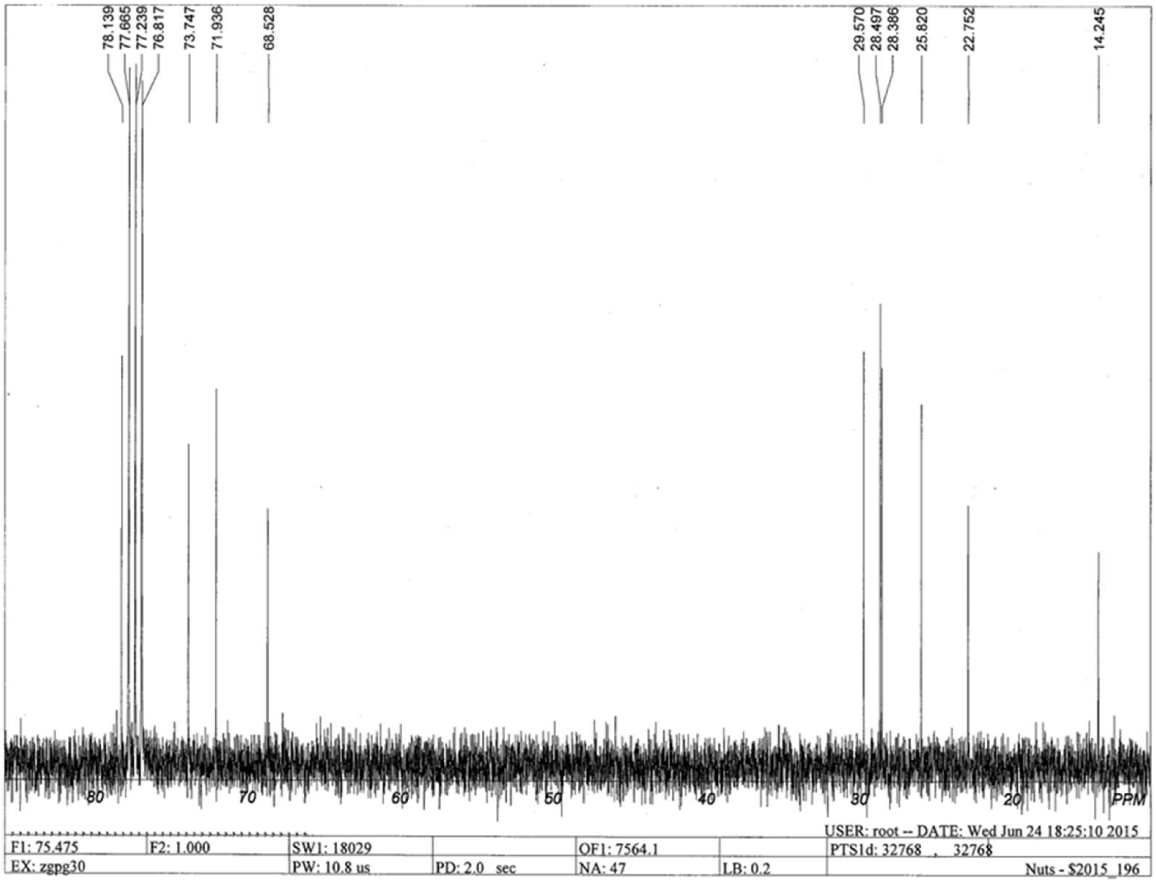


Appendix E NMR Data for Furanic Ethers

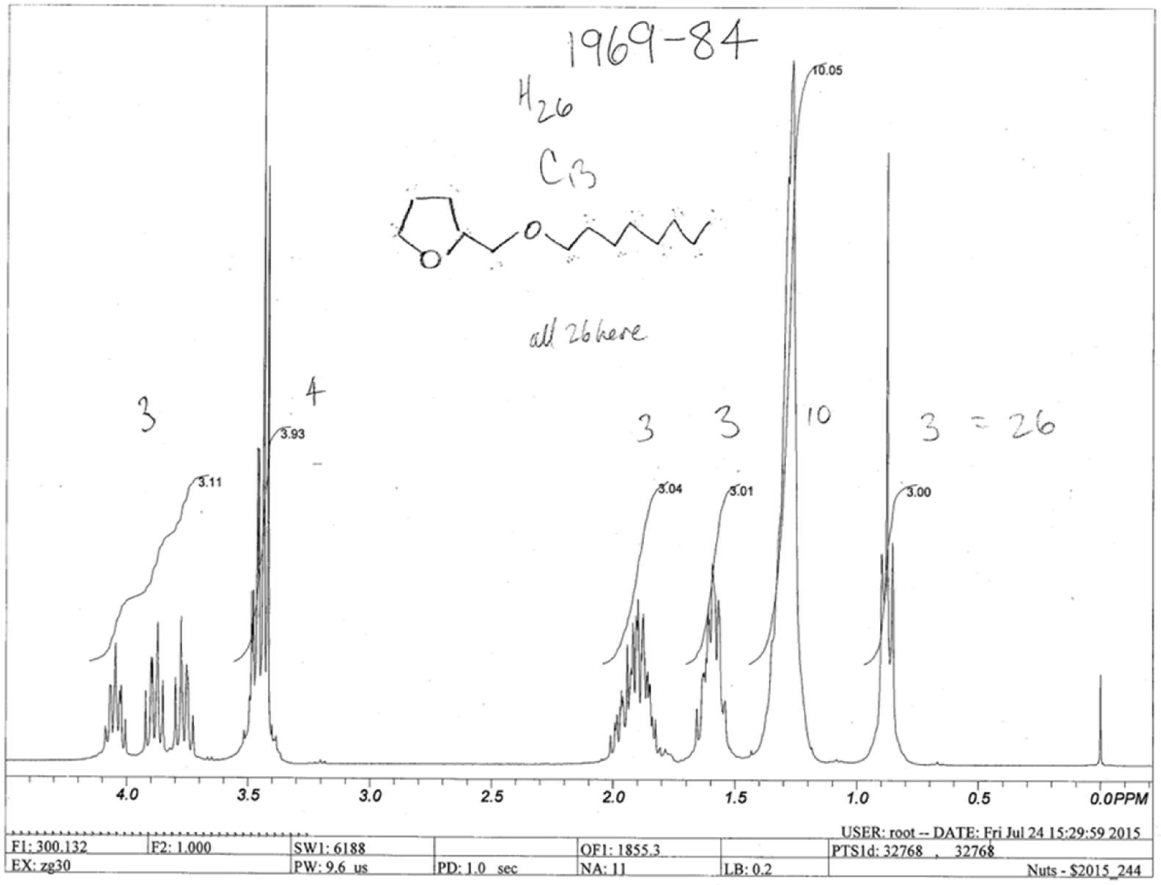
Proton NMR of pentyl ether of furfuryl alcohol (**68**)



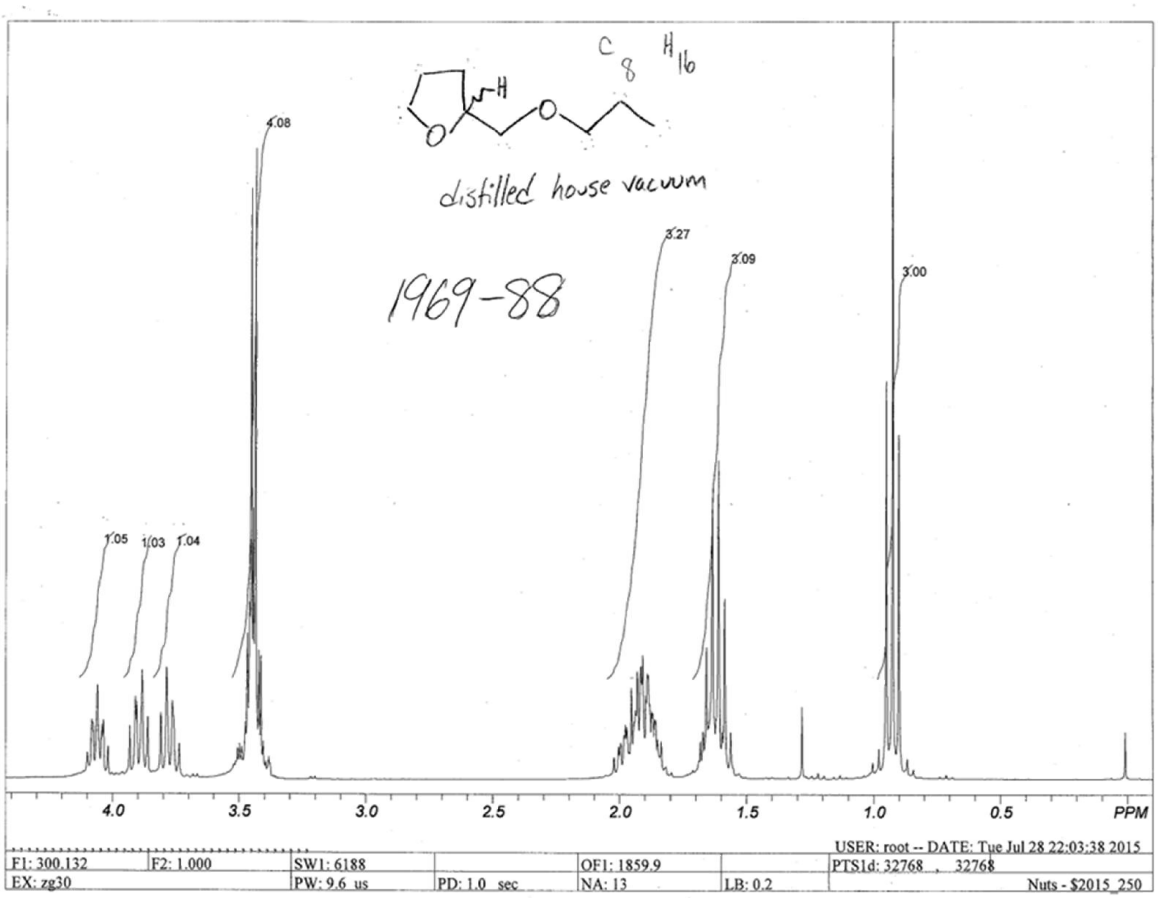
Carbon NMR of pentyl ether of furfuryl alcohol (**68**)



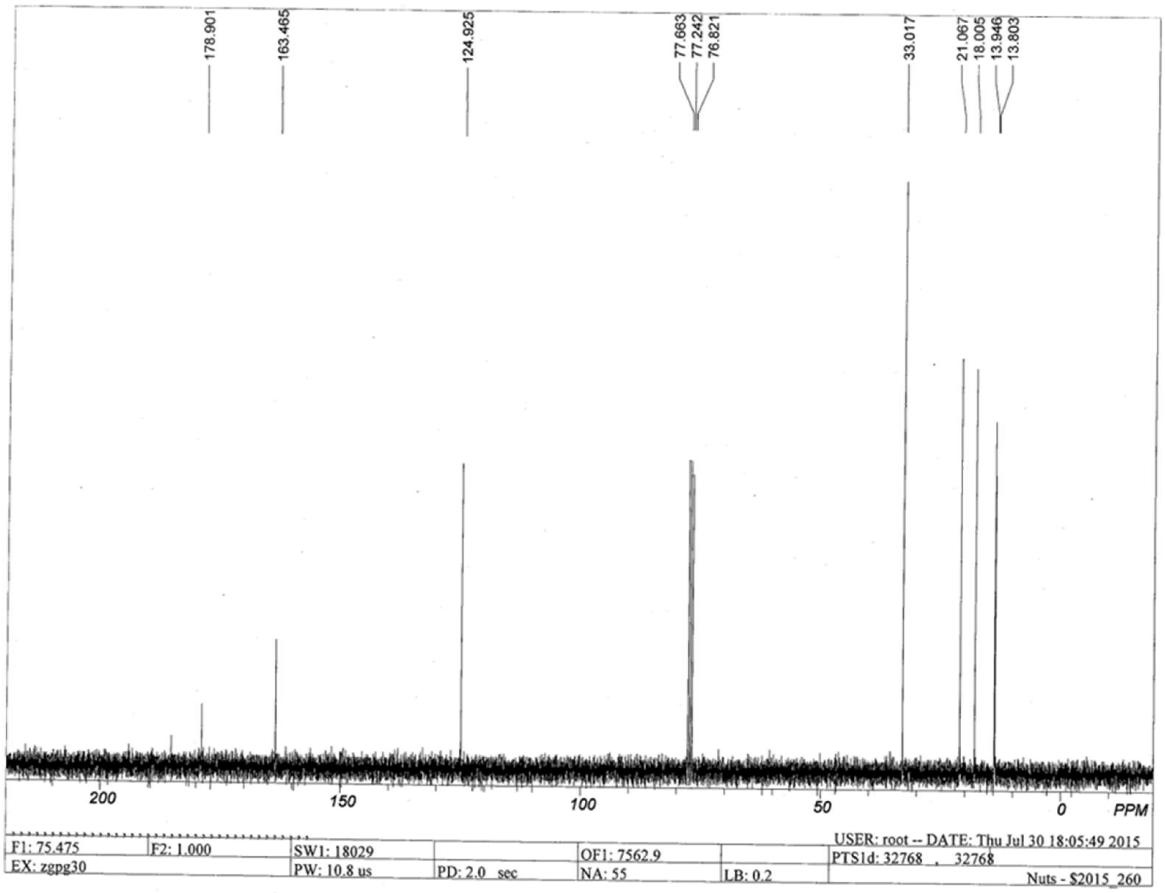
Proton NMR of octyl ether of furfuryl alcohol (**84**)



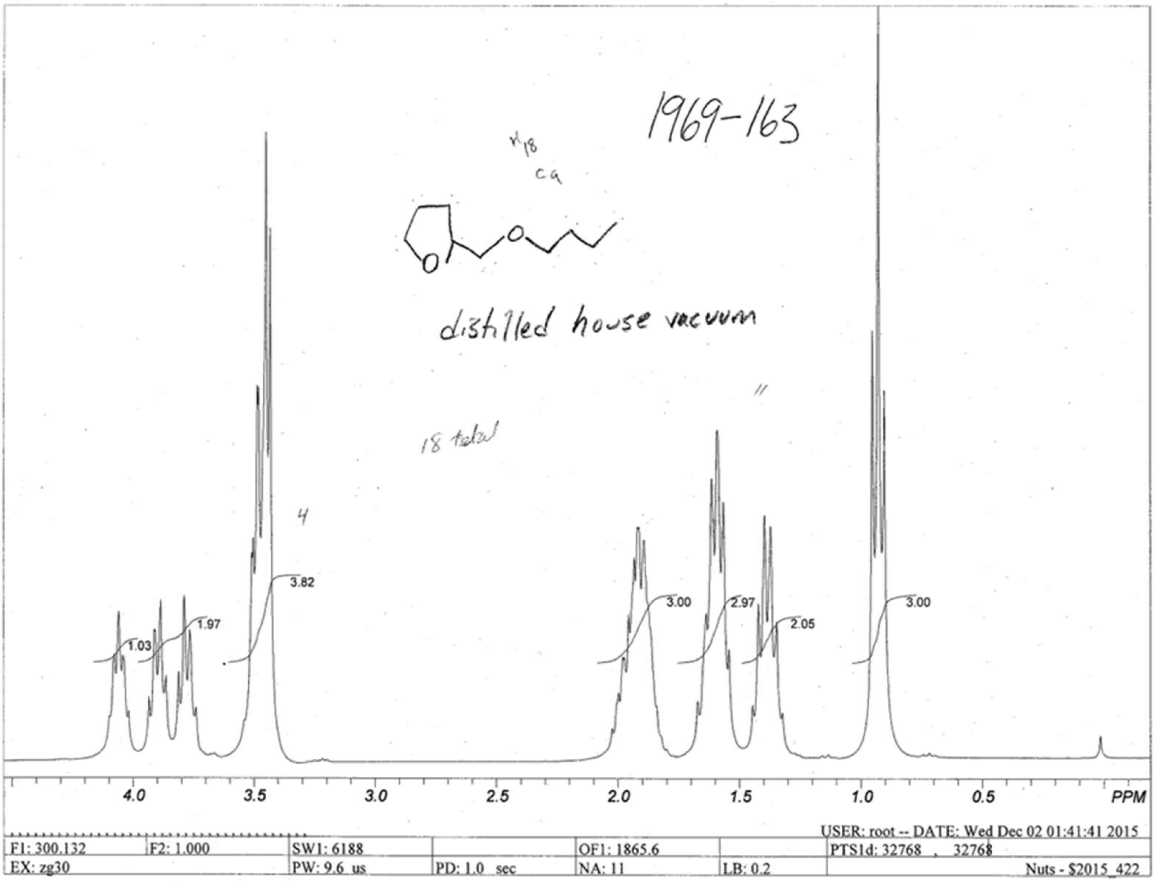
Proton NMR of propyl ether of furfuryl alcohol (**88**)



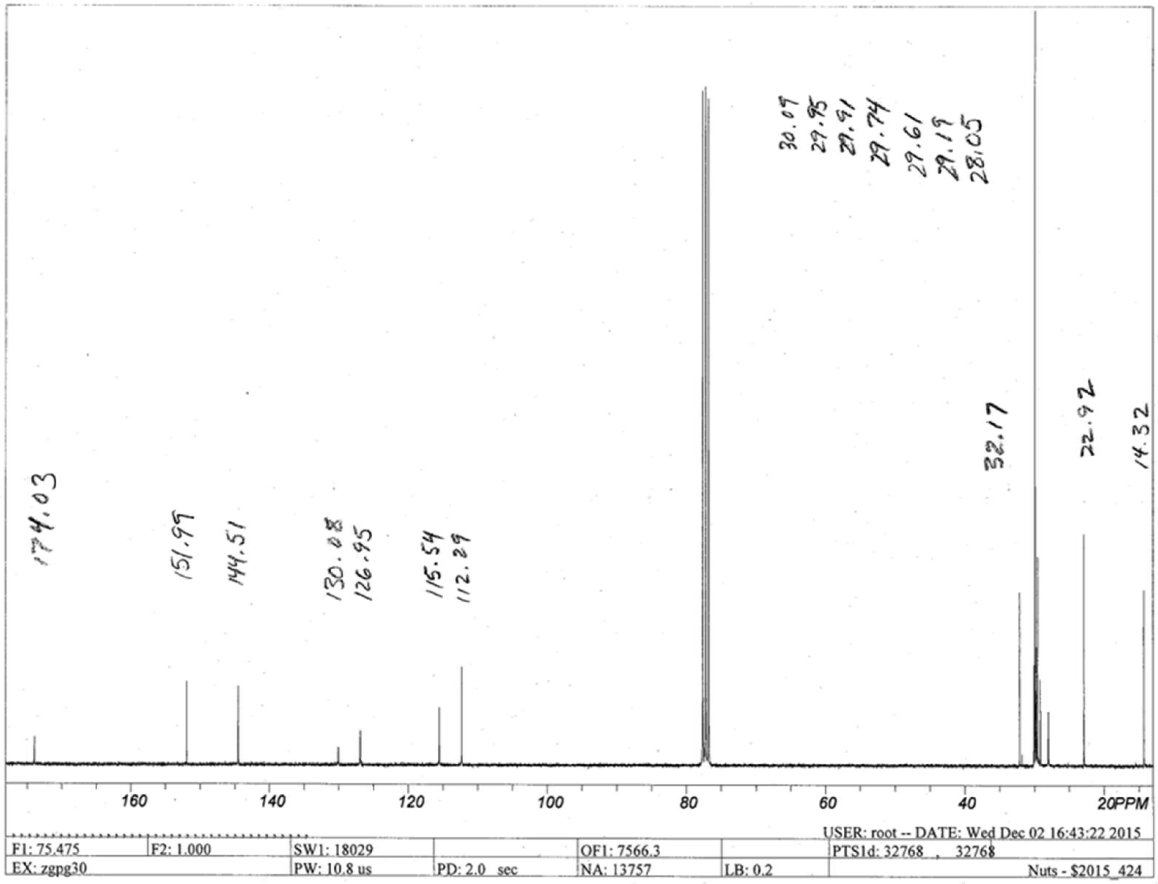
Carbon NMR of propyl ether of furfuryl alcohol (**88**)



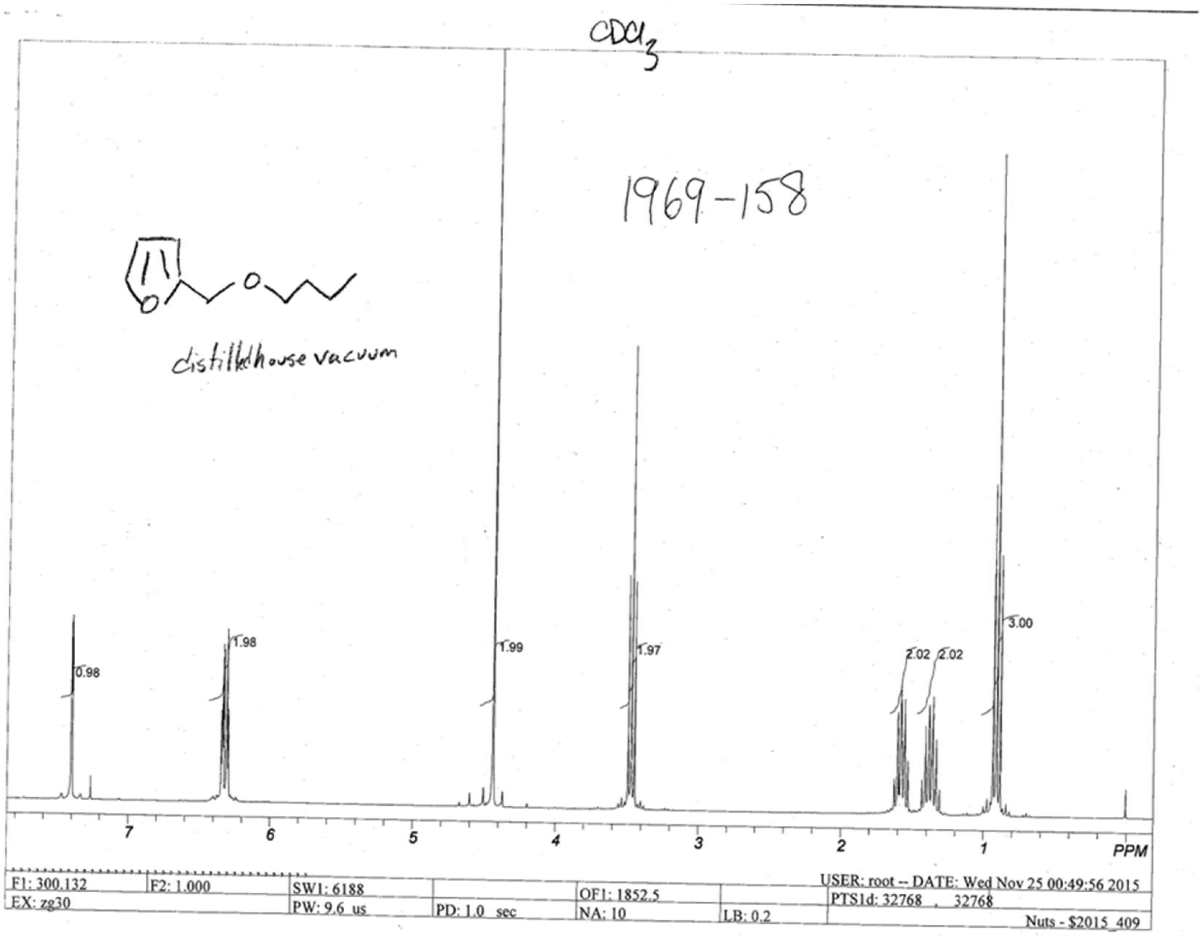
Proton NMR of butyl ether of furfuryl alcohol (**163**)



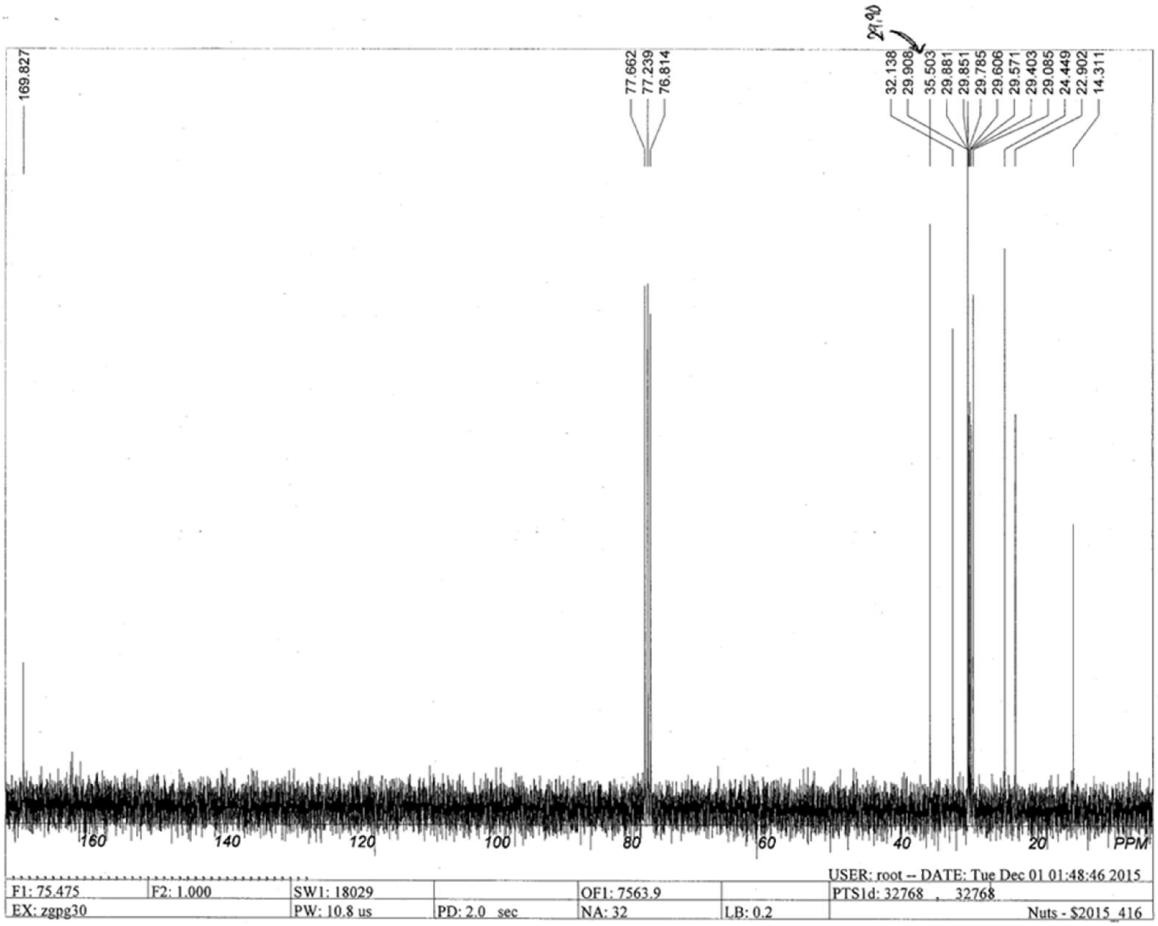
Carbon NMR of butyl ether of furfuryl alcohol (**163**)



Proton NMR of butyl ether of furfuryl alcohol (**158**)

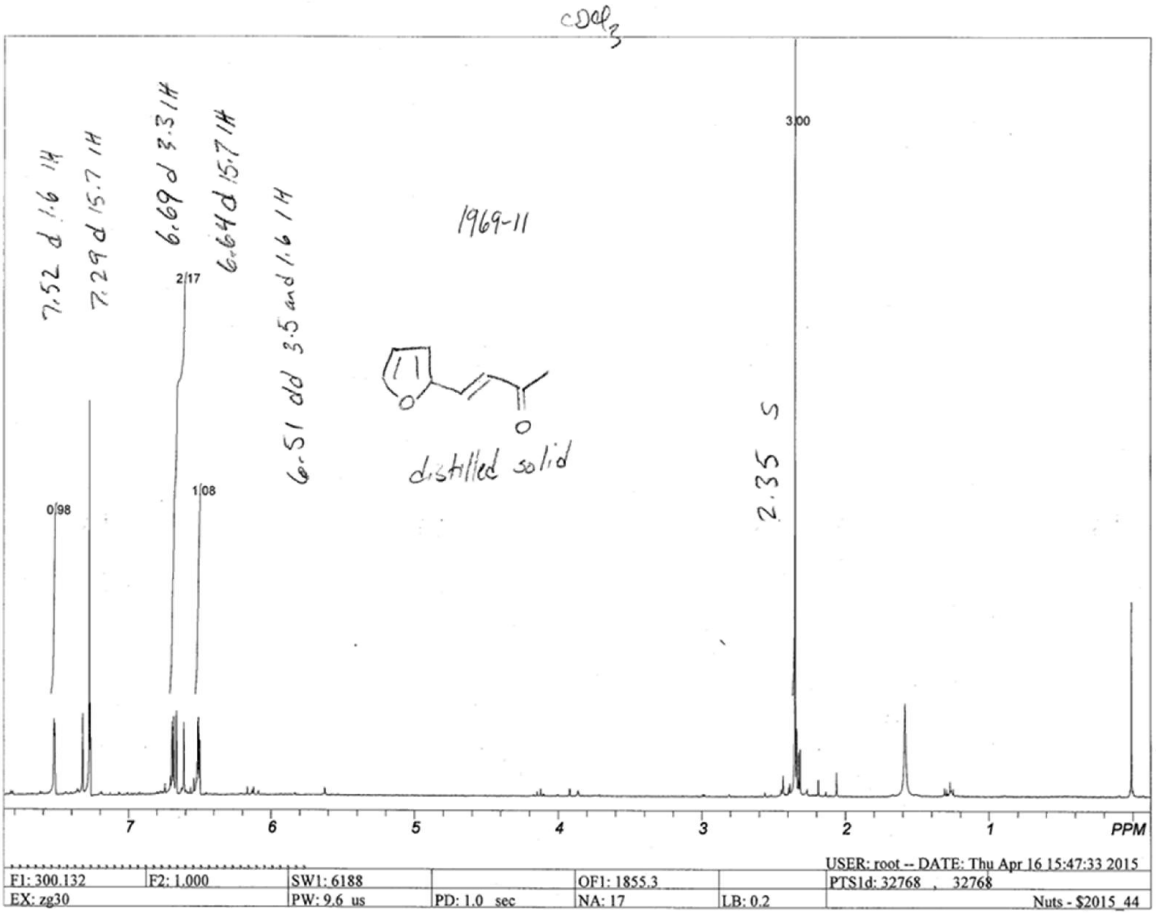


Carbon NMR of butyl ether of furfuryl alcohol (**158**)

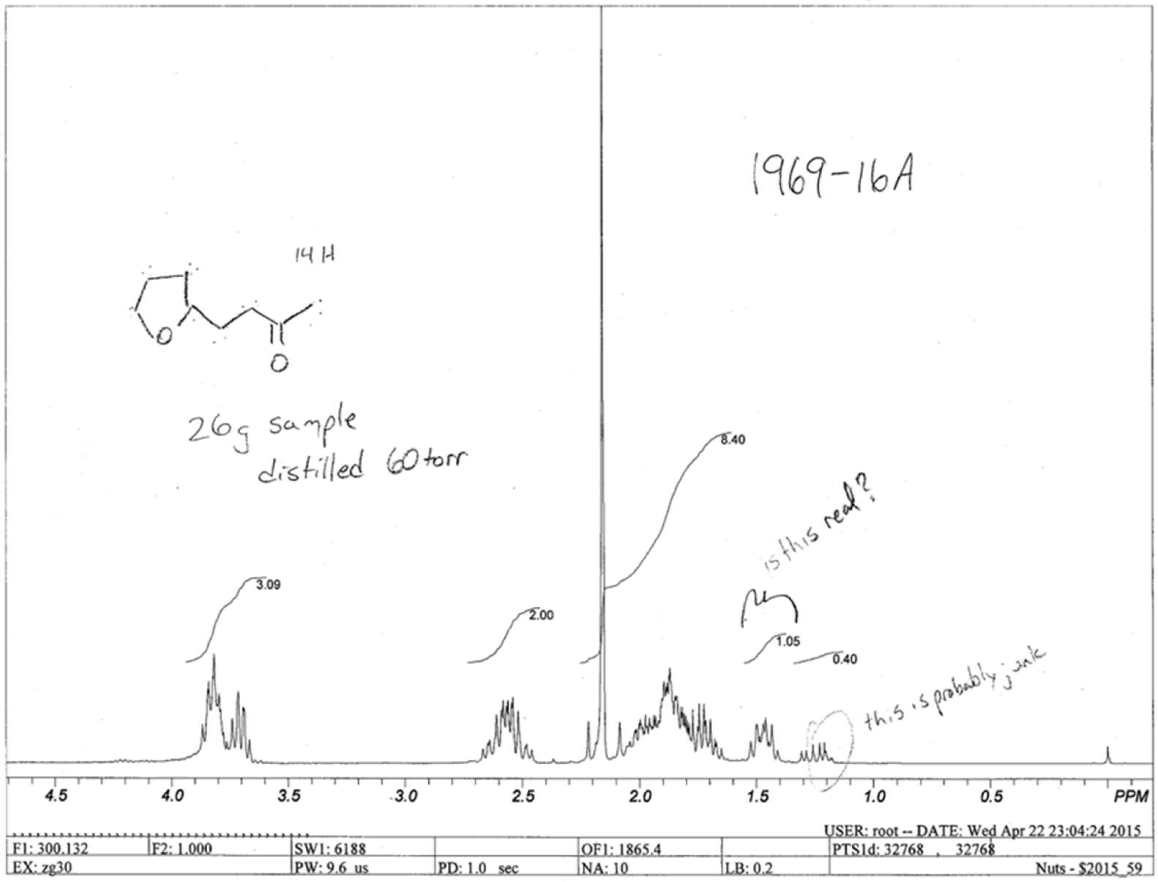


Appendix F NMR Data for Furanic Ketones

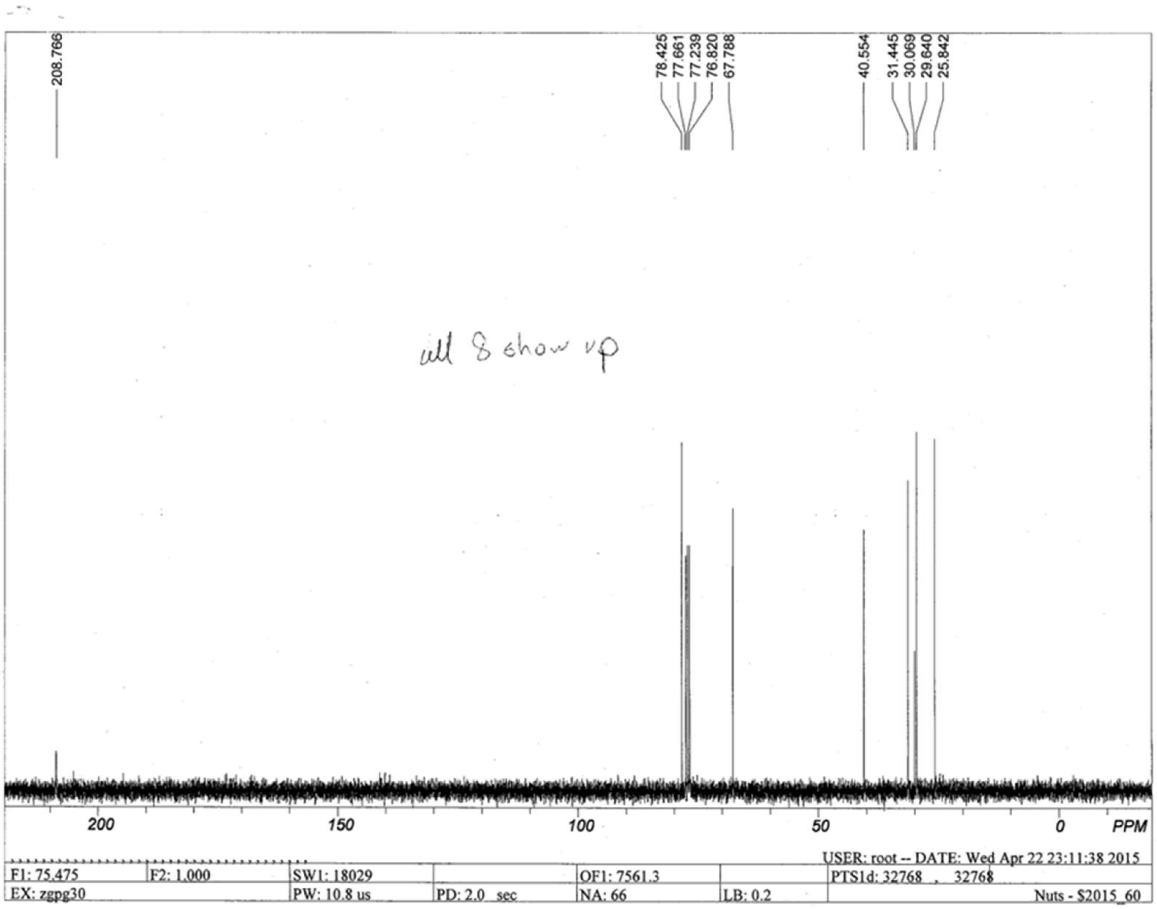
Proton NMR of furfurylideacetone (**11**)



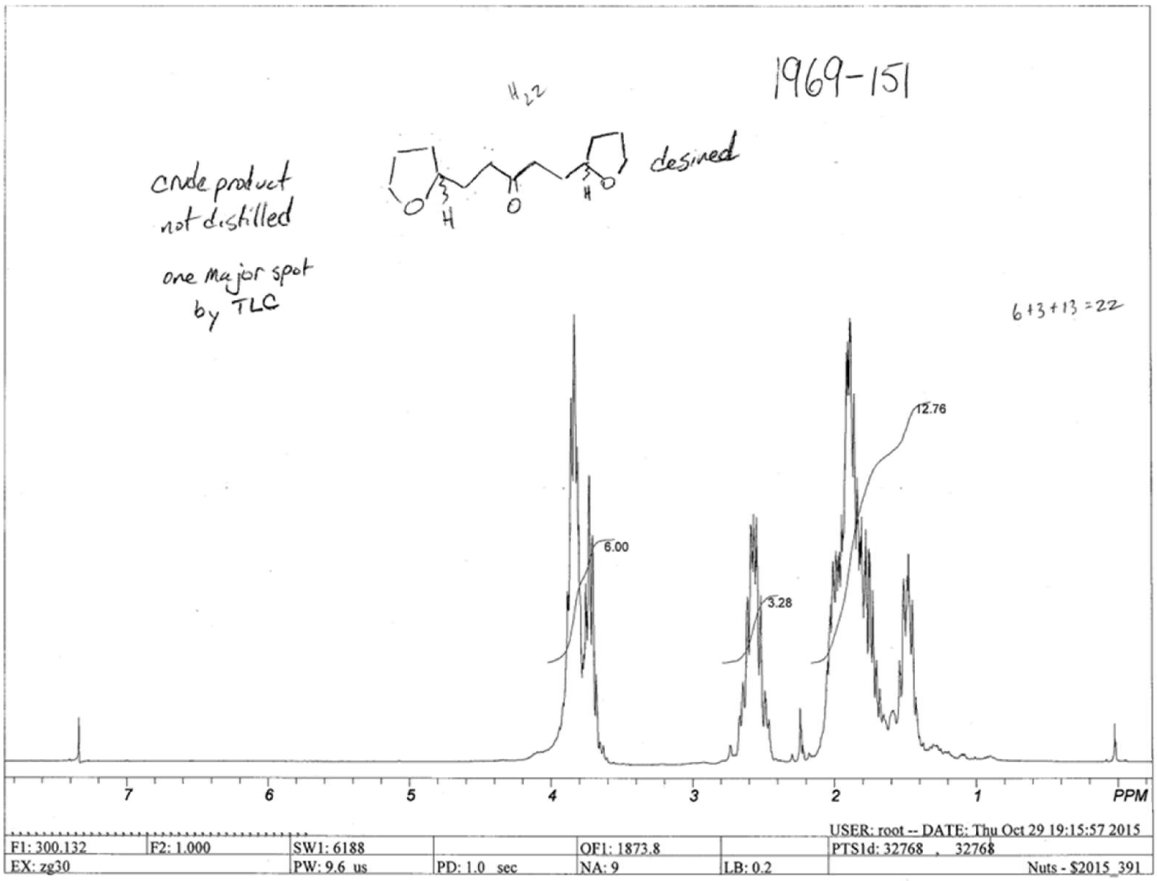
Proton NMR of tetrahydrofuranyl ketone (**17**)



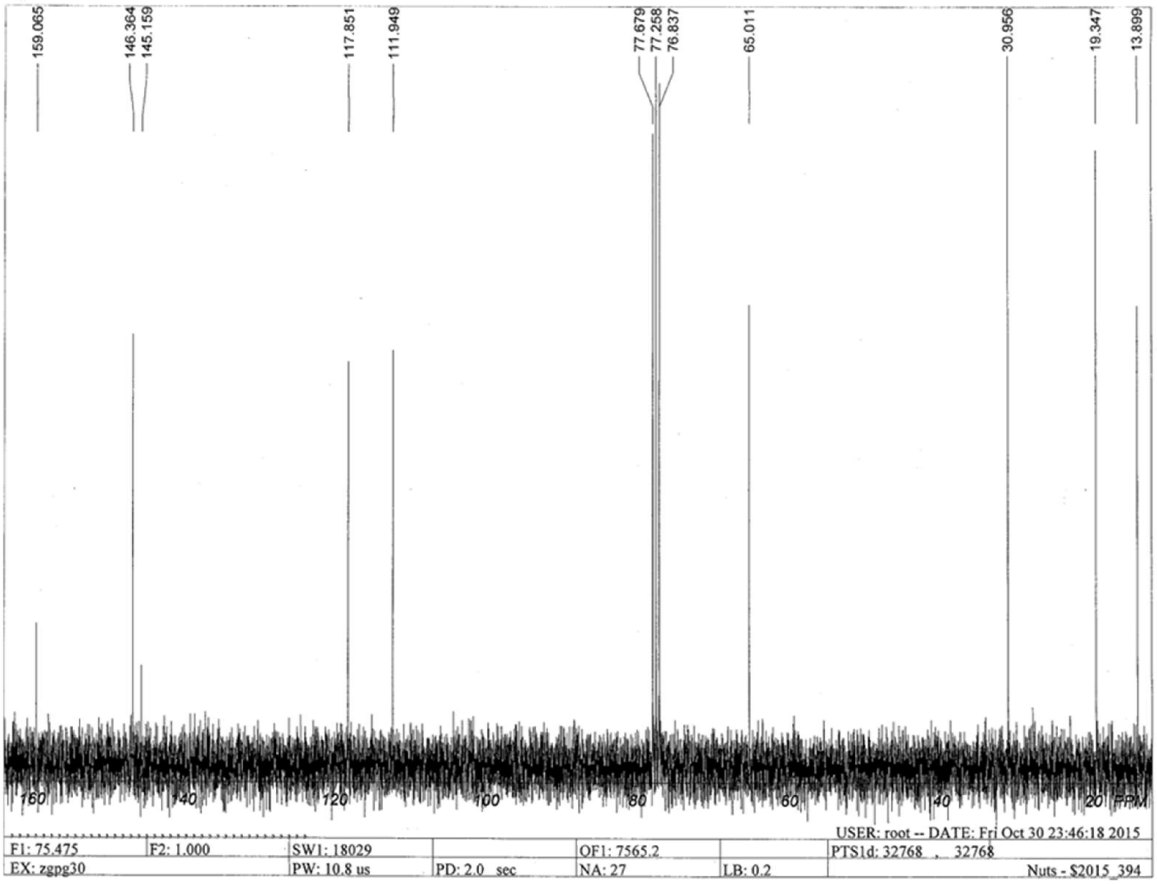
Proton NMR of tetrahydrofuranyl ketone (**17**)



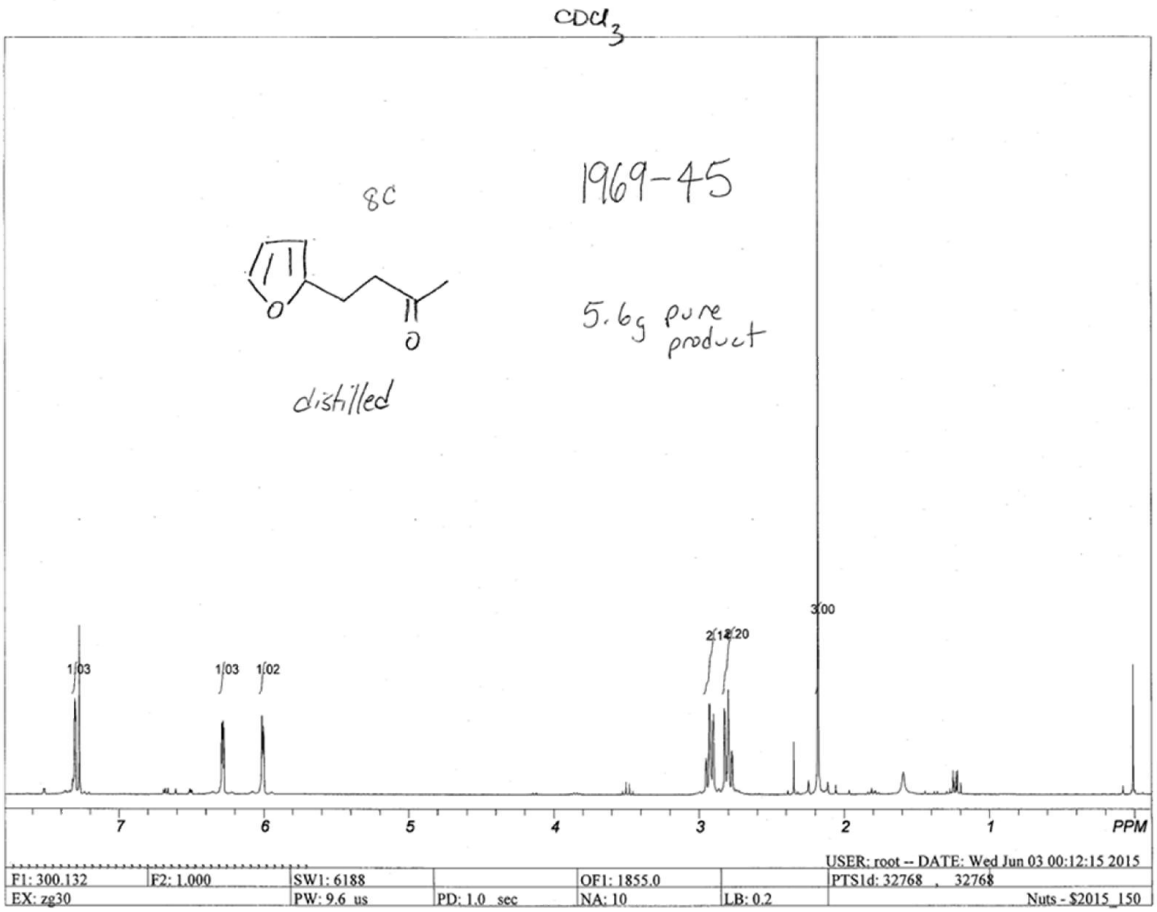
Proton NMR of saturated dodecahydro furanyl ketone (**151**)



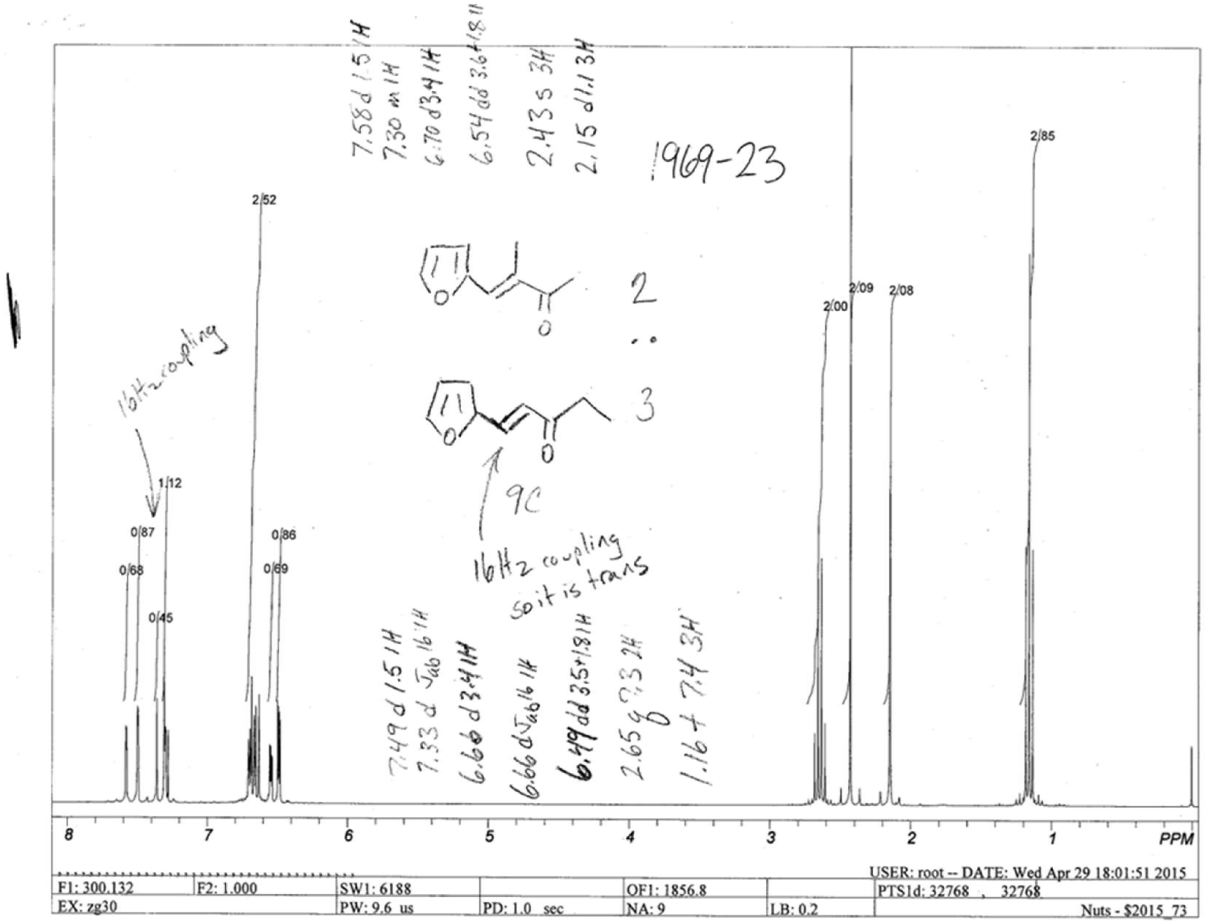
Carbon NMR of saturated dodecahydro furanyl ketone (**151**)



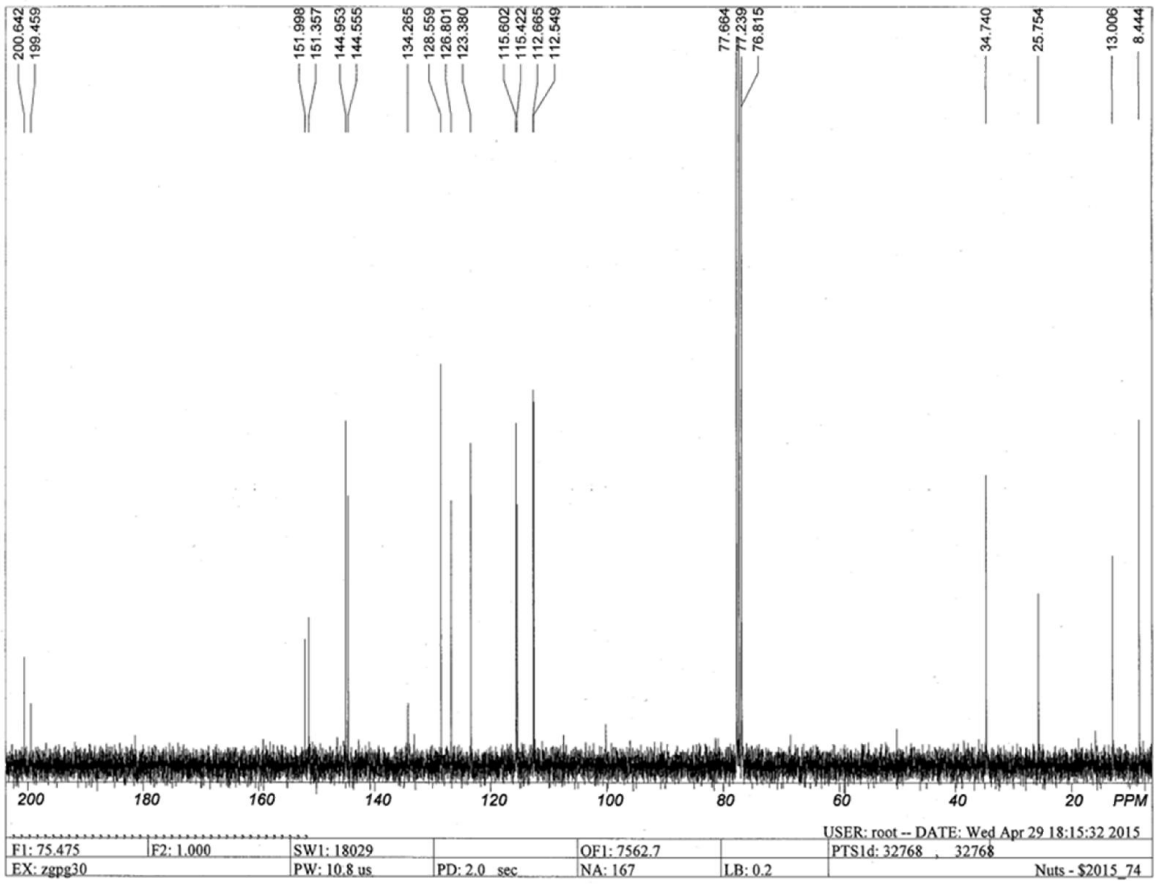
Proton NMR of dihydro furanyl ketone (**45**)



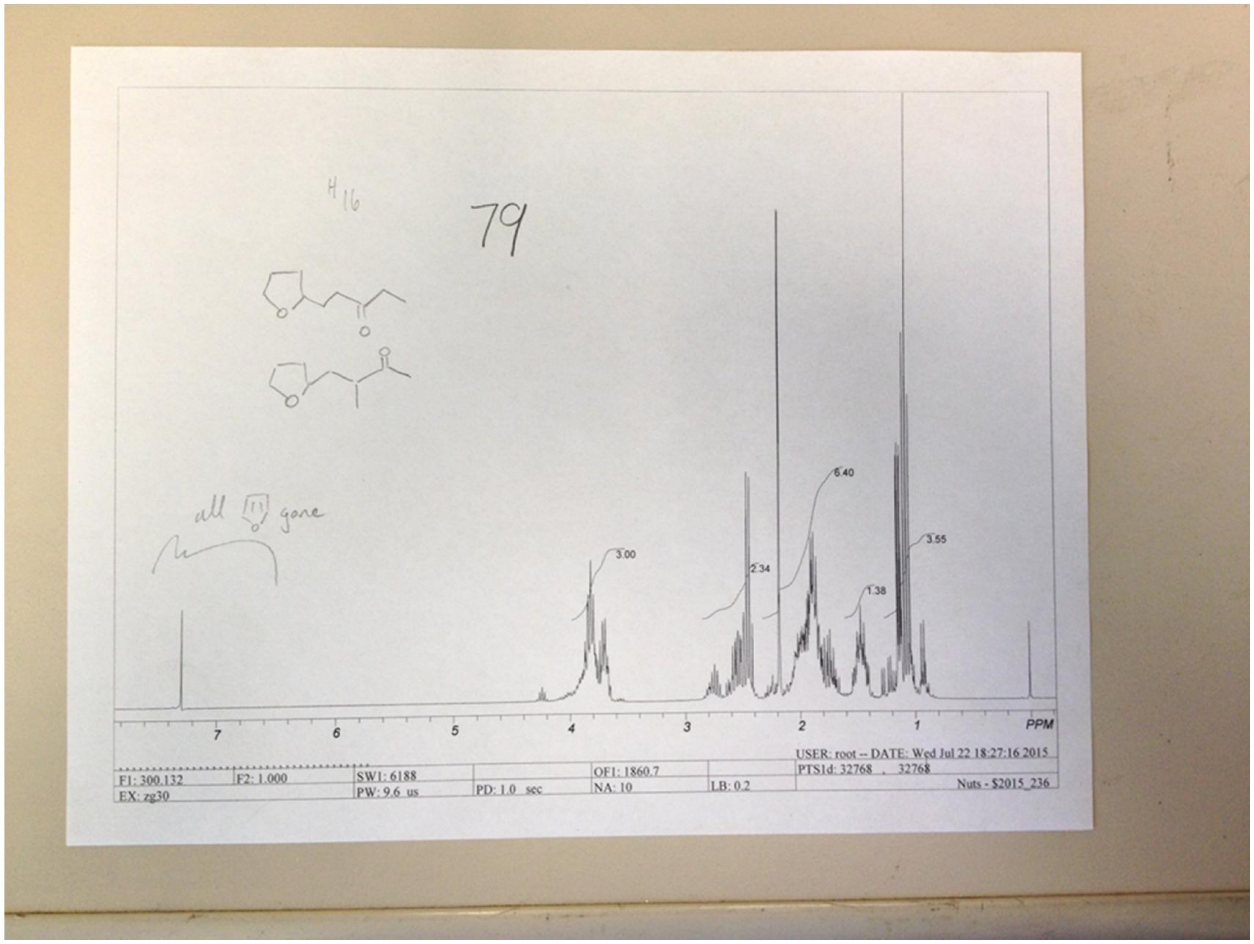
Proton NMR of furfurylidenone (**23**)



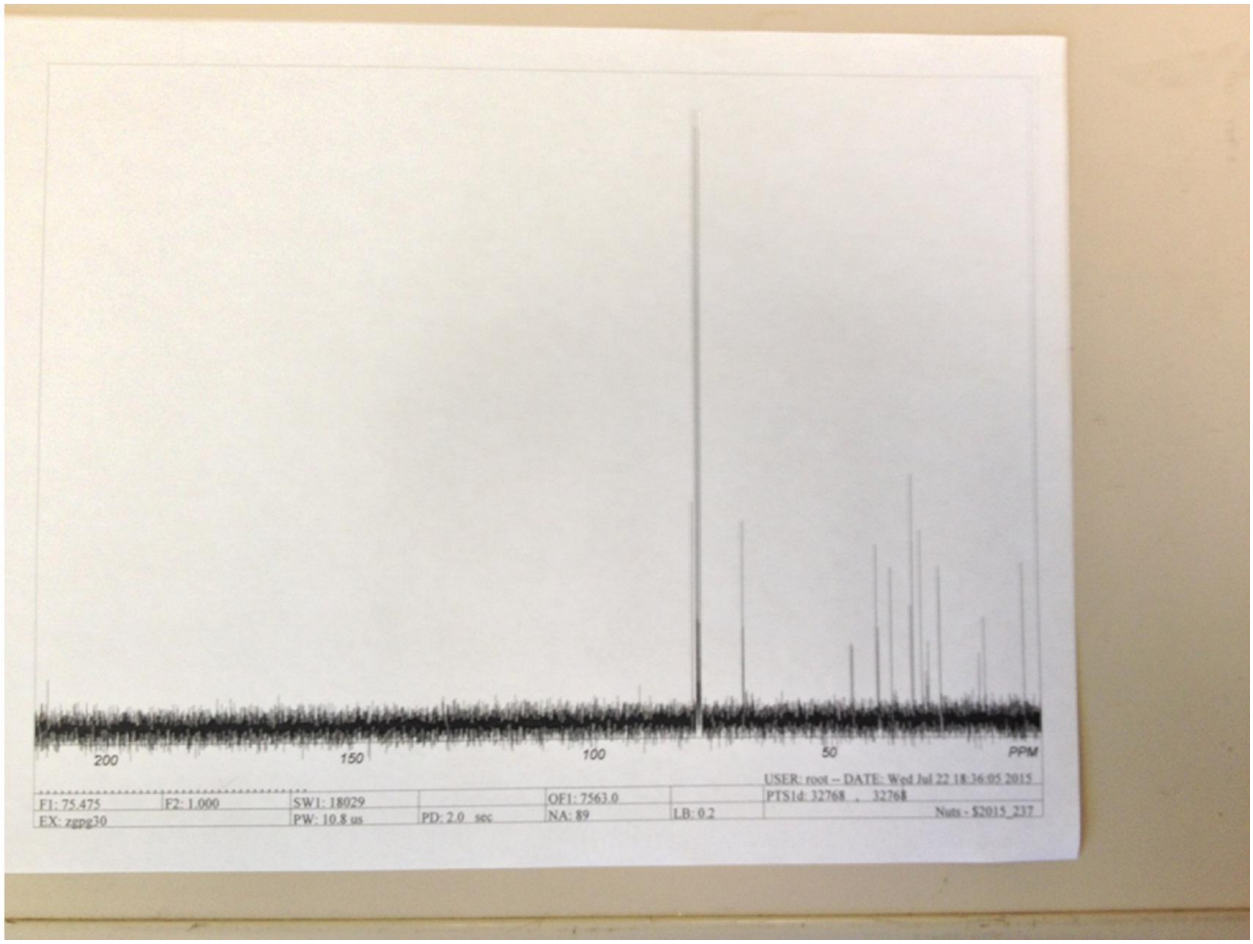
Carbon NMR of furfurylidenone (**23**)



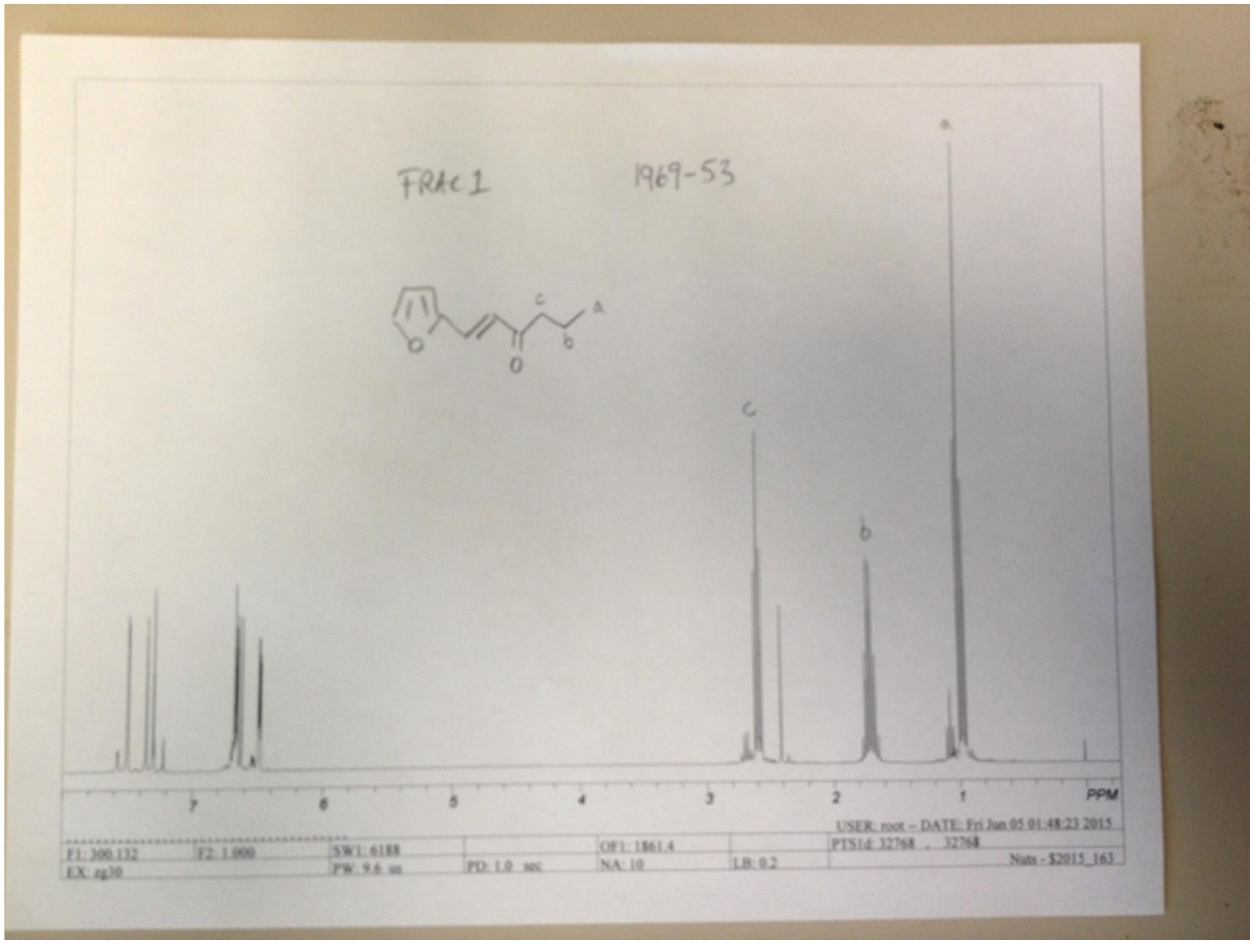
Proton NMR of tetrahydrofuranyl ketone (**79**)



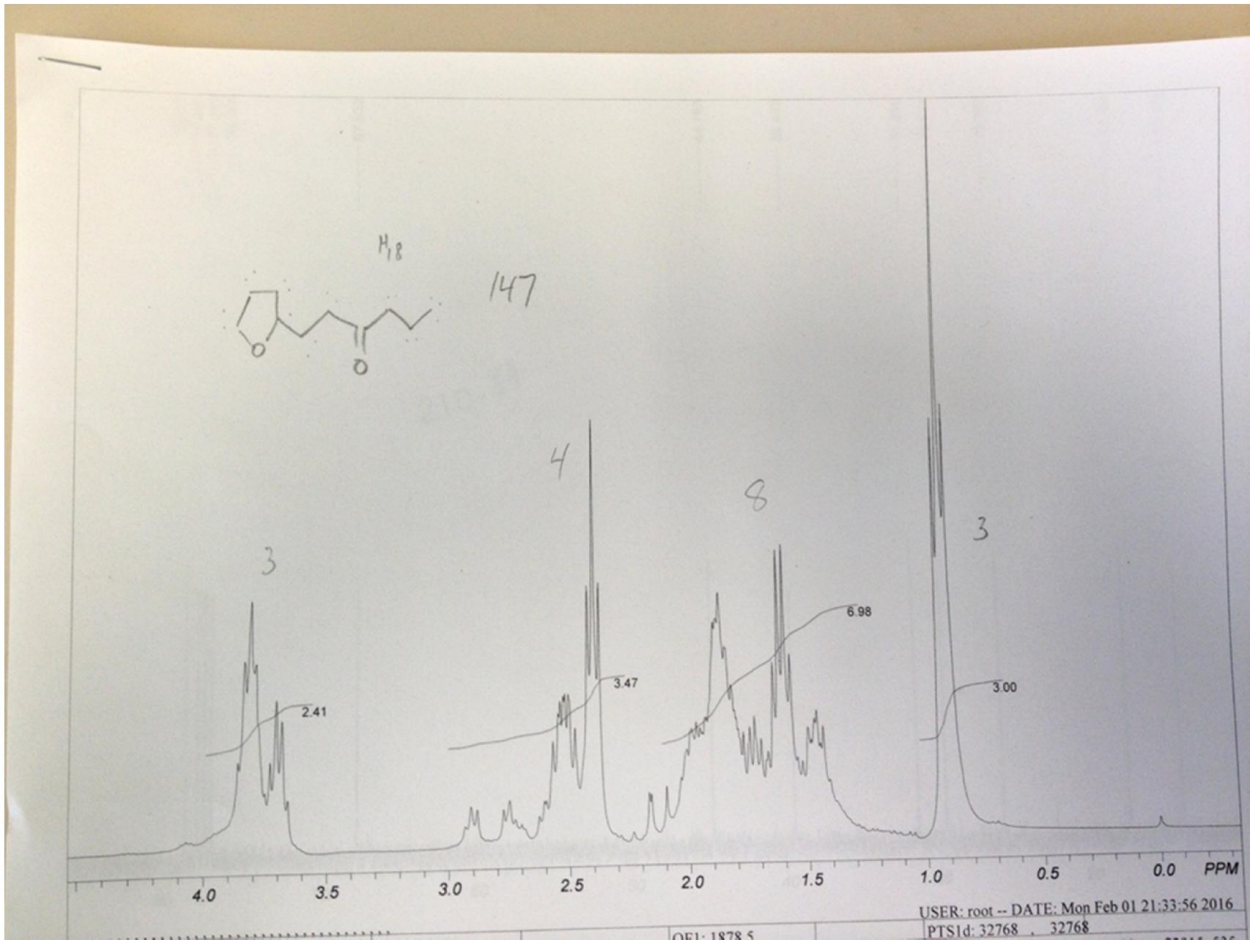
Carbon NMR of tetrahydrofuranyl ketone (**79**)



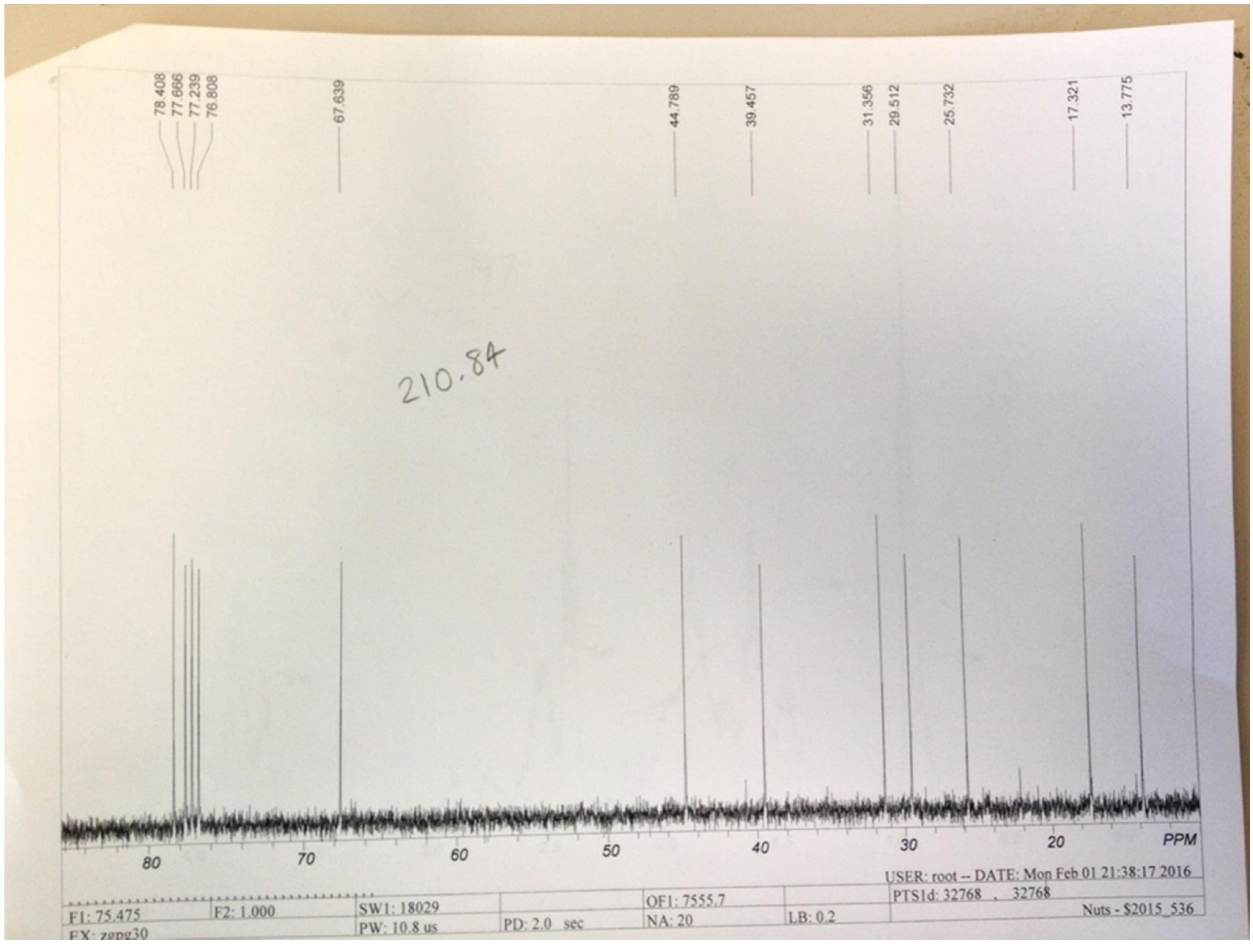
Proton NMR of furfurylidenone (**53**)



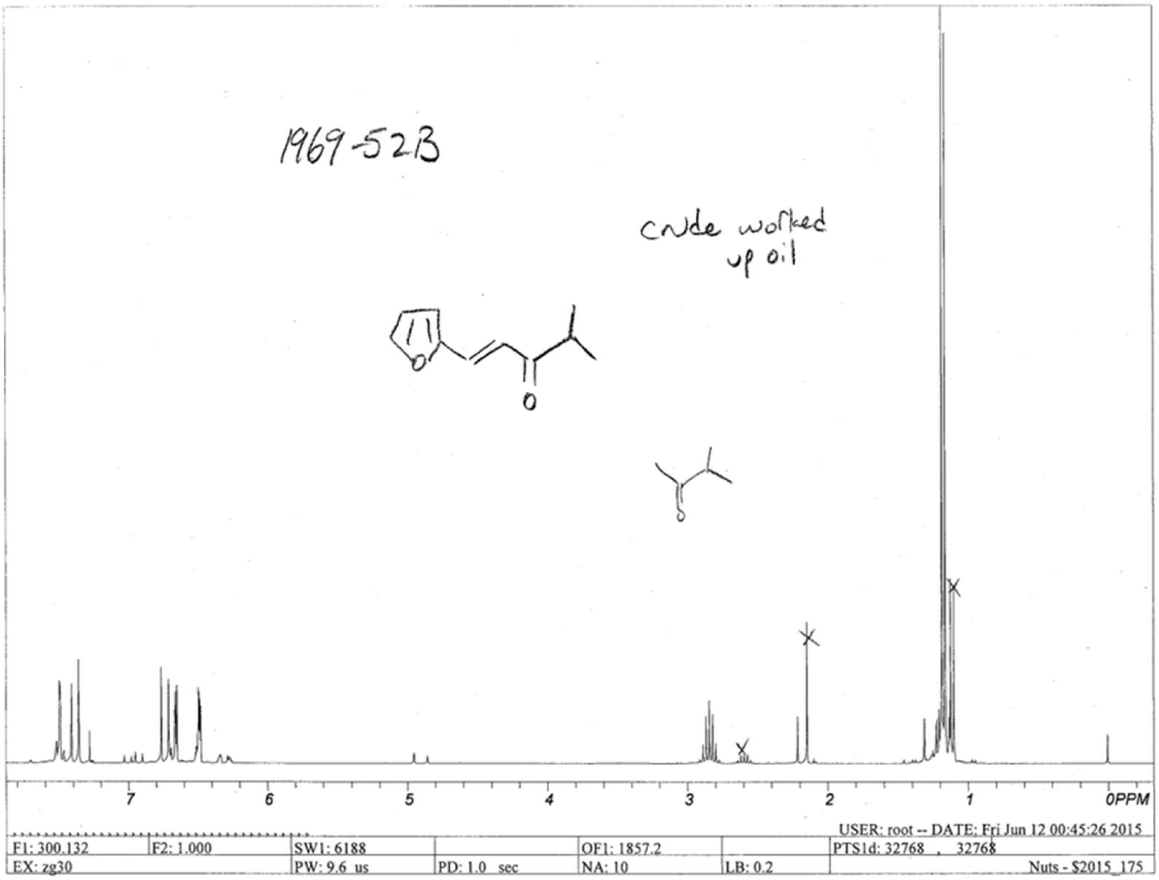
Proton NMR of tetrahydrofuranyl ketone (**147**)



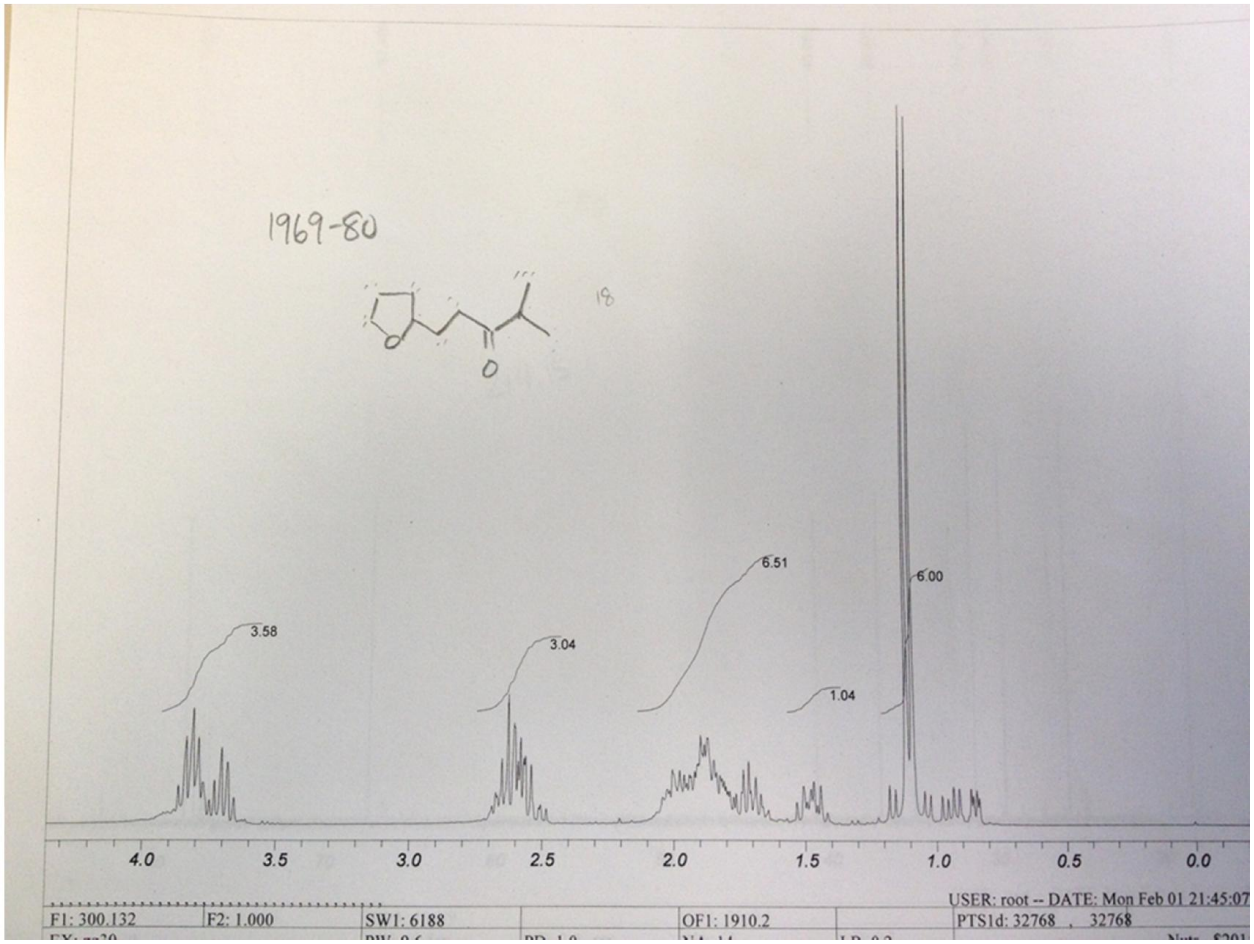
Carbon NMR of tetrahydrofuranyl ketone (**147**)



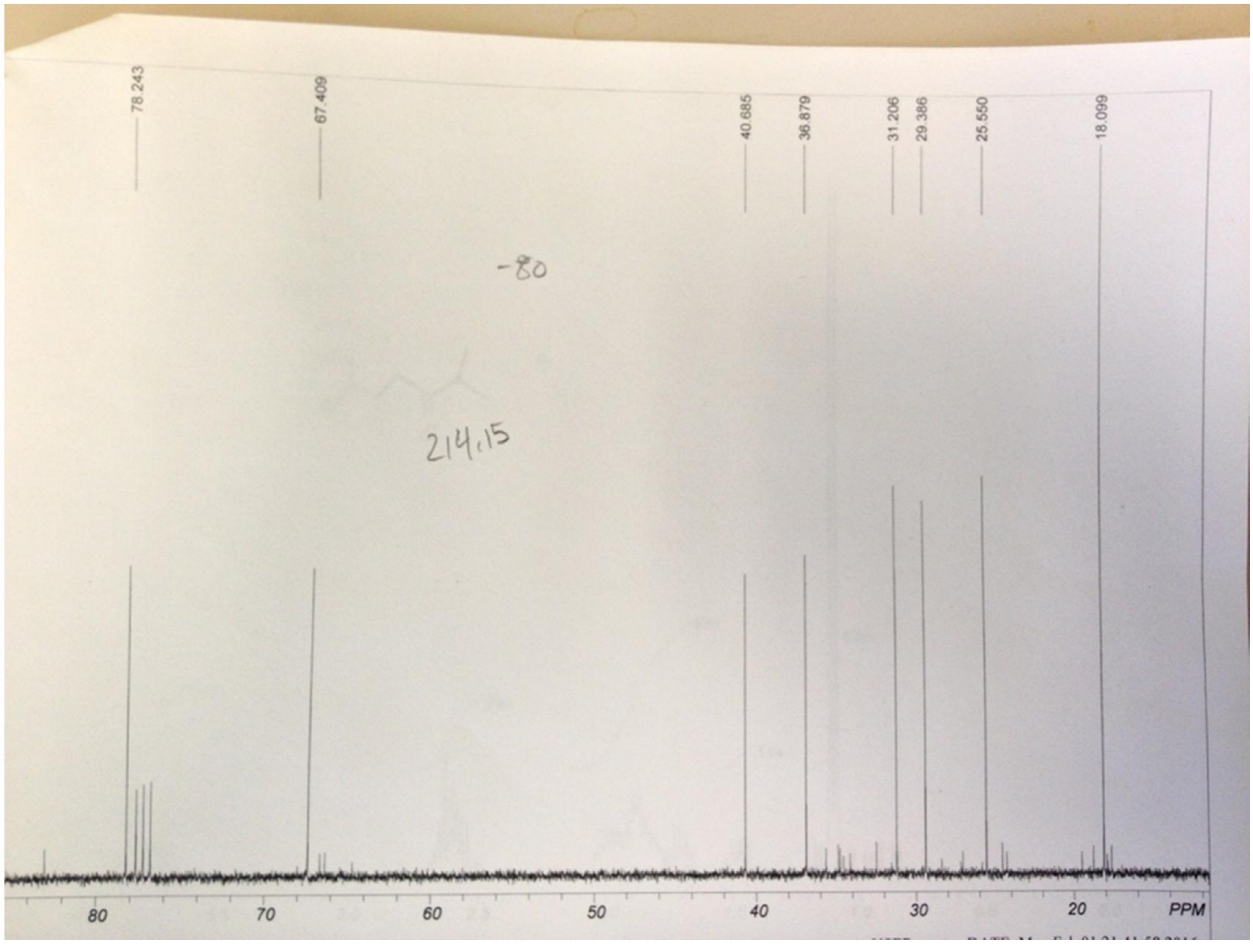
Proton NMR of furfurylidenone (**52B**)



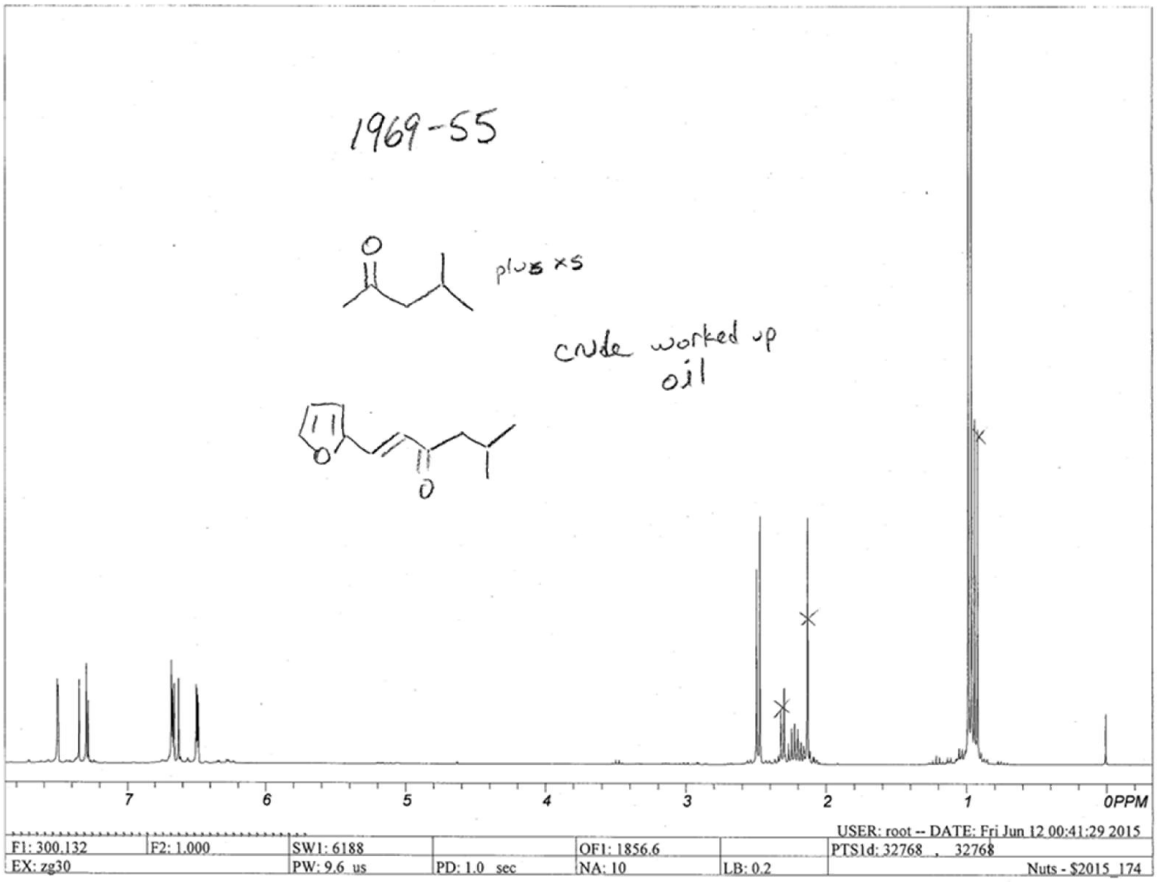
Proton NMR of tetrahydrofuranyl ketone (**80**)



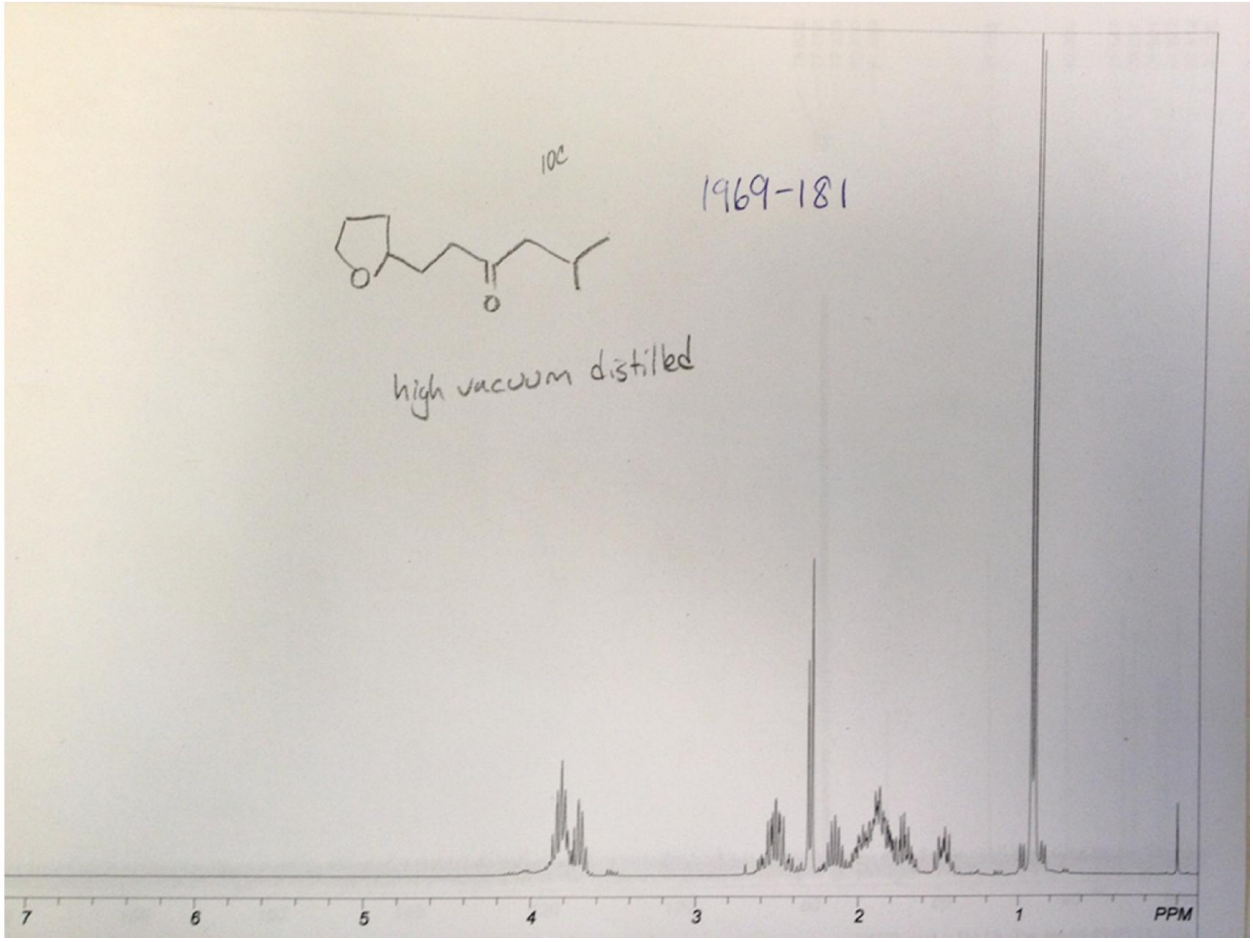
Carbon NMR of tetrahydrofuranyl ketone (**80**)



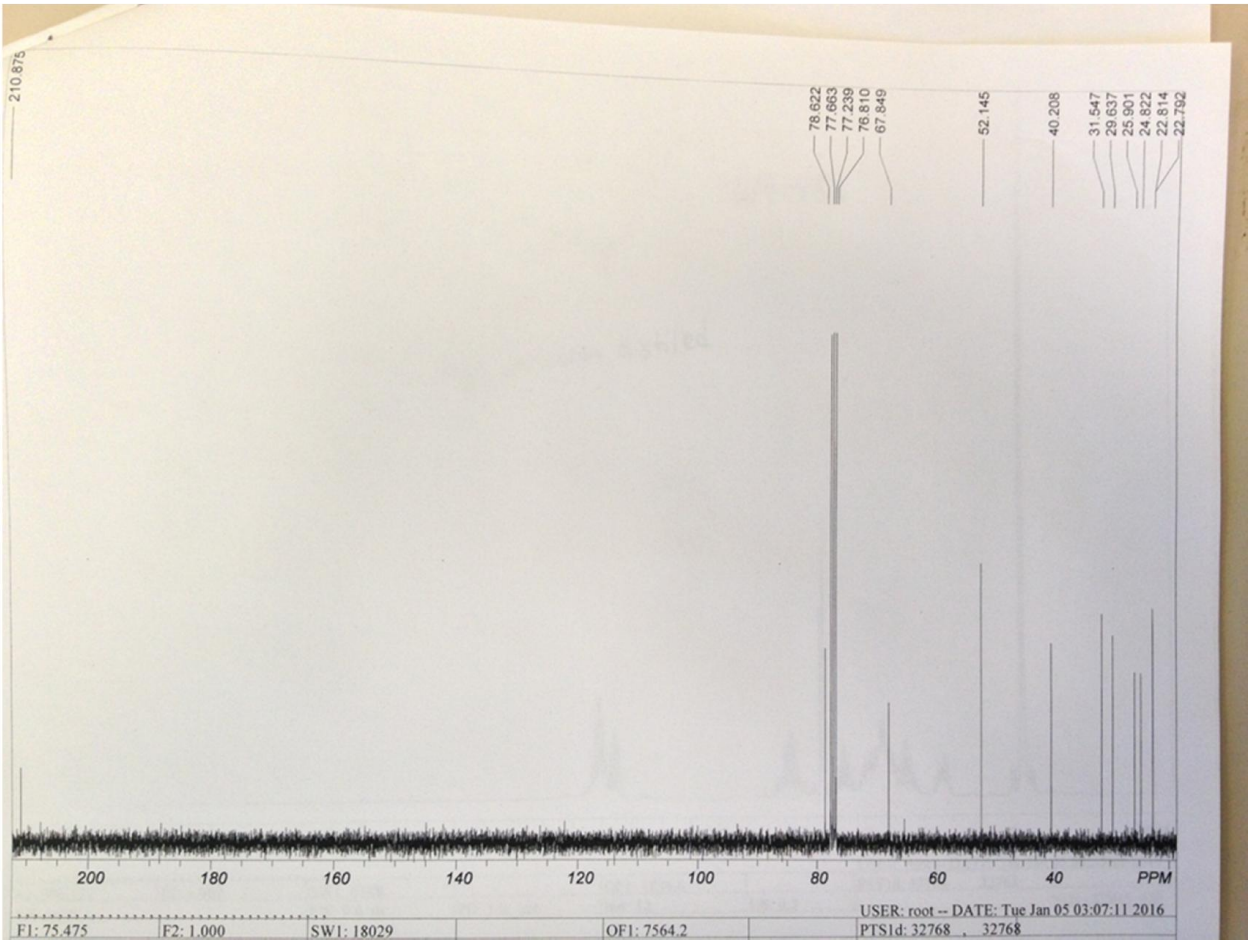
Proton NMR of furfurylidenone (**55**)



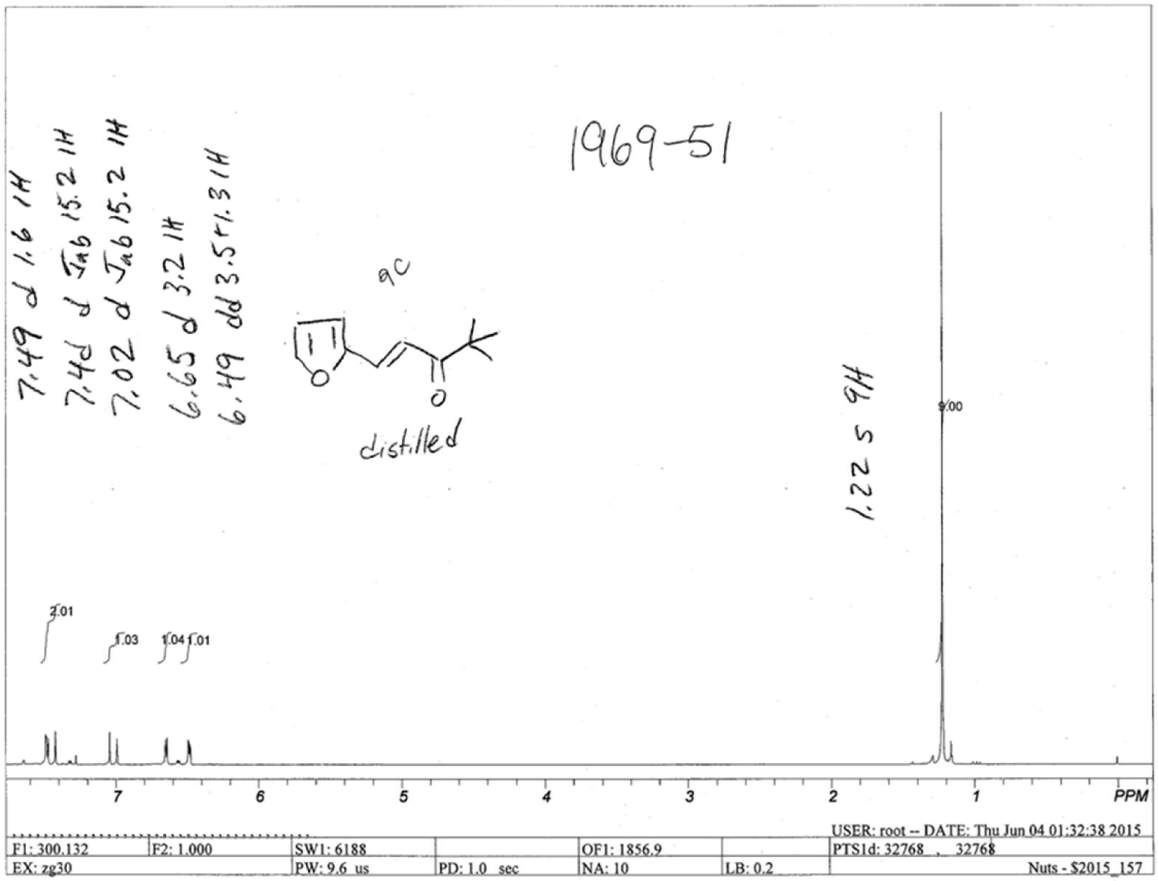
Proton NMR of tetrahydrofuranyl ketone (**82**)



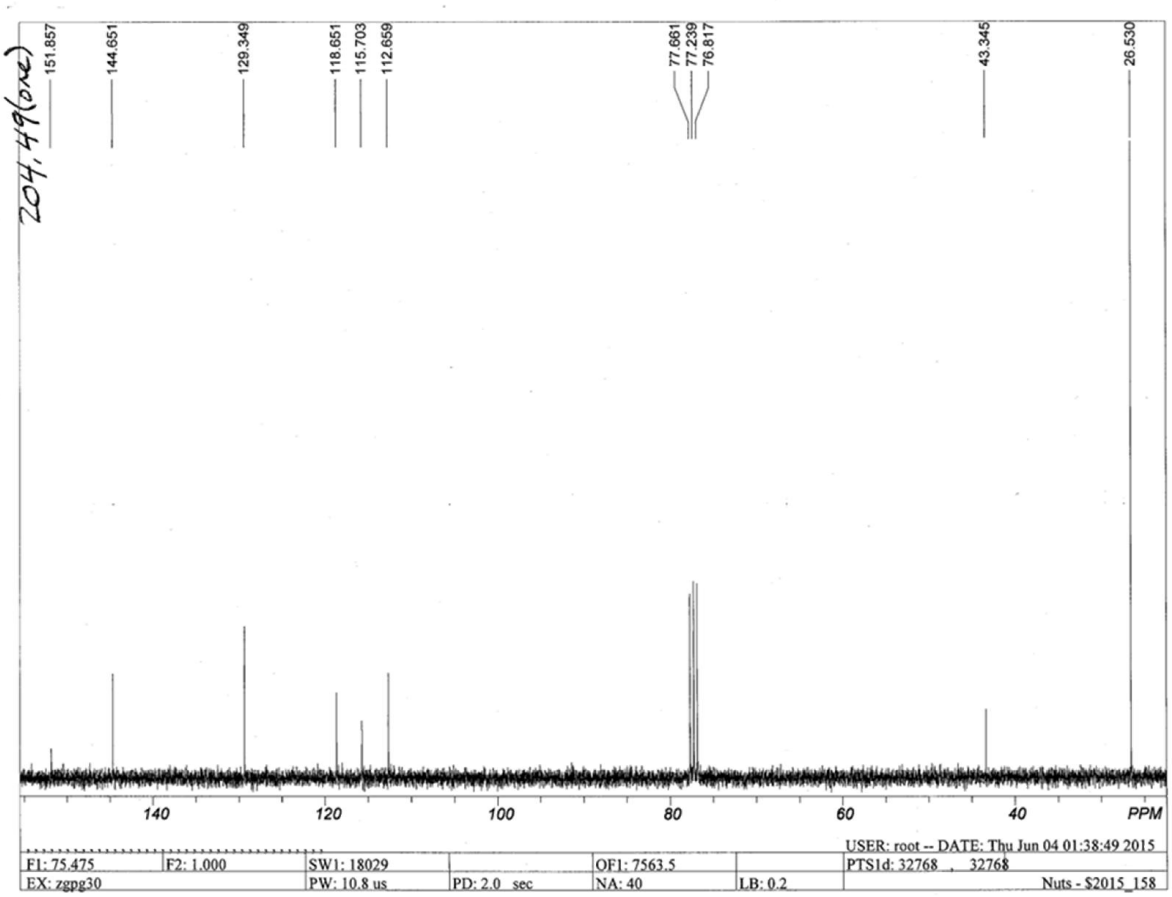
Carbon NMR of tetrahydrofuranyl ketone (**82**)



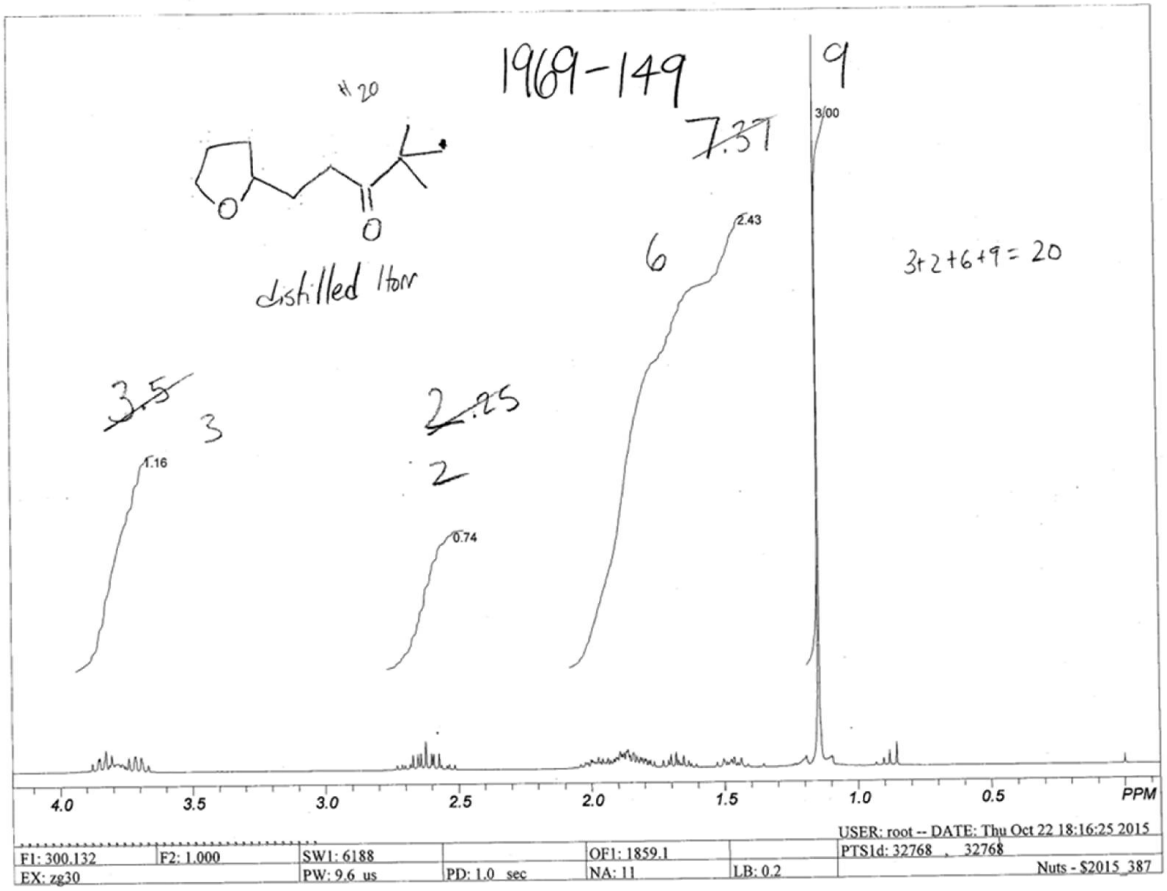
Proton NMR of furfurylidenone (**51**)



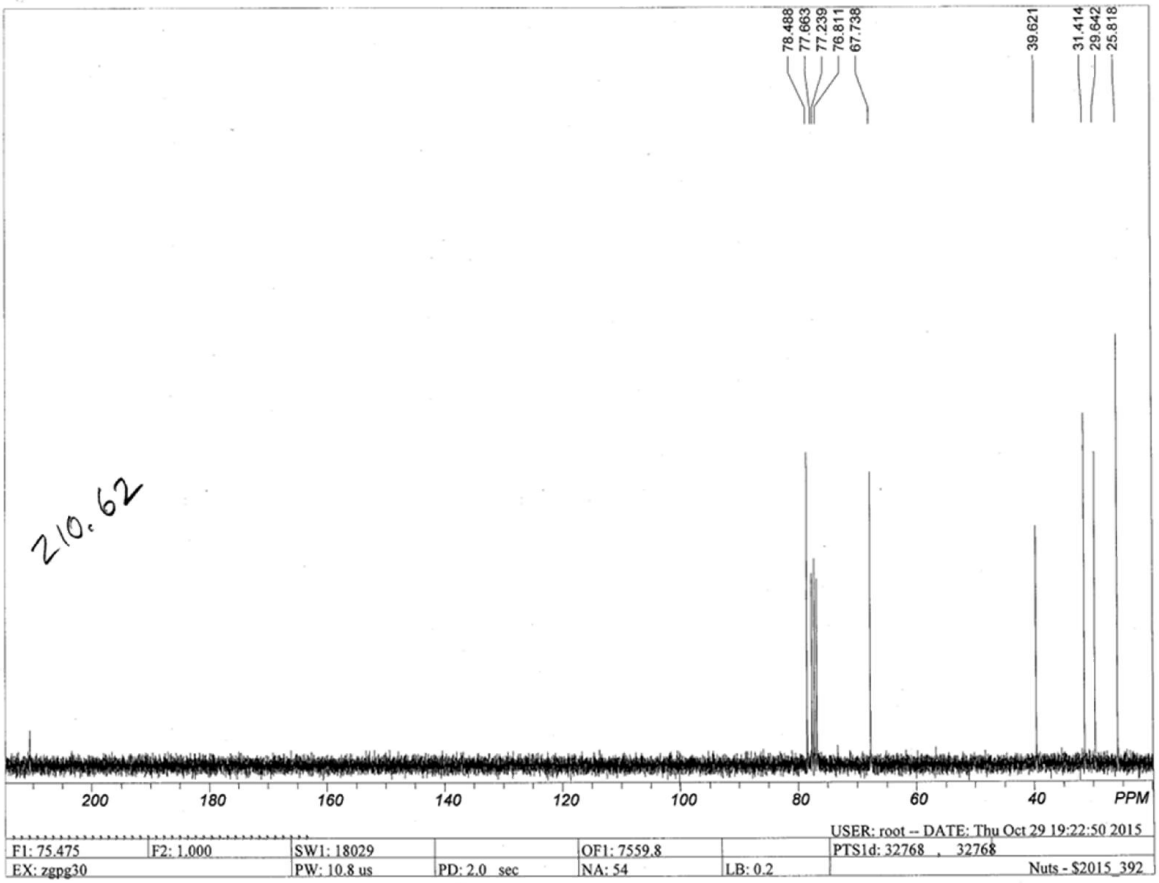
Carbon NMR of furfurylidenone (**51**)



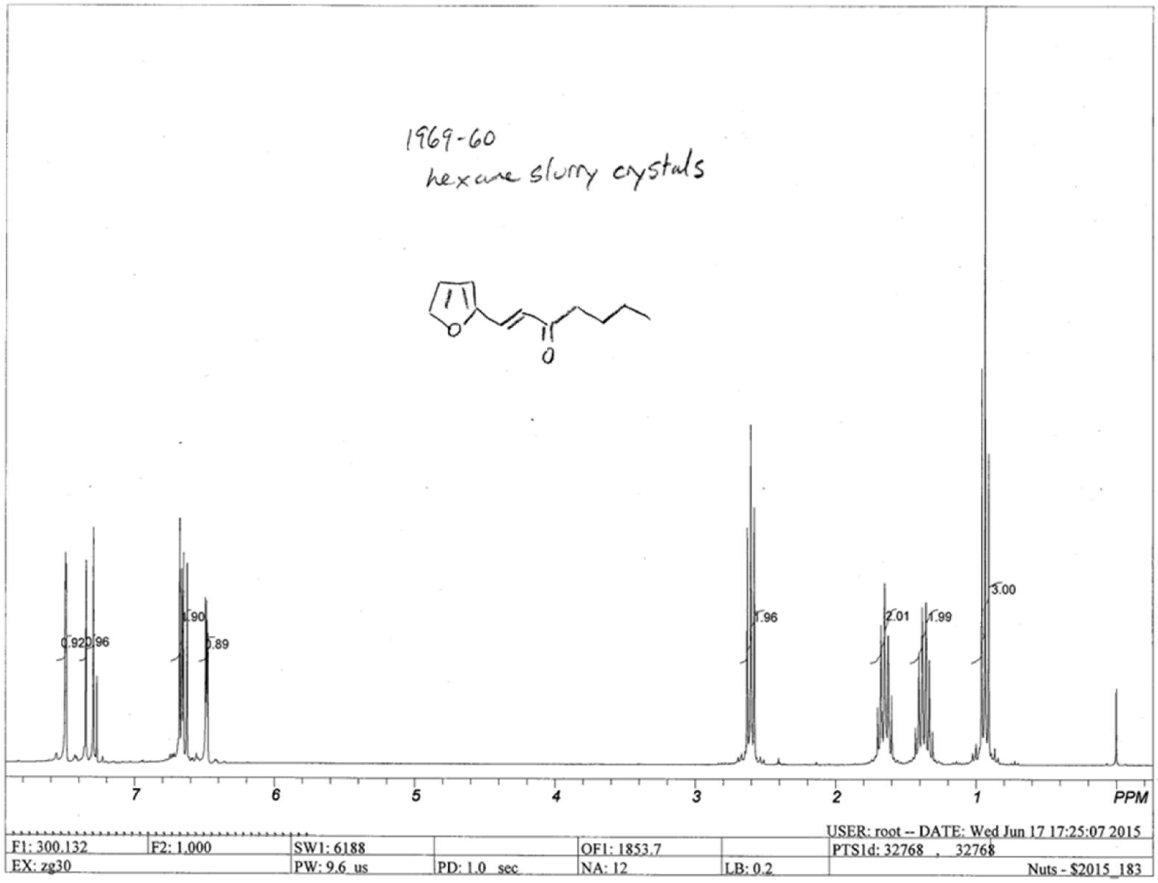
Proton NMR of tetrahydrofuranyl ketone (**149**)



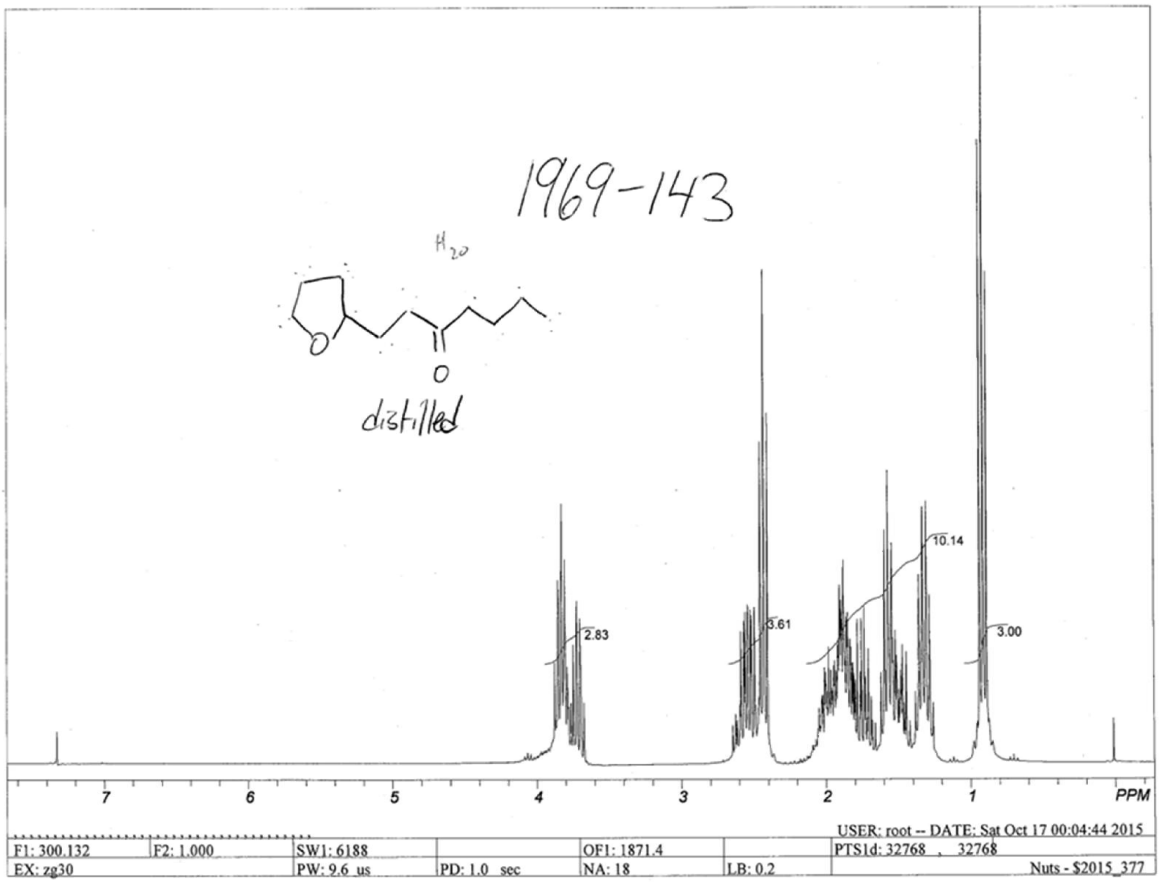
Carbon NMR of tetrahydrofuranyl ketone (**149**)



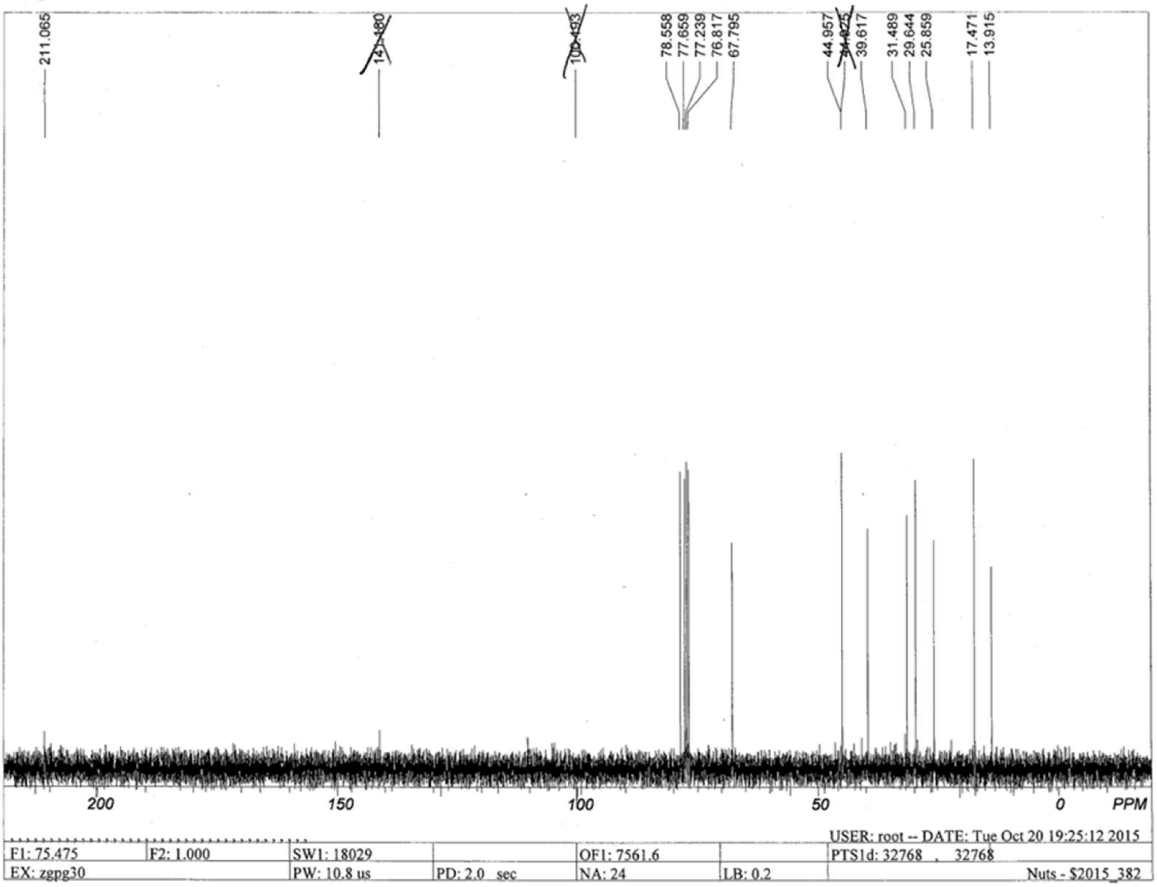
Proton NMR of furfurylidenone (**60**)



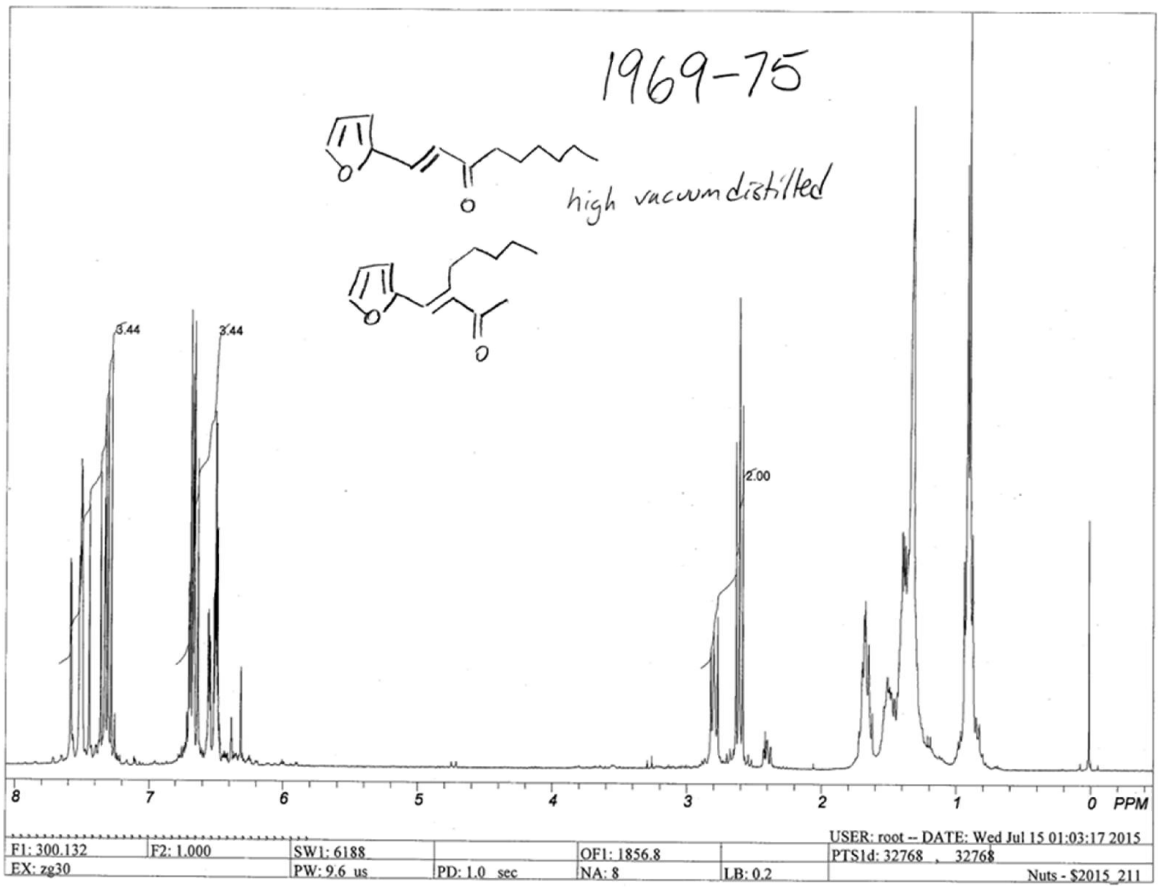
Proton NMR of tetrahydrofuranyl ketone (**143**)



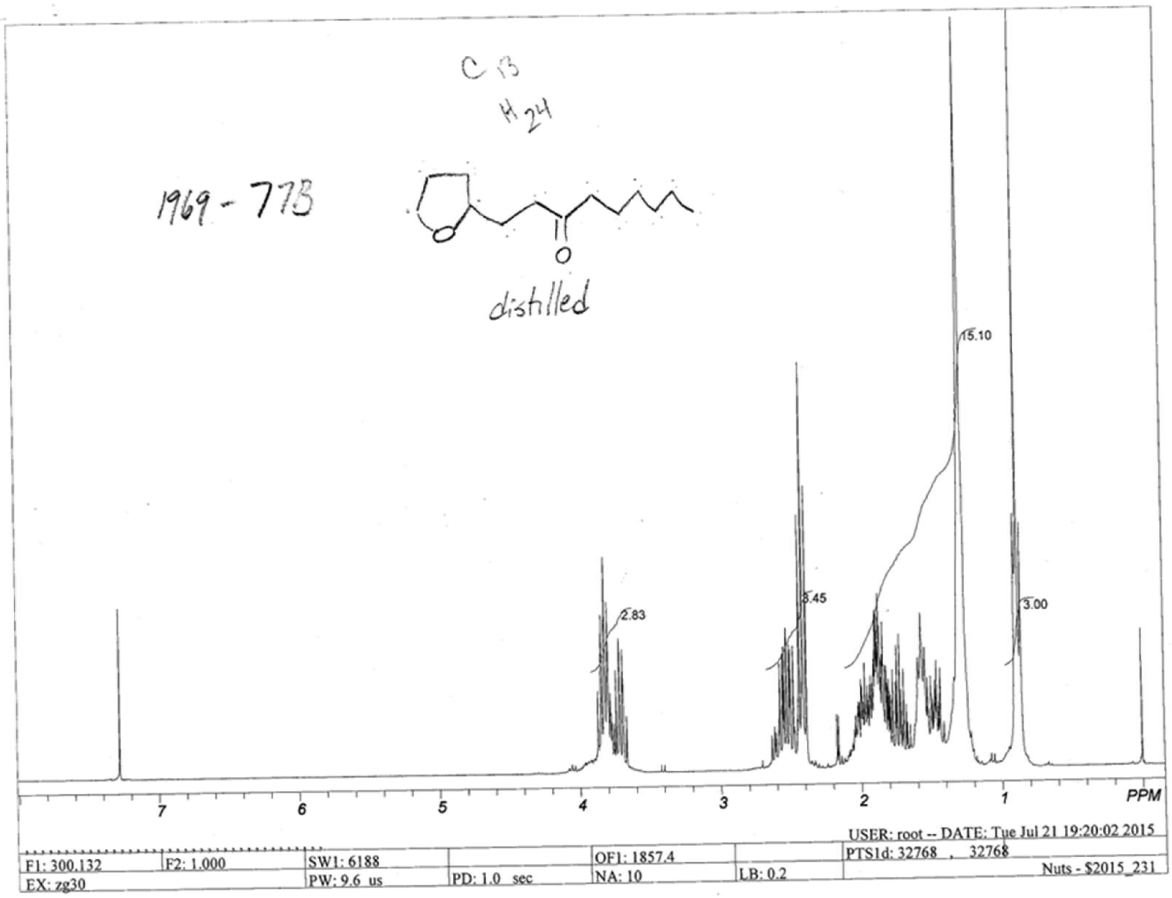
Carbon NMR of tetrahydrofuranyl ketone (**143**)



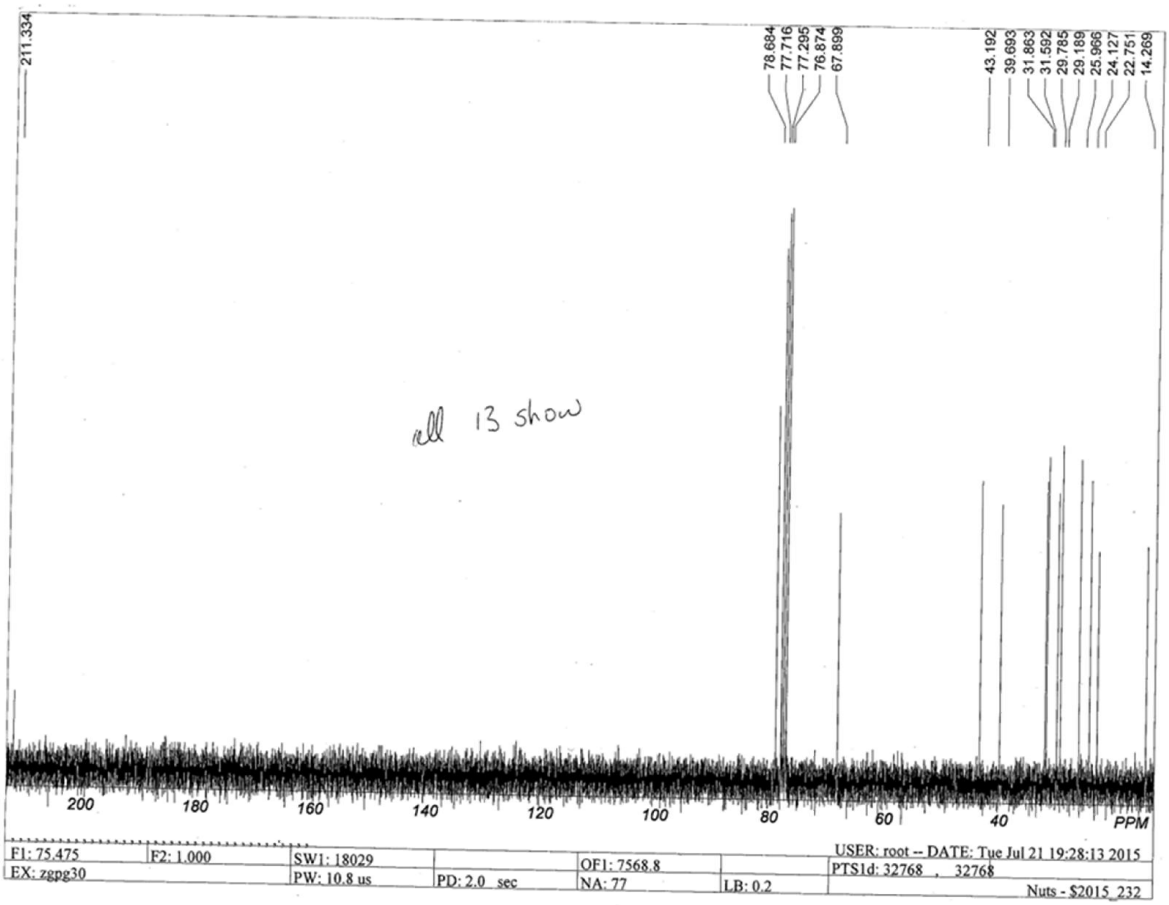
Proton NMR of furfurylidenone (**77A**)



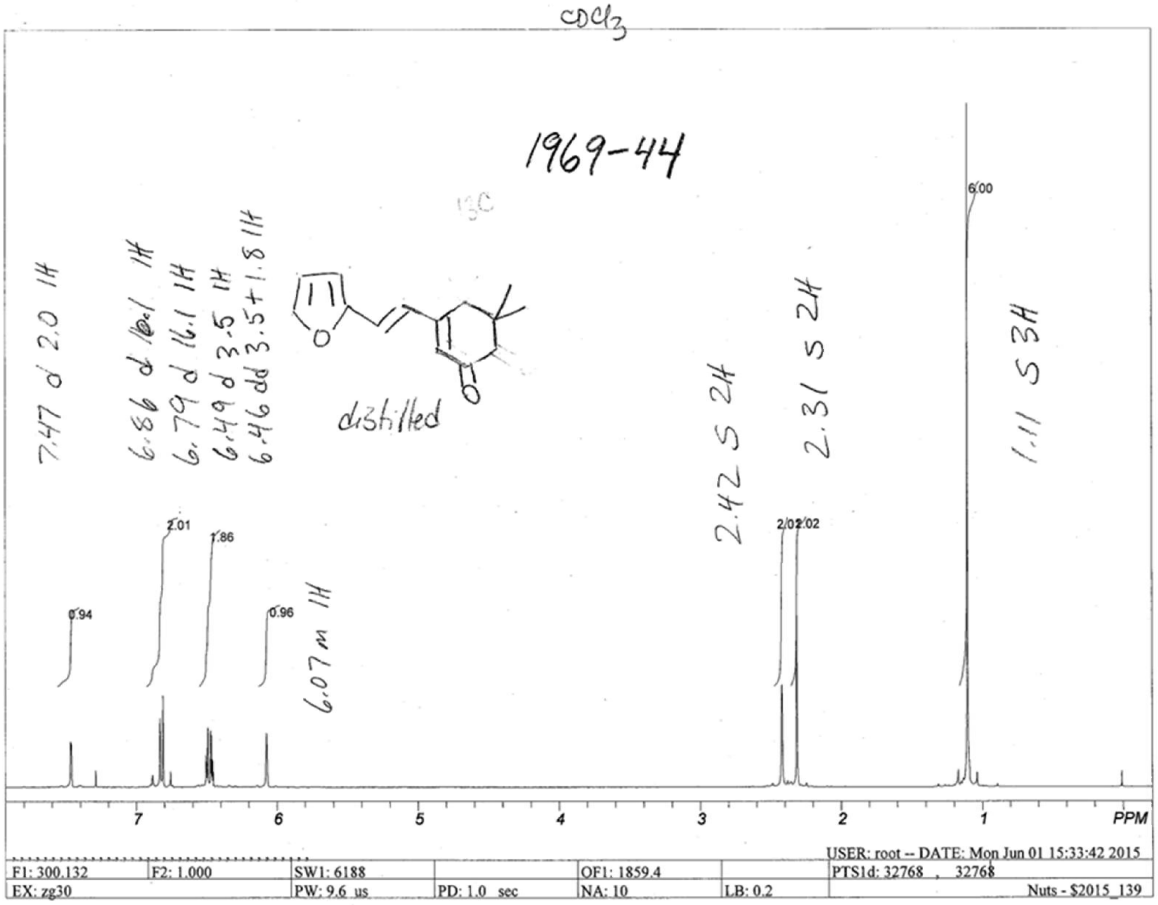
Proton NMR of tetrahydrofuranyl ketone (**77B**)



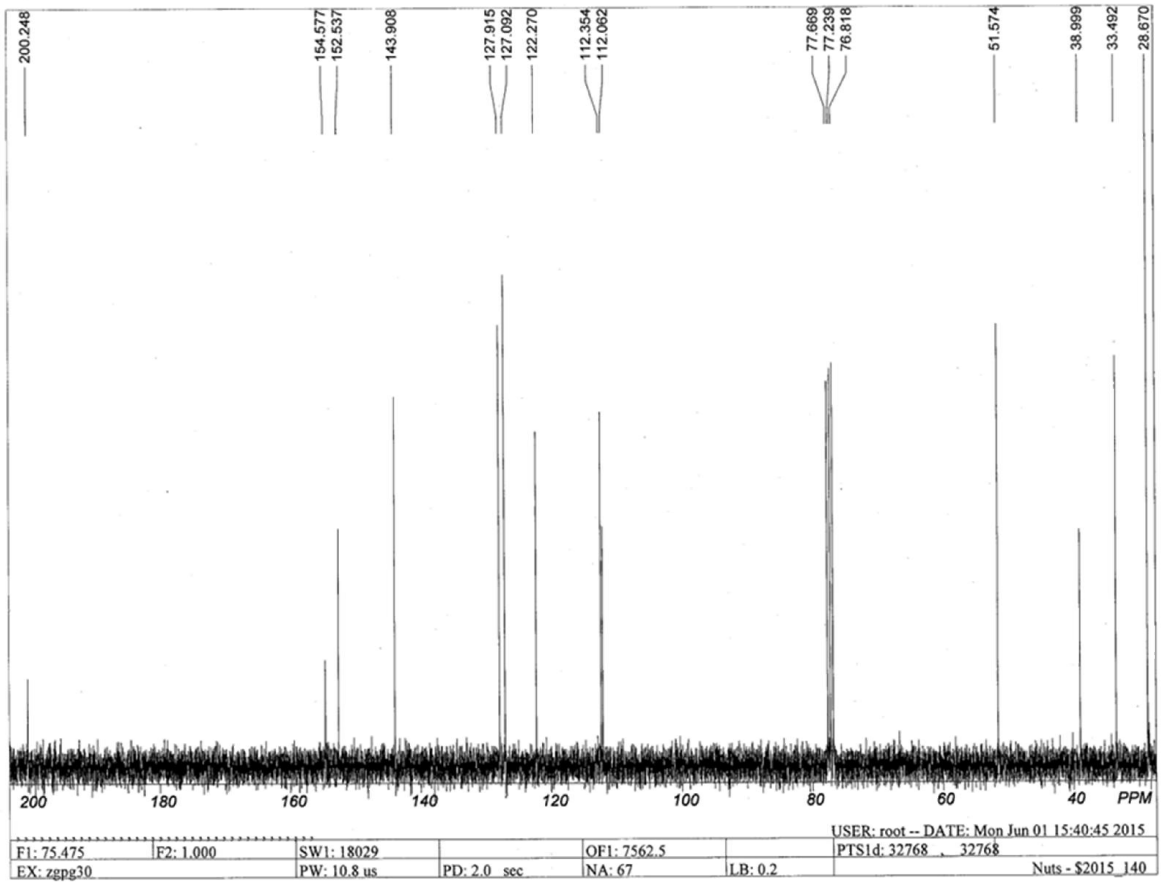
Carbon NMR of tetrahydrofuranyl ketone (**77B**)



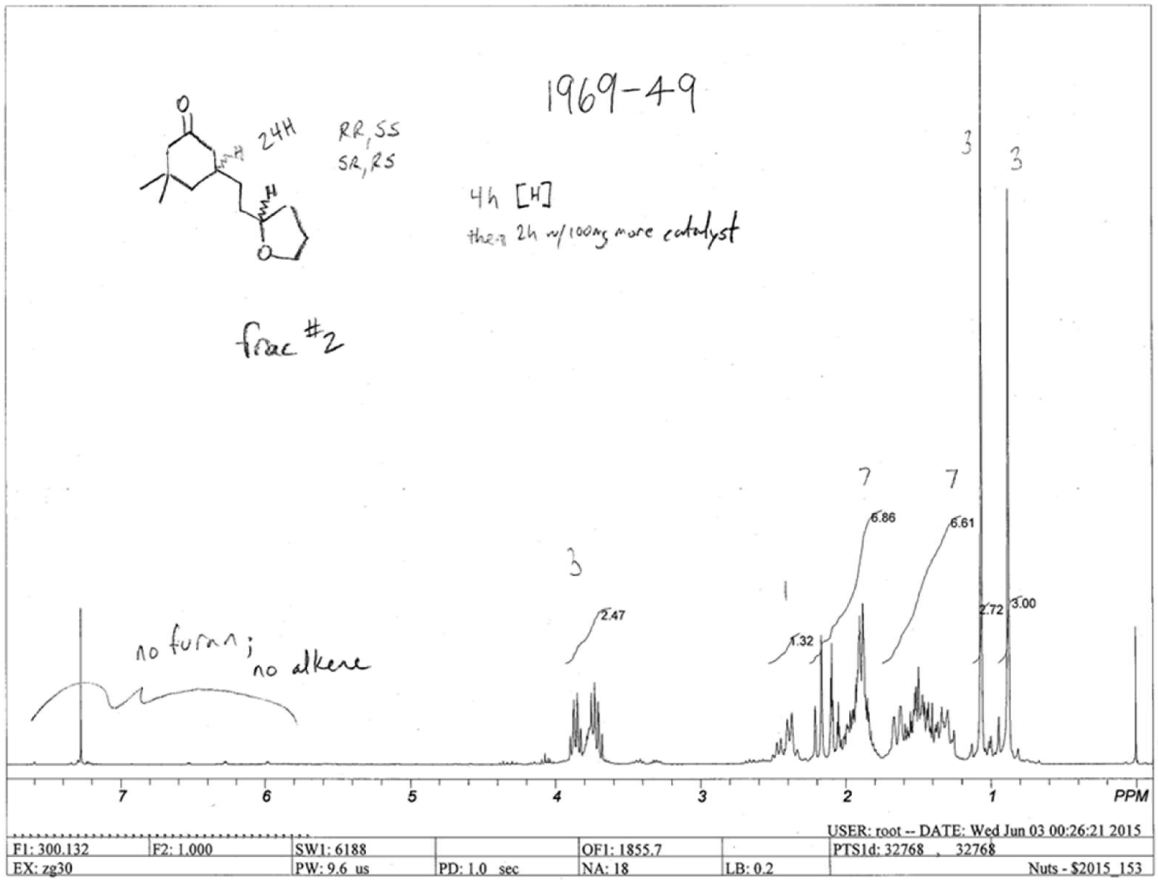
Proton NMR of furfurylidenone (**44**)



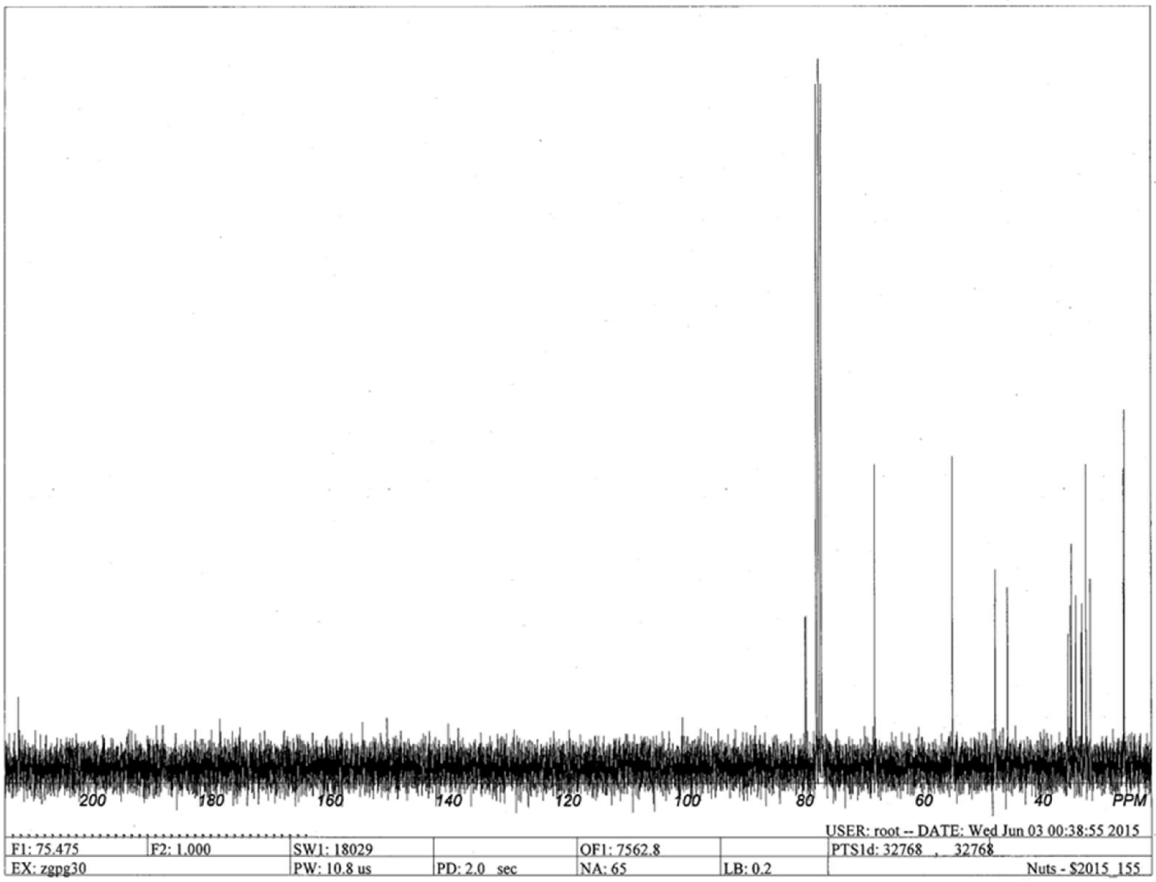
Carbon NMR of furfurylidenone (**44**)



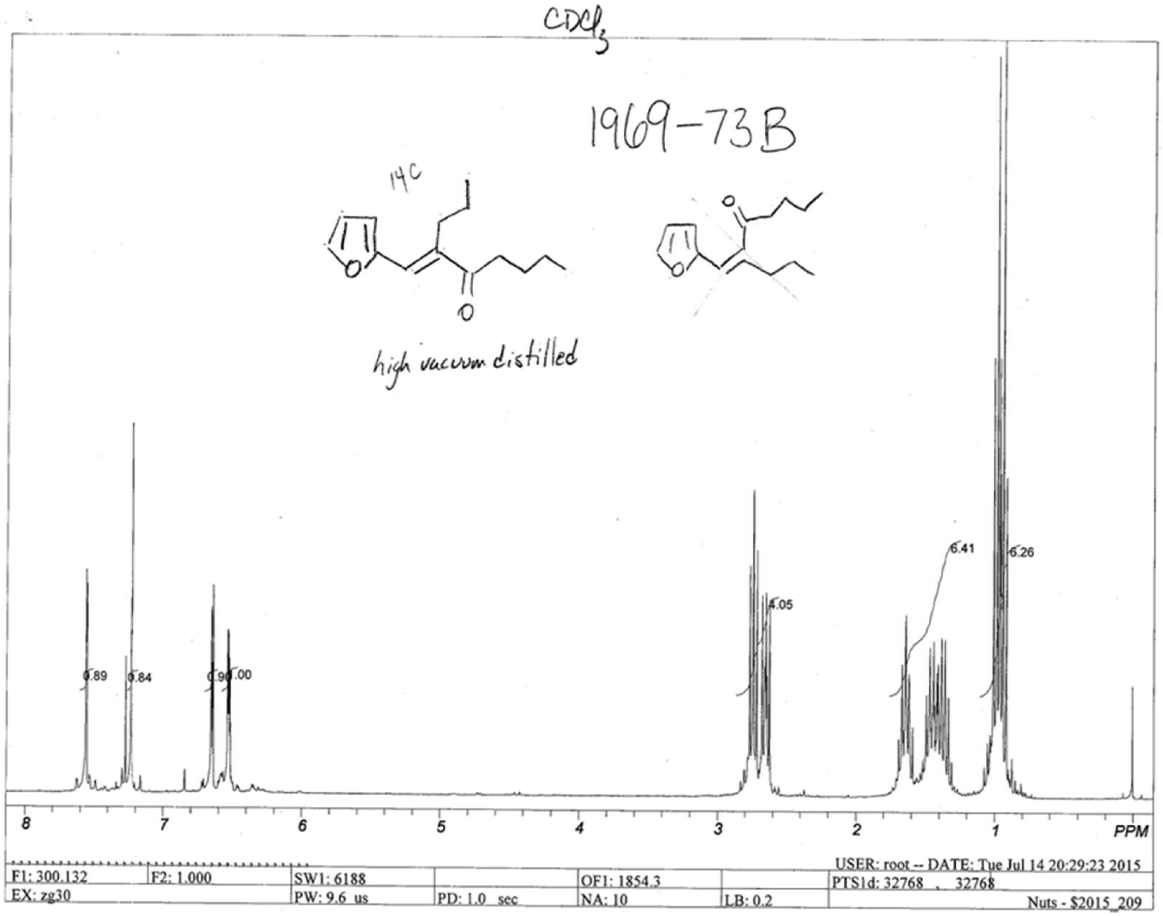
Proton NMR of tetrahydrofuranyl ketone (**49**)



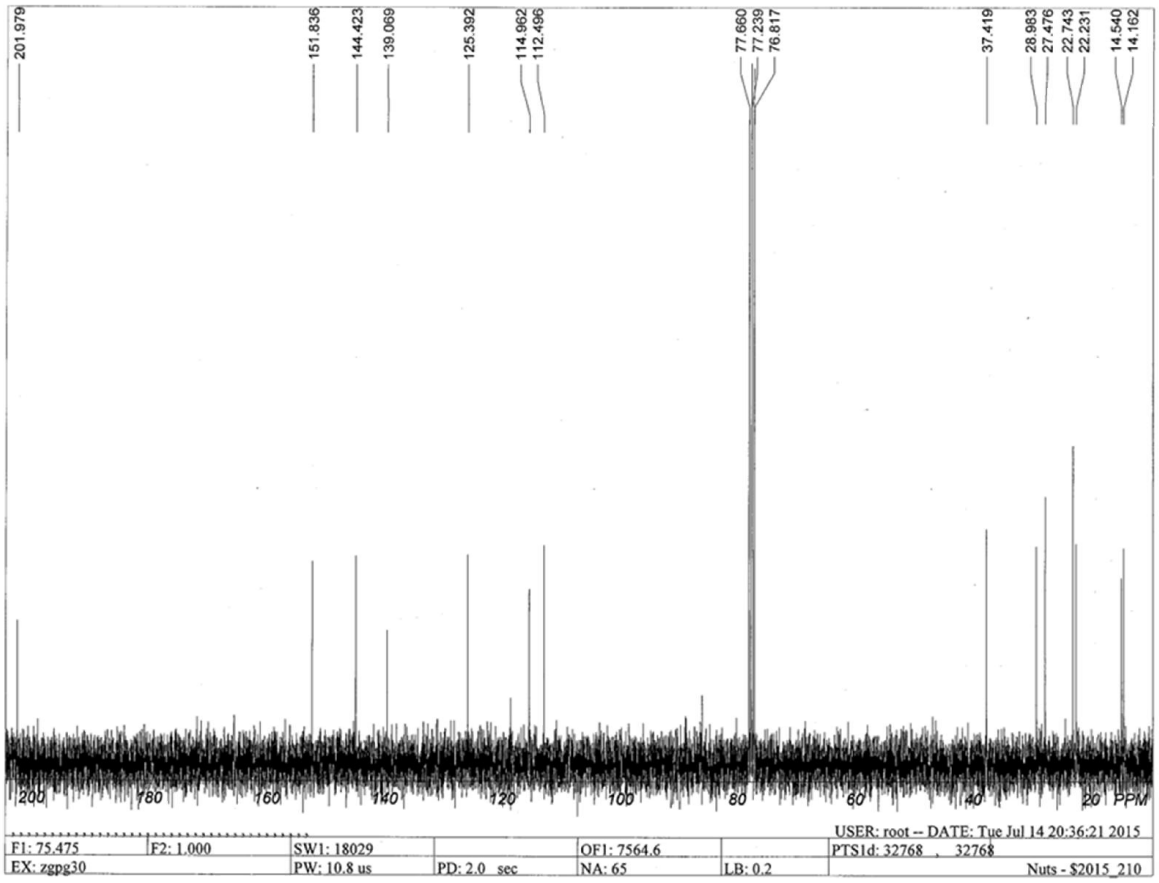
Carbon NMR of tetrahydrofuranyl ketone (**49**)



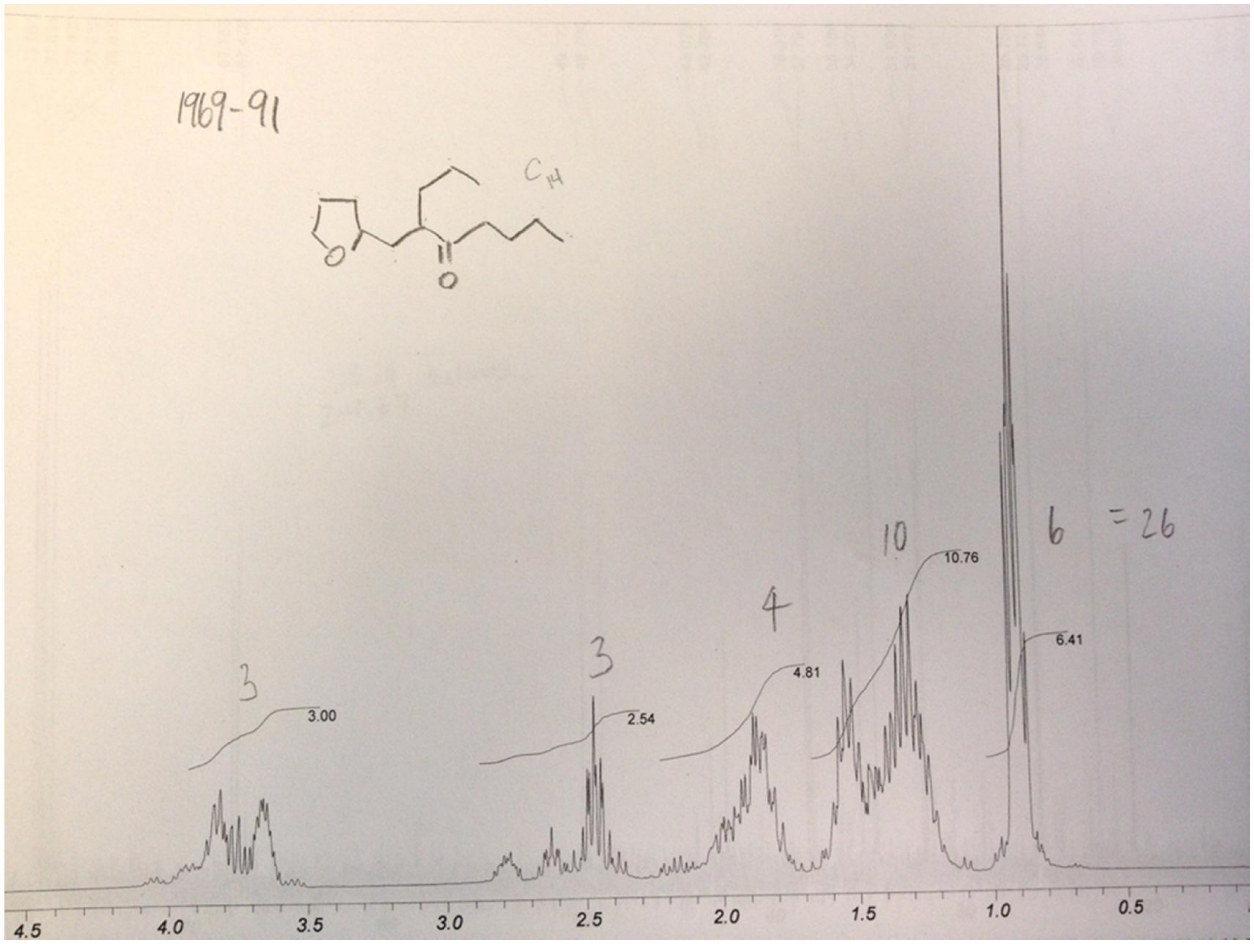
Proton NMR of furfurylidenone (**73B**)



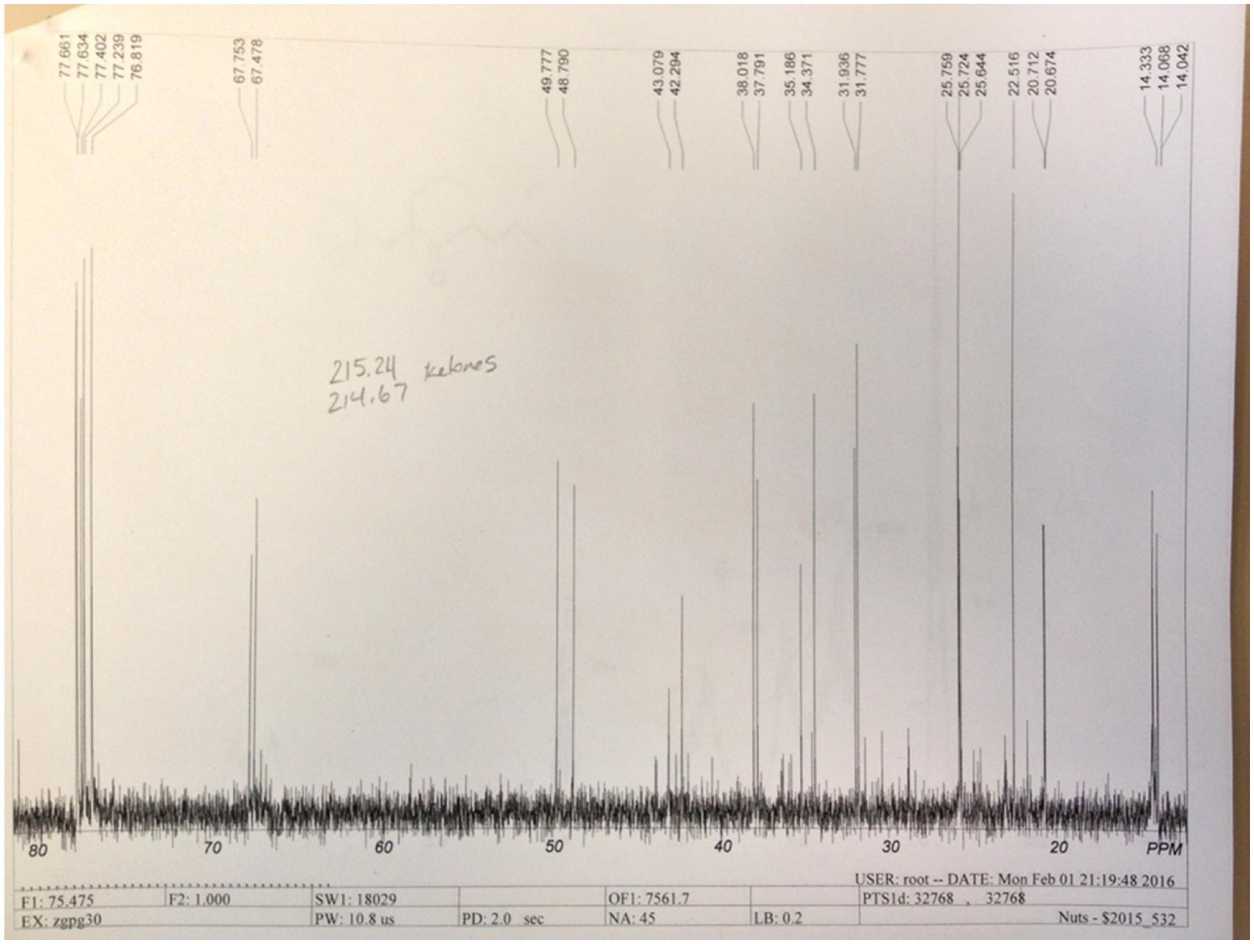
Carbon NMR of furfurylidenone (**73B**)



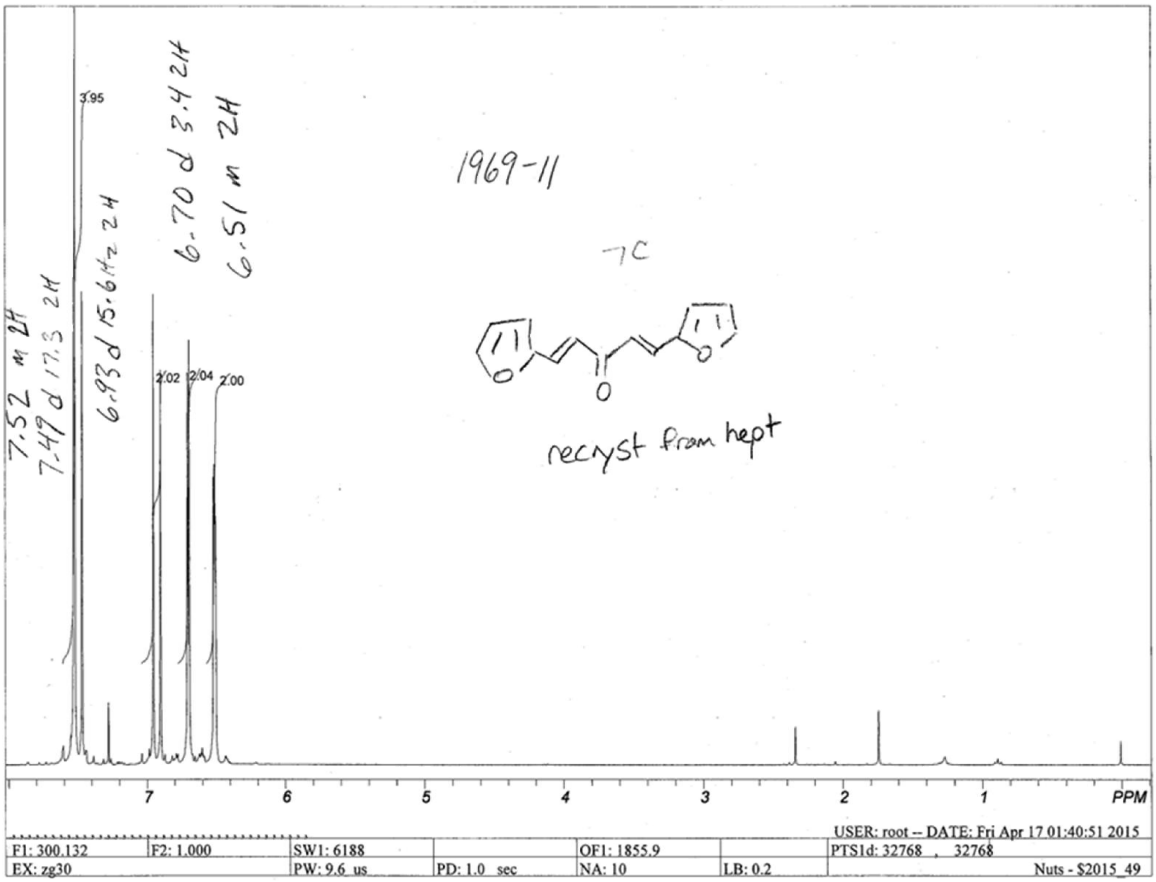
Proton NMR of tetrahydrofuranyl ketone (**91**)



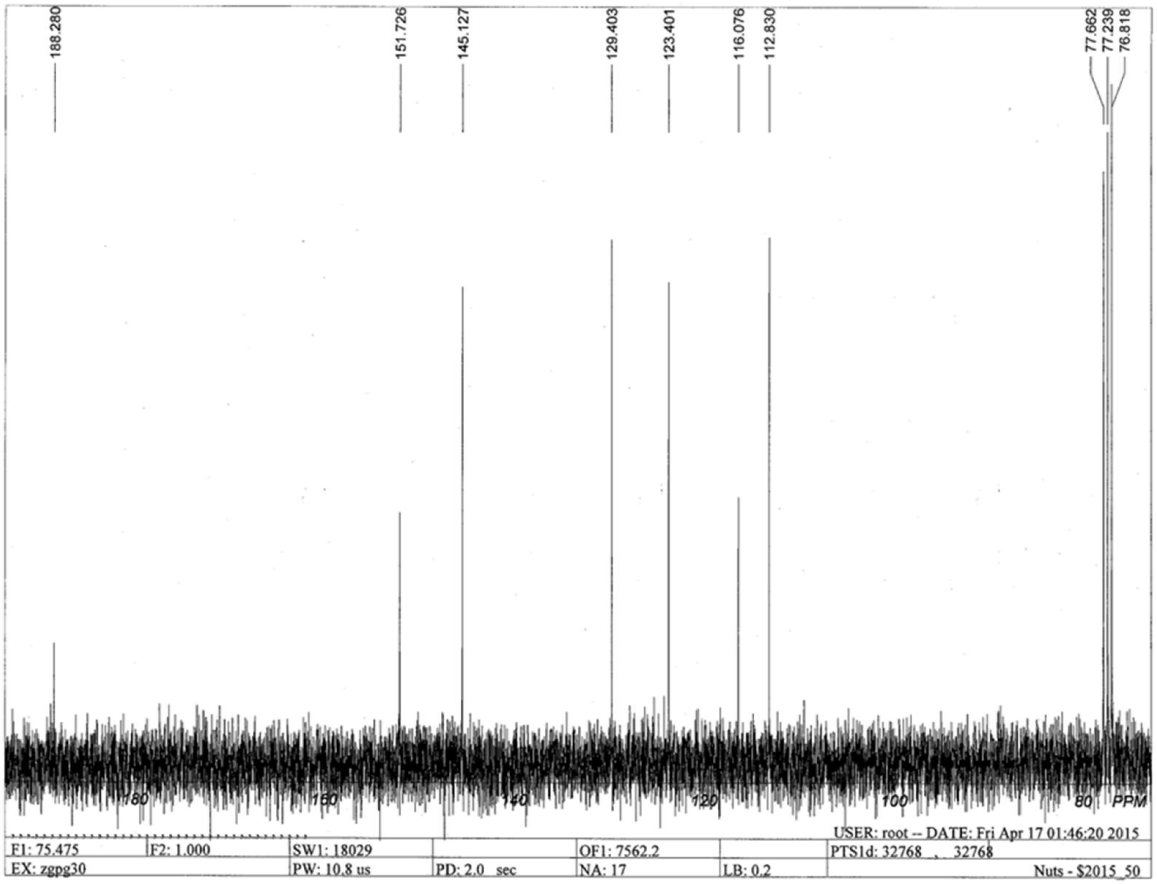
Carbon NMR of tetrahydrofuranyl ketone (**91**)



Proton NMR of dimeric furfurylidenone from acetone (**33**)

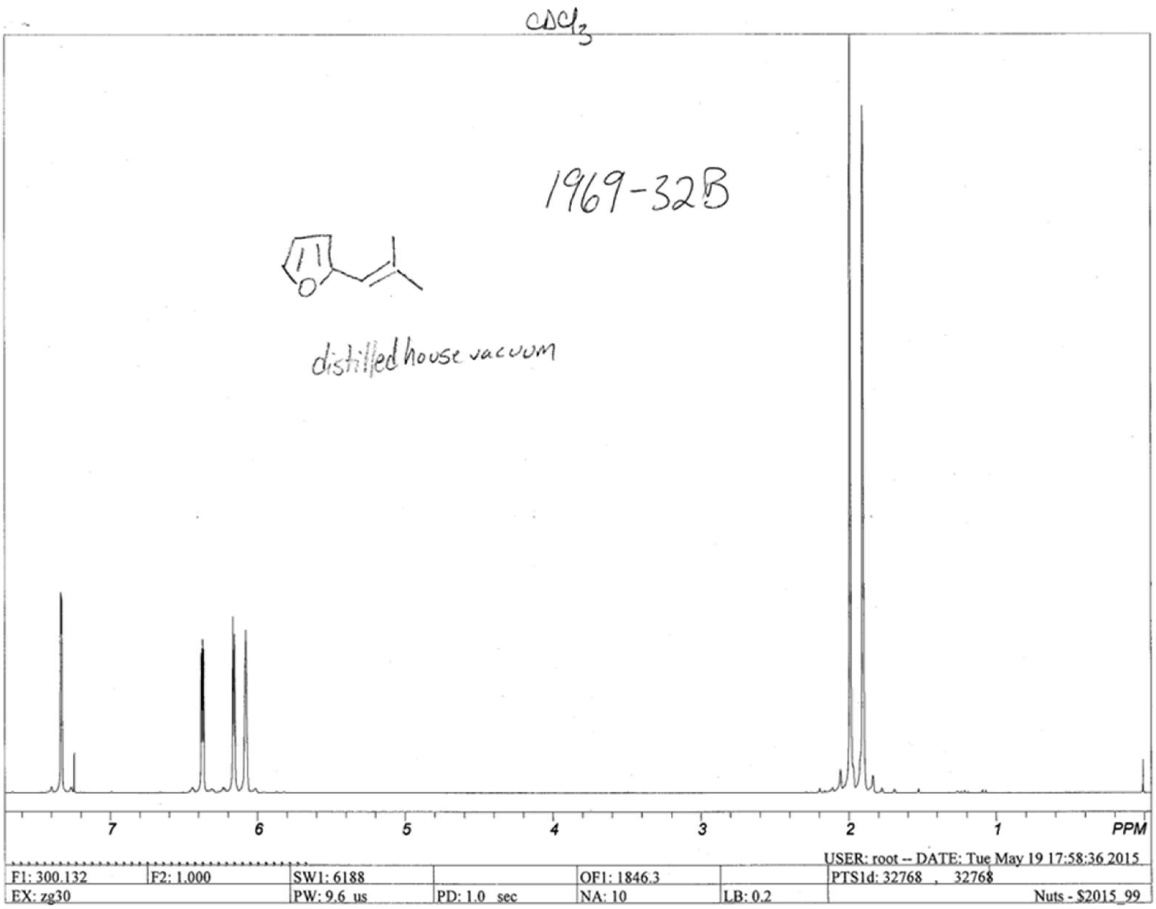


Carbon NMR of dimeric furfurylidenone from acetone (**33**)

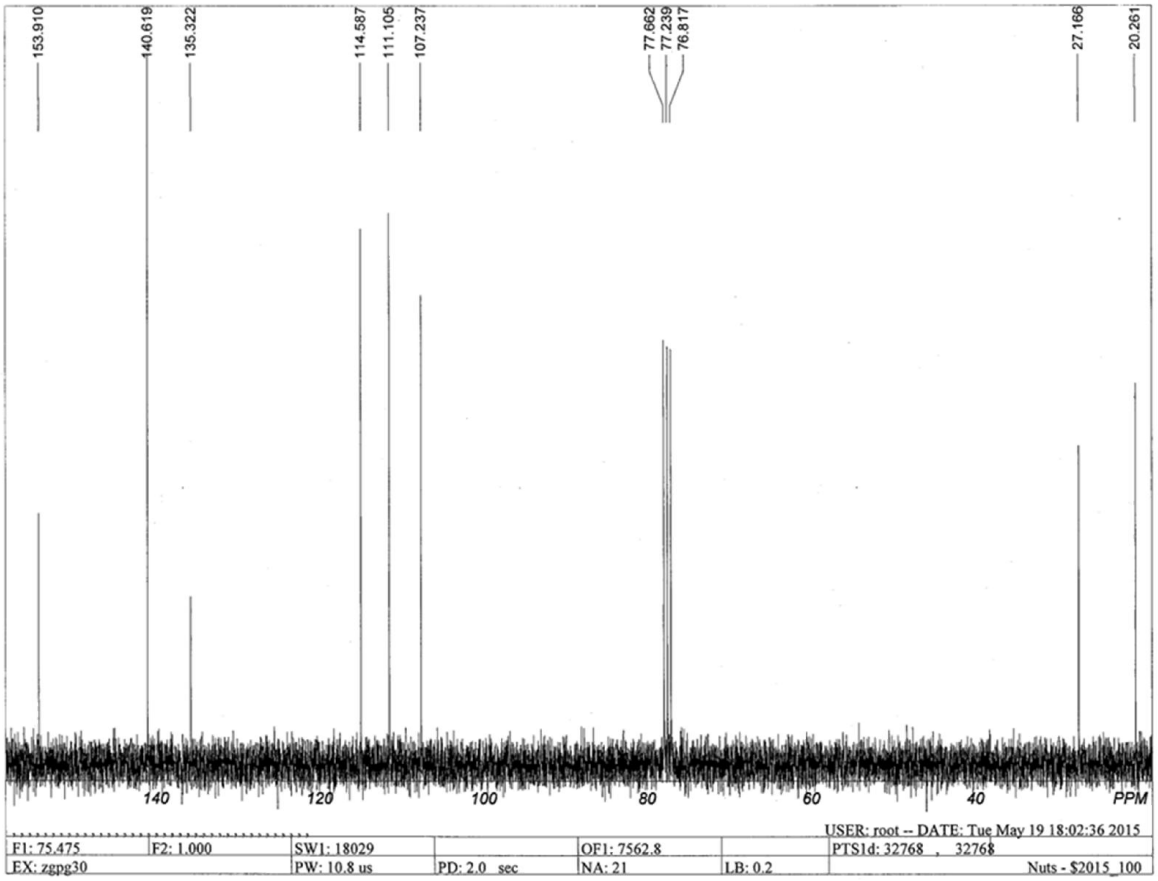


Appendix G NMR Data of Furan Solvents from Perkin Reaction

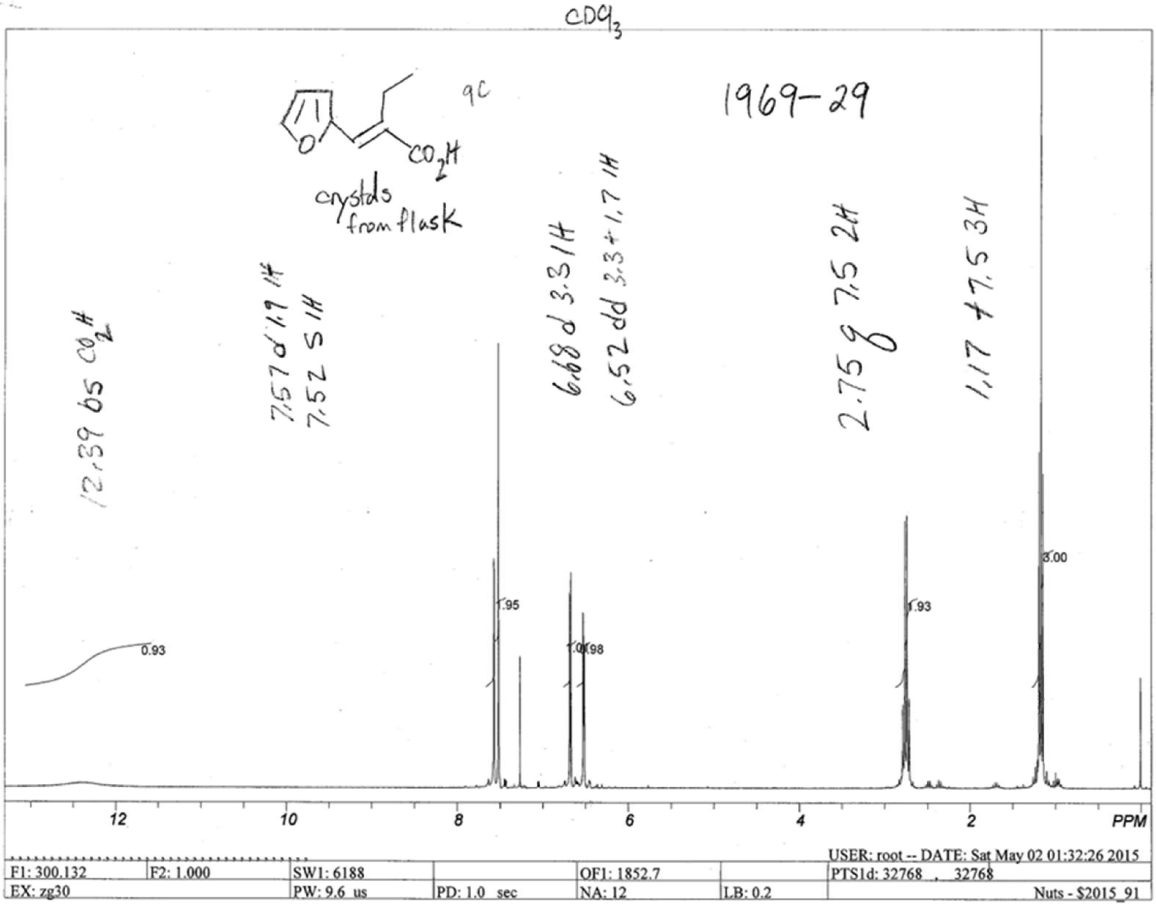
Proton NMR of isobutenylfuran (**85B**)



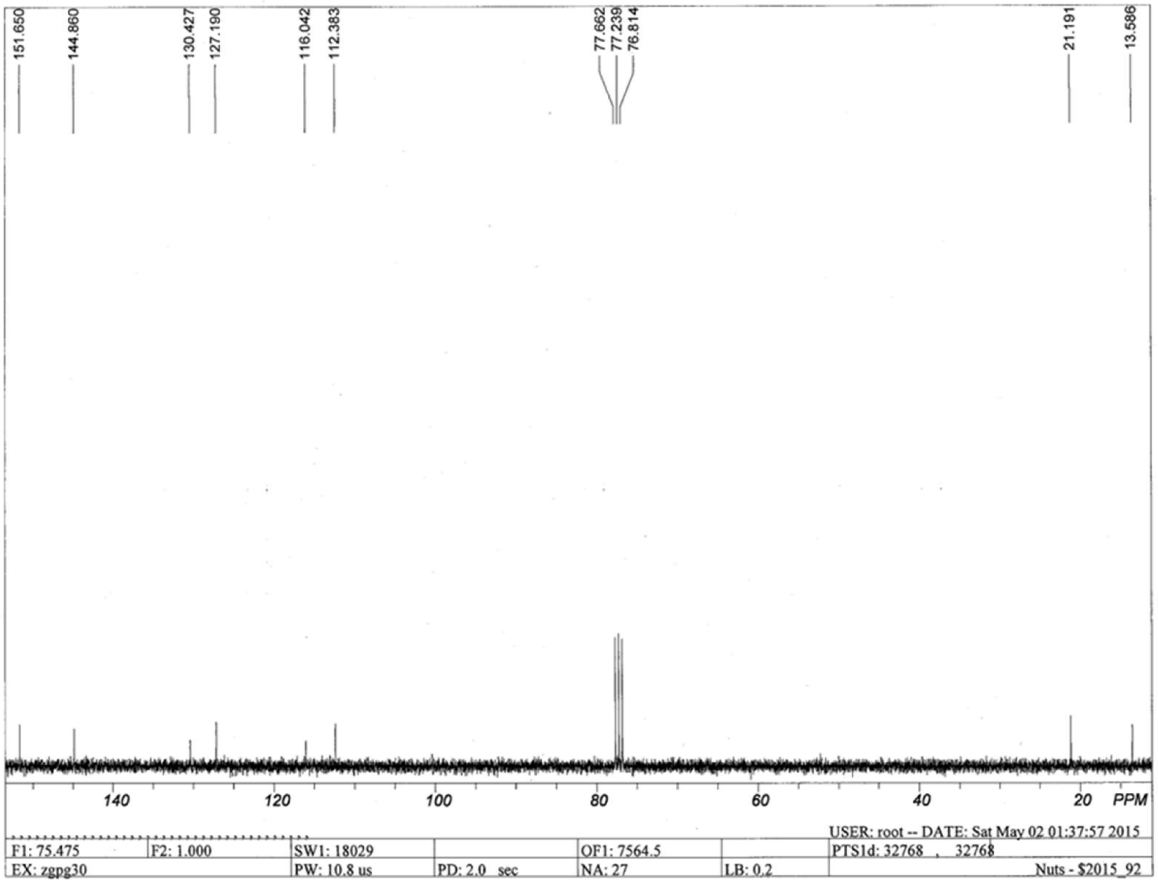
Carbon NMR of isobutenylfuran (**85B**)



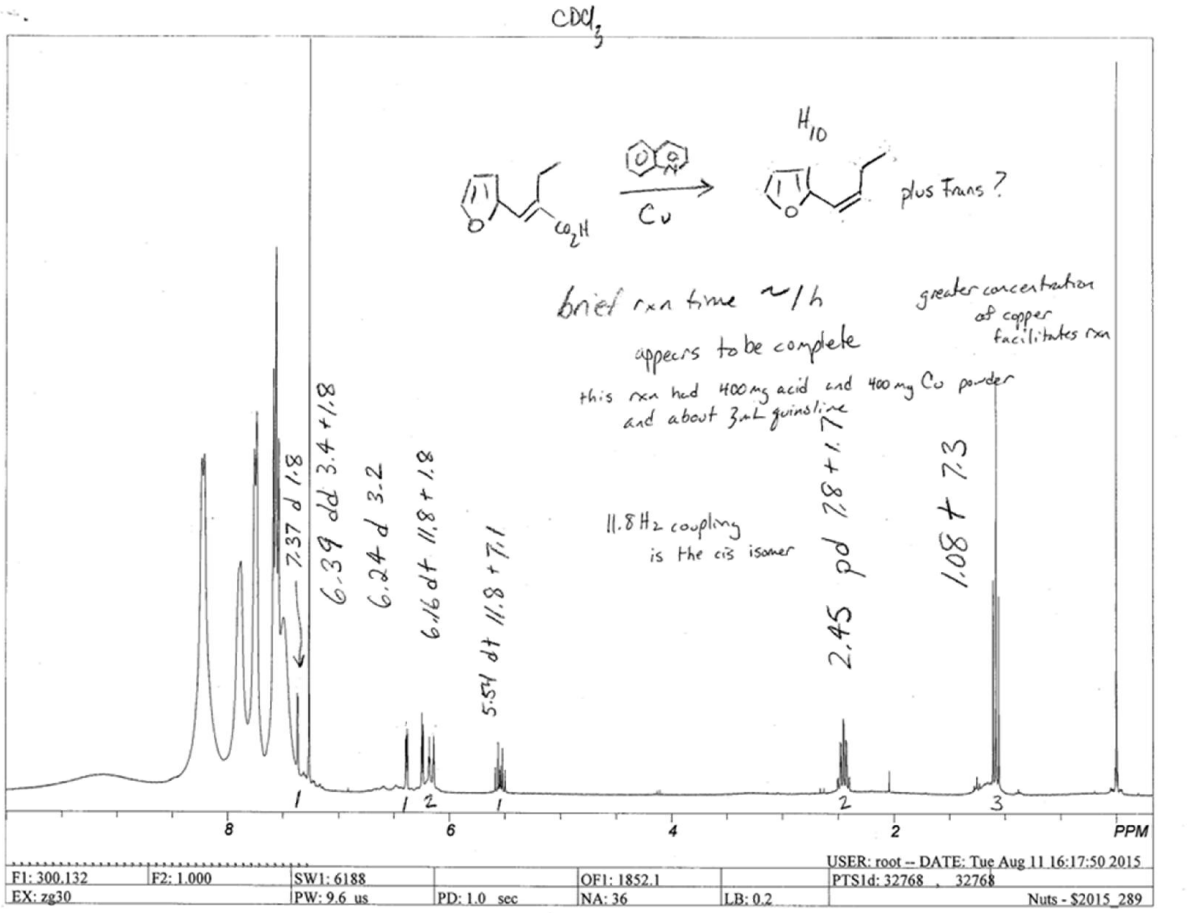
Proton NMR of furanacrylic acid (**113**)



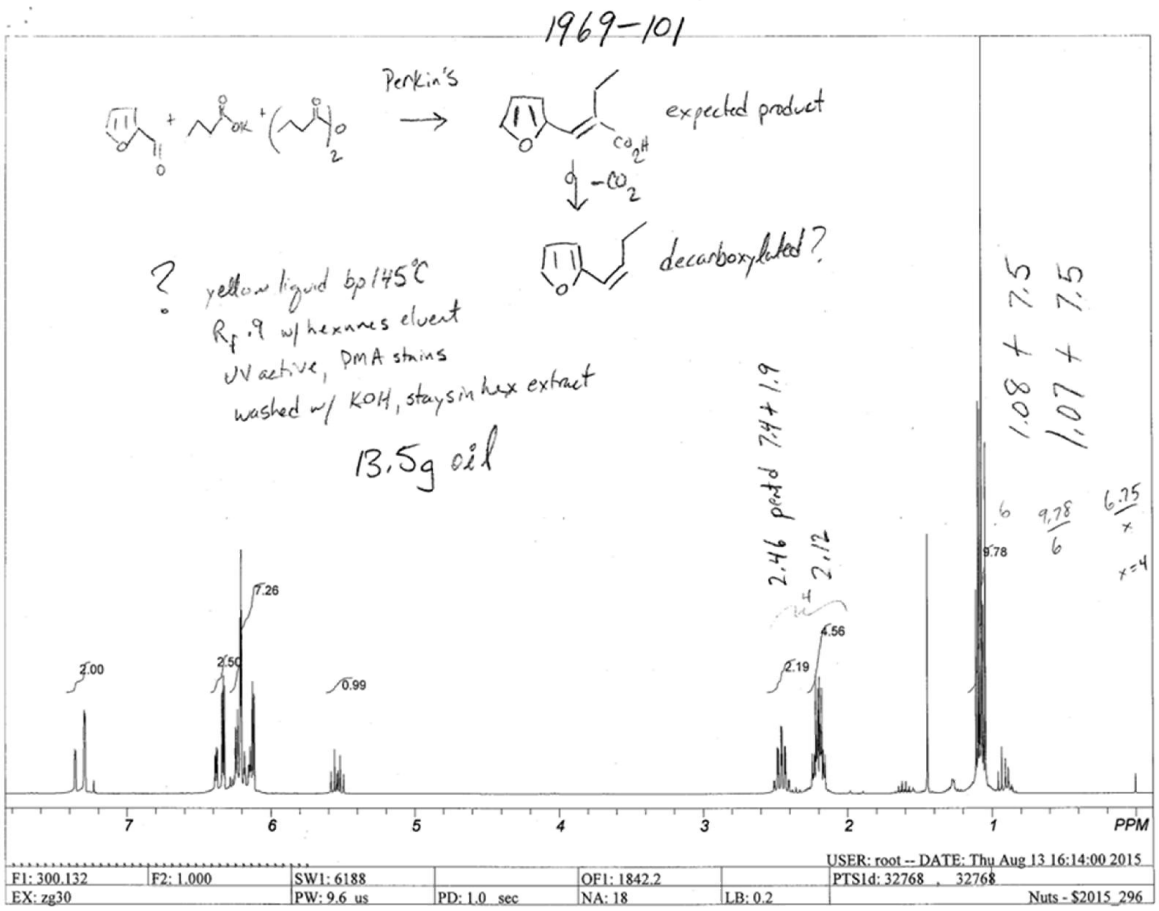
Carbon NMR of furanacrylic acid (**113**)



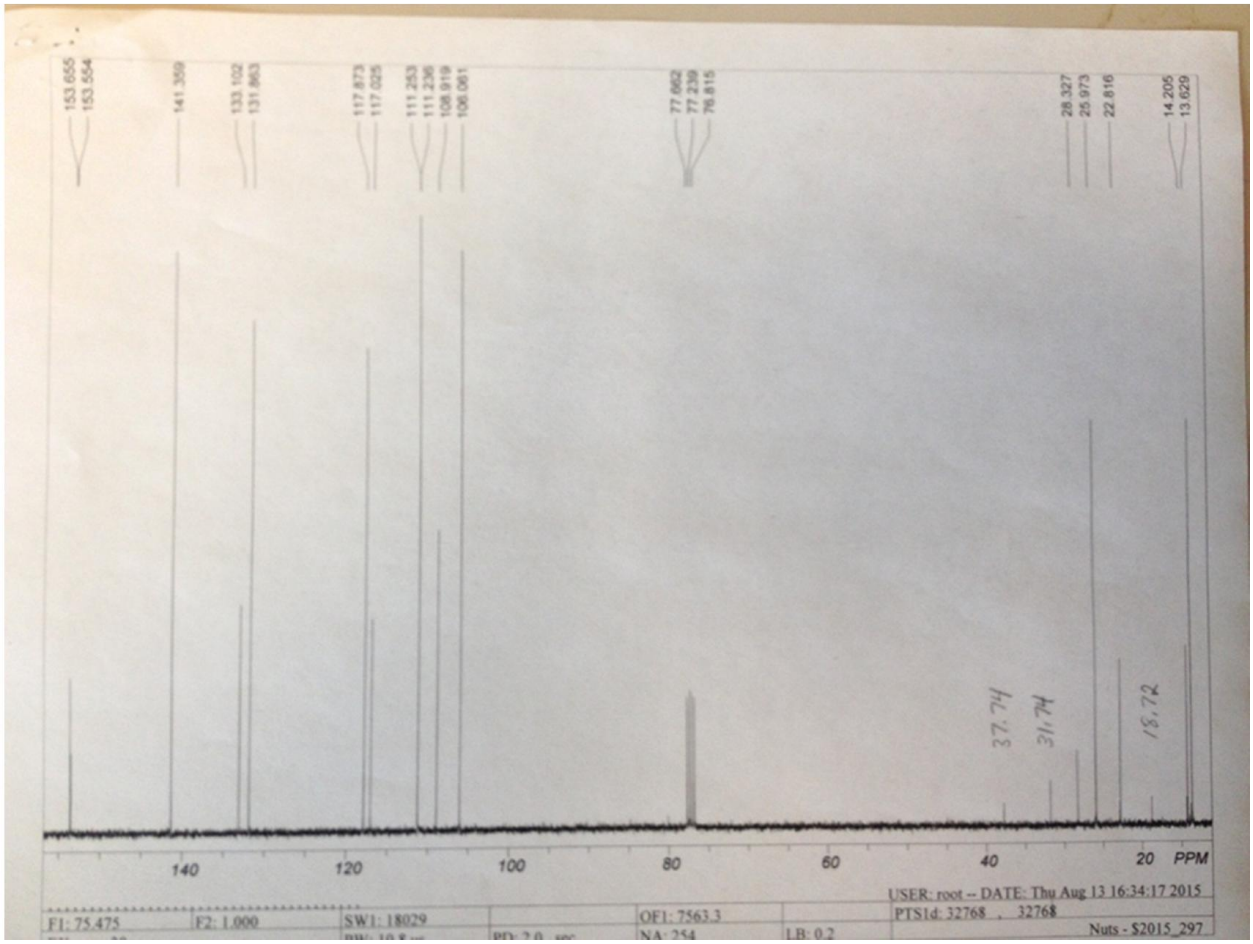
Proton NMR of cis butenylfuran (**90**)



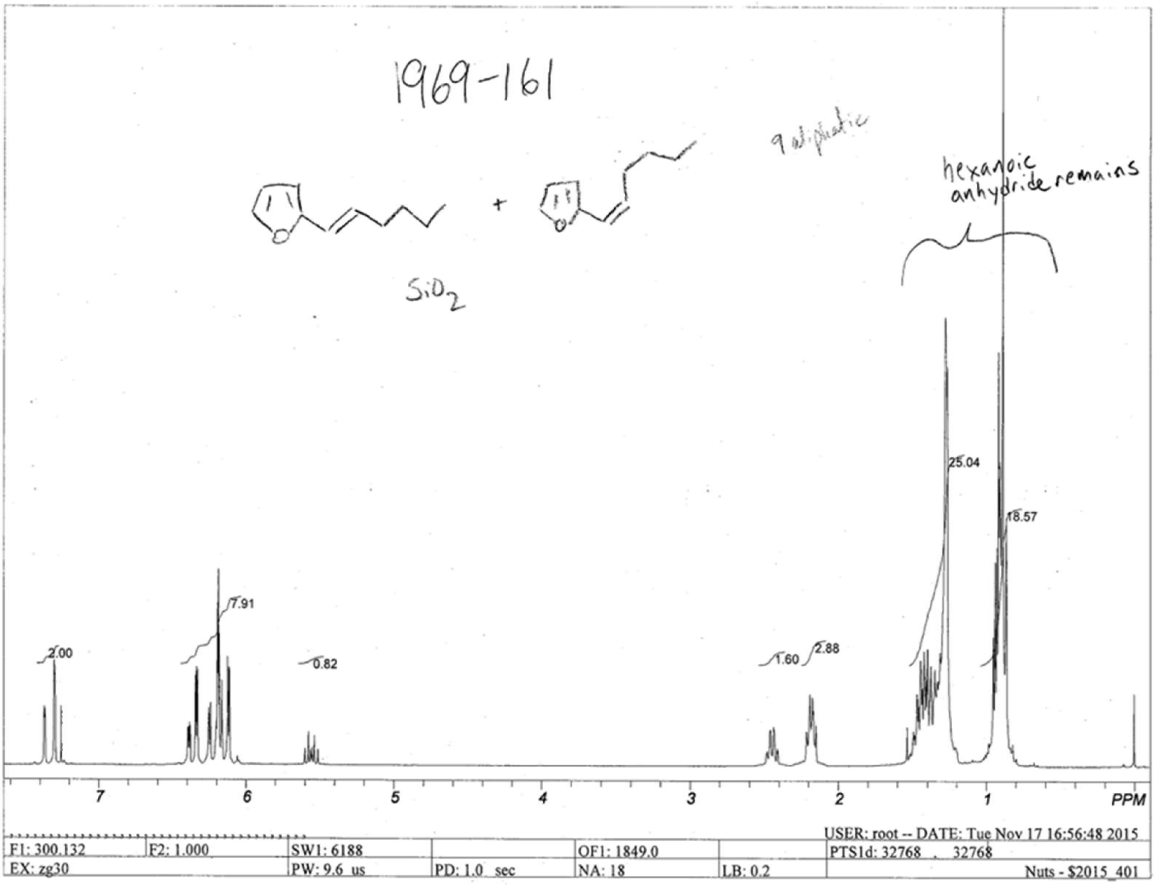
Proton NMR of butenylfuran (**101B**)



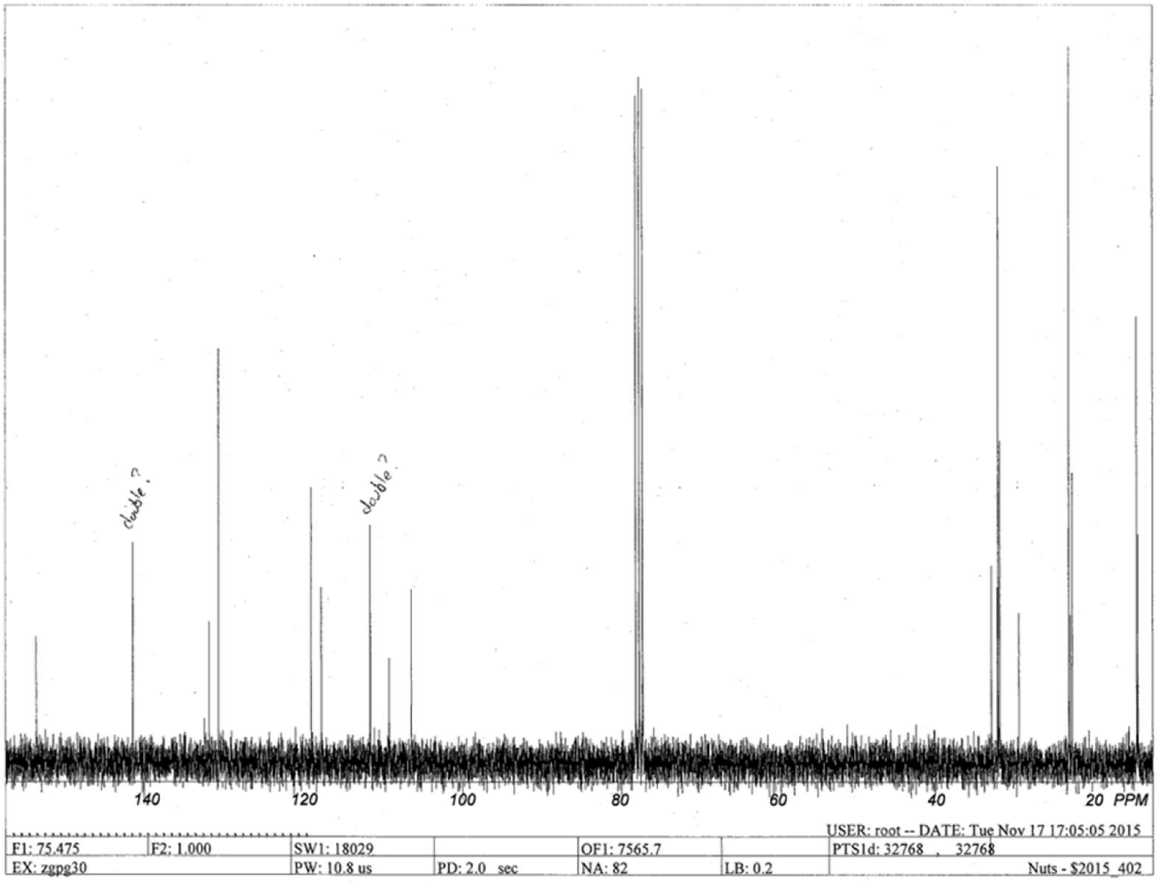
Carbon NMR of butenylfuran (**101B**)



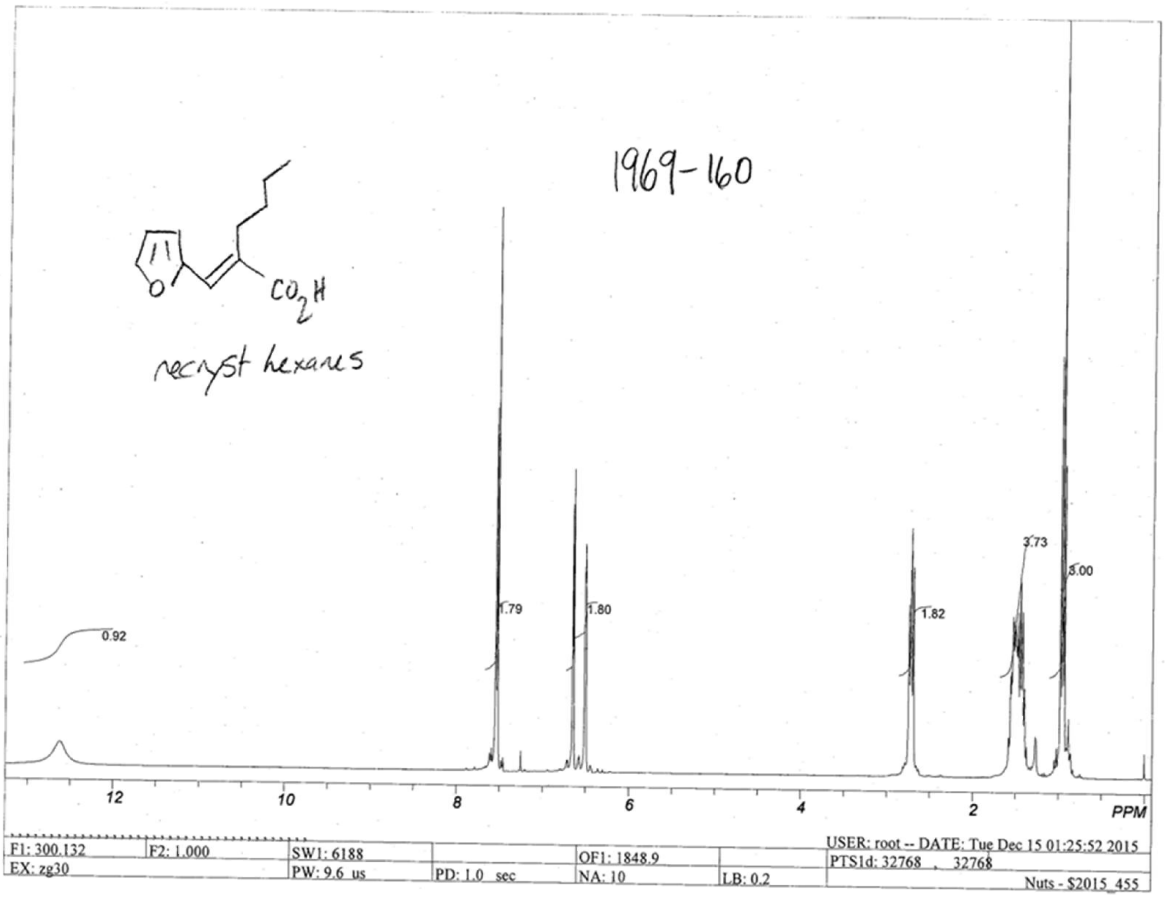
Proton NMR of hexenylfuran (**160A**)



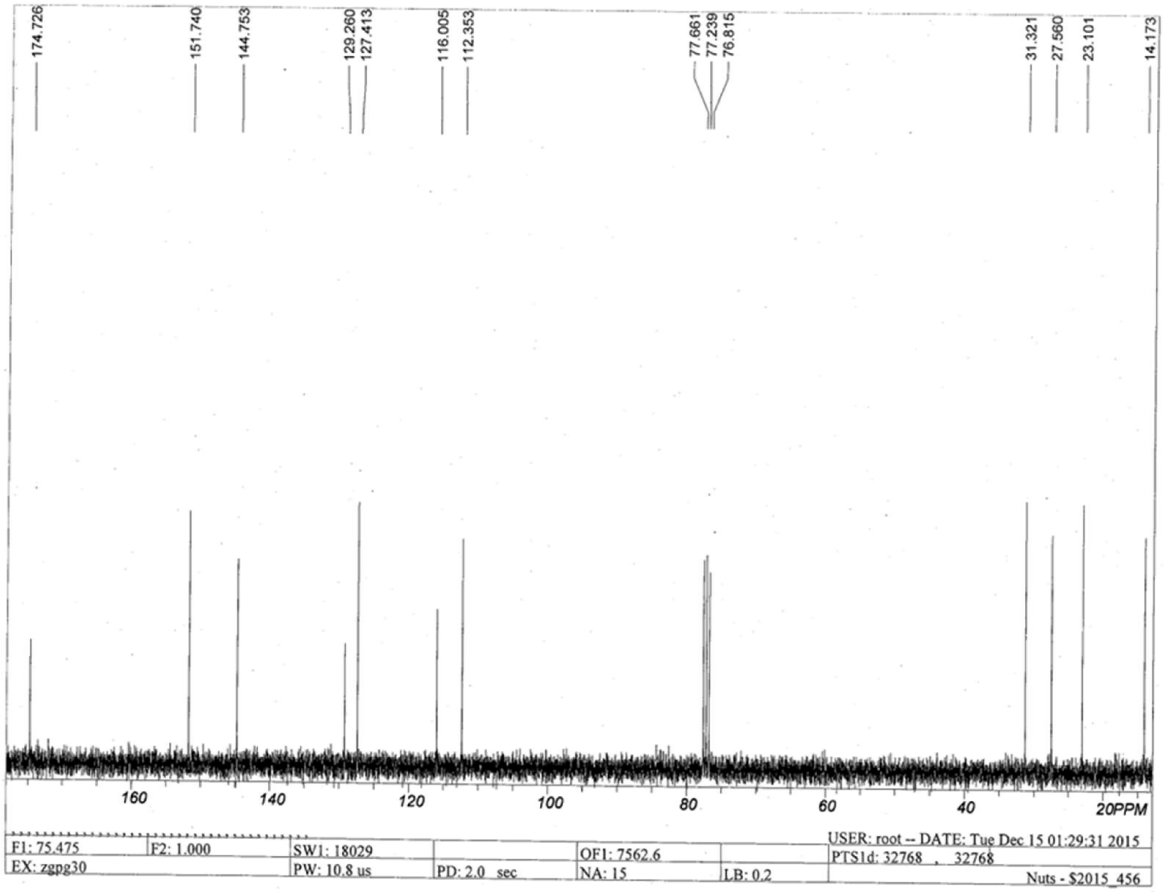
Carbon NMR of hexenylfuran (**160A**)



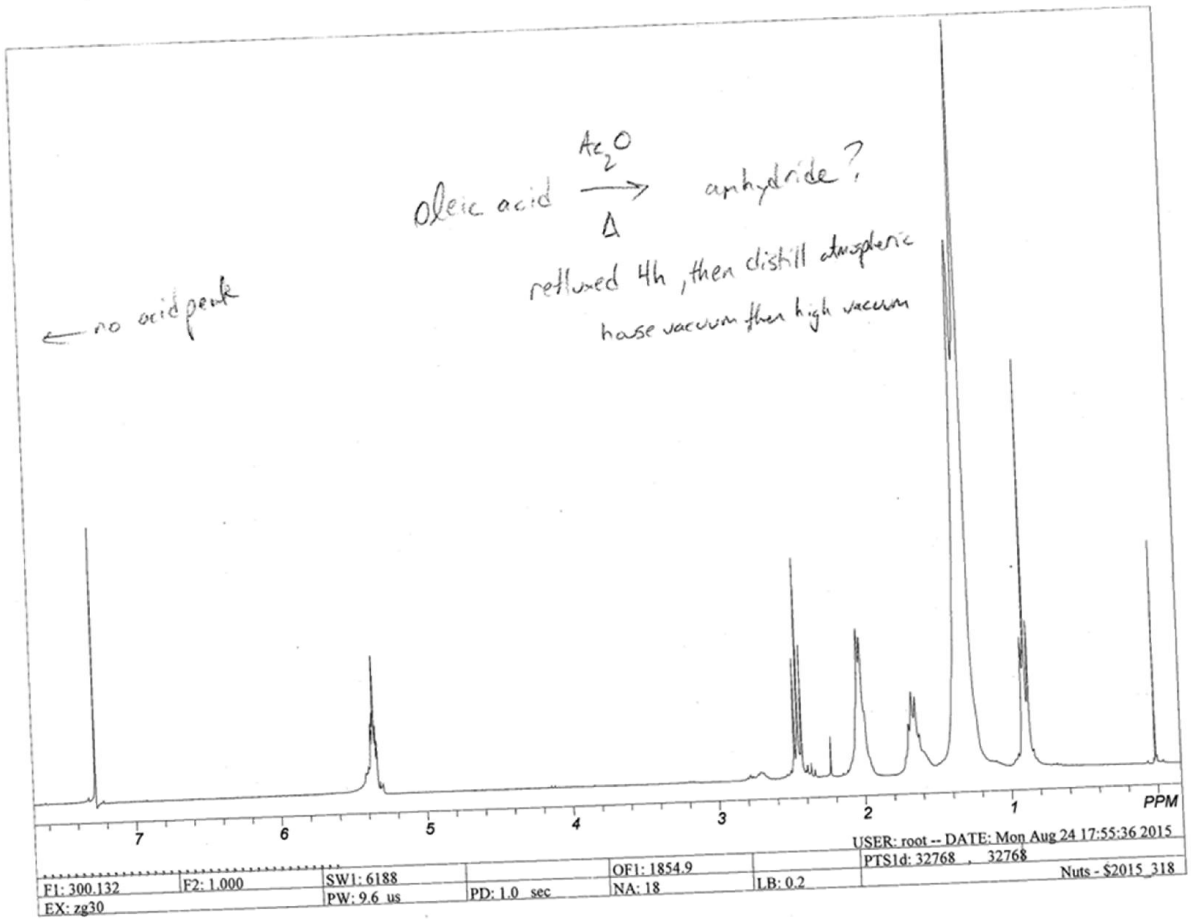
Proton NMR of furanacrylic acid (**160B**)



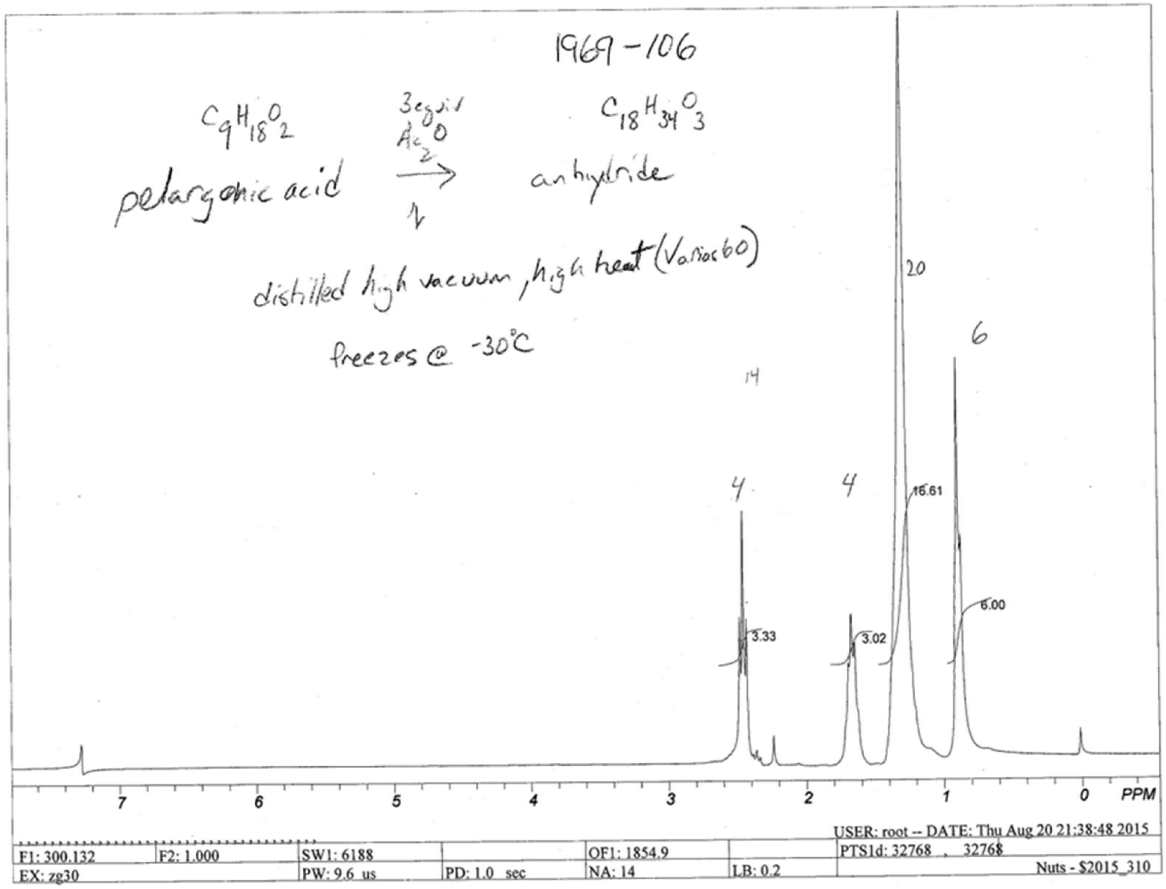
Carbon NMR of furanacrylic acid (**160B**)



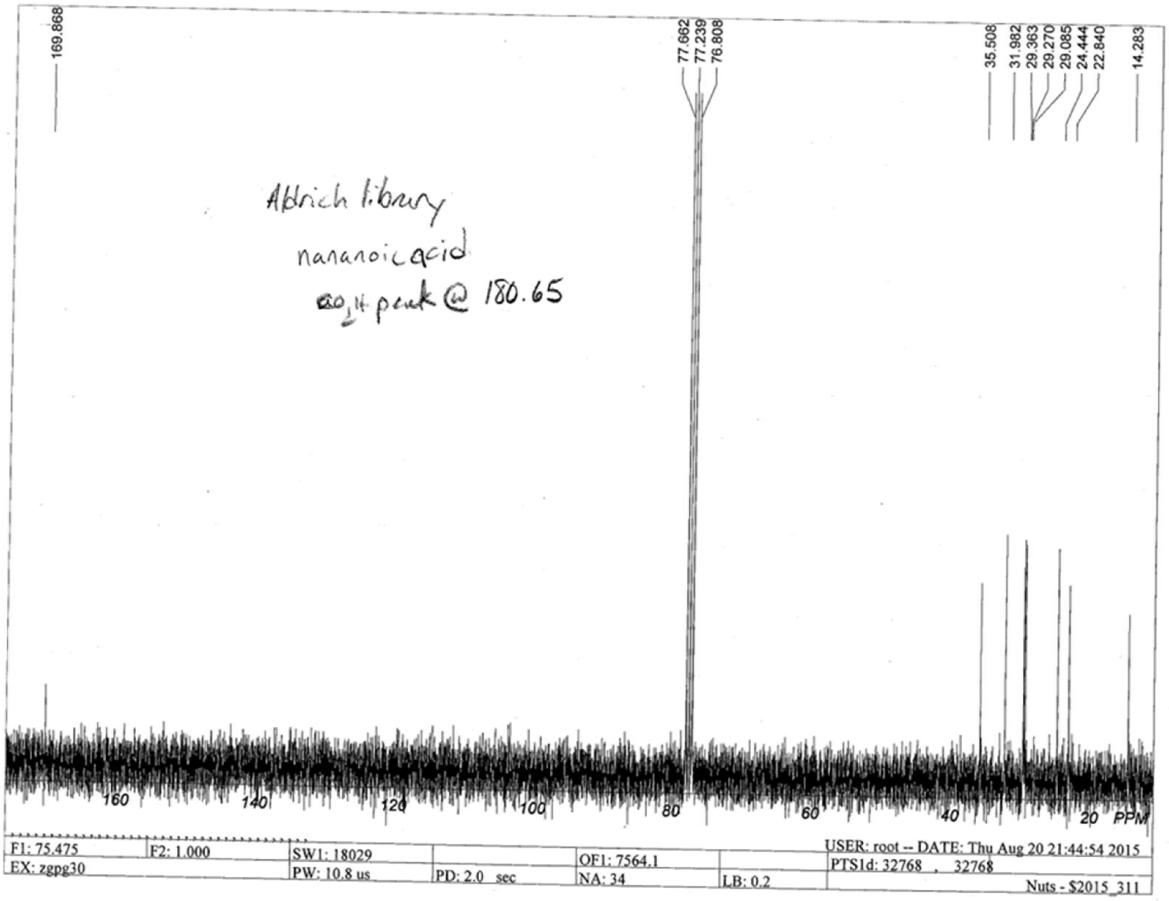
Proton NMR of oleic anhydride (**108A**)



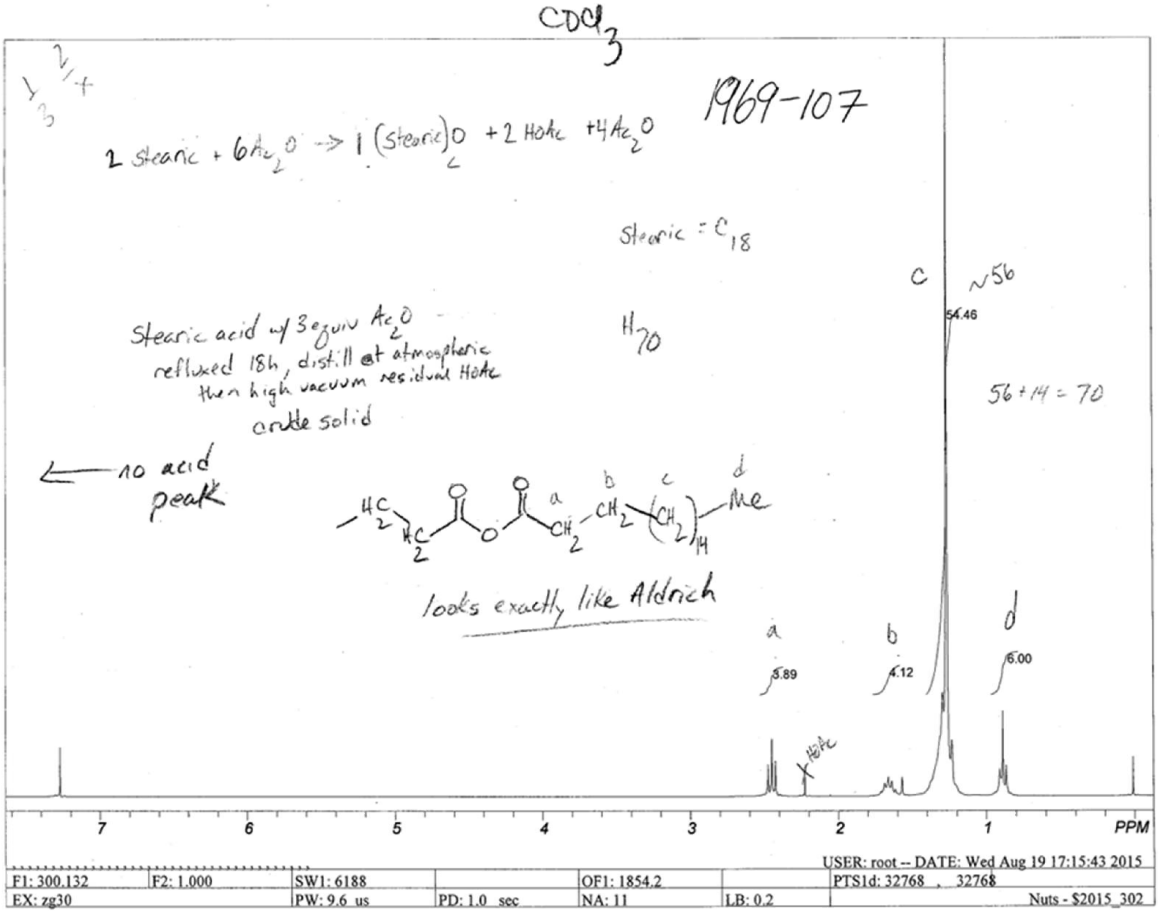
Proton NMR of pelargonic anhydride (**106A**)



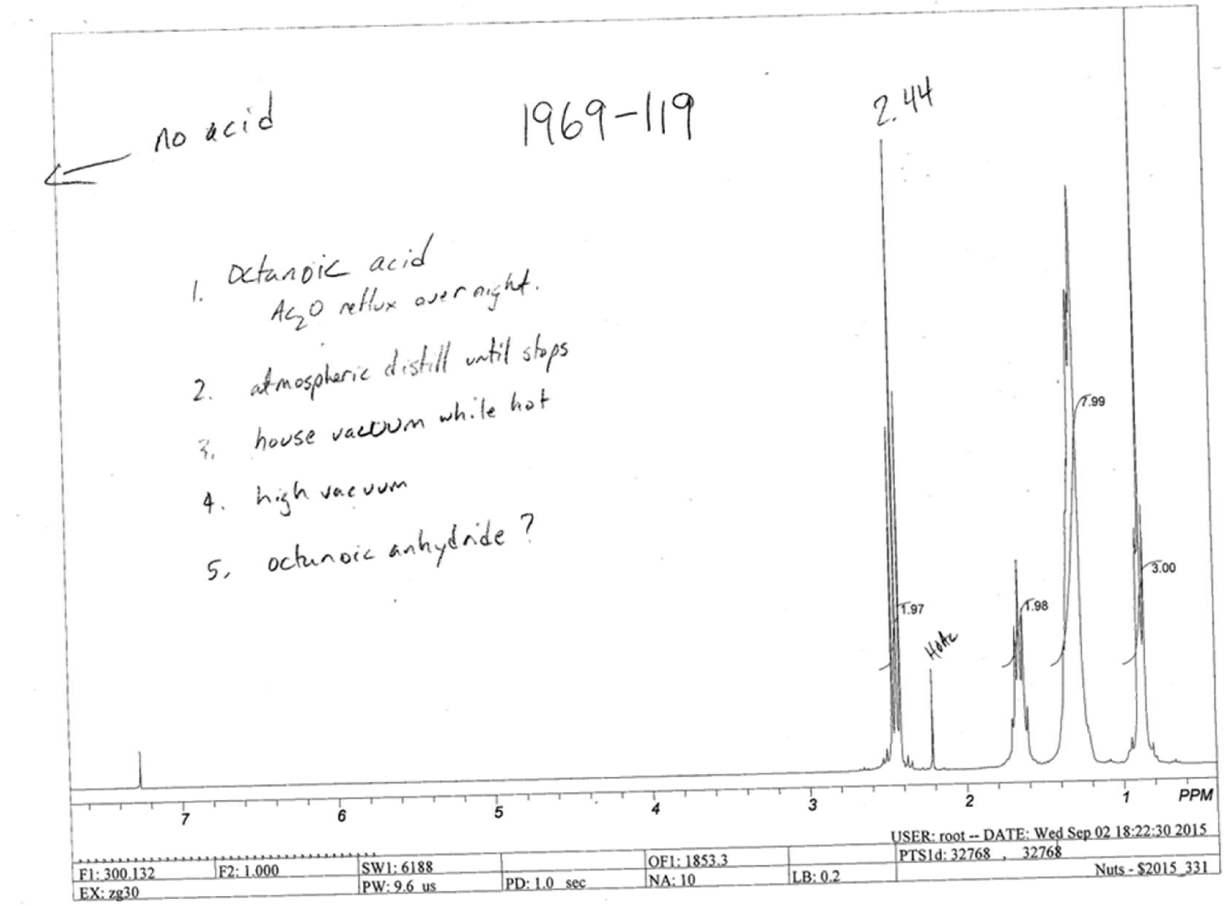
Carbon NMR of pelargonic anhydride (**106A**)



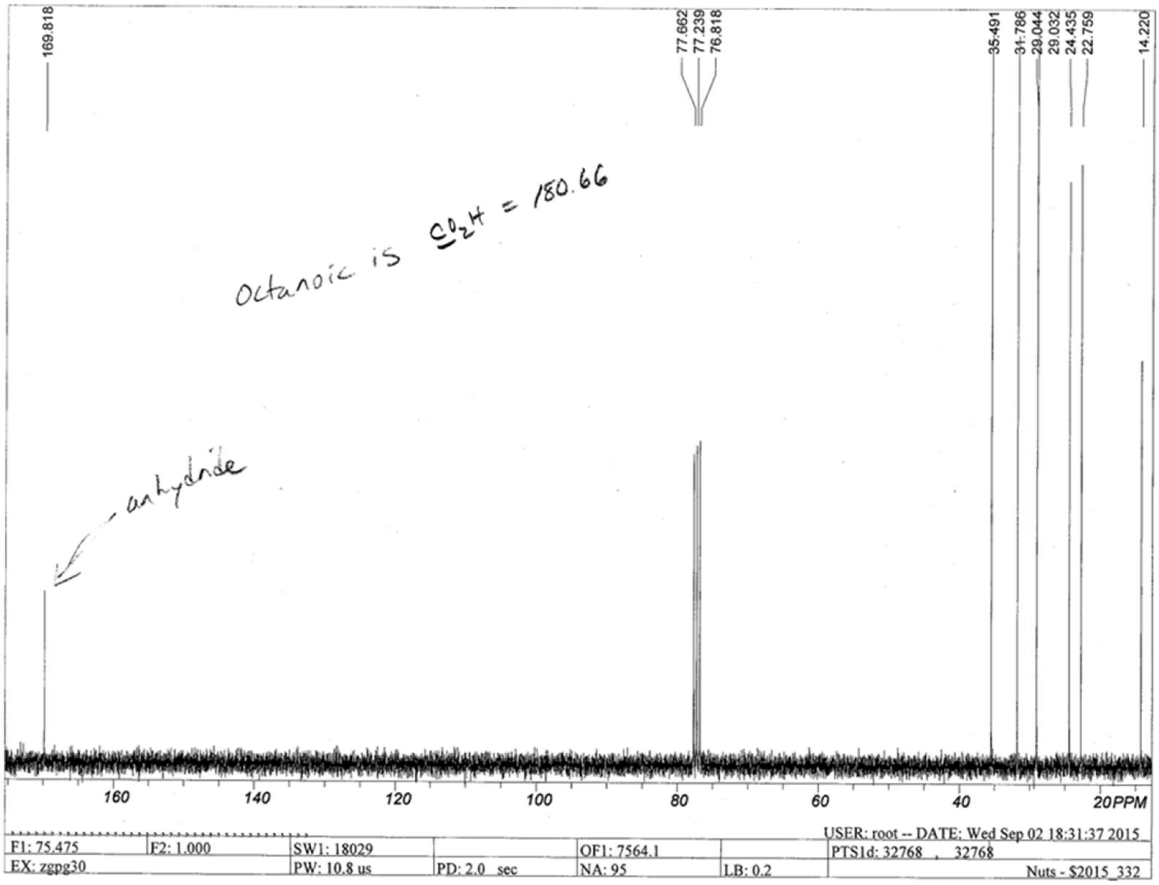
Proton NMR of stearic anhydride (**107A**)



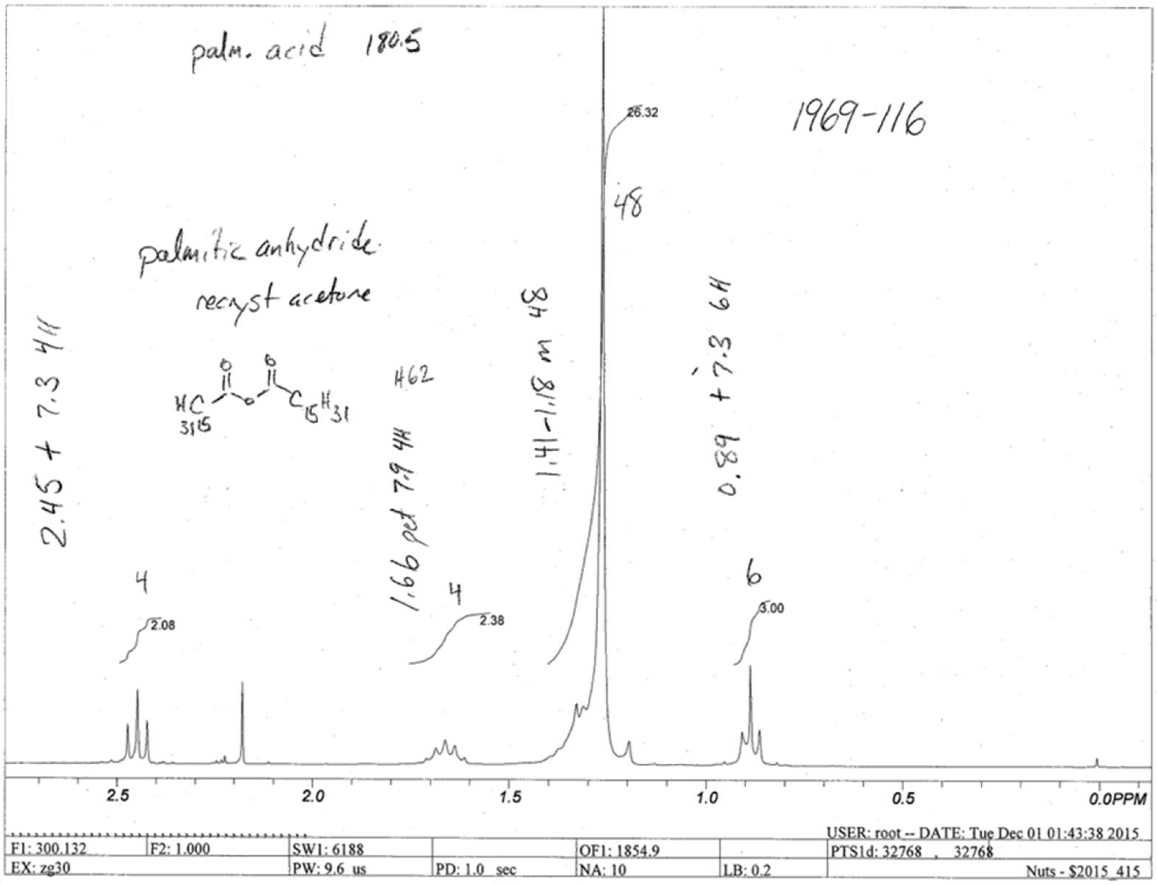
Proton NMR of octanoic anhydride (**119A**)



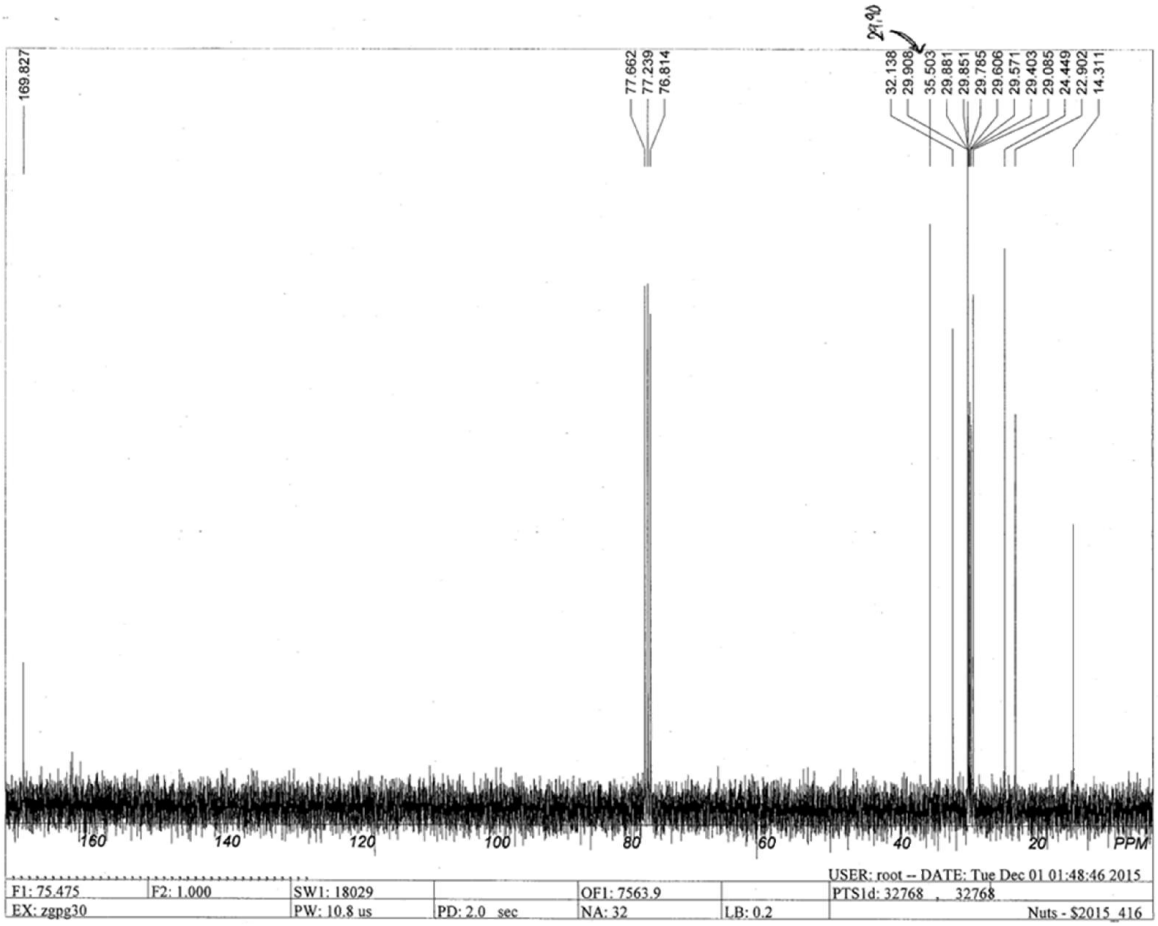
Carbon NMR of octanoic anhydride (**119A**)



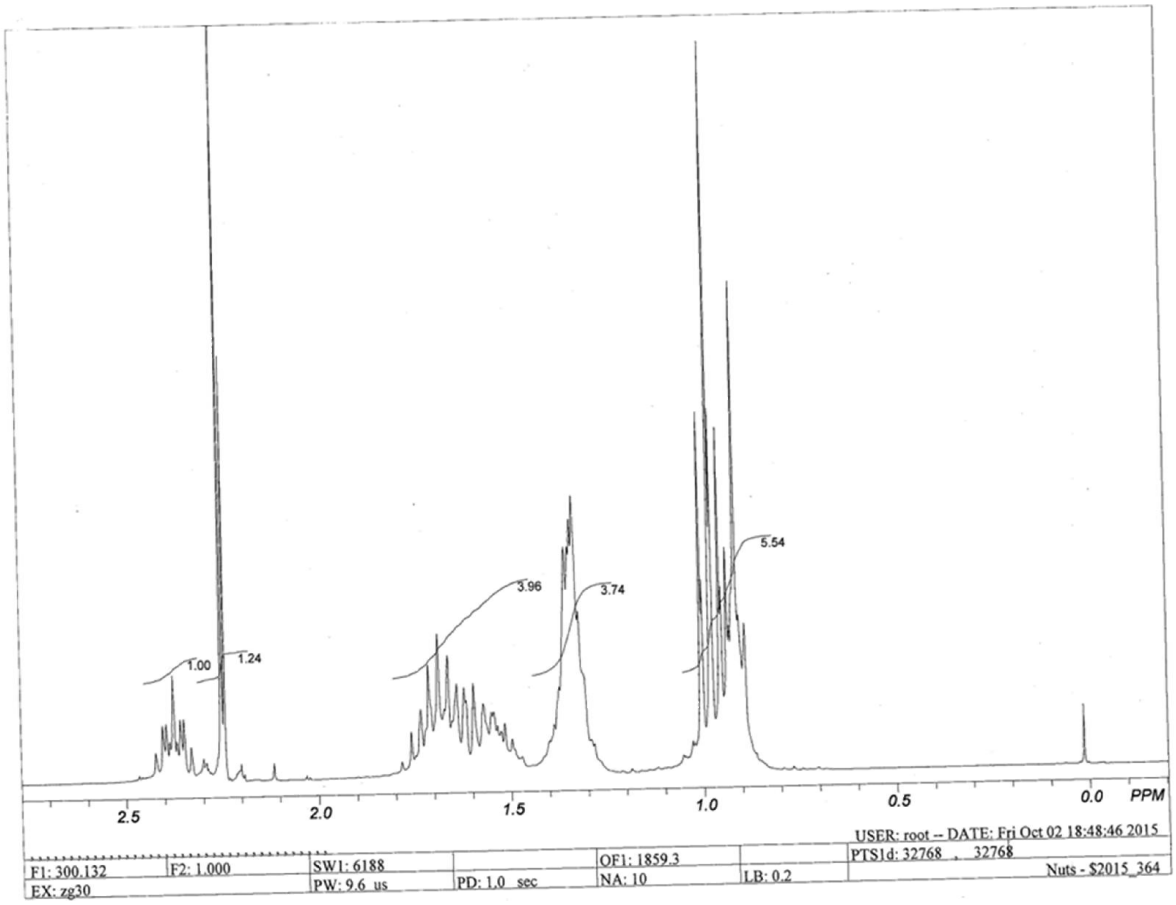
Proton NMR of palmitic anhydride (**116A**)



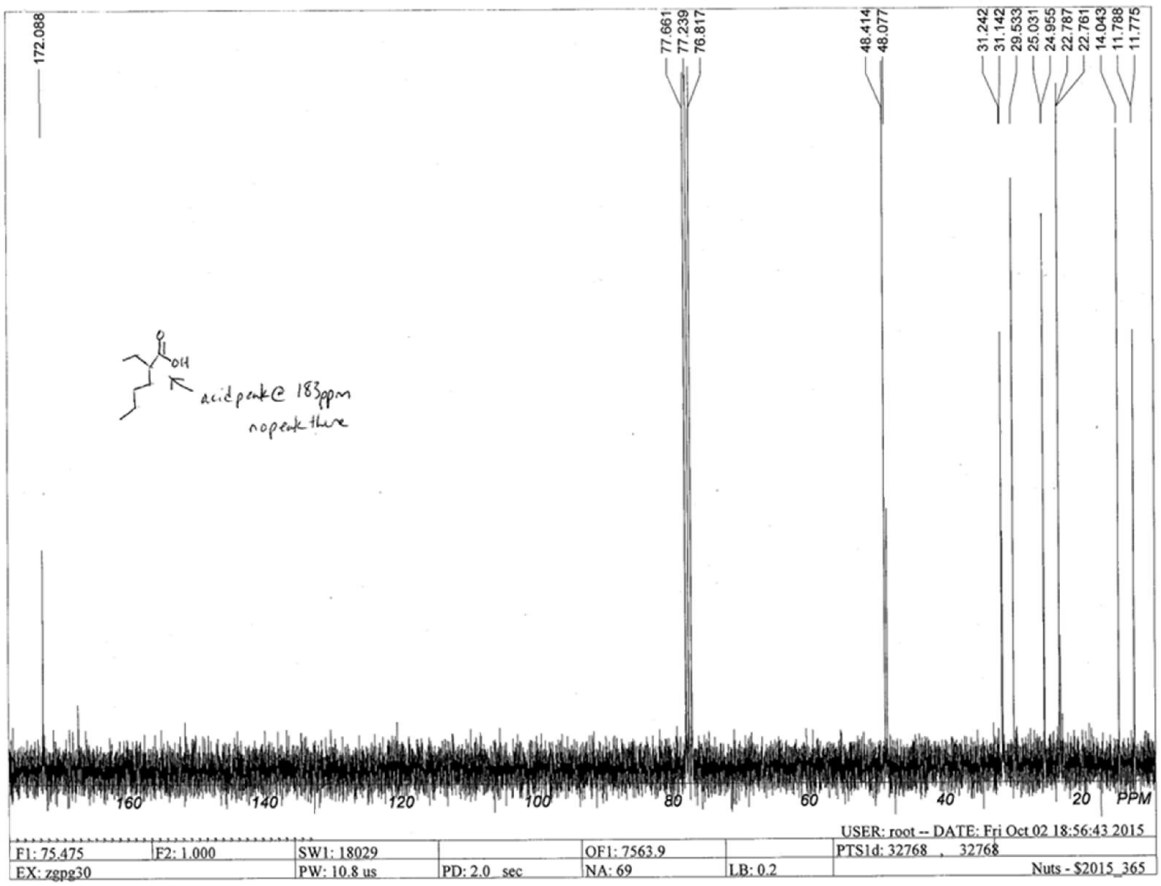
Carbon NMR of palmitic anhydride (**116A**)



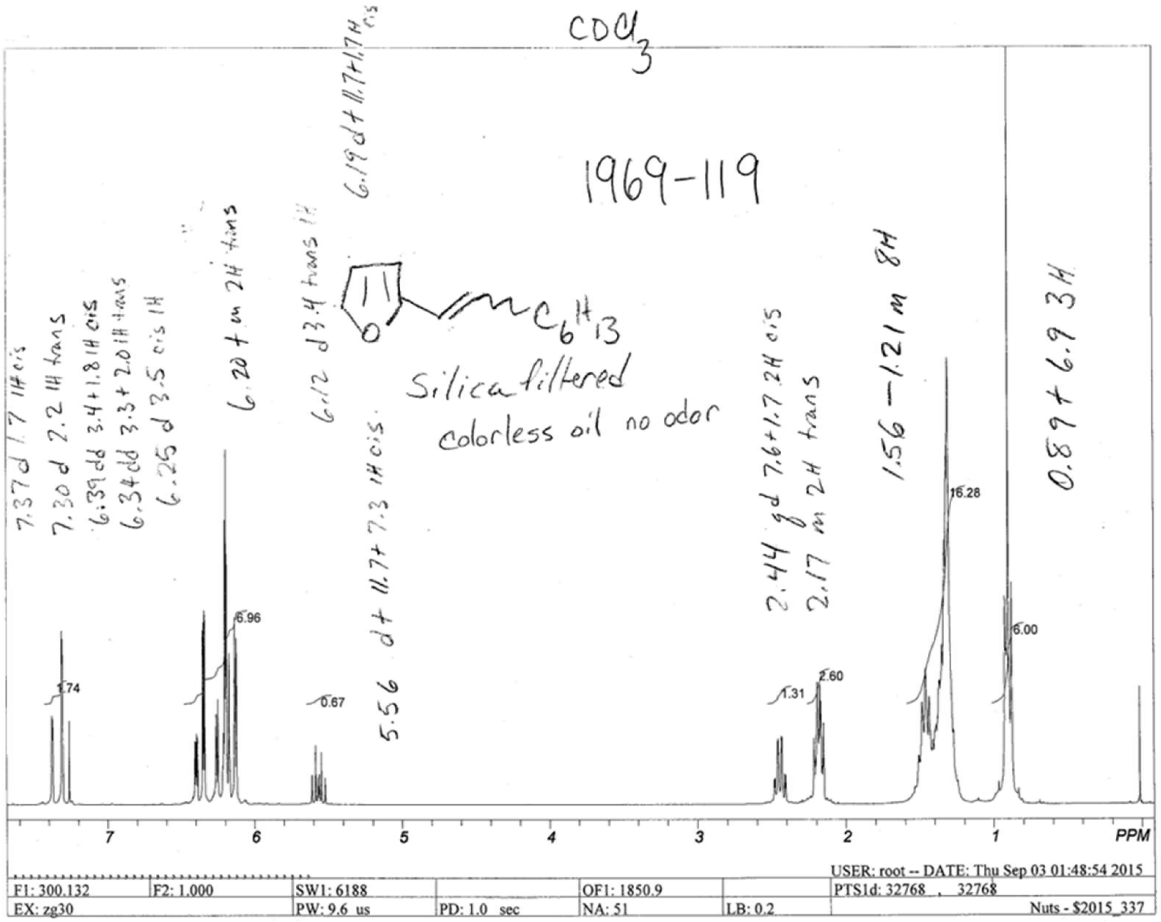
Proton NMR of 2-ethylhexanoic anhydride (**131**)



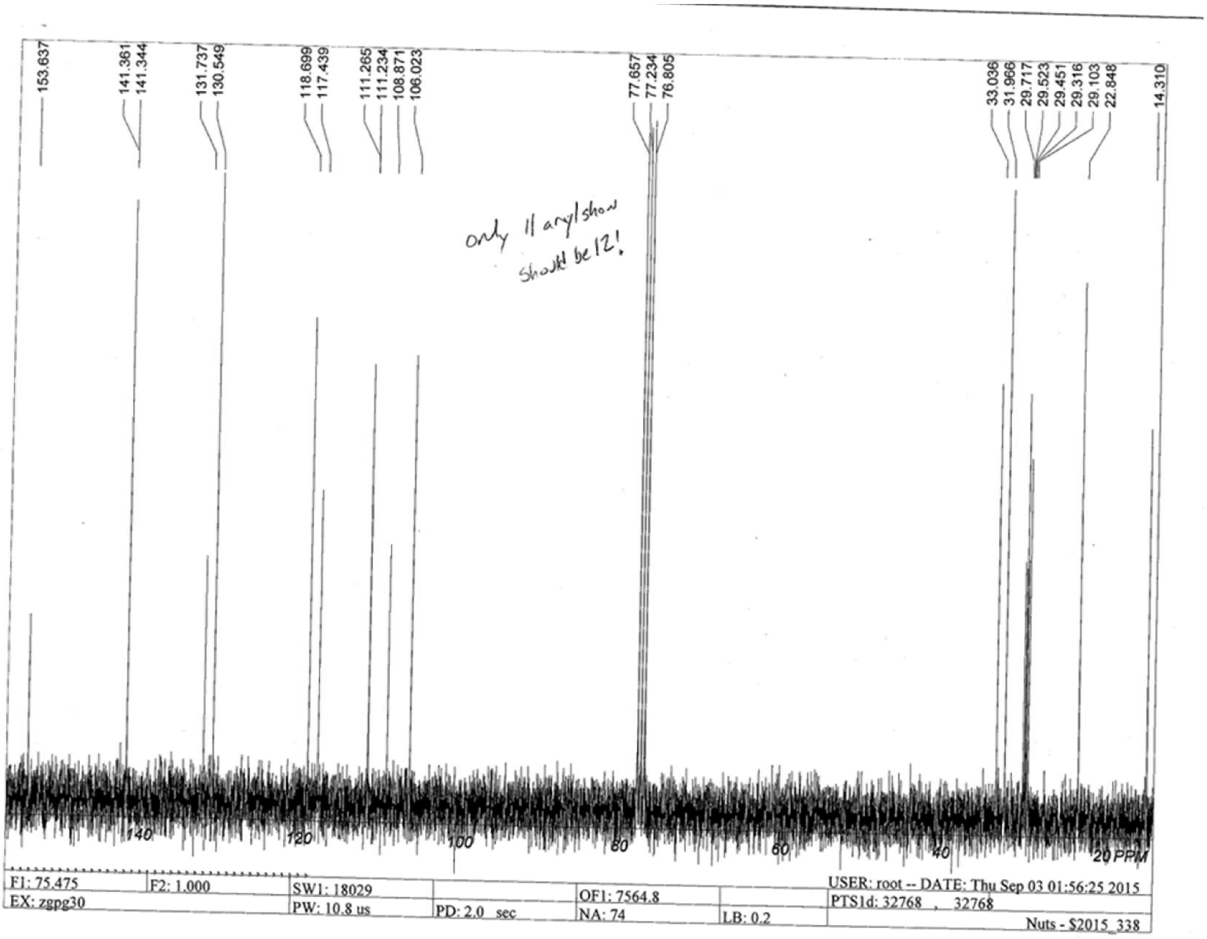
Carbon NMR of 2-ethylhexanoic anhydride (**131**)



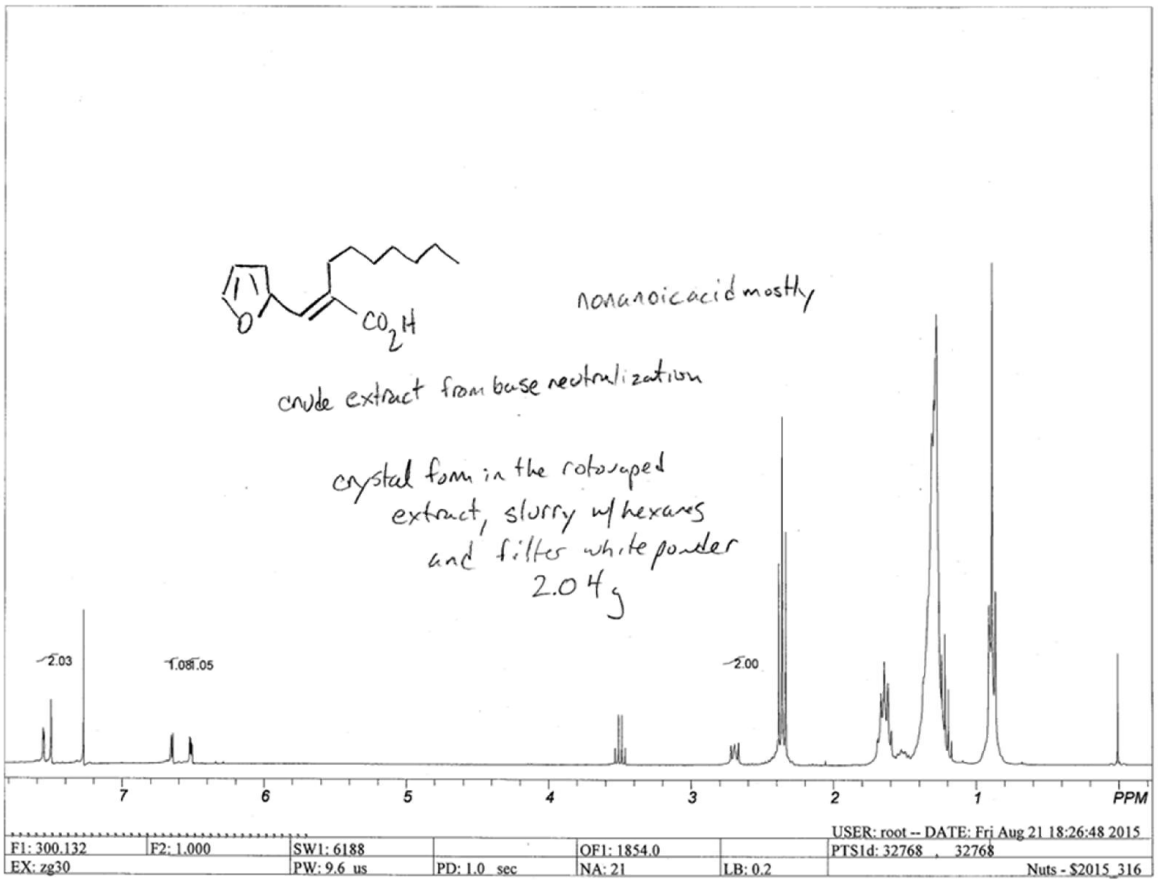
Proton NMR of octenylfuran (**119B**)



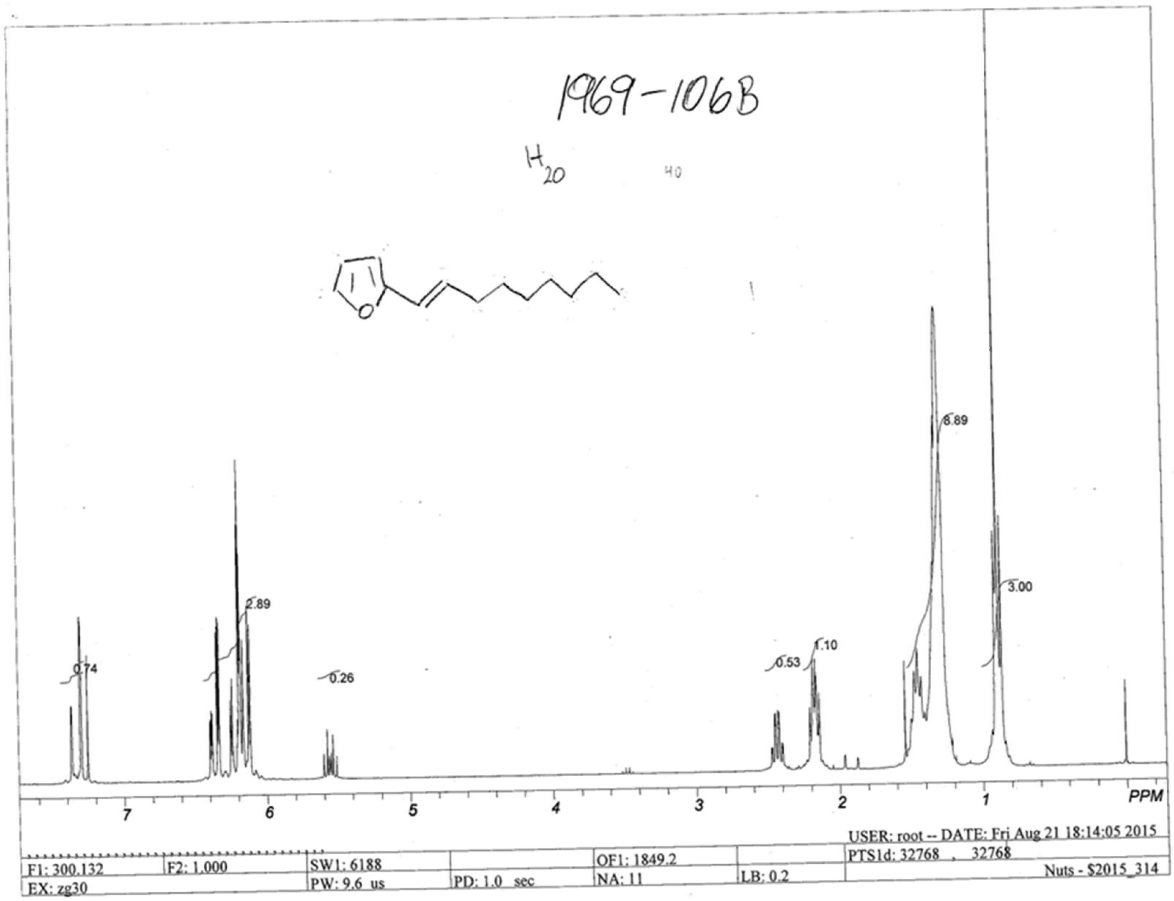
Carbon NMR of octenylfuran (**119B**)



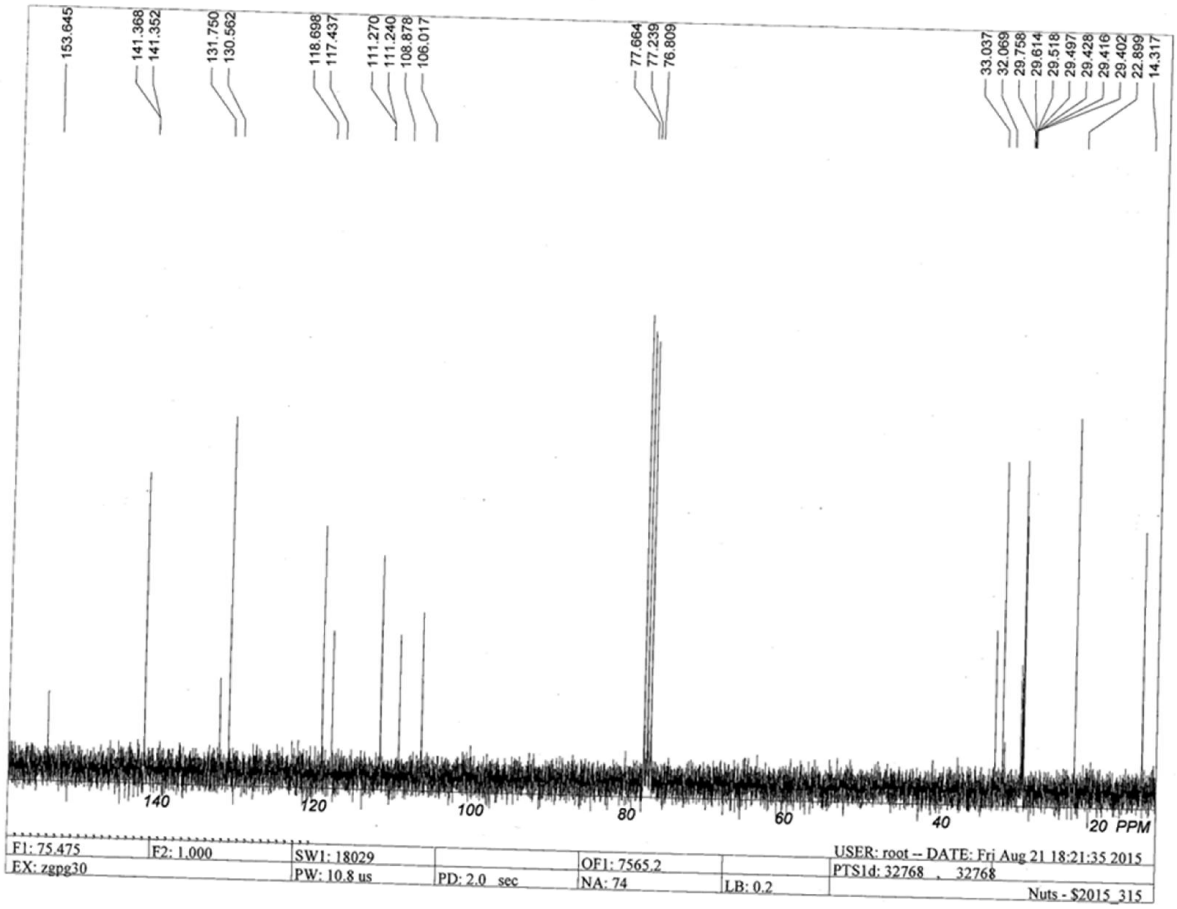
Proton NMR of furanacrylic acid (**106C**)



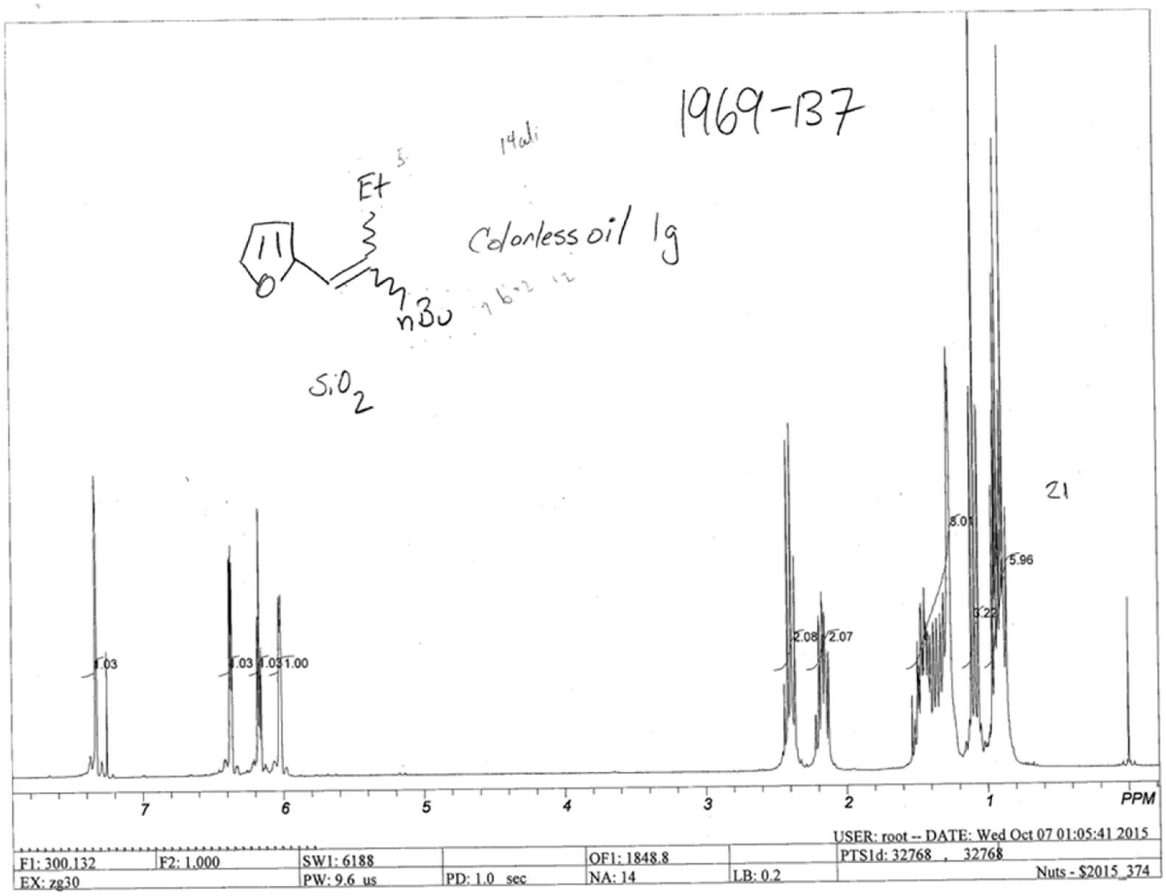
Proton NMR of furanyl alkene (**106B**)



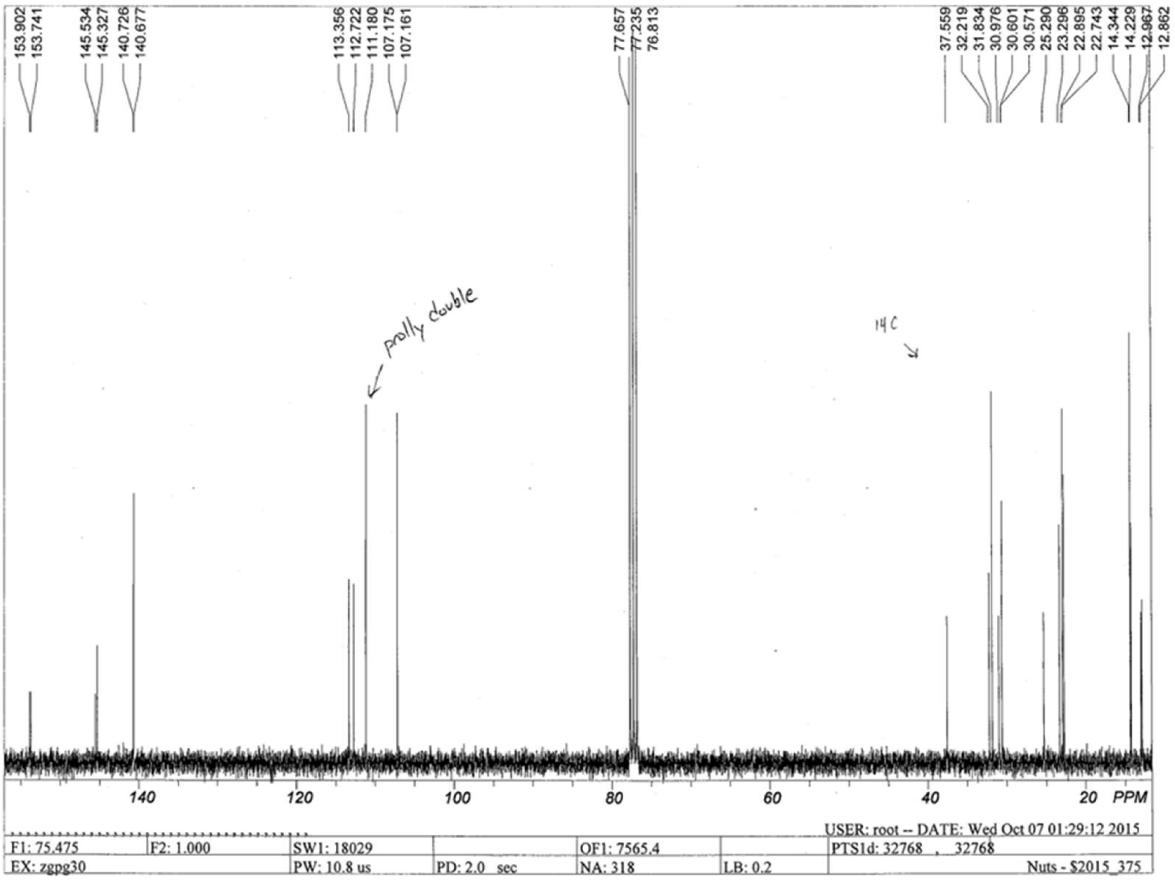
Carbon NMR of furanyl alkene (**106B**)



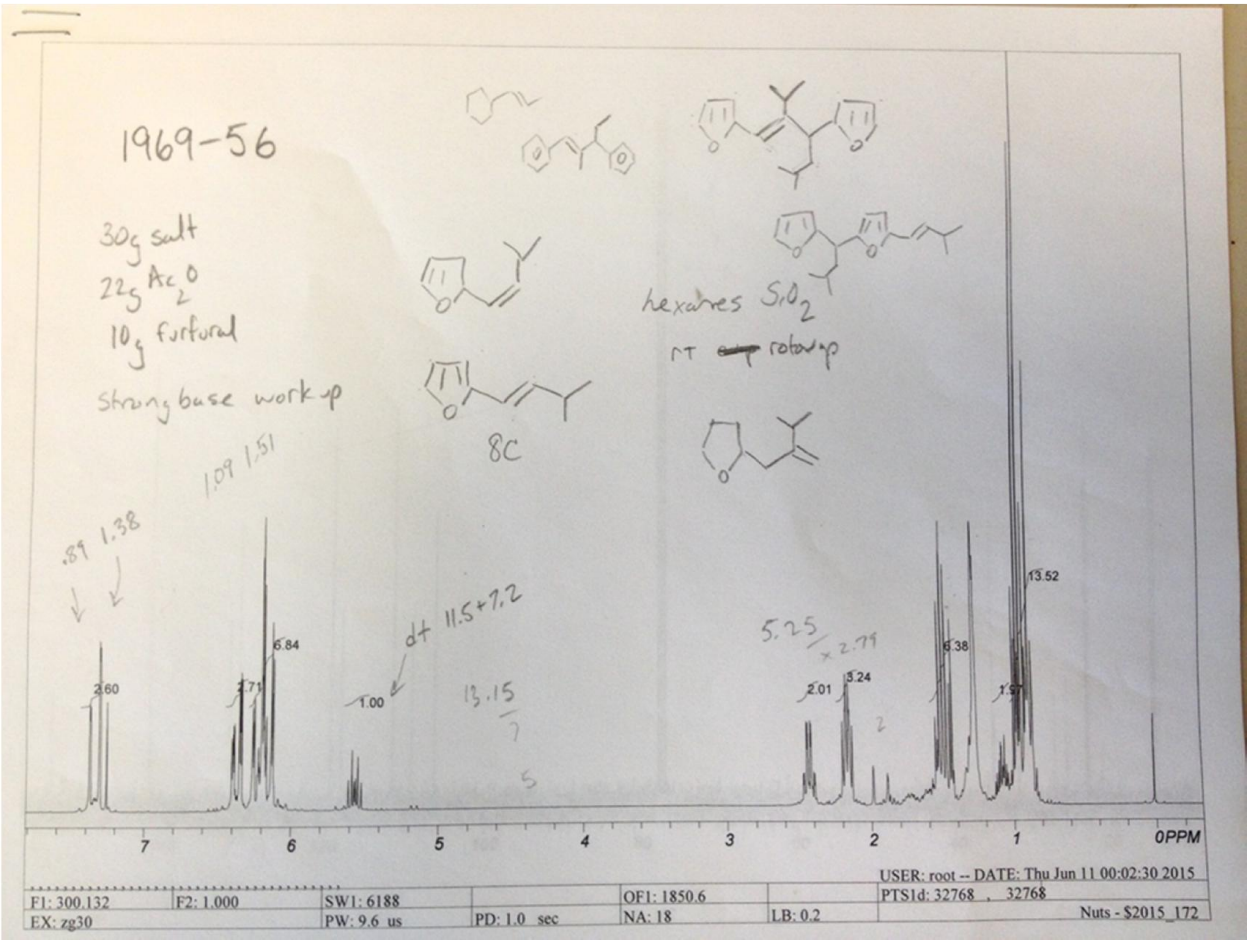
Proton NMR of alkenylfuran (**137**)



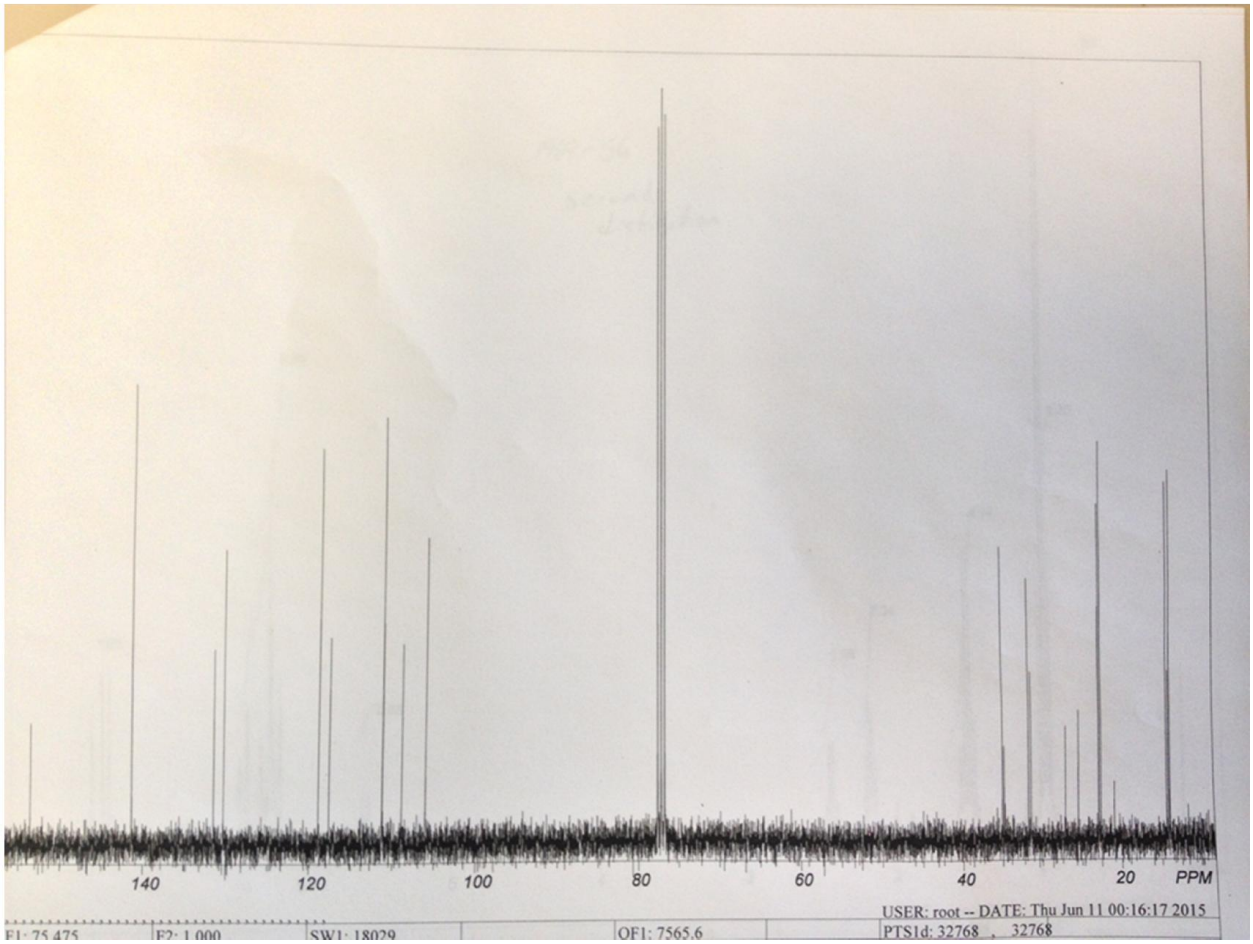
Carbon NMR of alkenylfuran (**137**)



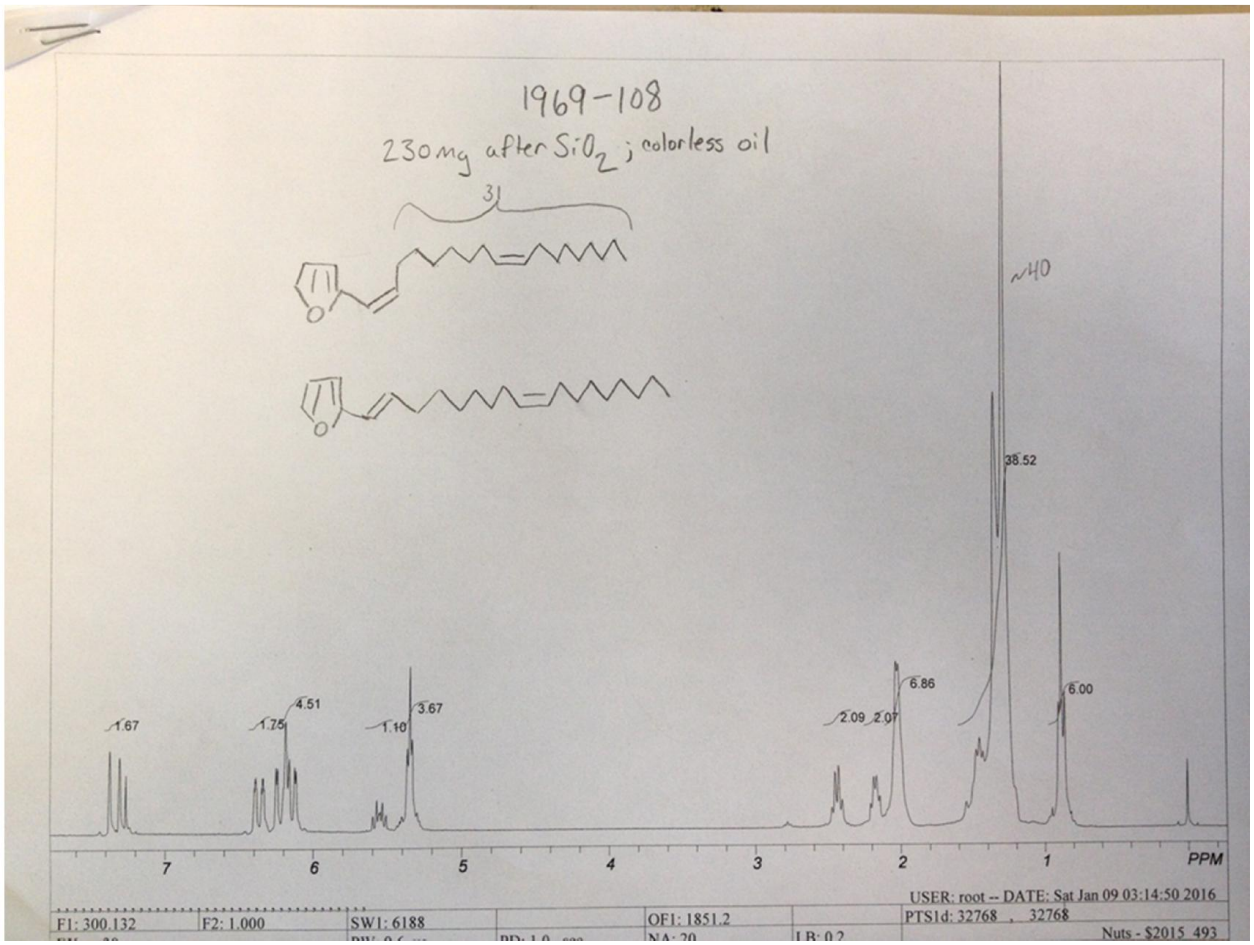
Proton NMR of isopentenylfuran (**56**)



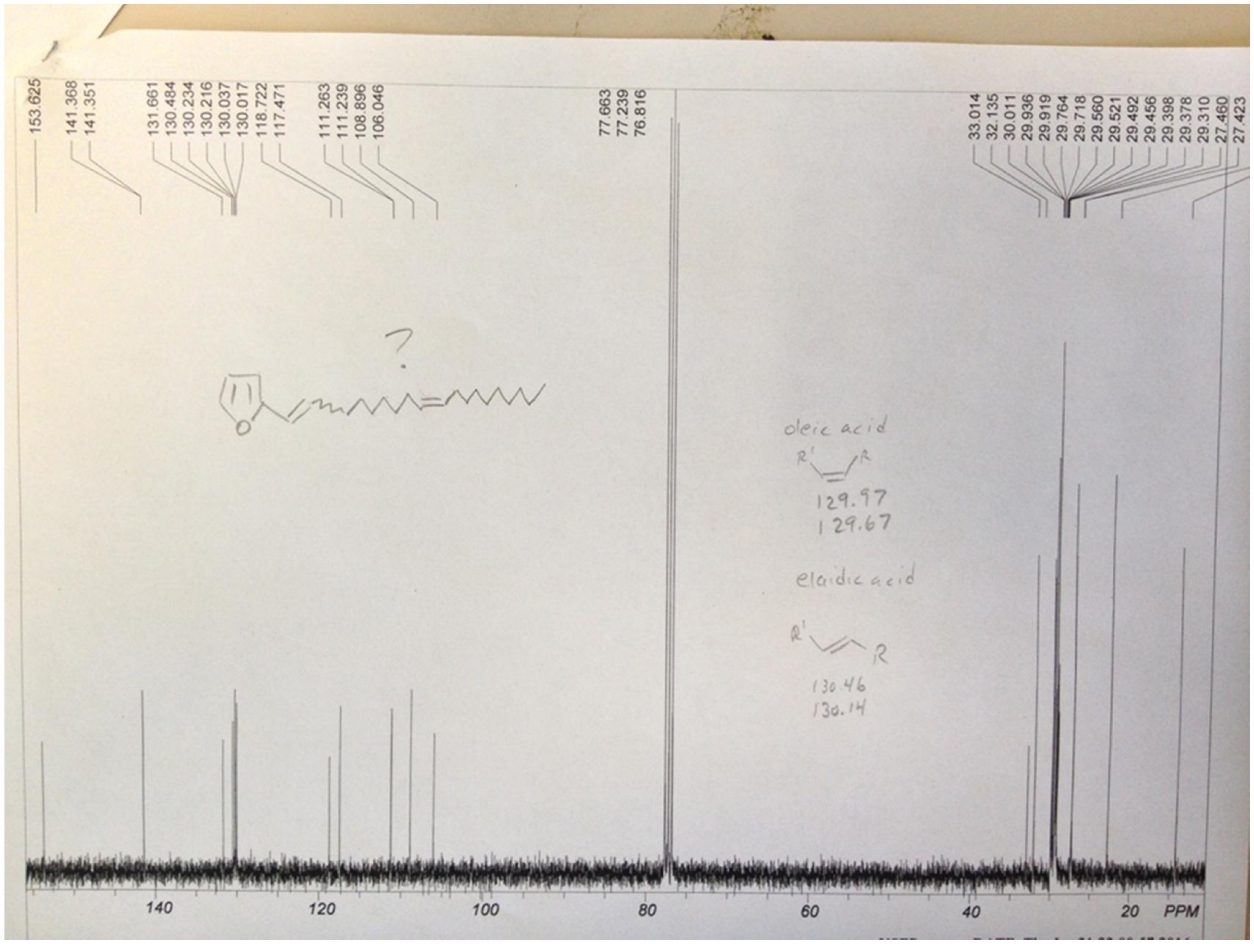
Carbon NMR of isopentenylfuran (**56**)



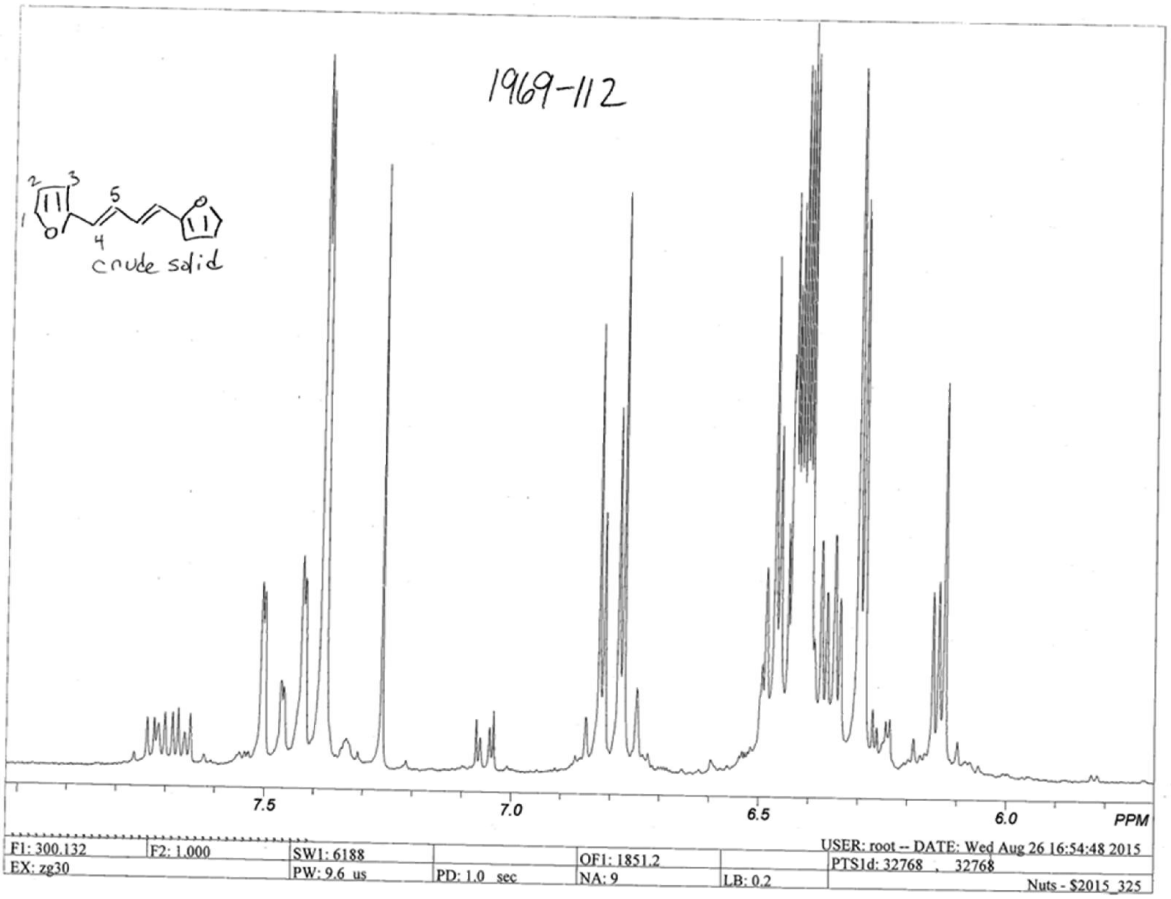
Proton NMR alkeneylfuran (**108**)



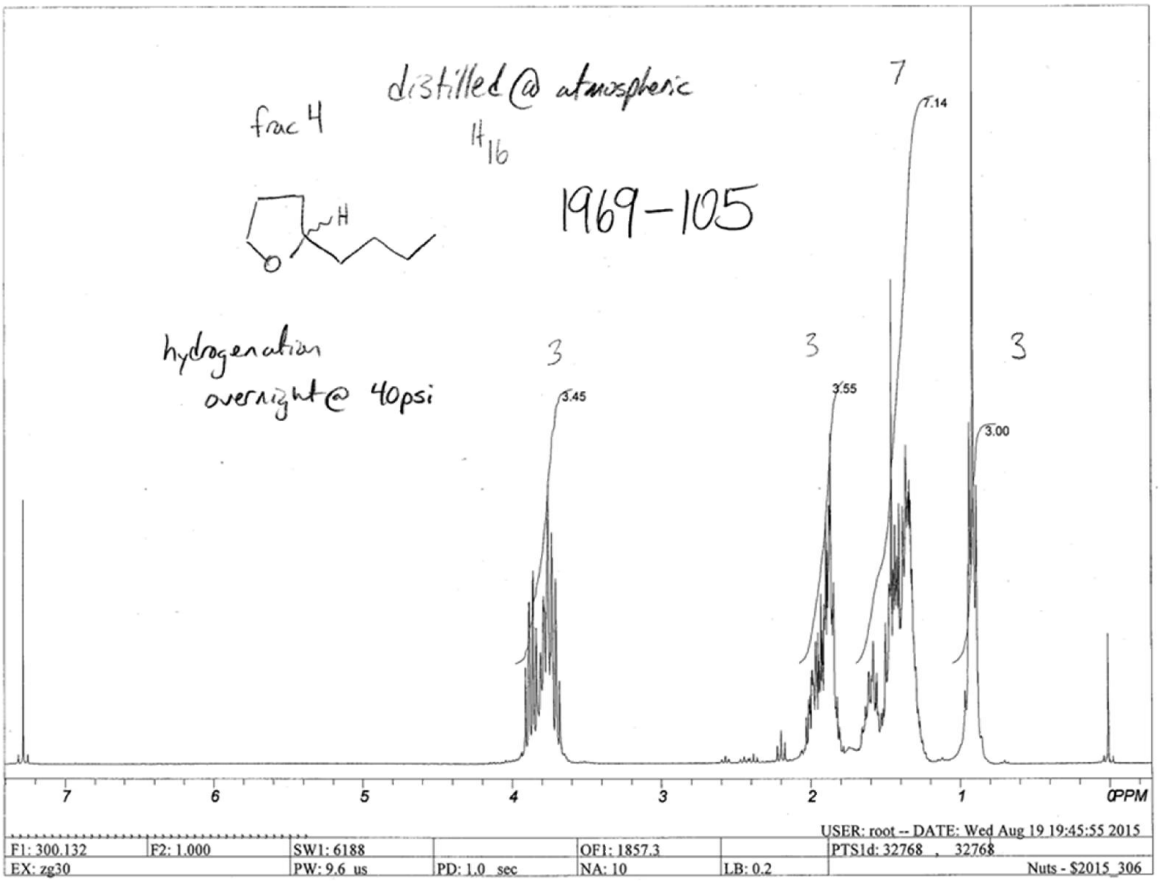
Carbon NMR alkeneylfuran (**108**)



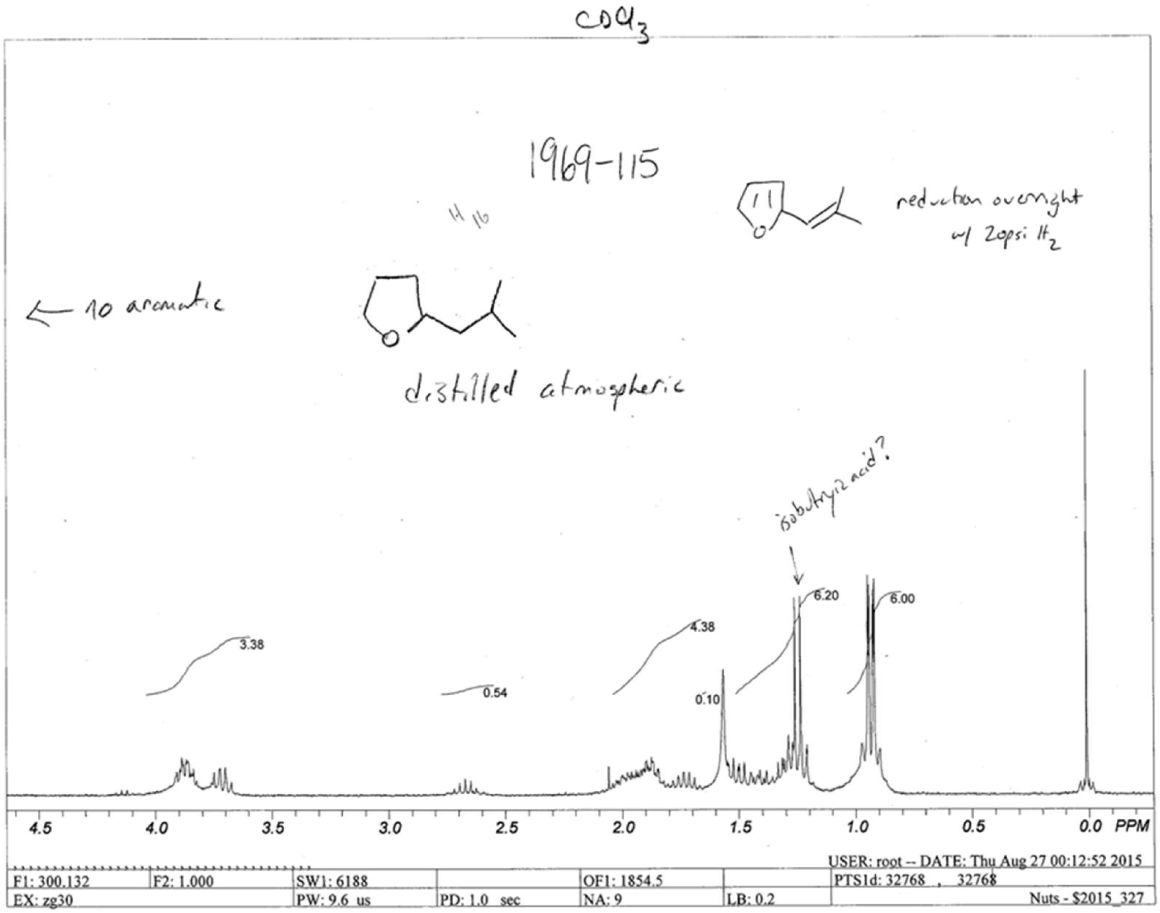
Proton NMR of alkenylfuran (**112**)



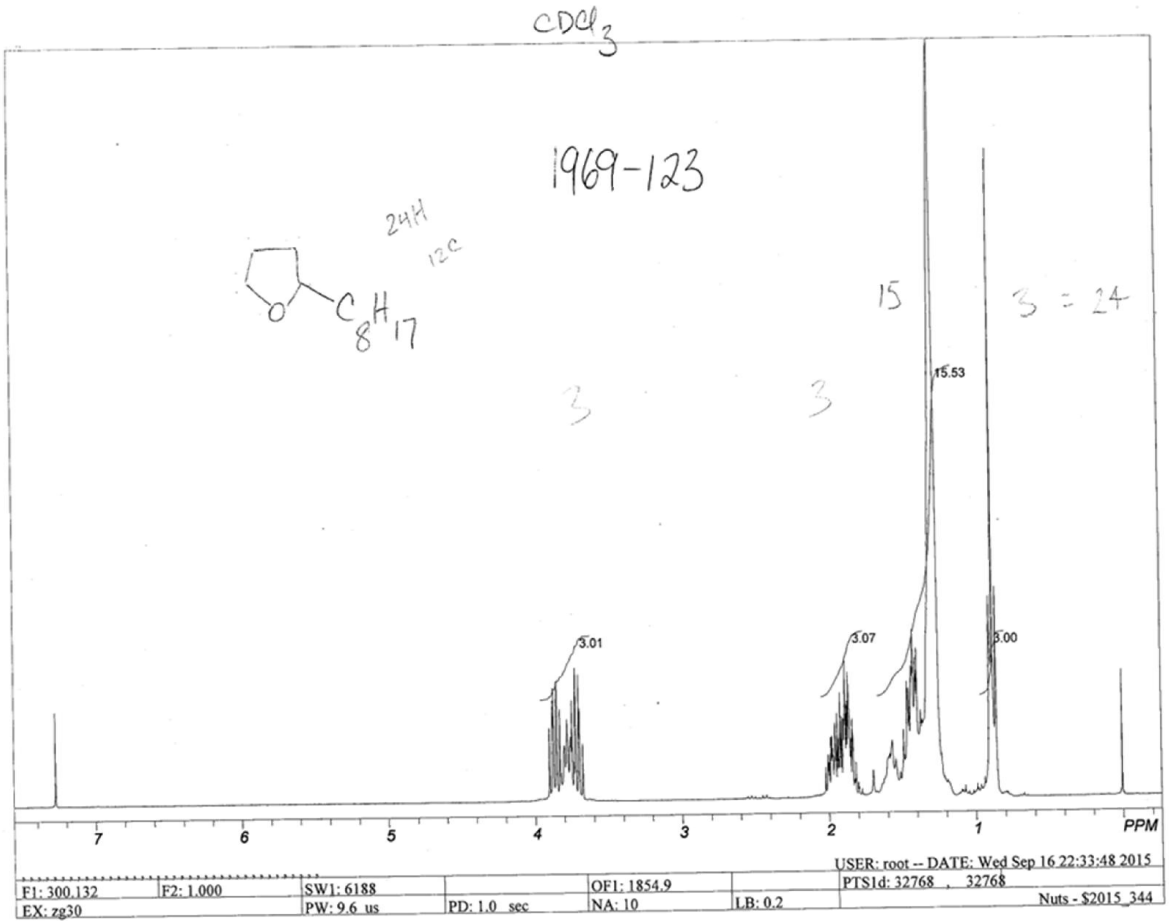
Proton NMR of alkyltetrahydrofuran (**105**)



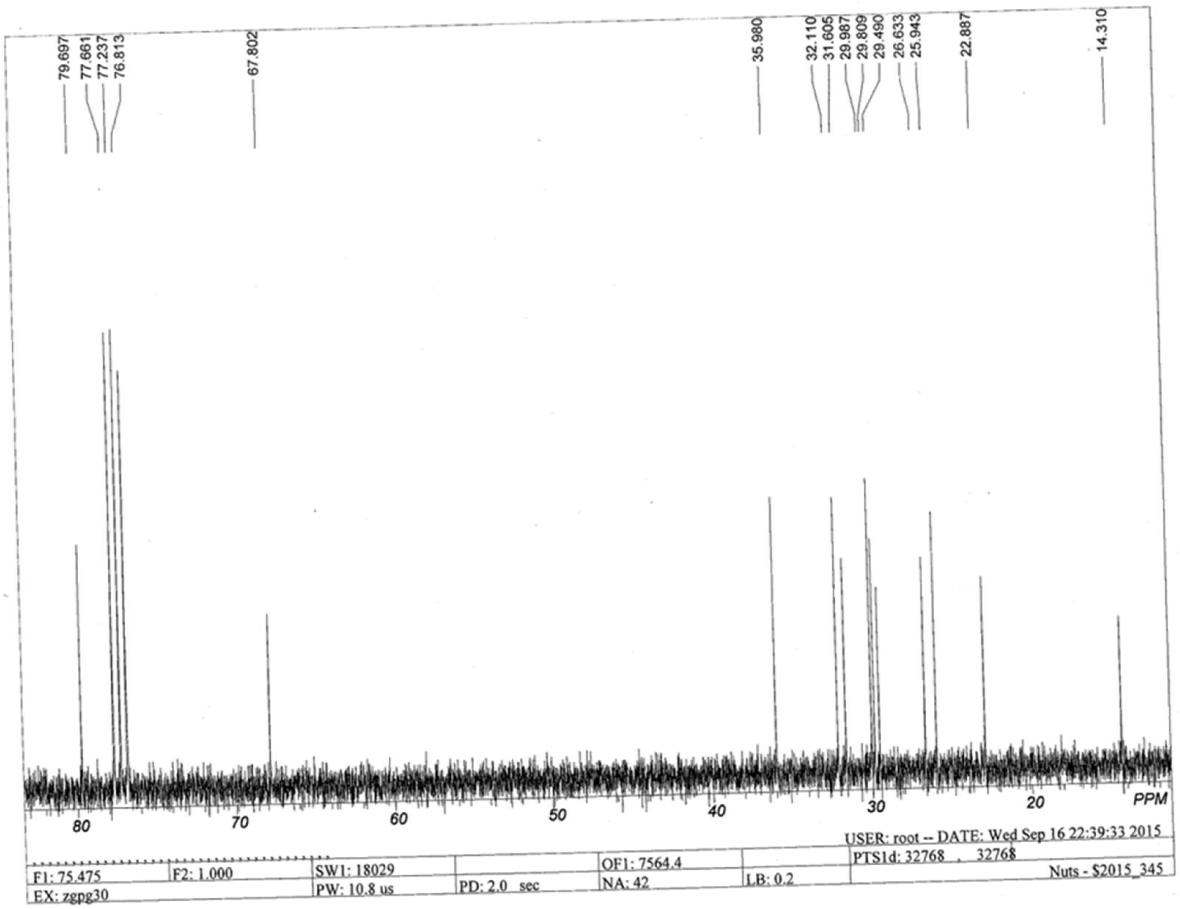
Proton NMR of alkylfuran (**115**)



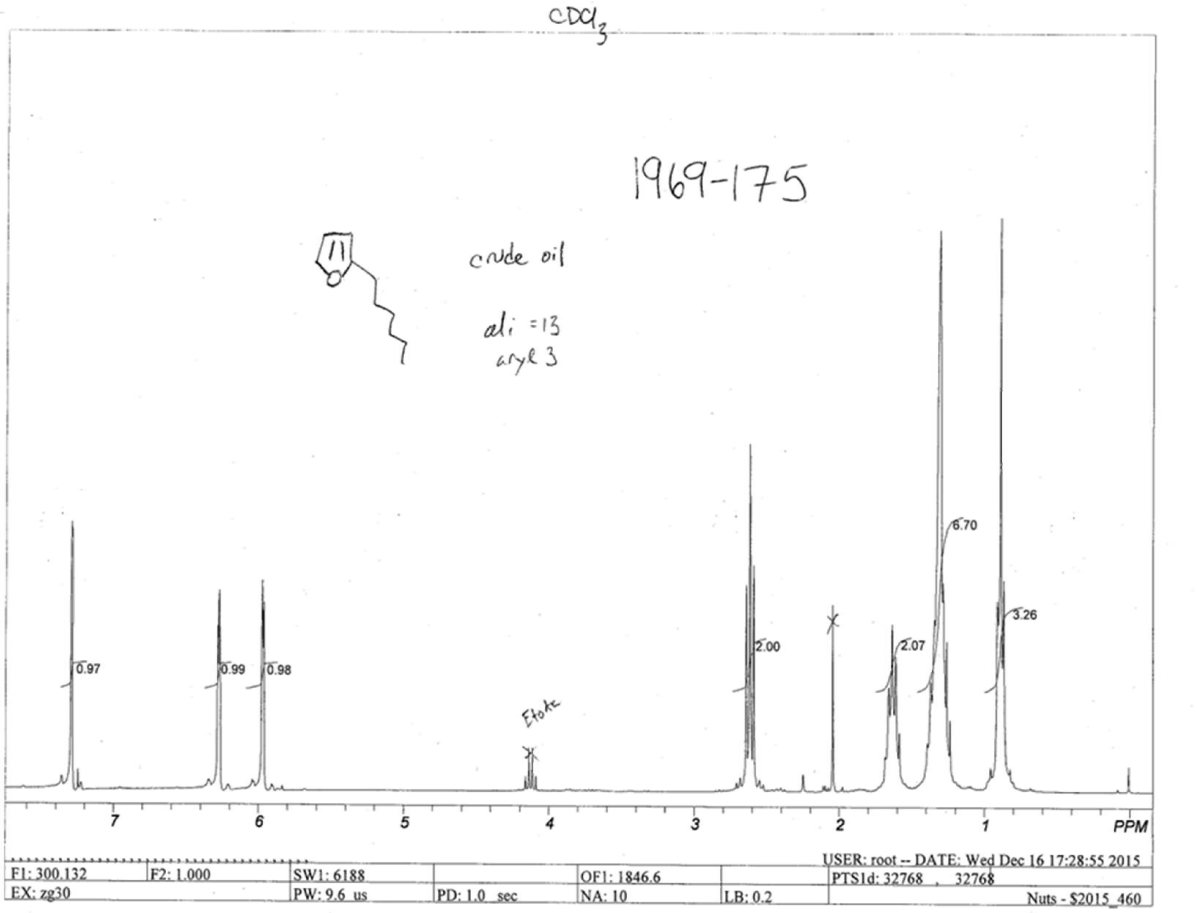
Proton NMR of alkytetrahydrofuran (**123**)



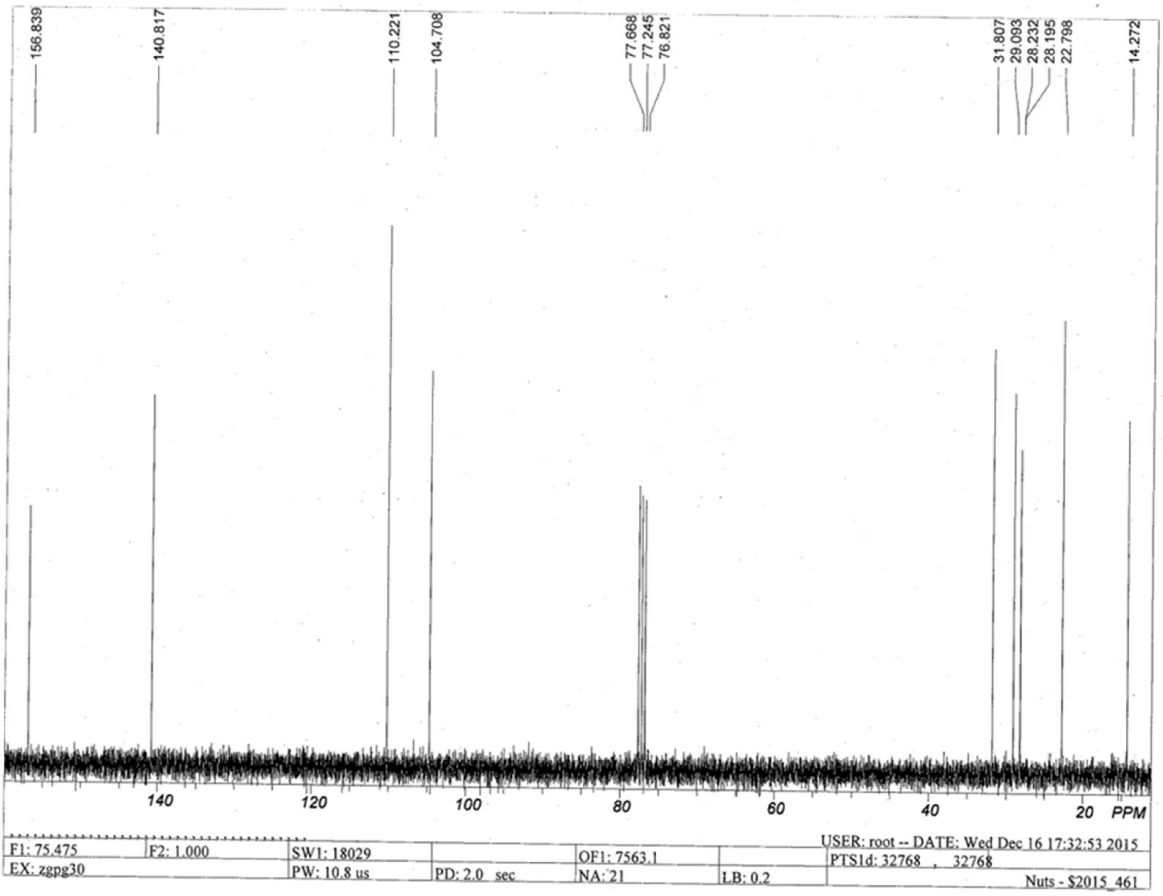
Carbon NMR of alkytetrahydrofuran (**123**)



Proton NMR of alkyfuran (**175**)

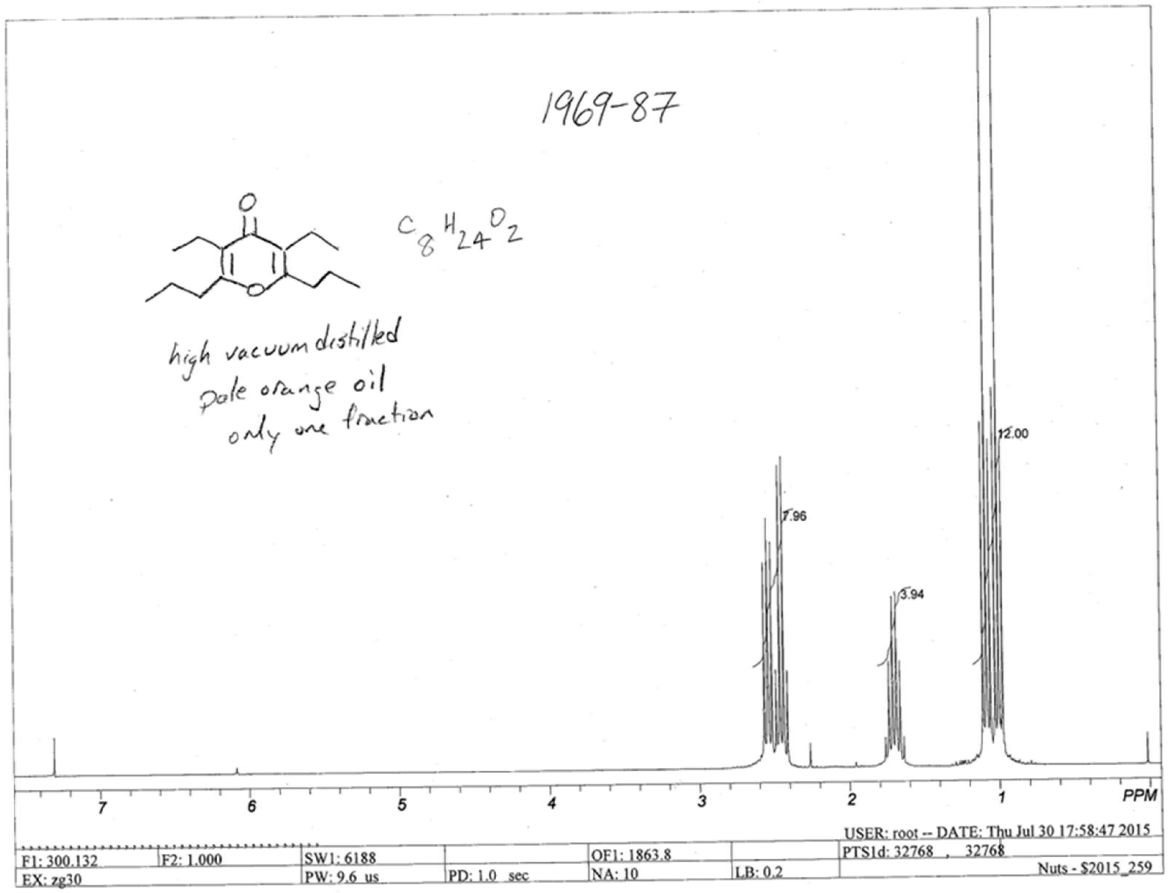


Carbon NMR of alkyfuran (**175**)

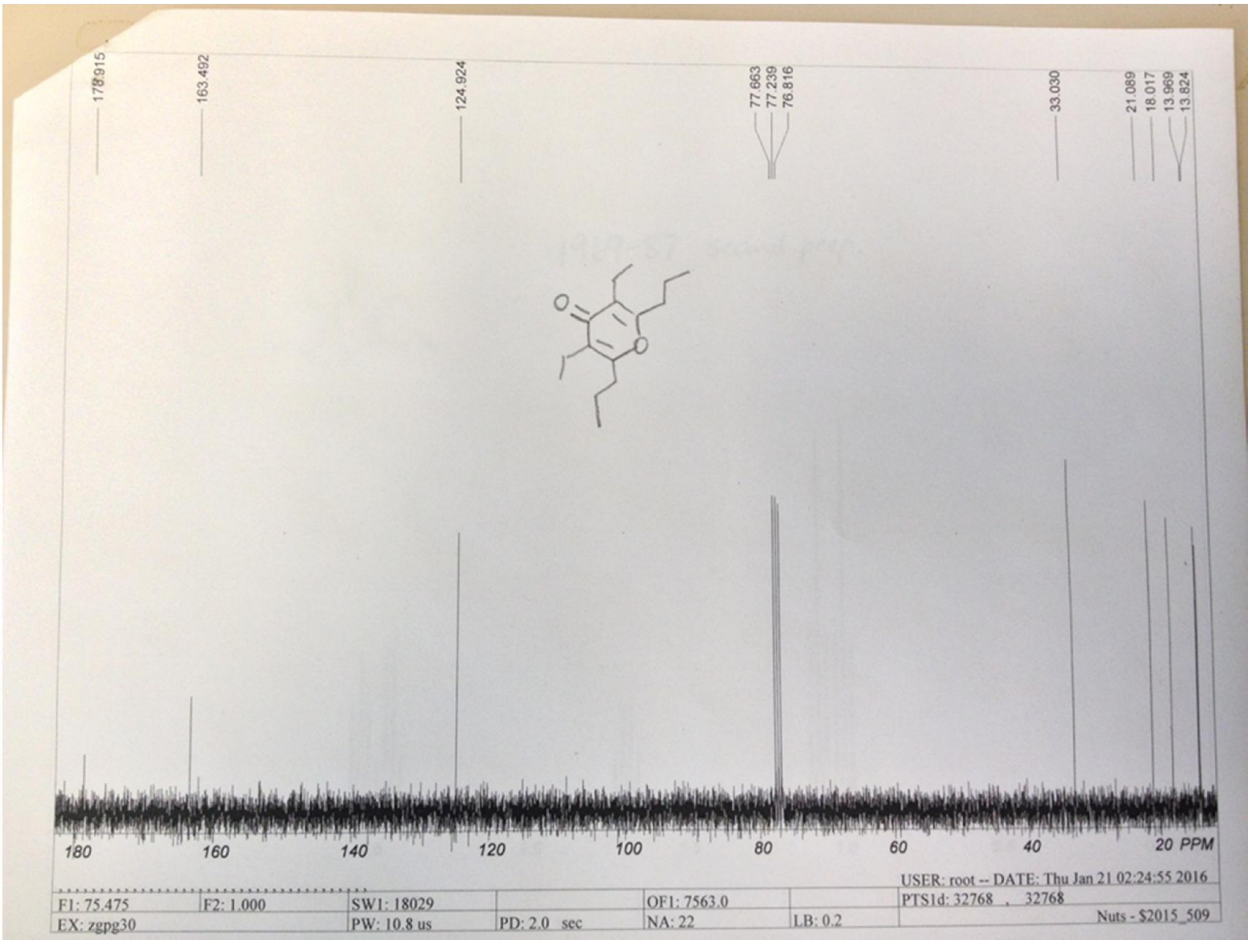


Appendix H NMR Data for Pyrone Solvent

Proton NMR of 2,6-dipropyl-3,5-diethyl-4-pyranone (**87**)

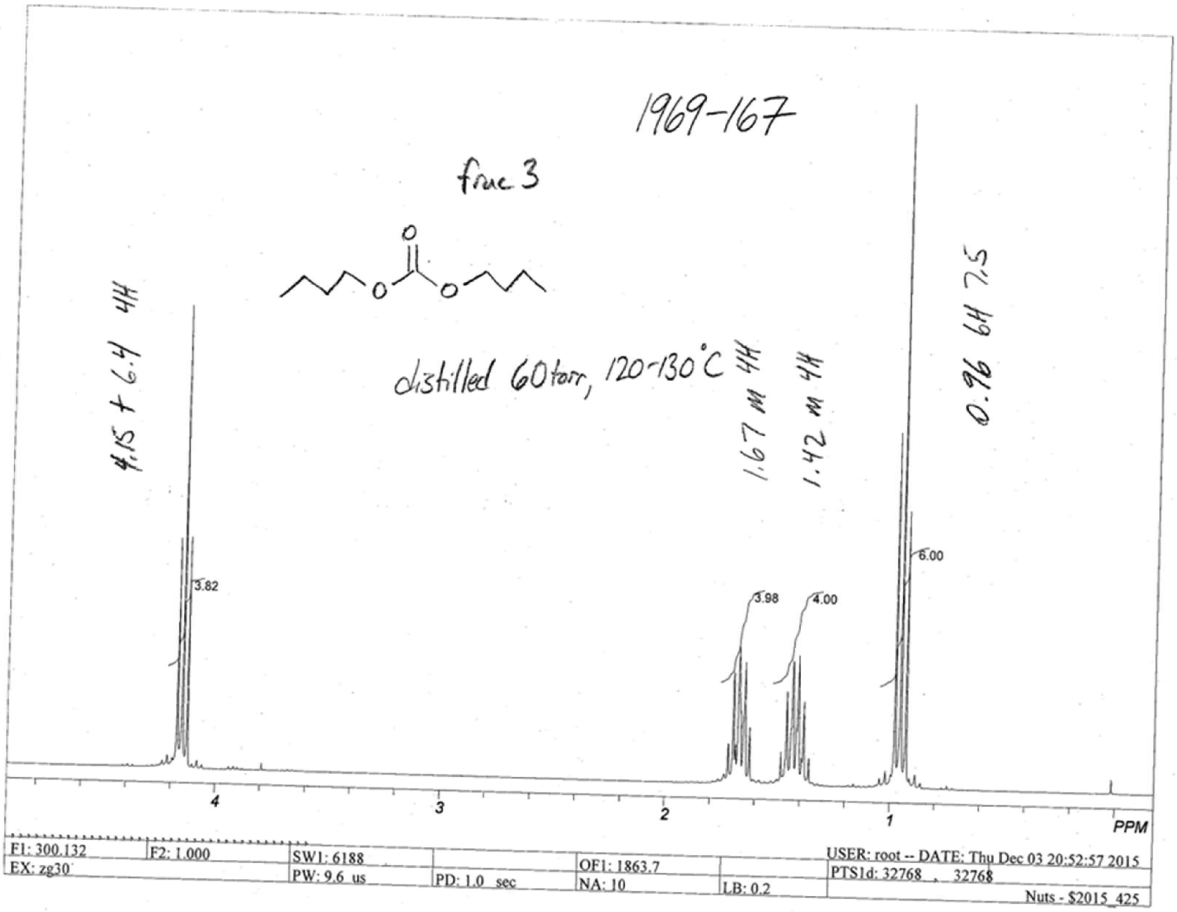


Carbon NMR of 2,6-dipropyl-3,5-diethyl-4-pyranone (**87**)

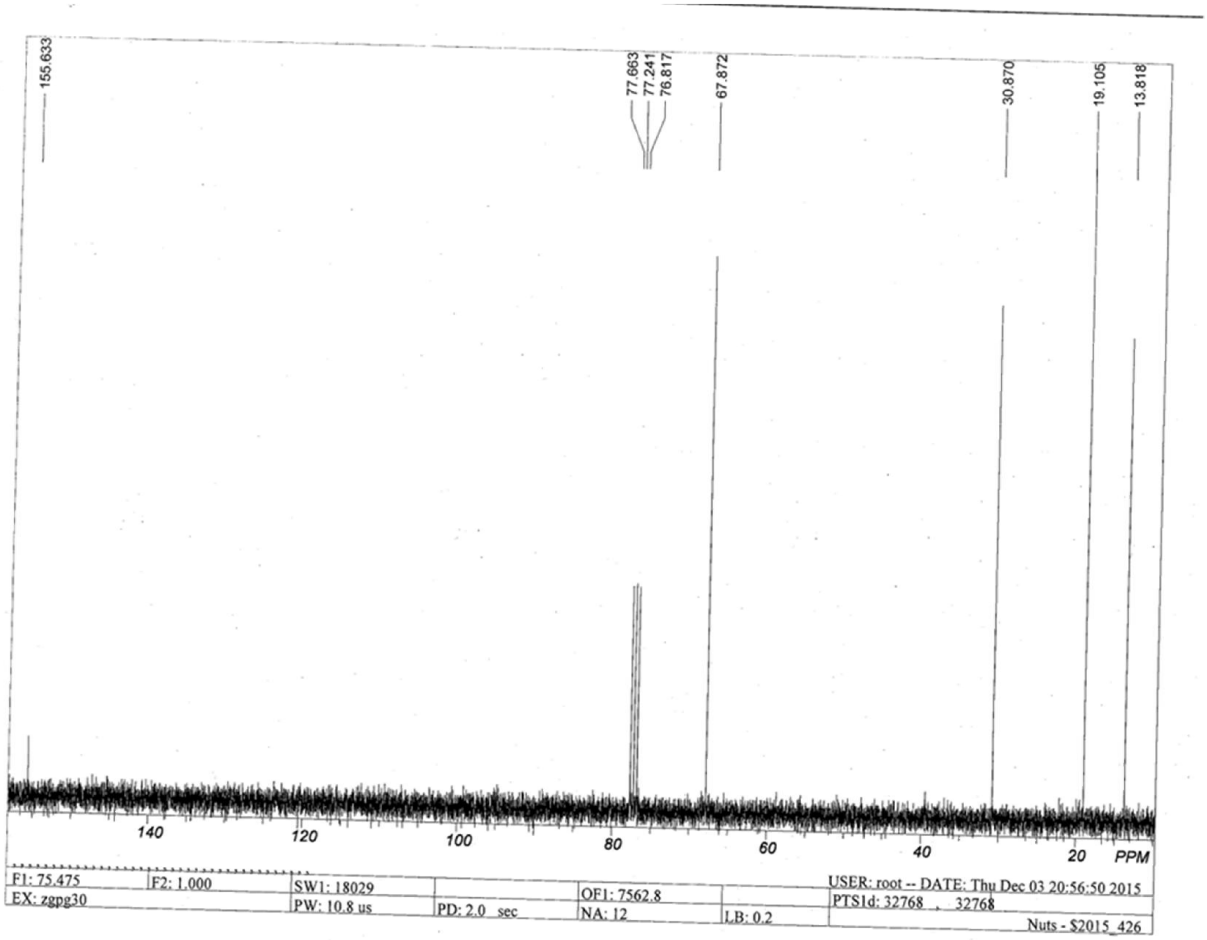


Appendix I NMR Data for Furanic carbonate, dialkyl carbonate and *N*,*O*-dialkyl carbamate solvents

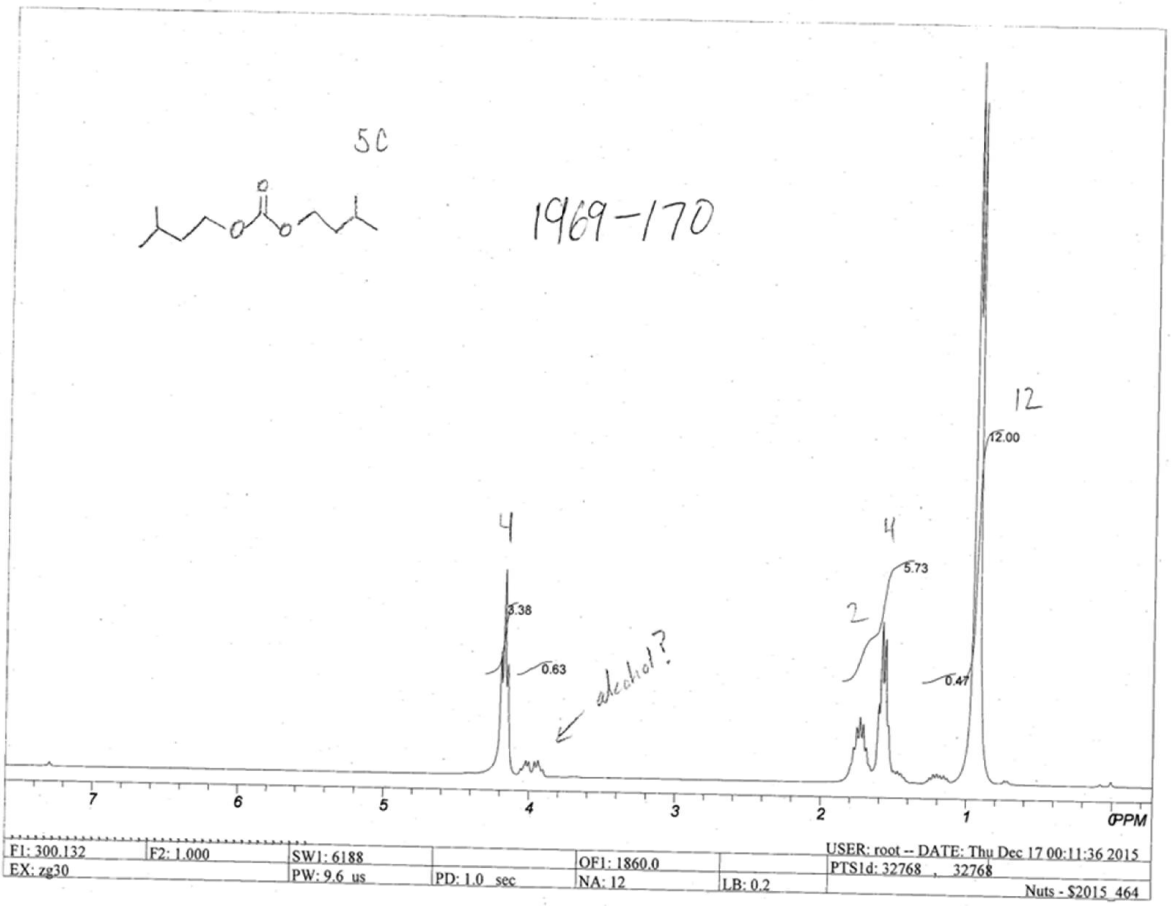
Proton NMR of dibutyl carbonate (**167**)



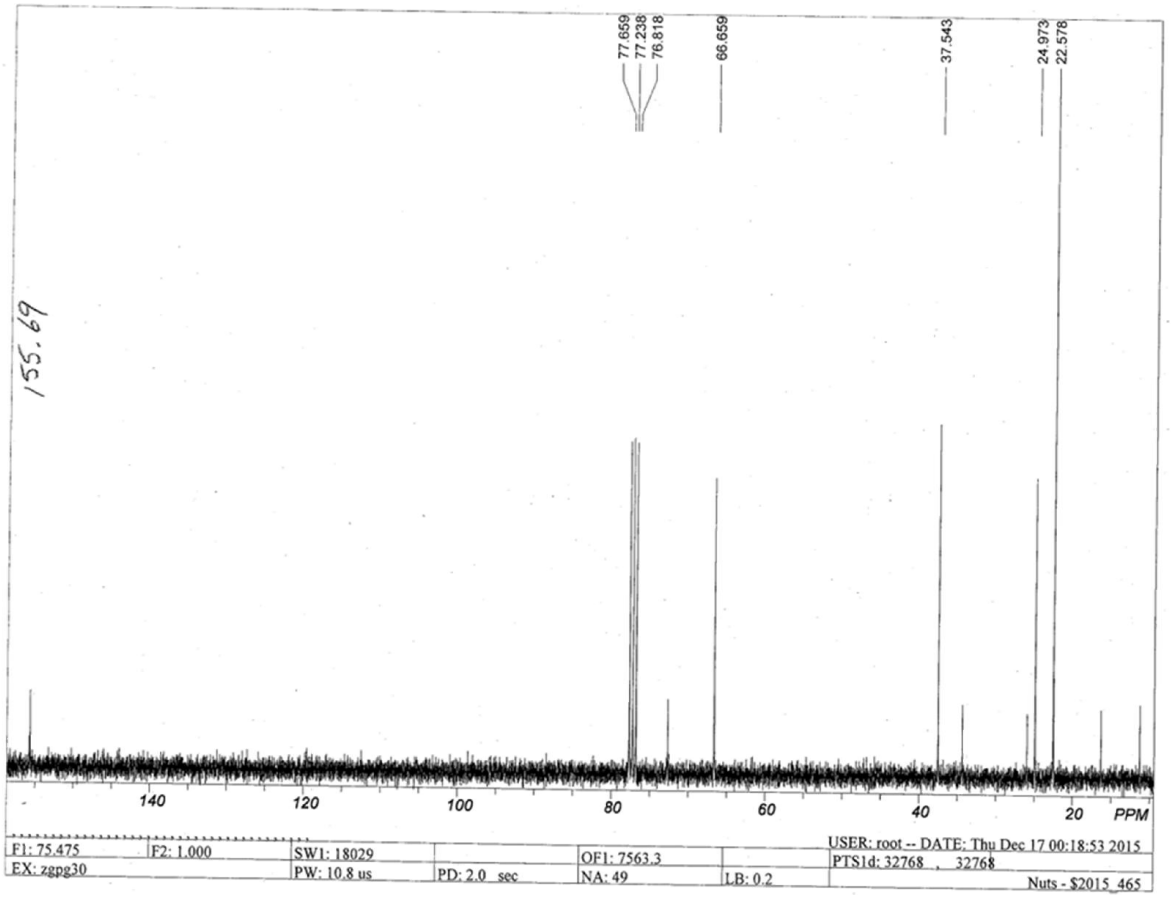
Carbon NMR of dibutyl carbonate (**167**)



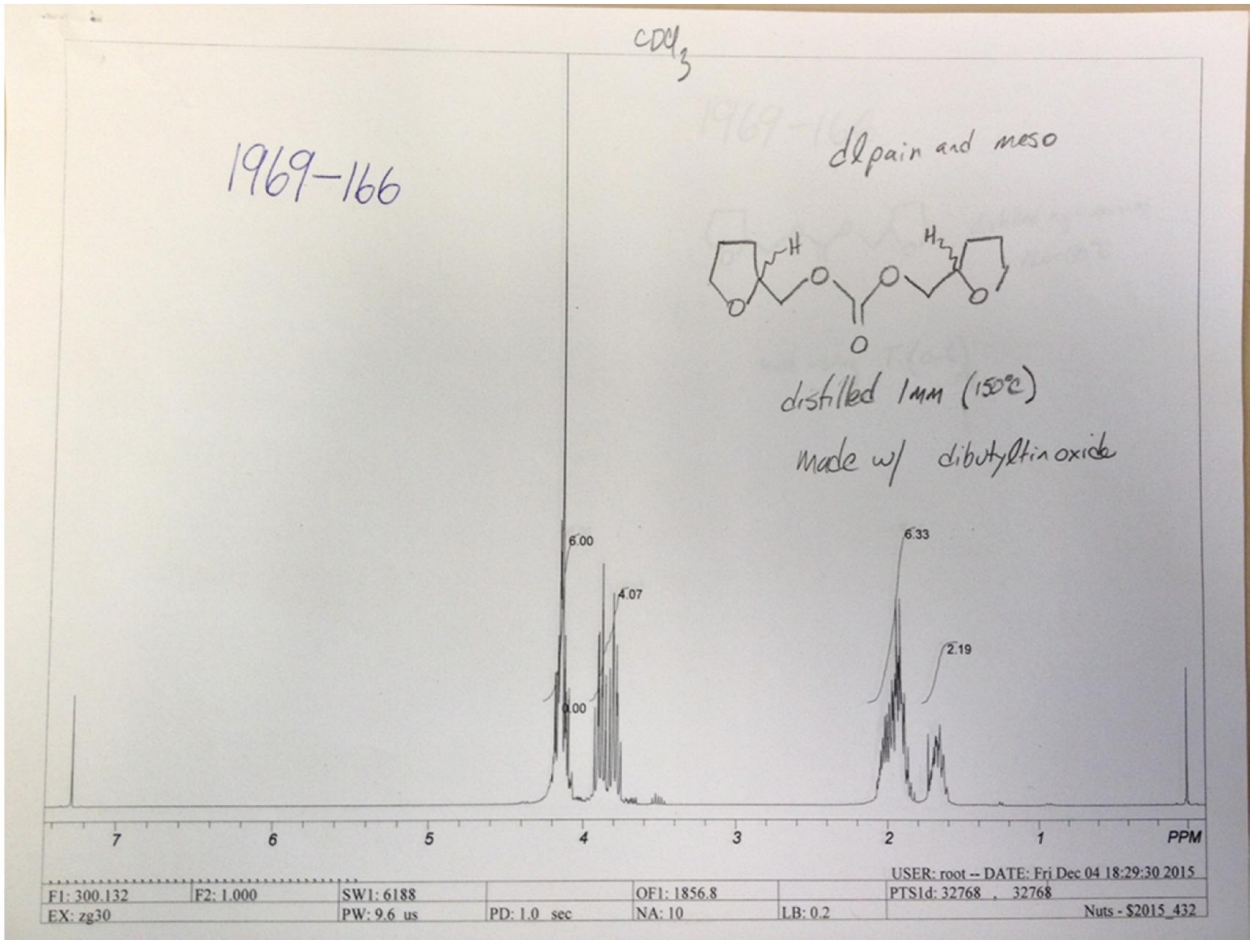
Proton NMR of diisoamyl carbonate (**170**)



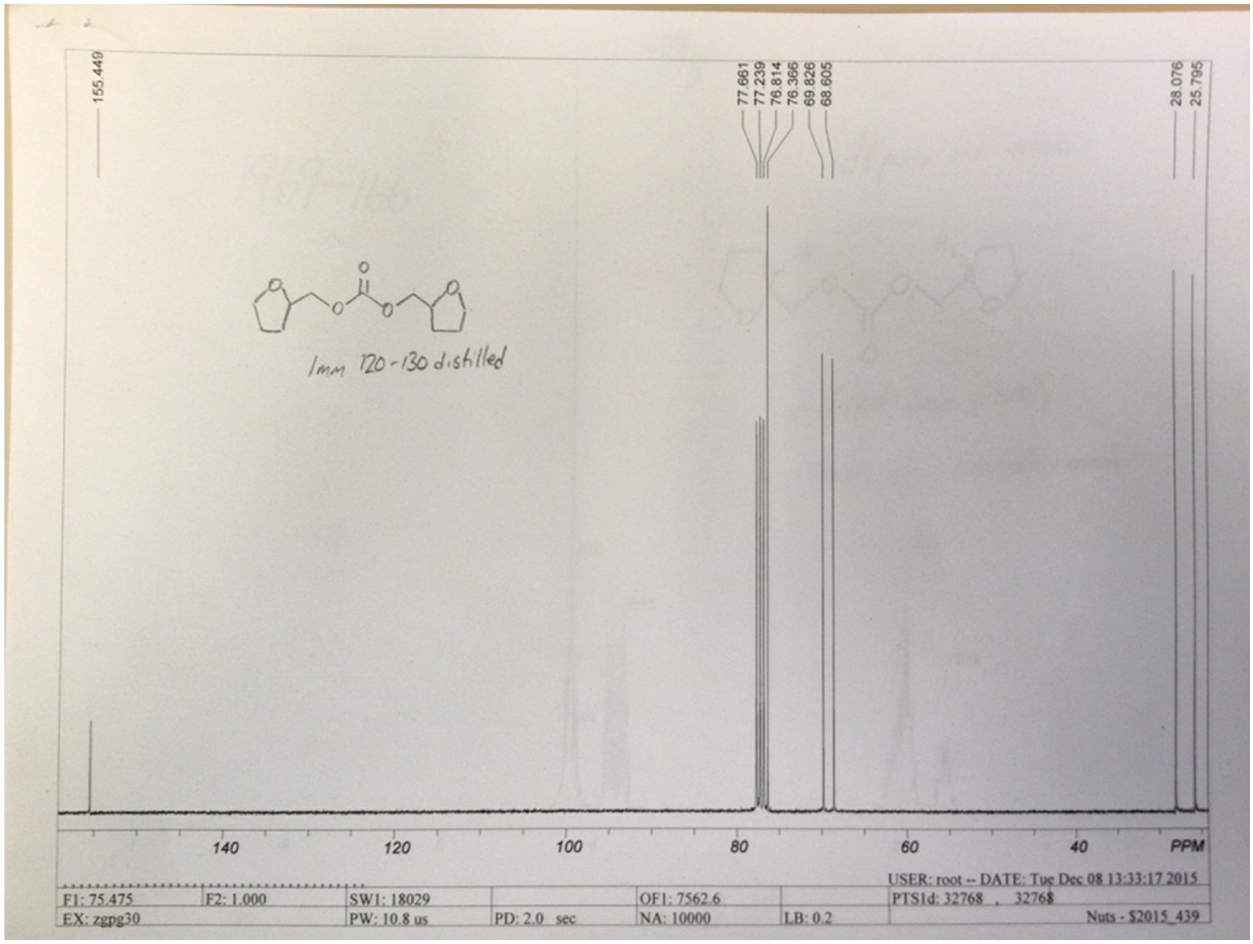
Carbon NMR of diisoamyl carbonate (**170**)



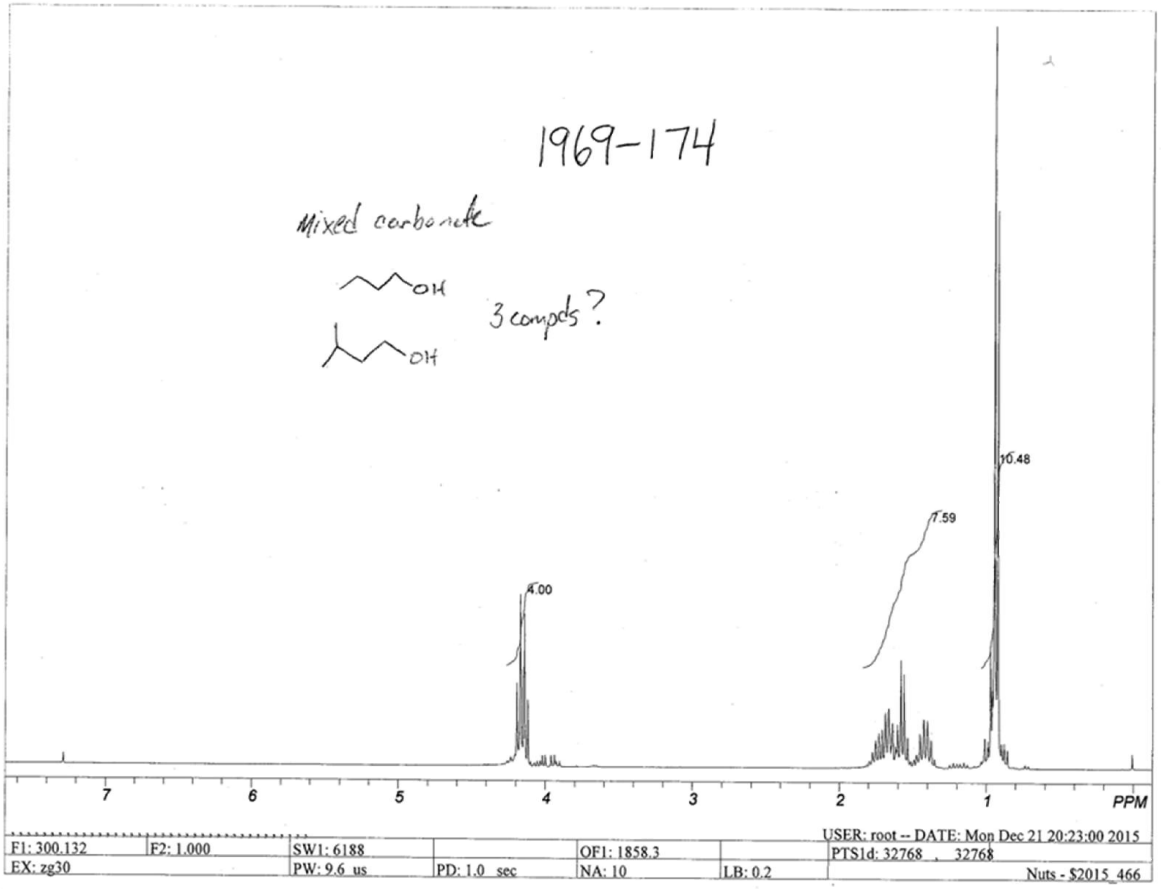
Proton NMR of difuranyl carboanate (**166**)



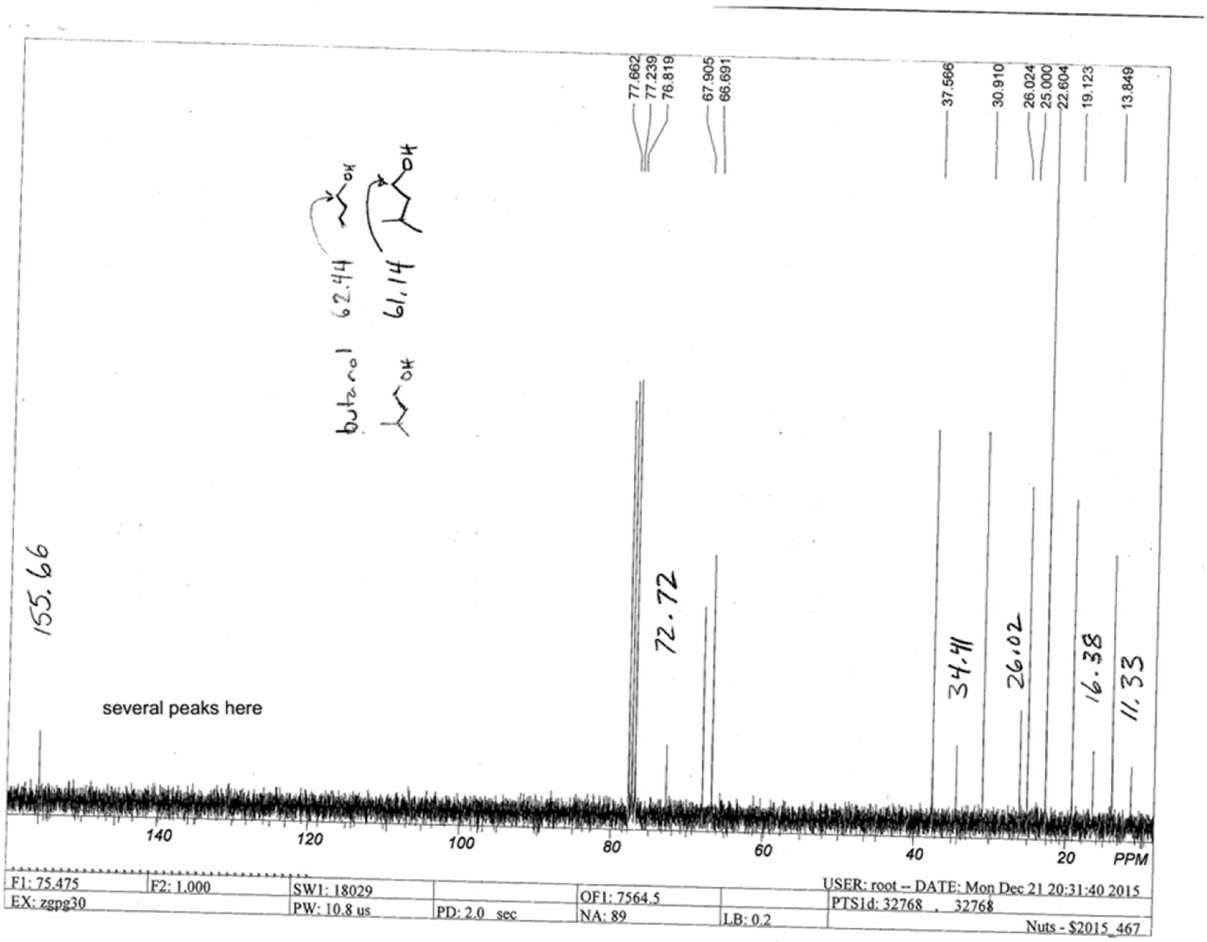
Carbon NMR of difuranyl carbonate (**166**)



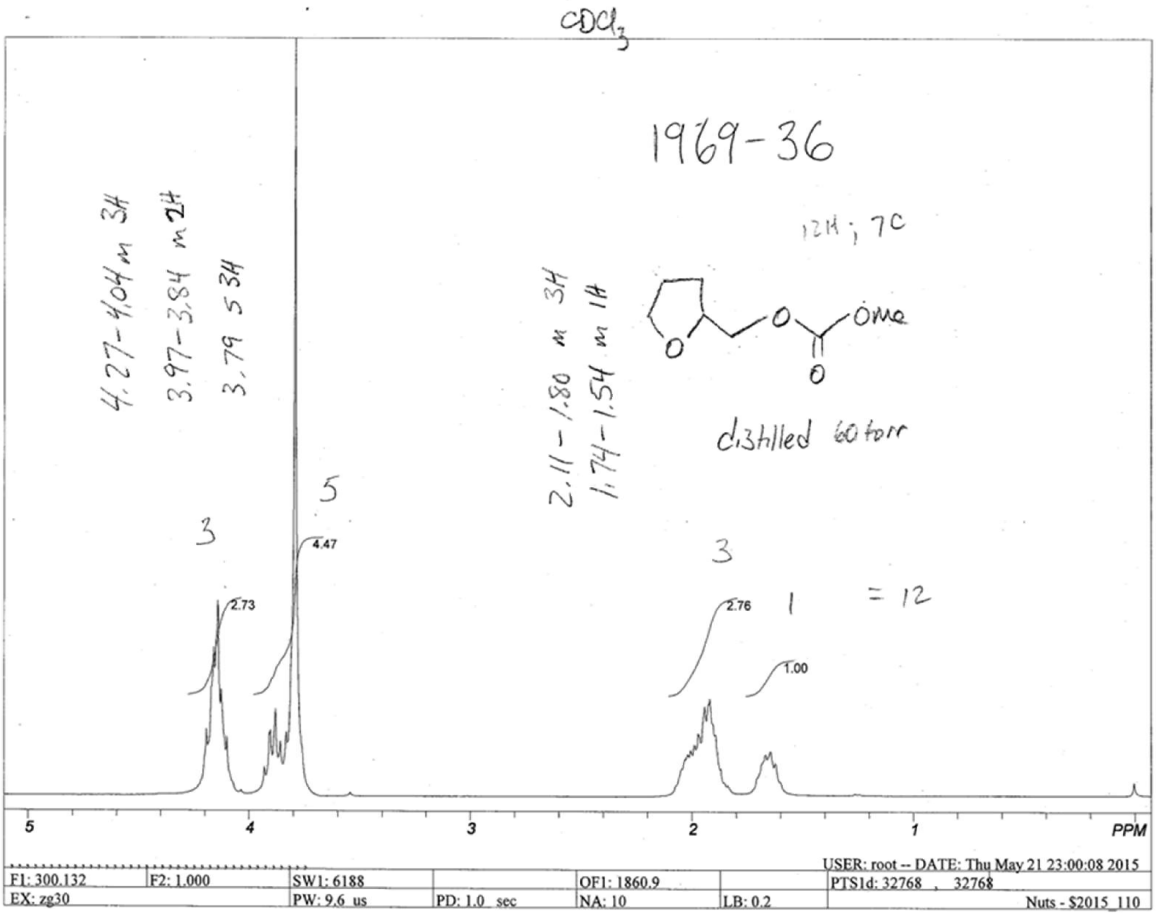
Proton NMR of mixed carbonate from butyl and isoamyl alcohols (**174**)



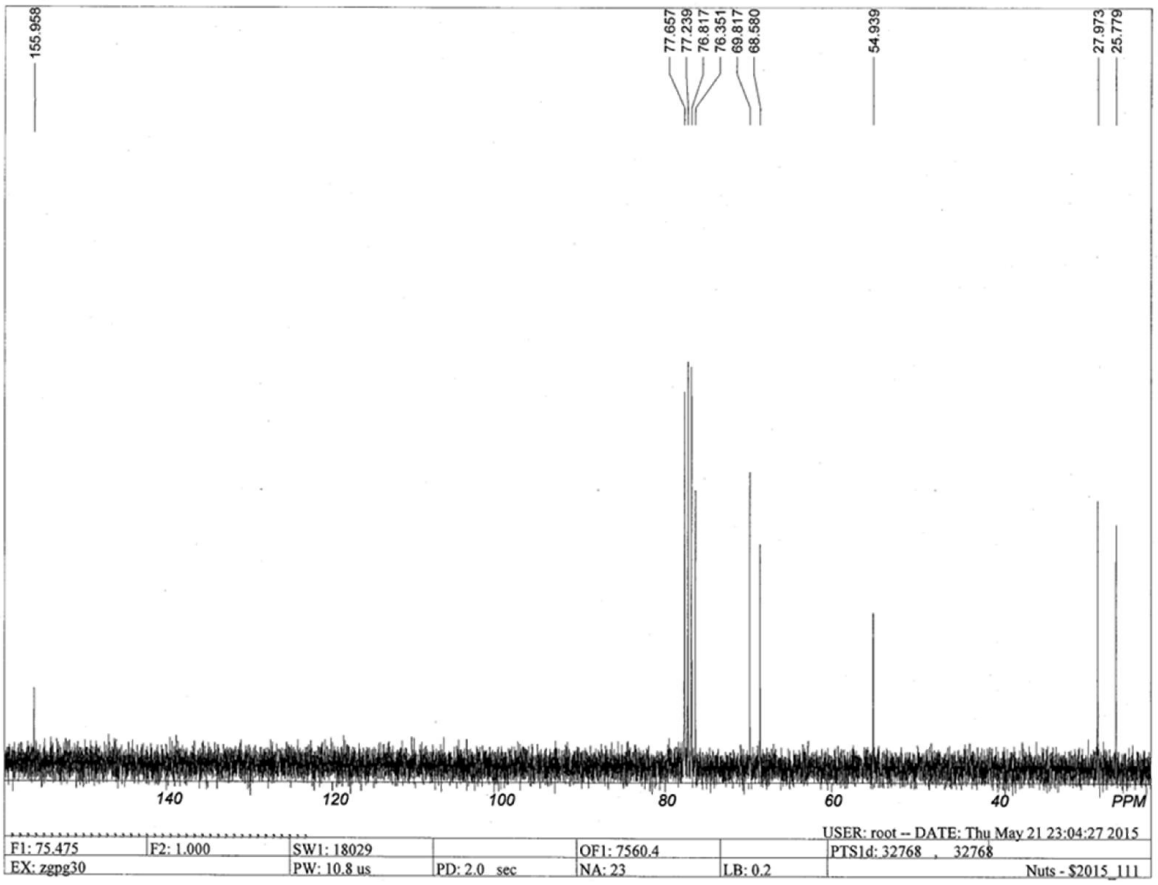
Carbon NMR of mixed carbonate from butyl and isoamyl alcohols (**174**)



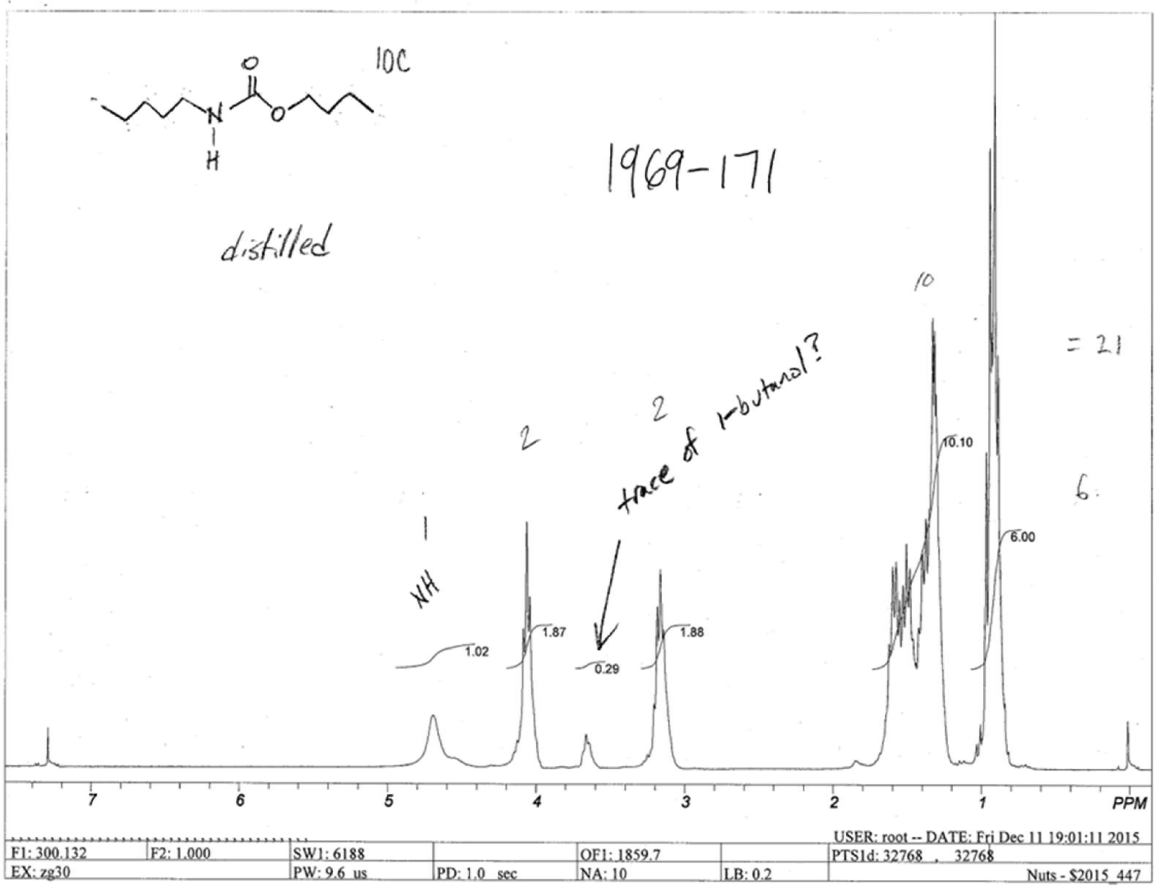
Proton NMR of tetrahydrofuranyl carbonate (**36**)



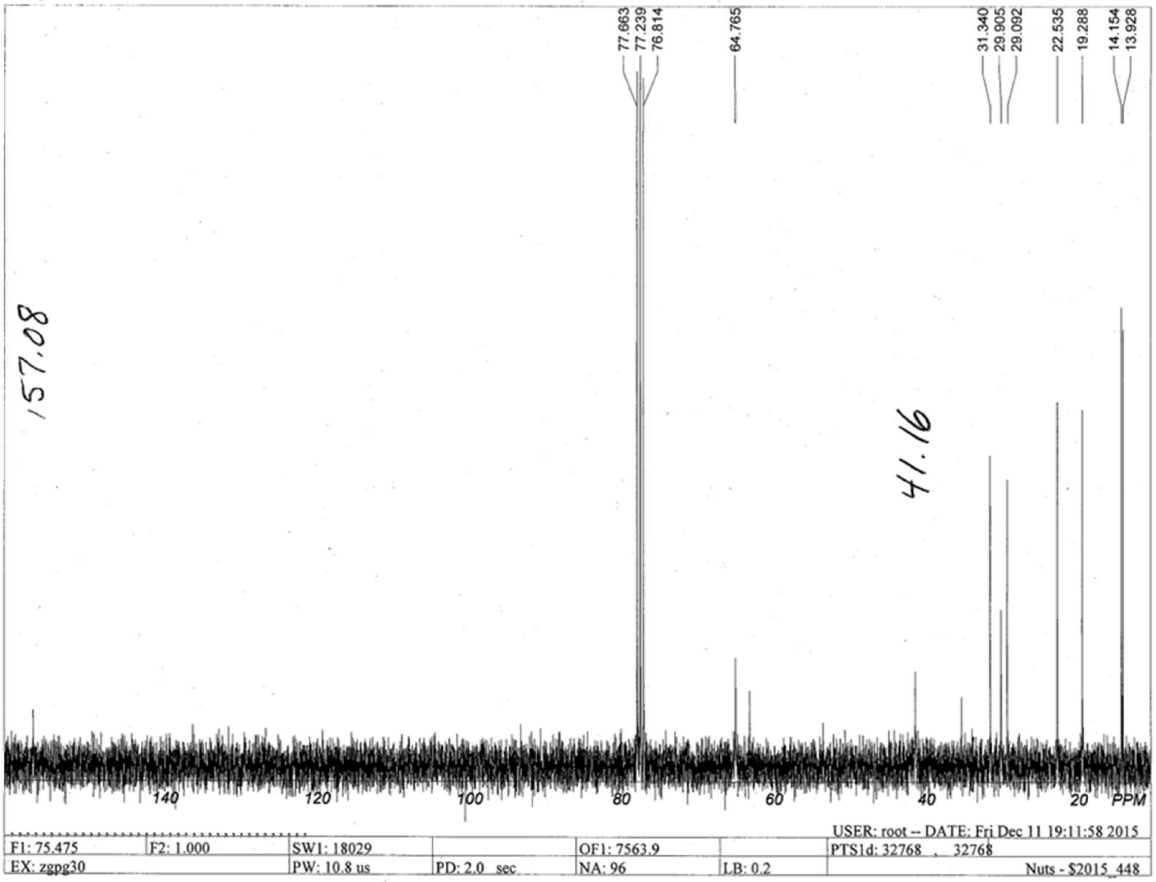
Carbon NMR of tetrahydrofuranyl carbonate (**36**)



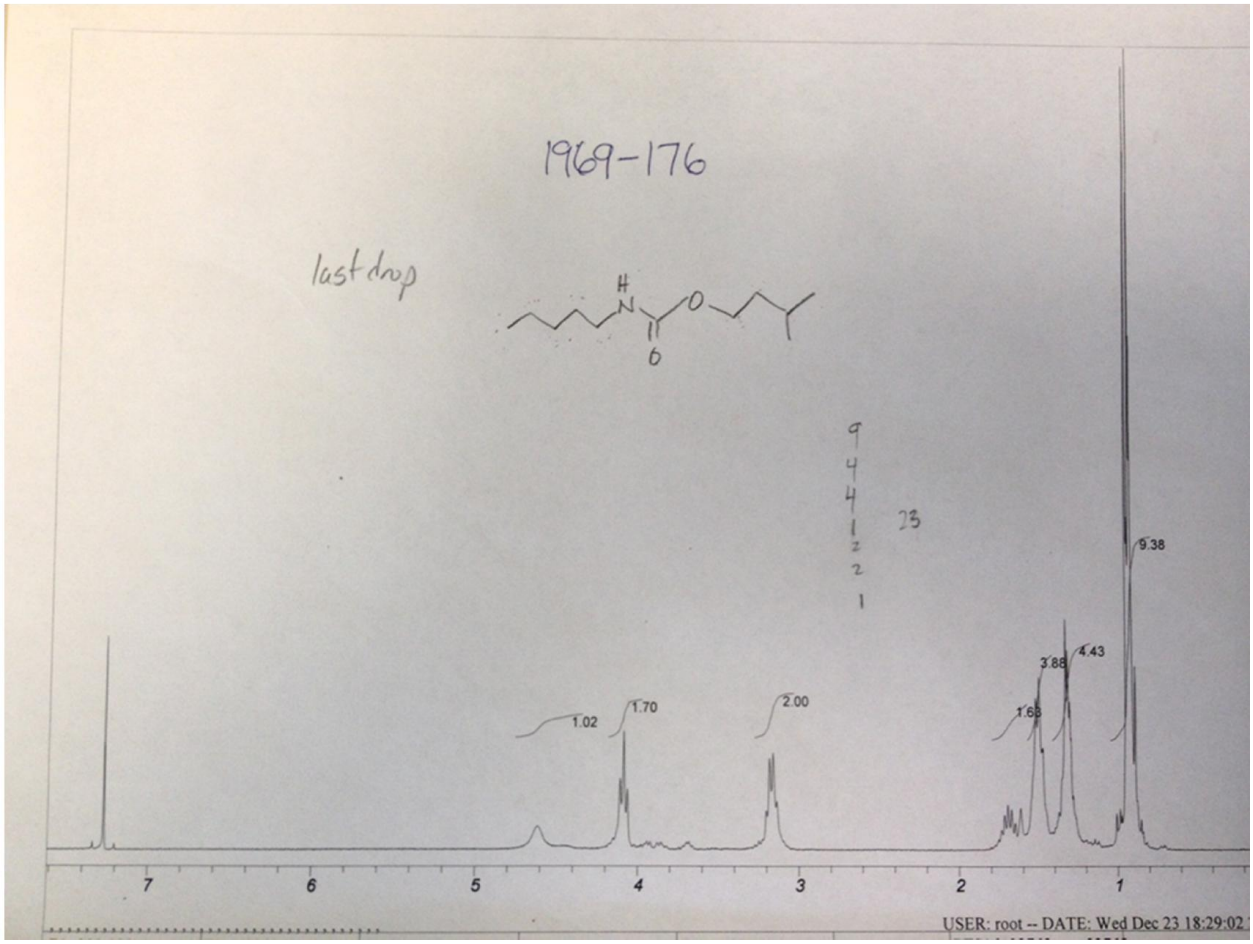
Proton NMR of carbamate (**171**)



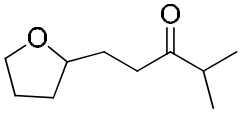
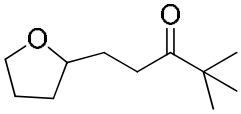
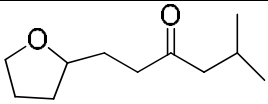
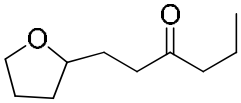
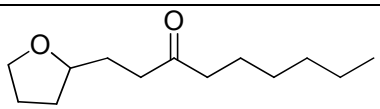
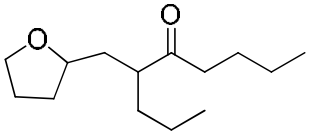
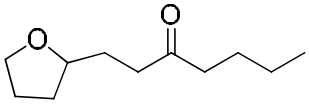
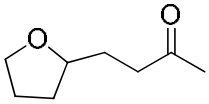
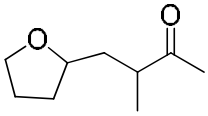
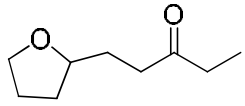
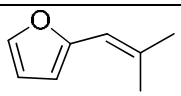
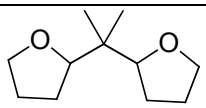
Carbon NMR of carbamate (**171**)

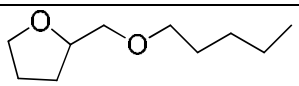
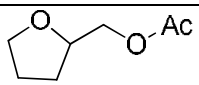
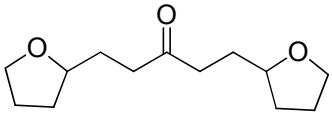
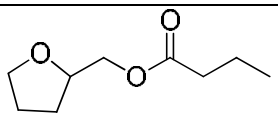
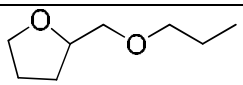
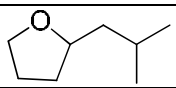
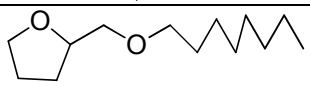
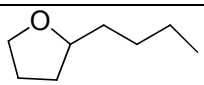
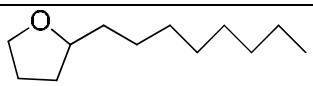
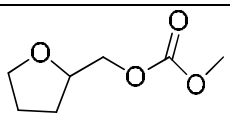
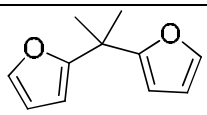
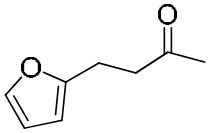


Proton NMR of carbamate (**176**)

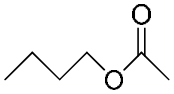
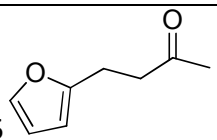
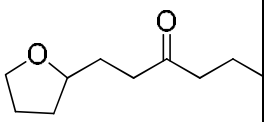
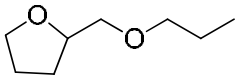
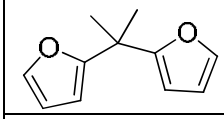
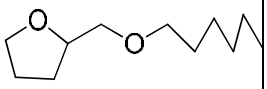
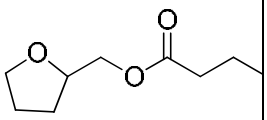


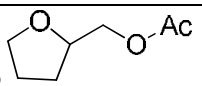
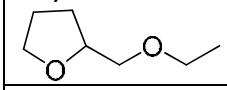
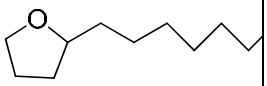
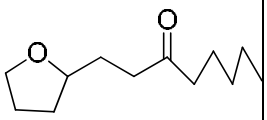
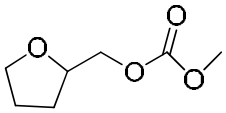
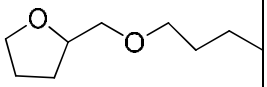
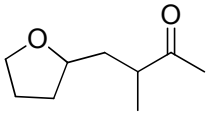
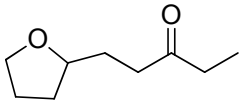
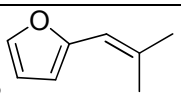
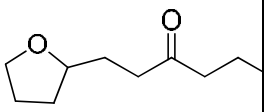
Appendix J Raw Flash Point Data for Furanic Solvents in Triplicate

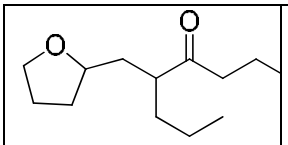
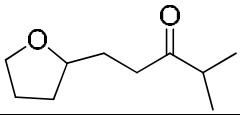
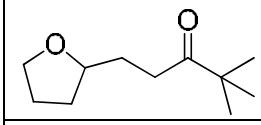
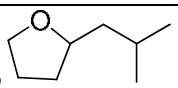
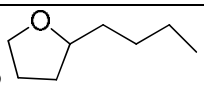
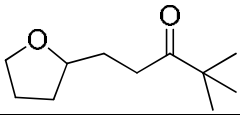
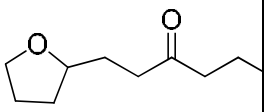
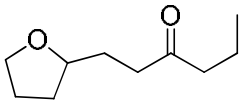
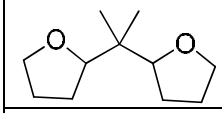
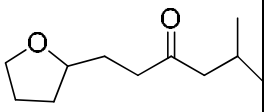
Solvent	Chemical Structure	Formula	Molecular Mass	Flash Point (C)
80		C10H18O2	170	90 90 90
149		C11H20O2	184	97 97 98
82		C11H20O2	184	106 106 107
147		C10H18O2	170	98 98 98
77B		C13H24O2	212	129 130 129
91		C14H26O2	226	122.7 122.7 123.7
143		C11H20O2	184	112.7 111.7 112.7
17		C8H14O2	142	82 83 82
79	  mixture	C9H16O2	156	82.8 81.8 81.8 80.8
85B		C8H10O	122	36.8 33.8 36.8
83B		C11H20O2	184	97.0 98.0 98.1

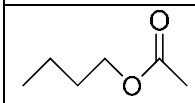
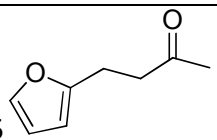
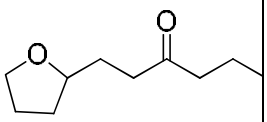
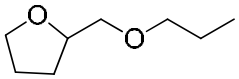
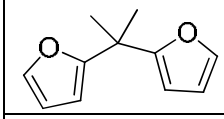
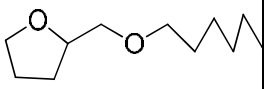
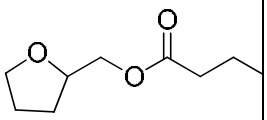
68		C10H20O2	172	84.1 84.0 85.0
35		C7H12O3	144	84.0 83.9 83.9
151		C13H22O3	226	154.9 149.0 155.0 150.0
37		C9H16O3	172	97.9 98.9 96.9
88		C8H16O2	144	53.7 55.7 56.8
115		C8H16O	128	31.8 32
84		C13H26O2	214	118.9 120.9 120.8
105		C8H16O	128	<20 Can't run
123		C12H24O	184	78.0 81.0 83.0
36		C7H12O4	160	100 102 103
30 dimer		C11H12O2	176	76.7 75.7 77.7
45		C8H10O2	138	78.0 80.0 83.0

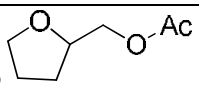
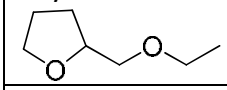
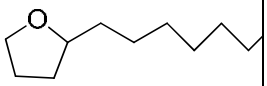
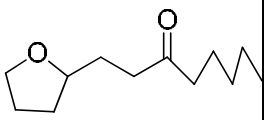
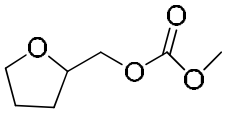
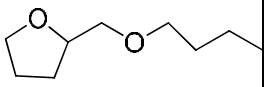
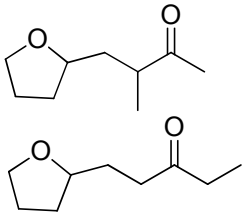
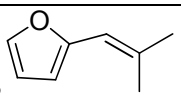
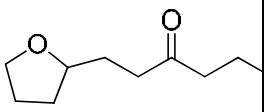
Appendix K Raw Evaporation Data of Furanic and other solvents

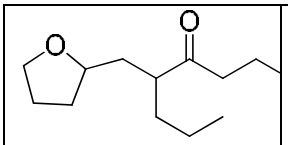
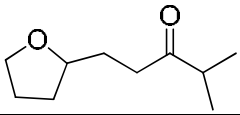
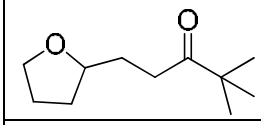
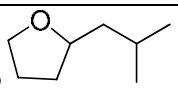
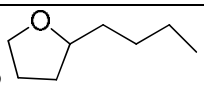
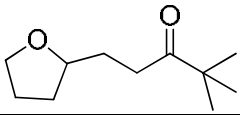
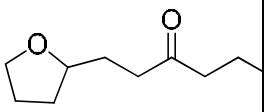
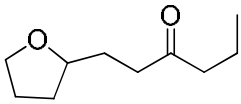
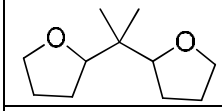
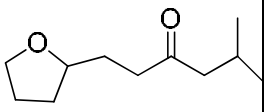
			88 Hours				160 Hours	328 hours	Solvent evap/ 328 h (rate)	Rate normalized to nBuOAc X100
			Solvent remaining	Solvent evaporated	Solvent evaporated/88 h (rate)	Rate normalized to nBuOAc	Solvent remaining	Solvent remaining		
nBuOAc 			1.36	0.64	0.0072	1	0.98	0.43	.00479	100
45 			2	0	0	0	1.99	1.95	.0001	2
151 			2	0	0	0	1.99	1.99	0	0
88 			1.92	0.08	0.0009	0.125	1.83	1.69	.0009	18.7
30 dimer 			1.99	0.01	0.0001	0.013	1.93	1.91	.0002	4.1
84 			2	0	0	0	1.98	1.98	.00006	1.2
37 			2	0	0	0	1.99	1.96	.0001	2

35 			2	0	0	0	1.98	1.95	.0001	2
2-ethyoxymethyltetrahydrofuran 			1.84	0.16	0.0018	0.25	1.67	1.44	.0017	35.5
123 			2	0	0	0	1.96	1.94	.00018	3.8
78 			2	0	0	0	2.03	2.02	0	0
36 			2	0	0	0	1.99	1.98	.00006	1.2
68 			1.99	0.01	0.0001	0.013	1.95	1.93	.0002	4
79   mixture			2	0	0	0	1.97	1.93	.0002	4
85B 			1.8	0.2	0.0022	0.3	1.66	1.41	.0018	3.8
143 			2	0	0	0	2	2.02	0	0
91			2	0	0	0	1.99	1.98	.00006	1.2

										
80 			2	0	0	0	1.99	1.95	.0001	2
149 			2	0	0	0	1.98	1.93	.0002	4
115 			1.7	0.3	0.0034	0.47	1.55	1.25	.0022	46
105 			1.66	0.34	0.0038	0.53	1.48	1.23	.0023	48
149 			1.99	0.01	0.0001	0.013	1.97	1.96	.0001	2
77B 			2	0	0	0	2	1.97	.0001	2
147 			2	0	0	0	2	1.97	.0001	2
83B 			2	0	0	0	2	1.98	.0000 6	1.2
82 			2	0	0	0	2	2.0	0	0

			88 Hours				160 Hours	328 hours	Solvent evap/ 328 h (rate)	Rate normalized to nBuOAc X100
			Solvent remaining	Solvent evaporated	Solvent evaporated/88 h (rate)	Rate normalized to nBuOAc	Solvent remaining	Solvent remaining		
 nBuOAc			1.36	0.64	0.0072	1	0.98	0.43	.00479	100
 45			2	0	0	0	1.99	1.95	.0001	2
151 			2	0	0	0	1.99	1.99	0	0
88 			1.92	0.08	0.0009	0.125	1.83	1.69	.0009	18.7
30 dimer 			1.99	0.01	0.0001	0.013	1.93	1.91	.0002	4.1
84 			2	0	0	0	1.98	1.98	.00006	1.2
37 			2	0	0	0	1.99	1.96	.0001	2

35 			2	0	0	0	1.98	1.95	.0001	2
2-ethyoxymethyltetrahydrofuran 			1.84	0.16	0.0018	0.25	1.67	1.44	.0017	35.5
123 			2	0	0	0	1.96	1.94	.00018	3.8
78 			2	0	0	0	2.03	2.02	0	0
36 			2	0	0	0	1.99	1.98	.00006	1.2
68 			1.99	0.01	0.0001	0.013	1.95	1.93	.0002	4
79  mixture			2	0	0	0	1.97	1.93	.0002	4
85B 			1.8	0.2	0.0022	0.3	1.66	1.41	.0018	3.8
143 			2	0	0	0	2	2.02	0	0
91			2	0	0	0	1.99	1.98	.00006	1.2

										
80 			2	0	0	0	1.99	1.95	.0001	2
149 			2	0	0	0	1.98	1.93	.0002	4
115 			1.7	0.3	0.0034	0.47	1.55	1.25	.0022	46
105 			1.66	0.34	0.0038	0.53	1.48	1.23	.0023	48
149 			1.99	0.01	0.0001	0.013	1.97	1.96	.0001	2
77B 			2	0	0	0	2	1.97	.0001	2
147 			2	0	0	0	2	1.97	.0001	2
83B 			2	0	0	0	2	1.98	.0000 6	1.2
82 			2	0	0	0	2	2.0	0	0

solvent	Remaining after 213 H	Amount evaporated	Solvent evaporated/213 H (rate)	Rate normalized to nBuAc	Rate normalized to nBuAc X 100		
nBuAc	0.73	1.27	0.00596	1	100		
PRF680II	1.78	0.22	0.001	0.168	16.8		
NAVSOLVE	1.86	0.14	0.000657	0.11	11		
NAVHFC	1.81	0.19	0.00089	0.15	15		

Appendix L MIL-PRF-680C, "Performance Specification Degreasing Solvent"

NOT MEASUREMENT SENSITIVE

MIL-PRF-680C
25 March 2010
SUPERSEDING
MIL-PRF-680B
26 October 2006

PERFORMANCE SPECIFICATION

DEGREASING SOLVENT

This specification is approved for use by all Departments and Agencies of the Department of Defense.

1. SCOPE

1.1 Scope. This specification covers degreasing solvent that consists of five types of petroleum distillates. The different types are referred to as "Stoddard solvent", "141 degrees Fahrenheit (°F) (60.6 degrees Celsius (°C)) solvent", "200°F (93.3°C) solvent", "141°F d-limonene blended solvent" and "Low Volatile Organic Compound (VOC) solvent". They are used for degreasing of machine parts in equipment maintenance.

1.2 Classification. Degreasing solvents are of the following types (see 6.2).

Type I	- Low flash point (Stoddard solvent) (Military Symbol SD-1)
Type II	- High flash point (Military Symbol SD-2)
Type III	- Very high flash point (200°F) (Military Symbol SD-3)
Type IV	- High flash point with citrus odor (Military Symbol SD-4)
Type V	- Low VOC solvent (Military Symbol SD-5)

1.2.1 NATO classification:

Type I	- S-752
Type II	- S-753
Type III	- S-760
Type IV	- None
Type V	- None

2. APPLICABLE DOCUMENTS

Beneficial comments (recommendations, additions, deletions) and any pertinent data which may be of use in improving this document should be addressed to: U.S. Army Tank-Automotive Research & Development Center, ATTN: RDTA-EN/ STND/TRANS, Warren, MI 48397-5000, or email dami_standardization@conus.army.mil. Since contact information can change, you may want to verify the currency of this address information using the ASSIST online database at https://assist.daps.dla.mil .

AMSC N/A FSC 6850

2.1 General. The documents listed in this section are specified in sections 3, 4, and 5 of this specification. This section does not include documents cited in other sections of this specification or recommended for additional information or as examples. While every effort has been made to ensure the completeness of this list, document users are cautioned that they must meet all specified requirement documents cited in sections 3, 4, and 5 of this specification, whether or not they are listed.

2.2 Government documents.

2.2.1 Specifications, standards, and handbooks. The following specifications, standards, and handbooks form a part of this document to the extent specified herein. Unless otherwise specified, the issues of these documents are those cited in the solicitation or contract.

STANDARD

FEDERAL

FED-STD-791 - Lubricants, Liquid Fuels and Related Products; Methods of Testing.

(Unless otherwise indicated, copies of the above specifications, standards, and handbooks are available from the Document Automation and Production Service, 700 Robbins Avenue, Building 4D, Philadelphia, PA 19111-5094 or at https://assist.daps.dla.mil.

2.2.2 Other Government documents, drawings and publications. The following other Government documents, drawings, and publications form a part of this document to the extent specified herein. Unless otherwise specified, the issues of these documents are those cited in the solicitation or contract.

ENVIRONMENTAL PROTECTION AGENCY (EPA)

EPA Method 420.1 - Methods for Phenolics, Total Recoverable (Spectrophotometric, Manual 4-AAP with Distillation)
EPA Method 3585 - Method for Waste Dilution for Volatile Organics.
EPA Method 8260B - Method for Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS).

(Application for copies should be addressed to the US EPA Headquarters, 401 M Street SW, mail code 3204, Washington, DC 20460 or at http://www.epa.gov).

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT (SCAQMD)

SCAQMD Method 313 - Determination of Volatile Organic Compounds (VOC) by Gas Chromatography/Mass Spectrometry (GC/MS).

(Application for copies should be addressed to the South Coast Air Quality Management District, 21865 Copley Drive, Diamond Bar, CA 91765 or at http://www.aqmd.gov)

2.3 Non-Government publications. The following document forms a part of this document to the extent specified herein. Unless otherwise specified, the issues of the documents which are DoD adopted are those listed in the issue of the DoDISS cited in the solicitation.

Unless otherwise specified, the issues of these documents are those cited in the solicitation or contract.

AMERICAN SOCIETY FOR QUALITY (ASQ)

Z1.4	- Sampling Procedures and Tables for Inspection by Attributes (DoD adopted).

(Application for copies should be addressed to the American Society for Quality, P.O. Box 3005, Milwaukee, WI 53201-3005 or at http://www.asq.org).

ASTM INTERNATIONAL

D 56	- Standard Test Method for Flash Point by Tag Closed Cup Tester
D 86	- Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure
D 130	- Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test
D 156	- Standard Test Method for Saybolt Color of Petroleum Products (Saybolt Chromometer Method)
D 235	- Standard Test Method for Mineral Spirits (Petroleum Spirits) (Hydrocarbon Dry-Cleaning Solvent)
D 847	- Standard Test Method for Acidity of Benzene, Toluene, Xylenes, Solvent Naphthas, and Similar Industrial Aromatic Hydrocarbons
D 1133	- Standard Test Method for Kauri-Butanol Value of Hydrocarbon Solvents
D 1296	- Standard Test Method for Odor of Volatile Solvents and Diluents
D 1298	- Standard Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
D 1353	- Standard Test Method for Nonvolatile Matter in Volatile Solvents for Use in Paint, Varnish, Lacquer, and Related Products
D 2879	- Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope
D 3257	- Standard Test Method for Aromatics in Mineral Spirits by Gas Chromatography
D 4057	- Standard Practice for Manual Sampling of Petroleum and Petroleum Products
D 4177	- Standard Practice for Automatic Sampling of Petroleum and Petroleum Products

F 483	- Standard Practice for Total Immersion Corrosion Test for Aircraft Maintenance Chemicals
F 945	- Standard Test Method for Stress-Corrosion of Titanium Alloys by Aircraft Engine Cleaning Materials
F 1110	- Standard Test Method for Sandwich Corrosion Test

(Application for copies should be addressed to ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959 or at http://www.astm.org).

SOCIETY OF AUTOMOTIVE ENGINEERS (SAE) INTERNATIONAL

AMS-QQ-A-250	- Aluminum and Aluminum Alloy, Plate and Sheet, General Specification for (DoD adopted).
AMS 2470	- Anodic Treatment of Aluminum Alloys Chrome Acid Process (DoD adopted).
AMS M 3171	- Magnesium Alloy, Processes for Pretreatment and Prevention of Corrosion on (DoD adopted).
AMS 4377	- Magnesium Alloy, Sheet and Plate 3.0A1-1.0Zn-0.20Mn (AZ31B-H24) Cold Rolled, Partially Annealed
AMS 4911	- Titanium Alloy Sheet, Strip, and Plate, 6AI-4V Annealed
AMS 5046	- Carbon Steel Sheet, Strip, and Plate, (SAE 1020 and 1025) Annealed

(Application for copies should be addressed to 400 Commonwealth Drive, Warrendale, PA 15096-0001 or at http://www.sae.org).

2.4 Order of precedence. Unless otherwise noted herein or in contact, in the event of a conflict between the text of this specification and the references cited herein, the text of this specification takes precedence. Nothing in this specification, however, supersedes applicable laws and regulations unless a specific exemption has been obtained.

3. REQUIREMENTS

3.1 Qualification. Solvents furnished under this specification shall be products that are authorized by the qualifying activity for listing on applicable qualified products list before contract award (see 4.2 and 6.3). Any change in the formulation of a qualified product will necessitate its requalification.

3.2 Materials. The hydrocarbon solvent shall be a virgin grade or recycled solvent derived from petroleum distillates, fraction from reclaiming and re-refining processes, or a mixture of these fractions. The d-limonene and hydrocarbon blended solvent is permitted as a Type IV solvent. The EPA exempt materials and hydrocarbon blended solvent is also permitted as a Type V solvent. The resultant solvent must be produced in such a manner as is necessary to meet the specified requirements.

3.3 Appearance. The solvent shall be clear and free from suspended matter and undissolved water when observed at a temperature between 60.1 and 78.1°F (15.6 and 25.6 °C).

3.4 Toxicity. The solvent shall have no adverse effects on human health when used as intended (see 6.1 and 6.6).

3.5 Carcinogenicity. The solvent shall contain no chemicals listed as carcinogens (see 6.7). Any carcinogenic components in the solvent in a concentration of 0.1 percent (%) or greater by weight (wt) or volume (vol) will be regarded as the presence of a carcinogen in the solvent.

3.6 Hazardous Air Pollutants. The solvent shall contain no chemicals listed as Hazardous Air Pollutants (HAPs) (see 6.7). Any HAP components in the solvent in a concentration of 1.0 percent (%) or greater by weight (wt) or volume (vol) will be regarded as the presence of a HAP in the solvent. The product containing less than 1 % of HAP shall be considered as a HAP free solvent. For carcinogenic HAPs see 3.5.

3.7 Physical and chemical property requirements. The solvents shall conform to the physical and chemical requirements in Table I when tested as specified in Table II.

TABLE I. Degreasing solvent properties.

Characteristics	Type I	Type II	Type III	Type IV	Type V
Flash point (pt), °C (°F)	38-60	61–92	93-116	61–92	61-92
	(100-140)	(141-198)	(200-241)	(141-198)	(141-198)
Distillation, °C:					
Initial boiling pt., minimum (min)	149	177	220	171	177
Dry point, °C, maximum (max)	208	212	300	240	212
Kauri-Butanol value	27 to 45	27 to 45	27 to 45	27 to 45	NR 4/
Aromatic content, vol %, max	1	1	1	1	1
Total phenol content, parts per million (ppm), max	0.5	0.5	0.5	0.5	0.5
Dichlorobenzene, milligrams per liter (mg/L), max	0.5	0.5	0.5	0.5	0.5
Benzene, mg/L, max	0.5	0.5	0.5	0.5	0.5
Tetrachloroethylene, mg/L, max	0.7	0.7	0.7	0.7	0.7
Trichloroethylene, mg/L, max	0.5	0.5	0.5	0.5	0.5
Apparent specific gravity, 60/60°F	0.754 to 0.820	0.754 to 0.820	0.754 to 0.840	0.754 to 0.820	0.754 to 0.980
Total chlorine content (ppm), Max	100	100	100	100	100
Non-volatile residue, (mg/100 mL), max	8	8	8	8	8
Color, min	25	25	25	25	25
Odor 1/	Low & non-residual	Low & non-residual	Low & non-residual	Citrus & non-residual	Low & non-residual
Corrosion, copper, max 2/	1b	1b	1b	1b	1b
Sandwich corrosion, max	1	1	1	1	1
Total immersion	Pass	Pass	Pass	Pass	Pass

corrosion 3/					
Titanium stress corrosion	No cracking	No cracking	No cracking	No cracking	No cracking
Acidity	Neutral	Neutral	Neutral	Neutral	Neutral
Doctor test	Negative	Negative	Negative	Negative	Negative
Vapor pressure, millimeters of Mercury (mm Hg) @ 20ºC, max	7.0	2.0	0.4	2.0	1.0
Soil cleaning test, %, min	85	85	85	88	85
VOC, g/l, max	NR	NR	NR	NR	25

1/ Samples of MIL-PRF-680C, Type III, having satisfactory low odor characteristics shall be used as reference standards.
2/ Test for three hours at 100 °C (212ºF).
3/ See 4.4.2
4/ Not required

4. VERIFICATION

4.1 Classification of inspections. The inspection requirements specified herein are classified as follows:

a. Qualification inspection (see 4.2)
b. Conformance inspection (see 4.3).

4.1.1 Inspection conditions. Unless otherwise specified, all inspections shall be performed in accordance the test conditions specified in 4.4.

4.2 Qualification inspection. The qualification inspection shall consist of all tests specified herein. Failure of any test shall be cause for rejection.

4.3 Conformance inspection. Conformance inspection shall consist of a sample for tests (see 4.3.2), samples for examination of filled containers (see 4.3.3), and the tests specified in Table II except for sandwich corrosion, total immersion corrosion, and titanium stress corrosion.

4.3.1 Lot. A lot shall consist of solvents from one batch or tank offered for delivery at one time. If material cannot be identified by batch or lot, a lot shall consist of not more than 10 000 gallons offered for delivery at one time (see 6.2).

4.3.2 Sampling for tests. Sampling of a lot for test purposes shall be in accordance with ASTM D 4057 or D 4177.

4.3.3 Sample for examination of filled containers. A random sample of filled unit containers and a sample of shipping containers fully prepared for delivery shall be selected from each lot of solvent in accordance with ASQ Z1.4.

4.4 Methods of inspection.

4.4.1 Tests. Tests shall be performed in accordance with the applicable methods specified in Table II and 4.4.2 through 4.4.3 to determine conformance with the requirements specified in 3.6.

TABLE II. Test methods for inspections.

Characteristic	ASTM methods	Other methods
Flash point	D 56	
Distillation	D 86	
Kauri-Butanol value	D 1133	
Aromatic content	D 3257	
Apparent specific gravity	D 1298	
Color	D 156	
Odor	D 1296	
Non-volatile residue	D 1353	
Copper corrosion	D 130	
Sandwich corrosion	F 1110	
Total immersion corrosion	F 483	
Titanium stress corrosion	F 945	
Acidity	D 847	
Doctor test	D 235	
Vapor pressure	D 2879	
Total phenol content		EPA 420.1
Total dichlorobenzene content		EPA 3585 and 8260B
Total benzene content		EPA 3585, 8260B
Total trichloroethylene		EPA 3585, 8260B
Total tetrachloroethylene		EPA 3585, 8260B
Soil cleaning test		FED-STD-791 Method,7502
VOC test		SCAQMD 313

4.4.2 Total immersion corrosion. The solvents shall not show any indication of staining, etching, pitting, or localized, or cause weight change to an average of three (3) test panels greater than that shown in Table III.

TABLE III. Alloy and maximum average weight loss.

Alloy	Average of 3 panels wt. loss, max milligrams per square centimeter (mg/cm^2/168 hrs)
Magnesium (AZ 31B-H24) AMS 4377 surface treated in accordance with AMS-M-3171, Type III	0.50
Aluminum, AMS-QQ-A-250, T3 surface, treatment in accordance with AMS 2470	0.15
Titanium, AMS 4911, 6AL-4V	0.10
Steel, AMS 5046, Grade 1020	0.25

4.4.3 Soil cleaning test. The test shall be conducted according to the solvent soil test method described in FED-STD-791D, Method 7502. The ultrasonic cleaner mentioned in this test method should be selected using two chemical materials (i.e., toluene and water). The cleaning power of water is found zero percent while toluene is 92-96 %. If the test results obtain the outside of these values when test with these chemical materials, the ultrasonic cleaner is not applicable to be used as a test apparatus mentioned in FED-STD-791D, Method 7502. The acceptable limit for each type of solvent is defined in Table I.

4.4.4 Total chlorine content. The total chlorine content of the solvent shall be determined by a gas chromatographic method, microcoulometric or by the use of a portable test kit for the quantitative analysis of chlorine (see 6.6). Nonconformance to Table I shall constitute failure of this test.

5. PACKAGING

5.1 Packaging. For acquisition purpose, the packaging requirements shall be as specified in the contract or order (see 6.2). When actual packaging of materiel is to be performed by DoD personnel, these personnel need to contact the responsible packaging activity to ascertain requisite packaging requirements. Packaging requirements are maintained by the Inventory Control Point's packaging activity with the Military Department or Defense Agency, or within the Military Department's System Command. Packaging data retrieval is available from the managing Military Department's or Defense Agency's automated packaging files, CD-ROM products, or by contracting the responsible packaging activity.

6. NOTES

(This section contains information of a general or explanatory nature that may be helpful, but is not mandatory.)

6.1 Intended use. These solvents are hydrocarbon-based solvents and are used as degreasers and cleaners for painted or unpainted metal parts. However, the compatibility between existing paints and solvents should be verified prior to use. It is recommended that these solvents should be used with an appropriate recirculated parts washer. No other commercial specification is available to cover these military applications.

6.1.1 Type I. Type I (Stoddard solvent) is intended for use where a low odor solvent with fast drying characteristics is desired. This solvent is currently defined as a flammable material due to its low flash point. It is recommended that the alternative solvents for Type I are Types II, III and IV. When Type I solvent is used indoors, ventilation should be sufficient to prevent the accumulation of vapors above allowable limits.

6.1.2 Type II. Type II (low odor with high flash point solvent) is intended for use where a solvent with a higher flash point is desired. It is recommended over Type I for safety and regulatory reasons. When Type II solvent is used indoors, ventilation should be sufficient to prevent the accumulation of vapors above allowable exposure limits.

6.1.3 Type III. Type III (low odor with very high flash point solvent) is intended to be used where confined atmospheric conditions require a cleaner that conforms to the Federal Government's directives for reduced hazardous materials.

6.1.4 Type IV. Type IV (citrus odor with high flash point) is intended for use where a solvent with a high flash point and strong solvency is desired. This solvent is formulated with petroleum based hydrocarbon solvents and d-limonene additive. When Type IV solvent is used indoors, ventilation should be sufficient to prevent the accumulation of vapors above allowable exposure limits.

6.1.5 Type V. Type V (Low VOC solvent) is intended for use where solvent confined atmospheric conditions require a cleaner that conforms to the Federal and Local Government's directives for reducing VOC of solvent.

6.2 Acquisition requirements. Acquisition documents must specify the following:

a. Title, number and date of this specification.
b. Type and quantity (see 1.2. and 4.3.1).
c. Issue of ASSIST to be cited in the solicitation, and if required, the specific issue of individual documents referenced (see 2.2.1 and 2.3).
d. Packaging requirements (see 5.1)

6.3 Qualification. With respect to products requiring qualification, awards will be made only for products which are at the time of award of contract, qualified for inclusion in Qualified Product List QPL No. 680 whether or not such products have actually been so listed by that date. The attention of the contractors is called to these requirements, and manufacturers are urged to arrange to have the products that they propose to offer to the Federal Government tested for qualification in order that they may be eligible to be awarded contracts or purchase orders for the products covered by this specification.

6.3.1 Specification preparing activity. Information and instructions regarding qualification inspection under this specification may be obtained from the Department of the Army, TACOM-TARDEC, ATTN: AMSRD-TAR-E/268, 6501 E. 11 Mile Road, Warren, MI 48397-5000.

6.4 International standardization. Certain provisions of this specification are the subject of international standardization agreement (NATO STANAG 1135, ANNEX C). When amendment, revision, or cancellation of this specification is proposed which would affect or violate the international agreement concerned, the preparing activity will take appropriate reconciliation action through international channels, including departmental standardization offices, if required.

6.5 Disposal actions. Disposal of this product should be in accordance with local, state and Federal regulations. Care should be taken to avoid mixing used MIL-PRF-680 with other waste materials, especially those containing halogenated solvents. However, these solvents can be recycled instead of disposal.

6.6 Material Safety Data Sheets. Contracting officers will identify those activities requiring copies of completed Material Safety Data Sheets (MSDSs) prepared in accordance with FED-STD-313. The pertinent Government mailing addresses for submission of data are listed in FED-STD-313; and 29 CFR 1910.1200 requires that the MSDS for each hazardous chemical used in an operation must be readily available to personnel using the material. Contracting officers will identify the activities requiring copies of the MSDS (see 3.4 and 4.4.4).

6.7 Definitions.

6.7.1 Carcinogens. The Occupational Safety and Health Administration (OSHA) definition of carcinogens are those chemicals / processes appearing in lists 1, 2A, and 2B of the International Agency for Research on Cancer (IARC) [1/]; substances known to be carcinogenic and occupational exposures associated with a technological process known to be carcinogenic by the National Toxicology Program (NTP) Report on Carcinogens (latest annual report) [2/]; and OSHA regulated carcinogens.

6.7.2. Hazardous Air Pollutant (HAP). HAP is defined as any substance listed under Section 112 of the Clean Air Act or its modifications. The text of the Clean Air Act, listed pollutants and modifications are kept by the Environmental Protection Agency (EPA) and are accessible through the website: http://www.epa.gov

1/ Copies of these volumes may be found in medical libraries or through the World Health Organization, 1211 Geneva 27, Switzerland.

2/ Copies may be obtained from the Public Health Service, National Toxicology Program, Public Information Office, P.O. Box 12233, MD B2-04, Research Triangle Park, NC 27709 or at http://ntp-server.niehs.nih.gov

6.8 Subject term (key word) listing.

d-limonene
d-limonene/hydrocarbon blended solvent (type IV)
Mineral Spirits
Naphtha
Petroleum Spirits (USA)
Stoddard Solvent (type I)
141 F Solvent (type II)
200 F Solvent (type III)
Low VOC Solvent (type V)

6.9 Changes from previous issues. Marginal notations are not used in this revision to identify changes with respect to the previous issue due to the extensiveness of the changes.

Custodians:
Army - AT
Air Force - 68
Navy – AS

Preparing Activity:
Army - AT

(Project 6850-2010-007)

Review Activities:
Army - AV, EA, MD1, MI, MR, SM
Air Force - 03, 11, 50
Navy - MC, SH
DLA - GS, GS3, DP
DTRA - DS
GSA/GSS - FAS
MISC – MP

NOTE: The activities listed above were interested in this document as of the date of this document. Since organizations and responsibilities can change, you should verify the currency of the information above using the ASSIST Online database at https://assist.daps.dla.mil.

Appendix M Product Information for Mobilgrease33, a MIL-PRF-23827 grease

Mobilgrease 33

Synthetic Aviation Grease

Product Description

Mobilgrease 33 is a high-performance lithium-complex grease designed for general-purpose aircraft use. Its consistency is between the NLGI grades 1 and 2. Mobilgrease 33 utilizes a 100% polyalphaolefin base oil and premium additives which ensure outstanding lubrication performance over a wide temperature range and operating conditions.

Features and Benefits

The lithium complex thickener system provides excellent structural stability and resistance to water wash-out. Polyalphaolefin base oil is used in Mobilgrease 33 because of its exceptional thermal/oxidative resistance potential, low volatility, and superb low-temperature capability, without the potential vulnerability of an ester base oil to degradation from reaction with water. The synthetic polyalphaolefin base oil offers excellent low-temperature mobility/pumpability and very low starting and running torque values. In addition, the state-of-the art additive system in Mobilgrease 33 provides superior rust and wear protection and load-carrying capacity compared to aviation greases that meet the minimum requirements of the MIL-PRF-23827 specification.

Features	Mobilgrease 33, with its unique features, provides the following advantages and potential benefits: Advantages and Potential Benefits
High viscosity index polyalphaolefin basestock	Very wide operating temperature range - outstanding high and low temperature performance.
Good storage stability	Excellent lubricant film protection at high temperatures
Resistance to degradation by water (hydrolysis)	Grease structure integrity maintained - low oil separation
Low volatility	Exceptional resistance to thermal and oxidative degradation Long grease and lubricated part service life
Extreme-pressure characteristics	No risk of corrosion induced by acidic base oil degradation products
High resistance to water washout	Little vulnerability to significant base oil loss by evaporation in service
	Excellent protection against wear, corrosion, and rusting Excellent bearing and component protection
	Prevention of excessive wear, even under shock load
	Excellent grease performance in adverse weather and other water-exposure conditions

Applications

Mobilgrease 33 is a true multipurpose aviation grease intended for use in highly loaded anti-friction bearings, gears, and actuators as well as instruments, high speed bearings (though not recommended for wheel bearings), and general airframe lubrication, over operating temperatures from -100°F to 250°F (-73°C to 121 °C). It can be used in all applications for which the aircraft manufacturer specifies U.S. Military Specification MIL-PRF-23827, Type I (Grease, Aircraft and Instrument, Gear and Actuator Screw, Grease thickened with metallic soap), Boeing BMS 3-33B (Grease, Aircraft, General Purpose), and Airbus AIMS09-06-002/SAE AMS3052 (Grease, General Purpose, Airframe, Low Temperature Range, Lithium Thickened). Mobilgrease 33 is listed in the Qualified Products List of Airbus, Boeing, and the U.S. Military for these specifications. The NATO Code Number for Mobilgrease 33 is G-354.

Specifications and Approvals

Mobilgrease 33	Is Approved Against	Meets
Airbus AIMS09-06-002	X	
Boeing BMS 3-33B Type 1	X	
MIL-PRF-23827C, Amendment 2, Type I	X	
NATO G-354	X	
SAE AMS3052	X	

Typical Properties

Airbus

Boeing BMS MIL-PRF- AIMS09-06- „ ■

Test Methods3-33B 23827 Type I 002/ SAE $_3 3^5 (\cdot|)^{i\ greaSe}$

RequirementsRequirementsAMS3052

Requirements

NLGI Grade				1 1/2
Thickener Type	Lithium Complex	Metallic Soap	Lithium Complex	Lithium Complex
Color	Visual Green to Blue		Blue Green	Blue Green
Structure/Consistency	Smooth, free Smooth, free from lumps		Smooth, free from lumps and visual impurities	Pass
Odor	No rancid, Olfactory perfume, or alcohol odor	No rancid, perfume, or alcohol odor		Pass
Viscosity of Base Oil, cSt	ASTM D 445			
at 40 °C				12.5
at 100 °C				3.2
Dropping Point, °C (°F)	ASTM D 2265 205 (401) min 165 (329) min 200 (392) min 255 (491)			
Low Temp. Torque at -73°C (-100°F), Nm	DEF STAN 05-50 Part 62, ASTMD1478			
Starting	0.75 max	1.00 max	0.75 max	0.52
Running, after 1 Hr	0.10 max	0.10 max	0.10 max	0.06
Low Temp. Torque with 10% water at -73°C (-100°F), Nm	DEF STAN 05-50 Part 62, ASTMD1478			
Starting			1.00 max	0.67
Running, after 1 Hr			0.20 max	0.09
	DEF STAN			

Penetration at 25°C (77°F), mm/10	**05-50 Part 63, ASTMD217**			
Unworked		**200 min**		**285**
60 Strokes Worked	**265-315**	**270-310**	**265-315**	**292**
100,000 Strokes Worked	**FTM 313 265-385**	**270-375**	**Report**	**330**
Penetration, 100,000 Strokes Worked with 10% water, mm/10	**DEF STAN 05-50 Part 63, ASTMD217**		**Report**	**330**
Oil Separation, 30 Hrs at 100°C, wt %	**ASTM D 6184 8 max**	**5 max**	**6 m ax**	**4**
Evaporation Loss, 22 Hrs at 100°C, wt %	**ASTM D 2595**	**2 m ax**		**1**
Evaporation Loss, 500 Hrs at 121°C, wt %	**ASTM D 2595 10 max**	**10 max 8.7**		

Copper Strip Corrosion, 24 Hrs at 100°C ASTM D 4048 1b max 1b max 1b max 1b

AMS4640 Al/Ni Bronze Corrosion, 24 Hrs at 100°C	No ASTM D 4048 appearance change		No appearance change	Pass
Four Ball Wear, scar dia., 1200rpm/40kg/1hr/75°C, mm	ASTM D 2266 0.9 max		0.90 max	0.4
Load Wear index, kgf	ASTM D 2596 60 min	30 min	60 min	110
Weld Load, kgf	ASTM D 2596		280 min	700
Timken OK Load, lbf	ASTM D 2509 50 min			55
Rust Protection, 48 Hrs at 125°F, >1 mm dia Spots	ASTMD1743	0 in 2 out of 3 bearings		0,0,0
SKF EMCOR Rust, 3% NaCl, rating	ASTM D 6138 0, 0		0, 0	0,0
Water Washout, 1 Hr at 38°C (100 °F), wt %	ASTMD1264	20 max		3
Water Washout, 1 Hr at 79°C (174 °F), wt %	ASTM D 1264 7.5 max		10 max	6
High Temperature Performance, Hrs at 121°C	ASTM D 3336 1,000 min	1,000 min	1,000 min	2,200+
Oxidation Stability, pressure drop in kPa	ASTM D 942			
100 Hrs at 99°C	70 max	70 max	50 max	11
500 Hrs at 99°C	105 max	105 max	105 max	25
Fretting Wear, mg loss	ASTM D 4170 0.9 max		Report	0.6
Dynamic Bearing Life, No of cycles	BMS 3-33-8.2 30,000 min			Pass
Navy Gear Wear Test, mg loss/1000 cycles	FTM 335			
2.3 kg load		2.5 max		1.1
4.5 kg load		3.5 max		1.6
Dirt Count, Particles/mL	FTM 3005			
25-74 Micron Size	1000 max	1000 max		0
75 Micron or Larger	0	0		0
Storage SteMhy, 6 months rrt not;, 3457 mm/10				
Unworked	ASTM D 217 200 min	200 min		289
60x worked	ASTMD217			288
60x worked, Difference from Unworked	ASTMD217 ±30			-1
Difference from Original	ASTMD217	±30	±30	2
Elastomer Compatibility, 168 Hrs at 70°C, % vol change	FTM 3603			
Nitrile (NBR-L, AMS3217/2)	-2.0 to +25.0		-2.0 to +25.0	+12.6
Thermoplastic Compatibility, 70 Hrs at 100°C, % vol change	ASTM D 4289			
Hytrel 6356 + 0.5% carbon black	± 5.0			3.4
Delrin 100 AF (ASTM D 4181)	± 2.0			+0.1
PTFE (Teflon) (AMS 3652)	± 2.0			+0.1

Nylatron GS	**± 1.0**	**-0.5**

(1) Values may vary within modest ranges

Health and Safety

Based on available toxicological information, this product is not expected to produce adverse effects on health when used and handled properly. Information on use and handling, as well as health and safety information, can be found in the Material Safety Data Sheet (MSDS), which can be obtained from your local distributor or via the Internet on http://www.exxonmobil.com/lubes.

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4-2013

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http://www.exxonmobil.com

Due to continual product research and development, the information contained herein is subject to change without notification. Typical Properties may vary slightly.

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Appendix N Material Safety Data Sheet for NavHFC

ECOLINK.

Safety Data Sheet (SDS)

OSHA HazCom Standard 29 CFR 1910.1200(g) and GHS Rev 03.

Reviewed on 05/07/2015

1 Identification

· **Product identifier**

· **Trade name: NAVHFC**

· **Relevant identified uses of the substance or mixture and uses advised against**
Hydraulic Fluid Cleaner

· **Product description**

Product Name	Part No.	Packaging
NAVHFC	241-55	55 Gal Drum
NAVHFC	241-15	15 Gal Drum
NAVHFC	241-5	5 Gal Pail
NAVHFC	241-1	4 x 1 Gal Case

· **Application of the substance / the mixture** Hydraulic Fluid Cleaner

· **Details of the supplier of the safety data sheet**

· **Manufacturer/Supplier:**
Ecolink
2177 Flintstone Drive, Ste. A
Tucker, GA 30084
www.ecolink.com
800-886-8240 or 770-621-8240 (8-5 EST)
email: info@ecolink.com

· **Emergency telephone number:**
Inside the U.S.: 800-535-5053 (INFOTRAC, 24 HOURS)
Outside the U.S.: 352-323-3500 (INFOTRAC, 24 HOURS)

2 Hazard(s) identification

· **Classification of the substance or mixture**

GHS08 Health hazard

Asp. Tox. 1 H304 May be fatal if swallowed and enters airways.

GHS07

Skin Irrit. 2 H315 Causes skin irritation.
Skin Sens. 1 H317 May cause an allergic skin reaction.
STOT SE 3 H336 May cause drowsiness or dizziness.

Flam. Liq. 4 H227 Combustible liquid.

· **Label elements**

· **GHS label elements**
The product is classified and labeled according to the Globally Harmonized System (GHS).

· **Hazard pictograms**

GHS07 GHS08

(Contd. on page 2)

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COLINK.

Safety Data Sheet (SDS)

OSHA HazCom Standard 29 CFR 1910.1200(g) and GHS Rev 03.

Reviewed on 05/07/2015

Trade name: NAVHFC

· **Signal word** Danger

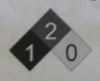
· **Hazard-determining components of labeling:**
Distillates (petroleum), hydrotreated light
d-limonene
Isoparaffinic Hydrocarbon

· **Hazard statements**
Combustible liquid.
Causes skin irritation.
May cause an allergic skin reaction.
May cause drowsiness or dizziness.
May be fatal if swallowed and enters airways.

· **Precautionary statements**
Keep away from flames and hot surfaces. – No smoking.
Avoid breathing dust/fume/gas/mist/vapors/spray.
Use only outdoors or in a well-ventilated area.
Wear protective gloves / eye protection / face protection.
Wear protective gloves.
Wash thoroughly after handling.
Contaminated work clothing must not be allowed out of the workplace.
If swallowed: Immediately call a poison center/doctor.
Specific treatment (see supplementary first aid instructions on this Safety Data Sheet).
IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
Call a poison center/doctor if you feel unwell.
Wash contaminated clothing before reuse.
If skin irritation occurs: Get medical advice/attention.
If skin irritation or rash occurs: Get medical advice/attention.
Do NOT induce vomiting.
In case of fire: Use for extinction: CO2, powder or water spray.
If on skin: Wash with plenty of water.
Take off contaminated clothing and wash it before reuse.
Store locked up.
Store in a well-ventilated place. Keep container tightly closed.
Store in a well-ventilated place. Keep cool.
Dispose of contents1container in accordance with local/regional/national/international regulations.

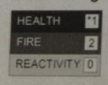
· **Classification system:** NFPA1HMIS Definitions: 0-Least, 1-Slight, 2-Moderate, 3-High, 4-Extreme

· **NFPA ratings (scale 0 - 4)**



Health = 1
Fire = 2
Reactivity = 0

· **HMIS-ratings (scale 0 - 4)**



Health = *1
Fire = 2
Reactivity = 0

· **Hazard(s) not otherwise classified (HNOC):** None known

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(Contd. on page 3)

COLINK.

Safety Data Sheet (SDS)

OSHA HazCom Standard 29 CFR 1910.1200(g) and GHS Rev 03.

Reviewed on 05/07/2015

Trade name: NAVHFC

3 Composition/information on ingredients

· **Chemical characterization: Mixtures**
· **Description:** Mixture of substances listed below with nonhazardous additions.
· **Dangerous Components:**

CAS: 64742-47-8	Distillates (petroleum), hydrotreated light Asp. Tox. 1, H304; Aquatic Chronic 2, H411; Skin Irrit. 2, H315; STOT SE 3, H336; Flam. Liq. 4, H227	25-50%
CAS: 64742-48-9	Isoparaffinic Hydrocarbon Asp. Tox. 1, H304; Flam. Liq. 4, H227	25-50%
CAS: 5989-27-5 RTECS: GW 6360000	d-limonene Aquatic Acute 1, H400; Aquatic Chronic 1, H410; Skin Irrit. 2, H315; Skin Sens. 1, H317; Flam. Liq. 4, H227	≤ 2.5%

4 First-aid measures

· **Description of first aid measures**
· **After inhalation:**
In case of symptoms arising from inhalation of fumes, mists or vapor: Remove casualty to a quiet and well ventilated place if safe to do so. If the casualty is unconscious and not breathing, ensure that there is no obstruction to air passage ways and give artificial respiration by trained personnel. If necessary, give external cardiac massage and obtain immediate medical assistance. If the casualty is breathing, place in a recovery position and administer oxygen by trained personnel if necessary. Seek medical attention if breathing remains difficult.
In case of unconsciousness, place patient securely on side position for transportation.
· **After skin contact:**
Immediately wash with water and soap and rinse thoroughly.
If skin irritation occurs, consult a doctor.
· **After eye contact:**
Rinse opened eye for several minutes under running water. If symptoms persist, consult a doctor.
· **After swallowing:**
Rinse out mouth and then drink plenty of water.
Do not induce vomiting.
If vomiting does occur, repeat fluid administration
If vomiting occurs, the head should be kept low so that the vomit does not enter the lungs (aspiration).
Once the vomiting ceases, place the person in the recovery position with the legs slightly raised.
If symptoms develop and1or persist, seek medical attention.
· **Information for doctor:**
· **Most important symptoms and effects, both acute and delayed:**
No further relevant information available.
· **Indication of any immediate medical attention and special treatment needed**
No further relevant information available.

5 Fire-fighting measures

· **Extinguishing media**
· **Suitable extinguishing agents:** Regular foam, water fog, carbon dioxide or dry chemical. Class B.

(Contd. on page 4)

COLINK.

Safety Data Sheet (SDS)

OSHA HazCom Standard 29 CFR 1910.1200(g) and GHS Rev 03.

Reviewed on 05/07/2015

Trade name: NAVHFC

· **Special hazards arising from the substance or mixture**
Combustible liquid. Vapors can travel to a source of ignition and flash back.
Explosive mixtures may occur at temperatures at or above flashpoint.
If incinerated product will release the following toxic fumes: Carbon Oxides, and unburnt hydrocarbon particulate.
· **Advice for firefighters** Use water spray to cool unopened containers.
· **Protective equipment:**
As in any fire, wear self-contained breathing apparatus pressure-demand (NIOSH approved or equivalent), and full protective gear to prevent contact with skin and eyes.

6 Accidental release measures

· **Personal precautions, protective equipment and emergency procedures**
Wear protective equipment. Keep unprotected persons away.
Ensure adequate ventilation
Keep people at a distance and stay upwind.
Avoid contact with skin, eyes and clothing.
Keep away from ignition sources
· **Environmental precautions:** Do not allow to enter sewers/surface or ground water.
· **Methods and material for containment and cleaning up:**
Absorb with liquid-binding material (ie. sand, diatomite, universal binders), do NOT use sawdust.
Dispose contaminated material as waste according to section 13.
Ensure adequate ventilation.
Dispose of the collected material according to regulations.
· **Reference to other sections**
See Section 7 for information on safe handling.
See Section 8 for information on personal protection equipment.
See Section 13 for disposal information.

7 Handling and storage

· **Handling:**
· **Precautions for safe handling**
Avoid contact with skin, eyes and clothing
Keep away from sources of ignition.
Ensure good ventilation/exhaustion at the workplace.
Prevent formation of aerosols and spray mists.
Keep receptacles tightly sealed.
· **Information about protection against explosions and fires:**
Do not spray on a naked flame or any incandescent material.
Protect from heat.

· **Conditions for safe storage, including any incompatibilities**
Store away from strong acids, strong bases, strong oxidizing agents and strong reducing agents.
· **Storage:**
· **Requirements to be met by storerooms and receptacles:**
Store in a well ventilated place.
Store in a cool, dry place away from sparks and flame.
Do not store in direct sunlight.

(Contd. on page 5)

Safety Data Sheet (SDS)

OSHA HazCom Standard 29 CFR 1910.1200(g) and GHS Rev 03.

Reviewed on 05/07/2015

Trade name: NAVHFC

· **Penetration time of glove material**
The exact break-through time has to be determined and observed by the manufacturer of the protective gloves.

· **Eye protection:**

Goggles or safety glasses with side shields recommended.

· **Body protection:**

Protective work clothing

9 Physical and chemical properties

· **Information on basic physical and chemical properties**
· **General Information**

· **Appearance:**	
Form:	Liquid
Color:	Colorless
· **Odor:**	Mild, citrus-Terpene
· **Odor threshold:**	Not determined.
· **pH-value:**	Not determined.
· **Change in condition**	
Melting point/Melting range:	Not determined.
Boiling point/Boiling range:	176-215 °C (349-419 °F)
· **Flash point:**	61 °C (142 °F)
· **Flammability (solid, gaseous):**	Not applicable.
· **Ignition temperature:**	
Decomposition temperature:	Not determined.
· **Auto igniting:**	Product is not self-igniting.
· **Danger of explosion:**	Not determined.
· **Explosion limits:**	
Lower:	0.7 Vol %
Upper:	7.0 Vol %
· **Vapor pressure @ 20 °C (68 °F):**	<1.0 mm Hg
· **Density @ 20 °C (68 °F):**	0.777 g/cm3 (6.48 lbs/gal)
· **Relative density**	Not determined.
· **Vapor density**	5.0 (air=1)
· **Evaporation rate @ 20 °C (68 °F)**	<1.0 (nBuAc=1)

(Contd. on page 7)

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Safety Data Sheet (SDS)

OSHA HazCom Standard 29 CFR 1910.1200(g) and GHS Rev 03.

Reviewed on 05/07/2015

Trade name: NAVHFC

· **Primary irritant effect:**
· **on the skin:**
Irritant to skin and mucous membranes.
May cause an allergic skin reaction.
· **on the eye:** No irritating effect.
· **Sensitization:** Sensitization possible through skin contact.
· **Additional toxicological information:**
The product shows the following dangers according to internally approved calculation methods for preparations:
Irritant

· **Carcinogenic categories**
· **IARC (International Agency for Research on Cancer)**
Group 1 - Carcinogenic to humans
Group 2A - Probably carcinogenic to humans
Group 28 - Possibly carcinogenic to humans
Group 3 - Not classifiable as to its carcinogenicity to humans
Group 4 - Probably not carcinogenic to humans
5989-27-5 d-limonene 3

· **NTP (National Toxicology Program)**
None of the ingredients are listed.

· **OSHA-Ca (Occupational Safety & Health Administration)**
None of the ingredients are listed.

12 Ecological information

· **Toxicity**
· **Aquatic toxicity:**
5989-27-5 d-limonene
EC50 0.36 mg/l (daphnia) (OECD Test Guideline 202)
· **Persistence and degradability** No further relevant information available.
· **Behavior in environmental systems:**
· **Bioaccumulative potential** No further relevant information available.
· **Mobility in soil** No further relevant information available.
· **Additional ecological information:**
· **General notes:**
Do not allow product to reach ground water, water course or sewage system.
Danger to drinking water if even small quantities leak into the ground.
· **Results of PBT and vPvB assessment**
· **PBT:** Not applicable.
· **vPvB:** Not applicable.
· **Other adverse effects** No further relevant information available.

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(Contd. on page 9)

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Safety Data Sheet (SDS)

OSHA HazCom Standard 29 CFR 1910.1200(g) and GHS Rev 03.

Reviewed on 05/07/2015

Trade name: NAVHFC

13 Disposal considerations

· **Waste treatment methods**
· **Recommendation:**
Must not be disposed of together with household garbage. Do not allow product to reach sewage system.
NAVHFC is not considered a RCRA regulated substance. Soils removed during cleaning may affect the hazard classification of your waste stream. If your waste stream remains non- hazardous (you need to check), the waste may be disposed of like used oil (in most states). Please call us if you need additional disposal information.

· **Uncleaned packagings:**
· **Recommendation:**
Dispose of as unused product.
Disposal must be made according to official regulations.

14 Transport information

· **UN-Number**
· **DOT, ADR, IMDG, IATA** — Non-Regulated Material

· **UN proper shipping name**
· **DOT** — Non-Regulated Material
· **ADR**
· **IMDG**
· **IATA**

· **Transport hazard class(es)**

· **DOT**
· **Class** — Non-Regulated Material

· **ADR**

· **Class**
· **Label**

(Contd. on page 10)
us

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Safety Data Sheet (SDS)

OSHA HazCom Standard 29 CFR 1910.1200(g) and GHS Rev 03.

Reviewed on 05/07/2015

Trade name: NAVHFC

· IMDG, IATA

· Class	
· Label	
· Packing group	
· DOT	Non-Regulated Material
· ADR, IMDG, IATA	
· Environmental hazards:	
· Special marking (ADR):	
· Special marking (IATA):	
· Special precautions tor user	
· Danger code (Kemler):	
· EMS Number:	
· Transport in bulk according to Annex II of MARPOL73/78 and the IBC Code	Not applicable.
· Transport/Additional information:	
· ADR	
· Excepted quantities (EQ)	Code: E1 Maximum net quantity per inner packaging: 30 ml Maximum net quantity per outer packaging: 1000 ml
· IMDG	
· Limited quantities (LQ)	5L
· Excepted quantities (EQ)	Code: E1 Maximum net quantity per inner packaging: 30 ml Maximum net quantity per outer packaging: 1000 ml

15 Regulatory information

· Safety, health and environmental regulations/legislation specific tor the substance or mixture

· Sara

· Section 355 (extremely hazardous substances):

None of the ingredients are listed.

· Section 313 (Specific toxic chemical listings):

None of the ingredients are listed.

· TSCA (Toxic Substances Control Act):

All ingredients are listed.

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Safety Data Sheet (SDS)

OSHA HazCom Standard 29 CFR 1910.1200(g) and GHS Rev 03.

Reviewed on 05/07/2015

Trade name: NAVHFC

· **California Proposition 65**
· **Chemicals known to cause cancer:**
None of the ingredients are listed.
· **Chemicals known to cause reproductive toxicity for females:**
None of the ingredients are listed.
· **Chemicals known to cause reproductive toxicity for males:**
None of the ingredients are listed.
· **Chemicals known to cause developmental toxicity:**
None of the ingredients are listed.
· **Carcinogenic categories**
· **EPA (Environmental Protection Agency)**
None of the ingredients are listed.
· **TLV (Threshold Limit Value established by ACGIH)**
None of the ingredients are listed.
· **NIOSH-Ca (National Institute tor Occupational Safety and Health)**
None of the ingredients are listed.
· **GHS label elements**
The product is classified and labeled according to the Globally Harmonized System (GHS).
· **Hazard pictograms**

GHS07 GHS08

· **Signal word** Danger

· **Hazard-determining components of labeling:**
Distillates (petroleum), hydrotreated light d-limonene
Isoparaffinic Hydrocarbon
· **Hazard statements** Combustible liquid. Causes skin irritation.
May cause an allergic skin reaction. May cause drowsiness or dizziness.
May be fatal if swallowed and enters airways.
· **Precautionary statements**
Keep away from flames and hot surfaces. – No smoking. Avoid breathing dust/fume/gas/mist/vapors/spray.
Use only outdoors or in a well-ventilated area.
Wear protective gloves / eye protection / face protection. Wear protective gloves.
Wash thoroughly after handling.
Contaminated work clothing must not be allowed out of the workplace.
If swallowed: Immediately call a poison center/doctor.

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Safety Data Sheet (SDS)

OSHA HazCom Standard 29 CFR 1910.1200(g) and GHS Rev 03.

Reviewed on 05/07/2015

Trade name: NAVHFC

Specific treatment (see supplementary first aid instructions on this Safety Data Sheet).
IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
Call a poison center/doctor if you feel unwell.
Wash contaminated clothing before reuse.
If skin irritation occurs: Get medical advice/attention.
If skin irritation or rash occurs: Get medical advice/attention.
Do NOT induce vomiting.
In case of fire: Use for extinction: CO2, powder or water spray.
If on skin: Wash with plenty of water.
Take off contaminated clothing and wash it before reuse.
Store locked up.
Store in a well-ventilated place. Keep container tightly closed.
Store in a well-ventilated place. Keep cool.
Dispose of contents/container in accordance with local/regional/national/international regulations.

· **National regulations:**

The product is subject to be classified according with the latest version of the regulations on hazardous substances.

· **State Right to Know**

CAS: 64742-47-8	Distillates (petroleum), hydrotreated light Asp. Tox. 1, H304; Aquatic Chronic 2, H411; Skin Irrit. 2, H315; STOT SE 3, H336; Flam. Liq. 4, H227	25-50%
CAS: 64742-48-9	Isoparaffinic Hydrocarbon Asp. Tox. 1, H304; Flam. Liq. 4, H227	25-50%
CAS: 5989-27-5 RTECS: GW 6360000	d-limonene Aquatic Acute 1, H400; Aquatic Chronic 1, H410; Skin Irrit. 2, H315; Skin Sens. 1, H317; Flam. Liq. 4, H227	≤ 2.5%

All ingredients are listed.

· **Chemical safety assessment:** A Chemical Safety Assessment has not been carried out.

16 Other information

Ecolink, Inc. believes the information contained herein is accurate. However, Ecolink makes no warranty, expressed or implied, regarding the accuracy of this data or the results to be obtained by the use thereof. Ecolink, Inc. assumes no responsibility for injury from the use of the product described herein.

· **Date of preparation / last revision** 05/07/2015

· **Abbreviations and acronyms:**

ADR: The European Agreement concerning the International Carriage of Dangerous Goods by Road
ADN: The European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways
IMDG: International Maritime Code for Dangerous Goods
DOT: US Department of Transportation
IATA: International Air Transport Association
ACGIH: American Conference of Governmental Industrial Hygienists
EINECS: European Inventory of Existing Commercial Chemical Substances
ELINCS: European List of Notified Chemical Substances
CAS: Chemical Abstracts Service (division of the American Chemical Society)
NFPA: National Fire Protection Association (USA)
HMIS: Hazardous Materials Identification System (USA)

LINK.

Safety Data Sheet (SDS)

OSHA HazCom Standard 29 CFR 1910.1200(g) and GHS Rev 03.

Reviewed on 05/07/2015

Trade name: NAVHFC

LC50: Lethal concentration, 50 percent
LD50: Lethal dose, 50 percent
Flam. Liq. 4: Flammable liquids, Hazard Category 4
Skin Irrit. 2: Skin corrosion/irritation, Hazard Category 2
Skin Sens. 1: Sensitization - Skin, Hazard Category 1
STOT SE 3: Specific target organ toxicity - Single exposure, Hazard Category 3
Asp. Tox. 1: Aspiration hazard, Hazard Category 1
Aquatic Acute 1: Hazardous to the aquatic environment - AcuteHazard, Category 1
Aquatic Chronic 1: Hazardous to the aquatic environment - Chronic Hazard, Category 1
Aquatic Chronic 2: Hazardous to the aquatic environment - Chronic Hazard, Category 2

Appendix O Material Safety Data Sheet for Navsolve

Material Safety Data Sheet

NAVSOLVE®

Low VOC Cleaner/Degreaser

Rev. 01/16/2012

Is

ECOLINK.

2177-A Flintstone Drive FOR CHEMICAL EMERGENCY

Tucker, GA 30084 Call Infotrac

www.ecolink.com 800/535-5053 (24 HOURS)

email: info@ecolink.com

800/886-8240 or

770/621-8240 (9-5 EST)

Section I: Product Identification

Product name:NAVSOLVE®

Synonym: Siloxane/oxygenated solvent blend

Molecular Formula: N/A

The "Plain English" Section

Material Safety Data Sheets can be confusing. Federal

law requires us to print a great deal of technical

information, which probably won't help the non-scientist. ECOLINK includes this "PLAIN ENGLISH" section, written to address the questions and concerns of the average person. If you have additional health, safety or product questions, don't hesitate to call us at 800/886-8240.

Health Hazards: NAVSOLVE® is an industrial solvent. We call it "environmentally preferred" because it is intended to replace products that are more hazardous, (HCFC-141b, MEK, etc.). This does not mean that NAVSOLVE® is completely harmless. It is strong enough to remove industrial soils, so it can irritate your skin. We suggest you wear gloves, and avoid extended exposure to unprotected skin. Don't get it in your eyes, or breath large amounts of the vapor, (it will dry out your nasal passages). Used on a rag or from a spray bottle, the product won't produce fumes in any great quantity, (don't spray NAVSOLVE® under pressure without adequate ventilation). For more exposure and first aid information, refer to MSDS Section VI.

Fire Hazard: NAVSOLVE® is combustible.

Under no circumstance can you use this solvent around open or potential ignition sources, (think about

welding tools, sparks from equipment, smoking, etc).

Rags must be handled as combustible and deposited

into properly marked rag containers. If you are unsure

about the safest way to use NAVSOLVE®, please call

us and we will help!

Section II: Hazardous Components

Chemical Name

Decamethylcyclopentasiloxane

CAS No.

541-02-6

Approx. wt.%

50-70%

Exposure

10 ppm TWA: Supplier

Chemical Name

Octamethylcyclotetrasiloxane

CAS No.

556-67-2

Approx. wt.%

20-40%

Exposure Limit

ACGIH TLV: Not Established

OSHA PEL: Not Established

10 ppm TWA: Supplier

Chemical Name

Decamethyltetrasiloxane

CAS No.

141-62-8

Approx. wt.%

5-10%

Exposure

200 ppm TWA: Supplier

Chemical Name

Dipropylene Glycol n-Butyl Ether

CAS No.

29911-28-2

Approx. wt.%

1-5%

Exposure Limit

ACGIH TLV: Not Established

OSHA PEL: Not Established

Chemical Name

Hexylene Glycol

CAS No.

107-41-5

Approx. wt.%

0-1%

Exposure Limit

ACGIH Ceiling: 25 ppm:

ALL MATERIALS IN PRODUCT ARE TSCALISTED

RCRA REGULATED:

No

CERCLA (superfund):

N/A

DOT Regulated:

No

DOT Haz. Class:

None

DOT Shipping Name:

N/A

DOT Number:

N/A

?

Colorless liquid with mild odor.

~185°C

Negligible

0.960 - 0.970

<25 gm/l

<0.5 @ 20oC

Approx 0.04

>1.0

Section IV: Fire & Explosion Hazard Data

Flash Point (Method):

Bulk Liquid (TCC)

Flammable Limits:

LEL

UEL

Autoignition Temperature:

Extinguishing Media:

Water fog, alcohol foam, dry chemical, or CO2.

Special Fire Fighting Procedures:

Caution. Combustible. Clear area of unprotected personnel and isolate. Use full bunker gear including a positive pressure NIOSH approved self-contained breathing apparatus. Cool fire exposed containers with water.

Unusual Fire & Explosion Hazards:

Containers exposed to intense heat should be cooled with water to prevent vapor pressure buildup, which could result in container rupture. Container areas exposed to direct flame contact should be cooled with large quantities of water as needed to prevent weakening of container structure.

Section V: Reactivity Data

Stability: Stable

Conditions to Avoid:

Temperature extremes. Heat, sparks or open flame.

Incompatibility (materials to avoid): Avoid contact with strong oxidizing agents.

Hazardous Decomposition:

Carbon oxides, Silicone dioxide, Formaldehyde

Hazardous Polymerization:

Will not occur.

Section VI: Health Hazard Data

Primary Routes of Exposure:

Inhalation:

May cause slight irritation to respiratory passages. High vapor concentrations may cause drowsiness.

Eyes:

Direct contact will cause mild irritation

Skin Contact:

Repeated or prolonged contact can result in defatting and drying of the skin that may result in dermatitis.

First Aid:

Inhalation: Remove to fresh air. If breathing difficult, give oxygen. Call physician

Eyes: Irrigate immediately with water for at

least 15 minutes. Call physician.

Skin: Wash with soap and water. Launder

contaminated clothing and shoes before

reuse. If symptoms persist, seek

medical attention.

Carcinogen: NTP - Not Listed

IARC Monographs - None

OSHA REGS - Not Regulated

Section VII: Precautions for Safe Handling

HMIS Information:

Health - 1 /

Flammability - 2

HMIS Definition:

0 - Minimal 1 - Slight 2 - Moderate 3 - Serious 4 - Extreme

"/" in the Health Category denotes material does not target

any major organs.

"*" In the Health Category denotes material may target certain

organs.

Eye Protection:

Safety glasses with side shields if splashing is likely.

Protective Gloves:

Impervious gloves are recommended for prolonged or

repeated contact.

Respiratory Protection:

Use a NIOSH approved respirator if exposure limits are exceeded.

Ventilation: Well ventilated area.

Other Protective Clothing: None

Work Practices: Use with adequate ventilation. Wash hands after use.

Section VIII: Control Measures

Small Spill: Remove all sources of ignition. Handling equipment must be grounded. Wear protective equipment. Absorb liquid on absorbent material.

Large Spill: Remove all sources of ignition. Persons not wearing protective equipment should be excluded from area. Dike and contain. Pump into suitable tank/drum. Soak up residue with absorbent material.

Waste Disposal Method: NAVSOLVE® liquid is to be disposed of according to local, state, and federal regulations. Please call us if you need additional disposal information. Under RCRA, this material is not considered a hazardous waste.

Precautions To Be Taken In Handling & Storing: Keep away from heat, sparks and open flames. Keep away from hot surfaces. Use with adequate ventilation. Vapors may

accumulate and travel to ignition sources distant from handling site. Flash-fire can result. Keep containers closed when not in use. Empty containers can contain explosive vapors. Do not cut, grind, drill or weld near containers. Static electricity may create a fire hazard. Ground fixed equipment. Keep out of reach of children.

Other Precautions: Keep this and all chemicals out of the reach of children.

Section IX: Part Number, Packaging

Product Name	Part No.	Packaging	National Stock No.
NAVSOLVE®		55 Gal Drum	
NAVSOLVE®		15 Gal Drum	
NAVSOLVE®		5 Gal Pail	
NAVSOLVE®		4 x 1 Gal Cs	

DISCLAIMER: Ecolink, Inc. believes the information contained herein is accurate. However, Ecolink makes no warranty, expressed or implied, regarding the accuracy of this data or the results to be obtained by the use thereof. Ecolink, Inc. assumes no responsibility for injury from the use of the product described herein.

END OF MSDS

Appendix P Product Information for Nyco MIL-PRF-81322 Grease

GENERAL PURPOSE AIRCRAFT SYNTHETIC GREASE

NATO CODE G-395 - DCSEA 395/B (AIR 4222) - MIL-PRF 81322 G DEF-STAN 91-52 Iss.1 Amd.2 - XG-293

DESCRIPTION

Nyco Grease GN 22 is a NLGI 2, clay-thickened grease, based on a synthetic hydrocarbon oil with a viscosity of 7 cSt at 100°C. It is inhibited against corrosion, oxidation and contains anti-wear/extreme pressure additives.

It can be used from -65 to +177°C.

MAIN APPLICATIONS

Airframe multipurpose grease (doors, flaps, slaps, landing gear, THS, ...) of most civil and
military aircrafts and helicopters

Wheel bearings of most of civil and military aircrafts and helicopters

Main and tail rotor of helicopter

Airbus CML 03GBB1 ATR CML 04-004B CFMI CP 5076

In process of being replaced by **Nyco Grease GN 3058** for application in wheels bearings.

- Appearance	-	homogeneous, smooth brown	homogeneous, smooth grease	visual
- Viscosity of Base Oil at 40°C	mm^2/s	40	-	ASTM D 445
- Dropping point	°C	265	min. 232	ASTM D 566
- Worked penetrability	1/10 mm	276	265 - 320	ASTM D 217
After 60 strokes		330	max. 350	FTM-S-791-
- Oil separation, 30 h at 177°C	%w	5.1	2.0 - 8.0	ASTM D 6184
- Evaporation loss, 22 h at	%w	4.9	max. 10.0	ASTM D 2595
- Copper corrosion, 24h at	-	1a	max. 1 b	ASTM D 4048
- Steel on steel wear, 1h at	mm	0.7	max. 0.80	ASTM D 2266
- Load carrying capacity (LWI)	daN	36	min. 30.0	ASTM D 2596
- Bearing performance at	h	pass	> 400	ASTM D 3336
- Oxidation stability at 100°C,	kPa	21 / 63	max. 83 / max	ASTM D 942
- Water washout at 38°C	%w	2.0	max 20	ASTM D1264
- Torque at -54°C (starting / 1h)	Nm	0.24 / 0.04	max 1.00 / max 0.10	ASTM D1478
- Bearing corrosion test	-	pass	no corrosion	ASTM D 1743

- Elastomer NBR-L	%v	3	max. 10	ASTM D 4289

The values above are typical values. They do not constitute any contractual commitment.

Sales specifications are available on request. The present technical data sheet replaces all the previous editions.

Appendix Q Product Information for Dow Ucon OSP-18

Date 2015-10-20 (YYYY-MM-DD) Time 20:59:23 (Greenwich Mean Time) Page 1 of 1

THE DOW CHEMICAL COMPANY

CHEMICAL MARKETING CONCEPTS
INC
194 PICKETT DISTRICT RD
NEW MILFORD CT 06776-4415

Ship From: HOUSTON Palmer Whse
HOUSTON
United States

Certificate of Analysis

Product Number 00000362596
Product Name
UCON™ OSP-18 Lubricant

Delivery No. 806326937 /000010

Order Number 103999174

Date Shipped 2015-10-20 (YYYY-MM-DD)

Shipment No. 26224413

Customer Information

Customer Name CHEMICAL MARKETING CONCEPTS

Customer PO number 54900

Container ID 288-238963

Vehicle# 463-5298

Specification Number 000000175744

Batch Number D358EB1PCA
Manufacturing Date 2014-10-28 (YYYY-MM-DD)

Test	Unit	Lower Limit	Upper Limit	Value	Method
Viscosity @ 40degC	cSt	16.2	19.8	19.0	ASTM D445
Water	WT%	-	0.20	0.02	ASTM E203
Acid Number (as KOH)	mg/g	-	0.10	0.02	DOWM 100387
Color, Pt-Co		-	50	26	ASTM D5386

Quality Coordinator

For inquiries please contact Customer Service or local sales
® ™ Trademark of The Dow Chemical Company ("Dow") or an affiliated company of Dow

Appendix R Product Information for Croda Priolubes

CRODA

Certificate prepared at

Croda Inc.
8 Croda Way
Mill Hall PA 17751
USA

Certificate of Analysis

A quality management system registered to the international standard ISO 9001 was used to manufacture and test this material.

Customer details

Naval Air Warfare Center
Matthew Davis
Michelson Laboratory
1900 North Knox Road MS6303
China Lake CA 93555
USA

Customer Ref. B9V74GF9G-B9V74I3Q6
Inspection Lot 090000221919
C of A Printed. 01/20/2016
Croda Order No. 2108230
Croda Del. No. 82327981
Quantity. 1.000KG

Batch Details

Product Name: PRIOLUBE 1936-LQ-(MH)
Product Code: ES40526/SAMP
Batch No: 0001047881

Date of test: 10/28/2015
Date of manufacture: 10/14/2015
Retest date: 10/13/2017

Specification: REVISED 3-FEB-2010

Quality Control Results

Analytical Test Method No.	Characteristic	Specification Limit Lower	Upper	Value	Unit	Status
	Addendum 00	Pass or Fail		Pass	-	P
AU020000	APPEARANCE	CLEAR LIQUID		Pass	-	P
AU320200	COLOR (APHA)	0	500	60	APHA	P
EU0100A0	ACID VALUE	0.0	0.1	0.1	mg KOH/g	P
EU050000	HYDROXYL VALUE	0	3	2	mg KOH/g	P
FU070610	POUR POINT	-100	-51	-51	°C	P
FU2904A0	WATER CONTENT	0.0	0.1	0.1	%	P
FU340200	DENSITY (20°C)	0.909	0.914	0.912	g/ml	P
FU3802A0	VISCOSITY (40°C)	25.5	29.0	28.0	cSt	P
FU3802A0	VISCOSITY (100°C)	5.1	5.5	5.4	cSt	P
LU680130	FLASH POINT	220	999	236	°C	P

If you received only a sample of this product, please request updated specification before placing the first purchase order.

Batch Status: Pass
The quality tests on this batch are reported above. The tests carried out are those necessary to demonstrate compliance with our product specification and are not intended to guarantee the product as suitable for any application beyond those contained in the specification. We recommend you perform your own quality and or identification checks on receipt

Page 1 of 2

RODA

cate prepared at

Europe Limited
oda Nederland BV
e 1
BE Gouda
rlands

Certificate of Analysis

A quality management system registered to the international standard ISO 9001 was used to manufacture and test this material.

omer details

Naval Air Warfare Center
Matthew Davis
Michelson Laboratory
1900 North Knox Road MS6303
China Lake CA 93555
USA

Customer Ref.	B9V74GF9G-B9V74I3
Inspection Lot	090000209151
C of A Printed.	02/09/2016
Croda Order No.	2108230
Croda Del. No.	82346065
Quantity.	1.000KG

h Details

duct Name:	PRIOLUBE 1445-LQ-(GD)	**Date of test:**	06/02/2015
duct Code:	ESG1445/SAMP	**Date of manufacture:**	02/22/2011
h No:	0000517473	**Retest date:**	11/23/2016

cification: AMENDED 25-FEB-2010

lity Control Results

lytical Test nod No.	Characteristic	Specification Limit Lower	Upper	Value	Unit	Statu
	Addendum 00	Pass or Fail		Pass	-	P
00000	REVISION NUMBER	37.0		Pass	-	P
00100	ACID VALUE	0.0	1.0	0.7	mg KOH/g	P
00200	HYDROXYL VALUE	0	20	8	mg KOH/g	P
00700	SAPONIFICATION VALUE	185	193	191	mg KOH/g	P
00400	IODINE VALUE	82	92	86	g/100g	P
04600	POUR POINT	-100	-21	-30	°C	P
00600	LOVIBOND 1# YELLOW	0.0	15.0	4.4		P
00600	LOVIBOND 1" RED	0.0	3.0	0.9		P
02000	KIN.VISCOSITY 40°C	61.2	74.8	68.3	mm2/s	P
00300	MOISTURE	0	500	282	mg/kg	P

received only a sample of this product, please request updated specification before placing the first purchase

h Status: Pass

quality tests on this batch are reported above. The tests carried out are those necessary to demonstrate pliance with our product specification and are not intended to guarantee the product as suitable for any applica nd those contained in the specification. We recommend you perform your own quality and or identification che eceipt

Page 1 of 2

Appendix S ExxonMobil Polyalphaolefin Product Specifications Sheets

Fri Jan 09 2015 14:50 CST REF:10041342 FR:ExxonMob11 TO:7133361577 PG: 2 OF 2

ExxonMobil Oil Corp. - Synthetics
CERTIFICATE OF ANALYSIS

Customer Name:
Ship-To Address:

Customer Product Name: SPECTRASYN 10
Product Name / Grade : SPECTRASYN 10

Date Printed: 09 JAN 2015
Lot / Batch No.: USRC587D 8C-D 016

[redacted]
Del. Number:
Delivery Number:
Dispatch Point: ExxonMobil Oil Corp. - Synthetics
Rail/car/Vessel/Truck #:

Plant Dispatch Date: 12 JAN 2015
Letter of Credit Number:
Inspection Ref.: 000012080649

ANALYSIS

Property	UoM	Results	Specifications	Test Method
VISCOSITY AT 40C	cSt	68.5	65.0 - 74.8	ASTM D445
VISCOSITY AT 100C	cSt	10.4	9.4 - 10.9	ASTM D445
FLASH POINT, COC	°C	260	>= 250	ASTM D92
POUR POINT	°C	-45	<= -45	ASTM D5950/D97
SPECIFIC GRAVITY @ 15.6/15.6 C		0.836	-	ASTM D4052
APPEARANCE, -18C		BRIGHT & CLEAR	APPR - BRIGHT AND CLEAR,	VISUAL
TOTAL ACID NUMBER, mg KOH/g	mg/g	0.02	<= 0.05	ASTM D974(mod)
WATER	ppm	14	<= 50	ASTM D6304
COLOR, ASTM		0.5	<= 0.5	ASTM D1500
FLASH POINT,PMCC	°C	227	>= 135	ASTM D93

The product represented by this certificate is on-specification. Data contained herein were prepared pursuant to ExxonMobil's sampling and testing procedures in effect at the time of production. Test results listed on this certificate represent the most recent inspections conducted on the product, and can be from samples taken from a blender, storage tank, package, bulk shipping unit or a combination of these points. Some values shown may result from interpolation or correlation of other data. Applicable sampling and testing methods are available upon request and are subject to change without notice unless otherwise agreed in writing.

CofA form revision date : 21 AUG 2012

Page 1 of 1

ExxonMobil Oil Corp. - Synthetics
CERTIFICATE OF ANALYSIS

Customer Name:
Ship-To Address:

Customer Product Name: SPECTRASYN 5
Product Name / Grade : SPECTRASYN 5

Date Printed: 19 OCT 2015
Lot / Batch No.: B15K001

Sales Order Number: 10423458
Customer Order Number:

BoL Number:
Delivery Number:
Dispatch Point: ExxonMobil Oil Corp - Synthetics
Railcar/Vessel/Truck #:

Plant Dispatch Date: 21 OCT 2015
Letter of Credit Number:
Inspection Ref.: 000012202775

ANALYSIS

Property	UoM	Results	Specifications	Test Method
SPECIFIC GRAVITY @ 15.6/15.6 C		0.824	-	ASTM D4052
VISCOSITY AT 100C	cSt	5.1	4.5 - 5.5	ASTM D445
VISCOSITY AT -40C	cSt	4825	<= 5300	ASTM D445
POUR POINT	°C	-54	<= -51	ASTM D5950/D97
NOACK VOLATILITY	wt%	6.8	<= 8.0	D5800/DIN51581
TOTAL ACID NUMBER, mg KOH/g	mg/g	0.00	<= 0.05	ASTM D974(mod)
WATER	ppm	17	<= 50	ASTM D6304
APPEARANCE, -18C		BRIGHT & CLEAR	APPR - BRIGHT AND CLEAR.	VISUAL
-				
COLOR, ASTM		< 0.5	<= 0.5	ASTM D1500
FLASH POINT, COC	°C	246	>= 204	ASTM D92

The product represented by this certificate is on-specification. Data contained herein were prepared pursuant to ExxonMobil's sampling and testing procedures in effect at the time of production. Test results listed on this certificate represent the most recent inspections conducted on the product, and can be from samples taken from a blender, storage tank, package, bulk shipping unit or a combination of these points. Some values shown may result from interpolation or correlation of other data. Applicable sampling and testing methods are available upon request and are subject to change without notice unless otherwise agreed in writing.

CofA form revision date : 31 OCT 2006

Page 1 of 1

ExxonMobil Oil Corp. - Synthetics
CERTIFICATE OF ANALYSIS

Customer Name:
Ship-To Address:

Customer Product Name: SPECTRASYN 2
Product Name / Grade : SPECTRASYN 2

Date Printed: 12 NOV 2014
Lot / Batch No.: USRC800OCT 2016

[redacted]

Bol. Number:
Delivery Number:
Dispatch Point: ExxonMobil Oil Corp. - Synthetics
Railcar/Vessel/Truck #:

Plant Dispatch Date: 13 NOV 2014
Letter of Credit Number:
Inspection Ref.: 000012027183

ANALYSIS

Property	Unit	Results	Specifications	Test Method
SPECIFIC GRAVITY @ 15.6/15.6 C		0.798	-	ASTM D4052
VISCOSITY AT 100C	cSt	1.69	1.65 - 1.70	ASTM D445
VISCOSITY AT -40C	cSt	249	<= 270	ASTM D445
POUR POINT	°C	-64	<= -60	ASTM D5950/D97
FLASH POINT, COC	°C	168	>= 155	ASTM D92
TOTAL ACID NUMBER, mg KOH/g	mg/g	0.00	<= 0.05	ASTM D974(mod)
WATER	ppm	24	<= 50	ASTM D6304
APPEARANCE, -40C		BRIGHT & CLEAR	APPR - BRIGHT AND CLEAR,	VISUAL
-				
COLOR, ASTM		< 0.5	<= 0.5	ASTM D1500
VISCOSITY AT 40C	cSt	5.1	-	ASTM D445

The product represented by this certificate is on-specification. Data contained herein were prepared pursuant to ExxonMobil's sampling and testing procedures in effect at the time of production. Test results listed on this certificate represent the most recent inspections conducted on the product, and can be from samples taken from a blender, storage tank, package, bulk shipping unit or a combination of these points. Some values shown may result from interpolation or correlation of other data. Applicable sampling and testing methods are available upon request and are subject to change without notice unless otherwise agreed in writing.

CoA form revision date : 31 OCT 2005

Page 1 of 1

Appendix T Typical Commercial Degreasing/Parts Washing Equipment Used by the DoD

APW-35

Immersion Cleaning Adds Speed and Efficiency to Your Business

The APW-35 is a total immersion solvent-based parts washer that will tackle your toughest job. Constructed with the same high-quality craftsmanship Clarus Technologies is known for, the APW-35 is easy to use with many automated features that save time and money. Simply load parts into the gridded basket, choose a cycle duration from the touch screen panel and walk away! A high degree of cleanliness is achieved in a shorter amount of time with no handling or scrubbing.

CLARUS
ECHNOLOGIES
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Inland Technology Incorporated

Pollution Prevention By Design

IT-16

NSN 4250-01-381-8061

Specifications

Overall Dimensions	26" L x 17" W x 7" H
Inside Tub Dimensions	34"
Sill/Working Height	16 Gauge Steel
Tub Material Thickness	14 Gallons
Solvent Capacity	500 GPH
Pump Capacity	120 V, 60Hz, 7
Electrical Requirements	A
31" L x 22" W x 53" H	

401 East 27th Street, Tacoma, WA 98421
(253) 383-1177 • (800) 552-3100
inland@inlandtech.com
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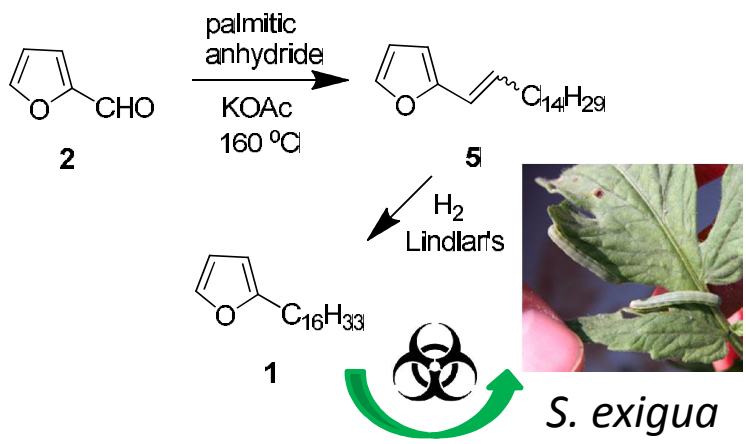
Appendix U Manuscript Published in the Online Journal ARKIVOC (Volume 2016, Part (v) pp. 242–248) Concerning Synthesis of Antifeedant Molecule Using Chemistry Developed During SERDP SEED Project WP-2523

Graphical Abstract

A new synthesis route for the preparation of the avocadofuran (2-hexadecylfuran) *Matthew C. Davis and Thomas J. Groshens*	

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A new synthesis route for the preparation of the avocadofuran (2-hexadecylfuran)

Matthew C. Davis* and Thomas J. Groshens

Chemistry & Materials Division, Michelson Laboratory,
Naval Air Warfare Center, China Lake, CA 93555, USA
E-mail: matthew.davis@navy.mil

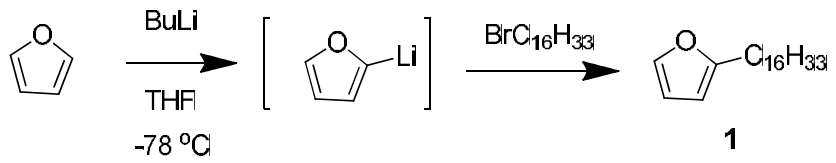
Abstract

A new synthetic route for the preparation of the insecticidal compound 2-hexadecylfuran is described in this study. The procedure starts from readily available furfuraldehyde and palmitic anhydride via two steps employing the Perkin reaction and resulting in a 25% overall yield. The method can be deemed as a practical and environmentally friendly route to prepare a potentially important class of insecticide.

Keywords: Furfuraldehyde, Perkin reaction, Lindlar catalyst, insecticide, avocadofurans

Introduction

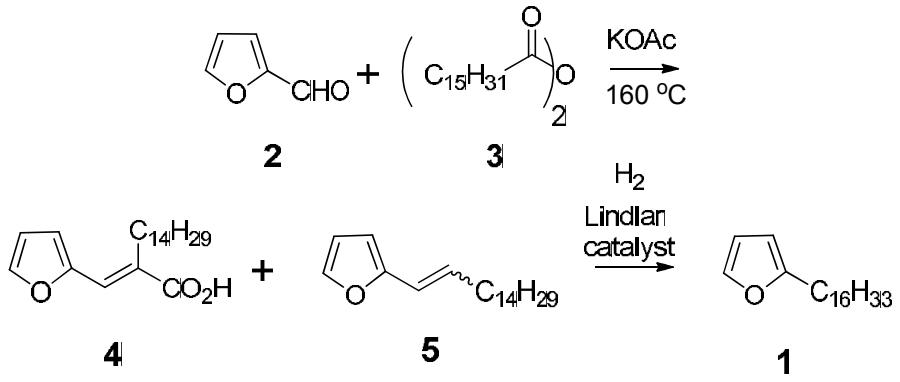
The avocadofurans are a family of natural products isolated from avocado (*Persia*) which consist of 2-alkylfurans with varying degrees and sites of unsaturation (double and triple bonds) in the alkyl chain.[1–3] Rodriguez-Soana and co-workers demonstrated that compounds structurally related to avocadofurans, saturated 2-alkylfurans with chain length of 14–18 carbon atoms, have inhibitory activity against larval growth of the agricultural insect beet army worm (*Spodoptera exigua*) and, therefore, such compounds could be useful insecticides in crop protection.[4,5] The synthetic route employed by Rodriguez-Soana et al. to prepare 2-hexadecylfuran (**1**) is shown in **Scheme 1**. Furan is deprotonated at the *alpha*-position by reaction with butyllithium at cryogenic temperature, afterwards 1-bromohexadecane was added for a nucleophilic substitution reaction.



Scheme 1. Original synthesis of 2-hexadecylfuran by Rodriguez-Soana *et al*.

Results and Discussion

As part of a study of the Perkin condensation, it was anticipated that the condensation of furfuraldehyde (**2**) with palmitic anhydride (**3**) might constitute a facile and inexpensive route to the insecticidal compound 2-hexadecylfuran (**1**) (**Scheme 2**). We now report the successful results of that investigation.



Scheme 2. New two-step synthesis of 2-hexadecylfuran by Perkin reaction followed by reduction.

Since the anhydride of palmitic acid is available only in small quantities for analytical purposes, it was conveniently prepared by reaction of palmitic acid with a 2.66 molar equiv. of acetic anhydride as dehydrating agent.[6,7] Thus, after refluxing for four hours, distillation of the mixture at atmospheric pressure removed the excess acetic anhydride and by-product acetic acid and gave a 78% yield of palmitic anhydride (**3**). Because palmitic acid and its anhydride have similar melting points, ^{13}C NMR was used to establish its structure and clearly showed the typical upfield shift of the carbonyl resonance of the anhydride (169.8 ppm) compared to that of the acid (180.5 ppm).

The Perkin condensation of **2** and **3** catalyzed by potassium acetate in a ratio of 1.85:1:1.09 was chosen owing to increased yields in similar reactions, (**Scheme 2**).[8–10] The mixture was heated in a controlled oil bath set to 160 °C for 4 hrs. The reaction quickly became dark brown in color and once the internal reaction temperature exceeded 110 °C, there appeared to be gas evolution. The work-up was complicated by the presence of large quantities of solids. The solids were collected, washed with ethyl acetate. Thin-layer chromatographic analysis of the filtrate on silica gel eluting with hexanes showed an unexpectedly fast moving non-polar component. It was isolated, purified by silica gel chromatography (elution with hexanes) and identified by ^{1}H NMR as a 1:1.85 mixture of *cis*- and *trans*-(2-furyl)hexadecene (**5**). In addition, the ^{13}C NMR showed twelve signals in the sp^{2}-hybridized region confirming that two diastereomers were present. The yield of **5** was only 26% based on **3**.

Evidently, under these conditions the anticipated product, 2-tetradecyl-3-(2-furyl)acrylic acid (**4**) underwent spontaneous decarboxylation to a considerable degree; two reports of Perkin condensation of benzaldehydes with stearic anhydride (another long chain fatty acid) make no mention of alkene products even though these reaction conditions were more vigorous (36 h at 170 °C[11] and 24 h at 210 °C,[12] respectively). This suggests that the decarboxylation might have been facilitated by the presence of furan ring, an hypothesis currently under study. It is known that Perkin reaction of **2** with isobutyric[13] and isopentanoic[14] anhydrides yields alkenes as the major product under conditions similar to these and even 3-(2-furanyl)acrylic acid can be made to decarboxylate, although at higher temperatures (> 250 °C).[15] The geometric isomerism of **5** is interesting to note since it clearly indicates that the intermediate acrylic acid **4** must have had trans configuration as proven in similar reactions.[16] Other *trans* 2,3-Disubstituted acrylic acids will undergo diastereospecific decarboxylation to *cis* alkenes by heating, with copper and quinolone for example (*e. g*. conversion of *trans*-1,2-diphenyl-acrylic acid to *cis*-stilbene).[17] The proportion of thermodynamically favored *trans* **5** likely resulted from isomerization of *cis* **5** in the hot reaction mixture.

In order to confirm these conclusions, the original solid removed by filtration (*vide supra*) was treated slurried with a 1:1 mixture of ethyl acetate and hexanes. Evaporation of the extract followed by crystallization from hexanes allowed the isolation of a small amount of pure

acrylic acid **4** in low yield (3.6%) sufficient for X-ray crystal analysis of single crystals grown as colorless plates by slow evaporation of a toluene solution and established that **4** had the expected *trans* geometry about the double bond (the furan ring and tetradecyl chain share one side), **Figure 1**. Low thermal disorder was observed in the conformationally flexible alkyl chain since the experiment was carried out at -100 °C.

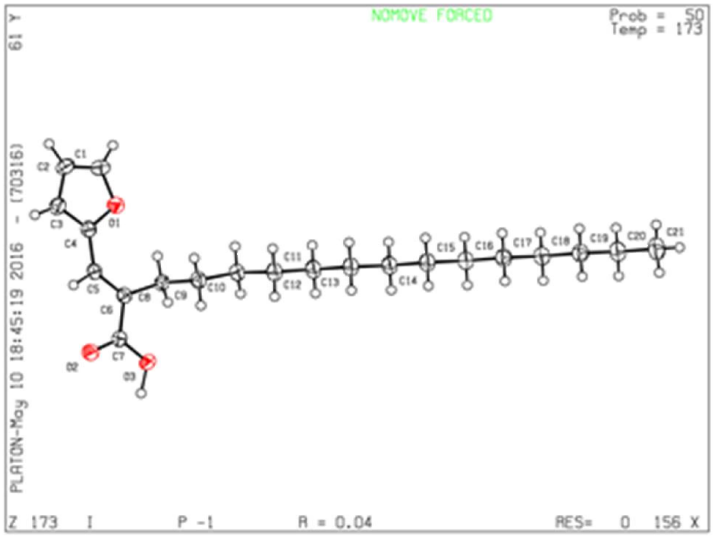


Figure 1. Thermal ellipsoid plot (50%) of acrylic acid **4**.

The final step to **1** involving the selective catalytic reduction of the alkene mixture **5** was accomplished using Lindlar catalyst. Although the Lindlar catalyst is best known for the diastereoselective reduction of alkynes to *cis*-alkenes, the catalyst can bring about further reduction of alkenes to dihydro derivatives which may be prevented when used in conjunction with amine poisons.[18] Other catalysts such as Pd/C led to reduction of the furan ring of **5** as well as the double bond. The furan ring has been shown to be a structural feature, vital for biological activity.[4,5]

Conclusions

A two-step synthesis of the insect anti-feedant 2-hexadecylfuran (**1**) was accomplished starting from inexpensive furfuraldehyde (**2**)[19–21] in 25% overall yield. Although the yield is low, the starting materials are inexpensive and are obtained from domestic agricultural sources.

Experimental Section

General. Mps were determined on a Meltemp II Electrothermal capillary melting point apparatus (Laboratory Devices, Holliston, MA) and are not corrected. $CDCl_3$ was used for all NMR experiments carried out on a Bruker Avance II 300 MHz spectrometer (^{1}H at 300 MHz, ^{13}C at 75 MHz). NMR data (free induction decay signals) were processed using NUTS software from Acorn NMR (Livermore, CA). All ^{1}H spectra are referenced to tetramethylsilane (Me_4Si) and all ^{13}C spectra are referenced to the solvent. Thin-layer chromatographies (TLC) were carried out on aluminum foil backed, silica gel plates (2–25 micron particle size, 60Å) and elution with a mixture of hexanes/EtOAc. The plates were visualized using UV lamp (254 nm) and/or by staining with 10% phosphomolybic acid in ethanol. Silica gel (grade 60, 60–200 micron, 60Å) for chromatography was obtained from Spectrum Chemical Mfg. Corp. (New Brunswick, NJ) and used as received. Palmitic acid, potassium acetate and acetic anhydride were obtained from Sigma-Aldrich (Milwaukee) and used as received. Furfuraldehyde (98%) also obtained from Sigma-Aldrich was distilled under reduced pressure (60 torr) prior to use. Lindlar's catalyst was purchased from Sigma-Aldrich. All other solvents and reagents were acquired commercially and used as received. Elemental analyses were carried out by Atlantic Microlab Inc. (Norcross, GA).

Palmitic acid anhydride (3). A round-bottomed flask equipped with magnetic stirring bar and reflux condenser was charged with palmitic acid (50 g, 195 mmol) and Ac_2O (53 g, 49 mL, 519 mmol, 2.66 equiv). The mixture was vigorously stirred and heated to reflux for 4 h. Afterwards, the condenser was exchanged for a distillation head and the volatiles were distilled at atmospheric pressure. The pot material solidified after cooling to ambient temperature. The crude product was recystallized from acetone to give **3**, soft, colorless platelets, yield 78%, 38 g, mp 58–62 °C (Lit.[22] 64 °C); ^{1}H NMR: δ_H 2.45 (t, *J* 7.3 Hz, 4H), 1.66 (pent, *J* 7.9 Hz, 4H), 1.41–1.18 (m, 48H), 0.89 (t, *J* 7.3 Hz, 6H); ^{1}H NMR: δ_C 169.83, 35.50, 32.14, 29.91, 29.90, 29.88, 29.85, 29.79, 29.61, 29.57, 29.40, 29.09, 24.45, 22.90, 14.31; Anal. Calcd for $C_{32}H_{62}O_3$ (494.8): C, 77.67; H, 12.63%. Found: C, 77.73; H, 12.71%.

2-Tetradecyl-3-(2-furyl)acrylic acid (4) and *cis*/*trans* 1-(2-furyl)hexadecene (5)

A round-bottomed flask equipped with magnetic stir bar and reflux condenser was charged with **2** (10 g, 8.6 mL, 104 mmol), **3** (28.4 g, 57 mmol) and KOAc (6 g, 61 mmol). The vigorously stirred mixture was heated in an oil bath set to 160 °C. After 4 h, the dark brown reaction mixture was cooled to rt whereupon it solidified. The residue was slurried with EtOAc (200 mL) and the insoluble material was removed by suction filtration and stored for later recovery of the excess palmitic acid. The ethyl acetate filtrate was evaporated *in vacuo* to a brown-colored semi-solid. It was slurried and triturated with a 1:1 mixture of EtOAc and hexanes and the insoluble light brown solid was collected and the filtrate was saved. The solid was dissolved in hot hexanes and treated with decolorizing charcoal (100 mg) and then filtered and evaporated to give **4**, colorless needles, yield 3.6%, 700 mg, mp. 82–84 °C; ^{1}H NMR: δ_H 11.14 (bs, CO_2H), 7.52 (s, 1H), 7.47 (s, 1H), 6.6 (d, *J* 2.6 Hz, 1H), 6.49 (bs, 1H), 2.68 (t, *J* 7.5 Hz, 2H), 1.50 (m, 2H), 1.25 (s, 22H), 0.88 (t, *J* 7.2 Hz, 3H); ^{1}H NMR: δ_C 174.03, 151.99, 144.51, 130.08, 126.95, 115.54,

112.29, 32.17, 30.09, 29.95 (overlapping signals), 29.91, 29.74, 29.61, 29.19, 28.05, 22.92, 14.32; Anal. Calcd for $C_{21}H_{34}O_3$ + 0.125 H_2O (336.3): C, 74.90; H, 10.25%. Found: C, 74.97; H, 10.12%.

The filtrate saved from the second slurry and trituration with a 1:1 mixture of EtOAc and hexanes was evaporated *in vacuo* leaving a brown colored semi-solid which was dissolved in hexanes (200 mL) with slight warming. The solution was passed through a cylindrical column (height 100 mm, radius 35 mm) of silica gel with elution with hexanes. The eluates containing the product were evaporated *in vacuo* to give **5**, colorless oil, yield 26%, 4.25 g, 35:65 mixture of *cis*:*trans* geometric isomers; ^{1}H NMR: δ_H 7.37 (d, *J* 1.7 Hz, 1H, *cis*), 7.31 (d, *J* 1.5 Hz, 1H, *trans*), 6.39 (dd, *J* 3.3 and 1.8 Hz, 1H, *cis*), 6.35 (dd, *J* 3.3 and 1.8 Hz, 1H, *trans*), 6.25 (d, *J* 3.6 Hz, 1H, *cis*), 6.18 (t, *J* 1.8 Hz, 2H, trans) 6.17 (dt, *J* 11.8 and 1.6 Hz, 1H, cis), 6.13 (d, *J* 3.5 Hz, 1H, *trans*), 5.56 (dt, *J* 11.9 and 7.2 Hz, 1H, *cis*), 2.44 (qd, *J* 7.5 and 1.8 Hz, 2H, *cis*), 2.18 (qm, *J* 6.9 Hz, 2H, *trans*), 1.45 (pent, *J* 7.1 Hz, 2H), 1.28 (m, 22H), 0.89 (t, *J* 6.9 Hz, 3H); ^{1}H NMR: δ_C 153.66, 153.65, 141.37, 141.35, 131.77, 130.58, 118.69, 117.44, 111.27, 111.24, 108.88, 106.03, 33.04, 32.17, 29.94, 29.93, 29.89, 29.86, 29.77, 29.76, 29.66, 29.60, 29.53, 29.50, 29.44 22.93, 14.35; Anal. Calcd for $C_{20}H_{34}O$ (290): C, 82.69; H, 11.80%. Found: C, 82.52; H, 11.87%.

2-Hexadecylfuran (1). A mixture of **5** (500 mg, 1.7 mmol), Lindlar catalyst (150 mg, 30 mol%) and EtOAc (20 mL) was shaken on a Parr™ hydrogenator under hydrogen at 15 torr. The reduction was complete in 40 min. The suspension was filtered through diatomaceous earth (Celite® 541) to remove the catalyst and the filtrate was evaporated *in vacuo* to give **1**, colorless oil, yield 98%, 490 mg; ^{1}H NMR: δ_H 7.30 (d, *J* 1.4 Hz, 1H), 6.29 (m, 1H), 5.98 (d, *J* 2.9 Hz, 1H), 2.62 (t, *J* 6.9 Hz, 2H), 1.64 (m, 2H), 1.32 (m, 2H), 1.27 (s, 24H), 0.89 (t, *J* 6.9 Hz, 3H); ^{13}C NMR: δ_C 156.97, 110.23, 104.72, 32.17, 29.94, 29.89, 29.96 (overlapping signals), 29.79, 29.61, 29.43, 28.27, 28.21, 22.92, 14.35; Anal. Calcd for $C_{20}H_{36}O$ (292): C, 82.12; H, 12.41%. Found: C, 82.26; H, 12.42%.

X-Ray Structure Determination of 4.

CCDC 1479181 (**4**) contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting CCDC 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Appendix V Manuscript Submitted for Public Release Concerning Solubility of Alcohols in Hydrocarbon Oils Drafted During SERDP SEED Project WP-2523

Alcohol Solubility in Hydrocarbon Base Oil

Matthew C. Davis

Chemistry & Materials Division, Naval Air Warfare Center, China Lake, California, 93555 USA

ABSTRACT: Twelve, small molecular weight alcohols from methanol to 1-hexanol were tested for solubility in polyalphaolefin and mineral oil. *Tert*-butanol, 1-pentanol, *tert*-pentanol and 1-hexanol could dissolve both 10 cSt PAO and mineral oil. *Tert*-pentanol and 1-hexanol could also dissolve high-viscosity PAO.

KEYWORDS: alcohols, solubility, hydrocarbons, solvents, degreasing

Industrial lubricants are most often manufactured from base oils containing an additives package. The base oils are commonly fractions from petroleum refining such as mineral oils (paraffinic and naphthenic) or they can be synthetic products such as polyol esters and polyalphaolefin (PAO). PAO are liquid hydrocarbon polymers made by the oligomerization of terminal alkene (e.g. 1-decene) followed by hydrogenation of the residual unsaturation. PAO are superior base oils as compared to mineral oils in nearly all key lubricant properties including pour point, viscosity index, volatility and both thermal and oxidative stability. Owing to these excellent properties and consistent quality, PAO base oils have gained widespread use in the manufacture of both liquid lubricants are greases for a variety of applications including crankcase oils, gas turbine oils, hydraulic fluids and roller bearings.

All such lubricated machinery must undergo periodic disassembly and inspection as part of a service schedule. The lubricant must be removed from the parts often using solvents such as trichloroethylene or mineral spirits (Stoddard solvent) in a process commonly referred to as degreasing. While these solvents are very effective they have environmental concerns and are not in keeping with the tenants of green chemistry. As part of a project to develop new degreasing solvents which might be equally effective to current technologies and less of a burden on the environment, investigations into the solubility of various organic liquids in base oils were made. It was thought that simple aliphatic alcohols could be an interesting solution as they are readily degraded by biological systems.[1,2] However, it is commonly thought that alcohols are very polar molecules and so less likely to dissolve thoroughly non-polar substances such as base oils. In this brief report, the qualitative solubility of some common, low molecular weight alcohols in a wide viscosity range of PAO along with mineral oil will be shown.

EXPERIMENTAL

PAO with kinematic viscosities of 2, 5, 10, 65 and 150 cSt (Spectrasyn™ and Spectrasyn Elite™ product lines) were obtained from the ExxonMobil Chemical Company.[3] Mineral oil USP was obtained from a local retail pharmacy. The aliphatic alcohols were obtained from Sigma-Aldrich in 99% purity and used as received. The solubility experiments were all conducted at room temperature. A clear glass test tube was charged with PAO or mineral oil (50 mg) and then alcohol (250 mg) was added. A 10X magnification hand loupe was helpful in noting changes. Upon gentle mixing, Schlieren texture was observed for hydrocarbon that dissolved in alcohol, owing to changes in density and the refraction of light during dissolution. Soluble mixtures were a single phase upon complete dissolution. Insoluble mixtures, however, appeared as an opaque emulsion during mixture returning to two phases shortly afterwards. All of the experiments were carried out similarly except for *tert*-butanol which was first melted by warming in the hand.

RESULTS AND DISCUSSION

A variety of PAO viscosities were tested since they have uses in different lubricant applications. The alcohols selected and the data from these solubility experiments are shown in the **Table**. The simplest alcohol, methanol, was unable to dissolve any hydrocarbon tested.[4] The next higher homolog, ethanol, was able to dissolve 2 cSt PAO, which is essentially the dimer of 1-decene ($C_{20}H_{46}$). The next higher homologs, 1-propanol and isopropanol, could not surpass ethanol. The isomers of butanol were interesting and were a step toward greater non-polar character. 1-Butanol was able to dissolve both 2 and 5 cSt PAO but 2-butanol lost the ability to dissolve 5 cSt PAO. Isobutanol could dissolve both 2 and 5 cSt PAO but *tert*-butanol was miscible with 2, 5 and 10 cSt PAO as well as mineral oil. The latter result is remarkable since *tert*-butanol is soluble in water yet has greater non-polar character than its isomers. Continuing on, 1-pentanol and the isomeric isoamyl alcohol showed solubility equivalent to that of *tert*-butanol (2–10 cSt PAO and mineral oil).[5] Similar to *tert*-butanol, a great leap in solubility was found in *tert*-pentanol which was miscible with all the hydrocarbons tested, 2–150 cSt PAO and mineral oil. Finally, 1-hexanol appears to represent the gateway to very non-polar character of primary alcohols since it also was soluble with all the base oils. This was unexpected when one considers that high-viscosity, 150 cSt PAO is a $(1\text{-decene})_n$ polymer with an weight average molecular weight (M_w) of ~ 9000 ($n \cong 63$).[6]

The data show a trend in that alcohols with tertiary structure provide best hydrocarbon solubility among isomers. But, another important consideration in degreasing operations is the risk of fire and as the flash points in the **Table** below show, tertiary alcohols are also the most flammable. Clearly, 1-hexanol has the highest flash point of all the alcohols tested owing to molecular weight. More importantly, branched isomers of hexanol were not necessary to achieve optimal hydrocarbon solubility.

On the horizon, the automotive industry will design engines around low viscosity crankcase lubricants (e.g. SAE 16, 6.1–8.2 cSt at 100 °C) for increased fuel economy so low molecular weight alcohols such as those studied here could become useful solvents in future degreasing processes. 1-Hexanol is produced industrially by the trimerization of ethylene followed by oxidation. However, the fascinating work by Dekishima *et al.* has shown that with genetic manipulation to extend short-chain fatty acid biosynthesis,

E. coli can produce 1-hexanol from glucose.[7,8] So microbial fermentation could eventually become a sustainable source for 1-hexanol and other useful medium-chain alcohols in the future.

REFERENCES

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2. *SIDS Initial Assessment Report for SIAM 22 for Long-Chain Alcohol (Tome 1 and 2)*, The Organization for Economic Co-operation and Development (OECD) 2006, retrieved from http://webnet.oecd.org.

3. Unless otherwise noted, kinematic viscosity values are reported at 100 °C which is the standard convention in the lubricants field.

4. These hydrocarbon base oils are mixtures within a molecular weight range which give a certain viscosity. Those alcohols which are described as insoluble may have dissolved lighter components of a base oil but such a detailed analysis was beyond the scope of this preliminary study.

5. From the *tert*-butanol and 1-pentanol data, the average molecular weight of the generic mineral oil was approximately that of a 10 cSt PAO since solubility in the latter was the indicator for mineral oil solubility.

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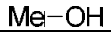
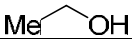
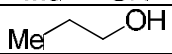
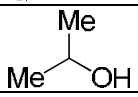
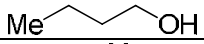
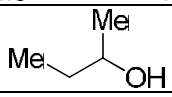
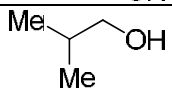
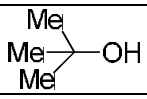
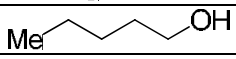
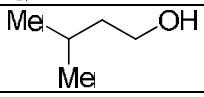
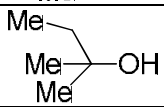
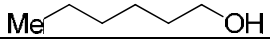
9. Collected from Safety Data Sheets made available from Sigma-Aldrich

Table. Solubility of Alcohols in Hydrocarbon Base Oil; Flash Point and Structure of the Alcohols.

			PAO (cSt @ 100 °C)					
Alcohol	Structure	Flash Point (°C)[9]	2	5	10	65	150	Min. Oil
methanol		9	i	i	i	i	i	i
ethanol		14	√	i	i	i	i	i
1-propanol		22	√	i	i	i	i	i
2-propanol		12	√	i	i	i	i	i
1-butanol		35	√	√	i	i	i	i
2-butanol		27	√	i	i	i	i	i
isobutanol		28	√	√	i	i	i	i
tert-butanol		11	√	√	√	i	i	√
1-pentanol		49	√	√	√	i	i	√
isoamylalcohol		43	√	√	√	i	i	√
tert-pentylalcohol		20	√	√	√	√	√	√
1-hexanol		60	√	√	√	√	√	√

√ = soluble; i = insoluble