

Multi-ion ionic liquids and a direct, reproducible, diversity-oriented way to make them

Alexandra C. Stenson, Kevin N. West, W. Matthew Reichert, Phiwat Klomkaew, Cody G. Cassity,
Breanna M. Dobyms, Benjamin Siu, and James H. Davis, Jr.

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Synthesis of Multi-ion IL system **1a**

A stock solution of a 1:1 (mol/mol) mixture of allyl bromide (Aldrich, 99%, Reagent Plus[®]) and n-bromopropane (Aldrich, 99%) was prepared by combining 30.64g (0.2534 mol) of the former with 31.15g (0.2534 mol) of the latter. This gives a two-component alkylating reagent which has an average molecular weight of 121.99g/mol [$\{\text{allyl bromide FW (120.98) + n-bromopropane FW (122.99)}\}/2$].

A 250 mL single-neck, round-bottomed flask was charged with a magnetic stir bar. Imidazole (7.71g, 0.1133 mol, Aldrich, 99%, Reagent Plus[®]) was then added, along with 12.02g (0.1133 mol) anhydrous Na₂CO₃ (Fisher Scientific, Lab Grade, >95%). To the mixed solids was then added 125 mL acetonitrile (Fisher Scientific, ACS Reagent Grade) and 27.65g (0.2266 moles) of the two-component alkylating reagent previously prepared (*vide supra*). The mixture was then fitted with a water-cooled condenser (capped with a CaCl₂-charged drying tube) and a heating mantle. The entire assembly was then secured to a magnetic stirrer which was then set to stir at 510 rpm. The mixture was heated to and maintained at 45° C. After 12 h a small sample of the solution was withdrawn, the acetonitrile evaporated, and the ¹H-NMR checked. It revealed conversion to be incomplete. Consequently, heating was continued for another 24 h (36 h total heating), at which time an NMR of the reaction mixture indicated that the reaction had reached completion. During the reaction period the suspended solid present (begins as Na₂CO₃) changed in appearance into a much finer-looking powder which accumulated at the flask sides (assumed to be NaBr and NaHCO₃). After cooling, the acetonitrile was removed *in vacuo*, leaving a pasty residue. A brisk stream of clean, compressed air was blown into this mass for 24 h to remove any residual molecular materials. The mixture was then taken up into 100 mL of hot, de-ionized water and stirring commenced. To this was added 40.0 g (0.125 mol) of solid KTF₂N [prepared in our laboratory by the neutralization of 80% aqueous HTf₂N (Iolitec USA) with KOH]. As the KTF₂N dissolved a copious quantity of a dense, pale-ivory liquid separated from the aqueous solution. After stirring overnight, the dense IL layer was separated, diluted with 200 mL of CH₂Cl₂, and the solution dried with anhydrous Na₂SO₄. Filtration of this suspension, followed by evaporation of the CH₂Cl₂, gave the final IL **1a**.

ADDITIONAL NOTES:

We have made **1a** and a number of other mixed-ion systems as of this writing. On occasion, when the alkylating agent mix employs an alkyl iodide, the final product has a medium to dark yellow color. This discoloration can often be diminished by dissolving the IL in methanol (specifically), heating to a boil, adding decolorizing carbon, and stirring overnight. Removal of the charcoal by filtration followed by removal of the methanol *in vacuo* gives a product with less color.

In repeated preparations of **1a** and other multi-imidazolium ion systems, we have generally found it advantageous to utilize 2.05-2.10 equivalents of the alkylating reagent relative to imidazole being employed. Even when the alkylating reagent component materials have relatively high boiling points, the excess is readily removed by the compressed-air treatment described.

For the repeat preparations of **1a**, two different batches of alkylating agent were prepared, one using reagents from TCI, and the other using TCI and Aldrich reagents together. Our aim was to introduce into the preparation opportunities for variation between the batches in order to gauge how sensitive to such variables our approach is with regard to being able to reproducibly generate a multi-ion system of consistent composition.

At the end of the reflux period, the precipitated NaBr and NaHCO₃ can be removed by filtration prior to removal of the acetonitrile *in vacuo*. However, we have not observed any improvement in the overall product quality or yield as a result of doing so.

Alkyl chlorides have been used successfully in conjunction with the present synthetic rubric. However, reactions in which they are used should be periodically assessed by NMR to gauge the extent of reaction. We have observed that reactions in which chlorides are employed can take up to 48 h to reach completion.

Procedures similar to the one used here have been reported before as a means to prepare N,N-dialkyl imidazolium salts for IL and imidazolidene-carbene applications (see references below). However, we have expressly found several of these have procedural elements that do not work well in our hands. Two of these of particular note are:

*The use of bicarbonate salts (rather than carbonate salts) as the base; in our hands, multi-ion ILs prepared in this way routinely did not reach completion, and were intractably contaminated with various partly-alkylated imidazole/imidazolium species.

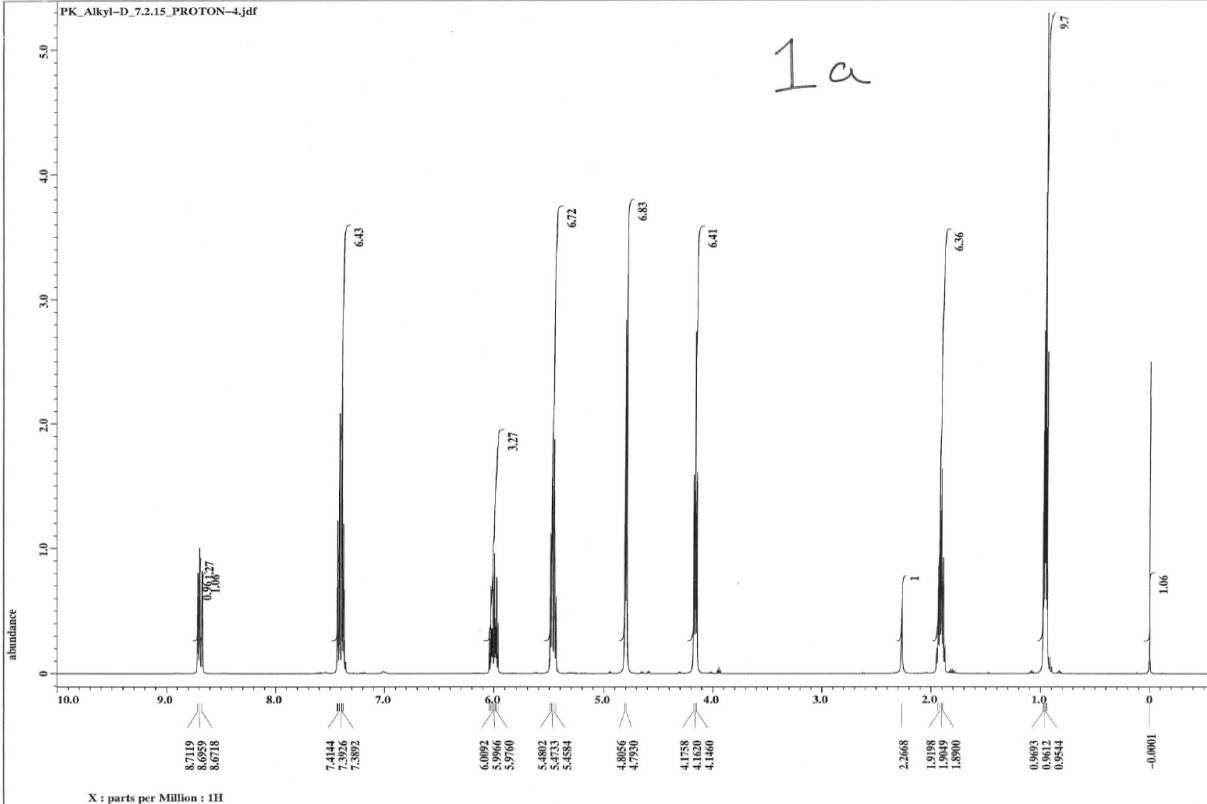
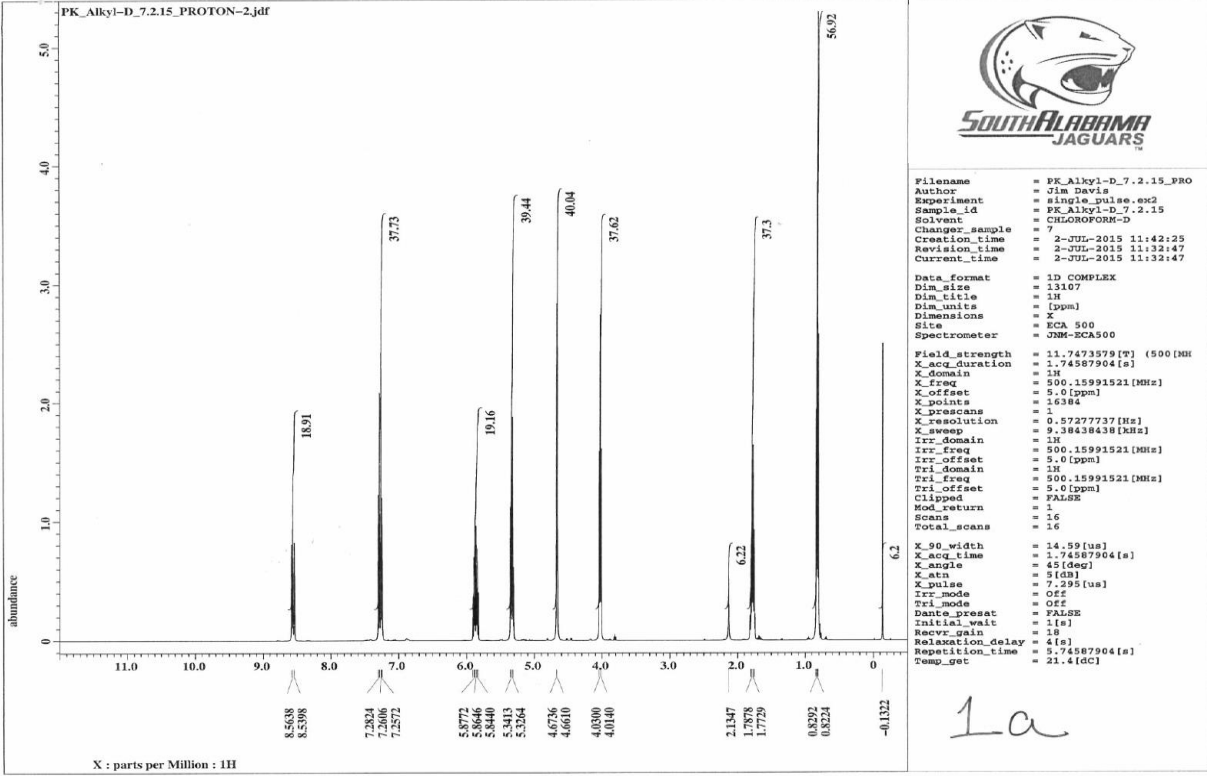
*The use of secondary alkyl halides as alkylating agents. In our hands, elimination (dehydrohalogenation) was a serious competing reaction to alkylation, and routinely led to overall incomplete alkylation and impure multi-ion mixtures.

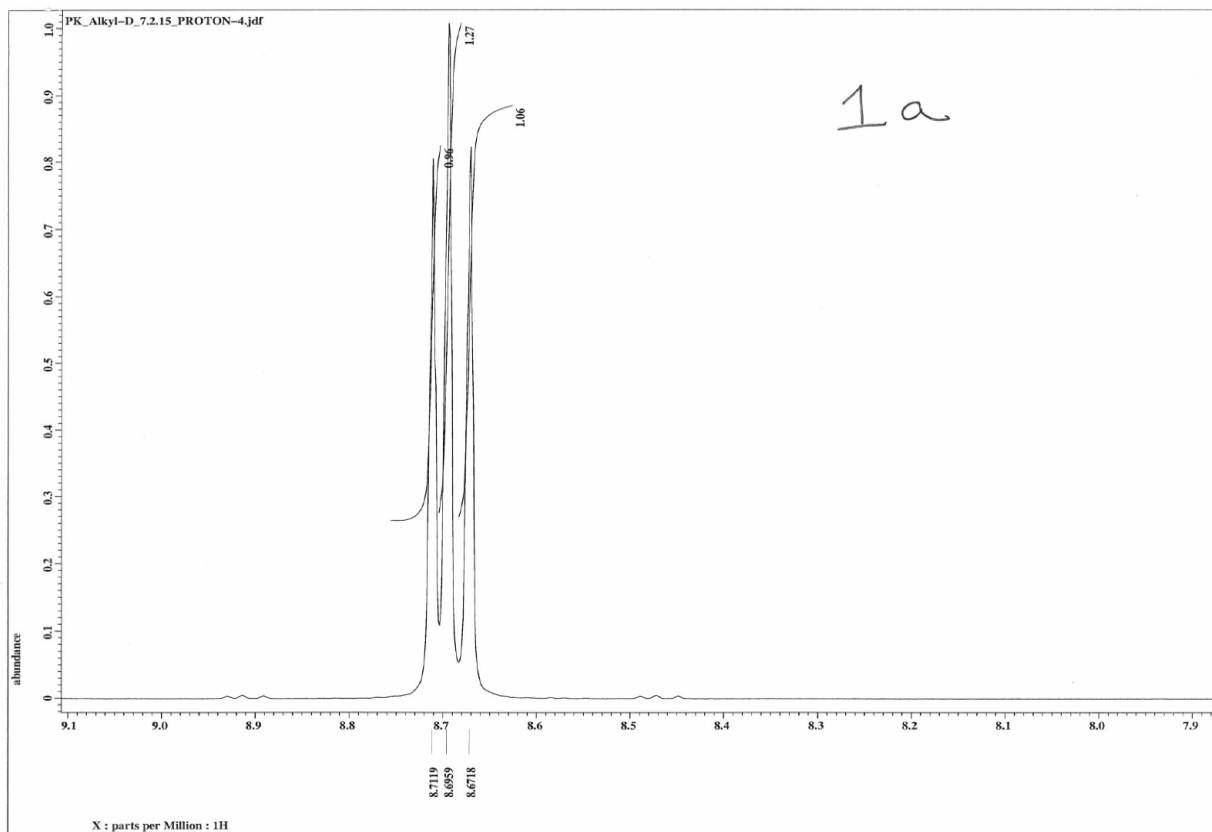
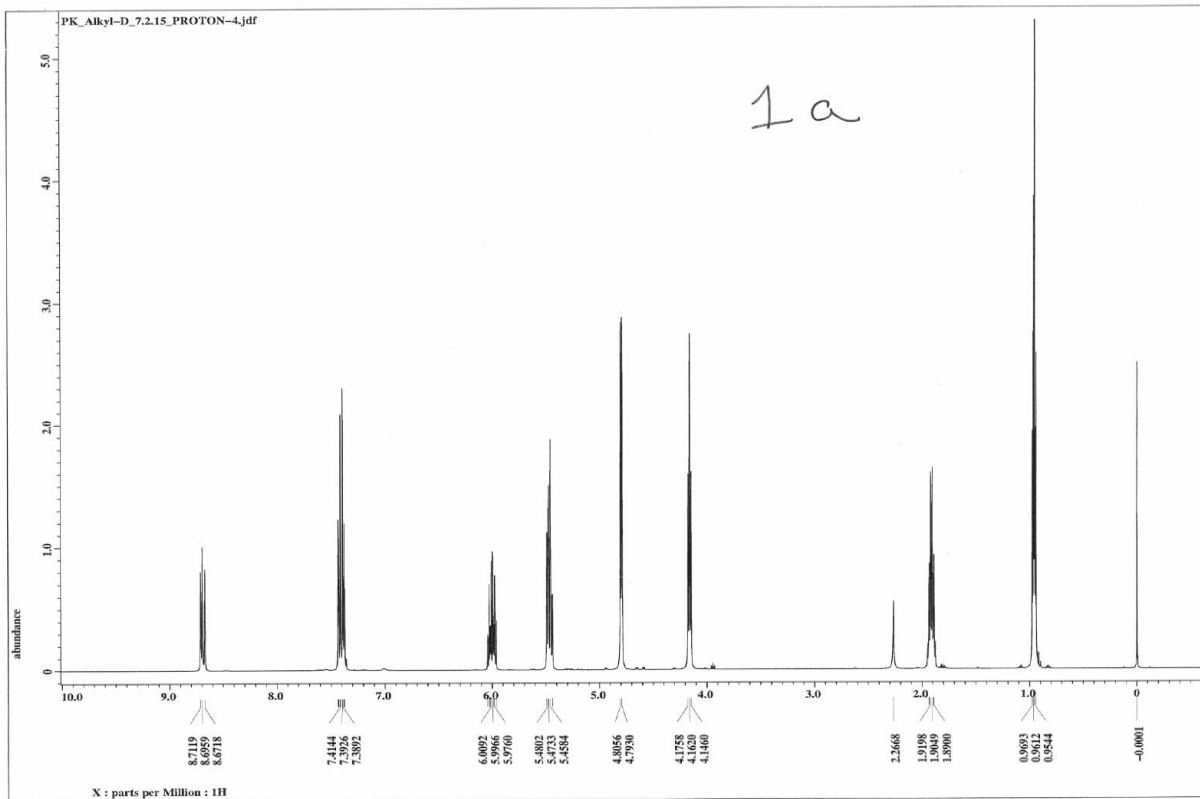
W. M. McDanel, M. G. Cowan, T. K. Carlisle, A. K. Swanson, R. D. Noble, D. L. Gin, *Polymer*, **2014**, *55*, 3305.

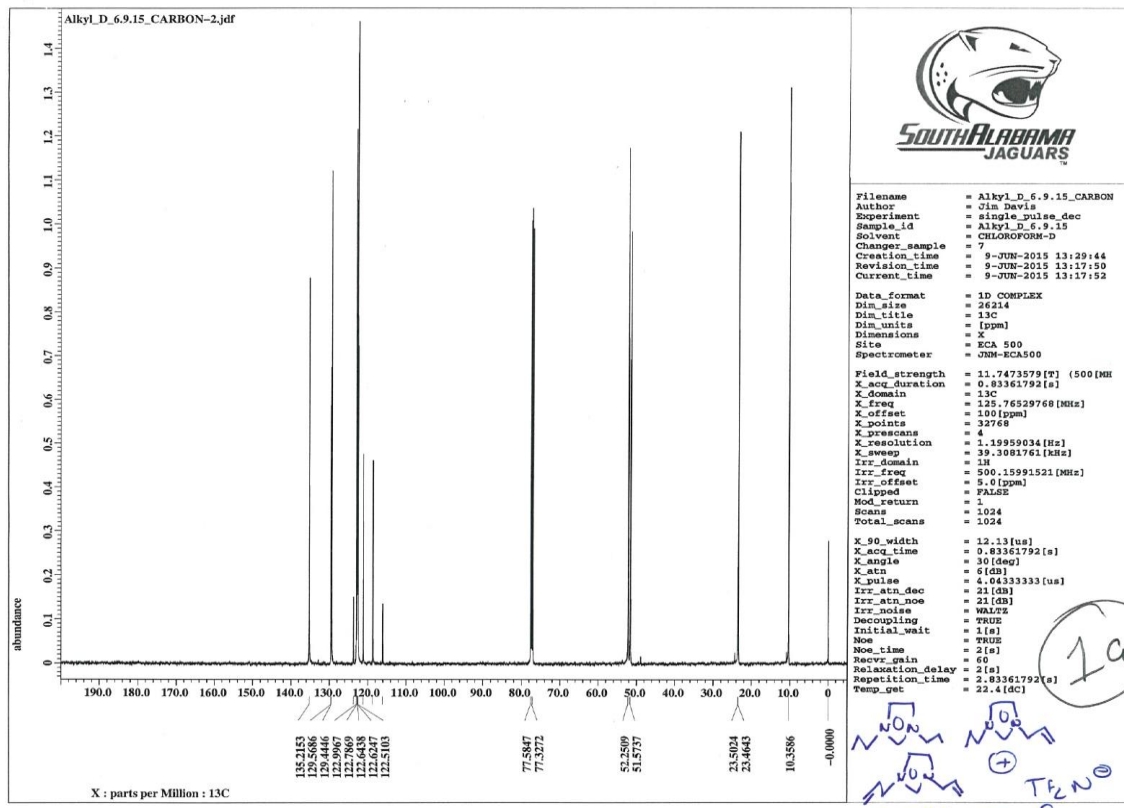
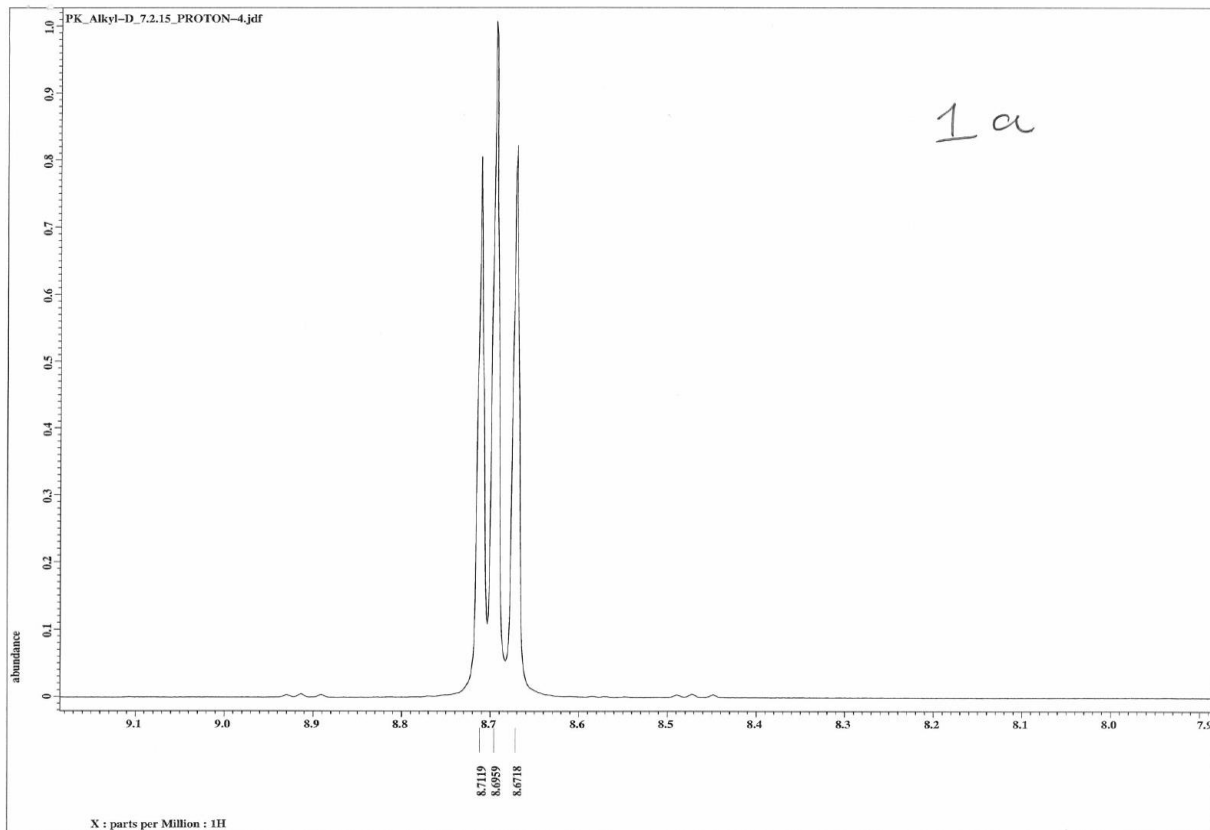
E. F. Hahn, B. Heidrich, A. Hepp, T. Pape, *J. Organomet. Chem.*, **2007**, *692*, 4630.

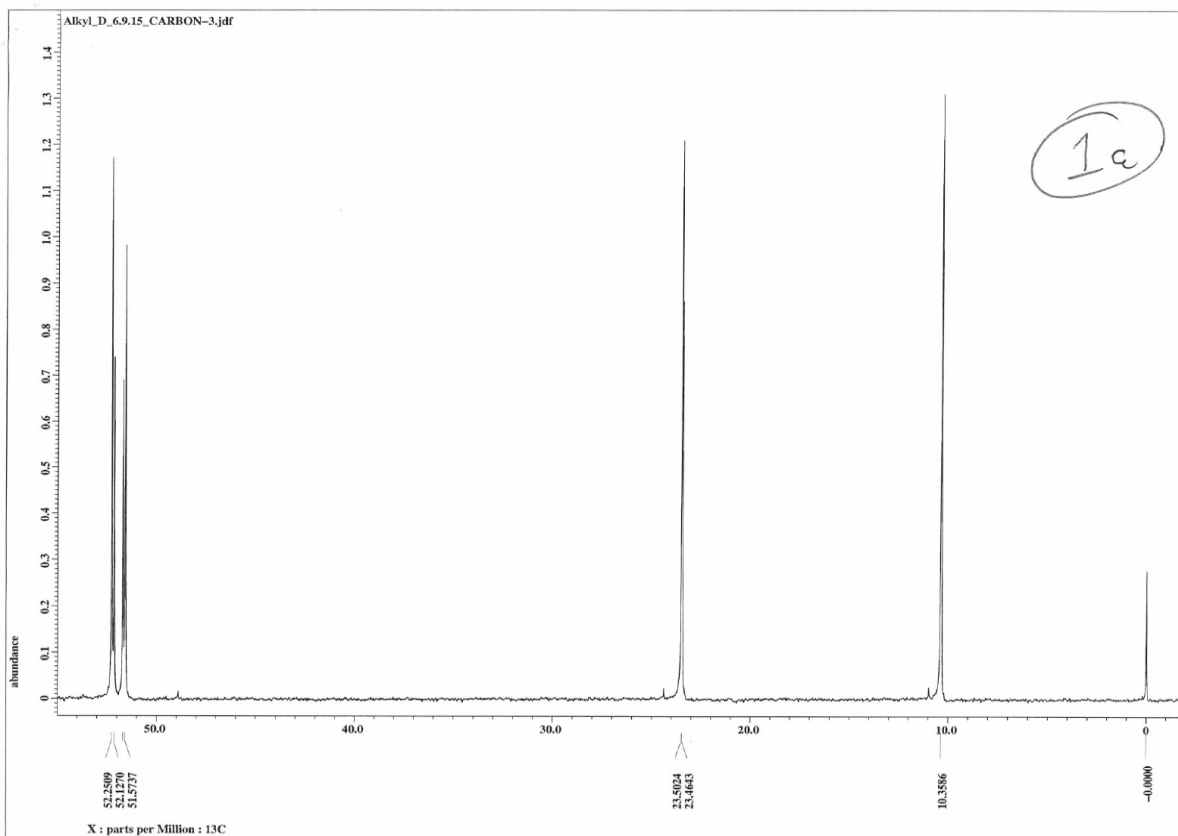
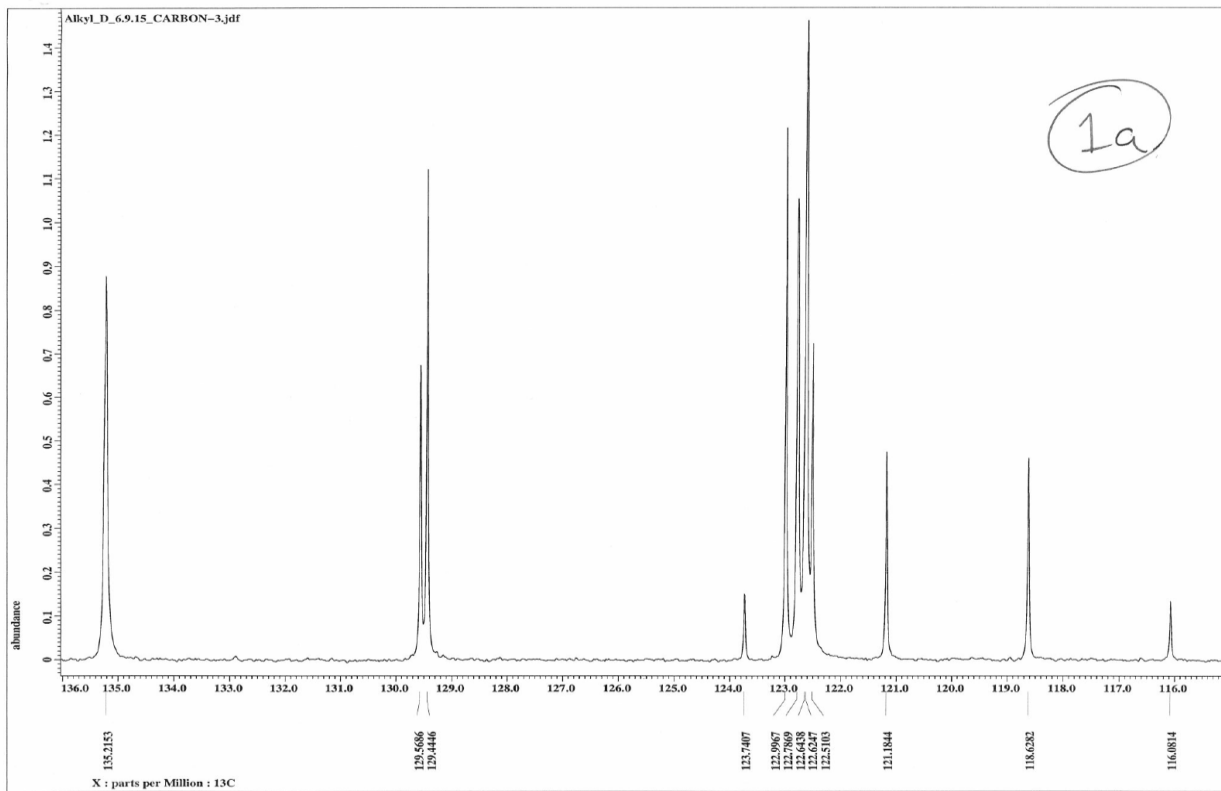
G.-H. Min, T. Yim, H. Y. Lee, D. H. Huh, E. Lee, J. Mun, S. M. Oh, Y. G. Kim, Young, *Bull. Korean Chem. Soc.*, **2006**, *27*, 847.

N. Kumar, R. Jain, *J. Heterocyc. Chem.*, **2012**, *49*, 370.



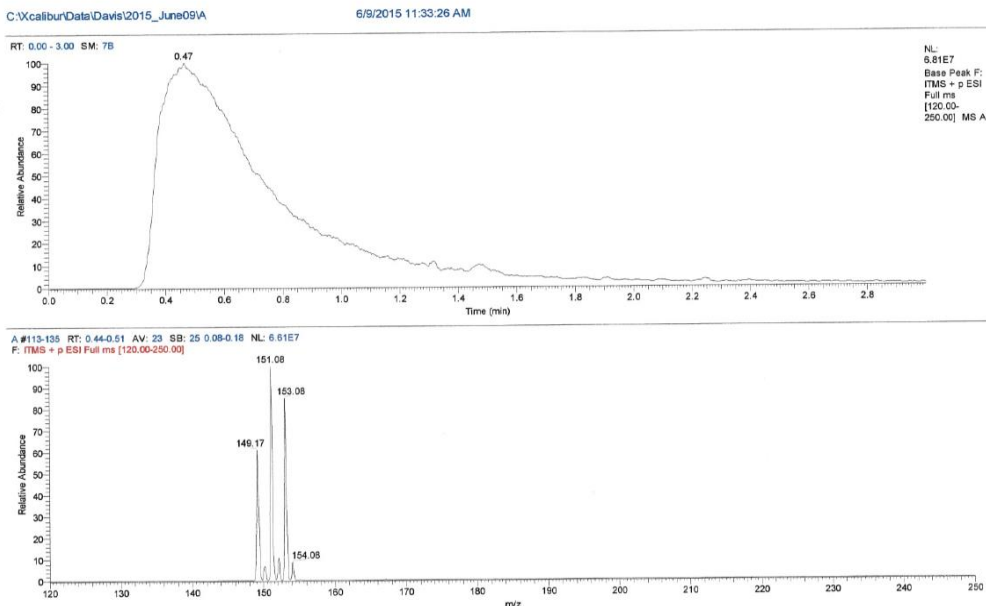






Allyl-Alkyl

1a



Atlantic Microlab, Inc.

No. JD Propyl Allyl 1 Batch A

Atlantic Blvd. Suite M
 Mobile, GA 30071
 atlanticmicrolab.com

Company/School University of South Alabama

Dept. Chemistry

Address Chem 223, USA Campus

City, State, Zip Mobile, AL, 36688

Analyst/Supervisor: Davis

Name James Davis

Date 06/04/2015

C# _____

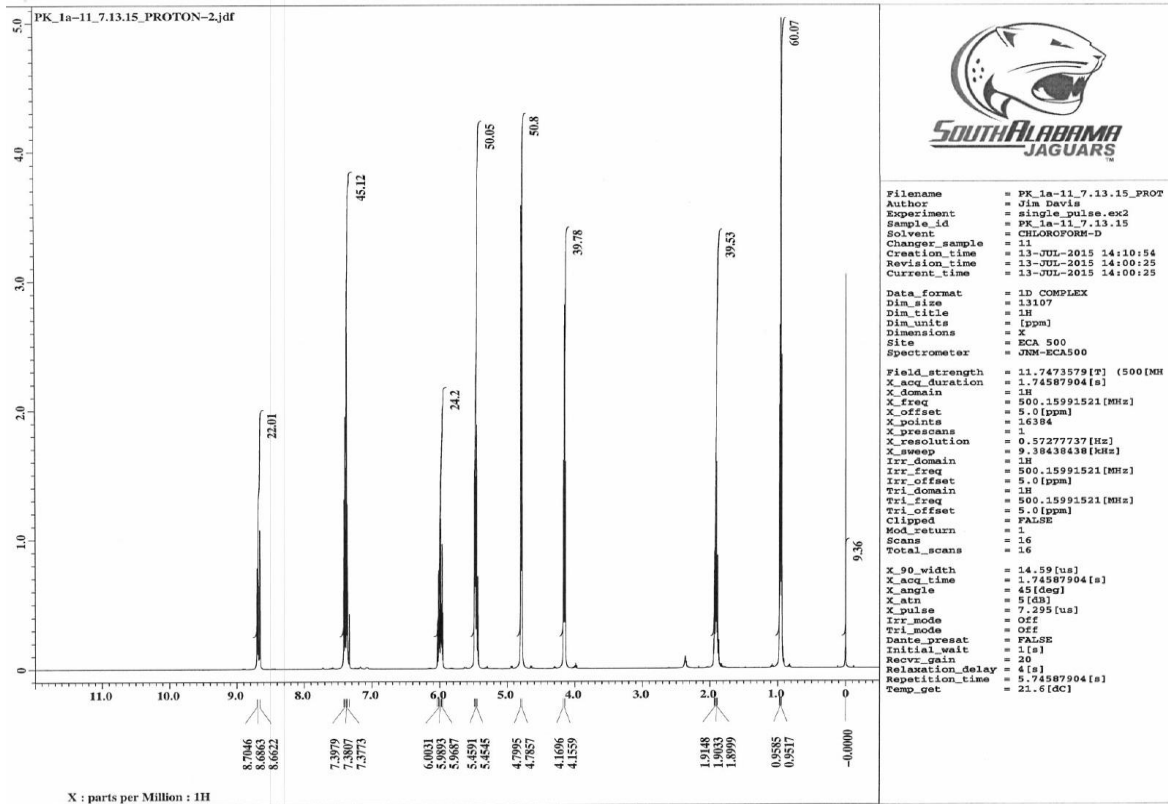
Phone (251) 751-0520

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H	3.51	3.56		
N	9.74	9.75		

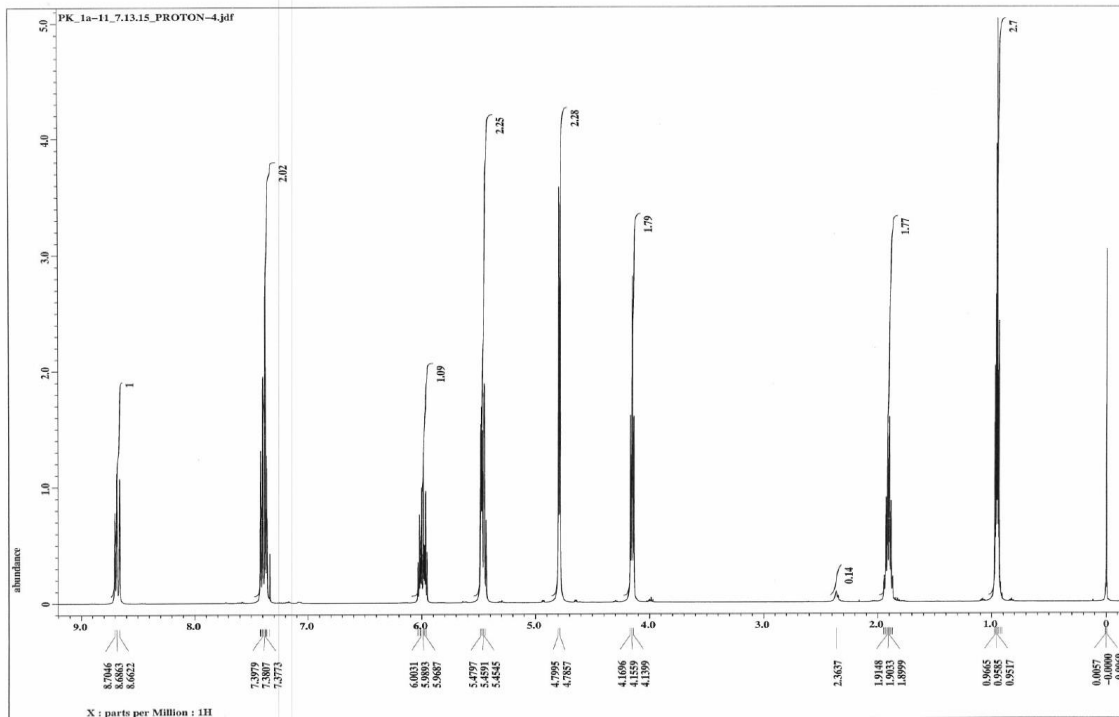
Elements C,H,N,O,S,F
 Present: _____
 Analyze CHN
 for: _____
 Hygroscopic Explosive
 M.P. LIQUID B.P. NONE
 To be dried: Yes No
 Temp. 80 Vac. HIGH Time >4 HRS
 Rush Service Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.
 Include Email Address or FAX # Below
jdavis@southalabama.edu

Received JUN 08 2015 Date Completed JUN 08 2015

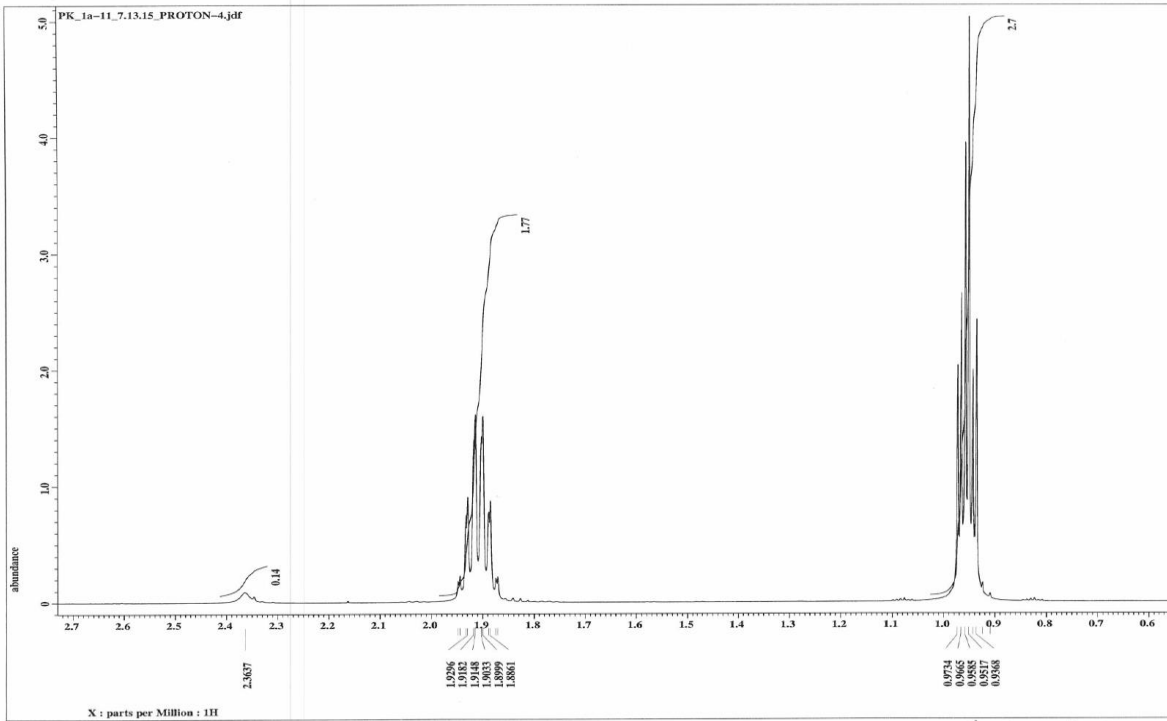
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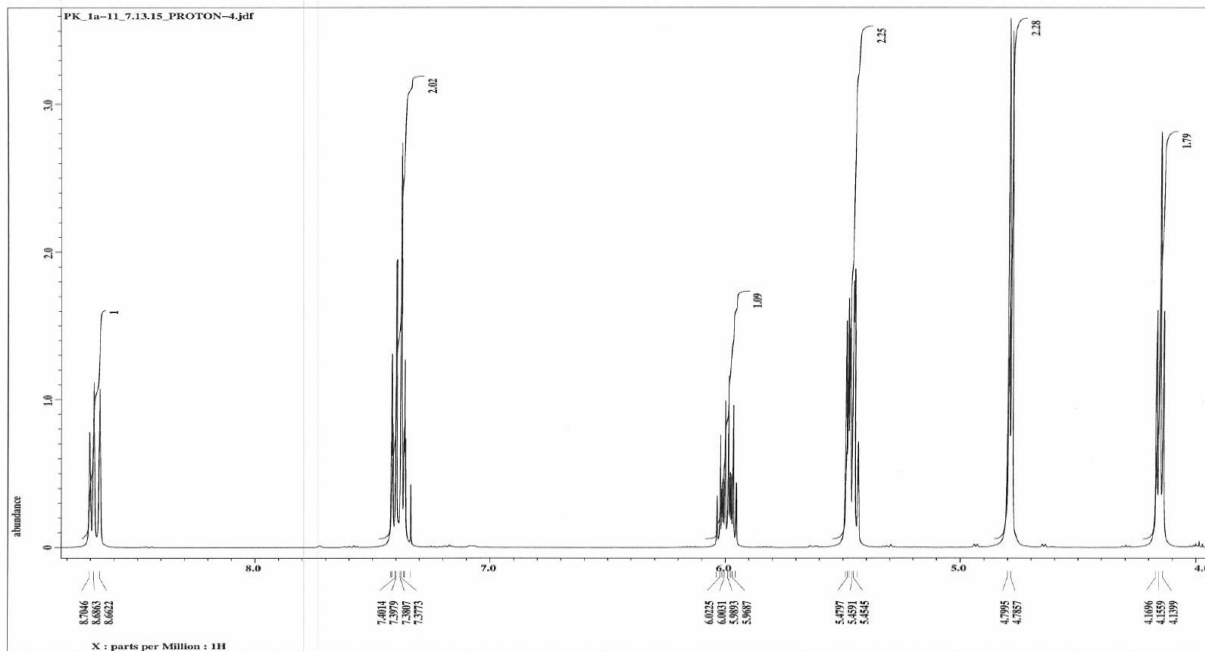
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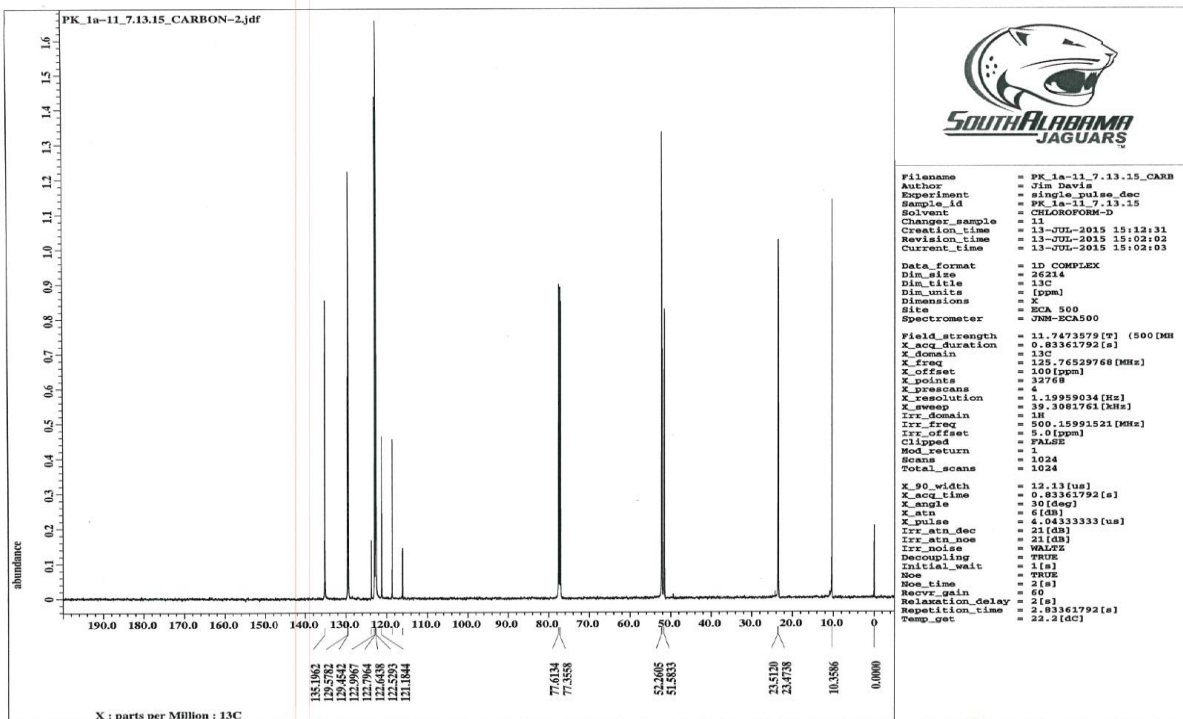
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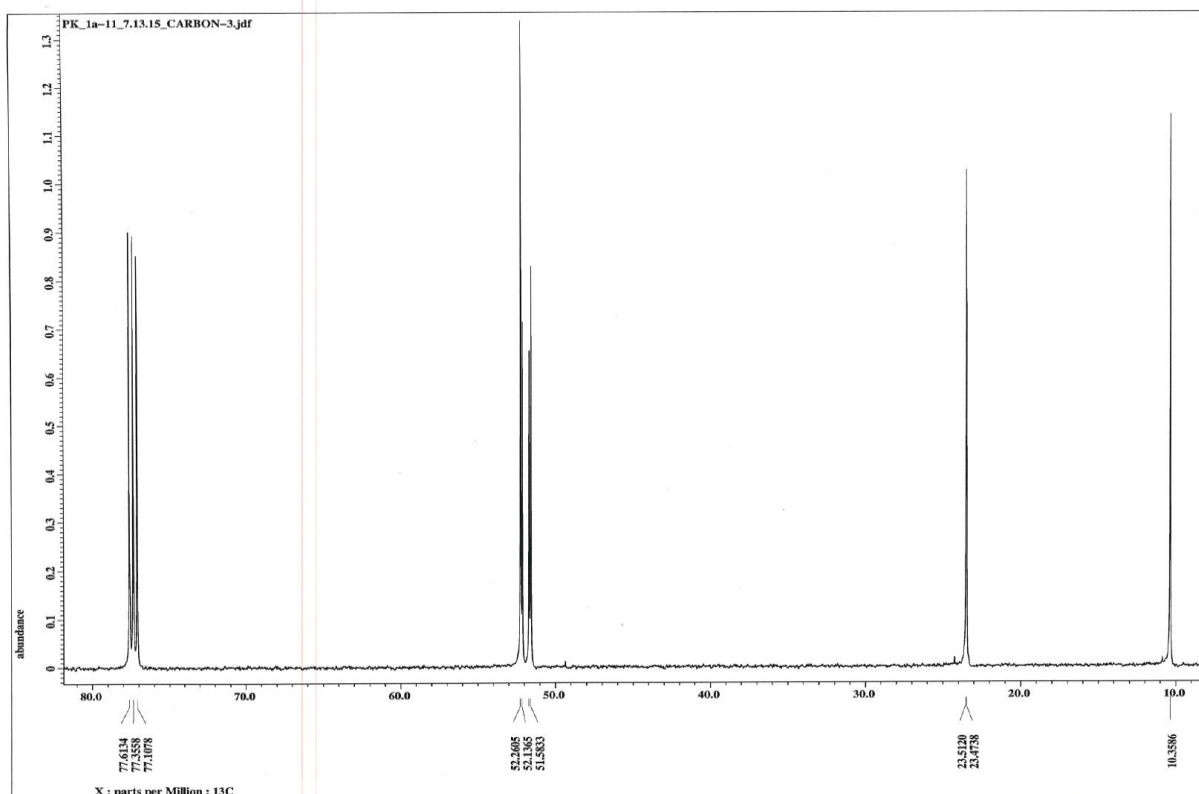
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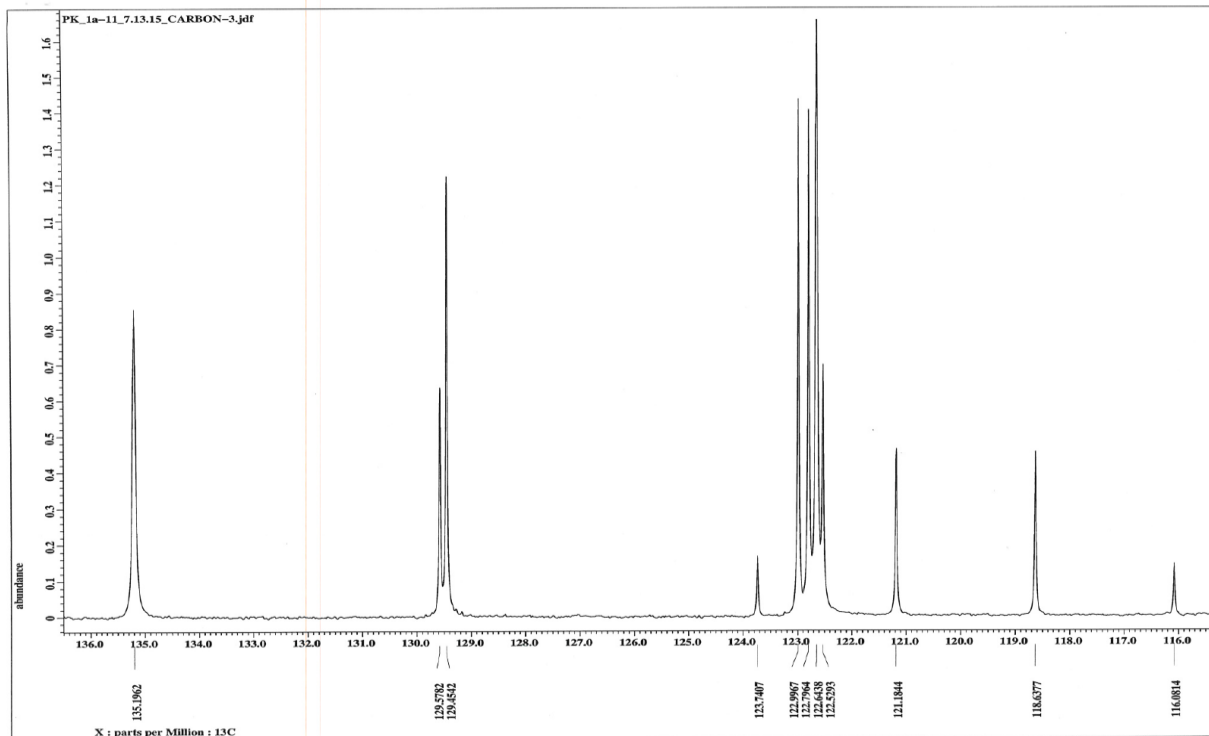
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1a b2



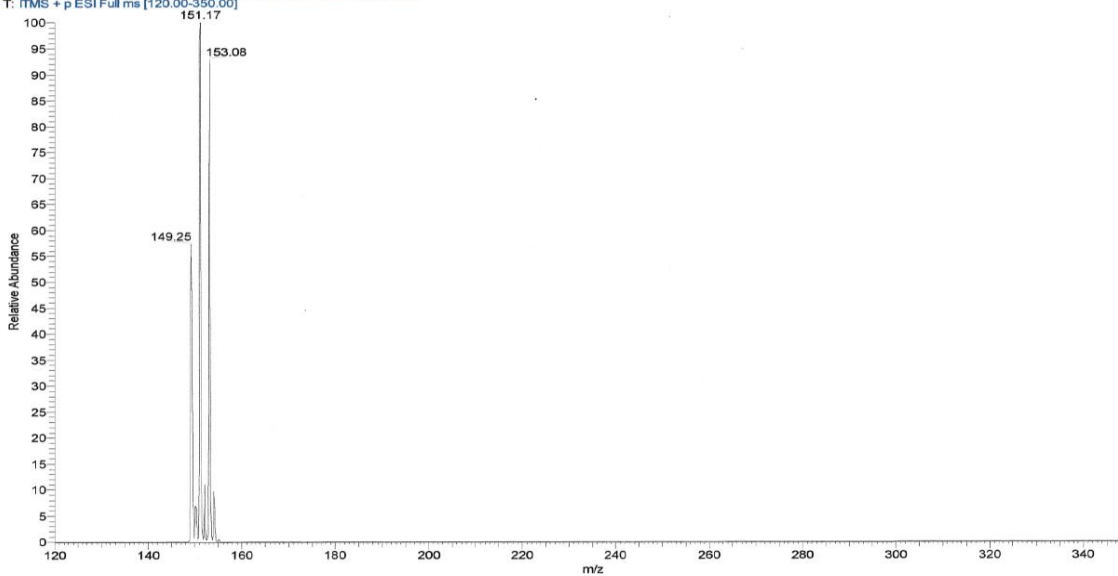
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1a b2

1a b2

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Atlantic Microlab, Inc.

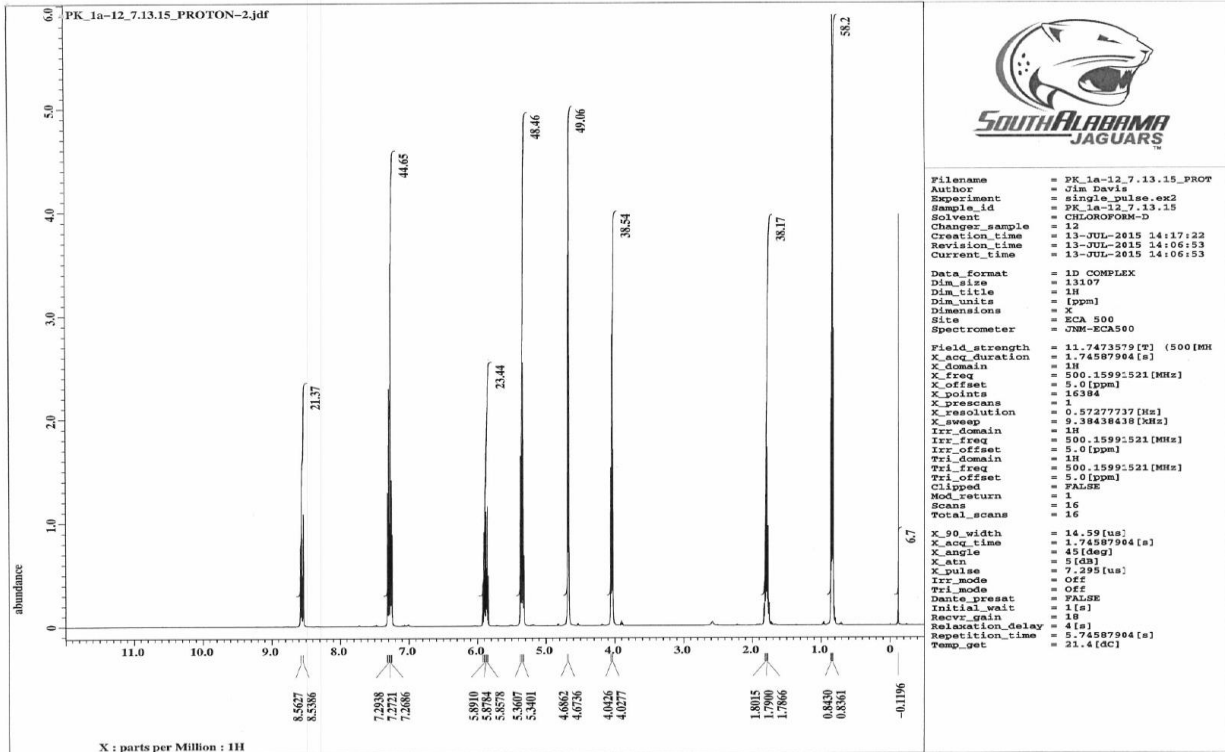
No. JD Propyl Allyl Batch B
 Atlantic Blvd. Suite M 1
 Moss, GA 30071
 atlanticmicrolab.com

Company/School South Alabama
 Dept. _____
 Address _____
 City, State, Zip _____
 Name _____ Date _____
 Phone JAMES DAVIS

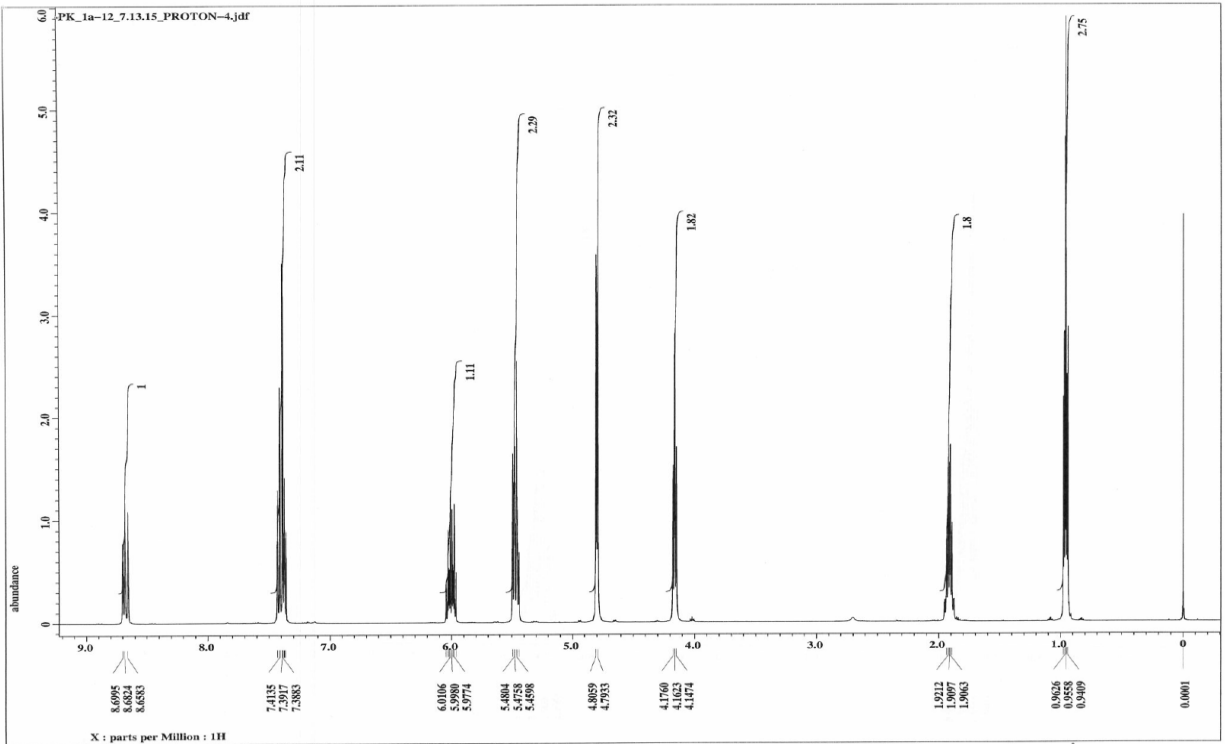
Analyst/Supervisor: Davis
 Accession #: _____

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H	3.51	3.60	<input type="checkbox"/>	<input type="checkbox"/>
N	9.74	9.56	<input type="checkbox"/>	<input type="checkbox"/>
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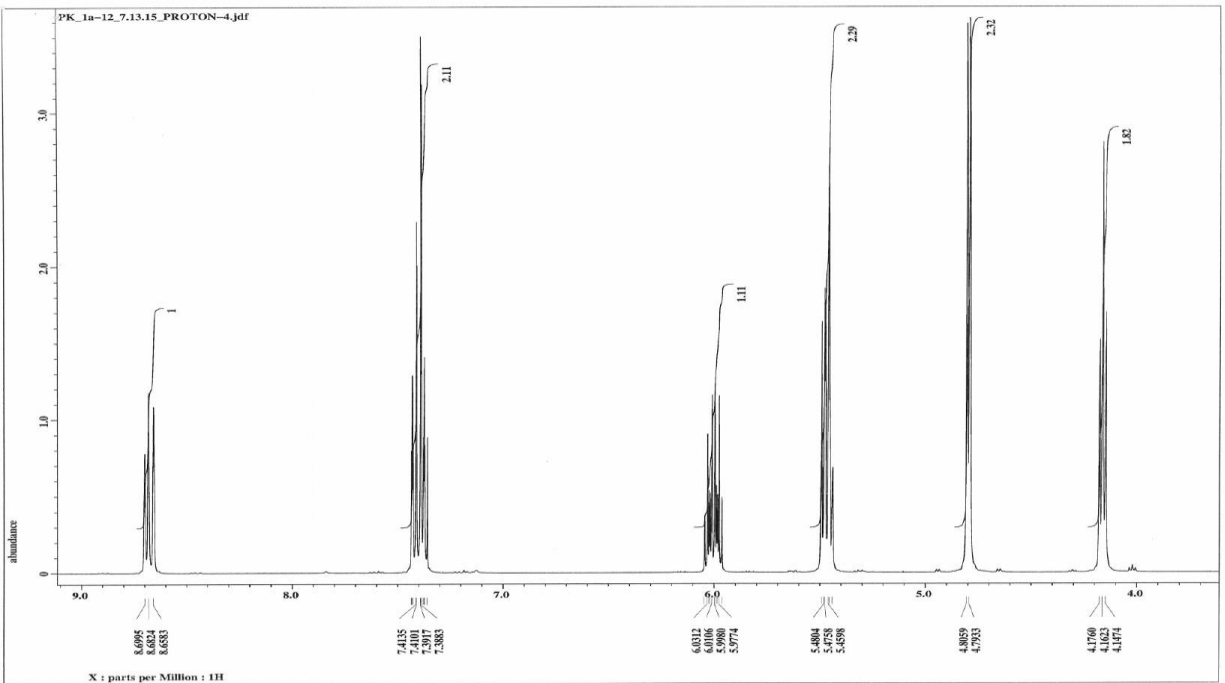
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 Remarks: 1 a batch 2



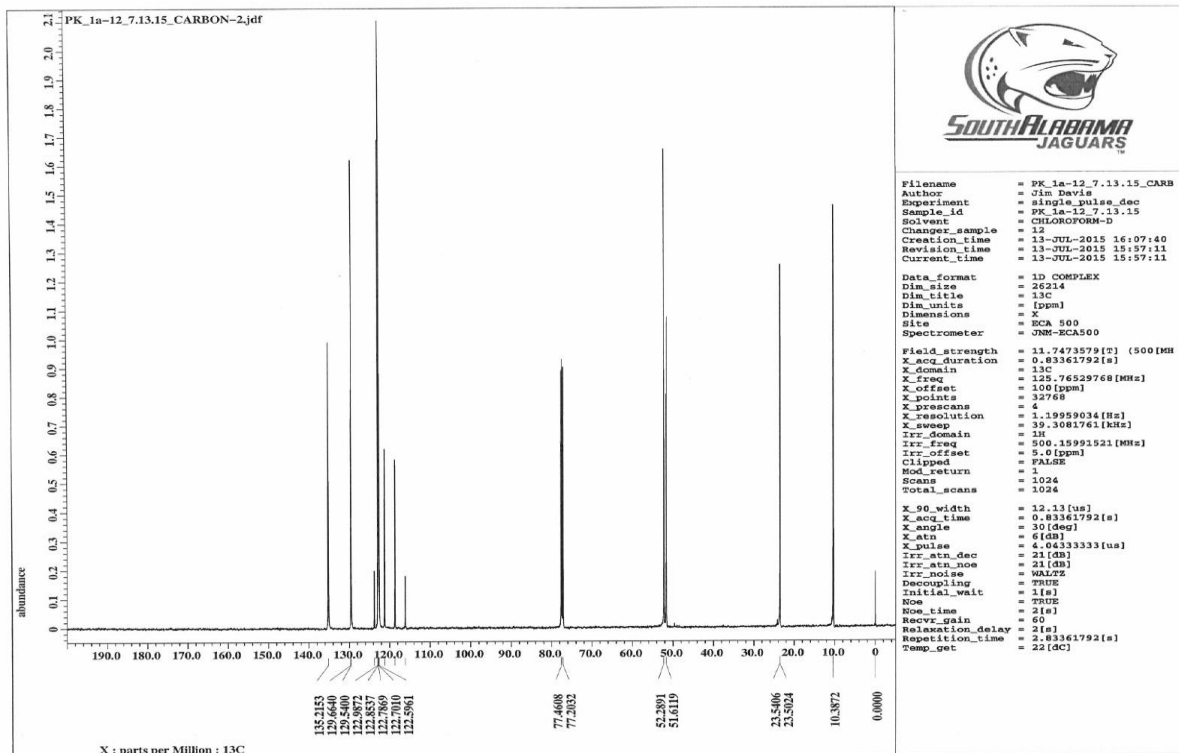
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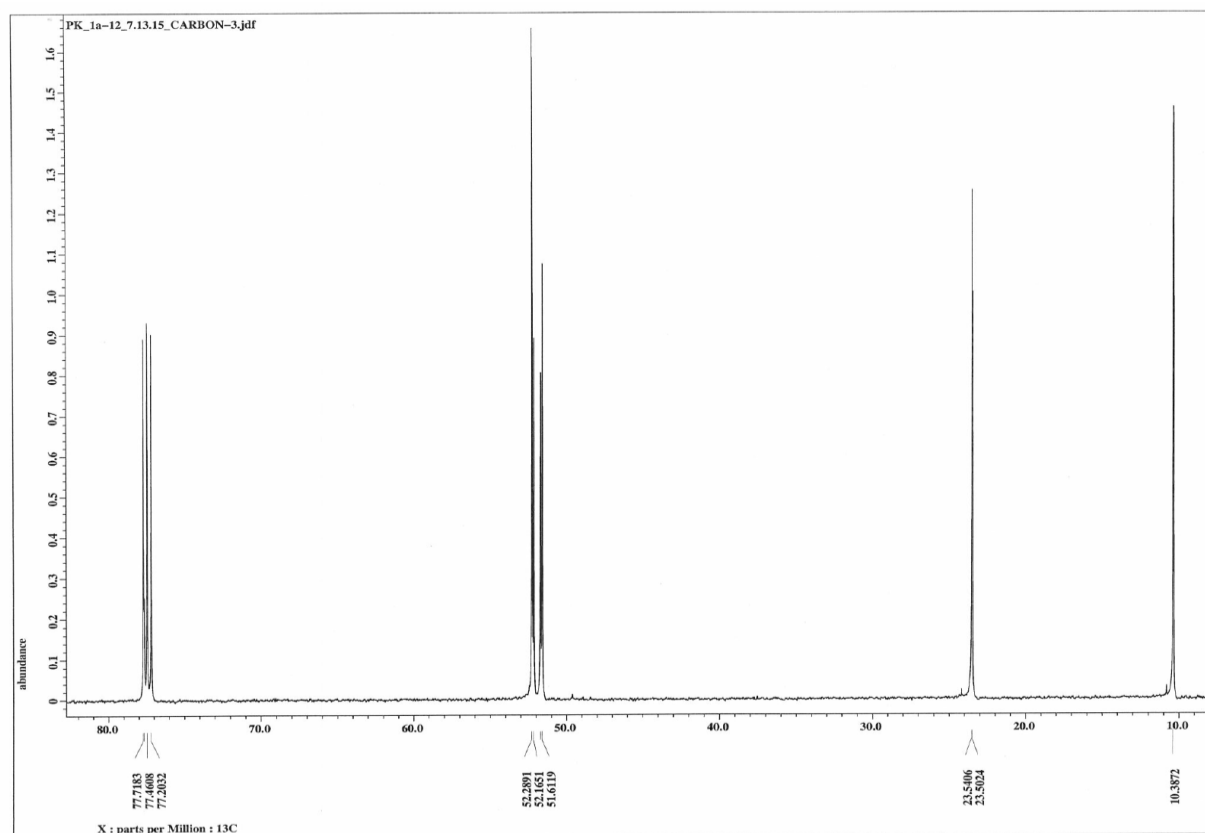
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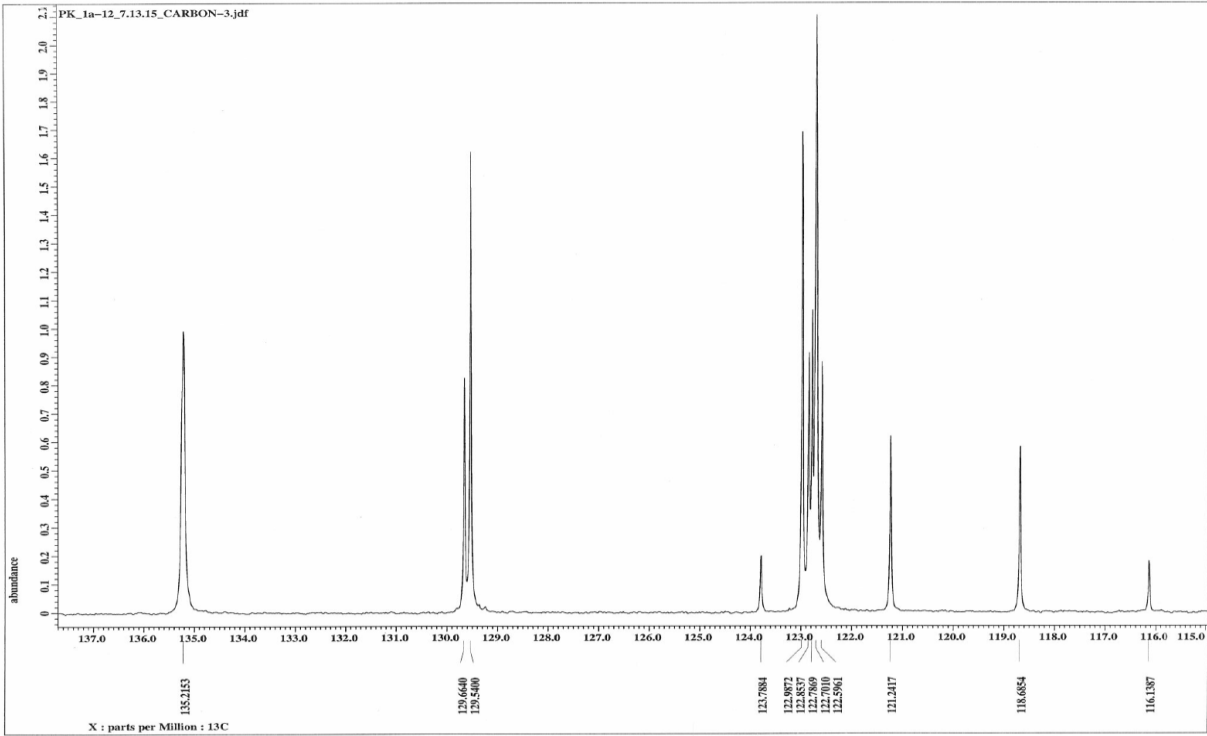
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1a b3

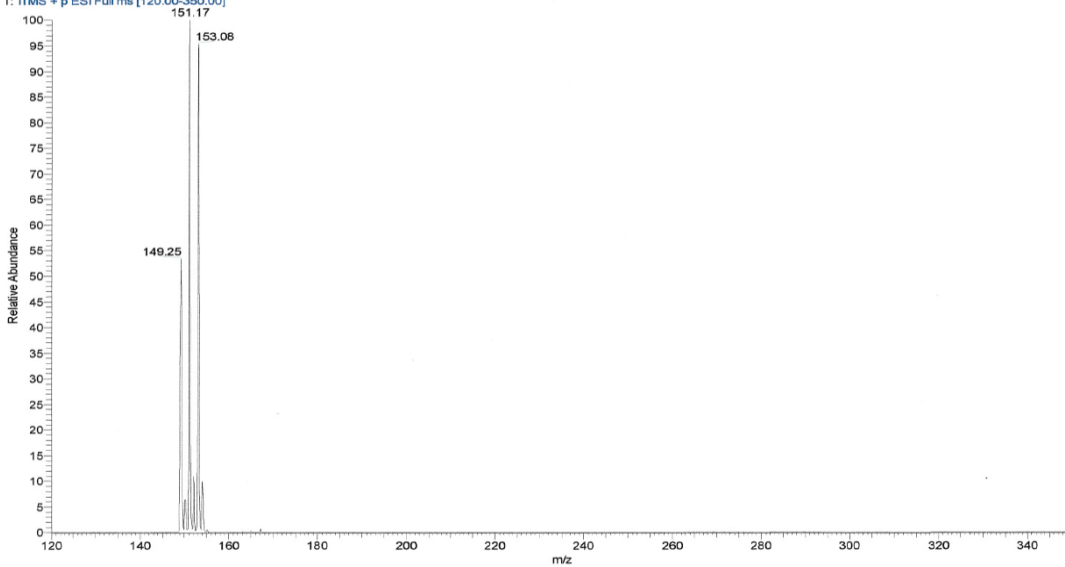


1a b3



1a b3

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T: ITMS + p ESI Full ms [120.00-350.00]



Atlantic Microlab, Inc.

No. JD (Propyl Allyl 1 Batch C)

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 atlanticmicrolab.com

Company/School University of South Alabama

Dept. Chemistry

Address Chem 223, USA Campus

City, State, Zip Mobile, AL, 36688

Analyst/Supervisor: Davis

Name James Davis Date 06/04/2015

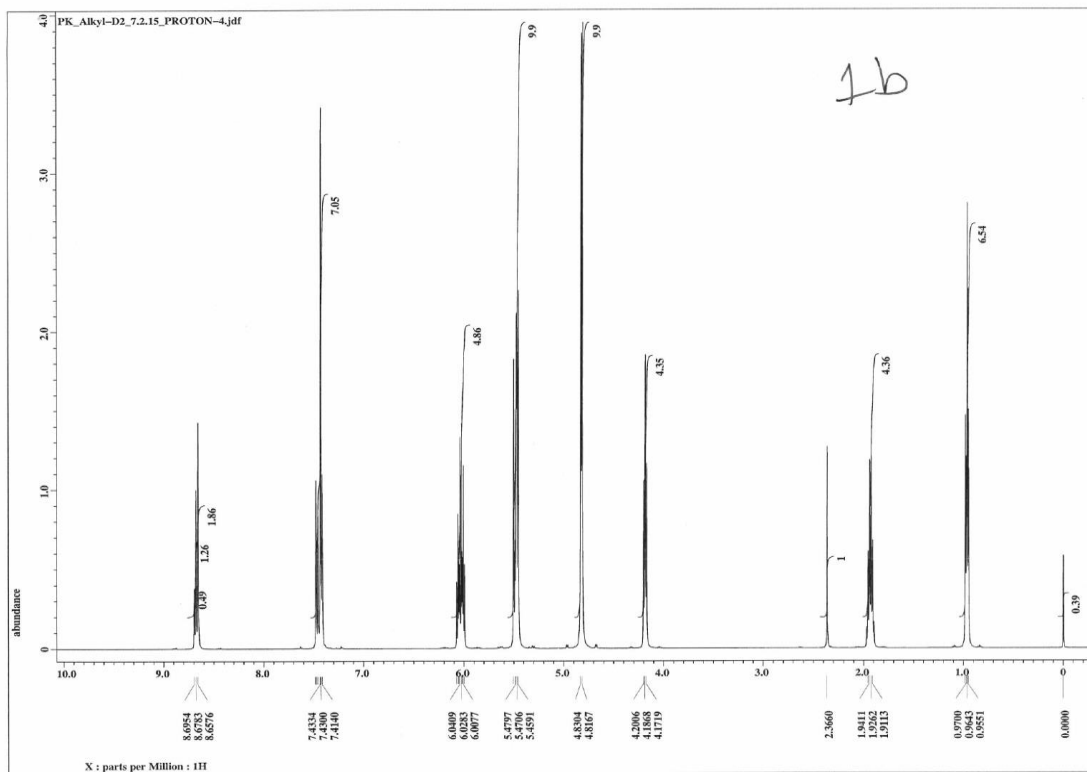
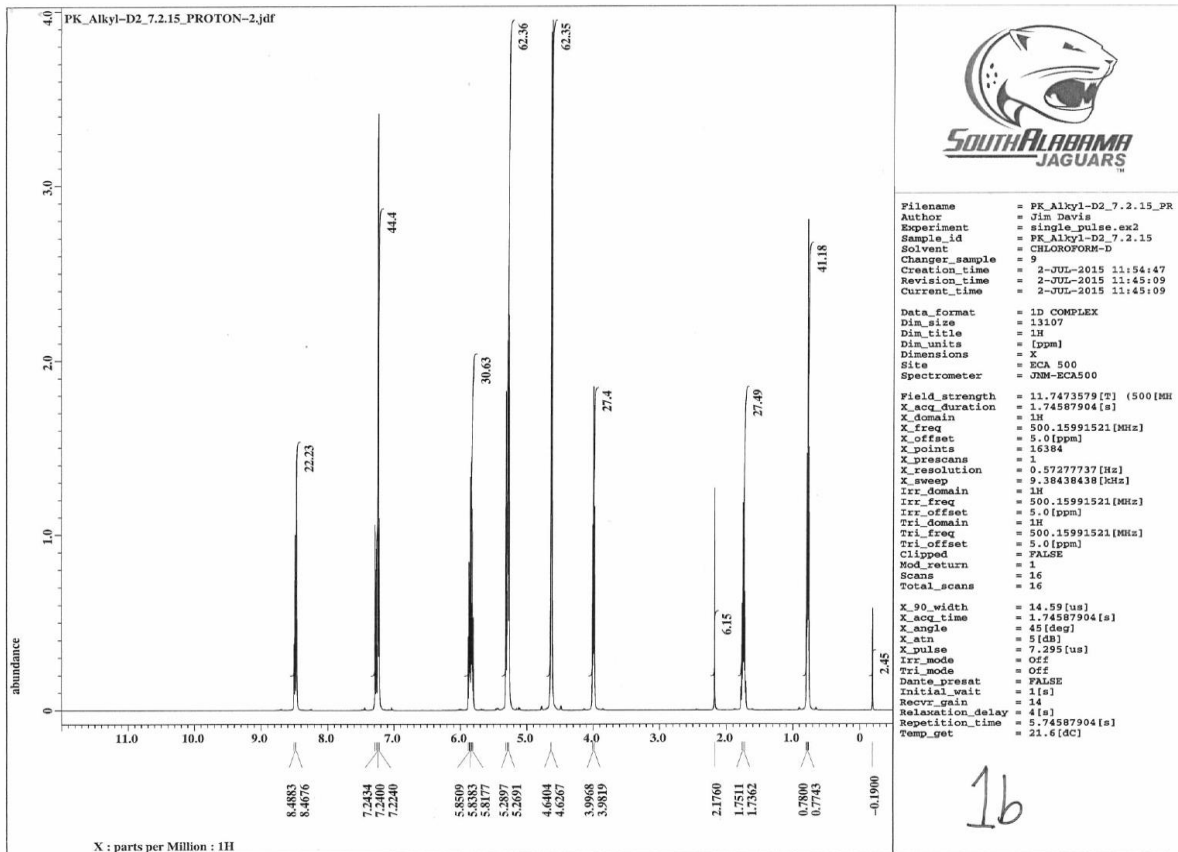
Phone # _____

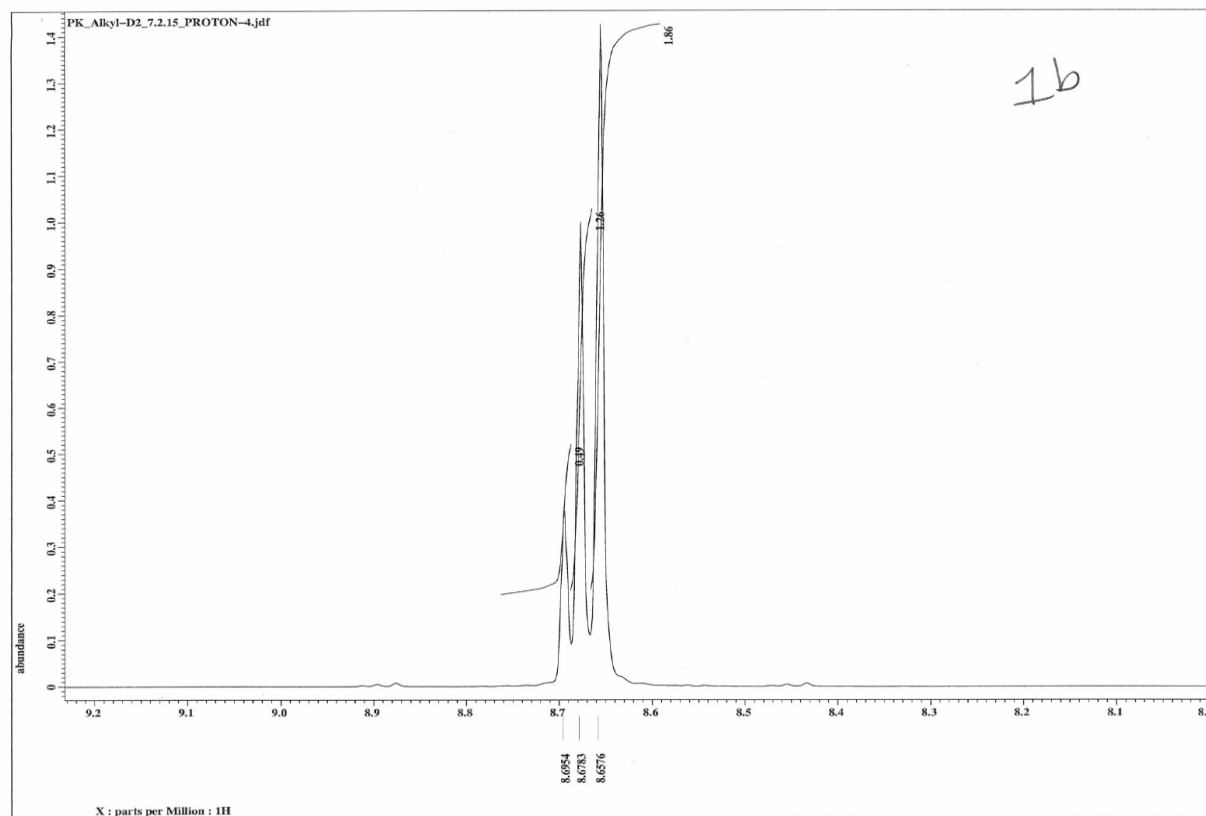
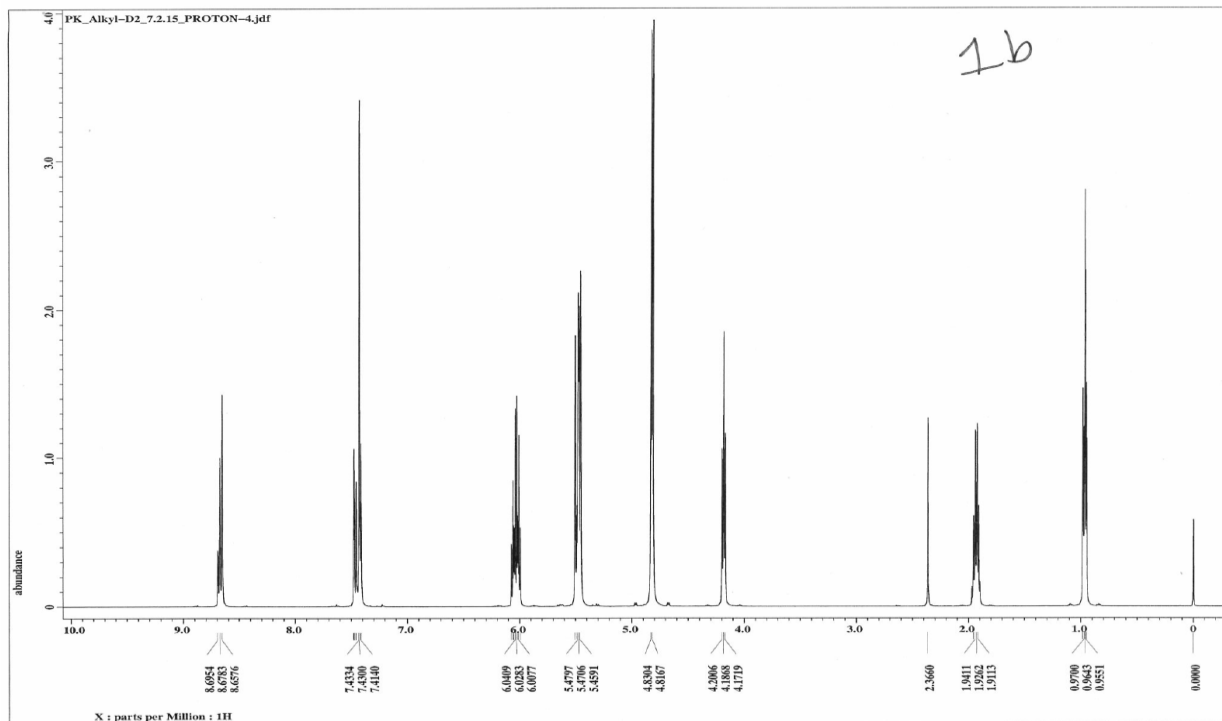
Phone (251) 751-0520

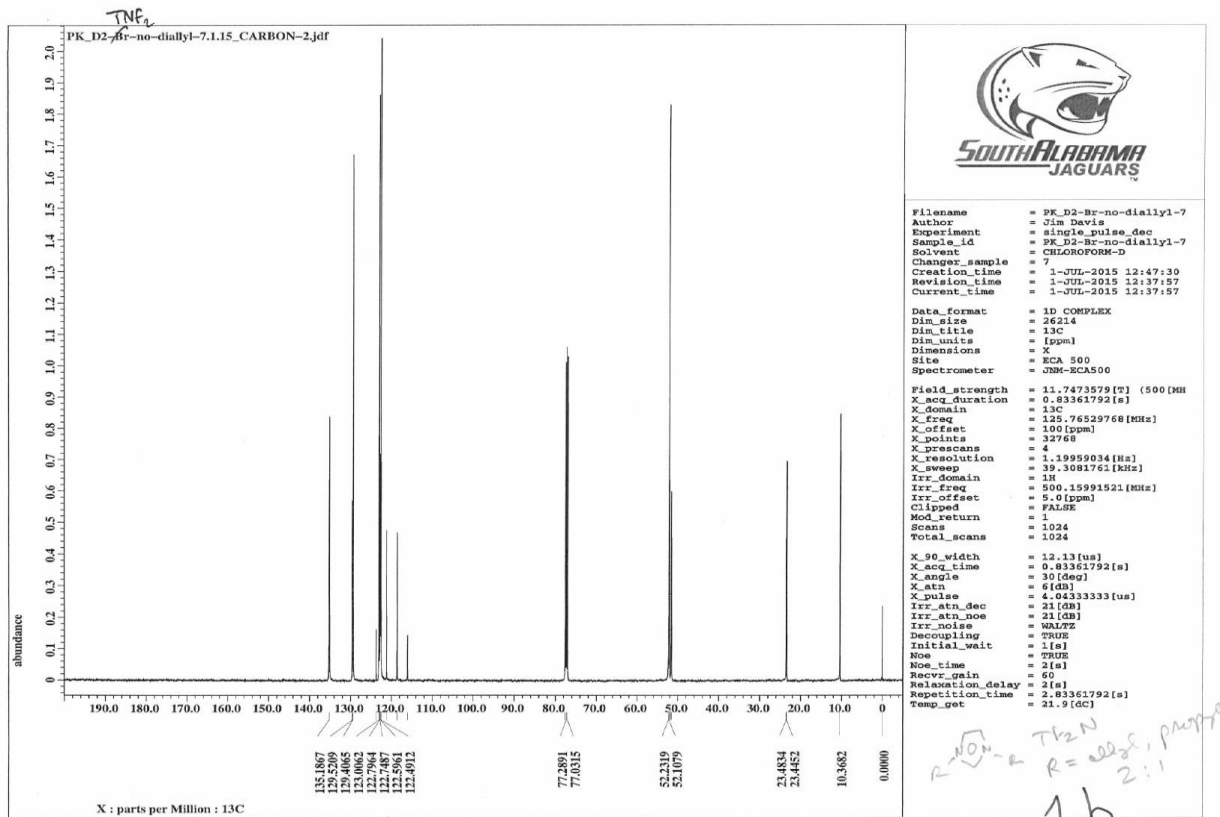
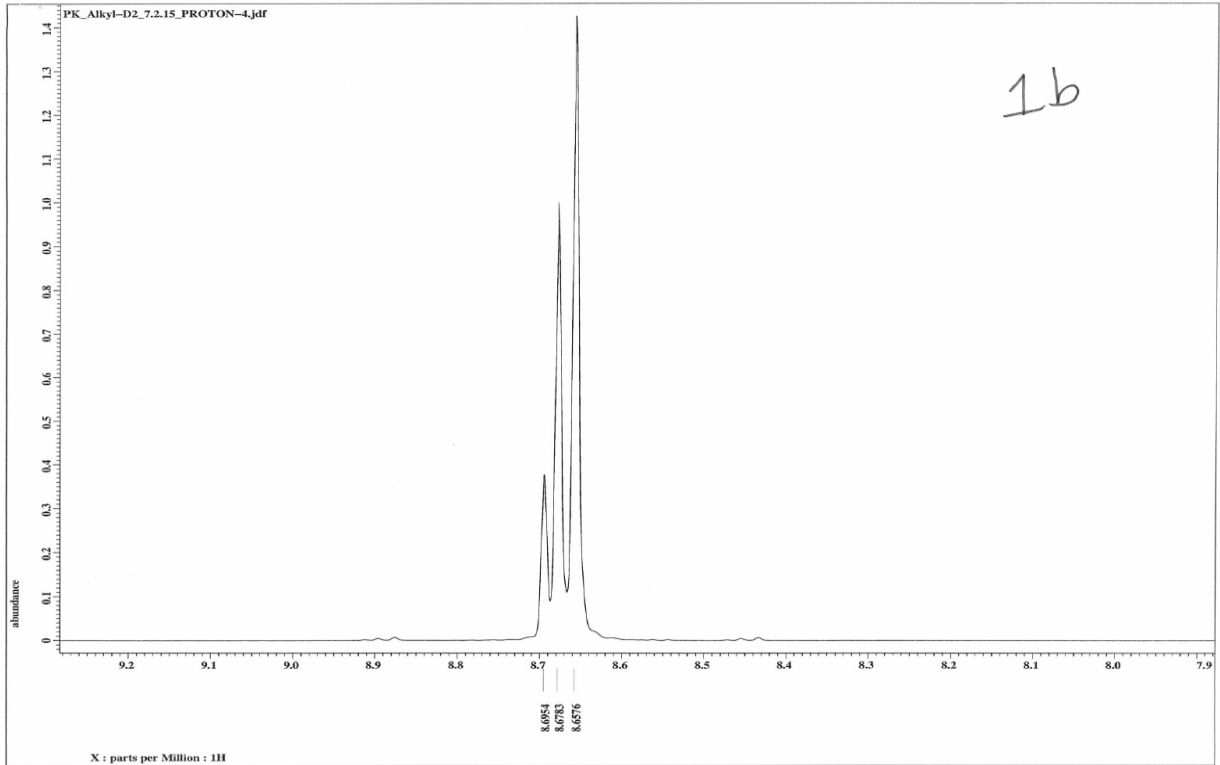
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	9.74	9.66	Hygroscopic <input type="checkbox"/> Explosive <input type="checkbox"/> M.P. <u>LIQUID</u> B.P. <u>NONE</u>	
			To be dried: Yes <input checked="" type="checkbox"/> No <input type="checkbox"/> Temp. <u>60</u> Vac. <u>HIGH</u> Time <u>>4 HRS</u>	
			Rush Service <input checked="" type="checkbox"/> <small>Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.</small>	
			Include Email Address or FAX # Below jdavis@southalabama.edu	

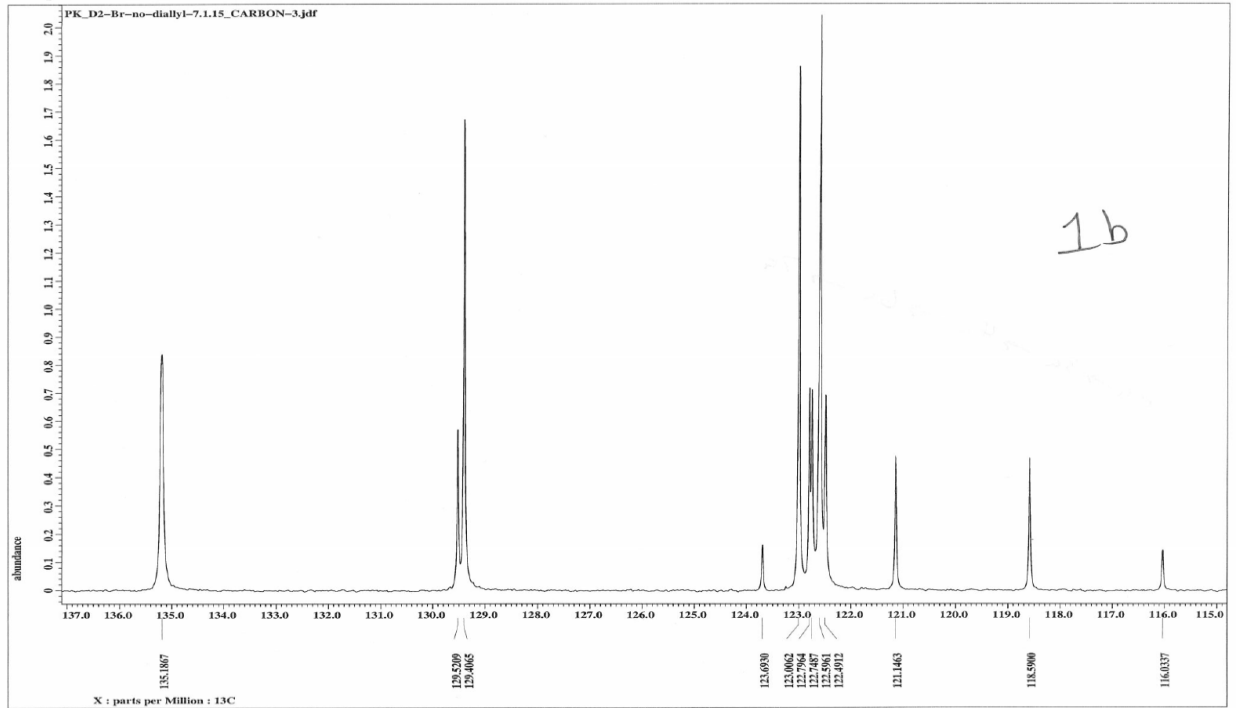
Received JUN 08 2015 Date Completed JUN 08 2015

Notes: 1 a batch, 3



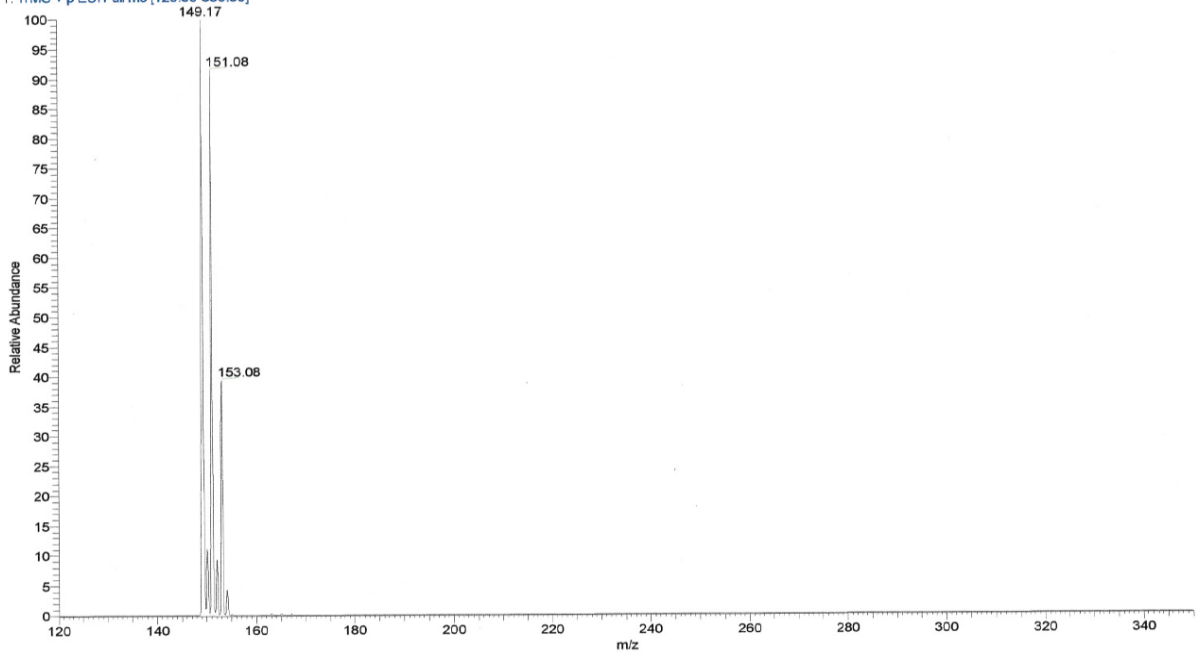






Smpl 1b

1b #87-101 RT: 0.36-0.41 AV: 15 SB: 16 0.13-0.20 NL: 4.58E7
T: FTMS + p ES/Full ms [120.00-350.00]



Atlantic Microlab, Inc.

Sample No. D-2 NT2N

Address: Atlantic Blvd. Suite M
Dallas, GA 30071
atlanticmicrolab.com

Company/School: University of South Alabama
 Dept.: Chemistry
 Address: Chem Bldg 223 6040 USA Driver South
 City, State, Zip: Mobile, AL 36688

Analyst/Supervisor: Davis
 CC#: Z 154679

Name: Jim Davis Date: 07/01/2015
 Phone: (251) 751-0520

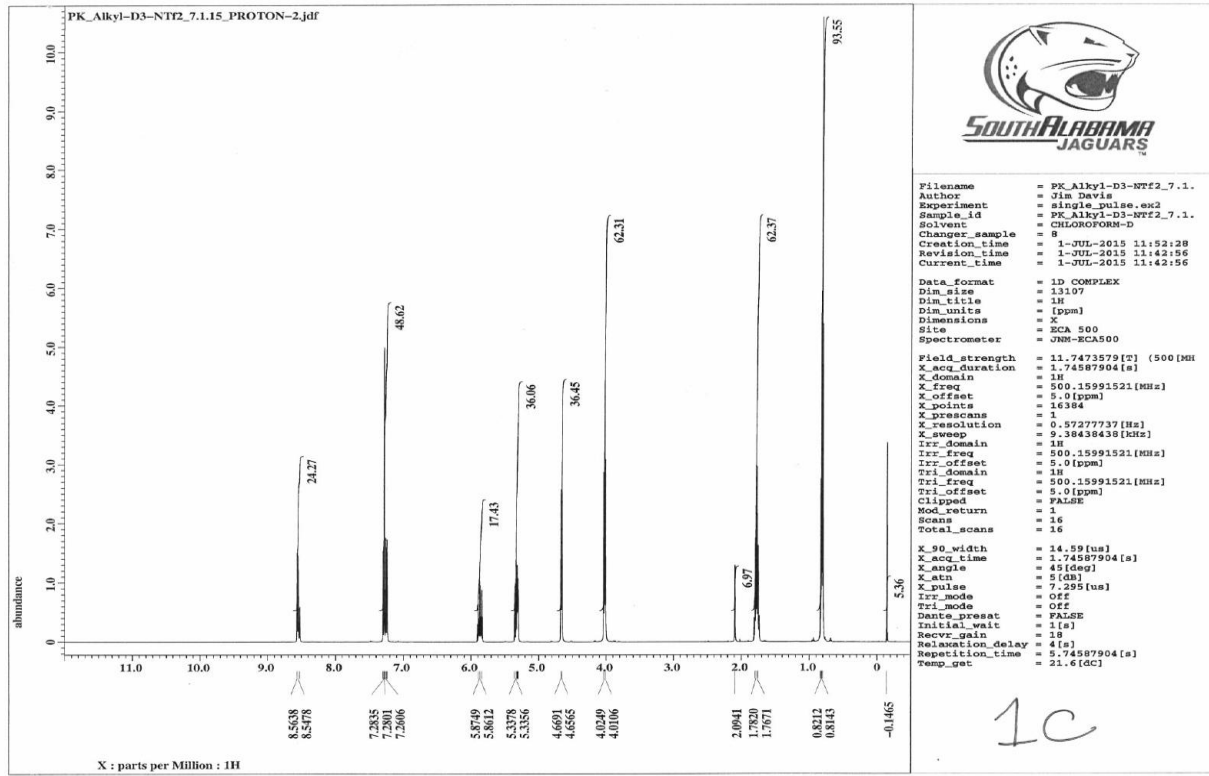
1b

Element	Theory	Found		Single <input checked="" type="checkbox"/>	Duplicate <input type="checkbox"/>
C	<u>JHD</u> 47.60	30.38	30.39	Elements CHNSOF Present: Analyze CHN for: Hygroscopic <input type="checkbox"/> Explosive <input type="checkbox"/> M.P. <u>LIQUID</u> B.P. <u>NONE</u> To be dried: Yes <input checked="" type="checkbox"/> No <input type="checkbox"/> Temp. <u>80C</u> Vac. <u>HIGH</u> Time <u>4HRS</u> Rush Service <input checked="" type="checkbox"/> <small>Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.</small> Include Email Address or FAX # Below jdavis@southalabama.edu	
H	<u>JHD</u> 5.92	3.22	3.20		
N	<u>JHD</u> 13.40	9.69	9.67		
NO CHARGE FOR DUPLICATES					

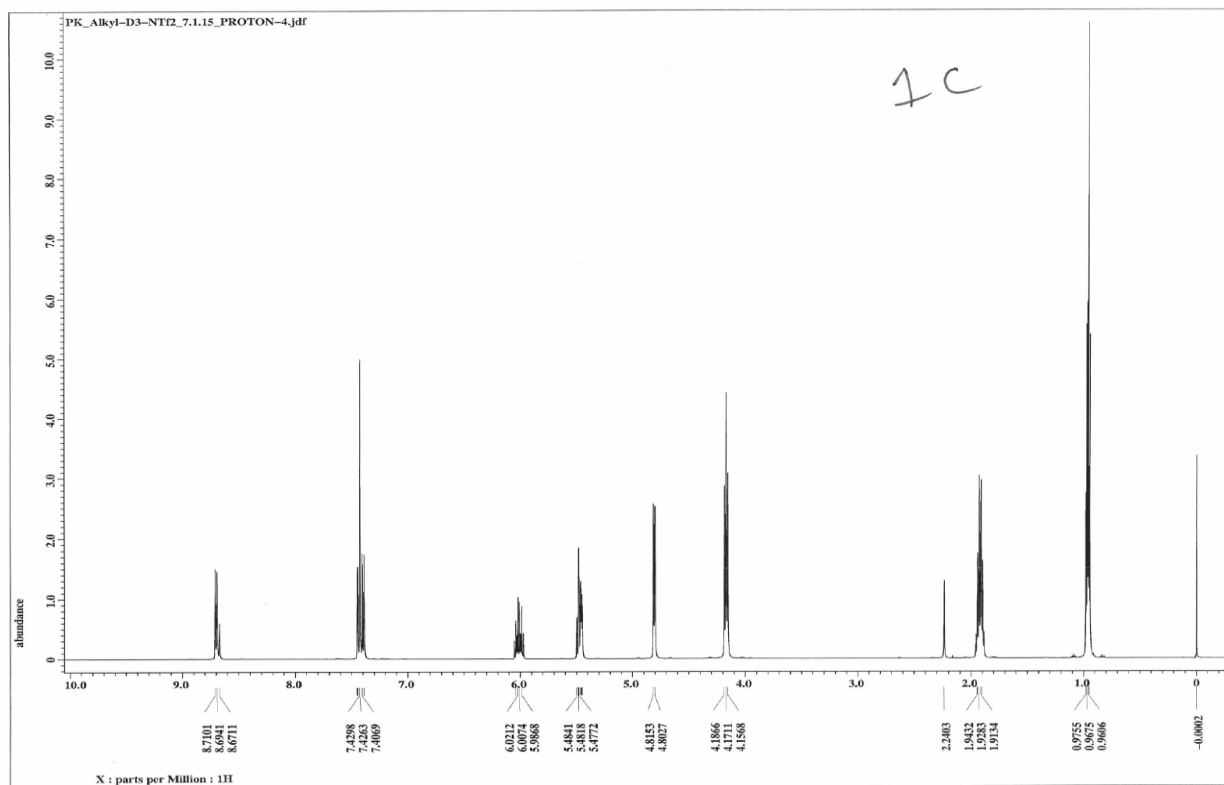
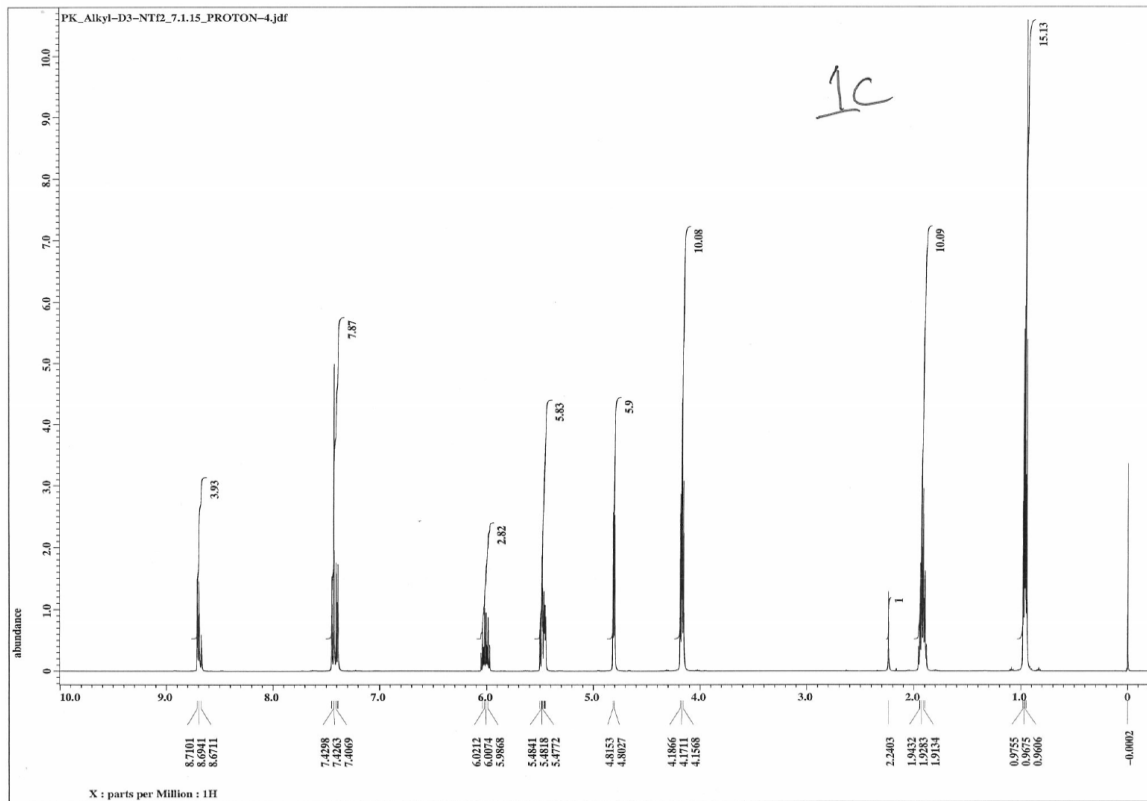
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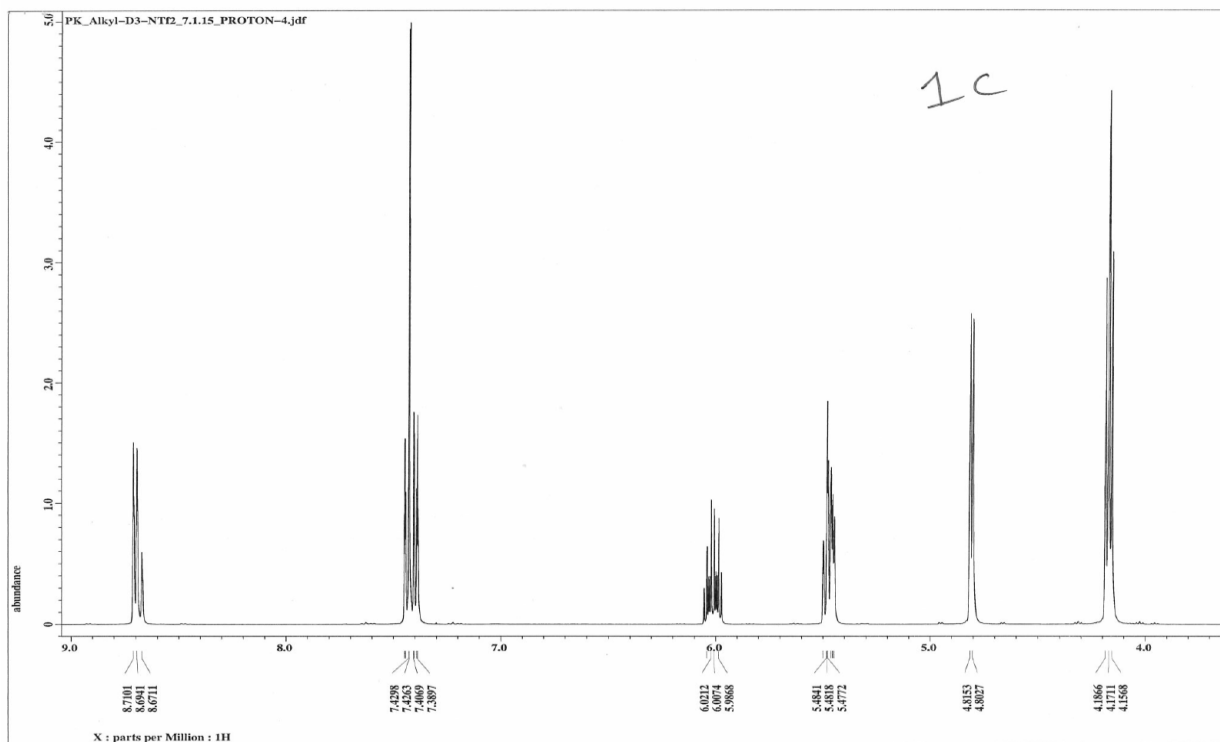
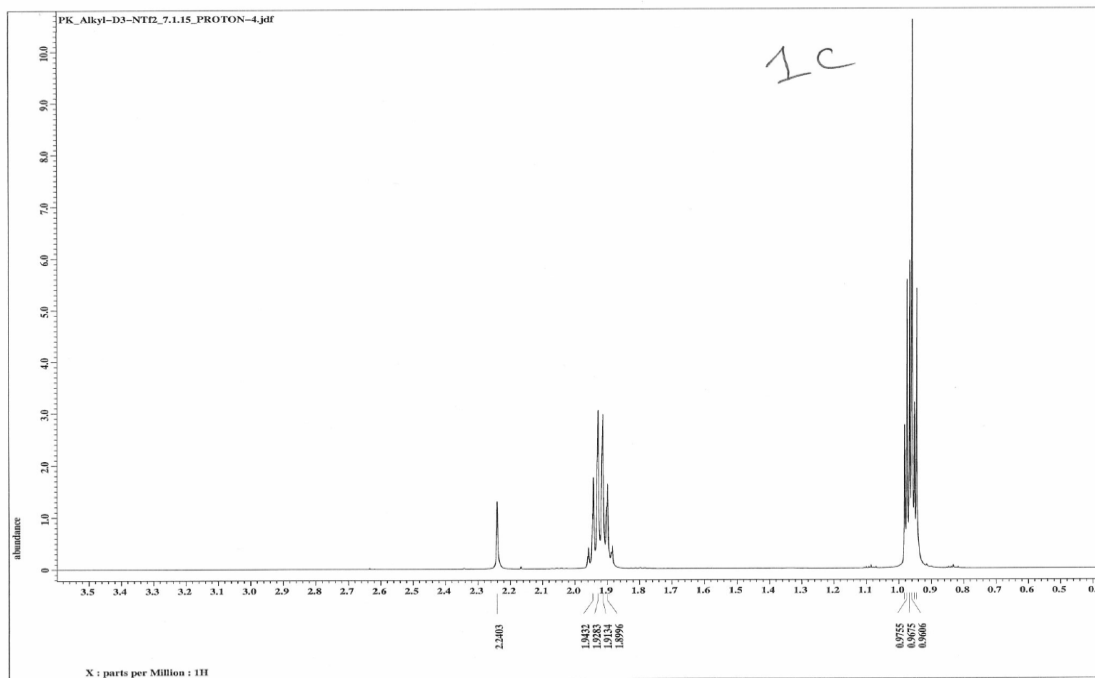
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 N: 9.76

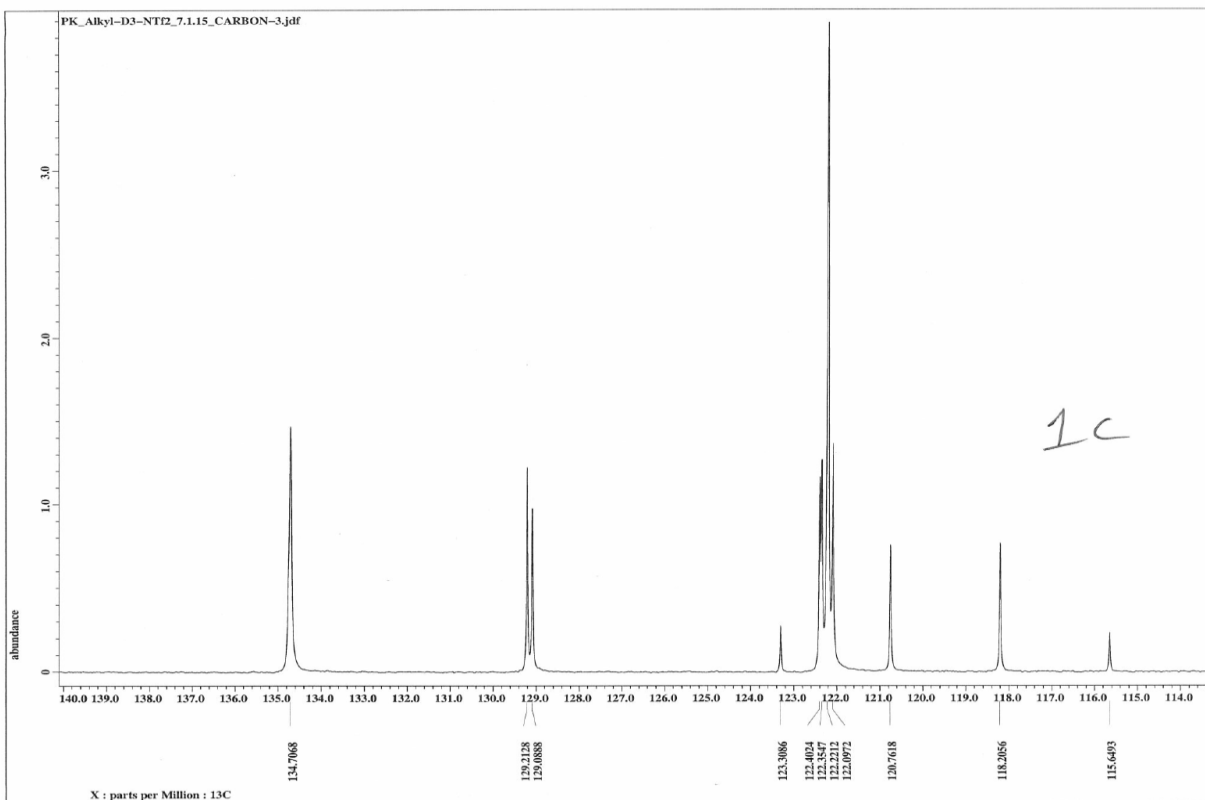
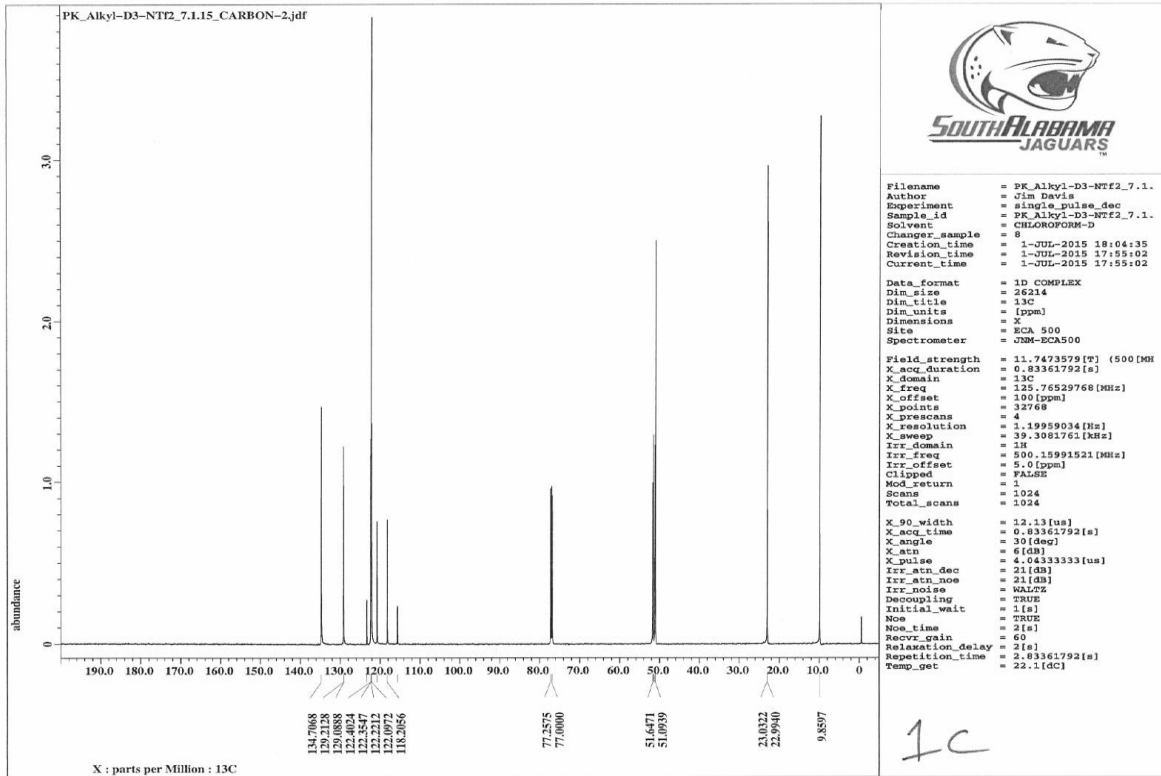
JHD



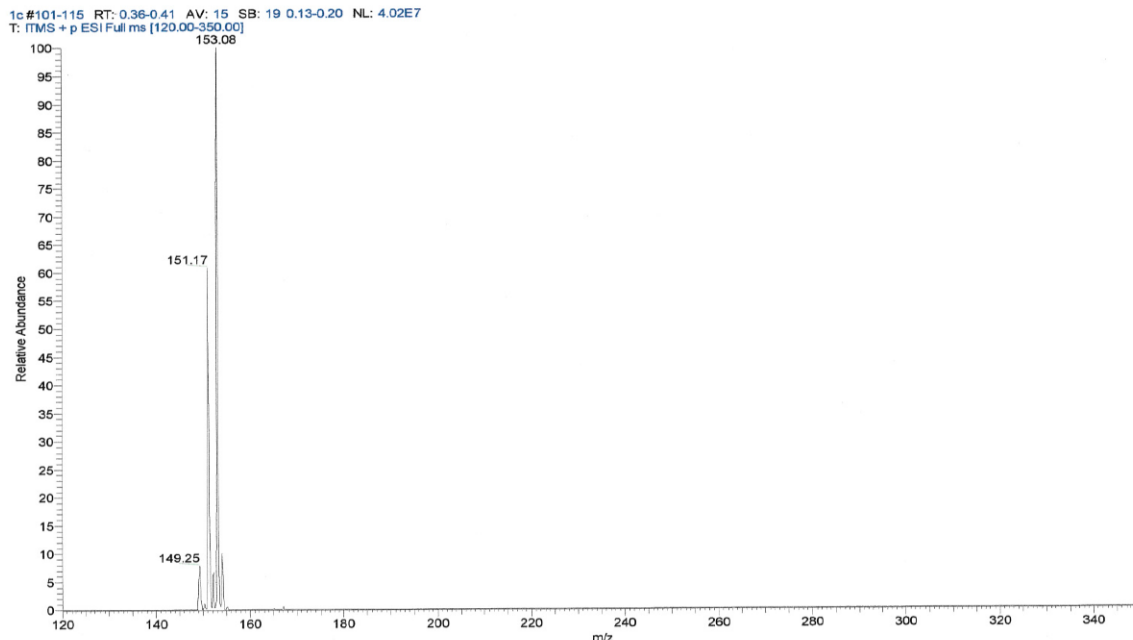
1c







Smpl 1c



Atlantic Microlab, Inc.

No. D-3Tf2N

Atlantic Blvd. Suite M
Mobile, GA 30071
atlanticmicrolab.com

Company/School University of South Alabama
Dept. Chemistry

Address Chem Bldg 223 6040 USA Drive South
City, State, Zip Mobile, AL 36688

Analyst/Supervisor: _____

Name Jim Davis Date 07/01/2015

Phone # _____

Phone (251) 751-0520

Element	Theory	Found		Single <input checked="" type="checkbox"/>	Duplicate <input type="checkbox"/>
<u>JHD</u>	<u>47.34</u>	30.61	30.55	Elements CHNOSF Present:	
<u>JHD</u>	<u>6.44</u>	3.62	3.52	Analyze CHN for:	
<u>JHD</u>	<u>13.32</u>	9.64	9.65	Hygroscopic <input type="checkbox"/> Explosive <input type="checkbox"/> M.P. <u>LIQUID</u> B.P. <u>NONE</u>	
		NO CHARGE FOR DUPLICATES		To be dried: Yes <input checked="" type="checkbox"/> No <input type="checkbox"/> Temp. <u>60C</u> Vac. <u>HIGH</u> Time <u>4 HRS</u>	
				Rush Service <input checked="" type="checkbox"/> <small>Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.</small>	
Include Email Address or FAX # Below <u>jdavis@southalabama.edu</u>					

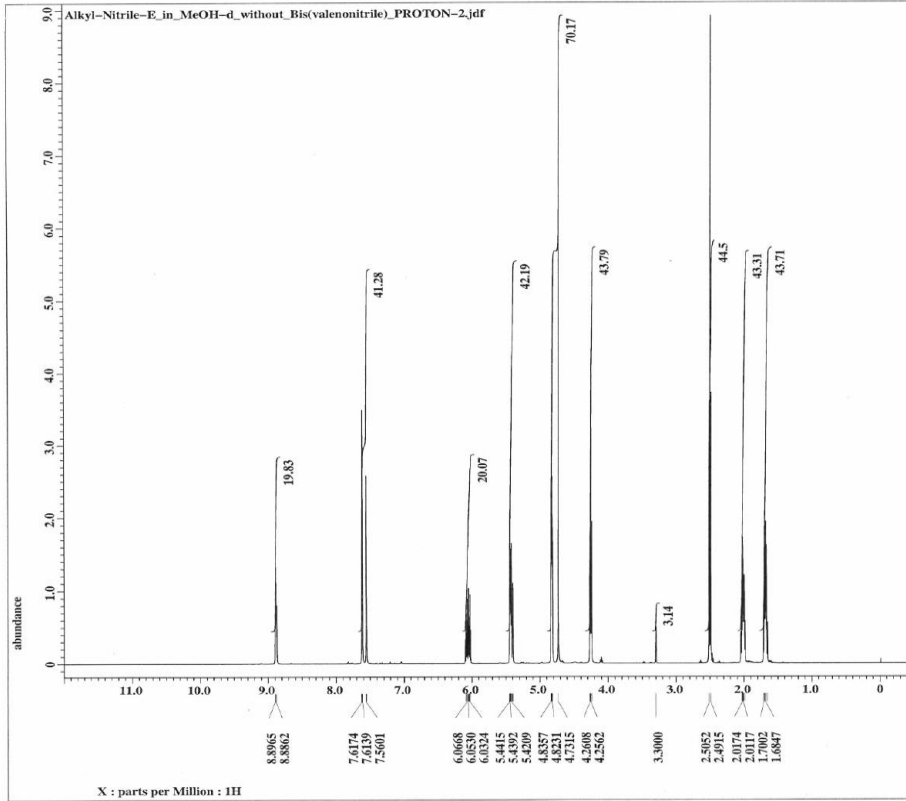

Received _____
Notes: _____

Date Completed _____

JUL 02 2015

JUL 02 2015

THESE THEORETICAL VALUES WERE MIS-CALCULATED.
ACTUAL THEORETICAL VALUES ARE C: 30.58, H: 3.66, N: 9.73

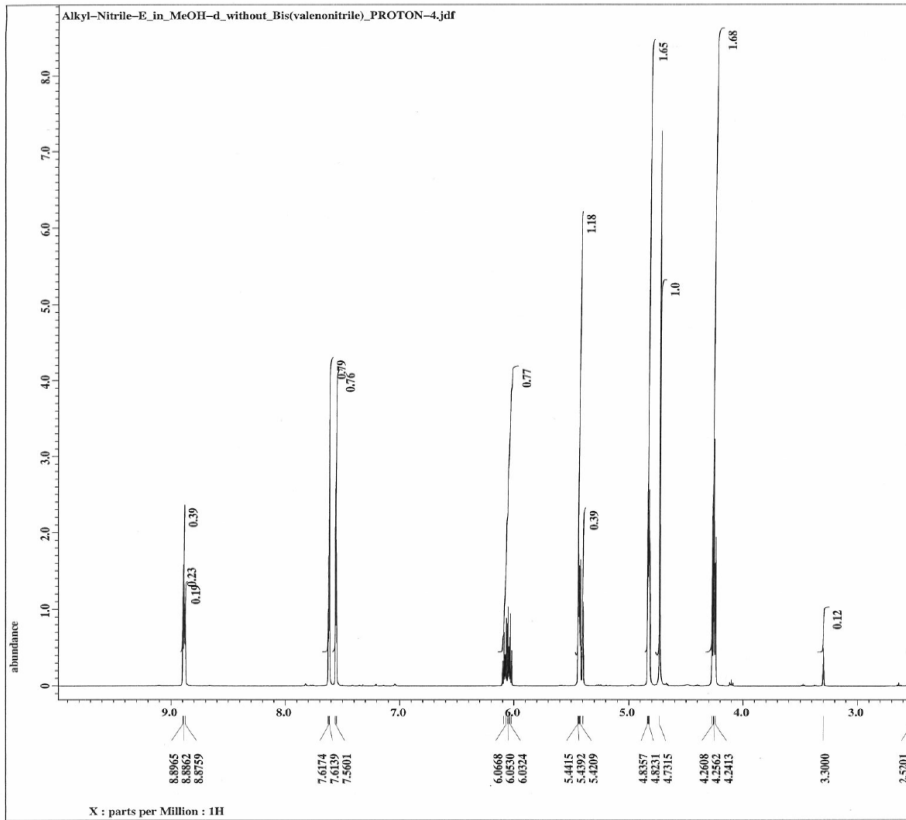
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Experiment = single_pulse.ex2
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Changer_sample = 7
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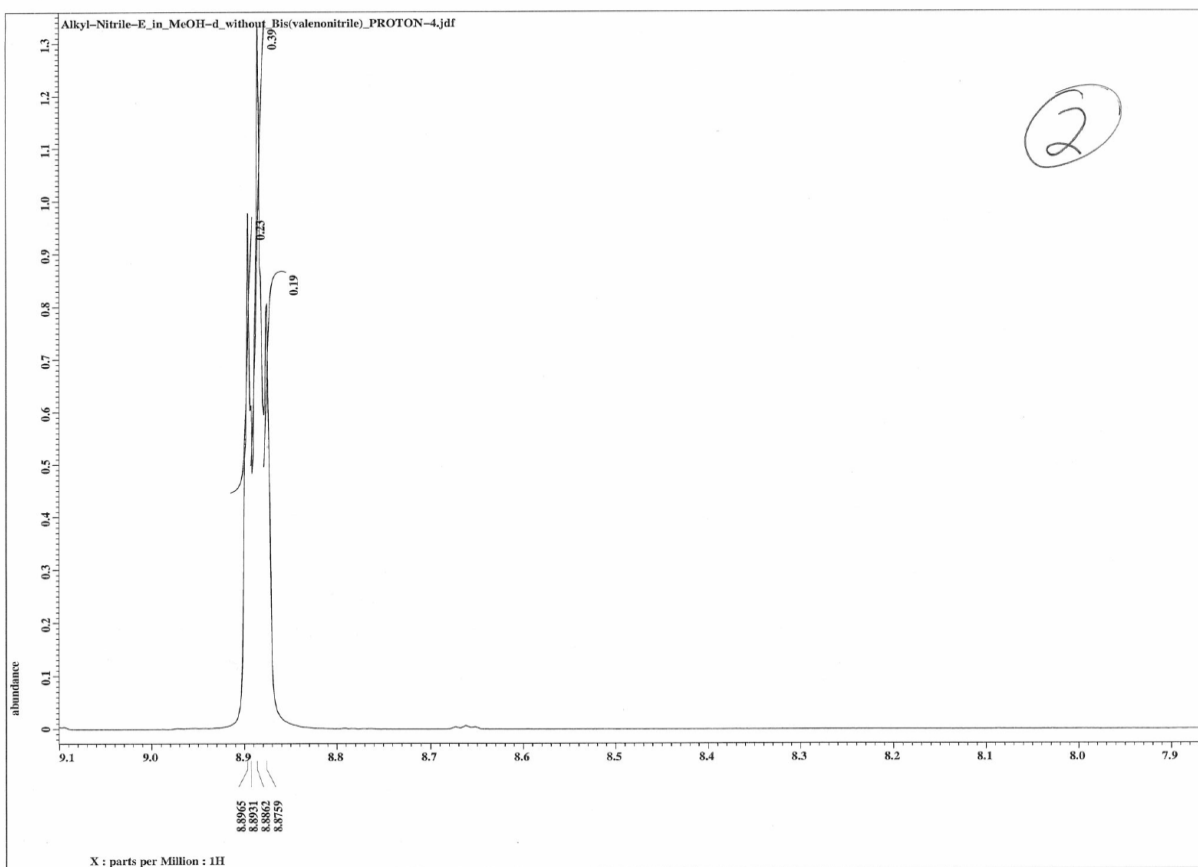
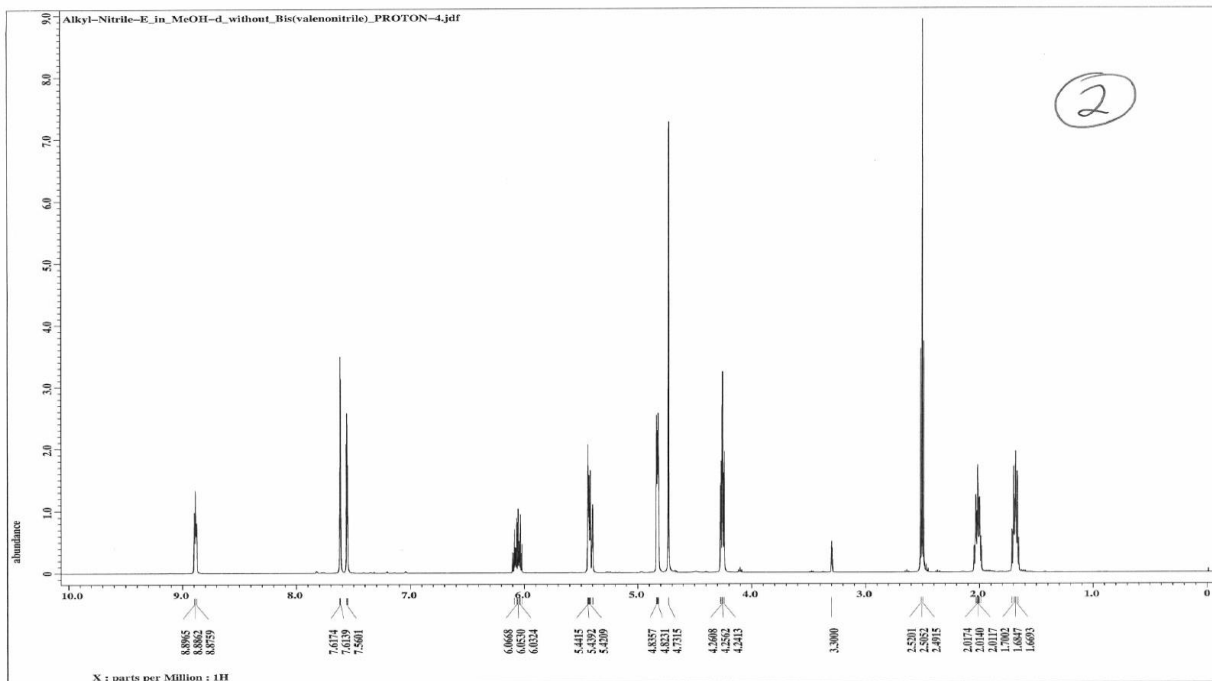
Data_format = 1D_COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

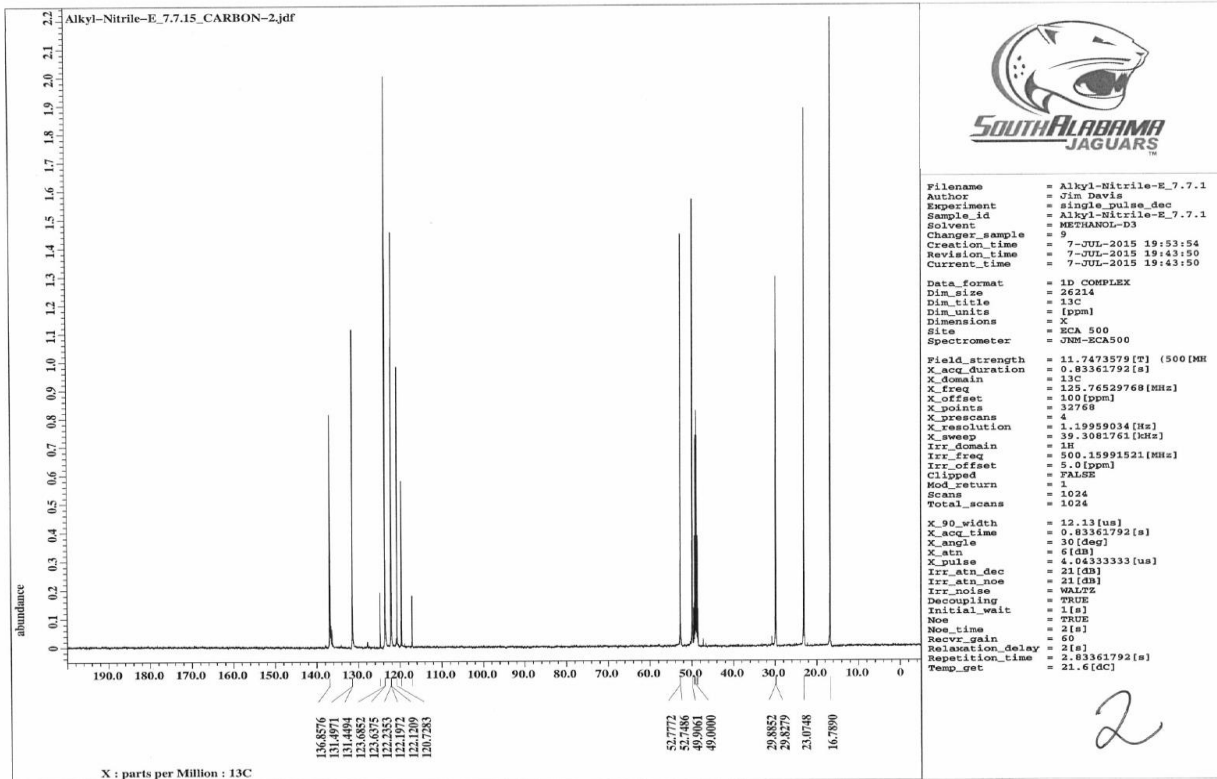
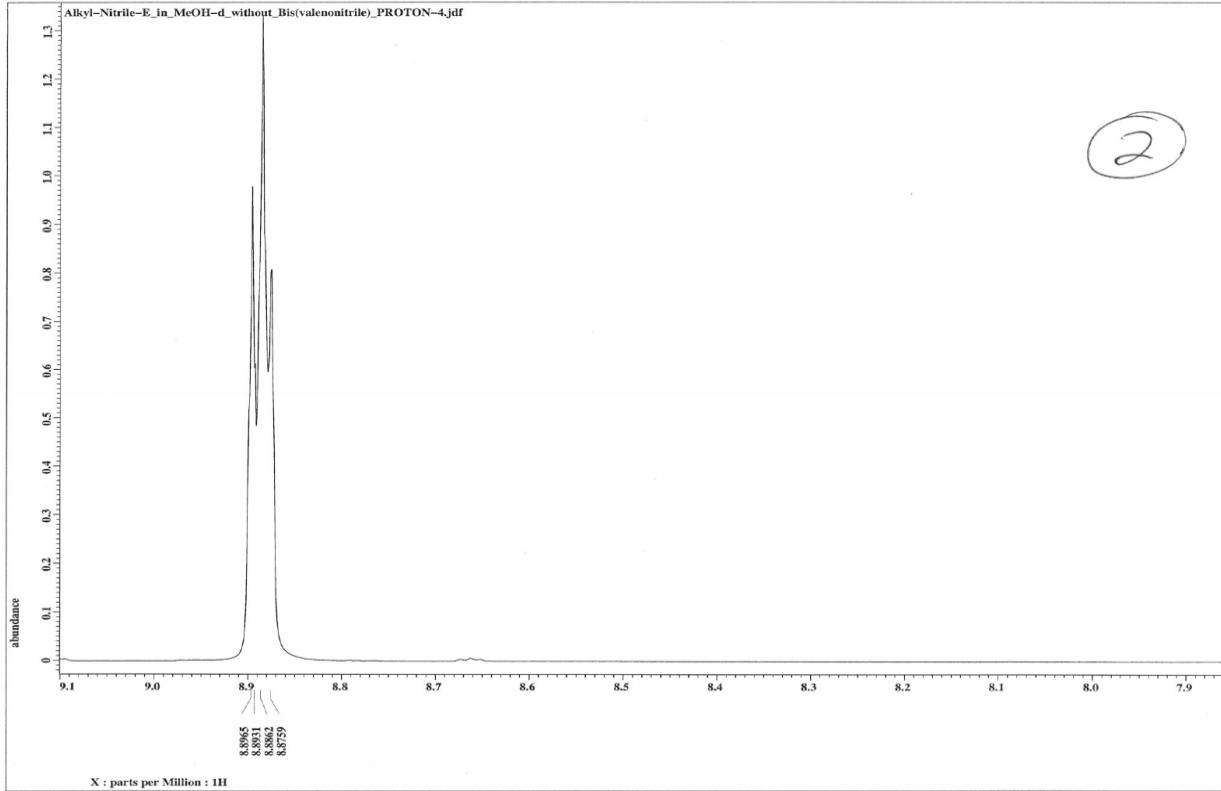
Field_strength = 11.747379 [T] (500 MHz)
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
X_acq = 1H
Xrr_domain = 1H
Xrr_freq = 500.15991521 [MHz]
Xrr_offset = 5.0 [ppm]
Xrr_domain = 1H
Xrr_freq = 500.15991521 [MHz]
Xrr_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 14.59 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 5 [dB]
X_pulse = 7.295 [us]
Xrr_mode = off
Xrr_mode = off
Dante_preset = FALSE
Initial_wait = [s]
Recvr_gain = 26
Relaxation_delay = 4 [s]
Repetition_time = 5.74587904 [s]
Temp_get = 22.1 [deg]
  
```

2



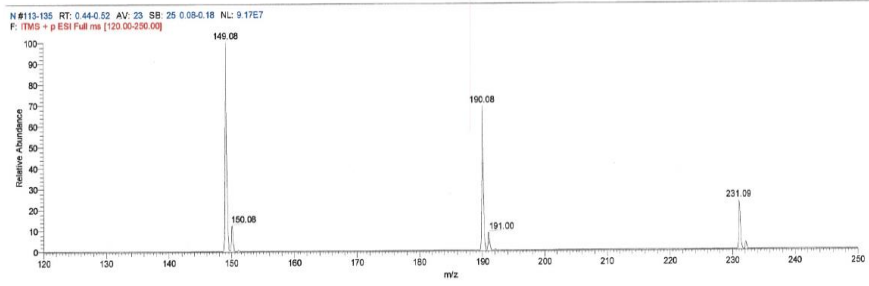
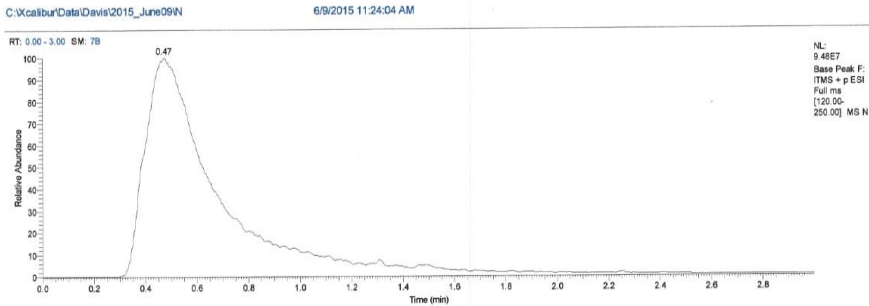
2





2

Nitrile-Alkyl



Atlantic Microlab, Inc.

No. JD Allyl Valeronitrile Batch A

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atlanticmicrolab.com

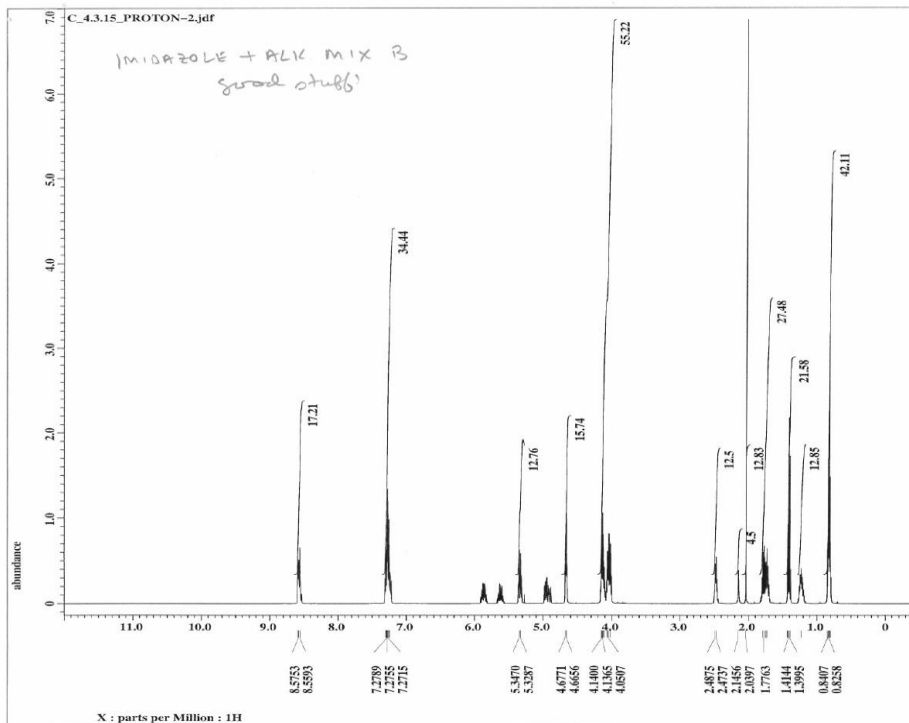

Company/School U of So Alabama
 Dept. Chem
 Address _____
 City, State, Zip _____
 Name James J Davis Date 6/4/15
 Phone _____

Analyst/Supervisor: Davis
C# _____

Element	Theory	Found	Single <input type="checkbox"/>	Duplicate <input type="checkbox"/>
C	33.19	33.22		
H	3.43	3.48		
N	11.91	11.95		
			Elements Present: Analyze for: <u>CHN</u> Hygroscopic <input type="checkbox"/> Explosive <input type="checkbox"/> M.P. _____ B.P. _____ To be dried: Yes <input checked="" type="checkbox"/> No <input type="checkbox"/> Temp. <u>60</u> Vac. <u>High</u> Time <u>24</u> Rush Service <input checked="" type="checkbox"/> Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM. Include Email Address or FAX # Below _____	

2

Received JUN 08 2015 Date Completed JUN 08 2015
Initials: _____

```

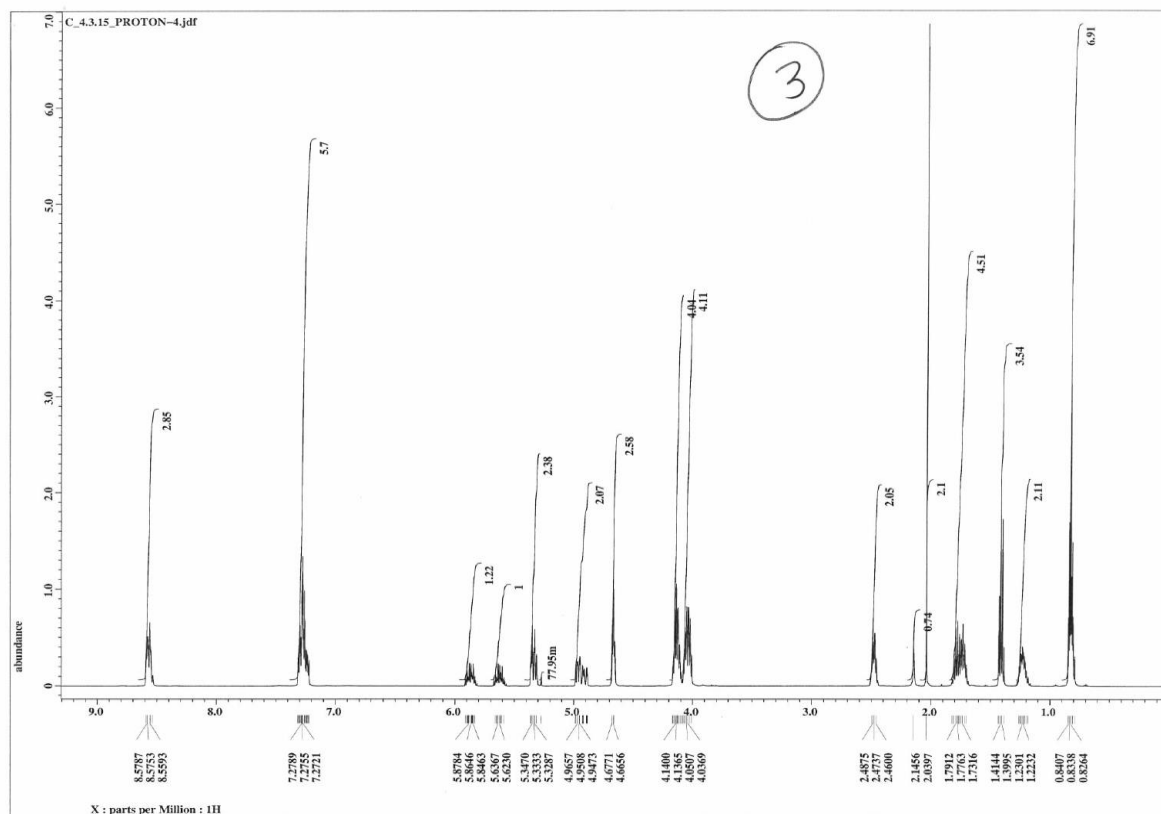
Filename      = C.4.3.15_PROTON-2.jdr
Author       = Jim Davis
Experiment   = single_pulse.ex2
Sample_id    = C.4.3.15
Solvent      = CHLOROFORM-D
Change_sample = 14
Creation_time = 3-APR-2015 15:04:50
Revision_time = 3-APR-2015 15:53:36
Current_time = 3-APR-2015 15:53:36

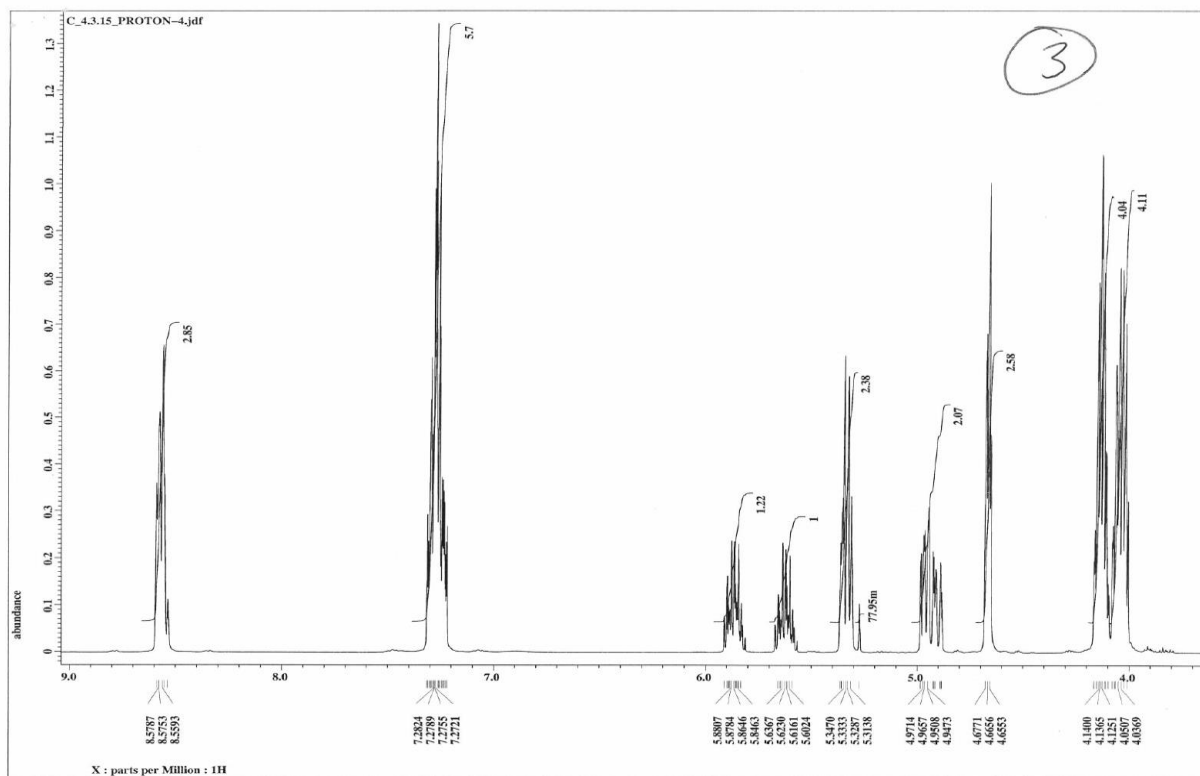
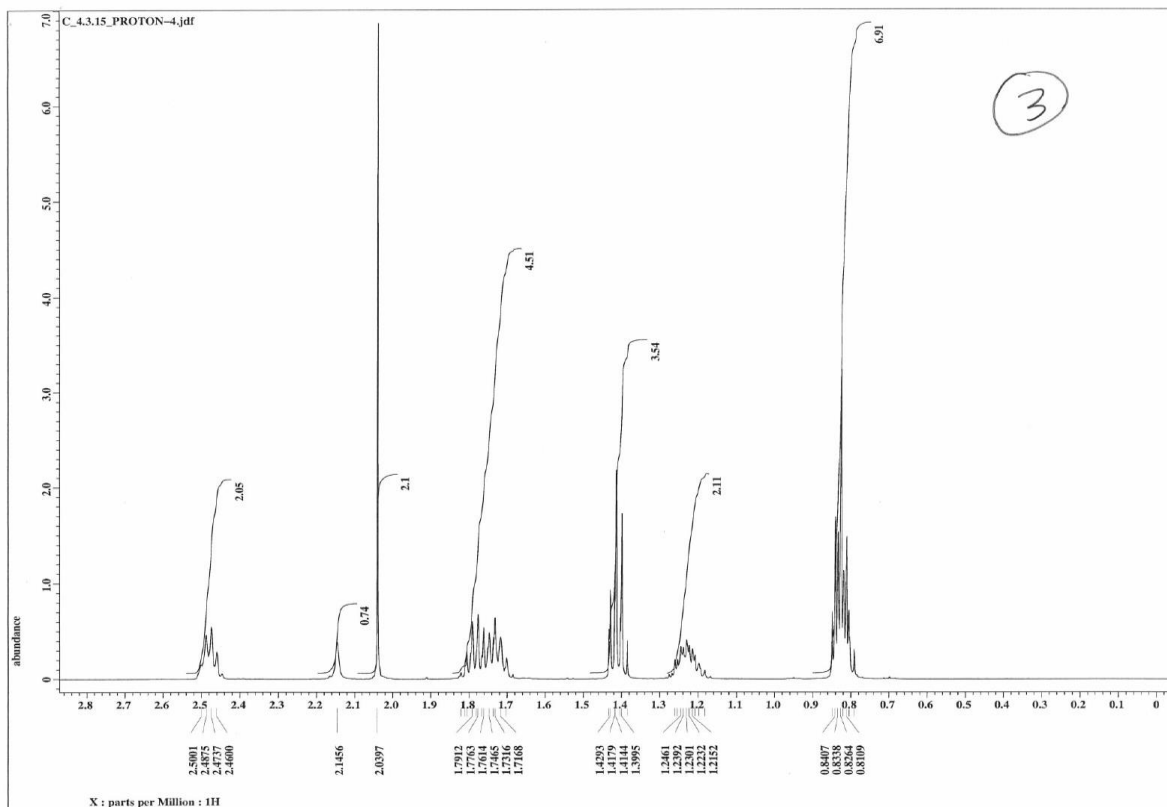
Data_format  = 1D COMPLEX
Dim_size     = 13107
Dim_scale    = 18
Dim_units    = [ppm]
Dimensions   = K
Site         = ECA 500
Spectrometer = JNM-ECA500

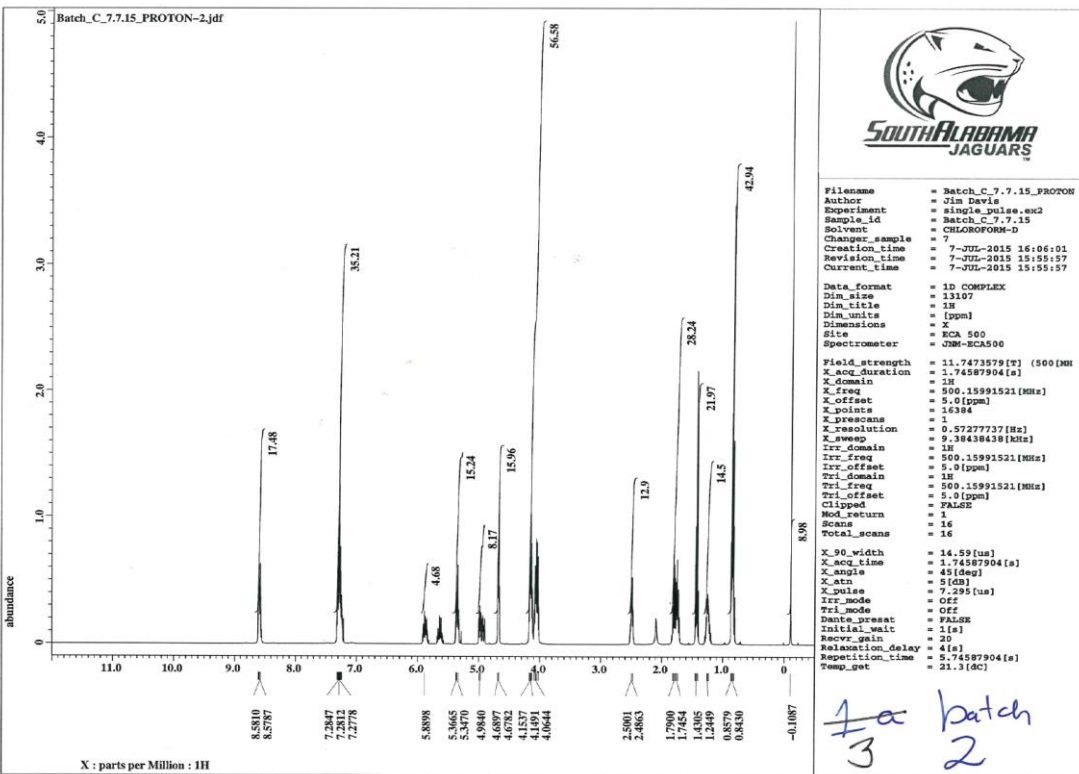
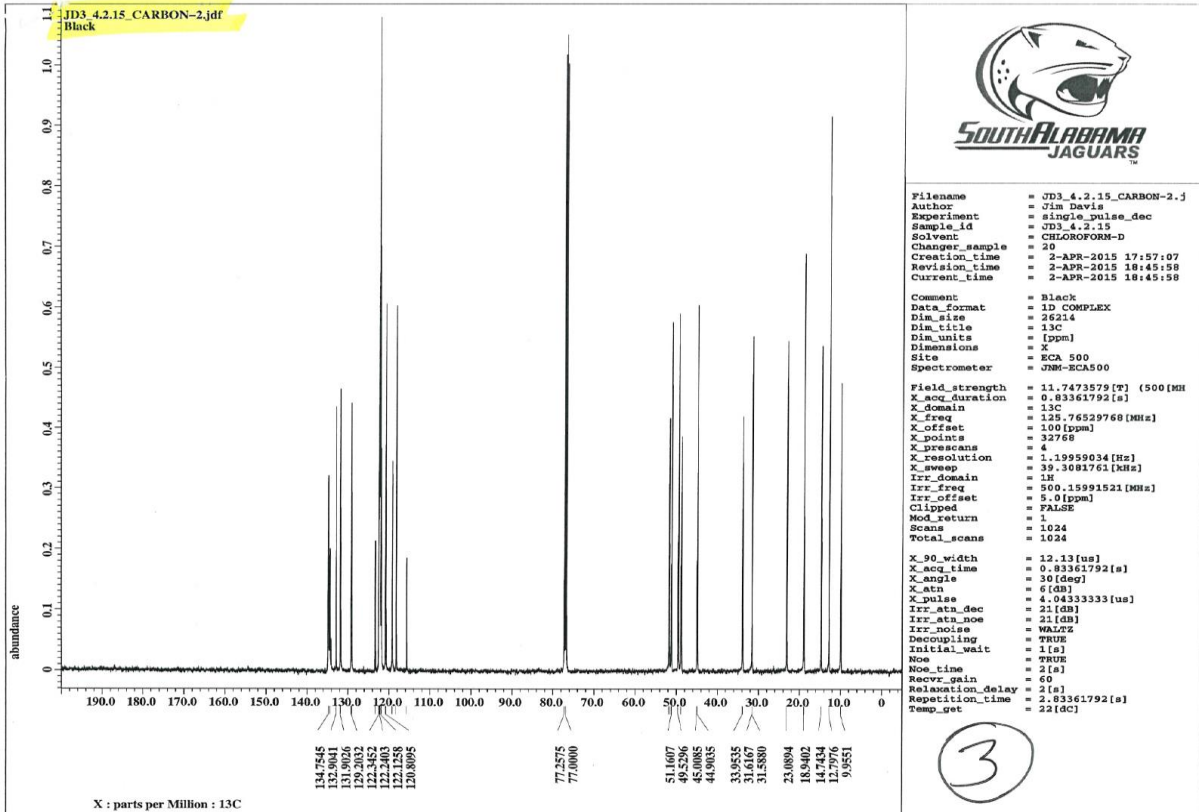
Field_strength = 11.7473579 [T] (500 [MH]
X_acq_duration = 1.74587904 [s]
X_domain       = 18
X_freq         = 500.15991521 [MHz]
X_offset       = 5.0 [ppm]
X_points       = 16384
X_prescans     = 1
X_resolution   = 0.57277737 [Hz]
X_sweep        = 9.38438438 [Hz]
F1_domain      = 18
F1_freq        = 500.15991521 [MHz]
F1_offset      = 5.0 [ppm]
F1_domain      = 18
F1_freq        = 500.15991521 [MHz]
F1_offset      = 5.0 [ppm]
Mod_return     = clipped
Mod_return     = 1
Scans          = 16
Total_scans    = 16

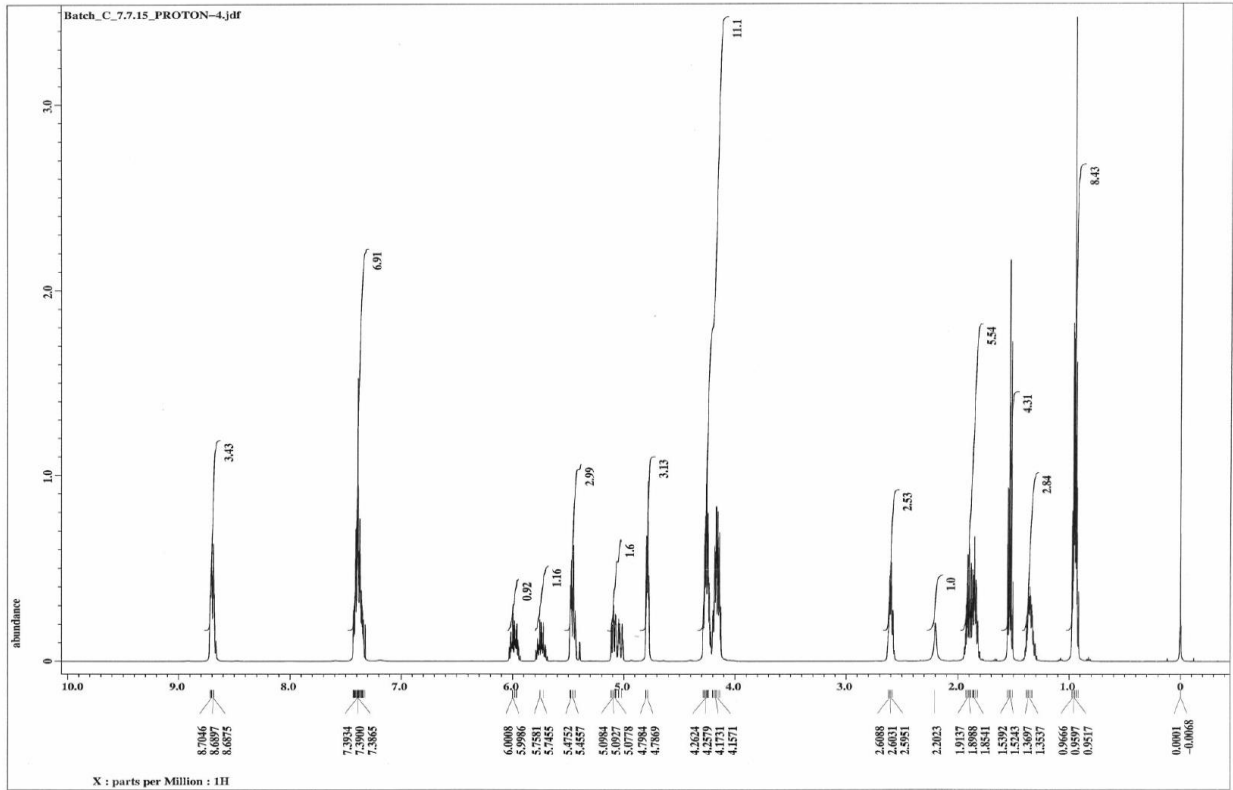
X_90_width    = 14.59 [us]
X_acq_time     = 1.74587904 [s]
X_angle        = 45 [deg]
X_atn          = 5 [dB]
X_pulse        = 7.29 [us]
F1_mode        = OFF
F1_mode        = OFF
Dante_present  = FALSE
Initial_wait   = 1 [s]
Recvz_gain     = 18
Relaxation_delay = 4 [s]
Repetition_time = 1.74587904 [s]
Temp_get       = 22.4 [C]
  
```

3

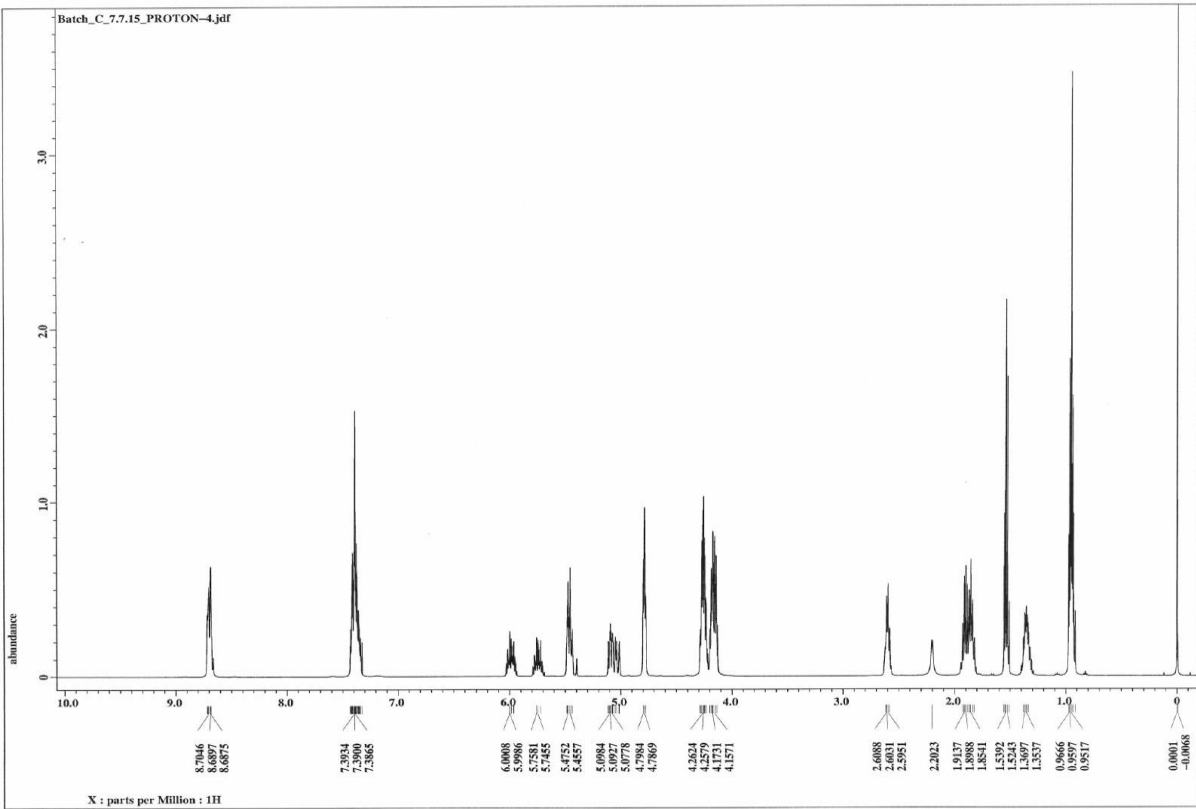




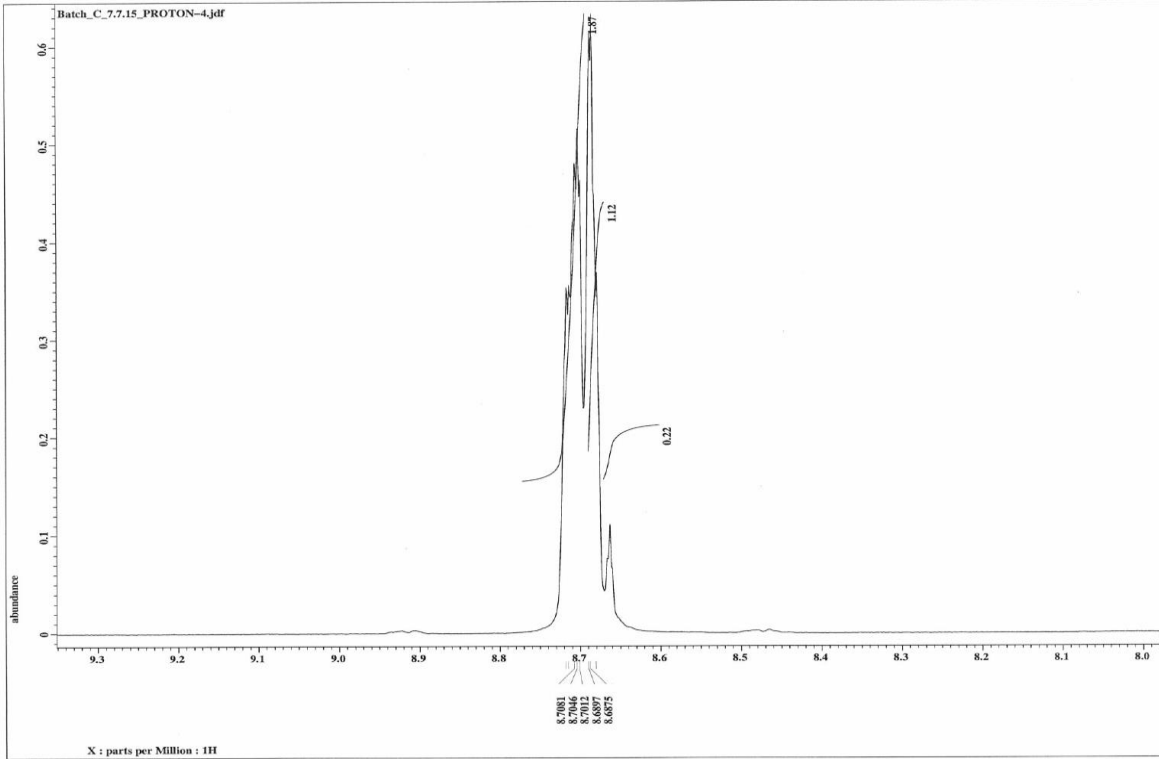




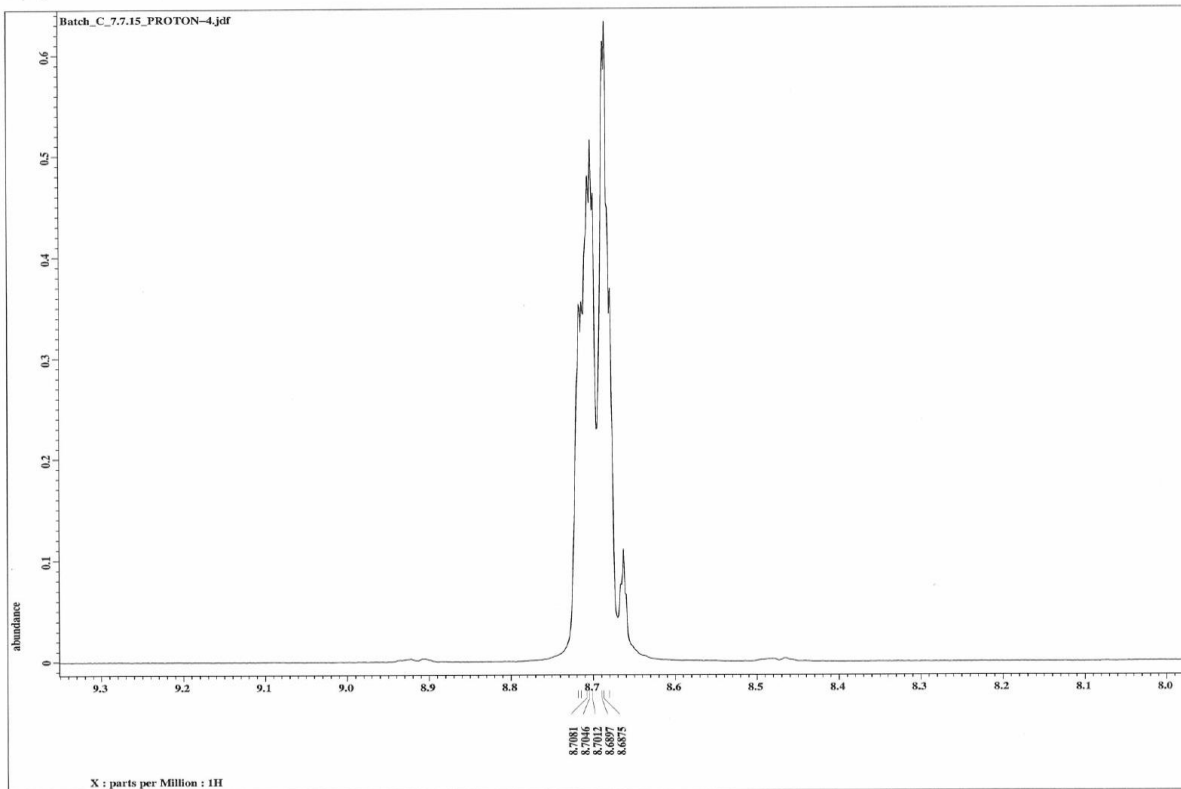
1a batch 2



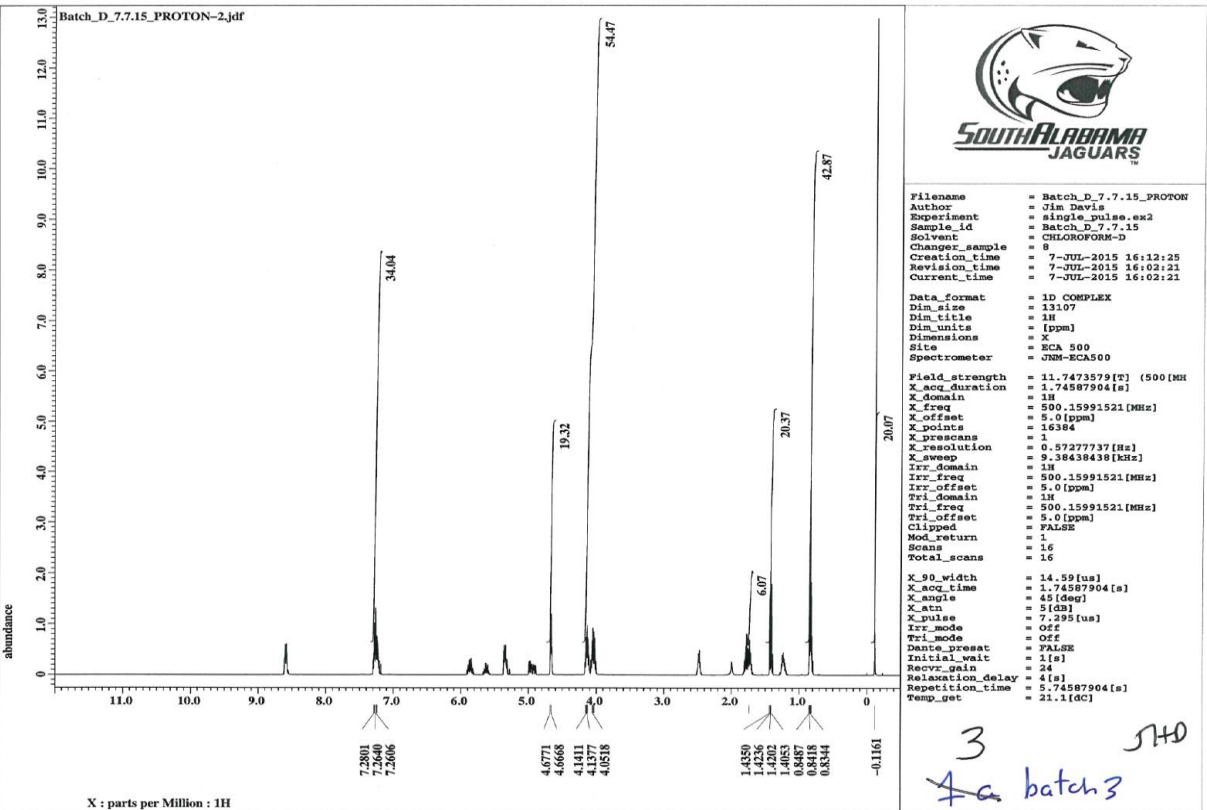
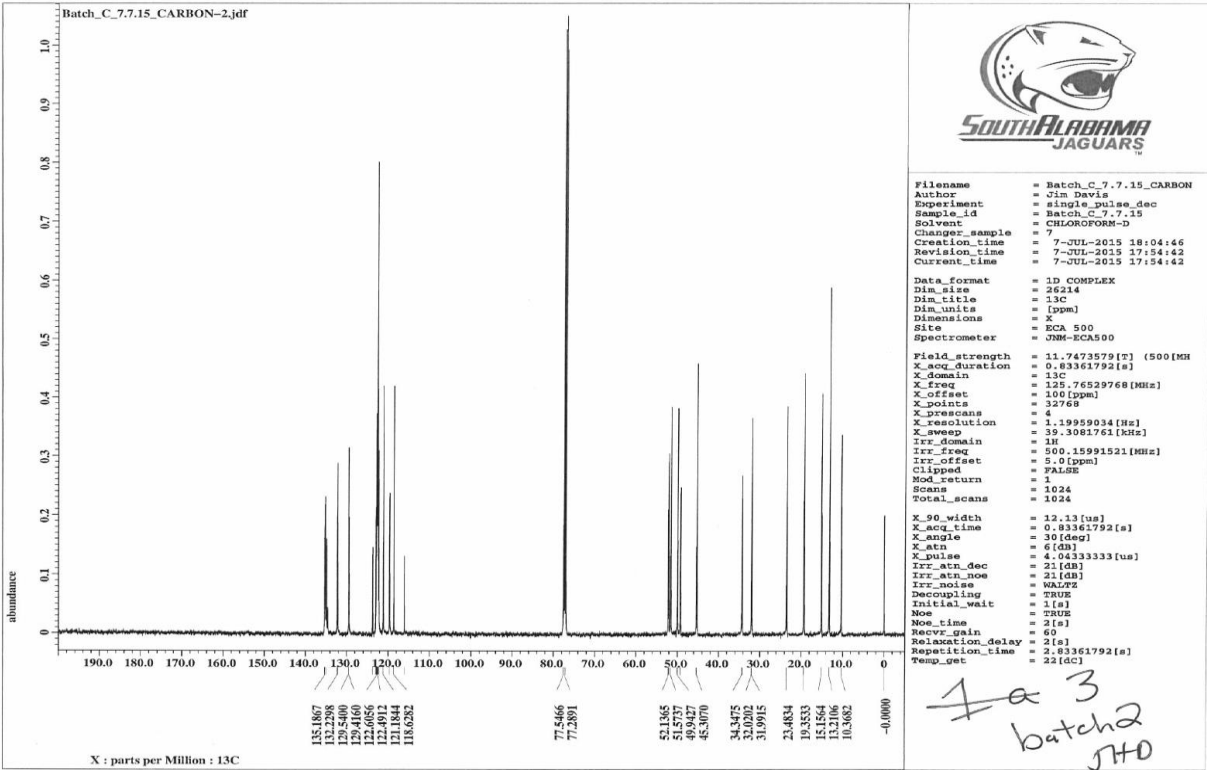
1a batch 2

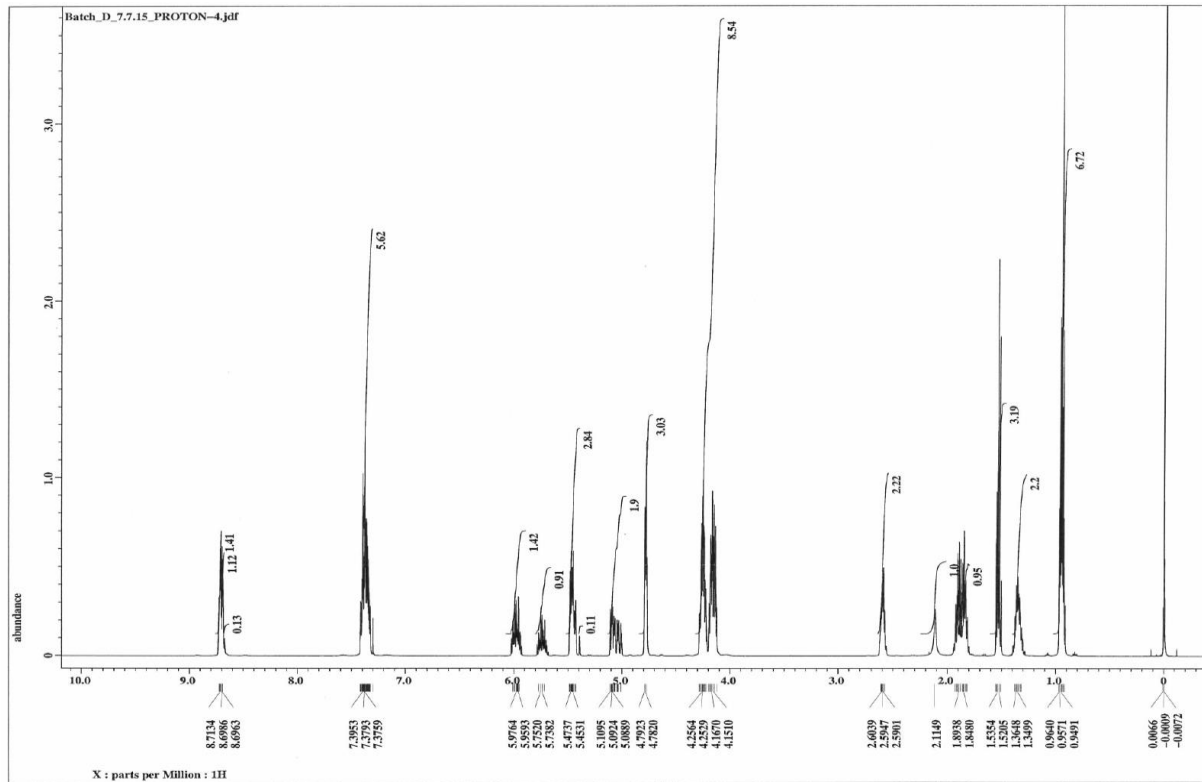


1a batch 2

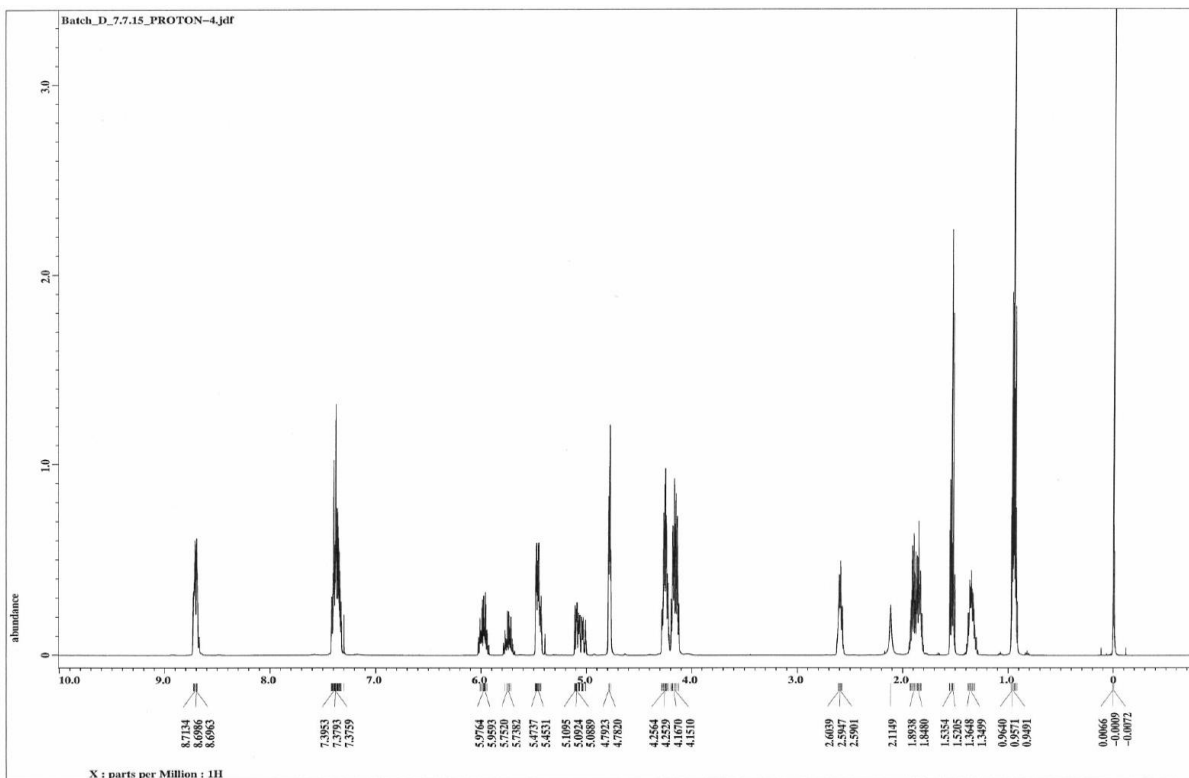


1a batch 2

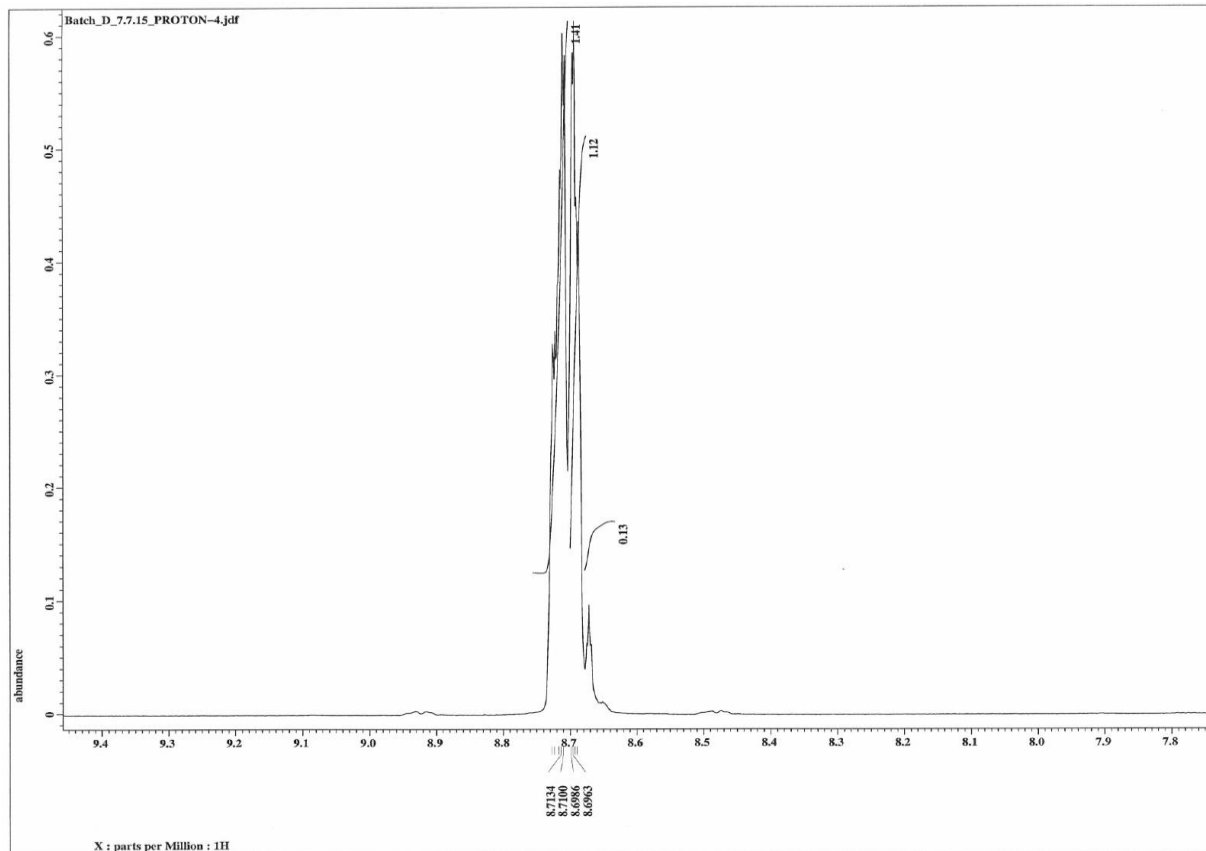




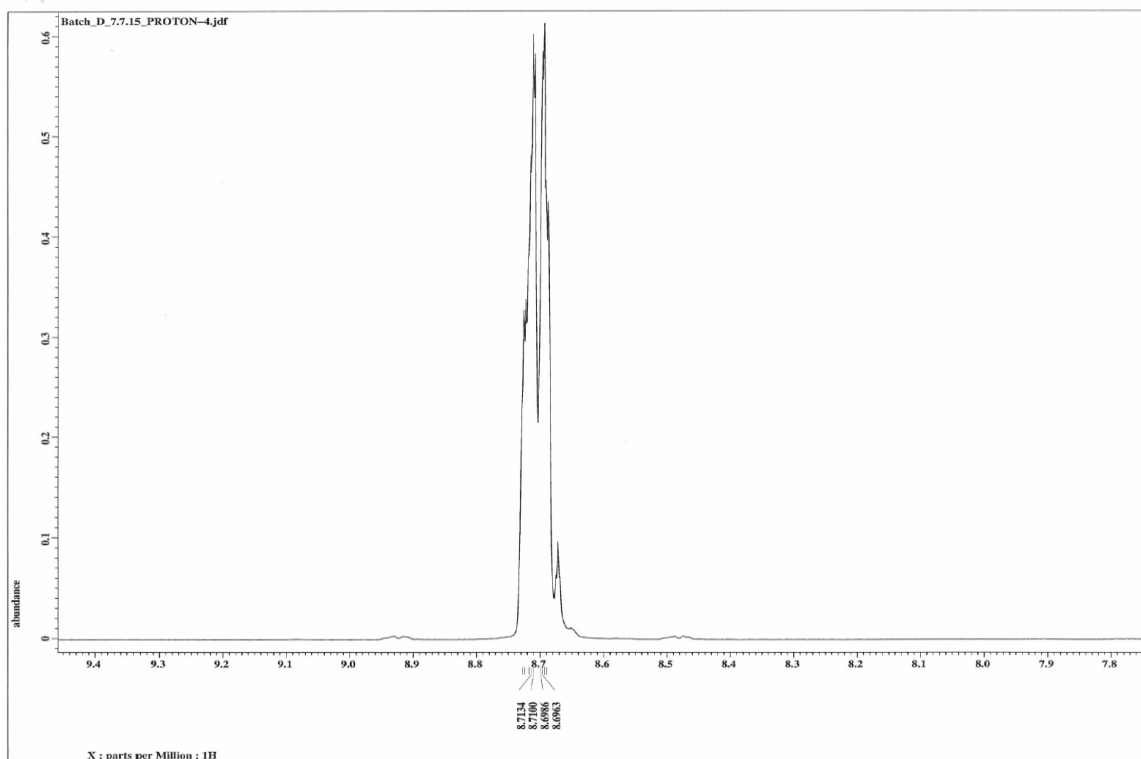
1 a batch 3

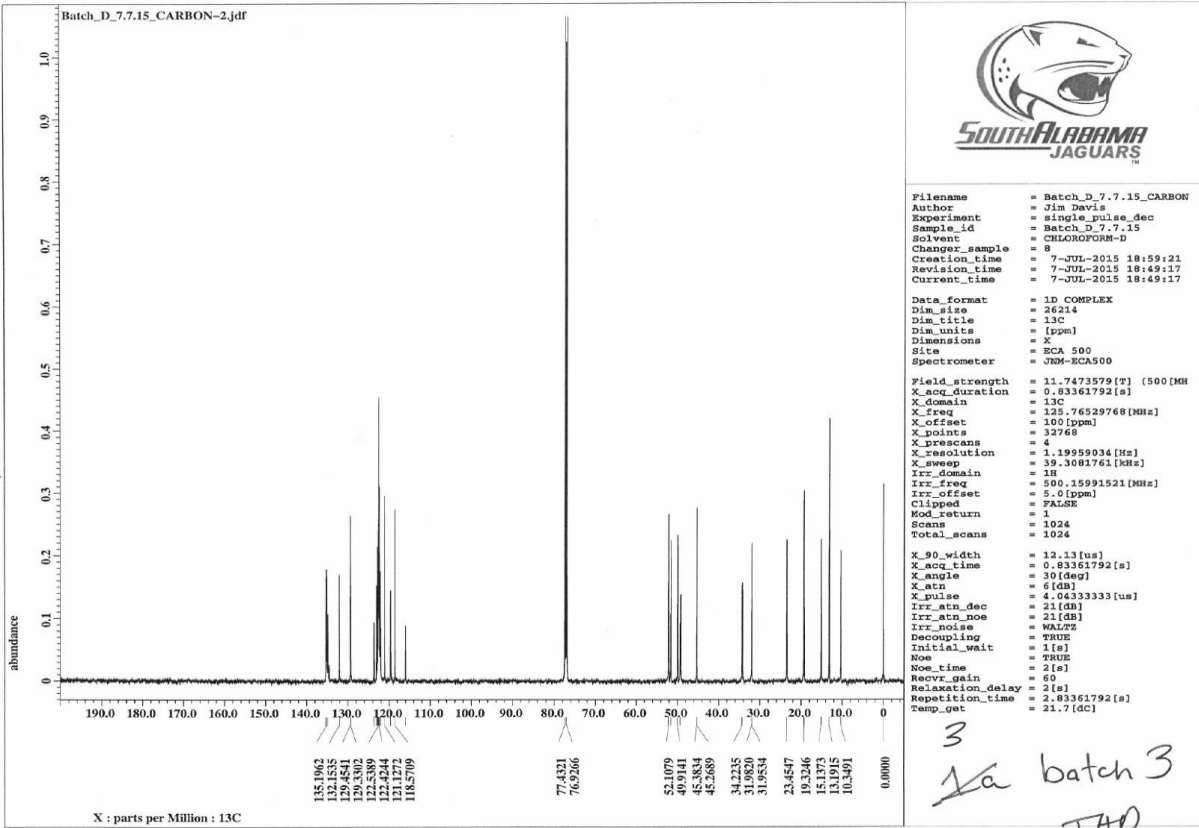


1 a batch 3



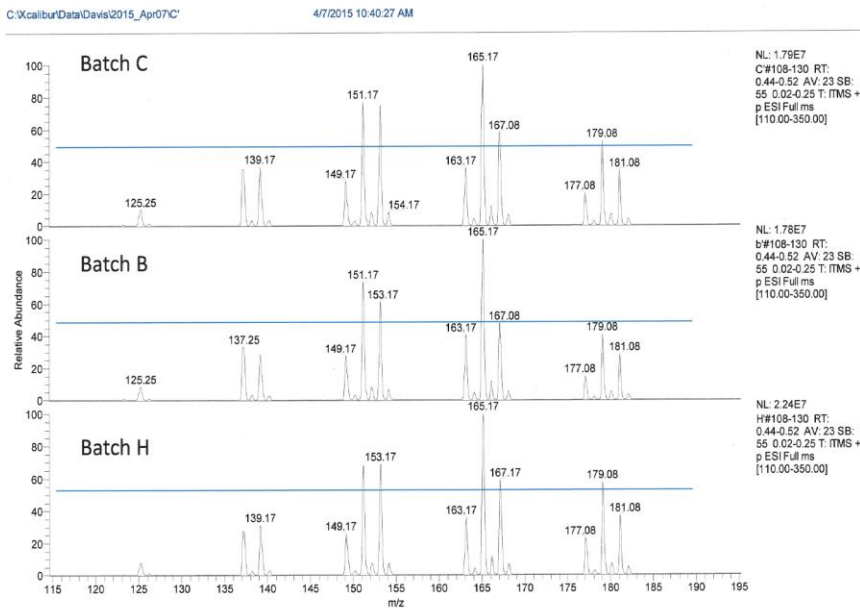
1 a beta?





Three Batches Stacked

3



NOTE: Three sets of two ions each have redundant masses: $m/z = 151, 153, 165$.

Atlantic Microlab, Inc.

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Dept. Chemistry

Address CHEM Bldg Room 223, USA Campus

City, State, Zip Mobile, AL, 36688

Analyst/Supervisor: Davis

Name James Davis

Date 04/08/2015

Lab# PO Z147846

Phone (251) 751-0520

Element	Theory	Found	Single <input checked="" type="checkbox"/>	Duplicate <input type="checkbox"/>
C	31.31	31.39	$\Delta < .4\%$	
H	3.73	3.67	$\Delta < .4\%$	
N	9.61	9.63	$\Delta < .4\%$	
Elements C, H, N, F, S, O Present: Analyze for: <u>CHN</u> Hygroscopic <input type="checkbox"/> Explosive <input type="checkbox"/> M.P. <u>liquid</u> - NO VAPOR PRESS. B.P. _____ To be dried: Yes <input checked="" type="checkbox"/> No <input type="checkbox"/> Temp. <u>60C</u> Vac. <u>high</u> Time <u>1 hour</u> Rush Service <input checked="" type="checkbox"/> <small>Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.</small> Include Email Address or FAX # Below <u>jdavis@southalabama.edu</u>				

Received APR 09 2015

Date Completed APR 09 2015

Remarks:

IL-3, 3x batches

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City, State, Zip Mobile, AL, 36688

Analyst/Supervisor: Davis

Name James Davis

Date 04/08/2015

Lab# PO Z147846

Phone (251) 751-0520

Element	Theory	Found	Single <input checked="" type="checkbox"/>	Duplicate <input type="checkbox"/>
C	31.31	31.43	$\Delta < .4\%$	
H	3.73	3.80	$\Delta < .4\%$	
N	9.61	9.73	$\Delta < .4\%$	
Elements C, H, N, F, S, O Present: Analyze for: <u>CHN</u> Hygroscopic <input type="checkbox"/> Explosive <input type="checkbox"/> M.P. <u>liquid</u> - NO VAPOR PRESS. B.P. _____ To be dried: Yes <input checked="" type="checkbox"/> No <input type="checkbox"/> Temp. <u>60C</u> Vac. <u>high</u> Time <u>1 hour</u> Rush Service <input checked="" type="checkbox"/> <small>Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.</small> Include Email Address or FAX # Below <u>jdavis@southalabama.edu</u>				

Received APR 09 2015

Date Completed APR 09 2015

Remarks:

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Analyst/Supervisor: Davis Name James Davis Date 04/08/2015
 C# PO Z147846 Phone (251) 751-0520

Element	Theory	Found	Single <input checked="" type="checkbox"/>	Duplicate <input type="checkbox"/>
C	31.31	31.37	$\Delta < .4\%$	
H	3.73	3.81	$\Delta < .4\%$	
N	9.61	9.74	$\Delta < .4\%$	

Elements C, H, N, F, S, O
 Present: _____
 Analyze CHN
 for: _____
 Hygroscopic Explosive
 M.P. liquid - NO VAPOR PRESS B.P. _____
 To be dried: Yes No
 Temp. 80C Vac. High Time 1 hour
 Rush Service Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.
 Include Email Address or FAX # Below
jdavis@southalabama.edu

Received APR 09 2015 Date Completed APR 09 2015
 Notes: _____

DSC Data and Acquisition

Thermal analysis was performed via differential scanning calorimetry. Data was collected on a TA Instruments Q2000. The samples were run in open pans, heated to 110°C at 10°C/min and held there for 10 minutes to degas and remove residual trace solvent. Next, they were cooled at 10°C/min to -85°C and held for 5 minutes. Data was then collected as the samples were heated at 10°C/min to 200°C.

The results are shown in Figure 2 (main text) for **1a** (solid), **2** (long dash) and **3** (short dash). Interestingly, no distinct solid/liquid phase transitions are observed, although a low temperature glass transition is indicated for **2**. The small thermal event at ~100°C for all samples, and is likely the loss of trace water. Samples were also run at scan rates of 1°C/min with similar thermal behavior (see Supplementary Information).

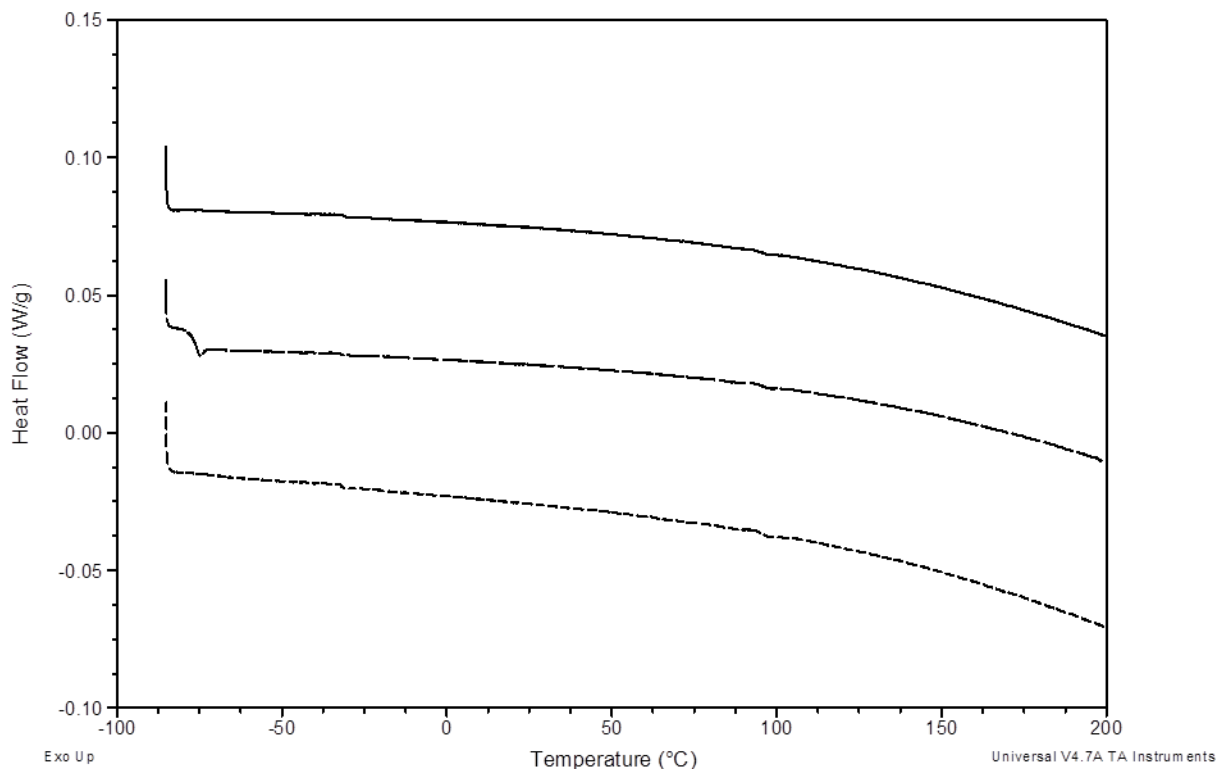


Figure SI-1. DSC traces compounds **1a** (solid), **2** (long dash) and **3** (short dash). The scan procedure is identical to that in the main body of the article, except that the data collection scan was run at 1°C/min. Like the scans obtained at 10°C/min, these results indicate no phase transitions discernable through thermal events for **1a** and **3**, with a low temperature glass transition observed for **2**. The thermal event at around 100°C is seen here as well, although diminished in relative magnitude. The y axis values have been offset, but not rescaled.

Water Determination (Karl Fisher)

Water contents for **1a-3** were not part of our original characterization panel, and were only acquired after a request by reviewers of the present manuscript (with which we were happy to comply). However, note that by the time the measurements were made the samples had been exposed to quite humid air for ca. 3 mos. and were not re-dried before doing the Karl Fisher experiments. Consequently, the values below probably represent water saturation values for the new ILs.

Sample	wt (g)	Water content (ppm)		
1a	trial 1	0.9775	1858.4277	average Stdv

	trial 2	1.135	1867.31	1859.849233	6.861345915
	trial 3	0.9166	1853.81		
1b	trial 1	0.7045	2526.448		
	trial 2	0.7217	2401.102	2471.261	64.00019935
	trial 3	0.8665	2486.233		
1c	trial 1	0.6456	2479.905		
	trial 2	0.6676	2536.87	2512.004333	29.1632861
	trial 3	0.722	2519.238		
2	trial 1	0.5207	1389.8599		
	trial 2	0.6705	1333.4236	1332.686833	57.5449875
	trial 3	0.7176	1274.777		
3	trial 1	0.71	4063.4135		
	trial 2	0.6975	4066.791	4057.247267	13.70963771
	trial 3	0.7513	4041.5373		