

SUPPORTING MATERIALS

Alkyl levulinate from furfuryl alcohol using CT151 Purolite as heterogenous catalyst: optimization, purification, and recycling

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CONTENTS

Pictures of furfuryl alcohol and ethyl levulinate degradation	2
Purolite and Amberlyst-15 physical and chemical characteristics	2
Synthesis of EtLev from FA varying temperatures and solvent amount	3
Preliminary investigation for catalyst recycling.....	4
¹ H-NMR, ¹³ C-NMR & Mass – Spectra	5

Pictures of furfuryl alcohol and ethyl levulinate degradation



Figure S1. Examples of the substrate/product degradation observed without previous filtration on basic alumina; starting from the left: reaction conducted in presence of H_2SO_4 , $\text{BF}_3\text{-O}(\text{Et})_2$ and Amberlyst-15 as acid catalysts.

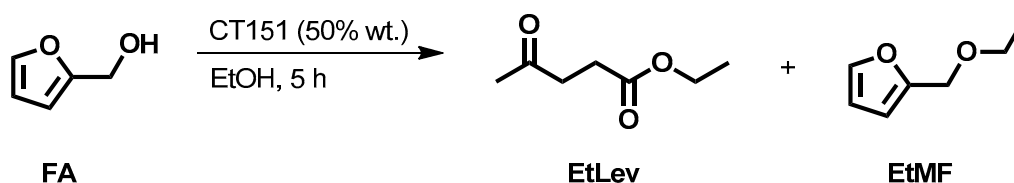
Purolite and Amberlyst-15 physical and chemical characteristics

Table S1. Purolite and Amberlyst-15 physical and chemical characteristics.^a

	CT275	CT269	CT151	Amberlyst-15
Polymer Structure	Macroporous polystyrene crosslinked with divinylbenzene			
Appearance	Spherical Beads			
Functional Group	Sulfonic Acid			
Ionic Form	H^+ form			
Particle Size Range	425 - 1200 μm			< 300 μm
Dry Weight Capacity	5.2 eq/kg (H^+ form)	5.2 eq/kg (H^+ form)	5.1 eq/kg (H^+ form)	≥ 4.7 eq/kg (H^+ form)
Moisture Retention	51 - 59 % (H^+ form)	51 - 57 % (H^+ form)	54 - 59 % (H^+ form)	$\leq 1.6\%$ (H^+ form)
Surface Area	20 - 40 m^2/g	35 - 50 m^2/g	15 - 25 m^2/g	53 m^2/g
Pore Volume	0.40 - 0.60 mL/g	0.30 - 0.50 mL/g	0.15 - 0.30 mL/g	0.40 mL/g
Median Pore Diameter	400 - 700 \AA	250 - 425 \AA	250 - 400 \AA	300 \AA
Temperature Limit	130 $^\circ\text{C}$	130 $^\circ\text{C}$	150 $^\circ\text{C}$	120 $^\circ\text{C}$

a) All information is available on the Purolite® website (<https://www.purolite.com/index>). All Amberlyst-15 information are available on the DuPont website (<https://www.dupont.com/content/dam/dupont/amer/us/en/water-solutions/public/documents/en/45-D00927-en.pdf>)

Synthesis of EtLev from FA varying temperatures and solvent amount



Scheme S1. Reaction scheme of EtLev synthesis.

Table S2. Synthesis of EtLev starting from FA at different temperatures.^a

#	Temp. (°C)	Conv. ^b (%)	¹ H-NMR Yield (%)	
			EtLev	EtMF
1	80	100	71	0
2	60	100	31	6
3	40	100	10	19
4	30	91	6	14
5	R.T.	50	5	16

a) Reaction conditions: **FA** (1.0 g) in ethanol (20.0 mL), CT151 (50% wt.) for 5h; b) Conversion determined via NMR.

Table S3. Synthesis of EtLev starting from FA employing different solvent amount.^a

#	EtOH (mL)	Conv. ^b (%)	¹ H-NMR Yield (%)	
			EtLev	EtMF
1	40	100	63	0
2	20	100	71	0
3	10	100	39	0
4	5	100	34	0

a) Reaction conditions: **FA** (1.0 g) in ethanol (20.0 mL), CT151 (50% wt.) for 5h; b) Conversion determined via NMR.

Preliminary investigation for catalyst recycling

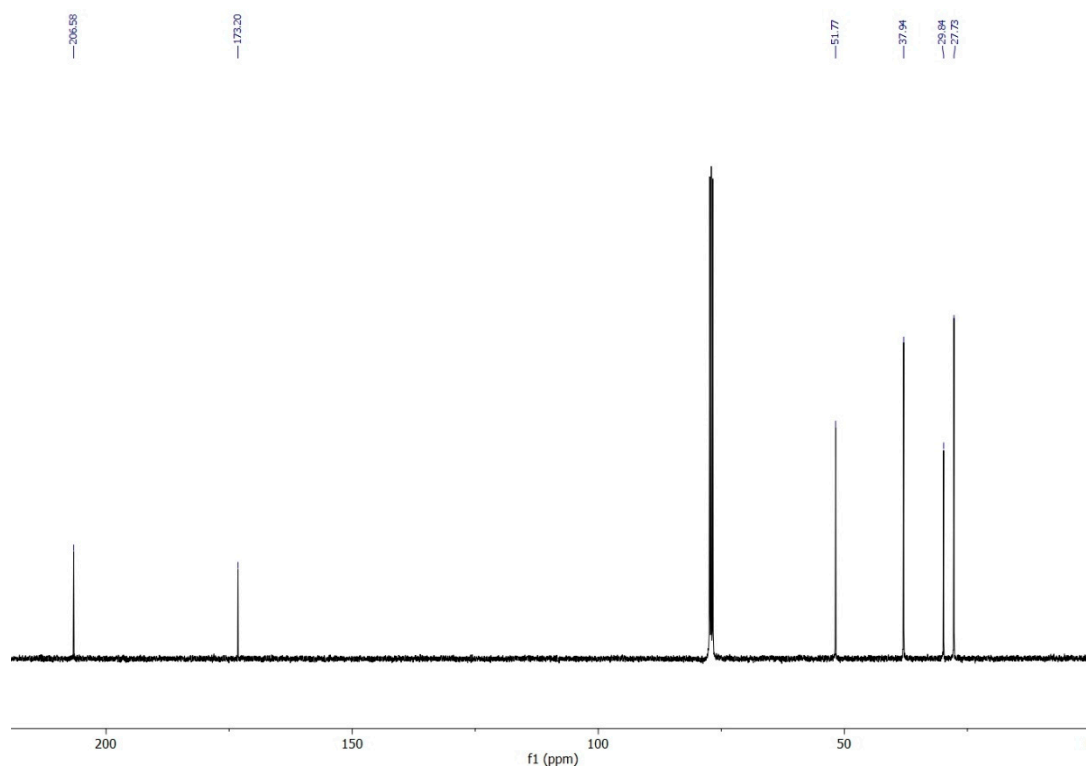
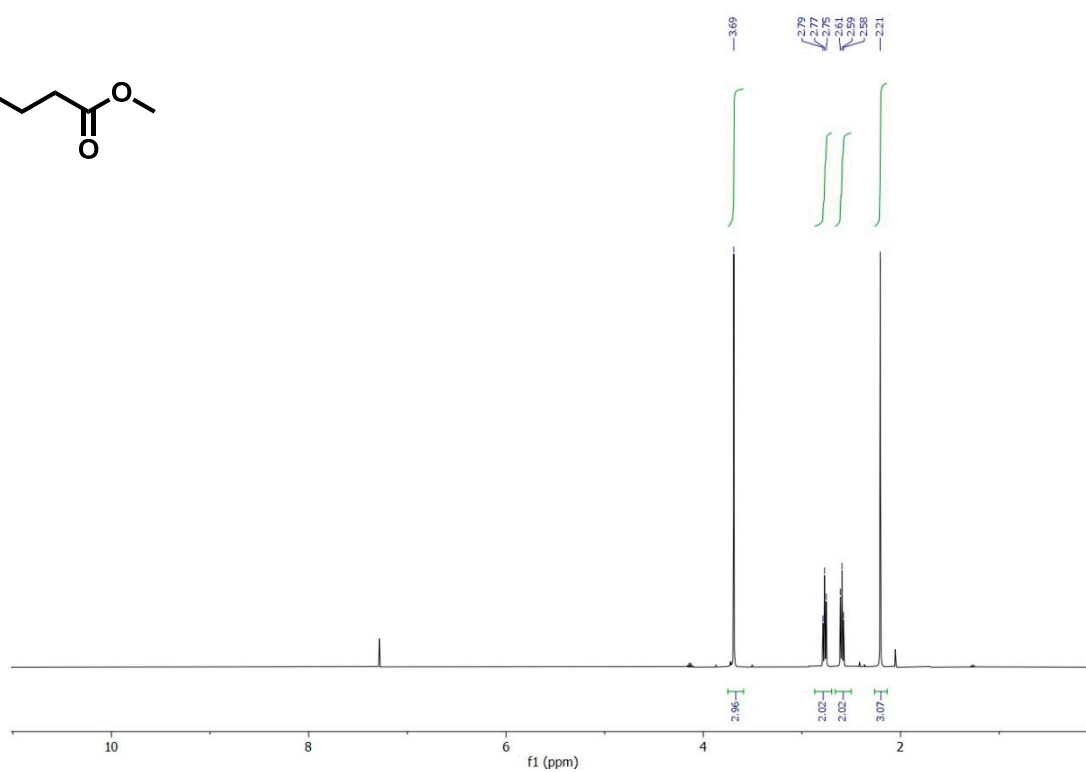
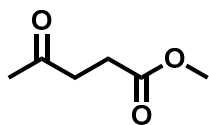
Table S4. Synthesis of EtLev starting from FA: Preliminary investigation for catalyst recycling.^a

	#	CT151 (% wt.)	¹ H-NMR Yield (%)	
			EtLev	EtMF
Stirring	1	50	71	0
No stirring	2	50	23	3
Nitrogen flow without stirring	3	50	57	0
No stirring	4	100	66	0

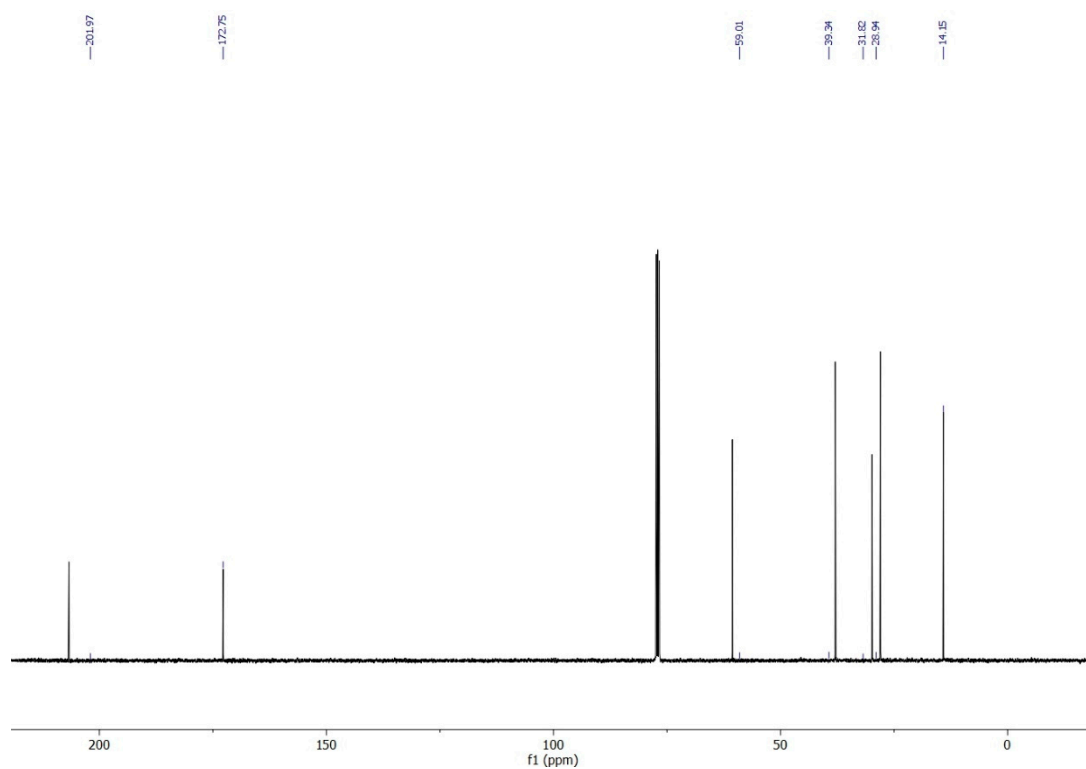
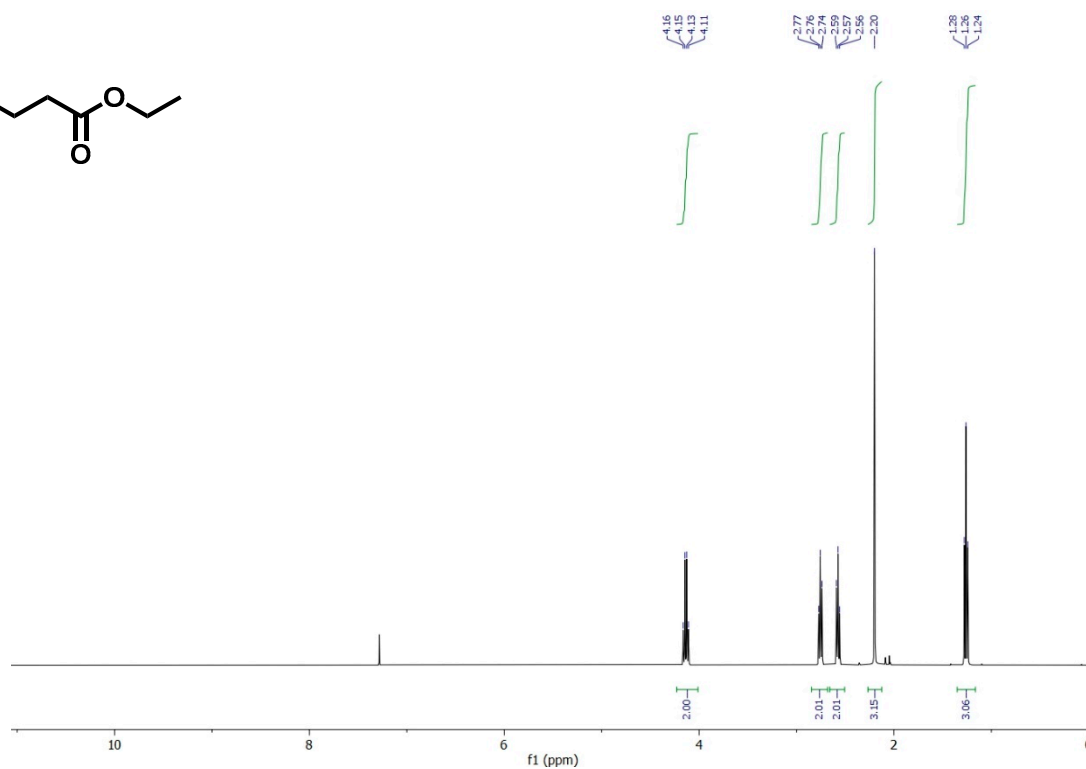
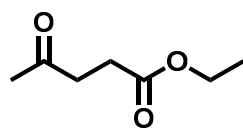
a) Reaction conditions: FA (1.0 g) in ethanol (20 mL), CT151 at 80 °C for 5h.

^1H -NMR, ^{13}C -NMR & Mass – Spectra

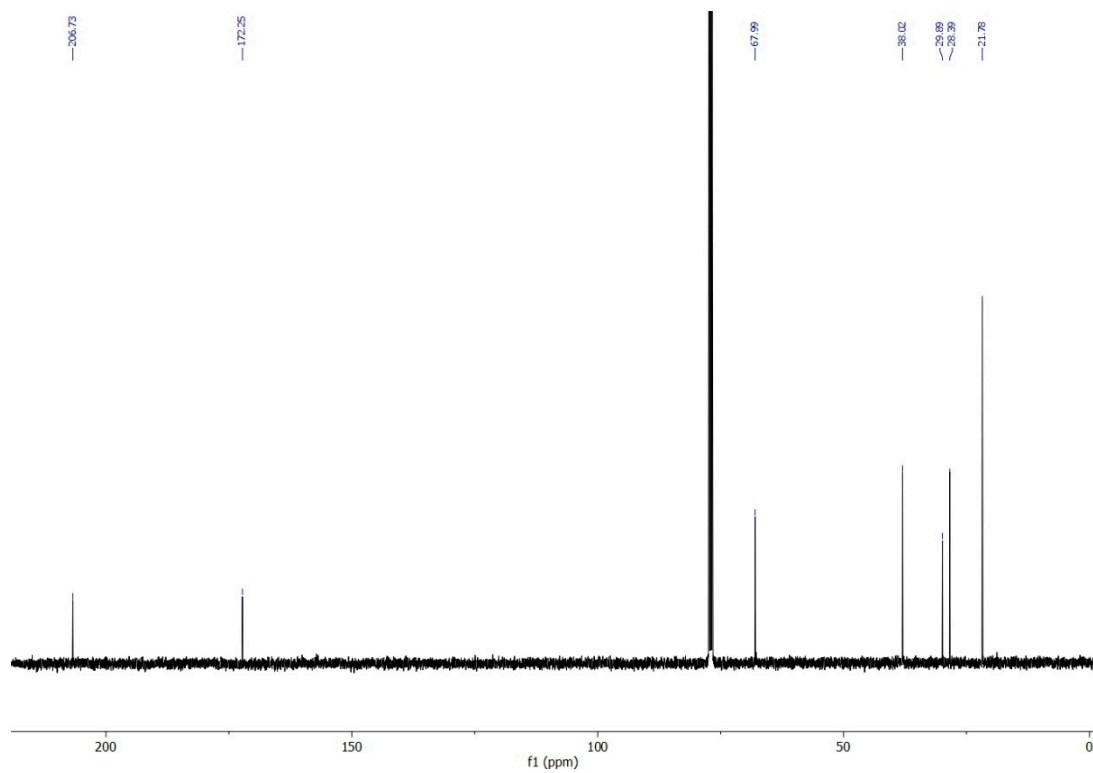
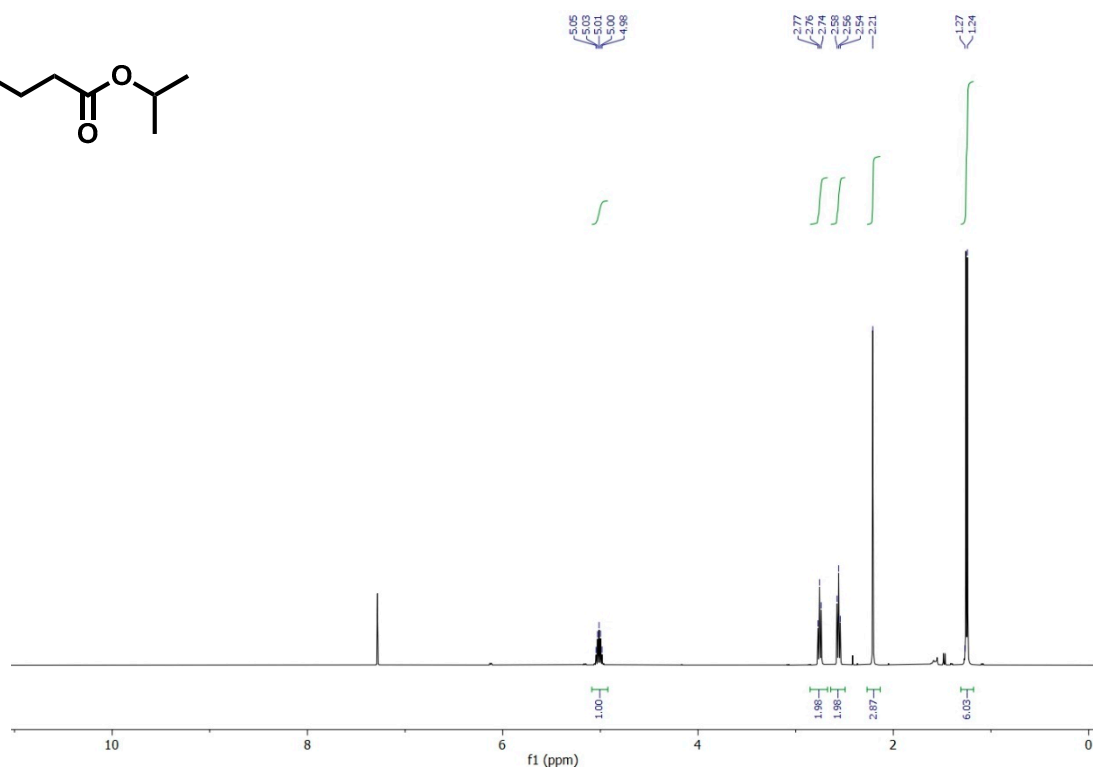
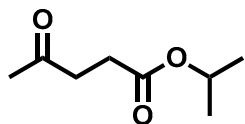
^1H -NMR, ^{13}C -NMR spectra of Methyl Levulinate (MeLev)



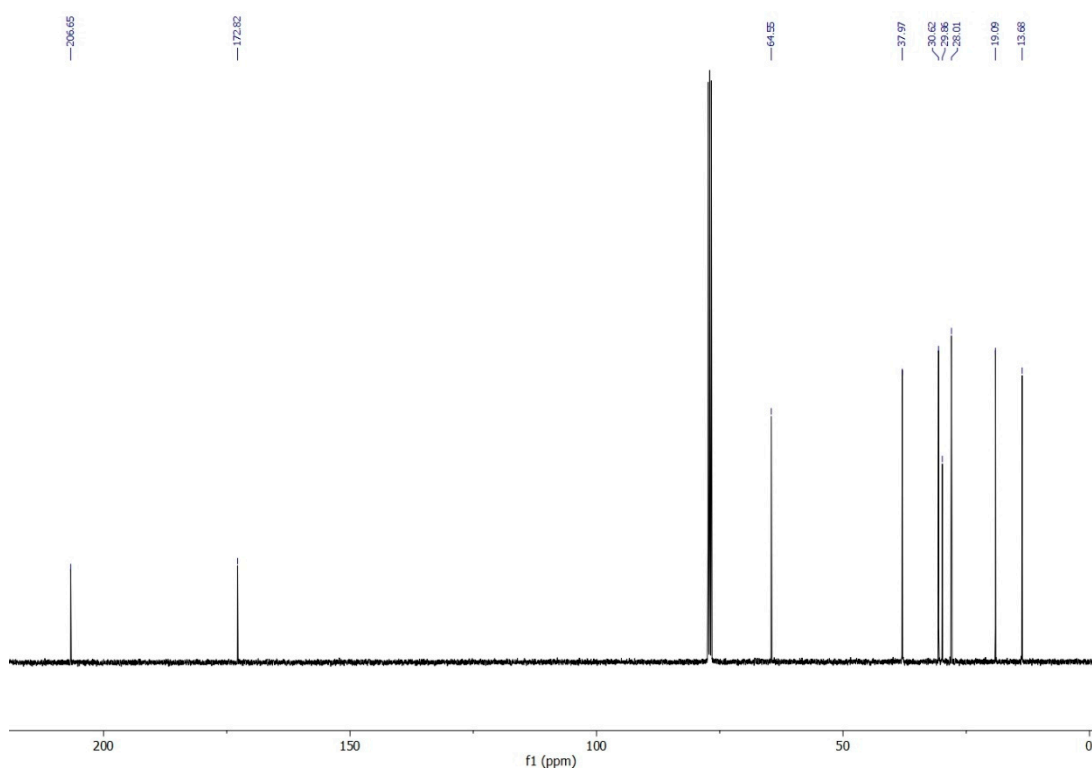
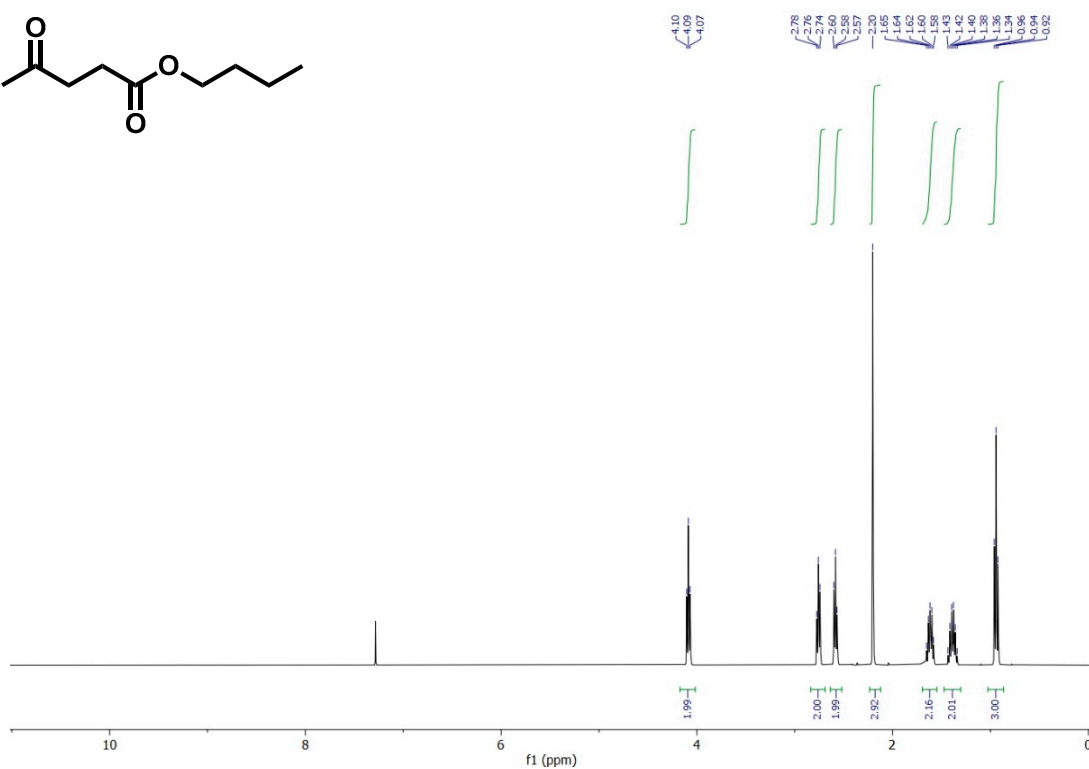
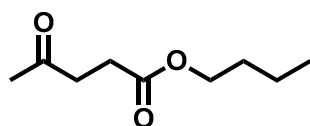
¹H-NMR, ¹³C-NMR spectra of Ethyl Levulinate (EtLev)

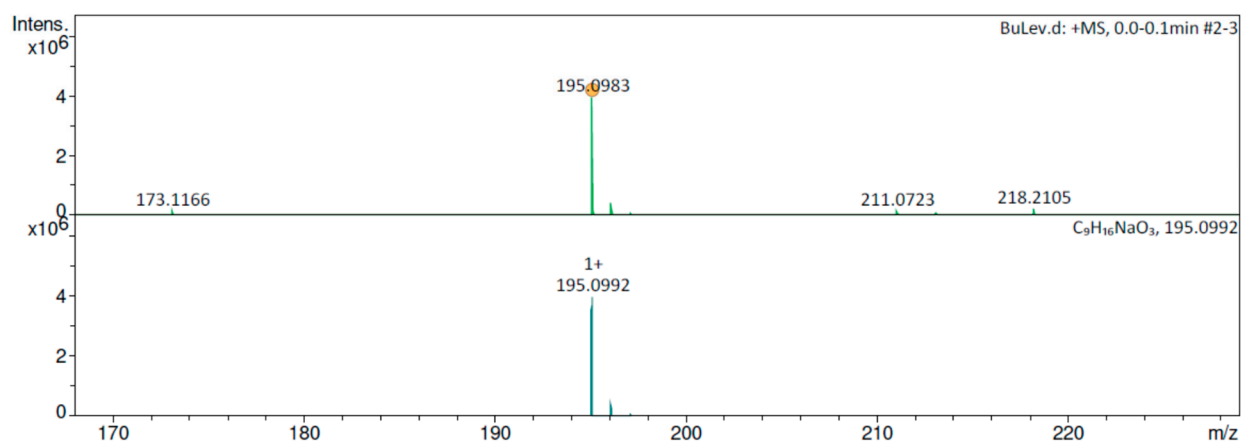
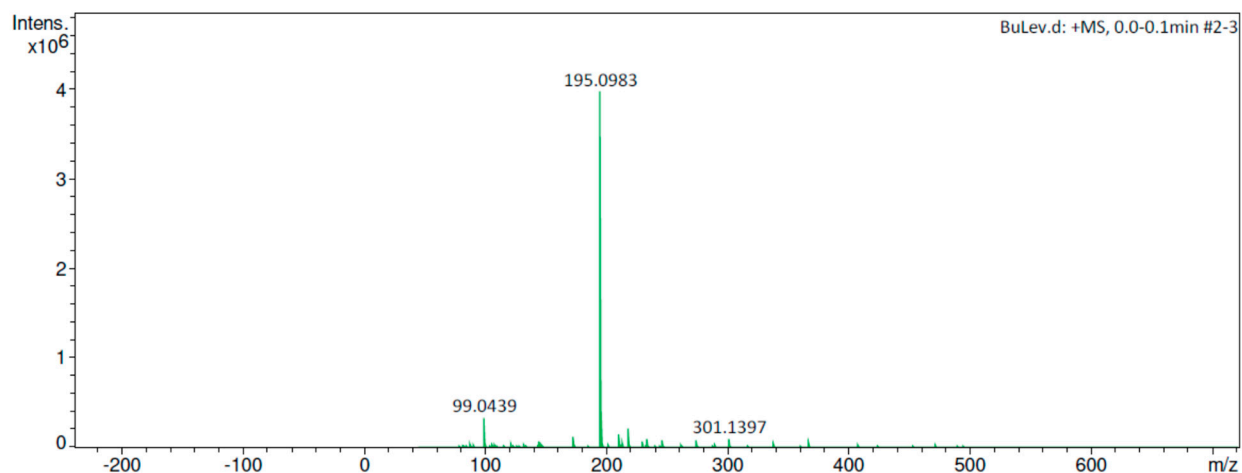


^1H -NMR, ^{13}C -NMR spectra of Isopropyl Levulinate (iPrLev)



^1H -NMR, ^{13}C -NMR and Hi-Res Mass Spectra of Butyl Levulinate (BuLev)





Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdB	e ⁻	Conf	N-Rule
195.0983	1	C ₉ H ₁₆ NaO ₃	195.0992	4.2	1.9	1	100.00	2.0	even		ok
	2	C ₅ H ₁₂ N ₆ NaO	195.0965	-9.6	15.4	2	40.18	3.0	even		ok

Analysis Info

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 Sample Name BuLev
 Comment

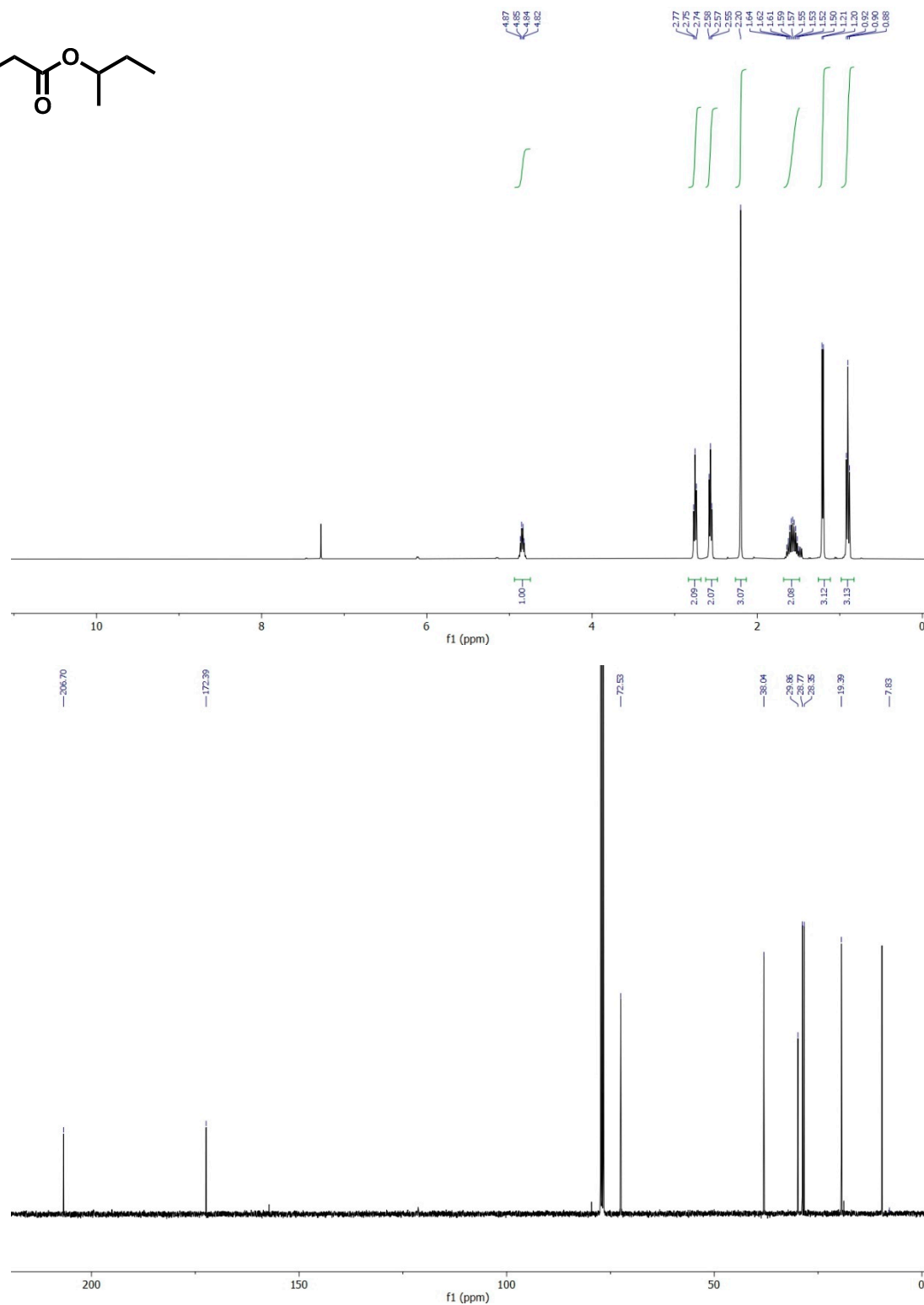
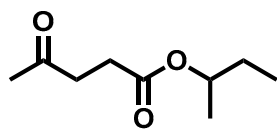
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Operator Demo User
 Instrument compact 8255754.20209

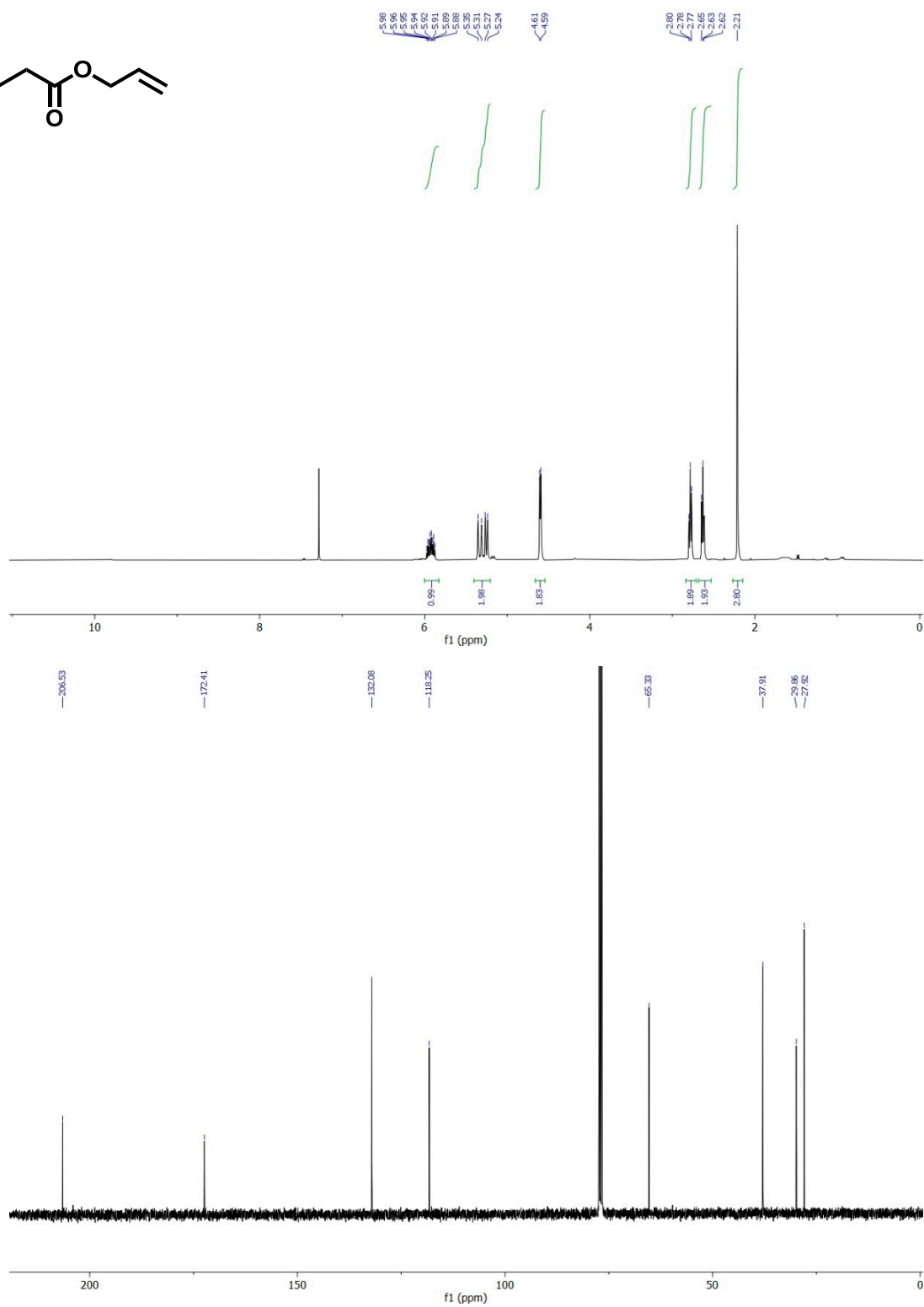
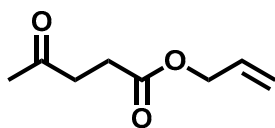
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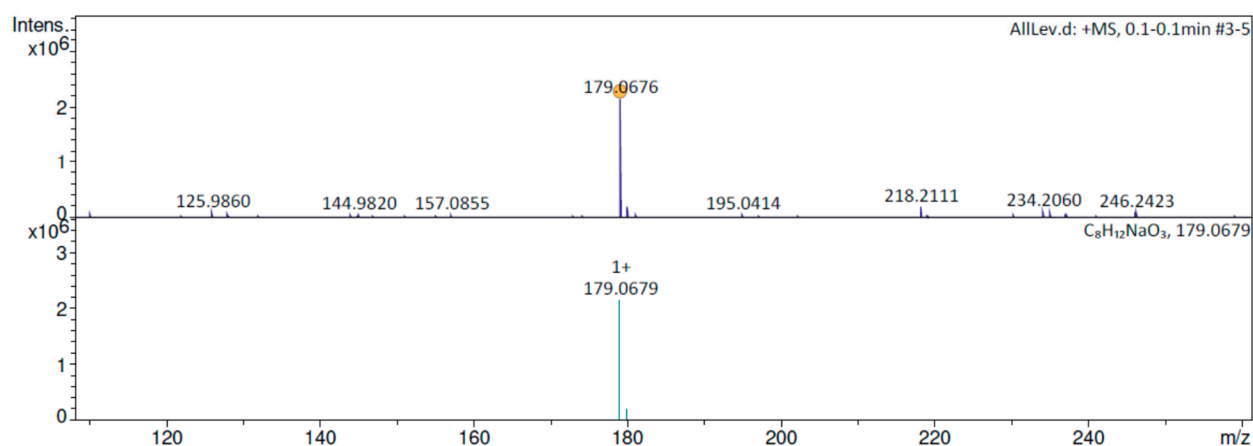
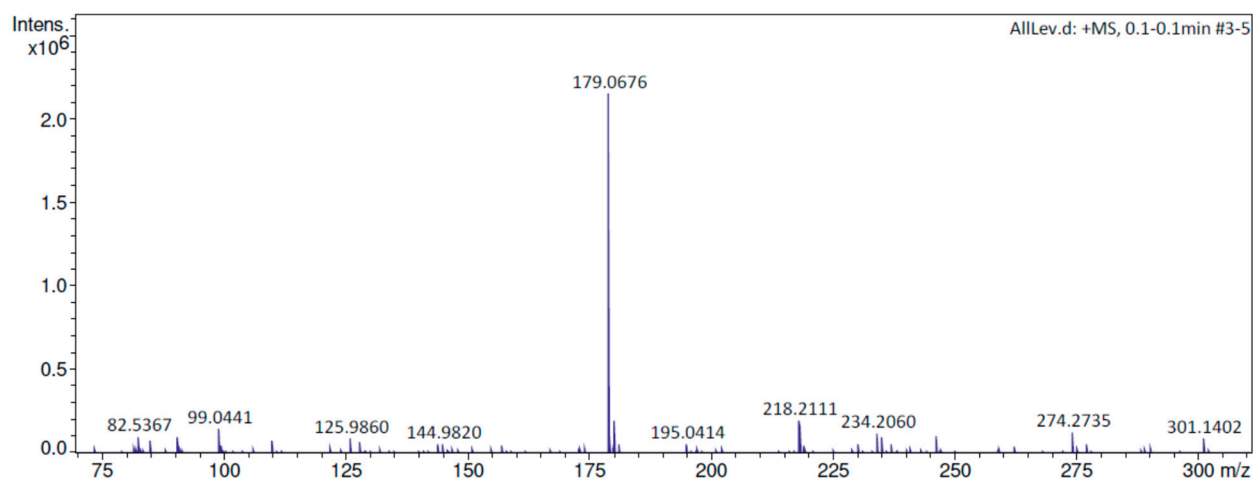
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	650.0 Vpp	Set Divert Valve	Source

^1H -NMR, ^{13}C -NMR spectra of *sec*-Butyl Levulinate (sBuLev)



^1H -NMR, ^{13}C -NMR and Hi-Res Mass spectra of Allyl Levulinate (AllLev)





Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdB	e ⁻	Conf	N-Rule
179.0676	1	C ₈ H ₁₂ NaO ₃	179.0679	1.7	8.1	1	100.00	3.0	even		ok
	2	C ₄ H ₈ N ₆ NaO	179.0652	-13.3	18.3	2	21.80	4.0	even		ok

Analysis Info

Analysis Name: D:\Data\Jack\LipidomicaEMA190521\Mattia210521\AllLev.d
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 Sample Name: AllLev
 Comment:

Acquisition Date: 5/21/2021 4:32:14 PM

Operator: Demo User
 Instrument: compact 8255754.20209

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	650.0 Vpp	Set Divert Valve	Source