Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPLEMENTARY INFORMATION

Furandicarboxylic acid methyl ester from galactaric acid via dimethyl carbonate chemistry

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CONTENTS

Table S1. Purolite and Amberlyst catalysts properties.

	CT275	CT269	CT151	Amb-15	Amb-36
Polymer structure	Macroporous polystyrene crosslinked with divinylbenzene				
Appearence	Spherical Beads				
Functional Group	Sulfonic Acid				
Ionic Form	H^+ form				
Particle Size Range		425 - 1200 µm		< 300 µm	600 – 850 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)	≥ 5.4 eq/kg (H^+ form)
Moisture Retention	51 - 59 % (H^+ form)	51 - 57 % (H^+ form)	54 - 59 % (H^+ form)	≤ 1.6% (H^+ form)	51 - 57 % (H^+ form)
Surface Area	20 - 40 m^2/g	35 - 50 m^2/g	15 - 25 m^2/g	53 m^2/g	33 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	0.20 mL/g
Average Pore Diameter	400 - 700 Å	250 - 425 Å	250 - 400 Å	300 Å	240 Å
Temperature Limit	130 °C	130 °C	150 °C	120 °C	150 °C

a) All information is available on the Purolite® website (https://www.purolite.com/index). All Amberlyst-15 information are available on the DuPont (https://www.dupont.com/content/dam/dupont/amer/us/en/watersolutions/public/documents/en/45-D00927-en.pdf) and Lenntech websites (https://www.lenntech.com/Data-sheets/Dow-Amberlyst-36-wet-L.pdf).

Compound synthesis

Synthesis of 2,5-furandicarboxylic acid dimethyl ester – FDME

Galactaric acid (1.0 g, 4.7 mmol, 1 mol eq.), Amberlyst-36 (0.5 g, 50 wt. %) and DMC (35 mL, 416 mmol, 88 mol eq.) were added in a 220 mL stainless steel autoclave at 200 °C for 2 h under stirring at 600 rpm. The autoclave was washed with dichloromethane and the reaction mixture filtered under vacuum with a small amount of celite. The resulting liquid was dried until the formation of a pale yellow solid. To further purify the product, the solid was dissolved in 20 mL of diethyl ether with a small amount of charcoal. The solution was heated at 35-40 °C and stirred for 30 minutes. The mixture was filtered through a paper filter and the transparent liquid was dried under vacuum. The pure FDME was isolated as a white powder with a yield of 70 %. The product formation was confirmed through proton and carbon NMR.

^{1}H NMR (400 MHz $CDCl_3$) δ ppm = 3.96 (s, 6H), 7.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm = 52.4, 118.5, 146.7, 158.4.

Synthesis of 2,5-furandicarboxylic acid diethyl ester – FDEE

Dimethyl galactarate (1 g, 4.2 mmol, 1 mol. eq.), Amberlyst-36 (0.5 g, 50 wt. %) and DEC (35 mL, 289 mmol, 69 mol. eq.) were added in a 220 mL stainless steel autoclave at 200 °C for 2 h under stirring at 600 rpm. The autoclave was washed with dichloromethane and the reaction mixture filtered under vacuum with a small amount of celite. The brown oil was purified via silica column chromatography with a mixture of hexane:ethyl acetate 7:3 as mobile phase. The pure FDEE was isolated as a light yellow liquid with a 38 % yield. The product formation was confirmed through proton and carbon NMR.

^{1}H NMR (400 MHz $CDCl_3$) δ ppm = 1.40-1.44 (t, 6H), 4.40-4.45 (q, 4H), 7.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm = 14.3, 61.6, 118.2, 147.0, 158.1.

Synthesis of dimethyl galactarate– Me-Gal

Me-Gal was synthesized according to the procedure already reported in the literature.[1]

Blank experiment - DMC and Amberlyst-36

Dried Amberlyst-36 (0.5 g – 50 wt. %) and 35 mL of DMC were added to a 220 mL stainless steel autoclave. The mixture was heated at 200 °C for 2 h under stirring reaching a maximum value of autogenous pressure of 90 bar. The solution was filtered on a paper filter to remove the solid catalyst and the amount of the residual liquid was 10 mL.

[1] M. E. Davis, H. Han, JP2019/108372, California Institute of Technology, 2019, A Location in patent: Paragraph 0230; 0231.

Table S2. Synthesis of FDME starting from dimethyl galactarate (Me-Gal) with different solvents

#	Me-Gal (g)	Solvent	T (°C)	Time (h)	P (bar)	Solv.polarity	Conv. (%)	FDME Yield (%)
3	1.0	DMC	200	2	95	0.232[a]	99	60
4	1.0	CH_3CN	200	2	20	0.460[b]	<5	0
5	1.0	Dioxane	200	2	10	0.164[b]	<5	0
6	1.0	Tert-butanol	200	2	55	0.389[b]	<5	0
7	1.0	Me-lactate	200	2	25	/	<5	traces
8	1.0	H_2O	200	2	20	1.00[b]	<5	0
9	1.0	DEC	200	2	75	0.185[b]	99	38[c]

Reaction conditions: 50 wt. % of Amb-36, 35 mL of solvent in a stainless steel autoclave under pressure. [a]W. Li, F. Galiano, J. Estager, J. M. Monbaliu, D. P. Debecker, A. Figoli, P. Luis; Journal of Membrane Sciences, 2018, 567, 303-310; [b] C. Reichardt, Chem. Rev, 1994, 94, 2319; [c] FDEE.

Catalyst recycling

Reaction conducted without stirring (#2; Table S3) Galactaric acid (Gal; 1.0 g), dried Amberlyst-36 (0.5 g; 50 wt. %) and 35 mL of DMC were added to a 220 mL stainless steel autoclave. The mixture was heated at 180 °C for 4 h without stirring, then the reaction mixture was worked up as previously reported and FDME was isolated in 60% yield.

First recycle (#3, Table S3)*:* The recovered catalyst was washed three times with methanol, oven dried at 100 °C overnight and reused in the next trial. FDME was isolated in 5% yield via column chromatography using a 7:3 hexane:ethyl acetate mixture as eluent phase.

Catalyst reactivation (#4, Table S3)*:* To the Amberlyst-36 recovered from the first recycle experiment (#3, Table S3) was added 30 mL of methanol and 1.5 mL of H_2SO_4. The solution was left overnight at room temperature, thus the catalyst beads were filtered, washed several times with methanol and dried at 100 °C. The dried Amb-36 was employed in the entry 4 Table S3 experiment. Both NMR spectroscopy and analysis via TLC did not show the presence of FDME.

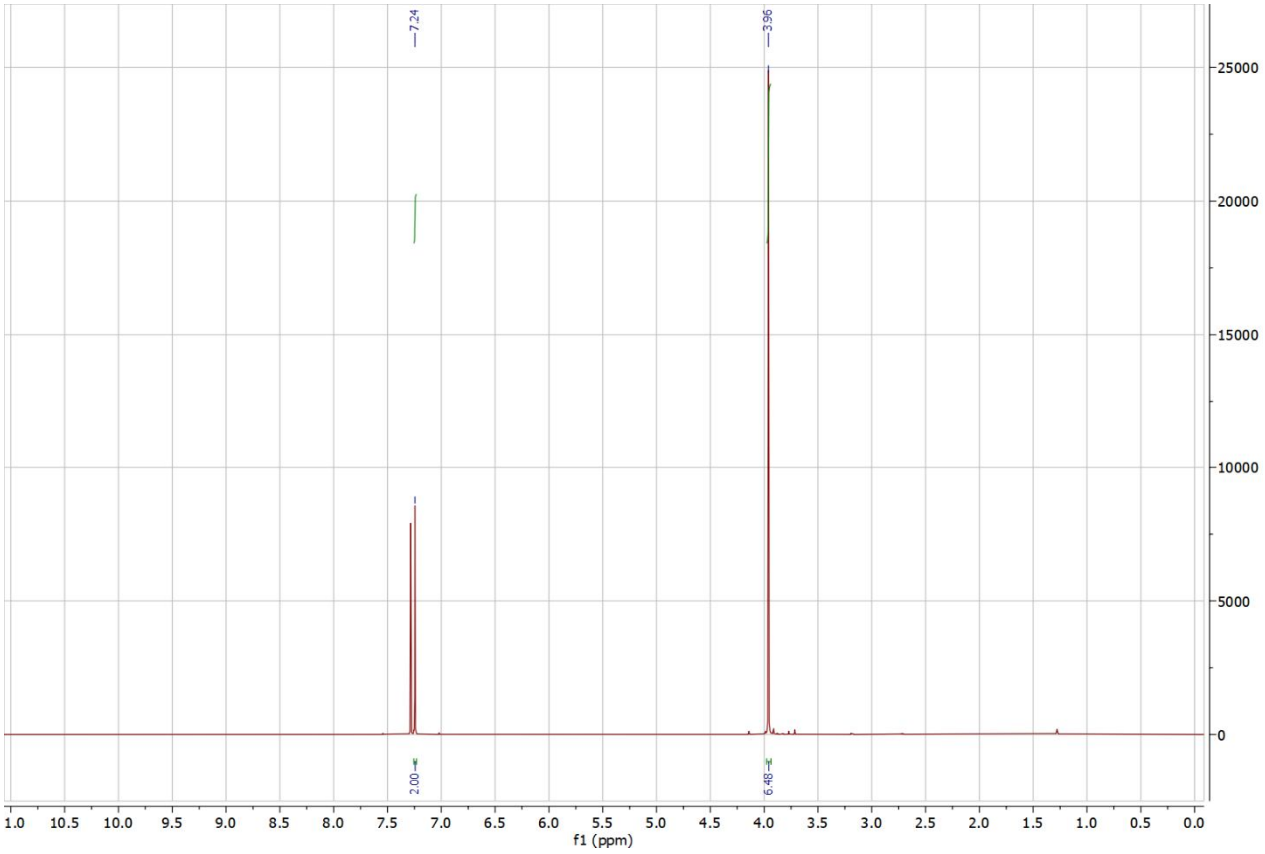
Table S3. Synthesis of FDME. Investigation on catalyst recycling and blank experiment

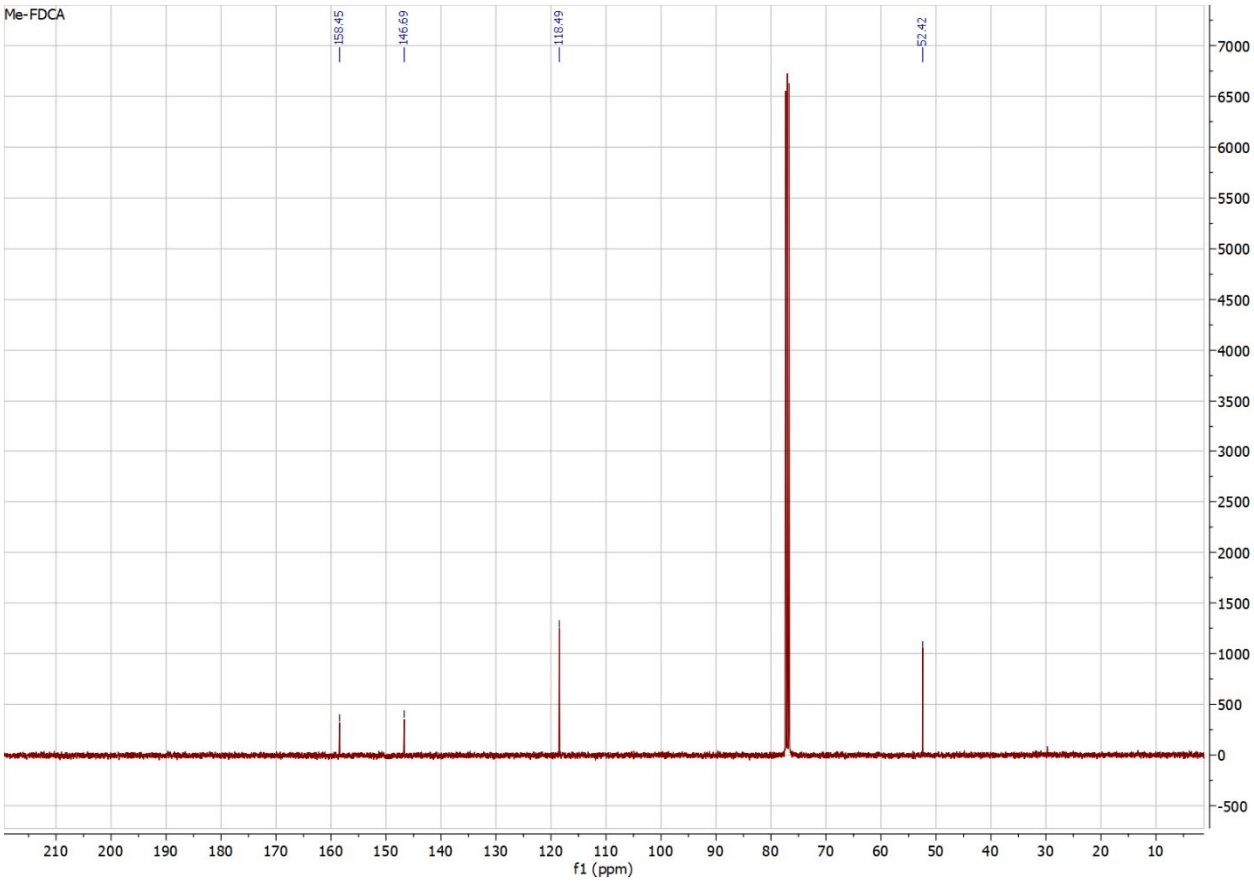
	#	Gal. (g)	T (°C)	P (bar)	FDME isolated Yield (%)
Stirring	1[a]	1	180	95	71
No stirring	2[b]	1	180	90	60
First recycle	3[b]	1	180	60	5[c]
Catalyst reactivation	4	1	180	20	n.d.

[a] Reaction conducted as #8, Table 2; [b] mixture filtered on a paper filter to recover the catalyst, solution purified with diethylether and charcoal; [c] FDME isolated through silica gel column chromatography using an 7:3 hexane:ethyl acetate mixture as eluent phase.

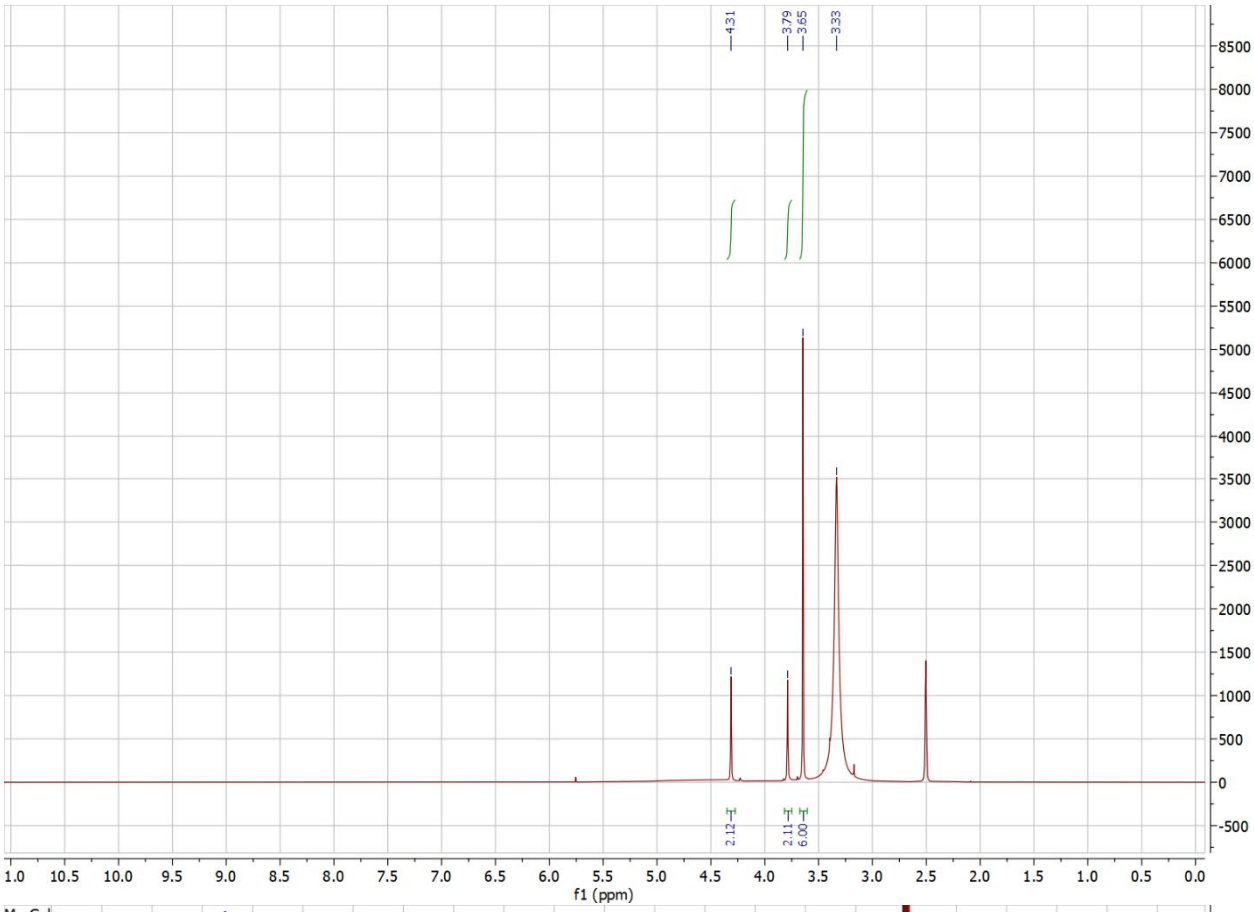
^{1}H and ^{13}C NMR spectra

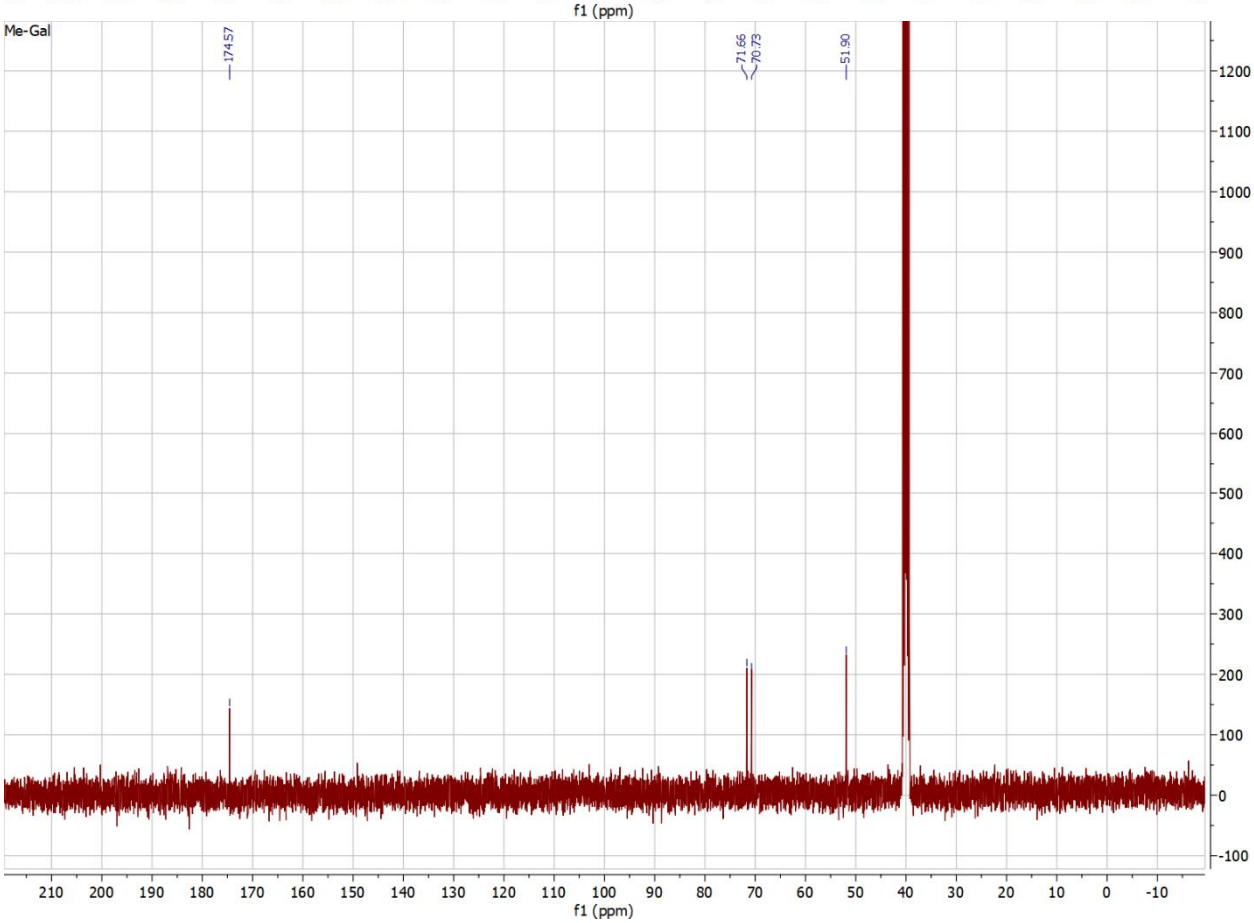
2,5-Furandicarboxylic acid dimethyl ester (FDME)



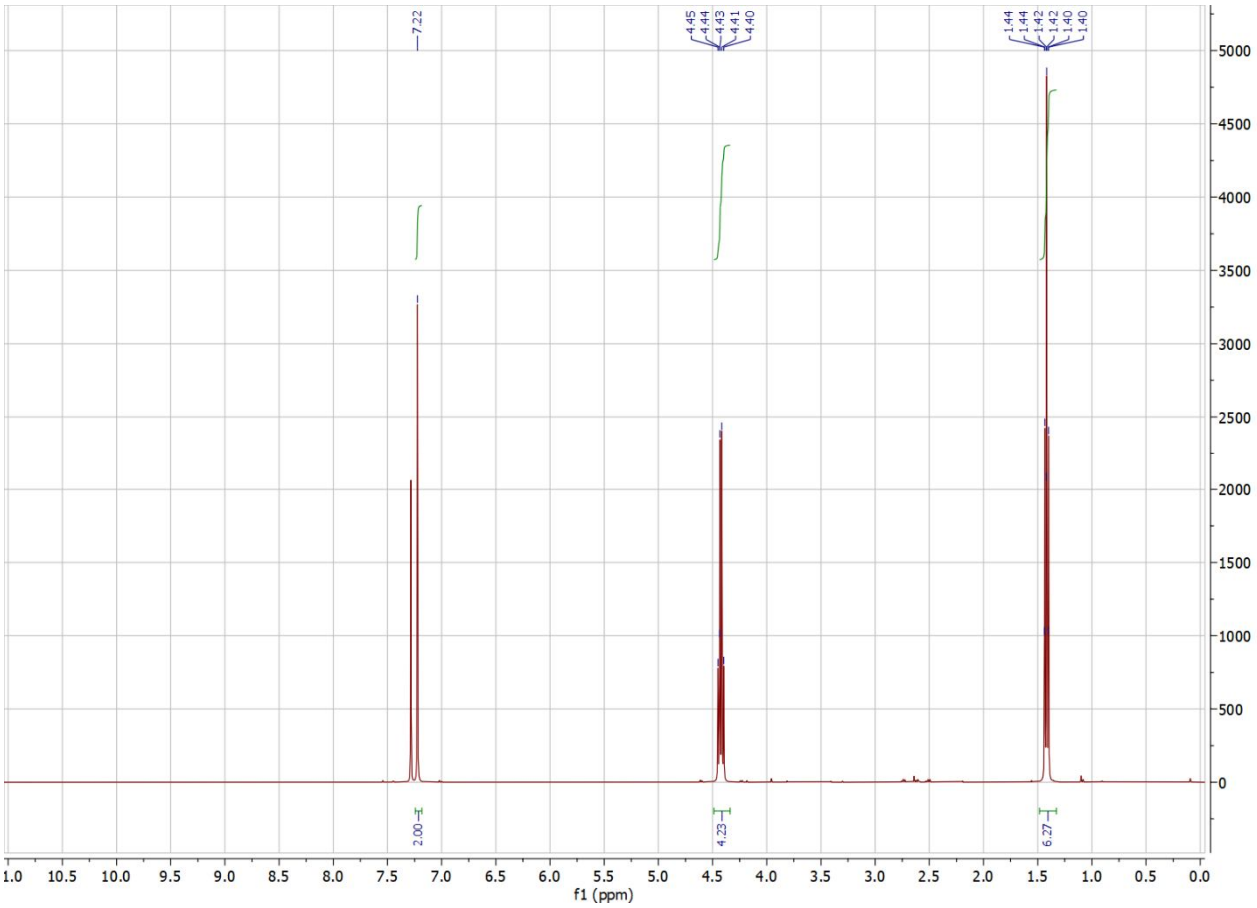


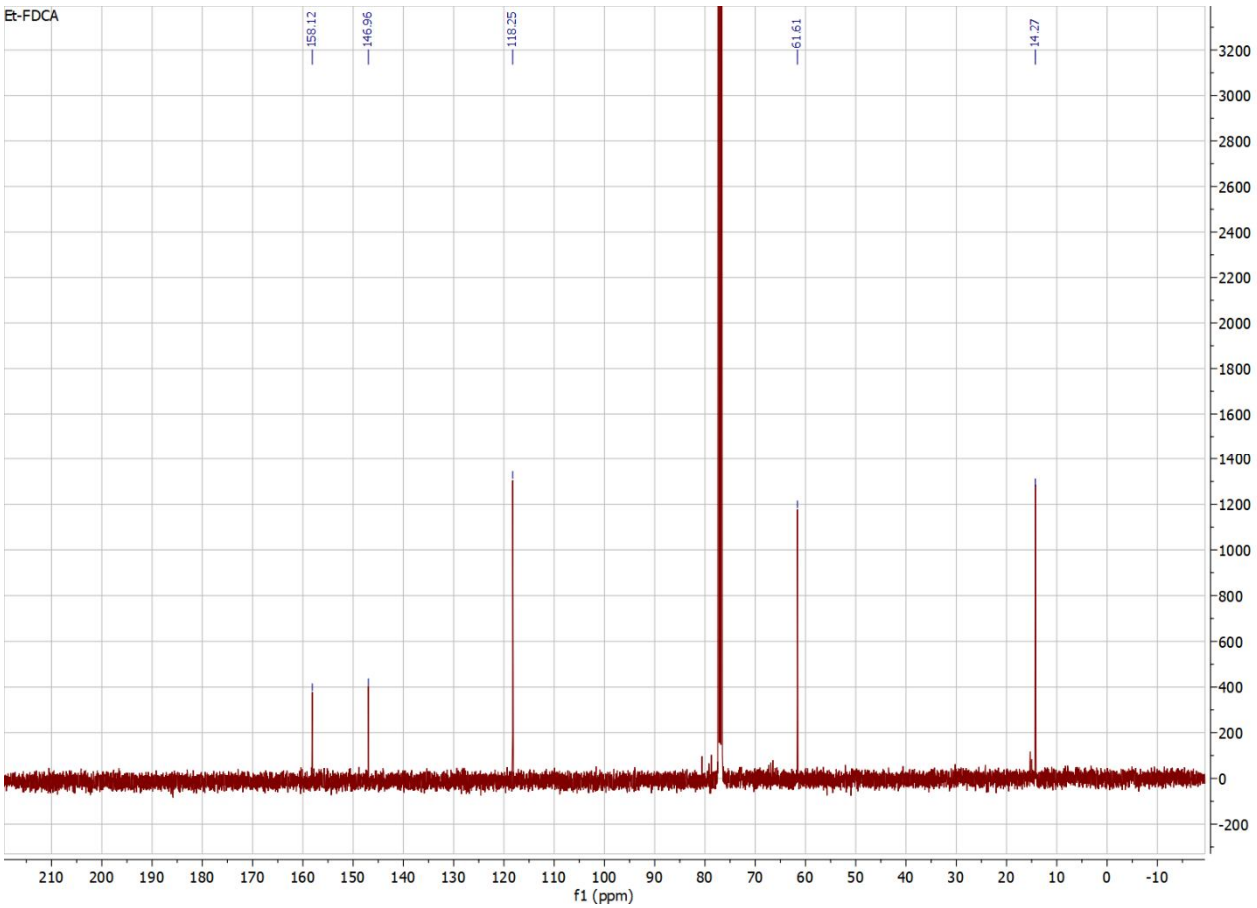
Dimethyl galactarate (Me-Gal)





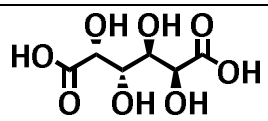
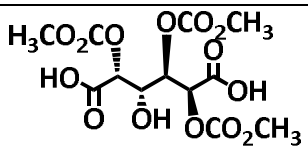
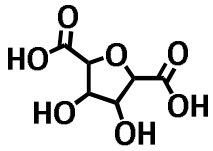
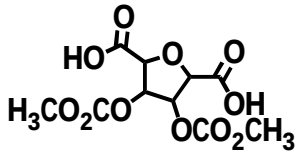
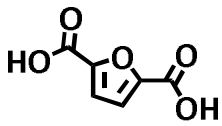
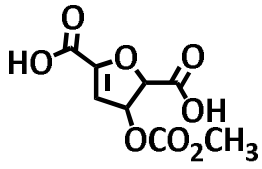
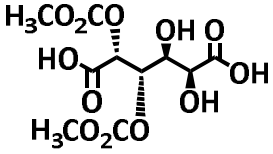
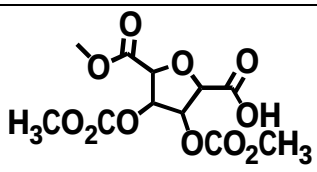
2,5-Furandicarboxylic acid diethyl ester (FDEE)

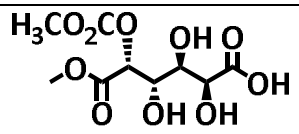
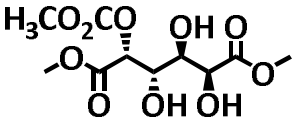
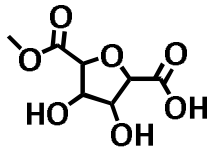
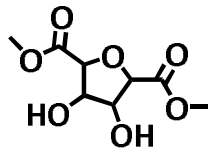
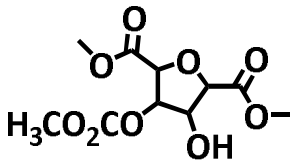
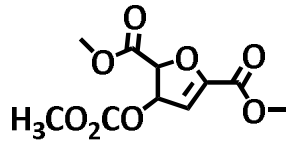
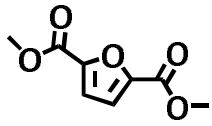
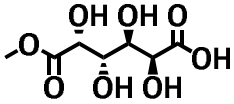
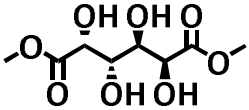
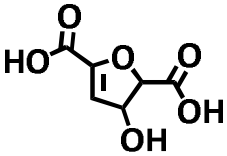
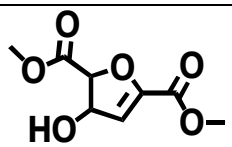




Hi-Res MS spectra of crude reaction mixtures at different reaction times in DMSO

Table S3. List of reaction intermediates detected through Hi-Res MS analysis employing positive (X) and (X) negative potential. Crosses represent the time at which each compound was detected.

#	Structure	T<200 °C			T =200 °C	T=200 °C		
		-35 min (82°C) 1 bar	-20 min (160°C) 6 bar	-10 min (184°C) 12 bar	0 (200°C) 25 bar	30 min (200°C) 65 bar	1 h (200°C) 80 bar	2h (200°C) 95 bar
2	 210.138	X X	X X	X X	X	X		
7	 384.246	X	X					
10	 192.123	X X	X X	X X	X			
15	 308.195	X	X	X	X	X		
21	 156.093	X	X	X	X	X	X X	X X
18	 232.144	X	X					
6	 326.210		X	X				
14	 322.222		X					

4	 282.201				X	X		
5	 296.228				X	X		
9	 206.150				X			XX
11	 220.177				X	X		
13	 278.213				X			X
19	 260.198				X			
22	 184.147				X	X	X	X
1	 224.165					X		
3	 238.192					X		X
16	 174.108					X		
17						X	X	X

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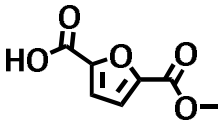
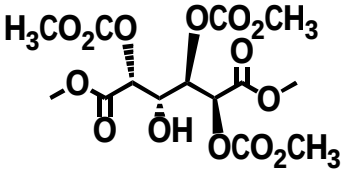
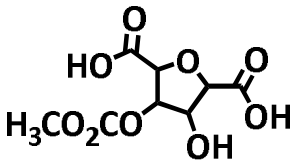
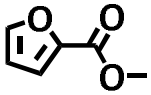
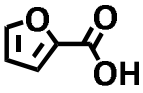
20	 170.120					X	X	X
8	 412.300						X	
12	 250.159						X	
24	 126.111						X	X
23	 112.084							X

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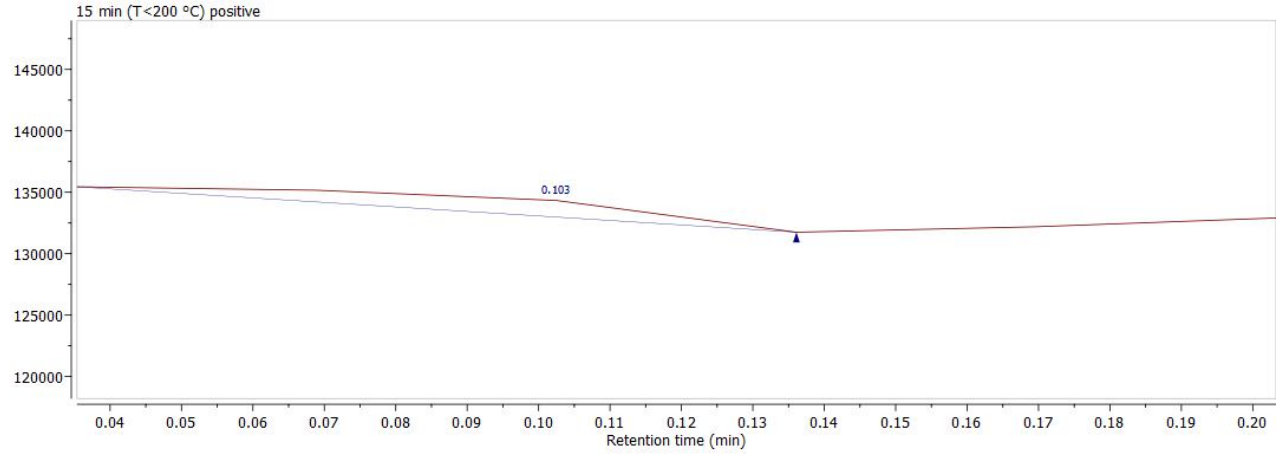

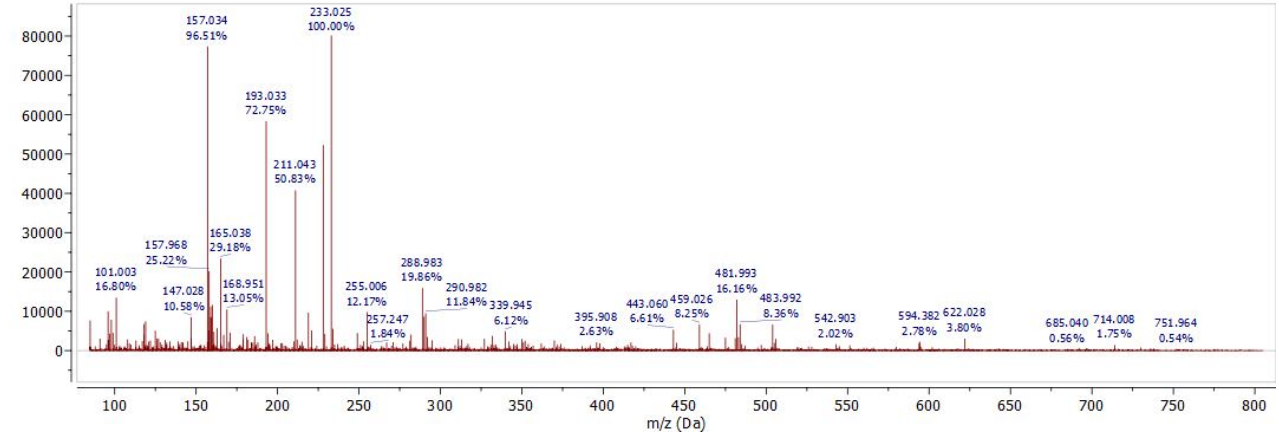

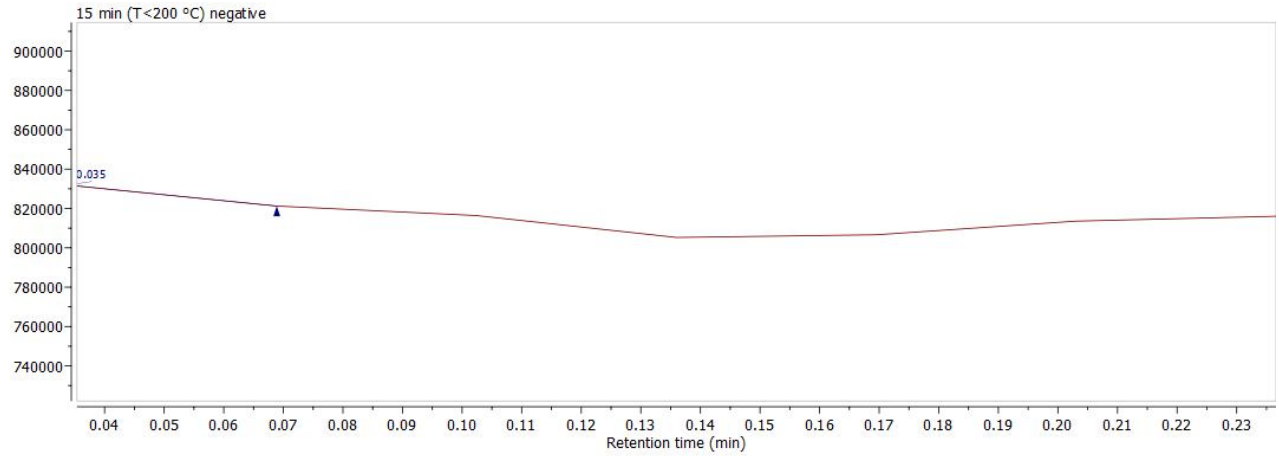

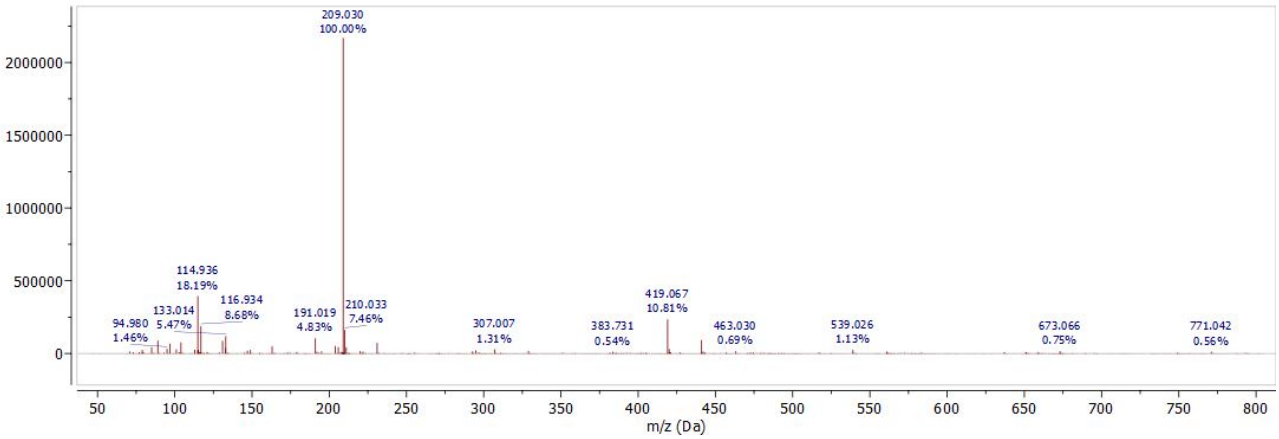

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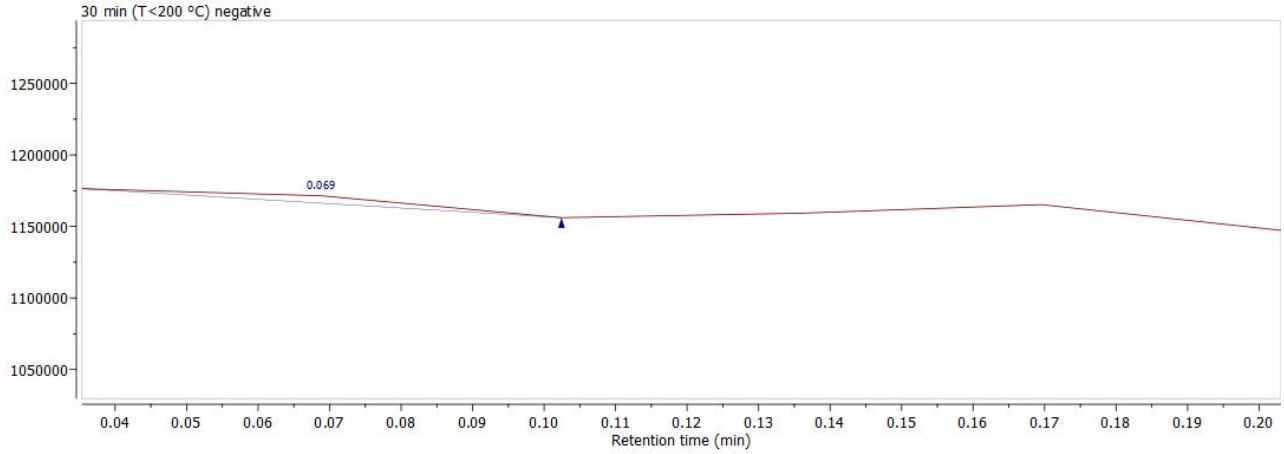

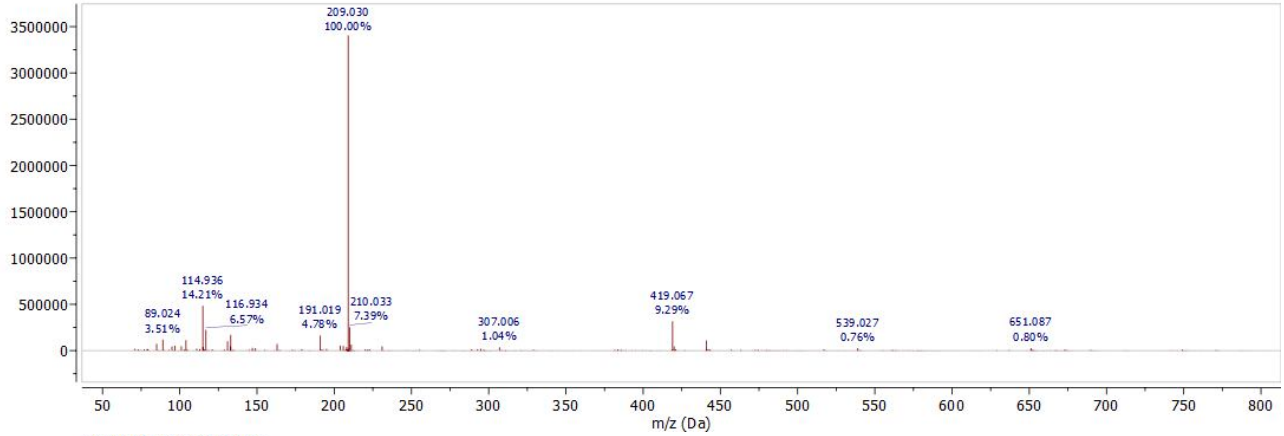

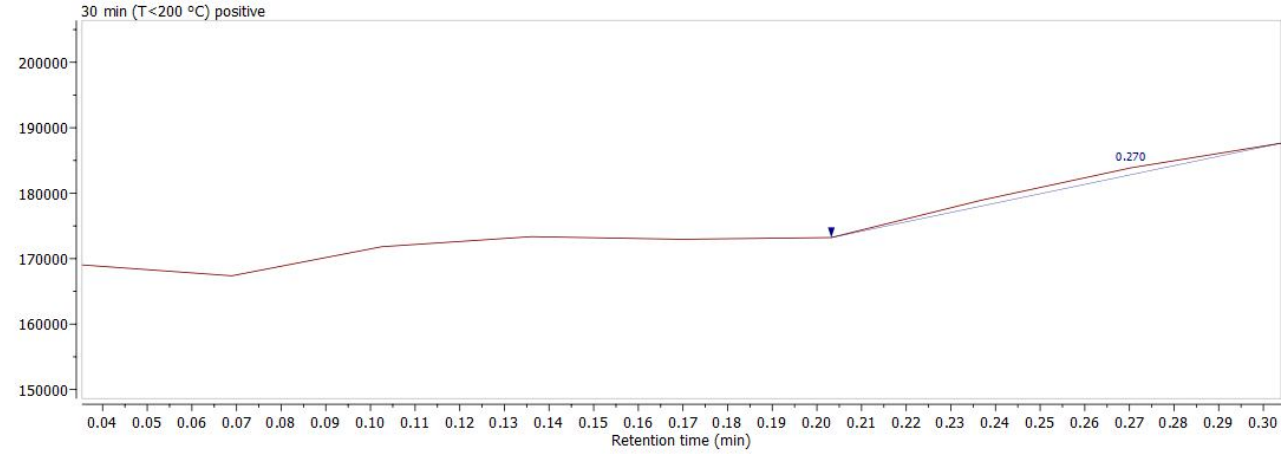

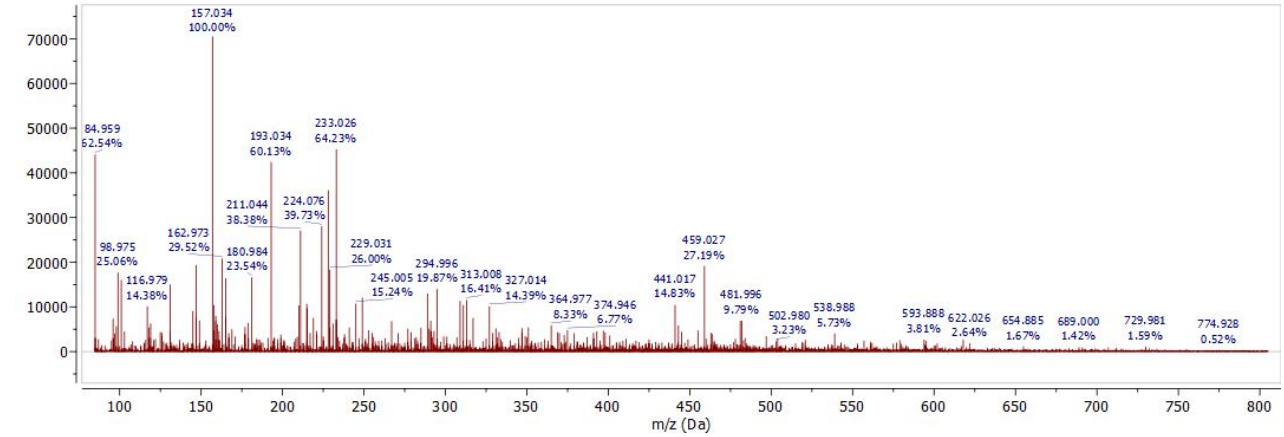

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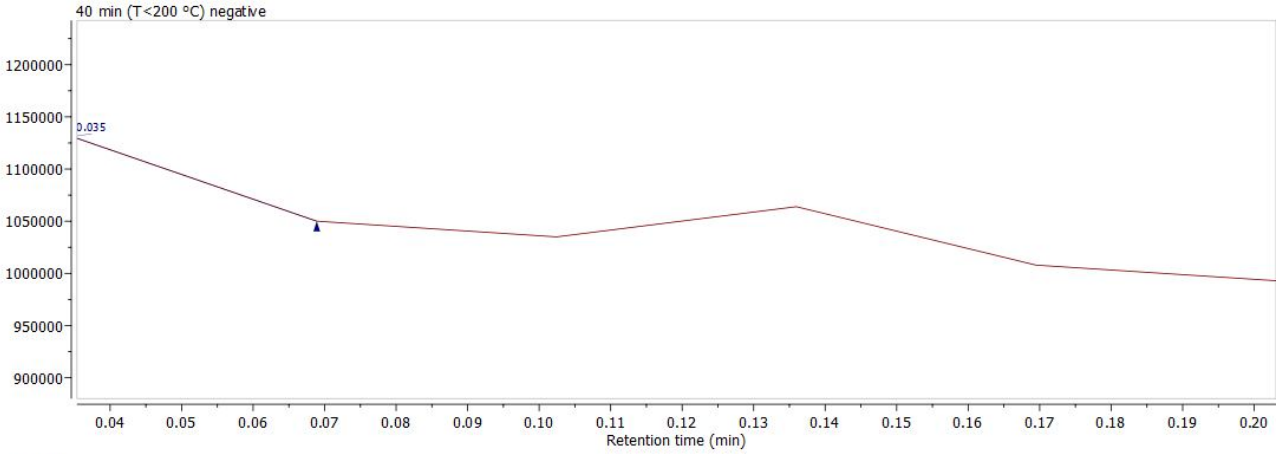
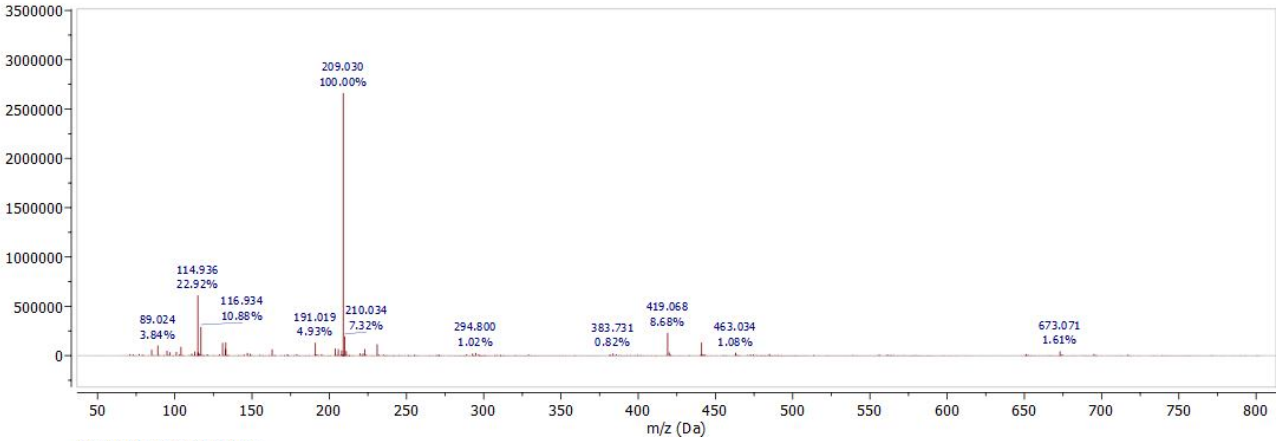
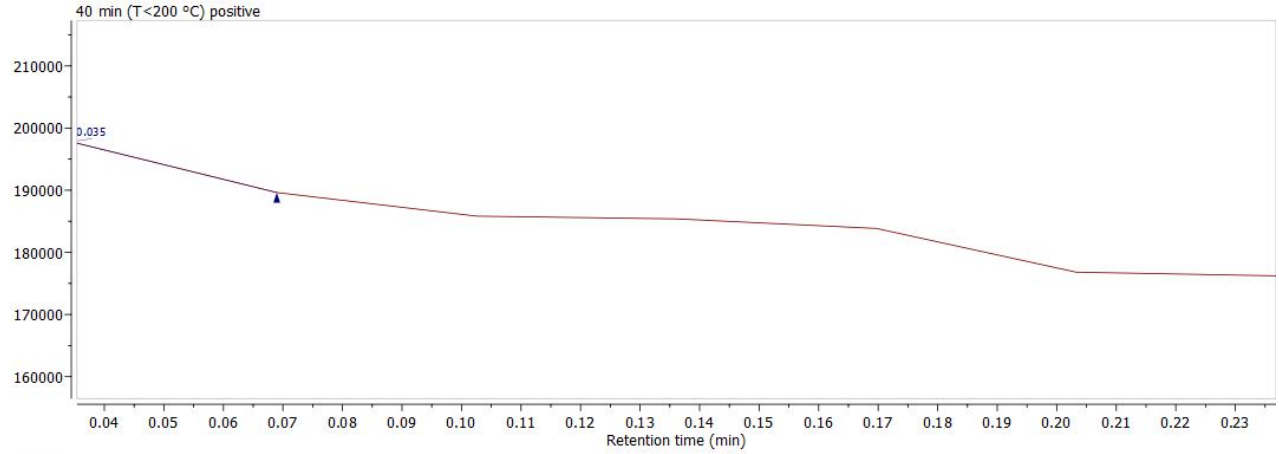
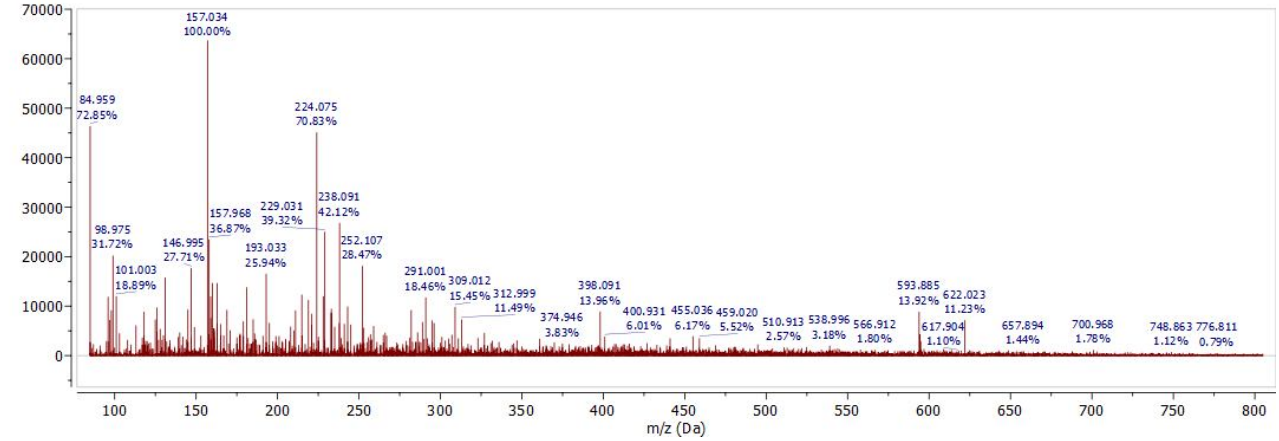
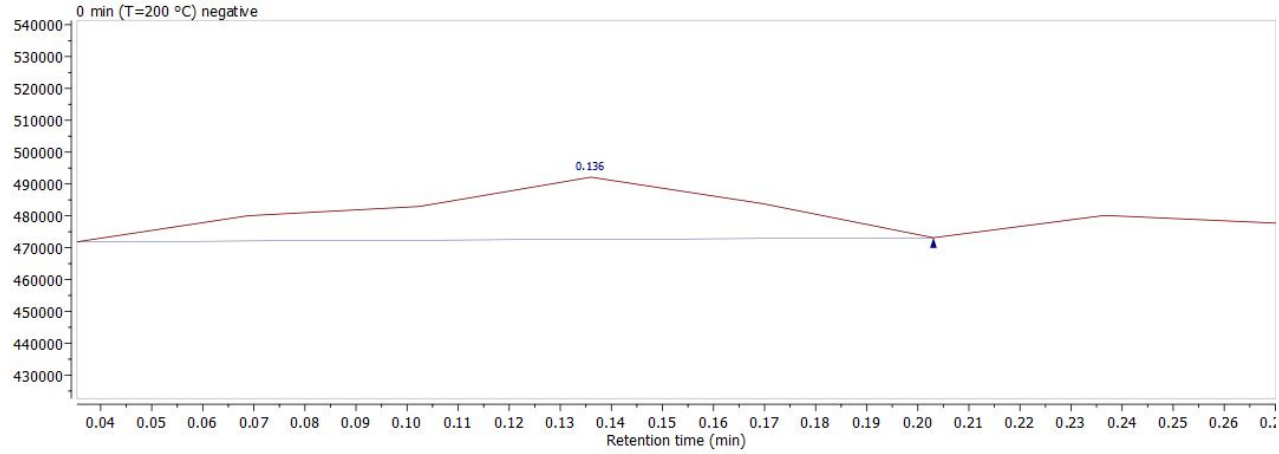


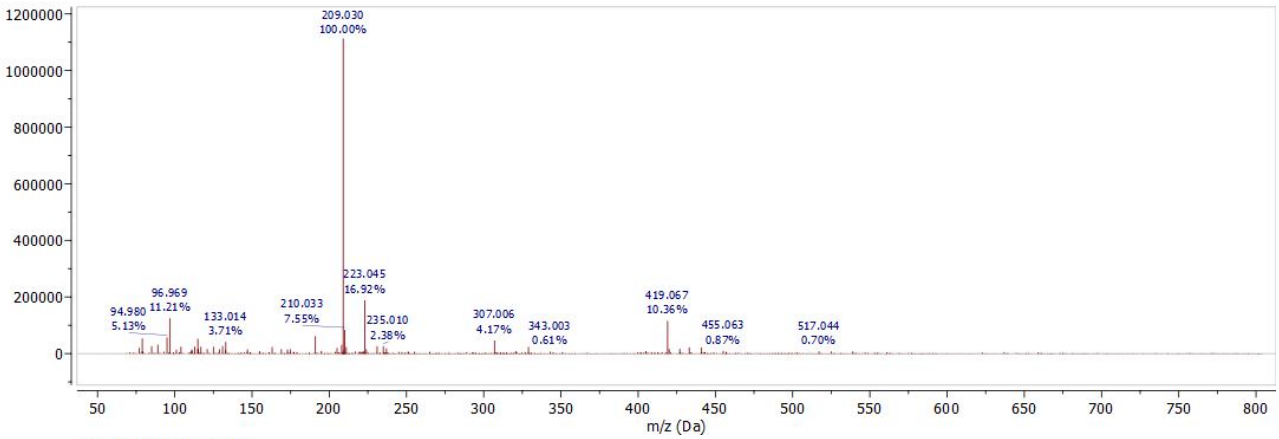


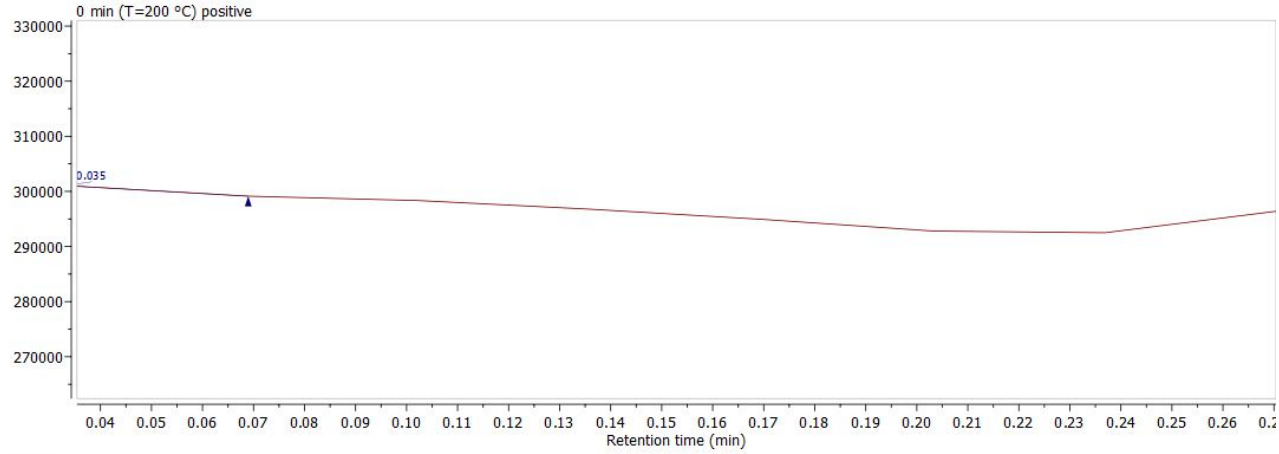


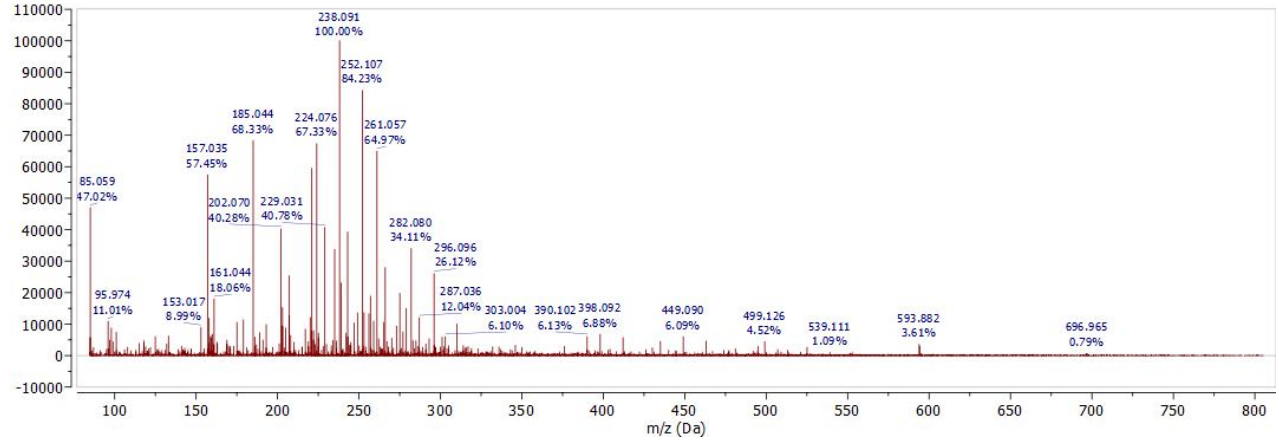


t = 0 minutes, T = 200 °C (positive and negative potential)

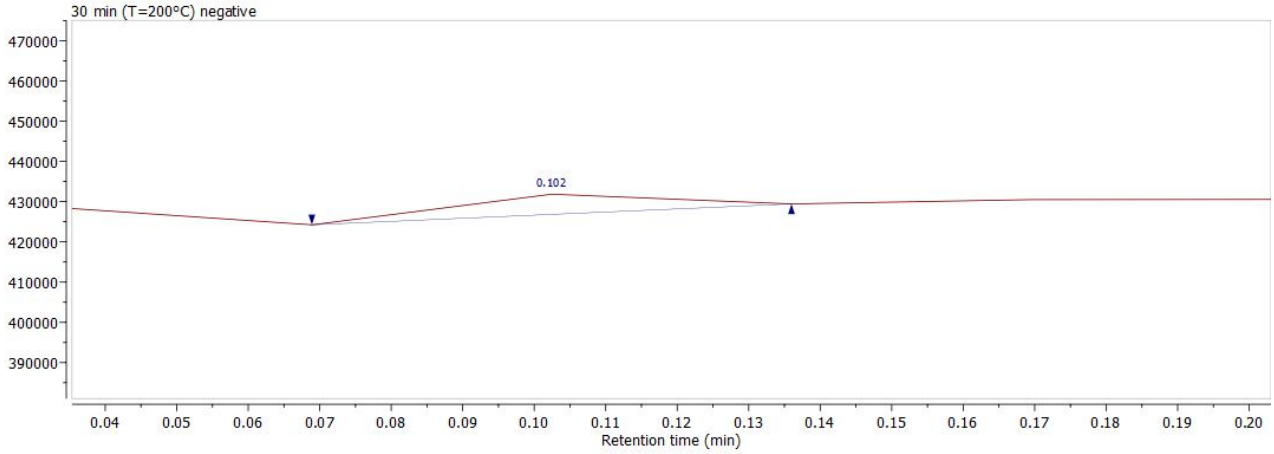


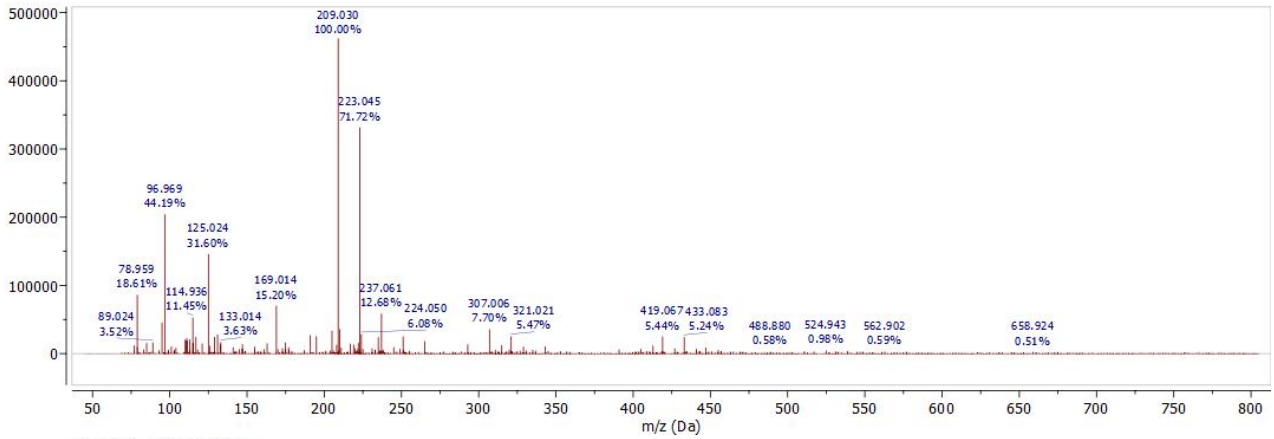


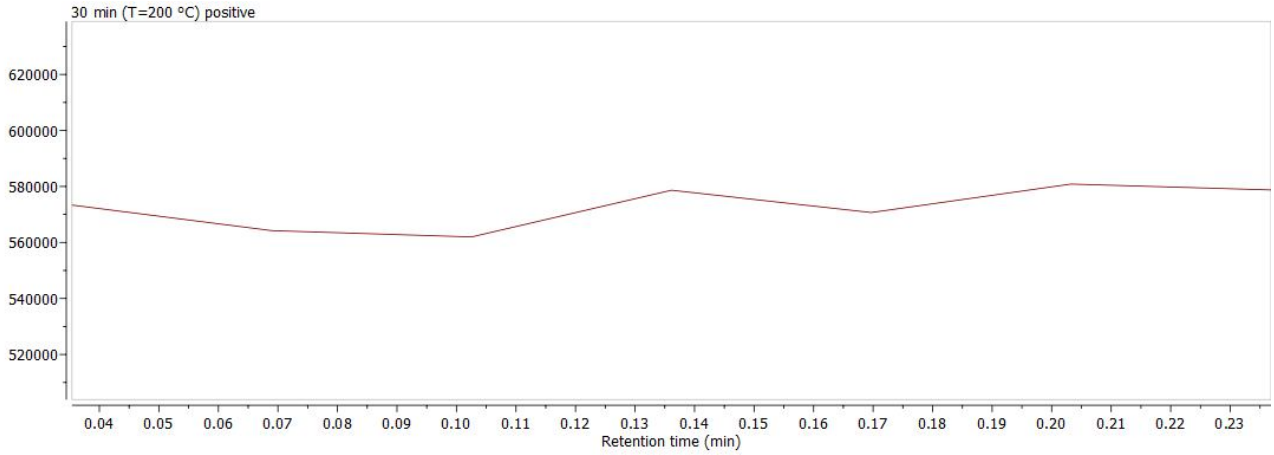


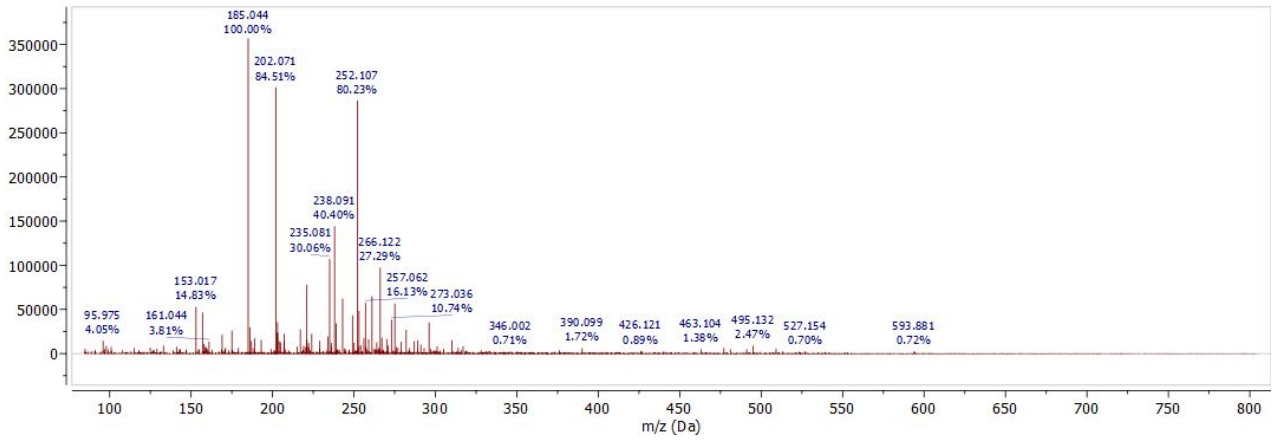


t = 30 minutes (T=200 °C) (positive and negative potential)

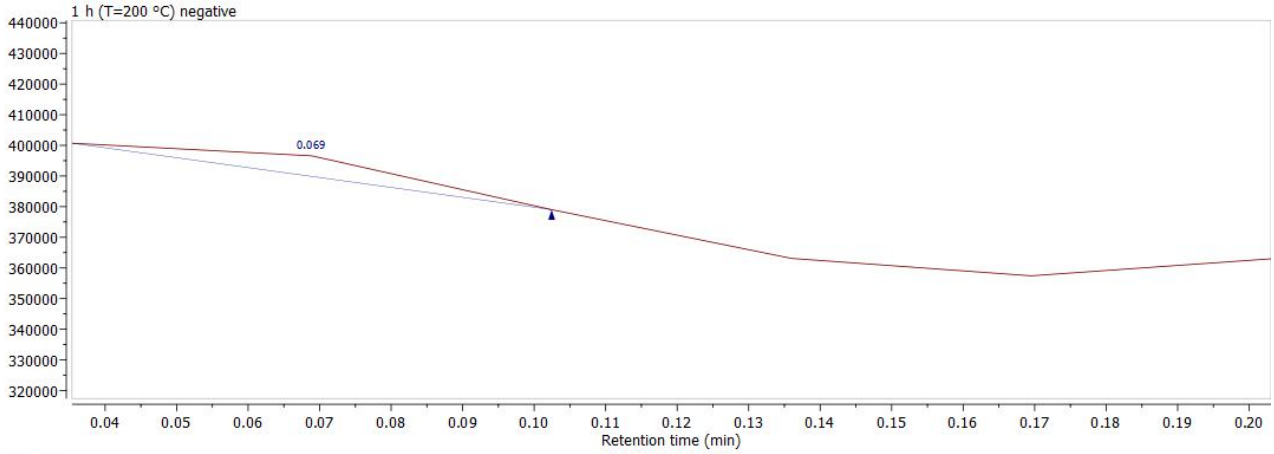


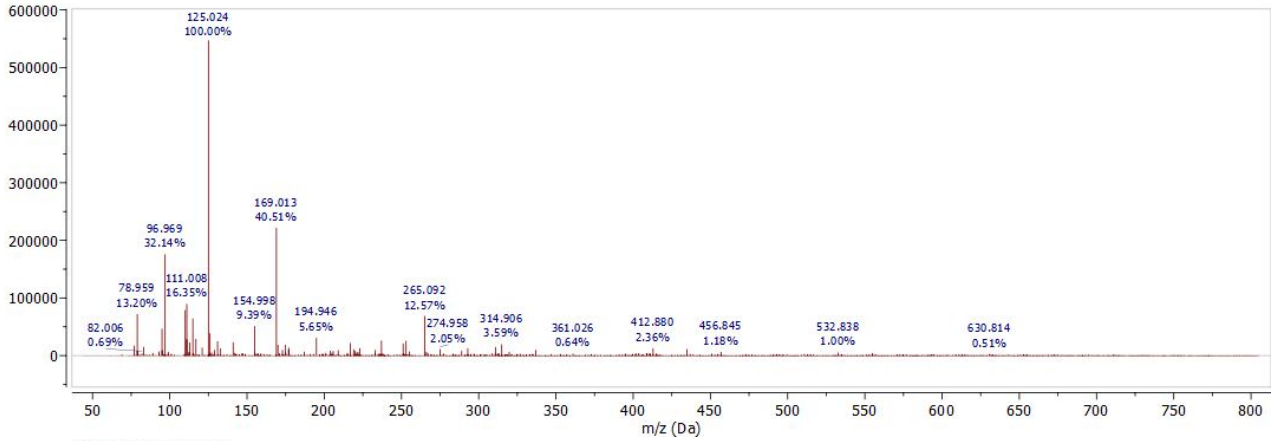


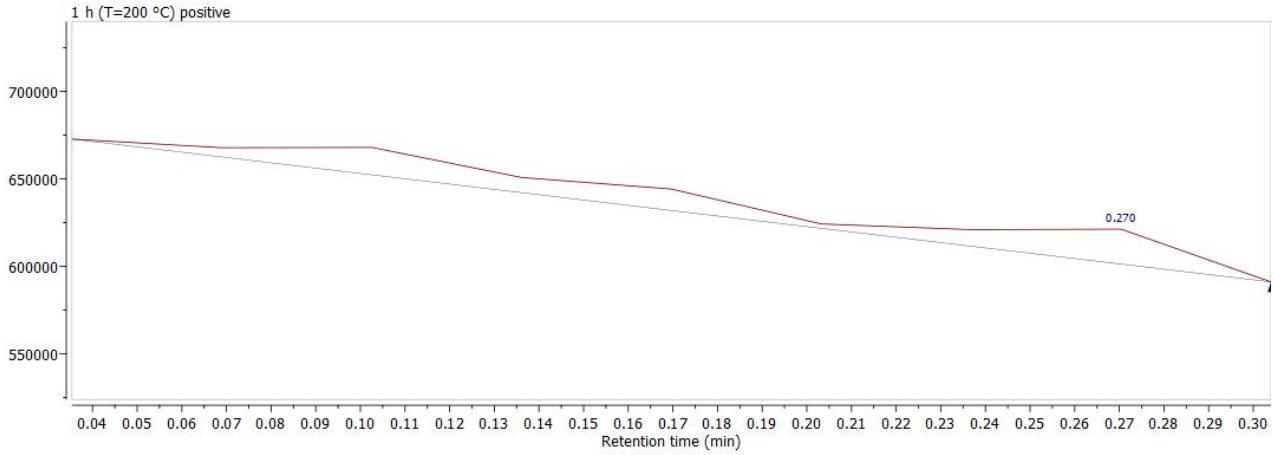


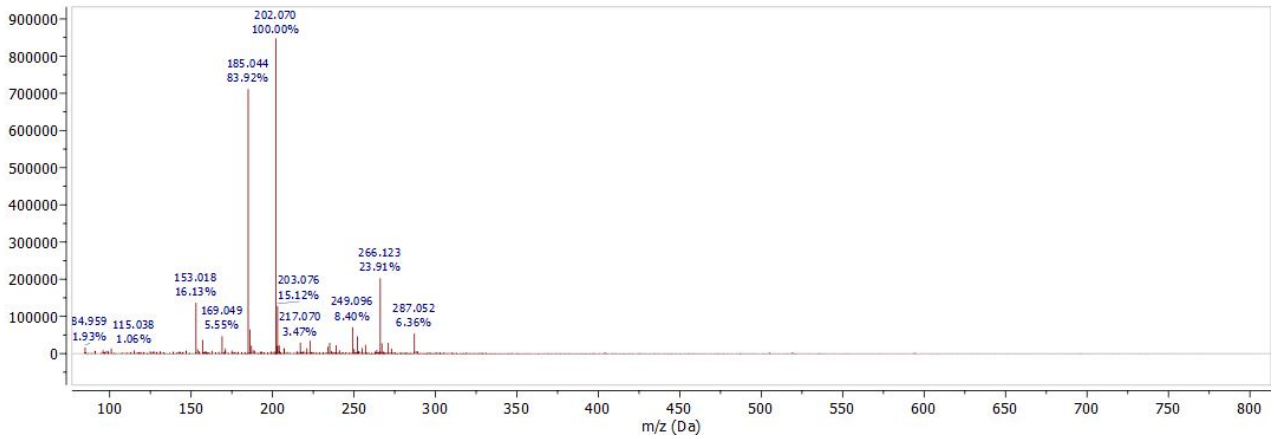


t = 1 hour (T=200 °C) (positive and negative potential)









t = 2 hours (T=200 °C) (positive and negative potential)