Supporting Information for the Communication Article

H_2-Free Heterogenous Route to Glycerol-Based Acrylics via Re-based Deoxydehydration

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Contents

1. Experimental

Catalytic experiments were conducted in stainless steel high-pressure stirred batch reactors (Parr 5000 Multi Reactor System). Each reactor had a total volume of 75 mL was independently heated, stirred magnetically and was equipped with a pressure gauge. In a typical catalytic experiment, 500 mg of aqueous GA (LD-2,3-dihydroxypropanoic acid; 20 – 22 wt % in water, TCI Chemicals) and 50.0 mL of methanol (MeOH; >99.8 %, J.T. Baker) was added vessel to give a ~20 mM solution. For the reaction, 45 mL of this solution, containing 0.001 mol of GA, was used. Rhenium was introduced into the reaction mixture either as a pre-reduced heterogeneous catalyst or as a homogeneous catalyst. In both cases, the molarity of Re was 0.04 mmol and the molar ratio of GA to Re was maintained at 25:1 for consistency. After, the reactor was closed, sealed and purged three times with N_2 (5.0, Messer) before purging and setting the process gas (N_2 or H_2) pressure to 5 bar_g. The stirring speed was set to 600 min^{-1}. The reactor was heated to the set temperature, being typically 150 °C (but also 120, 165 and 180 °C), with the rate of 4 K min^{-1} and kept isothermal for 72 h. The reactor was then cooled to room temperature, depressurized, purged with N_2 and opened to collect and analyze the product mixture.

Homogeneous catalysts, Re_2O_7, $(NH_4)ReO_4$, and $KReO_4$ (all ≥99 %, Sigma Aldrich), were used as received without pretreatment, while supported Re catalysts including Re/C, Re/TiO_2, Re/SiO_2, Re/Al_2O_3 or Re/H-ZSM-5 (each containing 5 wt % Re, all purchased from Riogen Inc.) underwent reductive pretreatment in a tubular furnace at 400 °C (3 h, 200 mL min^{-1} flow of pure H_2). The catalyst mass was either 10.0 mg (Re salts) or 140 mg (supported catalysts).

Ethanol (99.9 %, J.T. Baker), iso-propanol (>99.8 %, Merck), n-propanol (>99.5 %, Sigma-Aldrich), n-butanol (>99.9 %, Honeywell) and n-pentanol (>99 %, Sigma-Aldrich) were used as alternative solvents.

The catalysts were characterized by N2-physisorption, temperature-programmed reduction with H_2 (H_2-TPR), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). All characterization procedures and methods were conducted analogous to our previous work[1,2], where method details and procedures are described in detail.

2. Catalytic Data

Catalyst Screening

Table S1 Product yields after 72 h observed in the catalytic dehydroxylation of glyceric acid over different supported and unsupported Re catalysts in methanol at 150 °C under N_2 atmosphere. Moreover, supporting experiments with additional solid catalysts, under H_2 atmosphere (5 bar) and with non-reduced Re/C are shown. The experimental error is based on repeated experiments (Table S2).

Catalyst	Product yields / %				
	Acrylic acid	Methyl acrylate	Propanoic acid	Methyl propanoate	Methyl glycerate
Re/C	10.0 ± 2.0	46.2 ± 6.7	n.d.	4.4 ± 2.7	25.1 ± 11.4
Re/TiO_2	n.d.	3.2	n.d.	n.d.	22.6
Re/SiO_2	n.d.	0.9	n.d.	n.d.	92.3
Re/Al_2O_3	n.d.	0.4	n.d.	n.d.	84.4
Re/H-ZSM-5	n.d.	1.3	n.d.	n.d.	100.1
Re_2O_7[a]	n.d.	8.5	n.d.	n.d.	n.d.
$(NH_4)ReO_4$[a]	n.d.	13.4	n.d.	n.d.	n.d.
$KReO_4$[a]	n.d.	0.9	n.d.	n.d.	n.d.
Re/C+H-ZSM-5[b]	1.4	47.5	n.d.	2.5	n.d.
Re/C+Amberlyst[b]	n.d.	53.9	n.d.	12.8	n.d.
Re/C (H_2)[c]	4.2	54.4	n.d.	3.6	6.1
Re/TiO_2 (H_2)[c]	n.d.	6.0	n.d.	n.d.	n.d.
Re/SiO_2 (H_2)[c]	n.d.	2.0	n.d.	n.d.	82.6
Re/C not red.[a,d]	6.9[d]	5.4[d]	n.d.[d]	n.d.[d]	n.d.[d]
Re/C[d]	20.7 ± 3.1[d]	12.5 ± 2.4[d]	n.d.[d]	0.4 ± 0.2[d]	46.5 ± 8.9[d]

n.d. – not detected. [a] catalyst was used as obtained without reductive pretreatment experiment. [b] physical mixture of the two catalysts. [c] under 5 bar H_2 atmosphere. [d] experiment conducted only for 24 h.

Reproducibility of Catalytic Experiments

Table S2 Reproducibility of product yields after 10, 24 and 72 h observed in the catalytic dehydroxylation of glyceric acid over Re/C in methanol at 150 °C under N_2 atmosphere. Based on the replicated experiments the average yields are calculated as well as the standard deviation.

	Product yields after 10 h / %				
	Acrylic acid	Methyl acrylate	Propanoic acid	Methyl propanoate	Methyl glycerate
Experiment 1	19.6	5.3	n.d.	0.1	26.2
Experiment 2	15.5	4.6	n.d.	n.d.	47.5
Experiment 3	18.9	3.4	n.d.	n.d.	32.9
Average	18.0	4.4	n.d.	<0.1	35.5
Std. deviation	1.8	0.8	n.d.	0.1	8.9

	Product yields after 24 h / %				
	Acrylic acid	Methyl acrylate	Propanoic acid	Methyl propanoate	Methyl glycerate
Experiment 1	25.1	15.2	n.d.	0.5	25.4
Experiment 2	18.8	12.8	n.d.	0.6	63.3
Experiment 3	18.2	9.4	n.d.	0.2	50.8
Average	20.7	12.5	n.d.	0.4	46.5
Std. deviation	3.1	2.4	n.d.	0.2	15.7

	Product yields after 72 h / %				
	Acrylic acid	Methyl acrylate	Propanoic acid	Methyl propanoate	Methyl glycerate
Experiment 1	12.1	40.8	n.d.	2.8	n.d.
Experiment 2	10.6	42.2	n.d.	8.1	36.8
Experiment 3	7.3	55.7	n.d.	2.2	14.0
Average	10.0	46.2	n.d.	4.4	25.4
Std. deviation	2.0	6.7	n.d.	2.7	11.4

n.d. – not detected.

Reaction Condition Screening

Table S3 Product yields after 10 and 72 h observed in the catalytic dehydroxylation of glyceric acid over Re/C in methanol at different temperatures and at 150 °C under either inert (N_2) or reducing (H_2) atmosphere.

	Product yields after 10 h / %				
Conditions	Acrylic acid	Methyl acrylate	Propanoic acid	Methyl propanoate	Methyl glycerate
120 °C, N_2	11.7	0.4	n.d.	n.d.	13.9
150 °C, N_2	18.0 ± 1.8	4.4 ± 0.8	n.d.	<0.1	35.5 ± 8.9
165 °C, N_2	33.7	11.9	n.d.	1.3	24.7
180 °C, N_2	8.4	44.9	n.d.	11.8	n.d.
150 °C, H_2	33.6	4.9	n.d.	0.2	51.0
165 °C, H_2	41.9	16.0	n.d.	0.4	20.2
180 °C, H_2	42.5	30.6	15.4	4.6	n.d.
	Product yields after 72 h / %				
Conditions	Acrylic acid	Methyl acrylate	Propanoic acid	Methyl propanoate	Methyl glycerate
120 °C, N_2	4.6	6.1	n.d.	n.d.	51.2
150 °C, N_2	10.0 ± 2.0	46.2 ± 6.7	n.d.	4.4 ± 2.7	25.4 ± 11.4
165 °C, N_2	n.d.	25.7	n.d.	22.0	n.d.
180 °C, N_2	n.d.	5.7	n.d.	37.8	n.d.
150 °C, H_2	4.2	54.4	n.d.	3.6	6.1
165 °C, H_2	n.d.	18.3	n.d.	22.1	n.d.
180 °C, H_2	n.d.	0.5	n.d.	31.0	n.d.

n.d. – not detected.

Solvent screening

Table S4 Product yields after 72 h observed in the catalytic dehydroxylation of glyceric acid over Re/C catalysts at 150 °C under N_2 atmosphere in different alcohols.

Solvent	Product yields / %			
	Acrylic acid	Alkyl acrylate[a]	Propanoic acid	Alkyl propanoate[a]
Methanol	10.0 ± 2.0	46.2 ± 6.7	n.d.	4.4 ± 2.7
Ethanol	31.2	20.2	n.d.	10.4
iso-Propanol	14.1	3.5	54.0	6.1
n-Propanol	d.n.p.	20.8	n.d.	22.0
n-Butanol	d.n.p.	27.2	d.n.p.	5.4
n-Pentanol	d.n.p.	28.7	d.n.p.	3.8

d.n.p. – detection not possible (due to overlap with alcohol/aldehyde). n.d. – not detected. [a] esters with the respective alcohol that was used as solvent, *e.g.* ethyl esters in case of ethanol.

Pre-treatment of the catalyst

To test different reductive pretreatment of the catalyst, the experiment with 3 different reductive pretreatment was made on commercial Re/C from Riogen. The catalyst was not pretreated at all, the catalyst was exposed in the tubular furnace at 250 °C (3 h, 200 mL min^{-1} flow of pure H_2) and at 400 °C (3 h, 200 mL min^{-1} flow of pure H_2).

After pretreatment the catalytic test were made at the same reaction conditions at 150 °C, V (MeOH)=45 mL, n (glyceric acid)=0.001 mol, n(Re)=0.04mmol, molar ratio (glyceric acid:Re) = 25:1, 5 bar_g N_2. The results from the catalytic test are shown in the Table S5. As observed the pretreatment is beneficial, since it almost doubles the amount of methyl acrylate and triples the amount of acrylic acid.

Table S5 Product yields after 10 and 72 h observed in the catalytic dehydroxylation of glyceric acid over Re/C in methanol at different temperatures and under either inert (N_2) or reducing (H_2) atmosphere.

Entry	Conditions	Product yields after 72 h / %				
		Acrylic acid	Methyl acrylate	Propanoic acid	Methyl propanoate	Methyl glycerate
1	Untreated Re/C	6.2	24.3	n.d.	n.d.	38.1
2	Pretreatment in a tubular furnace at 250 °C (3 h, 200 mL min^{-1} flow of pure H_2).	6.3	44.4	n.d.	1.7	0.5
3	Pretreatment in a tubular furnace at 400 °C (3 h, 200 mL min^{-1} flow of pure H_2).	18.1	46.2	n.d.	4.4	n.d.

Hydrogen formation

Methanol serves as the hydrogen source and undergoes oxidation to formaldehyde on Re. During this process, H_2 is generated in the gas phase. To quantify the H_2 produced, a gas sample was extracted from the cooled reactor at room temperature. A gas sample was extracted after 72 h long reaction of glyceric acid DODH from the cooled reactor with the volume of headspace was 35 ml at the temperature 11.5 °C, and the pressure of reactor headspace was 1.4 bar_g. The sample was analysed by Agilent 490 Micro GC on the same day to quantify the detected compounds. The micro-GC has two different columns (PoraPLOT U, CP-Cox) and TCD detectors (thermal conductivity detector) to detect a wide range of gaseous compounds. The chromatogram of analysed gases is shown in Figure S1 and the amount of formed H_2 in the catalytic dehydroxylation of glyceric acid over Re/C (Table S6).

Table S6 Amount of formed H_2 in the catalytic dehydroxylation of glyceric acid over Re/C in methanol at 150 °C and under inert (N_2) atmosphere. The sample was taken after the reactors' headspace was cooled down to 11.5 °C and the pressure of reactor headspace was 1.4 bar_g.

Reaction conditions	Amount of formed H_2 / mol %	Amount of formed H_2 / mol
150 °C, 5 bar_g N_2	0.95	3.4×10^{-5}

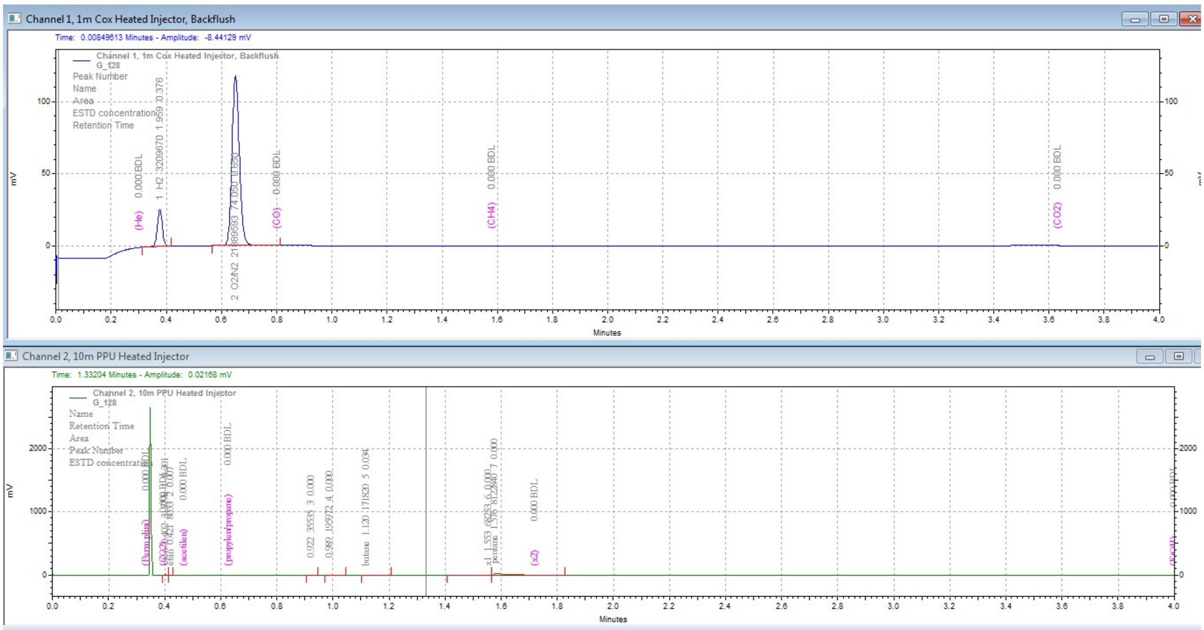


Figure S1 Chromatogram of detected compounds with TCD detector by Agilent 490 Micro GC on both channels for each column. On channel one, H_2 and N_2/O_2 are detected.

During the process, H_2 is used for DODH to acrylic acid and methyl acrylate and for further hydrogenation. This was considered to calculate the remaining H_2 that was used during the whole reaction pathway, proposed with our reaction scheme (Figure 4 in the Manuscript). The sum of the DODH products and hydrogenation products in the final reaction sample of the cooled down reaction mixture is 4.45×10^{-4} mol, which than equals to 4.62×10^{-4} mol of consumed H_2. Hydrogen is also dissolved in the liquid phase. This was calculated by the Henry's law, using the correlation for Henry's constant of solubility of H_2 in methanol.[3] The amount of soluble H_2 in the bulk phase is 3.8×10^{-6} mol. The sum of all measured H_2 in gas phase, dissolved in liquid phase and used for DODH and hydrogenation is 5.0×10^{-4} mol.

The consumption of methanol 1 mol produces 0.33 mol H_2 and 0.33 mol methylal, which confirms that methylal and H_2 are produced in a stoichiometric ratio 1:1.

$$3CH_3OH \rightarrow CH_2(OCH_3)_2 + H_2 + H_2O$$

Methylal quantification

The role of the hydrogen-donor solvent is also evident from the detection of its dehydrogenated product, methylal, in the product mixture (Figure S5). Additionally, methylal was quantified for two representative catalyst tests with Re/C at 150 °C in the presence of 5 bar_g of either N_2 or H_2 after 72 h. However, due to the unavailability of a methylal standard, direct quantification was not feasible. Instead, we employed the effective carbon number (ECN) concept, which simplifies calibration in the absence of authentic standards, especially in complex systems such as petrochemical and biomass processing [4].The methylal amount was calculated using THF calibration curve (Figure S2) as a reference and using the f_w from Table 2 published by Zhu [4] and the results for represented runs are shown in the Table S7.

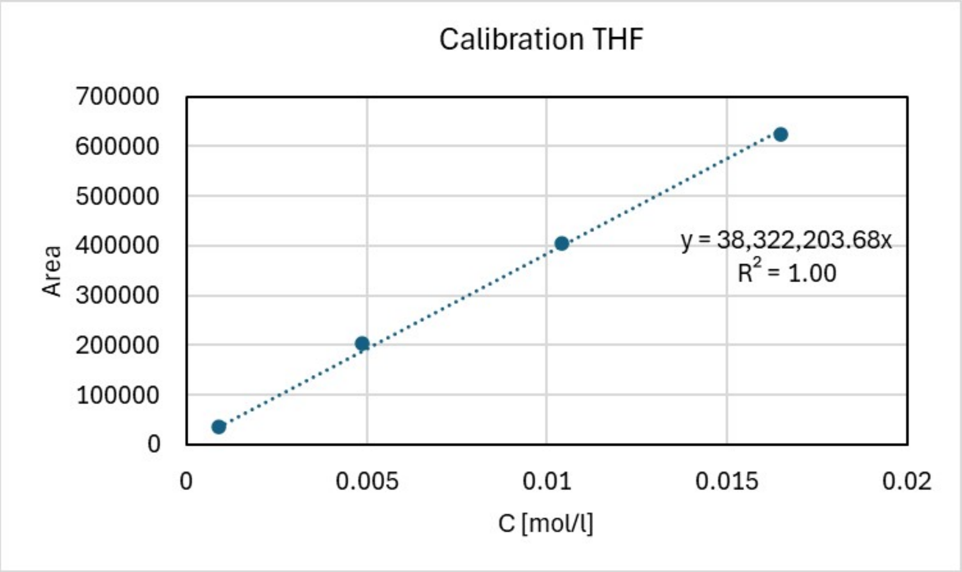


Figure S2 Calibration curve for THF standard, based on which methylal was quantified.

Table S7 Amount methylal formed in represented reaction.

Reaction conditions	Amount of methylal / mol
150 °C, 5 bar_g N_2	1.8×10^{-4}
150 °C, 5 bar_g H_2	1.3×10^{-5}

However, in the final cooled-down reactor after reaction under 5 bar_g N_2 and 150 °C, the methylal concentration was lower, 5.1×10^{-5} mol. This decrease is attributed to methanol condensation upon cooling and the dilution of the sample, which is also reflected in the lower concentrations of other analytes. If we compare results with the sum of all measured H_2 in gas phase, dissolved in liquid phase and used for DODH and hydrogenation, 5.0×10^{-4} mol, the amount of methylal is lower. The explanation for it should be that methanol might work as the source of more than one equivalent of H_2, for example via acetalization of formaldehyde to methylal might not be complete. Also, some methylal may have undergone further reaction, potentially to compounds that cannot be detected on the GCMS with the chosen method. The discrepancy may be also due to the quantification of methylal with THF and the method on GCMS, where methylal is not fully separated from MeOH.

Hot filtration test

To account for the potential homogenous reaction catalysed by leached rhenium, the hot filtration test was also conducted and a second reaction with supernatant was carried out. The reaction was carried out at 150 °C at 5 bar_g N_2 and V (MeOH)=45 mL, n (glyceric acid)=0.001 mol, n (Re)=0.04 mmol, molar ratio (glyceric acid:Re) = 25:1. The catalyst that was used for this reaction was Re/C, with 5 wt% of rhenium and pre-treated in a tubular furnace at 400 ˚C (3 h, 200 mL min^{-1} flow of pure H_2). The filter with pore diameters of 2 μm, was placed between the first reactor and second reactor. The assumption was that particles larger than 2 μm would be effectively filtered by the filters. At the reaction temperature (150 °C) and high reaction pressure (10 bar), the reaction mixture was filtered into the second parr reactor which was already preheated at 150 °C after 24 h of reaction, since the catalyst is very active at that time. Once the gas pressure equilibrium was reached following filtering, the reaction in the second reactor was continued and samples were collected and analysed by GCMS (as described below). After hot filtration and an additional 48 hours of reaction, the reactor was opened to check if any solid catalyst had passed through the filter, but no solid particles were observed.

The results obtained were compared. It can be seen (Figure S3) that no further deoxydehydration occurred after hot filtration. The DODH of methyl glycerate didn’t occur after hot filtration, as well as the DODH to acrylic acid. However, as expected the esterification of acrylic acid to methyl acrylate still proceeded after hot filtration, which explains the observed conversion of acrylic acid to methyl acrylate. The final product (methyl propanoate) was also not detected.

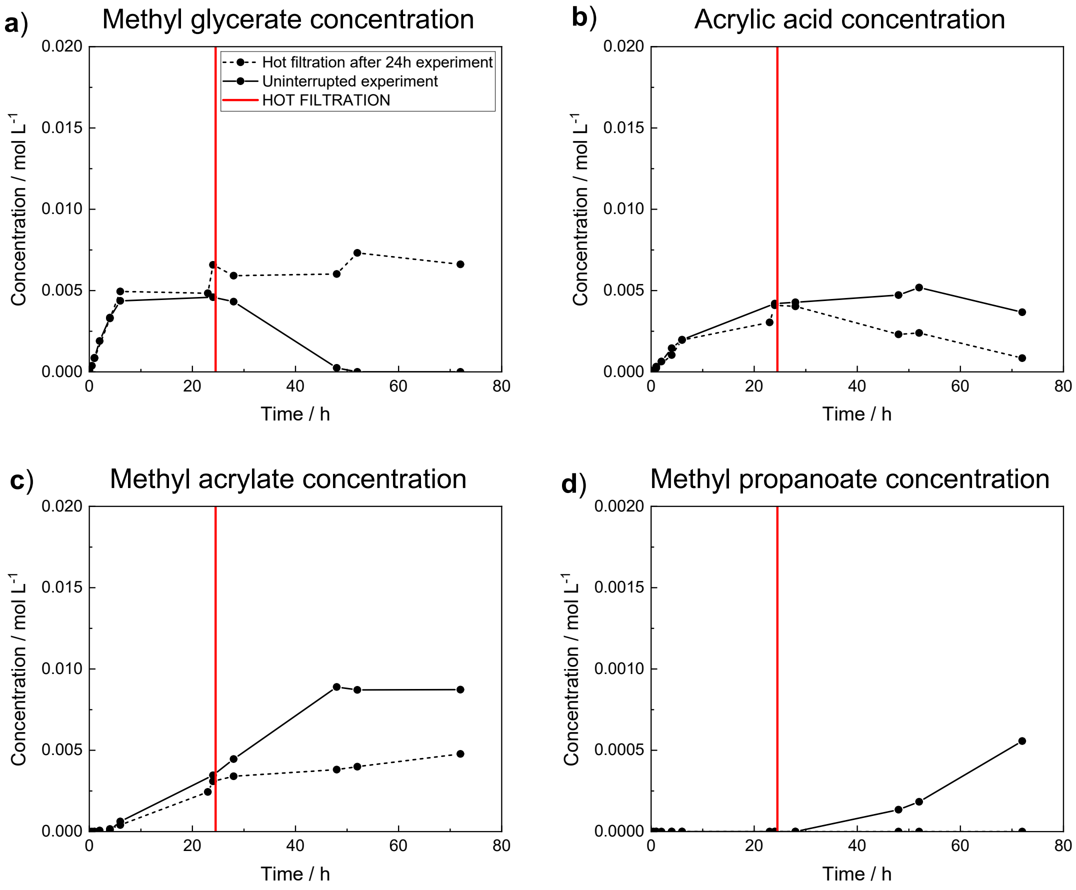


Figure S3: The formation of DODH or esterified products during uninterrupted (solid line) and filtered (dashed line) test.

Catalyst recycling test

The tendency of the metal rhenium to leach from solid supports is well known [5,6] . To evaluate the catalytic activity after the second reaction, a catalytic test was performed on the recycled catalyst. The catalyst was separated from the reaction mixture by centrifugation at 1500 rpm for 10 minutes, washed with MeOH and repeated three times. Afterward, the catalyst was dried and pretreated as usual at 400°C for 3 hours under a H_2 flow of 200 mL min^{-1} before reuse. The Figure S4 presents the results of catalyst recycling test done with Re/C. The reaction condition of initial and recycling experiment was 120 °C, 5 bar$_g$ N_2. Due to catalyst loss during reaction sampling or centrifugation, 30 mg of Re/C was used instead of 140 mg. However, the molar ratio of glyceric acid to Re remained the same as in the initial experiment, 25:1.

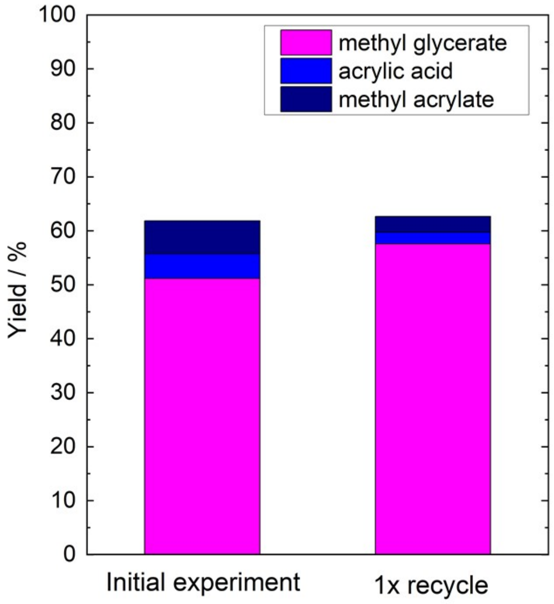


Figure S4: Catalyst recycling tests done with Re/C catalyst. RKC conditions: V (MeOH)= 45 mL, molar ratio (glyceric acid:Re) = 25:1, T = 120 °C, 5 bar_g N_2.

3. Catalyst characterization

The catalyst characterization techniques and detailed procedures are explained thoroughly in our previous work.[1] In this work all results are described in detail as well. The main properties of the catalyst are summarized in Table S8. The quantification of rhenium oxidation states from XPS are shown in Table S9.[1]

Table S8 Most important characterization properties of the Re supported catalyst used for glyceric acid conversion. The methods used are described in the paper and briefly in the footnote of the table.

Entry	Catalyst	Specific surface area[a] / $m^2 g^{-1}$	Total pore Volume[a] / $cm^3 g^{-1}$	Temperature at Maximum[b] / °C	H_2 uptake[b] / $cm^3 g^{-1}$	Re nanoparticles distribution[c] / nm
1	Re/C	1240	0.55	270	8.4	2.5 ± 0.9
2	Re/TiO_2	74	0.33	238	6.9	1.4 ± 0.5
3	Re/H-ZSM-5	334	0.24	230	7.6	1.9 ± 0.8
4	Re/SiO_2	148	0.59	320	10.8	1.5 ± 0.4
5	Re/Al_2O_3	159	0.50	410	12.5	2.0 ± 0.6

a – N_2 physisorption experiments at 77 K, specific surface area calculated with BET model.
b – Temperature-programmed reduction with H_2 (H_2-TPR).
c – For transmission electron microscopy (TEM), The particle size dTEM is given as an equivalent diameter, i.e., the diameter of a circle having the same surface area as the imaged particle.

Table S9 Approximative surface concentration of rhenium oxidation states calculated from the area ratios from XPS on pretreated Re supported catalyst used for glyceric acid conversion.

		Rhenium species / Approximate area %		
Entry	Catalyst	metallic Re	ReO_3	ReO_2
1	Re/C	10	65	25
2	Re/TiO_2	0	33	67
3	Re/SiO_2	100	0	0

4. Kinetic model

The kinetic model was formulated based on the proposed reaction pathway network. Whereas the molar (concentration) balance over time (*t*) for each component (j), (J is their number), in the liquid phase was solved as a set of ordinary differential equations.

$$\frac{dc_j}{dt} = \pm \sum^{I} r_i \cdot m_{cat}$$

Rate equations (*r*) for each reaction (*i*), (*I* is their number) are considered to be of an order of unity, hence only dependent on the reaction rate constant and the concentration of the propyl moiety in the liquid phase. Reaction rates, products of each reaction and reaction rate constants k_i listed for each reaction at various temperatures for inert (Table S10a) and reductive atmosphere (Table S10b).

The kinetic rate constants were determined by minimization of the sum of squared differences between all experimentally determined and calculated concentrations, for every experiment *m*, *M* is their number, and component *j*. Regression analysis was performed by using Nelder-Mead method for robust minimization of the objective function (f) and Levenberg-Marquardt algorithm for fine regression analysis and determination of 95% confidence intervals.

$$f(k_j) = \sum_{m=1}^{M} \sum_{j=1}^{J} \left(c_j^{exp} - c_j^{calc} \right)^2$$

Table S10a Kinetic rate constants for deoxydehydration over Re/C under inert atmosphere.

i	**Products**	r_i	**k_i at 120 °C ($h^{-1}\,g_{cat}^{-1}$)**	**k_i at 150 °C ($h^{-1}\,g_{cat}^{-1}$)**	**k_i at 165 °C ($h^{-1}\,g_{cat}^{-1}$)**	**k_i at 180 °C ($h^{-1}\,g_{cat}^{-1}$)**
1	MG	$k_1 \cdot C_{GA}$	0.03±0.01	0.36±0.027	0.64±0.06	1.12±0.23
2	AA	$k_2 \cdot C_{GA}$	0.012±0.006	0.21±0.029	0.49±0.06	1.1±0.22
3	MA	$k_3 \cdot C_{MG}$	0.003±0.002	0.27±0.03	0.95±0.06	3.07±0.23
4	MA	$k_4 \cdot C_{AA}$	0.001±0.001	0.12±0.02	0.12±0.08	0.12±0.08
5	PA	$k_5 \cdot C_{AA}$	<0.001	0.011±0.01	0.014±0.001	0.02±0.05
6	MP	$k_6 \cdot C_{MA}$	<0.001	0.013±0.031	0.06±0.03	0.22±0.01
7	MP	$k_7 \cdot C_{PA}$	n.a.	1.07±0.2	1.4±0.2	1.7±0.34

Table S10b Kinetic rate constants for deoxydehydration over Re/C under 5 bar_g hydrogen atmosphere.

i	**Products**	r_i	k_i **at 120 °C (h^{-1} g_{cat}^{-1})**	k_i **at 150 °C (h^{-1} g_{cat}^{-1})**	k_i **at 165 °C (h^{-1} g_{cat}^{-1})**	k_i **at 180 °C (h^{-1} g_{cat}^{-1})**
1	MG	$k_1 \cdot C_{GA}$	0.5±0.2	0.875±0.14	1.10±0.21	1.36±0.23
2	AA	$k_2 \cdot C_{GA}$	0.072±0.2	0.627±0.14	1.65±0.21	4.08±0.22
3	MA	$k_3 \cdot C_{MG}$	0.012±0.010	0.180±0.15	0.60±0.12	1.84±0.23
4	MA	$k_4 \cdot C_{AA}$	0.07±0.06	0.08±0.08	0.093±0.084	0.095±0.09
5	PA	$k_5 \cdot C_{AA}$	0.01±0.01	0.026±0.016	0.072±0.021	0.19±0.05
6	MP	$k_6 \cdot C_{MA}$	0.002±0.002	0.01±0.01	0.042±0.03	0.085±0.08
7	MP	$k_7 \cdot C_{PA}$	0.35±0.3	0.4±0.2	0.40±0.21	0.428±0.34

5. Product Analysis by GCMS

Further Experimental Details

Gas chromatography was conducted to analyze liquid samples taken from the reaction mixture using a Shimadzu GCMS-QP 2010 Ultra gas chromatograph equipped with a flame ionization detector (FID) and a quadrupole mass spectrometry (MS). A Zebron ZB-5MS capillary column (60 m x 0.25 mm x 0.25 µm) was used and the overall method was identical to the one reported previously for the adipate reaction system.[2] Quantification was based on FID peak areas and external calibrations of commercially available reference compounds were used to calculate product concentrations and, subsequently, product yields. While the reactant GA could not be detected, probably due to decomposition or low vapor pressure, glycerate esters could be detected as well as acrylic acid (AA) and propanoic acid (PP) and their esters, i.e., methyl acrylate (MA) and methyl propanoate (MP) in case of MeOH being the solvent (chromatograms of representative product mixtures in Figure S5).

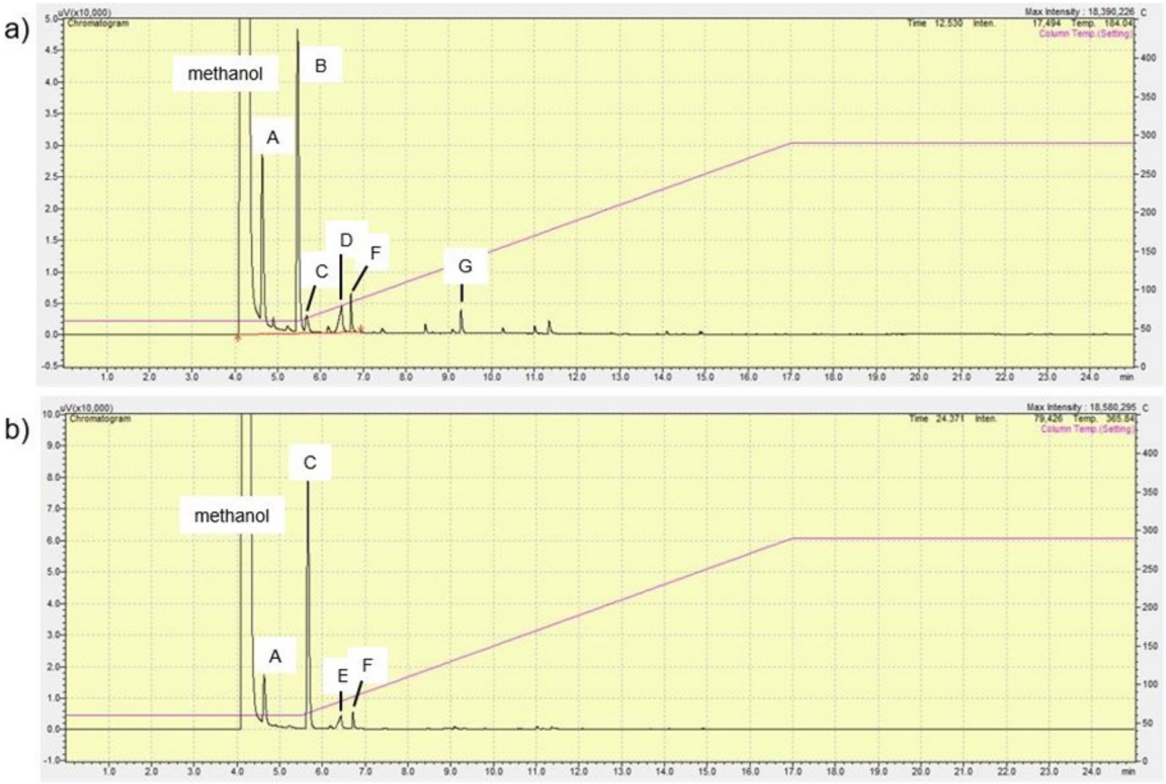
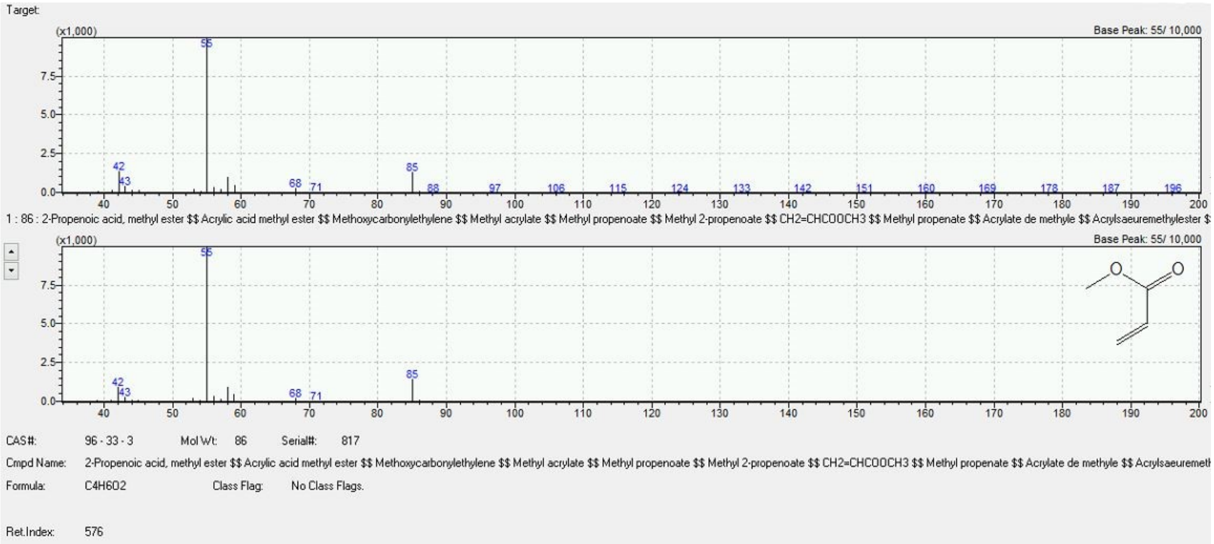


Figure S5 Gas chromatograms (FID signal, black lines) of representative product mixtures at harsh (a) and mild reaction (b) over supported Re catalyst. The pink line shows the GC oven temperature.
The following compounds were identified: A – methylal, oxidation product of methanol; B – methyl acrylate; C – methyl propanoate; D – acrylic acid; E – propanoic acid; F – methyl glycolate; G – methyl 3-methoxypropanoate.

Product Identification by Mass Spectrometry

The identity of each DODH compound was unambiguously confirmed by their respective MS fragmentation pattern (and comparison with library data) and representative examples are provided in Figure S6-S9 for the case of methanol as solvent. When other alcohols were used (see Table S4) the corresponding alkyl esters of acrylic acid and propanoic acid were unambiguously identified (Figures S9-S19).



1 : 86 : 2-Propenoic acid, methyl ester $$ Acrylic acid methyl ester $$ Methoxycarbonylethylene $$ Methyl acrylate $$ Methyl propenoate $$ Methyl 2-propenoate $$ CH2=CHCOOCH3 $$ Methyl propenate $$ Acrylate de methyle $$ Acrylsaeuremethylester $

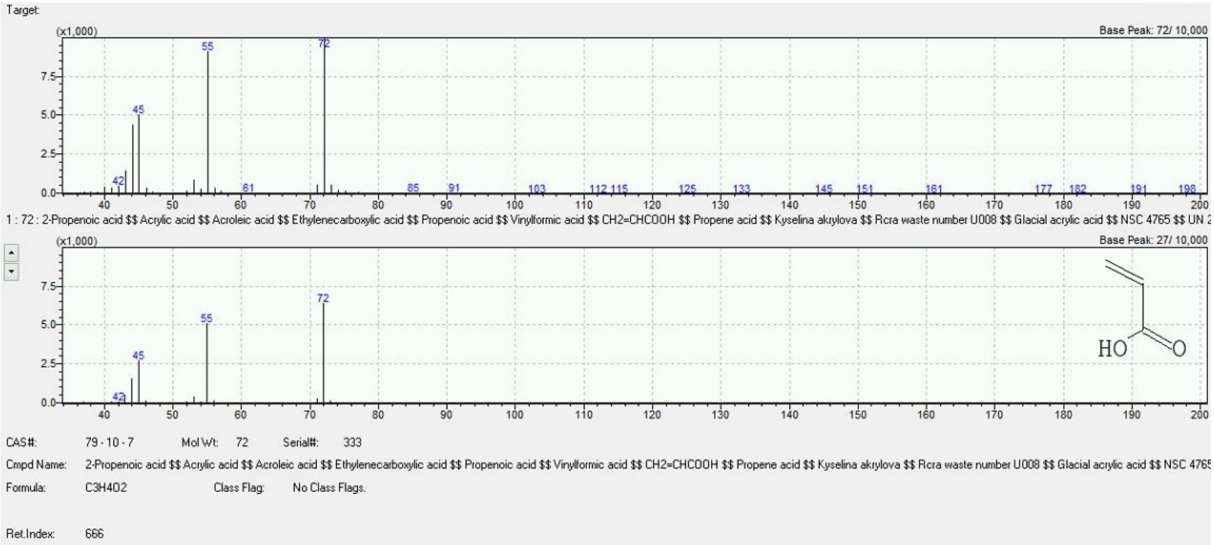
CAS#: 96 - 33 - 3 Mol Wt: 86 Serial#: 817

Cmpd Name: 2-Propenoic acid, methyl ester $$ Acrylic acid methyl ester $$ Methoxycarbonylethylene $$ Methyl acrylate $$ Methyl propenoate $$ Methyl 2-propenoate $$ CH2=CHCOOCH3 $$ Methyl propenate $$ Acrylate de methyle $$ Acrylsaeuremeth

Formula: C4H6O2 Class Flag: No Class Flags.

Ret.Index: 576

Figure S6 Mass spectrum of the peak in the chromatogram of reaction mixtures assigned to methyl acrylate based on the comparison with reference data (bottom).



1 : 72 : 2-Propenoic acid $$ Acrylic acid $$ Acroleic acid $$ Ethylenecarboxylic acid $$ Propenoic acid $$ Vinylformic acid $$ CH2=CHCOOH $$ Propene acid $$ Kyselina akrylova $$ Rcra waste number U008 $$ Glacial acrylic acid $$ NSC 4765 $$ UN 2

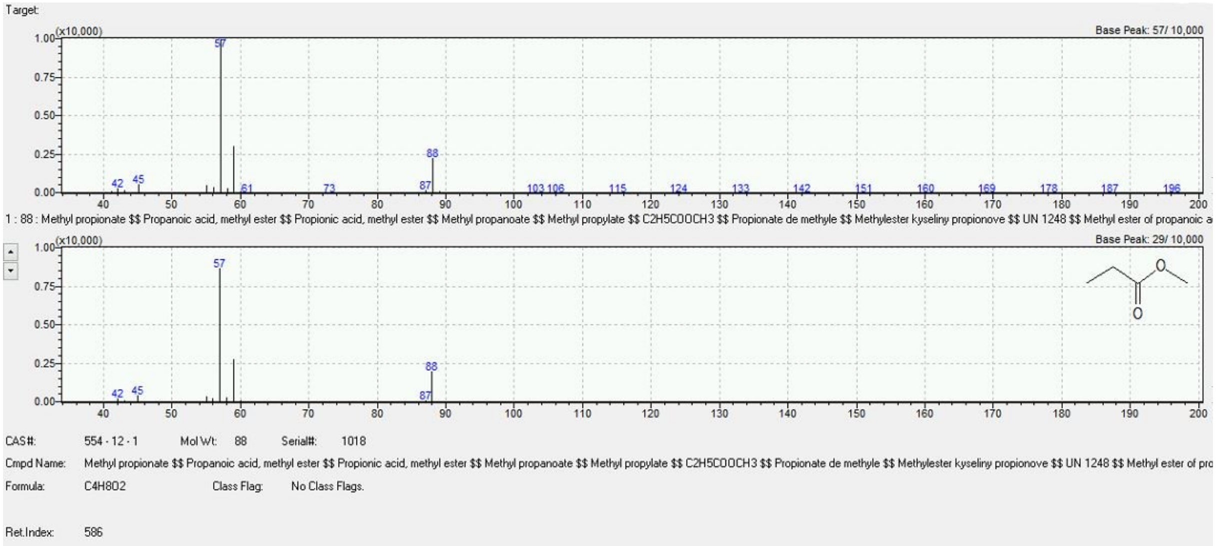
CAS#: 79 - 10 - 7 Mol Wt: 72 Serial#: 333

Cmpd Name: 2-Propenoic acid $$ Acrylic acid $$ Acroleic acid $$ Ethylenecarboxylic acid $$ Propenoic acid $$ Vinylformic acid $$ CH2=CHCOOH $$ Propene acid $$ Kyselina akrylova $$ Rcra waste number U008 $$ Glacial acrylic acid $$ NSC 4765

Formula: C3H4O2 Class Flag: No Class Flags.

Ret.Index: 666

Figure S7 Mass spectrum of the peak in the chromatogram of reaction mixtures assigned to acrylic acid based on the comparison with reference data (bottom).



1 : 88 : Methyl propionate $$ Propanoic acid, methyl ester $$ Propionic acid, methyl ester $$ Methyl propanoate $$ Methyl propylate $$ C2H5COOCH3 $$ Propionate de methyle $$ Methylester kyseliny propionove $$ UN 1248 $$ Methyl ester of propanoic a

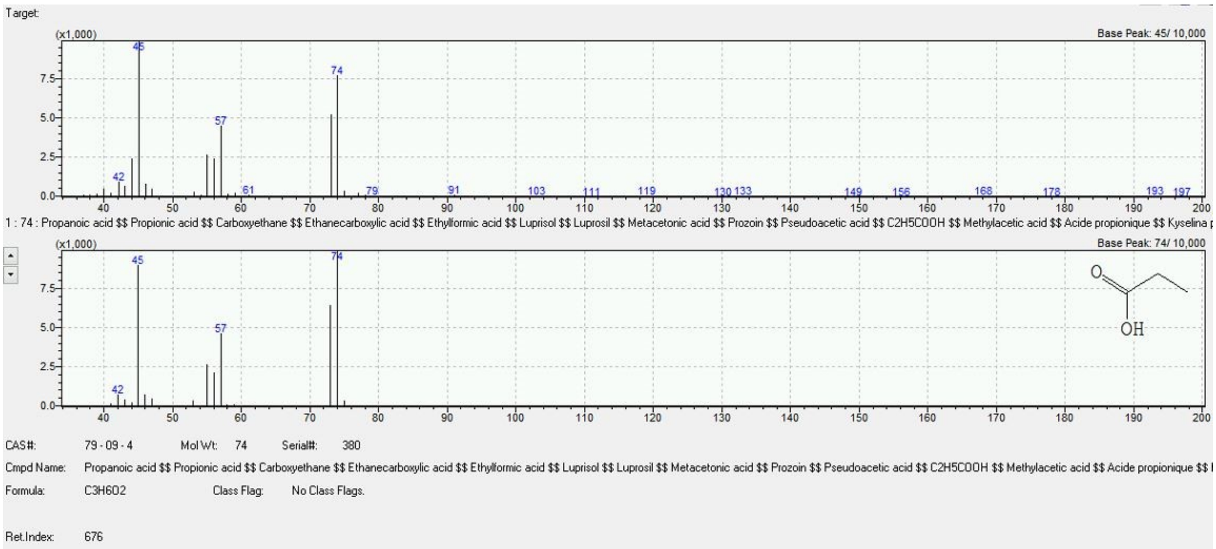
CAS#: 554 - 12 - 1 Mol Wt: 88 Serial#: 1018

Cmpd Name: Methyl propionate $$ Propanoic acid, methyl ester $$ Propionic acid, methyl ester $$ Methyl propanoate $$ Methyl propylate $$ C2H5COOCH3 $$ Propionate de methyle $$ Methylester kyseliny propionove $$ UN 1248 $$ Methyl ester of pro

Formula: C4H8O2 Class Flag: No Class Flags.

Ret.Index: 586

Figure S8 Mass spectrum of the peak in the chromatogram of reaction mixtures assigned to methyl propanoate based on the comparison with reference data (bottom).



1 : 74 : Propanoic acid $$ Propionic acid $$ Carboxyethane $$ Ethanecarboxylic acid $$ Ethylformic acid $$ Luprisol $$ Luprosil $$ Metacetonic acid $$ Prozoin $$ Pseudoacetic acid $$ C2H5COOH $$ Methylacetic acid $$ Acide propionique $$ Kyselina p

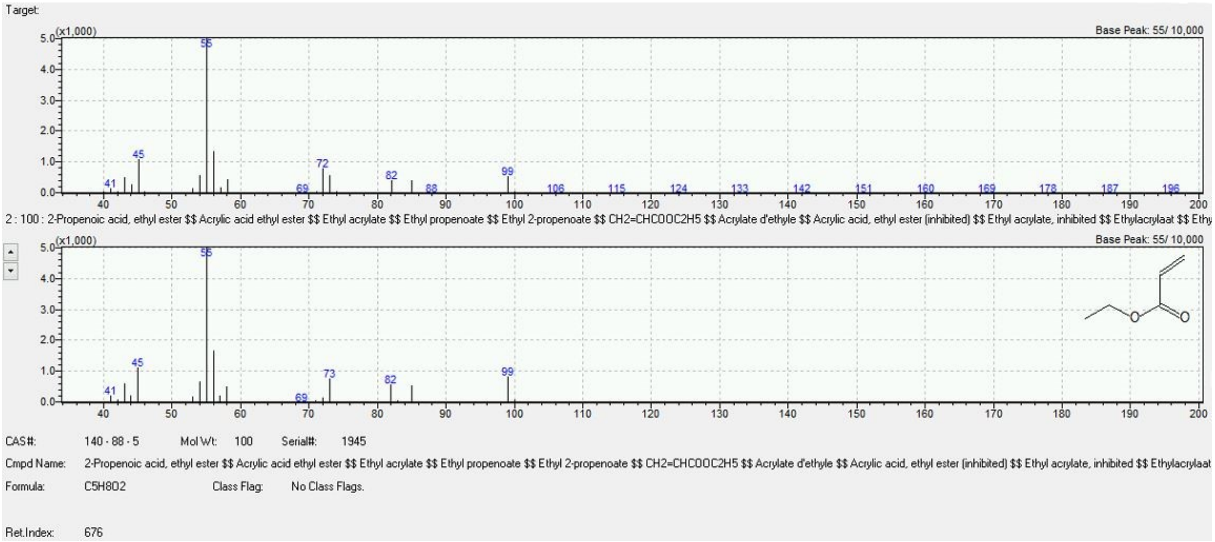
CAS#: 79 - 09 - 4 Mol Wt: 74 Serial#: 380

Cmpd Name: Propanoic acid $$ Propionic acid $$ Carboxyethane $$ Ethanecarboxylic acid $$ Ethylformic acid $$ Luprisol $$ Luprosil $$ Metacetonic acid $$ Prozoin $$ Pseudoacetic acid $$ C2H5COOH $$ Methylacetic acid $$ Acide propionique $$ I

Formula: C3H6O2 Class Flag: No Class Flags.

Ret.Index: 676

Figure S9 Mass spectrum of the peak in the chromatogram of reaction mixtures assigned to propanoic acid based on the comparison with reference data (bottom).



2 : 100 : 2-Propenoic acid, ethyl ester $$ Acrylic acid ethyl ester $$ Ethyl acrylate $$ Ethyl propenoate $$ Ethyl 2-propenoate $$ CH2=CHCOOC2H5 $$ Acrylate d'ethyle $$ Acrylic acid, ethyl ester (inhibited) $$ Ethyl acrylate, inhibited $$ Ethylacrylaat $$ Ethy

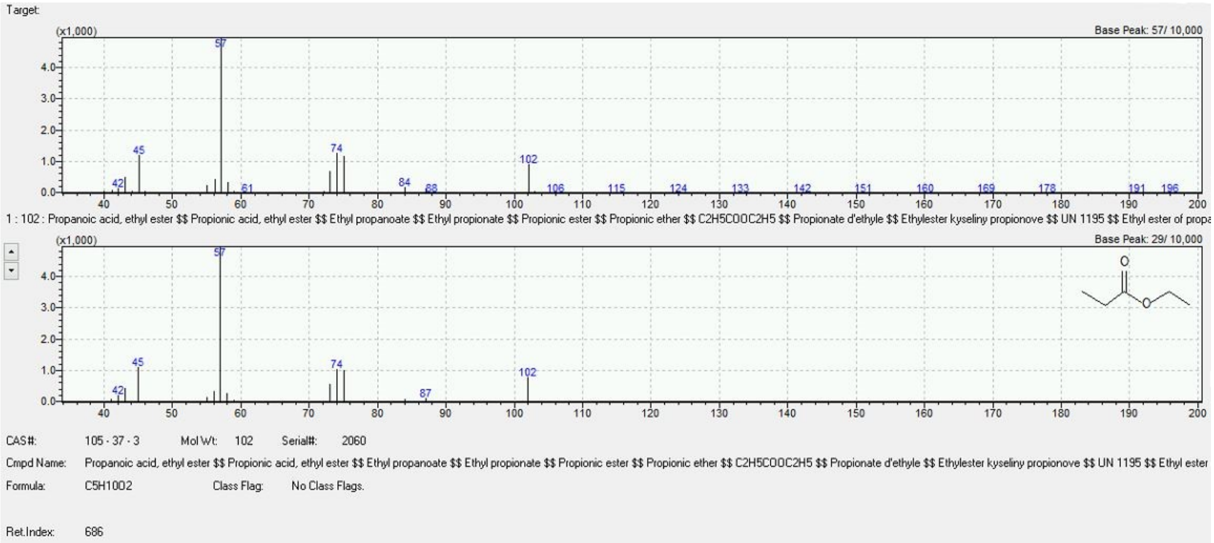
CAS#: 140 - 88 - 5 Mol Wt: 100 Serial#: 1945

Cmpd Name: 2-Propenoic acid, ethyl ester $$ Acrylic acid ethyl ester $$ Ethyl acrylate $$ Ethyl propenoate $$ Ethyl 2-propenoate $$ CH2=CHCOOC2H5 $$ Acrylate d'ethyle $$ Acrylic acid, ethyl ester (inhibited) $$ Ethyl acrylate, inhibited $$ Ethylacrylaat

Formula: C5H8O2 Class Flag: No Class Flags.

Ret.Index: 676

Figure S10 Mass spectrum of the peak in the chromatogram of reaction mixtures assigned to ethyl acrylate based on the comparison with reference data (bottom).



1 : 102 : Propanoic acid, ethyl ester $$ Propionic acid, ethyl ester $$ Ethyl propanoate $$ Ethyl propionate $$ Propionic ester $$ Propionic ether $$ C2H5COOC2H5 $$ Propionate d'ethyle $$ Ethylester kyseliny propionove $$ UN 1195 $$ Ethyl ester of propa

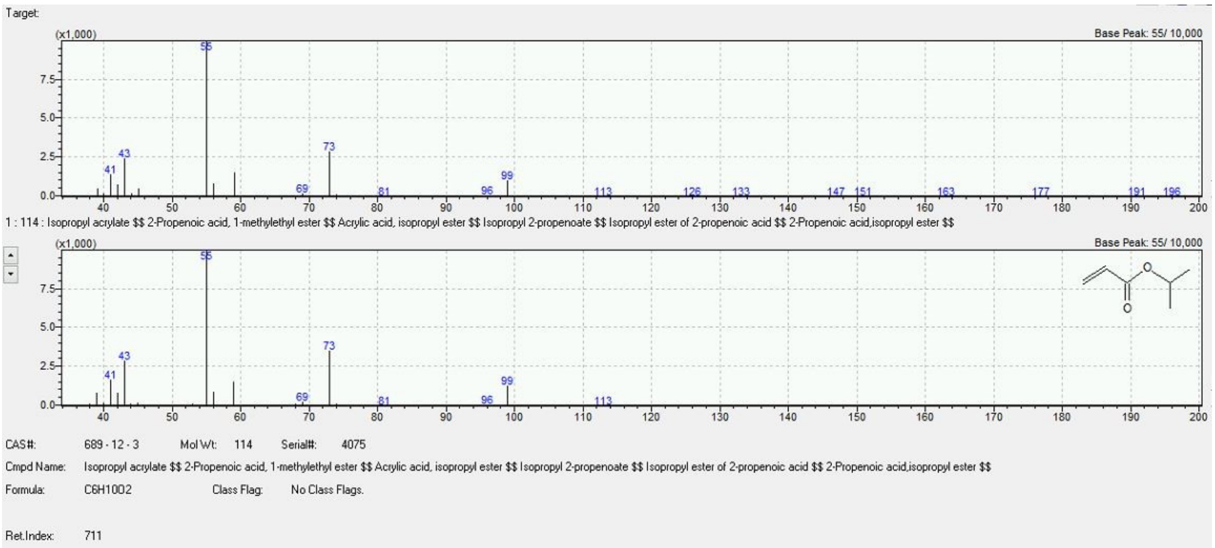
CAS#: 105 - 37 - 3 Mol Wt: 102 Serial#: 2060

Cmpd Name: Propanoic acid, ethyl ester $$ Propionic acid, ethyl ester $$ Ethyl propanoate $$ Ethyl propionate $$ Propionic ester $$ Propionic ether $$ C2H5COOC2H5 $$ Propionate d'ethyle $$ Ethylester kyseliny propionove $$ UN 1195 $$ Ethyl ester

Formula: C5H10O2 Class Flag: No Class Flags.

Ret.Index: 686

Figure S11 Mass spectrum of the peak in the chromatogram of reaction mixtures assigned to ethyl propanoate based on the comparison with reference data (bottom).



1 : 114 : Isopropyl acrylate $$ 2-Propenoic acid, 1-methylethyl ester $$ Acrylic acid, isopropyl ester $$ Isopropyl 2-propenoate $$ Isopropyl ester of 2-propenoic acid $$ 2-Propenoic acid,isopropyl ester $$

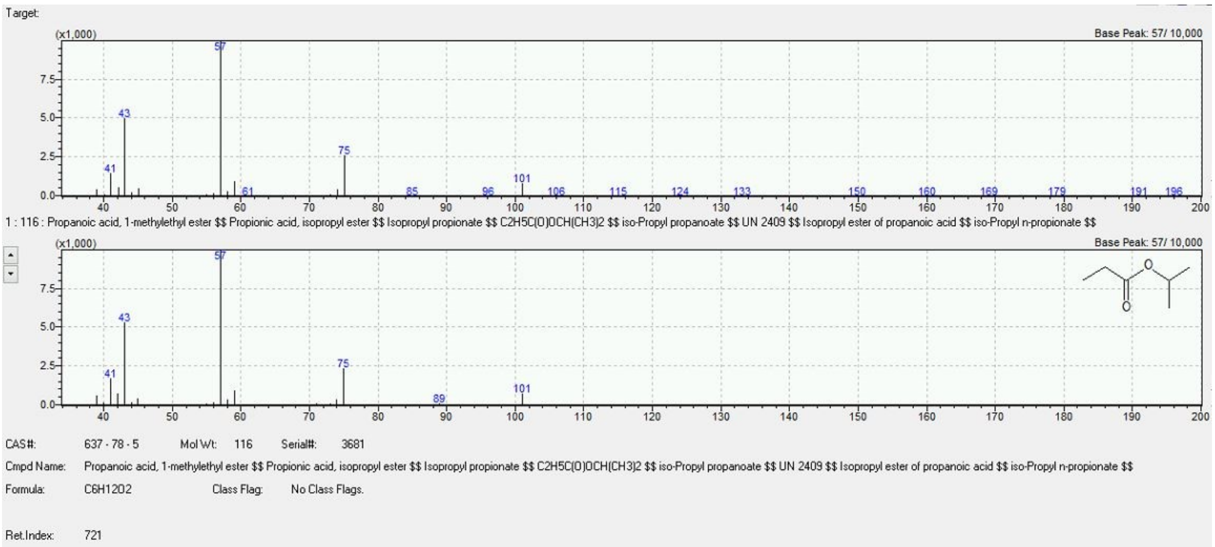
CAS#: 689 - 12 - 3 Mol Wt: 114 Serial#: 4075

Cmpd Name: Isopropyl acrylate $$ 2-Propenoic acid, 1-methylethyl ester $$ Acrylic acid, isopropyl ester $$ Isopropyl 2-propenoate $$ Isopropyl ester of 2-propenoic acid $$ 2-Propenoic acid,isopropyl ester $$

Formula: C6H10O2 Class Flag: No Class Flags.

Ret.Index: 711

Figure S12 Mass spectrum of the peak in the chromatogram of reaction mixtures assigned to *iso*-propyl acrylate based on the comparison with reference data (bottom).



1 : 116 : Propanoic acid, 1-methylethyl ester $$ Propionic acid, isopropyl ester $$ Isopropyl propionate $$ C2H5C(O)OCH(CH3)2 $$ iso-Propyl propanoate $$ UN 2409 $$ Isopropyl ester of propanoic acid $$ iso-Propyl n-propionate $$

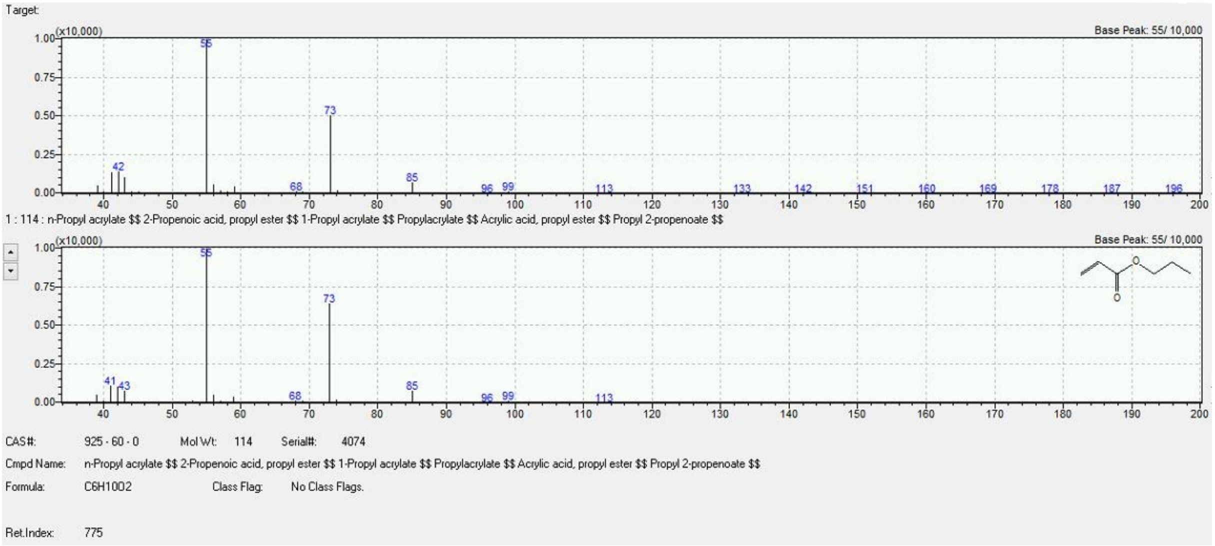
CAS#: 637 - 78 - 5 Mol Wt: 116 Serial#: 3681

Cmpd Name: Propanoic acid, 1-methylethyl ester $$ Propionic acid, isopropyl ester $$ Isopropyl propionate $$ C2H5C(O)OCH(CH3)2 $$ iso-Propyl propanoate $$ UN 2409 $$ Isopropyl ester of propanoic acid $$ iso-Propyl n-propionate $$

Formula: C6H12O2 Class Flag: No Class Flags.

Ret.Index: 721

Figure S13 Mass spectrum of the peak in the chromatogram of reaction mixtures assigned to *iso*-propyl propanoate based on the comparison with reference data (bottom).



1 : 114 : n-Propyl acrylate $$ 2-Propenoic acid, propyl ester $$ 1-Propyl acrylate $$ Propylacrylate $$ Acrylic acid, propyl ester $$ Propyl 2-propenoate $$

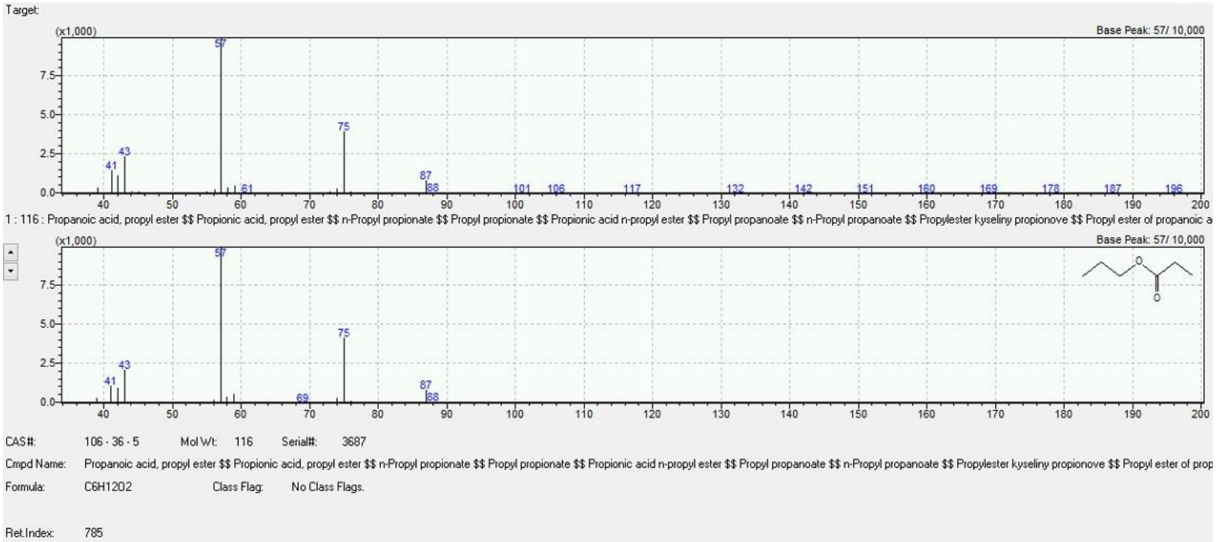
CAS#: 925 - 60 - 0 Mol Wt: 114 Serial#: 4074

Cmpd Name: n-Propyl acrylate $$ 2-Propenoic acid, propyl ester $$ 1-Propyl acrylate $$ Propylacrylate $$ Acrylic acid, propyl ester $$ Propyl 2-propenoate $$

Formula: C6H10O2 Class Flag: No Class Flags.

Ret.Index: 775

Figure S14 Mass spectrum of the peak in the chromatogram of reaction mixtures assigned to *n*-propyl acrylate based on the comparison with reference data (bottom).



1 : 116 : Propanoic acid, propyl ester $$ Propionic acid, propyl ester $$ n-Propyl propionate $$ Propyl propionate $$ Propionic acid n-propyl ester $$ Propyl propanoate $$ n-Propyl propanoate $$ Propylester kyseliny propionove $$ Propyl ester of propanoic a

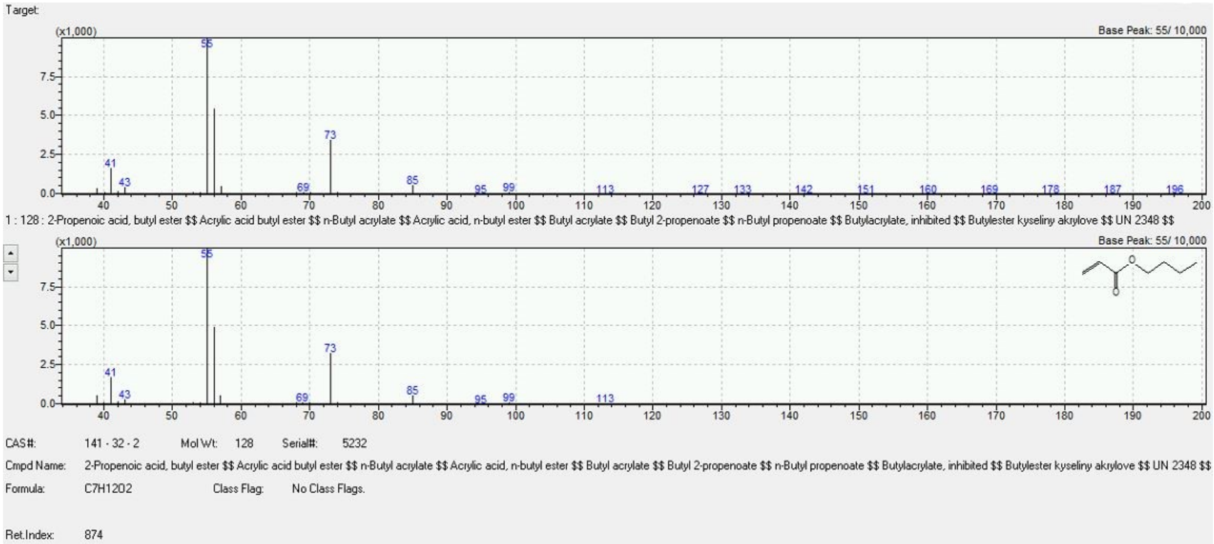
CAS#: 106 - 36 - 5 Mol Wt: 116 Serial#: 3687

Cmpd Name: Propanoic acid, propyl ester $$ Propionic acid, propyl ester $$ n-Propyl propionate $$ Propyl propionate $$ Propionic acid n-propyl ester $$ Propyl propanoate $$ n-Propyl propanoate $$ Propylester kyseliny propionove $$ Propyl ester of prop

Formula: C6H12O2 Class Flag: No Class Flags.

Ret.Index: 785

Figure S15 Mass spectrum of the peak in the chromatogram of reaction mixtures assigned to *n*-propyl propanoate based on the comparison with reference data (bottom).



1 : 128 : 2-Propenoic acid, butyl ester $$ Acrylic acid butyl ester $$ n-Butyl acrylate $$ Acrylic acid, n-butyl ester $$ Butyl acrylate $$ Butyl 2-propenoate $$ n-Butyl propenoate $$ Butylacrylate, inhibited $$ Butylester kyseliny akrylove $$ UN 2348 $$

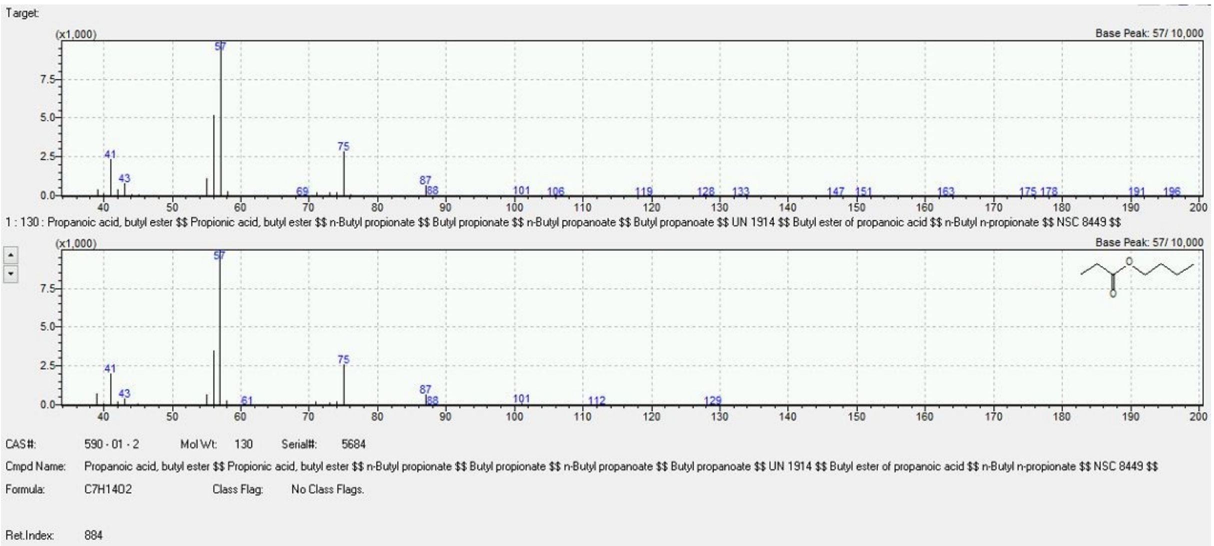
CAS#: 141 - 32 - 2 Mol Wt: 128 Serial#: 5232

Cmpd Name: 2-Propenoic acid, butyl ester $$ Acrylic acid butyl ester $$ n-Butyl acrylate $$ Acrylic acid, n-butyl ester $$ Butyl acrylate $$ Butyl 2-propenoate $$ n-Butyl propenoate $$ Butylacrylate, inhibited $$ Butylester kyseliny akrylove $$ UN 2348 $$

Formula: C7H12O2 Class Flag: No Class Flags.

Ret.Index: 874

Figure S16 Mass spectrum of the peak in the chromatogram of reaction mixtures assigned to *n*-butyl acrylate based on the comparison with reference data (bottom).



1 : 130 : Propanoic acid, butyl ester $$ Propionic acid, butyl ester $$ n-Butyl propionate $$ Butyl propionate $$ n-Butyl propanoate $$ Butyl propanoate $$ UN 1914 $$ Butyl ester of propanoic acid $$ n-Butyl n-propionate $$ NSC 8449 $$

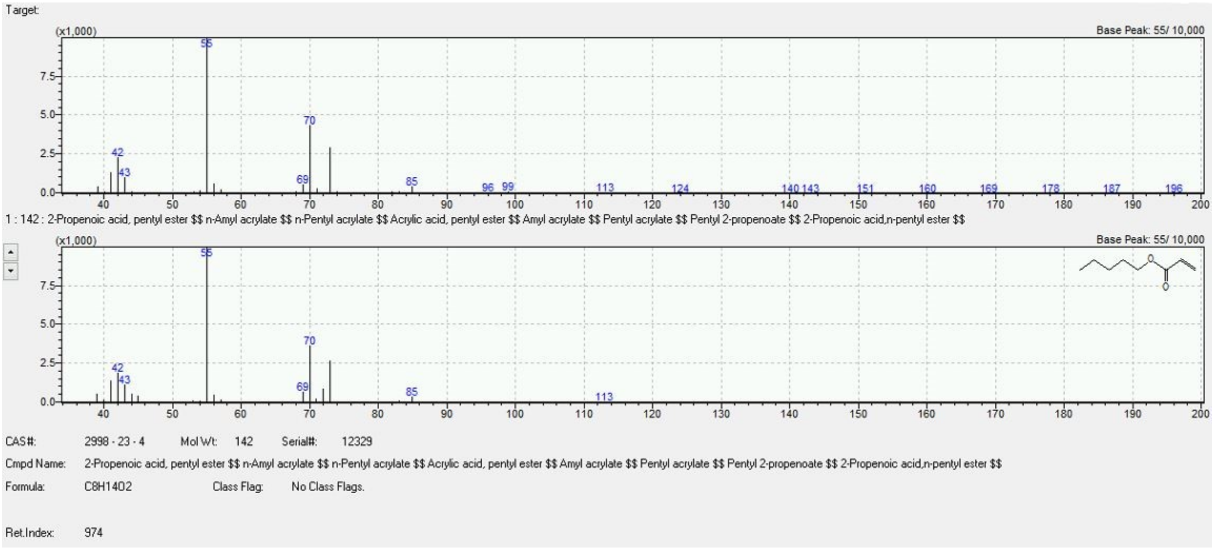
CAS#: 590 - 01 - 2 Mol Wt: 130 Serial#: 5684

Cmpd Name: Propanoic acid, butyl ester $$ Propionic acid, butyl ester $$ n-Butyl propionate $$ Butyl propionate $$ n-Butyl propanoate $$ Butyl propanoate $$ UN 1914 $$ Butyl ester of propanoic acid $$ n-Butyl n-propionate $$ NSC 8449 $$

Formula: C7H14O2 Class Flag: No Class Flags.

Ret.Index: 884

Figure S17 Mass spectrum of the peak in the chromatogram of reaction mixtures assigned to *n*-butyl propanoate based on the comparison with reference data (bottom).



1 : 142 : 2-Propenoic acid, pentyl ester $$ n-Amyl acrylate $$ n-Pentyl acrylate $$ Acrylic acid, pentyl ester $$ Amyl acrylate $$ Pentyl acrylate $$ Pentyl 2-propenoate $$ 2-Propenoic acid,n-pentyl ester $$

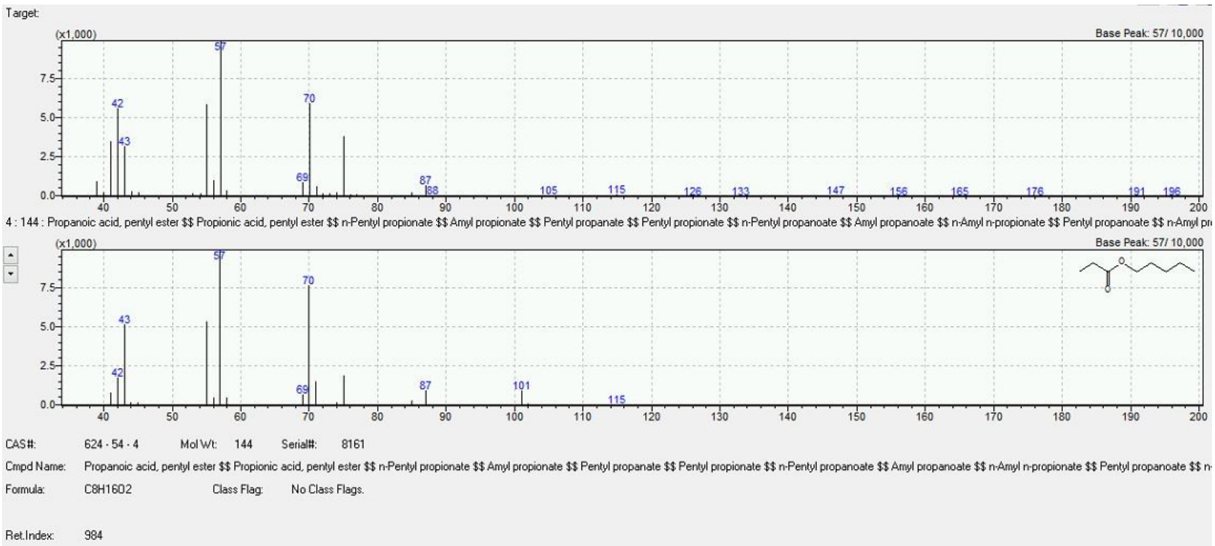
CAS#: 2998 - 23 - 4 Mol Wt: 142 Serial#: 12329

Cmpd Name: 2-Propenoic acid, pentyl ester $$ n-Amyl acrylate $$ n-Pentyl acrylate $$ Acrylic acid, pentyl ester $$ Amyl acrylate $$ Pentyl acrylate $$ Pentyl 2-propenoate $$ 2-Propenoic acid,n-pentyl ester $$

Formula: C8H14O2 Class Flag: No Class Flags.

Ret.Index: 974

Figure S18 Mass spectrum of the peak in the chromatogram of reaction mixtures assigned to *n*-pentyl acrylate based on the comparison with reference data (bottom).



4 : 144 : Propanoic acid, pentyl ester $$ Propionic acid, pentyl ester $$ n-Pentyl propionate $$ Amyl propionate $$ Pentyl propanate $$ Pentyl propionate $$ n-Pentyl propanoate $$ Amyl propanoate $$ n-Amyl n-propionate $$ Pentyl propanoate $$ n-Amyl pr

CAS#: 624 - 54 - 4 Mol Wt: 144 Serial#: 8161

Cmpd Name: Propanoic acid, pentyl ester $$ Propionic acid, pentyl ester $$ n-Pentyl propionate $$ Amyl propionate $$ Pentyl propanate $$ Pentyl propionate $$ n-Pentyl propanoate $$ Amyl propanoate $$ n-Amyl n-propionate $$ Pentyl propanoate $$ n-

Formula: C8H16O2 Class Flag: No Class Flags.

Ret.Index: 984

Figure S19 Mass spectrum of the peak in the chromatogram of reaction mixtures assigned to *n*-pently propanoate based on the comparison with reference data (bottom).

References

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