

## ***Supporting information***

**Efficient two-step production of biobased plasticizers:**

**Dehydration-hydrogenation of citric acid followed by Fischer esterification**

## Experimental details

**Table S1:** List with chemicals/materials used.

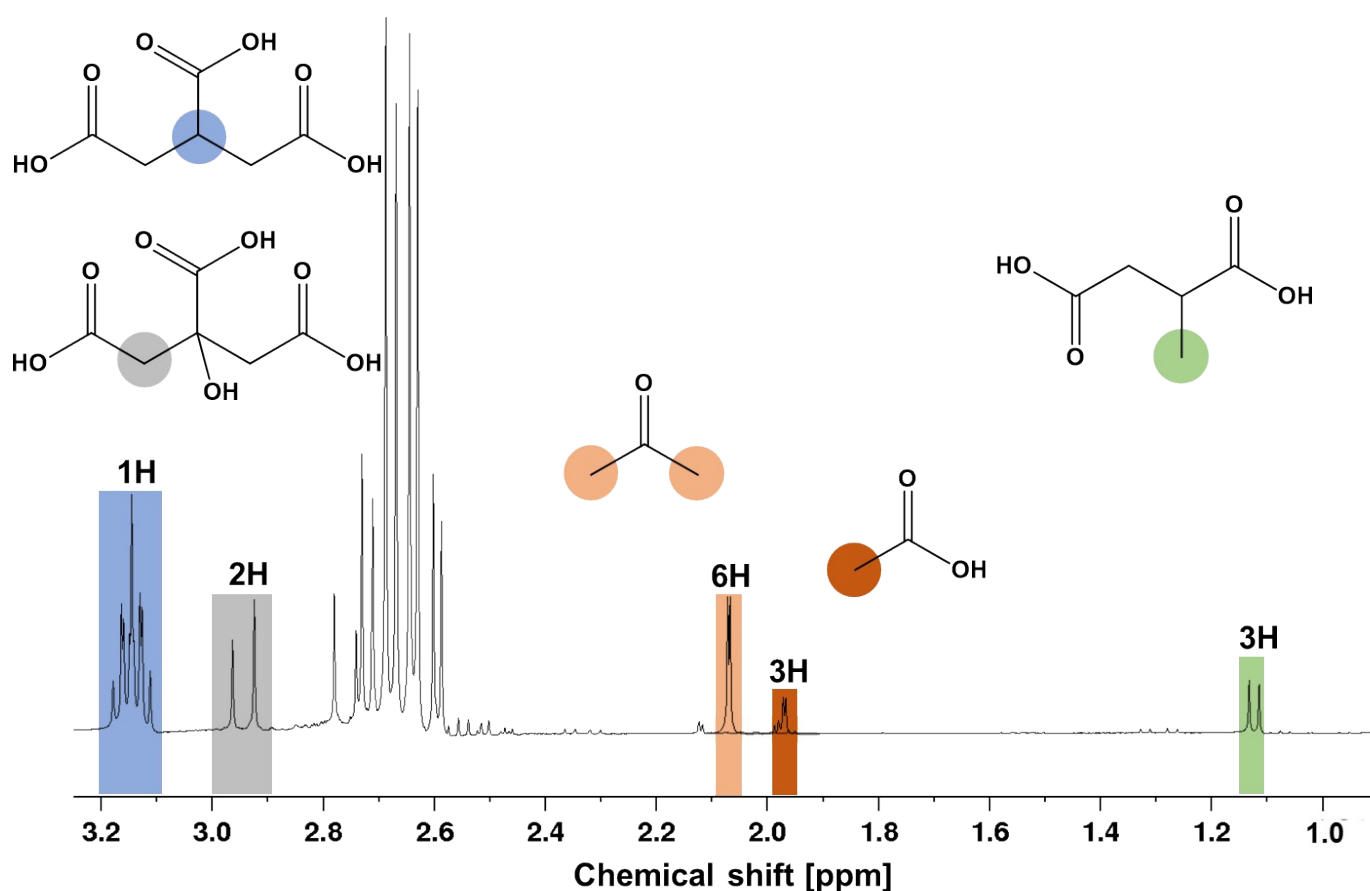
Chemicals	Supplier	Purity [%]
Aluminum (III) chloride	Sigma Aldrich	99.999
Aluminum (III) sulfate	Acros Organics	99.999
Aluminum (III) hydroxide	Acros Organics	-
Bismuth (III) chloride	Alfa Aesar	>97
Bismuth (III) oxy chloride	Alfa Aesar	-
Calcium (II) carbonate	Acros organics	98.5
Calcium (II) chloride	Merck	-
Dysprosium (III) chloride hexahydrate	Sigma Aldrich	99.9
Gallium(III) nitrate	Strem Chemicals, Inc.	99.9
Indium (II) chloride	Sigma Aldrich	99.9
Iron (III) chloride	Acros organics	>99
Iron(III) oxy hydroxide (Goethite)	Sigma Aldrich	-
Lanthanum (III) chloride	Alfa Aesar	99.99
Lanthanum (III) hydroxide	Sigma Aldrich	999
Lanthanum(III) trifluoromethanesulfonate	Alfa Aesar	99
Magnesium (II) chloride	Sigma Aldrich	-
Magnesium (II) oxide	Sigma ALdrich	99.99
Niobium (V) chloride	Alfa Aesar	99.99
Scandium(III) trifluoromethanesulfonate	Sigma Aldrich	99.995
Sodium (II) carbonate	Sigma Aldrich	-
Sodium (II) hydroxide	Th. Geyer GmbH & Co. KG	99.5
Sodium (II) sulfate	Acros Organics	99.9
Tin (II) chloride	Sigma Aldrich	99.99
Titanium (IV) chloride	Sigma Aldrich	99.9
Yttrium (III) chloride hexahydrate	Sigma Aldrich	-
Zinc (II) chloride	Sigma Aldrich	>98
Zirconium (IV) chloride	Sigma Aldrich	-
Zirconium (IV) hydroxide	Merck	-
Citric acid monohydrate	Sigma Aldrich	≥99.0
Di-ethylether	Fisher Scientific	≥99.5
Maleic acid	Tokyo Chemical Industries	>99.0
Methanol	Fisher Scientific	≥ 99.8
n-butanol	Sigma Aldrich	>99.4
<i>para</i> -Xylene	Acros Organics	99
Propane-1,2,3-tricarboxylic acid	Alfa Aesar	98
Palladium on carbon (5wt%)	Thermo Scientific	-
Boric acid	Sigma Aldrich	>99.5
Heteropoly acid (H <sub>13</sub> PWO <sub>40</sub> )	Fluka Analytics	-
Sulfuric acid	Fisher Scientific	>95
Carbon monoxide	Air Liquide	-
Hydrogen gas	Air Liquide	-
Nitrogen gas	Air Liquide	-
Deuterium oxide	Sigma Aldrich	99.9
Methanol-d <sub>4</sub>	Sigma Aldrich	99.8

## Dehydration-hydrogenation quantification

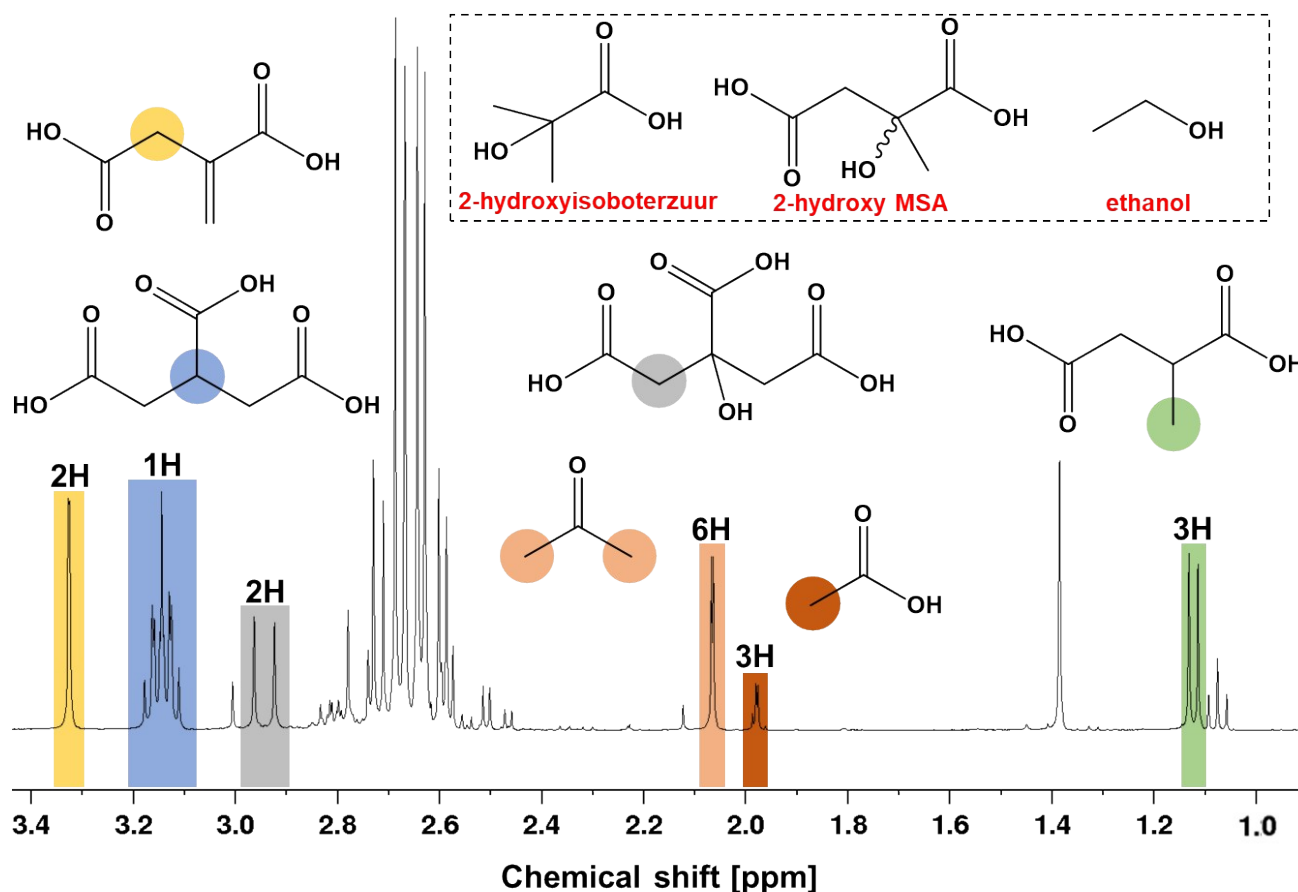
The amount of CA, PTA, MSA, IA and fragmentation products (*i.e.* acetone and acetic acid) were determined *via*  $^1\text{H-NMR}$  spectra. A typical  $^1\text{H-NMR}$  spectrum of a product mixture (*i.e.* dehydration-hydrogenation) is shown in figure S1 and figure S2. To determine the concentration of the different components, the peaks were integrated using the Bruker TopSpin 4.1.3 software with the use of an external standard (*i.e.* maleic acid, MA). A volume of 300  $\mu\text{L}$  external standard solution (0.067 M) was added to 200  $\mu\text{L}$  reaction mixture (0.1 M). For a given component X the area was determined with the peak area of the external standard set to 1. The carbon yields were calculated using the following formulas (with  $Y_{\text{CA}}$  consisting of both free citric acid and Al-citrate):

$$Y_{\text{CA}}[\%] = \frac{\text{Area}_{\text{CA}} * NH_{\text{MA}} * NC_{\text{CA}}}{NH_{\text{CA}} * NC_{\text{CA}}} + \frac{\text{Area}_{\text{Al-citrate}} * NH_{\text{MA}} * NC_{\text{CA}}}{NH_{\text{CA}} * NC_{\text{CA}}}$$

$$Y_{\text{X}}[\%] = \frac{\text{Area}_{\text{X}} * NH_{\text{MA}} * NC_{\text{X}}}{NH_{\text{X}} * NC_{\text{CA}}}$$



**Figure S1:** Typical  $^1\text{H-NMR}$  spectrum of a product mixture (dehydration-hydrogenation) with PTA (blue), CA (gray), acetone (orange), acetic acid (red) and MSA (green).



**Figure S2:** Typical <sup>1</sup>H-NMR spectrum of a product mixture (dehydration-hydrogenation) with IA (yellow), PTA (blue), CA (gray), acetone (orange), acetic acid (red) and MSA (green).

Additionally, HPLC was used to determine the concentration of PTA and CA in the product mixtures via the use of calibration curves (0.005 - 0.1 M for CA and 0.01 – 0.1 M for PTA). The linear relationship of both curves are shown below:

$$C_{CA}[M] = 1.00 * 10^{-5} * Area_{CA} + 0.0012 \quad \text{with } R^2 = 0.9998$$

$$C_{PTA}[M] = 2.00 * 10^{-5} * Area_{PTA} + 0.0014 \quad \text{with } R^2 = 0.9994$$

The concentrations of both CA and PTA could be calculated using the peak areas of CA and PTA. Integration was performed using the ChemStation ChemMain software with CA and PTA having a retention time of respectively 6.8 and 9.5 minutes. Concentrations were converted to the percentage relative to the initial concentration of CA (0.1 M or 1 M).

## Results

### Catalyst screening

Additional catalyst screening results, which contain water-stable Lewis acids, (Sc(OTf)<sub>3</sub> and La(OTf)<sub>3</sub>)<sup>1,2</sup>, oxophilic elements which form solids (TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O) in H<sub>2</sub>O (TiCl<sub>4</sub> and NbCl<sub>5</sub>)<sup>3,4</sup> and pure Brønsted acids (H<sub>3</sub>BO<sub>4</sub> and H<sub>13</sub>POW<sub>40</sub>). These reactions were performed in stainless steel reactor (12 mL) under standard conditions.

**Table S2:** Sequential dehydration - hydrogenation of citric acid. Screening of different homogenous Lewis acid catalysts.<sup>a</sup>

	Lewis Acid	Amount Cat. <sup>b</sup> [equiv.]	X <sup>c</sup> [%]	Carbon Yield [%]				Mass Balance <sup>h</sup>
				PTA <sup>d</sup>	MSA <sup>e</sup>	IA <sup>f</sup>	Fragm. <sup>g</sup>	
1*	-	-	17	10	4	0	1	98
<b>2</b>	-	-	<b>24</b>	<b>15</b>	<b>4</b>	<b>0</b>	<b>1</b>	<b>96</b>
3	AlCl <sub>3</sub> ·H <sub>2</sub> O	0.5	95	90	3	0	1	99
<b>4</b>	<b>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub></b>	<b>0.25</b>	<b>96</b>	<b>90</b>	<b>4</b>	<b>0</b>	<b>2</b>	<b>&gt;99</b>
5	Al(OH) <sub>3</sub>	0.5	88	85	2	0	0	99
6	Sc(OTf) <sub>3</sub>	0.5	23	21	1	0	1	96
7	La(OTf) <sub>3</sub>	0.5	13	13	0	0	0	95
8	TiCl <sub>4</sub>	0.5	29	29	0	0	0	89
9	NbCl <sub>5</sub>	0.5	29	28	1	0	0	94
10*	H <sub>3</sub> BO <sub>4</sub>	0.5	20	17	2	0	0	>99
11*	H <sub>13</sub> PWO <sub>40</sub>	0.5	11	10	0	0	1	>99
12	MgO	0.5	18	17	1	0	0	>99

<sup>a</sup> Reaction conditions: water (2 mL), 0.1 M citric acid, 0.5 mol% Pd<sup>0</sup>, 1 equivalent of H<sub>2</sub>SO<sub>4</sub>, 10 bar H<sub>2</sub>, 150°C and a reaction time of 20 h. <sup>b</sup> Amount of Lewis acid catalyst in equivalents with respect to citric acid. <sup>c</sup> Conversion *i.e.* the amount of citric acid that has reacted. <sup>d</sup> Propane-1,2,3-tricarboxylic acid. <sup>e</sup> Methyl succinic acid. <sup>f</sup> Itaconic acid. <sup>g</sup> Fragmentation products, which are represented by acetone and acetic acid. <sup>h</sup> Overall mass balance expressed in carbon yield.

\*No H<sub>2</sub>SO<sub>4</sub> added

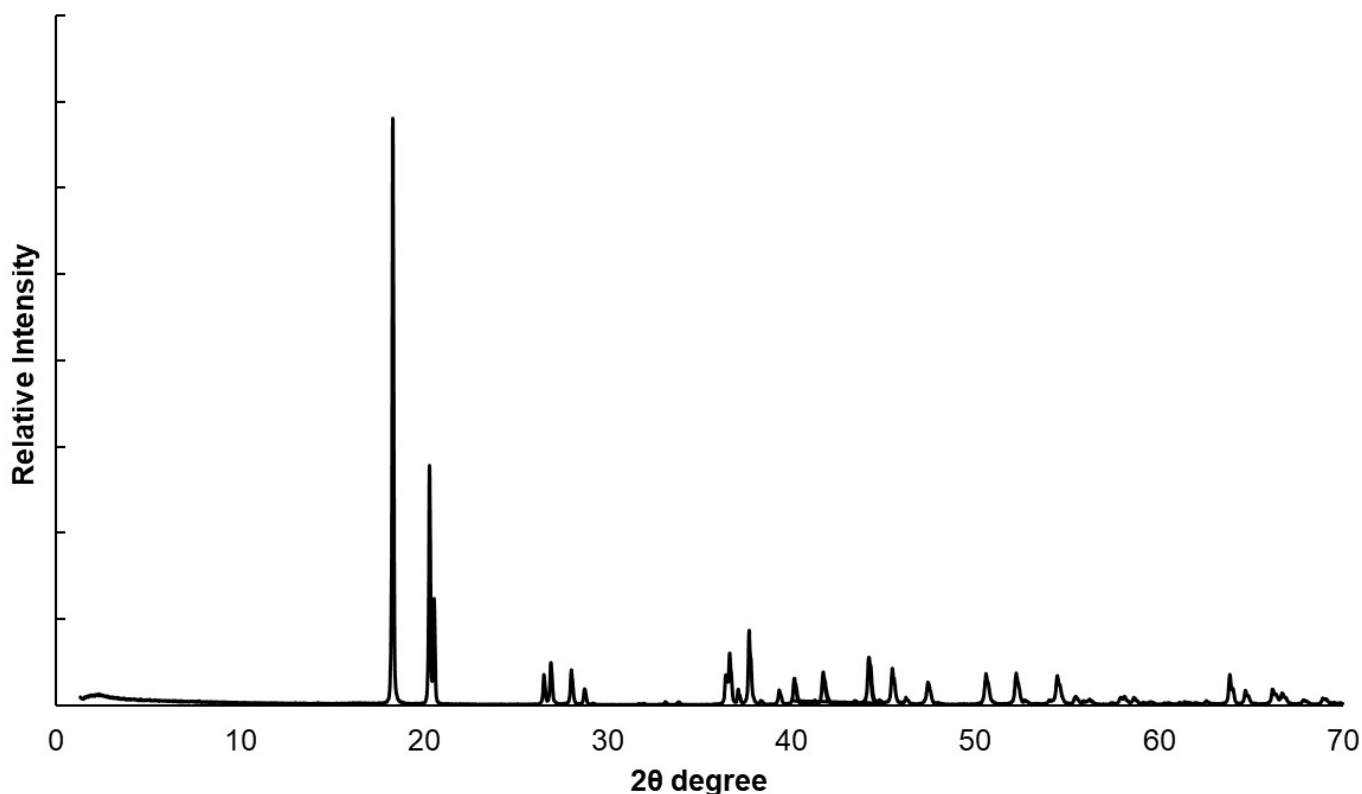
## Solubility Al(OH)<sub>3</sub>

**Table S3:** pH measurement of solutions which represent the different reaction mixtures with Al(OH)<sub>3</sub>.

CA [M]	Al(OH) <sub>3</sub>	Additive	pH <sup>a</sup>	Solubility at 20°C	Solubility at 80°C (stirred overnight)
0.1	0.5	/	1.57	Not in Sol.	Not in Sol.
0.1	0.5	0.5 eq. H <sub>2</sub> SO <sub>4</sub>	1.36	Not in Sol.	Not in Sol.
0.1	0.5	1 eq. H <sub>2</sub> SO <sub>4</sub>	1.22	Not in Sol.	Not in Sol.
0.1	0.5	2 eq. H <sub>2</sub> SO <sub>4</sub>	1.11	Not in Sol.	Clear Solution
1	0.5	1 eq. H <sub>2</sub> SO <sub>4</sub>	0.53	Not in Sol.	Clear Solution
1	0.5	2 eq. H <sub>2</sub> SO <sub>4</sub>	0.43	Not in Sol.	Clear Solution
1	0.25	/	1.68	Not in Sol.	Not in Sol.
1	0.25	0.1 eq. H <sub>2</sub> SO <sub>4</sub>	1.46	Not in Sol.	Not in Sol.
1	0.25	0.2 eq. H <sub>2</sub> SO <sub>4</sub>	1.34	Not in Sol.	Not in Sol.
1	0.25	0.5 eq. H <sub>2</sub> SO <sub>4</sub>	1.03	Not in Sol.	Colloidal Sol.

<sup>a</sup> pH measurements performed at 25°C using a SympHony VWR pH meter.

Low solubility of Al(OH)<sub>3</sub> resulted in a loss of substrate (*i.e.* citric acid) and lower PTA carbon yield due to adsorption of CA on the Al(OH)<sub>3</sub> particles and lower amounts of free Al<sup>3+</sup> ions. The presence of insoluble structures, like  $\alpha$ -Al(OH)<sub>3</sub> and  $\gamma$ -Al(OH)<sub>3</sub>, was suggested as a possible cause.<sup>5</sup> This was confirmed *via* XRD diffractogram of the commercially used Al(OH)<sub>3</sub>.



**Figure S3:** XRD diffractogram of commercially obtained Al(OH)<sub>3</sub>.<sup>5</sup>

## pH measurements $\text{Al}_2(\text{SO}_4)_3$

**Table S4:** pH measurement of solutions which represent the different reaction mixtures with  $\text{Al}_2(\text{SO}_4)_3$

CA [M]	$\text{Al}_2(\text{SO}_4)_3$	Additive	pH <sup>a</sup>	Solubility at 20°C	Solubility at 80 °C (stirred overnight)
0.1	0.25 eq.	/	1.76	Not in Sol.	Clear Solution
0.1	0.25 eq.	0.5 eq. NaOH	2.48	Not in Sol.	Clear Solution
0.1	0.25 eq.	1 eq. NaOH	3.15	Not in Sol.	Clear Solution
0.1	0.25 eq.	2 eq. NaOH	4.15	Not in Sol.	Clear Solution
0.1	0.25 eq.	0.5 eq. $\text{H}_2\text{SO}_4$	1.48	Not in Sol.	Clear Solution
0.1	0.25 eq.	1 eq. $\text{H}_2\text{SO}_4$	1.30	Not in Sol.	Clear Solution
0.1	0.25 eq.	2 eq. $\text{H}_2\text{SO}_4$	1.13	Not in Sol.	Clear Solution
1	0.125 eq.	0 eq. $\text{H}_2\text{SO}_4$	1.16	Not in Sol.	Clear Solution
1	0.125 eq.	0.5 eq. $\text{H}_2\text{SO}_4$	0.91	Not in Sol.	Colloidal Sol.

<sup>a</sup> pH measurements performed at 25°C using a SympHony VWR pH meter.

## CO chemisorption

**Table S5:** CO chemisorption measurements on hydrogenation catalyst, *i.e.*  $\text{Pd}^0/\text{C}$ .

Sample	$\text{Pd}^0$ dispersion [%]
$\text{Pd}^0/\text{C}$ before reaction	36.9
$\text{Pd}^0/\text{C}$ after reaction	38.7
$\text{Pd}^0/\text{C}$ after reaction with 20mol% Cysteine	3.34

\*Samples were washed with  $\text{H}_2\text{O}$  (3 times, 10 mL) and dried overnight (60°C) prior to the measurement

\*\*measurements were performed with a ChemBET Pulsar TPR/TPD

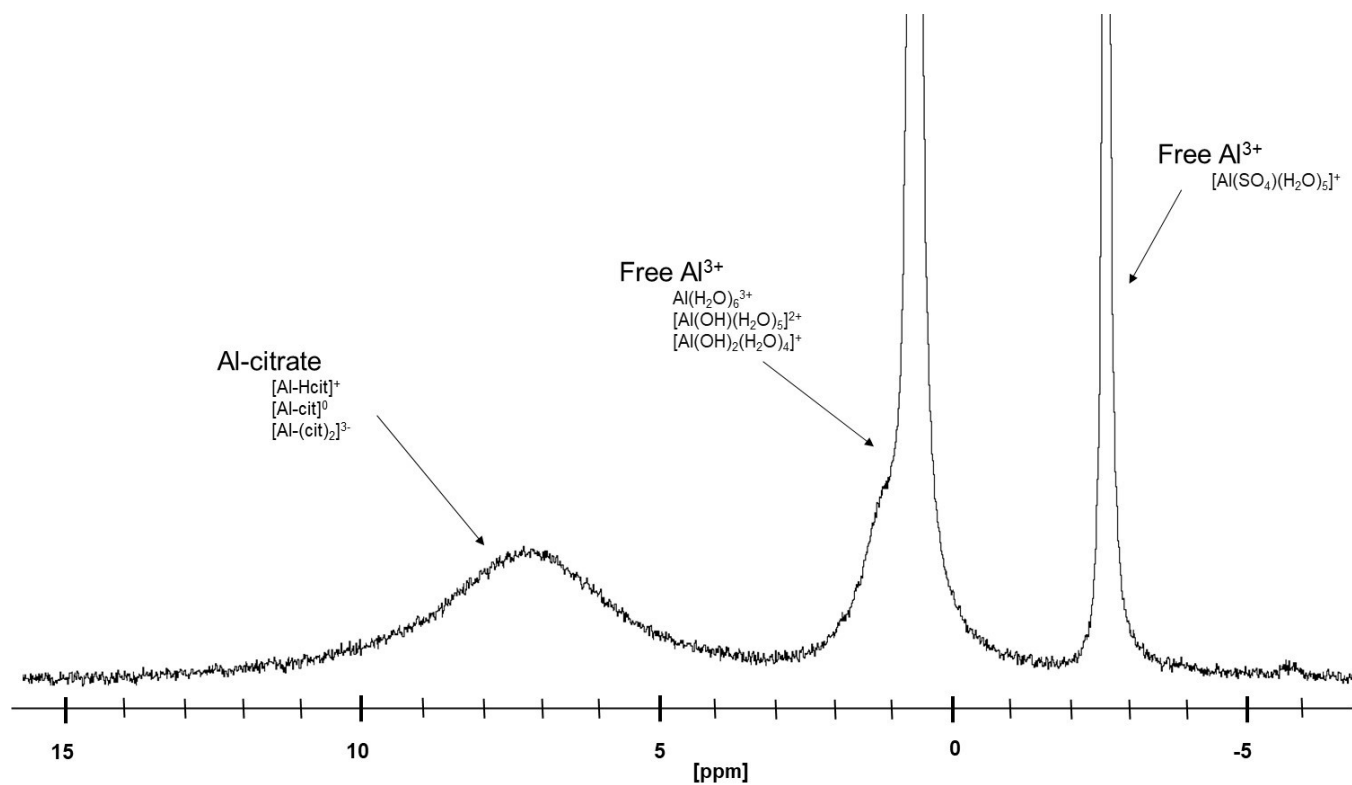
## ICP-OES measurements

**Table S6:** ICP-OES measurements on fresh (commercial) and recovered  $\text{Al}_2(\text{SO}_4)_3$  compared to theoretical amount of pure anhydrous  $\text{Al}_2(\text{SO}_4)_3$

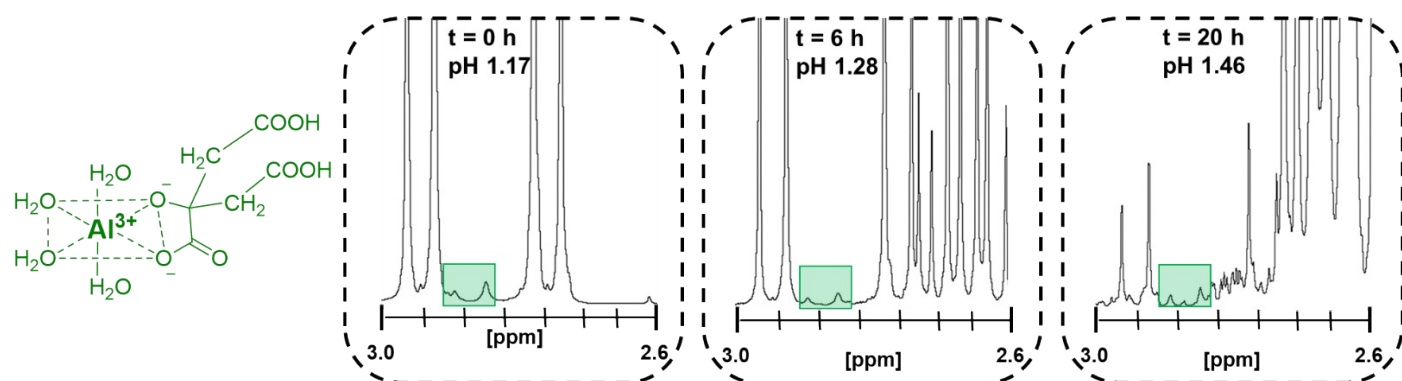
	Mass [mg]	Aluminum [%]	Anhydrous $\text{Al}_2(\text{SO}_4)_3$ [%]	Amount of $\text{H}_2\text{O}$ molecules in Hydrate
Anhydrous $\text{Al}_2(\text{SO}_4)_3$ *	/	15.75	100	0
Commercial $\text{Al}_2(\text{SO}_4)_3$	10	10.5	64.4	9.7
Recovered $\text{Al}_2(\text{SO}_4)_3$	10	10.3	63.1	9.9

\*Theoretical values

## $^{27}\text{Al}$ -NMR of aluminum-citrate complexes at different temperatures



**Figure S4:**  $^{27}\text{Al}$ -NMR spectra of mixture containing 1 M of citric acid and 0.125 eq.  $\text{Al}_2(\text{SO}_4)_3$  at  $25^\circ\text{C}$ .



**Figure S5:**  $^1\text{H}$ -NMR spectra and pH measurements of reaction mixtures (20 mL  $\text{H}_2\text{O}$ , 1 M of citric acid, 0.125 eq.  $\text{Al}^{3+}$  ( $\text{Al}_2(\text{SO}_4)_3$ ) and 5 mol%  $\text{Pd}^0$ ) at different reaction times (*i.e.* 0, 6 and 20 h). Reactions took place at  $150^\circ\text{C}$  with 20 bar of  $\text{H}_2$ . Highlighted boxes (green) show the presence of  $[\text{Al-Hcit}]^+$ .<sup>6-8</sup>

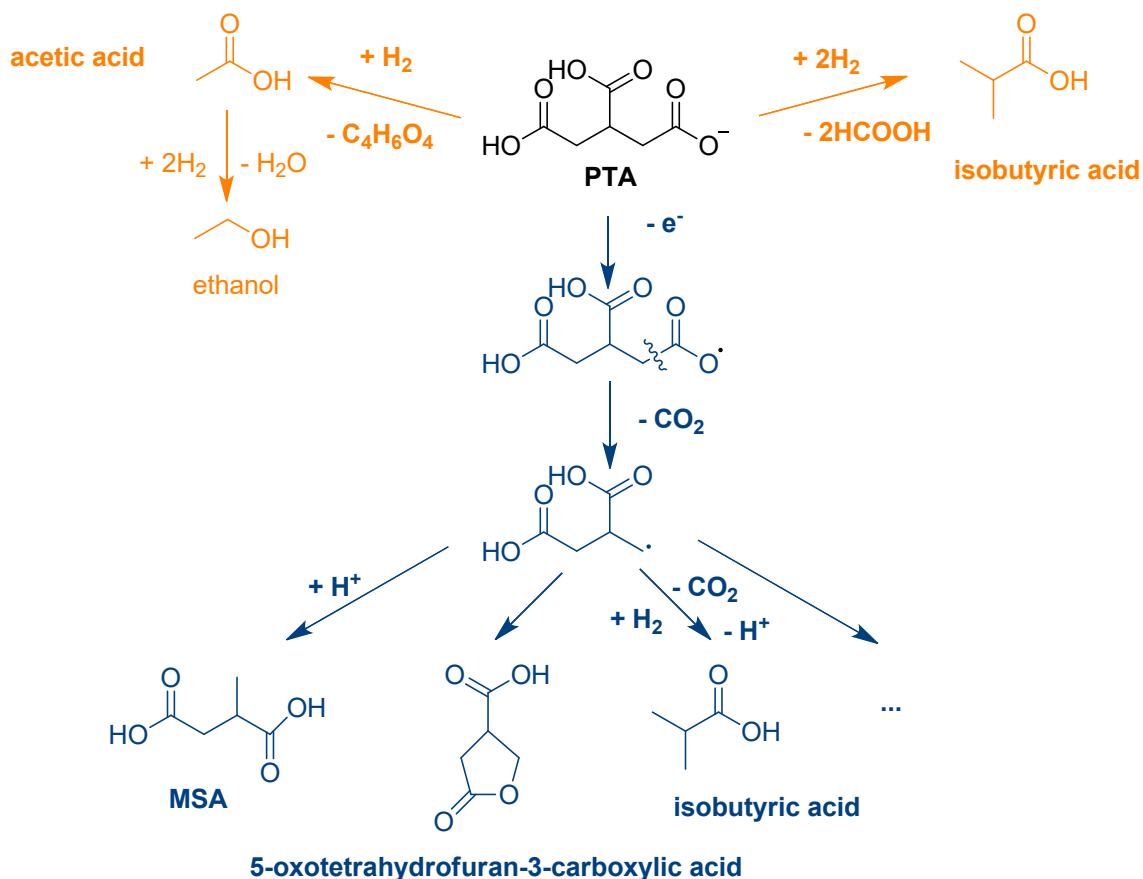


## Optimalisation: dehydration-hydrogenation of citric acid

**Table S7:** Sequential dehydration - hydrogenation of citric acid. Influence of different amounts of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, additives, temperature and higher substrate concentrations. <sup>a</sup>

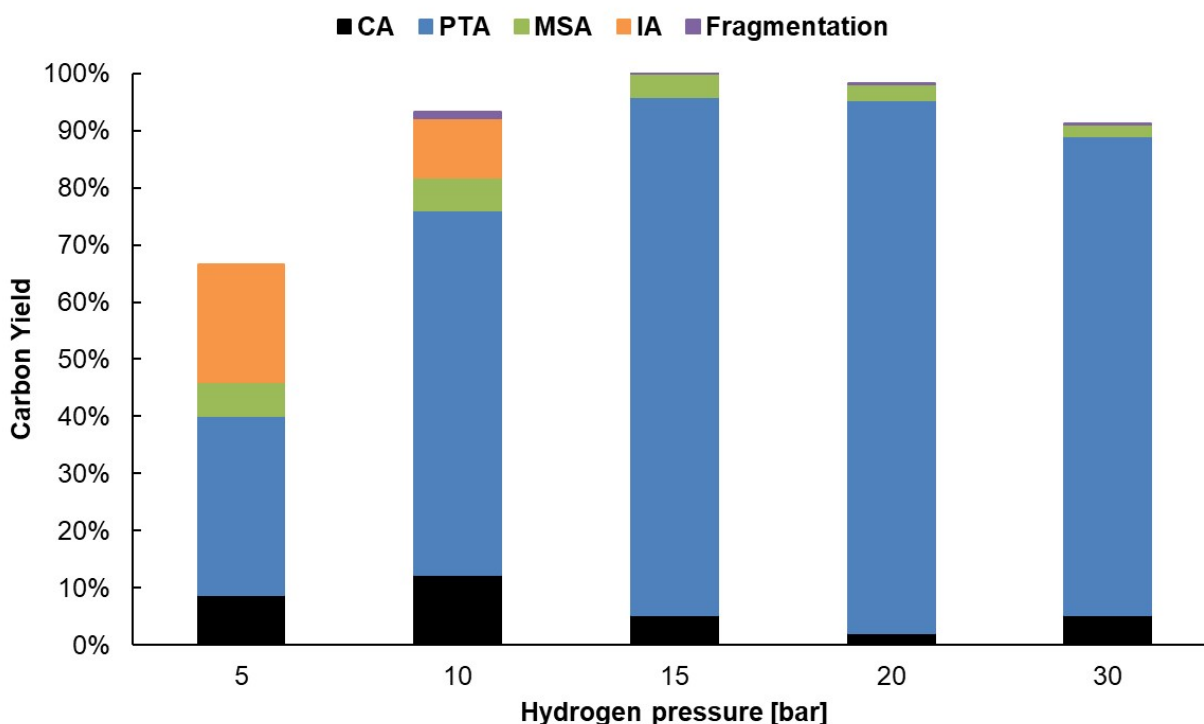
	Lewis Acid <sup>b</sup>	Amount Cat. <sup>c</sup> [eq.]	Additive [eq.]	Pd <sup>0</sup> /C <sup>d</sup> [mol%]	Conc. <sup>e</sup> [M]	P <sub>H<sub>2</sub></sub> [bar]	T [°C]	X [%]	Carbon Yield [%]				
									PTA <sup>g</sup>	MSA <sup>h</sup>	IA <sup>i</sup>	Fragm. <sup>j</sup>	Mass Balance <sup>k</sup>
1	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.065	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	60	54	1	0	0	95
2	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.125	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	91	85	4	0	2	>99
<b>3</b>	<b>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub></b>	<b>0.25</b>	<b>1 H<sub>2</sub>SO<sub>4</sub></b>	<b>0.5</b>	<b>0.1</b>	<b>10</b>	<b>150</b>	<b>96</b>	<b>90</b>	<b>4</b>	<b>0</b>	<b>2</b>	<b>&gt;99</b>
4	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.5	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	99	92	4	0	2	99
5	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	1	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	98	93	4	0	2	99
6	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	0 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	88	82	2	0	0	88
7	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	0.2 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	81	75	4	0	0	80
8	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	0.5 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	96	90	4	0	2	>99
9	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	2 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	>99	91	2	0	1	>99
10	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	0.2 NaOH	0.5	0.1	10	150	77	59	10	0	2	96
11	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	0.5 NaOH	0.5	0.1	10	150	74	57	15	0	1	97
12	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	1 NaOH	0.5	0.1	10	150	59	37	20	0	1	96
13	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	2 NaOH	0.5	0.1	10	150	34	8	16	0	1	91
14	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	130	26	24	0	0	1	99
15	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	140	75	73	0	0	1	>99
16	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	160	81	73	6	0	0	99
17	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	180	87	60	19	0	1	99
18	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.125	-	0.5	0.5	10	150	98	95	2	0	0	>99
19	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.5	10	150	52	51	0	0	0	>99
20	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.125	-	0.5	0.8	16	150	93	76	2	0	0	84
21	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	0.5 H <sub>2</sub> SO <sub>4</sub>	0.5	0.8	16	150	84	63	0	0	0	80
22	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.0625	-	0.5	1	20	150	91	73	0	0	0	82
<b>23</b>	<b>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub></b>	<b>0.125</b>	<b>-</b>	<b>0.5</b>	<b>1</b>	<b>20</b>	<b>150</b>	<b>90</b>	<b>88</b>	<b>1</b>	<b>0</b>	<b>0</b>	<b>&gt;99</b>
24	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	0.2 H <sub>2</sub> SO <sub>4</sub>	0.5	1	20	150	87	73	1	0	0	87

<sup>a</sup> Reaction conditions: water (2 mL), 20 h. <sup>b</sup> Lewis Acid catalyst. <sup>c</sup> Amount of Lewis acid catalyst in equivalents with respect to citric acid. <sup>d</sup> mol% of Pd (5 wt.% Pd<sup>0</sup>/C) with respect to citric acid. <sup>e</sup> Concentration of substrate citric acid. <sup>f</sup> Conversion *i.e.* the amount of citric acid that has reacted. <sup>g</sup> Propane-1,2,3-tricarboxylic acid. <sup>h</sup> Methyl succinic acid. <sup>i</sup> Itaconic acid. <sup>j</sup> Fragmentation products, which are represented by acetone and acetic acid. <sup>k</sup> Overall mass balance expressed in carbon yield.

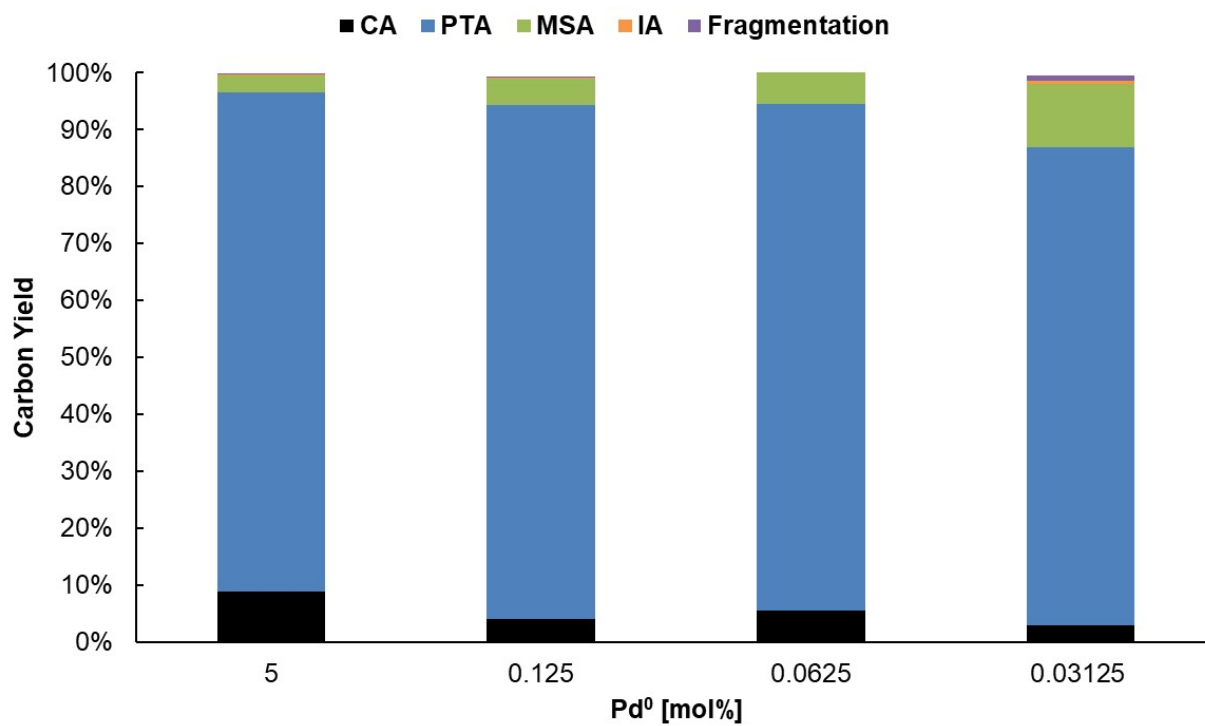


**Scheme S1:** Possible hydrogenolysis (orange) and fragmentation (blue) products starting from PTA.<sup>9,10</sup>

Additional reaction condition results, which contain varying the amount of hydrogen pressure ( $P_{H_2}$ ) and the amount of hydrogenation catalyst (*i.e.* Pd<sup>0</sup>/C). Performed in Hastelloy Premex reactor (60 mL) under standard conditions.



**Figure S6:** Influence of hydrogen pressure on the dehydration-hydrogenation of citric acid. Reaction in water (20 mL) with citric acid (20 mmol), Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (1.24 mmol), Pd<sup>0</sup>/C (0.5 mol% Pd<sup>0</sup>), 20 hours at 150°C. With different pressures of H<sub>2</sub> (5, 10, 15, 20 and 30 bar).



**Figure S7:** Influence of the amount of Pd<sup>0</sup> on the dehydration-hydrogenation of citric acid. Reaction in water (20 mL) with citric acid (20 mmol), Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (1.24 mmol), 20 hours with 20 bar H<sub>2</sub> at 150°C. With different amount of Pd<sup>0</sup> (0.3125; 0.625; 1.25 and 5 mol%).

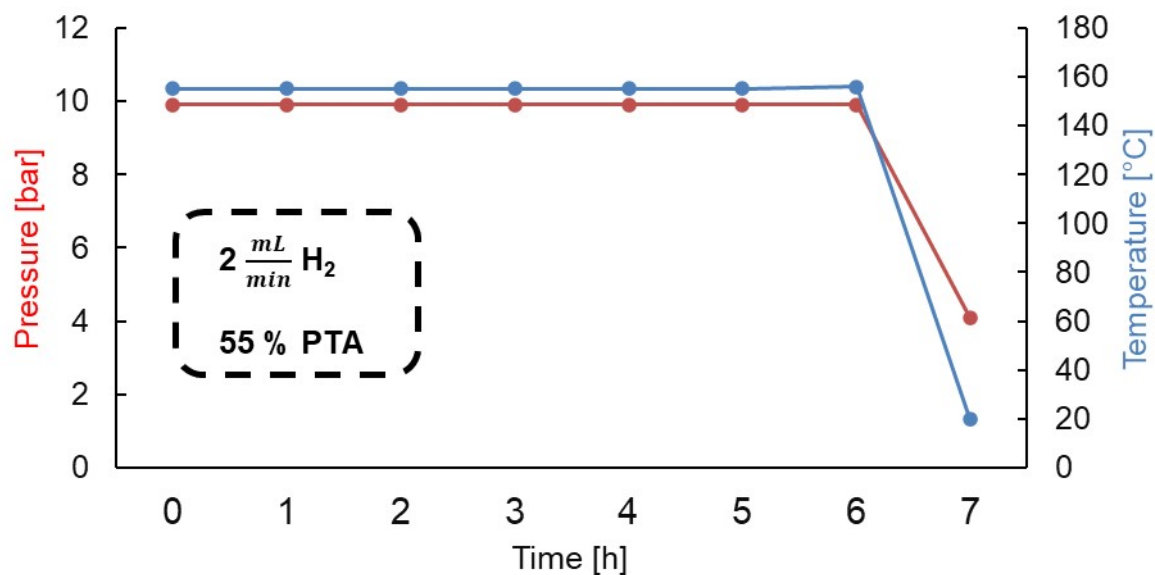
## Additional results Ga(NO<sub>3</sub>)<sub>3</sub>

**Table S8:** Sequential dehydration – decarboxylation -hydrogenation of citric acid. Influence of different amounts of Ga(NO<sub>3</sub>)<sub>3</sub>, additives, temperature and higher substrate concentration. <sup>a</sup>

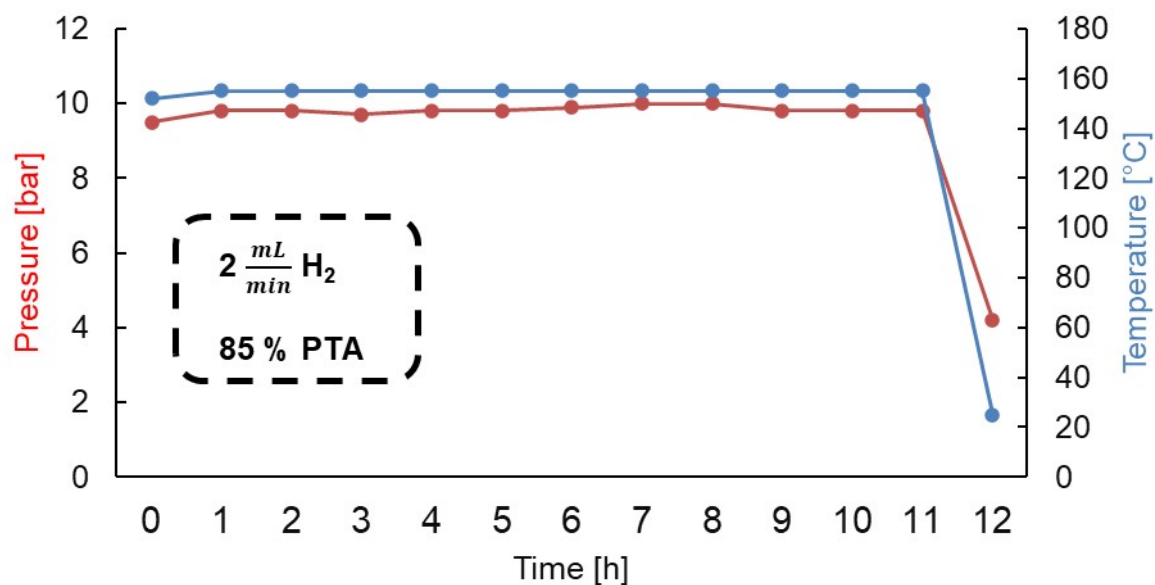
	Lewis Acid <sup>b</sup>	Amount Cat. <sup>c</sup> [eq.]	Additive [eq.]	Pd <sup>0</sup> /C <sup>d</sup> [mol%]	Conc. <sup>e</sup> [M]	P <sub>H2</sub> [bar]	T [°C]	X [%]	Carbon Yield [%]				Mass Balance <sup>k</sup>
									PTA <sup>g</sup>	MSA <sup>h</sup>	IA <sup>i</sup>	Fragm. <sup>j</sup>	
1	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.2	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	86	59	22	0	0	96
2	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.5	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	71	43	24	0	1	96
3	Ga(NO <sub>3</sub> ) <sub>3</sub>	1	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	76	24	34	0	1	83
4	Ga(NO <sub>3</sub> ) <sub>3</sub>	2	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	97	0	17	0	5	27
5	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.5	0.2 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	50	7	35	0	1	94
6	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.5	0.5 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	73	24	42	0	1	96
7	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.5	2 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	150	81	68	9	0	1	98
9	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.5	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	140	67	46	17	0	0	97
10	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.5	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	160	85	49	28	0	1	93
11	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.5	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	180	95	8	74	0	2	89
12	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.5	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	10	200	>99	8	80	0	1	89
13	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.5	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	5	150	74	42	27	0	1	95
14	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.5	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	20	150	66	46	14	0	0	95
15	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.5	1 H <sub>2</sub> SO <sub>4</sub>	0.5	0.1	30	150	70	42	23	0	1	95
<b>16</b>	<b>Ga(NO<sub>3</sub>)<sub>3</sub></b>	<b>0.2</b>	<b>2 H<sub>2</sub>SO<sub>4</sub></b>	<b>0.5</b>	<b>0.1</b>	<b>10</b>	<b>150</b>	<b>96</b>	<b>91</b>	<b>5</b>	<b>0</b>	<b>0</b>	<b>&gt;99</b>
<b>17</b>	<b>Ga(NO<sub>3</sub>)<sub>3</sub></b>	<b>0.2</b>	<b>-</b>	<b>0.5</b>	<b>0.1</b>	<b>5</b>	<b>200</b>	<b>&gt;99</b>	<b>0</b>	<b>63</b>	<b>0</b>	<b>1</b>	<b>65</b>
18	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.2	-	0.5	0.1	10	200	0	0	0	0	0	0
<b>19<sup>l</sup></b>	<b>Ga(NO<sub>3</sub>)<sub>3</sub></b>	<b>0.2</b>	<b>-</b>	<b>0.5</b>	<b>0.1</b>	<b>10</b>	<b>200</b>	<b>&gt;99</b>	<b>0</b>	<b>78</b>	<b>0</b>	<b>1</b>	<b>79</b>
20	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.5	1 H <sub>2</sub> SO <sub>4</sub>	0.5	1	20	150	60	44	0	0	1	84

<sup>a</sup> Reaction conditions: water (2 mL), 20 h. <sup>b</sup> Lewis Acid catalyst. <sup>c</sup> Amount of Lewis acid catalyst in equivalents with respect to citric acid. <sup>d</sup> mol% of Pd (5 wt.% Pd/C) with respect to citric acid. <sup>e</sup> Concentration of substrate citric acid. <sup>f</sup> Conversion *i.e.* the amount of citric acid that has reacted. <sup>g</sup> Propane-1,2,3-tricarboxylic acid. <sup>h</sup> Methyl succinic acid. <sup>i</sup> Itaconic acid. <sup>j</sup> Fragmentation products, which are represented by acetone and acetic acid. <sup>k</sup> Overall mass balance expressed in carbon yield. <sup>l</sup> Reaction conditions: water (2 mL), 6

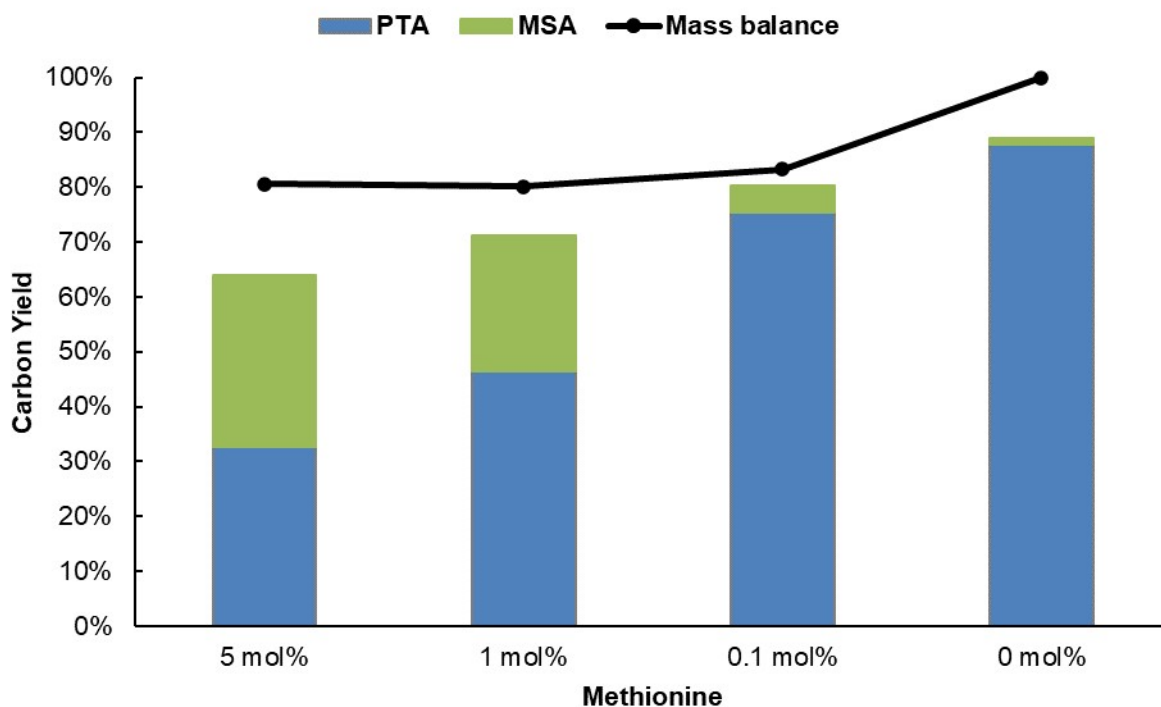
## Stability and robustness dehydration-hydrogenation system



**Figure S8:** Pressure and temperature profile of reaction (20 mL H<sub>2</sub>O, 1 M CA with 0.125 eq. Al<sub>2</sub>SO<sub>4</sub> and 5 mol% Pd<sup>0</sup>) at 150°C with a constant H<sub>2</sub> pressure of 10 bar. This resulted in a PTA carbon yield of 55% after 6 h of reaction time.



**Figure S9:** Pressure and temperature profile of reaction (20 mL H<sub>2</sub>O, 1 M CA with 0.125 eq. Al<sub>2</sub>SO<sub>4</sub> and 5 mol% Pd<sup>0</sup>) at 150°C with a constant H<sub>2</sub> pressure of 10 bar. This resulted in a PTA carbon yield of 85% after 12 h of reaction time.



**Figure S10:** Influence of amino acid methionine on dehydration-hydrogenation of citric acid. Reaction in water (2 mL) with citric acid (2 mmol),  $\text{Al}_2(\text{SO}_4)_3$  (0.25 mmol),  $\text{Pd}^0/\text{C}$  (0.5 mol%  $\text{Pd}^0$ ), 20 hours with 20 bar  $\text{H}_2$  at 150°C.

**Table S9:** Characterization of aqueous intermediate production stream (IPS) of the citric acid purification process, where only partial purification of citric acid has occurred, performed by Citribel.

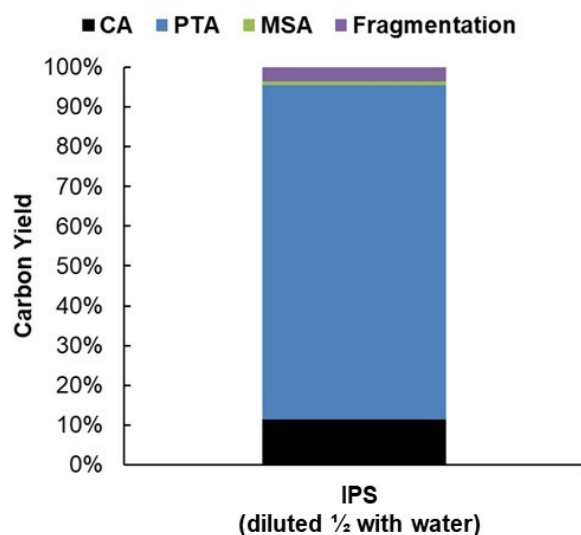
	pH <sup>a</sup>	Citric acid <sup>b</sup> [g/L]	Inorganics <sup>c</sup> [mg/L]	Organics <sup>d</sup> [mg/L]
IPS	0.91	432.62	1126.21	732.59

<sup>a</sup> pH measurements performed at 25°C using a Symphony VWR pH meter.

<sup>b</sup> citric acid + citrate determined *via* titration.

<sup>c</sup> Inorganics: sum of specific inorganic cations measured via ICP-OES.

<sup>d</sup> Organics: sum of specific organic acids (without citric acid) measured with HPLC.

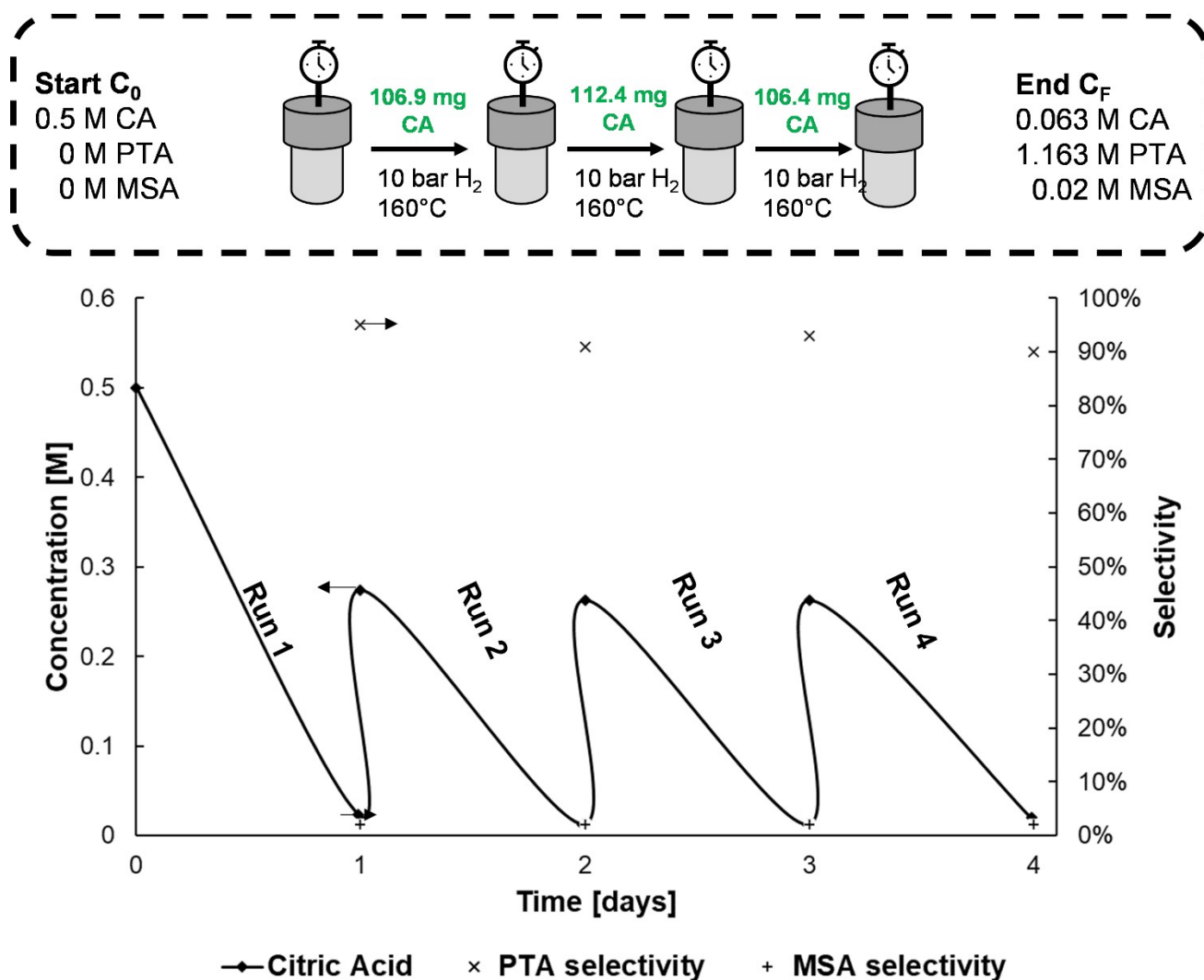


**Figure S11:** Dehydration-hydrogenation with aqueous IPS (diluted 1/2 with water) used as substrate,  $\text{Al}_2(\text{SO}_4)_3$  (0.25 mmol),  $\text{Pd}^0/\text{C}$  (0.5 mol%  $\text{Pd}^0$ ), 20 hours with 24 bar  $\text{H}_2$  at 150°C.

## Fed-batch experiment on dehydration-hydrogenation.

For a fed-batch experiment, the standard protocol was followed. Reaction started with 1 mmol of citric acid but after 24 h of reaction time, the reactor was cooled and a new amount of citric acid (0.5 mmol) was added to the existing reaction mixture and the reaction was repeated. This was repeated after 48 and 72 h. After 96 h, the liquid products were recovered by centrifugation (4000 rpm, 10 minutes) and analyzed by  $^1\text{H-NMR}$  spectroscopy and/or liquid chromatography (HPLC).

To obtain a large amount of PTA and evaluate the stability of the catalytic system over a longer period of time, a fed-batch experiment was performed. The initial amount of substrate ( $C_0$ ) was equal to 1 mmol citric acid ( $C_{0, \text{CA}} = 0.5 \text{ M}$ ) (Figure 7). After 24 h, 0.5 mmol citric acid was added together with again 10 bar  $\text{H}_2$ . This was repeated 3 times; hence a total amount of 2.5 mmol citric acid was processed during the fed-batch process. This resulted in an overall PTA carbon yield of 93% ( $C_{\text{F, PTA}} = 1.163 \text{ M}$ ).  $^1\text{H-NMR}$  measurements after the different stages of the fed-batch experiment showed that the selectivity to PTA and the conversion of citric acid remained constant over time, suggesting a stable catalytic system.



**Figure S12:** Fed-batch experiment of the dehydration-hydrogenation of citric acid. Reaction in water (2 mL) starting with citric acid (1 mmol),  $\text{Al}_2(\text{SO}_4)_3$  (0.5 mmol),  $\text{Pd}^0/\text{C}$  (0.5 mol%  $\text{Pd}^0$ ), 24 h with 10 bar  $\text{H}_2$  at 150°C. After 24 h an amount of citric acid (0.5 mmol) was added; the reactor was repressurized to 10 bar of  $\text{H}_2$  (repeated 3 times).

In view of the excellent PTA carbon yield obtained in the fed batch system, a constant pressure setup using a mass flow controller was designed to perform the reaction at a lower H<sub>2</sub> pressure of 10 bar (Figure S8 and S9, supp. Info). Similar PTA carbon yields were obtained, as in the batch experiments conducted at 20 bar H<sub>2</sub>, illustrating the potential of working at lower H<sub>2</sub> pressures, and thus the industrial relevancy of this system.



## Arrhenius plot

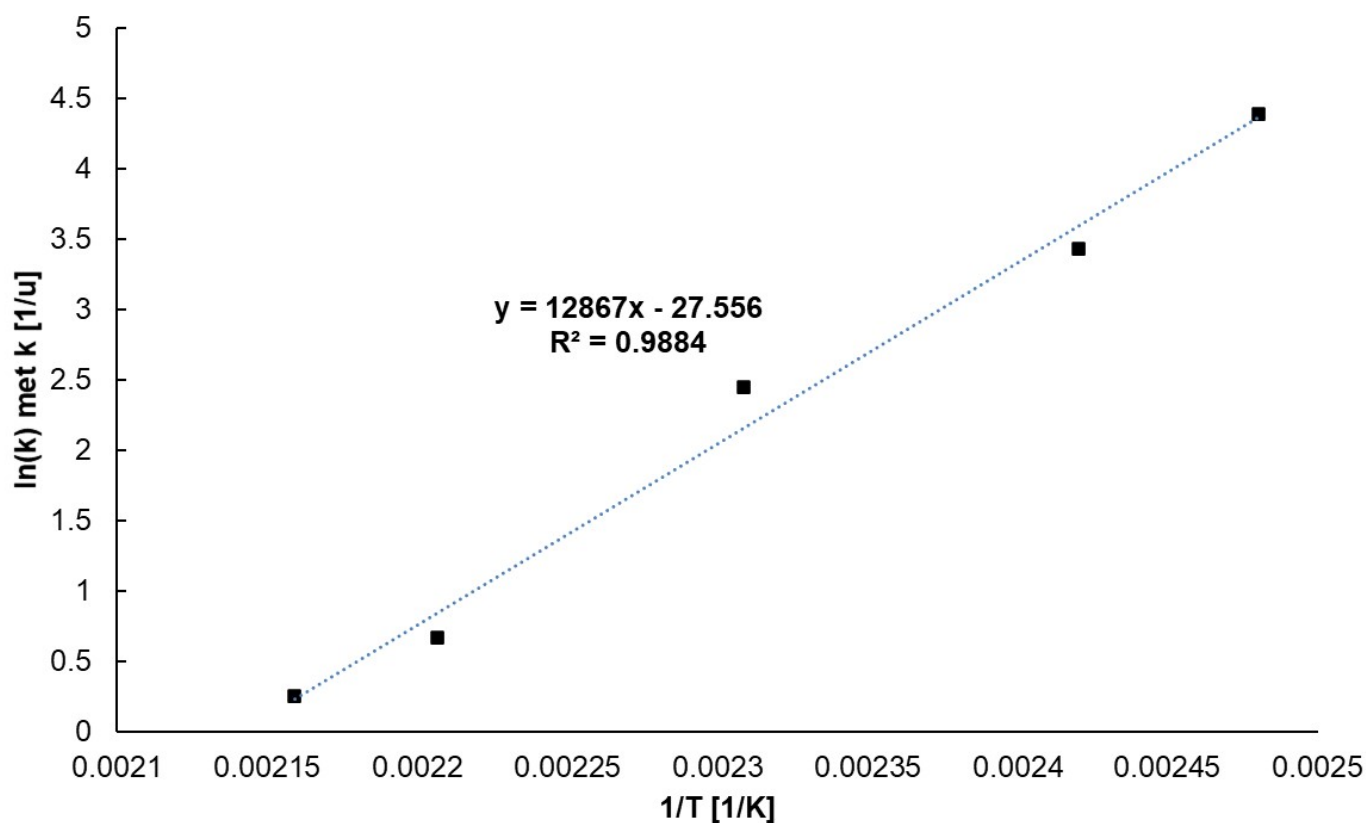
To study the influence of temperature on the reaction rate (dehydration of CA), an Arrhenius plot ( $\ln(k)$  versus  $1/T$ ) was obtained by performing reactions at different temperatures and reaction times each with a CA conversion of 5–15% (Table S9). It was assumed that the dehydration of CA is a first order reaction. Since a linear relationship is observed between  $\ln(k)$  and  $1/T$  is observed.

An activation energy ( $E_a$ ) of 105 kJ/mol was obtained. This relatively high value suggests the reaction rate of the dehydration will increase strongly with increasing temperature. However, at higher temperatures the newly formed aconitic acid is more prone to decarboxylation (*i.e.* formation of MSA).<sup>9</sup>

**Table S10:** Data points used for Arrhenius plot.

T [K]	1/T [1/K]	A <sub>0</sub> [M]	A <sub>F</sub> [M]	Tijd [u]	k [1/u]	ln(k)
403.15	0.00248	1.00	0.86	8	0.017065	-4.07071
413.15	0.00242	1.00	0.87	4	0.032283	-3.43323
433.15	0.00231	1.00	0.85	1	0.146413	-1.92132
453.15	0.00221	1.00	0.82	0.33	0.532174	-0.63078
463.15	0.00216	1.00	0.85	0.17	0.920870	-0.08244

\*Data points for the Arrhenius plot. T = reaction temperature, A<sub>0</sub> = concentration of CA at t = 0, A<sub>F</sub> = concentration of CA after reaction, k = reaction rate constant.

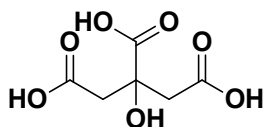


**Figure S13:** Arrhenius plot of the dehydration of citric acid.

## Product Identification

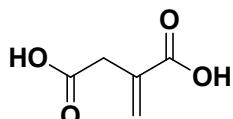
**General information:**  $^1\text{H-NMR}$  spectra in  $\text{D}_2\text{O}/\text{H}_2\text{O}$  were calibrated by setting the singlet signal of the external standard (*i.e.* maleic acid) to 6.302 ppm.

### Citric acid (1, MW = 192 g/mol)



$^1\text{H-NMR}$  (400 MHz,  $\text{H}_2\text{O}/\text{D}_2\text{O}$ ):  $\delta$  (ppm) = 2.94 (d, 2H,  $-\text{CH}_2-\text{COOH}$ ), 2.76 (d, 2H,  $-\text{CH}_2-\text{COOH}$ ).

### Itaconic acid (2, MW = 130 g/mol)

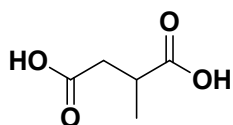


$^1\text{H-NMR}$  (400 MHz,  $\text{H}_2\text{O}/\text{D}_2\text{O}$ ):  $\delta$  (ppm) = 6.31 (s, 1H,  $\text{CH}_2=\text{C}(\text{COOH})-$ ), 5.83 (s, 1H,  $\text{CH}_2=\text{C}(\text{COOH})$ ), 3.36 (s, 2H,  $-\text{CH}_2-\text{COOH}$ ).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (400 MHz,  $\text{H}_2\text{O}/\text{D}_2\text{O}$ ):  $\delta$  (ppm) = 130.1 (1C,  $\text{CH}_2=\text{C}<$ ), 38.1 (1C,  $\text{COOH}-\text{CH}_2-$ ).

Carbons that do not couple with a proton, were not observed via HSQC.

### Methyl succinic acid (3, MW = 132 g/mol)

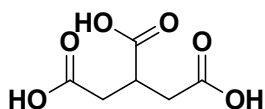


$^1\text{H-NMR}$  (400 MHz,  $\text{H}_2\text{O}/\text{D}_2\text{O}$ ):  $\delta$  (ppm) = 2.87-2.74 (m, 1H,  $-\text{CH}(\text{CH}_3)-\text{COOH}$ ), 2.60 (dd, 1H,  $-\text{CH}_2-\text{COOH}$ ), 2.48 (dd, 1H,  $-\text{CH}_2-\text{COOH}$ ), 1.11 (d, 3H,  $-\text{CH}(\text{CH}_3)-\text{COOH}$ ).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (400 MHz,  $\text{H}_2\text{O}/\text{D}_2\text{O}$ ):  $\delta$  (ppm) = 40.0 (1C,  $-\text{CH}_2-\text{COOH}$ ), 37.9 (1C,  $-\text{CH}(\text{CH}_3)-\text{COOH}$ ), 16.6 (1C,  $-\text{CH}(\text{CH}_3)-\text{COOH}$ ).

Carboxylic acid carbons could not be observed.

### Propane-1,2,3-tricarboxylic acid (4, MW = 176 g/mol)



$^1\text{H-NMR}$  (400 MHz,  $\text{H}_2\text{O}/\text{D}_2\text{O}$ ):  $\delta$  (ppm) = 3.14 (quint, 1H,  $-\text{CH}-(\text{CH}_2)_2$ ), 2.70 (dd, 2H,  $-\text{CH}-(\text{CH}_2)_2$ ), 2.60 (dd, 2H,  $-\text{CH}-(\text{CH}_2)_2$ ).

### Acetone (5, MW = 58 g/mol)

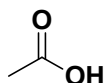


$^1\text{H-NMR}$  (400 MHz,  $\text{H}_2\text{O}/\text{D}_2\text{O}$ ):  $\delta$  (ppm) = 2.11 (s, 6H,  $\text{CH}_3-$ ).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (400 MHz,  $\text{H}_2\text{O}/\text{D}_2\text{O}$ ):  $\delta$  (ppm) = 30.2 (2C,  $\text{CH}_3-$ ).

Carbonyl carbon could not be observed.

**Acetic acid (6, MW = 60 g/mol)**

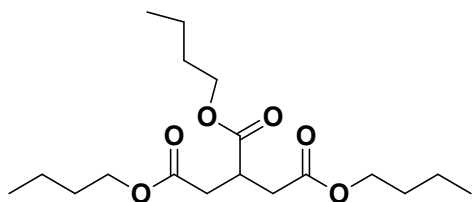


<sup>1</sup>H-NMR (400 MHz, H<sub>2</sub>O/D<sub>2</sub>O): δ (ppm) = 1.97 (s, 3H, CH<sub>3</sub>-).

<sup>13</sup>C{<sup>1</sup>H}-NMR (400 MHz, H<sub>2</sub>O/D<sub>2</sub>O): δ (ppm) = 176.9 (1C, -COOH), 20.6 (1C, CH<sub>3</sub>-).

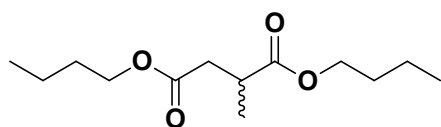
**General information: <sup>1</sup>H-NMR spectra in CD<sub>3</sub>OD were calibrated by setting the singlet signal of the external standard (*i.e.* *para*-xylene) to 7.045 ppm.**

**Tributyl propane 1,2,3 tricarboxylate (7, MW = 344 g/mol)**



<sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD): δ (ppm) = 4.11 (t, 6H, -CH<sub>2</sub>-O-), 3.23 (quin, 1H, -CH-(CH<sub>2</sub>-)<sub>2</sub>), 2.78 (dd, 2H, -CH-(CH<sub>2</sub>-)<sub>2</sub>), 1.63 (m, 6H, CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 1.41 (m, 6H, CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 0.97 (m, 9H, CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-).

**Dibutyl methylsuccinate (8, MW = 244 g/mol)**



<sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD): δ (ppm) = 4.10 (q, 4H, -CH<sub>2</sub>-O-), 2.89 (m, 1H, -CH(CH<sub>3</sub>COOCH<sub>2</sub>-)), 2.58 (dd, 2H, -CH<sub>2</sub>-CH-), 1.62 (m, 4H, CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42 (m, 4H, CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 1.21 (m, 3H, -CH(CH<sub>3</sub>COOCH<sub>2</sub>-)) 0.97 (m, 6H, CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-).

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