

# A recycling strategy for bio-aqueous phase *via* catalytic wet air oxidation to bio-based acetic acid solution

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## 1. Experimental

### 1.1. Catalyst preparation

ZrO<sub>2</sub> supported Pt and Ru catalysts were prepared by an incipient wetness impregnation method. A commercial ZrO<sub>2</sub> with particle size of 450 μm was first calcined at 350 °C under 100 ml min<sup>-1</sup> air in a tubular quartz reactor for 5 h. The water adsorbability on ZrO<sub>2</sub> was measured as 0.63 g H<sub>2</sub>O g<sup>-1</sup> ZrO<sub>2</sub>. H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and Ru(NO)(NO<sub>3</sub>)<sub>3</sub> were supplied by Sigma Aldrich and were used as the metal precursors. About 0.255 g Ru salt and 0.024 g Pt salt were desolved in 1.64 g H<sub>2</sub>O separately to prepare two bottles of homogeneous solution. Then *ca.* 2.6 g calcined ZrO<sub>2</sub> was added to the solution. After gentle mixing, the mixture stayed for about 12 h for impregnation. The wet mixture was dried at 100 °C under 100 ml min<sup>-1</sup> air in a tubular quartz reactor for 6 h, followed by calcining at 350 °C for 8 h. After cooling to room temperature under N<sub>2</sub>, H<sub>2</sub> was introduced to reduce the catalyst at 300 °C for 2 h. After cooling to room temperature under N<sub>2</sub>, the two catalysts were stored in a glassware and were ready for use.

### 1.2. Catalyst characterization

The loadings of Ru and Pt for the two catalysts were analyzed by X-ray fluorescence (XRF) on a PW1480 (Philips).

N<sub>2</sub> physisorption was performed on a Tristar 3000 (Micromeritics) at -196,15 °C. BET surface area was calculated according to Brunauer-Emmett-Teller (BET) method. Pore size distribution was calculated based on Barrett-Joyner-Halenda (BJH) method.

XRD patterns were recorded on a D2 PHASER Diffractometer (Bruker) using CuK<sub>α</sub> radiation with 1.5418 Å at 40 kV and 40 mA. The diffraction patterns were recorded in a range of 10-90° with each step of 0.05° for 2 s.

### 1.3. Catalytic wet air oxidation (CWAO) of bio-aqueous phase

CWAO experiments were carried out on a micro stirred reactor (Model 4590, reactor volume is 25 ml) with 4848 reactor Controller (Parr Instrument Company, USA). The synthetic air was used as the reactant gas and the initial air pressure was 20 bar at room temperature. 10 ml liquid and 50 mg catalyst were loaded to the reactor, followed by heating up to 270 °C. The pressure reached *ca.* 50 bar. The reactor was then maintained at this temperature under stirring at 1000 rpm for 3 h to perform CWAO reaction. The highest pressure during the experiment reached 85 bar.

### 1.4. Analysis

The liquid products were analyzed by a GC-MS (Agilent 6890N-5975) equipped with a capillary column (Agilent VF-1701ms, 60 m × 0.25 mm × 0.25 μm). Helium was used as carrier gas at a flow rate of 1.2 mL min<sup>-1</sup>. The injector temperature and split ratio were set at 280 °C and 100:1. The following temperature profile was applied: 40 °C for 5 min, raised up to 280 °C at 3 °C min<sup>-1</sup>, held at 280 °C for 10 min. The mass spectrum of all detected products was obtained at 70 eV (ionization energy) using the scan mode (m/z = 25 - 550). MS ion source and quadrupole temperatures were maintained at 230 °C and 150 °C. The identification of compounds was based on the obtained mass fragmentation patterns acquired by the coupled mass spectrometer using peak matching of corresponding chromatographic peaks with those of NIST database.

COD analysis was according to EPA-NERL: 410.1: Chemical Oxygen Demand by Titrimetry.

CHN elemental analysis was carried out on a Flash 2000 CHNS/O Elemental Analyzer (EA), which is calibrated with acetanilide.

## 2. Catalyst characterization

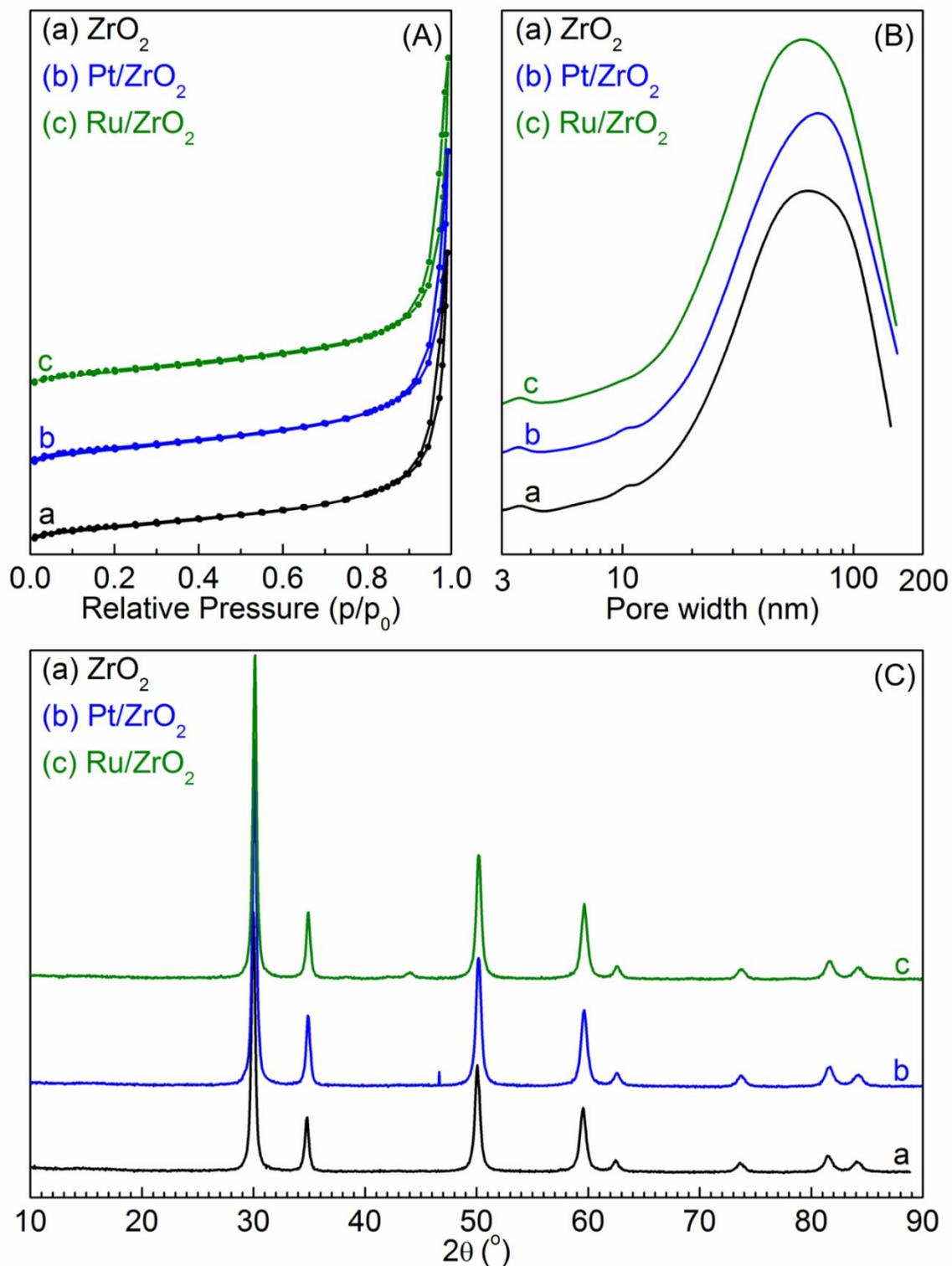


Fig. S1 N<sub>2</sub> adsorption-desorption isotherms (A), BJH pore size distribution (B), and XRD patterns (C) of ZrO<sub>2</sub> support (a) and the supported Pt/ZrO<sub>2</sub> (b) and Ru/ZrO<sub>2</sub> (c) catalysts.

### 3. GC-MS analysis

Table S1 Composition of bio-aqueous phase-FP analyzed by GC-MS

Library/ID	CAS No.	Area%	Group No.
1 Hexagol	002615-15-8	0.2	8
2 2-Propen-1-ol	000107-18-6	0.6	8
3 Ethyl Acetate	000141-78-6	0.7	9
4 2,3-Butanedione	000431-03-8	2.0	3
5 2-Butanone	000078-93-3	0.6	3
6 1,2-Ethanediol	000107-21-1	0.6	8
7 2-Propanamine, N-hydroxy-	005080-22-8	0.4	10
8 Methane, nitroso-	000865-40-7	0.5	10
9 Acetic acid	000064-19-7	30.8	1
10 2-Propanone, 1-hydroxy-	000116-09-6	15.2	3
11 2-Butanone, 3-hydroxy-	000513-86-0	0.4	3
12 Ethanol, 2,2'-oxybis-	000111-46-6	0.3	8
13 1-Hydroxy-2-butanone	005077-67-8	1.3	3
14 1,2-Ethanediol, monoacetate	000542-59-6	0.4	9
15 Butanedial	000638-37-9	1.1	6
16 2-Cyclopenten-1-one	000930-30-3	0.3	3
17 Furfural	000098-01-1	2.7	3
18 2-Pentanone, 4-hydroxy-4-methyl-	000123-42-2	1.4	3
19 Propanoic acid, 2-oxo-, ethyl ester	000617-35-6	0.4	9
20 2-Cyclopenten-1-one, 2-methyl-	001120-73-6	1.3	3
21 Ethanone, 1-(2-furyl)-	001192-62-7	0.4	3
22 2-Isopropoxyethylamine	081731-43-3	9.8	10
23 Butyrolactone	000096-48-0	0.8	3
24 2(5H)-Furanone	000497-23-4	2.2	4
25 Ethanol, 2-nitro-, propionate (ester)	005390-28-3	0.6	9
26 2(5H)-Furanone, 5-methyl-	000591-11-7	1.0	4
27 2(5H)-Furanone, 3-methyl-	022122-36-7	2.1	4
28 2-Furanone, 2,5-dihydro-3,5-dimethyl	1000196-88-1	0.3	4
29 Phenol	000108-95-2	0.4	5
30 Phenol, 2-methoxy-	000090-05-1	0.9	5
31 Propyl nitrite	000543-67-9	0.3	9
32 4-Methyl-5H-furan-2-one	006124-79-4	1.7	4
33 1-Butene, 1-methoxy-	029512-02-5	0.6	6
34 Ethanone, 1-oxiranyl-	004401-11-0	7.2	3
35 1,2,3-Propanetriol, diacetate	025395-31-7	0.5	9
36 1-Octadecene	000112-88-9	0.6	6
37 1H-Pyrrole-2-carboxylic acid	000634-97-9	0.7	2
38 (5-Ethylcyclopent-1-enyl)methanol	036431-59-1	0.4	9
39 Cyclohexanecarboxylic acid, 4-nitrophenyl ester	1000307-70-8	1.1	9
40 3,3-Dimethyl-2,4-pentane dione	003142-58-3	0.8	3
41 L-Cysteine, N-acetyl-S-[5-(acetylamino)-2-hydroxyphenyl]-	052372-86-8	0.3	10
42 4H-Pyrano[3,4-d]thiazol-4-one, 6,7-dihydro-	072579-00-1	0.6	10
43 D-Allose	002595-97-3	5.9	3

Group: 1-acetic acid, 2-other acids, 3-carbonyls, 4-furans, 5-phenols, 6-aliphatics, 7-aromatics, 8-alcohols, 9-esters, and 10-N-containing compounds.

Table S2 Composition of bio-aqueous phase-CC analyzed by GC-MS

Library/ID	CAS No.	Area%	Group No.
1 Methyl isocyanide	000593-75-9	0.3	10
2 2-Propen-1-ol	000107-18-6	0.4	3
3 Dimethylamine	000124-40-3	1.5	10
4 2-Butanone	000078-93-3	12.1	3
5 Propanenitrile	000107-12-0	1.6	10
6 2-Butanone, 3-methyl-	000563-80-4	0.9	3
7 1-Butanol	000071-36-3	7.0	8
8 2-Pentanone	000107-87-9	2.0	3
9 3-Pentanone	000096-22-0	0.8	3
10 Acetic acid	000064-19-7	4.8	1
11 Propanoic acid	000079-09-4	2.4	2
12 Cyclopentanone	000120-92-3	2.0	3
13 Pyrrole	000109-97-7	1.6	10
14 Propanoic acid, 2-methyl-	000079-31-2	0.2	2
15 Cyclopentanone, 2-methyl-	001120-72-5	0.3	3
16 2-Pentanone, 4-hydroxy-	004161-60-8	0.8	3
17 Acetamide	000060-35-5	2.1	10
18 2-Cyclopenten-1-one, 2-methyl-	001120-73-6	9.0	3
19 Acetamide, N,N-dimethyl-	000127-19-5	2.1	10
20 Ethanone, 1-(2-furanyl)-	001192-62-7	0.5	3
21 Acetamide, N-methyl-	000079-16-3	1.2	10
22 Cyclohexene, 1,2-dimethyl-	001674-10-8	0.8	6
23 2,4-Hexadiene, (Z,Z)-	006108-61-8	0.4	6
24 Hydrazine, 2-propenyl-	007422-78-8	0.5	10
25 N-Nitroso-2-methyl-oxazolidine	039884-53-2	0.6	10
26 Propanamide	000079-05-0	0.4	10
27 Propanamide, N,N-dimethyl-	000758-96-3	0.6	10
28 1H-Imidazole, 1-methyl-	000616-47-7	0.4	10
29 2-Cyclopenten-1-one, 2,3-dimethyl-	001121-05-7	1.3	3
30 2-Cyclopenten-1-one, 3-methyl-	002758-18-1	10.8	3
31 Aniline	000062-53-3	4.4	10
32 2-Cyclopenten-1-one, 3,4-dimethyl-	030434-64-1	1.3	3
33 2-Propen-1-amine, N-ethyl-N-methyl-	107995-54-0	0.5	10
34 2-Cyclopenten-1-one, 2,3-dimethyl-	001121-05-7	4.8	3
35 2-Cyclopenten-1-one, 2,3,4-trimethyl-	028790-86-5	0.9	3
36 2-Propen-1-amine, N-ethyl-N-methyl-	107995-54-0	0.5	10
37 Acetophenone	000098-86-2	0.9	3
38 Phenol	000108-95-2	16.9	5
39 Cyclopentanone, 3,4-bis(methylene)-	027646-73-7	0.4	3

Group: 1-acetic acid, 2-other acids, 3-carbonyls, 4-furans, 5-phenols, 6-aliphatics, 7-aromatics, 8-alcohols, 9-esters, and 10-N-containing compounds.

Table S3 Composition of H-0 analyzed by GC-MS

	Library/ID	CAS No.	Area%	Group No.
1	2-Propen-1-ol	000107-18-6	0.3	8
2	2-Pentanone	000107-87-9	0.5	3
3	2,3-Butanedione	000431-03-8	0.4	3
4	Acetic acid	000064-19-7	21.4	1
5	2-Propanone, 1-hydroxy-	000116-09-6	7.9	3
6	1-Hydroxy-2-butanone	005077-67-8	0.4	10
7	Furfural	000098-01-1	0.6	4
8	1,2-Propanediamine	000078-90-0	0.3	10
9	2-Cyclopenten-1-one, 2-methyl-	001120-73-6	0.4	3
10	Acetic acid, hydroxy-, methyl ester	000096-35-5	11.1	9
11	Butyrolactone	000096-48-0	0.6	9
12	2(5H)-Furanone	000497-23-4	1.8	4
13	Propanoic acid	000079-09-4	1.1	2
14	Ethyl N-hydroxyacetimidate	010576-12-2	0.8	10
15	Propanoic acid	000079-09-4	0.4	2
16	2(5H)-Furanone, 3-methyl-	022122-36-7	1.9	4
17	1,2,3,4-Butanetetrol, [S-(R*,R*)]-	002319-57-5	0.3	8
18	Phenol	000108-95-2	0.2	5
19	4-Isopropoxy-2-butanone	032541-58-5	0.2	9
20	Acetic acid, methoxy-, ethyl ester	003938-96-3	0.2	9
21	Phenol, 2-methoxy-	000090-05-1	0.5	5
22	Semioxamazine	000515-96-8	0.6	10
23	1,4-Diacetyl-3-acetoxymethyl-2,5-methylene-l-rhamnitol	1000128-41-9	0.3	3
24	3-Octene-2,5-dione, 6,6,7-trimethyl-, (E)-	060845-48-9	0.5	3
25	Ethanone, 1-oxiranyl-	004401-11-0	2.8	3
26	Phenol, 4-methyl-	000106-44-5	0.1	3
27	2,3,4,4-Tetramethyl-pentane-1,3-diol	1000188-09-0	0.3	8
28	Tetraacetyl-d-xylonic nitrile	1000130-04-4	0.7	10
29	1-Propene, 3-methoxy-2-methyl-	022418-49-1	0.7	3
30	Ethanone, 1-oxiranyl-	004401-11-0	10.9	3
31	4-Nonanone	004485-09-0	0.6	3
32	6-Methyl-3,7,9-trioxabicyclo[4.2.1]nonane	030120-65-1	0.2	3
33	1-Octadecene	000112-88-9	1.8	6
34	1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	1000098-14-8	0.3	10
35	Cyclohexanone, 3-methyl-, (R)-	013368-65-5	0.4	3
36	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	000067-47-0	0.5	3
37	4-Amino-6-hydroxypyrimidine	001193-22-2	1.0	10
38	7-Hydroxy-3-(1,1-dimethylprop-2-enyl)coumarin	056881-08-4	0.2	3
39	Diisopropyl methanephosphonate	001445-75-6	0.7	9
40	Cyclohexanecarboxylic acid, 4-nitrophenyl ester	1000307-70-8	1.6	9
41	1-Propene, 1-methoxy-2-methyl-	017574-84-4	1.2	3
42	1,2,3-Triazol-4-amine, 2-isopropyl-5-nitro-, 1-oxide	252555-86-5	0.5	10
43	4-Octen-3-one	014129-48-7	0.9	3
44	Benzaldehyde, 3-hydroxy-4-methoxy-	000621-59-0	0.4	3
45	N-Acetylpyrrolidone	000932-17-2	0.9	10
46	Cyclohexanecarboxylic acid, 4-tetradecyl ester	1000280-59-8	0.4	9
47	2-Acetylthiazole	024295-03-2	0.9	10
48	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	000498-02-2	0.9	3
49	Mannofuranoside, methyl 6-deoxy-3-O-methyl-, diacetate	029836-38-2	0.3	9
50	Tetraethylene glycol diethyl ether	004353-28-0	0.3	9
51	D-Allose	002595-97-3	17.0	3

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52	Heptanoic acid, 6-oxo-, ethyl ester	030956-41-3	0.4	9
53	Acetate, 2-(4-hydroxybutyl)cyclohexyl ester	1000196-73-2	0.6	9

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Group: 1-acetic acid, 2-other acids, 3-carbonyls, 4-furans, 5-phenols, 6-aliphatics, 7-aromatics, 8-alcohols, 9-esters, and 10-N-containing compounds.

Table S4 Composition of H-1 analyzed by GC-MS

	Library/ID	CAS No.	Area%	Group No.
1	2,3-Butanedione	000431-03-8	2.9	3
2	2-Butanone	000078-93-3	2.0	3
3	Acetic acid	000064-19-7	58.5	1
4	2,3-Pentanedione	000600-14-6	0.8	3
5	2-Propanone, 1-hydroxy-	000116-09-6	6.0	3
6	2-Butanone, 3-hydroxy-	000513-86-0	3.8	3
7	Propanoic acid	000079-09-4	2.0	2
8	1,2-Ethanediol	000107-21-1	0.9	3
9	Silane, trimethyl-	000993-07-7	0.8	10
10	2-Cyclopenten-1-one	000930-30-3	0.8	3
11	Furfural	000098-01-1	0.7	4
12	2-Cyclopenten-1-one, 2-methyl-	001120-73-6	2.1	3
13	Ethanone, 1-(2-furanyl)-	001192-62-7	0.8	3
14	2,5-Hexanedione	000110-13-4	4.5	3
15	Norvaline, 3-hydroxy-	002280-42-4	0.5	10
16	Butyrolactone	000096-48-0	1.5	3
17	2,4-Pentanedione, 3-ethyl-	001540-34-7	1.4	3
18	2-Cyclopenten-1-one, 3,4-dimethyl-	030434-64-1	0.5	3
19	2-Acetyl-5-methylfuran	001193-79-9	0.7	4
20	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	000080-71-7	3.3	3
21	3,6-Heptanedione	001703-51-1	0.9	3
22	Phenol	000108-95-2	0.6	5
23	2-Cyclopenten-1-one, 2,3,4-trimethyl-	028790-86-5	0.3	3
24	Phenol, 2-methoxy-	000090-05-1	1.1	5
25	Phenol, 2-methyl-	000095-48-7	0.5	5
26	Pentanoic acid, 4-oxo-	000123-76-2	1.2	2
27	Lomustine	013010-47-4	0.6	10
28	1H-Pyrazole, 1,5-dimethyl-	000694-31-5	0.5	10

Group: 1-acetic acid, 2-other acids, 3-carbonyls, 4-furans, 5-phenols, 6-aliphatics, 7-aromatics, 8-alcohols, 9-esters, and 10-N-containing compounds.

Table S5 Composition of **H-20** analyzed by GC-MS

	Library/ID	CAS No.	Area%	Group No.
1	2,3-Butanedione	000431-03-8	4.4	3
2	2-Butanone	000078-93-3	2.4	3
3	Acetic acid	000064-19-7	86.1	1
4	Propanoic acid	000079-09-4	2.2	2
5	2,5-Hexanedione	000110-13-4	3.8	3
6	Butyrolactone	000096-48-0	1.1	3

Group: 1-acetic acid, 2-other acids, 3-carbonyls, 4-furans, 5-phenols, 6-aliphatics, 7-aromatics, 8-alcohols, 9-esters, and 10-N-containing compounds.

Table S6 Composition of **H-3** analyzed by GC-MS

	Library/ID	CAS No.	Area%	Group No.
1	2,3-Butanedione	000431-03-8	6.9	3
2	2-Butanone	000078-93-3	2.5	3
3	Acetic acid	000064-19-7	80.8	1
4	2,3-Pentanedione	000600-14-6	0.6	3
5	2-Propanone, 1-hydroxy-	000116-09-6	1.9	3
6	Propanoic acid	000079-09-4	2.7	2
7	2,5-Hexanedione	000110-13-4	3.3	3
8	Butyrolactone	000096-48-0	1.4	3

Group: 1-acetic acid, 2-other acids, 3-carbonyls, 4-furans, 5-phenols, 6-aliphatics, 7-aromatics, 8-alcohols, 9-esters, and 10-N-containing compounds.

Table S7 Composition of **H-4** analyzed by GC-MS

	Library/ID	CAS No.	Area%	Group No.
1	2,3-Butanedione	000431-03-8	2.6	3
2	2-Butanone	000078-93-3	2.2	3
3	Acetic acid	000064-19-7	83.5	1
4	Propanoic acid	000079-09-4	2.6	2
5	1,2-Ethanediol	000107-21-1	0.6	8
6	2-Cyclopenten-1-one, 2-methyl-	001120-73-6	0.5	3
7	2,5-Hexanedione	000110-13-4	4.4	3
8	Butyrolactone	000096-48-0	1.2	3
9	2-Cyclopenten-1-one, 2,3-dimethyl-	001121-05-7	0.8	3
10	3,6-Heptanedione	001703-51-1	0.6	3
11	Phenol	000108-95-2	0.5	5
12	3-Penten-2-one, 4-methyl-	000141-79-7	0.6	3
13	2,3-Butanedione	000431-03-8	2.6	3

Group: 1-acetic acid, 2-other acids, 3-carbonyls, 4-furans, 5-phenols, 6-aliphatics, 7-aromatics, 8-alcohols, 9-esters, and 10-N-containing compounds.

Table S8 Composition of L-1 analyzed by GC-MS

	Library/ID	CAS No.	Area%	Group No.
1	Methyl vinyl ketone	000078-94-4	41.3	3
2	Acetic acid	000064-19-7	23.8	1
3	2-Butanone, 4-hydroxy-	000590-90-9	34.9	3

Group: 1-acetic acid, 2-other acids, 3-carbonyls, 4-furans, 5-phenols, 6-aliphatics, 7-aromatics, 8-alcohols, 9-esters, and 10-N-containing compounds.