

Electronic Supporting Information (ESI)

Upgrading 1-butanol to unsaturated, carbonyl and aromatic compounds: a new synthesis approach to produce important organic building blocks.

Jorge Mora Vargas,^a Luiz Henrique Tofaneli Morelato,^a Julieth Orduna Ortega,^{a,b} Mauricio Boscolo,^a and Gustavo Metzker^{a*}

^a *Sao Paulo State University (UNESP), Chemistry and Environmental Sciences Department (IBILCE), São José do Rio Preto, SP, Brazil.*

^b *Universidad Santiago de Cali, Facultad de Ciencias Básicas, Campus Pampalinda, Santiago de Cali, Colombia.*

* e-mail: g.metzker@unesp.br; Tel.: +55 17 3221-2477.

Table of Contents

1.	Experimental Section	ESI - 2
1.1	Reagents	ESI - 2
1.2	Synthesis of hydrotalcites (LDHs) and mixed metal oxides (MMOs)	ESI - 2
1.3	Physicochemical characterization of hydrotalcites (LDH) and mixed metal oxides (MMO).	ESI - 2
	1.3.1 - LDH and MMO characterization data	ESI - 3
1.4	Catalytic reactions	ESI - 9
2.	Products distribution by time	ESI - 11
3.	Catalyst characterization after reaction	ESI - 15
4.	Reaction products	ESI - 16
	4.1 - GC-MS total ion chromatograms (TIC)	ESI - 16
	4.2 - Retention times for GC-MS total ion chromatograms	ESI - 29
	4.3 - Tables	ESI - 30
5.	References	ESI - 34

1. Experimental Section

1.1 Reagents

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\geq 98\%$), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99 %) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, silica gel (particle size 70-230 mesh), Na_2CO_3 (99.5 %), 1-butanol (99.4 %) and methanol (99.8 %) were purchased from Sigma Aldrich and used without further purification.

1.2 Synthesis of hydrotalcites (LDHs) and mixed metal oxides (MMOs)

The hydrotalcite-like compound modified with Cu^{2+} ions (Cu_{20}LDH , catalytic precursor) was synthesized by co-precipitation method using a 3:1 molar ratio (sum of divalent cations Mg^{2+} and $\text{Cu}^{2+} = 3$ and trivalent cation $\text{Al}^{3+} = 1$) as described before in the literature.¹⁻³ A solution containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.36 mol L^{-1}), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.15 mol L^{-1}) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.09 mol L^{-1}) was prepared and added slowly in the sodium carbonate solution (0.16 mol L^{-1}) controlling the pH to 10 using a NaOH solution (4 mol L^{-1}), temperature ($60\text{ }^\circ\text{C}$) and constant stirring. The resulting solution was aged for 12 h at $60\text{ }^\circ\text{C}$. Posteriorly, the solid obtained was washed with deionized water until pH 7, filtered and dried at $100\text{ }^\circ\text{C}$ for 24 h. The same procedure was employed for obtention of the reference hydrotalcite (without Mg^{2+} substitution by Cu^{2+}) employed standard material. For the obtention of mixed metal oxides (MMO) hydrotalcites were calcined at $450\text{ }^\circ\text{C}$ for 5h giving rise to Cu_{20}MMO and MMO (reference material).

1.3 Physicochemical characterization of hydrotalcites (LDH) and mixed metal oxides (MMO).

Powder X-ray diffraction (XRD) patterns of LDHs and MMOs were obtained using a Rigaku model MiniFlex300 diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) operating at 40 kV and 30 mA at 2θ in the range of 5 to 70 degrees.

FTIR spectroscopy for LDHs was carried out using an ATR-FTIR Spectrum Two (PerkinElmer) spectrophotometer with an interval of $400\text{-}4000 \text{ cm}^{-1}$. Sample powder

was directly placed ATR crystal. FTIR spectra of the MMOs were not obtained due to the low wavenumber of metal oxides bands.

Thermal analysis (TGA) was carried out using a Perkin Elmer TGA 4000 thermogravimetric balance. The mass loss was measured from 100 °C to 500°C (10 °C min⁻¹) in N₂ flow (20 mL min⁻¹).

Basicity and acidity of MMOs were determined by the CO₂ and n-butylamine adsorption/desorption method, using the previous described TGA equipment. Approximately 15 mg of sample were treated at 450 °C for 20 min under dynamic nitrogen atmosphere (20 mL min⁻¹). After 20 minutes, the sample was cooled at 50 °C (for basicity) or 120 °C (for acidity). Subsequently, the nitrogen atmosphere was changed for CO₂ (20 mL min⁻¹) or N₂ saturated with n-butylamine (20 mL min⁻¹) for 5 min. The increase of mass caused by the adsorption CO₂ or n-butylamine was correlated with the basic and/or acid sites of the MMOs.

Surface area was measured by the BET (Brunauer, Emmett and Teller) method (N₂ adsorption) using a Gemini VII surface area analyzer (Micromeritics). Prior to BET measurements, the samples (50 mg) had the humidity removed by 30 minutes at 120 °C and N₂ flow.

1.3.1. LDH and MMO characterization data

Fig. S1 shows XRD patterns found for both hydrotalcites with (A) and without (B) 20 mol% substitution of Mg²⁺ by Cu²⁺. For both materials, seven diffraction peaks were found, corroborating with the XRD patterns previously reported for these materials.^{2,3}

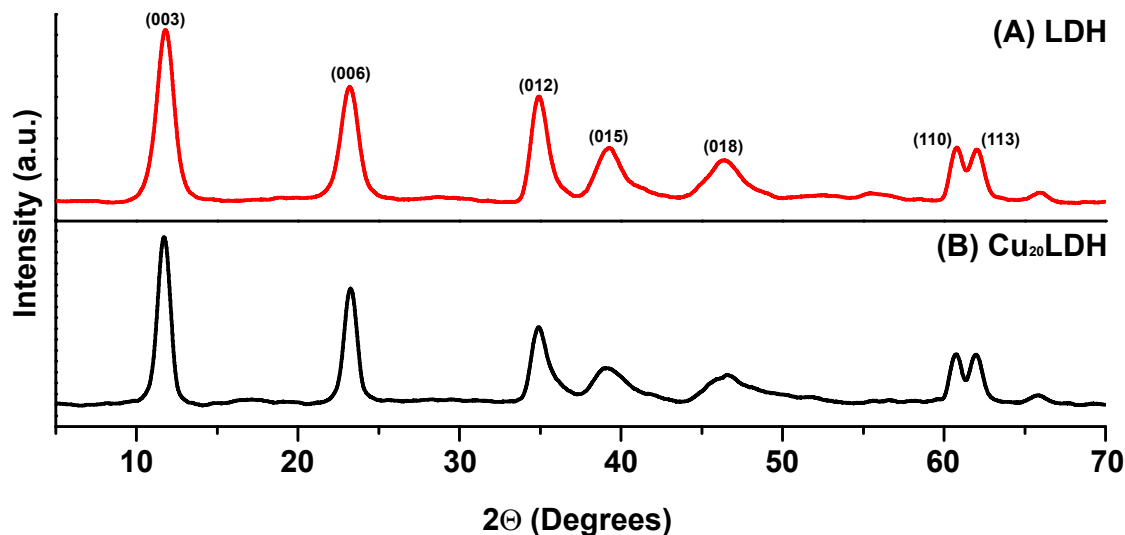


Fig. S1. XRD patterns for LDH (A) and Cu₂₀LDH (B). The Miller indexes are presented in top of the diffraction peaks.

Using the Scherrer equation was possible to calculate average cations distance (*a*), interlamellar distance (*c*) and crystallite size (*D*). Table S1 resumes these values.

Table S1. Crystallographic parameters for hydrotalcites (LDH).

Hydrotalcites	Crystallographic Parameters		
	<i>a</i> (Å)	<i>c</i> (Å)	<i>D</i> (Å)
LDH	3.0	16.8	203.9
Cu ₂₀ LDH	3.0	15.2	78.8

The partial substitution of Mg²⁺ for Cu²⁺ changed the interlamellar distance (*c*) and the crystallite size (*D*) of the Cu₂₀LDH material. Both observations are coherent with previous reports in the literature.^{2,3}

Infrared spectroscopy (ATR-FTIR) of the LDHs showed the expected bands for this type of material, as indicated in Fig. S2. The partial substitution of Mg²⁺ by Cu²⁺ did not lead to major changes comparing the IR spectra of both materials. Thus, since the IR fingerprint of the LDH materials is present, the IR contributed to confirm the successful synthesis of LDH materials.

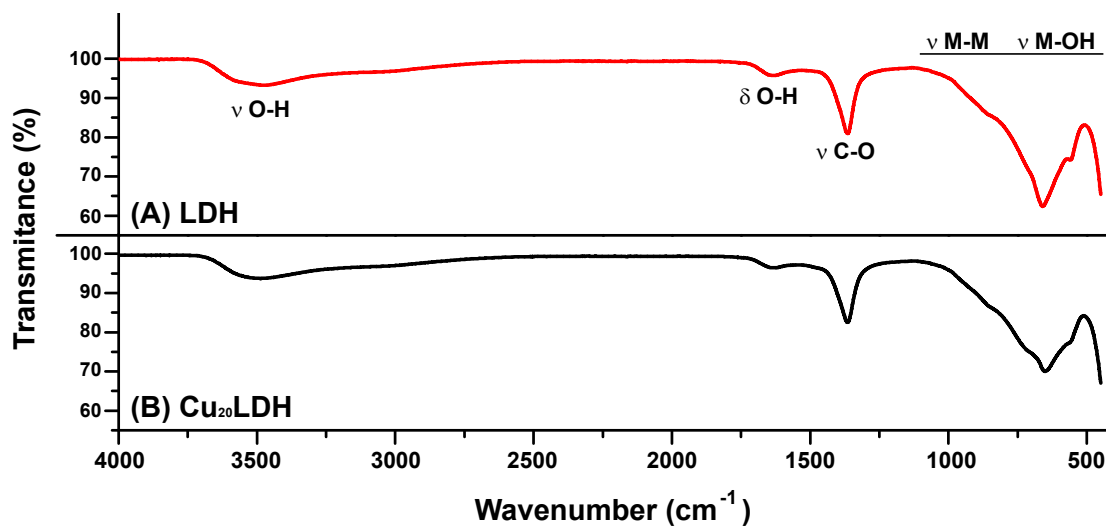


Fig. S2. ATR-FTIR spectra of LDH (A) and Cu₂₀LDH (B).

Thermogravimetric analysis of LDH and Cu₂₀LDH were performed aiming to verify the weight loss of both above-mentioned materials, Fig. S3. It is expected two thermal events for LDH materials: the first one in the range of 50 to 150 °C due to the loss of intralamellar and surface adsorbed water molecules and a second one in the range of 150 to and 350 °C due to the intralamellar carbonate decomposition. Both materials showed the two expected thermal events and the percentage of weight loss are coherent with previous data reported for LDH materials.^{2,3}

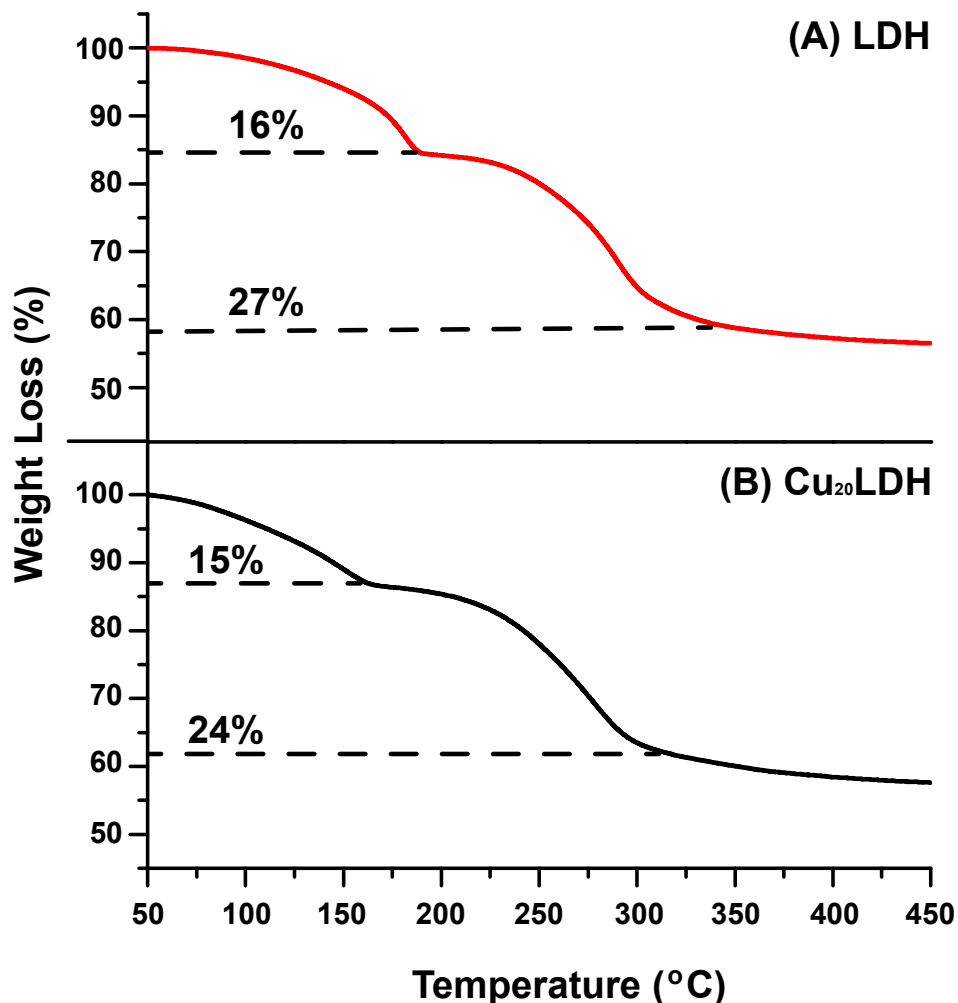


Fig. S3. TGA curves for LDH (A) and Cu₂₀LDH (B).

As observed in TGA curves of Fig. S3 the LDH materials in temperatures higher than 350 °C lost around 40% of weight due to the water and carbonate removal. These thermal events change the LDH structure, giving rise to the mixed metal oxides (MMO). On this perspective, the LDHs were submitted to calcination procedure (5h at 450°C) to completely transform LDHs to MMOs.

After calcination, the samples now referred as MMO and Cu₂₀MMO were submitted to XRD analysis. The XRD patterns for MMOs are depicted in Fig. S4.

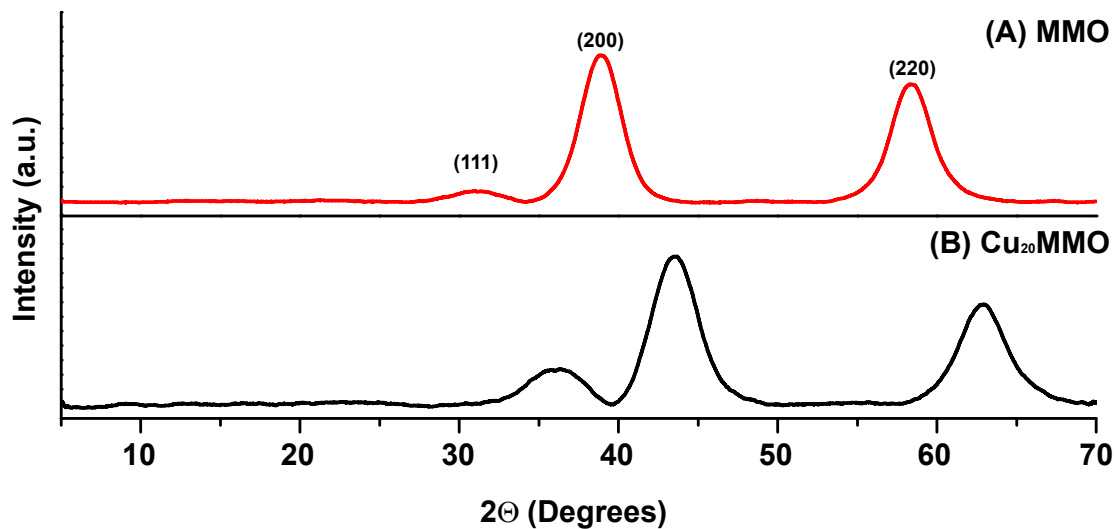


Fig. S4. XRD patterns for MMO (A) and Cu₂₀MMO (B). The Miller indexes are presented in top of the diffraction peaks.

Comparing the XRD patterns of Fig. S1 and Fig. S4, it indicates the completely conversion of LHDs into MMOs. Also, the pattern of three peaks observed are coherent with LDH materials transformed into MMO.^{2,3}

Finally, the obtained MMOs were submitted to surface area and acidity/basicity measurements. Table S2 shows the values found for MMO and Cu₂₀MMO.

Table S2. Surface area (S_{BET}), acidity and basicity for MMO and Cu₂₀MMO.

Mixed Metal	S_{BET}	Basicity	Acidity
Oxide	$\text{m}^2 \text{g}^{-1}$	$\text{mmols CO}_2 \text{g}^{-1}$	$\text{mmols n-butylamine g}^{-1}$
MMO	98.4 ± 1.6	0.93	8.08
Cu₂₀MMO	102.6 ± 1.9	1.96	6.83

The partial substitution of Mg²⁺ by Cu²⁺ did not lead substantial changes on the surface area values. However, the Cu₂₀MMO presented lower values of acidity and basicity comparing to the reference material. Also, the Cu₂₀MMO has more acidity than basic sites, which is the opposite observed for MMO. The surface area acidity and

basicity values found are in agreement with previously ones reported in the literature for this kind of material.^{2,3}

Although the calcination of the LDHs to obtention of MMOs was performed at 450°C and the catalytic reactions run at 550 and 600°C, there is no difference in the resulting MMO, as already described by Wang *et. al.*⁴ The Fig. S5 below shows the XRD patterns for the Cu₂₀MMO calcined at 450, 550 and 600°C indicating no structural or phase segregation in the catalyst.

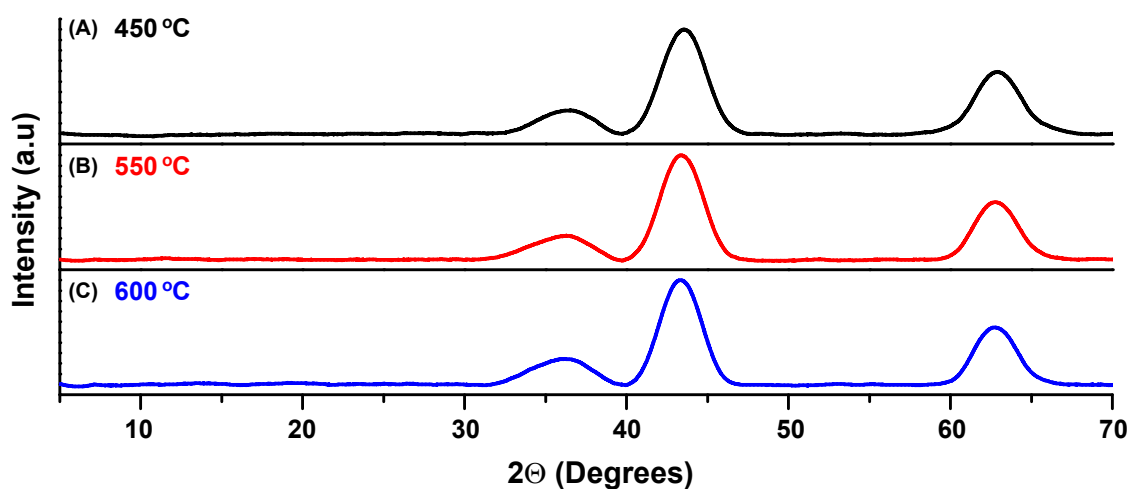


Fig. S5. XRD patterns for Cu₂₀MMO calcined at different temperatures. (A) 450°C; (B) 550°C and (C) 600°C.

1.4 Catalytic Reactions

The catalytic reactions were performed in a homemade fixed bed reactor as shown in the Fig.S6, below:

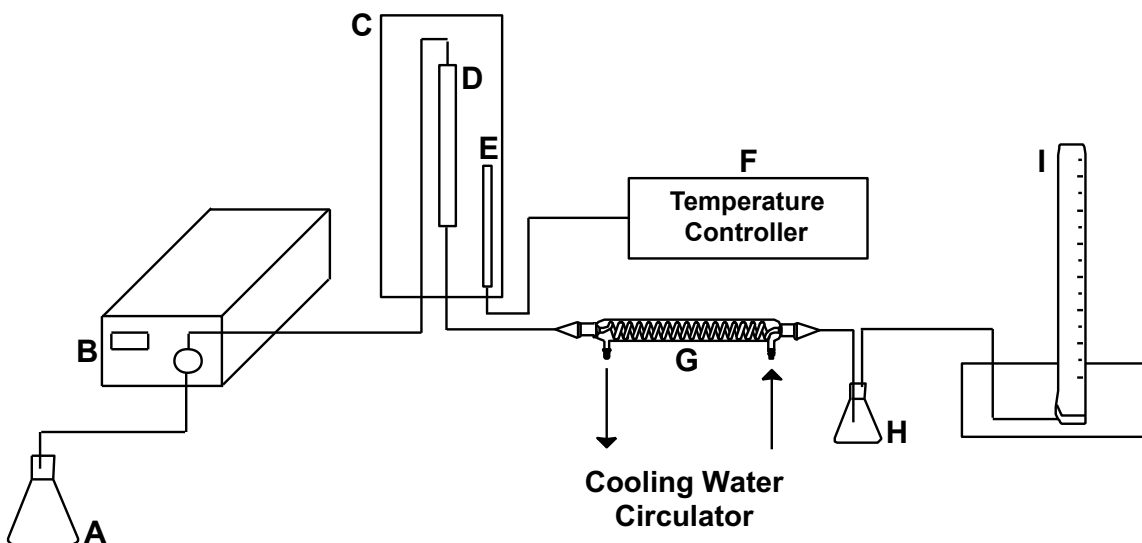


Fig.S6. Schematic representation of the fixed bed reactor. **A:** reactant reservoir; **B:** piston pump; **C:** oven; **D:** reactor column; **E:** thermocouple; **F:** temperature controller; **G:** condenser; **H:** products reservoir; **I:** graduated cylinder for gas measurement.

The reactant (100% 1-butanol or 1-butanol:methanol 7:3 (v/v) mixture) was pumped in a flow of 0.2 mL min^{-1} . In a first step, the reactant was vaporized by the oven heating in stainless steel tubing that was placed in parallel to the reactor column. This step aimed to guarantee that only reactant vapor passed through the reactor column and also avoided the utilization of an inert gas to drag the reactant.

The reactor column ($L = 12.0 \times \text{O.D.} = 1.0 \times \text{I.D.} = 0.5 \text{ cm}$) was packed with a mixture of 1.4 g of silica gel and 0.3 g of the desired catalyst. The reactant vapor flow percolated the column and was readily condensed after the column end by a continuous cooling-water circulator (-2°C). The condensed products were collected in the products reservoir (kept at -2°C) and the gas was conducted to a graduated cylinder aiming to measure the amount of gases generated by the reaction. Samples were collected every

30 minutes of reaction (total of 180 minutes) in 10 mL vials (hermetically sealed). The vials were kept at -20°C until the analysis.

The condensed products were identified and quantified by GC-MS, employing a Perkin-Elmer Clarus 680 chromatograph coupled with a 600T mass spectrometer detector. The analysis was performed in a BD-EN14103 capillary column (Agilent, 30 m x 0.32 mm x 0.25 μm), with injection volume of 1.0 μL (injector temperature of 250 °C). GC oven temperature program: isotherm for 10 minutes at 40 °C; heating at 10 °C min^{-1} until 160 °C; heating at 2 °C min^{-1} until 180 °C; heating at 10 °C min^{-1} until 240 °C; holding for 2 minutes at 240 °C. The ionization source was kept at 70eV and the m/z range was 40 to 300.

The samples for GC-MS analysis were prepared by adding 10 μL of the collected reactor effluent, 10 μL of ethyl dodecanoate as internal standard (final concentration of 17.2 ppm) and 980 μL of GC-MS grade methanol. The quantification was performed by correlation between the internal standard and reference standard compounds (butanol; isoamyl alcohol; ethyl ether; methyl isobutyl ketone, ethyl hexanoate, gamma-valerolactone, 3,4-dimethoxybenzyl alcohol) by calculating the correlation factors.

2. Products distribution by time

Graphics color code: red – alkenes; dark blue – aromatics; light blue – aldehydes; yellow – ethers; dark green – alkanes, light green – alcohols; purple – esters; gray – ketones.

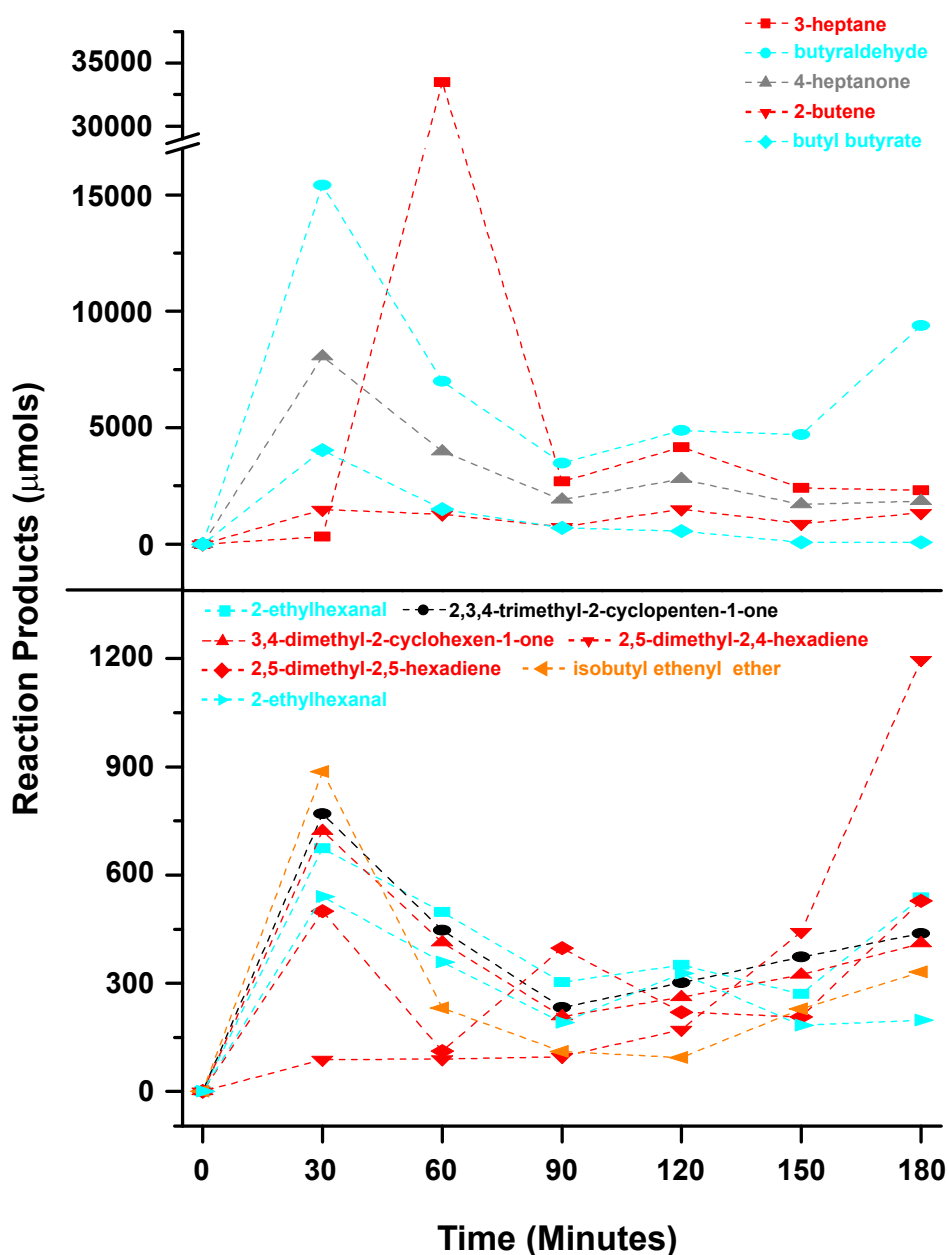


Fig. S7. Time profile of the main products found in the reaction of 1-butanol over Cu_{20}MMO catalyst. Conditions: Temp. = 550°C , 100% of 1-butanol, 3 hours of reaction.

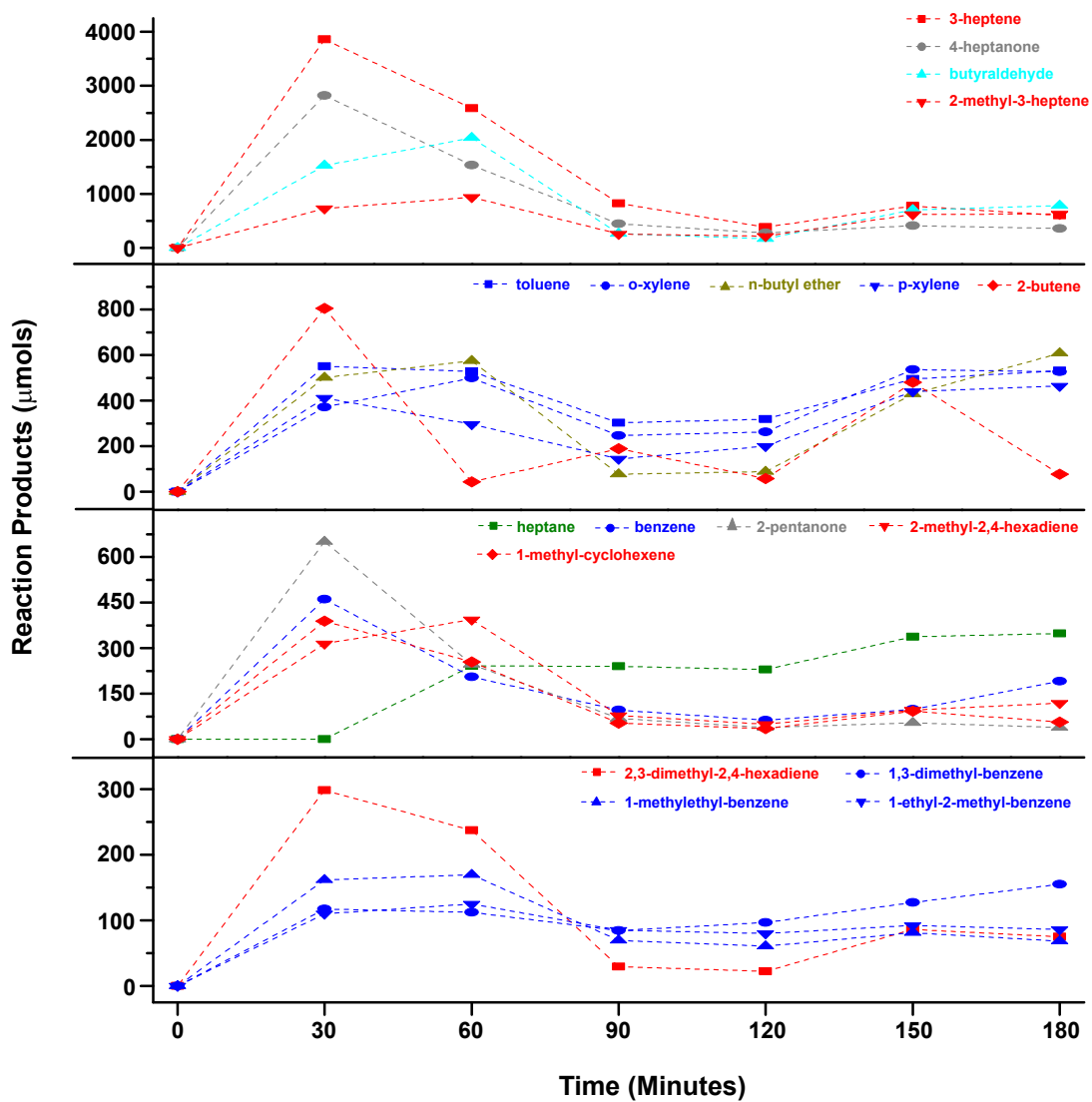


Fig. S8. Time profile of the main products found in the reaction of 1-butanol over Cu_{20}MMO catalyst. Conditions: Temp. = 600°C , 100% of 1-butanol, 3 hours of reaction.

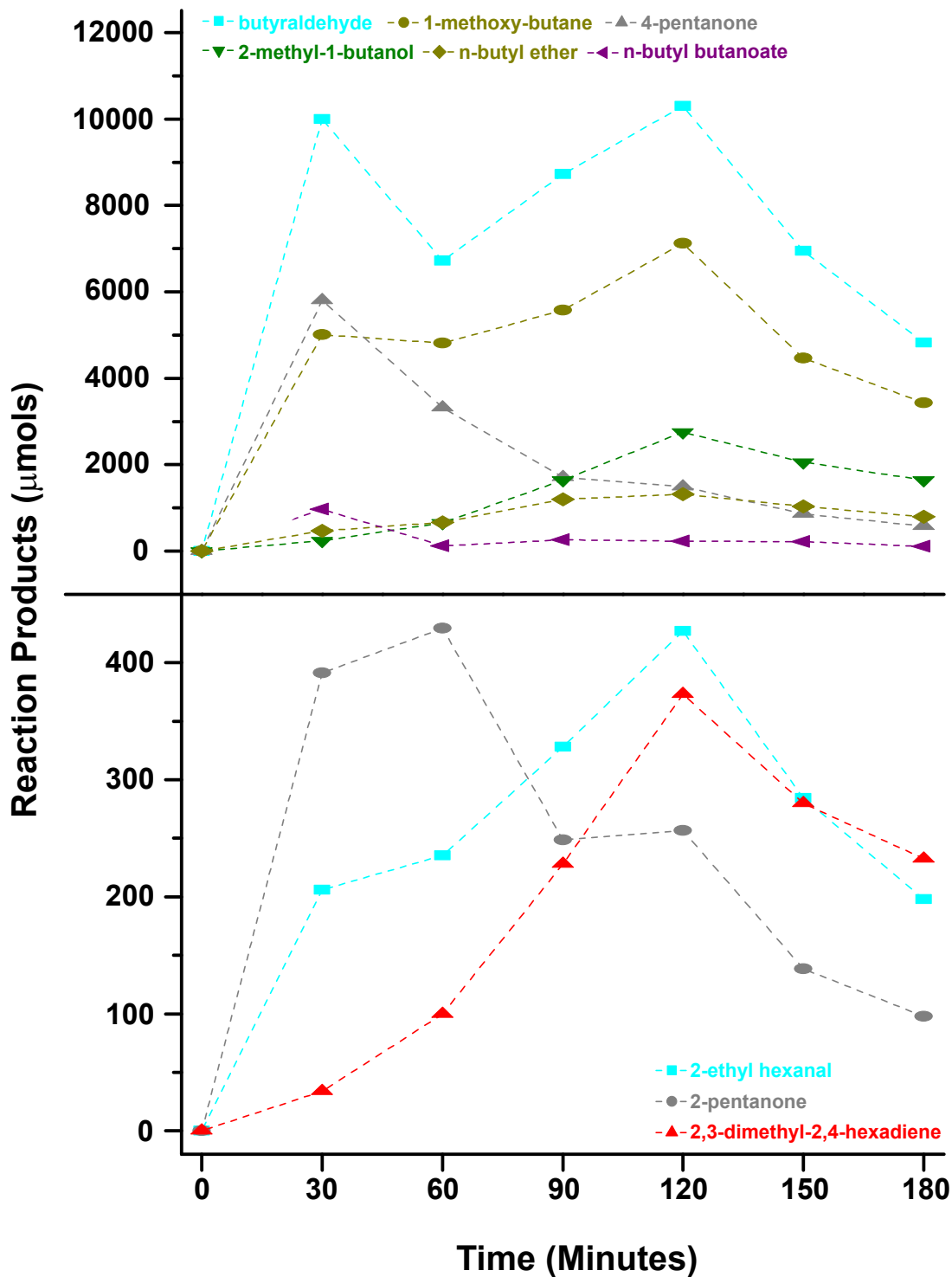


Fig. S9. Time profile of the main products found in the reaction of 1-butanol over Cu_{20}MMO catalyst. Conditions: Temp. = 550°C , 1-butanol:methanol 7:3 (v/v), 3 hours of reaction.

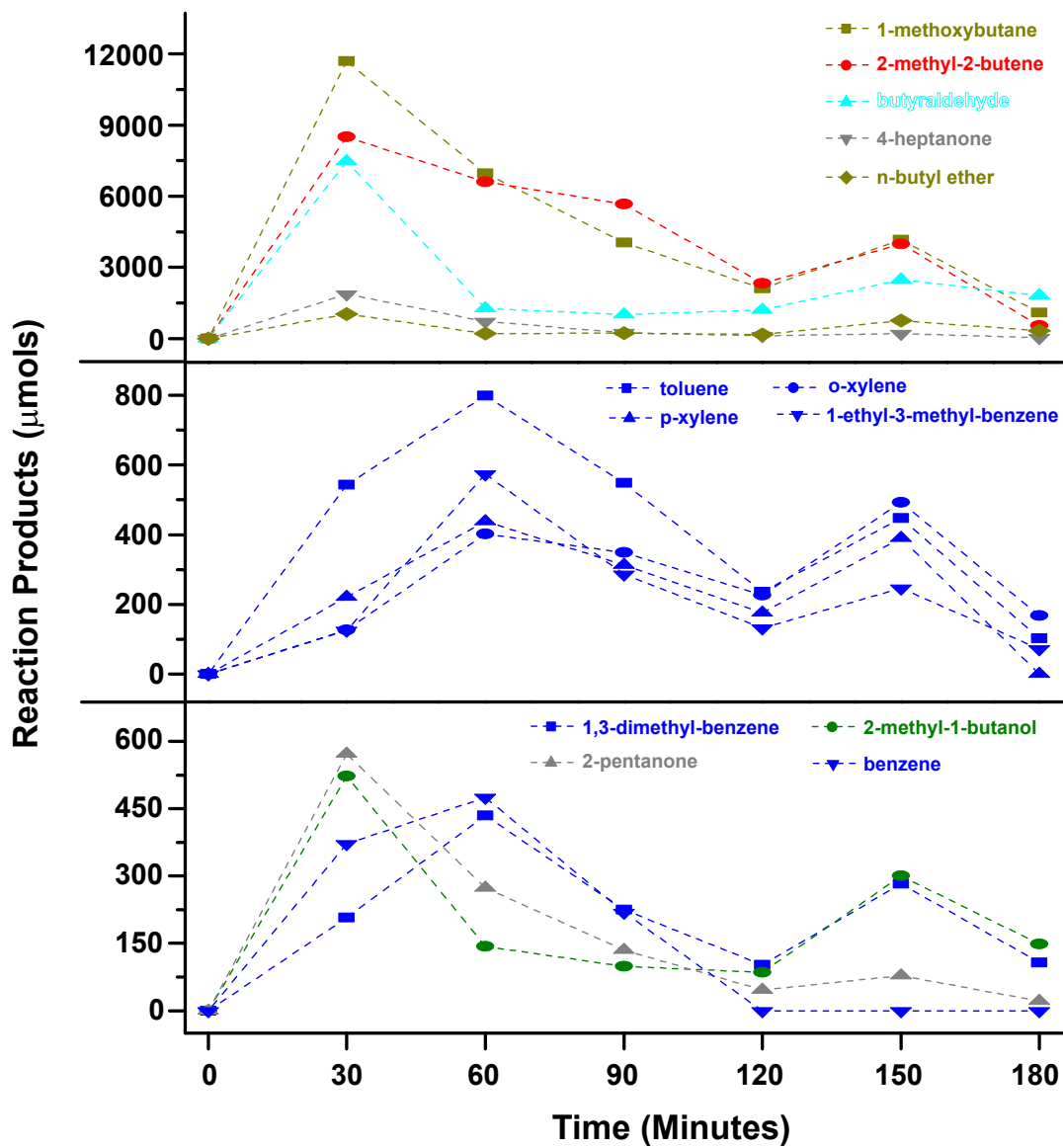


Fig. S10. Time profile of the main products found in the reaction of 1-butanol over Cu_{20}MMO catalyst. Conditions: Temp. = 600°C , 1-butanol:methanol 7:3 (v/v), 3 hours of reaction.

3. Catalyst characterization after reactions

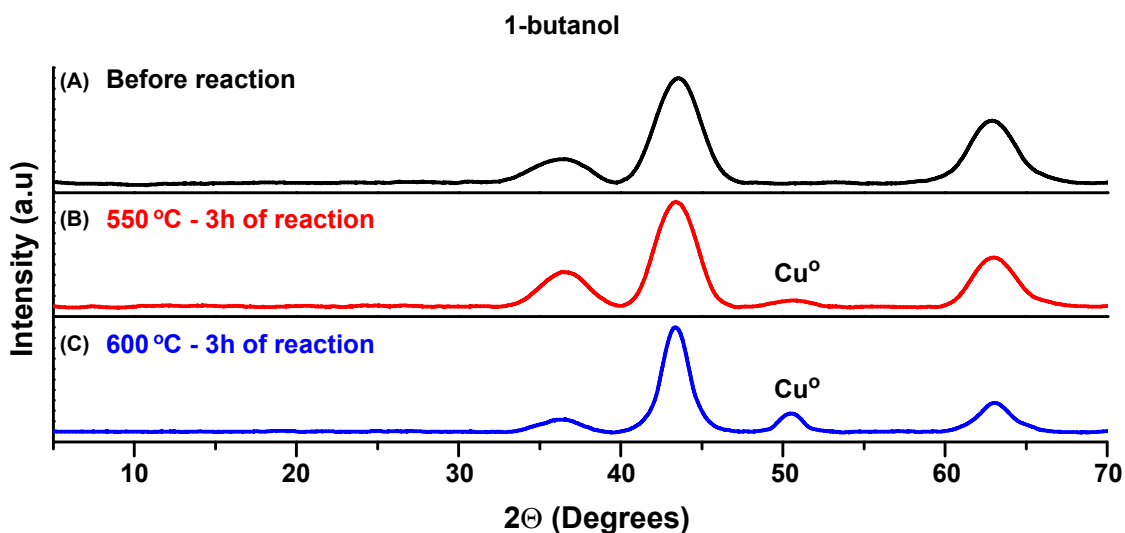


Fig. S11. XRD patterns for the Cu_{20}MMO catalyst with 100% of 1-butanol. (A) before reaction; (B) after 3 hours of reaction at 550°C. (C) after 3 hours of reaction at 600°C. The formation of Cu^0 species are indicated in the XRD patterns (B) and (C).

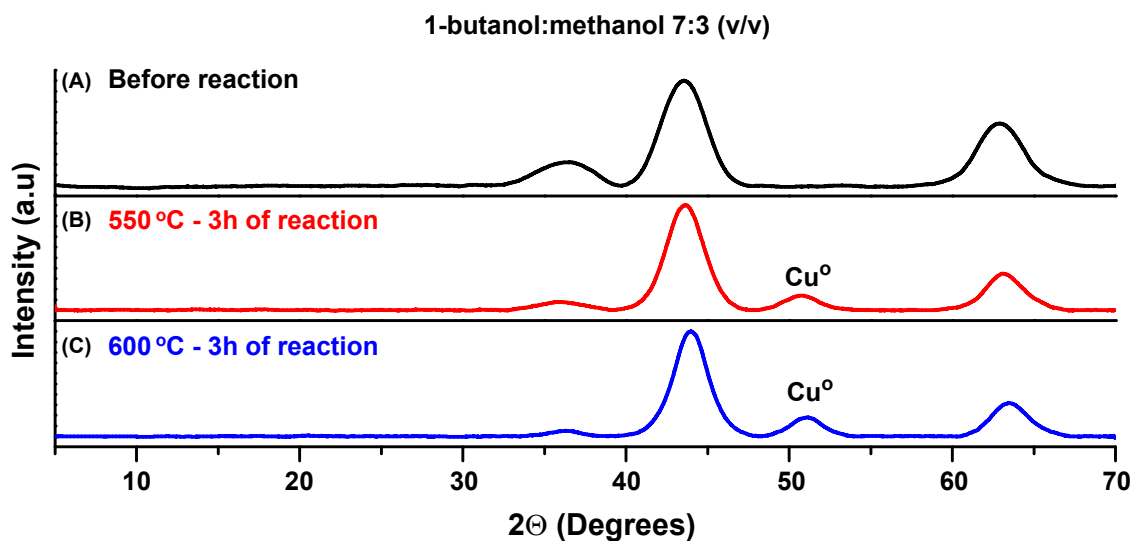


Fig. S12. XRD patterns for the Cu_{20}MMO catalyst with 1-butanol:methanol (7:3 v/v). (A) before reaction; (B) after 3 hours of reaction at 550°C. (C) after 3 hours of reaction at 600°C. The formation of Cu^0 species are indicated in the XRD patterns (B) and (C).

4. Reaction products

4.1 – GC-MS total ion chromatograms (TIC)

Fig. S13. GC-MS Total Ion Chromatograms (TIC) for the reaction products. Conditions: Catalyst Cu₂₀MMO; T = 550 °C; 100% of 1-butanol. The TICs were cut in three sections (A), (B) and (C) for better visualization.

Fig. S14. GC-MS Total Ion Chromatograms (TIC) for the reaction products. Conditions: Catalyst Cu₂₀MMO; T = 600 °C; 100% of 1-butanol. The TICs were cut in three sections (A), (B) and (C) for better visualization.

Fig. S15. GC-MS Total Ion Chromatograms (TIC) for the reaction products. Conditions: Catalyst Cu₂₀MMO; T = 550 °C; 1-butanol:methanol 7:3 (v/v). The TICs were cut in three sections (A), (B) and (C) for better visualization.

Fig. S16. GC-MS Total Ion Chromatograms (TIC) for the reaction products. Conditions: Catalyst Cu₂₀MMO; T = 600 °C; 1-butanol:methanol 7:3 (v/v). The TICs were cut in three sections (A), (B) and (C) for better visualization.

Fig. S13 (A)

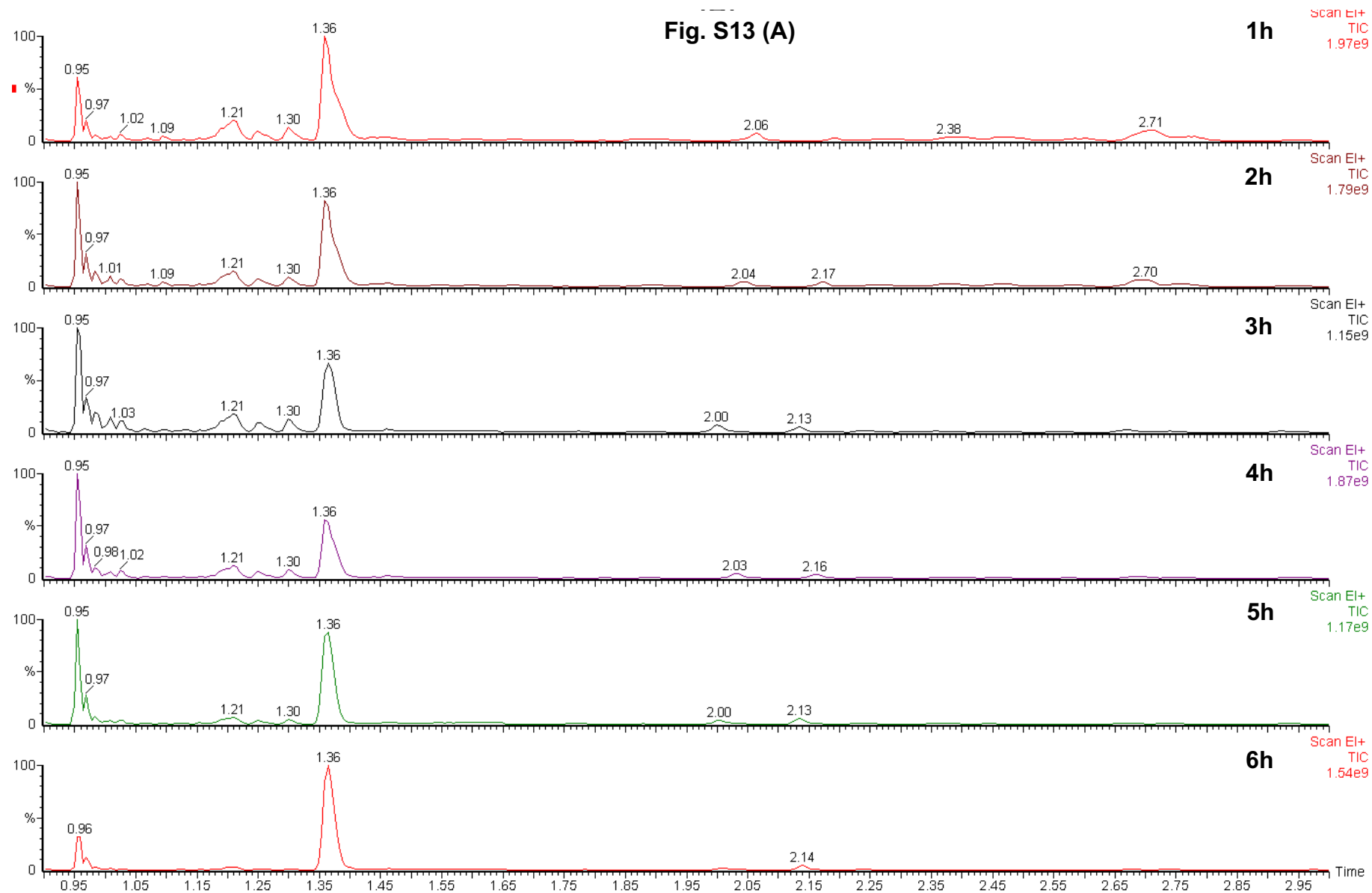


Fig. S13 (B)

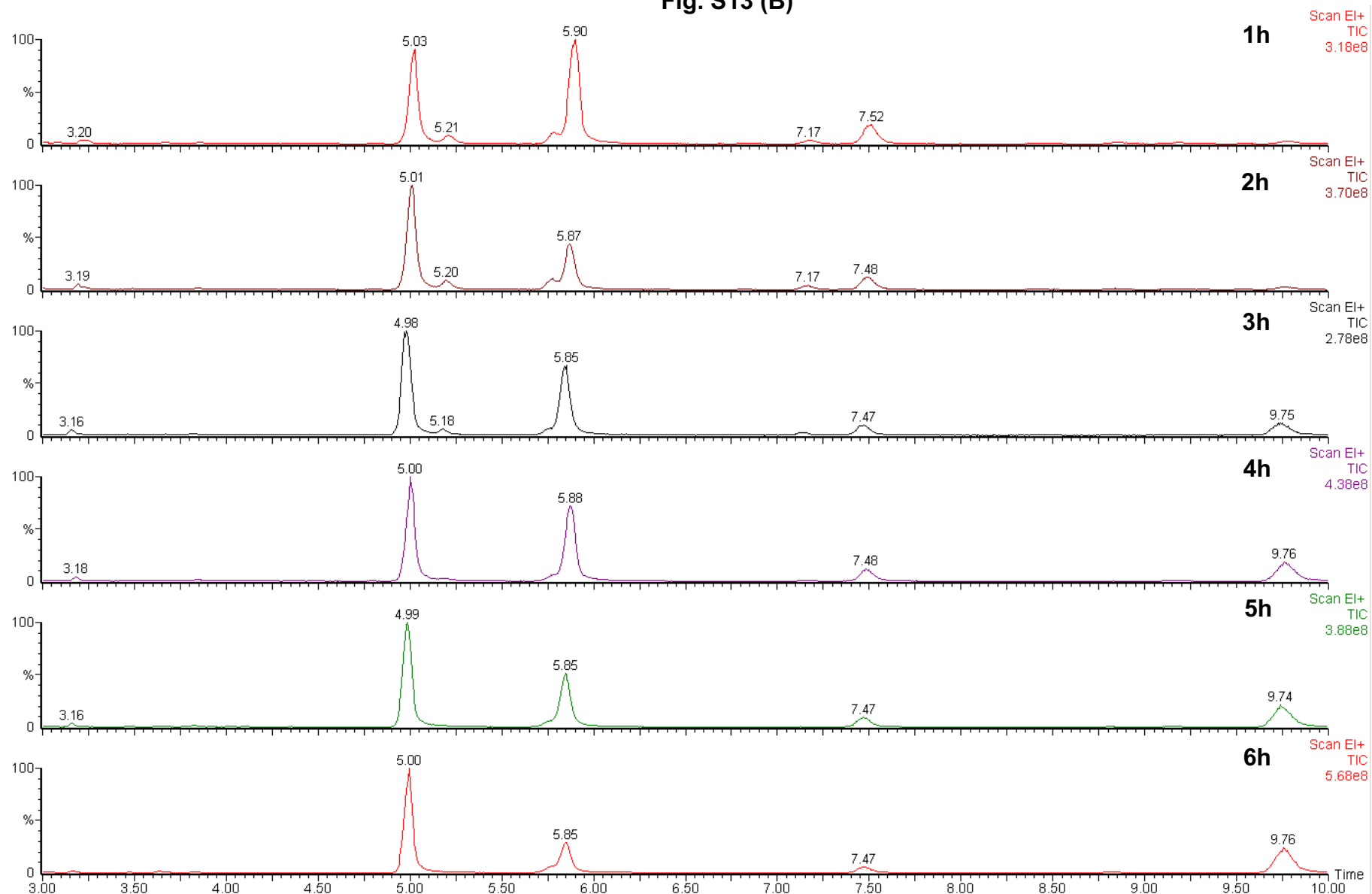


Fig. S13 (C)

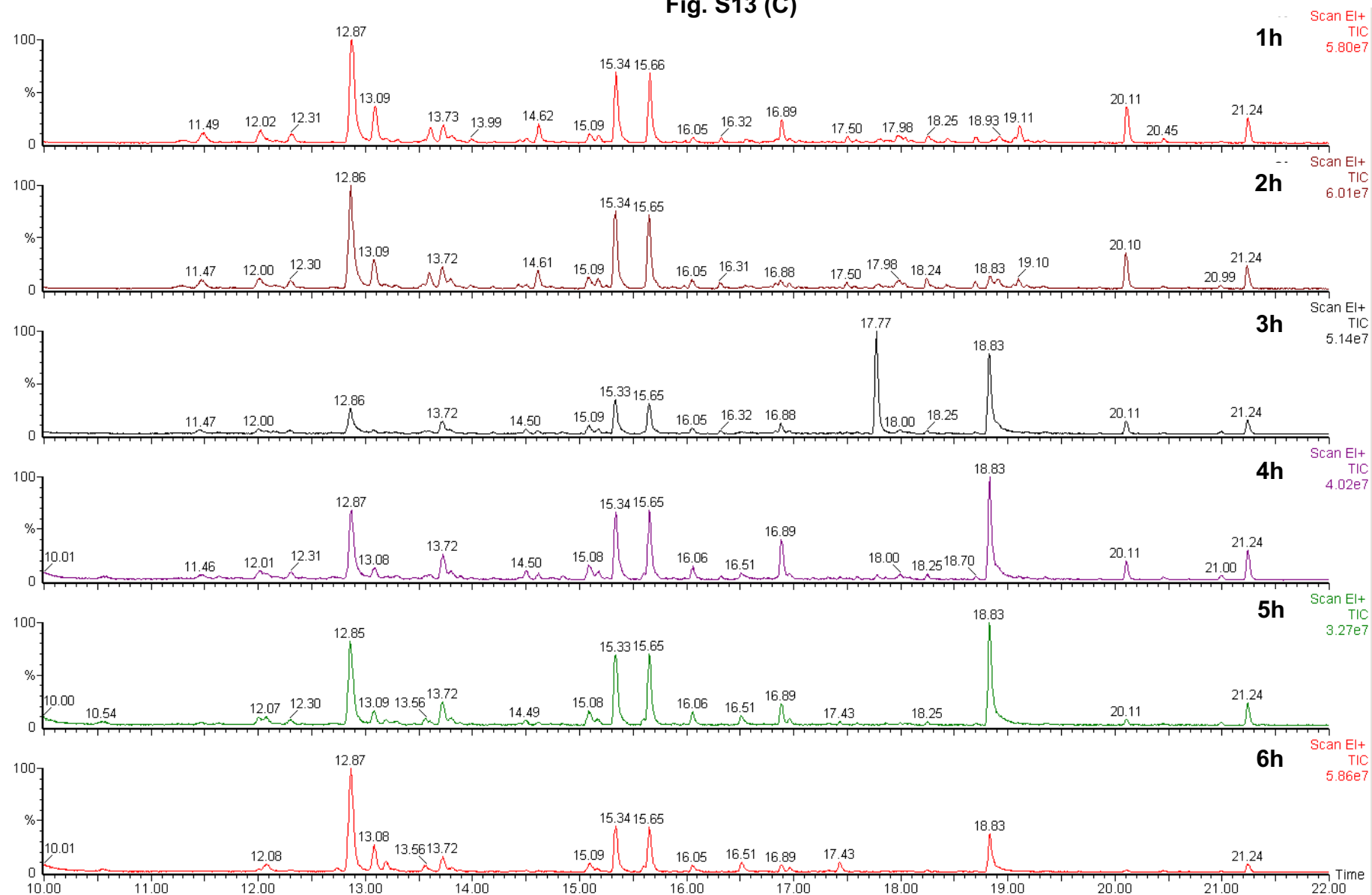


Fig. S14 (A)

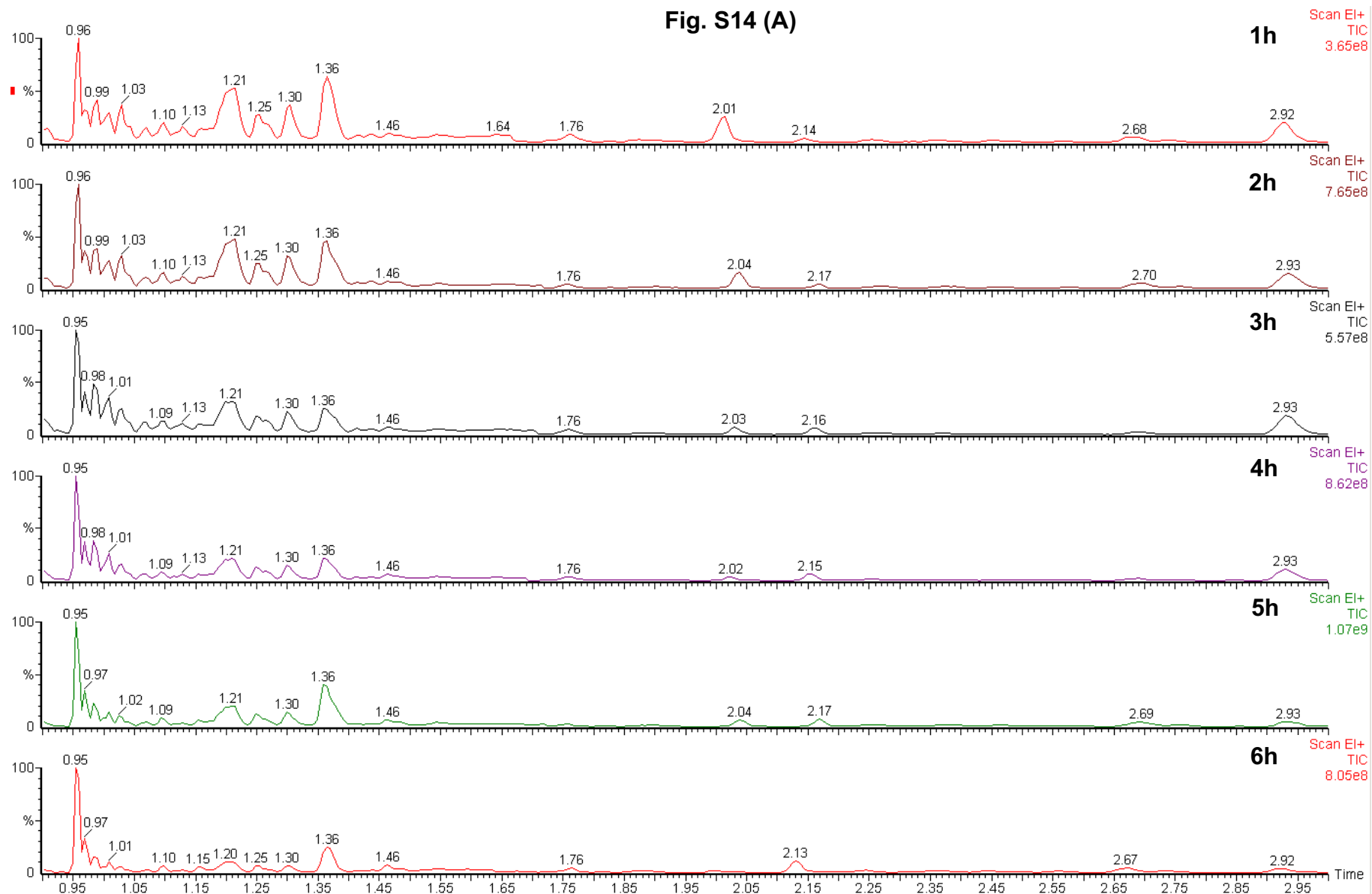


Fig. S14 (B)

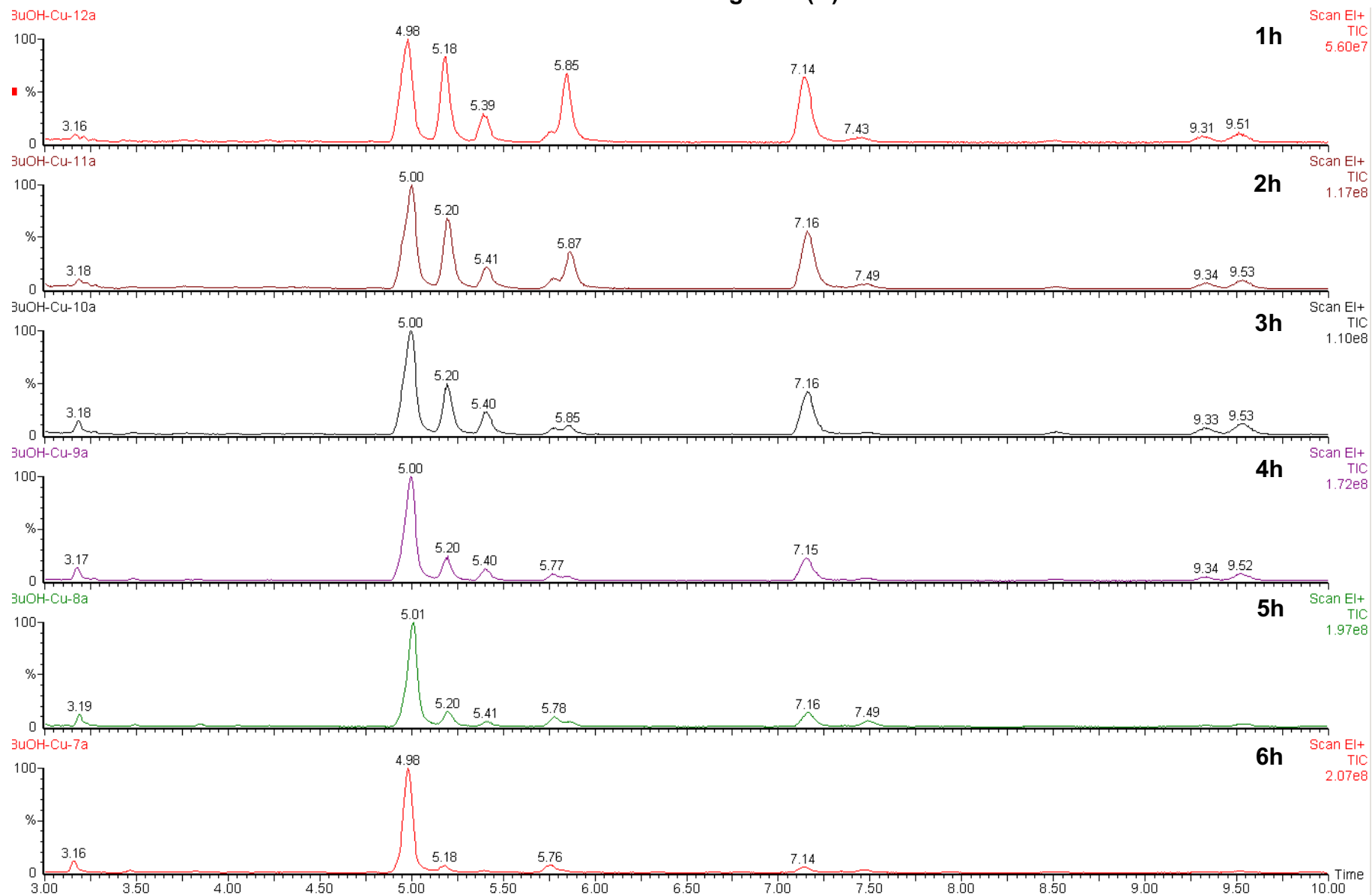


Fig. S14 (C)

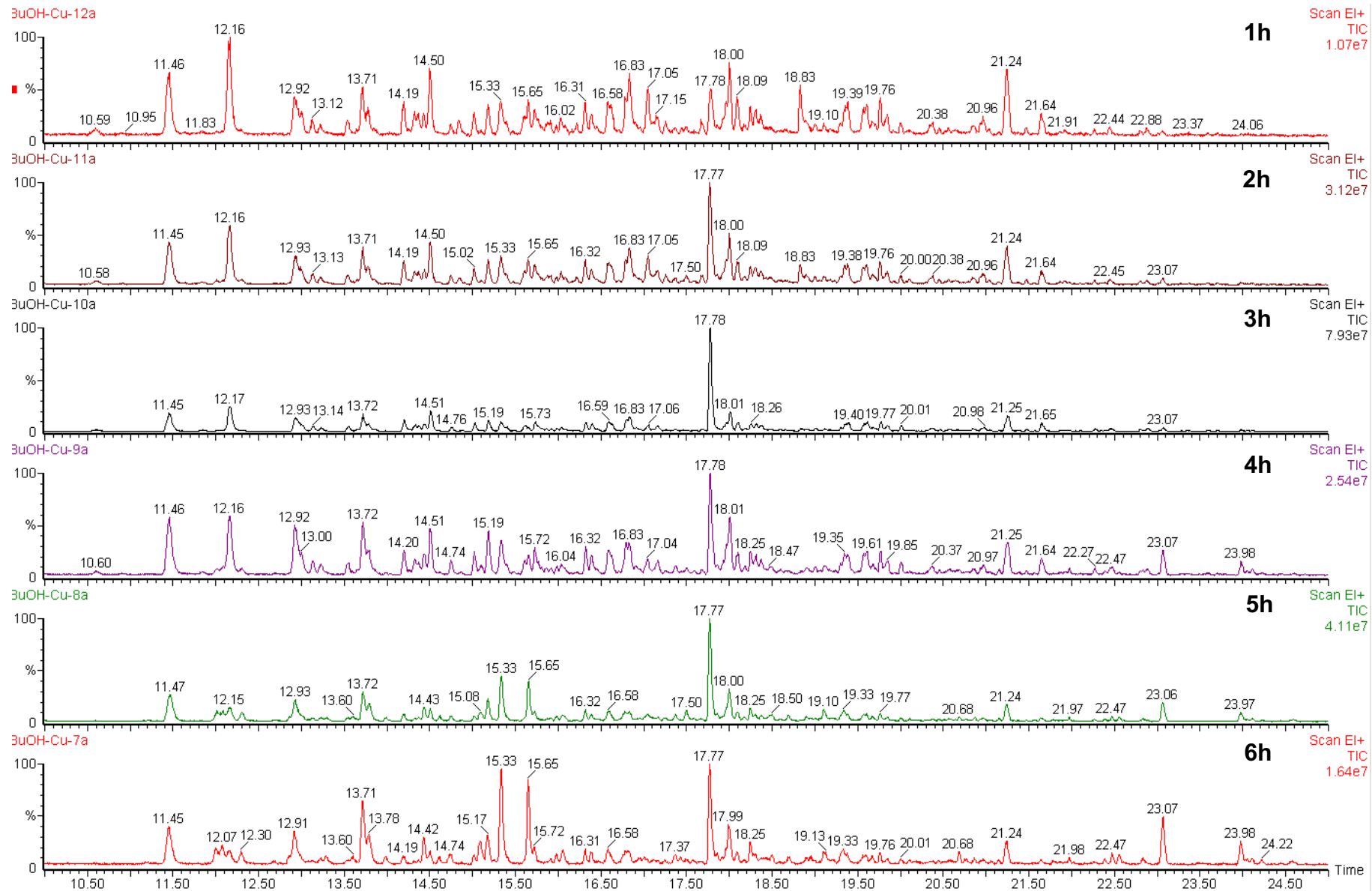


Fig. S15 (A)

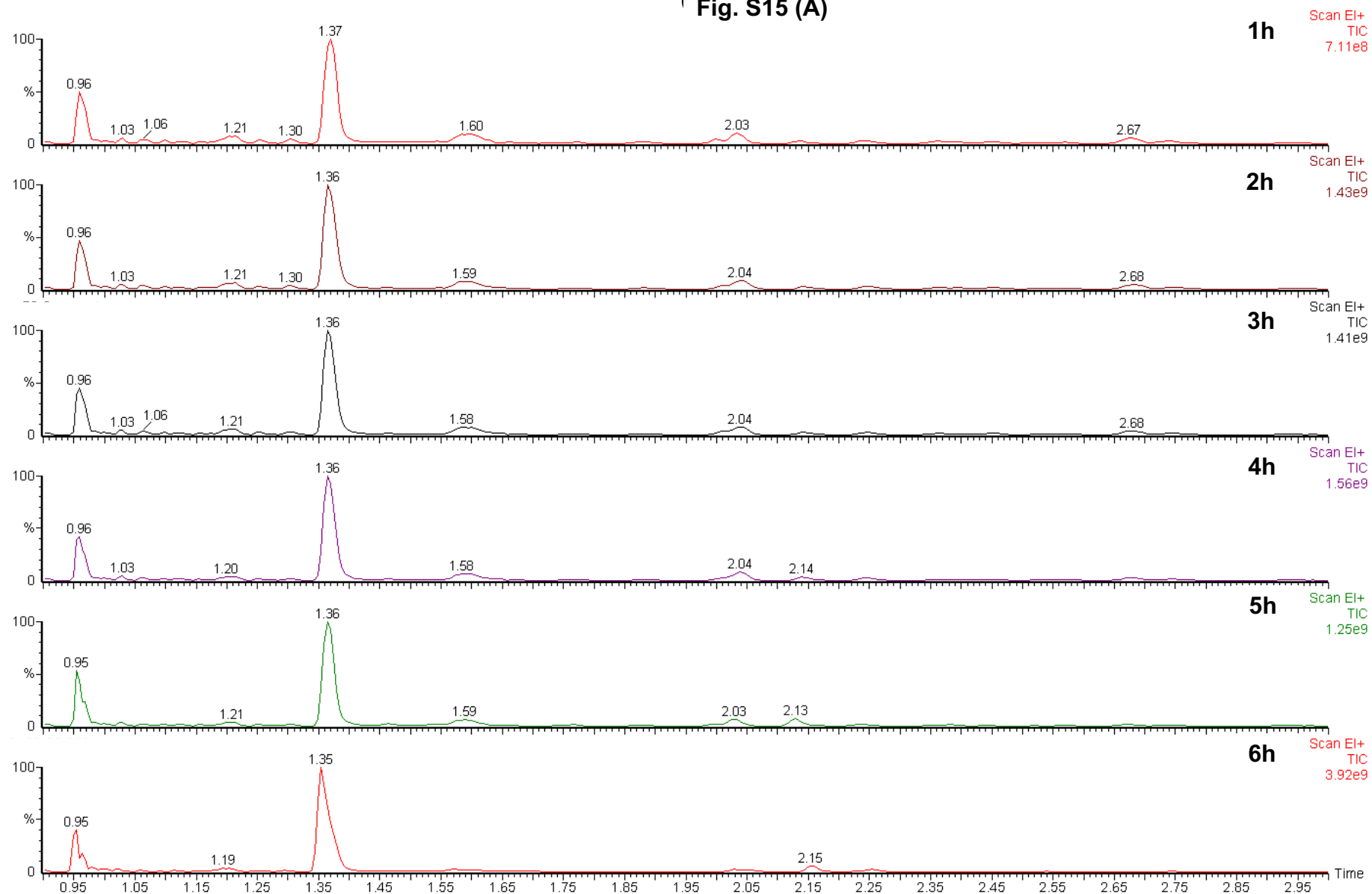


Fig. S15 (B)

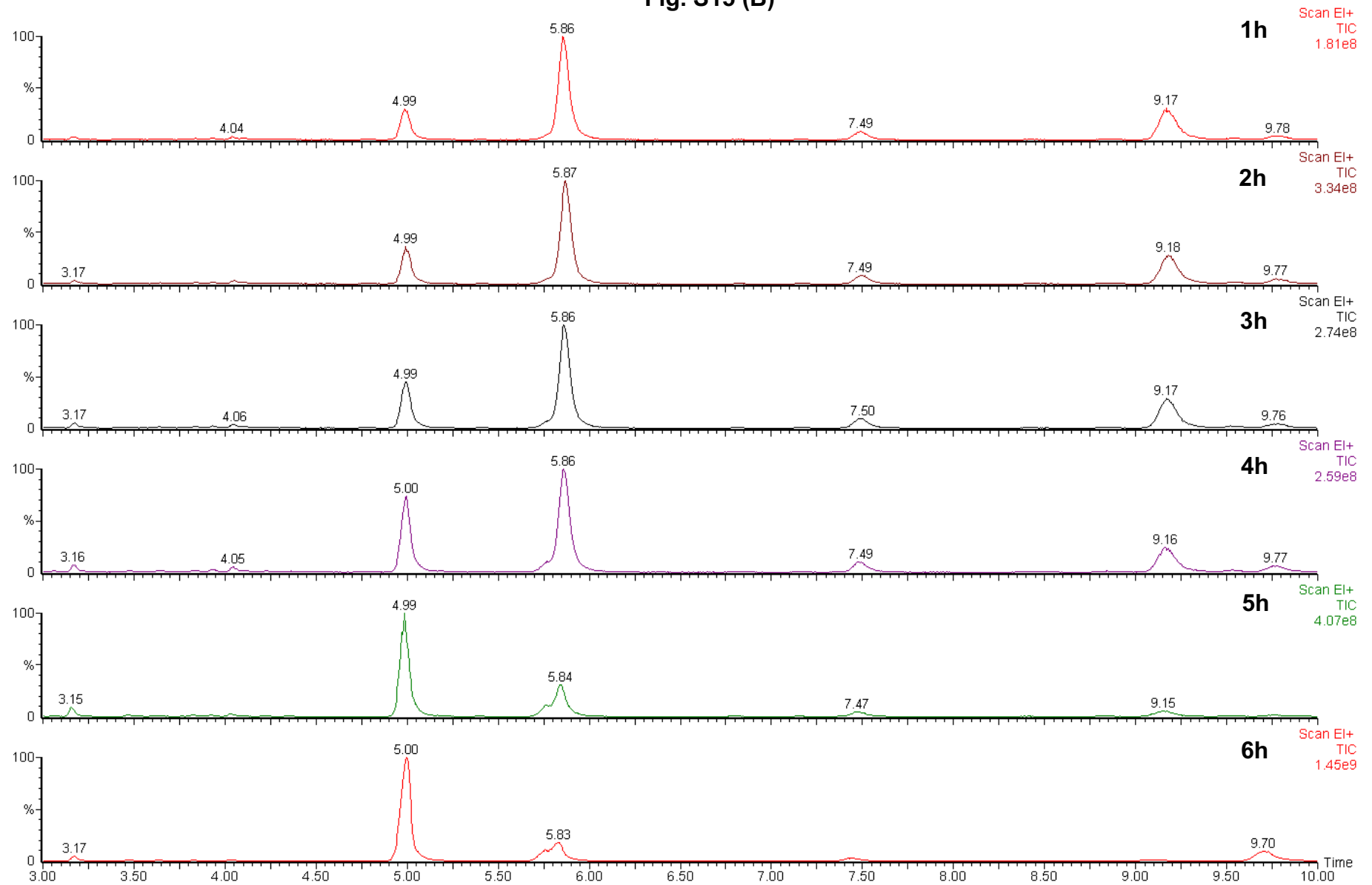


Fig. S15 (C)

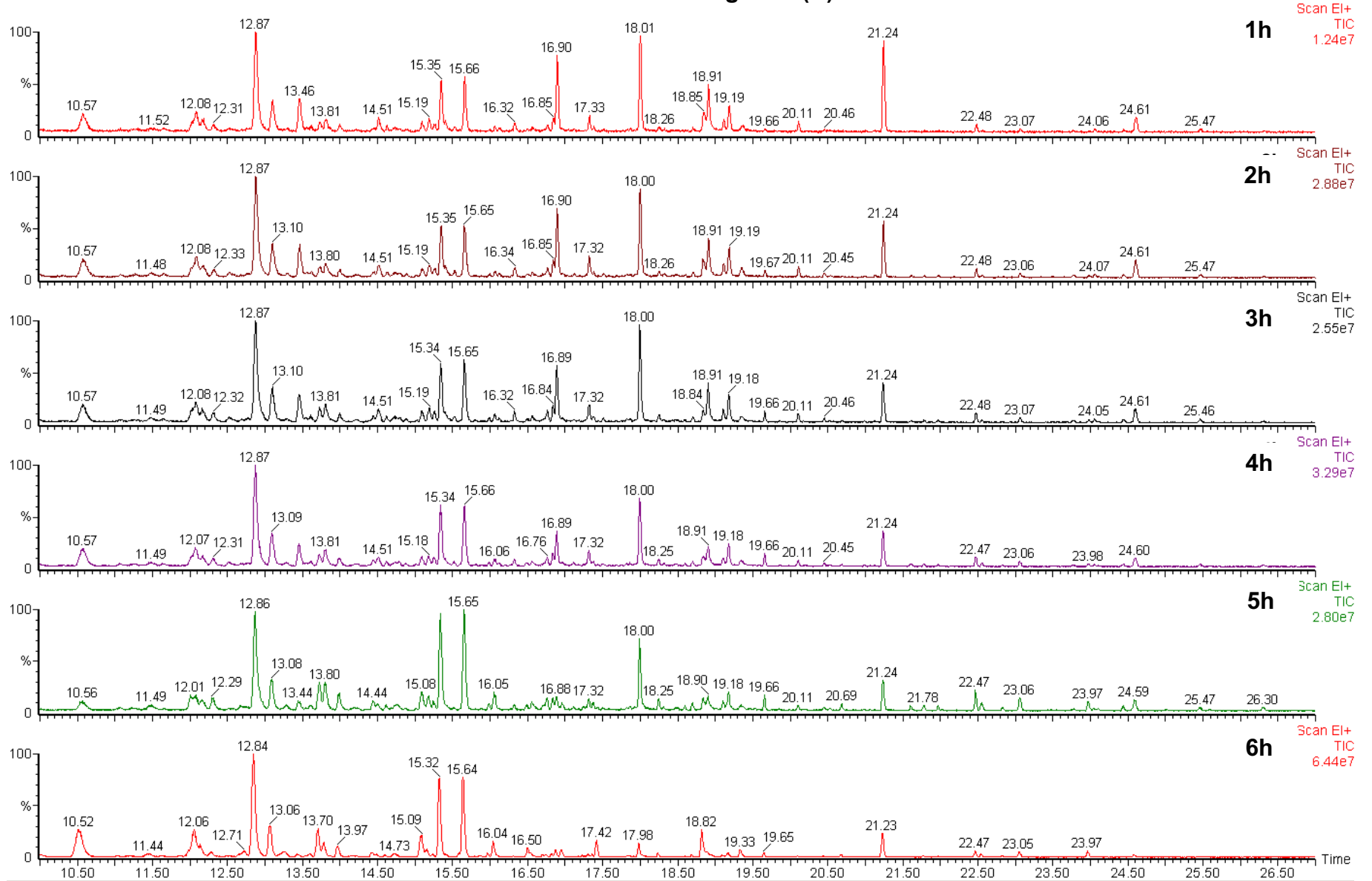


Fig. S16 (A)

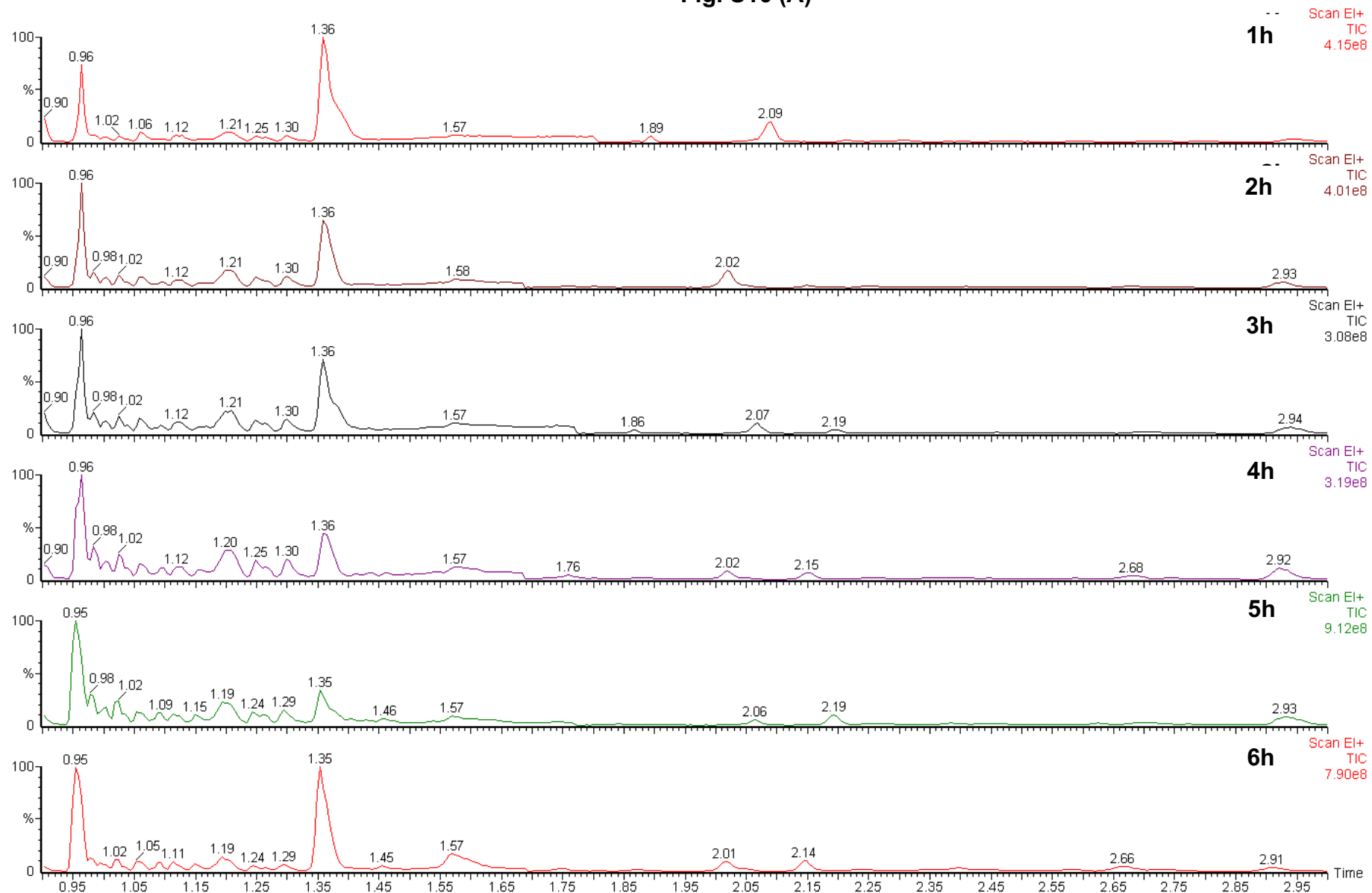


Fig. S16 (B)

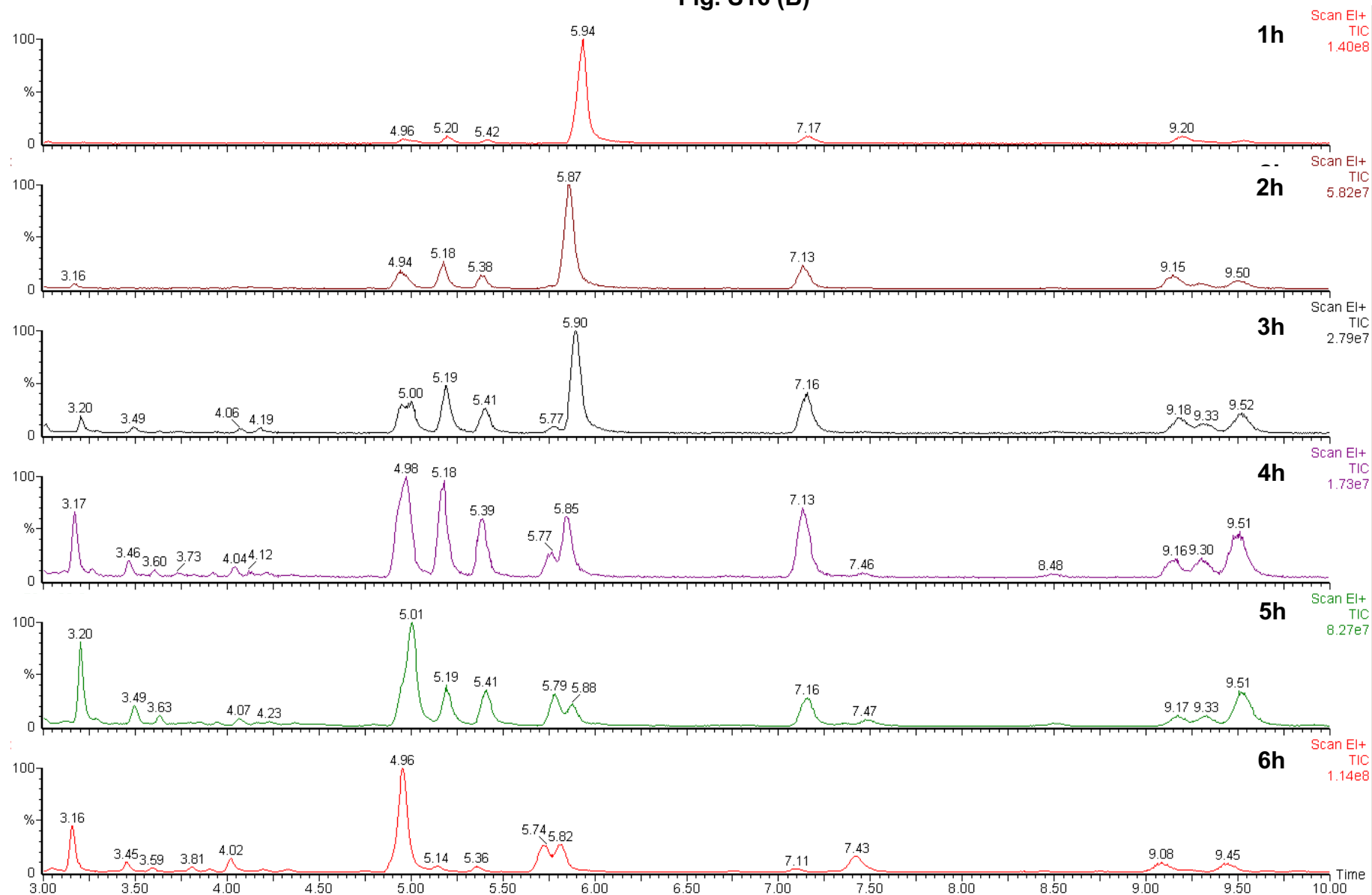
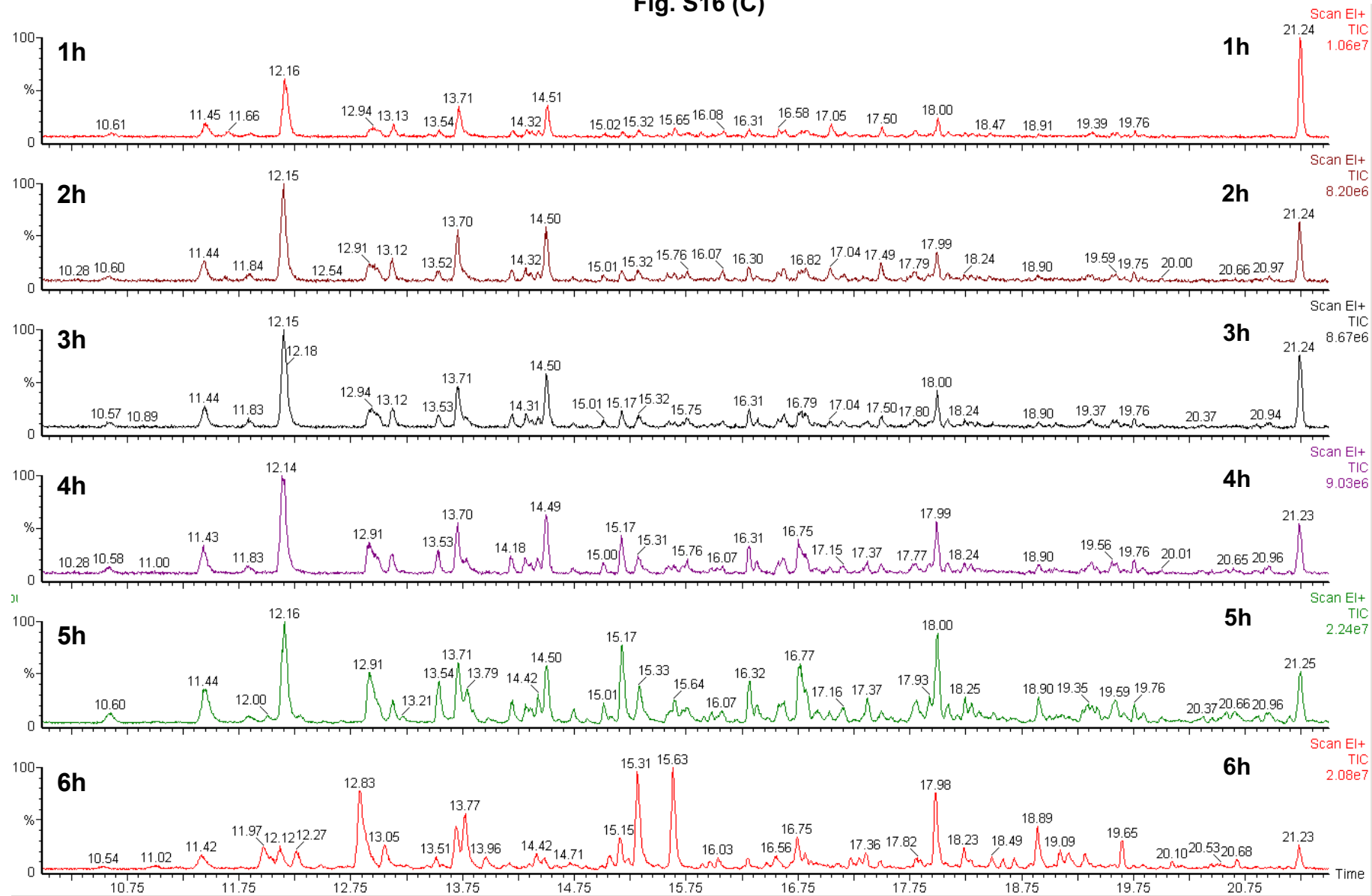


Fig. S16 (C)



4.2 - Retention times for GC-MS total ion chromatograms

0.78	2-butene	13.79	1-(1-methylethyl) cyclopentane
0.81	2-methyl-2-butene	13.80	2,3-dimethyl-2-cyclopenten-1-one
0.89	heptane	13.98	vinyl cyclohexanecarboxylate
0.95	3-heptene	14.20	4-ethyl-1,2-dimethyl-benzene
0.96	1-metoxi-butane	14.50	1-ethyl-2,4-dimethyl-benzene
1.20	2-methyl-3-heptene	15.01	1-etenil-3-ethyl-benzene
1.36	butyraldehyde	15.08	3-isobutyl-5-methyl-2-hexanone
1.46	2-methyl-2,4-hexadiene	15.16	1,3,5-diethyl-benzene
1.76	benzene	15.17	1,3-diethyl-5-methyl-benzene
2.01	Isobutyl ethenyl ether	15.32	2,3,4-trimethyl-2-cyclopenten-1-one
2.04	n-butyl ether	15.33	3-(1-methylethyl)-cyclohexene
2.13	2-pentanone	15.34	2,3,4-trimethyl-2-cyclopenten-1-one
2.24	1-methyl-cyclohexene	15.65	3,4-dimethyl-2-cyclohexen-1-one
2.25	methyl butanoate	15.73	1,4-diethyl-2-methyl-benzene
2.40	2-ethyl butyraldehyde	16.06	3-hepten-2-one
2.67	2,5-dimethyl-1,3-hexadiene	16.32	1,3,5-triethyl-benzene
2.92	toluene	16.51	butyl-2-ethyl hexanoate
3.16	3-hexanone	16.89	2-ethyl-1-hexanol
3.47	2-methyl-3-hexanone	16.96	5-ethyl-2,4-dimethyl-4-hepten-3-one
3.63	1-butoxy- <i>trans</i> -1-butene	17.32	4-ethyl-4-methyl-2-cyclohexen-1-one
3.83	hexanaldehyde	17.43	4-undecanone
4.03	2-methyl-2-butenaldehyde	17.78	2,2,5,5-tetramethyl-3-cyclopenten-1-one
4.98	4-heptanone	17.98	2,2,4,4-tetramethyl-3-cyclopenten-1-one
5.19	<i>p</i> -xylene	18.83	butanoic acid
5.36	1,3-dimethyl-benzene	19.17	3,4-dimethyl-4-ethyl-2-cyclohexen-1-one
5.41	1,3-dimethyl-benzene	19.33	2-methyl-butanoic acid
5.74	3-methyl-4-heptanone	19.65	3-ethyl-benzaldehyde
5.90	1-butanol	21.96	3,5-dimethyl-phenol
7.14	<i>o</i> -xylene	22.54	2-ethyl-5-methyl-phenol
7.47	2-ethylhexanaldehyde	23.07	4-methyl-phenol
9.11	2-methyl-1-butanol	23.98	2-ethyl-phenol
9.45	1-ethyl-2-methyl-benzene	24.60	2,4-bis(1-methylethyl)-phenol
9.51	1-ethyl-2-methyl-benzene		
9.76	butyl-butyrate		
10.52	butyl 2-methyl butanoate		
11.46	(1-methyl-ethyl)-benzene		
12.00	2,6-dimethyl-cyclohexanone		
12.16	1,2,3-trimethyl-benzene		
12.87	2-ethyl-hexenaldehyde		
12.92	1,3-diethyl-benzene		
13.71	4-nonanone		

4.3 – Tables

Table S3. Reaction Products for 1-butanol (100%) at 550 °C.

Products	Reaction Time / μmols						Sum	Selectivity
	30 min	60 min	90 min	120 min	150 min	180 min	(μmols)	(%)
3-heptene	302.5	33491.3	2678.8	4149.1	2406.7	2301.3	45329.7	31.2
butyraldehyde	15415.5	6981.6	3463.0	4878.1	4702.0	9374.9	44815.1	30.9
4-heptanone	8054.3	3981.4	1894.6	2788.0	1691.1	1850.0	20259.5	14.0
2-butene	1469.5	1272.0	739.0	1504.8	877.2	1339.5	7202.0	5.0
butyl-butyrate	4027.5	1503.6	692.4	545.8	61.2	73.3	6903.8	4.8
2-ethyl-hexanaldehyde	673.9	496.8	302.4	350.6	269.9	537.8	2631.5	1.8
2,3,4-trimethyl-2-cyclopenten-1-one	769.2	447.3	233.3	301.9	373.1	437.9	2562.8	1.8
3,4-dimethyl-2-cyclohexen-1-one	722.0	413.6	208.1	261.1	324.0	409.8	2338.5	1.6
2,5-dimethyl-2,4-hexadiene	89.0	89.5	96.9	171.5	442.6	1196.7	2086.1	1.4
isobutyl ethenyl ether	499.8	112.5	397.6	220.1	206.4	528.4	1964.9	1.4
2-ethyl-hexenaldehyde	887.1	231.6	111.4	93.5	228.4	331.8	1883.8	1.3
2-pentanone	539.6	358.2	191.2	327.6	183.0	197.7	1797.4	1.2
butyric acid	405.3	394.4	208.3	378.8	31.5	28.0	1446.4	1.0
Minors (7) < 1.0%*	733.5	504.7	384.2	565.3	428.7	1238.7	3855.1	2.7

Products by Chemical Class	Reaction Time / μmols						Sum	Selectivity
	30 min	60 min	90 min	120 min	150 min	180 min	(μmols)	(%)
Alkenes	1963.8	34933.4	3592.8	5982.1	3821.3	5457.7	55751.0	38.4
Aldehydes	17033.0	7752.2	3908.2	5363.8	5230.5	10280.8	49568.5	34.2
Ketones	8755.3	4457.5	2159.9	3227.2	1946.2	2151.7	22697.6	15.6
Esters	4027.5	413.6	208.1	261.1	324.0	409.8	5644.0	3.9
Cyclic (C5)	588.8	202.0	494.5	391.6	649.0	1725.1	4051.0	2.8
Ethers	698.0	175.3	420.6	253.2	226.8	588.8	2362.7	1.6
Carboxylic Acids	539.6	358.2	191.2	327.6	183.0	197.7	1797.4	1.2
Alcohols	214.9	201.2	177.8	222.4	211.3	417.7	1445.2	1.0

1-butanol Consumption and Gaseous Products							Yield (%)
1-butanol (total, μmols)							393414.0
1-butanol (not reacted, μmols)	12596.9	8868.4	5816.7	6935.7	2775.1	8301.4	45294.3
1-butanol consumption (%)	80.8	86.5	91.1	89.4	95.8	87.3	88.5
Condensed Products (μmols)	34589.0	50278.5	11601.4	16536.2	12225.8	19845.7	145076.6
Gaseous Products (μmols)							203043.1

* Heptene, 3-hepten-2-ol, metacrolein, 3-hexanone, 1-butoxy-trans-1-butene, hexanal, 3-hepten-2-one, 2-ethyl-1-hexanol, butyl-2-ethylhexanoate, 5-ethyl-2,4-dimethyl-4-hepten-3-one, 4-undecanone.

Table S4. Reaction Products for 1-butanol (100%) at 600 °C.

Products	Reaction Time / μmols						Sum (μmols)	Selectivity (%)
	30 min	60 min	90 min	120 min	150 min	180 min		
3-heptene	3855.9	2582.0	823.5	390.3	781.0	602.8	9035.4	19.1
4-heptanone	2819.3	1532.2	446.5	277.4	414.5	361.3	5851.3	12.4
butyraldehyde	1525.9	2042.4	269.3	171.7	705.7	788.4	5503.5	11.6
2-methyl-3-heptene	732.7	940.6	260.8	219.6	620.8	629.9	3404.4	7.2
toluene	549.8	528.3	302.8	318.8	495.0	531.2	2725.9	5.8
o-xylene	371.9	499.6	246.4	263.2	536.7	526.6	2444.3	5.2
n-butyl ether	500.5	574.9	76.4	87.8	429.4	607.8	2276.8	4.8
p-xylene	411.5	295.6	143.5	199.6	439.5	464.1	1953.7	4.1
2-butene	805.6	42.8	188.1	58.1	479.8	76.3	1650.7	3.5
heptane	0.0	240.9	240.6	228.7	337.8	347.6	1395.5	3.0
benzene	460.6	205.7	96.5	62.3	98.0	190.9	1114.0	2.4
2-pentanone	650.4	245.8	68.6	37.9	54.3	38.2	1095.2	2.3
2-methyl-2,4-hexadiene	314.9	393.6	77.6	49.4	96.2	118.6	1050.3	2.2
1-methyl-cyclohexene	388.5	254.1	52.3	35.0	92.0	56.2	878.1	1.9
2,3-dimethyl-2,4-hexadiene	298.1	237.0	29.2	22.0	86.1	75.1	747.5	1.6
1,3-dimethyl-benzene	117.0	112.1	84.6	96.5	127.5	155.0	692.7	1.5
1-methylethyl-benzene	161.6	169.5	69.2	60.5	81.0	68.6	610.5	1.3
1-ethyl-2-methyl-benzene	110.0	125.0	84.8	80.2	92.2	86.1	578.3	1.2
3-(1-methylethyl)-cyclohexene	243.0	146.9	23.4	18.2	31.5	24.2	487.3	1.0
1,2,3-trimethyl-benzene	66.3	73.5	50.2	75.1	95.4	97.0	457.5	1.0
Minors (15) < 1.0%*	1251.7	923.1	329.3	248.7	319.9	261.9	3334.6	7.1

Products by Chemical Class	Reaction Time / μmols						Sum (μmols)	Selectivity (%)
	30 min	60 min	90 min	120 min	150 min	180 min		
Alkenes	6815.7	4717.8	1466.1	802.9	2211.1	1604.0	17617.5	37.3
Aromatics (C6)	2749.9	2382.3	1251.1	1318.4	2147.5	2270.5	12119.6	25.6
Ketones	3786.3	1979.1	609.9	356.3	510.6	428.0	7670.2	16.2
Aldehydes	1619.3	2144.2	285.1	178.9	737.7	815.5	5780.8	12.2
Ethers	500.5	574.9	76.4	87.8	429.4	607.8	2276.8	4.8
Alkanes	0.0	240.9	240.6	228.7	337.8	347.6	1395.5	3.0
Cyclic (C5)	163.5	126.4	34.5	28.1	40.3	34.3	427.1	0.9

1-butanol Consumption and Gaseous Products							Yield (%)	
1-butanol (total, μmols)							393414.0	
1-butanol (not reacted, μmols)	0.0	238.7	72.8	80.4	487.4	763.4	1642.7	
1-butanol consumption (%)	100.0	99.6	99.9	99.9	99.3	98.8	99.6	
Condensed Products (μmols)	15635.1	12165.6	3963.6	3001.0	6414.4	6107.7	47287.5	12.1
Gaseous Products (μmols)							344483.8	87.9

* 3-hexanone, 2-ethylhexanal, 2,6-dimethylcyclohexanone, 1,3-diethylbenzene, 4-nonanone, 1- (1-methylethyl) cyclopentane, 4-ethyl-1,2-dimethylbenzene, 1-ethyl-2,4-dimethylbenzene, 1-ethenyl-3-ethylbenzene, 1,3-diethyl-5-methylbenzene, 3,4-dimethyl-2-cyclohexen-1-one, 1,4-diethyl-2-methylbenzene, 1,3,5-triethylbenzene, 4-methylphenol, 2-ethylphenol.

Table S5. Reaction Products for 1-butanol : methanol 7:3 (v/v) at 550 °C.

Products	Reaction Time / μmols						Sum (μmols)	Selectivity (%)
	30 min	60 min	90 min	120 min	150 min	180 min		
butyraldehyde	9995.4	6714.5	8728.1	10300.5	6948.1	4821.5	47508.0	38.5
1-methoxy-butane	5012.7	4808.8	5574.6	7122.7	4464.8	3427.2	30410.8	24.7
4-heptanone	5801.6	3319.3	1714.9	1497.2	863.7	573.9	13770.4	11.2
2-methyl-1-butanol	242.9	658.4	1648.1	2751.4	2059.3	1650.5	9010.7	7.3
n-butyl ether	470.4	667.3	1197.7	1320.5	1031.6	795.6	5483.1	4.4
n-butyl butanoate	965.9	119.6	265.9	228.5	223.3	113.9	1916.9	1.6
2-ethyl-hexanal	206.1	235.4	328.2	427.1	284.4	198.0	1679.2	1.4
2-pentanone	391.1	429.4	248.4	256.5	138.2	97.7	1561.3	1.3
2,3-dimethyl-2,4-hexadiene	33.7	99.7	228.1	373.1	279.7	232.3	1246.6	1.0
Minors (27) < 1.0%*	1720.2	2095	2086.4	2312.3	1566.3	944.4	10724.4	8.9

Products by Chemical Class	Reaction Time / μmols						Sum (μmols)	Selectivity (%)
	30 min	60 min	90 min	120 min	150 min	180 min		
Aldehydes	10551.7	7411.6	9598.4	11348.7	7646.9	5278.6	51836.0	42.0
Ethers	5542.3	5514.8	6838.1	8508.8	5536.9	4222.8	36163.6	29.3
Ketones	6461.1	4059.3	2110.2	1908.8	1081.2	724.5	16345.2	13.3
Alcohols	250.8	676.3	1699.1	2842.5	2134.0	1703.1	9305.8	7.5
Esters	1280.9	262.7	558.6	546.8	467.5	282.5	3399.0	2.8
Cyclic (C5)	329.6	604.1	548.6	616.7	389.8	247.2	2736.1	2.2
Aromatics (C6)	313.7	486.8	401.6	403.6	277.3	142.0	2024.9	1.6
Alkenes	33.7	99.7	228.1	373.1	279.7	232.3	1246.6	1.0
Carboxylic Acids	76.3	31.9	37.6	40.6	46.3	21.8	254.4	0.2

1-butanol Consumption, Condensed and Gaseous Products							Yield (%)	
1-butanol (total, μmols)							275388.0	
1-butanol (not reacted, μmols)	4202.4	5771.7	9797.2	13057.3	9854.6	7736.6	50419.8	
1-butanol consumption (%)	90.8	87.4	78.7	71.6	78.5	83.1	81.7	
Condensed Products (μmols)	24840.0	19147.4	22020.4	26589.8	17859.4	12855.0	123312.0	54.9
Gaseous Products (μmols)							101656.2	45.1

* Methyl butanoate, 2-ethyl butanal, 3-hexanone, 2-methyl-3-hexanone, 1-butoxy-trans-1-butene, hexanal, 2-methyl-2-butanal, butyl 2-methylbutanoate, 2-ethyl-2-hexenal, 2-ethylhexenal, 4-nonanone, 2,3-dimethyl-2-cyclopenten-1-one, vinyl cyclohexanecarboxylate, 3-isobutyl-5-methyl-2-hexanone, 2,3,4-trimethyl-2-cyclopenten-1-one, 3,4-dimethyl-2-cyclohexen-1-one, 2-ethylhexanol, 4-ethyl-4-methyl-2-cyclohexen-1-one, butanoic acid, 3,4-dimethyl-4-ethyl-2-cyclohexen-1-one, 2-methylbutanoic acid, 3-ethylbenzaldehyde, 2-ethyl-5-methylphenol, 4-methylphenol, 2-ethylphenol, 2,4-bis(1-methylethyl) phenol, 2,2,4,4-tetramethyl-3-cyclopenten-1-one.

Table S6. Reaction Products for 1-butanol : methanol 7:3 (v/v) at 600 °C.

Products	Reaction Time / μmols						Sum (μmols)	Selectivity (%)
	30 min	60 min	90 min	120 min	150 min	180 min		
1-methoxy butane	11695.0	6962.9	4049.4	2101.9	4158.0	1083.6	30050.8	30.1
2-methyl-2-butene	8496.9	6604.8	5663.4	2320.6	3982.5	550.8	27618.9	27.7
butyraldehyde	7462.8	1266.7	1014.3	1216.1	2489.2	1815.0	15264.1	15.3
4-heptanone	1875.9	729.8	259.9	104.8	209.6	40.5	3220.5	3.2
n-butyl ether	1034.8	216.6	233.3	178.9	752.7	333.0	2749.2	2.8
toluene	543.4	798.5	548.6	235.2	447.7	102.4	2675.8	2.7
o-xylene	126.3	401.7	348.6	226.2	492.6	167.7	1763.2	1.8
p-xylene	221.2	438.3	312.3	176.0	389.5	0.1	1537.4	1.5
1-ethyl-3-methyl-benzene	124.5	574.1	286.3	132.2	246.0	71.6	1434.7	1.4
1,3-dimethyl-benzene	207.0	435.1	224.5	102.4	282.7	106.7	1358.4	1.4
2-methyl-1-butanol	523.0	143.2	98.7	84.9	299.9	148.4	1298.0	1.3
2-pentanone	571.8	273.0	134.8	46.1	77.9	21.3	1125.0	1.1
benzene	371.7	474.8	218.3	0.0	0.0	0.0	1064.8	1.1
Minors (16) < 1.0%*	4458.6	2002.5	854.1	389.7	724.5	157.1	8586.6	8.6

Products by Chemical Class	Reaction Time / μmols						Sum (μmols)	Selectivity (%)
	30 min	60 min	90 min	120 min	150 min	180 min		
Ethers	12729.7	7179.5	4282.8	2280.8	4910.7	1416.6	32800.1	32.9
Alkenes	8893.0	6761.5	5758.5	2353.3	4032.2	564.3	28362.9	28.4
Aldehydes	8109.8	1423.2	1075.4	1245.4	2541.3	1815.0	16209.9	16.3
Cyclic (C6)	2683.6	3869.0	2348.7	1090.7	2249.1	528.4	12769.5	12.8
Ketones	3490.4	1494.1	548.1	204.5	316.6	75.5	6129.2	6.1
Alcohols	523.0	143.2	98.7	84.9	299.9	148.4	1298.0	1.3
Cyclic (C5)	1283.4	451.5	134.5	55.6	202.8	49.9	2177.7	2.2

1-butanol consumption, Condensed and Gaseous Products							Yield (%)		
1-butanol (total, μmols)							275388.0		
1-butanol (not reacted, μmols)	1884.6	482.5	458.4	826.9	3562.0	2821.7	7214.3		
1-butanol consumption (%)	95.9	98.9	99.0	98.2	92.2	93.9	96.4		
Condensed Products (μmols)	37712.9	21322.0	14246.6	7315.1	14552.6	4598.2	99747.3	37.1	
Gaseous Products (μmols)							168427.0	62.9	

* 2,3-dimethyl-1,3-hexadiene, 3-hexanone, 3-methyl-4-heptanone, 2-ethylhexanal, 1-ethyl-2-methylbenzene, 1,2,3-trimethylbenzene, 2-ethyl-2-hexenal, 4-nonanone, 2,3-dimethyl-2-cyclopenten-1-one, 1-ethyl-3,5-dimethylbenzene, 1,3,5-triethylbenzene, 2,3,4-trimethyl-2-cyclopenten-1-one, 3,4-dimethyl-2-cyclohexen-1-one, 2,2,5,5-tetramethyl-3-cyclopenten-1-one, 3,5-dimethylphenol, 2-methylphenol.

5. References

- [1] F. Cavani, F. Trifiro, A. Vaccari, *Catalysis Today*, 1991, **11**, 173-301.
- [2] J. A. Barrett, Z. R. Jones, C. Stickelmaier, N. Schopp, P. C. Ford, *ACS Sustainable Chemistry & Engineering*, 2018, **6**, 15119-15126.
- [3] M. Chui, G. Metzker, C. M. Bernt, A. T. Tran, A. C. B. Burtoloso, P. C. Ford, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 3158-3169.
- [4] K. K. Ramasamy, M. Gray, H. Job, D. Santosa, X. S. Li, A. Devaraj, A. Karkamkar, Y. Wang, *Topics in Catalysis*, 2016, **59**, 46-54.