Electronic Supplementary Material (ESI) for Green Chemistry.

Molybdenum carbide nanoparticles within carbon nanotubes as superior catalyst for γ-Valerolactone production via levulinic acid hydrogenation

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Supplementary Information

GC/MS Analysis

Figure S1-A shows the FID GC chromatogram obtained for the analysis of the liquid products obtained at 200 ºC and 30 bar using the 5% Ru/AC catalyst, with the most intense being related to γ-valerolactone. When the scale is zoomed it is possible to observe in Figure S1-B the presence of ten additional peaks with their chromatographic areas presented in Table S1. Table S1 also displays the name of the compounds associated to each peak that were identified by analysis of the MS spectrum.

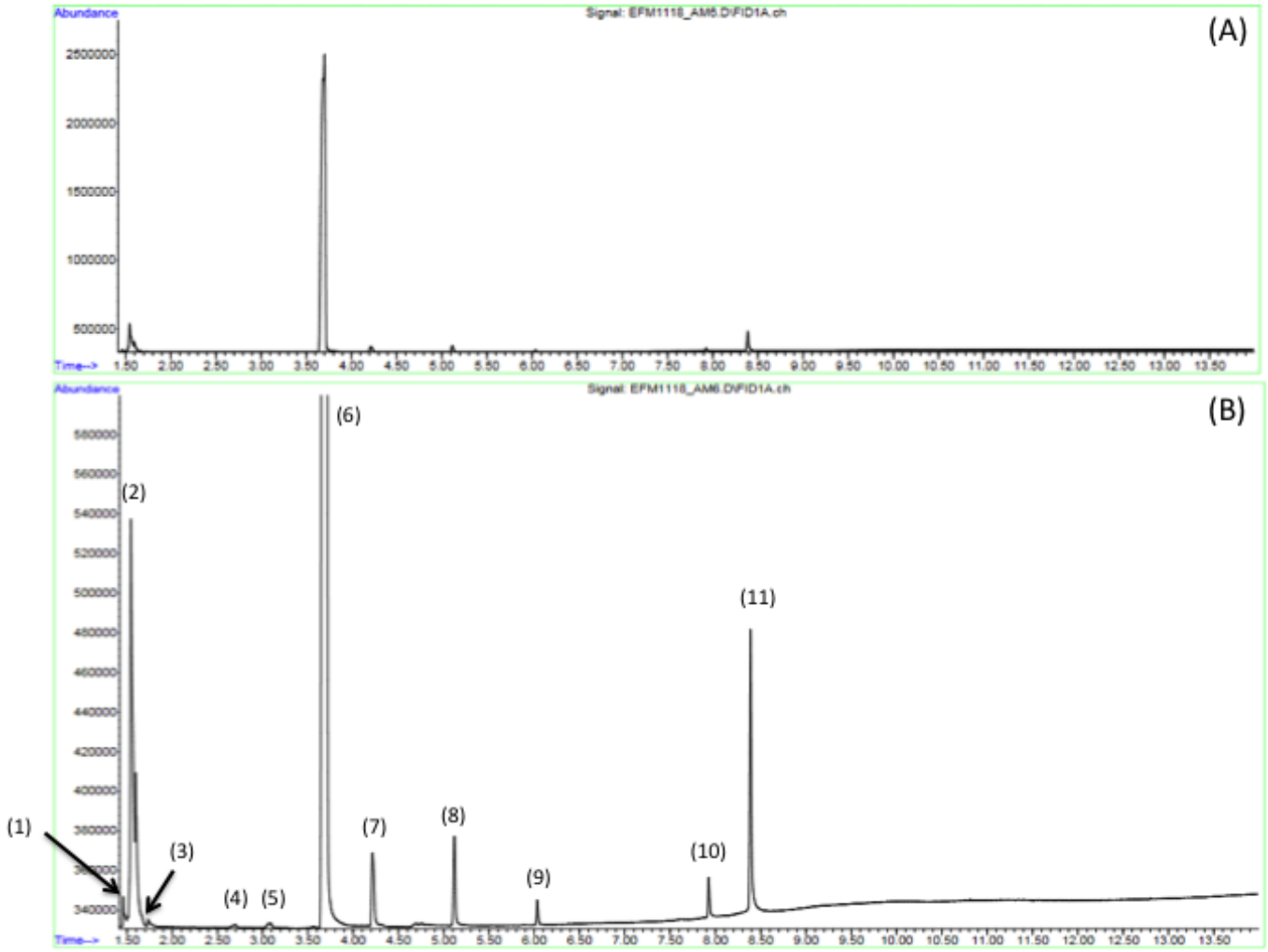

Figure S1 – FID GC chromatogram of the liquid sample obtained during the levulinic acid hydrogenation at 200 ºC and 30 bar using the 5% Ru/AC catalyst (A). Enlarged chromatogram to allow the visualization of the detected peaks (B).

Table S1 – Retention time, % of peak area and name of the identified compound for the peaks 1 to 11 shown in Figure S1-B.

Peak #	Retention time (min)	% Area	Identified Compound
1	1.457	0.181	N.I.
2	1.543	6.273	2-methyltetrahydrofuran
3	1.733	0.085	N.I.
4	2.696	0.069	α-angelic lactone
5	3.063	0.116	N.I.
6	3.702	88.301	γ-valerolactone
7	4.214	0.978	Pentanoic acid
8	5.117	0.864	1,4-pentanediol
9	6.035	0.206	N.I.
10	7.925	0.350	Levulinic acid
11	8.387	2.578	N.I

A thorough analysis of the mass spectroscopy spectra of the non-identified products was performed without allowing us to conclude about their nature. In particular, a comparison between the MS spectrum of the γ-hydroxyvaleric acid and those of the non-identified compounds was performed allowing us to conclude that none of the non-identified compounds is the this compound.

In Figure S2-A the FID GC chromatogram of the liquid sample obtained for 24 hours of reaction (200 ^{o}C and 30 bar) when Mo_2C/CNT was used as catalyst is presented. As in the previous case, the most intense peak is related to γ-valerolactone indicating that this was the major product. When the chromatogram is magnified one can see that there are more peaks than in the case of Figure S1-B, but their area account for about 9,4 % of the total area (Table S2). This result indicates that Mo_2C/CNT is more selective towards γ-valerolactone than the 5% Ru/AC catalyst because in the latter case the area of the by-products accounts for about 12 % of the total area.

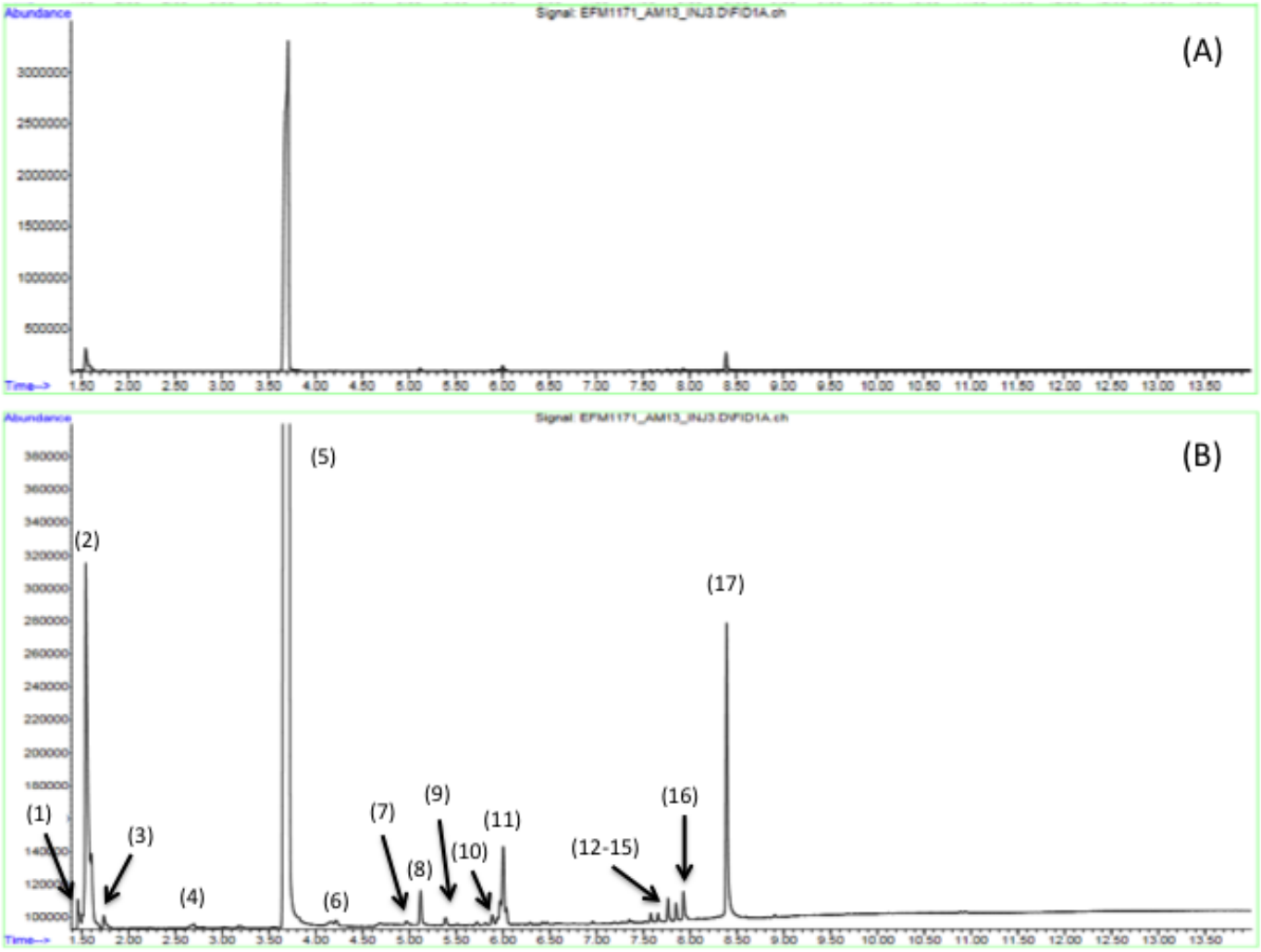

Figure S2 – FID GC chromatogram of the liquid sample obtained during the levulinic acid hydrogenation at 200 ºC and 30 bar using the Mo_2C/CNT catalyst (A). Enlarged chromatogram to allow the visualization of all detected peaks (B).

The retention time, percentage of area and name of the identified peaks are presented in Table S2.

Table S2 – Retention time, % of peak area and name of the identified compound for the peaks 1 to 17 shown in Figure S2-B.

Peak #	Retention time (min)	% Area	Identified Compound
1	1.458	0.177	N.I.
2	1.544	4.440	2-methyltetrahydrofuran
3	1.734	0.118	N.I.
4	2.696	0.079	α-angelic lactone
5	3.709	90.553	γ-valerolactone
6	4.218	0.154	Pentanoic acid
7	4.971	0.044	NI
8	5.119	0.290	1,4-pentanediol
9	5.300	0.073	N.I.
10	5.886	0.089	N.I.
11	6.002	1.033	N.I.
12	7.579	0.061	N.I.
13	7.655	0.057	N.I.
14	7.763	0.157	N.I.
15	7.849	0.119	N.I.
16	7.928	0.228	Levulinc acid
17	8.388	2.329	N.I

The fragmentation spectra of peaks 1 to 11 and 1 to 17 presented in Figures S1-B and S-2B are shown in Figures S3 to S18. The fragmentation spectra of peaks 2 and 3 were not possible to acquire because these compounds elute in retention times similar to that of the water solvent. The addition of 2-methyltetrahydrofuran to the sample to be analysed resulted in a sharp increase in the intensity of peak labeled 2 in Figures S1-B and S2-B, thus allowing the identification of the compound associated to the peak.

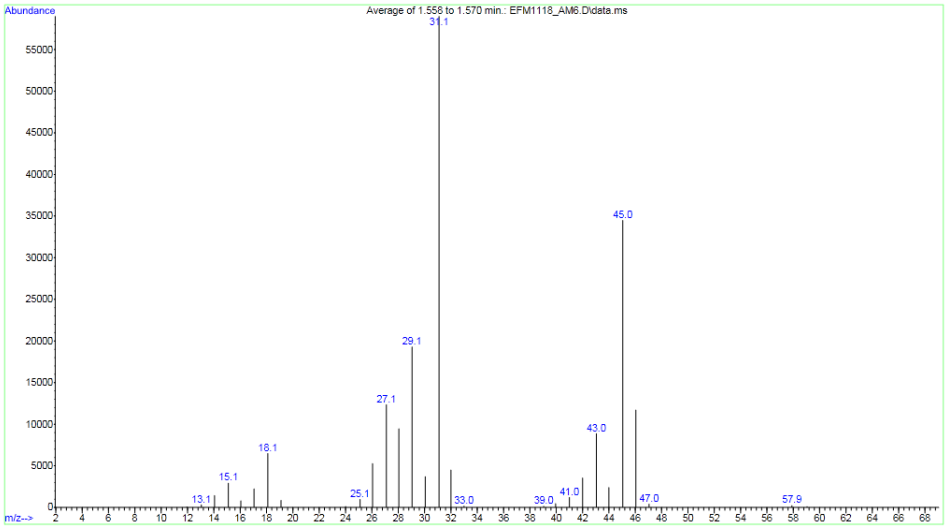

Figure S3 – M.S. fragmentation pattern of the compound associated to Peak #1 in Figures S1-B and S2-B.

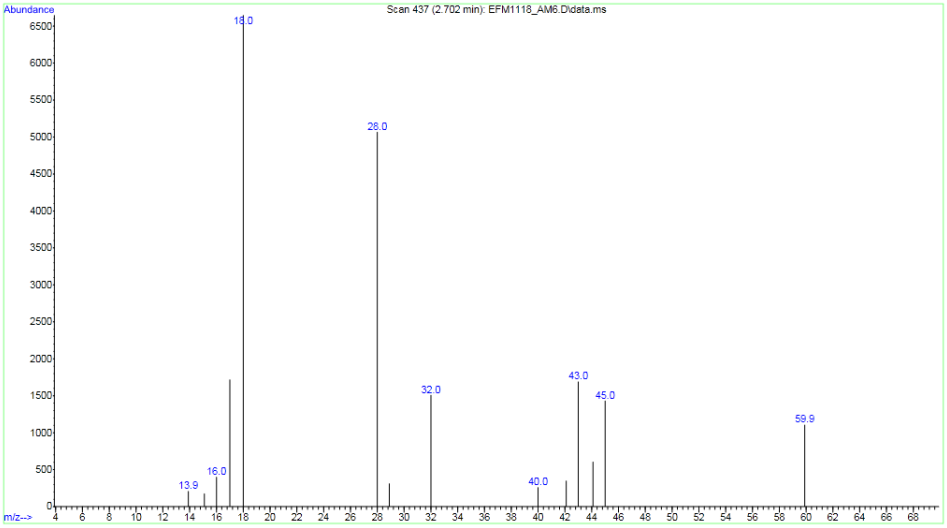

Figure S4 – M.S. fragmentation pattern of the compound associated to Peak #4 in Figure S1-B and S2-B. This pattern is in agreement with that of α-angelic lactone.

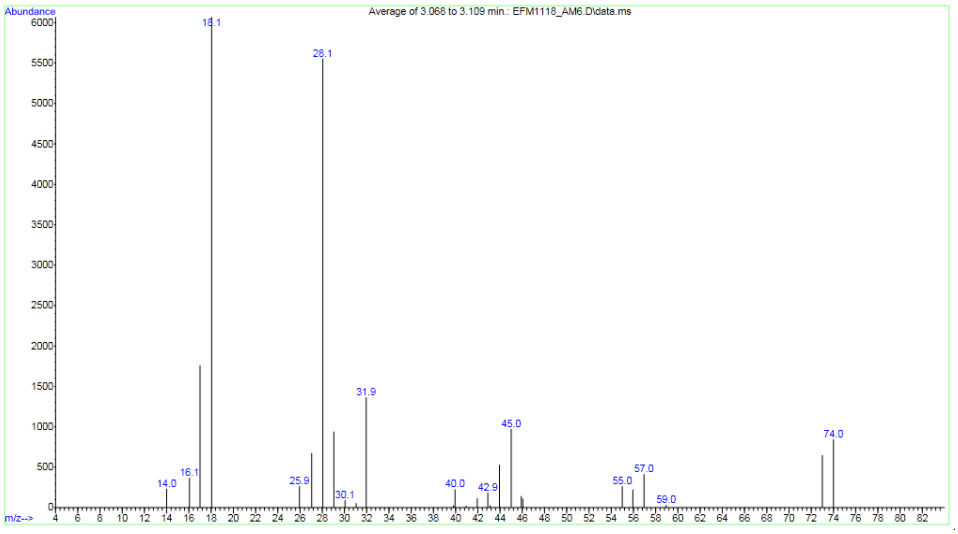

Figure S5 – M.S. fragmentation pattern of the compound associated to Peak #5 of Figure S1-B.

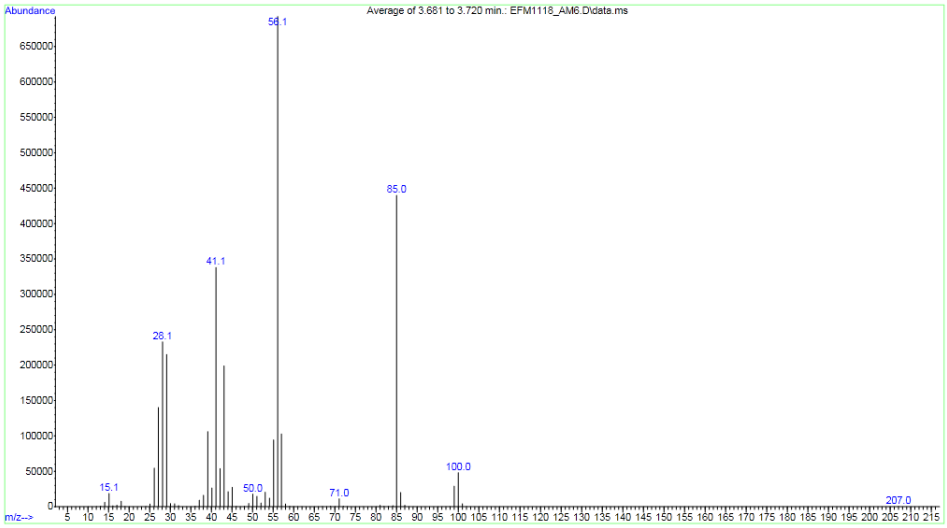

Figure S6 – M.S. fragmentation pattern of the compound associated to Peak #6 of Figure S1-B and Peak #5 in Figure S2-B. This pattern is in agreement with that of γ-valerolactone.

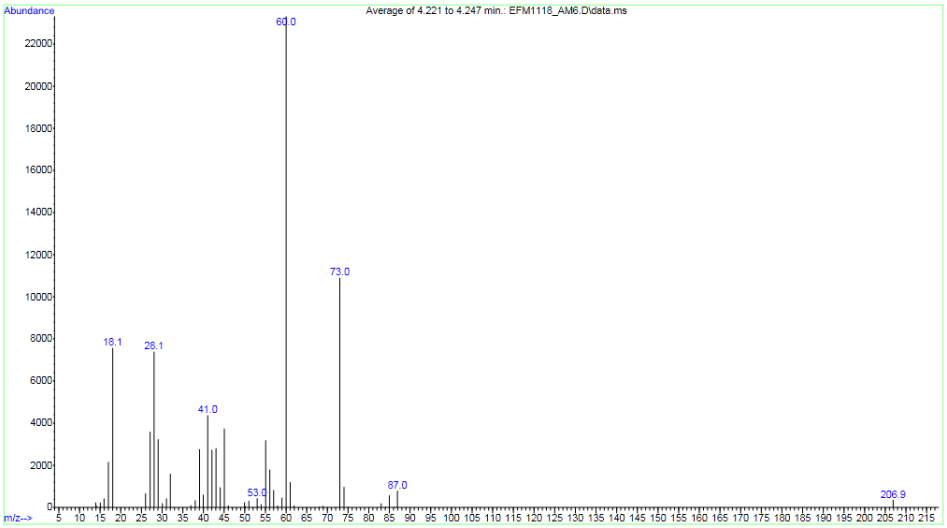

Figure S7 – M.S. fragmentation pattern of the compound associated to Peak #7 of Figure S1-B and to Peak #6 in Figure S2-B. This pattern is in agreement with that of pentanoic acid.

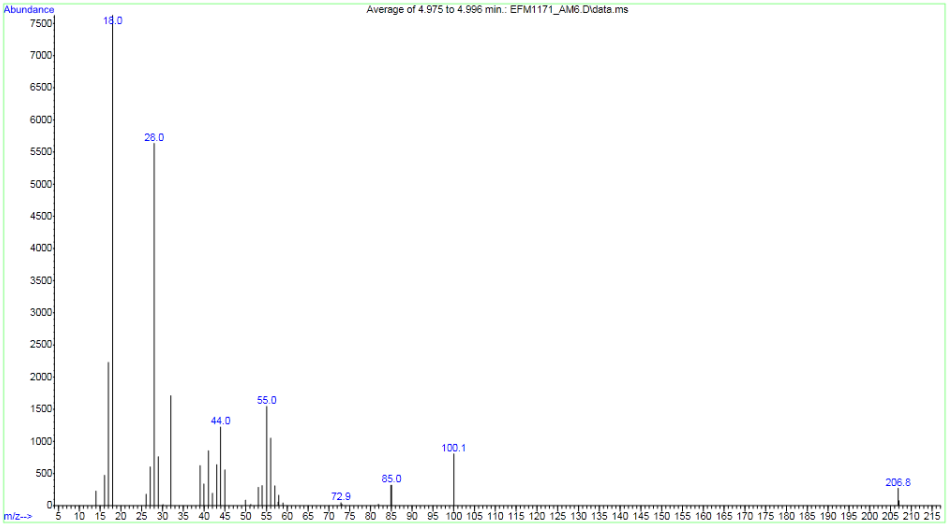

Figure S8 – M.S. fragmentation pattern of the compound associate to Peak #8 of Figure S-2.

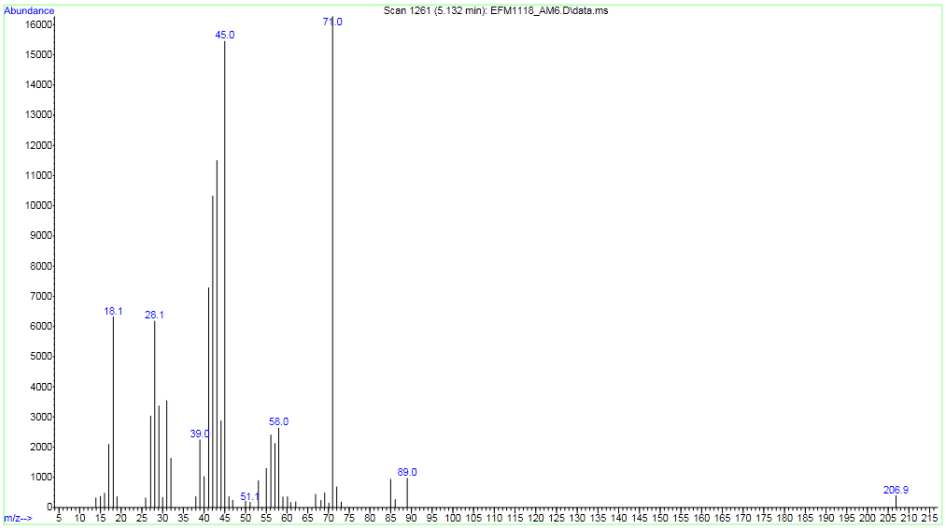

Figure S9 – M.S. fragmentation pattern of the compound associated to Peaks #8 in Figures S1-B and S2-B. This pattern is in agreement with that of 1,4-pentanediol.

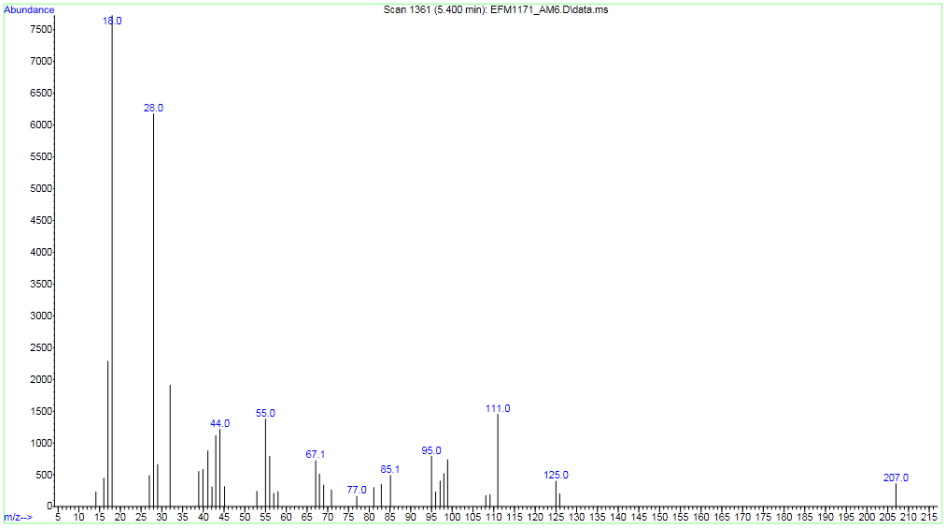

Figure S10 – M.S. fragmentation pattern of the compound associated to Peak #9 in Figure S2-B.

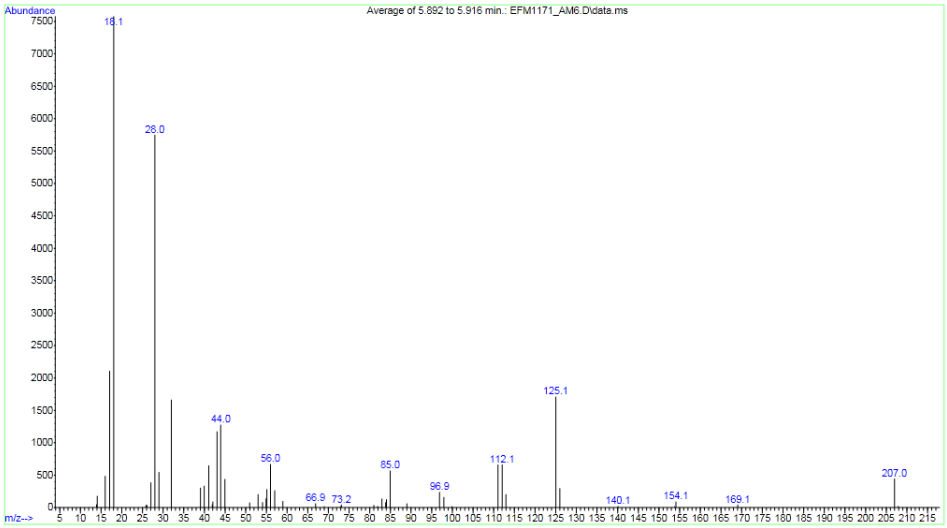

Figure S11 – M.S. fragmentation pattern of the compound associated to Peak #10 in Figure S2-B.

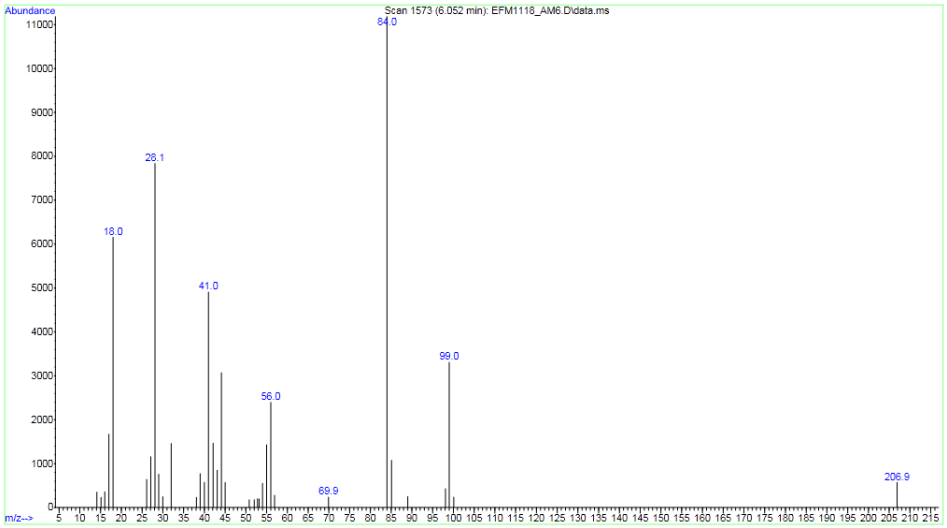

Figure S12 – M.S. fragmentation pattern of the compound associated to Peak #9 of Figure S1-B and Peak #11 in Figure S2-B.

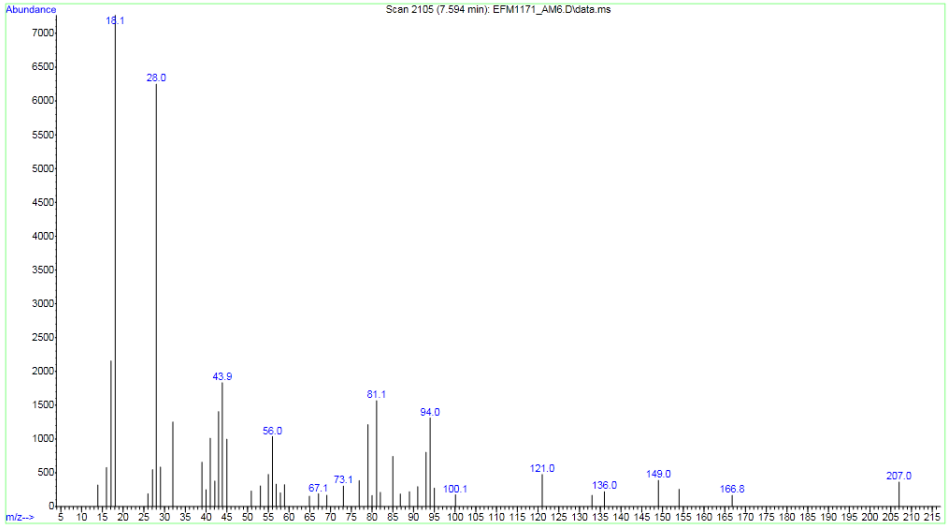

Figure S13 – M.S. fragmentation pattern of the compound associated to Peak #12 in Figure S2-B

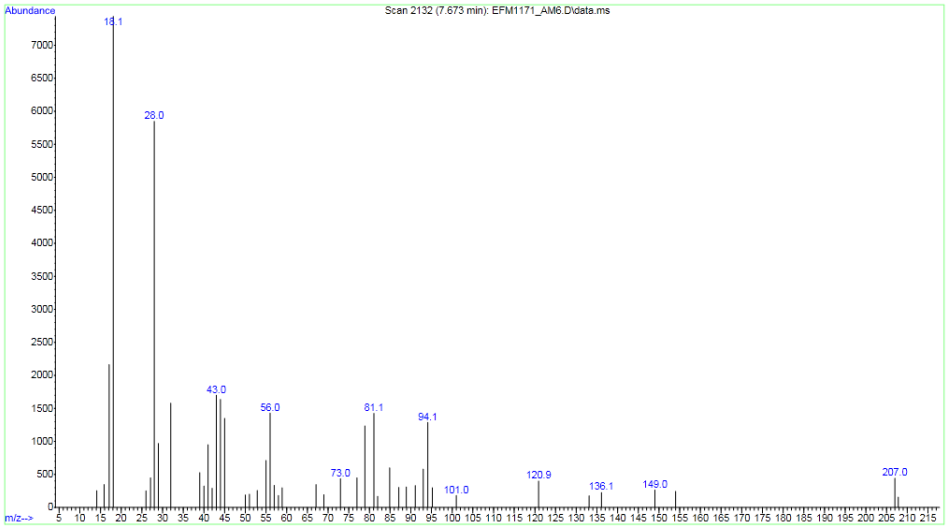

Figure S14 – M.S. fragmentation pattern of the compound associated to Peak #13 in Figure S2-B.

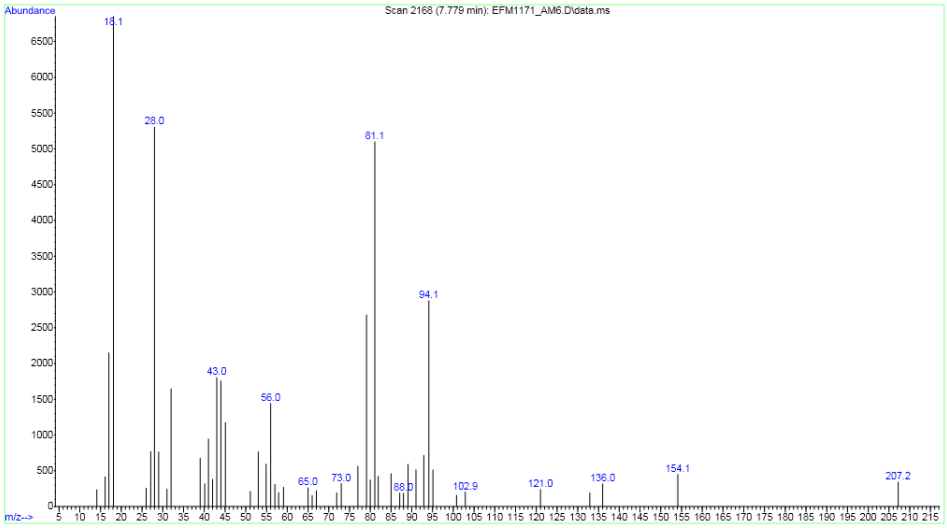

Figure S15 – M.S. fragmentation pattern of the compound associated to Peak #14 in Figure S2-B.

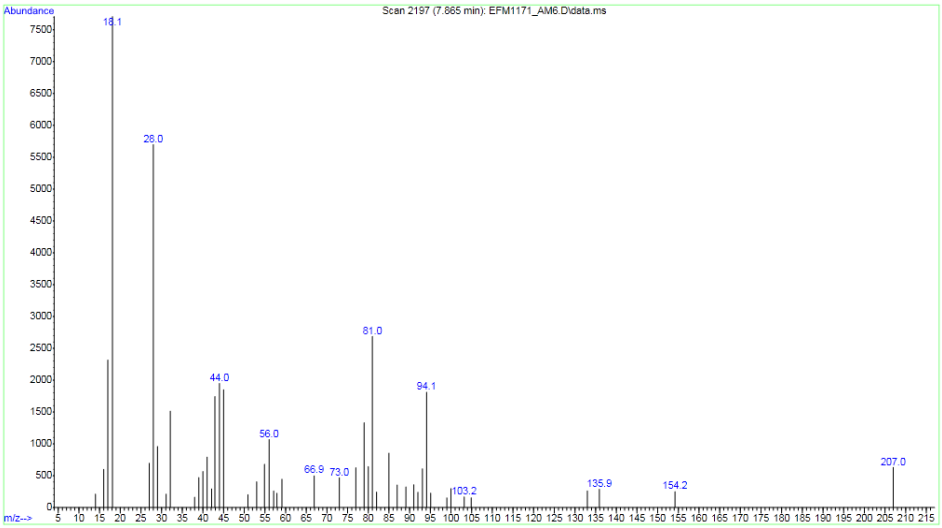

Figure S16 – M.S. fragmentation pattern of the compound associated to Peak #15 if Figure S2-B.

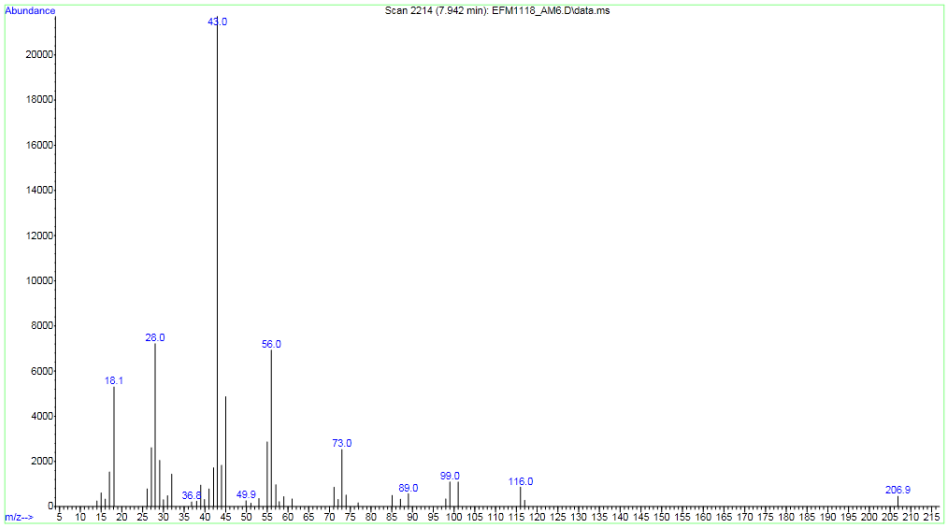

Figure S17 – M.S. fragmentation pattern of the compound associated to Peak #10 in Figure S1-B and Peak #16 in Figure S2-B. This pattern is in agreement with that of levulinic acid.

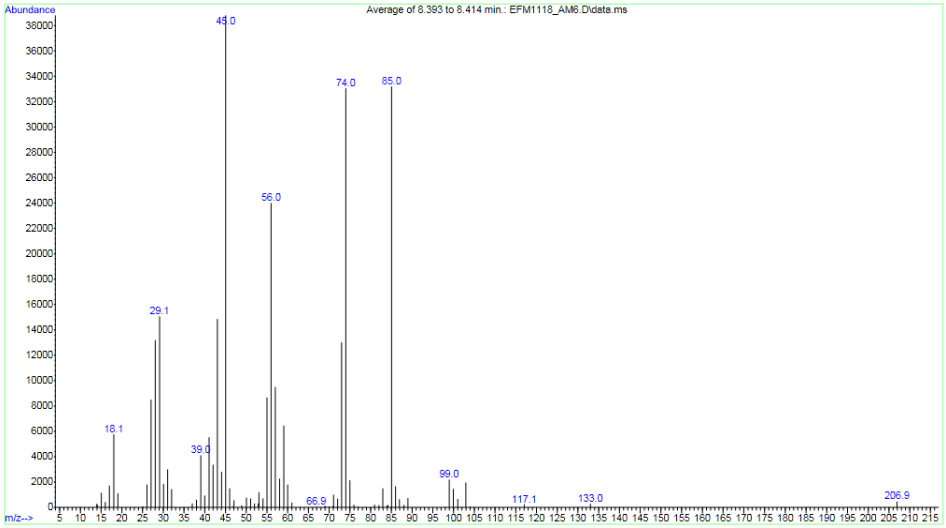

Figure S18 – M.S. fragmentation pattern of the compound associated to Peak #11 in Figure S1-B and to Peak #17 in Figure S2-B.