Electronic Supplementary Information (ESI)

Conversion of Levulinic Acid into γ-Valerolactone Using $Fe_3(CO)_{12}$: Mimicking a Biorefinery Setting by Exploiting Crude Liquors from Biomass acid Hydrolysis.

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Experimental Section: The reagents: triirondodecacarbonyl, iron(0) pentacarbonyl, triphenylphosphine, imidazole, pyridine, formic acid (spectroscopic grade) levulinic acid and gamma-valerolactone were purchased from Sigma-Aldrich and used without further purification. The crude liquor from sugarcane bagasse acid hydrolysis was kindly provided by Brazilian Bioethanol Science and Technology Laboratory (CTBE). The initial concentration of levulinic and formic acids in the liquor were 0.87 and 0.95 mmol respectively. The complex $[Fe(CO)_3(PPh_3)_2]$ was synthetized and characterized as reported in the literature.[24] Deionized water (Milli-Q system) was used throughout the experiments. The reactions were conducted in stainless-steel (316 L alloy) homemade reactors (Volume = 10 mL) equipped with Vitton O-ring for sealing at 180°C for 15h period. For the reactions, the solution total volume was 5 mL. The reactors were heated using a mechanical stirrer coupled with an immersion thermocouple for temperature control. Teflon magnetic stirrers were introduced in the reactors for solution stirring during the reaction period. HPLC-MS analyses were conducted in a Shimadzu Prominence HPLC system coupled with a Bruker Esquire 4000 ion-trap mass spectrometer, using electrospray (ESI) as ion source. Chromatographic conditions: Shim-pak VP-ODS (C-18, 250L × 4.6) column. Mobile phase: (A) Water (0.1% Formic Acid) and (B) Acetonitrile (0.1% Formic Acid). Linear Gradient: 0-2 min, 5-95% B in A; 2-20 min, 80-20% B in A; 20-23 min, 80-20% B in A; 23-27 min, 5-95% B in A; 27-30 min, 5-95% B in A. ESI-MS conditions: temperature: 365°C; Dry Gas: 10 L min-1, Nebulizer Pressure: 50 psi, m/z range: 50-500. For the GVL quantification, the solution from the reactor were filtrated in HPLC filtering membranes (Chromafil, Macherey-Nagel) and doped with desired amounts of GVL standard. The obtained Total Ion Chromatograms

(TIC) were treated in the mass spectrometer software for the obtaining the Extracted Ion Chromatogram (EIC) for GVL (m/z = 101.8). Using the areas of the GVL EIC peaks, the samples were fortificated with desired aliquots of GVL standard solution.

Samples preparation for the reaction: 1 mmol of LA (116mg = 100 μL), 4 mmol of FA (181 mg = 150 μL), 4 mmol of base (py: 316 mg = 320 μL / ImN: 272 mg) were added in the reactor. Milli-Q water was added for a V_T = 5.0 mL. This solution was sonicated for 10 min, the desired amount of catalyst added (according Table 1) and the reactor was immediately sealed. The reactors were progressively heated until the desired temperatures (Table 1).

GVL quantification: GVL was quantified in the samples by running the Total Ion Chromatogram (TIC) and then using the Exctracted Ion Chromatogram (EIC) in the m/z = 100.8). The quantification was performed by sample fortification. The area of the peak at retention time (r_t) 14.8 min (relative to GVL and confirmed by the injection of GVL standard) was calculated in the samples, immediately after the reaction and then fortificated with GVL. Using the Equation 1:

$$C_s = [(A_s + C_{ds}) / (A_T)] / (1\text{-}A_s) \quad \textbf{(1)}$$

Where: C_s: GVL sample concentration; C_{ds}: GVL sample concentration + GVL fortification concentration; As: area of GVL peak in the EIC on the r_t = 14.8 min in each sample. A_T: area of sample fortificated with GVL peak in the EIC on r_t = 14.8 min for each sample.

The samples analyses were conducted as follows: 480μL of filtered reactor solution were fortificated with 20 μL of GVL solution prepared using a commercial GVL standard (C_{GVL} = 0.20 mol L^{-1}), giving a concentration of GVL in the sample of C_{ds} = 8mmol L^{-1}. The EIC were obtained and the A_T was calculated. The same sample without fortification was injected, substituting the 20 μL of GVL for 20 μL of Milli-Q water, to

keep the dilution factor and the A_s was calculated. With the $C_{ds,}$ A_T and A_s values and using the equation 1, the concentration of GVL in the samples (C_s) were calculated.

For the crude liquor treated with activated charcoal, the samples were diluted 10X before the injection in the LC-ESI-MS. Consequently, the final C_s obtained was corrected by a factor of 10.

Table S1 - Conversion of LA to GVL using selected Fe(0) complexes as precursor catalysts.

Entry[a]	**Catalyst**	**Conc. mol%**	**Base**	**Temp °C**	**Time h**	**FA (equiv.)**	**GVL**[c] **%**
1	$[Fe(CO)_5]$	1	py	150	15	4	<5
2	$[Fe(CO)_5]$	4	py	150	15	4	<5
3	$[Fe(CO)_5]$	12	py	150	15	4	<5
4	$[Fe_3(CO)_{12}]$	1	py	150	15	4	<5
5	$[Fe_3(CO)_{12}]$	12	py	150	15	4	9
6	$[Fe(CO)_3(P)_2]$	1	py	150	15	4	<5
7	$[Fe(CO)_3(P)_2]$	4	py	150	15	4	<5
8	$[Fe(CO)_3(P)_2]$	12	py	150	15	4	<5
9	$[Fe(CO)_3(P)_2]$[b]	1	py	150	15	4	<5
10	$[Fe(CO)_3(P)_2]$[b]	4	py	150	15	4	<5
11	$[Fe(CO)_3(P)_2]$[b]	12	py	150	15	4	<5
12	$[Fe_3(CO)_{12}]$	4	Et_3N	150	15	4	<5
13	$[Fe_3(CO)_{12}]$	4	DBU	150	15	4	<5
14	$[Fe_3(CO)_{12}]$	4	ImN	180	15	1	6
15	$[Fe_3(CO)_{12}]$	4	ImN	180	15	2	26

[a] Conditions: aqueous solution of LA (1 mmol), FA (4 mmol), base (4 mmol); [b] catalyst generated *in situ* by the addition of 2.5 equivalents of P = PPh_3 regarding to Fe; [c] yields determined by HPLC-MS (exctracted Ion Chromatogram, EIC, with sample fortification. See ESI). ImN = imidazole; py = pyridine.

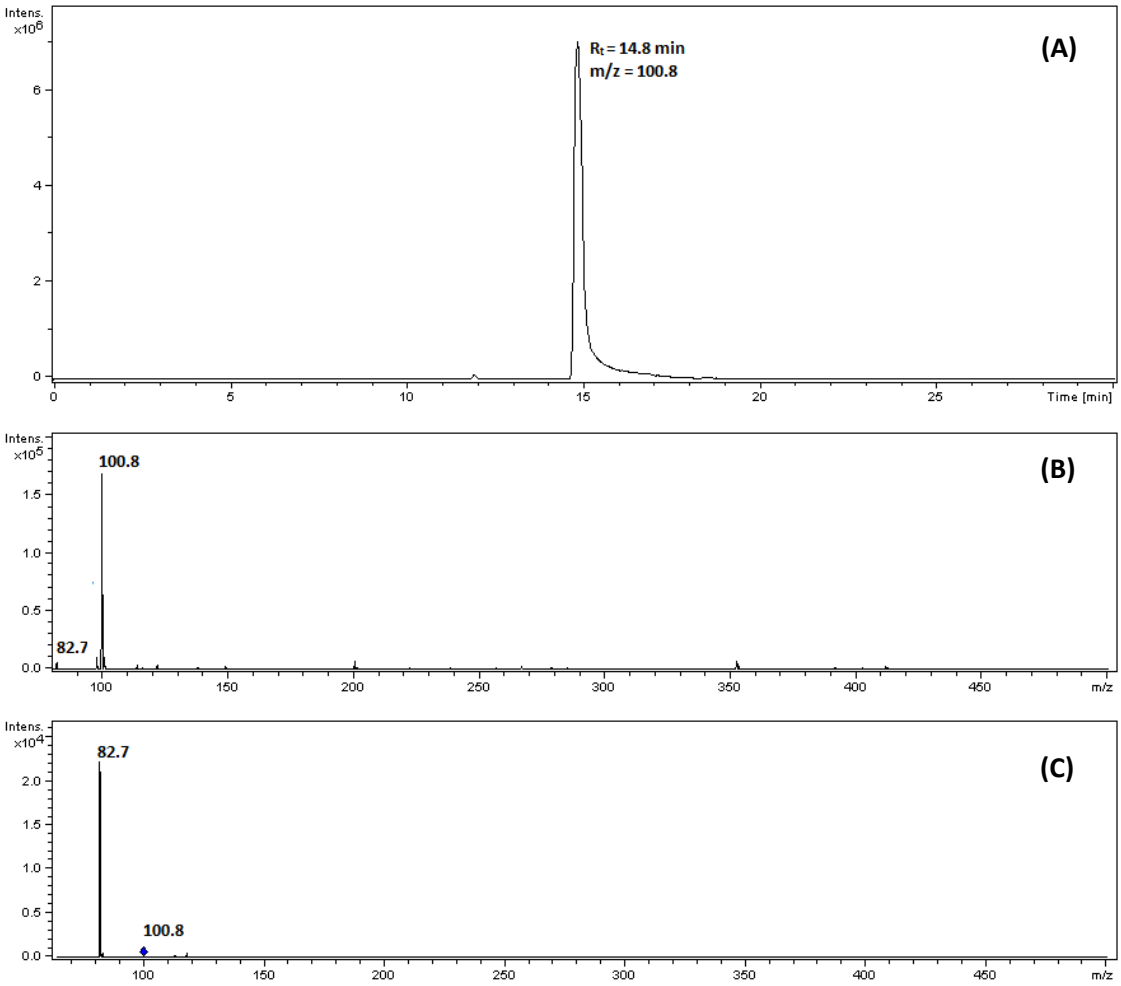
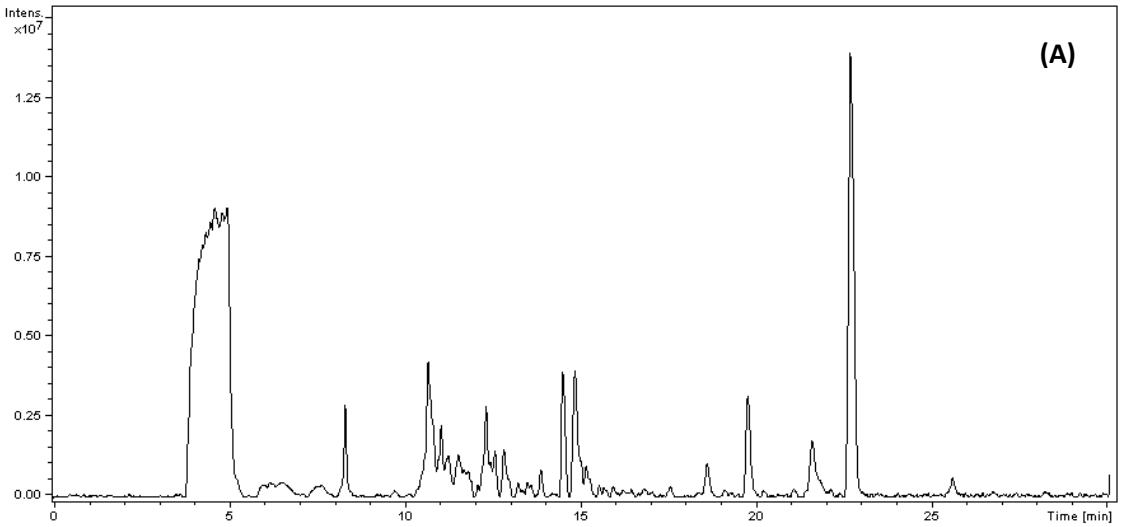


Figure S1. (A)EIC (m/z = 100.8) for GVL standard (C_{GVL} = 5.0×10^{-4} mol L^{-1}); (B) Mass spectrum for the R_t = 14.8 min (GVL). (C) MS/MS for the m/z = 100.8.



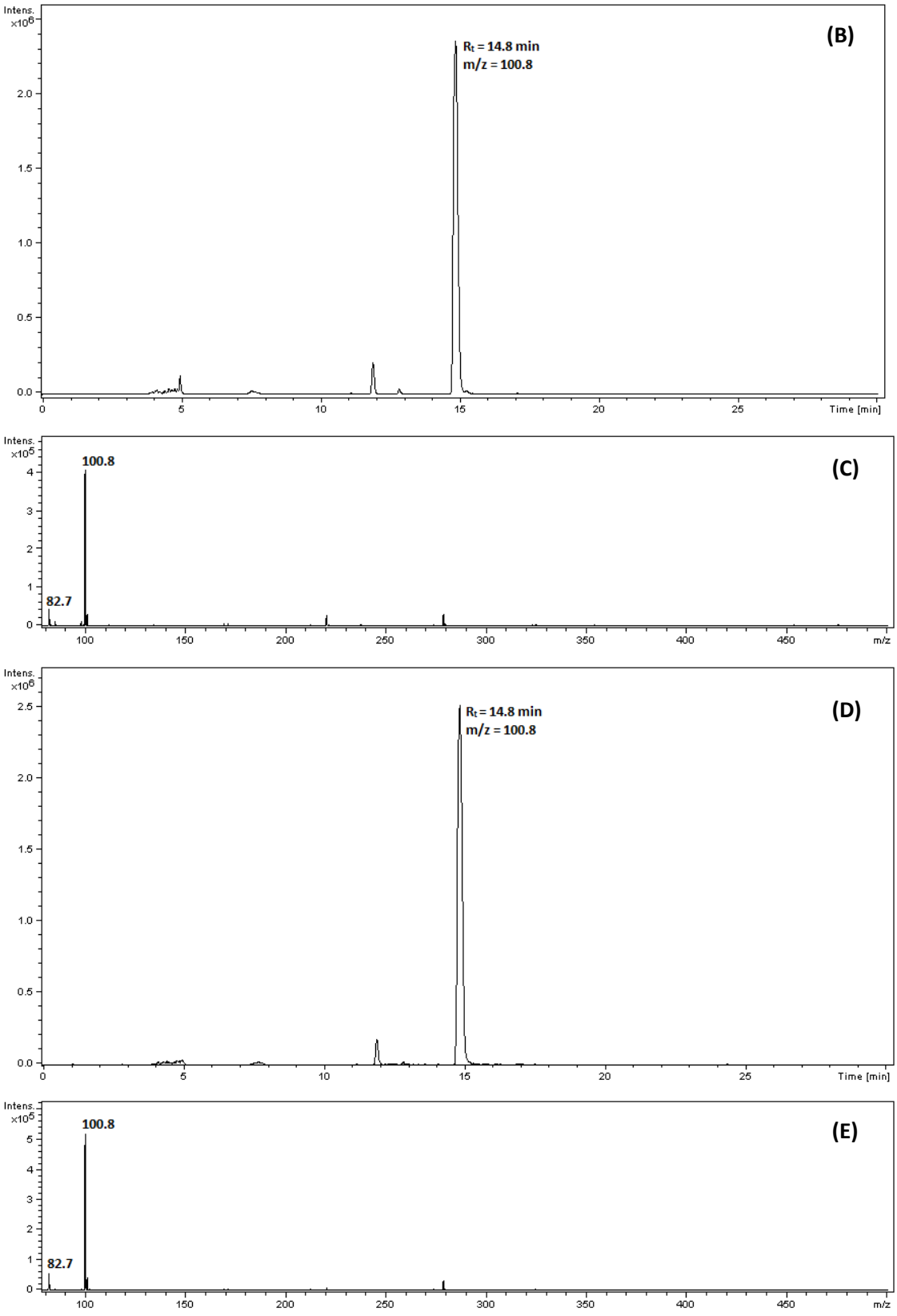
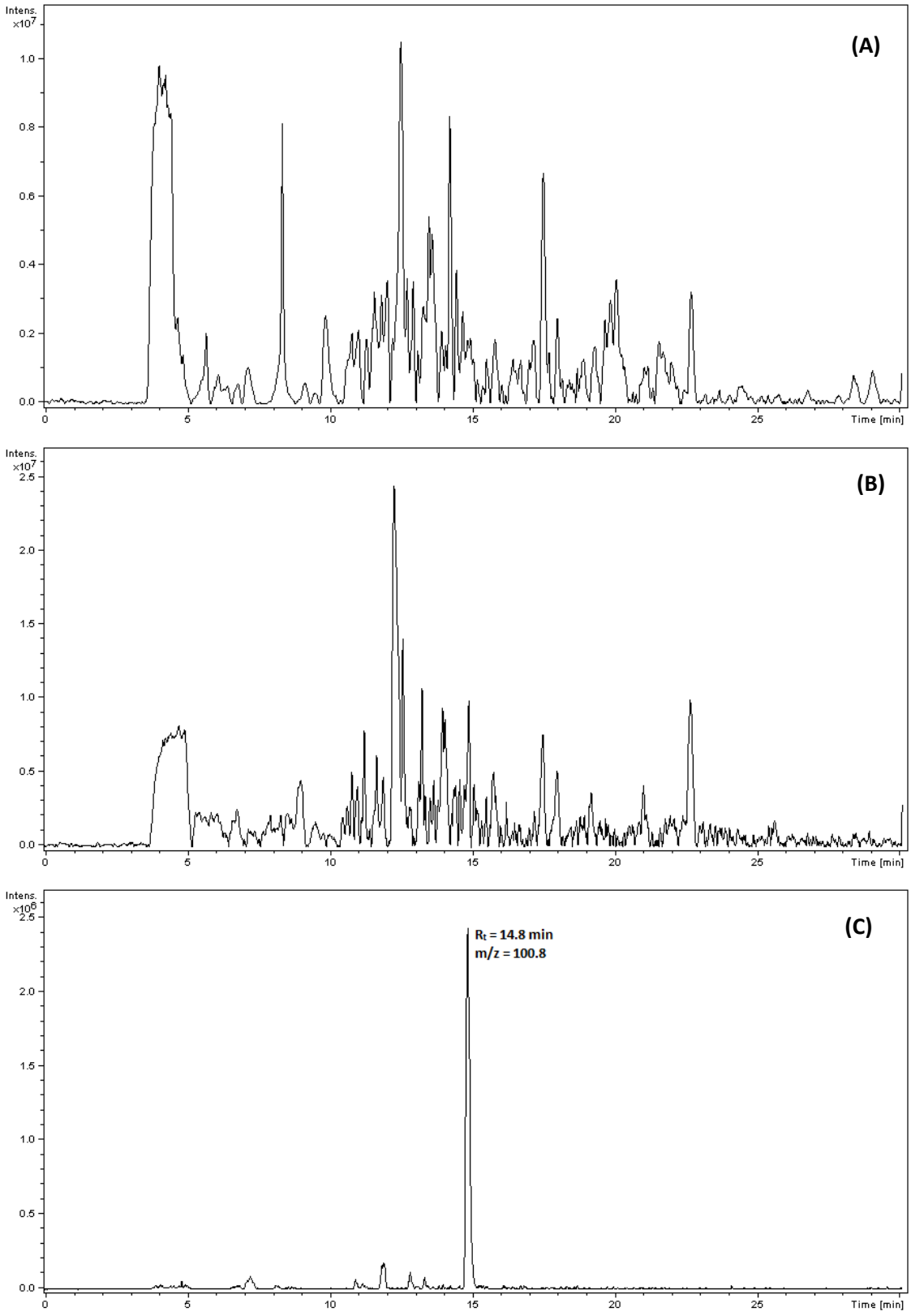


Figure S2. (A) TIC for the conversion of LA in GVL (conditions: entry **5**, Table 1 in manuscript); (B) EIC (m/z = 100.8) for (A). (C) Mass spectrum for the R_t = 14.8 min

(GVL) in the spectrum (B); (D) EIC (m/z = 100.8) for the (A) doped with GVL standard; (E) Mass spectrum for the R_t = 14.8 min (GVL) in the spectrum (D).



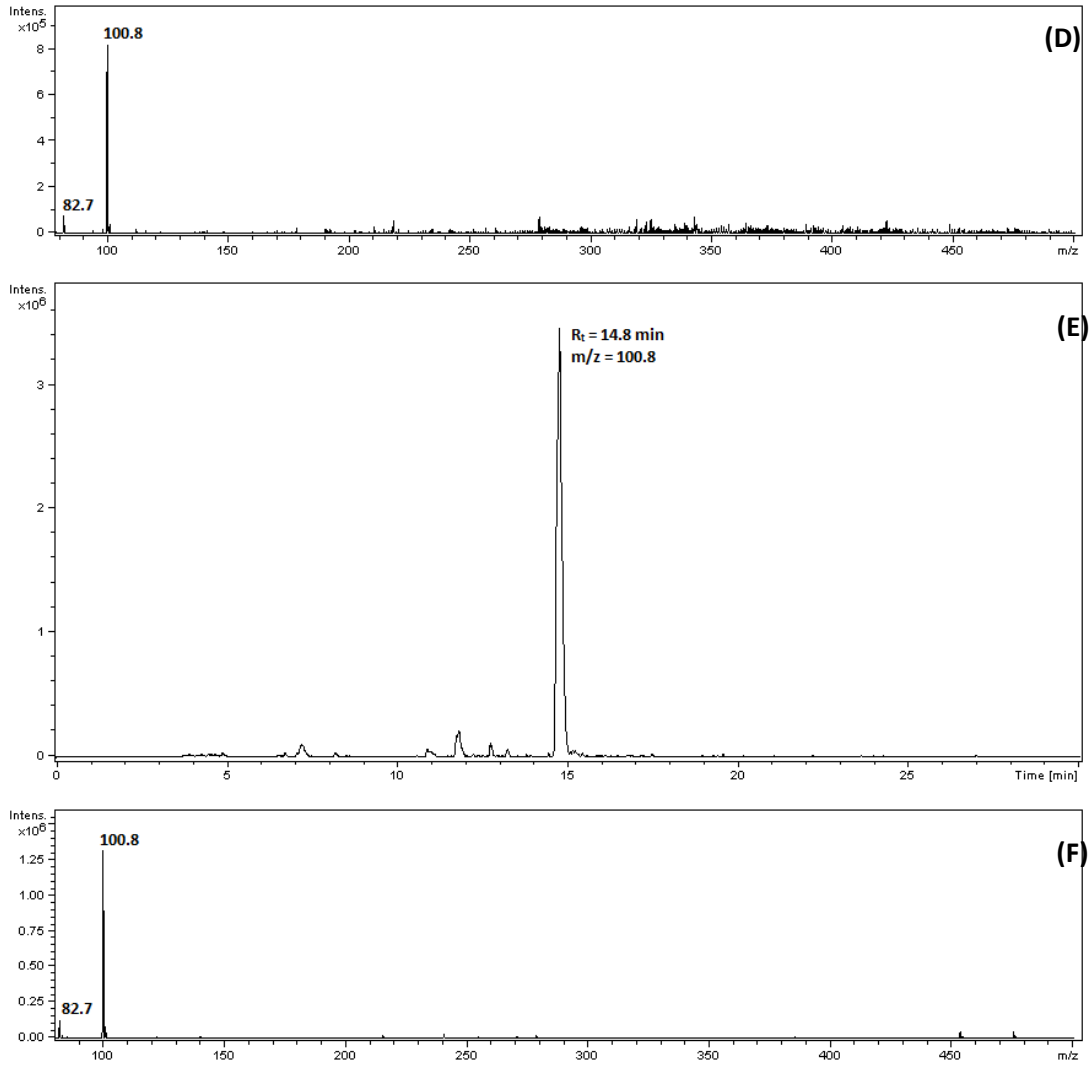
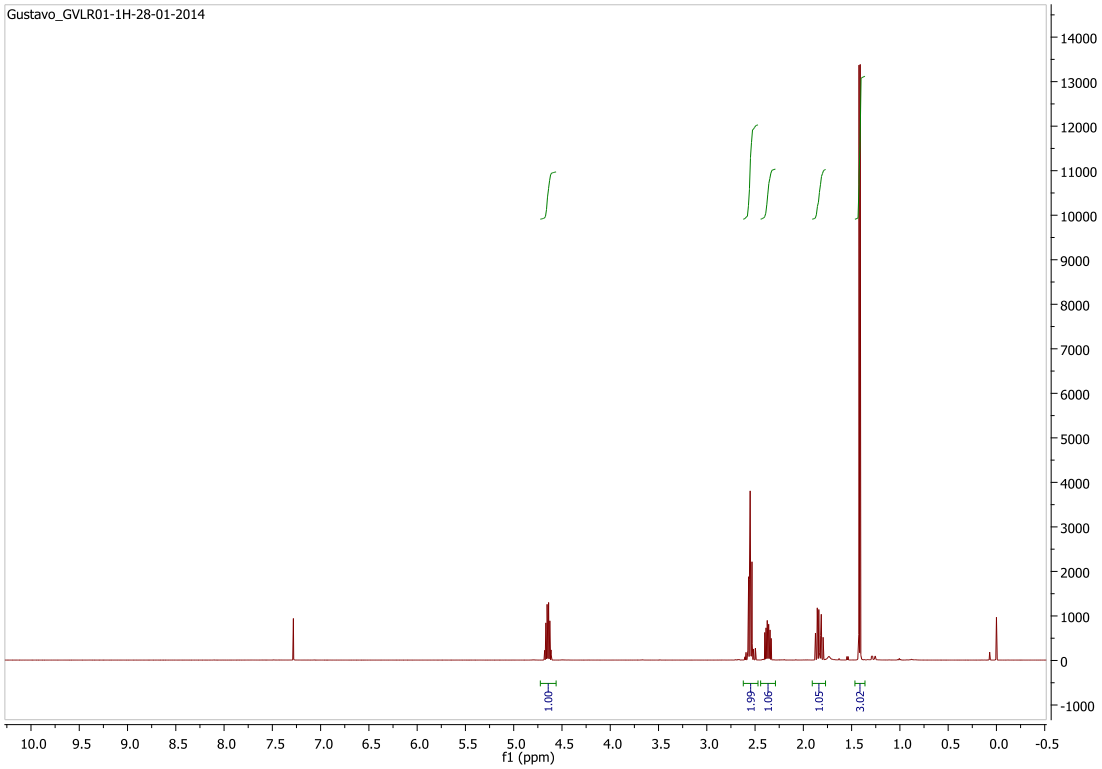


Figure S3. (A) TIC for the active charcoal treated crude liquor; (B) TIC for the active charcoal treated crude liquor after the reaction (conditions: entry 5, Table 1, 10 equiv. of base instead of 4 equiv.); (C) EIC (m/z = 100.8) for (B); (D) Mass spectrum for the R_t = 14.8 min (GVL) in the spectrum (C); (E) EIC (m/z = 100.8) for the (B) doped with GVL standard; (F)Mass spectrum for the R_t = 14.8 min (GVL) in the spectrum (E).

GVL isolation: aiming to obtain a NMR spectrum of GVL from the reaction, the following procedure was performed: GVL was extracted from the water solution with 5 portions of ethyl acetate. Then, the organic phase was dried with sodium sulphate, concentrated in a rotary evaporator, and purified by flash column chromatography, using silica gel (eluent: ethyl acetate/hexane 1:1). The purified product was dried under vacuum and the NMR spectrum was then collected in deuterated chloroform.

^{1}H NMR SPECTRA OF ISOLATED GVL ($CDCl_3$, 500 MHz)



^{13}C NMR SPECTRA OF ISOLATED GVL ($CDCl_3$, 125 MHz)

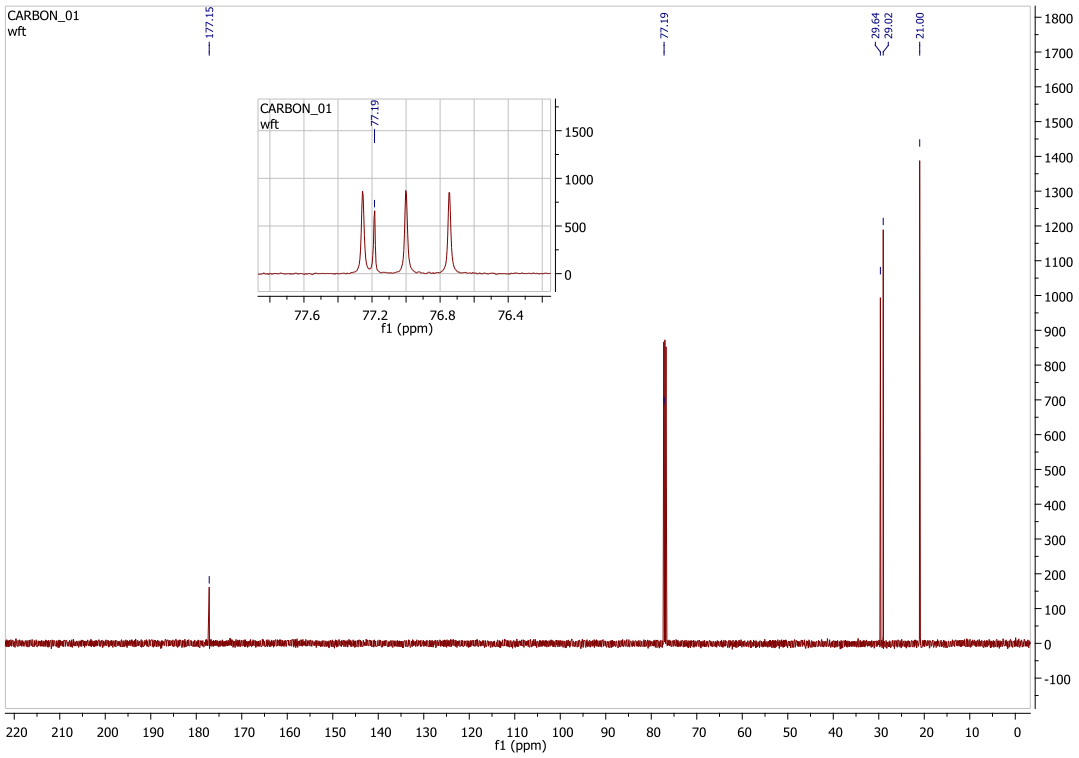


Figure S4. NMR spectra of isolated GVL

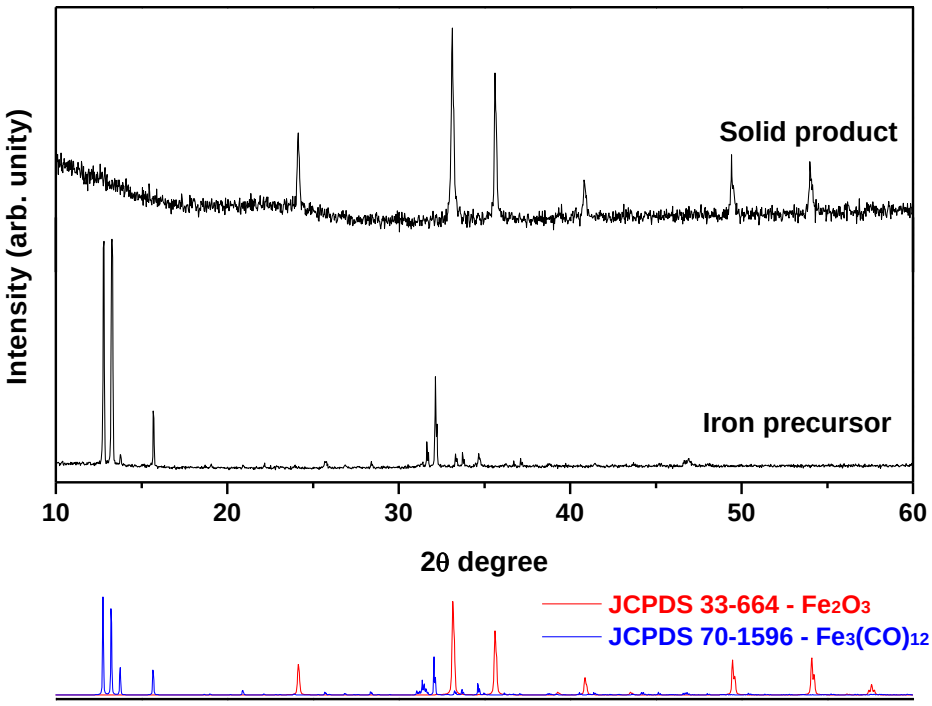


Figure S5. X-rays analysis of the solid obtained at the end of the reaction after centrifugation and of $[Fe_3(CO)_{12}]$.

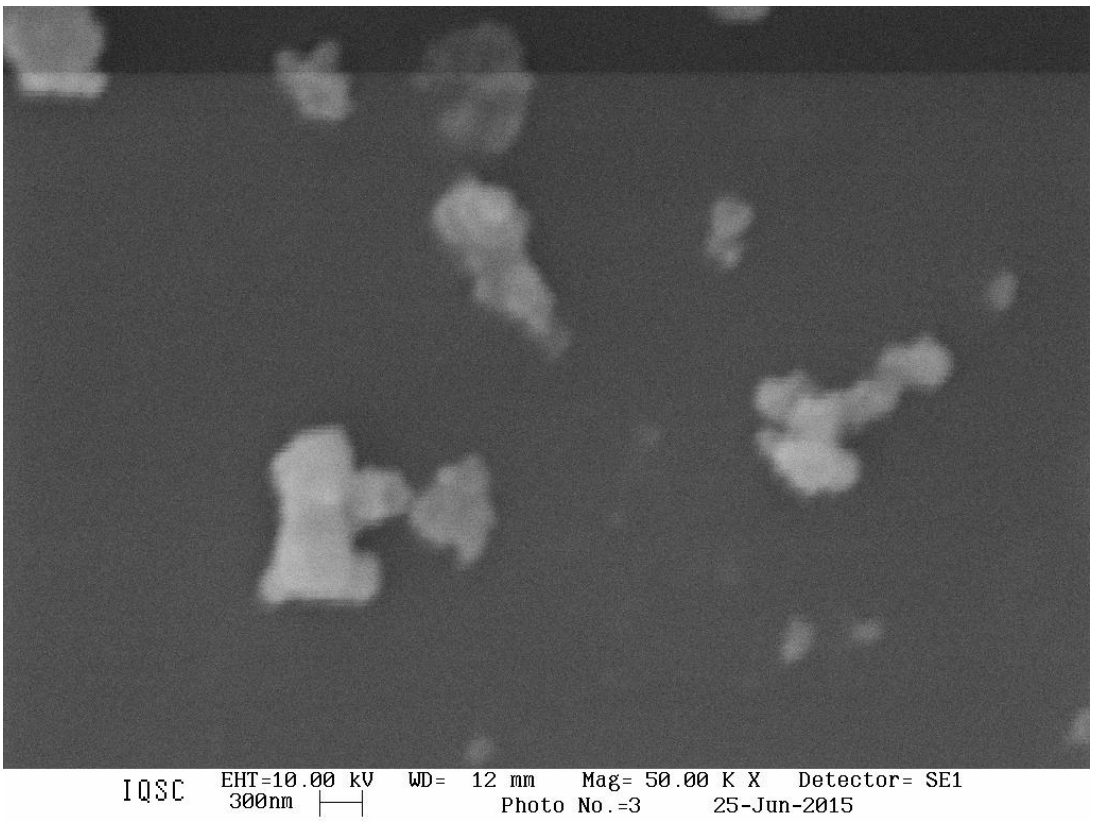


Figure S6. MEV of Fe_2O_3 obtained at the end of the reaction after centrifugation.