

## A Choline Chloride/DMSO solvent for the direct synthesis of diformylfuran from carbohydrates in the presence of heteropolyacids

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### Characterization of the Mo-Keggin catalysts

#### I- FTIR analysis

FTIR spectra of samples present the four characteristic peaks of the Keggin structure observed in the regions 1060-1080, 1000-960, 840-910, 800-760 respectively. Those peaks are attributed to  $\nu(\text{P}-\text{O}_a)$ ,  $\mu(\text{Mo}=\text{O}_d)$ ,  $\mu(\text{Mo}-\text{O}_b-\text{Mo})$ ,  $\mu(\text{Mo}-\text{O}_c-\text{Mo})$ . The vibration mode and position of the peaks is sensitive to the hydration degree of catalysis.<sup>1</sup>

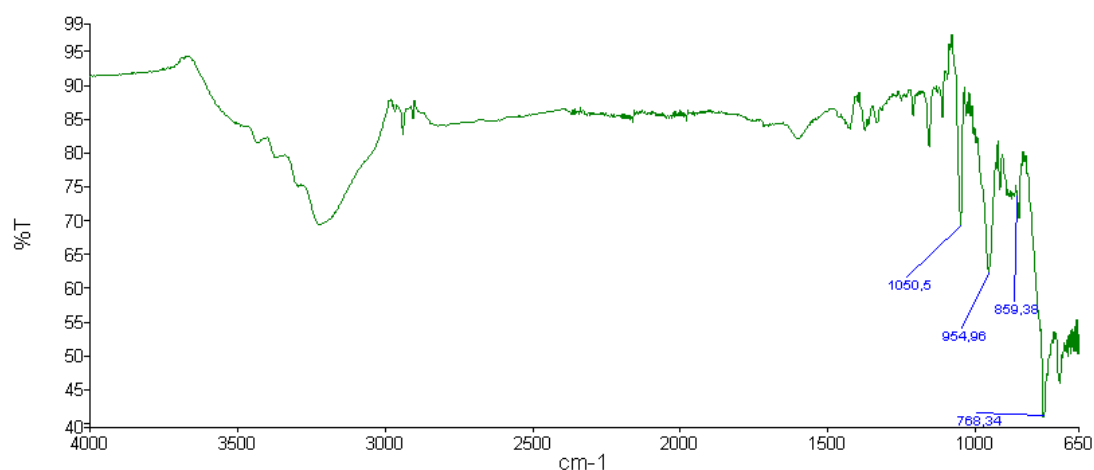


Figure S1. FTIR spectra of HPMo catalyst

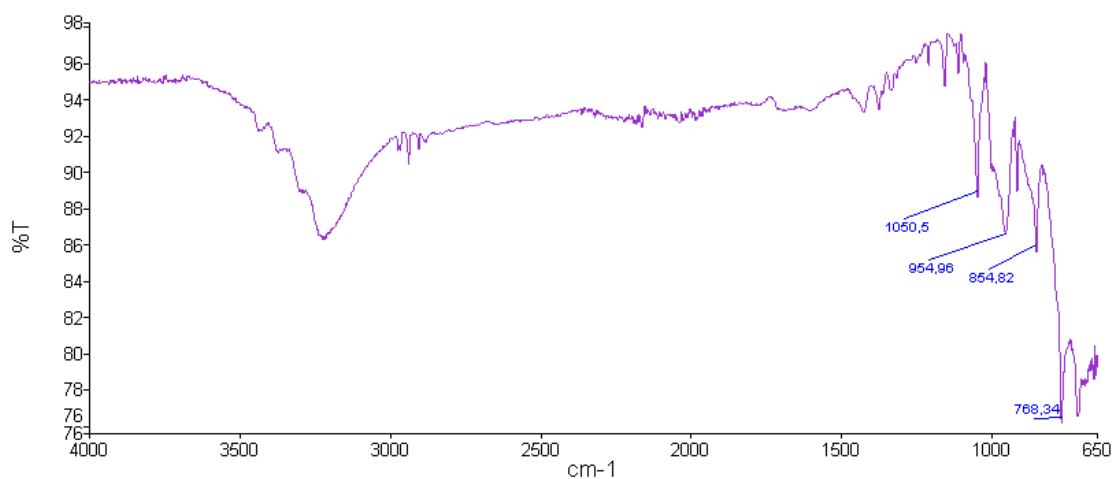


Figure S2. FTIR spectra of HPMoV.

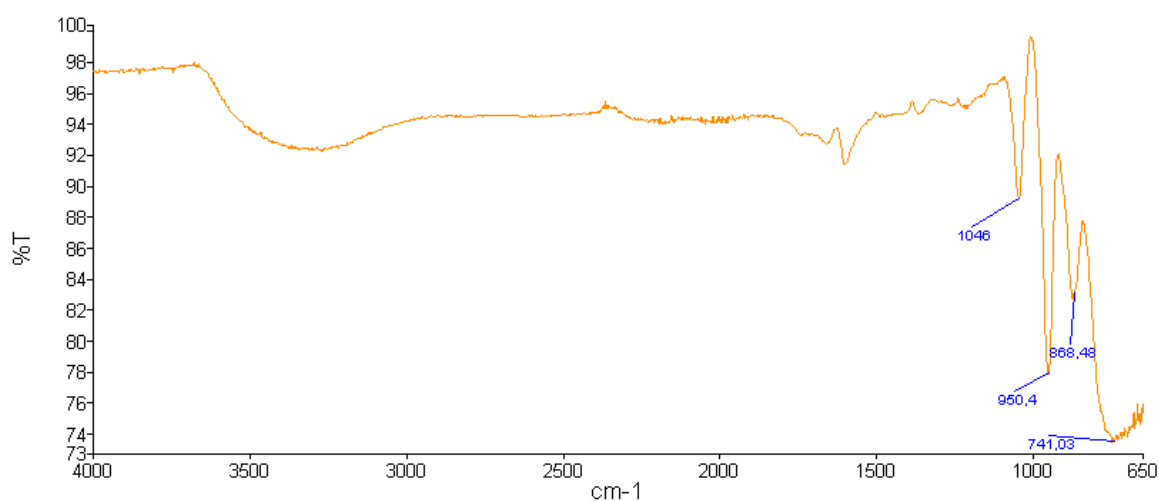


Figure S3. FTIR spectra of HPMoV<sub>2</sub>

## II- Nitrogen physisorption: Surface area

Measurements of the adsorption of nitrogen at 77°K provide data for the calculation of the surface area by use of the Brunauer-Emmett-Teller (BET) theory. Evidently these solid acids have little or no porosity, the BET surface areas as calculated from the adsorption of nitrogen are low (of the order of 5 m<sup>2</sup>/g or less).<sup>2</sup> Specific surface areas of HPMo, HPMoV and HPMoV<sub>2</sub> are 2, 3 and 1 m<sup>2</sup>/g respectively.

## III- XRD analysis

Usually, heteropoly acids crystallize with a large number of water molecules depending on solution acidity and temperature.<sup>3</sup> At low temperature, highly hydrated compounds (29-30H<sub>2</sub>O) are observed. These crystals are not stable at room temperature and loose water quickly, giving rise to 13-14H<sub>2</sub>O hydrates, generally with poor crystallinity due to the dehydration process.

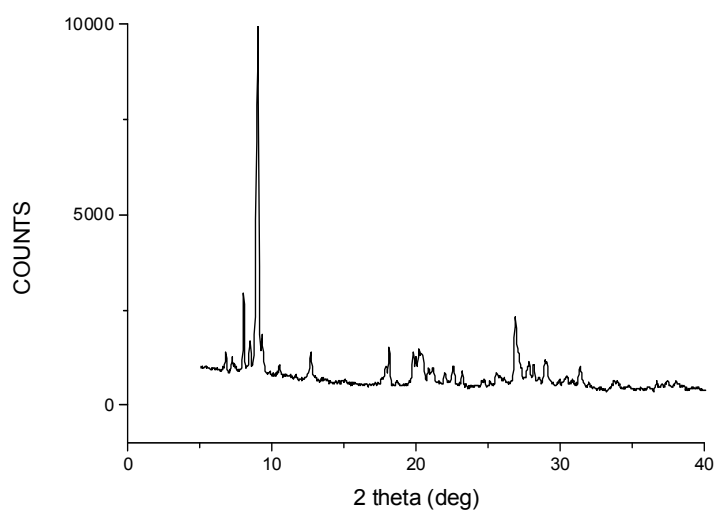


Figure S4. XRD analysis of HPMo catalyst

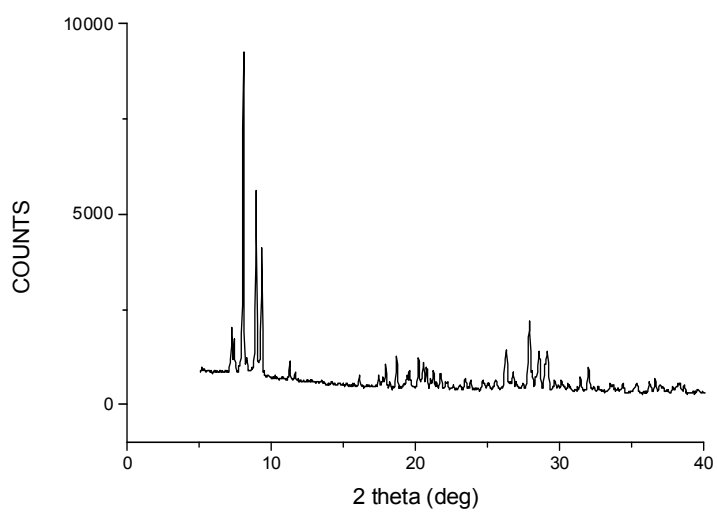


Figure S5. XRD analysis of HPMoV catalyst

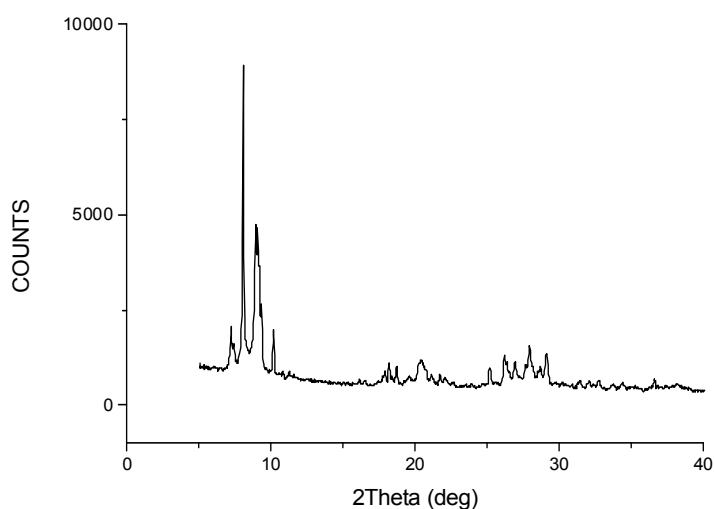


Figure S6. XRD analysis of HPMoV<sub>2</sub> catalyst

#### IV Thermal analysis TGA-TDA)

Substitution of one or two atoms of vanadium for molybdenum in the H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> Keggin unit induces a noticeable change in its dehydration properties.<sup>4</sup>

Comparing the three samples, the thermal analysis indicate that the temperature of the endothermic peak maximum associated with the loss of constitutional water decreases with the increase of the amount of vanadium introduced in the polyanion. For HPMo, a sharp exothermic peak centered at 437.51°C is observed. It is associated with the irreversible destruction of the Keggin units in O<sub>2</sub> flow. Another peak, not accompanied with a loss of weight, is observed at 520.67°C, probably due to the rearrangement of the oxide structure resulting from the first step of the Keggin unit decomposition. HPMoV exhibits a broad single exothermic peak at 454°C associated with the destruction of the Keggin unit in a single step. For HPMo V<sub>2</sub>, the thermal analysis indicates overlapping exothermic peaks at temperature 428°C a decomposition of the Keggin unit.

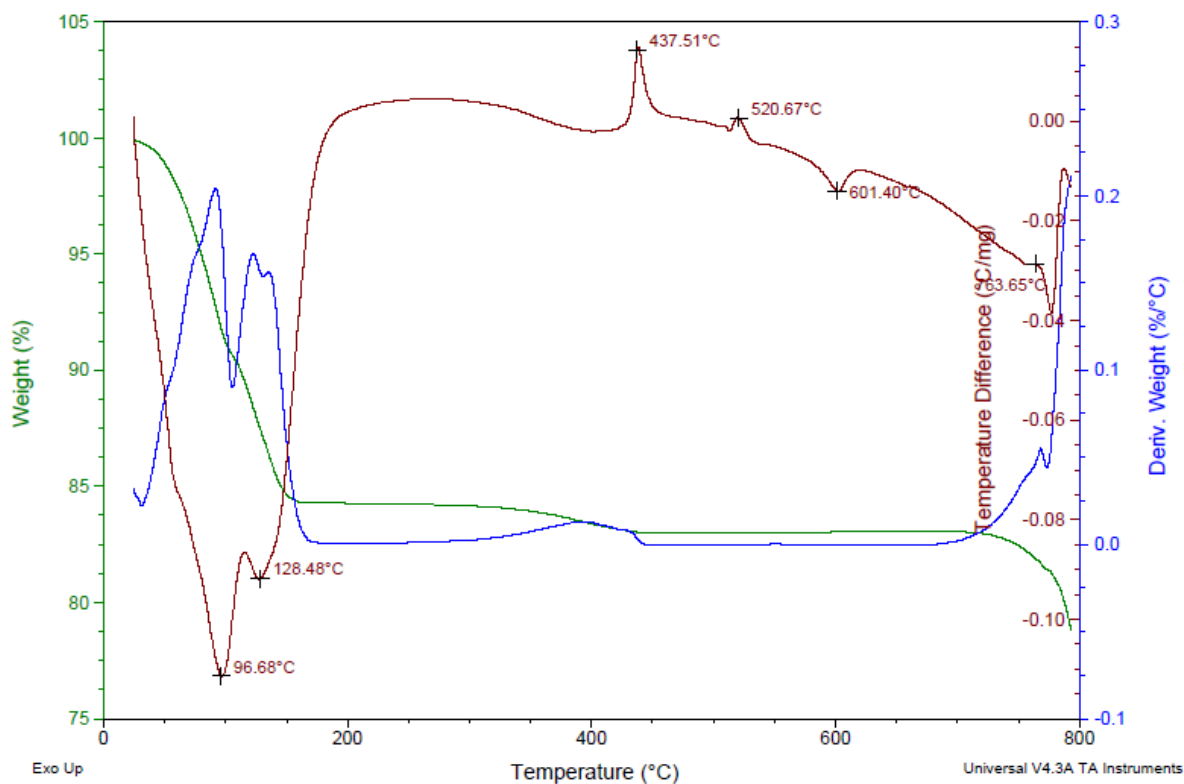


Figure S7. Thermal Analysis of HPMo catalyst

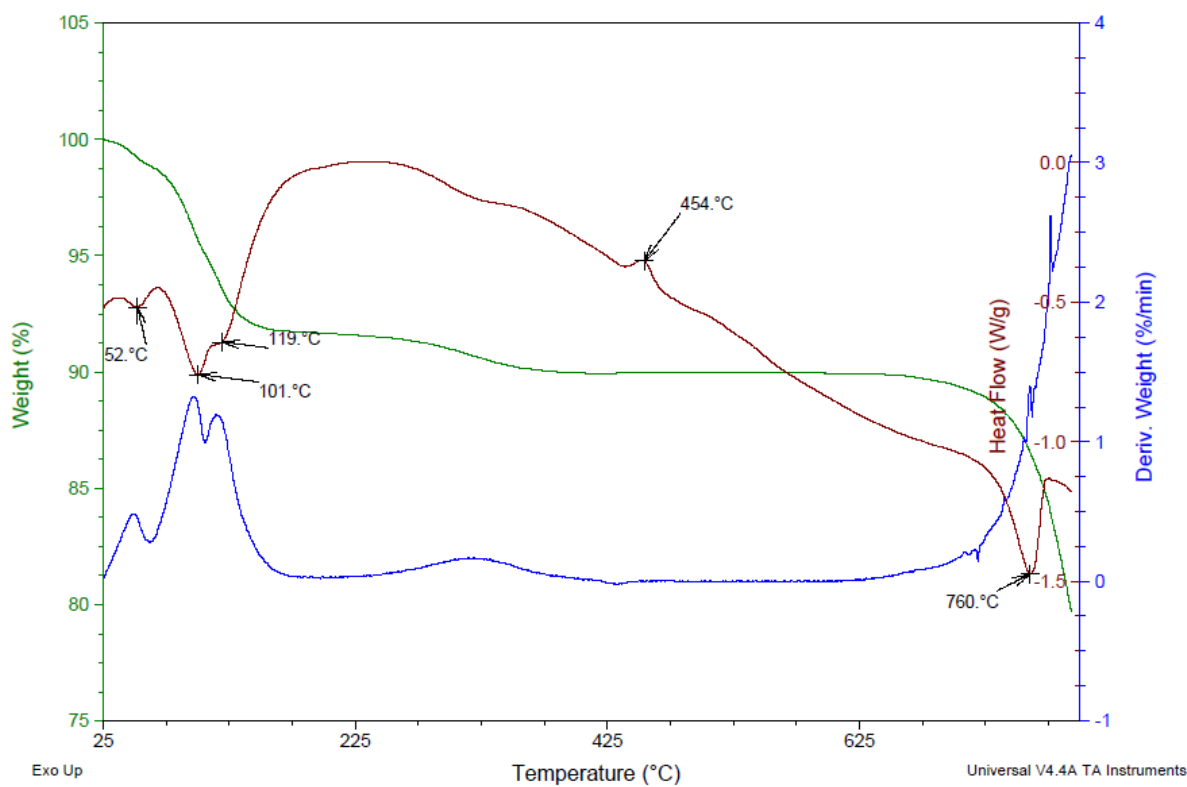


Figure S8. Thermal Analysis of HPMoV catalyst

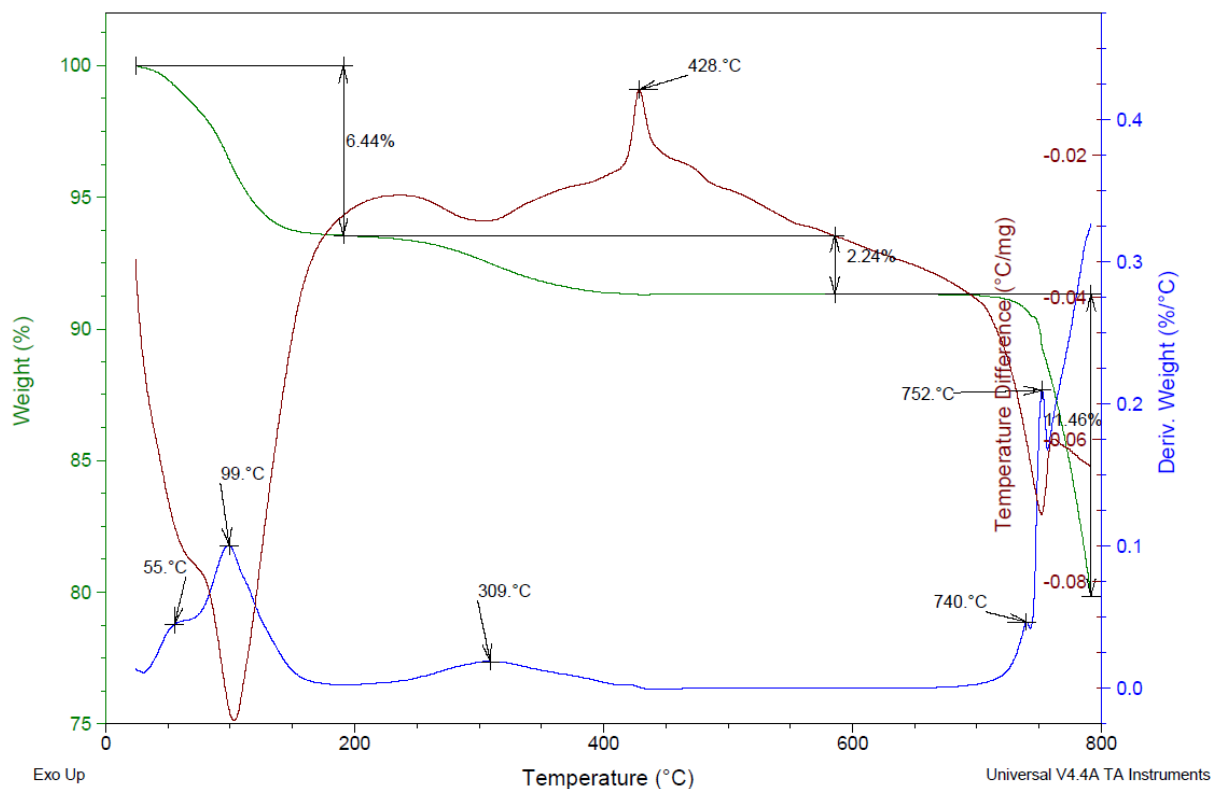


Figure S9. Thermal analysis Analysis of HPMoV<sub>2</sub> catalyst

**Catalytic performance of Mo-Keggin catalysts**

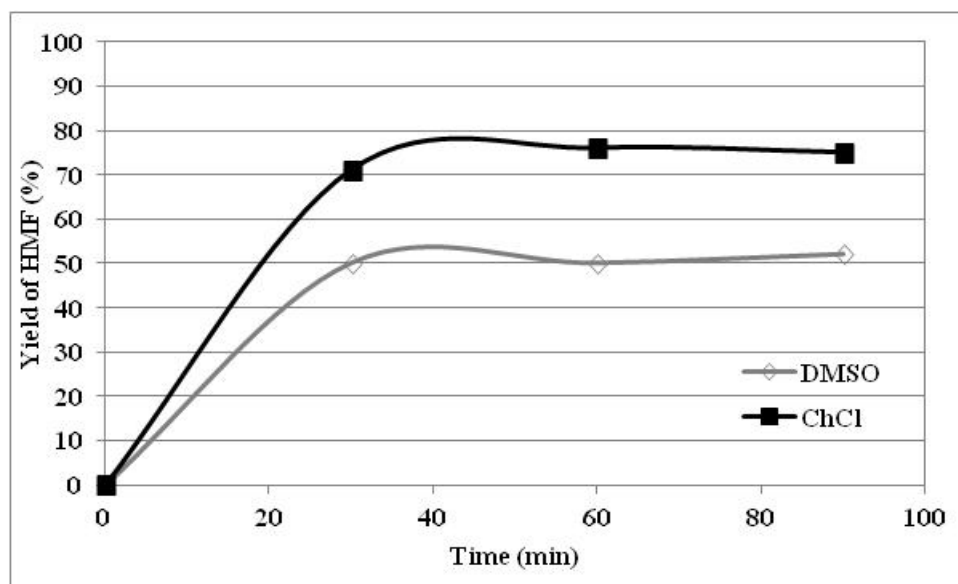


Figure S10: Dehydration of 20 wt% of fructose in the presence of 7 wt% of HPMoV at 120°C. Effect of the nature of the solvent.

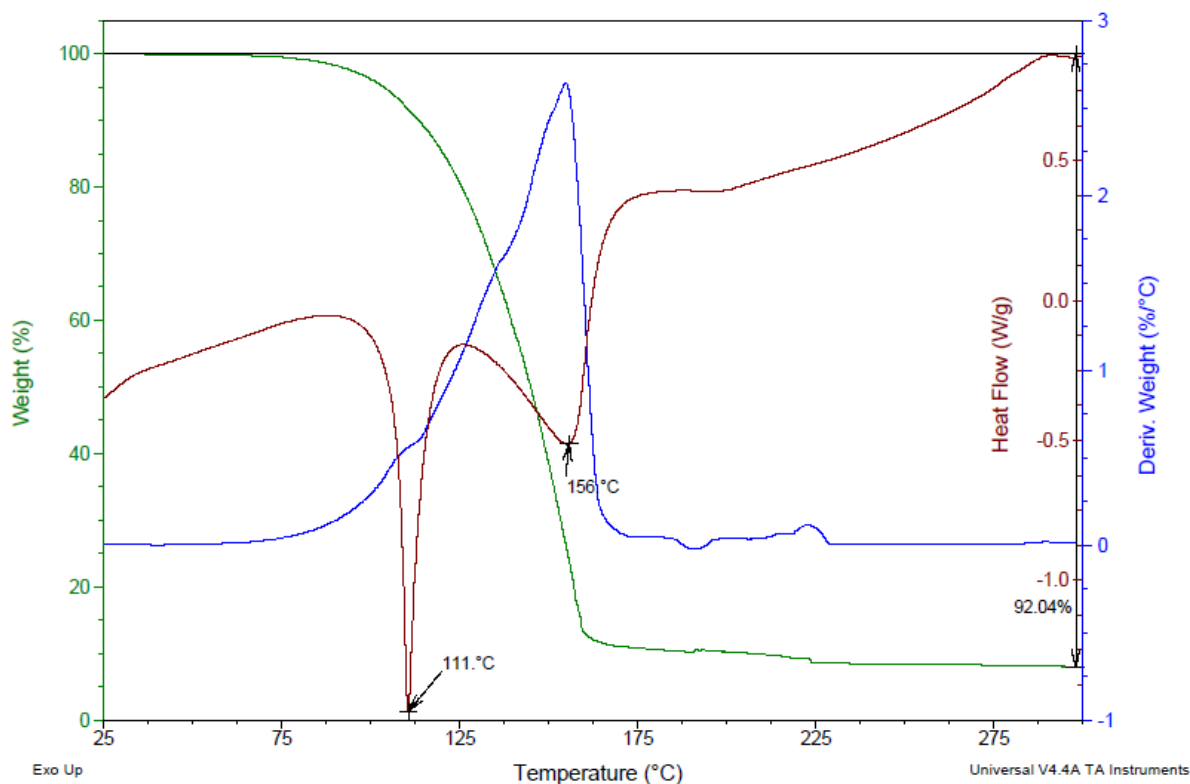


Figure S11. Thermal analysis of DFF

### Mechanism pathway

The mass spectrometry was carried out using a quadripole PRISMA 200 BALZERS/PFEIFFER, 70 eV.

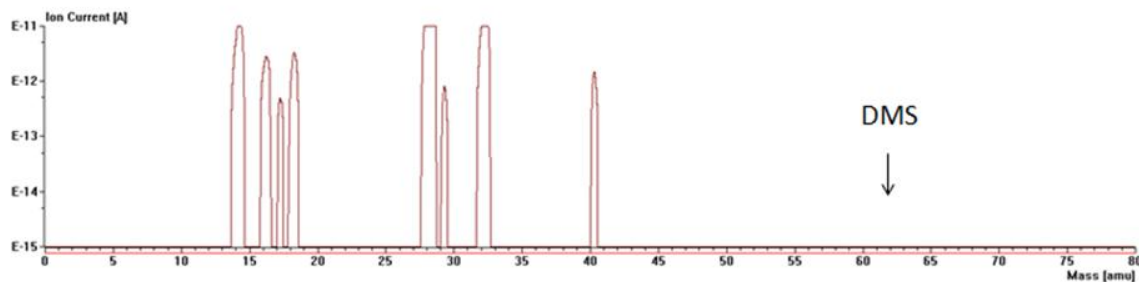


Figure S12. Analysis of the compounds released during the oxidation of fructose in the presence of ChCl/DMS (65/35) without catalyst at 120°C under air flow. DMS = dimethylsulfide

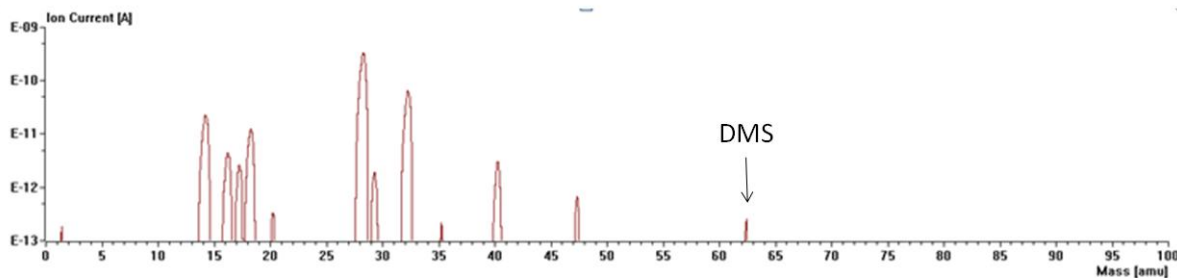


Figure S13. Analysis of the compounds released during the oxidation of fructose in the presence of ChCl/DMS (65/35) and 7 wt% of HPMoV at 120°C under air flow. DMS = dimethylsulfide

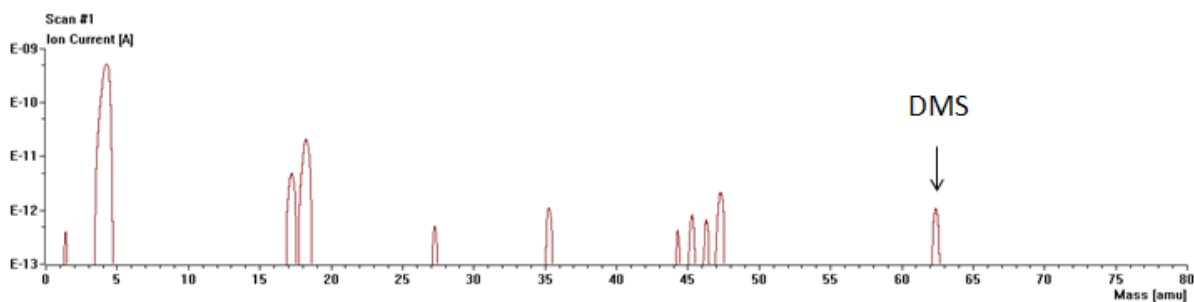


Figure S14. Analysis of the compounds released during the oxidation of fructose in the presence of  $\text{ChCl/DMS}$  (65/35) and 7 wt% of HPMoV at  $120^\circ\text{C}$  under helium flow. DMS = dimethylsulfide

## References

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2. J. B. Moffat, *J. Mol. Cat.*, 1989, **52**, 169.
3. M. Fournier C.Feumi-Jantou, C.Rabia, G.Herve, S. Launey, *J. Mater. Chem.*, 1992, 2, 971.
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