

Supplementary Materials

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p-TSA promoted reaction spectra

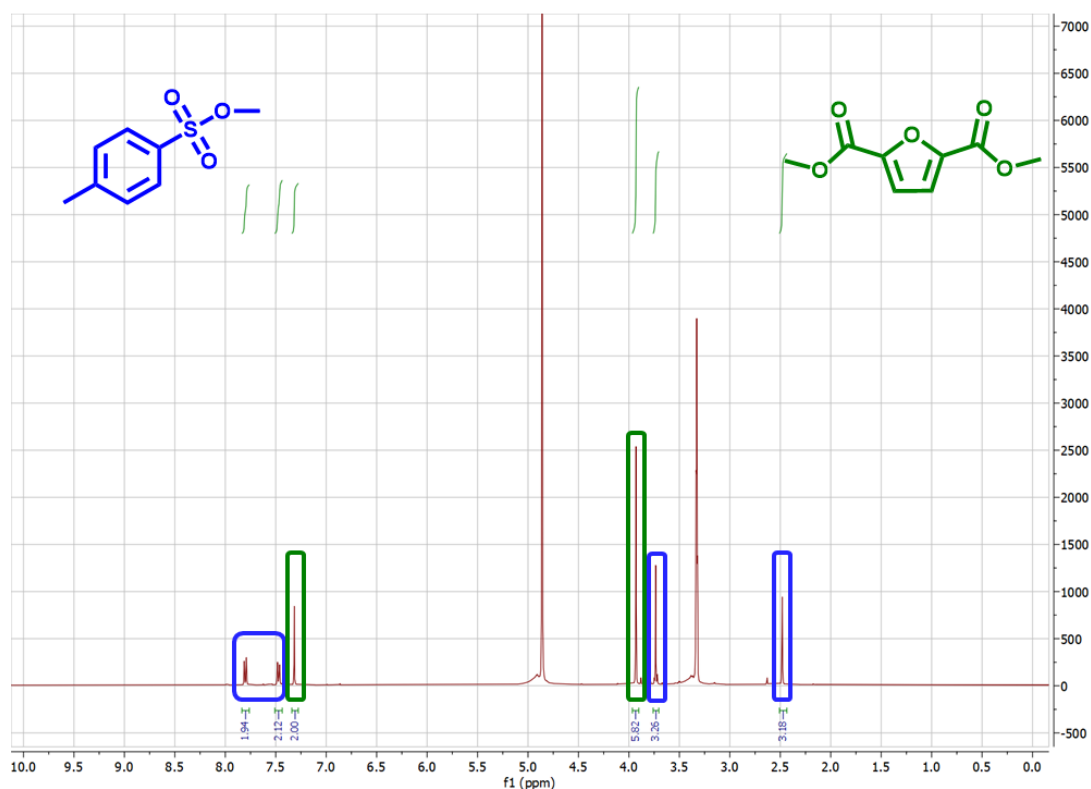


Figure S1. ^1H -NMR (MeOD) spectra of the reaction conducted employing p-TSA. The reaction mixture was purified via silica column chromatography using hexane and ethyl acetate at a ratio of 7:3 as the eluent phase. Methyl-p-TSA and FDME were barely separable.

Effect of reaction time on FDME formation

Table S1. Effect of reaction time on FDME formation.^a

#	time (h)	Pressure (Bar)	DMC (mL)	Yield ^b (%)
1	1	22	35	30
2	2	25	35	54
3	3	30	35	56
4	4	31	35	59
5	6	50	35	61
6	8	50	35	68
7	17	60	35	70

^a Reaction conditions: 1.0 g of galactaric acid, 0.95 g (50% mol.) of $\text{Fe}_2(\text{SO}_4)_3$ in 35 mL of DMC in an autoclave at 200 °C under magnetic stirring (500 rpm). ^b Isolated yield through a flash silica column chromatography with a mixture of hexane and ethyl acetate at a ratio of 7:3 as the eluent phase and N_2 flow.

Additional reactions

As galactaric acid is insoluble in DMC at room temperature, some trials were conducted to improve its solubility by adding tetraethylammonium bromide (TEAB) and DMSO as co-solvents of the reaction (Table S1).

Table S2. Additional reactions for FDME synthesis: TEAB, molecular sieves, and the addition of DMSO.^a

Galactaric acid (g)	Additive (g)	Time (h)	Pressure (bar)	Temperature (°C)	Yield (%)
1	TEAB (0.1)	2	25	200	n.d.
1	TEAB (1)	2	30	200	n.d.
1	Molecular sieves	2	18	200	Traces
4	DMSO/DMC (20/35 mL)	8	62	180	n.d.
4	DMSO/DMC (5/35 mL)	8	40	180	n.d.

^a Reaction conditions: 1.0 g of galactaric acid, 0.959 g (50% mol. eq.) of Fe₂(SO₄)₃ in 35 mL of DMC in an autoclave under magnetic stirring (500 rpm).

The addition of TEAB and DMSO did not favor FDME formation. It is possible that the enhanced solubility of galactaric acid in DMC at low temperatures led to the formation of different side products, originated from diverse reaction pathways and not recognizable by NMR. Moreover, to remove the water molecules formed during the triple dehydration reaction with the aim of boosting the reaction thermodynamics toward FDME formation, some trials employing molecular sieves as porous water absorbers were performed. The molecular sieves were not able to withstand the high temperature and pressure generated during the reaction and therefore disintegrated after 2 h of reaction.

Crystallization trials

An alternative to the silica flash column chromatography method for the isolation of FDME was also studied. In this regard, FDME crystallization tests were performed using different solvent mixtures (Table S3).

Table S3. FDME crystallization trials.

#	Solvents	Crystals	Yield ^a (%)
1	Et ₂ O	n.d.	n.d.
2	Hexane/CHCl ₃	Yellow crystals	Traces
3	Hexane/EtAc	n.d.	n.d.
4	THF/Hexane	n.d.	n.d.
5	DCM	n.d.	n.d.
6	H ₂ O/MeOH	Brown crystals	20 (53) ^b
7	TBME	Yellow crystals	traces
8	2-MeTHF	n.d.	n.d.
9	Acetone/Hexane	n.d.	n.d.
10	EtAc	n.d.	n.d.

^a Yield after crystallization. ^b Total yield of FDME crystals and FDME after extraction with H₂O–EtAc.

A mixture of hexane, chloroform, and TBME allowed to obtain traces of FDME as yellow crystals (#2,7; Table S3). However, the best performing crystallization solvent was composed of a mixture of water and methanol, which allowed the isolation of brown FDME crystals directly from the reaction crude (#6; Table S3). Once the reaction mixture was filtered and dried, it was added to 50 mL of boiling water under stirring. Since FDME is normally insoluble in water, a minimum amount of methanol was added until complete dissolution was achieved. Afterward, the solution was gradually cooled to room temperature and then placed in the fridge overnight. The precipitated brown crystals were filtered and dried, providing an isolated yield of approximately 20%. The FDME-rich water was then extracted with EtAc. Upon collection and drying of the organic phase, an additional amount of yellow solid FDME was obtained, providing a total yield of 53%. Despite

the brown color, the FDME crystals analyzed via NMR presented a pure product without any trace of impurities (see Figure S2 and S3).

X-ray powder diffraction (XRPD) analyses

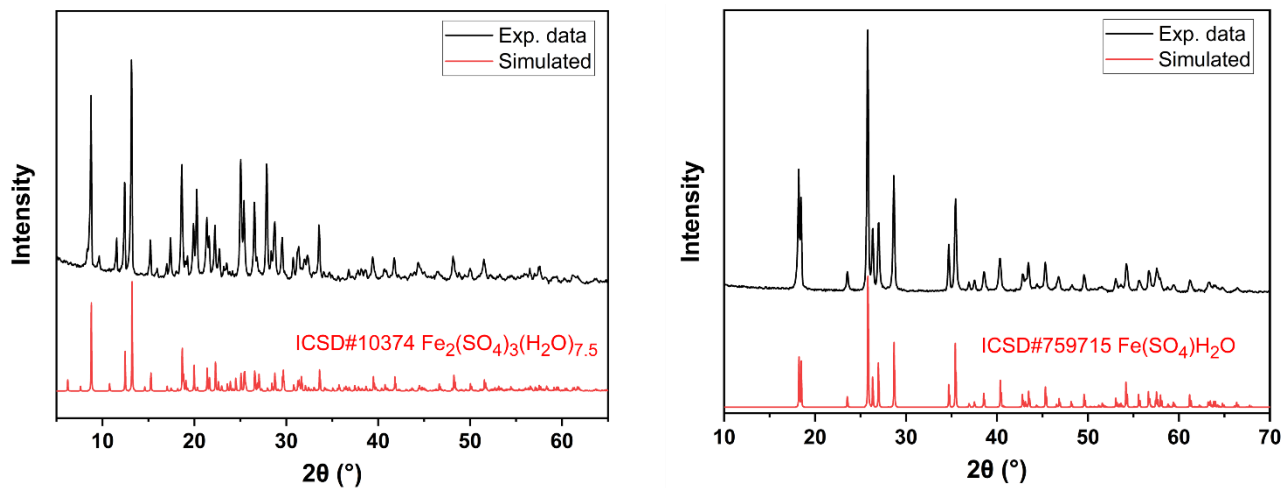


Figure S2. X-ray powder diffraction (XRPD) analyses of the clean Fe₂(SO₄)₃ (left) and of the Lewis acid after standard reaction with 1.0 g of galactaric acid (right).

Reaction crude and purified FDME spectra

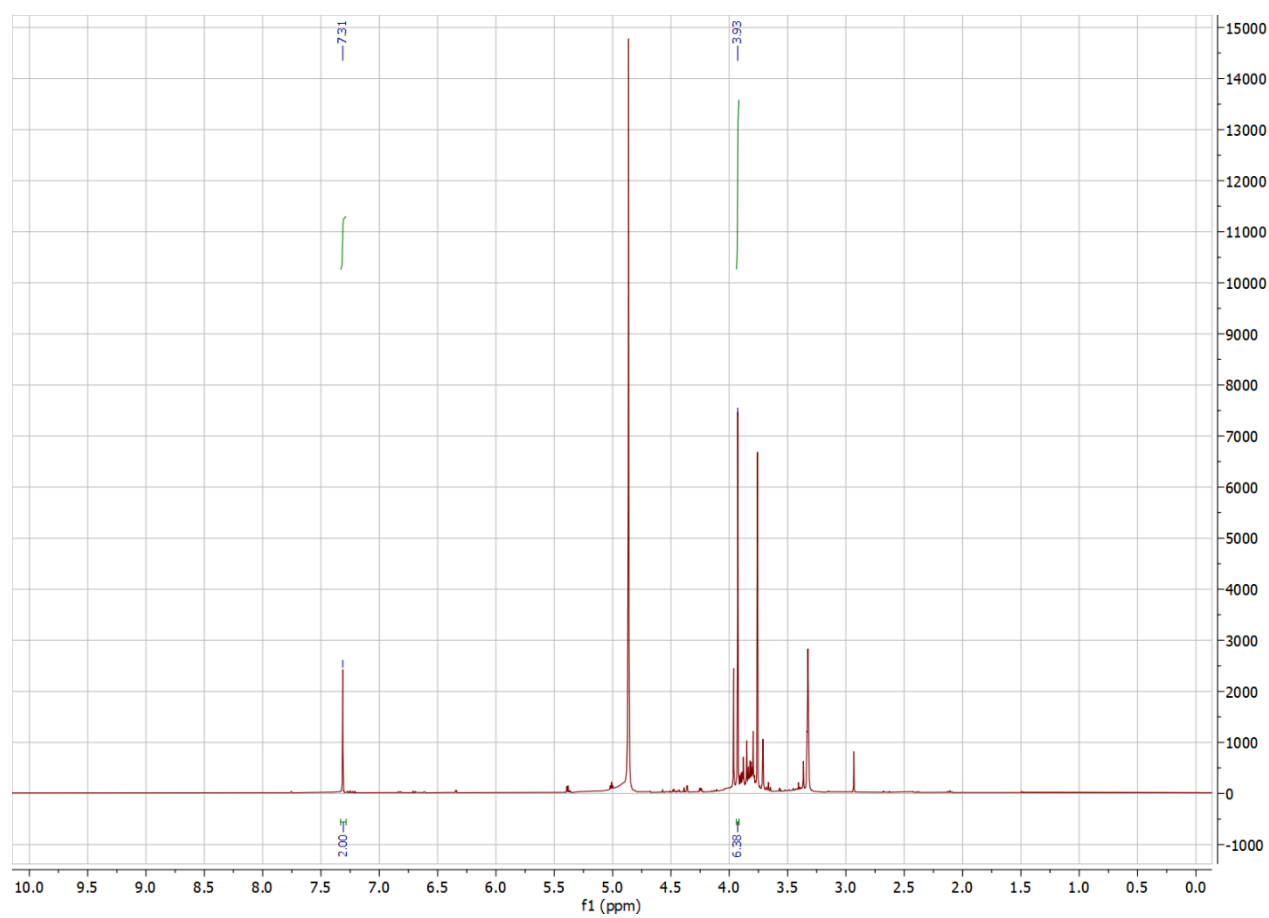


Figure S3. ^1H -NMR (MeOD) spectra of the reaction crude after filtration of $\text{Fe}_2(\text{SO}_4)_3$.

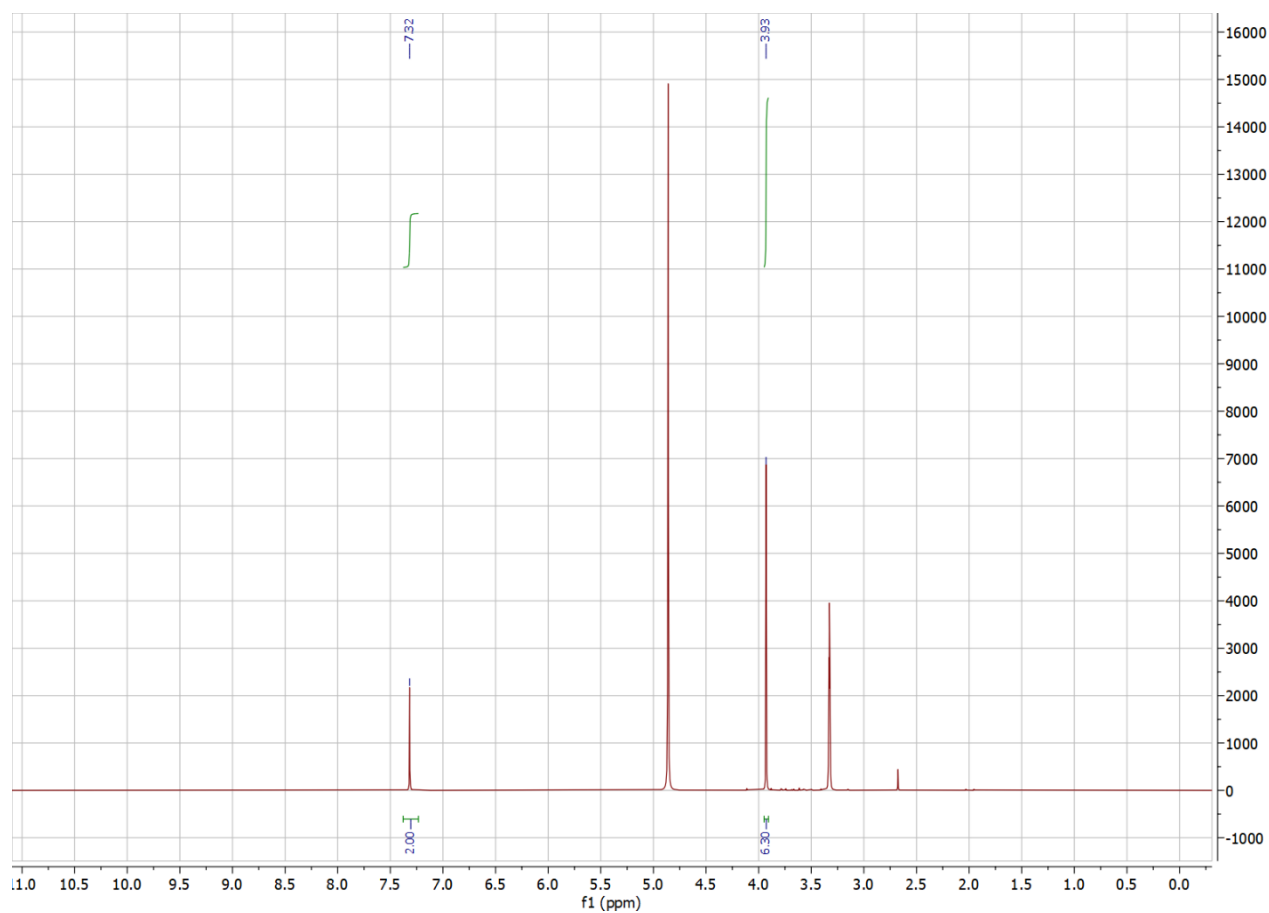


Figure S4. ^1H -NMR (MeOD) spectra of the purified FDME (white crystals).