

Electronic Supporting Information

Confinement of Fe-Al-PMOF catalytic sites favours the formation of pyrazoline from ethyl diazoacetate with unusual sharp increase of selectivity upon recycling

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This PDF file includes:

Experimental details

Supplementary Figures S1 to S22

Contents

1. Chemicals and Methods	3
2. Synthesis of iron porphyrins and Fe-Al-PMOF	4
3. Characterization of Fe-Al-PMOF	9
4. Catalytic study	13
5. References	23

1. Chemicals and Methods

All chemicals were obtained from commercial sources and used without further purification. Ethyl diazoacetate containing ~ 13 wt% of dichloromethane was purchased from Sigma-Aldrich. The tetrakis(4-carboxyphenyl)porphyrin was obtained from TCI chemicals.

Powder X-Ray diffraction (PXRD) was performed on a PANalytical XpertPro MRD diffractometer with a Cu K α 1 radiation ($\lambda = 1.540598 \text{ \AA}$) used with 40 kV and 30mA settings in θ/θ mode, reflection geometry.

The Energy Dispersive Spectroscopy analysis was performed by scanning electron microscopy on FEI Quanta 250 FEG and Zeiss Merlin Compact microscopes in the microscopy center of Lyon1 University. Samples were mounted on stainless pads and sputtered with ~2 nm of carbon to prevent charging during observation.

Thermogravimetric analysis (TGA) was performed with a TGA/DSC 1 STARe System from Mettler Toledo. Around 5 mg of sample is heated at a rate of 10 K·min⁻¹ from 25 to 800 °C, in a 70 μ l alumina crucible, under air atmosphere (20 mL·min⁻¹).

Infrared spectroscopy was performed with a Nicolet 380 FT-IR spectrometer coupled with the Attenuated Total Reflectance (ATR) accessory.

Mass spectrometry was performed in the Centre Commun de Spectrométrie de Masse (CCSM) in Lyon 1 University on a MicrOTOFQ II – Bruker in electrospray Ionisation mode (ESI)

Surface areas were measured by N₂ adsorption and desorption at 77.3 K using a BEL Japan Belsorp Mini apparatus volumetric adsorption analyzer. The sample was pre-activated under vacuum at 160°C prior to sorption measurement. The BET surface calculations was performed using points at the pressure range $0 < P/P^0 < 0.10$

The ⁵⁷Fe Mossbauer spectra were recorded at 300 K and 77K in a transmission geometry using a ⁵⁷Co/Rh source mounted on an electromagnetic drive with a triangular velocity form and a bath cryostat.

GC-MS analysis was performed on a Hewlett Packard GC system 6890 with a Roticap-5 column (He carrier gas, 30m x 0.25 mm) coupled with a Hewlett Packard MS selective detector 5973 (electron impact ionization at 70 eV). ¹H NMR spectra were recorded using a Bruker AM 250 spectrometer.

2. Synthesis of iron porphyrins and Fe-Al-PMOF

5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinato-Fe(III)-hydroxide - Fe(OH)TCPP

Free base meso-tetra(4-carboxyphenyl)porphyrin tetramethyl ester was prepared by a classical Adler Longo method¹ starting from pyrrole and methyl 4-formyl benzoate. Iron insertion was performed in quantitative yield by refluxing this porphyrin with 1.4 equivalents of iron (II) chloride in DMF for 12 hours. The iron tetra(4-carboxyphenyl)porphyrin tetramethyl ester (FeP) was recovered by precipitation in DMF/water/1M HCl mixture and filtered. The ester functions were hydrolyzed to carboxylic acid by refluxing overnight in a mixture of THF and aqueous NaOH solution (100 equivalents of NaOH). The desired compound was precipitated by careful addition of 2M HCl solution, filtered and dried under vacuum. The iron tetrakis(4-carboxyphenyl)porphyrin FeTCPP(OH) was obtained in quantitative yield. ESI-MS, m/z: found - 844.12, [M⁺]; calculated for; [C₄₈H₂₈N₄O₈]⁺ - 844,1257. FTIR, ν cm⁻¹: 2950 (w, broad, carboxylic acid OH stretch), 1690 (m, TCPP C=O stretch), 1604 (m, aromatic C=C stretch). UV-vis in 0.1M NaOH, λ_{max} /nm: 409, 568, 609.

Metal Organic Framework Fe-Al-PMOF

Direct synthesis method: iron tetrakis(4-carboxyphenyl)porphyrin (82.5 mg, 0.094 mmol) and AlCl₃·6H₂O (30 mg, 0.125 mmol) were added to the mixture of 2.5 mL of DMF and 2.5 mL of deionized water in a Teflon reactor. The resulting mixture was stirred and degassed with argon at room temperature during 10 minutes. The reaction mixture was sealed in a stainless-steel autoclave, heated at 190 °C for 16 hours (the temperature was increased over 3 hours to reach the isotherm) and cooled down to room temperature over 4 hours. The solid was recovered by centrifugation, washed three times with DMF and heated in 10 mL DMF at 80 °C for 12 hours. Then the solid was washed again with DMF (three times) followed by washing with acetone (three times). After drying under air, the MOF was obtained as a dark brown solid (42 mg, 48 % yield).

Synthesis optimization: For the direct synthesis method, solvent composition and temperature were optimized in order to obtain a crystalline material.

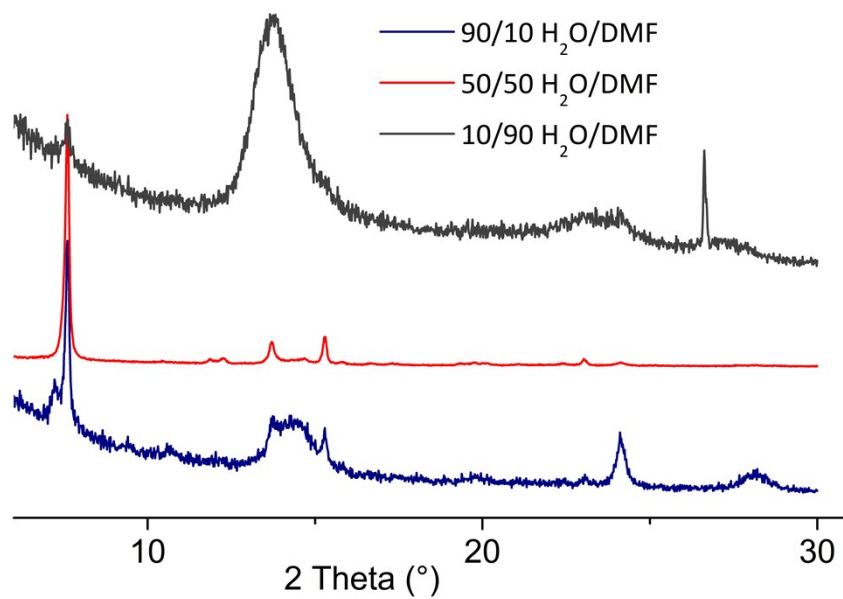


Figure S1. Direct synthesis of Fe-Al-PMOF at 190°C: influence of solvent composition.

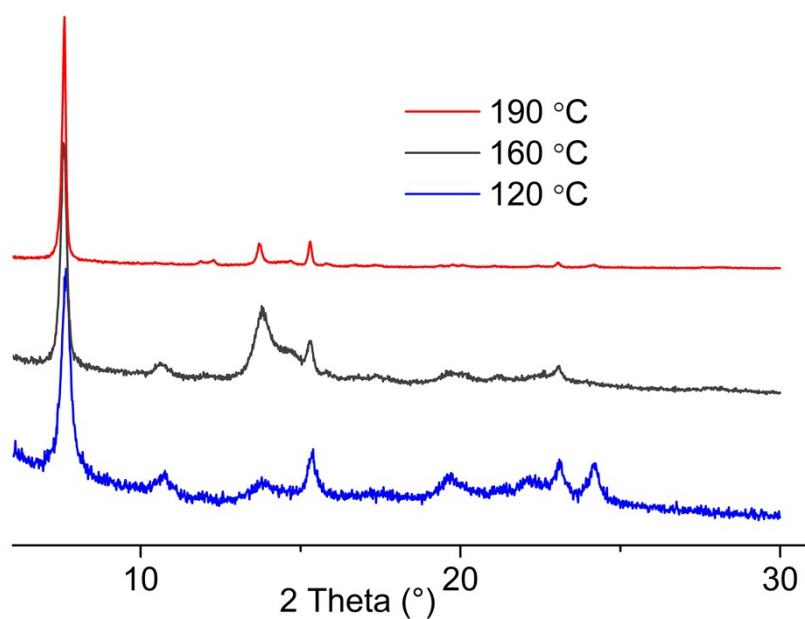


Figure S2. Direct synthesis of Fe-Al-PMOF using the solvent composition 50/50 $\text{H}_2\text{O}/\text{DMF}$: influence of the reaction temperature

Post-synthesis iron insertion method: H₂-Al-PMOF was prepared following the published experimental procedure². To a suspension of H₂-Al-PMOF (50 mg, 0.057 mmol) in 0.3 mL of methanol, 3.4 mL of a 0.1 M Fe(SCN)₂ solution in MeOH (0.34 mmol) and 5.4 mg of ascorbic acid were added. The vial was closed and the reddish suspension was heated at 100 °C for 48 hours. Then, the solid was recovered by centrifugation and was washed three times with DMF and three times with methanol. After drying in air, the MOF was obtained as a dark brown solid (35 mg, 65% yield).

LeBail fit on the Fe-Al-PMOF samples

Direct synthesis Fe-Al-PMOF refined cell:

6.439(3) 31.49(3) 16.33(2) 90 90 90

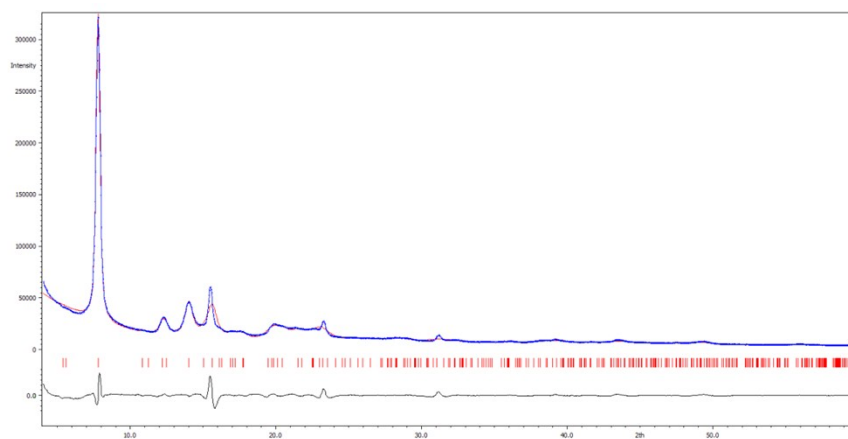


Figure S3. LeBail analysis for directly synthesised Fe-Al-PMOF (blue: observed, red: calculated, black: difference)

PSM Fe-Al-PMOF refined cell

6.5984(4) 32.098(5) 16.722(3) 90 90 90

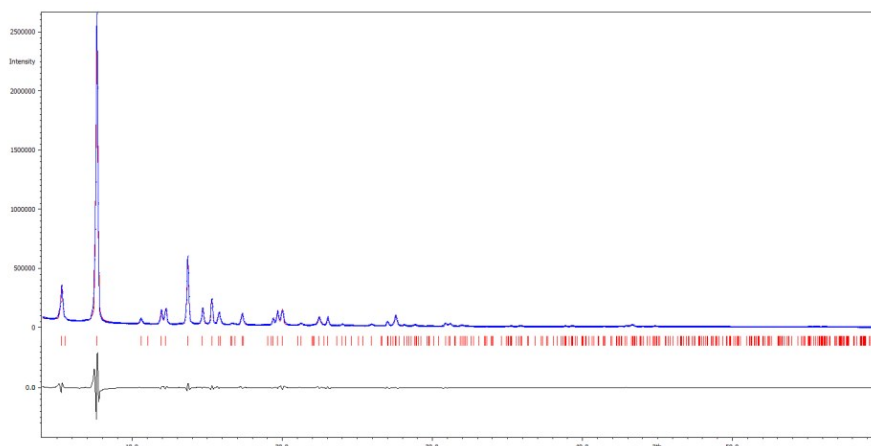


Figure S4. LeBail analysis for PSM Fe-Al-PMOF (blue: observed, red: calculated, black: difference)

Summary of refined cell parameters for H₂-Al-PMOF and all the Fe-Al-PMOF samples

sample	H ₂ -Al-PMOF (see ref 2)	Fe-Al-PMOF by PSM	Fe-Al-PMOF direct synthesis	Fe-Al-PMOF direct synthesis after 5 catalytic runs (see Fig S.14)
space group	C _{mmm}	C _{mmm}	C _{mmm}	C _{mmm}
a (Å)	6.5812(4)	6.5984(4)	6.439(3)	6.521(5)
b (Å)	31.978(3)	32.098(5)	31.49(3)	31.82(3)
c (Å)	16.862(2)	16.722(3)	16.33(2)	16.84(2)
V (Å ³)	3548.7	3541.6	3311.1	3494.3

UV-vis analysis of digested MOF samples obtained by methods 1 and 2

To determine the iron insertion yield, the prepared MOF solids were dissolved in 0.1M NaOH aqueous solution and the UV-vis spectra were recorded. By a quantitative analysis, Comparison of the UV-vis absorption of the resulting porphyrin solutions with the spectra of H₂-TCPP and Fe-TCPP samples allowed evaluating the yield of the iron insertion. Maximum iron insertion rate of 70% was determined using the synthesis conditions described above.

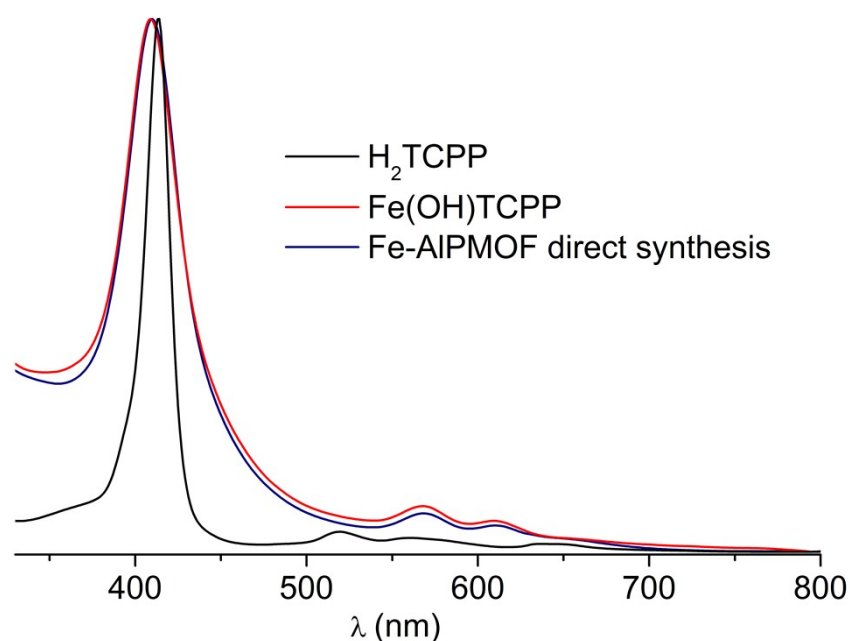


Figure S5. Comparison of UV-vis spectra of Fe-Al-PMOF prepared by direct synthesis method with those of the corresponding free base and iron porphyrins in 0.1 M NaOH solution.

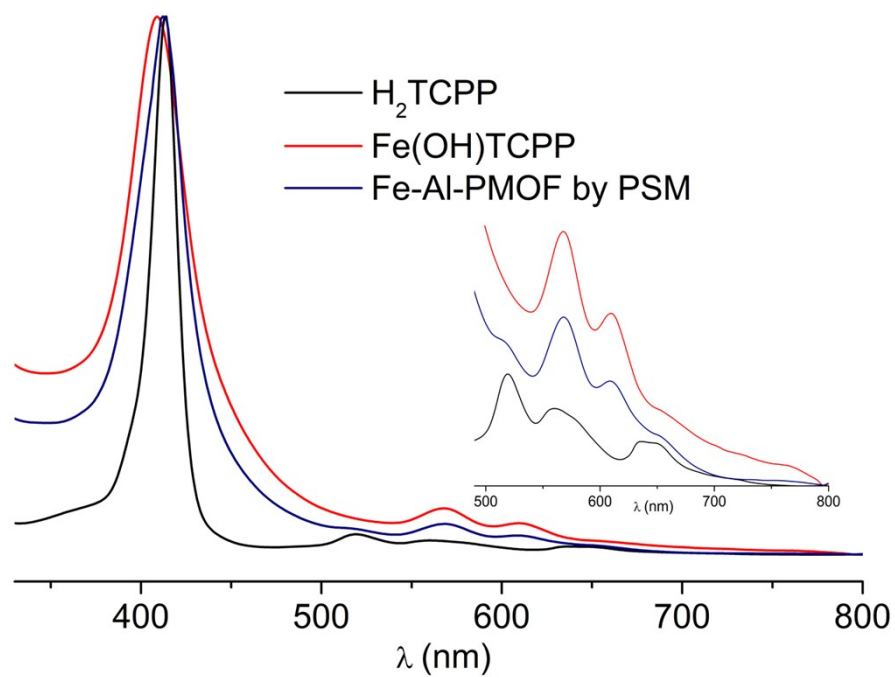


Figure S6. Comparison of UV-vis spectra of Fe-Al-PMOF prepared by post synthesis metallation method with those of the corresponding free base and iron porphyrins in 0.1 M NaOH solution

3. Characterization of Fe-Al-PMOF

Thermogravimetric analysis

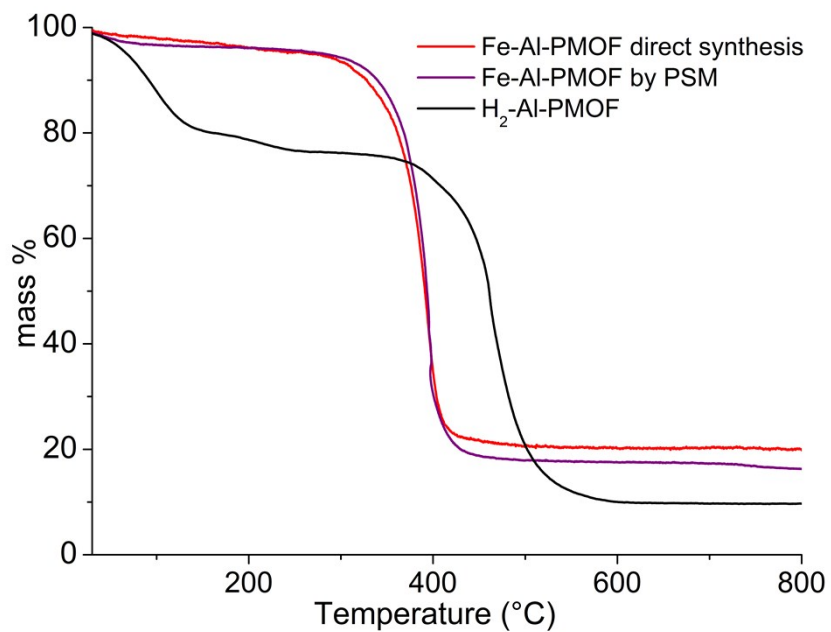


Figure S7. TGA curves for H₂-Al-PMOF (black), Fe-Al-PMOF by PSM (purple) and Fe-Al-PMOF by direct synthesis (red). TGA was performed under air flow (20 mL min⁻¹) at a 10°C min⁻¹ heating rate.

Scanning Electron Microscopy and Energy Dispersive Spectroscopy data

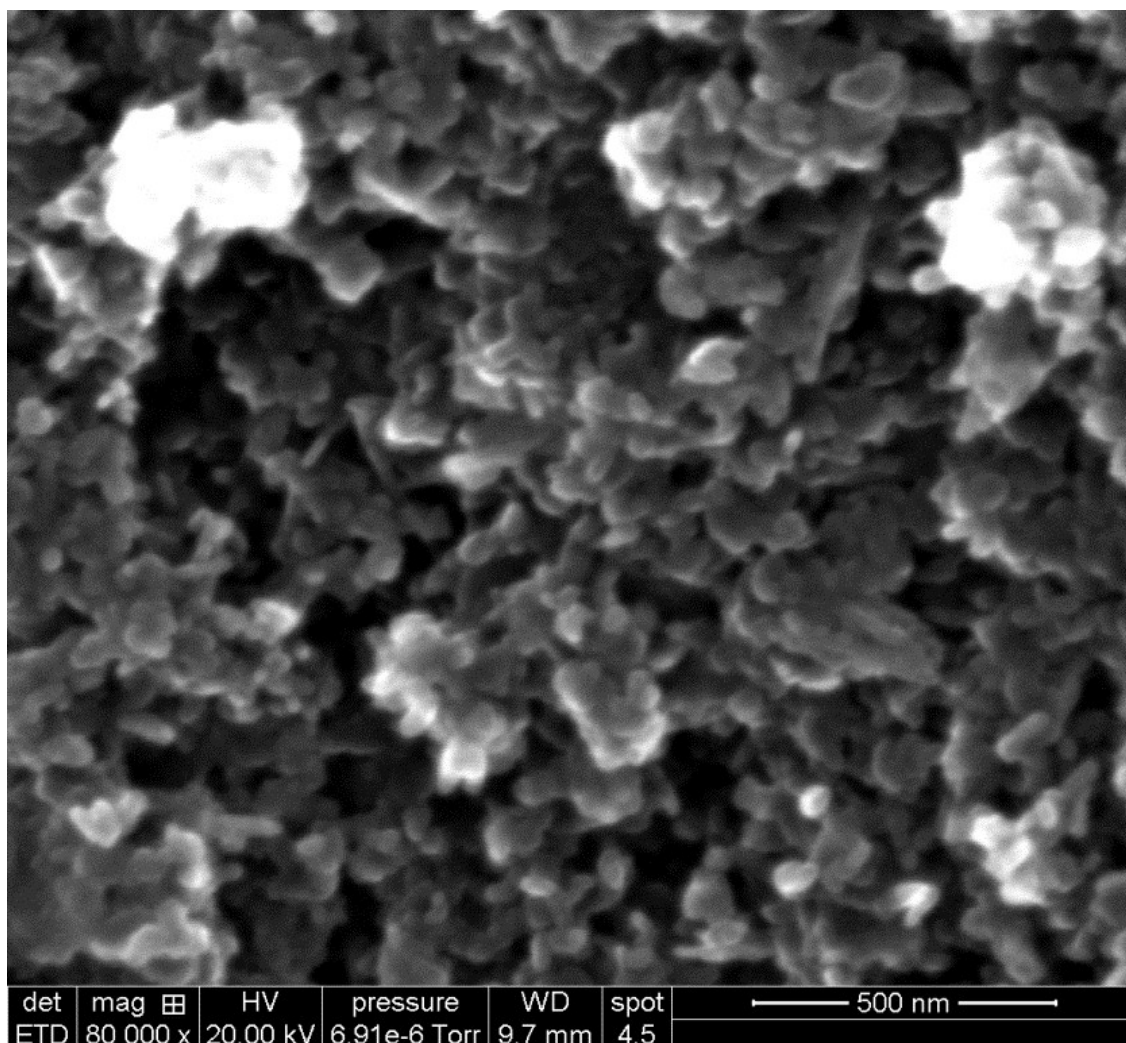


Figure S8. SEM image of directly synthesised Fe-Al-PMOF

Table S1. EDS analysis of directly synthesised Fe-Al-PMOF

	1	2	3	4	5	Average relative atomic ratio
Al (atomic %)	3.96	3.63	4.99	5.39	7.46	2
Fe (atomic %)	1.83	1.86	1.75	1.95	3.06	0.85

UV-vis spectroscopy of digested Fe-Al-PMOF samples showed the absence of free base porphyrin, the slight excess of Al in EDS analyses is due to a minor amount of boehmite impurity which can be formed during the direct Fe-Al-PMOF synthesis.

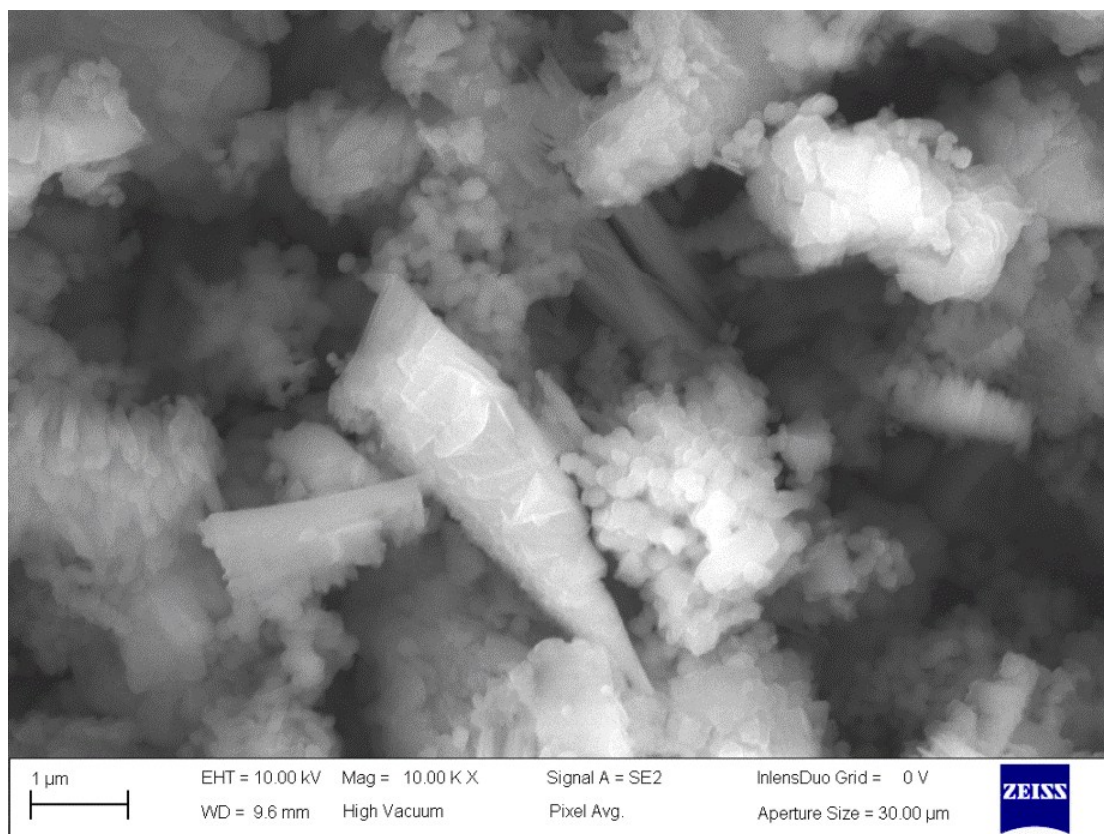


Figure S9. SEM image of Fe-Al-PMOF obtained by post synthesis metal insertion.

Table S2. EDS analysis on the Fe-Al-PMOF obtained by post synthesis metal insertion.

	1	2	3	4	5	6	Average relative atomic ratio
Al (atomic%)	4.64	5.06	4.91	4.43	2.43	7.46	2.0
Fe (atomic%)	1.53	1.76	1.58	1.54	0.88	3.06	0.7

EDS analysis indicated an average rate of 70% of iron insertion in the porphyrin.

Mössbauer Spectrometry

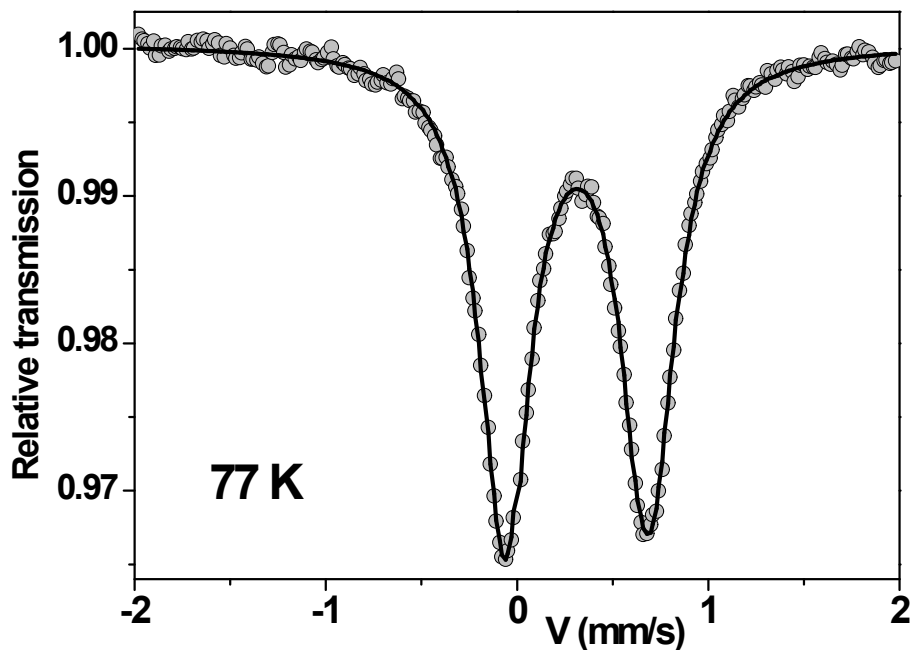


Figure S10. Mössbauer spectrum of Fe-Al-PMOF obtained by direct synthesis.

The isomer shift and quadrupole splitting values lie in the range of those reported for five-coordinate high-spin iron(III) porphyrins³: $\delta = 0.42$ mm/s, $\Delta E_Q = 0.74$ mm/s (values relative to α -Fe at 300K) at 77 K.

It is important to emphasize that the asymmetry of the quadrupolar doublet is due to the presence of a preferential orientation resulting from the platelet shaped particle sample: indeed, one clearly observes a change in the lines intensities ratio by rotating the sample respect to the γ -beam.

4. Catalytic study

Investigation of the cyclopropanation of styrene with ethyl diazoacetate using the Fe-Al-PMOF and FeP catalysts

Fe-Al-PMOF obtained by direct synthesis method was used in the catalytic studies due to the higher iron metallation degree. The reaction mixture containing 1 μmol of iron porphyrin (1.20 mg of Fe-Al-PMOF or 0.94 mg of FeP) and 1 mmol of styrene (115 μL) in 0.735 mL of toluene was placed in a 3 mL vial and was degassed with argon for 5 minutes. Ethyl diazoacetate (contains 13% CH_2Cl_2 , 0.15 mL, 1.2 mmol) was added to the reaction mixture with a syringe. The resulting mixture was stirred at 60 °C under maintained inert atmosphere. The reaction progress was followed by GC-MS method: at appropriate times, 10 μL of the reaction mixture was withdrawn and diluted with 400 μL of acetonitrile prior to GC-MS analysis.

Investigation of the formation of 3,4,5-triethyl-4,5-dihydro-1H-pyrazole-3,4,5-tricarboxylate (1) from ethyl diazoacetate using Fe-Al-PMOF and FeP catalysts

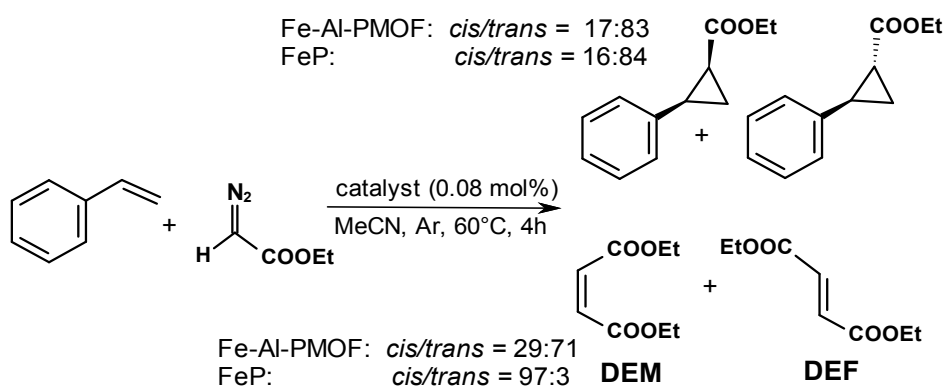
The reaction mixture containing 1 μmol of iron porphyrin (1.20 mg of Fe-Al-PMOF or 0.94 mg of FeP) in 0.85 mL of toluene was placed in a 3 mL vial and was degassed with argon for 5 minutes. Ethyl diazoacetate (contains 13% CH_2Cl_2 , 0.15 mL, 1.2 mmol) was added to the reaction mixture with a syringe. The resulting mixture was stirred at 60 °C under maintained inert atmosphere. The reaction progress was followed by GC-MS method: at appropriate times, 10 μL of the reaction mixture was withdrawn and diluted with 400 μL of acetonitrile prior to GC-MS analysis. The product yields were determined by NMR analysis of the reaction mixtures.

3,4,5-triethyl-4,5-dihydro-1H-pyrazole-3,4,5-tricarboxylate (**1**): MS-EI, m/z : 286 (0.13 %) $[\text{M}]^+$, calculated for $\text{C}_{12}\text{H}_{18}\text{O}_6\text{N}_2$: 286; 241 (2.10 %), $[\text{M}-\text{OC}_2\text{H}_5]^+$; 213 (23.40 %), $[\text{M}-\text{COOC}_2\text{H}_5]^+$; 167 (24.47 %); 141 (14.39 %); 95 (100 %). ^1H NMR (CDCl_3): 1.22-1.40 (9H, CH_2CH_3), 4.15-4.38 (6H, CH_2CH_3), 4.39 (d, 1H, **CH**), 4.73 (d, 1H, **CH**), 6.84 (s, 1H, **NH**). Spectral data for **1** correspond to data published in the literature.⁴

Investigation of the cyclopropanation of styrene by ethyl diazoacetate in the presence of Fe-Al-PMOF

Catalytic properties of the directly prepared Fe-Al-PMOF were initially evaluated in the cyclopropanation of styrene by ethyl diazoacetate (EDA) at 60°C in MeCN and compared with those of the soluble iron tetrakis(4-methoxycarbonylphenyl)porphyrin (FeP) (Scheme S1).

The *cis/trans* ratios of cyclopropanation products were almost the same for heterogeneous Fe-Al-PMOF and homogeneous FeP catalysts indicating no influence of the porous structure on the stereoselectivity of cyclopropanation (Fig. S12 and S13). The lack of the notable influence of the porous structure on the *cis/trans* cyclopropanation ratio can be explained as follows. In the first step, the iron porphyrin complex reacts with EDA to form the iron carbene complex $\text{PFe}=\text{C}(\text{H})(\text{COOC}_2\text{H}_5)$ which was published in numerous papers on the reactivity of FeP with diazo carbene precursors.^{5,6} Then, the olefin substrate preferentially attacks this carbene complex from less hindered side⁷ in homogeneous conditions and in MOF cages to furnish cyclopropanation products with similar *cis/trans* selectivity in both cases. This explains the lack of cage effect on the reaction outcome.



Scheme S1. Reaction of styrene with EDA in the presence of FeP and Fe-Al-PMOF.

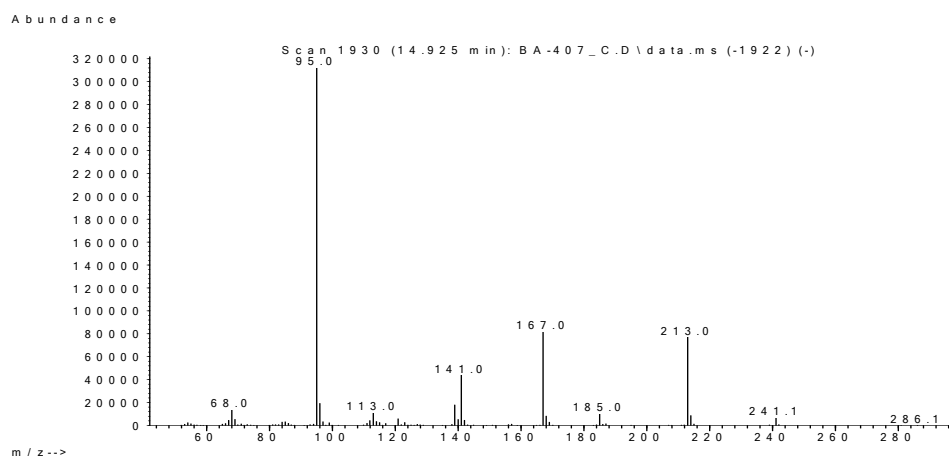


Figure S11. Mass spectrum (EI, 70 eV) of 3,4,5-triethyl-4,5-dihydro-1H-pyrazole-3,4,5-tricarboxylate (1).

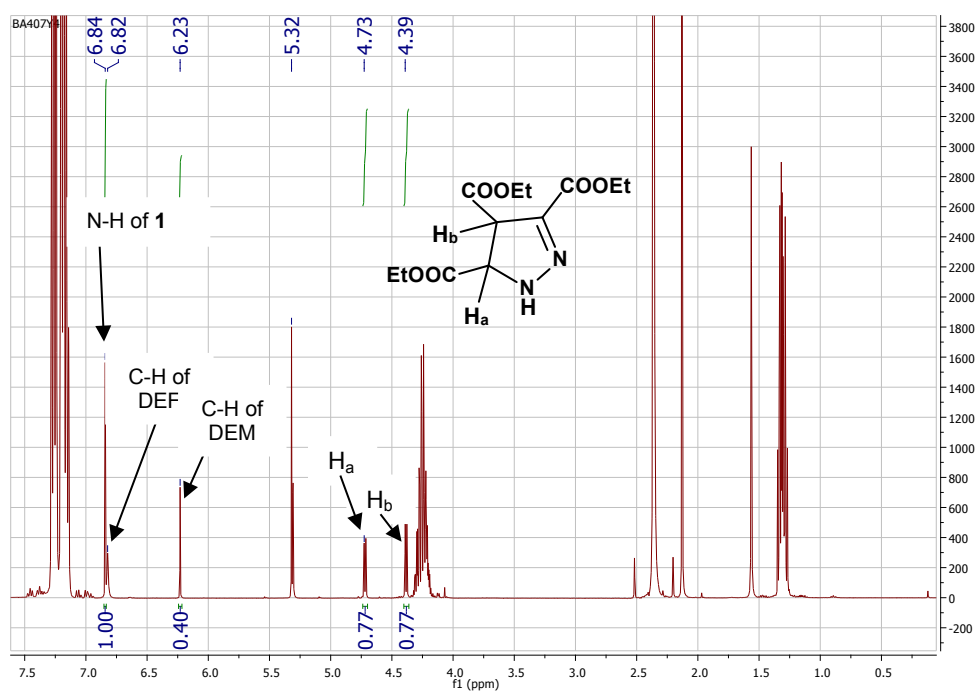


Figure S12. Typical ^1H NMR analysis of the reaction mixture obtained in the reaction of EDA with Fe-AL-PMOF in toluene at 60°C .

Recycling study

To investigate the recyclability of the Fe-Al-PMOF the amount of reagents were increased by factor 3. After completing reaction with EDA, the solid was recovered by centrifugation and washed with toluene for 5 times. The recovered solid was directly used for the following runs.

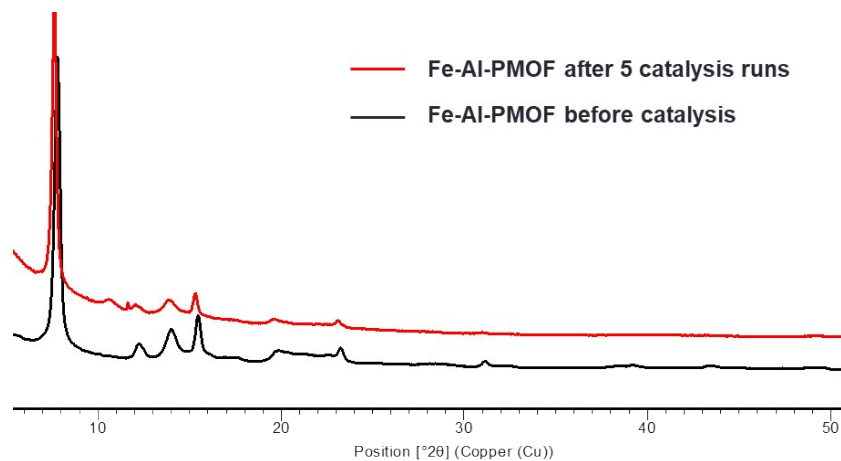


Figure S13. Powder X-ray diffraction (PXRD) patterns of Fe-Al-PMOF catalyst before catalysis and after 5 catalytic runs.

LeBail fit in the Fe-Al-PMOF after catalysis.

Refined cell: 6.521(5) 31.82(3) 16.84(2) 90 90 90

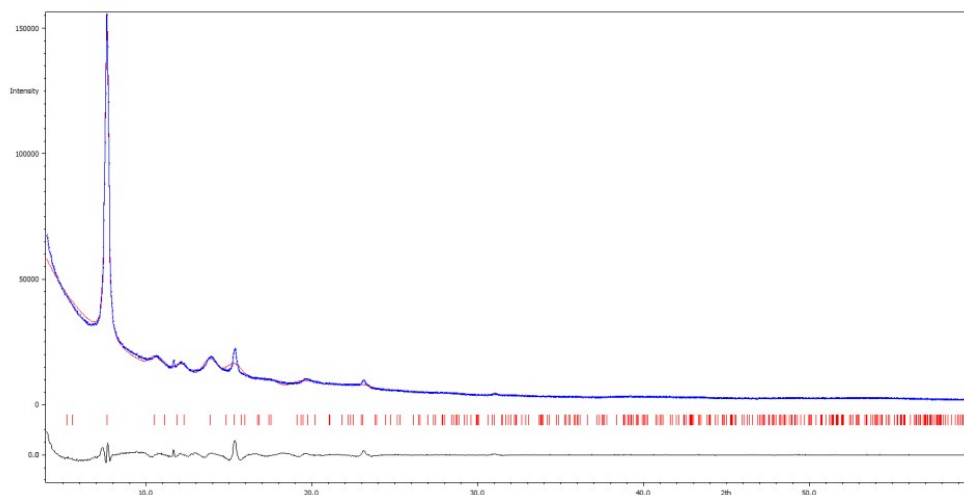


Figure S14. LeBail analysis of the Fe-Al-PMOF catalyst after 5 catalytic runs (blue: observed, red: calculated, black: difference). The very low intensity peak at $2\theta = 11.65^\circ$ does not correspond to the MOF phase.

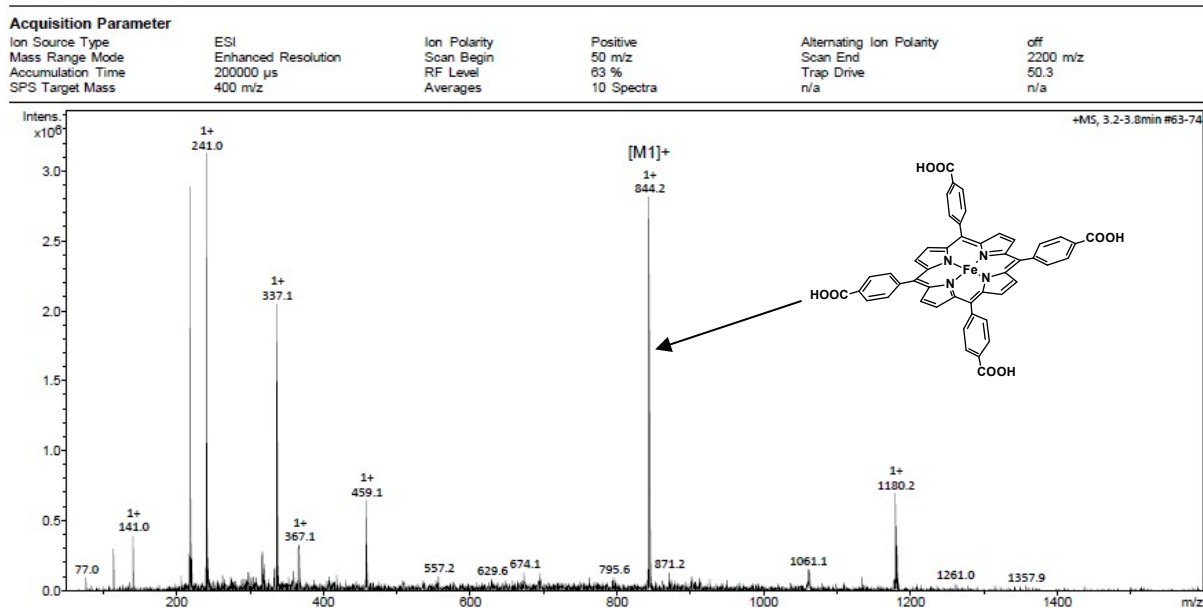


Figure S15a. Mass-spectrum (electrospray ionization) of the solution obtained by dissolving of the initial Fe-Al-PMOF in 0.1 M NaOH solution and the FeP structure.

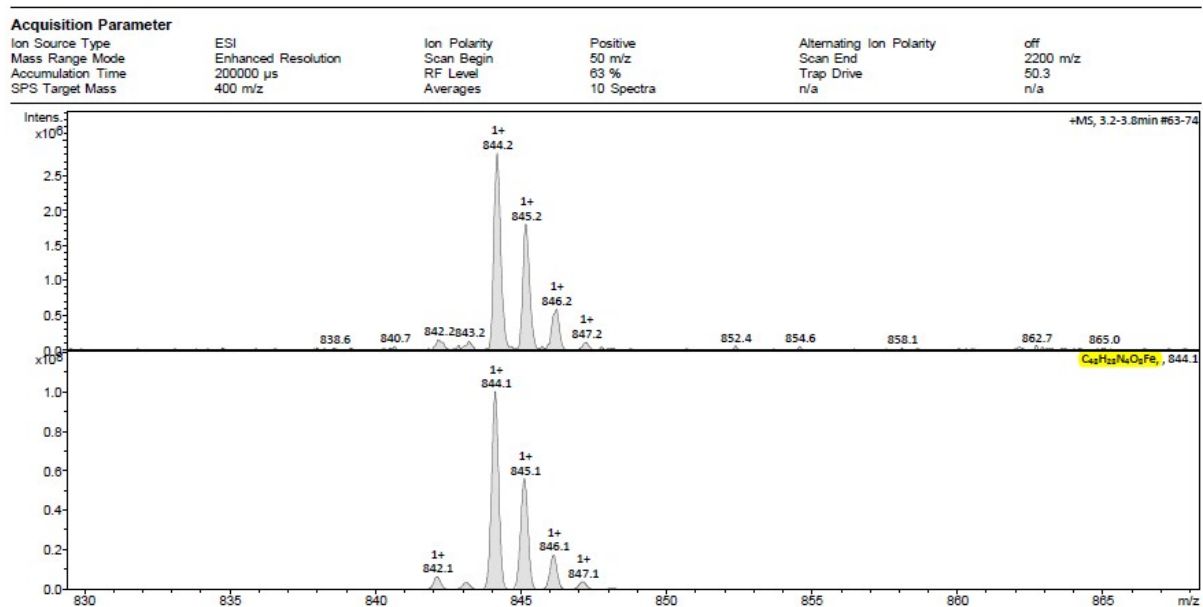


Figure S15b. Experimental molecular peak cluster of the $[\text{FeP}]^+$ complex in ESI-MS spectrum and calculated molecular peak cluster for $\text{C}_{48}\text{H}_{28}\text{N}_4\text{O}_8\text{Fe}$.

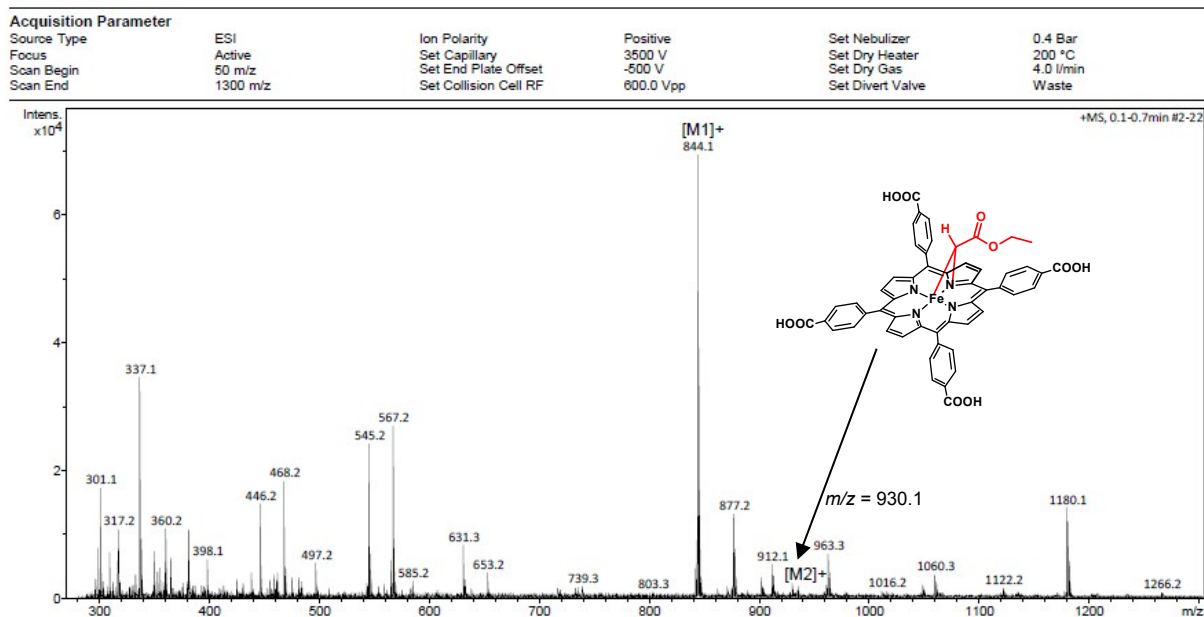


Figure S16a. Mass-spectrum (electrospray ionization) of the solution obtained by dissolving of the recycled Fe-Al-PMOF in NaOH solution and proposed structure of the carbene adduct of FeP.

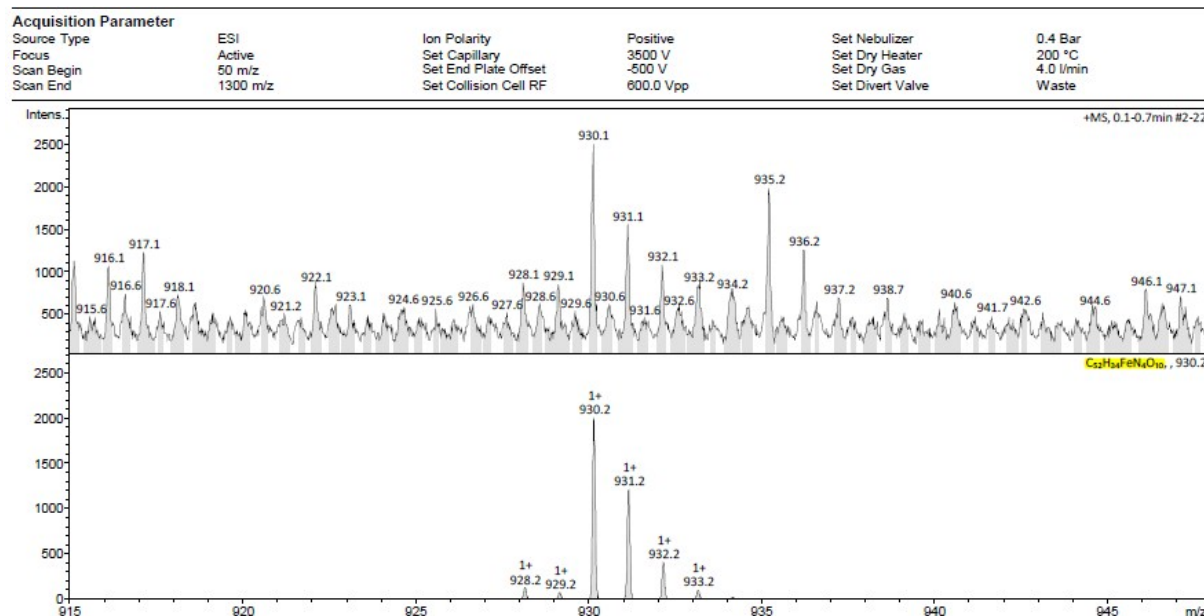


Figure S16b. Experimental molecular peak cluster of the $[\text{FeP} + \text{CHCOOC}_2\text{H}_5]^+$ complex in ESI-MS spectrum and calculated molecular peak cluster for $\text{C}_{52}\text{H}_{34}\text{N}_4\text{O}_{10}\text{Fe}$. Low intensity of the $[\text{FeP} + \text{CHCOOC}_2\text{H}_5]^+$ signal can be explained by its possible degradation in 0.1 M NaOH solution upon the dissolving the solid Fe-Al-PMOF.

GC-MS analyses of reaction products

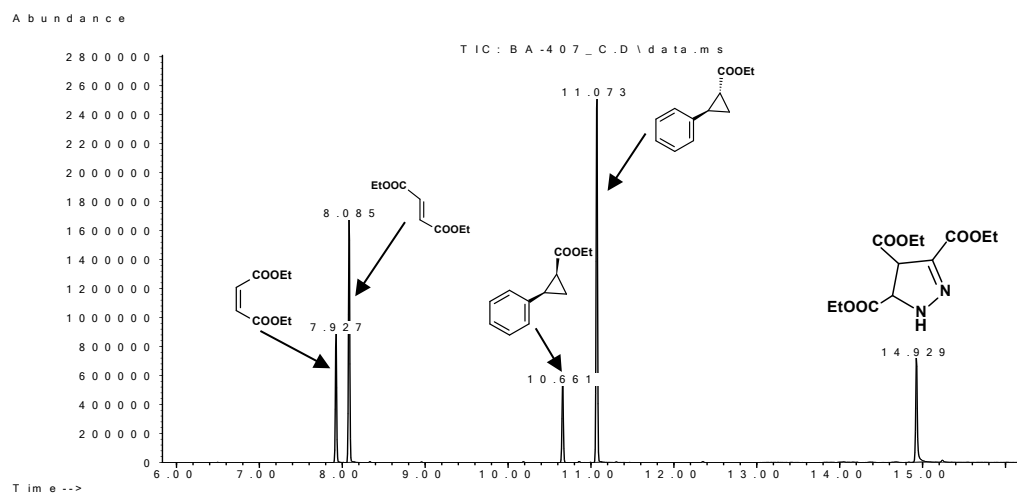


Figure S17. GC-MS analysis of the final reaction mixture in the reaction of EDA with styrene catalyzed by Fe-Al-PMOF.

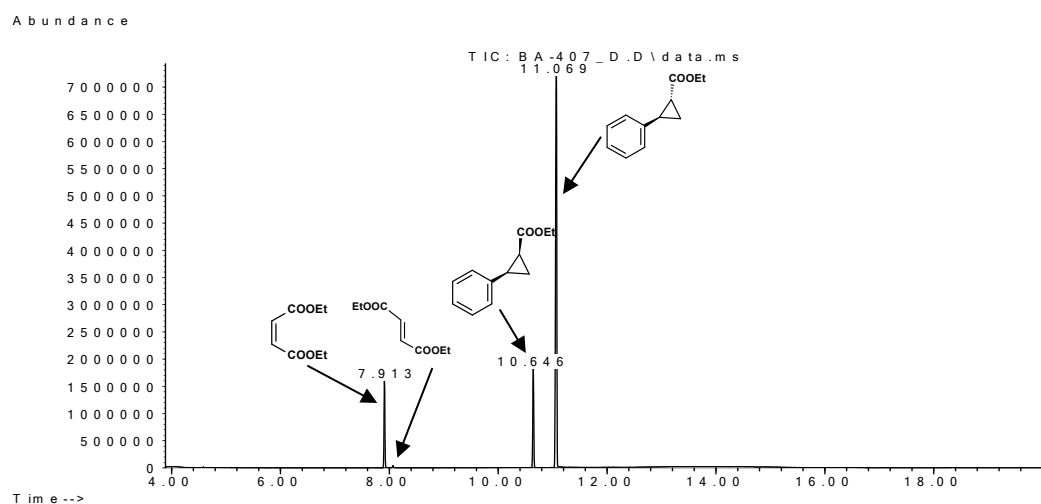


Figure S18. GC-MS analysis of the final reaction mixture in the reaction of EDA with styrene catalyzed by FeP.

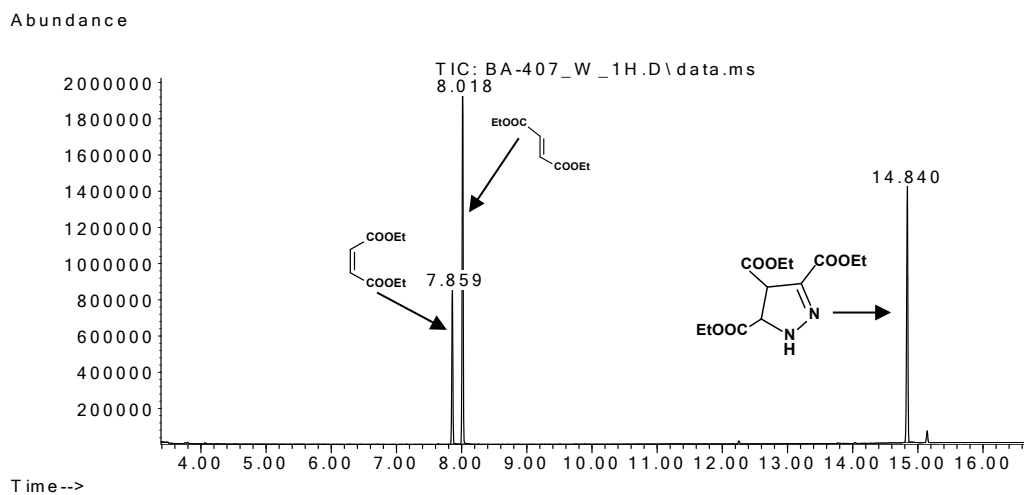


Figure S19. GC-MS analysis of the final reaction mixture in the reaction of EDA with Fe-Al-PMOF in toluene at 60°C. The DEM / DEF ratio obtained with Fe-Al-PMOF depended on the solvent nature. The *cis/trans* ratios of 21:79, 29:71 and 34:66 were observed in CH₂Cl₂, MeCN and PhMe, respectively. Upon decrease of the reaction temperature, the yield of **1** dropped to 12 and 27 % at 25 and 40°C, respectively.

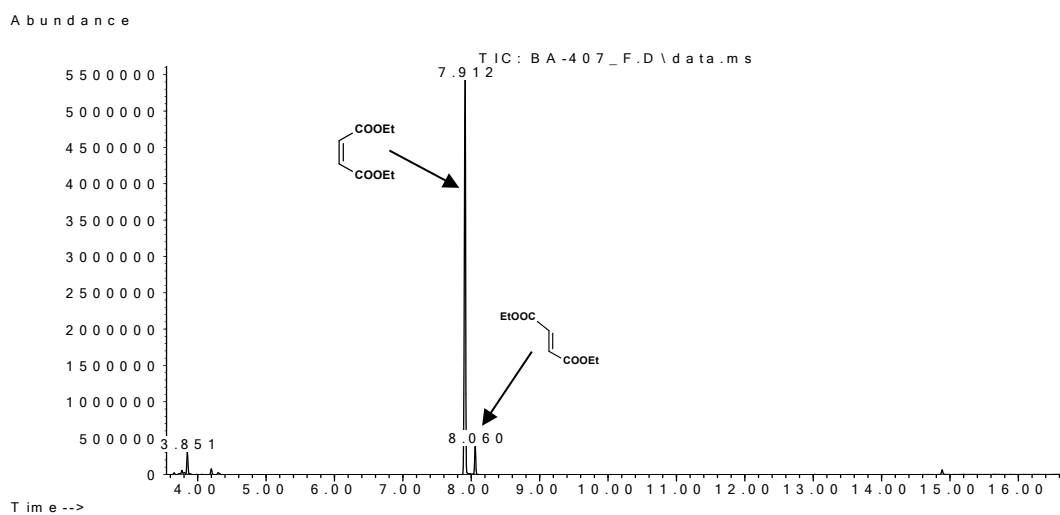


Figure S20. GC-MS analysis of the final reaction mixture in the reaction of EDA with FeP in toluene.

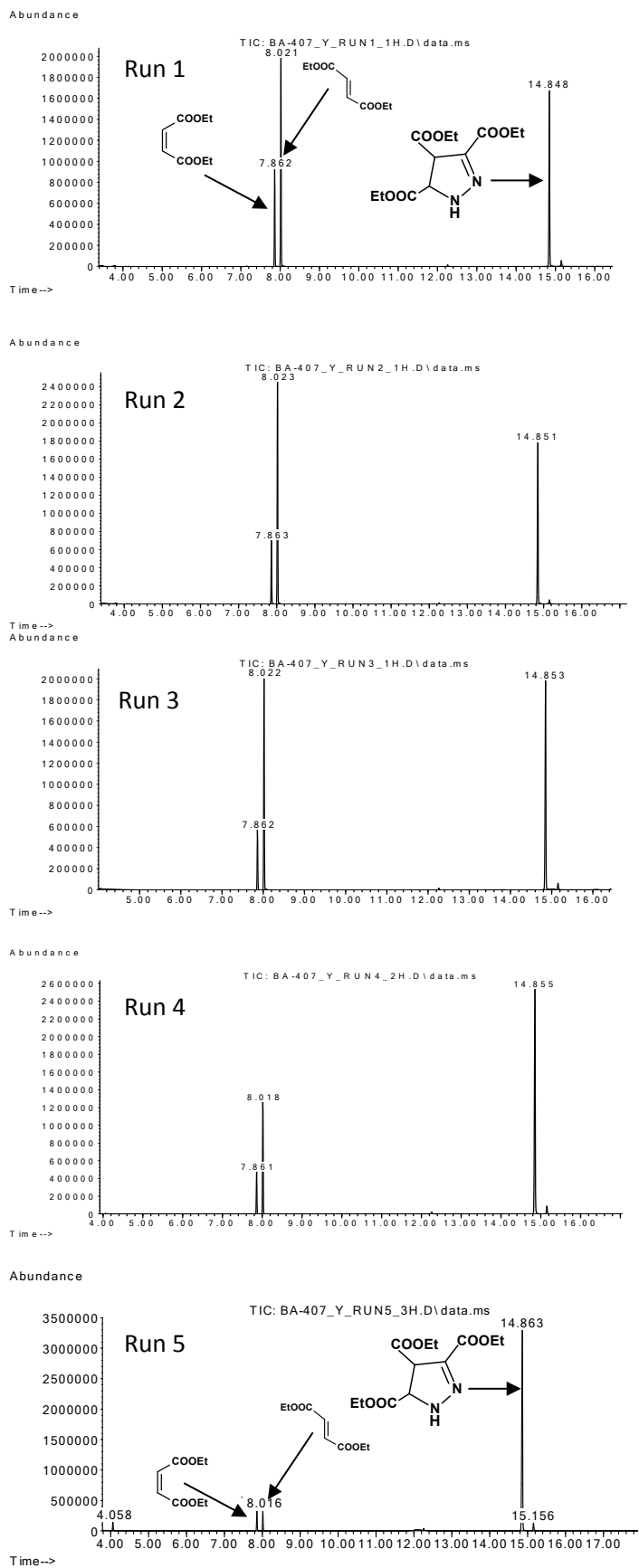


Figure S21. Recycling study: GC-MS analyses of the five consecutive reactions of EDA with the same sample of Fe-Al-PMOF.

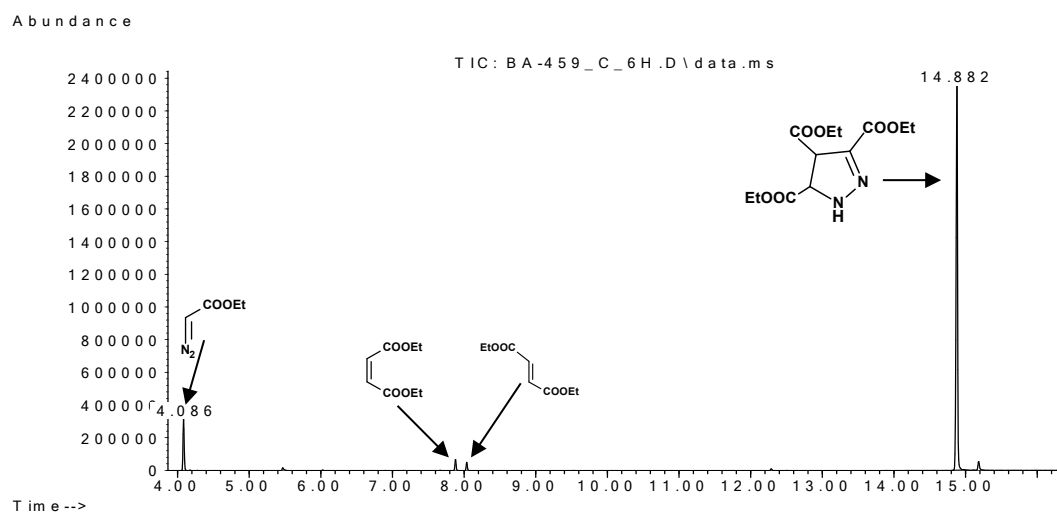


Figure S22. Highly selective formation of pyrazoline **1** in the presence of small amount of Fe-Al-PMOF catalyst (0.008 mol%, 1:12000 catalyst/EDA ratio).

References

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