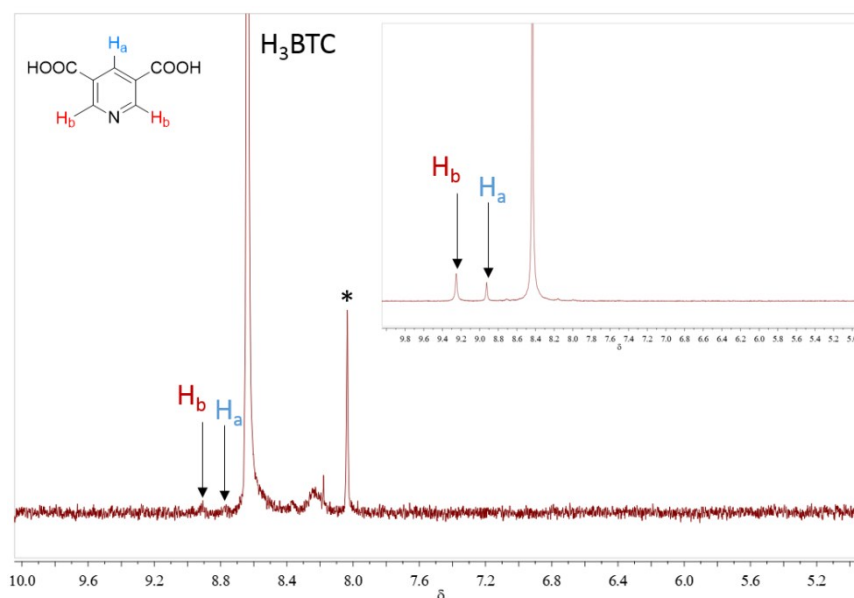
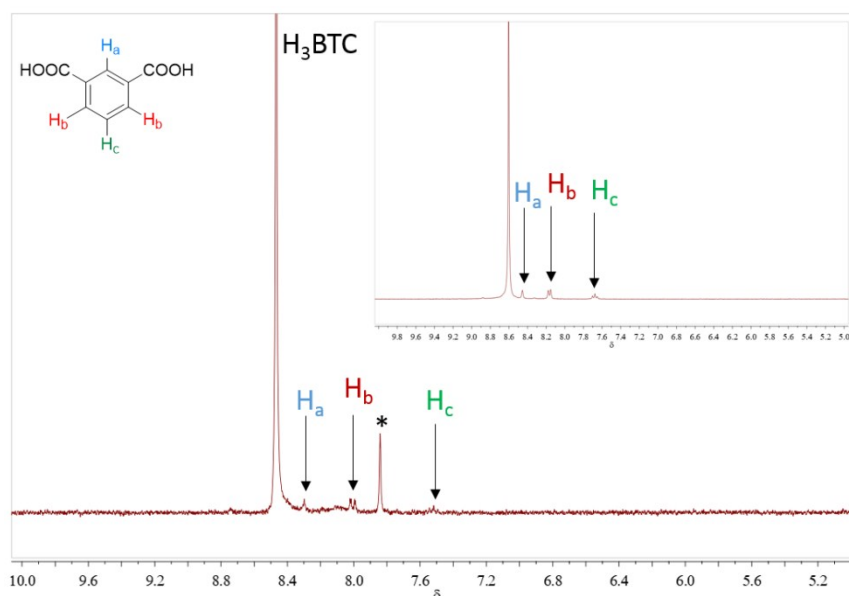


Supporting Information

Catalytic properties of pristine and defect-engineered Zr-MOF-808 Metal Organic Frameworks

H. –H. Mautschke, F. Drache, I. Senkovska, S. Kaskel and F. X. Llabrés i Xamena^{a*}



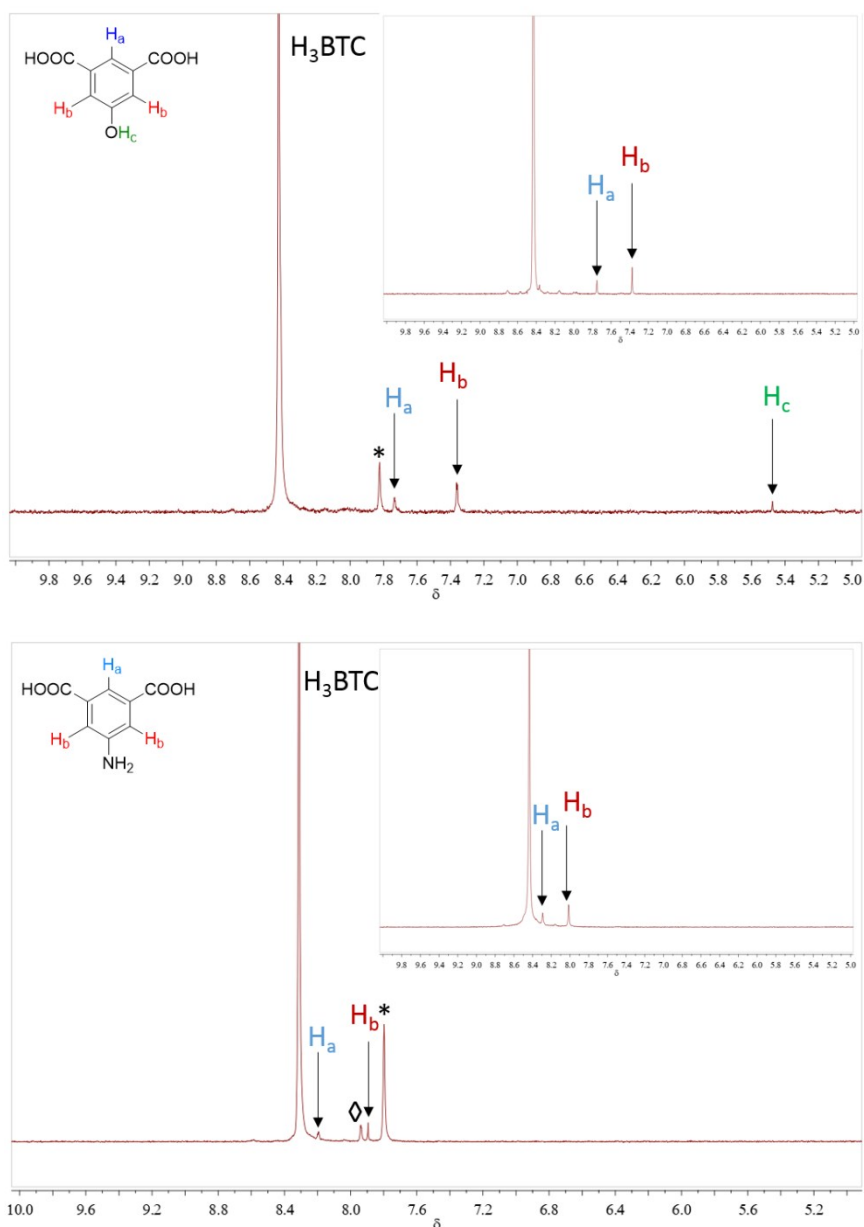


Figure S1. ¹H NMR spectra of digested DE-MOFs. From top to bottom: MOF-808-IP, MOF-808-Pydc, MOF-808-OH and MOF-808-NH₂. The insets show in each case the ¹H NMR spectra obtained for physical mixtures of H₃BTC (95%) and the corresponding defective linker (5%) recorded under analogous conditions as for MOF-808 compounds. * and ◇ indicate the presence of small amounts of DMF and formic acid, respectively.

Table S1. Incorporation of defective linkers in the DE-MOF-808 compounds, as calculated from the ¹H NMR shown in Figure S1.

Sample	%Defective linker
MOF-808-IP	3%
MOF-808-Pydc	~2%
MOF-808-OH	7%
MOF-808-NH ₂	4%

Table S2. Summary of the textural properties of pristine and defect-engineered MOF-808 compounds.

Sample	S_{BET} (m^2g^{-1}) ^a	V_p (cm^3g^{-1})	Pore size (\AA) ^b
MOF-808	1345	0.60	18.2
MOF-808-IP	1558	0.73	17.3
MOF-808-Pydc	1592	0.74	17.3
MOF-808-OH	1537	0.71	17.5
MOF-808-NH ₂	1436	0.67	17.4

^a Calculated in the range $0.05 < P/P^0 < 0.3$. ^b Pore size distribution was evaluated from the Dubinin-Stoeckli equation [M. M. Dubinin, N. S. Polyakov and L. I. Kataeva, *Carbon*, 1991, **29**, 481-488.]

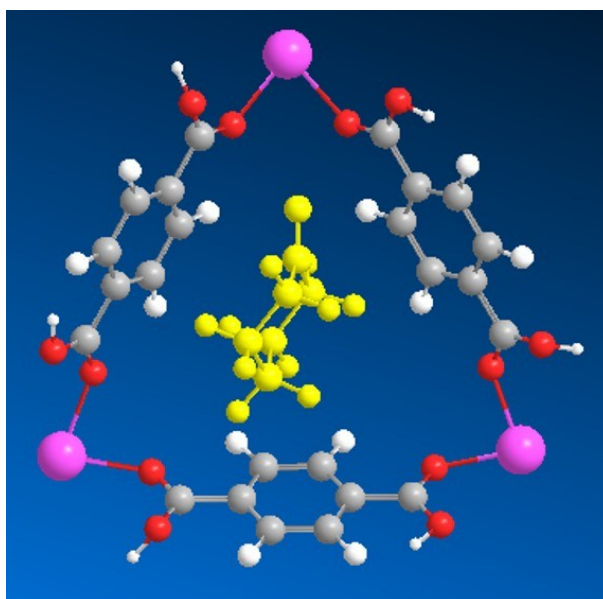


Figure S2: Dimensions of cyclohexanone (CH) relative to the pore openings of UiO-66. The figure shows a CH molecule (in yellow) placed at the center of the triangular windows of the Zr-MOF. All the atoms of the MOF have been fixed at the crystallographic positions and the CH molecule has been optimized with the MM2 force field as implemented in Chem3D Pro 12.0. Color code: C, grey; O, red; H, white; Zr, pink.

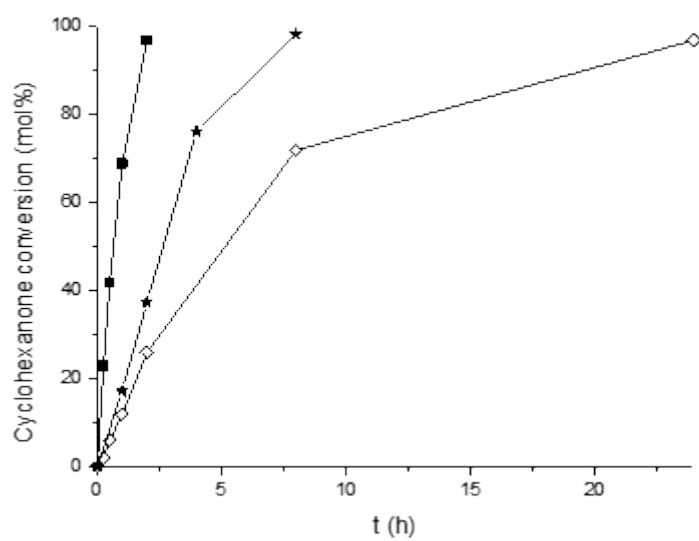


Figure S3. Conversion of cyclohexanone over UiO-66 (\diamond), DUT-67 ($*$) and MOF-808 (\blacksquare).

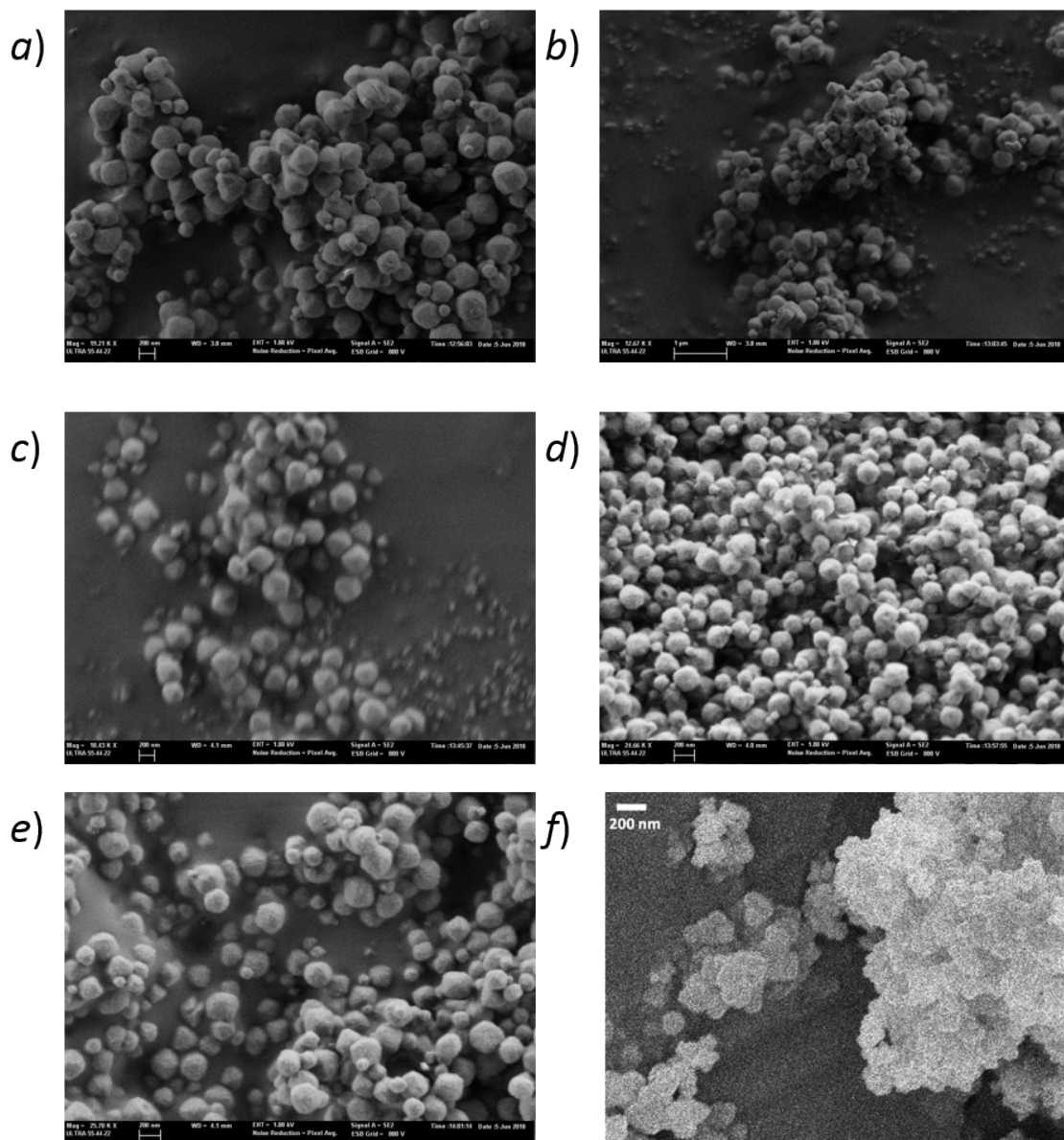


Figure S4. Scanning-Electron Microscopy images of: a) MOF-808; b) MOF-808-IP; c) MOF-808-Pydc; d) MOF-808-OH; e) MOF-808-NH₂; and f) UiO-66.

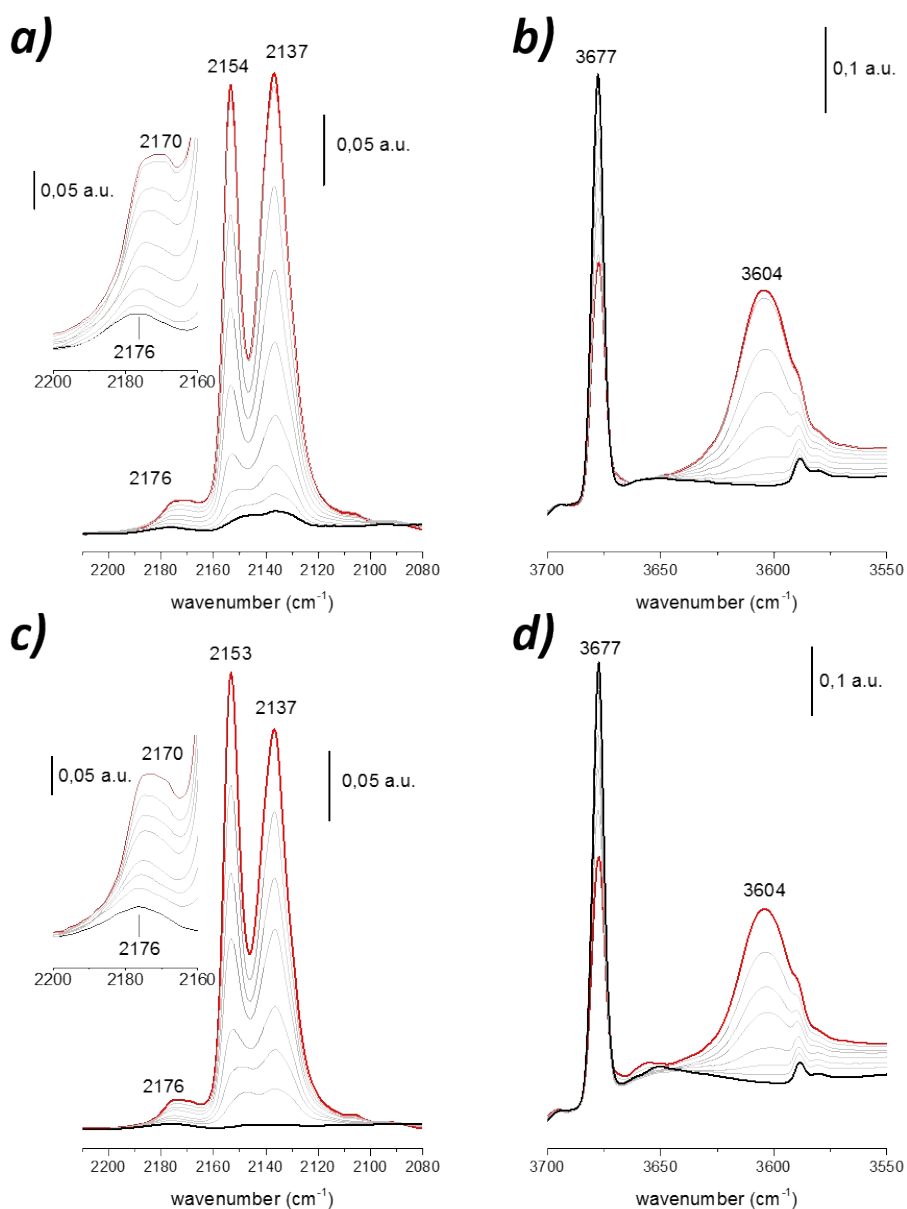


Figure S5. FTIR spectra of CO adsorbed at 77 K on pristine MOF-808 previously activated at 120°C under vacuum; in the C-O (*a*) and O-H (*b*) stretching regions. For the lowest CO equilibrium pressure ($\sim 10^{-2}$ Torr), a single IR absorption band is seen at 2176 cm^{-1} which can be assigned to the C-O stretching mode of $\text{Zr}^{4+}\cdots\text{CO}$ adducts formed onto Zr^{4+} open metal sites of MOF-808. Upon increasing the equilibrium pressure of CO, the band at 2176 cm^{-1} progressively broadens and shifts towards lower wavenumbers and a new shoulder become visible at *ca.* 2170 cm^{-1} . (see the inset for a better definition). This new band reflects the formation of multi-carbonyl species on the Zr^{4+} open metal sites. Additionally, a new band develops at 2154 cm^{-1} , that correspond to CO adsorbed onto the $\mu^3\text{-OH}$ groups of the Zr_6 clusters. Note in parts *b*) and *d*) the progressive erosion of the $\nu(\text{OH})$ band of these OH groups at 3677 cm^{-1} and the appearance of a new, broader band at 3604 cm^{-1} ($\Delta\nu(\text{O-H}) = -73 \text{ cm}^{-1}$) indicative of mild acid sites. Finally, at the highest CO equilibrium pressure, an additional CO

absorption band is observed at 2137 cm^{-1} , corresponding to CO physisorbed inside the pores of MOF-808.

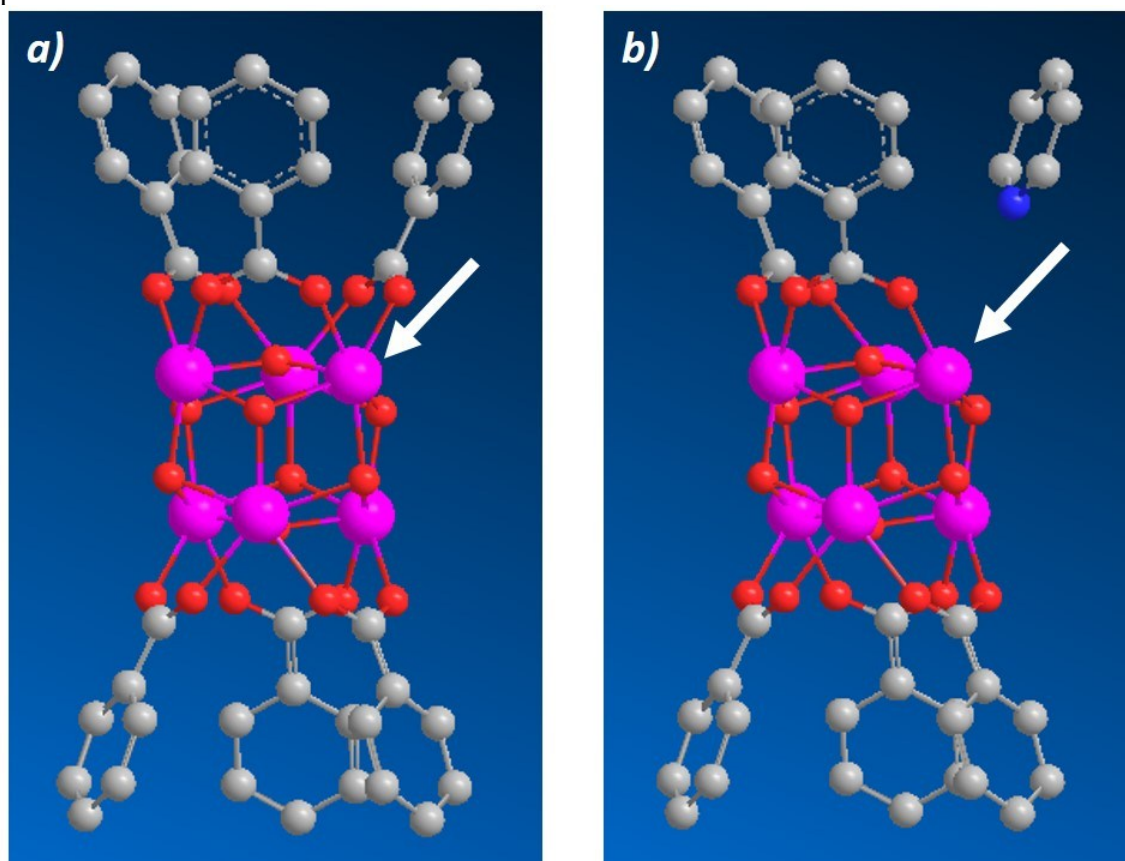


Figure S6: Detail of the Zr₆ oxoaggregates in (a) pristine MOF-80 and (b) MOF-808-Pydc, evidencing the less sterically crowded environment of the Zr ions (indicated with a white arrow) in the latter material. Color code: C, grey; O, red; H, white; Zr, pink. H atoms are omitted for clarity.

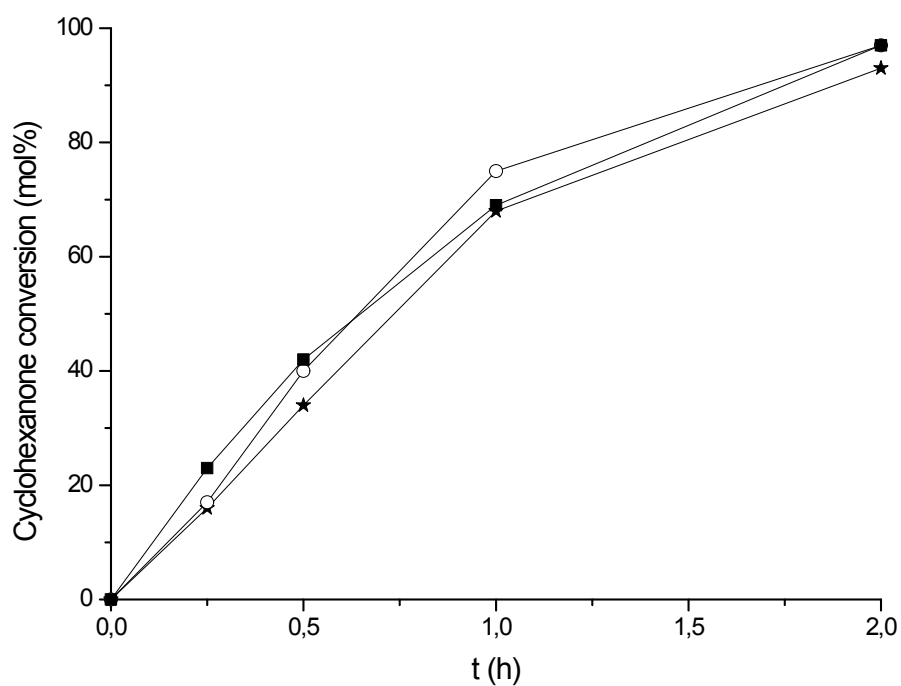


Figure S7. Conversion of cyclohexanone over MOF-808 (■), MOF-808-OH (○) and MOF-808-NH₂ (*).

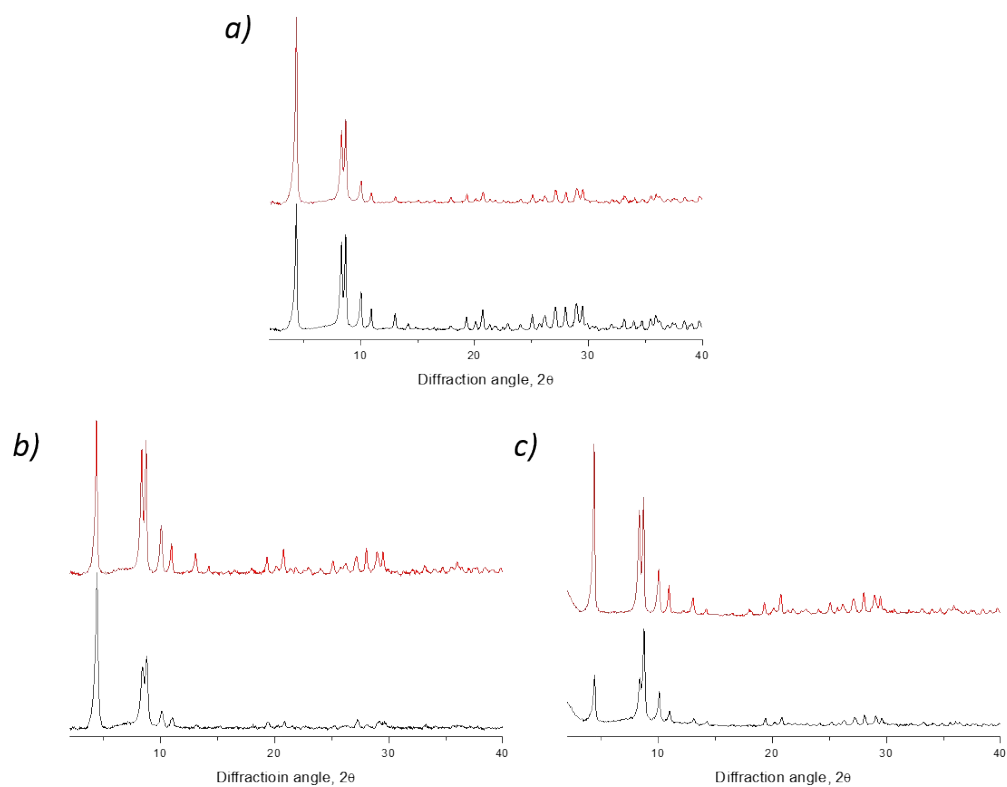


Figure S8. X-ray diffraction patterns (Cu K α radiation) of fresh (*top*) and used (*bottom*) MOF-808 (a), MOF-808-IP (b) and MOF-808-Pydc (c).

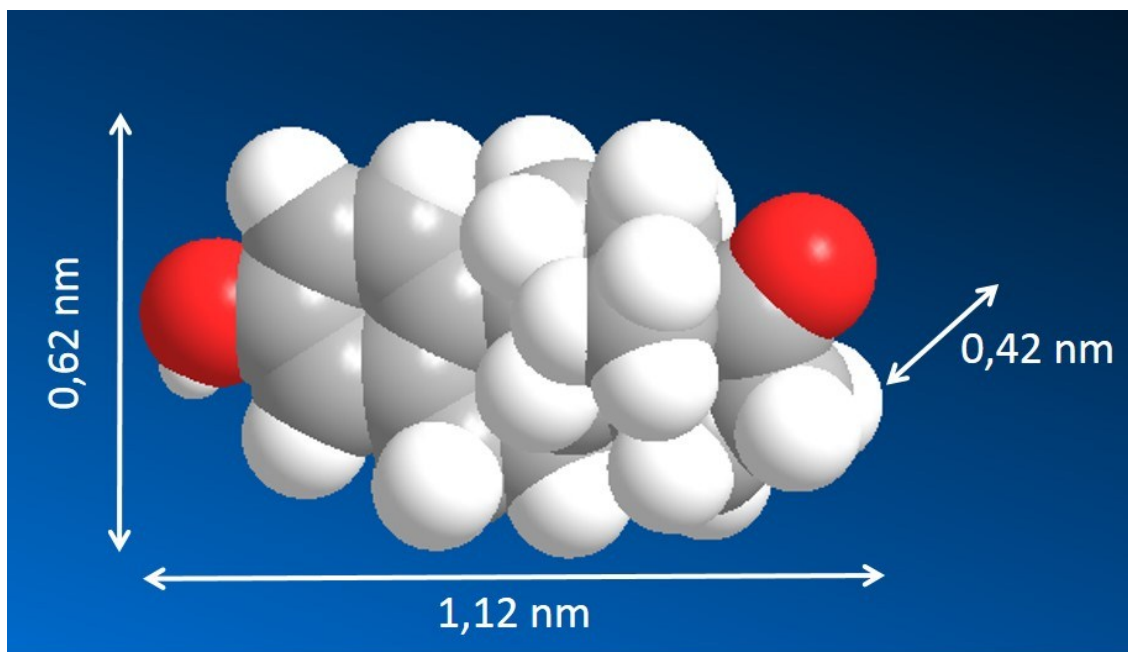


Figure S9. Approximate dimensions of estrone (E1), as obtained from the optimized structure using MOPAC2016.

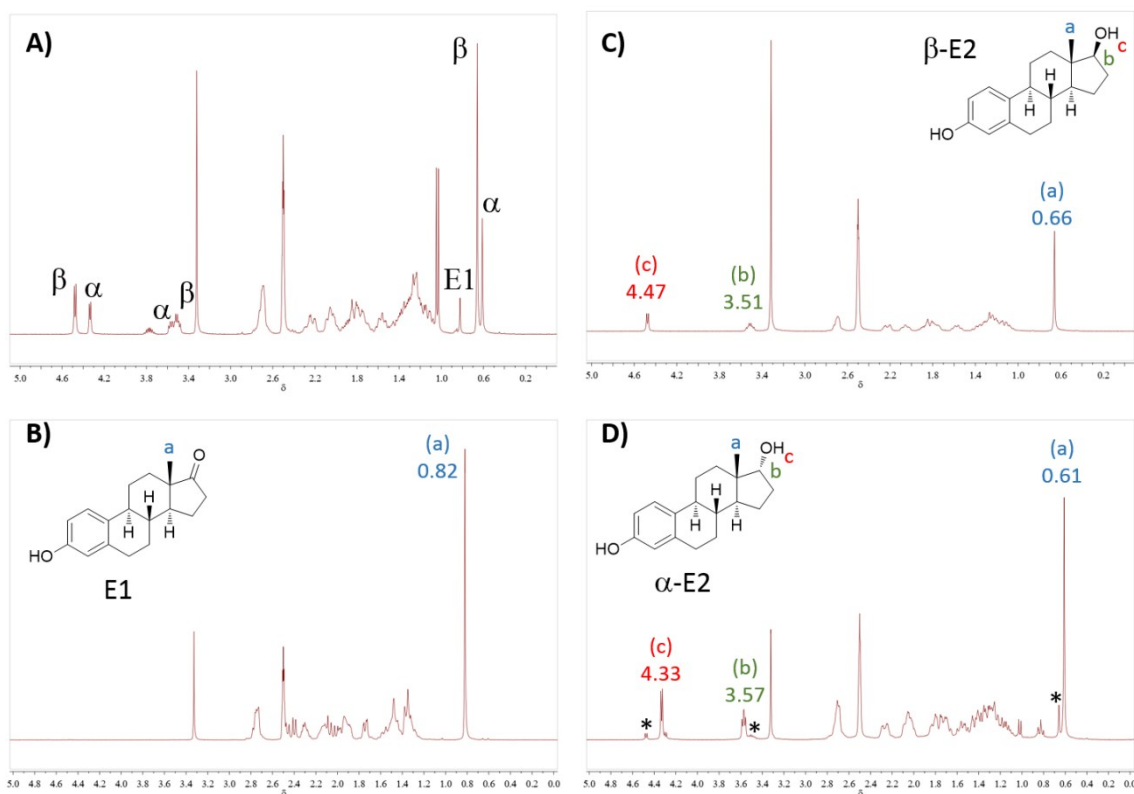


Figure S10. ^1H NMR spectra of: (A) the reaction crude obtained at almost full estrone conversion (some estrone still left, marked with E1); and reference spectra of (B) estrone, (C) 17- β -estradiol (β -E2), and (D) 17- α -estradiol (α -E2). The most prominent peaks of each compound have been indicated. In (D), the asterisks mark some traces of β -E2 detected together with α -E2.

The values of diastereomeric α -E2: β -E2 ratio reported in Table 2 of the main text have been calculated from both the ratios of peaks at 0.61/0.66 and 4.33/4.47, for α -E2 and β -E2 respectively.