SUPPORTING INFORMATION

Single-Crystal-to-Single-Crystal Post-Synthetic Modification of a Metal-Organic Framework via Ozonolysis

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S1. Materials and Characterization

Materials. Zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, purity ≥ 99.5%), formic acid (purity > 98%), potassium iodide (KI), *N,N*-diethylformamide (DEF) and anhydrous granular $CaCl_2$ (2-6 mm) were purchased from Sigma-Aldrich Co. *N,N*-dimethylformamide (DMF) and acetone were obtained from Fisher Chemical. 2-ethenylbenzene-1,4-dicarboxylic acid (purity >97%) was obtained from iChemicals Co. All the reagents and solvents were used without further purification unless otherwise specified. Deionized water was obtained with a Milli-Q® system (18.2 MΩ·cm). Pyrex tubes (outØ5mm x inØ3.4mm; length: 50 cm) were purchased from VIDRASA S.A. The tubes were bent into a U-shape with a flame torch prior to any ozonolysis process. A constant ozone flux was obtained using an ozone generator (model N1668A, 10.4 mmol/h O_3 at room temperature) purchased from Ozonotec.

Characterization. Powder X-Ray Diffraction (PXRD) patterns were recorded on an X'Pert PRO MPD analytical diffractometer (Panalytical) at 45 kV, 40 mA using CuKα radiation (λ = 1.5419 Å). Elemental Analysis measurements were performed on a Flash EA 2000 CHNS (Thermo Fisher Scientific) analyzer. Field-Emission Scanning Electron Microscopy (FE-SEM) images were collected on a FEI Magellan 400L scanning electron microscope at an acceleration voltage of 2.0 KV, using aluminum as support. ^{13}C NMR spectra were recorded on an Bruker Avance 500 NMR spectrometer (static magnetic field of 11.7 T) operating at Larmor frequencies of 500.1 MHz (^1H) or 125.8 MHz (^{13}C). The samples were packed in rotors (o.d.: 4 mm) and analyzed at 10 kHz MAS frequency. ^{13}C chemical shifts were referenced to the carbon signal in TMS at 0 ppm. The Cross-Polarization with Polarization Inversion (CPPI)[1] spectrum of **ozo-ZrBDC** was recorded using a pulse-inversion duration of 50 μs. ^1H step small-phase incremental alternation (SPINAL-64)[2] decoupling was applied during the ^{13}C signal acquisition (~ 80 kHz RF field). Nitrogen adsorption and desorption measurements were done at 77 K using an Autosorb-IQ-AG analyser.

Crystallography. Single-Crystal X-Ray Diffraction (SCXRD) data of **ZrEBDC** and **ZrBDC-COOH** were collected at 100(2) K in BL13-XALOC beamline[3] at the ALBA synchrotron, on a single-axis goniometer with a Pilatus 6M detector using a monochromatic X-ray beam (λ = 0.75253 Å and λ = 0.82653 Å, respectively). The data were indexed, integrated and scaled using the XDS program.[4] Absorption corrections were not applied. The **ZrEBDC** structure was solved by direct methods and subsequently refined by correction of F^2 against all reflections, using SHELXS2013 and SHELXL2013 within the WinGX package and OLEX2.[5-7] Single-crystal diffraction data for **ozo-ZrBDC** was collected in beamline I19-1 at Diamond Light Source, UK, on a fixed-chi goniometer with a Pilatus 2M detector (silicon (111) monochromatic radiation, λ = 0.6889 Å).[8] Data were processed using XiA.[9] Two different refinements were completed for this sample. In the first one, the

framework cubic symmetry was maintained, and the residual electron density corresponding to the trioxolane groups was accounted by means of the program Squeeze. In a second refinement, the crystal structure was refined in the *C2* space group, in order to refine the position of the trioxolane groups, which were refined as rigid bodies with the use of the FRAG and EADP instructions. The position of the carbon atoms bound to the linker phenyl ring could be readily identified in the difference density maps, and used to set the position of rigid body fragments, whose conformation was obtained from DFT calculations.

Computational Details. All calculations were performed at the DFT level using the M06 functional[10] with an ultrafine grid[11] as implemented in Gaussian09.[12] This functional accounts for dispersion interactions and has a good performance on inorganic systems.[13] The Zr atom was described by means of an effective core potential SDD for the inner electron and its associated double-ζ basis set for the outer ones,[14] complemented with a set of f-polarisation function.[15] The 6-31G basis set was used for the C atoms, 6-31G(d) for the O atoms and 6-31G(p,d), for H atoms.[16] The two possible structures were fully optimized in gas phase. Both structures were identified as minimum points in the potential energy surface by determining the absence of imaginary frequencies in the Hessian matrix. All energy values correspond to Gibbs energies in kcal mol^{-1}. Structures optimized without any geometrical restriction resulted in folded geometry (Structures **A** and **B** in Figure S5a), which would impose a tension in the solid-state structure that could hardly allow the formation of crystalline samples. Therefore, an additional set of optimizations was carried out restricting to 180º the value of the dihedral angle described by the planes Zr_a-Zr_b-C_a (Figure S5b) and Zr_b-C_a-C_b. Although unrestricted re-optimization always tends to the folded structure, the energetic difference between restricted an unrestricted was very small. In fact, frequency calculations in all restricted and unrestricted structures resulted only in positive values of frequencies. Therefore, the potential energy surface in the region of calculated geometries was very shallow and all structures found, both folded and straight, can be, as a matter of fact, considered as minimums of energy. The geometries relevant to elucidate the crystal structure are the ones that keep the dihedral angle Zr_a-Zr_b-C_a-C_b value at 180º (Structures **C** and **D** in Figure S5b). Therefore, the following structural discussion is focused on such structures.

Structural Discussion of optimized geometries. The main structural feature distinctive of structures **C** and **D** is the interaction that triozolane cycle establishes with the $\{Zr_6(RCOO)_{12}(OH)_4O_4\}$ cluster. First, in structure **C** two H-bonding interactions can be described with the proton that corresponds to the fragment O-C(H)-O, one with a $H\cdots O_{(benzoate)}$ distance of 2.24 Å and the other one with a $H\cdots O_{(formiate)}$ distance of 2.41 Å. On the other hand, in structure **D** two H-bonding are established with one of the protons in the fragment $O\text{-}C(H)_2\text{-}O$, which can be discerned by a $H\cdots O_{(benzoate)}$ distance of 2.66 Å and a $H\cdots O_{(formiate)}$ distance of 2.37 Å. Such multiple supramolecular interactions orientate the triozolane cycle fixing two positions of the rotation trough the $C_{(arom)}$-$CH_{(triozolane)}$ bond: one for structure **C** and another one for structure **D**. Such rotation positions, which can be defined by the

dihedral angle $C1_{(arom)}$- $C2_{(arom)}$-$C3_{(triozolane)}$-$H_{(triozolane)}$ (Figure S5c; 23º for **C** and 162º for **D**), are two plausible conformations that could be found in the crystal structure. In fact, the crystal structure can be interpreted as a mixture of both situations, which can be found randomly in different positions of the structure. In addition, in order to maximize H-bonding interactions, phenyl groups also rotates around the $C_{(carbox)}$- $C_{(arom)}$ bond. This rotation can be described by the dihedral angle $C1_{(arom)}$- $C2_{(arom)}$-$C_{(carboxy)}$-$O_{(carboxy)}$ (Figure S5c; 29º for **C** and 36º for **D**). This additional rotation, also associated to the interaction between the metallic cluster and the triozolane cycle, adds an additional uncertainty in the location of carbon atoms in of the phenyl group.

Coordinates of optimized geometries

Structure A

Zr	2.117637000	-2.029536000	-0.669704000
Zr	0.345549000	-1.034259000	2.226930000
O	1.002978000	1.138551000	2.149263000
O	0.695081000	-0.833630000	-1.590741000
O	2.035238000	-0.850242000	1.036972000
O	3.462583000	0.602147000	3.062981000
O	-1.131746000	-3.029185000	-1.908859000
O	1.042601000	-3.681357000	-1.740365000
O	4.815873000	-0.161169000	0.853637000
C	-0.154957000	-3.802433000	-2.134241000
O	1.813696000	-0.727437000	3.895514000
C	2.923461000	-0.120400000	3.952315000
C	5.073605000	-1.329890000	0.439828000
O	-0.924640000	0.093493000	3.689201000
O	3.002428000	-2.111347000	-2.729361000
O	1.201638000	-3.057662000	2.675547000
O	2.344377000	-3.697260000	0.814308000
C	2.962134000	-1.306285000	-3.705976000
C	1.954640000	-3.829633000	2.011724000
O	-1.538286000	-2.239035000	2.468574000
O	-2.563248000	-2.243994000	0.437551000
C	-2.492109000	-2.498226000	1.679450000
O	0.108981000	-2.293211000	0.352438000
Zr	-0.466154000	2.041756000	0.670190000
Zr	1.308834000	1.045021000	-2.224474000
O	2.995668000	0.018641000	-1.104337000
O	-0.785644000	-0.004286000	0.826164000
O	1.360766000	1.714024000	-0.259303000
O	-0.795054000	1.162061000	-1.392235000
O	4.162191000	2.328944000	-0.405253000
O	-3.151303000	0.136555000	-0.704445000
O	-2.662543000	2.117700000	0.274237000
O	2.803148000	3.092708000	1.801160000
O	0.627757000	3.742922000	1.639273000
C	-3.479285000	1.238192000	-0.153681000
O	3.130232000	2.339118000	-2.433842000
C	4.012461000	2.708445000	-1.603991000
C	-4.934616000	1.539529000	-0.051127000
C	1.852185000	3.921340000	1.909771000
O	2.481720000	-0.135040000	-3.730583000
O	-1.451336000	2.069104000	2.689361000
O	0.554498000	3.116668000	-2.634023000
O	-0.584912000	3.762271000	-0.772386000
C	-1.522293000	1.207941000	3.614749000
C	-0.085506000	3.944823000	-1.921476000
O	-0.097363000	0.641742000	-3.925079000
O	-1.749143000	-0.679568000	-3.085240000
C	-5.332731000	2.881746000	-0.074087000
C	-5.906831000	0.524375000	0.027716000
C	-7.258651000	0.873693000	0.033452000
C	-7.647584000	2.211079000	-0.019140000
C	-1.142688000	-0.067667000	-4.013130000
C	-6.683270000	3.218495000	-0.064650000
C	-5.531798000	-0.920489000	0.159223000
C	-6.085270000	-2.913743000	-0.747397000

O	-6.490905000	-1.596025000	0.979759000
O	-6.128882000	-2.945267000	0.682929000
O	-5.621043000	-1.616180000	-1.088527000
Zr	2.914056000	1.026535000	0.929748000
Zr	-1.263588000	-1.012293000	-0.925176000
O	4.304099000	-2.126385000	-0.173962000
H	-0.376003000	-4.696291000	-2.733627000
H	3.480192000	-0.221303000	4.893965000
H	6.094466000	-1.691767000	0.623563000
H	3.411726000	-1.662595000	-4.642854000
H	2.300665000	-4.731776000	2.534393000
H	-3.362019000	-3.011758000	2.113331000
H	2.119308000	4.912897000	2.300108000
H	-2.170531000	1.464169000	4.463750000
H	-0.237990000	4.940319000	-2.360701000
H	-4.566231000	3.648129000	-0.107509000
H	-8.000773000	0.086230000	0.101086000
H	-1.585227000	-0.151975000	-5.014974000
H	-6.982041000	4.260499000	-0.093324000
H	-7.080831000	-3.067594000	-1.179590000
H	-5.382373000	-3.695579000	-1.049531000
H	4.746698000	3.437132000	-1.973862000
H	3.853037000	0.023199000	-1.541615000
H	-1.451426000	1.615942000	-1.930534000
H	-0.177577000	-3.201595000	0.490544000
H	1.072811000	1.584295000	2.999372000
H	-8.701773000	2.466113000	-0.015114000
H	-4.538921000	-1.067926000	0.583906000

Structure B

Zr	2.268416000	-1.679988000	1.094066000
Zr	0.886245000	1.428574000	2.070408000
O	1.149089000	2.430796000	0.050365000
O	0.534664000	-1.759881000	-0.035120000
O	2.290467000	0.390197000	0.949247000
O	3.786734000	2.774547000	0.379940000
O	-0.950247000	-3.031494000	2.088473000
O	1.297700000	-3.371238000	2.210882000
O	4.843379000	0.403454000	-0.358870000
C	0.086755000	-3.687937000	2.401561000
O	2.547934000	2.921009000	2.283717000
C	3.535799000	3.204868000	1.543934000
C	5.214843000	-0.565838000	0.366108000
O	-0.281547000	3.345650000	2.119839000
O	2.783973000	-3.545712000	-0.039829000
O	2.133110000	0.721494000	3.797004000
O	3.018509000	-1.280352000	3.172439000
C	2.438062000	-3.968748000	-1.182207000
C	2.872229000	-0.294744000	3.953774000
O	-0.704558000	1.146125000	3.628501000
O	-2.051075000	-0.528981000	2.879569000
C	-1.719704000	0.389935000	3.684647000
O	0.540513000	-0.805500000	2.277141000
Zr	-0.681565000	1.717708000	-1.094982000
Zr	0.703489000	-1.388156000	-2.069558000
O	2.709238000	-1.063403000	-1.046358000
O	-0.619850000	0.829171000	0.780382000
O	0.985436000	0.632785000	-1.686921000
O	-1.218868000	-0.479421000	-1.278064000
O	3.579164000	0.642479000	-2.920903000
O	-3.242190000	-0.270029000	0.487295000
O	-2.865324000	1.530560000	-0.828887000
O	2.514549000	3.012293000	-2.179959000
O	0.267740000	3.358212000	-2.299587000
C	-3.622766000	0.759485000	-0.147469000
O	2.227330000	-1.024869000	-3.678199000
C	3.164934000	-0.181490000	-3.789032000
C	-5.055782000	1.184661000	-0.086355000
C	1.473924000	3.596981000	-2.602622000
O	1.771143000	-3.359937000	-2.069825000
O	-1.316545000	3.525083000	0.099251000
O	-0.434727000	-0.625835000	-3.840523000
O	-1.316544000	1.377329000	-3.218340000
C	-1.069134000	3.884470000	1.288296000
C	-1.070741000	0.449921000	-4.044300000
O	-0.898558000	-2.948382000	-2.244038000
O	-2.097347000	-2.805446000	-0.318689000
C	-5.262942000	2.571130000	-0.035472000
C	-6.171060000	0.324840000	-0.090007000

C	-7.451736000	0.883434000	-0.021080000
C	-7.646097000	2.259358000	0.071729000
C	-1.821853000	-3.299591000	-1.452500000
C	-6.542837000	3.109202000	0.061341000
C	-6.136075000	-1.172973000	-0.174929000
C	-5.011159000	-2.903734000	0.745148000
O	-5.138536000	-1.646608000	-1.074754000
O	-5.095570000	-3.020816000	-0.680283000
O	-5.825661000	-1.787482000	1.074152000
Zr	2.812326000	1.199889000	-0.888838000
Zr	-1.220955000	-1.147078000	0.886577000
O	4.493262000	-1.449293000	0.916151000
H	-0.085222000	-4.643859000	2.915299000
H	4.256278000	3.923704000	1.957640000
H	6.297613000	-0.660288000	0.526459000
H	2.769316000	-4.983881000	-1.440420000
H	3.446849000	-0.332347000	4.889408000
H	-2.385598000	0.540469000	4.545229000
H	1.638776000	4.422665000	-3.308400000
H	-1.593734000	4.784693000	1.638390000
H	-1.467387000	0.590105000	-5.058979000
H	-4.393222000	3.218582000	-0.074674000
H	-8.311538000	0.220047000	-0.043110000
H	-2.466516000	-4.122592000	-1.787695000
H	-6.675551000	4.183978000	0.115497000
H	-3.982750000	-2.729946000	1.072530000
H	-5.418002000	-3.835119000	1.149465000
H	3.694016000	-0.172774000	-4.751797000
H	3.465791000	-1.489936000	-1.460896000
H	-2.031669000	-0.663576000	-1.762910000
H	0.435255000	-1.135831000	3.174909000
H	1.291238000	3.382395000	0.069515000
H	-8.650930000	2.661666000	0.136660000
H	-7.113507000	-1.547529000	-0.514004000

Structure C

Zr	-2.112561000	-1.997286000	0.779765000
Zr	-0.446819000	-1.103788000	-2.212388000
O	-1.083490000	1.077726000	-2.172094000
O	-0.644846000	-0.789701000	1.609858000
O	-2.087093000	-0.869229000	-0.962343000
O	-3.582179000	0.539500000	-2.970826000
O	1.174735000	-2.997035000	1.917555000
O	-1.011485000	-3.628186000	1.856192000
O	-4.852175000	-0.147022000	-0.690274000
C	0.199854000	-3.752445000	2.203979000
O	-1.979533000	-0.830009000	-3.828684000
C	-3.084996000	-0.213598000	-3.859400000
C	-5.103622000	-1.300291000	-0.232056000
O	0.772358000	-0.030890000	-3.756718000
O	-2.916356000	-2.009462000	2.874483000
O	-1.337238000	-3.131115000	-2.567752000
O	-2.411402000	-3.705288000	-0.645260000
C	-2.829143000	-1.175893000	3.823676000
C	-2.070381000	-3.875971000	-1.852615000
O	1.421023000	-2.327746000	-2.490301000
O	2.528546000	-2.285451000	-0.502984000
C	2.404940000	-2.571066000	-1.733054000
O	-0.146493000	-2.312366000	-0.312922000
Zr	0.454649000	2.006429000	-0.779721000
Zr	-1.213726000	1.113248000	2.209376000
O	-2.953813000	0.072161000	1.187901000
O	0.739699000	-0.045810000	-0.885559000
O	-1.337109000	1.727103000	0.231514000
O	0.861000000	1.183589000	1.292725000
O	-4.126025000	2.371870000	0.470247000
O	3.161111000	0.100937000	0.531258000
O	2.673031000	2.057197000	-0.496213000
O	-2.849003000	3.058684000	-1.809074000
O	-0.663504000	3.692418000	-1.748717000
C	3.487930000	1.199212000	-0.026477000
O	-3.011180000	2.432858000	2.453602000
C	-3.923287000	2.786340000	1.649374000
C	4.938778000	1.531548000	-0.038073000
C	-1.895868000	3.874920000	-1.976976000
O	-2.336150000	-0.009940000	3.793784000
O	1.349537000	1.970759000	-2.840330000
O	-0.421079000	3.188783000	2.526220000
O	0.659169000	3.763989000	0.606977000

C	1.377667000	1.081763000	-3.741221000
C	0.202769000	3.987009000	1.767202000
O	0.254682000	0.747939000	3.865789000
O	1.855852000	-0.619977000	3.003126000
C	5.313405000	2.879039000	0.007921000
C	5.926897000	0.528727000	-0.057207000
C	7.271269000	0.896685000	0.021728000
C	7.636471000	2.239878000	0.098966000
C	1.293093000	0.026192000	3.935221000
C	6.657424000	3.234000000	0.084268000
C	5.578363000	-0.922882000	-0.205302000
C	6.120543000	-2.898175000	0.747296000
O	6.592737000	-1.587727000	-0.964766000
O	6.236102000	-2.940593000	-0.677808000
O	5.605602000	-1.609995000	1.050576000
Zr	-2.943198000	1.019173000	-0.875252000
Zr	1.284490000	-1.010316000	0.873579000
O	-4.317354000	-2.086597000	0.373890000
H	0.435965000	-4.632036000	2.818540000
H	-3.679672000	-0.335786000	-4.774973000
H	-6.134239000	-1.657079000	-0.364121000
H	-3.244848000	-1.498607000	4.787989000
H	-2.445068000	-4.789121000	-2.334870000
H	3.252953000	-3.102447000	-2.188412000
H	-2.169459000	4.857983000	-2.384011000
H	1.990678000	1.308572000	-4.624087000
H	0.382619000	4.993211000	2.170274000
H	4.535123000	3.634201000	-0.008524000
H	8.027637000	0.120186000	0.000963000
H	1.771939000	-0.036143000	4.921856000
H	6.939805000	4.279882000	0.131652000
H	7.097110000	-3.021787000	1.229826000
H	5.423664000	-3.694562000	1.023447000
H	-4.634370000	3.534153000	2.026222000
H	-3.793221000	0.099635000	1.657916000
H	1.535346000	1.644308000	1.802098000
H	0.125821000	-3.226988000	-0.437960000
H	-1.183351000	1.501764000	-3.030287000
H	8.685119000	2.509822000	0.160977000
H	4.612985000	-1.088504000	-0.686939000

Structure D

Zr	-2.274336000	-1.771562000	-0.919469000
Zr	-1.001546000	1.290987000	-2.149731000
O	-1.202744000	2.417012000	-0.187533000
O	-0.494717000	-1.744684000	0.137919000
O	-2.337777000	0.303172000	-0.906860000
O	-3.857067000	2.691176000	-0.423230000
O	0.928364000	-3.121502000	-1.971506000
O	-1.314584000	-3.512885000	-1.966856000
O	-4.830944000	0.352172000	0.510903000
C	-0.106621000	-3.816844000	-2.193810000
O	-2.705187000	2.734262000	-2.386006000
C	-3.666088000	3.047617000	-1.623170000
C	-5.211622000	-0.667999000	-0.135477000
O	0.118311000	3.222714000	-2.371100000
O	-2.702952000	-3.569675000	0.350339000
O	-2.300109000	0.450588000	-3.774712000
O	-3.117316000	-1.522020000	-2.985641000
C	-2.301674000	-3.912382000	1.501643000
C	-3.024366000	-0.586677000	-3.833982000
O	0.533790000	0.937772000	-3.750881000
O	1.948774000	-0.655463000	-2.950599000
C	1.564067000	0.202437000	-3.798690000
O	-0.615371000	-0.943682000	-2.228133000
Zr	0.690563000	1.814948000	0.918002000
Zr	-0.587310000	-1.246782000	2.149835000
O	-2.639410000	-1.026849000	1.194443000
O	0.565698000	0.802035000	-0.888098000
O	-0.925893000	0.739126000	1.651543000
O	1.286836000	-0.357001000	1.219988000
O	-3.464241000	0.778498000	2.995105000
O	3.242565000	-0.226989000	-0.632261000
O	2.856802000	1.660454000	0.551256000
O	-2.486010000	3.115322000	2.058871000
O	-0.243860000	3.508848000	2.060418000
C	3.623432000	0.829899000	-0.045638000
O	-2.048909000	-0.813819000	3.796409000
C	-2.998153000	0.018372000	3.894295000

C	5.073807000	1.203323000	-0.018612000
C	-1.441054000	3.744497000	2.398939000
O	-1.611839000	-3.236143000	2.319936000
O	1.225651000	3.560188000	-0.409972000
O	0.607063000	-0.344532000	3.817338000
O	1.429557000	1.624325000	3.027152000
C	0.922311000	3.834897000	-1.608252000
C	1.232378000	0.751255000	3.922615000
O	1.051706000	-2.758758000	2.362137000
O	2.142862000	-2.738571000	0.369834000
C	5.330225000	2.581602000	-0.085993000
C	6.159768000	0.312435000	0.087894000
C	7.458447000	0.833168000	0.108652000
C	7.703116000	2.199789000	0.004301000
C	1.937721000	-3.154369000	1.548532000
C	6.629061000	3.080782000	-0.092265000
C	6.083228000	-1.181965000	0.189680000
C	4.984294000	-2.912478000	-0.756807000
O	5.035517000	-1.627150000	1.046825000
O	5.002418000	-3.007574000	0.672291000
O	5.818560000	-1.805007000	-1.064999000
Zr	-2.796872000	1.218723000	0.898315000
Zr	1.210335000	-1.163329000	-0.893418000
O	-4.495131000	-1.570629000	-0.660315000
H	0.063441000	-4.799826000	-2.654484000
H	-4.419619000	3.723328000	-2.050565000
H	-6.297949000	-0.792800000	-0.242146000
H	-2.600877000	-4.914863000	1.836997000
H	-3.636858000	-0.695004000	-4.739587000
H	2.193020000	0.311601000	-4.692694000
H	-1.593751000	4.610401000	3.057757000
H	1.406543000	4.723844000	-2.036305000
H	1.667020000	0.965138000	4.908530000
H	4.481666000	3.255677000	-0.132038000
H	8.293198000	0.145677000	0.209442000
H	2.614029000	-3.941951000	1.904787000
H	6.797684000	4.149680000	-0.160630000
H	3.974046000	-2.735863000	-1.134804000
H	5.402747000	-3.852545000	-1.127615000
H	-3.486871000	0.078204000	4.876393000
H	-3.370673000	-1.438802000	1.665353000
H	2.114690000	-0.504351000	1.691988000
H	-0.539870000	-1.327626000	-3.107348000
H	-1.367879000	3.362230000	-0.261273000
H	8.722061000	2.570501000	0.010928000
H	7.033829000	-1.574066000	0.580762000

S2. Synthesis

Synthesis of bulk ZrEBDC. Bulk **ZrEBDC** was prepared using an adapted version of a standard solvothermal synthesis.[17] $ZrOCl_2 \cdot 8H_2O$ (2.5 g, 7.8 mmol) was added into a solvent mixture of DMF/formic acid (40 mL/15 mL) in a 100-mL screw-capped jar and sonicated for 15 min. 2-ethenylbenzene-1,4-dicarboxylic acid (**H_2EBDC**) 1.5 g (7.8 mmol) was added to the solution, which was further sonicated for 15 min. The jar was then transferred to a preheated oven and kept at 120 °C for 12 hours. A white crystalline material was collected and was washed three times with 50 mL of fresh DMF. The bulk particles were rinsed in 150 mL of acetone, which was replaced twice every 12 h. Finally, the solid powder was activated at 120 °C under vacuum for 12 h. (Yield: 2.2 g; 92% based on $ZrOCl_2 \cdot 8H_2O$). Elemental Analysis: Exp. C 32.77%, H 2.40%; Cal. C 32.61%, H 1.77%.

Synthesis of single crystals of ZrEBDC suitable for SCXRD. In a 100 mL Erlenmeyer flask, 240 mg (1.35 mmol) of $ZrOCl_2 \cdot 8H_2O$ and 250 mg (1.30 mmol) of H_2EBDC were dissolved in DEF (40 mL) under sonication. The resulting solution was divided into 20 scintillation vials, to each of which was added formic acid (2 mL). The samples were vortexed to homogenization and placed in an oven before being slowly heated to 135 °C (heating rate: 5 °C /min) for 72 h. Colorless octahedral crystals of **ZrEBDC** were harvested from the bottom and walls of the vials and treated as the bulk sample. (Yield: 110 mg; 20%).

Solid-gas phase procedure. Activated bulk **ZrEBDC** (50 mg) was grinded to homogenous powder and mixed with single-crystal **ZrEBDC**, and the resulting mixture was packed inside of a Pyrex tube stoppered by cotton pellets at both ends. The tube was then bent into a U-shape. A 0.1M solution of KI was added at the end of the setup to provide a color-based indicator of ozonolysis progression (from colorless to yellow). Before solid-gas ozonolysis, the sample was vacuumed for 10 min to remove all the residual moisture/solvents. Then, ozone (dried through $CaCl_2$) was steamed into the setup until a deep yellow color in the KI trap indicated full conversion (*ca.* 30 min). The bulk column was kept under vacuum for a further 10 min to remove all the unreacted ozone.

Soft-ligand exchange experiment. **ozo-ZrBDC** was immersed in a 0.2 M solution of 1,4-benzenedicarboxylic acid in DMF for one week. Afterwards, the supernatant was separated from the crystals by centrifugation and subsequently dried, and the resulting solid was dissolved in deuterated DMSO and analyzed by ^{1}H NMR.

Reduction and oxidation work up of Ozo-ZrBDC. Fully-converted **ozo-ZrBDC** (80 mg) was soaked in Me_2S (5% in 0.1M HCl/acetone) and H_2O_2 (10% aq.) under stirring for 12 h.

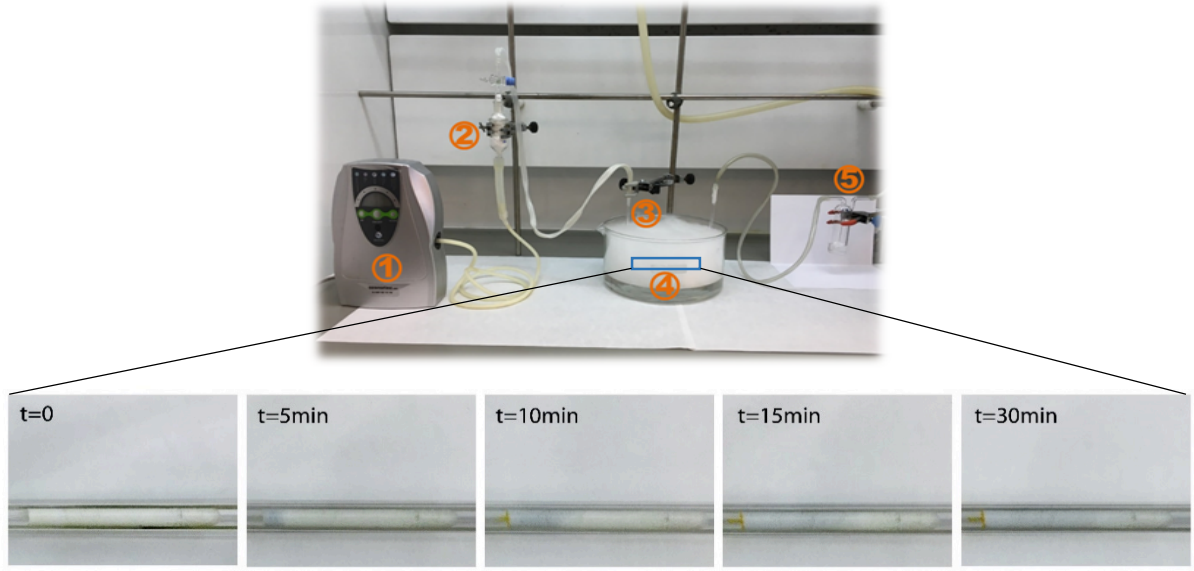

Figure S1. Laboratory set-up for performing ozonolysis experiments on MOF particles. ① Ozonator; ② Desiccator filled with granular $CaCl_2$; ③ U-shaped Pyrex tube containing the MOF column; ④ Basin keeping -78 °C with dry ice/acetone mixture; ⑤ Gas trap filled with aqueous KI solution. Bottom row: photos showing the gradual color change in the bulk column to indicate ozonolysis progression.

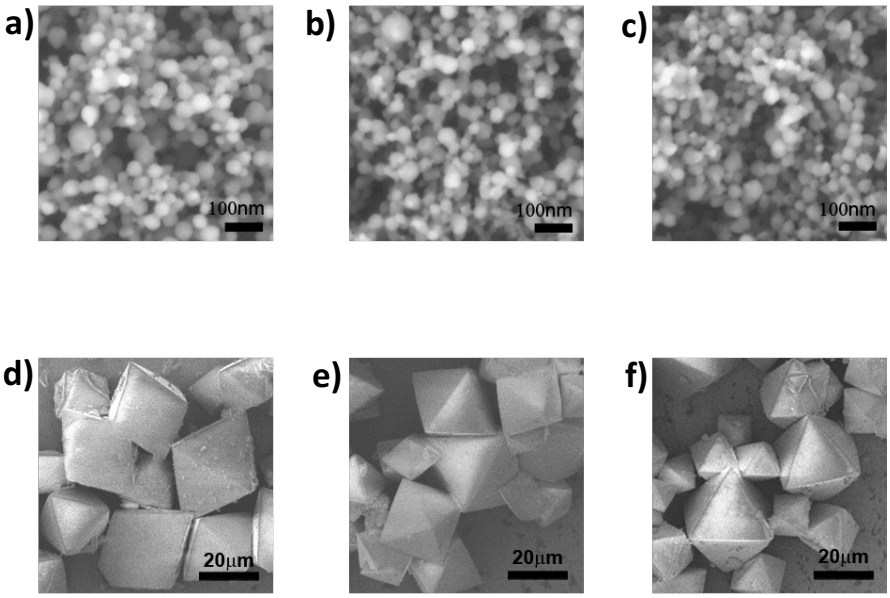

Figure S2. SEM images of bulk a) **ZrEBDC**, b) **ozo-ZrBDC** and c) **ZrBDC-COOH**. Solid-gas phase, single-crystal-to-single-crystal transformation of octahedral single-crystals: d) **ZrEBDC**, e) **ozo-ZrBDC**, and f) **ZrBDC-COOH**.

S3. Single-Crystal XRD Analysis

Table S1. Crystal and structural refinement data for **ZrEBDC, ozo-ZrBDC, ZrBDC-COOH.**

Compound	**ZrEBDC**	**ozo-ZrBDC[a]**	**ozo-ZrBDC[b]**	**ZrBDC-COOH**
Empirical formula	$C_{60}O_{40}Zr_6$	$C_{40.8}O_{35}Zr_6$	$C_{44}O_{44.5}H_{4.6}Zr_6$	$Zr_6C_{45.6}O_{48}$
Formula weight	1907.92	1632.27	1792.40	1819.78
Crystal system	Cubic	Cubic	Monoclinic	Cubic
Space group	*Fm-3m*	*Fm-3m*	*C2*	*Fm-3m*
CCDC reference	1589286	1589288	1589287	1589289
Unit cell dimensions				
a (Å)	20.740(4)	20.720(2)	20.747(4)	20.740(4)
b (Å)	20.740(4)	20.720(2)	20.747(4)	20.740(4)
c (Å)	20.740(4)	20.720(2)	14.670(3)	20.740(4)
β (°)			135.00(3)	
v ($Å^3$)	8921.3(1)	8895.0(3)	4465(2)	8921.3(1)
Z	4	4	2	4
F(000)	6272	3155	1729.0	3533
θ range (°)	2.778 – 26.670	2.97 - 72.29	2.97 - 72.29	1.978 - 33.814
Tot., Uniq.Data, R(int)	28302, 513, 0.121	68423, 1636, 0.1208	68694, 27598, 0.1047	29683, 632, 0.058
Final R indices [I/ sigma(I)>2]	R1 = 0.1012 wR2 = 0.2626	R1 = 0.0379 wR2 = 0.1129	R1 = 0.0616 wR2 = 0.1620	R1 = 0.0339 wR2 = 0.1482
Min. and Max. Resd. Dens. [$e/Å^3$]	-3.05, 1.34	-0.5, 1.29	-0.84, 3.19	-0.38, 1.24
GOF	1.243	1.137	1.1015	1.449

a: Data corresponding to refinement not including disorder model for the oxonale groups. Residual electron density in the cavities was accounted with the Platon Squeeze program. Details are copied below. b: Data corresponding to refinement carried out with a monoclinic cell in order to reduce the number of symmetry equivalent positions of the organic linkers. Note that due to the large correlation of the artificially generated independent positions of the framework atoms, a number of these were isotropically refined, also resulting in higher Rvalues.

Squeeze details of Ozo-ZrBDC:

Summary and Remarks: N = NOTE, W = WARNING, E = ERROR

N: Maximum Residue Number Reduced (Round ARU to 0.1 units)
N: No S.U.'s (esd) on observed/calculated parameters.
N: Maximum allowed number of residues reduced
N: DISORDERED structure - ATOMS with Pop. .LT. 1.0 are not moved or as a group.
N: No-Hydrogen atoms in this structure

N: Number of moved primary input atoms: 9
W: Number of (Carbon) Atoms with no sp(x) assignment 1
N: Number of Ignored Lines on INPUT 4
of which blank in column 1 4
N: Number of modified (= #) ATOM labels 2
W: Number of unusual anisotropic displacement parameters 1
N: Total Potential Solvent Accessible Void Vol (SOLV-Map Value) ... 3466 Ang^3
N: Electron Count Voids / Cell = 657

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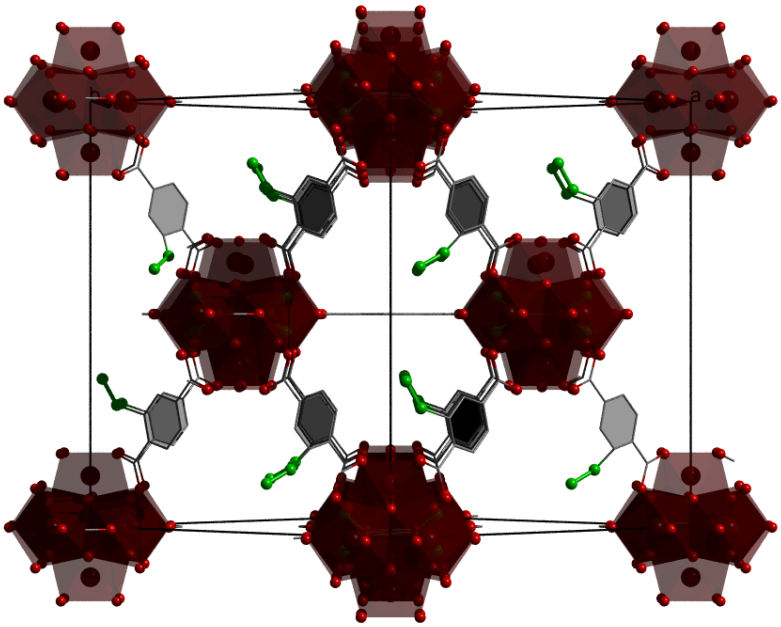


Figure S3. Backbone illustration of single-crystal structure of **ZrEBDC**. The olefinic side-chains of the EBDC linkers are highlighted in green. The zirconium oxide clusters are colored in brown and the aromatic carbons, in grey.

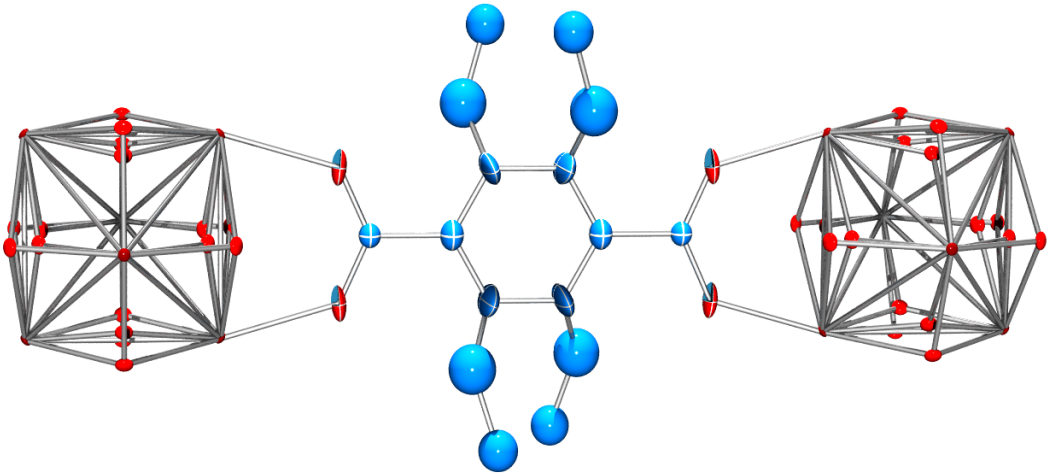
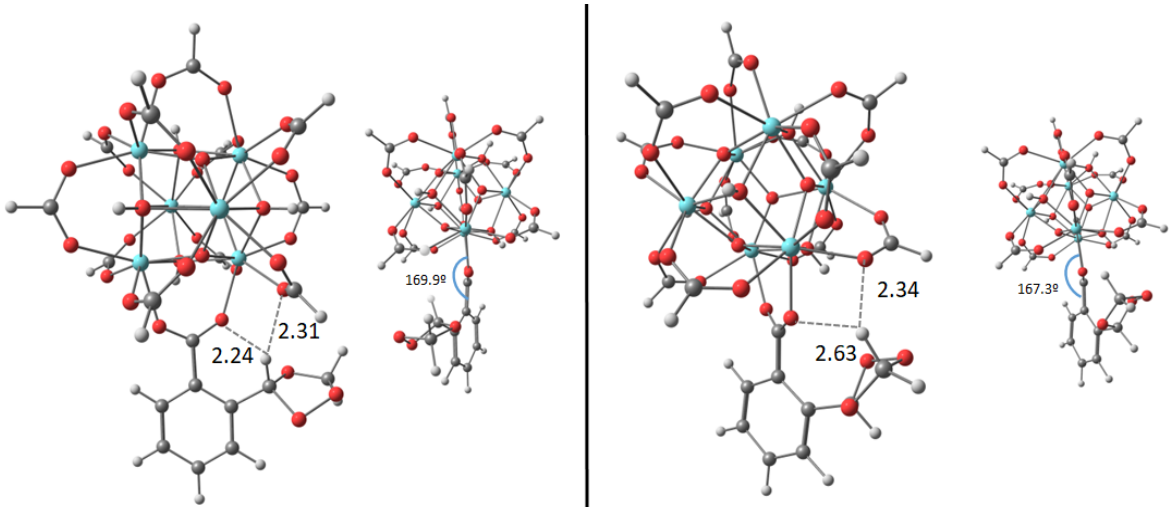


Figure S4. ORTEP drawing of **EBDC** linker as found in the crystal structure of **ZrEBDC.** The four equivalent ethenyl group positions are distorted.

a) **Structures optimized without any geometric restriction**



Structure A

Sum of electronic and thermal Free Energies:

-3689.975465

ΔG = 0 Kcal/mo l

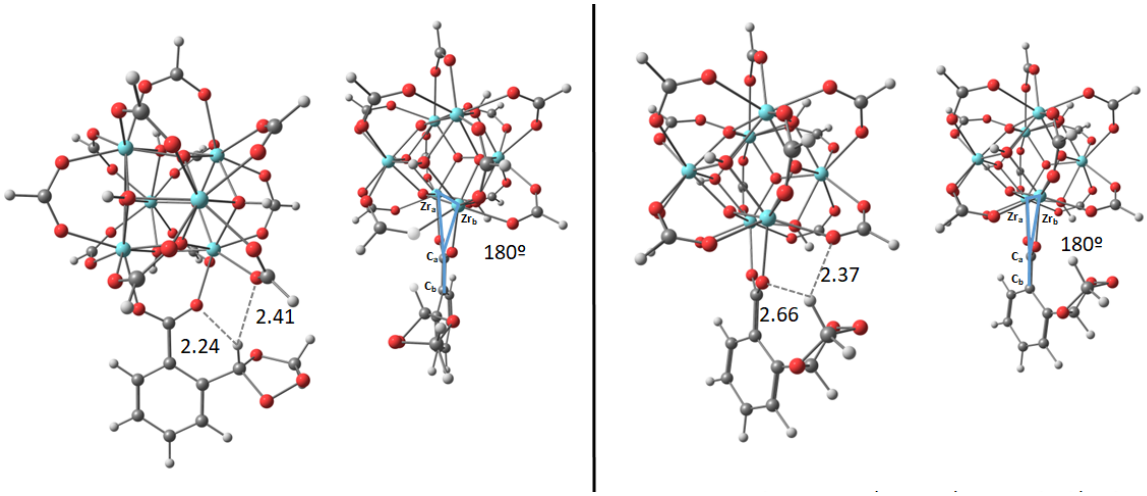
Structure B

Sum of electronic and thermal Free Energies:

-3689.972847

ΔG = +1.6 Kcal/mol

b) **Structures optimized restricting to 180º the value of Zr_a-Zr_b-C_a-C_b dihedral angle**



Structure C

Sum of electronic and thermal Free Energies:

-3689.975158

ΔG = +0.2 Kcal/mol

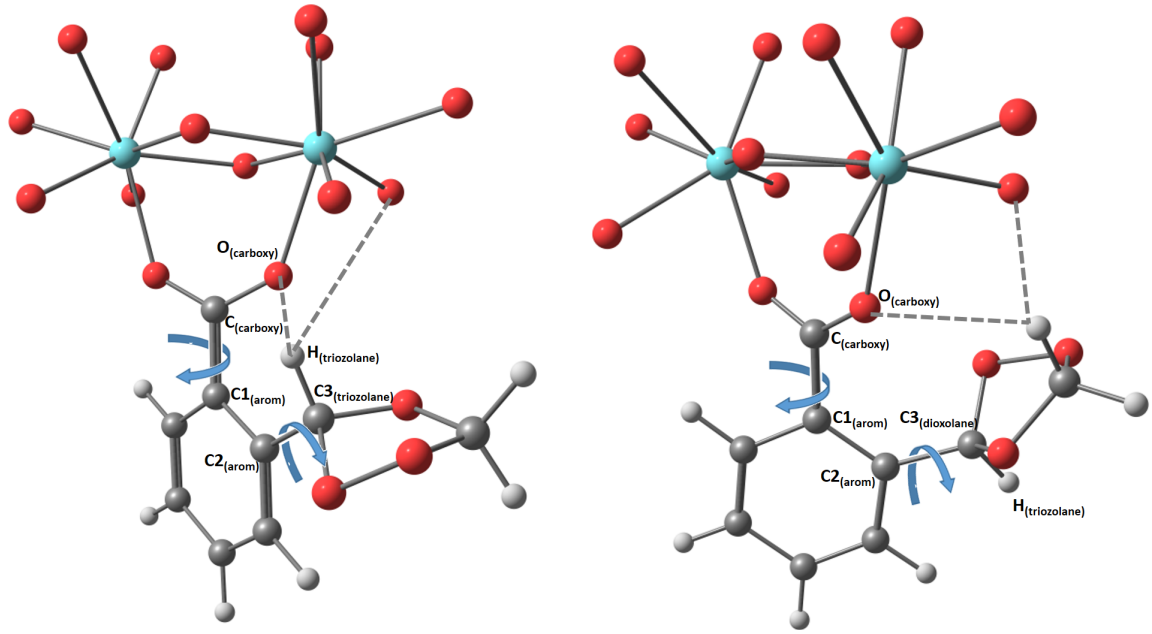
Structure D

Sum of electronic and thermal Free Energies:

-3689.973143

ΔG = +1.5 Kcal/mol

c)



Structure C **Structure D**

Figure S5. a) Structures A and B: Optimized geometries of model fragment without using any geometric restriction. **b)** Structures C and D: Optimized geometries of model fragment fixing to 180º the value of Zr_a-Zr_b-C_a-C_b dihedral angle. **c**) Simplified drawing of structures C and D. Curve arrows indicate rotations found accounting for maximization of hydrogen bonding interactions (noted as dashed lines).

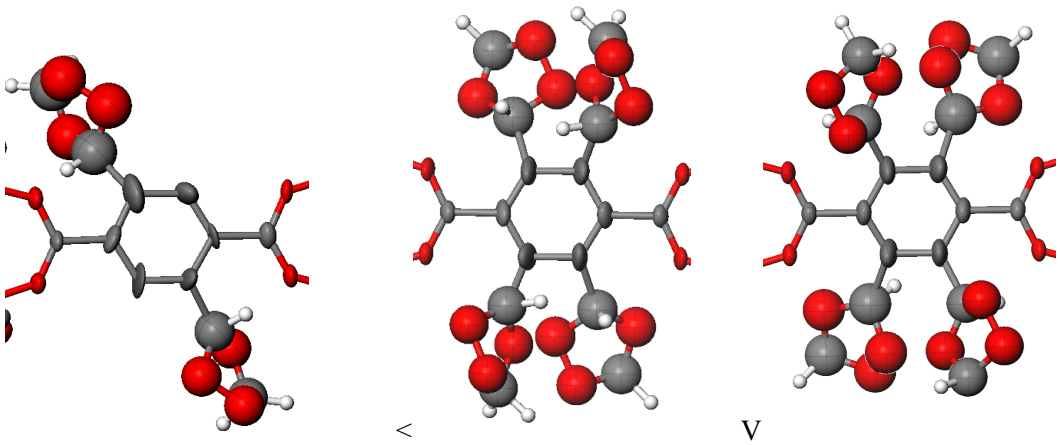


Figure S6. ORTEP drawing of **ozo-BDC** linker as found in the crystal structure of **ozo-ZrBDC.**

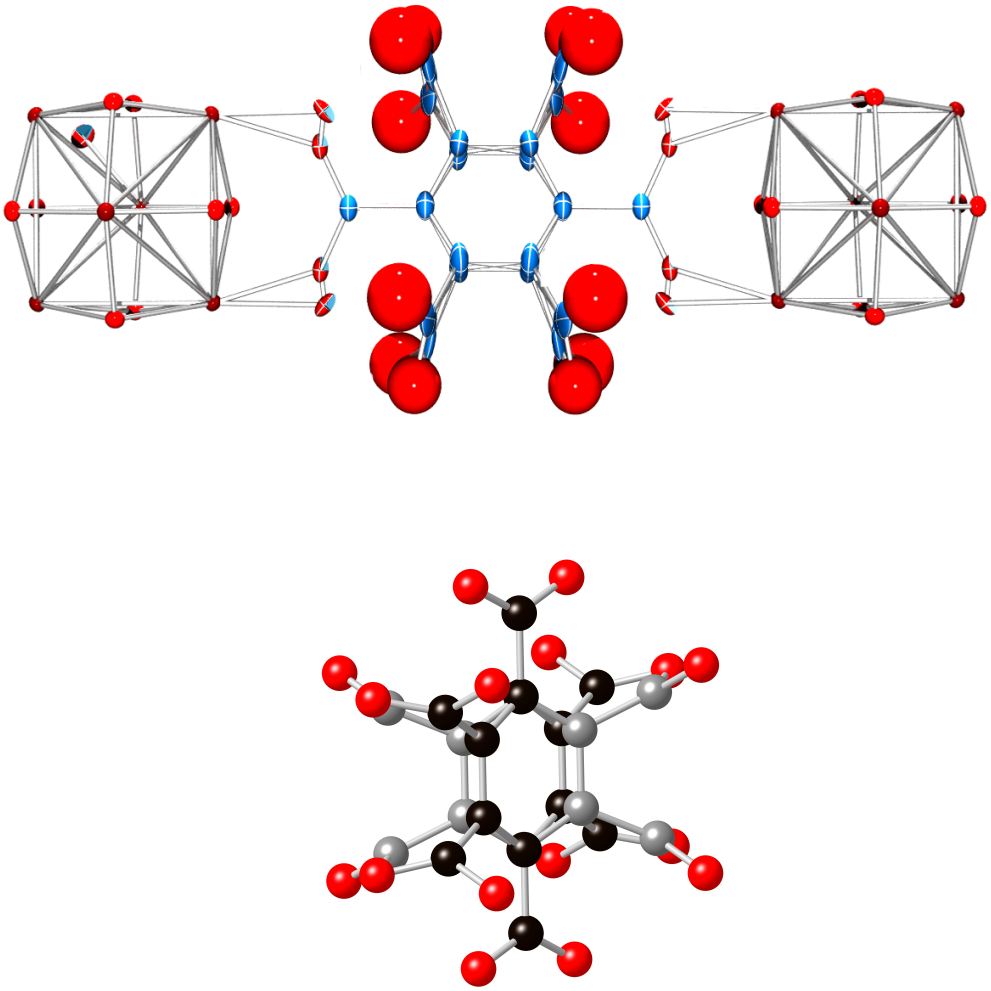


Figure S7. Top: ORTEP drawing **BDC-COOH** linker as found in the crystal structure of **ZrBDC-COOH** after oxidative work up, showing the disorder of the phenyl ring and the carboxylic group. Bottom: Disorder model in the organic linker in **ZrBDC-COOH**: Two orientations are defined for the phenyl ring and the corresponding pending carboxylate C atom, represented in black and grey color, respectively. The position of one of the oxygen atoms of the pending carboxylate groups is shared for the two possible orientations.

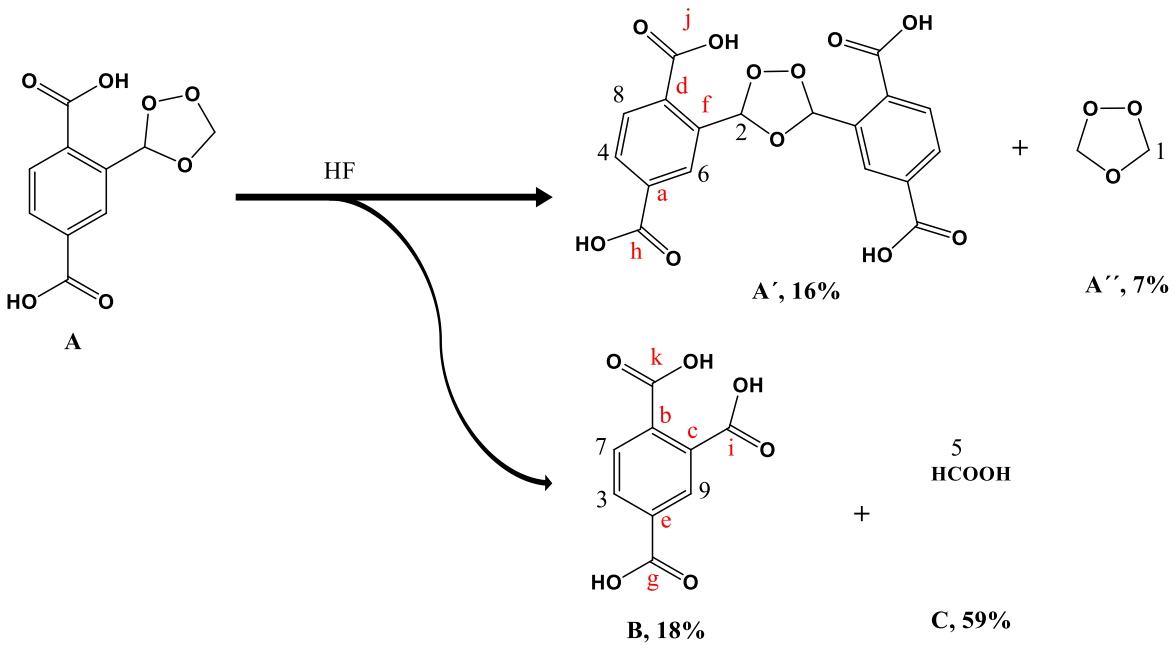
S4. Study of the Degree of Functionalization versus Ozonolysis Time

For this study, we systematically studied the ozonolysis using various reaction times (5 min, 10 min, 15 min and 30 min). To this end, the degree of functionalization was monitored by recording the ^{1}H NMR spectra of the digested samples (5% HF/DMSO-d_6), and then compared each one to that of the starting **ZrEBDC** (see Figures S8-S12). The digestion was done by adding 120 μL 5% HF in D_2O to 20 mg of dry **ZrEBDC** or **ozo-ZrBDC** powder in a 2 mL Eppendorf tube. The resulting mixture was sonicated for 5 min to afford a slurry, which was treated with 0.5 mL DMSO-d_6 and finally, sonicated for 5 more min.

The ^{1}H NMR spectrum of the digested **ZrEBDC** showed the characteristic peaks of three non-equivalent olefinic protons at δ = 7.29 ppm, δ = 5.77 ppm and δ = 5.41 ppm, integrating in a 1:1:1 ratio (see Figure S8). In contrast, the spectrum of the fully converted **ozo-ZrBDC** confirmed a quantitative fading of all the olefinic signals in approximately 30 min of solid-gas interaction, together with the appearance of new signals, including two peaks of interest, at δ = 6.70 ppm and δ = 4.58 ppm (see Figure S12). These latter signals fall within the typical range of chemical shifts for the expected trioxolane moiety,[18,19] but their relative integration does not match the expected 1:2 ratio for the CH and CH_2 protons in the five-membered ring.

Due to the instability of trioxolane moiety under aggressive digestion conditions, the fully ozonized linker **trioxolane-BDC** was subjected to two different degradation pathways. To fully identify these species, the digested **ozo-ZrBDC** sample was further analyzed by 1D-NMR and 2D-NMR (NOESY, DOSY, DEPT135, HSQC and HMBC; see Figures S13-19). After an in-depth analysis of the digested product, four different entities were properly identified in the mixture (see Scheme S1). First, the two, symmetric **cross-ozonation** products of the target **trioxolane-BDC** were properly identified (**A'** and **A''**). Second, both products of the **acid-induced hydrolysis** of the initial trioxolane were identified (**B** and **C**). Further step-by-step identification of these moieties is presented hereafter, divided by the techniques used and employing the same nomenclature as in **Scheme S1**, for clarity.

Finally, the degree of conversion of the olefinic groups into 1,2,4-trioxolane rings was calculated by comparing the combined integration of two peaks, one at 7.73 ppm (corresponding to H3 of 1,2,4-benzenetricarboxylate) and one at 6.70 ppm (corresponding to H2 of the trioxolane-metathesis product A'), versus the olefinic peak at 5.77 ppm (corresponding to EBCD) (see Supporting Informations for labels, Scheme S1).



Scheme S1. Representation of the species formed after digestion of **ozo-ZrBDC** with 5% HF in d_6-DMSO. Carbon atoms with attached protons are labeled with black numbers (**1-9**) and quaternary carbon atoms, with red letters (**a-k**).

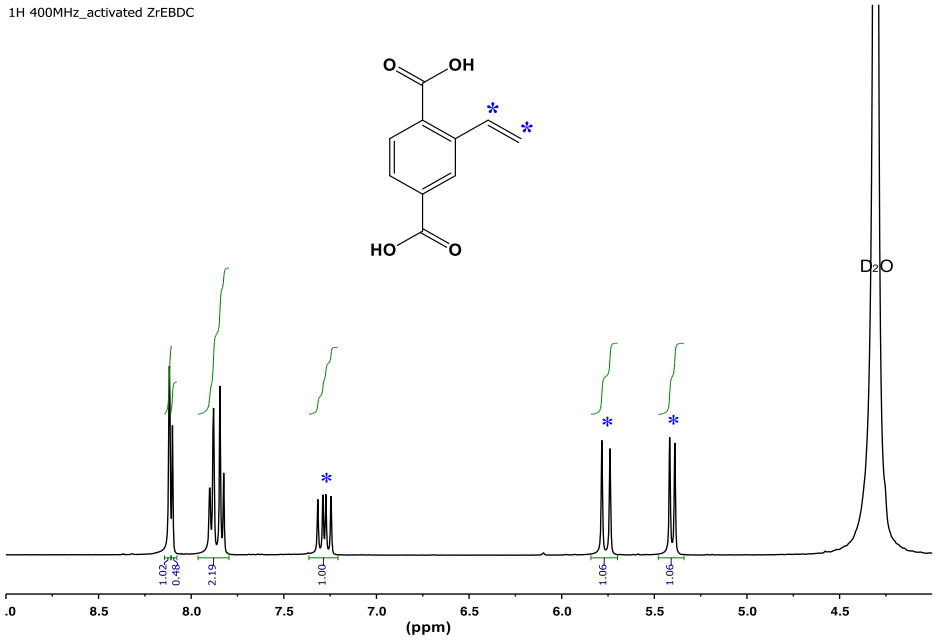


Figure S8. [1]H NMR spectrum of digested activated **ZrEBDC**.

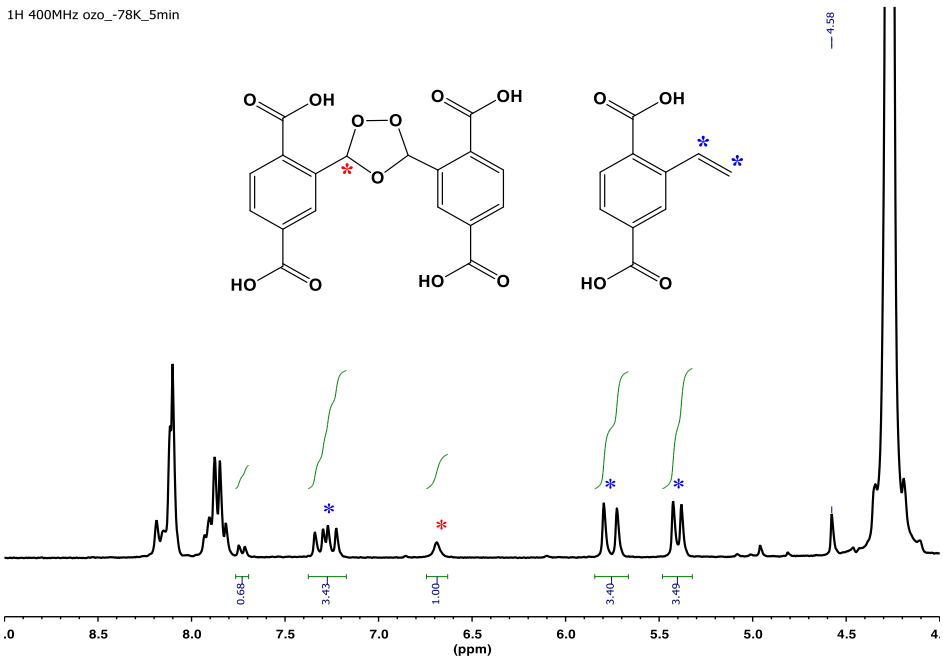


Figure S9. [1]H NMR spectrum of the digested **ZrEBDC** sample after ozonolysis for 5 min. Calculated integration of olefinic proton signals and newly generated proton signals indicated a conversion of 33%.

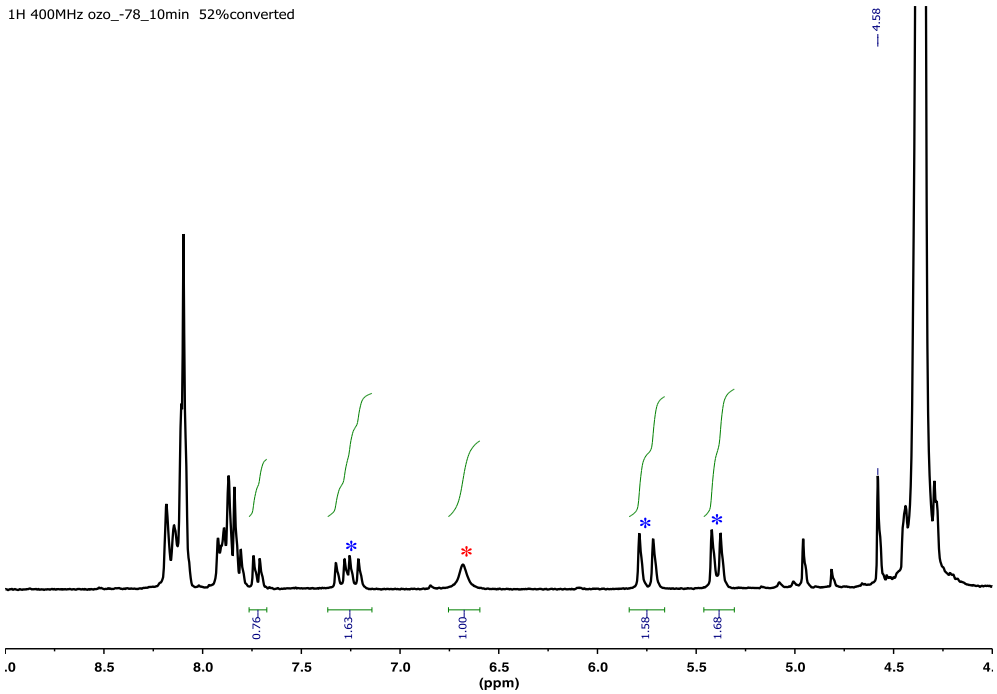


Figure S10. [1]H NMR spectrum of the digested **ZrEBDC** sample after ozonolysis for 10 min. Calculated integration of olefinic proton signals and newly generated proton signals indicated a conversion of 52%.

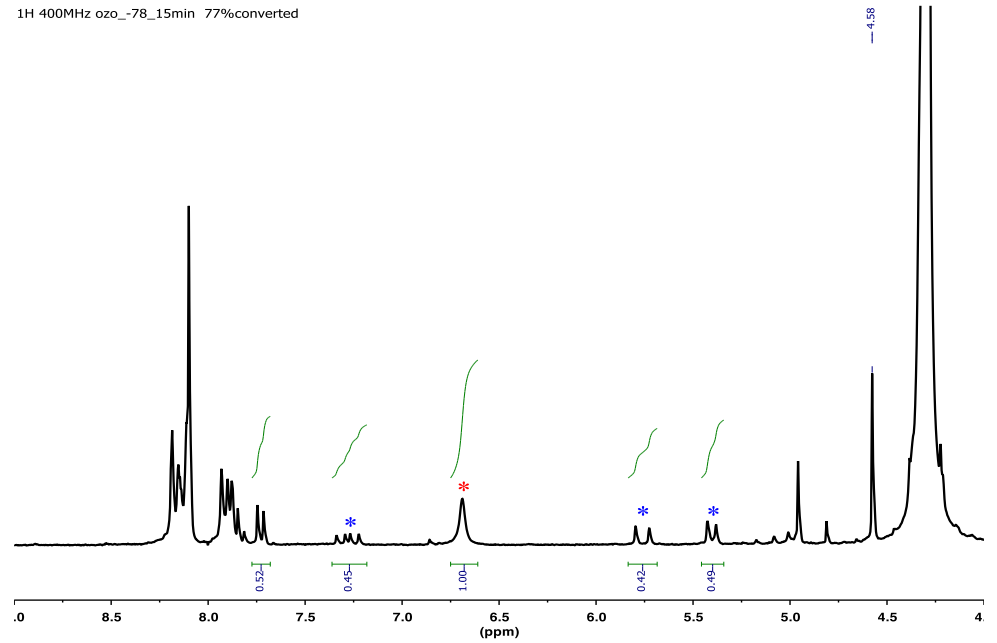


Figure S11. [1]H NMR spectrum of the digested **ZrEBDC** sample after ozonolysis for 15 min. Calculated integration of olefinic proton signals and newly generated proton signals indicated a conversion of 77%.

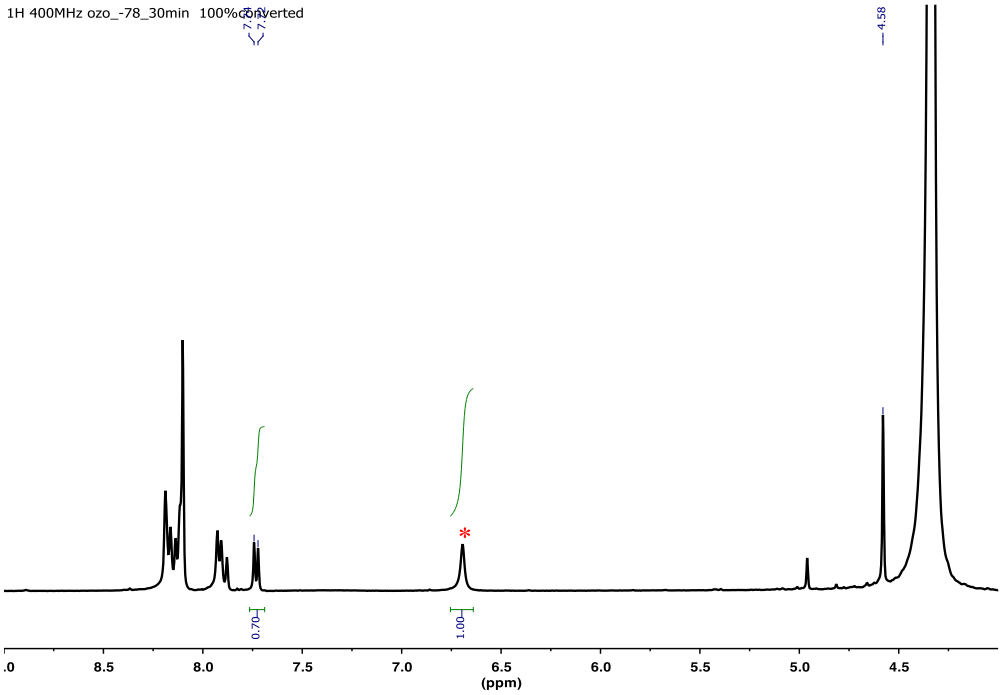


Figure S12. ^{1}H NMR spectrum of the digested **ZrEBDC** sample after ozonolysis for 30 min. Calculated integration of olefinic proton signals and newly generated proton signals indicated a conversion of 100%.

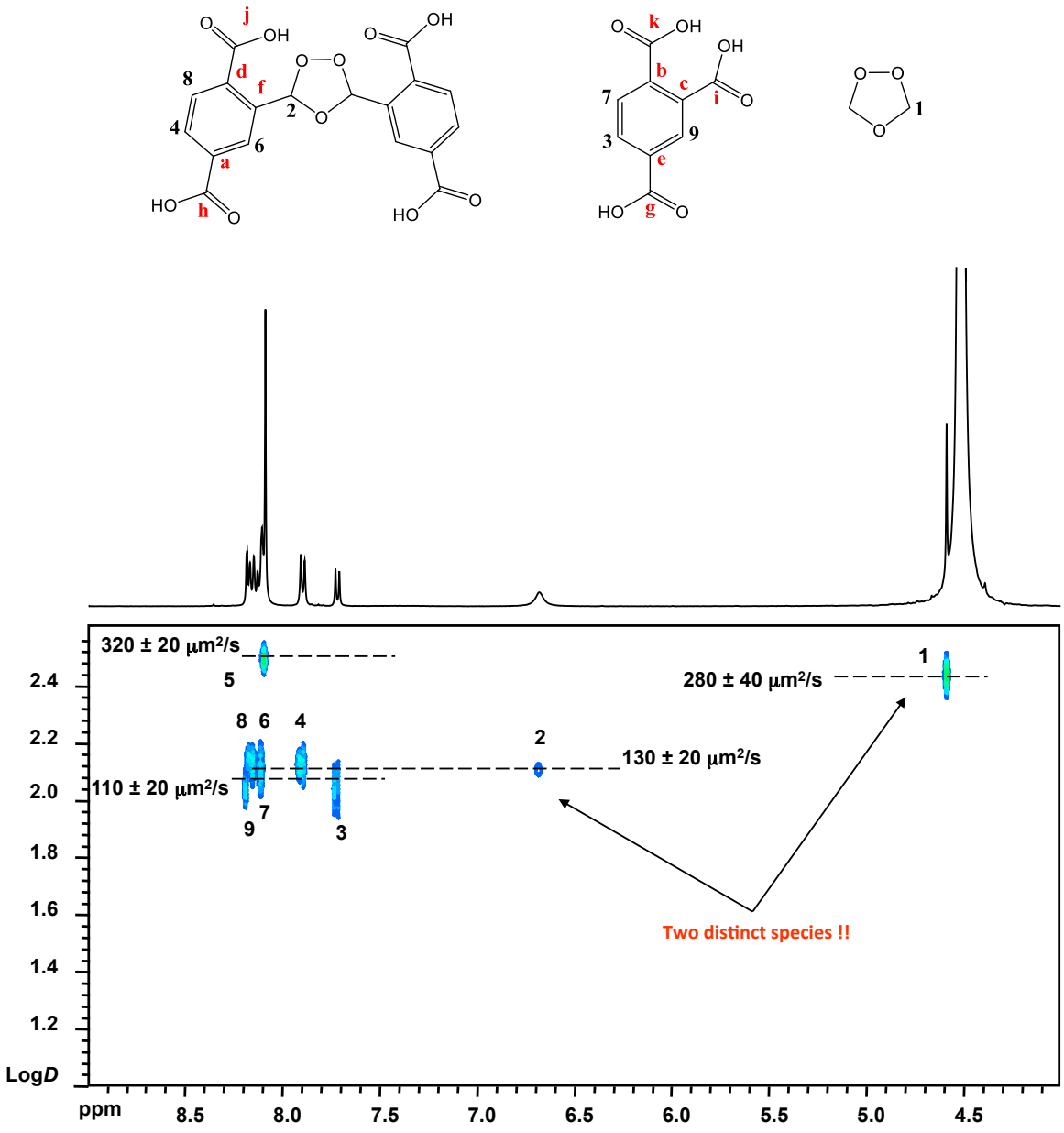


Figure S13. ^{1}H DOSY NMR spectrum of digested **ozo-ZrBDC** in HF/DMSO-d_6, showing four ensembles of resonances with different diffusion coefficients. Note that signals **1** and **2,** which appear in the range of trioxolane moieties, correspond to two distinct species.

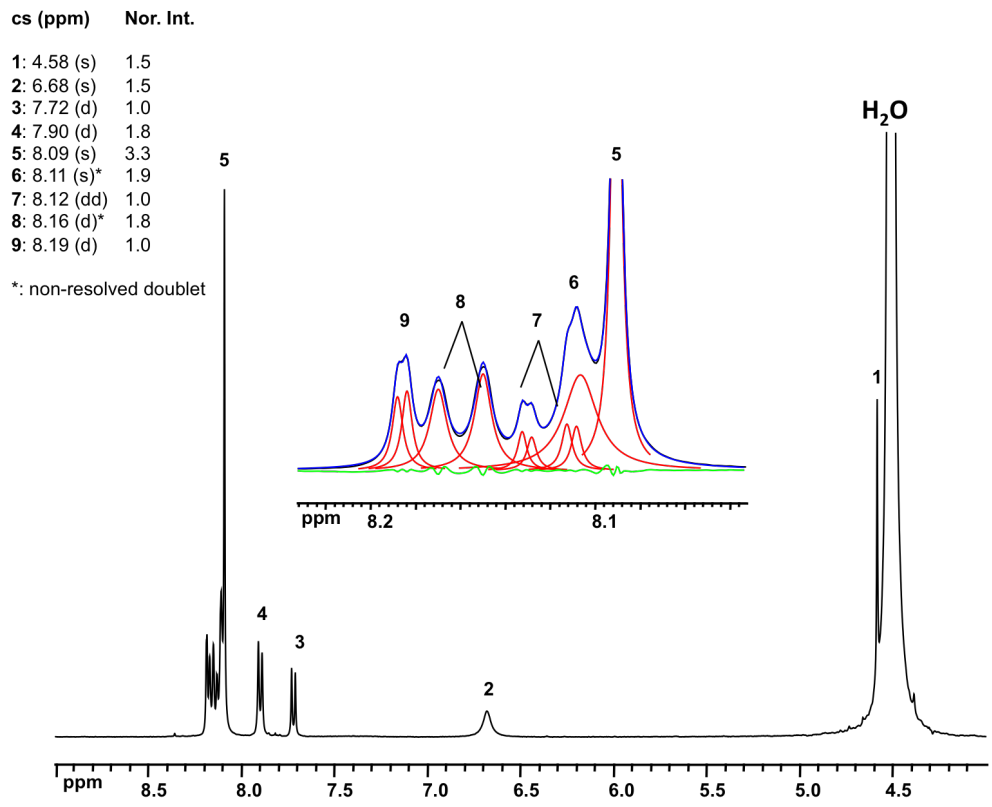


Figure S14. [1]H NMR spectrum of digested **ozo-ZrBDC** in HF/DMSO-d_6, showing nine H resonances (labeled **1** to **9)** that should correspond to the 1,2,4-trioxolane derivatives and their decompositions products. Insert: spectra (from 8.04 ppm to 8.23 ppm) focused on the aromatic region combined with fitted peaks (red lines).

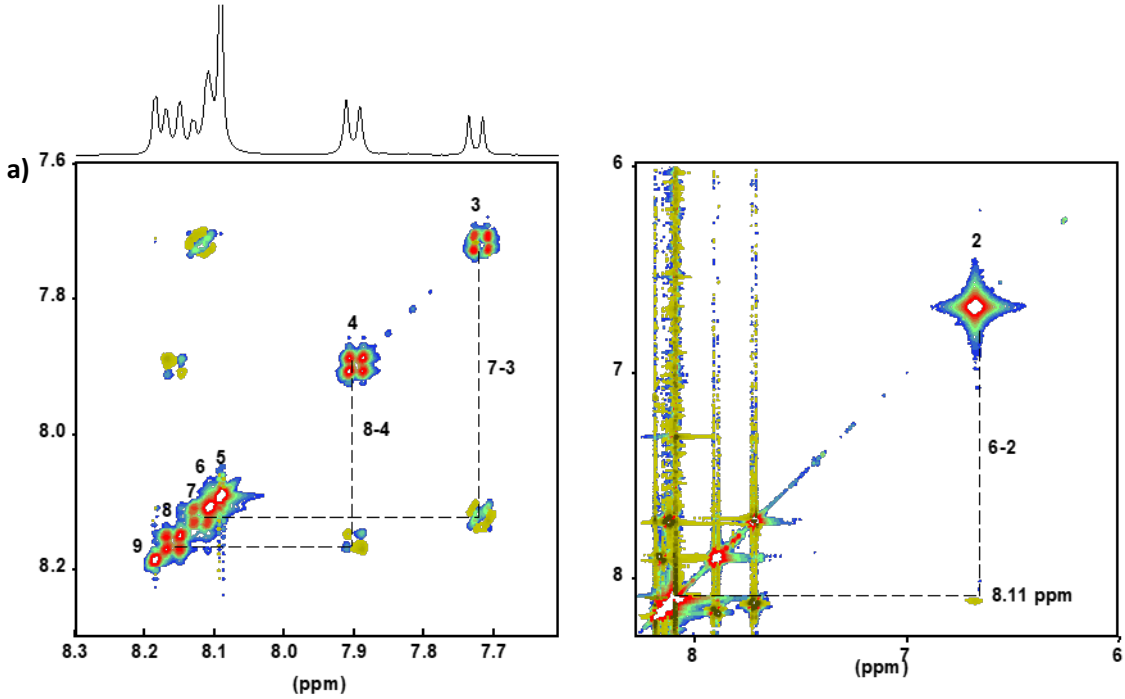


Figure S15. ^{1}H NOESY NMR spectrum of digested **ozo-ZrBDC** in HF/DMSO-d_6, showing the spatial proximities between: a) the adjacent aromatic protons (peaks **7** and **3**; and peaks **8** and **4**) and b) protons **2** and **6** over two neighboring bonds.

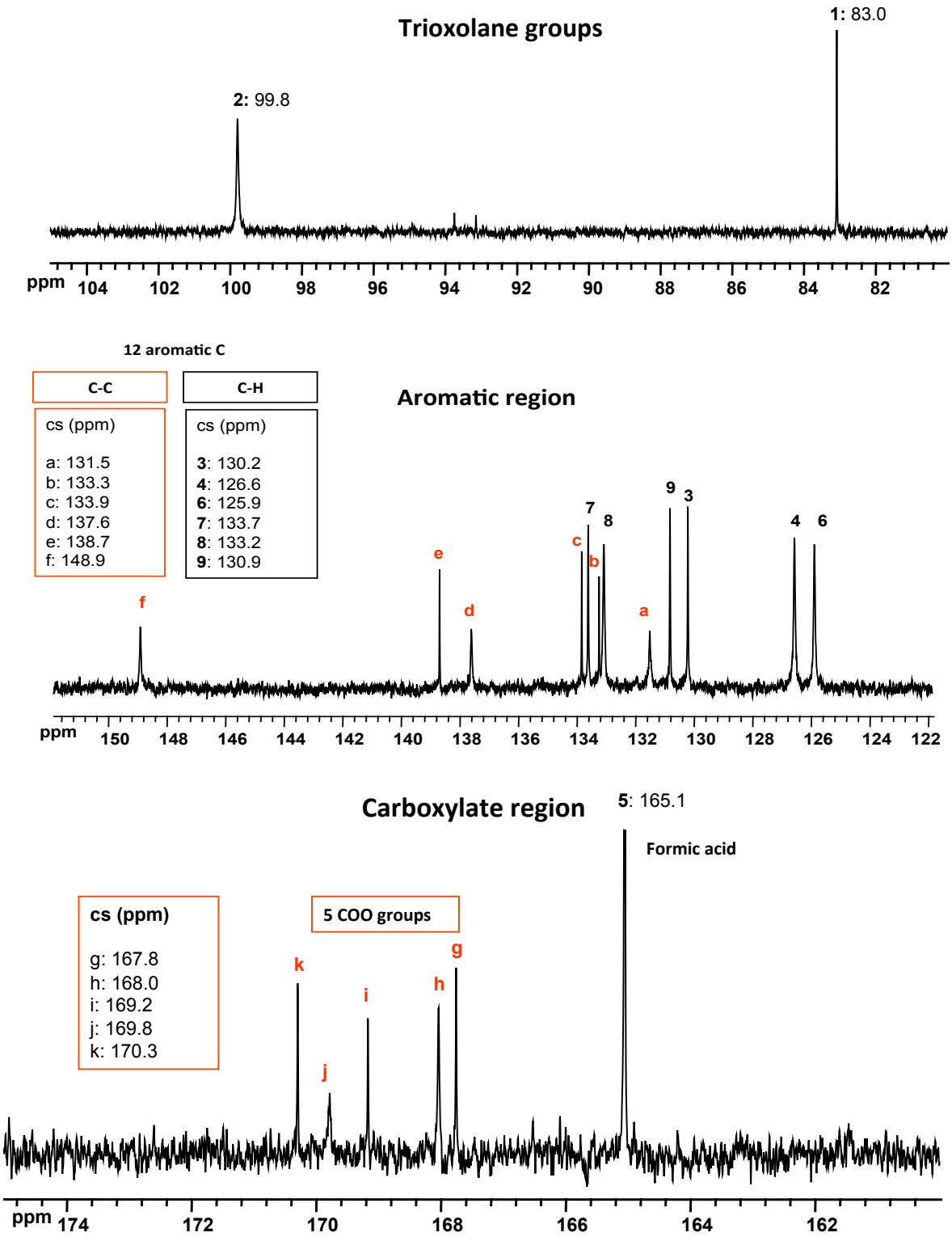


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of digested **ozo-ZrBDC** in HF/DMSO-d_6, showing the twenty different carbon atoms labeled **1-9** (attached to H) and **a-k** (attached to C and carbonyls). The two groups of resonances are differentiated by comparing DEPT135 and direct polarization experiments.

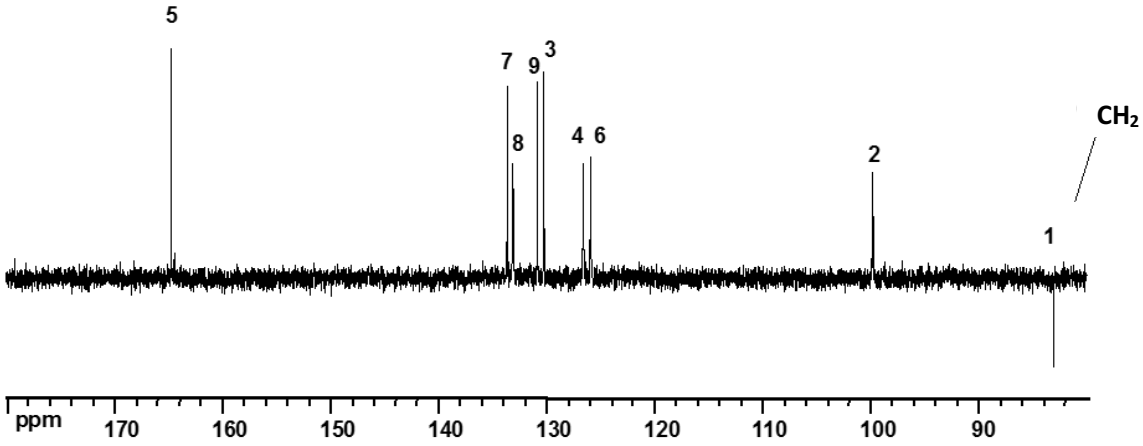


Figure S17. $^{13}C\{^{1}H\}$ DEPT135 NMR spectrum of digested **ozo-ZrBDC** in HF/DMSO-d_6 that enables differentiation of the **CH** groups from the **CH_2** groups. Note that all the nine carbon atoms bear one proton, except for C1, which is attached to two protons.

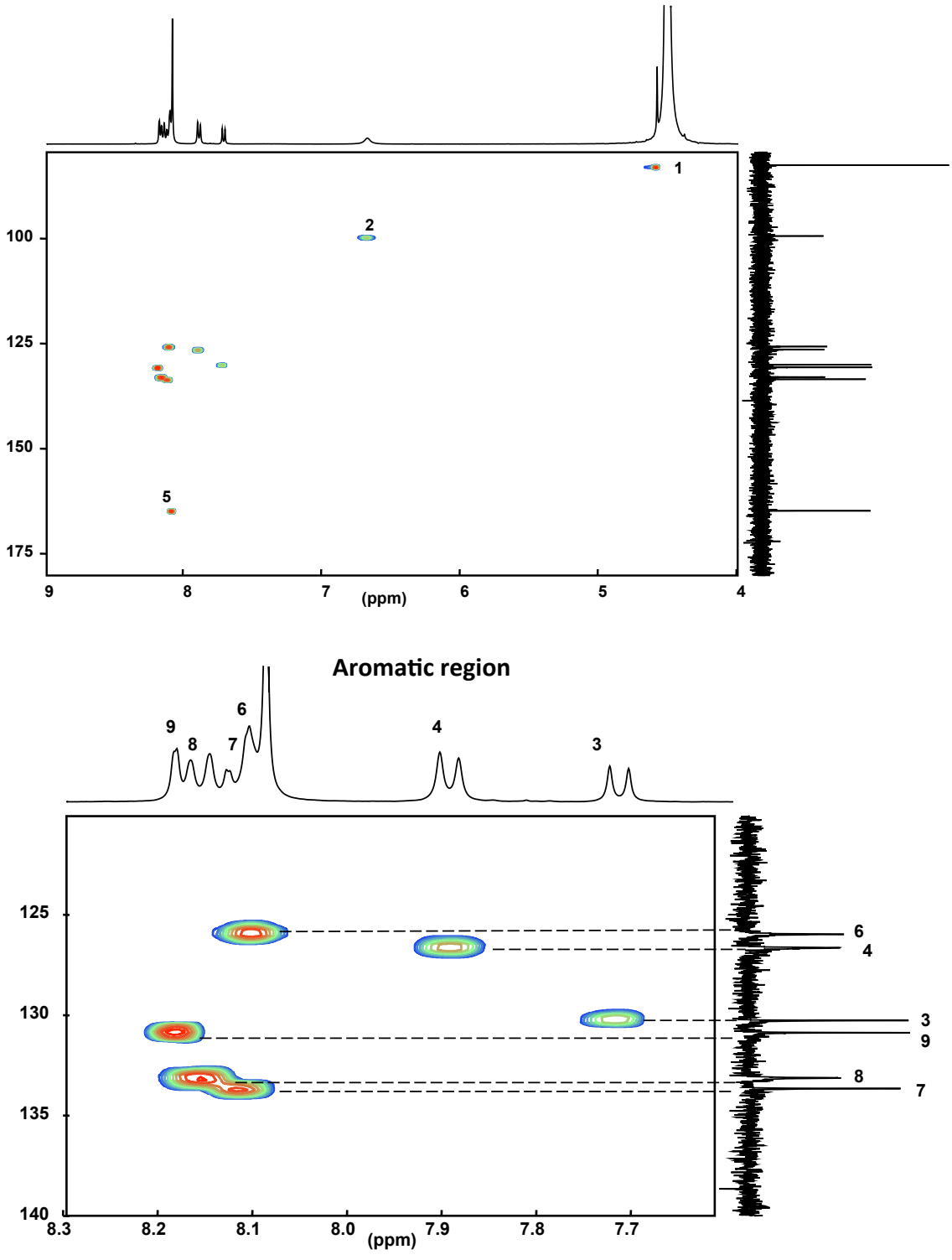


Figure S18. $^{13}C\{^{1}H\}$ HSQC NMR spectra of digested **ozo-ZrBDC** in HF/DMSO-d_6, showing the nine hydrogen atoms attached to the nine carbon atoms (**1**-**9**).

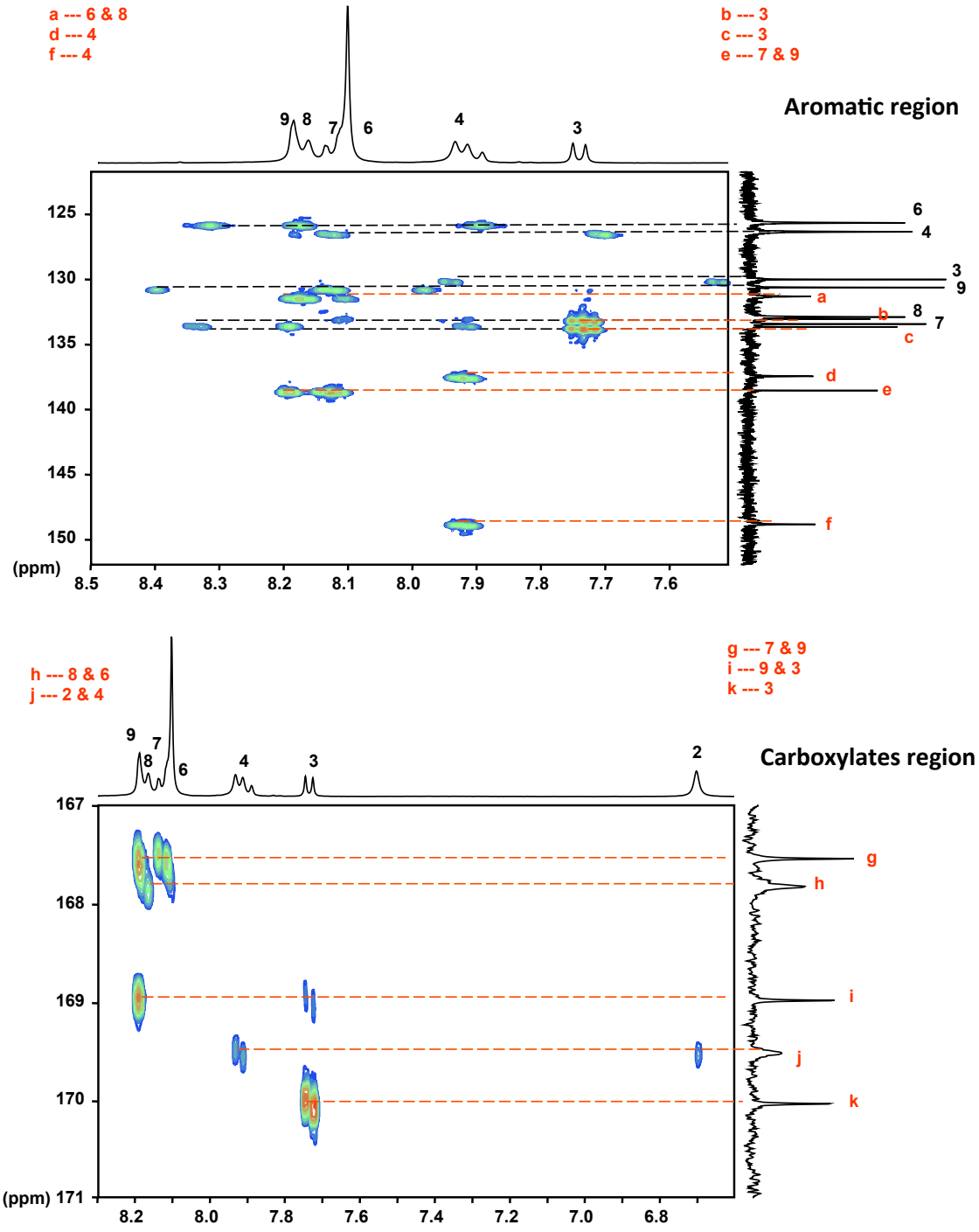


Figure S19. $^{13}C\{^{1}H\}$ HMBC NMR spectra of digested **ozo-ZrBDC** in HF/DMSO-d_6, enabling the complete assignment of carbon resonances. The quaternary carbons could be identified based on long-range J^{2}_{CH} and J^{3}_{CH} couplings.

S5. ^{1}H NMR Analysis of the Oxidation and Reduction of Ozo-ZrBDC

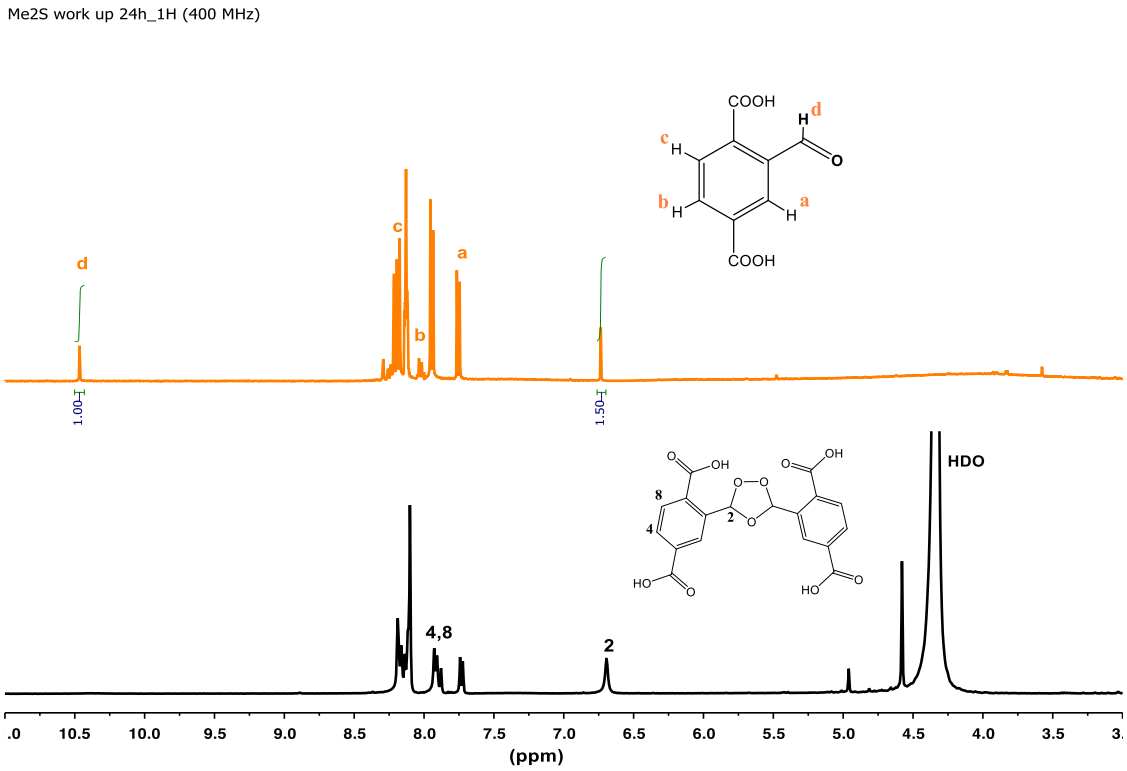


Figure S20. ^{1}H NMR spectrum of the digested **CHO**-functionalized **ZrBDC** resulting from soaking **ozo-ZrBDC** in Me_2S for 12 h (orange), compared to that of the digested **ozo-ZrBDC** (black). The degree of the conversion of the trioxolane ring into aldehyde groups (40%) was calculated by comparing the integration of the peak at 10.5 ppm to that of the peak at 6.7 ppm. Note that worked-up HF digested sample was dried before its dissolution in DMSO-d^6.

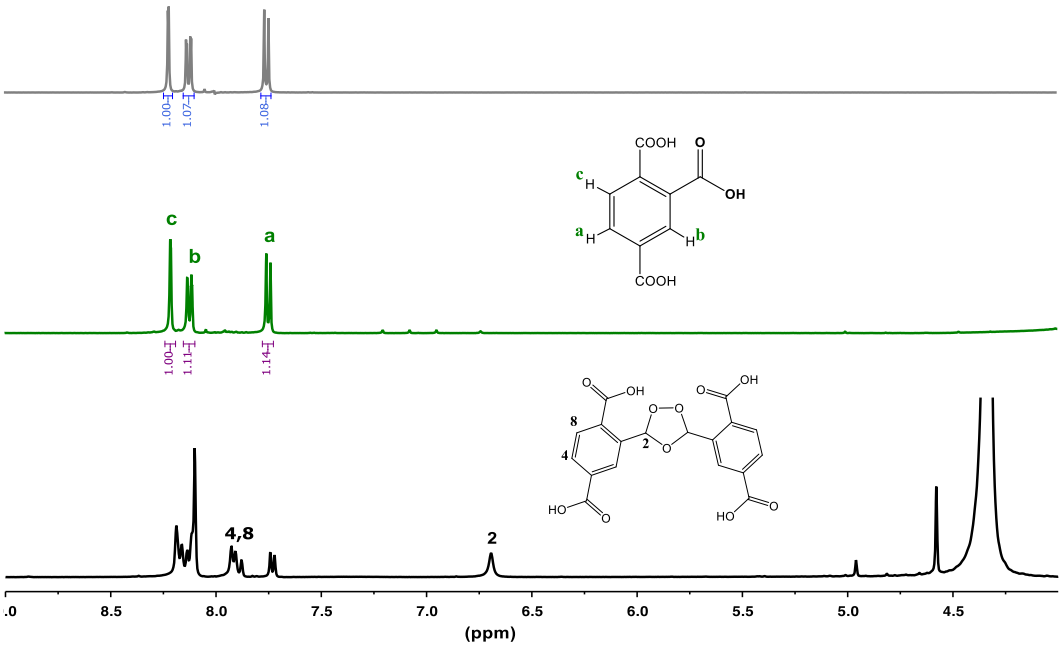


Figure S21.[1]H NMR spectrum of digested **ZrBDC-COOH** resulting from exposing **ozo-ZrBDC** in H_2O_2 (10% aq.) for 12 h (green), compared to that of the digested **ozo-ZrBDC** (black). Top: the spectrum of pure 1,2,4-benzenetricarboxylic acid (grey) is shown for reference. Note that worked-up HF digested sample was dried before its dissolution in DMSO-*d*[6].

S6. Powder X-Ray Diffraction Analysis

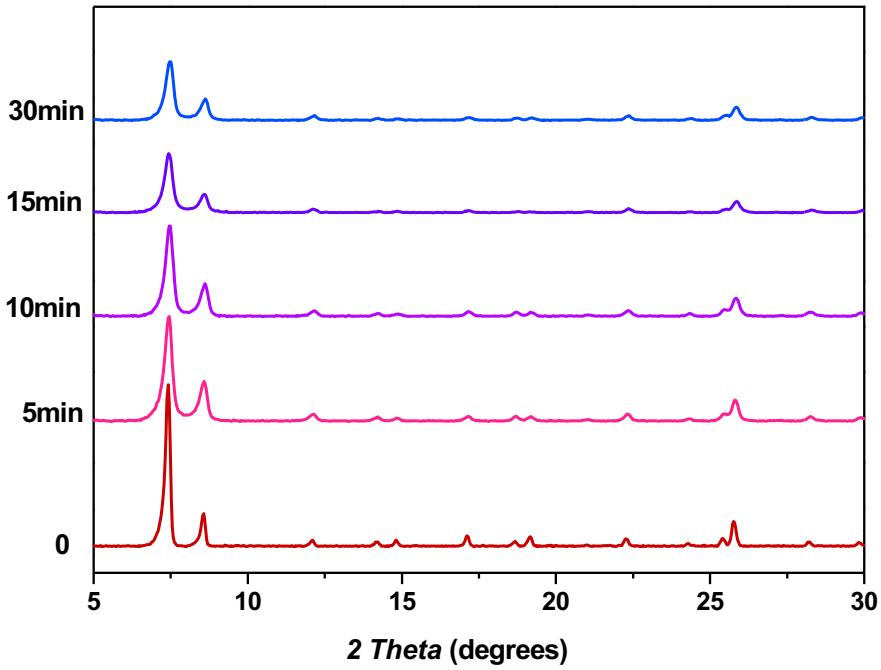


Figure S22. PXRD of **ZrEBDC** during the ozonolysis at -78 °C, in function of the reaction time (from red to blue: 0 min, 5 min, 10 min, 15 min and 30 min).

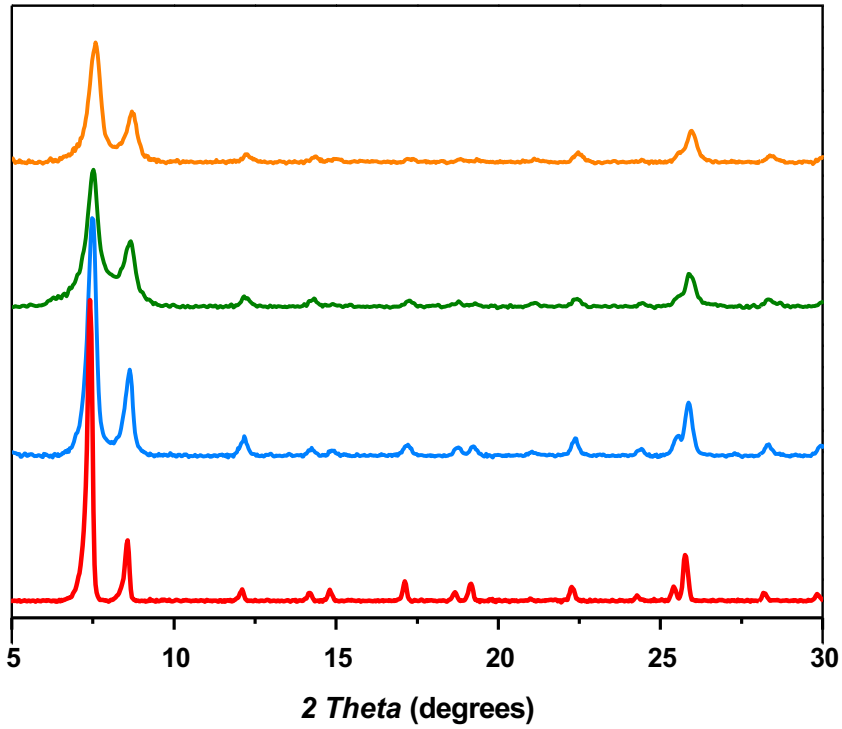
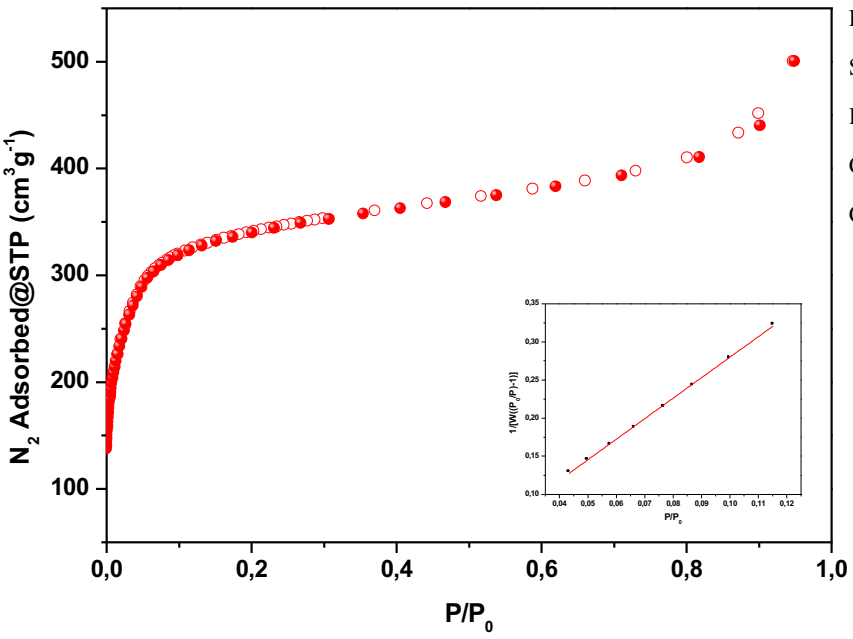


Figure S23. PXRD of **ZrEBDC** (red), **ozo-ZrBDC** (blue), **ZrBDC-COOH** (green) and **ozo-ZrBDC** partially functionalized with **CHO** groups (orange).

S7. BET Measurements



BET surface area: 1298 m²/g

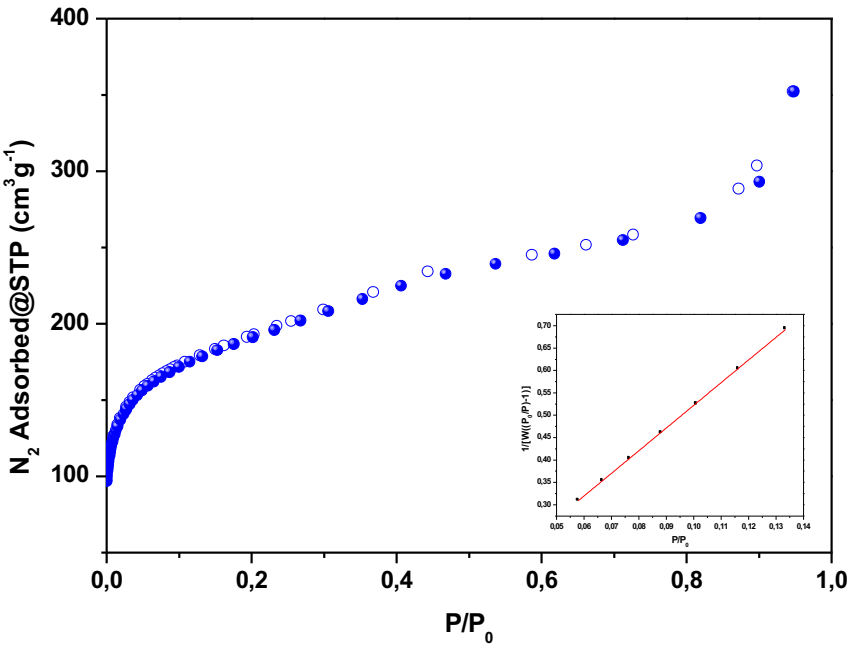
Slope: 2.96 g/cm^3 STP

Intercept: 0.0108 g/cm^3 STP

Correlation coefficient: r = 0.9996

C constant: 248

Figure S24. N_2 adsorption isotherm and BET liner fit for **ZrEBDC**.



BET surface area: 685 m²/g

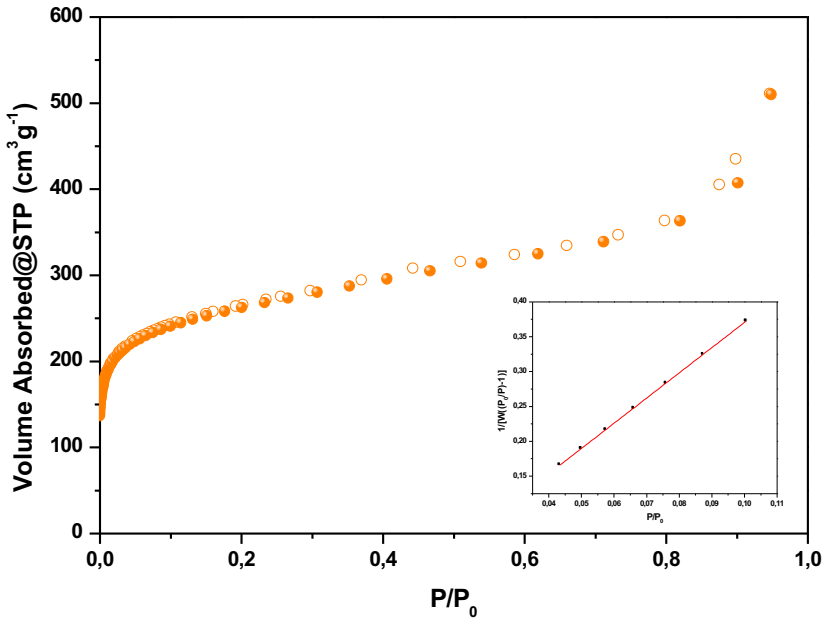
Slope: 5.06 g/cm^3 STP

Intercept: 0.0159 g/cm^3 STP

Correlation coefficient: r = 0.99997

C constant: 318

Figure S25. N_2 adsorption isotherm and BET liner fit for **ozo-ZrBDC**.



BET surface area: 960 m²/g

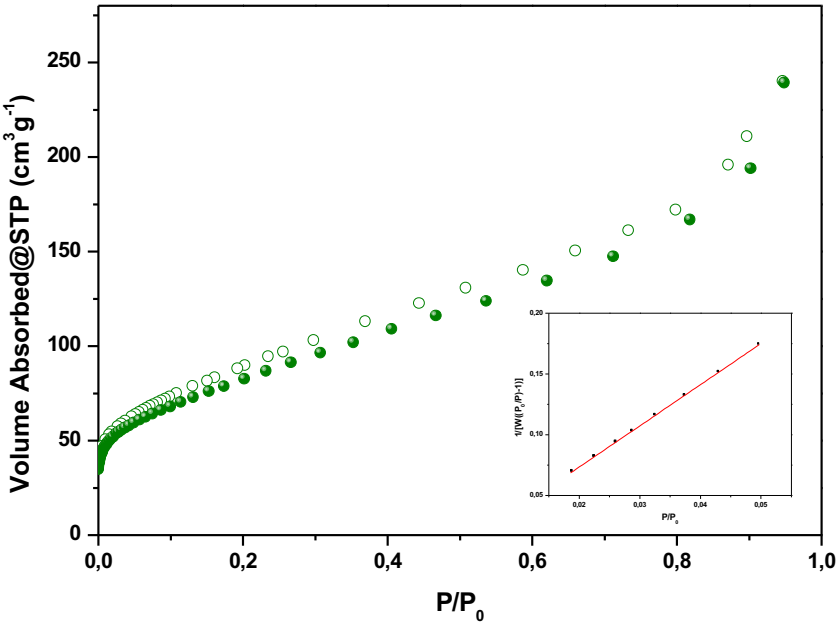
Slope: 3.617 g/cm^3 STP

Intercept: 0.00886 g/cm^3 STP

Correlation coefficient: r = 0.99999

C constant: 409

Figure S26. N_2 adsorption isotherm and BET liner fit for **ozo-ZrBDC** partially functionalized with **CHO** groups.



BET surface area: 301 m²/g

Slope: 3.34 g/cm^3 STP

Intercept: 0.0054 g/cm^3 STP

Correlation coefficient: r = 0.9996

C constant: 622

Figure S27. N_2 adsorption isotherm and BET liner fit of **ZrBDC-COOH**.

References

(1) Wu, X.; Zilm K.W. *J. Magn. Reson*. **1993**, *102*, 205.

(2) Fung, B.M.; Khitrin, A. K.; Ermolaev, K., *J. Magn. Reson.* **2000,** *142*, 97.

(3) Juanhuix, J.; Gil-Ortiz, F.; Cuní, G.; Colldelram, C.; Nicolás, J.; Lidón, J.; Boter, E.; Ruget, C.; Ferrer, S.; Benach, J. *J. Synchrotron Rad.* **2014**, 21, 679.

(4) Kissel, L. ; Pratt, R.H. *Acta Cryst. Sec.A* **1990,** 46, 170.

(5) Sheldrick, G. M.; Dauter, Z.; Wilson, K.S.; Hope, H.; Sieker, L. C. *Acta Cryst.* **1993**, D49, 18.

(6) Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3.

(7) a) Farrugia, L. J.; *J. Appl. Cryst.* **2012**, 45, 849. b) Dolomanov, O.V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, 42, 339.

(8) Allan, D.; Nowell, H.; Barnett, S.; Warren, M.; Wilcox, A.; Christensen, J.; Saunders, L.; Peach, A.; Jooper, M.; Zaja, L.; Patel, S.; Cahill, L.; Marshall, R.; Trimnell, S.; Foster, A.; Bates, T.; Williams, M.; Hathaway, P.; Winter, G.; Gerstel, M.; Wooley, R. *Crystals* **2017**, 7, 336.

(9) Winter, G. *J. Appl. Crystallogr* **2010**, 43, 186.

(10) (a) Cramer C. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.*, **2009**, *11*, 10757. (b) Zhao Y.; Truhlar, D. G. *Theor. Chem. Acc.*, **2008**, *120,* 215.

(11) Wheeler, S. E.; Houk, K. N. *J. Chem. Theory Comput.*, **2010**, *6*, 395.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J.A.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.; Kudin, K.N.; Staroverov, V. N.; Keith, T.; Kobayashi, K.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M., Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox D. J. *Gaussian 09 (Revision D.01)*, Gaussian, Inc., Wallingford CT, 2011.

(13) (a) Zhao Y.; Truhlar, D. G. *Acc. Chem. Res.*, **2008**, *41*, 157. (b) Zhao Y.; Truhlar, D. G. *Chem. Phys. Lett.*, **2011**, *502*, 1.

(14) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H; Preuss, H. *Theor. Chim. Acta*, **1990**, *77*, 123

(15) Ehlers, A. W.; Bohme, M.; Dapprich, S.; Gobbi, A.; Hollwarth, A.; Jonas, V.; Kohler, K. F.; Stegmann, R.; Veldkamp A.; Frenking, G. *Chem. Phys. Lett.*, **1993**, *208*, 111.

(16) (a) Hehre, W. J.; Ditchfield R.; Pople, J. A. *J. Chem. Phys.*, **1972**, *56*, 2257. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees D. J.; Pople, J. A. *J. Chem. Phys.*, 1982, **77**, 3654.

(17) Furukawa, H.; Gándara, F.; Zhang, Y. B.; Jiang, J.; Queen, W. L.; Hudson, M. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2014**, *136*, 4369.

(18) Soriano, N. U.; Migo, V. P.; Matsumura, M. *Chem. Phys. Lipids* **2003**, 126, 133.

(19) Sega, A.; Zanardi, I.; Chiasserini, L.; Gabbrielli, A.; Bocci, V.; Travagli, V. *Chem. Phys. Lipids* **2010**, 163, 148.