Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Make room for iodine: Systematic pore tuning of multivariate metal-organic frameworks for the catalytic oxidation of aromatic diols using hypervalent iodine.

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Supplementary Information

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S1 Experimental Details

S1.1 General Methods

Aluminum chloride hexahydrate (99.0%, Acros Organics), zirconium tetrachloride (98.0%, Merck KGaA), terephthalic acid (H_2BDC, >99.0%, TCI), 2-aminoterephthalic acid ($H_2BDC\text{-}NH_2$, 99.0%, Acros Organics), hydroquinone (>99.5%, Merck KGaA), 2,5-dibromohydroquinone (97%, Alfa Aesar), methylhydroquinone (>98.0%, TCI), 2,5-di-tert-butylhydroquinone (97%, Ark Pharm, Inc.), tert-butylhydroquinone (97%, Acros Organics), chlorohydroquinone (90%, Acros Organics), N,N-dimethylformamide (DMF, >99.9%, EMD Millipore), hydrochloric acid (36.5-38.0% BDH), dichloromethane (99.9%, Fisher Scientific), meta-chloroperoxybenzoic acid (70.0-75.0%, Acros Organics), hydrogen peroxide (30.0%, Fisher Scientific), potassium permanganate (>99.0%, J.T.Baker), sulfuric acid 96.0%, J.T.Baker), dimethyl sulfoxide-d_6 (DMSO-d_6, >99.0%, Cambridge Isotope Laboratories), dimethyl sulfone (>99.0%, TCI), ethyl acetate (99.9%, Fisher Scientific), tert-butyl hydroperoxide (70.0% aq. sol., Alfa Aesar), ethanol (99.5%, Pharmco-AAPER), methanol (>99.9%, Fisher Scientific), acetonitrile (>99.9%, Fisher Scientific), urea hydrogen peroxide adduct (97.0%, Alfa Aesar), nitromethane (>98.0%, Alfa Aesar), deuterium oxide (>99.0%, Cambridge Isotope Laboratories), sodium deuteroxide solution 40 wt. % in D_2O (>99.0%, Acros Organics), potassium iodide (>99.0%, Fisher Scientific), acetone (>99.7%, Macron Fine Chemicals), sodium bisulfite (98.5%, Fisher Scientific) and sodium nitrite (>99.0%, J.T.Baker) were used as purchased without further purification. All measurements, unless noted otherwise, were carried out at 298 K and NMR chemical shifts were given in ppm. The ^1H NMR spectra were referenced to the

residual ^{1}H residue in the deuterated solvent. All IR spectra were obtained using a Nicolet iS 5 FT-IR spectrometer equipped with a diamond ATR accessory.

S2 Synthesis

S2.1 Preparation of 2-iodoterephthalic acid (H_2BDC-I)

2-Iodoterephthalic acid was synthesized as previously reported using Sandmeyer reaction.[1] (Figure S1)

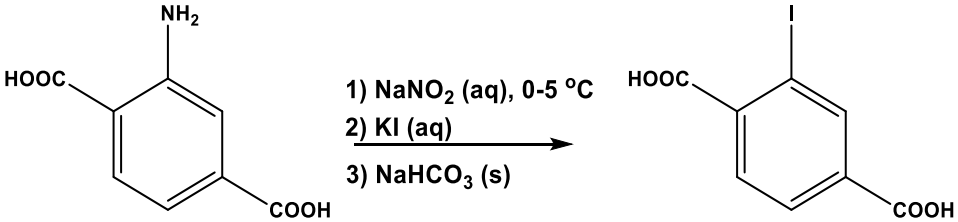

Figure S1. Preparation of 2-iodoterephthalic acid

S2.2 Preparation of dimethyl 2-iodobenzene-1,4-dicarboxylate

Dimethyl 2-iodobenzene-1,4-dicarboxylatewas prepared through a Fischer esterification (Figure S2).[2] 2-Iodoterephthalic acid (1.50 g, 5.6 mmol) was combined in methanol (10 mL) with good stirring. Concentrated H_2SO_4 (0.5 mL) was added dropwise, and the reaction mixture was refluxed with stirring overnight. Methanol was removed and resulting material was dissolved in dichloromethane and washed with water. The aqueous phase was further extracted with water (2x). The organic phases were combined and dried over $MgSO_4$ before being taken to dryness to yield a light brown crystalline solid (1.2 g, 67%). H NMR ($CDCl_3$) δ3.95 (s, 3H), 3.96 (s, 3H), 7.81 (d, 1H), 8.05 (dd, 1H), 8.63 (d, 1H).

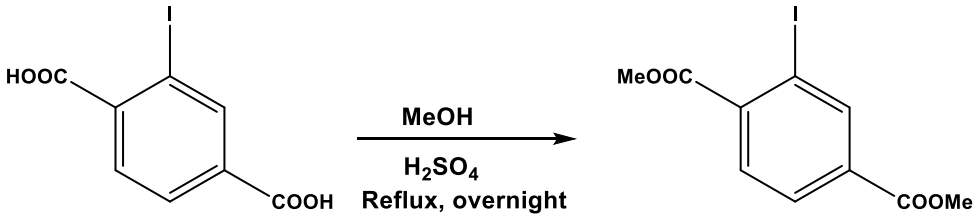

Figure S2. Preparation of dimethyl 2-iodobenzene-1,4-dicarboxylate

S2.3 Synthesis of MTV-UiO-66 (Zr)

The MTV-UiO-66 (Zr) frameworks were synthesized via solvothermal methods adapted from the literature preparation of UiO-66.[3] $ZrCl_4$ was added to N,N-dimethylformamide (DMF). The mixture of ligands was dissolved in DMF with a small amount of deionized water was added to the first solution. Amounts are provided in Table S1. The reaction mixtures were heated at 100 °C for 3 days to yield the MTV-UiO-66 (0, 25, 50, 75, or 100%-I) MOFs. The solids were washed with hot DMF (x3) and soaked for 16 h in hot methanol (x1) prior to being heated at 150 °C for 16 hours under vacuum.

Table S1. Composition of the reaction mixtures in synthesis of the MTV-UiO-66 (Zr)

MTV-MOFs	Reagents Amount (mmol)					Yield (mg)
	$ZrCl_4$	H_2BDC[a]	H_2BDC-I	H_2O	DMF	
UiO-66 0%-I	8.60	8.60	0.00	11.11	1420.71	310
UiO-66 25%-I	8.60	6.45	2.15	11.11	1420.71	380
UiO-66 50%-I	8.60	4.30	4.30	11.11	1420.71	400
UiO-66 75%-I	8.60	2.15	6.45	11.11	1420.71	390
UiO-66 100%-I	8.60	0.00	8.60	11.11	1420.71	430

a) H_2BDC: 1,4-benzenedicarboxylic acid

S2.4 Synthesis of MTV-MIL-53 (Al) in water.

Preparations of MTV-MIL-53 (0, 25, 50, 75, or 100%-I) MOFs were carried out under hydrothermal conditions in a 23 mL Teflon-lined stainless-steel autoclave using aluminum chloride hexahydrate, terephthalic acid, 2-iodoterephthalic acid, and deionized water (6.0 mL). The procedure was adapted from the reported procedure for preparing MIL-53 0%-I.[4] The chloride salt was chosen as the nitrate salt used in the original procedure led to oxidation of the linker. The amounts that were used are reported in Table S2. The reaction was performed for three days at 220 °C. The as-synthesized MOF, MIL-53(as), was obtained after filtering and washing with deionized water. In order to empty the pores of residual materials, the as-synthesized MOF was washed with DMF (x3) and treated with hot methanol for 16 hours followed by heating at 320 °C for 3 days in air.

Table S2. Composition of the reaction mixtures in synthesis of the MTV-MIL-53 (Al)

MTV-MOFs	Reagents Amount (mmol)				Yield (mg)
	$AlCl_3.6H_2O$	H_2-BDC	H_2BDC-I	H_2O	
MIL-53 0%-I	4.00	2.00	0.00	333	230
MIL-53 25%-I	4.00	3.00	1.00	333	230
MIL-53 50%-I	4.00	1.00	1.00	330	210
MIL-53 75%-I	4.00	1.00	3.00	330	350
MIL-53 100%-I	4.00	0.00	2.00	330	260

S2.5 Synthesis of multivariate MIL-53 25%-I (Al) with DMF.

Multivariate MIL-53 25%-I (DMF) was prepared under solvothermal conditions by adapting a previously reported synthesis of MIL-53.[5] Aluminum chloride hexahydrate (2.1 mmol, 0.51 g), I-H_2BDC (0.51 g, 3.1 mmol), H_2BDC (0.30 g, 1.0 mmol) was added to 30 mL DMF. The mixture was

placed in a 100 mL Teflon-lined stainless-steel autoclave and heated for 72 h at 120 °C in an oven under static conditions. (Yield: 550 mg)

S2.6 Single crystal growth experiment

Single crystals of MIL-53 100%-I was obtained by mixing 0.1207 g (0.5 mol) $AlCl_3 \cdot 6H_2O$ and 0.1465 g (0.5 mol) 2-iodoterephthalic acid in a small vial placed in the autoclave reactor containing 5 ml of ultrapure H_2O as shown in Figure S3. The reactor was sealed in a stainless-steel chamber and heated to 220 °C for 12 days.[6] From the mixture a single phase of crystals (MIL-53 100%-I AS) could be observed, consistent with the PXRD. Single crystals were activated following the same procedure as used with the bulk powders. The crystals underwent a single crystal-to-single crystal transformation. Under inspection, two unique phases could be distinguished, one more prevalent than the other, MIL-53 100%-I Act Phase I and II, respectively.

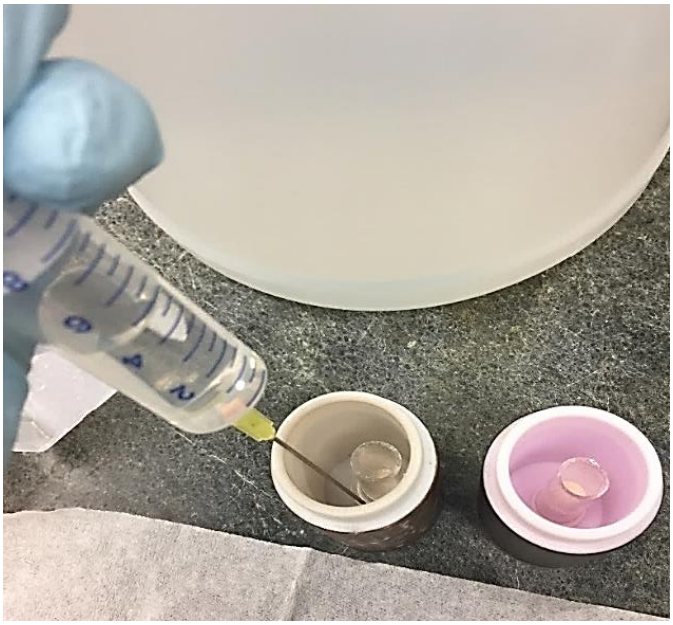

Figure S3. Experimental set-up for growth of single crystals of MIL-53 100%-I

S3 Crystallography

S3.1 Powder X-ray Diffraction

The diffraction patterns were collected on a Rigaku Ultima III powder diffractometer. X-ray diffraction patterns were obtained by using 2θ-θ scans with a range of 5-30°, step size = 0.05°, and scan time of 1 second/step. The X-ray source was Cu Kα radiation (λ=1.5418 Å) with an anode voltage of 40 kV and a current of 44 mA. The beam was then discriminated by Rigaku's Cross Beam optics to create a monochromatic parallel beam. Diffraction intensities were recorded on a scintillation detector after being filtered through a Ge monochromator. Powder mounts were prepared by packing the powder into a well on a glass slide.

S3.2 Single Crystal Diffraction

General Data Collection

Data were collected on a Bruker PLATFORM three circle diffractometer equipped with an APEX II CCD detector and operated at 1500 W (50kV, 30 mA) to generate (graphite monochromated) Mo Kα radiation (λ = 0.71073 Å). Crystals were transferred from the vial and placed on a glass slide in polyisobutylene. A Zeiss Stemi 305 microscope was used to identify a suitable specimen for X-ray diffraction from a representative sample of the material. The crystal and a small amount of the oil were collected on a MīTiGen cryoloop and transferred to the instrument where it was placed under a cold nitrogen stream (Oxford) maintained at 100 K throughout the duration of the experiment. The sample was optically centered with the aid of a video camera to insure that no translations were observed as the crystal was rotated through all positions.

A unit cell collection was then carried out. After it was determined that the unit cell was not present in the Cambridge Crystallographic Data Centre (CCDC) database a sphere of data was collected. Omega scans were carried out with a 20 sec/frame exposure time for MIL-53 100%-I AS and α-MIL-53 100%-I Act and 70 sec/frame for β-MIL-53 100%-I Act. All structures were collected with a rotation of 0.50° per frame. After data collection, the crystal was measured for size, morphology, and color. These values are reported in Table S3.

Refinement Details

After data collection, the unit cell was re-determined using a subset of the full data collection. Intensity data were corrected for Lorentz, polarization, and background effects using the Bruker program APEX.[7] A semi-empirical correction for adsorption was applied using the program SADABS.[8] The SHELXL-2014,[9] series of programs was used for the solution and refinement of the crystal structure. During the initial refinement stage, the RIGU restraint was used globally to help produce reasonable thermal ellipsoids. After the Al, C, and O atoms of the MOF framework refined to a stable point, the partially occupied I sites were added in and were allowed to freely refine their SOF values. Once the model reached convergence, the I1A and I1B sites were added together and given a set total SOF value of 0.15 and 0.17 for the MIL-53 100%-I AS and α-MIL-53 100%-I Act structures respectively. The I2 site was allowed to continue refine further during sequential refinements. For β-MIL-53 100%-I Act, the partially occupied I sites were added in and were allowed to free refine their SOF values. Hydrogen atoms bound to carbon atoms were geometrically constrained using the appropriate AFIX commands and their SOF values were set

to offset the occupancies of the iodine atoms. The hydrogen atom (H1) bound to O1 was constrained using a DFIX command. After all of these atoms had been structurally determined, the disordered region of electron density within the framework was masked using the SQUEEZE/PLATON program.[10,11] For MIL-53-ACT, the SQUEEZE/PLATON routine suggested an electron count of 1 electron. For MIL-53 100%-I AS and β-MIL53 100%-I Act, an extinction correction was also suggested during the final refinement cycles, resulting in an extinction values of 0.1035 and 0.0595, respectively.

Table S3. Single crystal information and refinement parameters.

Identification code	**MIL-53 100%-I AS**	**α-MIL-53 100%-I Act**	**β-MIL-53 100%-I Act**
Crystal Color	Yellow	pale yellow	pale yellow
Crystal Habit	Block	Block	block
Empirical formula	C8 H4.19 Al I0.82 O5	C8 H4.36 Al I0.64 O5	C8 H4.30 Al I0.70 O5.25
Formula weight	310.83	288.67	300.1
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Imma	Imma	Imma
Unit cell dimensions	a = 16.501(4) Å α = 90°	a = 18.466(17) Å α = 90°	a = 17.107(11) Å α = 90 °.
	b = 6.6194(18) Å β = 90°	b = 6.635(5) Å β = 90°	b = 6.622(4) Å β = 90 °.
	c = 13.210(4) Å γ = 90°	c = 9.627(7) Å γ = 9°	c = 12.229(8) Å γ = 90 °.
Volume ($Å^3$), Z	1442.9(7), 4	1179.5(16), 4	1385.2(16), 4
Calculated density (g/cm^3)	1.431	1.626	1.439
Absorption coefficient (mm^{-1})	1.883	1.843	1.703
F(000)	594	557	557
Crystal size (mm^3)	0.250 x 0.230 x 0.190	0.250 x 0.230 x 0.180	0.380 x 0.215 x 0.165
Theta range for data collection	1.975 to 25.367°	2.206 to 25.500 °.	2.047 to 25.485 °.
Limiting indices	-19<=h<=19, -7<=k<=7, -15<=l<=15	-22<=h<=22, -8<=k<=7, -11<=l<=11	-20<=h<=20, -8<=k<=7, -14<=l<=14
Reflections collected / unique	6080 / 754 [R(int) = 0.0558]	5570 / 619 [R(int) = 0.0974]	6789 / 730 [R(int) = 0.0878]
Completeness to θ	25.242° (100%)	25.242° (100%)	25.242° (99.70%)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	754 / 61 / 80	619 / 60 / 66	730 / 51 / 75
Goodness-of-fit on F^2	1.123	1.183	1.149
Final R indices [I>2sigma(I)]	R1 = 0.1270, wR2 = 0.3491	R1 = 0.1352, wR2 = 0.3299	R1 = 0.1067, wR2 = 0.2786

R indices (all data)	R1 = 0.1326, wR2 = 0.3533	R1 = 0.1448, wR2 = 0.3346	R1 = 0.1215, wR2 = 0.2903
Largest diff. peak and hole (e/Å^3)	1.740 and -0.689	0.964 and -1.438	0.637 and -0.529

S4 Characterization

S4.1 PXRD Patterns of MTV-MOFs

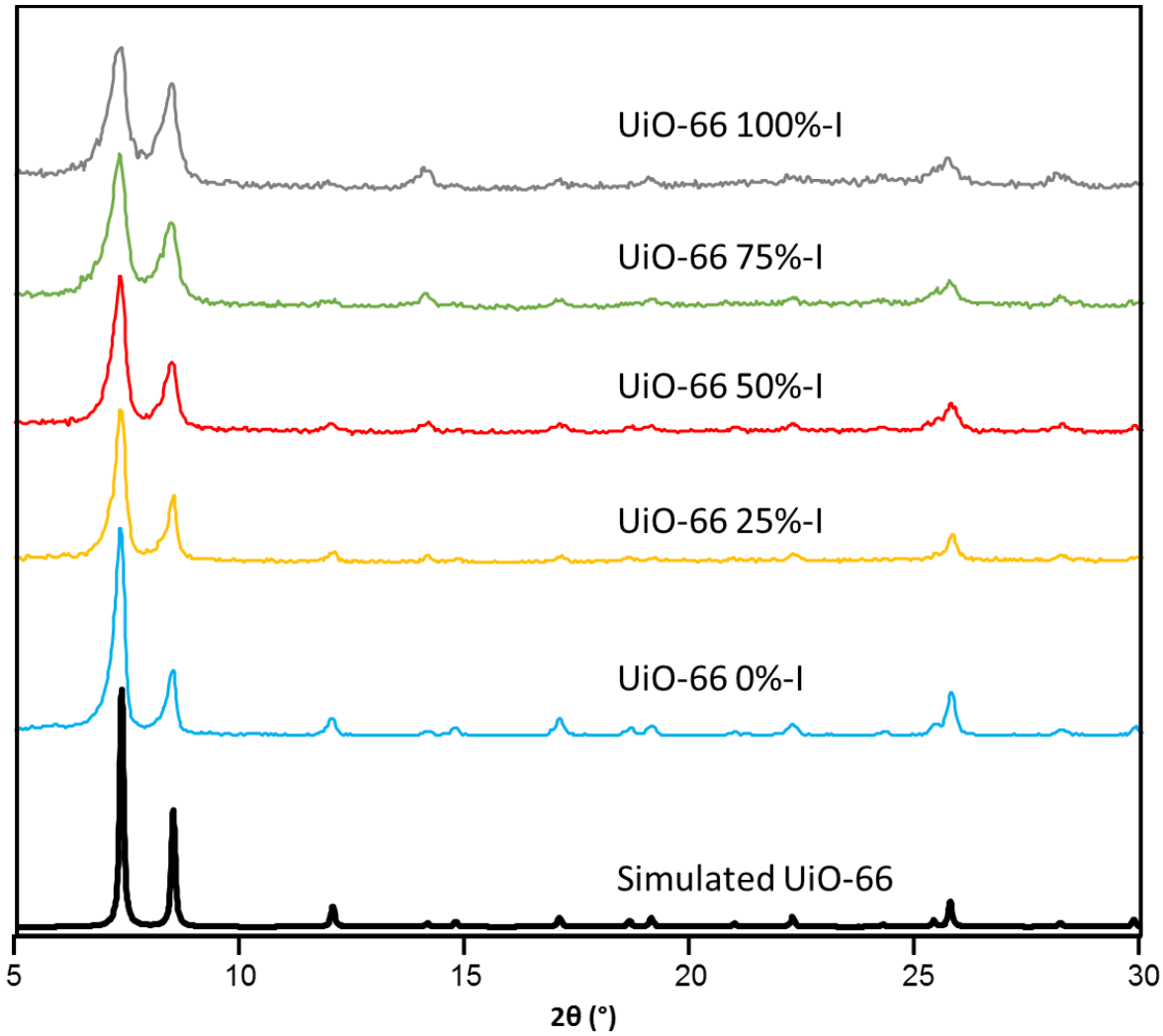

Figure S4. PXRD patterns of activated MTV-UiO-66 (0, 25, 50, 75 and 100%-I) and simulated UiO-66 0%-I.[12]

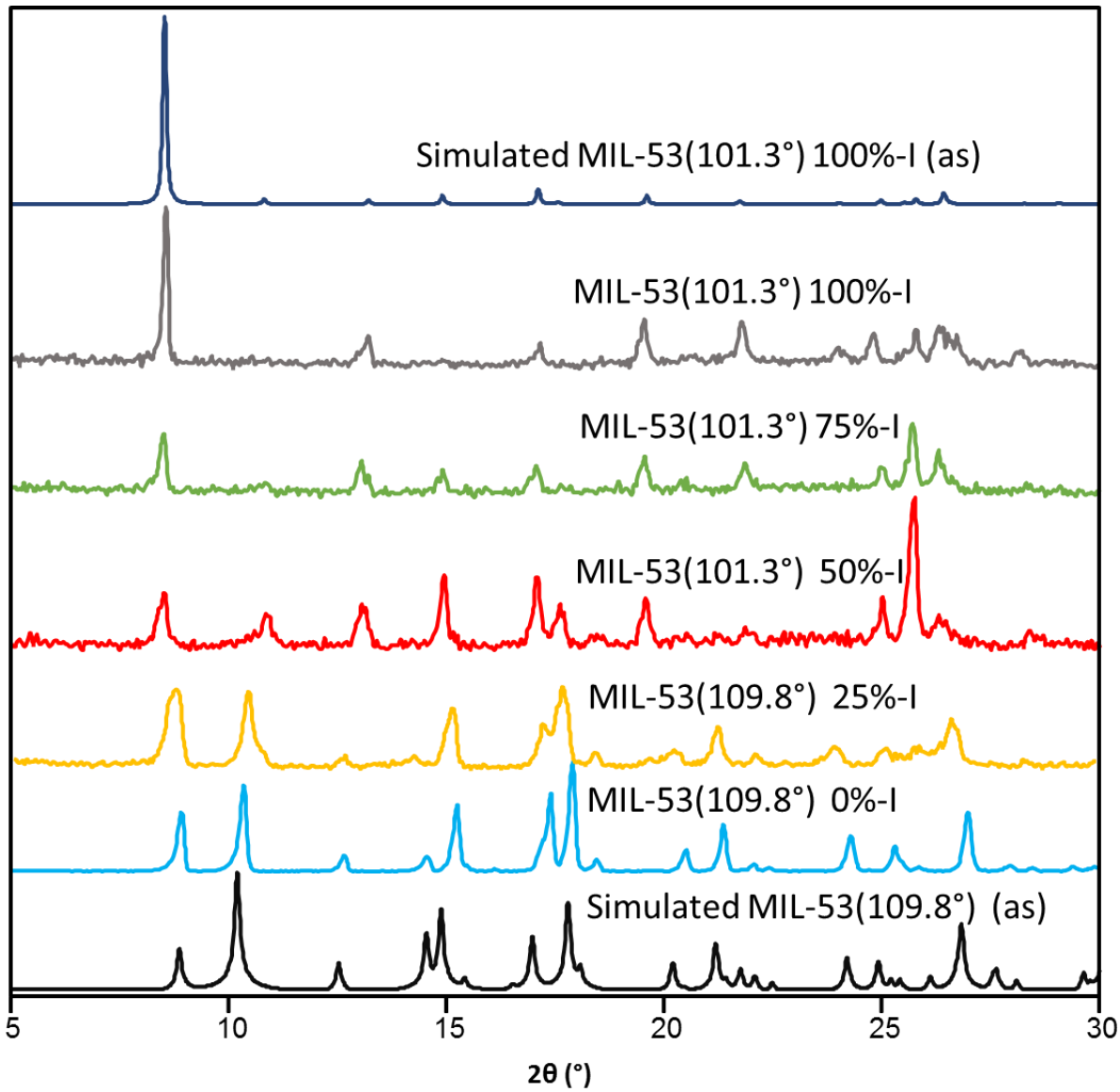

Figure S5. PXRD patterns of the as-synthesized MTV-MIL-53 (0, 25, 50, 75 and 100%-I) frameworks, simulated MIL-53(101.3°) 100%-I obtained from crystal growth in this study and simulated MIL-53(109.8°) 0%-I from literature.[13]

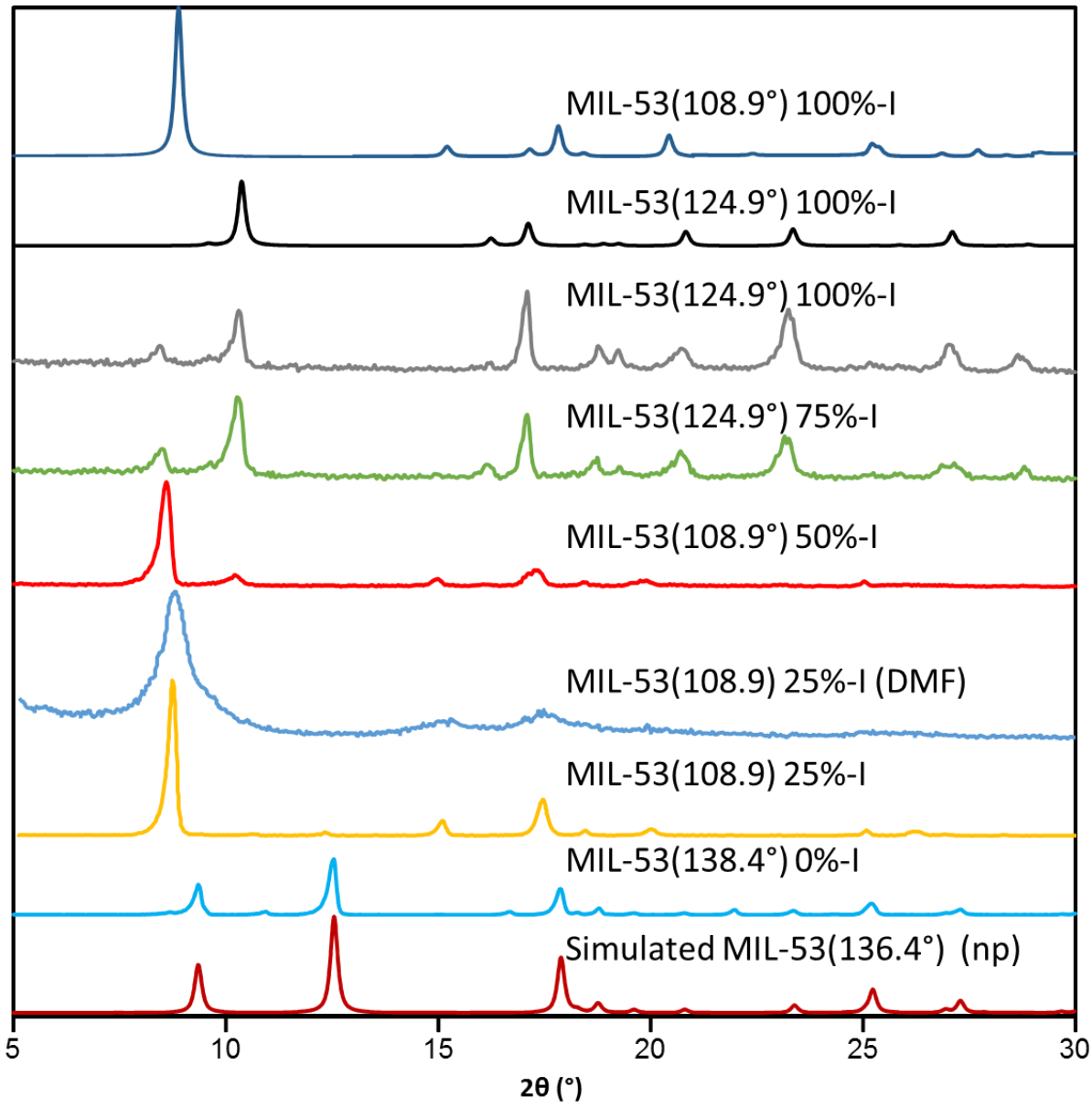

Figure S6. PXRD patterns of activated MTV MIL-53 (0, 25, 50, 75 and 100%-I) MOFs, MTV-MIL-53 25%-I synthesized in DMF, simulated MIL-53(136.4°),[14] activated MIL-53 (100%-I) 124.9° and 108.9° from single crystal structures.

S4.1 Crystal Size Estimation

Crystallite size estimation was done using Match! software (Phase Identification from Powder Diffraction) version 3.4.2 based on Scherrer equation and Corundum sample (Al_2O_3) as standard.

Equation S1. Scherrer equation to estimate crystallite sizes.

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where Scherrer constant k=0.94, wavelength λ=1.5418740 A (Cu-K_a), β as the full width of the peak at half maximum (FWHM) and θ is the Bragg angle.

Table S4. Estimate crystallite sizes for MIL-53 25% (HT, and DMF) by Scherrer equation.

MOFs	Estimated Crystallite Size (nm)[a]
MIL-53 25%-I (HT)	~70
MIL-53 25%-I (DMF)	~14

a) The calculation was performed with Match! software (Phase Identification from Powder Diffraction) version 3.4.2 based on Scherrer equation and corundum sample (Al_2O_3) as standard.

S4.2 IR Spectroscopy

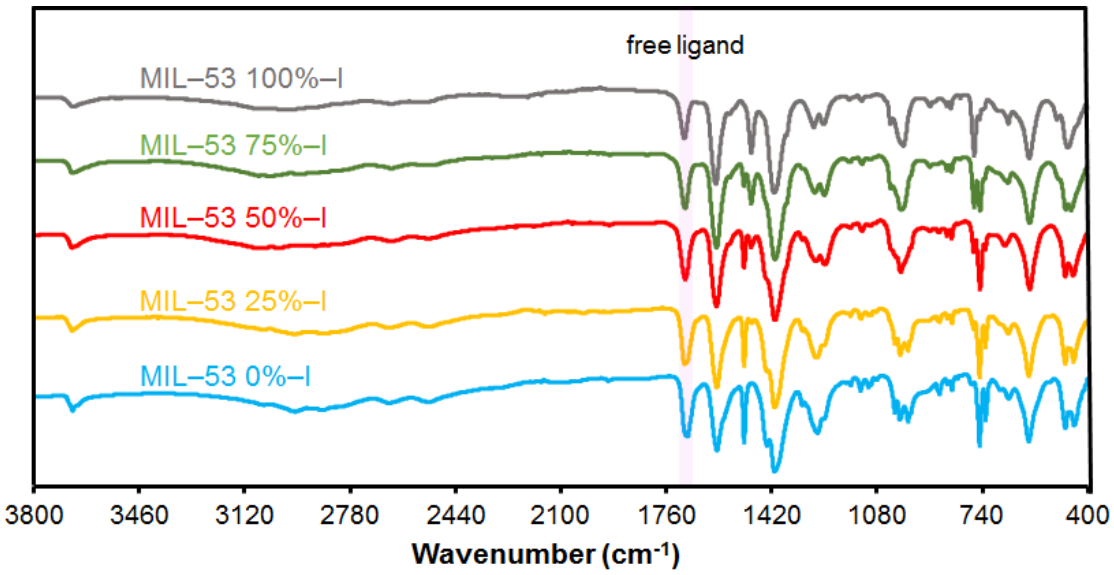

Figure S7. Di-ATR FTIR of as-synthesized MTV-MIL-53 (0, 25, 50, 75 and 100%-I) plotted as attenuation.

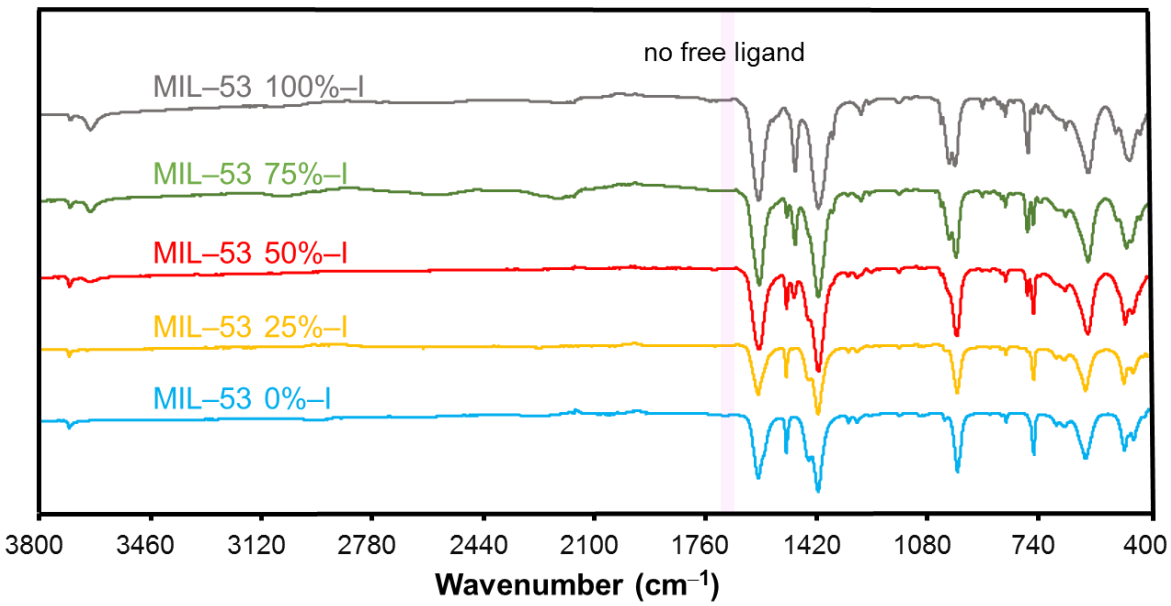

Figure S8. Di-ATR FTIR of activated MTV-MIL-53 (0, 25, 50, 75 and 100%-I) plotted as attenuation.

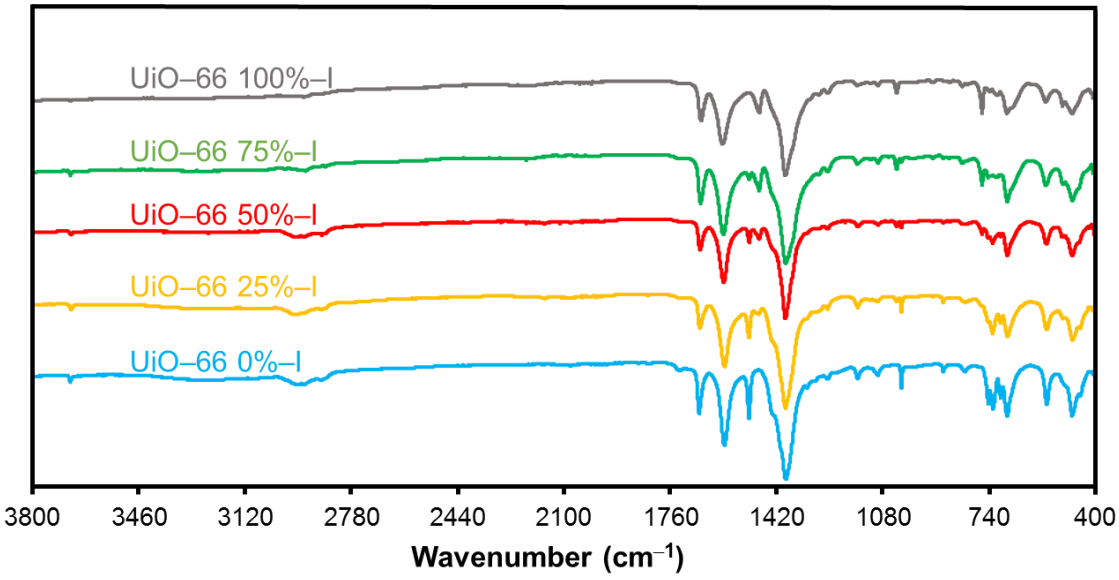

Figure S9. Di-ATR FTIR of activated MTV-UiO-66 (0, 25, 50, 75 and 100%-I) plotted as attenuation.

S4.3 Thermogravimetric Analysis (TGA) of MOFs

Thermogravimetric analysis under the air flow for MTV-UiO-66 25%-I (Figure S10) and MTV-MIL-53 25%-I (Figure S11) before and after the activation. For activated MTV-MOFs, no significant weight loss is seen until 420±20 ^{o}C. A big mass loss after 420±20 ^{o}C suggests that decomposition occurs. After decomposition, ~25 and ~35% of the starting weight remains for MTV-MIL-53 25%-I and MTV-UiO-66 25%-I respectively which corresponds to the formation of relevant metal oxide. Thermal decomposition under aerobic conditions for all multivariate activated MOFs as determined from TGA is summarized in Table S5.

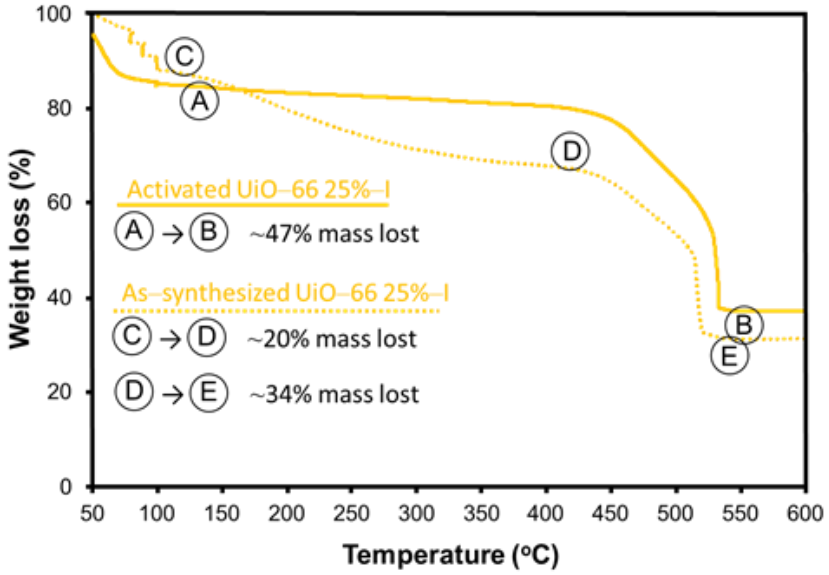

Figure S10. Thermogravimetric (TGA) analysis of MTV-UiO-66 25%-I under air before and after the activation.

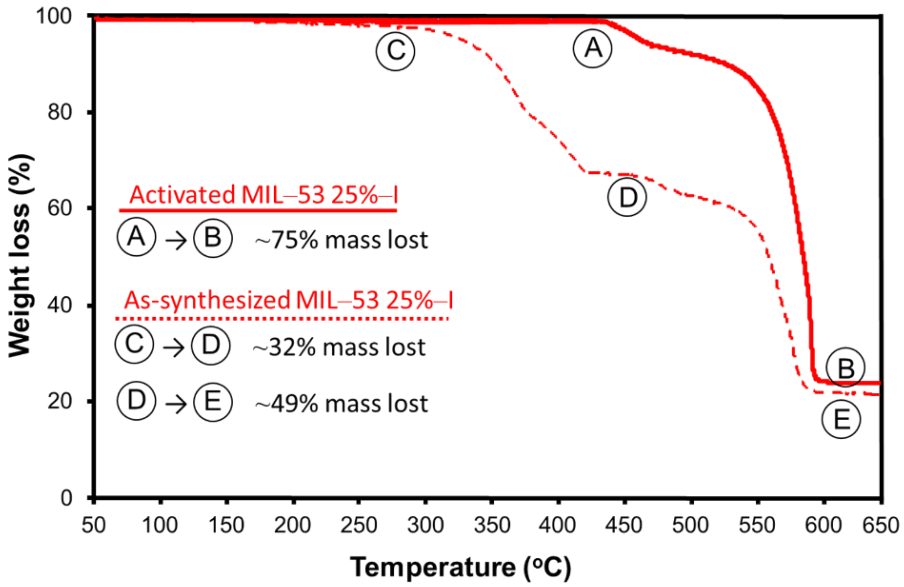

Figure S11. Thermogravimetric (TGA) analysis of MTV-MIL-53 25%-I under air before and after the activation.

Table S5. Comparison of onset temperature for thermal decomposition under aerobic conditions as determined from TGA of the MTV-MOFs (values shown are from activated MOFs).[a]

$IBDC^{2-}$ (%)[b]	Temperature (°C)	
	MIL-53	UiO-66
0%	535	500
25%	445	440
50%	420	455
75%	500	425
100%	490	400

a) 20 mg of activated MOFs under fellow of air (20 mL min^{-1}) with a heating rate of 10 °C min^{-1}.

S4.4 NMR Digestions

NMR digestions were performed on the MTV-MOFs to establish the ratio that the different ligands were incorporated and to ensure that no ligand decomposition had taken place. When aluminum nitrate was used as the salt for MIL-53 synthesis the NMR spectrum of the digested MOF was inconsistent with the spectrum of 2-iodoterephthalic acid. Digested MTV-UiO-66 was prepared by sonication 50 mg of in 500 µL $(CD_3)_2SO$ and 100 µL D_2SO_4. In case of MTV-MIL-53, 50 mg of the material was digested with 570 µL D_2O and 200 µL of NaOD solution 40 wt. % in D_2O by sonication. All the clear solutions were analyzed by ^1H NMR. For all other MTV-MOFs, the anticipated ratio of ligands was observed as shown.

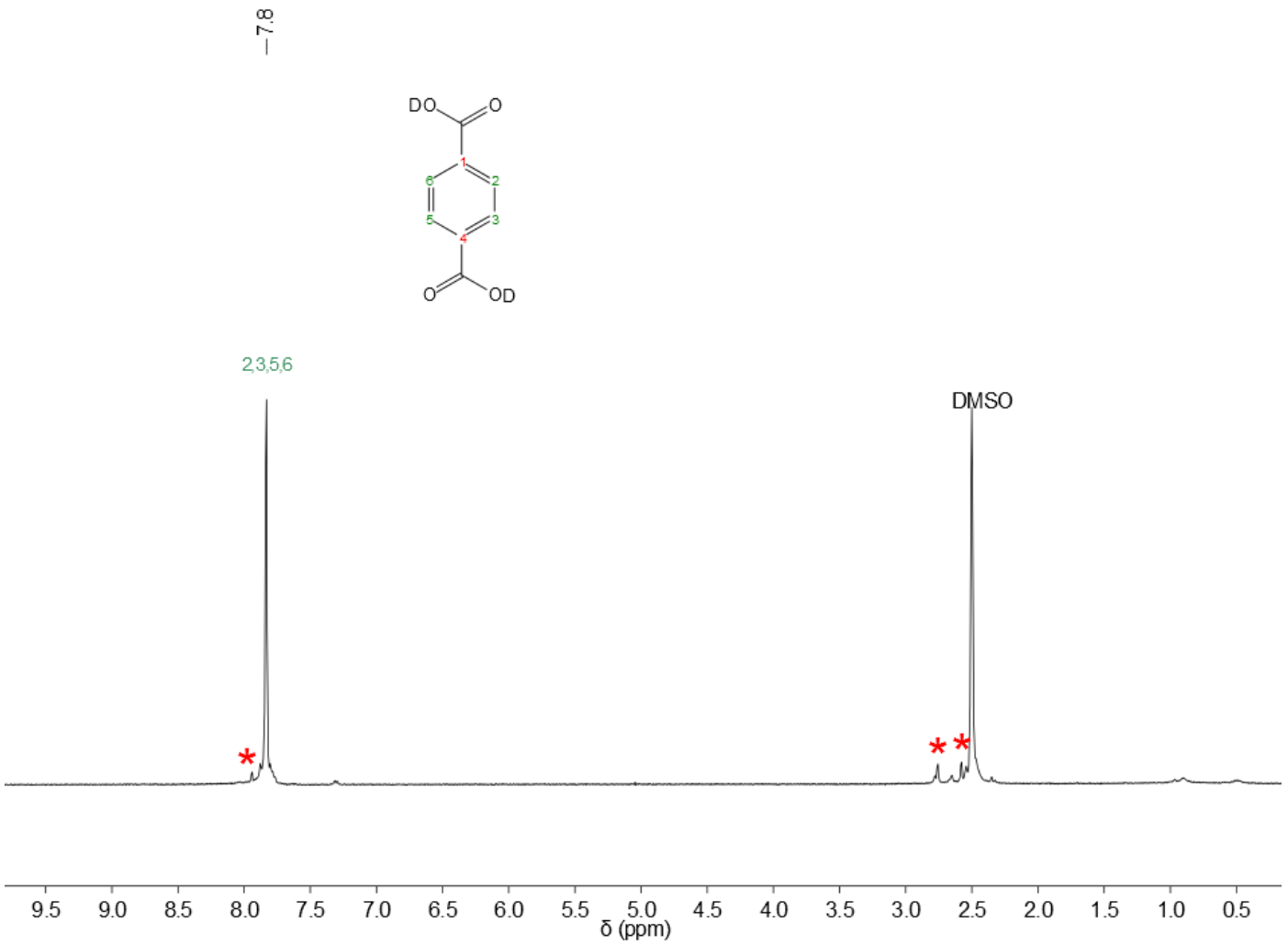

Figure S12. ^{1}H NMR spectrum for digested UiO-66 0%-I in 500 µL $(CD_3)_2SO$ and 100 µL D_2SO_4. Stars denote DMF.

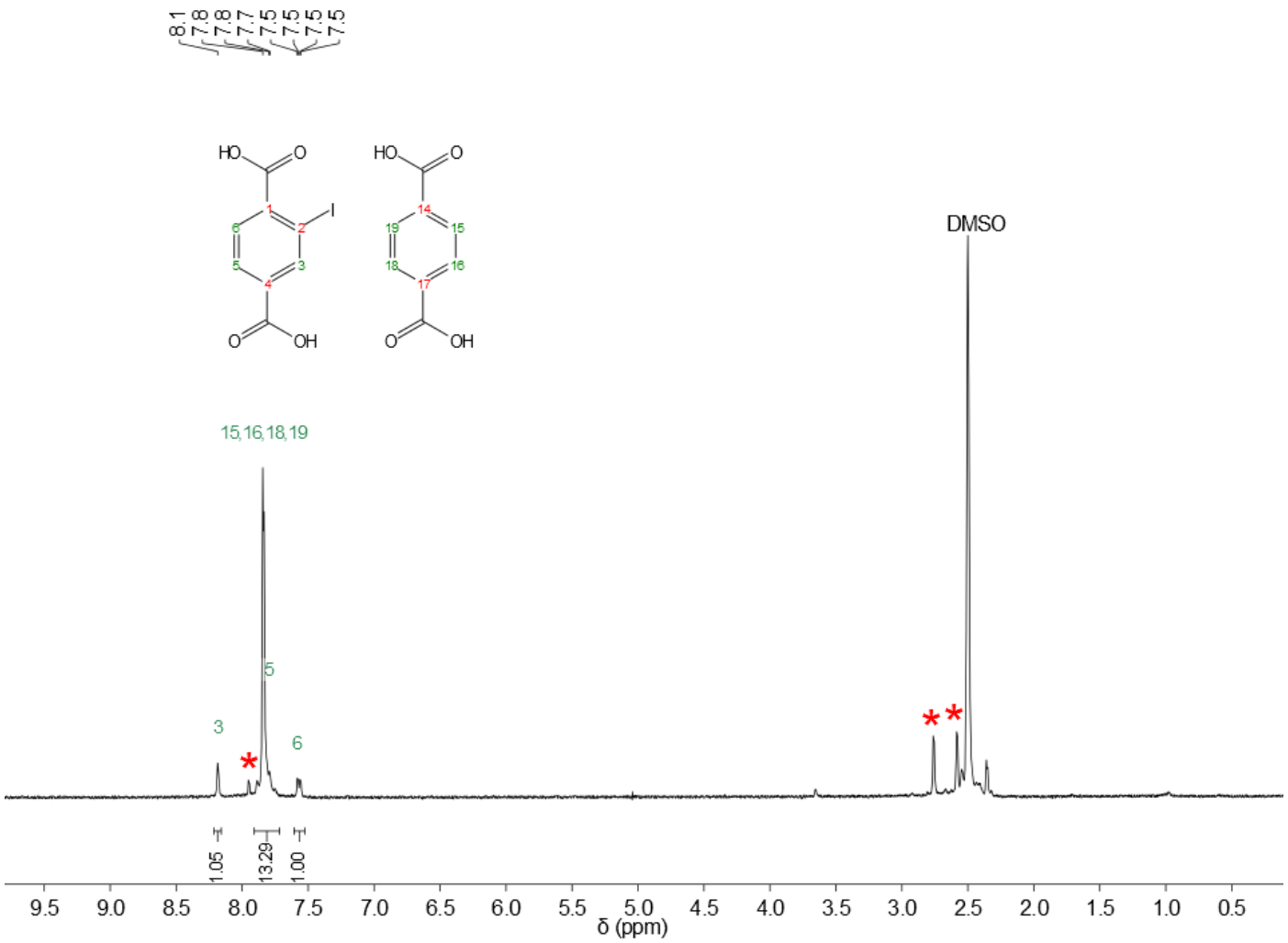

Figure S13. ^{1}H NMR spectrum for digested MTV-UiO-66 25%-I in 500 µL $(CD_3)_2SO$ and 100 µL D_2SO_4. Stars denote DMF.

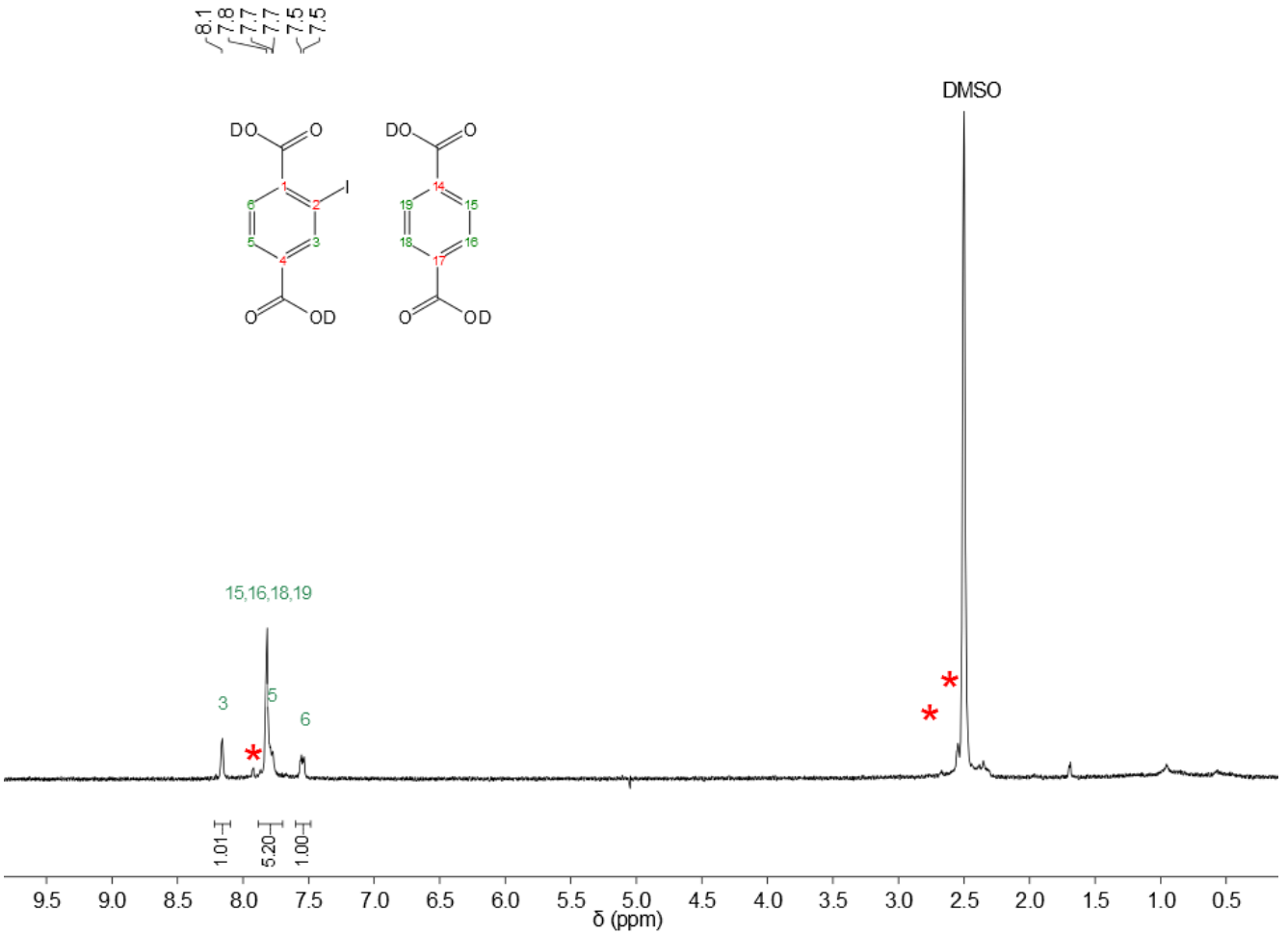

Figure 14. ^{1}H NMR spectrum for digested MTV-UiO-66 50%-I in 500 µL $(CD_3)_2SO$ and 100 µL D_2SO_4. Stars denote DMF.

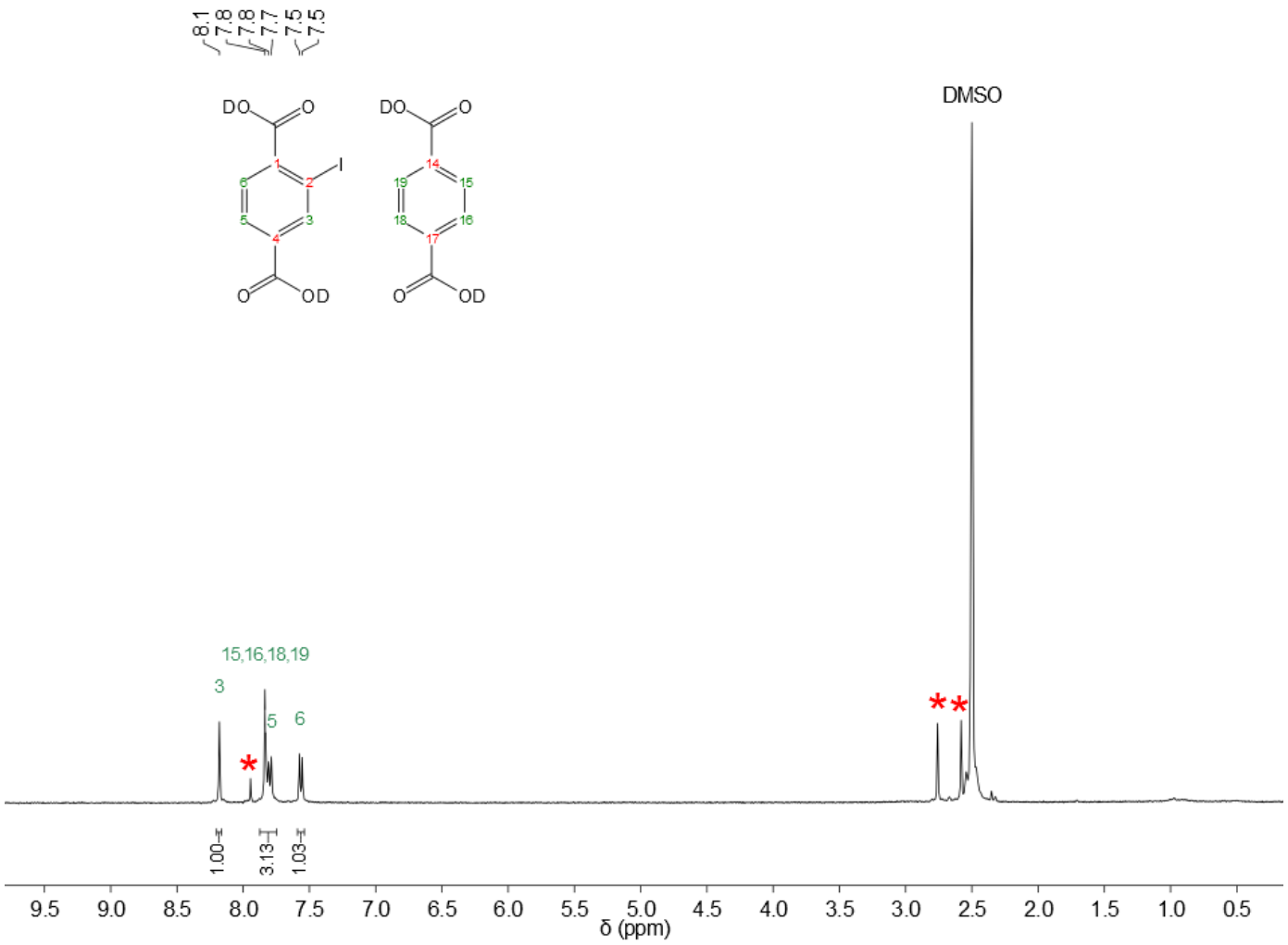

Figure S15. ^{1}H NMR spectrum for digested MTV-UiO-66 75%-I in 500 µL $(CD_3)_2SO$ and 100 µL D_2SO_4. Stars denote DMF.

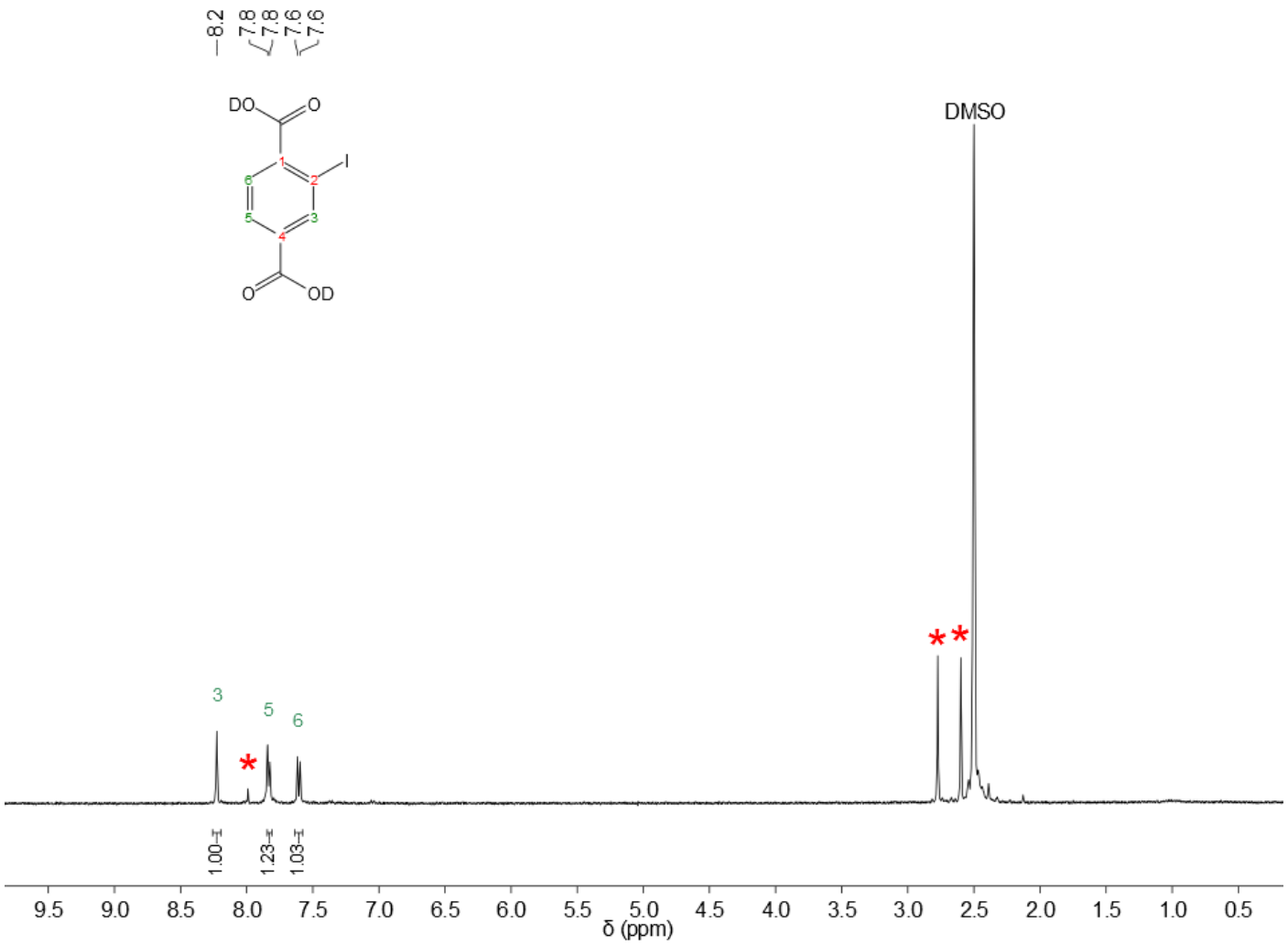

Figure S16. ^{1}H NMR spectrum for digested UiO-66 100%-I in 500 µL $(CD_3)_2SO$ and 100 µL D_2SO_4. Stars denote DMF.

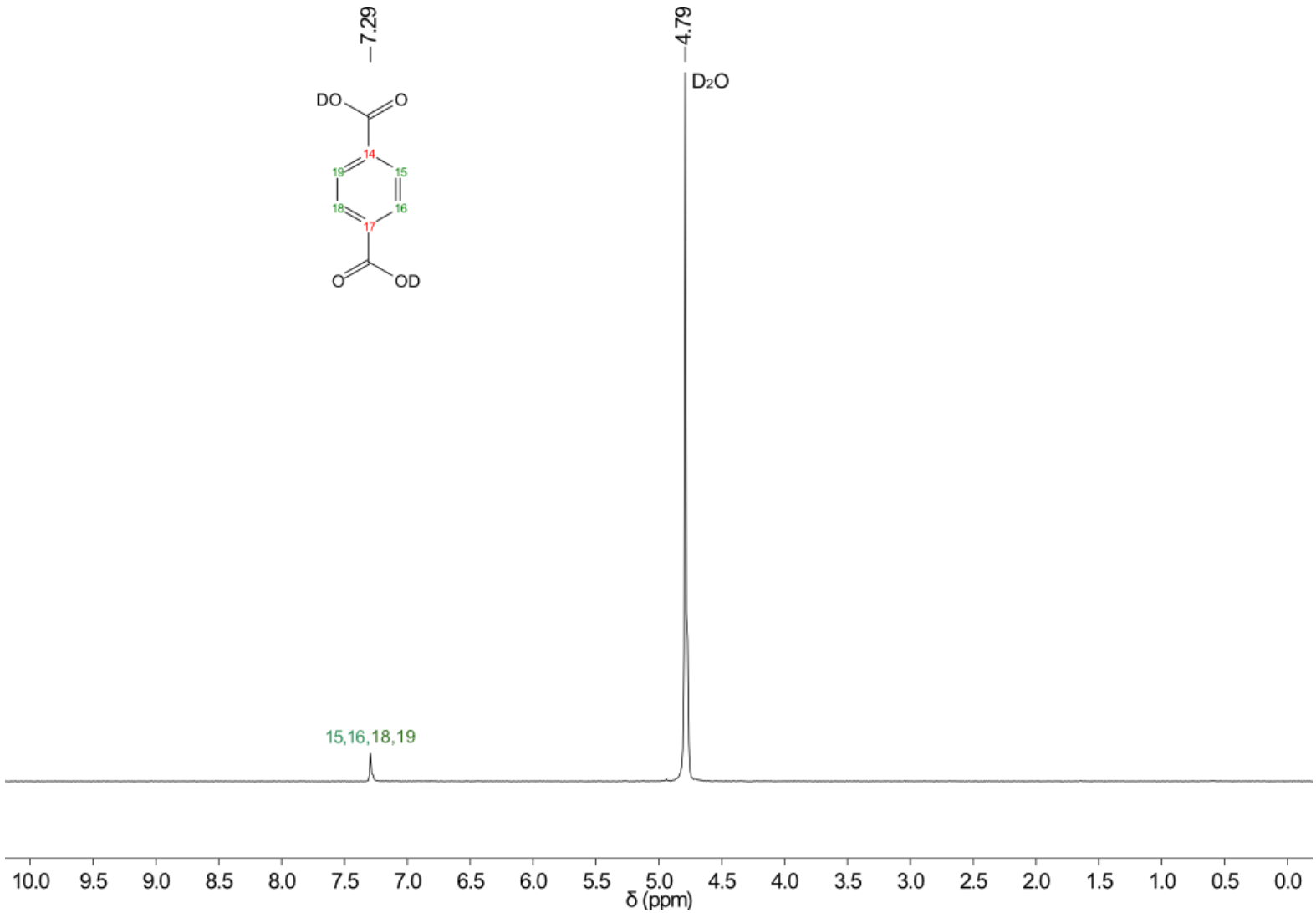

Figure S17. ^{1}H NMR spectrum for digested MIL-53 0%-I in 570 µL D_2O and 200 µL of NaOD solution 40 wt. % in D_2O.

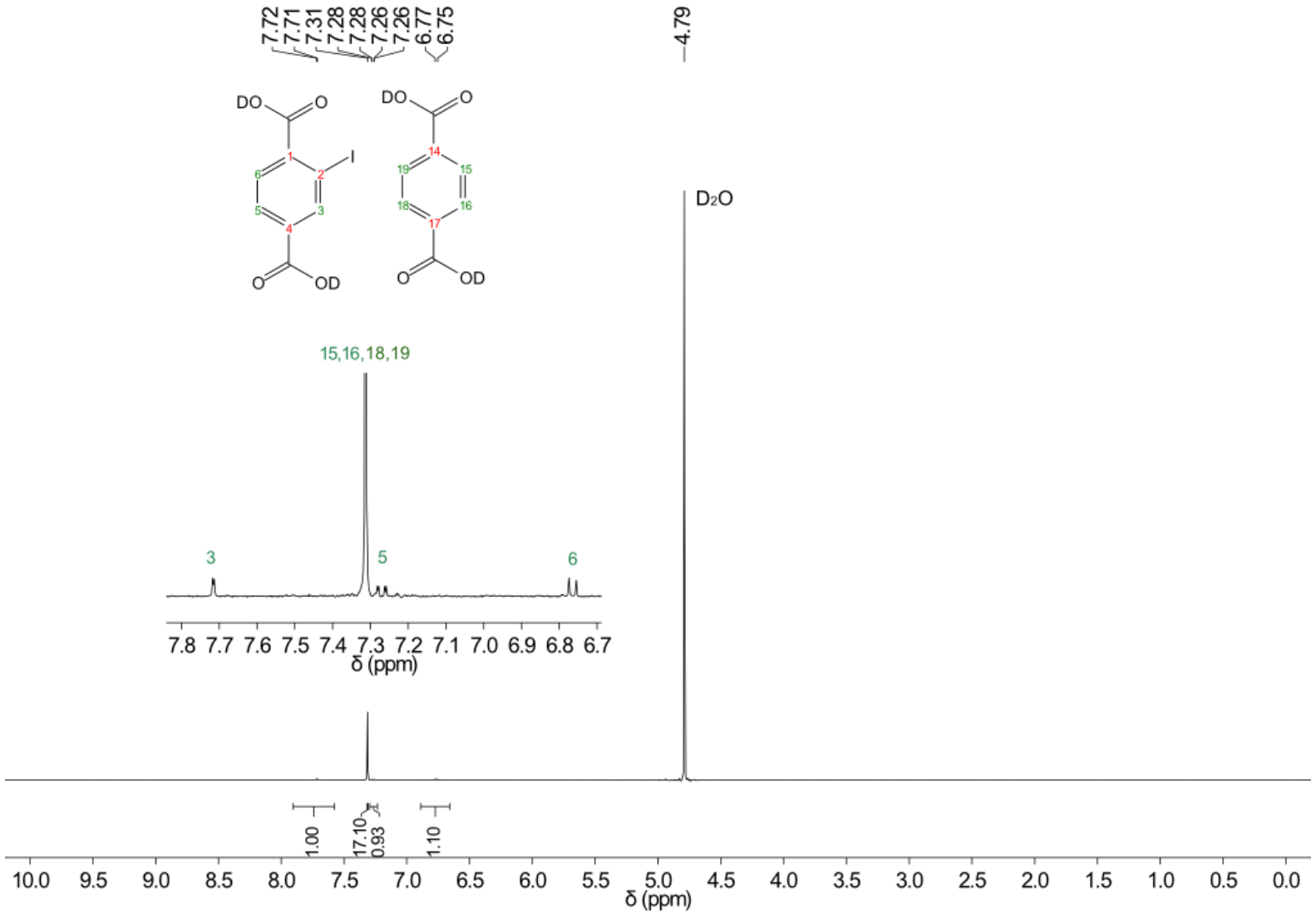

Figure S18. ^{1}H NMR spectrum for digested MTV-MIL-53 25%-I in 570 µL D_2O and 200 µL of NaOD solution 40 wt. % in D_2O.

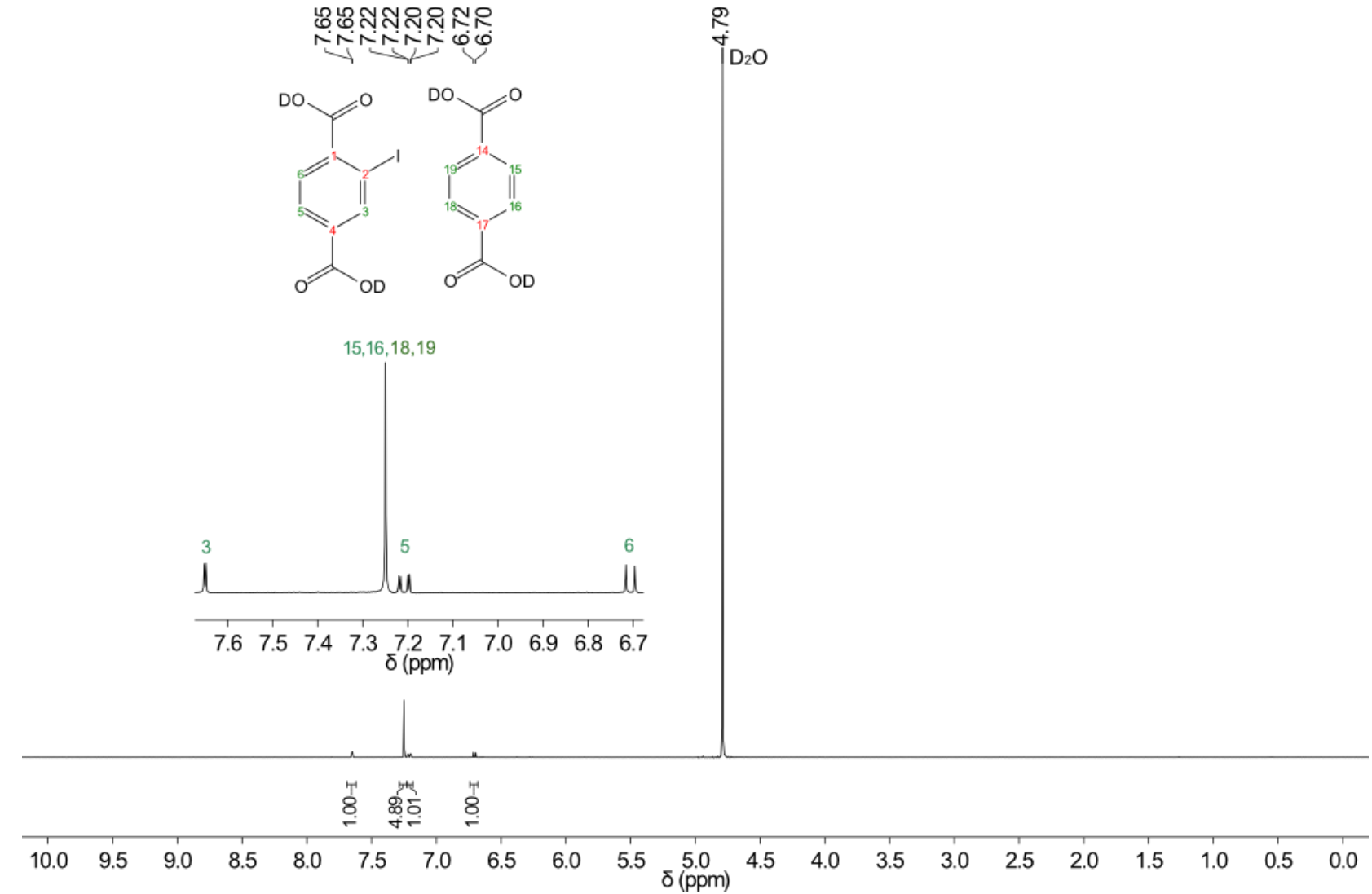

Figure S19. ^{1}H NMR spectrum for digested MTV-MIL-53 50%-I in 570 µL D_2O and 200 µL of NaOD solution 40 wt. % in D_2O.

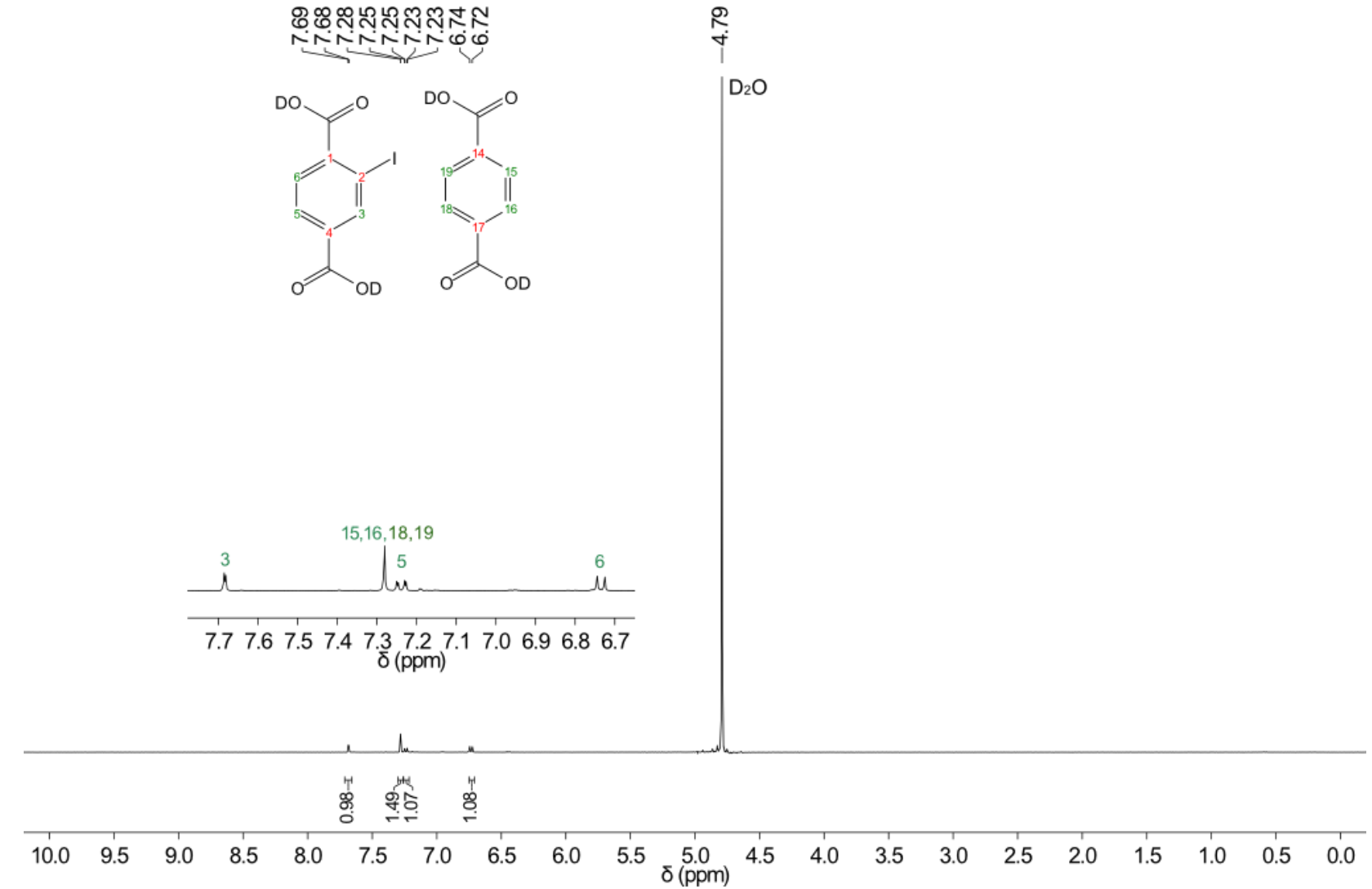

Figure S20. ^{1}H NMR spectrum for digested MTV-MIL-53 75%-I in 570 µL D_2O and 200 µL of NaOD solution 40 wt. % in D_2O.

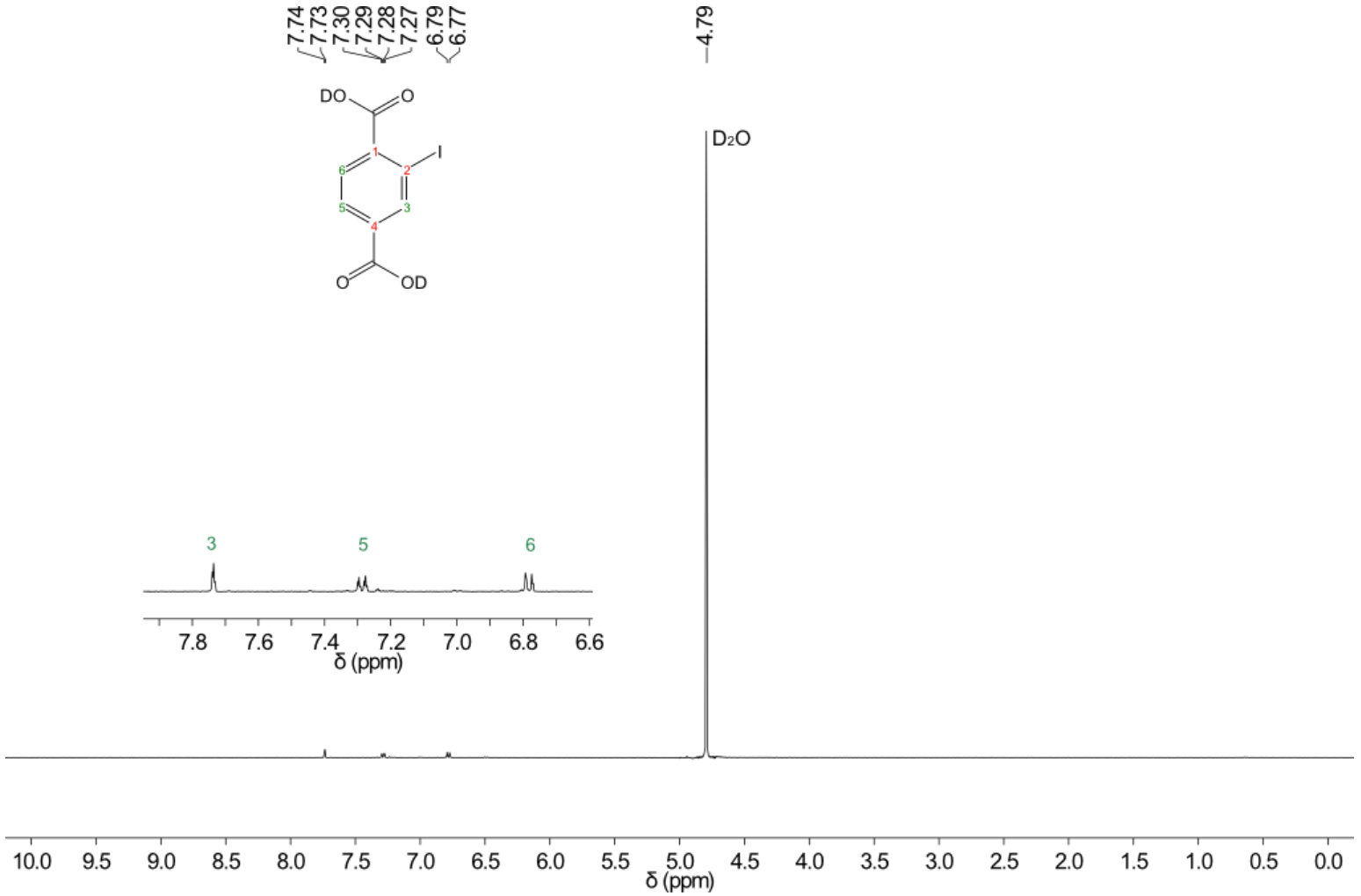

Figure S21. ^{1}H NMR spectrum for digested MIL-53 100%-I in 570 µL D_2O and 200 µL of NaOD solution 40 wt. % in D_2O.

S4.5 Nitrogen Adsorption

Nitrogen sorption measurements were performed at 77 K on a Quantichrome Autosorb iQ iQ gas sorption analyzer. Approximately 50 mg of the MOFs were added to a preweighed 6 mm sample cell. All samples were activated under vacuum at 200 °C for 13 hours under vacuum. The sample weight was then collected to accurately depict the activated weight. The activated MOFs had weights of approximately 40 mg, which were used as the final weight of the material. Analysis time of 20 hours and 15 minutes. Brunauer-Emmett-Teller surface areas and pore volumes were calculated using the DFT method in the Quantachrome ASiQwin software. The NLDFT equilibrium (cylinder/slit) model was chosen for the pore volume measurements.

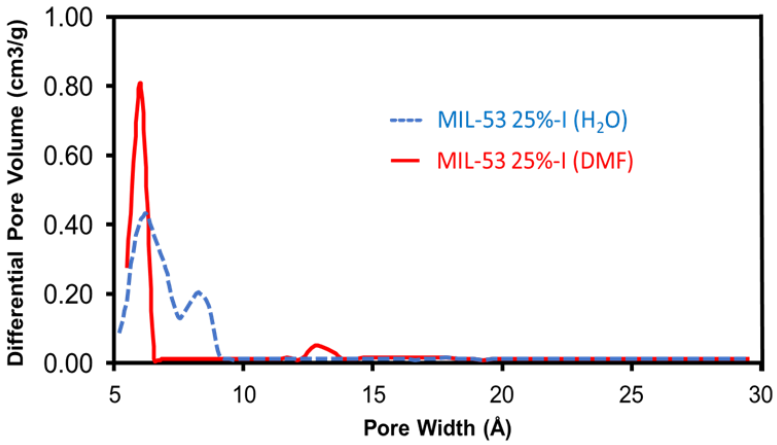

Figure S22. Pore volume distribution for the MTV-MIL-53 25%-I synthesized with H_2O and DMF.

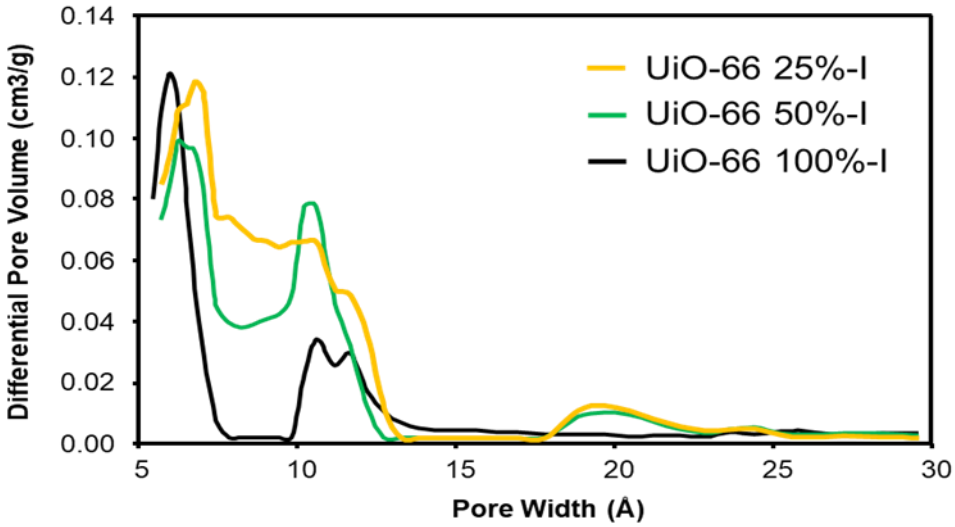

Figure S23. Pore volume distribution for the MTV-UiO-66 25, 50, and 100%-I.

S4.6 X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Physical Electronics PHI 5000 VersaProbe spectrometer (base pressure in the analysis chamber less than 1 × 10-7 Pa) using monochromatic Al Kα (hν = 1486.6 eV) X-ray source (25 W, 15 kV, 100 µm analysis spot size). The survey scans in the 0-1400 eV binding energy (BE) range were collected with a pass energy of 187.85 eV and a step of 0.8 eV. For the narrow energy scans, the pass energy was 23.5 eV with a step of 0.1 eV. To correct for sample charging, the BE of the spectra was referenced to the adventitious carbon C 1s BE at 284.8 eV.

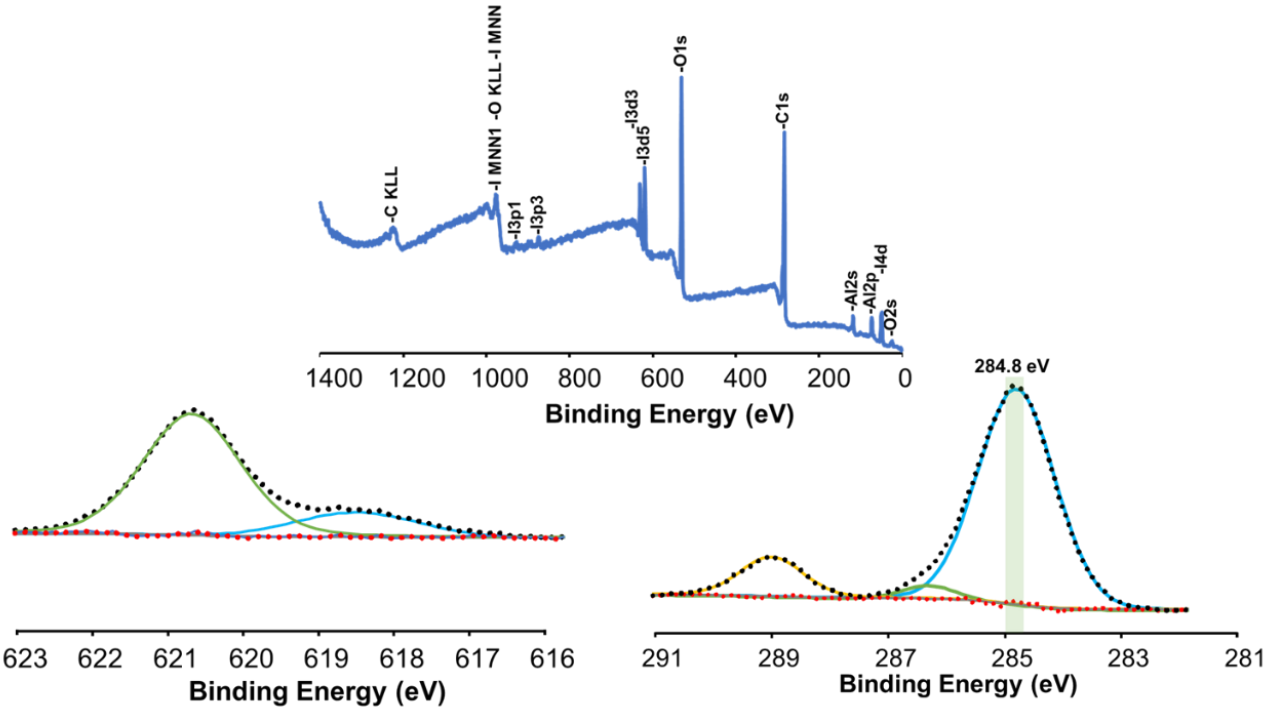

Figure S24. XPS spectra of MTV-MIL-53 50%-I: (top) survey scan; (bottom right) C 1s; (bottom left) I $3d_5$.

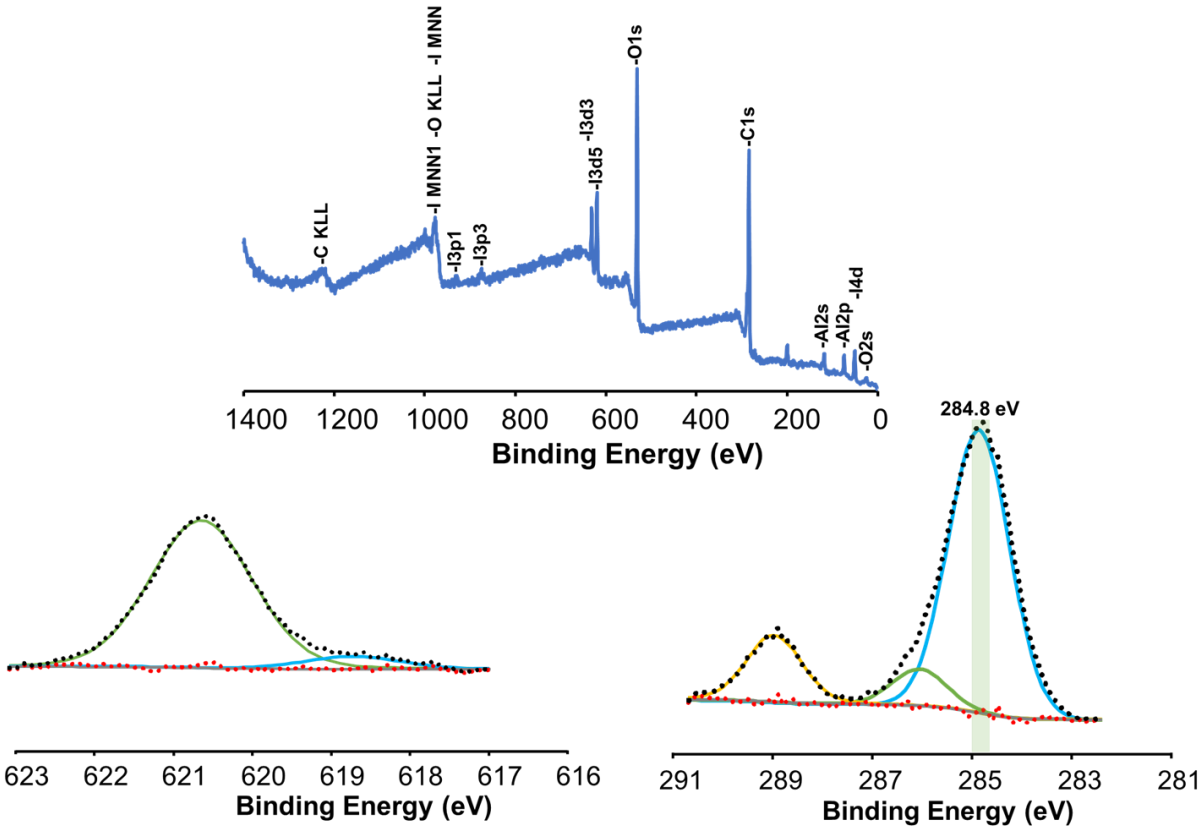

Figure S25. XPS spectra of oxidized MTV-MIL-53 50%-I: (top) survey scan; (bottom right) C 1s; (bottom left) I $3d_5$.

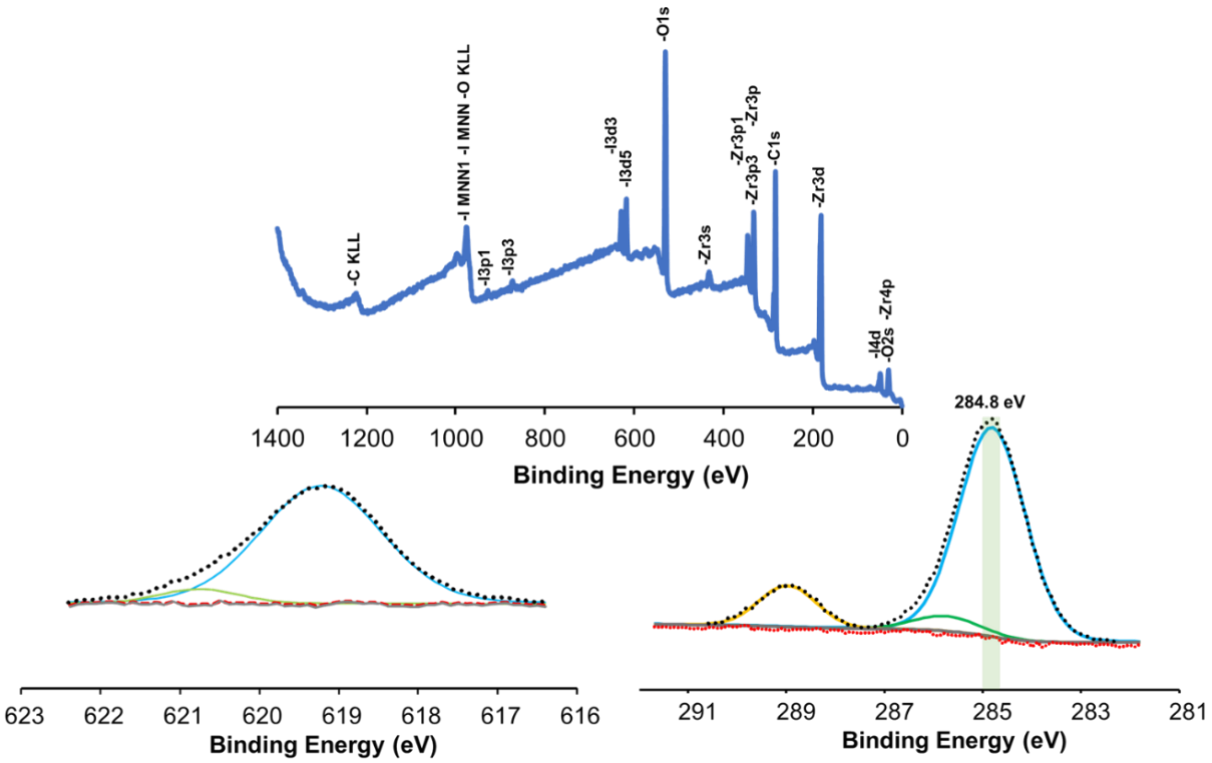

Figure 26. XPS spectra of MTV-UiO-66 25%-I: (top) survey scan; (bottom right) C 1s; (bottom left) I $3d_5$.

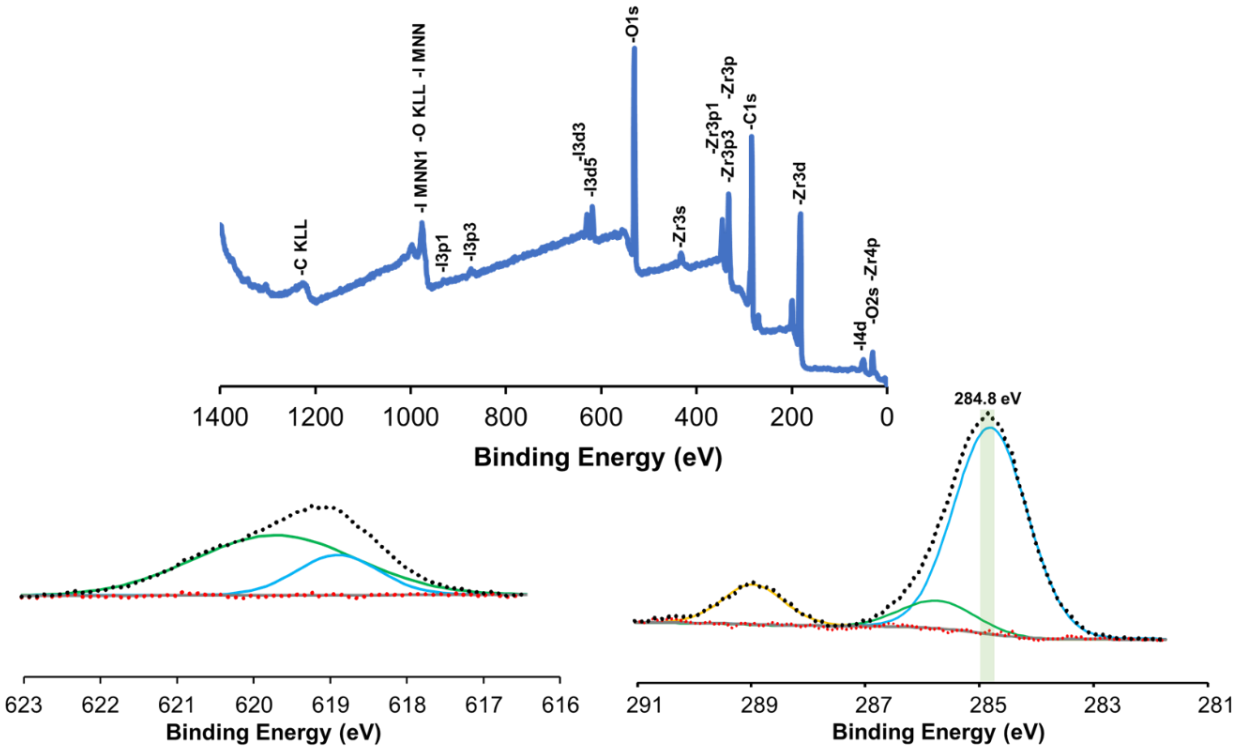

Figure S27. XPS spectra of oxidized MTV-UiO-66 25%-I: (top) survey scan; (bottom right) C 1s; (bottom left) I $3d_5$.

S5 Catalytic Experiments

S5.1 Typical Catalytic Reaction Procedure

In a typical catalytic reaction, the catalyst (20 mol%), co-oxidant (0.579 mmol, 0.0999) , and substrate (0.145 mmol, 0.0160 g) were mixed in the specified solvent or solvent mixture (4.0 mL) in a 2-dram clear glass vial. The vial was charged with a Teflon coated stir bar placed on the hot plate when it was 50 °C. After the specified time had been reached, the catalyst was separated using centrifugation and the liquid was decanted and 3 drops taken. The collcted sample was dissolved in the DMSO-d_6 to determine the catalytic conversion and yield via integration of the relevant peaks in the ^{1}H NMR spectrum. All control reactions were done in the absence of MOF.

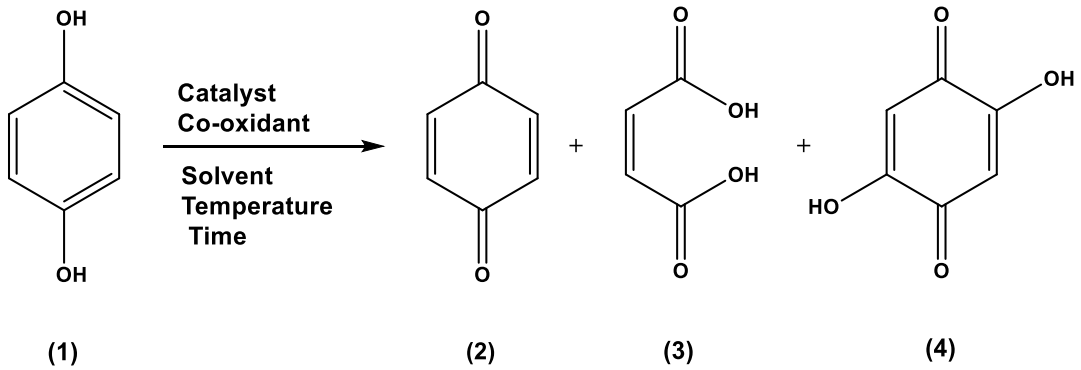

Figure S28. Observed products in the catalytic oxidation reaction of hydroquinone.

S5.2 Experimental procedure for multivariate MOFs catalyst optimization and esterified linker for oxidation of hydroquinone to benzoquinone.

0.3400 g (3.612 mmol) methylsulfonylmethane (MSM) as an internal standard and 0.3975 g (3.610 mmol) hydroquinone (HQ) as the substrate were dissolved in acetonitrile (ACN) to a final volume of 25.0 mL. 1.0 mL was taken and added to a 2-dram clear glass vial using a 1.0 mL volumetric pipet. 0.0999 g (70-75%, ~0.419 mmol, ~2.9 equivalent) meta-chloroperbenzoic acid (mCPBA) as co–oxidant was dissolved in 3.0 mL ACN and added to the reaction mixture. The reaction mixture was stirred in a closed cap vial at 50 °C. After 60 minutes, the catalyst was separated by centrifugation and 3 drops of the reaction mixture were dissolved in 0.5 mL of DMSO-d_6 to determine the catalytic conversion and yield as summarized in Table S6, Table S7 and Table S8.

S5.3 Results of All Catalytic Experiments

Table S6. Catalyst optimization for catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% MTV-UiO-66, ~2.9 equivalent meta-chloroperbenzoic acid (mCPBA), 4 mL acetonitrile (ACN) at 50 °C for 60 minutes.

Sample	Time (min)	Solvent	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	60	ACN	1.00	0.95	0.04	0.00	0.99	4	5
UiO-66 0%-I	60	ACN	1.00	0.93	0.07	0.00	1.00	7	7
UiO-66 25%-I	60	ACN	1.00	0.51	0.48	0.00	0.99	48	49
UiO-66 50%-I	60	ACN	1.00	0.86	0.13	0.00	0.99	13	14
UiO-66 75%-I	60	ACN	1.00	0.84	0.15	0.00	0.99	15	16
UiO-66 100%-I	60	ACN	1.00	0.95	0.04	0.00	0.99	4	5

Table S7. Catalyst optimization for catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% MTV-MIL-53, 2.9 equivalent meta-chloroperbenzoic acid (mCPBA), 4 mL acetonitrile (ACN) at 50 °C for 60 minutes.

Sample	Time (min)	Solvent	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	60	ACN	1.00	0.95	0.04	0.00	0.99	4	5
Mil-53 0%-I	60	ACN	1.00	0.97	0.03	0.00	0.99	3	3
Mil-53 25%-I	60	ACN	1.00	0.84	0.11	0.00	0.95	12	16
Mil-53 25%-I (DMF)	60	ACN	1.00	0.83	0.17	0.00	1.00	17	17
Mil-53 50%-I	60	ACN	1.00	0.91	0.08	0.00	0.99	8	9
Mil-53 75%-I	60	ACN	1.00	0.95	0.05	0.00	1.00	5	6
Mil-53 100%-I	60	ACN	1.00	0.94	0.05	0.00	0.99	5	6

Table S8. 2-Iodoterephthalate as a homogenous analogue of supporting iodine MOFs catalyst for catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% catalyst, 2.9 equivalent meta-chloroperbenzoic acid (mCPBA), 4 mL acetonitrile (ACN) at 50 °C for 60 minutes.

Sample	Time (min)	Solvent	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	60	ACN	1.00	0.95	0.04	0.00	0.99	4	5
2-Iodoterephthalate	60	ACN	1.00	0.02	0.88	0.06	0.96	97	98

S5.4 Experimental procedure for solvent variation for oxidation of hydroquinone to benzoquinone.

Experimental procedure for solvent variation was the same as the catalyst optimization. The solvent and time are summarized in Table S9, Table S10, Table S11 and Table S12.

Table S9. Solvent variation of MTV-UiO-66 25%-I for catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% catalyst, 2.9 equivalent meta-chloroperbenzoic acid (mCPBA), 4 mL specified solvent at 50 °C for 60 minutes.

Sample	Time (min)	Solvent	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	60	ACN	1.00	0.95	0.04	0.00	0.99	4	5
UiO-66 25%-I			1.00	0.50	0.48	0.00	0.98	48	49
Control	60	NM	1.00	0.85	0.08	0.06	0.99	8	15
UiO-66 25%-I			1.00	0.06	0.93	0.00	0.99	93	94
Control	60	EA	1.00	0.97	0.03	0.00	1.00	3	3
UiO-66 25%-I			1.00	0.37	0.63	0.00	1.00	63	63
Control	60	Acetone	1.00	0.95	0.03	0.00	0.98	4	5
UiO-66 25%-I			1.00	0.27	0.68	0.00	0.95	68	73
Control	60	EtOH	1.00	0.86	0.10	0.00	0.96	11	15
UiO-66 25%-I			1.00	0.01	0.97	0.00	0.98	98	98
Control	60	MeOH	1.00	0.0	0.94	0.00	0.98	95	96
UiO-66 25%-I			1.00	0.04	0.95	0.00	0.99	95	95

Table S10. Solvent variation of MTV-MIL-53 25%-I (DMF) for catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% catalyst, 2.9 equivalent meta-chloroperbenzoic acid (mCPBA), 4 mL specified solvent at 50 °C for 60 minutes.

Sample	Time (min)	Solvent	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	60	ACN	1.00	0.95	0.04	~ 0.00	0.99	4	5
Mil-53 25%-I			1.00	0.83	0.17	~ 0.00	1.00	17	17
Control	60	NM	1.00	0.86	0.08	0.06	1.00	8	15
Mil-53 25%-I			1.00	0.42	0.45	0.1	0.97	45	57
Control	60	EA	1.00	0.97	0.03	~ 0.00	1.00	3	3
Mil-53 25%-I			1.00	0.75	0.25	~ 0.00	1.00	25	25
Control	60	Acetone	1.00	0.95	0.04	~ 0.00	0.99	4	5
Mil-53 25%-I			1.00	0.83	0.06	~ 0.00	0.89	6	17
Control	60	EtOH	1.00	0.86	0.11	~ 0.00	0.97	11	15
Mil-53 25%-I			1.00	0.77	0.12	~ 0.00	0.89	12	23
Control	60	MeOH	1.00	0.04	0.94	~ 0.00	0.98	95	96
Mil-53 25%-I			1.00	0.02	0.97	~ 0.00	0.99	97	98

Table S11. Solvent variation of MTV-UiO-66 25%-I for catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% catalyst, 2.9 equivalent meta-chloroperbenzoic acid (mCPBA), 4 mL specified solvent at 50 °C for 2 minutes.

Sample	Time (min)	Solvent	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	2	ACN	1.00	0.95	0.04	0.00	0.99	4	5
UiO-66 25%-I			1.00	0.69	0.30	0.00	1.00	30	30
Control	2	NM	1.00	0.93	0.06	0.00	0.99	6	7
UiO-66 25%-I			1.00	0.06	0.77	0.15	0.98	77	94
Control	2	EA	1.00	1.00	0.00	0.00	1.00	0	0
UiO-66 25%-I			1.00	0.47	0.51	0.00	0.98	51	5
Control	2	Acetone	1.00	0.99	0.00	0.00	0.99	0	1
UiO-66 25%-I			1.00	0.34	0.66	0.00	1.00	66	66
Control	2	EtOH	1.00	0.96	0.04	0.00	1.00	4	4
UiO-66 25%-I			1.00	0.02	0.80	0.00	0.82	80	98
Control	2	MeOH	1.00	0.89	0.11	0.00	1.00	11	11
UiO-66 25%-I			1.00	0.07	0.92	0.00	0.99	92	93

Table S12. Solvent variation of MTV-MIL-53 25%-I (DMF) for catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% catalyst, 2.9 equivalent meta-chloroperbenzoic acid (mCPBA), 4 mL specified solvent at 50 °C for 2 minutes.

Sample	Time (min)	Solvent	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	2	ACN	1.00	0.95	0.04	0.00	0.99	4	5
Mil-53 25%-I			1.00	0.93	0.06	0.00	0.99	6	7
Control	2	NM	1.00	0.93	0.06	0.00	0.99	6	7
Mil-53 25%-I			1.00	0.71	0.23	0.04	0.98	24	28
Control	2	EA	1.00	1.00	0.00	0.00	1.00	0	0
Mil-53 25%-I			1.00	0.89	0.08	0.00	0.97	8	11
Control	2	Acetone	1.00	0.99	0.00	0.00	0.99	0	1
Mil-53 25%-I			1.00	0.97	0.03	0.00	1.00	3	3
Control	2	EtOH	1.00	0.96	0.04	0.00	1.00	4	4
Mil-53 25%-I			1.00	0.93	0.05	0.00	0.98	5	7
Control	2	MeOH	1.00	0.89	0.11	0.00	1.00	11	11
Mil-53 25%-I			1.00	0.56	0.42	0.00	0.98	42	44

S5.5 Experimental procedure for temperature variation for oxidation of hydroquinone to benzoquinone.

Experiment procedure for temperature variation was same as described for the catalyst optimization at specified temperature and solvent in 60 minutes as shown as Table S13 and Table S14.

Table S13. Control reactions for temperature variation of oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) at specified temperature in 4 mL solvent for 60 minutes.

Sample	Temp. (°C)	Time (min)	Solvent	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	0	60	ACN	1.00	0.99	0.00	0.00	0.99	0	1
	24	60	ACN	1.00	0.97	0.02	0.00	0.99	2	3
	50	60	ACN	1.00	0.95	0.04	0.00	0.99	4	5
	75	60	ACN	1.00	0.72	0.13	0.12	0.97	13	28
	75	60	Acetone	1.00	0.88	0.1	0.00	0.98	10	12
	75	60	EA	1.00	0.70	0.27	0.00	0.97	27	29
	75	60	NM	1.00	0.43	0.29	0.27	0.99	29	57
	75	60	EtOH	1.00	0.15	0.82	0.00	0.97	82	85
	75	60	MeOH	1.00	0.00	0.97	0.00	0.97	97	100

Table S14. Temperature variation of catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% MTV-MIL-53 25%-I (DMF), 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) at specified temperature in 4 mL solvent for 60 minutes.

Sample	Temp. (°C)	Solvent	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	50	ACN	1.00	0.95	0.04	0.00	0.99	4	5
	75		1.00	0.85	0.14	0.00	0.99	14	15
Mil-53 25%-I	50		1.00	0.83	0.17	0.00	1.00	17	17
	75		1.00	0.53	0.44	0.00	0.97	44	47
Control	50	Acetone	1.00	0.95	0.04	0.00	0.99	4	5
	75		1.00	0.88	0.1	0.00	0.98	10	12
Mil-53 25%-I	50		1.00	0.83	0.06	0.00	0.89	6	17
	75		1.00	0.82	0.12	0.05	0.99	12	18
Control	50	EA	1.00	0.97	0.03	0.00	1.00	3	3
	75		1.00	0.70	0.27	0.00	0.97	27	29
Mil-53 25%-I	50		1.00	0.75	0.25	0.00	1.00	25	25
	75		1.00	0.69	0.14	0.16	0.99	14	31

S5.5.1 Experimental procedure for co-oxidant loading variation for oxidation of hydroquinone to benzoquinone.

The experimental procedure for co-oxidant loading variation was the same as described for the catalyst optimization but with 1.45, 2.9, and 4.4 equivalents of meta-chloroperbenzoic acid (mCPBA) at 50 °C for 60 minutes as shown in Table S15.

Table S15. Co-oxidant loading variation for catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% catalyst, specified equivalent of meta-chloroperbenzoic acid (mCPBA) in 4 mL nitromethane (NM) at 50 °C for 60 minutes.

Sample	mCPBA	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	1.45 equiv.	1.00	0.82	0.09	0.08	0.99	9	18
Mil-53 25%-I (DMF)		1.00	0.7	0.27	0.03	1.00	27	30
UiO-66 25%-I		1.00	0.03	0.82	0.10	0.95	83	97
Control	2.9 equiv.	1.00	0.86	0.08	0.06	1.00	8	15
Mil-53 25%-I (DMF)		1.00	0.42	0.45	0.1	0.97	45	57
UiO-66 25%-I		1.00	0.06	0.93	0.00	0.99	93	94
Control	4.4 equiv.	1.00	0.67	0.17	0.12	0.96	17	32
Mil-53 25%-I (DMF)		1.00	0.47	0.40	0.09	0.96	40	52
UiO-66 25%-I		1.00	0.03	0.89	0.06	0.98	89	97

S5.5.2 Experimental procedure for variation of co-oxidant for oxidation of hydroquinone to benzoquinone.

The experiment procedure for variation of co-oxidant was same as described for the catalyst optimization with 2.9 equiv. of 3-chloroperbenzoic acid (mCPBA), 4 equiv. each of potassium peroxymonosulfate (Oxone), hydrogen peroxide (30 % (w/w) in H_2O) (H_2O_2), tert-butyl hydroperoxide (70 wt. % in H_2O) (^tBuOOH), and hydrogen peroxide - urea (Hyperol) in 4 mL nitromethane/ water (3:1 v:v) as the solvent at 50 °C for 60 minutes as shown in Table S16 and Table S17.

Table S16. Co-oxidant variation for catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% MTV-UiO-66 25%-I, 2.9 equivalent of specified co-oxidant in in nitromethane/ water (3:1 v:v) at 50 °C for 60 minutes

Sample	Co-oxidant	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	mCPBA	1.00	0.72	0.00	0.05	0.77	0	28
UiO-66 25%-I		1.00	0.23	0.74	0.00	0.97	75	76
Control	Oxone	1.00	0.84	0.00	0.06	0.90	0	15
UiO-66 25%-I		1.00	0.20	0.77	0.00	0.97	78	80
Control	H_2O_2	1.00	0.94	0.00	0.05	0.99	0	6
UiO-66 25%-I		1.00	0.72	0.24	0.00	0.96	24	28
Control	^tBuOOH	1.00	0.92	0.00	0.05	0.97	0	8
UiO-66 25%-I		1.00	0.32	0.06	0.61	0.99	6	68
Control	Hyperol	1.00	0.90	0.00	0.08	0.98	0	10
UiO-66 25%-I		1.00	0.75	0.09	0.15	0.99	9	25

Table S17. Co-oxidant variation for catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% MTV-MIL-53 25%-I (DMF), 2.9 equivalent of specified co-oxidant in in nitromethane/ water (3:1 v:v) at 50 °C for 60 minutes

Sample	Co-oxidant	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	mCPBA	1.00	0.72	0.00	0.05	0.77	0	28
Mil-53 25%-I		1.00	0.51	0.37	0.10	0.98	37	49
Control	Oxone	1.00	0.84	0.00	0.06	0.90	0	15
Mil-53 25%-I		1.00	0.14	0.70	0.16	1.00	70	86
Control	H_2O_2	1.00	0.94	0.00	0.05	0.99	0	6
Mil-53 25%-I		1.00	0.82	0.00	0.03	0.85	0	18
Control	^{t}BuOOH	1.00	0.92	0.00	0.05	0.97	0	8
Mil-53 25%-I		1.00	0.90	0.00	0.07	0.97	0	10
Control	Hyperol	1.00	0.90	0.00	0.08	0.98	0	10
Mil-53 25%-I		1.00	0.93	0.04	0.00	0.97	4	7

S5.5.3 Experimental procedure for variation of the mol% of catalyst for oxidation of hydroquinone to benzoquinone.

The experimental procedure for temperature variation was same as described for the catalyst optimization with different mol% of catalyst (20, 10, 5, and 1) and 4 equivalent oxone in nitromethane/water (3:1 v:v) at 50 °C for 60 minutes as shown in Table S18.

Table S18. Catalyst mol% variation for catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) using 4 equivalent oxone in nitromethane/water (3:1 v:v) at 50 °C for 60 minutes .

Sample	Catalyst (mol %) based on I	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	0	1.00	0.84	0.00	0.06	0.90	0	15
UiO-66 25%-I	20	1.00	0.20	0.78	0.00	0.98	78	80
	10	1.00	0.16	0.77	0.06	0.99	77	83
	5	1.00	0.33	0.51	0.15	0.99	51	67
	1	1.00	0.51	0.31	0.16	0.98	31	49
Mil-53 25%-I (DMF)	20	1.00	0.14	0.70	0.16	1.00	70	86
	10	1.00	0.34	0.46	0.19	0.99	45	66
	5	1.00	0.55	0.34	0.11	1.00	34	45
	1	1.00	0.64	0.23	0.12	0.99	23	36

S5.5.4 Experimental procedure for recyclability test of multivariate MOFs.

The recyclability tests for MTV-UiO-66 25%-I and MTV-MIL-53 25%-I were same as described for the catalyst optimization with ~2.9 equiv. metachloroperbenzoic acid (mCPBA) in 4 mL nitromethane (NM) at 50 °C for 60 minutes as shown in Table S19. After each run, the catalyst was separated using centrifugation and the liquid was decanted and 3 drops of liquid were dissolved in 0.5 mL DMSO-d_6 to determine the catalytic conversion and yield of catalytic conversion of hydroquinone (HQ) to benzoquinone (BQ). The leftover

catalyst was washed three times with nitromethane and acetone. To the dried catalyst were added prepared 1.00 mL of prepared solution of (MSM:HQ) as described before, 2.9 equivalent of meta-chloroperbenzoic acid (mCPBA), and 4 mL nitromethane (NM). The closed cap 2 dram clear glass vial was placed on the hot plate when temperature was 50 °C for 60 minutes.

Table S19. The recyclability test for catalysts with 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) in 4 mL nitromethane at 50 °C for 60 minutes.

Sample	Run	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	-	1.00	0.86	0.08	0.06	1.00	8	15
UiO-66 25%-I	1st	1.00	0.06	0.93	0.00	0.99	93	94
	2nd	1.00	0.52	0.43	0.03	0.98	43	48
	3rd	1.00	0.71	0.26	0.03	1.00	26	29
	4th	1.00	0.7	0.26	0.04	1.00	26	30
Mil-53 25%-I (DMF)	1st	1.00	0.42	0.45	0.1	0.97	45	57
	2nd	1.00	0.54	0.43	0.03	1.00	43	46
	3rd	1.00	0.52	0.43	0.03	0.98	43	47
	4th	1.00	0.52	0.41	0.03	0.96	41	47

S5.5.5 Split test for multivariate MOFs.

In order to study of any possible leaching of incorporated linkers in the multivariate MOFs during catalytic oxidation reaction of hydroquinone to benzoquinone split test was done with 1 equivalent methylsulfonylmethane (MSM) as internal standard, 1 equivalent hydroquinone (HQ) as substrate, ~ 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) as co-oxidant in 4 mL acetonitrile (ACN). The split test for MTV-UiO-66 25%-I and MTV-MIL-53 25%-I was done at 50 °C and 75 °C, respectively. For each catalyst, two reactions were running under the same condition simultaneously. For MTV-UiO-66 25%-I, after 2 minutes one of the reactions was interrupted and the catalyst was separated using centrifugation. The hot filtrate was immediately transferred to another vial and the reaction was then allowed to continue under the same conditions. In case of MTV-MIL-53 25%-I, after 30 minutes one of the reactions was interrupted and the catalyst was separated using centrifugation. Hot filtrate immediately was transferred to another vial and reaction was then allowed to continue under the same conditions. After 60 minutes no significant yield and conversion change was observed after filtration. The observed catalytic yields and conversions were summarized in Table S20 and Table S22.

Table S20. Split test of MTV-UiO-66 25%-I with 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) in 4 mL acetonitrile (ACN) at 50 °C.

Sample	Time (min)	Temp. (°C)	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	2	50	1.00	0.95	0.04	0.00	0.99	4	5
	60		1.00	0.95	0.04	0.00	0.99	4	5
UiO-66 25%-I	2		1.00	0.67	0.30	0.00	0.97	30	30
Filtration was done after 2 min	60		1.00	0.66	0.33	0.00	0.99	33	34
UiO-66 25%-I	60		1.00	0.51	0.48	0.00	0.99	48	49

Table S21. Catalytic oxidation of hydroquinone derivatives in the presence of 20 mol% MTV-UiO-66 25%-I and MTV-MIL-53 25%-I (DMF) as catalysts, 2.9 equivalent meta-chloroperbenzoic acid (mCPBA), 4 mL nitromethane for 60 minutes.

Substrate	Sample	Temp. (°C)	Normalized integrated intensity of MSM	Normalized integrated intensity of substrate	Normalized integrated intensity of desired product	Normalized integrated intensity of byproducts	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
2,5-dibromohydroquinone	Control	50	1.00	0.94	0.05	0.00	0.99	5	6
	UiO-66 25%-I		1.00	0.2	0.72	0.00	0.92	72	80
	MIL-53 25%-I		1.00	0.83	0.15	0.00	0.98	15	16
2-chlorohydroquinone	Control	50	1.00	0.75	0.24	0.00	0.99	24	25
	UiO-66 25%-I		1.00	0.35	0.64	0.00	0.99	64	65
	MIL-53 25%-I		1.00	0.54	0.44	0.00	0.98	44	46
2,5-di-tert-butylhydroquinone	Control	24	1.00	0.58	0.41	0.00	0.99	41	42
	UiO-66 25%-I		1.00	0.04	0.95	0.00	0.99	95	95
	MIL-53 25%-I		1.00	0.56	0.43	0.00	0.99	43	44
	UiO-66 25%-I		1.00	0.58	0.41	0.00	0.99	42	42
tert-butylhydroquinone	Control	24	1.00	0.68	0.3	0.00	0.98	31	32
	UiO-66 25%-I		1.00	0.35	0.62	0.00	0.97	62	65

	MIL-53 25%-I		1.00	0.65	0.34	0.00	0.99	34	35
methylhydroquinone	Control	24	1.00	0.69	0.3	0.00	0.99	29	31
	UiO-66 25%-I		1.00	0.4	0.57	0.00	0.97	57	59
	MIL-53 25%-I		1.00	0.7	0.29	0.00	0.99	36	37

Table S22. Split test of MTV-MIL-53 25%-I (DMF), 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) in 4 mL acetonitrile (ACN).

Sample	Time (min)	Temp. (°C)	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	10	75	1.00	0.93	0.07	0.00	1.00	7	7
	30		1.00	0.80	0.09	0.10	0.99	9	20
	60		1.00	0.72	0.13	0.12	0.97	13	28
MIL-53 25%-I	10		1.00	0.84	0.16	0.00	1.00	16	16
	30		1.00	0.74	0.22	0.01	0.97	22	26
Filtration was done after 30 minutes	60		1.00	0.75	0.24	0.00	0.99	24	25
MIL-53 25%-I	60		1.00	0.53	0.44	0.00	0.97	44	47

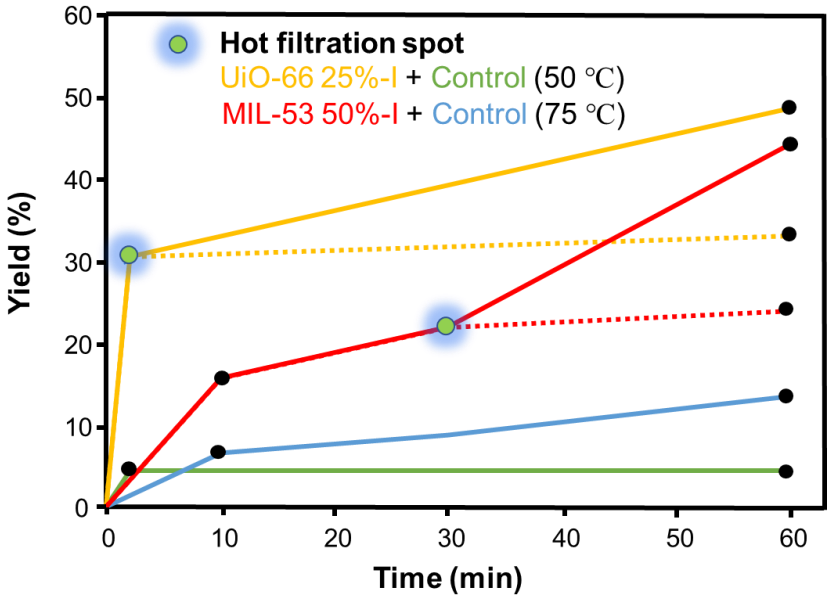

Figure S29. Split test where catalysts (MTV-UiO-66 25%-I in yellow, MTV-MIL-53 25%-I in red, no catalyst in green and blue) were hot filtered from the reaction mixture after 2 minutes for MTV-UiO-66 25%-I and 10 minutes for MTV-MIL-53 25%-I. Samples were characterized after 1 hour.

S6 UiO-66 25%-I surface-modification with benzoic acid

S6.1 Surface modification procedure

UiO-66 25%-I (0.651 mmol, 0.2 g) was suspended in 10 mL DMF with 30 equivalents of benzoic acid (19.53 mmol, 2.4 g) per Zr in the framework. An additional 10 mL of DMF was added to the mixture and it was heated up to 120 °C with gentle stirring. After 48 h, the reaction mixture was filtered and washed with hot DMF (x3) and soaked for 16 h in hot methanol (x1) prior to being heated at 150 °C for 16 hours under vacuum.

The PXRD pattern showed that the treated MOF remained crystalline (Figure S30). Digestion analysis confirmed the persistence of 25% of 2-iodoterephthalic acid in the framework (Figure S31) along with the incorporation of benzoate.

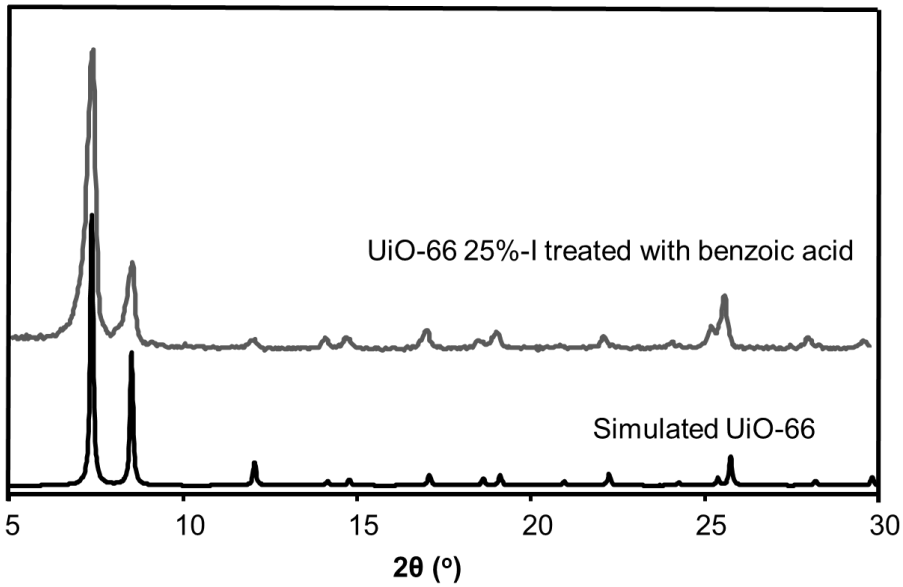

Figure S30. PXRD patterns of benzoic acid treated MTVUiO-66 25%-I, and simulated UiO-66 0%-I

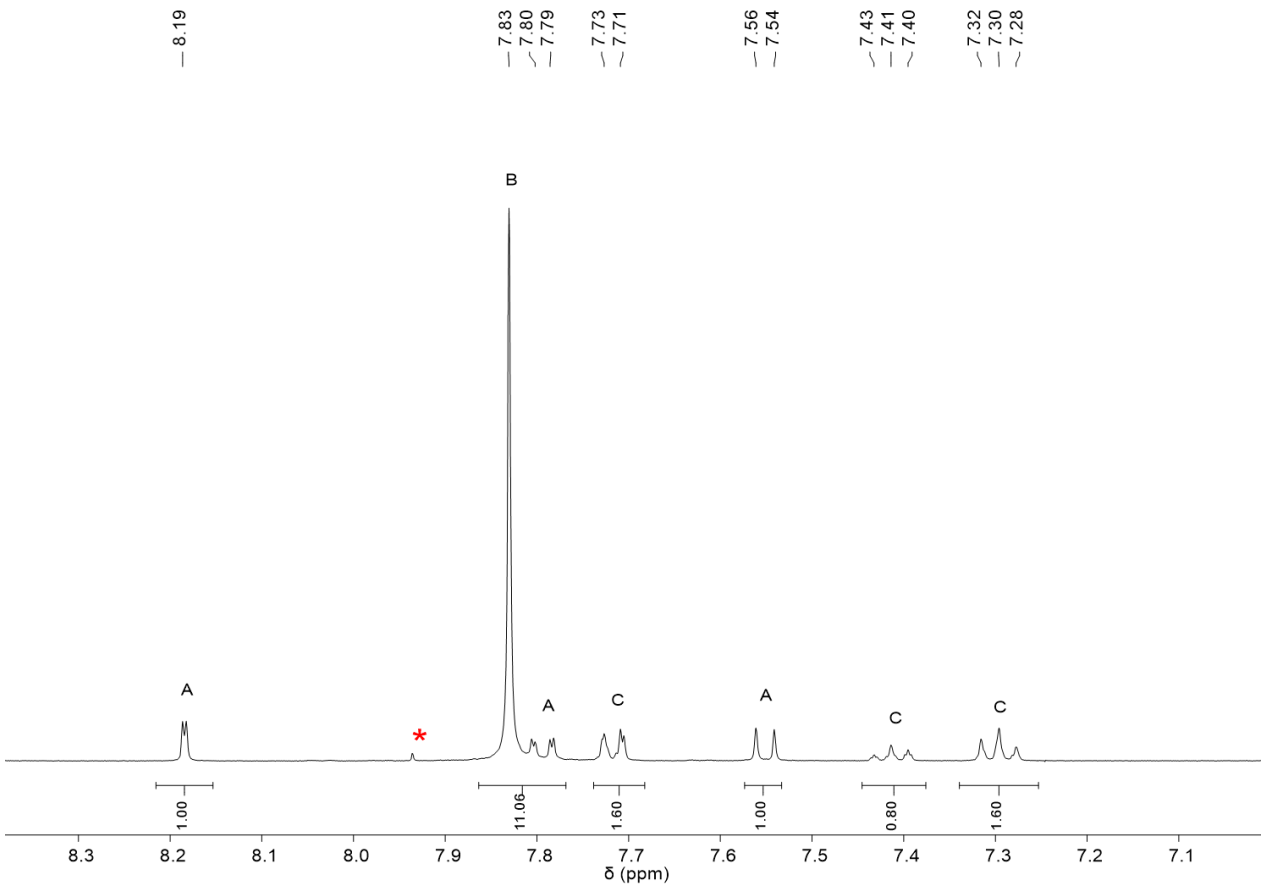

Figure S31. ^{1}H NMR spectrum for digested treated MTV-UiO-66 25%-I with benzoic acid in 500 µL $(CD_3)_2SO$ and 100 µL D_2SO_4. A: H_2I-BDC, B: H_2BDC, and C: $HO_2CC_6H_5$. Star denotes DMF.

S6.2 Test of catalytic activity of surface modified MOF

Methylsulfonylmethane (0.3400 g, 3.612 mmol) as an internal standard and 0.3975 g (3.610 mmol) of hydroquinone (HQ) were dissolved in nitromethane to a final volume of 25.0 mL. 1.0 mL was taken and added to a 2-dram clear glass vial using a 1.0 mL volumetric pipet. 20% mol of benzoic acid treated UiO-66 25%-I was loaded to the vial. 0.0999 g (70-75%, ~0.419 mmol, ~2.9 equivalent) meta-chloroperbenzoic acid (mCPBA) was dissolved in 3.0 mL of nitromethane and added to the reaction mixture. The reaction mixture was stirred in a closed cap vial at 50 °C. After 60 minutes, the catalyst was separated by centrifugation and 3 drops of the reaction mixture were dissolved in 0.5 mL of DMSO-d_6 to determine the catalytic conversion and yield.

S7 Computational Details and Results

Calculations were performed using the ORCA 3.0.3 quantum chemistry program package from the development team at the Max Planck Institute for Bioinorganic Chemistry.[15] The LDA and GGA functionals employed were those of Perdew and Wang (PW-LDA, PW91).[16] In addition, all calculations were carried out using the Zero-Order Regular Approximation (ZORA).[17,18] For all calculations the def2-TZV(pp) basis sets were used for all atoms.[19,20] Spin-restricted Kohn-Sham determinants were chosen to describe the closed shell wavefunctions, employing the RI approximation and the tight SCF convergence criteria provided by ORCA. Analytical frequencies calculations were performed on optimized structures to provide an estimate of the C–I stretching frequency. (Table S23)

Table S23. DFT calculated C–I stretching frequencies

Molecule	ν_{C-I} **(cm^{-1})**
iodobenzene	260
Me_2IBDC	205

Estimates of XPS chemical shift differences were determined by comparing orbital energies of the occupied core orbitals in the optimized geometries. (Table S24)

Table S24. DFT calculated core orbital energies (eV).

Molecule	**I $3d_{5/2}$**	**$\Delta E(I^{III}–I^{I})$**
iodobenzene	−606.26	-
Me_2IBDC	−606.40	-
$((AcO)_2I)C_6H_5$	−608.45	−2.19
$((OH)_2I)C_6H_5$	−608.12	−1.86

S7.1 DFT Minimized Cartesian Coordinates

Table S25. Cartesian coordinates for IC_6H_5 (iodobenzene).

Atom	**x**	**y**	**z**
C	1.356910	0.094285	0.022542
C	0.638252	1.280953	-0.135223
C	-0.755935	1.264496	-0.167923
C	-1.435853	0.053202	-0.042126
C	-0.730950	-1.141580	0.116265
C	0.662593	-1.108466	0.147292
I	1.741234	-2.912021	0.387440
H	2.444080	0.109757	0.048180
H	1.178717	2.221439	-0.233207
H	-1.311100	2.192728	-0.291006
H	-2.524510	0.030013	-0.066316
H	-1.263435	-2.084803	0.214081

Table S26. Cartesian coordinates for H_2IBDC.

Atom	x	y	z
C	1.380518	0.072682	-0.005548
C	0.537541	1.190904	-0.155305
C	-0.842778	1.085755	-0.141814
C	-1.429722	-0.173711	0.027881
C	-0.615953	-1.299067	0.175213
C	0.775605	-1.191205	0.158879
I	1.771151	-3.051995	0.363481
H	1.024122	2.155553	-0.282981
H	-1.465805	1.968153	-0.259759
H	-1.096696	-2.265708	0.304305
C	2.842988	0.414323	-0.044376
O	3.256417	1.532379	-0.295094
C	-2.907333	-0.382920	0.066016
O	-3.449053	-1.437375	0.336312
O	3.653179	-0.626319	0.225621
C	5.063517	-0.326938	0.191240
H	5.563655	-1.268665	0.427375
H	5.352965	0.031036	-0.802661
H	5.307777	0.441895	0.932202
O	-3.585238	0.748451	-0.252817
C	-5.020515	0.612711	-0.241719
H	-5.408994	1.595905	-0.515769
H	-5.337793	-0.146138	-0.965473
H	-5.369554	0.320297	0.754788

Table S27. Cartesian coordinates for $((AcO)_2I)C_6H_5$ ((diacetoxyiodo)benzene).

Atom	x	y	z
C	-1.672781	1.323538	-1.956854
C	-2.276920	2.405516	-2.599603
C	-2.211356	3.681545	-2.040067
C	-1.543675	3.881741	-0.831841
C	-0.941498	2.807711	-0.174129
C	-1.015271	1.543684	-0.750692
I	-0.095348	-0.106538	0.244988
H	-1.728338	0.327108	-2.388637
H	-2.796904	2.245260	-3.542749
H	-2.682096	4.522408	-2.546745
H	-1.490801	4.876408	-0.391983
H	-0.415713	2.963043	0.764890
O	1.702543	1.205621	0.025149

O	-2.188692	-0.888987	0.146652
C	2.664168	0.495719	0.568248
C	-2.102651	-2.058618	0.736209
C	4.020412	1.164324	0.551960
H	4.755062	0.523079	1.043479
H	3.965221	2.133637	1.060555
H	4.324348	1.355937	-0.483790
C	-3.397812	-2.838501	0.777892
H	-3.336299	-3.614070	1.544999
H	-3.551861	-3.317225	-0.197656
H	-4.248022	-2.174800	0.962345
O	-1.043980	-2.497472	1.200549
O	2.475858	-0.627470	1.049846

Table S28. Cartesian coordinates for $((HO)_2I)C_6H_5$ ((dihydroxyiodo)benzene).

Atom	**x**	**y**	**z**
I	2.402409	6.767402	1.008879
O	0.843189	8.172527	0.812741
O	3.908231	5.305128	1.205556
H	4.034000	5.156449	2.157667
C	1.361906	3.874773	0.939743
C	0.923766	5.187810	1.015880
C	0.398336	2.862124	0.941243
H	0.718374	1.823181	0.874970
C	-1.361854	4.510190	1.102298
H	-2.419418	4.761165	1.171539
C	-0.415079	5.538531	1.095838
C	-0.958190	3.177119	1.023704
H	-1.702277	2.382097	1.026757
H	0.680311	8.282037	-0.139051
H	-0.701187	6.588004	1.152612
H	2.427734	3.658272	0.879705

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