Supporting Information for

Robust, Sustainable Synthesis of Al-Based MOFs From Waste Aluminum

M.C. Lawrence, R.S. Horne, M.L. Reid-Hall, B.A. Blight*,
University of New Brunswick, Fredericton, NB, Canada

Table of Contents

Instrumentation

Powder X-Ray diffraction patterns were collected on a Malvern P'Analytical Empyrean Powder X-Ray diffractometer equipped with a copper radiation source. N_2 gas adsorption was measured on a Micrometrics Tristar II Plus at 77 K. Samples were activated on a Micrometrics SmartVac prep. Smaples were activated under vacuum at 150 ˚C for 1 or 10 hours. NMR spectra were collected on a Bruker AVANCE NEO 400 MHz at room temperature. Scanning electron microscopy images were collected on a JEOL 2011 STEM microscope from the University of New Brunswicks Microscopy and Microanalysis facility. TGA were measured on a Rigaku STA8122 from C-therm Technologies Ltd. under air with a flow rate of 100 mL/min and heating at 10 degrees/min. Nuclear magnetic resonance was preformed on a Bruker Avance NEO 400 at 25 ˚C, using the quantitative ERERIC program and water as an internal standard. Samples were dissolved in 3 drops of D_2SO_4 and 0.7 mL of DMSO-H6.

Synthesis

AlFum (H_2O, DMF)

In a 50 mL round bottom flask equipped with a stir bar, 162 mg (1.0 mmol) of aluminum formate, 145 mg fumaric acid (1.25 mmol) and 6 mL H_2O or DMF were combined and stirred. This mixture was heated to a reflux at 100 ˚C in H_2O or 120 ˚C in DMF for 96 hours. The resulting white powder was collected in a centrifuge tube and washed thoroughly with DMF, water and EtOH subsequentially. The synthesized AlFum was dried at 90 ˚C prior to activation and analysis.[1] 97.9 mg of white powder was isolated after drying.

MOF-303

In an 8-dram vial, 240 mg (1.0 mmol, 1 eq.) of aluminum formate, 258 mg 1-*H*-pyrazole-3,5-dicarboxylic acid (1.25 mmol, 1.25 eq.), 0.4 mL 1M NaOH, and 4.6 mL H_2O were combined and stirred. This mixture was placed in an oven and heated at 100 ˚C for 24 hours. The resulting white powder was collected in a centrifuge tube and washed thoroughly with water and EtOH subsequentially. The synthesized MOF-303 was dried at 90 ˚C prior to activation and analysis.[2] 201.6 mg of white powder was isolated after drying.

CAU-10

The CAU-10s were made in a similar fashion to already published procedures. In a 4-dram glass vial ALF, the organic ligand (Figure S1), DMF and water were combined and heated at 100 ˚C overnight. The samples were cooled to room temperature, and the resulting white powder was transferred to a 15 mL centrifuge tube, centrifuged at 4000 rpm for 5 minuets, the solvent decanted, and the resulting white powder was resuspended in DMF and centrifuged at 4000 rpm for 5 minuets. This was repeated 3 times and then the DMF was replaced with ethanol, and the process was repeated 3 times, and the samples were placed in an oven and dried at 100 ˚C.[3]

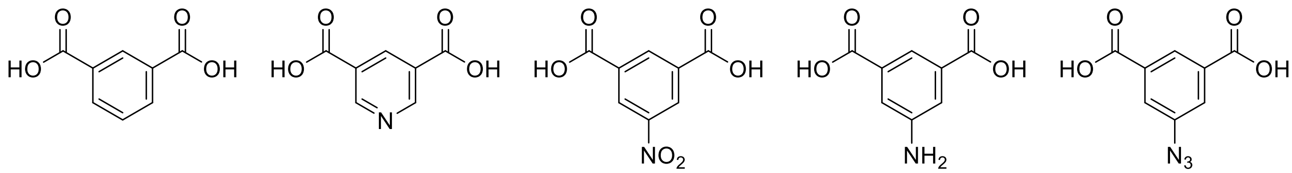
Table S1: Reaction conditions for the synthesis of CAU-10-X MOFs

	ALF (mg)	Ligand (mg)	DMF (mL)	H_2O (mL)	Isolated Mass (mg)
CAU-10	98 (0.605 mmol)	99 (0.596 mmol)	1	4	43.3
CAU-10-py	98 (0.605 mmol)	100 (0.593 mmol)	1	4	37.1
CAU-10-NO_2	99 (0.611) mmol)	146 (0.692 mmol)	1	4	57.6
CAU-10-NH_2	98 (0.605 mmol)	110 (0.608 mmol)	1	4	71.0
CAU-10-N_3	98 (0.605 mmol)	125 (0.605 mmol)	1	4	27.4

* CAU-10-NH_2 required the addition of 0.5 mL of 1M NaOH

Supporting Information for

Robust, Sustainable Synthesis of Al-Based MOFs From Waste Aluminum



CAU-10 CAU-10-py CAU-1-NO_2 (L1) CAU-10-NH_2 CAU-10-N_3 (L2)

Figure S1: Ligands for CAU-10-X MOF synthesis

Synthesis of CAU-10-R ligands:

3-Nitroisophthalic acid (L1):

In a 50 mL RBF, 1.093 g (6.58 mmol, 1.0 eq.) isophthalic acid was dissolved in 15 mL concentrated H_2SO_4. To this solution, 1.0 mL concentrated HNO_3 was added dropwise with strong stirring. The RBF was then fitted with a reflux condenser and the solution was heated at 80 ˚C for 3 hours. After this period of time, the reaction contents were cooled and then poured over ice. The product was collected via vacuum filtration as a white solid and dried in air at 50 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.78 (s, 2H), 8.75 (s, 1H).[4]

3-Azoisophthalic acid (L2):

To a 100 mL RBF 1.000 g (5.52 mmol, 1.0 eq.) 5-aminoisophthalic acid was added followed by 10 mL H_2O, 2 mL concentrated HCl (12 M), and a stir bar then the reaction vessel chilled to 0 ˚C in an ice bath. A solution containing 0.469 g (5.52 mmol, 1.0 eq.) $NaNO_3$ in 5 mL of H_2O was then added with strong stirring at 0 ˚C and left to stir for 30 minutes under N_2. After stirring, a solution of 0.359 g (5.52 mmol, 1.0 eq.) NaN_3 in 2.5 mL H_2O was then added dropwise to the solution, ensuring the temperature remained constant at 0 ˚C. This mixture was allowed to stir for 30 minutes. The product was collected as an off-white solid by vacuum filtration and dried in air at 50 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 (s, 1H), 7.38 (s, 2H).[5]

CAU-15

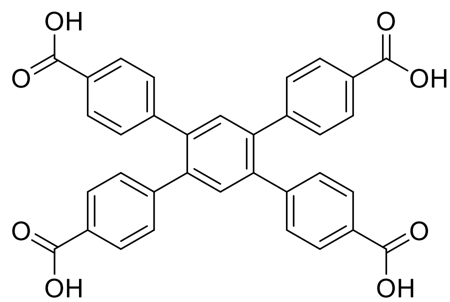
In a 4-dram glass vial 98 mg of ALF (0.605 mmol) and 99 mg of phthalic acid (0.596 mmol) were combined and 1 mL of DMF and 4 mL of water was added, the sample sonicated for 3 minutes and placed in a 100 ˚C oven overnight. The samples were cooled to room temperature, and the resulting white powder was transferred to a 15 mL centrifuge tube, centrifuged at 4000 rpm for 5 minuets, the solvent decanted, and the resulting white powder was resuspended in DMF and centrifuged at 4000 rpm for 5 minuets. This was repeated 3 times and then the DMF was replaced with ethanol, and the process was repeated 3 times, and the samples were placed in an oven and dried at 100 ˚C.[6] 45.4 mg of white powder was isolated after drying

CAU-21

In a 4-Dram glass vial 107 mg of ALF (0.660 mmol) and 175 mg of benzophenone-4,4'-dicarboxylic acid (0.684 mmol) were combined, and 0.75 mL of DMF, 0.5 mL of water, and 25 mg of benzoic acid (0.205 mmol) was added. The resulting solution was sonicated for 5 minuets. The resulting solution was placed in the oven at 100 ˚C overnight. The sample was cooled to room temperature, and the resulting powder was transferred to a 15 mL centrifuge tube, centrifuged at 4000 rpm for 5 minuets, the solvent decanted, and the resulting white powder was resuspended in DMF and centrifuged at 4000 rpm for 5 minuets. This was repeated 3 times and then the DMF was replaced with ethanol, and the process was repeated 3 times, and the samples were placed in an oven and dried at 100 ˚C.[7] 83.2 mg of white powder was isolated after drying.

CAU-9

Synthesis of CAU-9 ligand (L3):



CAU-9 (L3)

Figure S2: Ligand for CAU-9 Synthesis

In a three-neck 250 mL RBF, 1.003 g (2.55 mmol, 1 eq.) 1,2,4,5-tetrabromobenzene, 2.460 g (13.67 mmol, 5 eq.) 4-methoxycarbonylphenyl boronic acid, 2.800 g (13.19 mmol, 5 eq.) K_3PO_4 tribasic, and 29.5 mg (0.03 mmol, 0.01 eq.) $Pd(PPh_3)_4$ were combined with a stir bar. The reaction vessel was fitted with a reflux condenser and two rubber septa before establishing an inert environment by purging under vacuum and backfilling with N_2, cycling five times. 100 mL of degassed 1,4-dioxane was then added via cannula and the reaction heated to 90 ˚C for 4 days. The reaction was cooled to room temperature, after removing volatiles, the crude mixture was extracted with DCM/H_2O and the organic layer washed with brine. After removing volatiles again, the crude mixture was dissolved in a 1:1 v/v mixture of THF:1M NaOH (total volume 100 mL) and heated to reflux overnight. The reaction mixture was then acidified with 2 M HCl and the product collected as a white precipitate by vacuum filtration and dried in air at 50 ˚C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 12.98 (s, 4H), 7.84 (d, 8H), 7.58 (s, 2H), 7.38 (d, 8H).[8]

Synthesis of CAU-9 MOF

In a 25 mL Teflon lined autoclave, 108 mg of ALF (0.667 mmol) and 100 mg of **L3** (0.179 mmol) were combined with 4 mL of DMF and 2 mL of water. The solution was sonicated for 5 minutes and placed in a 150 ˚C oven overnight. The sample was cooled to room temperature, and the resulting powder was transferred to a 15 mL centrifuge tube, centrifuged at 4000 rpm for 5 minuets, the solvent decanted, and the resulting white powder was resuspended in DMF and centrifuged at 4000 rpm for 5 minuets. This was repeated 3 times and then the DMF was replaced with ethanol, and the process was repeated 3 times, and the samples were placed in an oven and dried at 100 ˚C.[8] 23.7 mg of white-gray powder was isolated after drying.

MIL-53(Al)-TDC

In a G30 microwave tube, 100 mg (0.615 mmol, 1.0 eq.) ALF and 127 mg (0.738 mmol, 1.2 eq.) 2,5-thiophenedicarboxylic acid (TDC) were combined with 5 mL H_2O and 1 mL DMF. The solution was sonicated for 5 minutes then reacted in the microwave reactor for 21 minutes at 140 ˚C. After cooling to 55 ˚C, the reaction mixture was transferred to a 15 mL centrifuge tube, centrifuged at 4000 rpm for 5 minuets, the solvent decanted, and the resulting white powder was resuspended in DMF and centrifuged at 4000 rpm for 5 minuets. This was repeated 3 times and then the DMF was replaced with ethanol, and the process was repeated 3 times, and the samples were placed in an oven and dried at 100 ˚C.[9]

Powder X-Ray Diffraction

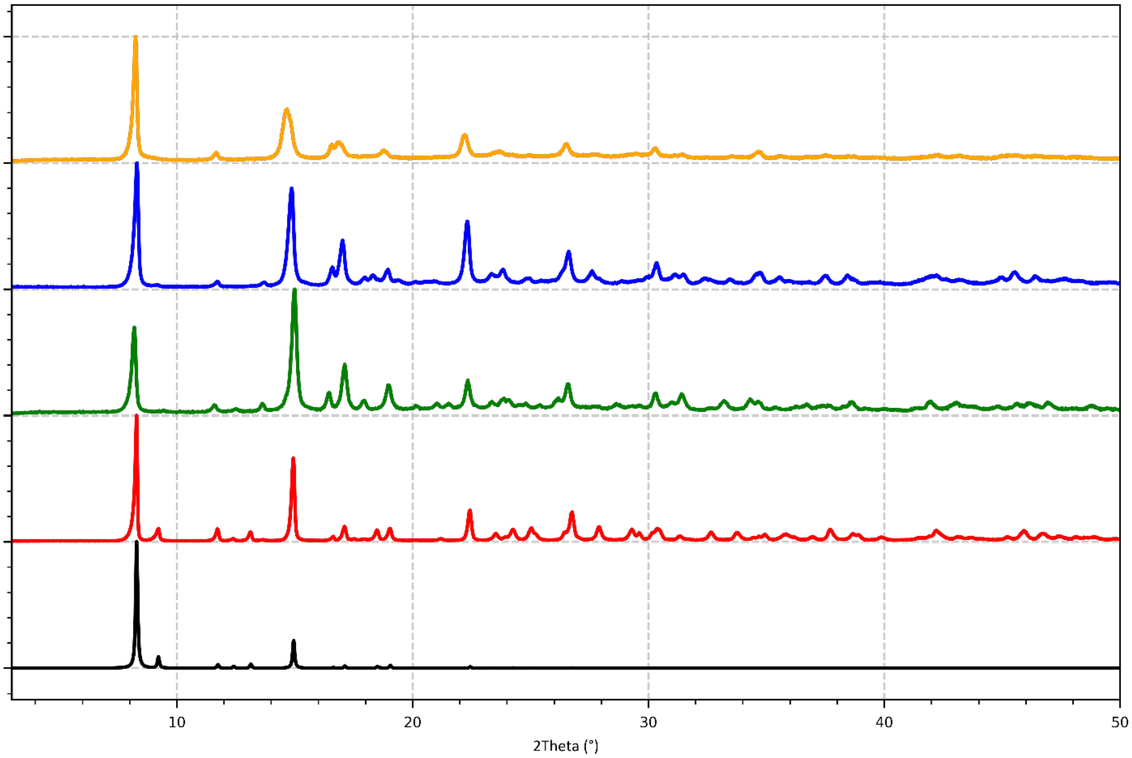


Figure S3: PXRD pattern of CAU-10's. Simulated (black trace), CAU-10 (red trace), CAU-10-NO_2 (green trace), CAU-10-NH_2 (blue trace), CAU-10-N_3 (yellow trace).

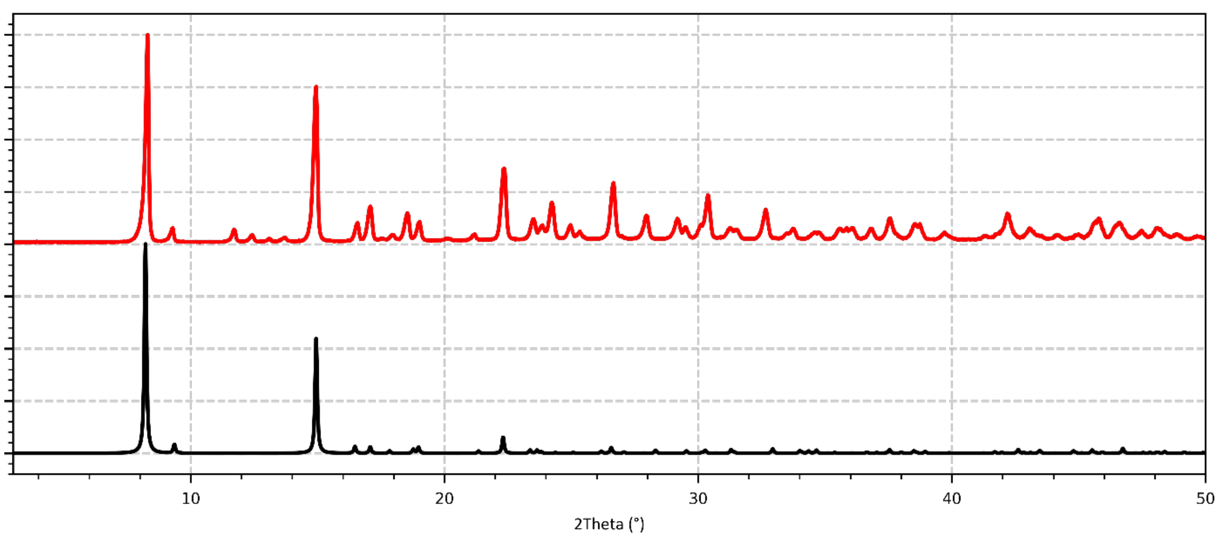


Figure S4: PXRD pattern of CAU-10-Py. Black trace simulated pattern, red trace experimental.

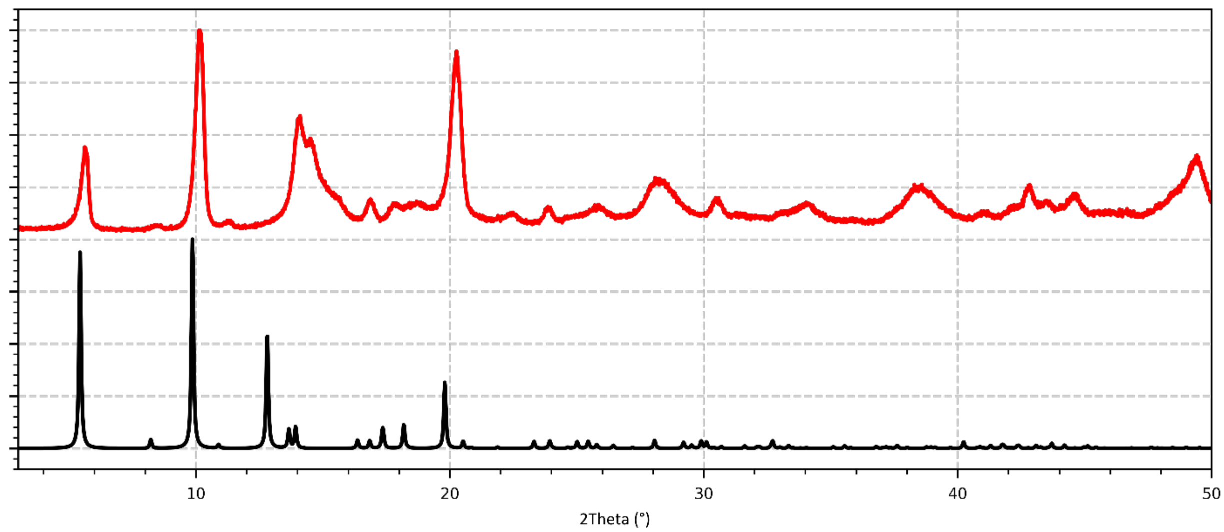


Figure S5: PXRD pattern of CAU-9. Black trace simulated pattern, red trace experimental.

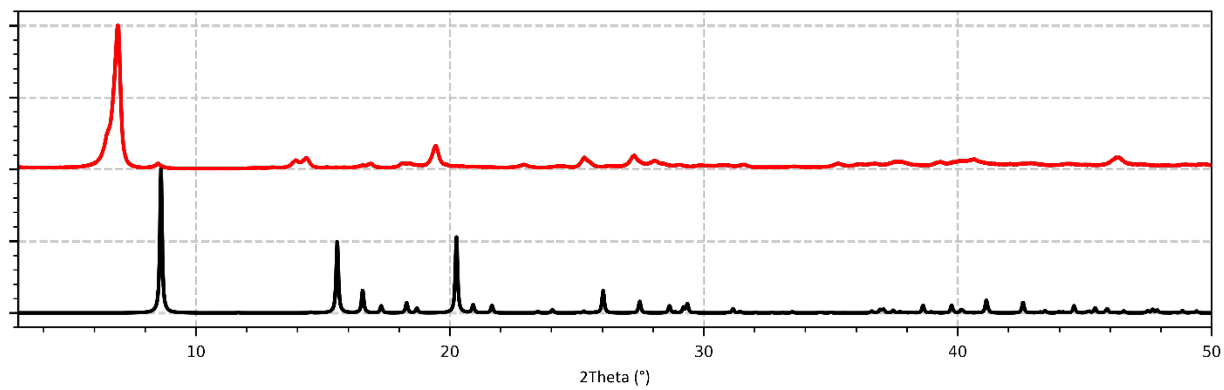


Figure S6: PXRD pattern of CAU-15. Black trace simulated pattern, red trace experimental. It should be noted that the PXRD pattern does not match that of simulated CAU-15, rather it matches that of inactivated CAU-15 found in the literature.[6]

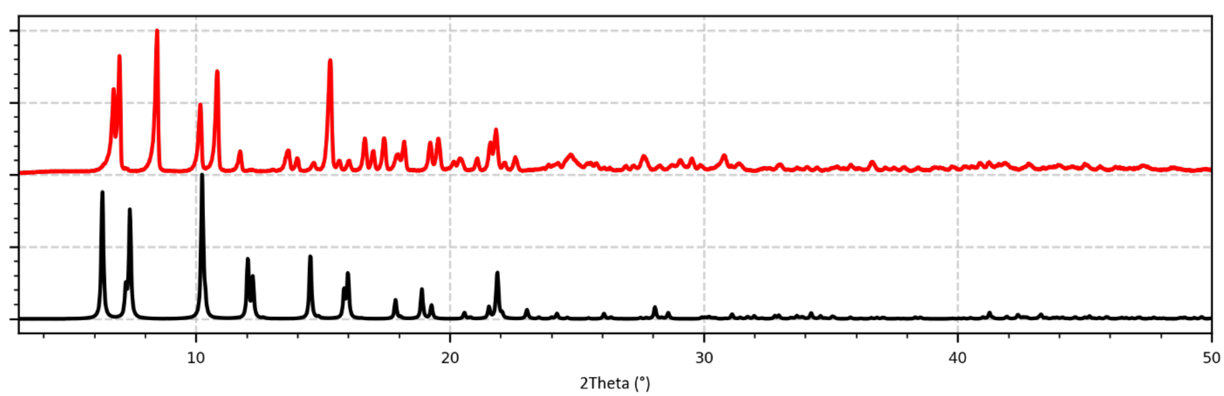


Figure S7: PXRD pattern of CAU-21. Black trace simulated pattern, red trace experimental.

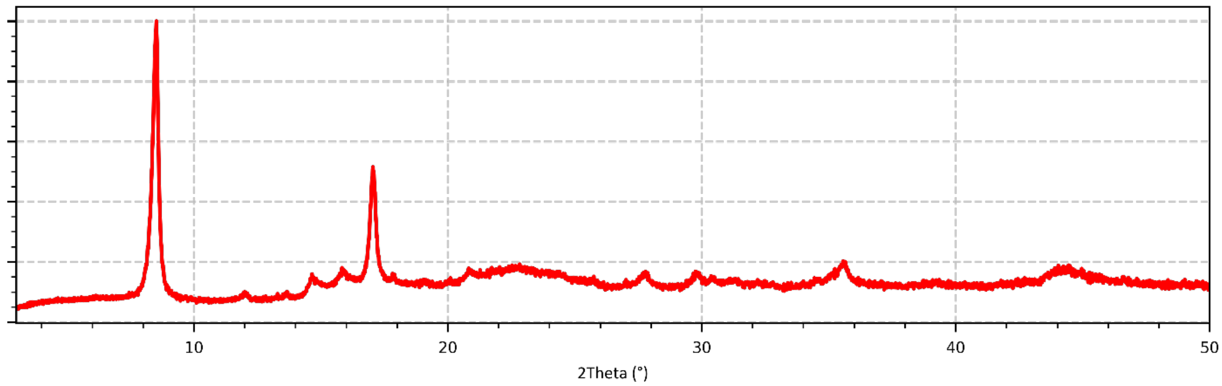


Figure S8: PXRD of MIL-53(Al)-TDC. There is no easily accessible CIF file, however this pattern matches other experimentally published diffractograms.[9,10]

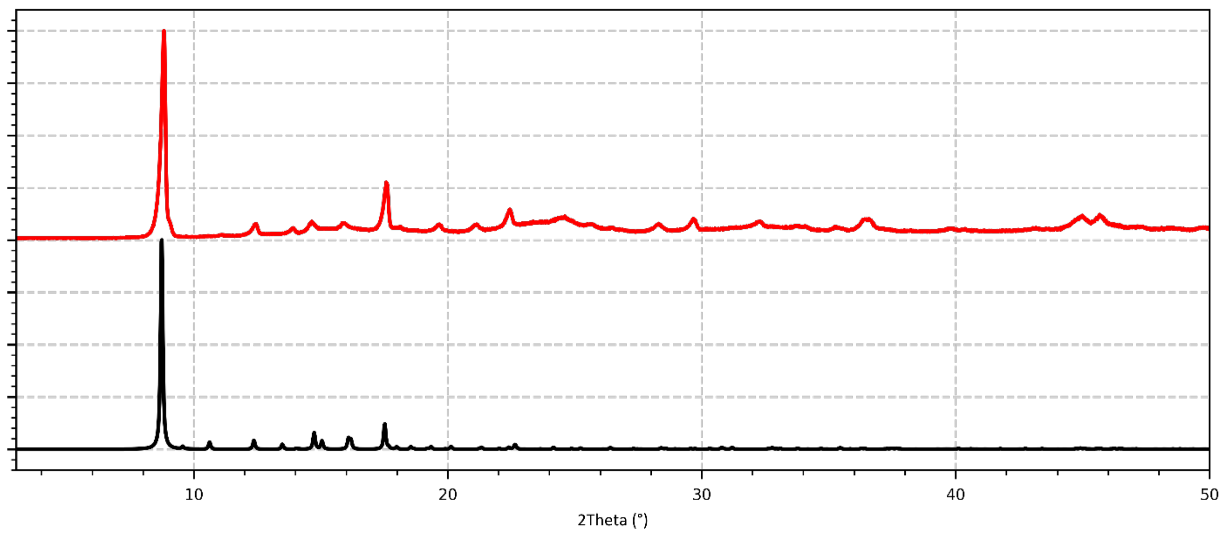


Figure S9: PXRD pattern of MOF-303. Black trace simulated pattern, red trace experimental.

N_2 Gas adsorption

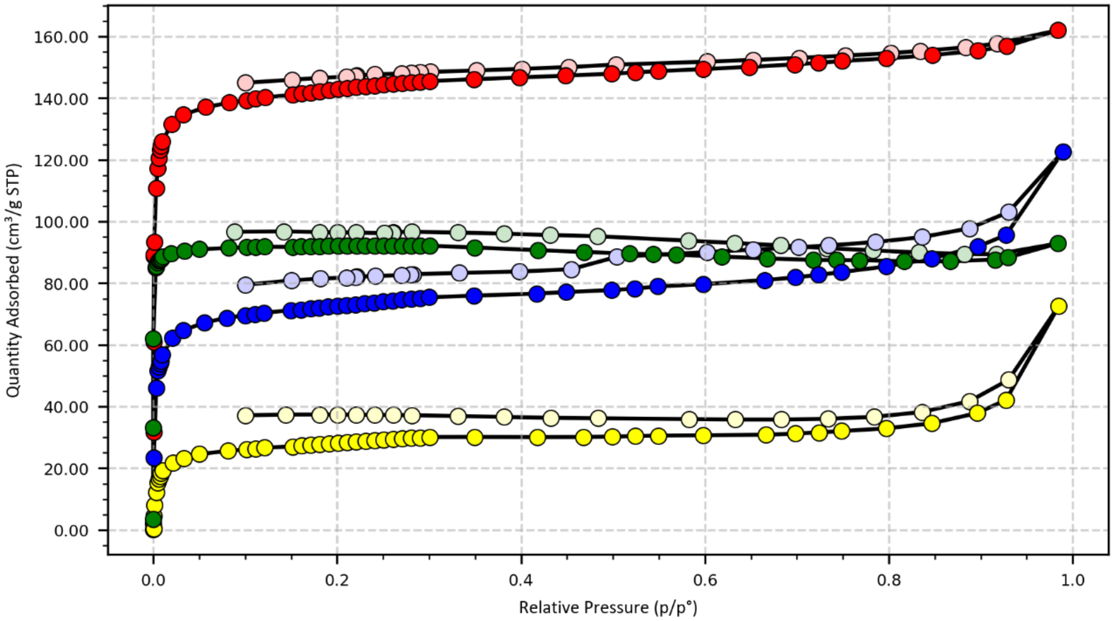


Figure S10: Nitrogen isotherms measured at 77 K for the CAU series of MOFs. CAU-10 (red), CAU-10-NH_2 (blue), CAU-10-NO_2 (green), CAU-10-N_3 (yellow).

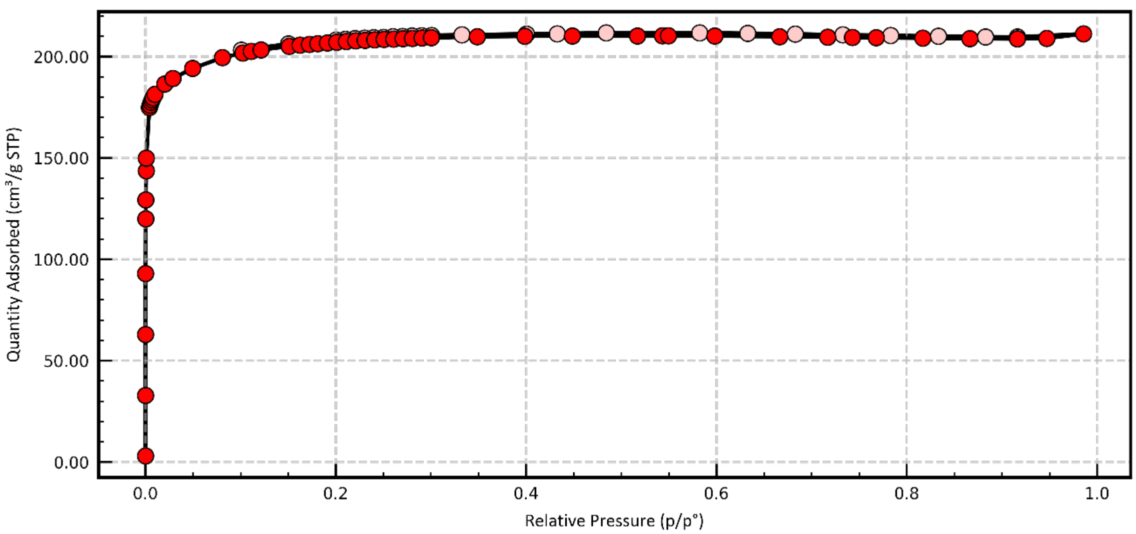


Figure S11: Nitrogen isotherms measured at 77 K for CAU-10-Py.

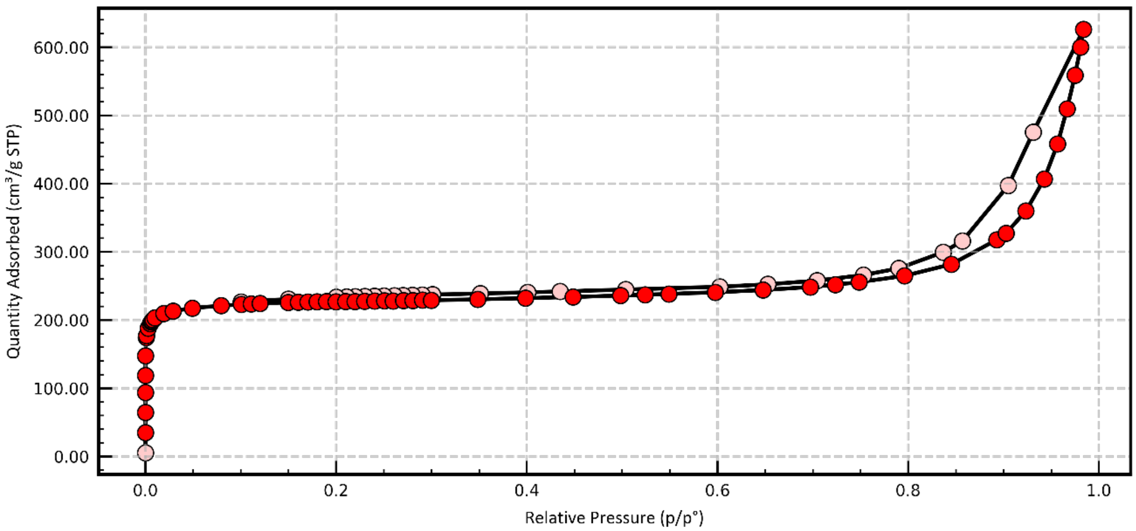


Figure S12: Nitrogen isotherms measured at 77 K for CAU-9.

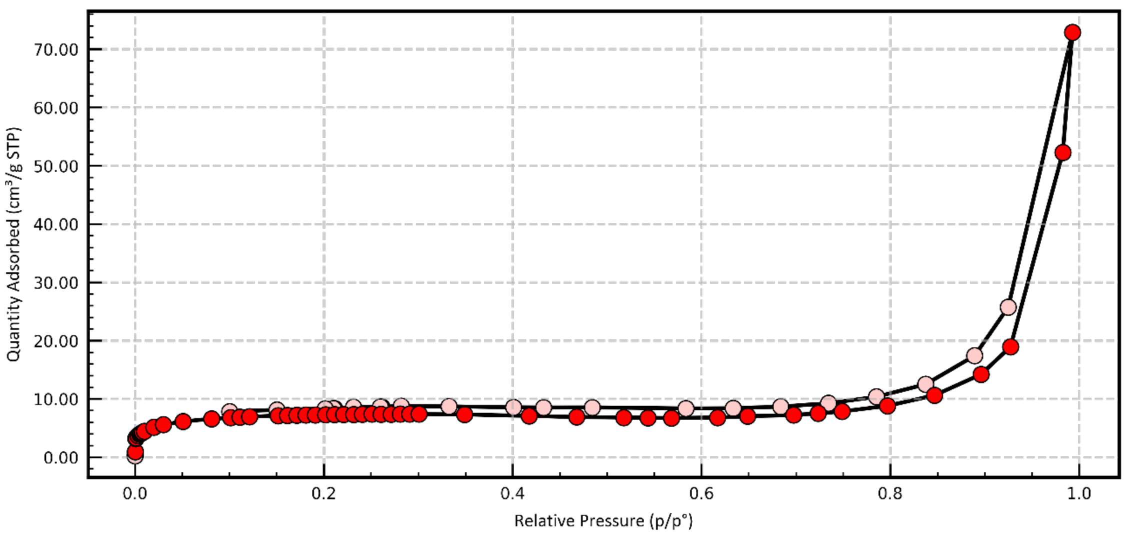


Figure S13: Nitrogen isotherms measured at 77 K for CAU-15.

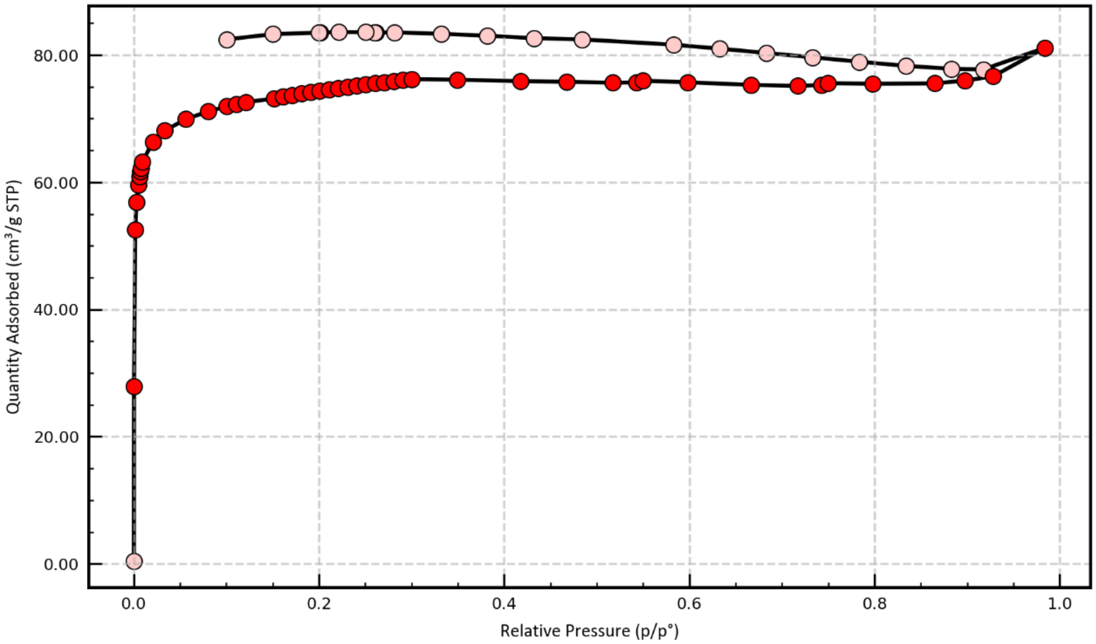


Figure S14: Nitrogen isotherms measured at 77 K for CAU-21.

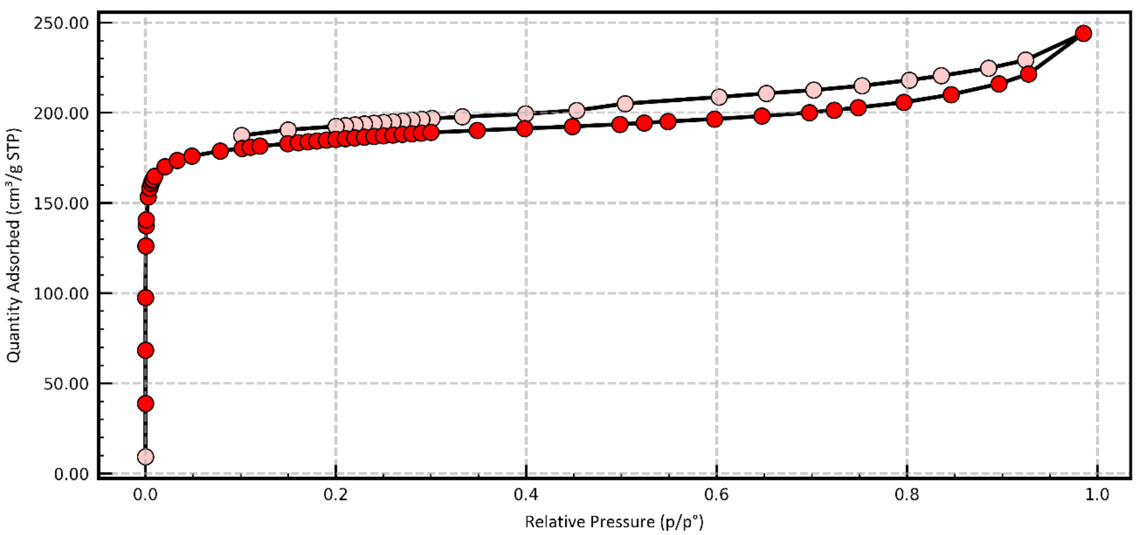


Figure S15: Nitrogen isotherms measured at 77 K for MIL-53(Al)-TDC.

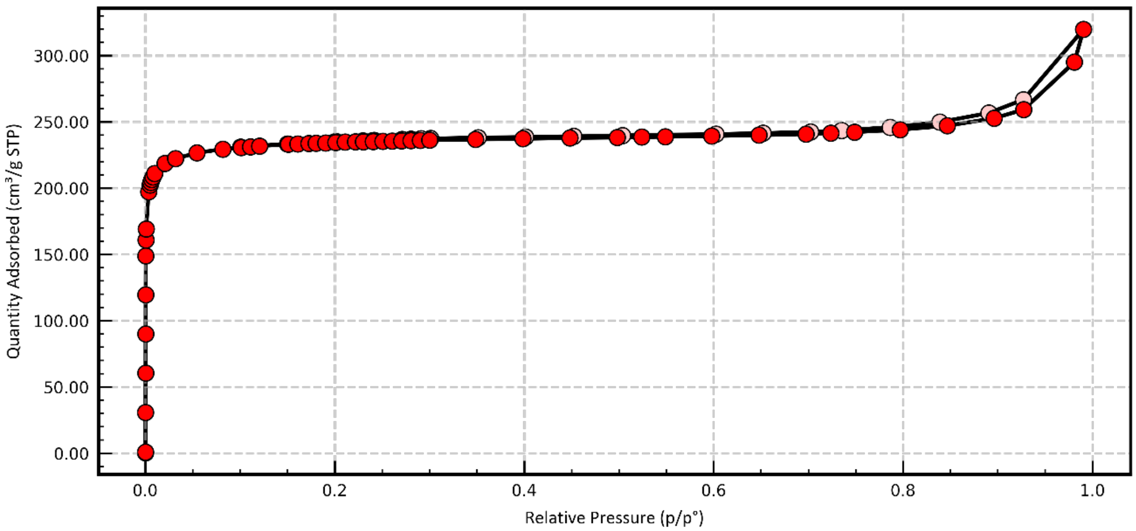


Figure S16: Nitrogen isotherms measured at 77 K for Al-Fum.

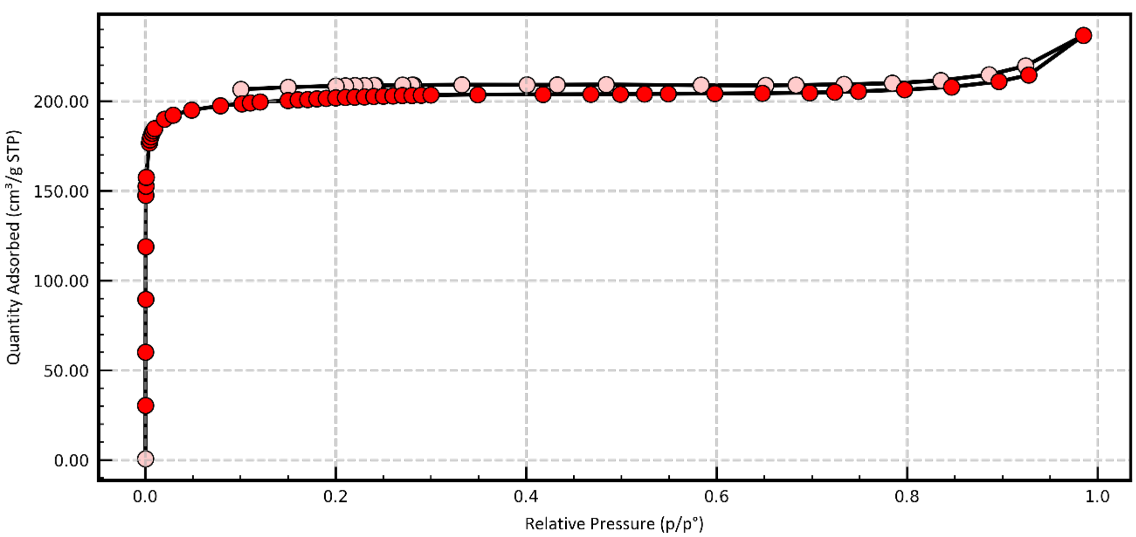


Figure S17: Nitrogen isotherms measured at 77 K for MOF-303.

Scanning Electron Microscopy

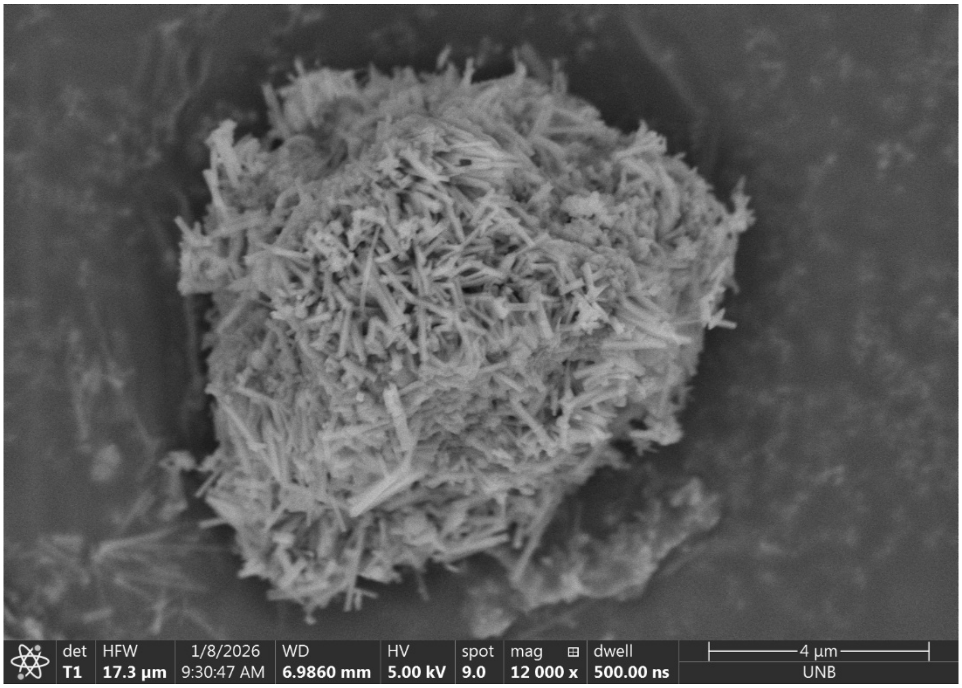


Figure S18: SEM image of MOF-303

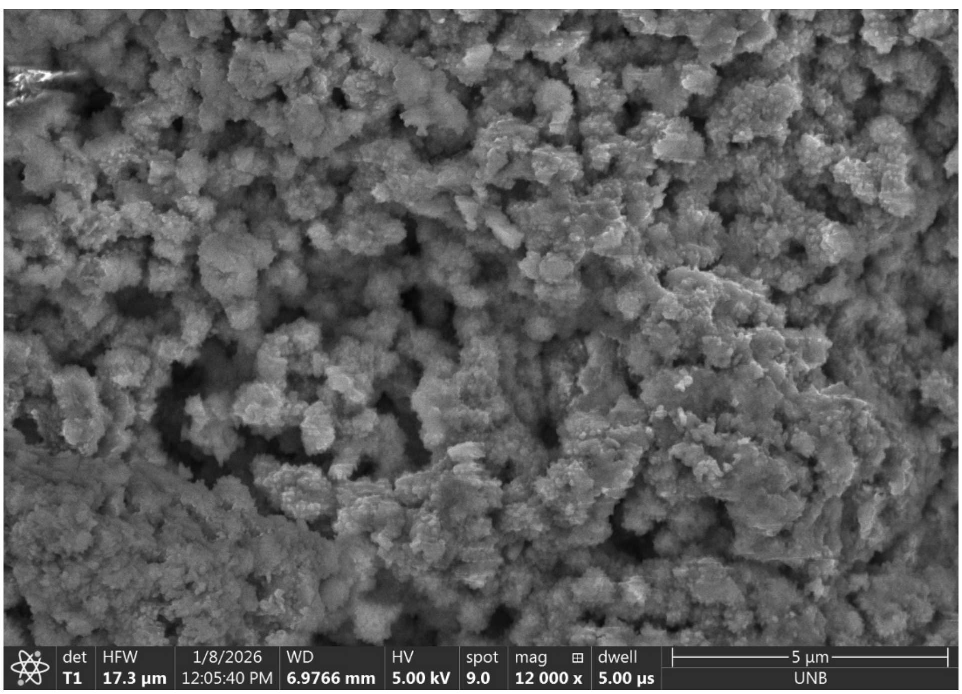


Figure S19: SEM image of Al-TDC

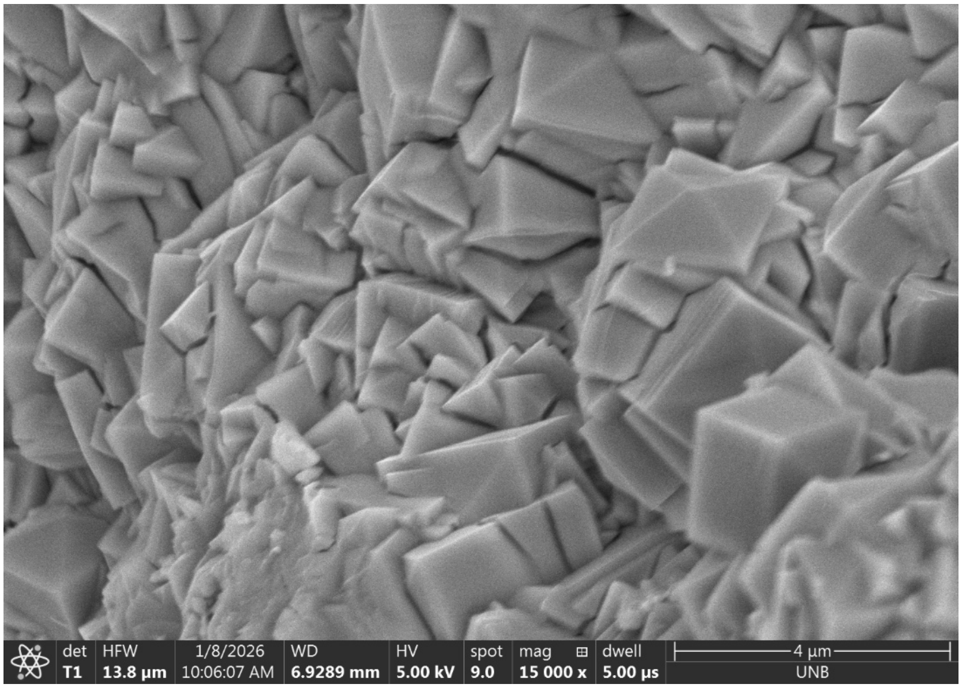


Figure S20: SEM image of CAU-10

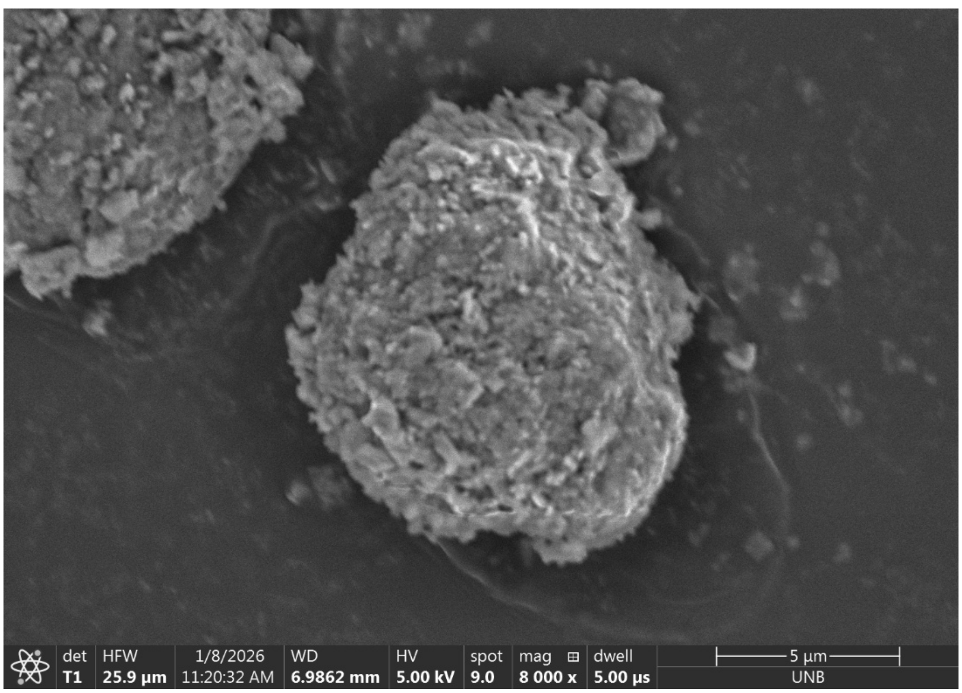


Figure S21: SEM image of CAU-10-N_3

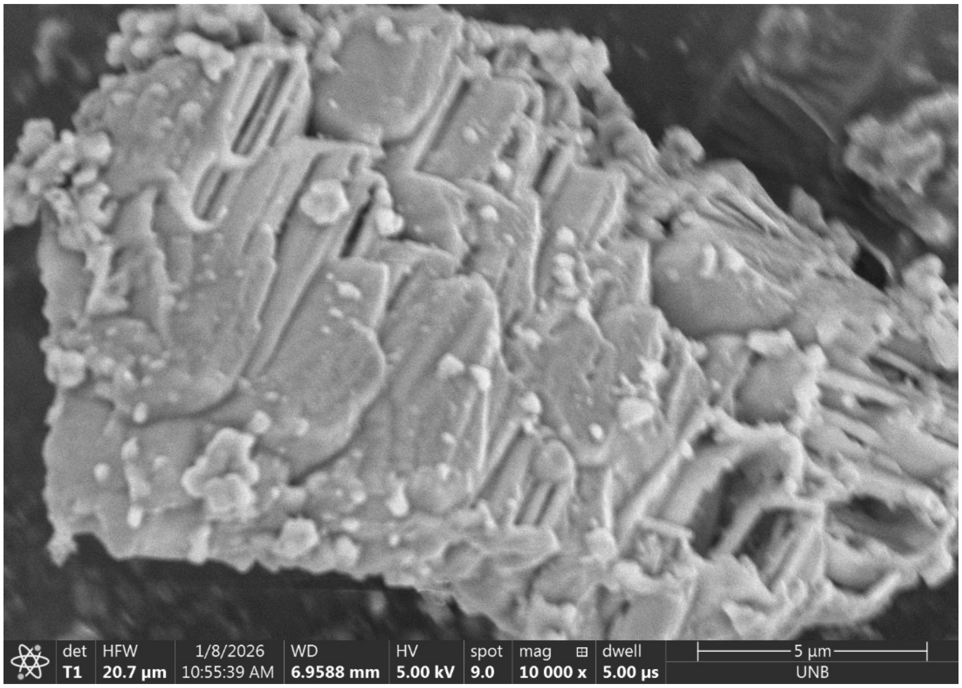


Figure S22: SEM image of CAU-10-NH_2

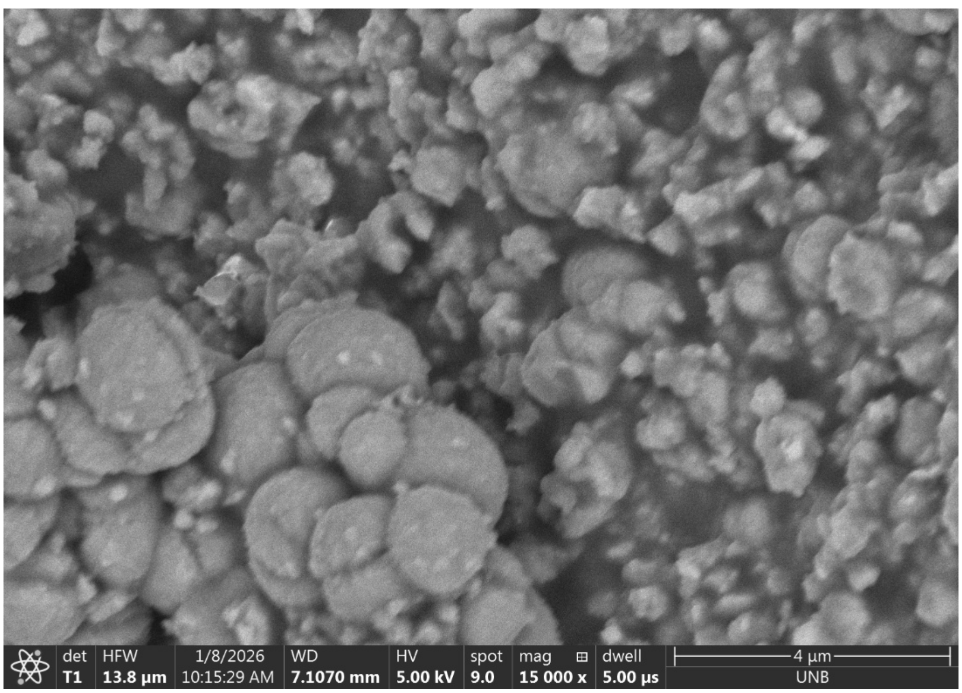


Figure S23: SEM image of CAU-10-NO_2

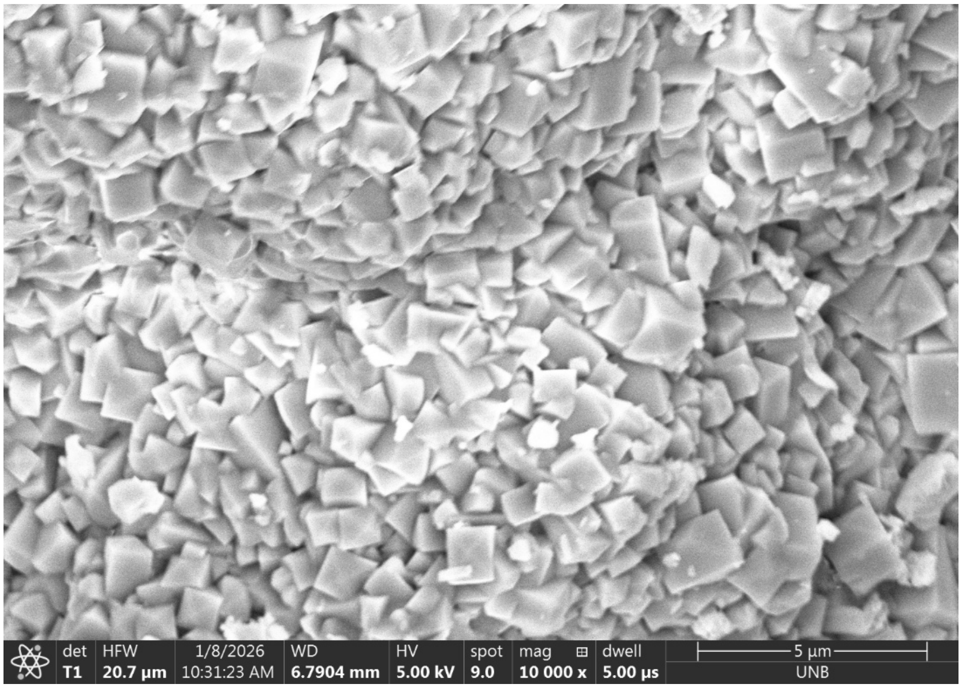


Figure S24: SEM image of CAU-10-py

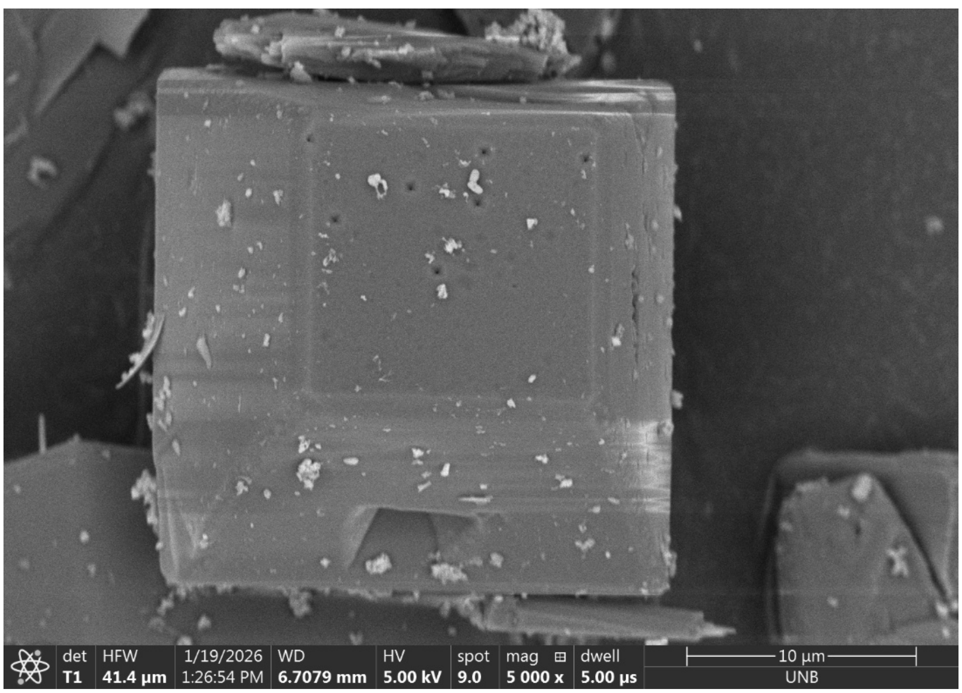


Figure S25: SEM image of CAU-21

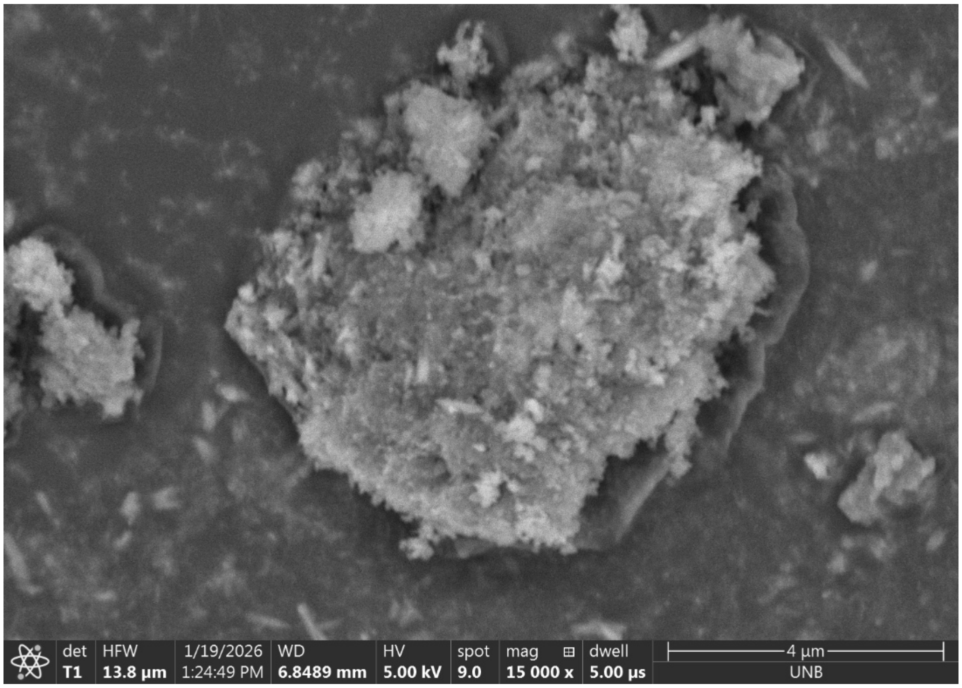


Figure S26: SEM image of CAU-9

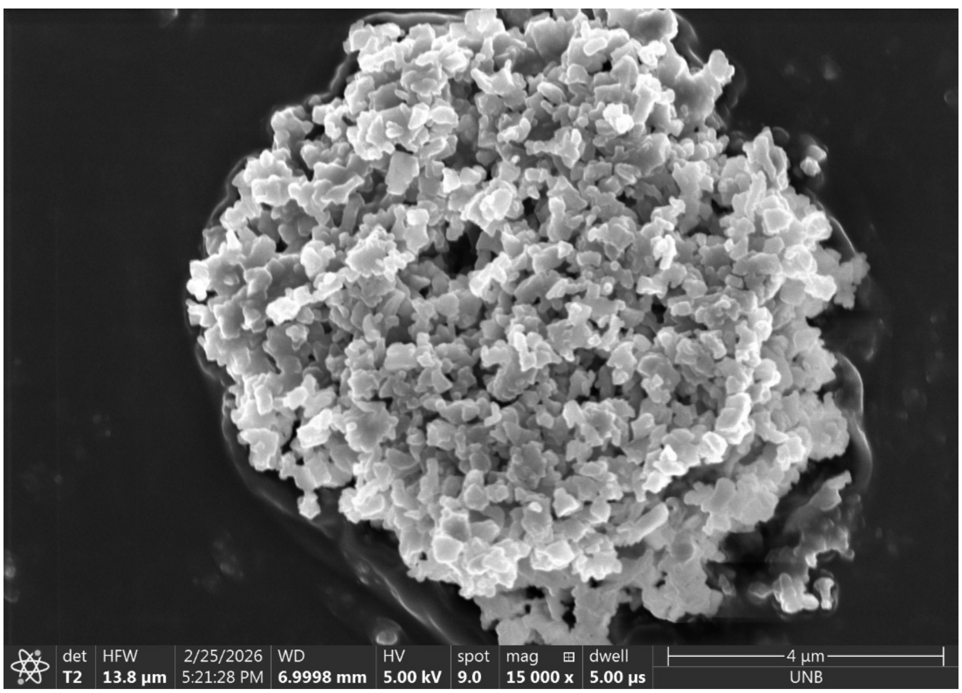


Figure S27: SEM image of Al-Fum

Thermogravimetric Analysis

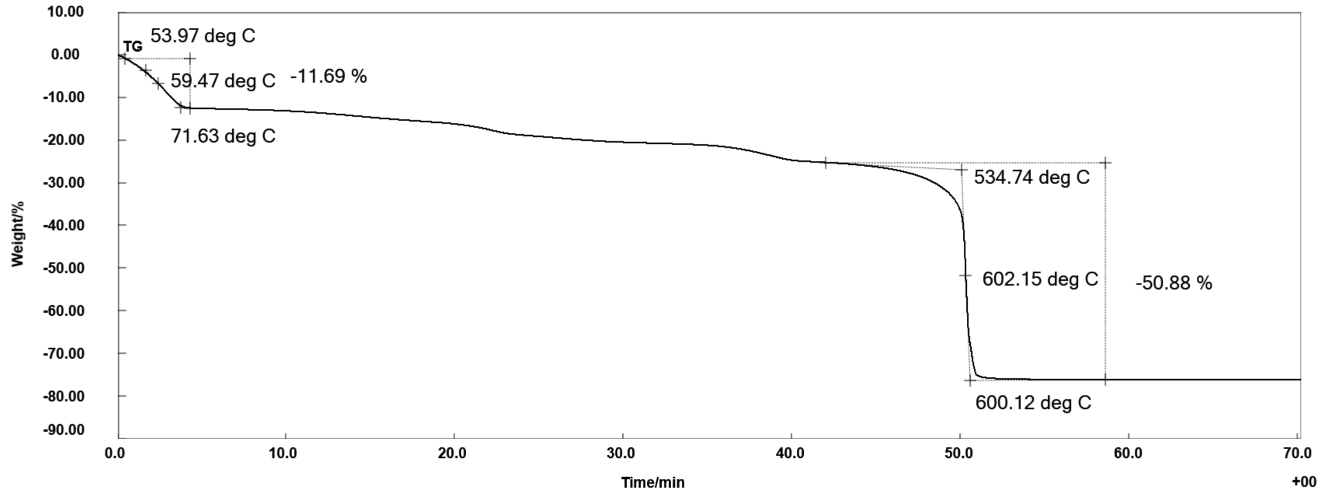


Figure S28: Thermogravimetric analysis of CAU-10

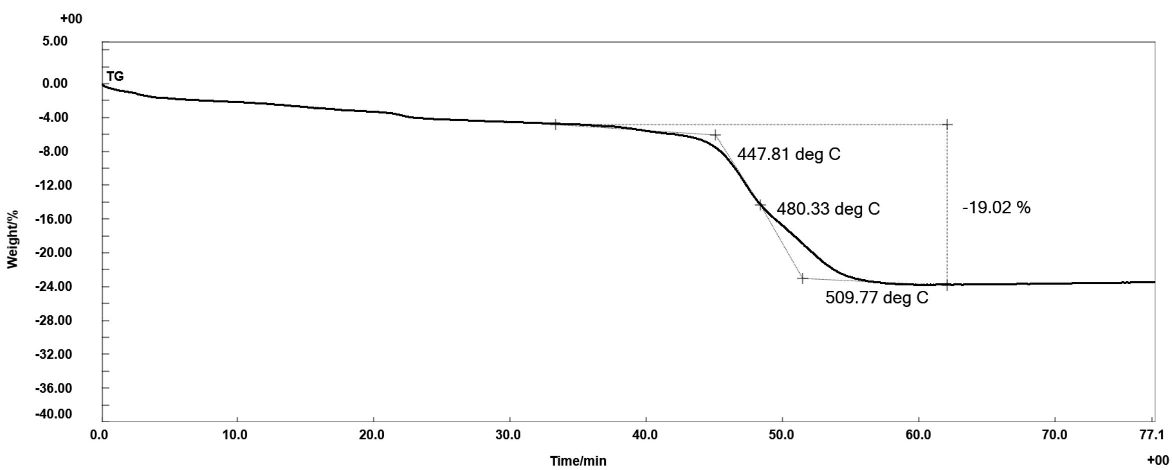


Figure S29: Thermogravimetric analysis of CAU-10-NO_2

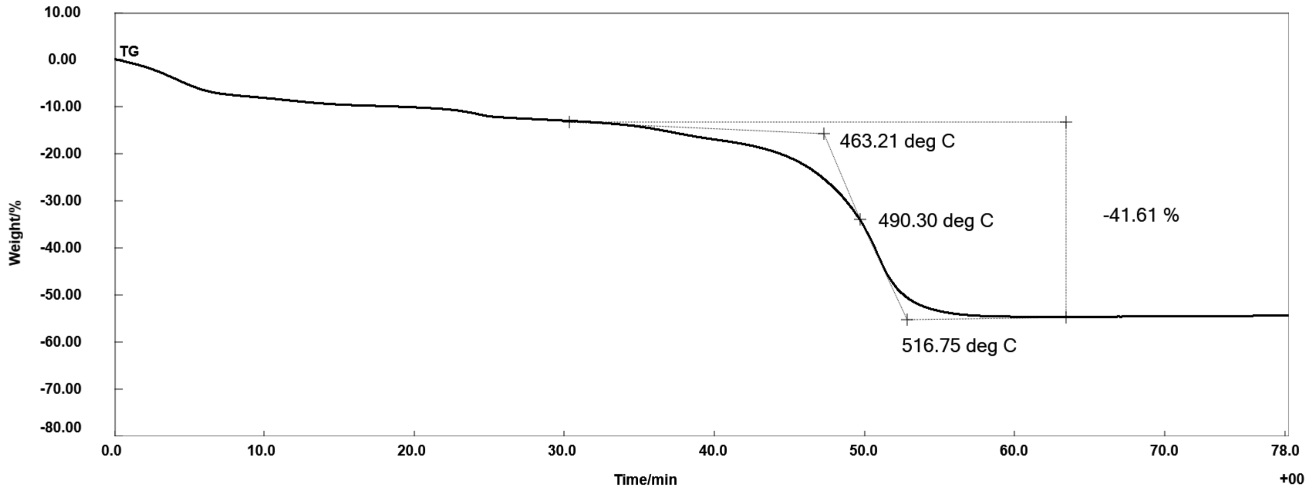


Figure S30: Thermogravimetric analysis of CAU-10-NH_2

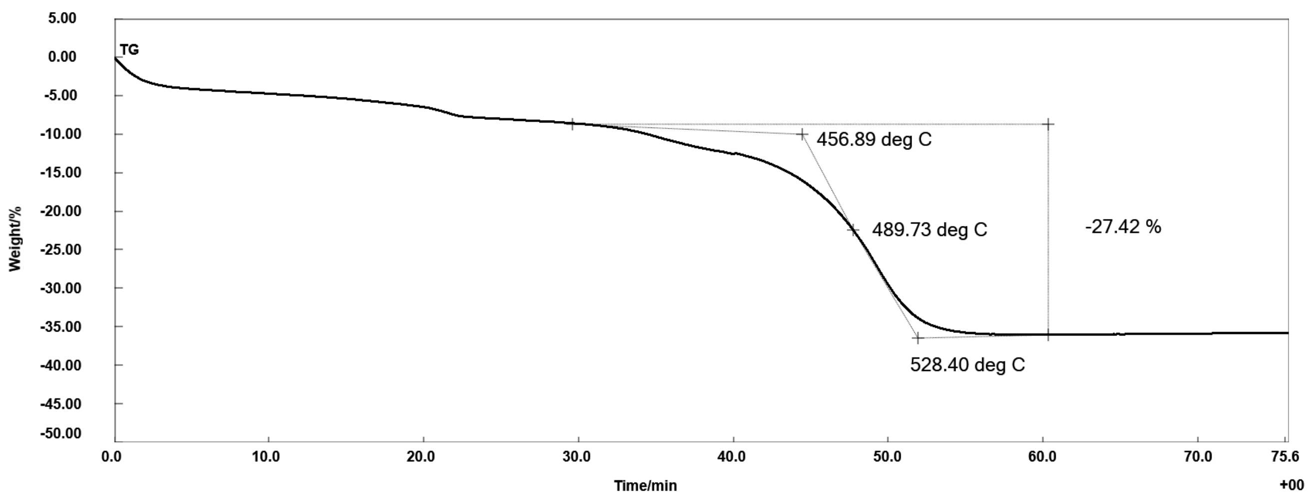


Figure S31: thermogravimetric analysis of CAU-10-N_3

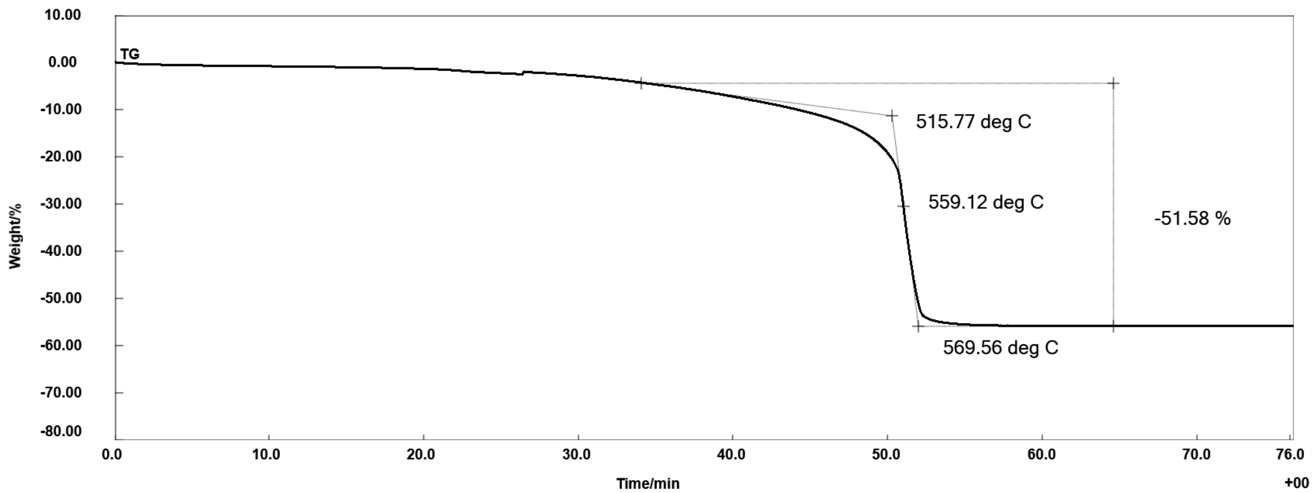


Figure S32: Thermogravimetric analysis of CAU-9

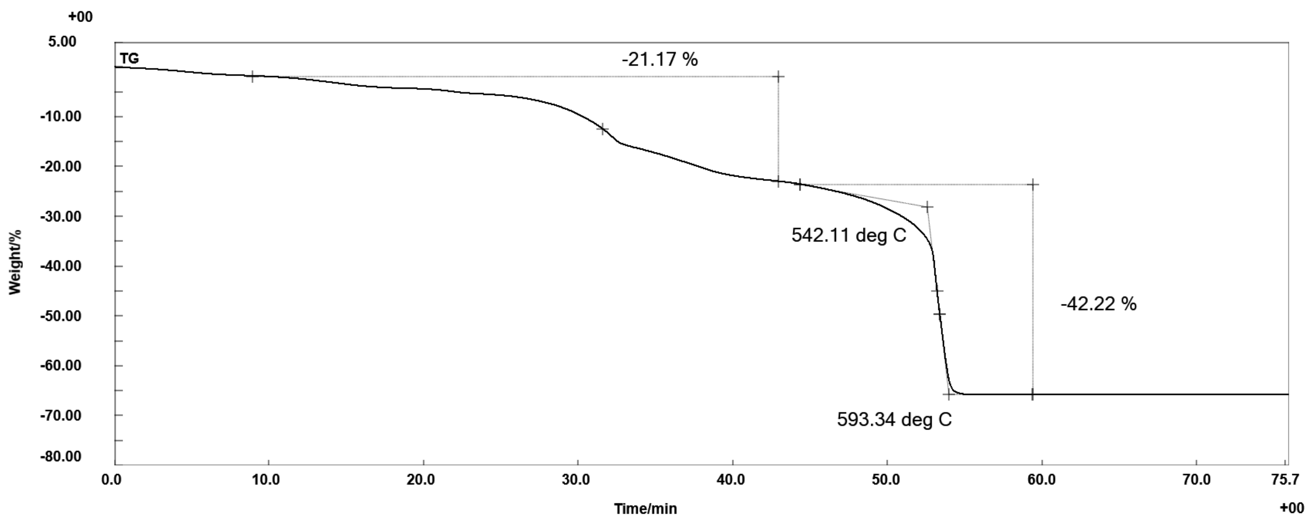


Figure S33: Thermogravimetric analysis of CAU-21

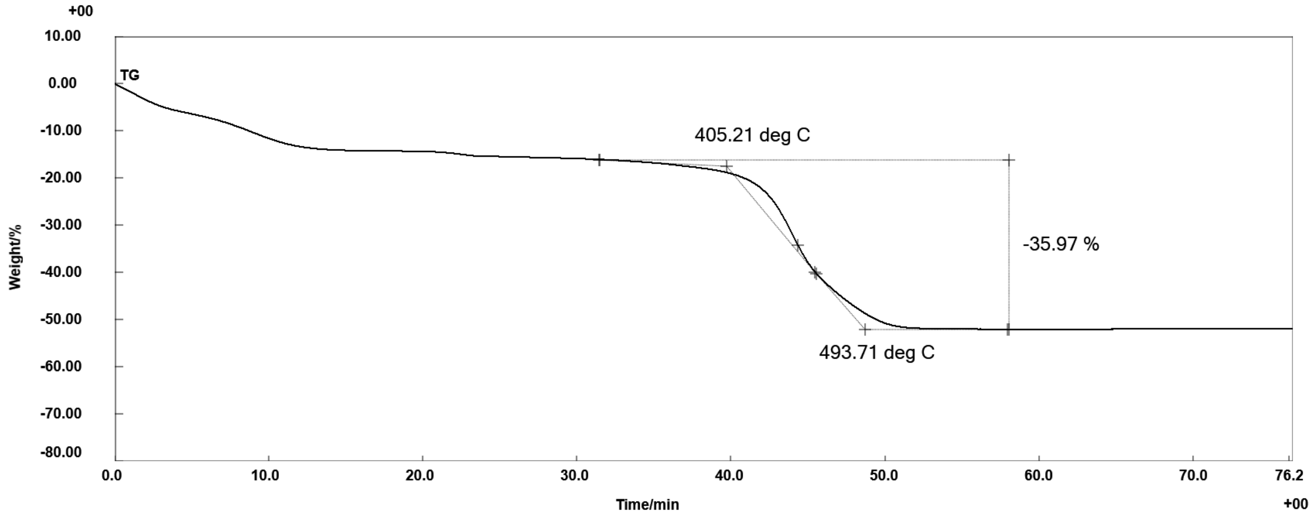


Figure S34: Thermogravimetric analysis of MOF-303

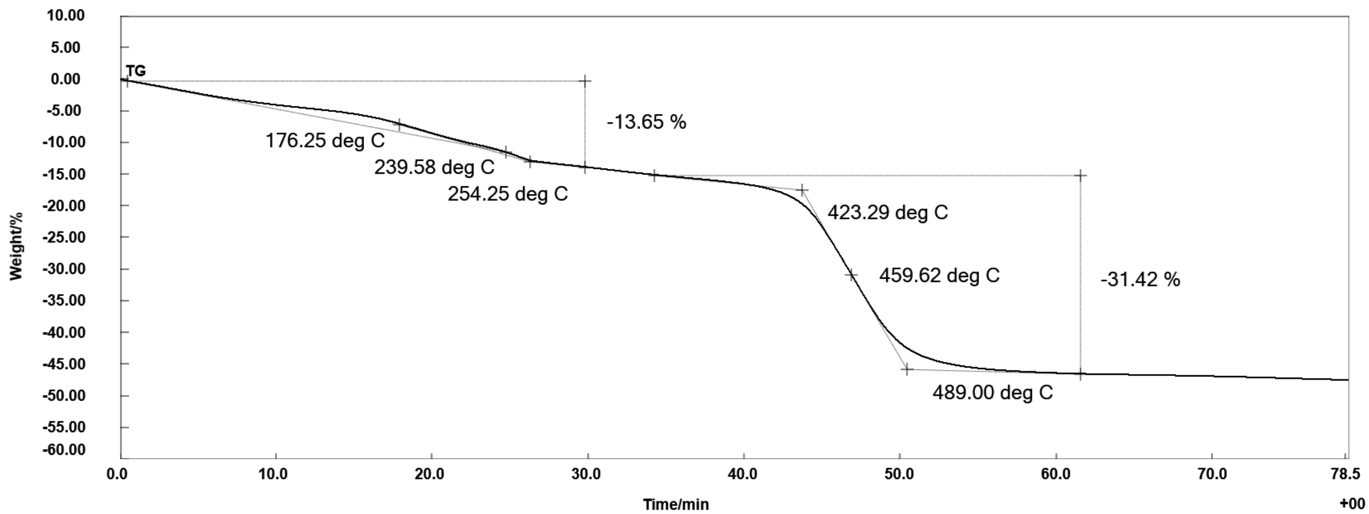


Figure S35: Thermogravimetric analysis of Al-MIL-53-TDC

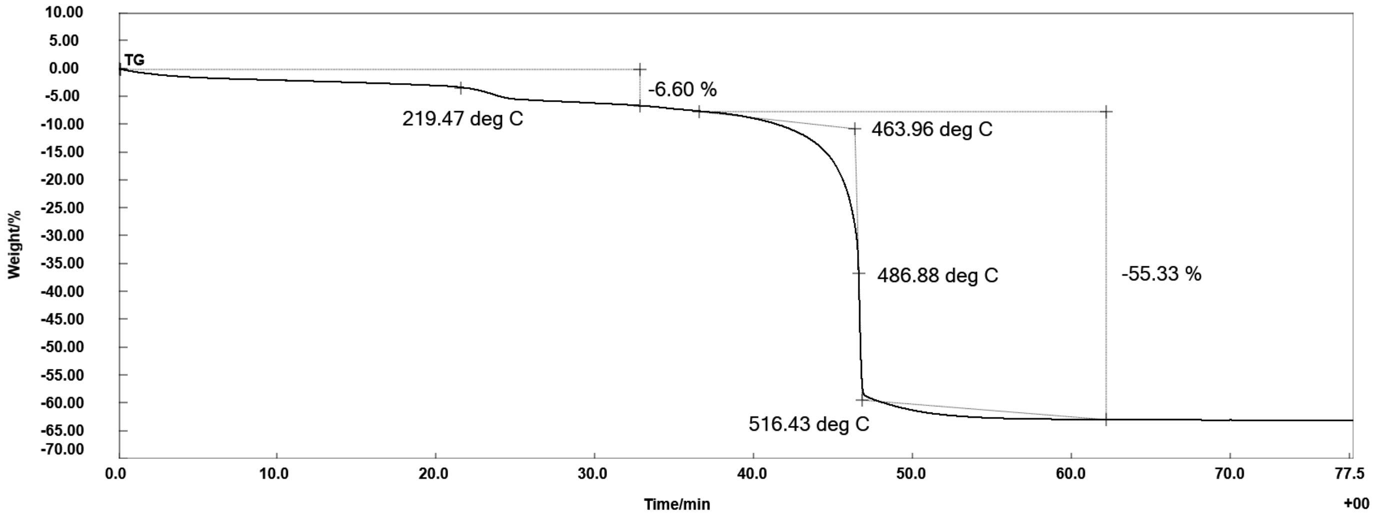


Figure S36: Thermogravimetric analysis of Al-Fum

Nuclear Magnetic Resonance

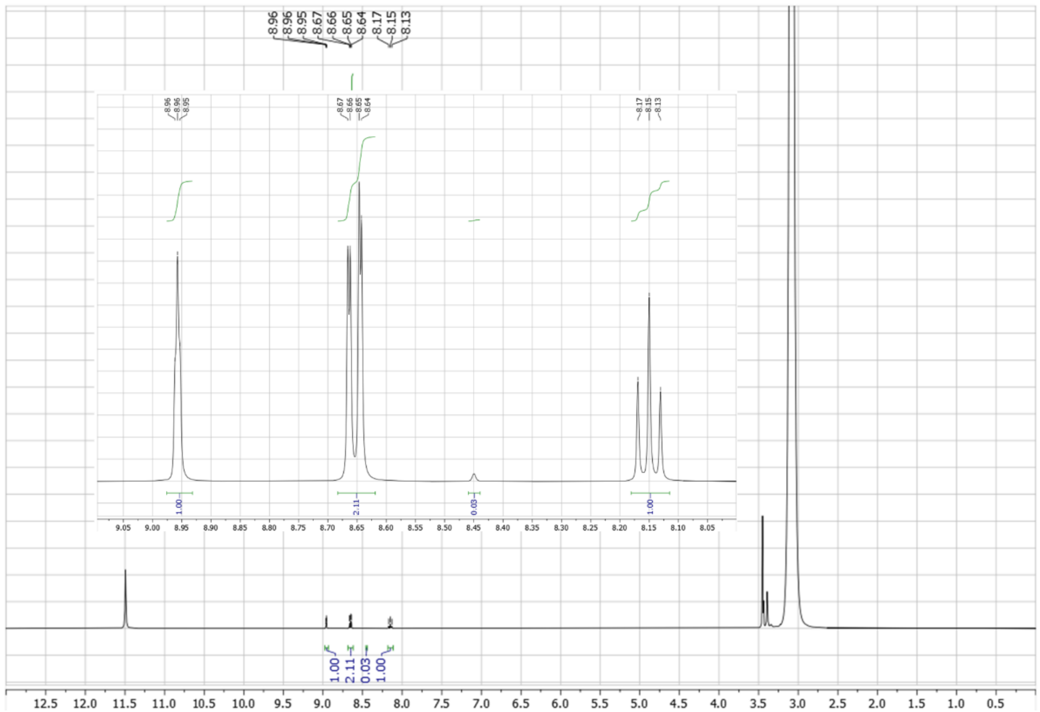


Figure S36: NMR of CAU-10-H in DMSO-H6 and D_2SO_4

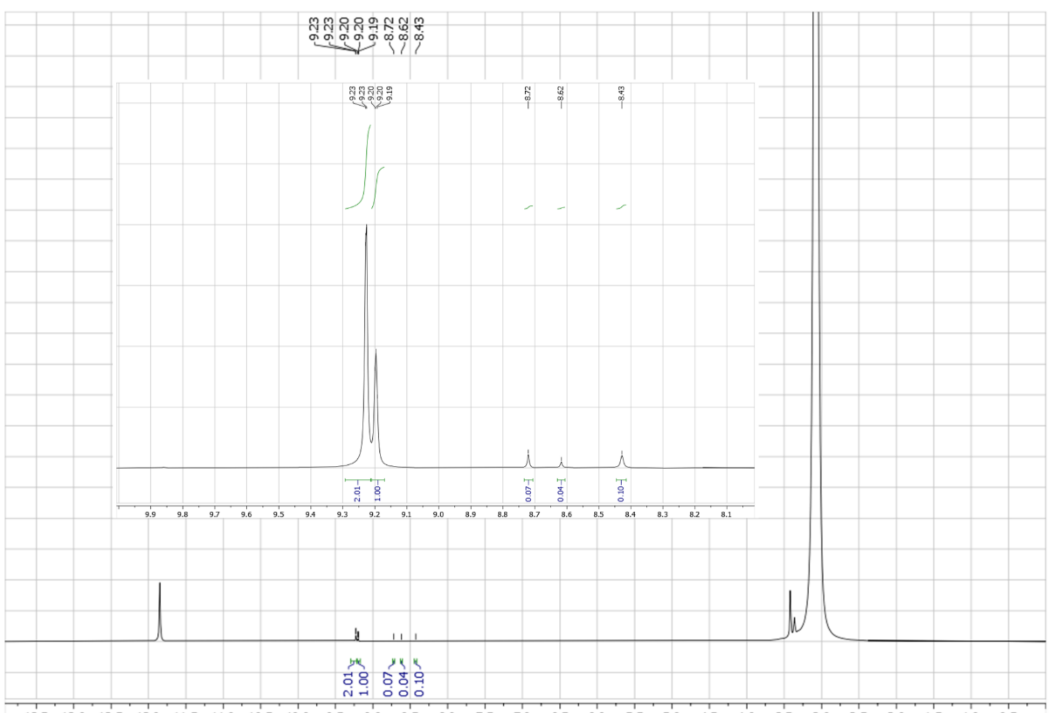


Figure S37: NMR of CAU-10-NO_2 in DMSO-H6 and D_2SO_4

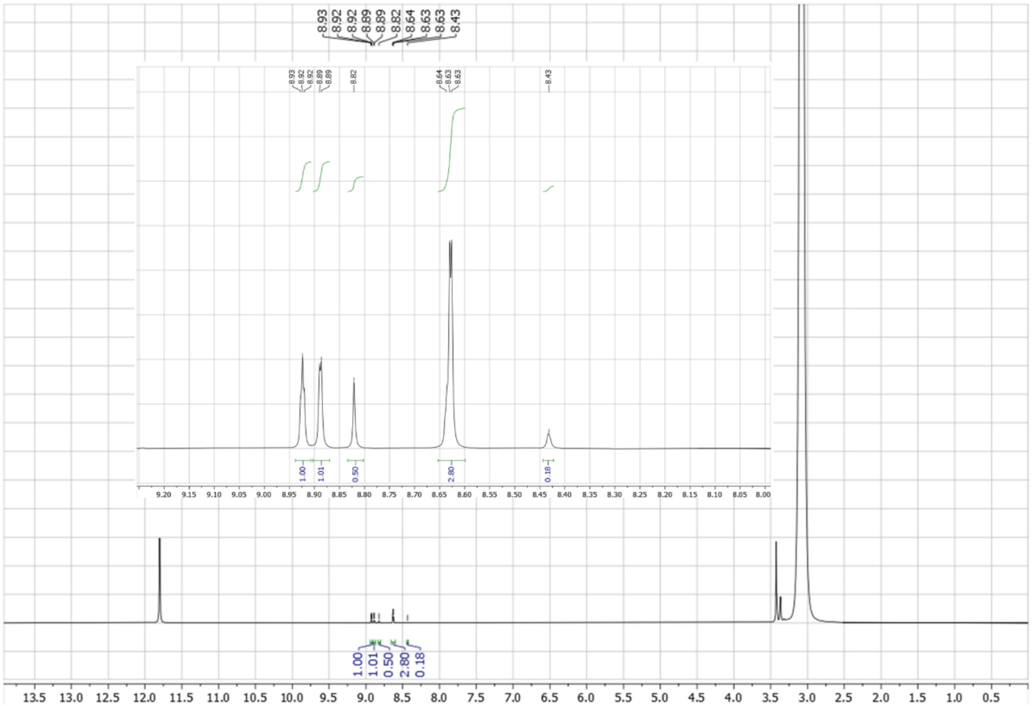


Figure S38: NMR of CAU-10-NH_2 in DMSO-H6 and D_2SO_4. The splitting pattern is not what we expect from the ligand 3-aminoisopthalic acid, we believe this is due to the acid catalysed formation of an amide.

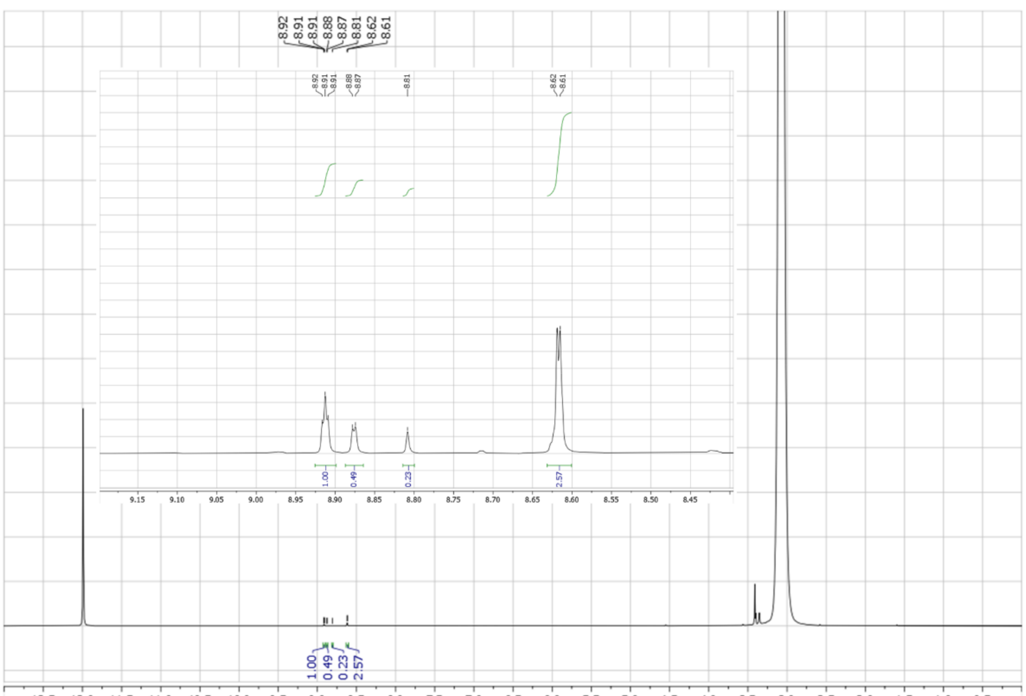


Figure S39: NMR of CAU-10-N_3 in DMSO-H6 and D_2SO_4. The splitting pattern is not what we expect from the ligand 3-azoisophthalic acid, we believe this is due to the loss of N_2 followed by the acid catalysed formation of an amide.

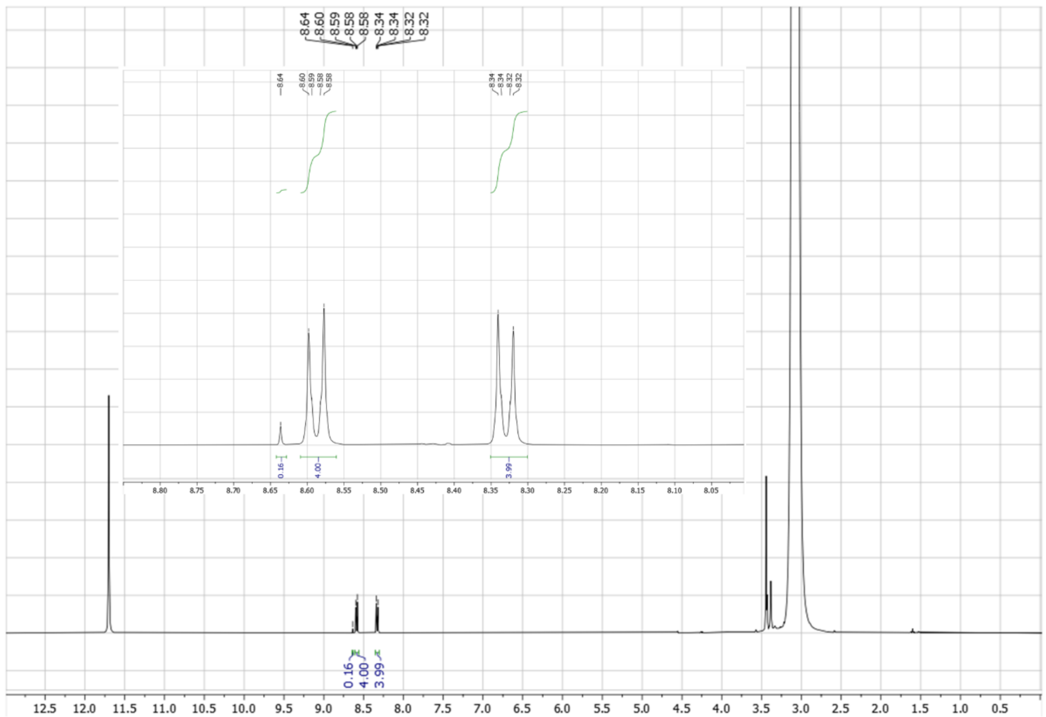


Figure S40: NMR of CAU-21 in DMSO-H6 and D_2SO_4

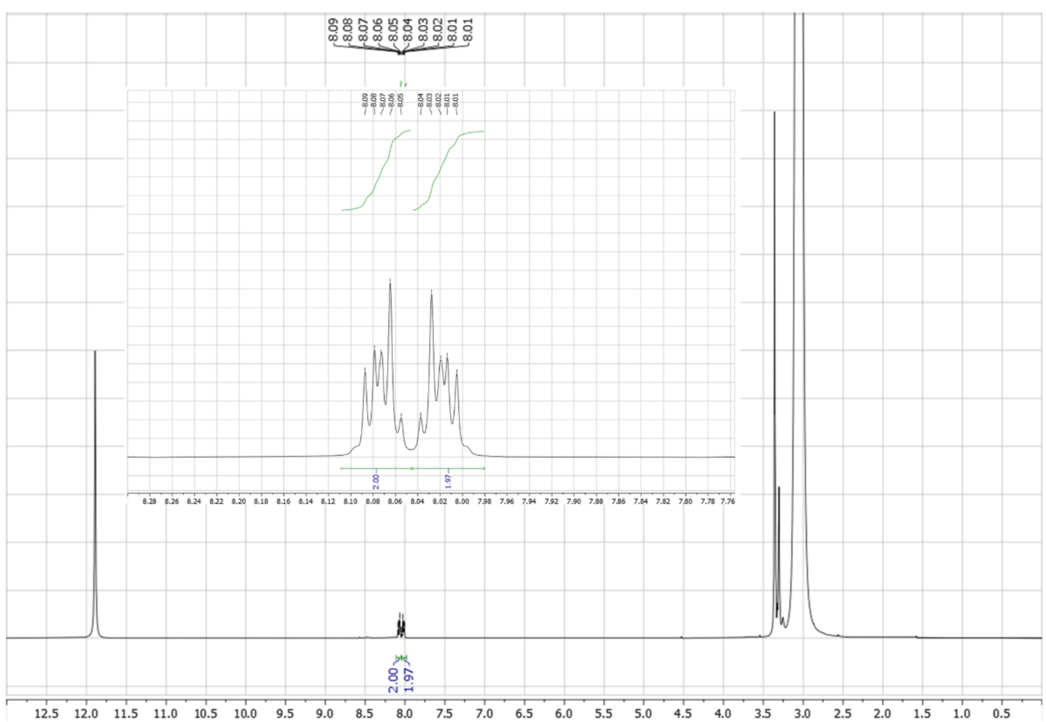


Figure S41: NMR of CAU-15 in DMSO-H6 and D_2SO_4

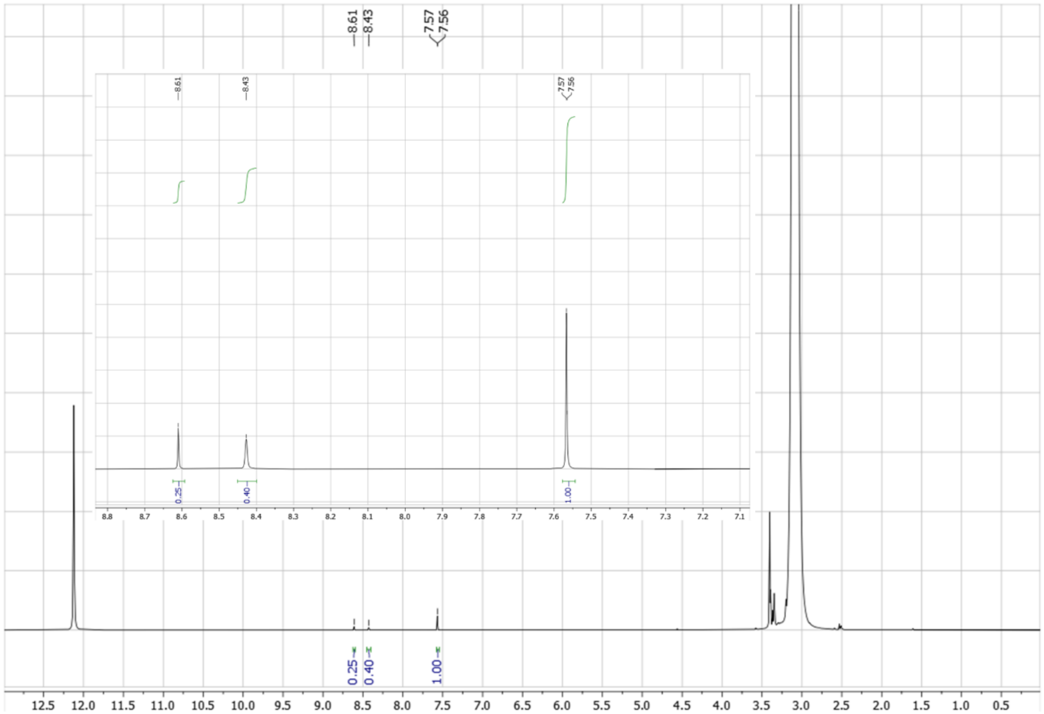


Figure S42: NMR of MOF-303 in DMSO-H6 and D_2SO_4

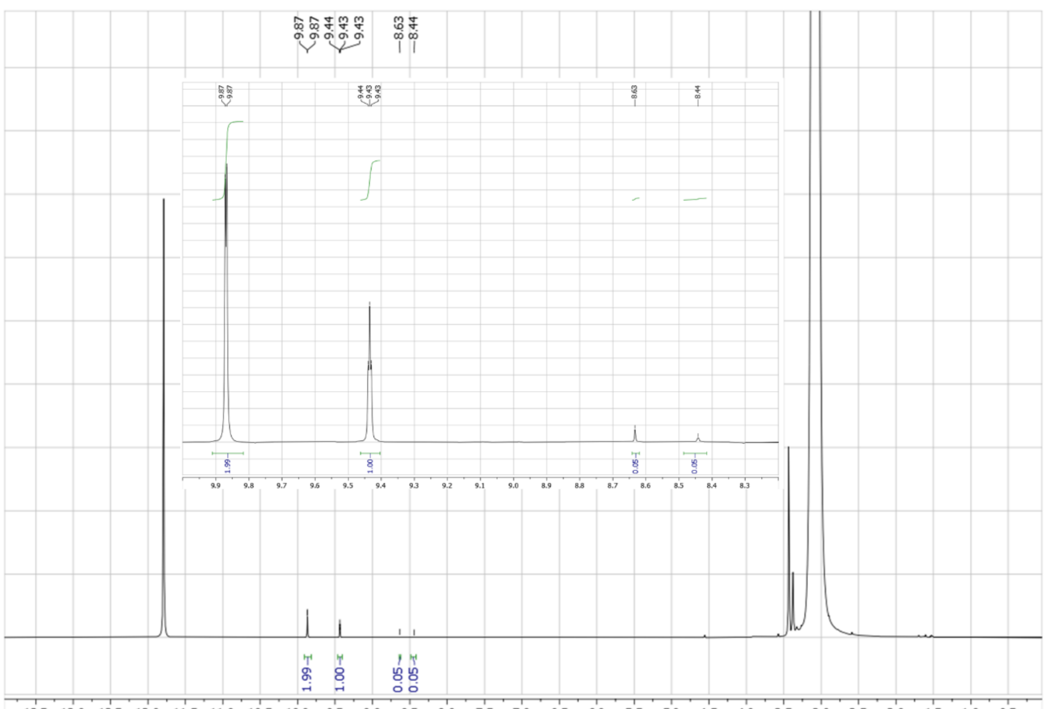


Figure S43: NMR of CAU-10-py in DMSO-H6 and D_2SO_4

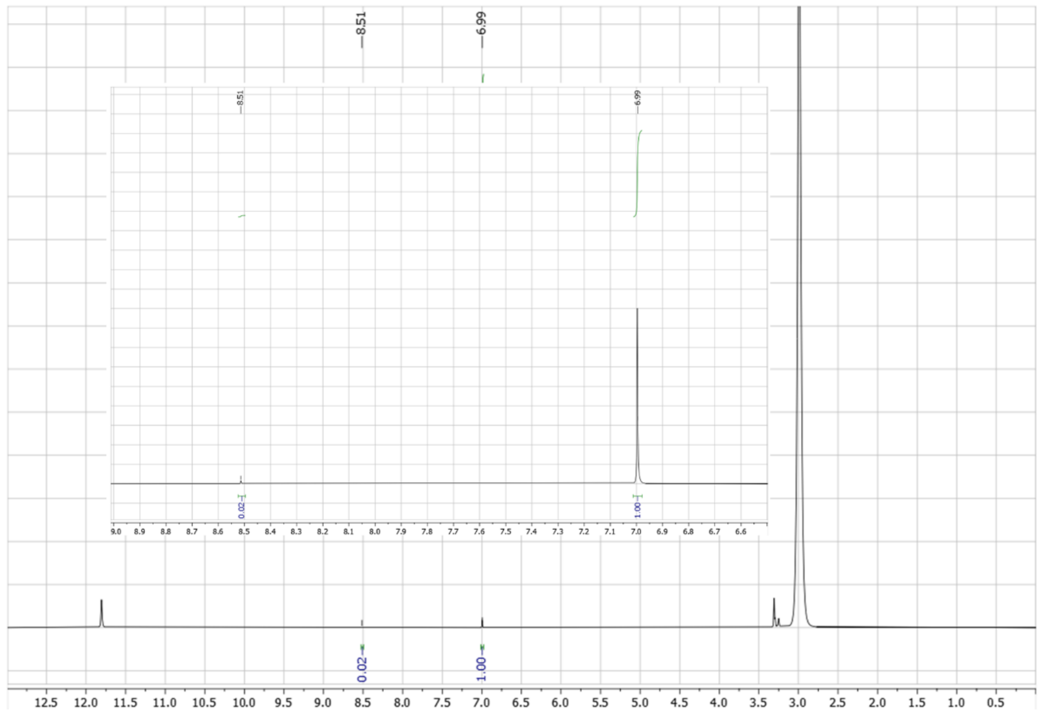


Figure S44: NMR of Al-Fum in DMSO-H6 and D_2SO_4

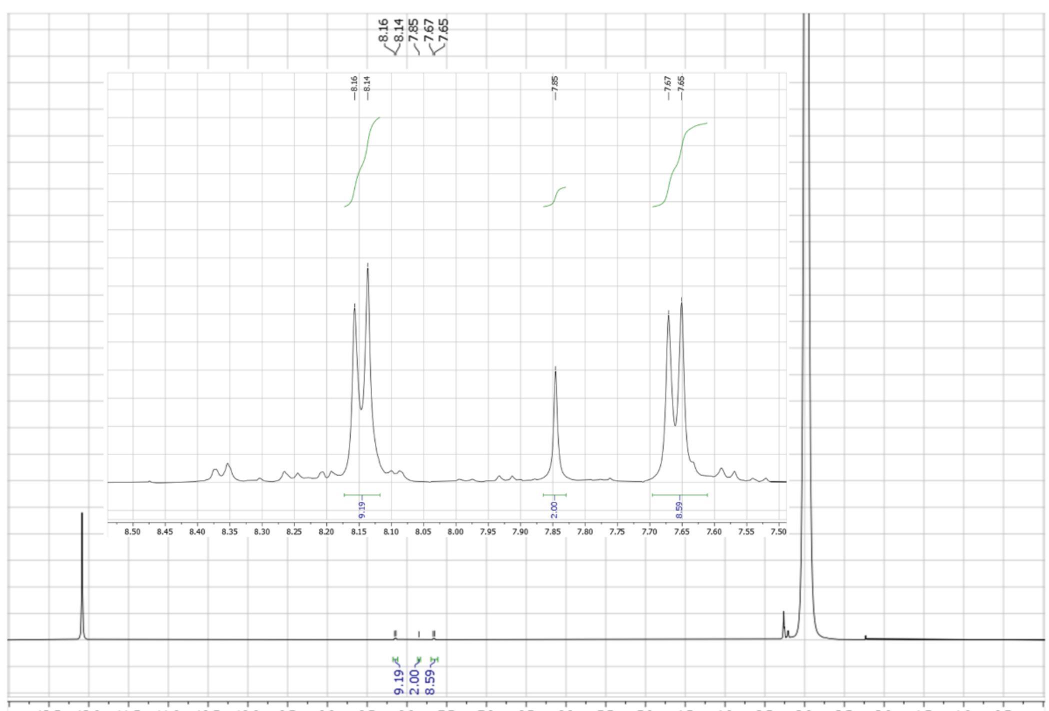


Figure S45: NMR of CAU-9 in DMSO-H6 and D_2SO_4

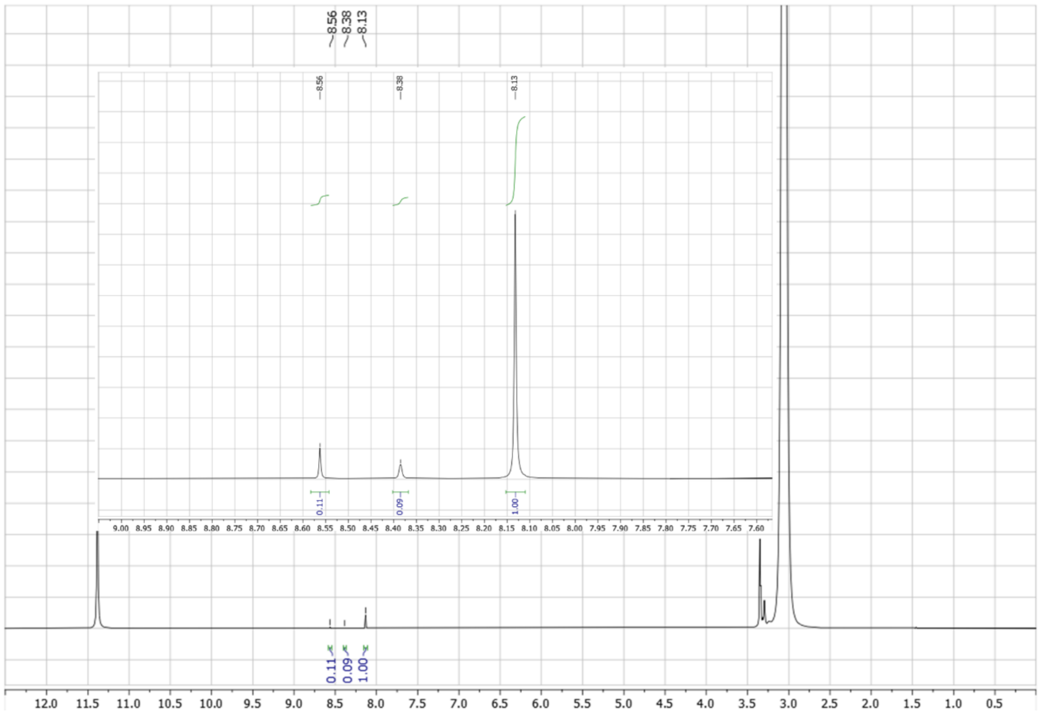


Figure S46: NMR of MIL-53(Al)-TDC in DMSO-H6 and D_2SO_4.

References:

1 J. A. Coelho, A. M. Ribeiro, A. F. P. Ferreira, S. M. P. Lucena, A. E. Rodrigues and D. C. S. de Azevedo, *Ind. Eng. Chem. Res.*, 2016, **55**, 2134–2143.
2 Z. Zheng, H. L. Nguyen, N. Hanikel, K. K.-Y. Li, Z. Zhou, T. Ma and O. M. Yaghi, *Nat Protoc*, 2023, **18**, 136–156.
3 M. V. Solovyeva, A. I. Shkatulov, L. G. Gordeeva, E. A. Fedorova, T. A. Krieger and Y. I. Aristov, *Langmuir*, 2021, **37**, 693–702.
4 V. Seabra, J. M. R. Gonçalves, A. L. S. Moura, V. G. Luna, P. H. O. Santiago, J. Ellena and B. S. Lima-Neto, *Transit Met Chem*, 2025, **50**, 115–125.
5 H.-P. Li, J.-W. Wang, Z. Dou, L.-Z. Wu, Y. Wang, Y. Liang and Q.-G. Zhai, *Chemical Engineering Journal*, 2024, **492**, 152125.
6 H. Reinsch, D. De Vos and N. Stock, *Zeitschrift für anorganische und allgemeine Chemie*, 2013, **639**, 2785–2789.
7 M. Krüger, A. K. Inge, H. Reinsch, Y.-H. Li, M. Wahiduzzaman, C.-H. Lin, S.-L. Wang, G. Maurin and N. Stock, *Inorg. Chem.*, 2017, **56**, 5851–5862.
8 M. Krüger, R. Siegel, A. Dreischarf, H. Reinsch, J. Senker and N. Stock, *Microporous and Mesoporous Materials*, 2015, **216**, 27–35.
9 N. Tannert, S.-J. Ernst, C. Jansen, H.-J. Bart, S. K. Henninger and C. Janiak, *J. Mater. Chem. A*, 2018, **6**, 17706–17712.
10 A. López-Olvera, J. A. Zárate, E. Martínez-Ahumada, D. Fan, M. L. Díaz-Ramírez, P. A. Sáenz-Cavazos, V. Martis, D. R. Williams, E. Sánchez-González, G. Maurin and I. A. Ibarra, *ACS Appl. Mater. Interfaces*, 2021, **13**, 39363–39370.