Supporting Information for:

Tuning Water Adsorption, Stability, and Phase in Fe-MIL-101 and Fe-MIL-88 Analogs with Amide Functionalization

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Experimental Procedures

Reagents were obtained from commercial vendors and used without modification, unless stated in the experimental details.

Synthesis of 2-(acetylamido) terephthalic acid. 2-Aminoterephthalic acid (4.891 g, 27 mmol) and acetyl chloride (2.543 g, 32.4 mmol) were added to a 250 ml RBF with 100 ml of THF and stirred under reflux at 80˚C for 12 hours. Solvent was removed under vacuum at 50 ˚C, leaving a tan solid behind. 30 ml of $CHCl_3$ was added to the crude product, stirred until powder was fully dispersed and under reduced pressure, solvent was removed via Büchner funnel. Two more washings with $CHCl_3$ were performed to obtain pure product 5.484 g pure product (91 % yield). ^{1}H-NMR (400MHz, DMSO): δ = 11.00 (s, 2H, OH), 8.99 (d, 1H, CH), 8.04 (d, 1H, CH), 7.66 (dd, 1H, CH), 2.15 (s, 6H, CH_3).

Synthesis of 2-(propyonylamido) terephthalic acid. 2-Aminoterephthalic acid (4.891 g, 27 mmol) and propyonyl chloride (2.998 g, 32.4 mmol) were added to a 250 ml RBF along with 100 ml of THF and stirred under reflux at 80˚C for 12 hours. Solvent was removed under vacuum at 50 ˚C, leaving a tan solid behind. 30 ml of $CHCl_3$ was added to the crude product, stirred until powder was fully dispersed and under reduced pressure, solvent was removed via Büchner funnel. Two more washings with $CHCl_3$ were performed to obtain pure product 5.316 g pure product (83 % yield). ^{1}H-NMR (400 MHz, DMSO): δ = 11.06 (s, 1H, NH), 9.05 (d, 1H, CH), 8.05 (d, 1H, CH), 7.65 (dd, 1H, CH), 2.43 (q, 2H, CH_2), 1.12 (t, 3H, CH_3).

Synthesis of 2-(butyrylamido) terephthalic acid. 2-Aminoterephthalic acid (4.891 g, 27 mmol) and butyryl chloride (3.452 g, 32.4 mmol) were added to a 250 ml RBF along with 100 ml of THF and stirred under reflux at 80˚C for 12 hours. Solvent was removed under vacuum at 50 ˚C, leaving a tan solid behind. 30 ml of $CHCl_3$ was added to the crude product, stirred until powder was fully dispersed and under reduced pressure, solvent was removed via Büchner funnel. Two more washings with $CHCl_3$ were performed to obtain pure product 5.969 g pure product (88 % yield). ^{1}H-NMR (400 MHz, DMSO): δ = 11.06 (s, 1H, NH), 9.04 (d, 1H, CH), 8.04 (d, 2H, CH), 7.65 (dd, 1H, CH), 2.38 (t, 2H, CH_2) 1.63 (m, 2H, CH_2), 0.93 (t, 3H, CH_3).

Synthesis of 2-(lauroylamido) terephthalic acid. 2-Aminoterephthalic acid (4.891 g, 27 mmol) and lauroyl chloride (7.437 g, 32.4 mmol) were added to a 250 ml RBF along with 100 ml of THF and stirred under reflux at 80˚C for 12 hours. Solvent was removed under vacuum at 50 ˚C, leaving a tan solid behind. 30 ml of $CHCl_3$ was added to the crude product, stirred until powder was fully dispersed and under reduced pressure, solvent was removed via Büchner funnel. Two more washings with $CHCl_3$ were performed to obtain pure product 6.415 g pure product (68 % yield). ^{1}H-NMR (400MHz, DMSO): δ = 11.07 (s, 1H, NH), 9.04 (d, 1H, CH), 8.04 (d, 1H, CH), 7.65 (dd, 1H, CH), 2.39 (t, 2H, CH_2), 1.62 (m, 2H, CH_2), 1.23 (m, 16H, CH_2), 0.83 (s, 3H, CH).

Synthesis of 2-(3,3,5-trimethylhexanoylamido) terephthalic acid. 2-Aminoterephthalic acid (4.891 g, 27 mmol) and 3,3,5-trimethylhexanoyl chloride (2.998 g, 32.4 mmol) were added to a 250 ml RBF along with 100 ml of THF and stirred under reflux at 80˚C for 12 hours. Solvent was removed under vacuum at 50 ˚C, leaving a tan solid behind. 30 ml of $CHCl_3$ was added to the crude product, stirred until powder was fully dispersed and under reduced pressure, solvent was removed via Büchner funnel. Two more washings with $CHCl_3$ were performed to obtain pure

product 8.156 g pure product (94 % yield). ^{1}H-NMR (400MHz, DMSO): δ = 11.06 (s, 1H, NH), 9.04 (d, 1H, CH), 8.04 (d, 1H, CH), 7.65 (dd, 1H, CH),

Synthesis of 2-(cyclohexanoylamido) terephthalic acid. 2-Aminoterephthalic acid (4.891 g, 27 mmol) and cyclohexanoyl chloride (4.750 g, 32.4 mmol) were added to a 250 ml RBF along with 100 ml of THF and stirred under reflux at 80˚C for 12 hours. Solvent was removed under vacuum at 50 ˚C, leaving a white solid behind. 30 ml of $CHCl_3$ was added to the crude product, stirred until powder was fully dispersed and under reduced pressure, solvent was removed via Büchner funnel. Two more washings with $CHCl_3$ were performed to obtain pure product 6.828 g pure product (72 % yield). ^{1}H-NMR (400MHz, DMSO): δ = 11.12 (s, 1H, NH), 9.07 (d, 1H, CH), 8.06 (d, 1H, CH), 7.67 (dd, 1H, CH), 2.34 (m, 1H, CH), 1.92 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 1.31 (m, 6H, CH_2).

Synthesis of 2-(phenylacetal) terephthalic acid. 2-Aminoterephthalic acid (4.891 g, 27 mmol) and phenylacetal chloride (5.009 g, 32.4 mmol) were added to a 250 ml RBF along with 100 ml of THF and stirred under reflux at 80˚C for 12 hours. Solvent was removed under vacuum at 50 ˚C, leaving a tan solid behind. 30 ml of $CHCl_3$ was added to the crude product, stirred until powder was fully dispersed and under reduced pressure, solvent was removed via Büchner funnel. Two more washings with $CHCl_3$ were performed to obtain pure product 6.138 g pure product (76 % yield). ^{1}H-NMR (400MHz, DMSO): δ = 11.10 (s, 1H, NH), 9.05 (s, 1H, CH), 8.02 (d, 1H, CH), 7.66 (dd, 1H, CH), 7.33 (t, 5H, CH), 3.78 (s, 2H, CH_2).

Synthesis of 2-(naphthoylamido) terephthalic acid. 2-Aminoterephthalic acid (4.891 g, 27 mmol) and naphthoyl chloride (6.176 g, 32.4 mmol) were added to a 250 ml RBF along with 100 ml of THF and stirred under reflux at 80˚C for 12 hours. Solvent was removed under vacuum at 50 ˚C, leaving a tan solid behind. 30 ml of $CHCl_3$ was added to the crude product, stirred until powder was fully dispersed and under reduced pressure, solvent was removed via Büchner funnel. Two more washings with $CHCl_3$ were performed to obtain pure product 6.52 g pure product (72 % yield). ^{1}H-NMR (400MHz, DMSO): δ = 12.27 (s, 1H, NH), 9.30 (d, 1H, CH), 8.57 (d, 1H, CH), 8.12 (m, 3H, CH), 8.02 (m, 1H, CH), 7.77 (m, 1H, CH), 7.66 (m, 2H, CH).

Synthesis of 2-(isobutyrylamido) terephthalic acid. 2-Aminoterephthalic acid (4.891 g, 27 mmol) and isobutyryl chloride (3.452 g, 32.4 mmol) were added to a 250 ml RBF along with 100 ml of THF and stirred under reflux at 80˚C for 12 hours. Solvent was removed under vacuum at 50 ˚C, leaving a white solid behind. 30 ml of $CHCl_3$ was added to the crude product, stirred until powder was fully dispersed and under reduced pressure, solvent was removed via Büchner funnel. Two more washings with $CHCl_3$ were performed to obtain pure product 5.73 g pure product (76 % yield). ^{1}H-NMR (400MHz, DMSO): δ = 11.14 (s, 1H, NH), 9.05 (d, 1H, CH), 8.05 (d, 1H, CH), 7.66 (dd, 1H, CH), 2.58 (m, 1H, CH), 1.17 (d, 6H, CH_3).

Synthesis of Cr-MIL-101. In a 20 mL Parr Vessel, $CrNO_3 \cdot 9\ H_20$ (0.800 g, 3.2 mmol) was combined with terephthalic acid (0.332 g, 3.0 mmol) along with 9.6 mL of deionized water and 100 µL of HF. The solution was heated to 220 ℃ in an oven for 8 hours and allowed to cool to room temperature. The solid was washed three times with deionized water and 3 times ethanol over the course of a 72-hour period. The product was allowed to dry, via vacuum filtration, under ambient conditions, until a free-flowing crystalline powder was obtained.

Synthesis of Fe-MIL-101. In a 20 mL vial, $FeCl_3 \cdot 6\ H_20$ (0.514 g,1.9mmol) was combined with terephthalic acid (0.299 g, 1.8 mmol) along with 12 mL of dimethyl formamide (DMF). Mixture was sonicated until no solid remained in solution. The solution was heated to 110 ℃ in a dry bath for 20 hours, during which time a precipitate formed, and allowed to cool to room temperature. The solid was washed three times with dimethyl formamide (DMF) and 3 times with dichloromethane (DCM), over the course of a 72-hour period. The product was allowed to dry, via vacuum filtration, under ambient conditions, until a free-flowing crystalline powder was obtained.

Synthesis of Fe-MIL-101-acetylamido. In a 20 mL vial, $FeCl_3 \cdot 6\ H_20$ (0.270 g,1.0mmol) was combined with 2-(acetylamido) terephthalic acid (0.201 g, 0.9 mmol) along with 12 mL of dimethyl formamide (DMF). Mixture was sonicated until no solid remained in solution. The solution was heated to 110 ℃ in a dry bath for 20 hours, during which time a precipitate formed, and allowed to cool to room temperature. The solid was washed three times with dimethyl formamide (DMF) and 3 times with dichloromethane (DCM), over the course of a 72-hour period. The product was allowed to dry, via vacuum filtration, under ambient conditions, until a free-flowing crystalline powder was obtained.

Synthesis of Fe-MIL-101-propyonylamido. In a 20 mL vial, $FeCl_3 \cdot 6\ H_20$ (0.270 g,1.0mmol) was combined with 2-(propyonylamido) terephthalic acid (0.213 g, 0.9 mmol) along with 12 mL of dimethyl formamide (DMF). Mixture was sonicated until no solid remained in solution. The solution was heated to 110 ℃ in a dry bath for 20 hours, during which time a precipitate formed, and allowed to cool to room temperature. The solid was washed three times with dimethyl formamide (DMF) and 3 times with dichloromethane (DCM), over the course of a 72-hour period. The product was allowed to dry, via vacuum filtration, under ambient conditions, until a free-flowing crystalline powder was obtained.

Synthesis of Fe-MIL-101-butyrylamido. In a 20 mL vial, $FeCl_3 \cdot 6\ H_20$ (0.270 g, 1.0mmol) was combined with 2-(butyrylamido) terephthalic acid (0.226 g, 0.9 mmol) along with 12 mL of dimethyl formamide (DMF). Mixture was sonicated until no solid remained in solution. The solution was heated to 110 ℃ in a dry bath for 20 hours, during which time a precipitate formed, and allowed to cool to room temperature. The solid was washed three times with dimethyl formamide (DMF) and 3 times with dichloromethane (DCM), over the course of a 72-hour period. The product was allowed to dry, via vacuum filtration, under ambient conditions, until a free-flowing crystalline powder was obtained.

Synthesis of Fe-MIL-101-lauroylamido. In a 20 mL vial, $FeCl_3 \cdot 6\ H_20$ (0.270 g,1.0mmol) was combined with 2-(lauroylamido) terephthalic acid (0.314 g, 0.9 mmol) along with 12 mL of dimethyl formamide (DMF). Mixture was sonicated until no solid remained in solution. The solution was heated to 110 ℃ in a dry bath for 20 hours, during which time a precipitate formed, and allowed to cool to room temperature. The solid was washed three times with dimethyl formamide (DMF) and 3 times with dichloromethane (DCM), over the course of a 72-hour period. The product was allowed to dry, via vacuum filtration, under ambient conditions, until a free-flowing crystalline powder was obtained.

Synthesis of Fe-MIL-101-trimethylhexanoylamido. In a 20 mL vial, $FeCl_3 \cdot 6\ H_20$ (0.270 g,1.0mmol) was combined with 2-(3,3,5-trimethylhexanoylamido) terephthalic acid (0.289 g, 0.9

mmol) along with 12 mL of dimethyl formamide (DMF). Mixture was sonicated until no solid remained in solution. The solution was heated to 110 ℃ in a dry bath for 20 hours, during which time a precipitate formed, and allowed to cool to room temperature. The solid was washed three times with dimethyl formamide (DMF) and 3 times with dichloromethane (DCM), over the course of a 72-hour period. The product was allowed to dry, via vacuum filtration, under ambient conditions, until a free-flowing crystalline powder was obtained.

Synthesis of Fe-MIL-101-cyclohexanoylamido. In a 20 mL vial, $FeCl_3 \cdot 6\ H_20$ (0.270 g,1.0mmol) was combined with 2-(cyclohexanoylamido) terephthalic acid (0.261 g, 0.9 mmol) along with 12 mL of dimethyl formamide (DMF). Mixture was sonicated until no solid remained in solution. The solution was heated to 110 ℃ in a dry bath for 20 hours, during which time a precipitate formed, and allowed to cool to room temperature. The solid was washed three times with dimethyl formamide (DMF) and 3 times with dichloromethane (DCM), over the course of a 72-hour period. The product was allowed to dry, via vacuum filtration, under ambient conditions, until a free-flowing crystalline powder was obtained.

Synthesis of Fe-MIL-101-phenylacetalamido. In a 20 mL vial, $FeCl_3 \cdot 6\ H_20$ (0.270 g,1.0mmol) was combined with 2-(phenylacetal) terephthalic acid (0.257 g, 0.9 mmol) along with 12 mL of dimethyl formamide (DMF). Mixture was sonicated until no solid remained in solution. The solution was heated to 110 ℃ in a dry bath for 20 hours, during which time a precipitate formed, and allowed to cool to room temperature. The solid was washed three times with dimethyl formamide (DMF) and 3 times with dichloromethane (DCM), over the course of a 72-hour period. The product was allowed to dry, via vacuum filtration, under ambient conditions, until a free-flowing crystalline powder was obtained.

Synthesis of Fe-MIL-101-naphthoylamido. In a 20 mL vial, $FeCl_3 \cdot 6\ H_20$ (0.270 g,1.0mmol) was combined with 2-(naphthoyl) terephthalic acid (0.302 g, 0.9 mmol) along with 12 mL of dimethyl formamide (DMF). Mixture was sonicated until no solid remained in solution. The solution was heated to 110 ℃ in a dry bath for 20 hours, during which time a precipitate formed, and allowed to cool to room temperature. The solid was washed three times with dimethyl formamide (DMF) and 3 times with dichloromethane (DCM), over the course of a 72-hour period. The product was allowed to dry, via vacuum filtration, under ambient conditions, until a free-flowing crystalline powder was obtained.

Synthesis of Fe-MIL-88b-acetalamido. In a 20 mL vial, $FeCl_3 \cdot 6\ H_20$ (0.270 g,1.0mmol) was combined with 2-(acetalamido) terephthalic acid (0.201 g, 0.9 mmol) along with 12 mL of dimethyl formamide (DMF). Mixture was sonicated until no solid remained in solution. ~2 g One solid piece of $Nd_2Fe_{14}B$ (~2 g) was added to the solution and it was heated to 110 ℃ in a dry bath for 20 hours, during which time a precipitate formed. The solution was allowed to cool to room temperature and the $Nd_2Fe_{14}B$ was removed. The remaining solid was washed three times with dimethyl formamide (DMF) and 3 times with dichloromethane (DCM), over the course of a 72-hour period. The product was allowed to dry, via vacuum filtration, under ambient conditions, until a free-flowing crystalline powder was obtained.

Synthesis of Fe-MIL-88b-acetalamido (iron-salt free synthesis). In a 20 mL vial, 2-(acetalamido) terephthalic acid (0.201 g, 0.9 mmol) was combined with 12 mL of dimethyl

formamide (DMF). Mixture was sonicated until no solid remained in solution. One solid piece of $Nd_2Fe_{14}B$ (~2 g) was added to the solution and it was heated to 110 ℃ in a dry bath for 20 hours, during which time a precipitate formed. The solution was allowed to cool to room temperature and the $Nd_2Fe_{14}B$ was removed. The remaining solid was washed three times with dimethyl formamide (DMF) and 3 times with dichloromethane (DCM), over the course of a 72-hour period. The product was allowed to dry, via vacuum filtration, under ambient conditions, until a free-flowing crystalline powder was obtained.

Synthesis of Fe-MIL-88b-propyonylamido. In a 20 mL vial, $FeCl_3 \cdot 6\ H_20$ (0.270 g,1.0mmol) was combined with 2-(propyonylamido) terephthalic acid (0.213 g, 0.9 mmol) along with 12 mL of dimethyl formamide (DMF). Mixture was sonicated until no solid remained in solution. ~2 g One solid piece of $Nd_2Fe_{14}B$ (~2 g) was added to the solution and it was heated to 110 ℃ in a dry bath for 20 hours, during which time a precipitate formed. The solution was allowed to cool to room temperature and the $Nd_2Fe_{14}B$ was removed. The remaining solid was washed three times with dimethyl formamide (DMF) and 3 times with dichloromethane (DCM), over the course of a 72-hour period. The product was allowed to dry, via vacuum filtration, under ambient conditions, until a free-flowing crystalline powder was obtained.

Synthesis of Fe-MIL-88b-propyonylamido (iron-salt free synthesis). In a 20 mL vial, 2-(propyonylamido) terephthalic acid (0.213 g, 0.9 mmol) was combined with 12 mL of dimethyl formamide (DMF). Mixture was sonicated until no solid remained in solution. One solid piece of $Nd_2Fe_{14}B$ (~2 g) was added to the solution and it was heated to 110 ℃ in a dry bath for 20 hours, during which time a precipitate formed. The solution was allowed to cool to room temperature and the $Nd_2Fe_{14}B$ was removed. The remaining solid was washed three times with dimethyl formamide (DMF) and 3 times with dichloromethane (DCM), over the course of a 72-hour period. The product was allowed to dry, via vacuum filtration, under ambient conditions, until a free-flowing crystalline powder was obtained.

X-Ray Diffraction

Powder X-ray diffraction experiments Figure S51.-S55. were collected on 11-BM at the Advanced Photon Source Argonne National Laboratory. Samples were loaded into 1.5 mm quartz capillaries in air and sealed with wax. Samples were collected at a wavelength of 0.4127 Å.

Pawley Refinements

Pawley refinements were performed on functionalized MIL-101 materials in TOPAS academic.[1] Previously published MIL-101 (Cr) space group (Fd3-m) and unit cell (a = 88.87 Å) was used as a starting point for fitting.[2] All Pawley fits of functionalized materials confirmed the same phase as MIL-101 (Fe) topology with unit cells ranging from a = 89.3 - 89.8 Å.

Gas Adsorption Measurements

Low-pressure gas adsorption measurements were obtained on a Micromeritics Tristar II PLUS, a Micromeritics Tristar 3000, or a Micromeritics 3Flex. 77 K baths were made using liquid N_2. 298 K baths utilized a Micromeritics temperature-controlled bath.

Nuclear Magnetic Resonance Spectra, 400 MHz

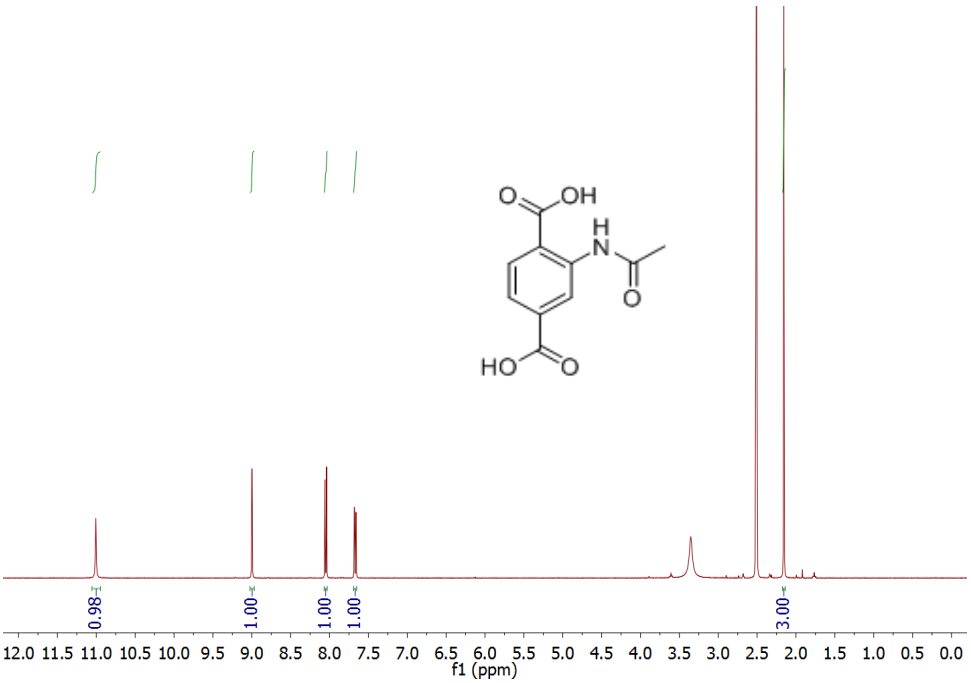

Figure S1. NMR spectra of 2-(acetylamido) terephthalic acid**.**

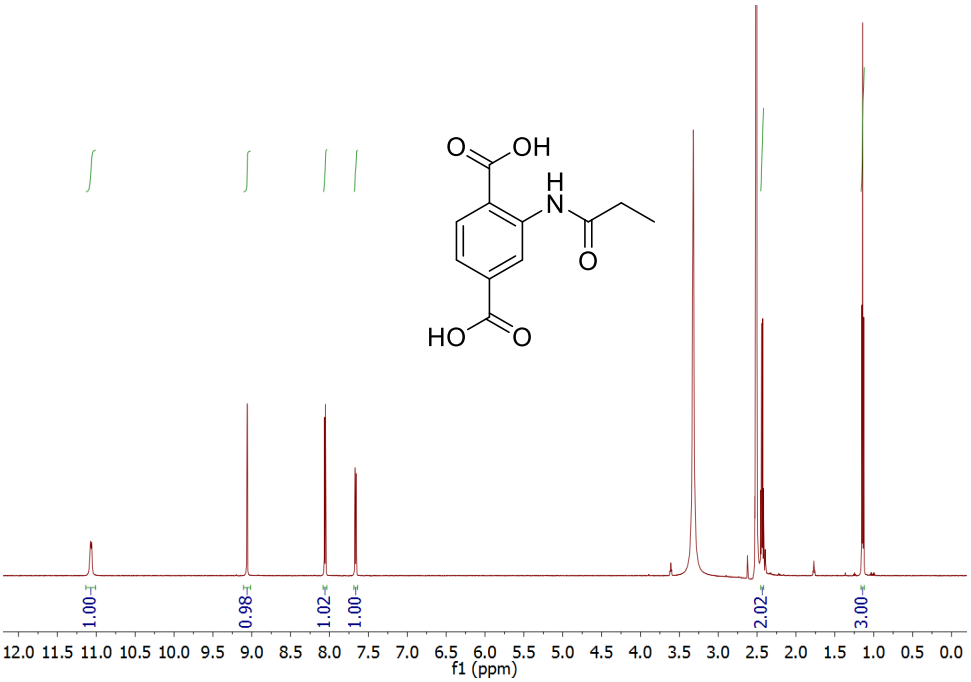

Figure S2. NMR spectra of 2-(propyonylamido) terephthalic acid.

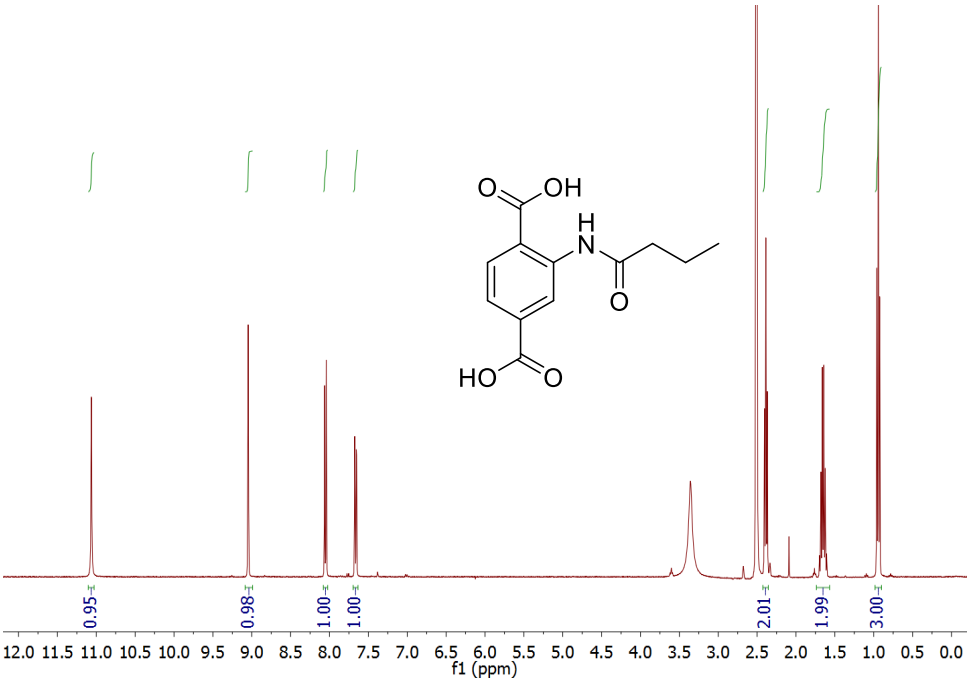

Figure S3. NMR spectra of 2-(butyrylamido) terephthalic acid.

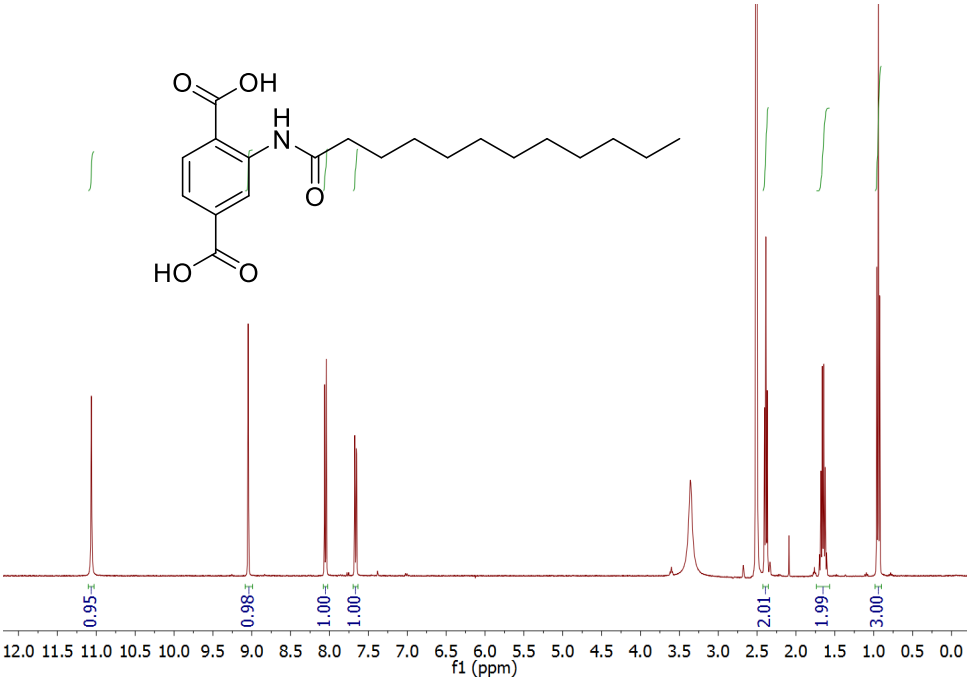

Figure S4. NMR spectra of 2-(lauroylamido) terephthalic acid.

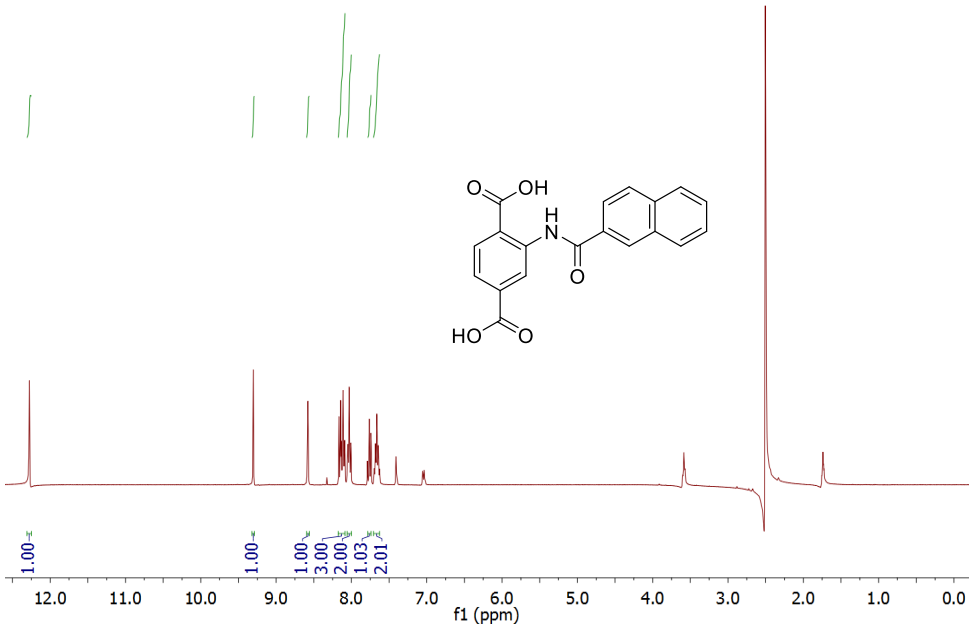

Figure S5. NMR spectra of 2-(naphthoyl) terephthalic

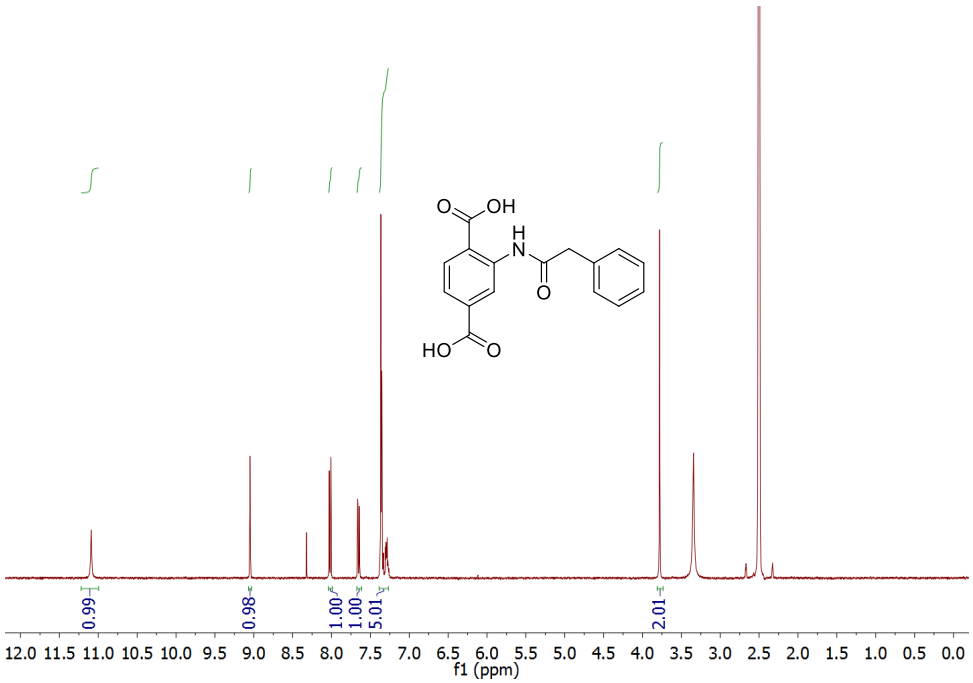

Figure S6. NMR spectra of 2-(phenylacetal) terephthalic acid.

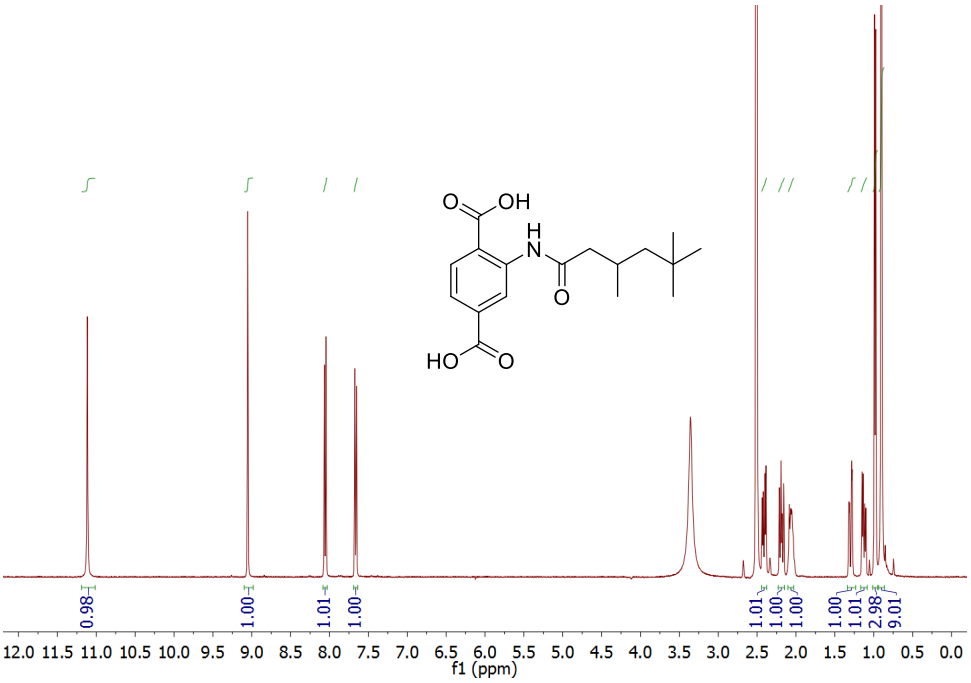

Figure S7. NMR spectra of 2-(3,3,5 trimethylhexanoyl) terephthalic acid.

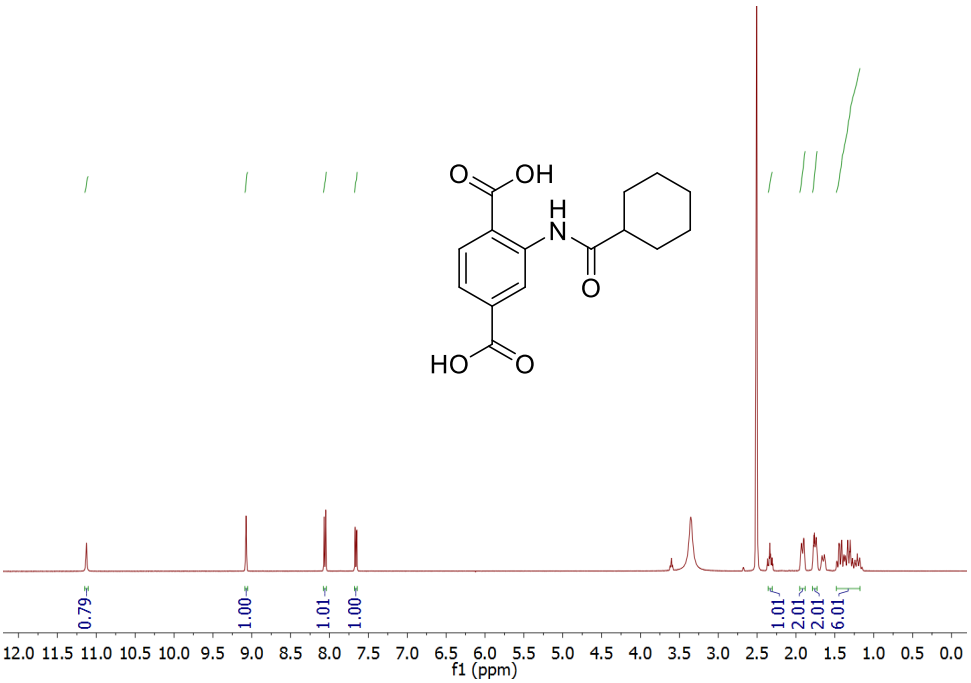

Figure S8. NMR spectra of 2-(cycohexanoyl) terephthalic acid.

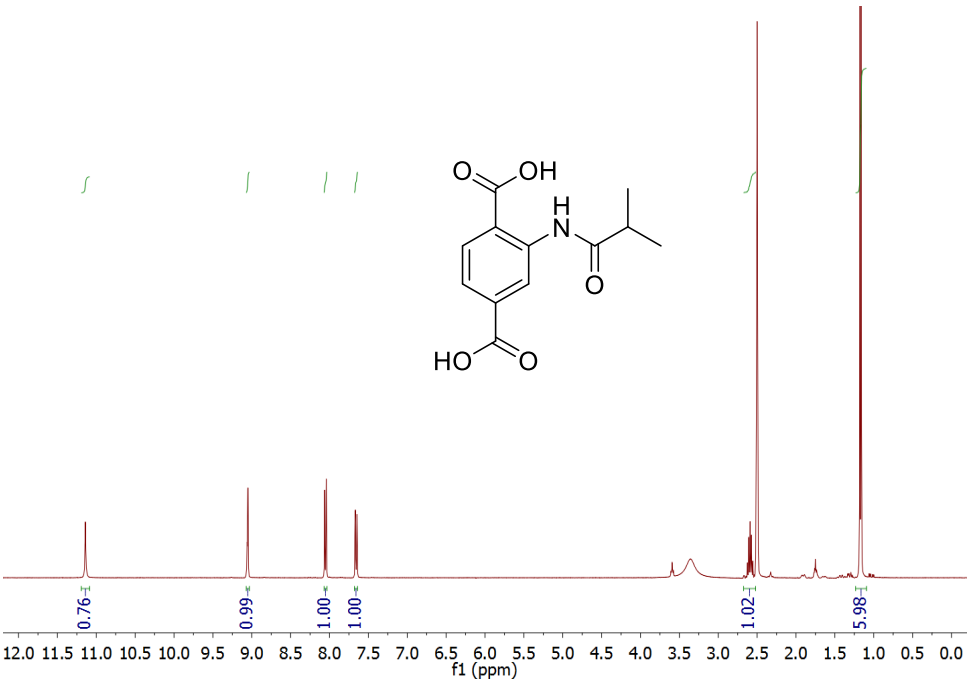

Figure S9. NMR spectra of 2-(isobutyryl) terephthalic acid.

Powder X-ray Diffraction Patterns, APS

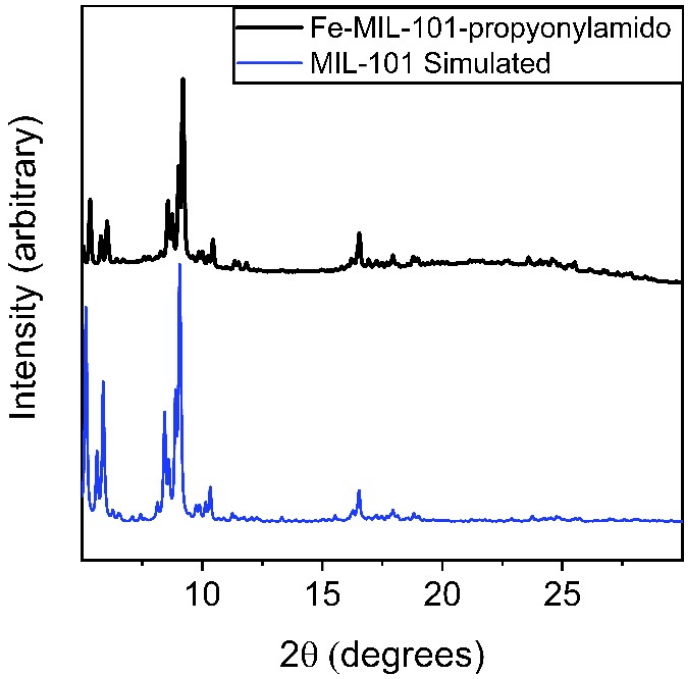

Figure S10. Powder X-ray diffraction pattern for solvothermally prepared Fe-MIL-101-propyonylamido, as compared to the simulated pattern for Cr-MIL-101.

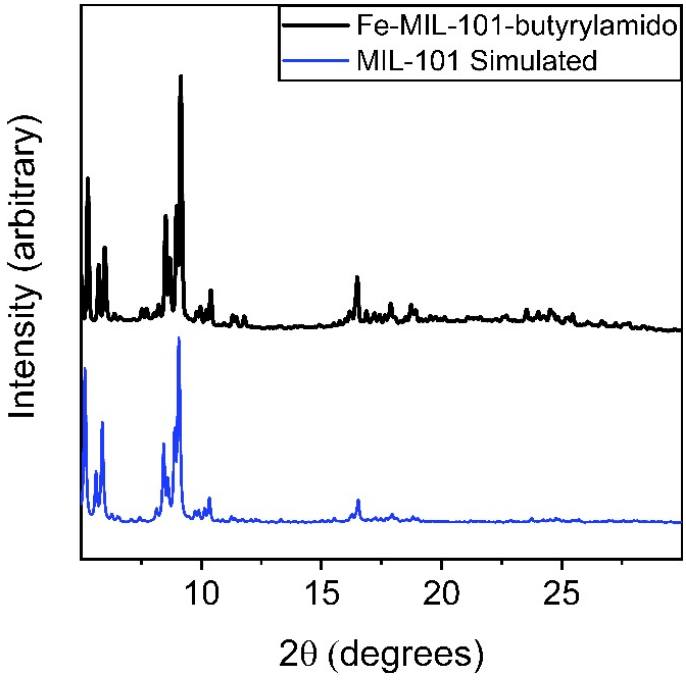

Figure S11. Powder X-ray diffraction pattern for solvothermally prepared Fe-MIL-101-butyrylamido, as compared to the simulated pattern for Cr-MIL-101.

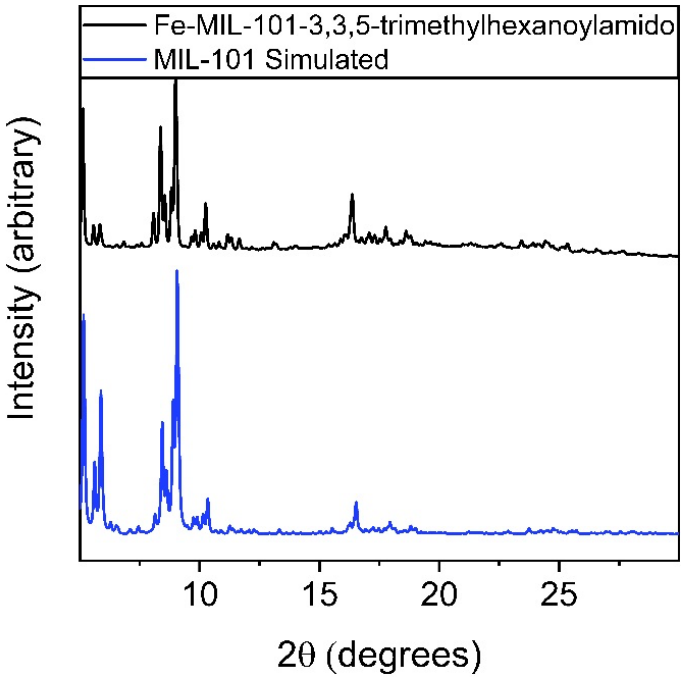

Figure S12. Powder X-ray diffraction pattern for solvothermally prepared Fe-MIL-101-3,3,5-trimethylhexanoylamido, as compared to the simulated pattern for Cr-MIL-101.

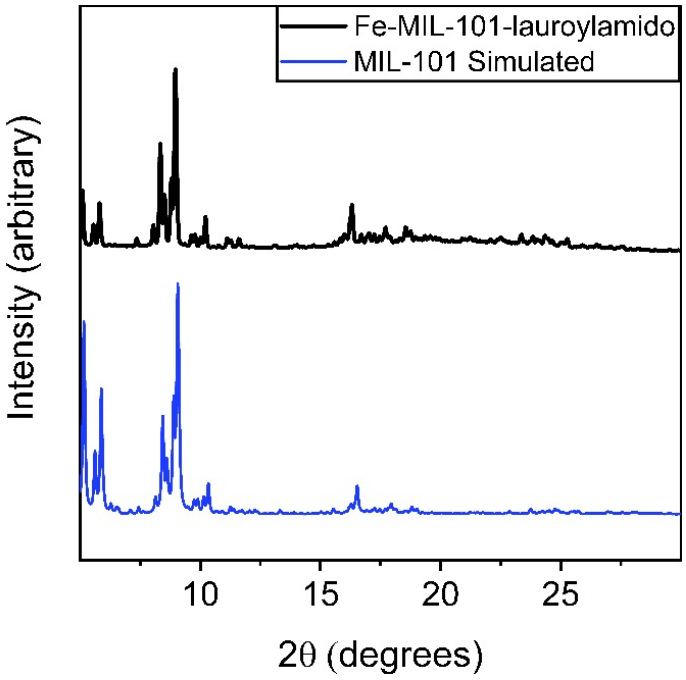

Figure S13. Powder X-ray diffraction pattern for solvothermally prepared of Fe-MIL-101-lauroylamido, as compared to the simulated pattern for Cr-MIL-101.

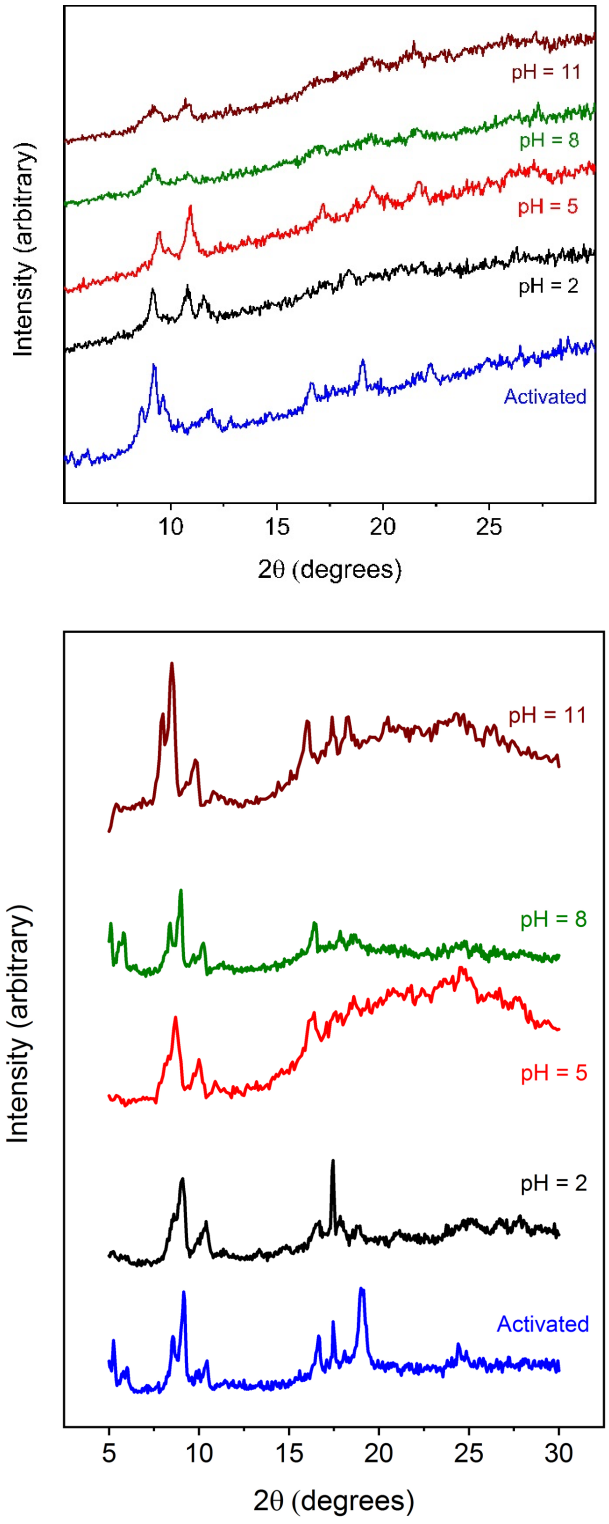

Figure S14. Powder X-ray diffraction patterns of Fe-MIL-101 (top) and Cr-MIL-101 (bottom) treated with an acidic/basic aqueous solution for 12 hours and two weeks, respectively.

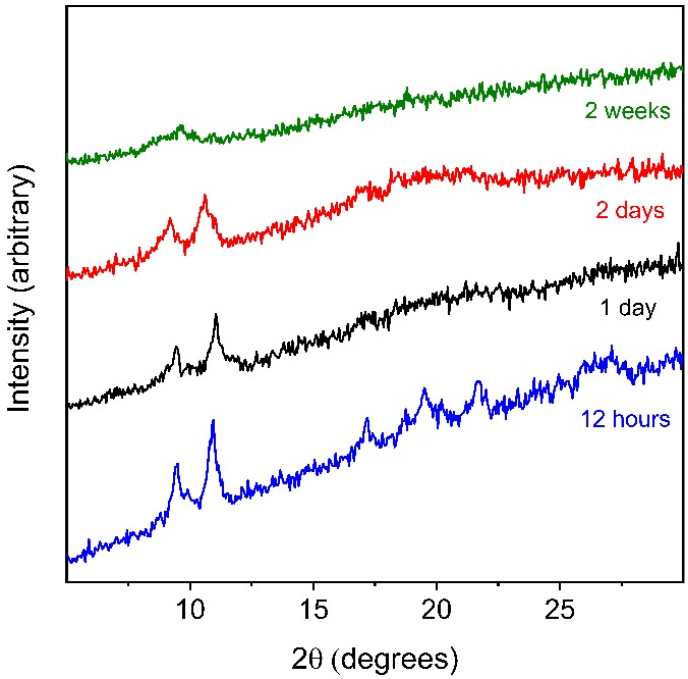

Figure S15. Powder X-ray diffraction patterns of Fe-MIL-101 treated with an aqueous pH = 5 solution for 12 hours to 2 weeks.

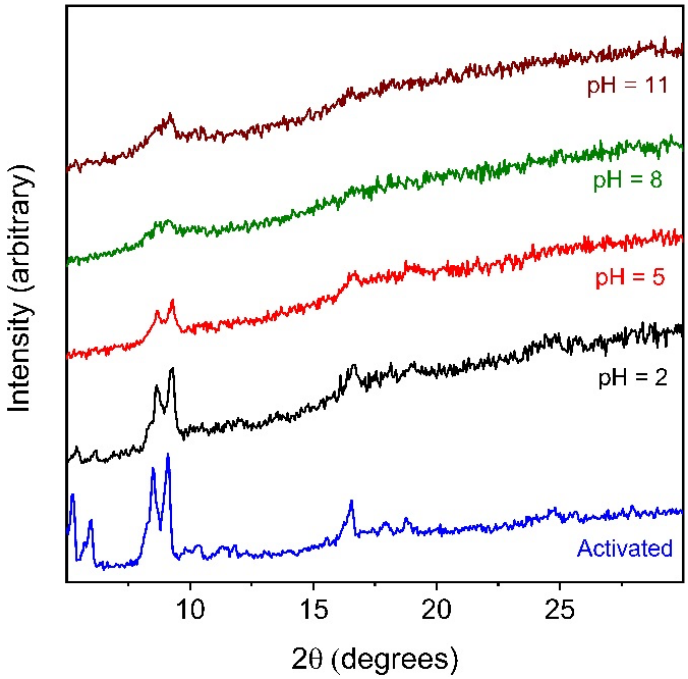

Figure S16. Powder X-ray diffraction patterns of Fe-MIL-101-buyrylamido treated with an acidic/basic aqueous solution for 12 hours.

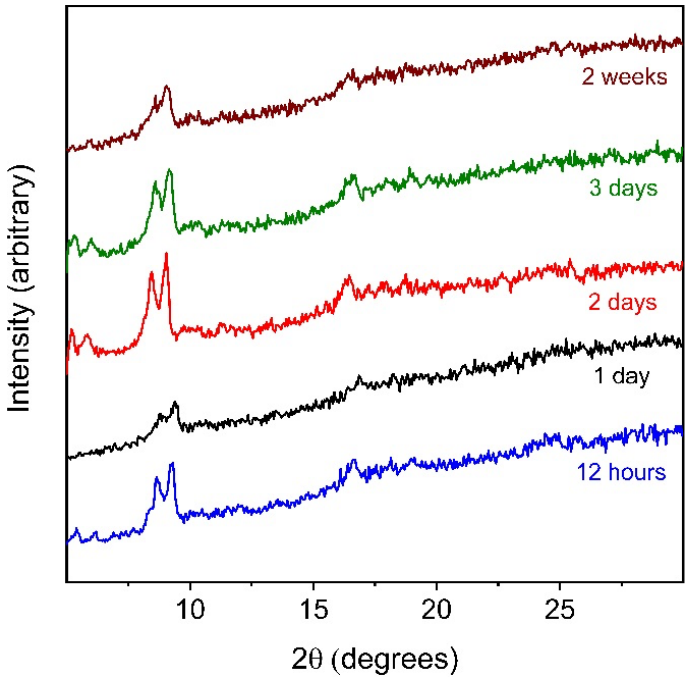

Figure S17. Powder X-ray diffraction patterns of Fe-MIL-101butyrylamido treated with a pH = 2 aqueous solution for 12 hours to 2 weeks.

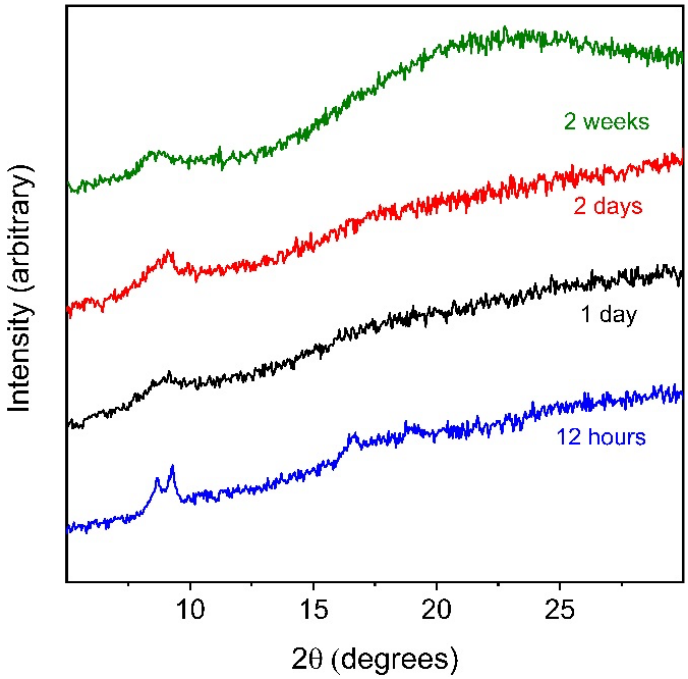

Figure S18. Powder X-ray diffraction patterns of Fe-MIL-101-butyrylamido treated with a pH = 5 aqueous solution for 12 hours to 2 weeks.

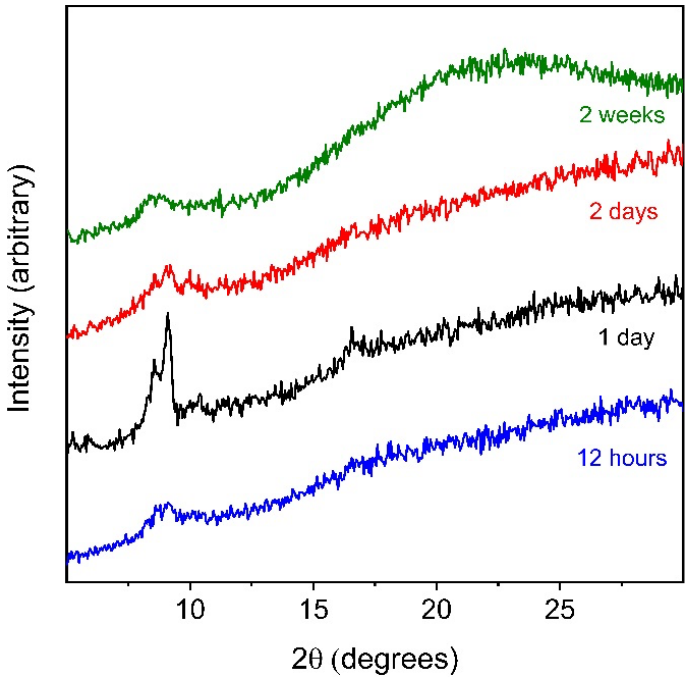

Figure S19. Powder X-ray diffraction patterns of Fe-MIL-101-butyrylamido treated with a pH = 8 aqueous solution for 12 hours to 2 weeks.

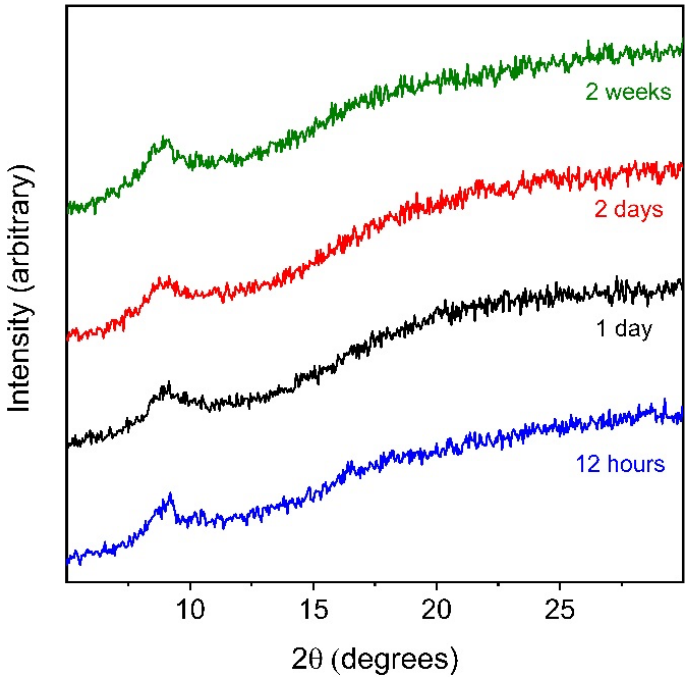

Figure S20. Powder X-ray diffraction patterns of Fe-MIL-101-butyrylamido treated with a pH = 11 aqueous solution for 12 hours to 2 weeks.

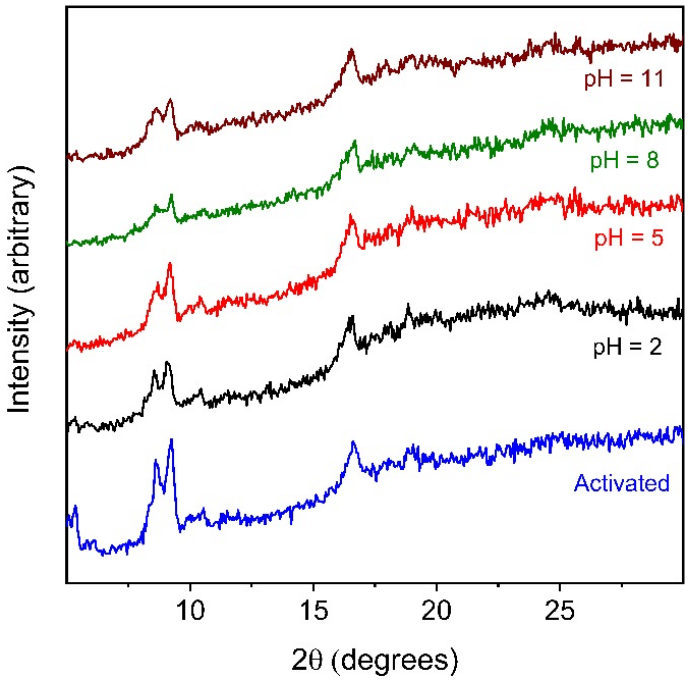

Figure S21. Powder X-ray diffraction patterns of Fe-Mil-101-lauroylamido treated with an acidic/basic aqueous solution for 12 hours.

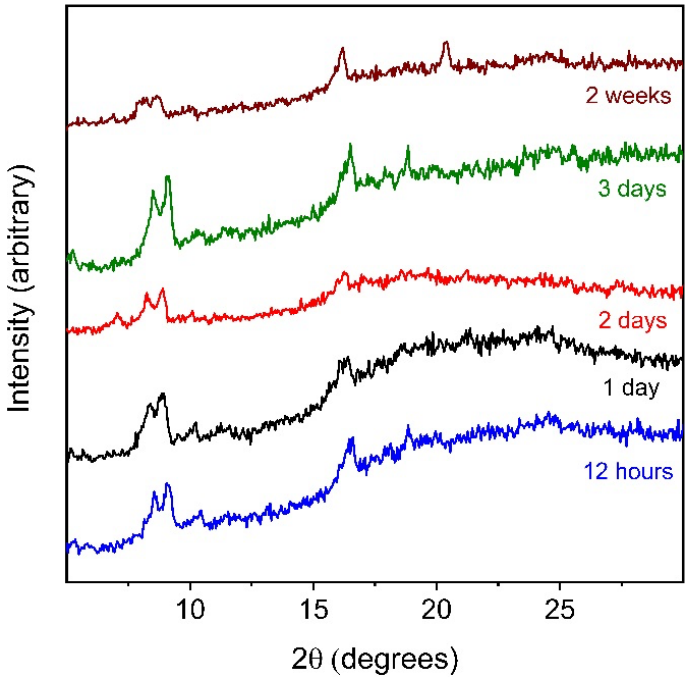

Figure S22. Powder X-ray diffraction patterns of Fe-MIL-101-lauroylamido treated with an aqueous pH = 2 solution for 12 hours to 2 weeks.

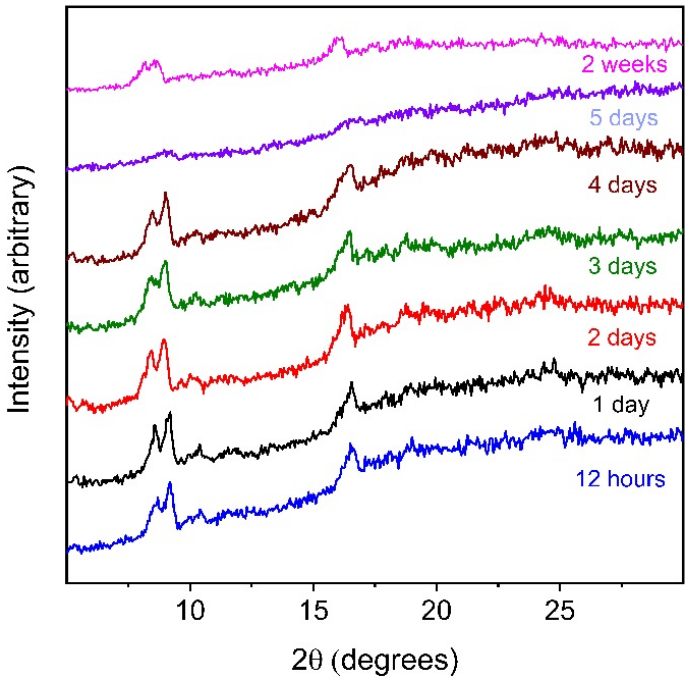

Figure S23. Powder X-ray diffraction patterns of Fe-MIL-101-lauroylamido treated with an aqueous pH = 5 solution for 12 hours to 2 weeks.

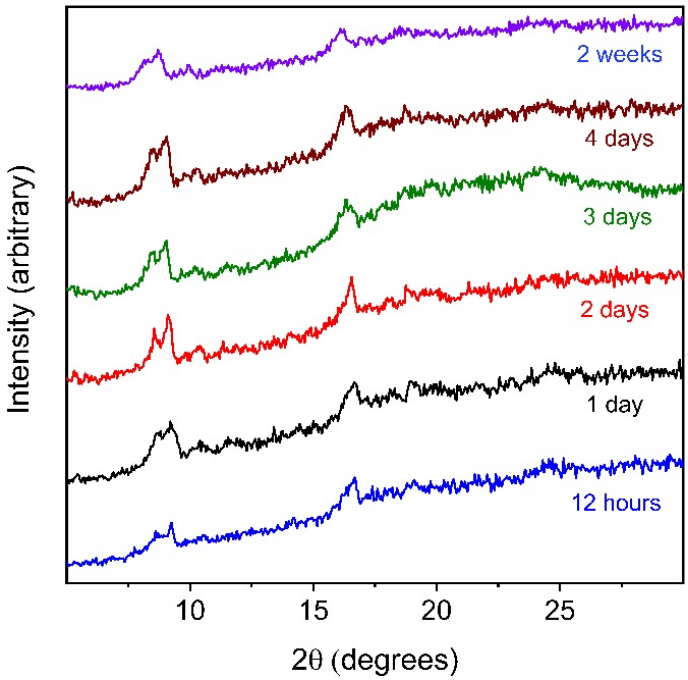

Figure S24. Powder X-ray diffraction patterns of Fe-MIL-101-lauroylamido treated with an aqueous pH = 8 solution for 12 hours to 2 weeks.

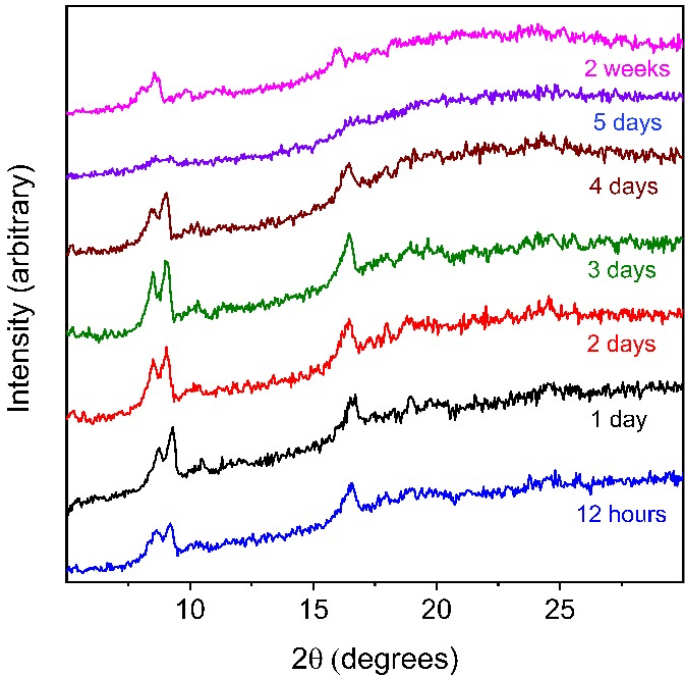

Figure S25. Powder X-ray diffraction patterns of Fe-MIL-101-lauroylamido treated with an aqueous pH = 11 solution for 12 hours to 2 weeks.

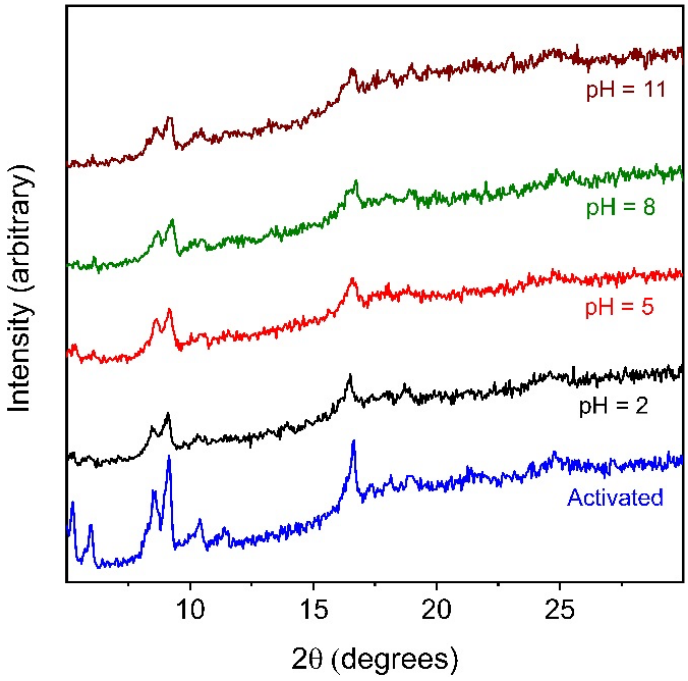

Figure S26. Powder X-ray diffraction patterns of Fe-MIL-101-trimethylhexanoylamido treated with an acidic/basic aqueous solution for 12 hours.

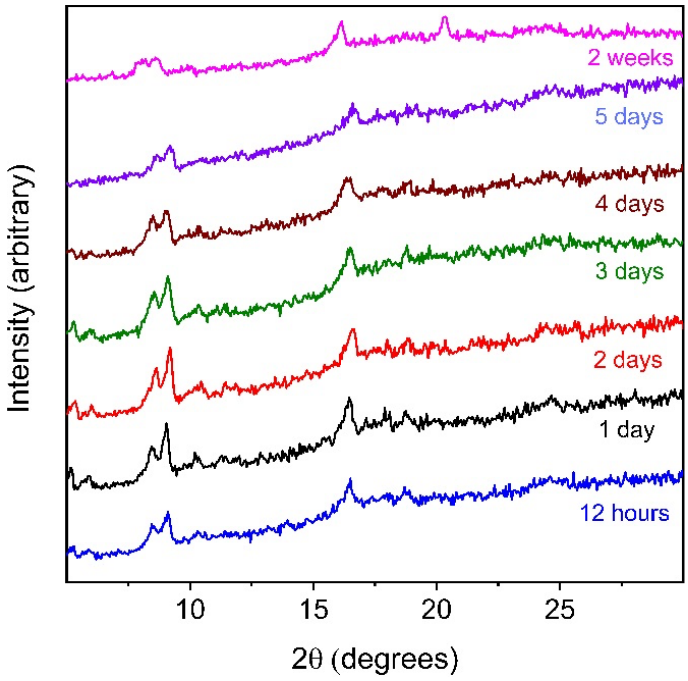

Figure S27. Powder X-ray diffraction patterns of Fe-MIL-101-trimethylhexanoylamido treated with an aqueous pH = 2 solution for 12 hours to 2 weeks.

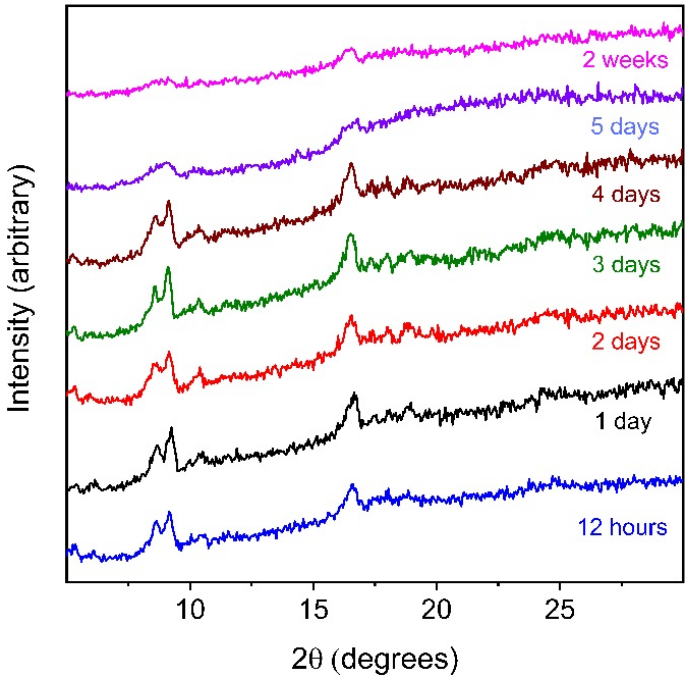

Figure S28. Powder X-ray diffraction patterns of Fe-MIL-101-trimethylhexanoylamido treated with an aqueous pH = 5 solution for 12 hours to 2 weeks

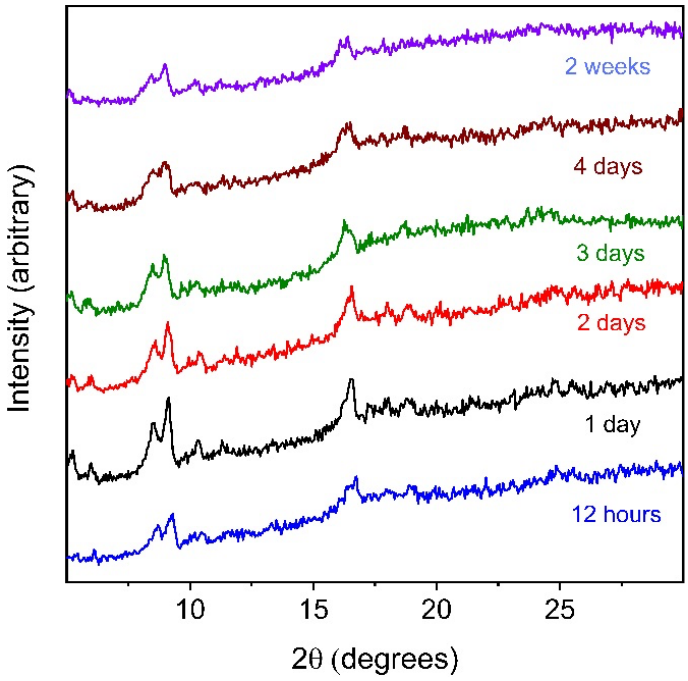

Figure S29. Powder X-ray diffraction patterns of Fe-MIL-101-trimethylhexanoylamido treated with an aqueous pH = 8 solution for 12 hours to 2 weeks

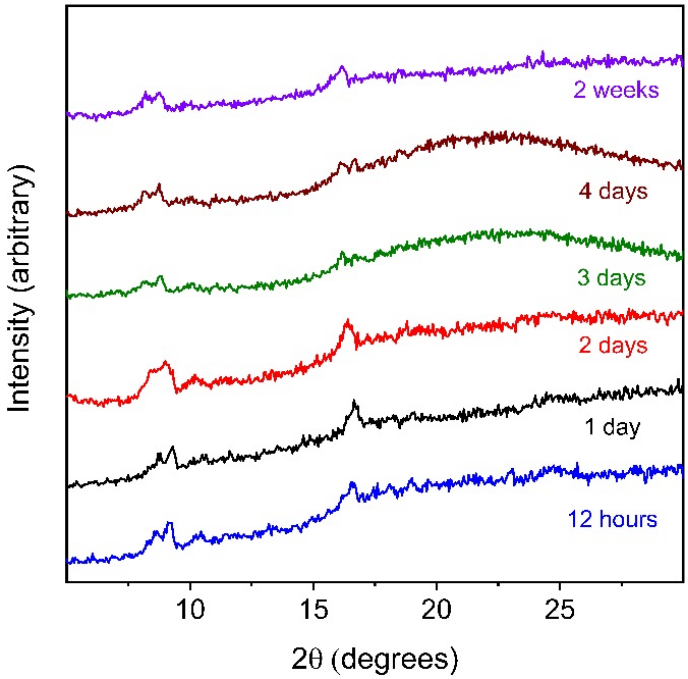

Figure S30. Powder X-ray diffraction patterns of Fe-MIL-101-trimethylhexanoylamido treated with an aqueous pH = 11 solution for 12 hours to 2 weeks

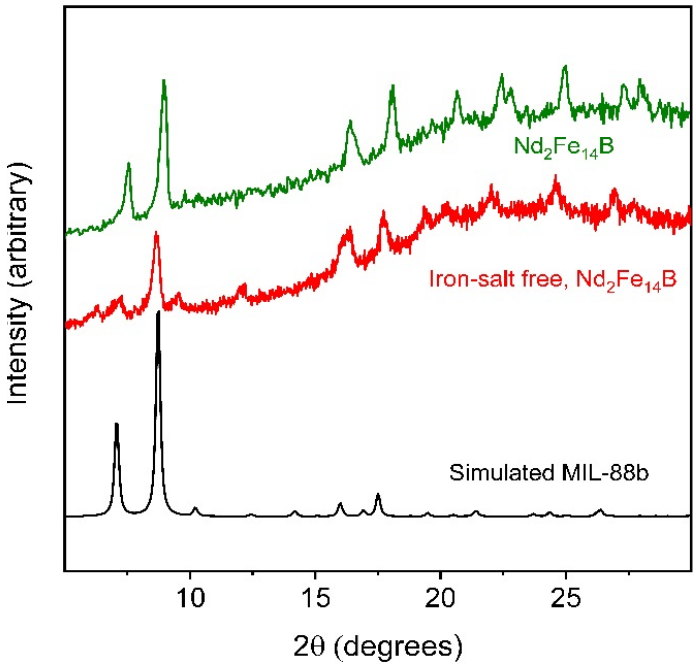

Figure S31. Powder X-ray diffraction patterns of Fe-MIL-88b-propyonylamido synthesized with the use of $Nd_2Fe_{14}B$, as compared to simulated Fe-MIL-88b.

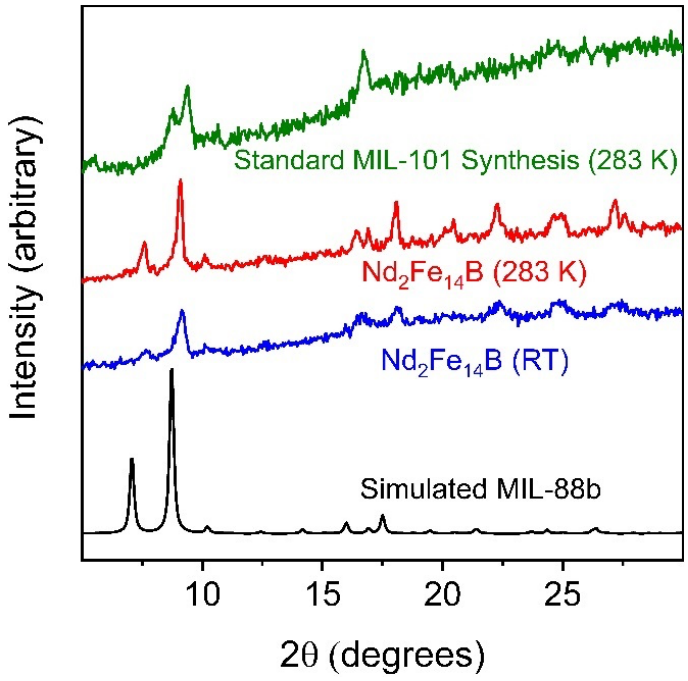

Figure S31. Powder X-ray diffraction patterns of Fe-MIL-88b-acylamido synthesized with the use of $Nd_2Fe_{14}B$, as compared to Fe-MIL-101-acylamido and the simulated Fe-MIL-88b.

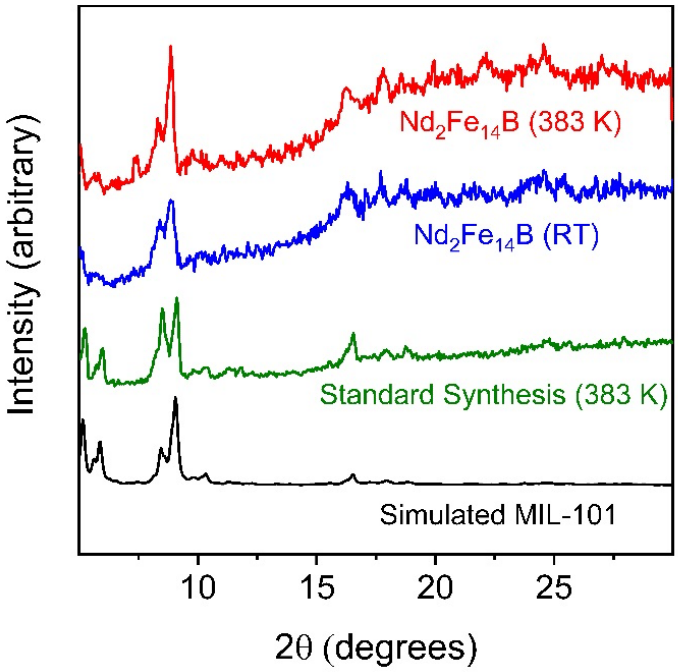

Figure S32. Powder X-ray diffraction patterns of Fe-MIL-10-propionylamino synthesized with and without the use of $Nd_2Fe_{14}B$, as compared to simulated Fe-MIL-101.

Table S1. BET (Langmuir) surface areas of select samples after water adsorption. Unless otherwise noted, data are based on 77 K N_2 isotherms.

	Initial S.A. (m^2/g) BET (Lang.)	After H_2O S.A. (m^2/g) BET (Lang.)	After 2nd H_2O S.A. (m^2/g) BET (Lang.)	After 2nd H_2O S.A. (m^2/g) BET (Lang.) CO_2 @ 195 K
MIL-101-butyrylamido	1949 (2486)	177 (189)	59 (61)	191 (389)
MIL-101-trimethylhexamido	1425 (1757)	1124 (1428)	848 (1101)	507 (1512)
MIL-101-lauroylamido	929 (1177)	38 (39)	21 (29)	226 (379)

N_2 Isotherms

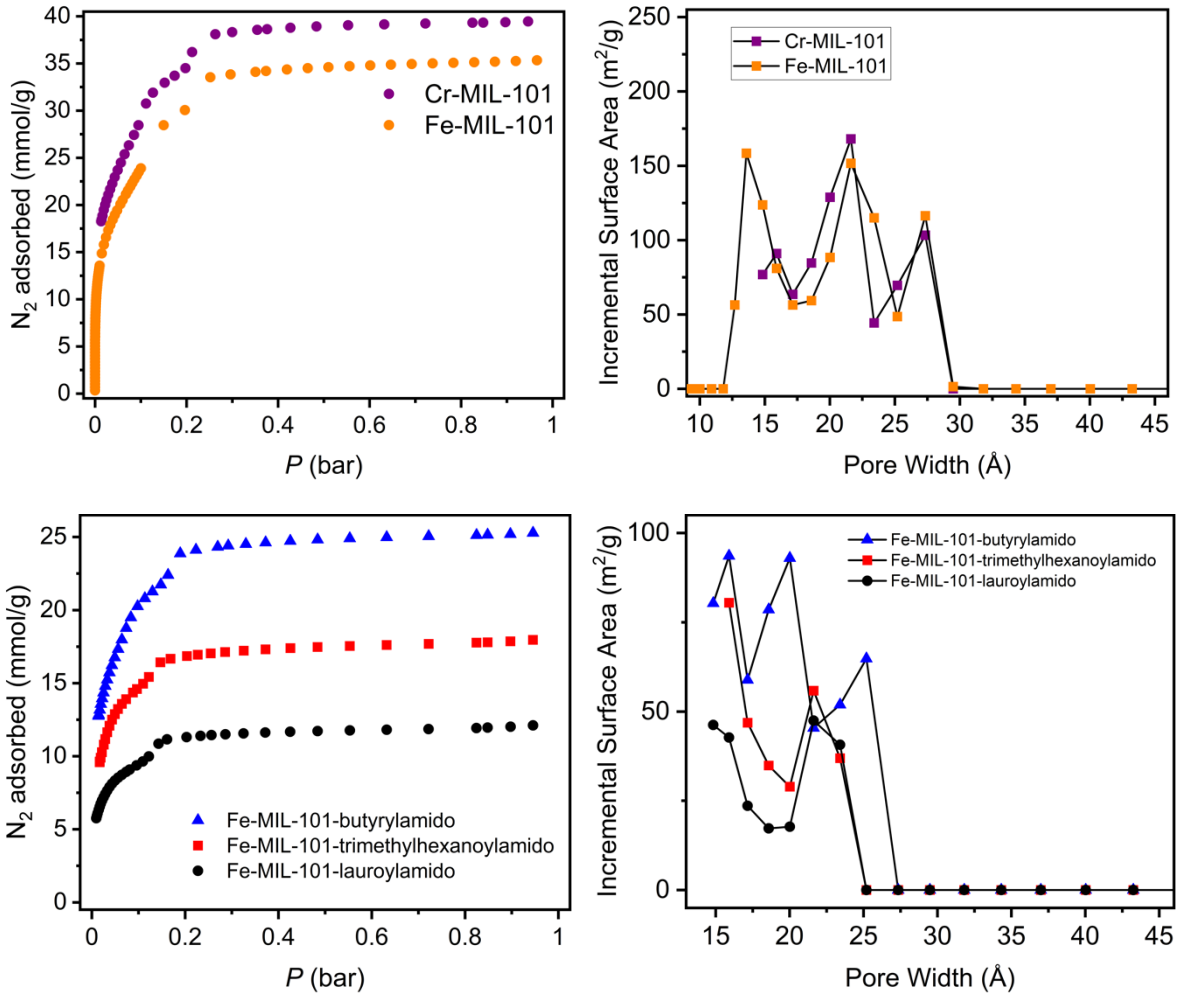

Figure S33. N_2 isotherms and corresponding pore size distributions for Fe-MIL-101 and Cr-MIL-101 (top) and select amide-functionalized materials (bottom).

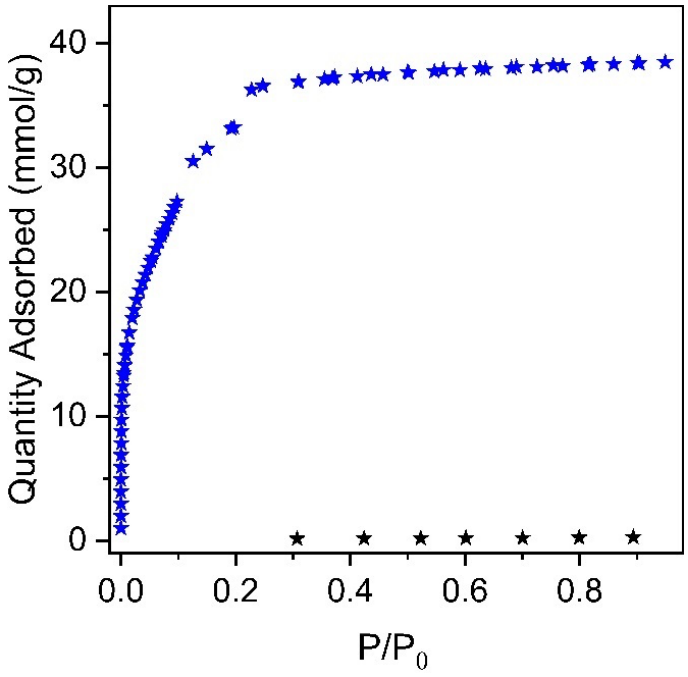

Figure S34. N_2 isotherm for Fe-MIL-101, before (blue star) and after (black star) exposure to water vapor.

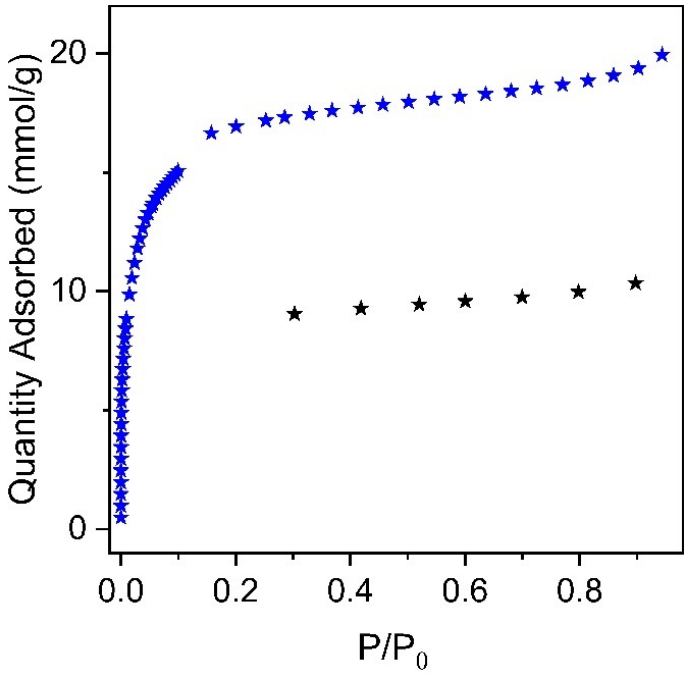

Figure S35. N_2 isotherm for Fe-MIL-101-trimethylhexanoylamido, before (blue star) and after (black star) exposure to water vapor.

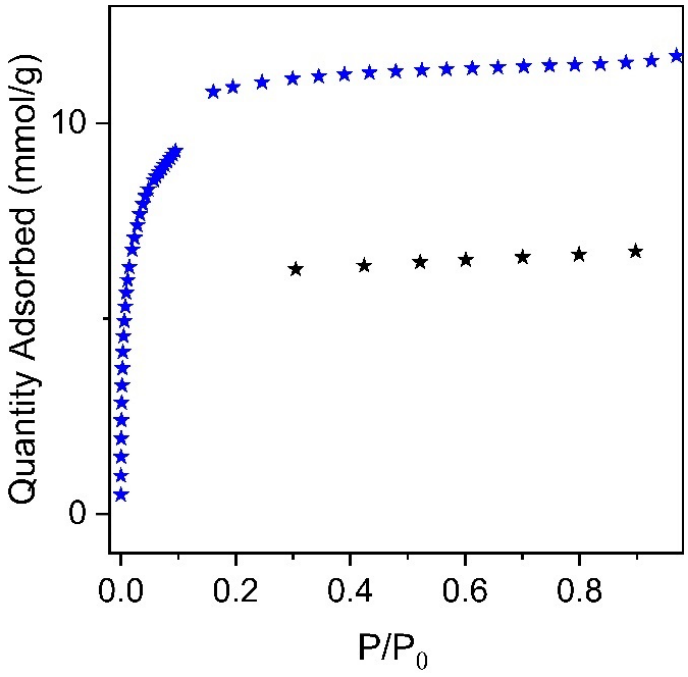

Figure S36. N_2 isotherm for Fe-MIL-101-lauroylamido, before (blue star) and after (black star) exposure to water vapor.

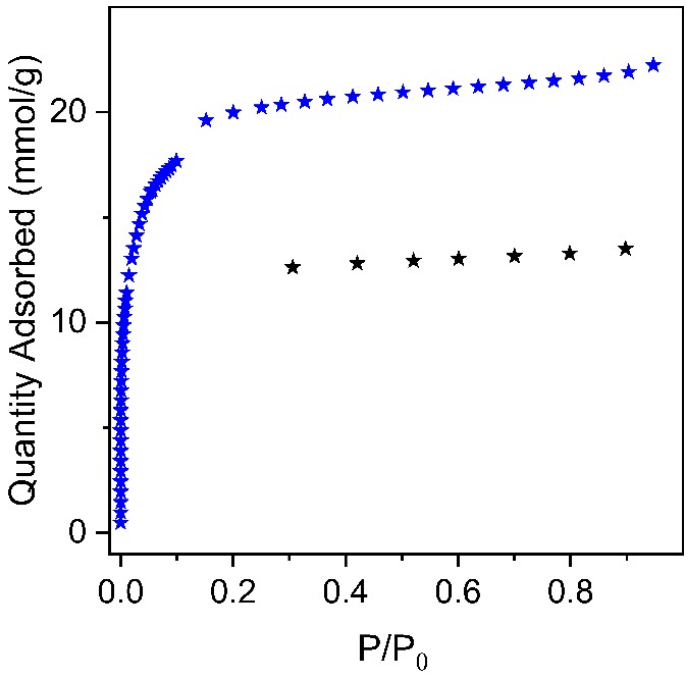

Figure S37. N_2 isotherm for Fe-MIL-101-phenylamido, before (blue star) and after (black star) exposure to water vapor.

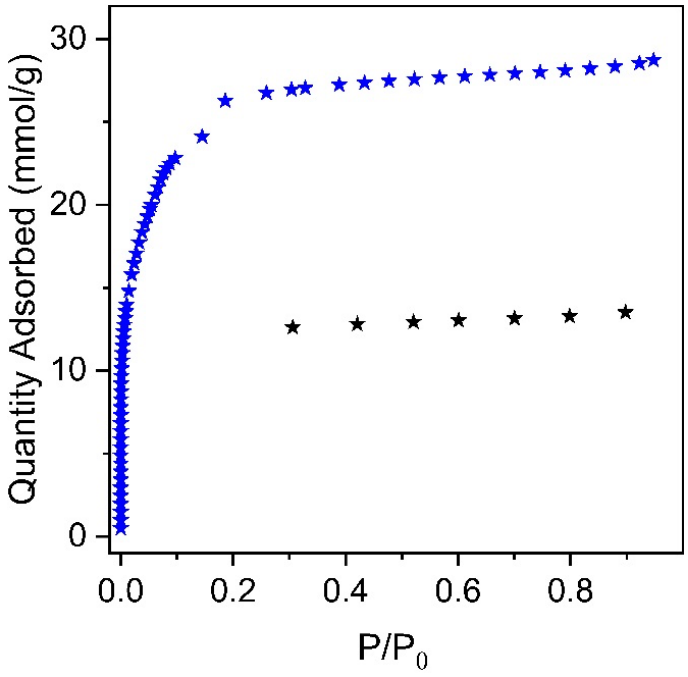

Figure S38. N_2 isotherm for Fe-MIL-101-propyonylamido, before (blue star) and after (black star) exposure to water vapor.

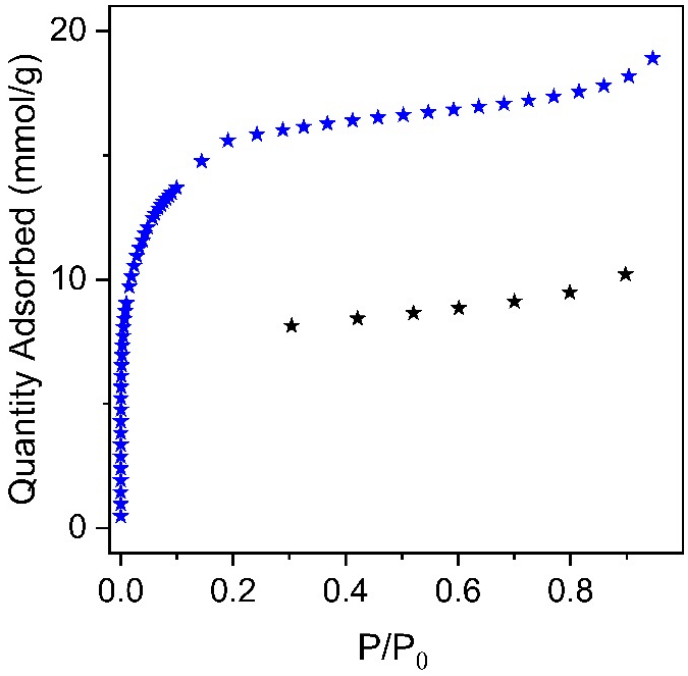

Figure S39. N_2 isotherm for Fe-MIL-101-naphthoylamido, before (blue star) and after (black star) exposure to water vapor.

H_2O Isotherms

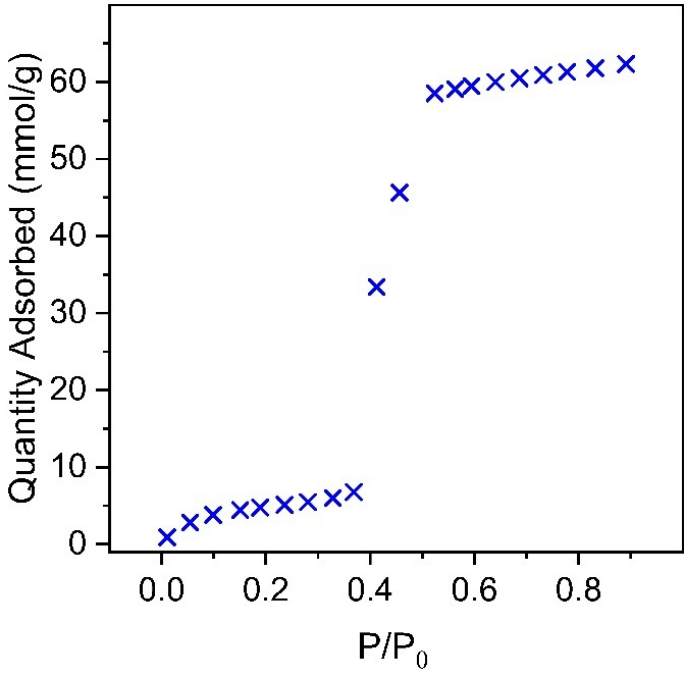

Figure S40. Water adsorption isotherms for Cr-MIL-101.

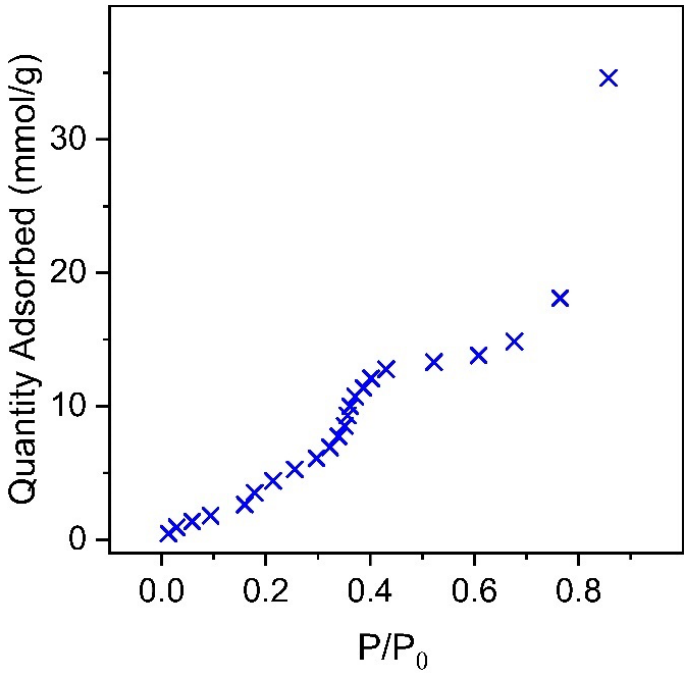

Figure S41. Water adsorption isotherms for Fe-MIL-101.

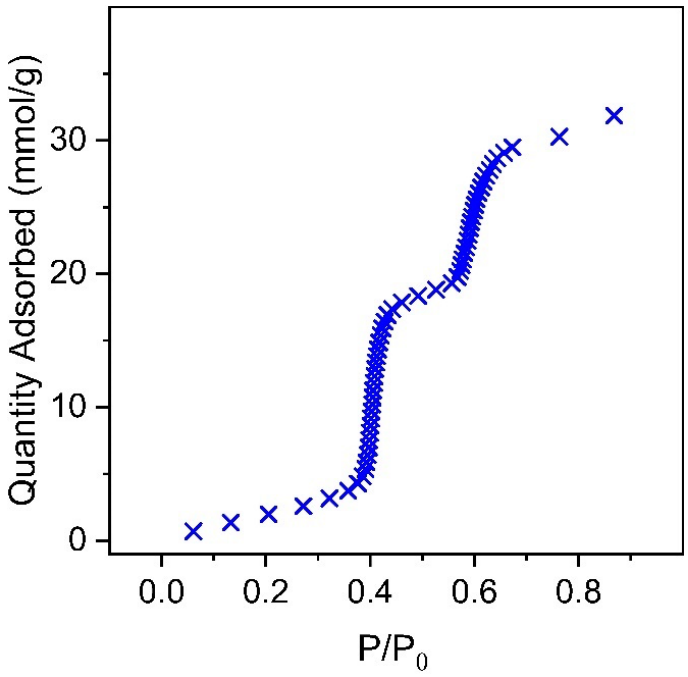

Figure S42. Water adsorption isotherms for Fe-MIL-101-butyrylamido.

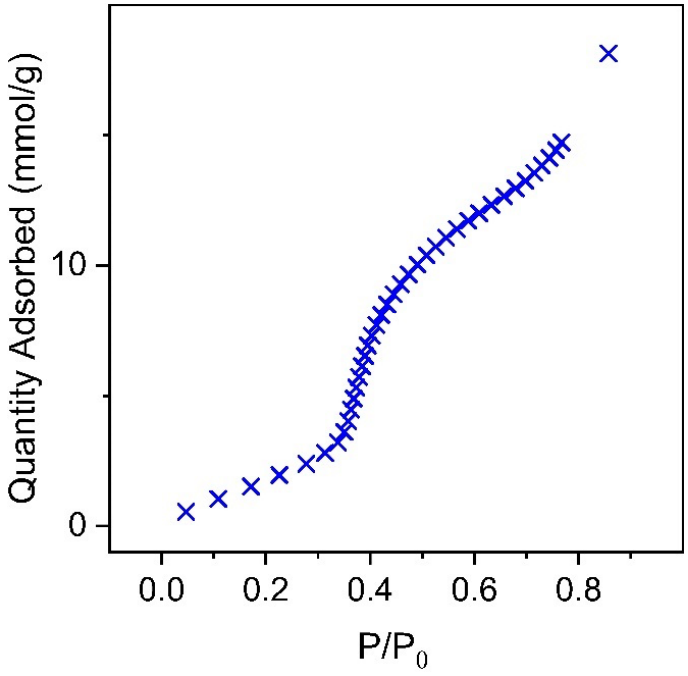

Figure S43. Water adsorption isotherms for Fe-MIL-101-3,3,5-trimethylhexanoylamido.

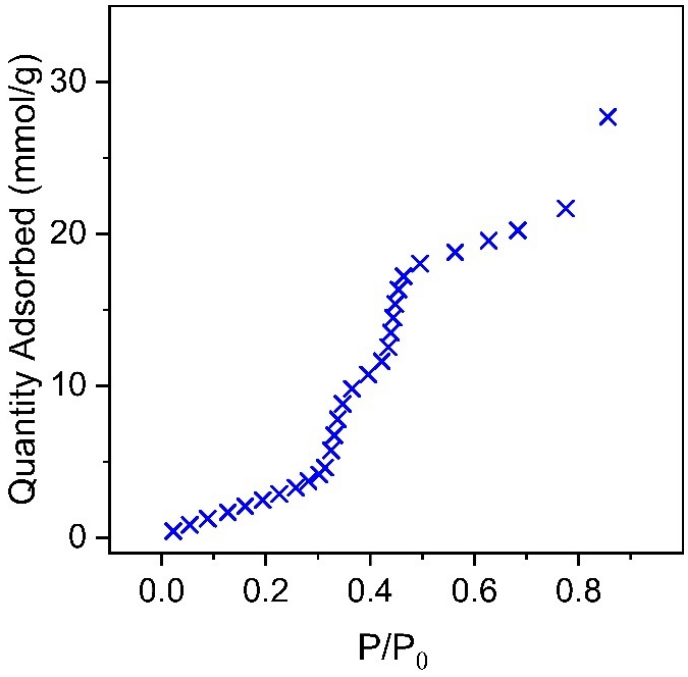

Figure S44. Water adsorption isotherms for Fe-MIL-101-naphthoylamido.

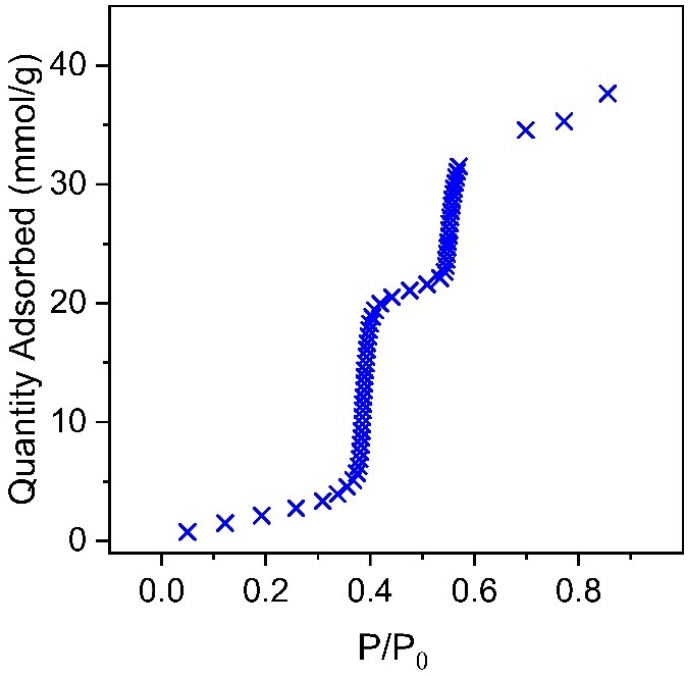

Figure S45. Water adsorption isotherms for Fe-MIL-101-propanoylamido.

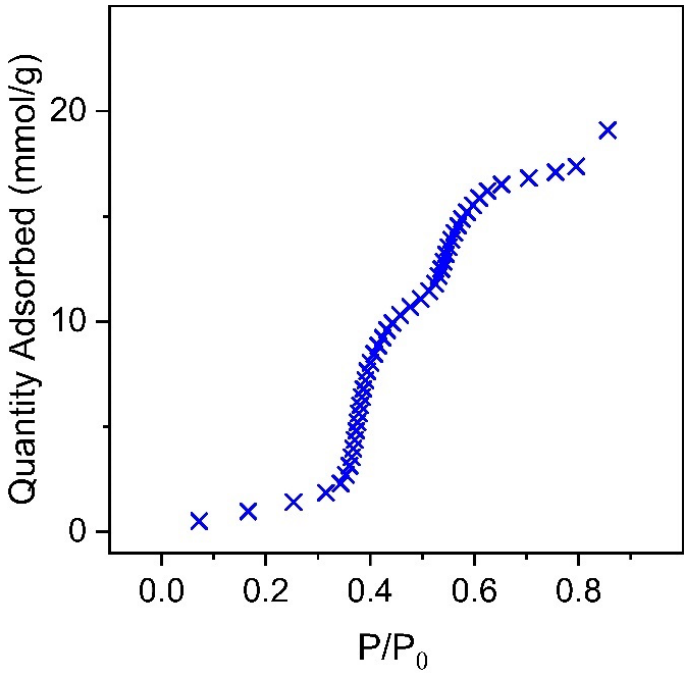

Figure S46. Water adsorption isotherms for Fe-MIL-101-phenylamido.

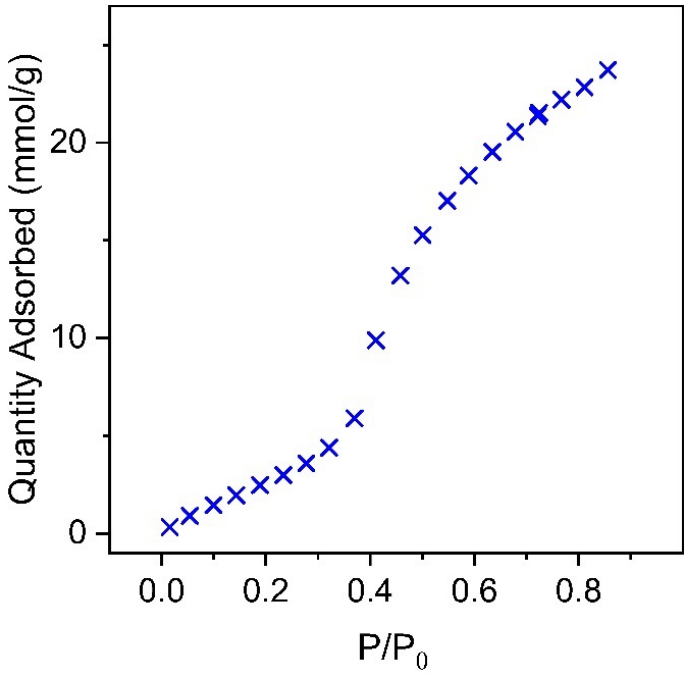

Figure S47. Water adsorption isotherms for Fe-MIL-101-cyclohexanoylamido.

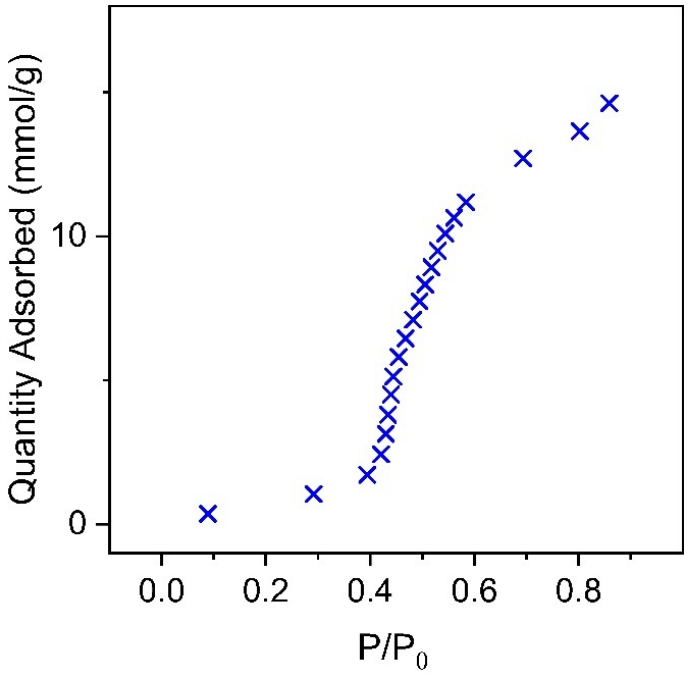

Figure S48. Water adsorption isotherms for Fe-MIL-101-lauroylamido.

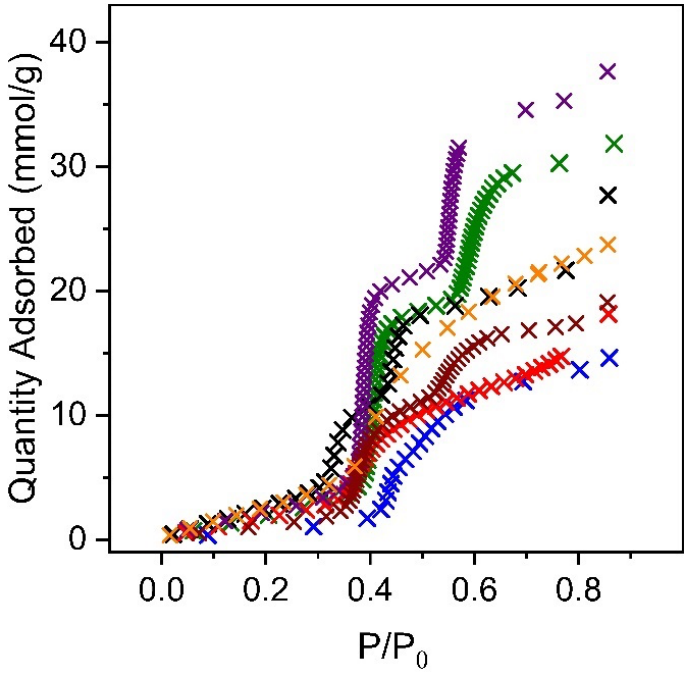

Figure S49. Water adsorption isotherms for Fe-MIL-101-propyonylamido (purple), Fe-MIL-101-butyrylamido (green), Fe-MIL-101-naphthoylamido (black), Fe-MIL-101-cyclohexanoylamido (orange), Fe-MIL-101-phenylamido (maroon), Fe-MIL-101-3,3,5-trimethylhexanoylamido (red) and Fe-MIL-101-lauroylamido (blue).

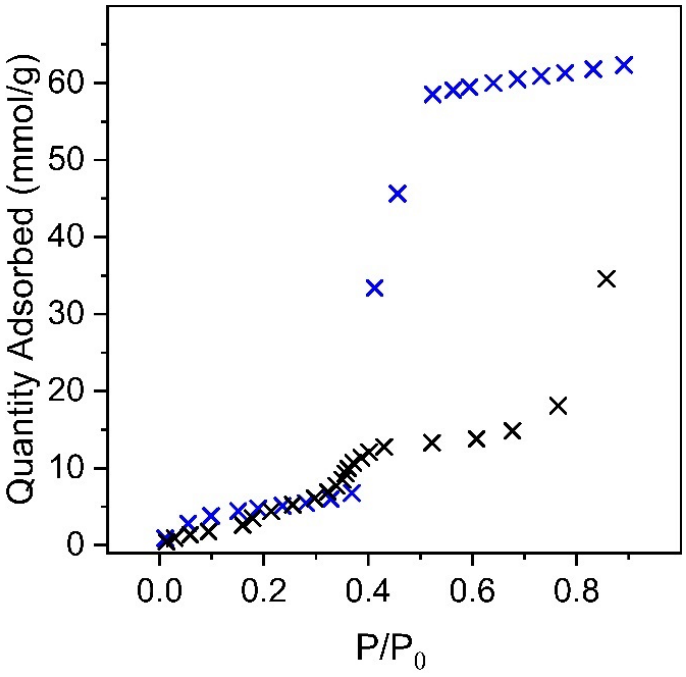

Figure S50. Water adsorption isotherm for Fe-MIL-101 (black) and Cr-MIL-101 (blue).

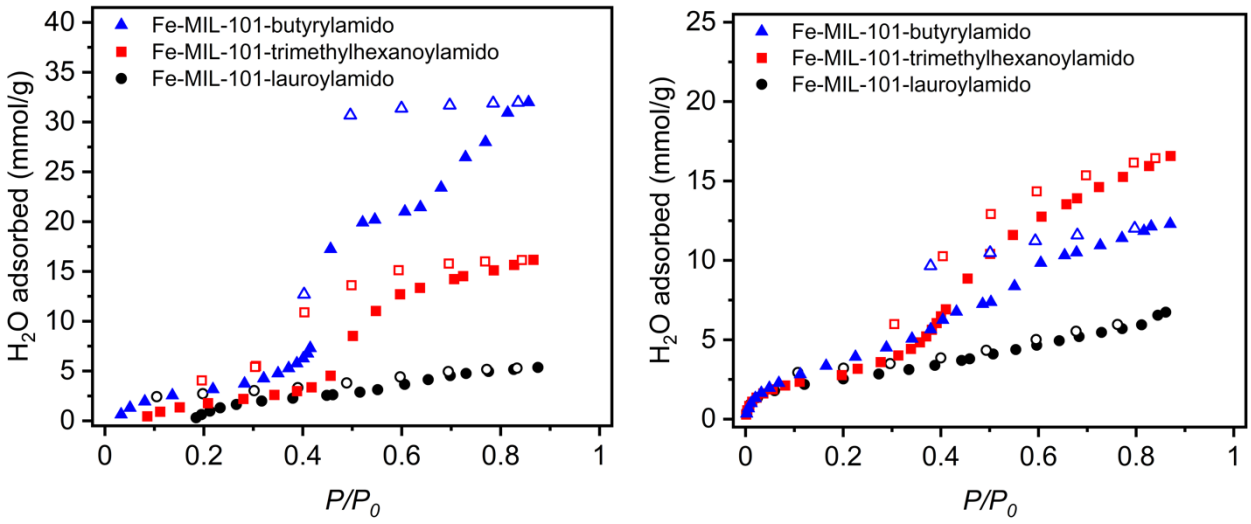

Figure S51. Water adsorption isotherms for select amide-functionalized materials. First cycle (left) and second cycle (right).

Pawley Refinements

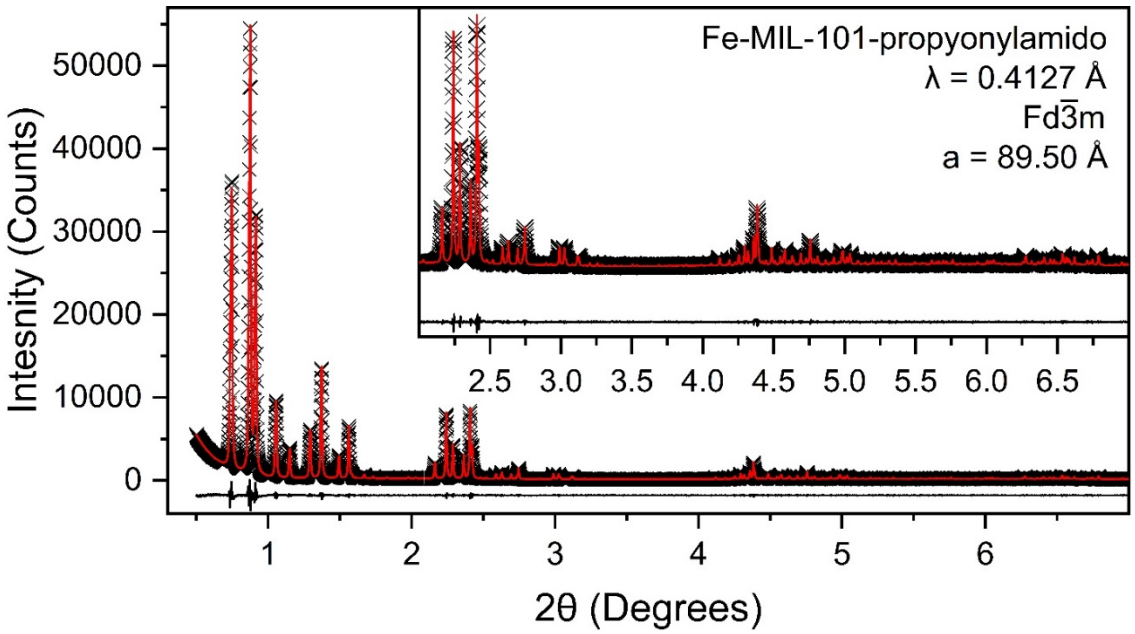

Figure S52. Pawley refinement of Fe-MIL-101-propyonylamido with the X-ray powder data (black X), fit (red line), and difference curve (black line). Resulting Fit statistics were R_{wp} = 4.31 %, R_p = 3.22 %, and GoF = 1.28.

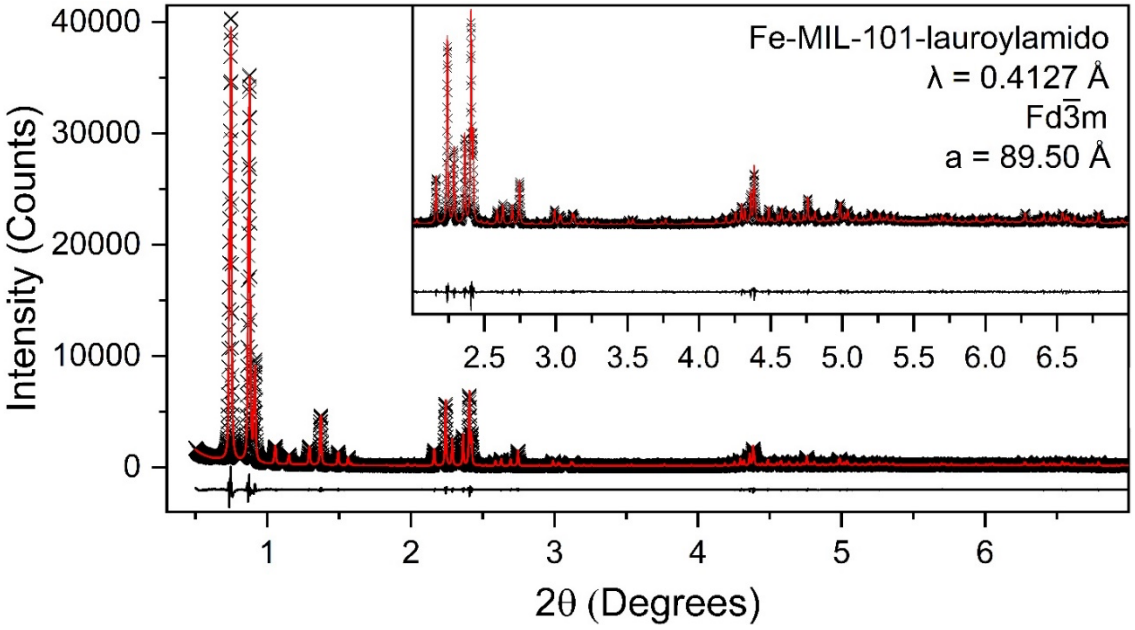

Figure S53. Pawley refinement of Fe-MIL-101-lauroylamido with the X-ray powder data (black X), fit (red line), and difference curve (black line). Resulting Fit statistics were R_{wp} = 5.63 %, R_p = 4.29 %, and GoF = 1.36.

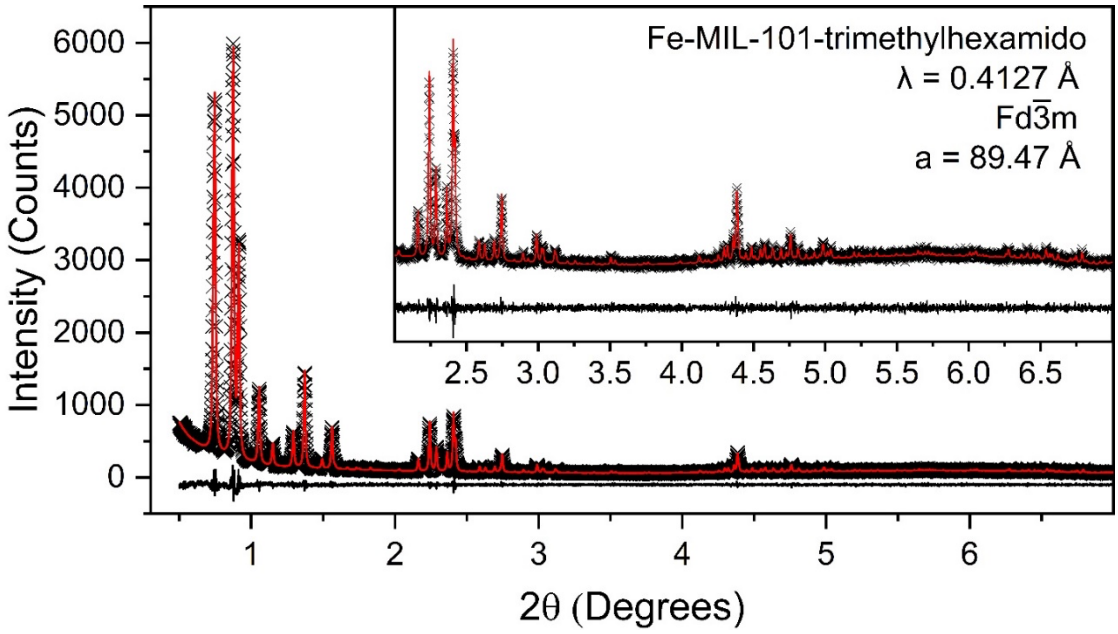

Figure S54. Pawley refinement of Fe-MIL-101-triemthylhexamido with the X-ray powder data (black X), fit (red line), and difference curve (black line). Resulting Fit statistics were R_{wp} = 6.65 %, R_p = 4.85 %, and GoF = 0.92 .

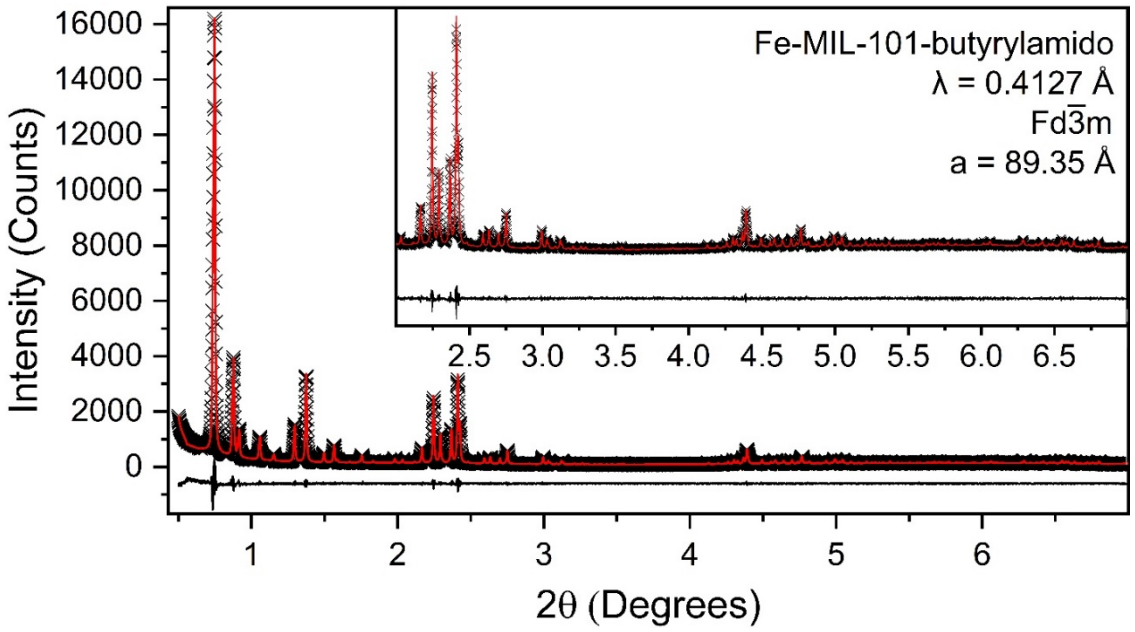

Figure S55. Pawley refinement of Fe-MIL-101-prop with the X-ray powder data (black X), fit (red line), and difference curve (black line). Resulting Fit statistics were R_{wp} = 6.97 %, R_p = 5.53 %, and GoF = 1.20 .

Thermogravimetric Analysis

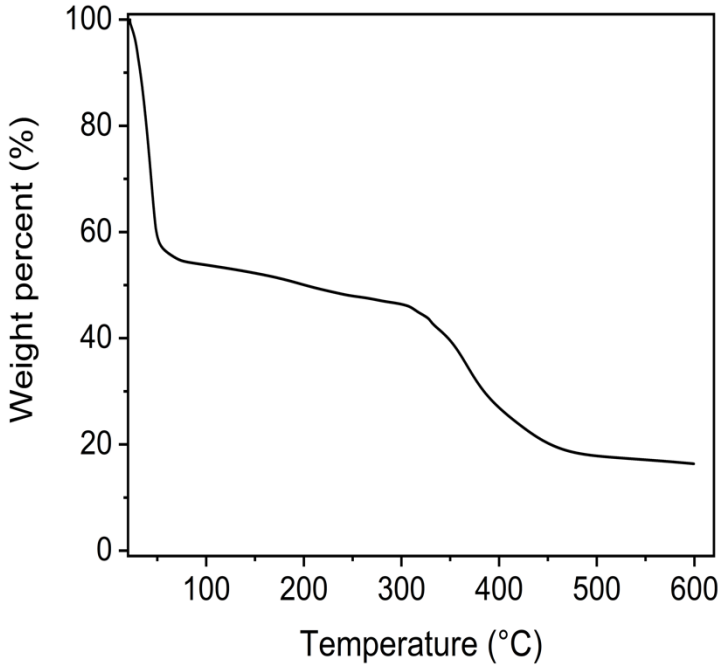

Figure S56. Thermogravimetric analysis for Cr-MIL-101.

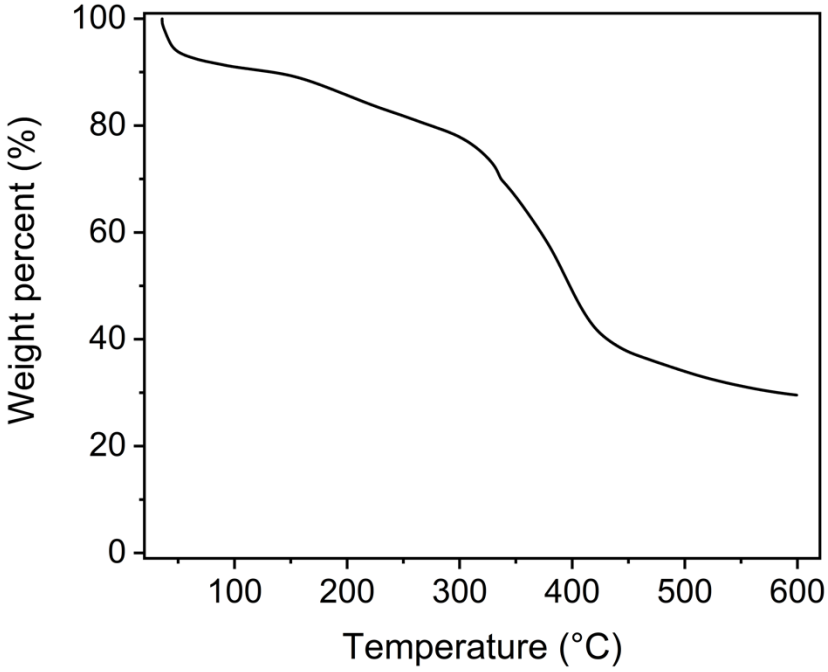

Figure S57. Thermogravimetric analysis for Fe-MIL-101.

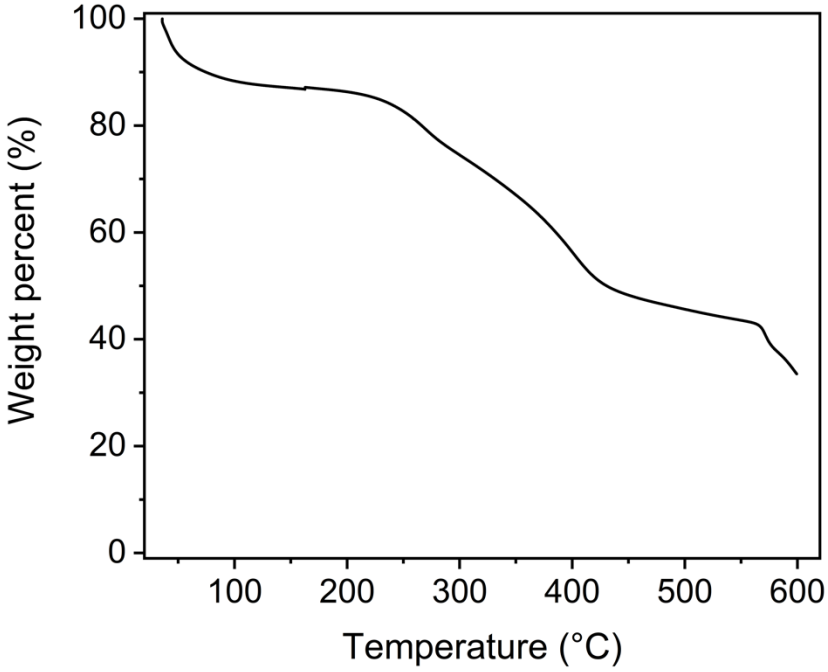

Figure S58. Thermogravimetric analysis for Fe-MIL-101-butyrylamido.

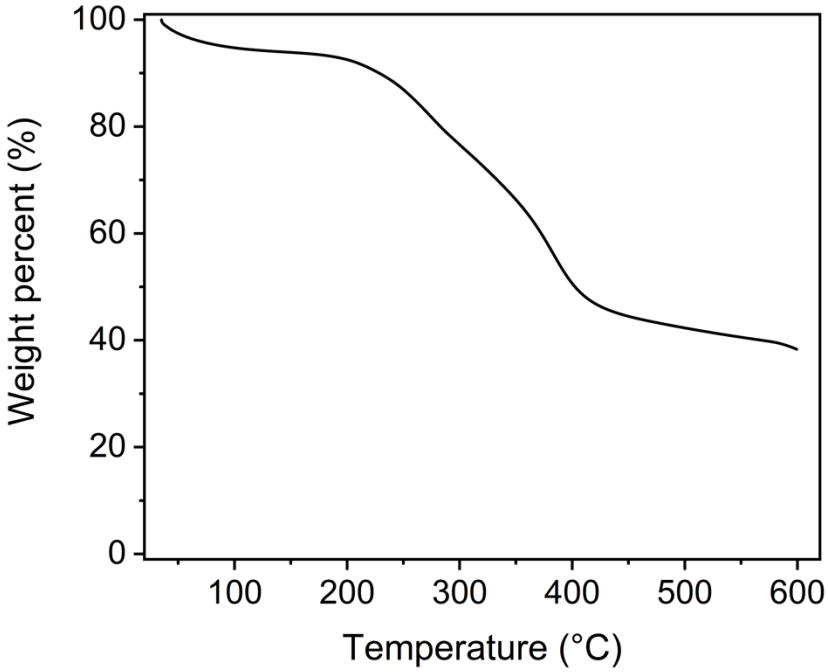

Figure S59. Thermogravimetric analysis Fe-MIL-101-3,3,5-trimethylhexanoylamido.

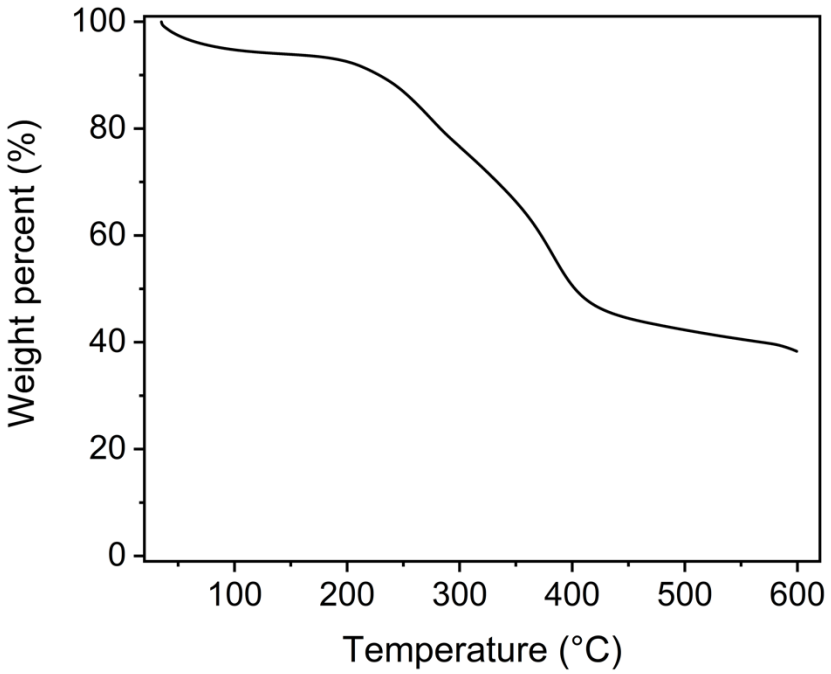

Figure S60. Thermogravimetric analysis Fe-MIL-101-3,3,5-trimethylhexanoylamido.

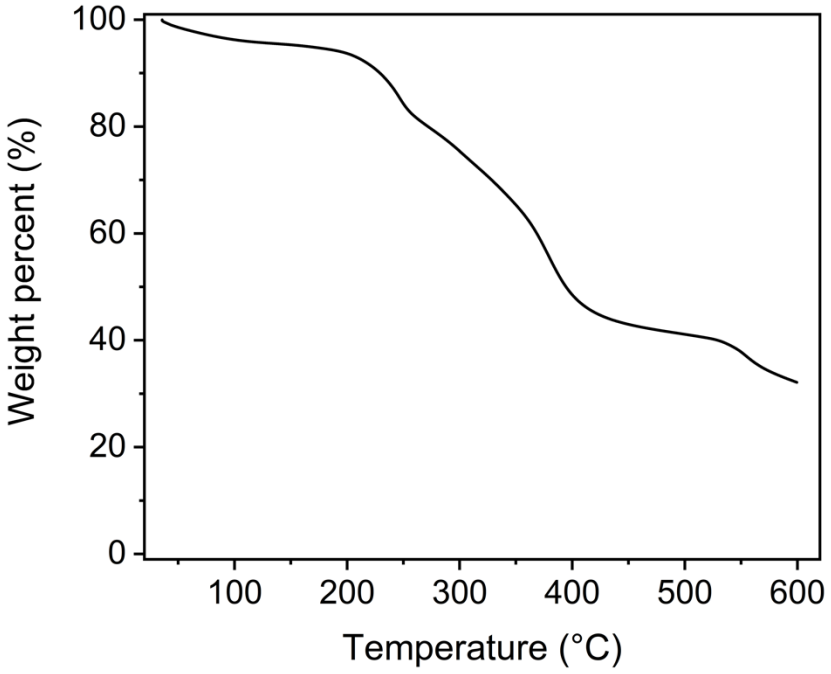

Figure S61. Thermogravimetric analysis Fe-MIL-101-lauroylamido.

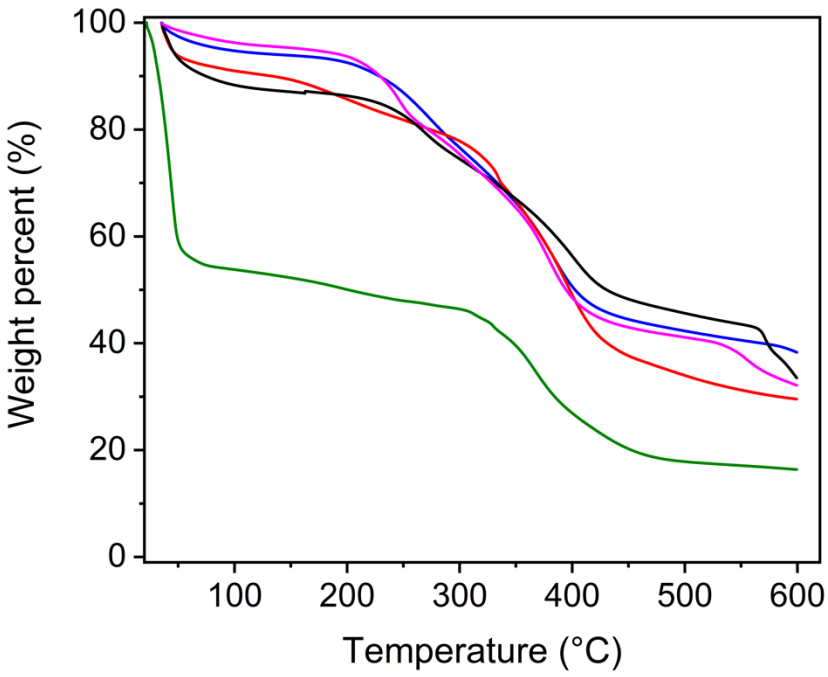

Figure S62. Thermogravimetric analysis of Cr-MIL-101 (Green), Fe-MIL-101 (orange), Fe-MIL-101-butyrylamido (black), Fe-MIL-101-3,3,5-trimethylhexanoylamido (blue), and Fe-MIL-101-lauroylamido (pink).

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