Systematic Pore Hydrophobicization to Enhance the Efficiency of an Amine-Based MOF Catalyst – Supporting Information

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MATERIALS

All chemicals were used as received from commercial sources unless otherwise noted. Isopropyl isocyanate (98%), tert butyl isocyanate (97%) and tetradecyl isocyanate (97%) were purchased from Sigma Aldrich. Hexyl isocyanate (99%) and 2-aminoterephthalic acid (BDC-NH_2) (99%) were purchased from Thermo Scientific. Meso-*α*,*β*-di(4-pyridyl) glycol (>98%) (DPG) and malononitrile (97%) were purchased from TCI. Sulfuric acid-d_2 (D_2SO_4, 98 wt.% in D_2O, 99.5+% atom D) was purchased from Acros Organics. *N*,*N*-dimethylformamide (DMF), toluene, acetonitrile and benzaldehyde were purchased from Fisher Scientific (ACS certified). Zinc nitrate hexahydrate from Strem Chemicals and 1,4-Diazabicyclo[2.2.2]octane (DABCO) (95%) was purchased from Oakwood Products. Dimethyl sulfoxide-d_6 (d_6-DMSO, 99.9 atom % D) was purchased from Cambridge Isotopes Laboratories.

SYNTHETIC PROCEDURES

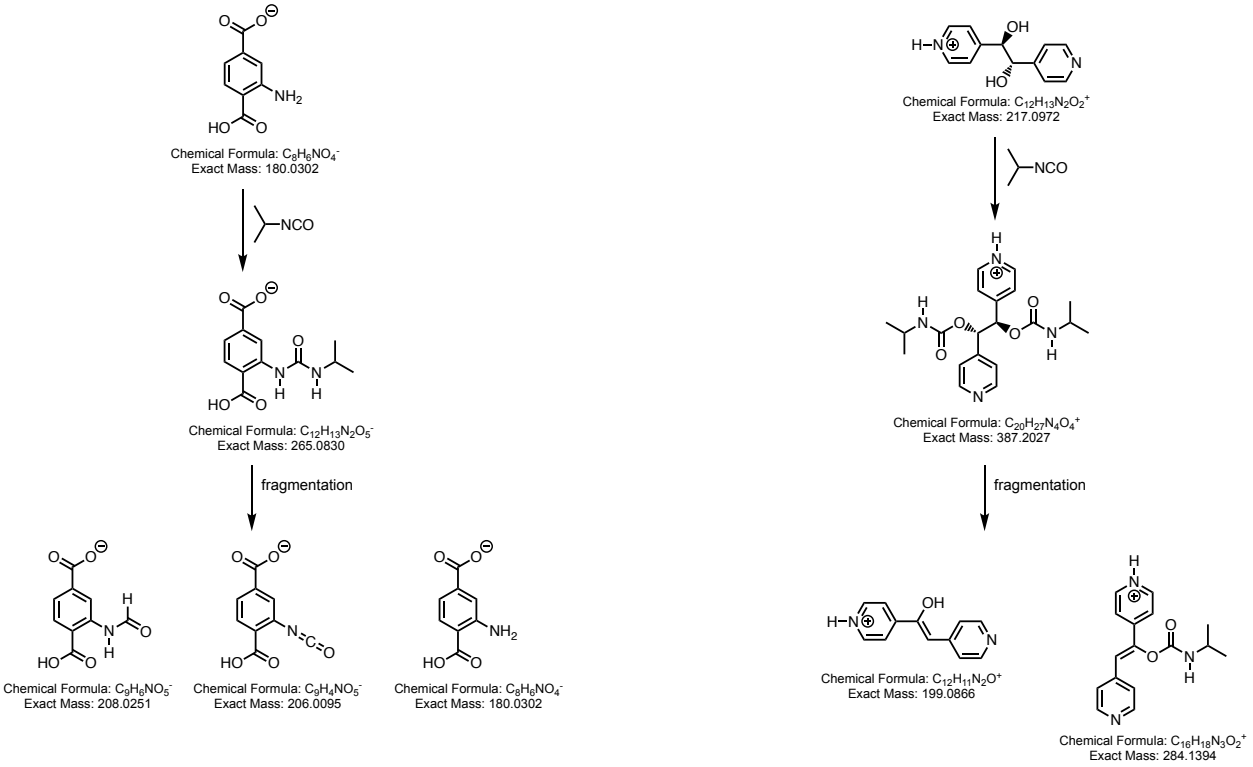
KSU-1 was synthesized according to the literature procedure.[26]

General procedure for the reaction of MOF materials with isocyanates.
In a typical experiment, ~ 10mg of KSU-1 (0.012mmol) (–OH (0.025mmol) and –NH_2 (0.025mmol)) as-synthesized in DMF was transferred to a 1-dram vial. Then, 2mL of a 0.2 M solution of the isocyanate (0.4 mmol) in acetonitrile were added to the vial. The reaction was left at 80 °C with continuous mixing on a Corning LSE Low Speed Orbital Shaker. Samples of the reacted MOF were taken at 3h, washed in acetonitrile 3 times filtered, and digested for analysis.

General procedure for catalysis
MOF material (0.0075mmol) was introduced into a 0.10 mL glass vial. Benzaldehyde (0.5 mmol; 50.8 uL) and malononitrile (0.55 mmol; 36.5 mg) were then added and the vial was sealed. For reactions in solvent, MOF material (0.0075mmol) was introduced into a 0.10 mL glass vial. Benzaldehyde (0.0625 mmol; 6.35 uL) and malononitrile (0.068 mmol; 4.5 mg) were then added and the vial was sealed 250 μL of toluene were added, and for those with internal standard, 14.2 μL (0.08 mmol) of dodecane were also added. The resultant suspension was allowed to react at 50 °C for 30 min. After quenching by cooling to room temperature, the product dissolved with $CHCl_3$ to separate the solid catalyst. The supernatant was analyzed by ^{1}H-NMR and the yield determined by integration of signals using disappearance of the starting material to appearance of product.

HIGH-RESOLUTION MASS SPECTROMETRY (HRMS)

MOF samples (~5mg) were placed in a solution of DABCO (10 mg) and 0.25ml of DMSO in a 2-dram vial. The vial was sonicated for ~ 1 min then heated at 80 °C overnight. A small amount of residue was filtered out and the resulting solution was analyzed using a Xevo G2-XS QTof quadrupole time-of-flight mass spectrometer coupled with an ACQUITY M-class UPLC and a NanoLockSpray dual electrospray ion source. Mass spectra were acquired in “eXtreme Resolution” mode.



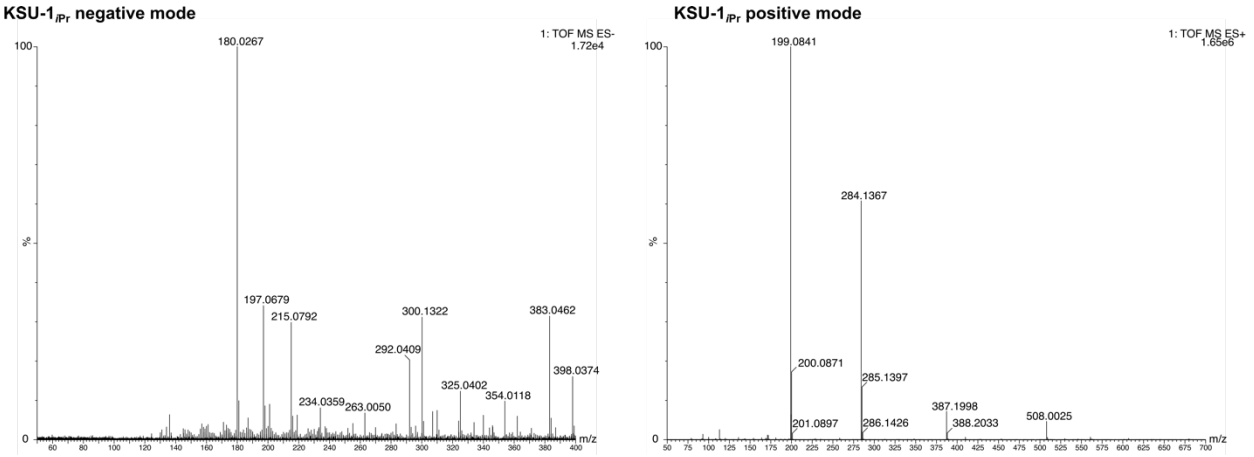
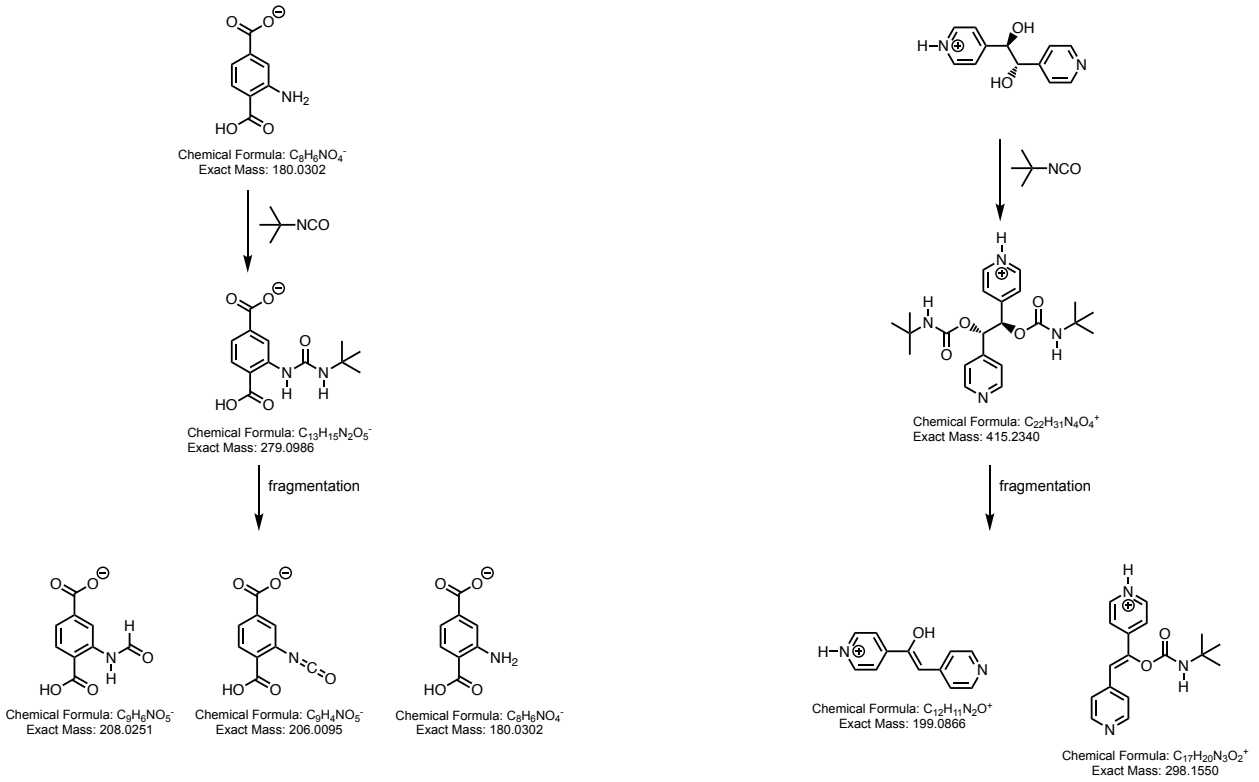


Figure S1: HRMS of **KSU-1** after reacting with isopropyl isocyanate to form **KSU-1$_{iPr}$**. Left: the negative mode has no indication of the BDC urea product (m/z = 265.0267), though the [BDC-NH_2-H^+] starting material peak could also be a fragmentation product. Right: the positive mode has m/z peaks corresponding to [$DPG_{dicarbamate}$+H^+] (m/z = 284.1394) and its various fragmentation products.



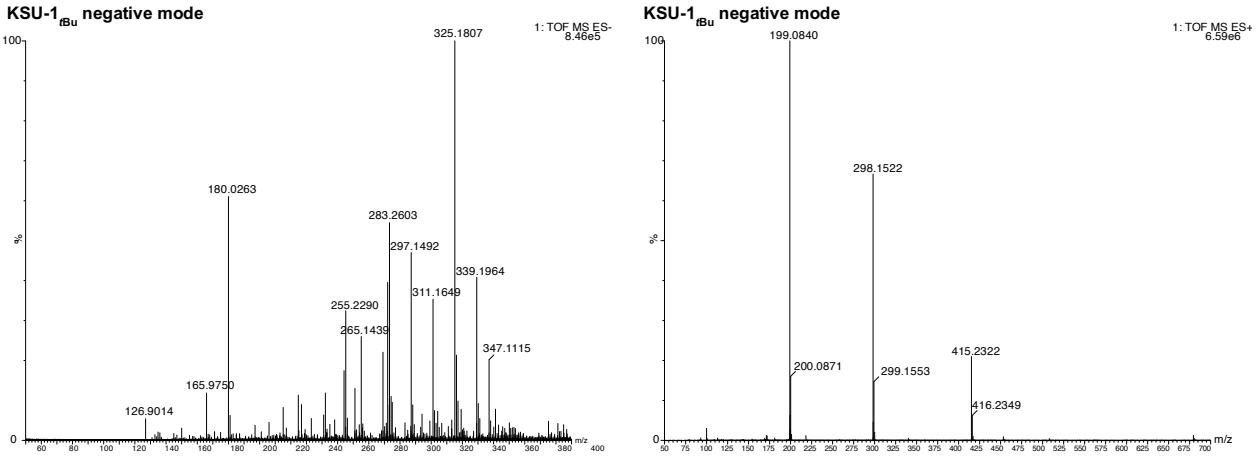
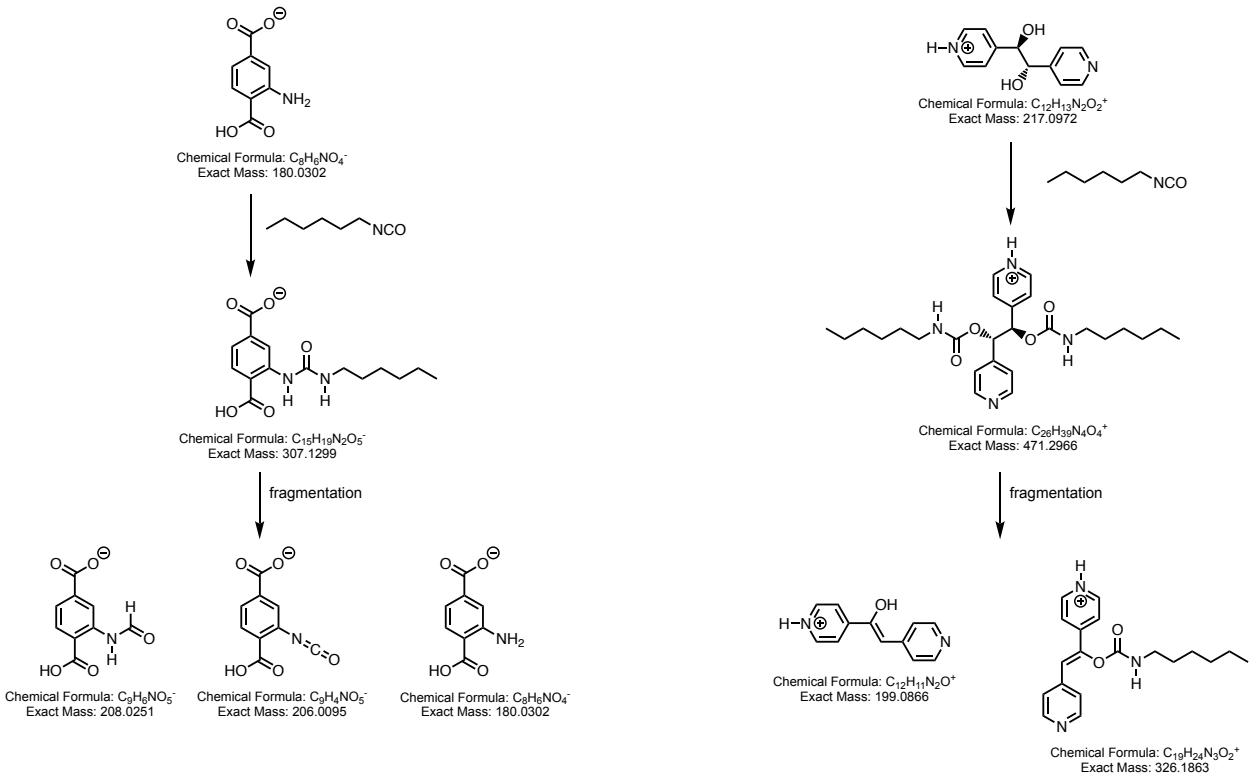


Figure S2: HRMS of **KSU-1** after reacting with *tert*-butyl isocyanate to form **KSU-1$_{tBu}$**. Left: the negative mode has no indication of the BDC urea product (m/z = 279.0986), though the [BDC-NH_2-H^+] starting material peak could also be a fragmentation product (note the presence of an unidentified mass at m/z = 339.1964 that appears to lose successive numbers of –CH_2 groups). Right: the positive mode has m/z peaks corresponding to [$DPG_{dicarbamate}$+H^+] (m/z = 415.2322) and its various fragmentation products.



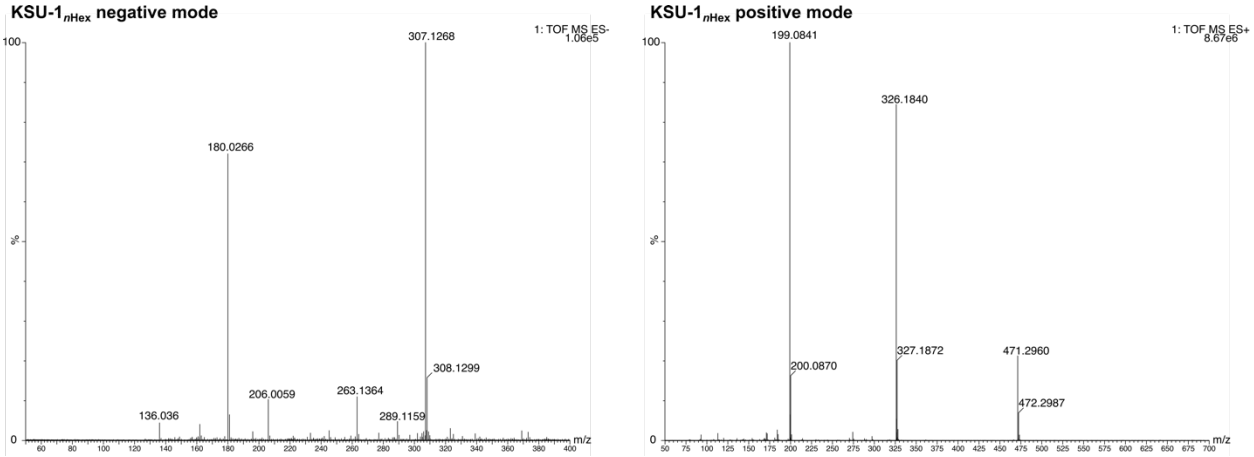
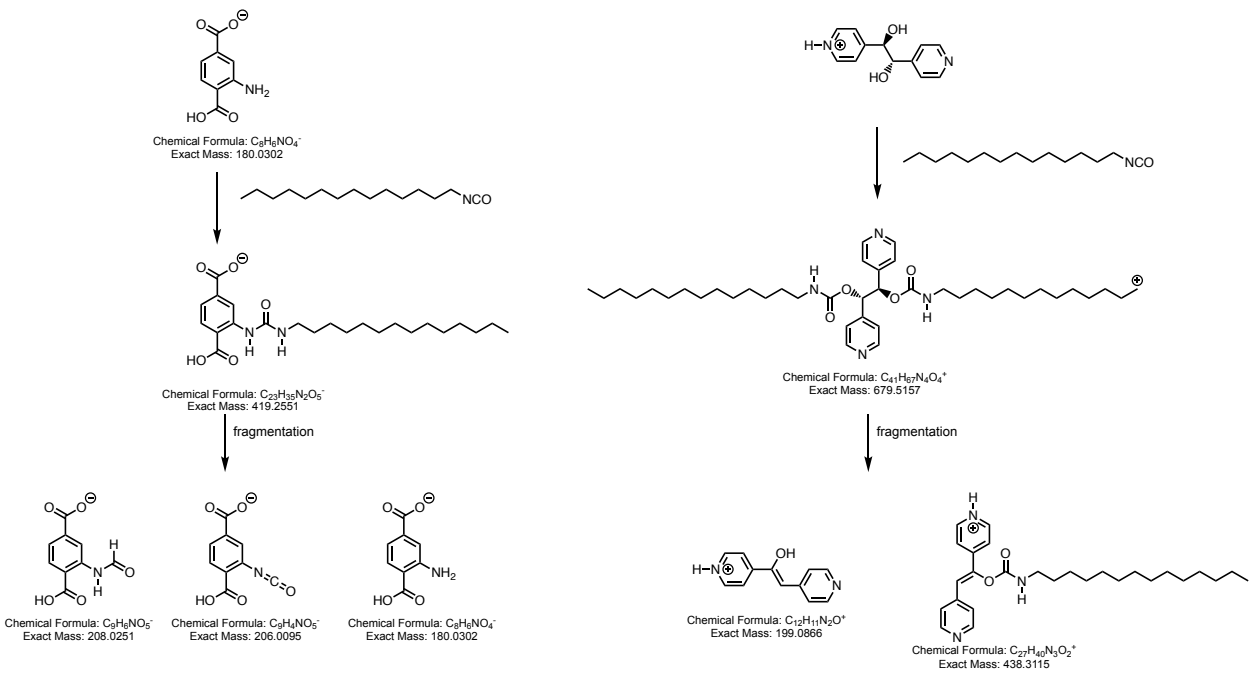


Figure S3: HRMS of KSU-1 after reacting with *n*-hexyl isocyanate to form **KSU-1$_{nHex}$**. Left: the negative mode indicates the presence of the BDC urea product (m/z = 307.1268), and the [BDC-NH_2-H^+] starting material peak could also be a fragmentation product. Right: the positive mode has m/z peaks corresponding to [$DPG_{dicarbamate}$+H^+] (m/z = 471.2960) and its various fragmentation products.



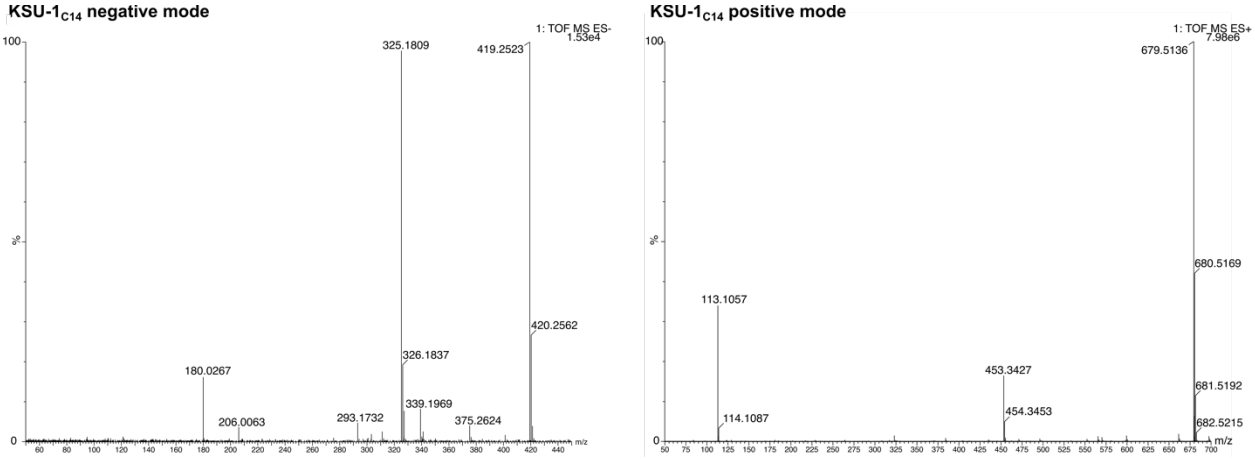


Figure S4:HRMS of KSU-1 after reacting with tetradecyl isocyanate to form **KSU-1$_{C14}$**. Left: the negative mode indicates the presence of the BDC urea product (m/z = 419.2523), and the [BDC-NH_2-H^+] starting material peak could also be a fragmentation product. Right: the positive mode has m/z peaks corresponding to [$DPG_{dicarbamate}$-CH_3^-] (m/z = 679.5136).

POWDER X-RAY DIFFRACTION (PXRD)

Powder diffraction was recorded on a Bruker AXS D8 Advance Phaser diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu Kα radiation (λ = 1.5418 Å) over a range of 4° < 2θ < 40° in 0.02° steps with a 0.5 s counting time per step. Samples were collected from the bottom of the reaction vial as a thick suspension in DMF and spread on a Si-Einkristalle plate immediately before PXRD measurements.

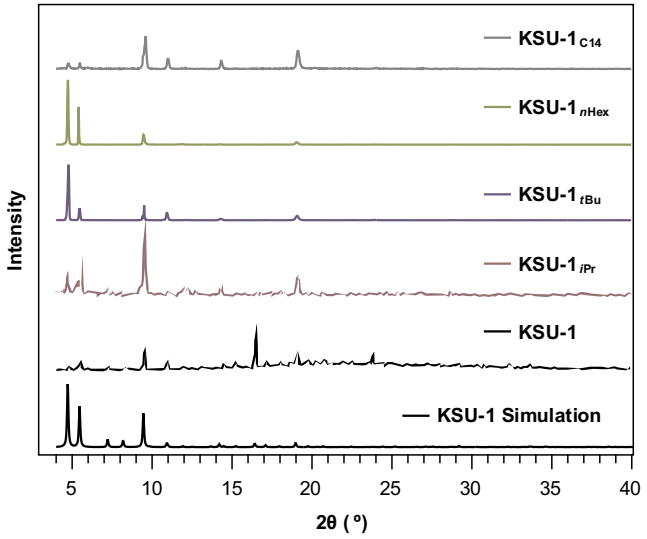


Figure S5. The PXRD patterns of the simulated **KSU-1**, the experimental **KSU-1**, and the **KSU-1** after reacting with the alkyl isocyanates **KSU-1**$_{i\text{Pr}}$ and **KSU-1**$_{t\text{Bu}}$, **KSU-1**$_{n\text{Hex}}$, and **KSU-1**$_{n\text{C14}}$ respectively.

THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis was performed on a TGA 8000 (PerkinElmer Inc., Waltham, MA, USA) interfaced with a PC using Pyris software. Samples were heated at a rate of 10 ºC/min under a nitrogen atmosphere. All samples were extensively solvent exchanged with fresh toluene prior to analysis.

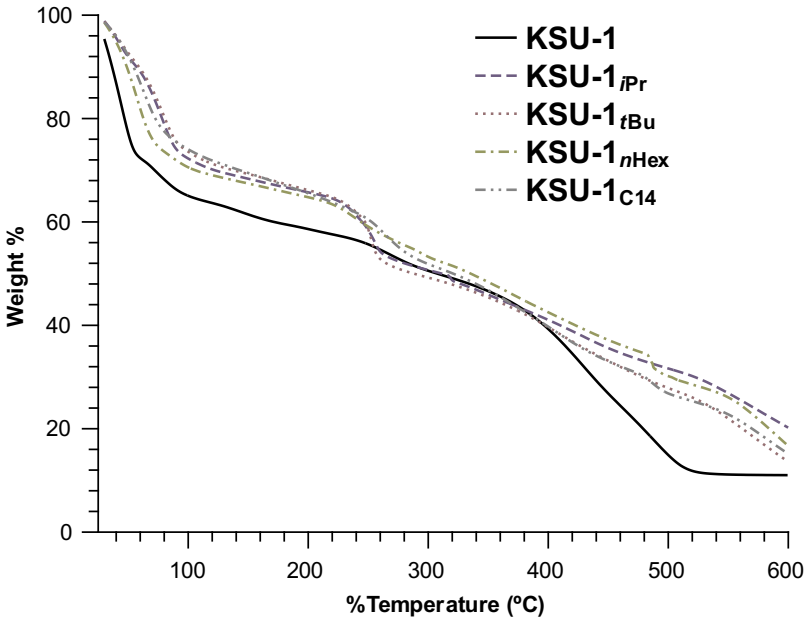


Figure S6. TGA data for as-synthesized **KSU-1, KSU-1**$_{i\text{Pr}}$ and **KSU-1**$_{t\text{Bu}}$, **KSU-1**$_{n\text{Hex}}$, and **KSU-1**$_{n\text{C14}}$ exchanged with toluene.

PROTON NUCLEAR MAGNETIC RESONANCE (^{1}H-NMR)

Spectra were recorded on a Bruker Avance NEO spectrometer (400 MHz for 1H, Bruker BioSpin, Billerica, MA, USA). NMR chemical shifts are reported in ppm against a residual solvent resonance as the internal standard (δ(*d*$_6$-DMSO) = 2.5 ppm). In a typical analysis, MOF materials stored in DMF were solvent exchanged with $CHCl_3$, isolated by vacuum filtration, and then evacuated in a vacuum oven at 80 °C overnight. Evacuated MOF samples (5-6 mg) were transferred into an NMR tube and *d*$_6$-DMSO (0.55 mL) was added. Subsequently, D_2SO_4 (0.09 mL, 98% w/w in D_2O) was also added. The tubes were capped and sonicated until all the solid was dissolved (~ 1 min).

Dodecane calibration curve

Benzaldehyde (0.5 mmol; 50.8 uL) and dodecane (0.5 mmol; 113.6 uL) were then added into two separate half vial followed by 2.00 mL of toluene in each vial to make a 0.50M solution. These solutions were then diluted to make 0.250 M, 0.200 M, 0.150 M, 0.100 M and 0.0500 M solutions. Aliquots for each solution were analyzed by ^{1}H-NMR and the ratio of benzaldehyde and dodecane in each standard was determined by integration of dodecane signal at 0.89ppm vs benzaldehyde signal at 10.03ppm.

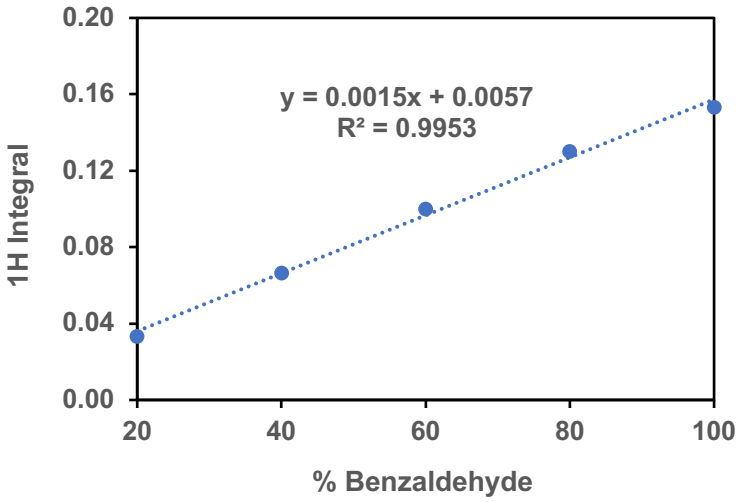


Figure S7: Calibration curve of the benzylidenemalononitrile proton with dodecane internal standard.

Table S1: Comparison of conversions obtained comparing the integral of the benzylidenemalononitrile proton to that of the dodecane internal standard (I.S.) vs comparing to the benzaldehyde (BA) proton.[a]

Entry	Catalyst	% Conversion					
		30 min. (I.S.)	30 min. (BA)	3 h (I.S.)	3 h (BA)	6 h (I.S.)	6 h (BA)
1	no catalyst	0	0	0	0	0	0
2	**KSU-1**	37	37	75	77	90	97
3	**KSU-1**$_{iPr}$	37	37	87	90	96	97
4	**KSU-1**$_{tBu}$	42	44	90	90	96	100
5	**KSU-1**$_{nHex}$	54	57	89	90	96	97
6	**KSU-1**$_{C14}$	58	64	92	90	97	100

[a]0.0625 mmol benzaldehyde, 0.068 mmol malononitrile, 0.083 mmol dodecane, 250 µL toluene,12 mol% catalyst, 50 °C.