A general description of metal-organic frameworks and their syntheses.

Metal-organic frameworks (MOFs) combine the stability, confinement, and matrix-isolation of heterogeneous catalysts with the molecular tunability of homogeneous catalysts. Post-synthetic metalation is one route to accessing active catalysts, but post-synthetic metalation risks the metal ions appending to unintended sites of the framework, such as bridging inorganic oxo units. Bottom-up assembly from organometallic species, on the other hand, often leads to metallolinker decomposition or ligand redistribution within the MOF.

Too access these catalysts:

**Materials.** The following reagents were purchased from commercial vendors and used as received. Benzyl alcohol (99 %, Alfa Aesar), aniline (≥ 99 %, Alfa Aesar), NaOH (≥ 98 %, pellets (anhydrous), Sigma Aldrich), trimethylsilyl cyanide (98 %, Sigma Aldrich), scandium triflate (99 %, Sigma Aldrich), Biphenyl-3,3′,5,5′-tetracarboxylic acid (H₄BPTC) (≥ 99.7 %, Sigma Aldrich), chloroform (≥ 99 %, ≥ 0.056 % of H₂O, Sigma Aldrich), chloroform-d (99.8 atom % D, ≥ 0.056 % of H₂O, Sigma Aldrich), DMSO-d₆ (99.9 atom % D, Sigma Aldrich), deuterium chloride solution (35 wt. % in D₂O, ≥ 99 atom % D, Sigma Aldrich), dichloromethane (≥ 99.8 %, Sigma Aldrich), HCl (36.5 wt. % in H₂O, Sigma Aldrich), THF (anhydrous, ≥ 99.9 %, Sigma Aldrich), DMF (≥ 99.8 %, Sigma Aldrich) and petroleum ether (puriss. p.a., high boiling, bp 60-80 °C, Sigma Aldrich) were purchased from commercial vendors and used as received.

**MFM-300(Sc) Synthesis and characterization.** Following a previously reported procedure,[¹] scandium triflate (0.030g, 0.061 mmol) and H₄BPTC (0.010 g, 0.030 mmol) were mixed in THF (4.0 ml), DMF (3.0 ml), water (1.0 ml) and HCl (36.5 %, 2 drops). The resultant slurry mixture was stirred until complete dissolution occurred. The solution was then placed in a pressure tube and heated in an oil bath to 75 °C for 72 h. The tube was cooled down to room temperature at a rate of 0.1 °C/min, and the colorless crystalline product was separated by filtration, washed with DMF (5.00 ml) and dried in air. Samples were handled under standard Schlenk techniques unless otherwise stated. N-Benzylideneaniline was synthesized and purified as previously reported.[²] Powder X-ray diffraction (PXRD) data were collected on a Bruker Advanced D4 diffractometer using Cu Kα radiation (λ = 1.5456 Å , 40 kW/ 40mA, 2θ = 5 – 50ϕ, phi rotation = 20 rotation/min, at 1 sec exposure per step with 5001 steps and using 0.5 mm glass capillaries). NMR spectra were recorded on Varian Gemini 400 MHz spectrometers at 25 °C using a 5 mm probe.

**Catalytic generation of 2-phenyl-2-phenylaminoacetanitrile.** The synthesized MFM-300(Sc) (approximately 22 mg) were washed with DMF (5 X 4.0 mL) and subsequently chloroform (5 X 4.0 mL), the chloroform was degassed with Ar after each exchange, and the crystals were allowed to soak 1 h between exchanges. The crystals were activated to remove the pore-filling solvent at 60°C for 16 hours and stored inside a glove box. Further, MFM-300(Sc) sample (2 mg, 0.0023 mmol) was placed in a 4.0 mL glass vial, and CDCl₃ (0.07 mol% H₂O, 1.5 ml), N-Benzylideneaniline (31.5 mg, 0.173 mmol), and trimethylsilyl cyanide (86.21 mg, 0.869 mmol) were added and the vial sealed at RT for 96 h. This process was repeated 5 more times to obtain the results in Table 1. The extent of conversion was calculated by comparing the reduction in the integral of the alkene CH resonance of N-Benzylideneaniline at 8.46 ppm and the appearance of a new secondary amine NH resonance from 2-Phenyl-2-phenylaminoacetanitrile at 4.27 ppm.