Electronic Supplementary Information

Remarkable Lewis Acid Catalytic Performance of the Scandium Trimesate Metal Organic Framework MIL-100(Sc) for C-C and C=N Bond-forming Reactions

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Contents

S1. General experimental

Chemicals were purchased from commercial suppliers. Dry solvents were used in reactions that were carried out under N_2. Mass spectrometry was carried out by the ESPSRC National Mass Spectrometry Service Centre, Swansea University, using Waters ZQ4000, Thermofisher LTQ Orbitrap XL and Finnigan MAT 900 XLT Instruments. EDX measurements were obtained by a JEOL 5600 SEM with an Oxford INCA Energy 200 EDX system. Thin layer chromatography was carried out on pre-coated 0.2 Å Machery-Nagel Polygram SIL G/UV254 silicon plates. Absorption under UV light was visualised as well as thermal decomposition after immersion in aqueous solution of potassium permanganate if required. Column chromatography was performed using Davisil silica gel Fluorochem 60 Å, particle size 35-70 micron.

^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and ^{31}P NMR were carried out using a Bruker Avance 400 spectrometer at 400 Hz or Bruker Avance 300 spectrometer at 300 Hz. Chemical shift information for each signal is given in part per million (ppm) relative to trimethylsilane (TMS). Chemical shifts for ^{19}F are relative to $CFCl_3$ and ^{31}P relative to phosphoric acid. The number of protons is denoted by nH reported from their resonance signal and the multiplicity represented by s, d, t, m and br where s is singlet, d is double, t is triplet, m is multiplet and br is broad. Coupling constants (J) are quoted to the nearest 0.1 Hz. All spectra were recorded at room temperature in varying solvents which are given in the parentheses.

Powder X-ray diffraction (PXRD) patterns were collected on MOFs using PANalytical Empyrean and STOE STAD i/p diffractometers using Cu $K_{\alpha 1}$ X-radiation (λ = 1.54056 Å).

Thermogravimetric analysis (TGA) was carried out using a Netzsch TG209 and TGA 760. Adsorption isotherms for N_2 were obtained at 77 K using a Micromeritics Tristar II 3020 and for CO_2 at 196 K using a Hiden IGA automatic gravimetric Porosimeter. Elemental analyses were performed on organic compounds and metal organic frameworks by Elemental Analysis Service, London Metropolitan University, London, UK.

S2. Synthesis of known metal organic frameworks

STA-12(Ni),[1] CPO-27(Ni),[2] HKUST-1,[3] MIL-88B(Sc),[4] MIL-100(Sc),[4] MIL-100(Cr) and MIL-101(Cr) were all synthesised according to published methods and confirmed to be pure by comparison of the measured PXRDs with reported patterns. MIL-100(Fe) was supplied by Johnson-Matthey. As an example synthesis of **MIL-100(Sc)**, the most active catalyst in this work, benzene-1,3,5-tricarboxylic acid (BTC, Aldrich, 95%, 0.43 mmol, 0.0905 g) and scandium nitrate (0.86 mmol, 0.2454 g) were dissolved in dimethylformamide, DMF (Acros, 98%, 20 mL) and heated in a Teflon lined steel autoclave at 423 K for 48 hours. The resulting solid was washed with ethanol and water and dried at 60 °C. Product identification was carried out using powder x-ray diffraction showing highly crystalline product (Figure S2.1). The reported structure of MIL-100(Cr),[5] modified by substitution of Sc for Cr and using the refined unit cell parameter, was used to simulate an expected pattern for MIL-100(Sc) confirming assignment of the product as MIL-100(Sc).

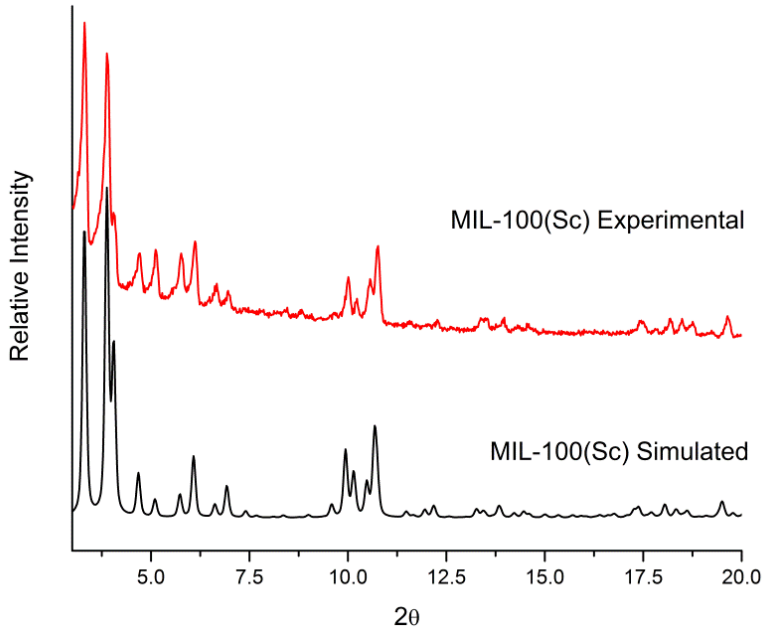


Figure S2.1 Comparison of PXRD (Cu $K_{\alpha 1}$, λ = 1.54056 Å) of MIL-100(Sc) with that simulated using the reported structure of MIL-100(Cr), substituting Cr by Sc and using the refined unit cell parameter, *a* = 75.436(8) Å in cubic *F d*-3*m*.

The synthesis of **MIL-101(Sc)** reported in our previous paper[4] was also modified. An aqueous 1.45 M $ScCl_3$ solution (0.58 mmol $ScCl_3$) and terephthalic acid (BDC, Aldrich, >98%, 0.64 mmol) were mixed in N,N-dimethylformamide, DMF (Acros Organics, 4.0 ml), and ethanol (VWR, 99.8%, 5 ml). The homogenized reactions mixture was transferred to a Teflon-lined autoclave and heated at 80 ^{o}C for 1 day. After heating, the autoclave was cooled and the mixture filtered, washed with DMF and dried at 60 °C overnight. The product was identified as MIL-101(Sc) by comparison of the PXRD profile with a pattern simulated using the reported structure of MIL-101(Cr),[6] (Figure 2.2) and characterised by TGA and N_2 adsorption (Figure 2.3). Extended evacuation at 120 °C led to loss of crystallinity, so that for catalysis samples were only dried at 60 °C.

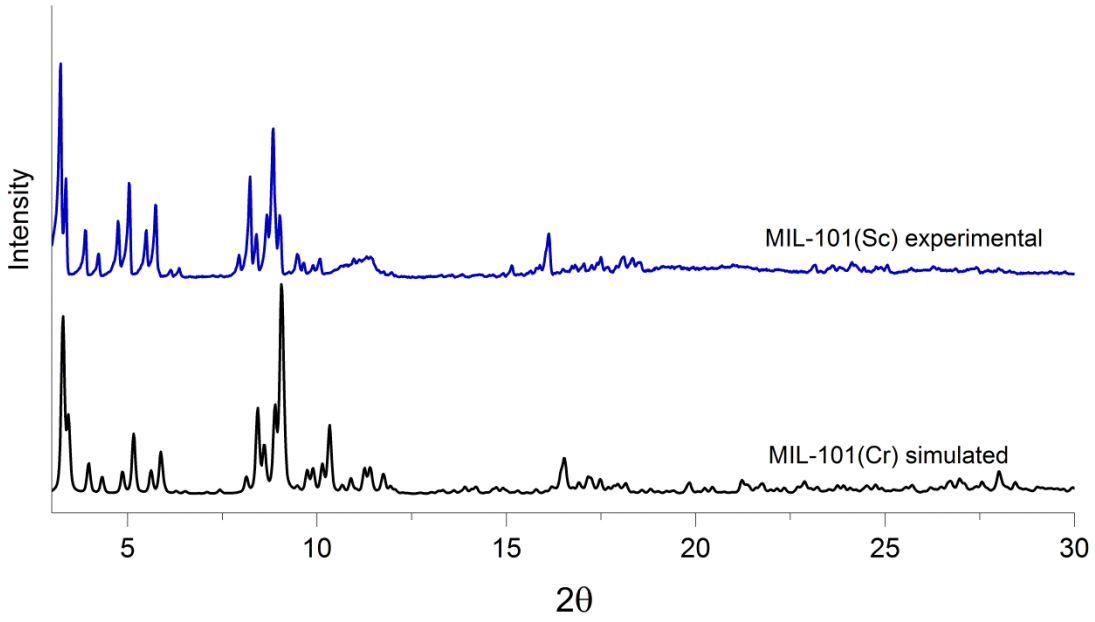


Figure S2.2 Powder x-ray diffraction pattern of MIL-101(Sc) (in blue) compared with a pattern simulated from the reported structure of MIL-101(Cr) (black).

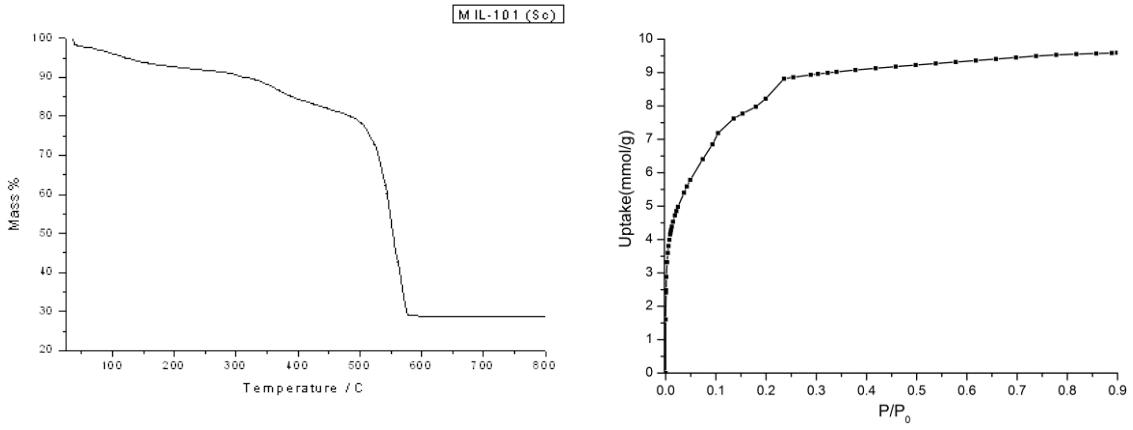
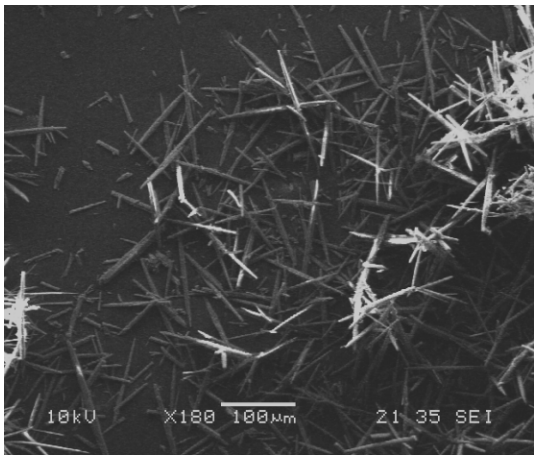


Figure S2.3 (left) TGA analysis of as-prepared MIL-101(Sc) heated at 10 °C min^{-1}, (right) N_2 adsorption at -196 °C. Sample degassed in vacuum at 60 °C prior to adsorption.

S3. Synthesis and structural analysis of MIL-68(Sc) and MIL-88D(Sc)

S3.1 MIL-68(Sc) MIL-68(Sc) was prepared by reaction of scandium chloride (0.46 mmol, 1.45 M aqueous solution) and terephthalic acid (0.46 mmol) in DMF (3.0 ml), water (5.0 ml), and ethanol (5 ml) heated at 90 °C for 12 hours in a Teflon-lined Parr autoclave. After heating, the autoclave was cooled and the mixture filtered, washed with ethanol and dried at 60 °C overnight. The acicular

crystals > 100 μm long (Figure S3.1) were suitable for single crystal analysis. EDX confirms the presence of scandium and TGA indicates the structure loses around 8 wt% before the major weight loss starts at 400 °C, corresponding to the carboxylate decomposition.



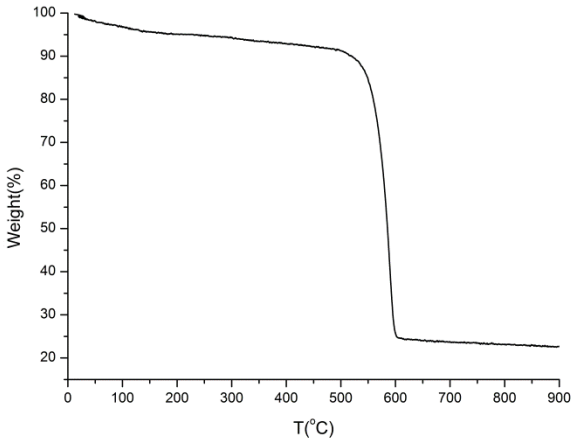


Figure S3.1 (Left) SEM of crystals of MIL-68(Sc)

Figure S3.2 TGA of as-prepared MIL-68(Sc)

Single crystal analysis indicated that the material was indeed MIL-68(Sc), *Cmcm a* = 21.577(7) Å, *b* = 37.523(11) Å, *c* = 7.320(2) Å, but the data was not of sufficent quality to complete the refinement (wR = 24.5%). Instead, the single crystal structure was used as a starting model that was Rietveld refined against laboratory powder diffraction using the GSAS suite of programs,[7] and using constraints to maintain the framework with chemically reasonable distances. Some extra-framework scattering was located in the narrow channel of MIL-68(Sc) in positions reported by Volkringer *et al.* for DMF molecules in MIL-68(In).[8] A satisfactory fit to the data was achieved confirming the structural assignment (R_{wp} = 5.25, R_p = 3.80, Figure S3.3). A cif file is available. Chemical analysis of as-prepared MIL-68(Sc), assuming inclusion of DMF as reported in the indium analogue was responsible for all the N in the solid, suggests a composition Sc(OH)(BDC)•0.3DMF (calculated C, 43.0 wt%; H, 2.9%; N 1.9%: measured C, 45.2%; H 2.5%, N 1.9%). Only a small fraction of the estimated DMF was located by diffraction, presumably due to disorder.

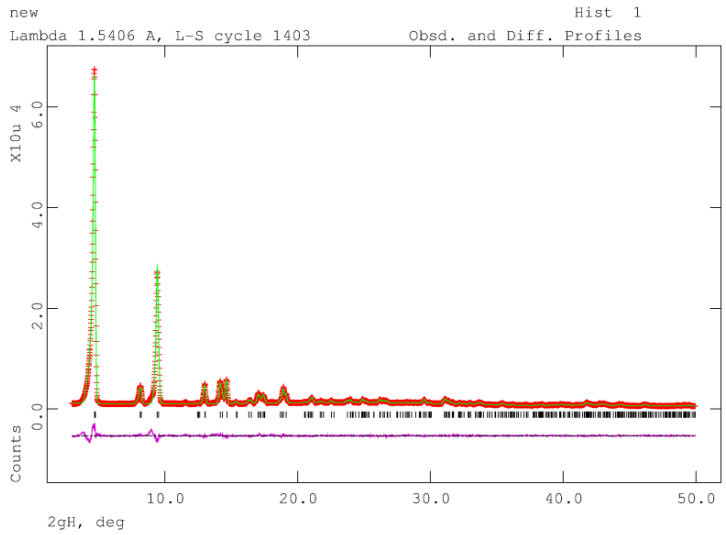


Figure S3.3 Rietveld plot of the refinement of the structure of as-prepared MIL-68(Sc)

N_2 adsorption at -196 °C on a heated (200 °C) sample re-activated at 120 °C under vacuum gave a low uptake, but that measured for CO_2 at – 77 °C was much higher (Figure S3.4). For a range of other permanently porous solids, our measurements show that the uptake in mmol g^{-1} at pore filling for N_2 (p/p_o = 0.9; T = -196 °C) is *ca*. 1.27× that of CO_2 at pore filling (p/p_o = 0.5, -77 °C), suggesting that the density of CO_2 under those conditions is 1.24× that of liquid N_2, i.e. 1.0 g cm^{-3}. This gives a pore volume of 0.6 cm^3 g^{-1} for MIL-68(Sc) as measured by CO_2 adsorption.

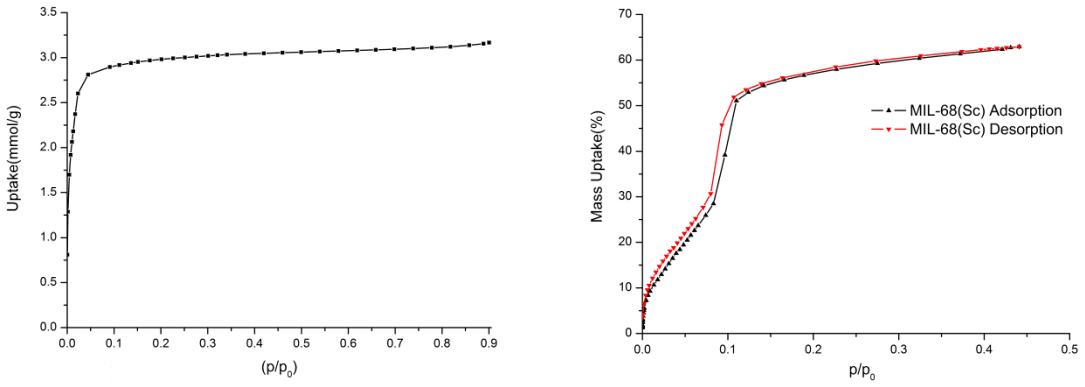


Figure S3.4 Adsorption isotherms of MIL-68(Sc) for (left) N_2 at -196 °C and (right) CO_2 at -77 °C.

To confirm that the pores of the as-prepared material were accessible to molecules larger than CO_2, 80 mg of the as-prepared MIL-68(Sc) was immersed in a solution of 0.15 mL of N-(2-Hydroxyethyl)ethylenediamine ($C_4H_{12}N_2O$) in 5 mL toluene. The solid was filtered and dried, and the N content found to increase from 1.9% to 7.7%, indicating uptake of 28 wt% of the amine.

S3.2 MIL-88D(Sc) Biphenyl-4,4'-dicarboxylic acid (H_2BPDC, Aldrich, 97%, 0.50 mmol, 0.1211 g) and scandium nitrate (0.5 mmol, 0.143 g) were dissolved in diethylformamide, DEF (Alfa Aesar, 98%, 6 mL) and heated in a Teflon-lined steel autoclave at 110 °C for 72 hours. The resulting solid was washed with ethanol and dried at 60 °C.

Initial identification of the product as MIL-88D(Sc) was achieved using PXRD in the following way. Firstly, the PXRD of the calcined solid subsequently immersed in methanol was indexed by the Lebail method[9] within the GSAS suite of programs[7] to give a hexagonal unit cell in *P* -62*c* of *a* = 21.734(4) Å, *c* = 21.913(5) Å. This is consistent with the MIL-88D structure in a partially open state, so that a model was constructed to fit that unit cell. The predicted diffraction pattern from the model shows reasonable agreement with that observed, but the low permanent porosity (see below) and the small amount of flexibility in the structure suggested that the material could be an interpenetrated version of the structure, as recently reported for Fe and In 4,4'-biphenyldicarboxylates.[10,11] Comparison of powder diffraction pattern of the as-prepared scandium containing solid with that simulated from the interpenetrated In analogue[11] (Figure S3.5) suggests the structure is strongly interpenetrated.

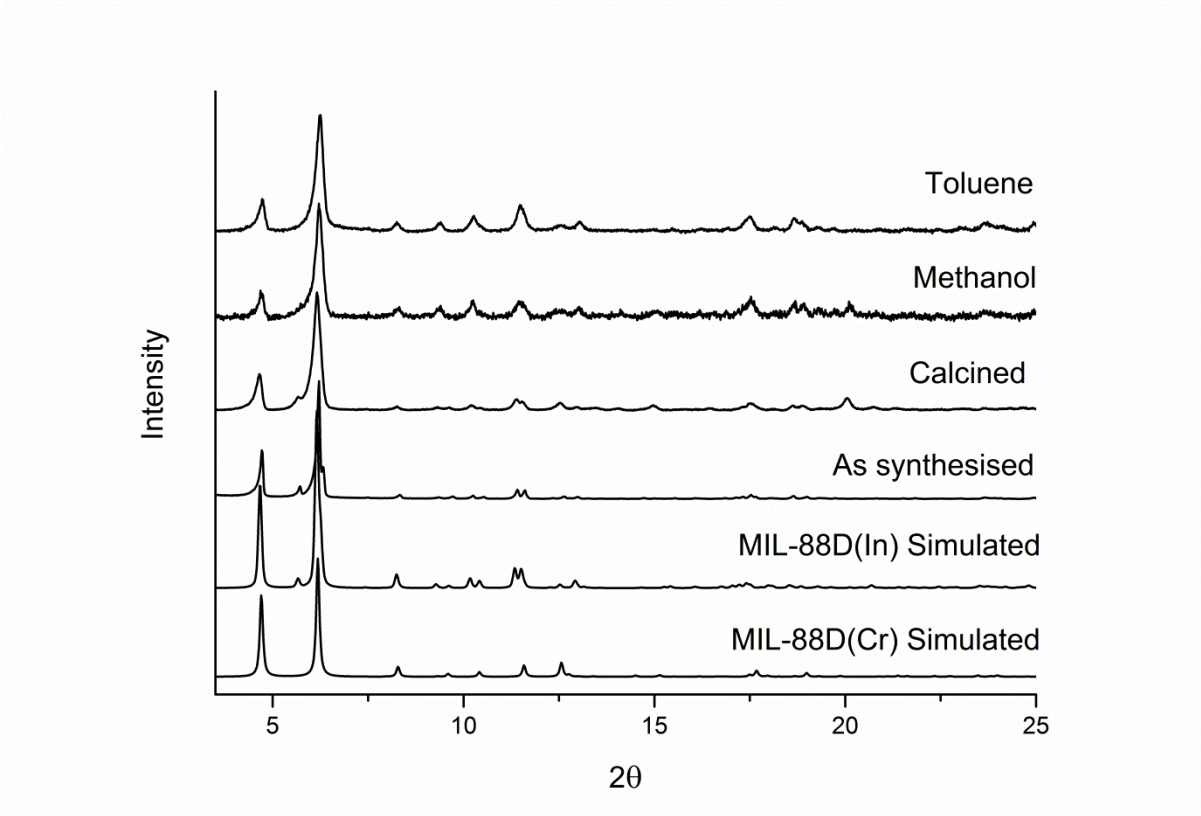


Figure S3.5 Powder x-ray diffraction pattern of as-synthesised, calcined and also calcined and subsequently immersed in methanol or toluene, compared with simulated patterns from reported structures for MIL-88D(Cr) and also for an interpenetrated indium version of MIL-88D.[11]

MIL-88D(Sc) was further characterised by TGA of the as-prepared material, which indicated loss of included solvent until around 300 °C, and structural breakdown beginning at this temperature. Additionally, N_2 adsorption at 77 K was measured (Figure S3.7).

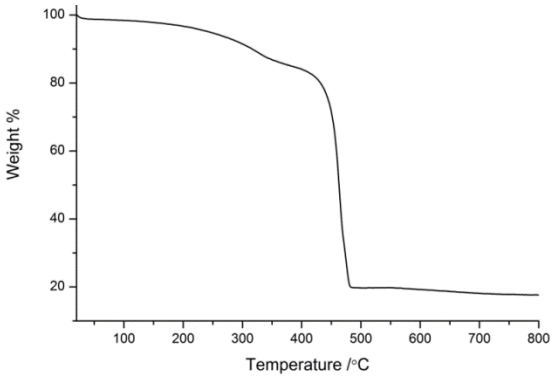


Fig. S3.6 TGA of as-prepared MIL-88D(Sc) at 5 °C min^{-1}.

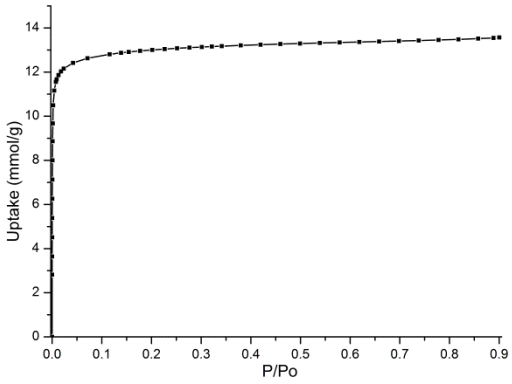


Fig. S3.7 N_2 (-196 °C) isotherm of MIL-88D(Sc).

S4. Preparation of scandium-exchanged zeolite Beta

Zeolite H-Beta (Zeolyst CP811E-22 H-Beta, Si/Al=17) was exchanged four times with Sc^{3+} using 3 M $Sc(NO_3)$(aq) at room temperature for 24 hrs. EDX indicated scandium was included, with a final molar Sc/Al ratio of 0.6 (2.7 wt% Sc). The crystallinity and porosity was retained (Figures S4.1 and S4.2). For H-β the BET surface area was 477 m^2 g^{-1} and after exchange with scandium it was 457 m^2 g^{-1}.

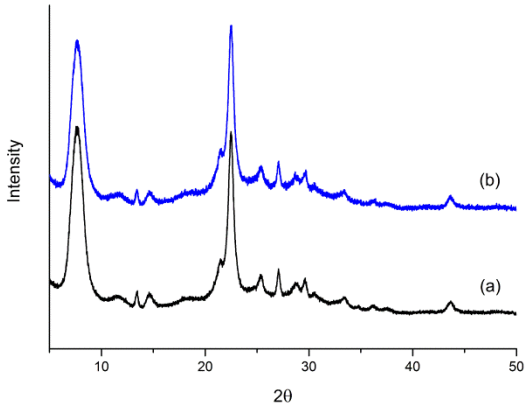


Figure S4.1 PXRD of (a) zeolite H-β and (b) Sc-β.

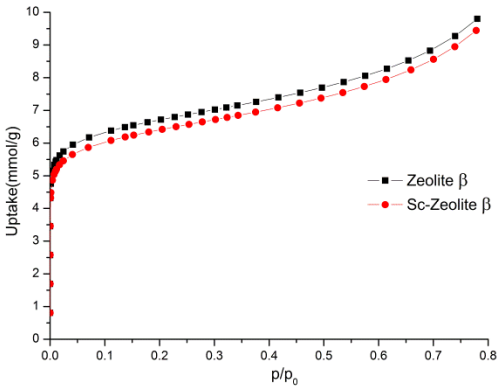
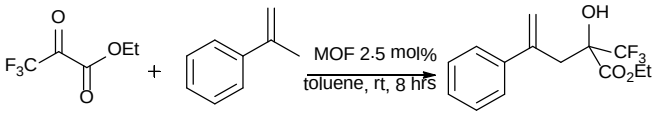


Fig. S4.2 N_2 adsorption (77 K) for H-β and Sc-β.

S5. Details of the carbonyl ene reaction

5.1 *Catalysed formation of ethyl-2-hydroxy-4-phenyl-2-trifluoromethyl)pent-4-enoate*

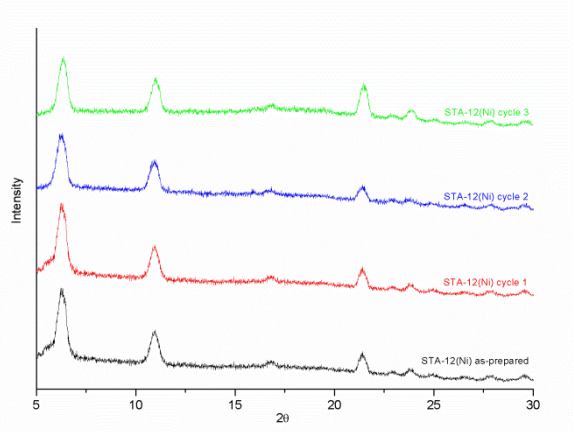


MOF catalyst was activated by heating under vacuum for 5 hrs between 150°C - 250°C or in the case of MIL-100(Sc) by washing with methanol and MIL-101(Cr) was activated according to literature (heated under solvothermal conditions for 12hrs at 90°C in EtOH (20ml) and further washed using NH_4Cl). Ethyl trifluoropyruvate (0.298 ml, 2.25 mmol), α-methylstyrene (0.351 ml, 2.7 mmol, 1.2 eq) and 1-fluoronapthalene (0.29 ml, 2.25 mmol, 1 eq) were added to a solution of activated MOF in toluene (5 ml). The solution was stirred for 8 h at room temperature under N_2. The reaction mixture was filtered and the solute concentrated in vacuo and purified by column chromotography using a hexane:ethyl acetate (6:1) mixture yielding a colourless oil (0.649 g, 99%). This compound has been reported previously from a different synthetic procedure.[12]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 – 7.13 (m, 5H), 5.30 (s, 1H), 5.19 (s, 1H), 3.93 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.74 (s, 1H), 3.53 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.20 (d, *J* = 14.0 Hz, 1H), 2.95 (d, *J* = 14.0 Hz, 1H), 1.01 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) 169.37, 141.48, 141.27, 128.57, 128.13, 127.2, 123.8 (q, J_{cf} 286.2), 119.82, 77.63 (q, J_{cf} 28.7), 63.89, 37.45, 13.92. ^{19}F NMR (282 MHz, $CDCl_3$) δ -78.9. ESI [M+H] calculated 289.1046 found 289.1046. $C_{14}H_{15}F_3O_3$ (Found C, 58.17; H, 5.08; Required C, 58.33; H, 5.24)

Reusability of catalyst

Used catalyst was filtered off after reaction and the crystallinity checked by PXRD.



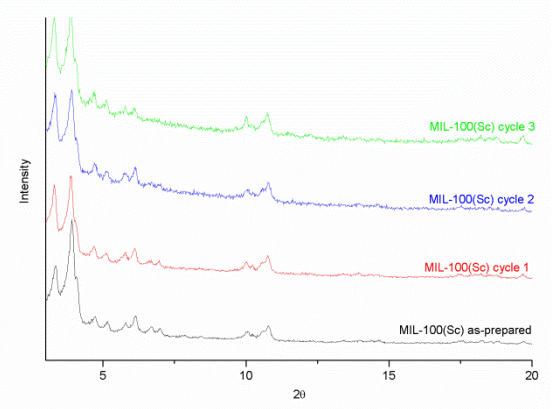


Figure S5.1 PXRD patterns of recovered (left) STA-12 (Ni) and (right) MIL-100(Sc) after each cycle in the carbonyl ene reaction

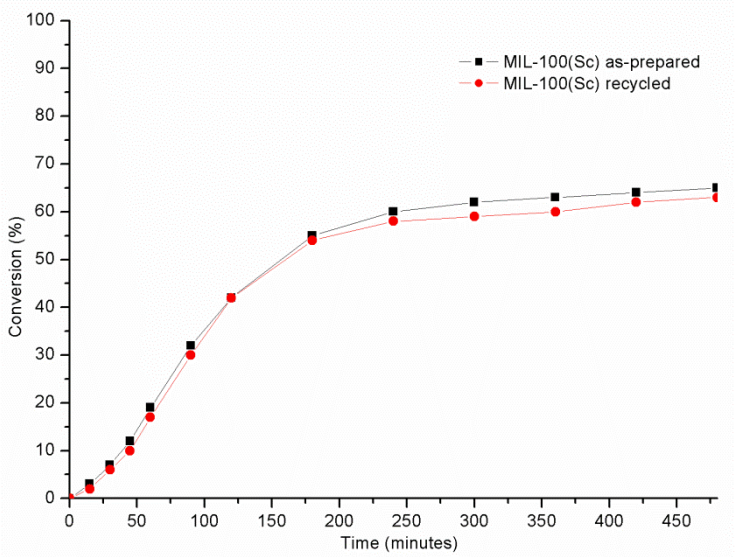


Figure S5.2 Graph showing conversion vs time for carbonyl ene reaction of α-methyl styrene with ethyltrifluoropyruvate over 8 h using as-prepared and recycled MIL-100(Sc). ^{1}H NMR taken at regular intervals using 1-fluoronaphthalene as internal standard.

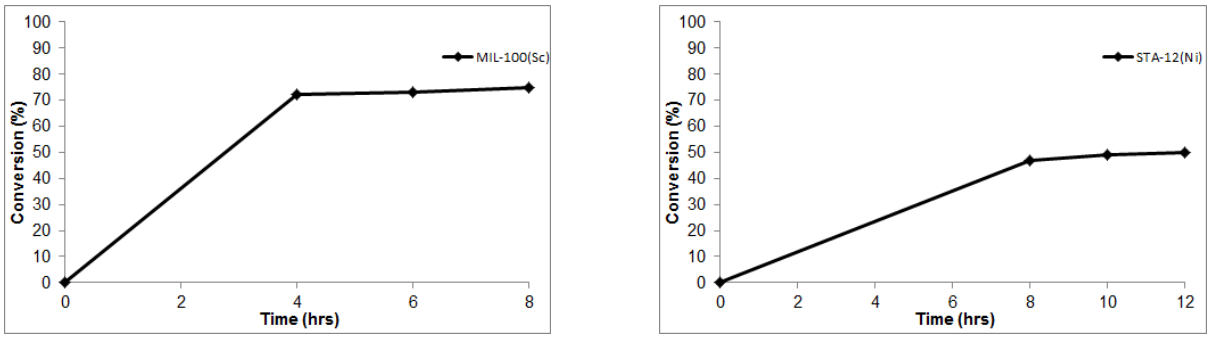
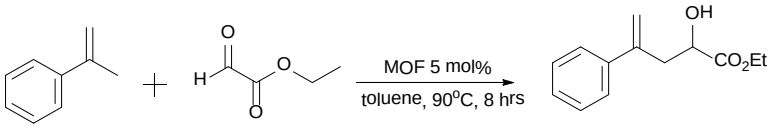


Figure S5.3 Conversion vs time curves from reaction where (left) MIL-100 (Sc) was removed after 4 h and (right) STA-12(Ni) was removed after 8 h for the carbonyl ene reaction of α-methylstyrene with Ethyl trifluoropyruvate.

5.2 *Catalysed formation of Ethyl-2-hydroxy-4-phenyl-2-pent-4-enoate*

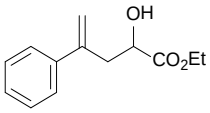


Formation of ethyl glyoxylate monomer

Ethyl glyoxylate polymer was heated to 110°C for 30 mins. The temperature was increased to 130°C to distil off excess toluene. The temperature was further increased to 150°C to distil ethyl glyoxylate monomer.

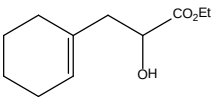
Ene reaction to give ethyl-2-hydroxy-4-phenylpent-4-enoate

Ethylglyoxalate (0.1 ml, 1 mmol) and α-methyl styrene (1 mmol, 1 eq) was added to a solution of activated MOF (5 mol%) in toluene (5 ml). The solution was stirred for 8hrs at 90°C under N_2. Reaction mixture was filtered under suction, concentrated in vacuo and purified by column chromotography using hexane : ethyl acetate (5:1) mixture yielding a colourless oil (0.187 g, 89%). This compound has been reported previously from a different synthetic procedure.[13]



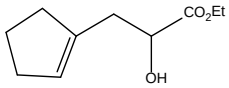
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.30 – 7.17 (m, 3H), 5.32 (s, 1H), 5.13 (s, 1H), 4.25 – 4.12 (m, 1H), 4.11 – 3.86 (m, 2H), 2.99 (dd, *J* = 14.4, 4.5 Hz, 1H), 2.77 (dd, *J* = 14.4, 7.6 Hz, 1H), 2.66 (br s, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.41, 143.61, 140.36, 128.36, 127.70, 126.43, 116.23, 69.16, 61.62, 40.53, 14.11. ESI [M+H] calculated 222.1046 found 222.1049. $C_{12}H_{16}O_3$ (Found C, 70.95; H, 7.35; Required C 70.89; H, 7.32). Pure product of ethyl-2-hydroxy-4-phenylpent-4-enoate was also obtained without polymer cracking

5.3 *Ene reaction to give Ethyl 3-cyclohexenyl-2-hydroxypropanoate*



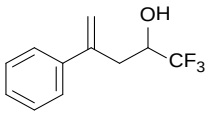
Ethylglyoxalate (0.1 ml, 1 mmol) and methylene cyclohexane (1 mmol, 1 eq) was added to a solution of activated MOF (5 mol%) in toluene (5 ml). The solution was stirred for 8hrs at 90°C under N_2. Reaction mixture was filtered under suction, concentrated in vacuo to obtain pure product in a 99% yield (0.197 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.45 (s, 1H), 4.31 – 4.15 (m, 3H), 2.81 (br s, 1H), 2.36 (dd, *J* = 13.9, 4.6 Hz, 1H), 2.21 (dd, *J* = 13.9, 7.9 Hz, 1H), 1.92 (m, 4H), 1.52 (dtd, *J* = 15.6, 5.8, 3.0 Hz, 4H), 1.22 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 174.86, 132.99, 125.14, 69.26, 61.32, 43.21, 28.37, 25.24, 22.77, 22.14, 14.15. ESI [M+H] calculated 198.125 found 198.237. $C_{12}H_{16}O_3$ (Found C, 66.42; H, 9.02; Required C 66.64; H, 9.15).

5.4 *Ene reaction to give Ethyl 3-cyclopentyl-2-hydroxypropanoate*



Ethylglyoxalate (0.1 ml, 1 mmol) and methylene cyclohexane (1 mmol, 1 eq) was added to a solution of activated MOF (5 mol%) in toluene (5 ml). The solution was stirred for 8hrs at 90°C under N_2. Reaction mixture was filtered under suction, concentrated in vacuo to obtain pure product in a 99% yield (0.184 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.43 (s, 1H), 4.24 (dd, *J* = 7.3, 4.6 Hz, 1H), 4.15 (qd, *J* = 7.4, 1.3 Hz, 2H), 2.86 (br s, 1H), 2.53 (dd, *J* = 14.0, 5.2 Hz, 1H), 2.41 (dd, *J* = 14.6, 7.3 Hz, 1H), 2.29 – 2.15 (m, 4H), 1.79 (p, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). δ ^{13}C NMR(75 MHz, $CDCl_3$) 174.7, 133.7, 126.1, 69.43, 61.42, 42.3, 34.5, 32.3, 22.7, 14.71.

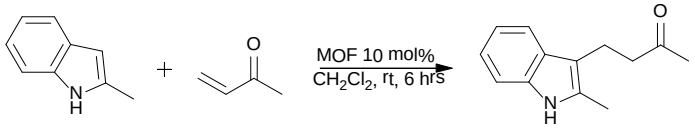
5.5 *Ene reaction to give (1-Methylene-3-hydroxy-4,4,4-trifluorobutyl)-benzol*



Hemiacetal (0.1 ml, 1 mmol) and methylene cyclohexane (1 mmol, 1 eq) was added to a solution of activated MOF (5 mol%) in toluene (5 ml). The solution was stirred for 8hrs at 90°C under N_2. Reaction mixture was filtered under suction, concentrated in vacuo to obtain pure product in a 99% yield (0.214g). *(1-Methylene-3-hydroxy-4,4,4-trifluorobutyl)-benzol* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.15 (m, 5H), 5.34 (s, 1H), 5.13 (s, 1H), 3.93 – 3.78 (m, 1H), 2.95 (dd, *J*= 14.8, 1.8 Hz, 1H), 2.57 (dd, *J* = 14.8, 10.2 Hz, 1H), 2.40 (br s, 1H). δ ^{13}C NMR(75 MHz, $CDCl_3$) 141.49, 138.30, 127.63, 127.03, 125.83, 125.14, 115.69, 67.66 (q J= 31 Hz), 34.66. ^{19}F NMR (282 MHz, $CDCl_3$) δ -79.99. ESI [M+H] calculated 216.067 found 216.012. $C_{12}H_{16}O_3$ (Found C, 61.04; H, 5.11; Required C 61.11; H, 5.13).

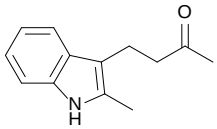
S6. Conjugate addition of indole to electron-deficient olefins

6.1 *Formation of 4-(2-methyl-3-indolyl)butan-2-one*



MOF (10 mol%) was heated to 150-250°C under vacuum for 5hrs, 2-methyl indole (0.1312 g, 1 mmol), methyl vinyl ketone (0.083 ml, 1 mmol), 1-methylnapthalene (0.07 ml, 0.5mmol) and CH_2Cl_2 (5 ml) was added and stirred for 6 hrs at RT. The reaction mixture was filtered and solution washed with water (5 ml), product extracted by CH_2Cl_2 (2×5 ml) and dried ($MgSO_4$). The product was concentrated in vacuo and purified by column chromatography hexane: ethyl acetate (4:1), yielding a

yellow oil (0.2 g, 99%). This compound has been reported previously from a different synthetic procedure.[14]



^{1}H NMR (400MHZ, $CDCl_3$): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.44 – 7.28 (m, 1H), 7.13 – 7.05 (m, 1H), 7.04 – 6.90 (m, 2H), 2.86 (t, *J* = 7.8 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.21 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.80, 135.78, 131.78, 128.68, 121.36, 119.54, 118.19, 110.87, 110.68, 44.66, 30.69, 18.88, 11.96. ESI [M+H] calculated 202.1226 found 202.1227. $C_{13}H_{15}NO$ (Found C, 77.62; H, 7.42; N, 6.85; Required C, 77.58; H, 7.51; N, 6.96)

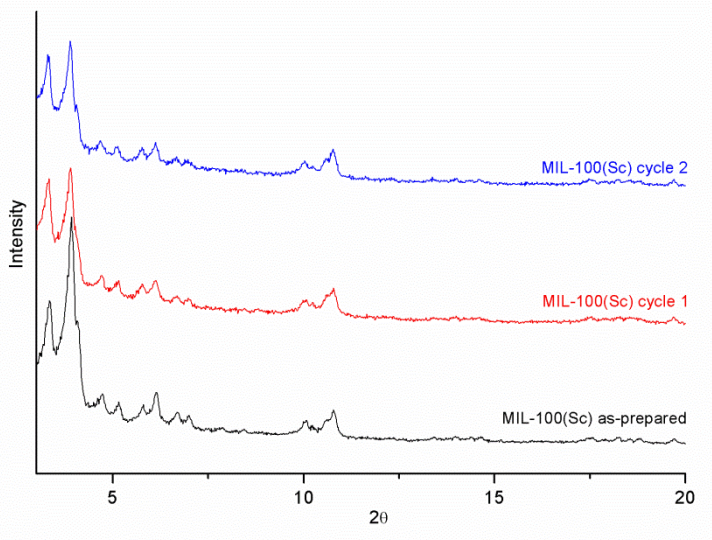


Figure S6.1 PXRD patterns obtained of MIL-100(Sc) recovered materials after each cycle in the conjugate addition of indole to electron-deficient olefins.

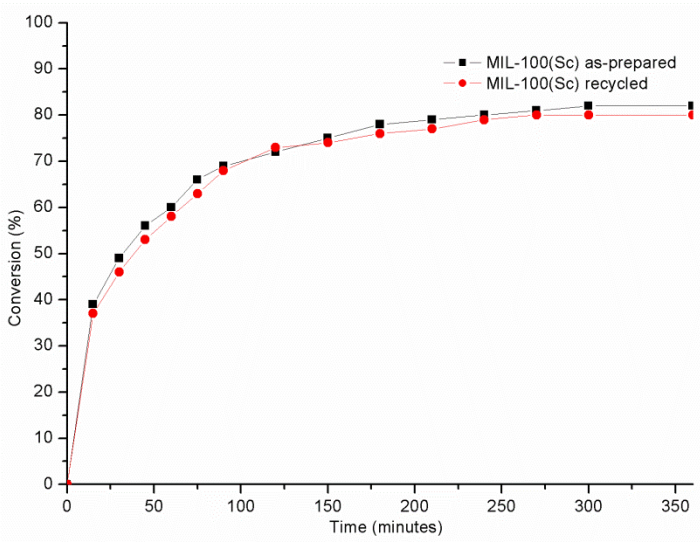


Figure S6.2 Graph showing conversion of as-prepared and recycled MIL-100(Sc) over 6 hrs cycle in the conjugate addition of indole to electron-deficient olefins.

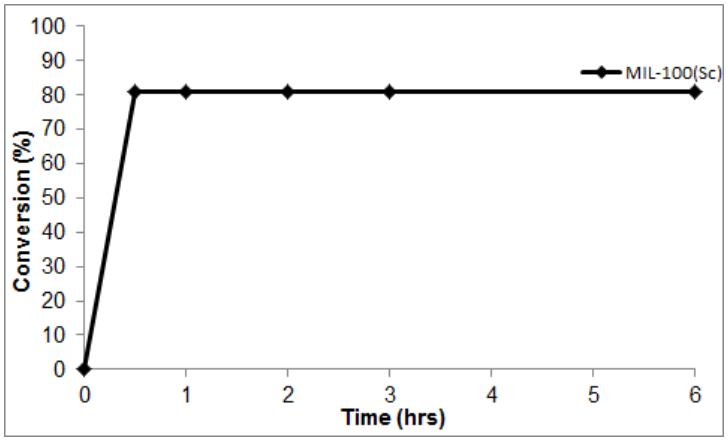


Figure S6.3 Graph showing Conversion vs time for MIL-100 (Sc) for reaction between 2-methylindole and methyl vinyl ketone which catalyst is removed after 4 hours, reaction was continued with no catalyst present and no further conversion is observed

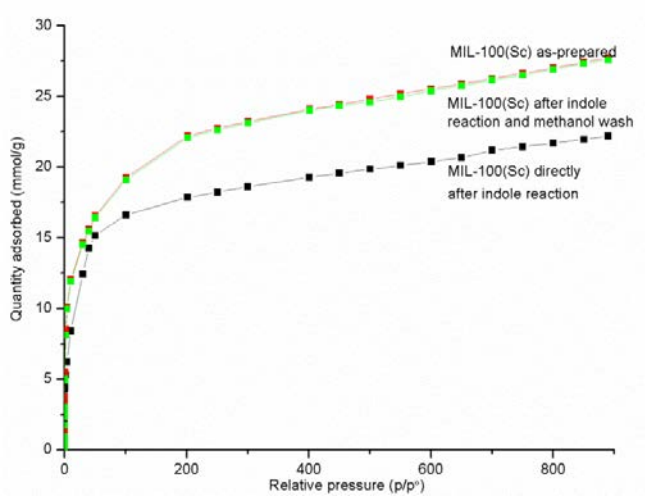
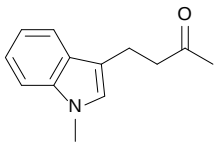


Figure S6.4 Adsorption isotherm of MIL-100(Sc) before indole reaction (red), directly after indole reaction (black) and after reaction and methanol washing (green)

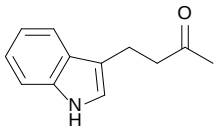
6.2 *Formation of 4-(1-methyl-1H-indol-3-yl)butan-2-one*



Experimental procedure similar to that for the synthesis of 4-(1-methyl-3-indolyl)butan-2-one.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.21 – 7.07 (m, 2H), 7.00 (ddd, *J* = 8.0, 6.6, 1.4 Hz, 1H), 6.71 (s, 1H), 3.58 (s, 3H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.01 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.21, 137.48, 128.05, 126.85, 122.05, 119.23, 119.19, 114.09, 109.72, 44.77, 33.01, 30.52, 19.71. ESI [M+H] calculated 202.1226 found 202.1221. $C_{13}H_{15}NO$ (Found C, 77.69; H, 7.45; N, 6.88; Required C, 77.58; H, 7.51; N, 6.96)

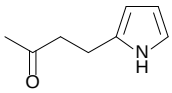
6.3 *Formation of 4-(1H-indol-3-yl)butan-2-one*



Experimental procedure as for synthesis of 4-(1-methyl-3-indolyl)butan-2-one.

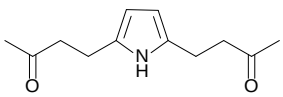
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 6.9 Hz, 1H), 7.15 – 6.98 (m, 2H), 6.88 (s, 1H), 2.97 (t, *J* = 7.4 Hz, 2H), 2.76 (t, *J* = 7.4 Hz, 2H), 2.06 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.32, 136.71, 127.58, 122.45, 121.91, 119.70, 119.07, 115.54, 111.61, 44.51, 30.50, 19.77. ESI [M+H] calculated 188.107 found 188.1069. $C_{12}H_{13}NO$ (Found C, 76.84; H, 6.99; N, 7.39; Required C, 76.98; H, 6.99; N, 7.48).

6.4 *Formation of 4-(1H-pyrrole-2-yl)butan-2-one and 4'4'-(1H-pyrrole-2,5-diyl)bis(butan-2one)*



MOF (10 mol%) was heated to 150-250°C under vacuum for 5hrs, 2-methyl indole (0.1312 g, 1 mmol), methyl vinyl ketone (0.083 ml, 1 mmol), 1-methylnapthalene (0.07 ml, 0.5mmol) and CH_2Cl_2 (5 ml) was added and stirred for 6 hrs at RT. The reaction mixture was filtered and solution washed with water (5 ml), product extracted by CH_2Cl_2 (2×5 ml) and dried ($MgSO_4$). The product was concentrated in vacuo and separated into mono and di substituted pyrroles by column chromatography hexane: ethyl acetate (4:1) with an overall yield of 89% (0.017 g, 0.158 g). This compound has been reported previously from a different synthetic procedure.[14]

4-(1H-pyrrole-2-yl)butan-2-one ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (s, 1H), 6.58 (td, *J* = 2.6, 1.6 Hz, 1H), 6.01 (q, *J* = 2.8 Hz, 1H), 5.85 – 5.71 (m, 1H), 2.84 – 2.68 (m, 4H), 2.09 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.84, 126.05, 117.14, 108.25, 105.69, 44.58, 30.51, 21.68. $C_8H_{11}NO$ (Found C, 70.13; H, 8.06; N, 10.11; Required C, 70.01; H, 8.06; N, 10.26)

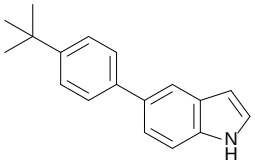


4'4'-(1H-pyrrole-2,5-diyl)bis(butan-2one) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, 1H), 5.64 (d, *J* = 2.6 Hz, 2H), 2.75 – 2.61 (m, 8H), 2.09 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.55, 130.83, 105.18,

44.40, 30.44, 21.91. $C_{12}H_{17}NO_2$ (Found C, 69.91; H, 8.02; N, 10.11; Required C, 70.01; H, 8.06; N, 10.26)

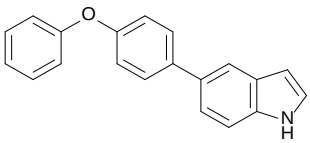
6.5 Synthesis of larger substrates for the indole reaction

6.5.1 *Synthesis of 5-(4-(tert-butyl)phenyl)-1H-indole via Suzuki coupling reaction*



tert-phenylboronic acid (0.79 g, 4.46 mmol, 1.75 eq.), $[PdCl_2(PCy_3)_2]$ (9.41 $\times 10^{-3}$ g, 1.27 $\times$ 10^{-3} mmol, 4 mol%) and potassium phosphonate (1.62g, 7.65 mmol, 3 eq) where charged in a flask with argon. Dry degassed toluene (10 ml) and bromoindole (0.5 g, 2.55 mmol) was added to the flask and the reaction mixture was heated to 90°C. This was left to stir at 90°C for 16 hrs under argon. The reaction was concentrated in vacuo and purified by column chromatography hexane: ethyl acetate (5:1). Yielding a white crystalline powder (0.39 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.78 (dt, *J* = 1.6, 0.8 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.46 – 7.27 (m, 4H), 7.14 (dd, *J* = 3.2, 2.4 Hz, 1H), 6.52 (ddd, *J* = 3.0, 2.1, 0.8 Hz, 1H), 1.30 (s, 9H). ^{13}C NMR (300 MHz, $CDCl_3$) 149.21, 139.64, 135.20 133.29, 128.37, 127.0, 125.61, 124.74, 121.92, 119.07, 111.16, 103.01, 34.51, 31.46. $C_{18}H_{19}N$(Found C, 86.63; H, 7.59; N, 5.62; Required C, 86.7; H 7.59; N 5.62). ESI [M+H] calculated 250.159 found 250.1593. Mp: 162-163°C. υ_{max}(KBr)/cm^{-1} 3434(NH), 2953(CH), 1463 (C=C), 1407 (C=C), 1384 (CH3), 1264 (CN), 1096, 885, 810, 723.

6.5.2 *Synthesis of 5-(4-phenoxyphenyl)-1H-indole via Suzuki coupling reaction*

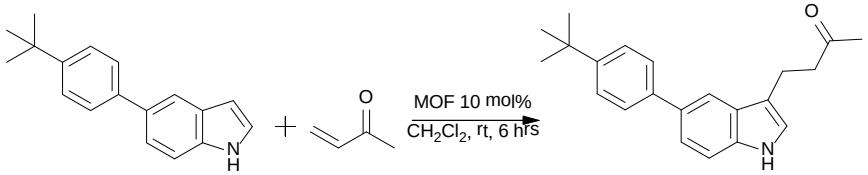


Phenoxyphenylboronic acid (0.955 g, 4.46 mmol, 1.75 eq.), $[PdCl_2(PCy_3)_2]$ (9.41 $\times 10^{-3}$ g, 1.27 $\times$ 10^{-3} mmol, 4 mol%) and potassium phosphonate (1.62 g, 7.65 mmol, 3 eq) where charged in a flask with argon. Dry degassed toluene (10 ml) and bromoindole (0.5 g, 2.55 mmol) was added to the flask and the reaction mixture was heated to 90°C. This was left to stir at 90°C for 16 hrs under argon. The reaction was concentrated in vacuo and purified by column chromatography hexane: ethyl acetate (5:1). Yielding a brown solid (0.37 g, 52%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.74 (s, 1H), 7.56 – 7.46 (m, 2H), 7.34 (d, *J* = 1.2 Hz, 2H), 7.29 – 7.20 (m, 2H), 7.13 (dd, *J* = 5.8, 3.0 Hz, 1H), 7.06 – 6.94 (m, 5H), 6.51 (dd, *J* = 3.1, 2.0 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.42, 156.01, 137.85, 135.09, 132.80, 129.82, 128.65,

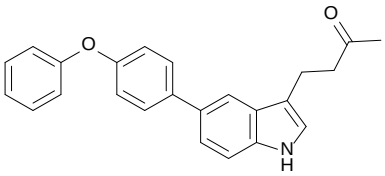
128.44, 124.97, 123.21, 121.79, 119.24, 119.04, 118.86, 111.34, 103.01. ESI [M+H] calculated 286.1226 found 286.123. $C_{19}H_{15}NO$ (Found C, 84.19; H,5.31; N,4.91; Required C, 84.36; H, 5.42; N, 4.98). Mp: 120-122°C. υ_{max}(KBr)/cm^{-1} [1]3340(NH), 2927 CH), 1586, 1488(C=C), 1465 (C=C), 1235 (C-N), 1165 (C-O), 1020, 805, 755.

6.6 Conjugate addition of large substrate indole to electron-deficient olefins



$ScOTf_3$ (1 mol%) was added to a flask flushed with nitrogen. 2-methyl indole (0.1534 g, 1 mmol), methyl vinyl ketone (0.1 ml, 1.2 mmol), and CH_2Cl_2 (5 ml) was added and stirred for 6 hrs at RT. The reaction mixture was filtered and solution washed with water (5 ml), product extracted by CH_2Cl_2 (2×5 ml) and dried ($MgSO_4$). The product was concentrated in vacuo and purified by column chromatography hexane: ethyl acetate (4:1), yielding a yellow oil.

4-(5-(4-tert-butyl)phenyl-1H-indol-3-yl)butan-2-one ^{1}H NMR (300 MHz, $CDCl_3$) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.71 – 7.65 (m, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.33 (m, 3H), 7.28 (d, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 2.2 Hz, 1H), 2.99 (t, *J* = 7.4 Hz, 2H), 2.77 (t, *J* = 7.4 Hz, 2H), 2.05 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (300 MHz, $CDCl_3$) δ ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.79, 148.22, 138.62, 134.65, 131.75, 126.58, 125.97, 124.58, 121.11, 120.81, 115.98, 114.38, 110.32, 43.02, 30.39, 29.03, 18.28. ESI [M+H] calculated 320.2009 found 320.2014. $C_{22}H_{25}NO_2$ (Found C, 82.95; H, 7.95; N, 4.55; Required C, 82.72; H 7.89; N 4.38)

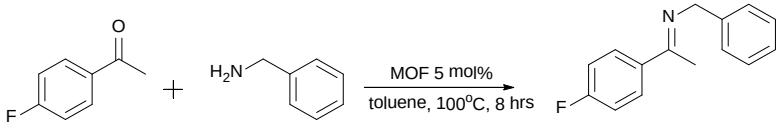


Experimental procedure as for the synthesis of 4-(5-(4-tert-butyl)phenyl-1H-indol-3-yl)butan-2-one.

4-(5-(4-phenoxyphenyl)-1H-indol-3-yl)butan-2-one ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.65 (s, 1H), 7.51 (dt, *J* = 8.5, 2.1 Hz, 2H), 7.31 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.04 – 6.93 (m, 5H), 6.88 (s, 1H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.76 (t, *J* = 7.4 Hz, 2H), 2.04 (s, 3H). ESI [M+H] calculated 356.1645 found 356.1649. $C_{24}H_{21}NO_2$ (Found C, 81.22; H, 5.82; N, 3.72; Required C, 81.10; H 5.96; N 3.94

S7 Imine synthesis over MOFs

7.1 *Imine synthesis of (E)-N-(1-(4-fluorophenyl)ethylidene)(phenyl)methanamine*



MOF (5 mol%) was heated to 150-250 °C under vacuum for 5hrs, 4' – Fluoroacetophenone (0.65 mmol), benzylamine (0.13 mmol), 1-methylnapthalene (0.4 mmol) and toluene (5 ml) were added and stirred at 100°C for 8 hrs. The reaction mixture was diluted using toluene, filtered through Na_2SO_4 and washed using 0.1M HCl solution and concentrated in vacuo to yield product (0.147 g, 99%).

^{1}H NMR (300 MHz, C_6D_6) δ 7.97 (ddd, *J* = 8.5, 5.3, 2.6 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.46 (td, *J* = 6.7, 6.2, 1.7 Hz, 2H), 7.40 – 7.28 (m, 2H), 7.19 – 7.11 (m, 2H), 4.81 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ 166.32, 141.24, 137.90, 131.61, 129.51, 129.39, 129.16, 128.43, 127.35, 56.38, 16.24. ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.38. . $C_{15}H_{14}FN$ Found C, 79.14; H, 6.19; N, 6.11; Required C, 79.27; H 6.21; N 6.16.

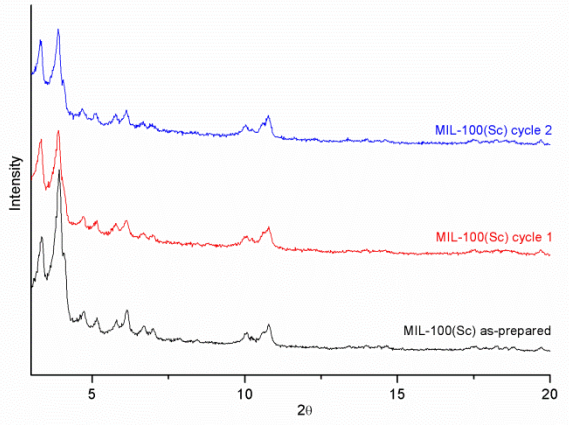
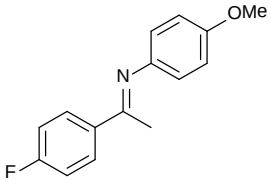


Figure S7.1 PXRD patterns of recovered MIL-100(Sc) after each cycle in the imine synthesis

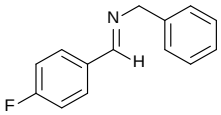
7.2 *Imine synthesis of (E)-N-(1- (4-fluorophenyl)^{1}H ethylidene)4-methoxyaniline*



MOF (5 mol%) was heated to 150-250 °C under vacuum for 5hrs, 4' – Fluoroacetophenone (0.65 mmol), 4-methoxyaniline (0.13 mmol), 1-methylnapthalene (0.4 mmol) and toluene (5 ml) were added and stirred at 100°C for 8 hrs. The reaction mixture was diluted using toluene, filtered through Na_2SO_4, washed using 0.1M HCl solution and concentrated in vacuo to yield product (0.158 g, 99%).

^{1}H NMR (300 MHz, MeOD) δ 7.93 – 7.79 (m, 2H), 7.15 – 7.00 (m, 2H), 6.91 – 6.78 (m, 2H), 6.70 – 6.58 (m, 4H), 3.70 (s, 1H), 2.15 (s, 2H). ^{19}F NMR (282 MHz, C_6D_6) δ -111.29 (s). . $C_{15}H_{14}FNO$ (Found C, 74.05; H, 5.81; N, 5.73; Required C, 74.06; H 5.8; N 5.76.

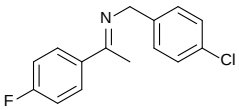
7.3 *Imine synthesis of Benzylidenebenzylamine*



MOF (5 mol%) was heated to 150-250 °C under vacuum for 5hrs, 4' – Fluorobenzaldehyde (0.65 mmol), benzylamine (0.65 mmol), 1-methylnapthalene (0.4 mmol) and toluene (5 ml) were added and stirred at room temperature for 8 hrs. The reaction mixture was diluted using toluene, filtered through Na_2SO_4 and concentrated in vacuo.

^{1}H NMR (300 MHz, C_6D_6) δ 8.53 (s, 1H), 7.79 – 7.76 (m, 2H), 7.49 – 7.45 (m, 3H), 7.36 – 7.32 (m, 4H), 7.26 – 7.27 (m, 1H), 4.85 (s, 2H), ^{13}C NMR (75 MHz, C_6D_6) δ 161.9, 137.2, 136.5, 130.9, 130.1, 128.7, 128.6, 127.8, 126.1, 64.8. ^{19}F NMR (282 MHz, C_6D_6) δ -106.82.

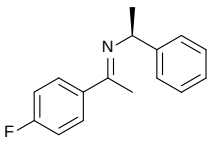
7.4 *Imine synthesis of 1-(4-chlorophenyl)-N-(1-(4-fluorophenyl)ethylidene)methanamine*



MOF (5 mol%) was heated to 150-250 °C under vacuum for 5hrs, 4' – Fluoroacetophenone (1.17 mmol), 4-chlorobenzylamine (0.65 mmol), 1-methylnapthalene (0.4 mmol) and hexane (5 ml) were added and stirred at 70°C for 8 hrs. The reaction mixture was diluted using toluene, filtered through Na_2SO_4, washed using methanol and concentrated in vacuo to yield product (0.155 g, 91%).

^{1}H NMR (300 MHz, C_6D_6) 7.80-7.73 (m, 2H), 7.34-7.10 (m, 3H), 6.97-6.89 (m, 2H), 4.31 (s, 2H), 1.74 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6) 164.2 (s), 140.4 (s), 133.0 (s), 129.4 (d, J=8.39 Hz), 129.1 (s), 128.8 (s), 128.4 (s), 128.1 (s), 115.5 (d, J=21.46 Hz), 55.2 (s), 15.2 (s). ^{19}F NMR (282 MHz, C_6D_6) -112.15 (s).

7.4 *Imine synthesis of 1-(4-fluorophenyl)ethylidene-1-phenylethanamine*



MOF (5 mol%) was heated to 150-250 °C under vacuum for 5hrs, 4' – Fluoroacetophenone (0.65 mmol), 4-chlorobenzylamine (1.3 mmol), 1-methylnapthalene (0.4 mmol) and hexane (5 ml) were added and stirred at 100°C for 8 hrs using dean stark apparatus to remove excess water. The reaction

mixture was diluted using hexane, filtered through Na_2SO_4, washed using methanol and concentrated in vacuo to yield product (0.151 g, 96%).

^{1}H NMR (300 MHz, C_6D_6) 7.83-7.76 (m, 2H), 7.59-7.55 (m, 2H), 7.37-7.17 (m, 3H), 6.96-6.90 (m, 2H), 4.70 (q, J=6.6 Hz, 1H), 1.79 (s, 3H), 1.59 (d, J=6.6 Hz, 3H). ^{19}F NMR (282 MHz, C_6D_6) -112.59.

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