Electronic Supplementary Information

A 3-D diamondoid MOF catalyst based on in-situ generated [Cu(L)$_2$] N-heterocyclic carbene (NHC) linkers: hydroboration of CO$_2$

Alexandre Burgun,[a] Rachel S. Crees,[a] Marcus L. Cole,[b] Christian J. Doonan[a] and Christopher J. Sumby[a]*

[a] School of Chemistry & Physics, The University of Adelaide, Adelaide, Australia. CJS: Phone +61 8 8313 7406. Fax. +61 8 8313 4358. Email: christopher.sumby@adelaide.edu.au

[b] School of Chemistry, University of New South Wales, Sydney, Australia.

1.   General experimental details

Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago (North Dunedin, New Zealand). Infrared spectra were collected on a Perkin-Elmer Spectrum 100 using a UATR sampling accessory. NMR spectra were recorded on a Varian Gemini 300 MHz or a 500 MHz NMR spectrometer at 23 °C using a 5 mm probe. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer STA-6000 instrument under a constant flow of N_2 at a temperature increase rate of 10 °C/min. Powder X-ray diffraction data were collected on a Rigaku Hiflux Homelab system using Cu Kα radiation with an R-Axis IV++ image plate detector. Samples were mounted on plastic loops using paratone-N and data collected by scanning 90° in Φ for 120 s exposures. The data were converted into xye format using the program Datasqueeze 2.2.2, Datasqueeze Software; Wayne, Pennsylvania, U.S.A., 2010. Simulated powder X-ray diffraction patterns were generated from the single crystal data using Mercury 3.0. Energy-dispersive X-ray spectroscopy (EDX) was performed on a Philips XL30 field emission scanning electron microscope. Catalytic reactions were carried out with standard Schlenk techniques under argon. THF was distilled from sodium/benzophenone. Unless otherwise stated, all chemicals were obtained from commercial sources and used as received. **H₃LCl**[1] and $[Cu(CH_3CN)_4]PF_6$[2] were prepared according to the methods described in the literature.

2.   Synthesis of [Zn₄O{Cu(L)₂}₂] (1)

H₃LCl (20 mg, 0.058 mmol), $Zn(NO_3)_2$ 6H₂O (17.3 mg, 0.058 mmol) and $[Cu(CH_3CN)_4]PF_6$ (10.8 mg, 0.029 mmol) were combined and dissolved in DMF (5 mL) in a 20 mL glass vial with a Teflon-lined screw cap. The mixture was heated at 120°C for 14 days resulting in pale yellow crystals. The crystals were washed with fresh DMF (×6), methanol (×5) and dried under vacuum to yield the dried sample **1-***dried* (14 mg, 59%). Anal. Calc. for $C_{68}H_{40}N_8O_{17}Cu_2Zn_4$ 3H₂O: C, 48.51; H, 2.75; N, 6.65. Found: C, 48.29; H, 2.62; N, 6.60%. ν_{max}(neat, cm^{-1}): 1606 (s, C=O), 1555 (m, C=C), 1511 (w, C=C), 1377 (s).
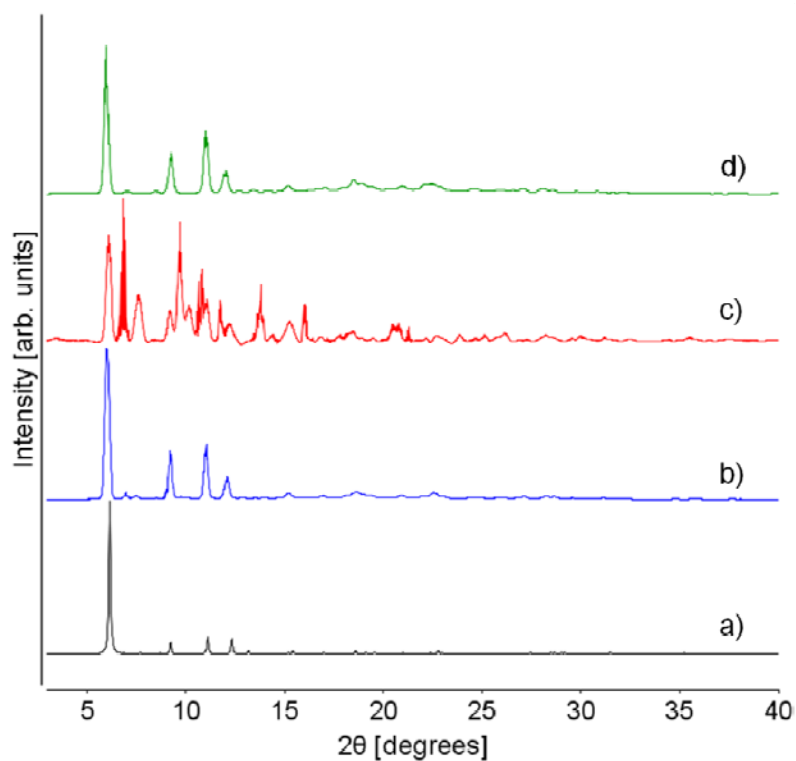
Figure S1. PXRD patterns of [Zn$_4$O{Cu(**L**)$_2$}$_2$] (**1**): a) simulated from the single crystal data, b) in DMF , c) in DCM (which shows both **1** and **1**-*dried*), and d) in THF.

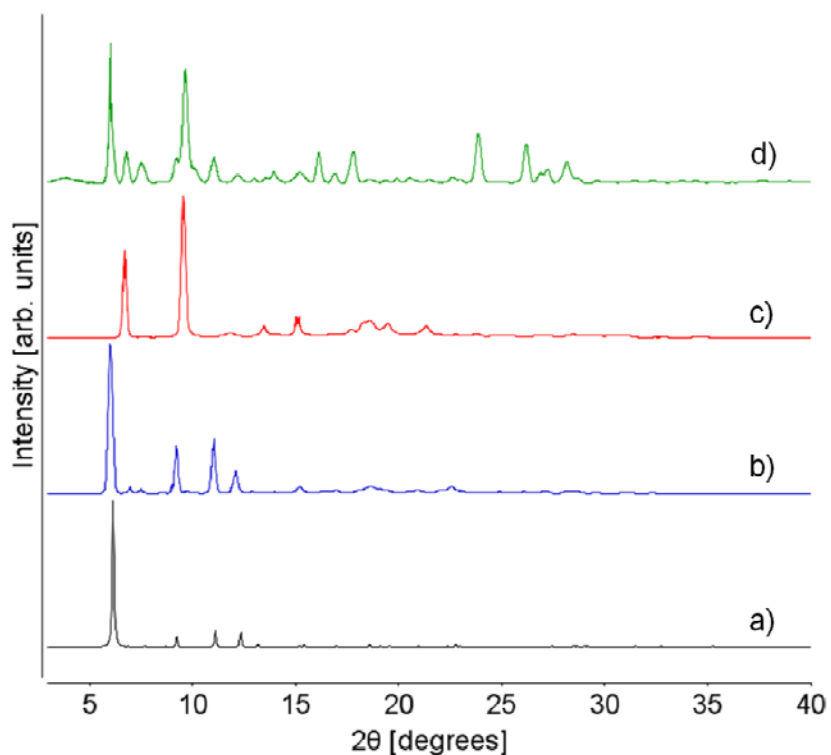**Figure S2**. PXRD patterns of [Zn$_4$O{Cu(**L**)$_2$}$_2$] (**1**): a) simulated from the single crystal data, b) as-synthesised, c) dried, and d) resolvated in DMF.
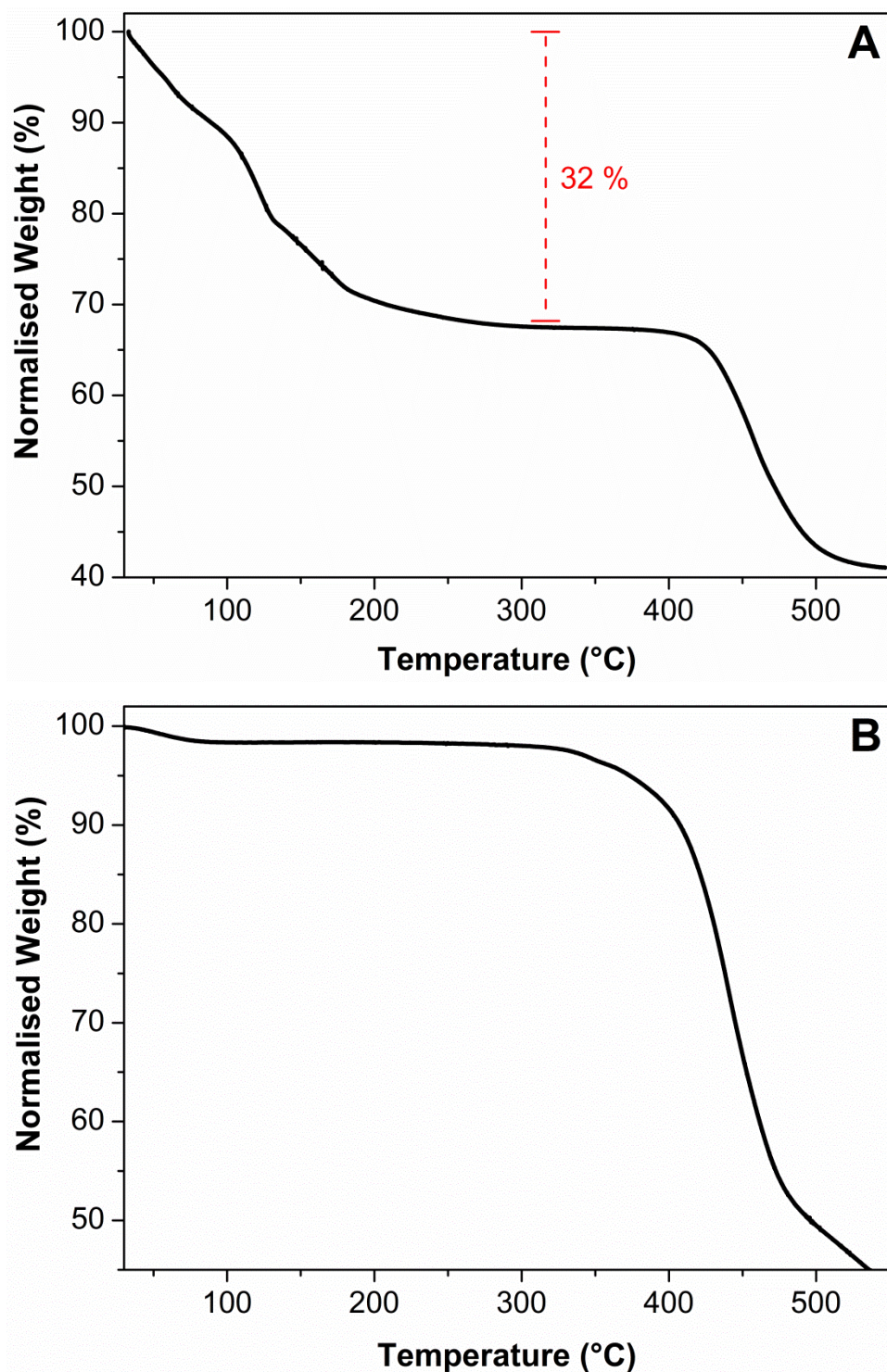
3.   Thermogravimetric Analysis

Figure S3. A. TGA trace of an as-synthesized sample of **1**. The weight loss of 32% corresponds to solvent molecules lost from the pores of the material. The MOF is thermally stable up to ~400°C. **B.** TGA trace **1**-*dried*.

4. Energy Dispersive X-ray spectroscopy (EDX)

Table S1. Atomic ratio of Zn and Cu in **1** determined by EDX.

Atomic ratio	Cu	Zn
MOF **1**	0.53	1.00

EDX results are calculated as an average of four areas of a sample (3 mm^2 of crystalline sample). Atomic ratio are normalised to Zn content.
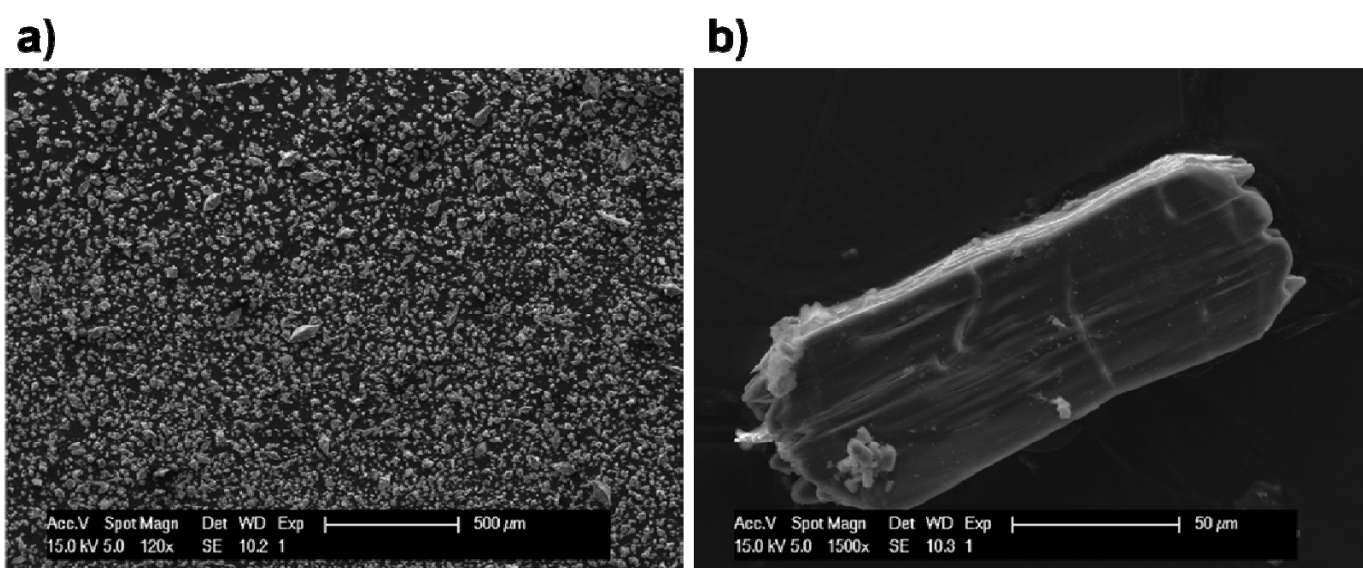

Figure S4. SEM images of **1**. (a) An example of an area of crystals used for analysis. (b) An example of a single crystal.

5.   X-Ray Crystallography

A crystal of **1** was mounted on a plastic loop using paratone-N oil and X-ray diffraction data collected with Mo-Kα radiation (λ = 0.7107 Å) on an Oxford Diffraction X-calibur diffractometer at 110(2) K. The data set was corrected for absorption and the structures were solved by direct methods using SHELXS-97[3] and refined by full-matrix least squares on F^2 by SHELXL-97,[4] interfaced through the program X-Seed.[5]   All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions, unless specified otherwise in additional details below. Details of data collections and structure refinements are given in Table S2.

Refinement special details for **1**: The structure of this MOF possesses large voids containing a considerable number of diffuse electron density peaks that could not be adequately modelled as solvent. The SQUEEZE routine of PLATON[6] was applied to the collected data, which resulted in significant reductions in R_1 and wR_2. R_1 and wR_2 before SQUEEZE routine: 19.93%, 51.4%; after SQUEEZE routine: 12.37%, 37.60%.

Table S2. X-ray experimental data for **1**.

Empirical formula	$C_{68}H_{40}Cu_2N_8O_{17}Zn_4$
Formula weight	1627.62
Crystal system	Orthorhombic
Space group	*Ibca*
a (Å)	28.1305(9)
b (Å)	26.1877(8)
c (Å)	28.1745(17)
α (º)	90
β (º)	90
γ (º)	90
Volume (Å^3)	20755.4(16)
Z	8
Density (calc.) (Mg/m^3)	1.042
Absorption coefficient (mm^{-1})	1.361
F(000)	6528
Crystal size (mm^3)	0.20 x 0.18 x 0.09
θ range for data collection (º)	2.57 - 29.17
Reflections collected	12711
Observed reflections [R(int)]	6666 [0.1060]
Goodness-of-fit on F^2	1.143
R_1 [I>2σ(I)]	0.1237
wR$_2$ (all data)	0.3760
Largest diff. peak and hole (e.Å^{-3})	1.455 and -1.372

6.   Catalysis

General procedure for Table 1, Entry 3 and Table S3.

MOF **1** (14 mg, 0.0086 mmol, 2.5 mol %) soaked in THF (1.2 mL) was charged in a 50 mL Schlenk under argon. CO_2 (~ 1atm) was then introduced using a balloon by purging the system (×4). Pinacol borane (50 µL, 0.344 mmol) was added dropwise to the solution and the resulting mixture was stirred for 24 h at 35°C. **1** was then removed from the reaction mixture by filtration and NEt_3 (36 µL, 0.258 mmol) and benzylamine (19 µL, 0.172 mmol) were added to the solution under argon. After stirring for 48 h at 65°C, the resulting mixture was directly passed through a pad of silica gel eluting with ethyl acetate. The solvent was then evaporated under vacuum and the residue was directly analysed by ^{1}H NMR spectroscopy in $CDCl_3$.

Spectroscopic data for *N*-formyl benzylamine were consistent with the previously reported data for this compound.[7] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.29 (s, 0.8H), 8.22 (d, J = 12 Hz, 0.2H), 7.30 (m, 5H), 5.76 (s(br), 1H), 4.50 (d, *J* = 6 Hz , 1.6H), 4.43 (d, *J* = 6 Hz , 0.4H). ^{13}C NMR (CDCl3, 150 MHz): δ 164.7, 161.0, 137.7, 129.1, 129.0, 128.2, 128.0, 127.9, 127.1, 45.8, 42.4. HRMS *m/z*: found 136.0764 [M + H]$^+$, calcd 136.0762 for C_8H_9NO.
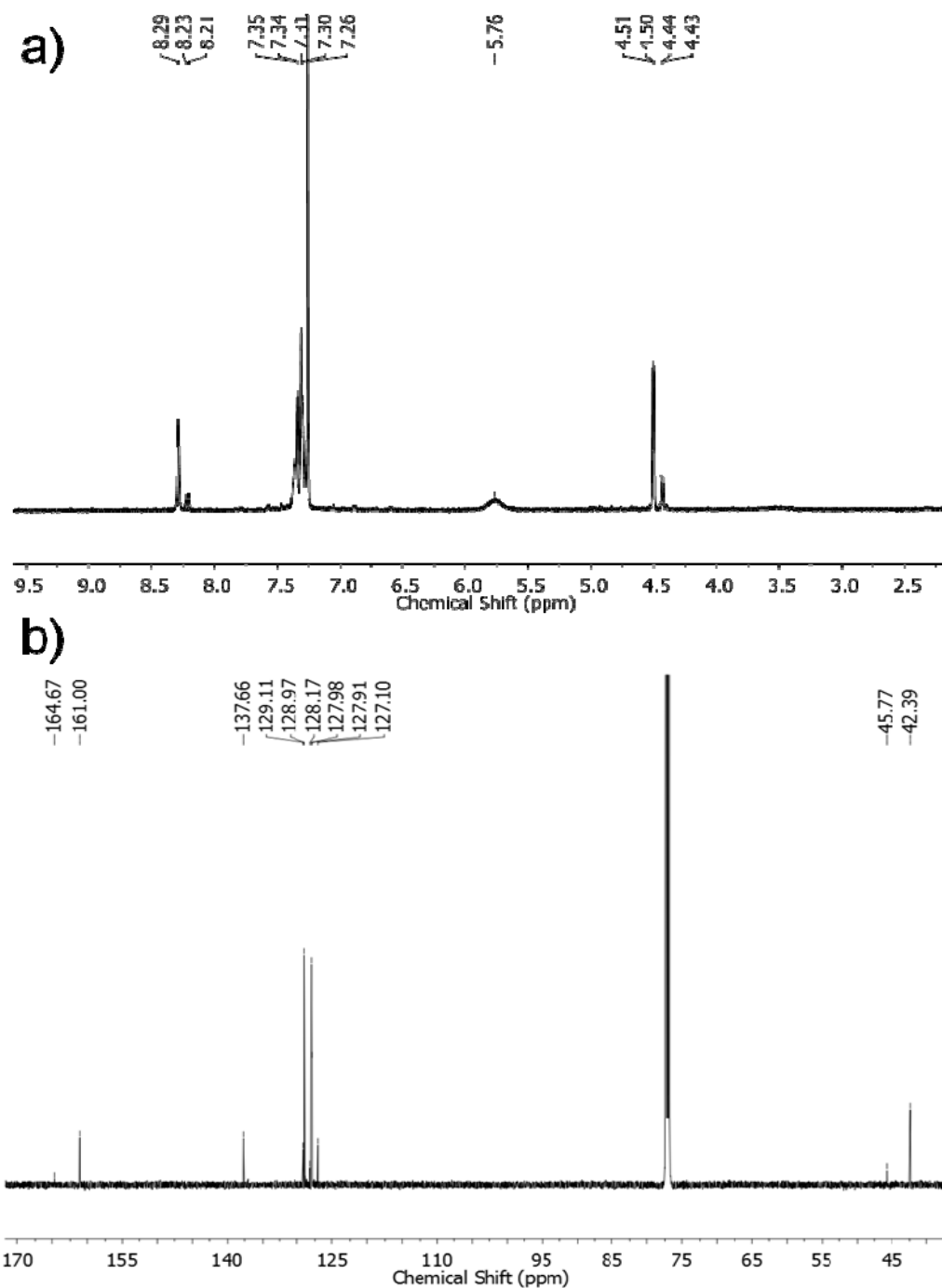
Figure S5. a) ^{1}H NMR spectrum of *N*-formyl benzylamine. b) ^{13}C NMR spectrum of *N*-formyl benzylamine.

Table S3. Recyclability tests for **1** using 5 mol % loading.

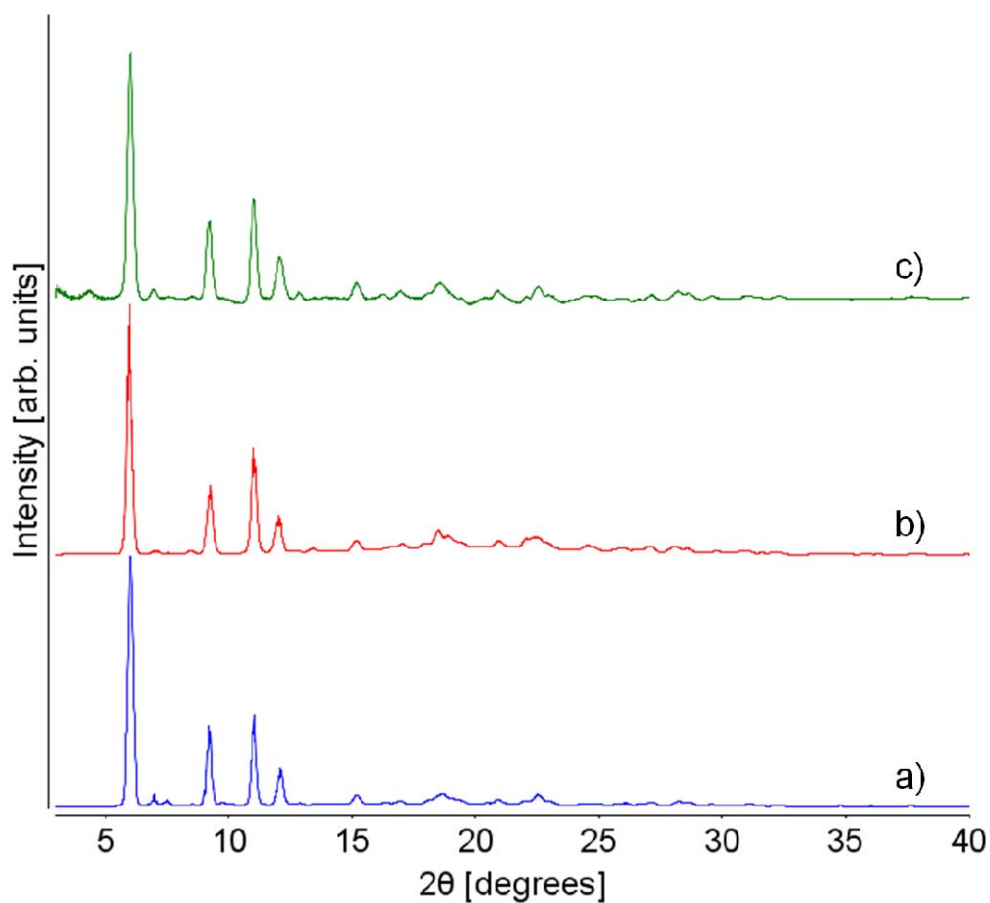| Cycle	1	2	3	4	5
conv. (%)[a]	92	62	53	52	51

[a] Determined by ^{1}H NMR spectroscopy.

Figure S6. PXRD patterns of **1**: a) as-synthesised, b) after 1st catalytic cycle, and c) after 5th catalytic cycle.

Table S4. Cu concentration in the reaction mixture as measured by ICP-MS after one catalytic cycle.

mol % Cu[a]	Conc. Cu [ppb]	% Cu leached
5	50±2	0.023%

[a] 1 mol % Cu = 0.5 mol % MOF.

7. References

1. S. Sen, N. N. Nair, T. Yamada, H. Kitagawa, P. K. Bharadwaj, *J. Am. Chem. Soc.*, 2012, **134**, 19432.
2. G. J. Kubas, *Inorg. Synth.*, 1979, **19**, 90.
3. G. M. Sheldrick, *Acta Crystallogr*., 1990, **A46**, 467.
4. G. M. Sheldrick, SHELXL-97, University of Gottingen, Gottingen, Germany, 1997.
5. L. J. Barbour, *J. Supramol. Chem.* 2001, **1,** 189.
6. A. L. Spek, Platon, *Acta Cryst.,* 1990, **A46**, C34.
7. M. Suchy, A. A. H. Elmehriki, R. H. E. Hudson, *Org. Lett.*, 2011, **13**, 3952.