Electronic Supplementary Material (ESI) for Dalton Transactions.

Analysing the Role of Anions in the Synthesis of Catalytic Active Urea-based MOF

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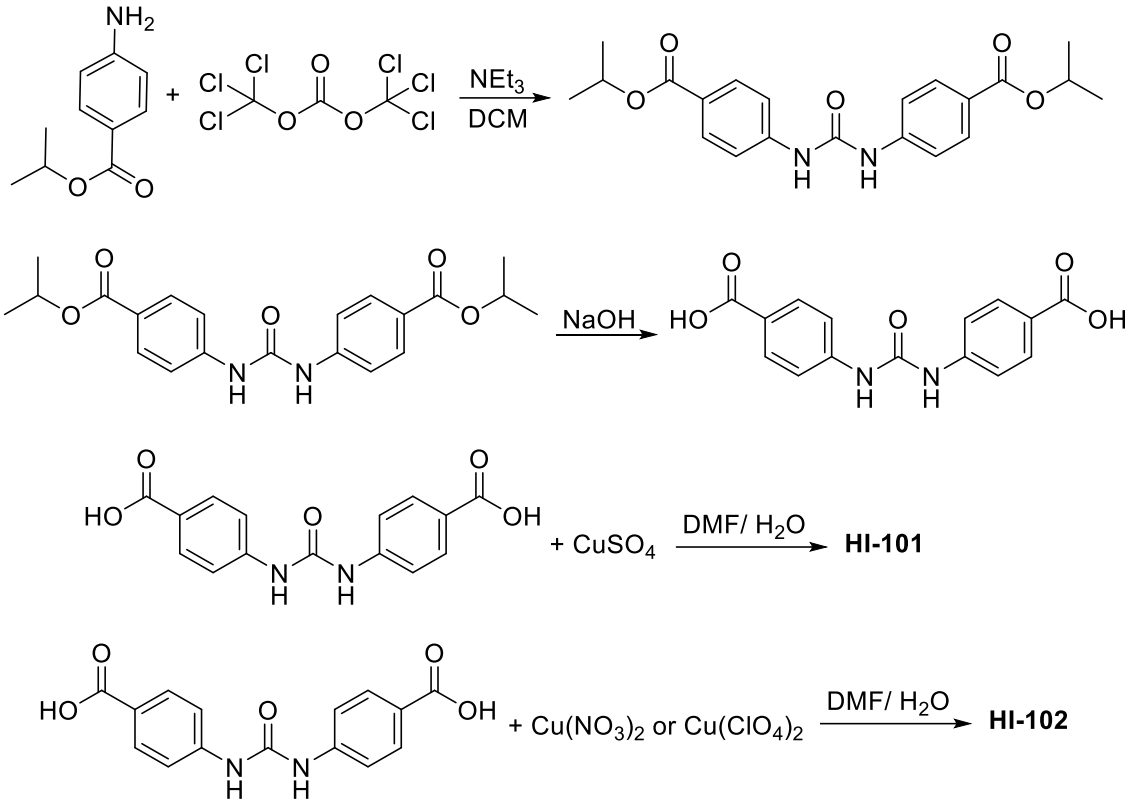
1. Synthesis of the H_2L Ligand and **HI-101**



Scheme S1: Synthetic route of the urea functionalized ligand and MOFs.

2. Crystallization details

Table S1: Reaction of H_2L (0.1 mmol) and copper(II) salts (0.1 mmol) in various solvents.

Ligand Solvent	Copper(II) salts solvent	Observation
DMF (5.0 mL)	Water (3.0 mL)	Needle shaped crystal with $CuSO_4.5H_2O$
DMA (5.0 mL)	Water (3.0 mL)	Needle shaped microcrystals with $CuSO_4.5H_2O$
DMSO (5.0 mL)	Water (3.0 mL)	Blue precipitate
DEF (5.0 mL)	Water (3.0 mL)	Needle shaped microcrystals with $CuSO_4.5H_2O$
DEA (5.0 mL)	Water (3.0 mL)	Needle shaped microcrystals with $CuSO_4.5H_2O$
DMF (5.0 mL)	DMF (3.0 mL)	Blue precipitate
DMF (5.0 mL)	MeOH (10.0 mL)	Blue precipitate
DMF (5.0 mL)	EtOH (10.0 mL)	Blue precipitate

Table S2: Reaction of H_2L (30.0 mg) with various copper(II) salts in DMF (5.0 mL)/water (3.0 mL)

Copper salt	Amount (mg)	Observation
$CuSO_4.5H_2O$	25.0	Needle shaped crystal
$Cu(ClO_4)_2.6H_2O$	37.0	Plate shaped microcrystals
$Cu(NO_3)_2.3H_2O$	24.1	Plate shaped microcrystals
$Cu(OAc)_2.H_2O$	20.0	Blue precipitate
$CuCl_2$	13.3	Yellow precipitate

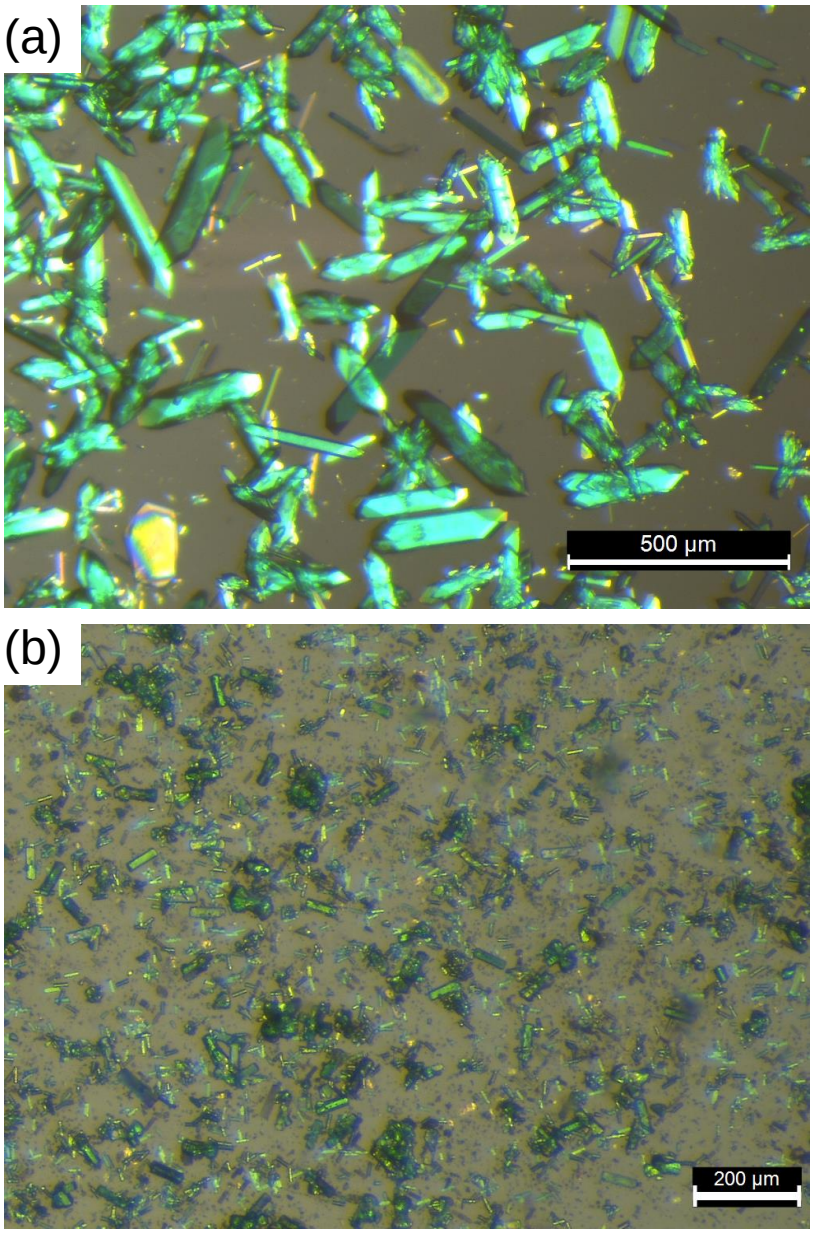


Figure S1: Crystals obtained from the metalation of H_2L ligand: (a) with $CuSO_4$ and (b) with $Cu(NO_3)_2$ or $Cu(ClO_4)_2$.

3. X-ray crystallography

Table S3: Crystal data of the MOFs

Crystal data	**HI-101**	**HI-102**
Empirical formula	$[C_{24}H_{31}CuN_5O_8]_n$	$[C_{21}H_{24}CuN_4O_7]_n$
Colour	Green	Green
Formula weight	581.08	507.98
Crystal size (mm)	0.13 x 0.07 x 0.04	0.18 x 0.06 x 0.03
Crystal system	Tetragonal	Orthorhombic
Space group	*P*4/mcc	*P*bca
a (Å)	15.2686(3)	18.2919(5)
b (Å)	15.2686(3)	9.4420(3)
c (Å)	29.2342(6)	25.3572(7)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume ($Å^3$)	6815.4(3)	4379.5(2)
Z	8	8
$D_{calc.}(g/cm^3)$	1.133	1.541
F(000)	2448	2104
μ CuKα (mm^{-1})	1.285	1.862
Temperature (K)	250(2)	240(2)
Reflections collected/ unique/observed [I>2σ(I)]	37664/3094/2175	31808/4141/3450
Data/restraints/parameters	3094/0/107	4141/0/302
Goodness of fit on F^2	1.099	1.172
Final R indices [I>2σ(I)]	R_1 = 0.0767 wR_2 = 0.2625	R_1 = 0.0632 wR_2 = 0.1641
R indices (all data)	R_1 = 0.1000 wR_2 = 0.2821	R_1 = 0.0759 wR_2 = 0.1713

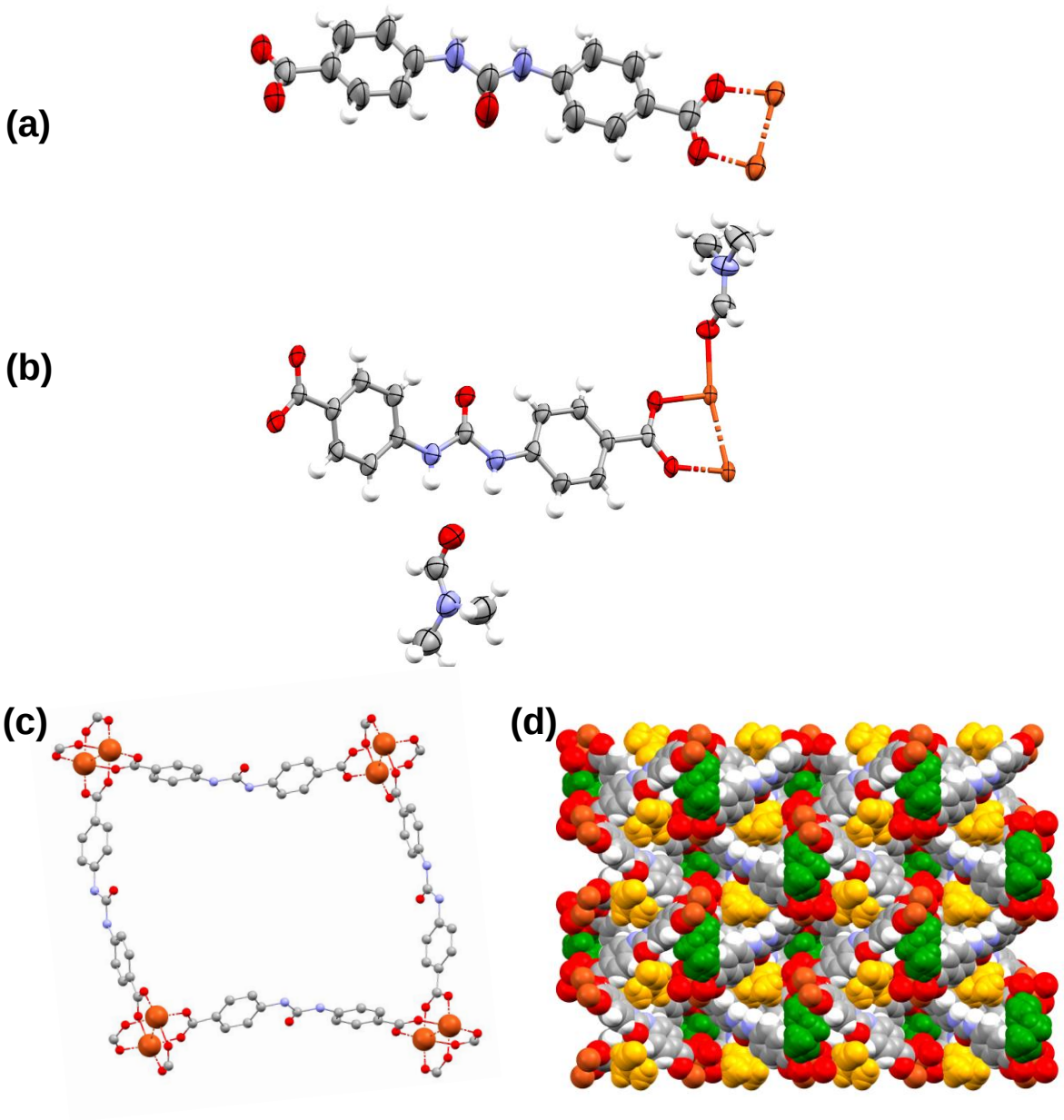


Figure S2: Thermal ellipsoidal plot (50% probability) of (a) **HI-101** and (b) **HI-102** (Color code: carbon-grey, nitrogen-blue, oxygen-red, hydrogen-white and copper-dark orange), (c) square grid network of **HI-102** and (d)space fill model of **HI-102** displaying the coordinated (green colour) and the solvent DMF molecules (orange) occupying the smaller and bigger pores, respectively.

4. Powder X-ray powder diffraction (PXRD)

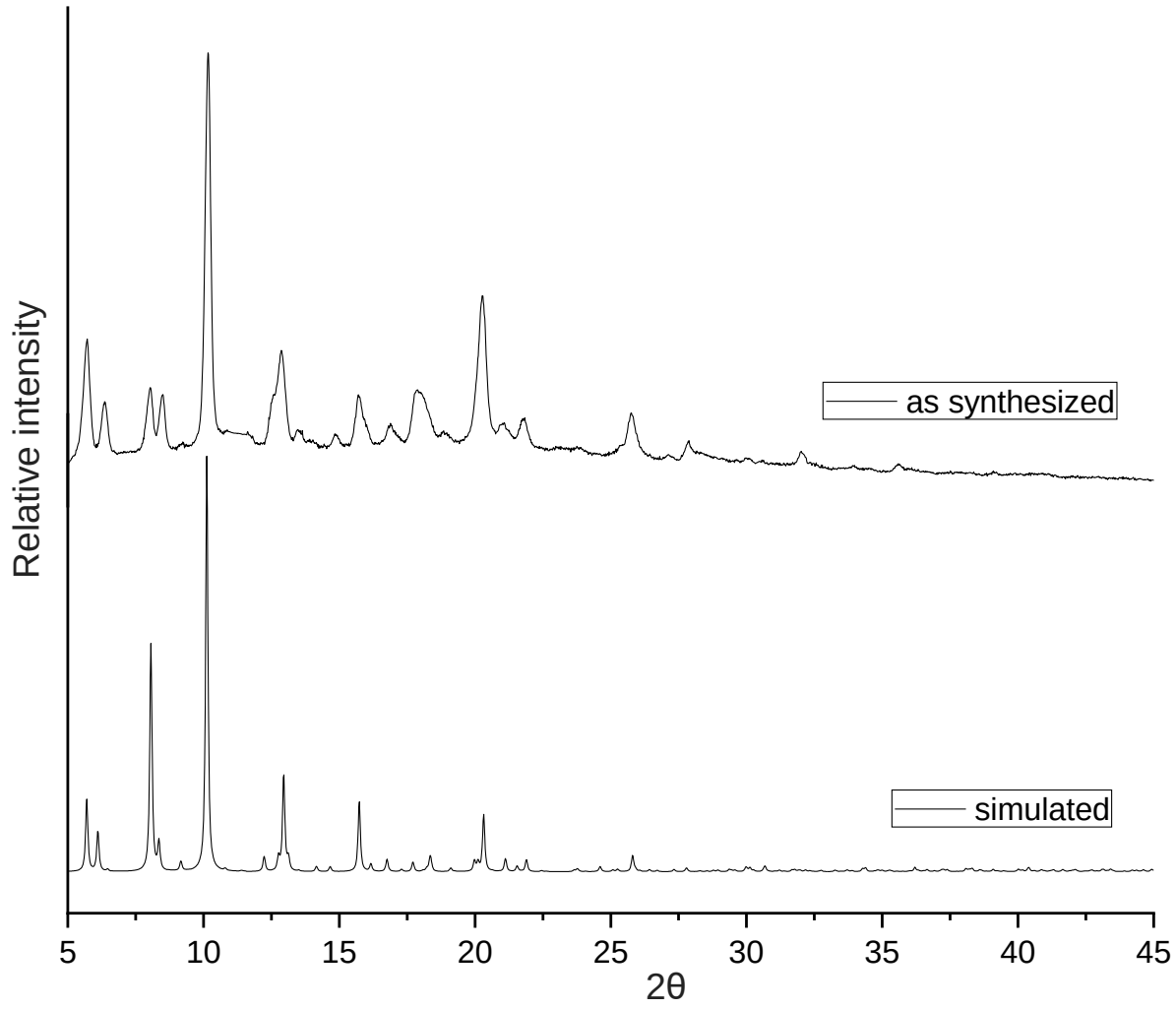


Figure S3: PXRD of simulated and as synthesized **HI-101**.

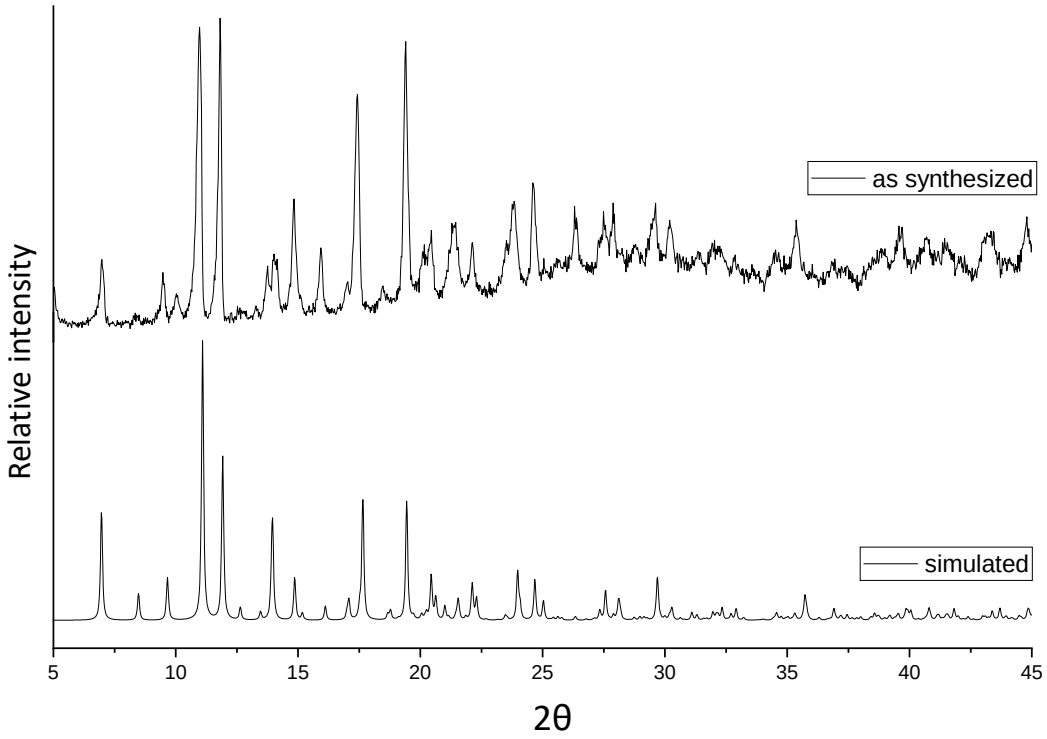


Figure S4: PXRD of simulated and as synthesized **HI-102**.

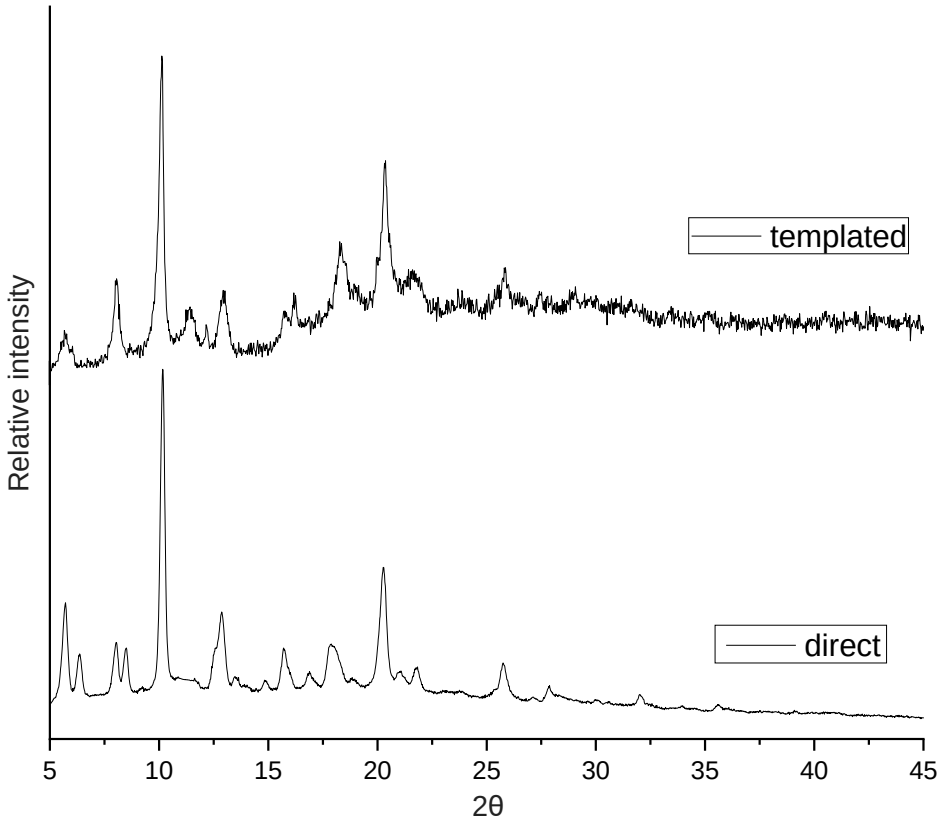


Figure S5: PXRD of **HI-101**: Direct synthesized from $CuSO_4.5H_2O$ and **H_2L**; and anion-templated synthesis from $Cu(NO_3)_2.3H_2O$, Na_2SO_4 and **H_2L** (Entry 3, Table S4).

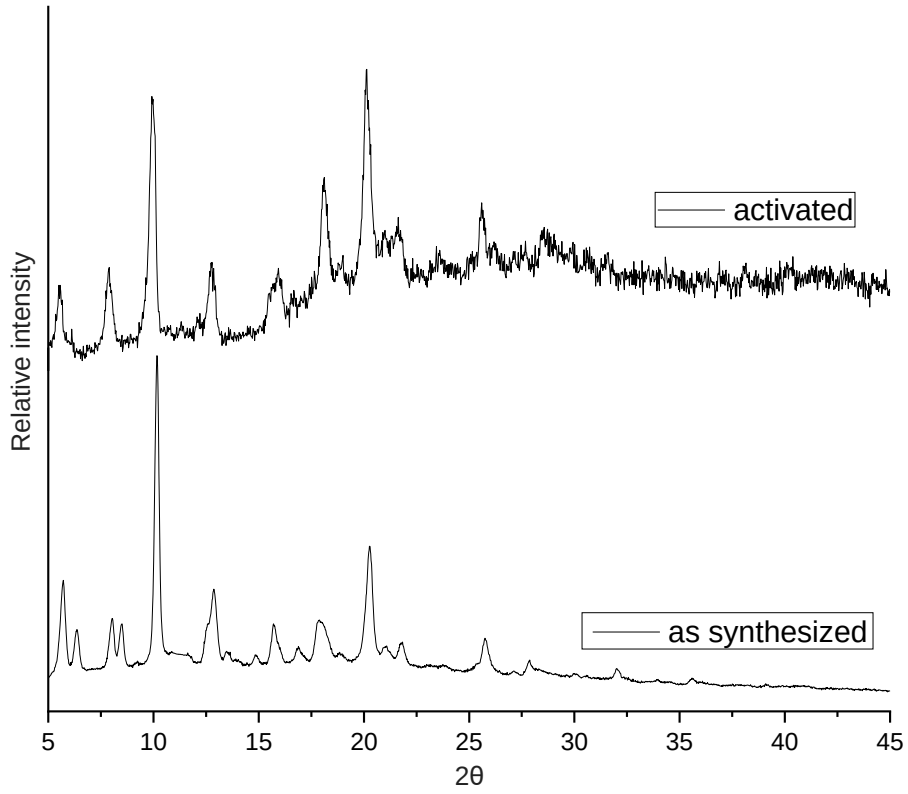


Figure S6: PXRD of the fresh crystals of **HI-101** and crystals after drying at 70.0 °C under vacuum for 12 hours.

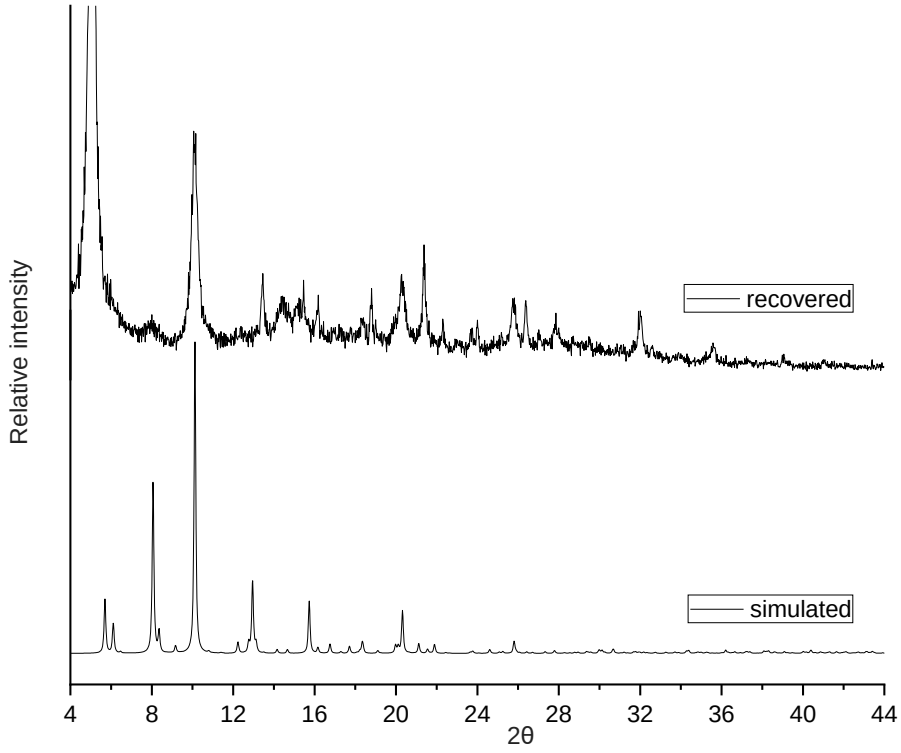


Figure S7: Comparison of PXRD pattern of simulated **HI-101** and the recovered **HI-101** after the CO_2 fixation reaction.

5. Anion-templated Synthesis

Table S4: Reaction of H_2L (0.1 mmol in DMF) with various salts (0.1 mmol in water)

Entry	Copper(II) salt	Additive salt (amount)	Observation
1	$CuSO_4.5H_2O$	-	Needle-shaped crystal (Similar to Figure S1a)
2	$Cu(NO_3)_2.3H_2O$	$(NH_4)_2SO_4$ (0.1 mmol)	Needle-shaped crystal (Similar to Figure S1a)
3	$Cu(NO_3)_2.3H_2O$	Na_2SO_4 (0.1 mmol)	Needle-shaped crystal (Similar to Figure S1a)
4	$Cu(NO_3)_2.3H_2O$	Na_2SO_4 (0.05 mmol)	Needle-shaped crystal (Similar to Figure S1a)
5	$Cu(NO_3)_2.3H_2O$	Na_2SO_4 (0.025 mmol)	Needle-shaped crystal (Similar to Figure S1a)
6	$Cu(NO_3)_2.3H_2O$	Na_2SO_4 (0.0125 mmol)	Blue precipitate + microcrystals
7	$Cu(NO_3)_2.3H_2O$	$NaBF_4$ (0.1 mmol)	Blue precipitate
8	$Cu(NO_3)_2.3H_2O$	Na_3PO_4 (0.1 mmol)	Immediate blue precipitate
9	$Cu(ClO_4)_2.6H_2O$	$(NH_4)_2SO_4$ (0.1 mmol)	Needle-shaped crystal (Similar to Figure S1a)
10	$Cu(ClO_4)_2.6H_2O$	Na_2SO_4 (0.1 mmol)	Needle-shaped crystal (Similar to Figure S1a)

6. Thermogravimetric Analysis (TGA)

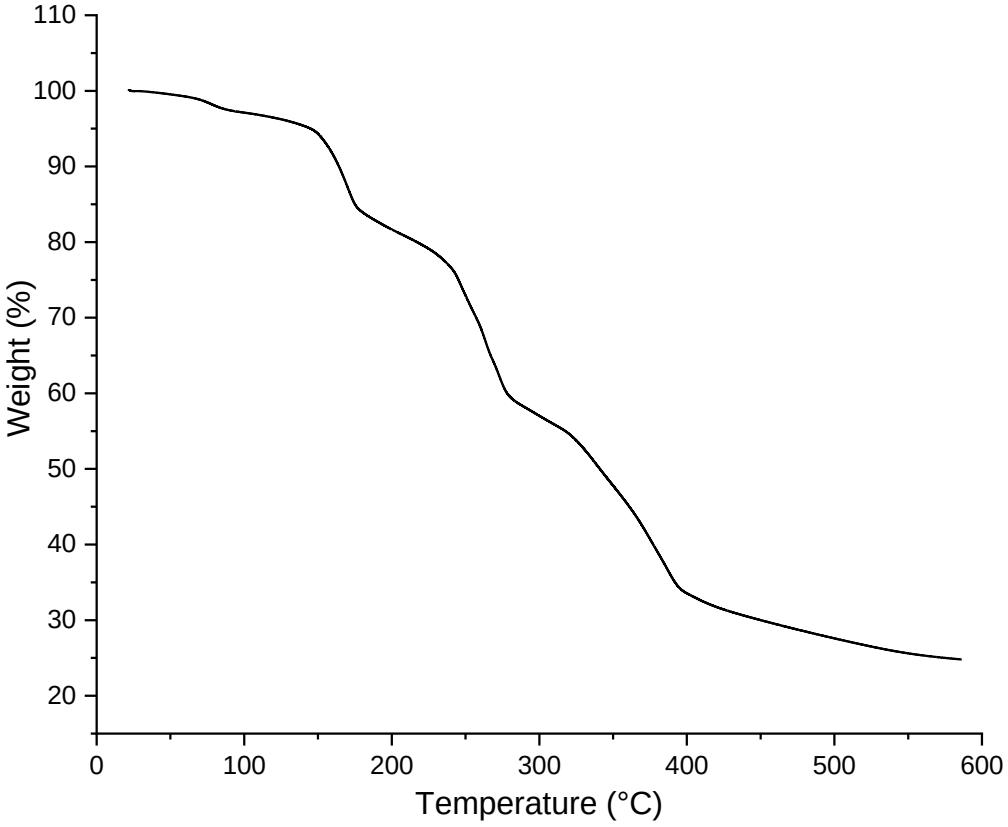


Figure S8: TGA of as synthesized **HI-101**.

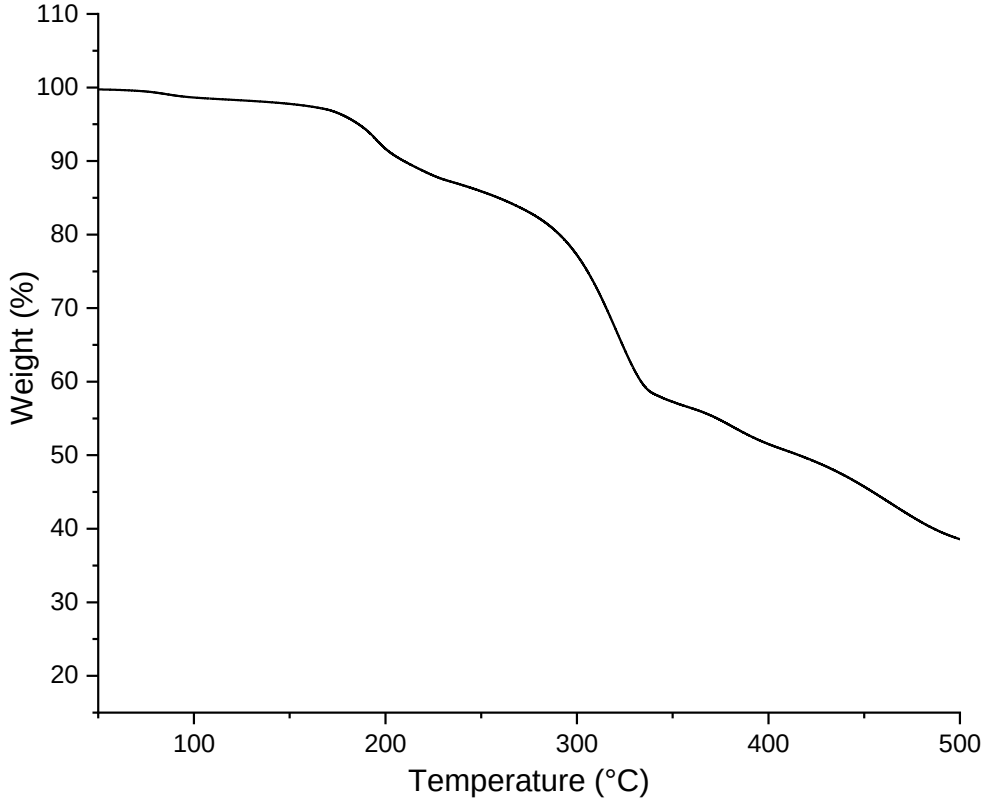


Figure S9: TGA of **HI-101** dried at 70.0 °C for 12 h.

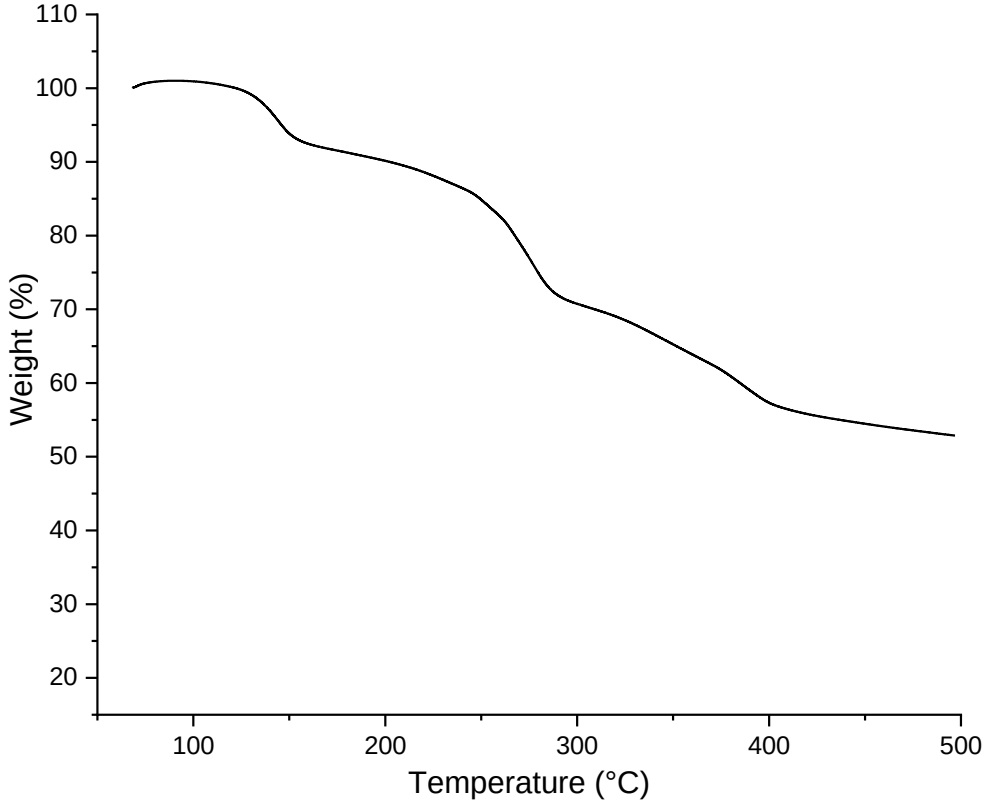


Figure S10: TGA of as synthesized **HI-102**.

7. Catalytic activity of HI-101

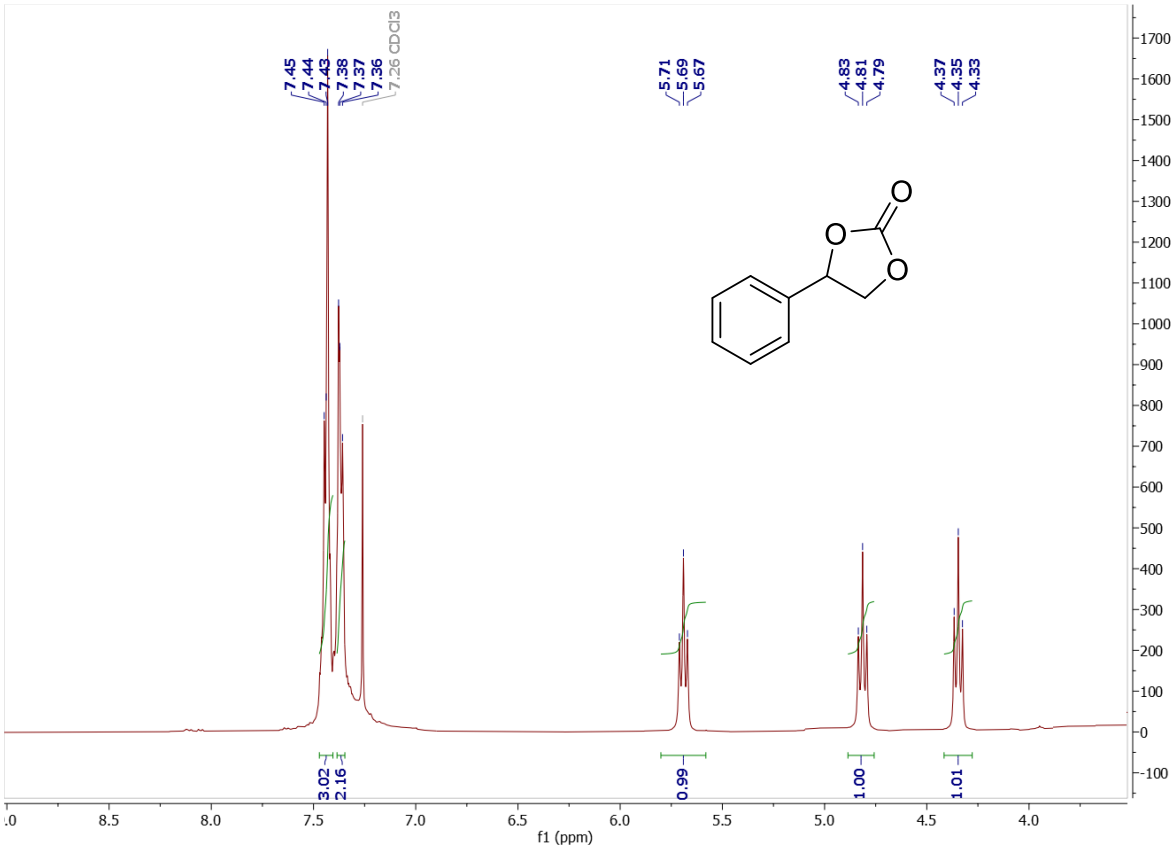


Figure S11: ^{1}H-NMR spectrum of the product obtained from **HI-101** catalyzed CO_2 fixation reaction of styrene oxide.

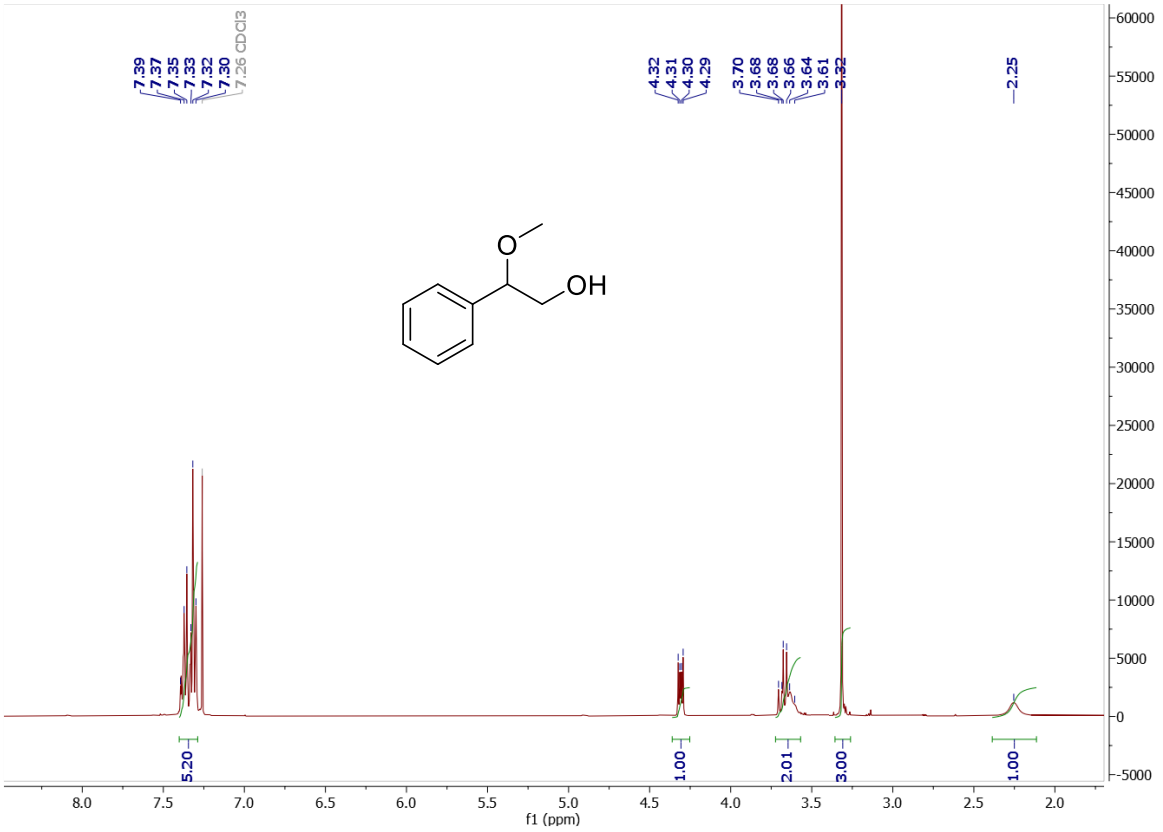


Figure S12: [1]H-NMR spectrum of the product obtained from **HI-101** catalyzed methanolysis reaction of styrene oxide.

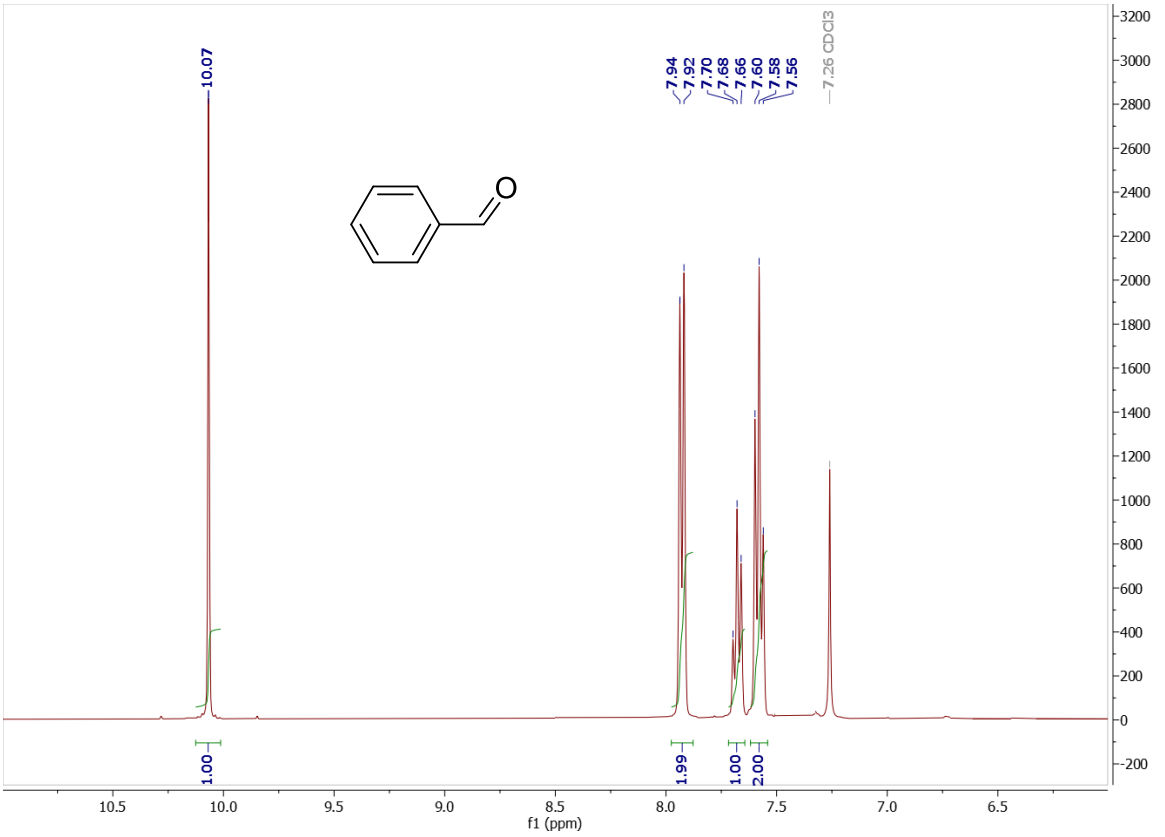


Figure S13: [1]H-NMR spectrum of the product obtained from **HI-101** catalyzed oxidation reaction of benzyl alcohol.