Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Investigating the Melting Behaviour of Polymorphic Zeolitic Imidazolate Frameworks

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Table S1: Optimisation of ZIF-76-mbIm synthesis. Blue) Investigation of the volume of NaOH used. Increasing the volume of NaOH increased the yield but too much led to the formation of a mixed phase product. Synthesis 3 gave optimal purity and yield (highlighted in yellow). Synthesis 4 had a greater yield; though infrequently produced a mixed phase product. Green) Investigation of changing the ratio of Im and mbIm. Increasing the content of Im led to a mixed phase product and further increases gave phase pure TIF-4.

Reaction Number	NaOH		Im		mbIm		Result	Yield (mg)	Yield (%)
	ml	mmol	g	mmol	g	mmol			
1	0	0	0.12	1.76	0.11	0.83	ZIF-76-mbIm single crystals	14	6
2	0.13	0.33	0.12	1.76	0.11	0.83	ZIF-76-mbIm powder	108	48
3	0.26	0.65	0.12	1.76	0.11	0.83	ZIF-76-mbIm powder	152	67
4	0.39	0.98	0.12	1.76	0.11	0.83	ZIF-76-mbIm powder	200	89
5	0.52	1.30	0.12	1.76	0.11	0.83	Mixed phase ZIF-76-mbIm and TIF-4	169	75
6	0.26	0.65	0.120	1.763	0.110	0.832	ZIF-76-mbIm powder	152	67
7	0.26	0.65	0.124	1.827	0.103	0.783	Mixed phase ZIF-76-mbIm and TIF-4	163	72
8	0.26	0.65	0.130	1.914	0.092	0.696	Mixed phase ZIF-76-mbIm and TIF-4	171	76
9	0.26	0.65	0.136	2.001	0.080	0.609	Mixed phase ZIF-76-mbIm and TIF-4	116	51
10	0.26	0.65	0.142	2.088	0.069	0.522	TIF-4 powder	99	44
11	0.26	0.65	0.148	2.174	0.058	0.439	TIF-4 powder	110	49

Effect of Organic Linker Chemistry on Thermal Behaviour

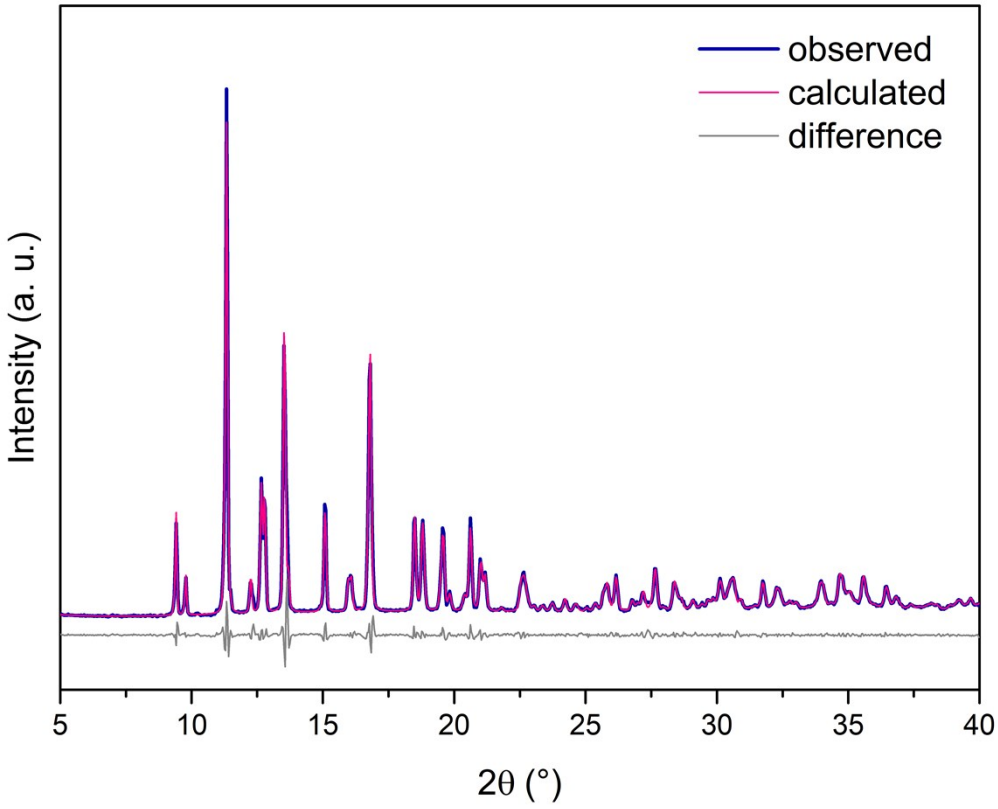

Figure S1: Pawley refinement of powder X-ray diffraction data of TIF-4. Initial parameters were obtained from the previously reported CIF of TIF-4.[1] It should be noted that TIF-4 prepared in this work has a different stoichiometry $[Zn(Im)_{1.8}(mbIm)_{0.2}]$ to that reported previously $[Zn(Im)_{1.5}(mbIm)_{0.5}]$, explaining the small difference in lattice parameters.

Table S2. Data from Pawley refinement of TIF-4

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for TIF-4[1]
8.715	*Pbca*	*a* = 15.4879(19) Å	*a* = 15.6251(9) Å
		b = 15.822(2) Å	*b* = 16.3217(9) Å
		c = 18.187(2) Å	*c* = 18.1244(10) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

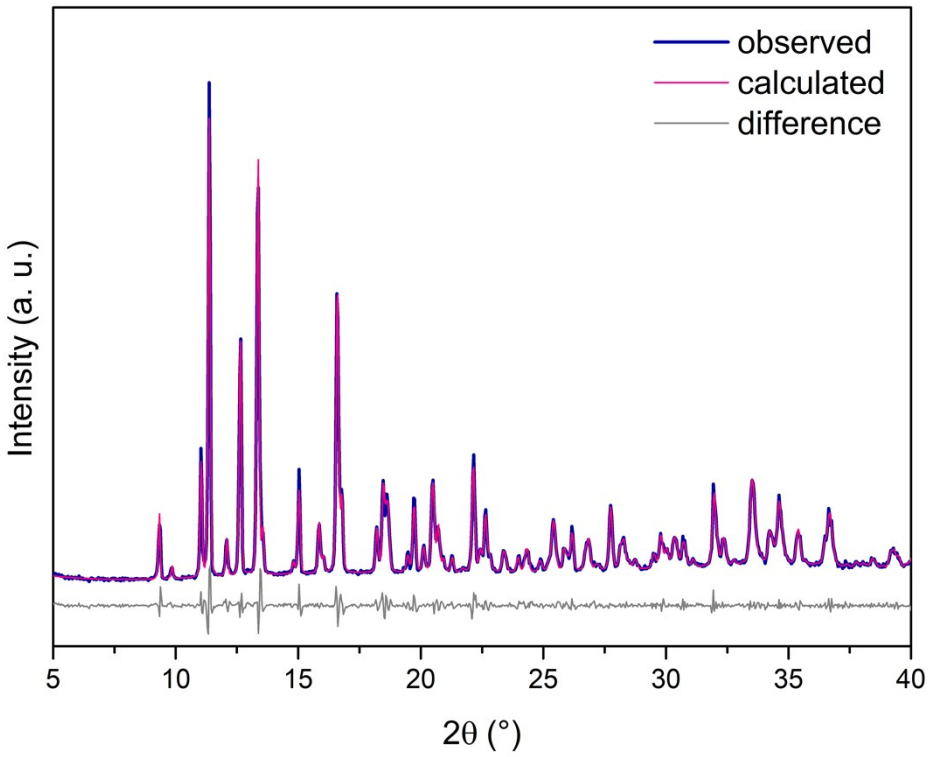

Figure S2: Pawley refinement of powder X-ray diffraction data of ZIF-UC-5. Initial parameters were obtained from the CIF previously reported for ZIF-UC-5.[2] It should be noted that ZIF-UC-5 has a different stoichiometry $[Zn(Im)_{1.8}(ClbIm)_{0.2}]$ to that previously reported $[Zn(Im)_{1.63}(mbIm)_{0.37}]$, explaining the small difference in lattice parameters.

Table S3. Data from Pawley refinement of ZIF-UC-5

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-UC-5[2]
8.215	*Pbca*	*a* = 15.646(2) Å	*a* = 15.7260(8) Å
		b = 16.087(2) Å	*b* = 16.0184(11) Å
		c = 18.029(3) Å	*c* = 18.1617(10) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

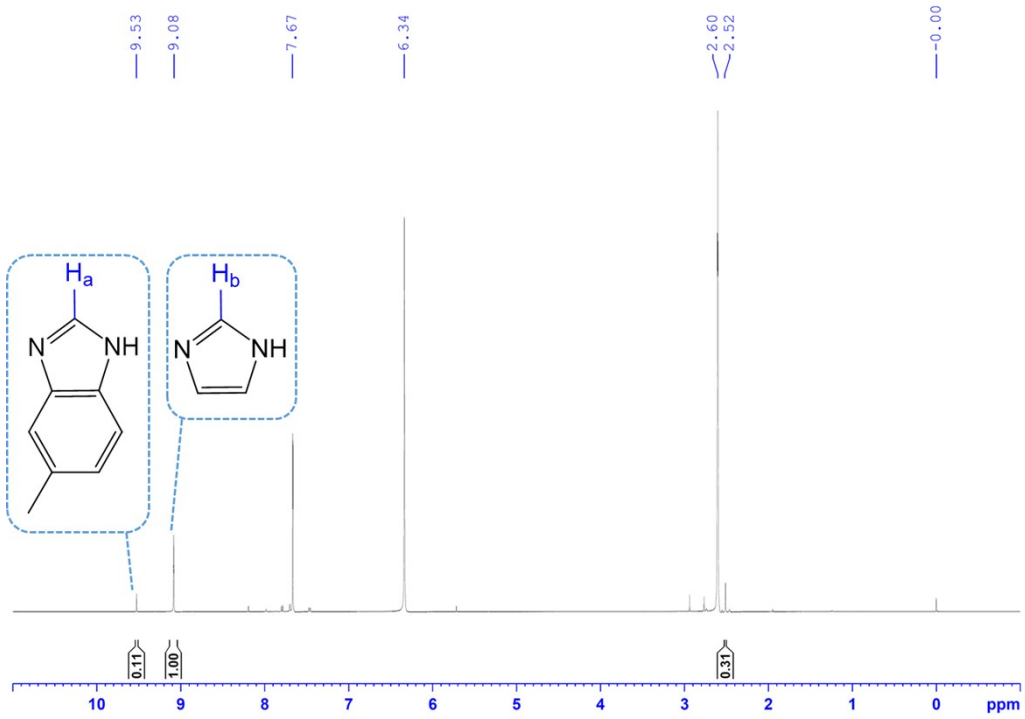

Figure S3: ^{1}H nuclear magnetic resonance spectrum of TIF-4.

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.53 (1H, s, H_a), 9.08 (1H, s, H_b), 7.67 (5H, m, aromatic), 6.34 (H_2O/HCl), 2.60 (DMSO), 2.52 (3H, s, Me), 0.00 (TMS).

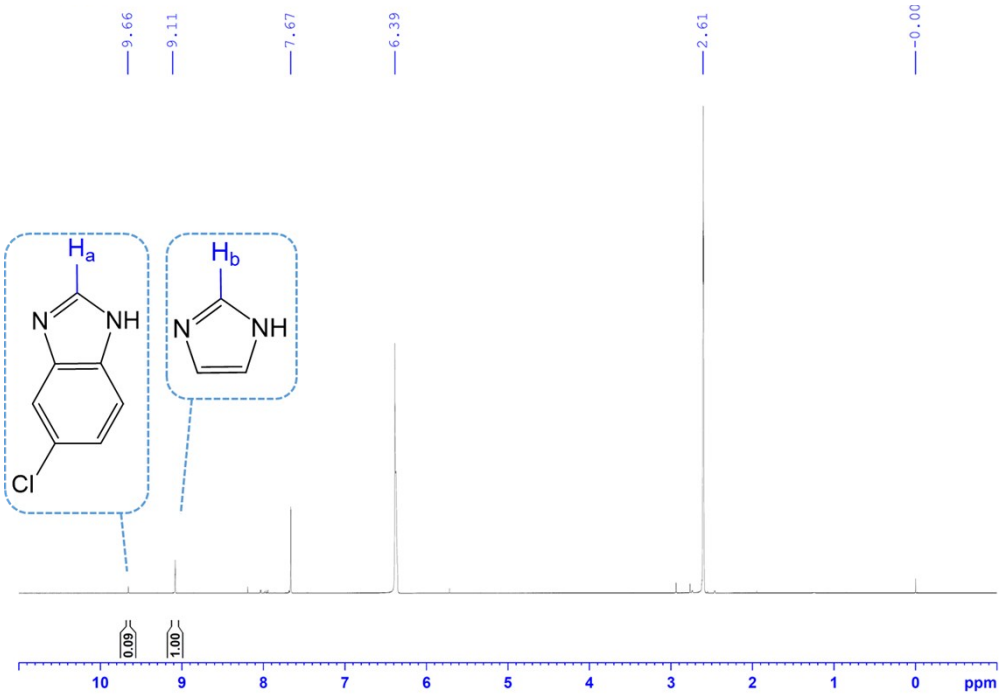

Figure S4: ^{1}H nuclear magnetic resonance spectrum of ZIF-UC-5.

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.66 (1H, s, H_a), 9.11 (1H, s, H_b), 7.67 (5H, m, aromatic), 6.39 (H_2O/HCl), 2.61 (DMSO), 0.00 (TMS).

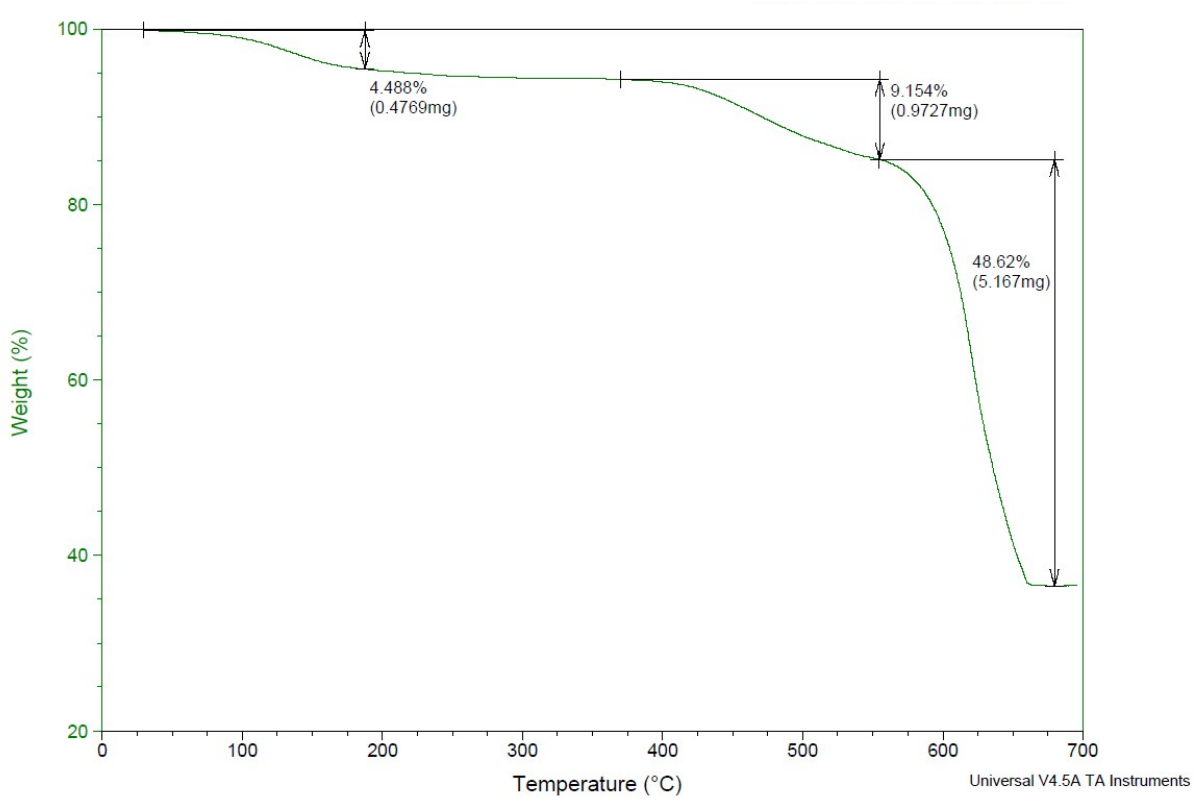

Figure S5: Thermogravimetric analysis of TIF-4.

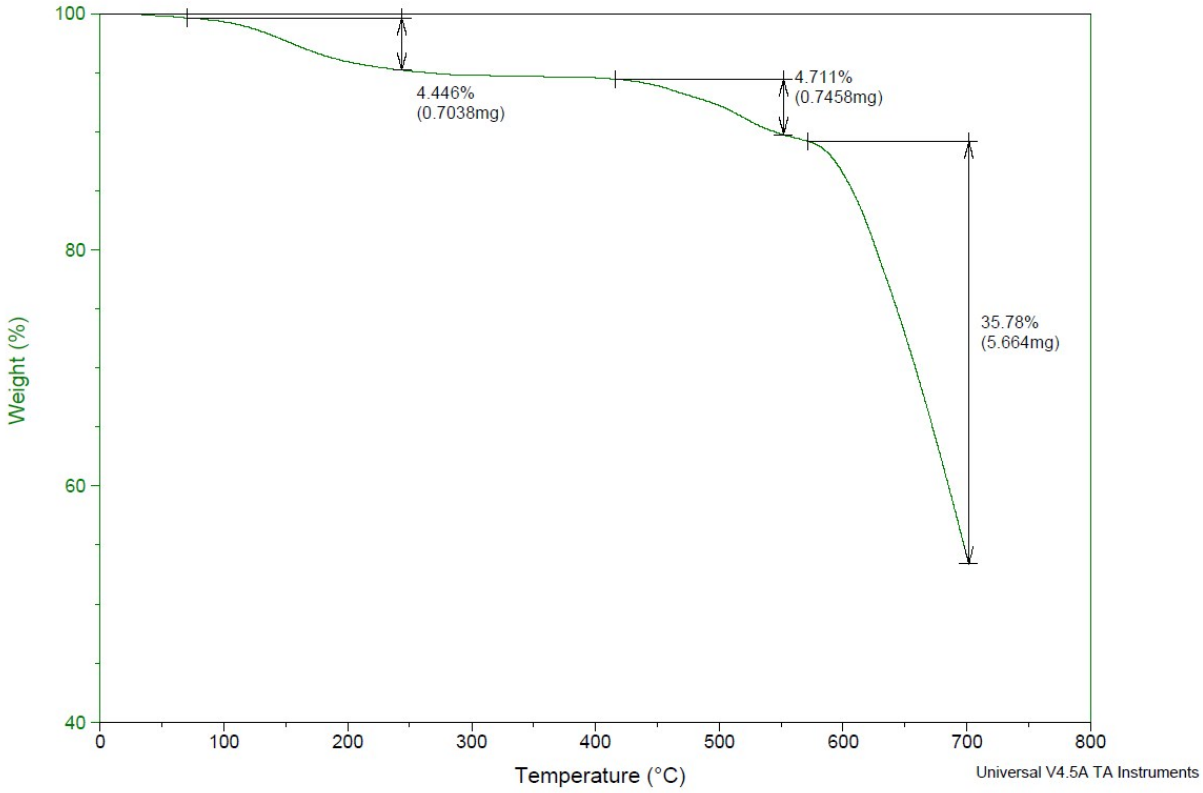

Figure S6: Thermogravimetric analysis of ZIF-UC-5.

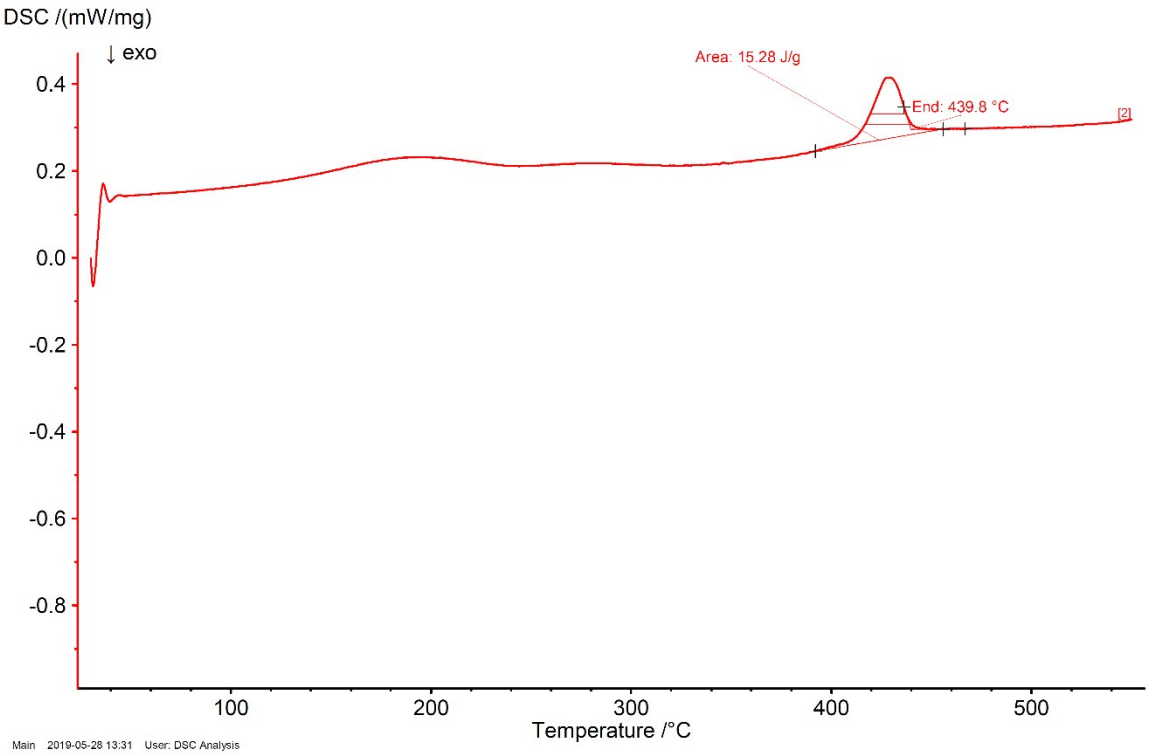

Figure S7: Differential scanning calorimetry of TIF-4 heated to 550 °C.

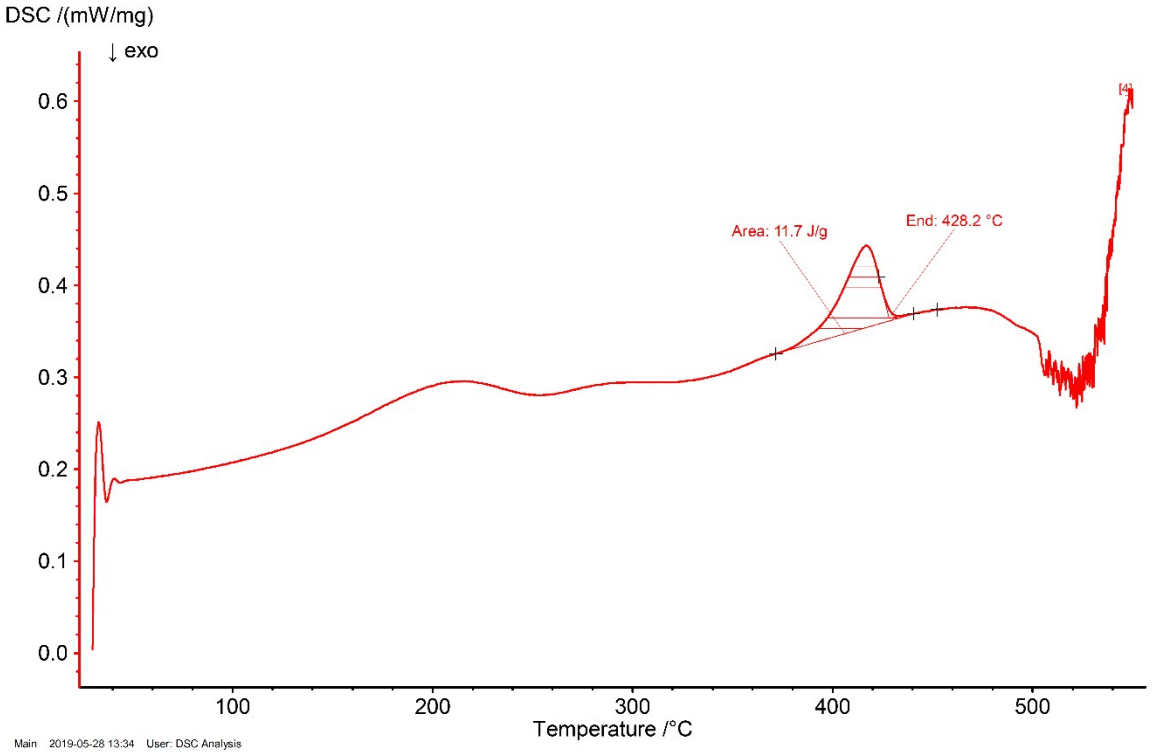

Figure S8: Differential scanning calorimetry of ZIF-UC-5 heated to 550 °C.

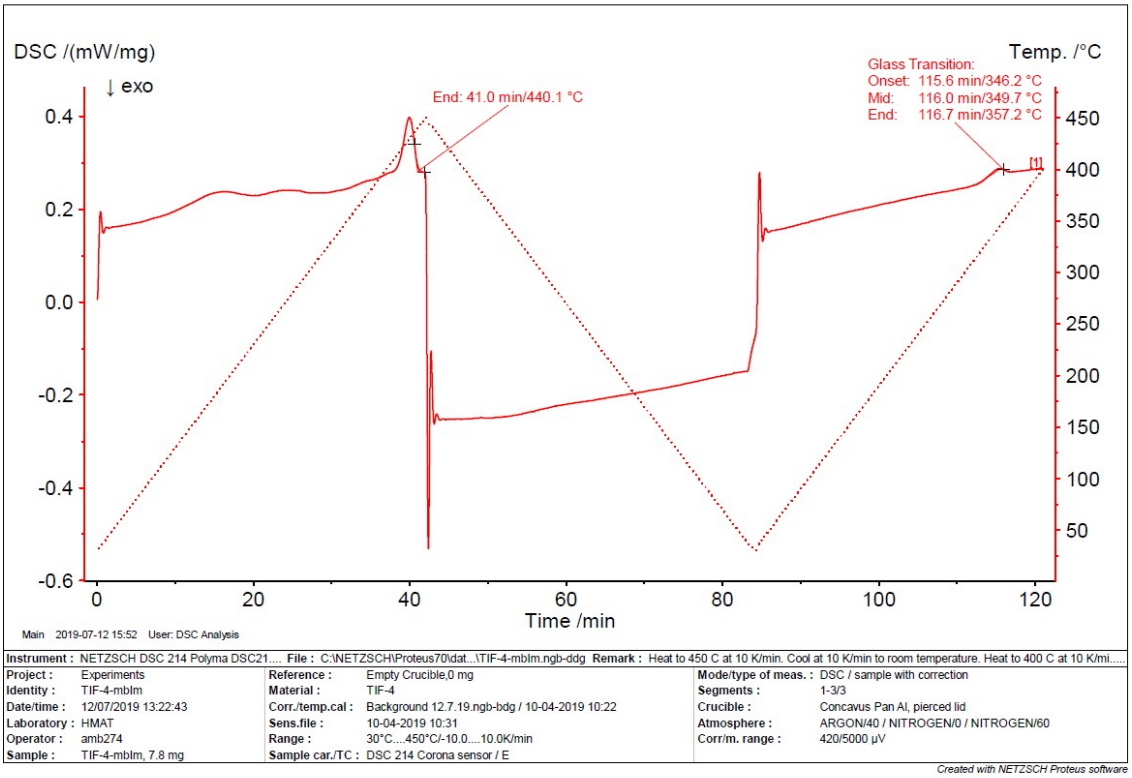

Figure S9: Differential scanning calorimetry of TIF-4 heated to 450 °C, cooled to 30 °C then heated to 400 °C.

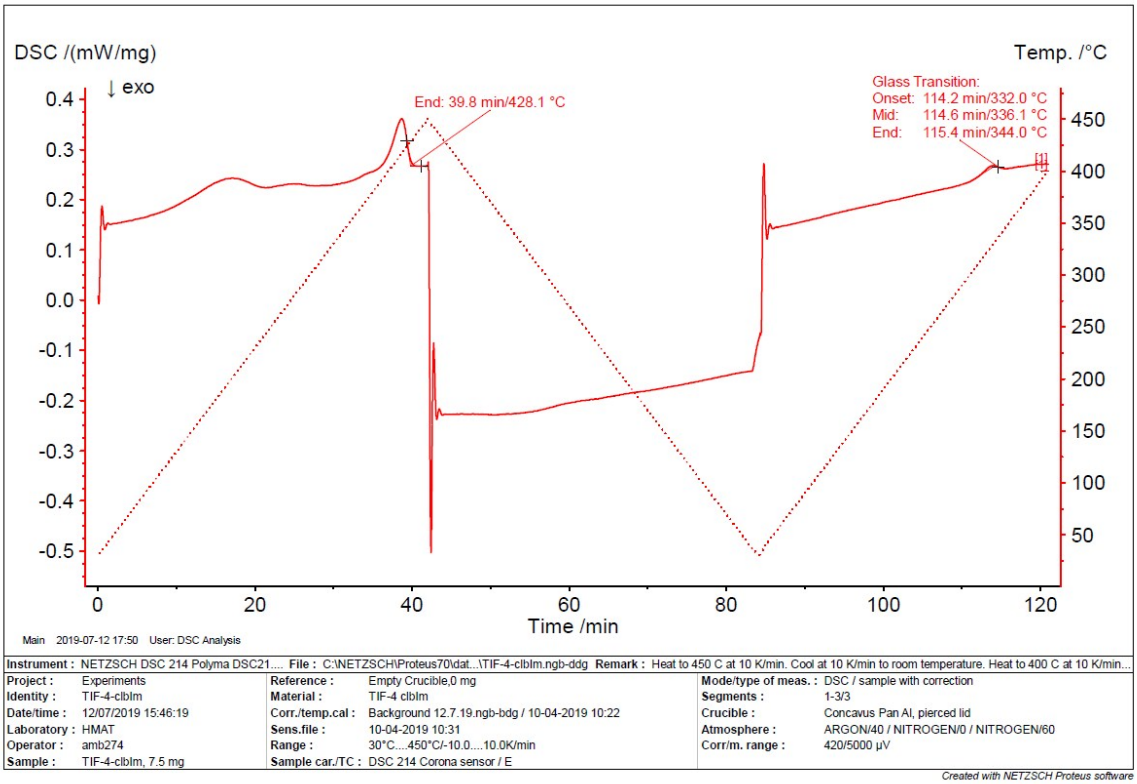

Figure S10: Differential scanning calorimetry of ZIF-UC-5 heated to 450 °C, cooled to 30 °C then heated to 400 °C.

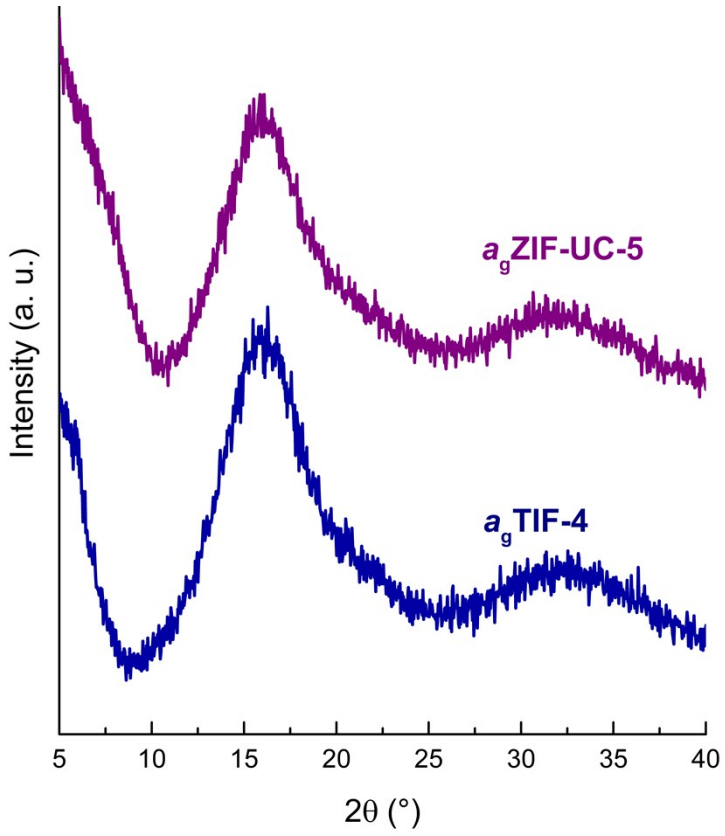

Figure S11: Powder X-ray diffraction patterns of TIF-4 and ZIF-UC-5 after glass formation.

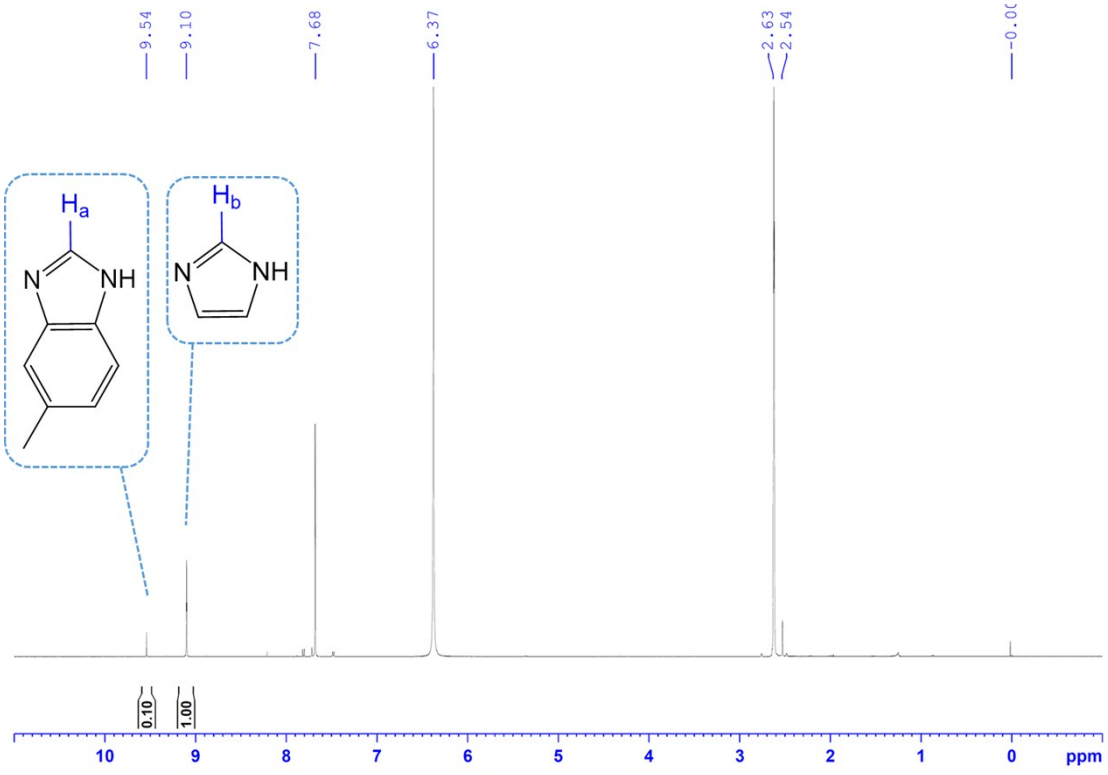

Figure S12: ^{1}H nuclear magnetic resonance spectrum of a_gTIF-4.

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.54 (1H, s, H_a), 9.10 (1H, s, H_b), 7.68 (5H, m, aromatic), 6.37 (H_2O/HCl), 2.63 (DMSO), 2.54 (3H, s, Me), 0.00 (TMS).

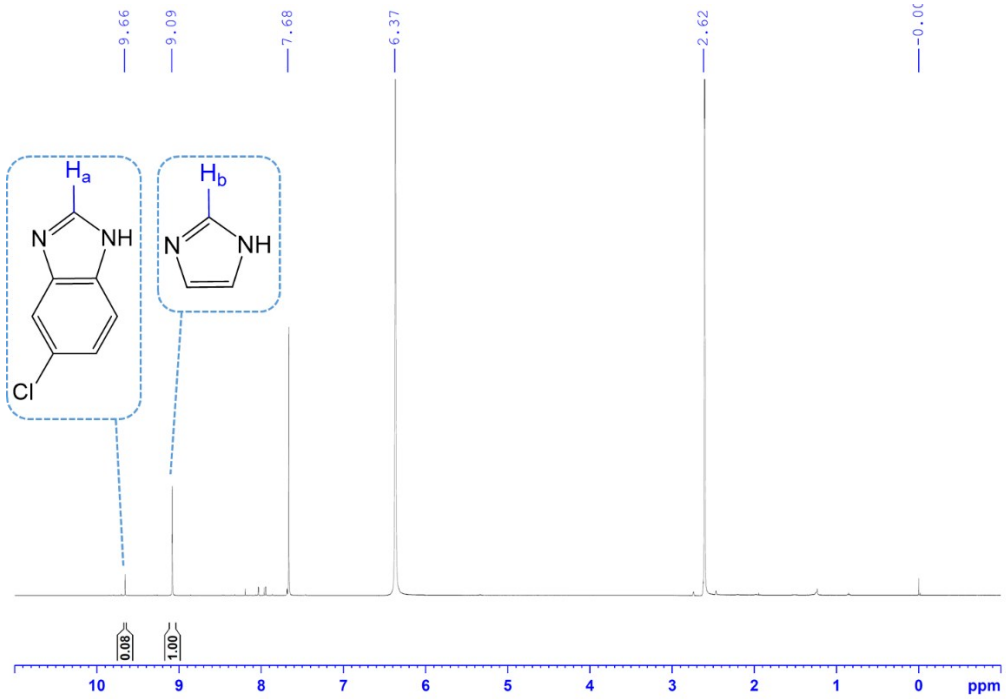

Figure S13: ^{1}H nuclear magnetic resonance spectrum of a_gZIF-UC-5.

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.66 (1H, s, H_a), 9.09 (1H, s, H_b), 7.68 (5H, m, aromatic), 6.37 (H_2O/HCl), 2.62 (DMSO), 0.00 (TMS).

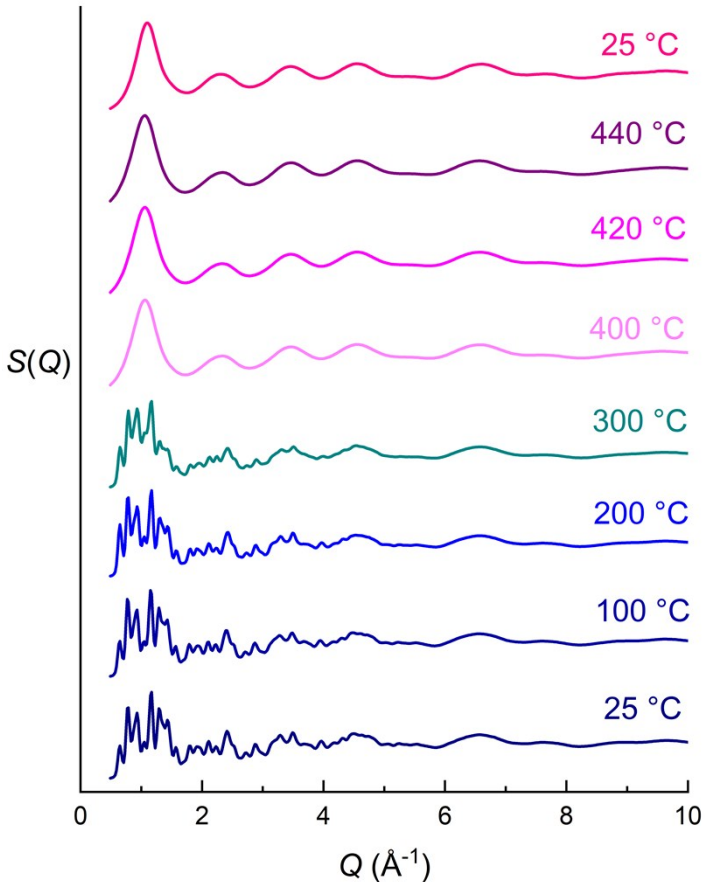

Figure S14: Variable temperature total scattering structure factors of TIF-4.

Optimisation of ZIF-76-mbIm Synthesis

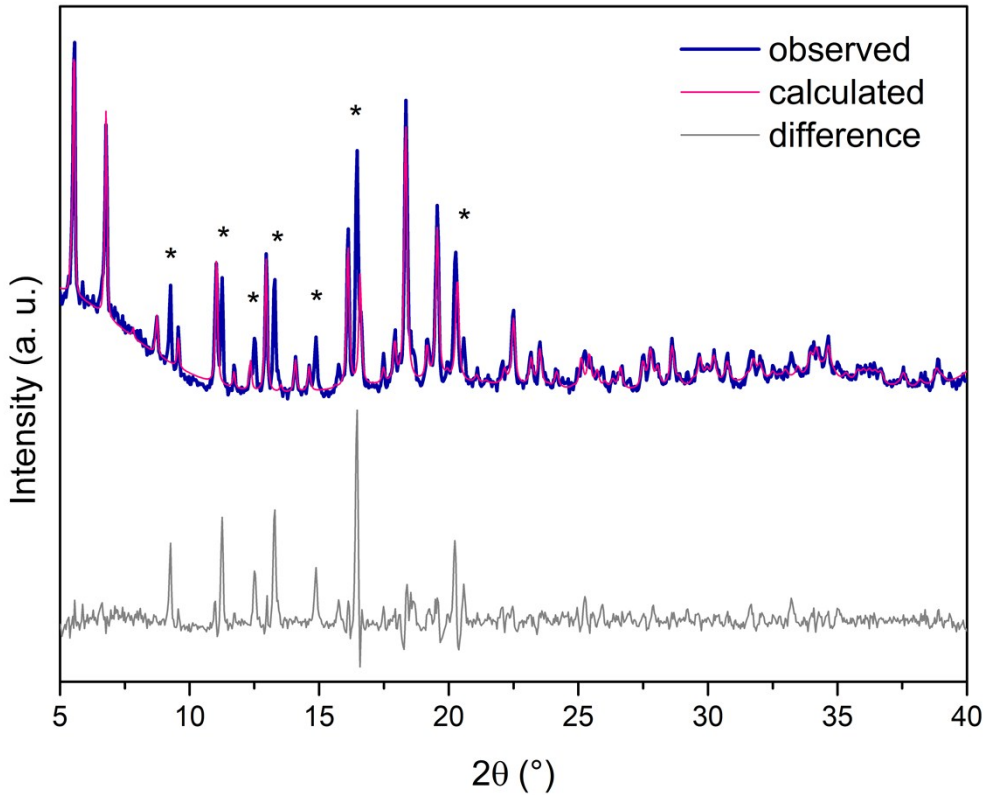

Figure S15: Pawley refinement of powder X-ray diffraction data of ZIF-76-mbIm mixed phase (1.30 mmol NaOH). Asterisks mark additional peaks that did not fit the model. Initial parameters were obtained from the previously reported CIF of ZIF-76.[3] The different benzimidazolate linkers contained by ZIF-76 and ZIF-76-mbIm explain the small difference in lattice parameters.

Table S4. Data from Pawley refinement of ZIF-76-mbIm mixed phase (1.30 mmol NaOH)

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-76[3]
20.379	*P-43m*	*a* = 22.741(5) Å	*a* = 22.6702(2) Å
		b = 22.741(5) Å	*b* = 22.6702(2) Å
		c = 22.741(5) Å	*c* = 22.6702(2) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

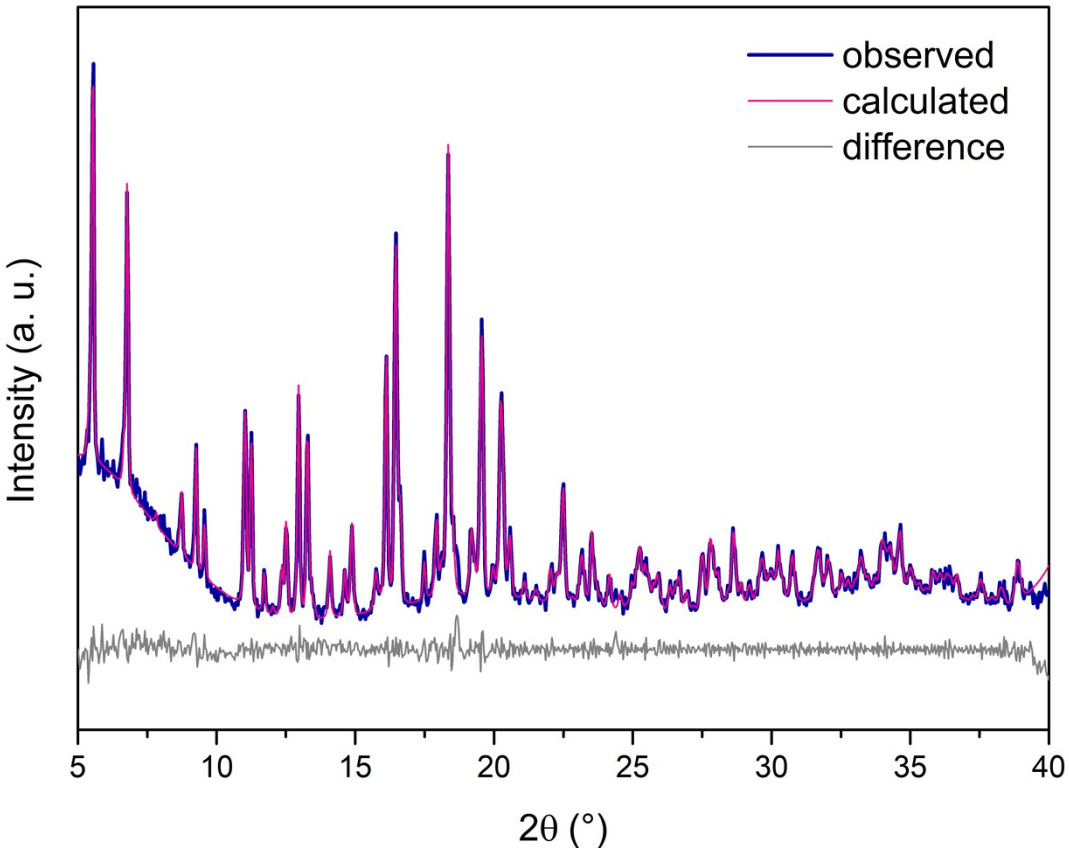

Figure S16: Pawley refinement of powder X-ray diffraction data of ZIF-76-mbIm mixed phase (1.30 mmol NaOH). Initial parameters were obtained from the previously reported CIFs of ZIF-76 and TIF-4.[1,3]

Table S5. Data from Pawley refinement of ZIF-76-mbIm mixed phase (1.30 mmol NaOH)

R_{wp}	**Space Group**	**Lattice Parameters ZIF-76-mbIm**	**Lattice Parameters Reported for ZIF-76[3]**	**Space Group**	**Lattice Parameters TIF-4**	**Lattice Parameters Reported for TIF-4[1]**
8.122	*P-43m*	*a* = 22.732(4) Å	*a* = 22.6702(2) Å	*Pbca*	*a* = 15.850(5) Å	*a* = 15.6251(9) Å
		b = 22.732(4) Å	*b* = 22.6702(2) Å		*b* = 16.168(4) Å	*b* = 16.3217(9) Å
		c = 22.732(4) Å	*c* = 22.6702(2) Å		*c* = 18.203(6) Å	*c* = 18.1244(10) Å
		α = 90 °	α = 90 °		α = 90 °	α = 90 °
		β = 90 °	β = 90 °		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °		γ = 90 °	γ = 90 °

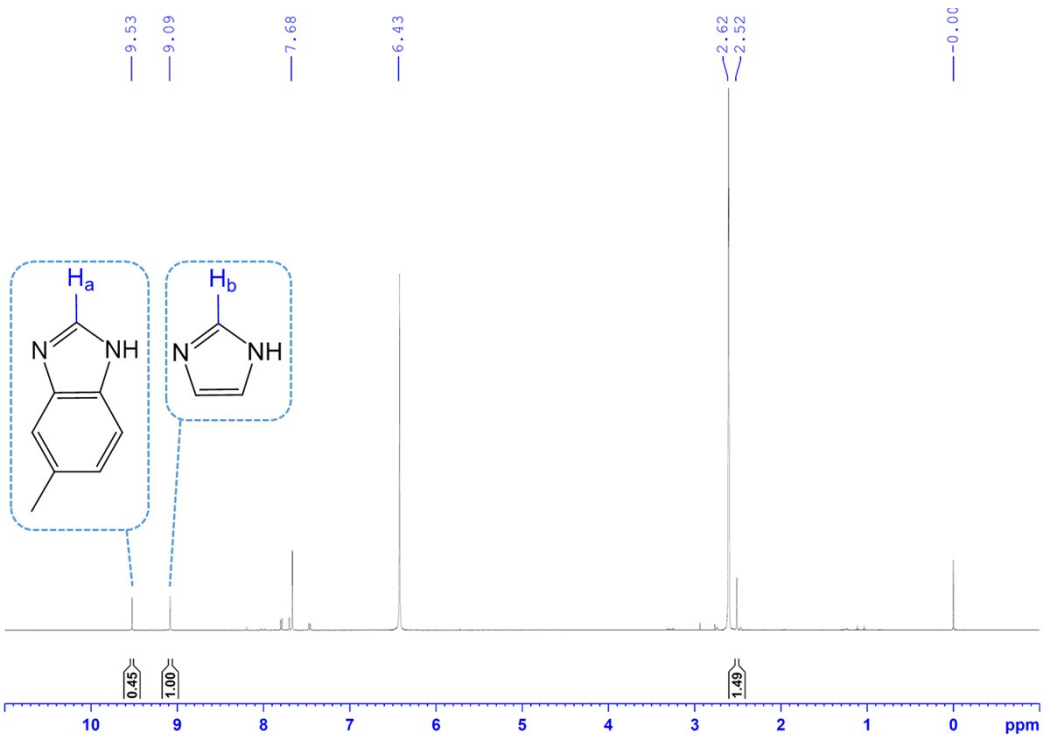

Figure S17: ^{1}H nuclear magnetic resonance spectrum of ZIF-76-mbIm mixed phase (1.30 mmol NaOH).

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.53 (1H, s, H_a), 9.09 (1H, s, H_b), 7.68 (5H, m, aromatic), 6.43 (H_2O/HCl), 2.62 (DMSO), 2.52 (3H, s, Me), 0.00 (TMS).

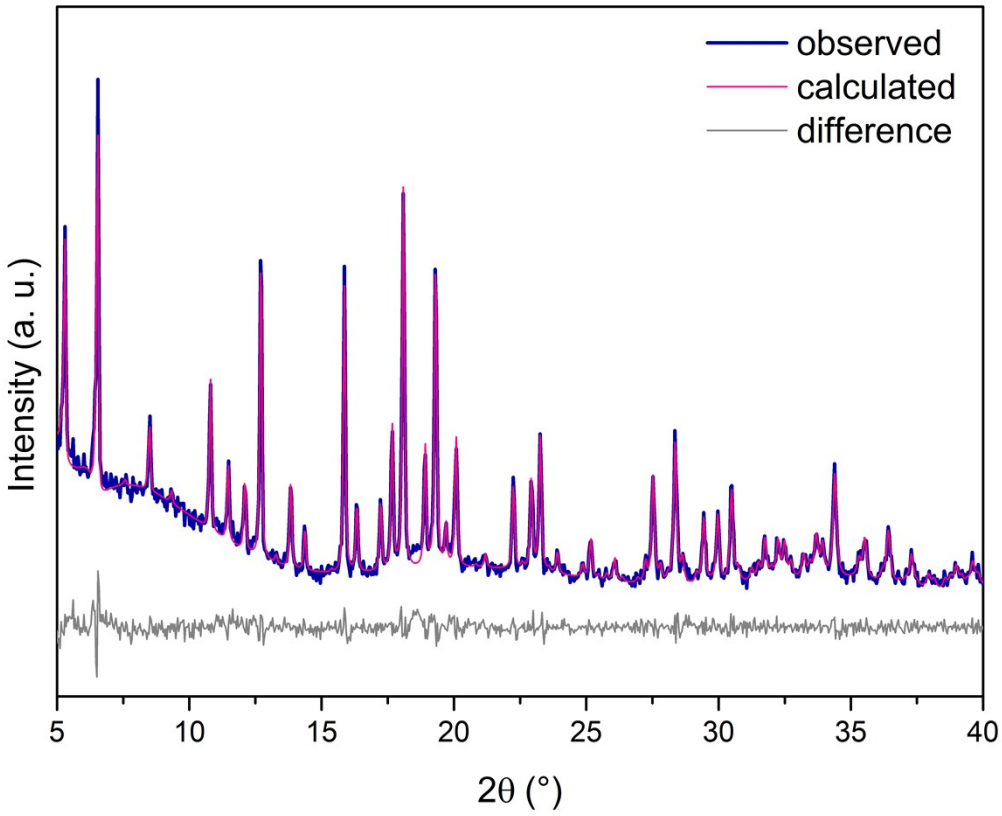

Figure S18: Pawley refinement of powder X-ray diffraction data of ZIF-76-mbIm (0 mmol NaOH). Initial parameters were obtained from the previously reported CIF of ZIF-76.[3]

Table S6. Data from Pawley refinement of ZIF-76-mbIm (0 mmol NaOH)

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-76[3]
6.782	*P-43m*	*a* = 22.7505(10) Å	*a* = 22.6702(2) Å
		b = 22.7505(10) Å	*b* = 22.6702(2) Å
		c = 22.7505(10) Å	*c* = 22.6702(2) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

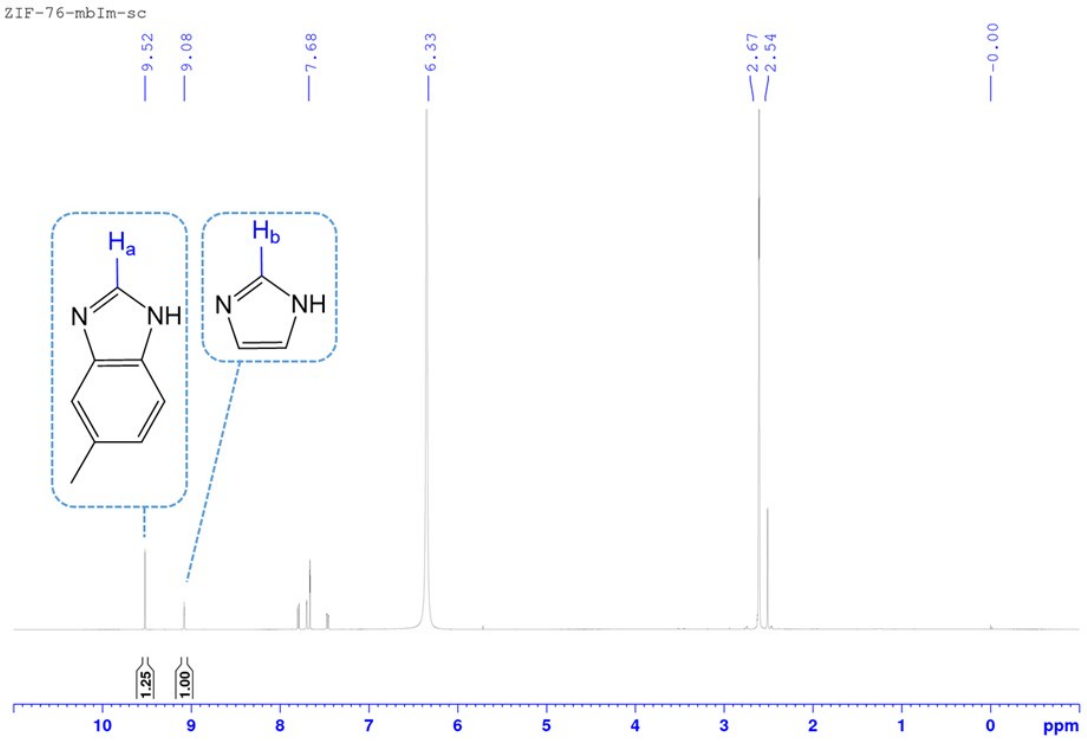

Figure S19: ^{1}H nuclear magnetic resonance spectrum of ZIF-76-mbIm (0 mmol NaOH).

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.52 (1H, s, H_a), 9.08 (1H, s, H_b), 7.68 (5H, m, aromatic), 6.33 (H_2O/HCl), 2.67 (DMSO), 2.54 (3H, s, Me), 0.00 (TMS).

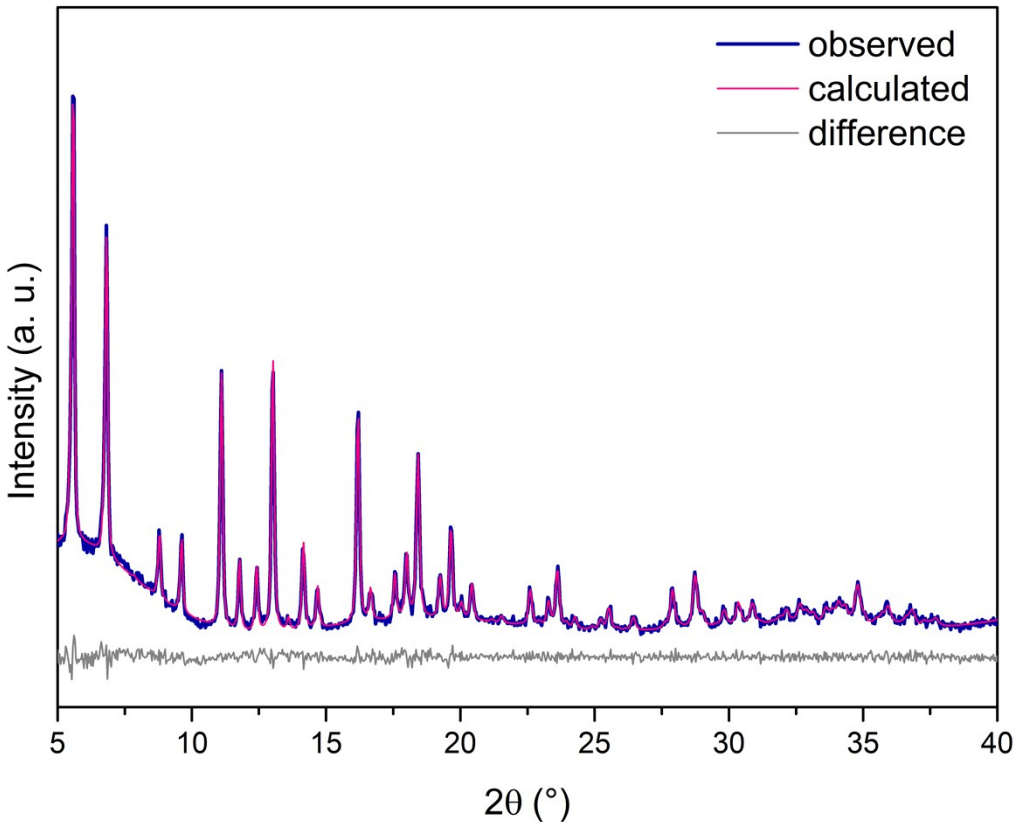

Figure S20: Pawley refinement of powder X-ray diffraction data of ZIF-76-mbIm (0.33 mmol NaOH). Initial parameters were obtained from the previously reported CIF of ZIF-76.[3]

Table S7. Data from Pawley refinement of ZIF-76-mbIm (0.33 mmol NaOH)

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-76[3]
6.603	*P-43m*	*a* = 22.6602(17) Å	*a* = 22.6702(2) Å
		b = 22.6602(17) Å	*b* = 22.6702(2) Å
		c = 22.6602(17) Å	*c* = 22.6702(2) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

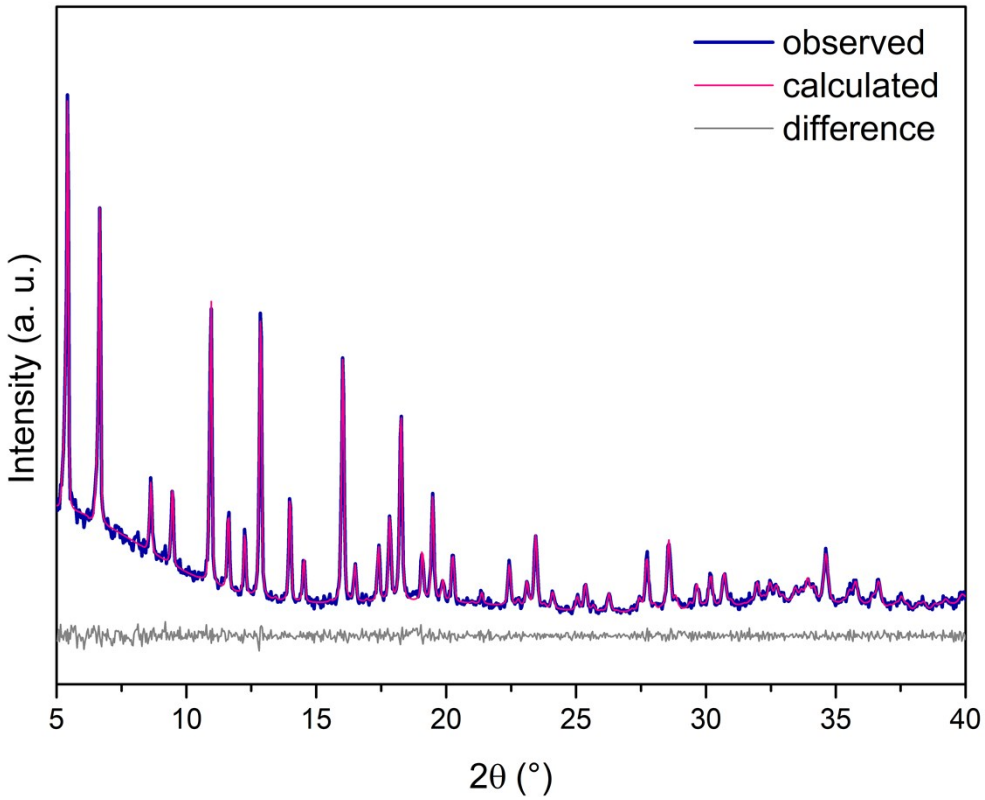

Figure S21: Pawley refinement of powder X-ray diffraction data of ZIF-76-mbIm (0.65 mmol NaOH). Initial parameters were obtained from the previously reported CIF of ZIF-76.[3]

Table S8. Data from Pawley refinement of ZIF-76-mbIm (0.65 mmol NaOH)

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-76[3]
5.969	*P-43m*	*a* = 22.6736(11) Å	*a* = 22.6702(2) Å
		b = 22.6736(11) Å	*b* = 22.6702(2) Å
		c = 22.6736(11) Å	*c* = 22.6702(2) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

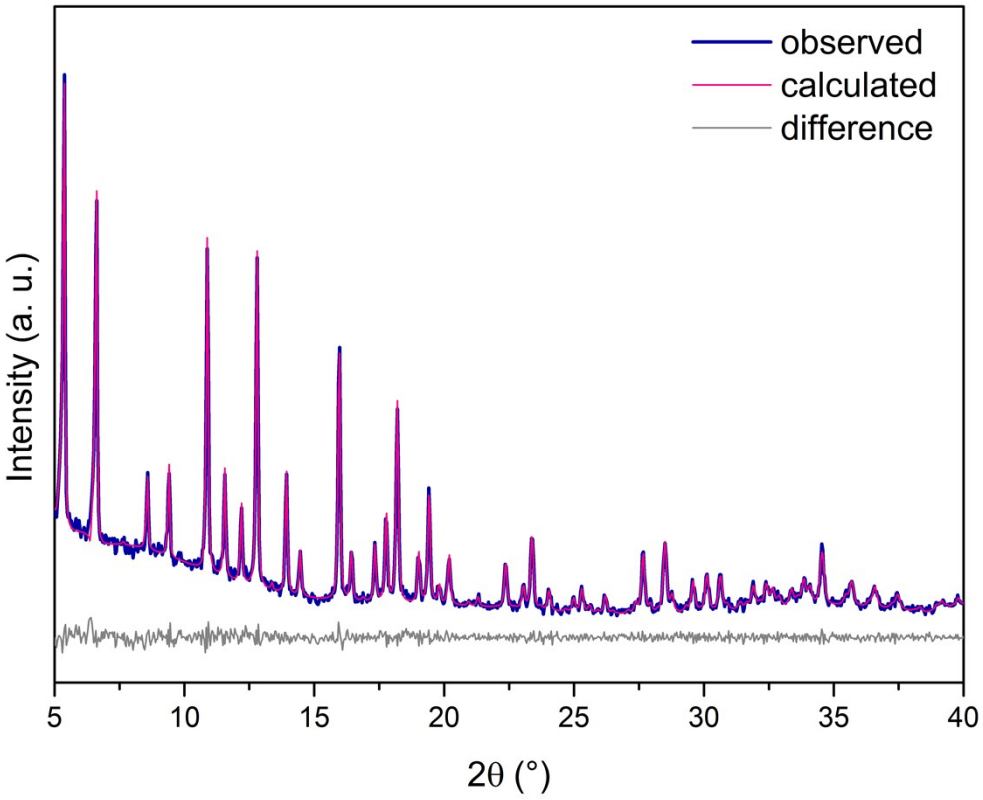

Figure S22: Pawley refinement of powder X-ray diffraction data of ZIF-76-mbIm (0.98 mmol NaOH). Initial parameters were obtained from the previously reported CIF of ZIF-76.[3]

Table S9. Data from Pawley refinement of ZIF-76-mbIm (0.98 mmol NaOH)

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-76[3]
6.321	*P-43m*	*a* = 22.6828(11) Å	*a* = 22.6702(2) Å
		b = 22.6828(11) Å	*b* = 22.6702(2) Å
		c = 22.6828(11) Å	*c* = 22.6702(2) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

Single Crystal X-ray Diffraction Experimental and Details of ZIF-76-mbIm Structure Refinement
CCDC Deposition Number: 1990640

An Oxford Diffraction Gemini E Ultra diffractometer with an Atlas CCD area detector was used to collect the single crystal X-ray diffraction data in this work. This was operated at 1200 W (35 kV, 35 mA) to produce Cu Kα radiation (λ = 1.54184 Å). A colourless crystal of ZIF-76-mbIm (0.25 × 0.20 × 0.18 mm) was selected, placed in a borosilicate loop (0.5 mm diameter) using Hampton Research Paratone-N oil and mounted in the diffractometer. The experiment was performed at 293(2) K. A total of 9161 reflections were collected within a θ range of 2.755 to 63.881°. From those reflections, 3425 were unique and 2610 of these were greater than 2σ(I). Negligible intensity decay occurred during collection. Structure solution was performed using SUPERFLIP (a charge-flipping based program) and the refinement was performed using SHELXL both in the WinGX suite version 2018.2.[4–6] ZIF-76-mbIm was solved to give a structure with a cubic *P-43m* space group, with Z = 24. Partial structural solutions for ZIF-76-mbIm were also found in space groups *Pm-3m* and *P23*. However, the best refinement for ZIF-76-mbIm was obtained with the *P-43m* space group. Interestingly, alternative structure solutions were also observed in the original structure solution of ZIF-76 with the *P-43m* space group also giving the best refinement.[3]

All non-hydrogen atoms were refined anisotropically apart from the carbon atoms within the mbIm linkers which were refined isotropically. It should be noted that several of the atomic coordinates that we have assigned to solvent molecules are on special positions. They also exhibited high thermal displacement parameters and high estimated standard deviations. Consequently, we were unable to successfully model the solvent molecules in the crystal structure. As a solution to this, individual oxygen atoms were used to model additional electron density within the pores. The largest errors in the structure solution are caused by this approximate assignment of the additional electron density. A similar strategy was employed in the original structure solution of ZIF-76.[3]

ZIF-76-mbIm contains 1.20 Im and 0.80 mbIm per Zn atom. From the four linker positions in the asymmetric unit, two are fully occupied by unsubstituted Im and mbIm respectively and the other two are disordered between both linkers: one with 0.55 mbIm, 0.45 Im and the other one is 0.05 mbIm, 0.95 Im. In these two positions, the imidazolate ring perfectly overlaps the imidazolate moiety of the larger linker. A second nitrogen triangle is created in the framework by rotating one of the Zn-N bonds by 60°, creating additional disorder. This was also observed in the original structure solution of ZIF-76.[3] The fully occupied Im position is located about a mirror plane. In both disordered positions, carbon atoms of the methyl groups in mbIm are related by mirror symmetry, although only one of these positions is filled for any given mbIm. Although the precision of this structural model is low, it is consistent with the previously reported structure of ZIF-76.[3] Final full matrix least-squares refinement on F^2 converged to R1 = 0.1156 (F >2σF)) and wR2 = 0.2989, with GOOF = 1.365.

Table S10. Crystal data and structure refinement for ZIF-76-mbIm.

Chemical formula	$C_{10}\ H_{9.2}\ N_4\ Zn_1,\ O_{0.3}$
Formula weight	256.08 g/mol
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system	Cubic
Space group	*P-43m*
Unit cell dimensions	*a* = 22.6840(6) A˚ α = 90°
	b = 22.6840(6) A˚ β = 90°
	c = 22.6840(6) A˚ γ = 90°
Volume	11672.4(9) $Å^3$
Density (calculated)	0.865 g/cm^3
Absorption coefficient	1.643
F(000)	3216.0
Crystal size	0.25 x 0.20 x 0.18 mm^3
Theta range for data collection	2.7548 – 59.8430°
Index ranges	-18 <= h <= 22, -25 <= k <= 26, -21 <= l <= 24
Reflections collected	9161
Independent reflections	3425
Completeness to theta = 64.56°	97.60 %
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3425 / 19 / 175
Goodness-of-fit on F^2	1.365
Final *R* indices [I>2sigma(I)]	*R*1 = 0.1156, wR2 = 0.2989
R indices (all data)	*R*1 = 0.1424, wR2 = 0.3534
Largest diff. peak and hole	1.413 and -0.518 e. $Å^{-3}$

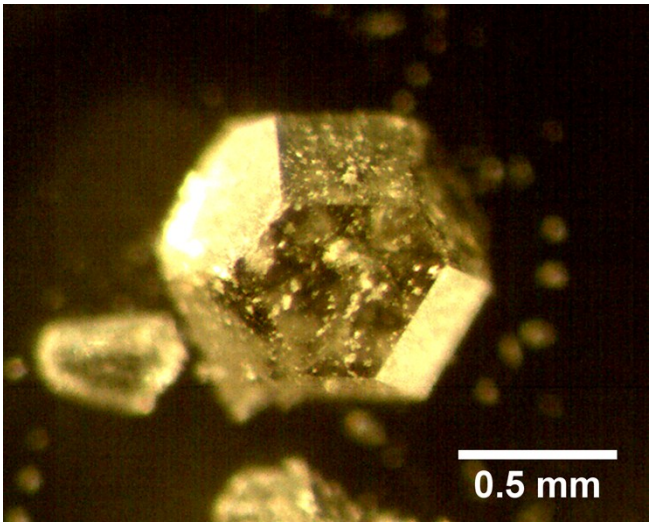

Figure S23: Microscope image of a single crystal of ZIF-76-mbIm.

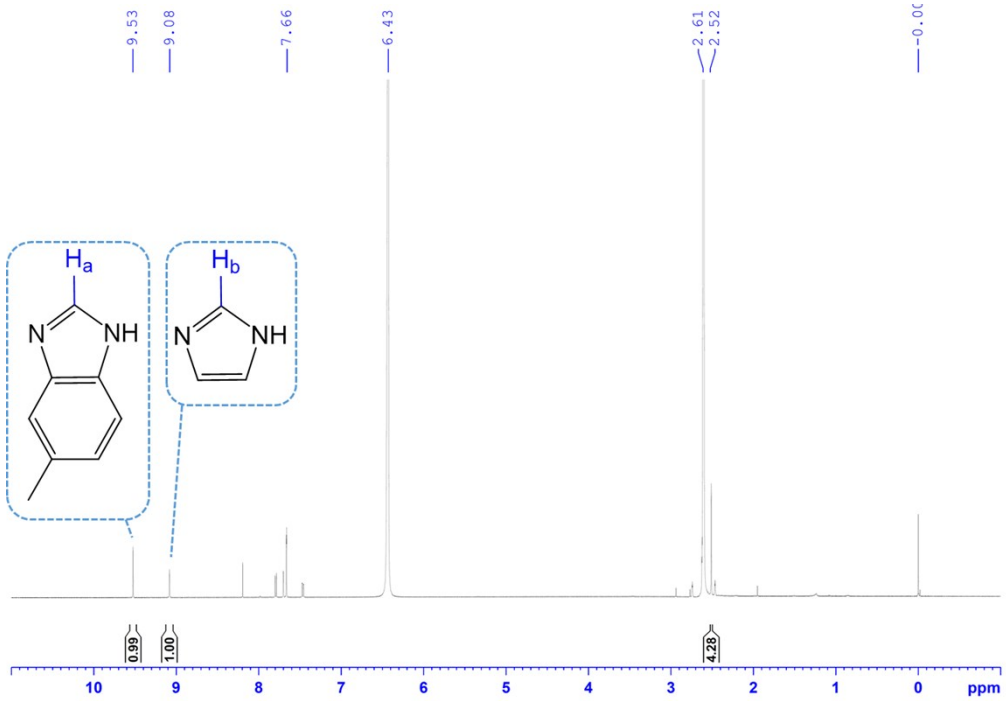

Figure S24: ^{1}H nuclear magnetic resonance spectrum of ZIF-76-mbIm.

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.53 (1H, s, H_a), 9.08 (1H, s, H_b), 7.66 (5H, m, aromatic), 6.43 (H_2O/HCl), 2.61 (DMSO), 2.52 (3H, s, Me), 0.00 (TMS).

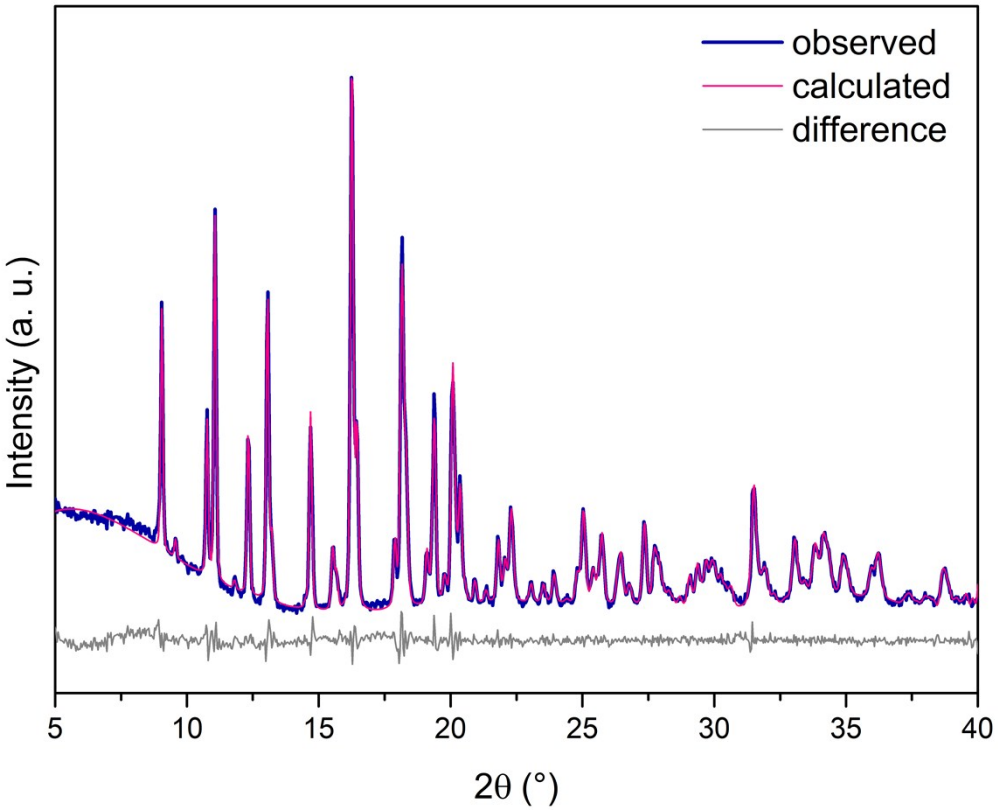

Figure S25: Pawley refinement of powder X-ray diffraction data of ZIF-76-mbIm (5.0:1 Im:mbIm). Initial parameters were obtained from the previously reported CIF of TIF-4.[1]

Table S11. Data from Pawley refinement of ZIF-76-mbIm (5.0:1 Im:mbIm)

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for TIF-4[1]
6.102	*Pbca*	*a* = 15.790(3) Å	*a* = 15.6251(9) Å
		b = 16.160(3) Å	*b* = 16.3217(9) Å
		c = 18.138(3) Å	*c* = 18.1244(10) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

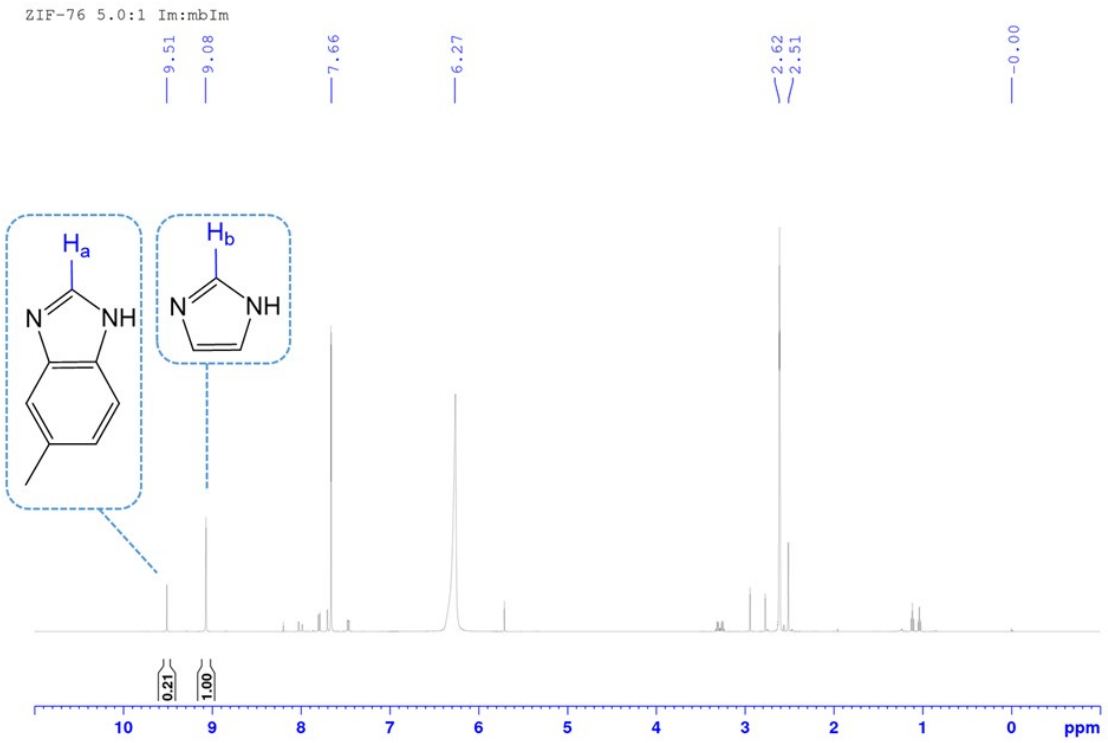

Figure S26: ^{1}H nuclear magnetic resonance spectrum of ZIF-76-mbIm (5.0:1 Im:mbIm).

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.51 (1H, s, H_a), 9.08 (1H, s, H_b), 7.66 (5H, m, aromatic), 6.27 (H_2O/HCl), 2.62 (DMSO), 2.51 (3H, s, Me), 0.00 (TMS).

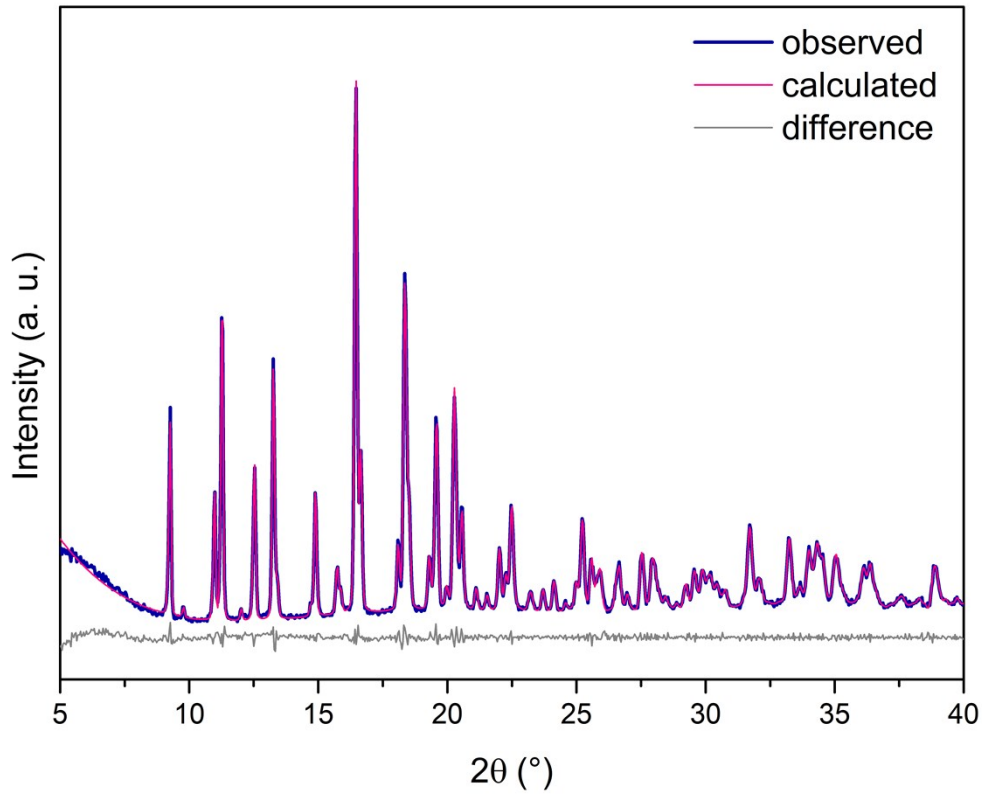

Figure S27: Pawley refinement of powder X-ray diffraction data of ZIF-76-mbIm (4.0:1 Im:mbIm). Initial parameters were obtained from the previously reported CIF of TIF-4.[1]

Table S12. Data from Pawley refinement of ZIF-76-mbIm (4.0:1 Im:mbIm)

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for TIF-4[1]
5.357	*Pbca*	*a* = 15.8285(16) Å	*a* = 15.6251(9) Å
		b = 16.1845(18) Å	*b* = 16.3217(9) Å
		c = 18.176(2) Å	*c* = 18.1244(10) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

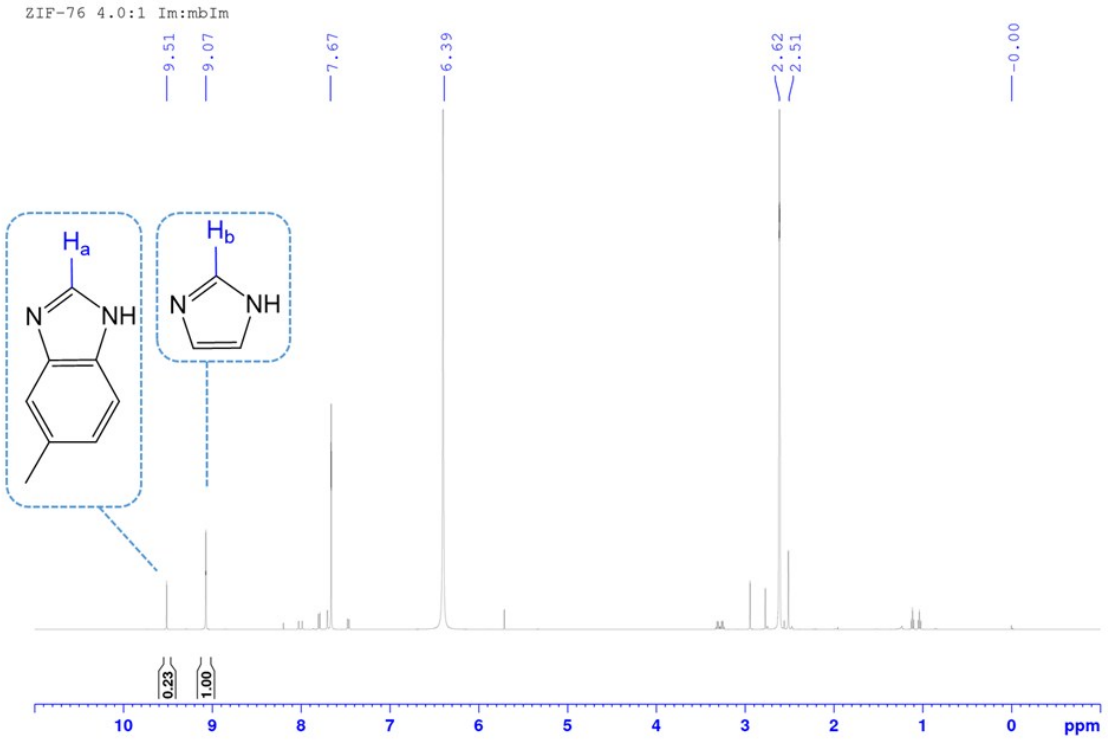

Figure S28: ^{1}H nuclear magnetic resonance spectrum of ZIF-76-mbIm (4.0:1 Im:mbIm).

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.51 (1H, s, H_a), 9.07 (1H, s, H_b), 7.67 (5H, m, aromatic), 6.39 (H_2O/HCl), 2.62 (DMSO), 2.51 (3H, s, Me), 0.00 (TMS).

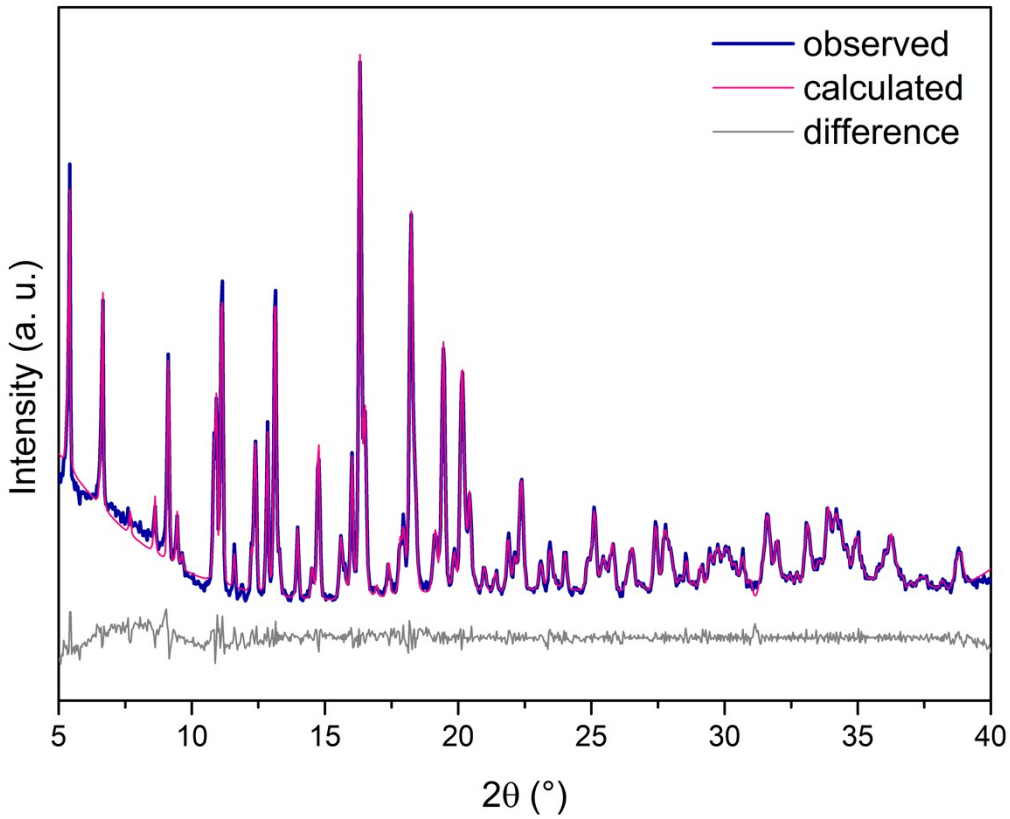

Figure S29: Pawley refinement of powder X-ray diffraction data of ZIF-76-mbIm (3.3:1 Im:mbIm). Initial parameters were obtained from the previously reported CIFs of ZIF-76 and TIF-4.[1,3]

Table S13. Data from Pawley refinement of ZIF-76-mbIm (3.3:1 Im:mbIm)

R_{wp}	**Space Group**	**Lattice Parameters ZIF-76-mbIm**	**Lattice Parameters Reported for ZIF-76[3]**	**Space Group**	**Lattice Parameters TIF-4**	**Lattice Parameters Reported for TIF-4[1]**
6.602	*P-43m*	*a* = 22.654(4) Å	*a* = 22.6702(2) Å	*Pbca*	*a* = 15.803(4) Å	*a* = 15.6251(9) Å
		b = 22.654(4) Å	*b* = 22.6702(2) Å		*b* = 16.169(4) Å	*b* = 16.3217(9) Å
		c = 22.654(4) Å	*c* = 22.6702(2) Å		*c* = 18.157(7) Å	*c* = 18.1244(10) Å
		α = 90 °	α = 90 °		α = 90 °	α = 90 °
		β = 90 °	β = 90 °		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °		γ = 90 °	γ = 90 °

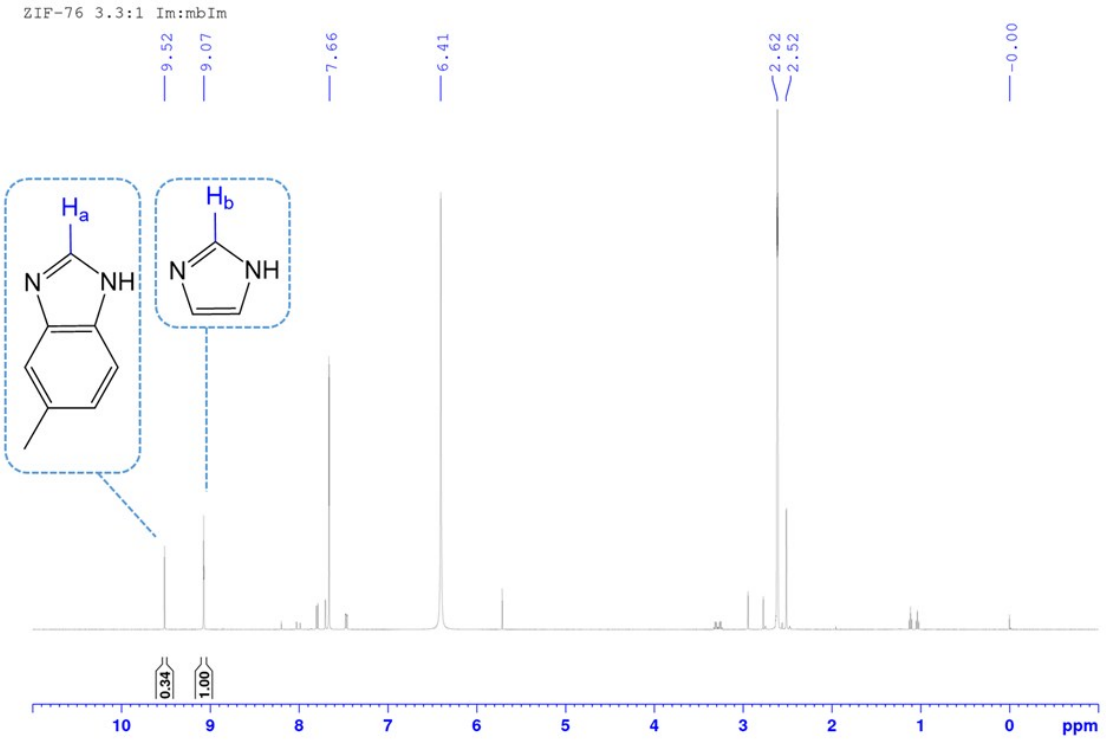

Figure S30: ^{1}H nuclear magnetic resonance spectrum of ZIF-76-mbIm (3.3:1 Im:mbIm).

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.52 (1H, s, H_a), 9.07 (1H, s, H_b), 7.66 (5H, m, aromatic), 6.41 (H_2O/HCl), 2.62 (DMSO), 2.52 (3H, s, Me), 0.00 (TMS).

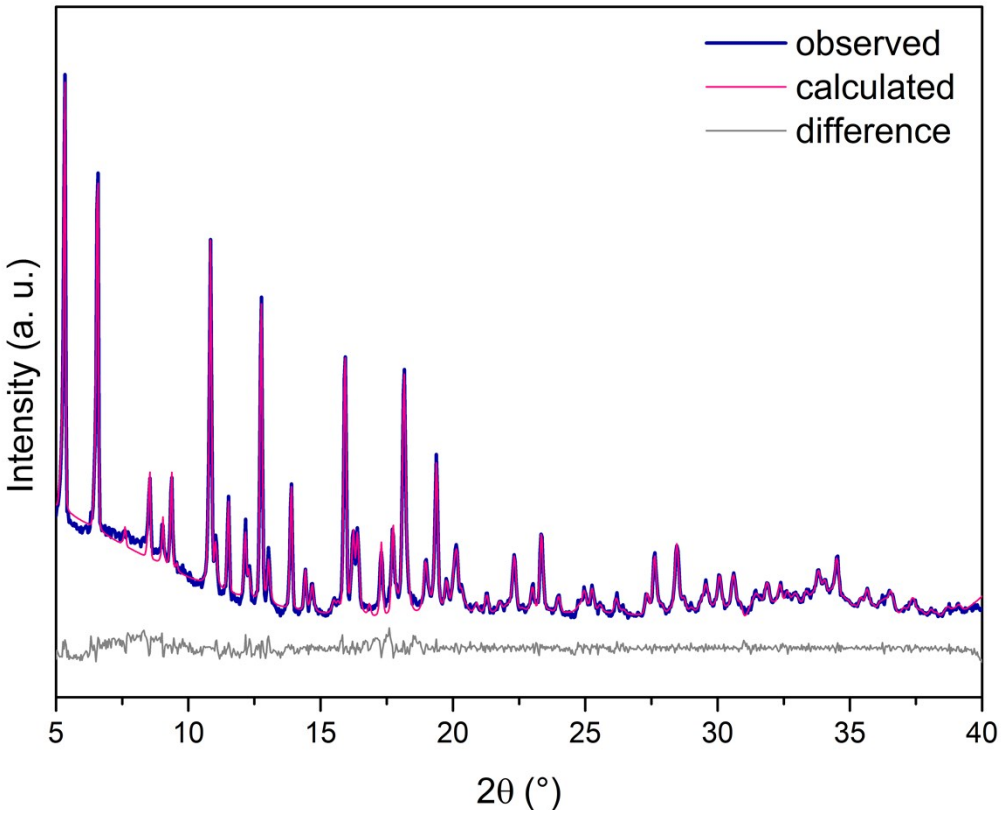

Figure S31: Pawley refinement of powder X-ray diffraction data of ZIF-76-mbIm (2.8:1 Im:mbIm). Initial parameters were obtained from the previously reported CIFs of ZIF-76 and TIF-4.[1,3]

Table S14. Data from Pawley refinement of ZIF-76-mbIm (2.8:1 Im:mbIm)

R_{wp}	**Space Group**	**Lattice Parameters ZIF-76-mbIm**	**Lattice Parameters Reported for ZIF-76[3]**	**Space Group**	**Lattice Parameters TIF-4**	**Lattice Parameters Reported for TIF-4[1]**
6.660	*P-43m*	*a* = 22.682(3) Å	*a* = 22.6702(2) Å	*Pbca*	*a* = 15.810(10) Å	*a* = 15.6251(9) Å
		b = 22.682(3) Å	*b* = 22.6702(2) Å		*b* = 16.202(9) Å	*b* = 16.3217(9) Å
		c = 22.682(3) Å	*c* = 22.6702(2) Å		*c* = 18.1168(16) Å	*c* = 18.1244(10) Å
		α = 90 °	α = 90 °		α = 90 °	α = 90 °
		β = 90 °	β = 90 °		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °		γ = 90 °	γ = 90 °

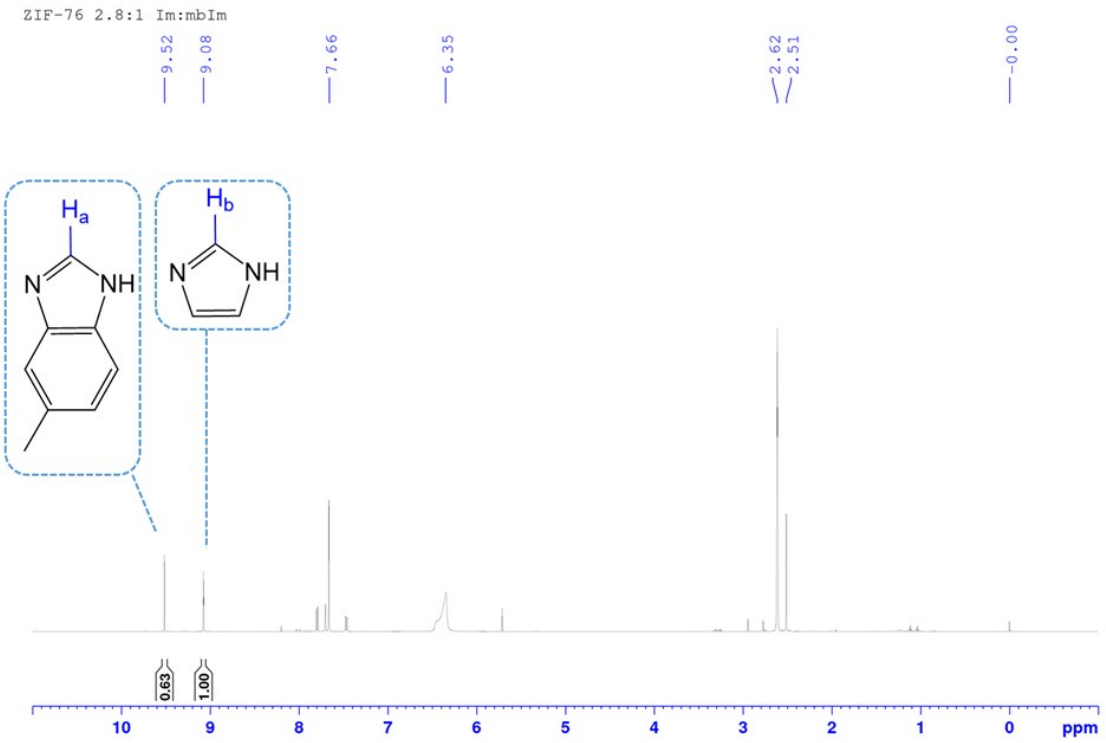

Figure S32: ^{1}H nuclear magnetic resonance spectrum of ZIF-76-mbIm (2.8:1 Im:mbIm).

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.52 (1H, s, H_a), 9.08 (1H, s, H_b), 7.66 (5H, m, aromatic), 6.35 (H_2O/HCl), 2.62 (DMSO), 2.51 (3H, s, Me), 0.00 (TMS).

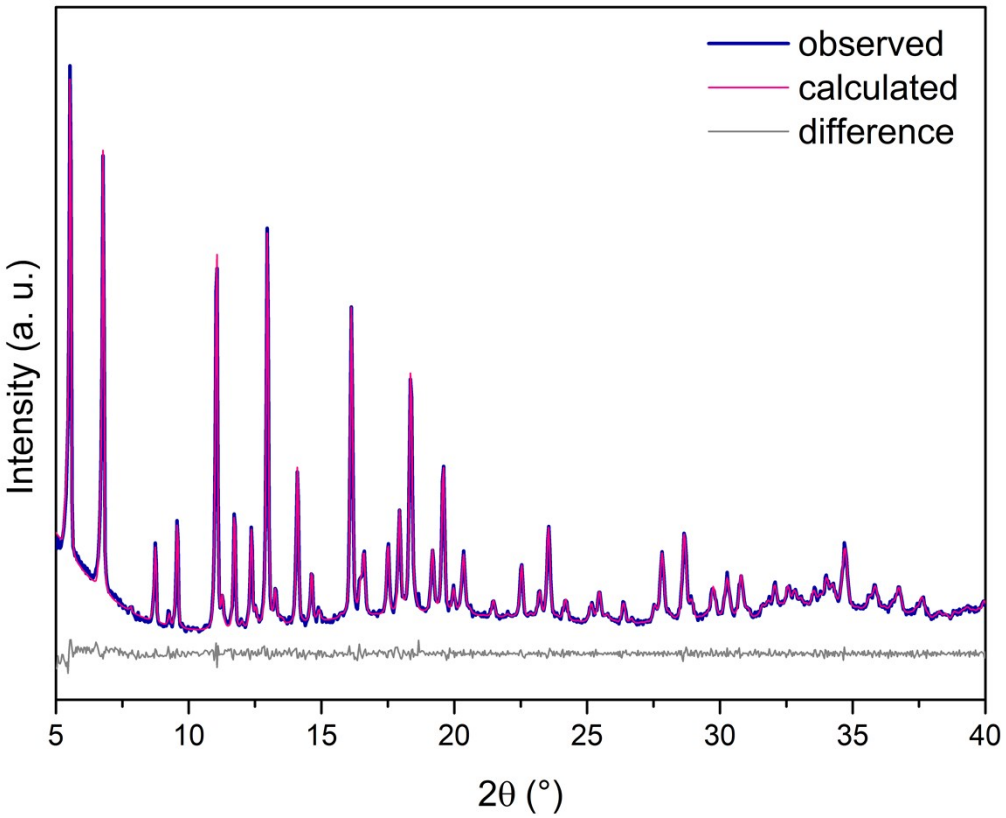

Figure S33: Pawley refinement of powder X-ray diffraction data of ZIF-76-mbIm (2.3:1 Im:mbIm). Initial parameters were obtained from the previously reported CIFs of ZIF-76 and TIF-4.[1,3]

Table S15. Data from Pawley refinement of ZIF-76-mbIm (2.3:1 Im:mbIm)

R_{wp}	Space Group	Lattice Parameters ZIF-76-mbIm	Lattice Parameters Reported for ZIF-76[3]	Space Group	Lattice Parameters TIF-4	Lattice Parameters Reported for TIF-4[1]
4.717	*P-43m*	*a* = 22.6904(14) Å	*a* = 22.6702(2) Å	*Pbca*	*a* = 15.759(17) Å	*a* = 15.6251(9) Å
		b = 22.6904(14) Å	*b* = 22.6702(2) Å		*b* = 16.182(10) Å	*b* = 16.3217(9) Å
		c = 22.6904(14) Å	*c* = 22.6702(2) Å		*c* = 18.22(3) Å	*c* = 18.1244(10) Å
		α = 90 °	α = 90 °		α = 90 °	α = 90 °
		β = 90 °	β = 90 °		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °		γ = 90 °	γ = 90 °

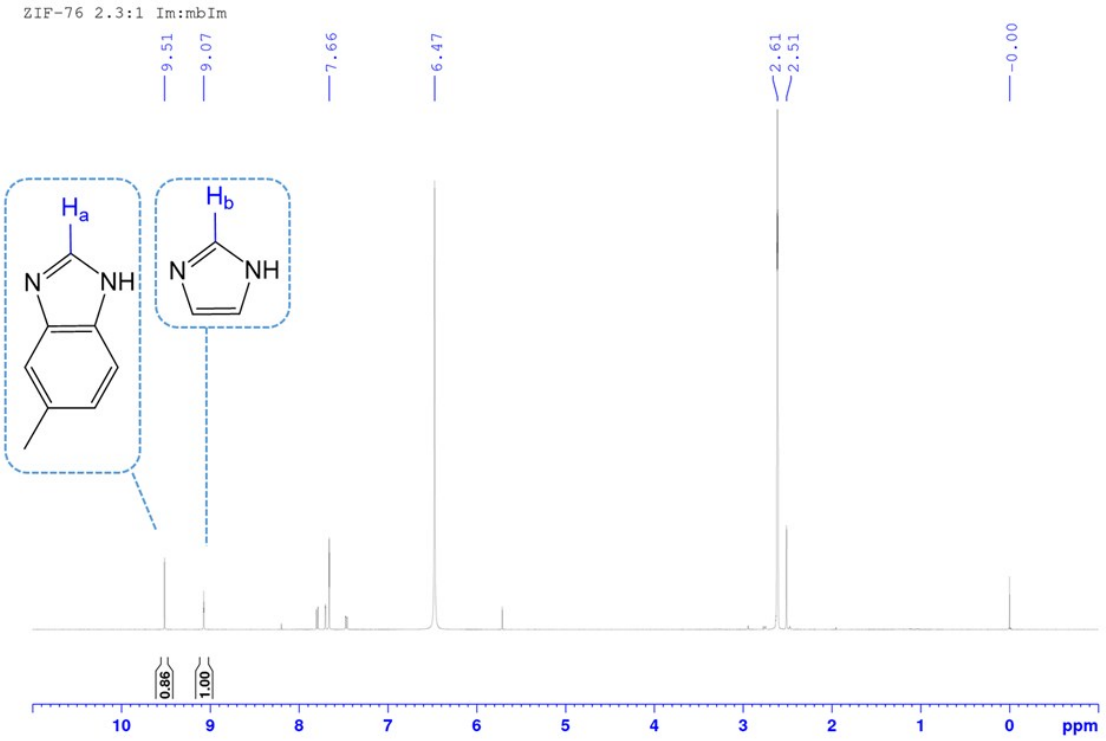

Figure S34: ^{1}H nuclear magnetic resonance spectrum of ZIF-76-mbIm (2.3:1 Im:mbIm).

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.51 (1H, s, H_a), 9.07 (1H, s, H_b), 7.66 (5H, m, aromatic), 6.47 (H_2O/HCl), 2.61 (DMSO), 2.51 (3H, s, Me), 0.00 (TMS).

Figure S35: Pawley refinement of powder X-ray diffraction data of ZIF-76-mbIm (2.0:1 Im:mbIm). Initial parameters were obtained from the previously reported CIF of ZIF-76.[3]

Table S16. Data from Pawley refinement of ZIF-76-mbIm (2.0:1 Im:mbIm)

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-76[3]
5.969	*P-43m*	*a* = 22.6736(11) Å	*a* = 22.6702(2) Å
		b = 22.6736(11) Å	*b* = 22.6702(2) Å
		c = 22.6736(11) Å	*c* = 22.6702(2) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

Figure S36: ^{1}H nuclear magnetic resonance spectrum of ZIF-76-mbIm (2.0:1 Im:mbIm).

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.53 (1H, s, H_a), 9.08 (1H, s, H_b), 7.66 (5H, m, aromatic), 6.43 (H_2O/HCl), 2.61 (DMSO), 2.52 (3H, s, Me), 0.00 (TMS).

Effect of Framework Topology on Thermal Behaviour

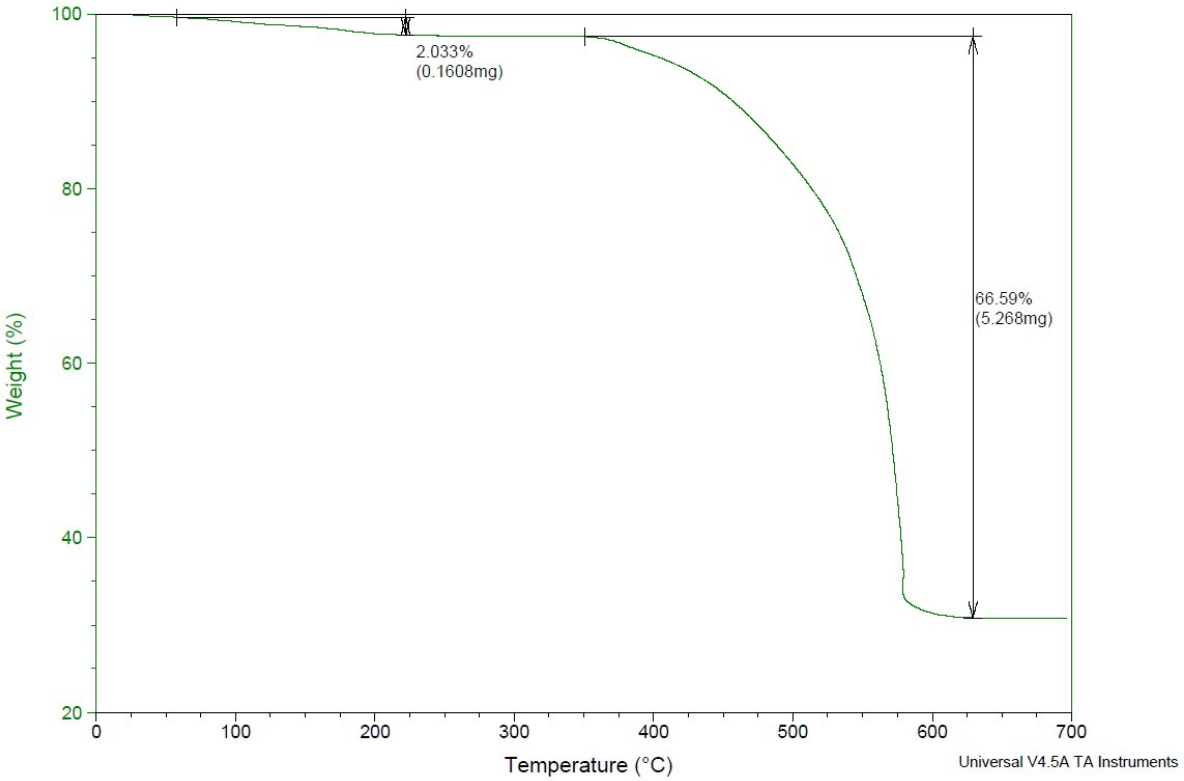

Figure S37: Thermogravimetric analysis of ZIF-76-mbIm.

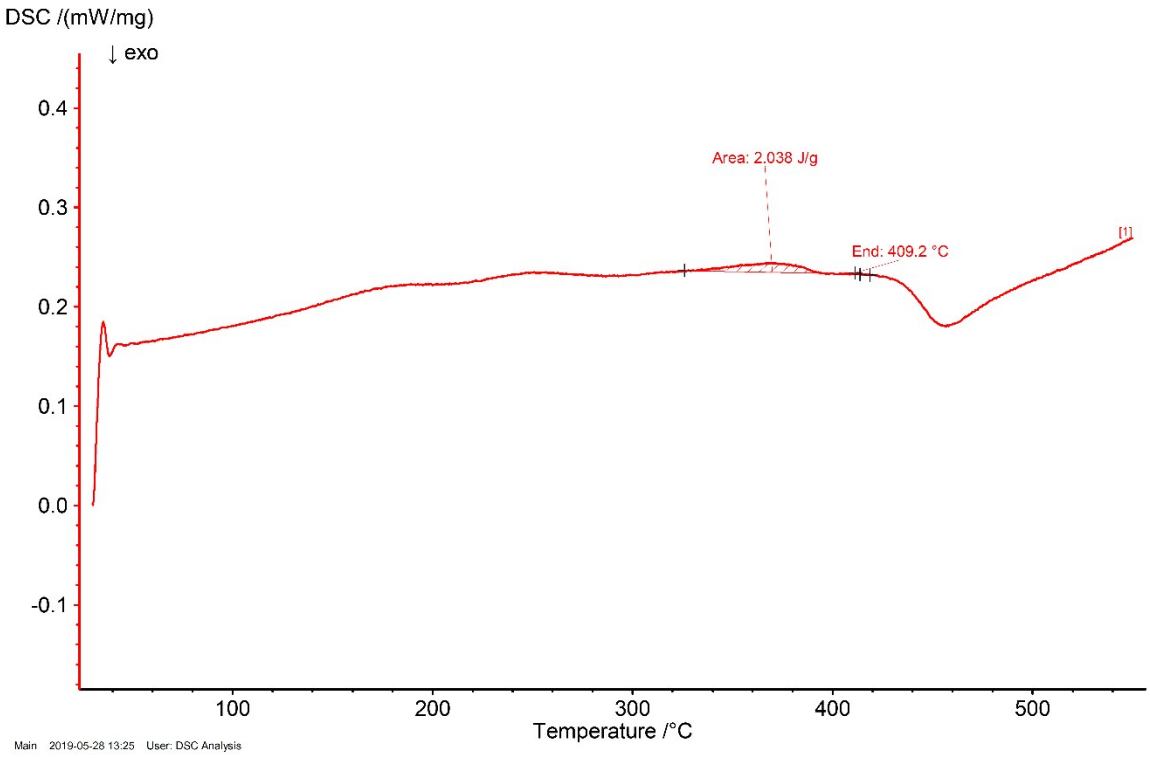

Figure S38: Differential scanning calorimetry of ZIF-76-mbIm heated to 550 °C.

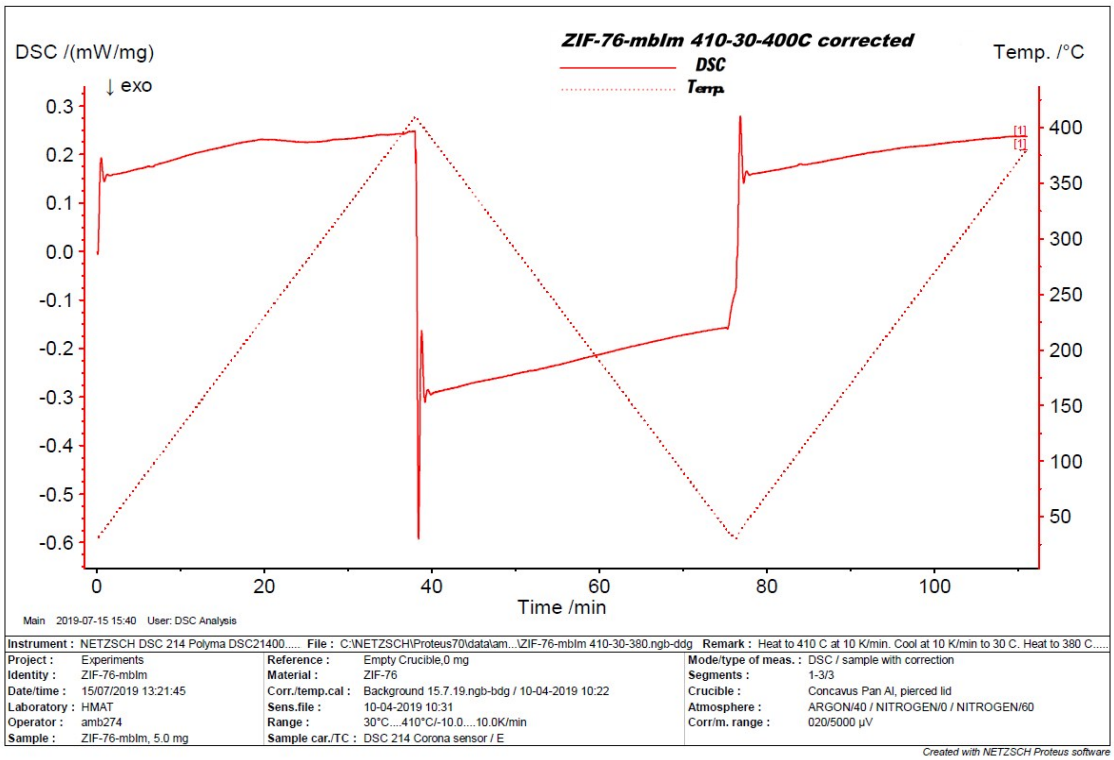

Figure S39: Differential scanning calorimetry of ZIF-76-mbIm heated to 410 °C, cooled to 30 °C then heated to 400 °C.

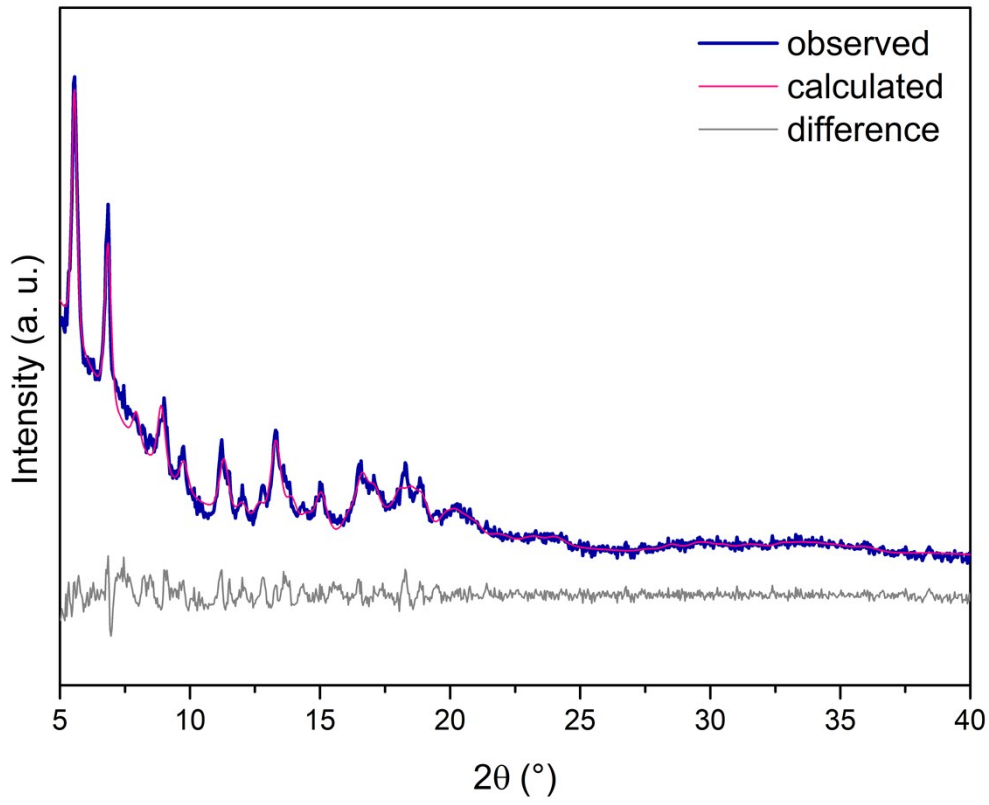

Figure S40: Pawley refinement of powder X-ray diffraction data of ZIF-76-mbIm after heating to 410 °C. Initial parameters were obtained from the previously reported CIF of ZIF-76.[3] This demonstrates that the sample was still crystalline and that the structure retained reflections that indexed to the ZIF-76 crystal structure. However, given the quality of this refinement, these parameters are not necessarily meaningful.

Table S17. Data from Pawley refinement of ZIF-76-mbIm after heating to 410 °C

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-76[3]
7.186	*P-43m*	*a* = 21.75(2) Å	*a* = 22.6702(2) Å
		b = 21.75(2) Å	*b* = 22.6702(2) Å
		c = 21.75(2) Å	*c* = 22.6702(2) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

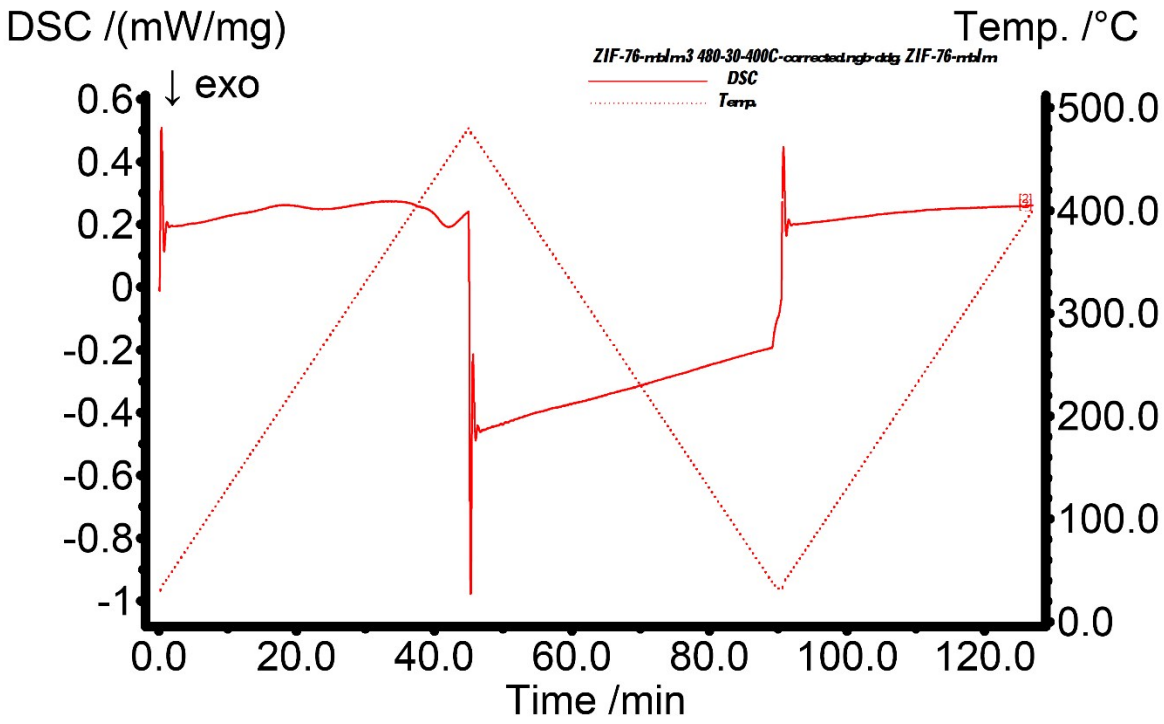

Figure S41: Differential scanning calorimetry of ZIF-76-mbIm heated to 480 °C, cooled to 30 °C then heated to 400 °C.

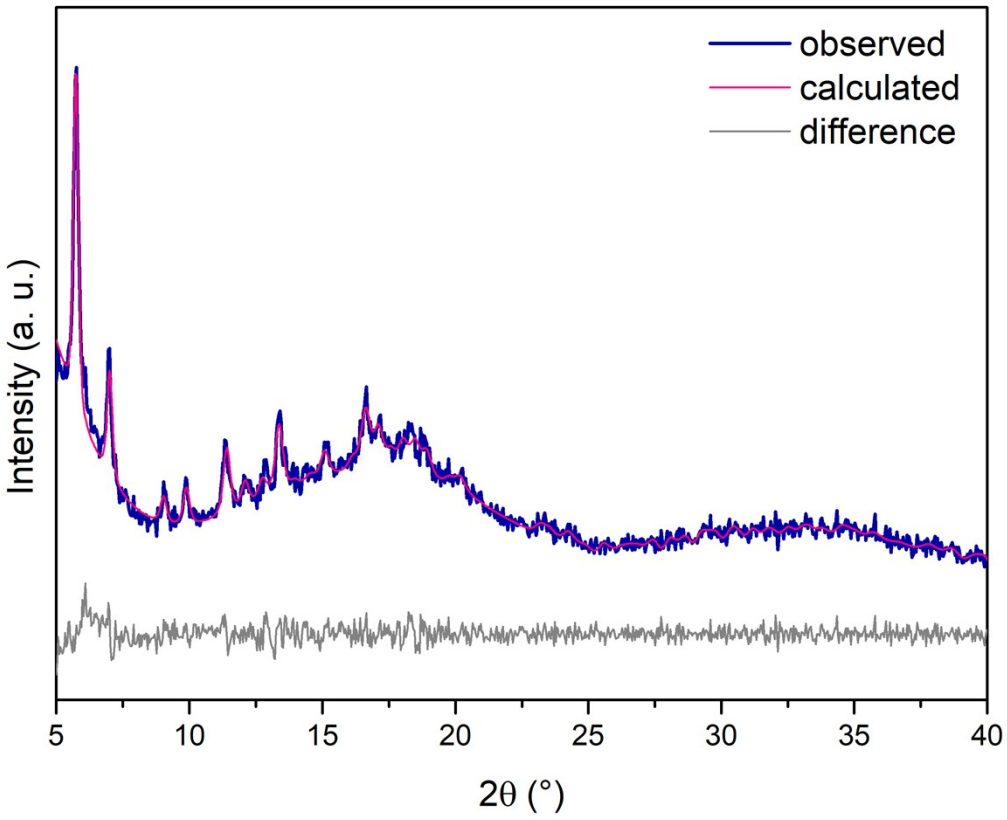

Figure S42: Pawley refinement of powder X-ray diffraction data of ZIF-76-mbIm after heating to 480 °C. Initial parameters were obtained from the previously reported CIF of ZIF-76.[3] This demonstrates that the sample was still crystalline and that the structure retained reflections that indexed to the ZIF-76 crystal structure. However, given the quality of this refinement, these parameters are not necessarily meaningful.

Table S18. Data from Pawley refinement of ZIF-76-mbIm after heating to 480 °C

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-76[3]
5.754	*P-43m*	*a* = 22.066(18) Å	*a* = 22.6702(2) Å
		b = 22.066(18) Å	*b* = 22.6702(2) Å
		c = 22.066(18) Å	*c* = 22.6702(2) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

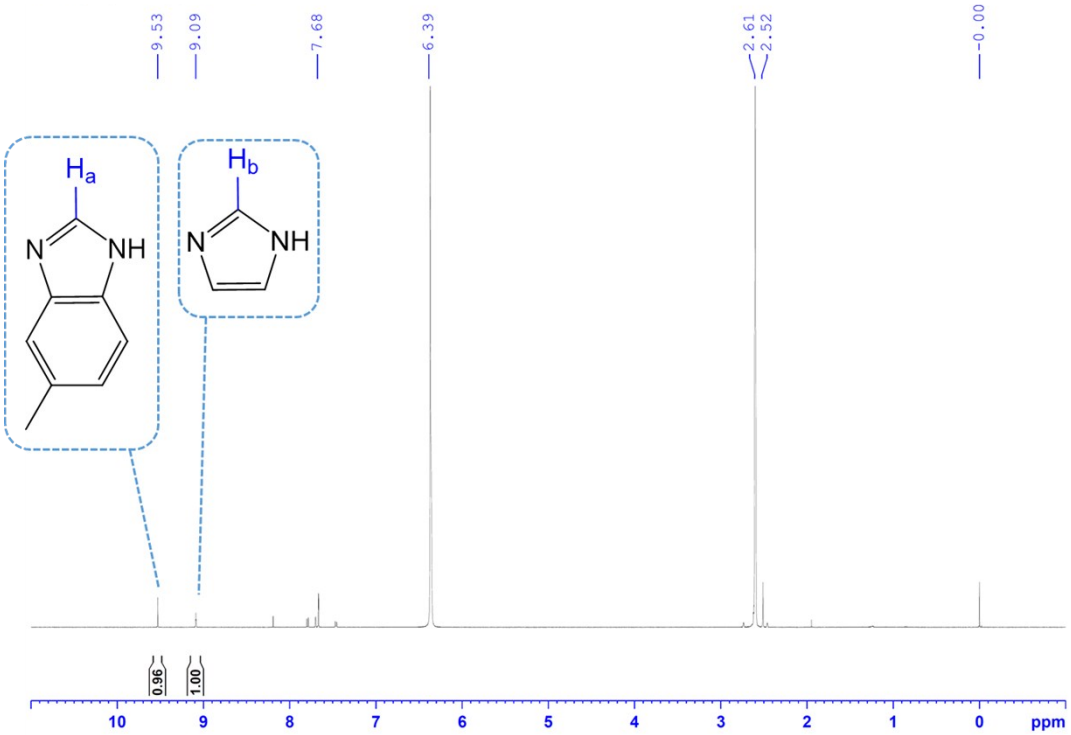

Figure S43: ^{1}H nuclear magnetic resonance spectrum of ZIF-76-mbIm after heating to 410 °C.

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.53 (1H, s, H_a), 9.09 (1H, s, H_b), 7.68 (5H, m, aromatic), 6.39 (H_2O/HCl), 2.61 (DMSO), 2.52 (3H, s, Me), 0.00 (TMS).

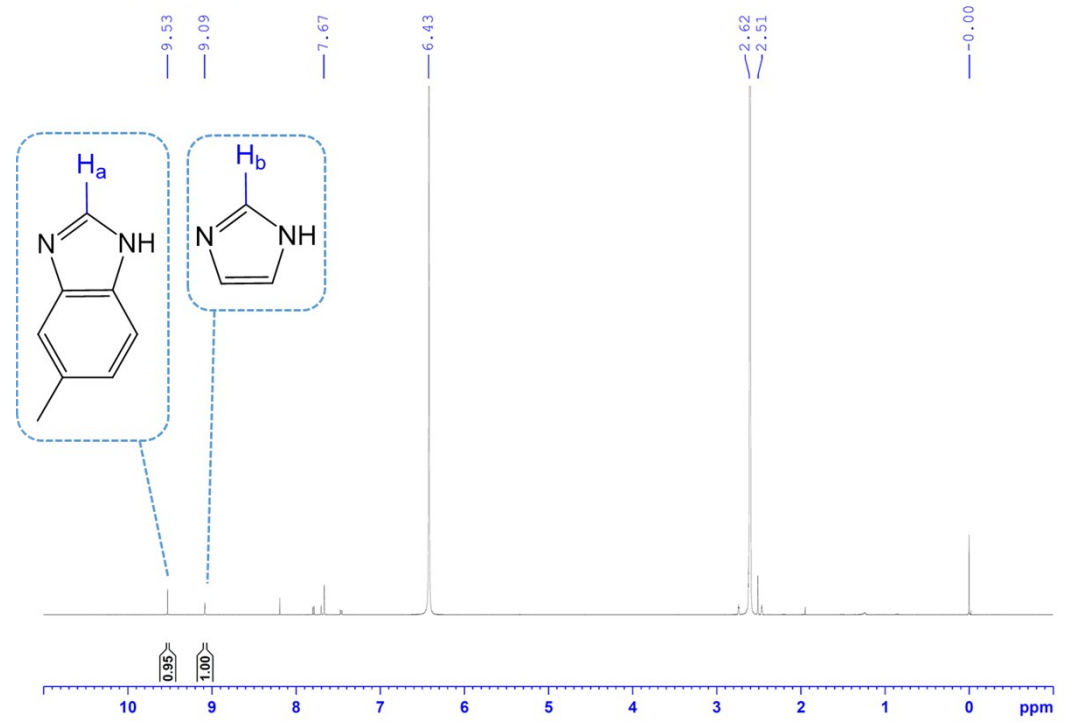

Figure S44: ^{1}H nuclear magnetic resonance spectrum of ZIF-76-mbIm after heating to 480 °C.

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.53 (1H, s, H_a), 9.09 (1H, s, H_b), 7.67 (5H, m, aromatic), 6.43 (H_2O/HCl), 2.62 (DMSO), 2.51 (3H, s, Me), 0.00 (TMS).

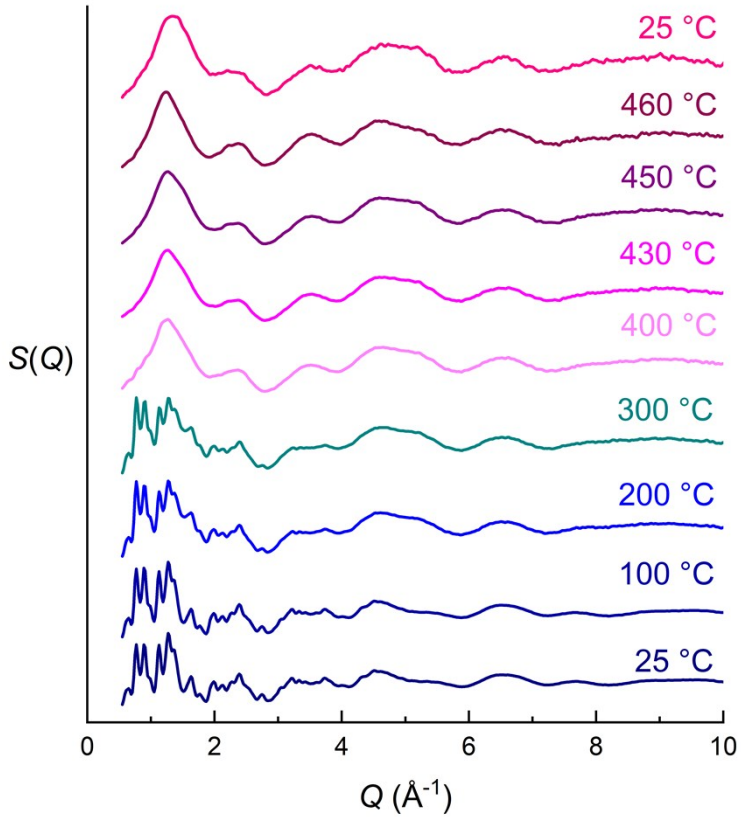

Figure S45: Variable temperature total scattering structure factors of ZIF-76-mbIm.

Figure S46: ^{1}H nuclear magnetic resonance spectrum of ZIF-76-mbIm mixed phase (mixture of ZIF-76-mbIm and TIF-4).

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.53 (1H, s, H_a), 9.09 (1H, s, H_b), 7.68 (5H, m, aromatic), 6.43 (H_2O/HCl), 2.62 (DMSO), 2.52 (3H, s, Me), 0.00 (TMS).

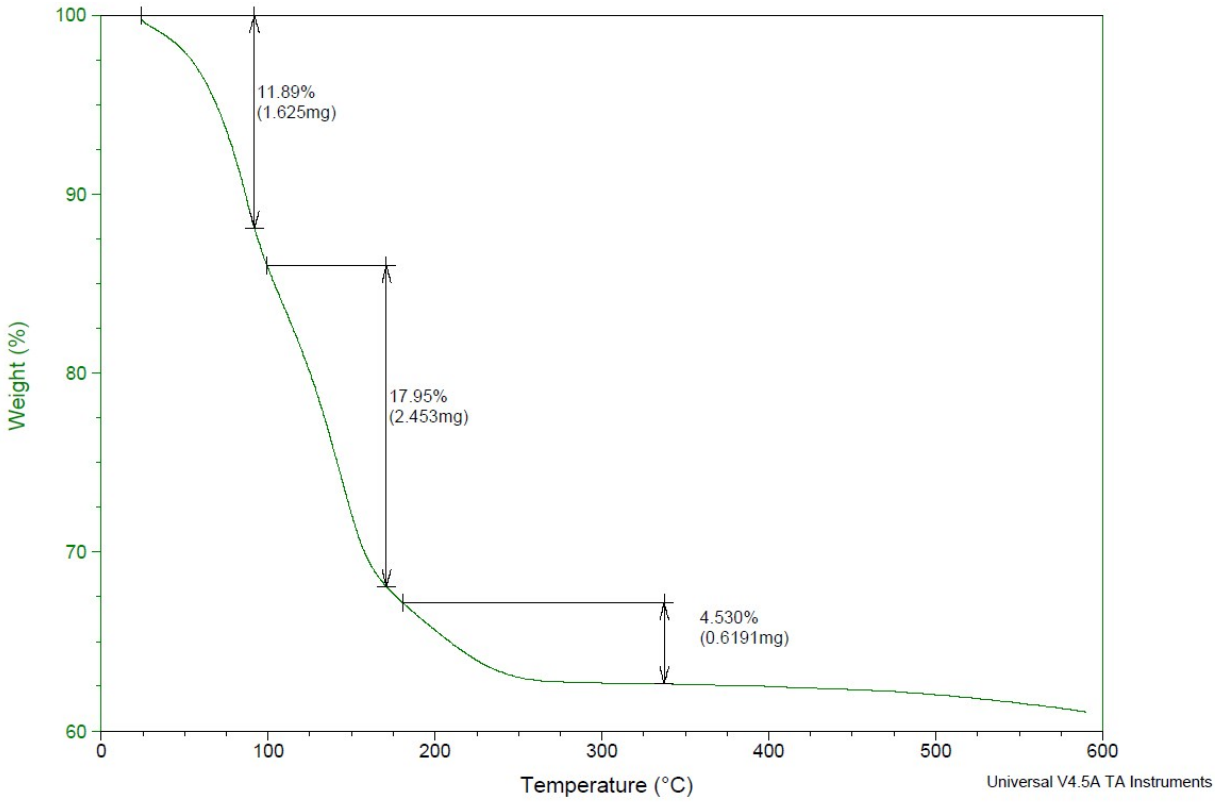

Figure S47: Thermogravimetric analysis of ZIF-76-mbIm mixed phase (ZIF-76-mbIm and TIF-4) before activation.

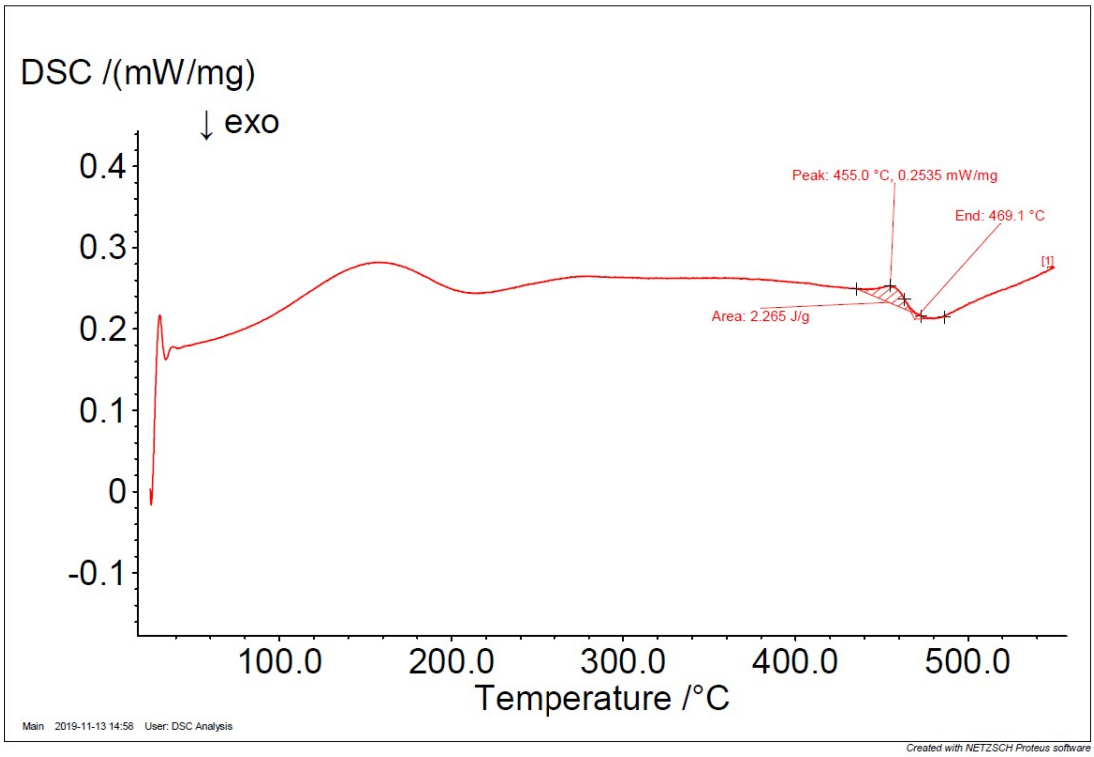

Figure S48: Differential scanning calorimetry of ZIF-76-mbIm mixed phase (ZIF-76-mbIm and TIF-4) heated to 550 °C.

Effect of Organic Linker Chemistry on ZIF-76

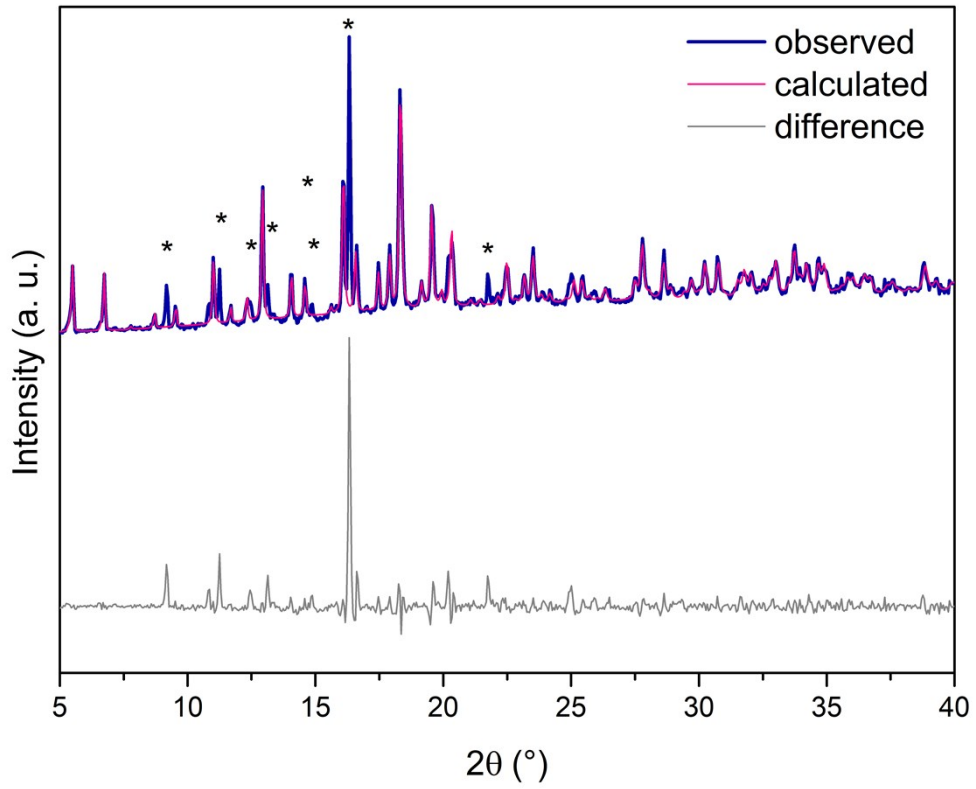

Figure S49: Pawley refinement of powder X-ray diffraction data of ZIF-76 mixed phase. Initial parameters were obtained from the previously reported CIF of ZIF-76.[3]

Table S19. Data from Pawley refinement of ZIF-76 mixed phase

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-76[3]
15.166	*P-43m*	*a* = 22.699(4) Å	*a* = 22.6702(2) Å
		b = 22.699(4) Å	*b* = 22.6702(2) Å
		c = 22.699(4) Å	*c* = 22.6702(2) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

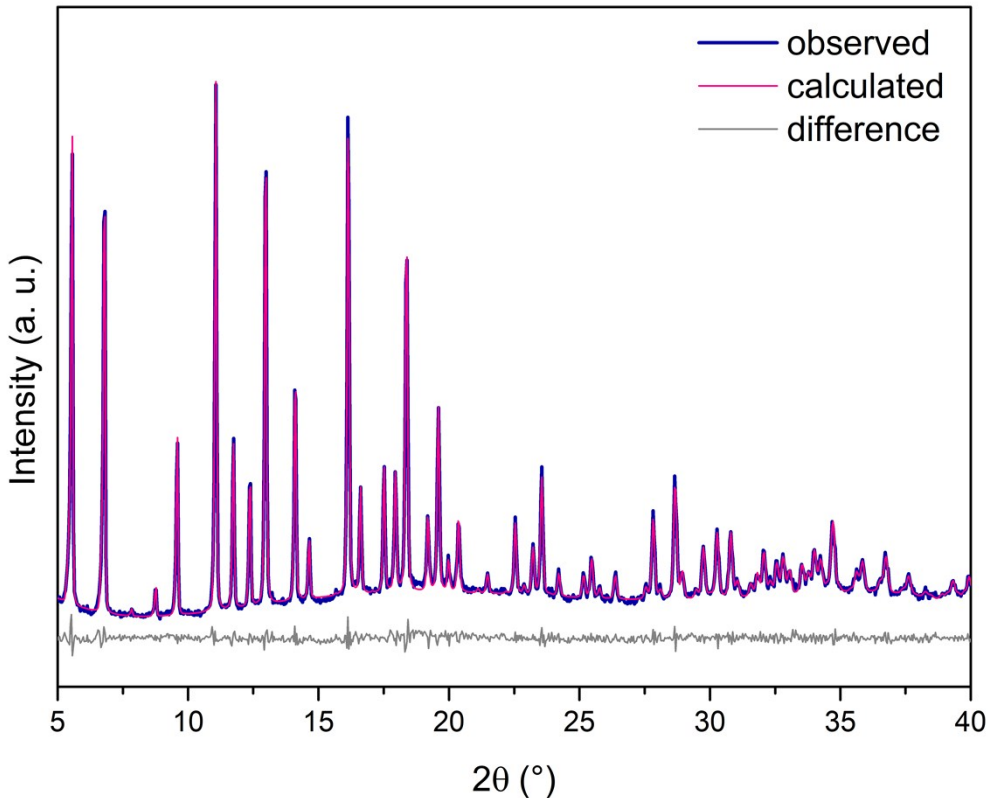

Figure S50: Pawley refinement of powder X-ray diffraction data of ZIF-76 phase pure. Initial parameters were obtained from the previously reported CIF of ZIF-76.[3]

Table S20. Data from Pawley refinement of ZIF-76 phase pure

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-76[3]
5.461	*P-43m*	*a* = 22.6977(6) Å	*a* = 22.6702(2) Å
		b = 22.6977(6) Å	*b* = 22.6702(2) Å
		c = 22.6977(6) Å	*c* = 22.6702(2) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

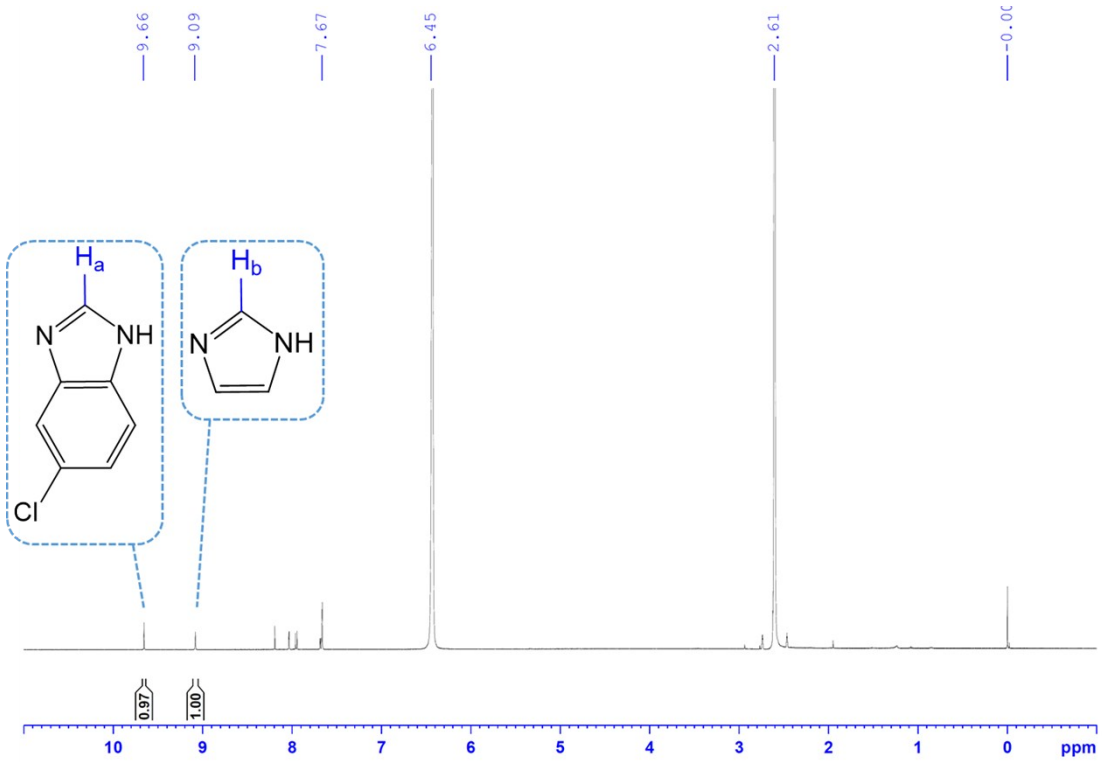

Figure S51: ^{1}H nuclear magnetic resonance spectrum of ZIF-76.

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.66 (1H, s, H_a), 9.09 (1H, s, H_b), 7.67 (5H, m, aromatic), 6.45 (H_2O/HCl), 2.61 (DMSO), 0.00 (TMS).

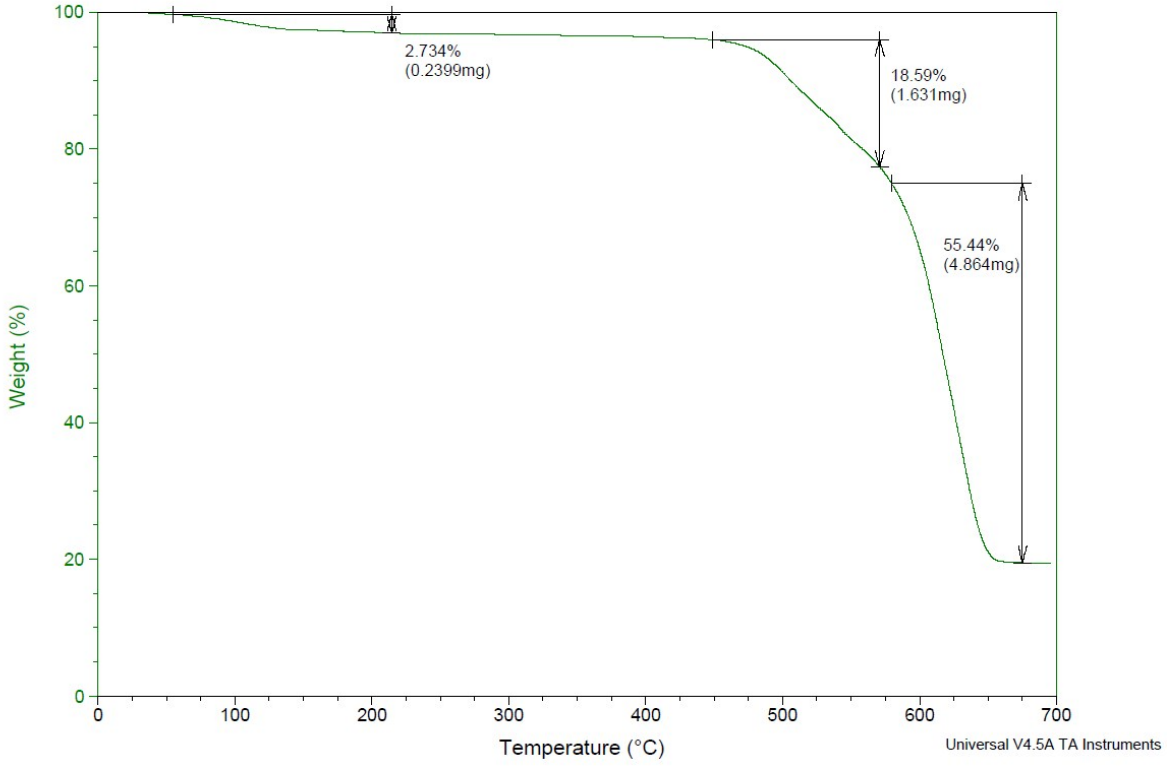

Figure S52: Thermogravimetric analysis of ZIF-76.

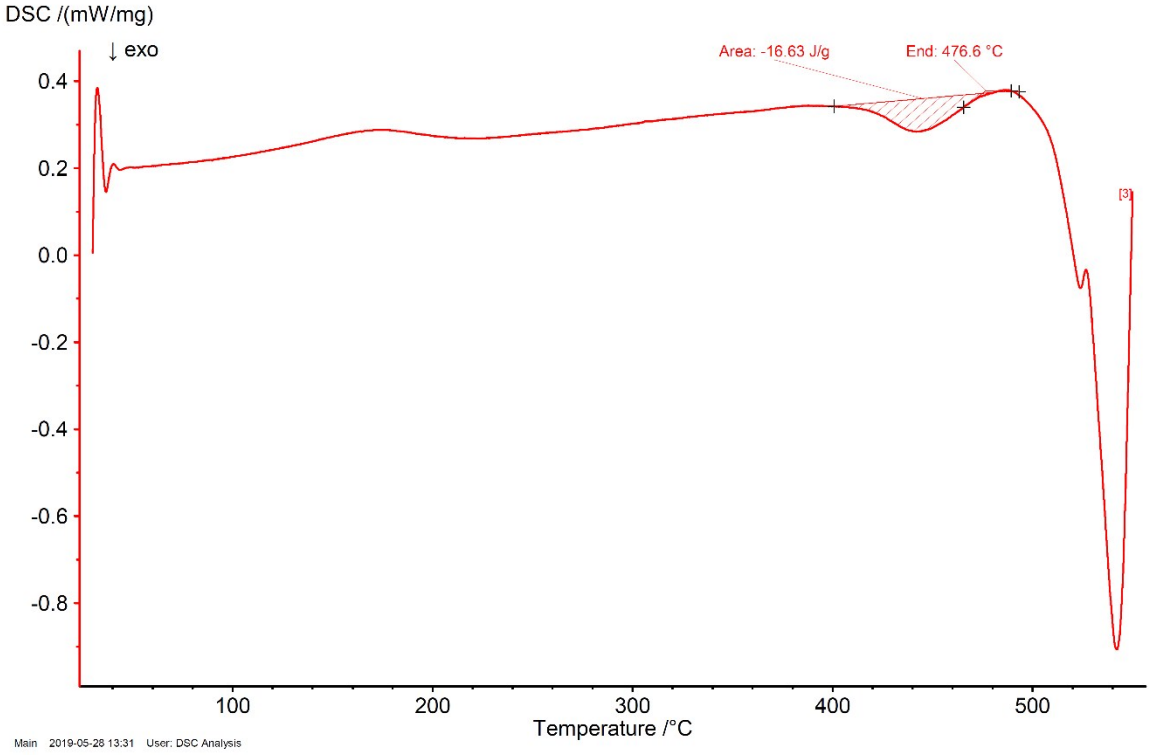

Figure S53: Differential scanning calorimetry of ZIF-76 heated to 550 °C.

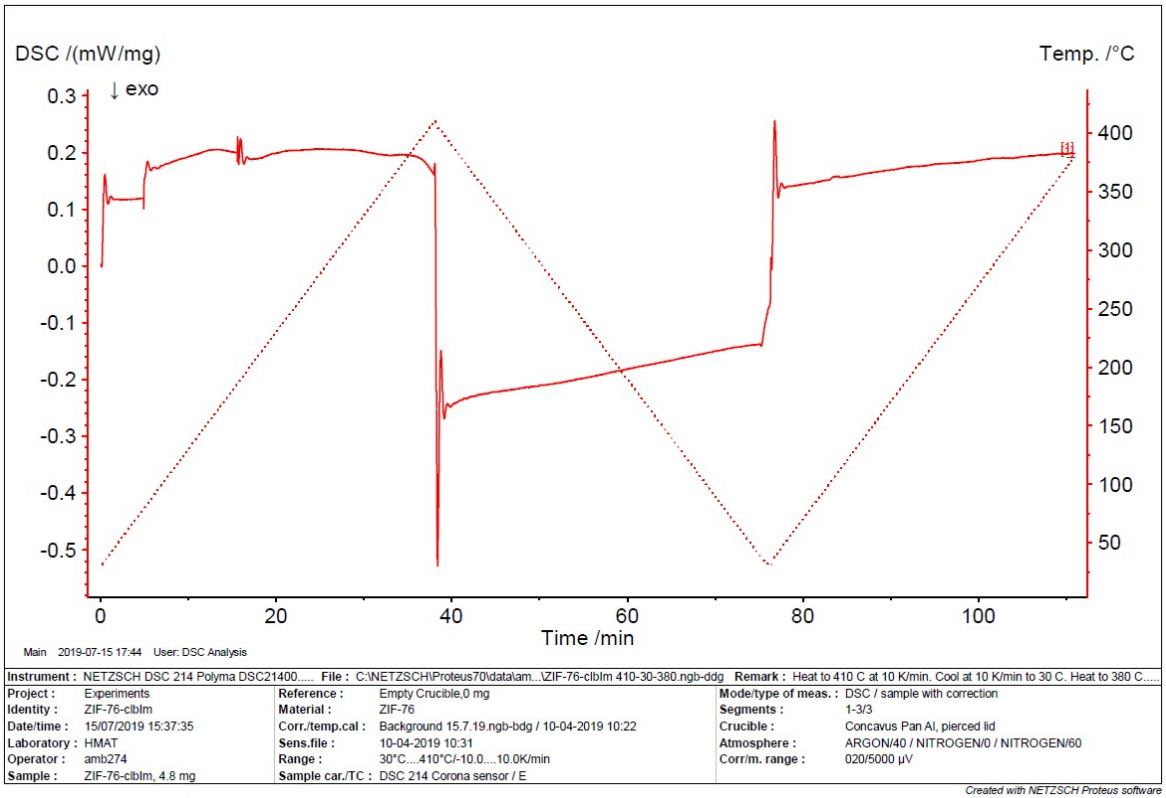

Figure S54: Differential scanning calorimetry of ZIF-76 heated to 410 °C, cooled to 30 °C then heated to 400 °C.

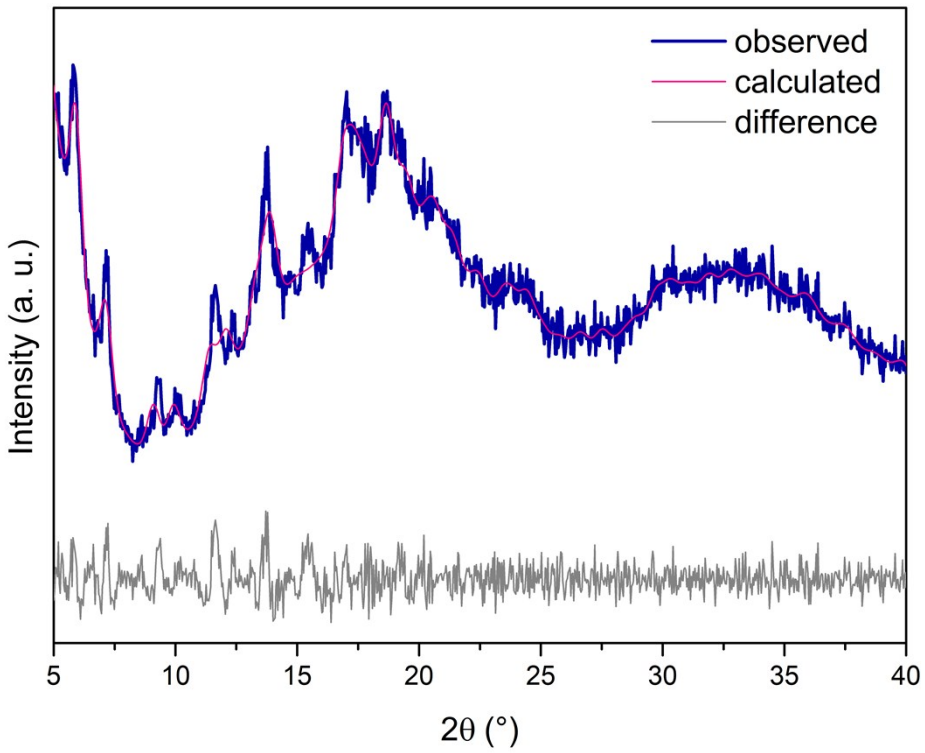

Figure S55: Pawley refinement of powder X-ray diffraction data of ZIF-76 after heating to 410 °C. Initial parameters were obtained from the previously reported CIF of ZIF-76.[3] This demonstrates that the sample was still crystalline and that the structure retained reflections that indexed to the ZIF-76 crystal structure. However, given the quality of this refinement, these parameters are not necessarily meaningful.

Table S21. Data from Pawley refinement of ZIF-76 after heating to 410 °C

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-76[3]
5.497	*P-43m*	*a* = 22.83(8) Å	*a* = 22.6702(2) Å
		b = 22.83(8) Å	*b* = 22.6702(2) Å
		c = 22.83(8) Å	*c* = 22.6702(2) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

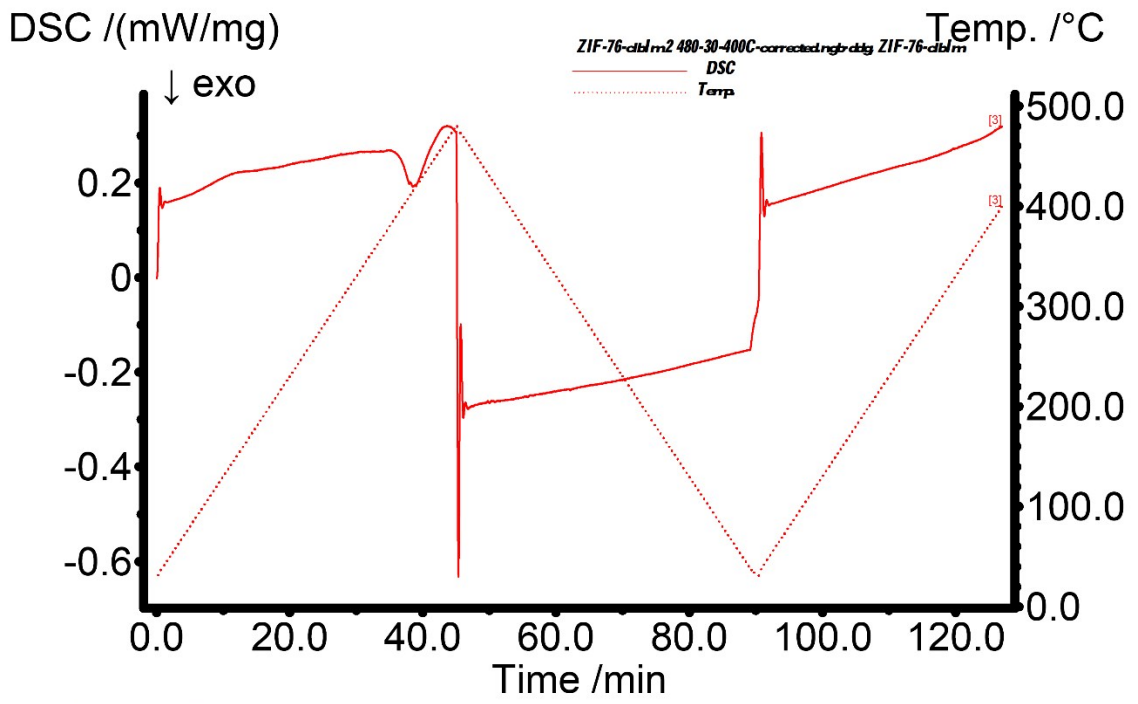

Figure S56: Differential scanning calorimetry of ZIF-76 heated to 480 °C, cooled to 30 °C then heated to 400 °C.

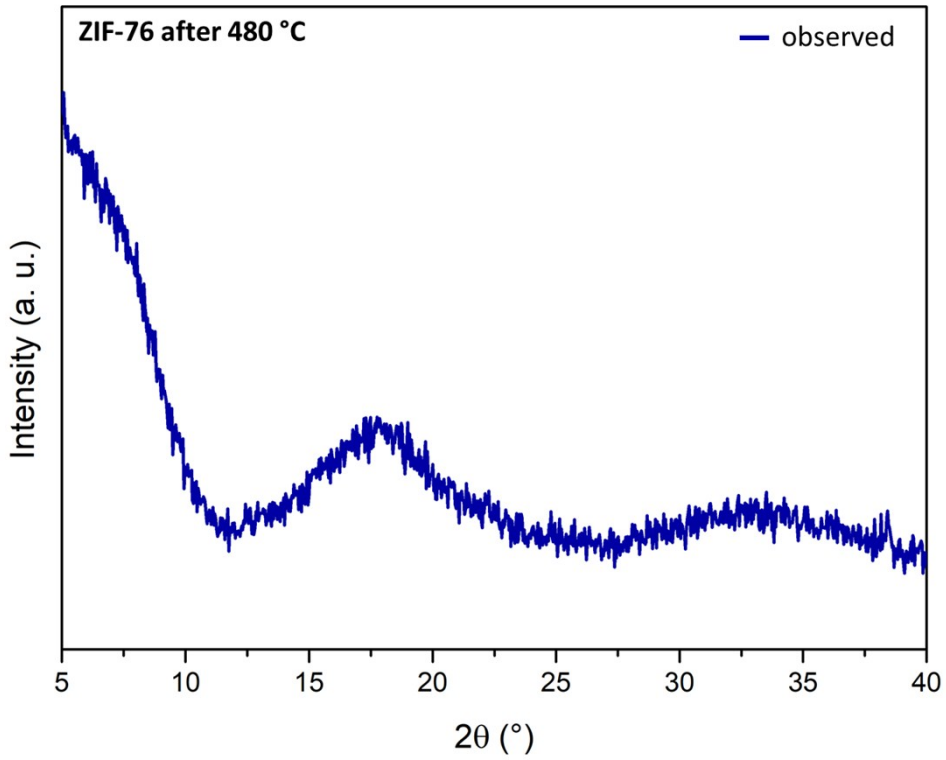

Figure S57: Powder X-ray diffraction pattern of ZIF-76 after heating to 480 °C.

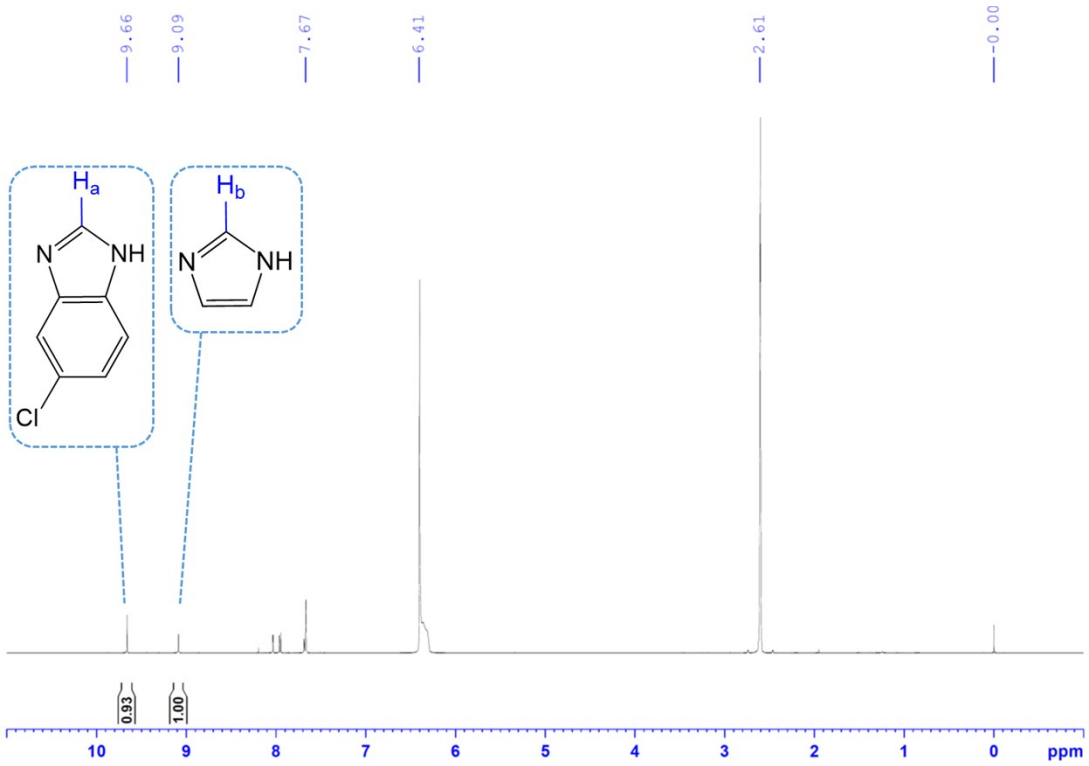

Figure S58: ^{1}H nuclear magnetic resonance spectrum of ZIF-76 after heating to 410 °C.

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.66 (1H, s, H_a), 9.09 (1H, s, H_b), 7.67 (5H, m, aromatic), 6.41 (H_2O/HCl), 2.61 (DMSO), 0.00 (TMS).

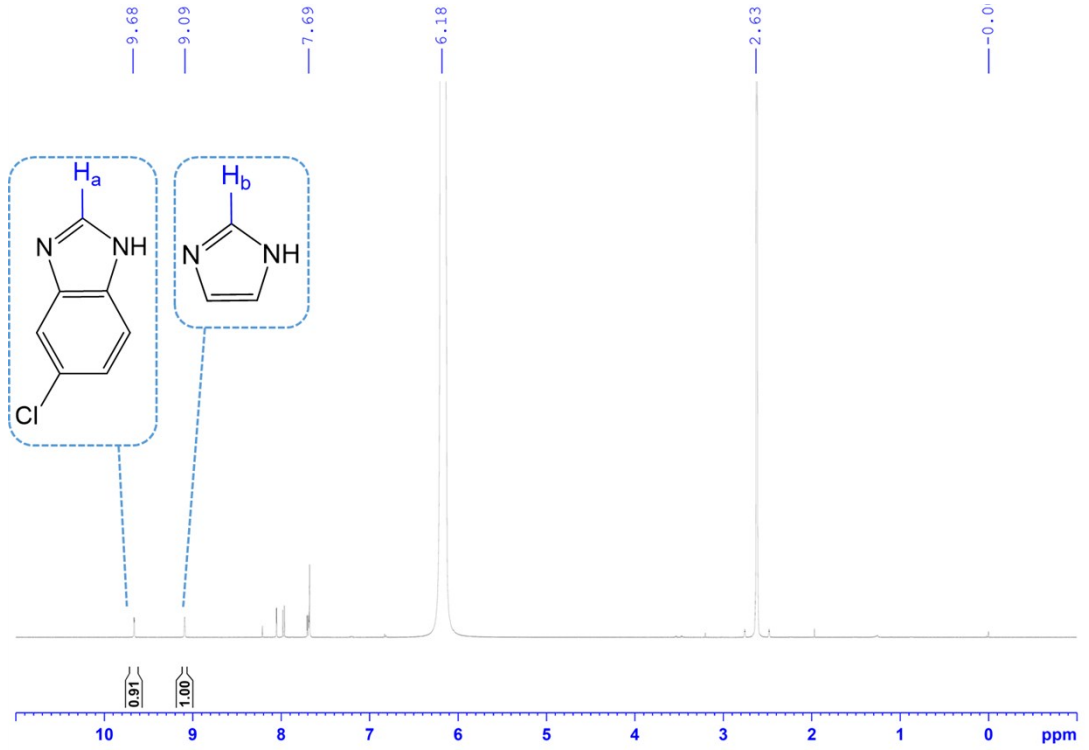

Figure S59: ^{1}H nuclear magnetic resonance spectrum of ZIF-76 after heating to 480 °C.

δH (500 MHz; DCl(20%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.68 (1H, s, H_a), 9.09 (1H, s, H_b), 7.69 (5H, m, aromatic), 6.18 (H_2O/HCl), 2.63 (DMSO), 0.00 (TMS).

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