

# Solvent-Assisted Ligand Exchange (SALE) For Enhancement of Catalysis Based Reaction the Capability of Epoxide Ring-Opening on Three Amide-Functionalized Metal-Organic Frameworks

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## 1. Experimental Section

### 1.1. Synthesis of the ligands

#### 1.1.1. Synthesis of bpta, bpfb and bpfn

The simple route for the synthesis of amide-containing compounds is the coupling of an acid chloride with an amine group. Note here that the acid chloride-amine reaction is exothermic. Therefore, all organic reactions performed in this study were carried out at low temperature in the presence of triethylamine (TEA) to capture in situ the generated side product HCl. Synthesis of bpta 4-aminopyridine (1.882 g; 20 mmol) and 2.84 ml of TEA (20.4 mmol) were dissolved in 50 ml of dry THF. Then, terephthaloyl chloride (2.030 g; 10 mmol) was added into this solution and heated under reflux for 24 h. The resulting yellow suspension was filtered, dried under ambient conditions, and poured into an aqueous saturated solution of Na<sub>2</sub>CO<sub>3</sub> (50 ml). The resulting white solid was finally filtered and dried, obtaining the pure ligand bpta in ca. 73 % yield.

#### Synthesis of bpfb and bpfn

1,5-diaminonaphthalene (1.580 g; 10 mmol; for bpfn) and 1,4-phenylenediamine (1.081 g; 10 mmol; for bpfb) were dissolved in 50 ml of dry THF containing 2.84 ml of TEA (20.4 mmol). Then, isonicotinoyl chloride hydrochloride (3.560 g, 20 mmol) was added into these solutions and heated under reflux for 24 h. Both reactions were then treated as above indicated for the

synthesis of bpta. The yellowish powders were filtered and dried, obtaining the pure ligands in ca. 82 % (bpfb) and 87 % (bpfn) yields.

### **Synthesis of the ligand N1, N3-di(pyridine-4-yl) malonamide (S)**

The S spacer was synthesized by mixture of 0.07gr malonyl dichloride (0.5mmol) and 0.09gr of 4-amino pyridine (1mmol) in 40cc dry THF. After adding 8cc TEA (Triethylamine), put the mixture be refluxed in Ar condition for 24h. The resulting brown suspension was filtered, dried under ambient conditions, and poured into an aqueous saturated solution of Na<sub>2</sub>CO<sub>3</sub> (50 ml). The resulting light brown solid was finally filtered and dried, obtaining the pure ligand S in ca. 73 % yield.

### **NMR of parent MOFs and SALE samples**

Approximately 5 mg of each MOFs were placed in an NMR tube and dissolved in 100  $\mu$ L of D<sub>2</sub>SO<sub>4</sub> and 0.6 mL of d<sub>6</sub>-DMSO by sonication. Once a homogeneous solution was obtained, the <sup>1</sup>H NMR spectra were obtained.

### **Activation Method**

The trapped guest molecules can be removed by exchanging the synthesized parent crystals (TMU-49), (TMU-50) and (TMU-51) and daughter crystals (TMU-49S), (TMU-50S) and (TMU-51S) With soaked MOFs in 3 mL of acetonitrile solvent for 2 days, and added fresh acetonitrile every 24 h. At last, the CH<sub>3</sub>CN solution was decanted, and the activated crystals were dried at 100 °C for at least 24 h. The activation is confirmed by FT-IR spectroscopy, elemental analysis, and powder X-ray diffraction. Absence of the peak at range 1665-1670 cm<sup>-1</sup> in the FT-IR spectrum of parent and daughter activated samples confirms the removal of DMF molecules after activation.

FT-IR data (KBr pellet, cm<sup>-1</sup>): selected bands: 3359 (w), 2929 (w), 1599 (s), 1518 (s), 1382 (m), 1303 (w), 1182 (m), 1022 (w), 841 (w), 783 (w), 535 (w).

### **Computational details**

All DFT calculations were performed using the GAMESS suite of programs. The geometry of the ligands was optimized at the B3LYP/6-31+G\* level of theory. The LANL2DZ basis set with the corresponding effective core potential was used for the metal cations. Molecular electrostatic potentials (MEPs) of the isolated ligand were obtained on the 0.001 au surface by means of the SAS-WFA program using the wave functions generated at the aforementioned level of theory. The Mulliken charge density analysis of the free ligands was performed at the B3LYP/6-31+G\* level using the GAMESS.

## **Crystallography**

Crystallographic data for TMU-49 and TMU-50 were collected at 100 K at XALOC beamline at ALBA synchrotron 36 ( $\lambda = 0.79474 \text{ \AA}$  and  $0.82653 \text{ \AA}$ , respectively) and the SCXRD for TMU-51 was collected at 293 K on a Bruker AXS SMART Apex diffractometer using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data were indexed, integrated, and scaled using the XDS37 and IMOSFLM38 programs. Absorption correction was not applied.

## **Catalysis Experiments.**

In a typical reaction, the amide-based MOFs 15 mg were added to a CH<sub>3</sub>OH solution (3 mL) containing the epoxide substrate (0.2 mmol). The reaction mixture was stirred at 60 °C for the indicated times mentioned in Table 1 of the manuscript. Then the reaction mixture was cooled to room temperature and analysed by GC analysis using internal-standard method.

## **Catalyst Recycling**

The recycling of TMU-49, TMU-50, and TMU-51 as the parent samples and the daughter compounds were examined for the methanolysis of styrene oxide. After stirring for 40 h, the heterogeneous mixture was allowed to settle completely followed by decanting the supernatant liquid. The sample of catalysts were filtered off after 40 h reaction, washed with excess MeOH and dried at 80 °C under vacuum at room temperature. The recovered catalyst was reused without further purification for the second run with fresh styrene oxide and methanol.

## **Typical Procedure for the Methanolysis of other Epoxides**

The prepared amide MOF catalysts is suspended in a MeOH (3 mL) solution of epoxide (15 mg) and stirred at 60 °C for different hours. Then, the solid catalysts were filtered off. Determination of the major product was performed based on an internal-standard method. All standards samples for determination of the major products in the reaction mixture were prepared using the separated methanolysis reactions of the epoxides in the presence of catalytic amount of HCl. Since the prominent product in this acidic condition is adduct owing to steric reasons, their retention time for GC analysis was revealed in this manner. For this reaction, 2 drop of the concentrated HCl was added to the solution of epoxides and MeOH (3 ml). The progress of the reaction was monitored using GC analysis.

**Table S1. Crystal data and structure refinement of TMU-49**

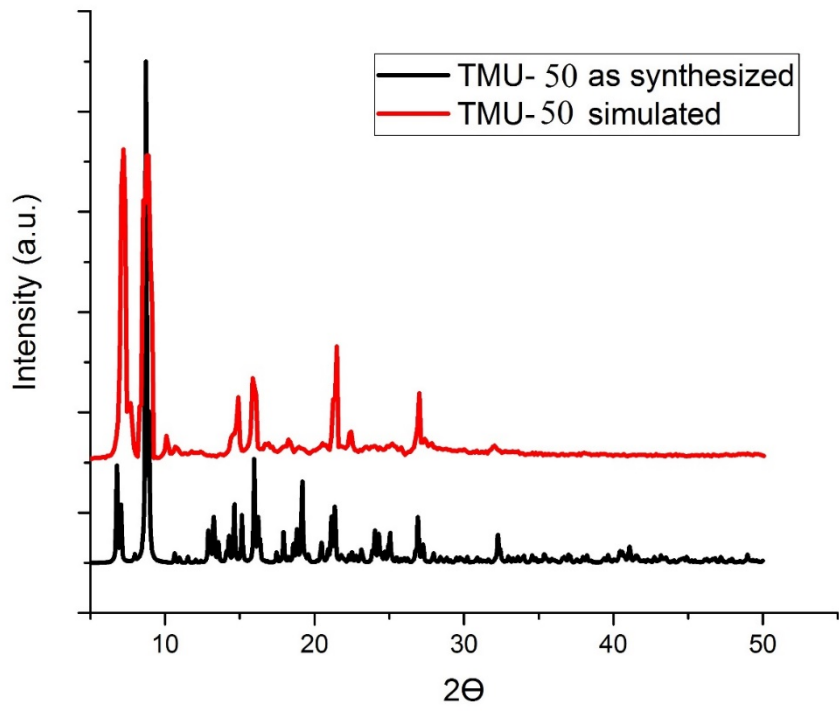
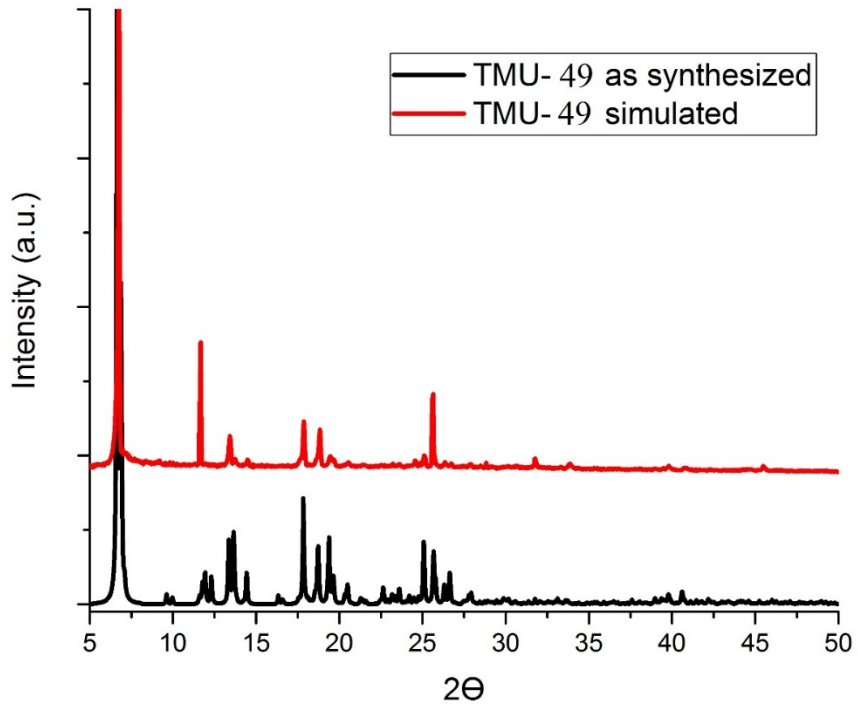
Empirical formula	C <sub>32</sub> H <sub>22</sub> Co N <sub>4</sub> O <sub>7</sub> ,C <sub>3</sub> H <sub>7</sub> N O
CCDC	1849856
Chemical formula weight	635.48
Crystal system	Triclinic
Space group	P -1
Temperature (K)	193(2)
Wavelength, MoK $\alpha$ (Å)	0.71073
a (Å)	9.9159(7)
b(Å)	14.941(2)
c (Å)	15.0690(11)
$\alpha$ (°)	112.459(14)
$\beta$ (°)	99.528(13)
$\gamma$ (°)	105.874(10)
Cell volume (Å <sup>3</sup> )	1890.74
Z	2
Z'	0
R -Factor(%)	6.77
goodness_of_fit_ref (GOF)	1.055
R_factor_gt	0.069
crystal_size_max	0.150
crystal_size_mid	0.06
crystal_size_min	0.04
crystal_F_000	785.2
reflns_number_total	6710
crystal_colour	pale red
crystal_description	prism

**Table S2. Crystal data and structure refinement of TMU-50**

Empirical formula CCDC	C32 H24 Co N4 O7 1849857
Chemical formula weight	635.48
Crystal system	monoclinic
Space group	P 21/n
Temperature (K)	193(2)
Wavelength, MoK $\alpha$ (Å)	0.71073
a (Å)	15.2997(12)
b (Å)	16.1519(13)
c (Å)	25.122(2)
$\alpha$ (°)	90
$\beta$ (°)	90.051(2)
$\gamma$ (°)	90
Cell volume (Å <sup>3</sup> )	6208.13
Z	8
Z'	0
R -Factor(%)	5.11
goodness_of_fit_ref (GOF)	1.070
R_factor_gt	0.0515
crystal_size_max	0.180
crystal_size_mid	0.150
crystal_size_min	0.120
crystal_F_000	2416.0
reflns_number_total	10910
crystal_colour	pink
crystal_description	Prism

**Table S3. Crystal data and structure refinement of TMU-51**

Empirical formula	C <sub>50</sub> H <sub>32</sub> Co <sub>2</sub> N <sub>4</sub> O <sub>12</sub> ,2(C <sub>3</sub> H <sub>7</sub> N O),0.86(C <sub>3</sub> H <sub>7</sub> N O)
CCDC	1849863
Chemical formula weight	635.48
Crystal system	orthorhombic
Space group	P n a 21
Temperature (K)	193(2)
Wavelength, MoK $\alpha$ (Å)	
a (Å)	24.5947(18)
b(Å)	15.6607(11)
c (Å)	16.3428(12)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
Cell volume (Å <sup>3</sup> )	6294.76
Z	4
Z'	0
R -Factor(%)	6.21
goodness_of_fit_ref (GOF)	1.008
R_factor_gt	0.0052
crystal_size_max	0.18
crystal_size_mid	0.08
crystal_size_min	0.03
crystal_F_000	2360
reflns_number_total	12722
crystal_colour	colourless
crystal_description	stick



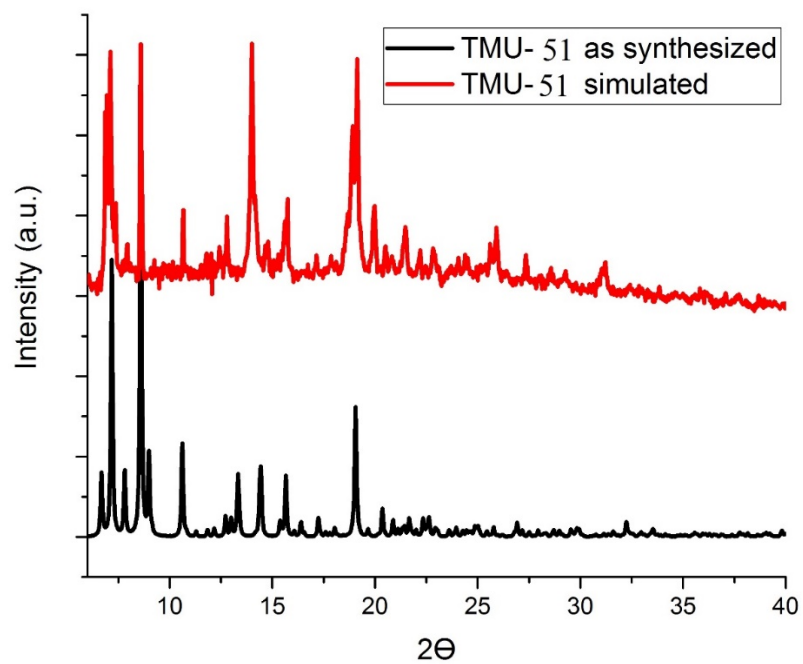


Fig. S1: PXRd spectra (black) of the synthesized TMU-49, 50, 51 and the simulated PXRd curve (red)



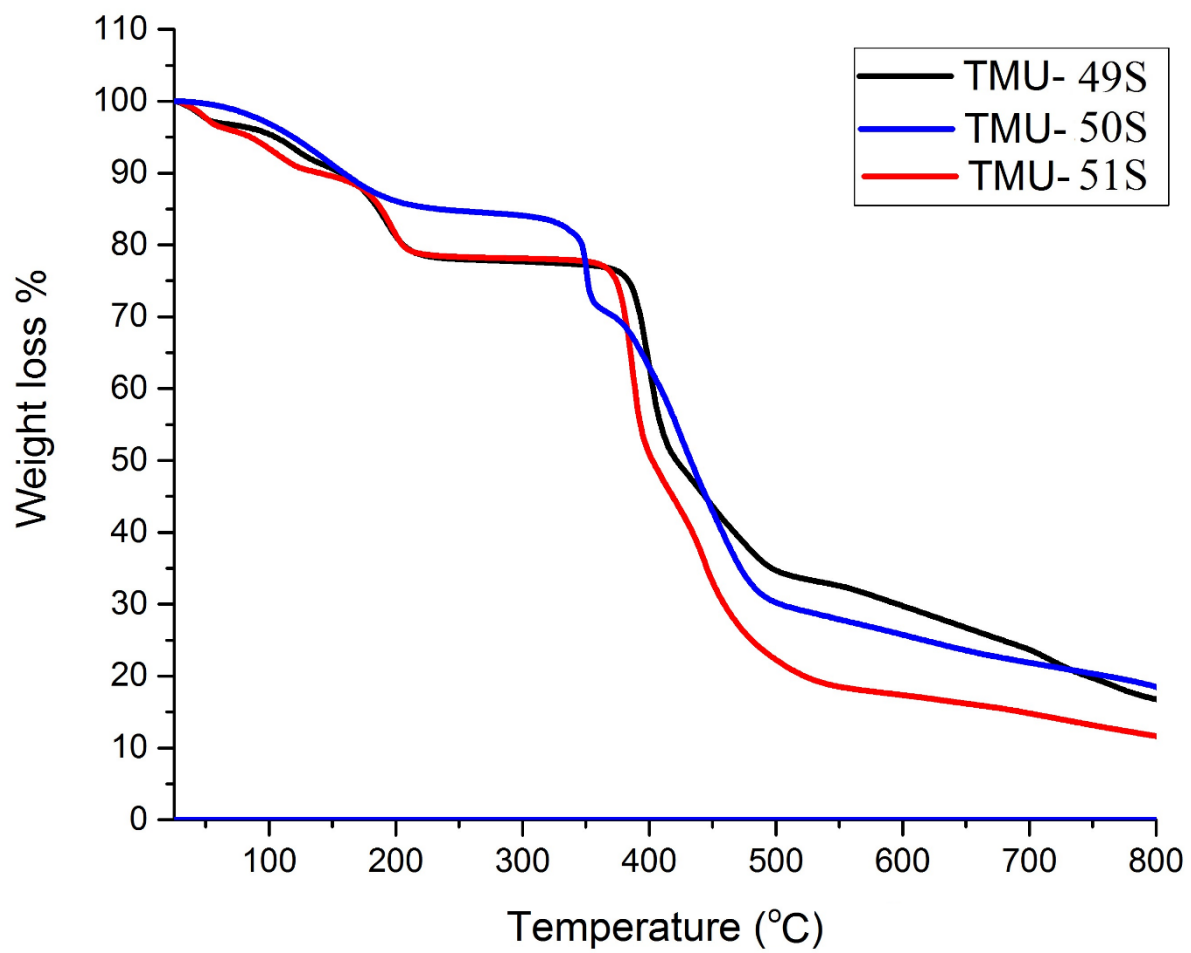
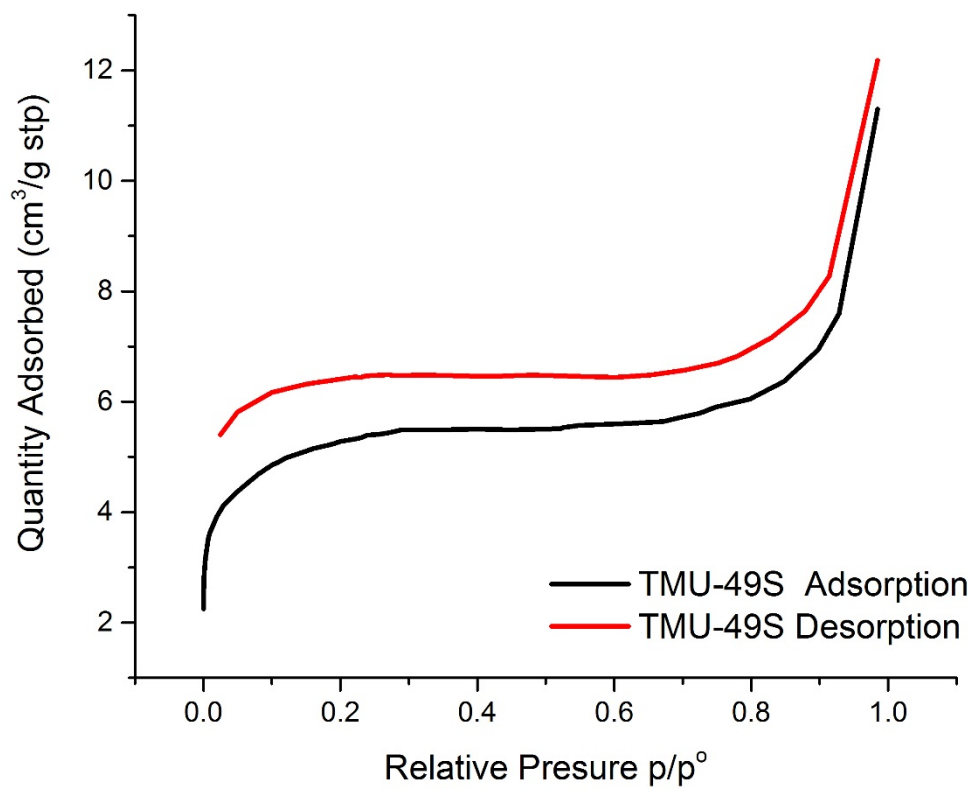
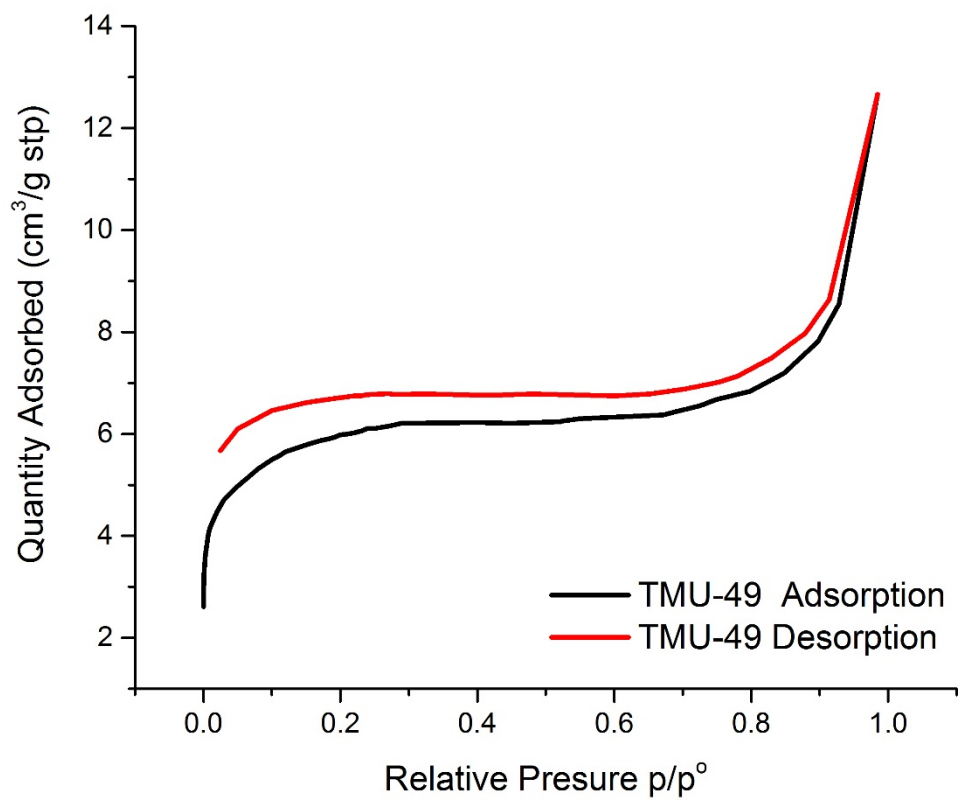


Fig. S2: Thermal analysis gravimetric of TMU-49, TMU-50 and TMU-51



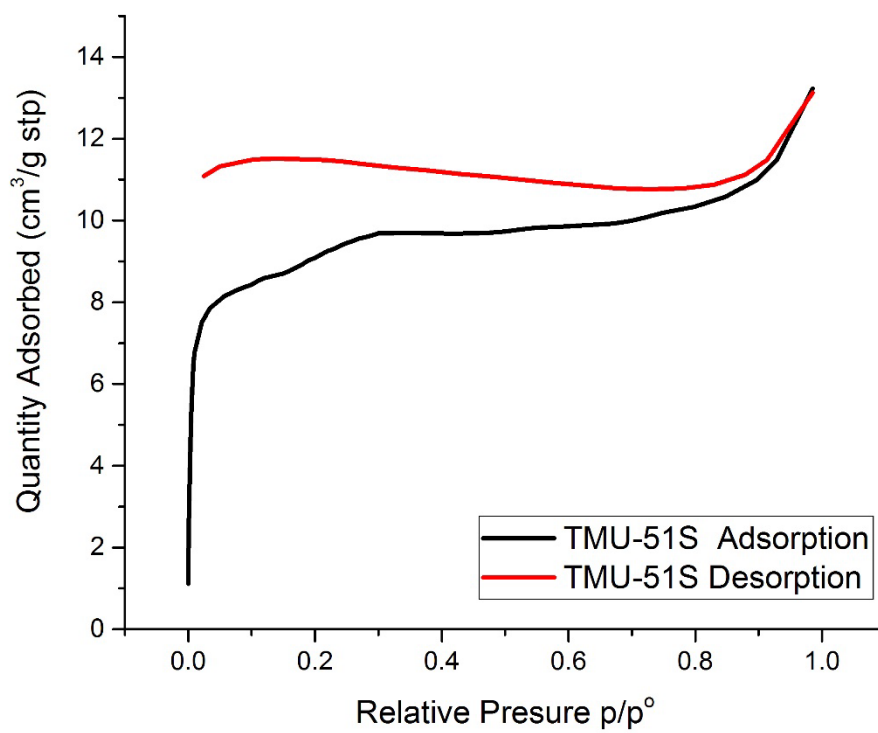
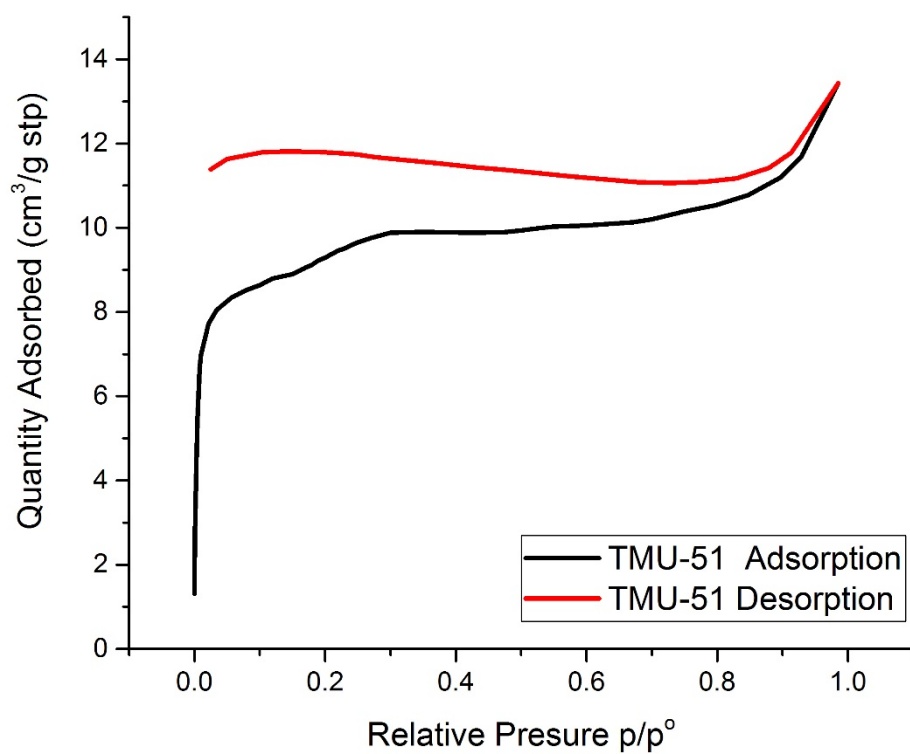
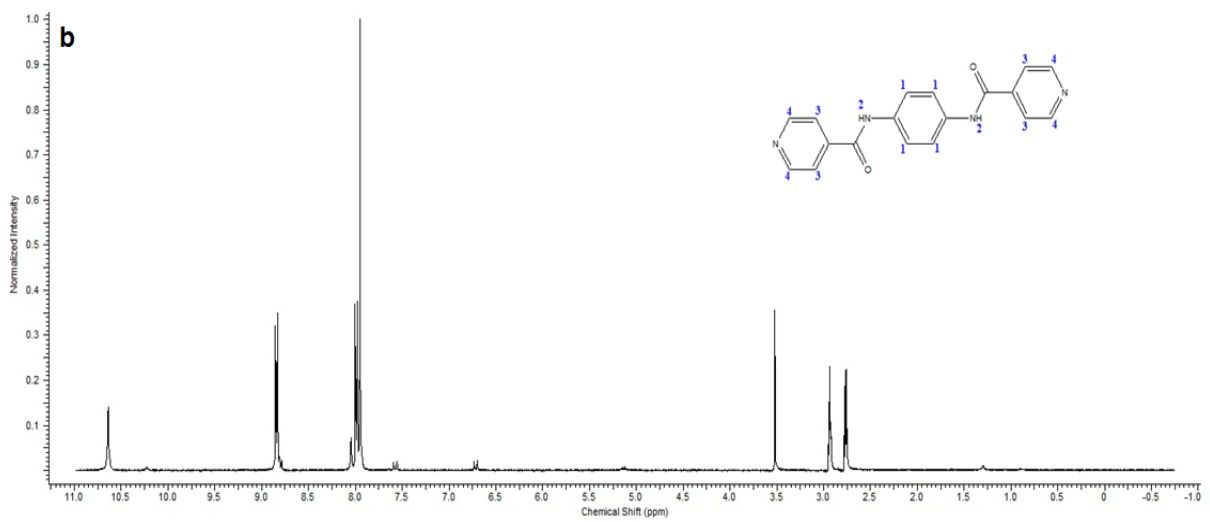
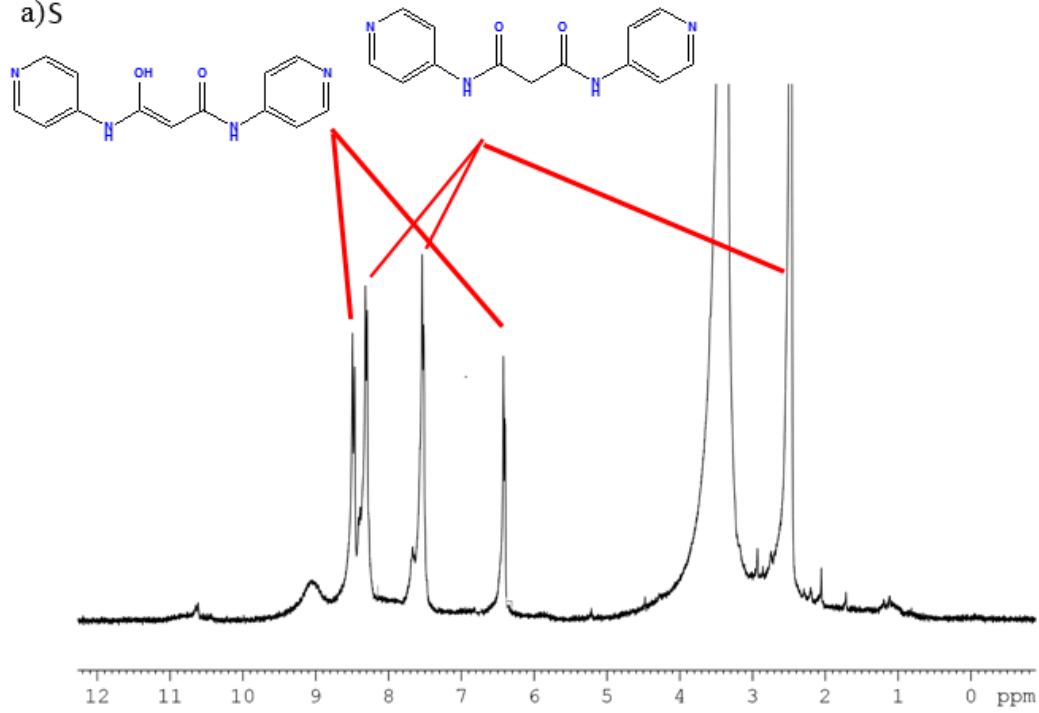
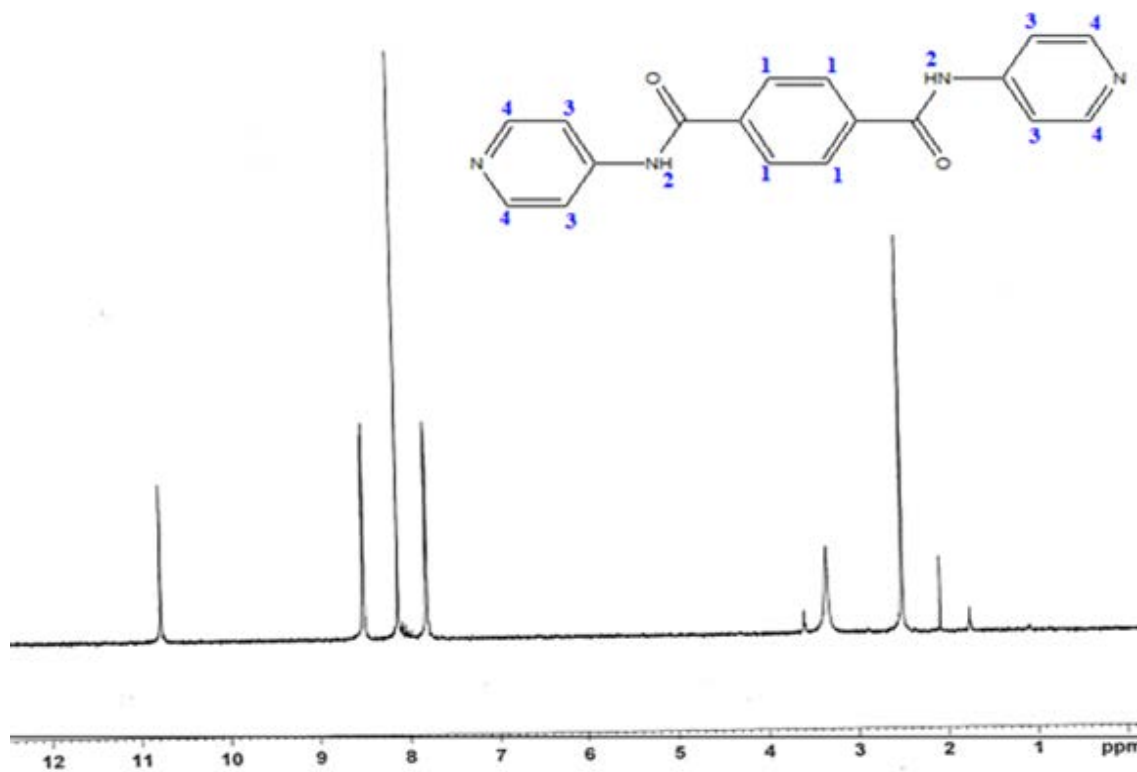


Fig. S3: Nitrogen adsorption-desorption isotherms at 77 K for TMU-49, 49S, 51 and 51S

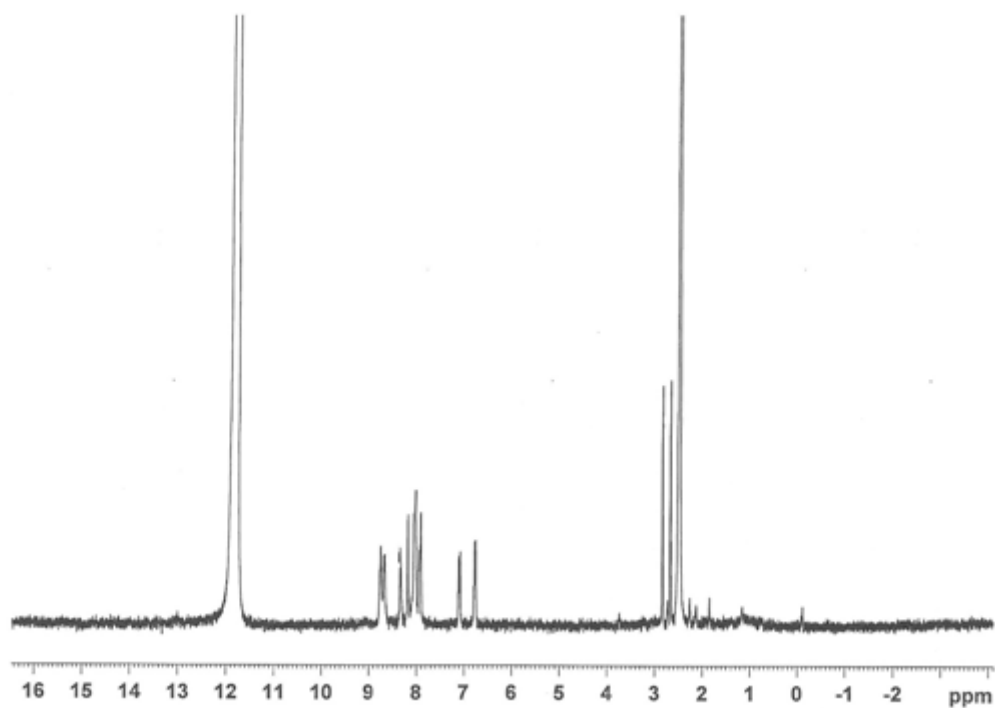
a) S



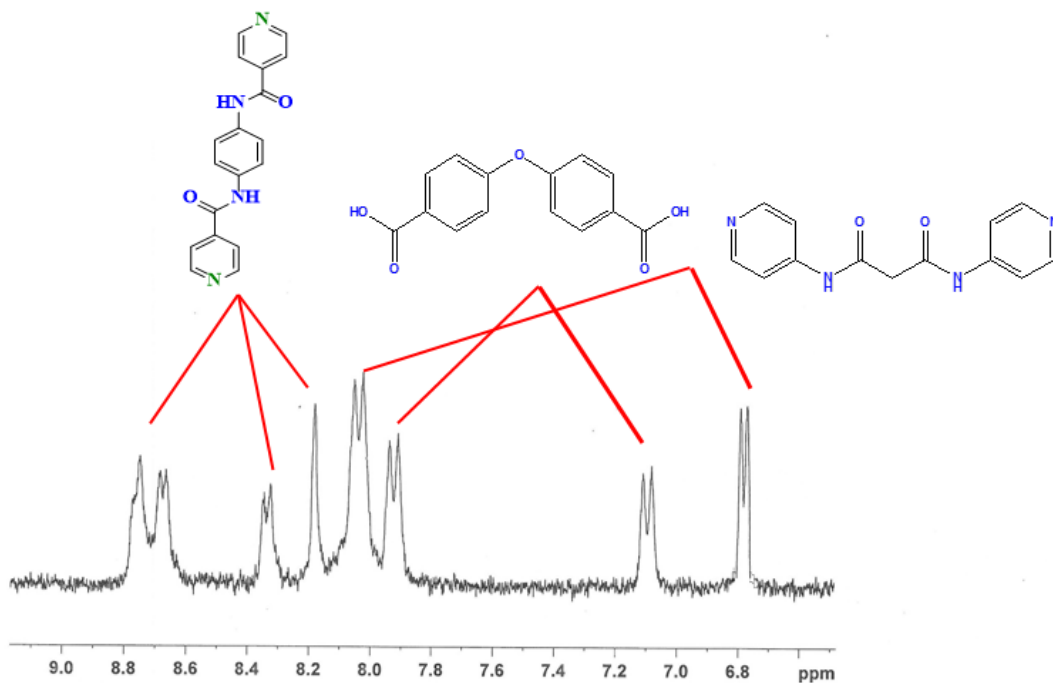
C



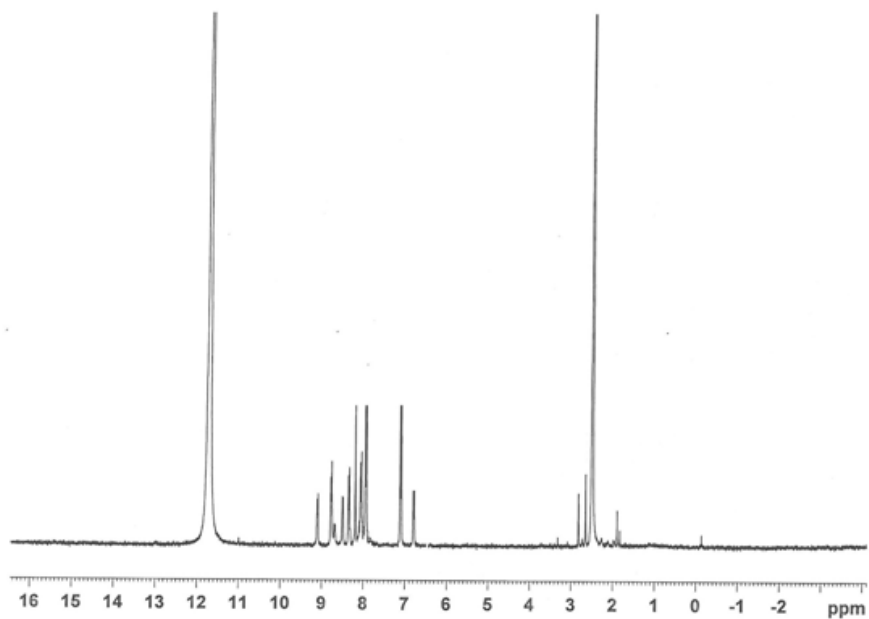
d)TMU-49S



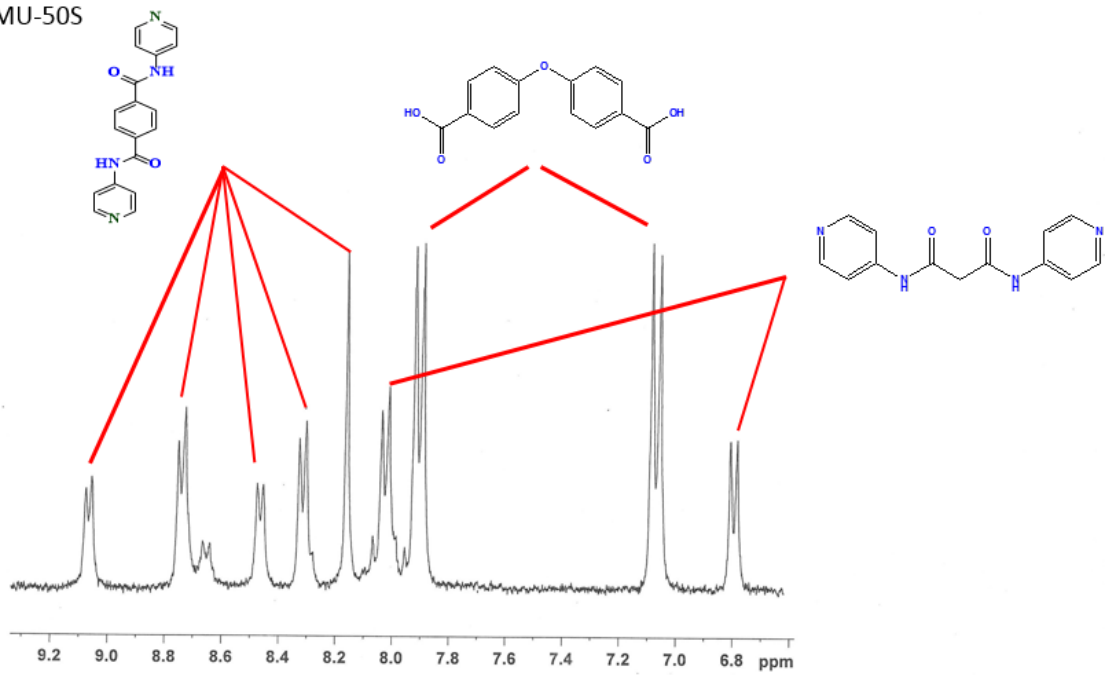
d')TMU-49S



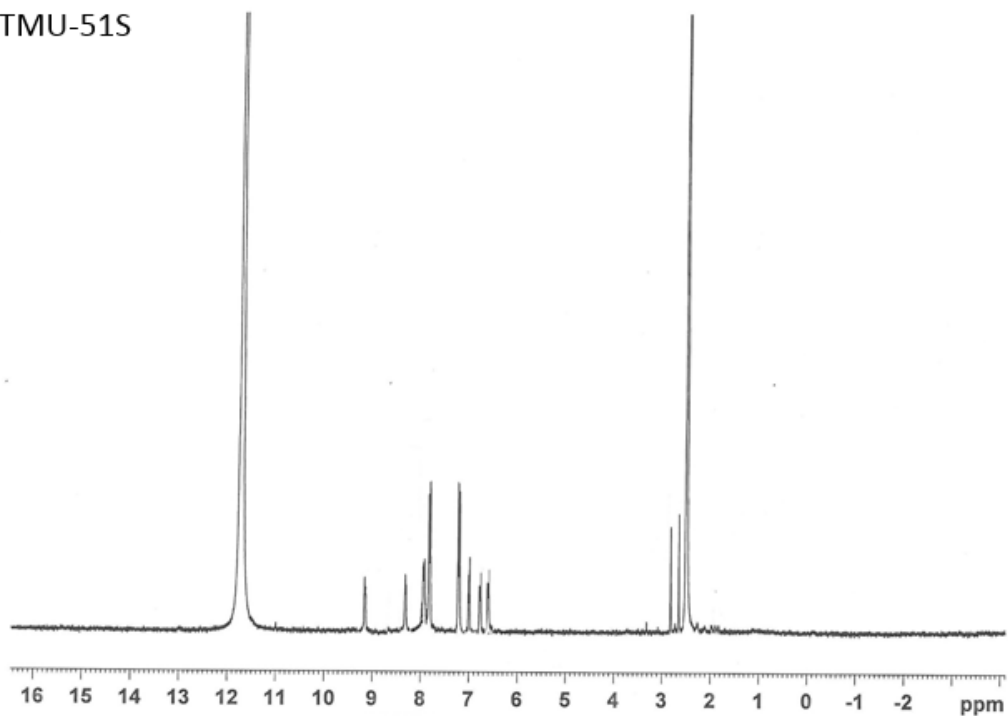
e)TMU-50S



e')TMU-50S



f)TMU-51S



f')TMU-51S

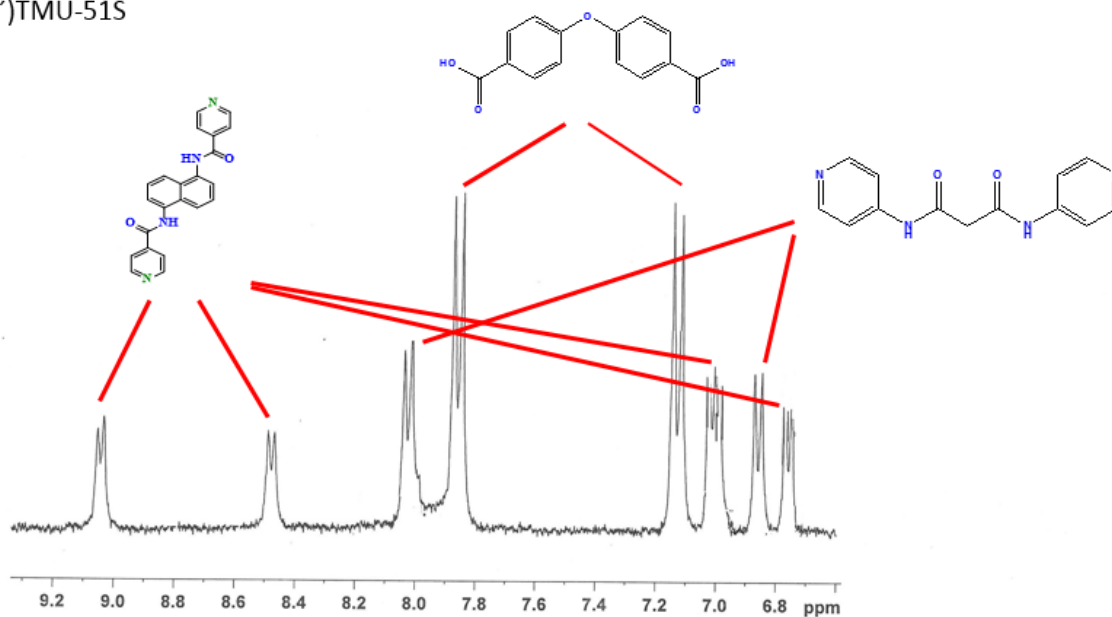


Fig. S4: NMR of compound TMU-49S, 50S and 51S (a: S ligand, b: bpta, c: bpfb d: NMR spectrum of TMU-49 d': expanded spectrum of TMU-49 e: NMR spectrum of TMU-50 e': expanded spectrum of TMU-50 f: NMR spectrum of TMU-51 f': expanded spectrum of TMU-51)



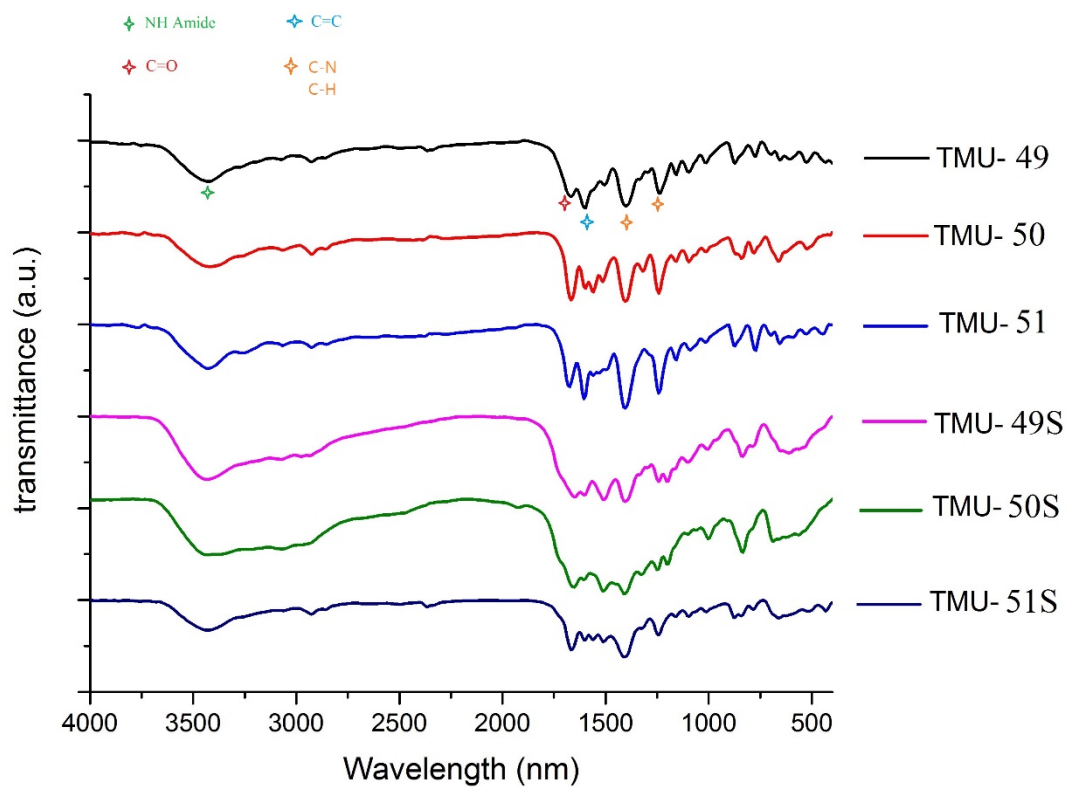


Fig. S5: IR spectroscopy of the TMU-49 (black), TMU-50 (red) and TMU-51 (blue), The IR spectroscopy of TMU-49S (pink), TMU-50S (green) and TMU-51S (dark blue).

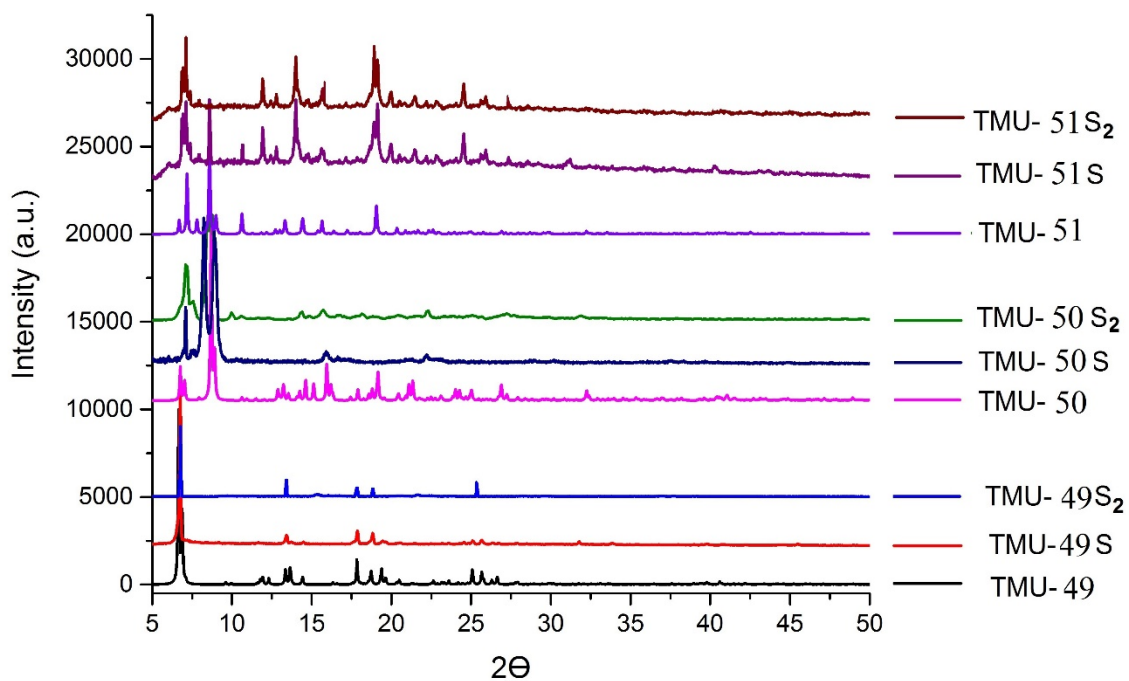
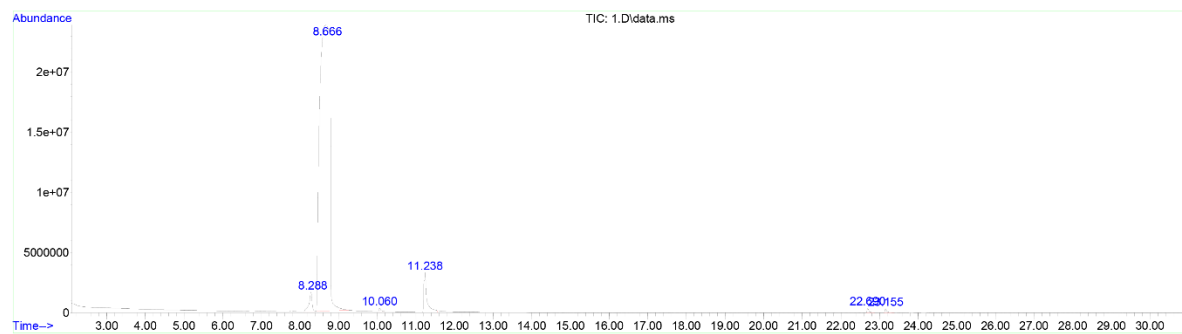


Fig.S6: PXRD patterns of simulated, daughter MOFs and recycled daughter MOFs of TMU-49, 50 and 51.

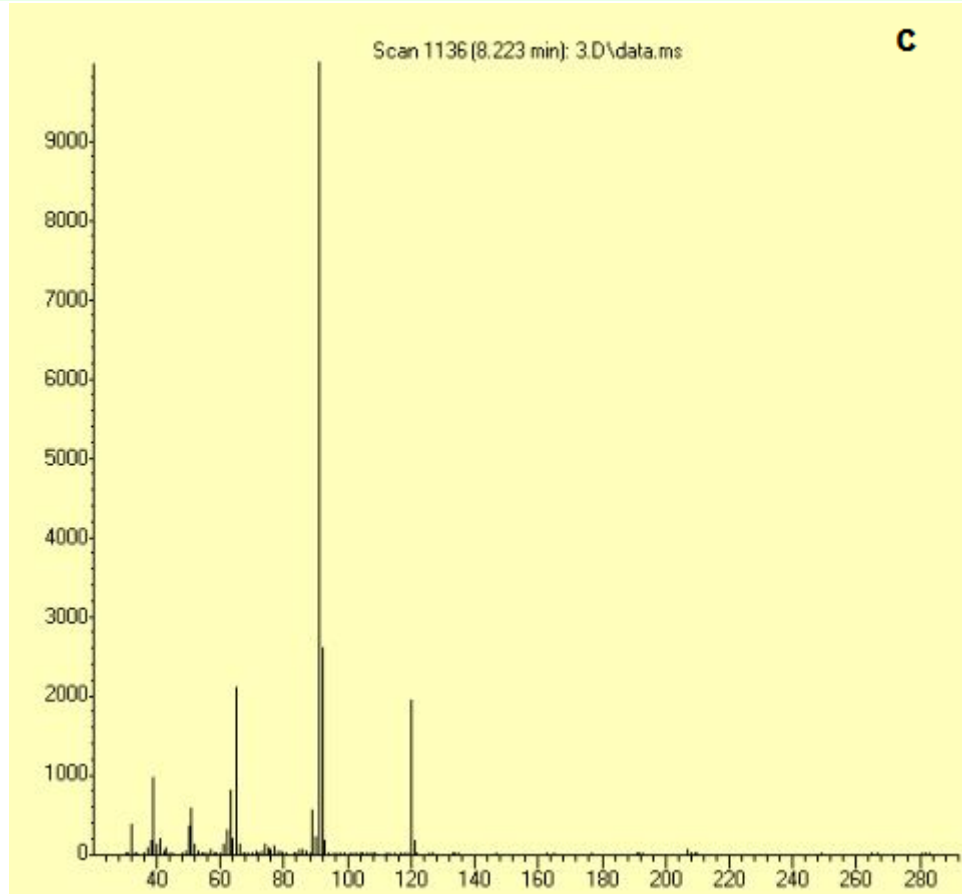
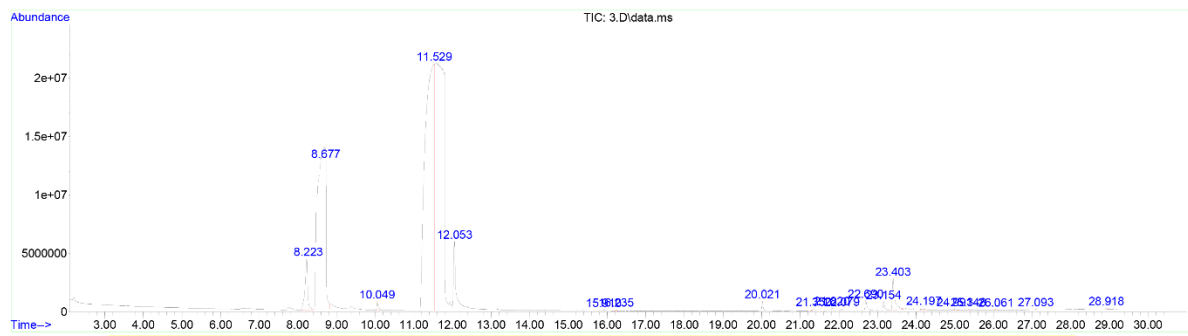
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Operator :  
Acquired : 21 May 2018 20:20 using AcqMethod 30time.M  
Instrument : Agilent Online  
Sample Name:  
Misc Info :  
Vial Number: 1

a



File :D:\Data file GC-MS\1397\Dr.esrafily\3.D  
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**b**



**C**

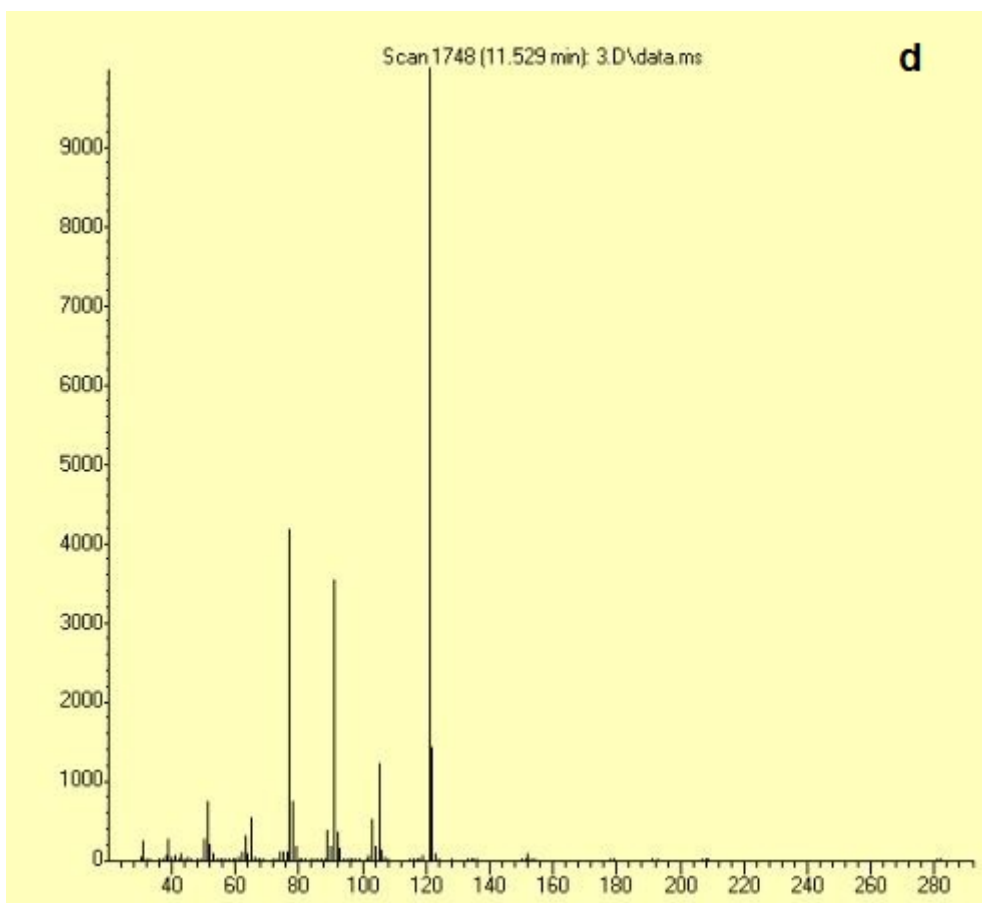


Fig. S7: GC-Mass chromatograms (a: for control reaction) and (b: catalyzed by TMU-50S) and mass analysis related to them (c: epoxy styrene and d: 2-Methoxy-2-phenylethanol)