

## Supporting Information

### **Metal–organic frameworks constructed from crown ether-based 1,4-benzenedicarboxylic acid derivatives**

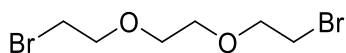
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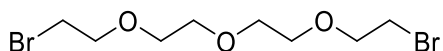
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## Syntheses of Starting Materials



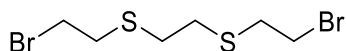
### 1,2-Bis(2-bromoethoxy)ethane

200 mL dichloromethane (DCM) was cooled to  $-78\text{ }^{\circ}\text{C}$  by using a mixture of  $\text{CO}_2$ /isopropanol. Under stirring, *N*-bromosuccinimid (NBS, 8.72 g, 49 mmol) and triphenylphosphine (12.84 g, 49 mmol) were added. After 10 min, triethyleneglycol (3.30 g, 22 mmol) was added and the solution was stirred overnight and the temperature was slowly increased to room temperature. The DCM was removed in vacuo and the product was taken up on silica gel. The product was then purified by flash chromatography over a short column with 1.3 L of hexane/ethyl acetate (4 : 1). After removal of the solvents in vacuo, the product was isolated as a colorless oil and dried in vacuum overnight. Yield: 5.20 g (86 %).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.83 (t, 4H,  $J = 6.2$  Hz), 3.69 (s, 4H), 3.48 (t, 4H,  $J = 6.2$  Hz). ESI-MS(+):  $m/z = 293.88$   $[\text{M} + \text{NH}_4]^+$ , 298.94  $[\text{M} + \text{Na}]^+$ .



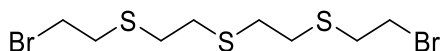
### 1-Bromo-2-[2-[2-(2-bromoethoxy)ethoxy]ethoxy]ethane

200 mL DCM was cooled to  $-78\text{ }^{\circ}\text{C}$  by using a mixture of  $\text{CO}_2$ /isopropanol. Under stirring NBS (8.72 g, 49 mmol) and triphenylphosphine (12.84 g, 49 mmol) were added. After 10 min, triethyleneglycol (4.27 g, 22 mmol) was added and the solution was stirred overnight and the temperature was slowly increased to room temperature. The DCM was removed in vacuo and the product was taken up on silica gel. The product was then purified by flash chromatography over a short column with 1.3 L of hexane/ethyl acetate (4 : 1). After removal of the solvents in vacuo the product was isolated as a colorless oil and dried in vacuum overnight. Yield: 6.37 g (91 %).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.82 (t, 4H,  $J = 6.3$  Hz), 3.68 (s, 8H), 3.48 (t, 4H,  $J = 6.3$  Hz). ESI-MS(+):  $m/z = 320.86$   $[\text{M} + \text{NH}_4]^+$ , 337.90  $[\text{M} + \text{NH}_4]^+$ , 342.91  $[\text{M} + \text{Na}]^+$ .



### **1,2-Bis(2-bromoethylthio)ethane**

3,6-Dithia-1,8-octanediol (4.00 g, 22 mmol) was dissolved in 50 mL DCM and the solution was cooled to 0 °C in an ice bath under nitrogen. Under stirring phosphorous tribromide (4.5 mL, 48 mmol) was added dropwise using a syringe over the course of 10 min. The reaction was maintained at 0 °C for 2 h and then allowed to come to room temperature overnight. The reaction was quenched by adding 10 mL H<sub>2</sub>O at 0 °C, and then neutralized by adding saturated NaHCO<sub>3</sub> solution. The mixture was filtered and the organic phase was collected and dried by rotavap to yield white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.49 (t, 4H, *J* = 8 Hz), 2.98 (t, 4H, *J* = 8 Hz), 2.79 (S, 4H). ESI-MS(+): *m/z* = 226.89 [M + H – HBr]<sup>+</sup>, 198.89 [M + H – HBr – C<sub>2</sub>H<sub>4</sub>]<sup>+</sup>, 168.95 [M + H – HBr – SC<sub>2</sub>H<sub>4</sub>]<sup>+</sup>.<sup>2,3</sup>



### **1-Bromo-2-[2-[2-(2-bromoethylthio)ethylthio]ethylthio]ethane**

1,2-Bis(2-hydroxyethylthio)ethane<sup>1</sup> (1.98 g, 8.2 mmol) was dissolved in 25 mL DCM and the solution was cooled to 0 °C in an ice bath under nitrogen. Under stirring phosphorous tribromide (1.7 mL, 18 mmol) was added dropwise using a syringe over the course of 10 min. The reaction was maintained at 0 °C for 2 h and then allowed to come to room temperature overnight. The reaction was quenched by adding 10 mL H<sub>2</sub>O at 0 °C, and then neutralized by adding saturated NaHCO<sub>3</sub> solution. The mixture was filtered and the organic phase was collected and dried by rotavap to yield white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.49 (t, 4H, *J* = 8 Hz), 2.99 (t, 4H, *J* = 8 Hz), 2.79 (S, 8H). ESI-MS(+): *m/z* = 312.87 [M + Na – HBr]<sup>+</sup>, 279.09 [M + NH<sub>4</sub> – HBr – C<sub>2</sub>H<sub>4</sub>]<sup>+</sup>, 118.98 [M + H – 2HBr – C<sub>2</sub>H<sub>4</sub> – SC<sub>2</sub>H<sub>4</sub>]<sup>+</sup>.<sup>2,3</sup>

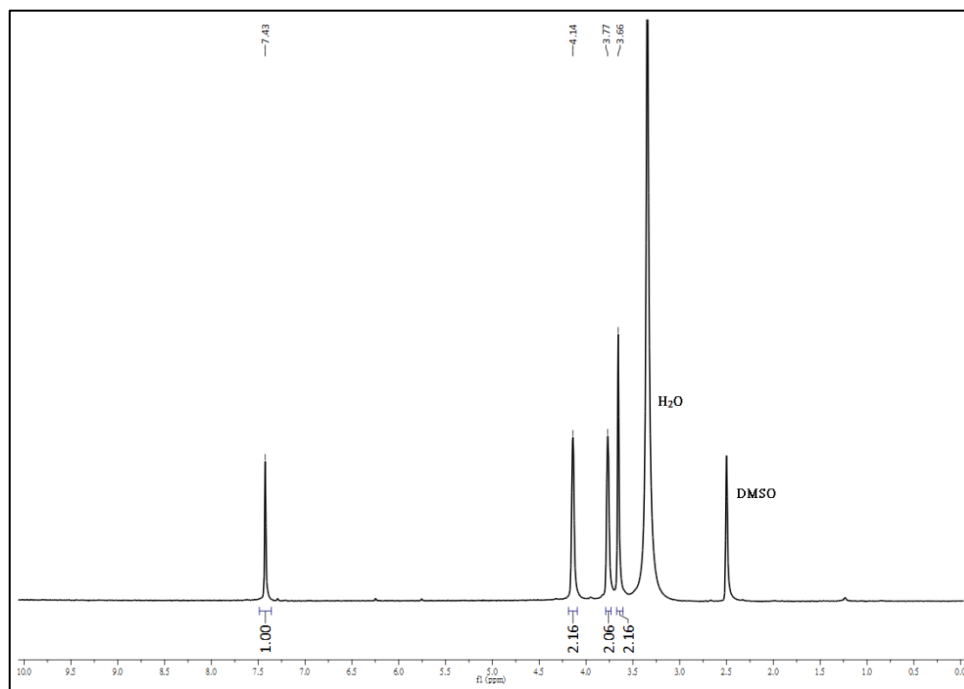


Figure S1.  $^1\text{H}$  NMR spectrum of L1.

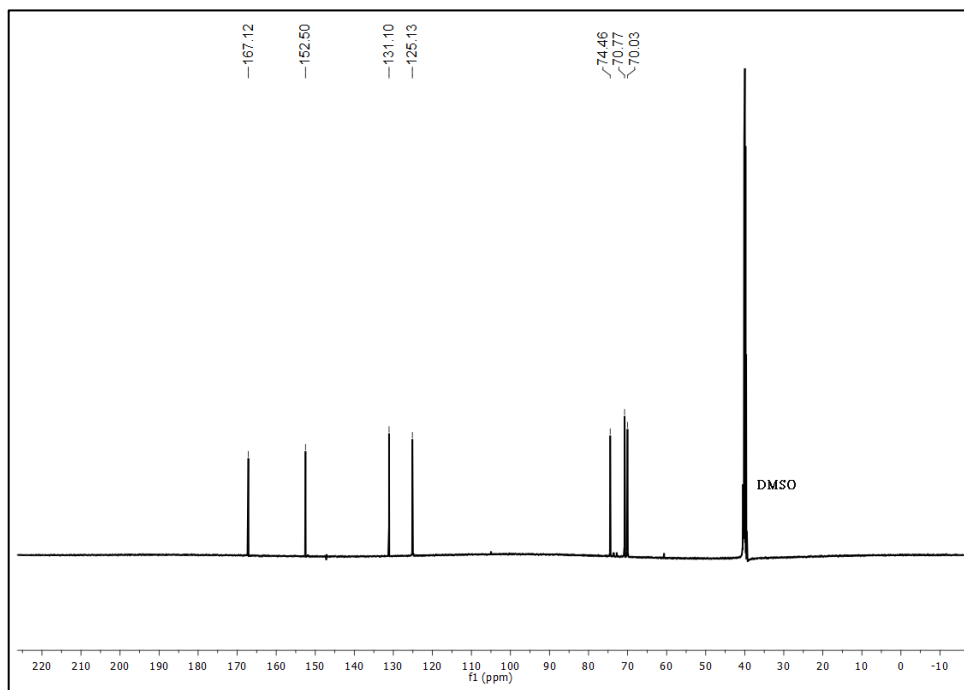
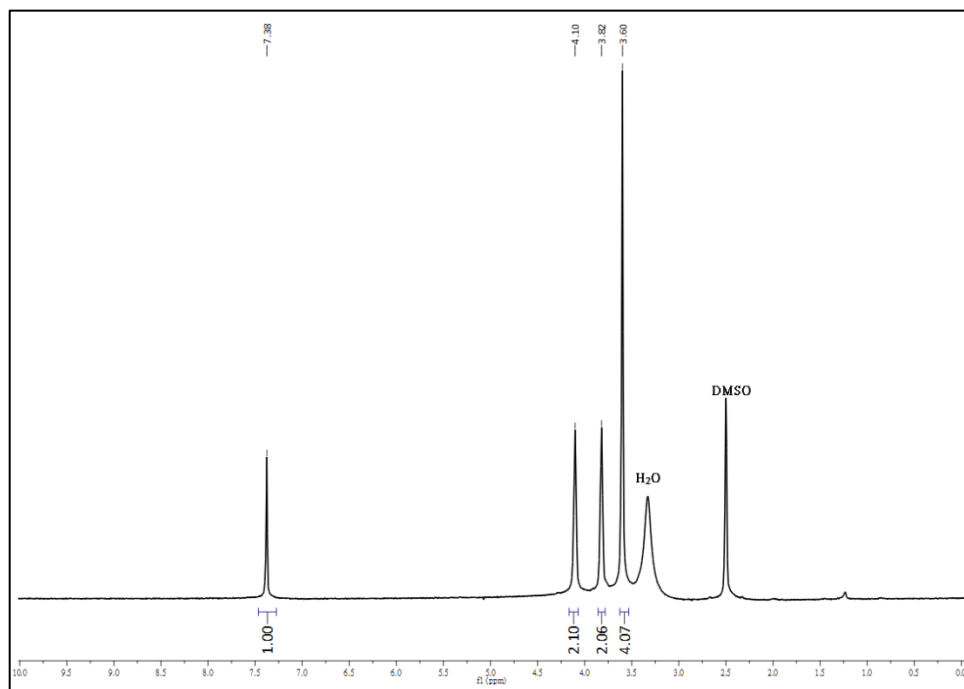
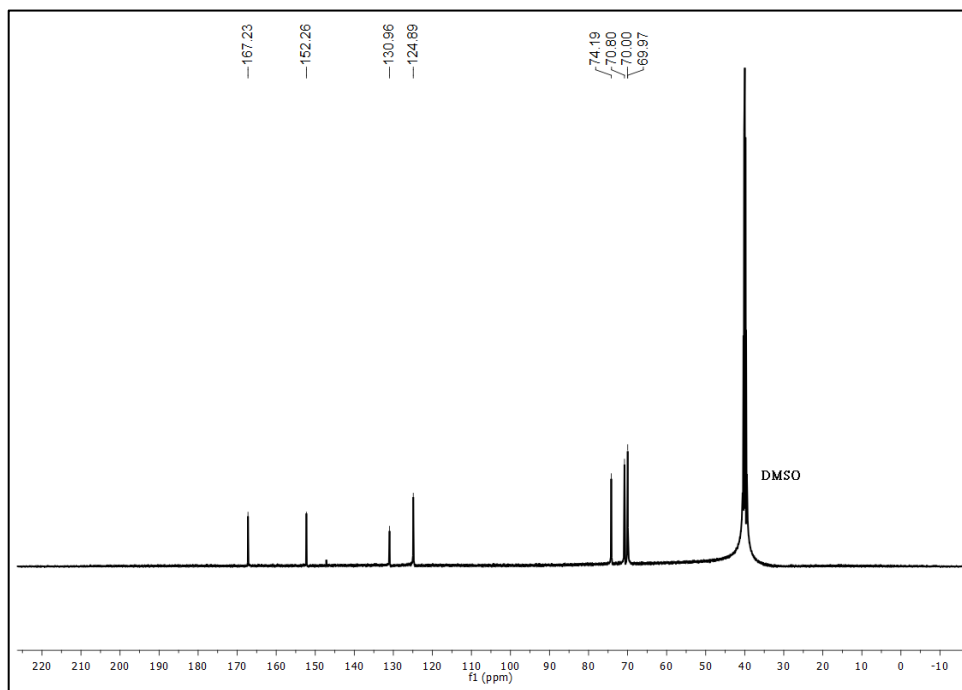


Figure S2.  $^{13}\text{C}$  NMR spectrum of L1.



**Figure S3.**  $^1\text{H}$  NMR spectrum of L2.



**Figure S4.**  $^{13}\text{C}$  NMR spectrum of L2.

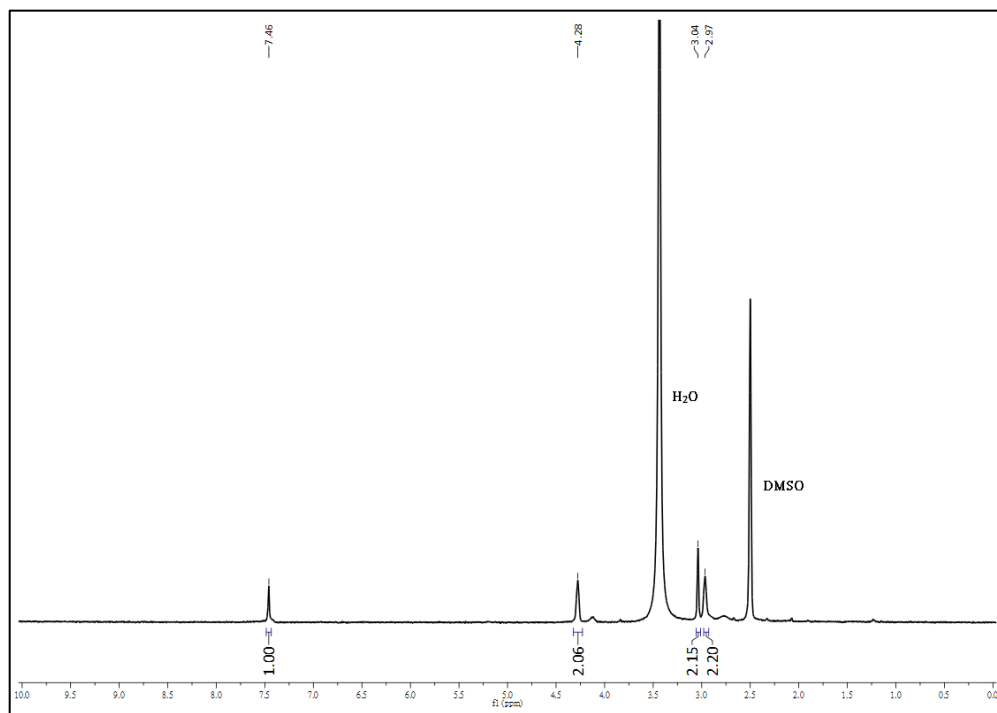


Figure S5.  $^1\text{H}$  NMR spectrum of L3.

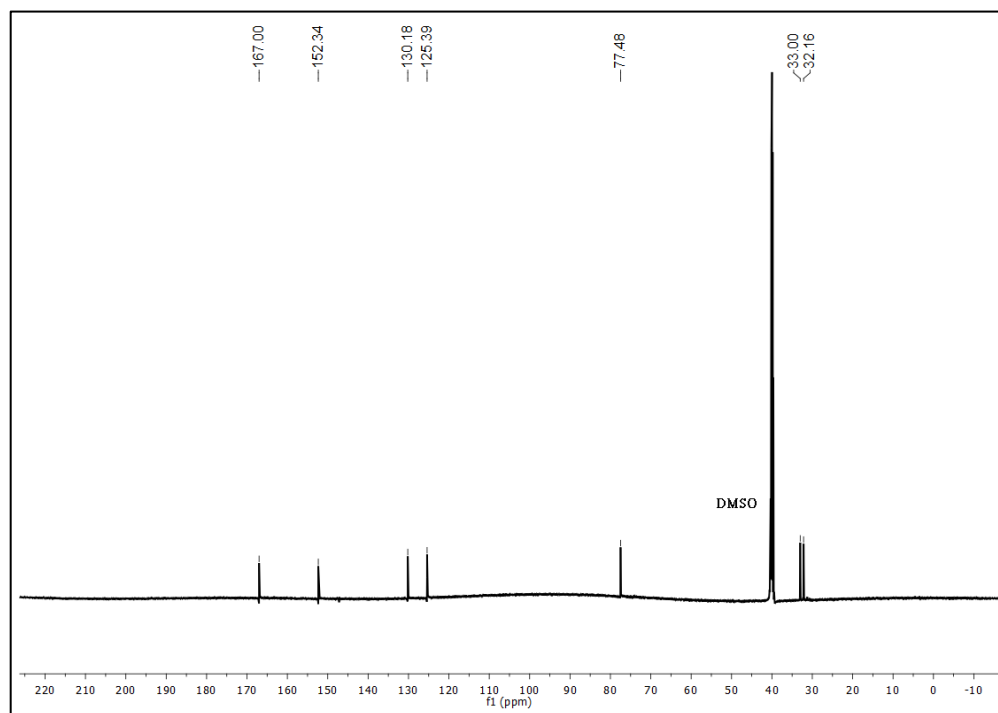
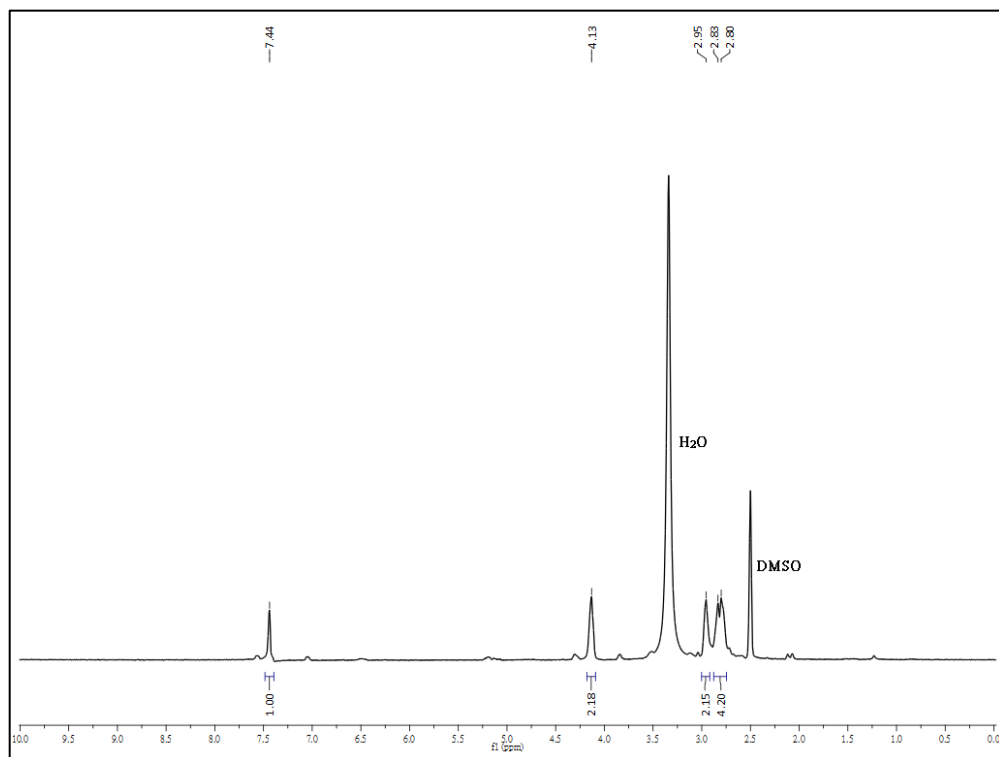
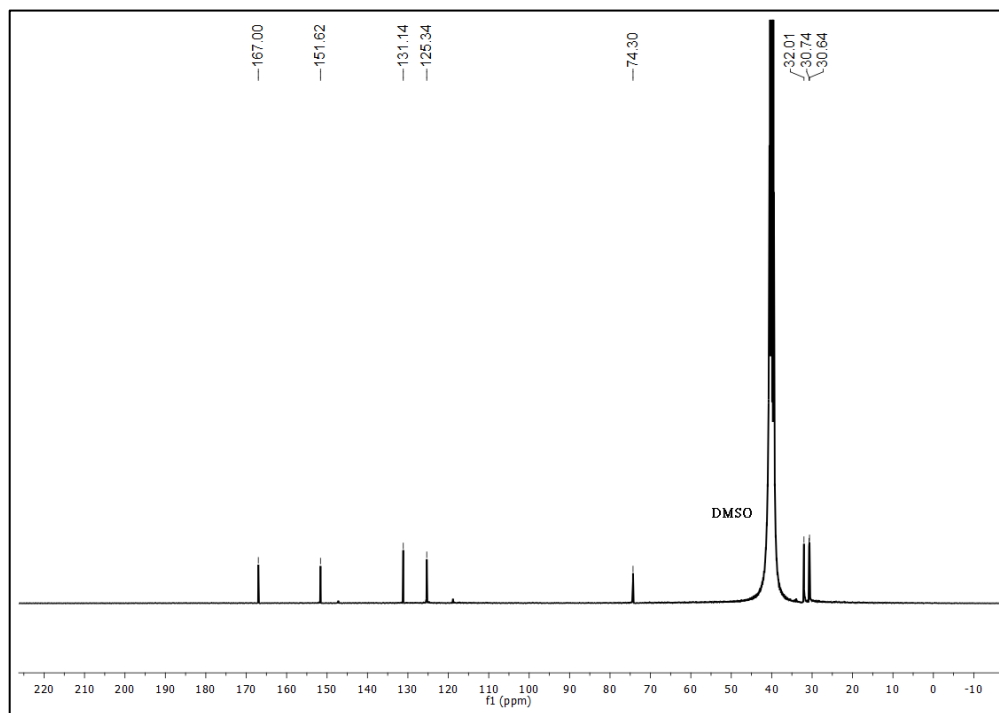


Figure S6.  $^{13}\text{C}$  NMR spectrum of L3.



**Figure S7.** <sup>1</sup>H NMR spectrum of **L4**.



**Figure S8.** <sup>13</sup>C NMR spectrum of **L4**.

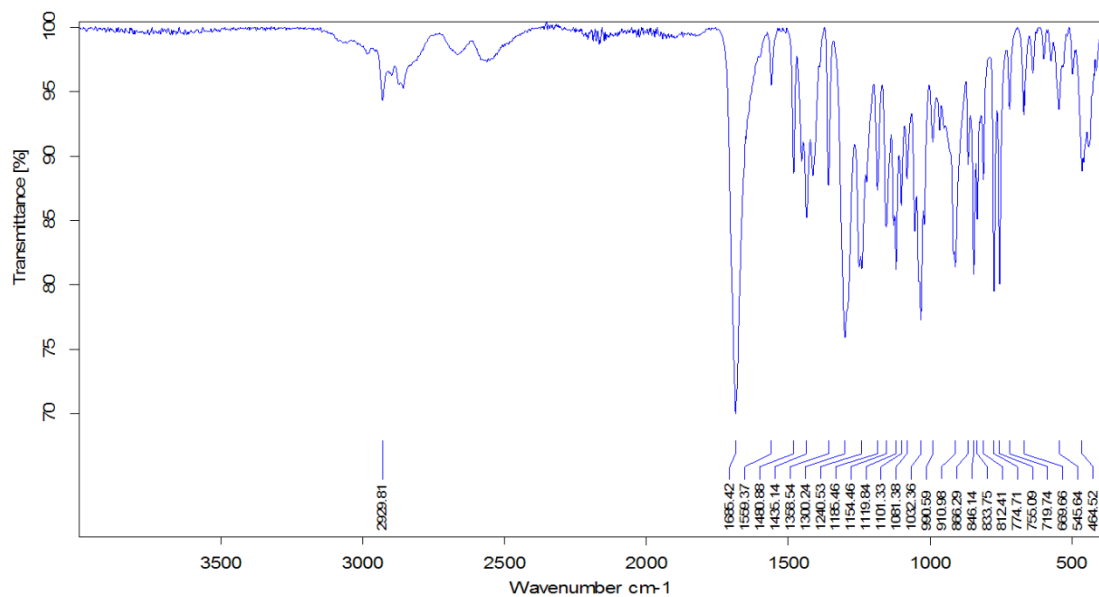


Figure S9. FTIR spectrum of L1.

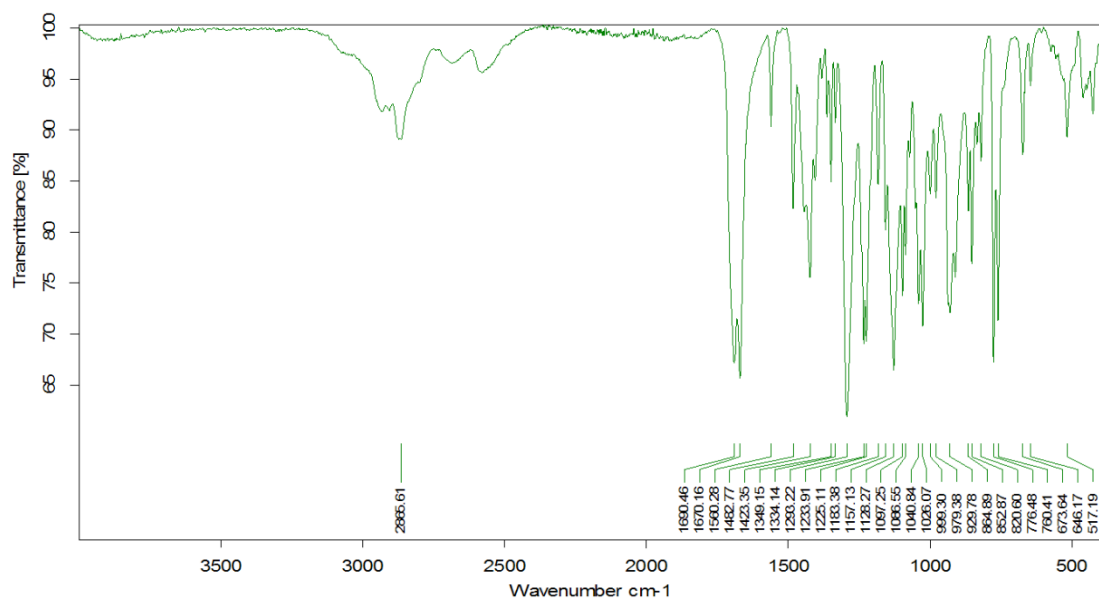
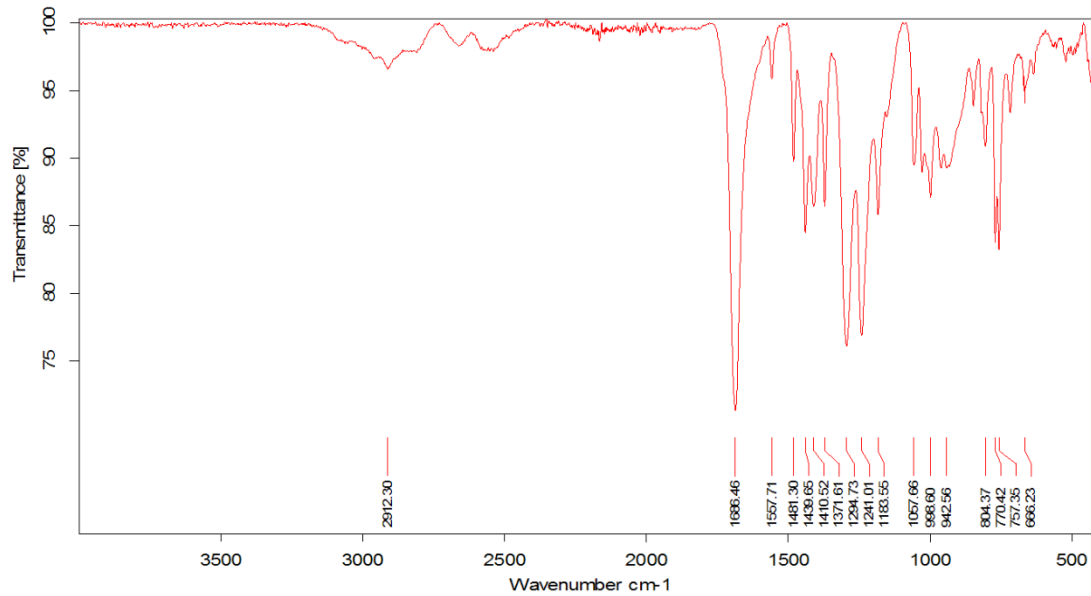
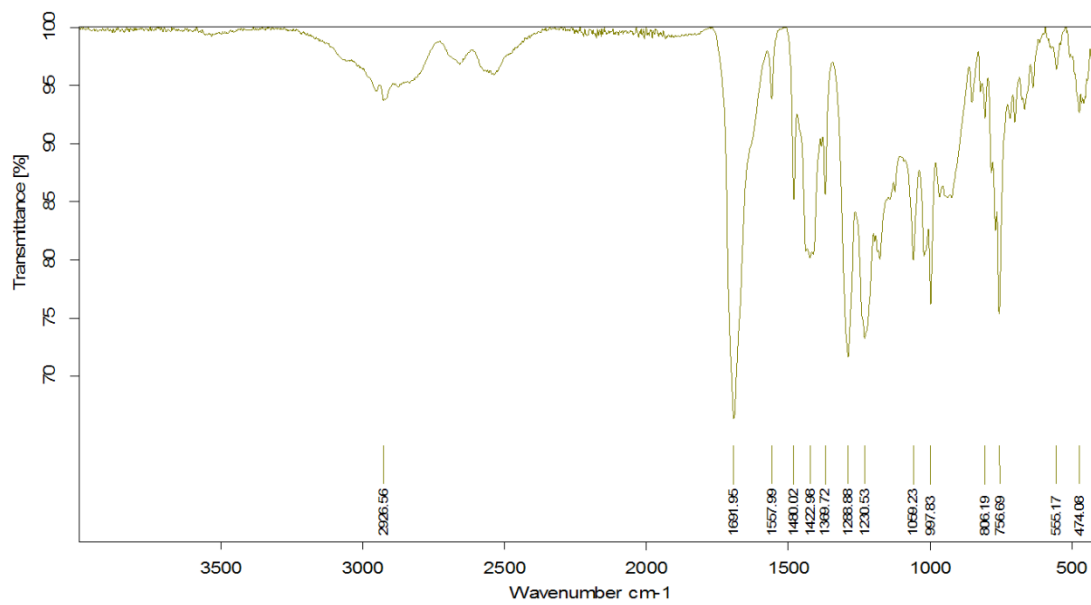


Figure S10. FTIR spectrum of L2.

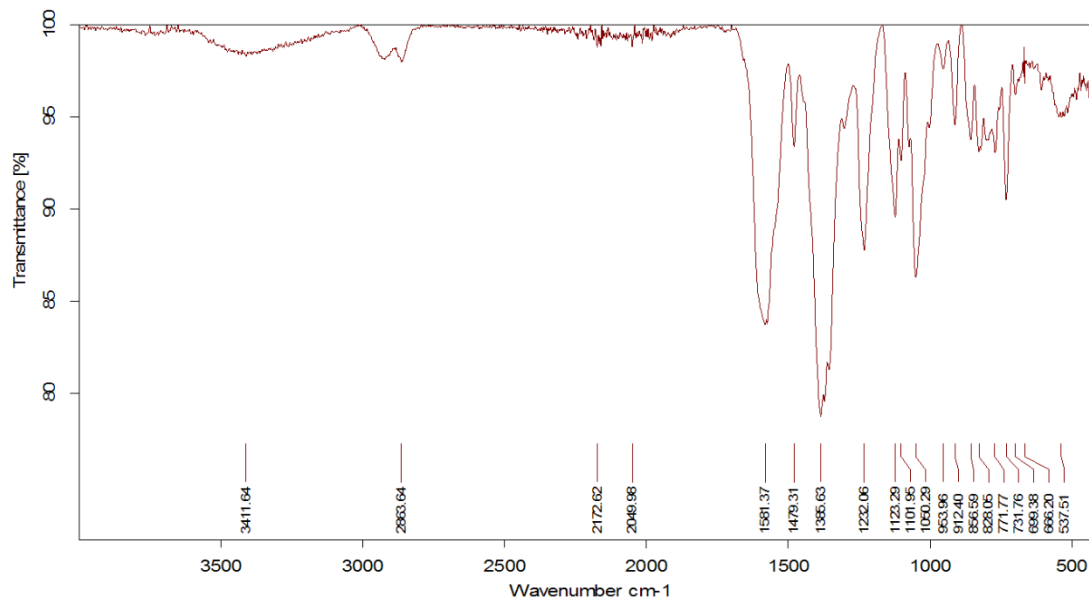




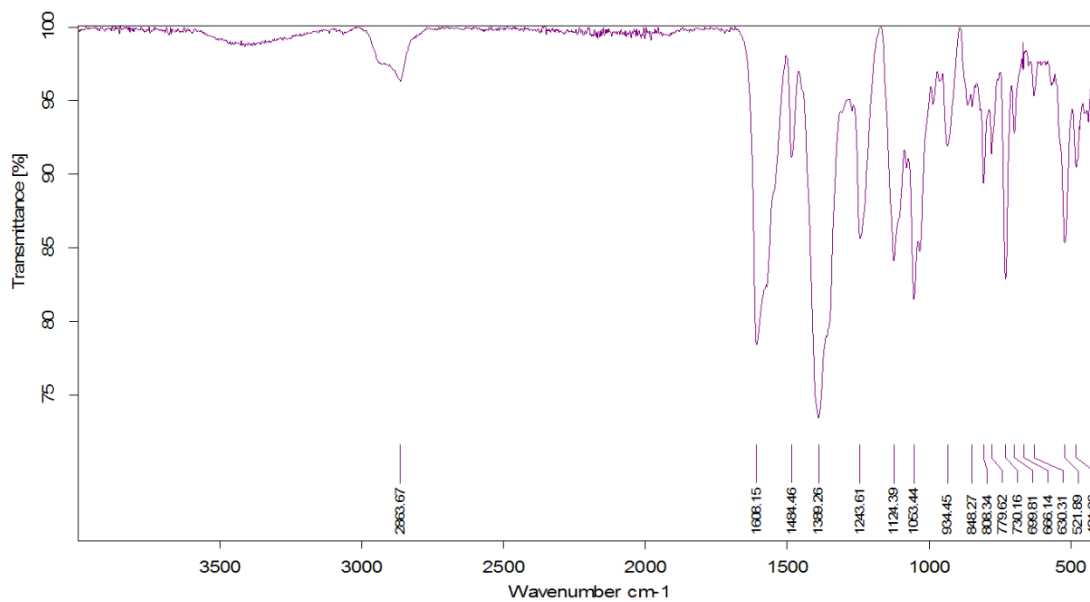
**Figure S11.** FTIR spectrum of L3.



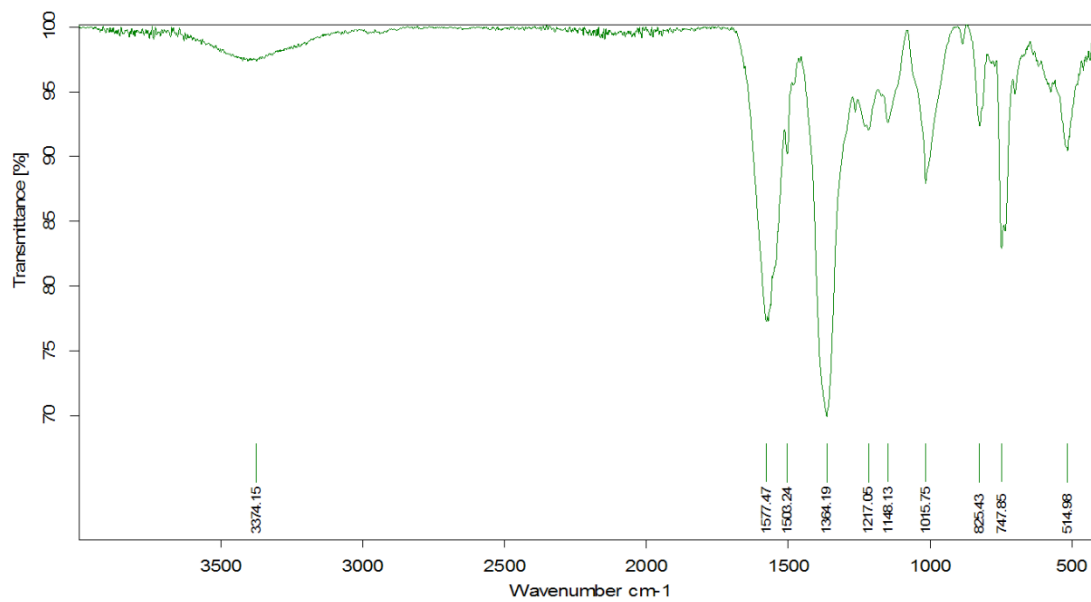
**Figure S12.** FTIR spectrum of L4.



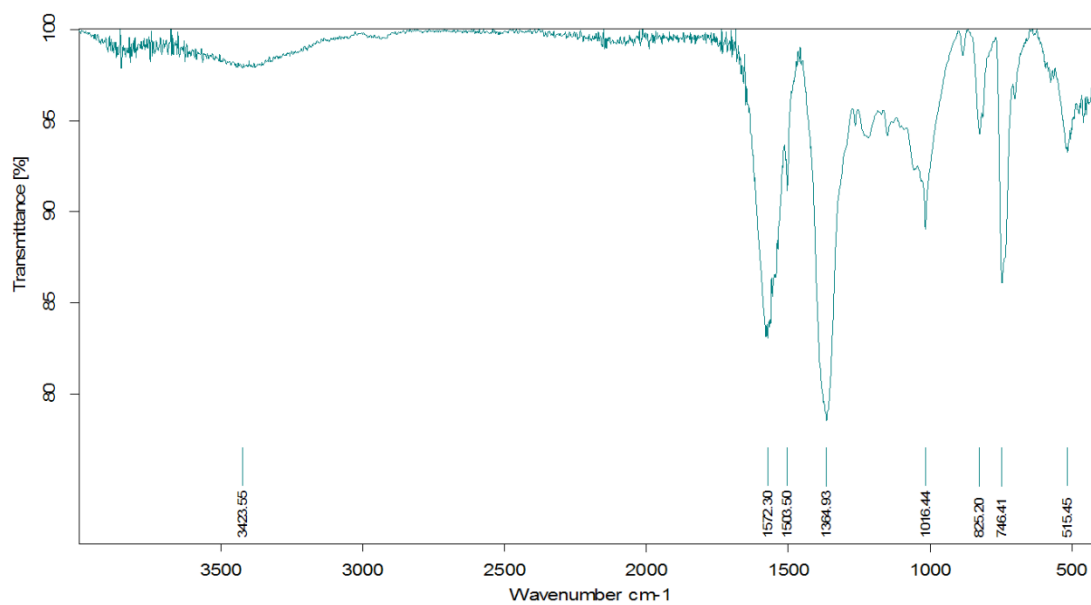
**Figure S13.** FTIR spectrum of IRMOF-1-L1.



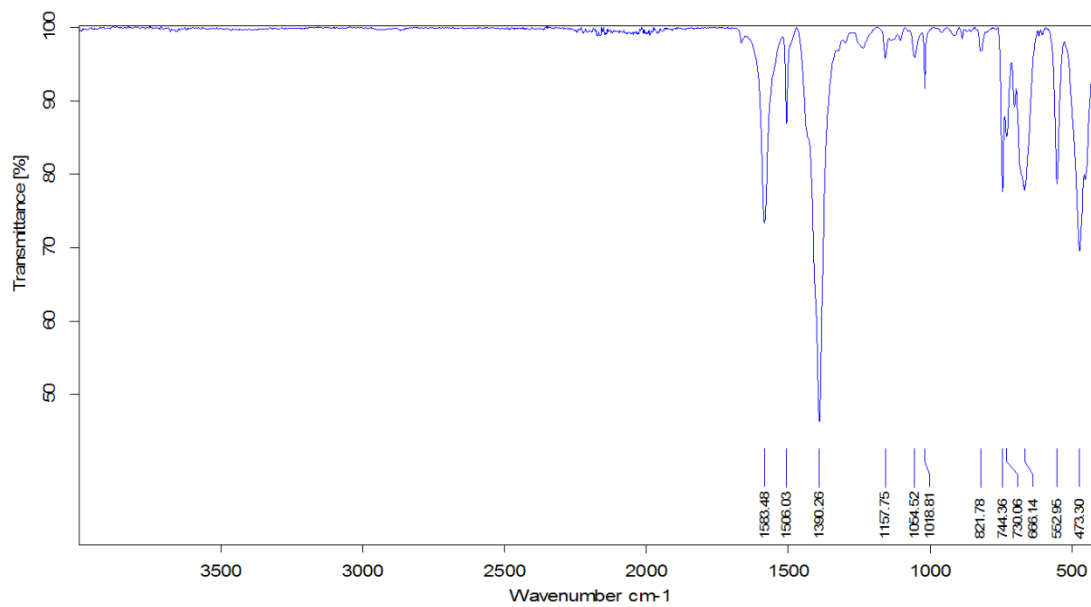
**Figure S14.** FTIR spectrum of IRMOF-1-L2.



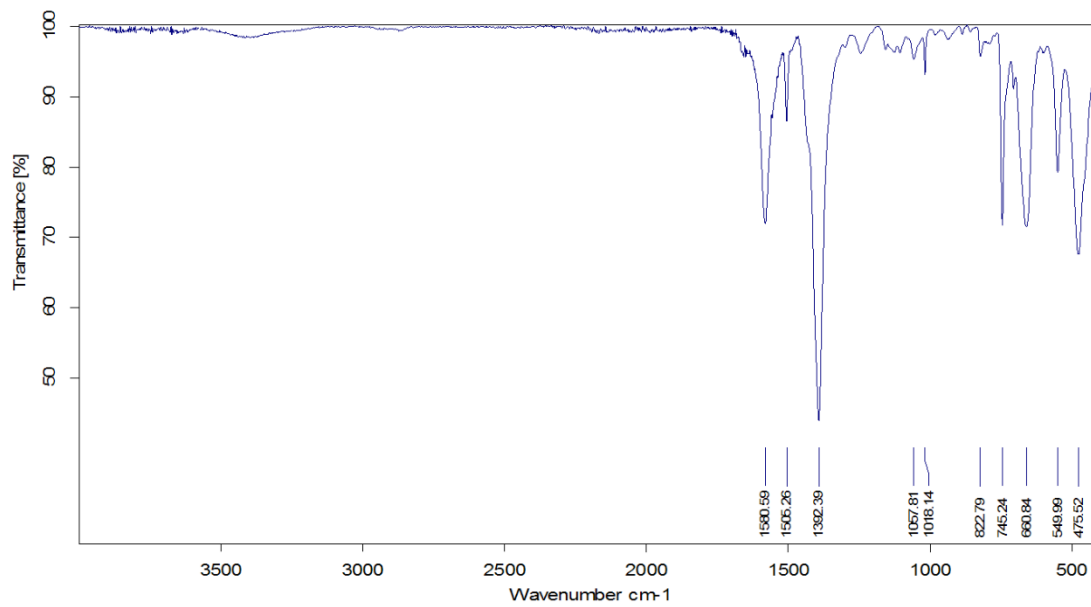
**Figure S15.** FTIR spectrum of IRMOF-1-L3.



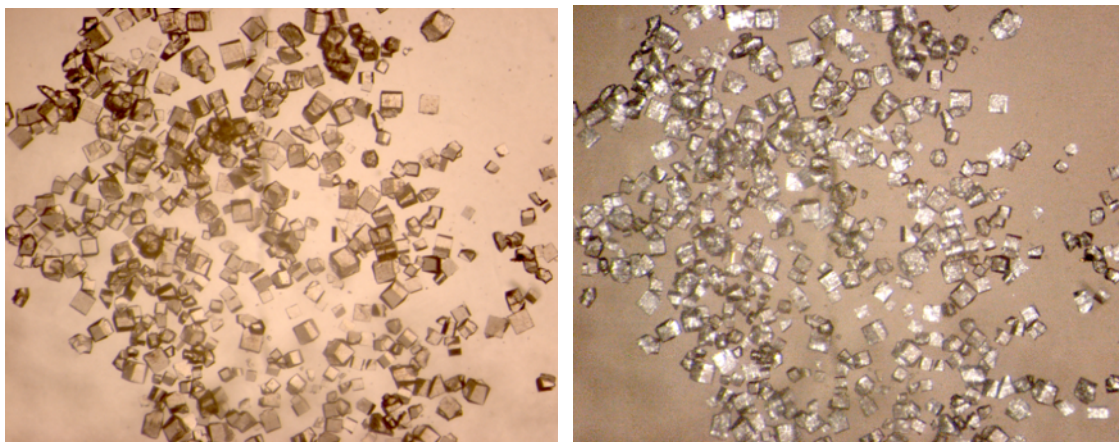
**Figure S16.** FTIR spectrum of IRMOF-1-L4.



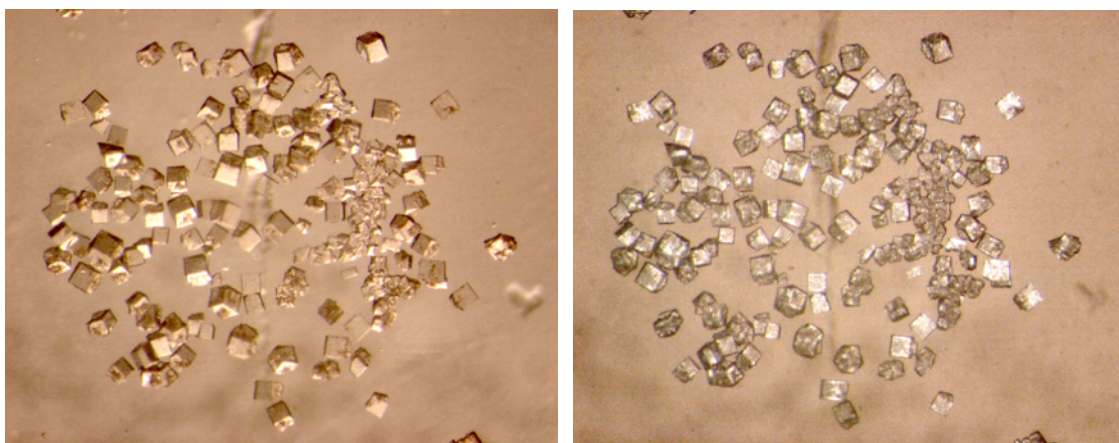
**Figure S17.** FTIR spectrum of UiO-66-L1<sub>0.33</sub>.



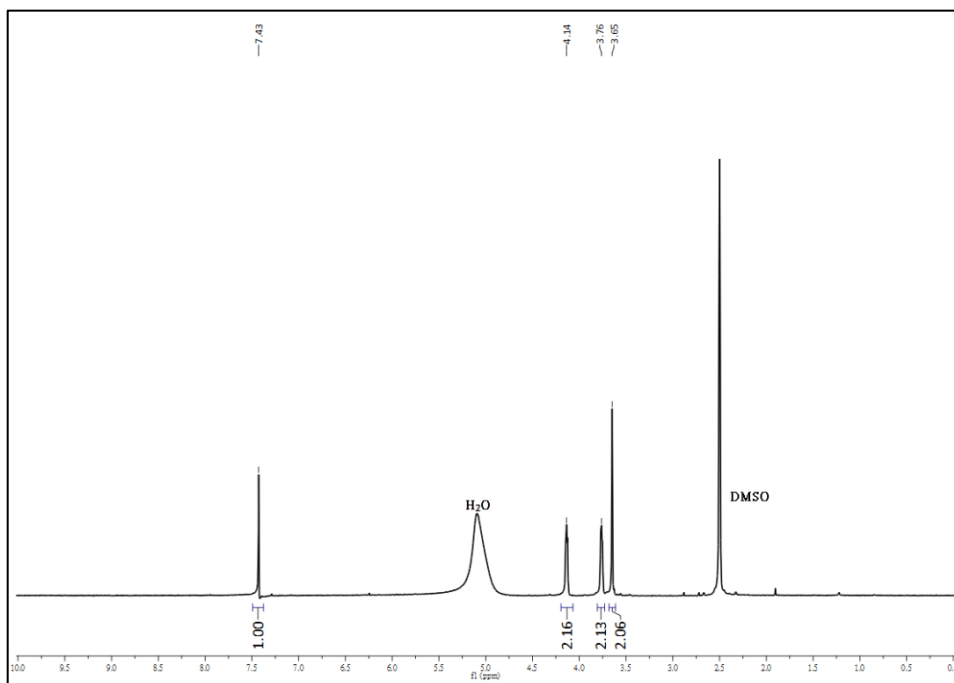
**Figure S18.** FTIR spectrum of UiO-66-L2<sub>0.25</sub>.



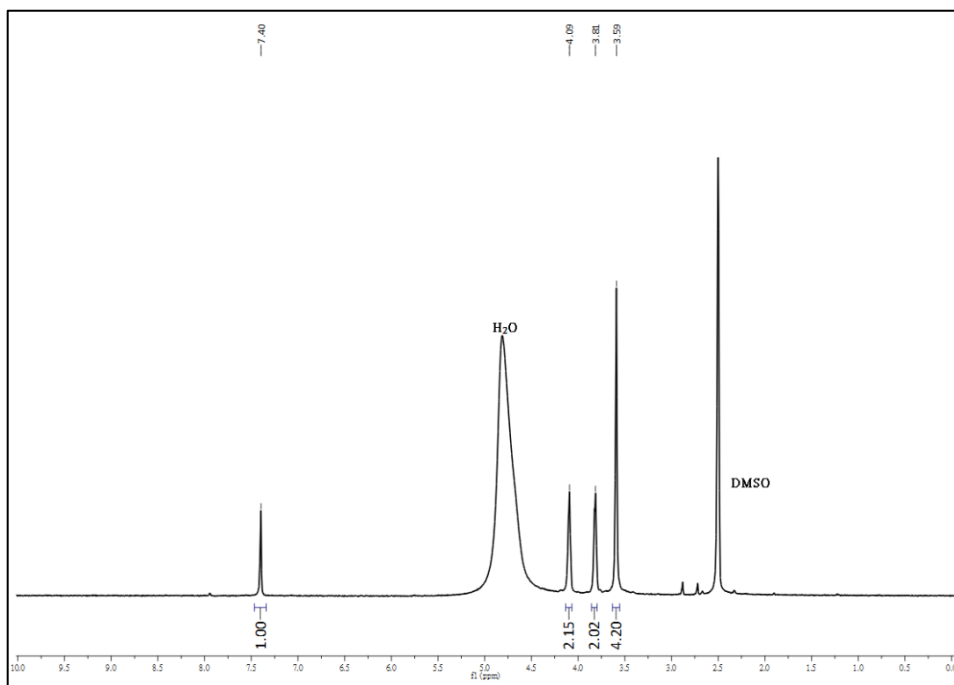
**Figure S19.** Pictures of the crystals of IRMOF-1-L1 under normal light (left) and polarized light (right).



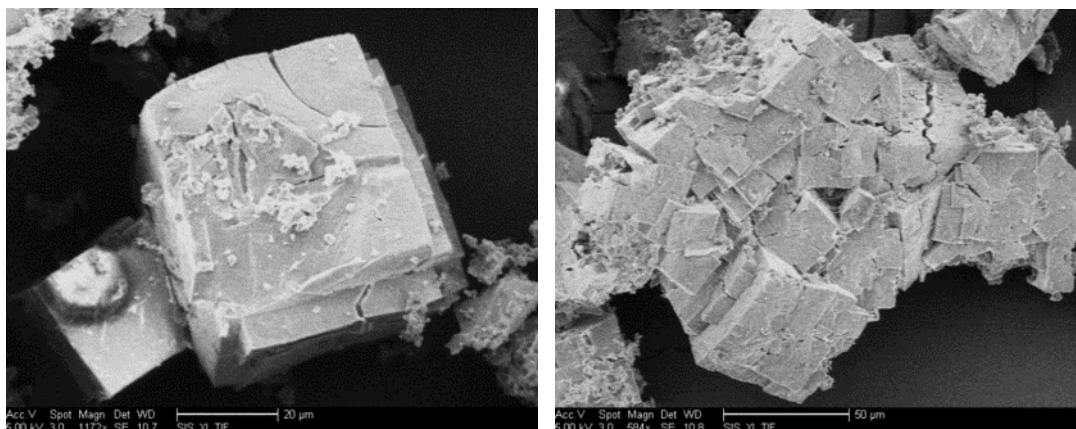
**Figure S20.** Pictures of the crystals of IRMOF-1-L2 under normal light (left) and polarized light (right).



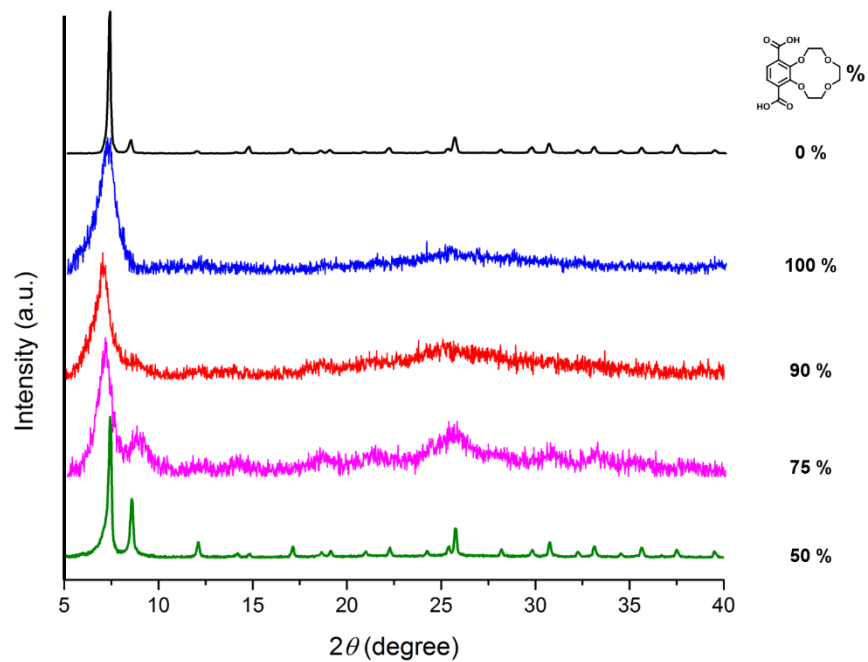
**Figure S21.**  $^1\text{H}$  NMR spectrum of digested IRMOF-1-L1.



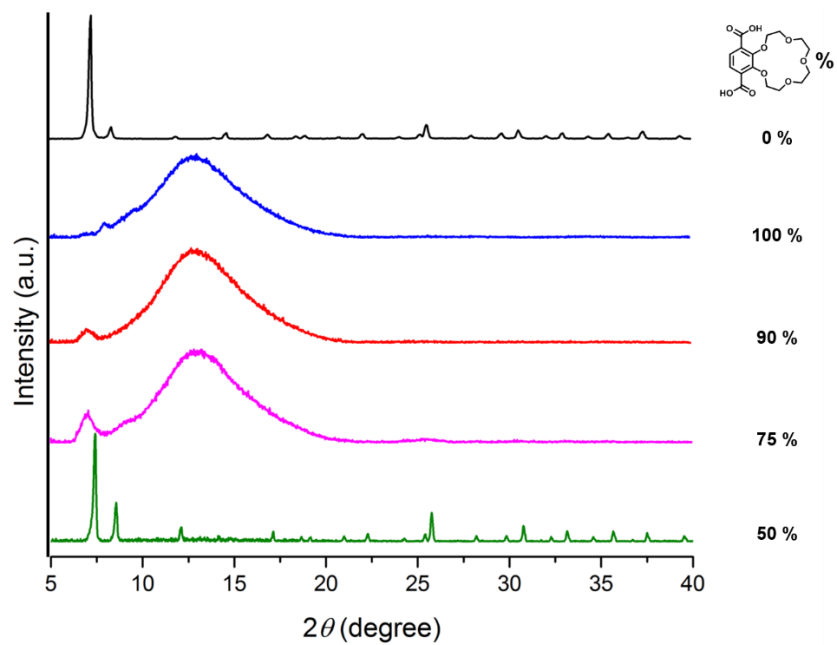
**Figure S22.**  $^1\text{H}$  NMR spectrum of digested IRMOF-1-L2.



**Figure S23.** SEM images of the crystals of IRMOF-1-L3 (left) and IRMOF-1-L4 (right).

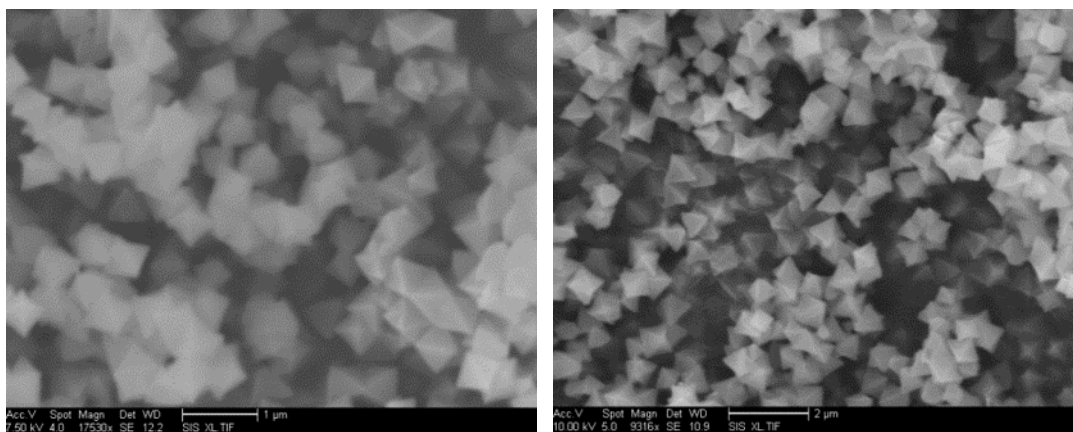


**Figure S24.** PXRD patterns of Zr-based MOFs synthesized from different amounts of **L1** (**L1** + bdc = 100%).

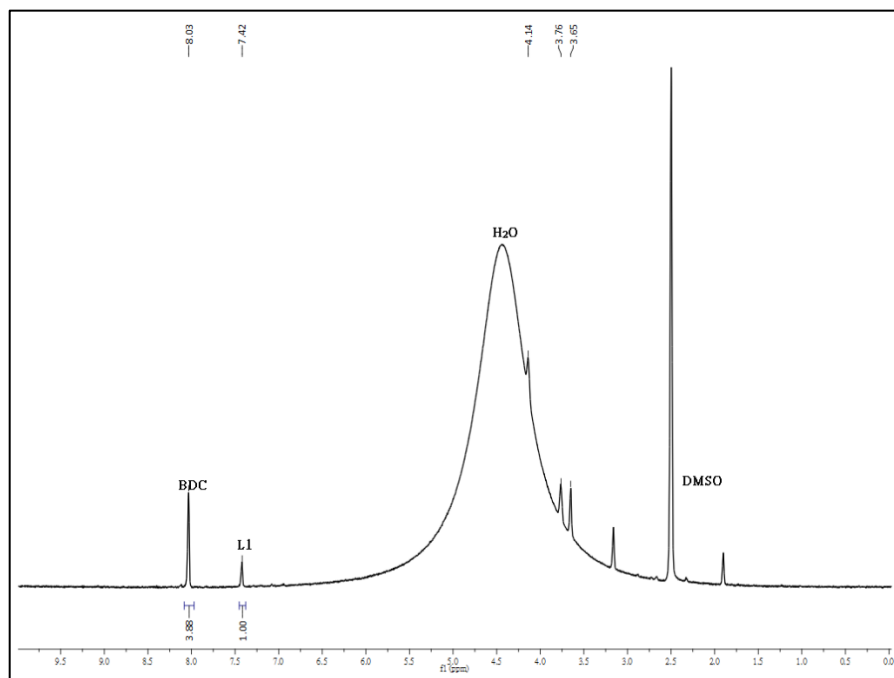


**Figure S25.** PXRD patterns of Zr-based MOFs synthesized from different amounts of **L2** (**L2** + bdc = 100%).

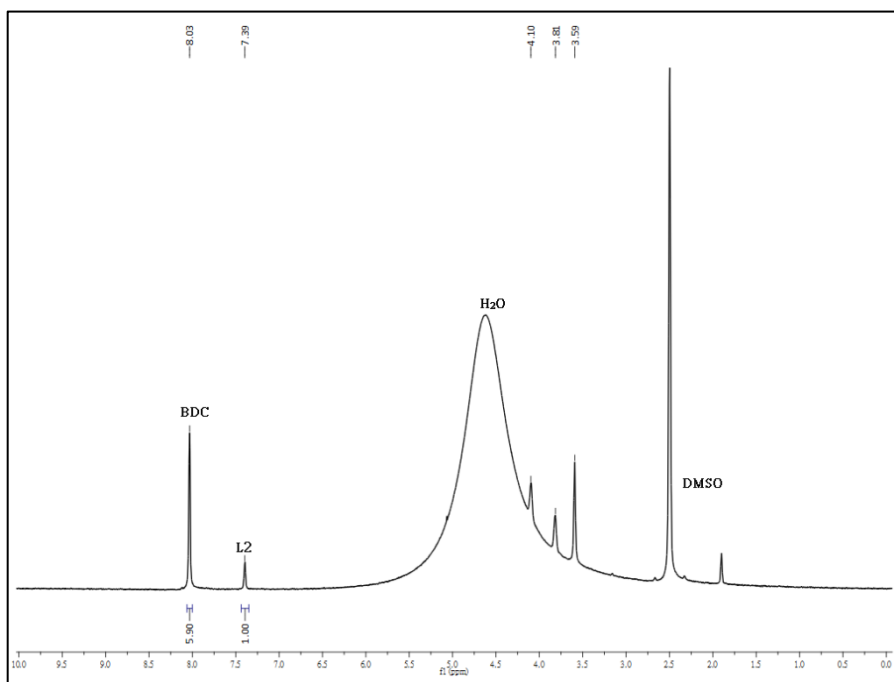




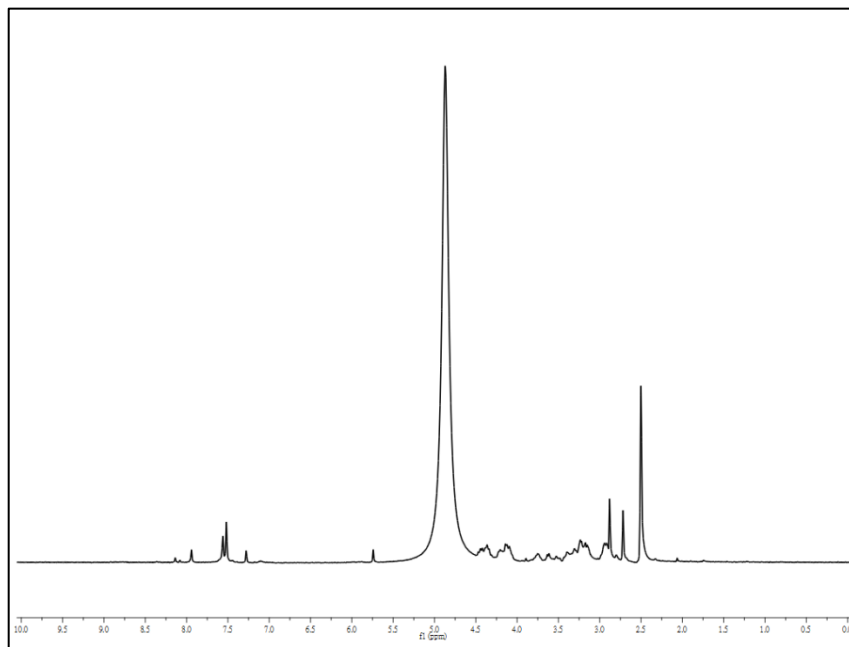
**Figure S26.** SEM images of the crystals of UiO-66-L1<sub>0.33</sub> (left) and UiO-66-L2<sub>0.25</sub> (right).



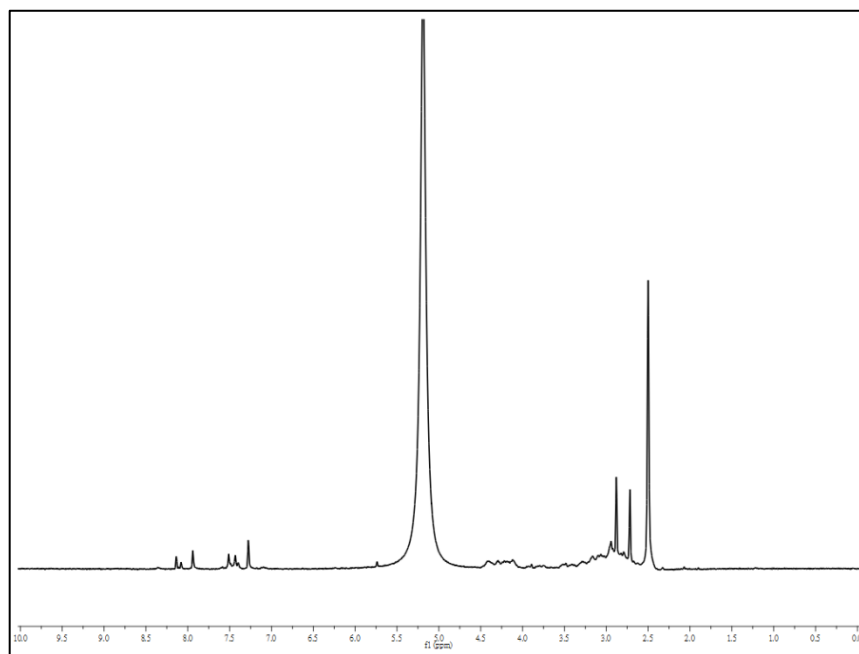
**Figure S27.**  $^1\text{H}$  NMR spectrum of digested UiO-66-L1<sub>0.33</sub>.



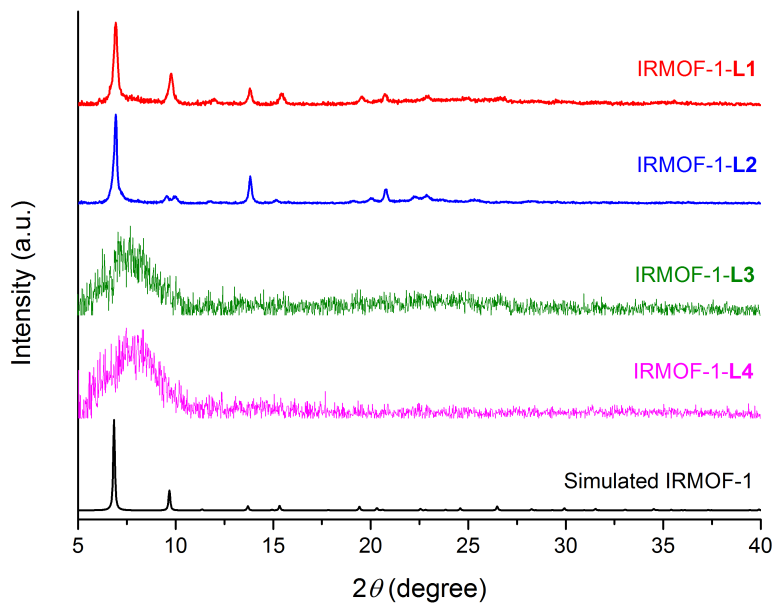
**Figure S28.**  $^1\text{H}$  NMR spectrum of digested UiO-66-L2<sub>0.25</sub>.



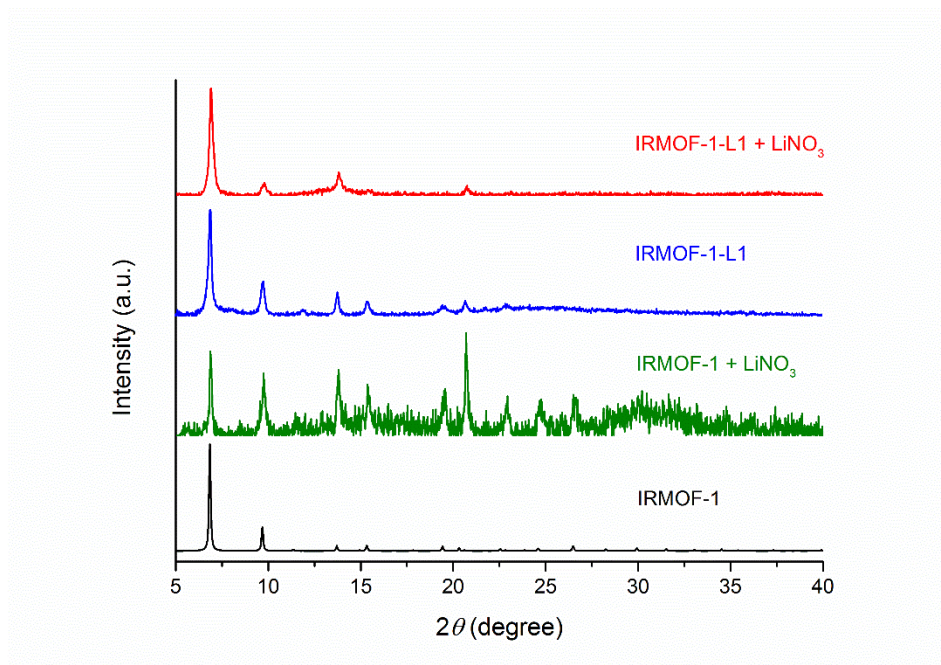
**Figure S29.**  $^1\text{H}$  NMR spectrum of digested IRMOF-1-L3. Broad and shifted peaks indicate possible coordination of the thiocrown ether to Zn ions.



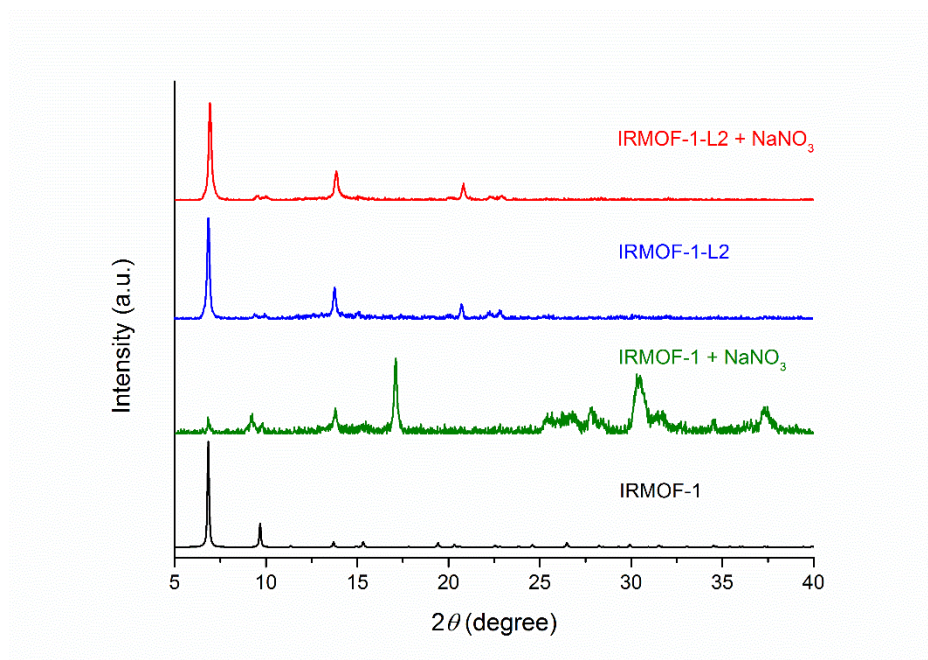
**Figure S30.**  $^1\text{H}$  NMR spectrum of digested IRMOF-1-L4. Broad and shifted peaks indicate possible coordination of the thiocrown ether to Zn ions.



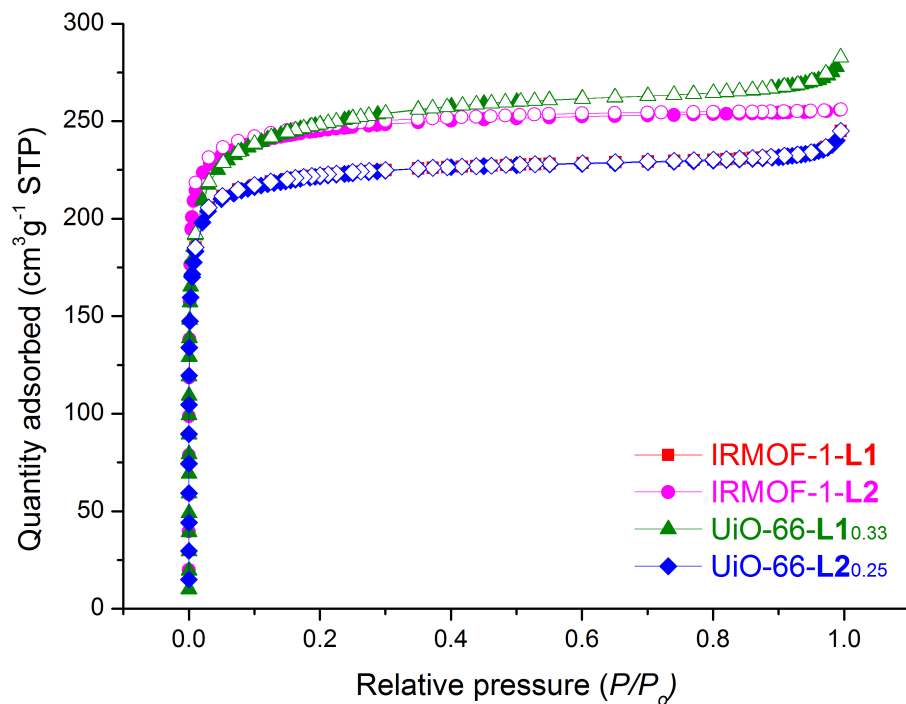
**Figure S31.** PXRD patterns of IRMOF-1-L1-L4 activated at 150 °C under vacuum.



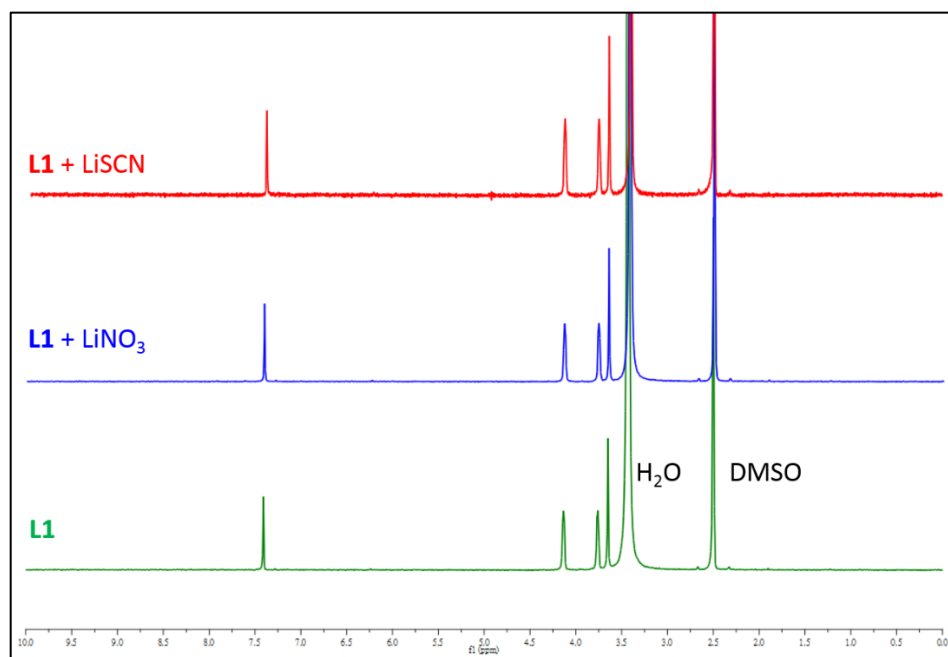
**Figure S32.** PXRD patterns of IRMOF-1 and IRMOF-1-L1 before and after soaking in 0.1 M  $\text{LiNO}_3$ /DMF solution for 1 d.



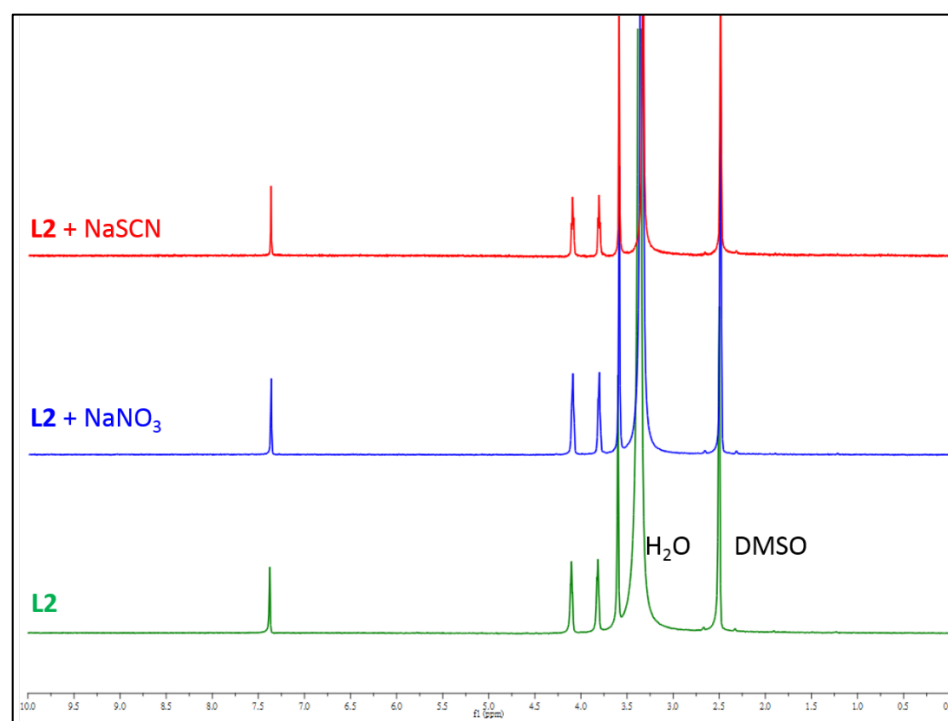
**Figure S33.** PXRD patterns of IRMOF-1 and IRMOF-1-L2 before and after soaking in 0.1 M  $\text{NaNO}_3$ /DMF solution for 1 d.



**Figure S34.** 77K N<sub>2</sub> sorption isotherms of IRMOF-1-L1 and -L2, and UiO-66-L1<sub>0.33</sub> and -L2<sub>0.25</sub> after soaking the materials in 0.1 M LiNO<sub>3</sub> (for L1) or NaNO<sub>3</sub> (for L2) in DMF solution for 1 d. Samples were activated at 150 °C under vacuum. Filled shape: adsorption; open shape: desorption.



**Figure S35.**  $^1\text{H}$  NMR spectra of L1 in  $\text{DMSO-}d_6$  titrated in excess equivalents of alkali metals.



**Figure S36.**  $^1\text{H}$  NMR spectra of L2 in  $\text{DMSO-}d_6$  titrated in excess equivalents of alkali metals.

**Table S1.** Elemental Analyses of Activated MOFs.

	Molecular Formula	Element	Wt% Calc	Wt% Exp <sup>b</sup>	Difference
IRMOF-1-L1 <sup>a</sup>	Zn <sub>4</sub> O(C <sub>14</sub> H <sub>14</sub> O <sub>8</sub> ) <sub>3</sub>	C	41.71%	34.38%	-7.09%
	Mw = 1208.29	H	3.50%	4.24%	0.74%
	g/mol	N	0.00%	0.00%	0.00%
IRMOF-1-L2	Zn <sub>4</sub> O(C <sub>16</sub> H <sub>18</sub> O <sub>9</sub> ) <sub>3</sub>	C	42.97%	38.19%	-3.78%
	Mw = 1340.45	H	4.06%	4.67%	0.61%
	g/mol	N	0.00%	0.00%	0.00%
IRMOF-1-L3	Zn <sub>4</sub> O(C <sub>14</sub> H <sub>14</sub> O <sub>6</sub> S <sub>2</sub> ) <sub>3</sub>	C	38.63%	30.55%	-8.08%
	Mw = 1304.66	H	3.24%	3.55%	0.31%
	g/mol	N	0.00%	0.00%	0.00%
IRMOF-1-L4	Zn <sub>4</sub> O(C <sub>16</sub> H <sub>18</sub> O <sub>6</sub> S <sub>3</sub> ) <sub>3</sub>	C	38.79%	23.78%	-15.01%
	Mw = 1485.00	H	3.67%	2.90%	0.77%
	g/mol	N	0.00%	0.00%	0.00%
UiO-66-L1 <sub>0.33</sub>	Zr <sub>6</sub> (OH) <sub>4</sub> O <sub>4</sub> (C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> ) <sub>4</sub> (C <sub>14</sub> H <sub>14</sub> O <sub>8</sub> ) <sub>2</sub>	C	36.80%	26.15%	-10.65
	Mw = 1956.35	H	2.47%	4.22%	1.75%
	g/mol	N	0.00%	0.00%	0.00%
UiO-66-L2 <sub>0.25</sub>	Zr <sub>6</sub> (OH) <sub>4</sub> O <sub>4</sub> (C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> ) <sub>4.5</sub> (C <sub>16</sub> H <sub>18</sub> O <sub>9</sub> ) <sub>1.5</sub>	C	36.94%	27.19%	-9.75%
	Mw = 1949.36	H	2.53%	4.58%	2.05%
	g/mol	N	0.00%	0.00%	0.00%

<sup>a</sup> All samples were activated at 150 °C under vacuum unless noted otherwise.<sup>b</sup> Based on two independent samples in duplicate.



**Table S2.** Brunauer-Emmett-Teller (BET) Surface Area Measurements and Isothermic Heats ( $Q_{st}$ ) of H<sub>2</sub> Adsorption of IRMOFs after Activation at 150 °C under Vacuum.

IRMOFs	BET (m <sup>2</sup> /g)	Pore Size (Å)	H <sub>2</sub> $Q_{st}$ (kJ/mol)
IRMOF-1	3180 ± 32	12.68	5.16
IRMOF-1-L1	1204 ± 10	10.90	5.83
IRMOF-1-L1 soaked in 0.1 M LiNO <sub>3</sub> /DMF 1d	1137 ± 9	10.90	5.76
IRMOF-1-L1 soaked in 0.1 M LiSCN/CH <sub>3</sub> CN 1d	Lost crystallinity		
IRMOF-1-L1 soaked in 0.1 M LiNO <sub>3</sub> /DMF 60 °C 1d	Lost crystallinity		
IRMOF-1-L2	899 ± 35	11.79	6.52
IRMOF-1-L2 soaked in 0.1 M NaNO <sub>3</sub> /DMF 1d	916 ± 7	11.79	6.50
IRMOF-1-L2 soaked in 0.1 M NaSCN/CH <sub>3</sub> CN 1d	Lost crystallinity		
IRMOF-1-L2 soaked in 0.1 M NaNO <sub>3</sub> /DMF 60 °C 1d	Lost crystallinity		

**Table S3.** BET Surface Area Measurements and  $Q_{st}$  of  $H_2$  Adsorption of UiO-66s after Activation at 150 °C under Vacuum.

UiO-66s	BET ( $m^2/g$ )	Pore Size ( $\text{\AA}$ )	$H_2$ $Q_{st}$ (kJ/mol)
UiO-66	$1336 \pm 33$	9.76	8.00
UiO-66- <b>L1</b> <sub>0.33</sub>	$999 \pm 74$	9.29	7.57
UiO-66- <b>L1</b> <sub>0.33</sub> soaked in 0.1 M LiNO <sub>3</sub> /DMF 1d	$926 \pm 6$	9.61	8.11
UiO-66- <b>L1</b> <sub>0.33</sub> soaked in 0.1 M LiSCN/CH <sub>3</sub> CN 1d	$977 \pm 4$	9.29	7.52
UiO-66- <b>L1</b> <sub>0.33</sub> soaked in 0.1 M LiNO <sub>3</sub> /DMF 60 °C 1d	$922 \pm 6$	9.29	7.83
UiO-66- <b>L2</b> <sub>0.25</sub>	$795 \pm 15$	9.29	7.69
UiO-66- <b>L2</b> <sub>0.25</sub> soaked in 0.1 M NaNO <sub>3</sub> /DMF 1d	$832 \pm 7$	9.29	7.02
UiO-66- <b>L2</b> <sub>0.25</sub> soaked in 0.1 M LiSCN/DMF 1d	$784 \pm 7$	8.57	6.95
UiO-66- <b>L2</b> <sub>0.25</sub> soaked in 0.1 M NaSCN/CH <sub>3</sub> CN 1d	$841 \pm 6$	8.57	6.20
UiO-66- <b>L2</b> <sub>0.25</sub> soaked in 0.1 M NaNO <sub>3</sub> /DMF 60 °C 1d	$820 \pm 7$	8.57	7.20

## References

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