

Supplementary Information for

Three Component Controls in Pillared Metal-Organic Frameworks for Catalytic Carbon Dioxide Fixation

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1. Synthesis of DMOF(M)s

DMOF(Co): $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (58 mg, 0.20 mmol), BDC ligand (33 mg, 0.20 mmol), DABCO (22 mg, 0.20 mmol) and DMF (4 mL) were placed in a scintillation vial. After stirring for 10 minutes, the purple gel was formed. This gel was filtered using a filter with a fritted disc of fine porosity. The solution was then transferred to a 20 mL size Teflon lined autoclave and heated at 120 °C for 48 h. The resulting crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with 5 mL chloroform over three days, replacing the old chloroform with fresh chloroform every 24 h.

DMOF(Ni): $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (58 mg, 0.20 mmol), BDC ligand (33 mg, 0.20 mmol), DABCO (11 mg, 0.10 mmol) and DMF (4 mL) were placed in a scintillation vial. After stirring for 10 minutes, the green gel was formed. This gel was filtered using a filter with a fritted disc of fine porosity. The solution was then transferred to a 20 mL size Teflon lined autoclave and heated at 120 °C for 48 h. The resulting crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with 5 mL chloroform over three days, replacing the old chloroform with fresh chloroform every 24 h.

DMOF(Cu): $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (48 mg, 0.20 mmol), BDC ligand (33 mg, 0.20 mmol), DABCO (22 mg, 0.20 mmol) and DMF (4 mL) were placed in a scintillation vial. After stirring for 10 minutes, the vial was heated at 120 °C for 24 h. The powders were then isolated by centrifugation and residual DMF and ligand precursors were removed from the material by washing with 5 mL DMF three times. The solvent was then exchanged with 5 mL chloroform over three days, replacing the old chloroform with fresh chloroform every 24 h.

DMOF(Zn): $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (60 mg, 0.20 mmol), BDC ligand (33 mg, 0.20 mmol), DABCO (36 mg, 0.32 mmol) and DMF (4 mL) were placed in a scintillation vial. After stirring for 10 minutes, the gel was formed. This gel was filtered using a filter with a fritted disc of fine porosity. The solution was then transferred to a 20 mL size scintillation vial and heated at 120 °C for 48 h. The resulting transparent crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with 5 mL chloroform over three days, replacing the old chloroform with fresh chloroform every 24 h.

2. CO₂ Cycloaddition with epoxide

Dried MOF catalyst (0.2 mmol of metal, 2 mol %) and co-catalyst (0.1 mmol, 0.1 mol %) were added to a 15 mL size stainless-steel autoclave. Epoxide (10 mmol) was added to this sealed vessel using a syringe. The autoclave was initially operated at a pressure of 10 bar CO₂ and then heated at the indicated conditions (100 °C for 2 h or 3 h), respectively. After completion autoclave had been cooled and vented, and then a small portion of sample mixture was taken for analysis by ¹H NMR.

3. Synthesis of DMOF(Zn)-R

DMOF(Zn)-NH₂[S1]: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (59 mg, 0.20 mmol), BDC-NH₂ ligand (36 mg, 0.20 mmol), DABCO (36 mg, 0.32 mmol) and DMF (5 mL) were placed in a scintillation vial. After stirring for 10

minutes, the yellow gel was formed. This gel was filtered using a filter with a fritted disc of fine porosity. The solution was then transferred to a 20 mL size scintillation vial and heated at a rate of 2.5 °C/min from room temperature to 100 °C. The temperature was then hold for 12 h and then cooled to temperature at a rate of 2.5 °C/min. The resulting brown crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with 5 mL chloroform over three days, replacing the old chloroform with fresh chloroform every 24 h.

DMOF(Zn)-OH [S1]: Zn(NO₃)₂·6H₂O (59 mg, 0.20 mmol), BDC-OH ligand (36 mg, 0.20 mmol), DABCO (36 mg, 0.32 mmol) and DMF (5 mL) were placed in a scintillation vial. After stirring for 10 minutes, the ivory precipitate was formed. This gel was filtered using a filter with a fritted disc of fine porosity. The solution was then transferred to a 20 mL size Teflon lined autoclave and heated at a rate of 2.5 °C/min from room temperature to 100 °C. The temperature was then hold for 12 h and then cooled to temperature at a rate of 2.5 °C/min. The resulting pale-yellow crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with 5 mL chloroform over three days, replacing the old chloroform with fresh chloroform every 24 h.

DMOF(Zn)-1,4-NDC [S2]: Zn(NO₃)₂·6H₂O (59 mg, 0.20 mmol) and 1,4-NDC ligand (44 mg, 0.20 mmol) were dissolved in 3 mL of DMF. To this mixture, DABCO (12 mg, 0.10 mmol) was added. Upon adding, a white precipitate formed. This precipitate was filtered using a filter with a fritted disc of fine porosity. The solution was then transferred to a scintillation vial and heated at 120 °C for 48 h. The resulting crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with 5 mL chloroform over three days, replacing the old chloroform with fresh chloroform every 24 h.

DMOF(Zn)-2,6-NDC [S3]: All reactants were dissolved separately. Zn(NO₃)₂·6H₂O (312 mg, 1.05 mmol) in 5 mL DMF, 2,6-NDC ligand (227 mg, 1.05 mmol) in 10 mL of DMF, and DABCO (59 mg, 0.525 mmol) in 5 mL DMF. The mixture was stirred for 10 min, transferred to 50 mL size Teflon lined autoclave and heated at 120 °C for 48 h. The resulting solid were then washed three times with 5 mL of DMF. The solvent was then exchanged with 5 mL chloroform over three days, replacing the old chloroform with fresh chloroform every 24 h.

4. ¹H NMR of DMOF(Zn)-R after acid digestion and crystal images

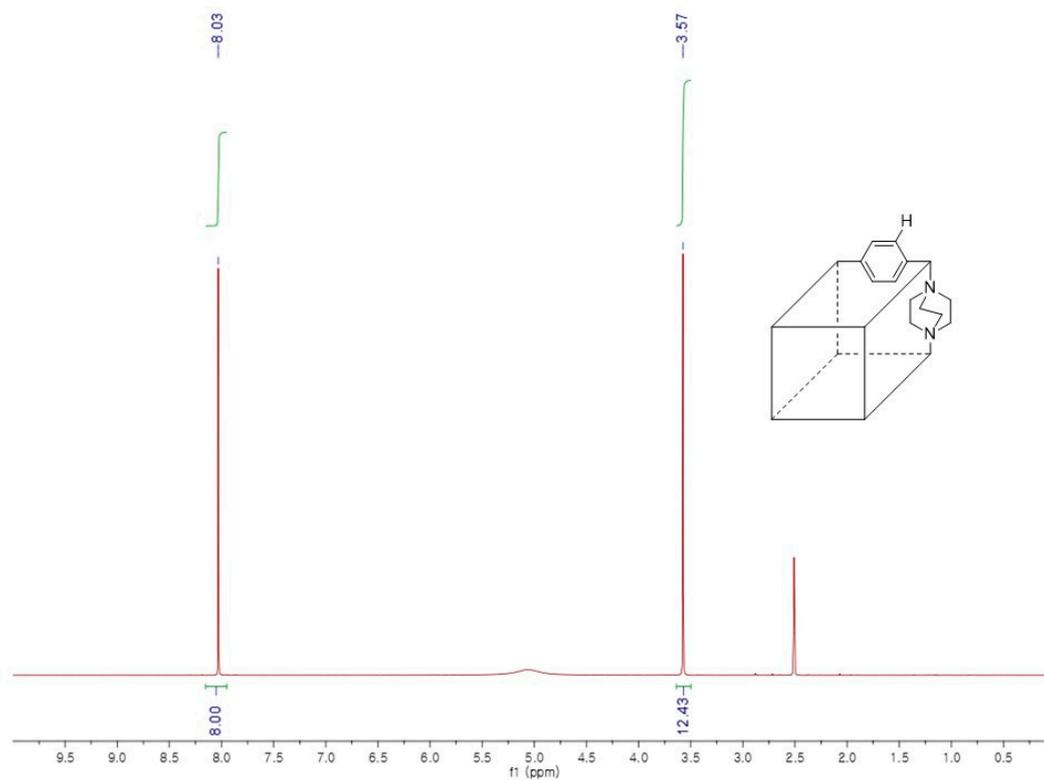


Figure S1. ^1H NMR of DMOF(Zn) after acid digestion.

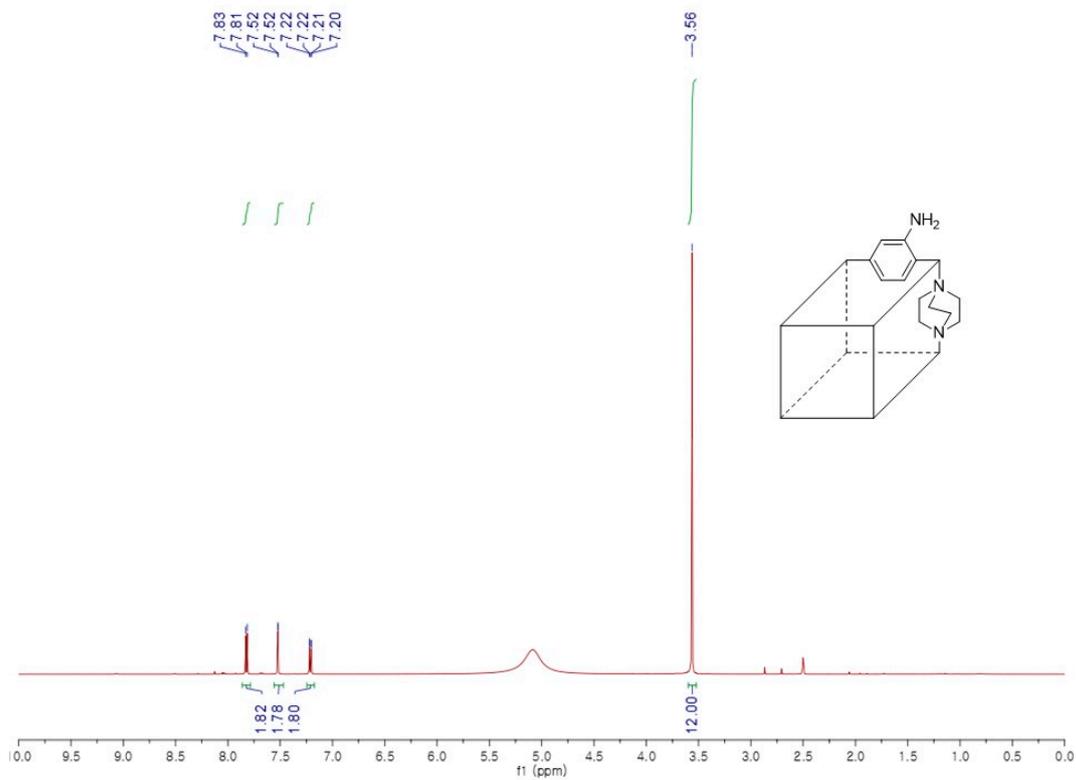


Figure S2. ^1H NMR of DMOF(Zn)-NH₂ after acid digestion.

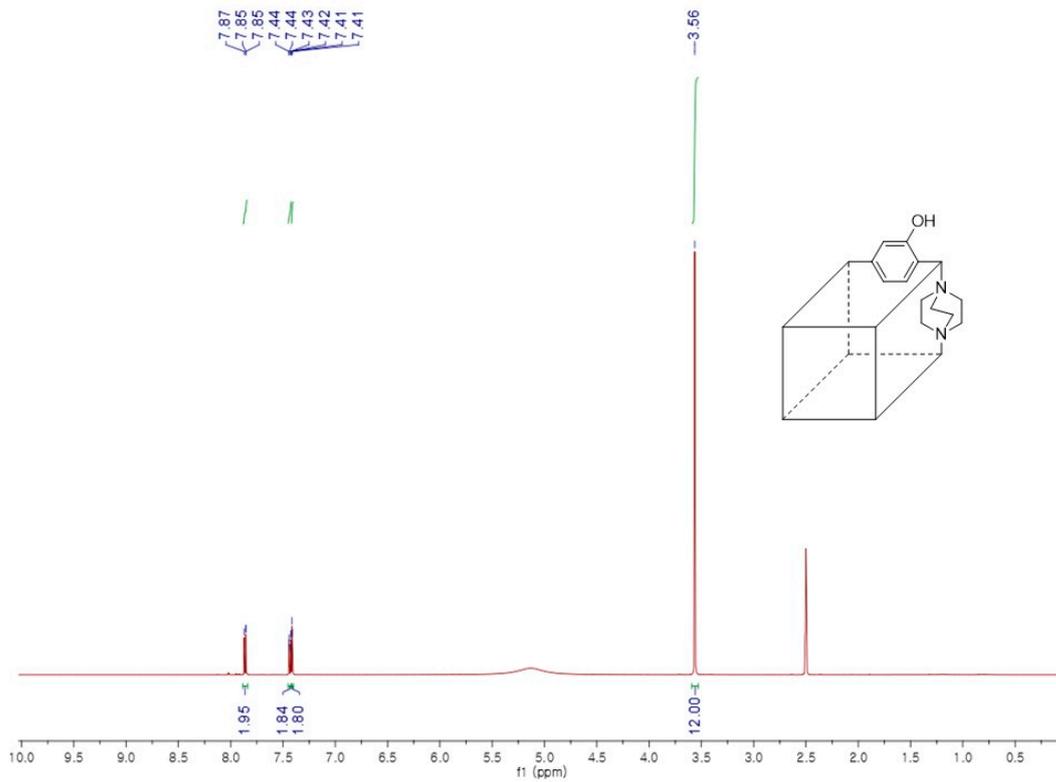


Figure S3. ^1H NMR of DMOF(Zn)-OH after acid digestion.

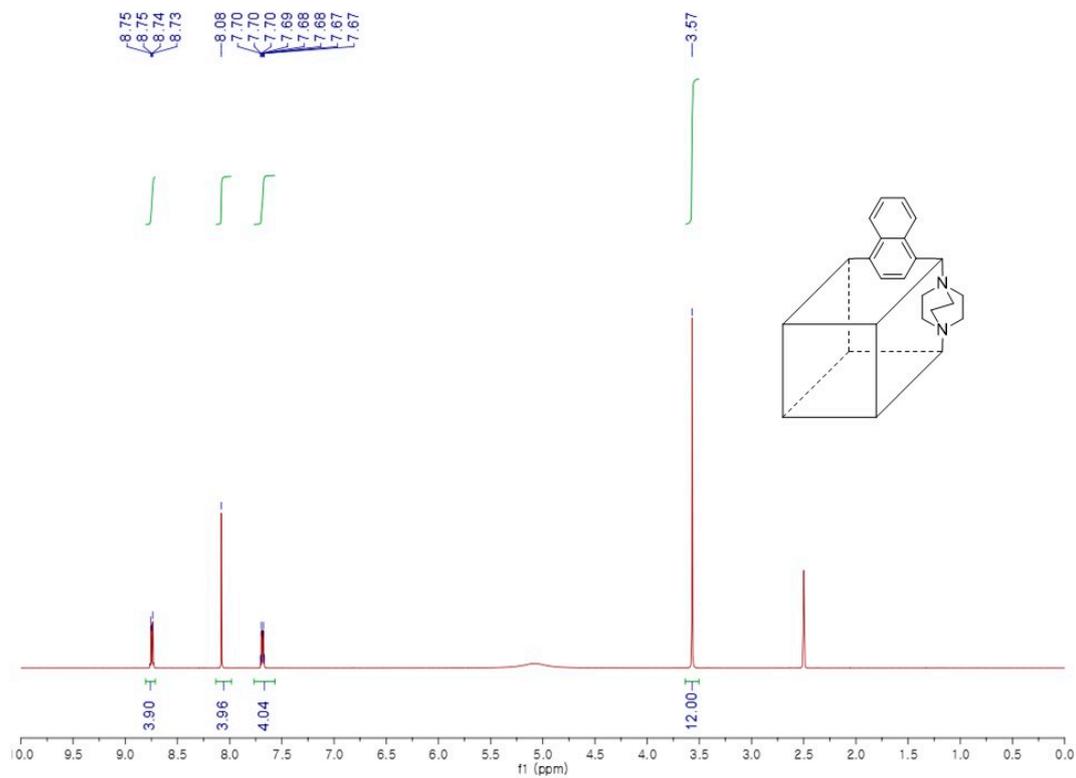


Figure S4. ^1H NMR of DMOF(Zn)-1,4-NDC after acid digestion.

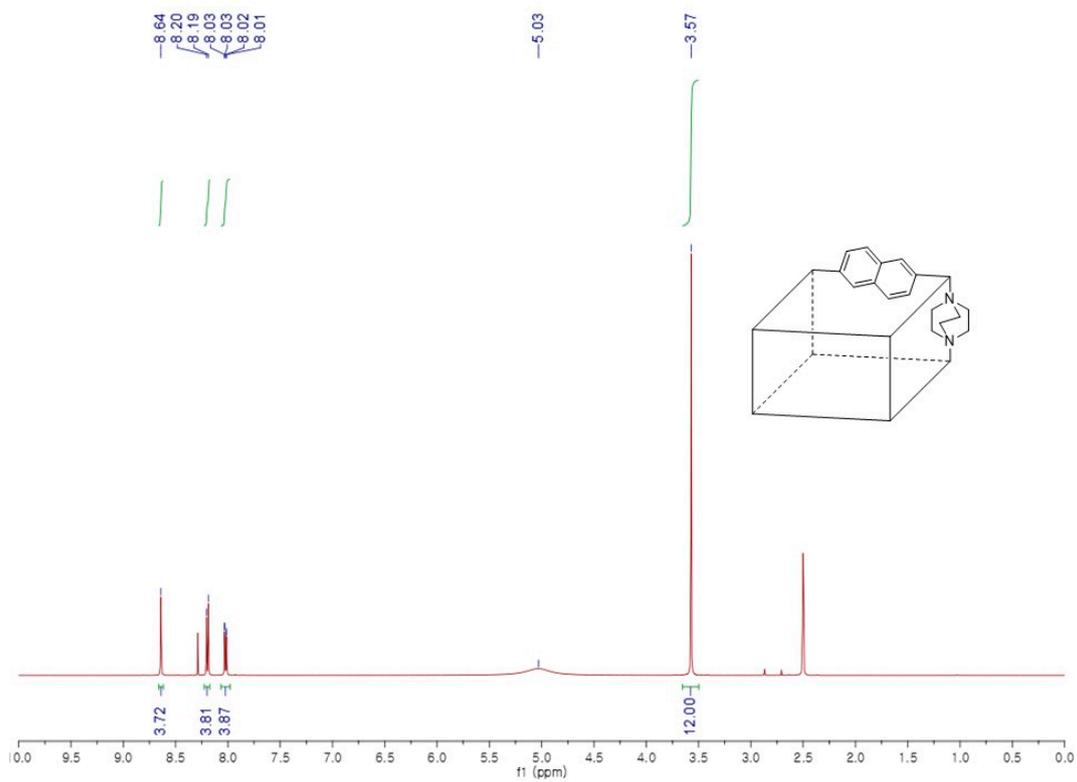


Figure S5. ^1H NMR of DMOF(Zn)-1,5-NDC after acid digestion.

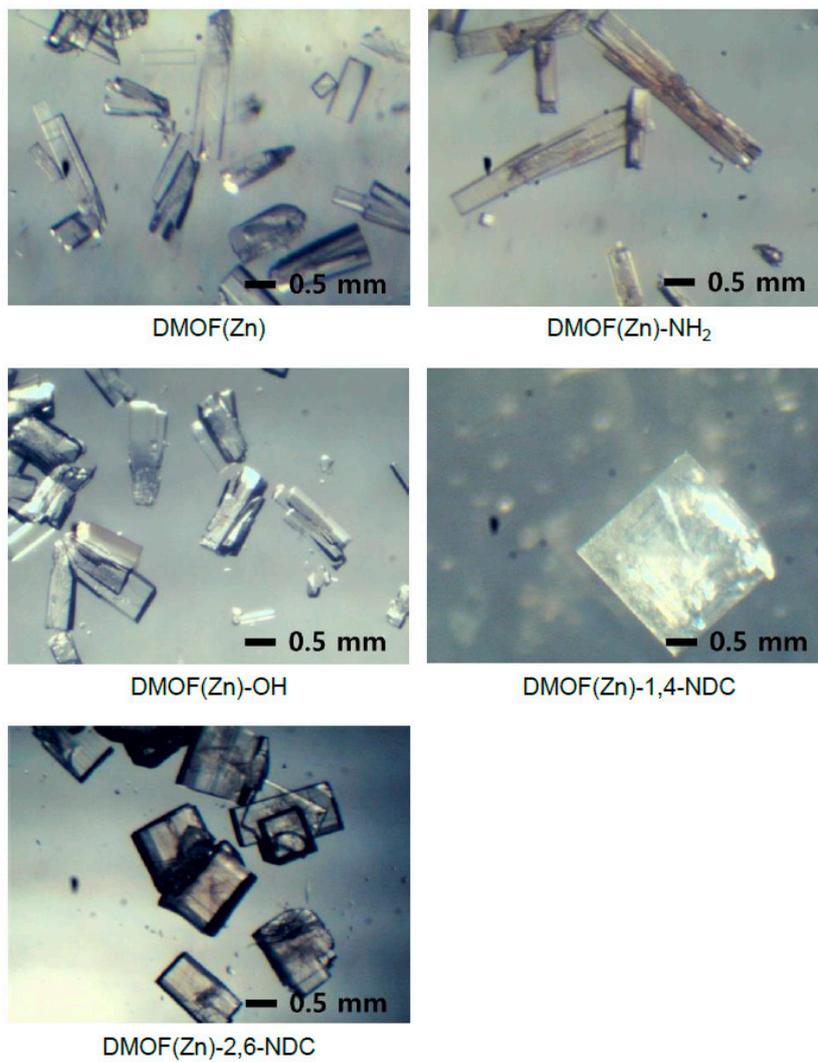


Figure S6. Crystal images of functionalized DMOFs.

5. Synthesis of BMOF(Zn)-R

BMOF(Zn)-H [S4]: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (71 mg, 0.24 mmol) , BDC ligand (39 mg, 0.24 mmol) and BPY (18 mg, 0.12 mmol) were dissolved in DMF/EtOH (1:1, 20 mL). The mixture was stirred for 10 min, transferred to 50 mL size Teflon lined autoclave and heated at 90 °C for 24 h. The resulting white block-shaped crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with chloroform (5 mL) over three days, replacing the old chloroform with fresh chloroform every 24 h.

BMOF(Zn)-NH₂: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (90 mg, 0.30 mmol) , BDC-NH₂ ligand (55 mg, 0.30 mmol) and BPY (23 mg, 0.15 mmol) were dissolved in DMF/EtOH (1:1, 25 mL). The mixture was stirred for 1 h, transferred to 50 mL size 50 mL scintillation vial and heated at 90 °C for 24 h. The resulting solid was then washed three times with 5 mL of DMF. The solvent was then exchanged with 20 mL chloroform over three days, replacing the old chloroform with fresh chloroform every 24 h.

BMOF(Zn)-OH: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (90 mg, 0.30 mmol) and BDC-OH ligand (55 mg, 0.30 mmol) and BPY (24 mg, 0.15 mmol) were dissolved in 4.5 mL of DMF. Upon adding, a ivory precipitate formed. This precipitate was filtered using a filter with a fritted disc of fine porosity. The solution was divided into 4 scintillation vials and added 5 mL of DMF to each vial. And it was heated at a rate of 0.5 °C/min from room temperature to 90 °C. The temperature was then hold for 24 h and then cooled to temperature at a rate of 1.0°C/min. The resulting pale yellow crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with 5 mL chloroform over three days, replacing the old chloroform with fresh chloroform every 24 h.

BMOF(Zn)-1,4-NDC [S5]: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (90 mg, 0.30 mmol) , 1,4-NDC (65 mg, 0.30 mmol) and BPY (23 mg, 0.15 mmol) were dissolved in DMF/EtOH (1:1, 25 mL). The mixture was stirred for 1 h, transferred to 50 mL size 50 mL scintillation vial and heated at 90 °C for 24 h. The resulting solid was then washed three times with 5 mL of DMF. The solvent was then exchanged with 20 mL chloroform over three days, replacing the old chloroform with fresh chloroform every 24 h.

BMOF(Zn)-2,6-NDC [S5]: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (90 mg, 0.30 mmol) 2,6-NDC (65 mg, 0.30 mmol) and BPY (23 mg, 0.15 mmol) were dissolved in DMF/EtOH (1:1, 25 mL). The mixture was stirred for 1 h, transferred to 50 mL size 50 mL scintillation vial and heated at 90 °C for 24 h. The resulting solid was then washed three times with 5 mL of DMF. The solvent was then exchanged with 20 mL chloroform over three days, replacing the old chloroform with fresh chloroform every 24 h.

6. ^1H NMR of BMOF(Zn)-R after acid digestion and SEM images

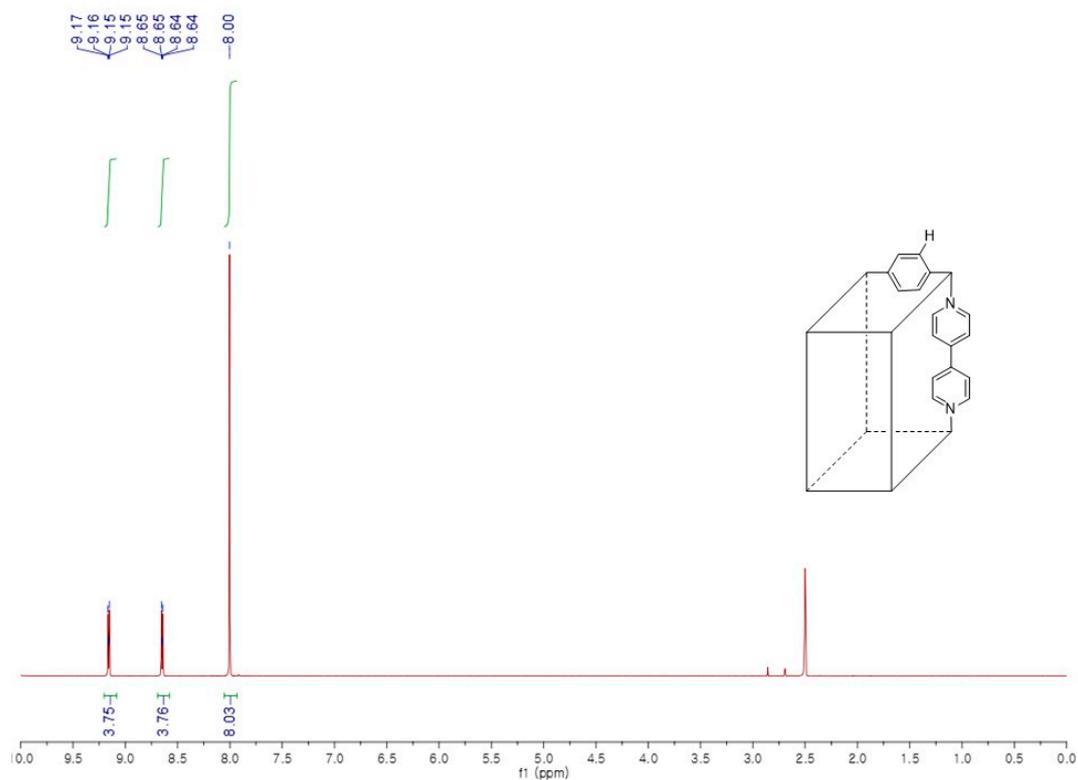


Figure S7. ^1H NMR of BMOF(Zn) after acid digestion.

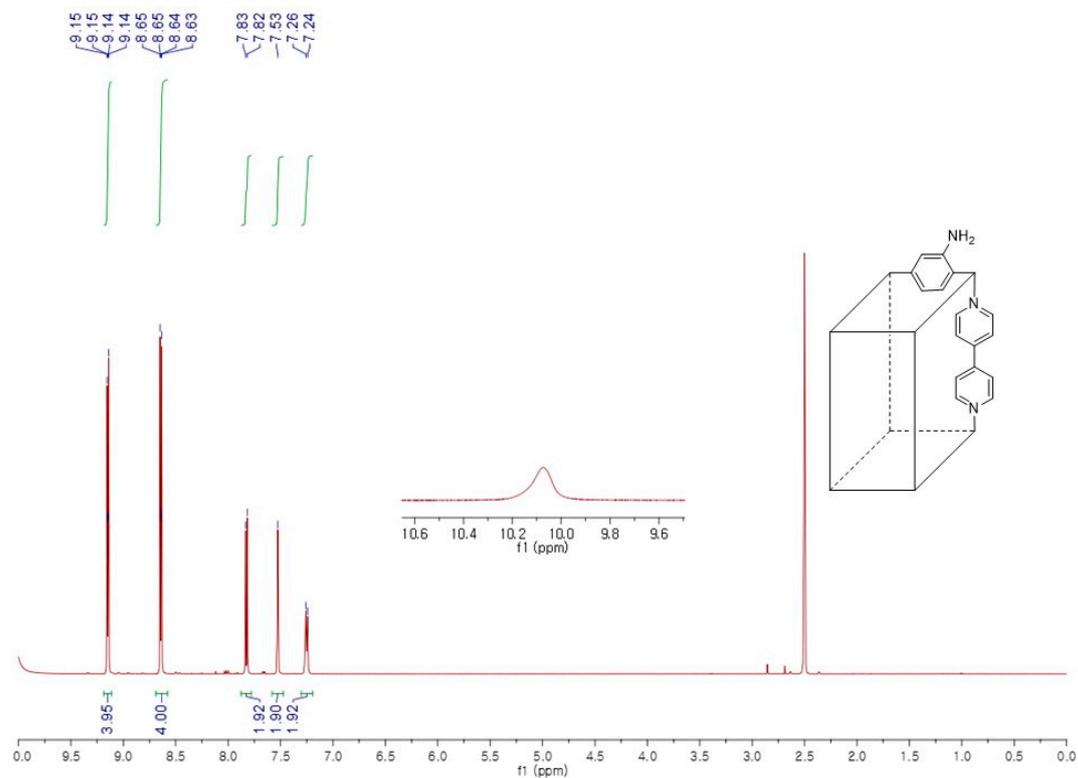


Figure S8. ^1H NMR of BMOF(Zn)-NH₂ after acid digestion.

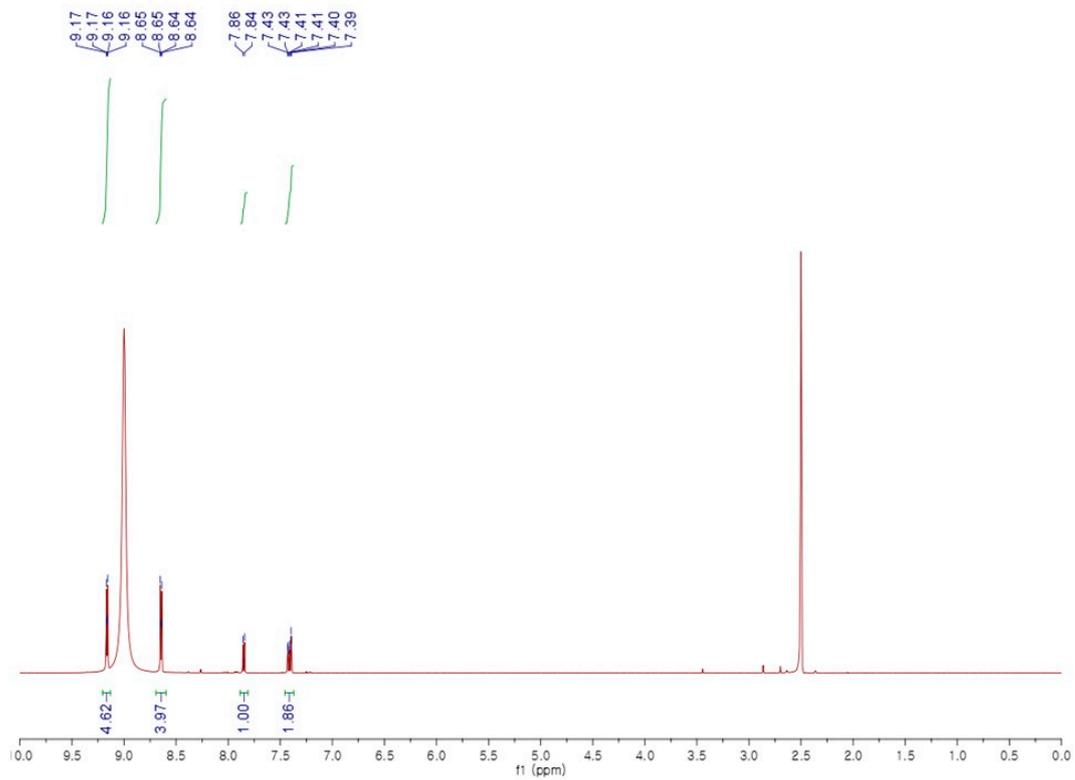


Figure S9. ^1H NMR of BMOF(Zn)-OH after acid digestion.

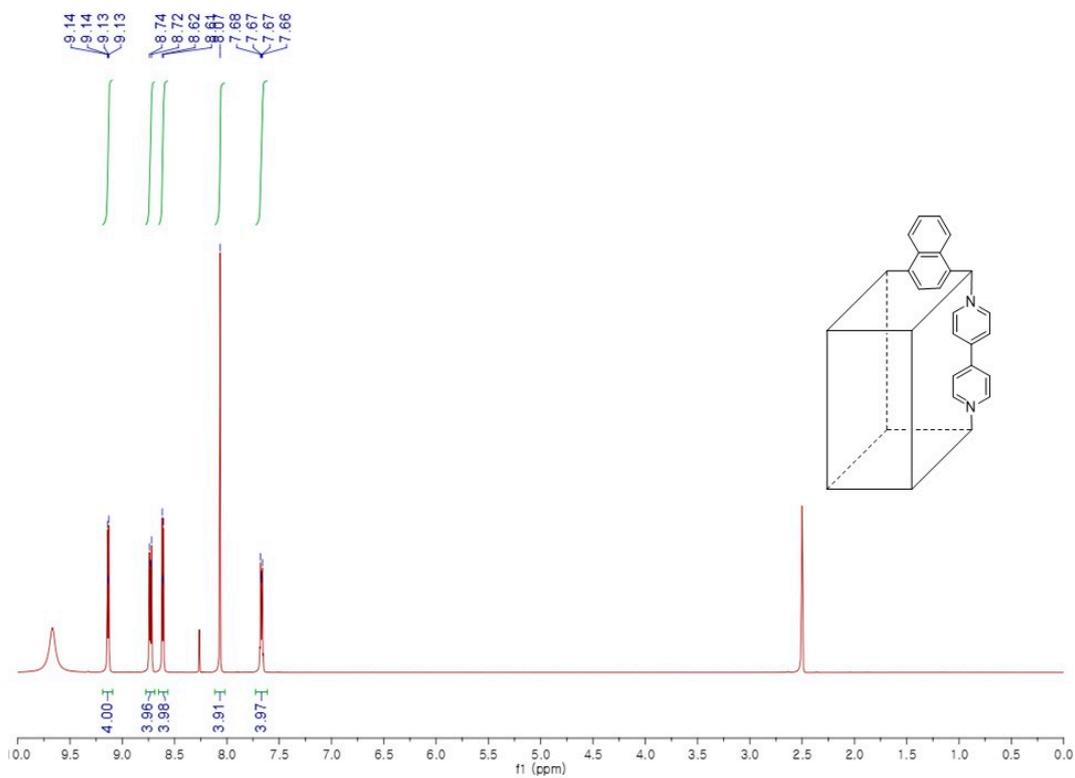


Figure S10. ^1H NMR of BMOF(Zn)-1,4-NDC after acid digestion.

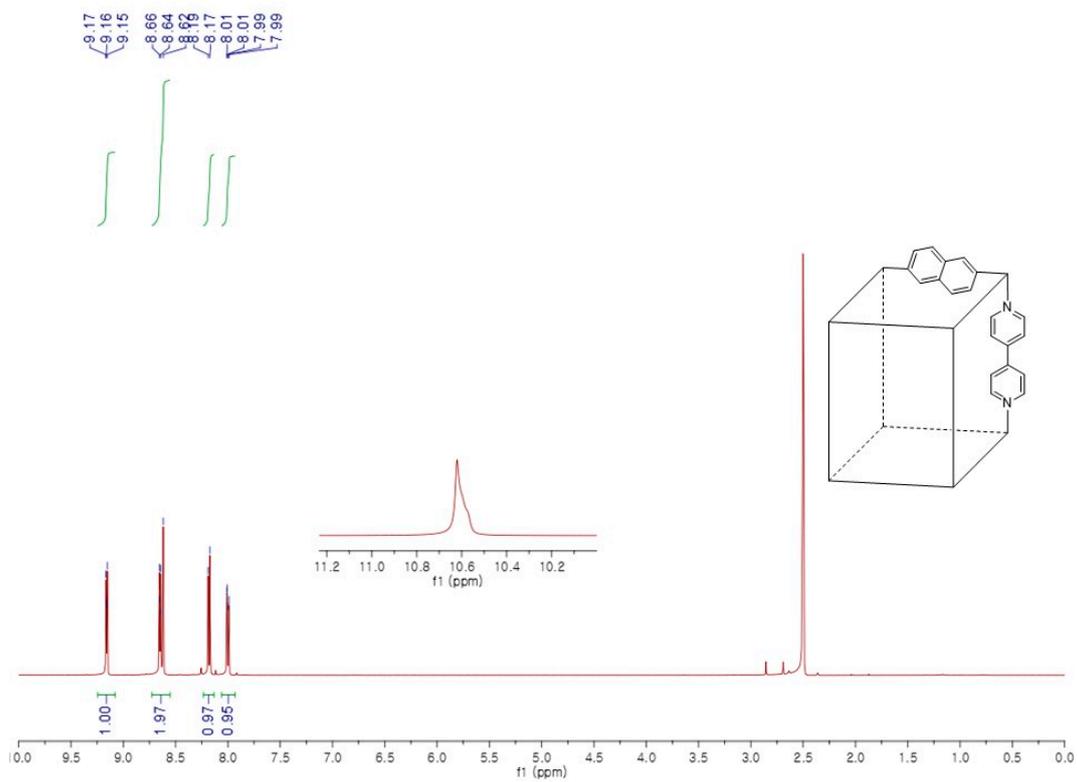
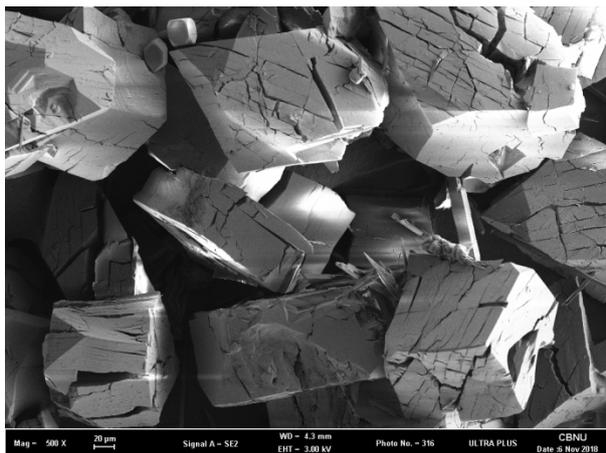


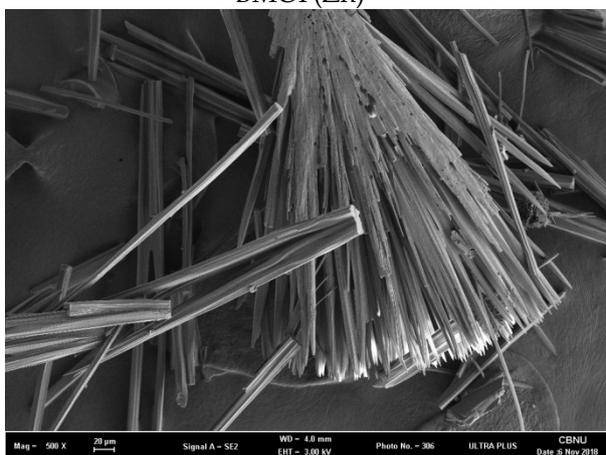
Figure S11. ^1H NMR of BMOF(Zn)-2,6-NDC after acid digestion.



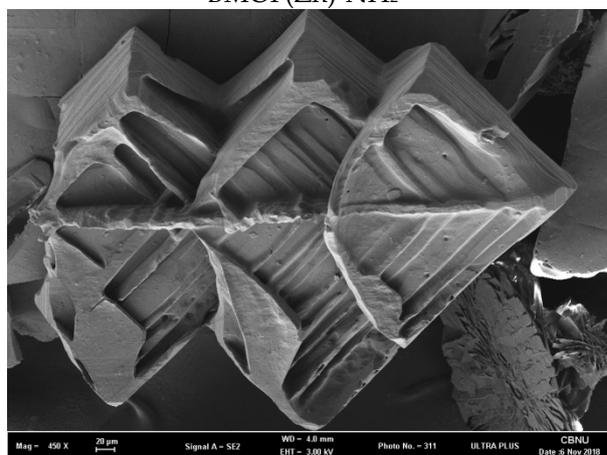
BMOF(Zn)



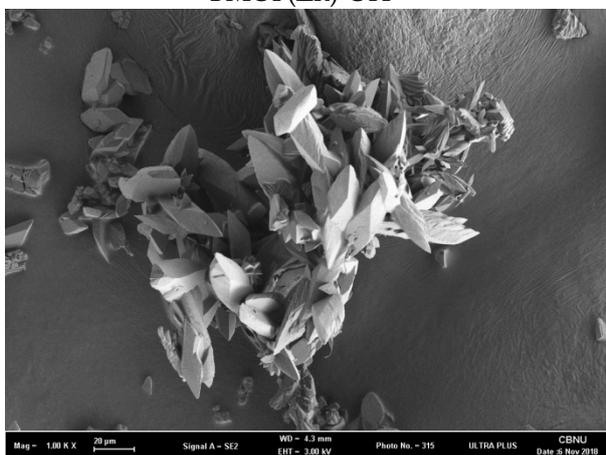
BMOF(Zn)-NH₂



BMOF(Zn)-OH



BMOF(Zn)-1,4-NDC



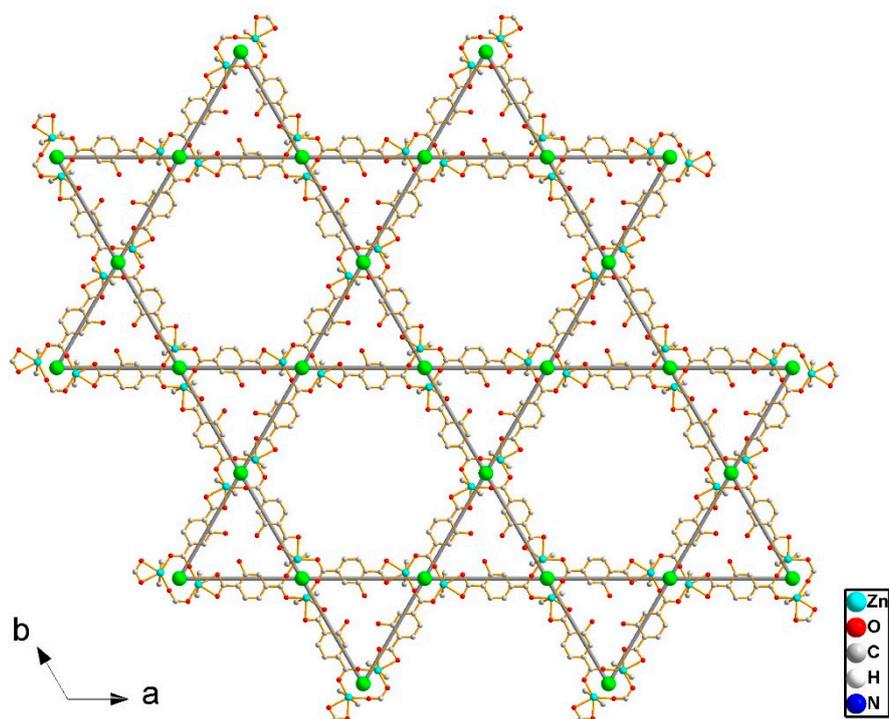
BMOF(Zn)-2,6-NDC

Figure S12. SEM image of functionalized BMOF(Zn)s.

7. X-ray crystallographic Data for BMOF(Zn)-OH and Characterizations

Single crystal of BMOF(Zn)-OH was coated with Paratone oil and mounted onto a glass capillary. The crystallographic measurements were performed on a Bruker D8QUEST CCD area detector diffractometer with a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by a full-matrix least-squares method on F^2 by using the SHELXTL/PC package, resulting in X-ray crystallographic data of BMOF(Zn)-OH in CIF format (Cambridge Crystallographic Data Centre, CCDC 1873485). Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The detailed crystallographic data are given in Table S1 and S2.

(a)



(b)

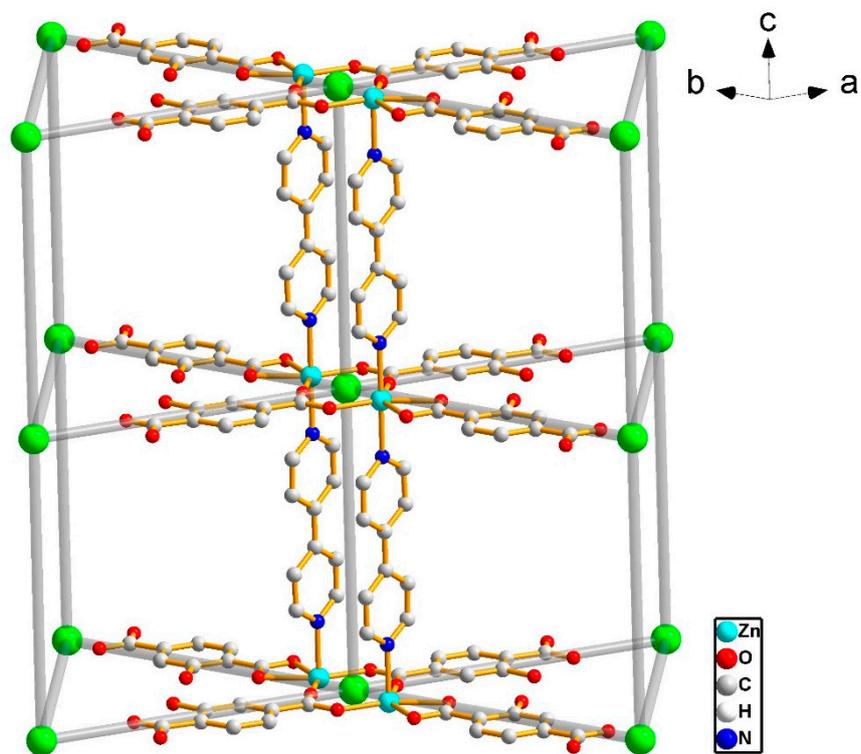


Figure S13. Structure of BMOF(Zn)-OH (a) top view (b) SBU-focused structure.

Table S1. Crystallographic data and parameters for **BMOF(Zn)-OH**.

Compound	BMOF(Zn)-OH
Formula	C ₁₈ H ₁₂ N ₂ O ₅ Zn
Formula weight	401.67
Crystal system	Hexagonal
Space group	<i>P6/m</i>
<i>a</i> (Å)	24.8543(19)
<i>b</i> (Å)	24.8543(19)
<i>c</i> (Å)	11.3862(9)
α (°)	90
β (°)	90
γ (°)	120
<i>V</i> (Å ³)	6091.3(10)
<i>Z</i>	6
ρ_{calc} (g cm ⁻³)	0.657
μ (mm ⁻¹)	0.618
<i>F</i> (000)	1224
<i>T</i> (K)	173(2)
Scan mode	<i>multi-scan</i>
<i>hkl</i> range	-28 < <i>h</i> < 28, -28 < <i>k</i> < 28, -13 < <i>l</i> < 13
Measd reflns	68270
Unique reflns [<i>R</i> _{int}]	3466 [0.1779]
Reflns used for refinement	3466
Refined parameters	148
<i>R</i> ₁ ^[a] (<i>I</i> > 2σ(<i>I</i>))	0.0941
<i>wR</i> ₂ ^[b] all data	0.2495
GOF on <i>F</i> ²	1.179
ρ_{fin} (max/min) (e Å ⁻³)	1.370, -2.193

$$^{\text{[a]}}R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^{\text{[b]}}wR_2 = \left\{ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right\}^{1/2}.$$

Table S2. Selected bond lengths (Å) and angles (deg) for **BMOF(Zn)-OH**.

Compound	BMOF(Zn)-OH
	lengths
Zn-O1	2.036(8)
Zn-O2'	2.026(7)
Zn-N1	2.148(5)
Zn-N1'	2.148(5)
Zn-O3	2.287(10)
Zn-O4	2.184(9)
Zn-C8	2.517(12)
	angles
O2'-Zn-O1	122.3(3)
O2'-Zn-N1'	90.15(15)
O1-Zn-N1'	88.90(16)
O2-Zn-N1	90.15(15)
O1-Zn-N1	88.90(16)
N1'-Zn-N1	177.6(3)
O2'-Zn-O4'	147.7(4)
O1-Zn-O4'	90.0(4)
N1'-Zn-O4'	90.52(14)
N1-Zn-O4'	90.52(14)
O2'-Zn-O3'	88.8(3)
O1-Zn-O3'	148.9(3)
N1'-Zn-O3'	91.22(15)
N1-Zn-O3'	91.21(15)
O4'-Zn-O3'	58.9(4)
O2'-Zn-C8'	118.6(4)
O1-Zn-C3'	119.1(4)
N1'-Zn-C3'	90.99(14)
N1-Zn-C3'	90.99(14)
O4'-Zn-C3'	29.1(4)
O3'-Zn-C3'	29.8(4)

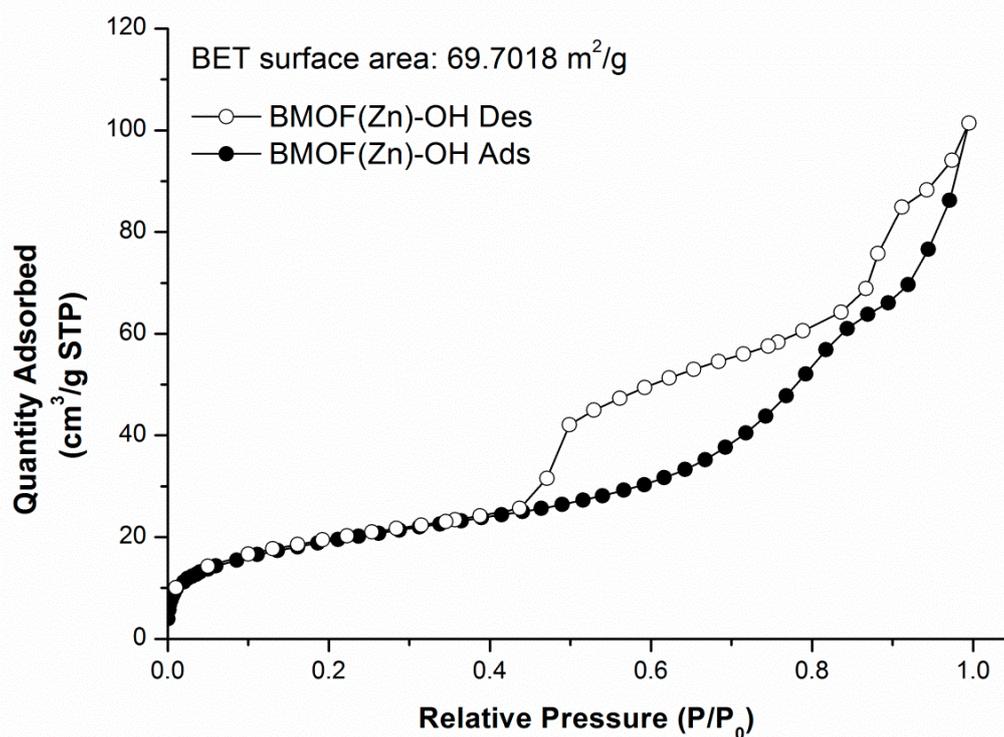


Figure S14. N₂ full isotherm (77 K) for BMOF(Zn)-OH.

Table S3. Reported BET value of DMOF and BMOF series.

DMOF	DMOF(Zn)	DMOF(Zn)-NH ₂	DMOF(Zn)-OH	DMOF(Zn)-1,4-NDC	DMOF(Zn)-2,6-NDC
BET value	1450 m ² /g[S6]	1320 m ² /g[S7]	1111 m ² /g[S8]	1000 m ² /g[S2]	710 m ² /g[S3]
BMOF	BMOF(Zn)	BMOF(Zn)-NH ₂	BMOF(Zn)-OH	BMOF(Zn)-1,4-NDC	BMOF(Zn)-2,6-NDC
BET value	1070 m ² /g[S9]	Not determined	70 m ² /g	Not determined	180 m ² /g[S9]

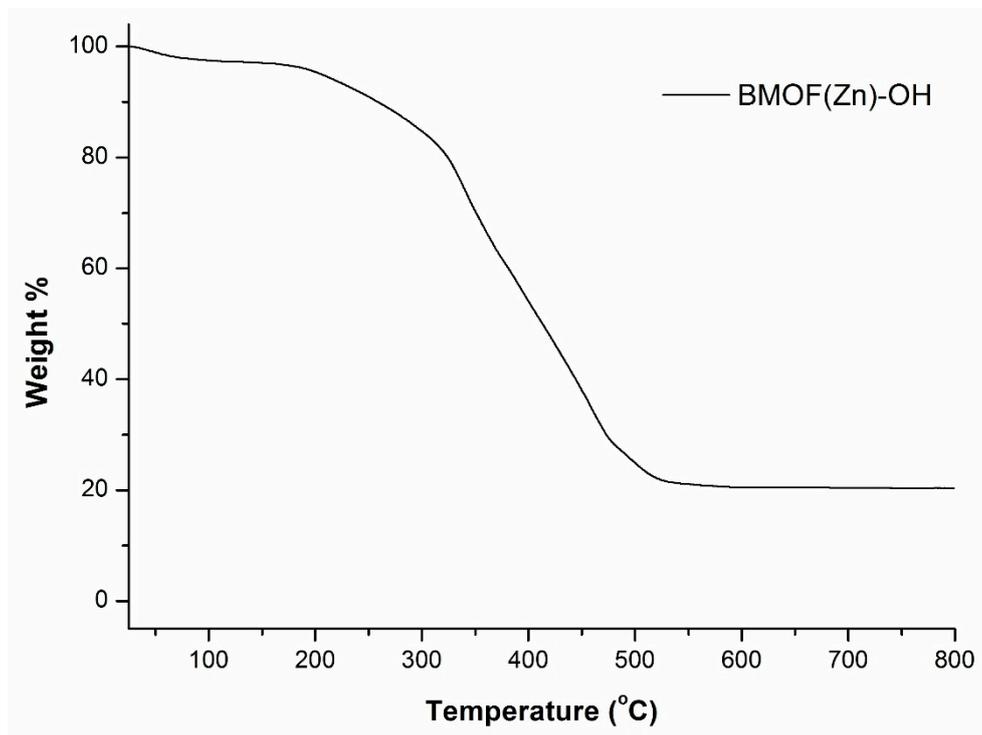


Figure S15. Thermogravimetric analysis of BMOF(Zn)-OH.

8. Recycle Test

BMOF(Zn)-NH₂ (100 mg, 0.31 mmol of Zn) catalyst and TBABr (48.2 mg, 0.15 mmol) co-catalyst were added to a 15 mL size stainless-steel autoclave. After sealing of reactor, propylene oxide (1.1 mL, 15.4 mmol) was added to the mixture using syringe. The autoclave was initially operated at a pressure of 10 bar of CO₂, and then heated at 100 °C for 2 h. After completion autoclave had been cooled and vented, the BMOF(Zn)-NH₂ catalysts were recovered by simple centrifugation (>3000 rpm). Recovered BMOF(Zn)-NH₂ was fully washed with dichloromethane 20 mL (to remove remaining propylene oxide, TBABr, and product, three times) and CHCl₃ 20 mL (three times), and then dried under vacuum for overnight.

Table S4. Recycle test results from BMOF(Zn)-NH₂ catalyzed CO₂ cycloaddition with PO.

Cycle	1st	2nd	3rd
Conversion (%)	78	75	75

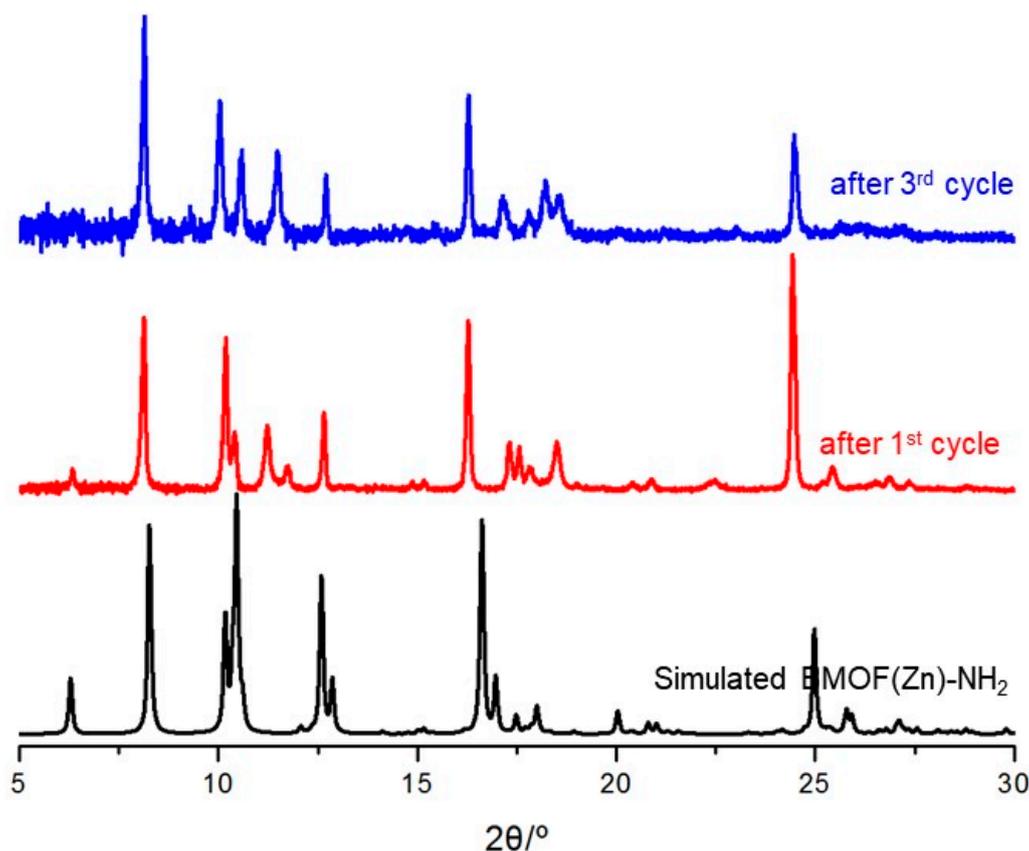


Figure S16. PXRD patterns of BMOF(Zn)-NH₂ before and after reaction.

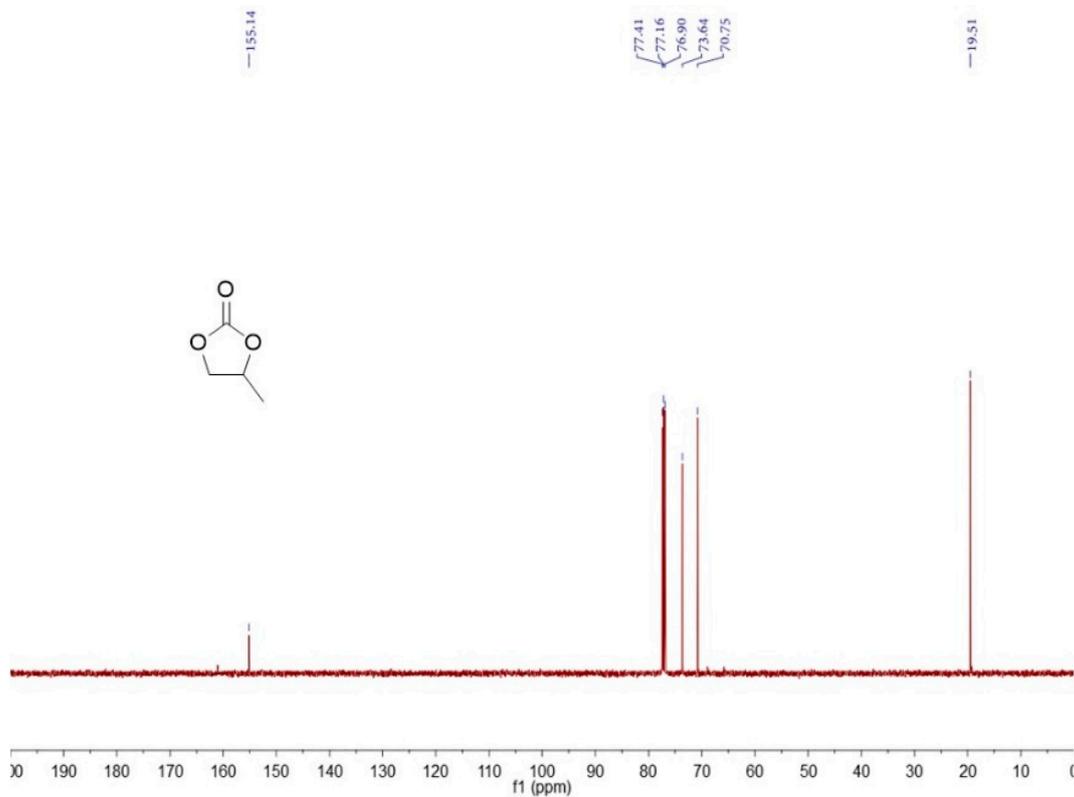
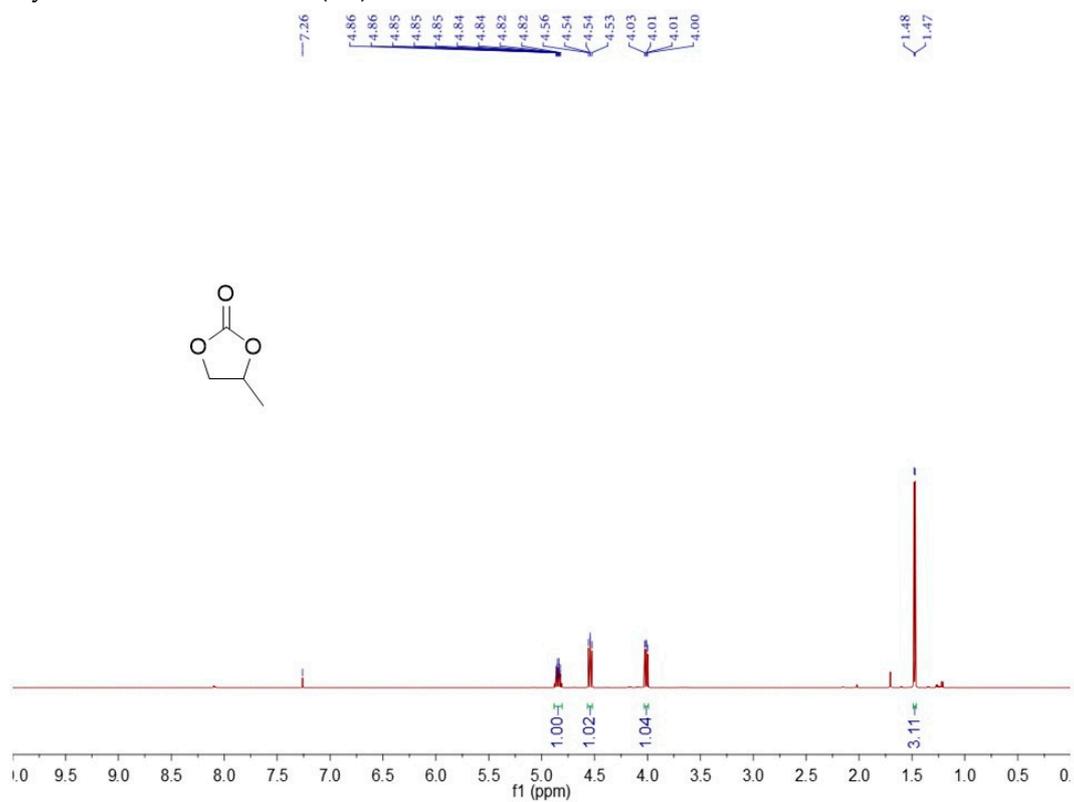
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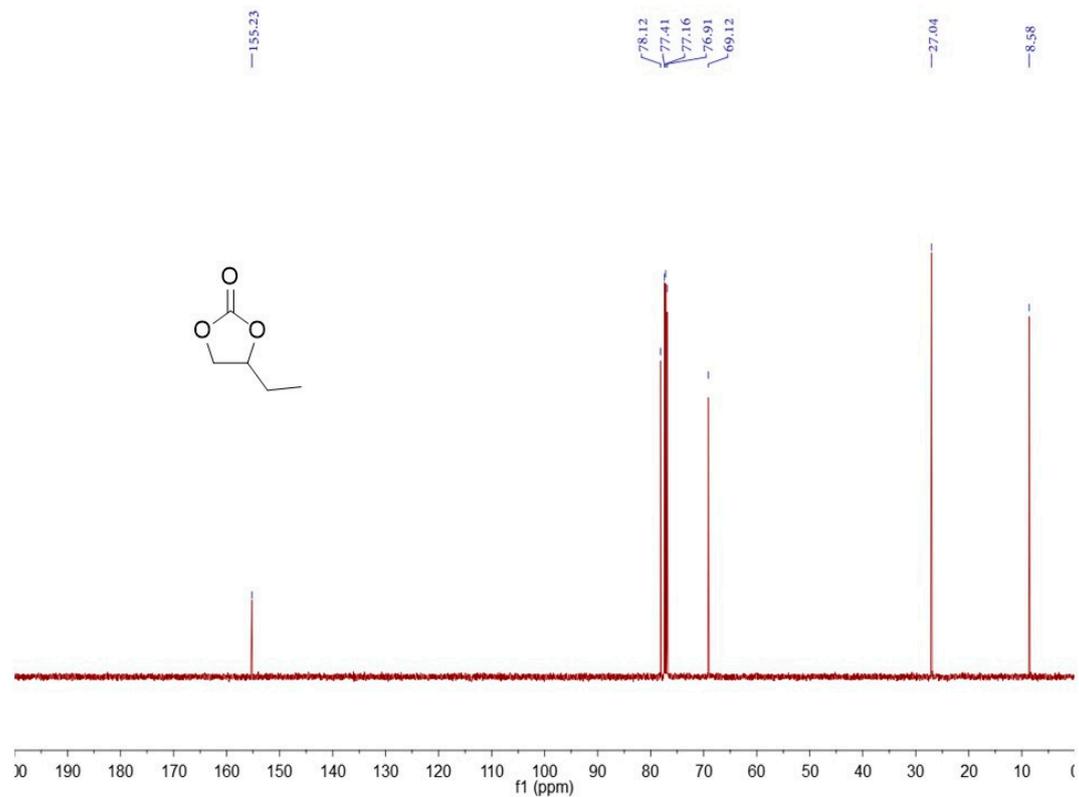
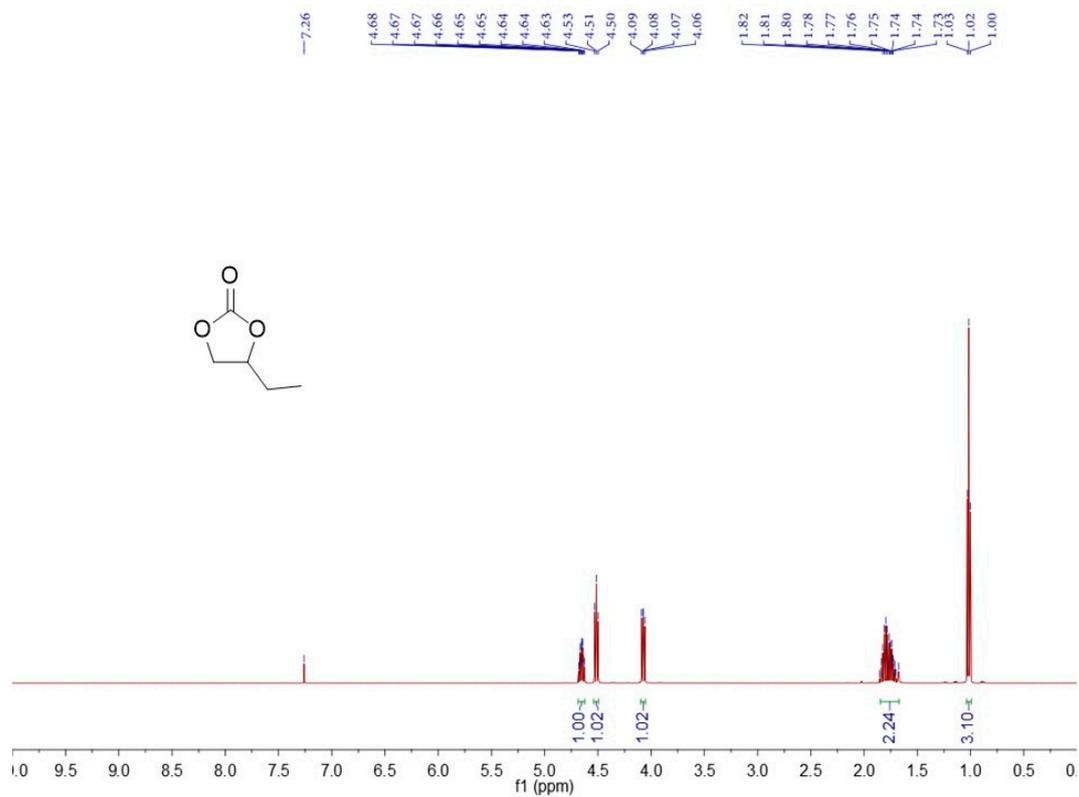
Appendix I

^1H and ^{13}C NMR of the obtained compounds

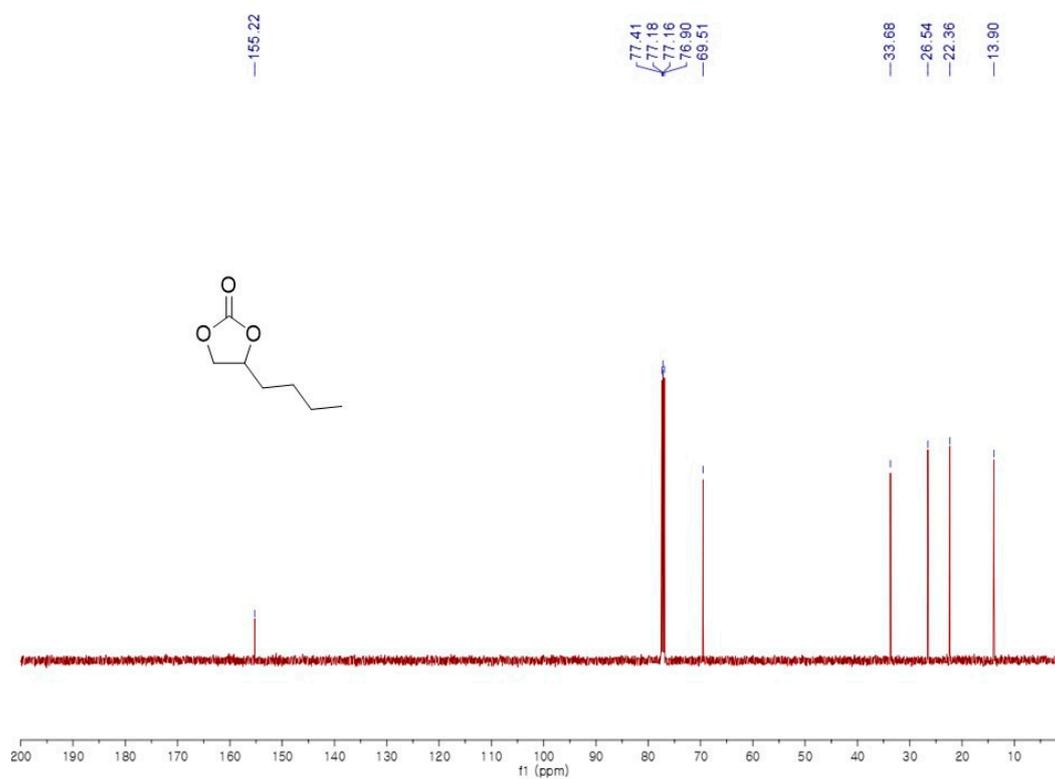
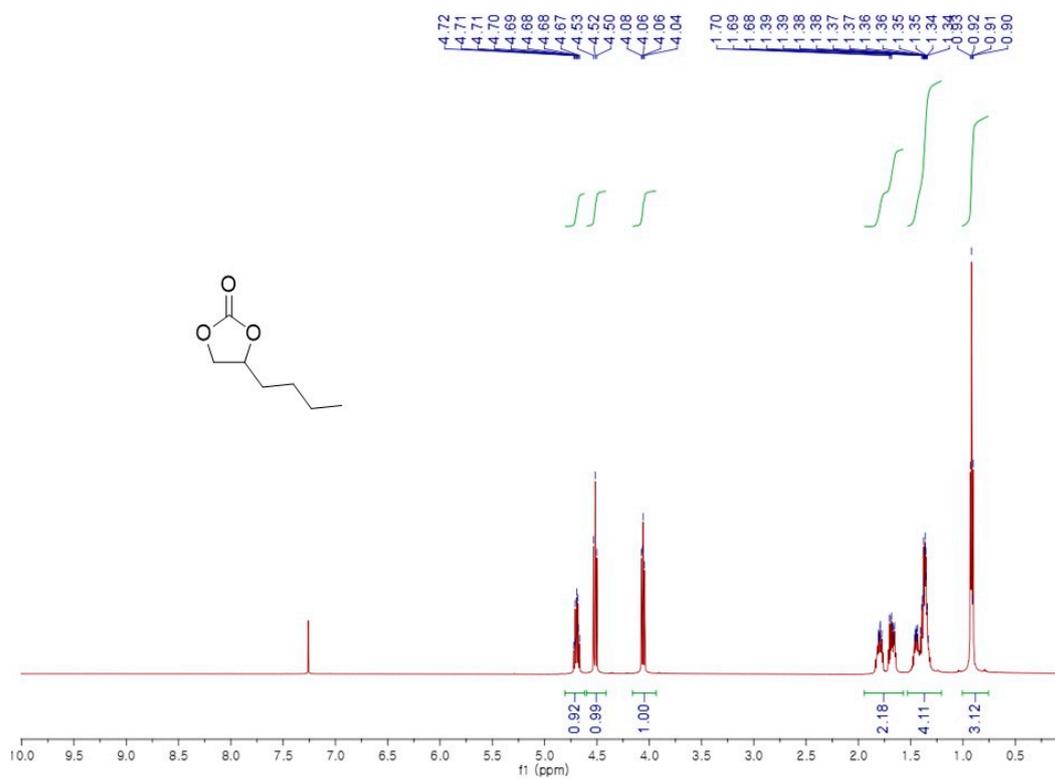
4-Methyl-1,3-dioxolan-2-one (2a)



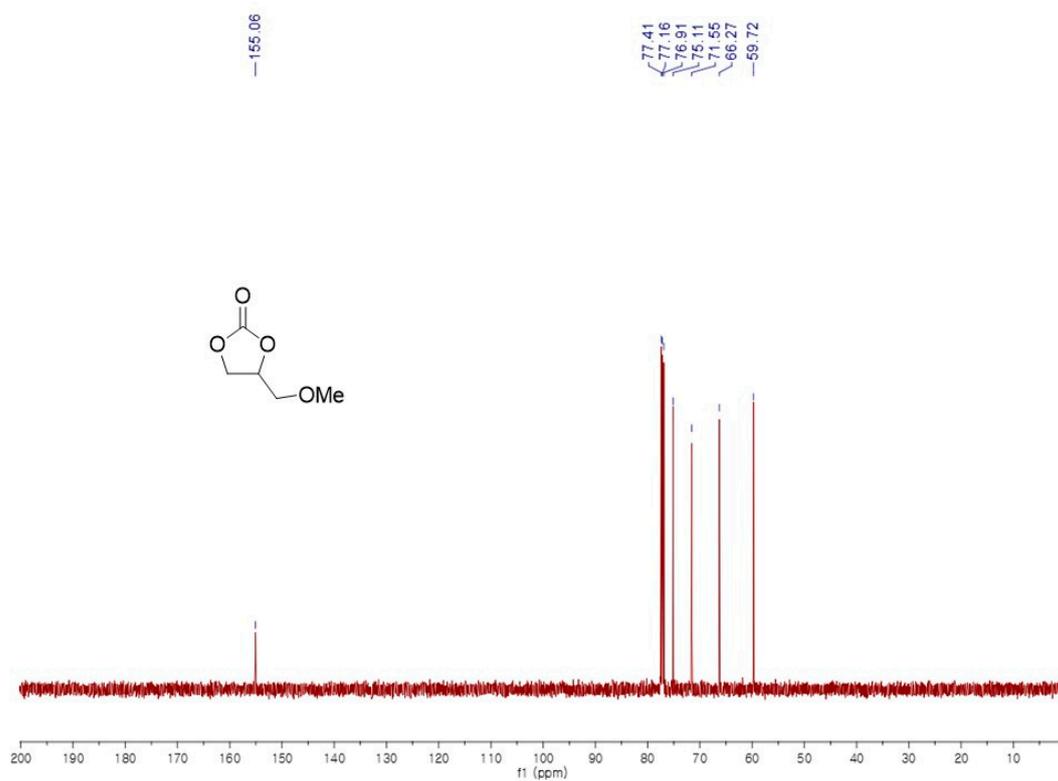
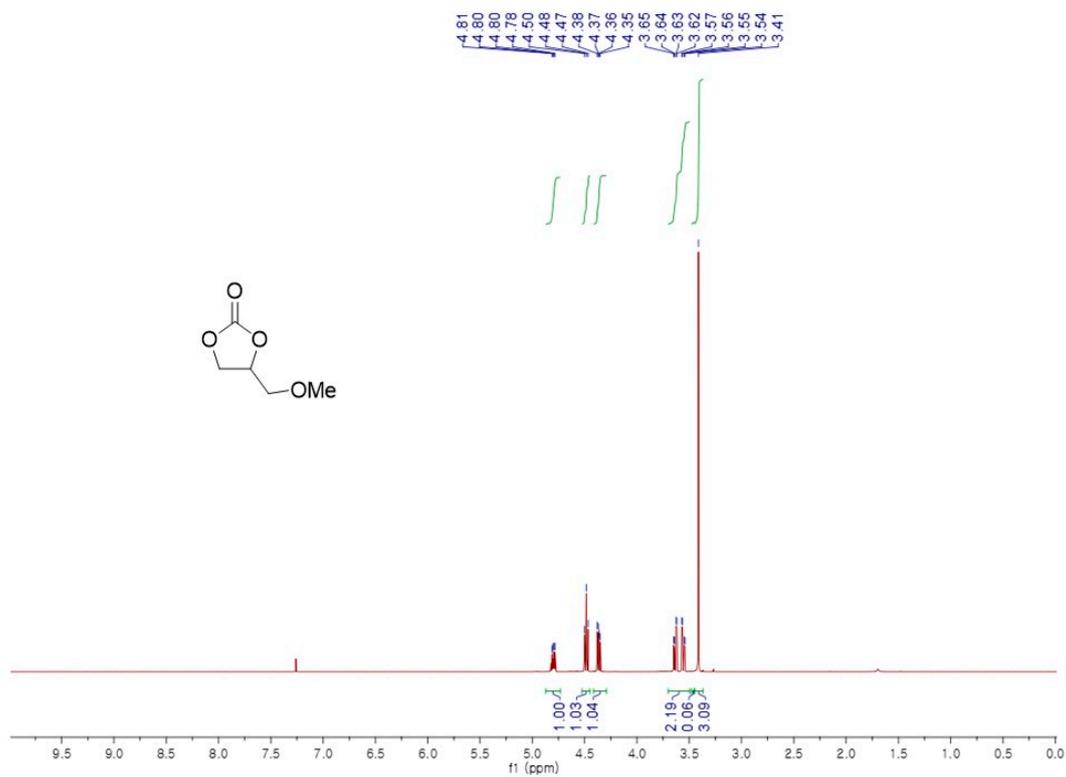
4-Ethyl-1,3-dioxolan-2-one (2b)



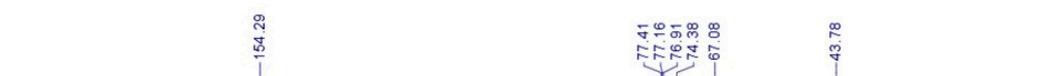
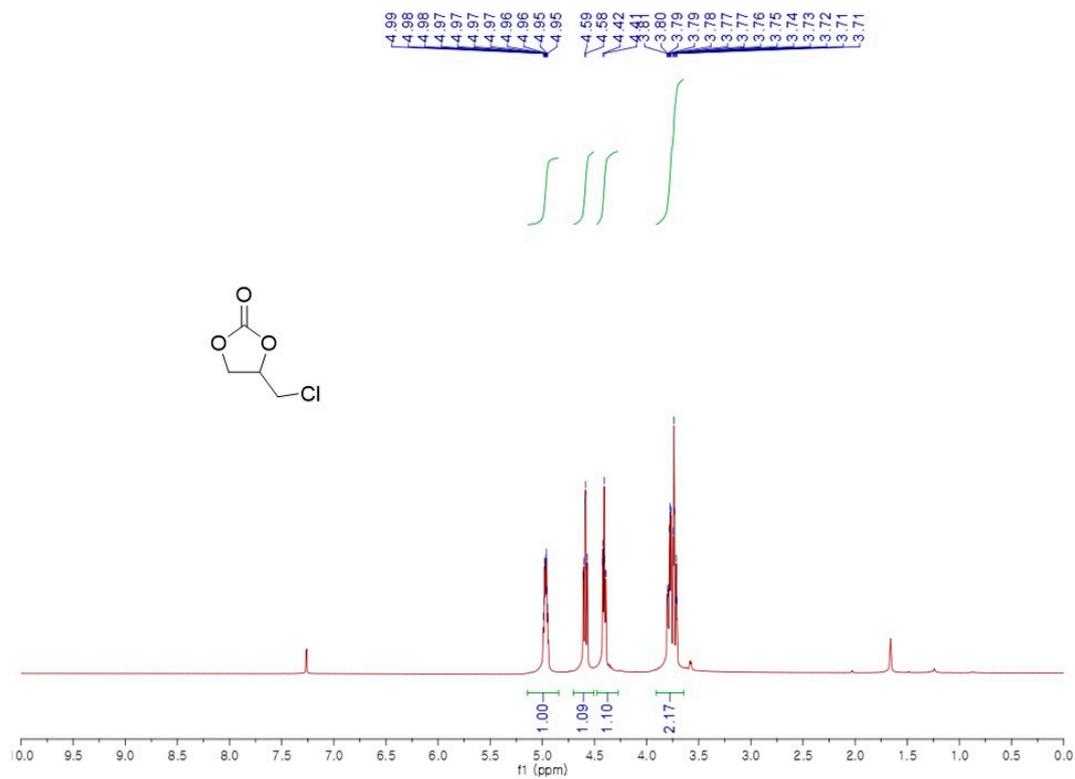
4-Butyl-1,3-dioxolan-2-one (2c)



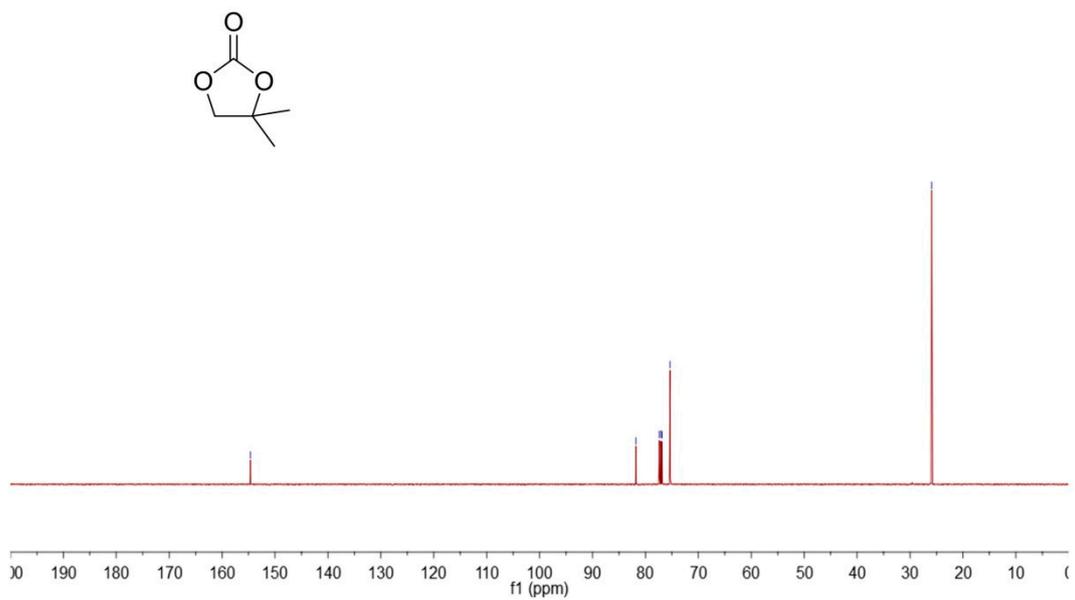
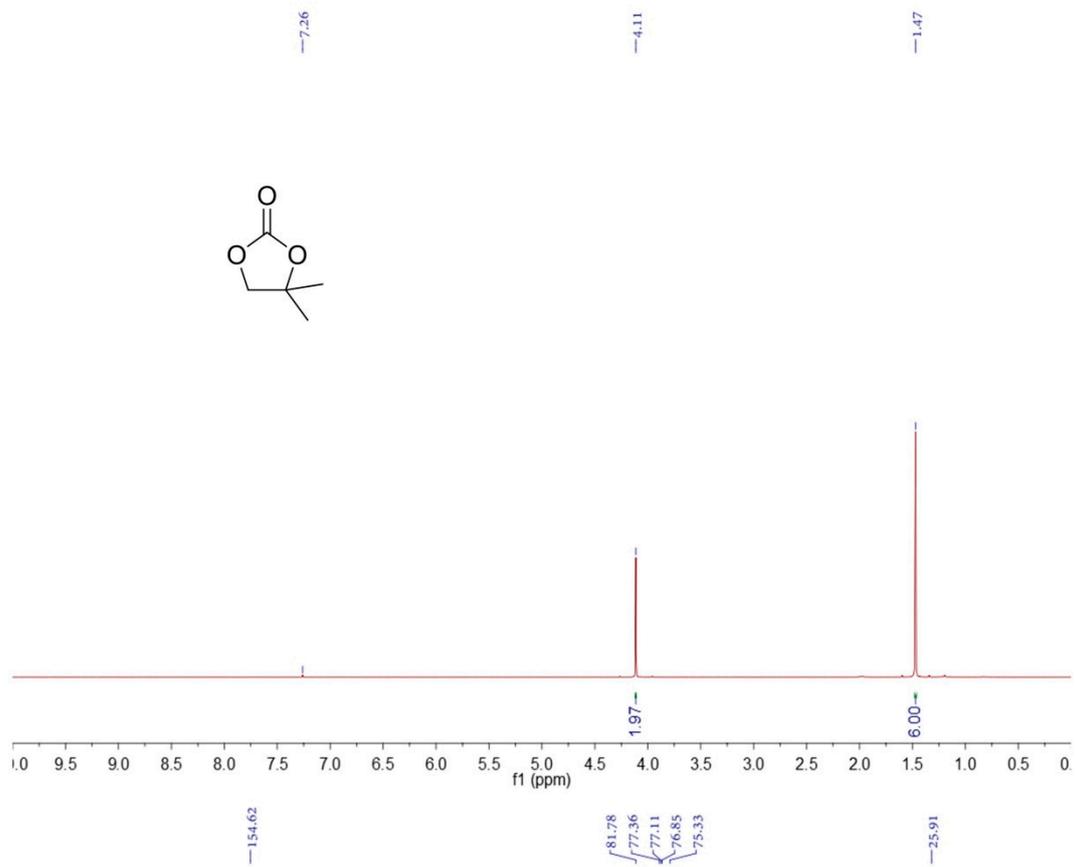
4-(Methoxymethyl)-1,3-dioxolan-2-one (**2d**)



4-(Chloromethyl)-1,3-dioxolan-2-one (**2e**)



4,4-Dimethyl-1,3-dioxolan-2-one (2f)



Hexahydrobenzo[d][1,3]dioxol-2-one (2g)

