Supporting Information

Catalytic CO_2 Fixation over a Robust Lactam-Functionalized Cu(II) Metal Organic Framework

Shagufi Naz Ansari[a+], *Pawan Kumar*[a+], *Anoop K. Gupta*[a], *Pradeep Mathur**[a] *and Shaikh M. Mobin*[a,b,c*]

[a] *Discipline of Chemistry,* [b]*Discipline of Metallurgy Engineering and Materials Science (MEMS),* [c]*Discipline of Biosciences and Biomedical Engineering (BSBE), Indian Institute of Technology Indore, Simrol, Khandwa Road, Indore 453552, India.*

*Corresponding author: Dr. Shaikh M. Mobin, E-mail: *xray@iiti.ac.in; Tel: +91 7312438752*

[+]Shagufi Naz Ansari and Pawan Kumar contributed equally to the work.

Table S1. Crystal structure and refinement parameters for **Cu-MOF**.

Parameters	**{[Cu(L)(DMF)]·1.5(H_2O)}$_n$ (Cu-MOF)**
Empirical formula	$C_{19}H_{19}CuN_2O_{7.5}$
Formula wt.	458.91
Crystal system	Trigonal
Space group	*R*-3
a, Å	21.8786(3)
b, Å	21.8786(3)
c, Å	21.3088(3)
α (deg)	90
β (deg)	90
γ (deg)	120
V, Å^3	8833.4(3)
Z	18
ρ_{calc} g/cm^3	1.461
μ, mm^{-1}	1.150
Temperature (K)	100(2)
θ max	29.118
F(000)	3978
Refl. collected	33671
Independent refl.	4978
GOOF	1.088
Final R indices (R_1[a], wR_2[b]) [I>2σ(I)]	R_1 = 0.0479, wR_2 = 0.0479
R indices (R_1[a], wR_2[b]) (all data)	R_1 = 0.1249, wR_2 = 0.1366
CCDC	1904186

[a]$R_1 = \sum(|Fo| - |Fc|)/\sum |Fo|$. [b]$R_2 = [\sum\{w(Fo^2 - Fc^2)^2\}/\sum\{w(Fo^2)^2\}]^{1/2}$.

Table S2. Selected bond distances (Å) and bond angles (º) in **Cu-MOF**.

{[Cu(L)(DMF)]·1.5(H_2O)}$_n$ (Cu-MOF)					
Bond Distances (Å)					
Cu01—Cu01	2.6116(6)	Cu01—O002	1.993(2)	Cu01—O003	1.966(2)
Cu01—O004	1.978(2)	Cu01—O005	1.954(2)	Cu01—O007	2.150(2)
O006—C00I	1.220(4)	N008—C00I	1.382(4)		
Bond Angles (°)					
O002–Cu01–Cu01	83.41(6)	O002–Cu01–O007	91.13(10)	O003–Cu01–Cu01	82.84(6)
O003–Cu01–O002	91.01(9)	O003–Cu01–O004	90.06(10)	O003–Cu01–O007	100.94(10)
O004–Cu01–Cu01	85.59(6)	O004–Cu01–O002	168.73(9)	O004–Cu01–O007	99.69(10)
O005–Cu01–Cu01	85.99(6)	O005–Cu01–O002	88.42(10)	O005–Cu01–O003	168.81(9)
O005–Cu01–O004	88.36(10)	O005–Cu01–O007	90.25(10)	O007–Cu01–Cu01	173.44(8)
C00Q–O007–Cu01	119.4(3)	O006–C00I–N008	126.2(3)	C00G–N008–C00L	120.4(3)
C00I–N008–C00G	127.0(3)	N00P–C00Q–O007	145.9(8)		

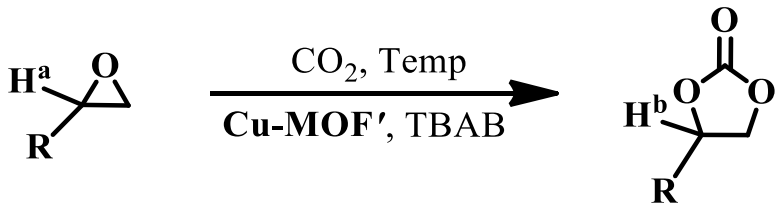
Table S3. ICP-MS data for **Cu-MOF** catalyst after 4 catalytic cycles.

Catalyst	**ICP-MS (ppm)**
Cu-MOF	0.45

(%) conversion calculation:

The conversion was calculated from 1H NMR according to equation (1). NMR results showed that there is no formation of side products. The sole product is only the cyclic carbonate.

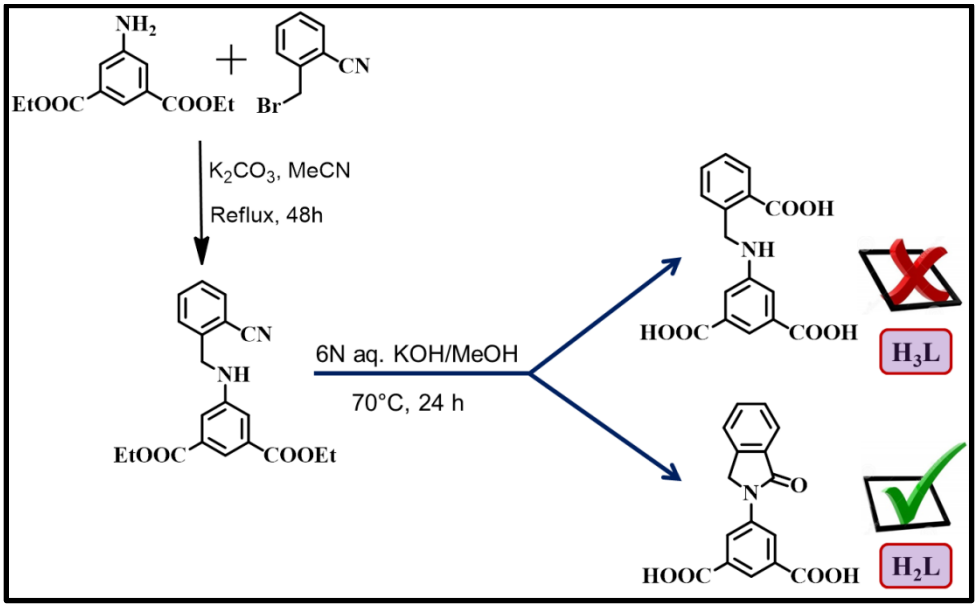
Conversion = *I*Hb / (*I*Ha+*I*Hb)



Ha and Hb belongs to the starting material and the product respectively

Synthesis of H_2L

The ligand H_2L was synthesized in several steps as shown in scheme S1.



Scheme S1. The synthetic scheme for preparation of **H_2L.**

Synthesis of diethyl 5-((2-cyanobenzyl)amino)isophthalate

In an N^2 atmosphere, 5-Aminoisophthalic acid diethyl ester (2 g, 8.4 mmol) was taken in a round-bottom flask and added dry acetonitrile (100 mL) and dry K_2CO_3 (1.7 g, 12.6 mmol) were mixed in a round-bottom flask under an inert atmosphere, and the mixture was stirred for 30 min at 80 °C. The mixture was treated with 2-(bromomethyl)benzonitrile (1.65 g, 8.4 mmol), and the resulting solution was refluxed for 24 h. At the end of this period, it was allowed to cool to room temperature and poured in ice-cold water (75 mL) to obtain a white solid that was collected by filtration and dried in air. Yield: 2.7g (91%). ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C, Me_4Si): δ = 8.8003(s, 2H, Ar-H), 8.4001 (s, 1H, N-H), 7.6911 (d, 1H, J = 6.88 Hz, Ar-H), 7.5380 - 7.4605 (m, 4H, Ar-H), 4.9692 (s, 2H), 4.4153 (q, 4H, J = 7.18 Hz, -CH_2-), 1.4148 (t, 6H, J = 7.16 Hz, -CH_3) ppm (**Figure S1**); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C, Me_4Si): δ =165.97,

150.92, 145.77, 138.05, 131.81, 131.32, 128.28, 124.71, 124.43, 122.95, 121.73, 101.83, 61.58, 53.46, 14.44 ppm (**Figure S2**); ESI-MS: m/z $[M+H]^+$ 353.15 (100%) (**Figure S3**).

Synthesis of 5-(1-oxoisoindolin-2-yl)isophthalic acid (H_2L)

Compound obtained as above (2 g, 5.17 mmol) was hydrolyzed by refluxing it with 6(N) NaOH solution (20 mL) for 24 h. After cooling to 5 °C, the resulting solution was acidified with 6(N) HCl solution to obtain a white precipitate. It was collected by filtration, washed thoroughly with water, and dried in air. Yield: 1.35 g (80%). It has been characterized by ^{1}H, ^{13}C NMR, mass Spectrometry, elemental analysis. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 °C, Me_4Si): δ = 8.6766 (s, 2H, Ar-H), 8.2290 (s, 1H, -NH), 7.7869 – 7.7679 (d, 1H, J = 7.60Hz, Ar-H), 7.6720 – 7.6572 (m, 2H, Ar-H), 7.5433 – 7.5037 (m, 1H, Ar-H), 5.1083 (s, 2H, -CH_2-) ppm (**Figure S4**); ^{13}C NMR (DMSO-d_6, 100 MHz, 25 °C, Me_4Si): δ = 167.64, 167.05, 141.68, 140.66, 133.01, 132.66, 132.50, 128.83, 125.60, 124.04, 123.94, 123.69, 50.97 ppm (**Figure S5**); ESI-MS: m/z $[M]^+$ 298.07 (100) (**Figure S6**).

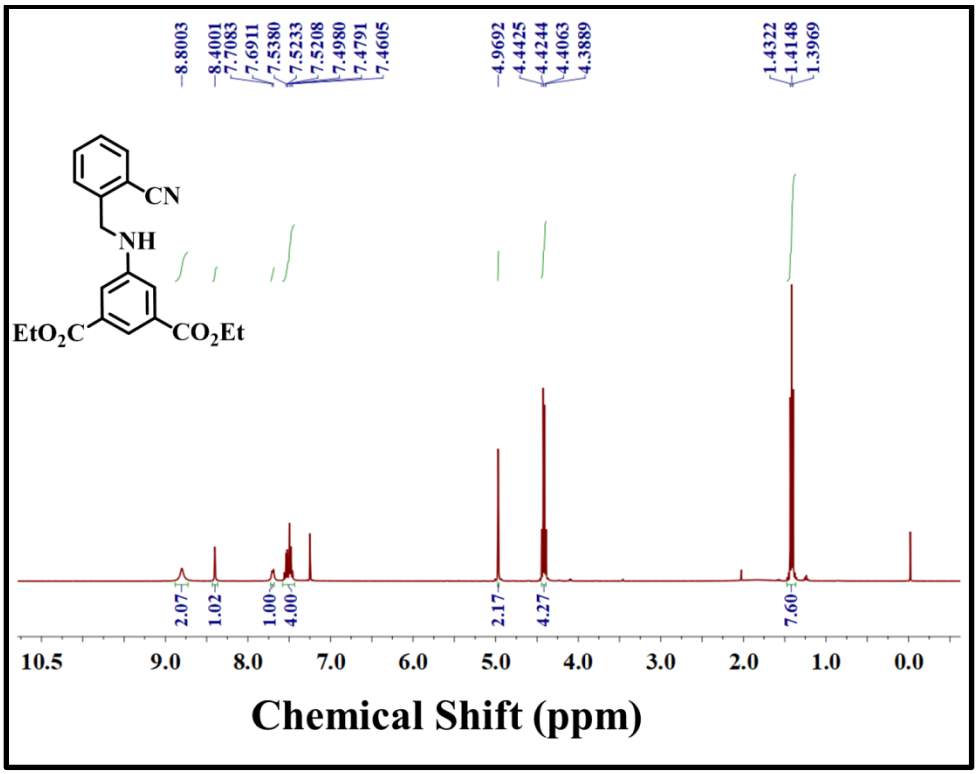


Figure S1. The ^{1}H NMR spectrum of diethyl 5-(2-cyanobenzyloxy)isophthalate.

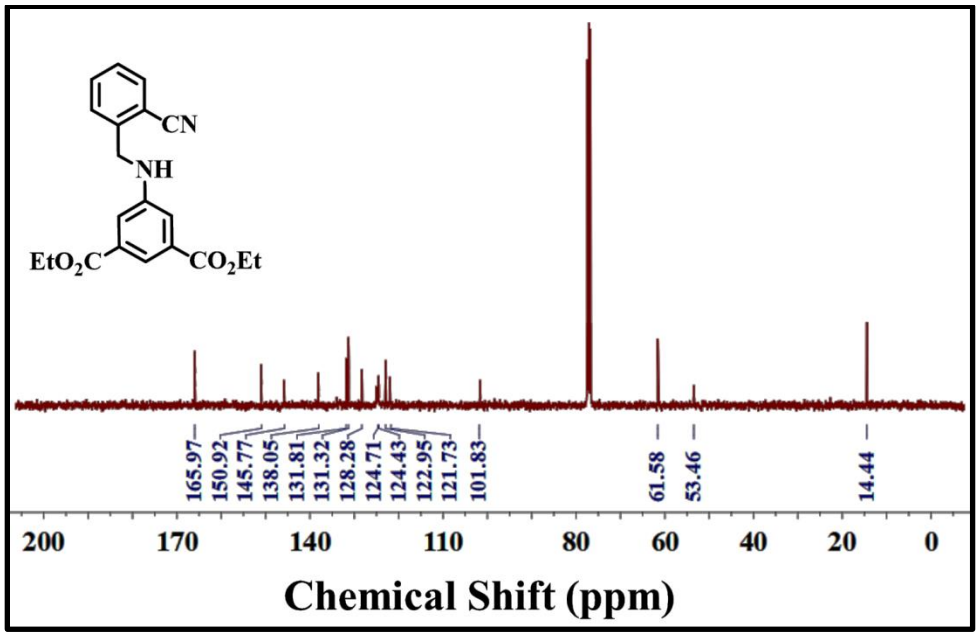


Figure S2. The ^{13}C NMR spectrum of diethyl 5-(2-cyanobenzyloxy)isophthalate.

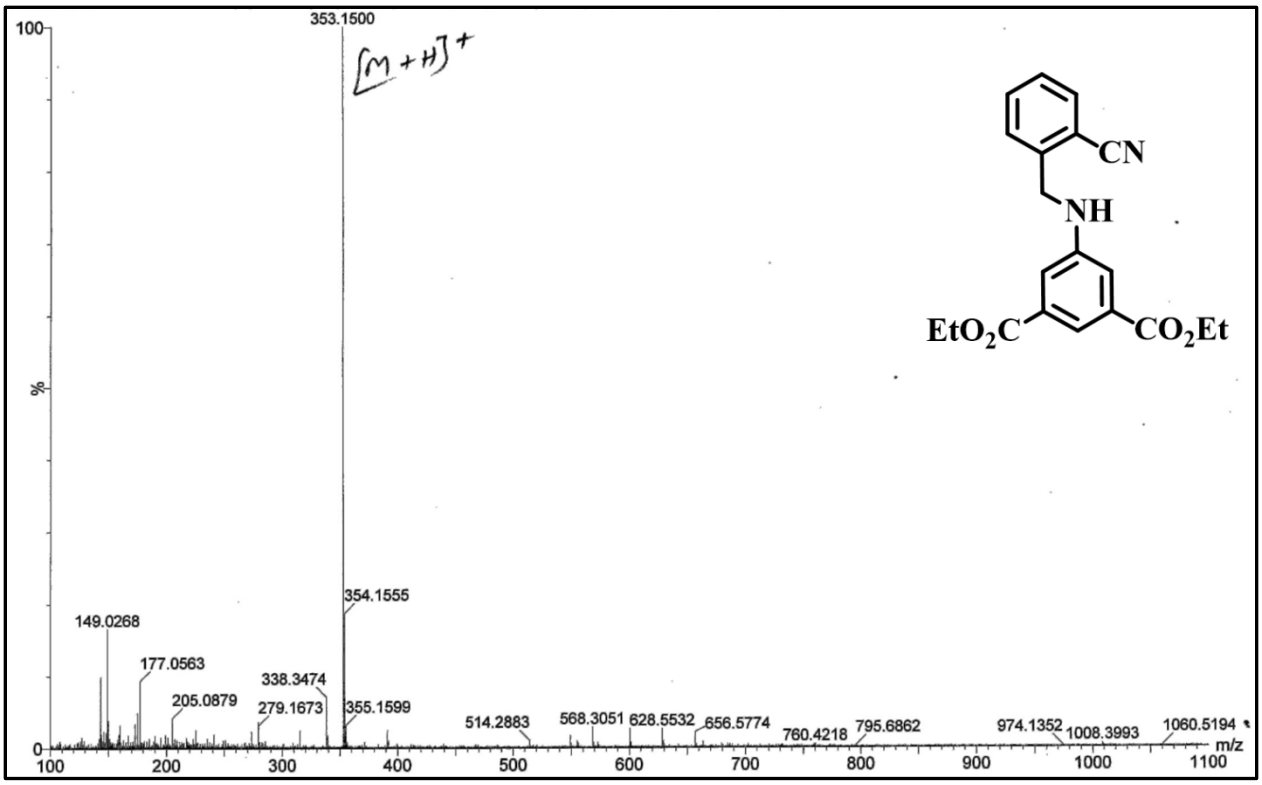


Figure S3. ESI-MS spectrum of diethyl 5-(2-cyanobenzyloxy)isophthalate.

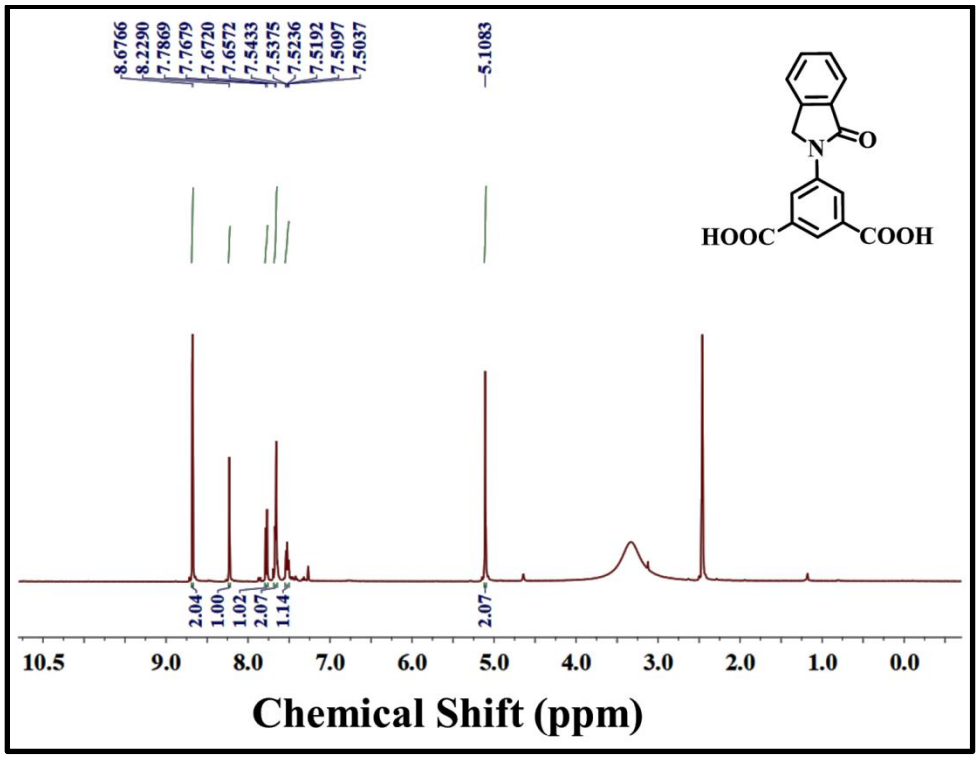


Figure S4. The ^{1}H NMR spectrum of 5-(2-carboxybenzyloxy)isophthalic acid (**H_2L**).

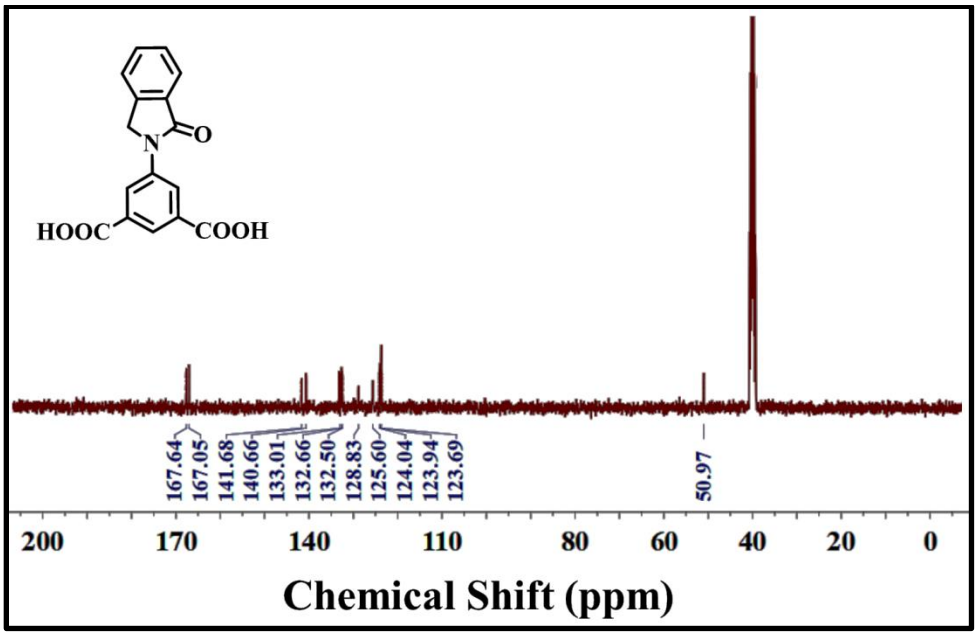


Figure S5. The ^{13}C NMR spectrum of 5-(2-carboxybenzyloxy)isophthalic acid (**H_2L**).

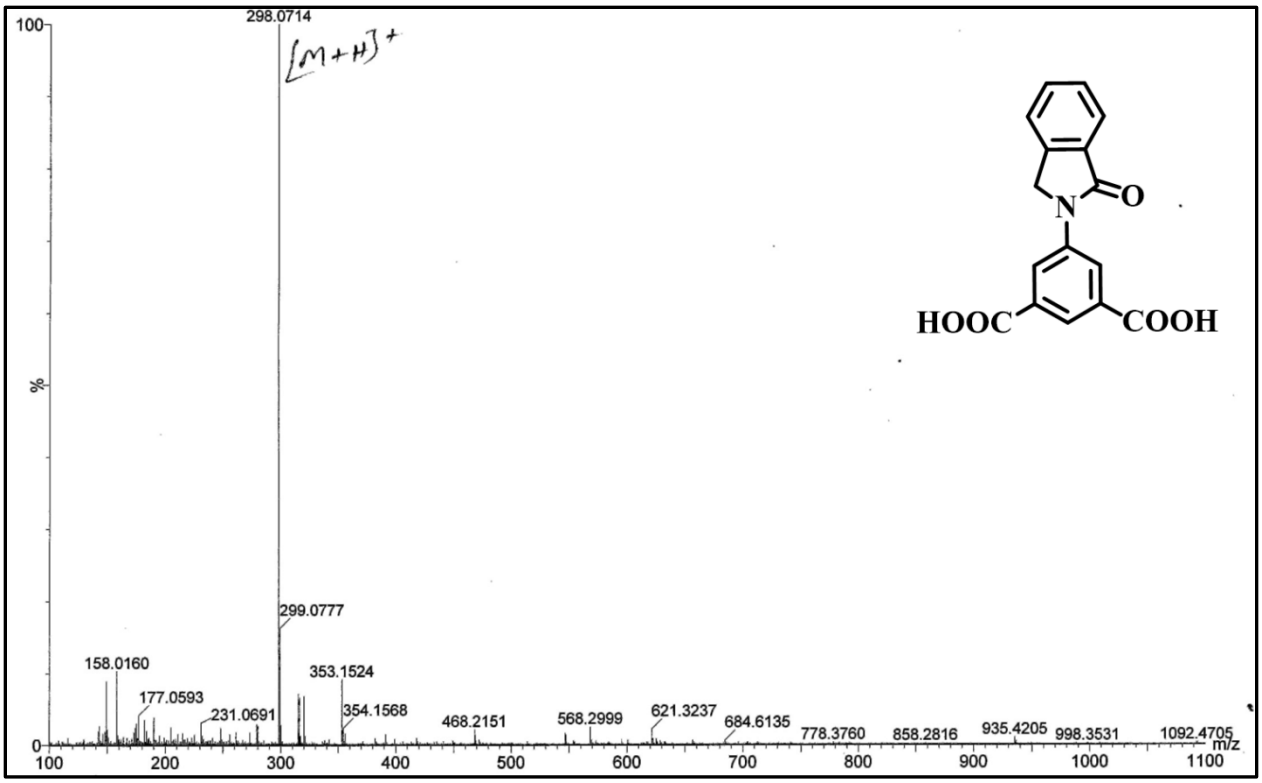


Figure S6. ESI-MS spectrum of 5-(2-carboxybenzyloxy)isophthalic acid (**H_2L**).

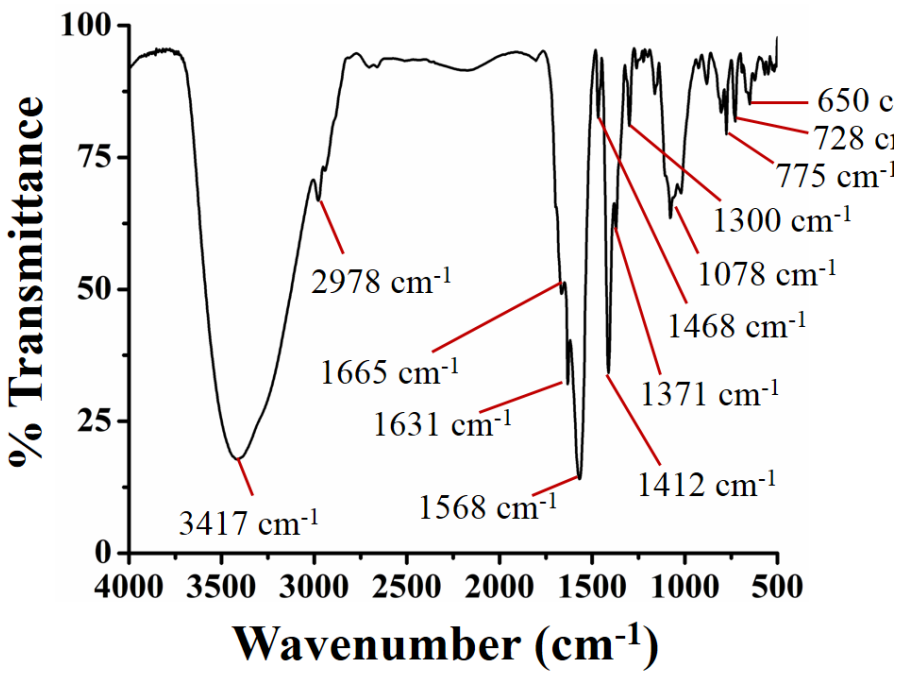


Figure S7. FT-IR spectrum of **Cu-MOF**.

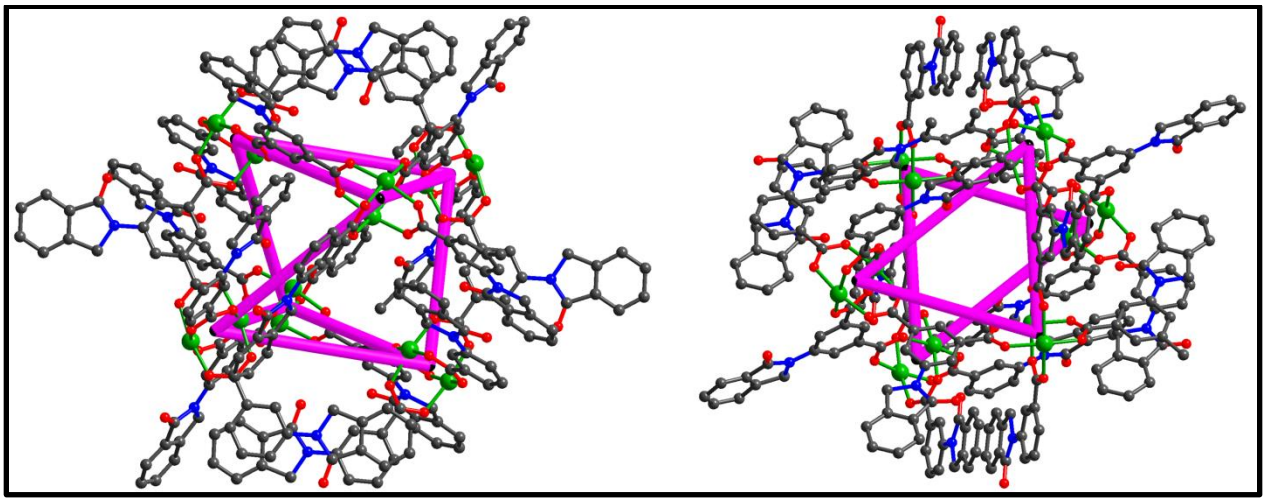


Figure S8. Representation of supramolecular building block (SBB) in **Cu-MOF**.

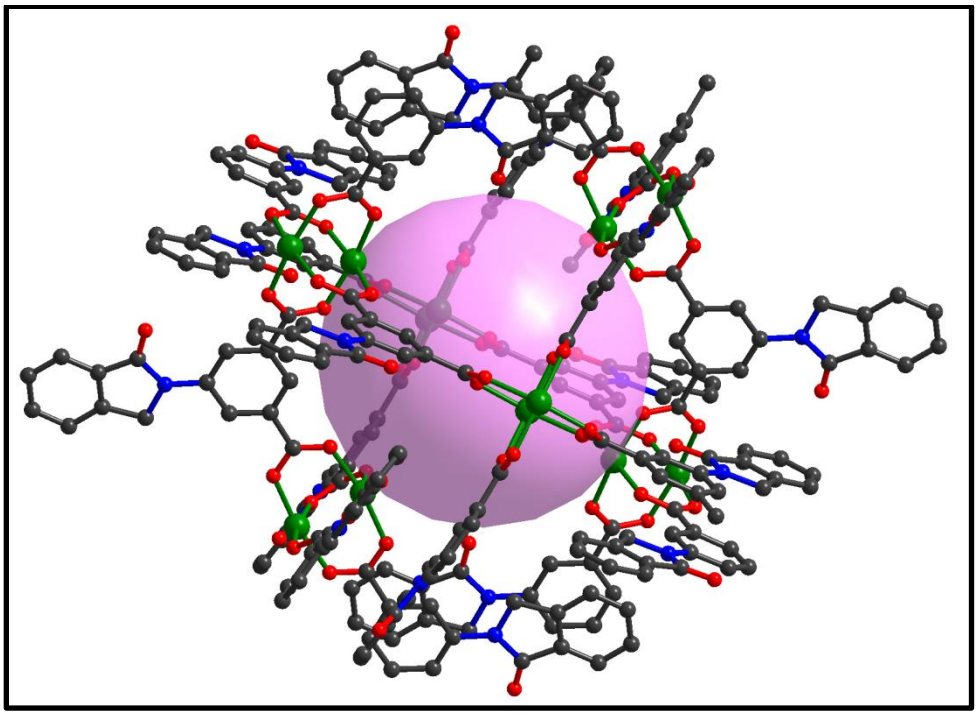


Figure S9. Representation of the internal spherical cage in the SBB of the **Cu-MOF**.

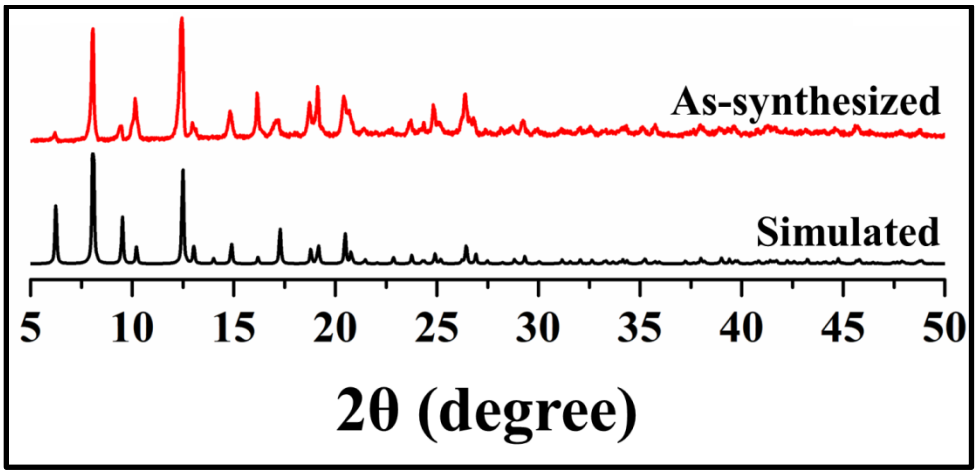


Figure S10. Powder X-ray diffraction patterns of simulated (Black) and as-synthesized (Red) of **Cu-MOF**.

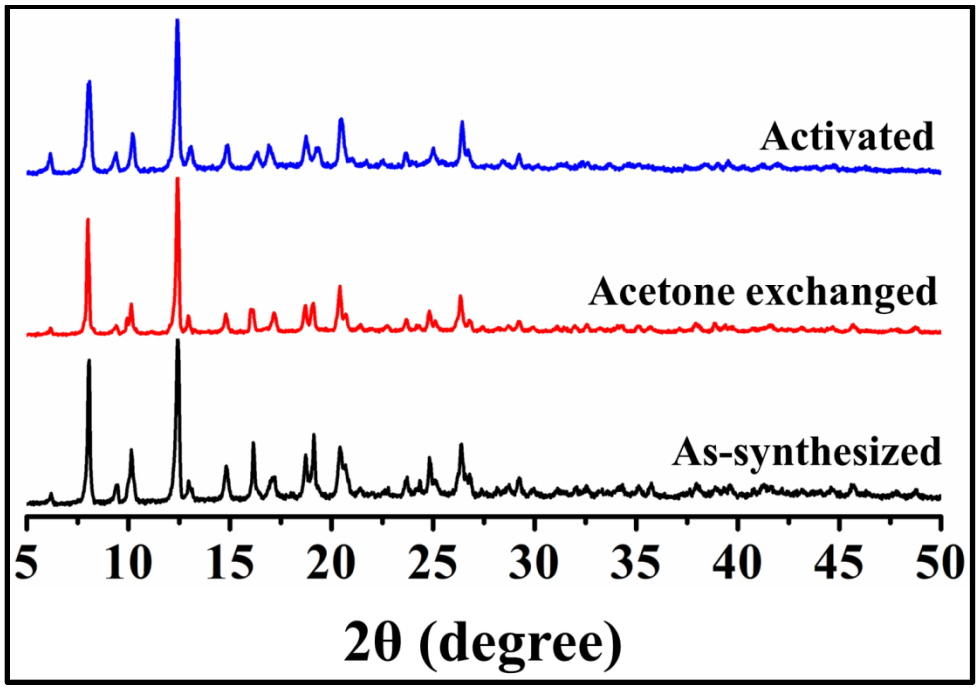


Figure S11. Powder X-ray diffraction patterns of simulated (Black) and as-synthesized (Red) of **Cu-MOF**.

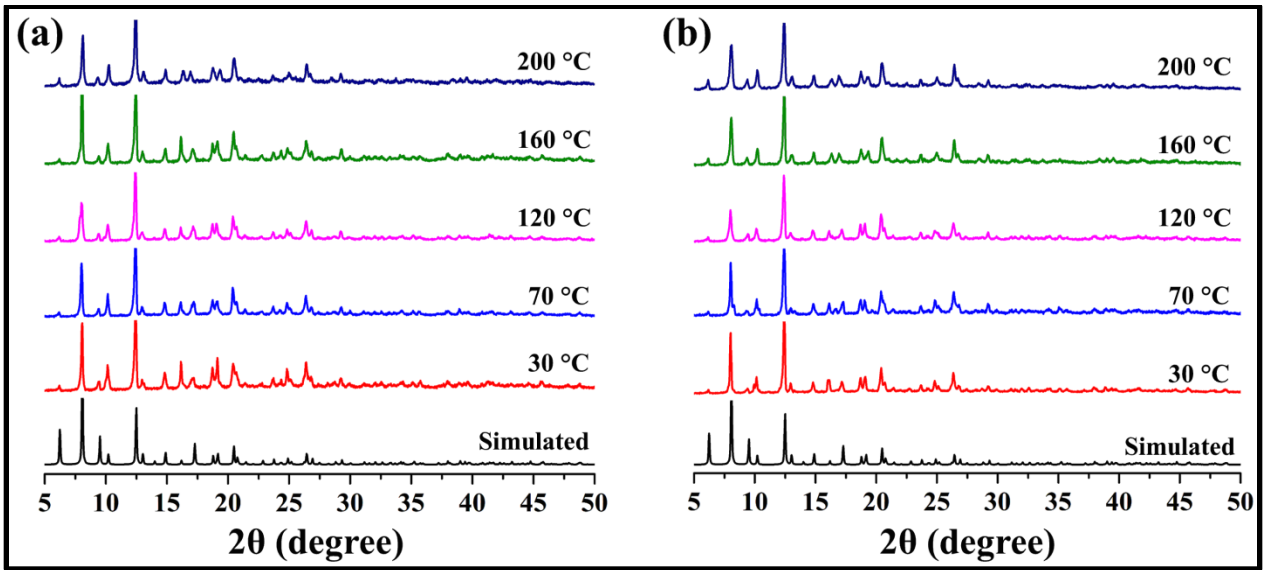


Figure S12. Powder X-ray diffraction patterns of simulated (Black) and as-synthesized (Red) of **Cu-MOF**.

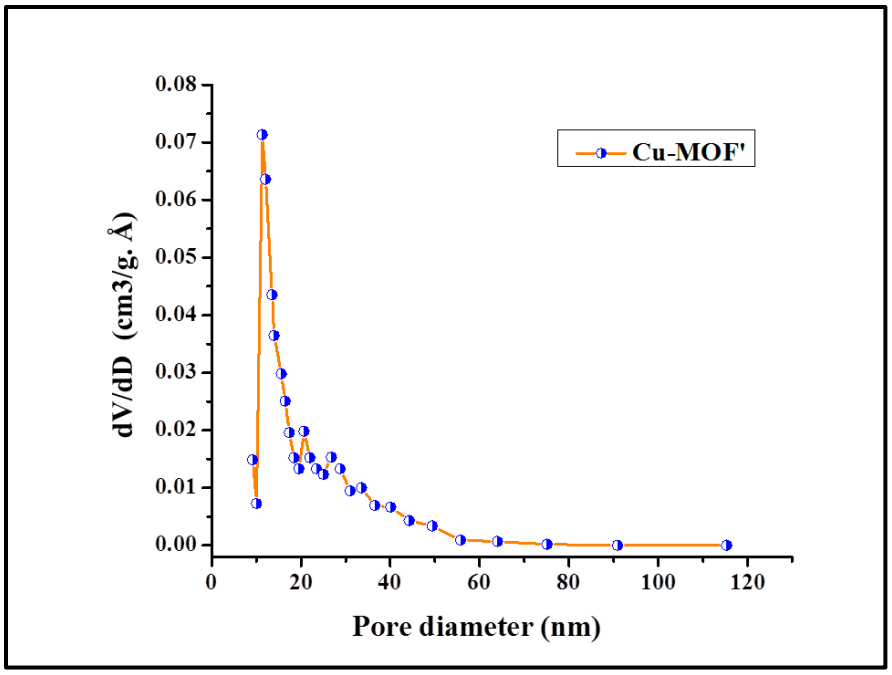


Figure S13. Pore-size distribution calculated from the isotherms.

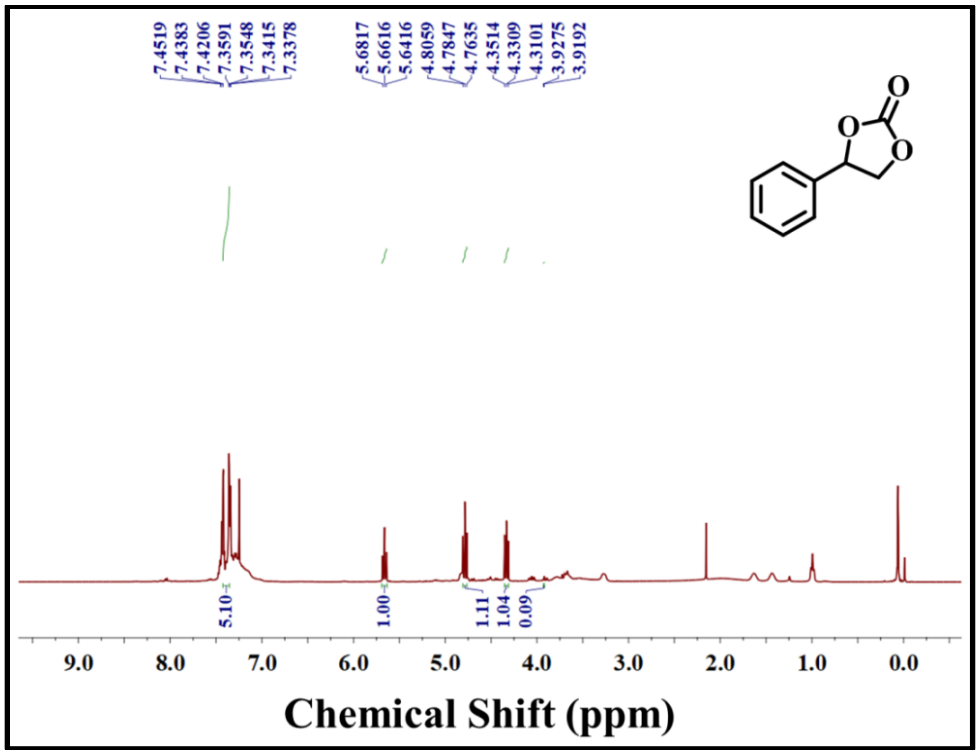


Figure S14. ^{1}H NMR of 4-phenyl-1,3-dioxolan-2-one: (400 MHz, $CDCl_3$): δ = 7.4519 – 7.3378 (m, 5H, Ar–H), 5.6616 (t, *J* = 8.04 Hz, 1H, -CH), 4.7847 (t, *J* = 8.48 Hz, 1H, -CH_2), 4.3309 (t, *J* = 8.2 Hz, 1H, -CH_2) ppm..

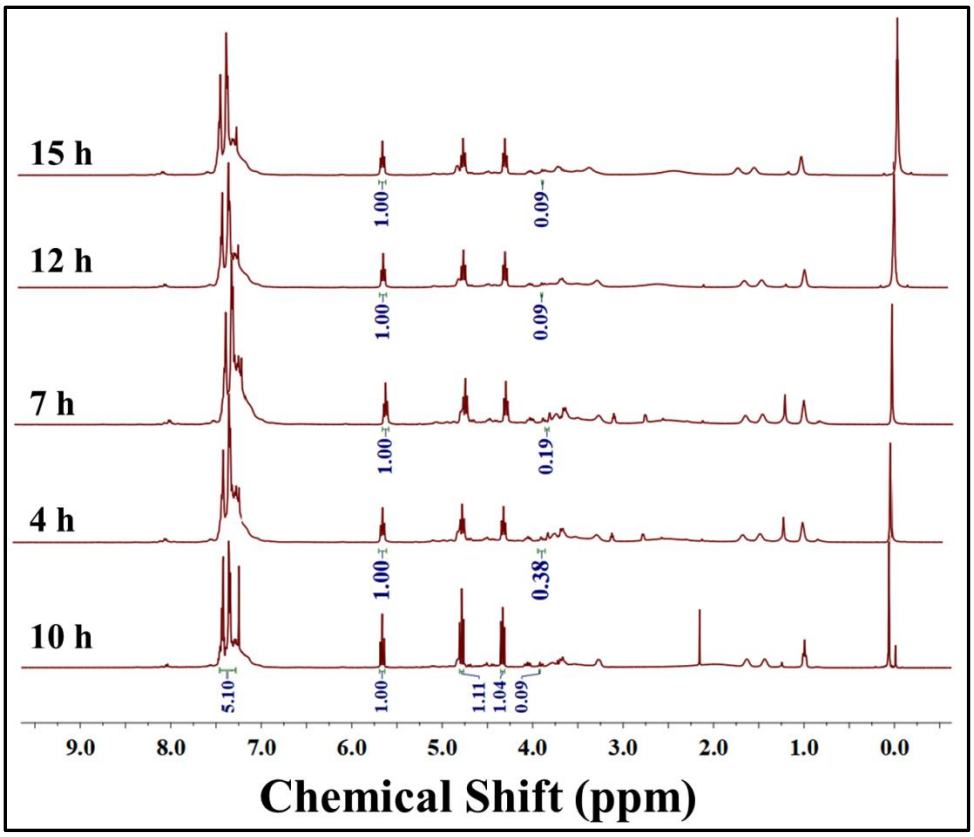


Figure S15. ^{1}H NMR of 4-phenyl-1,3-dioxolan-2-one at different time.

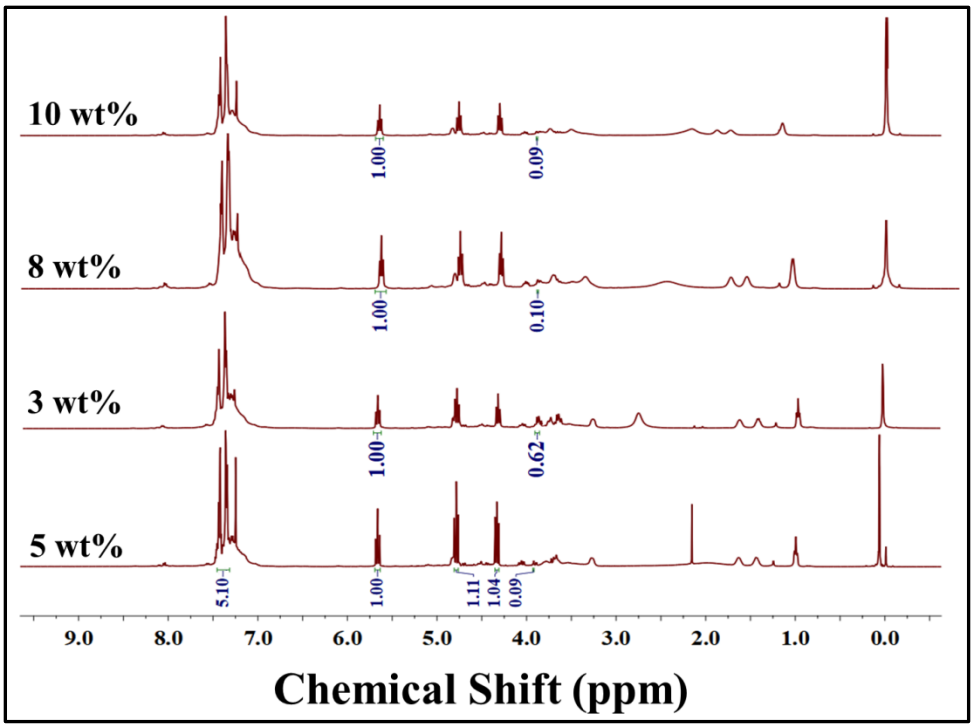


Figure S16. ^{1}H NMR of 4-phenyl-1,3-dioxolan-2-one at different catalyst loading.

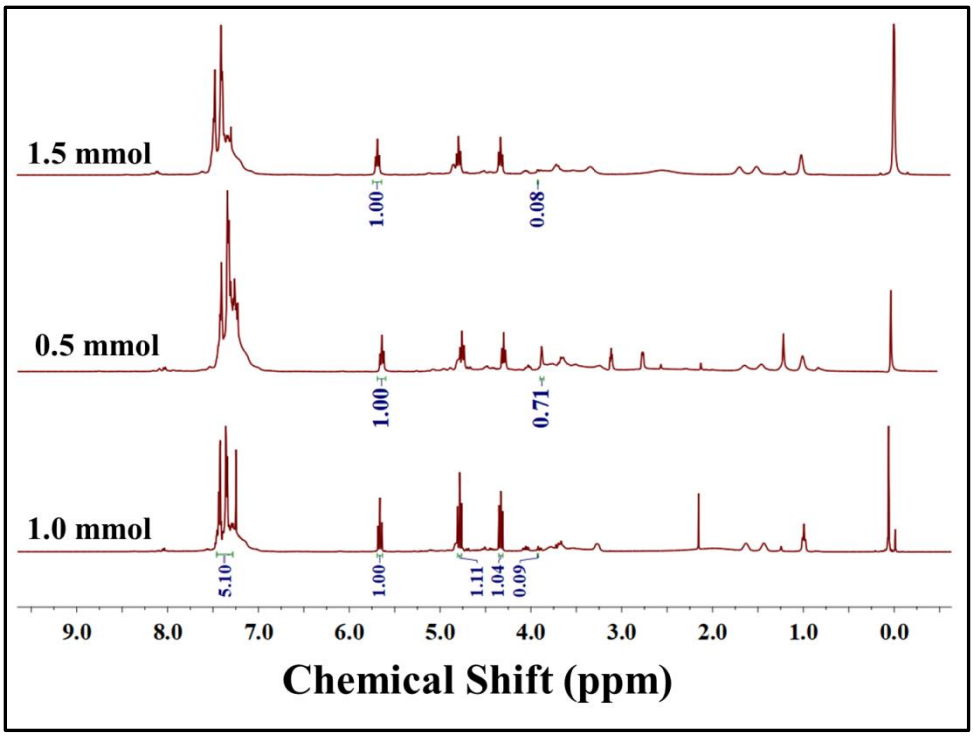


Figure S17. ^{1}H NMR of 4-phenyl-1,3-dioxolan-2-one at different co-catalyst loading.

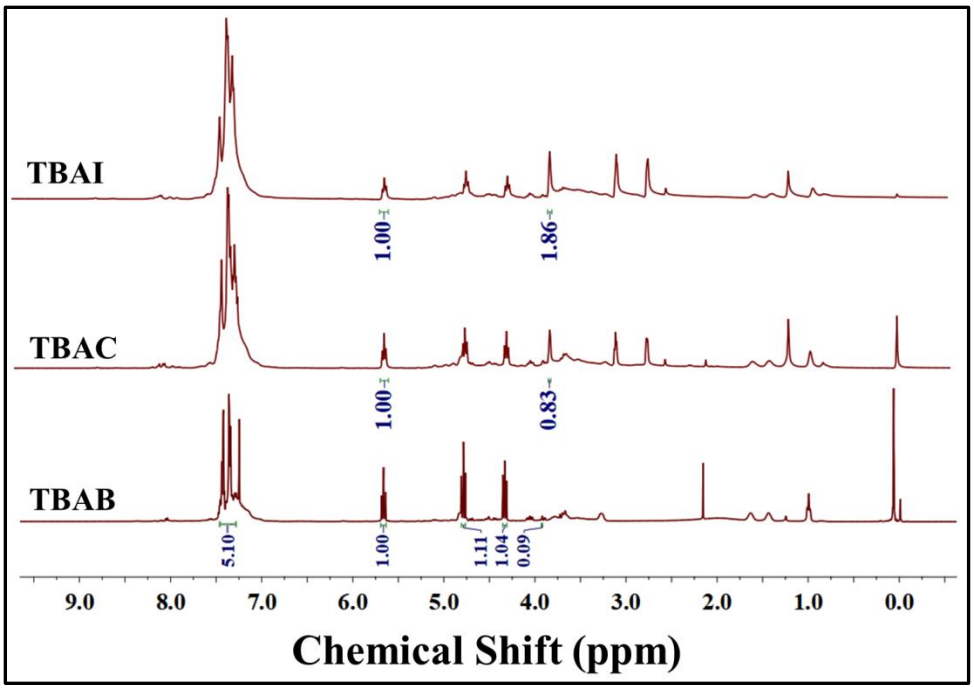


Figure S18. ^{1}H NMR of 4-phenyl-1,3-dioxolan-2-one after utilizing the different tetrabutyl ammonium halide.

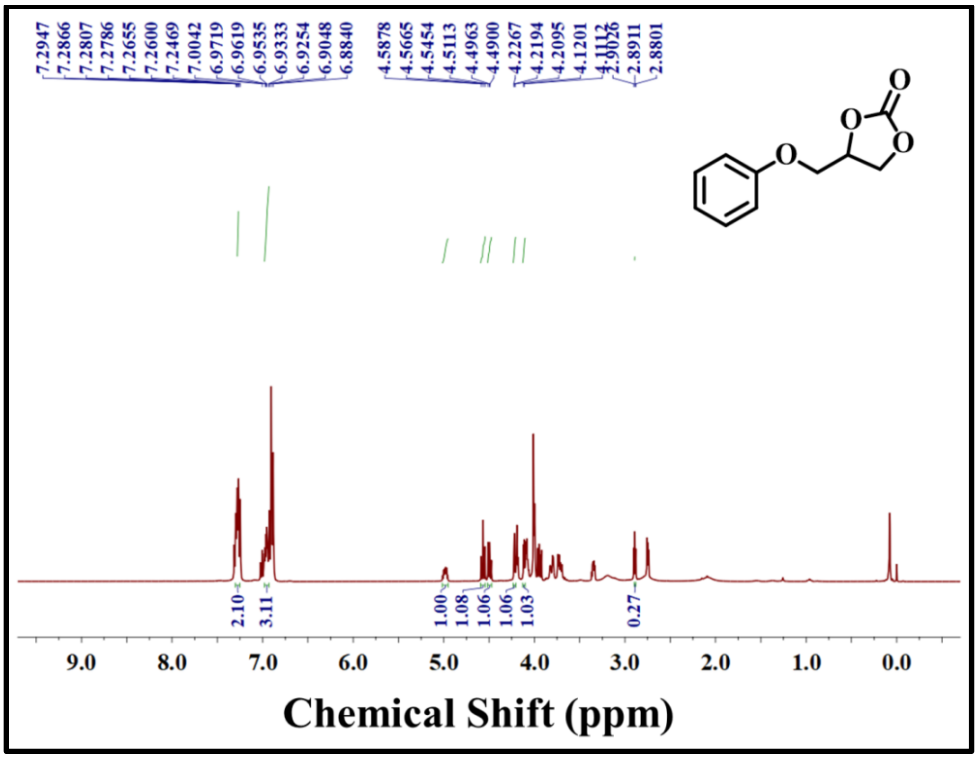


Figure S19. ^{1}H NMR of 4-(phenoxymethyl)-1,3-dioxolan-2-one: (400 MHz, $CDCl_3$): δ = 7.2947 – 7.2469 (m, 2H, Ar–H), 7.0042 – 6.8840 (m, 3H, Ar–H), 5.0019 – 4.9568 (m, 1H, -CH), 4.5665 (t, J = 8.52 Hz, 1H, -CH_2), 4.5113 – 4.4749 (m, 1H, -CH_2), 4.2267 – 4.2095 (m, 1H, -CH_2), 4.1201 – 4.1112 (m, 1H, -CH_2) ppm.

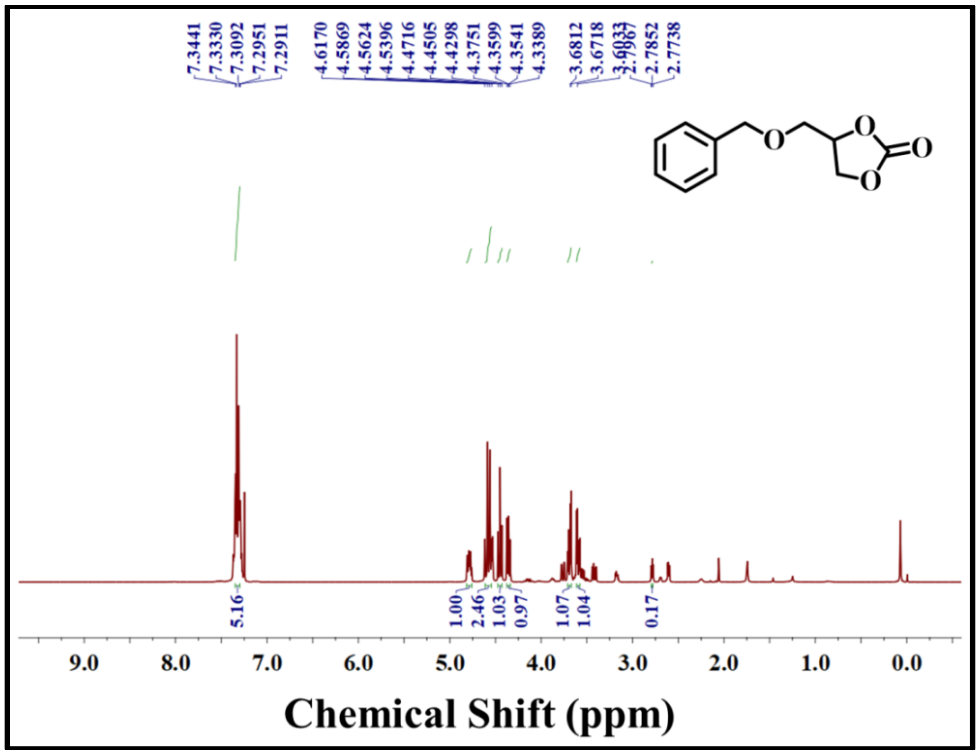


Figure S20. ^{1}H NMR of 4-((benzyloxy)methyl)-1,3-dioxolan-2-one: (400 MHz, $CDCl_3$): δ = 7.3441 – 7.2911 (m, 5H, Ar-H), 4.8158 – 4.7609 (m, 1H, -CH), 4.6170 – 4.5396 (m, 2H, -CH_2), 4.4505 (t, J = 8.32 Hz, 1H, -CH_2), 4.3751 – 4.3389 (m, 1H, -CH_2) 3.7086 – 3.6718 (m, 1H, -CH_2), 3.6126 – 3.5759 (m, 1H, -CH_2) ppm.

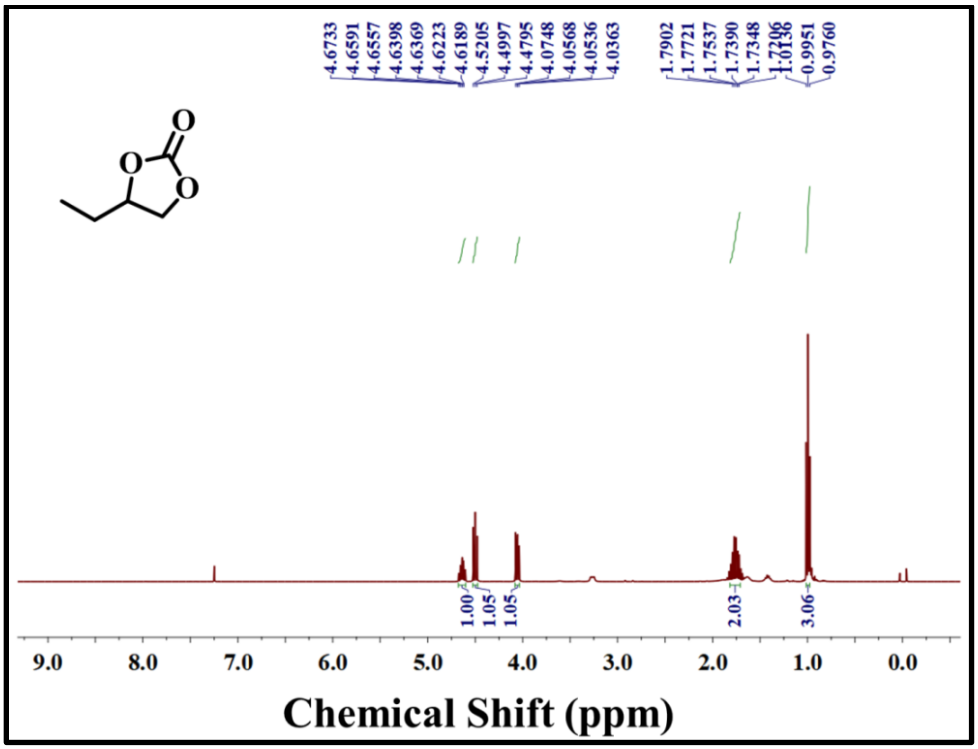


Figure S21. ^{1}H NMR of 4-ethyl-1,3-dioxolan-2-one: (400 MHz, $CDCl_3$): δ = 4.6557 – 4.6223 (m, 1H, -CH), 4.4997 (t, J = 8.32 Hz, 1H, -CH_2), 4.0748 – 4.0363 (m, 1H, -CH_2), 1.8260 – 1.6852 (m, 2H, -CH_2), 0.9951 (t, J = 7.40 Hz, 3H, -CH_3) ppm.

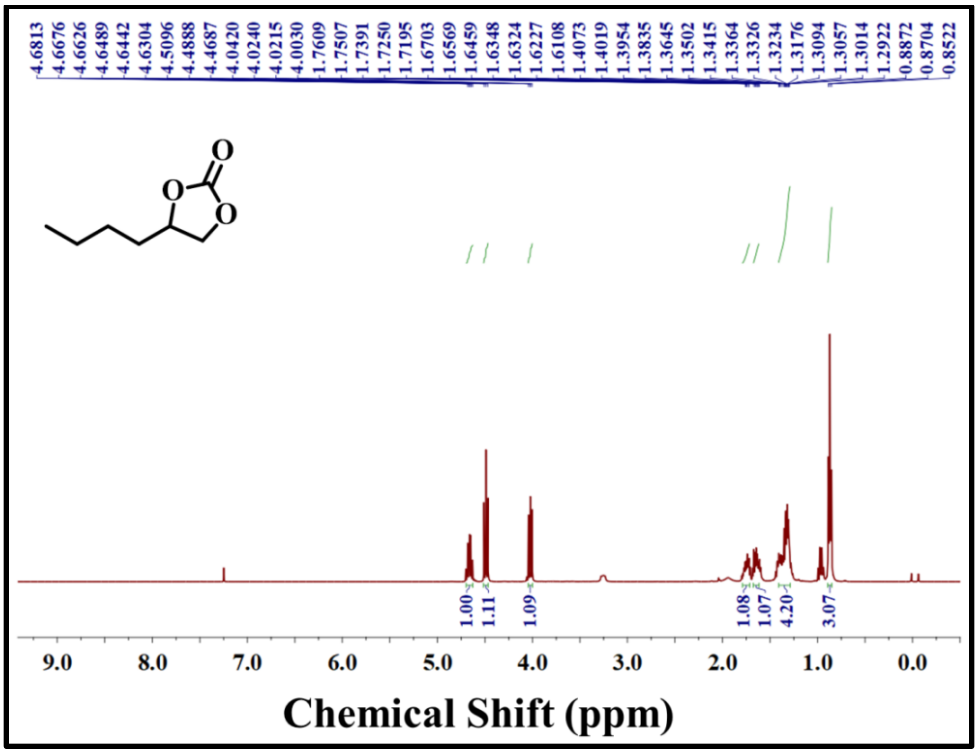


Figure S22. ^{1}H NMR of 4-butyl-1,3-dioxolan-2-one: (400 MHz, $CDCl_3$): δ = 4.7003 – 4.6304 (m, 1H, -CH), 4.4888 (t, J = 8.32 Hz, 1H, -CH_2), 4.0420 – 4.0030 (m, 1H, -CH_2), 1.7609 – 1.6108 (m, 2H, -CH_2), 1.4019 – 1.2922 (m, 4H, -CH_2-CH_2), 0.8704 (t, J = 6.72 Hz, 3H, -CH_3) ppm.

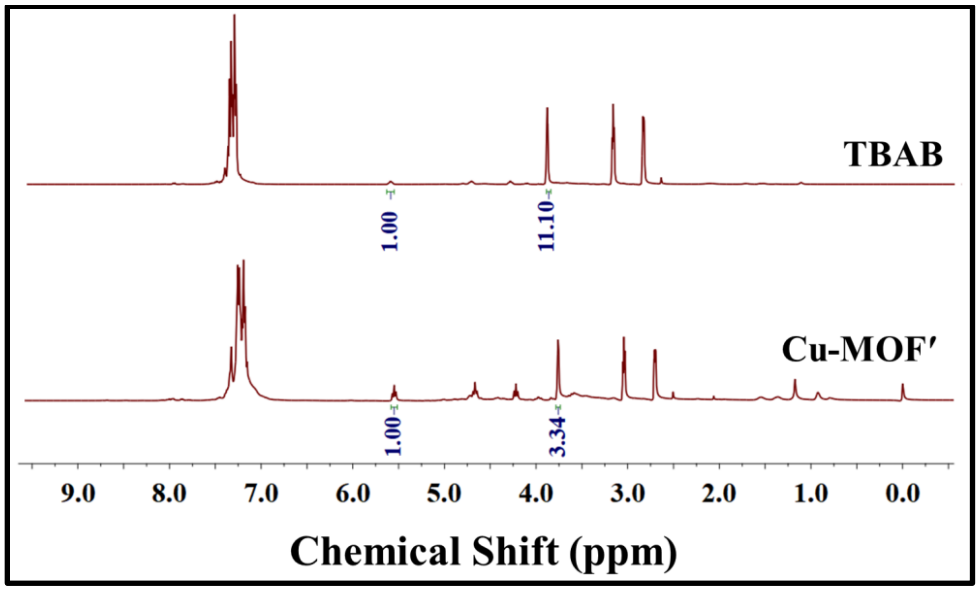


Figure S23. ^{1}H NMR of 4-phenyl-1,3-dioxolan-2-one for the control experiments.

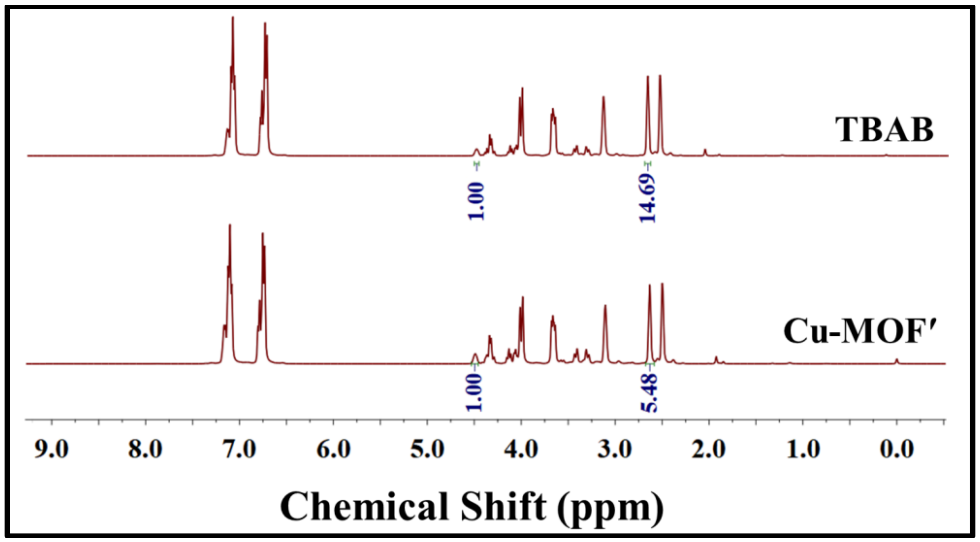


Figure S24. ^{1}H NMR of 4-(phenoxymethyl)-1,3-dioxolan-2-one for the control experiments.

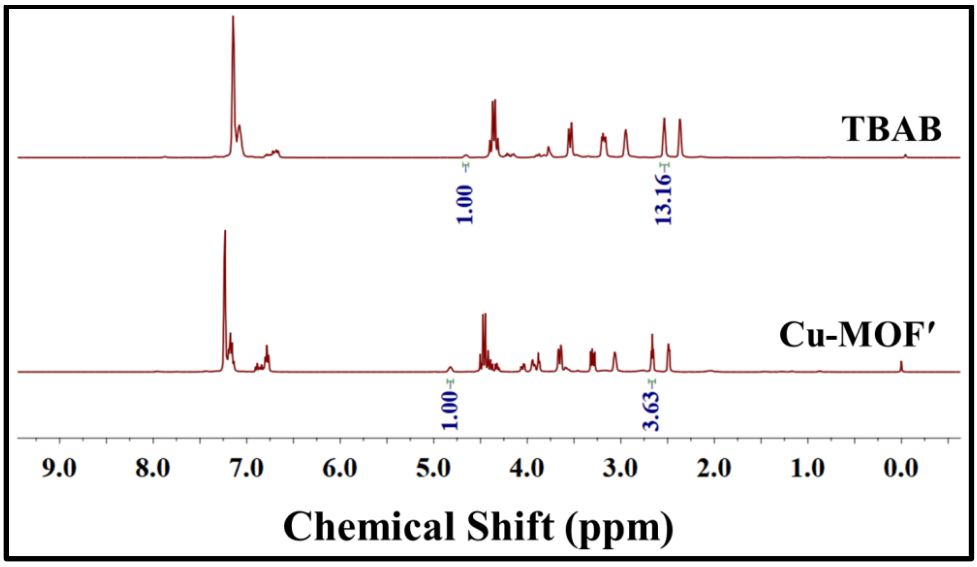


Figure S25. ^{1}H NMR of 4-((benzyloxy)methyl)-1,3-dioxolan-2-one for the control experiments.

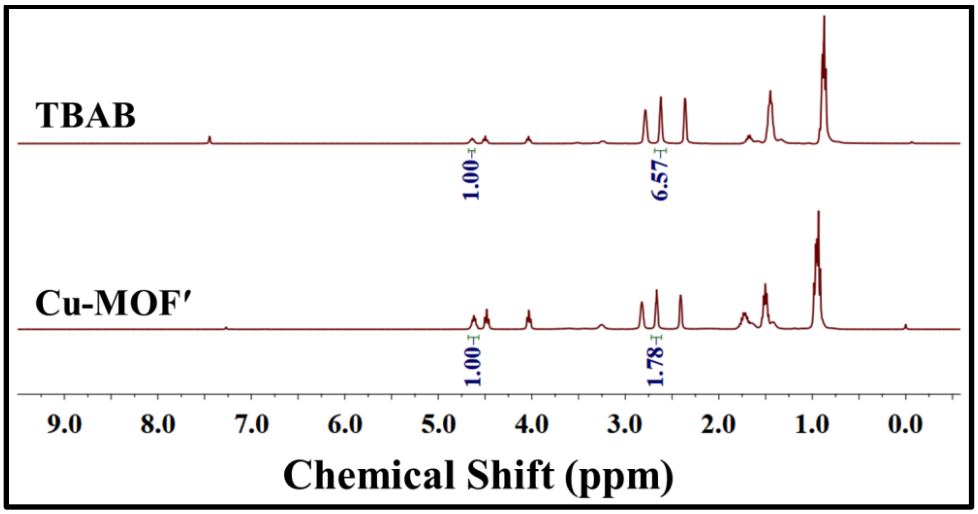


Figure S26. ^{1}H NMR of 4-ethyl-1,3-dioxolan-2-one for the control experiments.

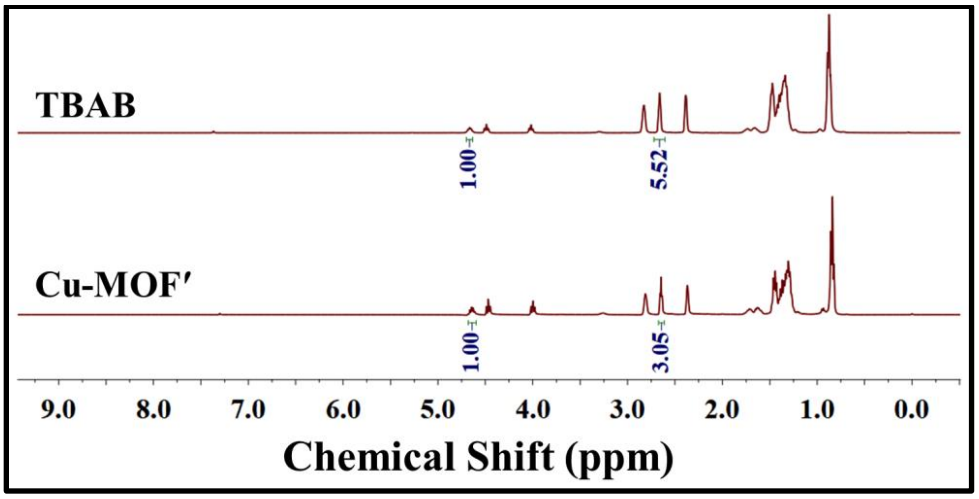


Figure S27. ^{1}H NMR of 4-butyl-1,3-dioxolan-2-one for the control experiments.