Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

An uncoordinatedly tertiary nitrogen based tricarboxylate Calcium network with Lewis acid-base dual catalytic sites for cyanosilylation of aldehydes

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Contents

1. General Information

All reagents were purchased from Energy Chemical and used without further purification. ^1H NMR and ^{13}C NMR were recorded on Bruker Avance III DM 600 MHz. IR spectrum on KBr pellet was obtained using a Nicolet iS50 spectrometer in the region of 4000-400 cm^{-1}. ~~UV-vis spectrum were tested on UV 25500 UV/vis/near-IR spectrophotometer.~~ PXRD patterns were measured on Rigaku D/Max-2500 diffractometer with Cu target tube at 40 kV and 30 mA. Thermogravimetric analyses (TGA) were performed on Shanghai yinnuo 1000 B under N_2 atmosphere at a heating rate of 10 °C min^{-1}. The sorption isotherms for N_2 (77 K) and CO_2 (298 K and 273 K) gas were measured with ASPS 2020 gas sorption analyzer. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Fisher SCIENTIFIC using Al Kα X-ray source. Binding energies (BE) were calibrated by setting the measured BE of C 1s to 284.65 eV. Scanning electron microscope energy-dispersive X-ray spectroscopy (SEM-EDS) analyses were conducted on a JSM-7500F SEM equipped with an EDAX CDU leap detector. ICP-OES analysis was performed on PerkinElmer Optima 8000 Plasma Emission Spectrometer. GC analysis was performed on Agilent Technologies with 7890B GC system.

2. Crystal Structure Data of 1

Table S1. Crystal data and structure refinement parameters for **1** ~~Table~~

MOF Code	**1**
Formula	$C_{86}H_{70}Ca_3N_4O_{16}$
Fw	1536
T/K	293(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	8.7338(5)
b/Å	12.7784(9)
c/Å	21.2690(19)
α/°	73.111(7)
β/°	84.390(6)
γ/°	76.799(5)
Volume/Å^3	2210.1(3)
Z	1
ρ_{calc}g/cm^3	1.154
μ/mm^{-1}	0.249
F(000)	802.0
Reflections collected	18661
Independent reflections	9410
Data/restraints/parameters	9410/45/539
R_{int}	0.0512
Goodness-of-fit on F^2	0.959
$R1$, $wR2$ [I>=2σ (I)]	0.0906, 0.2329
$R1$, $wR2$ [all data]	0.1374, 0.2637

Table S2. Selected bond lengths (Å) and bond Angles (°) for **1**.

Bond length (Å)		**Bond Angle** (°)	
Ca1−O1	2.298(3)	O1−Ca1−O2	94.21(12)
Ca1−O2	2.321(3)	O1−Ca1−O3	174.51(12)
Ca1−O3	2.398(3)	O1−Ca1−O4	133.43(11)
Ca1−O4	2.625(3)	O1−Ca1−O5	83.40(12)
Ca1−O5	2.397(3)	O1−Ca1−O6	83.08(12)
Ca1−O6	2.618(3)	O4−Ca2−Ca1	44.43(7)
Ca1−O8	2.288(4)	O4−Ca2−O7	96.22(11)
Ca2−O4	2.294(3)	O6−Ca2−Ca1	44.18(8)
Ca2−O6	2.277(3)	O6−Ca2−O4	81.32(11)
Ca2−O7	2.360(3)	C11−N1−C27	119.3(3)
N1−C11	1.420(5)	C14−N1−C11	120.0(3)
N1−C14	1.408(5)	C14−N1−C27	120.4(3)
N1−C27	1.421(5)	O1−C1−O2	124.4(4)
C1−C2	1.500(5)	O1−C1−C2	117.3(4)
C3−C4	1.383(5)	O2−C1−C2	118.2(3)
C5−C6	1.392(5)	C3−C2−C1	120.3(4)
C8−C9	1.397(6)	C3−C2−C7	119.5(3)
C10−C11	1.379(6)	C7−C2−C1	120.2(3)
C12−C13	1.382(6)	C2−C3−C4	120.0(4)
C14−C15	1.394(6)	C5−C4−C3	121.2(4)
C16−C17	1.389(6)	C4−C5−C6	118.5(4)
C17−C18	1.378(6)	C4−C5−C8	120.7(4)
C20−C21	1.404(6)	C6−C5−C8	120.8(4)
C21−C22	1.373(6)	C7−C6−C5	120.5(4)
C23−C24	1.378(6)	C2−C7−C6	120.3(4)
C24−C25	1.389(6)	C9−C8−C5	121.4(4)
C27−C28	1.374(6)	C13−C8−C5	121.7(4)
C29−C30	1.399(5)	C10−C9−C8	120.9(4)
C30−C31	1.377(6)	C9−C10−C11	121.8(4)
C31−C32	1.379(5)	C12−C11−C10	118.3(4)
C34−C35	1.374(5)	C11−C12−C13	120.5(4)
C36−C37	1.492(5)	C12−C13−C8	121.5(4)
C38−C39	1.389(5)	C19−C14−C15	117.6(4)
C39−C40	1.377(5)	C16−C15−C14	120.4(4)

Symmetry transformations used to generate equivalent atoms: ^{1}+X,-1+Y,1+Z; ^{2}1-X,-Y,2-Z; ^{3}1+X,+Y,1+Z; ^{4}2-X,1-Y,1-Z; ^{5}1+X,1+Y,+Z; ^{6}1-X,1-Y,-Z; ^{7}2-X,2-Y,-Z ^{1}+X,-1+Y,1+Z; ^{2}1-X,-Y,2-Z; ^{3}1+X,+Y,1+Z; ^{4}2-X,1-Y,1-Z; ^{5}+X,1+Y,-1+Z; ^{6}1+X,1+Y,+Z; ^{7}1-X,1-Y,-Z; ^{8}2-X,2-Y,-Z; ^{9}-1+X,+Y,-1+Z; ^{10}-1+X,-1+Y,+Z

3. Physical Characterizations of 1

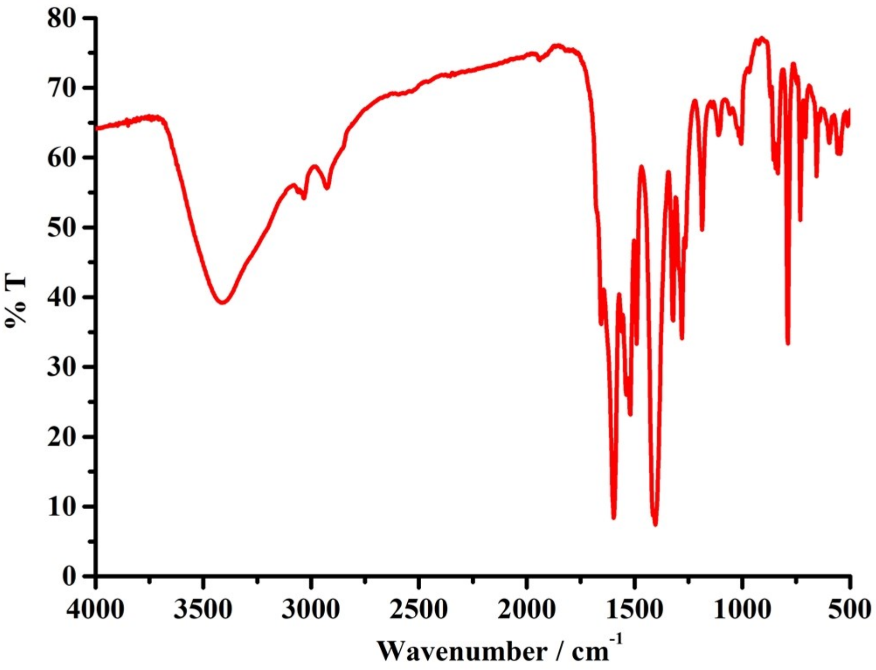


Figure S1. IR spectrum of **1**

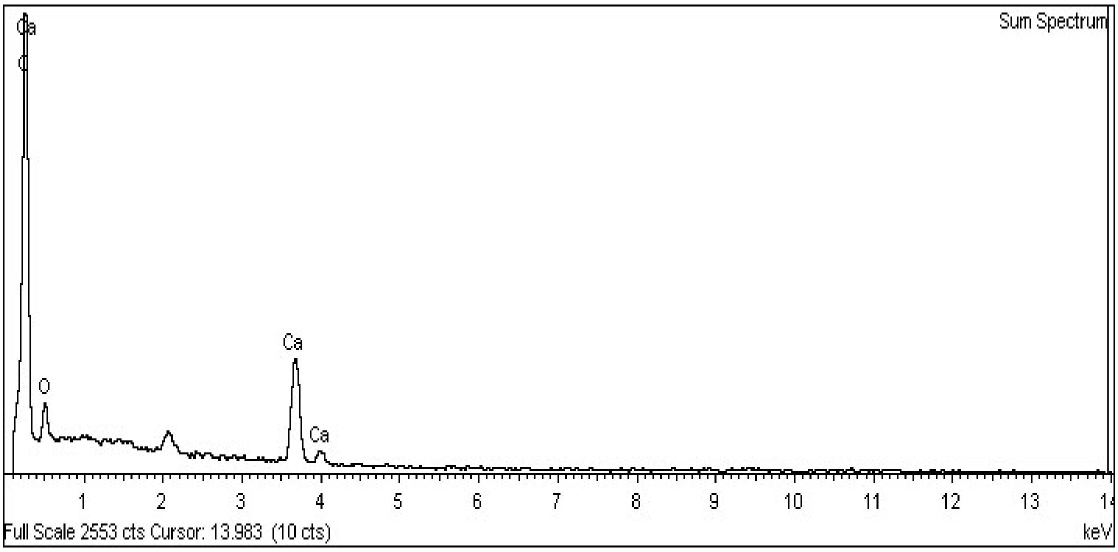


Figure S2. EDS spectrum of **1**

4. Stability Study of 1

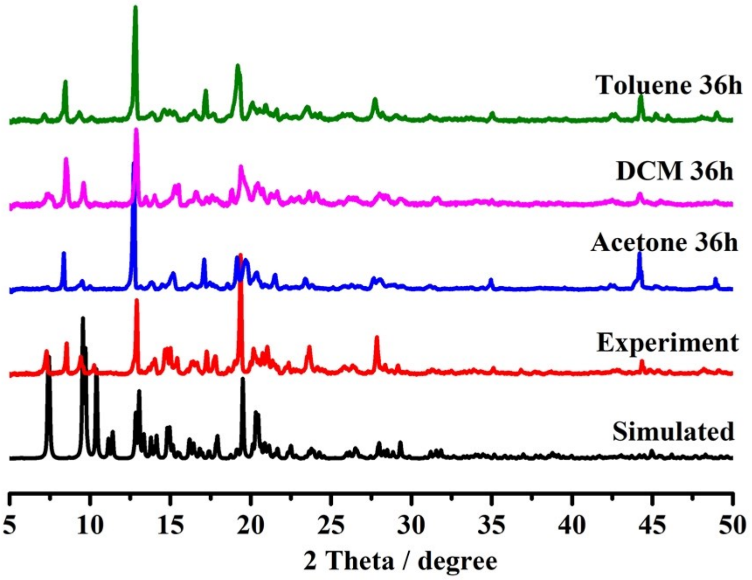


Figure S3. PXRD patterns of **1** upon treatment in different organic solvents for 36 h

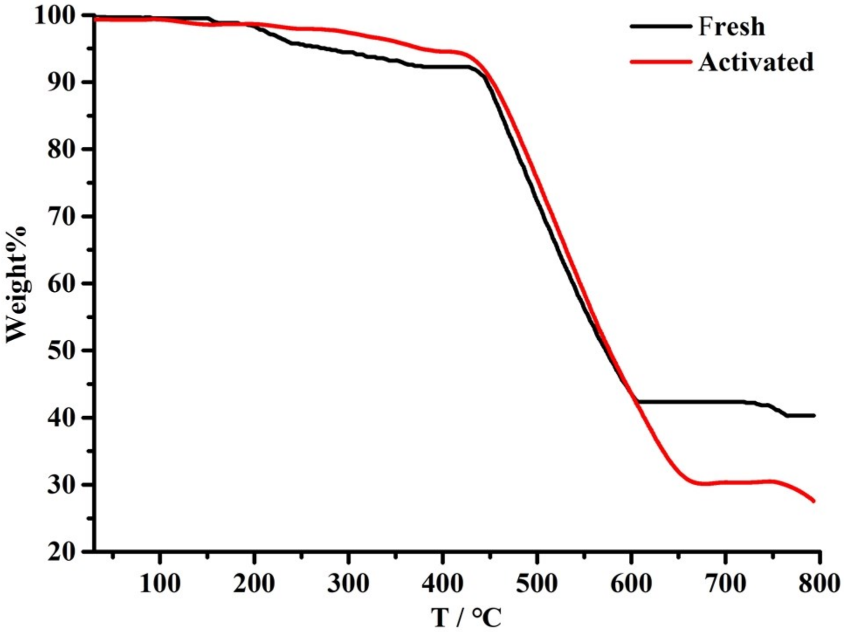


Figure S4. TG curves of fresh and activated **1** sample

5. Gas Adsorption of 1

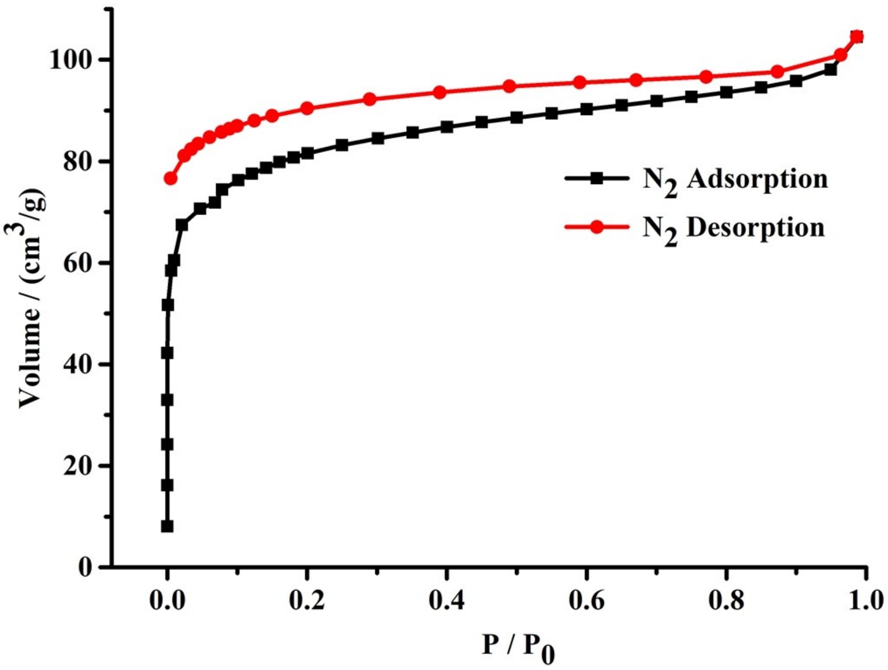


Figure S5. N_2 adsorption-desorption isotherms of **1** at 77K

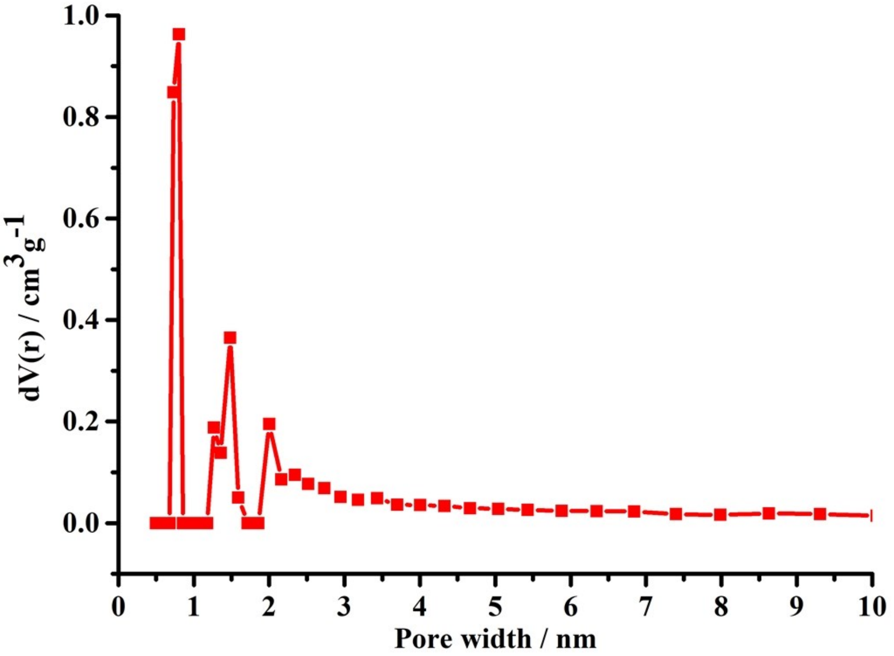


Figure S6. Density functional theory pore distribution plot of **1**

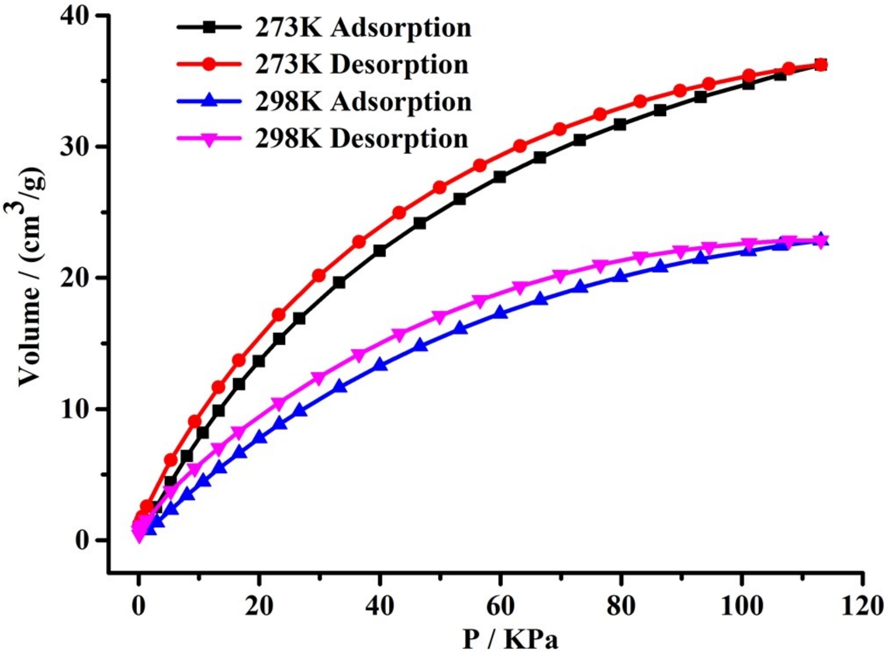
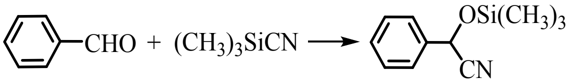


Figure S7. CO_2 adsorption-desorption isotherms of **1** at 273 and 298K

6. Catalytic Results

Table S3. Optimization of reaction condition for cyanosilylation of Aldehydes



Entry	Molar Ratio of Reactants	Weight of **1**	Time	Yield [a] / %
1[b]	1:1.2	5 mg	10 h	20
2	1:1.2	5 mg	12 h	83
3	1:1.2	10 mg	12 h	87
4	1:2.0	5 mg	6 h	99
5[c]	1:2.0	5 mg	3 h	86
6[d]	1:2.0	0 mg	6 h	12
7[e]	1:2.0	3 mg	6 h	99
8[f]	1:2.0	7 mg	6 h	50
9[g]	1:2.0	5 mg	6 h	6

[a] Determined by ^{1}H NMR; [b] Took place in air, while the others under Ar; [c] In toluene; [d] Without any catalyst; [e] Ca(OAc)$_2$ (0.01 mmol) as catalyst; [f] H$_3$TCBPA (0.01 mmol) as catalyst; [g] H$_3$BTB (0.01 mmol) as catalyst.

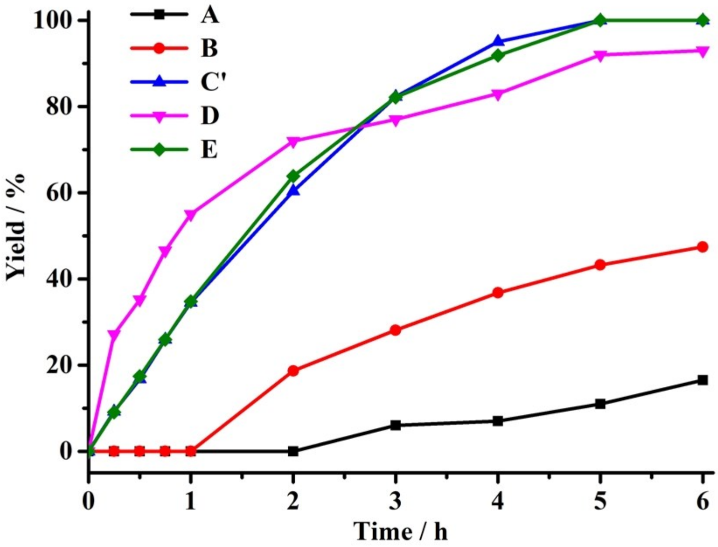


Figure S8. Time conversion plots for the optimization of reaction conditions. A, B, D, E corresponded to the same reaction conditions in Figure 2. In C' the ratio between benzaldehyde and $(CH_3)_3SiCN$ was 1:2, while in C (Figure 2) was 1:1.2. Yields were determined by GC.

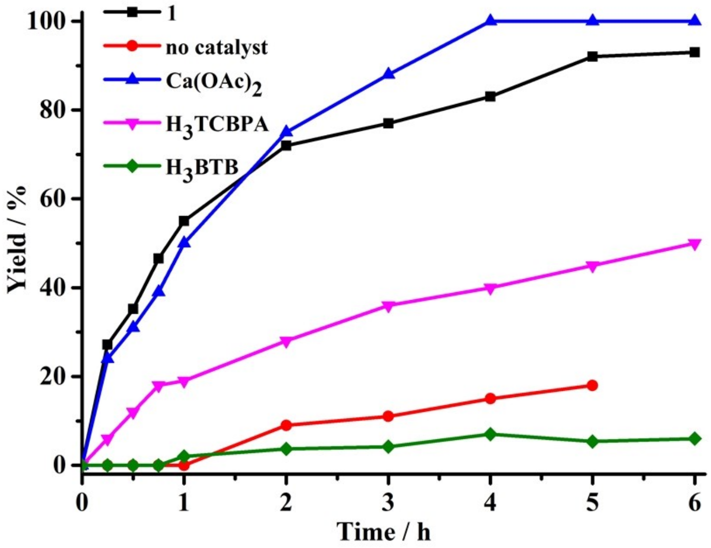


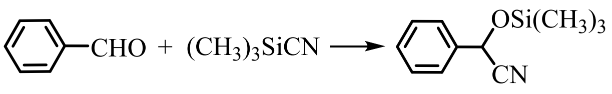
Figure S9. Time conversion plots for the comparison of **1**, without any catalyst, $Ca(OAc)_2$, H_3TCBPA and H_3BTB. Yields were determined by GC.

Table S4. Catalytic results of reported Lewis acid MOFs-based catalysts for cyanosilylation of aldehydes

Entry	Catalyst and Loading	Catalytic active site	Temperature	Time	Yield	Ref.[a]
1	$Zn_{0.29}$-STU-2, 4 mol%	Mn^{2+}, Zn^{2+}	r.t.	12 h	100 %	43
2	$[(Cu_4O_{0.27}Cl_{0.73})_3(H_{0.5}BTT)_8]$, 1 mol%	Cu^{2+}	40 °C	--	96 %	44
3	BINAPDA-Zr-MOF, 1 mol%	Zr^{4+}	r.t.	5 h	45 %	30
4	$[Cd_2(NiL^1)(CdL^2)][Cd_2(NiL^1)(H_2L^2)]_6DMF\cdot5MeOH$, 1 mol%	Cd^{2+}, Ni^{2+}	r.t.	24 h	95 %	45
5	Ce-MDIP1, 2 mol%	Ce^{3+}	r.t.	24 h	95 %	46
6	1 • Cd, 0.6 mol%	Cd^{2+}	r.t.	18 h	94 %	47
7	**1**, 0.3 mol%	Ca^{2+}, N	r.t.	6 h	99%	This work

[a] References in main text

Table S5. Recycling experiments for cyanosilylation of Aldehydes



Run	Yield (%)
1	99
2	99
3	99
4	99
5	99
6	99

Table S6. Catalytic results of reported MOFs-based catalysts for CO_2 addition to epoxides.

Entry	Catalyst and Loading	Cocatalyst	Pressure	Temperature	Time	Yield	Ref.[a]
1	$C_{54}H_{56}Mn_4N_6O_2$ 2 mol [Mn]%	TBAB	1 atm	80 °C	8 h	99 %	49
2	UiO-66-BAT 2 mol%	TBAI	5 bar	50 °C	6 h	95 %	50
3	Gd-MOF 0.47 mol%	TBAB	2 MPa	80 °C	5 h	98 %	51
4	1 0.3 mol%	TBAB	CO_2 balloon	100 °C	8 h	91 %	This work

[a] References in main text

7. Catalytic Procedure

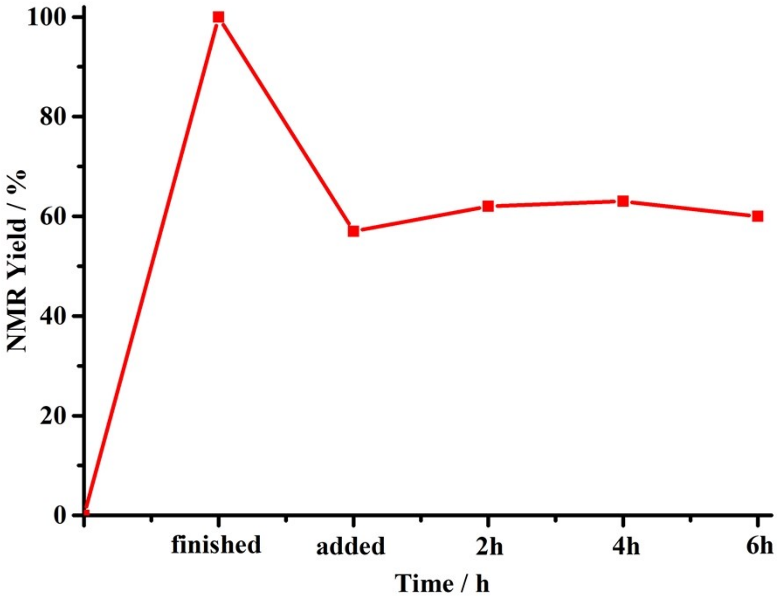


Figure S10. NMR Yiels vs. Time in thermal filtration experiment of **1** in cyanosilylation of aldehydes

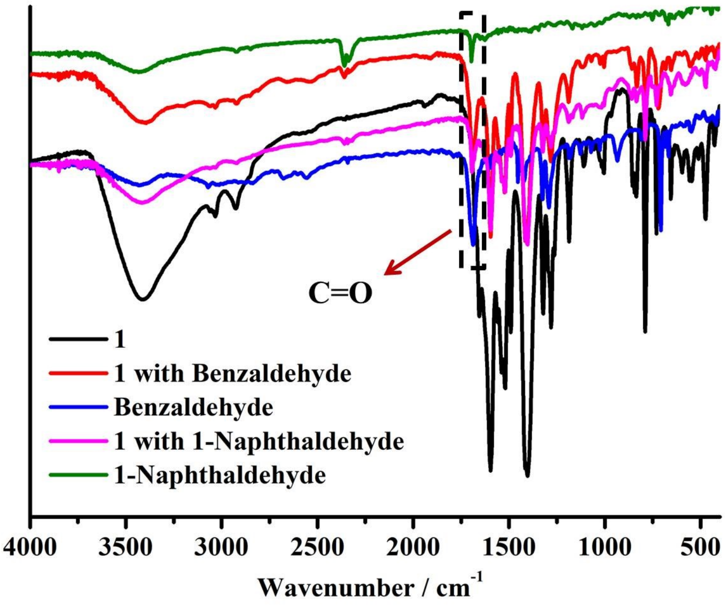


Figure S11. FT-IR of 1-naphthaldehyde, benzaldehyde, **1** and **1** after immersing in benzaldehyde or 1-naphthaldehyde solution for 24h

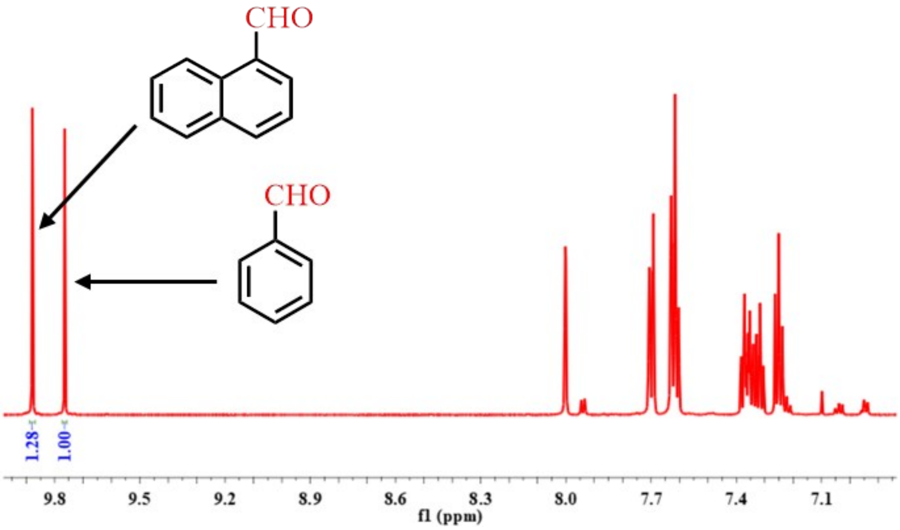


Figure S12. Mole ratio of benzaldehyde and 1-naphthaldehyde after stirring with **1** for 12 h

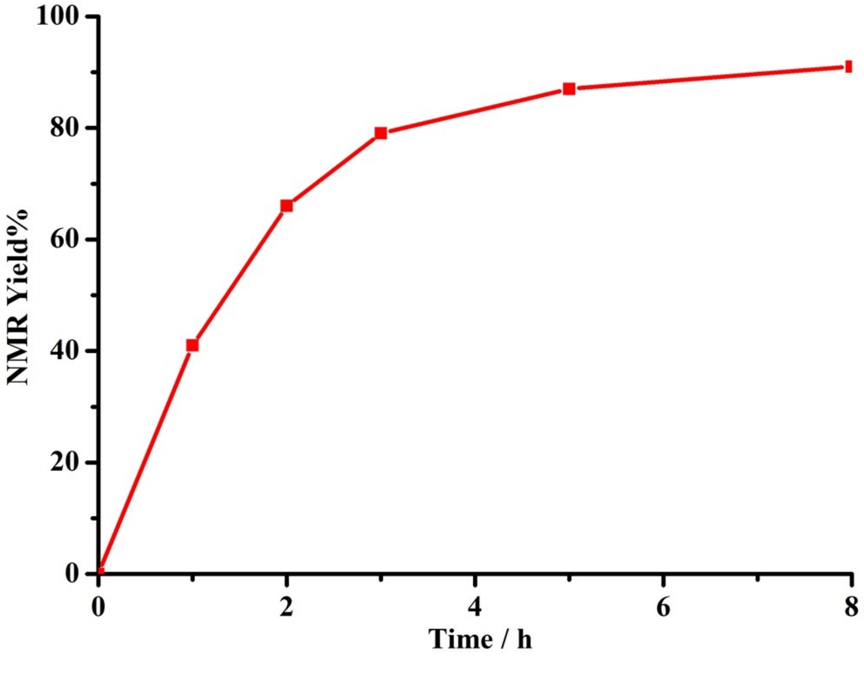


Figure S13. Time conversion plot of styrene oxide reacted with CO_2. Yields were determined by ^1H NMR

8. Chemical stability of 1 during catalysis

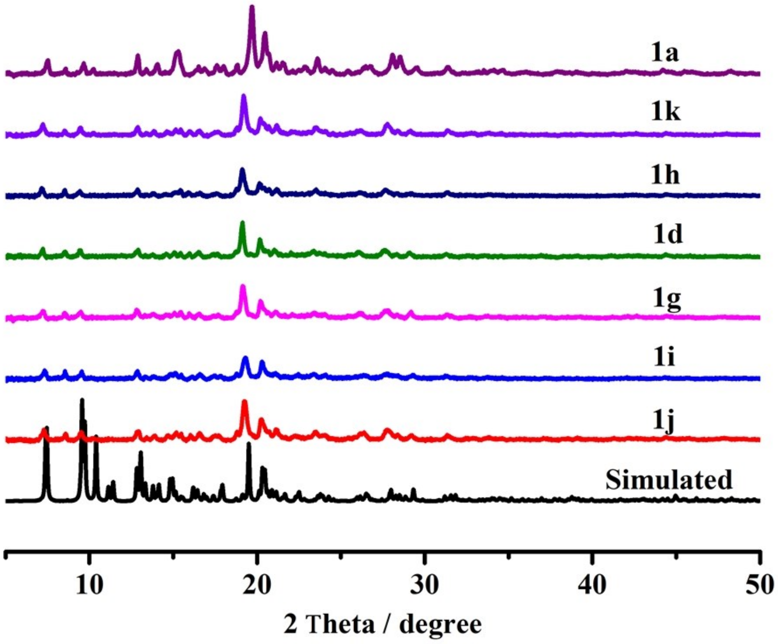


Figure S14. PXRD patterns of **1** after cyanosilylation of aldehydes

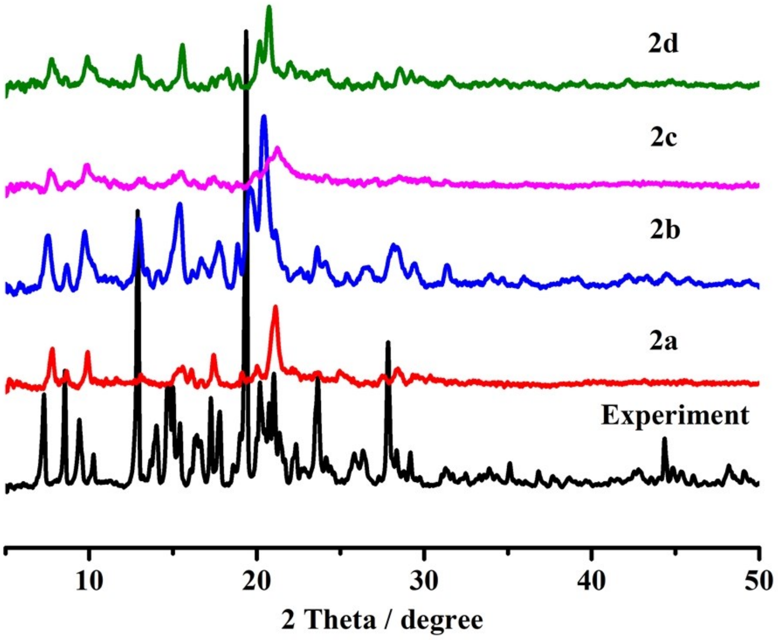
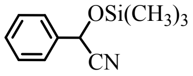
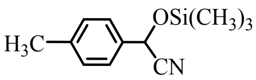


Figure S15. PXRD patterns of **1** before and after conversion of CO_2 with epoxides

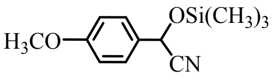
9. Characterization of products



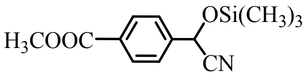
^{1}H NMR (600 MHz, $CDCl_3$) of **1a**: δ 7.48 (d, 2H, *J* = 7.4 Hz), 7.43-7.36 (m, 3H), 5.51 (s, 1H), 0.24 (s, 9H). Consistent with reported values [*J. Am. Chem. Soc.*, 2014, **136**, 1746-1749]



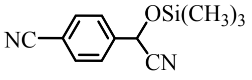
^{1}H NMR (600 MHz, $CDCl_3$) of **1b**: δ 7.26 (d, 2H, *J* = 8.0 Hz), 7.09 (d, 2H, *J* = 8.2 Hz), 5.37 (s, 1H), 2.24 (s, 3H), 0.12 (d, 9H, *J* = 0.9 Hz). Consistent with reported values [*Inorg. Chem.*, 2017, **56**, 3036-3043].



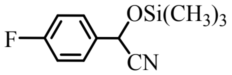
^{1}H NMR (600 MHz, $CDCl_3$) of **1c**: δ 7.37 (d, 2H, *J*=8.7), 6.90 (d, 2H, *J*=8.8), 5.43 (s, 1H), 3.76 (s, 3H), 0.19 (s, 9H). Consistent with reported values [*Inorg. Chem.*, 2017, ***56***, 3036-3043].



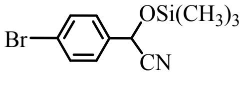
^{1}H NMR (600 MHz, $CDCl_3$) of **1d**: δ 7.99 (d, 2H, *J*=8.4), 7.48 (d, 2H, *J*=8.2), 5.52 (s, 1H), 3.83 (s, 3H), 0.17 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): δ -0.30, 53.65, 63.31, 126.35, 127.22, 130.28, 131.26, 141.03, 166.41.



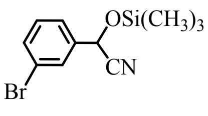
^{1}H NMR (600 MHz, $CDCl_3$) of **1e**: δ 7.64 (d, 2H, *J*=8.4), 7.55 (d, 2H, *J*=8.2), 5.55 (s, 1H), 0.19 (s, 9H). Consistent with reported values [*Inorg. Chem.*, 2017, **56**, 3036-3043]. ^{13}C NMR (151 MHz, $CDCl_3$): δ -0.23, 62.95, 113.43, 127.01, 132.88, 141.31.



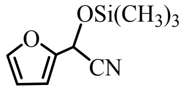
^{1}H NMR (600 MHz, $CDCl_3$) of **1f**: δ 7.46-7.41 (m, 2H), 7.09-7.03 (m, 2H), 5.47 (s, 1H), 0.20 (s, 9H).^{13}C NMR (151 MHz, $CDCl_3$): δ -0.17, 63.14, 116.16, 128.46, 132.48, 162.48, 164.12.



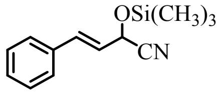
^{1}H NMR (600 MHz, $CDCl_3$) of **1g**: δ 7.50-7.47 (m, 2H), 7.33-7.29 (m, 2H), 5.44 (s, 1H), 0.19 (s, 9H). Consistent with reported values [*J. Am. Chem. Soc.*, 2014, **136**, 1746-1749]



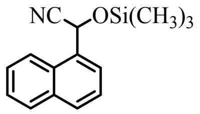
^{1}H NMR (600 MHz, $CDCl_3$) of **1h**: δ 7.58 (t, 1H, *J*=1.7), 7.46-7.44 (dd, 1H, *J*=7.5, 1.2), 7.34-7.36 (m, 1H), 7.24-7.23 (t, 1H, *J*=7.9), 5.45 (s, 1H), 0.19 (s, 9H). Consistent with reported values [*Synlett*, 2011, **4**, 551-554]



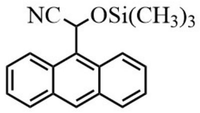
^{1}H NMR (600 MHz, $CDCl_3$) of **1i**: δ 7.40 (dd, 1H, *J*=1.8, 0.8), 6.48 (d, 1H, *J*=3.3), 6.34 (dd, 1H, *J*=3.3, 1.9), 5.51 (s, 1H), 0.14 (s, 9H). Consistent with reported values [*J. Am. Chem. Soc.*, 2014, **136**, 1746-1749]



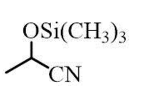
^{1}H NMR (600 MHz, $CDCl_3$) of **1j**: δ 7.28 (d, 2H, *J*=7.3), 7.23 (t, 2H, *J*=7.4), 7.20-7.17 (m, 1H), 6.69 (d, 1H, *J*=15.7), 6.07 (dd, 1H, *J*=15.8, 6.0), 5.00 (dd, 1H, *J*=6.0, 1.3), 0.15 (s, 9H). Consistent with reported values [*J. Am. Chem. Soc.*, 2014, **136**, 1746-1749]



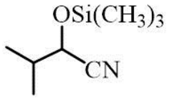
^{1}H NMR (600 MHz, $CDCl_3$) of **1k**: δ 7.95 (s, 1H), 7.89-7.82 (m, 3H), 7.58 (dd, 1H, *J*=8.5, 1.8), 7.54-7.50 (m, 2H), 5.68 (s, 1H), 0.29 (s, 9H). Consistent with reported values [*J. Am. Chem. Soc.*, 2014, **136**, 1746-1749]



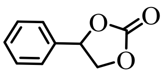
^{1}H NMR (600 MHz, $CDCl_3$) of **1l**: δ 8.41 (d, J = 8.9 Hz, 2H), 8.18 (s, 1H), 7.73 (d, J = 8.4 Hz, 2H), 7.44 (ddd, J = 8.9, 6.5, 1.2 Hz, 2H), 7.28 (dd, J = 7.9, 7.0 Hz, 2H), 6.87 (s, 1H), 0.00 (s, 9H).Consistent with reported values [*J. Am. Chem. Soc.*, 2014, **136**, 1746-1749].^{13}C NMR (151 MHz, $CDCl_3$): δ -0.07, 58.21, 123.63, 125.33, 126.05, 127.30, 129.50, 129.59, 130.68, 131.55.



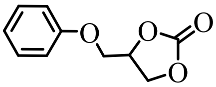
^{1}H NMR (600 MHz, $CDCl_3$) of **1m**: δ 4.49 (q, J = 6.7, 1H), 1.49 (d, J = 6.7, 3H), 0.16 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): δ -0.31, 23.11, 57.37, 127.14.



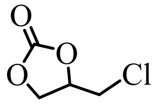
^{1}H NMR (600 MHz, $CDCl_3$) of **1n**: δ 4.13 (d, J = 5.8, 1H), 2.01-1.85 (m, 1H), 1.00 (d, J = 6.7, 3H), 0.97 (d, J = 6.8, 3H), 0.16 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): δ -0.33, 17.39, 17.71, 34.00, 67.38, 127.22.



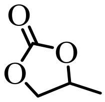
^{1}H NMR (600 MHz, $CDCl_3$) of **2a**: δ 7.41 (m, 3H), 7.37-7.31 (m, 2H), 5.71-5.62 (m, 1H), 4.84-4.73 (m, 1H), 4.36-4.24 (m, 1H). Consistent with reported values [*Applied Catalysis B: Environmental,* 2019, **254**, 380-390].



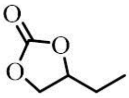
^{1}H NMR (600 MHz, $CDCl_3$) of **2b**: δ 7.23-7.18 (m, 2H), 6.91 (td, *J*=7.4, 0.9, 1H), 6.83-6.80 (m, 2H), 4.94 (ddt, *J*=6.8, 6.0, 3.5, 1H), 4.49 (t, *J*=8.5, 1H), 4.40 (dd, *J*=8.6, 5.9, 1H), 4.13 (dd, *J*=10.9, 3.3, 1H), 4.00 (dd, *J*=10.9, 3.6, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 66.26, 67.01, 74.47, 114.68, 121.90, 129.69, 155.00, 157.00. Consistent with reported values [*Applied Catalysis B: Environmental,* 2019, **254**, 380-390].



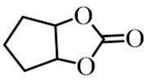
^{1}H NMR (600 MHz, $CDCl_3$) of **2c**: δ 4.96 (td, *J*=8.7, 5.2, 1H), 4.59-4.50 (m, 1H), 4.39-4.30 (m, 1H), 3.66-3.59 (m, 2H). Consistent with reported values [*Dalton Trans.,* 2019*,* **48***,* 7612-7618].



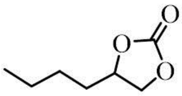
^{1}H NMR (600 MHz, $CDCl_3$) of **2d**: δ 4.86-4.77 (m, 1H), 4.51 (t, *J*=8.1, 1H), 3.97 (t, *J*=7.8, 1H), 1.45-1.43 (m, 3H). Consistent with reported values [*Applied Catalysis B: Environmental,* 2019, **254**, 380-390].



^{1}H NMR (600 MHz, $CDCl_3$) of **2e**: δ 4.61 (m, 1H), 4.48 (t, J=8.2, 1H), 4.03 (dd, J=8.4, 7.0, 1H), 1.80-1.66 (m, 2H), 0.97 (t, J=7.4, 3H). Consistent with reported values [*Dalton Trans.,* 2019*,* **48***,* 7612-7618].



^{1}H NMR (600 MHz, $CDCl_3$) of **2f**: δ 5.10-5.06 (m, 2H), 2.11 (ddd, J=7.0, 5.0, 1.4, 2H), 1.83-1.69 (m, 4H). Consistent with reported values [*Applied Catalysis B: Environmental,* 2019, **254**, 380-390].



^{1}H NMR (600 MHz, $CDCl_3$) of **2g**: δ 4.62-4.59 (m, 1H), 4.45-4.41 (m, 1H), 3.98-3.94

(m, 1H), 1.70-1.66 (m, 1H), 1.61-1.56 (m, 1H), 1.42-1.29 (m, 4H) 0.82-0.77 (m, 3H). Consistent with reported values [*Chem. Lett.*, 2017, **46**, 968-969].