$Sc_2(pydc)_2$ Unit Based 1D, 2D and 3D Metal-Organic Frameworks as Heterogeneous Lewis Acid Catalysts for Cyanosilylation

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Fig. S1 Powder X-ray diffraction patterns of the simulated and as-synthesized sample **1**, indicating the phase purity of the as-synthesized sample. The green line shows the powder X-ray diffraction patterns of sample **1** after catalysis.

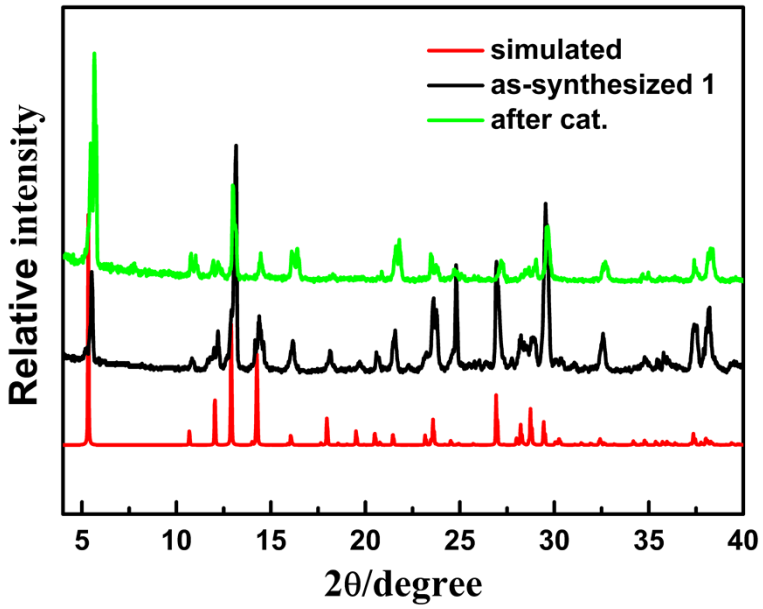


Fig. S2 Powder X-ray diffraction patterns of the simulated and as synthesized sample **2**, indicating the phase purity of the as-synthesized sample. The green line shows the powder X-ray diffraction patterns of sample **2** after fourth catalysis.

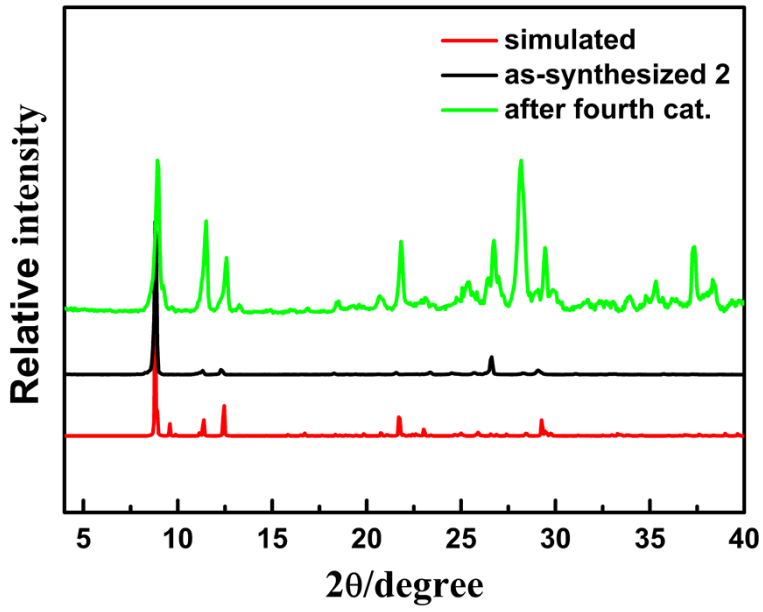


Fig. S3 Powder X-ray diffraction patterns of the simulated and as synthesized sample **3**, indicating the phase purity of the as-synthesized sample. The blue line shows the powder X-ray diffraction patterns of sample **3** immersed in water at room temperature for 5 days and the green line shows the powder X-ray diffraction patterns of sample **3** after catalysis.

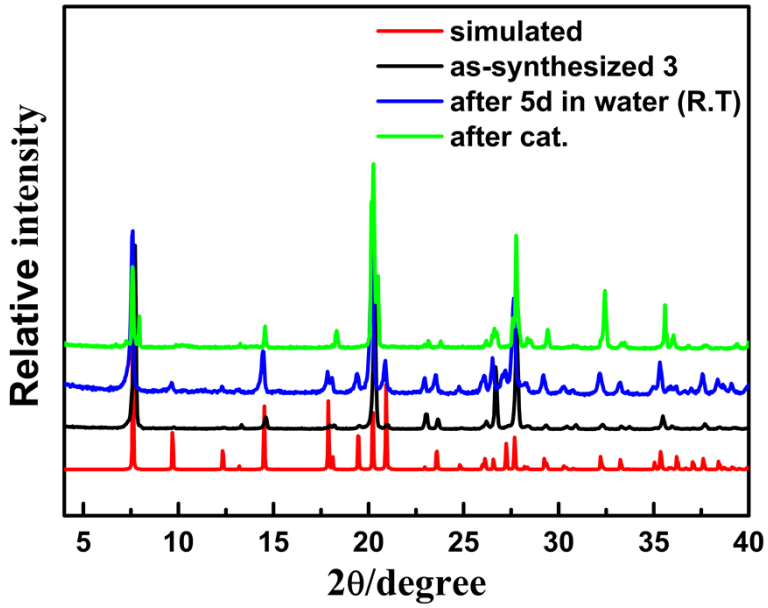


Fig. S4 IR spectra for compound **1**, compound **2** and compound **3**.

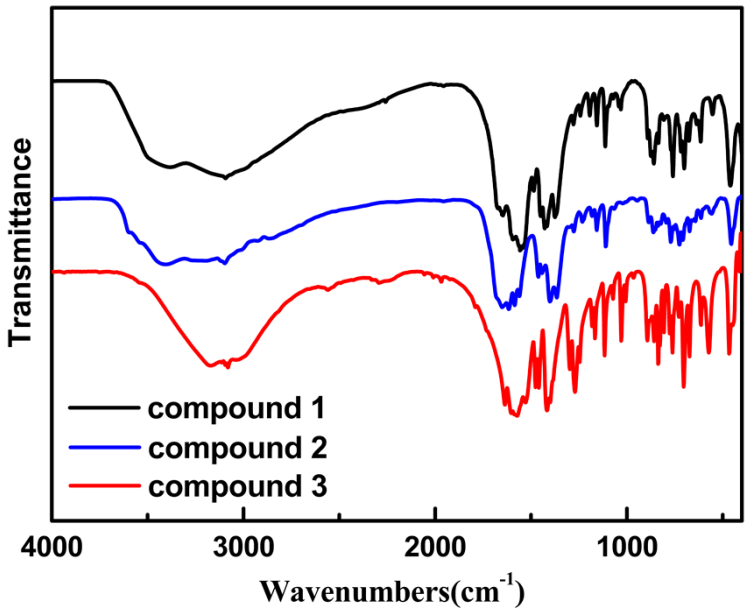


Fig. S5 The coordination and geometry for Sc1 atom in compound **1**.

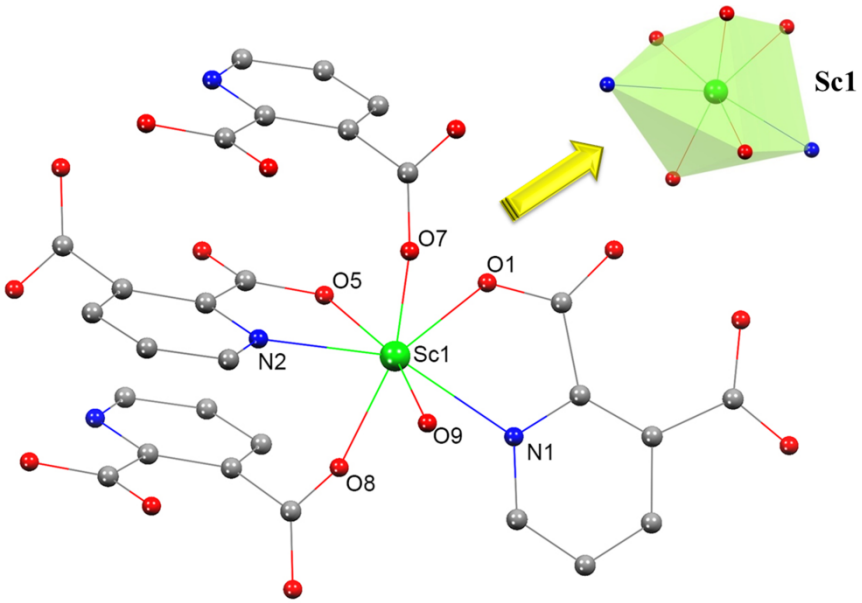


Fig. S6 The coordination and geometry for Sc1, and Sc2 atoms in compound **2**.

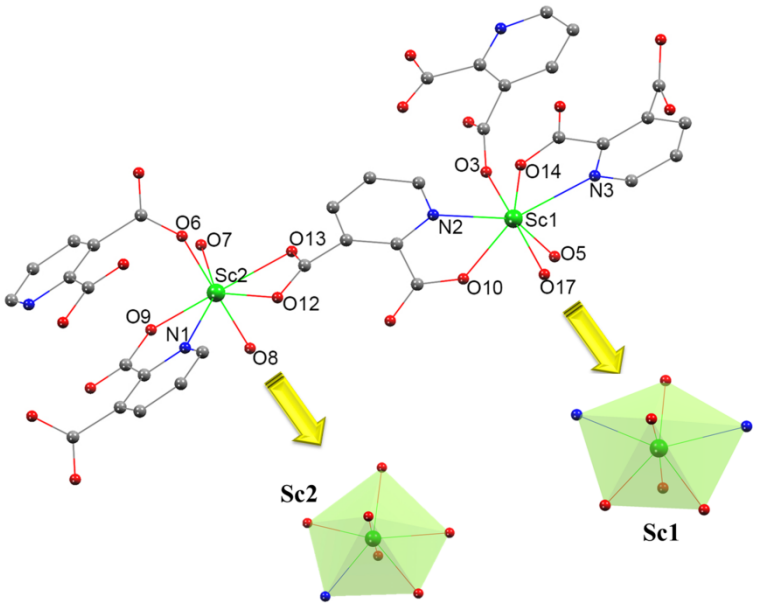


Fig. S7 Hydrogen-bonding interaction between the S-shaped chains and waved-like chains along [100] direction of compound **2**;

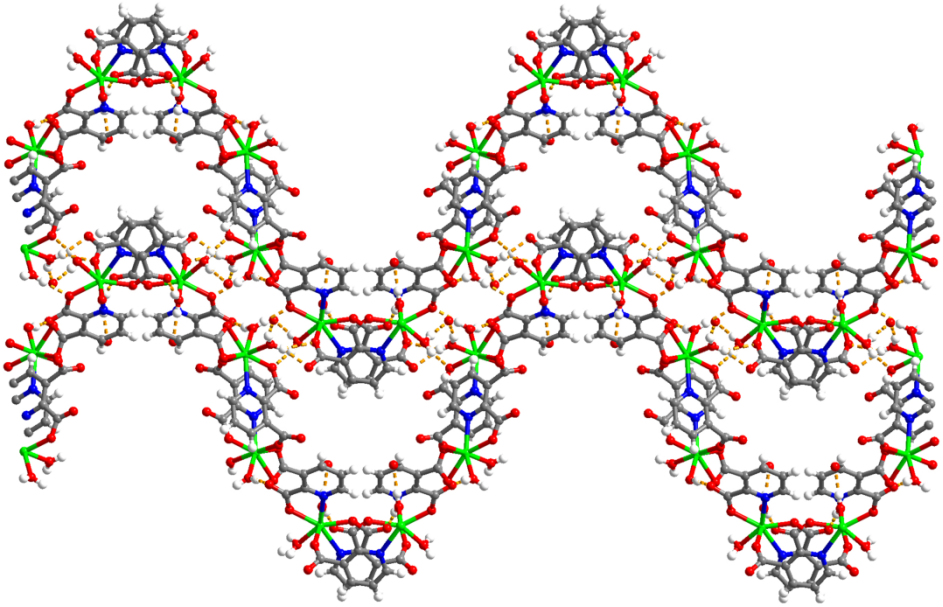


Fig. S8 The coordination and geometry for Sc1 atom in compound **3**.

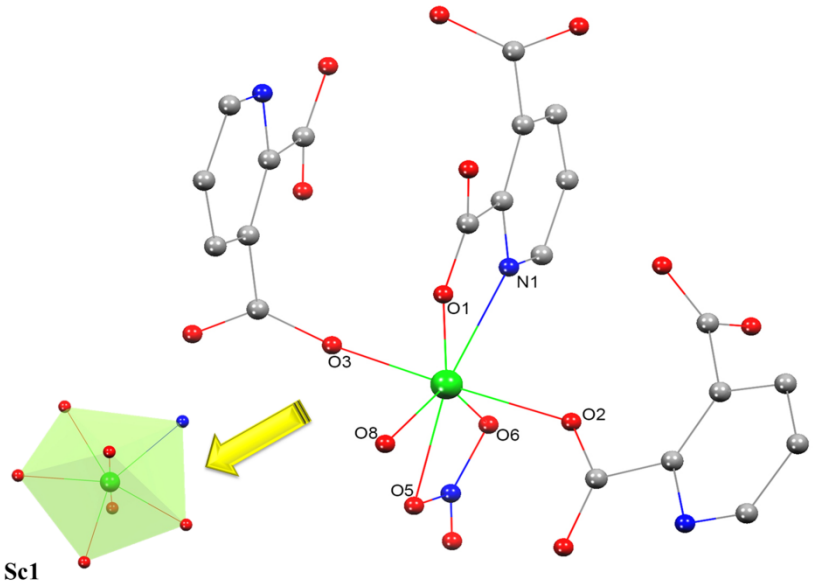


Fig. S9 a) a schematic representation of the **nbo-a** net; b) Space-filling representations of compound **3** viewed along the *c* axes.

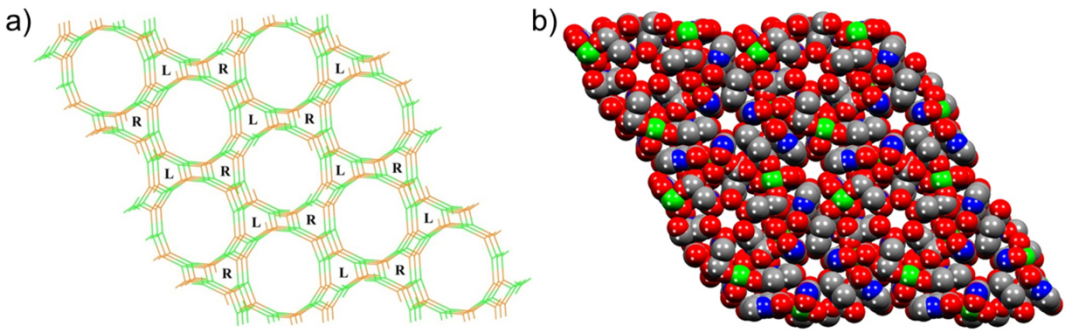


Fig. S10 Coordination modes for the H_2pydc ligand (I-V). Color scheme: carbon = gray, nitrogen = blue, oxygen = red, metal = green.

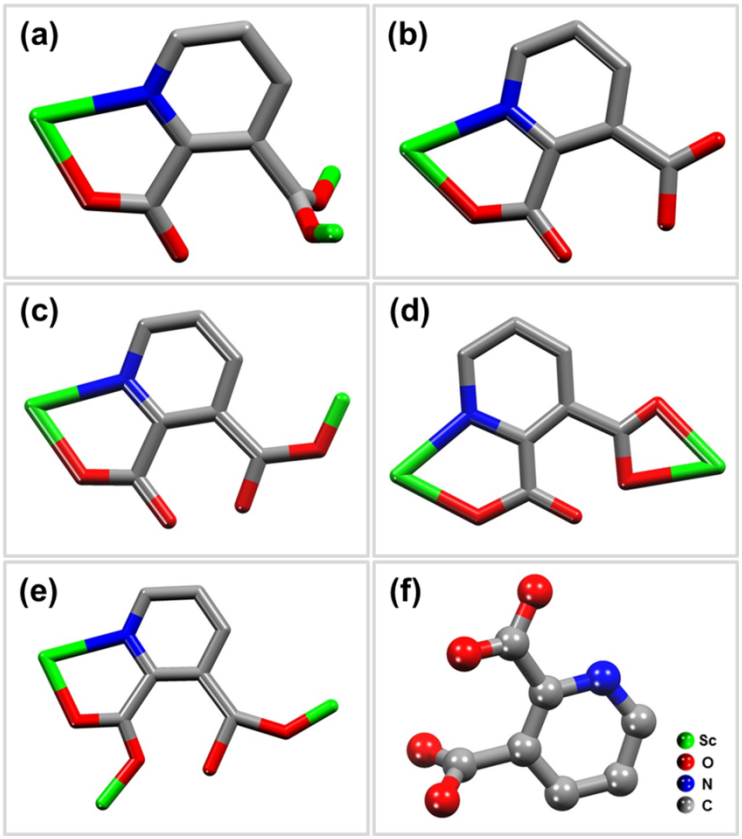


Fig. S11 TGA curve for compound **1** and compound **2**.

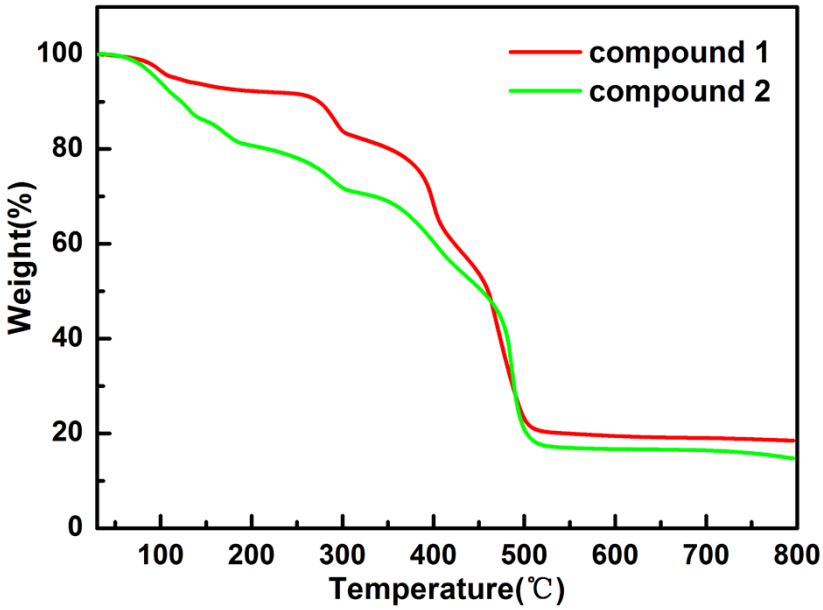


Fig. S12 TGA curve for compound **3**.

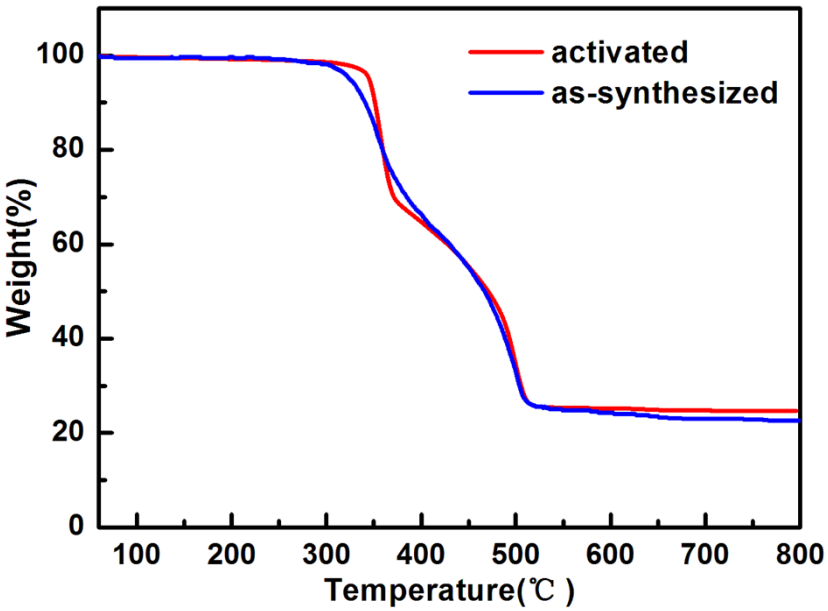


Fig. S13 The variable-temperature powder XRD patterns of compound **3**.

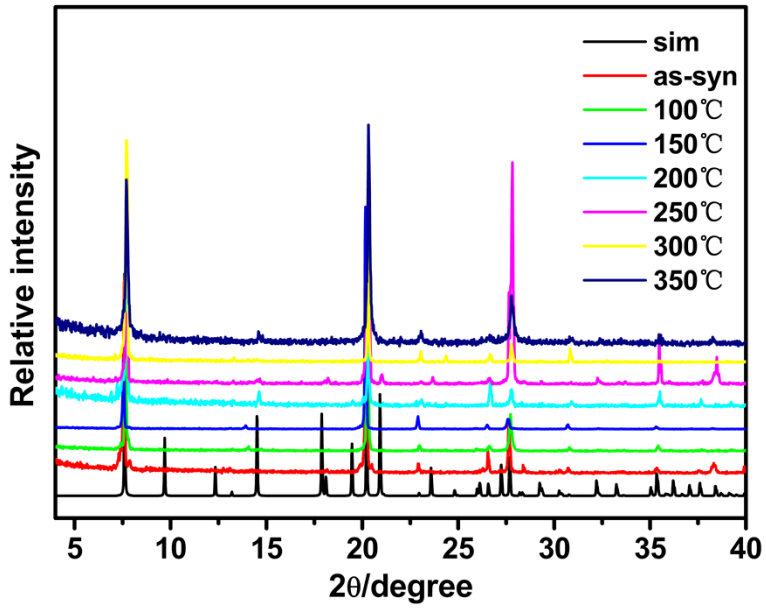
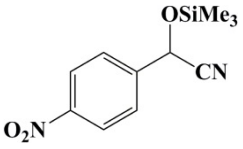


Fig. S14 ^{1}H NMR spectrum for the cyanosilylation of p-nitrobenzaldehyde.

^{1}H NMR (300 MHz, CD_3CN) δ = 8.21(d, J = 8.8 Hz, 2H), 7.67(d, J = 8.8 Hz, 2H), 5.80(s, 1H), 0.17(s, 9H).



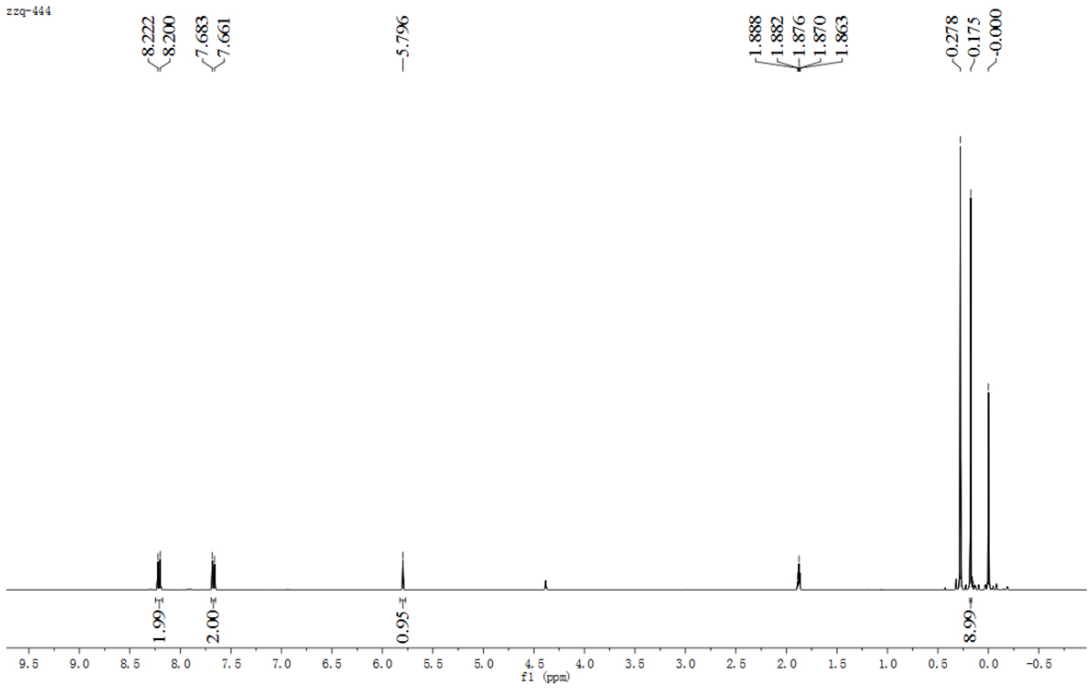


Table S1. Bond lengths [Å] and angles [º] for compound **1**.

N(1)-Sc(1)	2.419(4)	O(8)-Sc(1)#2	2.110(3)
N(2)-Sc(1)	2.355(4)	O(9)-Sc(1)	2.126(3)
O(1)-Sc(1)	2.130(3)	Sc(1)-O(8)#2	2.110(3)
O(5)-Sc(1)	2.091(3)	Sc(1)-O(7)#1	2.146(3)
O(7)-Sc(1)#1	2.146(3)		
O(5)-Sc(1)-O(8)#2	86.68(11)	O(5)-Sc(1)-N(2)	71.46(12)
O(5)-Sc(1)-O(9)	161.09(13)	O(8)#2-Sc(1)-N(2)	79.40(12)
O(8)#2-Sc(1)-O(9)	86.60(12)	O(9)-Sc(1)-N(2)	89.92(12)
O(5)-Sc(1)-O(1)	78.23(13)	O(1)-Sc(1)-N(2)	137.79(13)
O(8)#2-Sc(1)-O(1)	127.93(13)	O(7)#1-Sc(1)-N(2)	78.32(12)
O(9)-Sc(1)-O(1)	119.52(13)	O(5)-Sc(1)-N(1)	117.52(13)
O(5)-Sc(1)-O(7)#1	96.82(11)	O(8)#2-Sc(1)-N(1)	77.49(13)
O(8)#2-Sc(1)-O(7)#1	155.00(13)	O(9)-Sc(1)-N(1)	78.09(13)
O(9)-Sc(1)-O(7)#1	82.19(11)	O(1)-Sc(1)-N(1)	66.84(13)
O(1)-Sc(1)-O(7)#1	76.85(13)	O(7)#1-Sc(1)-N(1)	121.38(13)
N(2)-Sc(1)-N(1)	154.48(13)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y, -z+1 #2 -x, -y, -z+1

Table S2. Hydrogen bonds for compound **1** [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(7)...O(2)	0.927	1.522	2.432	166.57
O(9)-H(9A)...O(10) #3	0.851	1.788	2.632	170.99
O(9)-H(9B)...O(6)#4	0.850	1.850	2.700	177.28
O10-H(10)...O(4) #4	0.845	1.968	2.806	171.40
O(10)-H(11)...O(1)	0.851	2.258	3.072	160.03
O(10)-H(11)...O(5)	0.851	2.258	3.194	129.09

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y, -z+1 #2 -x, -y, -z+1 #3 x, y, z-1

#4 x, -y+1/2, z+1/2

Table S3. Bond lengths [Å] and angles [º] for compound **2**.

O(6)-Sc(2)#1	2.033(4)	O(9)-Sc(2)	2.129(4)
N(1)-Sc(2)	2.323(5)	O(10)-Sc(1)	2.193(4)
N(2)-Sc(1)	2.411(5)	O(12)-Sc(2)	2.208(4)
N(3)-Sc(1)	2.444(5)	O(13)-Sc(2)	2.303(4)
O(3)-Sc(1)#2	2.027(5)	O(14)-Sc(1)	2.095(4)
O(5)-Sc(1)	2.185(4)	O(17)-Sc(1)	2.135(5)
O(7)-Sc(2)	2.190(5)	Sc(1)-O(3)#3	2.027(5)
O(8)-Sc(2)	2.117(5)	Sc(2)-O(6)#1	2.033(4)
O(3)#3-Sc(1)-O(14)	97.51(18)	O(8)-Sc(2)-O(7)	91.2(2)
O(3)#3-Sc(1)-O(17)	172.52(19)	O(9)-Sc(2)-O(7)	80.42(17)
O(14)-Sc(1)-O(17)	89.6(2)	O(6)#1-Sc(2)-O(12)	91.78(18)
O(3)#3-Sc(1)-O(5)	86.63(18)	O(8)-Sc(2)-O(12)	92.06(19)
O(14)-Sc(1)-O(5)	143.16(17)	O(9)-Sc(2)-O(12)	144.58(17)
O(17)-Sc(1)-O(5)	86.3(2)	O(7)-Sc(2)-O(12)	134.49(17)
O(3)#3-Sc(1)-O(10)	90.15(17)	O(6)#1-Sc(2)-O(13)	95.12(17)
O(14)-Sc(1)-O(10)	141.53(16)	O(8)-Sc(2)-O(13)	84.18(19)
O(17)-Sc(1)-O(10)	85.59(18)	O(9)-Sc(2)-O(13)	152.61(17)
O(5)-Sc(1)-O(10)	74.63(16)	O(7)-Sc(2)-O(13)	78.18(18)
O(3)#3-Sc(1)-N(2)	89.33(18)	O(12)-Sc(2)-O(13)	57.08(17)
O(14)-Sc(1)-N(2)	73.42(16)	O(6)#1-Sc(2)-N(1)	87.48(18)
O(17)-Sc(1)-N(2)	94.87(19)	O(8)-Sc(2)-N(1)	96.68(19)
O(5)-Sc(1)-N(2)	143.40(17)	O(9)-Sc(2)-N(1)	70.99(17)
O(10)-Sc(1)-N(2)	69.02(15)	O(7)-Sc(2)-N(1)	148.24(18)
O(3)#3-Sc(1)-N(3)	89.76(17)	O(12)-Sc(2)-N(1)	76.08(17)
O(14)-Sc(1)-N(3)	68.79(15)	O(13)-Sc(2)-N(1)	133.12(18)
O(17)-Sc(1)-N(3)	90.76(18)	O(6)#1-Sc(2)-C(21)	91.23(18)
O(5)-Sc(1)-N(3)	74.66(16)	O(8)-Sc(2)-C(21)	90.53(19)
O(10)-Sc(1)-N(3)	149.24(16)	O(9)-Sc(2)-C(21)	168.31(18)
N(2)-Sc(1)-N(3)	141.73(16)	O(7)-Sc(2)-C(21)	105.9(2)
O(6)#1-Sc(2)-O(8)	174.9(2)	O(12)-Sc(2)-C(21)	28.74(19)
O(6)#1-Sc(2)-O(9)	99.34(17)	O(13)-Sc(2)-C(21)	28.57(17)
O(8)-Sc(2)-O(9)	79.36(17)	N(1)-Sc(2)-C(21)	104.8(2)
O(6)#1-Sc(2)-O(7)	83.71(18)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2, -y, -z+2 #2 x, -y+1/2, z-1/2 #3 x, -y+1/2, z+1/2

Table S4. Bond lengths [Å] and angles [º] for compound **3**.

Sc(1)-O(3)#1	2.028(4)	Sc(1)-O(6)	2.235(5)
Sc(1)-O(8)	2.117(5)	Sc(1)-O(5)	2.235(5)
Sc(1)-O(2)#2	2.121(4)	Sc(1)-N(1)	2.327(5)
Sc(1)-O(1)	2.139(4)		
O(3)#1-Sc(1)-O(8)	94.9(2)	O(1)-Sc(1)-O(6)	150.01(18)
O(3)#1-Sc(1)-O(2)#2	176.0(2)	O(3)#1-Sc(1)-O(5)	87.3(2)
O(8)-Sc(1)-O(2)#2	89.05(18)	O(8)-Sc(1)-O(5)	76.6(2)
O(3)#1-Sc(1)-O(1)	92.31(19)	O(2)#2-Sc(1)-O(5)	93.48(19)
O(8)-Sc(1)-O(1)	76.65(19)	O(1)-Sc(1)-O(5)	153.14(18)
O(2)#2-Sc(1)-O(1)	88.73(18)	O(6)-Sc(1)-O(5)	56.85(18)
O(3)#1-Sc(1)-O(6)	88.3(2)	O(3)#1-Sc(1)-N(1)	85.93(19)
O(8)-Sc(1)-O(6)	133.2(2)	O(8)-Sc(1)-N(1)	147.9(2)
O(2)#2-Sc(1)-O(6)	88.87(19)	O(2)#2-Sc(1)-N(1)	90.78(18)
O(1)-Sc(1)-N(1)	71.29(17)	O(6)-Sc(1)-N(1)	78.86(18)
O(5)-Sc(1)-N(1)	135.35(19)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2/3, -y+1/3, -z+1/3 #2 -y+1/3, x-y-1/3, z-1/3

Table S5. Comparison of the three compounds with some other MOFs materials for cyanosilylation of *p*-nitrobenzaldehyde.

MOFs Materials	Time (h)	Conversion (%)	Reference
Ce-TTS	1h	>99%	1
Compound **2**	1.5h	99%	This work
Tb-PT1	1.5h	90.5%	2
MCM-Er	2.5h	82%	3
Compound **3** (after activation)	5.5h	99%	This work
Compound **1**	8h	99%	This work
$\{[CdL_2(DMF)_2]\cdot(ClO_4)_2\cdot(2DMF)\}_n$	14h	80%	4
Tb-TCA	4h	47%	5
Compound **3**	24h	85.2%	This work
In(OH)(H_2O)(1,4-bdc)	94h	100%	6

Reaction conditions

This work: Me_3SiCN (1.2 mmol); p-nitrobenzaldehyde (0.5 mmol); catalysts, 0.05 mmol (10 mol %); room temperature;

Reference 1: Me_3SiCN (0.20m); aldehyde (0.08m); Ce-TTS (1.6 mm) at room temperature under N_2 for 1 hour in 2 mL DMF/$CHCl_3$ (v/v=1:99) solution;

Reference 2: Me_3SiCN (0.6 mmol); aldehyde (0.5 mmol); CH_2Cl_2 (0.5 mL); Tb-PT1 or Sm-PT1 (0.005 mmol); 20 ℃, 1.5 h;

Reference 3: 40 mg of MCM-Er in diethyl ether at room temperature;

Reference 4: Me_3SiCN (2.64 mmol); aldehyde (1.32 mmol); DCM (10 mL); catalyst (5 wt%) is added at 0 ℃;

Reference 5: Me_3SiCN (1.2 mmol); aldehyde (0.5 mmol); Tb-TCA catalysts, 0.01 mmol (2 mol%); room temperature under N_2 for 4 h;

Reference 6: Me_3SiCN (1.2 mmol); p-nitrobenzaldehyde (0.5 mmol); catalysts, 0.05 mmol (10 mol %); room temperature.

Reference

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