## Supplementary Information for

# Porous and Robust Lanthanide Metal-Organoboron Frameworks as Water Tolerant Lewis Acid Catalysts

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#### 1. Materials and General Procedures.

All of the chemicals are commercial available, and used without further purification. Elemental analyses of C, H and N were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectrum was recorded (400-4000 cm<sup>-1</sup> region) on a Nicolet Magna 750 FT-IR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR experiments were carried out on a MERCURYplus 400 spectrometer operating at resonance frequencies of 100.63 MHz. Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of  $10^{\circ}$ C min<sup>-1</sup> on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu K $\alpha$  radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. The known MOF Nd(trimesate) was synthesized and activated according to the literature (Gustafsson and Zou et al. *Chem. Mater.* **2010**, 22, 3316)

**X-ray Crystallography.** Single-crystal XRD data for the compounds was collected on on a Bruker SMART Apex II CCD-based X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.54178$  Å) at 123 K. The empirical absorption correction was applied by using the SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Göttingen, Göttingen, Germany, 1996). The structure was solved using direct method, and refined by full-matrix least-squares on F2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Göttingen, Germany, 1997). All non-H atoms were refined anisotropically. Crystal data and details of the data collection are given in Table S1. The selected bond distances and angles are presented in Tables S2-S3.

### 2. Synthesis of the ligand H<sub>3</sub>L



To a solution of tris(bromoduryl)borane (3.88g, 6.0mmol) in dry THF (150ml) was added dropwise a pentane solution of *t*-BuLi (1.1M, 33ml, 36.5mmol) at -78°C. After stirring at -78 °C for 1h the reaction mixture was allowed to warm up to -60 °C and dry CO<sub>2</sub> was aerated to the reaction mixture while keeping the temperature below -50 °C. The reaction mixture was warmed up to room temperature after aerating CO<sub>2</sub> for 1h and stirred overnight. The reaction mixture was concentrated under reduced pressure. After addition of water, the mixture was extracted with Et<sub>2</sub>O. The extract was washed with brine, dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by washing with hexane to afford tris(carbonylduryl)borane (2.6g, 80%) as a white solid. <sup>1</sup>HNMR (DMSO, 400MHz)  $\delta$  : 2.04 (s, 18H), 1.90 (s, 18H). <sup>13</sup>C NMR (DMSO,

400MHz)  $\delta$  : 172.62, 149.28, 138.66, 136.24, 128.85, 20.00, 17.59. ESI-MS: m/z 541.4 (Calcd m/z 541.3 [M-H]<sup>+</sup>) (see Figure S9)

# 3. Synthesis of MOFs 1 and 2 and the cation exchange

A mixture of LnCl<sub>3</sub>·6H<sub>2</sub>O (0.01 mmol), H<sub>3</sub>L (0.005 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.005 mmol) was placed in a small vial containing THF (1.0 mL), DMF (0.5mL) and EtOH (0.5 mL). The vial was sealed, heated at 80 °C for two days, and allowed to cool to room temperature. The crystals of **1** (purple) and **2** (colorless) suitable for X-ray diffraction were collected by filtration, washed with diethyl ether, and dried in air. Compound **2** was synthesized in a similar procedure by using corresponding salt La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O. The products can be bes formulated [Me<sub>2</sub>NH<sub>2</sub>][Ln<sub>4</sub>(CO<sub>3</sub>)L<sub>4</sub>(DMF)<sub>m</sub>(H<sub>2</sub>O)<sub>2</sub>]·nH<sub>2</sub>O (**1**: Ln = Nd, m = 2, n = 12; **2**: Ln = La, m = 4, n = 6) on the basis of microanalysis, IR, and TGA. While the single-crystal diffraction showed that the products have the formula [Me<sub>2</sub>NH<sub>2</sub>][Nd<sub>4</sub>(CO<sub>3</sub>)L<sub>4</sub>(DMF)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (**1**) and [Me<sub>2</sub>NH<sub>2</sub>][La<sub>4</sub>(CO<sub>3</sub>)L<sub>4</sub>(DMF)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (**2**). This difference may be attributed to the fact that only part of the disordered guest molecules could be located in the Single-crystal structure solution. Yield: **1**, 72 %; **2**, 67 %.

Elemental Analysis and IR for compound 1 (Nd):

Anal (%). Calcd for C143H202B4N4Nd4O43: C, 52.28; H, 6.20; N, 1.71. Found: C, 51.90; H, 6.15; N, 1.69.

IR (KBr, cm<sup>-1</sup>): 3411(s), 2991(w), 2929(m), 1656(m), 1531(s), 1423(s), 1277(s), 1099(m), 1079(w), 1043(m), 1002(w), 979(m), 870(m), 854(m), 781(w), 675(m), 632(m).

Elemental Analysis and IR for compound 2 (La):

Anal (%). Calcd for C149H208B4La4N6O41: C, 53.61; H, 6.28; N, 2.52. Found: C, 52.93; H, 6.21; N, 2.50.

IR (KBr, cm<sup>-1</sup>): 3411(s), 2991(w), 2929(m), 1653(m), 1548(s), 1417(s), 1276(s), 1099(m), 1076(w), 1040(m), 1004(w), 978(m), 869(m), 852(m), 790(w), 672(m), 632(m).

Na<sup>+</sup>-exchange experiment with crystalline powder of 1. Freshly ground crystalline powder of 1 (20 mg) was placed in a saturate aqueous solution of NaCl (8 mL). Then, the mixture was heated in a 10 mL capped vial at 40 °C for 4 days. The exchanged product was then isolated by filtration, washed several times with water, acetone, and ether. Inductively coupled plasma (ICP) analysis on the exchanged sample revealed that the molar ratio of Nd to Na is 4:1. Elemental analysis result (%): C, 50.37; H, 5.81; N, 0.83. Thus, the ion-exchanged product can be formulated as  $[Na_2][Nd_4(CO_3)L_4(DMF)_2(H_2O)_2]\cdot 10H_2O$  [Anal (%). Calcd: C, 50.97; H, 5.85; N, 0.86]. While powder XRD experiment indicates that the framework and crystallinity of 1 are retained upon exchange of the cation.

# 4. Experimental procedure and product characterization for the allylation reaction, the Diels-Alder reaction and the Strecker reaction in water:

# 4.1 The allylation reactions:

All reactions were carried out in 10 mL Schlenk flasks. To a suspension of evacuated 1 (0.02 mmol, 2 mol %) in water (2 mL) was added SDS (0.20 mmol), aldehyde or ketone (1 mmol) and tetraallyltin (0.4 mmol). This mixture was stirred at room temperature for 18-48h and then the solid catalyst was filtered and washed with water and EtOAc. The filtrate was extracted with EtOAc, and the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the residue passed through column packed with silica gel to afford the pure allylated product. Other reactions and control reactions were carried out under otherwise identical conditions as indicated in the text. NMR data are consistent with reported data (Kobayashi, S. et al. *J. Org. Chem.* **1993**, *58*, 6958). The substrate formylcoronene was synthesized accoding to the published procedure (Dale T. J.; Rebek, Jr. *J. Am. Chem. Soc.* **2006**, 128, 4500-4501).



## Phenylbut-3-en-1-ol

Yield 99.1%; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 2.42 (d, 1H), 2.48-2.52 (m, 2H), 4.68-4.72 (m, 1H), 5.12-5.18 (m, 2H), 5.75-5.85 (m, 1H), 7.27-7.36 (m, 5H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ 43.99, 73.59, 118.46, 126.10, 127.74, 128.61, 134.74, 144.17.



# 1-Naphthalen-1-yl-but-3-en-1-ol

Yield 83.6%; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 2.57-2.64 (m, 2H), 2.72-2.78 (m, 1H), 5.17-5.25 (m, 2H), 5.47-5.50 (m, 1H), 5.88-5.98 (m, 1H), 7.46-7.56 (m, 3H), 7.66 (d, 1H), 7.80 (d, 1H), 7.89-7.91 (m, 1H), 8.06-8.09 (m, 1H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ 43.08, 70.29, 118.35, 123.21, 123.35, 125.73, 125.78, 126.29, 128.20, 129.23, 130.58, 134.06, 135.14, 139.82.



#### 1-(4-Nitrophenyl)but-3-en-1-ol

Yield 98.3%; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 2.41-2.53 (m, 2H), 2.68 (s, 1H), 4.81-4.84 (m, 1H), 5.09-5.14 (m, 2H), 5.69-5.79 (m, 1H), 7.49-7.50 (m, 2H), 8.12-8.15 (m, 2H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ44.03, 72.42, 119.66, 123.79, 126.80, 126.81, 133.44, 147.38, 151.46.



# 1-(4-Methylphenyl)but-3-en-1-ol

Yield 87.3%; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  2.30 (d, 1H), 2.36 (s, 3H), 2.49-2.52 (m, 2H), 4.67-4.70 (m, 1H), 5.12-5.18 (m, 2H), 5.76-5.86 (m, 1H), 7.17 (d, 2H), 7.25 (d, 2H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  21.37, 43.94, 73.50, 118.25, 126.09, 129.30, 134.94, 137.33, 141.26.



## Phenyl-5-hexen-3-ol

Yield 90.8%; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 1.77-1.83 (m, 3H), 2.16-2.36 (m, 2H), 2.66-2.86 (m, 2H), 3.67-3.70 (m, 1H), 5.12-5.18 (m, 2H), 5.78-5.88 (m, 1H), 7.18-7.32 (m, 5H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ 32.26, 38.66, 42.28, 70.15, 118.53, 126.03, 128.61, 128.65, 134.82, 142.26.



# 1-Phenylhexa-1,5-dien-3-ol

Yield 95.7%; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 2.41-2.45 (m, 2H), 2.51 (s, 1H), 4.36 (d, 1H), 5.15-5.22 (m, 2H), 5.83-5.94 (m, 1H), 6.23-6.29 (m, 1H), 6.59-6.63 (m, 1H), 7.24-7.41 (m, 5H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ 42.24, 72.04, 118.50, 126.77, 127.89, 128.83, 130.54, 131.95, 134.43, 136.96.



# 3-Methyl-1-phenyl-5-hexen-3-ol

Yield 45.5%; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 1.27 (s, 3H), 1.77-1.81 (m, 2H), 2.31 (d, 2H), 2.70-2.74 (m, 2H), 5.14-5.19 (m, 2H), 5.85-5.96 (m, 1H), 7.18-7.31 (m, 5H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ 26.99, 30.50, 43.94, 46.70, 72.28, 119.09, 125.99, 128.56, 128.65, 134.07, 142.74.



# 3-Methyl-1-phenyl-hexa-1,5-dien-3-ol

Yield 81.4%; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  1.40 (s, 3H), 1.93 (s, 1H), 2.34-2.48 (m, 2H), 5.14-5.19 (m, 2H), 5.80-5.91 (m, 1H), 6.31 (d, 1H), 6.61 (d, 1H), 7.22-7.40 (m, 5H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  28.17, 47.58, 72.60, 119.50, 126.65, 127.65, 128.79, 133.82, 136.46, 137.15.



#### **Biphenylbut-3-en-1-ol**

Yield 83.2%; <sup>1</sup>H NMR (CDCl3, 400 MHz)  $\delta$  2.13 (d, 1H), 2.53-2.59 (m, 2H), 4.78-4.80 (m, 1H), 5.16-5.23 (m, 2H), 5.82-5.88 (m, 1H), 7.33-7.37 (m, 1H), 7.42-7.47 (m, 4H), 7.58-7.61 (m, 4H) ; <sup>13</sup>C NMR (400MHz, CDCl3):  $\delta$  44.02, 73.27, 118.74, 126.50, 127.29, 127.39, 127.49, 128.98, 134.64, 140.70, 141.06, 143.12°



# 1-(corone-1-yl)but-3-en-1-ol

Yield 33.2%; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  8.78-9.15 (m, 11H, ArH) , 6.05(m, 1H, vinylH) , 5.98 (d, 1H,) , 5.10 (dd, 1H, viny2H) , 5.03 (dd, 1H, viny2H) , 2.88 (dd, 2H, - CH<sub>2</sub>-); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): 40.72 , 136.64 , 128.77 , 128.64, 128.59, 128.46, 128.38, 127.06, 126.86, 126.80, 126.75, 126.72, 126.65, 126.46, 126.30, 123.91, 122.79, 122.50 , 122.41 , 122.09 , 121.94 , 121.74 , 121.32 , 117.462 , 70.62 , 44.18.

### 4.2. The Diels-Alder reaction:

The reaction was carried out in a 10 mL Schlenk flask. To a suspension of evacuated 1 (0.02 mmol, 2 mol%) in water (2 mL) was added SDS (0.20 mmol), 3-acryloyl-1,3-oxazolidin-2-one (1 mmol) and cyclopentadiene (3 mmol). This mixture was stirred at room temperature for 12 h and then the solid catalyst was filtered and washed with water and EtOAc. The filtrate was extracted with EtOAc, and the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the residue passed through column packed with silica gel to afford the pure product. Yield: quant. (100%). NMR data are consistent with reported data (Narasaka, K.et al, *J. Am. Chem. Soc.* **1989**, *111*, 5340).



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.29-1.40 (m, 3H), 1.82-1.88 (m, 1H), 2.84 (d, 1H), 3.20 (s, 1H), 3.81-3.96 (m, 3H), 4.29-4.33 (m, 2H), 5.75-5.78 (m, 1H), 6.07-6.14 (m, 1H). The *endo/exo* ratio was determined by integration of the olefinic protons of the exo diastereomer [ $\delta$  6.18 (m, 2H)], endo/exo=91:9.

### 4.3 The Strecker reaction:

The reaction was carried out in a 10 mL Schlenk flask. To a suspension of evacuated 1 (0.02 mmol, 2 mol%) in water (2 mL) was added SDS (0.20 mmol), benzaldehyde (1 mmol), aniline (1 mmol) and tributyltin cyanide (1.5 mmol). This mixture was stirred at room temperature for 12 h and then the solid catalyst was filtered and washed with water and EtOAc. The filtrate was extracted with EtOAc, and the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the residue passed through column packed with silica gel to afford the pure product. Yield: 75%. NMR data are consistent with reported data ((Kobayashi, S. et al. *J. Am. Chem. Soc.* **1997**, *119*, 10049)).



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 4.08 (d, 1H), 5.43 (d, 1H), 6.78 (d, 2H), 6.80-6.94 (m, 1H), 7.25-7.31 (m, 2H), 7.44-7.50 (m, 3H), 7.60-7.62 (m, 2H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ 50.44, 114.42, 118.48, 120.50, 127.50, 129.57, 129.75, 129.81, 134.19, 144.93 $_{\circ}$ 

Identification code	1 (Nd)	1 (La)
Empirical formula	C143H182B4Nd4N4O33	C149H196B4N6La4O35
Formula weight	3105.13	3230.00
Temperature (K)	123	123
Wavelength (Å)	1.54178	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	Pnna	Pnna
Unit cell dimensions	a = 37.6140(15) Å b = 27.2860(11) Å c = 18.2151(7) Å $\alpha = \beta = \gamma = 90^{\circ}$	a = 37.927(3) Å b = 27.1472(19) Å c = 18.4835(12) Å $\alpha = \beta = \gamma = 90^{\circ}$
Volume ( $Å^3$ ), Z	18694.8(13), 4	19031(2), 4
Density (calculated) (mg/m <sup>3</sup> )	1.103	1.127
Absorption coefficient (mm <sup>-1</sup> )	8.795	0.940
F(000)	6367	6640
Theta range for data collection (°)	2.92 to 55.00	1.23 to 25.00
Limiting indices	-37<=h<=39, -27<=k<=28, -19<=l<=19	-45<=h<=45, -31<=k<=32, - 15<=l<=21
Reflections collected	110592	133736
Independent reflections	11470 (Rint = 0.1086)	16714 (Rint = 0.1378)
Completeness to theta	55.00°, 97.5%	25.00°, 99.7%
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data / restraints / parameters	11470/ 30 / 738	16714 / 38 / 687
Goodness-of-fit on F <sup>2</sup>	1.012	1.015
Final R indices [I>2sigma(I)]	R1=0.0832, wR2=0.1812	R1=0.0609, wR2=0.1566
R indices (all data)	R1=0.1147, wR2=0.1949	R1=0.1201, wR2=0.1973
Largest diff. peak and hole (e.Å <sup>-3</sup> )	1.990 and -1.073	1.457 and -1.186

5. Table S1. Crystal data and structure refinement for 1 and 2.

# 6. Table S3. Selected bond lengths (Å) and angles (°) for 1.

Nd(1)-O(5)#1	2.407(7)
Nd(1)-O(14)	2.413(3)
Nd(1)-O(9)#2	2.427(7)
Nd(1)-O(2)	2.427(7)
Nd(1)-O(12)#3	2.503(8)
Nd(1)-O(16)	2.528(8)
Nd(1)-O(15)	2.545(7)
Nd(1)-O(11)#3	2.612(9)
Nd(1)-O(13)	2.724(6)
Nd(1)-C(59)#3	2.868(14)
Nd(2)-O(3)#4	2.390(7)
Nd(2)-O(6)#1	2.392(7)
Nd(2)-O(4)#5	2.396(7)
Nd(2)-O(13)	2.454(6)
Nd(2)-O(1)	2.465(6)
Nd(2)-O(10)	2.485(7)
Nd(2)-O(7)	2.511(10)
Nd(2)-O(8)	2.688(15)
B(1)-C(27)	1.619(12)
B(1)-C(5)	1.619(12)
B(1)-C(16)	1.624(12)
B(2)-C(49)	1.60(2)
B(2)-C(38)#1	1.616(11)
B(2)-C(38)	1.616(10)
B(3)-C(56)	1.58(2)
B(3)-C(63)	1.631(10)
B(3)-C(63)#6	1.631(12)
O(5)#1-Nd(1)-O(14)	110.8(2)
O(5)#1-Nd(1)-O(9)#2	136.6(3)
O(14)-Nd(1)-O(9)#2	73.4(3)
O(5)#1-Nd(1)-O(2)	74.8(3)
O(14)-Nd(1)-O(2)	120.6(3)
O(9)#2-Nd(1)-O(2)	142.3(3)
O(5)#1-Nd(1)-O(12)#3	75.9(3)
O(14)-Nd(1)-O(12)#3	145.9(3)
O(9)#2-Nd(1)-O(12)#3	79.5(3)
O(2)-Nd(1)-O(12)#3	93.5(3)
O(5)#1-Nd(1)-O(16)	67.5(3)
O(14)-Nd(1)-O(16)	73.3(2)
O(9)#2-Nd(1)-O(16)	73.3(3)

O(2)-Nd(1)-O(16)	142.2(3)
O(12)#3-Nd(1)-O(16)	79.4(3)
O(5)#1-Nd(1)-O(15)	149.7(3)
O(14)-Nd(1)-O(15)	70.8(2)
O(9)#2-Nd(1)-O(15)	73.5(3)
O(2)-Nd(1)-O(15)	78.8(2)
O(12)#3-Nd(1)-O(15)	120.7(3)
O(16)-Nd(1)-O(15)	136.5(3)
O(5)#1-Nd(1)-O(11)#3	115.0(3)
O(14)-Nd(1)-O(11)#3	134.2(3)
O(9)#2-Nd(1)-O(11)#3	72.4(3)
O(2)-Nd(1)-O(11)#3	74.6(3)
O(12)#3-Nd(1)-O(11)#3	50.8(3)
O(16)-Nd(1)-O(11)#3	123.2(3)
O(15)-Nd(1)-O(11)#3	70.8(3)
O(5)#1-Nd(1)-O(13)	76.6(2)
O(14)-Nd(1)-O(13)	49.2(3)
O(9)#2-Nd(1)-O(13)	122.5(2)
O(2)-Nd(1)-O(13)	78.4(2)
O(12)#3-Nd(1)-O(13)	152.4(3)
O(16)-Nd(1)-O(13)	90.8(3)
O(15)-Nd(1)-O(13)	84.0(2)
O(11)#3-Nd(1)-O(13)	146.0(2)
O(3)#4-Nd(2)-O(6)#1	151.7(2)
O(3)#4-Nd(2)-O(4)#5	121.4(3)
O(6)#1-Nd(2)-O(4)#5	76.4(2)
O(3)#4-Nd(2)-O(13)	79.2(3)
O(6)#1-Nd(2)-O(13)	84.9(2)
O(4)#5-Nd(2)- $O(13)$	76.4(2)
O(3)#4-Nd(2)-O(1)	79.9(2)
O(6)#1-Nd(2)-O(1)	74.3(2)
O(4)#5-Nd(2)-O(1)	143.4(2)
O(13)-Nd(2)-O(1)	79.7(2)
O(3)#4-Nd(2)-O(10)	75.2(2)
O(6)#1-Nd(2)-O(10)	132.9(2)
O(4)#5-Nd(2)- $O(10)$	75.4(2)
O(13)-Nd(2)-O(10)	123.1(2)
O(1)-Nd(2)-O(10)	141.1(2)
O(3)#4-Nd(2)-O(7)	98.3(4)
O(6)#1-Nd(2)-O(7)	87.9(3)
O(4)#5-Nd(2)-O(7)	121.8(4)
O(13)-Nd(2)-O(7)	158.2(4)
O(1)-Nd(2)-O(7)	78.5(4)

O(10)-Nd(2)-O(7)	76.2(3)
O(3)#4-Nd(2)-O(8)	133.3(3)
O(6)#1-Nd(2)-O(8)	68.6(3)
O(4)#5-Nd(2)-O(8)	77.1(4)
O(13)-Nd(2)-O(8)	146.1(3)
O(1)-Nd(2)-O(8)	111.2(3)
O(10)-Nd(2)-O(8)	68.8(3)
O(7)-Nd(2)-O(8)	45.3(4)
C(27)-B(1)-C(5)	118.5(8)
C(27)-B(1)-C(16)	120.2(8)
C(5)-B(1)-C(16)	121.3(8)
C(49)-B(2)-C(38)#1	118.6(9)
C(49)-B(2)-C(38)	118.6(7)
C(38)#1-B(2)-C(38)	122.7(15)
C(56)-B(3)-C(63)	120.0(6)
C(56)-B(3)-C(63)#6	120.0(8)
C(63)-B(3)-C(63)#6	120.1(14)

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1/2,-z+3/2 #2 x-1/2,y,-z+2 #3 x-1/2,-y+1/2,z-1/2 #4 -x,-y+1,-z+2 #5 -x,y-1/2,z+1/2 #6 x,-y+1/2,-z+5/2 #7 x+1/2,-y+1/2,z+1/2 #8 -x,y+1/2,z-1/2 #9 x+1/2,y,-z+2

# 7. Table S3. Selected bond lengths (Å) and angles (°) for 2.

La(1)-O(6)#22.446(8)La(1)-O(4)#32.456(9)	
La(1)-O(4)#3 2.456(9)	
La(1)-O(1) 2.462(8)	
La(1)-O(16) 2.481(7)	
La(1)-O(12)#4 2.564(10)	)
La(1)-O(9)#5 2.593(7)	
La(1)-O(13) 2.643(12)	
La(2)-O(10) 2.472(9)	
La(2)-O(5)#2 2.474(9)	
La(2)-O(2) 2.475(8)	
La(2)-O(15) 2.487(3)	
La(2)-O(8) 2.554(10)	
La(2)-O(17) 2.624(10)	
La(2)-O(14) 2.626(11)	
La(2)-O(7) 2.657(10)	
La(2)-O(16) 2.784(8)	
La(2)-C(34) 2.992(12)	
La(2)-C(73) 3.067(9)	
C(5)-B(1) 1.620(15)	
C(12)-B(1) 1.613(14)	
C(23)-B(1) 1.615(14)	
C(38)-B(2) 1.637(11)	
C(45)-B(2) 1.59(2)	
C(56)-B(3) 1.59(2)	
C(59)-B(3) 1.608(12)	
B(2)-C(38)#2 1.637(11)	
B(3)-C(59)#6 1.608(12)	
O(3)#1-La(1)-O(6)#2 154.2(3	)
O(3)#1-La(1)-O(4)#3 118.7(3	)
O(6)#2-La(1)-O(4)#3 71.7(3)	)
O(3)#1-La(1)-O(1) 86.2(3)	
O(6)#2-La(1)-O(1) 74.3(3)	
O(4)#3-La(1)-O(1) 141.2(3)	
O(3)#1-La(1)-O(16) 76.5(3)	
O(6)#2-La(1)-O(16) 83.8(3)	
O(4)#3-La(1)-O(16) 77.3(3)	
O(1)-La(1)-O(16) 81.0(3)	
O(3)#1-La(1)-O(12)#4 130.1(4	4)
O(6)#2-La(1)-O(12)#4 71.3(3	)

O(4)#3-La(1)-O(12)#4	85.8(4)
O(1)-La(1)-O(12)#4	100.7(3)
O(16)-La(1)-O(12)#4	153.3(3)
O(3)#1-La(1)-O(9)#5	75.8(3)
O(6)#2-La(1)-O(9)#5	129.5(3)
O(4)#3-La(1)-O(9)#5	73.3(3)
O(1)-La(1)-O(9)#5	145.1(3)
O(16)-La(1)-O(9)#5	122.0(3)
O(12)#4-La(1)-O(9)#5	70.9(3)
O(3)#1-La(1)-O(13)	72.1(4)
O(6)#2-La(1)-O(13)	114.7(4)
O(4)#3-La(1)-O(13)	143.6(4)
O(1)-La(1)-O(13)	69.2(3)
O(16)-La(1)-O(13)	137.5(4)
O(12)#4-La(1)-O(13)	64.9(4)
O(9)#5-La(1)-O(13)	76.8(3)
O(10)-La(2)-O(5)#2	137.4(3)
O(10)-La(2)-O(2)	142.6(3)
O(5)#2-La(2)-O(2)	74.6(3)
O(10)-La(2)-O(15)	72.2(3)
O(5)#2-La(2)-O(15)	110.3(3)
O(2)-La(2)-O(15)	121.0(3)
O(10)-La(2)-O(8)	80.5(3)
O(5)#2-La(2)-O(8)	77.2(3)
O(2)-La(2)-O(8)	92.7(3)
O(15)-La(2)-O(8)	146.3(3)
O(10)-La(2)-O(17)	73.6(3)
O(5)#2-La(2)-O(17)	148.7(3)
O(2)-La(2)-O(17)	78.8(3)
O(15)-La(2)-O(17)	70.2(2)
O(8)-La(2)-O(17)	120.7(4)
O(10)-La(2)-O(14)	73.0(3)
O(5)#2-La(2)-O(14)	67.8(3)
O(2)-La(2)-O(14)	142.4(3)
O(15)-La(2)-O(14)	73.3(3)
O(8)-La(2)-O(14)	80.2(4)
O(17)-La(2)-O(14)	136.3(3)
O(10)-La(2)-O(7)	73.1(3)
O(5)#2-La(2)-O(7)	115.5(3)
O(2)-La(2)-O(7)	74.6(3)
O(15)-La(2)-O(7)	134.1(3)
O(8)-La(2)-O(7)	49.5(3)
O(17)-La(2)-O(7)	71.9(3)

O(14)-La(2)-O(7)	122.7(4)
O(10)-La(2)-O(16)	120.7(3)
O(5)#2-La(2)-O(16)	75.8(3)
O(2)-La(2)-O(16)	79.8(3)
O(15)-La(2)-O(16)	48.6(3)
O(8)-La(2)-O(16)	153.0(3)
O(17)-La(2)-O(16)	83.5(3)
O(14)-La(2)-O(16)	90.0(3)
O(7)-La(2)-O(16)	147.3(3)
C(12)-B(1)-C(23)	120.5(9)
C(12)-B(1)-C(5)	120.6(9)
C(23)-B(1)-C(5)	118.9(9)
C(45)-B(2)-C(38)	120.2(7)
C(45)-B(2)-C(38)#2	120.2(6)
C(38)-B(2)-C(38)#2	119.7(13)
C(56)-B(3)-C(59)#6	118.7(8)
C(56)-B(3)-C(59)	118.7(8)
C(59)#6-B(3)-C(59)	122.5(16)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1 #2 x,-y+3/2,-z+1/2 #3 -x+2,y+1/2,z+1/2 #4 x+1/2,-y+3/2,z-1/2 #5 x+1/2,-y+3/2,z+1/2 #6 x,-y+3/2,-z+3/2 #7 -x+2,y-1/2,z-1/2 #8 x-1/2,-y+3/2,z-1/2 #9 x-1/2,-y+3/2,z+1/2 8. Figure S1. Space filling modes of the two isomers of the ligands  $\Delta$ -L (left) and  $\Lambda$ -

L (right) in 1 and 2.



9. Figure S2. (a) The asymmetric unit, (b) the Nd<sub>4</sub> cluster, (c) the space filling mode and (d) the (3,12)-connected network with a topology of 3,12T2 (binary ttd) in MOF
1. The guest molecules and hydrogen atoms were not included for clarity in (a)-(c).





10. Figure S3. (a) The asymmetric unit, (b)  $La_4$  cluster, (c) the 3D structure and (d) the space filling mode of MOF 2 (the guest molecules and hydrogen atoms were not included for clarity).





(d)

**11. Figure S4. TGA curves of 1 and 2.** (The weight losses of **1** and **2** estimated from the compositions obtained from the elemental analysis are slightly different from those obtained by TGA, which might be due to that some of adsorbed guest molecules had already been removed by applying a He flow before the elemental analysis.)



12. Figure S5. The  $N_2$  adsorption isotherm of 1 (a) and 2 (b), the sampel after soaking in  $H_2O$  for 7 days (c) and the recycled sample after 3 runs of catalysis.





13. Figure S6. PXRD patterns of 1 and 2 and the simulated patterns, as well as variable-temperature PXRD patterns for 1.



14. Figure S7. The PXRD patterns of 1 after heating in boiling water, methanol and benzene for 7 days and of the evacuated 1.



15. Figure S8. The PXRD patterns of the recycled catalytic sample of 1.



16. Figure S9. ESI-MS of Ligand H<sub>3</sub>L.



17. Figure S10. <sup>1</sup>H and <sup>13</sup>C NMR spectra of H<sub>3</sub>L (a) and (b), and Solution <sup>1</sup>H NMR showing the absence of the ligand L from the solution during the reactivity study







18. Figure S11. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the product for the allylation reaction, the Diels-Alder reaction and the Strecker reaction.









<sup>13</sup>C NMR

























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