# 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 $\mathrm{C}, \mathrm{H}$ and N were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR ( KBr pellet) spectrum was recorded ( $400-4000 \mathrm{~cm}^{-1}$. region) on a Nicolet Magna 750 FT-IR spectrometer. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ 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 $10^{\circ} \mathrm{C} \min ^{-1}$ on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using $\mathrm{Cu} \mathrm{K} \alpha$ 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 $\mathrm{Cu}-\mathrm{K} \alpha$ radiation $(\lambda=1.54178$ $\AA$ ) 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 $\mathrm{H}_{3} \mathrm{~L}$



To a solution of tris(bromoduryl)borane ( $3.88 \mathrm{~g}, 6.0 \mathrm{mmol}$ ) in dry THF ( 150 ml ) was added dropwise a pentane solution of $t-\mathrm{BuLi}(1.1 \mathrm{M}, 33 \mathrm{ml}, 36.5 \mathrm{mmol})$ at $-78^{\circ} \mathrm{C}$. After stirring at $-78^{\circ} \mathrm{C}$ for 1 h the reaction mixture was allowed to warm up to $-60^{\circ} \mathrm{C}$ and dry $\mathrm{CO}_{2}$ was aerated to the reaction mixture while keeping the temperature below $-50{ }^{\circ} \mathrm{C}$. The reaction mixture was warmed up to room temperature after aerating $\mathrm{CO}_{2}$ for 1 h and stirred overnight. The reaction mixture was concentrated under reduced pressure. After addition of water, the mixture was extracted with $\mathrm{Et}_{2} \mathrm{O}$. The extract was washed with brine, dried over anhydrous $\mathrm{MgSO}_{4}$ and concentrated under reduced pressure. The crude product was purified by washing with hexane to afford tris(carbonylduryl)borane $(2.6 \mathrm{~g}, 80 \%)$ as a white solid. ${ }^{1} \mathrm{HNMR}$ (DMSO, 400 MHz ) $\delta: 2.04(\mathrm{~s}, 18 \mathrm{H}), 1.90(\mathrm{~s}, 18 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (DMSO,
$400 \mathrm{MHz}) \delta: 172.62,149.28,138.66,136.24,128.85,20.00,17.59$. ESI-MS: m/z 541.4 (Calcd m/z $\left.541.3[\mathrm{M}-\mathrm{H}]^{+}\right)$(see Figure S9)

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

A mixture of $\mathrm{LnCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.01 \mathrm{mmol}), \mathrm{H}_{3} \mathbf{L}(0.005 \mathrm{mmol})$ and $\mathrm{K}_{2} \mathrm{CO}_{3}(0.005$ mmol ) was placed in a small vial containing THF ( 1.0 mL ), DMF $(0.5 \mathrm{~mL})$ and EtOH $(0.5 \mathrm{~mL})$. The vial was sealed, heated at $80^{\circ} \mathrm{C}$ for two days, and allowed to cool to room temperature. The crystals of $\mathbf{1}$ (purple) and $\mathbf{2}$ (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 $\mathrm{La}\left(\mathrm{NO}_{3}\right)_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$. The products can be bes formulated $\left[\mathrm{Me}_{2} \mathrm{NH}_{2}\right]\left[\mathrm{Ln}_{4}\left(\mathrm{CO}_{3}\right) \mathrm{L}_{4}(\mathrm{DMF})_{\mathrm{m}}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \cdot \mathrm{nH}_{2} \mathrm{O}(\mathbf{1}: \mathrm{Ln}=$ $\mathrm{Nd}, \mathrm{m}=2, \mathrm{n}=12 ; \mathbf{2}: \mathrm{Ln}=\mathrm{La}, \mathrm{m}=4, \mathrm{n}=6$ ) on the basis of microanalysis, IR , and TGA. While the single-crystal diffraction showed that the products have the formula $\left[\mathrm{Me}_{2} \mathrm{NH}_{2}\right]\left[\mathrm{Nd}_{4}\left(\mathrm{CO}_{3}\right) \mathrm{L}_{4}(\mathrm{DMF})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \cdot 2 \mathrm{H}_{2} \mathrm{O}$ (1) and $\left[\mathrm{Me}_{2} \mathrm{NH}_{2}\right]\left[\mathrm{La}_{4}\left(\mathrm{CO}_{3}\right) \mathrm{L}_{4}(\mathrm{DMF})_{4}\right.$ $\left.\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \cdot 2 \mathrm{H}_{2} \mathrm{O}(2)$. 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, $\mathrm{cm}^{-1}$ ): 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 ( $\mathrm{KBr}, \mathrm{cm}^{-1}$ ): 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).
$\mathbf{N a}^{+}$-exchange experiment with crystalline powder of 1 . Freshly ground crystalline powder of $\mathbf{1}(20 \mathrm{mg})$ was placed in a saturate aqueous solution of $\mathrm{NaCl}(8 \mathrm{~mL})$. Then, the mixture was heated in a 10 mL capped vial at $40^{\circ} \mathrm{C}$ 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, $50.37 ; \mathrm{H}, 5.81 ; \mathrm{N}, 0.83$. Thus, the ionexchanged product can be formulated as $\left[\mathrm{Na}_{2}\right]\left[\mathrm{Nd}_{4}\left(\mathrm{CO}_{3}\right) \mathbf{L}_{4}(\mathrm{DMF})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \cdot 10 \mathrm{H}_{2} \mathrm{O}$ [Anal (\%). Calcd: C, $50.97 ; \mathrm{H}, 5.85 ; \mathrm{N}, 0.86]$. While powder XRD experiment indicates that the framework and crystallinity of $\mathbf{1}$ 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 ( $0.02 \mathrm{mmol}, 2 \mathrm{~mol} \%$ ) 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 1848 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 $\mathrm{Na}_{2} \mathrm{SO}_{4}$. 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\%; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 2.42(\mathrm{~d}, 1 \mathrm{H}), 2.48-2.52(\mathrm{~m}, 2 \mathrm{H}), 4.68-4.72(\mathrm{~m}$, $1 \mathrm{H}), 5.12-5.18(\mathrm{~m}, 2 \mathrm{H}), 5.75-5.85(\mathrm{~m}, 1 \mathrm{H}), 7.27-7.36(\mathrm{~m}, 5 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 400 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 43.99,73.59,118.46,126.10,127.74,128.61,134.74,144.17$.


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

Yield $83.6 \%$; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 2.57-2.64(\mathrm{~m}, 2 \mathrm{H}), 2.72-2.78(\mathrm{~m}, 1 \mathrm{H}), 5.17-$ $5.25(\mathrm{~m}, 2 \mathrm{H}), 5.47-5.50(\mathrm{~m}, 1 \mathrm{H}), 5.88-5.98(\mathrm{~m}, 1 \mathrm{H}), 7.46-7.56(\mathrm{~m}, 3 \mathrm{H}), 7.66(\mathrm{~d}, 1 \mathrm{H}), 7.80$ $(\mathrm{d}, 1 \mathrm{H}), 7.89-7.91(\mathrm{~m}, 1 \mathrm{H}), 8.06-8.09(\mathrm{~m}, 1 \mathrm{H}){ }^{13}{ }^{3} \mathrm{C}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 43.08,70.29$, $118.35,123.21,123.35,125.73,125.78,126.29,128.20,129.23,130.58,134.06,135.14$, 139.82 .


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

Yield $98.3 \%$; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 2.41-2.53(\mathrm{~m}, 2 \mathrm{H}), 2.68(\mathrm{~s}, 1 \mathrm{H}), 4.81-4.84(\mathrm{~m}$, $1 \mathrm{H}), 5.09-5.14(\mathrm{~m}, 2 \mathrm{H}), 5.69-5.79(\mathrm{~m}, 1 \mathrm{H}), 7.49-7.50(\mathrm{~m}, 2 \mathrm{H}), 8.12-8.15(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 44.03,72.42,119.66,123.79,126.80,126.81,133.44,147.38$, 151.46.


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

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


## Phenyl-5-hexen-3-ol

Yield $90.8 \%$; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.77-1.83(\mathrm{~m}, 3 \mathrm{H}), 2.16-2.36(\mathrm{~m}, 2 \mathrm{H}), 2.66-$ $2.86(\mathrm{~m}, 2 \mathrm{H}), 3.67-3.70(\mathrm{~m}, 1 \mathrm{H}), 5.12-5.18(\mathrm{~m}, 2 \mathrm{H}), 5.78-5.88(\mathrm{~m}, 1 \mathrm{H}), 7.18-7.32(\mathrm{~m}, 5 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR (400MHz, $\mathrm{CDCl}_{3}$ ): $\delta 32.26,38.66,42.28,70.15,118.53,126.03,128.61,128.65$, 134.82, 142.26.


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

Yield $95.7 \%$; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 2.41-2.45(\mathrm{~m}, 2 \mathrm{H}), 2.51(\mathrm{~s}, 1 \mathrm{H}), 4.36(\mathrm{~d}, 1 \mathrm{H})$, 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, $5 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 42.24,72.04,118.50,126.77,127.89,128.83,130.54$, 131.95, 134.43, 136.96.


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

Yield $45.5 \%$; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.27(\mathrm{~s}, 3 \mathrm{H}), 1.77-1.81(\mathrm{~m}, 2 \mathrm{H}), 2.31(\mathrm{~d}, 2 \mathrm{H})$, 2.70-2.74 (m, 2H), 5.14-5.19 (m, 2H), 5.85-5.96 (m, 1H), 7.18-7.31 (m, 5H); ${ }^{13}$ C NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 26.99,30.50,43.94,46.70,72.28,119.09,125.99,128.56,128.65$, 134.07, 142.74.


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

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


Biphenylbut-3-en-1-ol
Yield 83.2\%; ${ }^{1} \mathrm{H}$ NMR (CDCl3, 400 MHz$) \delta 2.13(\mathrm{~d}, 1 \mathrm{H}), 2.53-2.59(\mathrm{~m}, 2 \mathrm{H}), 4.78-4.80$ $(\mathrm{m}, 1 \mathrm{H}), 5.16-5.23(\mathrm{~m}, 2 \mathrm{H}), 5.82-5.88(\mathrm{~m}, 1 \mathrm{H}), 7.33-7.37(\mathrm{~m}, 1 \mathrm{H}), 7.42-7.47(\mathrm{~m}, 4 \mathrm{H}), 7.58-$ $7.61(\mathrm{~m}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C}$ 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 $33.2 \%$; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.78-9.15(\mathrm{~m}, 11 \mathrm{H}, \mathrm{ArH}), 6.05(\mathrm{~m}, 1 \mathrm{H}$, vinylH), $5.98(\mathrm{~d}, 1 \mathrm{H}),, 5.10(\mathrm{dd}, 1 \mathrm{H}$, viny 2 H$), 5.03(\mathrm{dd}, 1 \mathrm{H}$, viny 2 H$), 2.88(\mathrm{dd}, 2 \mathrm{H},-$ $\mathrm{CH}_{2}-$ ); ${ }^{13} \mathrm{C}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $40.72,136.64,128.77,128.64,128.59,128.46$, $128.38,127.06,126.86,126.80,126.75,126.72,126.65,126.46,126.30,123.91,122.79$, $122.50,122.41,122.09,121.94,121.74,121.32,117.462,70.62$, 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 ( $0.02 \mathrm{mmol}, 2 \mathrm{~mol} \%$ ) 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 $\mathrm{Na}_{2} \mathrm{SO}_{4}$. 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).

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 1.29-1.40(\mathrm{~m}, 3 \mathrm{H}), 1.82-1.88(\mathrm{~m}, 1 \mathrm{H}), 2.84(\mathrm{~d}, 1 \mathrm{H}), 3.20(\mathrm{~s}$, 1 H ), 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 $[\delta 6.18(\mathrm{~m}, 2 \mathrm{H})$ ], 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 $\mathbf{1}$ ( $0.02 \mathrm{mmol}, 2 \mathrm{~mol} \%$ ) in water ( 2 mL ) was added SDS ( 0.20 mmol ), benzaldehyde ( 1 $\mathrm{mmol})$, 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 $\mathrm{Na}_{2} \mathrm{SO}_{4}$. 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)).

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 4.08(\mathrm{~d}, 1 \mathrm{H}), 5.43(\mathrm{~d}, 1 \mathrm{H}), 6.78(\mathrm{~d}, 2 \mathrm{H}), 6.80-6.94(\mathrm{~m}, 1 \mathrm{H})$, 7.25-7.31 (m, 2H), 7.44-7.50 (m, 3H), 7.60-7.62 (m, 2H); ${ }^{13} \mathrm{C}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $50.44,114.42,118.48,120.50,127.50,129.57,129.75,129.81,134.19,144.93$ 。

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

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

6. Table S3. Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 1 .

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


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


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

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
\# $9 \mathrm{x}+1 / 2, \mathrm{y},-\mathrm{z}+2$
7. Table S3. Selected bond lengths ( $\mathbf{A}$ ) and angles $\left({ }^{\circ}\right)$ for 2.

| $\mathrm{La}(1)-\mathrm{O}(3) \# 1$ | 2.425(9) |
| :---: | :---: |
| $\mathrm{La}(1)-\mathrm{O}(6) \# 2$ | 2.446 (8) |
| $\mathrm{La}(1)-\mathrm{O}(4) \# 3$ | 2.456 (9) |
| $\mathrm{La}(1)-\mathrm{O}(1)$ | $2.462(8)$ |
| $\mathrm{La}(1)-\mathrm{O}(16)$ | 2.481(7) |
| $\mathrm{La}(1)-\mathrm{O}(12) \# 4$ | 2.564(10) |
| $\mathrm{La}(1)-\mathrm{O}(9) \# 5$ | $2.593(7)$ |
| $\mathrm{La}(1)-\mathrm{O}(13)$ | 2.643(12) |
| $\mathrm{La}(2)-\mathrm{O}(10)$ | 2.472(9) |
| $\mathrm{La}(2)-\mathrm{O}(5) \# 2$ | 2.474(9) |
| $\mathrm{La}(2)-\mathrm{O}(2)$ | 2.475 (8) |
| $\mathrm{La}(2)-\mathrm{O}(15)$ | 2.487(3) |
| $\mathrm{La}(2)-\mathrm{O}(8)$ | 2.554(10) |
| $\mathrm{La}(2)-\mathrm{O}(17)$ | 2.624(10) |
| $\mathrm{La}(2)-\mathrm{O}(14)$ | 2.626(11) |
| $\mathrm{La}(2)-\mathrm{O}(7)$ | 2.657(10) |
| $\mathrm{La}(2)-\mathrm{O}(16)$ | 2.784(8) |
| $\mathrm{La}(2)-\mathrm{C}(34)$ | 2.992(12) |
| $\mathrm{La}(2)-\mathrm{C}(73)$ | 3.067(9) |
| $\mathrm{C}(5)-\mathrm{B}(1)$ | 1.620 (15) |
| $\mathrm{C}(12)-\mathrm{B}(1)$ | 1.613(14) |
| $\mathrm{C}(23)-\mathrm{B}(1)$ | 1.615(14) |
| $\mathrm{C}(38)-\mathrm{B}(2)$ | 1.637(11) |
| $\mathrm{C}(45)-\mathrm{B}(2)$ | 1.59(2) |
| $\mathrm{C}(56)-\mathrm{B}(3)$ | 1.59(2) |
| $\mathrm{C}(59)-\mathrm{B}(3)$ | 1.608(12) |
| $\mathrm{B}(2)-\mathrm{C}(38) \# 2$ | 1.637(11) |
| B(3)-C(59)\#6 | 1.608(12) |
| $\mathrm{O}(3) \# 1-\mathrm{La}(1)-\mathrm{O}(6) \# 2$ | 154.2(3) |
| $\mathrm{O}(3) \# 1-\mathrm{La}(1)-\mathrm{O}(4) \# 3$ | 118.7(3) |
| $\mathrm{O}(6) \# 2-\mathrm{La}(1)-\mathrm{O}(4) \# 3$ | 71.7(3) |
| $\mathrm{O}(3) \# 1-\mathrm{La}(1)-\mathrm{O}(1)$ | 86.2(3) |
| $\mathrm{O}(6) \# 2-\mathrm{La}(1)-\mathrm{O}(1)$ | 74.3(3) |
| $\mathrm{O}(4) \# 3-\mathrm{La}(1)-\mathrm{O}(1)$ | 141.2(3) |
| $\mathrm{O}(3) \# 1-\mathrm{La}(1)-\mathrm{O}(16)$ | 76.5(3) |
| $\mathrm{O}(6) \# 2-\mathrm{La}(1)-\mathrm{O}(16)$ | 83.8(3) |
| $\mathrm{O}(4) \# 3-\mathrm{La}(1)-\mathrm{O}(16)$ | 77.3(3) |
| $\mathrm{O}(1)-\mathrm{La}(1)-\mathrm{O}(16)$ | 81.0(3) |
| $\mathrm{O}(3) \# 1-\mathrm{La}(1)-\mathrm{O}(12) \# 4$ | 130.1(4) |
| $\mathrm{O}(6) \# 2-\mathrm{La}(1)-\mathrm{O}(12) \# 4$ | 71.3(3) |


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


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

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
\# $9 \mathrm{x}-1 / 2,-\mathrm{y}+3 / 2, \mathrm{z}+1 / 2$
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 $\mathbf{S 2}$. (a) The asymmetric unit, (b) the $\mathrm{Nd}_{4}$ 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).
(a)

(b)

(c)

(d)

10. Figure S3. (a) The asymmetric unit, (b) $\mathrm{La}_{4}$ 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).
(a)

(b)

(c)


무룽․
(d)

11. Figure S4. TGA curves of $\mathbf{1}$ and 2. (The weight losses of $\mathbf{1}$ and $\mathbf{2}$ 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 $\mathbf{S 5}$. The $\mathbf{N}_{2}$ adsorption isotherm of 1 (a) and 2 (b), the sampe 1 after soaking in $\mathbf{H}_{2} \mathrm{O}$ for $\mathbf{7}$ days (c) and the recycled sample after 3 runs of catalysis.

(b)

(c)

(c)

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

(b)

(c)

14. Figure $S 7$. 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 $\mathrm{H}_{3} \mathrm{~L}$.


17. Figure S10. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of $\mathrm{H}_{3} \mathrm{~L}$ (a) and (b), and Solution ${ }^{1} \mathrm{H}$ NMR showing the absence of the ligand $L$ from the solution during the reactivity study
(a)



(c)


Solution ${ }^{1} \mathrm{H}$ NMR showing the absence of the ligand $\mathbf{L}$ (2.04 and1.98 ppm) from the solution during the reactivity study

18. Figure S11. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of the product for the allylation reaction, the DielsAlder reaction and the Strecker reaction.
${ }^{1}$ H NMR

${ }^{13} \mathrm{C}$ NMR
$\left.\right|_{1} ^{\text {寺 }}$

$\left.\right|_{\mid} ^{\substack{\circ \\ \hline \\ \hline}}$

${ }^{1} \mathrm{H}$ NMR


LuUUUUUUUUUJJJJ

${ }^{13}$ C NMR


| 0 |
| :---: |
| $\dot{W}$ |
| $\dot{j}$ |
| $\mid$ |


${ }^{1} \mathrm{H}$ NMR




${ }^{13} \mathrm{C}$ NMR

${ }^{1} \mathrm{H}$ NMR

 Tin

$\rightarrow$


${ }^{13} \mathrm{C}$ NMR






## ${ }^{1} \mathrm{H}$ NMR

##   TIIIII


${ }^{13} \mathrm{C}$ NMR



ホี゙

${ }^{1} \mathrm{H}$ NMR



${ }^{13} \mathrm{C}$ NMR




${ }^{1} \mathrm{H}$ NMR




${ }^{13} \mathrm{C}$ NMR

|  | 웅웅앙 |
| :---: | :---: |
|  |  |
|  |  |




${ }^{1} \mathrm{H}$ NMR

${ }^{13} \mathrm{C}$ NMR

${ }^{1}$ H NMR

${ }^{13}$ C NMR
 WLuwIIDIDID



${ }^{1} \mathrm{H}$ NMR


${ }^{1} \mathrm{H}$ NMR



${ }^{1} \mathrm{H}$ NMR




${ }^{13} \mathrm{C}$ NMR



