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# Improved Enantioselectivity of Immobilized Chiral Bisoxazolines by Partial Precapping of the Siliceous Mesocellular Foam Support with Trimethylsilyl Groups

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**Abstract:** Siliceous mesocellular foams (MCF) were partially surface-modified with trimethylsilyl (TMS) groups prior to the immobilization of chiral *tert*-butylbisoxazolines. The resulting MCF-supported bisoxazoline-Cu(I) catalyst showed superior enantioselectivity (up to 95% *ee*) in asymmetric cyclopropanation,

compared to that supported on MCF without TMS precapping. This heterogenized catalyst also exhibited excellent recyclability.

**Keywords:** chiral bisoxazoline; copper; cyclopropanation; immobilization; mesoporous silica

## Introduction

Chiral bisoxazolines (BOX) have been used in a wide variety of asymmetric reactions as one of the most efficient classes of chiral ligands.<sup>[1]</sup> Conventionally, a low substrate/catalyst ratio is used to obtain high enantioselectivity and reactivity for BOX ligands. This, combined with the high cost of the ligands, has limited the practical application of chiral BOX catalysts. These drawbacks could be tackled by immobilizing BOX ligands on supports,<sup>[2]</sup> which would facilitate the catalyst recovery and reuse, and allow for continuous packed-bed reactor operations.

Most of the successfully heterogenized BOX ligands were immobilized on insoluble or soluble polymer supports.<sup>[3–8]</sup> Although the silica support is more mechanically robust and thermally stable, only very few successful silica-supported BOX catalysts have been reported;<sup>[9–12]</sup> most silica-supported bisoxazoline catalysts showed poor enantioselectivities in asymmetric cyclopropanation reactions.

As a nitrogen-based ligand, BOX shows a strong interaction with the silica surface. This is evident by the low  $R_f$  values of BOX on TLC plates when dichloromethane is used as the eluent. Such a strong interaction can affect the formation of metal complexes after covalent immobilization of BOX ligands, resulting in low enantioselectivity and regioselectivity. Although precapping of the remaining silanol groups on the silica surface after immobilization of BOX ligands can increase the enantioselectivities,<sup>[10–12]</sup> further im-

provement is required to achieve heterogenized catalysts with comparable performances as their homogeneous counterparts.

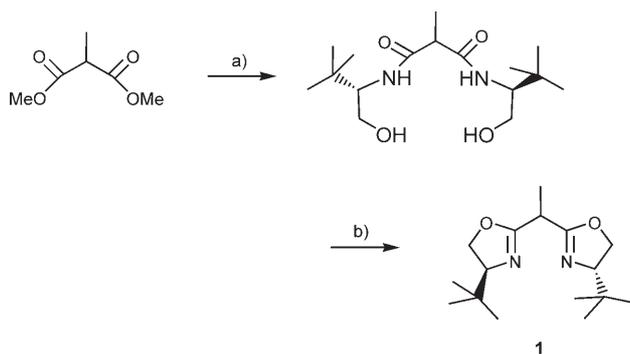
In modifying the silica surface with 3-aminopropyltriethoxysilane, a new approach has been developed to prevent the strong interaction between the amine groups and the silanol groups of the silica surface prior to precapping of the remaining silanol groups.<sup>[13]</sup> However, a different solution is required to immobilize nitrogen-containing ligands, such as BOX.

Herein, we report the successful development of a novel and simple approach to reduce the strong interactions between the ligands and the silica surface in the covalent immobilization of chiral BOX.

## Results and Discussion

Polymer-supported BOX ligands with one linker group have demonstrated high reactivity and enantioselectivity, despite breaking the  $C_2$  symmetry of the BOX ligands.<sup>[5–7]</sup> Bulky substituents on the bridge carbon of BOX decreased the regioselectivity in asymmetric cyclopropanation reactions.<sup>[3,12]</sup> Therefore, in our attempt, chiral BOX ligands were also immobilized onto mesoporous solids by one linker group (Scheme 1). A two-step process gave 68% overall yield for *tert*-butylbisoxazoline with a methyl substituent at the bridge carbon of **1**.

This BOX ligand was easily modified to obtain a trimethoxysilane linker group, which could react with



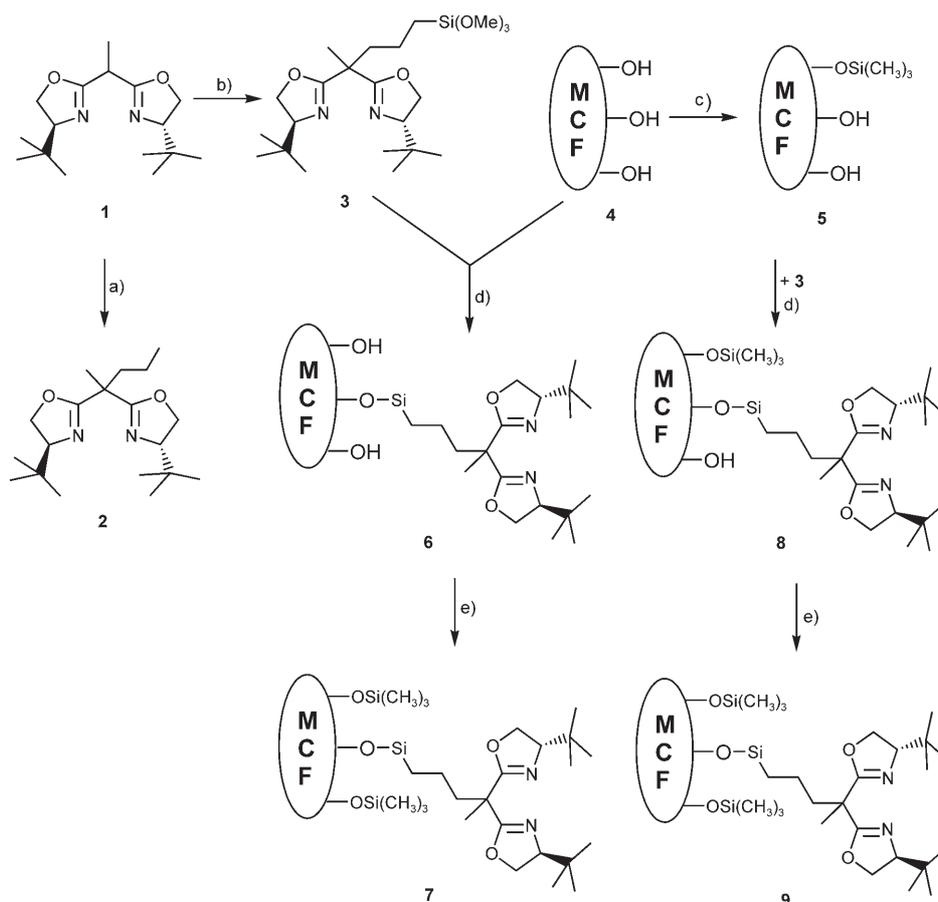
**Scheme 1.** a) (*S*)-*tert*-leucinol, 90 °C, 85%; b) *p*-toluenesulfonic chloride, triethylamine, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, room temperature, 80%.

a silanol group on the silica surface (Scheme 2). Bisoxazoline **1** was reacted with methyllithium (MeLi) or LiN(SiMe<sub>3</sub>)<sub>2</sub> to give a lithiated product, which was reacted with 3-iodopropyltrimethoxysilane to give trimethoxysilane-modified BOX. The modified BOX **3**

was easily anchored onto siliceous MCF<sup>[14]</sup> with a high loading (0.268 mmol g<sup>-1</sup>) (Scheme 2).

The surface of MCF was partially modified with TMS groups prior to the immobilization of BOX ligands in preparing **8**. Hexamethyldisilazane (HMDS) (0.4 mmol) was added to the MCF (1.0 g) well-dispersed in toluene to produce TMS-modified MCF **5** (0.794 mmol g<sup>-1</sup> by elemental analysis). This modification not only allowed for the uniform BOX immobilization onto the partially TMS-precapped MCF by preventing the strong interaction between the ligands and the support surface, but also provided for ease of control in the amount of ligands loaded.

To examine the effect of partial TMS-precapping of MCF, the modified BOX **3** was also directly immobilized onto unmodified MCF **4** to yield **6** (Scheme 2). In preparing the final MCF-supported BOX catalysts **7** and **9**, the remaining silanol groups in **6** and **8**, respectively, were capped with TMS groups by vapor phase grafting of HMDS. Excess HMDS was added to a closed reactor system under high vacuum, and then vaporized to react with the free silanol groups of



**Scheme 2.** a) i) MeLi, THF, -50 °C, 1 h; ii) 3-iodopropane, THF, -50 °C, then warmed to room temperature overnight. b) i) MeLi, THF, -50 °C, 1 h; ii) 3-iodopropyltrimethoxysilane, THF, -50 °C, then warmed to room temperature over 2 days. c) HMDS, toluene, room temperature to 60 °C. d) toluene, 120 °C, 24 h. e) HMDS, vapor phase reaction, 75 °C.

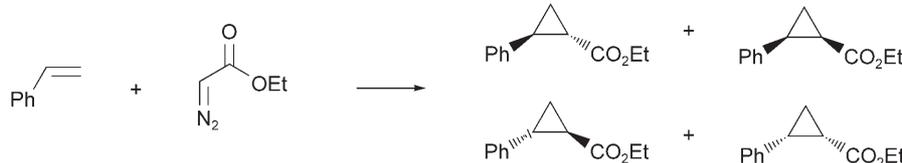
MCF at *ca.* 75°C. The extra, unreacted HMDS was readily removed under vacuum. This method allowed for the easy and efficient TMS-postcapping of the residual silanol groups without using any organic medium. Photoacoustic Fourier-transform infrared (PA-FT-IR) spectroscopy and elemental analysis confirmed that more TMS capping was achieved on the support surface by the vapor phase reaction than by the wet chemical route.

The immobilized BOX ligands formed BOX-Cu(I) complexes on reaction with Cu(I) triflate in CH<sub>2</sub>Cl<sub>2</sub>. The resulting heterogenized catalysts were examined for the asymmetric cyclopropanation of styrene (Table 1). The species **9**:CuOTf, whose MCF support was modified with TMS both before and after BOX immobilization, provided excellent enantioselectivity and reactivity. This heterogenized BOX-Cu(I) catalyst offered 95% enantiomeric excess (*ee*) for the *trans* isomer, and 92% *ee* for the *cis* isomer. Species **9**:CuOTf was successfully recycled five times without loss of enantioselectivity and reactivity. Even with a very small amount of this heterogenized catalyst (0.2 mol%, TON of 500), high reactivity and enantioselectivity (94% *ee* for the *trans* isomer and 91% *ee* for the *cis* isomer) were attained. A slightly higher *trans/cis* ratio (67/33) and the same enantioselectivity were achieved by **9**:CuOTf when the reaction medium was changed from CH<sub>2</sub>Cl<sub>2</sub> to toluene.

A homogeneous ligand **2** was synthesized with a similar structure to **3**. Both **2** and **3** did not have C<sub>2</sub> symmetry any more due to their different substituents at the bridge carbon. The homogeneous catalyst **2**:CuOTf showed a lower enantioselectivity (86% *ee* for the *trans* isomer and 84% *ee* for the *cis* isomer) and a slightly higher *trans/cis* ratio (68/32) than the heterogeneous catalyst **9**:CuOTf. Such increased enantioselectivity after immobilization was also observed in a polymer-supported catalyst.<sup>[5,7]</sup>

The species **6**:CuOTf, a BOX-Cu(I) catalyst immobilized on unmodified MCF, showed a significantly lower *trans/cis* ratio (59/41) and a lower enantioselectivity (82% *ee* for the *trans* isomer and 79% *ee* for the *cis* isomer). This inferior performance could be attributed to the presence of surface silanol groups on the MCF support, which were not capped with TMS. When **6** was subjected to TMS postcapping by vapor phase reaction, **7** was obtained. The species **7**:CuOTf showed a higher *trans/cis* ratio (64/36) and enantioselectivity (90% *ee* for the *trans* isomer and 87% *ee* for the *cis* isomer), compared to **6**:CuOTf. However, its catalytic properties still could not match those of **9**:CuOTf. Unlike **9**:CuOTf, **7**:CuOTf was not subjected to precapping, which served towards pretreating the surface of MCF with TMS prior to the introduction of the BOX ligands. The TMS precapping might have provided for a better dispersion of BOX ligands on the silica support, reducing their interactions with

**Table 1.** Asymmetric cyclopropanation of styrene.<sup>[a]</sup>



Catalyst	Run no.	Catalyst [mol%]	Yield [%] <sup>[b]</sup>	<i>trans/cis</i> ratio <sup>[b]</sup>	% <i>ee trans</i> <sup>[d]</sup>	% <i>ee cis</i> <sup>[d]</sup>
<b>2</b> :CuOTf	1	2	80	68/32	86	84
<b>6</b> :CuOTf	1	2	70	59/41	82	79
<b>7</b> :CuOTf	1	2	73	64/36	90	87
<b>9</b> :CuOTf	1	2	80 (78 <sup>[c]</sup> )	65/35	95	92
	2	2	76	65/35	95	91
	3	2	78	65/35	95	91
	4	2	76	64/36	94	90
	5	2	77 (75 <sup>[c]</sup> )	64/36	95	89
<b>9</b> :CuOTf	1	0.2	78	66/35	94	91
<b>9</b> :CuOTf <sup>[e]</sup>	1	2	72	67/33	95	92
<b>9</b> :Cu(OTf) <sub>2</sub> <sup>[f]</sup>	1	2	86	65/35	94	92

<sup>[a]</sup> Conditions: styrene/EDA = 1.2, CH<sub>2</sub>Cl<sub>2</sub>, Ar, 25°C. EDA was added slowly over 2 h, and the reaction medium was further stirred for another hour.

<sup>[b]</sup> Determined by means of a GC calibration factor between *n*-dodecane and the product.

<sup>[c]</sup> Yield of isolated product.

<sup>[d]</sup> Determined by GC (Chiraldex<sup>TM</sup> B-PM, 50 m × 0.25 mm I.D.).

<sup>[e]</sup> In toluene.

<sup>[f]</sup> Reduced by phenylhydrazine before use.

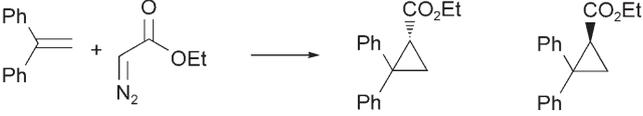
each other and with the surface silanol groups on the MCF a priori. Both **9**:CuOTf and **7**:CuOTf were subjected to postcapping by vapor phase reaction following the ligand immobilization; this would serve towards minimizing subsequent interactions between the ligands and the MCF surface. However, if there were preexisting strong interactions between the ligands and the MCF surface, such interactions would not be removed by the postcapping. These interactions might prevent proper complexing between the ligands and Cu, thereby affecting the enantioselectivity and reactivity of the catalyst. This might explain the inferior performance of **7**:CuOTf compared to **9**:CuOTf. These results illustrated that TMS precapping and postcapping of the silica support were both important towards optimizing the enantioselectivity and reactivity of the heterogenized BOX catalysts.

The heterogeneous catalyst **9**:CuOTf was also applied to the asymmetric cyclopropanation of 1,1-diphenylethylene (Table 2) and 2-methylpropene (Table 3). For 1,1-diphenylethylene, high enantioselectivity (92% *ee*) was obtained over two runs. 2-Methyl-

propene was cyclopropanated by **9**:CuOTf under the similar reaction conditions as those reported for the homogeneous catalyst [0.1 mol% catalyst, TON = 1000, 2-methylpropene/EDA = 7, addition of ethyl diazoacetate (EDA) for 5 h].<sup>[15]</sup> Catalyst **9**:CuOTf offered high enantioselectivity (92% *ee*) and high yield (90%) over 2 runs, achieving a total TON of 2000. The best insoluble polymer-supported BOX showed only 53% yield with a much lower conversion of 66%, even after 44 h under these conditions.<sup>[7]</sup> Catalyst **9**:CuOTf also showed excellent chemoselectivity (95%).

Due to the poor solubility of CuOTf and Cu(OTf)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>, long reaction times are required to complex CuOTf and Cu(OTf)<sub>2</sub> with the MCF-immobilized BOX. To reduce the complex formation time, Cu(OTf)<sub>2</sub> was completely dissolved in tetrahydrofuran (THF), and then added to the MCF-immobilized BOX ligands **9** dispersed in THF. The resulting catalyst was washed thoroughly with THF, and dried under vacuum. The elemental analysis showed that most BOX ligands (>98%) formed complexes with the copper added. In the case of highly cross-linked polymer-supported BOX, only ca. 60% of the supported ligands formed complexes with copper.<sup>[7]</sup> This suggested that the TMS-modified mesoporous silica with an ultrahigh surface area was more effective, providing greater catalyst accessibility with the monolayer immobilization of catalyst on the support surface. The complexes were reduced by phenylhydrazine before the catalytic reaction, and then used in the asymmetric cyclopropanation of styrene. Although the *ee* value was slightly lower than that of heterogenized **9**:CuOTf prepared directly in CH<sub>2</sub>Cl<sub>2</sub>, superb recyclability was achieved. Catalyst **9**:CuOTf prepared in THF maintained high enantioselectivity (92% *ee* for the *trans* isomer and 90% *ee* for the *cis* isomer) and *trans/cis* ratio (65/35) over 12 runs (Figure 1). When the reaction time was cut by half (to 1.5 h) for the 11th run, the catalyst provided the same enantioselectivity with only slightly lower yield (75%).

**Table 2.** Asymmetric cyclopropanation of diphenylethylene by **9**:CuOTf.



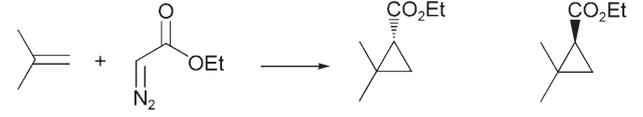
Run no.	Catalyst [mol %]	Yield [%] <sup>[b]</sup>	% <i>ee</i> <sup>[c]</sup>
1	2	73	92
2	2	74	92

<sup>[a]</sup> Conditions: 1,1-diphenylethylene/EDA = 2, CH<sub>2</sub>Cl<sub>2</sub>, Ar, 25 °C. EDA was added slowly over 2 h, and the reaction medium was further stirred for another hour.

<sup>[b]</sup> Yield of isolated product.

<sup>[c]</sup> Determined by HPLC (Chiralcel OD-H, hexane:2-propanol = 99.4:0.6).

**Table 3.** Asymmetric cyclopropanation of 2-methylpropene by **9**:CuOTf.<sup>[a]</sup>



Run no.	Catalyst [mol %]	Yield [%] <sup>[b]</sup>	% <i>ee</i> <sup>[c]</sup>
1	0.1	90	92
2	0.1	90	92

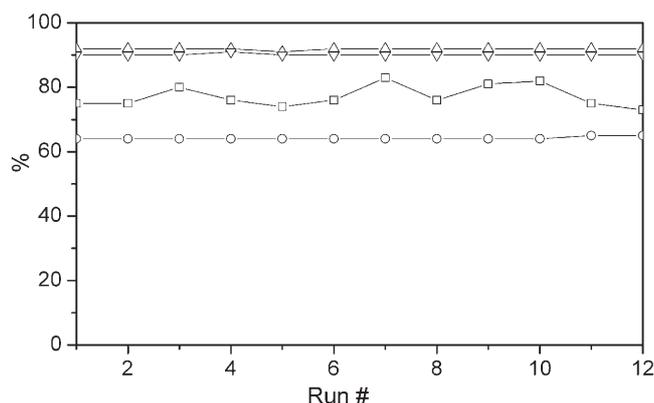
<sup>[a]</sup> Conditions: 2-methylpropene/EDA = 7, CH<sub>2</sub>Cl<sub>2</sub>, Ar. EDA was added slowly over 5 h at 0 °C; the reaction medium was then warmed to room temperature over 14 h.

<sup>[b]</sup> Yield of isolated product.

<sup>[c]</sup> Determined by GC (Chiraldex™ G-TA, 50 m × 0.25 mm I.D.).

## Conclusions

Chiral BOX ligands were effectively immobilized onto a mesoporous silica support, which was partially modified with TMS groups before ligand introduction. Following the ligand immobilization, the support was postcapped with TMS groups. This two-step modification of siliceous MCF support led to superior catalyst enantioselectivity. The resulting MCF-immobilized BOX-Cu(I) catalyst provided 95% *ee* for the *trans* isomer and 92% *ee* for the *cis* isomer, and 80% yield for the asymmetric cyclopropanation of styrene. It was also successfully recycled 12 times without losing



**Figure 1.** % Yield (□), % *trans* isomer (○), % *ee* for *trans* isomer (△), and % *ee* for *cis* isomer (▽) for the asymmetric cyclopropanation of styrene over **9**:CuOTf prepared in THF. *Conditions*: styrene/EDA = 1.2, CH<sub>2</sub>Cl<sub>2</sub>, Ar, 25 °C. For the first 10 runs, EDA was added slowly over 2 h, and the reaction medium was further stirred for another hour. For runs 11 and 12, EDA was added slowly over 1 h, and the reaction medium was further stirred for another 30 min.

any enantioselectivity and reactivity. This heterogenized chiral BOX catalyst is expected to show high enantioselectivity for various asymmetric reactions.

The partial TMS precapping of MCF represents an effective means of preparing a suitable silica support for immobilizing a wide variety of chiral BOX ligands and nitrogen-containing ligands. This approach can be applied to achieve well-dispersed chiral ligands without strong interactions with the silica surface, so that excellent enantioselectivity, reactivity and recyclability can be attained.

## Experimental Section

### Synthesis of BOX Ligand **1** with One Methyl Group at the Carbon Bridge

Dimethyl methylmalonate (1.78 g, 12.2 mmol) and (*S*)-*tert*-leucinol (3.0 g, 25.6 mmol) were heated to 90 °C under an argon flow, which removed the methanol generated during the reaction. After 12 h, white solids were obtained. To remove the remaining (*S*)-*tert*-leucinol, high vacuum was applied at 60 °C. Dihydroxymethylmalonodiamide (3.27 g, 10.37 mmol) was obtained with a high yield (85%).

A 100-mL Schlenk flask was charged with dihydroxymethylmalonodiamide (2.87 g, 9.08 mmol), 4-(dimethylamino)pyridine (DMAP, 0.12 g, 0.99 mmol), and 40 mL of CH<sub>2</sub>Cl<sub>2</sub>. Triethylamine (6 mL, 43.5 mmol) was then added. A solution of *p*-toluenesulfonyl chloride (3.77 g, 19.8 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added. The resulting bright yellow solution was stirred at room temperature for 27 h. It was diluted with 20 mL of CH<sub>2</sub>Cl<sub>2</sub>, and washed with saturated NH<sub>4</sub>Cl. The aqueous layer was back-extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The combined organic extracts were washed with saturated NaHCO<sub>3</sub>. The aqueous layer was back-ex-

tracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum. The concentrated liquors were purified by flash chromatography to give product **1**; yield: 2.03 g (7.26 mmol, 80%); [α]<sub>D</sub><sup>23</sup>: -93.3 (*c* 1.05, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 4.17 (m, 2H), 4.08 (m, 2H), 3.85 (m, 2H), 3.54 (q, *J* = 7.3 Hz, 1H), 1.48 (d, *J* = 7.3 Hz, 3H), 0.881 (s, 9H), 0.878 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 165.5, 165.3, 75.5, 68.9, 34.0, 33.8, 25.7, 25.6, 15.2; anal. calcd. for C<sub>16</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>: C 68.53, H 10.07, N 9.99; found: C 68.14, H 10.22, N 9.84; HR-MS: *m/z* = 281.2231, calcd. for [M + H]<sup>+</sup>: 281.2229

### Synthesis of Homogeneous BOX **2**

MeLi (0.516 mL, 1.6 M in Et<sub>2</sub>O, 0.825 mmol) was added into the solution of BOX **1** (0.21 g, 0.75 mmol) in 10 mL of THF at -50 °C. After stirring for 30 min, 3-iodopropane (0.110 mL, 1.13 mmol) was added, and the solution was warmed to room temperature. After stirring overnight, aqueous NH<sub>4</sub>Cl was added to the reaction mixture, and the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with brine, and then dried over MgSO<sub>4</sub>, filtered, and rotary-evaporated to give the crude product. The crude product was purified by flash column chromatography to obtain product **2**; yield: 170 mg (70%); [α]<sub>D</sub><sup>23</sup>: -43.7 (*c* 1.05, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 4.6 (m, 4H), 3.83 (m, 2H), 1.96 (m, 1H), 1.81 (m, 1H), 1.46 (s, 3H), 1.30 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.86 (s, 18H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 168.2, 168.0, 75.5, 75.3, 68.72, 68.69, 42.4, 38.7, 33.9, 33.8, 25.8, 25.7, 21.4, 17.7, 14.5; anal. calcd. for C<sub>19</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub>: C 70.76, H 8.69, N 9.92; found: C 70.35, H 8.52, N 9.75; HR-MS: *m/z* = 323.2705, calcd. for [M + H]<sup>+</sup>: = 323.2699.

### Synthesis of MCF (**4**)

Spherical MCF particles were synthesized by modifying the conventional MCF synthesis method.<sup>[14]</sup> Triblock copolymer P123 (4 g) was dissolved in an acidic solution (10 mL of HCl and 65 mL of H<sub>2</sub>O). Trimethylbenzene (TMB) (3.4 mL) was then added, and the resulting solution was heated to 37–40 °C with vigorous stirring. After 2 h of stirring, 9.2 mL of tetraethoxysilane (TEOS) were added and stirred for 5 min. The solution was transferred to an autoclave, and aged at 40 °C for 20 h under static conditions. To increase the pore size, NH<sub>4</sub>F (46 mg) in 5 mL of water was added to the solution prior to aging at 100 °C. It was then aged at 100 °C for 24 h. The resulting precipitate was filtered, washed with water and ethanol, and dried. The white powder obtained was calcined in air at 550 °C for 6 h. Surface area = 561 m<sup>2</sup>g<sup>-1</sup>; window pore size = 16 nm; cell pore size = 28 nm; average particle size = 5 μm.

### Partial Modification of MCF (**5**)

MCF (3.0 g) was degassed at 120 °C overnight under vacuum before reaction. HMDS (253 μL, 1.2 mmol) was

added to a suspension of MCF in toluene (20 mL). The mixture was stirred at room temperature under argon for 5 h, and then heated at 60 °C overnight. The resulting suspension was filtered, washed with methanol, and then dried under vacuum. Elemental analysis: found (wt %): C 2.86, H 0.94; loading of TMS groups: 0.794 mmol g<sup>-1</sup>.

### Immobilization of BOX onto Unmodified MCF (6)

MeLi (0.516 mL, 1.6 M in Et<sub>2</sub>O, 0.825 mmol) was added into the solution of BOX **1** (0.21 g, 0.75 mmol) in 10 mL of THF at -50 °C. After stirring for 30 min, 3-iodopropyltrimethoxysilane (0.148 mL, 0.75 mmol) was added, and the solution was warmed to room temperature. After stirring for 2 days at room temperature, THF was evaporated and toluene was added. The toluene solution was added to MCF **4** (2.0 g), which has been dried at 150 °C overnight. The resulting suspension was then heated to 120 °C with stirring for 1 day, filtered, and washed thoroughly with toluene, CH<sub>2</sub>Cl<sub>2</sub>, and methanol. PA-FT-IR:  $\nu$ =2957, 1663, 1089, 842, 811, 460 cm<sup>-1</sup>; elemental analysis: found (wt %): C 7.63, H 1.45, N 0.78; loading of BOX: 0.279 mmol g<sup>-1</sup>.

### TMS Modification of BOX-Immobilized MCF 6 (7)

MCF-supported BOX **6** (1.0 g) was degassed at 80 °C overnight. Excess HMDS (0.75 mL) was added to the solid under vacuum. The flask was cooled down using liquid N<sub>2</sub> under vacuum. It was sealed and then warmed to room temperature. After that, the flask was placed in the oven at 75 °C for 5 h. After reaction, excess HMDS was removed under vacuum. PA-FT-IR:  $\nu$ =2957, 1663, 1089, 842, 811, 460 cm<sup>-1</sup>; elemental analysis: found (wt %): C 10.91, H 2.05, N 0.71; loading of BOX: 0.254 mmol g<sup>-1</sup>.

### Immobilization of BOX onto Partially TMS-Modified MCF 5 (8)

The same procedure as for **6** was applied, except that partially TMS-capped MCF **5** (2.0 g, 0.794 mmol TMS/g of MCF) was used instead of unmodified MCF **4**. PA-FT-IR:  $\nu$ =2957, 1663, 1089, 842, 811, 460 cm<sup>-1</sup>.

### Further TMS Modification of BOX-Immobilized MCF 8 (9)

The same procedure as for **7** was applied except that **8** was used instead of **6**. PAS-FT-IR:  $\nu$ =2957, 1663, 1089, 842, 811, 460 cm<sup>-1</sup>; <sup>13</sup>C CP/MAS NMR (100 MHz):  $\delta$ =170.7, 168.0, 76.0, 67.9, 57.7, 50.1, 42.6, 33.2, 24.7, 18.0, 12.5, 0.5; <sup>29</sup>Si CP/MAS NMR (75 MHz):  $\delta$ =14.3, -50.0, -57.0, -65.8, -100.28, -107.58; elemental analysis: found (wt %): C 11.45, H 2.25, N 0.73; loading of BOX: 0.268 mmol g<sup>-1</sup>.

### Cyclopropanation of Styrene by MCF-Supported BOX Catalysts

(CuOTf)<sub>2</sub>-toluene (0.011 mmol) or Cu(OTf)<sub>2</sub> (0.022 mmol) was added to the MCF-immobilized BOX (0.022 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL). The mixture was stirred at room temperature for 3 days. In the case of Cu(OTf)<sub>2</sub>, phenylhydrazine (0.023 mmol) was added to reduce the copper. After the addition of styrene (153  $\mu$ L, 1.32 mmol), a solution of EDA (1.1 mmol, diluted with 2 mL of CH<sub>2</sub>Cl<sub>2</sub>) was added over 2 h using a syringe pump. The mixture was stirred for 1 h and then centrifuged. The solution portion was collected, and the *trans/cis* ratio and yield were determined by gas chromatography (GC). The enantiomeric excess was determined by GC using a Cyclodex-B column (50 m  $\times$  0.25 mm I.D.). The precipitate was washed with CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and then centrifuged three times. The recovered catalyst was reused directly for the next experiment.

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