

Electronic Supplementary Information (ESI)

General Synthesis

MCF was synthesized according to the literature procedure.^{1,2} Other chemicals were purchased from commercial suppliers, and were used without further purification. IndaBOX, anhydrous THF, toluene, anhydrous CH₂Cl₂ and dicyclopentadiene were purchased from Aldrich. 3-Iodopropyltrimethoxysilane, (p-chloromethyl)phenyltrimethoxysilane and ((chloromethyl)phenylethyl)trimethoxysilane were purchased from Gelest. IR spectra were obtained in photoacoustic mode on a Bio-rad FTS-60A spectrometer. ¹³C and ²⁹Si CPMAS NMR spectra were obtained through Spectral Data Services, Inc. The water content in the water-saturated dichloromethane was determined by the coulometric Karl-Fisher titration.

Preparation of 2

MeLi (1.4 M in ether, 2.18 ml, 3.05 mmol) was added to a solution of indaBOX (480 mg, 1.45 mmol) in THF (20 ml) at -50°C. After stirring the mixture at -50°C for 1 hr, 3-iodopropyltrimethoxysilane (0.572 ml, 2.90 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 3 days. THF was evaporated under vacuum. Toluene was added, and the soluble part was collected by centrifuge and washed with toluene. The resulting toluene solution was added to MCF (3.0 g), which has been dried under vacuum at 180°C for 1 day. The suspension was stirred at 80°C for 3 days, filtered through a filter funnel, and washed with toluene (20 ml × 3), acetone (20 ml × 3), water (20 ml × 10), methanol (20 ml × 3) and CH₂Cl₂ (20 ml × 3). After drying in vacuum, the desired product was obtained.

¹³C CPMAS NMR (ppm): -3, 17, 28, 38, 49, 76, 83, 127, 141, 167

²⁹Si CPMAS NMR (ppm): -110, -100, -90, -65, -59, -51, 28, 6

IR (cm⁻¹): 3372, 2954, 2845, 1643, 1082, 807, 462

Elemental Analysis: C: 14.06%, H: 2.01%, N: 0.97%, I: < 0.80%

Loading of IndaBOX: 0.346 mmol/g

Yield from IndaBOX: 93%

Preparation of 3 and 4

MeLi (1.4 M in ether, 2.18 ml, 3.05 mmol) was added to a solution of indaBOX (480 mg, 1.45 mmol) in THF (20 ml) at -50°C. After stirring the mixture at -50°C for 1 hr, (p-chloromethyl)phenyltrimethoxysilane (0.596 ml, 2.90 mmol) or ((chloromethyl)phenylethyl)-trimethoxysilane (0.713 ml, 2.90 mmol) was added dropwise. The

mixture was stirred at room temperature for 2 hr, and then heated to 50°C. The mixture was stirred at 50°C for 3 days, and THF was evaporated under vacuum. Toluene was added, and the soluble portion was collected by centrifugation and washed. The resulting toluene solution was added to MCF (3.0 g), which has been dried under vacuum at 180°C for 1 day. The suspension was stirred at 80°C for 3 days, filtered through a filter funnel, and washed with toluene (20 ml × 3), acetone (20 ml × 3), water (20 ml × 10), methanol (20 ml × 3) and CH₂Cl₂ (20 ml × 3). After drying in vacuum, the desired product was obtained.

3: IR (cm⁻¹): 3605, 3364 (br), 2949, 2846, 1642, 1605, 1087, 809, 749, 458

Elemental Analysis: C: 18.28%, H: 1.56%, N: 0.96%

Loading of IndaBOX: 0.343 mmol/g

Yield from IndaBOX: 92%

4: IR (cm⁻¹): 3605, 3364 (br), 2949, 2846, 1645, 1607, 1086, 809, 749, 458

Elemental Analysis: C: 19.01%, H: 1.72%, N: 0.97%, Cl: 0.17%, Li: 106 ppm

Loading of IndaBOX: 0.346 mmol/g

Yield from IndaBOX: 93%

TMS-Capping of Free Silanol Groups by Hexamethyldisilazane (HMDS) (2a, 3a, and 4a)

Catalysts **2**, **3** and **4** (700 mg) were dried at 80°C for 2 days. Excess HMDS (700 μl) was added to the dried catalysts in hexane (10 ml). The suspension was stirred at room temperature for 3 days, filtered through a filter funnel, and washed with CH₂Cl₂ (10 ml × 3), acetone (10 ml × 3), methanol (10 ml × 3) and CH₂Cl₂ (10 ml × 3). After drying in vacuum, the desired products were obtained.

2a: IR (cm⁻¹): 3469, 2954, 2848, 1648, 1606, 1089, 845, 809, 749, 460

Elemental Analysis: C: 17.02%, H: 2.36%, N: 0.94%

Loading of IndaBOX: 0.336 mmol/g

3a: IR (cm⁻¹): 3435, 2954, 1648, 1608, 1089, 845, 809, 460

Elemental Analysis: C: 20.28%, H: 2.41%, N: 0.87%

Loading of IndaBOX: 0.311 mmol/g

4a: IR (cm⁻¹): 3469, 2954, 2848, 1648, 1606, 1089, 845, 809, 749, 460

Elemental Analysis: C: 20.44%, H: 1.78%, N: 0.91%, Cl: 0.17%, Li: 29 ppm

Loading of IndaBOX: 0.325 mmol/g

Methyldiphenylsilyl-Capping of Free Silanol Groups by 1,1,3,3-Tetraphenyldimethyldisilazane (TPDMS) (2b)

Heterogenized indaBOX **2** (1.0 g) was dried under vacuum at 80°C for 2 days. Toluene (15 ml) and TPDMS (1.0 g) were added. The mixture was stirred at 80°C for 3 days. The suspension was filtered through a filter funnel, and washed with toluene (15 ml x 3), acetone (15 ml x 3), methanol (15 ml x 5) and CH₂Cl₂ (15 ml x 3). After drying in vacuum, the desired product was obtained.

IR (cm⁻¹): 2958, 2846, 1640, 1591, 801, 698

Elemental Analysis: C: 15.32%, H: 1.83%, N: 0.97%

Loading of IndaBOX: 0.346 mmol/g

Octyldimethylsilyl-Capping of Free Silanol Groups by 1,3-Di-n-Octyltetramethyldisilazane (DOTMS) (2c)

The procedure was the same as for **2a**, except that DOTMS (1.0 ml) was used instead of HMDS.

IR (cm⁻¹): 2959, 2924, 2855, 1647, 1460, 1083, 805

Elemental Analysis: C: 18.79%, H: 2.56%, N: 0.96%

Loading of IndaBOX: 0.343 mmol/g

Perfluorooctyldimethylsilyl-Capping of Free Silanol Groups by (Tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane (F-ODMS) (2d)

Heterogenized indaBOX **2** (1.0 g) was dried under vacuum at 80°C for 2 days. CH₂Cl₂ (10 ml) and NEt₃ (3 ml) were added, and then F-ODMS (1.0 ml) were introduced dropwise. The mixture was stirred at room temperature for 3 days. The suspension was filtered through a filter funnel, and washed with CH₂Cl₂ (15 ml x 3), acetone (15 ml x 3), methanol (15 ml x 5) and CH₂Cl₂ (15 ml x 3). After drying in vacuum, the desired product was obtained.

IR (cm⁻¹): 2957, 2848, 1642, 1237, 1191, 1084, 898, 805, 745, 709

Elemental Analysis: C: 17.83%, H: 1.77%, N: 0.76%, F: 14.99%

Loading of IndaBOX: 0.271 mmol/g

Preparation of 9

Non-porous colloidal silica was prepared according to literature.³ IndaBOX was immobilized onto the colloidal silica with a propyl linker, as described for **2**. The catalyst was capped with TMS, as described for **2a**.

Typical Diels-Alder Reaction

Cu(ClO₄)₂·6H₂O (10 mg, 0.027 mmol) was added to MCF-immobilized indaBOX (82

mg, 0.027 mmol) in CH₂Cl₂ (5 ml). The mixture was stirred at room temperature for 3 days. The dienophile (38 mg, 0.270 mmol) was added and the mixture was stirred for 1 hr. The mixture was brought to the desired temperature, and freshly cracked cyclopentadiene (3 equivalents) was added at once. The products were analyzed by HPLC. For recycling studies, the mixture was centrifuged and washed 4 times with CH₂Cl₂ (10 ml). The recovered catalyst was used directly for the next run. After second run, water-saturated CH₂Cl₂ (1850 ppm H₂O) was used for the next run. After the third run, the catalyst was washed four times with the same water-saturated CH₂Cl₂.

Kinetic Experiments

Kinetic studies were performed with the use of *in situ* attenuated total reflection (ATR) FT-IR spectroscopy (ASI ReactIR 1000) with an attached FiberConduit™ DiComp™ 6-mm probe (Metler-Toledo Autochem) that could be inserted directly into a stirred reaction flask. The kinetics could be measured at -30°C by placing the reaction flask in a cooling bath with a magnetic stirrer.

Typical Cyclopropanation of Styrene

(CuOTf)₂·toluene (0.011 mmol) or Cu(OTf)₂ (0.022 mmol) was added to the MCF-immobilized bisoxazolines (0.022 mmol) in CH₂Cl₂ (4 ml). The mixture was stirred at room temperature for 5 days. In the case of Cu(OTf)₂, phenylhydrazine (25 µl of a 5% solution) was added. After addition of styrene (153 µl, 1.32 mmol), a solution of ethyl diazoacetate (1.1 mmol, diluted with 2 ml of CH₂Cl₂) was added over 3 hr using a syringe pump. The mixture was stirred for 2 hr and then centrifuged. The solution portion was collected, and the trans/cis ratio and yield were analyzed by GC. To determine the exact yield, a calibration curve between n-decane and the products (purified by column chromatography) was obtained with seven different decane/product ratios. The enantiomeric excess was determined by GC using a Cyclodex-B column. The precipitate was washed with CH₂Cl₂ (10 ml), and then centrifuged 3 times. The recovered catalyst was reused directly for the next experiment.

References

1. D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science* 1998, **279**, 548.
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3. S. B. Yoon, K. Sohn, J. Y. Kim, C.-H. Shin, J.-S. Yu and T. Hyeon, *Adv. Mater.* 2002,

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