

Experimental

NMR spectra were taken using a Bruker AC 200 or 300 MHz. Melting points were measured with a Kofler heating system (type WME). IR spectra were taken with a Perkin-Elmer "Spectrum 1" spectrometer.

Preparation of indaBOX diol (**2**): 2.843 gr. of indaBOX **1** (1 eq) and 0.647 gr. of paraformaldehyde (2.5 eq.) were weighed into a 100 ml flask. CH_2Cl_2 (34 ml) was added, a CaCl_2 tube was adjusted, and the suspension was stirred. Dioxane (8.6 ml) and H_2O (1.6 ml) were added, followed by a solution of Et_3N (3.4 ml) in THF (24.5 ml), which was added over a period of 1-3 hr. The solids dissolved gradually during the period of the addition. The solution was mixed for 3 days in r.t., then poured into 150 ml of pentane. A precipitate appeared at once. It was filtered, washed with pentane, water, and pentane again, and left to dry in the air, giving a yield of 75-85%.

IR (cm^{-1}): 3649, 3174 (br), 1652, 1479, 1459, 1372, 1210, 1195, 1167, 1080, 1016, 855, 746, 713, 650.

NMR (peaks in ppm, J s in Hz): 7.45 (2H, m), 7.30 (6H, m), 5.54 (2H, d, $J = 8$), 5.27 (2H, dd, $J_1 = 8$, $J_2 = 4$), 3.96 (4H, AA' system, $J = 12$), 3.38 (2H, dd, $J_1 = 7$, $J_2 = 18$), 3.03 (2H, d, $J = 18$), 1.65 (2H, br s (OH)).

Microanalysis: calculated: C: 70.75%; H: 5.68%; N: 7.17%; O: 16.39%. Found: C: 68.76%; H: 5.72%; N: 7.02%;

m.p. 169°C, corrected by comparison to benzimide (m.p. 163°C).

Preparation of activated silica: silica (Matrex Si-60 from Millipore, particle size 70-200 μ , ca. 13 g) was refluxed with HCl (33%, 50 ml) for ca. 2 h. It was filtered and washed with water. After drying (vacuum, 70-80° C, 24 h), about 10-11 g of activated silica were obtained.

Preparation of catalyst **4** - grafting of ligand **2** onto silica: The functionalized ligand **2** (1.5 mmol, 0.5857 g) was dissolved in dry DMF (approx. 7 ml) and dry Et_3N (0.75 ml, 5 mmol), under Ar. 3-(Isocyanatopropyl)triethoxysilane (3.3 mmol, 0.8175 g, 0.82 ml) was added over a period of 10-20 minutes, at r.t.. The solution was stirred for ca. 48 h. A polystyrene- NH_2 resin (0.8715 g of 1.1 mmol NH_2/g resin) was added in order to capture the excess isocyanate. The mixture was stirred for another hour, following which the amine resin was filtered off and washed with CH_2Cl_2 . The solvents (including most of the DMF) were evaporated, and the resulting oil was added to a suspension of activated silica (4.00 g) in

toluene (30 ml). The suspension was refluxed overnight, then filtered through a sinter and washed with toluene followed by ethyl acetate and CH_2Cl_2 . After drying overnight in vacuum, 4.6720 g of the resulting catalyst were obtained.

IR (cm^{-1}): 3429, 2981 (very small), 1648 (oxazolines), 1095 (very br), 800, 476.

IR taken after use for catalysis of the reaction of **4** with CPD, using $\text{Cu}(\text{OTf})_2$ or $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ - essentially the same (sometimes small peaks at 1780, 1700 indicated the presence of some product or substrate which were not entirely washed away).

Microanalysis: found: C: 9.65%; H: 1.72%; N: 1.41%, Si: 38.85% (O: the rest = 48.37%).

Since there are exactly 4 Nitrogen atoms per ligand the ratio mmol ligand per gram of **4** can be calculated as follows:

$$0.0141[\text{g N to g 4}]/\{14.007[\text{g N to mol N}]*4[\text{mol N to mol ligand}]\}*1000[\text{mmol/mol}] = \\ 0.252 [\text{mmol ligand per gram of 4}]$$

weight of silica recuperated: 4.5016 g.

thus overall mmol of indaBOX: 1.13 mmol.

Yield from indaBOX diol: $(1.13/1.5)*100 = 75.5\%$

Catalyst **4'**: protecting the silanol groups of catalyst **4**: Catalyst **4** (1 g) was mixed in TMSIM (4.7 ml, 0.032 mole) for 1 h at 60°C. It was filtered and washed with MeOH (5x20 ml). After drying in vacuum overnight the catalyst weighed 1.0125 g, and was analyzed: C: 12.36%; H: 2.06%; N: 1.41%; Si: 37.40%. I.e.: 0.252 mmol ligand/g **4'**.

IR (cm^{-1}): 3434 (smaller than the same peak for **4**, indicating less OH groups), 2964 (CH_3), 1655 (oxazolines), 1091 (very br), 845, 802, 758, 474.

Catalyst **4''** was prepared in a similar manner, but mixing for 72 hours.

Microanalysis: C: 12.69%; H: 2.22%; N: 1.22%; Si: 35.33%. I.e.: 0.217 mmol ligand/g **4''**

IR: similar, but the peak for CH_3 is relatively bigger.

% Cu before use of the silica (calculated from amounts of catalyst **4''** and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ put at 1/1 molar ratios): 1.46%.

% Cu according to elemental analysis after use: 1.21%.

Products **5,7,9** were prepared according to the literature (see references in text).

Catalytic tests of silica-grafted BOX with $\text{Cu}(\text{OTf})_2$: catalyst **4** (0.0567 mmol, 8 mol%, 0.3626 g) was mixed with $\text{Cu}(\text{OTf})_2$ (0.0567 mmol, 8 mol%, 0.0205 g) in dry CH_2Cl_2 (10 ml) overnight under Ar. The appropriate dienophile (1 eq, 0.7086 mmol) was added, and mixing was continued for an hour. The mixture was brought to the appropriate temperature and freshly cracked CPD (5 eq, 3.54 mmol, 0.293 ml) was added over about an hour. The reaction was sampled to detect full conversion and analyzed by HPLC, GC. Workup was performed by filtration or by addition of CH_2Cl_2 , centrifuging and removal of the solvent (repeated 3 times). The silica thus recovered was then dried in vacuum before recycling.

Catalytic tests of silica-grafted BOX with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: catalyst **4** (or **4'** or **4''**) (0.0567 mmol, 10 mol%, 0.2495 g) was mixed with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mol%, 0.0193 g) in CH_2Cl_2 overnight. The appropriate dienophile (1 eq, 0.628 mmol) was added, and mixing was continued for an hour. The mixture was brought to the appropriate temperature and freshly cracked CPD (5 eq, 3.14 mmol, 0.259 ml) was added over about an hour. The reaction was sampled to detect full conversion and analyzed by HPLC, GC. Workup was performed by filtration or by addition of CH_2Cl_2 , centrifuging and removal of the solvent (repeated 3 times). The silica thus recovered was used directly for the next experiment.