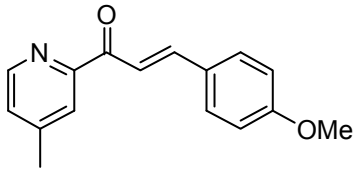
Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information: Ligand denticity controls enantiomeric preference in DNA-based asymmetric catalysis

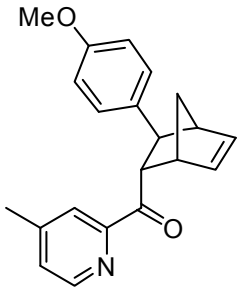
General remarks

Salmon testes DNA was obtained from Sigma. Cyclopentadiene **2** was freshly prepared from its dimer prior to use. Aza-chalcone **1a**, α,β-unsaturated 2-acyl imidazoles **1c**, **1d**, Cu(4,4'-dmbpy)$(NO_3)_2$ (Cu-L1), Cu(bpy)$(NO_3)_2$ (Cu-L2), and L8 were prepared following published procedures.[1-4] Salmon testes DNA was dialyzed extensively against MOPS buffer (20 mM, pH 6.5) prior to use. ^{1}H-NMR, and ^{13}C-NMR spectra were recorded on a Varian 400 (400 and 100 MHz) in $CDCl_3$. Chemical shifts (δ) are quoted in ppm using residual solvent as internal standard (δ_C 77.0 and δ_H 7.26 for $CDCl_3$). Mass spectra (HRMS) were recorded on an AEI MS-902. Enantiomeric excess determination was performed by HPLC analysis using UV-detection. Flash chromatography was performed using silica gel 60 Å (Merck, 200-400 mesh). The Diels-Alder catalysis experiments employing copper complexes Cu-L1 – Cu-L6,[1] or ligands L7 – L10,[5] and the Friedel-Crafts experiments[6] were performed according to the procedures described elsewhere.

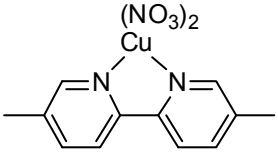
DFT calculations: Geometry optimizations were carried out with the Turbomole program package[7] coupled to the PQS Baker optimizer[8] at the ri-DFT level using the BP86[9] functional and the resolution-of-identity (ri) method.[10] We used the SV(P) basis set[11] for the geometry optimizations of all stationary points. Improved energies were obtained from single point calculations at the DFT/b3-lyp level[12] using the Turbomole def-TZVP basis set.[13]



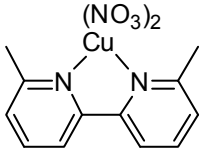
3-(4-Methoxy-phenyl)-1-(4-methyl-2-pyridinyl)-2-penten-1-one (**1b**). To 40 mL water at 5°C was added 2-acetyl-4-methylpyridine (1.0 g, 7.4 mmol), 4-methoxybenzaldehyde (0.95 g, 7.0 mmol), and 4 mL 10% NaOH. The solution was left at 5 °C overnight without stirring. The yellow precipitate was filtered and recrystallized from EtOH, yielding **1b** (0.75 g, 42%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.45 (s, 3H), 3.83 (s, 3H), 6.91 (d, 2H, J = 8.6 Hz), 7.27 (d, 1H, J = 4.3 Hz), 7.67 (d, 2H, J = 8.5 Hz), 7.90 (d, 1H, J = 15.9 Hz), 8.00 (s, 1H), 8.16 (d, 1H, J = 16.0 Hz), 8.57 (d, 1H, J = 4.7 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 21.0, 55.3, 114.2, 118.7, 123.6, 127.5, 127.9, 130.6, 144.4, 148.2, 148.6, 154.3, 161.6, 189.6. HRMS Calcd for MH+ $C_{16}H_{16}NO_2$ 254.1181, found 254.1176.



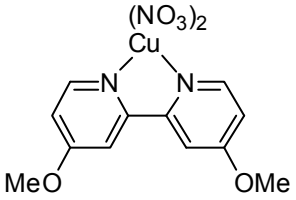
[3-(4-Methoxy-phenyl)bicyclo[2.2.1]hept-5-en-2-yl](4-methyl-2-pyridinyl)methanone (**3a**). Purified by column chromatography (SiO_2, EtOAc:pentane 1:4). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.59 (dd, 1H, J = 8.5 Hz, J = 1.7 Hz), 2.05 (d, 1H, J = 8.4 Hz), 2.41 (s, 3H), 3.02 (d, 1H, J = 1.5 Hz), 3.38 (dd, 1H, J = 4.9 Hz, J = 0.9 Hz), 3.51 (s, 1H), 3.77 (s, 3H), 4.47 (dd, 1H, J = 5.1 Hz, J = 3.4 Hz), 5.81 (dd, 1H, J = 5.6 Hz, J = 2.8 Hz), 6.48 (dd, 1H, J = 5.6 Hz, J = 3.2 Hz), 6.82 (d, 2H, J = 8.8 Hz), 7.22 – 7.27 (m, 3H), 7.81 (m, 1H), 7.53 (d, 1H, J = 4.9 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 21.1, 44.8, 48.1, 48.7, 49.6, 54.3, 55.3, 113.7, 123.0, 127.7, 128.5, 132.8, 136.7, 139.4, 148.1, 148.7, 153.5, 157.7, 201.5. Ee's were determined by HPLC analysis (Chiralcel-AD, heptane/iPrOH 99:1, 1 mL/min). Retention times: 23.9 (exo), 27.1 (exo), 32.1 (endo), and 34.8 (endo) mins. HRMS Calcd for MH+ $C_{21}H_{22}NO_2Na$ 343.1548, found 343.1543.



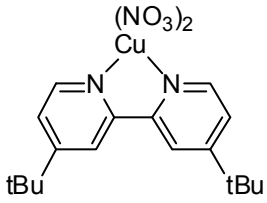
[Cu(5,5'-dimethyl-2,2'-dipyridyl)(NO_3)$_2$] (Cu-L3). To a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.10 g, 0.41 mmol) in ethanol was added 5,5'-dimethyl-2,2'-dipyridyl (L3) (38 mg, 0.24 mmol), dissolved in ethanol. The solution was left standing for 2 h. The blue solid was filtered and washed with ethanol. Yield: 52 mg, 63%. Anal. Cald for $C_{12}H_{12}CuN_4O_6$: C, 38.77 H, 3.25 N, 15.07. Found: C, 38.22 H, 3.25 N, 14.74.



[Cu(6,6'-dimethyl-2,2'-dipyridyl)(NO_3)$_2$] (Cu-L4). To a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.10 g, 0.41 mmol) in ethanol was added 6,6'-dimethyl-2,2'-dipyridyl (L4) (38 mg, 0.24 mmol), dissolved in ethanol. The green precipitate was filtered and washed with ethanol. Yield: 44 mg, 53%. Anal. Cald for $C_{12}H_{12}CuN_4O_6$: C, 38.77 H, 3.25 N, 15.07. Found: C, 38.19 H, 3.22 N, 14.81.



[Cu(4,4'-dimethoxy-2,2'-dipyridyl)(NO_3)$_2$] (Cu-L5). To a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.10 g, 0.41 mmol) in ethanol (2 mL) was added 4,4'-dimethoxy-2,2'-dipyridyl (L5) (45 mg, 0.24 mmol), dissolved in ethyl acetate (7 mL). The solution was left standing for 4 h. The blue crystals were filtered and washed with ethanol and ethyl acetate. Yield: 61 mg, 64%. Anal. Cald for $C_{12}H_{12}CuN_4O_8$: C, 35.7 H, 3.00 N, 13.88. Found: C, 35.6 H, 2.99 N, 13.89.



[Cu(4,4'-di-*tert*-butyl-2,2'-dipyridyl)(NO_3)$_2$] (Cu-L6). To a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.10 g, 0.41 mmol) in ethanol was added 4,4'-di-*tert*-butyl-2,2'-dipyridyl (L6) (55 mg, 0.24 mmol), dissolved in ethanol. The solution was left standing for 12 h. The blue crystals were filtered and washed with ethanol. Yield: 81 mg, 74%. Anal. Cald for $C_{18}H_{24}CuN_4O_6$: C, 47.42 H, 5.31 N, 12.29. Found: C, 47.18 H, 5.33 N, 12.18.

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