SUPPORTING INFORMATION
FOR
Polymer-Supported Pyridine-bis(oxazoline). Application to
Ytterbium Catalyzed Silylcyanation of Benzaldehyde

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General Methods: Benzaldehyde, CH₂Cl₂ and MeCN were distilled over CaH₂. TMSCN was purchased from Aldrich. Unless otherwise noted all ¹H and ¹³C NMR spectra were recorded in CDCl₃, on a 400 MHz instrument (Bruker Avance 400 MHz). Chemical shifts are reported in ppm relative to the solvent as internal standard. Enantiomeric excesses were determined by GC analysis using a chiral column (Supelco Gamma-DEX^{TM} -120).

4-Bromopyridine-2,6-dicarboxylic acid dimethyl ester (**3**)

Chelidamic acid and phosphorus pentabromide were heated for 3 h at 90 °C. The dark brown liquid was diluted with CHCl₃ (25 mL) and filtered. The filtrate was cooled to 0 °C and MeOH (100 mL) was added dropwise. The precipitated solid was filtered off and recrystallized from MeOH to afford 4.1 g (86%) of the product as a pale brown solid: m.p. 157 °C; ¹H NMR δ 8.40 (s, 2H), 3.97 (s, 6H); ¹³C NMR δ 164.4, 149.5, 136.6, 131.8, 53.9.

4-Bromopyridine-2,6-dicarboxylic acid bis[*[(R)-2-hydroxy-1-phenylethyl]amide*] (**4**)

A mixture of **3** (2.74 g, 10 mmol) and (*R*)-phenylglycinol (2.74 g, 20 mmol) was stirred at 120 °C for 16 h. The solid obtained was dissolved in hot EtOAc (25mL), cooled to 25 °C, and the clear yellow solution was poured into 150 mL of hexane. The precipitated white solid was filtered off and washed with hexane. The organic solution was concentrated in vacuo and the residue was dissolved in hot EtOAc (25 mL). The operation described above was repeated and the combined solids were dried giving 3.86 g (80%) of the product: m.p. 84 °C; [α]_D²⁰ +35.5 (*c* 0.50, CH₃Cl); ¹H NMR δ 8.68 (d, *J* = 7.9, 2H), 8.24 (s, 2H), 7.23 (m, 10H), 5.11 (m, 2H), 3.85 (d, *J* = 5.0 Hz, 4H), 3.54 (br s, 2H); ¹³C NMR δ 163.1, 150.1, 139.0, 136.7, 129.3, 128.9, 128.4, 127.1, 66.2, 56.2.

4-Bromo-2,6-bis[(*R*)-4-phenyloxazolin-2-yl]pyridine (1)

A solution of **4** (1.45 g, 3 mmol), TsCl (1.24 g, 6.5 mmol) and Et₃N (4 mL) in CH₂Cl₂ (10 mL) was refluxed for 24 h. The mixture was diluted with CH₂Cl₂ (10 mL) and washed with 1N NaOH (10 mL). The aqueous phase was extracted with CH₂Cl₂ (3 × 10 mL) and the combined organic solutions dried (Na₂SO₄). After evaporation, the crude product was purified by recrystallization from ethanol to yield 956 mg (71%) of **1** as a white solid: m.p. 196 °C; [α]_D²⁰ +74.6 (c 0.54, CH₃Cl); ¹H NMR δ 8.46 (s, 2H), 7.27 (m, 10H), 5.39 (dd, *J* = 8.7 and 10.3 Hz, 2H), 4.87 (dd, *J* = 8.7 and 10.3 Hz, 2H), 4.37 (t, *J* = 8.7 Hz, 2H); ¹³C NMR δ 163.0, 148.1, 141.8, 134.4, 129.9, 129.3, 128.4, 127.4, 76.2, 70.8.

4-(6-Carboxyl-1-hexenyl)-2,6-bis[(*R*)-4-phenyloxazolin-2-yl]pyridine (5)

CuI (5 mg, 0.026 mmol) was added to a solution of **1** (1.12 g, 2.5 mmol), 5-hexynoic acid (900 mg, 8 mmol), Pd(OAc)₂ (19 mg, 0.085 mmol), triphenylphosphine (44 mg, 0.168 mmol), and Et₃N (3 mL) in CH₂Cl₂ (10 mL). The resulting mixture was heated for 1.5 h at reflux. The solution was diluted with CHCl₃ (10 mL) and washed with a phosphate buffer solution (pH 6.5) (3 × 10 mL). The aqueous phase was extracted with CHCl₃ (3 × 10 mL) and the combined organic solutions dried (Na₂SO₄). After evaporation of the solvent, the residue was purified by column chromatography on silica gel (eluent: CH₂Cl₂/MeOH 10/1). The solid obtained was

washed with ether and dried to give 898 mg (75%) of **5** as a brown solid: m.p. 125 °C; $[\alpha]_D^{20}$ +3.9 (*c* 0.31, CH₃Cl); ¹H NMR δ 8.27 (s, 2H), 7.26 (m, 10H), 5.39 (dd, *J* = 8.5 and 10.3 Hz, 2H), 4.87 (dd, *J* = 8.5 and 10.3 Hz, 2H), 4.36 (t, *J* = 8.5 Hz, 2H), 2.43 (m, 4H), 1.83 (m, 2H); ¹³C NMR δ 177.4, 163.8, 147.1, 141.9, 134.4, 129.3, 128.9, 128.3, 127.3, 97.2, 78.7, 76.1, 70.5, 32.9, 23.6, 19.3. An analytically pure sample was obtained by recrystallization from EtOAc. Anal. Calcd for C₂₉H₂₅N₃O₄: C, 72.64; H, 5.25; N, 8.76. Found: C, 72.27; H, 5.29; N, 8.69.

4-(4-Hydroxy-1-butynyl)-2,6-bis[(*R*)-4-phenyloxazolin-2-yl]pyridine (**6**)

Compound **6** was prepared according to the procedure described above for **5** starting from **1** (1.12 g, 2.5 mmol), 3-butyne-1-ol (561 mg, 8 mmol), Pd(OAc)₂ (19 mg, 0.085 mmol), triphenylphosphine (44 mg, 0.168 mmol), CuI (5 mg, 0.026 mmol), and Et₃N (3 mL) in CH₂Cl₂ (10 mL). The crude product was purified by recrystallization from ethanol yielding 941 mg (86%) of the pure product as a white solid: m.p. 221 °C; $[\alpha]_D^{20}$ +8.0 (*c* 0.24, CH₃Cl); ¹H NMR δ 8.32 (s, 2H), 7.34 (m, 10H), 5.45 (dd, *J* = 10.3 and 8.6 Hz, 2H), 4.92 (dd, *J* = 10.3 and 8.6 Hz, 2H), 4.42 (t, *J* = 8.6 Hz, 2H), 3.80 (t, *J* = 6.3 Hz, 2H), 2.76 (t, *J* = 6.3 Hz, 2H), 1.88 (br s, 1H); ¹³C NMR δ 163.6, 147.4, 142.0, 134.0, 129.3, 128.8, 128.3, 127.2, 94.7, 79.4, 77.6, 76.0, 70.8, 61.2, 24.2. Anal. Calcd for C₂₇H₂₃N₃O₃: C, 74.12; H, 5.30; N, 9.60. Found: C, 73.96; H, 5.29; N, 9.57.

4-(1-Hexynyl)-2,6-bis[(*R*)-4-phenyloxazolin-2-yl]pyridine (**7**)

Compound **7** was prepared according to the procedure described above for **5** starting from **1** (500 mg, 1.1 mmol), 1-hexyne (290 mg, 3.53 mmol), Pd(OAc)₂ (8.5 mg, 0.044 mmol), triphenylphosphine (19.7 mg, 0.075 mmol), CuI (2.3 mg, 0.012 mmol), and Et₃N (1.4 mL) in CH₂Cl₂ (5 mL). The crude product was purified by column chromatography on silica gel (eluent: EtOAc/hexane/CH₂Cl₂ 1/1/2) yielding 368 mg (74%) of the pure product as a yellow solid: m.p. 117 °C; $[\alpha]_D^{20} +3.8$ (c 0.53, CH₃Cl); ¹H NMR δ 8.30 (s, 2H), 7.34 (m, 10H), 5.45 (dd, *J* = 10.3 and 8.6 Hz, 2H), 4.92 (dd, *J* = 10.3 and 8.6 Hz, 2H), 4.42 (t, *J* = 8.6 Hz, 2H), 2.42 (t, *J* = 7.1 Hz, 2H), 1.57 (m, 2H), 1.46 (m, 2H), 0.93(t, *J* = 7.3 Hz, 3H); ¹³C NMR δ 163.7, 147.2, 142.1, 129.3, 128.8, 128.3, 127.2, 77.64, 75.9, 70.8, 30.6, 22.3, 19.6, 13.9.

Polymer-bound ligand **5** (**8**)

DCC (23 mg, 0.11 mmol) was added to a suspension of TentaGel® MB-OH (0.4 mmol/g, 225 mg, 0.090 mmol), compound **5** (48 mg, 0.099 mmol) and DMAP (2 mg, 0.016 mmol) in dry CH₂Cl₂ (2 mL). The reaction mixture was stirred for 48 h at room temperature before the polymer was filtered off and washed with MeOH (2 mL), EtOH (2 mL), THF/H₂O 1:1 (2 mL) and MeOH (2 mL) and then dried in vacuo overnight, resulting in 263 mg of polymer containing 1.03% N, corresponding to 0.25 mmol ligand/g of polymer (74% assuming 0.4 mmol functional groups/g of TentaGel MB-OH). ¹³C NMR (100.6 MHz) δ 173.2, 163.6,

147.3, 144.7, 135.9, 130.4, 129.2, 128.7, 128.2, 127.2, 97.2, 70.7-82.5 (several signals), 69.5, 64.4, 62.0, 40.8, 33.2, 25.1, 19.2.

Polymer-bound ligand **6** (**9**)

This polymer was prepared according to the procedure described for **7** starting from TentaGel® HL-COOH (0.37 mmol/g, 243 mg 0.090 mmol), compound **6** (43 mg, 0.099 mmol), DCC (23 mg, 0.11 mmol), DMAP (2 mg, 0.016 mmol) and dry CH₂Cl₂ (2 mL). After drying under vacuum overnight, polymer **8** was obtained as pale yellow beads (278 mg) containing 1.88% N corresponding to 0.27 mmol ligand/g polymer (84% for 0.37 mmol functional groups/g TentaGel HL-COOH): ¹³C NMR (100.6 MHz) δ 178.0, 173.4, 172.4, 129.4, 127.3, 70.0-78.1 (several signals), 67.5, 66.7, 64.3, 60.9, 54.3, 54.1, 39.7, 38.1, 31.4, 30.4, 28.6, 26.5, 25.8.

General procedure for ytterbium catalyzed asymmetric addition of TMSCN to benzaldehyde

A solution of pybox ligand (0.041 mmol) and YbCl₃ (5.7, 0.02 mmol) in acetonitrile was stirred at room temperature for 1 h under nitrogen before benzaldehyde (20 l 0.204 mmol) was added. The reaction mixture was cooled to 0 °C and TMSCN (32.7 l, 0.245 mmol) was added. The mixture was stirred for 30 min before analyzed by GC. Spectral data are in accordance with those previously published: Yang, W.-B.; Fang, J.-M. *J. Org. Chem.* 1998, 63, 1356-1359. (Suppl. Information).

General procedure for ytterbium catalyzed asymmetric addition of TMSCN to benzaldehyde using polymer-bound ligand

Two stock solutions were prepared: S1 containing benzaldehyde in dry MeCN (c = 0.40M) and S2 consisting of TMSCN in dry MeCN (c = 0.48M). The two stock solutions were kept at 0 °C before being used. Ytterbium trichloride (2.8 mg, 0.01 mmol) and the ligand (0.02 mmol)

were transferred to a reaction vessel and agitated for 1 h in dry MeCN (0.4 mL) under nitrogen. The solvent was removed by filtration under nitrogen and S1 (0.25 mL, 0.1 mmol of benzaldehyde) and S2 (0.25 mL, 0.12 mmol of TMSCN) were added. The reaction mixture was agitated for 30 min, the solvent was removed, and the product analyzed by GC. Spectral data are in accordance with those previously published: Yang, W.-B.; Fang, J.-M. *J. Org. Chem.* **1998**, *63*, 1356-1359. (Suppl. Information). After the reaction(s) the polymer-supported ligand was washed with 5 mL each of the following solvents: MeCN, H₂O, CH₂Cl₂, DMF, MeOH, acetone, and CH₂Cl₂. The polymer was then dried for more than 5 h before being reused as ligand in the catalytic reaction.