Supporting information

Efficient Asymmetric Oxidation of Sulfides and Kinetic Resolution of Sulfoxides Catalyzed by Vanadium Salan System

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Content	Page
I. General Experimental	S2
II. Synthesis procedures and spectra data of ligands	S2
III. Characterization data for sulfoxides	S4
IV. References	S6

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Content	Page
I. General Experimental	S2
II. Synthesis procedures and spectra data of ligands	S2
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I. General Experimental

All reactions were conducted under air. All reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. Toluene and THF were distilled from sodium/benzophenone. CCl₄, CH₂Cl₂ and CH₃CN were distilled from CaH₂. CHCl₃ was dried with K₂CO₃ and distilled from P₂O₅.

Enantiomeric excesses of the sulfoxides were determined by HPLC analysis on chiral columns (Daicel Chiralcel OD-H or OB-H column), with UV detection at 254 nm.

II. Synthesis procedures and spectra data of ligands

Typical procedure for the synthesis of the salan ligands:
(*R,R*)-N,N'-bissalicyl-1,2-diaminocyclohexane (1)¹. In a 100 mL three-necked flask, (*R,R*)-N,N'-bissalicylidene-1,2-diaminocyclohexane (6.44 g, 20 mmol) was dissolved in 40 mL of absolute methanol, then sodium borohydride (6.1 g, 160 mmol) in 60 mL of absolute methanol was added with the yellow color disappeared. The mixture was heated to reflux for 30 minutes. Then the mixture was cooled to room temperature and the same volume of water was added. The secondary amine was precipitated and was collected by vacuum filtration, washed with water and dried, the crude product was further purified with recrystallization (acetone/petroleum ether = 1/2) gave **1** as a white solid (5.9 g, 90% yield), mp 117-119 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.20-7.16 (m, 2H), 7.0 (d, 2H, *J* = 8.0 Hz), 6.92 (d, 2H, *J* = 8.0 Hz), 5.63 (s, 2H), 4.07 (d, 2H, *J* = 13.5 Hz), 3.92 (d, 2H, *J* = 13.5 Hz), 2.05 (s, 2H), 2.19-2.18 (m, 2H), 1.74 (s, 2H), 1.26-1.24 (m, 4H); ¹³C-NMR (CDCl₃, 300 MHz) δ 158.2, 129.2, 128.7, 123.3, 120.0, 117.1, 60.3, 50.2, 31.1, 24.5; IR (KBr) 3325, 3298, 2932, 2861, 1593, 1483, 1367, 1265, 1020, 873 cm⁻¹.

(*R,R*)-*N,N'*-bis(3,5-di-*tert*-butylsalicyl)-1,2-diaminocyclohexane (2)¹. White solid, mp 139-142 °C; H NMR (CDCl₃, 300 MHz) δ 7.23 (d, 2H, J = 2.3 Hz), 6.85 (d, 2H, J = 2.3 Hz), 4.03 (d, 2H, J = 13.5 Hz), 3.92 (d, 2H, J = 13.5 Hz), 2.4 (m, 2H), 2.1 (m, 2H), 1.8 (m, 2H), 1.37 (s, 18H), 1.27 (s, 18H), 1.2 (m, 4H); IR (KBr) 3295, 2957, 2862, 1606, 1483, 1362, 1239, 875 cm⁻¹; ¹³C-NMR δ 154.3, 141.1, 136.2, 123.3, 123.1, 122.6, 60.1, 51.1, 35.0, 34.3, 31.9, 30.9, 29.8, 24.1.

(*S,S*)-*N,N'*-bissalicyl-1,2-diamino-1,2-diphenylethane (3)². White solid, mp 162-164 °C; H NMR (CDCl₃, 300 MHz) δ 7.29-7.27 (m, 6H), 7.19-7.17 (m, 2H), 6.98-6.95 (m, 4H), 6.90 (d, 2H, J = 9 Hz), 6.81-6.75 (m, 4H), 4.05 (s, 2H), 3.88 (d, 2H, J = 13.5 Hz), 3.63 (d, 2H, J = 13.5 Hz); IR (KBr) 3454, 3029, 2906, 2373, 1618, 1589, 1490, 1453, 1253, 1024, 845, 755, 698 cm⁻¹; ¹³C-NMR δ 158.1, 137.6, 129.4, 129.0, 128.9, 128.5, 122.4, 119.7, 116.9, 77.8, 77.4, 77.0, 66.7, 50.5.

(*S,S*)-*N,N'*-bis(3,5-di-*tert*-butylsalicyl)-1,2-diamino-1,2-diphenylethane (4)². White solid, mp 167-170 °C; H NMR (CDCl₃, 300 MHz) δ 7.27-7.20 (m, 8H), 6.99-6.96 (m, 4H), 6.67 (s, 2H), 4.07 (s, 2H), 3.81 (d, 2H, J = 13.5 Hz), 3.64 (d, 2H, J = 13.5 Hz), 1.45 (s, 9H), 1.24 (s, 9H); IR (KBr) 3454, 2961, 2367, 1627, 1567, 1480, 1434, 1360, 1234, 1024, 876, 758, 699 cm⁻¹.

(*R,R*)-*N,N'*-bissalicyl-*N,N'*-dimethyl-1,2-diaminocyclohexane (5)³. Under argon, to a solution of (*R,R*)-*N,N'*-bissalicyl-1,2-diaminocyclohexane (1.3 g, 4 mmol) in THF (30 mL) was added *n*-BuLi (2.5 M solution in *n*-hexane, 18 mmol) dropwise at 0 °C. After stirred for 1.5h, the mixture was allowed to warm to ambient temperature. Iodomethane (1.17 mL, 18 mmol) was added slowly and stirring was continued for another 6 h. Then to the result mixture was added 50 mL of water, and extracted with CH₂Cl₂ (5×30 mL). The combined organic layer was dried over anhydrous Na₂SO₄. The volatiles were removed using a rotary evaporator. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) gave **5** (0.9 g, 60% yield) as a white solid, mp 120 °C, [α _D²⁵] -6.7 (c 0.5, CH₂Cl₂); H NMR (CDCl₃, 300 MHz) δ 7.22-7.17 (m, 2H), 7.02-7.00 (m, 2H), 6.87-6.78 (m, 4H), 3.87 (d, 2H, J = 13.5 Hz), 3.66 (d, 2H, J = 13.5 Hz), 2.75-2.72 (m, 2H), 2.25 (s, 6H), 2.06-2.02 (m, 2H), 1.85-1.83 (m, 2H), 1.27-1.17 (m, 4H); ¹³C NMR (CDCl₃, 300

MHz) δ 158.24, 129.47, 129.40, 122.74, 119.42, 116.85, 62.35, 57.38, 35.95, 25.68, 22.68; FAB-MS m/z 354 (M^+), 276, 247, 219, 141, 110, 70, 44; IR (KBr) 3422.6, 2988.4, 2945.6, 2862.7, 1612.0, 1588.0, 1488.1, 1456.5, 1373.1, 1348.1, 1284.6, 1256.1, 1243.8, 1027.4, 761.5 cm^{-1} ; Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{N}_2\text{O}_2$: C, 74.50; H, 8.47; N, 7.91. Found C, 74.37; H, 8.36; N, 7.85. (Perkin-Elmer 240C)

III. Characterization data for sulfoxides

Phenyl methyl sulfoxide. H NMR (300 MHz, CDCl_3) δ 7.67 (m, 2H), 7.55 (m, 3H), 2.74 (s, 3H); Retention time [min]: (S) 21.01, (R) 36.20 (Chiralcel OB-H, hexane/2-propanol = 4/1, flow rate = 0.5 mL/min); or Chiralcel OD-H, hexane/2-propanol = 9:1, flow rate = 0.5 mL/min)

p-Tolyl methyl sulfoxide. H NMR (300 MHz, CDCl_3) δ 7.40-7.41 (m, 4H), 2.69 (s, 3H), 2.40 (s, 3H); Retention time [min]: (S) 16.06, (R) 35.15 (Chiralcel OB-H, hexane/2-propanol = 4/1, flow rate = 0.5 mL/min).

m-Bromophenyl methyl sulfoxide. H NMR (300 MHz, CDCl_3) δ 7.82 (s, 1H), 7.64 (m, 1H), 7.56 (m, 1H), 7.42 (m, 1H), 2.74 (s, 3H); Retention time [min]: (S) 21.36, (R) 32.56 (Chiralcel OB-H, hexane/2-propanol = 4/1, flow rate = 0.5 mL/min).

o-Bromophenyl methyl sulfoxide H NMR (300 MHz, CDCl_3) δ 7.89 (d, 1H, J = 9 Hz), 7.55-7.50 (m, 2H), 7.37-7.29 (m, 1H), 2.78 (s, 3H); Retention time [min]: (S) 18.52, (R) 28.24 (Chiralcel OB-H, hexane/2-propanol = 4/1, flow rate = 0.5 mL/min).

p-Chlorophenyl methyl sulfoxide H NMR (300 MHz, CDCl_3) δ 7.57 (d, 2H, J = 8.7 Hz), 7.48 (d, 2H, J = 8.7 Hz), 2.70 (s, 3H); Retention time [min]: (S) 17.73, (R) 26.15 (Chiralcel OB-H, hexane/2-propanol = 4/1, flow rate = 0.5 mL/min).

p-isopropylphenyl methyl sulfoxide. H NMR (300MHz, CDCl_3) δ 7.56 (d, 2H, J = 8.4 Hz), 7.36 (d, 2H, J = 9 Hz), 2.95 (m, 1H), 2.71 (s, 3H), 1.25 (d, J = 6.9 Hz, 6H); Retention time [min]: (S) 10.55, (R) 11.62 (Chiralcel OB-H, hexane/2-propanol = 4/1, flow rate = 0.5 mL/min).

p-Tolyl phenyl sulfoxide. H NMR (300 MHz, CDCl_3) δ 7.30-7.22 (m, 7H), 7.02 (m, 2H), 4.05 (m, 2H), 2.41 (s, 3H); Retention time [min]: (S) 25.38, (R) 30.39

(Chiralcel OD-H, hexane/2-propanol = 9/1, flow rate = 0.5 mL/min).

Phenyl benzyl sulfoxide. H NMR (300 MHz, CDCl₃) δ 7.47-7.38 (m, 4H), 7.29-7.25 (m, 4H), 7.0 (m, 2H), 4.08 (s, 2H); Retention time [min]: (S) 27.02, (R) 32.86 (Chiralcel OD-H, hexane/2-propanol = 9/1, flow rate = 0.5 mL/min).

m-Anisyl methyl sulfoxide. H NMR (300 MHz, CDCl₃) δ 7.35 (d, 1H, J = 7.9 Hz), 7.20 (s, 1H), 7.08 (d, 1H, J = 7.6 Hz), 6.95 (d, 1H, J = 9.9 Hz), 3.8 (s, 3H), 2.67 (s, 3H); Retention time [min]: (S) 22.72, (R) 35.74 (Chiralcel OB-H, hexane/2-propanol = 4/1, flow rate = 0.5 mL/min).

p-Anisyl methyl sulfoxide. H NMR (300 MHz, CDCl₃) δ 7.60 (d, 2H, J = 9 Hz), 7.03 (d, 2H, J = 9 Hz), 3.86 (s, 3H), 2.70 (s, 3H); Retention time [min]: (R) 29.31, (S) 32.55 (Chiralcel OD-H, hexane/2-propanol = 9/1, flow rate = 0.5 mL/min).

o-Nitrophenyl methyl sulfoxide. H NMR (300 MHz, CDCl₃) δ 8.41-8.32 (m, 2H), 8.02-7.37 (m, 2H), 2.82 (s, 3H); Retention time [min]: (R) 50.92, (S) 54.60 (Chiralcel OD-H, hexane/2-propanol = 9/1, flow rate = 0.5 mL/min).

m--Nitrophenyl methyl sulfoxide. H NMR (300 MHz, CDCl₃) δ 8.52 (s, 1H), 8.38 (d, 1H, J = 8.0 Hz), 8.02 (d, 1H, J = 7.8 Hz), 7.79 (d, 1H, J = 7.9 Hz), 2.81 (s, 3H); (R) 50.92, (S) 54.60 (Chiralcel OD-H, hexane/2-propanol = 9/1, flow rate = 0.6 mL/min).

p-Fluorophenyl methyl sulfoxide. H NMR (300 MHz, CDCl₃) δ 7.65-7.60 (m, 2H), 7.21-7.16 (m, 2H), 2.68 (s, 3H); Retention time [min]: (S) 18.90, (R) 27.01 (Chiralcel OB-H, hexane/2-propanol = 4/1, flow rate = 0.5 mL/min).

tert-Butyl methyl sulfoxide. H NMR (300 MHz, CDCl₃) δ 2.36 (s, 3H), 1.25 (s, 9H); Enantioselectivity excess measured by NMR upon addition of (*R*)-(-)-3,5-dinitro-*N*-(1-phenylethyl)benzamide.

tert-Butyl isopropyl sulfoxide. H NMR (300 MHz, CDCl₃) δ 2.91 (m, 1H), 1.35-1.32 (m, 3H), 1.27 (s, 9H), 1.26-1.24 (m, 3H); Enantioselectivity excess measured by NMR upon addition of (*R*)-(-)-3,5-dinitro-*N*-(1-phenylethyl)benzamide.

tert-Butyl n-butyl sulfoxide. H NMR (300 MHz, CDCl₃) δ 2.60-2.52 (m, 2H), 2.02-1.83 (m, 2H), 1.68-1.50 (m, 2H), 1.31 (s, 9H), 1.07-1.03 (m, 3H); Enantioselectivity excess measured by NMR upon addition of (*R*)-(-)-3,5-dinitro-*N*-(1-phenylethyl)benzamide.

IV. References

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