

Chiral dinuclear vanadium(V) catalysts for oxidative coupling of 2-naphthols

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General

¹H and ¹³C NMR spectra were recorded with a JEOL JNM-EX270 FT NMR spectrometer (¹H NMR 270 MHz, ¹³C NMR 67.7 MHz). All signals are expressed as ppm downfield from tetramethylsilane used as an internal standard. ⁵¹V-NMR spectra were recorded on a JEOL JNM-LA600 (158 MHz) spectrometer in CD₃OD or CD₂Cl₂ with VOCl₃ as an external standard (0 ppm). FT-IR spectra were recorded on a Perkin-Elmer system 2000 FT-IR. Optical rotations were measured with a JASCO P-1030 polarimeter. HPLC analyses were performed on a JASCO HPLC system (JASCO PU-980 pump and UV-975 UV/Vis detector) using a mixture of hexane and *i*-PrOH as an eluent. X-ray crystallographic analyses were carried out with a RIGAKU AFC-7R, and all calculations were performed using the crystal structure determination package of Molecular Structure Corporation. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL JMS-600H. High resolution mass (HRMS) spectra were recorded on a JEOL JMS-D 300. ESI-TOF mass spectra were recorded on a JEOL JMS-T100LC. Elemental analysis was performed on a Perkin-Elmer 2400. Analytical TLC was performed on Merck silica gel plates with 60 F₂₅₄ indicator. Visualization was accomplished with UV light and phosphomolybdic acid. Column chromatography on SiO₂ was performed with Kanto Silica Gel 60 (40-100 μm). Commercially available organic and inorganic compounds were used without further purification, except for the solvent, which was distilled by a known method before use.

Crystallographic data

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 666356. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk. or www: <http://www.ccdc.cam.ac.uk>).

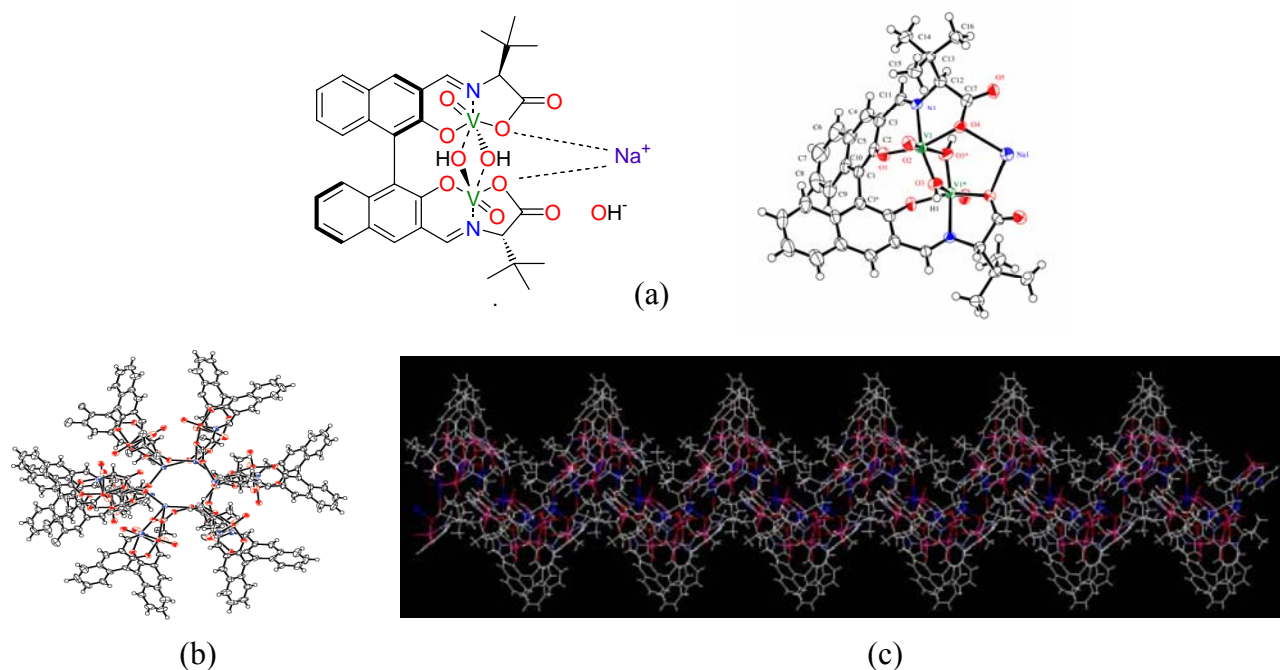


Figure ESI-1. (a) Structure of the dinuclear vanadium(V) complex as an adduct of NaOH (A hydrogen atom was not detected for the hydroxide (O2)); molecular aggregation of the vanadium(V) complex: (b) top view and (c) side view

Synthetic procedure of (*R,S,S*)-2a

A round-bottomed flask (100 mL) was charged with (*R*)-3,3'-diformyl-2,2'-dihydroxy-1,1'-binaphthyl (342 mg, 1.0 mmol), (*S*)-*tert*-leucine (289 mg, 2.2 mmol), MS 3Å (1.0 g) and EtOH (30 mL). The reaction mixture was refluxed at 80 °C for 2 h to generate a red-orange suspension and the consumption of

(*R*)-3,3'-diformyl-2,2'-dihydroxy-1,1'-binaphthyl was monitored by TLC (acetone/hexane = 1/3). After evaporation of EtOH, the residue was suspended in CH₂Cl₂ (20 mL) and then VOCl₃ (0.38 mL, 4.0 mmol) was added under Ar. The reaction mixture was stirred for 12 h, and filtered by Celite to remove MS 3Å. The filtrate was evaporated and the resulting black solid was dissolved in MeOH (*ca.* 20 mL) and the solvent was evaporated again. The residue was dissolved in CH₂Cl₂ (*ca.* 50 mL) and washed with H₂O (4 × *ca.* 40 mL), and the aqueous layer was extracted with CH₂Cl₂ (4 × *ca.* 40 mL). The combined extract was dried over anhydrous Na₂SO₄ and concentrated under vacuum to give (*R_a,S,S*)-**2a** (461 mg, 63%) as a black powder. Complex (*R_a,S,S*)-**2a** (952 mg, 1.3 mmol) and NaOH (57 mg, 1.4 mmol) were dissolved in MeOH (44 mL) and the resulting dark-brown solution was filtered through a membrane filter. Ether (*ca.* 350 mL) was added to the filtrate, and the solution was allowed to stand at room temperature for 3-7 days. Dark-brown needles (266 mg, 27%) were obtained as (*R_a,S,S*)-**2a**-NaOH salt. The needles (296 mg, 0.38 mmol) were suspended in CH₂Cl₂ and neutralized with 5 N HCl (aq) (77 μL, 0.38 mmol). The reaction mixture was diluted with water and extracted with CH₂Cl₂ two times. The extract was dried over Na₂SO₄ and then filtered. The organic solvent was removed by evaporation. After drying under vacuum, an extra pure (*R_a,S,S*)-**2a** (194 mg, 69%) resulted as a black powder. (*R_a,S,S*)-**2a**: ¹H-NMR (270 MHz, CD₃OD): δ 8.96 (s, 2H, CH=N), 8.48 (s, 2H, Ar-H), 8.06 (t, *J* = 4.7 Hz, 2H, Ar-H), 7.70 (t, *J* = 4.9 Hz, 2H, Ar-H), 7.44-7.38 (m, 4H, Ar-H), 4.23 (s, 2H, CH-*t*-Bu), 1.25 (s, 18H, *t*-Bu); ¹³C-NMR (67.7 MHz, CD₃OD): δ 167.9, 138.7, 137.6, 130.6, 130.5, 129.6, 127.4, 125.3, 124.1, 83.8, 38.8, 28.2; ⁵¹V-NMR (CD₃OD): δ -557.2. IR (cm⁻¹): 3436 (O-H), 1683 (C=N), 1608 (C=O), 996 (V=O); ESI-TOF-LRMS (MeOH): Found: *m/z* 783 [M-2(OH)+2(OMe)+Na]⁺; CSI-TOF-LRMS (CH₂Cl₂): Found: *m/z* 1511 [2(M+Na+H)]⁺. Anal. Calcd for C₃₄H₃₆N₂O₁₁V₂: C, 54.41; H, 4.83; N, 3.73. Found: C, 53.98; H, 4.60; N, 3.56.

Synthetic procedure of (*R_a,S,S*)-**2b**

A round-bottomed flask (50 mL) was charged with (*R*)-5,5',6,6',7,7',8,8'-octahydro-3,3'-diformyl-BINOL (70 mg, 0.2 mmol), (*S*)-*tert*-leucine (58 mg, 0.44 mmol), MS 3Å (*ca.* 500 mg) and EtOH (7 mL). The reaction mixture was refluxed at 80 °C for 30 min to generate a yellow suspension and the consumption of (*R*)-5,5',6,6',7,7',8,8'-octahydro-3,3'-diformyl-BINOL was monitored by TLC (acetone:hexane = 1:3). After evaporation of EtOH, the residue was suspended in CH₂Cl₂ (10 mL), and then VOCl₃ (75 μL, 0.8 mmol) was added to give a dark green solution. The reaction mixture was stirred for 6 h under Ar, and filtered with Celite to remove MS 3Å. The filtrate was evaporated to afford a dark green solid. The resulting solid was dissolved in MeOH (15 mL) and the solvent was evaporated again. The residue was washed with water (*ca.* 50 mL) and Et₂O (*ca.* 50 mL). Drying under vacuum gave (*R_a,S,S*)-**2b** (84 mg, 56%) as a dark green powder. ¹H-NMR (270 MHz, CD₃OD): δ 8.59 (s, 2H, CH=N), 7.41 (s, 2H, Ar-H³), 4.12 (s, 2H, CH-*t*-Bu), 2.89 (br, 4H, CH₂), 2.34 (br, 4H, CH₂), 1.82 (br, 8H, CH₂), 1.19 (s, 18H, *t*-Bu); ¹³C-NMR (67.7 MHz, CD₃OD): δ 168.1 x 2, 148.3, 135.6, 134.8 x 2, 131.9, 102.0, 84.8, 39.4, 31.6, 31.2, 29.1, 29.0, 25.1; IR (cm⁻¹): 3449 (O-H), 1686 (C=N), 1611 (C=O), 1001 (V=O); ESI-TOF HRMS: Found: *m/z* 791.1929 [M-2(OH)+2(OMe)+Na]⁺. Calcd for C₃₆H₄₆N₂NaO₁₀V₂: 791.1929.

Synthetic procedure of (*S*)-**3**

A round-bottomed flask (50 mL) was charged with 3-formyl-2-naphthol (86 mg, 0.5 mmol), (*S*)-*tert*-leucine (58 mg, 0.5 mmol), MS 3Å and EtOH (7 mL). The reaction mixture was refluxed at 80 °C for 4 h to generate a red suspension and the consumption of 3-formyl-2-naphthol was monitored by TLC (acetone:hexane = 1:3). After evaporation of EtOH, the residue was suspended in CH₂Cl₂ (*ca.* 8 mL) and then VOCl₃ (0.09 mL, 1 mmol) was added. The reaction mixture was stirred for 15 h under Ar and filtered by Celite to remove MS 3Å. The filtrate was evaporated to afford a dark green solid. The resulting solid was dissolved in MeOH and the solvent was evaporated again. The residue was washed sequentially with water and ether. Drying under

vacuum gave (*S*)-**3** as a dark green powder (69 mg, 38%). FAB-LRMS: Found: m/z 368 ($M+H$)⁺; IR (cm^{-1}): 3439 (O-H), 1661 (C=N), 1615 (C=O), 992 (V=O); ¹H-NMR (269.6 MHz, CD₃OD): δ 8.95 (br, 2H, CH=N), 4.24 (br, 2H, CH-*t*-Bu), 1.25 (s, 9H, *t*-Bu); ESI-TOF HRMS: Found: m/z 404.0679 [$M\text{-OH+OMe+Na}$]⁺. Calcd for C₁₈H₂₀NNaO₅V: 404.0679.

Representative procedure for oxidative coupling of 2-naphthols by vanadium(V) catalysts

A round-bottom flask (20 mL) was charged with a CH₂Cl₂ solution (1 mL) of the corresponding 2-naphthol (0.2 mmol). Vanadium catalyst (0.01 mmol) was added as a powder to the solution, and the reaction mixture was stirred while monitoring the consumption of 2-naphthols by TLC (acetone/hexane = 1/3). The reaction mixture was purified by silica gel column chromatography (acetone/hexane = 1/4) to obtain the coupling product.