Supplementary Information

General considerations:

Dry dichloromethane (CH₂Cl₂) was distilled under N₂ from P₂O₅ and kept over 4 Å molecular sieves. Other solvents and reactants of high quality were purchased from commercial suppliers. ¹H NMR and ¹³C NMR spectra were recorded at 270 and 67.5 MHz on a Jeol GSX 270 WB, using CDCl₃ and TMS as internal standard (NMR spectra were then reported in ppm relative to the non deuterated solvent peak). δ values are given in parts per million (ppm), coupling constants (J values) are given in Hertz (Hz), and multiplicities of 1 H NMR signals are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet; Ar, aromatic. Values with asterisk* can be inverted. High-resolution mass (HRMS) measurements for exact mass determination were performed on a ZABSpec TOF Micromass at the Centre Régional de Mesures Physiques de l'Ouest. Samples were ionized whether with an electrospray ion source (ESI = ElectroSpray Ionization) or by LSIMS (Liquid Secondary Ion Mass Spectrometry) ionization. IRFT spectra were run on a Perkin Elmer 16 PC spectrometer (KBr pellets, v: cm⁻¹). Thin layer chromatography was performed on silica gel 60F254 plates (Merck). Column chromatography was performed using silica gel (63-200 µm, Kieselgel 60, Merck). Optical rotations were recorded with a Perkin Elmer 341 automatic polarimeter at 20 °C at the sodium line; $[\alpha]_D$ are given in 10⁻¹ deg cm² g⁻¹.

Synthesis: Ligand 2:



To a solution of usnic acid 1 (3 g, 8.71 mmol, 2 eq) in THF/EtOH (20:80) (40 mL) was added dropwise 1,2-diaminoethane (292 μ L, 4.36 mmol, 1 eq.). After stirring at 80 °C for 4 h, the mixture was concentrated under reduced pressure. The residue was diluted with dichloromethane and washed with water (to eliminate the unreactive diamine), dried over anhydrous sodium sulfate. After filtration, 1 eq of an aminomethyl resin (0.4-0.6 mmol/g) was added into the filtrate for removing excess of usnic acid. The suspension was stirred overnight at rt. After filtration, the filtrate was evaporated under reduced pressure. Recrystallization from CH₂Cl₂/EtOH (5/5) yield pure ligand **2**.

Rf =0.26 (CH₂Cl₂/MeOH, 98/2); $[\alpha]_D^{20}$ = + 419 (*c* 0.5, CH₂Cl₂);¹H NMR (270 MHz, CDCl₃) δ 1.70 (s, 6H, C<u>H₃-10</u>), 2.09 (s, 6H, C<u>H₃-15</u>), 2.66 (s, 6H, C<u>H₃-12</u>), 2.67 (s, 6H, C<u>H₃-14</u>), 3.86 (m, 4H, H-a, H-b), 5.80 (s, 2H, H-4), 11.70 (s, 2H, H-9), 13.55 (s, 2H, H-7), 13.96 (s, 2H, NH); NMR ¹³C (67.5 MHz, CDCl₃) δ 7.44 (CH₃-15), 18.16 (CH₃-12), 31.21 (CH₃-14), 31.81 (CH₃-10), 42.58 (CH₂-a,b), 57.58 (C-9b), 101.39 (C-6), 102.13 (C-2), 102.30 (C-4), 104.78 (C-9a), 108.20 (C-8), 155.74 (C-6a), 158.08 (C-9), 163.57 (C-7), 174.64 (C-4a), 175.45 (C-11), 191.03 (C-3), 198.71 (C-1), 200.60 (C-13); FTIR: 3200-2250 (OH, NH), 1697 (CO-1), 1620 (CO-13), 1550 (ketoenamine system); HRMS (ESI) (*m/z*) calcd for C₃₈H₃₆N₂O₁₂Na (M + Na)⁺ 735.2166; found 735.2179.

Complex 3



To a solution of ligand **2** (0.5 g, 0.7 mmol, 1 eq) in CH₂Cl₂ (10 mL) was added 1 eq of copper(II) acetate monohydrate and methanol (2 mL). The resulting mixture was allowed at rt for 24 h. The precipitate was filtered and washed with CH₂Cl₂. Recrystallization from CH₂Cl₂/EtOH (5/5) afford complex **3**, violet crystals (0.1 g, 93%). Rf = 0.48 (CH₂Cl₂/ethyl acetate, 90/10); $[\alpha]_D^{20} = + 286$ (*c* 0.084, CH₂Cl₂); FTIR: 3200-2250 (OH), 1701 (CO-1), 1629 (CO-13), 1550 (imine), 1447 & 1402 (CO-3); HRMS (ESI) (*m/z*) calcd for C₃₈H₃₄N₂O₁₂Na⁶³Cu (M + Na)⁺ 796.1305; found 796.1296.

Complex 4



To a solution of ligand **2** (0.1 g, 0.14 mmol, 1 eq) in CH_2Cl_2 (5 mL) was added 1 eq of nickel(II) acetate tetrahydrate and methanol (1mL). The resulting mixture was allowed at rt for 24 h. The precipitate was filtered and washed with CH_2Cl_2 . Recrystallization from $CH_2Cl_2/EtOH$ (5/5) yield pure orange complex **4** (0.1 g, 93%).

Rf = 0.6 (CH₂Cl₂/MeOH, 9.9/0.1); $[α]_D^{26}$ = + 130 (*c* 0.28, CH₂Cl₂); ¹H NMR (270 MHz, CDCl₃) δ 1.71 (s, 6H, C<u>H₃-10</u>), 2.10 (s, 6H, C<u>H₃-15</u>), 2.45 (s, 6H, C<u>H₃-12</u>), 2.67 (s, 6H, C<u>H₃-14</u>), 3.26 (m, 4H, H-a, H-b), 5.87 (s, 2H, H-4), 11.78 (s, 2H, H-9), 13.44 (s, 2H, H-7); NMR ¹³C (67.5 MHz, CDCl₃) δ 7.55 (<u>CH₃-15</u>), 21.37 (<u>CH₃-12</u>), 31.29 (<u>CH₃-14</u>), 31.60 (<u>CH₃-10</u>), 54.01 (<u>CH₂-a,b</u>), 58.11 (C-9b), 100.04 (C-6), 101.57 (C-9a), 104.87 (C-4), 107.59 (C-2), 108.19 (C-8), 156.11 (C-6a), 158.15 (C-9), 163.66 (C-7), 171.02 (C-11), 173.75 (C-4a), 183.46 (C-3), 199.19 (C-1), 200.64 (C-13); FTIR: 3200-2250 (OH), 1696 (CO-1), 1629 (CO-13), 1544 (imine), 1450 & 1410 (CO-3); HRMS (ESI) (*m/z*) calcd for C₃₈H₃₄N₂O₁₂Na⁵⁸Ni (M + Na)⁺ 791.1363; found 791.1337.

7,9-Di-O-benzylusnic acid 5:8



A suspension of (+)-usnic acid (0.5 g, 1.45 mmole, 1 eq) and tetramethylammonium hydroxide pentahydrate (0.865g, 4.78 mmole, 3.3 eq) in hexamethylphosphoramide (15 mL) was stirred at 0°C for 2h under a nitrogen atmosphere. To the resulting maroon solution was added benzyl bromide (0.786 g, 4.6 mmole, 3.2 eq) and the reaction allowed to stir at 0 °C for 3 h. The reaction mixture was diluted with cold distilled water (50 mL) and extracted once with cyclohexane (20 mL) to eliminate the excess benzyl bromide. The aqueous phase was acidified with 1 M hydrochloric acid, and extracted with ethyl acetate (3 x 40 mL). The combined extracts were washed with water (2 x 50 mL), dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography using cyclohexane/ethyl acetate 90/10 to afford 7,9-Di-O-benzylusnic acid as yellow solid (200 mg, 26%).

Rf = 0.6 (hexane/ethyl acetate, 5/5); $[\alpha]_D^{20} = + 138$ (*c* 1, CH₂Cl₂); $[\alpha]_D^{20} = + 119$ (*c* 1, CH₃CN); ¹H NMR (270 MHz, CDCl₃) δ 1.83 (s, 3H, C<u>H₃-10</u>), 2.31 (s, 3H, C<u>H₃-15</u>), 2.50 (s, 3H, C<u>H₃-14</u>), 2.58 (s, 3H, C<u>H₃-12</u>), 4.91 (s, 2H, C<u>H₂-16</u>), 5.33 (AB q, *J*=10 Hz, 2H, C<u>H₂-18</u>), 5.85 (s, 1H, H-4), 7.30-7.60 (m, 10H, 2 x C₆H₅), 18.04 (s, 1H, H-3); NMR ¹³C (67.5 MHz, CDCl₃) δ 10.83 (CH₃-15), 25.00 (CH₃-12), 30.66 (CH₃-14), 32.14 (CH₃-10), 60.59 (C-9b), 75.53 (CH₂-16), 76.53 (CH₂-18), 98.19 (C-4), 106.53 (C-2), 116.75 (C-6), 116.96 (C-9a), 123.14 (C-8), 127.92 (C-17c), 128.03 (C-19c), 128.36, 128.42, 128.53, 128.65 (C-17a,b,d,e; C-19a,b,d,e), 136.14 (C-17f), 137.41 (C-19f), 153.04(C-6a), 157.27(C-9), 157.69 (C-7), 178.92 (C-4a), 191.15 (C-3), 193.78 (C-1), 196.21 (C-11), 197.59 (C-13).

Ligand 6:



To a solution of usnic acid 1 (0.4 g, 0.76 mmol, 2 eq) in THF/EtOH (20:80) (15 mL) was added dropwise 1,2-diaminoethane (25 μ L, 0.38 mmol, 1 eq.). After stirring at 80 °C for 5 h, the mixture was concentrated under reduced pressure. Purification by column chromatography on silica gel (CH₂Cl₂/MeOH, 99/1) gave ligand **6** (40 mg, 15%) as a white solid.

Rf = 0.3 (CH₂Cl₂/MeOH, 9.5/0.5); $[\alpha]_D^{20} = + 66.6$ (*c* 0.47, CH₂Cl₂); ¹H NMR (270 MHz, CDCl₃) δ 1.77 (s, 6H, C<u>H₃-10</u>), 2.30 (s, 6H, C<u>H₃-15</u>), 2.40 (s, 6H, C<u>H₃-12</u>), 2.57 (s, 6H, C<u>H₃-14</u>), 3.70 (m, 4H, H-a, H-b), 4.89 (s, 4H, C<u>H₂-16</u>), 5.33 (AB q, *J*=10 Hz, 4H, C<u>H₂-18</u>), 5.68 (s, 2H, H-4), 7.30-7.60 (m, 20H, 4 x C₆H₅), 13.08 (s, 2H, NH); NMR ¹³C (67.5 MHz, CDCl₃) δ 10.79 (CH₃-15), 16.30 (CH₃-12), 30.26 (CH₃-14), 32.21 (CH₃-10), 42.67 (CH₂-a,b), 59.66 (C-9b), 75.04 (CH₂-16), 77.16 (CH₂-18), 101.49 (C-4), 103.76 (C-2), 116.61 (C-6), 117.47 (C-9a), 122.23 (C-8), 127.66 (C-17c), 127.82 (C-19c), 128.35, 128.38, 128.43, 128.63 (C-17a,b,d,e; C-19a,b,d,e), 136.40 (C-17f), 137.82 (C-19f), 153.72(C-6a), 157.00(C-9), 157.87 (C-7), 170.94 (C-11), 174.60 (C-4a), 190.18 (C-3), 196.47 (C-1), 197.96 (C-13); FTIR: 3368 (NH), 2850-3100 (CH al + CH ar), 1685 (CO-1; CO-13), 1569 (CO-3); HRMS (ESI) (*m/z*) calcd for C₆₆H₆₀N₂O₁₂Na (M + Na)⁺ 1095.4044; found 1095.4049.

Complex 7



To a solution of ligand **6** (0.05 g, 0.046 mmol, 1 eq) in CH_2Cl_2 (2.5 mL) was added 1 eq of copper(II) acetate monohydrate and methanol (0.5 mL). The reaction mixture was heated a few seconds and allowed at rt for 24 h. The resulting precipitate was filtered and washed with CH_2Cl_2 and purified by column chromatography using $CH_2Cl_2/MeOH$, 99.5/0.5 to afford complex 7 as pink solid (30 mg, 58%).

complex 7 as pink solid (30 mg, 58%). Rf = 0.2 (CH₂Cl₂/MeOH, 9.9/0.1); $[\alpha]_D^{20} = +380$ (*c* 0.092, CH₂Cl₂); FTIR: 2850-3100 (CH al + CH ar), 1686 (CO-1; CO-13), 1557 (imine), 1445 & 1399 (CO-3); HRMS (ESI) (*m/z*) calcd for C₆₆H₅₉N₂O₁₂⁶³Cu (M + H)⁺ 1134.3364; found 1134.3359.

Complex 8



To a solution of ligand **6** (0.05 g, 0.046 mmol, 1 eq) in CH_2Cl_2 (2.5 mL) was added 1 eq of nickel(II) acetate tetrahydrate and methanol (0.5mL). The resulting mixture was allowed at rt for 24 h. The precipitate was filtered and washed with CH_2Cl_2 . Recrystallization from $CH_2Cl_2/EtOH$ (5/5) yield pure red crystals **8** (0.051 g, 95%).

Rf = 0.4 (CH₂Cl₂/MeOH, 9.9/0.1); $[α]_D^{20}$ = - 503.6 (*c* 0.22, CH₂Cl₂); ¹H NMR (270 MHz, CDCl₃) δ 1.77 (s, 6H, C<u>H₃-10)</u>, 2.21 (s, 6H, C<u>H₃-12)</u>, 2.30 (s, 6H, C<u>H₃-15)</u>, 2.57 (s, 6H, C<u>H₃-14)</u>, 3.18 (m, 4H, H-a, H-b), 4.89 (s, 4H, C<u>H₂-16)</u>, 5.32 (AB q, *J*=11 Hz, 4H, C<u>H₂-18), 5.76 (s, 2H, H-4)</u>, 7.30-7.60 (m, 20H, 4 x C₆H₅); NMR ¹³C (67.5 MHz, CDCl₃) δ 10.78 (<u>C</u>H₃-15), 20.00 (<u>C</u>H₃-12), 28.94 (<u>C</u>H₃-14), 32.27 (<u>C</u>H₃-10), 53.99 (<u>C</u>H₂-a,b), 59.74 (C-9b), 75.16 (<u>C</u>H₂-16), 77.17 (<u>C</u>H₂-18), 99.21 (C-4), 107.76 (C-2), 116.69 (C-6), 117.48 (C-9a), 122.13 (C-8), 127.79 (C-17c, C-19c), 128.34, 128.40, 128.43, 128.64 (C-17a,b,d,e; C-19a,b,d,e), 136.49 (C-17f), 137.87 (C-19f), 154.15 (C-6a), 157.00 (C-9), 157.80 (C-7), 168.32 (C-11), 172.37 (C-4a), 179.13 (C-3), 198.05 (C-1), 198.74 (C-13); FTIR: 2850-3100 (CH al + CH ar), 1686 (CO-1; CO-13), 1546 (imine), 1451 & 1400 (CO-3); HRMS (ESI) (*m/z*) calcd for C₆₆H₅₈N₂O₁₂Na⁵⁸Ni (M + Na)⁺ 1151.3241; found 1151.3226.

Structure analysis for compound 2

C₃₈H₃₆N₂O₁₂, \dot{M} = 712.69, triclinic, P-1, *a* = 7.5006(6), *b* = 10.1555(7), *c* = 11.3793(9) Å, α = 72.374(6), β = 88.638(6), γ = 90.841(5) °, V = 825.64(11) Å³, Z = 1, D_X = 1.433 Mg.m⁻³, λ(MoKα) = 0.71069 Å, μ = 0.108 mm⁻¹, F(000) = 374, *T* = 295(2) K. The sample (0.30 x 0.30 x 0.12 mm) is studied on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatized MoKα radiation. The data collection (Crysalis, 2004) (2θ_{max} = 54°, omega scan frames via 0.7° omega rotation and 20 s per frame, range HKL: H -10,10 K -8,15 L -16,16) gives 7721 reflections. The data leads to 5566 independent reflections from which 3126 with I>2.0σ(I). The structure was solved with SIR-97 which reveals the non hydrogen atoms of the molecule. After anisotropic refinement, all the hydrogen atoms are found with a Fourier Difference. The whole structure was refined with SHELXL97 by the full-matrix least-square techniques (use of F square magnitude; x , y, z, β_{ij} for C and O atoms, x, y, z in riding mode for H atoms; 470 variables and 3126 observations with I>2.0σ(I); calc w=1/[σ²(Fo²) +(0.089P)²] where P=(Fo²+2Fc²)/3 with the resulting R = 0.0361, R_w = 0.0883 and S_w = 0.833, Δρ < 0.20eÅ⁻³ Atomic scattering factors from International Tables for X-ray Crystallography (1992). Ortep view was realized with PLATON98.

Structure analysis for compound 8

C₁₃₄H₁₁₈Cl₆N₄Ni₂O₂₄, M = 2498.44, monoclinic, P21, a = 15.912(2), b = 23.792(4), c = 17.535(2) Å, $\alpha = 90$, $\beta = 113.5190(1)$, $\gamma = 90$ °, V = 6087.0(15) Å³, Z = 2, D_X = 1.363 Mg.m³, λ (MoK α) = 0.71069 Å, $\mu = 0.515$ mm⁻¹, F(000) = 2600, T = 110(2) K. The sample (0.15 x 0.06 x 0.06 mm) is studied on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatized MoK α radiation. The data collection (Crysalis, 2004) ($2\theta_{max} = 54^{\circ}$, omega scan frames via 0.7° omega rotation and 20 s per frame, range HKL: H -24,24 K - 35,35 L -26,26) gives 96611 reflections. The data leads to 36765 independent reflections from which 10683 with I>2.0 σ (I). The structure was solved with SIR-97 which reveals the non hydrogen atoms of the molecule. After anisotropic refinement, all the hydrogen atoms are found with a Fourier Difference. The whole structure was refined with SHELXL97 by the full-matrix least-square techniques (use of F square magnitude; x , y, z, β_{ij} for C and O atoms, x, y, z in riding mode for H atoms; 1568 variables and 10683 observations with I>2.0 σ (I);

calc w=1/[$\sigma^2(Fo^2)$ +(0.089P)²] where P=(Fo²+2Fc²)/3 with the resulting R = 0.0622, R_w = 0.1245 and S_w = 0.701, $\Delta \rho < 0.73e Å^{-3}$ Atomic scattering factors from International Tables for X-ray Crystallography (1992). Ortep view was realized with PLATON98.