Supporting Information

General considerations

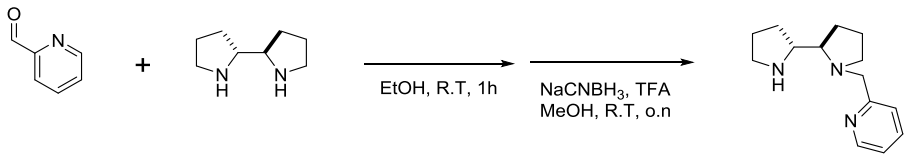
All manipulations of air-sensitive compounds were carried out using degassed solvents under an Ar atmosphere. 2,2'-bipyridine-6-carbaldehyde was purchased from HetCat, (*R,R*)-bipyrrolidine and (*S,S*)-bipyrrolidine were purchased from OBITER and used as received. All other chemicals were commercially available and used as received unless otherwise stated. Deuterated solvents were purchased from Aldrich or Cambridge Isotope Laboratories, Inc., and used as received.

Instruments and Methods

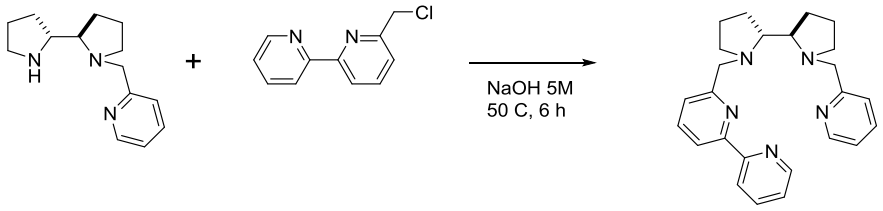
The NMR spectra were recorded on a Bruker Avance 400 spectrometer at 25 °C, unless otherwise stated. Chemical shifts (δ) are listed as parts per million and coupling constants (*J*) in Hertz. ^{1}H NMR spectra were referenced using the residual solvent peak at δ = 2.05 for Acetone-d_6 and δ = 7.26 for $CDCl_3$. ^{13}C NMR spectra were referenced using the residual solvent peak at δ = 206.26 and 29.84 for Acetone-d_6 and δ = 77.16 for $CDCl_3$.

X-ray diffraction measurements were performed on an ApexDuo (Bruker-AXS) diffractometer system, using MoKα (λ = 0.7107 Å) radiation. The analyzed crystals were grown by slow evaporation of acetone solutions and freeze-cooled to ca. 110 K. Mass spectra were obtained on a SYNAPT – High Definition Mass Spectrometry. Ionization methods: ESI (positive or negative) and APPI (atmospheric pressure photo ionization). The reported calculated and measured masses are based on the lightest isotope of each element rather than on the most abundant isotope. Ligands **1**, **2**[S1] and **3**[S2] were prepared according to published procedures.[S1]

Synthesis of the pentadentate ligand



(R,R)-1-(pyridin-2-ylmethyl)-2,2'-bipyrrolidine: (*R,R*)-bipyrrolidine (654 mg, 4.67 mmol) and 2-carbaldehyde pyridine (500 mg, 4.67 mmol) were reacted in ethanol (15 mL) for 1 h at R.T. The solvent was removed and the crude aminal was re-dissolved in MeOH (30 mL), cooled to 0 °C and treated with 2 equivalents of $NaCNBH_3$. The reaction mixture was allowed to stir for 10 min. at R.T, followed by the addition of 1 mL of TFA. The reaction was stirred under N_2 atmosphere over night and quenched by adding 50 mL of NaOH 4M and stirring the mixture for 1h. $CHCl_3$ (50 mL) was then added and the phases were separated. The aqueous phase was extracted twice with $CHCl_3$, the combined organic phases were dried over Na_2SO_4 and evaporated to give the pure product (98% yield) which was characterized according to the literature.[S3]



(R,R)-4: 6-chloromethyl-2,2'-bipyridine (332 mg, 1.62 mmol) and (*R,R*)-1-(pyridin-2-ylmethyl)-2,2'-bipyrrolidine (375 mg, 1.62 mmol) were reacted in NaOH 5M (10 mL) for 6 h at 50 ^{o}C. The reaction was then cooled to R.T, DCM (20 mL) was added and the phases were separated. The aqueous phase was extracted with DCM and the combined organic phases were dried over Na_2SO_4 and evaporated. The pure ligand was obtained by chromatography over Al_2O_3 (II-III) with 10% ethylacetate/hexane as yellow oil (90% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.66 (d, 1H, J = 4.2, ArH), 8.50 (d, 1H, J = 4.5 Hz, ArH), 8.39 (d, 1H, J = 7.7 Hz, ArH), 8.20 (d, 1H, J = 7.5 Hz, ArH), 7.79 (dd, 1H, J = 7.7 Hz, J= 1.7 Hz, ArH), 7.74 (t, 1H, J = 7.7 Hz, ArH), 7.59 (dd, 1H, J = 7.7 Hz, J= 1.7 Hz, ArH), 7.43 (d, 1H, J = 7.5 Hz, ArH), 7.41 (d, 1H, J = 7.7 Hz, ArH), 7.28 (m, 1H, ArH), 7.10 (m, 1H, ArH), 4.29 (d, 1H, J = 14.5 Hz, CH), 4.24 (d, 1H, J = 14.2 Hz, CH), 3.63 (d, 1H, J = 14.5 Hz, CH), 3.51 (d, 1H, J = 14.2 Hz, CH), 3.06 (m, 1H, CH), 3.00 (m, 1H, CH), 2.88 (m, 2H, CH), 2.31 (q, 1H, J = 8.5 Hz, CH), 2.24 (q, 1H, J = 8.5 Hz, CH), 2.88 (m, 2H, CH), 1.91 (m, 2H, CH), 1.83 (m, 4H, CH), 1.73 (m, 4H, CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.6 (C), 160.1 (C), 156.6 (C), 155.3 (C), 149.2 (CH), 148.9 (CH), 137.3 (CH), 137.0 (CH), 136.4 (CH), 123.6 (CH), 122.8 (2CH), 121.8 (CH), 121.3 (CH), 119.1 (CH), 65.6 (CH_2), 65.4 (CH_2), 61.4 (CH), 61.1 (CH), 55.5 (CH_2), 55.3 (CH_2), 26.2 ($2CH_2$), 23.7 ($2CH_2$). ESI-MS (calculated 400.2501): found 400.2493 (MH+).

Synthesis of complexes

[(R,R)-1-Ru][PF$_6$]$_2$ (mixture of stereoisomers): A solution of $RuCl_3$ hydrate (0.059 mmol) in a mixture of ethanol and water (3.5:1 mL) was degassed with argon for 2 min. in a pressure flask, sealed and heated to 120 ^{o}C. Upon the generation of "Ru blue" the solution was cooled to ambient temperature and a solution of (*R,R*)-**1** (0.059 mmol) in ethanol (1.5 mL) was added under a flow of argon. The reaction mixture was brought back to 120 ^{o}C and stirred under argon for 2 h. Upon completion the reaction was cooled to room temperature and saturated potassium hexafluorophosphate solution (8 mL, excess) was added. The reaction mixture was cooled to 0 °C to allow the complete precipitation of the complex. The precipitate was separated from the solution by centrifugation and the solids were washed with 3 portions of water. The complex was dried thoroughly under reduced pressure (95% yield). X-ray quality crystals were obtained by slow evaporation of 0.5 mL acetone solutions (containing about 10 mg of complex) from a loosely-capped 2.75 mL vial, over several days. ^{1}H NMR (Acetone-d_6, 400 MHz): δ = 8.85 (d, 1H, J = 8.2, ArH), 8.78 (d, 2H, J = 8.1 Hz, ArH), 8.71 (m, 2H, ArH), 8.28 (t, 1H, J = 8.1 Hz, ArH), 8.18 (t, 1H, J = 8.1 Hz, ArH), 8.06 (m, 5H, ArH), 7.84 (d, 1H, J = 7.9 Hz, ArH), 7.80 (d, 1H, J = 5.5 Hz, ArH), 7.40 (m, 2H, ArH), 5.05 (d, 1H, J = 18.7 Hz, CH), 4.77 (d, 1H, J = 16.1 Hz, CH), 4.63 (d, 1H, J = 18.7 Hz, CH), 4.09 (d, 1H, J = 16.1 Hz, CH), 3.28 (m, 1H, CH), 2.48 (m, 1H, CH), 2.34 (m, 2H, CH), 2.18 (m, 2H, CH), 1.81 (m, 3H, CH), 1.61 (m, 2H, CH). ESI-MS (calculated 717.1406): found 717.1404 ([M-PF_6]+).

$C_{30}H_{32}N_6Ru \cdot 2(PF_6)$, Mr = 867.62, monoclinic, space group C2, a = 25.132(2), b = 9.8199(7), c = 17.2577(16) Å, β = 131.012(5)°, V = 3213.8(5) Å^3, T = 110(2) K, Z = 4, μ(MoKa) = 0.692 mm^{-1}, ρ(calcd) = 1.793 g·cm^{-3}, 27997 reflections measured to θ = 28.36°, of which 7832 were unique (Rint = 0.026) and 7019 with I > 2σ(I). Final R1 = 0.0685 (wR2 = 0.1600) for the 7019 data above the intensity threshold, and R1 = 0.0611 (wR2 = 0.1538) for all unique data. CCDC 1469725

[2-Ru][PF$_6$]$_2$: Prepared from $RuCl_3$ hydrate and **2** according to the procedure for [(*R,R*)-**1**-Ru][PF_6]$_2$ in a similar yield. ^{1}H NMR (Acetone-*d$_6$*, 400 MHz): δ = 8.85 (d, 1H, J = 8.1, ArH), 8.79 (d, 2H, J = 8.0 Hz, ArH), 8.72 (d, 1H, J = 7.9, ArH), 8.30 (t, 1H, J = 7.9, ArH), 8.24 (t, 1H, J = 7.9, ArH), 8.08 (m, 3H, ArH), 7.99 (d, 1H, J = 7.9, ArH), 7.79 (d, 1H, J = 5.3, ArH), 7.69 (d, 1H, J = 4.9, ArH), 7.40 (m, 2H, ArH), 5.23 (d, 1H, J = 18.1 Hz, CH), 4.99 (d, 1H, J = 16.1 Hz, CH), 4.48 (d, 1H, J = 18.1 Hz, CH), 4.15 (d, 1H, J = 16.1 Hz, CH), 3.54 (s, 1H, CH), 2.96 (s, 1H, CH), 2.87 (m, 1H, CH), 2.74 (m, 1H, CH), 2.33 (m, 1H, CH), 2.23 (m, 2H, CH), 1.81 (s, 1H, CH), 1.75 (m, 1H, CH), 1.68 (m, 2H, CH), 1.42 (m, 1H, CH), 1.16 (m, 2H, CH). ^{13}C NMR (Acetone-*d$_6$*, 100 MHz): δ = 158.6 (C), 157.3 (C), 154.6 (C), 152.6 (CH), 136.7 (CH), 135.1 (CH), 127.0 (CH), 124.3 (CH), 123.8 (CH), 122.7 (CH), 70.1 (CH_2), 60.4 (CH_2), 44.8 (CH_3). ESI-MS (calculated 665.1096): found 665.1099 ([M-PF_6]+).

$C_{26}H_{28}N_6Ru \cdot 2(PF_6)$, Mr = 815.55, monoclinic, space group C2/c, a = 20.6432(17), b = 12.1018(9), c = 12.8802(11) Å, β = 110.019(3)°, V = 3023(4) Å^3, T = 110(2) K, Z = 4, μ(MoKa) = 0.729 mm^{-1}, ρ(calcd) = 1.792 g·cm^{-3}, 14132 reflections measured to θ = 28.32°, of which 3762 were unique (Rint = 0.026) and 3392 with I > 2σ(I). Final R1 = 0.0355 (wR2 = 0.0776) for the 3392 data above the intensity threshold, and R1 = 0.0304 (wR2 = 0.0737) for all unique data. CCDC 1469724

[(R,R)-3-Ru(CH$_3$CN)$_2$][PF$_6$]$_2$: A solution of $RuCl_3$ hydrate (0.059 mmol) in a mixture of ethanol and water (3.5:1 mL) was degassed with argon for 2 min. in a pressure flask, sealed and heated to 120 °C. Upon the generation of "Ru blue" the solution was cooled to ambient temperature and a solution of (*R,R*)-**3** (0.059 mmol) in ethanol (1.5 mL) was added under a flow of argon. The reaction mixture was brought back to 120 °C and stirred under argon for 2 h. Upon completion the reaction was cooled to ambient temperature for the second time and excess of acetonitrile (0.5 mL) was added. The reaction was stirred at 120 °C for an additional hour and cooled back to room temperature. Saturated potassium hexafluorophosphate solution (8 mL, excess) was added and the reaction mixture was cooled to 0 °C to allow the complete precipitation of the complex. The precipitate was separated from the solution by centrifugation and the solids were washed with 3 portions of water. The complex was dried thoroughly under reduced pressure. The crude reaction mixture pointed to the formation of a major product in a yield of (90+)%. X-ray quality crystals were obtained by slow evaporation of 0.5 mL acetone solutions (containing about 10 mg of complex) from a loosely-caped 2.75 mL vial, over several days. ^{1}H NMR (Acetone-*d$_6$*, 400 MHz): δ = 9.25 (d, 2H, J = 5.2, ArH), 8.00 (dd, 2H, J = 7.6 Hz, J = 1.4 Hz, ArH), 7.67 (d, 2H, J = 7.8 Hz, ArH), 7.59 (t, 2H, J = 6.5 Hz, ArH), 4.57 (d, 2H, J = 15.5 Hz, CH), 4.40 (d, 2H, J = 15.5 Hz, CH), 3.49 (m, 2H, CH), 2.70 (m, 2H, CH), 2.61 (2, 6H, CH), 2.23 (m, 4H, CH), 1.90 (m, 2H, CH), 1.50 (m, 2H, CH). ^{13}C NMR (Acetone-*d$_6$*, 100 MHz): δ = 161.3 (C), 154.1 (CH), 137.9 (CH), 128.0 (C), 125.5 (CH), 123.5 (CH), 74.0 (CH_2), 66.1 (CH_2), 57.3 (CH), 23.7 (CH_2), 23.4 (CH_2), 3.99 (CH_3). ESI-MS (calculated 645.1406): found 645.1407 ([M-PF_6]+).

$C_{24}H_{32}N_6Ru \cdot 2(PF_6)$, Mr = 795.56, trigonal, space group P31 2 1, a = 10.2422(2), b = 10.2422(2), c = 24.9887(6) Å, β = 90°, V = 2270.18(12) Å^3, T = 110(2) K, Z = 3, μ(MoKa) = 0.729 mm^{-1}, ρ(calcd) = 1.746 g·cm^{-3}, 14222 reflections measured to θ = 28.36°, of which 3775 were unique (Rint = 0.026) and 3743 with I > 2σ(I). Final R1 = 0.0199 (wR2 = 0.0476) for the 3743 data above the intensity threshold, and R1 = 0.0196 (wR2 = 0.0474) for all unique data. CCDC 1469726

[(R,R)-4-RuCl][PF$_6$]: Prepared from $RuCl_3$ hydrate and **4** according to the procedure for [(*R,R*)-**1**-Ru][PF_6]$_2$. The crude reaction mixture pointed to the formation of a major product in a yield of (90+)%. ^{1}H NMR (Acetone-*d$_6$*, 400 MHz): δ = 9.97 (d, 1H, J = 5.1, ArH), 8.51 (t, 2H, J = 8.5 Hz, ArH), 8.01 (m, 2H, ArH), 7.89 (m, 2H, ArH), 7.70 (m, 3H, ArH), 7.43 (t, 1H, J = 5.9 Hz, ArH), 4.64 (d, 1H, J = 14.6 Hz, CH), 4.47 (d, 1H, J = 14.6 Hz, CH), 4.21 (d, 1H, J = 15.6 Hz, CH), 3.52 (d, 1H, J = 15.6 Hz, CH), 3.42 (m, 1H, CH), 3.12 (m, 1H, CH), 2.96 (m, 2H, CH), 2.89 (m, 2H, CH), 2.71 (m, 1H, CH), 2.35 (m, 1H, CH), 2.21 (m, 1H, CH), 1.86 (m, 3H, CH), 1.66 (m, 1H, CH), 1.50 (m, 2H, CH). ^{13}C NMR (Acetone-*d$_6$*, 100 MHz): δ = 159.9 (C), 159.5 (C), 159.3 (C), 157.4 (C), 152.9 (CH), 152.6 (CH), 135.5 (CH), 134.2 (CH), 131.5 (CH), 126.5 (CH), 124.3 (2CH), 122.9 (CH), 122.9 (CH), 121.7 (CH), 74.2 (CH_2), 74.0 (CH_2), 68.4 (CH), 63.9 (CH), 57.2 (CH_2), 54.5 (CH_2), 24.7 (CH_2), 23.9 (CH_2), 22.5 (CH_2), 22.0 (CH_2). ESI-MS (calculated 530.1187): found 530.1192 ([M-PF_6]+).

[(R,R)-4-FeCl][PF$_6$]$_2$: A solution of $FeCl_3$ hexahydrate (0.059 mmol) in water (1 mL) was degassed with argon for 2 min. and treated with a solution of **4** (0.059 mmol) in ethanol (3.5 mL). The reaction mixture was stirred under argon atmosphere at room temperature for 2 h. Saturated potassium hexafluorophosphate solution (4 mL, excess) was added and the reaction mixture was cooled to 0 °C. The precipitate was separated from the solution by centrifugation and the solids were washed with 3 portions of water. The complex was dried thoroughly under reduced pressure (50% yield). X-ray quality crystals were obtained by slow evaporation of 0.5 mL acetone solutions (containing about 10 mg of complex) from a loosely-caped 2.75 mL vial, over several days.

$C_{25}H_{29}N_5FeCl \cdot 2(PF_6)$, Mr = 780.77, monoclinic, space group P21, a = 10.1753(10), b = 16.8389(17), c = 9.2498(9) Å, β = 112.218(3)°, V = 1467.2(3) Å^3, T = 110(2) K, Z = 2, μ(MoKa) = 0.819 mm^{-1}, ρ(calcd) = 1.767 g·cm^{-3}, 14427 reflections measured to θ = 28.44°, of which 6709 were unique (Rint = 0.026) and 6254 with I > 2σ(I). Final R1 = 0.045 (wR2 = 0.1078) for the 6254 data above the intensity threshold, and R1 = 0.041 (wR2 = 0.1053) for all unique data. CCDC 1469727

NMR spectra of ligands and complexes

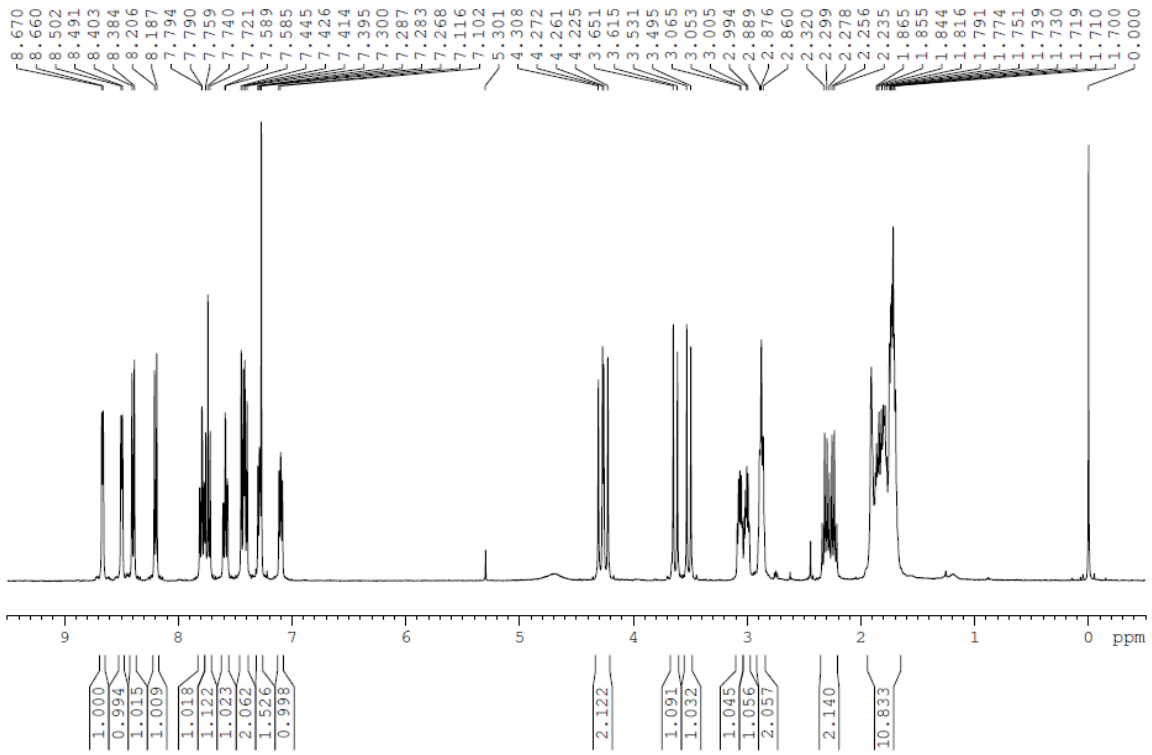


Fig. S1 ^{1}H NMR spectrum of (*R,R*)-**4**.

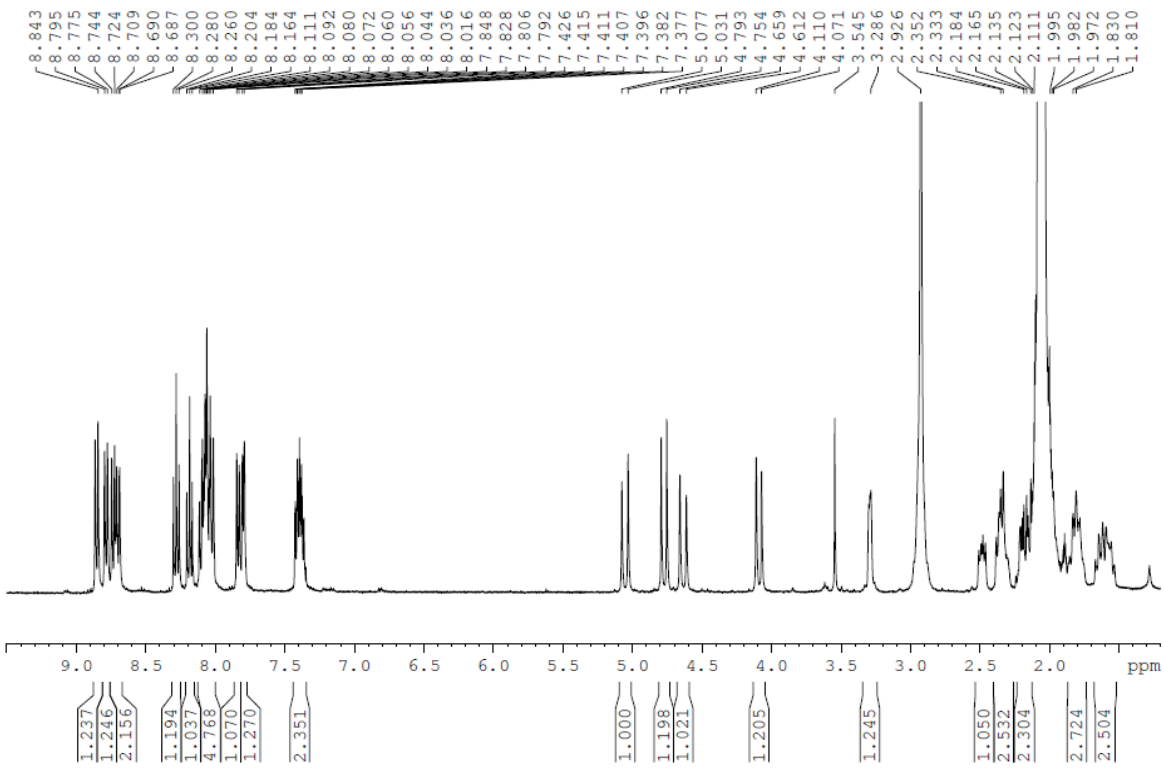


Fig. S2 ^{1}H NMR spectrum of [(*R,R*)-**1**-Ru][PF_6]$_2$ (mixture of stereoisomers).

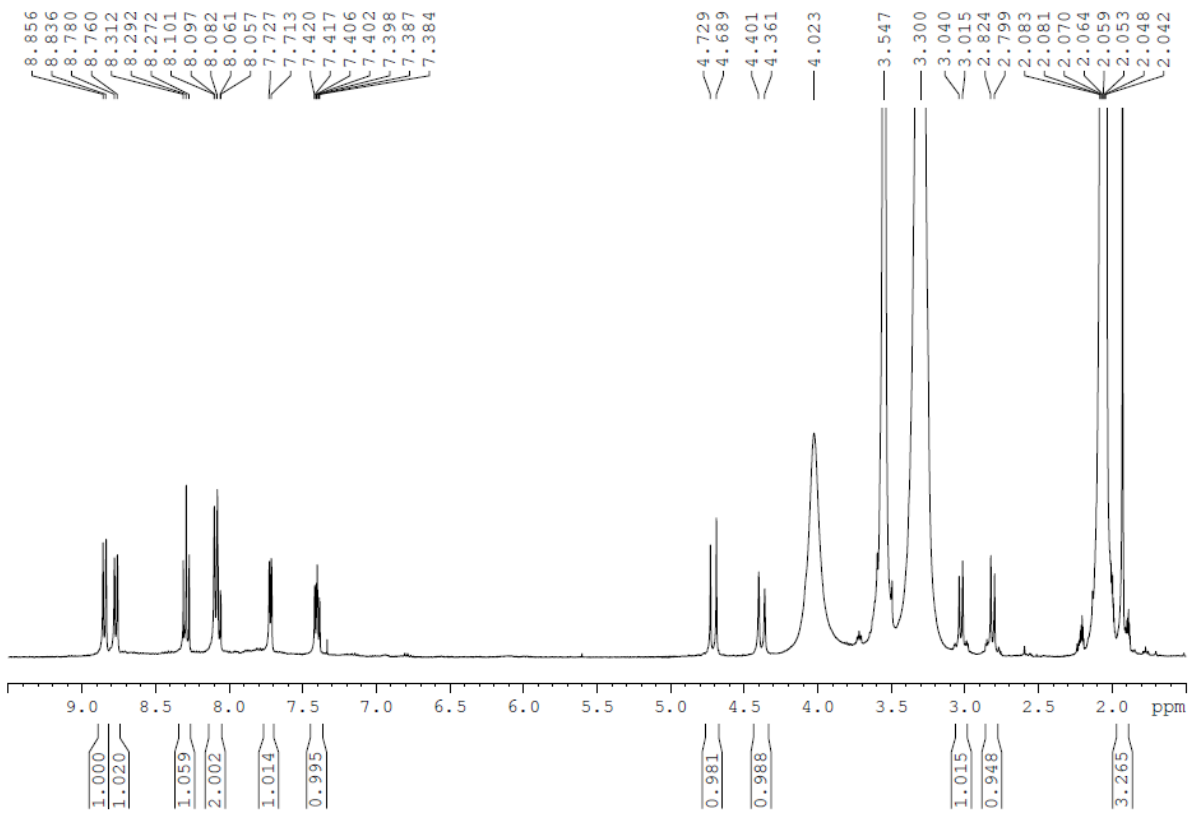


Fig. S3 ^{1}H NMR spectrum of [**2**-Ru][PF_6]$_2$.

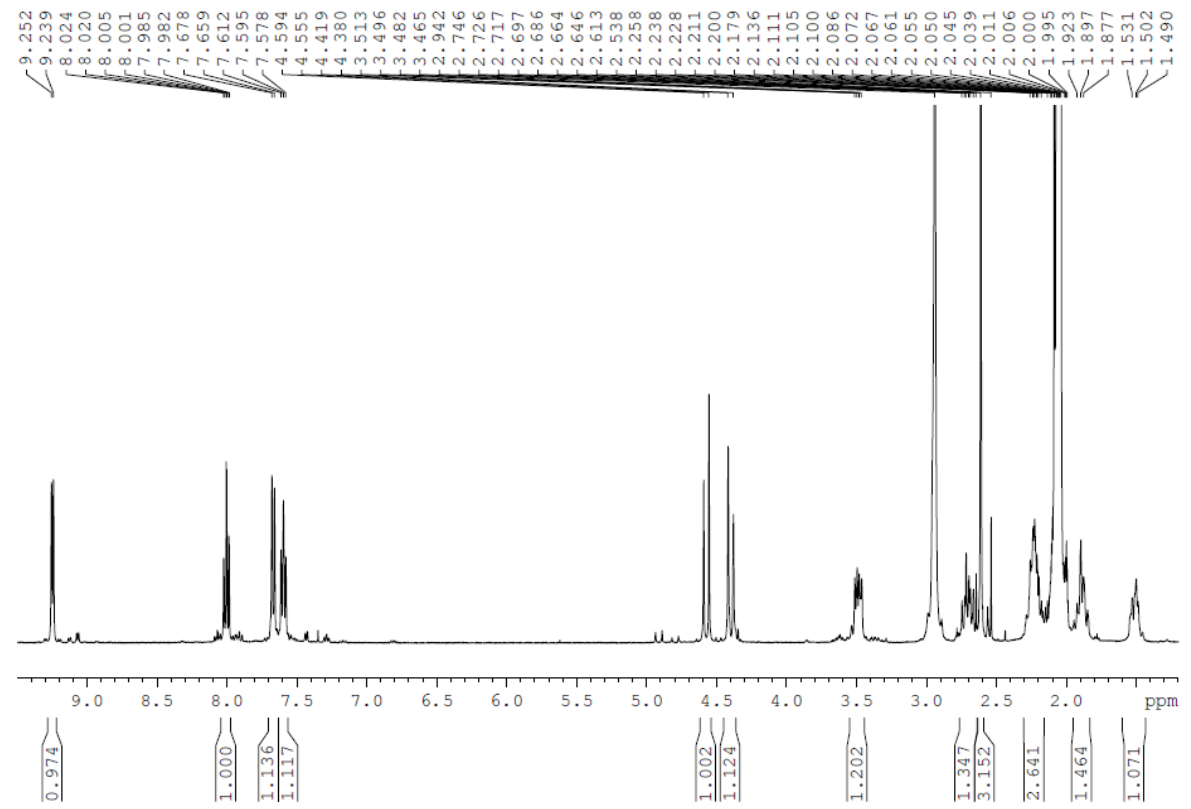


Fig. S4 ^{1}H NMR spectrum of [(*R,R*)-**3**-Ru(CH_3CN)$_2$][PF_6]$_2$.

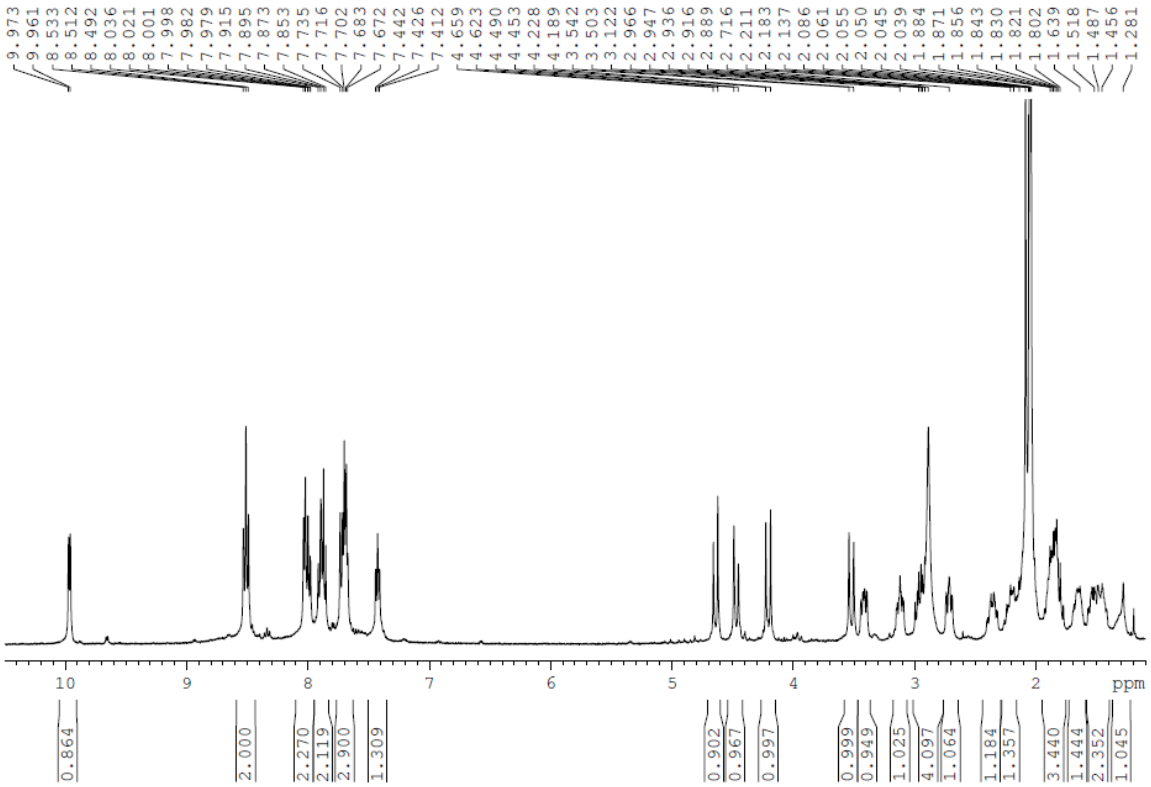


Fig. S5 ^{1}H NMR spectrum of [(*R,R*)-**4**-RuCl][PF_6]$_2$.

Absorbance and CD spectra of ligands and complexes

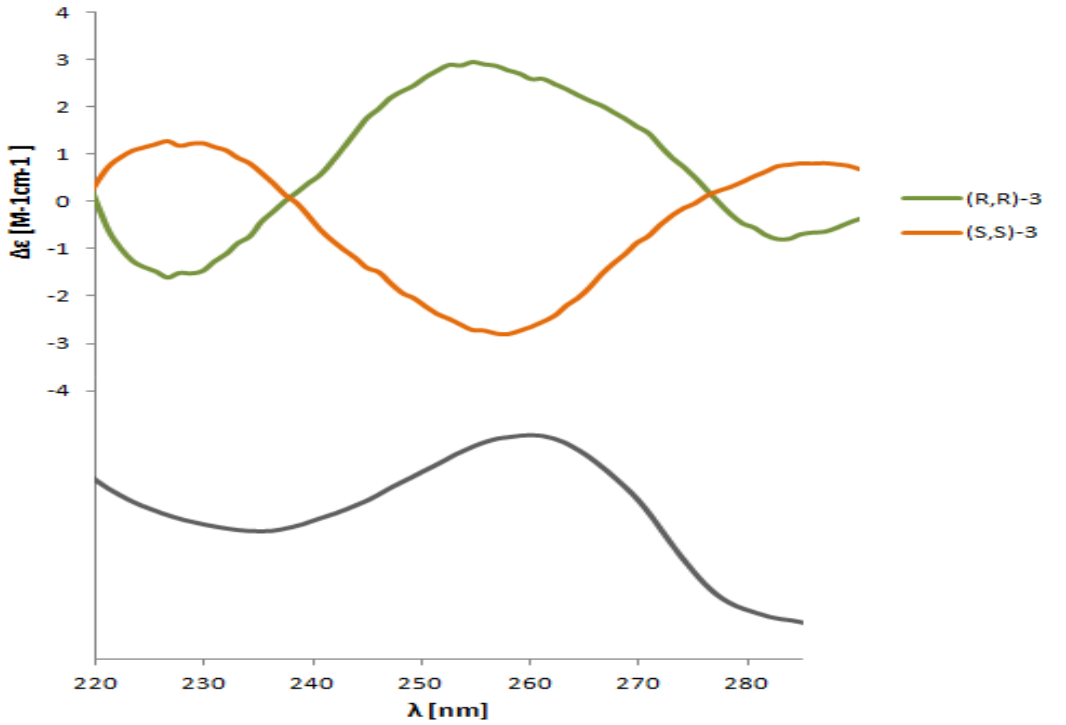


Fig. S6 Absorbance and CD spectra of ligand **3**.

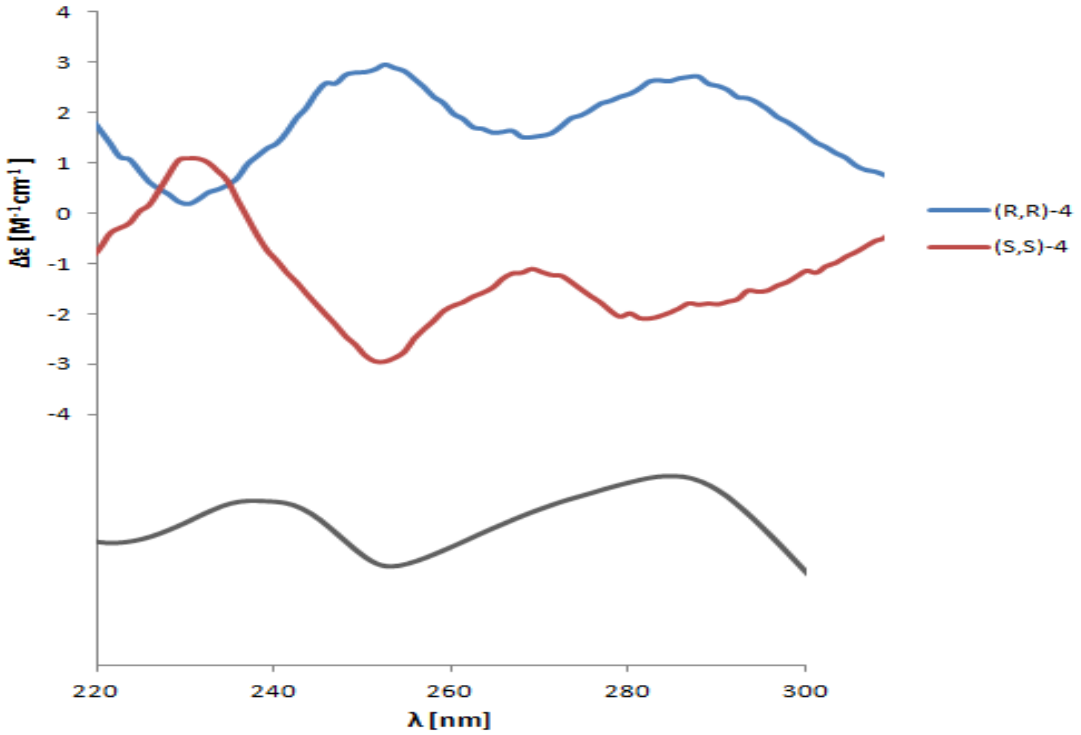


Fig. S7 Absorbance and CD spectra of ligand **4**.

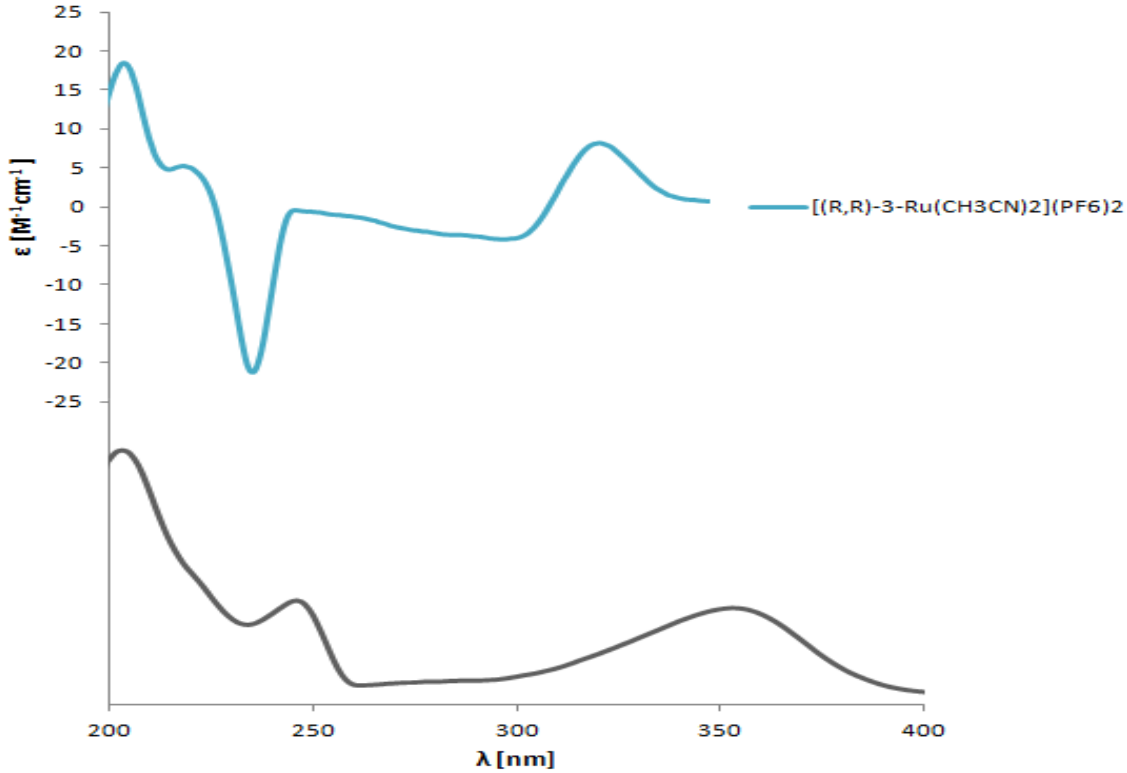


Fig. S8 Absorbance and CD spectra of [(*R,R*)-**3**-Ru(CH_3CN)$_2$][PF_6].

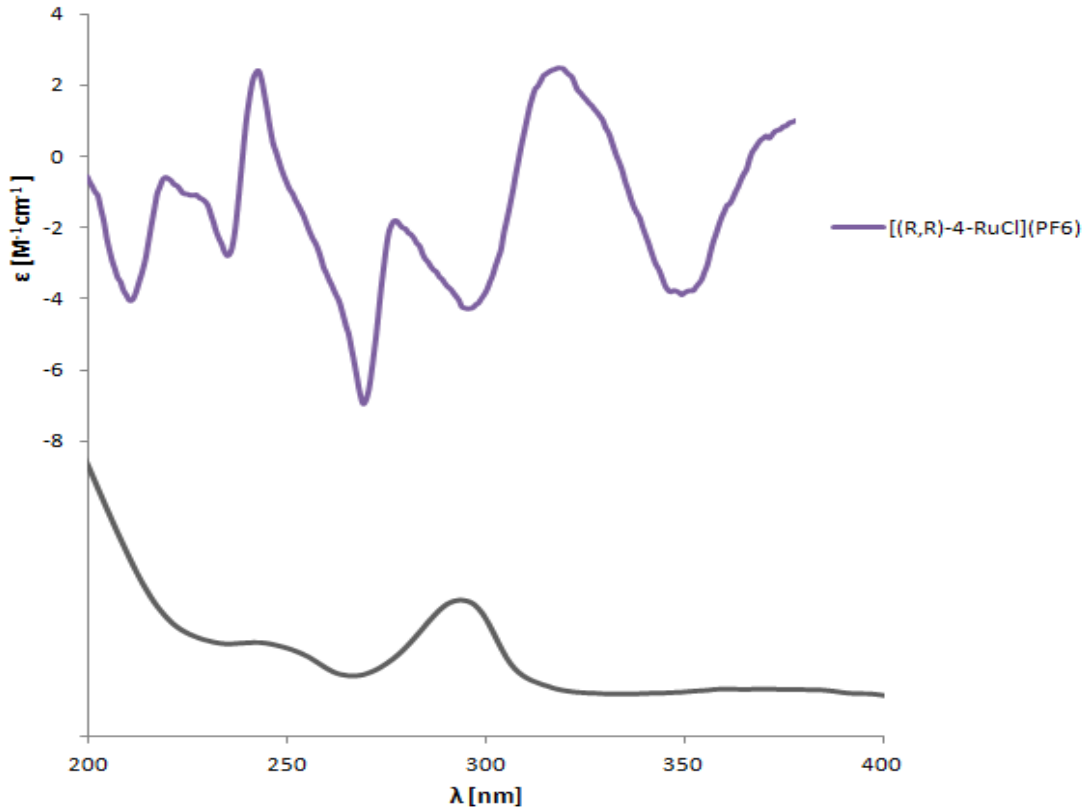


Fig. S9 Absorbance and CD spectra of [(*R,R*)-**4**-RuCl][PF_6].

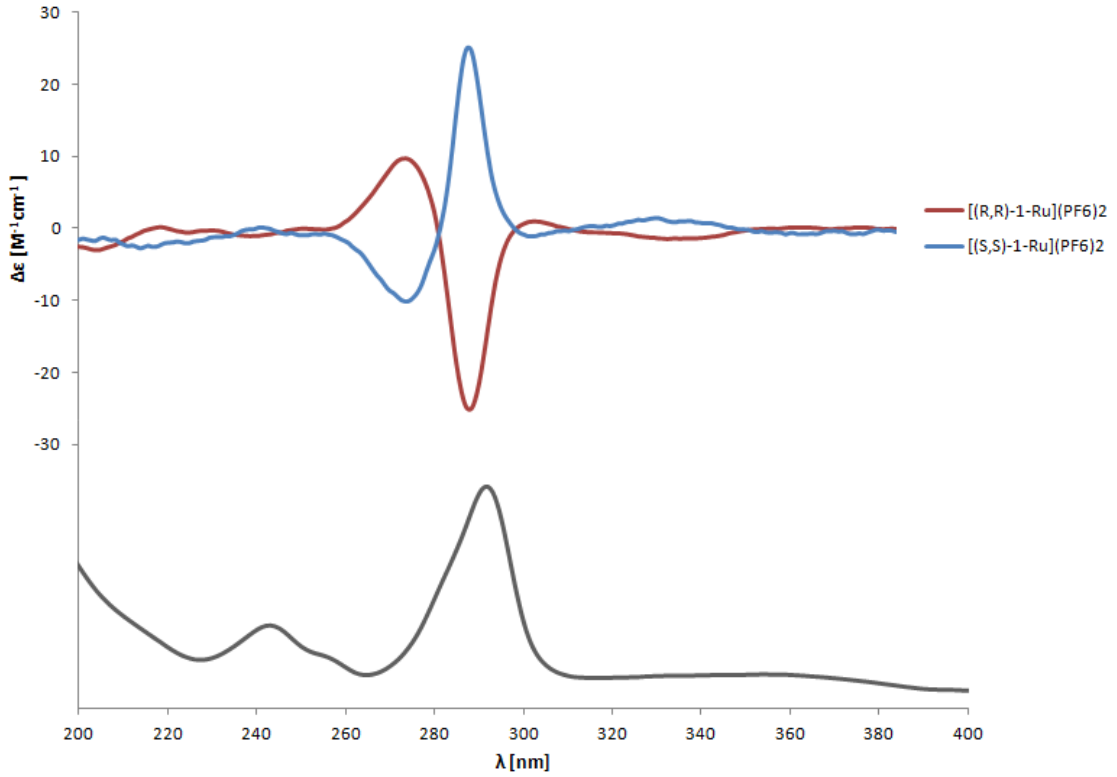


Fig. S10 Absorbance and CD spectra of [(*R,R*)-**1**-Ru][PF_6]$_2$ and [(*S,S*)-**1**-Ru][PF_6]$_2$.

References

S1. Y. Popowski, I. Goldberg and M. Kol, Chem. – Eur. J., DOI: 10.1002/chem.201505228.

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