Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

For

In situ generation of sulfoxide with predetermined chirality via structural template with a chiral-at-metal of ruthenium complex

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EXPERIMENTAL

Materials. 3-chloroperbenzoic acid (*m*-CPBA) and (*S*)-(-)-1,1'-binaphtol (S-binol) were bought from Aladdin and used without purification. Other reagent grade chemicals obtained from commercial sources were used as received. CD_3CN-d_3 was used in NMR experiments. $[Ru(bpy)_2Cl_2]\cdot 2H_2O$[1], 2-(isopropylthio)benzoic acid (OS-iPr)[2], Δ-$[Ru(bpy)_2(py)_2]$[O,O’-dibenzoyl-D-tartrate]$\cdot 12H_2O$[3] and Λ-$[Ru(bpy)_2(py)_2]$[O,O’-dibenzoyl-L-tartrate]$\cdot 12H_2O$[3] were synthesized according to methods described in the literatures.

(1) Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 4947.

(2) H. V. Huynh, C. H. Yeo and Y. X. Chew, *Organometallics*, 2010, **29**, 1479-1486.

(3) X. Hua and A. Zelewsky, *Inorg. Chem.*, 1995, 34, 5791–5797.

Physical Measurements.

Elemental (C, H, N and S) analyses were performed on an Elementar Vario EL analyzer. Electrospray ionization mass spectra (ESI-MS) were obtained on a Thermo LCQ DECA XP mass spectrometer. ^{1}H NMR spectra were obtained on a Varian Mercury-Plus 300 spectrometer. JASCO J-810 CD spectropolarimeter (1 sec response, 3.41 nm bandwidth, scanning speed of 200 nm/min, accumulation of 3 scans). HPLC analyses were carried out on a Shimadzu LC 20 with UV detector SPD-20A (Daicel Chiralpak AY-H column, 250 mm × 4.6 mm, Hexane/(EtOH: MeOH)/TFA=85/(3:1)15/0.3, flow rate:1mL/min, column temperature 35°C, 254 nm).

Synthesis of complexes

Δ-$[Ru(bpy)_2$ (OS-iPr)] PF_6 (**Δ-1**): Δ-$[Ru(bpy)_2(py)_2]$[O,O’-dibenzoyl-D-tartrate]$\cdot 12H_2O$ (560 mg, 0.5 mmol), OS-iPr (118 mg, 0.6 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and ethylene glycol (4 mL) were added into a 10 mL of three neck flask. The mixture was magnetically stirred and heated at 120 °C for 4 h under argon protection. Then, 15 mL saturated aqueous KPF_6 solution was added into the cooled reaction mixture. The aqueous phase was extracted with CH_2Cl_2 (3×15 mL), and the organic extracts were combined and subjected to silica gel chromatography with acetonitrile and later CH_3CN: H_2O: KNO_3(sat) = 50 : 6 : 2 as eluents. The product eluent was concentrated and the resulting material was dissolved in minimal amounts of ethanol/water, then an excess of solid KPF$_6$ was added to the above solution. The orange precipitate was collected, and washed with water twice, then dried under high vacuum to afford **Δ-1**. Yield: 306 mg (81%). The absolute configuration of **Δ-1** was determined by X-ray crystallography, and ee value is 98% obtained by ^{1}H NMR using S-Binol as a chiral shift reagent. Anal. Calcd for $C_{30}H_{27}F_6N_4O_2PRuS$: C 47.81, H 3.61, N 7.43, S 4.25. Found: C 47.56, H 3.77, N 7.53, S 4.04. ESI-MS: *m/z* = 608 [*M*-PF$_6$]$^{+}$. ^{1}H NMR (300.1 MHz, CD$_3$CN): δ 9.46 (d, 1H), 8.65 (*d*, 1H), 8.54 (*d*, 1H), 8.36 (*d*, 1H), 8.25 (*m*, 3H), 8.06 (*d*, 1H), 7.86 (*m*, 4H), 7.73 (*d*, 1H), 7.63 (*d*, 1H), 7.41 (*m*, 2H), 7.24 (*m*, 3H), 7.12 (*t*, 1H), 2.84 (*m*, 1H), 0.78 (*d*, 3H), 0.51 (*d*, 3H). CD (Δε / M^{-1} cm^{-1}, MeCN): 282nm (-42), 297nm (+106).

Λ-[Ru(bpy)$_2$ (OS-iPr)] PF$_6$ (**Λ-1**): The synthesis and isolation of the title complex were similar to those for **Δ-1**, with Λ-[Ru(bpy)$_2$(py)$_2$][O,O'-dibenzoyl-L-tartrate]·12H$_2$O in place of Δ-[Ru(bpy)$_2$(py)$_2$][O,O'-dibenzoyl-D-tartrate]·12H$_2$O. Yield: 306 mg (81%). The Λ-configuration was determined by CD spectroscopy, and the ee value is 98% obtained by ^{1}H NMR using S-Binol as a chiral shift reagent. Anal. Calcd for $C_{30}H_{27}F_6N_4O_2PRuS$: C 47.81, H 3.61, N 7.43, S 4.25. Found: C 47.65, H 3.80, N 7.32, S 3.94. ESI-MS: *m/z* = 608 [*M*-PF$_6$]$^{+}$. ^{1}H NMR (300.1 MHz, CD$_3$CN): δ 9.46 (d, 1H), 8.66 (*d*, 1H), 8.54 (*d*, 1H), 8.36 (*d*, 1H), 8.27 (*m*, 3H), 8.06 (*d*, 1H), 7.87 (*m*, 4H), 7.73 (*d*, 1H), 7.63 (*d*, 1H), 7.41 (*m*, 2H), 7.24 (*m*, 3H), 7.12 (*t*, 1H), 2.85 (*m*, 1H), 0.78 (*d*, 3H), 0.51 (*d*, 3H). CD (Δε / M^{-1} cm^{-1}, MeCN): 281(+40), 297 (-101).

Δ-[Ru(bpy)$_2${(R)-OSO-iPr}]PF$_6$ (**Δ-2**): Δ-1 (75 mg, 0.1 mmol) and m-CPBA (26 mg, 0.15 mmol) were dissolved in 50 mL of methanol. The reaction was stirred in the dark for 5 h at room temperature. The solvent was removed under reduce pressure, yielding a yellow-orange solid. Using Et$_2$O (3×20 mL) ultrasonic extract the solid for 10 min, the resulting solid was filtered, washed with Et$_2$O and air-dried. Yield: 73 mg (96%). The absolute configuration of **Δ-2** was determined by X-ray crystallography, and the ee value is 98% obtained by ^{1}H NMR using S-Binol as a chiral shift reagent. Anal. Calcd for $C_{30}H_{27}F_6N_4O_3PRuS$: C 46.82, H 3.54, N 7.28, S 4.17. Found: C 46.51, H 3.68, N 7.46, S 4.01. ESI-MS: m/z =624 [*M*-2PF$_6$]$^{+}$. ^{1}HNMR (300.1 MHz, CD$_3$CN) δ 9.22 (*d* 1H), 8.99 (*d* 1H), 8.60 (*d* 1H), 8.33 (*m* 3H), 8.28 (*d* 1H), 8.05 (*t* 2H), 7.93 (*m* 4H), 7.74 (*dd* 2H), 7.53 (*t* 1H), 7.37 (*t* 1H), 7.27 (*m* 3H), 3.14 (*m* 1H), 0.68 (*d* 3H), 0.58 (*d* 3H). CD (Δε / M^{-1} cm^{-1}, MeCN): 276nm (-13), 292nm (+52).

Λ-[Ru(bpy)$_2${(S)-OSO-iPr}] PF$_6$ (**Λ-2**): The synthesis and isolation of the title complex were similar to those for **Δ-2**, with Λ-1 (75 mg, 0.1 mmol) in place of Δ-1. Yield: 73 mg (96%). The absolute configuration of Λ-2 was determined by X-ray crystallography, and the ee value is 98% obtained by ^{1}H NMR using S-Binol as a chiral shift reagent. Anal. Calcd for $C_{30}H_{27}F_6N_4O_3PRuS$: C 46.82, H 3.54, N 7.28, S 4.17. Found: C 46.62, H 3.65, N 7.41, S 3.97. ESI-MS: m/z =624 [*M*-2PF$_6$]$^{+}$. ^{1}H NMR (300.1 MHz, CD$_3$CN) δ 9.22 (*d* 1H), 8.98 (*d* 1H), 8.60 (*d* 1H), 8.35 (*m* 3H), 8.28 (*d* 1H), 8.05 (*t* 2H), 7.91 (*m* 4H), 7.74 (*dd* 2H), 7.53 (*t* 1H), 7.37 (*t* 1H), 7.25 (*m* 3H), 3.15 (*m* 1H), 0.68 (*d* 3H), 0.58 (*d* 3H). CD (Δε / M^{-1} cm^{-1}, MeCN): 277 nm (+21), 293 nm (-51).

One-step method: Δ-[Ru(bpy)$_2$(py)$_2$][O,O'-dibenzoyl-D-tartrate]·12H$_2$O / Λ-[Ru(bpy)$_2$(py)$_2$][O,O'-dibenzoyl-L-tartrate]·12H$_2$O (112 mg, 0.1 mmol), OS-iPr (23.6 mg, 0.12 mmol), K$_2$CO$_3$ (6.9 mg, 0.05 mmol) and ethylene glycol (0.8 mL) were added into a 10 mL of three neck flask. The mixture was magnetically stirred and heated at 120 °C for 4h under argon protection. After cooling, methanol (50 mL) and *m*-CPBA (35 mg, 0.20 mmol) were added to the reaction mixture. The result solution was stirred in the dark at room temperature for 4 h. The methanol solvent was removed under reduced pressure, then the solution was washed with Et_2O (3×15 mL). After that, 5 mL saturated aqueous KPF_6 was added and the aqueous phase was extracted with CH_2Cl_2 (3×20 mL). The organic extracts were combined and subjected to silica gel chromatography with acetonitrile and later CH_3CN: H_2O: KNO_3(sat) = 50 : 6 : 2 as eluents. The product eluent was concentrated, the resulting material was dissolved in minimal amounts of ethanol/water. An excess of solid KPF_6 was added to the above solution, the orange precipitate was collected, washed with water twice, and dried under high vacuum to afford **Δ-2**/**Λ-2**. Yield: *ca.* 83%.

(R)-OSO-ipr: Λ -2 (77 mg, 0.1 mmol) and trifluoroacetic acid (76μL, 1 mmol) and CH_3CN (3 mL) were added into a 10 mL of three neck flask. The mixture was magnetically stirred and heated at 80 °C for 2 h under argon protection. The reaction mixture was cooled to room temperature and concentrated to give an orange solid. Then, H_2O (10 mL) was added to, the aqueous phase was extracted with Et_2O (3×15 mL). The Et_2O solutions were combined and dried over $MgSO_4$, then, filtered. The solvent was removed under reduced pressure and dried under high vacuum to give a light yellow powder. Yield: 90%. The e.e. value of 88.2% was determined by chiral HPLC analysis. Anal. Calcd for $C_{10}H_{12}O_3S$: C 56.58, H 5.70, S 15.11. Found: C 56.11, H 6.09, S 14.89. ESI-MS: m/z =211 [*M*-H]$^-$. ^{1}HNMR (300.1 MHz, $CDCl_3$) δ 8.18 (*m* 2H), 7.81 (*t* 1H), 7.59 (*t* 1H), 3.27(*m* 2H), 1.54 (*d* 1H), 0.98 (*t* 1H). CD (Δε / M^{-1} cm^{-1}, MeCN): 296nm (+108).

(*S*)-OSO-ipr: The synthesis and isolation of this complex were similar to those for (*R*)-OSO-ipr, with Δ-2 in place of Λ-2. Yield: ca. 90%. The e.e. value of 91.6% was determined by chiral HPLC analysis. Anal. Calcd for $C_{10}H_{12}O_3S$: C 56.58, H 5.70, S 15.11. Found: C 56.23, H 5.95, S 14.87. ESI-MS: m/z =211 [*M*-H]$^-$. ^{1}HNMR (300.1 MHz, $CDCl_3$) δ8.18 (*m* 2H), 7.81 (*t* 1H), 7.59 (*t* 1H), 3.27(*m* 2H), 1.54 (*d* 1H), 0.98 (*t* 1H). CD (Δε / M^{-1} cm^{-1}, MeCN): 296 nm (-110).

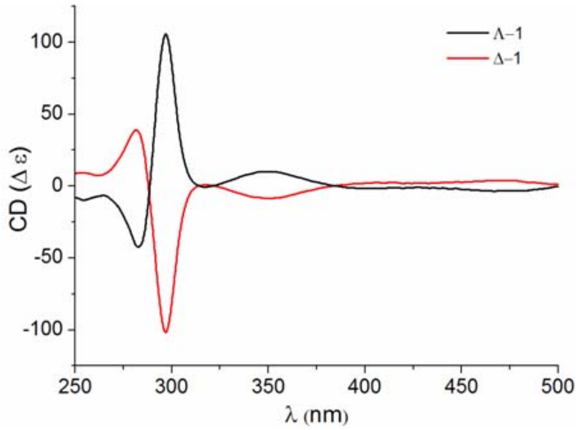

Fig. S1. CD spectra of Λ-1 and Δ-1 in CH_3CN (40 μM).

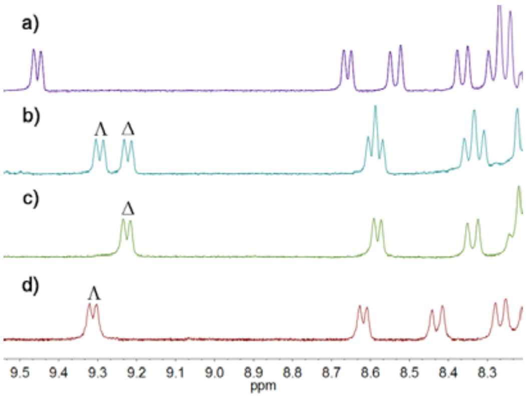

Fig. S2. The aromatic region ^{1}H NMR spectra in CD$_3$CN: a) in the absence of S-binol for rac-**1**; b) in the presence of 40 eq S-binol for rac-**1**; c) in the presence of 40 eq S-binol for **Δ-1**; d)in the presence of 40 eq S-binol for **Λ-1**.

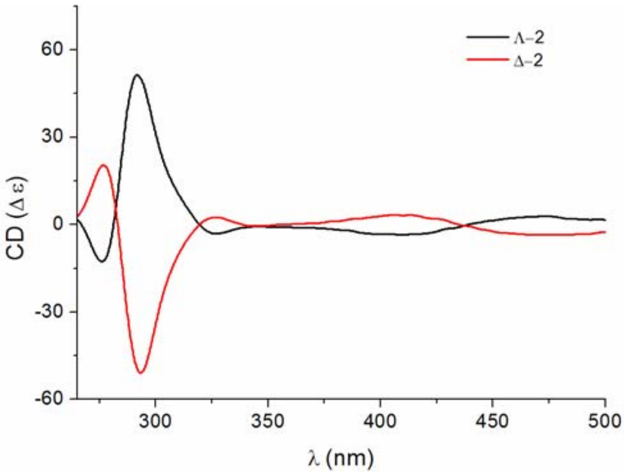

Fig. S3. CD spectra of Λ-2 and Δ-2 in CH$_3$CN (40 μM)..

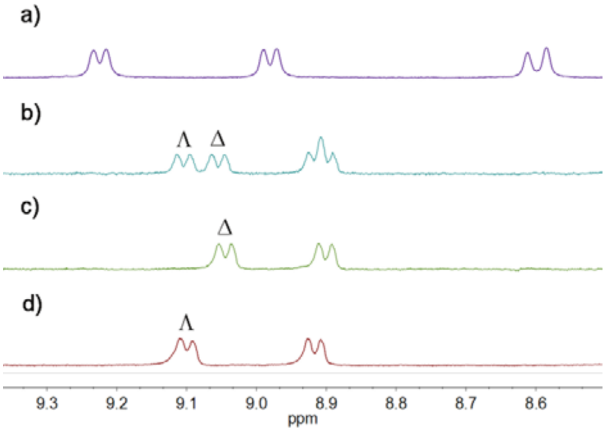

Figure S4. Excerpts of the aromatic region of the ^{1}H NMR spectra in CD$_3$CN): a) in the absence of S-binol for **rac-2**, b) in the presence of 40 eq S-binol for **rac-2**, c) in the presence of 40 eq S-binol for **Δ-2**, d) in the presence of 40 eq S-binol for **Λ-2**.

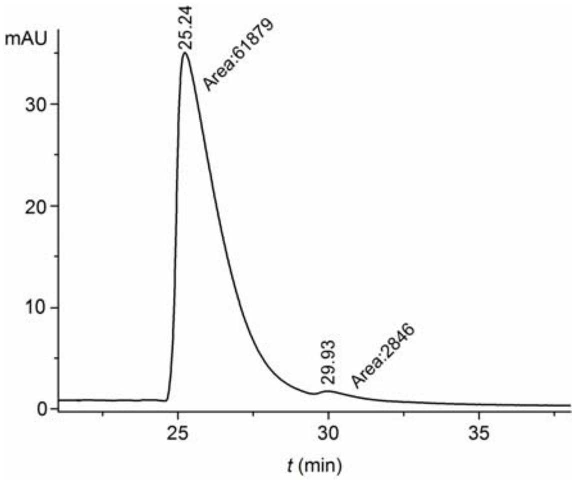

Figure S5. HPLC traces of Λ-[Ru(bpy)$_3$](PF$_6$)$_2$ (conditions: see, Z. Lin, M. A. Celik, C. Fu, K. Harms, G. Franking, E. Meggers, *Eur. Chem. J.* 2011, **17**, 1260.)