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# Enantioselective Oxidation of Thioethers to Sulfoxides by Means of a Structural Template with Chiral-at-Metal Ruthenium Complexes

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Treatment of *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ or $\Delta/\Lambda$-$[Ru(bpy)_2(py)_2]^{2+}$ (bpy = 2,2′-bipyridine, py = pyridine) with the prochiral thioether ligands 2-alkylthiobenzoic acid (HOS–R) produces the corresponding thioether complexes *rac*-$[Ru(bpy)_2(OS–R)](PF_6)$ (R = Me (*rac*-**1**), *i*Pr (*rac*-**2**), 2-benzylthiobenzonate (Bn) (*rac*-**3**)) and $\Delta/\Lambda$-$[Ru(bpy)_2(OS–R)](PF_6)$ (R = Me ($\Delta$-**1**/$\Lambda$-**1**), *i*Pr ($\Delta$-**2**/$\Lambda$-**2**), Bn ($\Delta$-**3**/$\Lambda$-**3**)) with retention of the configurations at chiral metal centers. In situ oxidation of the thioether complexes by *meta*-chloroperoxybenzoic acid provides the corresponding sulfoxide complexes *rac*-$[Ru(bpy)_2(OSO–R)](PF_6)$ (OSO–R is 2-alkylsulfinylbenzonate, R = Me (*rac*-**1a**), *i*Pr (*rac*-**2a**), Bn (*rac*-**3a**)), $\Delta$-$[Ru(bpy)_2\{(R)\text{-}OSO–R\}](PF_6)$ (R = Me ($\Delta$-**1a**), *i*Pr ($\Delta$-**2a**), Bn ($\Delta$-**3a**)), and $\Lambda$-$[Ru(bpy)_2\{(S)\text{-}OSO–R\}](PF_6)$ (R = Me ($\Lambda$-**1a**), *i*Pr ($\Lambda$-**2a**), Bn ($\Lambda$-**3a**)) in yields of 95% with 98% *ee* values. The absolute configurations at the metal centers and sulfur atoms were determined by means of X-ray crystallography. The results indicate that the configurations of the metal centers are retained and have the function of controlling sulfoxide chirality during the oxidation process. The $\Delta$ metal-centered configuration enantioselectively generates an *R*-configuration sulfoxide, and the $\Lambda$ configuration enantioselectively forms an *S*-configuration sulfoxide in the course of the in situ oxidation reaction, thereby resulting in a predetermined chirality of the sulfoxide ligands. The predetermined chirality of sulfoxides (*S*)-HOSO–R and (*R*)-HOSO–R were obtained by the treatments of the corresponding sulfoxide complexes $\Delta$-$[Ru(bpy)_2\{(R)\text{-}OSO–R\}](PF_6)$ and $\Lambda$-$[Ru(bpy)_2\{(S)\text{-}OSO–R\}](PF_6)$ with trifluoroacetic acid in yields of 90% with 83.5–92.9% *ee* values.

## Introduction

Chiral sulfoxides are of great interest for organic chemistry and biochemistry since they serve as intermediates in the synthesis of numerous sulfur-containing drugs and can also be widely used as auxiliary ligands in asymmetric synthesis.[1] Several approaches, including separation of a racemic mixture, transformation of a reagent from the chiral pool, and the use of a chiral catalyst for enantioselective synthesis, are used for the synthesis of chiral sulfoxides. Among them, the enantioselective transformations using a chiral catalyst are particularly attractive.[2–4] Many excellent asymmetric sulfoxidation reactions have been developed since the first enantioselective sulfoxidation was reported by the groups of Kagan[5] and Modena[6] in 1984. However, they still have certain disadvantages, which include low turnover numbers and enantiomeric excess (*ee*) value, the need to precisely control the reaction conditions and the water content, and overoxidation to sulfone, which has stimulated the search for new efficient catalysts and catalytic reactions.[1]

Relative to metal-dependent asymmetric catalysis based on a chiral ligand responsible for the asymmetric environment,[7] the use of a chiral-at-metal complex with an achiral ligand as a source for the asymmetric environment for catalysis has been still unexploited.[8] This might be limited to the lack of the available approach for the preparation of the chiral-at-metal complex in an enantiopure form and depends on its configurational stability in a catalysis reaction.[9] Octahedral ruthenium(II) complexes with a $d^6$ electron structure are very stable and good candidates for insight into the chiral-at-metal catalysis reaction. About ten years ago, Fontecave and co-workers reported the first instance of the enantioselective oxidation of thioethers to sulfoxides mediated by the chiral-at-metal complex $\Delta/\Lambda$-$[Ru(dmp)_2(MeCN)_2]^{2+}$ (dmp = 2,9-dimethyl-1,10-phenanthroline).[10] Although its stereoselectivity (*ee* is 7–18%) is modest, the chirality mediated by the "chiral-at-metal" opens a new approach for asymmetric synthesis of sulfoxide and encourages us to search for an efficient approach for the synthesis of chiral sulfoxides mediated by means of a chiral-at-metal ruthenium complex.

Previous studies have demonstrated that diastereoselectivity has occurred in the reaction of $[Ru(bpy)_2Cl_2]$ (bpy = 2,2′-bipyridine) and chiral sulfoxides,[9b,c,11] which has been successfully exploited for the auxiliary-mediated and catalytic synthesis of chiral ruthenium complexes by Meggers and co-workers.[9g,i] We perceive that octahedral stereocenters permit the straightforward generation of $\Delta$ and $\Lambda$ enantiomers, which might serve as a rigid scaffold for the generation of the enantiomeric sulfoxides. Crystal structural analysis of the racemic thioether complex $[Ru(bpy)_2(OS–Me)]^+$ (OS–Me = 2-methylthiobenzo-

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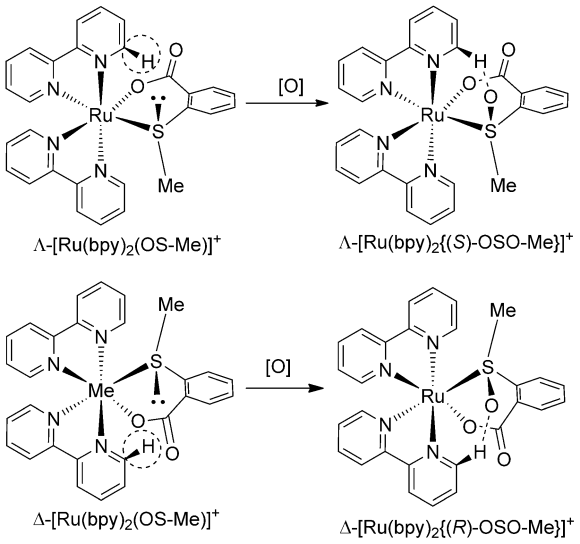


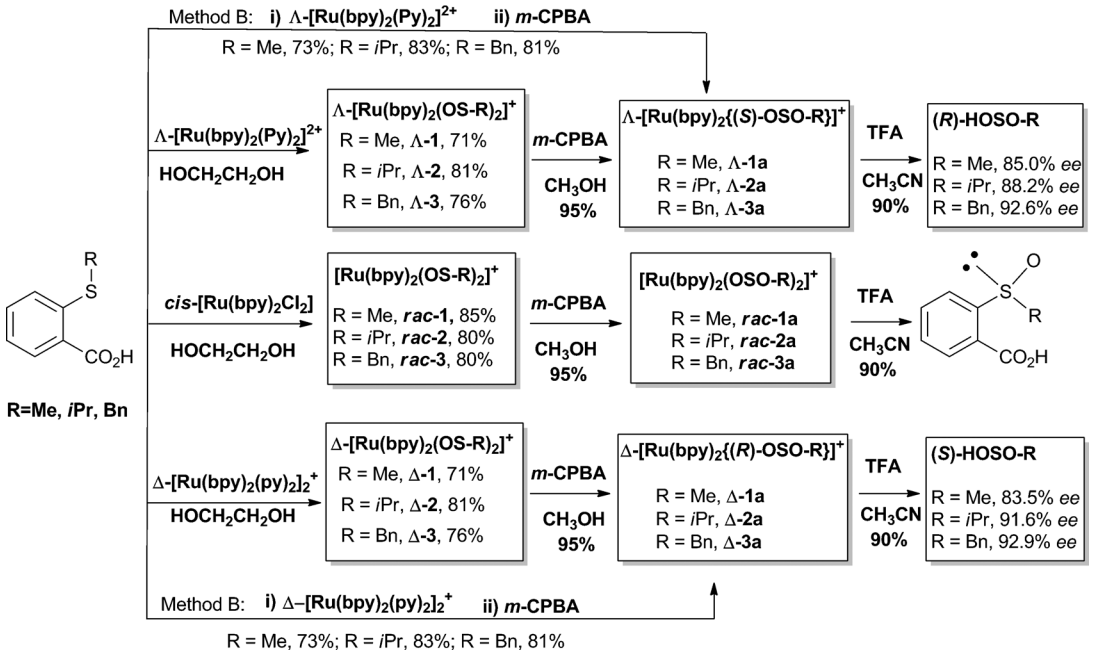

**Scheme 1.** In situ oxidation of prochiral thioether to chiral sulfoxide.

nate) indicates that the methyl group of the thioether always keeps away from the α-pyridyl proton to avoid steric congestion and the lone electron pair of the coordinated sulfur atom sits near the α-pyridyl proton (see Scheme 1).[12] That is to say, the position of the lone electron pair is predetermined in this kind of complex. When the thioether is oxidated in situ to the corresponding sulfoxide OSO–Me (OSO–Me = 2-methylsulfinylbenzonate), the adducted oxygen atom prefers to settle on the site near the α-pyridyl proton to form a hydrogen bond between them, thereby leading to the predetermined chirality of sulfoxide. Although the direct oxidation of metal-bound thiolato[13] and thioether[12,14] ligands has been reported, the oxidation of metal–thioether in situ to generate enantiomeric sulfoxide is unprecedented. The preliminary results for the successful synthesis of chiral sulfoxides (*R*)/(*S*)-2-isopropylsulfinylbenzoic acid (HOSO–*i*Pr) in situ in good *ee* values[15] led us to extend this approach to synthesize other chiral sulfoxides and systematically investigate the effect of the substituents of thioether on the enantioselectivity. In this study, we present the synthesis and characterization of a series of $Ru^{II}$ complexes with the prochirally chelate thioether ligands *rac*-[$Ru(bpy)_2$-(OS–R)]($PF_6$) (R = Me (*rac*-**1**), *i*Pr (*rac*-**2**), 2-benzylthiobenzonate (Bn) (*rac*-**3**)), Δ/Λ-[$Ru(bpy)_2$(OS–R)]($PF_6$) (R = Me (Δ-**1** and Λ-**1**), *i*Pr (Δ-**2** and Λ-**2**), Bn (Δ-**3** and Λ-**3**)), and their corresponding oxidation products *rac*-[$Ru(bpy)_2$(OSO–R)]($PF_6$) (R = Me (*rac*-**1 a**), *i*Pr (*rac*-**2 a**), Bn (*rac*-**3 a**)), Δ-[$Ru(bpy)_2${(*R*)-OSO–R}]($PF_6$) (R = Me (Δ-**1 a**), *i*Pr (Δ-**2 a**), Bn (Δ-**3 a**)) and Λ-[$Ru(bpy)_2${(*S*)-OSO–R}]($PF_6$) (R = Me (Λ-**1 a**), *i*Pr (Λ-**2 a**), Bn (Λ-**3 a**)). Moreover, the predetermined chirality of sulfoxides was also obtained by the treatments of the sulfoxide complexes with trifluoroacetic acid (TFA) in MeCN in good yields and *ee* values.

## Results and Discussion

### Synthesis and structural characterization of thioether complexes

The synthetic procedures for ruthenium complexes and sulfoxides are briefly summarized in Scheme 2. The racemic *cis*-[$Ru(bpy)_2Cl_2$][16] and chiral Δ/Λ-[$Ru(bpy)_2(py)_2$]$^{2+}$[17] (py = pyridine) were used as the precursors and treated with the prochiral thioether ligands HOS–R (R = Me, *i*Pr, and Bn) in ethylene glycol at 120 °C under argon protection. The corresponding racemic products [$Ru(bpy)_2$(OS–R)]($PF_6$) (*rac*-**1**, *rac*-**2**, and *rac*-**3**) were obtained in yields of 80–85 % after column chromatography




**Scheme 2.** A summary of the syntheses of sulfoxide compounds.

separation, and the corresponding chiral products Δ/Λ-[Ru(bpy)$_2$(OS–R)](PF$_6$) (Δ-**1**, Δ-**2**, Δ-**3** and Λ-**1**, Λ-**2**, Λ-**3**) were afforded in yields of 71–81% after column chromatography separation. Although *rac*-**1** and *rac*-**3** have been synthesized using different methods,[14b,c] they were also synthesized using the present procedure. As expected, circular dichroism (CD) spectra of the racemic complexes *rac*-**1**, *rac*-**2**, and *rac*-**3** are silent, whereas **Δ**/Λ-**1**, **Δ**/Λ-**2**, and **Δ**/Λ-**3** are optically active. The CD spectra of the two enantiomers are almost mirror images with a positive Cotton effect at 282 nm and a negative Cotton effect at 295 nm for Δ-**1**, and a negative Cotton effect at 281 nm and a positive Cotton effect at 295 nm for Λ-**1** (see Figure S1 in the Supporting Information), a positive Cotton effect at 282 nm and a negative Cotton effect at 297 nm for Δ-**2**, and a negative Cotton effect at 281 nm and a positive Cotton effect at 297 nm for Λ-**2** (see Figure S2), a positive Cotton effect at 282 nm and a negative Cotton effect at 297 nm for Δ-**3**, and a negative Cotton effect at 282 nm and a positive Cotton effect at 297 nm for Λ-**3** (see Figure S3), thereby suggesting that the configuration at the metal is the dominant factor in the appearance of the spectra.

The NMR spectra of the racemates and enantiomers were almost identical under the experimental conditions; however, the two enantiomers become distinguishable in the presence of (*S*)-1,1′-binaphthol ((*S*)-binol) as a chiral NMR spectroscopic shift reagent.[18] The resonance peak at $\delta = 9.09$ ppm for *rac*-**1** was split into a pair of peaks and shifted to $\delta = 8.97$ and 8.91 ppm (see Figure S4), at $\delta = 9.47$ ppm for *rac*-**2** was split and shifted to $\delta = 9.30$ and 9.22 ppm (see Figure S5), and at $\delta = 9.42$ ppm for *rac*-**3** was split and shifted to $\delta = 9.29$ and 9.23 ppm (see Figure S6). These peaks are assigned to the α-H of the pyridyl ring in bpy. Moreover, the peaks at $\delta = 8.97$ ppm for *rac*-**1**, $\delta = 9.30$ ppm for *rac*-**2**, and $\delta = 9.29$ ppm for *rac*-**3** are consistent with the corresponding Λ enantiomers, and the others are assigned to the corresponding Δ enantiomers. The spectra show very high enantiopurity in both Δ and Λ enantiomers, and these peaks can be used to determine *ee* values. The enantiopurities were found to be greater than 98% *ee* from the ratio of the integrals of the α-H peaks of the two enantiomers. The above results demonstrate that the metal-centered configurations are completely retained in the course of the reaction.

Single crystals of *rac*-**2**·H$_2$O were grown from a solution in methanol. It crystallizes in space group $P2_1/c$. As shown in Figure 1, the chelating thioether is bound to the [Ru(bpy)$_2$]$^{2+}$ moiety and features a slight twist of the phenyl ring relative to the carboxylate group. The Ru1–S1 distance is 2.331(1) Å, which is in accord with the reported value.[12,15] As expected, the isopropyl group of OS–*i*Pr is away from the α-H of the pyridyl ring to avoid steric congestion. The absolute metal-centered configuration of the Δ enantiomer was determined by X-ray crystallography for two complexes: one preliminary reported instance for Δ-**2**[15] in addition to Δ-**3** shown in Figure 1. It crystallizes in a chiral space group $P2_1$. The structure confirms a Δ configuration at the ruthenium center, which is consistent with the configuration of its parent, and the Flack parameter (−0.016(7)) is close to zero, thus demonstrating that the assignment of chirality at the metal center is correct and the absolute configuration at the metal center can be retained during the reaction. The Ru1–S1 distance (2.312(1) Å) is comparable to the reported one.[12,15] The benzyl group is away from the α-pyridyl proton to avoid steric congestion and π–π stacking with the bpy at a distance of 3.358 Å. Moreover, metal-centered configurations of all thioether complexes presented here were assigned relative to the two crystal structures by means of CD spectra.

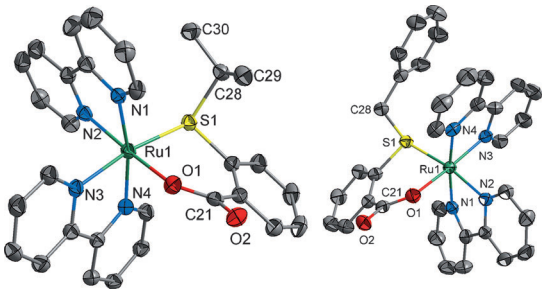



**Figure 1.** Crystal structures of *rac*-**2** (left, Ru1–S1 = 2.331(1) Å, Ru1–O1 = 2.087(2) Å, O1–Ru1–S1 = 90.27(6)°) and Δ-**3** (right, Ru1–S1 = 2.312(1) Å, Ru1–O1 = 2.081(3) Å, O1–Ru1–S1 = 89.63(8)°). ORTEP picture with thermal ellipsoids drawn at 50% probability. The anion and solvent molecules are omitted for clarity.

### In situ generation and structural characterization of sulfoxide complexes

The oxidation of the thioether complexes to the corresponding sulfoxide complexes was performed by the modified procedure of Rack[14b,c] with *meta*-chloroperoxybenzoic acid (*m*-CPBA) as an oxidant in methanol (see Scheme 2). It should be pointed out that the reaction time in OS–Bn complexes was prolonged to 24 h to afford a satisfactory yield because of an electron-withdrawing effect of the benzyl group. The excess amount of *m*-CPBA and its reduced product, 3-chlorobenzoic acid, were removed by ultrasonic extraction from the solid ruthenium product with diethyl ether. The yields were almost quantitative (95–97%) and no overoxidation product sulfone complex was found in the reaction. The other oxidant such as $H_2O_2$ was also tried to be used to oxidate the thioether complexes; however, the yield was very low. The identity and formulation of the corresponding complexes was confirmed by NMR spectroscopy, MS, and IR spectroscopy as well as by elemental analysis (see the Experimental Section).

A new signal at 1105 cm$^{-1}$ for **1a** and 1093 cm$^{-1}$ for **2a** and **3a**, which can be assigned to ν(S=O) in the S-bonded complexes and is in good agreement with the literature values for sulfoxide complexes,[19] indicates that the corresponding sulfoxide complexes are indeed generated in situ. The CD spectra of the enantiomers are almost mirror images, as shown in Figures 2 and Figure S7, thus indicating that the corresponding complexes are optically active.

The $^1$H and $^{13}$C chemical shifts of the alkyl groups (-S–*CH*-) at $\delta = 1.83$ and 15.61 ppm in **1**; $\delta = 2.85$ and 42.69 ppm in **2**; and $\delta = 3.81$, 3.21, and 44.23 ppm in **3** are lowfield-shifted relative

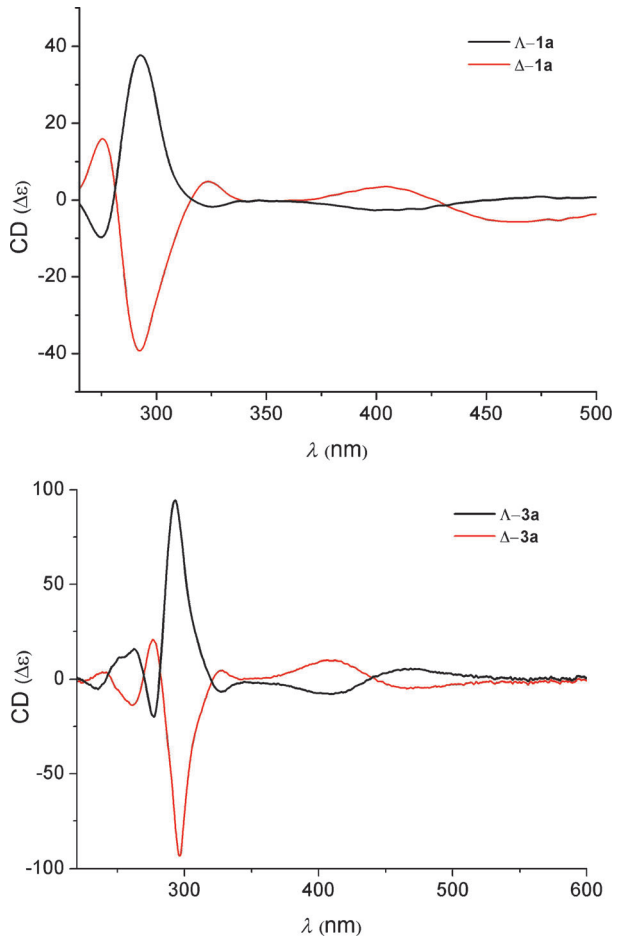



**Figure 2.** CD spectra of Λ-**1a** and Δ-**1a** (above), and Λ-**3a** and Δ-**3a** (below) in $CH_3CN$ (40 μM).

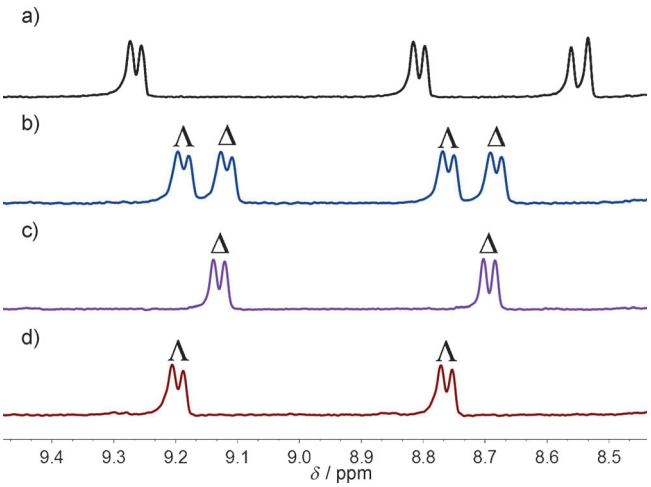



**Figure 3.** The excerpts of the aromatic region $^1$H NMR spectra in $CD_3CN$: (a) *rac*-**3a**, (b) *rac*-**3a** in the presence of (*S*)-binol (40 equiv), (c) Δ-**3a** in the presence of (*S*)-binol (40 equiv), and (d) Λ-**3a** in the presence of (*S*)-binol (40 equiv).

to the corresponding $\delta = 2.64$ and 47.44 ppm in **1a**; $\delta = 3.14$ and 59.66 ppm in **2a**; and $\delta = 4.14$, 3.82, and 64.10 ppm in **3a**, also indicating that the oxygen atom is definitely added to the sulfur atom because of the strong electron-withdrawing effect of the sulfoxide group. The excerpts of the aromatic region $^1$H NMR spectra in $CD_3CN$ are shown in Figure 3 and Figures S8 and S9. The peak at $\delta = 9.13$ ppm for *rac*-**1a**, $\delta = 9.22$ ppm for *rac*-**2a**, and $\delta = 9.27$ ppm for *rac*-**3a**, which are assigned to the α-H of the pyridine ring, is split into two peaks and highfield-shifted to $\delta = 9.01$ and 8.95 ppm, $\delta = 9.10$ and 9.05 ppm, and $\delta = 9.19$ and 9.12 ppm, respectively, in the presence of (*S*)-binol (40 equiv) as a chiral NMR spectroscopic shift reagent. These values are in accord with those of Λ and Δ enantiomers. The spectra show very high enantiopurity in both Δ and Λ enantiomers, and these peaks can be used to determine enantiomeric excesses. The *ee* values were found to be greater than 98% from the ratio of the integrals of the α-H peaks of the two enantiomers, thereby demonstrating that the metal-centered configurations are stable in the oxidation reaction.

Single-crystal structures of *rac*-**2a**·$H_2O$ and *rac*-**3a**·0.5 $CH_3OH$ were measured by X-ray diffraction. As shown in Figure 4 and Figure S10, the sulfoxide ligands are indeed generated in situ. The sulfur atoms are bound to $Ru^{II}$ ions with Ru1–S1 distances of 2.236(1) Å for *rac*-**2a** and 2.269(1) Å for *rac*-**3a**; these values are in accord with the reported distance for *rac*-**1a** (2.213(1) Å)[12] but shorter than those of thioether complexes (2.331(1) Å for *rac*-**2** and 2.312(1) Å for Δ-**3**). The S–O bond lengths of 1.478(2) Å for *rac*-**2a** and 1.505(5) Å for *rac*-**3a** are consistent with the reported bond lengths.[12,15] As expected, the methyl and benzyl groups of the sulfoxide ligands are far from the α-H of the pyridyl ring to avoid steric congestion and the added oxygen atoms indeed sit on the site near the α-pyridyl proton with a hydrogen bond to each other (C20···O3 = 3.430 Å for *rac*-**2a** and C10···O3 = 3.312 Å for *rac*-**3a**). The sulfoxide complexes are racemic; therefore, four isomers (Δ-*R*, Δ-*S*,

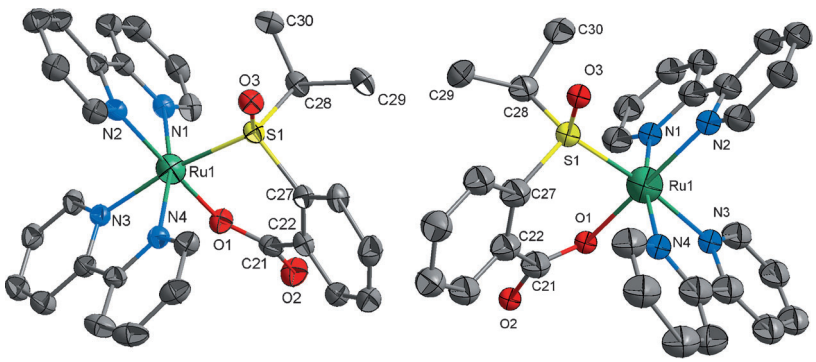



**Figure 4.** Crystal structures of *rac*-**2a** (Ru1–S1 = 2.236(1) Å, Ru1–O1 = 2.090(2) Å, S1–O3 = 1.478(2) Å; left, Δ-*R* isomer; right, Λ-*S* isomer). ORTEP picture with thermal ellipsoids drawn at 50% probability. The anion and solvent molecules are omitted for clarity.

Λ-*R*, and Λ-*S*) would be generated in theory during the oxidation reaction. However, structural analyses show that only two configurations Δ-*R* and Λ-*S* were found in the crystal structures. The absolute stereochemistry at the sulfur atom is assigned to the *R* configuration in the Δ metal-centered configuration according to the Cahn–Ingold–Prelog priority rules, and the *S* configuration of sulfoxide is named in the Λ metal-centered configuration complex. That is, the Δ metal-centered configuration enantioselectively generates the *R*-configuration sulfoxide, and the Λ configuration enantioselectively forms the *S*-configuration sulfoxide in the course of the oxidation reaction, thereby resulting in predetermined chirality for the sulfoxides. Moreover, the retention of the absolute metal-centered configuration and enantioselective generation of chiral sulfoxide complexes Δ-**2a** and Λ-**2a** in the course of oxidation reaction were also observed by means of X-ray crystallography, which have been reported by us recently.[15]

To optimize the synthetic procedures, a one-pot method was also developed. After reaction of the chiral precursors Δ/Λ-$[Ru(bpy)_2(py)_2]^{2+}$ with the prochiral HOS–R (R = Me, *i*Pr, and Bn) ligands in ethylene glycol for four hours, oxidant *m*-CPBA (2 equiv) in methanol was directly added to the above reaction mixtures. The corresponding sulfoxide complexes were obtained in yields of 73–83% after separation over several steps (see the Experimental Section). The CD spectra show that they are optically active. Their enantiopurities were determined by NMR spectra in the presence of (*S*)-binol as a chiral shift reagent. The *ee* values were found to be greater than 98% from the ratio of the integrals of the α-H peaks of the two enantiomers, thus demonstrating that the absolute configurations at the metal centers are retained over the course of reactions and the configurations of the metal centers have the function of controlling sulfoxide chirality in situ oxidation, thus leading to enantioselective oxidation of prochiral thioether to chiral sulfoxide.

### Acidolysis of sulfoxide complexes to afford chiral sulfoxides under retention of configuration

Following the method of Meggers et al.,[20] the sulfoxide ligands can be removed in the presence of acid since the binding strength of the sulfoxide ligand would be decreased through protonation of the carboxylate. Indeed, following treatments of the sulfoxide complexes with TFA in $CH_3CN$ at 80 °C for 2 h in the dark, the pure sulfoxides HOSO–R were isolated in yields of 90–92%. The chirality at metal centers and sulfoxides are configuration-stable under the experimental conditions.[15] To examine the influence of acidolysis conditions on the configuration of sulfoxide,[21] the acidolysis of Λ-**3a** was observed in various acids and solvents. When HCl (5 equiv) was used in place of TFA in $CH_3CN$, the acidolysis reaction went smoothly to afford the (*R*)-HOSO–Bn ligand in a yield of 96%. However, the *ee* value decreased to 7.9% as determined by $^1H$ NMR spectra using (*S*)-binol as a chiral shift reagent. Further experiments showed that (*R*)-HOSO–Bn is configuration-unstable under the experimental conditions.[22] When acetic acid (20 equiv) was added to the solution of Λ-**3a** in $CH_3CN$, no free ligand was obtained under similar conditions, thus indicating the acidolysis reaction was suppressed. By increasing the concentration of acetic acid the acidolysis reaction was promoted; however, the racemization occurred simultaneously, thereby demonstrating that an acid of appropriate strength plays a crucial role in the acidolysis reaction. Furthermore, $CH_3OH$ and $CH_2Cl_2$ solvents were used in place of $CH_3CN$ under identical conditions. However, the fact that only partial acidolysis reaction occurred to afford (*R*)-HOSO–Bn in yields of 43 and 57%, respectively, indicates that a coordinated solvent such as $CH_3CN$ is advantageous for the removal of the ligand. No significant racemization of sulfoxide was observed in $CH_2Cl_2$ and $CH_3OH$ solvents, and the enantiopurity came close to that in $CH_3CN$.

The identity and formulation of the corresponding compounds were confirmed by NMR spectroscopy, MS, and IR spectroscopy as well as elemental analysis (see the Experimental Section). As shown in Figure 5 and Figure S11, the sulfoxides are optically active. Their CD spectra are mirror images with a Cotton effect at 293 nm for (*R*)/(*S*)-HOSO–Me, 296 nm for (*R*)/(*S*)-HOSO–*i*Pr, and 300 nm for (*R*)/(*S*)-HOSO–Bn in $CH_2Cl_2$.

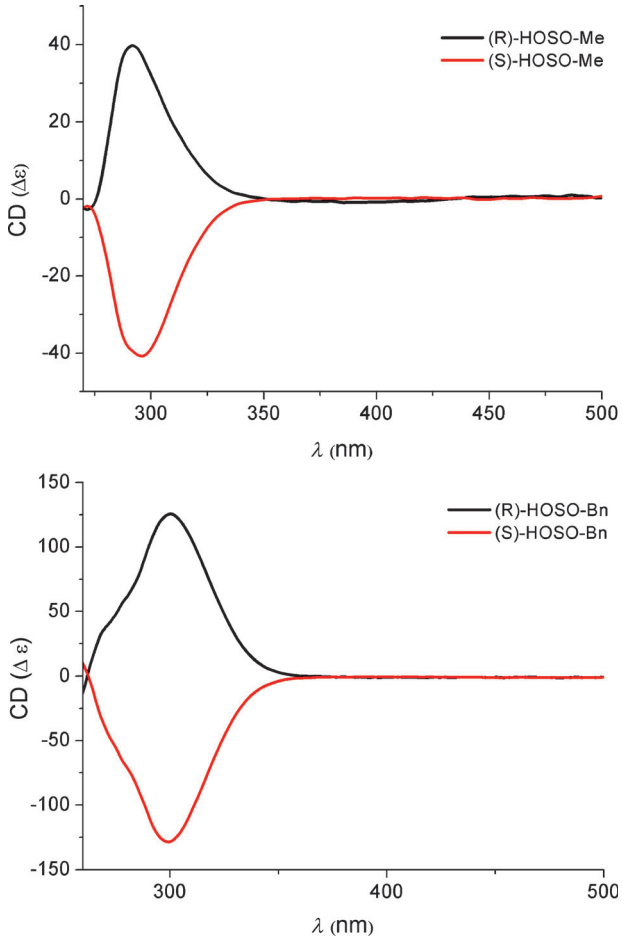



**Figure 5.** CD spectra of (*R*)/(*S*)-HOSO–Me (above) and (*R*)/(*S*)-HOSO–Bn (below) in $CH_2Cl$ (40 μM).

Although the NMR spectra of the two enantiomers are identical, the $^1$H NMR spectra of (*R*)/(*S*)-HOSO–Me and (*R*)/(*S*)-HOSO–Bn become distinguishable in the presence of (*S*)-binol (10 equiv) as a chiral NMR spectroscopic shift reagent. The methyl resonance peak at $\delta = 2.96$ ppm for HOSO–Me was split into a pair of peaks and shifted to $\delta = 2.82$ and 2.80 ppm in the presence of (*S*)-binol, which are in accord with the *R* and *S* enantiomers (see Figure S12), respectively. The enantiopurities were found to be 85.0% *ee* for the *R* configuration and 83.5% *ee* for the *S* configuration on the basis of the ratio of the integrals of the methyl peaks of the two enantiomers. For HOSO–Bn, the double peaks for methylene at $\delta = 4.48$ and 4.44 ppm were split into triple peaks at $\delta = 4.34$, 4.30, and 4.26 ppm in the presence of (*S*)-binol (see Figure S13). The *ee* values were found to be 92.9% for the *R* configuration and 92.5% for the *S* configuration from the ratio of the integrals of the methylene peaks of the two enantiomers. Furthermore, the enantiopurities of (*R*)-HOSO–Bn and (*S*)-HOSO–Bn were also determined by chiral HPLC analysis (see Figure 6) and found to

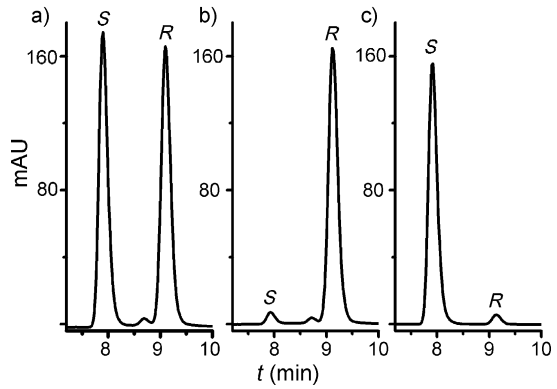



**Figure 6.** HPLC traces demonstrating the enantiopurity of synthetic HOSO–Bn: (a) *rac*-HOSO–Bn, (b) (*R*)-HOSO–Bn, and (c) (*S*)-HOSO–Bn.

be 92.6 and 92.9% *ee*, respectively. The enantiopurities calculated from the two techniques are comparable. We also attempted to measure the enantiopurities of (*R*)/(*S*)-HOSO–*i*Pr by means of their $^1$H NMR spectra using (*S*)-binol as a chiral shift reagent; however, the two enantiomers were indistinguishable under the experimental conditions. Therefore, their enantiopurities were estimated by chiral HPLC analysis (see Figure S14) and found to be 88.2% *ee* for (*R*)-HOSO–*i*Pr and 91.6% *ee* for (*S*)-HOSO–*i*Pr. The increase in *ee* values from the methyl (83.5 and 85.0%) to the isopropyl (88.2 and 91.6%) to the benzyl group (92.6 and 92.9%) indicates that the bulky substituent on thioether is advantageous for the enantioselectivity of sulfoxide. Apparently, the bulky substituent on sulfoxide should increase its stability during the acidolysis process.

The absolute configurations of (*R*)-HOSO–Me and (*R*)-HOSO–Bn were determined by means of X-ray crystallography. As shown in Figure 7, they all crystallize in the chiral space group $P2_12_12_1$. The structures verify an *R* configuration at the sulfur center, and the Flack parameters (0.01(2) for (*R*)-HOSO–Me and −0.01(2) for (*R*)-HOSO–Bn) are close to zero, thus demonstrating the assignment of chirality at the sulfur centers is correct. It should be pointed out that the absolute stereochemistry at the sulfur atoms changes from *S* to *R* upon removal of coordination according to the Cahn–Ingold–Prelog priority rules. The S1–O3 distances of 1.521(2) Å for (*R*)-HOSO–Me and 1.508(2) Å for (*R*)-HOSO–Bn are comparable to the reported ones (1.515(2) Å).[14b] Moreover, the sulfur atom configurations of all sulfoxides presented here were assigned relative to the two crystal structures by means of CD spectra.

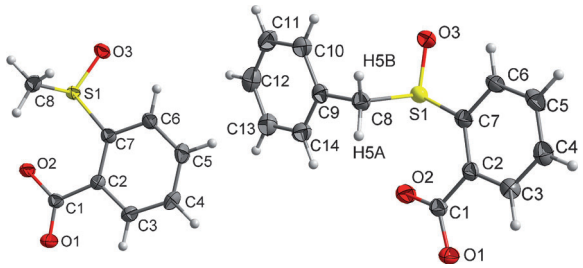



**Figure 7.** Crystal structures of (*R*)-HOSO–Me (left, S1–O3 = 1.521(2) Å, S1–C7 = 1.810(2) Å, S1–C8 = 1.793(2) Å, O3-S1-C8 = 103.9(1)°, O3-S1-C7 = 103.8(1)°, C7-S1-C8 = 98.6(1)°) and (*R*)-HOSO–Bn (right, S1–O3 = 1.508(2) Å, S1–C7 = 1.808(3) Å, S1–C8 = 1.831(2) Å, O3-S1-C8 = 101.8(1)°, O3-S1-C7 = 104.8(1)°, C7-S1-C8 = 99.6(1)°). ORTEP picture with thermal ellipsoids drawn at 50% probability.

## Conclusion

We have demonstrated here that the absolute configurations at the ruthenium centers of these complexes are completely retained during the formation of thioether complexes and oxidation in situ to generate sulfoxide complexes. Moreover, the configurations of the metal centers have the function of controlling sulfoxide chirality during the oxidation process, thus generating the predictable chirality of the sulfoxides. The chiral sulfoxides can be obtained by treatments of the corresponding sulfoxide complexes with TFA in $CH_3CN$ in high yields with retention of their configurations. The oxidation that generates enantiomeric sulfoxide in situ is unprecedented, which could provide a new approach for the enantioselective synthesis of sulfoxides.

## Experimental Section

### General procedures

All chemicals were commercially available and used as purchased unless otherwise noted. All manipulations were carried out under an Ar or $N_2$ atmosphere unless otherwise noted. The reactions that involved the formation of chiral ruthenium complexes were carried out in the dark as a precaution against light-induced decomposition and isomerization. Column chromatography was performed with silica gel (200–300 mesh) under reduced light. The precursors $[Ru(bpy)_2Cl_2]\cdot 2H_2O$,[16] Δ-$[Ru(bpy)_2(py)_2][O,O'$-dibenzoyl-D-tartrate$]\cdot 12H_2O$,[17] and Λ-$[Ru(bpy)_2(py)_2][O,O'$-dibenzoyl-L-tartrate$]\cdot 12H_2O$,[17] and the prochiral sulfide ligands OS–*i*Pr[23] and OS–Bn[24] were synthesized according to methods described in the literature. Elemental (C, H, N, and S) analyses were performed with an Ele-

mentar Vario EL analyzer. Electrospray ionization mass spectra (ESI-MS) were obtained with a Thermo LCQ DECA XP mass spectrometer. $^1$H and $^{13}$C NMR spectra were obtained with a Varian Mercury-Plus 300 spectrometer by using the chemical shift of the solvent as an internal standard. IR spectra were obtained with a Nicolet 330 FTIR spectrometer. CD spectra were recorded with a JASCO J-810 CD spectropolarimeter (1 s response, 3.41 nm bandwidth, scanning speed of 200 nm min$^{-1}$, accumulation of 3 scans). Chiral HPLC chromatogram analyses were carried out with a Shimadzu LC 20 with an SPD-20A UV detector (Daicel Chiralpak AY-H column, 250 mm × 4.6 mm, hexane/(EtOH/MeOH)/TFA = 85:(3:1)15:0.3, flow rate: 1 mL min$^{-1}$, column temperature 35 °C, 254 nm).

### General procedures for the preparation of the thioether complexes

A ruthenium precursor (0.5 mmol), thioether ligand HOS–R (0.6 mmol), $K_2CO_3$ (0.25 mmol), and ethylene glycol (4 mL) were added into a three-necked flask. The mixture was magnetically stirred and heated at 120 °C for 4 h under argon protection. Then a saturated aqueous $KPF_6$ solution (15 mL) was added to the cooled reaction mixture. $CH_2Cl_2$ (3 × 15 mL) was used to extract the product. The organic extract was subjected to silica gel column chromatography with $CH_3CN$ and later $CH_3CN/H_2O/KNO_3$ (saturated) = 100:1:0.4 solution as eluents. After removal of the solvent, water (20 mL) was used to dissolve the resulting product, and an excess amount of solid $KPF_6$ was added to the solution. Then $CH_2Cl_2$ (15 mL) was added to the solution and the layers were separated. The aqueous phase was extracted with $CH_2Cl_2$ (2 × 10 mL), and the combined organic phase were dried over $MgSO_4$, filtered, concentrated, and dried under high vacuum.

### Compound *rac*-1

Yield: 85% (*cis*-[Ru(bpy)$_2$Cl$_2$] was used as the precursor; EtOH (18 mL) and $H_2O$ (2 mL) were used as solvent at 90 °C for 6 h). Compound Δ-**1**: Yield: 71% (Δ-[Ru(bpy)$_2$(py)$_2$][*O*,*O*′-dibenzoyl-D-tartrate]·12 $H_2O$ was used as the precursor); *ee* 98% (determined by $^1$H NMR spectroscopy by using (*S*)-binol as a chiral shift reagent). $^1$H NMR (300.1 MHz, $CD_3CN$): $\delta$ = 9.09 (d, 1H), 8.79 (d, 1H), 8.47 (d, 1H), 8.34 (t, 3H), 8.17 (t, 1H), 7.92 (m, 3H), 7.77 (m, 3H), 7.57 (d, 1H), 7.48 (d, 1H), 7.40 (m, 2H), 7.27 (dd, 2H), 7.17 (t, 1H), 1.83 ppm (s, 3H); $^{13}$C NMR (75.5 MHz, $CD_3CN$): $\delta$ = 168.21, 160.45, 160.14, 159.02, 158.64, 155.09, 153.97, 153.50, 153.32, 143.92, 137.78, 137.11, 137.03, 136.50, 133.34, 132.17, 127.42, 126.84, 126.78, 126.22, 125.41, 124.76, 124.33, 124.04, 123.91, 123.52, 123.29, 15.61 ppm; IR (KBr): $\tilde{\nu}$ = 3433, 1601, 1550, 1467, 1443, 1426, 1365, 841, 763, 557 cm$^{-1}$; CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 282 (+42), 295 nm (−110 M$^{-1}$ cm$^{-1}$); ESI-MS: *m*/*z*: 581 [*M*−$PF_6$]$^+$; elemental analysis calcd (%) for $C_{28}H_{23}F_6N_4O_2PRuS$: C 46.35, H 3.19, N 7.72, S 4.42; found: C 46.21, H 3.25, N 7.64, S 4.35. Compound Λ-**1**: Yield: 71% (Λ-[Ru(bpy)$_2$(py)$_2$][*O*,*O*′-dibenzoyl-L-tartrate]·12 $H_2O$ was used as the precursor); CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 281 (−39), 295 nm (+108 M$^{-1}$ cm$^{-1}$).

### Compound *rac*-2

Yield: 80% (*cis*-[Ru(bpy)$_2$Cl$_2$] was used as the precursor). $^1$H NMR (300.1 MHz, $CD_3CN$): $\delta$ = 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 ppm (d, 3H); $^{13}$C NMR (75.5 MHz, $CD_3CN$): $\delta$ = 171.05, 159.81, 159.05, 158.88, 158.27, 155.33, 154.17, 152.42, 151.16, 142.93, 138.61, 137.97, 137.56, 136.65, 136.52, 133.62, 131.73, 130.38, 128.54, 127.96, 127.14, 126.93, 126.49, 124.77, 124.70, 124.22, 123.99, 42.69, 22.24, 21.59 ppm; IR (KBr): $\tilde{\nu}$ = 3428, 1593, 1552, 1464, 1444, 1361, 842, 763, 731, 557 cm$^{-1}$; ESI-MS: *m*/*z*: 608 [*M*−$PF_6$]$^+$; elemental analysis 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 3.98. Compound Δ-**2**: Yield: 81% (Δ-[Ru(bpy)$_2$(py)$_2$][*O*,*O*′-dibenzoyl-D-tartrate]·12 $H_2O$ was used as the precursor); *ee* 98% (determined by $^1$H NMR spectroscopy using (*S*)-binol as a chiral shift reagent); CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 282 (+42), 297 nm (−106 M$^{-1}$ cm$^{-1}$). Compound Λ-**2**: Yield: 81% (Λ-[Ru(bpy)$_2$(py)$_2$][*O*,*O*′-dibenzoyl-L-tartrate]·12 $H_2O$ was used as the precursor); *ee* 98% (determined by $^1$H NMR spectroscopy using (*S*)-binol as a chiral shift reagent); CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 281 (−40), 297 nm (+101 M$^{-1}$ cm$^{-1}$).

### Compound *rac*-3

Yield: 80% (*cis*-[Ru(bpy)$_2$Cl$_2$] was used as the precursor, reaction conditions: 120 °C, 6 h). $^1$H NMR (300.1 MHz, $CD_3CN$): $\delta$ = 9.42 (d, 1H), 8.59 (d, 1H), 8.37 (d, 1H), 8.29 (t, 2H), 8.20 (m, 2H), 7.97 (d, 1H), 7.84 (m, 4H), 7.69 (d, 1H), 7.26 (m, 6H), 7.10 (t, 2H), 6.98 (t, 2H), 6.62 (d, 2H), 3.81 (d, 1H), 3.21 ppm (d, 1H); $^{13}$C NMR (75.5 MHz, $CD_3CN$): $\delta$ = 170.41, 160.03, 159.10, 158.70, 158.12, 155.38, 154.05, 152.23, 151.20, 141.79, 138.51, 138.12, 137.63, 136.56, 134.88, 134.62, 133.99, 131.47, 130.30, 129.60, 129.57, 129.37, 129.22, 129.19, 128.52, 128.41, 127.07, 126.98, 126.65, 124.74, 124.65, 124.22, 124.14, 44.23 ppm; IR (KBr): $\tilde{\nu}$ = 3428, 1585, 1552, 1467, 1444, 1421, 1345, 841, 766, 728, 696, 557, 465 cm$^{-1}$; ESI-MS: *m*/*z*: 657 [*M*−$PF_6$]$^+$; elemental analysis calcd (%) for $C_{34}H_{27}F_6N_4O_2PRuS$: C 50.94, H 3.39, N 6.99, S 4.00; found: C 50.81, H 3.42, N 6.80, S 3.91. Compound Δ-**3**: Yield: 76% (Δ-[Ru(bpy)$_2$(py)$_2$][*O*,*O*′-dibenzoyl-D-tartrate]·12 $H_2O$ was used as the precursor); *ee* 98% (determined by $^1$H NMR spectroscopy using (*S*)-binol as a chiral shift reagent); CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 234 (−15), 282 (+62), 297 nm (−169 M$^{-1}$ cm$^{-1}$). Compound Λ-**3**: Yield: 76% (Λ-[Ru(bpy)$_2$(py)$_2$][*O*,*O*′-dibenzoyl-L-tartrate]·12 $H_2O$ was used as the precursor); *ee* 98% (determined by $^1$H NMR spectroscopy using (*S*)-binol as a chiral shift reagent); CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 235 (+15), 282 (−60), 297 nm (+165 M$^{-1}$ cm$^{-1}$).

### General procedures for the preparation of the sulfoxide complexes

Method A: A ruthenium thioether complex (2.5 mmol) and *m*-CPBA (5 mmol) were dissolved in methanol (100 mL). The solution was stirred at room temperature for 4 h. The solvent was removed under reduced pressure to yield a yellow-orange solid. Using $Et_2O$ (3 × 20 mL) to ultrasonically extract the solid for 10 min, the resulting solid was filtered, washed with $Et_2O$, and air-dried.

### Compound *rac*-1a

Yield: 95% (*rac*-**1** was used as the starting material). Compound Δ-**1a**: Yield: 95% (Δ-**1** was used as the starting material); *ee* 98% (determined by $^1$H NMR spectroscopy using (*S*)-binol as a chiral shift reagent). $^1$H NMR (300.1 MHz, $CD_3CN$): $\delta$ = 9.13 (d, 1H), 8.84 (d, 1H), 8.61 (d, 1H), 8.37 (m, 4H), 8.20 (d, 1H), 8.05 (t, 1H), 7.93 (m, 4H), 7.79 (m, 2H), 7.57 (t, 1H), 7.49 (d, 1H), 7.40 (t, 1H), 7.26 (t, 2H), 2.64 ppm (s, 3H); $^{13}$C NMR (75.5 MHz, $CD_3CN$): $\delta$ = 166.61, 158.83, 158.74, 158.46, 156.84, 156.10, 154.27, 152.66, 150.79, 143.99, 140.24, 140.02, 138.84, 138.35, 133.95, 133.78, 133.21,

132.35, 131.19, 128.91, 127.78, 127.64, 127.55, 125.43, 124.67, 124.62, 124.47, 47.44 ppm; IR (KBr): $\tilde{\nu}$ = 3431, 1604, 1557, 1466, 1446, 1425, 1367, 1105, 843, 764, 558 $cm^{-1}$; CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 275 (+16), 292 nm (−39 $M^{-1}cm^{-1}$); ESI-MS: *m/z*: 596 $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{28}H_{23}F_6N_4O_3PRuS$: C 45.29, H 3.26, N 7.54, S 4.32; found: C 45.11, H 3.45, N 7.34, S 4.21. Compound Λ-**1a**: Yield: 95% (Λ-**1** was used as the starting material); *ee* 98% (determined by $^1$H NMR spectroscopy using (*S*)-binol as a chiral shift reagent); CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 275 (−11), 293 nm (+38 $M^{-1}cm^{-1}$).

### Compound *rac*-2a

Yield: 96% (*rac*-**2** was used as the starting material). $^1$H NMR (300.1 MHz, $CD_3CN$): $\delta$ = 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 ppm (d, 3H); $^{13}$C NMR (75.5 MHz, $CD_3CN$) $\delta$ = 169.07, 158.90, 158.87, 158.69, 157.14, 156.26, 154.41, 152.72, 150.36, 140.08, 139.99, 139.22, 138.57, 138.24, 136.20, 133.53, 133.06, 131.20, 128.94, 127.61, 127.47, 127.17, 126.42, 125.35, 124.55, 124.43, 124.38, 59.66, 16.98, 14.97 ppm; IR (KBr): $\tilde{\nu}$ = 3429, 1603, 1556, 1455, 1445, 1359, 1093, 843, 765, 730, 555 $cm^{-1}$; ESI-MS: *m/z*: 624 $[M-PF_6]^+$; elemental analysis 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. Compound Δ-**2a**: Yield: 96% (Δ-**2** was used as the starting material); *ee* 98% (determined by $^1$H NMR spectroscopy using (*S*)-binol as a chiral shift reagent); CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 276 (+13), 292 nm (−52 $M^{-1}cm^{-1}$). Compound Λ-**2a**: Yield: 96% (Λ-**2** was used as the starting material); *ee* 98% (determined by $^1$H NMR spectroscopy using (*S*)-binol as a chiral shift reagent); CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 277 (−21), 293 nm (+51 $M^{-1}cm^{-1}$).

### Compound *rac*-3a

Yield: 97% (*rac*-**3** was used as the starting material, reaction time was 24 h). Compound Δ-**3a**: Yield: 95% (Δ-**3** was used as the starting material, reaction time was 24 h); *ee* 98% (determined by $^1$H NMR spectroscopy using (*S*)-binol as a chiral shift reagent). $^1$H NMR (300.1 MHz, $CD_3CN$): $\delta$ = 9.26 (d, 1H), 8.81 (d, 1H), 8.55 (d, 1H), 8.36 (m, 4H), 8.06 (t, 1H), 7.93 (m, 5H), 7.38 (m, 5H), 7.19 (m, 3H), 7.02 (t, 2H), 6.54 (d, 2H), 4.14 (d, 1H), 3.82 ppm (d, 1H); $^{13}$C NMR (75.5 MHz, $CD_3CN$): $\delta$ = 169.28, 158.83, 158.76, 158.55, 156.92, 156.22, 154.26, 152.63, 150.55, 140.38, 140.22, 140.17, 138.91, 138.40, 133.85, 133.10, 131.78, 131.75, 131.27, 131.26, 129.14, 129.13, 128.88, 128.72, 128.70, 127.91, 127.56, 127.54, 126.65, 125.61, 124.69, 124.57, 124.49, 64.10 ppm; IR (KBr): $\tilde{\nu}$ = 3440, 1595, 1557, 1468, 1446, 1424, 1349, 1093, 842, 766, 730, 698, 558, 505 $cm^{-1}$; CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 275 (+20), 292 nm (−92 $M^{-1}cm^{-1}$); ESI-MS: *m/z*: 673 $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{34}H_{27}F_6N_4O_3PRuS$: C 49.94, H 3.33, N 6.85, S 3.92; found: C 49.77, H 3.47, N 6.68, S 3.85. Compound Λ-**3a**: Yield: 95% (Λ-**3** was used as the starting material, reaction time was 24 h); *ee* 98% (determined by $^1$H NMR spectroscopy using (*S*)-binol as a chiral shift reagent); CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 275 (−20), 293 nm (+94 $M^{-1}cm^{-1}$).

Method B (one-pot method): Δ-[Ru(bpy)$_2$(py)$_2$][*O*,*O*′-dibenzoyl-D-tartrate]·12$H_2O$/Λ-[Ru(bpy)$_2$(py)$_2$][*O*,*O*′-dibenzoyl-L-tartrate]·12$H_2O$ (112 mg, 0.1 mmol), HOS–R (0.12 mmol), $K_2CO_3$ (6.9 mg, 0.05 mmol), and ethylene glycol (0.8 mL) were added into a 10 mL three-necked flask. The mixture was magnetically stirred and heated at 120 °C for 4 h (6 h for **3**) under argon protection. After cooling, methanol (50 mL) and *m*-CPBA (35 mg, 0.20 mmol) were added to the reaction mixture. The resulting solution was stirred at room temperature for 4 h (24 h for **3**). After that, the methanol solvent was removed under reduced pressure and a saturated aqueous $KPF_6$ solution (5 mL) was added. $CH_2Cl_2$ (3×20 mL) was used to extract the product, and the organic extract was subjected to silica-gel column chromatography with acetonitrile and later $CH_3CN/H_2O/KNO_3$ (saturated) = 100:1:0.4 as eluents. After removal of the solvent, water (10 mL) was used to dissolve the resulting product, and an excess amount of solid $KPF_6$ was added into the solution. Then $CH_2Cl_2$ (15 mL) was added to the solution and the layers were separated. The aqueous phase was further extracted with $CH_2Cl_2$ (2×10 mL), and the combined organic phase was dried over $MgSO_4$, filtered, concentrated, and dried under high vacuum. Yield: 73% for Δ-**1a** and Λ-**1a**, 83% for Δ-**2a** and Λ-**2a**, and 81% for Δ-**3a** and Λ-**3a**. The *ee* values are >98% (determined by $^1$H NMR spectroscopy using (*S*)-binol as a chiral shift reagent).

### General procedures for the preparation of the sulfoxide compounds

A ruthenium sulfoxide complex (0.1 mmol), trifluoroacetic acid (0.5 equiv), and $CH_3CN$ (3 mL) were added into a three-necked 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. After addition of $H_2O$ (10 mL) to the orange solid, the aqueous phase was extracted with $Et_2O$ (3×15 mL). The $Et_2O$ solutions were combined and dried over $MgSO_4$ and then filtered. The solvent was removed under reduced pressure and dried under high vacuum to give a white powder.

#### *rac*-HOSO–Me

Compound *rac*-**1a** was used as the starting material. Yield: 90%. (*S*)-HOSO–Me: Compound Δ-**1a** was used as the starting material. Yield: 90%; *ee* 83.5% (determined by $^1$H NMR spectroscopy using (*S*)-binol as a chiral shift reagent). $^1$H NMR (300.1 MHz, $CD_3Cl$): $\delta$ = 8.32 (d, 1H), 8.16 (d, 1H), 7.87 (t, 1H), 7.61 (t, 1H), 2.96 ppm (t, 3H); $^{13}$C NMR (75.5 MHz, $CD_3Cl$): $\delta$ = 167.98, 149.00, 134.40, 131.65, 130.68, 127.08, 124.35, 43.77 ppm; IR (KBr): $\tilde{\nu}$ = 2920, 2852, 2458, 1812, 1699, 1588, 1441, 1306, 1113, 1051, 972, 948, 802, 752, 693, 517 $cm^{-1}$; CD ($CH_2Cl_2$): $\lambda$ ($\Delta\varepsilon$) = 295 nm (−41 $M^{-1}cm^{-1}$); ESI-MS: *m/z*: 183 $[M-H]^-$; elemental analysis calcd (%) for $C_8H_8O_3S$: C 52.16, H 4.38, S 17.41; found: C 52.00, H 4.40, S 17.35. (*R*)-HOSO–Me: Compound Λ-**1a** was used as the starting material. Yield: 90%; *ee* 85.0% (determined by $^1$H NMR spectroscopy using (*S*)-binol as a chiral shift reagent); CD ($CH_2Cl_2$): $\lambda$ ($\Delta\varepsilon$) = 293 nm (+43 $M^{-1}cm^{-1}$).

#### *rac*-HOSO–*i*Pr

Compound *rac*-**2a** was used as the starting material. Yield: 91%. $^1$H NMR (300.1 MHz, $CDCl_3$) $\delta$ = 8.18 (m, 2H), 7.81 (t, 1H), 7.59 (t, 1H), 3.27 (m, 2H), 1.54 (d, 1H), 0.98 ppm (t, 1H); $^{13}$C NMR (75.5 MHz, $CD_3Cl$): $\delta$ = 167.92, 145.41, 133.38, 131.89, 130.39, 127.66, 126.08, 52.97, 18.80, 12.05 ppm; IR (KBr): $\tilde{\nu}$ = 2966, 2928, 2473, 1896, 1689, 1586, 1467, 1281, 1143, 1108, 1055, 1033, 963, 801, 759, 694, 536 $cm^{-1}$; elemental analysis 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 14.89; ESI-MS: *m/z*: 211 $[M-H]^-$. (*S*)-HOSO-*i*Pr: Compound Δ-**2a** was used as the starting material. Yield: approximately 90%; *ee* 91.6% (determined by chiral HPLC analysis); CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 296 nm

($-110\ M^{-1}cm^{-1}$). (*R*)-HOSO-*i*Pr: Compound Λ-**2a** was used as the starting material. Yield: approximately 90%; *ee* 88.2% (determined by chiral HPLC analysis); CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 296 nm ($+108\ M^{-1}cm^{-1}$).

### *rac*-HOSO–Bn

Compound *rac*-**3a** was used as the starting material. Yield: 92%. (*S*)-HOSO–Bn: Compound Δ-**3a** was used as the starting material. Yield: 90%; *ee* 92.9% (determined by chiral HPLC analysis). $^1$H NMR (300.1 MHz, $CD_3CN$): $\delta$ = 8.12 (d, 1H), 7.81 (d, 1H), 7.72 (t, 1H), 7.60 (t, 1H), 7.29 (m, 3H), 7.15 (m, 2H), 4.41 (d, 1H), 3.83 ppm (d, 1H); $^{13}$C NMR (75.5 MHz, $CD_3Cl$): $\delta$ = 168.37, 145.72, 133.79, 131.54, 131.21, 130.77, 130.65, 130.41, 128.65, 128.39, 128.36, 127.44, 125.75, 61.74 ppm; IR (KBr): $\tilde{\nu}$ = 2870, 2614, 2482, 1700, 1587, 1404, 1303, 1250, 1144, 1109, 1060, 1006, 793, 746, 695, 641, 496 $cm^{-1}$; CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 300 nm ($-128\ M^{-1}cm^{-1}$); ESI-MS: *m/z*: 259 $[M-H]^-$; elemental analysis calcd (%) for $C_{14}H_{12}O_3S$: C 64.60, H 4.65, S 12.32; found: C 64.55, H 4.67, S 12.9. (*R*)-HOSO–Bn: Compound Λ-**3a** was used as the starting material. Yield: 90%; *ee* 92.6% (determined by chiral HPLC analysis); CD (MeCN): $\lambda$ ($\Delta\varepsilon$) = 300 nm ($+126\ M^{-1}cm^{-1}$).

### Crystallographic analysis

Crystals suitable for X-ray diffraction were grown from $CHCl_3$ solutions layered with hexane for (*R*)-HOSO–Me and (*R*)-HOSO–Bn, from $CH_2Cl_2$ solutions layered with toluene for Δ-**2**, Δ-**2a**, and Λ-**2a**, and from $CH_2Cl_2$ solutions layered with $CH_3CH_2OH$ for Δ-**3**. Single crystals of *rac*-**2**, *rac*-**2a**, and *rac*-**3a** were grown from $CH_3OH$ solutions. Single-crystal X-ray diffraction data were collected with a Rigaku R-AXIS Spider IP diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å, for *rac*-**2**, *rac*-**2a**, and *rac*-**3a**) at 150 K or an Oxford Gemini S Ultra CCD area detector diffractometer with graphite-monochromated $Cu_{K\alpha}$ radiation ($\lambda$ = 1.54178 Å, for Δ-**2**, Δ-**2a**, Λ-**2a**, Δ-**3**, (*R*)-HOSO–Me, and (*R*)-HOSO–Bn) at 160 K. All of the data were corrected for absorption effects using the multiscan technique. The structures were solved by direct methods using SHELXS-97 programs[25] and refined by full-matrix least-squares technique on $F^2$ using SHELXL-97 programs.[26] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms of the ligands were generated geometrically.

CCDC 1001979 (*rac*-**2**·$H_2O$), 990972 (Δ-**2**·0.25 $CH_2Cl_2$·0.25 $H_2O$), 1001980 (*rac*-**2a**·$H_2O$), 990805 (Δ-**2a**·0.5 $H_2O$), 990806 (Λ-**2a**·0.5 $H_2O$), 1001981 (Δ-**3**·$CH_3CH_2OH$), 1001978 (*rac*-**3a**·0.5 $CH_3OH$), 1001983 ((*R*)-HOSO–Me), and 1001982 ((*R*)-HOSO–Me) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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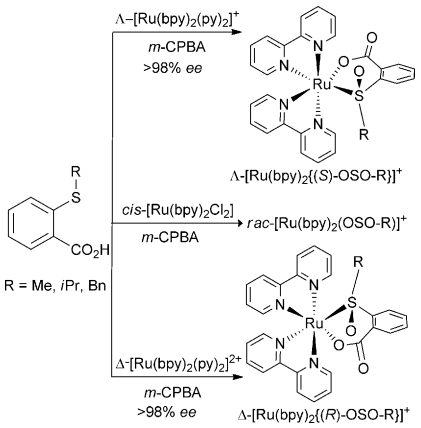
**Delta force**: Treatment of Δ-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ (bpy = 2,2′-bipyridine, py = pyridine) or Λ-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ with thioether ligands, then oxidation in situ, provides the corresponding Δ-[Ru(bpy)$_2${(*R*)-OSO–R}]$^+$ or Λ-[Ru(bpy)$_2${(*S*)-OSO–R}]$^+$ with 98% *ee* values, which can be converted into the corresponding chiral sulfoxides in yields of 90% with 83–93% *ee* values (see scheme).

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**Enantioselective Oxidation of Thioethers to Sulfoxides by Means of a Structural Template with Chiral-at-Metal Ruthenium Complexes**