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Chiral (Mercaptophenyl)oxazolines as Auxiliaries for Asymmetric Coordination Chemistry

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(4*S*)-2-(4-Isopropyl-4,5-dihydrooxazol-2-yl)-4-nitrobenzenethiol {(*S*)-**TS**} and its *tert*-butyl derivative {(*S*)-**TS**′} were developed as chiral auxiliaries for the asymmetric synthesis of polypyridyl ruthenium complexes. In their deprotonated form, these (mercaptophenyl)oxazolines were used as bidentate ligands and allowed the efficient transfer of chirality from the oxazoline moiety to the ruthenium stereocenter. After the induction of the absolute metal-centered configuration, the auxiliaries were labilized by converting the coordinated thiolate into a thioether ligand upon methylation with Meerwein salt, followed by the thermal replacement with 2,2′-bipyridine or 1,10-phenanthroline ligands under retention of configuration to afford octahedral polypyridyl ruthenium complexes with high enantiomeric excesses. These thiol-based auxiliaries complement our previously developed acid-labile chiral auxiliaries and thus expand the toolbox for the asymmetric synthesis of chiral ruthenium complexes.

Introduction

Chiral octahedral metal complexes attract increasing attention in the field of catalysis,[1] materials sciences,[2] and life sciences.[3] Typically, their chemical, physical and biological characteristics are closely related to the stereochemical arrangement of the ligands around the metal center with only one stereoisomer exhibiting the desired properties.[4] To circumvent a cost- and time-consuming separation by chiral resolution techniques of stereoisomers formed during synthesis, a stereoselective synthetic route, i.e. an asymmetric synthesis, is often the strategy of choice, but general and convenient methods to obtain stereochemically pure octahedral metal complexes are still rare.[5] Regarding the auxiliary-mediated asymmetric synthesis of octahedral coordination compounds, a few methods were developed over the last decades using for example tartrate,[6] monodentate chiral sulfoxides,[7] chiral cleavable linkers,[8] or chiral counterions[9] as auxiliaries.[10] Unfortunately, these methods either provide only moderate stereochemical induction or their application is limited with respect to their scope. Hence, more broadly applicable methods for the stereoselective synthesis of enantiopure compounds with metal-centered chirality are demanded.

A few years ago, our group started investigations in this field and established the concept of auxiliary-mediated asymmetric coordination chemistry using *chelating* ligands. The formation of a bidentate chelate prevents the auxiliary from rotation around the metal-ligand bond resulting in an improved stereoinduction. We applied carefully tailored chiral bidentate auxiliaries such as salicyloxazolines (**Salox**),[11] sulfinylphenols (**SO** and **SO**′),[12] a binaphthyl ligand (**HO-MOP**),[13] and a simple sulfinamide (**ASA**)[14] which all transfer their chiral information efficiently to an octahedral metal center and are removed afterwards in a traceless fashion under complete retention of the configuration at the metal (Figure 1). However, all current reaction sequences are based on an acid-induced auxiliary substitution. To in-

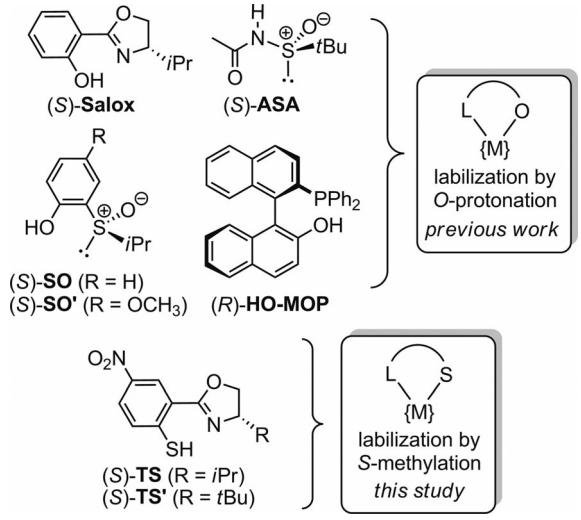

Figure 1. Comparison of previously developed and in this study introduced chelating chiral auxiliaries for the asymmetric synthesis of polypyridyl ruthenium complexes.

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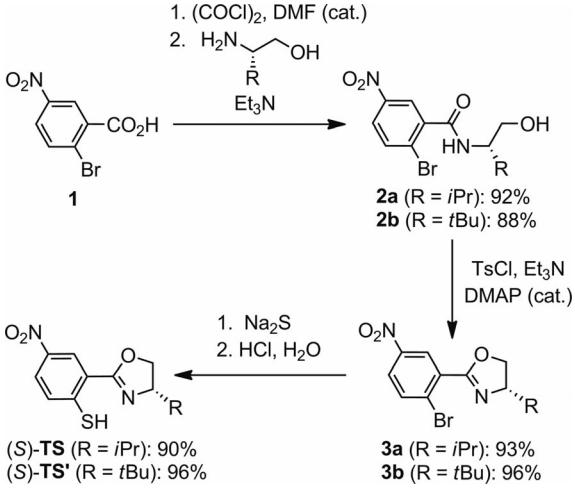
crease the scope of available methods for asymmetric coordination chemistry, we were therefore seeking new strategies with respect to the induction of the auxiliary replacement. We here wish to report our progress into this direction and present (4*S*)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-4-nitrobenzenethiol {(*S*)-**TS**} and its *tert*-butyl derivative {(*S*)-**TS′**} as chiral auxiliaries for the asymmetric synthesis of chiral polypyridyl ruthenium complexes (Figure 1).

Results and Discussion

Synthesis of (Mercaptophenyl)oxazolines

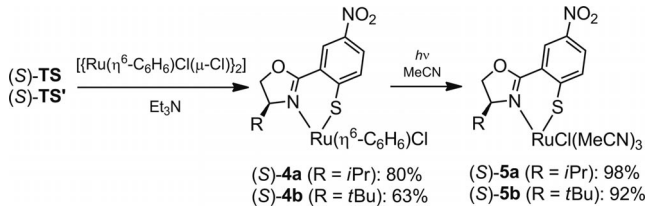
We selected the chiral (mercaptophenyl)oxazolines (*S*)-**TS** (R = *i*Pr) and (*S*)-**TS′** (R = *t*Bu) as our new generation of chiral auxiliaries (Figure 1). In comparison to the previously established salicyloxazolines, the hydroxy group is replaced by a thiol and an additional nitro group at the aromatic backbone is supposed to stabilize the aromatic thiol towards air oxidation.[15] The synthesis of these auxiliary ligands started from the commercially available 2-bromo-5-nitrobenzoic acid (**1**) following a procedure reported by Bauer et al. for the first two reaction steps.[16] Accordingly, **1** was converted quantitatively into 2-bromo-5-nitrobenzoyl chloride using oxalyl chloride and catalytic amounts of DMF (Scheme 1). By reacting the crude acid chloride with a chiral amino alcohol in the presence of triethylamine the stereochemical information was introduced to obtain hydroxybenzamide **2a**, **b**. 4-Toluenesulfonyl chloride, triethylamine, and catalytic amounts of DMAP effected the cyclization reaction and the oxazoline moiety in **3a**, **b** was formed. Finally the bromo substituent in **3a**, **b** was replaced in a nucleophilic aromatic substitution reaction with sodium sulfide and acidic aqueous work-up afforded the corresponding (mercaptophenyl)oxazoline (*S*)-**TS** (R = *i*Pr) or (*S*)-**TS′** (R = *t*Bu). Further purification by suspending the crude product in anhydrous toluene and subsequent filtration allowed isolation of the auxiliary in a salt-free fashion in an overall yield of ≥ 76% over three steps. The auxiliary is storable at –20 °C under argon for months but decomposes when stored in solution under air.



Scheme 1. Synthesis of the chiral (mercaptophenyl)oxazolines (*S*)-**TS** and (*S*)-**TS′**. TsCl = 4-toluenesulfonyl chloride, DMAP = 4-(dimethylamino)pyridine.

Synthesis of Precursor Complexes

To provide a suitable precursor complex that acts as a starting point for the asymmetric coordination chemistry, auxiliary ligand (*S*)-**TS** was treated with [{Ru(η⁶-C_6H_6)-Cl(μ-Cl)}$_2$] in acetonitrile in the presence of triethylamine at room temperature for 4 h (Scheme 2). The resulting benzene half-sandwich complex was stable enough to be purified by column chromatography to afford (*S*)-**4a** in a yield of 80%. In case of the *tert*-butyl derivative (*S*)-**TS′**, the reaction time had to be extended to 5 h. Subsequent silica gel column chromatography allowed isolation of (*S*)-**4b** only in a moderate yield of 63%. The increased reaction time and limited stability during column chromatography are most likely an effect of the sterically more demanding *tert*-butyl group. It hinders the coordination at the metal center and favors the decomposition of the formed half-sandwich complex (*S*)-**4b**. Alternatively, it was also possible to utilize the crude auxiliary ligand in the synthesis of (*S*)-**4a**, **b** without lowering the yield. Remaining salts from the ligand synthesis were removed subsequently by column chromatography. The pseudo-tetrahedral complexes (*S*)-**4a** and (*S*)-**4b** can exist as two different diastereomers. However, it was not possible to make a statement with respect to diastereoselectivity of this reaction as (*S*)-**4a**, **b** underwent a solvent dependent epimerization at the ruthenium center. This is in accordance with observations made by Brunner and Davies for structurally similar arene half-sandwich complexes.[17] Subsequently, the benzene ligand in (*S*)-**4a**, **b** was exchanged against substitutionally labile ligands which are crucial for further diastereoselective introduction of polypyridyl ligands. Accordingly, treatment of (*S*)-**4a**, **b** with UV-irradiation in acetonitrile followed by evaporation of solvents afforded (*S*)-**5a**, **b** without the need of further purification. The precursor complexes (*S*)-**5a**, **b** are sensitive to air and should be prepared freshly when used in diastereoselective synthesis experiments.

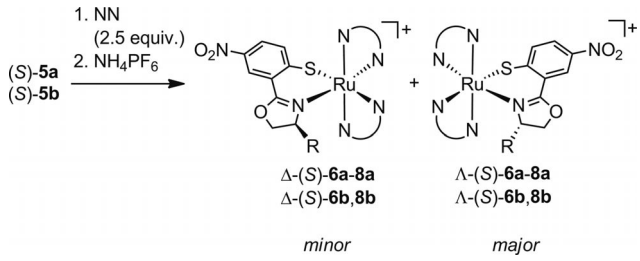


Scheme 2. Synthesis of the precursor complexes (*S*)-**5a**, **b** as starting points for asymmetric coordination chemistry.

Diastereoselective Coordination Chemistry

The precursor complex (*S*)-**5a** was treated with 2.5 equiv. of 2,2′-bipyridine (bpy), 5,5′-dimethyl-2,2′-bipyridine (dmbpy), or 1,10-phenanthroline (phen) to afford the com-

plexes Λ-(*S*)-**6a**–**8a** diastereoselectively, favoring the formation of the Λ-configuration at the ruthenium center in analogy to our previous salicyloxazoline system (Scheme 3).[11] The diastereoselectivity of this conversion originates from the steric demand of the alkyl group at the stereocenter located in close proximity to the coordinating nitrogen atom of the oxazoline moiety. Thus, incoming bidentate ligands arrange in a fashion resulting in minimal steric interaction with the alkyl chain. Crystal structures published by Meggers et al. for the related (*S*)-**Salox** system support this explanation.[11]



Scheme 3. Diastereoselective coordination chemistry with (mercaptophenyl)oxazoline complexes (*S*)-**5a**, **b**. NN = 2,2′-bipyridine [Λ-(*S*)-**6a**, **b**], 5,5′-dimethyl-2,2′-bipyridine [Λ-(*S*)-7**a**], or 1,10-phenanthroline [Λ-(*S*)-**8a**, **b**]. See Table 1 for reaction conditions.

Determination of Absolute Metal-Centered Configuration

Unfortunately, it was not possible to obtain single crystals suitable for X-ray analysis. The auxiliaries (*S*)-**TS** and (*S*)-**TS′** exhibit a structure very similar to (*S*)-**Salox** and the same configuration at the chiral carbon atom in 4-position of the oxazoline moiety which determines the metal-centered chirality emerged upon coordination of two polypyridines to the ruthenium center. As the configuration of previously published (*S*)-**Salox** bearing bis(polypyridyl) ruthenium complexes was identified by crystal structure analysis as Λ,[11] the resulting metal-centered configuration of diastereomers formed by the reaction of (*S*)-**5a** with polypyridines was expected to be the same. Hence, assignment of the absolute configuration at the ruthenium center was achieved by means of CD spectroscopy for diastereomeric complexes synthesized in this work relative to CD data of (*S*)-**Salox** containing diastereomers as Λ.[11] The CD spectrum of Λ-(*S*)-**6a** is shown in Figure 2 in comparison with the structurally similar (*S*)-**Salox** bearing diastereomeric complex Λ-[Ru(bpy)$_2${(*S*)-**Salox**-H}]PF$_6$.

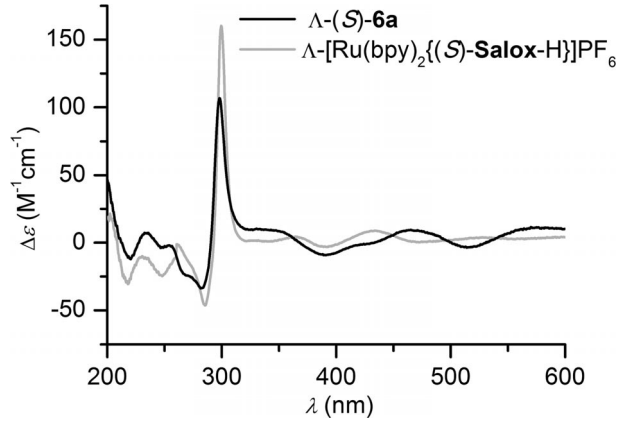


Figure 2. CD spectrum of the diastereomeric complex Λ-(*S*)-**6a** (*dr* = 59:1) (black line) compared with data of the structurally analogous complex Λ-[Ru(bpy)$_2${(*S*)-**Salox**-H}]PF$_6$ (*dr* = 120:1) (grey line) according to ref.[11b] Spectra were recorded in acetonitrile at concentrations of 0.2 mM.

Determination of Diastereomeric Ratios

The ratios of formed Λ-(*S*)- and Δ-(*S*)-diastereomers were determined from ^{1}H NMR spectra of the diastereomerically enriched purified product by peak integration and comparison of the integral values. Signals chosen for this purpose were those of the protons in *ortho* position to a coordinating nitrogen atom of one polypyridyl ligand. For example, the reaction of (*S*)-**5a** with bpy (2.5 equiv.) in chlorobenzene at a concentration of 5 mM at 110 °C for 3 h afforded Λ-(*S*)-**6a** with a diastereoselectivity of 59:1 (Figure 3, a). A 1:1 mixture of Λ/Δ-(*S*)-**6a** served as the reference for peak identification (Figure 3, b).

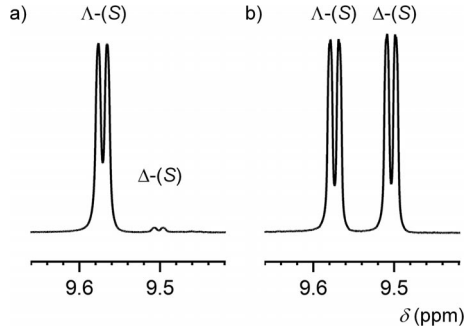


Figure 3. ^{1}H NMR spectra excerpts (500 MHz, CD_3CN) of (a) the reaction that afforded Λ-(*S*)-**6a** with a high diastereoselectivity (*dr* = 59:1) and (b) a 1:1 mixture Λ/Δ-(*S*)-**6a**. Depicted are the signals of the protons in *ortho* position to a coordinating nitrogen atom of one bipyridyl ligand.

Solvent Dependence of Diastereoselectivity

The extent of the stereoselectivity strongly depends on the solvent chosen for this reaction. For the reaction of (*S*)-**5a** with bpy, the best solvent regarding diastereoselectivity turned out to be chlorobenzene as a slightly polar noncoordinating solvent affording Λ-(*S*)-**6a** with a high *dr* (59:1, 62% yield) (Table 1, entry 1). This observation is in accordance with the results obtained for the (*S*)-**Salox** system.[11] A polar aprotic solvent like DMF led to a modest diastereoselectivity of 16:1 but a significantly increased yield (79%) (Table 1, entry 4). In ethanol as an example for a polar protic solvent direct conversion into $[Ru(bpy)_3]^{2+}$ was observed additionally to the formation of diastereomeric product complex, thus excluding ethanol as a suitable solvent. Other reaction parameters like concentration, temperature, and the number of equivalents of introduced polypyridine were also investigated but did not show a significant effect on the diastereoselectivity. In general, the trends observed in this work are comparable to results obtained for the (*S*)-**Salox** system studied previously.[11]

Table 1. Diastereoselective coordination chemistry with (mercaptophenyl)oxazoline complexes (*S*)-**5a**, **b**.[a]

Entry	Precursor	NN	Solvent	Time	Product	Yield	*dr*[b]
1	(*S*)-**5a**	bpy	C_6H_5Cl	3 h	Λ-(*S*)-**6a**	62%	59:1
2	(*S*)-**5a**	dmbpy	C_6H_5Cl	3 h	Λ-(*S*)-**7a**	64%	40:1
3	(*S*)-**5a**	phen	C_6H_5Cl	1 h	Λ-(*S*)-**8a**	68%	56:1
4	(*S*)-**5a**	bpy	DMF	90 min	Λ-(*S*)-**6a**	79%	16:1
5	(*S*)-**5a**	phen	DMF	45 min	Λ-(*S*)-**8a**	80%	23:1
6	(*S*)-**5b**	bpy	DMF	90 min	Λ-(*S*)-**6b**	72%	34:1
7	(*S*)-**5b**	phen	DMF	45 min	Λ-(*S*)-**8b**	64%	93:1

[a] Conditions: 5 mM precursor, 2.5 equiv. of NN = 2,2′-bipyridine (bpy), 5,5′-dimethyl-2,2′-bipyridine (dmbpy), or 1,10-phenanthroline (phen), 110 °C. [b] Determined by ^{1}H NMR spectroscopy.

Ligand Dependence

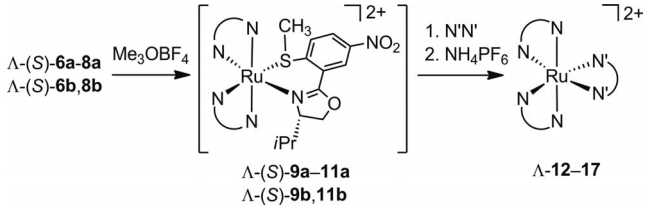
In addition to bpy, dmbpy and phen were introduced as bidentate ligands. Contrasting to the observations made for the (*S*)-**Salox** system, the reaction of (*S*)-**5a** with dmbpy as a sterically more demanding bipyridine derivative did not result in higher selectivities for Λ-(*S*)-**7a** (*dr* = 40:1, 64% yield) (Table 1, entry 2).[11] In the case of phen, the diastereomeric ratio obtained for the resulting ruthenium complex Λ-(*S*)-**8a** was 56:1 (68% yield) (Table 1, entry 3), similar to the *dr* found for Λ-(*S*)-**6a**. However, the reaction time could be reduced to 1 h as also observed for the related (*S*)-**Salox** system.[11] Overall, for all investigated polypyridyl ligands, diastereoselectivities and yields for reactions with the precursor (*S*)-**5a** were satisfactory and in the same range.

Influence of Alkyl Substituent in the 4-Position of the Oxazoline

Due to its close proximity to the metal center, the steric demand of the alkyl chain in 4-position of the oxazoline moiety should affect the diastereoselectivity of complex formation significantly.[11] We found that an increase of the bulkiness of the auxiliary ligand by introduction of a sterically more demanding alkyl chain (*tert*-butyl vs. isopropyl) in 4-position of the oxazoline moiety led to a higher diastereoselectivity. But – carried out in the same solvent chlorobenzene – this was achieved at the expense of the yield of the reaction. As the solvent screening gave high yields but low selectivities in DMF when (*S*)-**5a** was used as a precursor, we decided to react (*S*)-**5b** with bpy in DMF. After a reaction time of 90 min, Λ-(*S*)-**6b** was isolated with a *dr* of 34:1 in a yield of 72% (Table 1, entry 6). For phen as polypyridyl ligand, quantitative conversion of starting material was reached already after 45 min to afford Λ-(*S*)-**8b** with a high *dr* of 93:1 and an acceptable yield of 64% (Table 1, entry 7). As expected, diastereomeric complexes Λ-(*S*)-**6b** and Λ-(*S*)-**8b** were formed with an improved selectivity and yields even higher than obtained for the formation of Λ-(*S*)-**6a** and Λ-(*S*)-**8a** in DMF. Unfortunately, as a trade-off, the stability of complexes bearing auxiliary ligand (*S*)-**TS′** is significantly lower than (*S*)-**TS** with the result that the diastereomers decomposed more easily when exposed to air.

Replacement of the Auxiliary Ligand Under Retention of Configuration

The final step of the stereoselective synthesis of tris(polypyridyl) ruthenium complexes includes the replacement of the auxiliary against a third polypyridyl ligand under retention of the configuration at the metal center, requiring the weakening of the auxiliary-metal bond. In this work, this was achieved by a methylation of the thiolate complexes Λ-(*S*)-**6a**–**8a** and Λ-(*S*)-**6b**, **8b**. For example, the reaction of Λ-(*S*)-**6a** with trimethyloxonium tetrafluoroborate (2 equiv.) in dichloromethane at room temperature for 3 h and subsequent reaction of the intermediate complex with an excess of bpy (15 equiv.) in acetonitrile at 110 °C for 24 h in a sealed vessel afforded Λ-**12** in a yield of 68% (Scheme 4 and Table 2, entry 1).



Scheme 4. Replacement of the thiophenolato ligand under retention of configuration induced by methylation with the Meerwein salt. N′N′ = bpy (Λ-**12**), dmbpy (Λ-**13**), phen (Λ-**14**), or 4,4′-dimethoxy-2,2′-bipyridine (dmobpy) (Λ-**15**–**17**). See Table 2 for details.

Table 2. Ligand activation and substitution under retention of configuration.

Entry	Starting mat.	*dr*[a]	Reaction cond.	N′N′	Product	Yield	*er*[f,g]
1	Λ-(*S*)-**6a**	59:1	Me_3OBF_4[b]	bpy	Λ-**12**	68%	43:1
2	Λ-(*S*)-**7a**	40:1	Me_3OBF_4[b]	dmbpy	Λ-**13**	74%	26:1
3	Λ-(*S*)-**8a**	56:1	Me_3OBF_4[b]	phen	Λ-**14**	61%	36:1
4	Λ-(*S*)-**6a**	59:1	Me_3OBF_4[c]	dmobpy	Λ-**15**	74%	35:1
5	Λ-(*S*)-**7a**	40:1	Me_3OBF_4[c]	dmobpy	Λ-**16**	79%	27:1
6	Λ-(*S*)-**8a**	56:1	Me_3OBF_4[c]	dmobpy	Λ-**17**	76%	34:1
7	Λ-(*S*)-**6b**	34:1	Me_3OBF_4[c]	dmobpy	Λ-**15**	85%	23:1
8	Λ-(*S*)-**8b**	93:1	Me_3OBF_4[c]	dmobpy	Λ-**17**	86%	42:1
9	Λ-(*S*)-**6a**	59:1	MeI[d]	dmobpy	Λ-**15**	< 7%	n.d.
10	Λ-(*S*)-**6a**	59:1	MeI/$AgPF_6$[e]	dmobpy	Λ-**15**	39%	48:1
11	Λ-(*S*)-**6a**	59:1	TFA[f]	bpy	Λ-**12**	n.d.	n.d.

[a] Determined by ^{1}H NMR spectroscopy. [b] Conditions: (i) CH_2Cl_2, 50 mM, 2 equiv. Me_3OBF_4, room temp., 3 h. (ii) MeCN, 100 mM, 15 equiv. N′N′, 110 °C, sealed vial, 24 h. [c] Conditions: (i) CH_2Cl_2, 50 mM, 2 equiv. Me_3OBF_4, room temp., 3 h. (ii) MeCN, 100 mM, 15 equiv. dmobpy, 110 °C, sealed vial, 20 h. [d] Conditions: (i) MeCN, 50 mM, 5 equiv. MeI, room temp., 5 h. (ii) MeCN, 100 mM, 15 equiv. dmobpy, 110 °C, sealed vial, 20 h. [e] Conditions: (i) MeCN, 50 mM, 5 equiv. MeI, 10 equiv. $AgPF_6$, room temp., 5 h. (ii) MeCN, 100 mM, 15 equiv. dmobpy, 110 °C, sealed vial, 20 h. [f] Conditions: MeCN, 50 mM, 5 equiv. TFA, 15 equiv. bpy, 110 °C, sealed vial, 12 h. Traces of product formed. [g] Determined by chiral HPLC (see experimental section and Supporting Information for conditions).

The enantiomeric ratio of the product complex Λ-**12** was determined by chiral HPLC analysis to be 43:1. The HPLC trace of the enantioenriched complex is displayed in part a of Figure 4 compared with the trace for the racemic mixture

Λ/Δ-**12** as a reference (Figure 4, b). Comparison of the *dr* (59:1) before replacement of the auxiliary ligand and the *er* (43:1) of the enantiomerically enriched product Λ-**12** demonstrates that the substitution occurred within experimental errors without any significant loss of stereochemical information at the metal center. The absolute stereochemistry of Λ-**12** was assigned relative to published CD data as the Λ-configuration at the ruthenium center.[11]

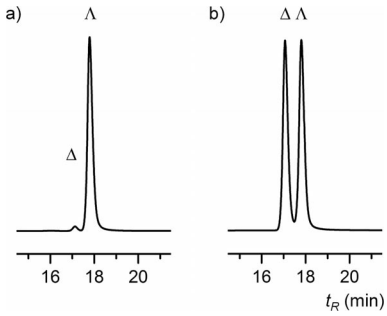


Figure 4. HPLC traces of (a) enantioenriched Λ-$[Ru(bpy)_3](PF_6)_2$ (Λ-**12**) (*er* = 43:1) synthesized from Λ-(*S*)-**6a** and (b) the racemic mixture Λ/Δ-**12**. HPLC conditions: Daicel Chiralpak IA (250 × 4.6 mm); solvent A = 0.1% TFA (aq), solvent B = acetonitrile (flow rate 0.5 mL/min, column temperature 40 °C, UV-absorption detected at 254 nm, 15–30% B in 20 min).

Diastereomeric complexes Λ-(*S*)-**7a** and Λ-(*S*)-**8a** were also converted into their corresponding tris-homoleptic polypyridyl ruthenium complexes Λ-**13** (*er* = 26:1, 74% yield) and Λ-**14** (*er* = 36:1, 61% yield) under reaction conditions applied for the synthesis of Λ-**12** (Table 2, entries 2 and 3). The *er* values and yields were in the same range as for Λ-**12**. This method is also applicable for the introduction of different bidentate ligands like 4,4′-dimethoxy-2,2′-bipyridine (dmobpy) to obtain heteroleptic polypyridyl ruthenium complexes. By methylation of the diastereomeric complexes Λ-(*S*)-**6a**–**8a** and subsequent reaction with dmobpy (15 equiv.) the corresponding complexes Λ-**15**–**17** were formed. Due to the electron-rich character of the dmobpy ligand the reaction time for the substitution step was slightly reduced to 20 h. In comparison with reactions that afforded homoleptic complexes, the yields marginally increased (74–79%) whereas the *er* was not affected (Table 2, entries 4–6). The auxiliary (*S*)-**TS′** in diastereomeric complexes Λ-(*S*)-**6b**, **8b** was also replaced against dmobpy under standard reaction conditions (Table 2, footnote [c]). The yields were negligibly higher than for complexes prepared by reaction of Λ-(*S*)-**6a**, **8a** (Table 2, entry 7 and 8). This might be an effect of the sterically more demanding alkyl substituent in 4-position of the oxazoline moiety in the auxiliary which makes the ligand cleaved more easily from the diastereomer.

Finally, to verify the regioselectivity of the methylation step, we isolated the product of the methylation reaction with Λ-(*S*)-**9a** by column chromatography and subsequent anion metathesis as the PF_6 salt. Two-dimensional NMR experiments (HMBC) revealed a ^3J coupling between the methyl protons and the quaternary sp^2-hybridized carbon atom in 1-position of the aromatic system of the coordinated auxiliary ligand. Furthermore, the comparison of the NMR spectrum with data of a 1:1 diastereomeric mixture of complexes obtained from the reaction of racemic *cis*-$[Ru(bpy)_2Cl_2]$ with the corresponding thioether showed a match in chemical shifts for one set of signals. Additionally, HRMS confirms the presence of the sulfido complex Λ-(*S*)-**9a**.

It is worth mentioning that other methylating agents were also tested. Initially the diastereomerically enriched complex Λ-(*S*)-**6a** was treated with methyl iodide (5 equiv.) in acetonitrile at room temperature for 5 h. Subsequent addition of an excess of dmobpy (15 equiv.) and heating to 110 °C in a sealed vessel for 20 h resulted in formation of product as analyzed by TLC (Table 2, entry 9). However, the isolated yield was very low so no chiral HPLC analysis was performed to determine the enantiopurity of the product complex Λ-**15**. To increase the electrophilicity of methyl iodide (5 equiv.), silver hexafluorophosphate (10 equiv.) was added as an activating agent and the reaction was repeated under the same conditions. This time Λ-**15** was isolated in a yield of 39% and an *er* of 48:1 (Table 2, entry 10). To achieve higher conversion, trimethyloxonium tetrafluoroborate as an even stronger methylation electrophile was required. For comparison with the previously reported (*S*)-**Salox** system, we also tried to activate the auxiliary ligand using acid.[11] Accordingly, heating of complex Λ-(*S*)-**6a** in presence of trifluoroacetic acid (5 equiv.) and bpy (15 equiv.) in acetonitrile at 110 °C in a sealed vial (standard conditions for auxiliary cleavage) resulted in poor conversion (Table 2, entry 11). Even if the reaction time was increased to 12 h, Λ-**12** was isolated only in traces (TLC, HRMS).

Conclusions

In summary, we here introduced the (mercaptophenyl)-oxazolines (*S*)-**TS** and (*S*)-**TS′** which provide high stereochemical control of the metal-centered configuration of polypyridyl ruthenium complexes. Contrasting to previously reported acid-mediated methods, labilization of the auxiliary ligand was achieved by chemoselective methylation at the sulfur atom, thus converting it from a strong coordinating thiolate to a more labile thioether. Hence, in the presence of polypyridine ligands, the methylated auxiliary was susceptible to substitution under retention of configuration, resulting in the formation of tris(polypyridyl) ruthenium complexes with high enantiomeric purities. Thus, these thiol-based auxiliaries complement our previously developed chiral auxiliaries and expand the toolbox for the asymmetric synthesis of chiral ruthenium complexes.

Experimental Section

General Methods and Materials: All reactions were carried out under argon atmosphere using dried glassware. Stereoselective coordination chemistry was performed in the dark to avoid light-induced

decomposition or racemization. Chemicals were purchased from Sigma Aldrich, Alfa Aesar, or Acros Organics and used without further purification. L-Valinol[18] and [{Ru(η^6-C_6H_6)Cl(μ-Cl)}$_2$][19] were prepared according to published procedures. Solvents were dried with calcium hydride (acetonitrile, dichloromethane, DMF), sodium (toluene), or sodium/benzophenone (THF) and distilled freshly prior to use. Chlorobenzene (HPLC grade) was used without further drying. Column chromatography was performed on silica gel (230–400 mesh). Photolytic reactions were performed using a Heraeus UV Reactor System equipped with a mercury medium pressure lamp (UV immersion lamp TQ 150, 150 W), quartz cooling jacket and uranium filter. NMR spectra were recorded on a Bruker DPX 250 (250 MHz), Bruker Avance 300 (300 MHz), Bruker DRX 400 (400 MHz), or Bruker Avance 500 (500 MHz) spectrometer at 298 K. Infrared spectra were recorded on a Bruker Alpha FTIR instrument. High-resolution mass spectra were obtained with a Finnigan LTQ-FT instrument using electrospray mass ionization. CD spectra were recorded on a JASCO J-810 CD spectropolarimeter (200–600 nm, band width 1 nm, scanning speed 50 nm/min, accumulation of 5 scans, cell length 1 mm). Chiral HPLC chromatograms were obtained on an Agilent 1200 Series HPLC System using a Daicel Chiralpak IA or IB column (250 × 4.6 mm); solvent A: 0.1% TFA (aq), solvent B: acetonitrile (flow rate 0.5 mL/min, column temperature 40 °C, UV-absorption detected at 254 nm). Diastereomeric ratios were determined by ^{1}H NMR spectroscopy ($c \approx 35$ mM, NS = 1024) and enantiomeric ratios by chiral HPLC. See the Supporting Information for the synthesis and reactions of (*S*)-**TS′**.

2-Bromo-5-nitrobenzoyl Chloride: 2-Bromo-5-nitrobenzoic acid (**1**) (4.92 g, 20.0 mmol) was suspended in dichloromethane (100 mL). After addition of DMF (77 μL, 1.00 mmol) the suspension was cooled to 0 °C, oxalyl chloride (2.62 mL, 30.0 mmol) was added dropwise and stirring at 0 °C continued for another 30 min. The reaction mixture was warmed up to room temp. upon which the reaction mixture became clear and evolution of gas (HCl) was observed. The solution was stirred at room temp. for 4 h and evaporation of solvents afforded a pale yellow solid that was used directly for the synthesis of benzamide **2a**, **b** without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.86 (d, J = 2.6 Hz, 1 H), 8.27 (dd, J = 8.8, 2.6 Hz, 1 H), 7.95 (d, J = 8.8 Hz, 1 H) ppm. IR (film): $\tilde{\nu}$ = 3101, 1788, 1758, 1602, 1572, 1526, 1453, 1343, 1294, 1253, 1189, 1106, 1043, 994, 931, 912, 836, 736, 671, 641, 571, 474 cm^{-1}.

(2*S*)-2-Bromo-*N*-(1-hydroxy-3-methylbutan-2-yl)-5-nitrobenzamide (2a): To a solution of L-valinol (2.27 g, 22.0 mmol) in dichloromethane (75 mL), triethylamine (5.6 mL, 40.0 mmol) was added and cooled to 0 °C. 2-Bromo-5-nitrobenzoyl chloride (5.29 g, 20.0 mmol) in dichloromethane (60 mL) was added dropwise yielding a suspension. After warming up to room temp. stirring continued for another 4 h at room temp. The reaction mixture was diluted with dichloromethane (100 mL), washed with water, 0.2 M $NaHSO_4$ (aq.), water, $NaHCO_3$ (satd. aq.), and water (100 mL each). Solvents were evaporated in vacuo and recrystallization from ethanol/hexane afforded **2a** (6.05 g, 18.3 mmol, 92%) as colorless needles. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.35 (d, J = 9.0 Hz, 1 H), 8.19–8.14 (m, 2 H), 7.96 (dd, J = 8.5, 0.5 Hz, 1 H), 4.70 [t(dd), J = 5.7 Hz, 1 H], 3.81–3.72 (m, 1 H), 3.51–3.47 (m, 2 H), 1.91 (sept, J = 6.7 Hz, 1 H), 0.95 (d, J = 6.8 Hz, 3 H), 0.90 (d, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 165.3, 146.3, 140.7, 134.2, 126.7, 124.8, 123.3, 61.1, 56.6, 28.2, 19.7, 18.1 ppm. IR (neat): $\tilde{\nu}$ = 3395, 3254, 3089, 2963, 2876, 1644, 1607, 1555, 1526, 1462, 1391, 1345, 1066, 1033, 921, 831, 738, 494 cm^{-1}. HRMS: *m*/*z* calcd. for $C_{12}H_{14}BrN_2O_4$ (M – H)$^-$ 329.0142, found 329.0145.

(4*S*)-2-(2-Bromo-5-nitrophenyl)-4-isopropyl-4,5-dihydrooxazole (3a): To a suspension of benzamide **2a** (1.80 g, 5.44 mmol) in dichloromethane (55 mL) were added triethylamine (2.3 mL, 16.3 mmol), 4-toluenesulfonyl chloride (2.07 g, 10.9 mmol), and DMAP (66 mg, 0.54 mmol), and it was heated to reflux for 20 h. After addition of water (2 mL), reflux continued for 1 h. The yellowish solution was cooled down to room temp. and diluted with dichloromethane (20 mL). The organic layer was washed with water, 0.2 M $NaHSO_4$ (aq.), water, $NaHCO_3$ (satd. aq.), water (30 mL each), dried with Na_2SO_4, and solvents were evaporated in vacuo. Subsequent purification by column chromatography (hexane/ethyl acetate, 10:1) afforded **3a** (1.59 g, 5.06 mmol, 93%) as a slightly yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.55 (d, J = 2.7 Hz, 1 H), 8.12 (dd, J = 8.8, 2.8 Hz, 1 H), 7.84 (d, J = 8.8 Hz, 1 H), 4.54–4.45 (m, 1 H), 4.26–4.17 (m, 2 H), 1.92 (sept, J = 6.7 Hz, 1 H), 1.07 (d, J = 6.8 Hz, 3 H), 1.00 (d, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.8, 146.7, 135.1, 131.4, 129.3, 126.3, 125.6, 73.3, 70.8, 32.7, 18.7, 18.3 ppm. IR (film): $\tilde{\nu}$ = 3103, 3083, 2359, 2929, 2903, 2872, 1656, 1607, 1569, 1526, 1465, 1415, 1386, 1341, 1307, 1275, 1243, 1111, 1026, 960, 913, 859, 833, 803, 737, 663, 574, 498, 450 cm^{-1}. HRMS: *m*/*z* calcd. for $C_{12}H_{14}BrN_2O_3$ [M + H]$^+$ 313.0182, found 313.0184.

(4*S*)-2-(4-Isopropyl-4,5-dihydrooxazol-2-yl)-4-nitrobenzenethiol [(*S*)-TS]: (Bromoaryl)oxazoline **3a** (500 mg, 1.60 mmol) was dissolved in acetonitrile (20 mL), purged with argon for 30 min, and cooled down to 0 °C. Sodium sulfide trihydrate (254 mg, 1.92 mmol) was added in one portion and purging with argon continued for 15 min. The resulting suspension turned red slowly. The reaction mixture was stirred at 0 °C for 2 h and then at room temp. for 18 h. Hydrochloric acid (1 M) was added until pH = 1, the yellow suspension was poured into a dropping funnel attached to Schlenk-flask, and diluted with dichloromethane (250 mL). The organic layer was collected and solvents were evaporated in vacuo. The crude product was suspended in anhydrous toluene (30 mL) and filtered through a Schlenk frit (D4). The residue was washed with anhydrous toluene (4 × 5 mL) to afford a clear yellow solution. Evaporation of solvents at 40 °C yielded (*S*)-**TS** (383 mg, 1.44 mmol, 90%) as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 15.97 [s(br), 1 H], 8.64 (d, J = 2.6 Hz, 1 H), 7.88 (dd, J = 9.2, 2.7 Hz, 1 H), 7.71 (d, J = 9.2 Hz, 1 H), 4.92 [t(dd), J = 9.5 Hz, 1 H], 4.61 (dd, J = 9.3, 7.3 Hz, 1 H), 4.37 [dt(ddd), J = 9.7, 7.3 Hz, 1 H], 2.00 (sept, J = 6.8 Hz, 1 H), 1.12 (d, J = 6.7 Hz, 3 H), 1.06 (d, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.1, 171.2, 140.4, 137.7, 126.6, 124.2, 116.0, 72.9, 65.7, 32.4, 18.3 (2 C) ppm. IR (film): $\tilde{\nu}$ = 3095, 2962, 2876, 2615, 1628, 1591, 1543, 1460, 1321, 1290, 1211, 1119, 1052, 920, 837, 776, 733, 674, 604, 535, 487, 438 cm^{-1}. HRMS: *m*/*z* calcd. for $C_{12}H_{13}N_2O_3S$ (M – H)$^-$ 265.0652, found 265.0653.

Benzene Half-Sandwich Complex (*S*)-4a: [{Ru(η^6-C_6H_6)Cl(μ-Cl)}$_2$] (150 mg, 300 μmol) and (*S*)-**TS** (192 mg, 720 μmol) were suspended in acetonitrile (15 mL) and purged with argon for 30 min. Triethylamine (105 μL, 750 μmol) was added and the red suspension was stirred at room temp. for 4 h. The reaction mixture was centrifuged and the remaining red residue was washed with diethyl ether until the solution remained colorless (3 × 8 mL). The crude product was purified over a short silica gel column (10 cm, DCM/MeOH, 50:1 → 20:1). Solvents were evaporated in vacuo to afford complex (*S*)-**4a** (230 mg, 479 μmol, 80%) as a dark red solid. The reaction was performed in the dark and subsequent work-up and purification procedure under reduced light to avoid light-induced decomposition. ^{1}H NMR (300 MHz, CD_3CN): δ = 8.36 (d, J = 2.2 Hz, 1 H), 7.76 (dd, J = 9.1, 2.2 Hz, 1 H), 7.59 (d, J = 9.1 Hz, 1 H), 5.61 (s, 6 H), 4.72 [dt(ddd), J = 9.2, 3.1 Hz, 1 H], 4.62 (dd, J = 9.0,

3.3 Hz, 1 H), 4.43 [t(dd), *J* = 9.1 Hz, 1 H], 3.07–2.98 (m, 1 H), 1.06 (d, *J* = 7.2 Hz, 3 H), 0.77 (d, *J* = 6.6 Hz, 3 H) ppm. IR (neat): $\tilde{\nu}$ = 3067, 2958, 2870, 1613, 1591, 1551, 1494, 1452, 1380, 1320, 1241, 1124, 1098, 1051, 1004, 967, 912, 863, 824, 737, 674, 604, 530, 468 cm^{-1}. HRMS: *m*/*z* calcd. for $C_{18}H_{19}N_2O_3RuS$ $(M - Cl)^+$ 445.0159, found 445.0156.

Precursor Complex (*S*)-5a: A photolysis reactor equipped with a cooling jacket and an uranium filter was charged with acetonitrile (210 mL). The solvent was purged with nitrogen for 30 min, complex (*S*)-**4a** (225 mg, 470 μmol) was added, and the red solution was irradiated with a mercury medium-pressure lamp for 1 h while purging with nitrogen continued. Solvents were evaporated in vacuo to provide precursor complex (*S*)-**5a** (243 mg, 463 μmol, 98%) as a purple black solid. (*S*)-**5a** was used in diastereoselective synthesis experiments without further purification and should not be stored for longer than approximately two weeks (–20 °C under argon atmosphere) as decomposition occurs. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.68 (dd, *J* = 2.4, 0.4 Hz, 1 H), 7.72 (dd, *J* = 9.1, 2.3 Hz, 1 H), 7.67 (dd, *J* = 9.1, 0.4 Hz, 1 H), 5.30 [dt(ddd), *J* = 9.1, 3.9 Hz, 1 H], 4.42 (dd, *J* = 8.8, 4.1 Hz, 1 H), 4.29 [t(dd), *J* = 9.0 Hz, 1 H], 2.85 (dsept, *J* = 7.0, 3.1 Hz, 1 H), 2.46 (s, 3 H), 2.38 (s, 3 H), 2.29 (s, 3 H), 0.96 (d, *J* = 7.0 Hz, 3 H), 0.69 (d, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 160.2, 140.6, 134.1, 127.6, 121.7, 121.6, 121.3, 120.8, 120.6, 73.0, 66.2, 28.8, 18.8, 13.8, 4.8, 4.6, 4.5 ppm. IR (film): $\tilde{\nu}$ = 3452, 2964, 2919, 2872, 2275, 2212, 1591, 1542, 1482, 1378, 1305, 1274, 1236, 1176, 1125, 1093, 1050, 969, 916, 865, 807, 730, 672, 644, 613, 538, 485 cm^{-1}. HRMS: *m*/*z* calcd. for $C_{18}H_{22}N_5O_3RuS$ $(M - Cl)^+$ 490.0485, found 490.0478.

Diastereoselective Synthesis. General Procedure: To a 5 mM solution of precursor complex (*S*)-**5a**, **b** (1.0 equiv.) was added polypyridine ligand (2.5 equiv.). The dark purple solution was purged with argon for 30 min and heated to 110 °C. The reaction mixture was allowed to cool down to room temp., solvents were evaporated in vacuo, and the crude product was purified by column chromatography (MeCN → MeCN/H_2O/satd. aq. KNO_3 300:3:1). After evaporation of solvents, the residue was redissolved in a minimum amount of ethanol/water, precipitated by addition of NH_4PF_6 (satd. aq.), and water was added to 12 mL. The suspension was centrifuged and the black precipitate was washed with water (2 × 10 mL) and dried under high vacuum to yield the diastereomeric complex as a black solid.

Λ-(*S*)-6a: According to the general procedure for diastereoselective synthesis, (*S*)-**5a** (150 mg, 286 μmol) was treated with 2,2′-bipyridine (112 mg, 714 μmol) in chlorobenzene (57 mL) for 3 h to afford Λ-(*S*)-**6a** (146 mg, 177 μmol, 62%) with a *dr* of 59:1. ^{1}H NMR (500 MHz, CD_3CN) (signals of major diastereomer listed only): δ = 9.57 (d, *J* = 5.4 Hz, 1 H), 8.69 (d, *J* = 5.5 Hz, 1 H), 8.66 (d, *J* = 2.5 Hz, 1 H), 8.51 (d, *J* = 8.1 Hz, 1 H), 8.41 (d, *J* = 8.2 Hz, 1 H), 8.38 (d, *J* = 8.1 Hz, 1 H), 8.26 (d, *J* = 8.1 Hz, 1 H), 8.12 [dt(ddd), *J* = 8.0, 1.4 Hz, 1 H], 8.01 [t(dd), *J* = 7.8 Hz, 1 H], 7.92 [dt(ddd), *J* = 8.0, 1.4 Hz, 1 H], 7.82 (d, *J* = 5.3 Hz, 1 H), 7.79 [dt(ddd), *J* = 8.2, 1.2 Hz, 1 H], 7.72 (dd, *J* = 9.0, 1.9 Hz, 1 H), 7.61–7.58 (m, 2 H), 7.52 (d, *J* = 9.0 Hz, 1 H), 7.30–7.27 (m, 2 H), 7.14–7.11 (m, 1 H), 4.52–4.48 (m, 2 H), 4.02–4.00 (m, 1 H), 0.23–0.18 (m, 4 H), 0.08–0.07 (m, 3 H) ppm. ^{13}C NMR (125 MHz, CD_3CN) (signals of major diastereomer listed only): δ = 163.3, 159.0, 158.3, 153.2, 152.4, 151.9, 151.5, 138.0, 137.9, 137.8, 137.2, 137.1, 136.3, 136.3, 128.0, 127.8, 127.5, 127.0, 125.0, 124.7, 124.6, 124.2, 123.9, 122.0, 75.9, 67.9, 30.4, 18.3, 13.2 ppm. IR (film): $\tilde{\nu}$ = 3076, 2963, 1587, 1544, 1487, 1449, 1380, 1306, 1270, 1234, 1127, 1091, 1050, 965, 837, 761, 732, 701, 669, 611, 555, 482, 425 cm^{-1}. CD (MeCN, 0.2 mM): λ/nm ($\Delta\varepsilon$/$M^{-1}cm^{-1}$) 221 (–13), 235 (+6), 283 (–36), 298 (+104), 391 (–10), 465 (+9), 514 (–4). HRMS: *m*/*z* calcd. for $C_{32}H_{29}N_6O_3RuS$ $(M - PF_6)^+$ 679.1066, found 679.1059.

Auxiliary Removal. General Procedure: An oven dried argon-flushed brown glass vial was charged with diastereomeric complex (1.0 equiv.) in dichloromethane (50 mM). Trimethyloxonium tetrafluoroborate (2.0 equiv.) was added, the vessel was sealed, and the suspension was stirred at room temp. for 3 h. Solvents were evaporated in vacuo. The residue was redissolved in acetonitrile (100 mM) and polypyridine ligand (15 equiv.) was added. The atmosphere in the vessel was exchanged by purging with argon and the sealed vial was heated to 110 °C (oil bath temperature). Evaporation of solvents followed and the sample was washed with small portions of diethyl ether (15 mL total). Purification by column chromatography (MeCN → MeCN/H_2O/satd. aq. KNO_3 50:3:1) and evaporation of solvents followed. The orange residue was redissolved in a minimum amount of ethanol/water (Λ-**12**–**14**) or water (Λ-**15**–**17**) and precipitated by addition of solid NH_4PF_6. Water was added to 10 mL and the suspension was centrifuged. The orange precipitate was washed with water (3 mL and 1 mL) and dried under high vacuum to afford the enantiomerically enriched polypyridyl ruthenium complex as an orange solid.

Λ-12: According to the general procedure for auxiliary removal, Λ-(*S*)-**6a** (20.0 mg, 24.3 μmol) was treated with trimethyloxonium tetrafluoroborate (7.2 mg, 48.6 μmol) in dichloromethane (490 μL). After evaporation of solvents, the residue was redissolved in acetonitrile (245 μL), 2,2′-bipyridine (57 mg, 365 μmol) was added, and heating for 24 h followed. Subsequent purification afforded Λ-**12** (14.2 mg, 16.5 μmol, 68%) with an *er* of 43:1. ^{1}H NMR (300 MHz, CD_3CN): δ = 8.50 (d, *J* = 8.2 Hz, 6 H), 8.05 (dt, *J* = 7.9, 1.4 Hz, 6 H), 7.73 (d, *J* = 5.3 Hz, 6 H), 7.39 (ddd, *J* = 7.2, 5.7, 1.2 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 157.9, 152.6, 138.7, 128.5, 125.2 ppm. IR (film): $\tilde{\nu}$ = 1604, 1445, 1312, 1268, 1165, 880, 833, 756, 731, 555, 418 cm^{-1}. CD (MeCN, 0.1 mM): λ/nm ($\Delta\varepsilon$/$M^{-1}cm^{-1}$) 219 (–38), 230 (–7), 239 (–27), 256 (+11), 277 (–146), 291 (+331), 321 (–20), 466 (+16). HRMS: *m*/*z* calcd. for $C_{30}H_{24}N_6Ru$ $(M - 2PF_6)^{2+}$ 285.0551, found 285.0547; *m*/*z* calcd. for $C_{30}H_{24}F_6N_6PRu$ $(M - PF_6)^+$ 715.0750, found 715.0731. HPLC: Daicel Chiralpak IA column, 15–30% B in 20 min: $t_{R(\Delta\text{-}12)}$ = 17.13 min ($A_{\Delta\text{-}12}$ = 50.19), $t_{R(\Lambda\text{-}12)}$ = 17.79 min ($A_{\Lambda\text{-}12}$ = 2150.04).

Supporting Information (see footnote on the first page of this article): Additional experimental procedures and analytical data including the synthesis and reactions with (*S*)-**TS′**.

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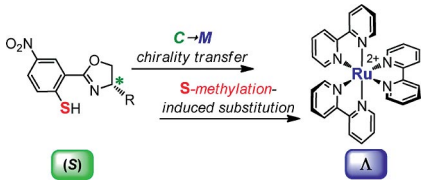
Asymmetric Coordination Chemistry

(Mercaptophenyl)oxazolines were used as chiral auxiliaries for the asymmetric synthesis of polypyridyl ruthenium complexes. Key step was the conversion of a coordinated thiolate into a labilized thioether upon methylation with Meerwein salt, followed by a thermal substitution with an achiral ligand under retention of configuration.



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