Tricyclic Sulfoxide–Alkene Hybrid Ligands for Chiral Rh(I) Complexes: The ‘Matched’ Diastereomer Catalyzes Asymmetric C–C Bond Formations.

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Abstract
Deprotonation of phenyl-dibenzo[b,f]tropolidene 8 with LDA/t-BuOK followed by quenching with either diastereomers of inexpensive glucose-based t-Bu-sulfinates (R)- or (S)-11 affords a sulfoxide-alkene hybrid ligand as diastereomeric pairs (S_s,S_c)-9 / (S_s,R_c)-10 and (R_s,R_c)-9 / (R_s,S_c)-10, respectively, which via chromatographic/recrystallization may be separated into the four isomers. The optically pure diastereomeric ligands (S_s,S_c)-9 and (S_s,R_c)-10 react with [RhCl(coe)_2]_2 to form the dinuclear complexes (R_s,S_c)-11 and (R_s,R_c)-12, respectively, in which the bidentate ligands coordinate the metal centers through the sulfur and alkene donor functions. These complexes catalyze the conjugate addition of arylboronic acids to cyclic Michael acceptors with enantioselectivities of up to 99% ee. DFT calculations show the preponderant influence of planar chirality of the ligand alkene function. The enantioselectivity switch observed between (R_s,S_c)-11 and (R_s,R_c)-12 is explained by the inverted cis-trans coordinations of the substrate molecules in catalytic steps.
Introduction

The development of new ligand designs for chiral metal complexes is paramount for the advancement of asymmetric catalysis.¹ For some time, we have been interested in hybrid P-alkene ligands such as 1 and 2 based on the tricyclic dibenz[b,f]azepine scaffold (see Table 1).² The azepine-alkene function has been proven to be hemilabile,³ a property imparting metal catalysts even with a L:M stoichiometry of 2:1 such as [Rh(I)₂][BF₄]⁴ and [Ir(I)₂Cl]⁵ high selectivity, activity, and stability. Apart from P-alkene ligands, chiral bis-alkenes,⁶ bis-sulfoxides,⁷ and in particular S(O)-alkene⁸ hybrids have emerged as ligands of choice for the asymmetric Hayashi-Miyaura reaction.⁹ The ease of synthesis and high stability of enantiopure sulfoxides and the recent finding that polarized R₂S⁺–O⁻ ligand functions appear to induce chirality also through electrostatic effects¹⁰ prompted us to extend the S(O)-alkene ligand architecture to tricyclic systems. Inspired by Knochel’s highly effective sulfoxide-alkene ³¹¹ and Liao’s stereoselectivity-switching S(O)-alkenes (both planar-chiral systems),¹² we recently disclosed the planar-chiral sulfonamide 4.¹³ Since this ligand proved stereochemically stable only at specific pH values, we were interested in replacing the sulfonamido S–N bond¹⁴ with the more robust sulfoxide S–C bond of the dibenzo-tropylidene analogue (i.e. replacing the N atom with a C–H moiety, see Table 1).¹⁵ Here, we describe a simple protocol for the stereodivergent synthesis of this new class of enantiopure, tricyclic sulfoxide-alkene ligands, which are a nice bidentate fit for Rh(I). We show that the rhodium complex of the matched ligand diastereomer¹⁶ is a highly selective catalyst for the asymmetric Hayashi-Miyaura reaction and provide mechanistic insight and a stereochemical model by DFT calculations.

Table 1. Inspiring chiral P-alkene and S-alkene ligands and the targeted tricyclic sulfoxide-alkene
**Results and discussion**

Exploring ways to construct the C–S bond of the sought after sulfoxide-tropylidene analogue of 4 we soon found out that common sulfinate electrophiles reacted cleanly only with *in situ* deprotonated phenyl-dibenzo[a,d]tropylidene 8 (at C9, see Scheme 1), while the use of more straightforward Grignard or lithium nucleophiles obtained from phenyl-dibenzo[a,d]tropylidenyl chloride invariably led to impure products. However, the limited scalability of published synthetic routes to 8\(^7\)\(^\text{17}\) prompted us to develop a 50 g scale Suzuki coupling of phenylboronic acid with the bromo alkene precursor 5.\(^8\)\(^\text{18}\) De-protection and reduction of product 6 routinely yields 20 g quantities of white crystalline 8 with a high melting point. In the crystal, 8 is a planar-chiral racemate with a boat-shaped tropylidene moiety while in solution at room temperature it inverts rapidly *via* a planar transition state with a DFT-calculated barrier of 13.1 kcal/mol.\(^9\)

**Scheme 1.** Multi-gram synthesis of 8 and its planar-chiral structure in the crystal

(i) PhB(OH)$_2$ (1 equiv), Pd(PPh$_3$)$_4$ (5 mol%), DME, reflux, 18h; (ii) HCl, THF, reflux 72h; (iii) AlCl$_3$, LiAlH$_4$, Et$_2$O/THF, reflux, 16h; Crystal structure of 8 (50% displacement ellipsoids, H atoms omitted). Selected distances (Å) and angles (º): C(1)–C(2) 1.3465(19), C(1)–C(2)–C(3) 128.71(13), C(2)–C(1)–C(15) 123.68(12), C(8)–C(9)–C(10) 110.97(11).

Before tackling the asymmetric synthesis of the ligand, its racemic form was isolated: Reacting deprotonated 8 with *rac*–tBu-S(O)Cl affords the diastereomeric pairs *rac*-9 + *rac*-10 because of the stereogenic benzyl C-atom.\(^10\) The isomers turned out to be readily separable by enantioselective HPLC (see Scheme 2), which indicated that stereochemically stable molecules should be amenable to
asymmetric synthesis. Indeed, deprotonation of 8 with LDA/KO\textsubscript{t}Bu\textsuperscript{21} followed by \textit{in situ} quenching at −78 °C with inexpensive glucose-derived sulfinate (R)-11\textsuperscript{22} in THF gives the alkene-sulfoxides (S\textsubscript{S},S\textsubscript{C})-9 and (S\textsubscript{S},R\textsubscript{C})-10 in a \textit{ca.} 5:3 diastereomeric mixture\textsuperscript{23} (see Scheme 3). The diastereomers are separated by Flash column chromatography/crystallization\textsuperscript{24} and isolated on gram scales and in excellent optical purity (verified by HPLC, see Figures S4 and S5 given as Supplementary Information). (S\textsubscript{S},S\textsubscript{C})-9 and (S\textsubscript{S},R\textsubscript{C})-10 are best identified by the characteristic singlet resonances of the \textit{t}-Bu-groups at 1.24 ppm and 1.19 ppm in their respective \textit{\textsuperscript{1}H} NMR spectra. The ligands do not epimerize in C\textsubscript{6}D\textsubscript{6} solution under prolonged heating at 60 °C.

**Scheme 2.** Symmetric synthesis of the \textit{t}-Bu-sulfoxide-alkene ligand giving rise to diastereomeric pairs of enantiomers \textit{rac}-9 + \textit{rac}-10 in a \textit{ca.} 1:1 ratio and their separation by chiral stationary phase HPLC. Trace shows area / retention times in minutes. Absolute configurations were assigned by single crystal XRD analysis of optically pure ligands, \textit{vide infra} and SI. Conditions: Daicel Chiralpak AD-H; flow rate: 0.7 mL/min; \textit{n}-hexane/\textit{i}-PrOH = 8:2.

In order to gain precise structural information for unambiguous assignment of the absolute configurations of the stereocenters in 9 and 10 and for identifying the HPLC peaks in Scheme 2, single crystal X-ray diffraction analyses were performed. The molecular structures are depicted in Figure 1 and confirm the expected (S)-configured sulfur atoms (C–S bond formation takes place with inversion of configuration) and, most importantly, reveal the absolute configurations of the carbon stereocenters, which are (S) and (R), respectively. The stereogenic sulfur and carbon atoms are pyramidal with average bond angles of 104.6° and 110.9° for 9 and 104.5° and 110.6° for 10, respectively. On the other hand, the phenyl substituted atoms C9 and C8 are perfectly trigonal planar in both structures (averaged
bond angles of 120.0°). As a proof of principle that all four stereoisomers may be accessible, the anion of 8 was also reacted with the (S)-11 diastereomer of the DAG-sulfinate to afford diastereomers (R₅,R₆)-9 and (R₅,S₆)-10 (Scheme 3). The crystal structure of (R₅,R₆)-9 is indeed the enantiomorph of (S₅,S₆)-9 (see Figure S7 in the Supporting Information) showing consistent stereochemistry and further confirming HPLC peak assignment.

**Scheme 3.** Stereodivergent syntheses of the diastereomeric S(O)-alkenes 9 and 10.
Figure 1. Molecular structures of \((S,S,C)-9\) (top) and \((S,R,C)-10\) (bottom) in the respective chiral crystals (50\% displacement ellipsoids, H atoms are omitted except on C1). Selected distances (Å) and angles (º) for \((S,S,C)-9\): S1–O1 1.4983(17), S1–C1 1.894(3), S1–C22 1.856(3), C8–C9 1.353(3), C9–C16 1.499(4), C22–S1–C1 101.82(11), O1–S1–C1 106.73(11), O1–S1–C22 105.15(11), C2–C1–S1 110.63(16), C8–C9–C16 116.6(2), C2–C1–C15 116.0(2); for \((S,R,C)-10\): S1–O1 1.5006(13), S1–C1 1.8714(17), S1–C16 1.8534(17), C8–C9 1.347(2), C8–C20 1.491(2), C16–S1–C1 100.32(8), O1–S1–C1 106.74(11), O1–S1–C16 114.0(2); for \((S,R,C)-10\): S1–O1 1.5006(13), S1–C1 1.8714(17), S1–C16 1.8534(17), C8–C9 1.347(2), C8–C20 1.491(2), C16–S1–C1 100.32(8), O1–S1–C1 106.74(11), O1–S1–C16 114.0(2); for \((S,R,C)-10\): S1–O1 1.5006(13), S1–C1 1.8714(17), S1–C16 1.8534(17), C8–C9 1.347(2), C8–C20 1.491(2), C16–S1–C1 100.32(8), O1–S1–C1 106.74(11), O1–S1–C16 114.0(2); for \((S,R,C)-10\): S1–O1 1.5006(13), S1–C1 1.8714(17), S1–C16 1.8534(17), C8–C9 1.347(2), C8–C20 1.491(2), C16–S1–C1 100.32(8), O1–S1–C1 106.74(11), O1–S1–C16 114.0(2).
The coordination behavior of (S,S,C)-9 and (S,R,C)-10 with Rh(I) was assessed by reacting two equivalents of the respective ligands with [RhCl(coe)₂]₂ (coe = cyclooctene) in benzene or toluene solution to yield almost quantitatively dinuclear complexes (R,S)-11 and (R,R)-12 as yellow-orange powders (Scheme 4). The complexes are soluble in CH₂Cl₂ but much less so in aromatic solvents. NMR spectra of complex 11 in CD₂Cl₂ solution show a mixture of syn/anti isomers in a 1:2 ratio, while complex 12 forms exclusively as the anti-isomer. The perfect anti-selectivity of ligand 10 in the synthesis of complex 12 parallels its superior enantioselectivity in catalysis (vide infra) and the strong diastereoselective interaction with the chiral stationary phase in HPLC separation causing a large difference in retention times (Scheme 2, vide supra). Single crystal X-ray diffraction analyses of the complexes confirm the bidentate coordination mode of the S-alkene ligands and show square planar coordination geometries around the chloro-bridged Rh-centers (see Figures 2 and 3). The butterfly-shaped Rh₂Cl₂ cores in 11 and 12 span wing angles of 120.4º and 167.5º, respectively. Exclusive anti-coordination is observed in both crystals. In both complexes, the trans influences exerted by the alkene vs. S-donors differ significantly: Rh–Cl distances trans to the S atoms are 0.06–0.08 Å longer than the corresponding bonds trans to the alkene donors. The bite angles of the ligands, measured between the centroids of the alkene functions and the S donors, are very similar at 93.7º in 11 (average value of two independent ligands) and 94.5º in 12. The coordinated alkene bonds (C9—C8 1.432(9), C34—C33 1.434(9) in 11; C7—C8 1.429(11) in 12) are ca. 0.08 Å longer than those in the respective free ligands 9 and 10 (1.353(3) and 1.347(2) Å, see Figure 1), and the C atoms bearing the phenyl substituents are slightly pyramidalized (sum of angles between C–C bonds are in the range of 354.1–355.1º). These observations reflect metal to alkene π-backbonding. Furthermore, the Rh–C distances to the phenyl-substituted C-atoms are on average 5 pm (for 11) and 8 pm (for 12) longer than the distances to the unsubstituted C-atoms.
**Scheme 4.** Synthesis of dinuclear Rh(I) complexes bearing ligands 9 and 10

\[
(S_{S,S})-9 + \text{[RhCl(coe)\textsubscript{2}]} \rightarrow (S_{S,R})-10, 97% \]

\[
\text{[RhCl(coe)\textsubscript{2}]} + (R,R)-11, 97% \rightarrow \text{[RhCl(coe)\textsubscript{2}]} + (R,R)-12, 97%
\]

**Figure 2.** Molecular structure of \textit{anti-}(R,S)-11 in the chiral crystal (50% displacement ellipsoids, H atoms are omitted). Selected distances (Å) and angles (º): Rh1—S1 2.1670(15), Rh1—Cl1 2.3777(15), Rh1—Cl2 2.4535(15), Rh1—C9 2.118(6), Rh1—C8 2.167(6), Rh2—Cl1 2.4414(15), Rh2—Cl2 2.3603(15), Rh2—C34 2.109(6), Rh2—C33 2.150(6), C9—C8 1.432(9), C34—C33 1.434(9), S1—O1 1.485(4), S1—C1 1.842(6), S1—C22 1.875(6).
Figure 3. Molecular structure of (R,R)-12 in the chiral crystal (50% displacement ellipsoids, H atoms are omitted). Selected distances (Å) and angles (°): Rh1–Cl1 2.4305(16), Rh1—Cl1A 2.3723(16), Rh1–C8 2.109(7), Rh1–C9 2.192(7), Rh1–S1 2.1590(17), S1–O1 1.481(5), S1–C1 1.846(7), S1–C22 1.880(7), C8–C9 1.429(11), C9–C16 1.482(10), Rh1A–C11–Rh1 98.68(6), S1–Rh1–Cl1A 92.56(6), C8–Rh1–Cl1 89.2(2), C9–Rh1–Cl1 93.96(19).

With well-characterized optically pure complexes 11 and 12 in hand, their performance in asymmetric catalysis was benchmarked in the Hayashi-Miyaura conjugate addition of arylboronic acids to enones (see Table 1). Standard reaction conditions consisted of a 1,4-dioxane/H₂O solvent system, Cs₂CO₃ additive, 40 °C, and a 3 mol% catalyst loading to ensure complete conversions (>95% isolated yields; optimization of catalyst activity was not a priority in this study).²⁸ Even though catalysts (R,S)-11 and (R,R)-12 bear identically configured sulfur donor atoms, entries 1 and 2, 4 and 5, and 14 and 15 reveal a preference for opposed configurations in the addition products. Clearly, the opposite planar chirality of the coordinated alkene functions that characterizes the two complexes is the overwhelming factor that determines the stereochemical outcome in these reactions. Additionally, complex (R,R)-12 displays vastly superior enantioselectivity, which identifies ligand 10 as the ‘matched’ ligand diastereomer with the two stereocenters working in synergy. The observation that enantioselection is predominantly governed by the planar chirality of the coordinated alkene function (and not the chirality of the S donor) has previously been made by Knochel and co-workers,¹¹ Liao and co-workers,¹² and by ourselves¹³ with similar S(O)-alkene ligand systems. In general, while catalyst 12 gives satisfactory enantioselectivities in additions of aryl nucleophiles to cyclohexenone, it compares favorably with the best S(O)-alkene ligands for additions to cyclopentenone and dihydropyranone.
Table 2. Catalytic performance of complexes 11 and 12 in the Hayashi-Miyaura conjugate addition reaction.

![Image](https://via.placeholder.com/150)

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In order to get a precise mechanistic picture of this reaction and to rationalize the disparate enantioselectivities observed for catalysts 11 and 12 (entries 1 and 2, 4 and 5, 14 and 15 in Table 2), the prototypical reaction of cyclohexenone 14a with phenylboronic acid 15a was investigated by DFT calculations. The first step of the catalytic cycle is well established and consists in transmetallation of the phenyl nucleophile from the boronic acid to the metal affording the nucleophile–rhodium intermediate (A in Figure 4).29 Starting from this species, set as zero point energy, the cyclohexenone electrophile presents its re or si face to the Rh–Ph bond via a [2+2] transition state leading to the (R)- or (S)-configured ketone, respectively, after hydrolysis. We focused on the coordination/insertion step affecting the enantioselectivity of the reaction. The energy profiles for 11 and 12 in Figure 4 show that phenyl coordination trans to the π-accepting alkene donor is favored in both cases (11-A and 12-A) while the alternative species A1 with the phenyl groups lying trans to the sulfoxide ligand are approximately 7 kcal/mol higher in energy. The approach of the enone to A occurs trans to the sulfoxide ligand via transition state A-B with an energy barrier of 8.8 and 5.0 kcal/mol for 11 and 12, respectively. From intermediate B the two catalysts behave differently: in the case of 11, the system prefers first to isomerize to the lower energy intermediate B1 with the phenyl cis to the alkene ligand, thereby gaining 5.0 kcal/mol, and then to insert via transition state B1-C, rather than to insert directly from B. In fact, both the B→B1 cis/trans isomerization barrier (12.6 kcal/mol calculated from A) and the following insertion barriers (16.5 and 19.0 kcal/mol leading to the (R) and (S)-configured products, respectively), are lower than the direct insertion barriers from B (18.4 and 20.7 kcal/mol for (R) and (S)-configured products, respectively), due to a strongly distorted square planar geometry of the corresponding transition states ascribed to steric repulsions between the ligand phenyl ring and the phenyl nucleophile. The free energy difference between the two competing transition states of 2.5 kcal/mol in favor of pro-(R) B1-C for 11 implies predominant insertion of the re face of the enone to

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<tr>
<td>30</td>
<td>(R&lt;sub&gt;s&lt;/sub&gt;,R&lt;sub&gt;c&lt;/sub&gt;)-12</td>
<td>14c</td>
<td>2-naph (15h)</td>
<td>16ch</td>
<td>94</td>
<td>(S)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Commercial aryl boronic acids were used as received. <sup>b</sup> Determined by enantioselective HPLC (see Supporting Information). <sup>c</sup> Absolute configurations are assigned by comparison with reported data. <sup>d</sup> Toluene instead of dioxane used. <sup>e</sup> Assumed configurations
the \((R)\)-product, in agreement with experiments. In the case of catalyst 12, on the contrary, the favored insertion step occurs from 12-B with the phenyl \textit{cis} to the sulfoxide ligand and with energy barriers of 14.9 and 10.6 kcal/mol for the \((R)\) and \((S)\)-configured products, respectively. The free energy difference between the two competing transition states of 4.3 kcal/mol in favor of pro-\((S)\) B-C explains the observed high enantioselectivity for the \((S)\)-product. The alternative pathway seeing the phenyl group \textit{trans} to the sulfoxide ligand was ruled out because it has higher energy barriers of 15.5 and 17.4 kcal/mol for \((R)\) and \((S)\)-configured products, respectively (see Figure S40 in the Supporting Information section for a detailed discussion). It is worth to note that the opposite \textit{cis}/\textit{trans} arrangements of the phenyl and enone substrate molecules in the favored intermediates and transition states for 11 and 12 are the result of steric effects of the opposite planar chirality of the phenyl-alkene ligand function. Thus, the theoretical comparison between the two catalysts is in nice agreement with experiments (even though the respective absolute \(\Delta G^\circ_{\text{re-si}}\) values are somehow overestimated by the calculations): The enantioselectivity of 12 in favor of the \((S)\)-configured insertion product is almost 2 kcal/mol higher than that displayed by 11 in favor of the \((R)\)-product.

![Figure 4](image-url)  

**Figure 4.** Energy profiles for the insertion step of the Hayashi-Miyaura conjugate addition of cyclohexanone and phenylboronic acid in presence of 11 (in blue) and 12 (in red). Free energies are in kcal/mol in 1,4-dioxane solvent.
Analysis of the favored transition state geometries 11 pro-(R) B1-C and 12 pro-(S) B-C in Figure 5 (top left and bottom right structures) highlights the cyclohexenone ring carbons placed in rather open space, anti to the S–t-Bu and the alkenyl phenyl groups, respectively. In contrast, the disfavored transition states 11 pro-(S) B1-C and 12 pro-(R) B-C are destabilized by steric repulsion between the cyclohexenone ring and ligand donor functions. In 11, enantio-differentiation of the cyclohexenone ring occurs by interaction with only one carbon atom of the cis-positioned S–t-Bu group with the planar-chiral phenyl-alkene ligand function trans to the enone having no influence (see Figure 5, top right). In 12, the cyclohexenone ring is cis to the phenyl-alkene ligand and, thus, this function becomes the determining steric factor with multiple steric clashes at short distances between the cyclohexenone and the ligand phenyl group (see Figure 5, bottom left).

Figure 5. Optimized geometries of the insertion transition states with 11 (top) and 12 (bottom).

Figure 6 schematically summarizes the differences between the two catalysts in the enantioselective insertion step and shows the steric maps around Rh calculated by the SambVca software. The maps
allow to rationalize the results discussed above in function of the symmetry of the catalytic pocket. In both cases, the phenyl group of the alkene donor of the ligand causes more encumbrance (northwest (NW) and southwest (SW) quadrants for 11 and 12, respectively) than the S–t-Bu donor (orange contours in the southeast quadrants (SE) denote one out of three methyl groups, which in solution rotate freely). The coordination environment for 11 (left diagram) is quasi-C$_2$ symmetric, while for 12 (right diagram) is quasi-C$_s$ symmetric, with both ligand donors obstructing the south quadrants.$^{32}$ As a consequence, with 12, the pro-(S) enantiospecific coordination of the enone is more forced than with 11 in order to avoid the clash of the cyclohexanone ring with the highly hindered alkene ligand in the SW quadrant (compare the substrate schemes in Figure 6c and the hindered quadrants in the maps).

**Figure 6.** a) Stereochemical model (top view) for the prediction of the sense of addition of 14a to 13a when using ligand $(S,S)$-9 (left) or ligand $(S,R)$-10 (right). b) Steric maps of the respective Rh(I) complexes $(R,S)$-11 and $(R,R)$-12 from crystallographic data. The steric maps are viewed down the z-axis; the orientation of the complexes is indicated on the left. Metal atoms, H atoms, and secondary ligands were excluded in the calculations. Sphere radii are 3.5 Å, and Bondi radii are scaled at 1.17. The isocontour scheme, in Å, is shown in the middle. Red and blue zones indicate the more and less hindered zones in the catalytic pocket, respectively. c) Ball-and-stick representation of the $(R)$ and $(S)$-configured product formations as in the favored transition states reported in Figure 5.
Conclusion

The stereoselective, divergent synthesis of the four possible isomers of a new tricyclic sulfoxide-alkene hybrid ligand has been demonstrated. Diastereomers 9 and 10 are excellent bidentate ligands for Rh(I), and the respective isolated complexes 11 and 12 catalyze the asymmetric Hayashi-Miyaura reaction. The superior enantioselectivity displayed by complex 12 bearing the ‘matched’ ligand diastereomer \((S,S,R,C)-10\) and the reversal and lowering of chiral induction observed with complex 11 bearing ligand diastereomer \((S,S,S,C)-9\) (with the sulfur donor of identical chirality as ligand \((S,S,R,C)-10\)) is explained by DFT calculations. 11 and 12 promote similar catalytic cycles with enantioselection occurring in the insertion step, with the difference that the favored insertion transition states in 11 and 12 present opposite cis/trans arrangements of the enone/phenyl substrates with respect to the ligand sulfur and alkene donors. We conclude that in electronically dissymmetric S-alkene ligand systems sterics and electronics (leading to trans effects in the square planar Rh(I) intermediates) are operative in the Hayashi-Miyaura reaction, and that ligand geometries that create quasi-\(C_2\) coordination environments on Rh should be avoided. This is in contrast to well established electronically and \(C_2\)-symmetric bis-alkene, bis-sulfoxide, and bis-phosphine systems. Finally, the remarkable enantioselectivities achieved with ligand 10 in its prototype version for the Hayashi-Miyaura reaction bodes well for other applications, not least because the simple synthetic protocol for this ligand is amenable to modification for steric and electronic optimization at both donor functions.

Experimental part

Experiments involving sensitive compounds were carried out under anaerobic and anhydrous conditions, using standard Schlenk and inert gas glove box techniques. Technical grade EtOAc and hexanes for flash column chromatography were purified by rotary evaporation. THF, Et\(_2\)O, and benzene were distilled from purple Na/Ph\(_2\)CO solutions, toluene from Na, pentane, C\(_6\)D\(_6\), and THF-D\(_8\) from Na\(_2\)K alloy, CH\(_3\)CN, CH\(_2\)Cl\(_2\), and CD\(_2\)Cl\(_2\) from CaH\(_2\), NEt\(_3\) and 1,4-dioxane from K. CD\(_3\)CN and CDCl\(_3\) were degassed with three freeze-pump-thaw cycles and then kept in a glove box over activated molecular sieves (3 and 4 Å, respectively). Arylboronic acids, LDA (purchased from Sigma-Aldrich), and DME (from TCI) were used as received. \(5^{,18}\) \((R)_5\)- and \((S)_5\)-1,2:5,6-Di-O-isopropylidene-\(\alpha\)-D-glucofuranosyl tert-butylsulfinate \((R)-11\) and \((S)-11\)\(^{,34}\) PhLi\(^{,35}\) \([RhCl(coe)]_2\)\(^{,36}\) tert-butanesulfinyl chloride\(^{,37}\) were prepared according to published procedures. LiAlH\(_4\) (Sigma-Aldrich) was extracted in Et\(_2\)O and used as snow-white crystalline powder. Elemental analyses (EA) were performed on a Euro
EA 3000 analyzer, and air-sensitive samples were handled and prepared in a glove box. NMR spectra were recorded on Jeol EX 270, ECP 400 or ECX 400 instruments operating at 269.71, 399.78, and 400.18 MHz for $^1$H; 67.82, 100.52, and 100.62 MHz for $^{13}$C; and at 161.83 and 162.00 MHz for $^{31}$P, respectively. Chemical shifts are given in ppm and are reported relative to residual solvent peaks as secondary standard. $^{38}$ Jeol’s Delta NMR Processing and Control Software was used to process and visualize the NMR data. $^{39}$ HPLC was performed on a Shimadzu LC10 series instrument.

**10-Phenyl-5,5-ethylenedioxy-5H-dibenzo[a,d]cycloheptene (6):** 5 (55.0 g, 168 mmol), phenylboronic acid (24.4 g, 197 mmol), and Pd(PPh$_3$)$_4$ (5.58 g, 4.80 mmol), degassed DME (1.38 L), and Na$_2$CO$_3$ (26.2 g, 247 mmol, 2 M in H$_2$O, 123.75 mL) were charged into a Schlenk vessel and the reaction mixture heated to reflux for 40 h. After cooling to room temperature CH$_2$Cl$_2$ (500 mL) and water (300 mL) were added. The organic phase was separated and the aqueous phase extracted with methylene chloride (3 x 150 mL). The combined organic phases were dried over anhydrous Na$_2$SO$_4$ and evaporation of the solvent provided solid crude 5, which was slurried in pentane (500 mL), filtered, and washed with additional pentane (3 x 150 mL) to yield a yellow solid (52 g, 95%). Mp: 145°C. EA (%): C 84.86, H 5.60; Calcd for C$_{23}$H$_{18}$O$_2$: C 84.64, H 5.56. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.92 – 7.86 (m, 2H, ArH), 7.52 – 7.17 (m, 12H, ArH), 4.25 (t, $^3$J$_{H,H}$ = 8.0 Hz, 2H, OC$_2$H$_2$R), 3.84 – 3.74 (m, 2H, OCH$_2$R) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$): δ 144.2, 143.4, 140.3, 139.3, 134.8, 133.4, 130.3, 129.5, 129.4, 129.1, 128.3, 128.1, 127.5, 127.3, 127.1, 123.5, 123.3, 106.5, 64.8, 64.2 ppm.

**10-Phenyl-5H-dibenzo[a,d]cycloheptene-5-one (7):** Aqueous HCl (0.56 L, 6.0 M, 3.4 mol) was added to a solution 6 (46.0 g, 141 mmol) in THF (500 mL) and the mixture refluxed for 3 d. After warming to RT, 1.0 M NaOH was added until pH > 7. The phases were separated, and the aqueous phase was extracted three times with EtOAc (350 mL). The combined organic phases were dried over anhydrous Na$_2$SO$_4$. The solvent was removed in vacuo. The crude liquid was distilled for remove glycol and the resulting solid was dissolved in EtOH (200 mL) and the suspension was heated to reflux. After 30 min, the mixture was filtered over Celite 545 (hot filtration). The orange solution was evaporated until crystals were forming. To favor further crystallization, the suspension allowed to chill in the fridge to yield the product 5 (36.0 g, 92%). Mp 120 °C. EA (%): C 89.11, H 4.89; Calcd for C$_{21}$H$_{14}$O: C 89.34, H 5.00. $^1$H NMR (270 MHz, CDCl$_3$): δ 8.02 – 7.98 (m, 2H, ArH), 7.61 – 7.38 (m, 9H, ArH), 7.24 – 7.17 (m, 2H, ArH) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$): δ 195.7, 144.1, 142.8, 141.1, 139.3, 134.8, 133.4, 130.3, 129.5, 129.4, 129.1, 128.3, 128.1, 127.5, 127.3, 127.1, 123.5, 123.3, 106.5, 64.8, 64.2 ppm.

**10-Phenyl-5H-dibenzo[a,d]cycloheptene (8):** $^{40}$ A solution of AlCl$_3$ (11.9 g, 89.5 mmol) in Et$_2$O (140 mL) was added to a solution of LiAlH$_4$ (3.39 g, 89.5 mmol) in Et$_2$O (140 mL). The resulting suspension
was stirred for 15 min at RT, followed by cooling to 0 °C. Then a solution of 7 (25.0 g, 88.6 mmol) in THF (115 mL) was added dropwise over 20 min and the mixture heated to reflux overnight. The resulting yellowish suspension was cooled to 0 °C and quenched with water (80 mL). The aqueous layer was separated and extracted with Et₂O (3 x 200 mL). The combined organic phases were washed with water (3 x 200 mL), dried over Na₂SO₄, and evaporated in vacuo (23.3 g, 98%). Mp 117°C. EA (%): C 93.69, H 5.93; Calcd for C₂₁H₁₆: C 93.99, H 6.01. ¹H NMR (270 MHz, CDCl₃): δ 7.48 – 7.31 (m, 11H, Ar H), 7.18 – 6.98 (m, 2H, Ar H), 3.77 (s, 2H, RCH₂R) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 144.1, 143.6, 140.2, 139.3, 136.4, 135.3, 129.9, 129.5, 129.2, 128.6, 128.3, 128.1, 127.4, 127.3, 127.1, 125.9, 125.6, 41.5 ppm.

rac-5-tert-butylsulfanyl-10-phenyl-5H-dibenzo[a,d]cycloheptene (rac-9 + rac-10): LDA (321 mg, 3.00 mmol) in THF (10 mL) was added dropwise to a stirred solution of 8 (400 mg, 1.50 mmol) in THF (15 mL). After stirring the reaction mixture overnight, rac-2-Methylpropane-2-sulfinic chloride (211 mg, 1.50 mmol) in THF (30 mL) was added. Stirring was continued for 4 h, then the solvent was removed in vacuo, the crude product purified by FLASH column chromatography (EtOAc), and the resulting yellow oil washed and slurried with pentane (75 mg, 13%). HPLC (Daicel Chiralpak AD-H column, hexane/i-PrOH: 8/2, 0.7 mL/min⁻¹): t_R1 = 10.70 min, t_R2 = 26.78 min, t_R3 = 28.33 min, t_R4 = 84.65 min.

5-((S)-tert-butylsulfanyl)-10-phenyl-5H-dibenzo[a,d]cycloheptene ((S,S)-9 and (S,R)-10): To a solution of 8 (5.00 g, 18.6 mmol) in THF (80 mL) at –78ºC under Ar, a solution of LDA (2.00 g, 18.7 mmol) in THF (25 mL) was added via a syringe in one portion, followed by slow addition of a solution of t-BuOK (2.09 g, 18.7 mmol) in THF (25 mL). The reaction mixture was stirred at –78ºC for 4 h. The reaction mixture was transferred via cannula to a solution of (R)-11 (5.65 g, 15.5 mmol) in THF (100 mL) at –78 ºC. The reaction was stirred at –78 ºC for 3 h and was allowed to warm slowly to RT under stirring overnight. After quenching the reaction with NH₄Cl aq. (75 mL, saturated), EtOAc (125 mL) was added. The aqueous phase was extracted with EtOAc (3 x 60 mL). The combined organic phases were washed with brine (60 mL) and dried over Na₂SO₄. The solvent was removed in vacuo to afford 4.25 g of the crude diastereomeric mixture, which was separated by column chromatography (hexane/AcOEt 2:1) to (S,S)-9 (2.65 g, 46%, ee 95%) and (S,R)-10 (1.59 g, 28%, ee 80 %) as white solids. Recrystallization of (S,S)-9 by layering a saturated and filtered THF solution with pentane affords material with ee > 99.5% (2.10 g, 36%). Mp: 143 ºC. [α]_D²⁵ = –165º (c = 1.0, CH₂Cl₂). EA (%): C 80.23, H 6.50, S 8.31; Calcd for C₂₅H₂₄O₂S: C 80.61, H 6.49, S 8.61. ¹H NMR (600 MHz, CDCl₃): δ 7.67 (d, J_HH = 6.0 Hz, 2H, ArH), 7.53 – 7.26 (m, 9H, ArH), 7.24 (m, 2H, ArH), 7.16
(d, \( J_{\text{HH}} = 6.0 \text{ Hz}, 1\text{H}, \text{Ar}H \)), 5.27 (s, 1H, S-CHR), 1.24 (s, 9H, C(CH\(_3\))\(_3\)) ppm. \(^{13}\text{C} \text{ NMR (151 MHz, CDCl}\(_3\))\): \(\delta 145.5, 144.2, 137.5, 136.6, 136.0, 135.4, 130.8, 130.7, 129.9, 129.7, 129.6, 129.3, 129.2, 128.5, 128.4, 127.9, 127.8, 127.6, 71.6, 55.7, 23.6 \text{ ppm. HPLC (Daicel Chiralpak AD-H column, hexane/iPrOH 9:1, 0.7 mLmin}^{-1}\)): \( t_{R2} = 23.34 \text{ min (major). Recrystallization of (S}_S,\text{R}_C)-10\) by layering a saturated and filtered EtOAc solution with hexane affords material with \( ee > 99.5\% \) (1.03 g, 18%). Mp: 136\(^{\circ}\text{C}. \ [\alpha]_D^{23} = – 20.6º (c = 1.0, \text{CH}_2\text{Cl}_2). \ EA (\%)\: C 80.76, H 6.48, S 8.49; \text{Calcd for C}_{25}\text{H}_{24}\text{OS: C 80.61, H 6.49, S 8.61.} \ H\text{ NMR (600 MHz, CDCl}\(_3\))\: \delta 7.42 – 7.26 (m, 12H, ArH), 7.14 – 7.08 (m, 2H, ArH), 5.16 (s, 1H, S-CHR\(_2\)), 1.19 (s, 9H, C(CH\(_3\))\(_3\)) ppm. \(^{13}\text{C} \text{ NMR (151 MHz, CDCl}\(_3\))\: \delta 143.8, 142.8, 137.2, 136.6, 135.8, 135.3, 131.8, 131.0, 130.9, 129.9, 129.3, 129.2, 129.0, 128.7, 128.5, 128.2, 127.8, 127.6, 70.8, 55.5, 23.8 \text{ ppm. HPLC (Daicel Chiralpak AD-H column, hexane/iPrOH: 8/2, 0.7 mLmin}^{-1}\): \( t_{R1} = 26.45 \text{ min (major). 5-(R}_S,\text{S}_C)-tert-butylsulfinyl-10-phenyl-5\text{-H-dibenzo[a,d]cycloheptene ( (R}_S,\text{R}_C)-9 \: + \: (R}_S,\text{S}_C)-10\):\(^{25}\) A solution of LDA (883 mg, 8.24 mmol) in THF (10 mL) was added slowly via syringe to a stirred solution of 8 (2.21 g, 8.24 mmol) in THF (40 mL) at –78 \(^{\circ}\text{C}, followed by slow addition of a solution of \( t\)-BuOK (925 mg, 8.24 mmol) in THF (10 mL). The reaction mixture was stirred at –78 \(^{\circ}\text{C for 4 h and then transferred via cannula to a solution (S)-11 (2.50 g, 6.86 mmol) in THF (20 mL) at –78 °C. The reaction was stirred at –78 °C and monitored by TLC (hexane/diethyl ether 1:1). Once the reaction was completed, it was quenched with saturated aq. NH\(_4\)Cl (75 mL). The aqueous phase was separated and extracted with EtOAc (3 x 60 mL). The combined organic phases were washed with brine (60 mL), dried over Na\(_2\)SO\(_4\), and the volatiles evaporated \textit{in vacuo} to give the crude diastereoisomeric mixture (4.25 g, 74\%, \( dr 5:3\)). This mixture was separated by column chromatography (hexane/AcOEt 2:1) and each of the diastereomers recrystallized by layering a saturated and filtered THF solution with pentane to yield (R\(_S,\text{R}_C)-9 (1.22 g, 48\%, \( ee = 89\%\)) and (R\(_S,\text{S}_C)-10 (0.62 g, 24\%, \( ee = 80\%\)) as white solids. (R\(_S,\text{R}_C)-9): \text{HPLC (Daicel Chiralpak AD-H column, hexane/iPrOH: 8/2, 0.7 mLmin}^{-1}\): \( t_{R} = 7.45 \text{ min (major), } t_{R} = 20.81 \text{ min (minor). \ EA (\%)\: C 80.74, H 6.48, S 8.28; \text{Calcd for C}_{25}\text{H}_{24}\text{OS: C 80.61, H 6.49, S 8.61.} \ H\text{ NMR (600 MHz, CDCl}\(_3\))\: \delta 7.54 (d, \( J_{\text{HH}} = 7.34 \text{ Hz, 2H, Ar}H\)), 7.40 – 7.20 (m, 9H, ArH), 7.13 (m, 2H, ArH), 7.02 (d, \( J_{\text{HH}} = 7.7 \text{ Hz, 1H}\)), 5.14 (s, 1H, S-CHR\(_2\)), 1.15 (s, 9H, C(CH\(_3\))\(_3\)) ppm. \(^{13}\text{C} \text{ NMR (151 MHz, CDCl}\(_3\))\: \delta 145.3, 144.1, 137.4, 136.4, 135.8, 130.7, 130.6, 129.7, 129.5, 129.2, 129.0, 128.7, 128.5, 128.2, 127.8, 127.6, 70.8, 55.5, 23.4 \text{ ppm.} (R\(_S,\text{S}_C)-10): \text{HPLC (Daicel Chiralpak AD-H column, hexane/iPrOH: 8/2, 0.7 mLmin}^{-1}\): \( t_{R} = 22.32 \text{ min (minor), } t_{R} = 69.76 \text{ min (major). \ 1H NMR (400 MHz, CDCl}\(_3\))\: \delta 7.47 – 7.31 (m, 12H, ArH), 7.31 – 7.15 (m, 2H, ArH), 5.22 (s, 1H, S-CHR\(_2\)), 1.24 (s, 9H, C(CH\(_3\))\(_3\)) ppm. \(^{13}\text{C} \text{ NMR (151 MHz, CDCl}\(_3\))\: \delta \)
[(S$_5$,S$_C$)-9]RhCl$_2$ ([R,S]-11): A solution of (S$_5$,S$_C$)-9 (286 mg, 0.766 mmol) in benzene (2.0 mL) was added dropwise to a stirred solution of [RhCl(COE)$_2$]$_2$ (275 mg, 0.383 mmol) in benzene (2.0 mL). The mixture was stirred for 2 h, then the volatiles were evaporated, and the crude product slurried in hexane (10 mL). The solid was separated by filtration and dried in vacuo to yield a yellow powder (379 mg, 97%). EA (%): C 58.88, H 4.78, S 6.01; Calcd for C$_{21}$H$_{16}$Cl$_2$S$_2$O$_2$Rh$_2$: C 58.77, H 4.73; S 6.28. NMR spectra indicate the presence of syn and anti isomers in a ratio of approximately 1 : 3. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.56 (d, $J_{HH} = 4$ Hz, 2H, ArH, major isomer), 8.20 (d, $J_{HH} = 8$ Hz, 2H, ArH, minor isomer), 7.26 – 6.44 (m, 26H, ArH, major isomer), 7.26 – 6.44 (m, 26H, ArH, minor isomer), 5.16 (s, 2H, S-C$_2$H$_2$R, minor isomer), 5.08 (s, 2H, S-C$_2$H$_2$R, major isomer), 1.20 (s, 18H, C(C$_3$H$_3$)$_3$, minor isomer), 1.04 (s, 18H, C(C$_3$H$_3$)$_3$, major isomer) ppm. $^{13}$C NMR (400 MHz, CD$_2$Cl$_2$): δ 146.31, 146.18, 139.91, 139.62, 138.91, 136.10, 136.00, 134.35, 131.57, 131.30, 130.87, 129.38, 128.92, 128.12, 127.74, 127.59, 127.34, 127.34, 125.65, 79.83, 78.00, 71.92, 71.45, 68.55, 63.04, 62.00, 26.39, 26.41 ppm. X-ray diffraction quality single crystals were grown from a filtered THF solution of the complex, which had been layered with pentane.

[(S$_5$,R$_C$)-10]RhCl$_2$ ([R,R]-12): A solution of (S$_5$,R$_C$)-10 (400 mg, 1.07 mmol) in benzene (4.0 mL) was added dropwise to a stirred solution of [RhCl(COE)$_2$]$_2$ (385 mg, 0.537 mmol) in benzene (4.0 mL), and the mixture was stirred overnight. After removing the solvent under reduced pressure, the residue was slurred in pentane (15 mL), filtered, and vacuum dried to afford a red-orange powder (566 mg, 97%). EA (%): C 58.84, H 4.85, S 6.04; Calcd. for C$_{21}$H$_{16}$Cl$_2$S$_2$O$_2$Rh$_2$: C 58.77, H 4.73; S 6.28. $^1$H NMR (270 MHz, benzene-D$_6$): δ 8.18 (d, $J_{HH} = 7.8$ Hz, 2H, ArH), 7.62 (d, $J_{HH} = 7.8$ Hz, 2H, ArH), 7.44 – 6.80 (m, 24H, ArH), 5.38 (s, 2H, S-C$_2$H$_2$R), 1.19 (s, 18H, C(C$_3$H$_3$)$_3$) ppm. X-ray diffraction quality single crystals were grown from a saturated and filtered benzene solution of the complex.

**General procedure for the asymmetric Hayashi-Miyaura reaction:** In an inert-gas glovebox, a capped 20 mL vial with a magnetic stir bar was charged with 1.0 equiv of enone, 2.0 equiv of boronic acid, and 0.03 equiv of either catalyst 11 or 12. The reactions were performed on a 1–2 mmol scale. 1,4-Dioxane (3.0–6.0 mL) was added and the reaction was stirred for 30 min at 40°C. 0.5 equiv of aqueous Cs$_2$CO$_3$ (1.0 M, 0.5–1.0 mL) was added by syringe and the reaction stirred for 24–28 h at 40°C. Aqueous workup was performed by the addition of H$_2$O (5–10 mL) and EtOAc (5–10 mL). The phases were separated and the aqueous phase further extracted with EtOAc (3 × 15 mL). The combined
organic phases were washed with brine (20 mL), dried over MgSO₄, filtered, and evaporated to dryness. The crude products, obtained as colorless or pale yellow oils or as white or off-white solids, were impregnated on silica G60 and purified by flash chromatography using n-hexane/EtOAc in varying ratios as eluent. This procedure affords practically quantitative isolated yields (>95%). Enantio-enriched products 16aa–16ai, 16ba–16be, 16bg–16bi, 16ca, 16cb, 16cf–16ci have been previously reported. For references, pertinent HPLC traces, and a general protocol for the synthesis of racemic reference substances, see the Supporting Information.

3-(3-methoxyphenyl)cyclopentan-1-one (16bf): The general procedure outlined in the experimental part was followed using catalyst 12 and 1.08 mmol of 2-cyclopenten-1-one. Purification by flash chromatography (hexane/EtOAc 9:1) afforded a colorless oil (202 mg, 98%). NMR spectroscopic data correspond to racemic reference substance (see SI). HPLC (Chiracel AS-H column, hexane/iPrOH 99:1, 0.6 mL min⁻¹): ee = 96%, tR₁ = 65.71 min, tR₂ = 69.98 min (major).

4-(4-(tert-butyl)phenyl)tetrahydro-2H-pyran-2-one (16cc): The general procedure was followed using catalyst 12 and 0.94 mmol of 5,6-dihydro-2H-pyran-2-one. Purification by flash chromatography (hexane/EtOAc 2:1) afforded a yellowish oil that slowly solidified at 0 ºC (218 mg, 99%). NMR spectroscopic data correspond to reference substance (see SI). HPLC (Daicel Chiralpak AD-H column, hexane/iPrOH 95:5, 0.7 mL min⁻¹): ee = 97%, tR₁ = 16.28 min (major), tR₂ = 17.24 min.

4-(4-fluorophenyl)tetrahydro-2H-pyran-2-one (16cd): The general procedure outlined in the experimental part was followed using catalyst 12 and 1.06 mmol of 5,6-dihydro-2H-pyran-2-one. Purification by flash chromatography (hexane/EtOAc 2:1) afforded a colorless oil that slowly solidified (196 mg, 95%). NMR spectroscopic data correspond to racemic reference substance (see SI). HPLC (Daicel Chiralpak AS-H column, hexane/iPrOH 8:2, 1.0 mL min⁻¹): ee = 94%, tR₁ = 25.28 min, tR₂ = 27.47 min (major).

4-(4-methoxyphenyl)tetrahydro-2H-pyran-2-one (16ce): The general procedure outlined in the experimental part was followed using catalyst 12 and 1.03 mmol of 5,6-dihydro-2H-pyran-2-one. Purification by flash chromatography (hexane/EtOAc 2:1) afforded a colorless oil that solidified on prolonged standing (203 mg, 95%). NMR spectroscopic data correspond to racemic reference substance (see SI). HPLC (Daicel Chiralpak AS-H column, hexane/iPrOH 6:4, 0.7 mL min⁻¹): ee = 94%, tR₁ = 35.80 min, tR₂ = 44.94 min (major).

Crystallographic information: CCDC-1965291 for rac-8, CCDC-1965292 for (R,S,R)-9, CCDC-1965293 for (S,S,R)-9, CCDC-1965294 for (S,R)-10, CCDC-1965295 for (R,S)-11, and CCDC-1965296 for (R,R)-12 contain the supplementary crystallographic data for this paper. The data can be
obtained free of charge from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Intensity data of 8 were collected using CuKα radiation (λ = 1.54184 Å) on an Oxford Diffraction SuperNova dual radiation diffractometer with mirror optics. Intensity data of single crystals of the other compounds were collected using MoKα radiation (λ = 0.71073 Å) either on a Bruker Smart APEX 2 diffractometer (curved graphite monochromator) for (R:S,RC)-9 and (S:S,S):-9 and a Bruker Kappa APEX 2 μS Duo diffractometer equipped with QUARZAR focusing Montel optics for (S:S,Rc)-10, (R:S)-11, and (R,R)-12. Data were corrected for Lorentz and polarization effects, semiempirical absorption corrections were performed on the basis of multiple scans using SADABS. The structures were solved by direct methods (SHELX XT 2014/5) and refined by full-matrix least-squares procedures on F² using SHELXL 2016/6. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in positions of optimized geometry, their isotropic displacement parameters were tied to those of the corresponding carrier atoms by a factor of either 1.2 or 1.5. Compound (R,S)-11 crystallized with four molecules of tetrahydrofuran in its asymmetric unit. In (R,R)-12 the complex molecule was situated on a crystallographic twofold rotation axis. This compound crystallized with a total of seven molecules of benzene per formula unit. Three out of the five independent benzene molecules were situated on crystallographic twofold rotation axes. Similarity restraints were applied to the anisotropic displacement parameters of the atoms of some solvent molecules. Pseudo-isotropic restraints were applied to the anisotropic displacement parameters of all carbon atoms. The overall crystal quality was rather poor. There were two significant residual electron density maxima observed. These were attributed to truncation effects as they could not be attributed to any disorder. There were also no signs of twinning (see also K value statistics).

Olex2 was used to prepare material for publication. Crystallographic data, data collection, and structure refinement details are given in Table S1 as Supplementary Information.

Computational details: Geometries were optimized with the Gaussian09 package using the PBE0-D3 functional. The electronic configuration of the system was described with the split-valence SVP basis set for main group atoms (C, H, S, and O) and the relativistic Stuttgart-Dresden effective core potential with the associated valence triple-ζ basis set for Rh. All geometries were confirmed as minimum or transition state through frequency calculations. The reported free energies were built through single point energy calculations on the PBE0-D3 geometries using the PBE0-D3 functional and the triple-ζ TZVP basis set for main group atoms. Solvent effects were included with the PCM model using 1,4-
dioxane as the solvent. To this PBE0-D3/TZVP electronic energy in solvent, thermal corrections were added from the gas-phase frequency calculations at the PBE0-D3/SVP level.

**Supporting Information**

NMR spectra of ligands, complexes, and catalysis products; ORTEP of (S,S)-9; HPLC traces of ligands and catalysis products; synthetic procedures for racemic reference substances.

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The authors declare no competing financial interests.

**Acknowledgements and declaration**

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Intrinsic Helical Chirality and Its Ferrocene Analogues *Organometallics* 2015, 34, 5374–5382.

20 The racemate also serves as reference substance for HPLC certification of stereochemical purity of the optically active ligands.

21 LDA/t-BuOK turned out to be the base of choice giving higher enantioselectivities and yields than either the pre-formed and isolated Li- and K-tropylidenides.


24 The high solubility difference of the two diastereomers in EtOAc makes their separation by crystallization a viable option, especially on larger scales.

25 Reaction conditions were not optimized, work in progress.

26 Structurally authenticated chiral S(O)-alkene complexes of Rh are quite rare. See references [11], [12(a)], and: Feng, X.; Wang, Y.; Wei, B.; Yang, J.; Du, H. Simple N-Sulfinyl-Based Chiral Sulfur-Olefin Ligands for Rhodium-Catalyzed Asymmetric 1,4-Additions *Org. Lett.* 2011, 13, 3300–3303.


28 (i) reactions in toluene are slower and less selective; (ii) base additive improves activity and selectivity in the following order: KOH < KF < K3PO4 ≈ Cs2CO3; (iii) catalyst loadings of < 1.5 mol% causes erosion of enantioselectivity.

29 Hayashi, T.; Takahashi, M.; Takaya, Y.; Ogasawara, M. Catalytic Cycle of Rhodium-Catalyzed

30 For similar stereochemical models featuring S(O)-alkene ligands, see references [11], [12a], and: Chen, Q.; Chen, C.; Guo, F.; Xia, W. Application of chiral *N*-tert-butylsulfanyl vinyl aziridines in Rh(I) catalyzed 1,4-addition of aryl boronic acids to cyclic enones. *Chem. Commun.* 2013, 49, 6433—6435.


32 The electrostatic maps show an inverted pattern and are less conclusive. See Figure S39 in the supporting information.


41 SADABS 2014/5, Bruker AXS area detector scaling and absorption correction *Bruker AXS, Inc.*, 2014, Madison WI., USA.


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