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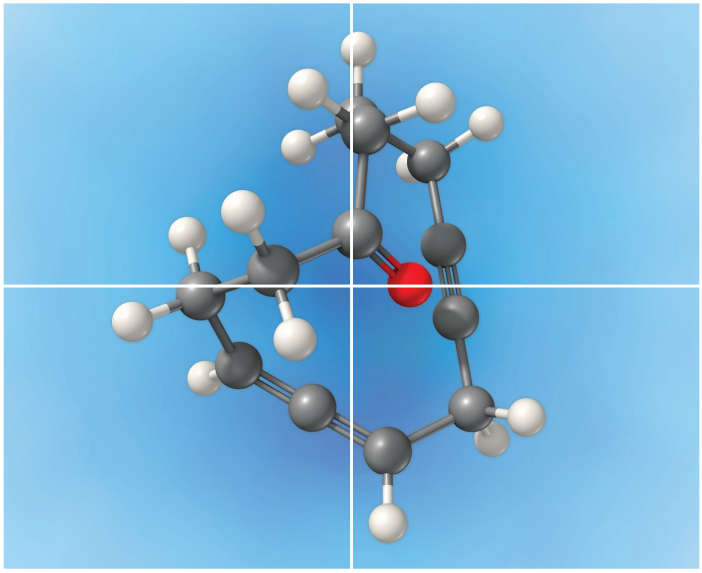

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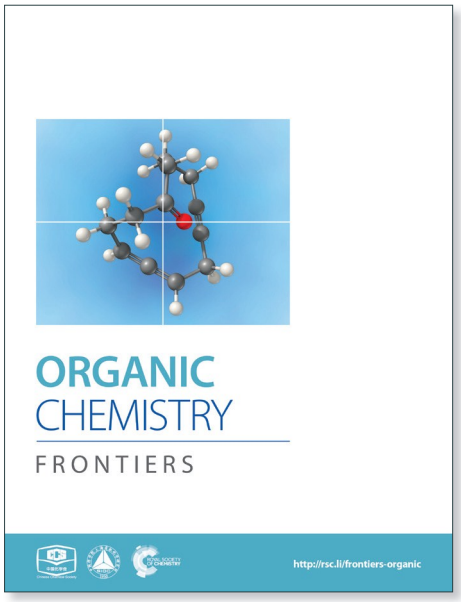

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Journal Name

ARTICLE

Chiral dirhodium catalysts derived from L-serine, L-threonine and L-cysteine: Design, synthesis and application

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A series of dirhodium tetrakis((4*S*)-3-(arylsulfonyl)oxazolidine-4-carboxylate), dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-(arylsulfonyl)oxazolidine-4-carboxylate) and dirhodium tetrakis((4*R*)-3-(arylsulfonyl)thiazolidine-4-carboxylate 1,1-dioxide) complexes with different *para*-substituted arylsulfonyl groups (e.g. $-NO_2$, -F, $-CF_3$, -Me, $-^tBu$, -OMe and $-^nC_{12}H_{25}$) derived from L-serine, L-threonine and L-cysteine, respectively, were prepared with yields in the range of 40-87% through refluxing ligands in water with $Na_4Rh_2(CO_3)_4$. These chiral Rh(II) complexes have been fully characterized by EA, IR, UV-vis, NMR and specific rotation measurements. They are found to be effective chiral catalysts for asymmetric aziridination and cyclopropanation reactions in terms of reactivity and enantioselectivity. They are extremely stable and can be stored for a long period (at least 18 months) on the bench without adversely affecting their reactivity and selectivity. The heterocycle rings as well as the substituents on the arylsulfonyl groups have critical effects on the degree of asymmetric induction. In the general, the higher enantioselectivity was observed in the reactions catalyzed by the oxazolidine-4-carboxylate-derived catalysts than the thiazolidine-4-carboxylate 1,1-dioxide-based catalysts. Among these 21 new Rh(II) catalysts, the uses of dirhodium tetrakis((4*S*)-3-((4-dodecylphenyl)sulfonyl)oxazolidine-4-carboxylate) (Rh_2(4*S*-DOSO)$_4$) and dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-((4-nitrophenyl)sulfonyl)oxazolidine-4-carboxylate) (Rh_2(4*S*,5*R*-MNOSO)$_4$) resulted in the highest levels of enantioselectivity in aziridination (94% ee) and cyclopropanation (98% ee) of styrene, respectively. The successful design and syntheses of these novel Rh(II) complexes enlarged the scope of accessible chiral dirhodium(II) catalysts.

Introduction

Chiral dirhodium(II) paddlewheel complexes are exceptional catalysts for a wide range of transformations.[1-5] They can react with iminoiodane and diazo compounds efficiently to form the important Rh(II) nitrenoid and carbenoid intermediates, respectively, which then undergo a number of highly selective reactions, including C-H bond functionalization and cycloaddition such as aziridination and cyclopropanation. Dirhodium carboxylates, dirhodium carboxamidates, dirhodium phosphates and *ortho*-metalated dirhodium(II) complexes are among the most efficient and widely used catalysts for metal-nitrene and metal-carbene transformations. Dirhodium carboxylates are very easy to handle, being stable to air, heat, and moisture. Among the chiral dirhodium carboxylates that had been used in nitrenoid/carbenoid reactions, four catalyst systems stood out, including dirhodium prolinates, *N*-phthaloyaminocarboxylates, *N*-naphthaloylaminocarboxylates and cyclopropanecarboxylates (Fig. 1).

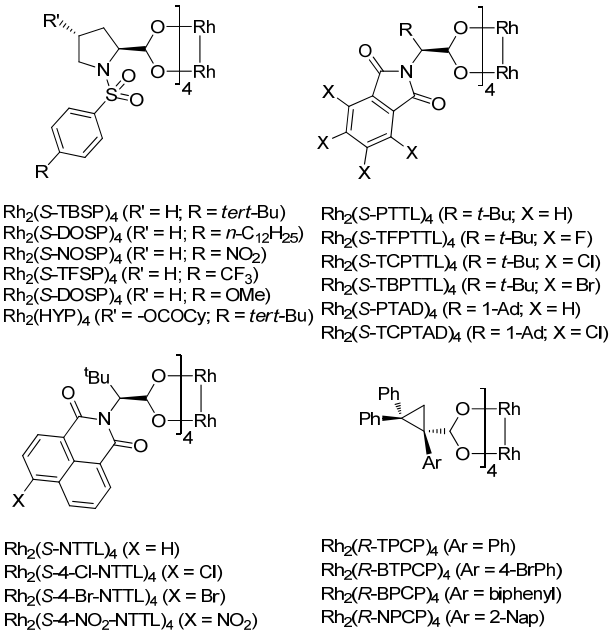

Fig. 1 Structures of chiral dirhodium carboxylates.

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† Electronic supplementary information (ESI) available: NMR spectra of the ligands and Rh(II) complexes; CIF files giving crystallographic data. See DOI: 10.1039/x0xx00000x

The synthesis and catalytic applications of dirhodium *N*-sulfonylprolinates were firstly studied by McKervey group, and then developed by Davies group. In the early 1990's McKervy developed different *N*-sulfonyl functionalized Rh(II) prolinates, and they found that the *tert*-butyl substituted complexe Rh_2(*S*-TBSP)$_4$ showed a remarkably improved diastereoselectivity and enantioselectivity in the cyclopropanation reactions with methyl phenyldiazoacetate.[6] Davies group developed *n*-dodecyl substituted complex Rh_2(*S*-DOSP)$_4$, which can be dissolved in pentane even at -78°C and displayed especially high asymmetric induction in the reactions of a variety of donor/acceptor carbenoids, including cycloaddition such as cyclopropanantion, cyclopropenation, [3+2] annulation, tandem cyclopropanation/Cope rearrangement, and three component coupling,[7] and X-H insertion such as carbenoid C-H insertions, combined C-H activation/cope rearrangement, and tandem ylide formation/[2,3]-sigmatropic rearrangement.[8] Hansen group developed chiral Rh(II) catalysts with 4-hydroxyproline-derived ligands.[9] The hydroxyl groups were O-acylated with acid chlorides such as lauroyl chloride and cyclohexylcarbonyl chloride. The formed Rh(II) catalysts efficiently promoted cyclopropanation and C-H insertion with high enantioselectivities (up to 93% ee).

The phthalimide derived Rh(II) complexes were developed by Hashimoto and co-workers.[10] The optimum catalyst can vary depending on the specific reaction, but usually the *tert*-leucine derived catalyst Rh_2(*S*-PTTL)$_4$,[10a] and its halogen-substituted complexes Rh_2(*S*-TFPTTL)$_4$ (X = F),[10b,c] Rh_2(*S*-TCPTTL)$_4$ (X = Cl)[10d-f] and Rh_2(*S*-TBPTTL)$_4$ (X = Br)[10g,h] gave the highest asymmetric induction. Later, Davies group developed the adamantylglycine derived complexes Rh_2(*S*-PTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$, which complemented with *tert*-leucine derived catalysts in nitrenoid and carbenoid reactions.[11] Impressively, Rh_2(*S*-TCPTAD)$_4$ (X = Cl) is an exceptional catalyst for enantioselective cyclopropanation of electron-deficient alkens[11e] and C-H amination.[11b]

Müller group designed and synthesized *N*-naphthaloyl-tethered chiral dirhodium tetracarboxylates, among which, Rh_2(*S*-NTTL)$_4$ and bromo-substituted Rh_2(*S*-4-Br-NTTL)$_4$ are the most efficient in terms of reactivities and selectivities.[12a-d] In conjunction with chiral sulfonimidamide-derived iminoiodanes, Rh_2(*S*-NTTL)$_4$ has been successfully employed in efficient diastereoselective intermolecular C-H amination.[12e,f] Compared to the former two chiral templates, rhodium *N*-naphthaloylaminocarboxylates have been less employed in asymmetric catalytic carbene transfer reactions.[13] The development of azavinyl carbenes highlighted its importance in organic synthesis. Rh_2(*S*-NTTL)$_4$ outperformed Rh_2(*S*-DOSP)$_4$ and Rh_2(*S*-PTTL)$_4$ in cyclopropanation and C-H bond activation when 1,2,3-triazoles are used as the azavinyl carbene sources.[14, 15]

Davies group for the first time prepared dirhodium triarylcyclopropanecarboxyalte complexes.[16] Like prolinate catalysts such as Rh_2(DOSP)$_4$, these catalysts showed high enantioselectivity in a series of donor/acceptor carbene transfer reactions. The advantages of Rh(II) cyclopropanecarboxylates include its ease of synthesis and its compatibility in dichloromethane as solvent, and most importantly, they can promote highly selective C-H functionalization of primary C-H bonds.[16c,d]

Our interests are to enlarge the scope of accessible chiral dirhodium catalysts, considering that the high need of new dirhodium(II) catalysts with different electronic and steric environments for the powerful C-C and C-N bond-forming processes in synthetic organic chemistry.[17-23] Herein, we report the design and synthesis of a series of dirhodium tetrakis((4*S*)-3-(arylsulfonyl)oxazolidine-4-carboxylate), dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-(arylsulfonyl)oxazolidine-4-carboxylate) and dirhodium tetrakis((4*R*)-3-(arylsulfonyl)thiazolidine-4-carboxylate 1,1-dioxide) complexes with different para-substituted arylsulfonyl groups (e.g. -NO_2, -F, -CF_3, -Me, -^{t}Bu, -OMe and -$^n C_{12}H_{25}$) derived from $_L$-serine, $_L$-threonine and $_L$-cysteine, respectively (Fig. 2). Their catalytic activities have been tested in nitrene and carbene transfer reactions.

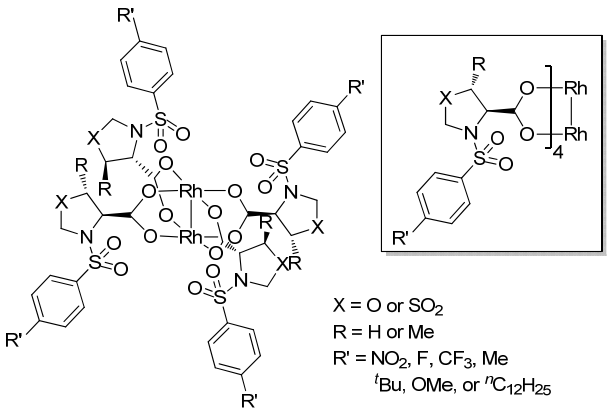


Fig. 2 Dirhodium tetrakis((4*S*)-3-(arylsulfonyl)oxazolidine -4-carboxylate) (X =O, R = H), dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-(arylsulfonyl)oxazolidine-4-carboxylate) (X = O, R = Me) and dirhodium tetrakis((4*R*)-3-(arylsulfonyl)thiazolidine-4-carboxylate 1,1-dioxide) (X = SO_2, R = H).

Results and discussion

Ligand design

Rhodium(II) prolinates have been shown to be effective in carbenen transfer reactions with high stereoselectivity and excellent enantioselectivity.[6-9] The catalytic results depended on the *N*-sulfonyl functionalities of the rhodium(II) prolinate complexes. Neither enlarging nor shrinking the ring size of the proline ring haven't necessarily affected the outcomes, and high levels of asymmetric induction were observed for both the *N*-4-*tert*-butylphenylsulfonyl azetidinecarboxylate complex and pipecolinate complex.[7a,24] Further modifications about the addition of the second heteroatom such as O, N, S into the proline ring, that is 1,3-oxazolidine-4-carboxylic acid, 1,3-imidazolidine-4-carboxylic acid and 1,3-thiazolidine-4-carboxylic acid and their derivatives, however, have been seldom studied.[25] Nevertheless, chiral dirhodium

oxazolidinones and imidazolidinones have been prepared and applied in nitrene and carbene transfer reactions, which offer advantages in the diastereo/enantio- control than Rh(II) pyrrolidones.[26-28]

Our catalysts are based on oxazolidine-4-carboxylate and thiazolidine-4-carboxylate, which are derived from natural available amino acids. Their structures are related to prolinates. The major advantages of our catalysts over Rh(II) prolinates lie in much more modifications can be made on them, as shown in Fig. 3. Synergistic effects of different hetero atoms of X (electronic effects), substituents of R on the methylene carbon (steric effects), and different R′ groups attached to the nitrogen (electronic effects and solubilities) could enrich the catalysis chemistry of the corresponding Rh(II) complexes. Appropriate combinations might endow the ligands with unique properties.

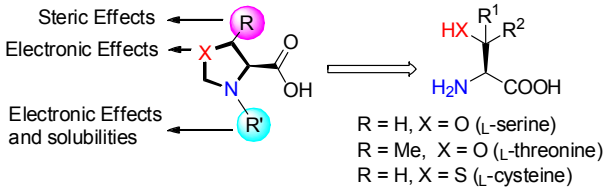


Fig. 3 Ligand design.

Syntheses and characterizations of ligands

Ligands (4*S*)-3-(arylsulfonyl)oxazolidine-4-carboxylic acids were synthesized from the reactions of (*S*)-oxazolidine-4-carboxylic acid and arylsulfonyl chlorides, whereas the former was prepared from the natural amino acid L-serine (Fig. 4).[29] L-Serine and formaldehyde, in aqueous medium, are in equilibrium with 1,3-oxazolidine-4-carboxylate: at pH value greater than 7 the oxazolidine adduct can be trapped under Schotten-Baumann conditions leading to the corresponding *N*-protected derivatives, which are then converted to 4-oxaproline compounds via the removal of the protecting group in acidic conditions. (4*S*,5*R*)-5-Methyl-3-(arylsulfonyl)oxazolidine-4-carboxylic acids and (4*R*)-3-(arylsulfonyl)thiazolidine-4-carboxylic acids were prepared in the similar way, starting from the natural amino acid L-threonine and L-cysteine, respectively. Ligands (*R*)-3-(arylsulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxides were then obtained from the oxidation of (*R*)-3-(arylsulfonyl)thiazolidine-4-carboxylic acids with urea-hydrogen peroxide (UHP).

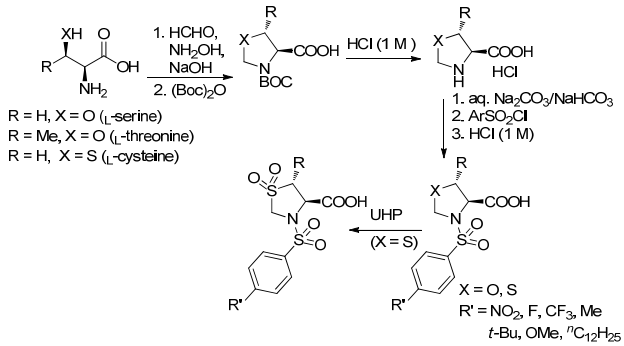


Fig. 4 Syntheses of ligands.

These ligands have been characterized by FTIR, NMR, HRMS-ESI, and optical rotation measurements. The IR spectra of these carboxylic acids displayed the characteristic asymmetric C=O stretching adsorption in the range of 1713-1770 cm^{-1}. The ^1H NMR (DMSO-d_6) spectra clearly exhibited the characteristic peaks of the protons in the oxazolidine or thiazolidine 1,1-dioxide heterocycles. Due to the larger electronegativity of the atom O than S, the protons on the carbon atoms next to these heteroatoms appeared at the lower field in oxazolidine ring than thiazolidine 1,1-dioxide ring. For example, (4*S*)-3-((4-(trifluoromethyl)phenyl)sulfonyl)oxazolidine-4-carboxylic acid (4*S*-TFSO) exhibited two doublet peaks at 5.17 and 4.57 ppm for the two protons attached to the carbon in the 2-position of the oxazolidine ring, and two doublet-doublet peaks (one of the peaks appeared as a pseudo triplet) at 3.93 and 3.73 ppm for the two protons attached to the carbon in the 5-position. In comparison, (4*R*)-3-((4-trifluoromethyl)phenyl)sulfonyl) thiazolidine-4-carboxylic acid 1,1-dioxide (4*R*-TFST) displayed two doublet peaks at 4.96 and 4.30 ppm for the protons attached to the carbon in the 2-position of the thiazolidine ring, and two doublet-doublet peaks at 3.68 and 3.56 ppm for the two protons attached to the carbon in the 5-position. In a similar way, as suggested by ^{13}C NMR spectra and DEPT ^{13}C NMR spectra, the two carbon nuclei next to the heteroatom O in the oxazolidine ring appeared with higher chemical shifts than those two carbon nuclei next to the atom S in the thiazolidine 1,1-dioxide ring. For example, as shown in ^{13}C NMR (DMSO-d_6) spectra, the carbon nuclei in the 2- and 5-position of the oxazolidine ring in 4*S*-TFSO appeared at 80.87 and 69.09 ppm, respectively, whereas the related carbon nuclei in 4*S*-TFST appeared at 62.40 and 51.73 ppm.

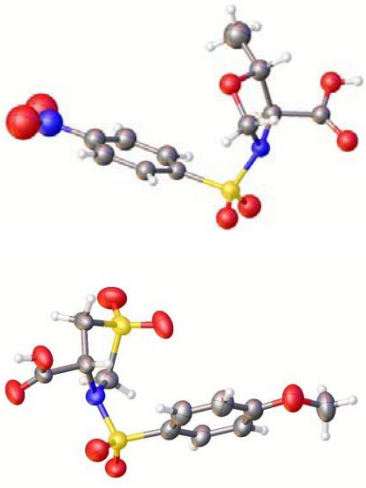


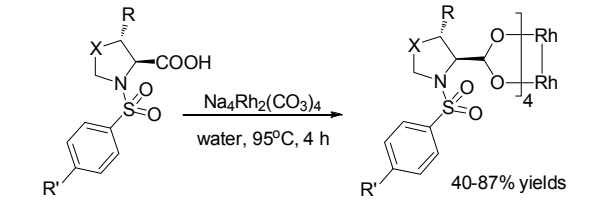
Fig. 5 Crystal structures of 4*S*,5*R*-MNOSO (up) and 4*R*-MOST (down)

The structures of (4*S*,5*R*)-5-methyl-3-((4-nitrophenyl)sulfonyl)-oxazolidine-4-carboxylic acid (4*S*,5*R*-MNOSO) and (4*R*)-3-((4-methoxyphenyl)sulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxide (4*R*-MOST) have been confirmed by the X-ray diffraction study, revealing that the sulfonamide moiety and the carboxylic acid group (-COOH) pointing to the different direction (Fig. 5). In contrast, an analysis of the

Cambridge Crystallographic Database (CCDB) indicated that the sulfonamide moiety and the carboxylic acid group (-COOH) (or ester group (-COOR)) in (*S*)-(arylsulfonyl)pyrrolidine-2-carboxylic acid (or their ester relatives) pointing to the same direction.[30] This indicated the importance of the heteroatom on the rings to their solid structures.

Rhodium complexes syntheses

The present chiral rhodium complexes (e.g. oxazolidine-4-carboxylate, 5-methyloxazolidine-4-carboxylate and thiazolidine-4-carboxylate 1,1-dioxide) were prepared in a similar procedure as the rhodium prolinate complexes by carbonate displacement using $Na_4Rh_2(CO_3)_4$ (Fig. 6).[31a] We ever tried high temperature ligand exchange with rhodium(II) acetate, which is another common synthesis method.[31b] However, the latter method has been discarded due to the much lower yields. In order to circumvent solubility problems in hydrocarbons, which seemed to be crucial for the high selectivities in the catalytic cyclopropanation reactions,[7] 4-*n*-dodecylpenylsulfonyl substituted Rh(II) complexes have been prepared. In addition, the strong electron-withdrawing (e.g. -NO_2) and electron-donating (e.g. -OMe) substituted Rh(II) complexes have been prepared to explore the electronic effects of *N*-sulfonyl functionalities on the catalytic results. After isolation and purification, these complexes are extremely stable and can be stored for long periods (at least 18 months) of time on the bench without adversely affecting their reactivity and selectivity in catalytic reactions. Endeavor to prepare Rh(II) thiazolidine-4-carboxylate failed, due to the strong coordination ability of the S atoms in the thiazolidine ring to metal centers. As soon as the thiazolidine-4-carboxylatic acid and $Na_4Rh_2(CO_3)_4$ were mixed in solution, the reaction solution turned purple, indicative of the coordination of S to Rh(II) atoms.[32]



Catalyst names:	X = O, R = H	X = O, R = Me	X = SO_2, R = H
R' = -NO_2	Rh_2(4*S*-NOSO)$_4$	Rh_2(4*S*,5*R*-MNOSO)$_4$	Rh_2(4*R*-NOST)$_4$
-F	Rh_2(4*S*-FLSO)$_4$	Rh_2(4*S*,5*R*-MFLSO)$_4$	Rh_2(4*R*-FLST)$_4$
-CF_3	Rh_2(4*S*-TFSO)$_4$	Rh_2(4*S*,5*R*-MTFSO)$_4$	Rh_2(4*R*-TFST)$_4$
-Me	Rh_2(4*S*-MESO)$_4$	Rh_2(4*S*,5*R*-MMESO)$_4$	Rh_2(4*R*-MEST)$_4$
-*t*-Bu	Rh_2(4*S*-TBSO)$_4$	Rh_2(4*S*,5*R*-MTBSO)$_4$	Rh_2(4*R*-TBST)$_4$
-OMe	Rh_2(4*S*-MOSO)$_4$	Rh_2(4*S*,5*R*-MMOSO)$_4$	Rh_2(4*R*-MOST)$_4$
-*n*-$C_{12}H_{25}$	Rh_2(4*S*-DOSO)$_4$	Rh_2(4*S*,5*R*-MDOSO)$_4$	Rh_2(4*R*-DOST)$_4$

Fig. 6 Rh(II) complexes syntheses.

The prepared Rh(II) complexes have been characterized by EA, FTIR, NMR and optical rotation measurements. The IR spectra of these Rh(II)-carboxylate complexes exhibited a strong asymmetric C=O stretching adsorption at 1612~1625 cm^{-1} and a relatively less strong symmetric C=O stretching adsorption at 1408~1420 cm^{-1}. Coordination of the carboxylate groups with Rh(II) atoms weaken the C=O bond, and thus resulting in absorption at a lower frequency than the free ligands (Rh_2(4*S*,5*R*-MNOSO)$_4$, 1613 cm^{-1} vs. 4*S*,5*R*-MNOSO, 1713 cm^{-1}).

The chemical shifts of the proton and carbon nuclei on the oxazoline rings of dirhodium complexes haven't displayed noticeable deviations from those of free ligands, whereas the carboxylate carbons of Rh(II) complex shifted to the lower field with a large extent compared to those of the free ligands in the NMR spectra, indicative of the coordination of Rh(II)-carboxylate. For example, the carboxyl carbon in 4*S*,5*R*-MNOSO appeared at 170.40 ppm, whereas the carboxylate carbon in Rh_2(4*S*,5*R*-MNOSO)$_4$ showed at 189.51 ppm in the ^{13}C NMR (acetone-d_6) spectra.

In order to explore the role of ligands on the electronic properties of the these new dirhodium(II) complexes, the UV-vis spectra were examined (Fig. 7). The λ_{max} for the two peaks in the visible region were ~ 590 and ~ 450 nm in acetone, which did not change greatly with different *N*-substituted oxazolidine-4-carboxylate or *N*-substituted thiazolidine-4-carboxylate 1,1-dioxide ligands, suggesting that these ligands did not significantly affect the electronic properties of the complex.[33]

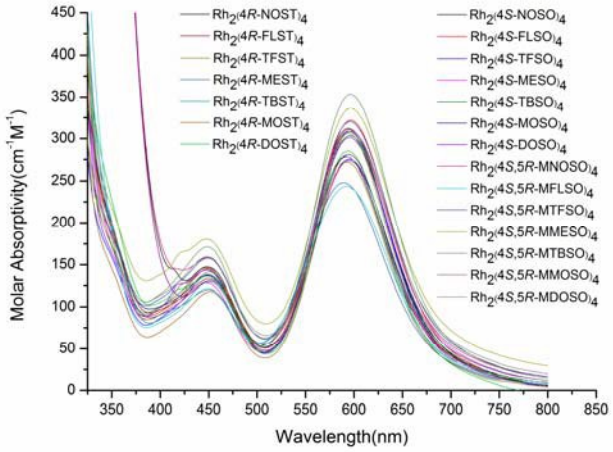
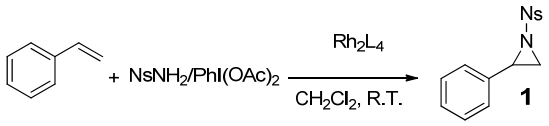


Fig. 7 UV-vis spectra of Rh(II) complexes in acetone (R. T.).

Catalytic nitrene transfer reactions

A limited number of chiral Rh(II) catalysts have been examined in aziridination reactions. A survey on the Rh(II)-catalyzed enantioselective aziridination of styrene disclosed that the rhodium(II) phosphate catalyst Rh_2(*R*-bnp)$_4$ gave the highest enantioselectivity (55% ee).[34] These results were unsatisfactory, considering that copper complexes with chiral bis(oxazoline) or salen ligands promoted the aziridination of olefins with exceptional enantioselectivities (up to 98% ee).[35] With our new catalysts in hand, we want to investigate their asymmetric induction in the aziridination reactions of olefins.

Table 1 Dirhodium catalyzed aziridination[a]



Entry	Catalyst	Yield, %	Ee, %
1	Rh_2(4*S*-NOSO)$_4$	85	47
2	Rh_2(4*S*-FLSO)$_4$	79	42
3	Rh_2(4*S*-TFSO)$_4$	96	46
4	Rh_2(4*S*-MESO)$_4$	68	35
5	Rh_2(4*S*-TBSO)$_4$	90	41
6	Rh_2(4*S*-MOSO)$_4$	66	50
7	Rh_2(4*S*-DOSO)$_4$	86	94
8	Rh_2(4*S*,5*R*-MNOSO)$_4$	92	88
9	Rh_2(4*S*,5*R*-MFLSO)$_4$	81	80
10	Rh_2(4*S*,5*R*-MFSO)$_4$	48	80
11	Rh_2(4*S*,5*R*-MMESO)$_4$	93	49
12	Rh_2(4*S*,5*R*-MTBSO)$_4$	55	55
13	Rh_2(4*S*,5*R*-MMOSO)$_4$	55	56
14	Rh_2(4*S*,5*R*-MDOSO)$_4$	92	89
15	Rh_2(4*R*-NOST)$_4$	89	13
16	Rh_2(4*R*-FLST)$_4$	93	16
17	Rh_2(4*R*-TFST)$_4$	90	9
18	Rh_2(4*R*-MEST)$_4$	90	14
19	Rh_2(4*R*-TBST)$_4$	88	55
20	Rh_2(4*R*-MOST)$_4$	91	13
21	Rh_2(4*R*-DOST)$_4$	90	79
22	Rh_2(*S*-NOSP)$_4$	69	-46
23	Rh_2(*S*-TFSP)$_4$	96	60
24	Rh_2(*S*-MOSP)$_4$	95	81
25	Rh_2(*S*-DOSP)$_4$	95	73
26	Rh_2(*S*-PTAD)$_4$	90	25
27	Rh_2(*S*-NTTL)$_4$	92	60
28[b]	Rh_2(4*S*,5*R*-MNOSO)$_4$	84	78
29[c]	Rh_2(4*S*,5*R*-MNOSO)$_4$	75	65
30[d]	Rh_2(4*S*,5*R*-MNOSO)$_4$	70	55
31[e]	Rh_2(4*S*,5*R*-MNOSO)$_4$	78	15

[a] Reaction conditions: To 2 mL of DCM were added sequentially MgO (29 mg, 0.72 mmol, 2.4 eq), $PhI(OAc)_2$ (152 mg, 0.45 mmol, 1.5 eq), styrene (47 mg, 0.45 mmol, 1.5 eq), $NsNH_2$ (61 mg, 0.30 mmol, 1.0 eq) and 2 mol% catalyst. The suspension was stirred vigorously overnight at room temperature until complete consumption of most starting material was indicated by TLC. [b] $PhCF_3$; [c] DCE; [d] CH_2Br_2; [e] toluene.

The Rh(II)-catalyzed aziridination of olefins proceed via intermediate metal nitrenes (M=NR), which are generated upon decomposition of iminoiodanes (PhI=NR) directly or formed *in situ* from the amine and oxidant (e.g. $PhI(OAc)_2$, PhIO) pair. In this work, the efficiency and enantioselectivity of the aziridination was tested with styrene, using $NsNH_2$/$PhI(OAc)_2$ as the nitrogen source (Table 1). The yields of the 1-((4-nitrophenyl)sulfonyl)-2-phenylaziridine (**1**) in the presence of all of the Rh(II) catalysts were rather high (up to 96%). The dodecyl substituted Rh(II) complexes (e.g. Rh_2(4*S*-DOSO)$_4$, Rh_2(4*S*,5*R*-MDOSO)$_4$ and Rh_2(4*R*-DOST)$_4$) gave high asymmetric inductions of 94%, 89% and 79% ee, respectively (entries 7, 14 and 21), which might be due to their good solubilities in organic solvents. In addition to these catalysts, another three 5-methyloxazolidine-4-carboxylate complexes (e.g. Rh_2(4*S*,5*R*-MNOSO)$_4$, Rh_2(4*S*,5*R*-MFLSO)$_4$ and Rh_2(4*S*,5*R*-MTFSO)$_4$) promote the aziridiantion reaction with high enantioselectivities (≥ 80% ee, entries 8-10). In the general, Rh(II) oxazolidine-4-carboxylate catalysts displayed higher enantioselectivities than Rh(II) thiazolidine-4-carboxylate 1,1-dioxide catalysts. Additional methyl group in the 5-position endowed the 5-methyloxazolidine-4-carboxylate complexes have higher asymmetric inductions than the corresponding Rh(II) oxazolidine-4-carboxylate catalysts.

In both systems of rhodium tetrakis((4*S*)-3-(arylsulfonyl)oxazolidine-4-carboxylate) and rhodium tetrakis((4*R*)-3-(arylsulfonyl)thiazolidine-4-carboxylate 1,1-dioxide), the electronic effects of the *N*-sulfonyl functionalities have negligible influence on the enantioselectivity results, the nitro- and methoxy- substituted oxazolidine carboxylate complexes gave the similar asymmetric induction (entries 1 vs. 6, and 15 vs. 20).

In contrast, the arylsulfonyl groups with different electronic effects have critical effects on the degree of asymmetric induction catalyzed by rhodium tetrakis((4*S*,5*R*)-5-methyl-3-(arylsulfonyl)oxazolidine-4-carboxylate). The asymmetric induction was good in the reactions catalyzed by the $-NO_2$, -F or $-CF_3$ functionalized catalysts (80-88% ee, entries 8-10), but only modest in the presence of –Me, -*tert*-Bu or –OMe substituted Rh(II) complexes (49-56% ee, entries 11-13).

Sulfonated rhodium prolinates Rh_2(*S*-NOSP)$_4$, Rh_2(*S*-TFSP)$_4$, Rh_2(*S*-MOSP)$_4$ and Rh_2(*S*-DOSP)$_4$ have been prepared according to the reported procedures (Figure 1),[31] and their activities have been tested in the aziridination of styrene. Under our standard reaction conditions, they gave rise to -46, 60, 81 and 73% ee, respectively (entries 21-25). Next, we have also examined the catalytic activities of Rh_2(*S*-PTAD)$_4$ and Rh_2(*S*-NTTL)$_4$, which are popular catalysts in nitrene transfer reactions,[11,12] and they led to the formation of the aziridine product in 25% and 60% ee, respectively (entries 26 and 27).

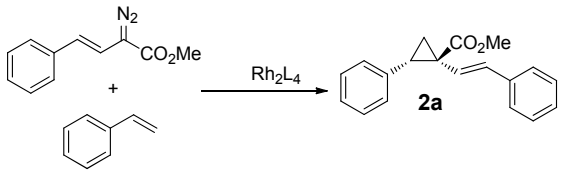
The effects of other solvents (e.g. $PhCF_3$, DCE, CH_2Br_2, toluene) on the enantioselectivity were also tested, and the enantiomeric excess was in the range of 15-78% ee using Rh_2(4*S*,5*R*-MNOSO)$_4$ as the catalyst (entries 28-31). Among the solvents that have been tested for catalytic aziridiantion reactions, it seemed that toluene was the worst choice and the asymmetric induction was only 15% ee.

Comparison on the catalytic data in the presence of different chiral Rh(II) catalysts, our catalysts Rh_2(4*S*-DOSO)$_4$ and Rh_2(4*S*,5*R*-MDOSO)$_4$ are so far the most effective Rh(II) catalysts in the aziridination reaction of styrene in terms of yields and enantioselectivities. We have further tested the catalytic capabilities of our catalysts in intramolecular C-H bond amination of sulfamate esters such as 2,3-dihydro-1*H*-inden-2-yl sulfamate developed by Du Bois.[19] The asymmetric inductions, however, were not satisfactory. The best result was only in modest asymmetric induction (40% ee) and achieved in Rh_2(4*S*,5*R*-MNOSO)$_4$-catalyzed amination reaction.

Catalytic cyclopropanantion reactions

Cyclopropanation of alkenes by transition metal catalysts with diazo compounds represents a straightforward approach to cyclopropanes, which are important in diverse areas of organic chemistry and biology. Especially, the optically pure cyclopropanes are critical to many applications, for example, asymmetric syntheses of cyclopropane amino acids and sertraline.[36] In the last two decades, the catalytic asymmetric cyclopropanation of alkenes with diazo carbonyl compounds in the presence of chiral rhodium catalysts offers significant potential as a general method for the synthesis of optically pure cyclopropanes.

Table 2 Dirhodium catalyzed cyclopropanation[a]



Entry	Catalyst	Yield, %	*E*-/*Z*-	Ee, %
1	Rh_2(4*S*-NOSO)$_4$	80	96:4	63
2	Rh_2(4*S*-FLSO)$_4$	92	95:5	81
3	Rh_2(4*S*-TFSO)$_4$	90	95:5	49
4	Rh_2(4*S*-MESO)$_4$	82	95:5	61
5	Rh_2(4*S*-TBSO)$_4$	90	96:4	71
6	Rh_2(4*S*-MOSO)$_4$	88	94:6	60
7	Rh_2(4*S*-DOSO)$_4$	84	95:5	65
8	Rh_2(4*S*,5*R*-MNOSO)$_4$	96	93:7	98
9	Rh_2(4*S*,5*R*-MFLSO)$_4$	90	93:7	83
10	Rh_2(4*S*,5*R*-MFSO)$_4$	85	92:8	94
11	Rh_2(4*S*,5*R*-MMESO)$_4$	93	93:7	88
12	Rh_2(4*S*,5*R*-MTBSO)$_4$	95	94:6	88
13	Rh_2(4*S*,5*R*-MMOSO)$_4$	86	93:7	92
14	Rh_2(4*S*,5*R*-MDOSO)$_4$	92	95:5	90
15	Rh_2(4*R*-NOST)$_4$	91	93:7	40
16	Rh_2(4*R*-FLST)$_4$	94	95:5	42
17	Rh_2(4*R*-TFST)$_4$	90	94:6	55
18	Rh_2(4*R*-MEST)$_4$	90	95:5	47
19	Rh_2(4*R*-TBST)$_4$	93	93:7	67
20	Rh_2(4*R*-MOST)$_4$	90	94:6	53
21	Rh_2(4*R*-DOST)$_4$	93	96:4	64
22	Rh_2(*S*-NOSP)$_4$	90	93:7	90
23[b]	Rh_2(4*S*,5*R*-MNOSO)$_4$	90	95:5	95
24[c]	Rh_2(4*S*,5*R*-MNOSO)$_4$	85	96:4	92
25[d]	Rh_2(4*S*,5*R*-MNOSO)$_4$	87	93:7	86
26[e]	Rh_2(4*S*,5*R*-MNOSO)$_4$	75	94:6	81
27[f]	Rh_2(4*S*,5*R*-MNOSO)$_4$	80	93:7	80
28[g]	Rh_2(4*S*,5*R*-MNOSO)$_4$	75	96:4	84
29[h]	Rh_2(4*S*,5*R*-MNOSO)$_4$	42	95:5	82

[a] Reaction conditions: A solution of diazo compound (40 mg, 0.2 mmol, 1.0 eq) in 1 mL toluene was added slowly to the solution of styrene (104 mg, 1.0 mmol, 5.0 eq), methyl benzoate (27 mg, 0.2 mmol, 1.0 eq) and 2 mol% catalyst in 1 mL toluene at -40℃. The resulting solution was vigorously stirred at -40℃ for two days until most diazo compound was completely consumed. [b] -40℃, no $PhCO_2Me$; [c] -30℃, no $PhCO_2Me$; [d] -20℃, no $PhCO_2Me$; [e] 0℃, no $PhCO_2Me$; [f] room temperature, no $PhCO_2Me$; [g] with 0.1 mol% catalyst; [h] with 0.01 mol% catalyst.

We have shown that our Rh(II) catalysts can efficiently promote azirdination reactions with moderate to high asymmetric inductions (up to 94% ee). Next, we explored the catalytic capabilities of our catalysts in cyclopropanation reactions. As the test reaction cyclopropanantion with vinyldiazoacetates such as (*E*)-methyl 2-diazo-4-phenylbut-3-enoate was chosen. This protocol employing $Rh_2(DOSP)_4$ as the catalyst and pentane as the solvent at -78°C has been successfully elaborated by Davies et al. and has transformed donor/acceptor substituted diazo compounds into cyclopropanes with different alkenes in high to excellent enantioselectivities (up to 98% ee).[7a] No attempt was made on our part to improve the Davies protocol; rather, it served as a well-established test reaction to investigate the effects of heterocycles and *N*-sulfonyl functionalities on the catalytic results of carbene transfer reactions.

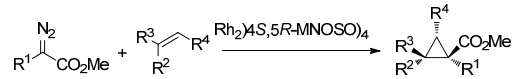
The evaluation of our catalysts was initially carried out using the cyclopropanation between the (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (1.0 eq) and styrene (5.0 eq) with 0.02 equiv of the catalyst and 1.0 eq of methyl benzoate as the additive and toluene as solvent at -40 °C as the standard reaction.[8m] The catalytic results are shown in Table 2. GC-MS analyses of the reaction mixtures suggest that excellent *E*-/Z-diastereoselectivities (ranging from 92:8 to 96:4, entries 1-21) were obtained. All the reactions proceeded in high to excellent yields ranging from 80 to 96%, and in moderate to excellent asymmetric induction (up to 98% ee). The absolute stereochemistry of the major isomer in all cases was 1*S*,2*S*, which was determined by comparison of the HPLC spectra with that of an authentic sample.[7a]

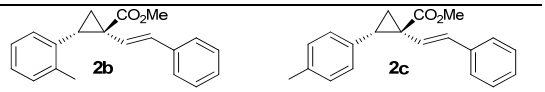
In the general, the higher enantioselectivity was observed in the reactions catalyzed by the oxazolidine-4-carboxylate-derived catalysts (49-81% ee, entries 1-7) than the thiazolidine-4-carboxylate 1,1-dioxide-based catalysts (40-67% ee, entries 15-21). Additional methyl group in the oxazolidine ring has largely enhanced the asymmetric inductions of the corresponding catalysts (83-98% ee, entries 8-14). Among the 21 Rh(II) complexes, dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-((4-nitrophenyl)sulfonyl)oxazolidine-4-carboxylate) (Rh_2(4*S*,5*R*-MNOSO)$_4$) displayed the highest efficiency in terms of yields and enantioselectivities (96% yield and 98% ee, entry 8). Electronic changes on the aryl ring had a minimal effect, considering that the electron-rich 4-methoxyphenyl derivative Rh_2(4*S*,5*R*-MMOSO)$_4$ also resulted in excellent asymmetric induction (92% ee, entry 13).

The 4-dodecylphenyl catalysts Rh_2(4*S*-DOSO)$_4$, Rh_2(4*S*,5*R*-MDOSO)$_4$ and Rh_2(4*R*-DOST)$_4$ were prepared due to the possibly good solubility induced by these functionalities. We have tested their solubilities, finding that they can be well dissolved in hydrocarbon solvent (e.g. toluene and pentane). It is noted that the success of the 4-dodecylphenyl prolinate catalyst $Rh_2(DOSP)_4$ was ascribed to its super solubility in hydrocarbon solvent.[7] Our results suggested that under our reaction conditions (in toluene at -40°C), the 4-dodecylphenyl catalyst Rh_2(4*S*,5*R*-MDOSO)$_4$ cannot compete with the nitro-functionalized catalyst Rh_2(4*S*,5*R*-MNOSO)$_4$. Their ligands have the same heterocycle ring, 5-methyloxazolidine, but they

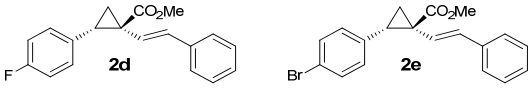
displayed 90 and 98% ee, respectively (entries 14 and 8). The other two 4-dodecylphenyl catalysts Rh_2(4*S*-DOSO)$_4$ and Rh_2(4*R*-DOST) cannot rival Rh_2(4*S*,5*R*-MNOSO)$_4$, neither, and the asymmetric inductions were modest (entries 7 and 21). On the other hand, the enantioselectivities of other nitro-functionalized Rh(II) catalysts Rh_2(4*S*-NOSO)$_4$ and Rh_2(4*R*-NOST)$_4$, whose ligands were composed of oxazolidine and thiazolidine 1,1-dioxide, respectively, were lower than Rh_2(4*S*,5*R*-MNOSO)$_4$ (entries 1, 8 and 15). For comparison, we have also run the same cycloaddition reaction using the nitro-functionalized Rh(II) prolinate (Rh_2(*S*-NOSP)$_4$, Figure 1) as the catalyst, resulting in 90% yield and 90% ee (entry 22). We ascribe the success of Rh_2(4*S*,5*R*-MNOSO)$_4$ to the synergistic effects of the electron-withdrawing O in the oxazolidine ring (electronic effect), the methyl substituent in the 5-position of the oxazolidine ring, which is next to the carboxylate group at the 4-position of the ring (steric effect), and the highly electron-withdrawing nitro substituent attached to the sulfonylphenyl group (electronic effect). Any one of these effects cannot alone elucidate the excellent enantioselectivity achieved in the Rh_2(4*S*,5*R*-MNOSO)$_4$-catalyzed cyclopropanation reaction.

Table 3 Substrate scope of catalytic cyclopropanation[a]

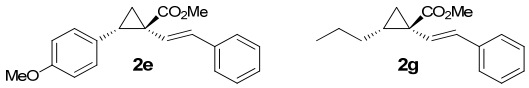




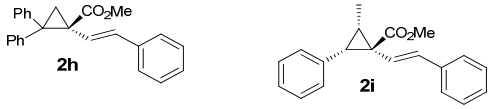
96%, 87% ee, 97:3 dr 93%, 88% ee, 95:5 dr



95%, 92% ee, 96:4 dr 92%, 90% ee, 97:3 dr



95%, 93% ee, 98:2 dr 70%, 92% ee, 97:3 dr



94%, 96% ee 90%, 88% ee, 98:2 dr

[a] Reaction conditions: A solution of diazo compound (40 mg, 0.2 mmol, 1.0 eq) in 1 mL toluene was added slowly to the solution of olefin (1.0 mmol, 5.0 eq), and 2 mol% Rh_2(4*S*,5*R*-MNOSO)$_4$ in 1 mL toluene at -40℃. The resulting solution was vigorously stirred at -40℃ for two days until most diazo compound was completely consumed.

After it was determined that Rh_2(4*S*,5*R*-MNOSO)$_4$ was an exceptional catalyst, we studied the effects of the additive methyl benzoate and the temperatures on the catalytic results, finding that the presence of methyl benzoate and low temperature have positive effects on the enantioselectivity of the cyclopropane product (entries 8, 23-27).[8m] Decreasing the catalyst loading from 2 to 0.1 mol% lowered the yield and enantioselectivity (75% yield and 84% ee, entry 28). Further decreasing the catalyst loading from 0.1 to 0.01 mol% did not alter the eneatioselectivity (82% ee), but the yield was much poorer (42%, entry 29).

The catalytic capabilities of Rh_2(4*S*,5*R*-MNOSO)$_4$ in intermolecular cyclopropanation reactions were further evaluated with the use of alkenes other than styrene (Table 3). Exceptional stereocontrol (> 95:5 *E*/*Z*) and enantiocontrol (88-93% ee) were achieved with substituted styrenes bearing either an electron-donating group (e.g. -Me and -OMe) or an electron–withdrawing group (e.g. -F and -Br) in the 4-position. The introduction of a 2-methyl group in 2-methyl styrene, and thus making the olefin substrate relatively crowded than styrene, does not largely reduce the enantioselectivity of the cyclopropane product **2b** (87% ee). High asymmetric induction was also found in the cyclopropantion of an aliphatic alkene (*n*-hexene), and the corresponding cyclopropane product **2g** was in 92% ee, although the yield is modest (70%). 1,1-Diphenylethene was also effective in Rh_2(4*S*,5*R*-MNOSO)$_4$-catalyzed cyclopropanation, leading the formation of the cyclopropane **2h** in 94% yield and 96% ee. (*Z*)-Methyl styrene gave the corresponding cyclopropane **2i** in high enantioselectivty (88% ee). However, the reaction with (*E*)-methyl styrene failed.

Conclusions

In summary, we have designed and synthesized a series of chiral Rh(II) complexes, dirhodium tetrakis((4*S*)-3-(arylsulfonyl)oxazolidine-4-carboxylate), dirhodium (4*S*,5*R*)-5-methyl-3-(arylsulfonyl)oxazolidine-4-carboxylic acids and dirhodium tetrakis((4*R*)-3-(arylsulfonyl)thiazolidine-4-carboxylate 1,1-dioxide), in which the *N*-sulfonyl functionalities included -NO_2, -F, -CF_3, -Me, -*tert*-Bu, -OMe and –*n*-dodecyl, which have been fully characterized by EA, IR, UV, NMR and optical rotation measurements. The capabilities of these Rh(II) complexes have been tested in nitrene and carbene transfer reactions. In the general, Rh(II) oxazolidinecarboxylate displayed higher enantioselectivities than Rh(II) thiazolidinecarboxylate 1,1-dioxide with the same arylsulfonyl groups. The *n*-dodecylphenyl substituted Rh(II) complexes (e.g. Rh_2(4*S*-DOSO)$_4$, Rh_2(4*S*,5*R*-MDOSO)$_4$ and Rh_2(4*R*-DOST)$_4$) gave high asymmetric inductions of 94%, 89% and 79% ee, respectively, in the aziridination reaction of styrene. Meanwhile, the nitro-functionalized catalyst Rh_2(4*S*,5*R*-MNOSO)$_4$ gave the best results in the cyclopropanantion reactions in terms of yields and enantioselectivities. Exceptional stereocontrol (> 93:7 *E*/*Z*) and enantiocontrol (up to 98% ee) were achieved with various olefins, which differ in steric and electronic factors. The preliminary results are encouraging. Studies are in progress to determine the full potential of these new dirhodium complexes in organic synthesis. In the carbene transfer reactions, additional methyl group in the 5-position endowed the 5-methyloxazolidine-4-

carboxylate complexes have higher asymmetric inductions than the corresponding Rh(II) oxazolidine-4-carboxylate catalysts. We are currently pursuing the modifications of the ligands (e.g. incorporating alkyl groups in the 5-position of the heterocyle ring) and syntheses of the second generation of Rh(II) thiazolidine-4-carboxylates, and the results will be published in due course.

Experimental section

General information

All the reagents in the present work were obtained from the commercial source and used directly without further purification. The elemental analyses were performed with Perkin-Elmer 240 elemental analyzer. HRESI-MS was performed by using a Bruker Daltonics ESI-Q-TOF maXis4G. Infrared spectra on KBr pellets were collected with a Nicolet/Nexus-670 FT-IR spectrometer in the region of 4000-400 cm^{-1}. UV-Vis spectra were tested on a Shimadzu/UV-3600 spectrophotometer. ^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra were recorded on a Bruker AVANCE III 400. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. HPLC spectra were obtained on HPLC of Agilent 1200 series. Specific rotations were measured on ADP440+B+S.

Cautions! Although we have not experienced any problem in the handling of diazo compounds, extreme care should be taken when manipulating them due to their explosive nature.

Syntheses of (4*S*)-3-(arylsulfonyl)oxazolidine-4-carboxylic acids

(4*S*)-3-(arylsulfonyl)oxazolidine-4-carboxylic acids were prepared with the similar procedure,[29] as exemplified by the synthesis of (4*S*)-3-((4-methoxyphenyl)sulfonyl)oxazolidine-4-carboxylic acid: (*S*)-oxazolidine-4-carboxylic acid hydrochloride (0.50 g, 3.25 mmol) was dissolved in a water (15 mL) solution of a mixture of Na_2CO_3 (0.82 g, 7.8 mmol) and $NaHCO_3$ (0.32 g, 3.90 mmol) at room temperature to give a clear solution, which was then cooled down in an ice bath.[13] An acetone (2 mL) solution containing *p*-methoxybenzenesulfonyl chloride (0.84 g, 4.1 mmol) was added slowly to the above solution with stirring. The whole reaction mixture was allowed to warm to room temperature. After stirring overnight, the reaction mixture was acidified with aqueous HCl (1 M) till the pH value of 2~3, and then extracted with EtOAc (30 ml × 3). The combined organic layer was washed with H_2O (30 ml x 2), brine (50 mL) and dried over Na_2SO_4, filtered. The solvent was removed by rotary evaporator and the crude product was obtained as white solid which was then purified by chromatography on silica gel.

(4*S*)-3-((4-Nitrophenyl)sulfonyl)oxazolidine-4-carboxylic acid (4*S*-NOSO). White solid, 0.56 g (57%). R_f = 0.54 (EtOAc : PE : HOAc = 100 : 50 :5). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.39 (d, J = 8.5 Hz, 2H), 8.18 (d, J = 8.5 Hz, 2H), 5.18 (d, J = 6.3 Hz, 1H), 4.60 (d, J = 6.3 Hz, 1H), 4.48 (dd, J = 7.9, 5.7 Hz, 1H), 3.94 (t, J = 8.7 Hz, 1H), 3.74 (dd, J = 8.7, 5.7 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.02, 150.85, 143.17, 129.86, 125.22, 81.48, 69.81, 59.38. FTIR (KBr, cm^{-1}): 3114 w, 2894 w, 1715 s, 1609 w, 1532 s, 1496 w, 1352 s, 1310s, 1167 s, 1101 w, 1056 w, 1010 w, 997 w, 927 m, 854 m, 742 m, 688 m, 660 m, 631 m, 574 m. HRMS (ESI) ($[M-H]^-$) Calcd. for $C_{10}H_9N_2O_7S$: 301.0136; Found: 301.0137.

(4*S*)-3-((4-Fluorophenyl)sulfonyl)oxazolidine-4-carboxylic acid (4*S*-FLSO). White solid, 0.67 g (75%). R_f = 0.50 (EtOAc : PE : HOAc = 100 : 50 :5) , $[\alpha]^{20}_D$ = -135.6 (c 3.62, acetone). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.11 – 7.91 (m, 2H), 7.48-7.42 (m, 2H), 5.13 (d, J = 6.6 Hz, 1H), 4.54 (d, J = 6.6 Hz, 1H), 4.40 (dd, J = 7.8, 6.0 Hz, 1H), 3.87 (t, J = 8.3 Hz, 1H), 3.70 (dd, J = 8.7, 5.9 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.10, 165.52 ($J_{C\text{-}F}$ = 249.75 Hz), 134.07, 131.40, 117.36 ($J_{C\text{-}F}$ = 21.75 Hz), 81.56, 69.76, 59.41. ^{19}F NMR (282 MHz, DMSO-d_6) δ 105.42. FTIR (KBr, cm^{-1}): 3110 w, 2895 m, 1713 s, 1595 s, 1495 s, 1353 m, 1298 s, 1205 s, 1170 s, 1156 s, 1101 m, 1070 m, 1057 m, 999 m, 926 s, 839 s, 686 s, 597 s, 545 s. HRMS (ESI) ($[M-H]^-$) Calcd. for $C_{10}H_9FNO_5S$: 274.0191; Found: 274.0199.

(4*S*)-3-((4-(Trifluoromethyl)phenyl)sulfonyl)oxazolidine-4-carboxylic acid (4*S*-TFSO). White solid, 0.60 g (57%). R_f = 0.60 (EtOAc : PE : HOAc = 20 : 10 : 1). $[\alpha]^{20}_D$ = -122.7 (c 5.76, acetone). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.14 (d, J = 8.1 Hz, 2H), 7.99 (d, J = 8.1 Hz, 2H), 5.17 (d, J = 6.3 Hz, 1H), 4.57 (d, J = 6.3 Hz, 1H), 4.45 (dd, J = 7.8, 6.0 Hz, 1H), 3.93 (t, J = 8.4 Hz, 1H), 3.73 (dd, J = 8.7, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.67, 141.10, 133.27 ($J_{C\text{-}F}$ = 33.0 Hz), 132.79, 128.81, 123.45 ($J_{C\text{-}F}$ = 272.0 Hz), 80.87, 69.09, 58.74. ^{19}F NMR (282 MHz, DMSO-d_6) δ -62.43. FTIR (KBr, cm^{-1}): 3400 br, 2896 w, 1714 s, 1433 w, 1406 w, 1354 s, 1329 s, 1298 w, 1257 w, 1170 s, 1111 m, 1064 m, 999 w, 927 m, 842 m, 717 m, 657 w, 630 w, 599 w, 570 w. HRMS (ESI) ($[M-H]^-$) Calcd. for $C_{11}H_9F_3NO_5S$: 324.0159; Found: 324.0155.

(4*S*)-3-Tosyloxazolidine-4-carboxylic acid (4*S*-MESO). White solid, 0.57 g (63%). R_f =0.50 (EtOAc : PE : HOAc = 100 : 100 :5), $[\alpha]^{20}_D$ = -168.2 (c 4.30, acetone). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.40 – 7.30 (m, 2H), 5.18 (d, J = 6.0 Hz, 1H), 4.72 (d, J = 6.0 Hz, 1H), 4.38 (t, J = 6.8 Hz, 1H), 3.95 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.44, 145.17, 134.09, 130.38, 128.03, 81.96, 69.74, 59.14, 22.09. FTIR (KBr, cm^{-1}): 3433 br, 2895 w, 1713 s, 1599 w, 1433 w, 1351 s, 1309 w, 1294 w, 1256 w, 1166 s, 1108 w, 1170 w, 997 w, 926 w, 885 w, 814 w, 712 w, 683 m, 579 m, 554 m, 465 w. HRMS (ESI) ($[M-H]^-$) Calcd. for $C_{11}H_{12}NO_5S$: 270.0442; Found: 270.0440.

(4*S*)-3-((4-(*tert*-Butyl)phenyl)sulfonyl)oxazolidine-4-carboxylic acid (4*S*-TBSO). Colorless crystals, 0.70 g (69%). R_f = 0.76 (EtOAc : PE : HOAc = 100 : 100 : 2) , $[\alpha]^{20}_D$ = -158.5 (c 4.48, acetone). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.81 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 5.10 (d, J = 6.3 Hz, 1H), 4.54 (d, J = 6.3 Hz, 1H), 4.36 (dd, J = 8.4, 6.0 Hz, 1H), 3.85 (t, J = 8.4 Hz, 1H), 3.70 (dd, J = 8.4, 6.0 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.40, 157.43, 135.00, 128.35, 127.13, 81.74, 69.81, 59.70, 35.87, 31.69. FTIR (KBr, cm^{-1}): 3416 w, 2897 m, 1713 s, 1597 s, 1598 w, 1497 m, 1467 w, 1443 w, 1348 s, 1307 m, 1257 s, 1157 s, 1114 m, 1069 w, 1026 w, 998 w, 926 m, 834 m, 685 m, 598 s, 554 s. HRMS (ESI) ($[M-H]^-$) Calcd. for $C_{14}H_{18}NO_5S$: 312.0911; Found: 312.0911.

(4*S*)-3-((4-Methoxyphenyl)sulfonyl)oxazolidine-4-carboxylic acid (4*S*-MOSO). White solid, 0.57 g (61%), R_f = 0.54 (EtOAc : Petroleum Ester : HOAc = 4 : 4 : 1), $[\alpha]^{20}_D$ = -153.0 (c 7.36, acetone). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.82 (d, J = 9.0 Hz, 2H), 7.11 (d, J = 9.0 Hz, 2H), 5.09 (d, J = 6.6 Hz, 1H), 4.52 (d, J = 6.6 Hz, 1H), 4.33 (dd, J = 7.2, 6.0 Hz, 1H), 3.84 (s, 3H), 3.82 (t, J = 7.8 Hz, 1H), 3.68 (dd, J = 8.7, 6.0 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.33, 163.71, 130.53,

129.10, 115.31, 81.59, 69.56, 59.56, 56.47. FTIR (KBr, cm^{-1}): 2988 m, 1713 s, 1597 s, 1580 m, 1498 m, 1464 w, 1442 w, 1348 s, 1306 m, 1257 s, 1156 s, 1113 m, 1069 w, 1026 w, 998 w, 926 m, 834 m, 685 m, 598 s, 554 s. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{11}H_{14}NO_7S$: 286.0380; Found: 286.0354.

(4*S*)-3-((4-Dodecylphenyl)sulfonyl)oxazolidine-4-carboxylic acid (4S-DOSO). Colorless oil, 1.10 g (61%), R_f = 0.31 (EtOAc : PE : HOAc = 7.5 : 30 : 1), $[\alpha]^{20}_D$ = -151.1° (c 13.44, acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.31 (m, 2H), 5.16 (d, *J* = 5.6 Hz, 1H), 4.70 (d, *J* = 5.6 Hz, 1H), 4.42 (m, 2H), 2.57 (m, 1H), 1.60 (m, 4H), 1.12 (m, 15H), 0.81 (m, 5H). FTIR (KBr, cm^{-1}): 3560 br, 2958 m, 2927 s, 2871 w, 2855 m, 1597 m, 1411 m, 1352 s, 1165 s, 1074 w, 982 w, 834 w, 655 w, 601 m, 575 w. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{23}H_{37}NO_5S$: 438.2320; Found: 438.2320.

Syntheses of (4*S*,5*R*)-5-methyl-3-(arylsulfonyl)oxazolidine-4-carboxylic acids

(4*S*,5*R*)-5-methyl-3-(arylsulfonyl)oxazolidine-4-carboxylic acids were prepared with the similar procedure,[29] as exemplified by the synthesis of (4*S*,5*R*)-3-((4-fluorophenyl)sulfonyl)-5-methyloxazolidine-4-carboxylic acid: (4*S*,5*R*)-5-methyloxazolidine-4-carboxylic acid hydrochloride (0.50 g, 3.25 mmol)[17] was dissolved in a water (15 mL) solution of a mixture of Na_2CO_3 (0.82 g, 7.8 mmol) and $NaHCO_3$ (0.32 g, 3.90 mmol) at room temperature to give a clear solution, which was then cooled down in an ice bath. An acetone (2 mL) solution containing *p*-fluorbenzenesulfonyl chloride (1.58 g, 4.1 mmol) was added slowly to the above solution with stirring. The whole reaction mixture was allowed to warm to room temperature. After stirring overnight, the reaction mixture was acidified with aqueous HCl (1 M) till the pH value of 2~3, and then extracted with EtOAc (30 ml × 3). The combined organic layer was washed with H_2O (30 ml x 2), brine (50 mL) and dried over Na_2SO_4, filtered. The solvent was removed by rotary evaporator and the crude product was obtained as white solid which was then purified by chromatography on silica gel.

(4*S*,5*R*)-5-methyl-3-((4-nitrophenyl)sulfonyl)-oxazolidine-4-carboxylic acid (4*S*,5*R*-MNOSO). Light yellow solid, 0.70 g (40%). R_f = 0.50 (EtOAc : PE : HOAc = 20 : 20 :1). $[\alpha]^{20}_D$ = -153.4 (c 7.08, acetone). ^{1}H NMR (400 MHz, acetone-d_6) *δ* 8.50 (m, 2H), 8.28 (m, 2H), 5.35 (d, *J* = 6.8 Hz, 1H), 4.71 (d, *J* = 6.8 Hz,1H), 4.11 (m, 1H), 3.94 (d, *J* = 7.1 Hz, 1H), 1.16 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6) *δ* 170.40, 151.71, 144.45, 130.42, 125.47, 81.80, 79.94, 66.04, 18.84. FTIR (KBr, cm^{-1}): 3435 br, 3114 w,1713 m, 1610 w, 1531 s, 1351 s, 1309 w, 1167 s, 1069 w, 927 w, 854 w, 741 m, 574 w, 468 w. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{11}H_{12}N_2O_7S$: 315.0292; Found: 315.0288.

(4*S*,5*R*)-5-methyl-3-((4-fluorophenyl)sulfonyl)-oxazolidine-4-carboxylic acid (4*S*,5*R*-MFLSO). Light yellow oil, 0.95 g (53%). R_f = 0.50 (EtOAc : PE : HOAc = 20 : 20 :1) , $[\alpha]^{20}_D$ = -132.6 (c 8.90, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) *δ* 8.01 (m, 2H), 7.45 (m, 2H), 5.24 (d, *J* = 7.1 Hz, 1H), 4.57 (d, *J* = 7.1 Hz, 1H), 3.97 (m, 1H), 3.72 (d, *J* = 7.0 Hz, 1H), 0.98 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 170.42, 165.07 (d, $J_{C\text{-}F}$= 252.8 Hz), 133.37 (d, *J* = 3.0 Hz), 131.08 (d, *J* = 9.7 Hz), 116.74 (d, *J* = 22.7 Hz), 80.60, 78.14, 65.02, 18.37. ^{19}F NMR (282 MHz, DMSO-d_6) *δ* -109.14. FTIR (KBr, cm^{-1}): 3420 br, 2980 w, 1737 s, 1494 s, 1295 m, 1352 s, 1238 m, 1170 s, 1156 s, 1089 m, 1075 w, 980 m, 842 s, 680 m, 591 s, 547 s. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{11}H_{12}FNO_5S$: 288.0347; Found: 288.0349.

(4*S*,5*R*)-5-methyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)-oxazolidine-4-carboxylic acid (4*S*,5*R*-MTFSO). White solid, 1.20 g (57%). R_f = 0.50 (EtOAc : PE : HOAc = 20 : 20 : 1). $[\alpha]^{20}_D$ = -132.3 (c 11.78, acetone). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.02 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 5.26 (d, *J* = 6.5 Hz, 1H), 4.70 (d, *J* = 6.5 Hz, 1H), 4.12 (m, 1H), 3.84 (d, *J* = 7.0 Hz, 1H), 1.22 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 173.85, 141.31, 135.53 (q, $J_{C\text{-}F}$= 33.0 Hz), 128.58, 126.74 (q, *J* = 3.6 Hz), 123.28 (d, *J* = 273.1 Hz), 81.38, 79.31, 65.22, 18.61.^{19}F NMR (377 MHz, $CDCl_3$) *δ* -63.21. FTIR (KBr, cm^{-1}): 3400 br, 2987 w, 1715 s, 1405 w, 1390 m,1324 s, 1296 w, 1259 w, 1227 w, 1185 s, 1133 s, 1107 m, 1062 m, 1015 w, 983 m, 889 w, 838 m, 717 s, 649 w, 617 s, 568 m, 428 m. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{12}H_{12}F_3NO_5S$: 338.0316; Found: 338.0311.

(4*S*,5*R*)-5-methyl-3-tosyloxazolidine-4-carboxylic acid (4*S*,5*R*-MMESO). White solid, 0.90 g (60%). R_f = 0.50 (EtOAc : PE : HOAc = 20 : 20 :1), $[\alpha]^{20}_D$ = -159.7 (c 9.00, acetone). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.75 (m, 2H), 7.34 (m, 2H), 5.23 (d, *J* = 6.7 Hz, 1H), 4.67 (d, *J* = 6.7 Hz, 1H), 4.09 (m, 1H), 3.76 (d, *J* = 7.1 Hz, 1H), 2.43 (s, 1H), 1.15 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 173.84, 145.05, 134.04, 130.22, 128.13, 81.44, 79.02, 65.31, 21.78, 18.55. FTIR (KBr, cm^{-1}): 3380 br, 2885 w,1737 s, 1598 w, 1348 s, 1278 w, 1161 s, 1089 s, 1071 w, 972 m, 818 w, 705 m, 665 s, 595 s, 546 s. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{12}H_{15}NO_5S$: 284.0598; Found: 284.0597.

(4*S*,5*R*)-5-methyl-3-((4-(tert-butyl)phenyl)sulfonyl)-oxazolidine-4-carboxylic acid (4*S*,5*R*-MTBSO). Colorless oil, 1.10 g (53%). R_f = 0.60 (EtOAc : PE : HOAc = 20 : 20 : 1) , $[\alpha]^{20}_D$ = -122.6 (c 8.60, acetone). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.78 (m, 2H), 7.54 (m, 2H), 5.25 (d, *J* = 6.6 Hz, 1H), 5.25 (d, *J* = 6.6 Hz, 1H), 4.67 (d, *J* = 6.7 Hz, 1H), 4.08 (m, 1H), 3.77 (d, *J* = 7.0 Hz, 1H), 1.32 (s, 9H), 1.11 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 173.74, 158.01, 134.07, 128.05, 126.56, 81.52, 79.00, 65.25, 35.40, 31.20, 18.51. FTIR (KBr, cm^{-1}): 3480 br, 2966 s, 1737 s, 1595 m, 1461 w, 1400 m, 1349 s, 1268 w, 1164 s, 1113 m, 1086 m, 1039 w, 980 m, 891 w, 844 m, 754 m, 637 s, 591 s, 554 w. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{15}H_{21}NO_5S$: 326.1068; Found: 326.1058.

(4*S*,5*R*)-5-methyl-3-((4-methoxyphenyl)sulfonyl)-oxazolidine-4-carboxylic acid (4*S*,5*R*-MMOSO). White solid, 0.85 g (47%), R_f = 0.60 (EtOAc : PE : HOAc = 20 : 20 : 1), $[\alpha]^{20}_D$ = -179.5 (c 7.80, acetone). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.76 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 5.17 (d, *J* = 6.8 Hz, 1H), 4.64 (d, *J* = 6.8 Hz, 1H), 4.04 (m, 1H), 3.82 (s, 3H), 3.71 (d, *J* = 7.1 Hz, 1H), 1.10 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 172.86, 163.89, 130.25, 128.26, 114.73, 81.35, 78.91, 65.32, 55.85, 18.53. FTIR (KBr, cm^{-1}): 3500 w, 2880 w, 1738 s, 1596 s, 1577 w, 1499 s, 1460 w, 1443 w, 1348 s, 1309 w, 1264 s, 1157 s, 1092 m, 1074 w, 1022 w, 980 w, 892 w, 836 m, 802 w, 673 s, 593 s, 557 s. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{12}H_{15}NO_6S$: 300.0547; Found: 300.0538.

(4*S*,5*R*)-3-((4-Dodecylphenyl)sulfonyl)-5-methyloxazolidine-4-carboxylic acid (4*S*,5*R*-MDOSO). Colorless oil, 1.10 g (61%). R_f = 0.31 (EtOAc : PE : HOAc = 7.5 : 30 : 1), $[\alpha]^{20}_D$ = -151.1° (c

13.44, acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.32 (m, 2H), 5.28 (d, *J* = 6.9 Hz, 1H), 4.69 (d, *J* = 6.9 Hz, 1H), 4.09 (m, 1H), 3.74 (m, 1H), 2.59 (m, 1H), 1.60 (m, 4H), 1.12 (m, 18H), 0.81 (m, 5H). FTIR (KBr, cm^{-1}): 3560 br, 2958 m, 2927 s, 2871 w, 2855 m, 1597 m, 1411 m, 1352 s, 1165 s, 1074 w, 982 w, 834 w, 655 w, 601 m, 575 w. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{23}H_{37}NO_5S$: 438.2320; Found: 438.2320.

Syntheses of (4*R*)-3-(arylsulfonyl)thiazolidine-4-carboxylic acids

(4*R*)-3-(arylsulfonyl)thiazolidine-4-carboxylic acids were prepared with the similar procedure,[29] as exemplified by the synthesis of (4*R*)-3-tosylthiazolidine-4-carboxylic acid: $_L$-4-Thiazolidinecarboxylic acid (1.00 g, 7.5 mmol) was dissolved in a water (30 mL) solution of a mixture of Na_2CO_3 (1.59 g, 15.0 mmol) and $NaHCO_3$ (0.63 g, 7.5 mmol) at room temperature to give a clear solution, which was then cooled down in an ice bath. An acetone (10 mL) solution containing 4-methylbenzene-1-sulfonyl chloride (1.80 g, 9.4 mmol) was added slowly to the above solution with stirring. The whole reaction mixture was allowed to warm to room temperature. After stirring for another 4 h, the reaction mixture was washed with Et_2O (5 mL * 5). The aqueous layer was collected, acidified with aqueous HCl (1 M) till the pH value around 2, extracted with EtOAc (30 ml × 3), washed with water until the pH value around 7, dried over anhydrous sodium sulfate, and then concentrated in vacuum.

(4*R*)-3-((4-Nitrophenyl)sulfonyl)thiazolidine-4-carboxylic acid. White solid, yield 0.89 g (74%). R_f = 0.72 (Petroleum ether: EtOAc: acetic acid = 30: 20: 2). ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 8.39 (d, *J* = 9.0 Hz, 2H), 8.08 (d, *J* = 9.0 Hz, 2H), 4.97 (dd, *J* = 6.9, 3.6 Hz, 1H), 4.74 (d, *J* = 9.0 Hz, 1H), 4.41 (d *J* = 9.0 Hz, 3.0 Hz, 1H), 3.32 (dd, *J* = 11.1, 3.6 Hz), 3.20 (dd, *J* = 11.1, 6.9 Hz, 1H).

(4*R*)-3-((4-Fluorophenyl)sulfonyl)thiazolidine-4-carboxylic acid. White solid, yield 0.90 g (75%). R_f = 0.42 (Petroleum ether: EtOAc: acetic acid = 30 : 20: 2). ^{1}H NMR (300 MHz, acetone-d_6) *δ* 7.85 (m, 2H), 7.17 (m, 2H), 4.84 (dd, *J* = 7.2, 3.4 Hz, 1H), 4.63 (d, *J* = 9.3 Hz, 1H), 4.35 (d, *J* = 9.3 Hz, 1H), 3.21 (dd, *J* = 11.5, 3.4 Hz, 1H), 3.01 (dd, *J* = 11.5，7.2 Hz, 1H). ^{19}F NMR, (282 MHz, acetone-d_6) *δ* -103.98.

(4*R*)-3-((4-Trifluoromethyl)phenyl)sulfonyl)thiazolidine-4-carboxylic acid. White solid, yield 1.09 g (85%). R_f =0.63 (Petroleum ether: EtOAc : acetic acid = 10: 10: 1). ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 8.02 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 4.96 (dd, *J* = 6.9, 3.3 Hz, 1H); 4.71 (d, *J* = 9.0 Hz, 1H), 4.42 (d, *J* = 9.0 Hz, 1H), 3.3 (dd, *J* = 11.4, 3.6 Hz, 1H), 3.15 (dd, *J* = 11.4, 6.9 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) *δ* -63.92.

(4*R*)-3-Tosylthiazolidine-4-carboxylic acid. White solids, yield 0.90 g (42%). R_f = 0.45 (Petroleum ether: EtOAc: acetic acid = 30: 20: 2). ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.75 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 4.86 (dd, *J* = 7.2, 3.6 Hz, 1H), 4.67 (d, *J* = 9.3 Hz, 1H), 4.44 (d, *J* = 9.3 Hz, 1H), 3.25 (dd, *J* = 11.4, 3.6 Hz, 1H), 2.96 (dd, *J* =11.4, 7.2 Hz, 1H), 2.45 (s, 3H).

(4*R*)-3-((4-(*tert*-Butyl)phenyl)sulfonyl)thiazolidine-4-carboxylic acid. White solid, yield 1.02 g (83%). R_f =0.34 (Petroleum ether: EtOAc: acetic acid = 30: 20: 2). ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.79 (d, *J* = 6.6 Hz, 2H), 7.55 (d, *J* = 6.6 Hz, 2H), 4.88 (dd, *J* = 7.2, 5.4 Hz，1H), 4.65 (d, *J* = 9.3 Hz, 1H), 4.45 (d, *J* = 9.3 Hz, 1H), 3.28 (dd, *J* = 11.4, 5.4 Hz, 1H), 2.98 (dd, *J* = 11.4, 7.2 Hz,1H), 1.36 (s, 9H).

(4*R*)-3-((4-Methoxyphenyl)sulfonyl)thiazolidine-4-carboxylic acid. Oil, yield 2.10 g (92 %). R_f =0.42 (Petroleum ether: EtOAc: acetic acid = 30: 20: 2). ^{1}H NMR (300 MHz, DMSO-d_6) *δ* 7.83 (d, *J* = 6.9 Hz, 2H), 7.10 (d, *J* = 6.9 Hz, 2H), 4.81 (dd, *J* = 7.3, 3.6 Hz，1H), 4.68 (d, *J* = 10.3 Hz, 1H), 4.32 (d, *J* = 10.3 Hz, 1H), 3.83 (s, 3H), 3.07 (dd, *J* = 11.4, 3.6 Hz, 1H), 2.78 (dd, *J* = 11.4, 7.3 Hz, 1H).

(4*R*)-3-((4-Dodecylphenyl)sulfonyl)thiazolidine-4-carboxylic acid. Oil, yield 1.95 g (59 %). R_f =0.38 (Petroleum ether: EtOAc: acetic acid = 20: 10: 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 4.90 (d, *J* = 4.1 Hz, 1H), 4.66 (d, *J* = 9.6 Hz, 1H), 4.44 (d, *J* = 9.6 Hz, 1H), 3.20 (d, *J* = 10.8 Hz, 1H), 2.87 (d, *J* = 4.1 Hz, 1H), 2.56 (m, 1H), 1.55 (m, 4H), 1.09 (m, 15H), 0.79 (m, 5H).FTIR (KBr, cm^{-1}): 3513 br, 2956 m, 2926 s, 2855 m, 1731 s, 1596 m, 1458 m, 1411 w, 1351 s, 1227 w, 1165 s, 1091 w, 1009 w, 828 w,648 w, 632 w, 595 s.

Syntheses of (4*R*)-3-(arylsulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxides

(4*R*)-3-(arylsulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxides were prepared with the similar procedure, as exemplified by the synthesis of (4*R*)-3-tosylthiazolidine-4-carboxylic acid 1,1-dioxide: A mixture of (*R*)-3-tosylthiazolidine-4-carboxylic acid (2.0 g, 6.96 mmol) and the finely powdered urea-hydrogen peroxide adduct (3.27 g, 34.79 mmol) in acetonitrile (3 mL) was heated at 85℃ for 4 h. After that, water (5 mL) was added to the reaction mixture, which was then acidified with HCl (1 M) till the pH value around 2, extracted with EtOAc (30 mL × 3), washed with water till the pH value around 7, and then dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to afford the crude product, which was purified by chromatography to deliver pure product.

(4*R*)-3-((4-Nitrophenyl)sulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxide (4*R*-NOST). Oyster solid, yield 0.98 g (88%) R_f = 0.59, (Petroleum ether: EtOAc: formic acid = 30: 20: 2). $[\alpha]^{15}_D$ = -62.2° (c 1.96, acetone). ^{1}H NMR (300 MHz, acetone-d_6): *δ* 8.45 (d, *J* = 9.0 Hz, 2H), 8.25 (d, *J* = 9.0 Hz, 2H), 5.39 (dd, *J* = 9.1, 4.1 Hz 1H), 4.90 (d, *J* = 11.8 Hz, 1H), 4.37 (d, *J* = 11.8 Hz 1H), 3.73 (dd, *J* = 13.5, 9.1Hz, 1H), 3.63(dd, *J* = 13.5, 4.1Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) *δ* 168.97, 150.13, 143.01, 129.14, 124.62, 62.35, 56.91, 51.28. FTIR (KBr, cm^{-1}): 3592 s, 3522 s, 3073 w, 3017 w, 2964 w, 2852 w, 2769 w, 2698 w, 2548w, 1739 s, 1608 s, 1530 s, 1355 s, 1332 s, 1224 m, 1161 s, 1124 s, 1090 s, 1043 s, 967 w, 921 w, 858 w, 769 s, 682 m, 468 m, 430 m. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{10}H_9N_2O_8S_2$: 348.9806; Found: 348.9784.

(4*R*)-3-((4-Fluorophenyl)sulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxide (4*R*-FLST). Oyster white solid, yield 1.23 g (56%) R_f = 0.29 (Petroleum ether: EtOAc: formic acid = 30: 20: 2). $[\alpha]^{15}_D$ = -58.8° (c 10.18, acetone). ^{1}H NMR (300 MHz, acetone-d_6) *δ* 8.05 (m, 2H), 7.39 (m, 2H), 5.28 (dd, *J* = 8.4, 4.5 Hz, 1H), 4.81 (d, *J* = 12.0 Hz，1H), 4.32 (d, *J* = 12 Hz, 1H), 3.60 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 169.80, 165.52 ($J_{C\text{-}F}$ = 251.0 Hz) 134.54, 131.25, 117.07 ($J_{C\text{-}F}$ = 23.0 Hz), 62.82, 57.43,

50.75, 31.09. ^{19}F NMR (377 MHz, acetone-d_6) δ -106.06. FTIR (KBr, cm^{-1}): 3554 br, 3109 s, 3023 s, 2955 s, 2601 w, 1732 s, 1625 m, 1591 s, 1494 s, 1408 s, 1333 s, 1297 s, 1232 s, 1157 s, 1089 s, 1041 m, 997 m, 915 m, 841 s, 820 s, 758 s, 727 w, 577 s, 545 s, 440 m. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{10}H_9FNO_6S_2$: 321.9861; Found: 321.9841.

(4*R*)-3-((4-Trifluoromethyl)phenyl)sulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxide (4*R*-TFST). Oyster white solid, yield 1.44 g (66 %). R_f = 0.37 (Petroleum ether: EtOAc: acetic acid = 30: 20: 2). $[\alpha]^{15}_D$ = -67.7° (c 8.98, acetone). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 5.14 (dd, *J* = 9.0 Hz, 4.5 Hz, 1H), 4.96 (d, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 12.0 Hz 1H), 3.68 (dd, *J* = 13.8, 9.0 Hz, 1H), 3.56 (dd, *J* = 13.8, 4.5 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 169.32, 141.50, 133.12 ($J_{C\text{-}F}$ = 24.8 Hz), 126.37, 126.39, 123.26 ($J_{C\text{-}F}$ = 270.8 Hz), 62.40, 57.11, 51.33. ^{19}F NMR (377 MHz, acetone-d_6) δ -63.66. FTIR (KBr, cm^{-1}): 3212 w, 2959 w, 1735 m, 1407 w, 1368 m, 1324 s, 1268 w, 1170 s, 1134 s, 1092 w, 1062 m, 1015 m, 996 w, 840 m, 756 m, 711 m, 613 s, 555 w, 431 w. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{11}H_9F_3NO_6S_2$: 371.98296; Found: 371.9829.

(4*R*)-3-Tosylthiazolidine-4-carboxylic acid 1,1-dioxide (4*R*-MEST). Oyster solid, yield 1.13 g (51%). R_f = 0.33 (Petroleum ether: EtOAc: acetic acid = 30: 20: 2). $[\alpha]^{15}_D$ = -47.2° (c 10.07, acetone). ^{1}H NMR (300 MHz, acetone-d_6) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 5.25 (t, *J* = 6.4 Hz, 1H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.30 (d, *J* = 11.9 Hz, 1H), 3.55 (d, *J* = 6.4 Hz, 2H), 2.44(s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 169.21, 144.31, 134.67, 129.31, 127.45, 62.89, 57.13, 51.61, 21.18. FTIR (KBr, cm^{-1}): 3219 s, 3025 w, 2972 w, 1760 s, 1434 w, 1332 s, 1286 w, 1269 w, 1229 w, 1190 s, 1113 m, 1088 m, 1056 w, 812 m, 762 s, 663 s, 578 s, 546 s, 466 m. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{11}H_{12}NO_6S_2$: 318.0112; Found: 318.0100.

(4*R*)-3-((4-(*tert*-Butyl)phenyl)sulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxide (4*R*-TBST). Oyster white solid, yield 0.97 g (42 %). R_f =0.51, (Petroleum ether: EtOAc: acetic acid = 30: 20: 2). $[\alpha]^{15}_D$ = -69.9° (c 8.97, acetone). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 5.07 (dd, *J* = 8.4, 4.8 Hz, 1H), 4.82 (d, *J* = 12.1 Hz, 1H), 4.24 (d, *J* = 12.1 Hz, 1H), 3.57 (dd, *J* = 13.8 Hz, 8.4 Hz, 1H), 3.53 (dd, *J* = 13.8 Hz, 4.8 Hz, 1H), 1.30 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 169.22, 156.75, 134.84, 127.29, 126.13, 62.72, 57.11, 51.21, 35.02, 30.80. FTIR (KBr, cm^{-1}): 3435 br, 2961 s, 1747 w, 1627 w, 1596 w, 1403 w, 1339 m, 1162 s, 1110 s, 806 w, 765 m, 631 m, 583 w, 553 w, 467 m. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{14}H_{18}NO_6S_2$: 360.0581; Found: 360.0576.

(4*R*)-3-((4-Methoxyphenyl)sulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxide (4*R*-MOST). Oyster white solid, yield 1.72 g (33%) R_f = 0.42 (Petroleum ether: EtOAc: acetic acid = 30: 20: 2). $[\alpha]^{15}_D$ = -66.6° (c 10.11, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 5.07 (t, *J* = 5.1 Hz, 1H), 4.83 (d, *J* = 12.3 Hz, 1H), 4.26 (d, *J* = 12.3 Hz, 1H), 3.87 (s, 3H), 3.57 (d, *J* = 5.1 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.89, 163.75, 130.37, 129.39, 115.07, 63.30, 56.26, 51.96. FTIR (KBr, cm^{-1}): 3207 br s, 3000 s, 2942 s, 1770 m, 1596 s, 1579 s, 1500 s, 1446 m, 1264 m, 1171 s, 1105 s, 1046 s, 1019 s, 995 m, 884 m, 806 s, 779 s, 733 s, 668 s, 579 s, 553 s, 445 s. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{11}H_{12}NO_7S_2$: 334.0061; Found: 334.0035.

(4*R*)-3-((4-dodecylphenyl)sulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxide (4*R*-DOST). Oil, yield 2.10 g (64 %). R_f =0.25 (Petroleum ether: EtOAc: acetic acid = 20: 10: 1). $[\alpha]^{25}_D$ = -61.3° (c 39.20, acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.34 (m, 2H), 5.15 (dd, *J* = 8.7, 3.4 Hz, 1H), 4.60 (d, *J* = 11.8 Hz, 1H), 4.41 (d, *J* = 11.8 Hz, 1H), 3.62 (dd, *J* = 8.7, 4.7 Hz, 1H), 3.31 (m, 1H), 2.62 (m, 1H), 1.65 (m, 4H), 1.17 (m, 15H), 0.86 (m, 5H).FTIR (KBr, cm^{-1}): 3552 br, 2958 m,2927 s, 2855 m, 1741 s, 1597 w, 1462 w, 1412 w, 1336 s, 1226 w, 1164 s, 1040 w, 919 w, 830 w,770 w, 650 w, 593 s. HRMS (ESI) ([M-H]$^-$) Calcd. for $C_{22}H_{35}NO_6S_2$: 472.1833; Found: 472.1825.

Syntheses of dirhodium tetrakis((4*S*)-3-(arylsulfonyl)oxazolidine-4-carboxylate)

Dirhodium tetrakis((4*S*)-3-(arylsulfonyl)oxazolidine-4-carboxylate) were prepared with the similar procedure,[31a] as exemplified by the synthesis of dirhodium tetrakis((*S*)-3-tosyloxazolidine-4-carboxylate): $Na_4Rh_2(CO_3)_4$ (122.6 mg, 0.228 mmol), which was then added in water (12 mL) and (*S*)-3-tosyloxazolidine-4-carboxylic acid (495 mg, 1.824 mmol).[14] The mixture was stirred at 95 °C for 4 h, during which time the catalyst color change from blue to green and the insoluble sticky matter clots on the stir bar. The reaction was cooled to room temperature and added to DCM (20 mL). The mixture was then washed sequentially with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and then concentrated *in vacuo*. The crude reaction mixture was purified on silica using ether to afford the product as a green solid.

Dirhodium tetrakis((4*S*)-3-((4-nitrophenyl)sulfonyl)-oxazolidine-4-carboxylate) (Rh_2(4*S*-NOSO)$_4$). Yield 192 mg (60%), $[\alpha]^{30}_D$ = -217.6° (c 1.36, acetone). R_f = 0.29 (EtOAc : PE = 1 : 1). ^{1}H NMR (300 MHz, acetone-d_6) δ 8.42 (*J* = 8.7 Hz, 2H), 8.14 (d, *J* = 8.7 Hz, 2H), 5.10 (d, *J* = 5.6 Hz, 1H), 4.52 (d, *J* = 5.6 Hz, 1H), 4.38 (dd, *J* = 7.5, 6.0 Hz, 1H), 4.02 (dd, *J* = 8.7, 7.5 Hz, 1H), 3.57 (dd, *J* = 8.7, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 188.89, 150.55, 143.94, 129.19, 124.46, 80.88, 70.30, 59.52. Anal. Calcd. for $C_{44}H_{46}N_8O_{31}Rh_2S_4$ ($Rh_2(NOSO)_4{\cdot}H_2O{\cdot}$EtOAc): C, 34.83%; H, 3.06%,; N, 7.39%; S, 8.45%; Found: C, 34.49%; H, 3.108%; N, 7.34%; S, 8.26%. FTIR (KBr, cm^{-1}): 3451 br, 3106 w, 2888 w, 1612 s, 1531 s, 1477 w, 1419 s, 1352 s, 1312 m, 1225 w, 1169 s, 1090 m, 1068 m, 1011 m, 937 m, 857 m, 739 s, 685 m, 626 s, 578 m, 455 m. UV-vis (acetone solution, λ (nm), ϵ (M^{-1}cm^{-1})): 593.5, 312.1; 447.5, 147.4

Dirhodium tetrakis((4*S*)-3-((4-fluorophenyl)sulfonyl)oxazolidine-4-carboxylate) (Rh_2(4*S*-FLSO)$_4$). Yield 154 mg (52%), $[\alpha]^{30}_D$ = -244.1° (c 0.90, acetone). R_f = 0.17 (EtOAc : PE = 1 : 1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.6, 5.0 Hz, 2H), 7.18 (t, *J* = 8.4 Hz, 2H), 5.00 (d, *J* = 5.4 Hz, 1H), 4.67 (d, *J* = 5.4 Hz, 1H), 4.12 (m, 1H), 3.93 (t, *J* = 8.4 Hz, 1H), 3.71 (m, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 188.94, 165.40 ($J_{C\text{-}F}$ = 251.0 Hz), 134.55, 130.73, 116.41 ($J_{C\text{-}F}$ = 23.0 Hz), 80.98, 70.02, 59.62. ^{19}F NMR (282 MHz, $CDCl_3$) δ -104.07. Anal. Calcd. for $C_{40}H_{38}F_4N_4O_{21}Rh_2S_4$ ($Rh_2(FLSO)_4{\cdot}H_2O$): C, 36.38%; H, 2.90%,; N, 4.24%; S, 9.71%; Found: C, 36.36%; H, 3.10%; N,

4.31%; S, 9.22%. FTIR (KBr, cm^{-1}): 3473 br, 3107 w, 3074 w, 2888 w, 1612 s, 1592 s, 1494 s, 1526 s, 1420 s, 1355 w, 1239 m, 1171 s, 1155 s, 1090 w, 1068 m, 1011 m, 935 m, 841 s, 764 w, 739 w, 677 s, 598 s, 548 s, 483 w. UV-vis (acetone solution, λ (nm), ϵ ($M^{-1}cm^{-1}$)): 597.5, 322.1; 449.5, 145.3.

Dirhodium tetrakis((4*S*)-3-((4-(trifluoromethyl)phenyl)sulfonyl)oxazolidine-4-carboxylate) (Rh_2(4*S*-TFSO)$_4$). Yield 199 mg (58%), $[\alpha]^{30}_D$ = -235.3° (c 1.00, acetone). R_f = 0.57 (EtOAc : PE = 1 : 1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 5.00 (d, *J* = 5.7 Hz, 1H), 4.70 (d, *J* = 5.2 Hz, 1H), 4.15 (m, 1H), 3.96 (t, *J* = 8.0 Hz, 1H), 3.75 (m, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 188.86, 142.36, 133.93 ($J_{C\text{-}F}$ = 33.0 Hz), 128.60, 126.50 ($J_{C\text{-}F}$ = 4.0 Hz),, 123.61 ($J_{C\text{-}F}$ = 270.0 Hz), 80.96, 70.12, 59.55. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.98. Anal. Calcd. for $C_{44}H_{40}F_{12}N_4O_{22}Rh_2S_4$ ($Rh_2(TFSO)_4{\cdot}2H_2O$): C, 34.34%; H, 2.62%,; N, 3.64%; S, 8.33%; Found: C, 34.33%; H, 2.54%; N, 3.69%; S, 8.33%. FTIR (KBr, cm^{-1}): 3466 br, 2893 w, 1613 m 1421 versus 1407 m, 1359 m, 1324 s, 1172 s, 1133 s, 1109 w, 1063 s, 1015 m, 936 s, 714 m, 625 m, 601 w, 429 w. UV-vis (acetone solution, λ (nm), ϵ ($M^{-1}cm^{-1}$)): 594.5, 308.8; 447.5, 138.3.

Dirhodium tetrakis((4*S*)-3-tosyloxazolidine-4-carboxylate) (Rh_2(4*S*-MESO)$_4$). Yield 148 mg (51%), $[\alpha]^{T}_D$ = -204.5° (c 1.16, acetone)., R_f = 0.48 (EtOAc : PE = 2 : 1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.6 Hz, 2H), 7.28 (d, *J* = 6.6 Hz, 2H), 4.99 (d, *J* = 5.5 Hz, 0H), 4.64 (d, *J* = 5.7 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 1H), 3.85 (t, *J* = 8.1 Hz, 1H), 3.68 (t, *J* = 6.9 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 188.94, 144.14, 135.20, 129.81, 127.74, 81.06, 69.91, 59.68, 20.56. Anal. Calcd. for $C_{50}H_{61}N_4O_{23.5}Rh_2S_4$ ($Rh_2(MESO)_4{\cdot}0.5H_2O{\cdot}1.5EtOAc$): C, 42.05%; H, 4.365%,; N, 4.59%; S, 8.332%; Found: C, 42.05%; H, 4.31%; N, 3.92%; S, 8.98%. FTIR (KBr, cm^{-1}): 3434 br, 2955 m, 2924 s, 2853 m, 1736 w, 1735 w, 1705 w, 1612 s, 1420 s, 1353 s, 1220 w, 1164 s, 1091 m, 1068 m, 1001 m, 934 m, 815 m, 764 w, 739 w, 705 w, 669 s, 598 s, 548 m, 470 w. UV-vis (acetone solution, λ (nm), ϵ ($M^{-1}cm^{-1}$)): 594.5, 273.8; 446.5, 128.7.

Dirhodium tetrakis((4*S*)-3-((4-(*tert*-butyl)phenyl)sulfonyl)oxazolidine-4-carboxylate) (Rh_2(4*S*-TBSO)$_4$). Yield 208 mg (63%), $[\alpha]^{30}_D$ = -247.4° (c 1.04, acetone). R_f = 0.41 (EtOAc : PE = 1 : 1) . ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 4.99 (d, *J* = 5.5 Hz, 1H), 4.64 (d, *J* = 5.5 Hz, 1H), 4.12 (t, *J* = 7.0 Hz, 1H), 3.86 (t, *J* = 8.0 Hz, 1H), 3.71 (dd, d, *J* = 8.4, 6.6 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, acetone-d_6) δ 188.96, 156.87, 135.21, 127.65, 126.24, 81.10, 69.91, 59.70, 34.85, 30.39. Anal. Calcd. for $C_{56}H_{76}N_4O_{22}Rh_2S_4$ ($Rh_2(TBSO)_4{\cdot}2H_2O$): C, 45.10%; H, 5.14%,; N, 3.76%; S, 8.60%; Found: C, 44.78%; H, 5.38%; N, 3.72%; S, 8.30%. FTIR (KBr, cm^{-1}): 3486 br, 3068 w, 2964 s, 2905 w, 2872 w, 1802 w, 1611 s, 1465 w, 1419 s, 1352 s, 1269 m, 1269 m, 1198 s, 1167 m, 1085 m, 1069 m, 1011 m, 935 m, 841 m, 753 m, 641 s, 593 s, 544 m, 486 w. UV-vis (acetone solution, λ (nm), ϵ ($M^{-1}cm^{-1}$)): 594.5, 303.7; 446.5, 144.0.

Dirhodium tetrakis((4*S*)-3-((4-methoxyphenyl)sulfonyl)oxazolidine-4-carboxylate) (Rh_2(4*S*-MOSO)$_4$). Yield 137 mg (45%), $[\alpha]^{30}_D$ = -256.7° (c 0.27, acetone). R_f = 0.47 (EtOAc : PE = 3 : 1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.02 (d, *J* = 5.6 Hz, 1H), 4.63 (d, *J* = 5.6 Hz, 1H), 4.14 (dd, *J* = 11.1, 7.2 Hz, 1H), 3.89 (dd, *J* = 11.1, 9.0 Hz, 1H), 3.83 (s, 3H), 3.72 (dd, *J* = 9.0, 7.2 Hz, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 189.01, 163.51, 129.93, 129.67, 114.39, 81.05, 69.88, 59.72, 55.27. Anal. Calcd. for $C_{48}H_{63}N_4O_{29.5}Rh_2S_4$ ($Rh_2(MOSO)_4{\cdot}3.5H_2O{\cdot}EtOAc$): C, 38.38%; H, 4.23%,; N, 3.73%; S, 8.54%; Found: C, 38.14%; H, 3.95%; N, 4.20%; S, 8.55%. FTIR (KBr, cm^{-1}): 3537 br, 2916 w, 1596 s, 1499 m, 1418 s, 1350 m, 1308 m, 1263 m, 1156 s, 1133 w, 1092 w, 1067 w, 1020 w, 933w, 836 w, 677 m, 560 s, 578 m. UV-vis (acetone solution, λ (nm), ϵ ($M^{-1}cm^{-1}$)): 594.5, 275.4; 449.5, 137.3.

Dirhodium tetrakis((4*S*)-3-((4-dodecylphenyl)sulfonyl)oxazolidine-4-carboxylate) (Rh_2(4*S*-DOSO)$_4$). Yield 92 mg (42%). R_f = 0.32 (EtOAc : PE = 1 : 3), $[\alpha]^{20}_D$ = -237.6° (c 1.01, acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (m, 2H), 7.28 (m, 2H), 5.05 (d, *J* = 5.0 Hz, 1H), 4.72 (d, *J* = 5.0 Hz, 1H), 4.21 (m, 1H), 3.85 (m, 2H), 2.64 (m, 1H), 1.60 (m, 4H), 1.15 (m, 15H), 0.85 (m, 5H). Anal. Calcd. for $C_{88}H_{136}F_{12}N_4O_{20}Rh_2S_4$ (Rh_2(4*S*-DOSO)$_4$): C, 55.51%; H, 7.20%; N, 2.94%; S, 6.74%; Found: C, 54.93%; H, 7.41%; N, 2.81%; S, 6.62%.FTIR (KBr, cm^{-1}): 3448 br, 2958 m, 2927 s, 2871 w, 2855 m, 1610 s, 1421 s, 1354 s, 1166 s, 1092 w, 1070 w, 936 m, 765 w, 657 w, 606 m, 577 w.

Syntheses of dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-(arylsulfonyl)oxazolidine-4-carboxylate)

Dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-(arylsulfonyl)oxazolidine-4-carboxylate) were prepared with the similar procedure,[31a] as exemplified by the synthesis of dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-tosyloxazolidine-4-carboxylate): $Na_4Rh_2(CO_3)_4$ (61.5mg ,0.114 mmol),[7a,19] which was then added in water (6 mL) and (4*S*,5*R*)-5-methyl-3-(phenylsulfonyl)oxazolidine-4-carboxylic acid (285mg, 8 equiv. ,0.912 mmol). The mixture was stirred at 95 °C for 4 h, during which time the catalyst color change from blue to green and the insoluble sticky matter clots on the stir bar. The reaction was cooled to room temperature and added to DCM (20 mL). The mixture was then washed sequentially with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and then concentrated *in vacuo*. The crude reaction mixture was purified on silica using ether to afford the product as a green solid.

Dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-((4-nitrophenyl)sulfonyl)oxazolidine-4-carboxylate) (Rh_2(4*S*,5*R*-MNOSO)$_4$). Yield 70 mg (40%), $[\alpha]^{30}_D$ = -276.5° (c 0.71, acetone) , R_f = 0.65 (EtOAc : PE = 1 : 1). ^{1}H NMR (400 MHz, acetone-d_6) δ 8.44 (m, 2H), 8.44 (m, 2H), 5.16 (d, *J* = 6.0 Hz, 1H), 4.48 (d, *J* = 6.0 Hz, 1H), 3.82 (m, 1H), 3.75 (d, *J* = 7.4 Hz, 1H), 1.09 (d, *J* = 5.9 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 189.51, 151.56, 145.00, 130.20, 125.44, 81.43, 80.38, 67.08, 18.59. Anal. Calcd. for $C_{45}H_{48}N_8O_{29.5}Rh_2S_4$ (Rh_2(4*S*,5*R*-MNOSO)$_4{\cdot}H_2O{\cdot}0.25EtOAc$): C, 35.87%; H, 3.21%; N, 7.44%; S, 8.51%; Found: C, 35.58%; H, 3.37%; N, 7.37%; S, 8.10%. FTIR (KBr, cm^{-1}): 3453 br, 3106 w, 1613 s, 1532 s, 1417 m, 1351 s, 1311 w, 1163 s, 1068 w, 856 w, 738 s, 685 m, 625 s, 579 w. Vis (DCM solution, λ (nm), ϵ ($M^{-1}cm^{-1}$)): 634.5, 242.8; 430.5, 171.2.

Dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-((4-fluorophenyl)sulfonyl)oxazolidine-4-carboxylate) (Rh_2(4*S*,5*R*-

MFLSO)$_4$). Yield 71 mg (45.5%), $[\alpha]^{30}_D$ = -246.5° (c 0.76, acetone) , R_f = 0.80 (EtOAc : PE = 1 : 1). ^{1}H NMR (400 MHz, acetone-d$_6$) δ 7.92 (m, 2H), 7.37 (m, 2H), 5.12 (d, *J* = 6.3 Hz, 1H), 4.49 (d, *J* = 6.3 Hz, 1H), 3.79 (m, 1H), 3.58 (d, *J* = 7.4 Hz, 1H), 1.01 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d$_6$) *δ* 189.61, 166.35 (d, $J_{C\text{-}F}$ = 253.0 Hz),, 135.55 (d, $J_{C\text{-}F}$ = 3.1 Hz), 131.78 (d, $J_{C\text{-}F}$ = 9.6 Hz), 117.32 (d, $J_{C\text{-}F}$ = 22.8 Hz), 81.58, 80.17, 67.18, 18.68. ^{19}F NMR (377 MHz, acetone-d$_6$) *δ* -103.85. Anal. Calcd. for $C_{48}H_{56}F_4N_4O_{24}Rh_2S_4$ (Rh$_2$(4*S*,5*R*-MFLSO)$_4$·2H$_2$O·EtOAc): C, 38.87%; H, 3.81%; N, 3.78%; S, 8.65%; Found: C, 38.76%; H, 3.70%; N, 4.21%; S, 8.16%. FTIR (KBr, cm^{-1}): 3448 br, 2979 w, 1612 s, 1592 m, 1493 m, 1417 s, 1352 s, 1295 w, 1240 m, 1169 m, 1155 s, 1090 m, 869 m, 771 m, 709 w, 677 m, 598 s, 548 m. Vis (DCM solution, *λ* (nm), *ϵ* (M^{-1}cm^{-1})): 626.5, 283.0; 433.0, 199.9.

Dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)oxazolidine-4-carboxylate) (Rh$_2$(4*S*,5*R*-MTFSO)$_4$). Yield 97 mg (53.0%), $[\alpha]^{30}_D$ = -275.4° (c 0.68, acetone) , R_f = 0.65 (EtOAc : PE = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.98 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 5.10 (d, *J* = 6.2 Hz, 1H), 4.76 (d, *J* = 6.2 Hz, 1H), 3.99 (m, 1H), 3.65 (d, *J* = 7.3 Hz, 1H), 1.02 (d, *J* = 5.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) *δ* 189.26, 140.83, 135.31 (q, $J_{C\text{-}F}$ = 33.0 Hz), 126.70 (d, $J_{C\text{-}F}$ = 3.2 Hz), 123.24 (d, $J_{C\text{-}F}$ = 273.0 Hz), 81.26, 79.65, 76.91, 66.29, 18.26. ^{19}F NMR (377 MHz, $CDCl_3$) *δ* -63.21. Anal. Calcd. for $C_{50}H_{52}F_{12}N_4O_{23}Rh_2S_4$ (Rh$_2$(4*S*,5*R*-MFLSO)$_4$·2H$_2$O·0.5EtOAc): C, 36.64%; H, 3.20%; N, 3.42%; S, 7.83%; Found: C, 36.60%; H, 3.41%; N, 3.34%; S, 7.37%. FTIR (KBr, cm^{-1}): 3462 br, 2981 w, 1614 s, 1418 m, 1406 w, 1324 s, 1253 w, 1167 s, 1134 s, 1063 m, 1016 w, 901 w, 844 m, 771 m, 714 m, 624 s, 601 w, 428 m. Vis (DCM solution, *λ* (nm), *ϵ* (M^{-1}cm^{-1})): 637.0, 236.6; 433.0, 169.2.

Dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-tosyloxazolidine-4-carboxylate) (Rh$_2$(4*S*,5*R*-MMESO)$_4$). Yield 105 mg (71%), $[\alpha]^{30}_D$ = -301.7° (c 0.89, acetone) , R_f = 0.70 (EtOAc : PE = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.70 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 5.06 (d, *J* = 5.9 Hz, 1H), 4.65 (d, *J* = 5.9 Hz, 1H), 4.04 – 3.83 (m, 1H), 3.62 (d, *J* = 7.3 Hz, 1H), 2.38 (s, 3H), 1.02 (d, *J* = 5.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 189.52, 144.44, 134.63, 130.07, 128.09, 81.22, 79.43, 66.40, 21.74, 18.30. Anal. Calcd. for $C_{50}H_{66}N_4O_{24}Rh_2S_4$ (Rh$_2$(4*S*,5*R*-MMESO)$_4$·3H$_2$O·0.5EtOAc): C, 41.67%; H, 4.62%; N, 3.89%; S, 8.90%; Found: C, 41.62%; H, 4.52%; N, 3.78%; S, 8.43%. FTIR (KBr, cm^{-1}): 3448 br, 2879 w,1612 s, 1418 s, 1350 s, 1251 w, 1161 s, 1090 m, 815 w, 771 m, 705 s, 599 s, 550 m. Vis (DCM solution, *λ* (nm), *ϵ* (M^{-1}cm^{-1})): 644.5, 257.5; 429.5, 191.9.

Dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-((4-(tert-butyl)phenyl)sulfonyl)oxazolidine-4-carboxylate) (Rh$_2$(4*S*,5*R*-MTBSO)$_4$). Yield 106 mg (60%), $[\alpha]^{30}_D$ = -325.9° (c 0.63, acetone) , R_f = 0.41 (EtOAc : PE = 1 : 1) . ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.73 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 5.09 (d, *J* = 5.7 Hz, 1H), 4.65 (d, *J* = 5.7 Hz, 1H), 3.97 (m, 1H), 3.62 (d, *J* = 7.1 Hz, 1H), 1.26 (s, 9H), 0.97 (d, *J* = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 189.45, 157.32, 134.64, 127.97, 126.35, 81.28, 79.43, 66.29, 35.31, 31.18, 18.18. Anal. Calcd. for $C_{62}H_{88}N_4O_{23}Rh_2S_4$ (Rh$_2$(4*S*,5*R*-MTBSO)$_4$·2H$_2$O·0.5EtOAc): C, 46.79%; H, 5.57%; N, 3.52%; S, 8.06%; Found: C, 46.66%; H, 5.44%; N, 3.62%; S, 7.64%. FTIR (KBr, cm^{-1}): , 3500 br, 2965 s, 1613 s, 1417 s, 1351 s, 1267 w, 1163 s, 1113 m, 1086 s, 1014 w, 984 w, 842 m, 771 m, 754 m, 640 s, 594 m, 542 w. Vis (DCM solution, *λ* (nm), *ϵ* (M^{-1}cm^{-1})): 638.0, 239.2; 428.0, 176.4.

Dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-((4-methoxyphenyl)sulfonyl)oxazolidine-4-carboxylate) (Rh$_2$(4*S*,5*R*-MMOSO)$_4$). Yield 74 mg (45%), $[\alpha]^{30}_D$ = -285.9° (c 0.95, acetone) , R_f = 0.40 (EtOAc : PE = 1 : 1). ^{1}H NMR (400 MHz, acetone-d$_6$) *δ* 7.77 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 5.08 (d, *J* = 6.2 Hz, 1H), 4.48 (d, *J* = 6.2 Hz, 1H), 3.89 (s, 3H), 3.79 (m, 1H), 3.52 (d, *J* = 7.4 Hz, 1H), 0.99 (d, *J* = 5.8 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d$_6$) *δ* 189.73, 164.47, 130.95, 130.70, 115.29, 81.67, 80.09, 67.30, 56.26, 18.77. Anal. Calcd. for $C_{50.4}H_{64.8}N_4O_{27.2}Rh_2S_4$ (Rh$_2$(4*S*,5*R*-MMOSO)$_4$·2H$_2$O·0.6EtOAc): C, 40.47%; H, 4.37%; N, 3.75%; S, 8.57%; Found: C, 40.36%; H, 4.32%; N, 3.85%; S, 8.14%. FTIR (KBr, cm^{-1}): 3517 br, 2977 w, 1612 s, 1596 s, 1498 m, 1416 m, 1347 m, 1309 w, 1156 s, 1092 w, 984 w, 836 w, 771 w, 877 m, 600 m, 558 m. Vis (DCM solution, *λ* (nm), *ϵ* (M^{-1}cm^{-1})): 641.0, 302.4; 427.5, 221.4.

Dirhodium tetrakis((4*S*,5*R*)-5-methyl-3-((4-dodecylphenyl)sulfonyl)oxazolidine-4-carboxylate) (Rh$_2$(4*S*,5*R*-MMOSO)$_4$). Yield 112 mg (50%). R_f = 0.47 (EtOAc : PE = 1 : 3), $[\alpha]^{20}_D$ = -259.8° (c 1.27, acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (m, 2H), 7.30 (m, 2H), 5.15 (d, *J* = 6.0 Hz, 1H), 4.69 (d, *J* = 6.0 Hz, 1H), 3.97 (m, 1H), 3.59 (m, 1H), 2.64 (m, 1H), 1.63 (m, 4H), 0.99 (m, 23H). Anal. Calcd. for $C_{92}H_{144}N_4O_{20}Rh_2S_4$ (Rh$_2$(4*S*,5*R*-MDOSO)$_4$): C, 56.37%; H, 7.40%; N, 2.86%; S, 6.54%; Found: C, 55.79%; H, 7.73%; N, 2.79%; S, 6.28%.FTIR (KBr, cm^{-1}): 3467 br, 2958 m, 2928 s, 2871 w, 2856 m, 1611 s, 1466 w, 1458 w, 1419 s, 1178 s, 1161 s, 1078 m, 985 w, 770 m, 677 w, 655 m, 605 s, 577 w.

Syntheses of dirhodium tetrakis((4*R*)-3-(arylsulfonyl)thiazolidine-4-carboxylate 1,1-dioxide)

Dirhodium tetrakis((4*R*)-3-(arylsulfonyl)thiazolidine-4-carboxylate 1,1-dioxide) were prepared with the similar procedure,[31a] as exemplified by the synthesis of dirhodium tetrakis((4*R*)-3-tosylthiazolidine-4-carboxylate 1,1-dioxide): $Na_4Rh_2(CO_3)_4$ (122.6 mg, 0.228 mmol), which was then added in water (12 mL) and (*R*)-3-tosylthiazolidine-4-carboxylic acid 1, 1-dioxide (582.4 mg, 1.824 mmol). The mixture was stirred at 95 °C for 4 h, during which time the catalyst color change from blue to green and the insoluble sticky matter clots on the stir bar. The reaction was cooled to room temperature and added to EtOAc (10 mL) with stirring, and then extracted with EtOAc (30 mL × 3). The combined organic layer was washed sequentially with saturated $NaHCO_3$ and brine, dried over anhydrous sodium sulfate, and then concentrated *in vacuo*. The crude reaction mixture was purified on silica using ether to afford the product as a green solid.

Dirhodium tetrakis((4*R*)-3-((4-nitrophenyl)sulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxide (Rh$_2$(4*R*-NOST)$_4$). Yield 203 mg (56 %), $[\alpha]^{30}_D$ = -144.9° (c 1.04, acetone). R_f = 0.47 (EtOAc : PE = 1 : 1) . ^{1}H NMR (300 MHz, acetone-d$_6$): *δ* 8.46 (m, 2H), 8.19 (m, 2H), 5.12 (dd, *J* = 8.40, 4.5 Hz,1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.11 (d, *J* = 12.0 Hz, 1H), 3.52 (dd, *J* = 13.5, 8.4 Hz, 1H), 3.40 (dd, *J* = 13.5, 4.5 Hz,

1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 186.99, 150.78, 143.70, 129.37, 124.56, 62.30, 57.79, 52.03. Anal. Calcd. for $C_{44}H_{46}N_8O_{35}Rh_2S_8$ (Rh_2(NOST)$_4$·H_2O·EtOAc): C, 30.92%; H, 2.71%; N, 6.56%; S 15.01%; Found: C, 30.53%; H, 2.94%; N, 6.55%; S, 14.72%. FTIR (KBr, cm^{-1}): 3543 br, 3107 m, 3020 m, 2963 m, 2871 w, 1624 s, 1532 s, 1478 w, 1414 s, 1351 m, 1226 m, 1265 s, 1089 m, 1044 m, 1008 m, 917 w, 895 w, 856 s, 822 w, 765 s 745 s, 684 m, 619 s, 566 m, 461 m, 433 m. Vis (acetone solution, λ (nm), ϵ (M^{-1}cm^{-1})): 595, 281.2; 450.5, 131.1.

Dirhodium tetrakis((4*R*)-3-((4-fluorophenyl)sulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxide (Rh_2(4*R*-FLST)$_4$). Yield 137 mg (40 %), $[\alpha]^{30}_D$ = -90° (c 1.00, acetone). R_f = 0.32 (EtOAc : PE = 1 : 1) . ^{1}H NMR (300 MHz, acetone-d_6): δ 7.96 (m, 2H), 7.39 (t, J = 8.6 Hz, 2H), 5.00 (m, 1H), 4.63 (m, 1H), 4.07 (m, 1H), 3.39 (m, 2H). ^{13}C NMR (100 MHz, acetone-d_6) δ 187.02, 165.61 ($J_{C\text{-}F}$ = 251 Hz), 164.35, 134.61, 116.53 ($J_{C\text{-}F}$ = 23 Hz), 62.55, 57.79, 52.11. ^{19}F NMR (377 MHz, acetone-d_6) δ -105.93. Anal. Calcd. for $C_{44}H_{48}F_4N_4O_{28}Rh_2S_8$ (Rh_2(FLST)$_4$·$2H_2O$·EtOAc): C, 32.64%; H, 2.99%,; N, 3.46%; S 15.84%; Found: C, 32.67%; H, 3.26%; N, 3.62%; S, 15.63%. FTIR (KBr, cm^{-1}): 3423 br, 3108 w, 3019 w, 2964 w, 1624 s, 1591 s, 1494 m, 1413 s, 1297 w, 1237 m, 1156 s, 1089 w, 1006 w, 841 m, 759 m, 671 m, 576 versus 545 m, 471 versus 447 w. Vis (acetone solution, λ (nm), ϵ (M^{-1}cm^{-1})): 593.5, 278.3; 449.5, 133.3.

Dirhodium tetrakis((4*R*)-3-((4-trifluoromethyl)phenyl)sulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxide (Rh_2(4*R*-TFST)$_4$). Yield 237 mg (61 %), $[\alpha]^{30}_D$ = -88.4° (c 1.01, acetone). R_f = 0.41 (EtOAc : PE = 1 : 1) . ^{1}H NMR (300MHz, acetone-d_6): δ 8.14 (d, J = 9.0 Hz, 6.0 Hz, 2H), 7.98 (d, J = 9.0 Hz, 2H), 5.05 (m,1H), 4.68 (d, J = 12.0 Hz, 1H), 4.15 (d, J = 12.0 Hz, 1H), 3.41 (m, 2H). ^{13}C NMR (100 MHz, acetone-d_6) δ 187.03, 142.11, 134.26 ($J_{C\text{-}F}$ = 33 Hz), 128.75, 126.55, 123.62 ($J_{C\text{-}F}$ = 271 Hz), 62.40, 57.77, 51.92. ^{19}F NMR (377 MHz, acetone-d_6) δ -63.49. Anal. Calcd. for $C_{60}H_{68}F_{12}N_4O_{32}Rh_2S_8$ (Rh_2(TFST)$_4$·4EtOAc): C, 35.20%; H, 3.35%,; N, 2.74%; Found: C, 35.20%; H, 3.58%; N, 3.25%. FTIR (KBr, cm^{-1}): 3542 br, 3020 w, 2966 m, 2872 w, 1624 s, 1408 s, 1324 s, 1270 w, 1225 w 1168 versus 1136 s, 1111 s, 1090 w, 1063 m, 1043 w, 1012 m, 917 w, 843 m, 763 m, 712 m, 635 s, 579 m, 553 m, 465 m, 432 m. Vis (acetone solution, λ (nm), ϵ (M^{-1}cm^{-1})): 593.5, 306.9; 450.5, 141.3.

Dirhodium tetrakis((4*R*)-3-tosylthiazolidine-4-carboxylate 1,1-dioxide) (Rh_2(4*R*-MEST)$_4$). Yield 247 mg (73 %), $[\alpha]^{30}_D$ = -119.3° (c 1.02, acetone). R_f = 0.47 (EtOAc : PE = 1 : 1) . ^{1}H NMR (300 MHz, acetone-d_6): δ 7.77 (d, J = 9.0 Hz 2H), 7.42 (d, J = 9.0 Hz, 2H), 4.91 (dd, J = 8.4, 5.1 Hz 1H), 4.57 (d, J = 12.0 Hz, 1H), 4.02 (d, J = 12.0 Hz, 1H), 3.35 (dd, J = 13.2, 5.1 Hz, 1H), 3.26 (dd, J = 13.2, 8.4 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 186.89, 163.84, 130.18, 129.66, 114.52, 62.81, 57.81, 55.42, 52.03. Anal. Calcd. for $C_{48}H_{58}N_4O_{27}Rh_2S_8$ (Rh_2(MEST)$_4$·H_2O·EtOAc): C, 36.37%; H, 3.69%,; N, 3.53%; S 16.18%; Found: C, 36.11%; H, 3.76%; N, 3.79%; S, 15.78%. FTIR (KBr, cm^{-1}): 3499 br, 3018 m, 2961 m, 1623 s, 1598 s, 1494 w, 1414 s, 1335 s 1224 w, 1161 s, 1090 m, 1041 m, 1004 w, 916 w, 867 w, 816 w, 757 w, 666 s, 612 w, 576 m, 547 m, 467 m, 436 m. Vis (acetone solution, λ (nm), ϵ (M^{-1}cm^{-1})): 589.5, 247.7; 450.5, 120.5.

Dirhodium tetrakis((4*R*)-3-((4-(*tert*-butyl)phenyl)sulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxide (Rh_2(4*R*-TBST)$_4$). Yield 328 mg (87%), $[\alpha]^{30}_D$ = -109.3° (c 1.04, acetone). R_f = 0.36 (EtOAc : PE = 1 : 1) . ^{1}H NMR (300 MHz, acetone-d_6): δ 7.84 (d, J = 9.0 Hz 2H), 7.64 (d, J = 9.0 Hz, 2H), 4.88 (dd, J = 8.4, 5.1 Hz, 1H), 4.55 (d, J = 12.0 Hz, 1H), 4.06 (d, J = 12 Hz 1H), 3.35 (dd, J = 13.5, 5.1 Hz, 1H), 3.22 (dd, J = 13.5, 8.4 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, acetone-d_6) δ 186.95, 157.40, 135.32, 127.75, 126.34, 62.80, 57.80, 51.81, 34.95. Anal. Calcd. for $C_{56}H_{76}N_4O_{26}Rh_2S_8$ (Rh_2(TBST)$_4$·$3H_2O$): C, 39.53%; H, 4.62%,; N, 3.29%; S 15.07%; Found: C, 39.73%; H, 4.67%; N, 3.32%; S, 14.69%. FTIR (KBr, cm^{-1}): 3349 br, 2964 m, 2871 m, 1625 s, 1595 s, 1462 w, 1412 m, 1336 s 1268 w, 1220 m, 1164 m, 1134 m, 1113 m, 1087 w, 1040 w, 840 w, 770 m, 637 m, 579 m, 553 m, 464 w. Vis (acetone solution, λ (nm), ϵ (M^{-1}cm^{-1})): 591.5, 278.8; 451, 129.7.

Dirhodium tetrakis((4*R*)-3-((4-methoxyphenyl)sulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxide (Rh_2(4*R*-MOST)$_4$). Yield 140 mg (40 %), $[\alpha]^{30}_D$ = -116.3° (c 0.98, acetone). R_f = 0.47 (EtOAc : PE = 1 : 1) .^{1}H NMR (400 MHz, acetone-d_6): δ 7.85 (d, J = 8.8 Hz, 2H), 7.14 (d, J = 8.8 Hz, 2H), 4.94 (dd, J = 8.8, 4.8 Hz, 1H), 4.59 (d, J = 12.0 Hz, 1H), 4.04 (d, J = 12.0 Hz, 1H), 3.38 (dd, J = 13.2, 4.8 Hz, 1H), 3.29 (dd, J = 13.2, 8.8 Hz, 1H), 2.96 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 186.89, 163.80, 130.18, 129.66, 114.52, 62.81, 57.81, 55.42, 52.03. Anal. Calcd. for $C_{44}H_{48}N_4O_{28}Rh_2S_8$ (Rh_2(MOST)$_4$·$4H_2O$·EtOAc): C, 33.85%; H, 3.79%,; N, 3.29%; S 15.06%; Found: C, 33.78%; H, 3.58%; N, 3.42%; S, 15.32%. FTIR (KBr, cm^{-1}): 3513 br, 3102 w, 3016 w, 2951 w, 2844 w, 1622 s, 1595 s, 1499 m, 1414 s, 1335 s, 1264 s, 1225 w, 1157 s, 1092 m, 1020 m, 869 w, 837 w, 805 w, 758 w, 671 m, 614 w, 579 m, 557 m, 466 w, 434 w. Vis (acetone solution, λ (nm), ϵ (M^{-1}cm^{-1})): 592.5, 271.9; 452.5, 118.0.

Dirhodium tetrakis((4*R*)-3-((4-dodecylphenyl)sulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxide (Rh_2(4*R*-DOST)$_4$). Yield 214 mg (45 %), $[\alpha]^{25}_D$ = -115.5° (c 1.32, acetone). R_f = 0.58 (EtOAc : PE = 1 : 2) . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 2H), 7.34 (m, 2H), 4.93 (s, 1H), 4.39 (m, 1H), 3.61 (d, J = 10.8 Hz, 1H), 3.43 (s, 1H), 3.08 (s, 1H), 2.59 (m, 1H), 1.58 (m, 4H), 1.18 (m, 15H), 0.84 (m, 5H). FTIR (KBr, cm^{-1}): 3447 br, 2957 m,2927 s, 2855 m, 1622 s, 1462 w, 1413 m, 1338 s, 1224 w, 1161 s, 1040 w, 854 w, 589 w.

General procedure for catalytic aziridination

To 2 mL of DCM were added sequentially MgO (29 mg, 0.72 mmol, 2.4 eq), $PhI(OAc)_2$ (152 mg, 0.45 mmol, 1.5 eq), styrene (47 mg, 0.45 mmol, 1.5 eq), $NsNH_2$ (61 mg, 0.30 mmol, 1.0 eq) and 2 mol % catalyst (the following data are related to Rh_2(4*S*-DOSO)$_4$-catalyzed reactions). The suspension was stirred vigorously overnight until complete consumption of most starting material was indicated by TLC. The solvent was removed in vacuum, and the residue underwent a flash silica chromatography to afford the pure 1-((4-nitrophenyl)sulfonyl)-2-phenylaziridine (**1**) as white solid (?? mg, ??%). R_f = 0.35 (EtOAc : PE = 1 : 5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (m, 2H),

8.17 (m, 2H), 7.30 (m, 3H), 7.20 (m, 2H), 3.88 (dd, *J* = 7.2, 4.6 Hz, 1H), 3.10 (d, *J* = 7.2 Hz, 1H), 2.49 (d, *J* = 4.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 150.83, 144.10, 134.32, 129.36, 128.93, 126.63, 124.54, 42.05, 36.75. 94% ee (AD-H, flow rate 0.8 ml/min, 10% *i*-PrOHin hexane), t_R= 33.62 min (major), t_R = 37.64 min (minor); $[\alpha]^{30}_D$ = +24.2° (c 0.80, acetone); HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_{12}O_4N_2S$: 327.0410; Found: 327.0399.

General procedure for catalytic cyclopropanantion

A solution of (*E*)-methyl 2-diazo-4-phenylbut-3-enoatemethyl (40.4 mg, 0.2 mmol, 1.0 eq) in 1 mL toluene was added slowly to the solution of olefin (1.0 mmol, 5.0 eq), and 2 mol% catalyst (the following data are related to Rh_2(4*S*,5*R*-MNOSO)$_4$-catalyzed reactions) in 1 mL toluene at -40℃. The resulting solution was vigorously stirred at -40℃for two days until most diazo compound was completely consumed. The solvent was removed in vacuum, and the residue was dissolved in deuterium solvents and analyzed by ^{1}H NMR to determine ratio of diastereomers (typically, only *E* isomer was observed). Flash silica chromatography of the crude residue afforded the pure cyclopropanecarboxylate product (1*S*,2*S*)-methyl 2-phenyl-1-((*E*)-styryl)cyclopropanecarboxylate (**2a**) as white solid (53 mg, 96%).

(1*S*,2*S*)-Methyl 2-Phenyl-1-((*E*)-styryl)cyclopropanecarboxylate (2a): White solid, yield 53 mg (96 %); R_f = 0.36 (EtOAc : PE = 1 : 20). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.21 (m, 4H), 7.13 (m, 6H), 6.33 (d, *J* = 16.0 Hz, 1H), 6.11 (d, *J* = 16.0 Hz, 1H), 3.75 (s, 3H), 2.99 (dd, *J* = 9.1, 7.4 Hz, 1H), 2.01 (ddd, *J* = 9.1, 5.0, 0.5 Hz, 1H), 1.81 (dd, *J* = 7.4, 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 174.37, 137.27, 135.71, 133.28, 129.30, 128.58, 128.20, 127.54, 126.98, 126.44, 124.29, 52.65, 35.18, 33.49, 18.82. 98% ee (OJ-H, flow rate 1.0 ml/min, 1% *i*-PrOH in hexanes), t_R= 19.56 min (major), t_R = 26.68 min (minor); $[\alpha]^{30}_D$ = -150.6° (c 1.16, acetone); HRMS (APCI) ($[M+H]^+$) Calcd. for $C_{19}H_{18}O_2$: 279.1380; Found: 279.1382.

(1*S*,2*S*)-Methyl 1-((*E*)-Styryl)-2-(*o*-tolyl)cyclopropanecarboxylate (2b): Colorless oil, yield 56 mg (96%); R_f = 0.32 (EtOAc : PE = 1 : 20). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.09 (m, 9H), 6.13 (m, 2H), 3.79 (s, 3H), 2.93 (t, *J* = 8.3 Hz, 1H), 2.26 (s, 3H), 2.06 (dd, *J* = 9.1, 5.0 Hz, 1H), 1.87 (dd, *J* = 7.5, 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 174.47, 138.83, 137.44, 134.27, 131.38, 129.80, 128.49, 127.36, 127.29, 126.28, 125.72, 123.74, 52.66, 35.16, 32.06, 19.84, 19.08. 90% ee (OD-H, flow rate 0.8 ml/min, 1% *i*-PrOH in hexane), t_R= 10.15 min (minor), t_R = 11.67 min (major); $[\alpha]^{30}_D$ = -29.8° (c 1.90, acetone); HRMS (APCI) ($[M+H]^+$) Calcd. for $C_{20}H_{20}O_2$: 293.1536; Found: 293.1537.

(1*S*,2*S*)-Methyl 1-((*E*)-Styryl)-2-(*p*-tolyl)cyclopropanecarboxylate (2c): White solid, yield 54 mg (93%); R_f = 0.32 (EtOAc : PE = 1 : 20). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.19 (m, 5H), 7.00 (m, 4H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.13 (d, *J* = 16.0 Hz, 1H), 3.74 (s, 3H), 2.95 (dd, *J* = 9.1, 7.4 Hz, 1H), 2.25 (s, 3H), 1.98 (dd, *J* = 9.1, 5.0 Hz, 1H), 1.77 (dd, *J* = 7.4, 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 174.43, 137.34, 136.53, 133.15, 132.59, 129.13, 128.92, 128.57, 127.49, 126.47, 124.43, 52.61, 35.03, 33.46, 21.24, 18.89. 88% ee (OJ-H, flow rate 0.8 ml/min, 1% *i*-PrOH in hexane), t_R= 19.43 min (major), t_R = 31.11 min (minor); $[\alpha]^{30}_D$ = -99.7° (c 2.17, acetone); HRMS (APCI) ($[M+H]^+$) Calcd. for $C_{20}H_{20}O_2$: 293.1536; Found: 293.1536.

(1*S*,2*S*)-Methyl 2-(4-Fluorophenyl)-1-((*E*)-styryl)cyclopropanecarboxylate (2d): Colorless oil, yield 56 mg (95%); R_f = 0.33 (EtOAc : PE = 1 : 20). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.22 (m, 7H), 6.96 (m, 2H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.18 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 3.03 (dd, *J* = 8.9, 7.5 Hz, 1H), 2.07 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.82 (dd, *J* = 7.5, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 174.18, 161.92 (d, $J_{C\text{-}F}$ = 245.3 Hz), 137.05, 133.31, 131.44 (d, $J_{C\text{-}F}$ = 3.1 Hz), 130.76 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.62, 127.65, 126.38, 123.97, 115.07 (d, $J_{C\text{-}F}$ = 21.4 Hz), 52.64, 34.36, 33.34, 18.84. ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.75. 90% ee (OJ-H, flow rate 0.5 ml/min, 1% *i*-PrOH in hexane), t_R= 40.48 min (major), t_R = 52.35 min (minor); $[\alpha]^{30}_D$ = -106.5° (c 1.80, acetone); HRMS (APCI) ($[M+H]^+$) Calcd. for $C_{19}H_{17}O_2F$: 297.1285; Found: 297.1289.

(1*S*,2*S*)-Methyl 2-(4-Bromophenyl)-1-((E)-styryl)cyclopropanecarboxylate (2e): Colorless oil, yield 66 mg(92%); R_f = 0.29 (EtOAc : PE = 1 : 20). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.34 (m, 2H), 7.21 (m, 5H), 6.99 (m, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.11 (d, *J* = 16.0 Hz, 1H), 3.75 (s, 3H), 2.93 (dd, *J* = 9.1, 7.3 Hz, 1H), 2.02 (ddd, *J* = 9.1, 5.2, 0.6 Hz, 1H), 1.77 (dd, *J* = 7.3, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 174.03, 136.90, 134.85, 133.69, 131.25, 130.86, 128.64, 127.73, 126.43, 123.69, 120.87, 52.69, 34.30, 33.74, 18.74. 90% ee (OJ-H, flow rate 0.8 ml/min, 3% *i*-PrOH in hexane), t_R= 19.78 min (major), t_R = 25.26 min (minor); $[\alpha]^{30}_D$ = -97.3° (c 2.00, acetone); HRMS (APCI) ($[M+H]^+$) Calcd. for $C_{19}H_{17}O_2Br$: 357.0485; Found: 357.0473.

(1*S*,2*S*)-Methyl 2-(4-Methoxyphenyl)-1-((E)-styryl)cyclopropanecarboxylate (2f): Colorless oil, yield 59 mg (95%); R_f = 0.25 (EtOAc : PE = 1 : 20). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.18 (m, 5H), 7.05 (m, 2H), 6.75 (m, 2H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.15 (d, *J* = 16.0 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 2.95 (dd, *J* = 9.1, 7.4 Hz, 1H), 1.99 (ddd, *J* = 9.1, 5.0, 0.5 Hz, 1H), 1.75 (dd, *J* = 7.4, 5.0 Hz,1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 174.36, 158.59, 137.28, 133.00, 130.27, 128.55, 127.66, 127.46, 126.40, 124.41, 113.61, 55.33, 52.54, 34.78, 33.32, 18.94. 94% ee (OJ-H, flow rate 1.0 ml/min, 1% *i*-PrOH in hexane), t_R= 39.10 min (major), t_R = 78.01 min (minor); $[\alpha]^{30}_D$ = -113.7° (c 1.80, acetone); HRMS (APCI) ([M+H]+) Calcd. for $C_{20}H_{20}O_3$: 309.1485; Found: 309.1491.

Methyl 2-Butyl-1-((E)-styryl)cyclopropanecarboxylate (2g): Colorless oil, yield 36 mg (70%); R_f = 0.46 (EtOAc : PE = 1 : 20). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.38 (m, 2H), 7.30 (m, 2H), 7.22 (m, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.31 (d, *J* = 16.0 Hz, 1H), 3.68 (s, 3H), 1.63 (m, 1H), 1.58 (m, 1H), 1.29 (m, 6H), 1.10 (dd, *J* = 6.6, 4.1 Hz, 1H), 0.84 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 175.21, 137.30, 131.91, 128.74, 127.57, 126.47, 124.90, 52.37, 31.92, 31.82, 30.75, 28.03, 22.56, 19.62, 14.25. 92% ee (OJ-H, flow rate 0.8 ml/min, 1% *i*-PrOH in hexane), t_R= 9.14 min (major), t_R = 9.81 min (minor); $[\alpha]^{30}_D$ = -102.5° (c 1.47, acetone); HRMS (APCI) ($[M+H]^+$) Calcd. for $C_{17}H_{22}O_2$: 259.1693; Found: 259.1695.

Methyl 2,2-Diphenyl-1-styrylcyclopropanecarboxylate (2h): White solid, yield 67 mg (94%); R_f = 0.33 (EtOAc : PE = 1 : 20). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.42 (m, 4H), 7.17 (m, 11H), 6.45 (d, *J* = 16.1 Hz, 0H), 6.18 (d, *J* = 16.1 Hz, 1H), 3.40 (s, 3H), 2.62

(d, *J* = 5.4 Hz, 1H), 2.05 (d, *J* = 5.4 Hz,1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.40, 142.37, 140.97, 137.51, 131.10, 130.14, 128.98, 128.57, 128.54, 128.50, 127.38, 127.05, 127.01, 126.87, 126.35, 52.06, 47.34, 39.09, 22.79. 96% ee (OJ-H, flow rate 1.0ml/min, 5% *i*-PrOH in hexane), t_R= 16.45 min (minor), t_R = 28.54 min (major); $[\alpha]^{30}_D$ = -137.7° (c 1.68, acetone); HRMS (APCI) ($[M+H]^+$) Calcd. for $C_{25}H_{22}O_2$: 355.1693; Found: 355.1679.

Methyl 2-Methyl-3-phenyl-1-((*E*)-styryl)cyclopropanecarboxylate (2i): Colorless oil, yield 53 mg (90%); R_f = 0.43 (EtOAc : PE = 1 : 20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (m, 10H), 6.69 (d, *J* = 16.5 Hz, 1H), 5.85 (d, *J* = 16.5 Hz, 1H), 3.76 (s,3H), 3.07 (d, *J* = 9.8 Hz, 1H), 2.28 (m, 1H), 1.19 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.79, 137.88, 135.05, 134.78, 131.10, 128.65, 128.47, 127.45, 126.84, 126.19, 122.32, 52.57, 36.45, 32.94, 28.01, 11.39. 90% ee (OD-H, flow rate 0.8 ml/min, 1% *i*-PrOH in hexane), t_R= 10.05 min (minor), t_R = 10.67 min (major); $[\alpha]^{30}_D$ = -38.1° (c 1.60, acetone); HRMS (APCI) ($[M+H]^+$) Calcd. for $C_{20}H_{20}O_2$: 293.1536; Found: 293.1532.

X-ray Crystallography

The diffraction data were collected with Agilent Technologies SuperNova X-ray diffractometer system for 4*S*,5*R*-MNOSO at 293 K and Oxford Gemini S Ultra diffractometer equipped with $Cu_{k\alpha}$ radiation (λ = 1.54178 Å) for (*R*)-3-((4-Methoxyphenyl)sulfonyl)thiazolidine-4-carboxylic acid 1,1-dioxide (4*R*-MOST) at 299 K. Using Olex2[37a], the structures were solved with the XS[37b] structure solution program using Direct Methods. 4*S*,5*R*-MNOSO was refined with the ShelXL[37b] refinement package and 4*R*-MOST was refined with the XL[37b] refinement package using Least Squares minimization. Anisotropical thermal factors were assigned to all of the non-hydrogen atoms. The positions of the hydrogen atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their respective patent atoms before the final cycle of least-squares refinement. A summary of the crystal structure refinement data is shown in Table S1, and selected bond angles and distances are listed in Table S2. Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 1055407 (4*S*,5*R*-MNOSO) and 1038152 (4*R*-MOST).

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Notes and references

1 (a) H. M. L. Davies, *Eur. J. Org. Chem.*, 1999, 2459; (b) J. Hansen, H. M. L. Davies, *Coord. Chem. Rev.*, 2008, **252**, 545.

2 (a) D. J. Timmons, M. P. Doyle, *J. Organomet. Chem*., 2001, **617-618**, 98; (b) M. P. Doyle, *J. Org. Chem.*, 2006, **71**, 9253.

3 P. Müller, C. Fruit, *Chem. Rev.*, 2003, **103**, 2905.

4 G. Pons, V. Dequirez, P. Dauban, *Angew. Chem. Int. Ed.*, 2012, **51**, 7384.

5 J. L. Roizen, M. E. Harvey, J. Du Bois, *Accounts Chem. Res.,* 2012, **45**, 911.

6 (a) M. Kennedy, M. A. McKervey, A. R. Maguire, G. H. P. Roos, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 361-362; (b) T. Ye, C. F. García, M. A. McKervey, *J. Chem. Soc.*, *Perkin Trans. 1*, 1995, 1373-1379; (c) C. F. García, M. A. McKervey, T. Ye, *Chem. Commun.* 1996, 1465-1466; (d) M. P. Doyle, Q.-L. Zhou, C. Charnsangavej, M. A. Longoria, M. A. McKervey, C. F. García, *Tetrahedron Lett.* **1996**, *37*, 4129-4132.

7 (a) H. M. L. Davies, P. R. Bruzinski, D. H. Lake, N. Kong, M. J. Fall, *J. Am. Chem. Soc.*, 1996, **118**, 6897; (b) H. M. L. Davies, P. R. Bruzinski, M. J. Fall, *Tetrahedron Lett.*, 1996, 37, 4133; (c) H. M. L. Davies, D. G. Stafford, B. D. Doan, J. H. Houser, *J. Am. Chem. Soc.*, 1998, **120**, 3326; (d) L. Deng, A. J. Giessert, O. O. Gerlitz, X. Dai, S. T. Driver, H. M. L. Davies, *J. Am. Chem. Soc.*, 2005, **127**, 1342; (e) Y. Lian, H. M. L. Davies, *J. Am. Chem. Soc.*, 2010, **132**, 440; (f) J. F. Briones, J. Hansen, K. I. Hardcastle, I. Autschbach, H. M. L. Davies, *J. Am. Chem. Soc.*, 2010, **132**, 17211; (g) H. Wang, D. M. Guptill, A. Varela-Alvarez, D. G. Musaev, H. M. L. Davies, *Chem. Sci.*, 2013, **4**, 2844; (h) B. T. Parr, S. A. Green, H. M. L. Davies, *J. Am. Chem. Soc.*, 2013, **135**, 4716; (i) C. Qin, H. M. L. Davies, *J. Am. Chem. Soc.*, 2013, **135**, 14516.

8 (a) H. M. L. Davies, T. Hansen, *J. Am. Chem. Soc.*, 1997, **119**, 9075; (b) H. M. L. Davies, T. Hansen, D. W. Hopper, S. A. Panaro, *J. Am. Chem. Soc.*, 1999, **121**, 6506; (c) H. M. L. Davies, T. Hansen, M. R. Churchill, *J. Am. Chem. Soc.*, 2000, **122**, 3063; (d) H. M. L. Davies, P. Ren, *J. Am. Chem. Soc.*, 2001, **123**, 2070; (e) H. M. L. Davies, C. Venkataramani, *Angew. Chem. Int. Ed.*, 2002, **41**, 2197; (f) H. M. L. Davies, Q. Jin, *J. Am. Chem. Soc.*, 2004, **126**, 10862; (g) H. M. L. Davies, A. M. Walji, *Angew. Chem. Int. Ed.*, 2005, **44**, 1733; (h) H. M. L. Davies, J. R. Manning, *J. Am. Chem. Soc.*, 2006, **128**, 1060; (i) H. M. L. Davies, X. Dai, M. S. Long, *J. Am. Chem. Soc.*, 2006, **128**, 2485; (j) Z. Li, H. M. L. Davies, *J. Am. Chem. Soc.*, 2010, **132**, 396; (k) J. H. Hansen, T. M. Gregg, S. R. Ovalles, Y. Lian, J. Autschbach, H. M. L. Davies, *J. Am. Chem. Soc.*, 2011, **133**, 5076; (l) Y. Lian, H. M. L. Davies, *J. Am. Chem. Soc.*, 2011, **133**, 11940; (m) H. M. L. Davies, C. Venkataramani, *Org. Lett.*, 2003, **5**, 1403.

9 H. T. Bonge, M. Kaboli, T. Hansen, *Tetrahedron Lett.,* 2010, **51**, 5375.

10 (a) S. Kitagaki, M. Anada, O. Kataoka, K. Matsuno, C. Umeda, N. Watanabe, S. Hashimoto, *J. Am. Chem. Soc.*, 1999, **121**, 1417; (b) H. Tsutsui, Y. Yamaguchi, S. Kitagaki, S. Nakamura, M. Anada, S. Hashimoto, *Tetrahedron: Asymmetry* 2003, **14**, 817; (c) M. Anada, M. Tanaka, T. Washio, M. Yamawaki, T. Abe, S. Hashimoto, *Org. Lett.*, 2007, **9**, 4559; (d) M. Yamawaki, H. Tsutsui, S. Kitagaki, M. Anada, S. Hashimoto, *Tetrahedron Lett.*, 2002, **43**, 9561; (e) N. Shimada, M. Anada, S. Nakamura, H. Nambu, H. Tsutsui, S. Hashimoto, *Org. Lett.*, 2008, **10**, 3603; (f) N. Shimada, T. Oohara, J. Krishnamurthi, H. Nambu, S. Hashimot, *Org. Lett.*, 2011, **13**, 6284; (g) J. Krishnamurthi, H. Nambu, K. Takeda, M. Anada, A. Yamano, S. Hashimoto, *Org. Biomol. Chem.*, 2013, **11**, 5374; (g) T. Goto, K. Takea, N. Shimada, H. Nambu, M. Anada, M. Shiro, K. Ando, S. Hashimoto, *Angew. Chem. Int. Ed.*, 2011, **50**, 6803-6808; (h) T. Goto, K. Takeda, M.; Anada, K. Ando, S. Hashimoto, *Tetrahedron Lett.*, 2011, **52**, 4200.

11 (a) R. P. Reddy, G. H. Lee, H. M. L. Davies, *Org. Lett.*, 2006, **8**, 3437; (b) R. P. Reddy, H. M. L. Davies, *Org. Lett.*, 2006, **8**, 5013; (c) R. P. Reddy, H. M. L. Davies, *J. Am. Chem. Soc.*, 2007, **129**, 10312; (d) B. D. Schwartz, J. R. Denton, Y. Lian, H. M. L.

Davies, C. M. Williams, *J. Am. Chem. Soc.*, 2009, **131**, 8329; (e) H. Wang, D. M. Guptill, A. Varela-Alvarez, D. G. Musaev, H. M. L. Davies, *Chem. Sci.*, 2013, **4**, 2844; (f) J. E. Spangler, Davies, H. M. L. *J. Am. Chem. Soc.*, 2013, **135**, 6802; (g) L. Lu, H. Wang, H. M. L. Davies, *Org. Lett.*, 2014, **16**, 3036.

12 (a) P. Müller, Y. Allenbach, E. Robert, *Tetrahedron: Asymmetry* 2003, **14**, 779; (b) P. Müller, G. Bernardinelli, Y. F. Allenbach, M. Ferri, H. D. Flack, *Org. Lett.*, 2004, **6**, 1725; (c) P. Müller, A. Ghanem, *Org. Lett.*, 2004, **6**, 4347; (d) A. Ghanem, M. G. Gardiner, R. M. Williamson, P. Müller, *Chem. Eur. J.*, 2010, **16**, 3291; (e) C. Liang, F. Robert-Peillard, C. Fruit, P. Müller, R. H. Dodd, P. Dauban, *Angew. Chem. Int. Ed.*, 2006, **45**, 4641; (f) C. Liang, F. Collet, F. Robert-Peillard, P. Müller, R. H. Dodd, P. Dauban, *J. Am. Chem. Soc.*, 2008, **130**, 343.

13 (a) D. Marcoux and A. B. Charette, *Angew. Chem., Int. Ed.*, 2008, **47**, 10155; (b) D. Marcoux, S. Azzi and A. B. Charette, *J. Am. Chem. Soc.*, 2009, **131**, 6970.

14 (a) S. Chuprakov,; S. W. Kwok,; L. Zhang,; L. Lercher,; V. V. Fokin, *J. Am. Chem. Soc.*, 2009, **131**, 18034; (b) N. Grimster, L. Zhang, V. V. Fokin, *J. Am. Chem. Soc.*, 2010, **132**, 2510; (c) M. Zibinsky, V. V. Fokin, *Org. Lett.*, 2011, **13**, 4870; (d) M. Zibinsky, V. V. Fokin, *Angew. Chem. Int. Ed.*, 2013, **52**, 1507; (e) S. W. Kwok, L. Zhang, N. P. Grimster, V. V. Fokin, *Angew. Chem. Int. Ed.*, 2014, **53**, 3452.

15 B. T. Parr, H. M. L. Davies, *Angew. Chem. Int. Ed.*, 2013, **52**, 10044.

16 (a) C. Qin, V. Boyarskikh, J. H. Hansen, K. I. Hardcastle, D. G. Musaev, H. M. L. Davies, *J. Am. Chem. Soc.*, 2011, **133**, 19198; (b) C. Qin, H. M. L. Davies, *J. Am. Chem. Soc.*, 2013, **135**, 14516; (c) C. Qin, H. M. L. Davies, *J. Am. Chem. Soc.*, 2014, **136**, 9792; (d) D. M. Guptill, H. M. L. Davies, *J. Am. Chem. Soc.*, 2014, **136**, 17718.

17 (a) M. Kim, J. Kwak, S. Chang, *Angew. Chem. Int. Ed.*, 2009, **48**, 8935; (b) H. J. Kim, M. Kim, S. Chang, *Org. Lett.*, 2011, **13**, 2368; (c) J. Kwak, M. Kim, S. Chang, *J. Am. Chem. Soc.*, 2011, **133**, 3780.

18 C.-Y. Zhou, J.-C. Wang, J. Wei, Z.-J. Xu, Z. Guo, K.-H. Low, C.-M. Che, *Angew. Chem. Int. Ed.*, 2012, **51**, 11376.

19 (a) C. G. Espino, P. M. When, J. Chow, J. Du Bois, *J. Am. Chem. Soc.*, 2001, **123**, 6935; (b) C. G. Espino, K. W. Fiori, M. Kim, J. Du Bois, *J. Am. Chem. Soc.*, 2004, **126**, 15378; (c) D. N. Zalatan, J. Du Bois, *J. Am. Chem. Soc.*, 2008, **130**, 9220.

20 (a) A. DeAngelis, O. Dmitrenko, G. P. A. Yap, J. M. Fox, *J. Am. Chem. Soc.*, 2009, **131**, 7230; (b) R. Panish, S. R. Chintala, D. T. Boruta, Y. Fang, M. T. Taylor, J. M. Fox, *J. Am. Chem. Soc.*, 2013, **135**, 9283.

21 (a) S. Chuprakov, F. W. Huang, V. Gevorgyan, *Angew. Chem. Int. Ed.*, 2007, **46**, 4757; (b) B. Chattopadhyay, V. Gevorgyan, *Org. Lett.*, 2011, **13**, 3746; (c) Y. Shi, V. Gevorgyan, *Org. Lett.*, 2013, **15**, 5394.

22 (a) H. Qiu, M. Li, L.-Q. Jiang, F.-P. Lv, L. Zan, C.-W. Zhai, M. P. Doyle, W.-H. Hu, *Nat. Chem.*, 2012, **4**, 733; (b) C. Jing, D. Xing, Y. Qian, T. Shi, Y. Zhao, W. Hu, *Angew. Chem. Int. Ed.*, 2013, **52**, 9289; (c) D. Zhang, H. Qiu, L. Jiang, F. Lv, C. Ma, W. Hu, *Angew. Chem. Int. Ed.*, 2013, **52**, 13356; (d) X. Xu, X. Guo, X. Han, L. Yang, W. Hu, *Org. Chem. Front.*, 2014, **1**, 181.

23 W.-B. Zhang, S.-D. Xiu, C.-Y. Li, *Org. Chem. Front.*, 2015, **2**, 47.

24 W. A. J. Starmans, L. Thijs, B. Zwanenburg, *Tetrahedron* 1998, **54**, 629.

25 R. T. Buck, D. M. Coe, M. J. Drysdale, L. Ferris, D. Haigh, C. J. Moody, N. D. Pearson, J. B. Sanghera, *Tetrahedron Asymmetry* 2003, **14**, 791.

26 (a) M. P. Doyle, R. J. Pieters, *J. Am. Chem. Soc.*, 1991, **113**, 1423; (b) M. P. Doyle, A. van Oeveren, L. J. Westrum, M. N. Protopopova, T. W. Clayton, Jr, *J. Am. Chem. Soc.*, 1991, **113**, 8982; (c) M. N. Protopopova, M. P. Doyle, *J. Am. Chem. Soc.*, 1992, **114**, 2755; (d) M. P. Doyle, M. Protopopova, P. Müller, D. Ena, E. A. Shapiro, *J. Am. Chem. Soc.*, 1994, **116**, 8492.

27 (a) M. P. Doyle, I. M. Phillips, W. Hu, *J. Am. Chem. Soc.*, 2001, **123**, 5366; (b) X. Xu, X. Xu, P. Y. Zavalij, M. P. Doyle, *Chem. Commun.*, 2013, **49**, 2762.

28 (a) M. P. Doyle, A. B. Dyatkin, G. H. P. Roos, F. Cañas, D. A. Pierson, A. van Oeveren, *J. Am. Chem. Soc.*, 1994, **116**, 4507; (b) M. P. Doyle, A. V. Kalinin, D. G. Ene, *J. Am. Chem. Soc.*, 1996, **118**, 8837; (c) M. P. Doyle, Y. Wang, P. Ghorbani, E. Bappert, *Org. Lett.*, 2005, **7**, 5035.

29 (a) M. Falorni, S. Conti, G. Giacomelli, S. Cossu, F. Soccolini, *Tetrahedron Asymmetry* 1995, **6**, 287; (b) M. R. Vishnumaya, V. K. Singh, *J. Org. Chem.*, 2009, **74**, 4289.

30 (a) D. Fattori, C. Rossi, C. I. Fincham, M. Berettoni, F. Calvani, F. Catrambone, P. Felicetti, M. Gensini, R. Terracciano, M. Altamura, A. Bressan, S. Giuliani, C. A. Maggi, S. Meini, C. Valenti, L. Quartara, *J. Med. Chem.*, 2006, **49**, 3602; b) K. N. Vijayadas, H. C. Davis, A. S. Kotmale, R. L. Gawada, V. G. Puranik, P. R. Rajamohanan, G. J. Sanjayan, *Chem. Commun.* 2012, **48**, 9747.

31 (a) J. Wu, Y. Chen, J. S. Panek, *Org. Lett.*, 2010, **12**, 2112; (b) H. J. Callot, F. Metz, *Tetrahedron* 1985, 41, 4495

32 S. A. Johnson, H. R. Hunt, H. M. Neumann, *Inorg. Chem.*, 1963, **2**, 960.

33 D. C. Wynne, M. M. Olmstead, P. G. Jessop, *J. Am. Chem. Soc.*, 2000**, 122**, 7638.

34 P. Müller, C. Baud, Y. Jacquier, M. Moran, I. Nägeli, *J. Phys. Org. Chem.*, **1996**, *9*, 341.

35 (a) D. A. Evans, M. M. Faul, M. T. Bilodeau, B. A. Anderson, D. M. Barnes, *J. Am. Chem. Soc.*, 1993, **115**, 5328; (b) Z. Li, K. R. Conser, E. N. Jacobsen, *J. Am. Chem. Soc.*, 1993, **115**, 5326; (c) S. Taylor, J. Gullick, P. McMorn, D. Bethell, P. C. B. Page, F. E. Hancock, F. King,; G. J. Hutchings, *J. Chem. Soc., Perkin Trans.*, 2001, **2**, 1724.

36 (a) E. J. Corey, T. G. Gant, *Tetrahedron Lett.,* 1994, **35**, 5373; (b) M. P. Doyle, D. C. Forbes, *Chem. Rev.,* 1998, **98**, 911.

37 (a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339; (b) G. M. Sheldrick, *Acta Cryst.,* 2008, **A64**, 112.