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Rhodium-Catalyzed Asymmetric Addition of Organoboronic Acids to Aldimines Using Chiral Spiro Monophosphite-Olefin Ligands: Method Development and Mechanistic Studies

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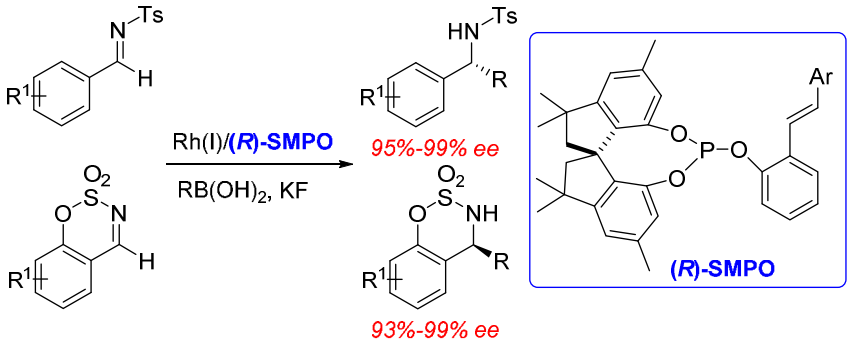


Abstract: The synthesis of a novel type of chiral spiro monophosphite-olefin (SMPO) ligands based on a hexamethyl-1,1'-spirobiindane scaffold was accomplished starting from Bisphenol C. The optimal ligand could serve as an elegant chiral bidentate ligand in the Rh-catalyzed asymmetric 1,2-addition of organoboronic acids to various acyclic/cyclic aldimines leading to chiral amines with high yields and excellent enantioselectivities. Detailed stereochemical models for enantioselective induction were elucidated through DFT calculations and postulated the origins of the higher enantioselectivity of phosphite-olefin ligands.

Introduction

The development of effective chiral ligands for transition-metal-catalyzed asymmetric reactions has become one of the most important and challenging goals of research in synthetic chemsitry.[1] Chiral phosphorus-based olefin ligands,[2] which combine the strongly coordinating phosphorus atom and the weakly coordinating olefin into one ligand molecule, have made impressive progress in asymmetric catalysis since the first demonstration by Grützmacher.[3] There have been reported structurally diverse P-olefin ligands with various kinds of skeletons, which had remarkable influence on catalytic performance in some cases. [3-7] These ligands have been used successfully for many asymmetric reactions, including hydrogenation, addition, allylic alkylation, amination, and intramolecular hydroacylation. Notably, Hayashi's phosphine–olefin[4] and Carreira's phosphoramidite–olefin[5] represented the great success of the promising class of ligands. Recently, Xu developed the first chiral binol- and H_8-binol-derived phosphite-olefin ligands for highly enantioselective catalysis.[7] Despite these achievements, the development of novel P-olefin ligands with excellent catalytic activities continues to be a search focus in a diverse range of asymmetric transformations. More importantly, the origins of the higher enantioselectivity of P-olefin ligands in transition-metal-catalyzed asymmetric reactions are still elusive.

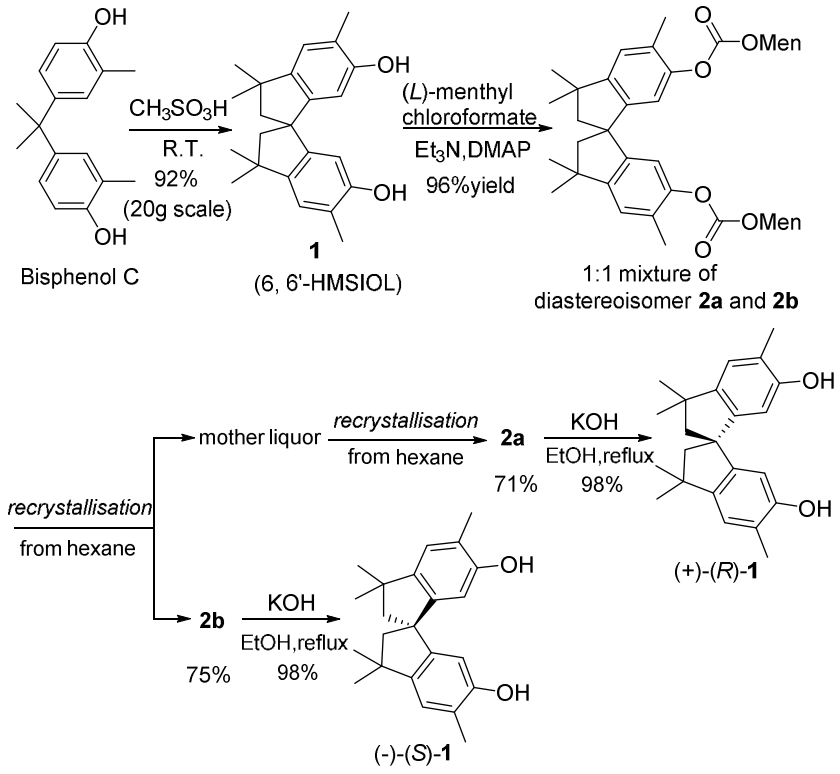
More recently, we developed new types of chiral phosphine-oxazoline ligands and bisphosphine ligands based on a hexamethyl-1,1'-spirobiindane backbone, and demonstrated their successful application in asymmetric catalysis.[8] Herein, we report the first synthesis of chiral spiro monophosphite-olefin (SMPO) ligands and their application in asymmetric reaction, and also elucidate the mechanism of stereocontrol through DFT calculations and NMR measurements. Importantly, the origins of the higher enantioselectivity of phosphite-olefin ligands in asymmetric catalysis are postulated for the first time.

Results and Discussion

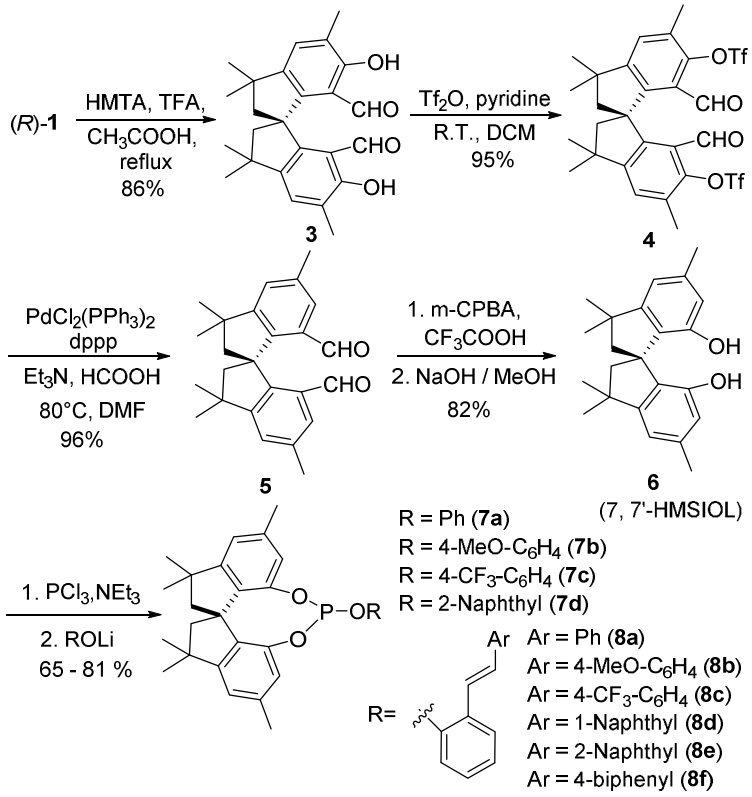
Our approach started with Bisphenol C (Scheme 1). Hexamethyl-1,1'-spirobiindane-6,6'-diol **1** (6, 6'-HMSIOL) was obtained in 92% yield by acid-catalyzed rearrangement.[8] Then, efficient chiral resolution

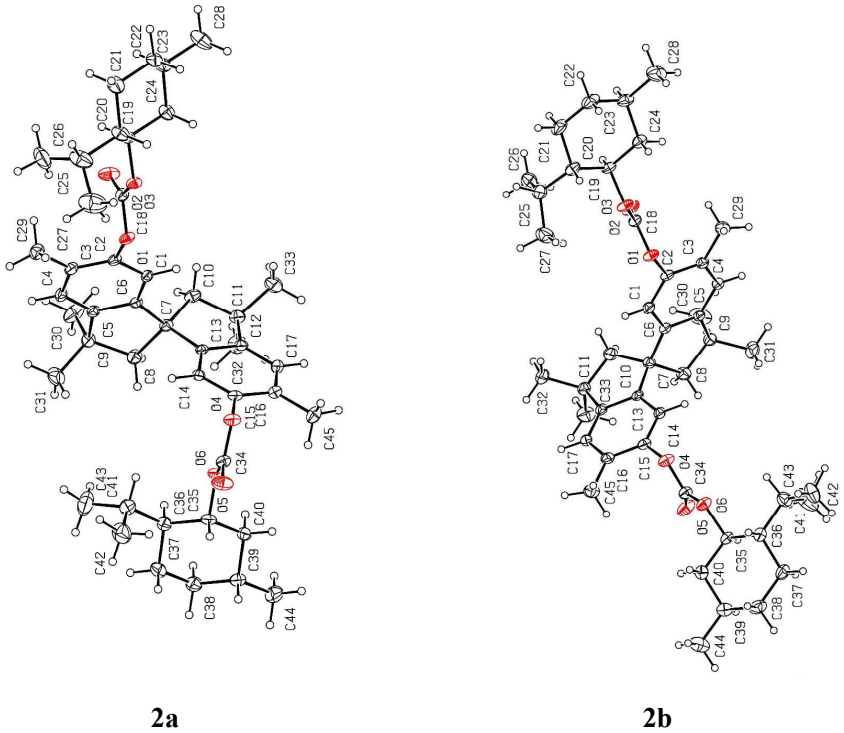
of **1** was accomplished utilizing (-)-menthyl chloroformate as a resolving agent. Notably, the two diastereomers of **2a** and **2b** were isolated by cycling recrystallization with good yields. Absolute configurations of **2a** and **2b** were confirmed by their X-ray structures, as shown in Figure 1. Both enantiomerically pure 6, 6'-HMSIOLs (*R*)-**1** and (*S*)-**1** were obtained in 98% yield after hydrolysis. Then, the new spiro phosphite ligands were synthesized from (*R*)-**1**, as shown in Scheme 2. The Duff reaction of (*R*)-**1** with hexamethylenetetramine (HMTA) provided the dialdehydes **3** in 86% yield. The subsequent esterification with Tf_2O afforded triflate **4** in 95% yield. The following Pd-catalyzed selective reduction with formic acid furnished spiro-aldehyde **5** in 96% yield. Then, the Baeyer-Villiger oxidation rearrangement and subsequent hydrolysis gave 7, 7'-HMSIOL **6** in 82% yield. Finally, a one-pot, two-step process afforded spiro monophosphite (SMPP) ligands **7a-d** and spiro monophosphite-olefin (SMPO) ligands **8a-f** in 65-81% yields.

Scheme 1. Synthesis and resolution of 6, 6'-HMSIOL



Scheme 2. Synthesis of chiral ligands

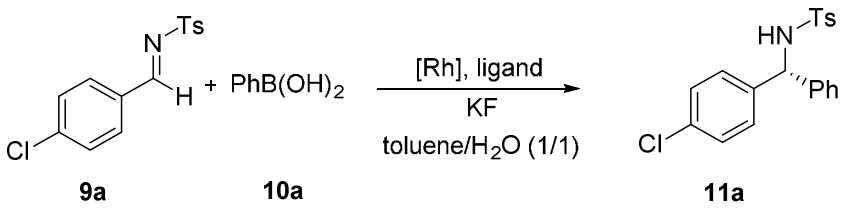




2a **2b**

Figure 1. X-ray crystal structures of 2a and 2b (The ellipsoids are drawn at 50% probability**)**

Table 1. Optimization of Reaction Parameters[a]



9a **10a** **11a**

Entry	Ligand	[Rh]	Yield [%][b]	*ee* [%][c]
1[d]	(*R*)-**7a**	$Rh(acac)(C_2H_4)_2$	52	-56
2[d]	(*R*)-**7b**	$Rh(acac)(C_2H_4)_2$	46	-57
3[d]	(*R*)-**7c**	$Rh(acac)(C_2H_4)_2$	27	-33
4[d]	(*R*)-**7d**	$Rh(acac)(C_2H_4)_2$	47	-35
5	(*R*)-**7a**	$Rh(acac)(C_2H_4)_2$	45	-64
6[d]	(*R*)-**8a**	$Rh(acac)(C_2H_4)_2$	trace	-
7	(*R*)-**8a**	$Rh(acac)(C_2H_4)_2$	83	97
8	(*R*)-**8b**	$Rh(acac)(C_2H_4)_2$	84	97
9	(*R*)-**8c**	$Rh(acac)(C_2H_4)_2$	82	98
10	(*R*)-**8d**	$Rh(acac)(C_2H_4)_2$	80	94
11	(*R*)-**8e**	$Rh(acac)(C_2H_4)_2$	85	99
12	(*R*)-**8f**	$Rh(acac)(C_2H_4)_2$	84	98
13	(*R*)-**8e**	$[RhCl(C_2H_4)_2]_2$	82	96
14	(*R*)-**8e**	$Rh(acac)(CO)_2$	83	-35
15	(*R*)-**8e**	$[Rh(COD)Cl]_2$	41	80
16	(*R*)-**8e**	$Rh(COD)_2BF_4$	10	3

[a]Reactions conditions: 0.05 mmol of **9a**, 0.1 mmol of **10a**, 3 mol % [Rh], 3 mol % ligand, and 0.2 mmol KF in 1 mL toluene/H_2O (1/1) at 35 °C for 20 h under N_2 atmosphere. [b]Isolated yields. [c]Determined by chiral HPLC analysis. [d] With 6 mol % ligand.

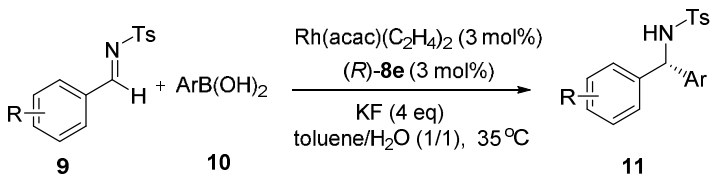
Our new ligands were applied to rhodium-catalyzed asymmetric reactions. First, the efficiency of new ligands was tested in the Rh-catalyzed asymmetric 1,2-addition of arylboronic acids to *N*-tosylarylimines. Highly efficient transition-metal-catalyzed asymmetric addition of arylboron reagents to *N*-tosylarylimines is the most versatile method to generate chiral diarylmethylamines.[9, 10] Initial experiments were investigated by the model reaction of *N*-tosylimine **9a** with phenylboronic acid **10a** (Table 1). When the reaction was carried out in the presence of 3 mol % of $Rh(acac)(C_2H_4)_2$ and 6 mol

% of SMPP **7** under aqueous KF-toluene at 35 ^{o}C for 20 h, the 1,2-addition product **11a** was obtained with low yield and enantioselectivity (Table 1, entries 1-4). The use of 3 mol % of **7a** (Table 1, entry 5) instead of 6 mol % (Table 1, entry 1) gave similar poor result. The use of 6 mol % of SMPO **8a** (Table 1, entry 6) instead of **7a** (Table 1, entry 1) resulted in no desired adduct. Notably, the use of 3 mol % of **8a** (Table 1, entry 7) instead of 6 mol % (Table 1, entry 6) resulted in good yield (83%) and excellent enantiomeric excess (97%). Furthermore, excellent result could be achieved in all case for the use of 3 mol % of SMPO **8a-f** (Table 1, entries 7-12), and the optimal ligand **8e** provided **11a** in 85% yield with 99% ee (Table 1, entry 11). Further evalutation of the Rh catalyst precursors indicated that only $[RhCl(C_2H_4)_2]_2$ gave the comparable result (Table 1, entries 13-16).

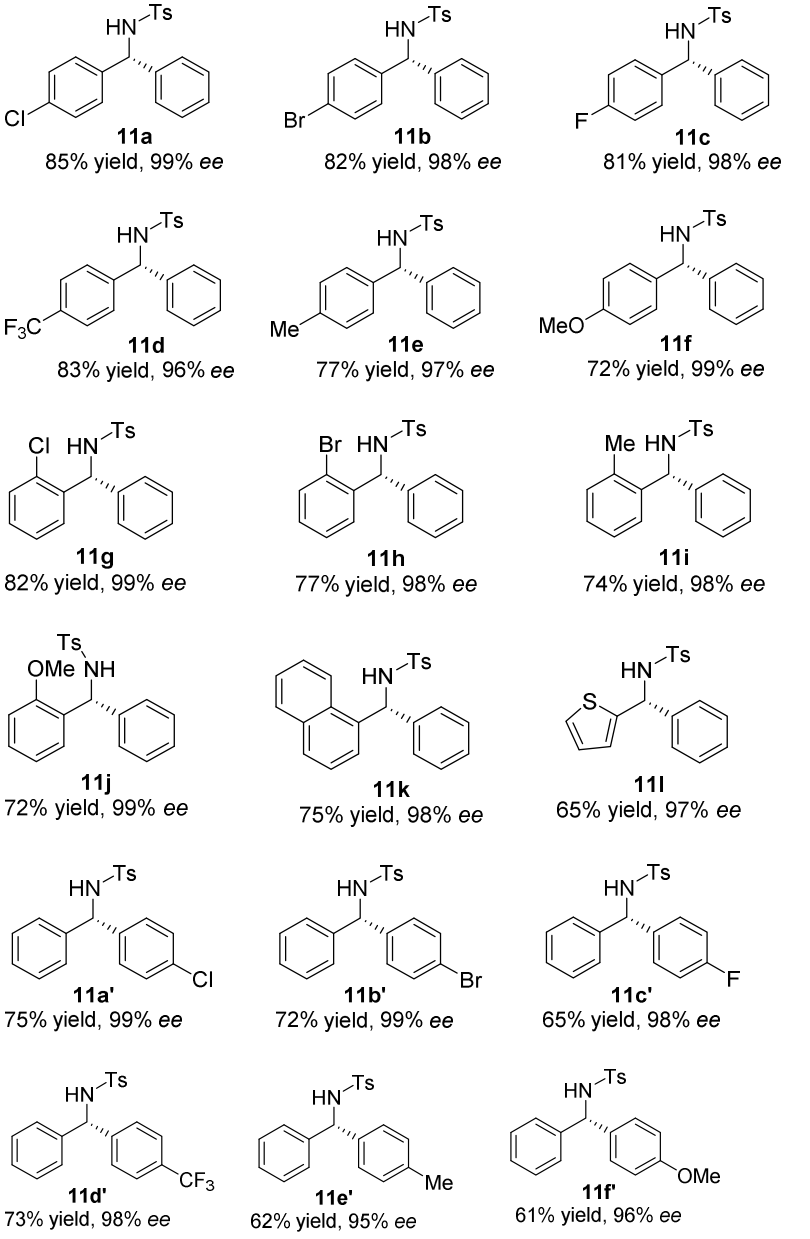
With the optimized conditions in hand, the scope of substrate was examined, and the result was summarized as shown in Table 2. Notably, high enantiomeric excess (95-99%) could be achieved when a wide variety of *N*-tosylarylimines with diverse steric and electronic properties were tested to react with arylboronic acids. The reaction enantiocontrol is not apparently impacted by the electronic nature of the phenyl ring of either imines or boronic acids. It is noteworthy that sterically encumbered *ortho*-substituted arylimines could also be smoothly employed to give excellent enantioselectivity and show apparently no influence on the yield (Table 2, **11g-j**). Meanwhile, naphthyl or thiopheneyl *N*-tosylimine could afford the corresponding products with high yields and excellent enantioselectivities (Table 2, **11k-l**). Moreover, various arylboronic acids afforded the corresponding products with high ees (Table 2, **11a'-d'** and **11e'-f'**). Interestingly, without changing the catalyst, only simply switching the aryl acceptor and donor of the substrates could provide both enantiomers of the corresponding product (Table 2, **11a-f** and **11a'-f'**).

Furthermore, we tested under the standard conditions the corresponding *N*-Nosylarylimine **9m** from para-chlorobenzaldehyde with phenylboronic acid **10a**. The corresponding diarylmethylamine product **11m** was obtained with 97% ee but low yield (37%). When we tested under the standard conditions the *N*-tosyl ketimine **9n** from para-fluoroacetophenone with phenylboronic acid **10a**, however, no reaction happened due to its very low reactivity.

Table 2. Substate Scope for Asymmetric Arylation of *N*-Tosylarylimines[a]



9 **10** **11**

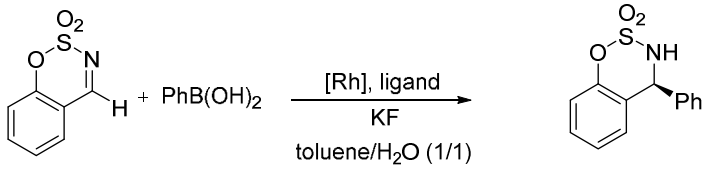


[a] Reactions conditions: 0.05 mmol of **9**, 0.1 mmol of **10**, 3 mol % $Rh(acac)(C_2H_4)_2$, 3 mol % (*R*)-**8e**, and 0.2 mmol KF in 1 mL toluene/H_2O (1/1) at 35 °C for 20 h under N_2 atmosphere. Yields are of isolated products. Enantioselectivity was determined by chiral HPLC.

Newly developed SMPO ligands **8** were also tested in the asymmetric addtion of cyclic *N*-sulfonyl aldimines with organoboronic acids.[7a, 9, 11] The reaction of cyclic *N*-sulfonyl aldimine **12a** with

phenylboronic acid **10a** was carried out in the presence of rhodium salts and chiral ligands to optimize the reaction conditions, as shown in Table 3. It was found that both (*R*)-**8b** and (*R*)-**8e** gave the excellent yield and the best ee value using $[RhCl(C_2H_4)_2]_2$ as the Rh catalyst precursor (Table 3, entries 3 and 6). The complex of (*R*)-**8b** and $Rh(acac)(C_2H_4)_2$ also gave the good yield and excellent enantioselectivity (Table 3, entry 8, 87%, 97% ee).

Table 3. Optimization of Reaction Parameters[a]



12a **10a** **13a**

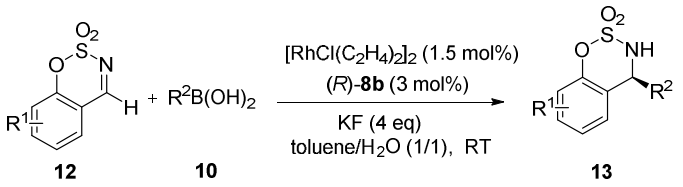
Entry	Ligand	[Rh]	Yield [%][b]	*ee* [%][c]
1[d]	(*R*)-**7a**	$[RhCl(C_2H_4)_2]_2$	85	-22
2	(*R*)-**8a**	$[RhCl(C_2H_4)_2]_2$	90	94
3	(*R*)-**8b**	$[RhCl(C_2H_4)_2]_2$	90	98
4	(*R*)-**8c**	$[RhCl(C_2H_4)_2]_2$	89	91
5	(*R*)-**8d**	$[RhCl(C_2H_4)_2]_2$	85	88
6	(*R*)-**8e**	$[RhCl(C_2H_4)_2]_2$	90	97
7	(*R*)-**8f**	$[RhCl(C_2H_4)_2]_2$	88	90
8	(*R*)-**8b**	$Rh(acac)(C_2H_4)_2$	87	97
9	(*R*)-**8b**	$Rh(acac)(CO)_2$	65	53
10	(*R*)-**8b**	$[Rh(COD)Cl]_2$	47	37
11	(*R*)-**8b**	$Rh(COD)_2BF_4$	43	15

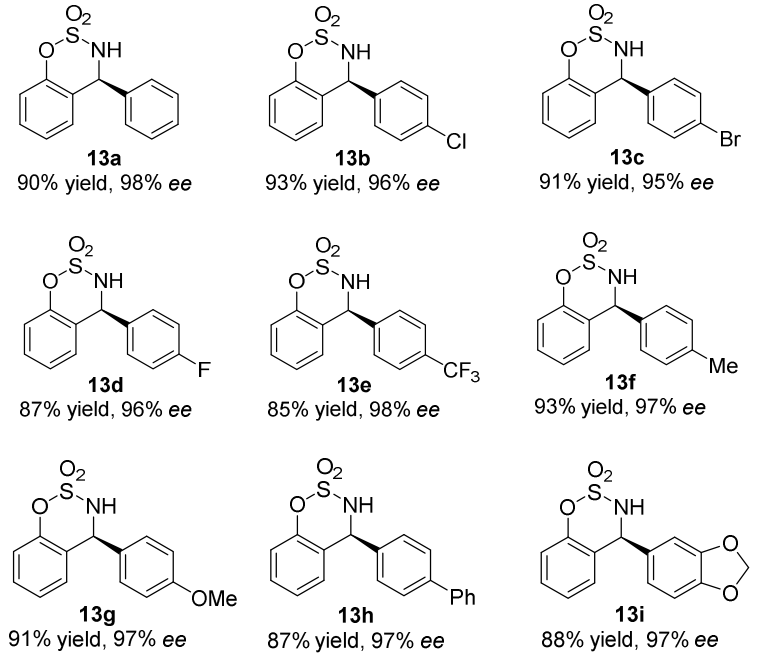
[a] Reactions conditions: 0.05 mmol of **12a**, 0.1 mmol of **10a**, 3 mol % [Rh], 3 mol % ligand, and KF (0.2 mmol) in toluene/H_2O (1/1, 1 mL) at 25 °C for 20 h under N_2 atmosphere. [b] Isolated yields. [c] Determined by chiral HPLC analysis. [d] With 6 mol % ligand.

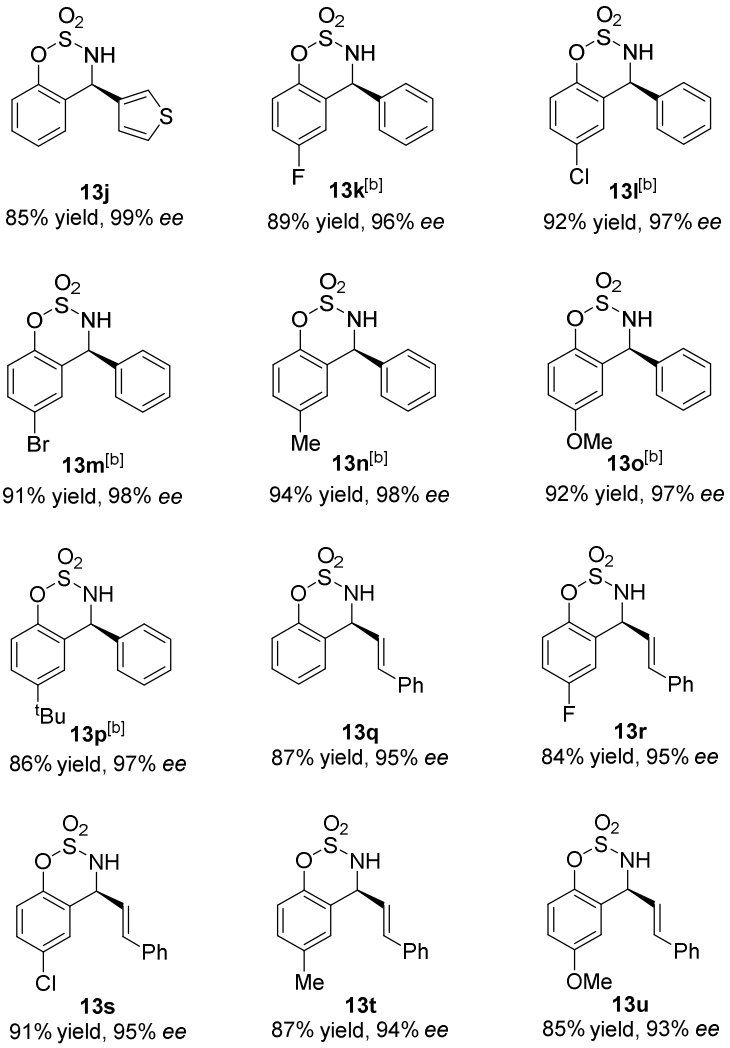
Under the optimized conditions (Table 3, entry 3), to our delight, the complex of (*R*)-**8b** and $[RhCl(C_2H_4)_2]_2$ showed near-perfect performance for such asymmetric transformation, as shown in Table 4. Notably, a wide range of arylboronic acids with electron-withdrawing or electron-donating

groups are suitable substrates to afford the corresponding products with high yields (85-93%) and excellent enantioselectivities (95%-98% ee) (Table 4, **13a-13i**). Meanwhile, heteroaryl 3-thiopheneylboronic acid also be successfully employed (Table 4, **13j**, 85% yield and 99% ee). Moreover, a range of acceptors were also applied in the addition reaction with phenylboronic acid to reveal excellent results using $[Rh(acac)(C_2H_4)_2]_2$ /(*R*)-**8b** as the catalyst (Table 4, **13k-13p**). It is noteworthy that styrylboronic acid reacted smoothly with various cyclic *N*-sulfonyl aldimines to afford the corresponding enantioselective styrylation products[7a] (Table 4, **13q-13u**). However, when we tested under the standard conditions the more challenging cyclic *N*-sulfonyl ketimine, such as 4-methylbenzo[e][1,2,3]oxathiazine 2,2-dioxide **12h** from 2-hydroxyacetophenone, no reaction happened due to its low reactivity.

Table 4. Substrate scope for asymmetric addtion of cyclic aldimines[a]







[a] Reactions conditions: 0.05 mmol of **12**, 0.1 mmol of **10**, 1.5 mol % $[RhCl(C_2H_4)_2]_2$, 3 mol % (*R*)-**8b**, and 0.2 mmol KF in 1 mL toluene/H_2O (1/1) at RT for 20 h under N_2 atmosphere. Yields are of isolated products. Enantioselectivity was determined by chiral HPLC. [b] With 3 mol % $Rh(acac)(C_2H_4)_2$.

Additionally, we have performed NMR measurements[7b] to investigate the coordination mode of (*R*)-**8e** to a Rh(I) cation (See Supporting Information for NMR spectra). Upon treatment of (*R*)-**8e** with $Rh(acac)(C_2H_4)_2$ (1.1 equiv) in CD_2Cl_2 at room temperature for 1 hour, the free phosphorus resonance (^{31}P NMR: δ 119.3 ppm) disappeared with the concomitant formation of new double peaks (δ 133.7 ppm) with the large Rh-P coupling (J_{Rh-P} = 309 Hz). In the ^{1}H NMR and ^{13}C spectra, obvious upfield shifts of the olefinic protons to 5.32 and 4.85 ppm and the olefinic carbons to 58.0 and 57.0 ppm were observed. All these NMR observations clearly disclose that the (*R*)-**8e** behaves as a P-olefin bidentate chelating ligand in Rh/(*R*)-**8e** complex.

We next explored the origins of ligand-controlled enantioselectivity with DFT calculations at the M06/6-311+G(d,p)-SDD-CPCM (toluene) // B3LYP/6-31G(d)-LANL2DZ level (see Supporting Information for computational details). Using *N*-tosylimine (**9a**) as the model substrate, the enantioselectivity-determining transition states for the C–C bond formation step between L_nRhPh and **9a** are located (Figure 2).[12] For the optimal monophosphite-olefin ligand (*R*)-**8e**, **TS14**, which leads to the favorable adduct, is 3.0 kcal/mol more favorable than the competing **TS15** (Figure 2a).[13] This computed enantioselectivity agrees well with the experimental observations (entry 11, Table 1). The insertion barrier for **TS14** is 13.1 kcal/mol, and that for **TS15** is 16.1 kcal/mol, which are surmountable under the experimental conditions (Figure S2). For the monophosphite ligand (*R*)-**7a**, our calculations showed that the bisligation is essential to promote the insertion, and the insertion transition states with only one monophosphite ligand coordination require unsurmountable barriers (Figure S3). **TS16** is 0.6 kcal/mol less favorable comparing with **TS17** (Figure 2b), which is in line with the reversed trend with ligand (*R*)-**7a** in experiments (entry 1, Table 1).

The conformational flexibility of the ligand leads the change of enantioselectivity. Topographic steric map is applied to elucidate the steric environment of the L_nRhPh moiety in the C–C bond formation transition states (Figure 2).[12] For (*R*)-**8e**, the bis-ligation of phosphine and alkene creates a rigid steric environment; the topographic steric maps of the L_nRhPh moiety in both **TS14** and **TS15** indicate a steric-demanding first quadrant (red region), which corresponds to the naphthyl group. Therefore, the steric-demanding naphthyl group has steric repulsions with the tosyl group in **TS15**, leading to the exceptional enantioselectivity. These steric repulsions are also reflected by the orientation of the naphthyl group of the ligand in **TS14** and **TS15** (Figure S4). For (*R*)-**7a**, this monophosphite ligand can rotate around the rhodium-phosphine bond, and the steric environment of the corresponding L_nRhPh moiety is quite flexible. Figure 2b showed the steric environments of the L_nRhPh moiety in **TS16** and **TS17**. Due to the ligand rotation, the steric-demanding spiro backbone of (*R*)-**7a** can avoid the tosyl group of *N*-tosylimine in both transition states; **TS16** has the steric-demanding red region in the first

quadrant, while **TS17** has the corresponding region in the fourth quadrant. This flexibility of steric environment results in the significantly diminished enantioselectivity of (*R*)-**7a** and the reversed trend. To further support our mechanistic rationale that the steric repulsions between tosyl group and naphthyl group in **TS15** are the leading factors that control the enantioselectivity, additional calculations were performed to clarify the explanation. By replacing the naphthyl group of the ligand with hydrogen, the computed free energy difference between **TS14** and **TS15** decreases from +3.0 kcal/mol to -1.4 kcal/mol (**TS-S25** vs. **TS-S26**, Figure S6). In addition, similar change was observed when we removed both the tosyl and naphthyl groups (**TS-S27** vs. **TS-S28**, Figure S6). The optimized structures and relative Gibbs free energies of the high-energy conformers of the insertion transition states are included in the Supporting Information (Figure S5).

Conclusion

In summary, a new class of chiral spiro monophosphite-olefin (SMPO) ligands based on the hexamethyl-1,1'-spiro biindane backbone has been developed. The optimal P-olefin ligand could serve as an elegant chiral bidentate ligand in the Rh-catalyzed asymmetric 1,2-addition of organoboronic acids to acyclic/cyclic aldimines with a broad range of substraes leading to chiral amines with high yields and excellent enantioselectivities. It has been disclosed that SMPO ligands are capable of coordinating to a rhodium(I) cation in the bidentate fashion at the phosphorus atom as well as at the olefinic double bond. Detailed stereochemical models for enantioselective induction of Rh/P-olefin catalyzed asymmetric reactions were elucidated through DFT calculations, and the origins of the higher enantioselectivity of phosphite-olefin ligands are postulated.

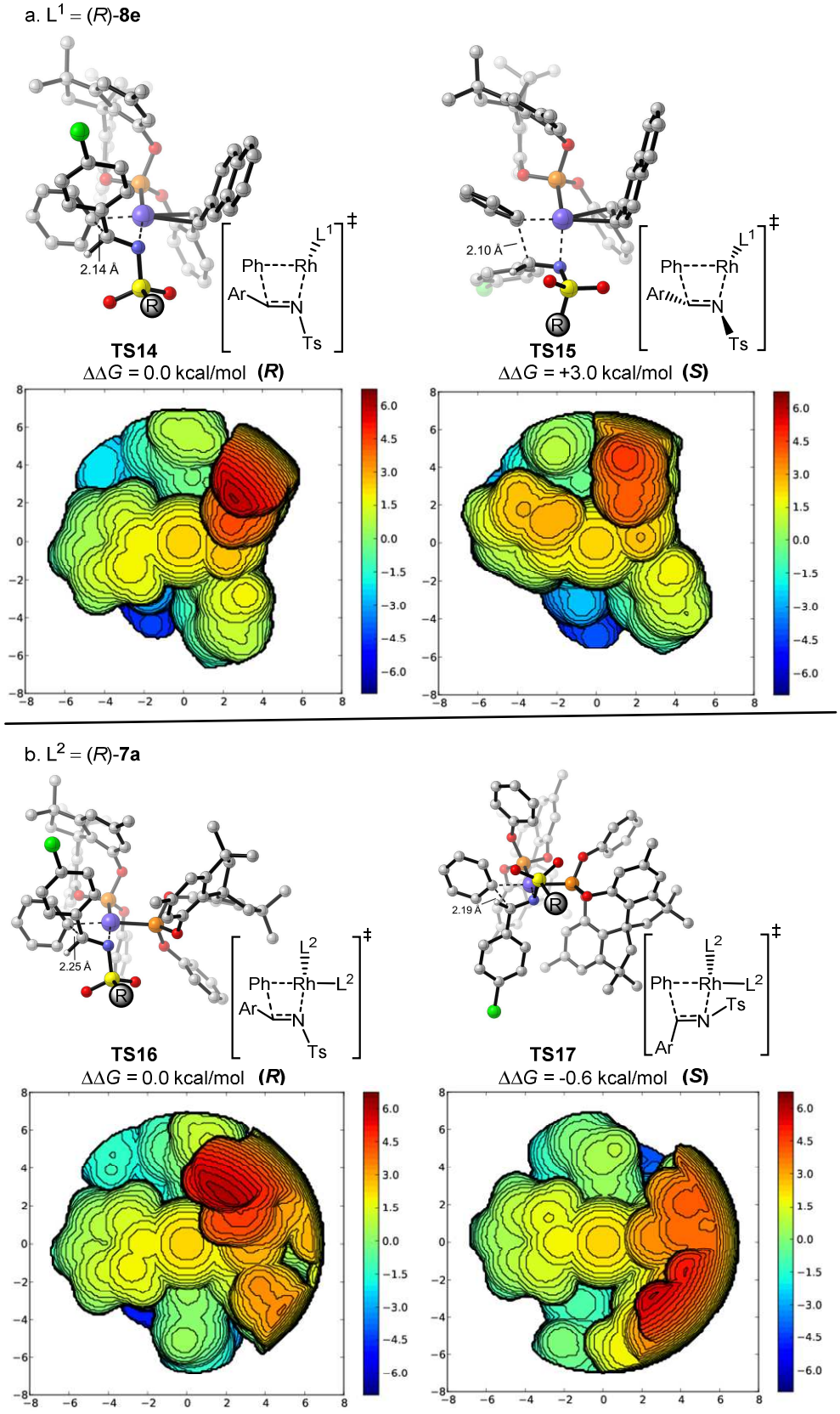


Figure 2. DFT-computed enantioselectivity-determining transition states and topographic steric maps with (*R*)-**8e** and (*R*)-**7a**.

Experimental Section

General information. All reactions were carried out in oven-dried glassware with magnetic stirring. All commercially available reagents were purchased and used without further purification, and all solvents were dried and purified according to standard methods prior to use. *N*-Tosylarylimines **9**[10b, 14] and cyclic *N*-sulfonyl aldimines **12**[15] were prepared according to the reported procedures. NMR spectrums were recorded on 400 NMR spectrometer at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, 162 MHz for ^{31}P. The chemical shifts were reported in $CDCl_3$ or DMSO-d_6 with tetramethylsilane (TMS) as internal standard. The following abbreviations were used to describe peak patterns where appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. Coupling constants were reported in Hertz (Hz). Infrared spectra were recorded on an ATR-FTIR spectrometer. HRMS were obtained using EI ionization or ESI ionization. Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at 20 °C. Enantiomeric excesses (ee) were determined by chiral high-performance liquid chromatography. HPLC analysis was performed using Chiralcel columns (Chiralcel OD-H, AD-H, IC-3, IF-3 column).

*Synthesis of 3,3,3',3',5,5'-Hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diol (**1**).*[8a] A 500 mL round bottom flask was charged with Bisphenol C (BPC, 51.2 g, 0.2 mol) and methanesulfonic acid (160 mL), and then the mixture was stirred at room temperature for 3 days. Additional methanesulfonic acid (100 mL) was added to the reaction system at the forth day and the reaction was continued to stir for another 2 days. The mixture was poured directly into the crushed ice and filtered. The filter cake was washed sequentially with saturated solution of $NaHCO_3$ and hot water. Then, the residue was recrystallized with ethyl acetate/petroleum ether followed by ethanol/water and dried to afford 6, 6'-HMSIOL (**1**) as a white solid (20.6 g, 92% yield). mp 249-250 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (s, 2H), 5.84 (s, 2H), 3.93 (s, 2H), 2.29 (d, *J* = 13.0 Hz, 2H), 2.20 (s, 6H), 2.15 (d, *J* = 13.0 Hz, 2H), 1.37 (s, 6H), 1.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 150.0, 144.5, 123.5, 122.9, 110.5, 59.4, 57.0, 43.1, 31.9, 30.1, 16.0; IR (film) γ = 3515, 2952, 2862, 1615, 1497, 1411, 1361, 1313, 1288, 1275, 1207, 1149, 1136, 1070, 1014, 886, 858, 758, 668 cm^{-1}; HRMS (EI, GC-TOF) m/z: [M^{+}] Calcd for $C_{23}H_{28}O_2$ 336.2089, found 336.2085.

*Chiral resolution of 6, 6'-HMSIOL (**1**).*

A solution of **1** (5.05 g, 15 mmol), triethylamine (9.6 mL, 69 mmol) and 4-dimethyl-aminopyridine (DMAP) (183 mg, 1.5 mmol) in methylene chloride (50 mL) was treated over 30 minutes with (-)-menthyl chloroformate (7.3 mL, 34.5 mmol). The resulting mixture was stirred at ambient temperature for 1 h, then the reaction mixture was washed with 1M hydrochloric acid, saturated solution of brine.

The organic phase was dried with anhydrous sodium sulfate and concentrated in vacuo to afford **2a** and **2b** as a mixture of diastereomeric diester (1:1). The diastereoisomer mixture of **2a** and **2b** was recrystallized from hexane to provide **2b** as a colorless solid (2.8 g, >99% d.r.). The mother liquor was concentrated in vacuo to provide a glassy solid, which was also recrystallized from hexane to give **2a** as a colorless solid (2.0 g, >99% d.r.). Furthermore cycling recrystallization of the resulting residue to provide **2a** (1.6 g) and **2b** (1.0 g), respectively.

*(R)-3,3,3',3',5,5'-Hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diyl bis((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) bis(carbonate) (**2a**).* White solid, 3.6 g, 71% yield, mp 154-156 ^{o}C; $[\alpha]_D^{20}$ = -158.0 (*c*1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 2H), 6.55 (s, 2H), 4.56 (m, 2H), 2.33 (d, J = 13.1 Hz, 2H), 2.22 (m, 8H), 2.10 (d, J = 11.9 Hz, 2H), 2.03-1.92 (m, 2H), 1.75 – 1.64 (m, 4H), 1.52 – 1.39 (m, 4H), 1.36 (s, 6H), 1.32 (s, 6H), 1.08 (m, 4H), 0.91 (m, 14H), 0.79 (d, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2 , 149.9, 149.2, 149.2, 128.7, 124.2, 117.1, 79.1, 59.4, 57.1, 47.0, 43.2 , 40.6, 34.1, 31.6, 31.4, 30.3, 26.2, 23.4, 22.0, 20.7, 16.4, 16.1; IR (film) γ= 2955, 2925, 2869, 1756, 1487, 1456, 1254, 1239 cm^{-1}; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd for $C_{45}H_{64}O_6Na$ 723.4601, found 723.4578.

*(S)-3,3,3',3',5,5'-Hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diyl bis((1R,2S,5R) -2-isopropyl-5-methylcyclohexyl) bis(carbonate) (**2b**).* White solid, 3.8 g, 75% yield, mp 101-103 ^{o}C; $[\alpha]_D^{20}$ = -87.4 (*c*1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 2H), 6.55 (s, 2H), 4.55 (m, 2H), 2.32 (d, J = 13.1 Hz, 2H), 2.23 (d, J = 13.2 Hz, 2H), 2.20 (s, 6H), 2.12 (d, J = 11.8 Hz, 2H), 2.01 (m, 2H), 1.68 (d, J = 12.3 Hz, 4H), 1.53 – 1.39 (m, 4H), 1.36 (s, 6H), 1.32 (s, 6H), 1.16 – 0.97 (m, 4H), 0.91 (m,14H), 0.80 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 149.9, 149.2, 128.8, 124.3, 117.2, 79.1, 59.5, 57.1, 47.0, 43.1, 40.6, 34.1, 31.6, 31.4, 30.3, 26.1, 23.3, 22.0, 20.7, 16.3, 16.2; IR (film) γ= 2955, 2927, 2869, 1755, 1486, 1456, 1254, 1239, 1159, 961 cm^{-1}; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd for $C_{45}H_{64}O_6Na$ 723.4601, found 723.4590.

A solution of **2a** (15.7 g, 22.5 mmol) and KOH (6.55 g, 117 mmol, 5.2 equiv.) in ethanol (200 mL) was heated under reflux for 2 hours, then concentrated in vacuo. The resulting residue was dissolved in methylene chloride (100 mL), then washed with 1M hydrochloric acid, saturated solution of brine, dried with anhydrous sodium sulfate and concentrated in vacuo followed by flash chromatography to provide **(*R*)-1** (7.4 g) in 98 % yield, as a white solid, mp 210-212 ^{o}C, $[\alpha]_D^{20}$ = +30.5 (*c*1.0, CH_2Cl_2).

2b (1.5 g, 2.25 mmol) was also applied to the aboved procedure to give (*S*)-**1** (0.74 g) in 98% yield, as a white solid, mp 210-212 ^{o}C, $[\alpha]_D^{20}$ = -30.4 (*c*1.0, CH_2Cl_2).

*Synthesis of (R)-6,6'-Dihydroxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-dicarbaldehyde [(R)-**3**]*. (*R*)-**1** (4.2 g, 12.5 mmol) was dissolved in trifluoroacetic acid (TFA, 150 mL) under nitrogen, and hexamethylenetetramine (HMTA, 10.5 g, 75 mmol) was added in one portion. The yellow solution was refluxed overnight and glacial acetic acid (150 mL) was added the next day. The solution then kept refluxing for 3 days. Until the starting diols were converted, 4 M HCl (150 mL) was added after cooling to 95 ^{o}C, and the mixture was stirred overnight. Then after cooling to room temperature, the mixture was poured into water and finally filtered to give the product (*R*)-**3** as a yellow solid (4.2 g, 86 % yield). mp ＞300 ^{o}C; $[\alpha]_D^{20}$ = -131.0 (*c*1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.01 (s, 2H), 9.57 (s, 2H), 7.20 (s, 2H), 2.57 (d, *J* = 13.5 Hz, 2H), 2.38 (d, *J* = 13.5 Hz, 2H), 2.26 (s, 6H), 1.37 (s, 6H), 1.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ194.7, 162.3, 149.6, 141.8, 132.6, 128.0, 113.7, 60.3, 57.8, 43.0, 32.0, 30.1, 15.6; IR (film) γ= 3379, 2966, 2925, 2876, 1636, 1604, 1468, 1393, 1384, 1273, 1162, 1092 cm^{-1}; HRMS (EI, GC-TOF) m/z: [M^+] Calcd for $C_{25}H_{28}O_4$ 392.1988, found 392.1990.

*Synthesis of (R)-7,7'-Diformyl-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diyl bis(trifluoromethanesulfonate) [(R)-**4**]*. To a solution of (*R*)-**3** (3.92 g, 10 mmol) and pyridine (2.42 mL, 30 mmol) in methylene chloride (60 mL), triflic anhydride (4.21 mL, 25 mmol) was added dropwise at 0 ^{o}C under a nitrogen atmosphere. The mixture was naturally raised to room temperature and stirred overnight. The reaction was diluted with dichloromethane, washed with 5% HCl aqueous, saturated solution of brine, saturated solution of $NaHCO_3$, and saturated solution of brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by flash chromatography on a silica gel column (ethyl acetate/petroleum ether = 1/50) to obtain the product (*R*)-**4** as a white solid (6.24 g, 95% yield). mp 160-162 ^{o}C; $[\alpha]_D^{20}$ = -158.7 (*c*1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ9.79 (s, 2H), 7.35 (s, 2H), 2.51 (d, *J* = 12.8 Hz, 2H), 2.45 (s, 6H), 2.42 (d, *J* = 12.8 Hz, 2H), 1.50 (s, 6H), 1.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ186.5, 153.5, 148.1, 146.2, 130.6, 130.0, 117.4(q, *J* = 320 Hz), 57.7, 56.5, 42.1, 31.4, 28.0, 15.8; IR (film) γ = 2962, 2870, 1704, 1565, 1455, 1423, 1405, 1215, 1183, 1140, 1048 cm^{-1}; HRMS (EI, GC-TOF) m/z: [M^+] Calcd for $C_{27}H_{26}O_8S_2F_6$ 656.0973, found 656.0981.

*Synthesis of (R)-3,3,3',3',5,5'-Hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-dicarbaldehyde [(R)-**5**]*. Under nitrogen, to a solution of (*R*)-**4** (6.56 g, 10 mmol), $PdCl_2(PPh_3)_2$ (280 mg, 0.4 mmol), and 1,3-bis (diphenylphosphino)propane (210 mg, 0.5 mmol) in DMF (100 mL), triethylamine (17 mL, 120 mmol) was added dropwise at 0 ^{o}C followed by the addition of formic acid (3

mL, 80 mmol). Then, the reaction mixture was raised to 80 °C and reacted for 1.5 hours. After cooling to room temperature, the resulting mixture was diluted with ethyl acetateand, and washed sequentially with water, saturated solution of $NaHCO_3$, and saturated solution of brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate / petroleum ether = 1/30) to afford product (*R*)-**5** as a yellow solid (3.44 g, 96% yield). mp 220-222 °C; $[\alpha]_D^{20}$ = -181.3 (*c*1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 2H), 7.53 (s, 2H), 7.25 (s, 2H), 2.56 (d, *J* = 13.2 Hz, 2H), 2.43 (d, *J* = 13.4 Hz, 2H), 2.41 (s, 6H), 1.45 (s, 6H), 1.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 152.4, 149.1, 137.2, 129.5, 128.4, 128.2, 58.8, 56.2, 42.4, 31.4, 28.6, 20.1; IR (film) γ = 3359, 2963, 2924, 2866, 1681, 1604, 1573, 1460, 1394, 1383, 1311, 1242, 1162cm^{-1}; HRMS (EI, GC-TOF) m/z: [M^+] Calcd for $C_{25}H_{28}O_2$ 360.2089, found 360.2092.

*Synthesis of (R)-3,3,3',3',5,5'-Hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diol [(R)-**6**]*. Under nitrogen atmosphere, to a solution of (*R*)-**5** (1.44 g, 4 mmol) in methylene chloride (150mL), *m*-chloroperbenzoic acid (*m*-CPBA) (3.2 g, 16 mmol, 85% active oxygen content) was added several portions at 0 °C followed by the addition of trifluoroacetic acid (TFA) (0.6 mL, 8 mmol). The mixture was naturally raised to room temperature and stirred overnight. The reaction solution was washed with saturated aqueous solution of Na_2SO_3, saturated solution of $NaHCO_3$, and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was redissolved in 40mL methyl alcohol, 1M NaOH aqueous (16 mL, 16 mmol) was added dropwise at 0 °C. Then, the mixture was naturally raised to room temperature and stirred overnight. After removal of the solvent, the residue was redissolved in methylene chloride, acidified by 3M HCl aqueous, washed with saturated solution of brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate / petroleum ether / glacial acetic acid= 5/100/1) to afford product (*R*)-**6** as a white solid (1.14 g, 82% yield). mp 165-167 °C; $[\alpha]_D^{20}$ = -124.8 (*c*1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.63 (s, 2H), 6.50 (s, 2H), 4.41 (s, 2H), 2.35 (d, J = 13.4 Hz, 2H), 2.30 (m, 8H), 1.38 (s, 6H), 1.33 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.0, 152.4, 140.7, 127.1, 116.1, 115.4, 55.9, 53.4, 44.1, 31.9, 29.6, 21.5; IR (film) γ = 3520, 2955, 2925, 2862, 1618, 1585, 1469, 1455, 1447 cm^{-1}; HRMS (EI, GC-TOF) m/z: [M^+] Calcd for $C_{23}H_{28}O_2$ 336.2089, found 336.2089.

General Procedure for Synthesis of Ligands (*R*)-7/(*R*)-8. At nitrogen atmosphere, to a solution of PCl_3 (0.25 mL, 0.5 mmol, 2.0 M solution in methylene chloride) in THF (10 mL), Et_3N (155 μL, 1.1 mmol) was added dropwise at 0 °C and cooled to -78 °C. A solution of (*R*)-**6** (168 mg, 0.5 mmol) in 2 mL THF was added at -78 °C, the reaction mixture was stirred at this temperature for 2h, naturally raised up to room temperature and stirred for another 1h. The mixture was cooled to -78 °C again, and treated

with lithium phenolates prepared from phenols (0.6 mmol) and butyllithium (0.375 mL, 0.6 mmol, 1.6 M solution in hexane) in THF (5 mL) at -30 °C. The resulted mixture was warmed slowly to room temperature and stirred overnight. The solvent was removed in vaccum and the residue was purified by flash chromatography (ethyl acetate / petroleum ether = 1/100) to afford the corresponding product (*R*)-**7** or (*R*)-**8**.

*Phenyl-[(R)-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobiindane-7,7'-diyl]-phosphite [(R)-**7a**]*. 148 mg, 65% yield ; white solid, mp 73-75 °C; $[\alpha]_D^{20}$ = +163.3 (*c*1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 2H), 7.11 (t, J = 7.4 Hz, 1H), 7.06 (m, 2H), 6.83 (s, 1H), 6.79 (s, 1H), 6.79 (s, 1H), 6.54 (s, 1H), 2.39 (d, J = 12.7 Hz, 2H), 2.36 (s, 3H), 2.28 (s, 3H), 2.05 (d, J = 12.5 Hz, 2H), 1.53 (s, 3H), 1.50 (s, 3H), 1.28 (s, 3H), 1.25 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 153.3, 152.8, 151.4, 151.3, 143.1, 143.1, 141.5, 141.5, 138.8, 138.8, 138.1, 138.1, 137.0, 135.5, 135.5, 128.6, 122.7, 121.6, 121.4, 121.4, 119.6, 119.6, 119.0, 118.76, 118.7, 55.7, 55.3, 54.7, 41.9, 41.3, 31.3, 30.9, 29.2, 29.0, 20.2, 20.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 118.94 ; IR (film) γ = 2959, 2916, 2856, 1613, 1586, 1487, 1474, 1452, 1414, 1362, 1321, 1308, 1291, 1261, 1231,1214, 1162cm^{-1}; HRMS (EI, GC-TOF) m/z: [M^+] Calcd for $C_{29}H_{31}O_3P$ 458.2011, found 458.2007.

*4-Methoxyphenyl-[(R)-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobiindane-7,7'-diyl]-phosphite [(R)-**7b**])*. 175 mg, 72% yield ; white solid, mp 64-66 °C; $[\alpha]_D^{20}$ = +145.5 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 6.4 Hz, 2H), 6.82 (s, 1H), 6.80 (s, 1H), 6.77 (s, 1H), 6.57 (s, 1H), 3.79 (s, 3H), 2.38 (d, J = 12.6 Hz, 2H), 2.35 (s, 3H), 2.29 (s, 3H), 2.04 (d, J = 12.2 Hz, 2H), 1.53 (s, 3H), 1.50 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ154.8, 153.3, 153.3, 152.8, 144.9, 143.1, 141.6, 141.5, 138.8, 138.1, 137.0, 135.5, 121.6, 121.4, 121.4, 119.7, 119.6, 119.6, 119.5, 119.0, 113.6, 55.6, 55.3, 54.7, 54.6, 41.9, 41.3, 31.3, 31.0, 29.2, 29.0, 20.2, 20.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 119.32; IR (film) γ = 2959, 2920, 2860, 1611, 1581, 1568, 1502, 1474, 1465, 1450, 1442, 1412, 1360, 1317, 1308, 1289, 1246, 1229, 1201, 1165cm^{-1}; HRMS (EI, GC-TOF) m/z: [M^+] Calcd for $C_{30}H_{33}O_4P$ 488.2116, found 488.2115.

*4-Trifluoromethylphenyl-[(R)-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobiindane-7,7'-diyl]-phosphite [(R)-**7c**]*. 186 mg, 71% yield; white solid, mp 49-51 °C; $[\alpha]_D^{20}$ = +161.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.55 (d, J = 8.7 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.85 (s, 1H), 6.80 (s, 1H), 6.78 (s, 1H), 6.48 (s, 1H), 2.41 – 2.35 (m, 5H), 2.25 (s, 3H), 2.03 (dd, J = 12.5, 2.1 Hz, 2H), 1.53 (s, 3H), 1.50 (s, 3H), 1.27 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 153.5, 153.0, 142.7, 142.7, 141.4, 141.3, 138.7, 138.3, 137.3, 135.4, 125.9(q, J = 4Hz), 124.8(q, J = 33Hz), 123.0(q, J = 272Hz), 121.4, 121.3, 121.3, 119.9, 119.2, 118.9, 118.8, 55.7, 55.4, 54.8, 41.9, 41.4, 31.2, 31.0, 29.2, 29.0, 21.6, 20.2, 20.0, 13.1;^{31}P NMR (162 MHz, $CDCl_3$) δ 117.22; IR (film) γ = 2963, 2916, 2860,

2357, 2331, 1611, 1583, 1512, 1472, 1444, 1414, 1360, 1321, 1263, 1229, 1169cm-1; HRMS (EI, GC-TOF) m/z: [M^+] Calcd for $C_{30}H_{30}F_3O_3P$ 526.1885, found 526.1888.

*2-Naphthyl-[(R)-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobiindane-7,7'-diyl]-phosphite [(R)-**7d**]*. 203 mg, 80% yield; white solid, mp 100-102 ^oC; $[\alpha]_D^{20}$ = +89.1 (*c*1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ7.79 (m, 3H), 7.46 (m, 3H), 7.19 (dd, J = 8.9, 2.3 Hz, 1H), 6.85 (s, 1H), 6.82 (s, 1H), 6.81 (s, 1H), 6.57 (s, 1H), 2.40 (d, J = 12.6 Hz, 2H), 2.37 (s, 3H), 2.26 (s, 3H), 2.06 (dd, J = 12.4, 3.7 Hz, 2H), 1.54 (s, 3H), 1.51 (s, 3H), 1.29 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ153.4, 153.3, 152.9, 149.1, 149.1, 143.1, 143.0, 141.6, 141.5, 138.8, 138.8, 138.2, 138.2, 137.1, 135.5, 133.0, 129.3, 128.7, 126.7, 126.2, 125.5, 123.8, 121.5, 121.5, 121.4, 119.7, 119.7, 119.6, 119.1, 114.3, 114.2,63.4, 55.7, 55.4, 54.7, 41.9, 41.4, 31.3, 30.9, 29.3, 29.0, 24.3, 20.2, 20.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 118.64 ; IR (film) γ= 2959, 2916, 2860, 1631, 1613, 1598, 1577, 1508, 1461, 1409, 1360, 1319, 1308, 1289, 1263, 1248, 1231, 1212, 1167cm^{-1}; HRMS (EI, GC-TOF) m/z: [M^+] Calcd for $C_{33}H_{33}O_3P$ 508.2167, found 508.2166.

*(E)-2,4,4,7,7,9-Hexamethyl-12-(2-styrylphenoxy)-4,5,6,7-tetrahydrodiindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocine [(R)-**8a**]*. 204 mg, 73% yield; white solid, mp 60-62 ^oC; $[\alpha]_D^{20}$ = +318 (*c*0.1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ7.71 – 7.64 (m, 1H), 7.39 (d, J = 7.3 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.28 – 7.18 (m, 3H), 7.15 – 7.03 (m, 3H), 6.83 (s, 1H), 6.77 (s, 1H), 6.74 (s, 1H), 6.51 (s, 1H), 2.40 (dd, J = 12.5, 10.4 Hz, 2H), 2.33 (s, 3H), 2.14 – 1.98 (m, 5H), 1.53 (s, 3H), 1.52 (s, 3H), 1.32 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 152.7, 149.0, 148.9, 143.1, 143.0, 141.6, 141.6, 138.7, 138.7, 138.2, 138.1, 137.3, 136.5, 135.6, 128.4, 127.7, 127.5, 127.4, 126.5, 125.6, 125.3, 122.7, 121.6, 121.4, 121.3, 119.6, 119.1, 117.9, 117.7, 55.6, 55.4, 54.9, 41.9, 41.4, 31.3, 31.2, 29.1, 29.1, 20.1, 20.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 119.16; IR (film) γ = 2963, 2916, 2860, 1616, 1596, 1573, 1485, 1450, 1412, 1360, 1321, 1308, 1289, 1261, 1229, 1208, 1182, 1165cm^{-1}; HRMS (EI, GC-TOF) m/z: [M^+] Calcd for $C_{37}H_{37}O_3P$ 560.2480, found 560.2476.

*(E)-12-(2-(4-Methoxystyryl)phenoxy)-2,4,4,7,7,9-hexamethyl-4,5,6,7-tetrahydrodiindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocine [(R)-**8b**]*. 238 mg, 81% yield ; white solid, mp 63-65 ^oC; $[\alpha]_D^{20}$ = +140 (*c* 0.1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (m, 1H), 7.37 – 7.29 (m, 2H), 7.25 – 7.13 (m, 2H), 7.10 (s, 1H), 6.97 (d, J = 3.7 Hz, 2H), 6.90 – 6.84 (m, 2H), 6.83 (s, 1H), 6.78 (s, 1H), 6.73 (s, 1H), 6.51 (s, 1H), 3.83 (s, 3H), 2.40 (dd, J = 12.5, 10.7 Hz, 2H), 2.33 (s, 3H), 2.13 – 2.00 (m, 5H), 1.53 (s, 3H), 1.52 (s, 3H), 1.33 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 153.3, 152.7, 148.8, 143.1, 141.6, 138.7, 138.1, 137.3, 135.6, 129.4, 128.0, 127.0, 125.0, 122.7, 121.6, 121.4, 119.5, 119.1, 117.9, 112.9, 55.6, 54.9, 54.3, 41.9, 41.4, 31.3, 29.1, 20.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 119.28 ; IR (film) γ = 2959, 2916, 2860, 2361, 2335, 2241, 1607, 1579, 1512, 1480, 1450, 1412, 1360, 1319, 1306,

1248, 1227, 1175cm^{-1}; HRMS (EI, GC-TOF) m/z: [M$^+$] Calcd for $C_{38}H_{39}O_4P$ 590.2586, found 590.2592.

*(E)-2,4,4,7,7,9-Hexamethyl-12-(2-(4-(trifluoromethyl)styryl)phenoxy)-4,5,6,7-tetrahydrodiindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocine [(R)-**8c**]*. 241 mg, 77% yield ; white solid, mp 68-70 ^{o}C; $[\alpha]_D^{20}$ = +254 (*c* 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.67 (d, J = 7.5 Hz, 1H), 7.56 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 7.33 – 7.22 (m, 2H), 7.18 – 7.10 (m, 2H), 7.03 (d, J = 16.5 Hz, 1H), 6.84 (s, 1H), 6.76 (s, 1H), 6.72 (s, 1H), 6.46 (s, 1H), 2.40 (t, J = 12.9 Hz, 2H), 2.34 (s, 3H), 2.14 – 1.99 (m, 5H), 1.53 (s, 3H), 1.53 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 152.8, 149.3, 143.0, 141.6, 140.0, 138.7, 138.2, 137.3, 135.7, 128.1(q, J = 32 Hz), 126.9, 126.7, 125.7, 125.5, 124.4, 124.2, 123.2(q, J = 272 Hz), 122.7, 121.5, 119.7, 117.9, 55.6, 54.9, 41.9, 41.4, 31.3, 29.3, 29.1, 20.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 119.02; IR (film) γ = 2959, 2925, 2860, 1613, 1573, 1485, 1450, 1414, 1362, 1323, 1261, 1231, 1165 cm^{-1}; HRMS (EI, GC-TOF) m/z: [M$^+$] Calcd for $C_{38}H_{36}F_3O_3P$ 628.2354, found 628.2354.

*(E)-2,4,4,7,7,9-Hexamethyl-12-(2-(2-(naphthalen-1-yl)vinyl)phenoxy)-4,5,6,7-tetrahydrodiindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocine [(R)-**8d**]*. 207 mg, 68% yield ; white solid, mp 67-69 ^{o}C; $[\alpha]_D^{20}$ = +217 (*c* 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 7.6 Hz, 1H), 7.82 (m, 4H), 7.60 (d, J = 7.1 Hz, 1H), 7.55 – 7.41 (m, 3H), 7.25 (d, J = 5.1 Hz, 2H), 7.20 – 7.10 (m, 2H), 6.82 (s, 1H), 6.72 (s, 1H), 6.70 (s, 1H), 6.52 (s, 1H), 2.37 (dd, J = 12.8, 3.6 Hz, 2H), 2.30 (s, 3H), 2.11 – 1.96 (m, 5H), 1.52 (s, 3H), 1.48 (s, 3H), 1.24 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 152.7, 149.1, 143.0, 141.6, 138.7, 138.1, 137.3, 135.5, 134.1, 132.6, 130.4, 128.0, 127.6, 127.5, 126.9, 125.8, 125.6, 125.0, 124.7, 122.8, 121.5, 119.5, 119.1, 118.1, 117.9, 63.4, 55.5,54.9, 41.9, 41.3, 31.2, 29.3, 24.3, 20.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 119.12; IR (film) γ = 2959, 2916, 2860, 1609, 1575, 1510, 1482, 1450, 1414, 1360, 1319, 1308, 1287, 1259, 1231, 1223, 1186, 1165 cm^{-1}; HRMS (EI, GC-TOF) m/z: [M$^+$] Calcd for $C_{41}H_{39}O_3P$ 610.2637, found 610.2632.

*(E)-2,4,4,7,7,9-Hexamethyl-12-(2-(2-(naphthalen-2-yl)vinyl)phenoxy)-4,5,6,7-tetrahydrodiindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocine [(R)-**8e**]*. 222 mg, 73% yield ; white solid, mp 91-93 ^{o}C; $[\alpha]_D^{20}$ = +285 (*c* 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.86 – 7.71 (m, 5H), 7.59 (m, 1H), 7.51 – 7.40 (m, 2H), 7.30 – 7.19 (m, 4H), 7.18 – 7.07 (m, 1H), 6.83 (s, 1H), 6.78 (s, 1H), 6.75 (s, 1H), 6.54 (s, 1H), 2.41 (t, J = 12.9 Hz, 2H), 2.31 (s, 3H), 2.15 – 2.01 (m, 5H), 1.54 (s, 3H), 1.53 (s, 3H), 1.35 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 152.7, 149.0, 148.9, 143.1, 143.0, 141.6, 141.6, 138.7, 138.7, 138.2, 138.1, 137.3, 136.5, 135.6, 128.4, 127.7, 127.4, 127.4, 126.5, 125.6, 125.3, 122.7, 121.6, 121.4, 121.3, 119.6, 119.1, 117.9, 117.7, 55.6, 55.4, 54.9, 41.9, 41.4, 31.3, 31.2, 29.1, 29.1, 20.1, 20.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 119.17; IR (film) γ = 2963, 2920, 2860, 1613, 1596, 1570, 1478, 1450,

1414, 1362, 1319, 1308, 1289, 1259, 1229, 1201, 1182, 1162cm^{-1}; HRMS (EI, GC-TOF) m/z: [M^{+}] Calcd for $C_{41}H_{39}O_3P$ 610.2637, found 610.2642.

*(E)-12-(2-(2-([1,1'-Biphenyl]-4-yl)vinyl)phenoxy)-2,4,4,7,7,9-hexamethyl-4,5,6,7-tetrahydrodiindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocine [(R)-**8f**]*. 219 mg, 69% yield ; white solid, mp 78-80 ^{o}C; $[\alpha]_D^{20}$ = +114 (*c* 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.72 – 7.66 (m, 1H), 7.66 – 7.60 (m, 2H), 7.57 (d, J = 8.3 Hz, 2H), 7.45 (m, 4H), 7.35 (m, 1H), 7.28 – 7.19 (m, 2H), 7.18 – 7.02 (m, 3H), 6.83 (s, 1H), 6.79 (s, 1H), 6.74 (s, 1H), 6.52 (s, 1H), 2.40 (t, J = 12.2 Hz, 2H), 2.33 (s, 3H), 2.16 – 2.00 (m, 5H), 1.53 (s, 3H), 1.53 (s, 3H), 1.34 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 152.7, 149.0, 143.1, 141.6, 139.7, 139.2, 138.7, 138.2, 137.4, 135.6, 127.9, 127.4, 126.3, 126.1, 125.9, 125.3, 122.7, 121.6, 121.4,119.6, 119.1, 118.0, 117.8, 55.6, 54.9, 41.9, 41.4, 31.3, 29.3, 20.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 119.20; IR (film) γ = 2959, 2920, 2860, 1613, 1596, 1573, 1519, 1487, 1450, 1409, 1360, 1317, 1308, 1289, 1261, 1231, 1210, 1182, 1165 cm^{-1}; HRMS (EI, GC-TOF) m/z: [M^{+}] Calcd for $C_{43}H_{41}O_3P$ 636.2793, found 636.2796.

General Procedure for Asymmetric Arylation of *N*-Tosylarylimines. Under a nitrogen atmosphere, Rh(acac)$(C_2H_4)_2$ (0.6 mg, 1.5 μmol), and **8e** (0.9 mg, 1.5 μmol) were dissolved in toluene (0.5 mL) in a dry schlenk tube. The mixture was stirred at room temperature for 1 h.Then, aldimine **9** (0.05 mmol), $ArB(OH)_2$ (0.1 mmol), KF (0.2 mmol) and water (0.5 mL) were added sequentially and the reaction mixture was stirred at 35 ^{o}C for 20 h. The mixture was cooled to room temperature and concentrated under reduced pressure, and then it was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1/8) to afford the corresponding product **11**.

*(R)-N-((4-Chlorophenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (**11a**).*[10d] 16 mg, 85% yield; white solid; mp 122-124 °C; 99% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 93/7, 0.8 mL/min, 230 nm), t_R (minor) 21.899 min, t_R (major) 30.665 min; $[\alpha]_D^{20}$ = +28.5 (*c* 0.23, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.3 Hz, 2H), 7.21 (m, 3H), 7.16 (m, 4H), 7.09 – 7.01 (m, 4H), 5.53 (d, J = 7.1 Hz, 1H), 5.18-5.16 (m, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 140.1, 139.0, 137.2, 133.4, 129.4, 128.8, 128.7, 128.6, 127.9, 127.3, 127.2, 60.8, 21.5; IR (film) γ = 3271, 3063, 3031, 2923, 2871, 2255, 1911, 1806, 1598, 1491 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M-H]$^{-}$ Calcd for $C_{20}H_{17}ClNO_2S$ 370.0669, found 370.0663.

*(S)-N-((4-Chlorophenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (**11a'**).*[10d] 14 mg, 75% yield; white solid; mp 121-123 °C; 99% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 93/7, 0.8 mL/min, 230 nm), t_R (major) 21.236 min, t_R (minor) 31.081 min;$[\alpha]_D^{20}$ = -91.7 (*c* 0.07, CH_2Cl_2).

*(R)-N-((4-Bromophenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (**11b**).*[10d] 17 mg, 82% yield; white solid; mp 115-117 °C; 98% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 80/20, 0.6 mL/min, 230 nm), t_R (minor) 13.757 min, t_R (major) 18.635 min; $[\alpha]_D^{20}$ = +32.7 (*c* 0.28, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.25 – 7.19 (m, 3H), 7.15 (d, J = 8.1 Hz, 2H), 7.08 – 7.02 (m, 2H), 7.00 (d, J = 8.4 Hz, 2H), 5.51 (d, J = 7.1 Hz, 1H), 5.19 (d, J = 7.1 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 160.9, 143.4, 140.32, 137.3, 136.3, 129.4, 129.2, 129.1, 128.7, 127.8, 127.3, 127.2, 115.5, 115.3, 60.7, 21.5; IR (film) γ = 3269, 3058, 3028, 2925, 2865, 1890, 1601, 1506, 1491 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{18}BrNO_2SNa$ 438.0140, found 438.0144.

*(S)-N-((4-Bromophenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (**11b'**).*[10d] 15 mg, 72% yield; white solid; mp 115-117 °C; 99% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 80/20, 0.6 mL/min, 230nm), t_R (major) 13.402 min, t_R (minor) 18.244 min; $[\alpha]_D^{20}$ = -128.8 (*c* 0.07, CH_2Cl_2).

*(R)-N-((4-Fluorophenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (**11c**).*[10f] 14 mg, 81% yield; white solid; mp 116-117 °C; 98% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 85/15, 0.8 mL/min, 230 nm), t_R (minor) 11.156 min, t_R (major) 13.678 min; $[\alpha]_D^{20}$ = -70.1 (*c* 0.05, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.3 Hz, 2H), 7.22-7.20 (m, 3H), 7.15 (d, J = 8.1 Hz, 2H), 7.10-7.05 (m, 4H), 6.91-6.87 (m, 2H), 5.55 (d, J = 7.1 Hz, 1H), 5.20 (d, J = 7.0 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 143.1, 140.7, 137.4, 132.8, 129.3, 128.6, 128.5, 127.5, 127.3, 127.2, 113.9, 60.8, 55.3, 21.5; IR (film): γ = 3276, 3062, 3030, 3004, 2954, 2930, 2836, 1610, 1586, 1512, 1495 cm^{-1}; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{18}FNO_2SNa$ 378.0940, found 378.0948.

*(S)-N-((4-Fluorophenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (**11c'**).*[10c] 11 mg, 65% yield; white solid; mp 117-118°C; 98% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 85/15, 0.8 mL/min, 230 nm), t_R (major) 10.973 min, t_R (minor) 13.86 min; $[\alpha]_D^{20}$ = +86.7 (*c* 0.04, CH_2Cl_2).

*(R)-4-Methyl-N-(phenyl(4-(trifluoromethyl)phenyl)methyl)benzenesulfonamide (**11d**).*[10b] 17 mg, 83% yield; white solid; mp 124-125°C; 96% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 85/15, 0.8 mL/min, 230 nm), t_R (minor) 10.902 min, t_R (major) 16.783 min; $[\alpha]_D^{20}$ = -32.4 (*c* 0.23, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.29 – 7.20 (m, 5H), 7.12 (d, J = 8.0 Hz, 2H), 7.05 (m, 2H), 5.61 (d, J = 7.2 Hz, 1H), 5.42 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 143.6, 139.7, 137.0, 129.7(q, J = 32 Hz), 129.4, 128.9, 128.1, 127.8, 127.3, 127.2, 125.4(q, J = 4 Hz), 61.0, 21.4; IR (film) γ = 3273, 3065, 3033, 2927, 2872, 1620, 1599, 1494, 1452, 1429, 1326, 1291, 1162, 1124 cm^{-1}; HRMS (ESI-TOF)*m/z*: $[M-H]^-$ Calcd for $C_{21}H_{17}F_3NO_2S$ 404.0932, found 404.0938.

*(S)-4-Methyl-N-(phenyl(4-(trifluoromethyl)phenyl)methyl)benzenesulfonamide (**11d'**).*[10b] 15 mg, 73% yield; white solid; mp 123-124 °C; 98% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 85/15, 0.8 mL/min, 230 nm), t_R (major) 11.049 min, t_R (minor) 17.464 min; $[\alpha]_D^{20}$ = +147.1 (*c* 0.05, CH_2Cl_2).

*(R)-4-Methyl-N-(phenyl(p-tolyl)methyl)benzenesulfonamide (**11e**).*[10f] 13 mg, 77% yield; white solid; mp 115-116 °C; 97% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 85/15, 0.8 mL/min, 230 nm), t_R (minor) 9.782 min, t_R (major) 13.220 min; $[\alpha]_D^{20}$ = +40.5 (*c* 0.32, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.23 – 7.17 (m, 3H), 7.13 (d, J = 8.0 Hz, 2H), 7.12 – 7.08 (m, 2H), 7.01 (d, J = 8.1 Hz, 2H), 6.97 (d, J = 8.1 Hz, 2H), 5.52 (d, J = 7.0 Hz, 1H), 5.08 (d, J = 7.0 Hz, 1H), 2.38 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 140.7, 137.6, 137.4, 129.3, 129.2, 128.5, 127.5, 127.3, 127.3, 127.2, 61.1, 21.5, 21.0; IR (film) γ= 3264, 3085, 3059, 3030, 2951, 2922, 2863, 1599, 1512, 1493, 1448, 1433 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M-H]^-$ Calcd for $C_{21}H_{20}NO_2S$ 350.1215, found 350.1220.

*(S)-4-Methyl-N-(phenyl(p-tolyl)methyl)benzenesulfonamide (**11e'**).* 11 mg, 62% yield; white solid; mp 116-117 °C; 95% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 85/15, 0.8 mL/min, 230 nm), t_R (major) 9.797 min, t_R (minor) 13.419 min; $[\alpha]_D^{20}$ = -314 (*c* 0.04, CH_2Cl_2).

*(R)-N-((4-Methoxyphenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (**11f**).*[10d] 13 mg, 72% yield; white solid; mp 127-129 °C; 99% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 85/15, 0.8 mL/min, 230 nm), t_R (minor) 14.027 min, t_R (major) 21.505 min; $[\alpha]_D^{20}$ = +19.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.56 (d, J = 8.3 Hz, 2H), 7.21-7.19 (m, 3H), 7.17 – 7.07 (m, 4H), 7.02 – 6.96 (m, 2H), 6.77 – 6.70 (m, 2H), 5.51 (d, J = 7.0 Hz, 1H), 5.10 (d, J = 6.9 Hz, 1H), 3.75 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 140.2, 137.2, 135.5, 134.0, 130.4, 129.3, 128.9, 128.6, 127.6, 127.5, 127.2, 126.6, 126.1, 125.7, 125.1, 123.4, 58.5, 21.5; IR (film) γ= 3251, 3041, 2922, 2853, 1597, 1507, 1493 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{21}NO_3SNa$ 390.1140, found 390.1142.

*(S)-N-((4-Methoxyphenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (**11f'**).*[10d] 11 mg, 61% yield; white solid; mp 127-128°C; 96% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 85/15, 0.8 mL/min, 230 nm), t_R (major) 13.811 min, t_R (minor) 21.782 min; $[\alpha]_D^{20}$ = -62.7 (*c* 0.27, CH_2Cl_2).

*(R)-N-((2-Chlorophenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (**11g**).*[10d] 15 mg, 82% yield; white solid; mp 165-167 °C; 99% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min, 230 nm), t_R (minor) 23.301 min, t_R (major) 26.716 min; $[\alpha]_D^{20}$ = -21.7 (*c* 0.56, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2H), 7.35-7.32(m, 1H), 7.25-7.19 (m, 4H), 7.18-7.12 (m, 4H), 7.08-7.06 (m, 2H), 5.91 (d, J = 7.2 Hz, 1H), 5.35 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 143.4, 139.3, 137.5, 137.0, 132.8, 129.9, 129.4, 129.3, 128.8, 128.7, 127.8, 127.3, 127.2, 127.0, 58.6, 21.5; IR (film) γ = 3321, 3063, 3030, 2974, 2924, 1596, 1489, 1471 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M-H]^-$ Calcd for $C_{20}H_{17}ClNO_2S$ 370.0669, found 370.0670.

(R)-N-((2-Bromophenyl)(phenyl)methyl)-4-methylbenzenesulfonamide ***(11h)****.*[10c] 16 mg, 77% yield; white solid; mp 168-171°C; 98% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min, 230 nm), t_R (minor) 24.922 min, t_R (major) 27.547 min; $[\alpha]_D^{20}$ = -25.7 (*c* 0.52, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 7.9 Hz, 1H), 7.37-7.35 (m, 1H), 7.25-7.14 (m, 6H), 7.10-7.03 (m, 3H), 5.91 (d, J = 6.9 Hz, 1H), 5.30 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 139.3, 139.0, 136.9, 133.2, 129.6, 129.5, 129.1, 128.7, 127.9, 127.6, 127.4, 127.3, 123.1, 60.6, 21.5; IR (film) γ = 3306, 3063, 3029, 2974, 2924, 2897, 1597, 1494, 1470, 1454 cm^{-1}; HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{20}H_{17}BrNO_2S$ 414.0164, found 414.0164.

(R)-4-Methyl-N-(phenyl(o-tolyl)methyl)benzenesulfonamide ***(11i)****.*[10c] 13 mg, 74% yield; white solid; mp 134-136 °C; 98% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 85/15, 0.8 mL/min, 230nm), t_R (major) 8.178 min, t_R (minor) 10.338 min; $[\alpha]_D^{20}$ = -130.1 (*c* 0.07, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 2H), 7.22-7.17 (m, 3H), 7.16-7.09 (m, 4H), 7.07-7.05 (m, 4H), 5.79 (d, J = 6.9 Hz, 1H), 5.03 (d, J = 6.9 Hz, 1H), 2.37 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 140.0, 138.2, 137.4, 135.5, 130.7, 129.3, 128.6, 127.6, 127.5, 127.2, 127.1, 126.2, 58.1, 21.5, 19.4; IR (film) γ = 3280, 3062, 3028, 2954, 2923, 2869, 1599, 1494 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M-H]^-$ Calcd for $C_{21}H_{20}NO_2S$ 350.1215, found 350.1218.

(R)-N-((2-Methoxyphenyl)(phenyl)methyl)-4-methylbenzenesulfonamide ***(11j)****.*[10c] 13 mg, 72% yield; white solid; mp 124-126 °C; 99% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 90/10, 0.8 mL/min, 230nm), t_R (major) 14.384 min, t_R (minor) 17.569 min; $[\alpha]_D^{20}$ = +216.8 (*c* 0.07, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.3 Hz, 2H), 7.24 – 7.12 (m, 6H), 7.04 (d, J = 8.1 Hz, 2H), 6.98 – 6.96 (m, 1H), 6.82 – 6.74 (m, 1H), 6.67 (d, J = 8.2 Hz, 1H), 5.81 (d, J = 9.2 Hz, 1H), 5.65 (d, J = 9.2 Hz, 1H), 3.59 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 142.3, 140.1, 137.0, 129.1, 128.5, 128.4, 127.6, 127.1, 126.6, 126.5, 126.3, 120.1, 110.6, 58.5, 54.7, 20.9; IR (film) γ = 3286, 3063, 3029, 2939, 2837, 1600, 1494 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M-H]^-$ Calcd for $C_{21}H_{20}NO_3S$ 366.1164, found 366.1168.

(R)-4-Methyl-N-(naphthalen-1-yl(phenyl)methyl)benzenesulfonamide ***(11k)****.*[10d] 15 mg, 75% yield; white solid; mp 174-176 °C; 98% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 85/15, 0.8 mL/min, 230 nm), t_R (major) 20.424 min, t_R (minor) 25.569 min; $[\alpha]_D^{20}$ = +40.2 (*c* 0.24, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, J = 7.3 Hz, 2H), 7.73 (d, J = 7.9 Hz, 1H), 7.51 (d, J = 8.2 Hz, 2H),

7.47 – 7.35 (m, 2H), 7.32 – 7.22 (m, 2H), 7.22 – 7.17 (m, 3H), 7.17 – 7.11 (m, 2H), 7.06 (d, J = 8.2 Hz, 2H), 6.31 (d, J = 7.1 Hz, 1H), 5.17 (d, J = 7.0 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 140.0, 139.5, 137.1, 131.6, 129.4, 129.1, 128.8, 127.9, 127.3, 127.2, 121.6, 60.8, 21.5; IR (film) γ = 3273, 3062, 3030, 2922, 2870, 1598, 1487 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{21}NO_2SNa$ 410.1191, found 410.1185.

*(R)-4-Methyl-N-(phenyl(thiophen-2-yl)methyl)benzenesulfonamide (**11l**).*[10d] 11 mg, 65% yield; white solid; mp 131-132°C; 97% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 90/10, 0.6 mL/min, 230 nm), t_R (minor) 20.599 min, t_R (major) 30.087 min; $[\alpha]_D^{20}$ = +4.7 (*c* 0.23, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.58 (d, J = 8.3 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.20 – 7.10 (m, 5H), 6.84 – 6.82 (m, 1H), 6.67 (d, J = 3.5 Hz, 1H), 5.79 (d, J = 7.4 Hz, 1H), 5.23 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.3, 140.1, 137.3, 129.4, 128.6, 128.0, 127.2, 127.1, 126.8, 126.2, 125.8, 57.4, 21.5; IR (film) γ = 3264, 3065, 2968, 2924, 2872, 1654, 1597 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M-H]^-$ Calcd for $C_{18}H_{16}NO_2S_2$ 342.0623, found 342.0621.

*(R)-4-(((4-Chlorophenyl)(phenyl)methyl)amino)-3-nitrobenzenesulfonic acid (**11m**).*[10f] 8 mg, 37% yield; white solid; mp 158-160°C; 97% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 80/20, 0.8 mL/min, 230nm), t_R (minor) 17.390 min, t_R (major) 31.308 min; $[\alpha]_D^{20}$ = -7.4 (*c* 0.27, CH_2Cl_2); ^{1}H NMR (600 MHz, acetone-d_6) δ 8.20 (d, J = 7.0 Hz, 2H), 8.00 (s, 1H), 7.92-7.90 (m, 3H), 7.26-7.21 (m, 8H), 5.78 (d, J = 9.2 Hz, 1H); ^{13}C NMR (151 MHz, acetone-d_6) δ 150.6, 148.1, 141.3, 140.8, 133.7, 130.1, 129.4, 129.3, 128.5, 128.4, 124.9, 79.3, 61.8; IR (film): γ = 3269, 1526, 1352, 1164, 1091, 843, 738, 554 cm^{-1}; HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{19}H_{14}ClN_2O_5S$ 401.0363, found 401.0378.

General Procedure for Asymmetric Addition of Cyclic Aldimines. Under a nitrogen atmosphere, $[RhCl(C_2H_4)_2]_2$ (0.3 mg, 0.75 μmol), and **8e** (0.9 mg, 1.5 μmol) were dissolved in toluene (0.5 mL) in a dry schlenk tube. The mixture was stirred at room temperature for 1 h. Then, aldimine **12** (0.05 mmol), $ArB(OH)_2$ (0.1 mmol), KF (0.2 mmol) and water (0.5 mL) were added sequentially and the reaction mixture was stirred at RT for 20 h. The mixture was cooled to room temperature and concentrated under reduced pressure, and then it was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1/8) to afford the corresponding product **13**.

*(S)-4-Phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13a**).*[8a] 13 mg, 90% yield; white solid; mp 133-134 °C; 98% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 90/10, 0.8 mL/min, 220 nm), t_R (minor) 14.606 min, t_R (major) 16.956 min; $[\alpha]_D^{20}$ = -25.7 (*c* 0.10, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.42 (m, 3H), 7.38 – 7.28 (m, 3H), 7.14 – 7.04 (m, 2H), 6.82 (d, J = 7.8 Hz, 1H), 5.90 (s, 1H), 4.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 137.9, 129.7, 129.6, 129.5, 128.8,

128.6, 125.3, 122.0, 118.9, 62.0; IR (film) γ = 3286, 3071, 3032, 2963, 2920, 2847, 1613, 1575, 1480, 1448, 1414, 1362, 1261, 1205, 1162 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M-H]^-$ Calcd for $C_{13}H_{10}NO_3S$ 260.0381, found 260.0397.

*(S)-4-(4-Chlorophenyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide(**13b**).*[8a] 14 mg, 93% yield; white solid; mp 140-142 °C; 96% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 90/10, 0.8 mL/min, 220 nm), t_R (minor) 12.521 min, t_R (major) 19.43 min; $[\alpha]_D^{20}$ = -16.7 (*c* 0.10, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.38 – 7.27 (m, 3H), 7.13 – 7.09 (m, 1H), 7.07 – 7.05 (m, 1H), 6.81 (d, J = 7.8 Hz, 1H), 5.88 (d, J = 5.0 Hz, 1H), 4.86 (d, J = 3.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 136.3, 135.6, 130.3, 130.0, 129.7, 128.4, 125.4, 121.5, 119.0, 61.3; IR (film): γ= 3273, 3067, 2925, 2843, 1616, 1596, 1577, 1491, 1448, 1422, 1369, 1293, 1246, 1201, 1171 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M-H]^-$ Calcd for $C_{13}H_9ClNO_3S$ 293.9992, found 293.9997.

*(S) -4-(4-Bromophenyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide(**13c**).*[8a] 15 mg, 91% yield; white solid; mp 128-130 °C; 95% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 90/10, 0.8 mL/min, 220 nm), t_R (minor) 13.038 min, t_R (major) 20.373 min; $[\alpha]_D^{20}$ = -22.4 (*c* 0.10, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.35 (td, J = 7.9, 0.8 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.11 (ddd, J = 9.1, 6.8, 1.0 Hz, 2H), 6.81 (d, J = 7.8 Hz, 1H), 5.88 (s, 1H), 4.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 135.8, 131.6, 129.5, 129.0, 127.4, 124.3, 122.8, 120.3, 118.0, 60.3; IR (film) γ = 3277, 2959, 2916, 2847, 1579, 1487, 1450, 1424, 1373, 1293, 1259, 1242, 1201, 1169 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M-H]^-$ Calcd for $C_{13}H_9BrNO_3S$ 337.9487, found 337.9493.

*(S)-4-(4-Fluorophenyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13d**).*[11e] 12 mg, 87% yield; white solid; mp 147-148 °C; 96% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 90/10, 0.8 mL/min, 220 nm), t_R (minor) 12.066 min, t_R (major) 15.876 min; $[\alpha]_D^{20}$ = -27.7 (*c* 0.10, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 3H), 7.17 – 7.09 (m, 3H), 7.07 – 7.05 (m, 1H), 6.81 (d, J = 7.8 Hz, 1H), 5.90 (d, J = 8.5 Hz, 1H), 4.84 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 162.0, 151.4, 133.8, 133.7, 130.8, 130.7, 129.9, 128.5, 125.4, 121.7, 119.0, 116.6, 116.4, 61.2; IR (film): γ= 3273, 3080, 2925, 1607, 1579, 1508, 1482, 1450, 1424, 1369, 1296, 1229, 1201, 1169 cm^{-1}; HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{13}H_9FNO_3S$ 278.0287, found 278.0276.

*(S)-4-(4-(Trifluoromethyl)phenyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13e**).*[8a] 14mg, 85% yield; white solid; mp 122-124°C; 98% ee; HPLC analysis: Chiralpak IF-3 (hexane/i-PrOH = 95/5, 0.6 mL/min, 220 nm), t_R (major) 8.37 min, t_R (minor) 9.522 min; $[\alpha]_D^{20}$ = -24.2 (*c* 0.10, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.30 (m, 1H), 7.12 – 7.00 (m, 2H), 6.73 (d, J = 7.7 Hz, 1H), 5.91 (s, 1H), 4.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 140.6, 130.8(q, J = 33 Hz), 129.1, 128.4, 127.3, 125.4(q, J = 4 Hz), 124.5, 122.6(q, J = 272 Hz), 120.0,

118.1, 60.3; IR (film) γ = 3273, 2962, 2925, 2856, 1620, 1581, 1482, 1454, 1424, 1371, 1326, 1259, 1205, 1171 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M-H]^-$ Calcd for $C_{14}H_9F_3NO_3S$ 328.0255, found 328.0268.

*(S)-4-(p-Tolyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13f**).*[8a] 13 mg, 93% yield; white solid; mp 118-119°C; 97% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 90/10, 0.8 mL/min, 220 nm), t_R (minor) 14.451 min, t_R (major) 16.061 min; $[\alpha]_D^{20}$ = -21.4 (*c* 0.10, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 1H), 7.27 – 7.17 (m, 4H), 7.10 – 7.04 (m, 2H), 6.82 (d, J = 7.8 Hz, 1H), 5.86 (s, 1H), 4.74 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 138.6, 133.9, 129.1, 128.6, 127.6, 127.6, 124.2, 121.2, 117.8, 60.7, 20.2; IR (film): γ = 3269, 3024, 2963, 2920, 2856, 2357, 2331, 1613, 1579, 1510, 1480, 1450, 1418, 1364, 1291, 1259, 1201, 1169 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M-H]^-$ Calcd for $C_{14}H_{12}NO_3S$ 274.0538, found 274.0540.

*(S)-4-(4-Methoxyphenyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13g**).*[11e] 13 mg, 91% yield; white solid; mp 112-114 °C; 97% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 90/10, 0.8 mL/min, 220 nm), t_R (minor) 24.675 min, t_R (major) 41.741 min; $[\alpha]_D^{20}$ = -21.7 (*c* 0.10, CH_2Cl_2);^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 1H), 7.29 – 7.21 (m, 2H), 7.11 – 7.05 (m, 2H), 6.97 – 6.90 (m, 2H), 6.84 (d, J = 7.8 Hz, 1H), 5.86 (s, 1H), 4.69 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 151.5, 130.1, 129.9, 129.7, 128.6, 125.2, 122.3, 118.8, 114.8, 61.5, 55.4; IR (film) γ = 3273, 2968, 2929, 2834, 1611, 1579, 1512, 1482, 1448, 1418, 1369, 1306, 1259, 1199, 1169 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M-H]^-$ Calcd for $C_{14}H_{12}NO_4S$ 290.0487, found 290.0483.

*(S)-4-([1,1'-Biphenyl]-4-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13h**).*[8a] 15 mg, 87% yield; white solid; mp 171-173°C; 97% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 95/5, 0.6 mL/min, 220 nm), t_R (minor) 31.744 min, t_R (major) 38.366 min; $[\alpha]_D^{20}$ = -15.2 (*c* 0.10, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.2 Hz, 2H), 7.62 – 7.57 (m, 2H), 7.48 – 7.44 (m, 2H), 7.43 – 7.37 (m, 3H), 7.36 – 7.32 (m, 1H), 7.13 – 7.07 (m, 2H), 6.88 (d, J = 7.7 Hz, 1H), 5.94 (s, 1H), 4.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ151.5, 142.6, 140.0, 136.7, 129.8, 129.3, 129.0, 128.6, 128.1, 127.9, 127.2, 125.3, 122.0, 118.9, 61.7; IR (film) γ = 3273, 3062, 3028, 2959, 2925, 2847, 1577, 1482, 1450, 1422, 1373, 1291, 1265, 1244, 1203, 1171 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M-H]^-$ Calcd for $C_{19}H_{14}NO_3S$ 336.0694, found 336.0705.

*(S)-4-(Benzo[d][1,3]dioxol-5-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13i**).*[8a] 13 mg, 88% yield; white solid; mp 123-125°C; 97% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 95/5, 0.6 mL/min, 220 nm), t_R (major) 47.45 min, t_R (minor) 50.304 min; $[\alpha]_D^{20}$ = -18.7 (*c* 0.10, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 1H), 7.16 – 7.07 (m, 1H), 7.05 (d, J = 8.3 Hz, 1H), 6.88 – 6.82 (m, 3H), 6.73 (d, J = 0.9 Hz, 1H), 6.00 (s, 2H), 5.81 (d, J = 8.3 Hz, 1H), 4.78 (d, J = 8.3 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 148.6, 148.5, 131.5, 129.8, 128.6, 125.3, 123.0, 122.0, 118.9, 108.8, 108.7, 101.7, 61.8; IR (film) γ = 3273, 3084, 2899, 2774, 1611, 1575, 1504, 1489, 1450, 1424, 1364, 1287, 1250, 1233, 1199, 1167 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M-H]$^-$ Calcd for $C_{14}H_{10}NO_5S$ 304.0280, found 304.0286.

*(R)-4-(Thiophen-3-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13j**).*[11e] 11 mg, 85% yield; white solid; mp 124-126 °C; 99% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 90/10, 0.8 mL/min, 220 nm), t_R (minor) 17.529 min, t_R (major) 18.087 min; $[\alpha]_D^{20}$ = -17.9 (*c* 0.23, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.37 – 7.30 (m, 1H), 7.14 – 7.10 (m, 1H), 7.07 – 6.99 (m, 2H), 6.93 (d, J = 7.8 Hz, 1H), 6.04 (d, J = 7.8 Hz, 1H), 4.84 (d, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 138.0, 129.9, 128.2, 127.9, 126.6, 125.9, 125.3, 121.7, 118.9, 56.9; IR (film) γ = 3264, 3105, 3054, 1577, 1478, 1448, 1420, 1392, 1371, 1287, 1276, 1257, 1205, 1188, 1167 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M-H]$^-$ Calcd for $C_{11}H_8NO_3S_2$ 265.9946, found 365.9943.

*(S)-6-Fluoro-4-phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13k**).* 12 mg, 89% yield; white solid; mp 154-157 °C; 96% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 90/10, 0.8 mL/min, 220 nm), t_R (minor) 6.522 min, t_R (major) 7.006 min; $[\alpha]_D^{20}$ = -58.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.51 – 7.43 (m, 3H), 7.53 – 7.33 (m, 2H), 7.08– 7.04(m, 2H), 6.55 – 6.52 (m, 1H), 5.87 (s, 1H), 4.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 157.9, 147.4, 147.4, 137.1, 129.9, 129.7, 128.7, 123.8, 123.7, 120.5, 120.4, 117.0, 116.8, 115.1, 114.9, 61.9, 61.9; IR (film) γ = 3276, 3067, 3028, 2925, 2852, 1626, 1592, 1482, 1454, 1420, 1373, 1343, 1291, 1255, 1235, 1207, 1160 cm^{-1}; HRMS(ESI-TOF) *m/z*: [M-H]$^-$ Calcd for $C_{13}H_9FNO_3S$ 278.0287, found 278.0292.

*(S)-6-Chloro-4-phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13l**).*[11e] 14 mg, 92% yield; white solid; mp 161-163 °C; 97% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 90/10, 0.8 mL/min, 220 nm), t_R (minor) 10.209 min, t_R (major) 10.952 min; $[\alpha]_D^{20}$ = -67.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 3H), 7.39 – 7.27 (m, 3H), 7.02 (d, J = 8.8 Hz, 1H), 6.80 (d, J = 1.8 Hz, 1H), 5.85 (s, 1H), 4.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 136.0, 129.5, 128.9, 128.7, 127.7, 127.3, 122.6, 119.3, 60.7; IR (film) γ = 3273, 3080, 3058, 3028, 2959, 2925, 2852, 1605, 1500, 1474, 1454, 1424, 1366, 1261, 1203, 1184, 1167 cm^{-1}; HRMS(ESI-TOF) *m/z*: [M-H]$^-$ Calcd for $C_{13}H_9ClNO_3S$ 293.9992, found 293.9994.

*(S)-6-Bromo-4-phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13m**).*[11e] 16 mg, 91% yield; white solid; mp 152-154 °C; 98% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 90/10, 0.8 mL/min, 220 nm), t_R (minor) 10.422 min, t_R (major) 11.065 min; $[\alpha]_D^{20}$ = -78.8 (*c* 1.0, CH_2Cl_2);; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 4H), 7.39 – 7.30 (m, 2H), 6.97 – 6.94 (m, 2H), 5.86 (s, 1H),

4.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 136.0, 131.8, 130.2, 128.9, 128.7, 127.7, 123.0, 119.6, 117.0, 60.6. IR (film) γ = 3277, 3032, 2959, 2920, 1472, 1454, 1422, 1396, 1366, 1336, 1302, 1261, 1244, 1199, 1184, 1165 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M-H]$^-$ Calcd for $C_{13}H_9BrNO_3S$ 337.9487, found 337.9486.

*(S)-6-Methyl-4-phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13n**).*[11e] 13 mg, 94% yield; white solid; mp 171-173°C; 98% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 90/10, 0.8 mL/min, 220 nm), t_R (minor) 17.436 min, t_R (major) 19.206 min; $[\alpha]_D^{20}$ = -32.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 3H), 7.35 – 7.32 (m, 2H), 7.19 – 7.08 (m, 1H), 6.97 (d, J = 8.4 Hz, 1H), 6.60 (s, 1H), 5.86 (s, 1H), 4.65 (s, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 138.1, 135.1, 130.4, 129.6, 129.5, 128.8, 128.6, 121.5, 118.6, 62.0, 20.7; IR (film) γ =3273, 3062, 3024, 2959, 2925, 2852, 1489, 1457, 1416, 1364, 1291, 1257, 1195, 1177 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M-H]$^-$ Calcd for $C_{14}H_{12}NO_3S$ 274.0538, found 274.0530.

*(S)-6-Methoxy-4-phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13o**).*[11e] 13 mg, 92% yield; white solid; mp 148-150 °C; 97% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 90/10, 0.8 mL/min, 220 nm), t_R (minor) 11.844 min, t_R (major) 12.627 min; $[\alpha]_D^{20}$ = -60.1 (*c* 1.0, CH_2Cl_2);; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.46 – 7.39 (m, 3H), 7.38 – 7.29 (m, 2H), 6.99 (d, J = 9.0 Hz, 1H), 6.86 – 6.83 (m, 1H), 6.29 – 6.28 (m, 1H), 5.84 (s, 1H), 4.79 (s, 1H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ156.5, 145.3, 137.8, 129.6, 129.5, 128.8, 122.8, 119.8, 115.2, 113.3, 62.1, 55.7; IR (film) γ = 3265, 3067, 3028, 3002, 2963, 2933, 2834, 2353, 2335, 1611, 1581, 1491, 1422, 1366, 1281, 1250, 1171 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M-H]$^-$ Calcd for $C_{14}H_{12}NO_4S$ 290.0487, found 290.0492.

*(S)-6-(tert-Butyl)-4-phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13p**).* 14 mg, 86% yield; white solid; mp 161-162 °C; 97% ee; HPLC analysis: Chiralpak IC-3 (hexane/i-PrOH = 90/10, 0.8 mL/min, 220 nm), t_R (minor) 7.494 min, t_R (major) 8.43 min; $[\alpha]_D^{20}$ = -67.2 (*c* 1.0, CH_2Cl_2);; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 3H), 7.38 – 7.31 (m, 3H), 6.99 (d, J = 8.7 Hz, 1H), 6.79 (d, J = 1.5 Hz, 1H), 5.89 (d, J = 8.4 Hz, 1H), 4.75 (d, J = 8.3 Hz, 1H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 148.3, 138.0, 129.5, 129.4, 128.8, 126.8, 125.4, 121.0, 118.3, 62.2, 34.4, 31.2; IR (film) γ = 3269, 3062, 3032, 2963, 2864, 1495, 1457, 1418, 1364, 1293, 1272, 1248, 1199, 1177 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M-H]$^-$ Calcd for $C_{17}H_{18}NO_3S$ 316.1008, found 316.1005.

*(S,E)-4-Styryl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**13q**).*[11g] 13 mg, 87% yield; colorless oil; 95% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm), t_R (minor) 21.236 min, t_R (major) 24.565 min; $[\alpha]_D^{20}$ = +5.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.47 – 7.42 (m, 2H), 7.41 – 7.30 (m, 4H), 7.25 – 7.15 (m, 2H), 7.06 (d, J = 8.2 Hz, 1H), 6.87

(d, J = 15.7 Hz, 1H), 6.29 (dd, J = 15.7, 8.6 Hz, 1H), 5.47 (t, J = 8.4 Hz, 1H), 4.83 (d, J = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 136.9, 135.1, 129.9, 129.0, 128.9, 127.8, 127.0, 125.4, 124.0, 121.2, 118.9, 77.2, 60.1; IR (film) γ = 3277, 3019, 2959, 2916, 2847, 1650, 1575, 1478, 1450, 1418, 1369, 1287, 1266, 1197, 1169 cm^{-1}; HRMS(ESI-TOF) *m/z*: [M-H]$^-$ Calcd for $C_{15}H_{12}NO_3S$ 286.0538, found 286.0538.

*(S,E)-6-Fluoro-4-styryl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**11r**).*[11h] 13 mg, 84% yield; colorless oil; 95% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm), t_R (minor) 20.171 min, t_R (major) 25.788 min; $[\alpha]_D^{20}$ = +6.3 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 2H), 7.43 – 7.32 (m, 3H), 7.11 – 7.00 (m, 2H), 6.97 – 6.93 (m, 1H), 6.88 (d, J = 15.7 Hz, 1H), 6.26 (dd, J = 15.7, 8.6 Hz, 1H), 5.43 (t, J = 8.4 Hz, 1H), 4.80 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 158.1, 146.8, 137.5, 134.9, 129.2, 128.9, 127.0, 123.2, 122.9, 122.8, 120.5, 120.5, 117.1, 116.8, 114.5, 114.3, 77.2, 60.0;IR (film) γ = 3273, 3080, 3058, 3024, 2959, 2920, 2847, 1654, 1626, 1592, 1577, 1482, 1420, 1373, 1285, 1255, 1203, 1158 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M-H]$^-$ Calcd for $C_{15}H_{11}FNO_3S$ 304.0444, found 304.0446.

*(S,E)-6-Chloro-4-styryl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide(**11s**).*[11h] 15 mg, 91% yield; colorless oil; 95% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm), t_R (minor) 23.051 min, t_R (major) 25.281 min; $[\alpha]_D^{20}$ = +5.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.43 – 7.32 (m, 3H), 7.34 – 7.28 (m, 1H), 7.19 (d, J = 2.2 Hz, 1H), 7.00 – 6.97 (m, 1H), 6.88 (d, J = 15.7 Hz, 1H), 6.28 – 6.22 (m, 1H), 5.41 (s, 1H), 4.90 (s, 1H);^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 136.6, 133.8, 129.6, 129.0, 128.1, 127.9, 126.6, 126.0, 122.0, 121.8, 119.3, 76.3, 58.9, 28.7; IR (film) γ = 3275, 3082, 3062, 3028, 2961, 2920, 2852, 1652, 1624, 1594, 1575, 1481, 1423, 1375, 1281, 1261, 1207, 1156 cm^{-1}; HRMS(ESI-TOF) *m/z*: [M-H]$^-$ Calcd for $C_{15}H_{11}ClNO_3S$ 320.0148, found 320.0146.

*(S,E)-6-Methyl-4-styryl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**11t**).*[7a] 13 mg, 87% yield; colorless oil; 94% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm), t_R (minor) 19.93 min, t_R (major) 22.348 min; $[\alpha]_D^{20}$ = +7.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.43 – 7.31 (m, 3H), 7.14 – 7.11 (m, 1H), 6.99 (d, J = 4.1 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 15.7 Hz, 1H), 6.28 (dd, J = 15.7, 8.6 Hz, 1H), 5.41 (t, J = 8.4 Hz, 1H), 4.76 (d, J = 8.2 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 136.7, 135.3, 135.2, 130.5, 128.9, 128.9, 128.0, 127.0, 124.2, 120.7, 118.6, 77.2, 60.1, 20.8; IR (film) γ = 3277, 3084, 3062, 3028, 2963, 2920, 2856, 1489, 1450, 1422, 1369, 1287, 1261, 1207, 1177 cm^{-1}; HRMS(ESI-TOF) *m/z*: [M-H]$^-$ Calcd for $C_{16}H_{14}NO_3S$ 300.0695, found 300.0687.

*(S,E)-6-Methoxy-4-styryl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**11u**).*[11g] 14 mg, 85% yield; colorless oil; 93% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 80/20, 0.8 mL/min, 254nm), t_R (minor) 27.465 min, t_R (minor) 33.804 min; $[\alpha]_D^{20}$ = +9.1 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.41 – 7.31 (m, 3H), 6.98 (d, J = 9.0 Hz, 1H), 6.87 (d, J = 2.9 Hz, 1H), 6.86 – 6.80 (m, 1H), 6.69 (d, J = 2.5 Hz, 1H), 6.28 (dd, J = 15.7, 8.6 Hz, 1H), 5.40 (t, J = 8.3 Hz, 1H), 4.75 (d, J = 8.2 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 144.7, 136.9, 135.1, 129.0, 128.9, 127.0, 124.0, 122.0, 119.8, 115.1, 112.6, 77.2, 60.2, 55.8; IR (film) γ = 3277, 3084, 3054, 3028, 2963, 2916, 2834, 1611, 1489, 1461, 1422, 1373, 1280, 1248, 1201, 1167 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M-H]^-$ Calcd for $C_{16}H_{14}NO_4S$ 316.0644, found 316.0638.

ASSOCIATED CONTENT

Supporting Information

This Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Details of the theory calculations; Copies of NMR and HPLC traces; crystallographic data for **2a** and **2b** (CIF).

Accession Codes

CCDC 1841337 (**2a**) and CCDC 1841338 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interests.

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