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The Proton of Alcohols as Hydrogen Source in Diboron-Mediated Nickel-Catalyzed Asymmetric Transfer Hydrogenation of Cyclic *N*-Sulfonyl Imines

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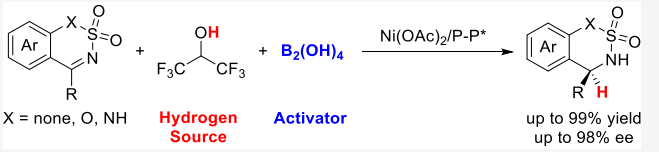
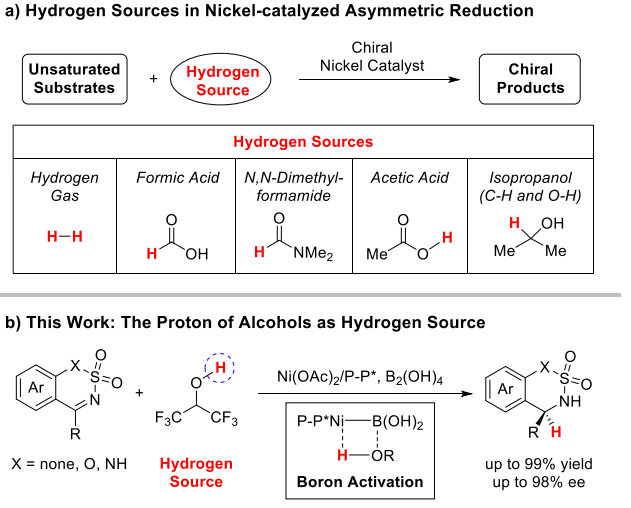
ABSTRACT: The proton of alcohols as the sole hydrogen source in diboron-mediated nickel-catalyzed asymmetric transfer hydrogenation of cyclic *N*-sulfonyl imines has been developed, providing the chiral cyclic sulfamidates in excellent enantioselectivities. The mechanistic investigations suggested that the proton of alcohols could be activated by tetrahydroxydiboron to form active nickel hydride species.



Transition-metal catalyzed asymmetric reduction is one of the most efficient approaches for the construction of optically active compounds and plays a crucial role in synthetic chemistry.[1] In comparison with the well-exploited noble transition-metal-catalyzed asymmetric reduction,[1] earth-abundant transition-metals such as manganese, iron, cobalt, copper, and nickel have recently attracted considerable attention in asymmetric reduction attributing to their relative abundance and lower cost.[2] Particularly, nickel-catalyzed asymmetric reduction has been extensively explored and a series of hydrogen sources have been developed (Scheme 1a).[2d−h,3−13] In 2008, Hamada and co-workers identified nickel-catalyzed asymmetric hydrogenation of α-amino-β-keto ester hydrochlorides using hydrogen gas as the hydrogen source.[3] Since this pioneering work, impressive progress has been achieved in nickel-catalyzed asymmetric hydrogenation of enamides, alkenes, ketones, imines and oximes with hydrogen gas by Chirik,[4] Zhang,[5] Zhang,[6] Deng,[7] Huang,[8] and our group.[9] Zhou and co-workers disclosed nickel-catalyzed asymmetric transfer hydrogenation of olefins, enamides and hydrazones, and asymmetric reductive amination of ketones using formic acid as hydrogen source and suggested that the formate decarboxylation on nickel catalyst formed active nickel-hydride species.[10] Asymmetric transfer hydrogenation of α,β-unsaturated esters with *N*,*N*-dimethylformamide as a hydrogen source catalyzed by nickel catalyst was also realized by Zhou's group.[11] Subsequently, an elegant nickel-catalyzed asymmetric umpolung hydrogenation of alkenes was reported utilizing acetic acid as the hydrogen source and indium powder as the terminal electron donor.[12] Additionally, nickel-catalyzed asymmetric transfer hydrogenation of imines with C−H and O−H of isopropanol as hydrogen source has been established.[13] Isopropanol underwent β-hydride elimination with a chiral nickel catalyst to *in situ* generate chiral nickel hydride species, which was applied in asymmetric transfer hydrogenation. Despite different types of hydrogen sources having been developed in nickel-catalyzed asymmetric reduction, the exploration of efficient and easy-handling hydrogen sources is still highly desirable.

The utilization of protons as a hydrogen source in reduction has gained considerable attention in recent years.[14] In contrast, asymmetric reduction with protons as a hydrogen source is less

Scheme 1. Hydrogen Sources in Nickel-Catalyzed Asymmetric Reduction



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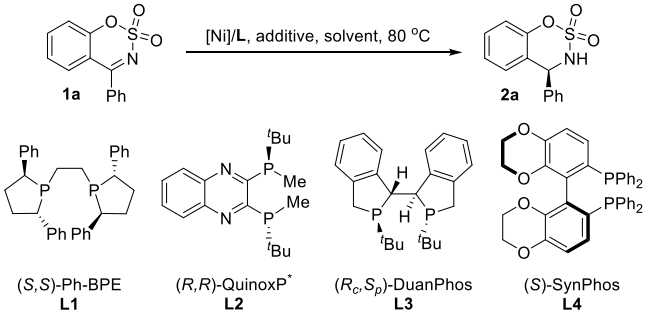
exploited.[12,15] In continuation of our efforts to utilize protons as a hydrogen source in transition-metal-catalyzed asymmetric reduction, we previously disclosed diboron-mediated palladium-catalyzed asymmetric transfer hydrogenation of 1,3-diketones and aromatic indoles using the proton of alcohols as the sole hydrogen source.[15b] Due to the advantages of earth-abundant nickel catalysts, we envisioned the proton of alcohols as the hydrogen source to directly form chiral nickel-hydride species via tetrahydroxydiboron activation in the presence of chiral nickel catalysts and their application in nickel-catalyzed asymmetric reduction. Herein, we report the proton of alcohols as a hydrogen source in diboron-mediated nickel-catalyzed asymmetric transfer hydrogenation of cyclic *N*-sulfonyl imines, delivering a variety of chiral cyclic sulfamidates in excellent enantioselectivities (Scheme 1b).

At the outset, six-membered cyclic *N*-sulfonyl imine **1a** was chosen as a model substrate to explore the proton of alcohols as the hydrogen source in diboron-mediated nickel-catalyzed asymmetric transfer hydrogenation. Pleasingly, the reaction was conducted successfully to deliver the desired product **2a** in 94% yield and 93% ee using the proton of hexafluoroisopropanol as the hydrogen source and tetrahydroxydiboron as the activator in the catalysis of $Ni(OAc)_2$/(*S*,*S*)-Ph-BPE (Table 1, entry 1). Using $Ni(COD)_2$ instead of nickel(II) precursors, the product **2a** was obtained in 39% yield and 83% ee (entry 4). Without nickel precursor, the reaction shut down (entry 5). To further improve the yield and enantioselectivity, some commercially available chiral bisphosphine ligands were examined. The more electron-rich bisphosphine ligands exhibited better results than the less donating bisphosphine ligands. (*R*,*R*)-QuinoxP* **L2** was the most efficient ligand in overall terms (entries 1, and 6−8). Subsequently, a series of alcoholic solvents were screened. Poor yield and enantioselectivity were observed in trifluoroethanol (entry 9). Finally, the influence of the diboron reagents was also explored. Trace product was achieved with bis(pinacolato)diboron ($B_2(pin)_2$) (entry 13). The yield diminished to 72% with 2.0 equiv of $B_2(OH)_4$ (entry 14). No reaction proceeded in the absence of $B_2(OH)_4$ (entry 15). When the reaction temperature was decreased, the yield was reduced to 28% (entry 16).

With optimal conditions, we turned our attention toward evaluating the scope of this transformation and the results were depicted in Scheme 2. For six-membered cyclic *N*-sulfonyl imines bearing an aryl group **1a**-**1h**, the electronic and steric properties of the substituent on the aromatic ring had only marginal influence on the yields and enantioselectivities. The imines with a methyl group at the 8-, 7-, 6- or 5-position of benzo ring were also suitable reaction substrates, giving the desired products **2i**-**2l** with good to excellent enantioselectivities. The asymmetric reduction of six-membered cyclic *N*-sulfonyl imines bearing an alkyl group **1l**-**1o** proceeded smoothly to provide the cyclic sulfamidate products **2l**-**2o** in high ee values. In the case of six-membered cyclic substrate containing a nitrogen atom, excellent yield and enantioselectivity were observed. When this nickel-catalyzed reduction of **1a** was conducted at 1.0 mmol scale under standard conditions, the yield and enantioselectivity could be retained.

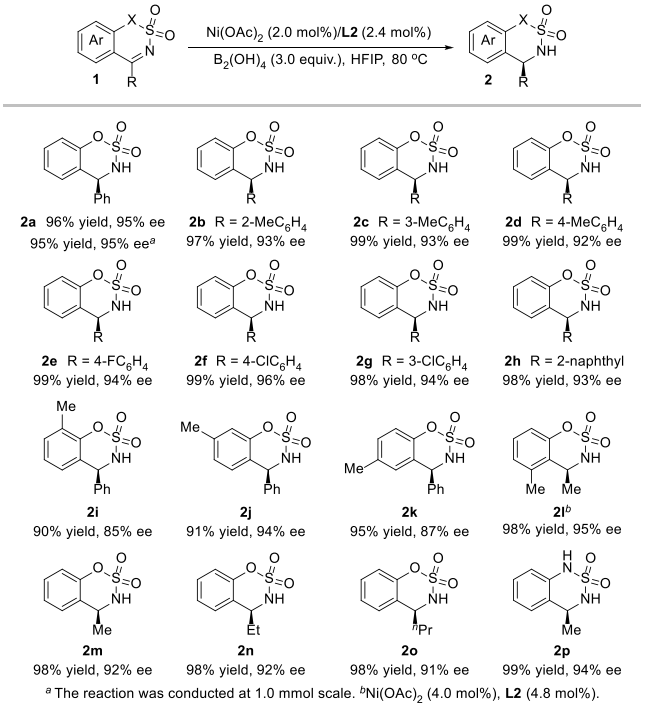
Table 1. Optimization of Reaction Conditions



entry[a]	[Ni]	L	solvent	additive	yield (%)[b]	ee (%)[c]
1	$Ni(OAc)_2$	**L1**	HFIP	$B_2(OH)_4$	94	93
2	$Ni(OTf)_2$	**L1**	HFIP	$B_2(OH)_4$	17	83
3	$NiCl_2$ (DME)	**L1**	HFIP	$B_2(OH)_4$	27	79
4	$Ni(COD)_2$	**L1**	HFIP	$B_2(OH)_4$	39	83
5	–	**L1**	HFIP	$B_2(OH)_4$	trace	–
6	$Ni(OAc)_2$	**L2**	HFIP	$B_2(OH)_4$	97	95
7	$Ni(OAc)_2$	**L3**	HFIP	$B_2(OH)_4$	36	62
8	$Ni(OAc)_2$	**L4**	HFIP	$B_2(OH)_4$	13	19
9	$Ni(OAc)_2$	**L2**	TFE	$B_2(OH)_4$	13	6
10	$Ni(OAc)_2$	**L2**	^{i}PrOH	$B_2(OH)_4$	trace	–
11	$Ni(OAc)_2$	**L2**	MeOH	$B_2(OH)_4$	trace	–
12[d]	$Ni(OAc)_2$	**L2**	MeOH	$B_2(OH)_4$	trace	–
13	$Ni(OAc)_2$	**L2**	HFIP	$B_2(pin)_2$	trace	–
14[e]	$Ni(OAc)_2$	**L2**	HFIP	$B_2(OH)_4$	72	94
15	$Ni(OAc)_2$	**L2**	HFIP	–	trace	–
16[f]	$Ni(OAc)_2$	**L2**	HFIP	$B_2(OH)_4$	28	94

[a]Reaction conditions: **1a** (0.20 mmol), [Ni] (2.0 mol %), **L** (2.4 mol %), additive (0.60 mmol), solvent (3.0 mL), 80 °C, 24 h. [b]Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [c]Determined by chiral HPLC. [d]Trifluoroacetic acid (0.50 mmol) was added. [e]$B_2(OH)_4$ (0.40 mmol) was used. HFIP = Hexafluoroisopropanol. [f]The reaction temperature was decreased to 60 °C. TFE = Trifluoroethanol. [g]PrOH = Isopropanol. MeOH = Methanol.

Scheme 2. Substrate Scope: Six-Membered Cyclic *N*-Sulfonyl Imines



[a]The reaction was conducted at 1.0 mmol scale. [b]$Ni(OAc)_2$ (4.0 mol%), **L2** (4.8 mol%).

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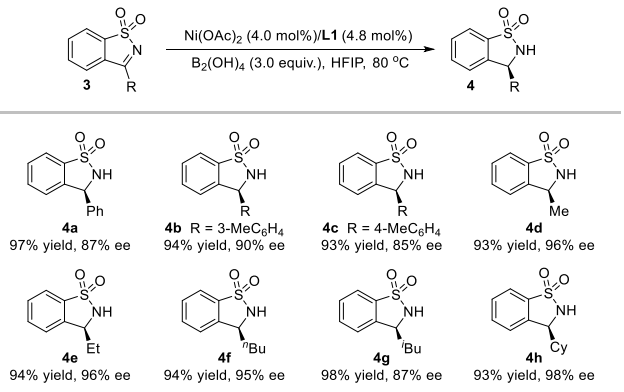
Additionally, five-membered cyclic *N*-sulfonyl imines also conducted the transfer hydrogenation successfully to give the target chiral cyclic sulfamidates with high yields and good to excellent enantioselectivities using (*S*,*S*)-Ph-BPE **L1** as ligand (Scheme 3). For aryl substituted imines, the reductive

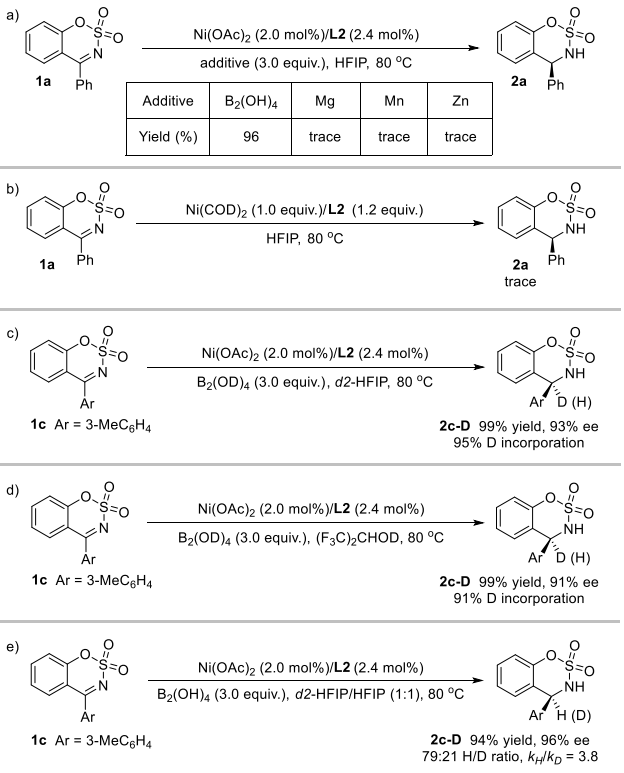
Scheme 3. Substrate Scope: Five-Membered Cyclic *N*-Sulfonyl Imines



products **4a**-**4c** were obtained in 85%−90% ee. Notably, alkyl substituted imines were favorable reaction substrates, providing the desired products in satisfying results. In the case of cyclohexyl substituted imine, the transfer hydrogenation gave the corresponding sulfamidate **4h** with 98% ee.

In order to gain insight into the mechanism of this asymmetric transfer hydrogenation, a series of experiments were conducted. When the additive tetrahydroxydiboron was replaced by reducing reagents including magnesium, manganese and zinc powder, trace product was observed (Scheme 4a), suggesting that the active nickel hydride species might not

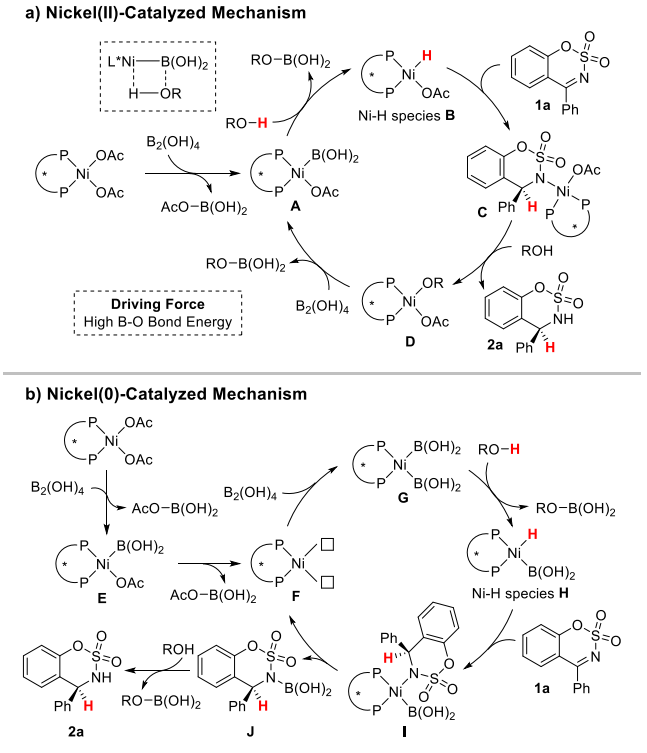
Scheme 4. Mechanistic Study Experiments



be formed via the reaction of the proton of hexafluoroisopropanol with nickel(0) catalyst.[12] To further identify it, another control experiment was performed. When 1.0 equiv of $Ni(COD)_2$ and 1.2 equiv of **L2** were utilized in the absence of tetrahydroxydiboron, the reaction shut down (Scheme 4b). This result could exclude the generation of nickel hydride species from the oxidative addition of nickel(0) catalyst with the O−H bond of alcohols. The product **2c-D** with 95% deuterium incorporation was acquired when the reaction of **1c** proceeded with prepared tetradeuteroxydiboron as activator and *d2*-HFIP as solvent under standard conditions (Scheme 4c). Using $(F_3C)_2CHOD$ as solvent, 91% deuterium incorporation was observed (Scheme 4d). These results indicated that the proton of alcohols was the sole hydrogen source for this asymmetric transfer hydrogenation. A kinetic isotope effect was explored by applying an equimolar mixture of *d2*-HFIP and HFIP, and the deuterium isotope effect of 3.8 was observed (Scheme 4e), demonstrating that hydrogen transfer might be involved in the rate-determining step.

Based on the aforementioned experimental results and previous report,[14c,15b] and considering that both nickel(II) precursor and nickel(0) precursor could facilitate this asymmetric transfer hydrogenation, two plausible mechanisms for the proton of alcohols as hydrogen source in asymmetric transfer hydrogenation were proposed and nickel(II)-catalyzed cycle might be the main catalytic process. One probable mechanism is the nickel(II)-catalyzed mechanism (Scheme 5a). Initial transmetalation between nickel(II) catalyst and

Scheme 5. Proposed Two Possible Mechanisms



tetrahydroxydiboron afforded the Ni−B intermediate **A**. Alcohols coordinated to the boron atom of intermediate **A** and hydrogen transferred from alcohols to nickel via σ-bond metathesis, generating chiral nickel hydride active species **B** through the four-membered transition state due to the high B−O bond energy. Subsequently, the enantioseletive migratory

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insertion of intermediate **B** into imine **1a** formed intermediate **C**. Finally, the protolysis of intermediate **C** delivered the desired chiral sulfamidate product **2a** and nickel(II) **D**, which underwent transmetalation with tetrahydroxydiboron to regenerate Ni−B species **A** and completed the catalytic cycle. The other possible mechanism is the nickel(0)-catalyzed mechanism (Scheme 5b). First, nickel(0) species **F** was produced by the reduction of the nickel(II) catalyst with tetrahydroxydiboron via transmetalation and reductive elimination.[16] The oxidative addition of the B−B bond in tetrahydroxydiboron to nickel(0) species **F** delivered Ni−B intermediate **G**. The boron atom of Ni−B intermediate could coordinate to the oxygen atom of alcohols, facilitating hydrogen transfer to furnish chiral nickel hydride species **H**. Subsequently, imine **1a** underwent migratory insertion with chiral nickel hydride species to give intermediate **I**. Finally, the reductive elimination of intermediate **I** occurred to regenerate nickel(0) species **F** and intermediate **J**, which could release the desired product **2a** via the protolysis with alcohol. It is worthy to note that the protolysis of intermediate **I** with alcohol could also deliver the desired product **2a** and nickel(II) species which could regenerate nickel(0) species via reductive elimination and complete the catalytic cycle.

In conclusion, the proton of alcohols as a hydrogen source in the diboron-mediated nickel-catalyzed asymmetric transfer hydrogenation of cyclic *N*-sulfonyl imines has been successfully developed. A myriad of chiral six-membered and five-membered cyclic sulfamidates could be conveniently synthesized in excellent yields and enantioselectivities. The mechanistic investigations suggested that the proton of alcohols could be activated by tetrahydroxydiboron to form active nickel hydride species and hydrogen transfer would be the rate-determining step. Further explorations on the application of the proton as hydrogen source in earth-abundant transition-metal-catalyzed asymmetric reduction are currently underway in our laboratory.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. ^{1}H NMR, ^{13}C{^{1}H} NMR and ^{19}F{^{1}H} NMR spectra were recorded at room temperature in $CDCl_3$ on a 400 MHz instrument with tetramethylsilane (TMS) as the internal standard. Enantiomeric excess was determined by HPLC analysis, using the chiral column described below in detail. Optical rotations were measured by polarimeter. Flash column chromatography was performed on silica gel (200−300 mesh). The heat source for all heating reactions is the oil bath. High-resolution mass spectrometry (HRMS) was measured on an electrospray ionization (ESI) apparatus using the time-of-flight (TOF) mass spectrometry. All reactions were monitored by TLC analysis.

Materials. The six-membered cyclic *N*-sulfonyl imines **1a-1g**, **1j-1k**, **1m-1p** and five-membered cyclic *N*-sulfonyl imines **3a-3h** can be synthesized according to the known literature procedures.[6a,17,18] Commercially available reagents and solvents were used throughout without further purification.

Procedures for Synthesis of Cyclic *N*-Sulfonyl Imines 1h, 1i and 1l. Formic acid (1.150 g, 0.94 mL, 25 mmol, 2.5 equiv) was added dropwise to chlorosulfonyl isocyanate (3.538 g, 2.2 mL, 25 mmol, 2.5 equiv) at 0 °C. The reaction mixture was stirred at room temperature for 1 h, giving sulfamoyl chloride as a white solid. Ketones (10 mmol) in *N*,*N*-dimethylacetamide (40 mL) was added to the synthesized sulfamoyl chloride in *N*,*N*-dimethylacetamide (10 mL) at 0 °C. Then the reaction mixture was stirred at room temperature for 10 min. Sodium hydride (1.000 g, 60 wt % in mineral oil, 25 mmol, 2.5 equiv) was added in several portions within 1 h at room temperature. Then, the mixture was heated at 50 °C overnight. After cooling to room temperature, water (30 mL) was added. The solution was extracted with ethyl acetate (40 mL × 3). Then the combined organic layer was washed with saturated brine (30 mL × 3) and dried by anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The crude residue was purified by flash column chromatography on silica gel using hexanes/ethyl acetate as eluent and recrystallized from dichloromethane and hexane to give *N*-sulfonyl imines.

*4-(Naphthalen-2-yl)benzo[e][1,2,3]oxathiazine 2,2-dioxide (**1h**).* 1.391 g, 45% yield, white solid, new compound, mp = 160−161 °C, R_f = 0.20 (hexanes/ethyl acetate 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31−8.22 (m, 1H), 8.04−7.90 (m, 3H), 7.87−7.75 (m, 2H), 7.74−7.70 (m, 1H), 7.69−7.56 (m, 2H), 7.46−7.34 (m, 2H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) δ 176.4, 154.7, 137.0, 135.4, 132.6, 132.4, 132.0, 130.9, 129.4, 129.1, 129.0, 128.0, 127.5, 126.0, 125.9, 119.5, 116.8. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{12}NO_3S$ 310.0532, found 310.0529.

*8-Methyl-4-phenylbenzo[e][1,2,3]oxathiazine 2,2-dioxide (**1i**).* 1.284 g, 47% yield, white solid, new compound, mp = 146−147 °C, R_f = 0.25 (hexanes/ethyl acetate 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79−7.71 (m, 2H), 7.70−7.63 (m, 1H), 7.63−7.58 (m, 1H), 7.57−7.51 (m, 2H), 7.49−7.41 (m, 1H), 7.31−7.21 (m, 1H), 2.46 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.9, 153.0, 138.5, 134.0, 133.2, 130.7, 129.5, 129.2, 128.9, 125.1, 116.5, 15.2. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{14}H_{12}NO_3S$ 274.0532, found 274.0534.

*4,8-Dimethylbenzo[e][1,2,3]oxathiazine 2,2-dioxide (**1l**).* 747 mg, 54% yield, white solid, new compound, mp = 118−119 °C, R_f = 0.30 (hexanes/ethyl acetate 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 2.78 (s, 3H), 2.70 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 179.7, 154.1, 139.7, 135.7, 130.3, 118.5, 117.4, 29.4, 24.1. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_9H_{10}NO_3S$212.0376, found 212.0360.

General Procedure for Nickel-Catalyzed Asymmetric Transfer Hydrogenation of Six-Membered Imines. The metal precursor nickel diacetate (0.7 mg, 0.0040 mmol, 2.0 mol %), chiral ligand (*R*,*R*)-QuinoxP* (1.6 mg, 0.0048 mmol, 2.4 mol %), six-membered cyclic *N*-sulfonyl imines **1** (0.20 mmol, 1.0 equiv) and tetrahydroxydiboron (53.8 mg, 0.60 mmol, 3.0 equiv) were added to the sealed tube. The sealed tube was taken into a glovebox filled with nitrogen, and hexafluoroisopropanol (3.0 mL) was added. The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the volatiles were removed under the reduced pressure. The crude residue was purified by silica gel column chromatography using hexanes/ethyl acetate or dichloromethane as eluent to give the chiral reductive products **2**. The enantiomeric excesses were determined by chiral HPLC. The racemates **2** could be coveniently prepared through reduction with sodium borohydride in methanol.

*(S)-(−)-4-Phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2a**).* 50.3 mg, 96% yield, white solid, known compound,[6a] R_f = 0.50 (hexanes/dichloromethane 2/1), 95% ee, $[\alpha]^{20}_D$ = −25.44 (*c* 1.01, CH_2Cl_2), [lit.:[6a] $[\alpha]^{20}_D$ = −27.5 (*c* 0.60, CH_2Cl_2) for 97% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.41 (m, 3H), 7.38−7.29 (m, 3H), 7.16−6.97 (m, 2H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.90 (d, *J* = 8.7 Hz, 1H), 4.82 (d, *J* = 8.7 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.6, 137.9, 129.8, 129.7, 129.6, 128.9, 128.7, 125.4, 122.1, 119.0, 62.1. HPLC (Chirapak AD-H column, *n*-Hexane/*i*-PrOH = 90/10, flow = 0.8 mL/min, l = 210 nm, 30 °C) t_R = 16.5 min (minor), 17.5 min (major).

*(−)-4-(o-Tolyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2b**).* 53.3 mg, 97% yield, white solid, known compound,[18] R_f = 0.60 (hexanes/dichloromethane 1/2), 93% ee, $[\alpha]^{20}_D$ = −69.13 (*c* 1.04, $CHCl_3$), [lit.:[18] $[\alpha]^{20}_D$ = +23.8 (*c* 1.01, $CHCl_3$) for 39% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.27 (m, 3H), 7.25−7.18 (m, 1H), 7.15−7.02 (m, 3H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.18 (d, *J* = 8.9 Hz, 1H), 4.65 (d, *J* = 8.9 Hz, 1H), 2.48 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.9, 137.6, 136.1, 131.5, 129.7, 129.6, 128.7, 128.4,

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127.2, 125.4, 122.1, 119.1, 58.6, 19.3. HPLC (Chirapak IC column, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.7 mL/min, l = 210 nm, 30 °C) t_R = 10.0 min (minor), 11.6 min (major).

*(−)-4-(m-Tolyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2c**).* 54.7 mg, 99% yield, colorless oil, known compound,[19] R_f = 0.55 (hexanes/dichloromethane 1/2), 93% ee, $[\alpha]^{20}_D$ = −14.40 (*c* 1.09, CH_2Cl_2), [lit.:[19] $[\alpha]^{20}_D$ = +12.1 (*c* 0.31, CH_2Cl_2) for 99% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.28 (m, 2H), 7.26−7.21 (m, 1H), 7.18−7.01 (m, 4H), 6.83 (d, *J* = 7.5 Hz, 1H), 5.85 (d, *J* = 8.7 Hz, 1H), 4.85−4.65 (m, 1H), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.6, 139.5, 137.9, 130.5, 129.8, 129.51, 129.46, 128.7, 125.9, 125.4, 122.3, 118.9, 62.1, 21.5. HPLC (Chirapak IC column, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.7 mL/min, l = 210 nm, 30 °C) t_R = 12.4 min (minor), 14.0 min (major).

*(−)-4-(p-Tolyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2d**).* 50.3 mg, 99% yield, white solid, known compound,[19] R_f = 0.50 (hexanes/ethyl acetate 10/1), 92% ee, $[\alpha]^{20}_D$ = −16.51 (*c* 1.09, CH_2Cl_2), [lit.:[19] $[\alpha]^{20}_D$ = +18.7 (*c* 0.12, CH_2Cl_2) for 93% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.28 (m, 1H), 7.26−7.19 (m, 4H), 7.14−6.95 (m, 2H), 6.82 (d, *J* = 8.3 Hz, 1H), 5.86 (d, *J* = 8.6 Hz, 1H), 4.75 (d, *J* = 8.6 Hz, 1H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.6, 139.8, 135.0, 130.2, 129.8, 128.8, 128.7, 125.3, 122.4, 118.9, 61.9, 21.4. HPLC (Chiracel AD-H column, *n*-Hexane/*i*-PrOH = 85/15, flow = 0.7 mL/min, l = 210 nm, 30 °C) t_R = 15.4 min (major), 17.0 min (minor).

*(−)-4-(4-Fluorophenyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2e**).* 55.4 mg, 99% yield, white solid, known compound,[20] R_f = 0.55 (hexanes/dichloromethane 2/1), 94% ee, $[\alpha]^{20}_D$ = −41.44 (*c* 1.11, CH_2Cl_2), [lit.:[20] $[\alpha]^{20}_D$ = −27.7 (*c* 0.10, CH_2Cl_2) for 96% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.29 (m, 3H), 7.19−7.09 (m, 3H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 5.90 (d, *J* = 8.6 Hz, 1H), 4.80 (d, *J* = 8.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J_{C-F} = 250.0 Hz), 151.6, 133.9 (d, J_{C-F} = 3.0 Hz), 130.9 (d, J_{C-F} = 8.3 Hz), 130.1, 128.6, 125.5, 121.8, 119.1, 116.7 (d, J_{C-F} = 22.0 Hz), 61.4. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ −111.06. HPLC (Chiracel IC column, *n*-Hexane/*i*-PrOH = 90/10, flow = 1.0 mL/min, l = 210 nm, 30 °C) t_R = 13.6 min (minor), 18.2 min (major).

*(−)-4-(4-Chlorophenyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2f**).* 58.3 mg, 99% yield, colorless oil, known compound,[20] R_f = 0.50 (hexanes/dichloromethane 1/2), 96% ee, $[\alpha]^{20}_D$ = −21.54 (*c* 1.17, CH_2Cl_2), [lit.:[20] $[\alpha]^{20}_D$ = −16.7 (*c* 0.10, CH_2Cl_2) for 96% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.38 (m, 2H), 7.38−7.27 (m, 3H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 5.87 (d, *J* = 8.0 Hz, 1H), 4.98 (d, *J* = 8.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.5, 136.3, 135.7, 130.4, 130.1, 129.8, 128.6, 125.5, 121.6, 119.0, 61.3. HPLC (Chirapak IC column, *n*-Hexane/*i*-PrOH = 70/30, flow = 0.7 mL/min, l = 210 nm, 30 °C) t_R = 8.2 (minor), 10.5 min (major).

*(−)-4-(3-Chlorophenyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2g**).* 58.2 mg, 98% yield, colorless oil, known compound,[21] R_f = 0.55 (hexanes/dichloromethane 1/2), 94% ee, $[\alpha]^{20}_D$ = −27.50 (*c* 1.16, CH_2Cl_2), [lit.:[21] $[\alpha]^{25}_D$ = −18.6 (*c* 0.86, CH_2Cl_2) for 98% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.30 (m, 4H), 7.27−7.22 (m, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.86 (d, *J* = 8.6 Hz, 1H), 4.90 (d, *J* = 8.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.5, 139.7, 135.3, 130.9, 130.1, 129.9, 129.1, 128.5, 127.2, 125.6, 121.3, 119.1, 61.4. HPLC (Chirapak IC column, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.8 mL/min, l = 210 nm, 30 °C) t_R = 10.8 min (major), 14.5 min (minor).

*(+)-4-(Naphthalen-2-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2h**).* 60.8 mg, 98% yield, colorless oil, known compound,[18] R_f = 0.60 (hexanes/ethyl acetate 5/1), 93% ee, $[\alpha]^{20}_D$ = +48.68 (*c* 1.22, $CHCl_3$), [lit.:[18] $[\alpha]^{25}_D$ = +46.5 (*c* 1.02, $CHCl_3$) for 98% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.80 (m, 4H), 7.65−7.50 (m, 2H), 7.42−7.30 (m, 2H), 7.16−7.00 (m, 2H), 6.90−6.78 (m, 1H), 6.06 (d, *J* = 8.5 Hz, 1H), 4.91 (d, *J* = 8.6 Hz, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 151.6, 135.0, 133.7, 133.3, 129.9, 129.8, 128.9, 128.8, 128.3, 128.0, 127.3, 127.1, 125.4, 125.3, 122.1, 119.0, 62.3. HPLC (Chirapak IC column, *n*-Hexane/*i*-PrOH = 80/20, flow = 1.0 mL/min, l = 230 nm, 30 °C) t_R = 10.7 min (minor), 17.8 min (major).

*(+)-8-Methyl-4-phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2i**).* 49.6 mg, 90% yield, white solid, known compound,[18] R_f = 0.55 (hexanes/ethyl acetate 5/1), 85% ee, $[\alpha]^{20}_D$ = +2.42 (*c* 0.99, $CHCl_3$), [lit.:[18] $[\alpha]^{25}_D$ = +2.28 (*c* 1.01, $CHCl_3$) for 98% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.39 (m, 3H), 7.38−7.29 (m, 2H), 7.17 (d, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 5.87 (d, *J* = 8.6 Hz, 1H), 4.89 (d, *J* = 8.6 Hz, 1H), 2.26 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.1, 138.2, 131.2, 129.6, 129.5, 128.9, 128.2, 126.2, 124.6, 121.9, 62.1, 15.6. HPLC (Chirapak AD-H column, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.8 mL/min, l = 210 nm, 30 °C) t_R = 7.4 min (major), 8.0 min (minor).

*(−)-7-Methyl-4-phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2j**).* 50.0 mg, 91% yield, white solid, known compound,[18] R_f = 0.70 (hexanes/ethyl acetate 5/1), 94% ee, $[\alpha]^{20}_D$ = −27.63 (*c* 0.93, $CHCl_3$), [lit.:[18] $[\alpha]^{25}_D$ = −29.4 (*c* 1.02, $CHCl_3$) for 95% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.39 (m, 3H), 7.38−7.29 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.86 (s, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 5.85 (d, *J* = 8.7 Hz, 1H), 4.79 (d, *J* = 8.7 Hz, 1H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.4, 140.4, 138.1, 129.6, 129.5, 128.9, 128.4, 126.3, 119.1, 119.0, 61.9, 21.1. HPLC (Chirapak AD-H column, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.8 mL/min, l = 210 nm, 30 °C) t_R = 10.0 min (minor), 14.1 min (major).

*(−)-6-Methyl-4-phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2k**).* 52.2 mg, 95% yield, white solid, known compound,[20] R_f = 0.65 (hexanes/ethyl acetate 5/1), 87% ee, $[\alpha]^{20}_D$ = −58.36 (*c* 1.04, CH_2Cl_2), [lit.:[20] $[\alpha]^{20}_D$ = −32.7 (*c* 1.0, CH_2Cl_2) for 98% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.41 (m, 3H), 7.39−7.30 (m, 2H), 7.12 (d, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.60 (s, 1H), 5.85 (d, *J* = 8.6 Hz, 1H), 4.78 (d, *J* = 8.6 Hz, 1H), 2.21 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.6, 138.1, 135.2, 130.5, 129.63, 129.56, 129.0, 128.8, 121.7, 118.7, 62.1, 20.9. HPLC (Chirapak AD-H column, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.8 mL/min, l = 210 nm, 30 °C) t_R = 9.3 min (minor), 10.5 min (major).

*(+)-4,5-Dimethyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2l**).* 41.9 mg, 98% yield, colorless oil, new compound, R_f = 0.65 (hexanes/ethyl acetate 5/1), 95% ee, $[\alpha]^{20}_D$ = +1.19 (*c*,0.84 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 5.05 (br s, 1H), 4.87−4.64 (m, 1H), 2.32 (s, 3H), 1.70 (*d*, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.2, 135.6, 128.9, 127.7, 123.3, 116.8, 52.4, 20.0, 19.1. HPLC (Chirapak IC column, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.8 mL/min, l = 210 nm, 30 °C) t_R = 11.2 min (minor), 12.8 min (major). HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_9H_{12}NO_3S$ 214.0532, found 214.0527.

*(−)-4-Methyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2m**).* 39.2 mg, 98% yield, pale yellow oil, known compound,[6a] R_f = 0.60 (hexanes/dichloromethane 1/1), 92% ee, $[\alpha]^{20}_D$ = −53.46 (*c*,0.78 CH_2Cl_2), [lit.:[6a] $[\alpha]^{20}_D$ = −57.3 (*c* 0.4, CH_2Cl_2) for 97% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.27 (m, 1H), 7.24−7.16 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.96−4.83 (m, 1H), 4.67 (d, *J* = 9.4 Hz, 1H), 1.71 (d, *J* = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.0, 129.6, 126.4, 125.6, 123.7, 118.8, 53.1, 20.2. HPLC (Chirapak AS-H column, *n*-Hexane/*i*-PrOH = 70/30, flow = 0.8 mL/min, l = 210 nm, 30 °C) t_R = 12.4 min (major), 14.8 min (minor).

*(−)-4-Ethyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2n**).* 41.8 mg, 98% yield, colorless oil, known compound,[22] R_f = 0.55 (hexanes/dichloromethane 1/1), 92% ee, $[\alpha]^{20}_D$ = −55.83 (*c* 0.84, $CHCl_3$), [lit.:[22] $[\alpha]^{20}_D$ = −82.2 (*c* 0.45, $CHCl_3$) for >99% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.27 (m, 1H), 7.25−7.14 (m, 2H), 6.97 (d, *J* = 8.1 Hz, 1H), 4.79−4.57 (m, 2H), 2.28−2.11 (m, 1H), 2.10−1.93 (m, 1H), 1.10 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.4, 129.5, 126.5, 125.5, 122.7, 118.9, 58.6, 27.0, 9.7. HPLC (Chirapak AD-H column, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.8 mL/min, l = 220 nm, 30 °C) t_R = 7.4 min (major), 8.2 min (minor).

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*(−)-4-Propyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (**2o**).* 44.5 mg, 98% yield, colorless oil, known compound,[5i] R_f = 0.60 (hexanes/dichloromethane 1/1), 91% ee, $[\alpha]^{20}_D$ = −70.00 (*c* 0.89, $CHCl_3$), [lit.[5i]: $[\alpha]^{20}_D$ = −77.6 (*c* 0.50, $CHCl_3$) for 98% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.25 (m, 1H), 7.24−7.11 (m, 2H), 7.02−6.87 (m, 1H), 4.85−4.57 (m, 2H), 2.18−1.86 (m, 2H), 1.67−1.39 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.3, 129.4, 126.4, 125.4, 123.0, 118.9, 57.1, 36.0, 18.5, 13.7. HPLC (Chirapak AD-H column, *n*-Hexane/*i*-PrOH = 90/10, flow = 0.8 mL/min, l = 210 nm, 30 °C) t_R = 11.4 min (major), 12.1 min (minor).

*(−)-4-Methyl-3,4-dihydro-1H-benzo[c][1,2,6]thiadiazine 2,2-dioxide (**2p**).* 39.2 mg, 99% yield, colorless oil, known compound,[6a] R_f = 0.70 (dichloromethane/ethyl acetate 50/1), 94% ee, $[\alpha]^{20}_D$ = −48.07 (*c* 0.78, CH_2Cl_2), [lit.:[6a] $[\alpha]^{20}_D$ = −46.0 (*c* 0.50, CH_2Cl_2) for 95% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.11 (m, 2H), 7.09−7.01 (m, 1H), 6.98 (br s, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 4.86−4.67 (m, 1H), 4.40 (d, *J* = 10.5 Hz, 1H), 1.66 (d, *J* = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 137.5, 128.8, 126.0, 124.7, 123.5, 118.3, 53.4, 19.6. HPLC (Chirapak AD-H column, *n*-Hexane/*i*-PrOH = 90/10, flow = 1.0 mL/min, l = 210 nm, 30 °C) t_R = 34.9 min (minor), 49.2 min (major).

General Procedure for Nickel-Catalyzed Asymmetric Transfer Hydrogenation of Five-Membered Imines. The metal precursor nickel diacetate (1.4 mg, 0.0080 mmol, 4.0 mol %), chiral ligand (*S*,*S*)-Ph-BPE (4.9 mg, 0.0096 mmol, 4.8 mol %), five-membered cyclic *N*-sulfonyl imines **3** (0.20 mmol, 1.0 equiv) and tetrahydroxydiboron (53.8 mg, 0.60 mmol, 3.0 equiv) were added to the sealed tube. The sealed tube was taken into a glovebox filled with nitrogen, and hexafluoroisopropanol (3.0 mL) was added. The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the volatiles were removed under the reduced pressure. The crude residue was purified by silica gel column chromatography using dichloromethane as eluent to give the chiral reductive products **4**. The enantiomeric excesses were determined by chiral HPLC. The racemates **4** could be coveniently prepared through reduction with sodium borohydride in methanol.

*(S)-(+)-3-Phenyl-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (**4a**).* 47.8 mg, 97% yield, white solid, known compound,[6a] R_f = 0.20 (dichloromethane), 87% ee, $[\alpha]^{20}_D$ = +82.08 (*c* 0.96, CH_2Cl_2), [lit.:[6a] $[\alpha]^{20}_D$ = +85.2 (*c* 0.50, CH_2Cl_2) for 90% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.74 (m, 1H), 7.62−7.49 (m, 2H), 7.45−7.29 (m, 5H), 7.18−7.06 (m, 1H), 5.72 (d, *J* = 4.1 Hz, 1H), 5.08 (d, *J* = 4.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 139.9, 138.8, 134.9, 133.5, 129.6, 129.4, 129.2, 127.7, 125.5, 121.3, 61.5. HPLC (Chiracel OJ-H column, *n*-Hexane/*i*-PrOH = 70/30, flow = 0.8 mL/min, l = 210 nm, 30 °C) t_R = 17.7 min (major), 19.2 min (minor).

*(+)-3-(m-Tolyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (**4b**).* 48.8 mg, 94% yield, white solid, known compound,[23] R_f = 0.35 (dichloromethane), 90% ee, $[\alpha]^{20}_D$ = +95.79 (*c* 0.98, $CHCl_3$), [lit.:[23] $[\alpha]^{20}_D$ = +100.27 (*c* 1.10, $CHCl_3$) for 97% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.77 (m, 1H), 7.62−7.48 (m, 2H), 7.30−7.24 (m, 1H), 7.23−7.07 (m, 4H), 5.67 (d, *J* = 4.1 Hz, 1H), 5.04 (d, *J* = 4.0 Hz, 1H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.0, 139.3, 138.7, 134.8, 133.4, 130.0, 129.6, 129.2, 128.2, 125.5, 124.8, 121.2, 61.5, 21.5. HPLC (Chiracel OJ-H column, *n*-Hexane/*i*-PrOH = 70/30, flow = 0.7 mL/min, l = 210 nm, 30 °C) t_R = 19.1 min (major), 21.5 min (minor).

*(+)-3-(p-Tolyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (**4c**).* 48.0 mg, 93% yield, white solid, known compound,[23] R_f = 0.50 (dichloromethane), 85% ee, $[\alpha]^{20}_D$ = +83.43 (*c* 0.96, CH_2Cl_2), [lit.:[23] $[\alpha]^{20}_D$ = +75.45 (*c* 1.10, $CHCl_3$) for 83% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.73 (m, 1H), 7.62−7.46 (m, 2H), 7.31−7.04 (m, 5H), 5.67 (d, *J* = 4.1 Hz, 1H), 5.05 (d, *J* = 4.1 Hz, 1H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.2, 139.1, 135.8, 134.9, 133.4, 130.0, 129.5, 127.6, 125.46, 121.2, 61.3, 21.3. HPLC (Chiracel OD-H column, *n*-Hexane/*i*-PrOH = 70/30, flow = 0.8 mL/min, l = 210 nm, 30 °C) t_R = 21.1 min (minor), 25.5 min (major).

*(−)-3-Methyl-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (**4d**).* 34.2 mg, 93% yield, colorless oil, known compound,[6a] R_f = 0.25 (dichloromethane/ethyl acetate 50/1), 96% ee, $[\alpha]^{20}_D$ = −34.70 (*c* 0.68, CH_2Cl_2), [lit.:[6a] $[\alpha]^{20}_D$ = −30.1 (*c* 0.40, CH_2Cl_2) for 94% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 4.90 (br s, 1H), 4.84−4.74 (m, 1H), 1.61 (d, *J* = 6.7 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.8, 135.6, 133.3, 129.3, 124.0, 121.3, 53.5, 21.5. HPLC (Chiracel OD-H column, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.8 mL/min, l = 210 nm, 30 °C) t_R = 14.0 min (major), 18.1 min (minor).

*(−)-3-Ethyl-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (**4e**).* 37.2 mg, 94% yield, colorless oil, known compound,[22] R_f = 0.40 (dichloromethane), 96% ee, $[\alpha]^{20}_D$ = −55.07 (*c* 0.67, $CHCl_3$), [lit.:[22] $[\alpha]^{20}_D$ = −46.7 (*c* 1.0, $CHCl_3$) for 96% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.62 (td, *J* = 7.6, 1.2 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 4.86 (br s, 1H), 4.73−4.54 (m, 1H), 2.13−1.98 (m, 1H), 1.89−1.75 (m, 1H), 1.03 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.3, 135.8, 133.2, 129.3, 124.2, 121.4, 59.1, 28.8, 10.0. HPLC (Chirapak AD-H column, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.8 mL/min, l = 210 nm, 30 °C) t_R = 12.1 min (major), 14.1 min (minor).

*(−)-3-Butyl-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (**4f**).* 42.6 mg, 94% yield, white solid, known compound,[23] R_f = 0.60 (dichloromethane), 95% ee, $[\alpha]^{20}_D$ = −51.42 (*c* 0.77, $CHCl_3$), [lit.:[23] $[\alpha]^{20}_D$ = −46.92 (*c* 0.78, $CHCl_3$) for 94% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.61 (td, *J* = 7.6, 1.2 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 4.90 (d, *J* = 4.1 Hz, 1H), 4.75−4.60 (m, 1H), 2.10−1.90 (m, 1H), 1.86−1.69 (m, 1H), 1.55−1.29 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.8, 135.7, 133.2, 129.3, 124.2, 121.4, 58.0, 35.6, 28.0, 22.5, 14.0. HPLC (Chirapak IC column, *n*-Hexane/*i*-PrOH = 70/30, flow = 0.7 mL/min, l = 210 nm, 30 °C) t_R = 20.2 min (major), 30.6 min (minor).

*(−)-3-Isobutyl-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (**4g**).* 44.3 mg, 98% yield, colorless oil, known compound,[23] R_f = 0.60 (dichloromethane), 87% ee, $[\alpha]^{20}_D$ = −60.71 (*c* 0.84, $CHCl_3$), [lit.:[23] $[\alpha]^{20}_D$ = −52.38 (*c* 0.42, $CHCl_3$) for 96% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.60 (td, *J* = 7.5, 1.3 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.36 (dd, *J* = 7.7, 0.9 Hz, 1H), 4.96 (d, *J* = 5.2 Hz, 1H), 4.76−4.64 (m, 1H), 1.97−1.82 (m, 1H), 1.79−1.64 (m, 2H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.5, 135.7, 133.2, 129.3, 124.2, 121.4, 56.2, 45.3, 25.6, 23.5, 21.5. HPLC (Chirapak OD-H column, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.8 mL/min, l = 210 nm, 30 °C) t_R = 10.4 min (major), 22.8 min (minor).

*(−)-3-Cyclohexyl-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (**4h**).* 46.9 mg, 93% yield, pale yellow solid, known compound,[22] R_f = 0.50 (dichloromethane), 98% ee, $[\alpha]^{20}_D$ = −48.96 (*c* 0.87, $CHCl_3$), [lit.:[22] $[\alpha]^{20}_D$ = −48.6 (*c* 1.00, $CHCl_3$) for 97% ee]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 4.84 (d, *J* = 5.1 Hz, 1H), 4.68−4.55 (m, 1H), 1.99−1.76 (m, 3H), 1.74−1.58 (m, 2H), 1.37−1.01 (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 139.1, 135.8, 133.1, 129.3, 124.5, 121.5, 63.0, 42.8, 30.8, 26.4, 26.0, 25.9, 25.8. HPLC (Chirapak IC column, *n*-Hexane/*i*-PrOH = 70/30, flow = 0.7 mL/min, l = 210 nm, 30 °C) t_R = 18.1 min (major), 42.5 min (minor).

Experiment at 1.0 mmol Scale. The metal precursor nickel diacetate (3.5 mg, 0.020 mmol), chiral ligand (*R*,*R*)-QuinoxP* (8.0 mg, 0.024 mmol), six-membered cyclic *N*-sulfonyl imine **1a** (259 mg, 1.0 mmol) and tetrahydroxydiboron (269 mg, 3.0 mmol) were added to the sealed tube. The sealed tube was taken into a glovebox filled with nitrogen, and hexafluoroisopropanol (1.5 mL) was added. The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the volatiles were removed under the reduced pressure. The crude residue was purified by silica gel column chromatography using dichloromethane as eluent to give the chiral reductive product (−)-**2a** (248 mg, 95% yield, 95% ee).

Mechanistic Study Experiments. *Reaction with Reducing Reagents as Additives.* The metal precursor nickel diacetate (0.7 mg, 0.0040 mmol), (*R*,*R*)-QuinoxP* (1.6 mg, 0.0048 mmol), cyclic *N*-

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sulfonyl imine **1a** (51.9 mg, 0.20 mmol) and additive (0.60 mmol) were added to the sealed tube. The sealed tube was taken into a glovebox filled with nitrogen, and hexafluoroisopropanol (3.0 mL) was added. The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the volatiles were removed under the reduced pressure. Trace product **2a** was observed by ^{1}H NMR.

Reaction Using Stoichiometric Ni(0) Catalyst. Cyclic *N*-sulfonyl imine **1a** (7.8 mg, 0.03 mmol) and (*R*,*R*)-QuinoxP* (12.0 mg, 0.036 mmol) were added to the sealed tube. The sealed tube was taken into a glovebox filled with nitrogen, and then bis(1,5-cyclooctadiene) nickel (8.3 mg, 0.03 mmol) and hexafluoroisopropanol (0.50 mL) were added. The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the volatiles were removed under the reduced pressure. Trace product **2a** was observed by ^{1}H NMR.

Deuterium Labeling Experiment Using d2-HFIP. A sealed tube with a stir bar was placed in an oil bath at 80 °C under vacuum for 2 h. Cyclic *N*-sulfonyl imine **1c** (27.3 mg, 0.10 mmol) was dissolved in dry toluene (4.0 mL), and the solvent was removed under vacuum. The above process for imine **1c** was repeated two more times, and the corresponding solid was dried under vacuum for 2 h, giving dried imine **1c**. Dried imine **1c**, synthesized tetradeuteroxydiboron (28.1 mg, 0.30 mmol) from tetrahydroxydiboron (26.9 mg, 0.30 mmol) and deuterium oxide (3.0 mL, 99.8% D, J&K Scientific),[15b] nickel diacetate (0.4 mg, 0.0020 mmol) and (*R*,*R*)-QuinoxP* (0.8 mg, 0.0024 mmol) were added to the dried sealed tube. The sealed tube was taken into a glovebox filled with nitrogen, and *d*2-hexafluoroisopropanol (1.0 mL, 99% D, Acros Organics) was added. The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the volatiles were removed under the reduced pressure. The crude residue was purified by silica gel column chromatography using dichloromethane as eluent to give the corresponding product **2c-D** (27.4 mg, 99% yield, 93% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.29 (m, 2H), 7.26−7.20 (m, 1H), 7.17−7.03 (m, 4H), 6.87−6.79 (m, 1H), 5.86 (d, J = 8.7 Hz, 0.05H), 4.73 (s, 1H), 2.37 (s, 3H). Deuterium incorporation was 95%. HPLC (Chirapak IC column, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.7 mL/min, l = 210 nm, 30 °C) t_R = 12.4 min (minor), 14.0 min (major).

Deuterium Labeling Experiment Using $(F_3C)_2$CHOD. A sealed tube with a stir bar was placed in an oil bath at 80 °C under vacuum for 2 h. Cyclic *N*-sulfonyl imine **1c** (27.3 mg, 0.10 mmol) was dissolved in dry toluene (4.0 mL), and the solvent was removed under vacuum. The above process for imine **1c** was repeated two more times, and the corresponding solid was dried under vacuum for 2 h, giving dried imine **1c**. Dried imine **1c**, synthesized tetradeuteroxydiboron (28.1 mg, 0.30 mmol) from tetrahydroxydiboron (26.9 mg, 0.30 mmol) and deuterium oxide (3.0 mL, 99.8% D, J&K Scientific),[15b] nickel diacetate (0.4 mg, 0.0020 mmol) and (*R*,*R*)-QuinoxP* (0.8 mg, 0.0024 mmol) were added to the dried sealed tube. The sealed tube was taken into a glovebox filled with nitrogen, and $(F_3C)_2$CHOD (1.0 mL, 98% D, Acros Organics) was added. The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the volatiles were removed under the reduced pressure. The crude residue was purified by silica gel column chromatography using dichloromethane as eluent to give the corresponding product **2c-D** (27.2 mg, 99% yield, 91% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.28 (m, 2H), 7.26−7.20 (m, 1H), 7.18−6.97 (m, 4H), 6.91−6.73 (m, 1H), 5.85 (d, J = 8.7 Hz, 0.09H), 4.75 (s, 1H), 2.37 (s, 3H). Deuterium incorporation was 91%. HPLC (Chirapak IC column, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.7 mL/min, l = 210 nm, 30 °C) t_R = 12.0 min (minor), 13.6 min (major).

Kinetic Isotope Effect. Asymmetric transfer hydrogenation of cyclic *N*-sulfonyl imine **1c** (27.3 mg, 0.10 mmol) was performed in *d*2-hexafluoroisopropanol (0.50 mL, 99% D, Acros Organics) and hexafluoroisopropanol (0.50 mL) under standard conditions, giving the corresponding product **2c-D** (25.8 mg, 94% yield, 96% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.29 (m, 2H), 7.26−7.21 (m, 1H), 7.18−7.03 (m, 4H), 6.83 (d, J = 7.8 Hz, 1H), 5.86 (d, J = 8.7 Hz, 0.79H), 4.69 (d, J = 8.1 Hz, 1H), 2.37 (s, 3H). A kinetic isotope effect of 3.8 was observed. HPLC (Chirapak IC column, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.7 mL/min, l = 210 nm, 30 °C) t_R = 12.3 min (minor), 13.9 min (major).

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying his study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.3c01773.

Copies of ^{1}H, ^{13}C{^{1}H},^{19}F{^{1}H} and HPLC spectra of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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