Rhodium-Catalyzed Highly Enantioselective Addition of Arylboronic Acids to Cyclic Aldimines: Practical Asymmetric Synthesis of Cyclic Sulfamidates

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Abstract: A highly efficient asymmetric arylation of cyclic *N*-sulfonyl aldimines with arylboronic acids catalyzed by a rhodium/sulfur–olefin ligand complex under mild conditions is described. A wide range 4-aryl-3,4-dihydro-1,2,3-benzoxathiazine 2,2-dioxides were obtained in extremely high yields (93–99%) and high enantiomeric purities (97–99% ee).

Key words: asymmetric catalysis, cyclization, arylation, rhodium, boron, ligands, sulfamidates, heterocycles

Chiral amines are ubiquitous in nature and commonly occur as key structural motifs in numerous biologically interesting compounds and pharmaceutical agents. Consequently, the discovery of efficient techniques for the asymmetric synthesis of various optically pure amines continues to be a pivotal subject in modern organic chemistry. Cyclic sulfamidates represent an intriguing class of amine derivatives that contain a sulfonamide functionality in the ring. They occur widely in pharmaceutical compounds for diverse medicinal uses[1] and they can also serve as versatile building blocks in various organic syntheses.[2] In general, cyclic sulfamidates are prepared from amino alcohols and diols in several steps.[2a,3] They can also be synthesized from alcohols through intramolecular sulfamate ester C−H insertion in the presence of binuclear rhodium carboxylate catalysts[4] or ruthenium porphyrin catalysts.[5,6] However, methods for creating stereogenic centers in these heterocycles through asymmetric catalysis are limited because of difficulties in achieving a high enantioselectivity.[5a,5d] Among the methods that do exist, direct asymmetric hydrogenation of the corresponding cyclic ketimines is reported to be the most efficient enantioselective route to chiral cyclic sulfamidates.[7] Surprisingly, although asymmetric addition to C=N double bonds in analogous imine compounds represents an alternative and direct route to chiral sulfamidates, it is only recently that a few examples of reactions of this type have been documented.[8]

The use of commercially available stable arylboronic acids to replace common organometallic reagents in transition metal-catalyzed C–C bond-forming reactions has recently also attracted a considerable degree of attention.[9] However, to the best of our knowledge, the asymmetric addition of arylboronic acids to benzene-fused cyclic *N*-sulfonyl aldimines remains unexplored. Therefore, the development of new catalytic systems capable of efficient synthesis of enantiomerically pure cyclic sulfamidates would be a highly desirable goal.

We recently designed a series of chiral sulfinamide/sulfoxide-based olefin ligands and used them in rhodium-catalyzed asymmetric reactions.[10,11] Simple linear *N*-cinnamylsulfinamide derivatives were found to be elegant chiral ligands for the 1,2-addition of arylboronic acids to α-keto esters and α-diketones, and gave a broad range of aryl α-hydroxy carbonyl compounds with very high enantioselectivities (up to 99% ee).[10d] Following an extensive study, we showed that equally simple branched sulfur–olefin ligands were more effective in promoting asymmetric addition of arylboronic acids to cyclic ketimines, affording a variety of highly enantiomerically enriched (up to 99% ee) quaternary carbon-containing benzosultams and benzosulfamidates.[10g]

In an attempt to broaden the scope of this chemistry, we surmised that the corresponding cyclic *N*-sulfonyl aldimines might also act as suitable substrates. We present a detailed survey of the asymmetric addition of such imines to arylboronic acids in the presence of rhodium catalysts under mild conditions to give a diversity of chiral cyclic sulfamidates in extremely high yields and high enantioselectivities (up to 99% ee).

We began by treating the cyclic *N*-sulfonyl aldimine **1a** with (4-methoxyphenyl)boronic acid (**2a**) under the conditions previously optimized for the asymmetric arylation of ketimines in the presence of the simple *N*-cinnamylsulfinamide **L1** as the chiral ligand (Scheme 1). The reaction proceeded at room temperature in the presence of dichlorotetrakis(cyclooctene)dirhodium {$[Rh(coe)_2Cl]_2$} (1.5 mol%) and ligand **L1** (3.3 mol%) in 1.5 M aqueous potassium fluoride/toluene to give the expected benzosulfamidate **3a** in moderate yield and promising enantioselectivity (54% ee). To follow up on this encouraging result, we performed further screening of other sulfur–olefin hybrid ligands with the aim of enhancing the reactivity and enantioselectivity of the reaction. Interestingly, the branched-chain sulfinamide ligand **L2** gave a much higher yield of the product (77%) with a similar enantiomeric excess (56% ee). Unlike the case of the arylation of cyclic ketimines,[10g] the stereocontrol was not affected by the use of the sterically hindered ligand **L3** with an *ortho*-methyl substituent on the phenyl ring, but this reaction gave a lower yield. To our delight, however, marked improve-

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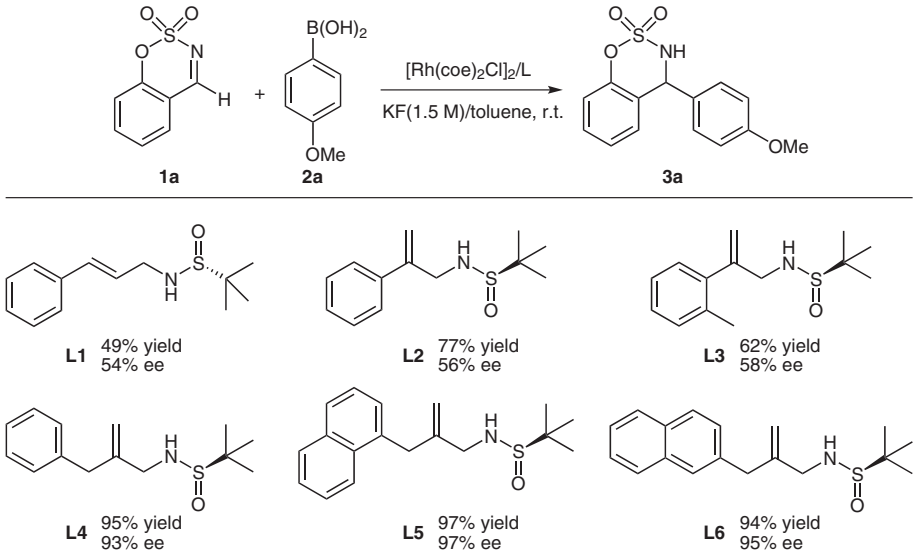
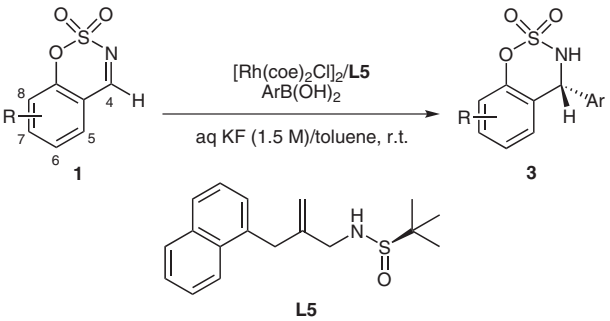


Scheme 1 Screening of ligands

ments in both enantioselectivity (93%) and yield (95%) were achieved when we used the benzyl-substituted ligand **L4**. The incorporation of a large naphthyl group was even more beneficial (**L5** and **L6**), the highest enantioselectivity (97% ee) and yield (97%) being observed when chiral sulfinamide **L5** was used as the ligand.

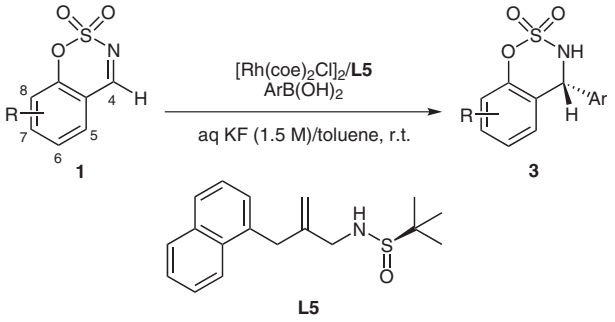
Having performed these optimization studies, we went on to make a thorough examination of the substrate scope and generality of the reaction, the results of which are summarized in Table 1. A wide range of arylboronic acids with various electronic and steric demands reacted successfully with a series of cyclic *N*-sulfonyl aldimines **1** to give the corresponding functionalized 3,4-dihydro-1,2,3-benzoxathiazine 2,2-dioxides **3** in excellent yields and extremely high enantioselectivities. The electronic properties of the arylboronic acids did not appear to affect the reactivity or enantioselectivity of the reaction (entries 1–11). In addition to the simple aldimine **1a**, derivatives with electron-donating or electron-withdrawing substituents in various positions on the aromatic ring were all found to be viable substrates, exhibiting high reactivities and giving highly optically active cyclic benzosulfamidates in excellent yields (entries 12–26). Notably, arylboronic acids and substrates with high degrees of steric hindrance also participated in smooth arylation reactions with excellent enantioselectivities (entries 5 and 10–12). In view of the high level of enantioselectivity and the exceptionally mild conditions that are required, this process represents the most enantioselective and the most convenient route to 3,4-dihydro-1,2,3-benzoxathiazine 2,2-dioxides.

Table 1 Asymmetric Addition of Arylboronic Acids to Cyclic *N*-Sulfonyl Aldimines Catalyzed by Dichlorotetrakis(cyclooctene)dirhodium and ligand **L5**



Entry[a]	R	Ar	Product	Yield[b] (%)	ee[c] (%)
1	H	4-$MeOC_6H_4$	**3a**	97	97
2	H	4-Tol	**3b**	96	99
3	H	4-ClC_6H_4	**3c**	96	99
4	H	Ph	**3d**	98	99
5	H	1-naphthyl	**3e**	99	99
6	H	2-naphthyl	**3f**	98	99
7	H	3-$MeOC_6H_4$	**3g**	96	99
8	H	3-Tol	**3h**	98	98
9	H	3-ClC_6H_4	**3i**	98	99
10	H	2-$MeOC_6H_4$	**3j**	99	99
11	H	2-Tol	**3k**	99	99
12	5,6-$(CH{=}CH)_2$	Ph	**3l**	96	99
13	6-OMe	Ph	**3m**	99	99
14	6-OMe	4-$MeOC_6H_4$	**3n**	98	97

Table 1 Asymmetric Addition of Arylboronic Acids to Cyclic *N*-Sulfonyl Aldimines Catalyzed by Dichlorotetrakis(cyclooctene)dirhodium and ligand **L5** (continued)



Entry[a]	R	Ar	Product	Yield[b] (%)	ee[c] (%)
15	6-Me	Ph	**3o**	99	99
16	6-Me	4-Tol	**3p**	99	99
17	6-Cl	Ph	**3q**	93	99
18	6-Cl	4-ClC_6H_4	**3r**	99	99
19	6-Cl	3-ClC_6H_4	**3s**	98	99
20	6-Cl	4-BrC_6H_4	**3t**	99	99
21	7-OMe	Ph	**3u**	99	99
22	8-OMe	Ph	**3v**	99	99
23	8-OMe	4-$MeOC_6H_4$	**3w**	96	97
24	8-Me	Ph	**3x**	99	99
25	8-Me	4-Tol	**3y**	98	99
26	8-Me	4-BrC_6H_4	**3z**	98	99

[a] *Reaction conditions*: **1** (0.25 mmol), $ArB(OH)_2$ (2.0 equiv), $\{[Rh(coe)_2Cl]_2\}$ (3 mol%), **L5** (3.3 mol%), 1.5 M aq KF (1.0 equiv)/toluene, r.t., 5−6 h.
[b] Isolated yield.
[c] By HPLC on a chiral column.

The absolute configuration of the newly created carbon stereocenter in product **3z** was shown to be *R* by means of X-ray crystallographic analysis (Figure 1).[12]

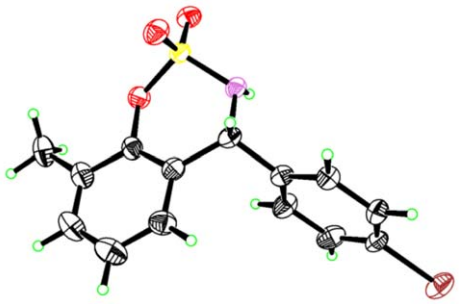
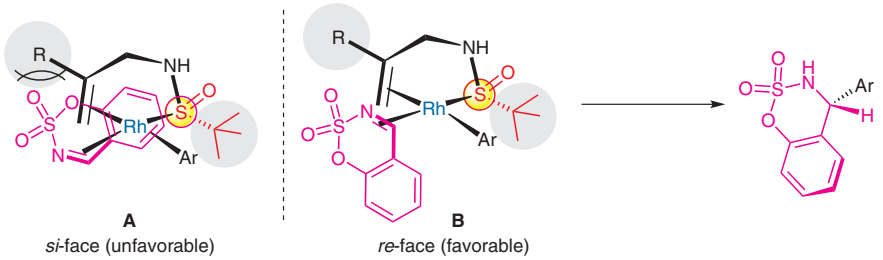


Figure 1 X-ray structure of **3z**

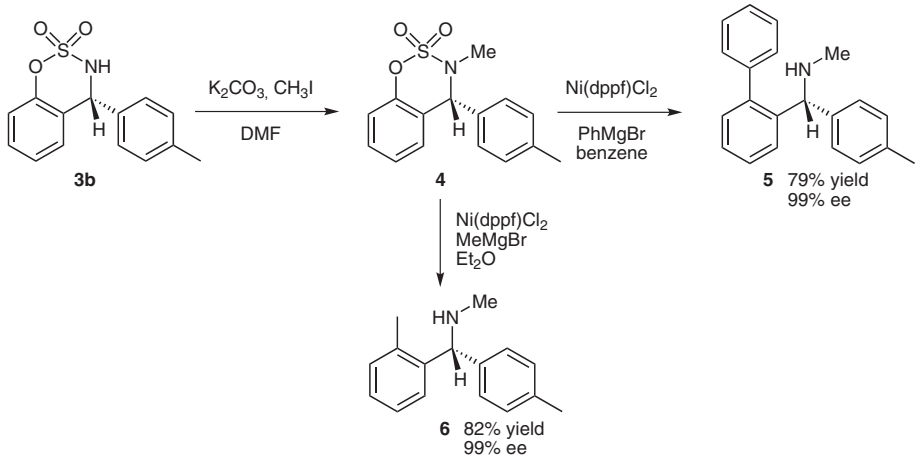
The stereochemical outcome of the reaction can be rationalized by considering an empirical transition state model[13,14] in which the arylrhodium species has a preferred conformation with the aryl group positioned *trans* to the olefin ligand and the *tert*-butyl moiety staggered (Scheme 2). The highly enantioselective formation of the *R*-product can be explained by *re*-face-selective coordination of the cyclic imine with rhodium, because an unfavorable steric interaction between the R group and the sulfonyl moiety of the imine substrate exists in transition state **A**, which is absent in transition state **B**.

The synthetic utility of the arylation product was exemplified by the conversion of product **3b** into cyclic sulfamate **4** by N-methylation (Scheme 3). Such aryl sulfamates have recently been shown to be highly effective in nickel-catalyzed Kumada cross-couplings.[15] As we had hoped, the reaction of sulfamate **4** with phenylmagnesium bromide under Du Bois's conditions[15b] smoothly gave the biaryl compound **5** in 79% yield with retained enantioselectivity (99% ee). Additionally, the cross-coupling reaction of cyclic sulfamate **4** and methylmagnesium bromide was also successful and gave the chiral diaryl derivative **6** in 82% yield and 99% ee.

In summary, we have developed a new, simple, practical, and enantioselective synthesis of 4-aryl-3,4-dihydro-1,2,3-benzoxathiazine 2,2-dioxides through the rhodium-catalyzed asymmetric addition of arylboronic acids with cyclic aldimines in the presence of a branched chiral *N*-alkenylsulfinamide ligand. This method is general and provides ready access to a wide range of functionalized derivatives of 4-aryl-3,4-dihydro-1,2,3-benzoxathiazine 2,2-dioxides in enantiomerically pure form and excellent



Scheme 2 Proposed transition-state model



Scheme 3 Further transformations of arylation product **3b**

yields under mild conditions, so that it is the most convenient and efficient approach to this class of target compounds. The newly designed sulfur–olefin ligands are promising and exciting ligands for asymmetric catalysis that should find a wide range of applications in asymmetric synthesis.

Commercially available reagents were purchased from J&K Chemical or Sigma-Aldrich and used directly without further purification. Toluene was distilled from sodium under nitrogen prior to use; THF was distilled from benzophenone-ketyl under nitrogen prior to use; other solvents were dried using standard procedures. Melting points were determined on a Buchi 510 melting point apparatus and are uncorrected. IR spectra were recorded on a Thermofisher Nicolet 7600 spectrophotometer. NMR spectra were recorded on a Varian spectrometer (300 MHz for ^{1}H, and 100 MHz for ^{13}C). Chemical shifts are reported on the δ scale in ppm referenced to $SiMe_4$ as an internal standard for ^{1}H NMR and chloroform-*d* (δ = 77.16) for ^{13}C NMR. High-resolution mass spectra were recorded on a MICROMASS Q-Tof ultima spectrometer. HPLC was performed on a JASCO 2000 instrument. X-ray crystallography was performed on a Bruker APEX 11.

4-Aryl-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxides 3; General Procedure

A soln of cyclic aldimine **1** (0.25 mmol), $[Rh(coe)_2Cl]_2$ (2.7 mg, 0.0075 mmol of Rh), ligand **L5** (2.5 mg, 0.00825 mmol), and $ArB(OH)_2$ (0.5 mmol) in toluene was stirred at r.t. for 30 min then 1.5 M aq KF (0.17 mL, 0.25 mmol) was added. The mixture was stirred at r.t. for 5–6 h then passed through a pad of silica gel with EtOAc (10 mL). The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, PE–EtOAc, 5:1).

(4*R*)-4-(4-Methoxyphenyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3a)

White solid; yield: 71 mg (97%; 97% ee); mp 112 °C.

HPLC: Chiralpak AD-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 13.2 min, 16.2 min (major).

IR (KBr): 3269, 2931, 1612, 1513, 1257, 1168, 1099, 1028, 850, 761 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 4.80 (d, *J* = 5.7 Hz, 1 H), 5.85 (d, *J* = 5.7 Hz, 1 H), 6.83 (d, *J* = 5.7 Hz, 1 H), 6.91–6.95 (m, 2 H), 7.03–7.11 (m, 2 H), 7.23–7.27 (m, 2 H), 7.32 (t, *J* = 5.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 54.9, 61.0, 114.3, 118.3, 121.9, 124.7, 128.2, 129.2, 129.4, 129.7, 151.0, 159.9.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{14}H_{13}NNaO_4S$: 314.0463; found: 314.0466.

(4*R*)-4-(4-Tolyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3b)

White solid; yield: 66 mg (96%; 99% ee); mp 130 °C.

HPLC: Chiralpak AD-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (85:15); flow = 0.7 mL/min; retention time: 16.1 min, 17.5 min (major).

IR (KBr): 3248, 2922, 1579, 1429, 1367, 1205, 1169, 1097, 891, 850 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 4.78 (s, 1 H), 5.86 (s, 1 H), 6.82 (d, *J* = 7.5 Hz, 1 H), 7.03–7.11 (m, 2 H), 7.20–7.23 (m, 4 H), 7.32 (t, *J* = 8.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 61.7, 118.7, 122.2, 125.2, 128.6, 128.6, 129.6, 130.1, 134.9, 139.6, 151.4.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{14}H_{13}NNaO_3S$: 298.0514; found: 298.0531.

(4*R*)-4-(4-Chlorophenyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3c)

White solid; yield: 71 mg (96%; 99% ee); mp 120 °C.

HPLC: Chiralpak AD-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (85:15); flow = 0.7 mL/min; retention time: 12.2 min, 13.5 min (major).

IR (KBr): 3236, 2922, 1579, 1431, 1371, 1201, 1167, 1092, 903, 849 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.88 (s, 1 H), 5.88 (s, 1 H), 6.81 (d, *J* = 5.7 Hz, 1 H), 7.05–7.13 (m, 2 H), 7.28–7.36 (m, 3 H), 7.40–7.43 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.2, 118.9, 121.4, 125.3, 128.4, 129.6, 129.9, 130.2, 135.6, 136.2, 151.4.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{13}H_{10}ClNNaO_3S$: 317.9968; found: 317.9977.

(4*R*)-4-Phenyl-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3d)

White solid; yield: 64 mg (98%; 99% ee); mp 144 °C.

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (70/30); flow = 0.6 mL/min; retention time: 11.3 min (major), 12.4 min.

IR (KBr): 3238, 2922, 1579, 1450, 1365, 1203, 1167, 1103, 893, 845 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.83 (s, 1 H), 5.90 (s, 1 H), 6.82 (d, *J* = 7.2 Hz, 1 H), 7.05–7.12 (m, 2 H), 7.31–7.37 (m, 3 H), 7.42–7.45 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.9, 118.8, 122.0, 125.2, 128.5, 128.8, 129.4, 129.5, 129.7, 137.8, 151.4.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{13}H_{11}NO_3S$: 284.0357; found: 284.0385.

(4*R*)-4-(1-Naphthyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3e)
White solid; yield: 77 mg (99%; 99% ee); mp 140 °C.

HPLC: Chiralpak AD-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 10.1 min, 12.1 min (major).

IR (KBr): 3276, 2924, 1583, 1454, 1371, 1192, 1171, 1103, 839, 760 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.25 (s, 1 H), 6.65 (s, 1 H), 6.86 (d, *J* = 7.8 Hz, 1 H), 7.04–7.13 (m, 2 H), 7.31–7.37 (m, 1 H), 7.42–7.58 (m, 4 H), 7.93–7.96 (m, 2 H), 8.02(s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 59.0, 119.1, 122.1, 122.7, 125.3, 125.4, 126.5, 127.4, 128.1, 128.3, 129.3, 129.7, 130.5, 134.2, 151.5.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{13}NNaO_3S$: 334.0514; found: 334.0498.

(4*R*)-4-(2-Naphthyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3f)
White solid; yield: 76 mg (98%; 99% ee); mp 132 °C.

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (70:30); flow = 0.7 mL/min; retention time: 11.6 min (major), 17.6 min.

IR (KBr): 3265, 2922, 1579, 1452, 1358, 1190, 1167, 1099, 879, 758 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.94 (s, 1 H), 6.07 (s, 1 H), 6.84 (d, *J* = 7.4 Hz, 1 H), 7.08 (t, *J* = 7.5 Hz, 2 H), 7.32–7.37 (m, 2 H), 7.54–7.60 (m, 2 H), 7.85–7.92 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 62.1, 118.9, 122.0, 125.2, 125.3, 127.0, 127.2, 127.8, 128.1, 128.6, 128.8, 129.7, 129.8, 133.1, 133.5, 134.8, 151.5.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{13}NNaO_3S$: 334.0514; found: 334.0510.

(4*R*)-4-(3-Methoxyphenyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3g)
White solid; yield: 70 mg (96%; 99% ee); mp 112 °C.

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 17.6 min (major), 19.7 min.

IR (KBr): 3236, 2920, 1589, 1427, 1373, 1259, 1201, 1171, 862, 750 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3 H), 5.00 (s, 1 H), 5.84 (s, 1 H), 6.83–6.87 (m, 2 H), 6.91–6.97 (m, 2 H), 6.99–7.03 (d, *J* = 7.4 Hz, 1 H), 7.06–7.11 (t, *J* = 7.5 Hz, 1 H), 7.29–7.37 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 61.9, 114.4, 115.0, 118.7, 120.9, 121.9, 125.2, 128.5, 129.7, 130.5, 139.1, 151.3, 160.2.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{14}H_{13}NNaO_4S$: 314.0463; found: 314.0478.

(4*R*)-4-(3-Tolyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3h)
White solid; yield: 67 mg (98%; 98% ee); mp 100 °C.

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 12.7 min (major), 14.4 min.

IR (KBr): 3257, 2922, 1579, 1429, 1369, 1211, 1169, 1099, 874, 750 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 4.79 (s, 1 H), 5.85 (d, *J* = 7.2 Hz, 1 H), 6.83 (d, *J* = 8.1 Hz, 1 H), 7.03–7.14 (m, 4 H), 7.23 (d, *J* = 7.5 Hz, 1 H), 7.32 (t, *J* = 7.5 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 61.9, 118.8, 122.1, 125.2, 125.8, 128.6, 129.3, 129.4, 129.6, 130.3, 137.8, 139.4, 151.4.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{14}H_{13}NNaO_3S$: 298.0514; found: 298.0541.

(4*R*)-4-(3-Chlorophenyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3i)
White solid; yield: 72 mg (98%; 99% ee); mp 106 °C.

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 13.3 min, 17.5 min (major).

IR (KBr): 3234, 2922, 1579, 1427, 1371, 1200, 1169, 1099, 858, 760 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.97 (s, 1 H), 5.86 (s, 1 H), 6.82 (d, *J* = 6.6 Hz, 1 H), 7.05 (d, *J* = 6.9 Hz, 1 H), 7.12 (t, *J* = 5.4 Hz, 1 H), 7.25 (d, *J* = 8.4 Hz, 1 H), 7.33–7.37 (m, 2 H), 7.39–7.43 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.3, 119.0, 121.2, 125.4, 127.1, 128.4, 129.0, 129.8, 130.0, 130.7, 135.2, 139.6, 151.4.

HRMS (ESI): *m/z* $[M - H]^-$ calcd for $C_{13}H_9ClNO_3S$: 293.9992; found: 293.9980.

(4*R*)-4-(2-Methoxyphenyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3j)
White solid; yield: 72 mg (99%; 99% ee); mp 111 °C.

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (70:30); flow = 0.7 mL/min; retention time: 11.7 min (major), 14.7 min.

IR (KBr): 3284, 2922, 1603, 1425, 1373, 1200, 1171, 1103, 820, 756 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.68 (s, 3 H), 5.72 (d, *J* = 7.5 Hz, 1 H), 5.91 (d, *J* = 7.5 Hz, 1 H), 6.68 (d, *J* = 5.7 Hz, 1 H), 6.96–7.09 (m, 4 H), 7.25–7.30 (m, 1 H), 7.33–7.36 (m, 1 H), 7.41–7.46 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 60.3, 112.1, 118.3, 121.3, 122.7, 124.5, 124.9, 126.8, 129.2, 131.0, 151.1, 157.2.

HRMS (ESI): *m/z* $[M - H]^+$ calcd for $C_{14}H_{12}NO_4S$: 290.0487; found: 290.0496.

(4*R*)-4-(2-Tolyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3k)
White solid; yield: 68 mg (99%; 99% ee); mp 114 °C.

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 10.2 min (major), 12.1 min.

IR (KBr): 3253, 2922, 1579, 1406, 1363, 1205, 1169, 1097, 854, 752 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.47, (s, 3 H), 4.77 (s, 1 H), 6.17 (s, 1 H), 6.83 (d, *J* = 7.8 Hz, 1 H), 7.03–7.06 (m, 1 H), 7.09–7.14 (m, 2 H), 7.19–7.24 (m, 1 H), 7.28–7.36 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 58.3, 118.8, 121.9, 125.2, 126.9, 128.2, 128.5, 129.3, 129.4, 131.2, 135.8, 137.3, 151.6.

HRMS (ESI): *m/z* $[M - H]^-$ calcd for $C_{14}H_{12}NO_3S$: 274.0538; found: 274.0525.

(1*R*)-1-Phenyl-1,2,7,8,9,10-hexahydronaphtho[1,2-*e*][1,2,3]oxathiazine 3,3-Dioxide (3l)
Light-yellow solid; yield: 75 mg (96%; 99% ee); mp 184 °C.

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (85:15); flow = 0.7 mL/min; retention time: 21.3 min, 23.1 min (major).

IR (KBr): 3296, 1593, 1456, 1419, 1200, 1082, 955, 835 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.91 (s, 1 H), 6.35 (s, 1 H), 7.24–7.28 (m, 3 H), 7.30–7.37 (m, 5 H), 7.39–7.45 (m, 1 H), 7.85 (d, *J* = 8.1 Hz, 1 H), 7.90 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 60.6, 114.1, 118.6, 124.2, 125.5, 127.3, 128.2, 128.8, 129.0, 129.2, 130.0, 131.2, 131.3, 138.5, 150.1.

HRMS (ESI): *m/z* $[M - H]^-$ calcd for $C_{17}H_{12}NO_3S$: 310.0538; found: 310.0524.

(4*R*)-6-Methoxy-4-phenyl-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3m)
White solid; yield: 72 mg (99%; 99% ee); mp 148 °C.

IR (KBr): 3278, 2924, 1612, 1493, 1429, 1369, 1201, 1171, 1036, 849, 764 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 3 H), 4.79 (s, 1 H), 5.84 (s, 1 H), 6.29 (d, *J* = 2.1 Hz, 1 H), 6.84–6.87 (m, 1 H), 6.99 (d, *J* = 6.6 Hz, 1 H), 7.35 (t, *J* =2.7 Hz, 2 H), 7.42–7.44 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 62.1, 113.2, 115.2, 119.8, 122.8, 128.8, 129.5, 129.6, 137.8, 145.3, 156.5.

HRMS (ESI): *m/z* $[M - H]^-$ calcd for $C_{14}H_{12}NO_4S$: 290.0487; found: 290.0504.

(4*R*)-6-Methoxy-4-(4-methoxyphenyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3n)
Colorless oil; yield: 79 mg (98%; 97% ee).

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (70:30); flow = 0.7 mL/min; retention time: 17.3 min (major), 23.9 min.

IR (KBr): 3269, 2939, 1612, 1489, 1254, 1171, 1030, 852 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.62 (s, 3 H), 3.80 (s, 3 H), 5.05 (d, *J* = 7.8 Hz, 1 H), 5.76 (d, *J* = 7.8 Hz, 1 H), 6.29 (d, *J* = 3.0 Hz, 1 H), 6.79–6.84 (m, 1 H), 6.91 (t, *J* = 9.0 Hz, 3 H), 7.24 (d, *J* = 9.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 57.3, 57.5, 63.4, 115.1, 116.6, 117.1, 121.5, 125.1, 131.6, 132.1, 147.1, 158.3, 162.1.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_{15}NNaO_5S$: 344.0569; found: 344.0577.

(4*R*)-6-Methyl-4-phenyl-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3o)
White solid; yield: 68 mg (99%; 99% ee); mp 168 °C.

HPLC: Chiralpak AD-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 10.5 min (major), 11.9 min.

IR (KBr): 3278, 2922, 1487, 1425, 1365, 1198, 1173, 1111, 858, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.19 (s, 3 H), 4.84 (s, 1 H), 5.83 (s, 1 H), 6.58 (s, 1 H), 6.91 (d, *J* = 8.7 Hz, 1 H), 7.10 (d, *J* = 8.4 Hz, 1 H), 7.32–7.35 (m, 2 H), 7.42–7.44 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6, 61.8, 118.4, 121.5, 128.5, 128.7, 129.3, 129.4, 130.2, 134.9, 137.8, 149.3.

HRMS (ESI): *m/z* $[M - H]^-$ calcd for $C_{14}H_{12}NO_3S$: 274.0538; found: 274.0521.

(4*R*)-6-Methyl-4-(4-tolyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3p)
White solid; yield: 72 mg (99%; 99% ee); mp 171 °C.

HPLC: Chiralpak AD-3 column (250 mm); detection: 220 nm; hexane–*i*-PrOH (90:10); flow = 0.7 mL/min; retention time: 22.7 min, 23.7 min (major).

IR (KBr): 3261, 2924, 1487, 1421, 1365, 1201, 1174, 1107, 850, 793 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 2.39 (s, 3 H), 4.82 (d, *J* = 6.3 Hz, 1 H), 5.81 (d, *J* = 6.3 Hz, 1 H), 6.60 (s, 1 H), 6.93 (d, *J* = 6.6 Hz, 1 H), 7.09–7.12 (m, 1 H), 7.21–7.26 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7, 21.3, 61.8, 118.5, 121.7, 128.7, 128.7, 130.1, 130.3, 135.0, 135.1, 139.5, 149.4.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_{15}NNaO_3S$: 312.0670; found: 312.0684.

(4*R*)-6-Chloro-4-phenyl-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3q)
White solid; yield: 69 mg (93%; 99% ee); mp 158 °C.

HPLC: Chiralpak AD-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 9.4 min (major), 10.6 min.

IR (KBr): 3288, 1473, 1427, 1367, 1207, 1169, 1113, 845, 781 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.86 (s, 1 H), 5.85 (s, 1 H), 6.80 (d, *J* = 2.7 Hz, 1 H), 7.01 (d, *J* = 9.0 Hz, 1 H), 7.27–7.35 (m, 3 H), 7.46 (t, *J* = 3.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.6, 120.2, 123.5, 128.2, 128.6, 129.6, 129.8, 130.4, 136.9, 149.9.

HRMS (ESI): *m/z* $[M - H]^-$ calcd for $C_{13}H_9ClNO_3S$: 293.9992; found: 294.0000.

(4*R*)-6-Chloro-4-(4-chlorophenyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3r)
Colorless oil; yield: 82 mg (99%; 99% ee).

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 9.1 min, 11.8 min (major).

IR (KBr): 3276, 2920, 1597, 1473, 1427, 1371, 1203, 1167, 1111, 849, 777 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.21 (s, 1 H), 5.82 (s, 1 H), 6.77 (m, 1 H), 6.99 (d, *J* = 6.6 Hz, 1 H), 7.27–7.31 (m, 3 H), 7.42–7.44 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.0, 120.4, 123.1, 128.2, 129.9, 130.1, 130.2, 130.7, 135.4, 136.0, 149.9.

HRMS (ESI): *m/z* $[M + Na]^-$ calcd for $C_{13}H_9Cl_2NNaO_3S$: 351.9578; found: 351.9586.

(4*R*)-6-Chloro-4-(3-chlorophenyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3s)
White solid; yield: 81 mg (98%; 99% ee); mp 178 °C.

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 10.6 min, 13.6 min (major).

IR (KBr): 3244, 3207, 1473, 1439, 1367, 1207, 1165, 1109, 849, 783 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.99 (s, 1 H), 5.81 (s, 1 H), 6.79–6.80 (m, 1 H), 7.02 (d, *J* = 6.6 Hz, 1 H), 7.22–7.25 (m, 1 H), 7.30–7.34 (m, 2 H), 7.39–7.46 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 60.7, 120.0, 122.4, 126.5, 127.7, 128.5, 129.7, 129.7, 130.3, 130.5, 135.1, 138.4, 149.4.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{13}H_9Cl_2NNaO_3S$: 351.9578; found: 351.9563.

(4*R*)-4-(4-Bromophenyl)-6-chloro-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3t)

White solid; yield: 93 mg (98%; 99% ee); mp 185 °C.

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 12.2 min, 13.5 min (major).

IR (KBr): 3255, 2922, 1647, 1473, 1423, 1375, 1211, 1171, 1109, 852, 777 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.02 (d, *J* = 6.3 Hz, 1 H), 5.80 (d, *J* = 6.6 Hz, 1 H), 6.77 (d, *J* = 2.1 Hz, 1 H), 6.99 (d, *J* = 6.6 Hz, 1 H), 7.22 (d, *J* = 6.3 Hz, 2 H), 7.30 (dd, *J* = 1.8, 6.6 Hz, 1 H), 7.59 (d, *J* = 6.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.1, 120.4, 123.0, 124.2, 128.1, 130.1, 130.5, 130.7, 132.9, 135.9, 149.9.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{13}H_9BrClNNaO_3S$: 395.9073; found: 395.9077.

(4*R*)-7-Methoxy-4-phenyl-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3u)

Light-yellow solid; yield: 72 mg (99%; 99% ee); mp 181 °C.

HPLC: Chiralpak AD-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 16.8 min (major), 20.3 min.

IR (KBr): 3205, 2920, 1626, 1427, 1367, 1200, 1151, 1090, 953, 798 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3 H), 4.79–4.81 (m, 1 H), 5.82 (d, *J* = 6.3 Hz, 1 H), 6.55–6.56 (m, 1 H), 6.63–6.72 (m, 2 H), 7.32–7.35 (m, 2 H), 7.42–7.44 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 61.4, 103.3, 112.1, 113.7, 128.6, 129.1, 129.3, 129.4, 137.9, 152.1, 160.3.

HRMS (ESI): *m/z* $[M - H]^-$ calcd for $C_{14}H_{12}NO_4S$: 290.0487; found: 290.0500.

(4*R*)-8-Methoxy-4-phenyl-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3v)

White solid; yield: 72 mg (99%; 99% ee); mp 144 °C.

HPLC: Chiralpak AD-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 16.9 min, 19.4 min (major).

IR (KBr): 3236, 2922, 1581, 1442, 1365, 1209, 1157, 1082, 870 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.89 (s, 3 H), 4.81 (s, 1 H), 5.91 (s, 1 H), 6.38 (d, *J* = 7.8 Hz, 1 H), 6.90 (d, *J* = 8.1 Hz, 1 H), 7.02 (t, *J* = 8.1 Hz, 1 H), 7.34–7.37 (m, 2 H), 7.42–7.45 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.2, 62.1, 111.8, 119.6, 123.0, 124.8, 128.8, 129.4, 129.5, 138.0, 141.3, 148.8.

HRMS (ESI): *m/z* $[M - H]^-$ calcd for $C_{14}H_{12}NO_4S$: 290.0487; found: 290.0503.

(4*R*)-8-Methoxy-4-(4-methoxyphenyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3w)

White solid; yield: 77 mg (96%; 97% ee); mp 191 °C.

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (70:30); flow = 0.7 mL/min; retention time: 23.8 min (major), 28.0 min.

IR (KBr): 3299, 2920, 1614, 1479, 1410, 1267, 1200, 1155, 1082, 876, 789 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3 H), 3.81 (s, 3 H), 5.01 (d, *J* = 8.7 Hz, 1 H),5.83 (d, *J* = 8.7 Hz, 1 H), 6.37 (d, *J* = 8.1 Hz, 1 H), 6.84 (d, *J* = 8.1 Hz, 1 H), 6.90–7.01 (m, 3 H), 7.28 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 57.3, 58.0, 63.5, 113.5, 116.5, 121.5, 125.3, 126.5, 131.9, 132.0, 143.0, 150.6, 162.1.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_{15}NNaO_5S$: 344.0569; found: 344.0575.

(4*R*)-8-Methyl-4-phenyl-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3x)

White solid; yield: 68 mg (99%; 99% ee); mp 142 °C.

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 8.2 min (major), 9.0 min.

IR (KBr): 3269, 2922, 1631, 1433, 1365, 1207, 1149, 879, 719 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 4.81 (s, 1 H), 5.88 (s, 1 H), 6.63 (d, *J* = 8.1 Hz, 1 H), 6.97 (t, *J* = 7.5 Hz, 1 H), 7.16 (d, *J* = 7.2 Hz, 1 H), 7.32–7.35 (m, 2 H), 7.40–7.43 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.6, 62.0, 121.8, 124.6, 126.1, 128.2, 128.8, 129.4, 129.5, 131.1, 138.2, 150.2.

HRMS (ESI): *m/z* $[M - H]^-$ calcd for $C_{14}H_{12}NO_3S$: 274.0538; found: 274.0531.

(4*R*)-8-Methyl-4-(4-tolyl)-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3y)

White solid; yield: 71 mg (98%; 99% ee); mp 174 °C.

HPLC: Chiralpak AD-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (85:15); flow = 0.7 mL/min; retention time: 11.2 min, 14.5 min (major).

IR (KBr): 3249, 2925, 1462, 1408, 1369, 1200, 1149, 872, 795 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3 H), 2.38 (s, 3 H), 4.87 (s, 1 H), 5.84 (s, 1 H), 6.64 (d, *J* = 5.7 Hz, 1 H), 6.96 (t, *J* = 6.0 Hz, 1 H), 7.15 (d, *J* = 6.3 Hz, 1 H), 7.22 (d, *J* = 6.6 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.5, 21.2, 61.7, 122.0, 124.4, 126.1, 128.0, 128.6, 130.0, 130.9, 135.1, 139.4, 149.9.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_{15}NNaO_3S$: 312.0670; found: 312.0654.

(4*R*)-4-(4-Bromophenyl)-8-methyl-3,4-dihydro-1,2,3-benzoxathiazine 2,2-Dioxide (3z)

White solid; yield: 87 mg (98%; 99% ee); mp 182 °C.

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (80:20); flow = 0.7 mL/min; retention time: 11.1 min (major), 14.1 min.

IR (KBr): 3286, 2922, 1597, 1412, 1367, 1200, 1155, 1011, 868, 775 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 4.97 (s, 1 H), 5.83 (s, 1 H), 6.61 (d, *J* = 5.7 Hz, 1 H), 6.98 (t, *J* = 5.7 Hz, 1 H), 7.17–7.19 (m, 1 H), 7.21–7.24 (m, 2 H), 7.53–7.57 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.5, 61.3, 121.2, 123.6, 124.7, 125.9, 128.3, 130.5, 131.3, 132.5, 137.1, 150.0.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{14}H_{12}BrNNaO_3S$: 375.9619; found: 375.9604.

Crystal data: $C_{14}H_{12}BrNO_3S$: T = 100 K, wavelength: 0.71073 Å. Crystal system: orthorhombic, space group: $P2_12_12_1$; unit cell dimensions: *a* = 9.6530(3) Å, *b* = 12.3548(4) Å, *c* = 24.1314(9) Å, V = 2877.93(17) $Å^3$, Z = 8, ρ_{calcd} = 1.635 g/cm^3; *F*; (000) = 1424. The final anisotropic full-matrix least-squares refinement on F^2 with 368 variables converged at *R*1 = 3.97% (4343), for the observed data and *wR*2 = 7.49% (6611) for all data. The goodness-of-

fit was 0.998. Data were corrected for absorption effects by using the multi-scan method (SADABS).[12]

Chiral Aryl Amines 5 and 6; General Procedure

A 10-mL Schlenk flask was charged with cyclic sulfamate **4** (0.4 mmol) under N_2, then 5 mol% of Ni(dppp)Cl_2 in benzene (4 mL) was added from a syringe. The resulting red suspension was treated with a 0.5–2 M soln of RMgX (0.8 mmol, 2 equiv) in Et_2O, and mixture was stirred at 55 °C for 15 h. The mixture was then cooled to 25 °C and the reaction was quenched by the addition of MeOH (500 μL). The resulting mixture was stirred vigorously for 5 min and then transferred to a recovery flask. All volatiles were removed by concentration under reduced pressure to give an oily residue that was treated with anhyd 2 M methanolic HCl (2 mL). The resulting orange solution was stirred at 55 °C for 6 h then cooled to 25 °C and poured carefully into a separatory funnel containing sat. aq $NaHCO_3$ (10 mL). The organic phase was separated and collected, and the aqueous solution was extracted with EtOAc (3 × 15 mL). The organic phases were combined, washed with sat. aq NaCl (10 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a residue that was purified by chromatography (silica gel, PE–EtOAc, 4:1).

(*R*)-1-Biphenyl-2-yl-*N*-methyl-1-(4-tolyl)methanamine (5)

Light-yellow oil; yield: 91 mg (79%; 99% ee).

HPLC: Chiralpak IC-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (99:1); flow = 0.5 mL/min; retention time: 12.7 min (major), 14.1 min.

IR (KBr): 3338, 3022, 2947, 1597, 1475, 1438, 1124, 804, 752, 702 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 2.29 (s, 3 H), 4.80 (s, 1 H), 7.03–7.06 (m, 4 H), 7.18–7.28 (m, 4 H), 7.35–7.42 (m, 4 H), 7.60–7.63 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 34.8, 64.1, 126.4, 126.9, 127.0, 127.4, 127.8, 127.9, 128.9, 129.4, 129.9, 136.2, 140.7, 141.2, 141.4, 141.9.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{21}H_{21}N$: calcd 287.1674; found: 287.1663.

(*R*)-*N*-Methyl-1-(2-tolyl)-1-(4-tolyl)methanamine (6)

Light-yellow oil; yield: 74 mg (82%; 99% ee).

HPLC: Chiralpak AY-H column (250 mm); detection: 220 nm; hexane–*i*-PrOH (97:3); flow = 0.7 mL/min; retention time: 7.3 min, 8.0 min (major).

IR (KBr): 3356, 2952, 2922, 1739, 1662, 1460, 1377, 1111, 814, 748 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 3 H), 2.30 (s, 3 H), 2.41 (s, 3 H), 4.84 (s, 1 H), 7.08–7.12 (m, 3 H), 7.13–7.15 (m, 1 H), 7.19–7.23 (m, 2 H), 7.24–7.25 (m, 1 H), 7.57 (d, *J* = 5.7 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.6, 21.1, 35.1, 64.9, 126.1, 126.2, 126.6, 127.9, 129.0, 130.5, 135.7, 136.5, 139.8, 141.4.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{16}H_{19}N$: calcd 225.1517; found: 225.1505.

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