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# Kinetic Resolution of [2.2]Paracyclophane-Derived Cyclic *N*-Sulfonylimines via Palladium-Catalyzed Addition of Arylboronic Acids

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Cite This: *J. Org. Chem.* 2021, 86, 1262−1272 Read Online

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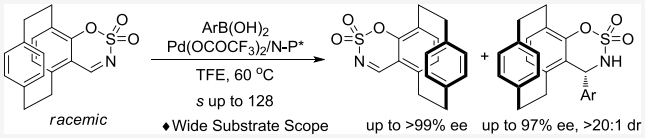
**ABSTRACT:** A facile method for kinetic resolution of [2.2]-paracyclophane-derived cyclic *N*-sulfonylimines based on palladium-catalyzed addition of arylboronic acids was developed, giving two kinds of planar chiral [2.2]paracyclophane derivatives in excellent diastereoselectivities and up to 99% of enantioselectivities with high selectivity factors (*s* up to 128).






[2.2]Paracyclophane derivatives are fascinating, considering their intriguing structural and electronic properties. As a result of their rigid scaffold, mono- and polysubstituted [2.2]-paracyclophanes are representative frameworks for planar chirality. Enantiopure [2.2]paracyclophanes have been successfully utilized as chiral materials, including mesoporous polymers, metal−organic frameworks, and circularly polarized light-emitting compounds.[1] Planar chiral [2.2]paracyclophanes have also found ample applications as one of the most commonly used classes of chiral inductors for asymmetric synthesis.[2] A major method for the optical resolution of planar chiral [2.2]paracyclophanes has been developed by chromatographic techniques or chiral reagents,[3] but there are few examples of the catalytic asymmetric process for accessing the enantioenriched [2.2]paracyclophanes.[4]

Cyclic *N*-sulfonylimines play an important role in the synthesis of functionalized benzosulfamidate heterocycles.[5] These chiral cyclic sulfamidate compounds display important biological activities including antiviral, antibiotic, anticonvulsant, anticancer, antiobesity, and antiosteoporosis activities.[6] Thus, some reactions exist using cyclic *N*-sulfonylimines for the synthesis of sulfamidate derivatives, involving asymmetric nucleophilic addition and hydrogenation (Scheme 1a).[7] Recently, palladium-catalyzed enantioselective addition of arylboronic acids has emerged as an efficient method for the rapid and diversified construction of central-chiral sulfamidates.[7a] Considering that the planar chiral [2.2]paracyclophane derivatives containing the sulfamidate motif have potential applications in organocatalysis and biologically active molecules and in connection with our previous work on the palladium-catalyzed kinetic resolution of [2.2]paracyclophane-derived acyclic *N*-sulfonylimines with arylboronic acids (Scheme 1b),[4g] we speculated this approach could be extended to kinetic resolution of [2.2]paracyclophane-derived cyclic *N*-sulfonylimines. The key point in the development of an efficient kinetic resolution method is to find a suitable chiral catalyst to distinguish the planar chirality of [2.2]paracyclophane-derived cyclic *N*-sulfonylimines. Herein, we report a facile method for kinetic resolution of [2.2]paracyclophane-derived cyclic *N*-sulfonylimines based on palladium-catalyzed addition of arylboronic acids. Two kinds of planar chiral [2.2]-paracyclophane derivatives could be obtained in excellent diastereoselectivities and enantioselectivities with high selectivity factors (Scheme 1c).

At the outset of the investigation, [2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-dioxide **1a** was chosen as model substrate for condition optimization. Based on previous work on asymmetric addition with arylboronic acids,[4g,8] bidentate phosphine-oxazoline ligands performed well for the palladium-catalyzed asymmetric addition of arylboronic acids to imines. In this context, the experiment was conducted using Pd(OCOCF$_3$)$_2$/(*S*)-$^t$Bu-Phox as a catalyst. To our delight, the reaction proceeded cleanly in TFE (2,2,2-trifluoroethanol) at 60 °C, albeit with low diastereoselectivity (Table 1, entry 1, *s* = 44.4). Aiming to further enhance the stereoselectivity, a number of ferrocene-derived phosphinooxazoline ligands with planar chirality were tested. High diastereoselectivity was obtained when using **L3** and **L4** as ligands (Table 1, entries 3 and 4). **L3** was selected as the best ligand considering the kinetic resolution selectivity factor. Changing the solvent to 1,2-dichloroethane, 1,4-dioxane, or hexafluoroisopropanol, the reactions gave worse results (Table 1, entries 6−8). In addition, the effects of reaction temperature and the amounts of phenylboronic acid were evaluated (Table 1, entries 9−12). Finally, the optimal reaction conditions were established: using Pd(OCOCF$_3$)$_2$/**L3** as a

**Received:** October 21, 2020
**Published:** December 18, 2020





https://dx.doi.org/10.1021/acs.joc.0c02509
*J. Org. Chem.* 2021, 86, 1262−1272

**Scheme 1. Kinetic Resolution of [2.2]Paracyclophane-Derived Cyclic Imines via Pd-Catalyzed Addition of Arylboronic Acids**

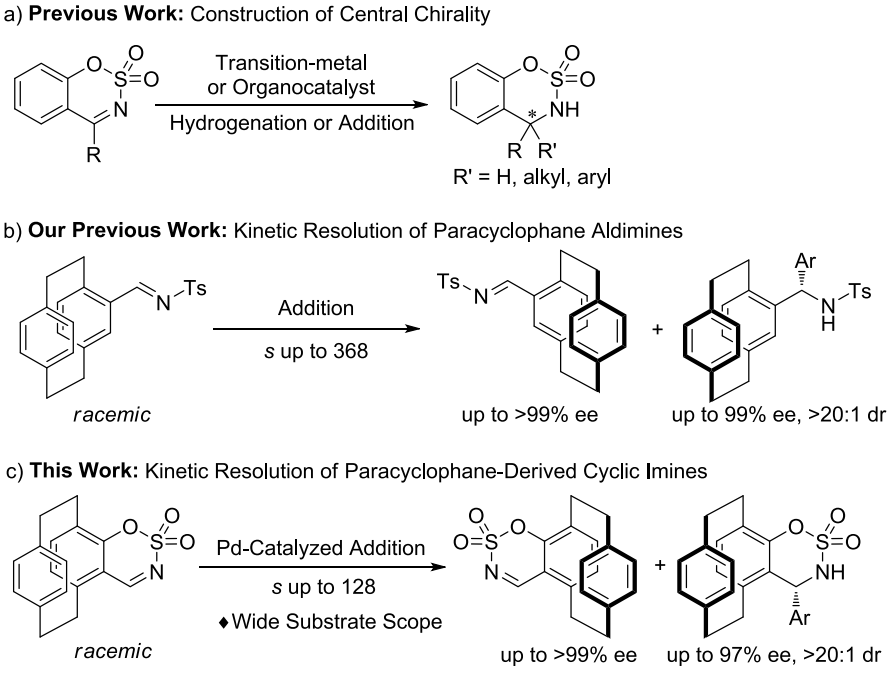
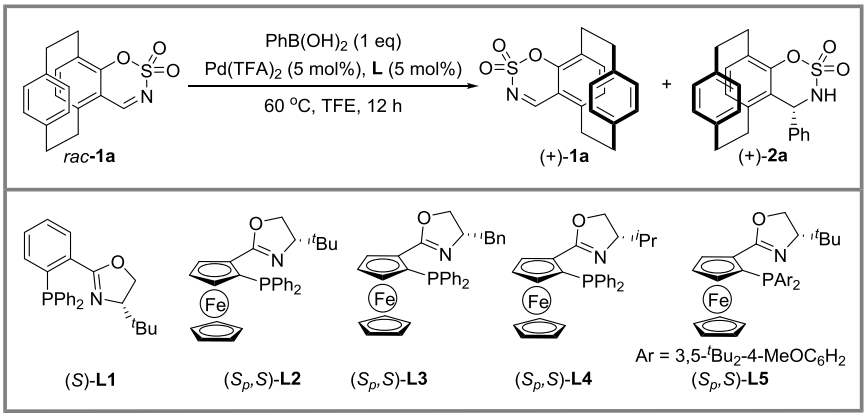



**Table 1. Optimization of the Kinetic Resolution**




| entry[a] | L | solvents | 1a conversion (%)[b] | 1a ee (%)[c] | 2a ee[c](dr)[b] | s[d] |
|---|---|---|---|---|---|---|
| 1 | L1 | TFE | 52 | 93.0 | 98.9 (8:1) | 44.4 |
| 2 | L2 | TFE | 51 | 97.0 | 99.1 (9:1) | 119.5 |
| 3 | L3 | TFE | 50 | 94.6 | 94.2 (>20:1) | 132.0 |
| 4 | L4 | TFE | 55 | 96.6 | 87.2 (>20:1) | 34.1 |
| 5 | L5 | TFE | 50 | 90.1 | 98.6 (16:1) | 59.2 |
| 6 | L3 | DCE | <5 | | | |
| 7 | L3 | 1,4-dioxane | <5 | | | |
| 8 | L3 | HFIP | <5 | | | |
| 9[e] | L3 | TFE | 30 | 40.5 | 96.3 (>20:1) | 52.6 |
| 10[f] | L3 | TFE | 51 | 96.3 | 91.5 (>20:1) | 103.2 |
| 11[g] | L3 | TFE | 51 | 96.4 | 93.8 (>20:1) | 105.2 |
| 12[h] | L3 | TFE | 40 | 63.2 | 96.8 (>20:1) | 71.9 |

[a]Conditions: *rac*-**1a** (0.10 mmol), $PhB(OH)_2$ (0.10 mmol), $Pd(OCOCF_3)_2$ (5.0 mol %), **L** (5.0 mol %), TFE (2.0 mL), 60 °C, 12 h. [b]Determined by $^1H$ NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. [c]Determined by chiral HPLC analysis. [d]Calculated selectivity factors: $C$ = conversion, $s = \ln[(1 - C)(1 - \text{ee of } \mathbf{1a})]/\ln[(1 - C)(1 + \text{ee of } \mathbf{1a})]$. [e]The reaction was carried out at 40 °C. [f]The reaction was carried out at 80 °C. [g]Using 1.5 equiv of $PhB(OH)_2$ (0.15 mmol). [h]Using 0.6 equiv of $PhB(OH)_2$ (0.06 mmol).

catalyst (5.0 mol % catalyst loading), arylboronic acid as a nucleophile (1.0 equiv), 2,2,2-trifluoroethanol (2.0 mL) as a solvent to perform the reaction at 60 °C, delivering excellent selectivity factor ($s$ = 132.0).



https://dx.doi.org/10.1021/acs.joc.0c02509
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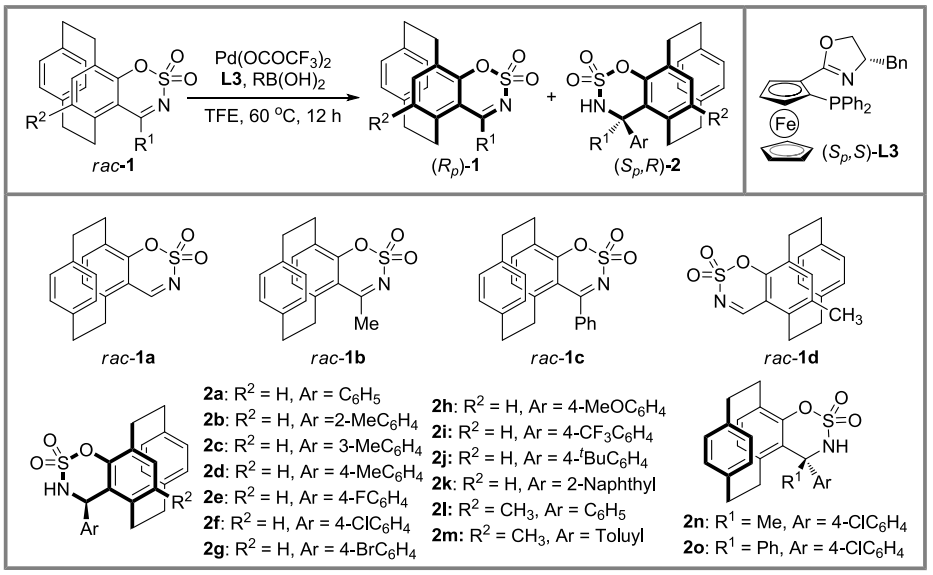
**Table 2. Substrate Scope for the Kinetic Resolution of [2.2]Paracyclophane Imines**




| entry[a] | *rac*-**1** conversion (%)[b] | **1** yield (%) | **1** ee (%)[c] | **2** | **2** yield (%) | **2** ee (%)[c] | **2** dr[b] | *s*[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | 51 | 48 | 97.3 | **2a** | 48 | 93.7 | >20:1 | 128.0 |
| 2 | 30 | 67 | 40.0 | **2b** | 28 | 94.2 | >20:1 | 42.9 |
| 3 | 52 | 45 | 95.6 | **2c** | 48 | 87.3 | >20:1 | 61.2 |
| 4 | 51 | 48 | 83.3 | **2d** | 49 | 79.7 | >20:1 | 23.3 |
| 5 | 52 | 46 | 98.7 | **2e** | 47 | 91.9 | >20:1 | 107.2 |
| 6 | 46 | 50 | 81.4 | **2f** | 45 | 97.1 | >20:1 | 111.3 |
| 7 | 40 | 59 | 63.6 | **2g** | 37 | 96.1 | >20:1 | 81.9 |
| 8 | 60 | 38 | 68.6 | **2h** | 59 | 45.9 | >20:1 | 5.3 |
| 9 | 20 | 78 | 23.5 | **2i** | 17 | 91.0 | >20:1 | 40.7 |
| 10 | 40 | 59 | 50.1 | **2j** | 36 | 75.6 | >20:1 | 11.5 |
| 11 | 24 | 75 | 29.8 | **2k** | 22 | 95.6 | >20:1 | 46.2 |
| 12 | 41 | 57 | 65.9 | **2l** | 38 | 97.1 | >20:1 | 74.9 |
| 13 | 30 | 69 | 36.4 | **2m** | 25 | 88.5 | >20:1 | 17.5 |
| 14 | <5 | | | **2n** | | | | |
| 15 | <5 | | | **2o** | | | | |

[a]Conditions: *rac*-**1** (0.20 mmol), $PhB(OH)_2$ (0.20 mmol), $Pd(OCOCF_3)_2$ (5.0 mol %), **L3** (5.0 mol %), TFE (4.0 mL), 60 °C, 12 h. [b]Determined by $^1H$ NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. [c]Determined by chiral HPLC analysis. [d]Calculated selectivity factors: $C$ = conversion, $s = \ln[(1 - C)(1 - \text{ee of } \mathbf{1})]/\ln[(1 - C)(1 + \text{ee of } \mathbf{1})]$.

After establishing the optimal conditions, we examined the substrate generality of kinetic resolution. A broad range of arylboronic acids could be resolved. The steric hindrance of the arylboronic acids had a negligible effect on the selectivity factor (Table 2, entries 2−4). In addition, the arylboronic acid bearing an *ortho* substituent showed very low reactivity. The electron-deficient arylboronic acids containing halo- or trifluoromethyl were also well tolerated (Table 2, entries 5−7 and 9). Arylboronic acids bearing electron-donating groups showed slightly higher activity than those bearing electron-withdrawing groups but with a very low selectivity factor (Table 2, entry 8). Moreover, the addition of 4-*tert*-butylphenylboronic acid and 2-naphthaleneboronic acid to imine **1a** proceeded smoothly (Table 2, entries 10 and 11). For aliphatic boronic acids including methylboronic acid and *trans*-2-phenylvinylboronic acid, no reaction occurred under the standard conditions. Besides, boronate esters including 2,4,4,5,5-pentamethyl-[1,3,2]dioxaborolane, 2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxoborole, and 4,4,5,5-tetramethyl-2-((*E*)-styryl)-[1,3,2]-dioxaborolane were not reactive. To further estimate the application possibility, [2.2]paracyclophane-derived cyclic *N*-sulfonylketimines (**1b**, **1c**) and 8-substituted [2.2]-paracyclophane-based cyclic *N*-sulfonylimine (**1d**) were synthesized. Probably owing to steric effects, no desired products were observed when **1b** and **1c** were used as substrates. Fortunately, the 8-substituted [2.2]paracyclophane-based cyclic *N*-sulfonylimine (**1d**) was also a suitable reaction partner, and the reaction worked well with moderate selectivity (Table 2, entries 12 and 13).

Next, the potential synthetic utility of this method was demonstrated. We performed a gram-scale reaction and derivatizations of recovered material ($R_p$)-**1a** and addition adduct ($S_p$,*R*)-**2a**. Gratifyingly, this strategy could be successfully applied to the scale-up reaction of *rac*-**1a** (2 mmol) with phenylboronic acid under the standard conditions (Scheme 2a), and the kinetic selectivity factor of this reaction was similar to those obtained in the small-scale reaction. The addition of phenylboronic acid and imine (+)-**1a** (49.6% ee) proceeded again to get the material (+)-**1a** with 99% ee. In addition, some transformations of [2.2]paracyclophane-based planar chiral imine ($R_p$)-**1a** were performed (Scheme 2b). Planar chiral products ($R_p$,*S*)-**2a**, ($R_p$,*S*)-**3**, and ($R_p$)-**4** were obtained in high


https://dx.doi.org/10.1021/acs.joc.0c02509
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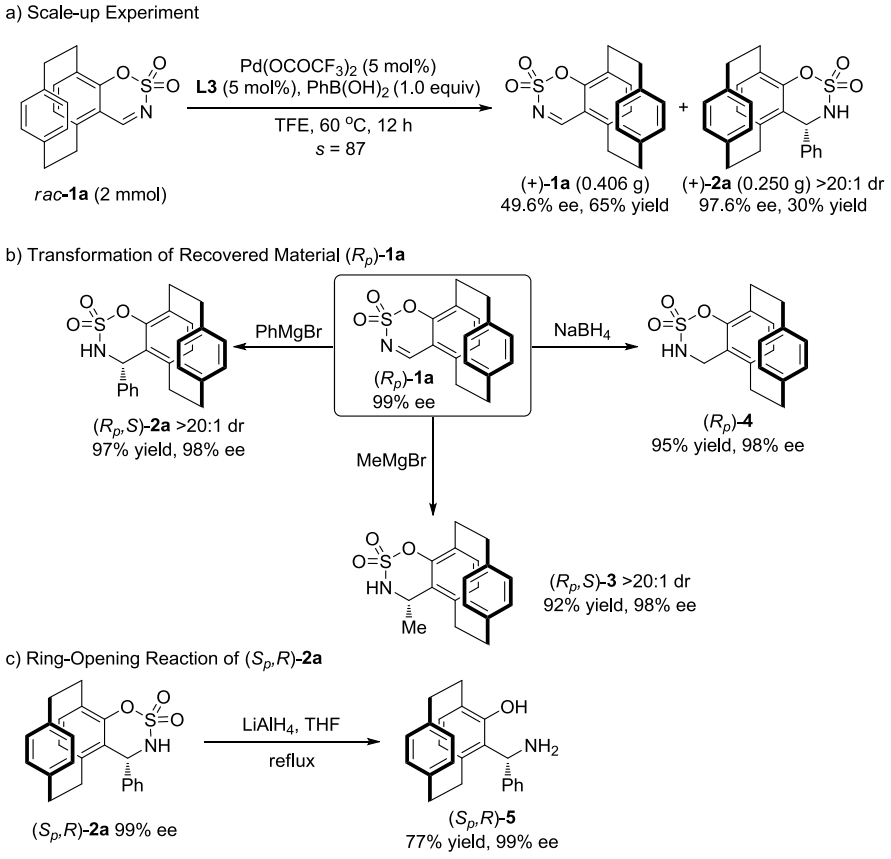
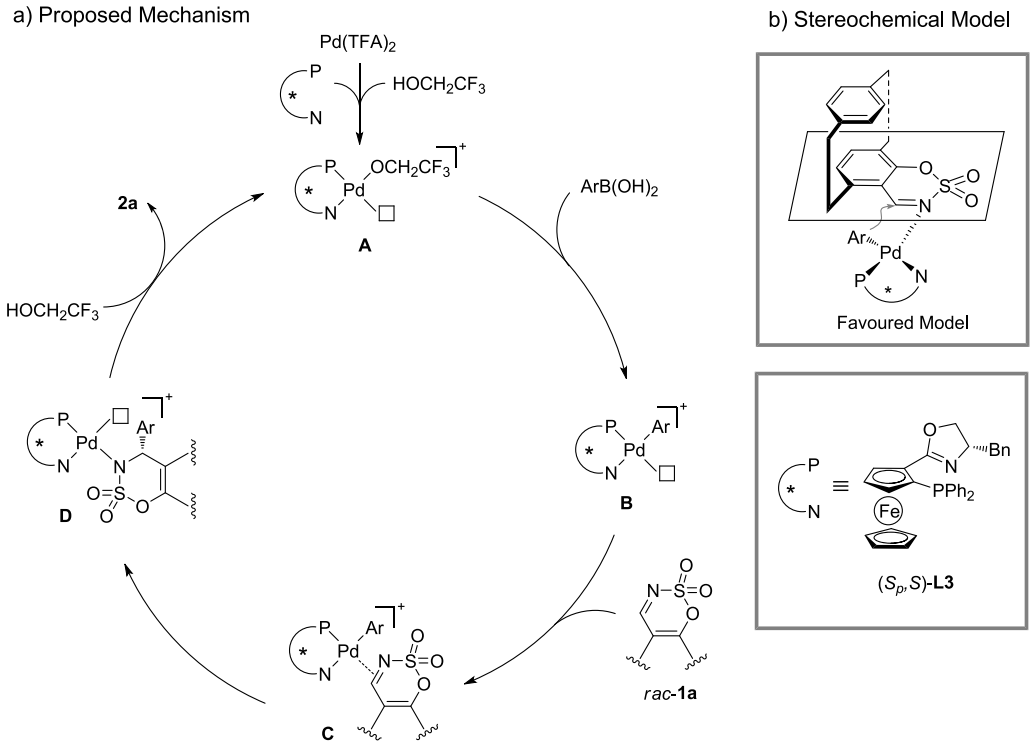
**Scheme 2. Scale-up Reaction and Elaborations of Recovered Material ($R_p$)-1a and Product ($S_p$,$R$)-2a**




**Scheme 3. Proposed Mechanism and Stereochemical Model**




yields with excellent retention of the enantiopurity. The carbon−nitrogen double bond of ($R_p$)-**1a** was reduced with sodium borohydride conveniently to ($R_p$)-**4**. When phenyl magnesium bromide and methyl magnesium bromide were used as nucleophiles to react with ($R_p$)-**1a**, good stereoselectivity was observed in these cases because of the substantial rigidity of the



https://dx.doi.org/10.1021/acs.joc.0c02509
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[2.2]paracyclophane backbone. With lithium aluminum hydride as the nucleophilic reagent, the ring opening of addition adduct ($S_p$,$R$)-**2a** was carried out to synthesize [2.2]paracyclophane-derived amino phenol ($S_p$,$R$)-**5** in 77% yield without the loss of optical purity (Scheme 2c).

To obtain more insight into the mechanism, we performed the addition of ($R_p$)-**1a** with 99% ee under the standard conditions, and no reaction occurred. According to the above experimental results and putative mechanism on palladium-catalyzed arylation of imines,[7h] a proposed mechanism was shown in Scheme 3a. First, the cationic palladium complex **A** was generated in the presence of $Pd(TFA)_2$, phosphinooxazoline ligand, and 2,2,2-trifluoroethanol. After that, the cationic palladium complex **A** underwent transmetalation with arylboronic acid to form Ar—Pd complex **B**. Coordination of cyclic *N*-sulfonylimine **1a** with **B** led to form intermediate **C**, which allowed insertion of the C═N bond into the Pd—C bond to form **D**. Alcoholysis of intermediate **D** afforded the addition product **2a** and regenerated the active Pd(II) complex **A**. The key to achieving kinetic resolution was the selective reaction of intermediate **B** with a single enantiomer of **1a**. On the basis of the above experimental results and absolute configuration of addition product ($S_p$,$R$)-**2a**, ($S_p$)-**1a** matched the ligand ($S_p$,$R$)-**L3**. The stereochemical model of this reaction was proposed as shown in Scheme 3b. The *N*-sulfonylimine **1a** coordinated with Pd(II) *cis* to an oxazoline motif with the benzene ring of the [2.2]paracyclophane framework oriented upward as a result of a steric effect, and the insertion of Ar—Pd species to **1a** occurred at the downward face. The favored model in which ($S_p$)-**1a** bound to the palladium center avoided the steric interaction between the benzyl group of oxazoline moiety and the benzene ring of [2.2]paracyclophane framework, giving the product **2a** with the observed ($S_p$,$R$) configuration.

In conclusion, we have demonstrated the feasibility of the kinetic resolution of [2.2]paracyclophane-derived cyclic *N*-sulfonylimine using the palladium-catalyzed addition of arylboronic acids. This strategy offers two kinds of planar chiral [2.2]paracyclophane derivatives in good diastereoselectivities (up to >20:1 dr) and excellent enantioselectivities (up to 99% ee) with high selectivity factors (*s* up to 128). This method not only provides easy access to the planar chiral [2.2]-paracyclophane-derived cyclic *N*-sulfonylimines but also offers a robust method for synthesizing cyclic sulfamidate derivatives bearing both planar and central chirality. The obtained enantioenriched derivatives incorporating reactive groups are suitable for late-stage functionalization. As a result, these compounds may reveal particular uses as synthetic intermediates to rapidly access more complex planar chiral [2.2]-paracyclophanes in their enantiopure form. Such work is ongoing, and the results will be reported in due course.

## EXPERIMENTAL SECTION

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 and $^{13}$C NMR spectra were recorded at 400 and 100 MHz with a Bruker spectrometer, respectively. $^{19}$F NMR spectra were recorded at 376 MHz with a Bruker spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as an internal standard when using $CDCl_3$ as a solvent for $^1$H NMR spectra. The following abbreviations were used to symbolize the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, brs = broad singlet. X-ray crystallography data were collected using a Bruker D8 Venture with 3.0 ius cu and 3.0 ius mo. Flash column chromatography was performed on silica gel (200−300 mesh). All reactions were monitored by TLC analysis. High-resolution mass spectrometry (HRMS (ESI-TOF) *m*/*z*) was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. The heat source in reaction procedures was an oil bath.

**Procedures for Synthesis of [2.2]Paracyclophane-Derived Cyclic *N*-Sulfonylimine.** [2.2]Paracyclophane-derived cyclic *N*-sulfonylimine **1** could be synthesized from substituted hydroxy[2.2]-paracyclophane and sulfamoyl chloride according to the literature procedures.[9] The substituted hydroxy[2.2]paracyclophane 5-formyl-4-hydroxy[2.2]paracyclophane, 5-acetyl-4-hydroxy[2.2]-paracyclophane, and 5-benzoyl-4-hydroxy[2.2]paracyclophane are known compounds and prepared by the literature procedures.[10] 4-Hydroxy-5-formyl-7-methyl[2.2]paracyclophane could be conveniently synthesized from 4-formyl-7-methyl[2.2]paracyclophane. 4-Formyl-7-methyl[2.2]-paracyclophane was prepared by the literature procedures.[4g]

Following a known literature procedure,[9] anhydrous formic acid (1.841 g, 1.51 mL, 40 mmol) was added dropwise to neat chlorosulfonyl isocyanate (5.661 g, 3.48 mL, 40 mmol) at 0 °C with rapid stirring. Vigorous gas evolution was observed during the addition process. The resulting viscous suspension was stirred at room temperature until gas evolution ceased (1−2 h). The liquid was removed to give the product sulfamoyl chloride ($H_2NSO_2Cl$).

*Method A.* To a solution of substituted hydroxy[2.2]paracyclophane (1.0 equiv) in *N*,*N*-dimethylacetamide (0.24 M) was quickly transferred at once solid $H_2NSO_2Cl$ (5.2 equiv) at 0 °C. Caution: the combination of these two compounds is slightly exothermic. The solution was allowed to warm to room temperature and was stirred for 12 h. The reaction was quenched by the addition of water (30 mL), and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). After drying over anhydrous sodium sulfate, filtration, and volatile removal under the reduced pressure, the crude residue was purified by silica gel column chromatography to afford the compound.

*Method B.* A mixture of substituted hydroxy[2.2]paracyclophane (1.0 equiv) was dissolved in toluene (0.10 M), and $H_2NSO_2Cl$ (2.0 equiv) was added. Then the reaction mixture was heated at reflux for 10 h. The reaction was quenched by the addition of water (30 mL), and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). After drying over anhydrous sodium sulfate, filtration, and volatile removal under the reduced pressure, the crude residue was purified by silica gel column chromatography as an eluent to afford the compound.

**[2.2]Paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1a).** The reaction was performed according to Method A using 5-formyl-4-hydroxy[2.2]paracyclophane (3.071 g, 12 mmol, 1.0 equiv) and $H_2NSO_2Cl$ (7.168 g, 62 mmol, 5.2 equiv) for 12 h, and the crude mixture was purified using hexanes and ethyl acetate as an eluent to give *N*-sulfonylimine **1a**: 2.371 g, 63% yield, yellow solid, mp = 232−234 °C. New compound: $R_f$ = 0.50 (hexanes/ethyl acetate 2:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.49 (s, 1H), 6.90−6.83 (m, 2H), 6.69−6.62 (m, 2H), 6.52−6.45 (m, 1H), 6.36−6.29 (m, 1H), 3.70−3.59 (m, 1H), 3.52−3.43 (m, 1H), 3.41−3.31 (m, 1H), 3.26−2.97 (m, 4H), 2.84−2.72 (m, 1H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 164.7, 153.8, 144.7, 143.1, 139.9, 137.8, 133.9, 133.0, 132.1, 131.1, 129.5, 128.2, 117.1, 35.5, 34.0, 31.5, 28.6. HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{16}NO_3S$ $[M + H]^+$, 314.0845; found, 314.0845.

**4-Methyl-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1b).** The reaction was performed according to Method A using 5-acetyl-4-hydroxy[2.2]paracyclophane (1.224 g, 4.6 mmol, 1.0 equiv) and $H_2NSO_2Cl$ (2.761 g, 23.9 mmol, 5.2 equiv) for 12 h, and the crude mixture was purified using hexanes and ethyl acetate as an eluent to give *N*-sulfonylimine **1b**: 1.301 g, 87% yield, yellow solid, mp = 183−185 °C. New compound: $R_f$ = 0.70 (hexanes/ethyl acetate 2:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.95−6.90 (m, 1H), 6.76−6.67 (m, 2H), 6.66−6.61 (m, 1H), 6.57−6.52 (m, 1H), 6.37−6.31 (m, 1H), 3.65−3.53 (m, 1H), 3.51−3.41 (m, 1H), 3.35−3.14 (m, 3H), 3.08−2.95 (m, 2H), 2.87−2.77 (m, 1H), 2.70 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 176.3, 154.0, 143.7, 142.0, 139.8, 137.8, 133.8, 133.7, 132.4, 130.4, 129.2, 117.7, 37.2, 35.9, 34.5, 28.5, 28.1. HRMS (ESI-


https://dx.doi.org/10.1021/acs.joc.0c02509
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TOF): $m/z$ calcd for $C_{18}H_{18}NO_3S$ $[M + H]^+$, 328.1002; found, 328.1004.

**4-Phenyl-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1c).** The reaction was performed according to Method B using 5-benzoyl-4-hydroxy[2.2]paracyclophane (1.641 g, 5.0 mmol, 1.0 equiv) and $H_2NSO_2Cl$ (1.155 g, 10.0 mmol, 2.0 equiv) for 10 h, and the crude mixture was purified using hexanes and ethyl acetate as an eluent to give *N*-sulfonylimine **1c**: 1.197 g, 63% yield, yellow solid, mp = 262−264 °C. New compound: $R_f$ = 0.30 (hexanes/ethyl acetate 20:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.78−7.57 (m, 3H), 7.53−7.43 (m, 2H), 7.05−6.97 (m, 1H), 6.80−6.75 (m, 1H), 6.74−6.62 (m, 2H), 6.53−6.48 (m, 1H), 6.41−6.35 (m, 1H), 3.62−3.48 (m, 1H), 3.46−3.32 (m, 1H), 3.08−2.96 (m, 1H), 2.93−2.73 (m, 4H), 2.48−2.34 (m, 1H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 175.0, 155.5, 146.0, 142.8, 139.4, 138.0, 137.4, 134.3, 133.6, 133.0, 132.4, 131.7, 131.4, 130.3, 128.9, 128.5, 116.3, 36.8, 35.9, 34.9, 28.2. HRMS (ESI-TOF): $m/z$ calcd for $C_{23}H_{20}NO_3S$ $[M + H]^+$, 390.1158; found, 390.1151.

4-Formyl-7-methyl[2.2]paracyclophane (2.466 g, 10 mmol) was dissolved in a 9:1 mixture of dichloro-methane/methanol (50 mL/50 mL). Then concentrated sulfuric acid (40 drops) and aqueous hydrogen peroxide (2.00 mL, 30% wt in water) were subsequently added, and the solution was stirred for 4 h. The mixture was quenched with aqueous sodium thiosulfate. The two phases were separated, and the aqueous phase was extracted with dichloromethane (50 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using hexanes and ethyl acetate as an eluent to afford 4-hydroxy-7-methyl[2.2]paracyclophane **6** (colorless solid, 1.904 g, 80% yield). Mp: 185−187 °C. New compound: $R_f$ = 0.30 (hexanes/ethyl acetate 20:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.08−7.01 (m, 1H), 6.86−6.80 (m, 1H), 6.49−6.44 (m, 1H), 6.43−6.38 (m, 1H), 6.08 (s, 1H), 5.51 (s, 1H), 4.66 (brs, 1H), 3.40−3.29 (m, 1H), 3.28−3.18 (m, 1H), 3.18−3.02 (m, 4H), 2.69−2.52 (m, 2H), 2.14 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 152.0, 139.9, 139.7, 139.0, 137.5, 132.9, 132.2, 129.7, 129.0, 128.9, 124.9, 123.5, 33.7, 33.5, 32.9, 30.9, 19.3. HRMS (ESI-TOF): $m/z$ calcd for $C_{17}H_{19}O$ $[M + H]^+$, 239.1430; found, 239.1430.

A dry 250 mL round-bottom flask was loaded with sodium hydride (0.152 g, 3.8 mmol, 60% wt) in a 9:1 mixture of anhydrous diethyl ether/*N*,*N*-dimethylformamide (18 mL:2 mL). 4-Hydroxy-7-methyl[2.2]paracyclophane **6** (0.773 g, 3.2 mmol) was added slowly, and the mixture was allowed to be stirred for 10 min at 0 °C; after that, chloromethyl methyl ether (2.2 mL, 4.8 mmol) was added under nitrogen while stirring. After 2 h, water (10 mL) was added, and the organic phase was separated and worked up as above. The crude product was purified by column chromatography on silica gel using hexanes and ethyl acetate as an eluent to afford 4-methoxymethoxy-7-methyl-[2.2]paracyclophane **7** (white solid, 0.596 g, 66% yield). Mp: 53−55 °C. New compound: $R_f$ = 0.30 (hexanes). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.91−6.85 (m, 1H), 6.83−6.77 (m, 1H), 6.50−6.44 (m, 1H), 6.42−6.36 (m, 1H), 6.08 (s, 1H), 5.91 (s, 1H), 5.16 (d, $J$ = 6.4 Hz, 1H), 5.05 (d, $J$ = 6.4 Hz, 1H), 3.55 (s, 3H), 3.47−3.36 (m, 1H), 3.30−3.19 (m, 1H), 3.16- 2.98 (m, 4H), 2.77−2.65 (m, 1H), 2.59−2.47 (m, 1H), 2.12 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 154.1, 140.0, 139.8, 139.0, 137.3, 132.7, 132.3, 130.7, 129.6, 128.8, 127.8, 122.0, 95.0, 56.4, 34.0, 33.7, 33.2, 31.1, 19.4. HRMS (ESI-TOF): $m/z$ calcd for $C_{19}H_{23}O_2$ $[M + H]^+$, 283.1693; found, 283.1690.

4-Methoxymethoxy-7-methyl[2.2]paracyclophane **7** (1.034 g, 3.7 mmol) was dissolved in diethyl ether (16 mL) containing *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.860 g, 1.10 mL, 7.4 mmol), and *n*-butyllithium (3.00 mL, 2.5 M in hexane, 7.4 mmol) was added at 0 °C under nitrogen while stirring. The mixture was allowed to react for 1.5 h at 0 °C, *N*,*N*-dimethylformamide (0.57 mL, 7.4 mmol) was added, and the reaction was allowed to proceed for 4 h at room temperature. Water was added, the organic phase was separated and washed with water, and the solvent was evaporated. The resulting crude oil was dissolved in tetrahydrofuran (4 mL), concentrated hydrochloric acid (2.00 mL) was added, and the mixture was kept at room temperature overnight. After neutralization with aqueous sodium bicarbonate, the mixture was extracted with dichloromethane (3 × 10 mL), and the solvent was evaporated at reduced pressure. The crude product was purified by column chromatography on silica gel using hexanes and ethyl acetate as an eluent to afford 4-hydroxy-5-formyl-7-methyl[2.2]paracyclophane **8** (yellow solid, 0.232 g, 19% yield). Mp: 145−147 °C. New compound: $R_f$ = 0.50 (hexanes/ethyl acetate 20:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 12.04 (s, 1H), 9.83 (s, 1H), 6.98−6.90 (m, 1H), 6.85−6.78 (m, 1H), 6.41−6.35 (m, 2H), 6.30−6.24 (m, 1H), 3.48−3.37 (m, 2H), 3.29−3.12 (m, 3H), 3.08−2.97 (m, 1H), 2.95−2.83 (m, 1H), 2.57−2.44 (m, 1H), 2.16 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 193.9, 160.9, 145.0, 143.3, 140.3, 137.9, 133.0, 132.8, 129.4, 128.9, 128.0, 127.0, 122.3, 34.4, 33.6, 29.3, 26.8, 19.8. HRMS (ESI-TOF): $m/z$ calcd for $C_{18}H_{19}O_2$ $[M + H]^+$, 267.1380; found, 267.1379.

**(8-Methyl[2.2]paracyclophano)[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1d).** The reaction was performed according to Method A using 4-hydroxy-5-formyl-7-methyl[2.2]paracyclophane **8** (0.232 g, 0.9 mmol, 1.0 equiv) and $H_2NSO_2Cl$ (0.543 g, 4.7 mmol, 5.2 equiv) for 12 h, and the crude mixture was purified using hexanes and ethyl acetate as an eluent to give *N*-sulfonylimine **1d**: 0.234 g, 72% yield, yellow solid, mp = 83−85 °C. New compound: $R_f$ = 0.50 (hexanes/ethyl acetate 5:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.53 (s, 1H), 6.91−6.84 (m, 2H), 6.53 (s, 1H), 6.45−6.39 (m, 1H), 6.34−6.28 (m, 1H), 3.50−3.15 (m, 5H), 3.14−3.01 (m, 2H), 2.75−2.60 (m, 1H), 2.23 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 165.0, 152.4, 145.1, 143.0, 139.8, 137.8, 135.7, 132.9, 132.7, 129.0, 128.8, 128.2, 117.3, 34.0, 33.8, 28.2, 26.7, 20.2. HRMS (ESI-TOF): $m/z$ calcd for $C_{18}H_{18}NO_3S$ $[M + H]^+$, 328.1002; found, 328.1003.

**General Procedure for Kinetic Resolution.** A Schlenk tube (25 mL) was charged with $Pd(OCOCF_3)_2$ (3.3 mg, 0.01 mmol, 5 mol %) and ($S_p$,*S*)-**L3** (5.0 mg, 0.01 mmol, 5 mol %) under nitrogen, and degassed anhydrous acetone (2.0 mL) was added. The mixture was stirred at room temperature for 1 h. The solvent was removed under a vacuum to give the catalyst. Then substrate *rac*-**1** (0.20 mmol), arylboronic acids (0.20 mmol) and 2,2,2-trifluoroethanol (4.0 mL) were added into the tube under nitrogen. The mixture was heated to 60 °C. After stirring at 60 °C for 12 h, the reaction mixture was cooled to room temperature, and the solvent was removed by rotary evaporation. The resulting mixture was dried under a vacuum, and the conversion of *rac*-**1** was confirmed by $^1$H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard. The solvent was removed under reduced pressure, and the recovered material (+)-**1** and addition product **2** were isolated by column chromatography on silica gel using hexanes and ethyl acetate as an eluent. The optical purity of products and starting materials was determined by chiral HPLC analysis.

**4-Phenyl-3,4-dihydro-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2a):** 37.9 mg, 48% yield, >20:1 dr, white solid, mp = 183−185 °C. New compound: $R_f$ = 0.50 (hexanes/ethyl acetate 10:1), 93.7% ee, $[\alpha]_D^{20}$ = +49.57 (*c* 0.94, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.39−7.30 (m, 3H), 7.26−7.20 (m, 2H), 7.03−6.97 (m, 1H), 6.90−6.82 (m, 1H), 6.63−6.55 (m, 3H), 6.39−6.32 (m, 1H), 5.51 (d, $J$ = 8.8 Hz, 1H), 4.63 (d, $J$ = 8.8 Hz, 1H), 3.46−3.34 (m, 1H), 3.29−3.16 (m, 1H), 3.10−2.90 (m, 3H), 2.82−2.70 (m, 1H), 2.62−2.45 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 151.6, 141.0, 139.9, 139.2, 138.5, 135.7, 133.4, 132.9, 131.6, 130.4, 129.2, 129.2, 129.1, 129.1, 128.3, 119.9, 61.3, 34.4, 34.0, 33.7, 29.1. HPLC: Chiracel IA column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 10.5 min (major) and 15.3 min. HRMS (ESI-TOF): $m/z$ calcd for $C_{23}H_{25}N_2O_3S$ $[M + NH_4]^+$, 409.1580; found, 409.1553.

**[2.2]Paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1a):** kinetic resolution from addition of imine **1a** with phenylboronic acid, 30.0 mg, 48% yield, 97.3% ee, $[\alpha]_D^{20}$ = +440.68 (*c* 0.70, $CHCl_3$). HPLC: Chiralcel OD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 19.6 min (major) and 23.8 min.

**4-Phenyl-3,4-dihydro-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2a′):** white solid, mp = 233−235 °C. New compound: $R_f$ = 0.30 (hexanes/ethyl acetate 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.87−7.71 (m, 2H), 7.64−7.42 (m, 3H), 6.65−6.55 (m, 3H), 6.51−6.45 (m, 1H), 6.33−6.26 (m, 1H), 5.46 (d, $J$ = 7.0 Hz, 1H), 5.37−5.29 (m, 1H), 5.10 (d, $J$ = 7.0 Hz, 1H), 3.57−3.40 (m, 1H),


https://dx.doi.org/10.1021/acs.joc.0c02509
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3.31−3.15 (m, 1H), 3.13−2.96 (m, 1H), 2.94−2.65 (m, 4H), 2.59−2.40 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.3, 139.9, 139.2, 138.6, 137.1, 136.2, 133.2, 132.9, 132.9, 131.2, 130.0, 129.5, 129.4, 128.9, 124.5, 61.2, 35.1, 34.6, 32.0, 28.7. HRMS (ESI-TOF): *m*/*z* calcd for $C_{23}H_{25}N_2O_3S$ $[M + NH_4]^+$, 409.1580; found, 409.1591.

**4-(*o*-Tolyl)-3,4-dihydro-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2b):** 23.0 mg, 28% yield, >20:1 dr, white solid, mp = 201−203 °C. New compound: $R_f$ = 0.50 (hexanes/ethyl acetate 5:1), 94.2% ee, $[\alpha]_D^{20}$ = +61.33 (*c* 0.60, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.28−7.22 (m, 2H), 7.09−6.97 (m, 2H), 6.92−6.86 (m, 1H), 6.83−6.77 (m, 1H), 6.65−6.53 (m, 3H), 6.36−6.29 (m, 1H), 5.75 (d, *J* = 9.3 Hz, 1H), 4.45 (d, *J* = 9.3 Hz, 1H), 3.45−3.34 (m, 1H), 3.29−3.19 (m, 1H), 3.09−2.89 (m, 3H), 2.82−2.72 (m, 1H), 2.62 (s, 3H), 2.57−2.48 (m, 1H), 2.41−2.31 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.9, 140.8, 140.0, 138.4, 137.5, 136.6, 135.6, 133.2, 132.7, 131.7, 130.9, 130.8, 129.3, 129.2, 129.1, 127.8, 126.8, 120.4, 57.8, 34.5, 34.5, 33.8, 29.0, 19.3. HPLC: Chiracel IA column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 10.8 min (major) and 21.5 min. HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{27}N_2O_3S$ $[M + NH_4]^+$, 423.1737; found, 423.1765.

**[2.2]Paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1a):** kinetic resolution from the addition of [2.2]paracyclophane imine **1a** with 2-methylphenylboronic acid, 42.0 mg, 67% yield, 40.0% ee. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 19.5 min (major) and 23.5 min.

**4-(*m*-Tolyl)-3,4-dihydro-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2c):** 39.0 mg, 48% yield, >20:1 dr, white solid, mp = 247−249 °C. New compound: $R_f$ = 0.45 (hexanes/ethyl acetate 5:1), 87.3% ee, $[\alpha]_D^{20}$ = +41.11 (*c* 0.90, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.24−7.18 (m, 1H), 7.18−7.13 (m, 1H), 7.09−7.04 (m, 1H), 7.03−6.96 (m, 2H), 6.88−6.81 (m, 1H), 6.64−6.54 (m, 3H), 6.37−6.30 (m, 1H), 5.47 (d, *J* = 9.0 Hz, 1H), 4.40 (d, *J* = 9.0 Hz, 1H), 3.48−3.35 (m, 1H), 3.29−3.18 (m, 1H), 3.09−2.90 (m, 3H), 2.83−2.72 (m, 1H), 2.59−2.47 (m, 2H), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.7, 141.1, 139.9, 139.2, 139.0, 138.5, 135.7, 133.3, 132.8, 131.7, 130.6, 130.0, 129.3, 129.1, 129.1, 129.0, 125.2, 120.2, 61.4, 34.5, 34.1, 33.8, 29.0, 21.5. HPLC: Chiracel IA column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 10.3 min (major) and 14.9 min. HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{27}N_2O_3S$ $[M + NH_4]^+$, 423.1737; found, 423.1751.

**[2.2]Paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1a):** kinetic resolution from the addition of [2.2]paracyclophane imine **1a** with 3-methylphenylboronic acid, 28.0 mg, 45% yield, 95.6% ee. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 19.4 min (major) and 23.4 min.

**4-(*p*-Tolyl)-3,4-dihydro-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2d):** 40.0 mg, 49% yield, >20:1 dr, white solid, mp = 259−261 °C. New compound: $R_f$ = 0.45 (hexanes/ethyl acetate 5:1), 79.7% ee, $[\alpha]_D^{20}$ = +39.30 (*c* 0.72, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.17−7.08 (m, 4H), 7.02−6.95 (m, 1H), 6.88−6.81 (m, 1H), 6.63−6.54 (m, 3H), 6.37−6.30 (m, 1H), 5.48 (d, *J* = 8.9 Hz, 1H), 4.53 (d, *J* = 8.8 Hz, 1H), 3.46−3.34 (m, 1H), 3.30−3.15 (m, 1H), 3.09−2.89 (m, 3H), 2.81−2.70 (m, 1H), 2.61−2.47 (m, 2H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.6, 141.1, 139.9, 139.1, 138.5, 136.3, 135.6, 133.3, 132.8, 131.6, 130.5, 129.8, 129.2, 129.1, 128.1, 120.2, 61.1, 34.5, 34.1, 33.8, 29.1, 21.3. HPLC: Chiracel IA column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 12.8 min (major) and 20.9 min. HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{24}NO_3S$ $[M + H]^+$, 406.1471; found, 406.1474.

**[2.2]Paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1a):** kinetic resolution from the addition of [2.2]paracyclophane imine **1a** with 4-methylphenylboronic acid, 30.0 mg, 48% yield, 83.3% ee. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 19.1 min (major) and 23.0 min.

**4-(4-Fluorophenyl)-3,4-dihydro-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2e):** 39.0 mg, 47% yield, >20:1 dr, white solid, mp = 224−226 °C. New compound: $R_f$ = 0.30 (hexanes/ethyl acetate 5:1), 91.9% ee, $[\alpha]_D^{20}$ = +52.69 (*c* 0.78, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.24−7.15 (m, 2H), 7.09−6.92 (m, 3H), 6.92−6.77 (m, 1H), 6.68−6.55 (m, 3H), 6.46−6.29 (m, 1H), 5.48 (d, *J* = 8.5 Hz, 1H), 4.91 (d, *J* = 8.5 Hz, 1H), 3.49−3.31 (m, 1H), 3.28−3.11 (m, 1H), 3.11−2.87 (m, 3H), 2.83−2.65 (m, 1H), 2.64−2.44 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.9 (C−F, $^1J_{C-F}$ = 248.6 Hz), 151.3, 140.6, 140.0, 138.4, 135.7, 135.0 (C−F, $^4J_{C-F}$ = 3.5 Hz), 133.6, 133.1, 131.5, 130.1, 130.1 (C−F, $^3J_{C-F}$ = 12.5 Hz), 129.5, 128.9, 119.4, 115.9 (C−F, $^2J_{C-F}$ = 21.7 Hz), 60.4, 34.3, 33.9, 33.5, 29.2. $^{19}F$ NMR (376 MHz, $CDCl_3$): δ −112.3. HPLC: Chiracel IA column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 10.3 min (major) and 13.2 min. HRMS (ESI-TOF): *m*/*z* calcd for $C_{23}H_{24}FN_2O_3S$ $[M + NH_4]^+$, 427.1486; found, 427.1471.

**[2.2]Paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1a):** kinetic resolution from the addition of [2.2]paracyclophane imine **1a** with 4-fluorophenylboronic acid, 29.0 mg, 46% yield, 98.7% ee. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 19.4 min (major) and 23.5 min.

**4-(4-Chlorophenyl)-3,4-dihydro-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2f):** 38.0 mg, 45% yield, >20:1 dr, white solid, mp = 247−249 °C. New compound: $R_f$ = 0.30 (hexanes/ethyl acetate 5:1), 97.1% ee, $[\alpha]_D^{20}$ = +44.21 (*c* 0.76, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.32−7.27 (m, 2H), 7.21−7.14 (m, 2H), 7.01−6.96 (m, 1H), 6.84−6.78 (m, 1H), 6.64−6.57 (m, 3H), 6.43−6.36 (m, 1H), 5.46 (d, *J* = 8.4 Hz, 1H), 4.94 (d, *J* = 8.5 Hz, 1H), 3.44−3.32 (m, 1H), 3.26−3.14 (m, 1H), 3.12−2.90 (m, 3H), 2.81−2.69 (m, 1H), 2.67−2.47 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.3, 140.5, 140.0, 138.4, 137.5, 135.8, 134.9, 133.6, 133.1, 131.4, 129.9, 129.7, 129.6, 129.2, 128.8, 119.0, 60.4, 34.2, 33.9, 33.5, 29.2. HPLC: Chiracel IA column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 11.3 min (major) and 12.6 min. HRMS (ESI-TOF): *m*/*z* calcd for $C_{23}H_{21}ClNO_3S$ $[M + H]^+$, 426.0925; found, 426.0927 ($^{35}Cl$) and 428.0898 ($^{37}Cl$).

**[2.2]Paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1a):** kinetic resolution from the addition of [2.2]paracyclophane imine **1a** with 4-chlorophenylboronic acid, 31.0 mg, 50% yield, 81.4% ee. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 19.3 min (major) and 23.3 min.

**4-(4-Bromophenyl)-3,4-dihydro-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2g):** 35.0 mg, 37% yield, >20:1 dr, white solid, mp = 247−249 °C. New compound: $R_f$ = 0.40 (hexanes/ethyl acetate 10:1), 96.1% ee, $[\alpha]_D^{20}$ = +41.00 (*c* 0.50, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.48−7.41 (m, 2H), 7.15−7.07 (m, 2H), 7.01−6.94 (m, 1H), 6.83−6.77 (m, 1H), 6.63−6.56 (m, 3H), 6.42−6.36 (m, 1H), 5.44 (d, *J* = 8.5 Hz, 1H), 4.90 (d, *J* = 8.5 Hz, 1H), 3.45−3.33 (m, 1H), 3.25−3.14 (m, 1H), 3.12−2.90 (m, 3H), 2.82−2.69 (m, 1H), 2.68−2.47 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.4, 140.5, 140.0, 138.4, 138.1, 135.8, 133.6, 133.1, 132.1, 131.4, 130.0, 129.9, 129.6, 128.7, 123.1, 119.0, 60.4, 34.2, 33.9, 33.5, 29.2. HPLC: Chiracel IC column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 9.2 min (major) and 10.2 min. HRMS (ESI-TOF): *m*/*z* calcd for $C_{23}H_{21}BrNO_3S$ $[M + H]^+$, 470.0420; found, 470.0419 ($Br^{79}$) and 472.0397 ($Br^{81}$).

**[2.2]Paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1a):** kinetic resolution from the addition of [2.2]paracyclophane imine **1a** with 4-bromophenylboronic acid, 37.0 mg, 59% yield, 63.6% ee. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 19.0 min (major) and 22.9 min.

**4-(4-Methoxyphenyl)-3,4-dihydro-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2h):** 50.0 mg, 59% yield, >20:1 dr, white solid, mp = 192−194 °C. New compound: $R_f$ = 0.50 (hexanes/ethyl acetate 5:1), 45.9% ee, $[\alpha]_D^{20}$ = +21.46 (*c* 0.82, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.18−7.11 (m, 2H), 7.01−6.95 (m, 1H), 6.87−6.80 (m, 3H), 6.62−6.54 (m, 3H), 6.37−6.31 (m, 1H), 5.47 (d, *J* = 8.7 Hz, 1H), 4.57 (d, *J* = 8.7 Hz, 1H), 3.79 (s, 3H), 3.44−3.34 (m, 1H), 3.27−3.16 (m, 1H), 3.08−2.89 (m, 3H), 2.81−2.69 (m, 1H),


https://dx.doi.org/10.1021/acs.joc.0c02509
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2.60−2.47 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.0, 151.5, 141.1, 139.9, 138.5, 135.6, 133.3, 132.9, 131.6, 131.3, 130.5, 129.5, 129.2, 129.2, 120.3, 114.4, 60.8, 55.4, 34.4, 34.1, 33.8, 29.1. HPLC: Chiracel IA column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 16.8 min (major) and 20.5 min. HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{24}NO_4S$ $[M + H]^+$, 422.1421; found, 422.1428.

**[2.2]Paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1a):** kinetic resolution from the addition of [2.2]paracyclophane imine **1a** with 4-methoxyphenylboronic acid, 24.0 mg, 38% yield, 68.6% ee. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 19.3 min (major) and 22.7 min.

**4-(4-Trifluoromethylphenyl)-3,4-dihydro-[2.2]-paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2i):** 16.0 mg, 17% yield, >20:1 dr, white solid, mp = 221−223 °C. New compound: $R_f$ = 0.45 (hexanes/ethyl acetate 10:1), 91.0% ee, $[\alpha]_D^{20}$ = +53.00 (*c* 0.20, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.62−7.54 (m, 2H), 7.41−7.34 (m, 2H), 7.01−6.94 (m, 1H), 6.82−6.75 (m, 1H), 6.67−6.58 (m, 3H), 6.45−6.39 (m, 1H), 5.56−5.48 (m, 1H), 4.98−4.89 (m, 1H), 3.49−3.34 (m, 1H), 3.26−3.14 (m, 1H), 3.13−3.02 (m, 2H), 3.02−2.92 (m, 1H), 2.83−2.71 (m, 1H), 2.69−2.58 (m, 1H), 2.55−2.44 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.4, 142.8, 140.4, 140.1, 138.3, 136.0, 133.8, 133.2, 131.4, 131.1 (C−F, $^2J_{C-F}$ = 32.5 Hz), 129.8, 129.8, 128.7, 128.6, 126.0 (C−F, $^3J_{C-F}$ = 3.6 Hz), 123.9 (C−F, $^1J_{C-F}$ = 272.3 Hz), 118.5, 60.5, 34.2, 33.9, 33.4, 29.3. $^{19}F$ NMR (376 MHz, $CDCl_3$): δ −62.7. HPLC: Chiracel AD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 9.4 and 10.3 min (major). HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{21}F_3NO_3S$ $[M + H]^+$, 460.1189; found, 460.1178.

**[2.2]Paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1a):** kinetic resolution from the addition of [2.2]paracyclophane imine **1a** with 4-trifluoromethylphenylboronic acid, 49.0 mg, 78% yield, 23.5% ee. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 19.3 min (major) and 23.3 min.

**4-(4-*tert*-Butylphenyl)-3,4-dihydro-[2.2]paracyclophano-[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2j):** 32.0 mg, 36% yield, >20:1 dr, white solid, mp = 119−121 °C. New compound: $R_f$ = 0.60 (hexanes/ethyl acetate 10:1), 75.6% ee, $[\alpha]_D^{20}$ = +37.78 (*c* 0.54, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.38−7.31 (m, 2H), 7.18−7.13 (m, 2H), 7.02−6.97 (m, 1H), 6.89−6.83 (m, 1H), 6.63−6.54 (m, 3H), 6.37−6.30 (m, 1H), 5.54−5.46 (m, 1H), 4.55−4.46 (m, 1H), 3.46−3.33 (m, 1H), 3.29−3.16 (m, 1H), 3.09−2.89 (m, 3H), 2.81−2.70 (m, 1H), 2.61−2.47 (m, 2H), 1.30 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.2, 151.6, 141.1, 139.9, 138.5, 136.1, 135.6, 133.3, 132.8, 131.6, 130.5, 129.3, 129.1, 127.9, 126.1, 120.3, 61.0, 34.8, 34.5, 34.1, 33.9, 31.4, 29.0. HPLC: Chiracel IA column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 10.5 min (major) and 13.7 min. HRMS (ESI-TOF): *m*/*z* calcd for $C_{27}H_{29}NaNO_3S$ $[M + Na]^+$, 470.1760; found, 470.1746.

**[2.2]Paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1a):** kinetic resolution from the addition of [2.2]paracyclophane imine **1a** with 4-*tert*-butylphenylboronic acid, 37.0 mg, 59% yield, 50.1% ee. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 19.0 min (major) and 22.8 min.

**4-(2-Naphthyl)-3,4-dihydro-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2k):** 19.0 mg, 22% yield, >20:1 dr, white solid, mp = 124−126 °C. New compound: $R_f$ = 0.50 (hexanes/ethyl acetate 10:1), 95.6% ee, $[\alpha]_D^{20}$ = +22.17 (*c* 0.23, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.86−7.79 (m, 2H), 7.79−7.73 (m, 1H), 7.72−7.67 (m, 1H), 7.55−7.45 (m, 2H), 7.38−7.32 (m, 1H), 7.06−7.00 (m, 1H), 6.92−6.85 (m, 1H), 6.65−6.56 (m, 3H), 6.40−6.34 (m, 1H), 5.68 (d, *J* = 8.8 Hz, 1H), 4.69 (d, *J* = 8.8 Hz, 1H), 3.54−3.38 (m, 1H), 3.30−3.17 (m, 1H), 3.11−2.92 (m, 3H), 2.88−2.71 (m, 1H), 2.62−2.44 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.7, 141.1, 140.0, 138.5, 136.4, 135.8, 133.5, 133.4, 133.2, 132.9, 131.7, 130.5, 129.3, 129.2, 128.3, 127.9, 127.7, 127.0, 126.8, 125.6, 119.9, 61.5, 34.4, 34.1, 33.8, 29.1. HPLC: Chiracel IA column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 15.4 min (major) and 24.5 min. HRMS (ESI-TOF): *m*/*z* calcd for $C_{27}H_{23}KNO_3S$ $[M + K]^+$, 480.1030; found, 480.1053.

**[2.2]Paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1a):** kinetic resolution from the addition of [2.2]paracyclophane imine **1a** with 2-naphthaleneboronic acid, 47.0 mg, 75% yield, 29.8% ee. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 19.3 min (major) and 23.3 min.

**4-(4-Phenyl)-3,4-dihydro-(8-methyl[2.2]paracyclophano)-[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2l):** 31.0 mg, 38% yield, >20:1 dr, white solid, mp = 220−222 °C. New compound: $R_f$ = 0.50 (hexanes/ethyl acetate 5:1), 97.1% ee, $[\alpha]_D^{20}$ = +79.99 (*c* 0.28, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.35−7.30 (m, 3H), 7.24−7.18 (m, 2H), 7.08−7.03 (m, 1H), 6.89−6.78 (m, 2H), 6.52−6.48 (m, 1H), 6.21 (s, 1H), 5.55 (d, *J* = 8.9 Hz, 1H), 4.39 (d, *J* = 8.9 Hz, 1H), 3.44−3.31 (m, 1H), 3.26−3.13 (m, 1H), 3.07−2.83 (m, 3H), 2.74−2.56 (m, 2H), 2.44−2.30 (m, 1H), 2.04 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.4, 139.8, 139.8, 139.5, 138.3, 138.0, 135.1, 132.1, 131.0, 129.5, 129.2, 129.0, 128.3, 128.3, 127.7, 119.9, 61.8, 34.1, 32.7, 29.3, 28.7, 20.5. HPLC: Chiracel IA column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 11.6 min (major) and 13.9 min. HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{27}N_2O_3S$ $[M + NH_4]^+$, 423.1737; found, 423.1735.

**(8-Methyl[2.2]paracyclophano)[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1d):** kinetic resolution from the addition of [2.2]paracyclophane imine **1d** with phenylboronic acid, 37.0 mg, 57% yield, 65.9% ee, $[\alpha]_D^{20}$ = +232.84 (*c* 0.42, $CHCl_3$). HPLC: Chiralcel AD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 11.2 and 13.1 min (major).

**4-(*p*-Tolyl)-3,4-dihydro-(8-methyl[2.2]paracyclophano)[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2m):** 21.0 mg, 25% yield, >20:1 dr, white solid, mp = 223−225 °C. New compound: $R_f$ = 0.60 (hexanes/ethyl acetate 5:1), 88.5% ee, $[\alpha]_D^{20}$ = +106.85 (*c* 0.35, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.15−7.02 (m, 5H), 6.88−6.77 (m, 2H), 6.52−6.46 (m, 1H), 6.19 (s, 1H), 5.51 (d, *J* = 8.9 Hz, 1H), 4.28 (d, *J* = 8.8 Hz, 1H), 3.44−3.29 (m, 1H), 3.27−3.11 (m, 1H), 3.06−2.85 (m, 3H), 2.75−2.54 (m, 2H), 2.43−2.30 (m, 4H), 2.03 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.3, 139.7, 139.6, 138.9, 138.3, 137.8, 136.9, 135.1, 132.0, 131.0, 129.8, 129.5, 128.2, 128.2, 127.6, 120.1, 61.5, 34.1, 32.7, 29.3, 28.7, 21.3, 20.5. HPLC: Chiracel AD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 16.0 min (major) and 22.7 min. HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{25}NNaO_3S$ $[M + Na]^+$, 442.1447; found, 442.1446.

**(8-Methyl[2.2]paracyclophano)[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1d):** kinetic resolution from the addition of [2.2]paracyclophane imine **1d** with 4-methylphenylboronic acid, 45.0 mg, 69% yield, 36.4% ee. HPLC: Chiralcel AD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 11.4 and 13.3 min (major).

**Synthesis of (−)-4-Phenyl-3,4-dihydro-[2.2]paracyclophano-[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2a).** To a solution of (+)-**1a** (63 mg, 0.20 mmol, 99% ee) in dry tetrahydrofuran (3.0 mL) was added phenyl magnesium bromide (1.00 mL, 1 M in THF, 1.00 mmol) at 0 °C under nitrogen. The reaction mixture was allowed to warm to room temperature and stirred at room temperature overnight. Water (5.0 mL) was added and extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine, dried by anhydrous sodium sulfate, and filtered. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel using hexanes and ethyl acetate as an eluent to afford sulfamidate (−)-**2a**: 76 mg, 97% yield, white solid. New compound: $R_f$ = 0.50 (hexanes/ethyl acetate 10:1), 98% ee, $[\alpha]_D^{20}$ = −55.78 (*c* 1.66, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.37−7.30 (m, 3H), 7.26−7.21 (m, 2H), 7.03−6.98 (m, 1H), 6.89−6.84 (m, 1H), 6.63−6.55 (m, 3H), 6.40−6.32 (m, 1H), 5.51 (d, *J* = 8.8 Hz, 1H), 4.77 (d, *J* = 8.8 Hz, 1H), 3.44−3.32 (m, 1H), 3.27−3.15 (m, 1H), 3.10−2.90 (m, 3H), 2.81−2.70 (m, 1H), 2.62−2.45 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.5, 140.9, 139.9, 139.1, 138.5, 135.6, 133.4, 132.9, 131.5, 130.3,


https://dx.doi.org/10.1021/acs.joc.0c02509
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129.2, 129.1, 129.1, 129.1, 128.3, 119.9, 61.2, 34.4, 34.0, 33.7, 29.1. HPLC: Chiracel IA column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 10.4 and 15.3 min (major).

**Synthesis of (−)-4-Methyl-3,4-dihydro-[2.2]-paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (3).** To a solution of (+)-**1a** (63 mg, 0.20 mmol, 99% ee) in dry tetrahydrofuran (3.0 mL) was added methyl magnesium bromide (0.34 mL, 3 M in $Et_2O$, 1.00 mmol) at 0 °C under nitrogen. The reaction mixture was allowed to warm to room temperature and stirred at room temperature overnight. Water (5.0 mL) was added and extracted with dichloromethane (10 mL × 3). The combined organic layer was washed with brine, dried by anhydrous sodium sulfate, and filtered. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel using hexanes and ethyl acetate as an eluent to afford sulfamidate (−)-**3**: 61 mg, 92% yield, white solid, mp = 223−225 °C. New compound: $R_f$ = 0.50 (hexanes/ethyl acetate 5:1), 98% ee, $[\alpha]_D^{20}$ = −46.61 (*c* 1.24, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.02−6.92 (m, 1H), 6.65−6.57 (m, 2H), 6.56−6.49 (m, 2H), 6.46−6.40 (m, 1H), 5.11 (d, *J* = 6.8 Hz, 1H), 4.46 (p, *J* = 7.1 Hz, 1H), 3.41−3.28 (m, 1H), 3.24−2.99 (m, 5H), 2.98−2.83 (m, 1H), 2.74−2.56 (m, 1H), 1.59 (d, *J* = 7.1 Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 149.6, 140.1, 138.3, 138.1, 134.6, 134.1, 133.3, 131.0, 129.6, 128.9, 128.3, 122.5, 53.7, 33.8, 32.6, 29.7, 22.6. HPLC: Chiracel OD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 9.5 and 10.6 min (major). HRMS (ESI-TOF): *m*/*z* calcd for $C_{18}H_{19}NNaO_3S$ $[M + Na]^+$, 352.0978; found, 352.0972.

**Synthesis of (−)-3,4-Dihydro-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (4).** Sodium tetrahydroborate (38 mg, 1.00 mmol) was added to a solution of aldimine (+)-**1a** (63 mg, 0.20 mmol, 99% ee) in methanol (5.0 mL). The reaction was performed at room temperature overnight. The reaction mixture was quenched by the addition of saturated aqueous ammonium chloride solution (15 mL). After being extracted with ethyl acetate (15 mL × 3), the combined organic layer was dried by anhydrous sodium sulfate, concentrated *in vacuo*, and then purified by silica gel chromatography using hexanes and ethyl acetate as an eluent to give product (−)-**4**: 60 mg, 95% yield, white solid, mp = 142−144 °C. New compound: $R_f$ = 0.60 (hexanes/ethyl acetate 5:1), 98% ee, $[\alpha]_D^{20}$ = −22.87 (*c* 1.36, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.99−6.85 (m, 1H), 6.77−6.65 (m, 1H), 6.61−6.49 (m, 3H), 6.43−6.33 (m, 1H), 4.74−4.60 (m, 1H), 4.35−4.15 (m, 2H), 3.40−3.26 (m, 1H), 3.21−2.76 (m, 6H), 2.74−2.59 (m, 1H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 151.0, 139.9, 138.8, 138.2, 134.7, 133.7, 133.2, 130.3, 129.5, 128.8, 128.0, 118.3, 45.1, 34.1, 33.8, 31.8, 29.3. HPLC: Chiracel IA column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 10.7 and 14.2 min (major). HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{21}N_2O_3S$ $[M + NH_4]^+$, 333.1267; found, 333.1266.

**Synthesis of (−)-5-(Amino(phenyl)methyl)[2.2]-paracyclophan-4-ol (5).** To a suspension of lithium aluminum hydride (30 mg, 0.80 mmol) in THF (4 mL) was added asolution of (+)-**2a** (78 mg, 0.20 mmol, 99% ee) dropwise. The mixture was refluxed overnight and then cooled to room temperature; aqueous potassium sodium tartrate was added to destroy the lithium aluminum hydride, and the aqueous layer was extracted with ethyl acetate (10 mL × 3). Then, the combined organic layers were dried and concentrated to provide the crude product. The residue was purified by column chromatography on silica gel using hexanes and ethyl acetate as an eluent to afford product (−)-**5**: 51 mg, 77% yield, white solid, mp = 150−152 °C. New compound: $R_f$ = 0.50 (hexanes/ethyl acetate 5:1), 99% ee, $[\alpha]_D^{20}$ = −226.98 (*c* 0.40, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.26−7.13 (m, 5H), 7.05−7.00 (m, 1H), 6.64−6.56 (m, 2H), 6.52−6.46 (m, 1H), 6.40−6.33 (m, 1H), 6.11−6.05 (m, 1H), 5.25 (s, 1H), 3.56−3.42 (m, 1H), 3.27−2.99 (m, 5H), 2.75−2.50 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 157.0, 144.1, 140.7, 138.5, 137.9, 134.6, 134.1, 132.7, 129.0, 129.0, 128.8, 127.7, 126.9, 126.1, 123.7, 57.7, 34.4, 34.0, 33.4, 30.6. HPLC: Chiracel OD-H column, 254 nm, 30 °C, *n*-hexane/*i*-PrOH = 60:40, flow = 0.6 mL/min, retention time 19.4 and 34.9 min (major). HRMS (ESI-TOF): *m*/*z* calcd for $C_{23}H_{23}ClNO$ $[M + Cl]^-$, 364.1474; found, 364.1485.

**Scale-up Reaction.** A Schlenk tube (250 mL) was charged with $Pd(OCOCF_3)_2$ (33.0 mg, 0.1 mmol, 5 mol %) and ($R_p$,*S*)-**L2** (53.0 mg, 0.1 mmol, 5 mol %) under nitrogen, and degassed anhydrous acetone (5.0 mL) was added. The mixture was stirred at room temperature for 1 h. The solvent was removed under a vacuum to give the catalyst. Then substrate *rac*-**1a** (626 mg, 2.00 mmol), phenylboronic acid (243 mg, 2.00 mmol), and 2,2,2-trifluoroethanol (40 mL) were added into the tube under nitrogen. The mixture was heated to 60 °C. After stirring at 60 °C for 12 h, the reaction mixture was cooled to room temperature, and the solvent was removed by rotary evaporation. The resulting mixture was dried under a vacuum; the conversion of *rac*-**1a** (34% conversion) and the diastereomeric ratio (>20:1 dr) of the addition product were confirmed by $^1$H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard. The solvent was removed *in vacuo*, and recovered material (+)-**1a** (406.0 mg, 65% yield with 49.6% ee) and addition product (+)-**2a** (250.0 mg, 30% yield with 97.6% ee) were isolated by column chromatography on silica gel using hexanes and ethyl acetate as an eluent.

*Determination of the Absolute Configuration of Compound* ***2f***. To determine the absolute configuration of addition product (+)-**2f**, the (+)-**2f** was obtained as a colorless crystal after the recrystallization from chloroform/hexanes. Based on single-crystal X-ray diffraction analysis, the structure of compound (+)-**2f** was determined as ($S_p$,*R*) 4-(4-chlorophenyl)-3,4-dihydro-[2.2]paracyclo-phano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-dioxide (see the Supporting Information). The CCDC number is 2023207. These details can be obtained free of charge via www.ccdc.com.ac.uk/data_request/cif from the Cambridge Crystallographic Data Centre.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02509.

Determination of absolute configuration and NMR and HPLC spectra (PDF)

### Accession Codes

CCDC 2023207 contains 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 emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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https://dx.doi.org/10.1021/acs.joc.0c02509
J. Org. Chem. 2021, 86, 1262−1272

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.joc.0c02509

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (21532006 and 21690074) and Chinese Academy of Sciences (XDB17020300 and SLH035) is acknowledged.

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https://dx.doi.org/10.1021/acs.joc.0c02509
*J. Org. Chem.* 2021, 86, 1262−1272