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Nickel-Catalyzed Asymmetric Hydrogenation for Kinetic Resolution of [2.2]Paracyclophane-Derived Cyclic *N*-Sulfonylimines

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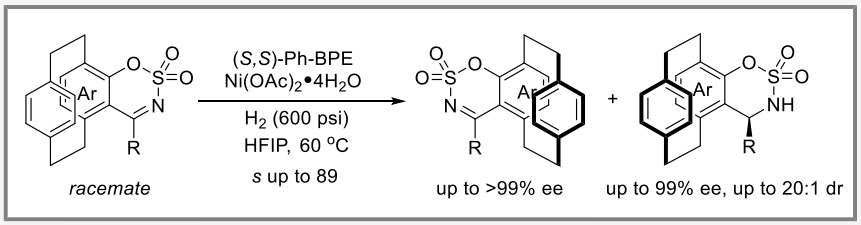

ABSTRACT: Nickel-catalyzed asymmetric hydrogenation for kinetic resolution of [2.2]paracyclophane-derived cyclic *N*-sulfonylimines was successfully developed. High selectivity factors were observed in most cases (*s* up to 89), providing the recovered materials and hydrogenation products in good yields with high levels of enantiopurity. The recovered materials and hydrogenation products are useful synthetic intermediates for the synthesis of planar chiral [2.2]paracyclophane-based compounds.

Transition-metal-catalyzed asymmetric hydrogenation has emerged as an effective method for the direct access to enantioenriched compounds.[1] This process is of great synthetic importance in the preparation of pharmaceuticals, natural products, agrochemicals, and so on. Kinetic resolution is one of powerful and practical strategies in asymmetric catalysis. However, transition-metal-catalyzed asymmetric hydrogenation is less applied in kinetic resolution compared with other basic transformations such as epoxidation and acylation.[2] The first application was reported in 1988 by Noyori who subjected cyclic allylic alcohols under hydrogen using Ru-BINAP as catalyst with up to 76 of selectivity factor.[3] Thereafter, two kinds of transition-metal-catalyzed asymmetric hydrogenation including asymmetric hydrogenation and asymmetric transfer hydrogenation were employed for kinetic resolution of racemic compounds (Scheme 1a). Kinetic resolution of racemic alkenes,[4] esters,[5] and imines[6] can be smoothly realized by transition-metal-catalyzed asymmetric hydrogenation using hydrogen gas as hydrogen source. Meanwhile, transition-metal-catalyzed asymmetric transfer hydrogenation using other types of hydrogen sources was also applied in the kinetic resolution of ketones,[7] aldehydes,[8] and alkenes.[9] Kinetic resolution of racemic unsaturated compounds *via* transition-metal-catalyzed asymmetric hydrogenation mainly focused on precious transition-metal catalytic systems including ruthenium, rhodium, and iridium. In contrast to these precious transition-metal catalysts, earth-abundant transition-metal catalysts exhibit potential advantages as they are cheap and environmentally friendly. Therefore, it is important and necessary to develop a kinetic resolution *via* earth-abundant transition-metal-catalyzed asymmetric hydrogenation.

Planar-chiral [2.2]paracyclophane derivatives have served as ligands or auxiliaries in asymmetric catalysis and stereoselective synthesis,[10] which can be utilized as chiral materials.[11] Reports concerning catalytic asymmetric processes were very finite.[8,12] As our contiguous efforts on the preparation of enantiopure [2.2]paracyclophanes through kinetic resolution, we previously reported palladium-catalyzed kinetic resolution of [2.2]-paracyclophane-derived *N*-sulfonylimines to afford paracyclophane derivatives with planar and central chirality.[8b,12d] In the past few years, asymmetric (transfer) hydrogenation using cheap and earth-abundant transition-metal catalytic systems has achieved considerable attention.[13] Recently, some important research works on nickel-catalyzed asymmetric hydrogenation of ketones, alkenes, imines, and enamides were realized by the Hamada,[14] Chirik,[15] Zhou,[16] Zhang,[17] and Zhang groups.[18] Despite great progress, nickel-catalyzed asymmetric hydrogenation for kinetic resolution has not been reported. Hence, the development of kinetic resolution *via* nickel-catalyzed asymmetric hydrogenation is still desirable. On the basis of previous reports on asymmetric hydrogenation of *N*-sulfonyl imines,[17a,18e,j,19] we conjectured that nickel-catalyzed asymmetric hydrogenation would enable a general approach for accessing the kinetic resolution of [2.2]-paracyclophane-derived cyclic *N*-sulfonylimines (Scheme 1b).

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Scheme 1. Kinetic Resolution *via* the Transition-Metal-Catalyzed Asymmetric Hydrogenation

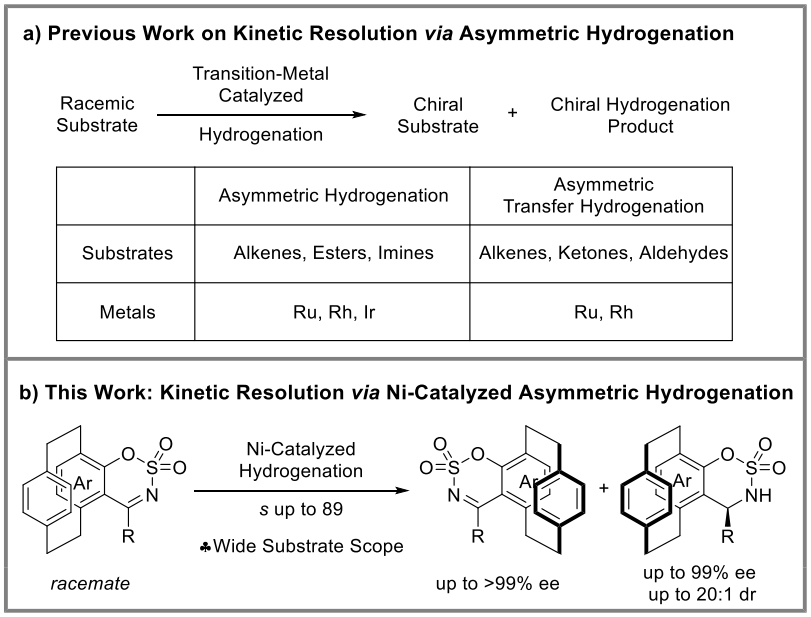
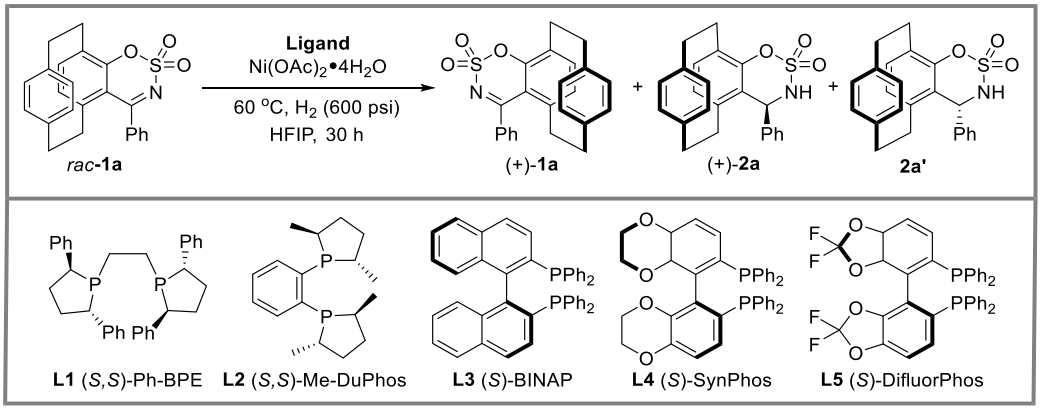


Table 1. Optimization of the Kinetic Resolution[a]



entry	solvent	L	1a conv. (%)[b]	1a ee (%)[c]	2a dr[b]	2a (2a′) ee (%)[c]	s[d]
1	TFE	**L1**	39	59.2	>20:1	95.7	47.5
2	HFIP	**L1**	36	53.1	>20:1	97.9	59.1
3	MeOH	**L1**	<5				
4	toluene	**L1**	<5				
5	DCM	**L1**	<5				
6	HFIP	**L2**	70	32.0	1.0:1	95.8 (77.1)	1.7
7	HFIP	**L3**	52	58.7	6.0:1	68.5 (85.1)	5.9
8	HFIP	**L4**	69	55.0	2.0:1	72.2 (96.8)	2.7
9	HFIP	**L5**	30	30.4	12.5:1	86.4	7.9
10[e]	HFIP	**L1**	56	99.2	9.4:1	92.4	42.8
11[f]	HFIP	**L1**	37	56.7	>20:1	96.5	100.9
12[g]	HFIP	**L1**	37	56.2	>20:1	96.1	80.1

[a]Conditions: *rac*-**1a** (0.10 mmol), $Ni(OAc)_2 \cdot H_2O$ (5.0 mol %), **L** (5.0 mol %), solvent (3.0 mL), H_2 (600 psi), 60 °C, 30 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 = conv., $s = \ln[(1 - C)(1 - \text{ee of } \mathbf{1a})]/\ln[(1 - C)(1 + \text{ee of } \mathbf{1a})]$. [e]The reaction was carried out at 80 °C. [f]Using 1.5 mL of HFIP. [g]The reaction was carried out at H_2 (1000 psi), using 1.5 mL of HFIP.

Herein, we reported nickel-catalyzed asymmetric hydrogenation for the kinetic resolution of [2.2]paracyclophane-derived cyclic *N*-sulfonylimines, providing a series of chiral [2.2]paracyclophane derivatives with excellent enantioselectivities.

In our initial studies, we commenced our investigation using racemic 4-phenyl-[2.2]paracyclophano[5,6-*d*]-1,2,3 benzoxathiazine 2,2-dioxide **1a** as the model substrate to optimize the reaction conditions. Results revealed that only trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP) were

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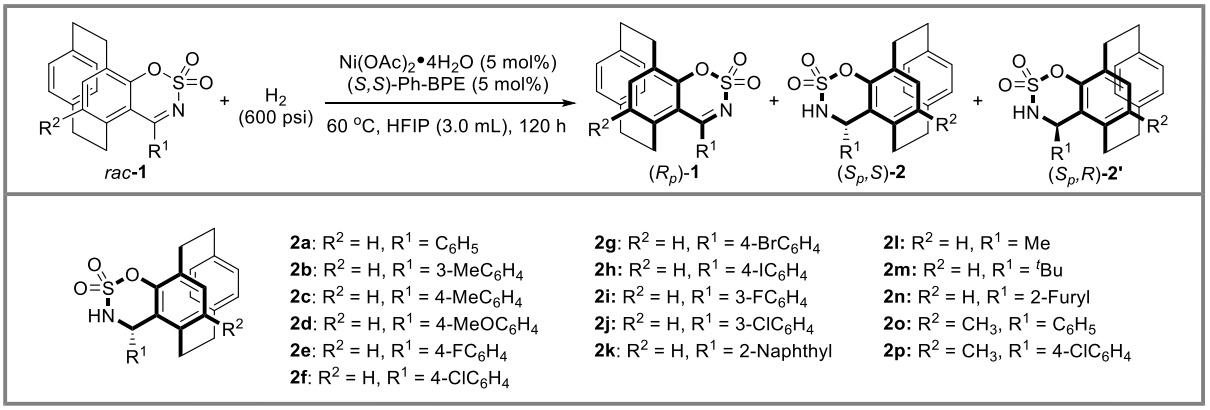
Table 2. Substrate Scope for Kinetic Resolution of [2.2]Paracyclophane-Derived *N*-Sulfonylmines 1[a]



entry	1	*rac*-1 conv. (%)[b]	1 yield (%)[c]	1 ee (%)[d]	2	2 + 2′ yield (%)[c]	2 (2′) ee (%)[d]	2 dr[b]	*s*[e]
1	**1a**	50	49	92.1	**2a**	50	93.0	>20:1	80.2
2	**1b**	53	46	98.8	**2b**	51	92.2	>20:1	76.3
3	**1c**	51	48	93.5	**2c**	49	95.1	9.2:1	64.7
4	**1d**	51	49	87.9	**2d**	46	95.2 (62.1)	1.5:1	34.2
5	**1e**	52	47	97.2	**2e**	50	93.3	15.0:1	78.5
6	**1f**	52	47	96.4	**2f**	51	93.4	15.0:1	68.8
7	**1g**	52	47	97.1	**2g**	51	94.3	14.0:1	77.1
8	**1h**	45	54	77.6	**2h**	44	97.3	>20:1	89.2
9	**1i**	51	48	91.4	**2i**	50	73.7	16.0:1	49.4
10	**1j**	55	44	98.8	**2j**	54	88.1	17.0:1	46.9
11	**1k**	52	46	96.9	**2k**	51	90.8	16.0:1	74.5
12[f]	**1l**	58	41	1.9	**2l**	56	99.0 (94.8)	1.1:1[j]	1.0
13[g]	**1m**	51	49	69.4	**2m**	50	94.7	14.0:1	10.2
14[h]	**1n**	56	43	17.2	**2n**	51	50.1 (98.0)	1.3:1	1.5
15[i]	**1o**	38	61	55.6	**2o**	37	97.2	15.0:1	35.9
16[i]	**1p**	22	77	26.3	**2p**	21	97.6	>20:1	37.0

[a]Conditions: *rac*-**1** (0.20 mmol). [b]Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. [c]Isolated yield. [d]Determined by HPLC. [e]Calculated selectivity factors: C = conv., $s = \ln[(1 - C)(1 - \text{ee of } \mathbf{1})]/\ln[(1 - C)(1 + \text{ee of } \mathbf{1})]$. [f]12 h. [g]$Ni(OAc)_2{\cdot}H_2O$ (25 mol %), (*S*,*S*)-Ph-BPE (5 mol %), 72 h. [h]30 h. [i]$Ni(OAc)_2{\cdot}H_2O$ (25 mol %), (*S*,*S*)-Ph-BPE (5 mol %), 40 °C, 176 h. [j]The absolute configuration of **2l′** was assigned as (R_p,*S*) according to previously reported literature (ref 12d).

effective, but no reaction occurred using other solvents including methanol, toluene, and dichloromethane (Table 1, entries 1−5). Up to 59.1 of selectivity factor was observed using hexafluoroisopropanol as solvent with 36% conversion of *rac*-**1a** (Table 1, entry 2). Aiming to further enhance the conversion, the ligand effect was tested. The other electron-rich ligand such as (*S*,*S*)-Me-DuPhos provided the diminished diastereoselectivity, albeit with high reactivity (Table 1, entry 6). When the axially chiral ligands (*S*)-BINAP, (*S*)-SynPhos, and (*S*)-DifluorPhos were examined, low selectivity factors were obtained (Table 1, entries 7−9). None of these gave further improvement. Among the ligands tested, (*S*,*S*)-Ph-BPE was the most effective. When the temperature was elevated, the values of diastereoselectivity and selectivity factor were low (Table 1, entry 10). An attempt with HFIP (1.5 mL) instead of HFIP (3.0 mL) resulted in a higher selectivity factor (Table 1, entry 11). When the reaction was run at 1000 psi of H_2 in HFIP (1.5 mL), the kinetic resolution efficiency diminished (Table 1, entry 12). Therefore, the optimal conditions were established as $Ni(OAc)_2{\cdot}4H_2O$ (5 mol %)/(*S*,*S*)-Ph-BPE (5 mol %)/H_2 (600 psi)/HFIP (1.5 mL)/60 °C.

With the optimized conditions in hand, an assortment of cyclic [2.2]paracyclophane-derived *N*-sulfonylimines may be used in reaction to generate the corresponding sulfamidate derivatives. These results are summarized in Table 2. The substrate **1b** bearing a 3-methyl group on the phenyl ring was hydrogenated smoothly in >20:1 dr (Table 2, entry 2). However, the asymmetric hydrogenation of substrate **1c** with a 4-methyl group proceeded well to afford product **2c** with 9.2:1 dr (Table 2, entry 3). The electron-donating group (methoxy) substituted at the *para* position on the phenyl ring caused an obvious decrease in the diastereoselectivity (Table 2, entry 4). Substrates with electron-withdrawing aryl substituents (R^1 = 4-FC_6H_4, R^1 = 4-ClC_6H_4, R^1 = 3-FC_6H_4, R^1 = 3-ClC_6H_4) can be successfully hydrogenated to give the corresponding sulfamidate derivatives in high diastereoselectivity (Table 2, entries 5, 6, 9, 10). Additionally, the reaction proceeded smoothly, giving the desired hydrogenation products in high diastereoselectivity and selectivity factor when other halogen groups were introduced at the 4-position of the phenyl ring (Table 2, entries 7 and 8). The naphthyl group was also tolerated in the reaction (Table 2, entry 11). When the aryl group was replaced by a methyl group, the hydrogenation of **1l** afforded low diastereoselectivity and selectivity factor, albeit with high reactivity (Table 2, entry 12). Changing the methyl group to *tert*-butyl, the kinetic resolution of **1m** (Table 2, entry 13) was more sluggish, resulting in 51% conversion with a 5:1 ratio of nickel salt to ligand after 72 h. In 2019, the Zhang group reported that adding excess nickel salt could improve the efficiency of the hydrogenation.[17a] Product **2m** shows better

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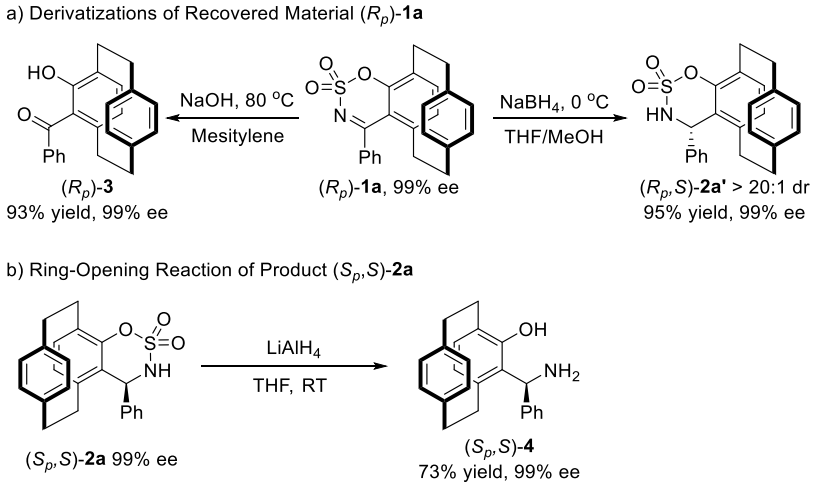
Scheme 2. Elaborations of Recovered Material (R_p)-1a and Product (S_p,S)-2a



diastereoselectivity than product **2l** probably owing to steric effects. The oxygen atom of 2-furyl on the *N*-sulfonylimine **1n** probably coordinated with Ni(II), leading to the low diastereoselectivity of **2n** (Table 2, entry 14). 8-Substituted [2.2]paracyclophane-based *N*-sulfonylimines **1o** and **1p** were synthesized to further estimate the application possibility. To raise the value of diastereoselectivity, the reaction was carried out at 40 °C. Meanwhile, a 5:1 ratio of nickel salt to ligand was used to improve the reactivity. The reaction proceeded well with high diastereoselectivity and moderate selectivity factor (Table 2, entries 15 and 16).

The absolute configuration of (+)-**2a** (increases to 99% ee by a simple recrystallization with chloroform and *n*-hexane) was unambiguously confirmed as (S_p,S) by X-ray crystallographic analysis. The configuration of recovered aldimines (−)-**1a** was assigned as R_p configuration by comparison with X-ray crystallographic data of the compound (+)-**2a**.[20]

The recovered material (R_p)-**1a** and hydrogenation product (S_p,S)-**2a** can be easily converted to other chiral building blocks without compromise of enantiomeric integrity (Scheme 2). For instance, imine (R_p)-**1a** was reduced with sodium borohydride to obtain **2a′** in 95% yield. Surprisingly, the isolated product **2a′** revealed to be a diastereomer of **2a** (evidenced by the nuclear magnetic resonance and high performance liquid chromatography), and the reason was not clear. The removal of the *N*-sulfonyl group of imine (R_p)-**1a** was also carried out in the presence of sodium hydroxide to provide the ketone (R_p)-**3** in 93% yield (Scheme 2a). In addition, treatment of the hydrogenation product (S_p,S)-**2a** with lithium aluminum hydride gave the amino phenol (S_p,S)-**4** in 73% yield without loss of optical purity (Scheme 2b).

In summary, nickel-catalyzed asymmetric hydrogenation for the kinetic resolution of the racemic [2.2]paracyclophane-derived cyclic *N*-sulfonylimines has been developed, giving a variety of chiral paracyclophane derivatives in excellent selectivity factor. The recovered materials and hydrogenation products are useful synthetic intermediates for the synthesis of planar chiral [2.2]paracyclophane-based compounds. Efforts to explore the nickel-catalyzed asymmetric hydrogenation for the kinetic resolution of other unsaturated compounds are ongoing in our laboratory.

EXPERIMENTAL SECTION

All reactions were carried out using the standard Schlenk techniques under an atmosphere of nitrogen, unless otherwise noted. Commercially available reagents and solvents were used without further purification. ^{1}H NMR spectra were recorded at 400 MHz with the Bruker spectrometer. ^{13}C NMR spectra were recorded at 100 MHz with the Bruker spectrometer. ^{19}F NMR spectra was recorded at 376 MHz with the Bruker spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard when using $CDCl_3$ as solvent for ^{1}H NMR spectra. Data are shown as follows: chemical shift δ (ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, brs = broad singlet). Flash column chromatography was carried out using 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. X-ray crystallography data were measured using a BRUKER D8 VENTURE with 3.0 Iμs CU and 3.0 Iμs MO.

Procedures for Synthesis of [2.2]Paracyclophane-Derived Imines. The [2.2]paracyclophane-derived *N*-sulfonylimines **1a**−**1n** were synthesized from 4-hydroxy-[2.2]paracyclophane in two steps, and the *N*-sulfonylimines **1o** and **1p** were synthesized from 4-hydroxy-7-methyl-[2.2]paracyclophane in two steps according to known literature procedures.[12d,21]

Racemic hydroxy[2.2]paracyclophane (0.673 g, 3 mmol) was dissolved in dry dichloromethane under nitrogen and then cooled to 0 °C. Titanium tetrachloride (0.853 g, 0.49 mL, 4.5 mmol, 1.5 equiv) was added to this solution, and the resulting mixture was stirred for 10 min at 0 °C. 4-Fluorobenzoyl chloride (0.523 g, 0.39 mL, 3.3 mmol, 1.1 equiv) was added at 0 °C with a syringe, and the solution was stirred for an additional 2 h at room temperature. The reaction was quenched with water (10 mL) and stirred for 15 min, and the aqueous layer was extracted with dichloromethane (3 × 20 mL) and dried with anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified by flash chromatography to yield acyl[2.2]paracyclophane.

A mixture of acyl[2.2]paracyclophane (0.850 g, 2.46 mmol) was dissolved in toluene (15 mL), and H_2NSO_2Cl (0.852 g, 7.38 mmol, 3.0 equiv) was added. H_2NSO_2Cl was prepared as described previously.[22] Then the reaction mixture was heated at reflux for 3 h. The reaction was quenched with water (10 mL), extracted with dichloromethane (3 × 20 mL), dried with anhydrous sodium sulfate, filtered, and concentrated under vacuum. The crude residue was purified by silica gel column chromatography using the hexanes/dichloromethane as eluent to give the desireable cyclic [2.2]-paracyclophane-derived cyclic *N*-sulfonylimines **1**.

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*4-Phenyl-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1a**).* 2.256 g, 53% yield, yellow solid, known compound, R_f = 0.40 (hexanes/acetone 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.66 (m, 2H), 7.65−7.57 (m, 1H), 7.53−7.44 (m, 2H), 7.06−6.96 (m, 1H), 6.81−6.70 (m, 2H), 6.69−6.62 (m, 1H), 6.55−6.48 (m, 1H), 6.42−6.34 (m, 1H), 3.60−3.47 (m, 1H), 3.44−3.32 (m, 1H), 3.10−2.95 (m, 1H), 2.95−2.74 (m, 4H), 2.51−2.34 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 155.5, 146.1, 142.8, 139.4, 138.0, 137.4, 134.3, 133.6, 133.0, 132.4, 131.7, 131.4, 130.3, 128.9, 128.4, 116.3, 36.8, 35.9, 34.9, 28.2.

*4-(m-Tolyl)-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1b**).* 0.385 g, 64% yield, yellow solid, mp = 178−180 °C, new compound, R_f = 0.40 (hexanes/acetone 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.50 (m, 1H), 7.50−7.30 (m, 3H), 7.07−6.95 (m, 1H), 6.81−6.70 (m, 2H), 6.70−6.62 (m, 1H), 6.56−6.47 (m, 1H), 6.43−6.34 (m, 1H), 3.61−3.48 (m, 1H), 3.45−3.32 (m, 1H), 3.10−2.96 (m, 1H), 2.94−2.74 (m, 4H), 2.55−2.37 (m, 1H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.2, 155.4, 146.1, 142.8, 139.4, 138.9, 138.0, 137.4, 134.3, 133.8, 133.5, 132.4, 131.7, 131.4, 130.5, 128.6, 128.4, 127.8, 116.4, 36.8, 35.9, 34.9, 28.2, 21.5. HRMS: Calculated for $C_{24}H_{22}NO_3S$ [M + H]$^+$ 404.1315, found: 404.1316.

*4-(p-Tolyl)-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1c**).* 0.641 g, 53% yield, yellow solid, mp = 193−195 °C, new compound, R_f = 0.40 (hexanes/acetone 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.46 (m, 2H), 7.35−7.25 (m, 2H), 7.06−6.94 (m, 1H), 6.80−6.61 (m, 3H), 6.55−6.46 (m, 1H), 6.42−6.31 (m, 1H), 3.61−3.45 (m, 1H), 3.44−3.29 (m, 1H), 3.08−2.95 (m, 1H), 2.94−2.75 (m, 4H), 2.54−2.38 (m, 1H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.9, 155.4, 146.1, 144.1, 142.7, 139.3, 138.0, 134.5, 134.2, 133.5, 132.4, 131.6, 131.4, 130.5, 129.6, 128.3, 116.3, 36.8, 35.8, 34.8, 28.1, 21.8. HRMS: Calculated for $C_{24}H_{22}NO_3S$ [M + H]$^+$ 404.1315, found: 404.1317.

*4-(4-Methoxyphenyl)-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1d**).* 0.489 g, 40% yield, yellow solid, mp = 279−281 °C, new compound, R_f = 0.30 (hexanes/acetone 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.48 (m, 2H), 7.05−6.88 (m, 3H), 6.81−6.62 (m, 3H), 6.55−6.44 (m, 1H), 6.42−6.32 (m, 1H), 3.89 (s, 3H), 3.60−3.45 (m, 1H), 3.43−3.29 (m, 1H), 3.09−2.74 (m, 5H), 2.62−2.45 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.0, 163.9, 155.3, 145.9, 142.6, 139.3, 138.0, 134.2, 133.4, 132.8, 132.4, 131.6, 131.4, 129.3, 128.2, 116.2, 114.3, 55.7, 36.8, 35.8, 34.8, 28.1. HRMS: Calculated for $C_{24}H_{22}NO_4S$ [M + H]$^+$ 420.1264, found: 420.1263.

*4-(4-Fluorophenyl)-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1e**).* 0.497 g, 41% yield, yellow solid, mp = 236−238 °C, new compound, R_f = 0.35 (hexanes/acetone 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.60 (m, 2H), 7.23−7.10 (m, 2H), 7.03−6.92 (m, 1H), 6.83−6.60 (m, 3H), 6.57−6.48 (m, 1H), 6.41−6.31 (m, 1H), 3.59−3.47 (m, 1H), 3.44−3.29 (m, 1H), 3.11−2.96 (m, 1H), 2.94−2.77 (m, 4H), 2.49−2.34 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.7, 165.8 ($J_{C\text{-}F}$ = 256.1 Hz), 155.5, 145.7, 143.0, 139.4, 137.9, 134.3, 133.7, 133.4 ($J_{C\text{-}F}$ = 3.3 Hz), 132.8 ($J_{C\text{-}F}$ = 9.3 Hz), 132.5, 131.7, 131.4, 128.6, 116.2 ($J_{C\text{-}F}$ = 22.0 Hz), 116.1, 36.8, 35.9, 34.8, 28.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −104.8. HRMS: Calculated for $C_{23}H_{19}FNO_3S$ [M + H]$^+$ 408.1064, found: 408.1067.

*4-(4-Chlorophenyl)-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1f**).* 0.615 g, 48% yield, yellow solid, mp = 233−235 °C, new compound, R_f = 0.40 (hexanes/acetone 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.59 (m, 2H), 7.52−7.42 (m, 2H), 7.03−6.94 (m, 1H), 6.81−6.62 (m, 3H), 6.55−6.49 (m, 1H), 6.39−6.32 (m, 1H), 3.59−3.47 (m, 1H), 3.44−3.31 (m, 1H), 3.09−2.96 (m, 1H), 2.94−2.77 (m, 4H), 2.50−2.34 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.7, 155.5, 145.7, 143.0, 139.7, 139.4, 137.9, 135.7, 134.3, 133.7, 132.5, 131.7, 131.6, 131.3, 129.2, 128.6, 116.0, 36.9, 35.9, 34.8, 28.2. HRMS: Calculated for $C_{23}H_{19}ClNO_3S$ [M + H]$^+$ 424.0769, found: 424.0762 (^{35}Cl) and 426.0734 (^{37}Cl).

*4-(4- Bromophenyl)-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1g**).* 0.565 g, 40% yield, yellow solid, mp = 237−239 °C, new compound, R_f = 0.40 (hexanes/ethyl acetate 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.80 (m, 2H), 7.50−7.35 (m, 2H), 7.03−6.93 (m, 1H), 6.81−6.62 (m, 3H), 6.54−6.47 (m, 1H), 6.39−6.32 (m, 1H), 3.60−3.46 (m, 1H), 3.45−3.33 (m, 1H), 3.11−2.94 (m, 1H), 2.94−2.76 (m, 4H), 2.52−2.34 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.1, 155.5, 145.7, 143.0, 139.4, 138.2, 137.9, 136.7, 134.3, 133.7, 132.5, 131.7, 131.6, 131.3, 128.6, 116.0, 100.8, 37.0, 35.9, 34.8, 28.2. HRMS: Calculated for $C_{23}H_{19}Br\ NO_3S$ [M + H]$^+$ 468.0264, found: 468.0269 (^{79}Br) and 470.0247 (^{81}Br).

*4-(4-Iodophenyl)-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1h**).* 0.380 g, 24% yield, yellow solid, mp = 265−267 °C, new compound, R_f = 0.35 (hexanes/ethyl acetate 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74−7.43 (m, 4H), 7.05−6.93 (m, 1H), 6.82−6.61 (m, 3H), 6.56−6.48 (m, 1H), 6.41−6.31 (m, 1H), 3.62−3.46 (m, 1H), 3.46−3.30 (m, 1H), 3.12−2.98 (m, 1H), 2.95−2.77 (m, 4H), 2.51−2.33 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.9, 155.5, 145.7, 143.1, 139.4, 137.9, 136.1, 134.3, 133.7, 132.5, 132.2, 131.7, 131.7, 131.3, 128.6, 128.3, 116.0, 36.9, 35.9, 34.8, 28.2. HRMS: Calculated for $C_{23}H_{19}INO_3S$ [M + H]$^+$ 516.0125, found: 516.0128.

*4-(3-Fluorophenyl)-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1i**).* 0.280 g, 23% yield, yellow solid, mp = 214−216 °C, new compound, R_f = 0.40 (hexanes/dichloromethane 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.39 (m, 3H), 7.37−7.28 (m, 1H), 7.04−6.94 (m, 1H), 6.83−6.62 (m, 3H), 6.56−6.49 (m, 1H), 6.40−6.32 (m, 1H), 3.61−3.47 (m, 1H), 3.44−3.31 (m, 1H), 3.09−2.96 (m, 1H), 2.95−2.77 (m, 4H), 2.50−2.32 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.6, 162.6 ($J_{C\text{-}F}$ = 248.6 Hz), 155.5, 145.8, 143.1, 139.4, 139.3 ($J_{C\text{-}F}$ = 7.7 Hz), 137.9, 134.3, 133.7, 132.5, 131.7, 131.3, 130.6 ($J_{C\text{-}F}$ = 7.9 Hz), 128.6, 126.1, 120.0 ($J_{C\text{-}F}$ = 21.2 Hz), 117.1 ($J_{C\text{-}F}$ = 23.6 Hz), 116.1, 36.8, 35.9, 34.8, 28.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −111.1. HRMS: Calculated for $C_{23}H_{19}FNO_3S$ [M + H]$^+$ 408.1064, found: 408.1063.

*4-(3-Chlorophenyl)-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1j**).* 0.506 g, 40% yield, yellow solid, mp = 200−202 °C, new compound, R_f = 0.45 (hexanes/dichloromethane 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.65 (m, 1H), 7.63−7.51 (m, 2H), 7.48−7.35 (m, 1H), 7.04−6.92 (m, 1H), 6.82−6.62 (m, 3H), 6.57−6.48 (m, 1H), 6.39−6.30 (m, 1H), 3.60−3.46 (m, 1H), 3.46−3.30 (m, 1H), 3.11−2.97 (m, 1H), 2.95−2.78 (m, 4H), 2.50−2.34 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.5, 155.5, 145.7, 143.2, 139.4, 138.9, 137.9, 135.1, 134.3, 133.8, 132.9, 132.5, 131.7, 131.3, 130.1, 130.0, 128.6, 128.5, 116.0, 36.8, 35.9, 34.8, 28.2. HRMS: Calculated for $C_{23}H_{19}ClNO_3S$ [M + H]$^+$ 424.0769, found: 424.0762 (^{35}Cl) and 424.0734 (^{37}Cl).

*4-(2-Naphthyl)-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1k**).* 0.359 g, 28% yield, yellow solid, mp = 143−145 °C, new compound, R_f = 0.40 (hexanes/dichloromethane 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38−8.11 (m, 1H), 8.03−7.83 (m, 3H), 7.82−7.49 (m, 3H), 7.14−6.95 (m, 1H), 6.84−6.69 (m, 2H), 6.68−6.60 (m, 1H), 6.59−6.50 (m, 1H), 6.45−6.36 (m, 1H), 3.62−3.48 (m, 1H), 3.45−3.28 (m, 1H), 3.10−2.98 (m, 1H), 2.96−2.70 (m, 4H), 2.47−2.34 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.9, 155.4, 146.1, 142.9, 139.4, 138.0, 135.3, 134.5, 134.2, 133.6, 132.5, 132.5, 131.7, 131.4, 129.5, 128.9, 128.7, 128.4, 128.0, 127.3, 126.0, 116.4, 36.8, 35.8, 34.8, 28.2. HRMS: Calculated for $C_{27}H_{22}NO_3S$ [M + H]$^+$ 440.1315, found: 440.1317.

*4-Methyl-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1l**).* 0.111 g, 28% yield, yellow solid, known compound, R_f = 0.30 (hexanes/ethyl acetate 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97−6.89 (m, 1H), 6.78−6.67 (m, 2H), 6.66−6.60 (m, 1H), 6.59−6.51 (m, 1H), 6.39−6.32 (m, 1H), 3.67−3.54 (m, 1H), 3.54−3.42 (m, 1H), 3.36−3.26 (m, 1H), 3.26−3.16 (m, 2H), 3.09−2.95 (m, 2H), 2.89−2.76 (m, 1H), 2.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 154.1, 143.7, 142.0, 139.9, 137.8, 133.8, 133.7, 132.4, 130.5, 129.3, 117.7, 37.2, 36.0, 34.6, 28.5, 28.2.

*4-tert-Butyl-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1m**).* 0.203 g, 8% yield, yellow solid, mp = 159−161 °C, new compound, R_f = 0.45 (hexanes/dichloromethane 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97−6.90 (m, 1H), 6.78−6.67 (m, 2H), 6.66−6.61 (m, 1H), 6.44−6.38 (m, 2H), 3.52−3.18 (m, 5H), 3.04−2.90

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(m, 2H), 2.86−2.74 (m, 1H), 1.39 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 189.9, 154.6, 143.5, 141.5, 139.8, 137.7, 134.1, 132.7, 132.5, 131.4, 131.3, 127.9, 116.1, 43.3, 39.4, 36.0, 34.7, 31.0, 28.4. HRMS: Calculated for $C_{21}H_{24}NO_3S$ $[M + H]^+$ 370.1471, found: 370.1473.

*4-(2-Furyl)-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1n**).* 0.190 g, 56% yield, yellow solid, mp = 233−235 °C, new compound, R_f = 0.30 (hexanes/ethyl acetate 5/1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.80−7.69 (m, 1H), 7.42−7.32 (m, 1H), 7.03−6.91 (m, 1H), 6.83−6.61 (m, 4H), 6.56−6.46 (m, 1H), 6.44−6.33 (m, 1H), 3.61−3.44 (m, 1H), 3.43−3.31 (m, 1H), 3.29−3.17 (m, 1H), 3.17−2.97 (m, 2H), 2.95−2.78 (m, 2H), 2.76−2.61 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.9, 155.4, 149.6, 148.7, 145.6, 143.0, 139.4, 138.1, 134.2, 133.2, 132.7, 131.5, 131.3, 127.8, 121.7, 114.8, 113.8, 35.9, 35.8, 34.7, 28.1. HRMS: Calculated for $C_{21}H_{18}NO_4S$ $[M + H]^+$ 380.0951, found: 380.0953.

*4-(4-Phenyl)-(8-methyl[2.2]paracyclophano)[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1o**).* 0.236 g, 41% yield, yellow solid, mp = 264−266 °C, new compound, R_f = 0.35 (hexanes/dichloromethane 1/1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77−7.54 (m, 3H), 7.50−7.41 (m, 2H), 7.15−7.05 (m, 1H), 6.95−6.89 (m, 1H), 6.64−6.56 (m, 1H), 6.37−6.27 (m, 2H), 3.56−3.44 (m, 1H), 3.41−3.29 (m, 1H), 3.05−2.67 (m, 5H), 2.39−2.26 (m, 1H), 2.16 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.2, 154.2, 145.5, 144.5, 139.1, 137.8, 137.2, 137.0, 134.6, 132.9, 131.0, 130.4, 130.3, 128.8, 127.8, 126.9, 117.5, 35.0, 34.4, 33.3, 27.5, 20.9. HRMS: Calculated for $C_{24}H_{22}NO_3S$ $[M + H]^+$ 404.1315, found: 404.1317.

*4-(4-Chlorophenyl)-(8-methyl[2.2]paracyclophano)[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1p**).* 0.354 g, 47% yield, yellow solid, mp = 286−288 °C, new compound, R_f = 0.30 (hexanes/dichloromethane 1/1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.71−7.55 (m, 2H), 7.50−7.40 (m, 2H), 7.12−7.05 (m, 1H), 6.95−6.90 (m, 1H), 6.62−6.56 (m, 1H), 6.36−6.29 (m, 2H), 3.56−3.43 (m, 1H), 3.41−3.26 (m, 1H), 3.07−2.64 (m, 5H), 2.40−2.25 (m, 1H), 2.16 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.9, 154.3, 145.1, 144.7, 139.6, 139.1, 137.4, 136.9, 136.2, 134.6, 131.7, 131.0, 130.3, 129.2, 127.9, 127.2, 117.3, 35.3, 34.4, 33.3, 27.5, 20.9. HRMS: Calculated for $C_{24}H_{21}ClNO_3S$ $[M + H]^+$ 438.0925, found: 438.0926 (^{35}Cl), 440.0897 (^{37}Cl).

General Procedure for Kinetic Resolution. Nickel acetate tetrahydrate (2.5 mg, 5 mol %), (*S,S*)-Ph-BPE (5.1 mg, 5 mol %), and substrate *rac*-**1** (0.20 mmol) were placed in a vial. They were then transferred to a nitrogen-filled glovebox, and the degassed anhydrous hexafluoroisopropanol (3.00 mL) was added. The vial was subsequently transferred into an autoclave into which hydrogen gas was charged. The reaction was stirred under H_2 (600 psi) at 60 °C in a stainless steel autoclave for 120 h. After carefully releasing hydrogen gas, the autoclave was opened and the reaction mixture was evaporated. The resulting mixture was concentrated under reduced pressure, and the conversion of *rac*-**1** was confirmed by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. The solvent was evaporated in *vacuo*; the recovered material **1** and reductive product **2** were isolated by column chromatography on silica gel using hexanes and ethyl acetate as eluent. The enantiomeric excess of products and starting materials was measured by chiral HPLC analysis.

*(+)-4-Phenyl-3,4-dihydro-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2a**).* 39.0 mg, 50% yield, >20:1 dr, white solid, known compound, R_f = 0.40 (hexanes/acetone 5/1), 93.0% ee, $[\alpha]^{20}_D$ = +56.36 (*c* 0.22, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.82−7.71 (m, 2H), 7.60−7.45 (m, 3H), 6.67−6.55 (m, 3H), 6.52−6.44 (m, 1H), 6.35−6.25 (m, 1H), 5.47 (d, *J* = 7.0 Hz, 1H), 5.36−5.28 (m, 1H), 5.07 (d, *J* = 7.0 Hz, 1H), 3.57−3.39 (m, 1H), 3.32−3.14 (m, 1H), 3.09−2.95 (m, 1H), 2.93−2.62 (m, 4H), 2.56−2.41 (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, 133.0, 132.9, 131.2, 130.0, 129.5, 129.4, 128.9, 124.5, 61.2, 35.2, 34.6, 32.1, 28.7. HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 18.8 min (major), 24.4 min (minor). **4-Phenyl-3,4-dihydro-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2a′)**: white solid, known compound, R_f = 0.45 (hexanes/acetone 5/1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.40−7.30 (m, 3H), 7.26−7.20 (m, 2H), 7.03−6.95 (m, 1H), 6.89−6.80 (m, 1H), 6.63−6.54 (m, 3H), 6.41−6.30 (m, 1H), 5.51 (d, *J* = 8.9 Hz, 1H), 4.51 (d, *J* = 8.9 Hz, 1H), 3.51−3.35 (m, 1H), 3.31−3.16 (m, 1H), 3.13−2.89 (m, 3H), 2.84−2.70 (m, 1H), 2.64−2.41 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.6, 141.0, 139.9, 139.1, 138.5, 135.7, 133.4, 132.9, 131.6, 130.5, 129.2, 129.2, 128.3, 119.9, 61.3, 34.4, 34.1, 33.7, 29.1. **(+)-4-Phenyl-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1a)**: 38.0 mg, 49% yield, 92.1% ee, $[\alpha]^{20}_D$ = +389.97 (*c* 0.62, $CHCl_3$). HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 9.1 min (minor), 10.5 min (major).

*(+)-4-(m-Tolyl)-3,4-dihydro-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2b**).* 41.0 mg, 51% yield, >20:1 dr, white solid, mp = 167−169 °C, new compound, R_f = 0.30 (hexanes/dichloromethane 1/1), 92.2% ee, $[\alpha]^{20}_D$ = +53.92 (*c* 0.56, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58−7.51 (m, 2H), 7.47−7.40 (m, 1H), 7.32−7.27 (m, 1H), 6.67−6.56 (m, 3H), 6.50−6.44 (m, 1H), 6.33−6.25 (m, 1H), 5.47−5.38 (m, 2H), 5.03 (d, *J* = 6.9 Hz, 1H), 3.53−3.40 (m, 1H), 3.30−3.18 (m, 1H), 3.10−2.97 (m, 1H), 2.93−2.63 (m, 4H), 2.55−2.41 (m, 1H), 2.49 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.4, 139.9, 139.2, 139.1, 138.6, 137.0, 136.2, 133.2, 133.0, 132.9, 131.3, 130.1, 129.9, 129.6, 129.4, 129.3, 125.9, 124.3, 61.1, 35.2, 34.6, 32.1, 28.7, 21.7. HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 14.7 min (major), 22.0 min (minor). HRMS: Calculated for $C_{24}H_{27}N_2O_3S$ $[M + NH_4]^+$ 423.1737, found: 423.1735. **(+)-4-(*m*-Tolyl)-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1b)**: 37.0 mg, 46% yield, 98.8% ee, $[\alpha]^{20}_D$ = +296.77 (*c* 0.78, $CHCl_3$). HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 8.5 min (minor), 9.6 min (major).

*(+)-4-(p-Tolyl)-3,4-dihydro-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2c**).* 40.0 mg, 49% yield, 9.2:1 dr, white solid, mp = 174−176 °C, new compound, R_f = 0.35 (hexanes/dichloromethane 1/1), 95.1% ee, $[\alpha]^{20}_D$ = +62.79 (*c* 0.68, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.68−7.61 (m, 2H), 7.39−7.31 (m, 2H), 6.65−6.55 (m, 3H), 6.49−6.42 (m, 1H), 6.32−6.24 (m, 1H), 5.41 (d, *J* = 6.8 Hz, 1H), 5.38−5.31 (m, 1H), 5.01 (d, *J* = 6.7 Hz, 1H), 3.54−3.39 (m, 1H), 3.30−3.16 (m, 1H), 3.09−2.96 (m, 1H), 2.94−2.68 (m, 4H), 2.60−2.47 (m, 1H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.2, 139.9, 139.4, 139.2, 138.6, 136.1, 134.0, 133.1, 132.9, 131.3, 130.0, 129.3, 128.9, 124.7, 61.0, 35.1, 34.6, 32.0, 28.7, 21.4. HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 18.6 min (major), 25.4 min (minor). HRMS: Calculated for $C_{24}H_{24}NO_3S$ $[M + H]^+$ 406.1471, found: 406.1470. **(+)-4-(*p*-Tolyl)-[2.2]paracyclophano-[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1c)**: 39.0 mg, 48% yield, 93.5% ee, $[\alpha]^{20}_D$ = +279.70 (*c* 0.72, $CHCl_3$). HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 9.1 min (minor), 11.5 min (major).

*(+)-4-(4-Methoxyphenyl)-3,4-dihydro-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2d**).* 23.0 mg, 46% yield, 1.5:1 dr, white solid, mp = 84−86 °C, new compound, R_f = 0.25 (hexanes/dichloromethane 1/1), 95.2% ee, $[\alpha]^{20}_D$ = +46.54 (c 0.26, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.76−7.62 (m, 2H), 7.14−7.00 (m, 2H), 6.69−6.53 (m, 3H), 6.53−6.41 (m, 1H), 6.35−6.22 (m, 1H), 5.47−5.31 (m, 2H), 5.00 (d, *J* = 6.3 Hz, 1H), 3.87 (s, 3H), 3.56−3.37 (m, 1H), 3.31−3.14 (m, 1H), 3.11−2.95 (m, 1H), 2.96−2.69 (m, 4H), 2.62−2.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 149.1, 139.9, 139.2, 138.6, 136.1, 133.0, 132.9, 132.9, 131.4, 130.4, 129.9, 129.4, 128.9, 125.0, 114.6, 60.8, 55.6, 35.1, 34.6, 31.9, 28.7. HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 22.6 min (major), 30.8 min (minor). HRMS: Calculated for $C_{24}H_{24}NO_4S$ $[M + H]^+$ 422.1421, found: 422.1420. **(+)-4-(4-Methoxyphenyl)-3,4-dihydro-[2.2]-paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2d′)**: 15.0 mg, 1.5:1 dr, white solid, known compound, R_f = 0.30 (hexanes/dichloromethane 1/1), 62.1% ee, $[\alpha]^{20}_D$ = +21.15 (*c* 0.26,

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$CHCl_3$), [lit.[12d]: $[\alpha]^{20}_D$ = +21.46 (*c* 0.82, $CHCl_3$) for 45.9% ee (S_p,*R*)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.10 (m, 2H), 7.05−6.93 (m, 1H), 6.89−6.79 (m, 3H), 6.64−6.51 (m, 3H), 6.38−6.30 (m, 1H), 5.51−5.42 (m, 1H), 4.54−4.45 (m, 1H), 3.79 (s, 3H), 3.47−3.33 (m, 1H), 3.29−3.15 (m, 1H), 3.11−2.88 (m, 3H), 2.82−2.69 (m, 1H), 2.61−2.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 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 (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 16.3 min (major), 20.1 min (minor). **(+)-4-(4-Methoxyphenyl)-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1d)**: 41.0 mg, 49% yield, 87.9% ee, $[\alpha]^{20}_D$ = +276.17 (*c* 0.84, $CHCl_3$). HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 11.4 min (minor), 15.7 min (major).

*(+)-4-(4-Fluorophenyl)-3,4-dihydro-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2e**).* 41.0 mg, 50% yield, 15.0:1 dr, white solid, mp = 84−86 °C, new compound, R_f = 0.35 (hexanes/dichloromethane 1/1), 93.3% ee, $[\alpha]^{20}_D$ = +92.10 (*c* 0.38, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.70 (m, 2H), 7.26−7.20 (m, 2H), 6.68−6.52 (m, 3H), 6.51−6.44 (m, 1H), 6.34−6.25 (m, 1H), 5.41 (d, *J* = 6.9 Hz, 1H), 5.37−5.28 (m, 1H), 5.04 (d, *J* = 6.9 Hz, 1H), 3.50−3.39 (m, 1H), 3.27−3.16 (m, 1H), 3.10−2.97 (m, 1H), 2.95−2.80 (m, 3H), 2.76−2.65 (m, 1H), 2.57−2.45 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.1 ($J_{C\text{-}F}$ = 249.6 Hz), 149.1, 139.9, 139.1, 138.5, 136.3, 133.1, 133.0, 133.0, 132.8 ($J_{C\text{-}F}$ = 3.5 Hz), 131.1, 131.0 ($J_{C\text{-}F}$ = 8.3 Hz), 129.8, 129.5, 124.9, 116.3 ($J_{C\text{-}F}$ = 21.6 Hz), 60.4, 35.1, 34.6, 31.9, 28.7. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −111.6. HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 21.7 min (major), 23.8 min (minor). HRMS: Calculated for $C_{23}H_{20}FNaNO_3S$ [M + Na]$^+$ 432.1040, found: 432.1047. **(+)-4-(4-Fluorophenyl)-[2.2]-paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1e)**: 38.0 mg, 47% yield, 97.2% ee, $[\alpha]^{20}_D$ = +329.83 (*c* 0.68, $CHCl_3$). HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 9.4 min (minor), 11.1 min (major).

*(+)-4-(4-Chlorophenyl)-3,4-dihydro-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2f**).* 43.0 mg, 51% yield, 15.0:1 dr, white solid, mp = 103−105 °C, new compound, R_f = 0.35 (hexanes/dichloromethane 1/1), 93.4% ee, $[\alpha]^{20}_D$ = +56.25 (*c* 0.64, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76−7.68 (m, 2H), 7.58−7.48 (m, 2H), 6.66−6.51 (m, 3H), 6.51−6.44 (m, 1H), 6.34−6.25 (m, 1H), 5.39 (d, *J* = 6.8 Hz, 1H), 5.36−5.30 (m, 1H), 5.05 (d, *J* = 6.9 Hz, 1H), 3.51−3.37 (m, 1H), 3.29−3.16 (m, 1H), 3.11−2.98 (m, 1H), 2.96−2.78 (m, 3H), 2.78−2.63 (m, 1H), 2.60−2.41 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.1, 139.9, 139.2, 138.4, 136.4, 135.4, 133.1, 133.0, 133.0, 131.1, 130.5, 129.8, 129.5, 129.5, 124.8, 60.4, 35.1, 34.6, 32.0, 28.7. HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 24.2 min (minor), 27.9 min (major). HRMS: Calculated for $C_{23}H_{21}ClNO_3S$ [M + H]$^+$ 426.0925, found: 426.0929 (^{35}Cl) and 428.0904 (^{37}Cl). **(+)-4-(4-Chlorophenyl)-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1f)**: 40.0 mg, 47% yield, 96.4% ee, $[\alpha]^{20}_D$ = +331.13 (*c* 0.78, $CHCl_3$). HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 10.1 min (minor), 12.1 min (major).

*(+)-4-(4-Bromophenyl)-3,4-dihydro-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2g**).* 48.0 mg, 51% yield, 14.0:1 dr, white solid, mp = 108−110 °C, new compound, R_f = 0.33 (hexanes/dichloromethane 1/1), 94.3% ee, $[\alpha]^{20}_D$ = +56.33 (*c* 0.60, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.59 (m, 4H), 6.68−6.52 (m, 3H), 6.51−6.44 (m, 1H), 6.37−6.27 (m, 1H), 5.42−5.30 (m, 2H), 5.04 (d, *J* = 7.0 Hz, 1H), 3.52−3.38 (m, 1H), 3.28−3.16 (m, 1H), 3.10−2.98 (m, 1H), 2.94−2.80 (m, 3H), 2.78−2.63 (m, 1H), 2.61−2.47 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.2, 139.9, 139.2, 138.4, 136.4, 135.9, 133.1, 133.0, 133.0, 132.5, 131.1, 130.8, 129.8, 129.5, 124.7, 123.6, 60.5, 35.1, 34.6, 32.0, 28.7. HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 25.1 min (minor), 29.9 min (major). HRMS: Calculated for $C_{23}H_{24}BrN_2O_3S$ [M + NH_4]$^+$ 487.0686, found: 487.0687 (^{79}Br) and 489.0668 (^{81}Br).

*(+)-4-(4-Bromophenyl)-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1g**).* 48.0 mg, 47% yield, 97.1% ee, $[\alpha]^{20}_D$ = +313.40 (*c* 0.76, $CHCl_3$). HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 10.6 min (minor), 12.7 min (major).

*(+)-4-(4-Iodophenyl)-3,4-dihydro-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2h**).* 46.0 mg, 44% yield, >20:1 dr, white solid, mp = 213-215 °C, new compound, R_f = 0.36 (hexanes/dichloromethane 1/1), 97.3% ee, $[\alpha]^{20}_D$ = +52.62 (*c* 0.80, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.82 (m, 2H), 7.57−7.44 (m, 2H), 6.69−6.41 (m, 4H), 6.36−6.25 (m, 1H), 5.40−5.31 (m, 2H), 5.05 (d, *J* = 7.0 Hz, 1H), 3.52−3.37 (m, 1H), 3.30−3.15 (m, 1H), 3.10−2.97 (m, 1H), 2.95−2.79 (m, 3H), 2.78−2.63 (m, 1H), 2.60−2.45 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.1, 139.9, 139.2, 138.4, 138.4, 136.6, 136.4, 133.1, 133.0, 133.0, 131.1, 130.9, 129.8, 129.5, 124.6, 95.2, 60.5, 35.1, 34.6, 32.0, 28.7. HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 25.4 min (major), 27.4 min (minor). HRMS: Calculated for $C_{23}H_{24}IN_2O_3S$ [M + NH_4]$^+$ 535.0547, found: 535.0546.

*(+)-4-(4-Iodophenyl)-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**1h**).* 56.0 mg, 54% yield, 77.6% ee, $[\alpha]^{20}_D$ = +228.11 (*c* 0.96, $CHCl_3$). HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 11.3 min (minor), 13.5 min (major).

*(+)-4-(3-Fluorophenyl)-3,4-dihydro-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2i**).* 41.0 mg, 50% yield, 16.0:1 dr, white solid, mp = 176−178 °C, new compound, R_f = 0.35 (hexanes/dichloromethane 1/1), 73.7% ee, $[\alpha]^{20}_D$ = +68.75 (*c* 0.80, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.45 (m, 3H), 7.24−7.15 (m, 1H), 6.67−6.53 (m, 3H), 6.52−6.44 (m, 1H), 6.35−6.27 (m, 1H), 5.41 (d, *J* = 7.1 Hz, 1H), 5.36−5.27 (m, 1H), 5.08 (d, *J* = 7.1 Hz, 1H), 3.55−3.37 (m, 1H), 3.33−3.14 (m, 1H), 3.12−2.97 (m, 1H), 2.94−2.79 (m, 3H), 2.79−2.64 (m, 1H), 2.62−2.46 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.1 ($J_{C\text{-}F}$ = 248.0 Hz), 149.2, 139.9, 139.3 ($J_{C\text{-}F}$ = 6.9 Hz), 139.2, 138.5, 136.4, 133.2, 133.0, 133.0, 131.0, 131.0 ($J_{C\text{-}F}$ = 8.1 Hz), 129.9, 129.5, 124.7 ($J_{C\text{-}F}$ = 2.9 Hz), 124.5, 116.4 ($J_{C\text{-}F}$ = 20.8 Hz), 116.3 ($J_{C\text{-}F}$ = 22.6 Hz), 60.4, 35.1, 34.6, 32.0, 28.7. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −110.7. HPLC (Chiralcel IB column, *n*-Hexane/*i*-PrOH = 70/30, flow rate = 0.8 mL/min, *I* = 254 nm, 30 °C) t_R = 8.7 min (major), 17.7 min (minor). HRMS: Calculated for $C_{23}H_{21}FNO_3S$ [M + H]$^+$ 410.1221, found: 410.1224. **(+)-4-(3-Fluorophenyl)-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1i)**: 39.0 mg, 48% yield, 91.4% ee, $[\alpha]^{20}_D$ = +357.27 (*c* 0.74, $CHCl_3$). HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, *I* = 254 nm, 30 °C) t_R = 10.9 min (minor), 12.2 min (major).

*(+)-4-(3-Chlorophenyl)-3,4-dihydro-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2j**).* 46.0 mg, 54% yield, 17.0:1 dr, white solid, mp = 212−214 °C, new compound, R_f = 0.25 (hexanes/dichloromethane 1/1), 88.1% ee, $[\alpha]^{20}_D$ = +79.37 (*c* 0.80, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82−7.73 (m, 1H), 7.72−7.64 (m, 1H), 7.58−7.42 (m, 2H), 6.70−6.55 (m, 3H), 6.54−6.46 (m, 1H), 6.36−6.27 (m, 1H), 5.39 (d, *J* = 7.0 Hz, 1H), 5.36−5.30 (m, 1H), 5.04 (d, *J* = 7.0 Hz, 1H), 3.53−3.39 (m, 1H), 3.29−3.17 (m, 1H), 3.11−2.97 (m, 1H), 2.96−2.80 (m, 3H), 2.78−2.63 (m, 1H), 2.60−2.47 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.2, 140.0, 139.2, 138.8, 138.4, 136.5, 135.2, 133.2, 133.0, 133.0, 131.0, 130.6, 129.8, 129.6, 129.3, 127.2, 124.4, 60.4, 35.1, 34.6, 32.0, 28.7. HPLC (Chiralcel IB column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 9.8 min (major), 16.5 min (minor). HRMS: Calculated for $C_{23}H_{20}ClNNaO_3S$ [M + Na]$^+$ 448.0745, found: 448.0740 (^{35}Cl) and 450.0711 (^{37}Cl). **(+)-4-(3-Chlorophenyl)-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1j)**: 37.0 mg, 44% yield, 98.8% ee, $[\alpha]^{20}_D$ = +317.48 (*c* 0.72, $CHCl_3$). HPLC (Chiralcel AD-H column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 11.2 min (major), 15.0 min (minor).

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*(+)-4-(2-Naphthyl)-3,4-dihydro-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2k**).* 45.0 mg, 51% yield, 16.0:1 dr, white solid, mp = 103−105 °C, new compound, R_f = 0.30 (hexanes/dichloromethane 1/1), 90.8% ee, $[\alpha]^{20}_D$ = +101.53 (*c* 0.78, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15−8.09 (m, 1H), 8.07−7.86 (m, 4H), 7.64−7.54 (m, 2H), 6.71−6.52 (m, 3H), 6.51−6.43 (m, 1H), 6.33−6.25 (m, 1H), 5.62 (d, *J* = 7.1 Hz, 1H), 5.43−5.32 (m, 1H), 5.17 (d, *J* = 7.1 Hz, 1H), 3.57−3.41 (m, 1H), 3.32−3.16 (m, 1H), 3.12−2.96 (m, 1H), 2.94−2.65 (m, 4H), 2.45−2.29 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.5, 139.9, 139.3, 138.5, 136.3, 134.4, 133.4, 133.4, 133.2, 133.0, 132.9, 131.3, 129.8, 129.4, 129.2, 128.3, 128.0, 128.0, 127.2, 127.1, 126.3, 124.3, 61.2, 35.1, 34.6, 32.2, 28.7. HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 19.0 min (major), 30.5 min (minor). HRMS: Calculated for $C_{27}H_{24}NO_3S$ $[M + H]^+$ 442.1471, found: 442.1477. **(+)-4-(2-Naphthyl)[2.2]-paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1k)**: 40.0 mg, 46% yield, 96.9% ee, $[\alpha]^{20}_D$ = +326.19 (*c* 0.74, $CHCl_3$). HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 10.8 min (minor), 15.5 min (major).

*(+)-4-Methyl-3,4-dihydro-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2l**).* The reaction was conducted for 12 h. 19.0 mg, 56% yield, 1.1:1 dr, white solid, mp = 153−155 °C, new compound, R_f = 0.45 (hexanes/dichloromethane/ethyl acetate 10/10/1), 99.0% ee, $[\alpha]^{20}_D$ = +11.58 (*c* 0.38, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79−6.60 (m, 3H), 6.55−6.41 (m, 2H), 6.40−6.24 (m, 1H), 4.55−4.34 (m, 2H), 3.47−3.36 (m, 1H), 3.24−2.99 (m, 5H), 2.98−2.84 (m, 1H), 2.83−2.72 (m, 1H), 1.94 (d, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.0, 140.4, 138.9, 138.1, 135.7, 133.4, 133.0, 131.7, 131.1, 129.4, 129.2, 127.8, 52.0, 35.3, 34.5, 31.4, 28.8, 18.7. HPLC (Chiralcel AD-H column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 14.6 min (major), 24.3 min (minor). HRMS: Calculated for $C_{18}H_{20}NO_3S$ $[M + H]^+$ 330.1158, found: 330.1154. **(−)-4-Methyl-3,4-dihydro-[2.2]-paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2l′)**: 18.0 mg, 1.1:1 dr, white solid, known compound, R_f = 0.50 (hexanes/dichloromethane/ethyl acetate 10/10/1), 94.8% ee, $[\alpha]^{20}_D$ = −47.00 (*c* 0.20, $CHCl_3$), [lit.[12b]: $[\alpha]^{20}_D$ = −46.61 (*c* 1.24, $CHCl_3$) for 98% ee (R_p,*S*)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99−6.90 (m, 1H), 6.64−6.49 (m, 4H), 6.47−6.40 (m, 1H), 4.91 (d, *J* = 7.1 Hz, 1H), 4.45 (p, *J* = 7.1 Hz, 1H), 3.45−3.28 (m, 1H), 3.26−2.99 (m, 5H), 2.99−2.85 (m, 1H), 2.75−2.58 (m, 1H), 1.59 (d, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.6, 140.1, 138.3, 138.1, 134.7, 134.1, 133.3, 131.1, 129.6, 128.8, 128.1, 122.5, 53.8, 33.9, 33.8, 32.7, 29.7, 22.5. HPLC (Chiralcel OD-H column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 9.4 min (minor), 10.7 min (major). **(−)-4-Methyl-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1l)**: 27.0 mg, 41% yield, 1.9% ee, $[\alpha]^{20}_D$ = −7.18 (*c* 0.78, $CHCl_3$). HPLC (Chiralcel OD-H column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 13.3 min (major), 15.2 min (minor).

*4-tert-Butyl-3,4-dihydro-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2m**).* Nickel acetate tetrahydrate (12.4 mg, 25 mol %) and (*S*,*S*)-Ph-BPE (5.1 mg, 5 mol %) were used in this reaction, and the reaction was conducted for 72 h. 37.0 mg, 50% yield, 14.0:1 dr, white solid, mp = 276−278 °C, new compound, R_f = 0.40 (hexanes/dichloromethane 1/1), 94.7% ee, $[\alpha]^{20}_D$ = +6.38 (*c* 0.58, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05−6.97 (m, 1H), 6.73−6.64 (m, 2H), 6.55−6.48 (m, 1H), 6.47−6.35 (m, 2H), 5.07 (d, *J* = 6.7 Hz, 1H), 4.14 (d, *J* = 6.8 Hz, 1H), 3.50−3.35 (m, 1H), 3.32−3.15 (m, 2H), 3.15−2.92 (m, 4H), 2.89−2.75 (m, 1H), 0.95 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.9, 140.4, 138.6, 138.4, 135.8, 133.3, 132.7, 132.3, 131.4, 130.7, 129.1, 120.5, 65.7, 37.6, 35.0, 34.8, 33.1, 29.1, 26.7. HPLC (Chiralcel IC column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 7.7 min (minor), 8.8 min (major). HRMS: Calculated for $C_{21}H_{26}NO_3S$ $[M + H]^+$ 372.1628, found: 372.1630. **(−)-4-*tert*-Butyl-[2.2]-paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1m)**: 36.0 mg, 49% yield, 69.4% ee, $[\alpha]^{20}_D$ = −318.49 (*c* 0.74, $CHCl_3$). HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 7.2 min (major), 7.8 min (minor).

*(−)-4-(2-Furyl)-3,4-dihydro-[2.2]paracyclophano[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2n**).* The reaction was conducted for 30 h. 22.0 mg, 51% yield, 1.3:1 dr, white solid, mp = 70−72 °C, new compound, R_f = 0.50 (hexanes/ethyl acetate 5/1), 50.1% ee, $[\alpha]^{20}_D$ = −41.74 (*c* 0.46, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.37 (m, 1H), 7.03−6.91 (m, 1H), 6.80−6.72 (m, 1H), 6.66−6.53 (m, 3H), 6.46−6.38 (m, 1H), 6.36−6.27 (m, 1H), 6.17−6.06 (m, 1H), 5.55 (d, *J* = 8.0 Hz, 1H), 5.09−4.95 (m, 1H), 3.48−3.32 (m, 1H), 3.24−2.91 (m, 4H), 2.81−2.64 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.8, 150.8, 143.1, 140.5, 140.0, 138.4, 135.7, 133.8, 133.2, 131.1, 129.7, 129.4, 128.4, 118.1, 110.9, 110.1, 54.8, 34.1, 34.0, 32.9, 29.4. HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 9.5 min (minor), 13.7 min (major). HRMS: Calculated for $C_{21}H_{23}N_2O_4S$ $[M + NH_4]^+$ 399.1373, found: 399.1372. **(+)-4-(2-Furyl)-3,4-dihydro-[2.2]-paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2n′)**: 17.0 mg, 1.3:1 dr, white solid, mp = 230−232 °C, new compound, R_f = 0.35 (hexanes/ethyl acetate 5/1), 98.0% ee, $[\alpha]^{20}_D$ = +13.18 (*c* 0.22, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.61 (m, 1H), 6.83−6.78 (m, 1H), 6.64−6.56 (m, 4H), 6.52−6.45 (m, 1H), 6.37−6.29 (m, 1H), 5.55 (d, *J* = 7.5 Hz, 1H), 5.41−5.33 (m, 1H), 4.96 (d, *J* = 7.4 Hz, 1H), 3.52−3.37 (m, 1H), 3.26−3.13 (m, 1H), 3.10−2.99 (m, 1H), 2.98−2.75 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.3, 148.7, 142.5, 139.9, 139.2, 138.9, 136.3, 133.1, 132.7, 132.6, 131.0, 130.0, 129.7, 123.4, 112.1, 110.3, 53.9, 35.1, 34.4, 31.7, 29.0. HPLC (Chiralcel IC column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 12.5 min (major), 14.8 min (minor). HRMS: Calculated for $C_{21}H_{23}N_2O_4S$ $[M + NH_4]^+$ 399.1373, found: 399.1375. **(+)-4-(2-Furyl)-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1n)**: 32.0 mg, 43% yield, 17.2% ee, $[\alpha]^{20}_D$ = +70.16 (*c* 0.60, $CHCl_3$). HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 10.2 min (minor), 11.1 min (major).

*(+)-4-(4-Phenyl)-3,4-dihydro-(8-methyl[2.2]paracyclophano)-[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2o**).* Nickel acetate tetrahydrate (12.4 mg, 25 mol %) and (*S*,*S*)-Ph-BPE (5.1 mg, 5 mol %) were used in this reaction, and the reaction was conducted for 176 h at 40 °C. 30.0 mg, 37% yield, 15.0:1 dr, white solid, mp = 238−240 °C, new compound, R_f = 0.30 (hexanes/dichloromethane 1/1), 97.2% ee, $[\alpha]^{20}_D$ = +102.31 (*c* 0.56, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.82 (m, 2H), 7.61−7.51 (m, 2H), 7.51−7.43 (m, 1H), 6.91−6.82 (m, 1H), 6.57−6.51 (m, 1H), 6.50−6.42 (m, 1H), 6.09 (s, 1H), 5.33 (d, *J* = 5.9 Hz, 1H), 5.02−4.96 (m, 1H), 4.92 (d, *J* = 5.8 Hz, 1H), 3.50−3.36 (m, 1H), 3.26−3.13 (m, 1H), 3.12−2.94 (m, 2H), 2.90−2.79 (m, 2H), 2.78−2.68 (m, 1H), 2.67−2.54 (m, 1H), 2.06 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.1, 139.3, 138.7, 137.9, 137.8, 137.3, 136.0, 131.5, 131.4, 130.0, 129.5, 129.3, 129.3, 128.1, 128.0, 126.4, 61.9, 34.3, 32.7, 28.1, 27.9, 20.6. HPLC (Chiralcel IB column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 13.0 min (major), 15.2 min (minor). HRMS: Calculated for $C_{24}H_{27}N_2O_3S$ $[M + NH_4]^+$ 423.1737, found: 423.1747. **(+)-4-(4-Phenyl)-(8-methyl[2.2]-paracyclophano)[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1o)**: 49.0 mg, 61% yield, 55.6% ee, $[\alpha]^{20}_D$ = +146.76 (*c* 0.96, $CHCl_3$). HPLC (Chiralcel AD-H column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, *I* = 254 nm, 30 °C) t_R = 8.8 min (minor), 10.1 min (major).

*(+)-4-(4-Chlorophenyl)-3,4-dihydro-(8-methyl[2.2]paracyclophano)[5,6-d]-1,2,3-benzoxathiazine 2,2-Dioxide (**2p**).* Nickel acetate tetrahydrate (12.4 mg, 25 mol %) and (*S*,*S*)-Ph-BPE (5.1 mg, 5 mol %) were used in this reaction, and the reaction was conducted for 176 h at 40 °C. 18.0 mg, 21% yield, >20:1 dr, white solid, mp = 246−248 °C, new compound, R_f = 0.25 (hexanes/dichloromethane 1/1), 97.6% ee, $[\alpha]^{20}_D$ = +88.12 (*c* 0.48, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.77 (m, 2H), 7.57−7.47 (m, 2H), 6.94−6.84 (m, 1H), 6.58−6.43 (m, 2H), 6.10 (s, 1H), 5.30 (d, *J* = 6.0 Hz, 1H), 5.16−5.06 (m, 1H), 4.88 (d, *J* = 6.0 Hz, 1H), 3.51−3.34 (m, 1H),

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3.26−3.15 (m, 1H), 3.14−2.95 (m, 2H), 2.94−2.82 (m, 1H), 2.81−2.58 (m, 3H), 2.06 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.2, 139.4, 138.6, 138.0, 137.8, 136.2, 135.5, 135.4, 131.7, 131.3, 131.0, 129.8, 129.5, 128.3, 128.2, 126.6, 61.2, 34.3, 32.8, 28.4, 27.9, 20.6. HPLC (Chiralcel IB column, *n*-Hexane/*i*-PrOH = 80/20, flow rate = 0.8 mL/min, I = 254 nm, 30 °C) t_R = 11.1 min (major), 15.3 min (minor). HRMS: Calculated for $C_{24}H_{23}ClNO_3S$ $[M + H]^+$ 440.1082, found: 440.1098 (^{35}Cl) and 442.1079 (^{37}Cl). **(+)-4-(4-Chlorophenyl)-(8-methyl[2.2]paracyclophano)[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (1p)**: 67.0 mg, 77% yield, 26.3% ee, $[\alpha]^{20}_D$ = +102.45 (*c* 1.22, $CHCl_3$). HPLC (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, I = 254 nm, 30 °C) t_R = 12.3 min (minor), 13.5 min (major).

Synthesis of (−)-4-Phenyl-3,4-dihydro-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-Dioxide (2a′). Sodium tetrahydridoborate (38 mg, 1.00 mmol, 5.0 equiv) was added to a solution of imine (+)-**1a** (78 mg, 0.20 mmol, 99% ee) in methanol (3.0 mL) and tetrahydrofuran (3.0 mL) at 0 °C. The reaction was performed at 0 °C overnight. The reaction mixture was quenched by addition of saturated aqueous ammonium chloride solution (15 mL). After being extracted with dichloromethane (15 mL × 3), the combined organic layer was dried by anhydrous sodium sulfate, concentrated in *vacuo*, then purification by silica gel chromatography using hexanes and dichloromethane as eluent to give the product (−)-**2a′**. 74 mg, 95% yield, >20:1 dr, white solid, known compound, R_f = 0.40 (hexanes/ethyl acetate 5/1), 99% ee, $[\alpha]^{20}_D$ = −60.00 (*c* 1.36, $CHCl_3$), [lit.[12b]: $[\alpha]^{20}_D$ = −55.78 (*c* 1.66, $CHCl_3$) for 98% ee (R_p,*S*)]. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38−7.29 (m, 3H), 7.26−7.20 (m, 2H), 7.03−6.97 (m, 1H), 6.89−6.82 (m, 1H), 6.65−6.53 (m, 3H), 6.39−6.31 (m, 1H), 5.51 (d, J = 8.9 Hz, 1H), 4.60 (d, J = 8.8 Hz, 1H), 3.46−3.33 (m, 1H), 3.28−3.17 (m, 1H), 3.11−2.89 (m, 3H), 2.83−2.69 (m, 1H), 2.62−2.46 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.6, 141.0, 139.9, 139.1, 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 (Chiralcel IA column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, I = 254 nm, 30 °C) t_R = 10.4 min (minor), 15.2 min (major).

Synthesis of (+)-4-Benzoyl-5-hydroxy[2.2]paracyclophane (3). To a stirred mixture of imine (R_p)-(+)-**1a** (78 mg, 0.20 mmol, 99% ee) in mesitylene (2.0 mL) was added sodium hydroxide (24 mg, 0.60 mmol, 3.0 equiv). The resulting mixture was stirred at 80 °C for 4 h. The solvent was removed in *vacuo*, and the residue was purified by column chromatography on silica gel using hexanes and ethyl acetate as eluent to afford the corresponding product (+)-**3**. 61 mg, 93% yield, yellow solid, the known compound, R_f = 0.60 (hexanes/ethyl acetate 20/1), 99% ee, $[\alpha]^{20}_D$ = +241.21 (*c* 1.06, C_6H_6), [lit.[23]: $[\alpha]^{20}_D$ = −254.4 (*c* 0.25, C_6H_6) for 99% ee (S_p)]. ^1H NMR (400 MHz, $CDCl_3$) δ 11.94 (s, 1H), 7.78−7.68 (m, 2H), 7.62−7.53 (m, 1H), 7.50−7.40 (m, 2H), 7.15−7.04 (m, 1H), 6.66−6.55 (m, 2H), 6.53−6.44 (m, 2H), 6.38−6.29 (m, 1H), 3.55−3.43 (m, 1H), 3.28−3.16 (m, 1H), 3.13−3.01 (m, 1H), 2.91−2.80 (m, 1H), 2.68−2.38 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.1, 162.0, 144.4, 140.7, 140.2, 140.1, 138.1, 132.9, 132.6, 132.2, 131.0, 129.5, 128.9, 128.5, 127.7, 126.8, 121.2, 37.0, 35.3, 34.0, 30.3. HPLC (Chiralcel AD-H column, *n*-Hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, I = 254 nm, 30 °C) t_R = 8.3 min (minor), 9.5 min (major).

Synthesis of (+)-5-(Amino(phenyl)methyl)[2.2]paracyclophan-4-ol (4). To a suspension of lithium aluminum hydride ($LiAlH_4$, 15 mg, 0.40 mmol, 2.0 equiv) in THF (4 mL) was added the solution of (S_p,*S*)-(+)-**2a** (78 mg. 0.20 mmol, 99% ee) dropwise. The reaction was performed at room temperature for 3 h, aqueous potassium sodium tartrate was added to destroy the lithium aluminum hydride, the aqueous layer was extracted with ethyl acetate (10 mL × 3), and 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 eluent to afford the product (+)-**4**. 48 mg, 73% yield, white solid, mp = 120−122 °C. new compound, R_f = 0.25 (hexanes/ethyl acetate 5/1), 99% ee, $[\alpha]^{20}_D$ = 0.91 (*c* 0.44, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.01−7.86 (m, 2H), 7.60−7.47 (m, 2H), 7.46−7.35 (m, 1H), 6.62−6.50 (m, 2H), 6.47−6.35 (m, 1H), 6.33−6.21 (m, 1H), 6.02−5.86 (m, 1H), 5.36−5.25 (m, 1H), 5.10 (brs, 2H), 4.56 (d, J = 7.7 Hz, 1H), 3.52−3.35 (m, 1H), 3.25−3.07 (m, 2H), 3.05−2.85 (m, 2H), 2.82−2.55 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.7, 142.3, 140.2, 140.1, 138.0, 134.9, 133.0, 132.0, 130.8, 129.2, 129.1, 129.0, 128.6, 127.3, 125.9, 123.6, 58.1, 34.9, 34.7, 32.0, 29.0. HPLC (Chiralcel OD-H column, *n*-Hexane/*i*-PrOH = 60/40, flow rate = 0.6 mL/min, I = 254 nm, 30 °C) t_R = 49.7 min (major). HRMS: Calculated for $C_{23}H_{23}ClNO$ $[M + Cl]^-$ 364.1474, found: 364.1474 (^{35}Cl) and 366.1477 (^{37}Cl).

Scale-Up Reaction. Nickel acetate tetrahydrate (12.0 mg, 5 mol %), (*S*,*S*)-Ph-BPE (25.0 mg, 5 mol %), and substrate *rac*-**1a** (1.0 mmol) were placed in a vial. They were then transferred to a nitrogen-filled glovebox, and the degassed anhydrous hexafluoroisopropanol (12 mL) was added. The vial was transferred into an autoclave into which hydrogen gas was charged. The reaction was stirred under H_2 (600 psi) at 60 °C in a stainless steel autoclave for 120 h. After release of the hydrogen gas, the autoclave was opened and the reaction mixture was evaporated. The resulting mixture was dried under vacuum; the conversion of *rac*-**1a** (57% conversion) and diastereomeric ratio (13:1 dr) of the hydrogenation product were confirmed by ^1H NMR analysis with 1,3,5-trimethoxybenzene as internal standard. The solvent was removed in *vacuo*; the recovered material (+)-**1a** (165 mg, 42% yield with 99.1% ee) and the hydrogenation product (+)-**2a** (198 mg, 51% yield with 89.2% ee) were isolated by column chromatography on silica gel using hexanes and dichloromethane as eluent.

Determination of the Absolute Configuration of Compound 2a. To determine the absolute configuration of hydrogenation product (+)-**2a**, the (+)-**2a** was obtained as a colorless crystal after the recrystallization from chloroform/hexanes. On the basis of single crystal X-ray diffraction analysis, the structure of compound (+)-**2a** was determined as (S_p,*S*) 4-(4-phenyl)-3,4-dihydro-[2.2]paracyclophano[5,6-*d*]-1,2,3-benzoxathiazine 2,2-dioxide (see the Supporting Information). The CCDC number is 2050047. These details can be obtained free of charge via www.ccdc.cam.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.1c01011.

NMR spectra of products; copies of ^1H, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$ spectra of all new compounds; X-ray crystallography data **2a** (PDF)

Accession Codes

CCDC 2050047 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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Notes

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