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Dearomatization of [2.2]Paracyclophane-Derived *N*-Sulfonylimines through Cyclopropanation with Sulfur Ylides

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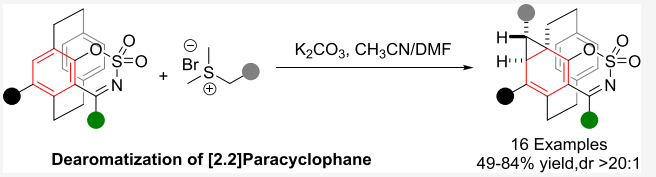
ABSTRACT: An unprecedented dearomatization of [2.2]-paracyclophane-derived cyclic *N*-sulfonylimines was conducted through cyclopropanation with sulfur ylides, giving a series of dearomative cyclopropanes with good yields. DFT calculations suggested that the dearomatization was attributed to the relatively weak aromaticity of [2.2]paracyclophane derivatives that resulted from the effect of the unique [2.2]paracyclophane skeleton and the electron-withdrawing *N*-sulfonyl group. Some downstream elaborations of the products were demonstrated.

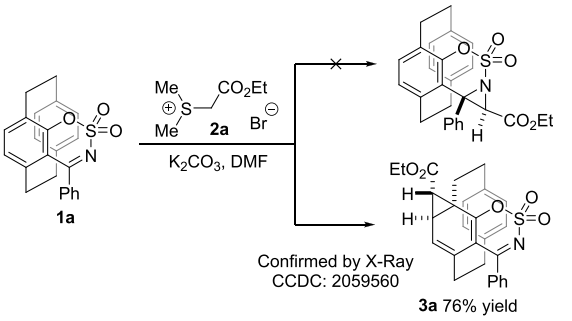


INTRODUCTION

Aromatic compounds can serve as bulk feedstocks in the chemical industry and play an important role in fundamental building blocks of living systems. The selective dearomatization reactions of the planar aromatic compounds provide a unique approach to access valuable three-dimensional molecules.[1] Dearomatization of heteroaromatics containing N or O atoms and phenols has progressed tremendously.[1] By contrast, there are few reports on the dearomatization of the carbocyclic rings of other arenes and their derivatives owing to dramatically improved resonance stabilization energy.[2] The [2.2]paracyclophane derivatives are widely prevalent in materials science.[3] In addition, they also could be used as chiral auxiliaries and ligands in stereoselective synthesis and asymmetric catalysis.[4] [2.2]Paracyclophane incorporates two highly strained benzene rings, which are locked by two ethylene bridges at their *para*-positions.[5] As a result of their ubiquitous scaffold, [2.2]paracyclophane derivatives can show unexpected chemical reactivities[6,7] and unique stereochemical features (planar chirality).[6c] Compared with other reactions, the dearomatization of [2.2]paracyclophanes has been less explored. Of the limited reports, Diels−Alder cycloaddition,[6b] hydrogenation,[6c] Birch reduction[6d−f] and carbene addition[6g,h] are reliable strategies. However, these reactions require harsh reaction conditions or afford a complex product mixture. In this regard, developing a mild and effective protocol for dearomatization of [2.2]paracyclophanes would diversify the [2.2]paracyclophane derivatives, which can serve as potential candidates for new [2.2]paracyclophane-derived ligands and materials that would be otherwise difficult to be prepared.

Recently, we had developed the kinetic resolution of the [2.2]paracyclophane-derived cyclic *N*-sulfonylimines.[8] During the course of this study, we attempted the aziridination of [2.2]paracyclophane-derived cyclic *N*-sulfonylimines with sulfur ylides.[9] To our surprise, no aziridine product was detected. The dearomatization was accompanied by cyclopropanation of the carbocyclic aromatic ring, affording **3a** with 76% yield (Scheme 1). This discovery suggested that the sulfur ylides were capable of disrupting the aromaticity of the carbocyclic ring. In this context, we began to study the dearomatization of [2.2]paracyclophane-derived cyclic *N*-sulfonylimines with sulfur ylides.

Scheme 1. Reaction of [2.2]Paracyclophane Derivatives with Sulfur Ylides and Dearomatization of [2.2]Paracyclophane Motif



RESULTS AND DISCUSSION

To begin our investigation, [2.2]paracyclophane-derived cyclic *N*-sulfonylimine *rac*-**1a** (1.0 equiv) and sulfonium salt **2a** (2.0 equiv) were chosen as model substrates. When the reaction was conducted in *N*,*N*-dimethylformamide (DMF), a series of

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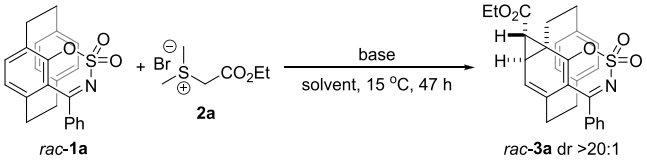
bases were examined. The reactions were shut down when triethylamine and lithium carbonate were used as the base (Table 1, entries 1 and 5). Using potassium hydroxide as the base led to an increase in the conversion of *rac*-**1a**, but the system was complex and only moderate 45% yield of *rac*-**3a** was obtained (entry 2). When sodium carbonate was also examined, the dearomatization was sluggish (entry 4). Potassium carbonate was found to be the optimal base after the screening of various bases (entry 3). Next, the effect of different solvents was tested. Acetonitrile and dichloromethane led to low reactivity (entries 6 and 7). Switching the solvent to ethanol gave only trace amount of *rac*-**3a** (entry 8). Thus, the next screening was focused on the mixed solvents. When the ratio of acetonitrile/*N*,*N*-dimethylformamide was 1:1, the yield of *rac*-**3a** (based on recovered starting materials) was increased up to 91% (entry 9). Hence, the optimal conditions were established: K_2CO_3 (3.0 equiv), CH_3CN/DMF (1:1).

Table 1. Optimization of Reaction Conditions

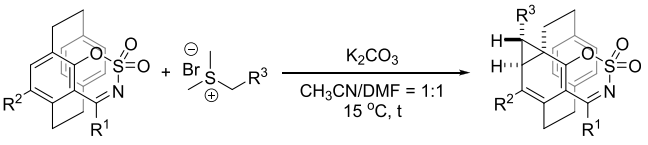


entry[a]	base	solvent	conv. (%)[b]	yield (%)[b]
1	Et_3N	DMF	<5	<5
2	KOH	DMF	91	45
3	K_2CO_3	DMF	89	76 (85)[c]
4	Na_2CO_3	DMF	13	13
5	Li_2CO_3	DMF	<5	<5
6	K_2CO_3	CH_3CN	39	37
7	K_2CO_3	DCM	23	21
8	K_2CO_3	EtOH	<5	<5
9	K_2CO_3	CH_3CN/DMF (1:1)	86	78 (91)[c]

[a]Reaction conditions: *rac*-**1a** (0.10 mmol), sulfonium salt **2a** (0.20 mmol, 2.0 equiv), base (0.30 mmol, 3.0 equiv), solvent (2.0 mL), 47 h. [b]Determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [c]Yield of *rac*-**3a** (brsm) = yield of *rac*-**3a**/conversion of *rac*-**1a**.

With the optimized conditions in hand, we evaluated the substrate scope and generality (Table 2). A series of sulfonium salts were examined. Ester- and amide-bearing sulfonium salts exhibited high activities, resulting in the formation of dearomative product **3a**-**3e** with excellent yields (entries 1−5). When R^3 was benzoyl, no reaction occurred under the standard conditions (entry 6). The reaction of a sulfonium salt bearing a cyano group was complex (entry 7). These unsatisfactory results might be ascribed to the electronic effect of the functional groups in the sulfonium salts. Then, a broad range of [2.2]paracyclophane-derived cyclic *N*-sulfonylimines *rac*-**1** were explored. The imines containing 3-MeC_6H_4 or 4-MeC_6H_4 were also well tolerated (Table 2, entries 8−9). Imine bearing electron-donating groups (R^1 = 4-$MeOC_6H_4$) showed lower reactivity than those bearing electron-withdrawing groups (R^1 = 4-FC_6H_4, 4-ClC_6H_4, 3-FC_6H_4, 3-ClC_6H_4), giving the dearomative product **3k** in 83% yield in 113 h (entry 11). Additionally, the reactions proceeded smoothly when R^1 was other halogen group (R^1 = 4-BrC_6H_4, 4-IC_6H_4), the desirable products **3m**-**3n** were obtained with moderate yields (entry 13−14). The naphthyl group was also tolerated (entry 17). 8-Substituted [2.2]paracyclophane-based *N*-sulfonylimine was synthesized to further estimate the substrate scope. Probably owing to steric effects, a moderate 49% yield was observed when the reaction was extended to 113 h (entry 18). The structures and relative configurations of **3a** and **3c′** were verified by the single crystal X-ray crystallographic analysis.[10,11] When this dearomatization was conducted on a 1.0 mmol scale under standard conditions, the yield and enantioselectivity of product **3j** could be retained (entry 19).

Table 2. Substrate Scope



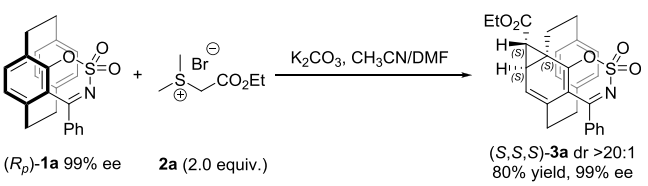
entry[a]	t (h)	R^1/R^2	R^3	yield (%)[b]
1	47	C_6H_5/H	CO_2Et	80 (**3a**)
2	47	C_6H_5/H	CO_2Me	77 (**3b**)
3	36	C_6H_5/H	$C(O)NEt_2$	70 (**3c**)[c]
4	36	C_6H_5/H	$C(O)NMe_2$	70 (**3d**)
5	36	C_6H_5/H	$C(O)NBn_2$	84 (**3e**)
6	72	C_6H_5/H	C(O)Ph	<5 (**3f**)
7	04	C_6H_5/H	CN	- (**3g**)[d]
8	47	3-MeC_6H_4/H	CO_2Et	84 (**3h**)
9	47	4-MeC_6H_4/H	CO_2Et	73 (**3i**)
10	12	4-FC_6H_4/H	CO_2Et	83 (**3j**)
11	113	4-$MeOC_6H_4$/H	CO_2Et	83 (**3k**)
12	12	4-ClC_6H_4/H	CO_2Et	78 (**3l**)
13	12	4-BrC_6H_4/H	CO_2Et	69 (**3m**)
14	12	4-IC_6H_4/H	CO_2Et	66 (**3n**)
15	12	3-ClC_6H_4/H	CO_2Et	82 (**3o**)
16	12	3-FC_6H_4/H	CO_2Et	82 (**3p**)
17	47	2-Naphthyl/H	CO_2Et	76 (**3q**)
18	113	C_6H_5/CH_3	CO_2Et	49 (**3r**)
19[e]	19	4-FC_6H_4/H	CO_2Et	74 (**3j**)

[a]Reaction conditions: *rac*-**1** (0.20 mmol), sulfonium salt **2** (0.40 mmol, 2.0 equiv), K_2CO_3 (0.60 mmol, 3.0 equiv), CH_3CN (2.0 mL), DMF (2.0 mL). [b]Isolated yield. [c]**3c**:**3c′** = 23.3:1. [d]The system is complex. [e]The reaction was conducted at 1.0 mmol scale.

Furthermore, a preliminary study on the enantioselective version of this dearomatization reaction was also tried. Using the planar-chiral [2.2]paracyclophane-derived cyclic *N*-sulfonylimine (R_p)-**1a** synthesized by our group,[8b] the desirable chiral product (*S*,*S*,*S*)-**3a** could be obtained with 99% ee and 80% yield (Scheme 2).

Control experiments were performed to probe the specificity of substrate **1** (Scheme 3). Under the above standard conditions, [2.2]paracyclophane aldimine **4a** reacted with two equivalents of sulfonium salt **2a** to give the aziridination **5a** in 80% yield (eq 1). In addition, **4a** reacted with two equivalents of sulfonium salt **2d** bearing amide to give the

Scheme 2. Synthesis of Chiral Dearomatization Product (*S*,*S*,*S*)-3a



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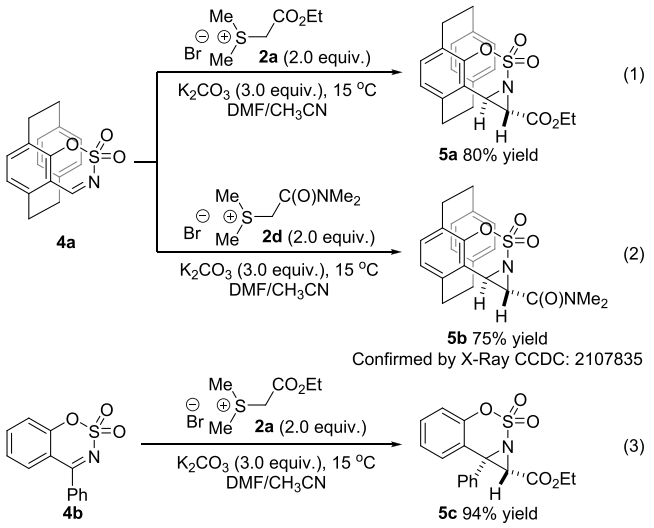
Scheme 3. Control Experiments



aziridination **5b** in 75% yield (eq 2), no dearomative product was observed. The single-crystal of **5b** was successfully obtained and confirmed the structure and relative configuration.[12] The result accounted for the preferential reaction of the benzene ring with the sulfur ylide in substrate **1**. When R^1 was aryl, the imine moiety of substrate **1** did not react with sulfur ylide, probably owing to steric effects. The reaction of simple cyclic ketimine **4b** with **2a** generated the only aziridination product **5c** in 94% yield (eq 3), which shows that both the [2.2]paracyclophane skeleton and ketimine had a critical role in dearomatization of [2.2]paracyclophane imines **1**.

To demonstrate the synthetic versatility of dearomative product **3a**, some downstream transformations of **3a** were conducted (Scheme 4). Selective reduction of **3a** with sodium borohydride delivered the amine **6** in 95% yield and >20:1 dr.[8b] Through coordination activation in the presence of Lewis acid boron trichloride, product **7** was obtained with 81% yield when dimethylamine was used as the nucleophile. The single-crystal of product **7** was successfully obtained and confirmed the structure and relative configuration.[13]

Parallel to experimental studies, density functional theory (DFT) calculations were performed to gain further mechanistic insights into the reaction and stereoselectivity. Here, some possible pathways leading to four different stereogenic products were explored in detail. As illustrated in Scheme 5, the sulfur ylide initially undergoes electrophilic addition with **1a**. Based on the configuration of possible products, four possible transition states (TS_{S1}, TS_{R1}, TS_{S2}, and TS_{R2}, see Scheme 5 and Figure S6) were identified for the first C−C bond formation. Among the four transition states, $TS1_{S1}$ was calculated to have the lowest barrier (20.0 kcal/mol, see the black line in Scheme 5), followed by $TS1_{R1}$, the barrier of which is 2.2 kcal/mol higher. Interestingly, both TS_{S1} and $TS1_{R1}$ are involved in C═C bond activation, rather than C═N bond activation. Compared to TS_{R1}, TS_{S2}, and TS_{R2} have even higher barriers, in which the sulfur ylide adds to the C═N bond of **1a** to finish the aziridination of cyclic *N*-sulfonylimines.

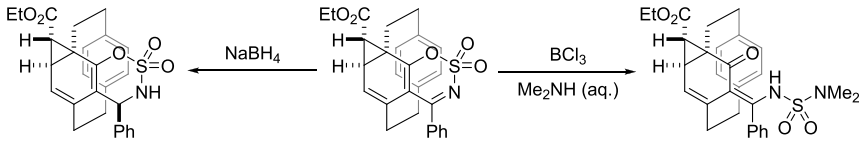
As for each pathway, the first C−C bond formation leads to the generation of an intermediate. Four different intermediates ($Int1_{S1}$, $Int1_{R1}$, $Int2_{S2}$, and $Int2_{R2}$, see Scheme 5) were located. At $Int1_{S1}$, an intramolecular S_N2-like step via a new transition state $TS2_{S1}$ occurs, involving the departure of $S(Me)_2$ and enabling the formation of the observed dearomative (*S*,*S*,*S*)-product $Prod_{S1}$. The total barrier of $TS2_{S1}$ was calculated to be 15.0 kcal/mol relative to that of **1a** plus the sulfur ylide. Three other transition states leading to different stereogenic products were also located and are presented in Scheme 5. Taken together, the computational results support the formation of the (*S*,*S*,*S*)-product as the most favored product, which is consistent with the experimental findings.

To confirm the disruption of the aromaticity in the cyclopropanation process, quantitative evaluations of the aromaticity of several compounds were performed. Two suggested measurements of aromaticity, namely multicenter bond indices (B3LYP/6-31G**)[14] and $NICS(1)_{ZZ}$ (the ZZ tensor component of the nuclear independent chemical shift values at the points 1 Å above the ring center) (B3LYP/6-31+G**) were chosen as the aromatic indices in this study.[15] Although the strong aromaticity of the selected benzene ring in **1a** and **5a** is exemplified by the negative $NICS(1)_{ZZ}$ values (−22.297 and −24.716) and large multicenter bond indices (0.056 and 0.066), it is also evident that the presence of the sulfonyl imine group and the paracyclophane skeleton in **1a** weakens the aromaticity of the benzene ring when compared to **1a** and **5a** with [2.2]paracyclophane (see Scheme 6). As expected, the aromaticity of the benzene ring in **3a** is destroyed, as indicated by the $NICS(1)_{ZZ}$ value and multicenter bond index of the ring, which are −0.863 and 0.008, respectively, typical values of a nonaromatic ring.

CONCLUSIONS

In conclusion, we have successfully developed an unprecedented dearomatization of the [2.2]paracyclophane-derived cyclic *N*-sulfonylimines via selective clopropanation with the sulfur ylides, giving the dearomative cyclopropane products with high site selectivity and diastereoselectivity in good yields. The mild conditions rendered this methodology compatible with diverse functional groups. Moreover, the diversification of the dearomative products was demonstrated, further showcasing the potential synthetic utility. We anticipated this methodology would provide a new platform for selective dearomatization of readily available [2.2]paracyclophane derivatives.

Scheme 4. Transformations of the Product 3a



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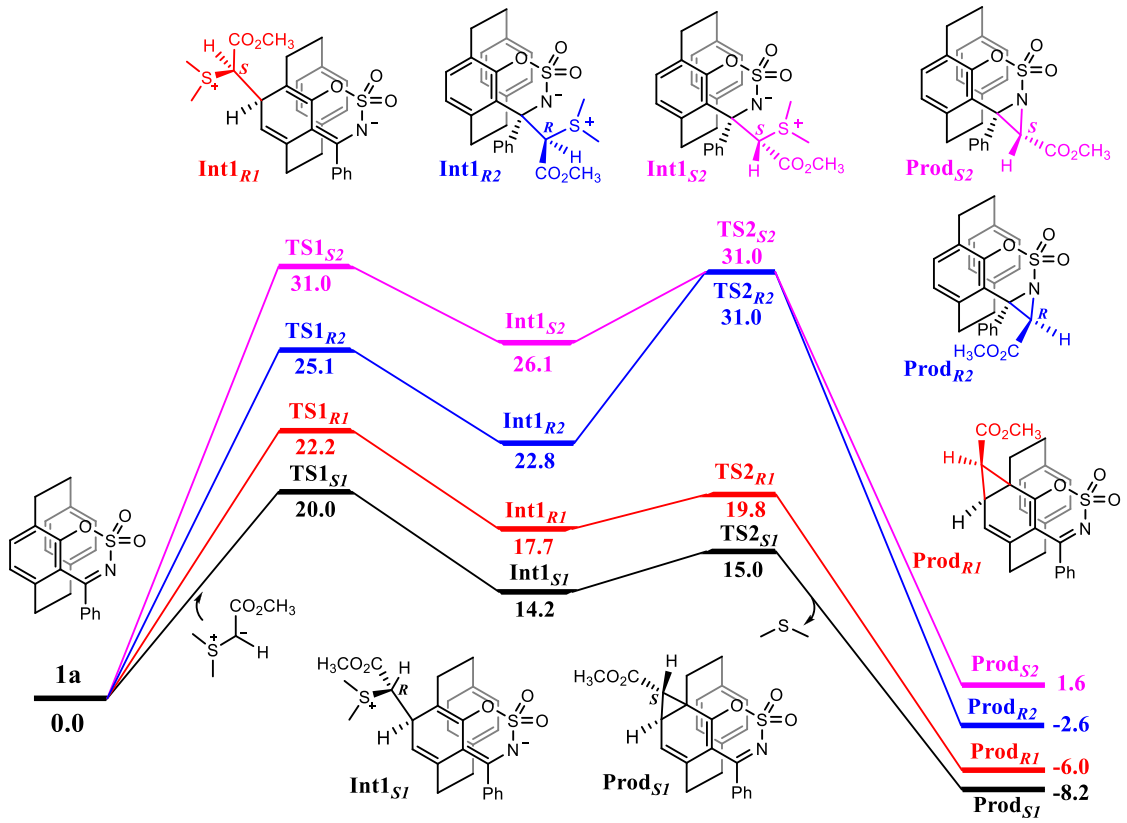
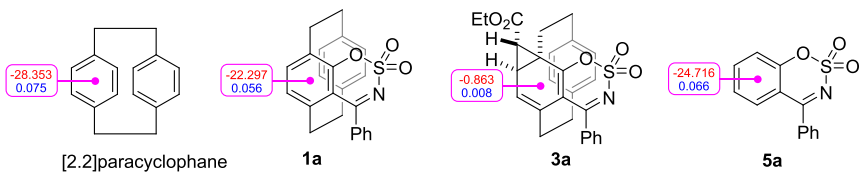
Scheme 5. Calculated Gibbs Energy Profile (kcal/mol) at the SMD-B3LYP-D3/def2-TZVPP//B3LYP-D3/def2-SVP-SDD Level for Four Different Reaction Pathways[a]



[a]For clarity, selected key structures of transition states are shown here. More details and data can be seen in Figures S5–S9.

Scheme 6. Evaluation of Aromaticity of the Selected Compounds[a]



[a]$NICS(1)_{ZZ}$ values are highlighted in red while multicenter bond indices are highlighted in blue. More details and data can be seen in Figure S10.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under an atmosphere of nitrogen using 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. ^1H NMR, $^{13}C\{^1H\}$ NMR and $^{19}F\{^1H\}$ NMR spectra were recorded at room temperature in $CDCl_3$ on a 400 MHz instrument with tetramethylsilane (TMS) as the internal standard. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. Optical rotations were measured by polarimeter. 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). The heat source for all heating reactions is the oil bath. High-resolution mass spectrometry (HRMS) was measured on an electrospray ionization (ESI) apparatus using the time-of-flight (TOF) mass spectrometry. All reactions were monitored by TLC analysis.

Materials. The [2.2]paracyclophane-derived *N*-sulfonylimines **1** were prepared according to the known methods.[8b] The sulfonium salts **2** were prepared according to the literature procedure.[16,17]

General Procedure for Dearomatization of [2.2]-Paracyclophanes. A mixture of [2.2]paracyclophane-derived cyclic *N*-sulfonylimines **1** (0.20 mmol), sulfonium salts **2** (0.40 mmol, 2.0 equiv) and potassium carbonate (83 mg, 0.60 mmol, 3.0 equiv) in acetonitrile (2.0 mL) and *N*,*N*-dimethylformamide (2.0 mL) was stirred at 15 °C for 12–113 h. Then ethyl acetate (10 mL) and water (10 mL) were added. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (20 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel using hexanes and ethyl acetate or hexanes and dichloromethane as eluent to give the desired dearomative products **3**.

*Ethyl 4-Phenyl-6a,7a-dihydro-7H-(5,7a)-cyclopropa[3,4]benzo-[1,2-e][1,2,3]oxathiazina-(1,4)-benze-nacyclohexaphane-7-carboxylate-2,2-dioxide (**3a**).* 76 mg, 80% yield, > 20:1 dr, yellow solid, mp = 226–228 °C, new compound, R_f = 0.45 (hexanes/ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59–7.46 (m, 3H), 7.44–7.37 (m, 2H), 7.26–7.23 (m, 1H), 7.18–7.44 (m, 1H), 7.09–7.03 (m, 1H), 6.89- 6.83 (m, 1H), 5.01 (d, J = 7.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.23–3.12 (m, 1H), 2.88- 2.51 (m, 4H), 2.47 (t, J = 6.6 Hz, 1H), 2.17–2.00 (m, 2H), 1.75–1.63 (m, 1H), 1.53 (d, J = 6.1 Hz,

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1H), 1.29 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 173.6, 171.6, 170.7, 140.0, 138.8, 136.1, 133.8, 132.9, 131.5, 131.0, 130.5, 129.6, 129.2, 129.1, 128.8, 110.3, 61.9, 35.5, 35.1, 34.4, 33.9, 33.2, 31.7, 26.7, 14.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{26}NO_5S$476.1526, found 476.1522 (Confirmed by X-ray, CCDC number: 2059560).

*Methyl 4-Phenyl-6a,7a-dihydro-7H-(5,7a)-cyclopropa[3,4]-benzo[1,2-e][1,2,3]oxathiazina-(1,4)-ben-zenacyclohexaphane-7-carboxylate-2,2-dioxide (**3b**).* 71 mg, 77% yield, > 20:1 dr, yellow solid, mp = 245−247 °C, new compound, R_f = 0.50 (hexanes/ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.57−7.46 (m, 3H), 7.44−7.37 (m, 2H), 7.26−7.23 (m, 1H), 7.16−7.12 (m, 1H), 7.08−7.03 (m, 1H), 6.89−6.83 (m, 1H), 5.01 (d, J = 7.0 Hz, 1H), 3.75 (s, 3H), 3.23−3.10 (m, 1H), 2.89−2.51 (m, 4H), 2.47 (t, J = 6.6 Hz, 1H), 2.17−1.97 (m, 2H), 1.74−1.62 (m, 1H), 1.54 (d, J = 6.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 173.6, 171.5, 171.1, 140.0, 138.8, 136.0, 133.7, 132.9, 131.5, 131.0, 130.4, 129.7, 129.2, 129.1, 128.8, 110.3, 52.7, 35.5, 35.2, 34.3, 33.9, 33.0, 31.6, 26.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{24}NO_5S$ 462.1371, found 462.1371.

*N,N-Diethyl 4-Phenyl-6a,7a-dihydro-7H-(5,7a)-cyclopropa[3,4]-benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxamide-2,2-dioxide (**3c**).* 70 mg, 70% yield, 23.3:1 dr, yellow solid, mp = 247−249 °C, new compound, R_f = 0.55 (hexanes/ethyl acetate = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58−7.49 (m, 3H), 7.45−7.37 (m, 2H), 7.25−7.20 (m, 1H), 7.18−7.13 (m, 1H), 7.08−7.02 (m, 1H), 6.90- 6.84 (m, 1H), 5.03 (d, J = 7.1 Hz, 1H), 3.60−3.43 (m, 1H), 3.42−3.20 (m, 3H), 3.18−3.05 (m, 1H), 2.88−2.48 (m, 5H), 2.19−2.06 (m, 1H), 1.73−1.65 (m, 2H), 1.56 (d, J = 6.0 Hz, 1H), 1.19−1.06 (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 173.6, 172.7, 166.2, 140.1, 138.8, 136.2, 133.6, 132.9, 131.6, 131.5, 131.1, 129.3, 129.0, 129.0, 128.8, 110.0, 42.3, 41.4, 35.6, 34.4, 33.4, 33.1, 32.7, 31.7, 27.3, 14.5, 13.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{31}N_2O_4S$ 503.1999, found 503.1996.

*N,N-Diethyl 4-Phenyl-6a,7a-dihydro-7H-(5,7a)-cyclopropa[3,4]-benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxamide-2,2-dioxide (**3c′**).* Three mg, 3% yield, yellow solid, mp = 250−252 °C, new compound, R_f = 0.20 (hexanes/ethyl acetate = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.73−7.63 (m, 2H), 7.54−7.47 (m, 1H), 7.45- 7.37 (m, 2H), 7.31−7.27 (m, 1H), 7.13−7.08 (m, 1H), 7.06−7.00 (m, 1H), 6.91−6.83 (m, 1H), 5.06 (d, J = 7.1 Hz, 1H), 3.67−3.40 (m, 2H), 3.29- 3.04 (m, 3H), 2.82- 2.50 (m, 4H), 2.30 (d, J = 9.4 Hz, 1H), 2.22 (dd, J = 9.3, 7.1 Hz, 1H), 2.17−2.07 (m, 1H), 1.60−1.53 (m, 2H), 1.13 (t, J = 7.2 Hz, 3H), 0.62 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 173.6, 167.4, 163.6, 139.8, 138.7, 136.2, 133.3, 132.6, 131.9, 130.4, 129.9, 129.7, 129.6, 129.5, 128.7, 111.8, 41.6, 39.0, 35.7, 35.0, 34.9, 34.6, 32.7, 31.9, 31.3, 13.7, 12.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{31}N_2O_4S$ 503.1999, found 503.1973 (Confirmed by X-ray, CCDC number: 2079416).

*N,N-Dimethyl 4-Phenyl-6a,7a-dihydro-7H-(5,7a)-cyclopropa-[3,4]benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxamide-2,2-dioxide (**3d**).* 66 mg, 70% yield, > 20:1 dr, yellow solid, mp = 215−217 °C, new compound, R_f = 0.55 (hexanes/ethyl acetate = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59−7.48 (m, 3H), 7.45−7.36 (m, 2H), 7.25−7.19 (m, 1H), 7.17−7.11 (m, 1H), 7.07−7.01 (m, 1H), 6.90- 6.83 (m, 1H), 5.02 (d, J = 7.1 Hz, 1H), 3.14−3.04 (m, 1H), 2.99 (d, J = 7.1 Hz, 6H), 2.85−2.75 (m, 1H), 2.75−2.50 (m, 4H), 2.18−2.06 (m, 1H), 1.73−1.61 (m, 2H), 1.59 (d, J = 6.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 173.5, 172.5, 167.1, 139.9, 138. 8, 136.1, 133.5, 132.9, 131.5, 131.4, 131.0, 129.3, 129.0, 128.9, 128.7, 110.0, 37.4, 36.2, 35.5, 34.3, 33.5, 33.4, 32.4, 31.5, 27.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{27}N_2O_4S$ 475.1686, found 475.1685.

*N,N-Dibenzyl 4-Phenyl-6a,7a-dihydro-7H-(5,7a)-cyclopropa-[3,4]benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxamide-2,2-dioxide (**3e**).* 105 mg, 84% yield, > 20:1 dr, yellow solid, mp = 219−221 °C, new compound, R_f = 0.30 (hexanes/ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.56−7.48 (m, 1H), 7.41−7.31 (m, 5H), 7.30−7.26 (m, 4H), 7.24−7.20 (m, 1H), 7.18−7.08 (m, 4H), 7.06- 7.00 (m, 1H), 7.00−6.94 (m, 2H), 6.87−6.81 (m, 1H), 5.12 (d, J = 14.5 Hz, 1H), 4.95 (d, J = 7.0 Hz, 1H), 4.51−4.34 (m, 3H), 3.22−3.06 (m, 1H), 2.83−2.66 (m, 4H), 2.62−2.48 (m, 1H), 2.11−1.97 (m, 1H), 1.88−1.75 (m, 1H), 1.61−1.53 (m, 1H), 1.50 (d, J = 6.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 173.5, 172.5, 168.6, 139.8, 138.9, 137.0, 136.6, 136.0, 133.6, 132.7, 131.6, 131.2, 131.0, 129.3, 129.1, 129.03, 128.99, 128.9, 128.7, 128.4, 128.0, 127.9, 126.1, 110.0, 51.0, 35.3, 34.3, 34.0, 33.9, 33.3, 31.6, 27.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{39}H_{35}N_2O_4S$ 627.2312, found 627.2318.

*Ethyl 4-(m-Tolyl)-6a,7a-dihydro-7H-(5,7a)-cyclopropa[3,4]-benzo[1,2-e][1,2,3]oxathiazina-(1,4)-ben-zenacyclohexaphane-7-carboxylate-2,2-dioxide (**3h**).* 82 mg, 84% yield, > 20:1 dr, yellow solid, mp = 210−212 °C, new compound, R_f = 0.45 (hexanes/ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43−7.31 (m, 2H), 7.27−7.19 (m, 3H), 7.17−7.11 (m, 1H), 7.08−7.02 (m, 1H), 6.89−6.82 (m, 1H), 5.00 (d, J = 7.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.21−3.11 (m, 1H), 2.86−2.50 (m, 4H), 2.47 (t, J = 6.6 Hz, 1H), 2.38 (s, 3H), 2.16−1.98 (m, 2H), 1.76−1.66 (m, 1H), 1.53 (d, J = 6.1 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 173.8, 171.5, 170.7, 140.0, 138.9, 138.8, 136.0, 133.7, 131.5, 131.0, 130.3, 129.7, 129.5, 129.1, 128.6, 126.5, 110.3, 61.9, 35.4, 35.1, 34.4, 33.9, 33.1, 31.6, 26.7, 21.4, 14.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{28}NO_5S$ 490.1683, found 490.1678.

*Ethyl 4-(p-Tolyl)-6a,7a-dihydro-7H-(5,7a)-cyclopropa[3,4]benzo-[1,2-e][1,2,3]oxathiazina-(1,4)-benze-nacyclohexaphane-7-carboxylate-2,2-dioxide (**3i**).* 71 mg, 73% yield, > 20:1 dr, yellow solid, mp = 224−226 °C, new compound, R_f = 0.50 (hexanes/ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44−7.37 (m, 2H), 7.26−7.23 (m, 1H), 7.22−7.17 (m, 2H), 7.16−7.11 (m, 1H), 7.08−7.03 (m, 1H), 6.88−6.83 (m, 1H), 5.00 (d, J = 7.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.22−3.08 (m, 1H), 2.88- 2.52 (m, 4H), 2.47 (t, J = 6.6 Hz, 1H), 2.41 (s, 3H), 2.18−1.98 (m, 2H), 1.82- 1.68 (m, 1H), 1.51 (d, J = 6.1 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 173.5, 171.4, 170.7, 144.0, 139.9, 138.8, 133.7, 133.2, 131.4, 131.0, 130.3, 129.7, 129.5, 129.4, 129.2, 110.2, 61.9, 35.5, 35.1, 34.3, 33.9, 33.2, 31.6, 26.6, 21.8, 14.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{28}NO_5S$ 490.1683, found 490.1682.

*Ethyl 4-(4-Fluorophenyl)-6a,7a-dihydro-7H-(5,7a)-cyclopropa-[3,4]benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxylate-2,2-dioxide (**3j**).* 82 mg, 83% yield, > 20:1 dr, yellow solid, mp = 230−232 °C, new compound, R_f = 0.50 (hexanes/ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61−7.48 (m, 2H), 7.26−7.21 (m, 1H), 7.17−7.01 (m, 4H), 6.90−6.84 (m, 1H), 5.03 (d, J = 7.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.24−3.11 (m, 1H), 2.89−2.53 (m, 4H), 2.48 (t, J = 6.6 Hz, 1H), 2.25−1.98 (m, 2H), 1.81−1.66 (m, 1H), 1.51 (d, J = 6.2 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.2, 172.0, 170.5, 165.6 (C−F, $^1J_{C-F}$ = 256.0 Hz), 140.0, 138.7, 133.7, 132.0 (C−F, $^4J_{C-F}$ = 3.0 Hz), 131.9 (C−F, $^3J_{C-F}$ = 9.0 Hz), 131.5, 131.0, 130.8, 129.3, 129.1, 116.2 (C−F, $^2J_{C-F}$ = 22.0 Hz), 110.1, 61.9, 35.5, 35.2, 34.3, 33.9, 33.3, 31.6, 26.7, 14.3. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ −104.59. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{27}H_{24}FNaNO_5S$ 516.1251, found 516.1248.

*Ethyl 4-(4-Methoxyphenyl)-6a,7a-dihydro-7H-(5,7a)-cyclopropa-[3,4]benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxylate-2,2-dioxide (**3k**).* 84 mg, 83% yield, > 20:1 dr, yellow solid, mp = 219−221 °C, new compound, R_f = 0.45 (hexanes/ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59−7.40 (m, 2H), 7.26−7.23 (m, 1H), 7.17−7.10 (m, 1H), 7.08−7.02 (m, 1H), 6.92−6.83 (m, 3H), 5.00 (d, J = 7.0 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 3.24−3.09 (m, 1H), 2.89−2.55 (m, 4H), 2.47 (t, J = 6.6 Hz, 1H), 2.26−2.10 (m, 1H), 2.09−1.96 (m, 1H), 1.92- 1.79 (m, 1H), 1.49 (d, J = 6.2 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 172.5, 171.3, 170.7, 163.7, 139.9, 138.8, 133.7, 131.7, 131.4, 130.9, 130.2, 129.8, 129.3, 128.0 114.1, 110.1, 61.8, 55.7, 35.5, 35.3, 34.3, 33.9, 33.2, 31.6, 26.5, 14.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{28}NO_6S$ 506.1632, found 506.1633.

*Ethyl 4-(4-Chlorophenyl)-6a,7a-dihydro-7H-(5,7a)-cyclopropa-[3,4]benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxylate-2,2-dioxide (**3l**).* 79 mg, 78% yield, > 20:1 dr, yellow solid, mp = 236−238 °C, new compound, R_f = 0.55 (hexanes/ethyl

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acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.43 (m, 2H), 7.42−7.36 (m, 2H), 7.26−7.21 (m, 1H), 7.17−7.11 (m, 1H), 7.06−7.00 (m, 1H), 6.89−6.83 (m, 1H), 5.03 (d, J = 7.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.22−3.08 (m, 1H), 2.89−2.52 (m, 4H), 2.48 (t, J = 6.6 Hz, 1H), 2.22−1.97 (m, 2H), 1.78−1.65 (m, 1H), 1.51 (d, J = 6.2 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 172.3, 172.1, 170.5, 140.0, 139.5, 138.7, 134.3, 133.7, 131.5, 131.0, 130.9, 130.6, 129.2, 129.09, 129.06, 110.1, 61.9, 35.6, 35.2, 34.3, 33.9, 33.3, 31.6, 26.7, 14.3. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{27}H_{25}ClNO_5S$ 510.1136 (^{35}Cl) and 512.1118 (^{37}Cl), found 510.1139 (^{35}Cl) and 512.1181 (^{37}Cl).

*Ethyl 4-(4-Bromophenyl)-6a,7a-dihydro-7H-(5,7a)-cyclopropa-[3,4]benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxylate-2,2-dioxide (**3m**).* 76 mg, 69%, > 20:1 dr, yellow solid, mp = 234−236 °C, new compound, R_f = 0.45 (hexanes/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58−7.49 (m, 2H), 7.46−7.32 (m, 2H), 7.26- 7.21 (m, 1H), 7.18−7.11 (m, 1H), 7.07−6.99 (m, 1H), 6.90−6.82 (m, 1H), 5.03 (d, J = 7.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.24−3.06 (m, 1H), 2.92- 2.52 (m, 4H), 2.48 (t, J = 6.6 Hz, 1H), 2.21−1.97 (m, 2H), 1.78−1.64 (m, 1H), 1.51 (d, J = 6.2 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 172.4, 172.1, 170.5, 140.0, 138.7, 134.8, 133.7, 132.2, 131.5, 131.0, 130.9, 130.7, 129.1, 128.1, 110.1, 62.0, 35.6, 35.1, 34.3, 33.9, 33.3, 31.6, 26.7, 14.4. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{27}H_{25}BrNO_5S$ 554.0631 (^{79}Br) and 556.0614 (^{81}Br), found 554.0634 (^{79}Br) and 556.0621 (^{81}Br).

*Ethyl 4-(4-Iodophenyl)-6a,7a-dihydro-7H-(5,7a)-cyclopropa-[3,4]benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxylate-2,2-dioxide (**3n**).* 79 mg, 66% yield, > 20:1 dr, yellow solid, mp = 240−242 °C, new compound, R_f = 0.35 (hexanes/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.72 (m, 2H), 7.26−7.20 (m, 3H), 7.18−7.11 (m, 1H), 7.07−7.00 (m, 1H), 6.90−6.82 (m, 1H), 5.02 (d, J = 7.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.23−3.11 (m, 1H), 2.91−2.51 (m, 4H), 2.48 (t, J = 6.6 Hz, 1H), 2.22−1.97 (m, 2H), 1.79−1.65 (m, 1H), 1.50 (d, J = 6.2 Hz, 1H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 172.6, 172.1, 170.5, 140.1, 138.7, 138.2, 135.4, 133.7, 131.5, 131.0, 130.9, 130.6, 129.12, 129.10, 110.0, 100.6, 62.0, 35.6, 35.2, 34.3, 33.9, 33.3, 31.6, 26.7, 14.4. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{27}H_{25}INO_5S$ 602.0493, found 602.0495.

*Ethyl 4-(3-Chlorophenyl)-6a,7a-dihydro-7H-(5,7a)-cyclopropa-[3,4]benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxylate-2,2-dioxide (**3o**).* 83 mg, 82% yield, > 20:1 dr, yellow solid, mp = 221−223 °C, new compound, R_f = 0.55 (hexanes/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.45 (m, 2H), 7.41−7.30 (m, 2H), 7.25−7.20 (m, 1H), 7.17−7.12 (m, 1H), 7.06−7.00 (m, 1H), 6.89- 6.82 (m, 1H), 5.04 (d, J = 7.0 Hz, 1H), 4.28−4.11 (m, 2H), 3.20−3.09 (m, 1H), 2.89−2.53 (m, 4H), 2.48 (t, J = 6.6 Hz, 1H), 2.25−1.98 (m, 2H), 1.77−1.63 (m, 1H), 1.52 (d, J = 6.2 Hz, 1H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 172.2, 172.0, 170.5, 140.0, 138.7, 137.6, 135.1, 133.6, 132.9, 131.5, 131.03, 130.99, 130.1, 129.1, 129.0, 128.9, 127.4, 110.1, 62.0, 35.5, 35.2, 34.3, 33.9, 33.3, 31.6, 26.7, 14.3. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{27}H_{25}ClNO_5S$ 510.1136 (^{35}Cl) and 512.1118 (^{37}Cl), found 510.1140 (^{35}Cl) and 512.1117 (^{37}Cl).

*Ethyl 4-(3-Fluorophenyl)-6a,7a-dihydro-7H-(5,7a)-cyclopropa-[3,4]benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxylate-2,2-dioxide (**3p**).* 81 mg, 82% yield, > 20:1 dr, yellow solid, mp = 222−224 °C, new compound, R_f = 0.55 (hexanes/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.34 (m, 1H), 7.29−7.20 (m, 4H), 7.17−7.11 (m, 1H), 7.07−6.99 (m, 1H), 6.91−6.82 (m, 1H), 5.03 (d, J = 7.0 Hz, 1H), 4.30−4.10 (m, 2H), 3.21−3.09 (m, 1H), 2.91−2.52 (m, 4H), 2.48 (t, J = 6.6 Hz, 1H), 2.21−2.00 (m, 2H), 1.76−1.64 (m, 1H), 1.52 (d, J = 6.2 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.2 (C−F, $^4J_{C-F}$ = 3.0 Hz), 172.1, 170.5, 162.5 (C−F, $^1J_{C-F}$ = 248.0 Hz), 140.0, 138.7, 137.9 (C−F, $^3J_{C-F}$ = 7.0 Hz), 133.6, 131.5, 131.0, 130.9, 130.6 (C−F, $^3J_{C-F}$ = 8.0 Hz), 129.0, 125.0 (C−F, $^4J_{C-F}$ = 3.0 Hz), 119.9 (C−F, $^2J_{C-F}$ = 21.0 Hz), 116.1 (C−F, $^2J_{C-F}$ = 23.0 Hz), 110.2, 61.9, 35.4, 35.1, 34.3, 33.8, 33.3, 31.6, 26.7, 14.3. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −110.89. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{27}H_{25}FNO_5S$ 494.1432, found 494.1433.

*Ethyl 4-(2-Naphthyl)-6a,7a-dihydro-7H-(5,7a)-cyclopropa[3,4]-benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxylate-2,2-dioxide (**3q**).* 80 mg, 76% yield, > 20:1 dr, yellow solid, mp = 230−232 °C, new compound, R_f = 0.45 (hexanes/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.94−7.80 (m, 3H), 7.67−7.54 (m, 2H), 7.55−7.46 (m, 1H), 7.31−7.27 (m, 1H), 7.19−7.13 (m, 1H), 7.11−7.05 (m, 1H), 6.89−6.83 (m, 1H), 5.05 (d, J = 7.0 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.27−3.12 (m, 1H), 2.84−2.48 (m, 5H), 2.15−2.02 (m, 2H), 1.74- 1.64 (m, 1H), 1.61 (d, J = 6.1 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 173.3, 171.6, 170.6, 139.9, 138.7, 135.2, 133.6, 133.2, 132.4, 131.4, 130.9, 130.5, 130.4, 129.5, 129.3, 129.1, 128.8, 128.5, 127.9, 127.2, 124.9, 110.3, 61.8, 35.5, 35.1, 34.2, 33.8, 33.2, 31.5, 26.6, 14.3. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{31}H_{28}NO_5S$ 526.1683, found 526.1685.

*Ethyl 6-Methyl-4-phenyl-6a,7a-dihydro-7H-(5,7a)-cyclopropa-[3,4]benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxylate-2,2-dioxide (**3r**).* 48 mg, 49% yield, > 20:1 dr, yellow solid, mp = 235−237 °C, new compound, R_f = 0.55 (hexanes/dichloromethane = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.45 (m, 3H), 7.41−7.34 (m, 3H), 7.04−7.00 (m, 1H), 6.99−6.93 (m, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.15- 3.00 (m, 1H), 2.93−2.79 (m, 1H), 2.78−2.53 (m, 3H), 2.35−2.19 (m, 1H), 2.15 (d, J = 6.1 Hz, 1H), 2.03−1.89 (m, 1H), 1.80 (s, 3H), 1.56−1.46 (m, 1H), 1.45 (d, J = 6.1 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 173.7, 170.8, 170.2, 139.4, 139.1, 136.3, 133.5, 132.7, 132.3, 129.8, 129.09, 129.06, 128.8, 128.7, 125.1, 113.3, 61.9, 40.3, 33.3, 32.9, 32.6, 32.0, 31.0, 26.6, 22.9, 14.3. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{28}H_{28}NO_5S$ 490.1683, found 490.1679.

Experiment at 1.0 mmol Scale. A mixture of [2.2]-paracyclophane-derived cyclic *N*-sulfonylimine **1d** (407 mg, 1.0 mmol), sulfonium salt **2a** (456 mg, 2.0 mmol, 2.0 equiv) and potassium carbonate (415 mg, 3.0 mmol, 3.0 equiv) in acetonitrile (10 mL) and *N*,*N*-dimethylformamide (10 mL) was stirred at 15 °C for 19 h. Then ethyl acetate (30 mL) and water (30 mL) were added. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (30 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The crude residue was purified by flash chromatography on silica gel using hexanes and ethyl acetate as eluent to give the desired dearomative product **3j** 364 mg, 74% yield.

Dearomatization of Chiral *N*-Sulfonylimine. A mixture of [2.2]paracyclophane-derived cyclic *N*-sulfonylimine (R_p)-**1a** (78 mg, 0.20 mmol, 99% ee), sulfonium salt **2a** (91 mg, 0.40 mmol, 2.0 equiv) and potassium carbonate (83 mg, 0.60 mmol, 3.0 equiv) in acetonitrile (2.0 mL) and *N*,*N*-dimethylformamide (2.0 mL) was stirred at 15 °C for 47 h. Then ethyl acetate (10 mL) and water (10 mL) were added. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes and dichloromethane as eluent to give chiral product (*S*,*S*,*S*)-**3a**.

*(+)-(S,S,S)-Ethyl 4-Phenyl-6a,7a-dihydro-7H-(5,7a)-cyclopropa-[3,4]benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxylate-2,2-dioxide (**3a**).* 75 mg, 80% yield, > 20:1 dr, yellow solid, R_f = 0.50 (hexanes/ethyl acetate = 5:1), 99% ee, $[\alpha]^{20}_D$ = +821.32 (c 1.38, $CHCl_3$). HPLC (Chiralpak IA column, *n*-Hexane/*i*-PrOH = 60/40, flow = 0.6 mL/min, l = 254 nm, 30 °C) t_R = 8.4 min (major), 11.4 min (minor).

Aziridination of Cyclic *N*-Sulfonylimines. A mixture of [2.2]paracyclophane-derived cyclic *N*-sulfonylimine **4a** (63 mg, 0.20 mmol), sulfonium salt **2a** (91 mg, 0.40 mmol, 2.0 equiv) and potassium carbonate (83 mg, 0.60 mmol, 3.0 equiv) in acetonitrile (2.0 mL) and *N*,*N*-dimethylformamide (2.0 mL) was stirred at 15 °C for 12 h. Then ethyl acetate (10 mL) and water (10 mL) were added to the mixture. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic

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layer was dried by anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes and dichloromethane as eluent to give the corresponding aziridination product **5a**.

*Ethyl 1,8b-Dihydro-azirino[1,2-c][2.2]paracyclophano[5,6-d][1,2,3]oxathiazina-1-carboxylate-3,3-dioxide (**5a**).* 64 mg, 80% yield, > 20:1 dr, white solid, mp = 63−65 °C, new compound, R_f = 0.60 (hexanes/dichloromethane = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00−6.95 (m 1H), 6.75−6.70 (m, 1H), 6.68−6.59 (m, 2H), 6.55 (d, J = 7.9 Hz, 1H), 6.43 (d, J = 7.9 Hz, 1H), 4.38−4.24 (m, 2H), 4.02 (d, J = 3.7 Hz, 1H), ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 149.0, 140.3, 139.8, 138.1, 136.7, 133.5, 132.6, 132.5, 131.3, 131.0, 129.8, 116.0, 62.9, 46.5, 43.6, 34.7, 34.4, 31.8, 28.6, 14.2. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{21}NaNO_5S$ 422.1033, found 422.1003.

A mixture of [2.2]paracyclophane-derived cyclic *N*-sulfonylimine **4a** (63 mg, 0.20 mmol), sulfonium salt **2d** (91 mg, 0.40 mmol, 2.0 equiv) and potassium carbonate (83 mg, 0.60 mmol, 3.0 equiv) in acetonitrile (2.0 mL) and *N*,*N*-dimethylformamide (2.0 mL) was stirred at 15 °C for 12 h. Then ethyl acetate (10 mL) and water (10 mL) were added to the mixture. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried by anhydrous sodium sulfate, and concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes and ethyl acetate as the eluent to give the corresponding aziridination product **5b**. The structure of product **5b** was assigned by single crystal X-ray diffraction analysis; the CCDC number is 2107835.

*N,N-Dimethyl 1,8b-Dihydro-azirino[1,2-c][2.2]paracyclophano-[5,6-d][1,2,3]oxathiazina-1-carboxamide-3,3-dioxide (**5b**).* 60 mg, 75% yield, > 20:1 dr, white solid, mp = 196−198 °C, new compound, R_f = 0.50 (hexanes/ethyl acetate = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00−6.94 (m, 1H), 6.78−6.72 (m, 1H), 6.66−6.57 (m, 2H), 6.55 (d, J = 7.9 Hz, 1H), 6.44 (d, J = 7.9 Hz, 1H), 4.19 (d, J = 4.0 Hz, 1H), 3.51 (d, J = 4.0 Hz, 1H), 3.43−3.28 (m, 2H), 3.26−3.11 (m, 6H), 3.02 (s, 3H), 3.01−2.89 (m, 2H), 2.84−2.74 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 163.7, 148.8, 140.6, 139.7, 138.4, 136.2, 133.6, 132.7, 132.2, 130.7, 130.3, 129.6, 117.2, 47.1, 44.8, 37.2, 36.1, 34.5, 34.1, 31.8, 28.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{23}N_2O_4S$ 399.1373, found 399.1373.

A reaction mixture of *N*-sulfonylimines **4b** (52 mg, 0.20 mmol), sulfonium salt **2a** (91 mg, 0.40 mmol, 2.0 equiv) and potassium carbonate (83 mg, 0.60 mmol, 3.0 equiv) in acetonitrile (2.0 mL) and *N*,*N*-dimethylformamide (2.0 mL) was stirred at 15 °C for 12 h. Then ethyl acetate (10 mL) and water (10 mL) were added to the mixture. The organic layer was separated, and the aqueous layer was extracted three times with ethyl acetate (10 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes and dichloromethane as eluent to give the corresponding aziridination product **5c**.

*8b-Phenyl-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]-oxathiazine-1-carboxylate-3,3-dioxide (**5c**).* 65 mg, 94% yield, > 20:1 dr, white solid, mp = 54−56 °C, new compound, R_f = 0.50 (hexanes/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.42 (m, 5H), 7.42−7.35 (m, 1H), 7.19−7.11 (m, 2H), 7.06−6.98 (m, 1H), 4.27 (s, 1H), 4.14−3.93 (m, 2H), 0.98 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 164.1, 149.1, 132.2, 131.0, 130.6, 129.6, 129.0, 128.9, 126.8, 121.6, 119.8, 62.4, 58.3, 49.2, 13.8. HRMS (ESI) m/z: $[M+NH_4]^+$ calcd for $C_{17}H_{19}N_2O_5S$ 363.1009, found 363.1000.

Reduction of Dearomatized Product 3a. Sodium tetrahydroborate (38 mg, 1.00 mmol, 5.0 equiv) was added to a solution of **3a** (95 mg, 0.20 mmol) in tetrahydrofuran (3.0 mL). The reaction was performed at room temperature for 1 h. The reaction mixture was quenched by the addition of saturated aqueous ammonium chloride solution (10 mL). After being extracted with dichloromethane (10 mL × 3), the combined organic layer was dried by anhydrous sodium sulfate and concentrated under reduced pressure. The diastereomeric ratio of the product **6** was determined by ^{1}H NMR analysis. The solvent was removed under reduced pressure; the residue was purified by flash chromatography on silica gel using hexanes and dichloromethane as eluent to give the desired reductive product **6**.

*Ethyl 4-Phenyl-4,6a,7,7a-tetrahydro-3H-(5,7a)-cyclopropa[3,4]-benzo[1,2-e][1,2,3]oxathiazina-(1,4)-benzenacyclohexaphane-7-carboxylate-2,2-dioxide (**6**).* 91 mg, 95% yield, > 20:1 dr, white solid, mp = 227−229 °C, new compound, R_f = 0.30 (hexanes/dichloromethane = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.29 (m, 4H), 7.26−7.22 (m, 1H), 7.18−7.13 (m, 1H), 7.12−7.06 (m, 2H), 6.85−6.79 (m, 1H), 5.15 (d, J = 8.3 Hz, 1H), 4.84 (d, J = 6.8 Hz, 1H), 4.26−4.11 (m, 3H), 3.19−2.97 (m, 2H), 2.91−2.76 (m, 1H), 2.68−2.47 (m, 2H), 2.38−2.25 (m, 1H), 2.00−1.74 (m, 3H), 1.41 (d, J = 5.9 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 172.5, 153.8, 139.8, 138.2, 137.1, 131.7, 131.6, 131.5, 131.33, 131.26, 129.52, 129.49, 128.6, 128.0, 109.5, 61.4, 60.2, 34.8, 34.4, 33.8, 33.3, 31.6, 27.9, 25.5, 14.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{28}NO_5S$ 478.1683, found 478.1681.

Ring-Opening of Dearomatized Product 3a. To a solution of compound **3a** (48 mg, 0.10 mmol) in dichloromethane (3.0 mL) was added boron trichloride (90.0 μL, 117 mg, 0.20 mmol, 2.0 equiv) was added dropwise. After 10 min, aqueous dimethylamine (0.20 mL, 1.00 mmol, 33 wt %, 10 equiv) was added at 0 °C. The reaction was performed at room temperature for 2 h, saturated aqueous ammonium chloride solution (10 mL) was added to the mixture. The organic layer was separated and the aqueous layer was extracted three times with dichloromethane (10 mL × 3). The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. Then, the crude residue was purified by flash chromatography on silica gel using hexanes and ethyl acetate (20/1−6/1) as eluents to give the desirable ring-opening product **7**. The structure of product **7** was assigned by single crystal X-ray diffraction analysis; the CCDC number is 2111966.

*Ethyl 4-(((N,N-Dimethylsulfamoyl)amino)(phenyl)methylene)-5-oxo-(3,6)-bicyclo[4.1.0]heptana-(1,4)-benzenacyclohexaphan-2-ene-7-carboxylate (**7**).* 42 mg, 81% yield, yellow solid, mp = 171−173 °C, new compound, R_f = 0.40 (hexanes/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.02 (s, 1H), 7.71−7.60 (m, 1H), 7.53−7.36 (m, 2H), 7.32−7.28 (m, 1H), 7.11−6.95 (m, 2H), 6.91−6.79 (m, 2H), 6.72−6.64 (m, 1H), 5.01 (d, J = 6.8 Hz, 1H), 4.22−4.02 (m, 2H), 3.15−3.01 (m, 1H), 2.94−2.81 (m, 1H), 2.72−2.58 (m, 2H), 2.50 (s, 6H), 2.38−2.25 (m, 1H), 2.05 (dd, J = 6.6, 5.7 Hz, 1H), 1.93−1.79 (m, 2H), 1.78−1.64 (m, 1H), 1.24 (t, J = 7.1 Hz, 3H), 1.16−1.03 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 199.7, 169.9, 148.3, 139.1, 138.3, 134.5, 132.5, 131.5, 131.1, 130.9, 130.7, 130.5, 130.1, 128.4, 128.2, 115.8, 61.4, 37.3, 36.6, 36.2, 35.5, 34.1, 31.3, 31.1, 25.0, 14.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{33}N_2O_5S$ 521.2105, found 521.2100.

■ ASSOCIATED CONTENT

Data Availability Statement

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

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.3c02052.

Copies of ^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H} spectra of all new compounds; crystal data and DFT (PDF)

Accession Codes

CCDC 2059560, 2079416, 2107835, and 2111966 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by 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

The authors declare no competing financial interest.

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