23, 130063-06-8; 24, 134594-16-4; 25, 130043-16-2; A, 119997-04-5; B, 134594-17-5; t-BuMe$_2$SiTf, 69739-34-0; PhCH=CHC(O)CH$_3$, 122-57-6; H$_3$CCOCH=C(CH$_3$)$_2$, 141-79-7; H$_2$C=CHCH$_2$Sn(Bu)$_3$, 24850-33-7; 1-acetylcyclopentene, 16112-10-0; 1-acetylcyclohexene, 932-66-1.

Supplementary Material Available: ^{1}H NMR spectra of compounds 7a', 7b, 7c, 8a-*cis*, 8a-*trans*, 8b-*cis*, 8b-*trans*, 8c, 8d, 10a, 10b, 14a, 15a, 16a–16c, 17b, 17c, 18a, 18c, 18d, 19a–19c, 21, 22, 23, 24, and 25 (33 pages). Ordering information is given on any current masthead page.

Lewis Acid Mediated Reaction of *N*-Phenyl-*S*-(4-methylphenyl)sulfoximidoyl Chloride with Alkenes

Michael Harmata,* R. J. Claassen II, and Charles L. Barnes

Department of Chemistry, University of Missouri—Columbia, Columbia, Missouri 65211

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The reaction of *N*-phenyl-*S*-(4-methylphenyl)sulfoximidoyl chloride (1) with alkenes in the presence of aluminum chloride leads to 2,1-benzothiazines in good yield. The reaction is regioselective, sometimes highly stereoselective, and is stereospecific with respect to alkene geometry. The mechanism can be formulated as a concerted cycloaddition between the iminosulfonium species 2 and the alkene to form a σ complex that subsequently rearomatizes to give the product.

The use of heterodiene cycloadditions in the construction of heterocyclic and carbocyclic organic compounds has been of considerable interest recently.[1] The facility with which these reactions are generally performed and their broad scope make them especially attractive in synthesis.[2] Heterodienes based on adjacent sulfur and nitrogen atoms are relatively rare and often not general with respect to reactivity. For example, *N*-sulfinylaniline has been used as the diene component in 4 + 2 cycloadditions, but only with reactive dienophiles.[3] Given the synthetic versatility associated with sulfur containing functional groups, it appeared that further study of this or related heterodiene systems was warranted. Herein we detail the results of such a study.

We recently reported the Lewis acid mediated reaction of *N*-phenyl-*S*-(4-methylphenyl)sulfoximidoyl chloride (1) with alkynes to produce benzothiazines 4 in good to high yield with high regioselectivity.[4,5] Although we initially believed the formation of the σ complex 3 to be stepwise, this process can, in principle, be formulated as a concerted cycloaddition between the iminosulfonium "heterodiene" 2 and the alkyne dienophile (Scheme I).[3,6] As part of our effort to explore the scope and mechanism of this process, we have examined alkenes as reactants and have found that the reaction is not only regioselective but sometimes highly stereoselective as well. Our results are shown in Table I.

Scheme I

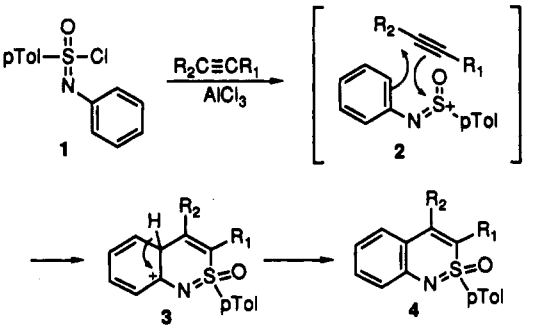
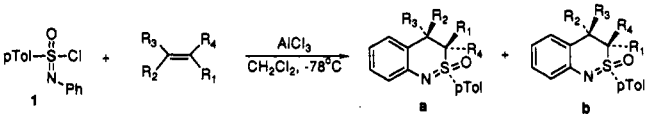


Table I. Reaction of 1 with Alkenes in the Presence of Lewis Acids



entry	R_1	R_2	R_3	R_4	products	yield[a] (%)	isomer ratio (a:b)
1	H	H	$-(CH_2)_4-$		5a/5b	91	25:1[c]
2	H	H	$-(CH_2)_3-$		6a/6b	81	5:1[b]
3	H	H	$-(CH_2)_5-$		7a/7b	70	2.4:1[b]
4	H	H	$-(CH_2)_6-$		8a/8b	76	2.1:1[b]
5	H	Et	H	Et	9a/9b	85	122:1[c]
6	H	H	Et	Et	10a/10b	85	2.3:1[c]
7	H	Bu	H	H	11a/11b	77	1.6:1[b]

[a] All yields are for chromatographically purified materials. [b] Isomer ratios were determined by HPLC analysis of crude reactions mixtures. [c] Isomer ratios were determined by weights of isolated products.

Entry 1 lists the intriguing result obtained with cyclohexene. Treatment of a mixture 1 and cyclohexene under either of our standard reaction conditions[4] gave a compound that was nearly a single isomer based on high-field ^{1}H and ^{13}C NMR and HPLC data. Two signals in the 300-MHz ^{1}H NMR of the major diastereomer 5a were

(1) For some recent examples and reviews, see: (a) Tietze, L. F. *J. Heterocycl. Chem.* **1990**, *27*, 47. (b) Tietze, L. F.; Fenner, J.; Anders, E. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1371. (c) Weinreb, S. M.; Scola, P. M. *Chem. Rev.* **1989**, *89*, 1525. (d) Taylor, E. C.; Macor, J. E. *J. Org. Chem.* **1989**, *54*, 1249, 4984. (e) Boger, D. L.; Kasper, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 1517. (f) Boger, D. L.; Robarge, K. D. *J. Org. Chem.* **1988**, *53*, 3373.

(2) Boger, D. L.; Weinreb, S. M. *Hetero Diels–Alder Methodology in Organic Synthesis*; Academic Press: San Diego, 1987.

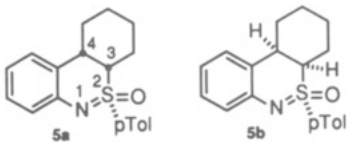
(3) For examples and leading references, see: (a) Hanson, P.; Wren, S. A. C. *J. Chem. Soc., Perkin Trans. 2* **1987**, 197. (b) Borthakur, D. R.; Prajapati, D.; Sandhu, J. S. *Heterocycles* **1986**, *24*, 2739. (c) Zoller, U.; Roan, P. *Tetrahedron Lett.* **1985**, 2813. (d) Hanson, P.; Stone, T. W. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2429. (e) Hanson, P.; Lewis, R. J.; Stone, T. W. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1719. (f) Maculso, A.; Hamer, J. *J. Org. Chem.* **1067**, *32*, 506. (g) Collins, G. R. *Ibid.* **1964**, *29*, 1688.

(4) Harmata, M.; Schlemper, E. O. *Tetrahedron Lett.* **1987**, 5997.

(5) These benzothiazines are cyclic sulfoximines. For reviews of sulfoximine chemistry, see: (a) Johnson, C. R. *Aldrichimica Acta* **1985**, *18*, 3. (b) Johnson, C. R. in *Comprehensive Organic Chemistry*; Jones, N. D., Ed.; Pergamon: Oxford, 1979; Vol. 3, Chapter 11. (c) Kennewell, P. E.; Taylor, J. B. *Chem. Soc. Rev.* **1975**, 189.

(6) Many other cationic heterodienes are known. Among them are the cationic thiabutadienes that undergo facile 4 + 2 cycloaddition with alkenes. For examples, see: (a) Tamura, Y.; Ishiyawa, K.; Mizuki, Y.; Maeda, H.; Ishibashi, H. *Tetrahedron Lett.* **1981**, 3773. (b) Wada, M.; Shigehisa, T.; Kitani, H.; Akiba, K. *Ibid.* **1983**, 1715. (c) Thakur, D. K.; Vankar, Y. D. *Synthesis* **1983**, 223.

0022-3263/91/1956-5059$02.50/0



highly supportive of the stereochemistry shown. A broadened doublet at 3.96 ppm assigned to the proton on carbon 4 had a width at half-height of about 10 Hz, suggesting an equatorial orientation. Further, a doublet of triplets at 3.16 ppm (J = 3.9, 12.2 Hz) assigned to the proton on carbon 3 suggested an axial orientation.[7] On the other hand, in **5b** resonances for protons on carbons 3 and 4 both occurred at ca. 3.23 ppm. Assuming the proximal oxygen of the sulfoximine functionality to be the origin of the downfield chemical shift of the proton on carbon 4 in **5a**, a stereochemical assignment could be made.[8] This assignment was ultimately confirmed by X-ray.[9]

The fascinating stereoselectivity observed in the reaction of **1** with cyclohexene prompted us to examine other cyclic alkenes with the expectation of high relative stereocontrol. Surprisingly, among the small- to medium-ring cycloalkenes studied, cyclohexene gave the highest degree of stereoselection. While all the cyclic alkenes showed complete cis selectivity with respect to the newly formed carbon–carbon and carbon–sulfur bonds, overall diastereoselectivity was highly variable. Still, the major stereoisomers for all the adducts derived from the cyclic alkenes possessed the same relative stereochemistry. Stereochemical assignments were made on the basis of comparison of the 300-MHz ^{1}H NMR spectra of each of the formal cycloaddition products with those of **5a** and **5b**. Resonances for protons on carbons 3 and 4 (benzothiazine numbering) were generally well-resolved for the major cis-anti diastereomers **5a–8a**, while significant overlap of these signals was observed for the cis-syn isomers **5b–8b**. Some ambiguity arose in the case of the cyclooctene adducts **8a** and **8b** but was resolved by an X-ray structure of **8b**.

More intriguing was the result obtained using (*E*)-3-hexene (Table I, entry 5). Incredible stereoselectivity was observed in this reaction *with retention of the geometry of the alkene*.[10] Although two isomers were formed from (*Z*)-3-hexene in almost equal amounts (Table I, entry 6), these presumably arose from different approaches (exo/endo) to **2**. In both **10a** and **10b**, the geometry of the alkene was retained. Thus, in the 3-hexene series this reaction appears to be completely stereospecific with respect to alkene geometry. Indeed, no evidence could be found for any stereochemical crossover with these two alkenes.[11] As for the major adducts from the cyclic alkenes, there is a syn relationship between the oxygen on sulfur and the hydrogen on carbon 3 in both **9a** and **10a**.

Finally, using 1-hexene we found the reaction to be regioselective in a Markovnikov sense as expected.[3] Stereoselectivity in this case was rather low (Table I, entry 7).[12,13]

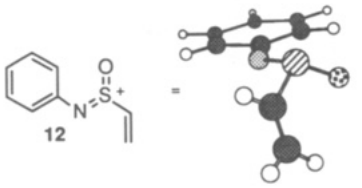


Figure 1.

While the mechanism of this reaction remains unclear, the retention of alkene stereochemistry with either (*E*)- or (*Z*)-3-hexene strongly suggests a concerted process.[14] Interestingly, an MNDO calculation of structure **12**, a model for iminosulfonium species **2**, yields a minimized geometry that very much resembles a diene.[15] The sulfur, nitrogen, and ipso and ortho carbons lie in the same plane (Figure 1). If the reaction is concerted, the Markovnikov regioselectivity suggests a high degree of asynchronicity in the cycloaddition step with significant accumulation of positive charge on the more substituted carbon of the alkene.

While of potential agricultural and pharmaceutical interest,[16] cycloadducts **5–11** also lend themselves to several unique and useful synthetic manipulations. For example, treatment of **5a** with potassium dimsylate in DMSO followed by basic hydrolysis produced *o*-cyclohexenylaniline in good yield (eq 1).[17]

(1)

In summary, we have discovered a regioselective and stereoselective reaction between unactivated alkenes and a reactive intermediate produced from the treatment of **1** with aluminum chloride. 2,1-Benzothiazines are produced in high yield. The reaction is stereospecific with respect to alkene geometry in the 3-hexene series. This suggests a concerted cycloaddition as the reaction mechanism, but further experimental evaluations of the mechanism and stereochemistry of this formal cycloaddition reaction are necessary to confirm this tentative hypothesis.

Experimental Section

General Methods. CH_2Cl_2 was freshly distilled from CaH_2 prior to use. Reactions were performed in oven- (120 °C) or flame-dried glassware under an inert atmosphere of N_2. Flash chromatography[18] was performed on 230–400 mesh silica gel (Merck) with technical grade solvents that were distilled prior

(7) When **5a** was treated with *n*-BuLi and the resulting anion quenched with D_2O, the signal at 3.16 ppm disappeared. Analysis of the ^{13}C NMR spectrum of **5a**-d_1 confirmed that deprotonation had taken place at C-3.

(8) (a) Lacombe, L.; Lavielle, S. *Org. Magn. Reson.* **1979**, *12*, 39. (b) Lett, R.; Marquet, A. *Tetrahedron* **1974**, *30*, 3365–3379.

(9) The conformation assigned on the basis of ^{1}H NMR data is the same in the crystal structure of **5a**. See the supplementary materials for details.

(10) The stereochemistry of **9a** was confirmed by X-ray.

(11) HPLC and GC analyses of purified products from these two reactions showed four separate products (two from each reaction) and no evidence of any loss of alkene stereochemistry in the cycloadducts **9** and **10**. Preliminary results suggest that preservation of alkene geometry upon cycloaddition is also observed in the stilbene series.

(12) Regiochemical and stereochemical assignments were made on the basis of ^{1}H and ^{13}C NMR data. Experiments designed to further substantiate these assignments are in progress.

(13) Though the number of examples in this work is limited, it would appear that stereoselectivity in this reaction is a function of the local conformation of alkyl groups attached to the alkene and is best only for certain 1,2-disubstituted alkenes. Interestingly, 1-methylcyclohexene reacts with **1** with only minor stereoselectivity. Harmata, M.; Claassen, R. J. Unpublished results from these laboratories.

(14) Very rapid collapse of an intermediate carbocation is also a possibility.

(15) MOPAC(MNDO), Version 5.0. The S–N–C–C dihedral angle is 8°. The structure in Figure 1 was generated using the Cartesian coordinates from the MOPAC output and CHEM-3D.

(16) Lombardino, J. G.; Kuhla, D. E. In *Advances in Heterocyclic Chemistry*; Katritsky, A. R.; Boulton, A. J., Eds.; Academic Press: New York, 1981; Vol 28, pp 73–126.

(17) Harmata, M.; Herron, B. Manuscript in preparation.

(18) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

to use with the exception of Et_2O, which was ACS reagent grade (Fischer) and was used without purification. TLC was performed on silica gel plates (Merck), 0.25 mm, with F_{254} fluorophore. Visualization was accomplished with UV light, iodine, and/or phosphomolybdic acid; ^1H NMR spectra were obtained at 300 MHz. ^{13}C spectra were obtained at 75.5 or 22.5 MHz. All NMR spectra were obtained as $CDCl_3$ solutions with TMS as the internal standard. IR spectra were obtained in CCl_4 solution. Intensities are reported as s (strong 67–100%), m (medium 34–66%), and w (weak 0–33%) with the following abbreviations: br (broadened) and sh (shoulder). X-ray diffraction data were obtained on an Enraf-Nonius CAD-4 diffractometer. Crystal structures were solved by direct-method software. Melting points are uncorrected.

General Procedure for Preparation of *N*-Phenyl-*S*-(4-methylphenyl)sulfoximidoyl Chloride (1).[19] A 50-mL flask equipped with a stirring bar, septum, and N_2 balloon was charged with *N*-phenyl-*p*-toluenesulfinamide[20] (0.8436 g, 3.65 mmol) and 18 mL of dry CH_2Cl_2 to give a ca. 0.2 M solution. The solution was then cooled to −78 °C in a 2-propanol/dry ice bath. *tert*-Butyl hypochlorite (0.4960 g, 545 μL, 4.57 mmol) was then added via a syringe over a 5-min period. The reaction was monitored by TLC, and upon completion (ca. 10 min) the solution was concentrated first on a rotary evaporator at 0 °C and then on a vacuum line for 5 min. The resulting product was a bright yellow solid that was reasonably stable at room temperature.

General Procedure for Reaction of *N*-Phenyl-*S*-(4-methylphenyl)sulfoximidoyl Chloride with Alkenes. The sulfoximidoyl chloride was prepared as described previously and then immediately treated as follows. The sulfoximidoyl chloride contained in a flask that was equipped with a stirring bar, septum, and N_2 balloon was dissolved in dry CH_2Cl_2 to give a ca. 0.2 M solution. The alkene (1.2 equiv) was then added via a syringe. This solution was then cooled to −78 °C. $AlCl_3$ (1.5 equiv, finely powdered with a mortar and pestal and weighed out under N_2) was then added in portions over a 10-min period. The reaction was monitored by TLC. Upon completion the reaction was quenched with 1 N HCl and then diluted with ethyl acetate. The organic phase was washed with water and brine. The organic phase was dried over $MgSO_4$ and the solvent removed under reduced pressure. The product was then chromatographically purified.

(±)-(5*S,4a*S**,10b*S**)-1,2,3,4,4a,10b-Hexahydro-5-(4-methylphenyl)-5λ⁴-dibenzo[*c*,*e*][1,2]thiazine 5-Oxide (5a) and (±)-(5*S**,4a*R**,10b*R**)-1,2,3,4,4a,10b-Hexahydro-5-(4-methylphenyl)-5λ⁴-dibenzo[*c*,*e*][1,2]thiazine 5-Oxide (5b).** Chromatography solvent: hexanes/Et_2O = 2/1; yield 91%. Recrystallization from hexane/CH_2Cl_2 gave an analytical sample of **5a**: mp 146–147 °C; ^1H NMR (300 MHz) δ 7.97 (d, 2 H, *J* = 8.2 Hz), 7.38 (d, 2 H, *J* = 8.2 Hz), 7.32 (d, 1 H, *J* = 7.8 Hz), 7.20 (t, 1 H, *J* = 7.4 Hz), 7.09 (d, 1 H, *J* = 7.9 Hz), 6.94 (t, 1 H, *J* = 7.4 Hz), 3.96 (d, broadened, 1 H, *J* = 3.3 Hz), 3.16 (dt, 1 H, *J* = 3.6, 12.2 Hz), 2.76 (d, 1 H, *J* = 15.0 Hz), 2.46 (s, 3 H), 1.81–1.03 (m, 7 H); ^{13}C NMR (22.5 MHz) δ 144.88, 144.70, 131.29, 130.27, 129.68, 127.77, 126.16, 124.18, 121.69, 120.62, 56.08, 32.72, 27.30, 24.80, 23.07, 21.58, 19.67; IR (CCl_4) 2939s, 1478s, 1270s, 1219s cm^{-1}; MS (70eV) *m*/*z* 312 (M^+ + 1, 20), 311 (M^+, 93), 283 (11), 282 (17), 281 (67), 219 (13), 209 (15), 208 (24), 207 (100), 192 (14), 191 (13), 172 (45), 170 (14), 144 (17), 143 (21), 131 (22), 130 (79), 117 (16), 115 (11), 106 (16), 91 (13), 77 (10), 73 (14), 69 (13), 39 (10). Anal. Calcd for $C_{19}H_{21}NOS$: C, 73.27; H, 6.80. Found: C, 73.06; H, 6.75. Further purification of the "flashed" mixture on the Chromatotron[21] (1-mm plate, hexanes/EtOAc = 3/1) gave an analytical sample of **5b** as an oil: ^1H NMR (300 MHz) δ 7.85 (d, 2 H, *J* = 8.4 Hz), 7.35 (d, 2 H, *J* = 8.0 Hz), 7.19 (dt, 1 H, *J* = 1.6, 7.5 Hz), 7.11 (dd, 1 H, *J* = 1.4, 7.7 Hz), 7.07 (dd, 1 H, *J* = 1.3, 8.0 Hz), 6.91 (dt, 1 H, *J* = 1.4, 7.4 Hz), 3.29–3.17 (m, 2 H), 2.50–2.32 (m, 4 H), 2.23–2.07 (m, 1 H), 2.00–1.63 (m, 4 H), 1.58–1.41 (m, 2 H); ^{13}C NMR (22.5 MHz) δ 144.88, 144.46, 136.00, 129.86, 129.02, 127.89, 124.08, 123.48, 120.38, 55.91, 38.39, 28.97, 22.95, 22.77, 22.06, 21.52; IR (CCl_4) 2936s, 1479s, 1266s (br), 1219s, 1108s cm^{-1}; MS (70eV) *m*/*z* 312 (M^+ + 1, 23), 311 (M^+, 94), 281 (21), 208 (10), 207 (34), 172 (40), 170 (17), 144 (17), 143 (25), 131 (20), 130 (100), 106 (24), 91 (15), 77 (10); exact mass calcd for $C_{19}H_{21}NOS$ 311.1344, found 311.1319.

(±)-(6*S,6a*S**,9a*S**)-6a,8,9,9a-Tetrahydro-6-(4-methylphenyl)-7*H*-cyclopenta[*e*]-6λ⁴-benzo[*c*][1,2]thiazine 6-Oxide (6a) and (±)-(6*S**,6a*R**,9a*R**)-6a,8,9,9a-Tetrahydro-6-(4-methylphenyl)-7*H*-cyclopenta[*e*]-6λ⁴-benzo[*c*][1,2]thiazine 6-Oxide (6b).** Chromatography solvent: hexanes/EtOAc = 5/1; yield 81%. Recrystallization from hexane/CH_2Cl_2 gave an analytical sample of **6a**: mp 104–105 °C; ^1H NMR (300 MHz) δ 8.01 (d, 2 H, *J* = 8.3 Hz), 7.37 (d, 2 H, *J* = 8.2 Hz), 7.23–7.11 (m, 2 H), 7.05 (dd, 1 H, *J* = 1.4, 8.0 Hz), 6.91 (dt, 1 H, *J* = 1.5, 7.3 Hz), 4.00 (dt, distorted, 1 H, *J* = 2.2, 6.6 Hz), 3.61–3.50 (m, 1 H), 2.45 (s, 3 H), 2.38–2.27 (m, 1 H), 2.27–2.14 (m, 1 H), 1.76–1.50 (m, 4 H); ^{13}C NMR (22.5 MHz) δ 144.76, 143.15, 133.37, 129.74, 129.38, 127.71, 127.53, 124.61, 123.12, 121.10, 59.78, 41.01, 34.33, 28.49, 22.00, 21.58; IR (CCl_4) 2957m, 1478s, 1267s, 1206s, 1111s cm^{-1}. Anal. Calcd for $C_{18}H_{19}NOS$: C, 72.69; H, 6.44. Found: C, 72.38; H, 6.43. Recrystallization from hexane/CH_2Cl_2 gave an analytical sample of **6b**: mp 143 °C, ^1H (300 MHz) δ 7.92 (d, 2 H, *J* = 8.4 Hz), 7.39 (d, 2 H, *J* = 8.0 Hz), 7.23–7.08 (m, 3 H), 6.92 (dt, 1 H, *J* = 1.4, 7.2 Hz), 3.58–3.40 (m, 2 H), 2.47 (s, 3 H), 2.48–2.38 (m 1 H), 2.34–2.14 (m, 2 H), 2.14–1.94 (m, 2 H), 1.83–1.63 (m, 1 H); ^{13}C NMR (75 MHz) δ 144.70, 143.05, 134.67, 130.04, 129.15, 127.87, 124.34, 123.32, 120.66, 58.79, 44.94, 34.60, 26.91, 22.44, 21.62; IR (CCl_4) 2946m, 1479s, 1264s, 1216s, 1102s cm^{-1}; exact mass calcd for $C_{18}H_{19}NOS$ 297.1187, found 297.1187.

(±)-(6*S,6a*S**,11a*S**)-6a,8,9,10,11,11a-Hexahydro-6-(4-methylphenyl)-7*H*-6λ⁴-benzo[*c*]cyclohepta[*e*][1,2]thiazine 6-Oxide (7a) and (±)-(6*S**,6a*R**,11a*R**)-6a,8,9,10,11,11a-Hexahydro-6-(4-methylphenyl)-7*H*-6λ⁴-benzo[*c*]cyclohepta[*e*][1,2]thiazine 6-Oxide (7b).** Chromatography solvent: hexanes/Et_2O, gradient 3/1 to 2/1; yield 70%. Recrystallization from hexane/CH_2Cl_2 gave an analytical sample of **7a**: mp 180 °C; ^1H NMR (300 MHz) δ 8.04 (d, 2 H, *J* = 8.4 Hz), 7.41 (d, 2 H, *J* = 8.1 Hz), 7.31–7.17 (m, 2 H), 7.09 (dd, 1 H, *J* = 1.4, 7.9 Hz), 6.93 (dt, 1 H, *J* = 1.4, 7.5 Hz), 4.09 (q, distorted, 1 H), 3.23 (quintet, distorted, 1 H, *J* = 4.2 Hz), 2.61–2.48 (m, 4 H), 2.20–2.07 (m, 1 H), 1.87–1.12 (m, 8 H); ^{13}C NMR (22.5 MHz) δ 144.87, 144.68, 131.58, 130.27, 129.76, 127.72, 126.55, 124.33, 123.62, 120.43, 58.11, 35.49, 30.63, 27.82, 25.42, 24.22, 23.01, 21.68; IR (CCl_4) 2931s, 1476s, 1254s (br), 1121s cm^{-1}; exact mass calcd for $C_{20}H_{23}NOS$: 325.1500, found 325.1505. Recrystallization from hexane/CH_2Cl_2 gave an analytical sample of **7b**: mp 127 °C; ^1H NMR (300 MHz) δ 7.84 (d, 2 H, *J* = 8.3 Hz), 7.35 (d, 2 H, *J* = 8.0 Hz), 7.16 (dt, 1 H, *J* = 1.6, 7.6 Hz), 7.08 (dd, 1 H, *J* = 1.4, 7.7 Hz), 7.04 (dd, 1 H, *J* = 1.3, 8.0 Hz), 6.89 (dt, 1 H, *J* = 1.4, 7.4 Hz), 3.41–3.30 (m, 2 H), 2.68–2.54 (m, 1 H), 2.45 (s, 3 H), 2.10–1.75 (m, 6 H), 1.54–1.39 (m, 3 H); ^{13}C NMR (22.5 MHz) δ 144.58, 144.04, 135.00, 129.86, 129.32, 129.02, 127.89, 126.58, 123.54, 120.56, 58.23, 42.20, 32.31, 29.45, 24.98, 24.44, 21.57, 17.77; IR (CCl_4) 2928s, 1479s, 1268s, 1204s, 1116s cm^{-1}. Anal. Calcd for $C_{20}H_{23}NOS$: C, 73.81; H, 7.12. Found: C, 73.58; H, 7.20.

(±)-(6*S,6a*S**,12a*S**)-6a,7,8,9,10,11,12,12a-Octahydro-6-(4-methylphenyl)-6λ⁴-benzo[*c*]cycloocta[*e*][1,2]thiazine 6-Oxide (8a) and (±)-(6*S**,6a*R**,12a*R**)-6a,7,8,9,10,11,12,12a-Octahydro-6-(4-methylphenyl)-6λ⁴-benzo[*c*]cycloocta[*e*][1,2]thiazine 6-Oxide (8a).** Chromatography solvent hexanes/Et_2O, gradient 4/1 to 3/1; yield 76%. Recrystallization from hexane/CH_2Cl_2 gave an analytical sample of **8a**: mp 189 °C; ^1H NMR (300 MHz) δ 8.01 (d, 2 H, *J* = 8.3 Hz), 7.38 (d, 2 H, *J* = 8.2 Hz), 7.25–7.19 (m, 2 H), 7.10 (dd, 1 H, *J* = 1.3, 7.9 Hz), 6.92 (dt, 1 H, *J* = 1.3, 7.4 Hz), 3.88–3.82 (m, 1 H), 3.50–3.45 (m, 1 H), 2.51–2.41 (m, 4 H), 2.17–2.05 (m, 1 H), 1.93–1.86 (m, 1 H), 1.77–1.15 (m, 9 H); ^{13}C NMR (22.5 MHz) δ 145.05, 144.76, 131.88, 130.28, 129.74, 127.89, 126.24, 124.61, 123.30, 120.32, 54.71, 35.76, 28.73, 27.84, 25.33, 24.62, 23.43, 21.64; IR (CCl_4) 2925m, 1474s, 1258s, 1222m, 1113m cm^{-1}. Anal. Calcd for $C_{21}H_{25}NOS$: C, 74.29; H, 7.42. Found: C, 74.26; H, 7.26. Recrystallization from hexane/CH_2Cl_2 gave an analytical sample of **8b**: mp 144 °C; ^1H NMR (300 MHz) δ 7.82 (d, 2 H, *J* = 8.3

(19) The procedure given here is a modification of that reported by Johnson: Johnson, C. R.; Wambsgans, A. *J. Org. Chem.* **1979**, *44*, 2278.

(20) The sulfinamide is prepared by reaction of aniline with *p*-toluenesulfinyl chloride in the presence of triethylamine.

(21) Harrison Research's preparative, centrifugally accelerated, radial, thin-layer chromatograph. Harrison Research, 840 Moana Court, Palo Alto, CA.

Hz), 7.29 (d, 2 H, J = 8.0 Hz), 7.18 (dt, 1 H, J = 1.5, 7.6 Hz), 7.07 (dd, 1 H, J = 1.4, 4.4 Hz), 7.05 (dd, 1 H, J = 1.4, 4.0 Hz), 6.88 (dt, 1 H, J = 1.3, 7.4 Hz), 3.49–3.41 (m, 1 H), 3.27–3.18 (m, 1 H), 2.54–2.38 (m, 4 H), 2.20–2.07 (m, 1 H), 1.96–1.66 (m, 7 H), 1.64–1.34 (m, 3 H); ^{13}C NMR (22.5 MHz) δ 144.70, 144.46, 135.70, 129.80, 129.38, 128.19, 127.89, 123.12, 120.26, 58.83, 37.55, 31.65, 28.67, 26.47, 24.61, 22.41, 21.58; IR (CCl_4) 2928m, 1479s, 1273s, 1219m, 1110m cm^{-1}; MS (70 eV) m/z 340 (M^+ + 1, 17), 339 (M^+, 71), 281 (12), 256 (10), 207 (23), 200 (42), 156 (12), 144 (20), 143 (14), 139 (15), 131 (15), 130 (100), 118 (22), 117 (10), 106 (13), 91 (13), 77 (12), 55 (12), 44 (10); exact mass calcd for $C_{21}H_{25}NOS$: 339.1657, found 339.1641.

(±)-(2*S,3*S**,4*R**)-3,4-Diethyl-3,4-dihydro-2-(4-methylphenyl)-2λ⁴-2,1-benzothiazine 2-Oxide (9a) and (±)-(2*S**,3*R**,4*S**)-3,4-Diethyl-3,4-dihydro-2-(4-methylphenyl)-2λ⁴-2,1-benzothiazine 2-Oxide (9b).** Chromatography solvent: hexanes/EtOAc = 3/1; yield 85%. Recrystallization from hexane/CH_2Cl_2 gave an analytical sample of **9a**: mp 123–124 °C; ^{1}H NMR (300 MHz) δ 7.93 (d, 2 H, J = 8.2 Hz), 7.36 (d, 2 H, J = 8.1 Hz), 7.20 (t, 1 H, J = 7.0 Hz), 7.09 (d, 1 H, J = 7.9 Hz), 7.02 (d, 1 H, J = 7.4 Hz), 6.88 (t, 1 H, J = 6.8 Hz), 3.29–3.24 (m, 1 H), 3.10 (t, broadened, 1 H, J = 7.9 Hz), 2.46 (s, 3 H), 2.27–1.97 (m, 2 H), 1.09 (t, 3 H, J = 7.3 Hz), 1.12–0.95 (m, 2 H), 0.71 (t, 3 H, J = 7.3 Hz); ^{13}C NMR (22.5 MHz) δ 144.63, 143.09, 133.85, 130.16, 129.62, 128.01, 123.42, 122.65, 120.14, 58.88, 43.93, 28.49, 22.47, 21.64, 12.88, 10.80; IR (CCl_4) 2935w, 1478s, 1269s, 1213m, 1116s cm^{-1}. Anal. Calcd for $C_{19}H_{23}NOS$: C, 72.80; H, 7.40. Found: C, 73.10; H, 7.46. Further purification of a mixture first on a Chromatotron[21] (1-mm plate; hexanes/EtOAc, gradient 19/1 to 4/1) and then by separation on HPLC (5 μm silica, 4.6 × 250 mm column, hexane/isopropanol = 99/1) gave an oil for an analytical sample of **9b**: ^{1}H NMR (300 MHz) δ 7.93 (d, 2 H, J = 8.3 Hz), 7.36 (d, 2 H, J = 8.2 Hz), 7.20 (t, 1 H, J = 7.3 Hz), 7.09 (d, 1 H, J = 4.8 Hz), 7.07 (d, 1 H, J = 4.4 Hz), 6.89 (t, 1 H, J = 7.4 Hz), 3.26 (dt, 1 H, J = 5.1, 7.5 Hz), 3.03 (q, 1 H, J = 6.1 Hz), 2.46 (s, 3 H), 2.25–2.10 (m, 1 H), 1.78–1.50 (m, 3 H), 0.99 (t, 3 H, J = 7.5 Hz), 0.74 (t, 3 H, J = 7.4 Hz); ^{13}C NMR (75 MHz) δ 144.37, 129.95, 129.60, 128.66, 124.20, 120.79, 61.80, 42.94, 25.78, 21.61, 21.30, 11.66, 10.81; IR (CCl_4) 2931m, 1478s, 1277s, 1216s, 1102s cm^{-1}; MS (70 eV) m/z 314 (M^+ + 1, 21), 313 (M^+, 92), 207 (17), 174 (45), 159 (15), 158 (38), 147 (12), 146 (70), 145 (50), 144 (55), 143 (13), 139 (100), 133 (18), 132 (48), 131 (24), 130 (78), 119 (44), 118 (43), 117 (34), 115 (13), 106 (10), 103 (11), 92 (11), 91 (41), 90 (13), 89 (11), 78 (10), 77 (28), 65 (22), 41 (12), 39 (16); exact mass calcd for $C_{19}H_{23}NOS$ 313.1500, found 313.1485.

(±)-(2*S,3*S**,4*S**)-3,4-Diethyl-3,4-dihydro-2-(4-methylphenyl)-2λ⁴-2,1-benzothiazine 2-Oxide (10a) and (±)-(2*S**,3*R**,4*R**)-3,4-Diethyl-3,4-dihydro-2-(4-methylphenyl)-2λ⁴-2,1-benzothiazine 2-Oxide (10b).** Chromatography solvent: hexanes/Et_2O = 3/1; yield 85%. Recrystallization from hexane/CH_2Cl_2 gave an analytical sample of **10a**: mp 84–85 °C; ^{1}H NMR (300 MHz, 50 °C) δ 7.99 (d, 2 H, J = 8.4 Hz), 7.30 (d, 2 H, J = 8.1 Hz) 7.20 (dt, 1 H, J = 1.2, 7.5 Hz) 7.12 (t, distorted, 2 H, J = 7.8 Hz), 6.89 (dt, 1 H, J = 1.4, 7.5 Hz), 3.38–3.19 (m, 2 H), 2.46 (s, 3 H), 2.19–2.01 (m, 1 H), 1.60 (septet, 1 H, J = 7.0 Hz), 1.30 (quintet, broadened, 2 H, J = 6.8 Hz), 1.06 (t, 3 H, J = 7.3 Hz), 0.58 (t, distorted, 3 H, J = 7.0 Hz); ^{13}C NMR (22.5 MHz) δ 144.76, 132.96, 130.63, 129.68, 128.01, 126.70, 126.10, 123.36, 120.38, 62.00 (broadened), 39.93, 21.58, 20.86, 18.48, 12.35, 12.16; IR (CCl_4) 2937s, 1477s, 1273s (br), 1218s, 1099s cm^{-1}. Anal. Calcd for $C_{19}H_{23}NOS$: C, 72.80; H, 7.40. Found: C, 72.64; H, 7.45. Recrystallization from hexane/CH_2Cl_2 gave an analytical sample of **10b**: mp 71–74 °C; ^{1}H NMR (300 MHz) δ 7.77 (d, 2 H, J = 8.3 Hz), 7.32 (d, 2 H, J = 8.0 Hz), 7.21 (dt, 1 H, J = 1.6, 6.7 Hz), 7.09 (dd, 1 H, J = 1.3, 7.9 Hz), 6.99 (dd, 1 H, J = 1.5, 7.5 Hz), 6.86 (dt, 1 H, J = 1.3, 7.3 Hz), 3.05 (dt, 1 H, J = 4.5, 9.9 Hz), 2.96 (dt, 1 H, J = 4.5, 9.7 Hz), 2.43 (s, 3 H), 2.17–1.76 (m, 4 H), 0.96–0.90 (m, 6 H); ^{13}C NMR (22.5 MHz) δ 144.64, 144.28, 136.53, 129.74, 129.38, 129.20, 128.19, 125.92, 122.94, 119.43, 61.98, 41.90, 21.52, 20.51, 17.17, 12.94, 10.86; IR (CCl_4) 2936s, 1478s, 1274s (br), 1229s, 1103s cm^{-1}. Anal. Calcd for $C_{19}H_{23}NOS$: C, 72.80; H, 7.40. Found: C, 72.65; H, 7.59.

(±)-(2*S,4*R**)-4-Butyl-3,4-dihydro-2-(4-methylphenyl)-2λ⁴-2,1-benzothiazine 2-Oxide (11a) and (±)-(2*S**,4*S**)-4-Butyl-3,4-dihydro-2-(4-methylphenyl)-2λ⁴-2,1-benzothiazine 2-Oxide (11b).** Chromatography solvent: hexanes/Et_2O = 10/1; yield 77%. Recrystallization from hexane/CH_2Cl_2 gave an analytical sample of **11a**: mp 101–102 °C; ^{1}H NMR (300 MHz) δ 7.89 (d, 2 H, J = 8.3 Hz), 7.34 (d, 2 H, J = 8.1 Hz), 7.21 (dt, 1 H, J = 1.6, 7.6 Hz), 7.11 (dd, 1 H, J = 1.3, 8.0 Hz), 7.07 (dd, 1 H, J = 1.4, 7.6 Hz), 6.91 (dt, 1 H, J = 1.3, 7.4 Hz), 3.52–3.42 (m, 1 H), 3.23–3.12 (m, 2 H), 2.44 (s, 3 H), 2.04–1.86 (m, 2 H), 1.54–1.25 (m, 4 H), 0.91 (t, 3 H, J = 7.0 Hz); ^{13}C NMR (22.5 MHz) δ 144.58, 137.13, 129.86, 128.73, 128.13, 127.83, 125.51, 123.66, 120.38, 51.55, 37.43, 33.02, 29.63, 22.47, 21.52, 13.96; IR (CCl_4) 2930s, 1478s, 1273s(br), 1221s, 1118s cm^{-1}. Anal. Calcd for $C_{19}H_{23}NOS$: C, 72.80; H, 7.40. Found: C, 73.10; H, 7.40. Recrystallization from hexane/CH_2Cl_2 gave an analytical sample of **11b**: mp 68–69 °C; ^{1}H NMR (300 MHz) δ 7.94 (d, 2 H, J = 8.4 Hz), 7.37 (d, 2 H, J = 8.0 Hz), 7.28–7.19 (m, 2 H), 7.12 (dd, 1 H, J = 1.5, 8.3 Hz), 6.93 (dt, 1 H, J = 1.5, 7.4 Hz), 3.50–3.38 (m, 2 H), 2.90 (t, 1 H, J = 13.1 Hz), 2.46 (s, 3 H), 2.14–2.01 (m, 1 H), 1.81–1.68 (m, 1 H), 1.43–1.23 (m, 4 H), 0.89 (t, distorted, 3 H, J = 6.8 Hz); ^{13}C NMR (22.5 MHz) δ 145.35, 144.82, 136.12, 129.98, 128.96, 128.13, 125.81, 125.63, 123.78, 120.50, 51.85, 33.56, 31.13, 28.32, 22.77, 21.64, 13.96; IR (CCl_4) 3091w (sh), 2932s, 1477s, 1280s (br), 1220s, 1118 s cm^{-1}; MS (70 eV) m/z 314 (M^+ + 1, 11), 313 (M^+, 46), 256 (21), 207 (26), 174 (12), 139 (33), 132 (12), 130 (17), 119 (13), 118 (100), 117 (15), 91 (20), 77 (10); exact mass calcd for $C_{19}H_{23}NOS$ 313.1500, found 313.1492.

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Supplementary Material Available: NMR spectral data of **5a/b–11a/b** and tables of interatomic distances, interatomic angles, and dihedral angles for non-hydrogen atoms for **5a**, **8b**, and **9a** (54 pages). Ordering information is given on any current masthead page.