Lewis Acid Mediated Reactions of *N*-Arylsulfonimidoyl Chlorides with Alkenes. Some Steric Effects of Alkene Substitution

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The Lewis acid-mediated reaction of *N*-phenyl-*S*-(4-methylphenyl)sulfonimidoyl chloride with alkenes was explored in order to determine the effect of alkene substitution on the stereochemical outcome of the reaction. With monosubstituted alkenes, benzothiazines are produced with relatively low diastereoselection, with one unique exception, trimethylsilylethene. 1,1-Disubstituted alkenes give products with even lower stereoselectivity. With trisubstituted alkenes, steric effects begin to change the course the reaction from one which can be rationalized as a cycloaddition to one which seems to definitely produce a carbocationic intermediate. Interestingly, the stereoselection observed in the reaction of (*E*)- and (*Z*)-2-butenes shows large deviations from the norm with (*E*)-2-butene giving rise to two diastereomeric benzothiazines in a ratio of 45:1.

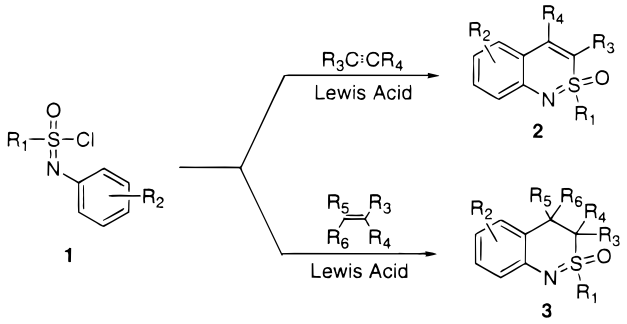
Introduction

The Lewis acid-mediated reaction of *N*-arylsulfonimidoyl chlorides with alkynes and alkenes is a powerful synthetic approach to the synthesis of benzothiazines such as **2** and **3** (Scheme 1).[1] The reaction is further characterized by a reasonable range of generality and compares very favorably with related methodology involving the direct cycloaddition of sulfinylanilines with alkenes, the latter reaction being possible only with strained alkenes.[2] Further, the product benzothiazines have tremendous potential as intermediates in organic synthesis, and their facile conversion to alkylanilines, alkenylanilines, and allylanilines has been demonstrated.[3] In an earlier study, we obtained some interesting results regarding the preparation of benzothiazines **2** from alkenes with respect to diastereoselectivity.[1b] We decided to investigate the matter more deeply and examine a series of alkenes with the aim of establishing a relationship between the number and size of substituents on the alkene and the diastereoselectivity of the reaction. This report details the results of that investigation.

Results and Discussion

Monosubstituted Alkenes. In this series, a small number of monosubstituted alkenes were chosen to examine the effect of steric interactions on the diastereoselectivity of the reaction with respect to carbon 4 of the benzothiazines formed in this reaction. The sulfonimidoyl chloride **4** was treated with monosubstituted alkenes in the presence of $AlCl_3$ at −78 °C in CH_2Cl_2 to produce benzothiazines in good to excellent yields. These results obtained are shown in Table 1.

Scheme 1



All crude reaction products were subjected to capillary GC analysis in order to determine the isomer ratios shown in Table 1. The extent of diastereoselectivity was small, ranging from 1.4:1 to 4.1:1, even for R_1 = *tert*-butyl. Interestingly, with (trimethylsilyl)ethene a reasonable diastereoselectivity was obtained (Table 1, entry 6). The size of the trimethylsilyl group is greater than that of the *tert*-butyl group.[4] Further, because of the greater carbon−silicon bond length vis-à-vis the carbon−carbon bond, that steric bulk is projected further away from the reactive alkene centers. Which factor is responsible for the observed diastereoselectivity is not known. It should be stated that we have shown in several cases that benzothiazine stereochemistry remains intact under the reaction conditions.[1b] The low yield associated with the formation of **10** can be attributed to the formation of a desilylated side product.[5]

The relative stereochemistry of the benzothiazines was assigned on the basis of NMR shift reagent studies. Lanthanide shift reagents are commonly used on organic

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(3) (a) Harmata, M.; Jones, D. E. *Tetrahedron Lett.* **1995**, *36*, 4769. (b) Harmata, M.; Kahraman, M. *Synthesis* **1995**, 713. (c) Harmata, M.; Kahraman, M. *Synthesis* **1994**, 142. (d) Harmata, M.; Herron, B. F. *Tetrahedron* **1991**, *47*, 8855.

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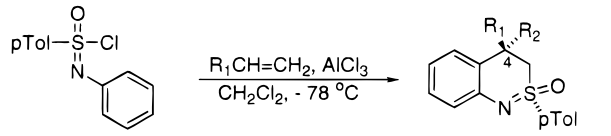
Table 1. Reactions of 4 with Monosubstituted Alkenes



4

a: R_1 = alkyl, R_2 = H
b: R_1 = H, R_2 = alkyl

entry	R_1	product	a:b[a]	yield[b] (%)
1	Et	**5**	1.5:1	90
2	*n*-Pr	**6**	1.6:1	66
3	*i*-Pr	**7**	2.4:1	78
4	Ph	**8**	1.4:1	62
5	*t*-Bu	**9**	4.1:1	65
6	TMS	**10**	10:1	35

[a] Determined by capillary GC analysis of crude reaction mixtures. [b] After chromatographic purification.

Table 2. Shift Reagent Study[a]

entry	benzothiazine	Δδ isomer **a**[b]	Δδ isomer **b**[b]
1	**5**	0.84	1.19
2	**6**	0.43	0.83
3	**7**	0.32	0.54
4	**8**	0.80	1.08
5	**9**	0.30	0.46
6	**10**	0.10	0.36

[a] Chemical shift change of the C-4 proton after addition of 20 mol % $Eu(fod)_3$. [b] Downfield, in ppm.

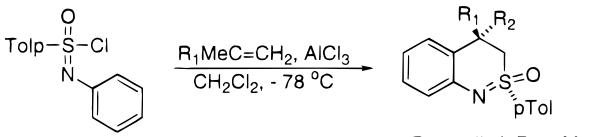
compounds to assign stereochemistry.[6] In our studies, $Eu(Fod)_3$ was chosen for the stereochemical assignments.

In most cases, separated diastereomers were subjected to this study with the same stock solution of $Eu(Fod)_3$. However, in a few cases, the mixture of isomers was used. While one isomer showed relatively large downfield shifts, the other showed smaller downfield shifts. The stereochemical assignments are based on the comparison of these shifts for each isomer. The results for this shift reagent study are shown in Table 2, which presents the changes in chemical shifts for the C-4 hydrogen of the benzothiazines after the addition of 20 mol % of $Eu(Fod)_3$.

It was anticipated that the hydrogen cis to the oxygen at S-2 would experience a greater downfield shift than the one situated trans since coordination of the shift reagent at the sulfoximine oxygen should perturb the C-4 cis hydrogen to a greater extent than one oriented trans. For example, the C-4 hydrogen of benzothiazine **9a** has a chemical shift of 3.05 ppm. However, after the addition of 20 mol % of $Eu(Fod)_3$, the same proton had moved to 3.35 ppm, a downfield shift of 0.30 ppm. On the other hand, the C-4 hydrogen of the minor isomer **9b** had a chemical shift of 3.04 ppm. After the addition of 20 mol % of shift reagent, this proton shifted to 3.50 ppm, a downfield shift of 0.46 ppm. The stereochemical assignments for **5** through **8** were made accordingly. These assignments were supported by X-ray structural determination of **9a** and **10b**.

To predict the relative stereochemistry, it is appropriate to mention the polarity of isomers. HPLC analysis of the crude reaction mixtures showed that the major isomers for **5**−**9** had shorter retention times relative to minor isomers. This result is also consistent with the data from the shift reagent study because alkyl or aryl groups which are cis to S-2 oxygen at the C-4 position would block the polar group and reduce the polarity of the isomer.

Table 3. Reactions of 4 with Disubstituted Alkenes



4

a: R_1 = alkyl, R_2 = Me
b: R_1 = Me, R_2 = alkyl

entry	R_1	product	a:b[a]	yield[b] (%)
1	Et	**11**	1.2:1	46
2	*i*-Pr	**12**	2.4:1	33
3	*t*-Bu	**13**	1.2:1	57

[a] Determined by capillary GC analysis of crude reaction mixtures. [b] After chromatographic purification.

Table 4. Shift Reagent Study for 11−13[a]

entry	benzothiazine	Δδ isomer **a**[b]	Δδ isomer **b**[b]
1	**11**	0.23	0.26
2	**12**	0.14	0.21
3	**13**	0.137	0.139

[a] Chemical shift change of the C-4 methyl group after addition of 20 mol % $Eu(fod)_3$. [b] Downfield, in ppm.

1,1-Disubstituted Alkenes. 1,1-Disubstituted alkenes were also studied to examine the effect of steric interactions on the diastereoselectivity of the reaction and to broaden the scope of the reaction. When the sulfonimidoyl chloride **4** was reacted with 1,1-disubstituted alkenes in the presence of $AlCl_3$ at −78 °C in CH_2Cl_2, the reaction yielded benzothiazines **11**−**13** (Table 3). To determine the isomer ratio (**a**/**b**) for benzothiazines **11**−**13**, all crude reaction mixtures were subjected to capillary GC analysis. Not surprisingly, the diastereoselection for these reactions was not very high. Yields for these reactions varied in a range of 33% to 57% due to the formation of side products.

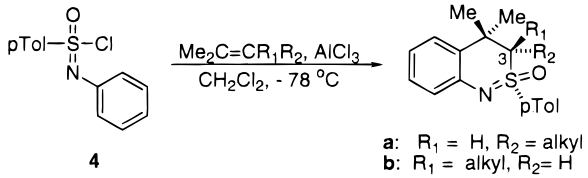
All benzothiazines were separated and subjected to NMR shift reagent study as mentioned above. It was anticipated that those methyl groups cis to the oxygen of sulfoximine functionality would experience a greater downfield shifts than those situated trans. These methyl shifts for benzothiazines **11**−**13** are listed in Table 4.

Benzothiazine **11a** exhibited a C-4 methyl resonance at 1.41 ppm. Isomer **11b** had the same methyl peak at 1.56 ppm. After the addition of 20 mol % $Eu(Fod)_3$, the methyl peaks shifted downfield by 0.23 and 0.26 ppm, respectively. The stereochemical assignments were made accordingly. Thus, the C-4 methyl group for **11a** was assigned as trans to the oxygen at S-2 position because it shifts less downfield than C-4 methyl group of **11b**. Because the change in chemical shifts in both isomers is comparable, the stereochemical assignments should be considered tentative. Nevertheless, the data are self-consistent. In all cases, it appears that the major isomers maintained the same relative stereochemistry in which there was a cis relationship between alkyl groups at C-4 position of benzothiazines and the oxygen of sulfoximine functionality.

According to these assignments, it is logical to expect that the major isomer would be less polar than the minor isomer. HPLC analysis of the crude reaction mixtures showed that the major isomers of **11**−**13** all had shorter retention times relative to their diastereomers.

(6) *Lanthanide Shift Reagents in Stereochemical Analysis*; Morrill, T. C., Ed.; VCH: Deerfield Beach, 1986.

Table 5. Reactions of 4 with Trisubstituted Alkenes



4

entry	R_1	product	a:b[a]	yield[b] (%)
1	Me	**16**	1.2:1	53
2	Et	**17**	1.6:1	53
3	*i*-Pr	**18**		*c*
4	*t*-Bu	**19**		*c*

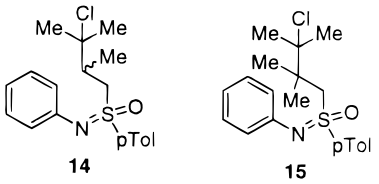
[a] Determined by capillary GC analysis of crude reaction mixtures. [b] After chromatographic purification. [c] Benzothiazine not formed.

Table 6. Shift Reagent for 16 and 17[a]

entry	benzothiazine	$\Delta\delta$ isomer **a**[b]	$\Delta\delta$ isomer **b**[b]
1	**16**	1.30	0.39
2	**17**	1.27	0.35

[a] Chemical shift change of the C-3 proton after addition of 20 mol % $Eu(fod)_3$. [b] Downfield, in ppm.

In addition to the benzothiazines mentioned, side products were observed in some cases. Chlorosulfoximine **14** was isolated in 11% yield as a 1.2:1 mixture of isomers in the formation of benzothiazine **12**. Similarly, **15** was obtained during the synthesis of **13** in 6% yield. Its structure was confirmed by X-ray analysis.

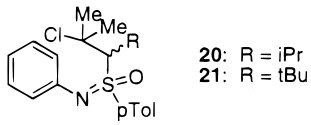


14 **15**

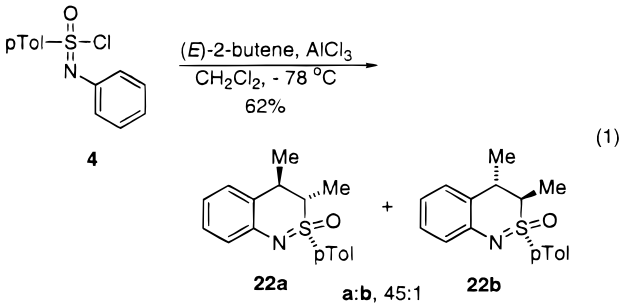
Trisubstituted Alkenes. These alkenes were studied to examine the effect of steric interactions on the diastereoselectivity in benzothiazine formation with respect to the C-3 position of benzothiazines. The results are summarized in Table 5. When 2-methyl-2-butene was treated with **4**, benzothiazine **16** was obtained in 53% yield as a 1.2:1 mixture of diastereomers. With 2-methyl-2-pentene, **17** was formed in 53% yield as a 1.6:1 mixture of diastereomers.

As for the relative stereochemical assignments, benzothiazines **16** and **17** were submitted to a shift reagent study. In this case, separation was not possible, even with HPLC, and mixtures had to be used. It was relatively easy to distinguish the C-3 proton for the major and the minor isomers by careful measurement of integration. It was seen that the C-3 hydrogens of benzothiazines **16a** and **16b** had chemical shifts of 3.20 and 2.96 ppm, respectively. After the addition of 20 mol % of $Eu(Fod)_3$, the C-3 protons of **16a** and **16b** moved to 4.50 and 3.35 ppm, respectively. The chemical shift changes were 1.30 and 0.39 ppm. The larger shift should correspond to the cis hydrogen at carbon 3, and the stereochemical assignments were made accordingly. The same result was found for benzothiazine **17** as well (Table 6). In both cases, the major isomer had a longer retention time on the HPLC column. This is also consistent with the stereochemical assignments.

Interestingly, as steric bulk on the alkene increased the course of the reaction changed. Reaction of **4** with 2,4-dimethyl-2-pentene gave a 34% yield of chlorosulfoximine **20** as a 2.4:1 mixture of isomers. Gas chromatographic analysis suggested only very small amounts of benzothiazine **18** may have been formed. The reaction with 2,4,4-trimethyl-2 pentene gave only chlorosulfoximine **21** as a single, but unassigned, stereoisomer in 48% yield.



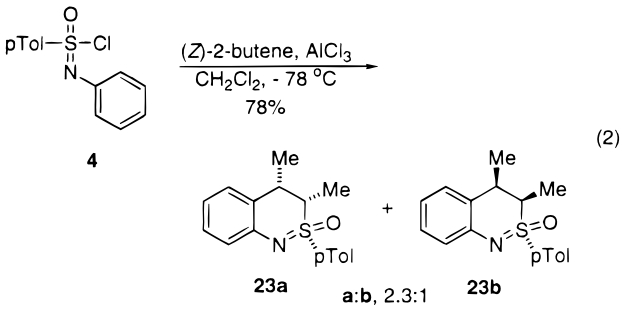
(*Z*)- and (*E*)-2-Butene. We had earlier reported some intriguing stereoselectivities in the reaction of **4** with (*Z*)- and (*E*)-3-hexene.[1b] To test the lower limit of this stereoselectivity, we examined the corresponding 2-butenes. Interestingly, when (*E*)-2-butene was reacted with sulfonimidoyl chloride **4** under the standard reaction conditions, benzothiazine **22** was obtained in 62% yield as a 45:1 mixture of isomers (eq 1). The relative



(1)

stereochemistry of cycloadduct **22a** was determined by X-ray crystallography. The minor isomer **22b** could not be isolated for further study, but it was assumed that it had the stereochemistry shown in analogy to our earlier work.[1b]

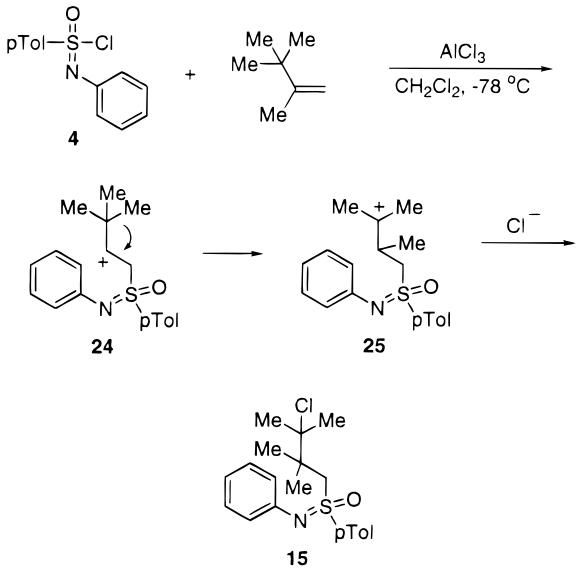
In the case of (*Z*)-2-butene, reaction with **4** gave the benzothiazine **23** in 78% yield with a diastereomer ratio of 2.3:1 (eq 2). The relative stereochemical assignment



(2)

for benzothiazines **23a**/**b** was made on the basis of NMR shift reagent study. The major isomer had two sets of multuplets at 3.94 and 3.17 ppm. Those peaks corresponded to C-3 and C-4 hydrogens, respectively. After 20 mol % $Eu(Fod)_3$ was added, those peaks shifted downfield 4.29 and 3.81 ppm, a difference of 0.35 and 0.64 ppm, respectively. On the other hand, the minor isomer had a multiplet at 3.23 ppm for the same two protons. After the NMR shift reagent study, those protons shifted to 3.40 ppm and 3.32 ppm, a difference

Scheme 2



of 0.17 and 0.11 ppm. On the basis of these data, the major isomer and minor isomers were assigned as **23a** and **23b**, respectively. It was expected that the major isomer **23a** should be more polar than **23b**, and this was observed with HPLC analysis of the product mixture.

Side Reactions and Mechanistic Possibilities. The mechanism of the reaction of **4** with alkenes is still in question. The stereochemical data we obtained previously and as well as that in this study suggests a concerted process or a stepwise one in which collapse of an intermediate carbocation to a σ complex is faster than bond rotation. The issue is still unresolved, but it is clear that carbocation intermediates are accessible in this reaction, particularly as steric hindrance increases as a result of alkene substitution.

Most telling in this regard is the formation of the chlorosulfoximines observed in this work. Their appearance clearly suggests a stepwise process as shown in Scheme 2 for the formation of **15** and is suggestive of the formation of carbocationic intermediates in general. Remaining to be answered are such questions as the mechanistic basis behind the high diastereoselectivity found with (*E*)-1,2-dialkylalkenes and the nature of the stereochemistry (retention/inversion) at sulfur in benzothiazine formation.

Summary

In summary, we have examined the effect of alkene substitution on the course and stereochemical outcome of the reaction of **4** with alkenes in the presence of a Lewis acid, aluminum chloride. This study helped to expand the scope of the reaction. The effects of substitution of diastereoselectivity seem to be minimal, except for (*E*)-1,2-disubstituted alkenes. The reasons for this are still not clear. Steric bulk on the alkene progressively steers the course of the reaction away from cycloaddition and benzothiazine formation in favor of electrophilic addition. Many mechanistic questions remain unanswered, and given the simplicity of this reaction and the synthetic utility of benzothiazines, further studies are warranted. Progress will be reported in due course.

Experimental Section

General Methods. See ref 1b. ^{1}H and ^{13}C spectra were obtained at 500 and 125.8 MHz, respectively. All NMR spectra were obtained as a solution in $CDCl_3$ with TMS as the internal standard unless otherwise stated. 2,4-Dimethyl-2-pentene was prepared as described in the literature.[7] All other chemicals were obtained from commercial sources.

General Procedure for the Preparation of *N*-Phenyl-*S*-(4-methylphenyl)sulfonimidoyl Chloride (4). A flame-dried 50 mL recovery flask equipped with a magnetic stir bar, a septum, and a nitrogen balloon was charged with 1.034 g (4.47 mmol, 1 equiv) of *N*-phenyl-*p*-toluenesulfinamide[8] and 21.9 mL of dry CH_2Cl_2 to give a 0.20 M solution. This solution was cooled to −78 °C in a 2-propanol/dry ice bath. *tert*-Butyl hypochlorite (0.545 mL, 4.56 mmol, 1.02 equiv) was added via a syringe over 5 min. The solution turned yellow after 10 min. The completion of the reaction was monitored by TLC. The product **4** can be obtained by evaporating the solvent and excess *t*-BuOCl on a rotary evaporator at 0 °C. However, all reactions were carried out in one pot as discussed below.

General Procedure for the Reaction of *N*-Phenyl-*S*-(4-methylphenyl)sulfonimidoyl Chloride (4) with Alkenes. Method A. In the case of gaseous alkenes, a solution of the sulfonimidoyl chloride (1.18 g, 4.47 mmol, 1 equiv), prepared as decribed above, was cooled to −78 °C in a 2-propanol/dry ice bath in the same flask equipped with a septum, magnetic stir bar, and a nitrogen balloon. Gaseous alkenes were passed through the solution of the sulfonimidoyl chloride solution for 10−15 min by using a simple gas line connected to a needle. Powdered $AlCl_3$ (1.789 g, 13 mmol, 3 equiv) was added to the reaction mixture in three portions over 15 min time period. The color of the solution turned brown. The alkene was continuously bubbled through the solution. The mixture was allowed to stir at −78 °C for 1 h. The reaction was monitored by TLC. It was quenched with 20 mL of 1 N HCl. It was poured into a separatory funnel along with 30 mL of ethyl acetate. The organic layer was washed with water (3 × 30 mL) and brine solution (1 × 30 mL), dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo to give the product as either a brownish viscous oil or light brown solid which was purified by either flash chromatography or MPLC.

Method B. In the case of liquid alkenes, the sulfonimidoyl chloride (1.18 g, 4.47 mmol, 1 equiv) prepared as described above was cooled to −78 °C in a 2-propanol/dry ice bath in the same flask equipped with a septum, magnetic stir bar, and nitrogen balloon. The alkene (5.36 mmol, 1.2 equiv) was added to this solution via a syringe at −78 °C. The solution was allowed to stir for 5−10 min, followed by the addition of 1.78 g (13 mmol, 3 equiv) of powdered $AlCl_3$ in three portions over a 15 min time period. The color of the solution turned brown immediately. The mixture was allowed to stir at −78 °C for 1 h. The reaction was monitored by TLC. The reaction was quenched and worked up as described for method A.

(±)-(2*S,4*R**)-3,4-Dihydro-4-ethyl-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (5a) and (±)-(2*S**,4*S**)-3,4-Dihydro-4-ethyl-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (5b). Method A.** Chromatography solvent: 6:1 hexane/ethyl acetate. Combined yield: 90%. Recrystallization from hexane/ethyl acetate gave an analytical sample of **5a**: mp 89−90 °C; ^{1}H (500 MHz, $CDCl_3$) δ 7.85 (d, 2H, J = 8.2 Hz), 7.30 (d, 2H, J = 8.2 Hz), 7.17 (dt, 1H, J = 0.7, 7.9 Hz), 7.07 (d, 1H, J = 7.8 Hz), 7.04 (d, 1H, J = 7.7 Hz), 6.86 (t, 1H, J = 7.4 Hz), 3.44 (dd, 1H, J = 5.2, 13.2 Hz), 3.14 (dd, 1H, J = 5.3, 13.2 Hz), 3.08−3.03 (m, 1H), 2.40 (s, 3H), 2.0−1.93 (m, 2H), 1.00 (t, 3H, J = 7.33 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 144.34, 136.8, 129.6, 128.4, 127.8, 125.0, 123.3, 120.1, 50.8, 38.8, 26.2, 21.3, 11.8. Anal. Calcd for $C_{17}H_{19}NSO$: C, 71.53; H, 6.71. Found: C, 71.53; H, 6.68.

Recrystallization from hexane/ethyl acetate gave an analytical sample of **5b**: mp 93−94 °C; ^{1}H (500 MHz, $CDCl_3$) δ 7.93 (dd, 2H, J = 1.8, 8.3 Hz), 7.36 (d, 2H, J = 8.1 Hz), 7.23−7.19 (m, 2H), 7.11 (dd, 1h, J = 1.3, 7.9 Hz), 6.92 (dt, 1H, J = 1.37, 7.5 Hz), 3.45−3.37 (m, 2H), 2.87 (dd, 1H, J = 1.8, 11.8 Hz),

(7) Shapiro, R. H.; Kolonko, K. J. *J. Org. Chem.* **1978**, *43*, 1404.
(8) Prepared by the reaction of aniline with *p*-toluenesulfinyl chloride in the presence of triethylamine.

2.44 (s, 3H), 2.17−2.11 (m, 1H) 1.86−1.77 (m, 1H), 0.96 (t, 3H, J = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 144.7, 135.9, 129.9, 128.9, 128.0, 125.6, 125.3, 123.7, 120.4, 51.4, 34.6, 24.2, 21.5, 10.5. Anal. Calcd for $C_{17}H_{19}NSO$: C, 71.53; H, 6.61. Found: C, 71.31; H, 6.69.

(±)-(2*S,4*R**)-3,4-Dihydro-2-(4-methylphenyl)-4-propyl-2λ^4-2,1-benzothiazine 2-Oxide (6a) and (±)-(2*S**,4*S**)-3,4-Dihydro-2-(4-methylphenyl)-4-propyl-2λ^4-2,1-benzothiazine 2-Oxide (6b). Method B.** Chromatography solvent: 3:1 hexane/ethyl acetate. Combined yield: 66%. Recrystallization from hexane/ethyl acetate gave an analytical sample of **6a**: mp 115−116 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, 2H, J = 8.2 Hz), 7.33 (d, 2H, J = 8.1 Hz), 7.21 (t, 1H, J = 0.8 Hz), 7.10 (d, 1H, J = 7.9 Hz), 7.05 (d, 1H, J = 7.2 Hz), 6.89 (t, 1H, J = 7.2 Hz), 3.46−3.42 (m, 2H), 2.91−2.86 (m, 1H) 2.43 (s, 3H), 1.98−1.90 (m, 2H), 1.55−1.47 (m, 1H), 1.42−1.32 (m, 1H), 0.94 (t, 3H, 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 144.6, 137.1, 129.9, 128.7, 128.1, 127.9, 125.5, 123.6, 120.4, 51.6, 37.1, 35.4, 21.5, 20.6, 13.8. Anal. Calcd for $C_{18}H_{21}NOS$: C, 72.20; H, 7.06. Found: C, 72.09; H, 7.05.

Flash chromatographic purification gave the analytical sample of **6b** as a yellow oil: ^{1}H (500 MHz, $CDCl_3$) δ 7.93 (d, 2H, J = 8.2 Hz), 7.35 (d, 2H, J = 8.1 Hz), 7.25−7.19 (m, 2H), 7.11 (d, 1H, J = 7.7 Hz), 6.91 (t, 1H, J = 7.0 Hz), 3.46−3.40 (m, 2H), 2.91−2.86 (m, 1H), 2.44 (s, 3H), 2.08−2.01 (m, 1H), 1.74−1.67 (m, 1H), 1.45−1.36 (m, 1H), 1.35−1.26 (m, 1H), 0.95 (t, 3H, J = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 144.7, 136.1, 129.9, 128.9, 128.0, 125.8, 125.6, 123.7, 120.4, 51.8, 33.6, 33.4, 21.5, 19.4, 14.0. Anal. Calcd for $C_{18}H_{21}NOS$: C, 72.20; H, 7.06. Found: C, 72.11; H, 6.95.

(±)-(2*S,4*R**)-3,4-Dihydro-4-(1-methylethyl)-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (7a) and (±)-(2*S**,4*S**)-3,4-Dihydro-4-(1-methylethyl)-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (7b). Method B.** Chromatography solvent: 6:1 hexane/ethyl acetate. Combined yield: 78%. Recrystallization from hexane/ethyl acetate gave an analytical sample of **7a**: mp 136−137 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, 2H, J = 8.0 Hz), 7.30 (d, 2H, J = 8.1 Hz), 7.19 (t, 1H, J = 7.8 Hz), 7.10 (d, 1H, J = 7.9 Hz), 7.02 (d, 1H, J = 7.5 Hz), 6.86 (t, 1H, J = 7.4 Hz), 3.67 (dd, 1H, J = 5.1 Hz, J = 13.6 Hz), 3.06 (dd, 1H, J = 4.8, 13.6 Hz), 2.81−2.78 (m, 1H), 2.51−2.44 (m, 1H), 2.40 (s, 3H), 1.33 (d, 3H, J = 6.6 Hz), 0.91 (d, 3H, J = 6.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 144.3, 137.7, 129.7, 129.0, 128.3, 128.0, 124.6, 123.3, 119.7, 49.8, 44.8, 28.0, 21.8, 21.4, 20.1. Anal. Calcd for $C_{18}H_{21}NOS$: C, 72.20; H, 7.06. Found: C, 72.33; H, 7.15.

Flash chromatographic purification gave the analytical sample of **7b** as a yellow oil: ^{1}H (500 MHz, $CDCl_3$) δ 7.96 (d, 2H, J = 8.3 Hz), 7.36 (d, 2H, J = 8.1 Hz), 7.21−7.17 (m, 2H), 7.11 (dd, 1H, J = 1.4, 8.8 Hz), 6.92 (dt, 1H, J = 1.4, 7.6 Hz), 3.37 (dd, 1H, J = 4.1, 12.5 Hz), 3.27−3.23 (m, 1H), 2.94 (dd, 1H, J = 12.09, 12.11 Hz), 2.71−2.65 (m, 1H), 2.44 (s, 3H), 1.05 (d, 3H, J = 6.8 Hz), 0.77 (d, 3H, J = 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 144.7, 135.9, 129.9, 128.9, 127.9, 126.1, 124.9, 124.0, 120.4, 48.0, 40.0, 26.7, 21.5, 21.1, 16.8. Anal. Calcd for $C_{18}H_{21}NOS$: C, 72.20; H, 7.06. Found: C, 71.88; H,7.15.

(±)-(2*S,4*R**)-3,4-Dihydro-2-(4-methylphenyl)-4-phenyl-2λ^4-2,1-benzothiazine 2-Oxide (8a) and (±)-(2*S**,4*S**)-3,4-Dihydro-2-(4-methylphenyl)-4-phenyl-2λ^4-2,1-benzothiazine 2-Oxide (8b). Method B.** Chromatography solvent (MPLC): 9:1 hexane/ethyl acetate. Combined yield: 62%. Recrystallization from hexane/ethyl acetate gave an analytical sample of **8a**: mp 145−146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, 2H, J = 8.3 Hz), 7.59−7.23 (m, 7H), 7.20−7.17 (m, 1H), 7.12 (dd, 1H, J = 1.2, 7.9 Hz), 6,76 (dt, 1H, J = 1.3, 7.6 Hz), 6.64 (d, 1H, J = 7.7 Hz), 4.74 (dd, 1H, J = 4.2, 14.1 Hz), 3.52 (dd, 1H, J = 4.3, 12.0 Hz), 3.20 (dd, 1H, J = 14.04, 12.1 Hz), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 145.1, 140.2, 134.8, 130.0, 129.2, 129.0, 128.9, 128.4, 128.2, 127.7, 125.2, 123.6, 120.4, 53.1, 40.7, 21.6. Anal. Calcd for $C_{21}H_{19}NOS$: C, 75.68; H, 5.75. Found: C, 75.47; H, 5.83.

Recrystallization from hexane/ethyl acetate gave an analytical sample of **8b**: mp 175−176 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, 2H, J = 8.3 Hz), 7.38−7.16 (m, 9H), 6.79 (dd, 1H, J = 1.4, 7.5 Hz), 6.59 (d, 1H, J = 7.7 Hz), 4.27 (dd, 1H, J = 8.2, 8.3 Hz), 3.67−3.65 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7,144.9, 139.1, 136.9, 130.0, 128.9, 128.9, 128.7, 128.6, 127.7, 127.6,126.6, 123.8, 120.8, 54.5, 42.5, 21.6. Anal. Calcd for $C_{21}H_{19}NOS$: C, 75.68; H, 5.75. Found: C, 75.88; H, 5.82.

(±)-(2*S,4*R**)-3,4-Dihydro-4-(1,1-dimethylethyl)-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (9a) and (±)-(2*S**,4*S**)-3,4-Dihydro-4-(1,1-dimethylethyl)-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (9b). Method B.** Chromatography solvent: 4:1 hexane/ethyl acetate. Yield: 65%. Recrystallization from hexane/ethyl acetate gave an analytical sample of **9a**: mp 173−174 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, 2H, J = 8.2 Hz), 7.29−7.22 (m, 3H), 7.12 (d, 1H, J = 8.0 Hz), 7.05 (d, 1H, J = 7.1 Hz), 6.89 (dt, 1H, J = 0.8, 7.5 Hz), 3.90 (dd, 1H, J = 1.5, 13.9 Hz), 3.10−3.03 (m, 2H), 2.41 (s, 3H), 1.15 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 143.9, 139.6, 130.4, 129.7, 128.3, 127.8, 123.5, 122.7, 119.7, 51.0, 49.2, 34.7, 28.5, 21.4. Anal. Calcd for $C_{19}H_{23}NOS$: C, 72.88; H, 7.39. Found: C, 73.06; H, 7.33.

Recrystallization from hexane/ethyl acetate gave an analytical sample of **9b**: mp 115−116 °C; ^{1}H NMR 500 MHz, $CDCl_3$) δ 7.97 (d, 2H, J = 8.2 Hz), 7.36 (d, 2H, J = 8.1 Hz), 7.25−7.20 (m, 2H), 7.14 (d, 1H, J = 7.6 Hz), 6.92 (t, 1H, J = 7.2 Hz), 3.70 (dd, 1H, J = 6.6, 14.2 Hz), 3.57 (dd, 1H, J = 6.2, 14.2 Hz), 3.03 (dd, 1H, J = 6.4 Hz), 2.45 (s, 3H), 1.00 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 144.3, 136.9, 129.8, 129.7, 128.4, 128.1, 125.0, 120.4, 53.6, 46.5, 34.3, 28.5, 21.5. Anal. Calcd for $C_{19}H_{23}NOS$: C, 72.88; H, 7.39. Found: C, 72.63; H, 7.24.

(±)-(2*S,4*R**)-3,4-Dihydro-2-(4-methylphenyl)-4-(trimethylsilyl)-2λ^4-2,1-benzothiazine 2-Oxide (10a) and (±)-(2*S**,4*S**)-3,4-Dihydro-2-(4-methylphenyl)-4-(trimethylsilyl)-2λ^4-2,1-benzothiazine 2-Oxide (10b). Method B.** Chromatography solvent: 9:1 hexene/ethyl acetate. Yield: 35%. Recrystallization from hexane/ethyl acetate gave an analytical sample of **10a**: mp 132−133 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.86 (d, 2H, J = 8.2 Hz), 7.33 (d, 2H, J = 8.2 Hz), 7.17−7.06 (m, 2H), 6.97 (d, 1H, J = 6.7 Hz), 6.86 (dt, 1H, J = 1.2, 7.2 Hz), 3.56 (dd, 1H, J = 3.1, 12.6 Hz), 3.14 (dd, 1H, J = 6.6, 12.6 Hz), 2.78 (dd, 1H, J = 3.1, 6.5 Hz), 2.44 (s, 3H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.8, 144.8, 136.7, 129.8, 128.7, 127.6, 126.8, 123.7, 123.3, 120.1, 49.3, 28.4, 21.5, −1.8. Anal. Calcd for $C_{18}H_{23}NOSSi$: C, 65.61; H, 7.04. Found: C, 65.43; H, 6.94.

Flash chromatographic purification gave **10b** as a solid. Recrystallization from hexane/ethyl acetate gave an analytical sample: mp 129−130 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.96 (d, 2H, J = 8.2 Hz), 7.38 (d, 2H, J = 8.2 Hz), 7.27−7.17 (m, 2H), 7.08 (dd, 1H, J = 1.4, 8.0 Hz), 6.86 (dt, 1H, J = 1.4, 7.5 Hz), 3.35 (dd, 1H, J = 4.0, 12.1 Hz), 3.06 (dd, 1H, J = 3.9, 15.0 Hz), 2.73 (dd, 1H, J = 12.1, 15.0 Hz), 2.46 (s, 3H), 0.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 145.9, 144.8, 135.2, 129.9, 129.1, 128.2, 127.4, 124.4, 123.3, 120.0, 49.0, 22.3, 21.6, −1.2. Anal. Calcd for $C_{18}H_{23}NOSSi$: C, 65.61; H, 7.04. Found: C, 65.87; H, 6.80.

(±)-(2*S,4*R**)-3,4-Dihydro-4-ethyl-4-methyl-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (11a) and (±)-(2*S**,4*S**)-3,4-Dihydro-4-ethyl-4-methyl-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (11b). Method B.** Chromatography solvent: 9:1 hexene/ethyl acetate. Yield: 46%. Recrystallization from hexane/ethyl acetate gave an analytical sample of **11a**: mp 91−92 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, 2H, J = 8.2 Hz), 7.32 (d, 2H, J = 8.1 Hz), 7.25 (dd, 1H, J = 1.0, 8.6 Hz), 7.18 (dt, 1H, J = 1.0, 8.0 Hz), 7.11 (dd, 1H, J = 0.9, 8.1 Hz), 6.92 (dt, 1H, J = 1.0, 7.7 Hz), 3.50 (d, 1H, J = 13.4 Hz), 2.88 (d, 1H, J = 13.4 Hz), 2.42 (s, 3H), 2.08−2.03 (m, 1H), 1.93−1.83 (m, 1H), 1.40 (s, 3H), 0.96 (t, 3H, J = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 144.1, 137.6, 129.8, 129.6, 128.5, 128.0, 125.2, 123.8, 120.4, 56.2, 38.9, 32.6, 25.2, 21.5, 8.9. Anal. Calcd for $C_{18}H_{21}NOS$: C, 72.20; H, 7.07. Found: C, 72.25; H, 6.69.

Flash chromatographic purification gave an analytical sample of **11b** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, 2H, J = 8.2 Hz), 7.36 (d, 2H, J = 8.1 Hz), 7.25−7.16

(m, 2H), 7.11 (d, 1H, J = 7.7 Hz), 6.93 (dt, 1H, J = 0.9, 7.6 Hz), 3.25 (d, 1H, J = 13.2 Hz), 3.17 (d, 1H, J = 13.3 Hz), 2.44 (s, 3H), 1.98−1.89 (m, 1H), 1.79−1.70 (m, 1H), 1.55 (s, 3H), 0.74 (t, 3H, J = 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 144.2, 137.0, 129.0, 128.7, 128.7, 127.8, 124.9, 124.6, 120.9, 56.5, 38.9, 33.4, 28.2, 21.5, 8.5. Anal. Calcd for $C_{18}H_{21}NOS$: C, 72.20; H, 7.07. Found: C, 72.45; H, 7.14.

(±)-(2*S,4*R**)-3,4-Dihydro-4-methyl-4-(1-methylethyl)-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (12a) and (±)-(2*S**,4*S**)-3,4-Dihydro-4-methyl-4-(1-methylethyl)-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (12b). Method B.** Chromatography solvent: 6:1 hexane/ethyl acetate. Yield: 33%. Flash chromatographic purification gave an analytical sample of **12a** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, 2H, J = 8.3 Hz), 7.30 (d, 2H, J = 8.0 Hz), 7.22−7.19 (m, 2H), 7.14 (dd, 1H, J = 1.2, 8.2 Hz), 6.91 (dt, 1H, J = 1.3, 7.7 Hz), 3.70 (d, 1H, J = 13.8 Hz), 2.78 (d, 1H, J = 13.8 Hz), 2.67−2.61 (m, 1H), 2.41 (s, 3H), 1.30 (s, 3H), 1.12 (d, 3H, J = 6.7 Hz), 0.79 (d, 3H, J = 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 144.2, 138.6, 129.8, 129.5, 128.3, 128.0, 126.5, 123.7, 119.8, 56.2, 42.1, 30.8, 21.5, 19.3, 17.9, 17.5. Anal. Calcd for $C_{19}H_{23}NOS$: C, 72.80; H, 7.39: Found: C, 72.57; H, 7.41.

Recrystallization from hexane/ethyl acetate gave an analytical sample of **12b** as white crystals: mp 139−140 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, 2H, J = 8.3 Hz), 7.37 (d, 2H, J = 8.1 Hz), 7.22 (dd, 1H, J = 1.2, 7.8 Hz), 7.15 (dt, 1H, J = 1.4, 7.9 Hz), 7.1 (dd, 1H, J = 1.3, 7.9 Hz), 6.92 (dt, 1H, J = 1.4, 7.8 Hz), 3.26 (d, 1H, J = 13.5 Hz), 3.23 (d, 1H, J = 13.5 Hz), 2.45−2.43 (m, 1H), 2.45 (s, 3H), 1.52 (s, 3H), 0.86 (d, 3H, J = 6.8 Hz), 0.63 (d, 3H, J = 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 143.9, 136.7, 129.9, 129.4, 128.8, 127.6, 125.4, 124.9, 120.9, 54.0, 41.8, 34.2, 25.6, 21.5, 17.6, 17.0. Anal. Calcd for $C_{19}H_{23}NOS$: C, 72.80; H, 7.39. Found: C, 72.54; H, 7.47.

(±)-(2*S,4*R**)-3,4-Dihydro-4-methyl-4-(1,1-dimethylethyl)-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (13a) and (±)-(2*S**,4*S**)-3,4-Dihydro-4-methyl-4-(1,1-dimethylethyl)-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (13b). Method B.** Chromatography solvent (MPLC): 9:1 hexanes/ethyl acetate. Yield: 57%. Recrystallization from hexane/ethyl acetate gave an analytical sample of **13a**: mp 136−137 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, 2H, J = 8.3 Hz), 7.29−7.27 (m, 3H), 7.20 (dt, 1H, J = 1.4, 8.0 Hz), 7.11 (dd, 1H, J = 1.2, 7.9 Hz), 6.90 (dt, 1H, J = 1.3, 7.8 Hz), 3.85 (d 1H, J = 14.8 Hz), 2.82 (d, 1H, J = 14.8 Hz), 2.39 (s, 3H), 1.39 (s, 3H), 1.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 143.9, 139.9, 129.7, 128.0, 127.7, 127.2, 123.6, 119.8, 56.6, 46.0, 37.4, 27.0, 26.0, 21.4. Anal. Calcd for $C_{20}H_{25}NOS$: C, 73.35; H, 7.69. Found: C, 73.46; H, 7.86.

Recrystallization from hexane/ethyl acetate gave an analytical sample of **13b**: mp 137−138 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, 2H, J = 8.3 Hz), 7.42−7.38 (m, 3H), 7.15 (dt, 1H, J = 1.4, 8.0 Hz), 7.06 (dd, 1H, J = 1.4, 7.8 Hz), 6.89 (dt, 1H, J = 1.4, 8.1 Hz), 3.65 (d, 1H, J = 13.7 Hz), 3.31 (d, 1H, J = 13.7 Hz), 2.46 (s, 3H), 1.63 (s, 3H), 0.92 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 144.2, 135.8, 130.0, 128.6, 128.4, 128.2, 127.9, 125.8, 120.4, 59.6, 45.1, 39.3, 26.5, 25.9, 21.6. Anal. Calcd for $C_{20}H_{25}NOS$: C, 73.35; H, 7.69. Found: C, 73.39; H, 7.69.

(±)-*N*-Phenyl-*S*-(3-chloro-2,2,3-trimethylbutyl)-*S*-(4-methylphenyl)sulfoximine (15) was formed as a side product during the preparation of **13**: chromatography solvent 10:1 hexane/ethyl acetate; yield: 6%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, 2H, J = 8.3 Hz), 7.27 (d, 2H, J = 8.2 Hz), 7.07 (dt, 2H, J = 1.8, 7.6 Hz), 6.97 (dt, 2H, J = 1.0, 8.4 Hz), 6.81 (t, 1H, J = 7.2 Hz), 3.68 (d, 1H, J = 14.4 Hz), 3.56 (d, 1H, J = 14.3 Hz), 2.37 (s, 3H), 1.56 (s, 3H), 1.54 (s, 6H), 1.31 (s 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 143.6, 137.7, 130.0, 128.8, 128.8, 123.3, 121.2, 78.4, 64.0, 43.7, 28.0, 27.8, 22.2, 21.5, 21.2.

(±)-(2*S,3*R**)-3,4-Dihydro-3,4,4-trimethyl-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (16a) and (±)-(2*S**,3*S**)-3,4-dihydro-3,4,4-trimethyl-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (16b). Method B.** Chromatography solvent (MPLC): 9:1 hexane/ethyl acetate. Combined yield: 53%. Recrystallization from hexane/ethyl acetate gave an analytical sample of the mixture of isomers: mp 124−125 °C; major isomer **16a** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, 2H, J = 8.3 Hz), 7.32 (d, 2H, J = 8.1 Hz), 7.24 (dd, 1H, J = 1.5, 7.7 Hz), 7.17 (dt, 1H, J = 1.5, 7.9 Hz), 7.09 (dd, 1H, J = 1.3, 7.9 Hz), 6.91−6.87 (m, 1H), 3.20 (q, 1H, J = 7.2 Hz), 2.42 (s, 3H), 1.63 (s, 3H), 1.41 (s, 3H), 0.81 (d, 1H, J = 7.2 Hz); minor isomer **16b** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, 2H, J = 8.3 Hz), 7.31 (d, 2H, J = 7.8 Hz), 7.27 (dd, 1H, J = 1.5, 7.9 Hz), 7.15 (dt, 1H, J = 1.6, 7.7 Hz), 7.04 (dd, 1H, J = 1.3, 7.9 Hz), 6.91−6.87 (m, 1H), 2.96 (q, 1H, J = 6.9 Hz), 2.41 (s, 3H), 1.44 (s, 6H), 1.35 (d, 3H, J = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 145.0, 143.4, 143.2, 135.3, 134.2, 131.2, 130.2, 129.8, 129.6, 129.6, 129.5, 129.5, 127.9, 125.2, 124.9, 123.9, 120.9, 120.6, 61.6, 59.4, 38.7, 38.4, 30.3, 27.2, 26.5, 24.0, 21.5, 12.9, 8.5. Anal. Calcd for $C_{18}H_{21}NOS$: C, 72.20; H, 7.07. Found: C, 72.40; H, 6.90.

(±)-(2*S,3*R**)-3,4-Dihydro-3-ethyl-4,4-dimethyl-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (17a) and (±)-(2*S**,3*S**)-3,4-Dihydro-3-ethyl-4,4-dimethyl-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (17b). Method B.** Chromatography solvent (MPLC): 10% ethyl acetate in hexanes. Combined yield: 53%. Recrystallization from hexane/ethyl acetate gave an analytical sample of a mixture of isomers: mp 34−36 °C; major isomer **17a** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, 2H, J = 1.6, 6.8 Hz), 7.28 (d, 1H, J = 7.9 Hz), 7.18 (dd, 2H, J = 1.5, 7.7 Hz), 7.13−7.08 (m, 2H), 6.86−6.84 (m, 1H), 2.91 (dd, 1H, J = 2.87, 6.57 Hz), 2.38 (s, 3H), 1.58 (s, 3H), 1.41 (s, 3H), 1.14−1.05 (m, 2H), 0.51 (t, 3H, J = 7.52 Hz); minor isomer: **17b** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, 2H, J = 6.8 Hz), 7.27 (d, 2H, J = 7.5 Hz), 7.22 (dd, 1H, J = 1.5, 7.9 Hz), 7.08−7.04 (m, 1H), 6.98 (dd, 1H, J = 1.1, 7.9 Hz), 6.84−6.82 (m, 1H), 2.74 (dd, 1H, J = 3.2, 5.7 Hz), 2.36 (s, 3H), 2.13−2.07 (m, 1H), 1.86−1.85 (m, 1H), 1.43 (s, 3H), 1.41 (s, 3H), 0.49 (t, 3H, J = 7.62 Hz); ^{13}C NMR (125 MHz, $CDCl_3$), δ 144.6, 144.5, 143.7, 143.0, 136.2 134.5, 131.5, 130.4, 130.3, 129.9, 129.6, 129.3, 127.9, 127.8, 125.3, 124.5, 123.8, 123.80, 120.9, 120.6, 69.2, 66.8, 39.6, 39.4, 30.3, 27.3, 25.9, 24.5, 21.6, 20.5, 17.3, 14.7, 13.2. Anal. Calcd for $C_{19}H_{23}NOS$: C, 72.84; H, 7.34. Found: C, 72.52; H, 7.16.

(±)-(2*S,3*S**,4*R**)-3,4-Dihydro-3,4-dimethyl-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (22a). Method A.** Chromatography solvent: 4:1 hexanes/ethyl acetate. Combined yield: 62%. Recrystallization from hexane/ethyl acetate gave an analytical sample of **22a**: mp 138−139 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, 2H, J = 8.3 Hz), 7.34 (d, 2H, J = 8.2 Hz), 7.19 (dt, 1H, J = 1.4, 8.0 Hz), 7.09−7.07 (m, 2H), 6.91 (dt, 1H, J = 1.2, 7.4 Hz), 3.25−3.19 (m, 1H), 3.09−3.03 (m, 1H), 2.44 (s, 3H), 1.54 (d, 3H, J = 7.3 Hz), 0.97 (d, 3H, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 143.4, 133.3, 130.3, 129.6, 128.0, 127.5, 125.8, 123.7, 120.7, 57.2, 38.5, 21.5, 19.4, 15.8. Anal. Calcd for $C_{17}H_{19}NOS$: C, 71.53; H, 6.71. Found: C, 71.60; H, 6.80.

(±)-(2*S,3*S**,4*S**)-3,4-Dihydro-3,4-dimethyl-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (23a) and (±)-(2*S**,3*R**,4*R**)-3,4-Dihydro-3,4-dimethyl-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine 2-Oxide (23b). Method A.** Chromatography solvent: 6:1 hexanes/ethyl acetate. Combined yield: 78%. Recrystallization from hexane/ethyl acetate gave an analytical sample of **23a**: mp 162−163 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, 2H, J = 1.7, 8.3 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.06 (dd, 1H, J = 1.2, 8.2 Hz), 6.91 (dt, 1H, J = 1.3, 7.5 Hz), 3.95−3.90 (m, 1H), 3.18−3.13 (m, 1H), 2.45 (s, 3H), 1.51 (d, 3H, J = 7.1 Hz), 0.66 (d, 3H, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 144.4, 131.9, 130.4, 129.7, 128.0, 125.9, 124.5, 122.9, 120.5, 54.9, 31.2, 21.6, 15.6, 9.1. Anal. Calcd for $C_{17}H_{19}NOS$: C, 71.53; H, 6.71. Found: C, 71.57; H, 6.71.

Further purification of the mixture on a Chromatotron (1 mm plate, 2% ethyl acetate in hexane) gave an oil, **23b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, 2H, J = 8.3 Hz), 7.28 (d, 2H, J = 8.0 Hz), 7.12 (dt, 1H, J = 1.5, 7.5 Hz), 7.06 (d, 1H, J = 8.0 Hz), 6.98−6.96 (m, 1H), 6.84 (dt, 1H, J = 1.2, 7.4 Hz), 3.22−3.16 (m, 2H), 2.38 (s, 3H), 1.39 (d, 3H, J = 7.2 Hz), 1.31 (d, 3H, J = 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 135.7, 130.2, 129.7, 129.7, 129.5, 129.1, 127.9, 127.6, 123.0, 120.3,

55.1, 36.8, 21.4, 15.9, 9.6. Anal. Calcd for $C_{17}H_{19}NOS$: C, 71.53; H, 6.71. Found: C, 71.61; H, 6.83.

(±)-*N*-Phenyl-*S*-)4-methylphenyl)-*S*-(3-chloro-2,3-dimethylbutyl)sulfoximine (14) was obtained in the preparation of **12**. Chromatography solvent: gradient MPLC using hexane/ethyl acetate as eluent. Yield: 11% as a mixture in a ratio of 1.2:1. Major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, 2H, J = 8.2 Hz), 7.28 (d, 2H, J = 8.0 Hz), 7.09−7.06 (m, 2H), 6.98−6.96 (m, 2H), 6.83−6.80 (m, 1H), 3.75 (dd, 1H, J = 0.61, 14.2 Hz), 3.04 (dd, 1H, J = 8.8, 14.3 Hz), 2.57−2.52 (m, 1H), 2.38 (s, 3H), 1.59 (s, 3H), 1.50 (s, 3H), 1.13 (d. 3H, J = 6.78 Hz); ^{13}C (125 MHz, $CDCl_3$) δ 145.2, 144.0, 135.8, 130.2, 129.2, 128.8, 123.2, 121.2, 73.3, 61.6, 40.7, 31.4, 29.7, 21.5, 16.1. Minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, 2H, J = 8.3 Hz), 7.30 (d, 2H, J = 8.0 Hz), 7.11−7.08 (m, 2H), 6.99 (dd, 2H, J = 1.1, 8.5 Hz), 6.85−6.82 (m, 1H), 3.67 (d, 1H, J = 14.4 Hz), 3.26 (dd, 1H, J = 8.9, 14.5 Hz), 2.39 (s, 3H), 2.28−2.23 (m, 1H), 1.44 (s, 3H), 1.43 (s, 3H), 1.31 (d, 3H, J = 6.8 Hz). Anal. Calcd for $C_{19}H_{24}ClNOS$: C, 65.25; H, 6.86. Found: C, 65.47; H, 6.84.

(±)-*N*-Phenyl-*S*-(4-methylphenyl)-*S*-[1-(methylethyl)-2-methyl-2-chloropropyl]sulfoximine (20). Method B. Chromatography solvent: 8:1 hexane/ethyl acetate. Yield: 34% as a mixture of isomers in a ratio of 2.4:1. Major isomer: mp 79−80 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, 2H, J = 8.4 Hz), 7.36 (d, 2H, J = 8.1 Hz), 7.25 (dd, 2H, J = 7.7, 1.5 Hz), 7.18 (dt, 1H, J = 7.8, 1.5 Hz), 7.09 (dd, 1H, J = 7.9, 1.4 Hz), 6.9 (dt, 1H, J = 7.5, 1.4 Hz), 3.26 (d, 1H, J = 1.7 Hz), 2.46 (s, 3H), 2.04−1.99 (m, 1H), 1.73 (s, 3H), 1.63 (s, 3H), 0.90 (d, 3H, J = 7.4 Hz), 0.44 (d, 3H, J = 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 143.7, 130.3, 129.7, 127.6, 123.8, 123.2, 121.0, 72.4, 39.6, 33.6, 29.1, 27.6, 21.6, 18.1. Anal. Calcd for $C_{20}H_{26}ClNOS$: C, 66.00; H, 7.20. Found: C, 66.37; H, 7.31.

***N*-Phenyl-*S*-(4-methylphenyl)-*S*-(2-chloro-2-methyl-1,1-dimethylethyl)propylsulfoximine (21). Method B.** Chromatography solvent: 7:1 hexane/ethyl acetate. Yield: 48%. **21**: mp 118−120 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, 2H, J = 8.3 Hz), 7.29−7.24 (m, 2H), 7.20 (d, 2H, J = 8.0 Hz), 7.16 (dt, 1H, J = 7.6, 1.4 Hz), 6.93−6.89 (m, 2H), 3.28 (s, 1H), 2.38 (s, 3H), 1.80 (s, 3H), 1.78 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 143.8, 137.0, 129.5, 128.0, 126.1, 122.4, 120.2, 76.1, 41.2, 37.2, 32.0, 28.9, 24.2, 21.4. Anal. Calcd for $C_{21}H_{28}ClNOS$: C, 66.73; H, 7.47. Found: C, 67.0; H, 7.70.

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Supporting Information Available: ^{1}H and ^{13}C NMR for **5**−**17** and **20**−**23**, selected IR and MS data, and X-ray crystallographic data for **9a**, **10b**, **15**, and **22** (94 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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