

Dichloroketene-Induced Cyclizations of Vinyl Sulfilimines: Application of the Method in the Synthesis of (\pm) -Desoxyeseroline

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The reactions of several aryl-, furanyl-, and vinyl-substituted sulfilimines with dichloroketene proceeded at 25 °C to yield thioalkyl-substituted γ-lactams. The overall process involves nucleophilic addition of the nitrogen atom of the sulfilimine onto the highly electrophilic dichloroketene to first generate a zwitterionic intermediate. A subsequent [3,3]-sigmatropic rearrangement is followed by intramolecular trapping of the Pummerer cation by the amido anion to furnish the observed γ -lactam product. Incorporation of donor groups on the aromatic ring of the sulfonyl functionality had little effect when aryl-substituted sulfilimines were used but exhibited a major effect on the efficiency of the reaction with furanyl-substituted systems. The placement of an electron donor group (i.e., OMe) on the sulfonyl aryl group enhances the nucleophilicity of the amido anion contained within the sulfonium ion intermediate and facilitates the rate of the 3,3-sigmatropic rearrangement. Styryl-substituted sulfilimines cyclize in a stereospecific manner and produce a 3:2-mixture of γ -lactams and the isomeric imino-lactone system. The heavily functionalized γ -lactams are easily converted to a variety of nitrogen containing substrates. The vinyl sulfilimine cyclization method was applied to the total synthesis of the Calabar alkaloid (\pm) -desoxyeseroline.

Introduction

Sulfur-carbon ylides represent important reagents in organic synthesis, particularly in reactions involving intramolecular rearrangement and intermolecular attack on substrates bearing an electrophilic carbon.¹ The reaction of a sulfonium ylide with carbonyl compounds to give epoxides has proven to be an important synthetic method.² In addition, sigmatropic rearrangements of sulfonium ylides constitute a powerful synthetic tool for regio-, stereo-, and enantioselective C-C bond formation.³ Sulfoxides have also been extensively studied because of their varied reactivity as a functional group for transformations into a variety of sulfur compounds.⁴ These

transformations are useful for the synthesis of drugs and sulfur-substituted natural products.^{5–7} The Pummerer reaction of sulfoxides has established itself as an extremely useful method for the preparation of α -substituted sulfides.8 The reaction has been widely studied and has received considerable attention as a valuable synthetic process. Pummerer thionium ions are generally formed by treating a sulfoxide bearing an α -hydrogen with acetic anhydride.9 Currently, Pummerer-based transformations are finding widespread application in carbo and heterocyclic synthesis by reaction of the initially generated thionium ion with internally disposed nucleophiles.¹⁰

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The additive Pummerer reaction^{11–18} represents one of the more interesting variants of the Pummerer process and occurs when a nucleophile displaces the acyloxy leaving group of a vinyl sulfonium ion through an $S_N 2'$ mechanism producing a saturated β -functionalized thionium species (3) (Scheme 1). Trapping with a second nucleophilic agent affords a product (4) formally derived by the sequential attack of two nucleophiles on an α . β dication. This sequence of reactions has been utilized by a number of research groups for the formation of carbonheteroatom and carbon-carbon bonds.¹⁷⁻²⁰

The Marino group developed a novel variation of the additive Pummerer reaction that produces γ -butyrolactones by the reaction of dichloroketene with vinyl sulfoxides.²¹ In general, the oxygen of a vinyl sulfoxide such as 5 first attacks dichloroketene to produce in situ the salt 6 (Scheme 2). The resulting enolate anion present in 6 then undergoes a 3,3-sigmatropic rearrangement to provide thionium ion intermediate 7. Finally, the resulting carboxylate anion adds to the neighboring thionium ion to furnish butyrolactone 8, which retains the geometry of the starting olefin.

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FIGURE 1. A comparison of some sulfur ylides.

SCHEME 2. Marino Vinyl Sulfoxide Protocol



As part of our continuing program designed to explore the use of thionium ions for heterocyclic synthesis,²² we became interested in developing some comparable additive Pummerer chemistry using sulfur-nitrogen ylides (sulfilimines). Consideration of the relative electronegativities of the atoms involved in this particular sulfur ylide leads to the prediction that the chemical behavior of sulfilimines should be intermediate between those of sulfonium ylides and sulfoxides (Figure 1). The properties of sulfilimines²³ are known to be similar to those exhibited by sulfoximines,²⁴ but the sulfilimines are more reactive, just as sulfonium ylides are more reactive than the corresponding oxosulfonium ylides.¹⁻³ To demonstrate that vinyl sulfilimines can be induced to undergo the additive Pummerer reaction,^{25,26} we decided to examine their reactions with dichloroketene with the intention of using the resulting γ -lactams for alkaloid synthesis.

Results and Discussion

Because oxindoles represent an important substructure associated with many biologically active natural products,²⁷ we thought that it might be possible to synthesize this heterocyclic ring system by treating an aryl sulfilimine such as 12 with dichloroketene as outlined in Scheme 3, Path B. Although various methods are avail-

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SCHEME 3. **Methods To Synthesize Oxindoles** Path A -- "Gassman Procedure"

(1) Cl [2,3] R1SCH2CO2Et (2) ArNHR R_2 9 (3) Et₃N 11 10

Path B-- "Modified Marino Protocol



able for the preparation of oxindoles,²⁸⁻³⁴ their synthesis is often limited by the availability of starting materials. The method reported by Gassman and co-workers,³⁵ which proceeds from a substituted aniline and ethyl (methylthio)acetate via chlorination of the sulfide and subsequent treatment with an arylamine and base, is one of the most generally useful methods in terms of scope, starting material availability, brevity, and reproducibility (Scheme 3, Path A). We reasoned that by simply switching the sulfur and nitrogen positions, it might be possible to use vinyl sulfilimines to prepare oxindoles according to the sequence outlined in Scheme 3, Path B. Thus, we expected that the reaction of arylsulfilimine of type 12 with dichloroketene would first afford zwitterion 13 where the nitrogen and sulfur atoms were interchanged relative to the analogous Gassman intermediate 10. A subsequent [3,3]-sigmatropic rearrangement would then deliver the Pummerer-thionium ion intermediate 14. Cyclization to **15** and loss of the mercaptan should yield the desired oxindole 16. We first examined the reaction of phenyl sulfilimine **17** with dichloroketene³⁶ in THF at 25 °C, which afforded oxindole 21 together with varying

SCHEME 4. Reaction of Aryl Sulfiliminines with Dichloroketene



amounts of methyl phenyl sulfide and amide 22 (Scheme 4).³⁷ Amide **22** is presumably derived by C–N cleavage of the N-sulfonyl lactam 15 in competition with mercaptan elimination, which leads to oxindole **21** (Scheme 3, Path B). Similar results were obtained using arylsubstituted sulfilimines 18-20 with the oxindole (i.e., 23-25) being formed in low yield (ca. 15-20%). Changing the substituent group on both aromatic rings to the more electron-donating methoxy group on the aryl sulfilimine (i.e., X = OMe(19) and $Ar = p - OMeC_6H_4(20)$) had only a minimal effect on the yield of oxindole formation (13-19%). Apparently, the key rate-determining step of the process (i.e., $13 \rightarrow 14$) possesses a relatively high activation energy as a consequence of the disruption of aromaticity. To minimize this difficulty, we opted to study the reaction of the more reactive naphthyl-substituted sulfilimine 26 with dichloroketene. In contrast to the results obtained with sulfilimine 17, the cyclization reaction of 26 proceeded in 56% yield and furnished 27 as the only detectable product that could be isolated from the crude reaction mixture.

Next, we turned our attention to the related reaction of several benzofuranyl-, indolyl-, and 2-furanyl-substituted sulfilimines. The results we obtained showed that these cyclizations also proceeded at rt in THF and furnished novel γ -lactams in good yield. Thus, the reaction of benzofuranyl (28)- and indolyl-substituted (29) sulfilimines with dichloroketene furnished the cyclized lactams 30 and 31 in 52% and 78% yield, respectively (Scheme 5). When the 2-furanyl-substituted sulfilimines 32 and 33 were used as the starting substrates, dihydrofuranyl γ -lactams 34 and 35 were formed in 58% and 40% yield, respectively. Interestingly, all of the γ -lactams that were isolated were unexpectedly robust and did not undergo loss of mercaptan even under somewhat forcing conditions (i.e., heat, acid).

In contrast to the results noted with aryl sulfilimines 17–20, where the incorporation of donor groups on the aromatic ring of the sulfonyl functionality had little effect, the situation was quite different with furanyl sulfilimines **36–39**. When sulfilimine **36** $(R_2 = p-NO_2C_6H_4)$ was treated with dichloroketene, no discernible quantities of

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SCHEME 6. Reaction of Furanyl Sulfilimines with Dichloroketene



lactam 40 were detected in the crude reaction mixture. On the other hand, the reaction of sulfilimine **39** ($R_2 =$ p-OMeC₆H₄), which contains an electron-donor group on the aromatic ring, with dichloroketene furnished γ -lactam 43 in 72% yield (Scheme 6). The less activated sulfilimines 37 $(R_2 = C_6H_5)$ and 38 $(R_2 = p-MeC_6H_4)$ afforded the expected γ -lactams but in 20% and 51% yield, respectively. Clearly, the overall efficiency of the furanyl-substituted sulfilimine cyclization is highly dependent on the nature of the substituent group attached to the sulfonyl aromatic ring. An electron donor group on R_2 (i.e., **39**) enhances the nucleophilicity of the amido anion contained within the sulfonium intermediate (13), thereby facilitating the rate of the 3,3-sigmatropic rearrangement, which we assume corresponds to the ratedetermining step in the overall process.

To further explore the scope and generality of the method, we carried out a series of reactions using a variety of vinyl-substituted sulfilimines as outlined in Schemes 7 and 9. The reaction of dichloroketene with acyclic sulfilimines 44-46 proceeded smoothly to give the expected γ -lactams 47–49 in 60–68% yield as the only isolable products. Most interestingly, when the styrylsubstituted sulfilimines 50-52 were treated with dichloroketene under identical experimental conditions, a 3:2 mixture of two isomeric compounds was obtained in ca. 75% yield. Separation of the mixture of products by silica gel chromatography afforded pure samples of both the expected N-tosyl γ -lactams 53-55 together with the isomeric imino-lactones 56-58. The carbonyl stretching frequency of the N-tosyl γ -lactam system appeared at 1765 cm^{-1} , whereas the lactone *N*-tosylimine showed an IR absorption at 1662 cm⁻¹.³⁸ Similar results were reported by Marino and Zou.²⁶ Some significant spectral differences between the two isomeric products were also noted in their ¹H and ¹³C NMR properties. In particular, the vicinal trans coupling constant for N-tosyl lactams **54** and **55** exhibits a value of J = 8.4 Hz, whereas the related coupling for 57 and 58 has a value of J = 10.8Hz (600 MHz in CDCl₃). The formation of a mixture of products is really not so surprising because both compounds are generated by either N- or O-alkylation³⁹ of the sulfonium ion 60 by the adjacent N-tosyl stabilized amido anion formed by the 3,3-sigmatropic rearrangement of 59 (Scheme 8). The complete stereospecificity of the cyclization process is undoubtedly related to the highly ordered transition state of the 3,3-sigmatropic rearrangement. The resulting Pummerer intermediate 60 is rapidly trapped by the amido anion before C-Cbond rotation can occur. What is so surprising, however, is that the formation of a mixture of isomeric γ -lactams and imino-lactones only occurs with these styryl-substituted sulfilimines. In no other case were we able to detect any of the less stable imino-lactone structure in the crude reaction mixture.⁴⁰ For example, the reaction of cyclic sulfilimines of type 61-63 with dichloroketene only afforded the *N*-tosyl γ -lactams **64**–**66** (Scheme 9).

As part of an effort to further broaden the utility of this cyclization protocol, we decided to carry out some simple chemical manipulations of these highly functionalized γ -lactams to probe their usefulness for the synthesis of various nitrogen containing substrates. It was anticipated that lactam 47, derived from the reaction of dichloroketene with S-ethyl-S-ethenyl-N-(toluene-4-sulfonyl)sulfilimine, could be used to prepare a variety of substituted pyrrolidine derivatives. Indeed, the reaction of 47 with zinc in the presence HOAc and TMEDA cleanly led to the dechlorinated lactam 67 in 88% yield. Oxidation of 67 with mCPBA followed by treatment with tertbutyldimethylsilyl trifluoromethane-sulfonate (Scheme 10) provided pyrrole 68 in 86% yield. This activated pyrrole corresponds to an attractive intermediate for the eventual synthesis of several pyrrolidine alkaloids (vide infra). N-(p-Toluenesulfonyl)pyrrolidine 69 was obtained in 83% yield when lactam 67 was reduced with BH₃·THF. We also subjected 47 to reduction with BH₃·THF and found that carbinolamide **70** was cleanly formed in 84% yield. Reduction of 47 with NaBH₄ followed by further reaction with zinc/HOAc furnished the 1,4-amino alcohol 71 in 81% yield.

The reactivity of γ -lactam **34**, which contains a fused dihydrofuran ring as part of its skeleton, was also investigated. Smooth dechlorination occurred when **34** was treated with zinc affording the novel heterocycle **72** in 84% yield (Scheme 11). The loss of the thioethyl group proved to be more difficult than originally anticipated. All of our attempts to induce the elimination of ethyl mercaptan from **34** with various thiophilic reagents failed. When treated with trifluoroacetic acid at 100 °C, **34** was smoothly converted into furan **73** in 71% yield by preferential elimination of the *N*-(*p*-toluenesulfonyl) group. However, by first oxidizing the thio group with mCPBA and then treating the resulting sulfone with

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SCHEME 7. **Reaction of Styryl Sulfilimines with Dichloroketene**



Mechanism of Sulfiliminine Reaction SCHEME 8.



Reaction of Cycloalkenyl Sulfilimines SCHEME 9. with Dichloroketene



SCHEME 10. Chemical Reductions of Compound 47



trimethylaluminum, it was possible to introduce a methyl substituent on the carbon atom adjacent to the two heteroatoms (i.e., formation of 74).

In an effort to more fully explore and exploit the sulfilimine/dichloroketene cyclization chemistry, we decided to pursue a synthesis of the Calabar alkaloid (\pm) - SCHEME 11. Chemical Transformations of **Compound 34**



desoxyeseroline (79) using our methodology to create the hexahydro[2,3-b]indole framework of the target. The pyrrolidinoindoline ring system containing a carbon substituent at the C-3a site is a widely distributed structural framework that has been obtained from a diverse array of natural sources.⁴¹ Physostigmine was isolated initially from the seeds of the African Calabar bean *Physostigma venenosum*⁴² and is known to be a potent reversible inhibitor of acetyl and butyrylcholinesterase and is employed to treat glaucoma.43 More recently, analogues of physostigmine (75) (Figure 2) have shown promise in the treatment of Alzheimer's disease.⁴⁴ The unique structural array and the interesting biological activities displayed by this class of compounds have made them attractive synthetic targets. As a result, many innovative methodologies toward the core hexahydropyrrolo[2,3-b]indole skeleton have been developed.⁴⁵ During the course of our work with sulfilimines, we were intrigued by the possibility of utilizing these ketene cyclizations for the synthesis of the Calabar alkaloids.

As was mentioned earlier, pyrrolo[2,3-*b*]indole **31** was easily prepared in 78% yield by treating the readily available indole 29 with dichloroketene. Subjecting this compound to zinc with acetic acid and TMDEA in ethanol at reflux followed by treatment with formic acid furnished

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FIGURE 2. Representatiave hexahydropyrrolo[2,3-*b*]indole alkaloids with a quaternary center at C-3*a*.

SCHEME 12. Synthesis of (\pm) -Desoxyeseroline



82 in 72% overall yield (Scheme 12). Removal of the *N*-tosyl group by reduction with sodium naphthalinide afforded **83** in 81% yield. Further reaction of **83** with sodium hydride/methyl iodide gave **84** in 87% yield. Reduction of **84** with BH₃·THF furnished desoxyeseroline (**79**)⁴⁶ in 80% yield, which had previously been converted to physostigmine by Fuji and co-workers.⁴⁷

In conclusion, we have disclosed a new and efficient method for the synthesis of highly functionalized γ -lactams. The overall process involves reaction of a vinylsubstituted sulfilimine with the highly electrophilic dichloroketene to first generate a zwitterionic intermediate. A subsequent [3,3]-sigmatropic rearrangement is followed by intramolecular trapping of the Pummerer cation by the amido anion to furnish the observed γ -lactam products. The heavily functionalized lactams are easily converted to a variety of nitrogen containing substrates. The vinyl sulfilimine cyclization method has been applied to the total synthesis of (\pm) -desoxyeseroline. This approach should also serve as a general method for access to other Calabar alkaloids and for preparing libraries of structurally diverse pyrrolo[2,3-b]indoles that may exhibit interesting biological activities.

Experimental Section

3,3-Dichloro-1-(toluene-4-sulfonyl)-1,3-dihydroindol-2one (21). To a mixture of 0.3 g (1.1 mmol) of sulfilimine 17^{48} and 0.65 g of Zn–Cu in 20 mL of THF was slowly added 0.44 mL (4.0 mmol) of trichloroacetyl chloride at 0 °C. The reaction mixture was stirred at rt for 20 min, filtered through a Celite column into an aqueous NaHCO₃ solution, and washed with EtOAc. The combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography to give 0.051 g (13%) of **21** as a clear oil: IR (neat) 1773, 1464, 1377, and 1180 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.44 (s, 3H), 7.30 (td, 1H, J = 8.0 and 0.8 Hz), 7.66 (d, 2H, J = 8.0 Hz), 7.48 (td, 1H, J = 8.0 and 0.8 Hz), 7.63 (dd, 1H, J = 8.0 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 22.0, 73.9, 114.5, 125.5, 126.5, 128.3, 128.5, 130.3, 132.8, 134.2, 136.6, 146.8, and 166.5.

A second fraction isolated from the chromatographic column contained 0.089 g (22%) of a yellow oil whose structure was assigned as *N*-[2,2-dichloro-2-(2-methyl-sulfanylphenyl)acetyl]-4-toluenesulfonamide (**22**): IR (neat) 1667, 1431, 1190, 1086, and 660 cm⁻¹; ¹H NMR (DMSO-*d*₆, 600 MHz) δ 2.36 (s, 3H), 2.40 (s, 3H), 7.22 (t, 1H, *J* = 7.5 Hz), 7.40 (d, 2H, *J* = 7.8 Hz), 7.44 (d, 1H, *J* = 7.5 Hz), 7.49 (d, 1H, *J* = 7.5 Hz), 7.60 (t, 1H, *J* = 7.5 Hz), and 7.80 (d, 2H *J* = 7.8 Hz); ¹³C NMR (DMSO-*d*₆, 150 MHz) δ 15.1, 21.1, 96.6, 123.9, 125.9, 127.3, 128.9, 129.2, 133.1, 133.9, 141.7, 143.5, and 168.7.

In addition to compounds **21** and **22**, 0.021 g (17%) of methyl phenyl sulfide was obtained as a colorless oil: ¹H NMR (CDCl₃, 300 MHz) δ 2.40 (s, 3H), 7.05 (m, 1H), 7.20–7.33 (m, 4H).

3,3-Dichloro-5-methyl-1-(toluene-4-sulfonyl)-1,3-dihydroindol-2-one (23). To a mixture of 0.25 g (0.81 mmol) of sulfilimine 1849 and 1.0 g of Zn-Cu in 4.0 mL of THF was slowly added 0.45 mL (4.1 mmol) of trichloroacetyl chloride in 5.0 mL of THF at 0 °C. The reaction mixture was stirred at rt for 20 min, filtered through Celite into a saturated aqueous NaHCO₃ solution, and washed with EtOAc. After the organic layer was separated, the aqueous layer was washed twice with EtOAc. The combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.034 g (13%) of **23** as a white solid: mp 105–107 °C; IR (neat) 1777, 1484, 1192, and 1180 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.37 (s, 3H), 2.42 (s, 3H), 7.25 (dd, 1H, J=8.4and 0.8 Hz), 7.33 (d, 2H, J = 8.4 Hz), 7.42 (d, 1H, J = 0.8 Hz), 7.77 (d, 1H, J = 8.4 Hz), and 7.95 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃, 100 MHz) & 21.2, 22.1, 74.2, 114.3, 125.8, 128.2, 128.3, 130.3, 133.4, 134.2, 134.3, 136.7, 146.7, and 166.7. Anal. Calcd for C₁₆H₁₃Cl₂NO₃S: C, 51.90; H, 3.54; N, 3.78. Found: C, 52.15; H, 3.53; N, 3.70.

3,3-Dichloro-5-methoxy-1-(toluene-4-sulfonyl)-1,3-dihydroindol-2-one (24). To a solution containing 1.0 mL (7.1 mmol) of 1-methoxy-4-methylsulfanyl-benzene in 20 mL of EtOH was added 2.0 g (7.1 mmol) of chloramine-T trihydrate. The mixture was stirred at rt for 1 h and concentrated under reduced pressure. The residue was purified by silica gel chromatography to give 1.7 g (74%) of sulfilimine **19** as a white solid: IR (neat) 1634, 1498, 1175, and 1139 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.30 (s, 3H), 2.77 (s, 3H), 3.78 (s, 3H), 6.91 (d, 2H, J = 8.8 Hz), 7.10 (d, 2H, J = 8.0 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 21.5, 39.2, 55.8, 115.5, 126.3, 126.5, 128.1, 129.3, 141.4, 141.7, and 163.1.

To a mixture of 0.2 g (0.6 mmol) of sulfilimine **19** and 0.79 g of Zn-Cu in 30 mL of THF was slowly added 0.35 mL (3.1 mmol) of trichloroacetyl chloride at 0 °C. The reaction mixture was stirred at rt for 20 min, filtered through Celite into a saturated aqueous NaHCO₃ solution, and washed with EtOAc. After the organic layer was separated, the aqueous layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.035 g (15%) of **24** as a clear oil: IR (neat) 1775, 1487, 1191, and 671 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.43 (s, 3H), 2.84 (s, 3H), 6.99 (dd, 1H, J = 9.2 and 2.8 Hz),

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7.13 (d, 1H, J = 2.8 Hz), 7.34 (d, 2H, J = 8.4 Hz), 7.81 (d, 1H, J = 9.2 Hz), and 7.95 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 22.0, 56.1, 74.2, 110.4, 115.8, 118.7, 128.2, 129.4, 129.6, 130.3, 134.3, 146.7, 158.3, and 166.7.

3,3-Dichloro-1-(4-methoxybenznesulfonyl)-1,3-dihydroindol-2-one (25). To the mixture of 0.1 g (0.3 mmol) of sulfilimine 20^{50} and 0.21 g of Zn-Cu in 16 mL of THF was slowly added 0.18 mL (1.6 mmol) of trichloroacetyl chloride at 0 °C. The reaction mixture was stirred at rt for 35 min, filtered through Celite into a saturated aqueous NaHCO₃ solution, and washed with EtOAc. The aqueous layer was washed twice with EtOAc, and the combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.02 g (19%) of 25 as a clear oil: IR (KBr) 1747, 1592, 1371, and 1164 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 3.88 (s, 3H), 7.01 (d, 2H, J=9.2 Hz), 7.28 (t, 1H, J=7.6 Hz), 7.48 (td, J = 7.6 and 1.2 Hz, 1H), 7.64 (dd, 1H, J =7.6 and 1.2 Hz), 7.92 (d, 1H, J = 7.6 Hz), and 8.04 (d, 2H, J =9.2 Hz); $^{13}{\rm C}$ NMR (CDCl_3, 100 MHz) δ 55.8, 114.3, 114.6, 125.3, 126.2, 128.2, 130.6, 132.6, 136.5, 164.9, and 166.4.

3,3-Dichloro-9b-ethylthio-1-(toluene-4-sulfonyl)-1,3,3a,9b-tetrahydrobenzo-[g]indol-2-one (27). To a mixture containing 0.1 g (0.3 mmol) of sulfilimine 26 and 0.15 g of Zn-Cu in 14 mL of THF at 0 °C was slowly added 0.2 mL (1.8 mmol) of trichloroacetyl chloride. After being stirred at rt for 45 min, the reaction mixture was filtered and EtOAc was added. The organic layer was washed with a saturated aqueous NaHCO₃ solution, brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.074 g (56%) of 27 as a colorless solid; mp 172-174 °C; IR (neat) 2927, 1754, 1372, 1223, 1176, 1049, 980, and 663 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.91 (t, 3H, J = 7.5 Hz), 1.94–2.05 (m, 1H), 2.48 (s, 3H), 2.75-2.86 (m, 1H), 3.28 (dd, 1H, J = 6.0 and 1.2 Hz), 5.99 (dd, 1H, J = 10.0 and 6.0 Hz), 6.88 (d, 1H, J = 10.0 Hz),7.17 (d, 1H, J = 7.8 Hz), 7.30–7.40 (m, 4H), 7.98 (d, 1H, J =7.8 Hz), and 8.24 (d, 2H, J = 8.1 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 13.1, 21.8, 27.2, 59.0, 78.4, 79.5, 117.7, 127.7, 127.9, 129.0, 129.2, 129.5, 129.9, 130.7, 131.0, 133.0, 134.8, 145.8, and 164.7. Anal. Calcd for $C_{21}H_{19}Cl_2NO_3S_2$: C, 53.85; H, 4.09; N, 2.99. Found: C, 53.73; H, 4.07; N, 2.87.

3,3-Dichloro-8a-ethylthio-1-(toluene-4-sulfonyl)-1,3,3a,8a-tetrahydro-2H-benzo-furo[2,3-b]pyrrol-2-one (30). To a mixture of 0.3 g (0.9 mmol) of sulfilimine 28 and 0.28 g of Zn-Cu in 45 mL of THF at rt was slowly added 0.4 mL (3.5 mmol) of trichloroacetyl chloride. After being stirred at rt for 45 min, the reaction mixture was filtered and EtOAc was added. The organic layer was washed with a saturated aqueous NaHCO3 solution, brine, dried over Na2SO4, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 0.2 g (52%) of **30** as a colorless solid: mp 126-128 °C; IR (KBr) 2968, 1757, 1595, 1478, 1379, 1258, 1115, 983, and 749 cm⁻¹; ¹H NMR $(\text{CDCl}_3, 300 \text{ MHz}) \delta 1.30 (t, 3\text{H}, J = 7.8 \text{ Hz}), 2.42 (s, 3\text{H}), 2.75 -$ 2.94 (m, 2H), 4.80 (s, 1H), 7.00 (d, 1H, J = 7.5 Hz), 7.04 (t, 1H, J = 7.5 Hz), 7.31 (d, 2H, J = 7.8 Hz), 7.33 (t, 1H, J = 7.5Hz), 7.48 (d, 1H, J = 7.5 Hz), and 8.06 (d, 2H, J = 7.8 Hz); ¹³C NMR (CDCl₃, 150 MHz) & 13.6, 21.8, 25.8, 65.6, 80.2, 106.5, 110.8, 121.2, 122.8, 128.0, 129.4, 129.5, 131.4, 133.9, 146.2, 157.5, and 163.2. Anal. Calcd for C₁₉H₁₇Cl₂NO₄S₂: C, 49.78; H, 3.74; N, 3.06. Found: C, 49.49; H, 3.78; N, 3.03.

tert-Butyl 3,3-Dichloro-8*a*-ethylthio-3*a*-methyl-2-oxo-1-(toluene-4-sulfonyl)-2,3,3*a*,8*a*-tetrahydro-1*H*-pyrrolo-[2,3-*b*]indole-8-carboxylate (31). To a mixture of 1.8 g (3.9 mmol) of sulfilimine 29 and 2.6 g of Zn-Cu in 200 mL of THF was slowly added 1.7 mL (16 mmol) of trichloroacetyl chloride at rt. The reaction mixture was stirred at 25 °C for 1 h, filtered through Celite into a saturated aqueous NaHCO₃ solution, and washed with EtOAc. The aqueous layer was washed with EtOAc, and the combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 1.5 g (78%) of **31** as a white solid: mp 180–182 °C; IR (neat) 1760, 1722, 1485, 1349, 1179, and 1081 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.19 (t, 3H, J = 7.6 Hz), 1.53 (s, 3H), 1.61 (s, 9H), 2.42 (s, 3H), 2.85 (dq, 1H, J = 11.2 and 7.6 Hz), 3.49 (dq, 1H, J = 11.2 and 7.6 Hz), 7.13 (td, 1H, J = 7.6 and 0.8 Hz), 7.25–7.29 (m, 3H), 7.33 (td, 1H, J = 7.6 and 0.8 Hz), 7.52 (d, 1H, J = 7.6 Hz), and 8.15 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 13.1, 17.7, 21.9, 27.4, 28.6, 65.0, 83.8, 86.1, 96.6, 117.8, 124.4, 124.5, 128.1, 129.4, 130.1, 130.2, 135.8, 142.4, 145.6, 150.2, and 165.1. Anal. Calcd for C₂₅H₂₈Cl₂-N₂O₅S₂: C, 52.54; H, 4.94; N, 4.90. Found: C, 52.48; H, 4.81; N, 5.00.

4,4-Dichloro-6a-ethylthio-6-(toluene-4-sulfonyl)-3a,4,6,6a-tetrahydrofuro[2,3-b]-pyrrol-5-one (34). To a mixture of 0.25 g (0.8 mmol) of sulfilimine 32 and 1.1 g of Zn-Cu in 15 mL of THF was slowly added 0.5 mL (4.2 mmol) of trichloroacetyl chloride at 0 °C. The reaction mixture was stirred at rt for 20 min, filtered through Celite into a saturated aqueous NaHCO₃ solution, and washed with EtOAc. The aqueous layer was washed with EtOAc, and the combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.2 g (58%) of **34** as a white solid; mp 133-134 °C; IR (neat) 3114, 1762, 1618, 1377, and 907 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.34 (t, 3H, J = 7.2 Hz), 2.42 (s, 3H), 2.28 (dq, 1H, J = 11.6 and 7.2 Hz), 2.90 (dq, 1H, J = 11.6 and 7.2 Hz), 4.43 (t, 1H, J = 2.4 Hz), 5.17 (dd, 1H, J = 2.8 and 2.4 Hz), 6.40 (dd, 1H, J = 2.8 and 2.4 Hz), 7.33 (d, 2H, J = 8.0 Hz), and 8.01 (d, 2H, J = 8.0 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 13.9, 22.0, 25.9, 66.4, 80.3, 102.8, 106.1, 129.5, 129.7, 134.2, 146.3, 146.5, and 163.5. Anal. Calcd for C15H15Cl2NO4S2: C, 44.12; H, 3.70; N, 3.43. Found: C, 44.07; H, 3.61; N, 3.36.

3a-Acetoxymethyl-6a-butythio-4,4-dichloro-6-(toluene-4-sulfonyl)-4,5,6,6*a*-tetrahydrofuro[2,3-*b*]pyrrol-5-one (35). To a mixture of 0.1 g (0.25 mmol) of sulfilimine **33** and 0.07 g of Zn-Cu in 13 mL of THF at 0 °C was added dropwise 0.1 mL (0.9 mmol) of trichloroacetyl chloride. After being stirred at rt for 30 min, the reaction mixture was filtered and EtOAc was added. The organic layer was washed with a saturated aqueous NaHCO3 solution, brine, dried over Na2SO4, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 0.05 g (40%) of 35 as a pale yellow oil: IR (KBr) 1763, 1752, 1224, 1077, 1032, and 676 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.96 (t, 3H, J = 7.1 Hz), 1.41-1.54 (m, 2H), 1.61-1.75 (m, 2H), 2.09 (s, 3H), 2.45 (s, 3H), 3.01-3.18 (m, 2H), 4.53 (d, 1H, J = 12.0 Hz), 4.86 (d, 1H, J = 12.0 Hz), 5.23 (d, 1H, J = 3.2 Hz), 6.41 (d, 1H, J = 3.2 Hz), 7.34 (d, 2H, J = 7.5 Hz), and 8.02 (d, 2H, J = 7.5 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 13.6, 20.8, 21.8, 22.0, 31.3, 31.7, 63.6, 67.9, 82.3, 106.4, 107.5, 129.4, 129.5, 134.1, 145.6, 146.1, 163.5, and 170.2. HRMS Calcd for C₂₀H₂₄- $Cl_2NO_6S_2 [M + H]^+$: 508.0417. Found: 508.0421.

6-(Benzenesulfonyl)-6a-(1-butylthio)-4,4-dichloro-3a,4,6,6a-tetrahydrofuro-[2,3-b]pyrrol-5-one (41). To the mixture of 0.1 g (0.3 mmol) of sulfilimine 37 and 0.2 g of Zn-Cu in 15 mL of THF was slowly added 0.2 mL (1.6 mmol) of trichloro-acetyl chloride at 0 °C. The reaction mixture was stirred at rt for 20 min, filtered through Celite into a saturated aqueous NaHCO₃ solution, and washed with EtOAc. The aqueous layer was washed twice with EtOAc. The combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.03 g (20%) of 41 as a pale yellow oil: IR (neat) 1764, 1385, 1229, 1190, 816 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 0.94 (t, 3H, J = 7.2 Hz), 1.40-1.47 (m, 2H), 1.64-1.72 (m, 2H), 2.79 (dt, 1H, J = 11.6and 7.6 Hz), 2.88 (dt, 1H, J = 11.6 and 7.6 Hz), 4.44 (t, 1H, J = 2.4 Hz), 5.18 (t, 1H, J = 2.4 Hz), 6.41 (t, 1H, J = 2.4 Hz),

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7.54–7.58 (m, 3H), 7.68 (m, 1H), and 8.15–8.18 (m, 2H); $^{13}\mathrm{C}$ NMR (CDCl₃, 100 MHz) δ 13.6, 22.1, 30.7, 31.1, 66.5, 80.1, 102.6, 106.0, 128.9, 129.3, 134.8, 137.0, 146.4, and 163.4.

6a-Butylthio-4,4-dichloro-6-(toluene-4-sulfonyl)-3a,4,6,-6a-tetrahydrofuro-[2,3-b]pyrrol-5-one (42). To a mixture of 0.5 g (1.5 mmol) of sulfilimine 38 and 0.4 g of Zn-Cu in 75 mL of THF at 0 °C was slowly added 0.4 mL (3.1 mmol) of trichloroacetyl chloride. After being stirred at 0 °C for 30 min, the reaction mixture was filtered and EtOAc was added. The organic layer was washed with a saturated aqueous NaHCO₃ solution, brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 0.34 g (51%) of ${\bf 42}$ as a pale yellow oil: IR (neat) 1763, 1384, 1088, 1038, 965, and 750 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.94 (t, 3H, J=9.8 Hz), 1.40–1.50 (m, 2H), 1.62-1.72 (m, 2H), 2.44 (s, 3H), 2.73-2.90 (m, 2H), 4.42 (t, 1H, J = 3.2 Hz), 5.17 (t, 1H, J = 3.2 Hz), 6.41 (t, 1H, J = 3.2 Hz), 7.34 (d, 2H, J = 11.2 Hz), and 8.02 (d, 2H, J =11.2 Hz); ¹³C NMR (CDCl₃, 100 MHz) & 13.6, 21.8, 22.1, 30.7, 31.1, 66.4, 80.2, 102.6, 106.0, 129.3, 129.5, 134.1, 146.1, 146.4, and 163.3.

6a-(1-Butylthio)-4,4-dichloro-6-(4-methoxybenznesulfonyl)-3a,4,6,6a-tetrahydrofuro[2,3-b]pyrrol-5-one (43). To the mixture of 0.1 g (0.29 mmol) of sulfilimine 39 and 0.19 g of Zn-Cu in 15 mL of THF was slowly added 0.16 mL (1.5 mmol) of trichloroacetyl chloride at 0 $^{\circ}\mathrm{C}.$ The reaction mixture was stirred at rt for 20 min, filtered through Celite into a saturated aqueous NaHCO₃ solution, and washed with EtOAc. The aqueous layer was washed twice with EtOAc. The combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.09 g (72%) of **43** as a pale yellow oil: IR (neat) 1772, 1358, 1264, 1164, 835 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 0.94 (t, 3H, J = 7.2 Hz), 1.41-1.49 (m, 2H), 1.63-1.71 (m, 2H), 2.78 (dt, 1H, J = 11.6 and 7.6 Hz), 2.87 (dt, 1H, J = 11.6 and 7.6 Hz), 3.88 (s, 3H), 4.43 (t, 1H, J = 2.4 Hz), 5.18 (t, 1H, J = 2.4 Hz), 6.41(t, 1H, J = 2.4 Hz), 6.99 (d, 2H, J = 9.2 Hz), and 8.09 (d, 2H, J = 9.2 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 13.6, 22.1, 30.7, 31.1, 55.7, 66.4, 80.3, 102.6, 105.9, 114.0, 128.2, 131.8, 146.4, 163.3, and 164.5.

3,3-Dichloro-5-ethylthio-1-(toluene-4-sulfonyl)pyrrolidin-2-one (47). To a mixture of 0.12 g (0.46 mmol) of sulfilimine 44 and 0.6 g of Zn-Cu in 10 mL of THF was slowly added 0.3 mL (2.3 mmol) of trichloroacetyl chloride at 0 °C. The reaction mixture was stirred at rt for 20 min, filtered through Celite into a cold saturated aqueous NaHCO3 solution, and washed with EtOAc. After the organic layer was separated, the aqueous layer was washed with EtOAc. The combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.11 g (68%) of 47 as a white solid: mp 135-136 °C; IR (neat) 1756, 1371, 1172, 1068, and 960 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 1.30 (t, 3H, J = 7.2 Hz), 2.45 (s, 3H), 2.89 (dq, 1H, J = 12.0and 7.2 Hz), 2.94 (dq, 1H, J = 12.0 and 7.2 Hz), 3.02 (dd, 1H, J = 15.0 and 3.6 Hz), 3.39 (dd, 1H, J = 15.0 and 7.2 Hz), 5.39 (dd, 1H, J = 7.2 and 3.6 Hz), 7.36 (d, 2H, J = 8.4 Hz), and 8.05 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ 14.9, 22.0, 28.4, 50.8, 62.3, 78.7, 129.3, 129.9, 134.3, 146.4, and 163.8. Anal. Calcd for $\rm C_{13}H_{15}Cl_2NO_3S_2:\ C,\ 42.39;\ H,\ 4.11;\ N,$ 3.80. Found: C, 42.41; H, 4.10; N, 3.81.

3,3-Dichloro-5-phenylthio-1-(toluene-4-sulfonyl)pyrrolidin-2-one (48). To a mixture of 0.1 g (0.34 mmol) of sulfilimine **45**⁵¹ and 0.7 g of Zn–Cu in 16 mL of THF was slowly added 0.3 mL (2.8 mmol) of trichloroacetyl chloride in 2 mL of THF at 0 °C. The reaction mixture was stirred at 0 °C for 15 min, filtered through Celite with a saturated aqueous NaHCO₃ solution, and washed with EtOAc. The aqueous layer was washed with EtOAc, and the combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.085 g (61%) of **48** as a white solid: mp 122–124 °C; IR (neat) 1760, 1374, 1173, and 663 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.43 (s, 3H), 2.98 (dd, 1H, J = 14.8 and 3.6 Hz), 3.26 (dd, 1H, J = 14.8 and 7.2 Hz), 5.59 (dd, 1H, J = 7.2 and 3.6 Hz), 7.32–7.44 (m, 7H), and 8.12 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 22.0, 48.5, 64.8, 78.7, 129.6, 129.7, 129.9, 130.0, 130.7, 134.1, 134.9, 146.6, and 163.8.

3,3-Dichloro-4,4,5-trimethyl-1-(toluene-4-sulfonyl)-5-(phenylthio)pyrrolidin-2-one (49). To a mixture of 0.2 g (0.57 mmol) of sulfimide 46 and 0.75 g of Zn-Cu in 20 mL of THF at 0 °C was slowly added 0.32 mL (2.9 mmol) of trichloroacetyl chloride in 9 mL of THF. After being stirred at 0 °C for 10 min, the reaction mixture was quenched with NaHCO₃ and the mixture was filtered and EtOAc was added. The organic layer was washed with a saturated aqueous NaHCO₃ solution, brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 0.15 g (59%) of $\mathbf{49}$ as a white solid: mp 113-115 °C; IR (KBr) 1754, 1368, 1263, 1176, 752, and 653 cm^-1; ¹H NMR (CDCl₃, 300 MHz) δ 1.26 (s, 3H), 1.63 (s, 3H), 1.68 (s, 3H), 2.45 (s, 3H), 7.35 (d, 2H, J = 8.4 Hz), 7.39–7.44 (m, 3H), 7.77 (dd, 2H, J = 8.0 and 1.3 Hz), and 8.18 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 19.9, 21.8, 24.0, 24.7, 54.1, 82.5, 88.4, 128.0, 129.3, 129.7, 130.0, 131.1, 134.4, 138.5, 145.7, and 164.4. Anal. Calcd for C₂₀H₂₁-Cl₂NO₃S₂: C, 52.40; H, 4.62; N, 3.06. Found: C, 52.27; H, 4.70; N. 3.07.

(Z)-3,3-Dichloro-4-phenyl-5-phenylthio-1-(toluene-4sulfonyl)pyrrolidin-2-one (53). To a mixture of 0.05 g (0.13 mmol) of sulfilimine 50 and 0.17 g of Zn-Cu in 5 mL of THF was slowly added 0.075 mL (0.66 mmol) of trichloroacetyl chloride at 0 °C. The reaction mixture was stirred at rt for 20 min, filtered through Celite with a saturated aqueous NaHCO₃ solution, and washed with EtOAc. The combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.042 g (60%) of ${\bf 53}$ as a colorless oil: IR (neat) 1765, 1373, 1175, and 1088 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 2.47 (s, 3H), 4.35 (d, 1H, J = 6.0Hz), 5.79 (d, 1H, J = 6.0 Hz), 7.18–7.26 (m, 5H), 7.34–7.41 (m, 5H), 7.63 (d, 2H, J = 7.2 Hz), and 8.15 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ 22.1, 59.4, 72.7, 82.4, 128.7, 128.8, 129.3, 129.4, 130.0, 130.8, 130.9, 133.4, 134.0, 134.3, 146.6, and 163.6; HRMS Calcd for $C_{23}H_{20}Cl_2NO_3S_2$ [M + H]+: 492.0256. Found: 492.0261.

The ¹H NMR spectrum of the crude reaction mixture also showed the presence of (*Z*)-*N*-(3,3-dichloro-4-phenyl-5-phenyl-sulfanyl-dihydrofuran-2-ylidene)-4-methyl-benzenesulfona-mide (**56**), which could be isolated with some difficulty from the chromatographic separation as a colorless oil: IR (neat) 1660, 1338, 1162, and 1086 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 2.45 (s, 3H), 4.21 (d, 1H, *J* = 4.8 Hz), 6.42 (d, 1H, *J* = 4.8 Hz), 6.91 (d, 2H, *J* = 7.8 Hz), 7.28 (t, 2H, *J* = 7.8 Hz), 7.35–7.39 (m, 4H), 7.47–7.49 (m, 2H), and 7.96 (d, 2H, *J* = 8.4 Hz).

(*E*)-3,3-Dichloro-4-phenyl-5-phenylthio-1-(toluene-4sulfonyl)pyrrolidin-2-one (54). To a mixture of 0.06 g (0.17 mmol) of sulfilimine 51 and 0.21 g of Zn-Cu in 5 mL of THF was slowly added 0.09 mL (0.83 mmol) of trichloroacetyl chloride at 0 °C. The reaction mixture was stirred at rt for 20 min, filtered through Celite with a saturated aqueous NaHCO₃ solution, and washed with EtOAc. The combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The ¹H NMR spectrum of the crude reaction mixture showed the presence of 54 and 57 in a 3:2 ratio. The residue was purified by flash silica gel chromatography to give 0.04 g (50%) of 54 as a colorless oil: IR (neat) 1764, 1375, 1173, and 1085 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 2.47 (s, 3H), 3.54 (d, 1H, J = 8.4 Hz), 5.66 (d, 1H, J = 8.4 Hz), 7.03 (d, 2H, J = 8.4 Hz), 7.21–7.26 (m, 4H), 7.34 (td, 1H,

⁽⁵¹⁾ Rayner, C. P.; Clark, A. J.; Rooke, S. M.; Sparey, T. J.; Tayor, P. C. J. Chem. Soc., Perkin Trans. 1 2000, 79.

J=7.8 and 0.6 Hz), 7.38–7.43 (m, 5H), and 8.16 (d, 2H, J=8.4 Hz); $^{13}\mathrm{C}$ NMR (CDCl₃, 150 MHz) δ 22.0, 59.6, 67.4, 83.4, 128.9, 129.5, 129.6, 129.7, 130.0, 130.1, 134.6, 135.8, 146.5, and 163.7. HRMS Calcd for $\mathrm{C_{23}H_{20}Cl_2NO_3S_2}$ [M + H]+: 492.0256. Found: 492.0262.

The second fraction isolated from the chromatographic column contained 0.02 g (27%) of (*E*)-*N*-(3,3-dichloro-4-phenyl-5-phenylsulfanyl-dihydrofuran-2-ylidene)-4-methyl-benzene-sulfonamide (**57**) as a colorless oil: IR (neat) 1662, 1336, 1164, and 1090 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 2.43 (s, 3H), 3.64 (d, 1H, J = 10.8 Hz), 6.11 (d, 1H, J = 10.8 Hz), 7.25 (d, 2H, J = 7.8 Hz), 7.32 (d, 2H, J = 8.4 Hz), 7.36–7.46 (m, 8H), and 7.93 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ 21.9, 61.3, 65.3, 84.2, 128.0, 128.3, 128.7, 129.1, 129.7, 129.9, 130.0, 130.3, 135.1, 137.5, 144.4, and 164.6; HRMS Calcd for C₂₃H₂₀-Cl₂NO₃S₂ [M + H]⁺: 492.0256. Found: 492.0261.

(E)-3,3-Dichloro-4-(4-methoxy-phenyl)-5-phenylsulfanyl-1-(toluene-4-sulfonyl)-pyrrolidin-2-one (55). To a mixture of 0.08 g (0.19 mmol) of sulfilimine 52 and 0.24 g of Zn-Cu in 5 mL of THF was slowly added 0.11 mL (1.0 mmol) of trichloroacetyl chloride at 0 °C. The reaction mixture was stirred at rt for 20 min, filtered through Celite with a saturated aqueous NaHCO₃ solution, and washed with EtOAc. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The ¹H NMR spectrum of the crude reaction mixture showed the presence of 55 and 58 in a 3:2 ratio. The residue was purified by flash silica gel chromatography to give 0.043 g (44%) of 55 as a colorless oil: IR (neat) 1764, 1516, 1174, and 1087 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.47 (s, 3H), 3.45 (d, 1H, J = 8.4Hz), 3.84 (s, 3H), 5.60 (d, 1H, J = 8.4 Hz), 6.92 (d, 2H, J = 8.4Hz), 7.02 (d, 2H, J = 7.2 Hz), 7.14 (d, 2H, J = 8.4 Hz), 7.23 (t, 2H, J = 7.2 Hz), 7.34 (t, 1H, J = 7.2 Hz), 7.40 (d, 2H, J = 8.4Hz), and 8.16 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 22.1, 55.5, 59.0, 67.5, 83.8, 114.4, 121.7, 128.9, 129.5, 129.6, 130.0, 130.1, 131.3, 134.6, 135.8, 146.4, 160.6, and 163.8.

The second fraction isolated from the chromatographic column contained 0.029 g (30%) of (*E*)-*N*-[3,3-dichloro-4-(4-methoxy-phenyl)-5-phenylsulfanyl-dihydrofuran-2-ylidene]-4-methyl-benzenesulfonamide (**58**): IR (neat) 1662, 1516, 1163, and 739 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.44 (s, 3H), 3.59 (d, 1H, *J* = 10.4 Hz), 3.84 (s, 3H), 6.06 (d, 1H, *J* = 10.4 Hz), 6.96 (d, 2H, *J* = 8.4 Hz), 7.18 (d, 2H, *J* = 8.4 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 7.40–7.46 (m, 5H), 7.94 (d, 2H, *J* = 8.4 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ 21.9, 55.5, 60.8, 84.5, 93.3, 114.5, 120.3, 127.9, 128.3, 129.7, 129.8, 130.3, 131.1, 135.1, 137.5, 144.4, 160.8, and 164.8.

3,3-Dichloro-6a-phenylthio-1-(toluene-4-sulfonyl)-hexahydrocyclopenta[b]-pyrrol-2-one (64). To a mixture of 0.05 g (0.15 mmol) of sulfilimine 61 and 0.18 g of Zn-Cu in 5 mL of THF was slowly added 0.08 mL (0.72 mmol) of trichloroacetyl chloride at 0 °C. The reaction mixture was stirred at rt for 20 min, filtered through Celite with a saturated aqueous NaHCO₃ solution, and washed with EtOAc. The organic layer was washed with brine, dried over MgSO4, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.04 g (63%) of 64 as a white solid: mp 129-131 °C; IR (neat) 1755, 1374, 1175, and 1086 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.00-2.04 (m, 2H), 2.10-2.15 (m, 2H), 2.44 (s, 3H), 2.51 (ddd, 1H, J = 14.0, 10.0, and7.2 Hz), 2.66 (ddd, 1H, *J* = 14.0, 7.2, and 3.6 Hz), 3.04 (t, 1H, J = 7.2 Hz), 7.21–7.29 (m, 4H), 7.33 (dt, 1H, J = 7.2 and 1.6 Hz), 7.36 (d, 2H, J = 8.0 Hz), and 8.14 (d, 2H, J = 8.0 Hz); ¹³C NMR (CDCl₃, 100 MHz) & 22.0, 25.9, 27.0, 41.5, 59.3, 83.5, 129.8, 129.9, 130.0, 130.3, 130.5, 134.3, 136.6, 146.3, and 164.9. Anal. Calcd for C₂₀H₁₉Cl₂NO₃S₂: C, 52.63; H, 4.20; N, 3.07. Found: C, 52.66; H, 4.09; N, 3.19.

3,3-Dichloro-7*a***-phenylthio-1-(toluene-4-sulfonyl)oc-tahydroindol-2-one (65).** To a mixture of 0.11 g (0.29 mmol) of sulfilimine **62** and 0.37 g of Zn-Cu in 20 mL of THF was slowly added 0.16 mL (1.5 mmol) of trichloroacetyl chloride at 0 °C. The reaction mixture was stirred at rt for 20 min,

filtered through Celite with a saturated aqueous NaHCO₃ solution, and washed with EtOAc. The combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.086 g (65%) of **65** as a white solid: mp 176–177 °C; IR (neat) 1753, 1376, 1176, and 1083 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.60–1.66 (m, 1H), 1.78–1.91 (m, 4H), 2.01–2.05 (m, 1H), 2.27–2.36 (m, 2H), 2.44 (s, 3H), 3.00–3.07 (m, 1H), 7.26–7.29 (m, 4H), 7.33–7.37 (m, 3H), and 8.10 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 20.5, 21.9, 22.0, 34.2, 48.6, 78.3, 84.9, 129.7, 129.8, 129.8, 129.9, 130.3, 134.6, 135.9, 146.1, and 164.0. Anal. Calcd for C₂₁H₂₁-Cl₂NO₃S₂: C, 53.62; H, 4.50; N, 2.98. Found: C, 53.37; H, 4.37; N, 3.02.

3,3-Dichloro-3a-methyl-6a-phenylthio-1-(toluene-4-sulfonyl)hexahydro-cyclopenta[b]pyrrol-2-one (66). To a mixture of 0.045 g (0.12 mmol) of sulfilimine 63 and 0.15 g of Zn-Cu in 5 mL of THF was slowly added 0.05 mL (0.48 mmol) of trichloroacetyl chloride at 0 °C. The reaction mixture was stirred at rt for 20 min, filtered through Celite with a saturated aqueous NaHCO3 solution, and washed with EtOAc. The aqueous layer was washed with EtOAc, and the combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.011 g (20%) of 66 as a colorless oil: IR (neat) 1758, 1369, and 1176 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.66 (s, 3H), 1.65-1.82 (m, 3H), 1.86-1.94 (m, 1H), 2.07-2.15 (m, 1H), 2.46 (s, 3H), 2.84-2.88 (m, 1H), 7.36 (d, 2 H, J = 8.0 Hz), 7.38–7.44 (m, 3H), 7.82– 7.85 (m, 2H), and 8.21 (d, 2H, J = 8.0 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 18.3, 21.6, 21.8, 40.1, 41.3, 62.6, 89.6, 113.3, 127.7, 129.4, 129.5, 129.8, 130.2, 135.9, 137.9, 144.1, and 165.9.

5-Ethylthio-1-(toluene-4-sulfonyl)pyrrolidin-2-one (67). To a mixture containing 0.05 g (0.14 mmol) of sulfide 47 and 0.17 g of Zn metal in 8 mL of EtOH was added 0.04 mL (0.7 mmol) of acetic acid and 0.1 mL (0.7 mmol) of TEMDA. The mixture was stirred at rt for 1 h and was then filtered through Celite. The solvent was removed under reduced pressure, and the residue was dissolved in EtOAc and washed with water. The organic layer was separated, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.034 g (88%) of 67 as a white solid: mp 114-116 °C; IR (neat) 1742, 1359, 1165, 1088, and 814 cm $^{-1}\mbox{;}$ $^1\rm H$ NMR (CDCl_3, 400 MHz) δ 1.25 (t, 3H, J = 7.2 Hz), 2.14–2.20 (m, 1H), 2.37–2.43 (m, 1H), 2.42 (s, 3H), 2.52-2.75 (m, 4H), 5.49 (d, 1H, J = 7.2 Hz), 7.30 (d, 2H, J = 8.0 Hz), and 8.02 (d, 2H, J = 8.0 Hz); ¹³C NMR (CDCl₃, 100 MHz) & 14.6, 21.9, 25.6, 29.5, 31.1, 64.7, 129.2, 129.5, 135.5, 145.4, and 172.6. Anal. Calcd for C₁₃H₁₇NO₃S₂: C, 52.15; H, 5.72; N, 4.68. Found: C, 52.30; H, 5.78; N, 4.66.

2-(tert-Butyl-dimethylsilanyloxy)-1-(toluene-4-sulfonyl)-1H-pyrrole (68). To a solution containing 0.06 g (0.2 mmol) of sulfide 67 in 5 mL of CH₂Cl₂ was added 0.07 g (0.4 mmol) of *m*-chloroperbenzoic acid at rt. The reaction mixture was stirred for 2 h and was then quenched by a saturated aqueous NaHCO₃ solution. The organic layer was separated, washed with a saturated aqueous NaHCO₃ solution, and dried over MgSO₄. Concentration under reduced pressure followed by flash silica gel chromatography provided 0.044 g (94%) of 1-(toluene-4-sulfonyl)-1,5-dihydropyrrol-2-one as a white solid: IR (neat) 1716, 1357, 1169, and 799 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 2.43 (s, 3H), 4.50 (quint, 2H, J = 1.8 Hz), 6.07 (dt, 1H, J = 6.0 and 1.8 Hz), 7.24 (dt, 1H, J = 6.0 and 1.8 Hz),7.33 (d, 2H, J = 7.8 Hz), and 7.95 (d, 2H, J = 7.8 Hz); ¹³C NMR (CDCl₃, 150 MHz) & 21.9, 52.5, 127.4, 128.2, 130.0, 135.5, 145.4, 146.7, and 168.5.

To a solution containing 0.04 g (0.17 mmol) of above pyrrolinone in 2 mL of CH_2Cl_2 at rt was added 0.07 mL (0.5 mmol) of 2,6-lutidine and 0.04 mL (0.18 mmol) of TBSOTf. The reaction mixture was stirred at rt for 15 min and was concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.05 g (86%) of **68**

as a clear oil: IR (neat) 1585, 1179, 1154, 843, and 672 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 0.18 (s, 6H), 0.93 (s, 9H), 2.39 (s, 3H), 5.15 (dd, 1H, J = 3.6 and 1.8 Hz), 5.98 (t, 1H, J = 3.6 Hz), 6.78 (dd, 1H, J = 3.6 and 1.8 Hz), 7.25 (d, 2H, J = 8.4 Hz), and 7.71 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ -4.8, 18.4, 21.8, 25.8, 92.3, 109.7, 113.9, 127.5, 129.8, 136.6, 143.4, and 144.7.

1-(Toluene-4-sulfonyl)-pyrrolidine (69). To a solution containing 0.03 g (0.1 mmol) of amide 67 in 2 mL of THF was added 0.3 mL of BH₃·THF (1.0 M in THF) at 0 °C. The reaction mixture was stirred for 20 h, quenched with MeOH, and concentrated under reduced pressure. Purification by flash silica gel chromatography gave 0.02 g (83%) of 69 as a white solid:⁵² ¹H NMR (CDCl₃, 600 MHz) δ 1.73–1.76 (m, 4H), 2.43 (s, 3H), 3.21–3.34 (m, 4H), 7.32 (d, 2H, J = 7.8 Hz), and 7.72 (d, 2H, J = 7.8 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ 21.7, 25.4, 48.1, 127.8, 130.0, 134.2, and 143.5. HRMS Calcd for C₁₁H₁₅-NO₂S [M + H]⁺: 226.0896. Found: 226.0898.

3,3-Dichloro-5-ethylthio-1-(toluene-4-sulfonyl)pyrrolidin-2-ol (70). To a solution containing 0.1 g (0.3 mmol) of sulfide 47 in 3 mL of THF at 0 °C was added 0.8 mL (0.8 mmol) of BH₃·THF (1.0 M). The reaction mixture was stirred at rt for 12 h and was then quenched with MeOH. The aqueous layer was extracted with EtOAc, and the combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.084 g (84%) of 70 as a white solid: mp 119-120 °C; IR (neat) 1343, 1165, and 1082 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 0.95 (t, 3H, J = 7.2 Hz), 2.31 (dq, 1H, J = 12.0 and 7.2 Hz), 2.41 (s, 3H), 2.49 (dq, 1H)J=12.0 and 7.2 Hz), 2.87 (dd, 1H, J=14.0 and 9.2 Hz), 2.98 (dd, 1H, J = 14.0 and 6.8 Hz), 3.60 (brs, 1H), 4.99 (dd, 1H)J = 9.2 and 6.8 Hz), 5.71 (s, 1H), 7.28 (d, 2H, J = 8.0 Hz), and 7.87 (d, 2H, J = 8.0 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 13.9, 21.8, 23.3, 49.3, 62.9, 86.2, 89.9, 128.0, 130.0, 137.3, and 144.2. Anal. Calcd for C13H17Cl2NO3S2: C, 42.16; H, 4.63; N, 3.78. Found: C, 42.20; H, 4.54; N, 3.83.

N-(4-Hydroxybutyl)-4-toluenesulfonamide (71). To a solution containing 0.05 g (0.14 mmol) of sulfide 47 in 2 mL of MeOH was added 0.026 g (0.67 mmol) of NaBH₄. The reaction mixture was stirred at rt for 20 min and quenched with water. The aqueous layer was extracted with EtOAc, and the combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. Purification by flash silica gel chromatography gave 0.037 g (92%) of N-(3,3dichloro-4-hydroxybutyl)-4-toluenesulfonamide as a white solid: mp 108–109 °C; IR (neat) 1305, 1151, and 1048 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 2.43 (s, 3H), 2.46 (t, 2H, J = 7.2Hz), 2.67 (t, 1H, J = 7.2 Hz), 3.30 (q, 2H, J = 7.2 Hz), 3.88 (d, 2H, J = 7.2 Hz), 4.98 (t, 1H, J = 7.2 Hz), 7.32 (d, 2H, J = 8.4Hz), and 7.75 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 21.8, 39.7, 43.7, 72.3, 91.6, 127.3, 130.1, 136.7, and 144.0. Anal. Calcd for C₁₁H₁₅Cl₂NO₃S: C, 42.32; H, 4.84; N, 4.49. Found: C, 42.27; H, 4.79; N, 4.56.

To a mixture containing 0.03 g (0.1 mmol) of the above amide and 0.12 g of Zn in 5 mL of EtOH were added 0.03 mL (0.5 mmol) of acetic acid and 0.07 mL (0.5 mmol) of TEMDA. The reaction mixture was stirred at rt for 1 h and was filtered through Celite. The solvent was removed under reduced pressure, and the residue was dissolved in EtOAc and washed with water. The organic layer was separated, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.021 g (88%) of **71** as a colorless oil.⁵³ ¹H NMR (CDCl₃, 400 MHz) δ 1.64 (m, 1H), 1.70 (quint, 2H, J = 6.0 Hz), 2.42 (s, 3H), 3.10 (q, 2H, J = 6.0 Hz), and 7.73 (d, 2H, J = 8.0 Hz).

6a-Ethylthio-6-(toluene-4-sulfonyl)-3a,4,6,6a-tetrahydrofuro[2,3-b]pyrrol-5-one (72). To a mixure containing 0.16 g (0.39 mmol) of sulfide **34** and 0.5 g of Zn metal in 15 mL of EtOH were added 0.12 mL (1.9 mmol) of acetic acid and 0.29 mL (1.9 mmol) of TEMDA. The mixture was stirred at rt for 1 h and was filtered through Celite. The solvent was removed under reduced pressure, and the residue was dissolved in EtOAc and washed with water. The organic layer was separated, dried over MgSO₄, and concentrated under reduced pressure. Silica gel chromatography gave 0.11 g (84%) of 72 as a white solid: mp 129–131 °C; IR (neat) 1740, 1371, 1174, and 1011 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.29 (t, 3H, J = 7.2 Hz), 2.39 (dd, 1H, J = 17.6 and 2.4 Hz), 2.40 (s, 3H), 2.65 (dq, 1H, J = 11.6 and 7.2 Hz), 2.76 (dd, 1H, J = 17.6 and 9.2 Hz), 2.79 (dq, 1H, J = 11.6 and 7.2 Hz), 3.80 (dq, 1H, J = 9.2 and 2.4 Hz), 5.01 (t, 1H, J = 2.4 Hz), 6.35 (t, 1H, J = 2.4 Hz), 7.28 (d, 2H, J = 8.4 Hz), and 7.99 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃, 100 MHz) & 13.8, 21.9, 25.0, 35.4, 49.2, 105.6, 108.8, 129.3, 129.4, 135.6, 145.1, 145.4, and 171.3. Anal. Calcd for C₁₅H₁₇NO₄S₂: C, 53.08; H, 5.05; N, 4.13. Found: C, 53.11; H, 5.08; N, 4.11.

N-{2,2-Dichloro-2-[2-(ethylthio)furan-3-yl]-acetyl}-4toluenesulfonamide (73). A solution containing 0.02 g (0.05) mmol) of sulfide 34 and 0.1 mL of TFA in 1 mL of toluene was sujected to microwave irradiation (200 W, 100 °C) for 30 min. The resulting mixture was diluted with H₂O and extracted with EtOAc. The organic layer was washed with a saturated aqueous NaHCO₃, brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 0.014 g (71%) of amide **73** as a yellow oil: IR (neat) 1721, 1638, 1408, and 1192 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.40 (t, 3H, J = 7.2 Hz), 2.42 (s, 3H), 3.16 (q, 2H, J = 7.2 Hz), 7.34 (d, 2H, J = 8.0 Hz), 7.34 (d, 1H, J = 2.0 Hz), 7.37 (d, 1H, J = 2.0 Hz), and 7.98 (d, 2H, J=8.0 Hz); $^{13}\mathrm{C}$ NMR (CDCl₃, 100 MHz) δ 15.0, 21.9, 25.2, 112.5, 116.4, 128.7, 129.9, 135.3, 143.4, 145.8, 158.5, 166.3, and 176.2.

4.4-Dichloro-6a-methyl-6-(toluene-4-sulfonyl)-3a.4.6.6atetrahydrofuro[2,3-b]pyrrol-5-one (74). To a solution containing 0.04 g (0.10 mmol) of sulfide 34 in 3 mL of CH_2Cl_2 at 0 °C was added 0.085 g (0.5 mmol) of *m*-chloroperbenzoic acid. After being stirred at rt for 32 h, the mixture was quenched with H₂O and extracted with EtOAc. The organic layer was washed with a saturated aqueous NaHCO₃, brine, and dried over Na₂SO₄. Concentration under reduced pressure followed by flash silica gel chromatography provided 0.03 g (70%) of 4, 4-dichloro-6a-ethane-sulfonyl-6-(toluene-4-sulfonyl)-3a, 4, 6, 6a-baby -3a, 4, 6a-baby -3a, 4, 6, 6a-baby -3a, 4, 6, 6a-baby -3a, 4, 6a-baby -3a, 4a-baby -3a, 4a-babtetrahydrofuro[2,3-b]pyrrol-5-one as a colorless oil: ¹H NMR $(CDCl_3, 400 \text{ MHz}) \delta 1.55 (t, 3H, J = 7.6 \text{ Hz}), 2.45 (s, 3H), 3.72$ (dq, 1H, J = 14.0 and 7.6 Hz), 3.84 (dq, 1H, J = 14.0 and 7.6Hz), 5.26 (t, 1H, J = 2.8 Hz), 5.36 (t, 1H, J = 2.8 Hz), 6.48 (t, 1H, J = 2.8 Hz), 7.36 (d, 2H, J = 8.0 Hz), and 8.07 (d, 2H, J = 8.0 Hz).

To a solution containing 0.02 g (0.05 mmol) of the above sulfone in 2 mL of CH₂Cl₂ at rt was added 0.1 mL (0.2 mmol) of AlMe₃ (2.0 M in toluene). After being heated at reflux for 36 h, the reaction mixture was quenched with a 10% aqueous solution of Rochelle salt and extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to provide 0.013 g (70%) of 74as a white solid: mp 147-148 °C; IR (KBr) 1765, 1376, 1038, 977, 817, and 665 cm $^{-1};$ $^1\rm H$ NMR (CDCl_3, 400 MHz) δ 2.27 (s, 3H), 2.44 (s, 3H), 3.97 (t, 1H, J = 2.4 Hz), 5.01 (t, 1H, J = 2.4Hz), 6.22 (t, 1H, J = 2.4 Hz), 7.32 (d, 2H, J = 8.0 Hz), and 7.96 (d, 2H, J = 8.0 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 24.7, 65.7, 80.9, 101.6, 102.0, 129.0, 129.5, 134.5, 145.8, 145.9, and 163.7. Anal. Calcd for C₁₄H₁₃Cl₂NO₄S: C, 46.42; H, 3.62; N, 3.87. Found: C, 46.54; H, 3.71; N, 3.90.

3a-Methyl-2-oxo-1-(toluene-4-sulfonyl)-2,3,3a,8a-tetrahydro-1H-pyrrolo[2,3-b]indole-8-carbaldehyde (82). To a mixture of 0.16 g (2.8 mmol) of **31**, 0.8 mL (14 mmol) of

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HOAc, and 1.9 mL (14 mmol) of TMEDA in 40 mL of EtOH was added 3.7 g (5.6 mmol) of Zn at rt. After being stirred for 2 h at rt, the reaction mixture was filtered through Celite into a saturated aqueous NaHCO₃ solution and extracted with EtOAc. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give 1.2 g (86%) of tert-butyl 8a-ethylthio-3amethyl-2-oxo-1-(toluene-4-sulfonyl)-2,3,3a,8a-tetrahydro-1Hpyrrolo[2,3-b]-indole-8-carboxylate as a white solid: mp 163-164 °C; IR (KBr) 1745, 1721, and 1597 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.19 (t, 3H, J=7.2 Hz), 1.69 (s, 9H), 2.34 (s, 3H), 2.49-2.57 (m, 1H), 2.67 (d, 1H, J = 17.6 Hz), 2.75-2.83 (m, 1H), 2.81 (d, 1H, J = 17.6 Hz), 6.90–7.03 (m, 2H), 7.14 (d, 2H, $J=8.0~\mathrm{Hz}),\,7.22$ (ddd, 1H, $J=8.4,\,6.4,\,\mathrm{and}\,2.4~\mathrm{Hz}),\,7.75$ (d, 1H, J = 8.4 Hz), and 7.80 (d, 2H, J = 8.0 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 12.4, 21.6, 22.3, 25.9, 28.4, 42.1, 54.9, 83.6, 99.2, 117.5, 122.5, 123.9, 128.7, 128.9, 129.0, 135.3, 140.2, 144.8, 151.6, and 170.3.

To a mixture of 0.53 g (1.0 mmol) of the above compound, 0.6 mL (10 mmol) of HOAc, and 1.4 mL (10 mmol) of TMEDA in 50 mL of EtOH was added 1.4 g (20 mmol) of Zn at rt. After being heated for 3 h at reflux, the reaction mixture was allowed to cool, filtered through Celite into a saturated aqueous NaHCO₃ solution, and extracted with EtOAc. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give 0.39 g (73%)of tert-butyl 2-ethylthio-3-methyl-3-[2-oxo-2-(toluene-4-sulfonylamino)-ethyl]-2,3-dihydroindole-1-carboxylate as a colorless oil: IR (neat) 1701, 1664, and 1597 cm⁻¹; ¹H NMR (CD₃OD, 400 MHz) δ 1.15 (t, 3H, J = 7.6 Hz), 1.44 (s, 3H), 1.55 (s, 9H), 2.24 (d, 1H, J = 14.8 Hz), 2.30 (d, 1H, J = 14.8 Hz), 2.45 (s, 3H), 2.45-2.60 (m, 2H), 5.67 (s, 1H), 6.92-7.01 (m, 2H), 7.17 (td, 1H, J = 8.0 and 1.6 Hz), 7.39 (d, 2H, J = 8.0 Hz), 7.55 (m, 1H), and 7.86 (d, 2H, J = 8.0 Hz); ¹³C NMR (CD₃OD, 100 MHz) δ 15.8, 19.7, 21.8, 26.7, 28.8, 47.3, 75.4, 83.1, 117.2, 123.7, 124.7, 129.3, 129.4, 129.5, 130.7, 137.9, 138.8, 146.3, 153.7, and 170.8.

A solution of 0.37 g (0.7 mmol) of the above compound in 20 mL of HCO₂H was stirred at rt for 4 h. The reaction mixture was concentrated under reduced pressure, and the resultant residue was dissolved in EtOAc and washed with a saturated aqueous NaHCO₃ solution. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was precipitated with EtOAc/hexane to provide 0.24 g (88%) of **82** as a white solid: mp 228–229 °C; IR (KBr) 2973, 1734, and 1684 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.50 (s, 3H), 2.36 (s, 3H), 2.88 (s, 3H), 6.07 (s, 1H), 7.11–7.25 (m, 5H), 7.76 (d, 2H, J = 8.4 Hz), 7.83 (d, 1H, J = 8.0 Hz), and 8.99 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.6, 24.6, 43.1, 46.8, 82.2, 117.7.6, 122.9, 126.1, 127.9, 129.3, 129.7, 135.1, 136.4, 137.7, 145.5, 162.0, and 170.5. HRMS Calcd for C₁₉H₁₈N₂O₄S [M + H]⁺: 371.1060. Found: 371.1060.

3a-Methyl-2-oxo-2,3,3a,8a-tetrahydro-1H-pyrrolo[2,3b]indole-8-carbaldehyde (83). To a solution containing 0.88 g (6.9 mmol) of naphthalene in 20 mL of THF was added 0.17 g (7.0 mmol) of sodium, and the mixture was stirred at rt for 45 min so as to produce sodium naphthalinide. The blue solution was cooled to -78 °C, and then a solution of 0.25 g (0.69 mmol) of 82 in 10 mL of THF was added. After being stirred for 1 h, the reaction was guenched with a saturated aqueous NH₄Cl solution and was allowed to warm to rt. The mixture was extracted with EtOAc, and the combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give 0.12 g (81%) of 83 as a white solid: mp 163-164 °C; IR (KBr) 3200, 1708, and 1677 cm $^{-1};$ $^1\!H$ NMR (CDCl_3, 400 MHz) δ 1.54 (rotamer A; s, 3H), 1.56 (rotamer B; s, 3H), 2.64 (rotamer B; d, 1H, J = 17.6 Hz), 2.66 (rotamer A; d, J=17.6 Hz, 1H), 2.72 (rotamer B; d, 1H, J=17.6 Hz), 2.80 (rotamer A; d, 1H, J=17.6 Hz), 5.48 (rotamer A; s, 1H), 5.59 (rotamer B; s, 1H), 6.73 (brs, 1H), 7.14–7.29 (rotamer B; m, 5H and rotamer A; m, 4H), 8.02 (rotamer A; d, 1H, J=8.4 Hz), 8.62 (rotamer A; s, 1H), and 8.96 (rotamer B; s, 1H); 13 C NMR (CDCl₃, 100 MHz) δ 26.6, 43.9, 46.11, 17.7, 109.6, 124.3, 125.5, 129.0, 137.3, 138.0, 158.2, and 175.0. HRMS Calcd for $C_{12}H_{12}N_2O_2$ [M + H]+: 217.0972. Found: 217.0971.

1,3a-Dimethyl-2-oxo-2,3,3a,8a-tetrahydro-1H-pyrrolo-[2,3-b]indole-8-carbaldehyde (84). To a solution containing 0.04 g (0.2 mmol) of 83 in 1.0 mL of THF at 0 °C was added 8.0 mg (0.34 mmol) of NaH. The mixture was stirred for 30 min at 0 °C, then 0.02 mL (0.32 mmol) of MeI was added, and the temperature was allowed to warm to rt with stirring over 5 h. The reaction mixture was quenched with a saturated aqueous NH₄Cl solution and was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na2- SO_4 , and concentrated under reduced pressure. The residue was purified by preparative thick layer chromatography to give 0.02 g (49%) of 84 as a colorless oil: IR (neat) 2961, 1686, and 1596 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.49 (rotamer B; s, 3H), 1.52 (rotamer A; s, 3H), 2.69 (rotamer A and B; d, 1H, J = 17.2 Hz), 2.84 (rotamer B; d, 1H, J = 17.2 Hz), 2.88 (rotamer B; s, 3H), 2.90 (rotamer A; d, 1H, J = 17.2 Hz), 2.94 (rotamer B; s, 3H), 5.28 (rotamer A; s, 1H), 5.74 (rotamer B; s, 1H), 7.16-7.32 (rotamer B; m, 5H, and rotamer A; m, 4H), 7.98 (rotamer A; d, 1H, J = 8.0 Hz), 8.68 (rotamer A; s, 1H), and 8.97 (rotamer B; s, 1H); $^{13}\mathrm{C}$ NMR (CDCl_3, 100 MHz) rotamer B: δ 25.9, 28.3, 43.4, 45.3, 81.4, 110.8, 117.6, 124.4, 125.9, 129.0, 138.3, 159.6, and 172.2. Rotamer A: δ 25.5, 26.7, 43.1, 45.9, 84.1, 110.8, 117.6, 123.2, 126.1, 129.0, 137.9, 159.0, and 171.8. HRMS Calcd for $C_{25}H_{30}N_2O_5S_2$ [M + H]⁺: 231.1128. Found: 231.1127.

The second fraction isolated by preparative thick layer chromatography contained 0.02 g (47%) of 1,3*a*-dimethyl-3,3*a*,8,8*a*-tetrahydro-1*H*-pyrrolo[2,3-*b*]indol-2-one as a colorless oil: IR (neat) 1686 and 1608 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.45 (s, 3H), 2.61 (d, 1H, J = 17.2 Hz), 2.81 (d, 1H, J = 17.2 Hz), 2.84 (s, 3H), 4.60 (brs, 1H), 4.88 (s, 1H), 6.65 (d, 1H, J = 8.0 Hz), 6.82 (t, 1H, J = 7.2 Hz), and 7.07–7.10 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 26.2, 26.8, 44.2, 47.1, 84.4, 110.7, 120.4, 123.1, 128.5, 135.9, 146.9, and 172.7.

A solution containing 0.02 g (0.1 mmol) of the above NHlactam was taken up in 1.0 mL of HCO_2H and was stirred at rt for 4 h. The reaction mixture was concentrated under reduced pressure. The resultant residue was dissolved in EtOAc and was washed with a saturated aqueous NaHCO₃ solution. The organic layers were then washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was precipitated from EtOAc/hexane to provide 0.02 g (87%) of **84**.

Desoxyeseroline (79). To a mixture containing 0.03 g (0.12 mmol) of 84 in 1.5 mL of THF was added 0.6 mL (0.6 mmol) of a 1.0 M solution of BH₃·THF complex in THF at rt. After being heated at reflux for 2 h, the reaction mixture was allowed to cool to rt and 2.0 mL of H₂O was added. The mixture was heated at reflux for another 1 h, cooled to rt, and extracted with EtOAc. The combined organic layer was dried over Na₂- SO_4 and was concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give 0.02 g (76%) of 78 as a colorless oil:⁴⁶ IR (neat) 1605 and 1491 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.45 (s, 3H), 1.90-2.10 (m, 2H), 2.56 (s, 3H), 2.60-2.66 (m, 1H), 2.74-2.79 (m, 1H), 2.95 (s, 3H), 4.16 (s, 1H), 6.42 (d, 1H, J = 7.6 Hz), 6.69 (t, 1H, J = 7.6 Hz), 7.00 (d, 1H, J = 7.6 Hz), and 7.10 (t, J =1H, $J=7.6~{\rm Hz});\,^{13}{\rm C}$ NMR (CDCl₃, 100 MHz) δ 27.3, 36.6, 38.2, 40.7, 52.7, 53.2, 97.3, 106.7, 117.7, 122.2, 127.8, 136.5, and 151.9.

Cyclizations of Vinyl Sulfilimines

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