A Triple Cascade Sequence as a Strategy for the Construction of the Erythrinane Skeleton

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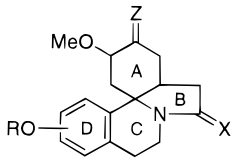
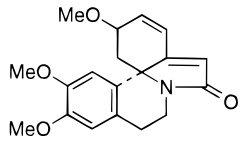
α-Thiocarbocations generated from Pummerer reactions of several *o*-imido sulfoxides were intercepted by adjacent carbonyl groups to produce α-amido-substituted isobenzofurans as transient intermediates. When an olefinic tether was present, intramolecular Diels−Alder cycloaddition occurred followed by a ring-opening−elimination sequence that produced an *N*-acyliminium ion. Deprotonation of the iminium ion led to oxindole derivatives in good yields. When the iminium ion contained both a blocking substituent, such as a carbomethoxy group, as well as an activated aromatic π-tether, the *N*-acyliminium ion intermediate underwent stereoselective spirocyclization to afford *cis*-3,4-benzoerythrinane or homoerythrinane derivatives in good yield. The overall triple cascade sequence represents an efficient one-pot approach toward the erythrina skeleton in which the spirocyclic ABC skeleton is assembled in a single operation. The scope and limitations of the triple cascade were explored by varying both the olefinic and nucleophilic tethers. The required sulfoxide precursors for these Pummerer-induced transformations were easily synthesized starting from 2-[(ethylthio)methyl]benzoic acid. The tandem Pummerer/Diels−Alder/*N*-acyliminium ion cyclization was used for the synthesis of indoloisoquinoline **38**. Since compound **38** was converted to **47** which, in turn, was transformed into erysotramidine (**2**), its preparation represents an extraordinarily facile, formal synthesis of this member of the Erythrina alkaloid family.

The *Erythrina* alkaloids are a widely distributed family of structurally interesting and biologically active natural products.[1−5] Many members of this family possess curare-like activity, and the alkaloidal extracts have been used in indigenous medicine.[3] A variety of pharmacological effects, including sedative, hypotensive, neuromuscular blocking, and CNS depressant properties are associated with the erythrinane skeleton.[1−3] The vast majority of naturally occurring Erythrina alkaloids possess the tetracyclic framework and substitution pattern shown in structure **1**. Numerous synthetic approaches into the Erythrina ring system have been developed[4,5] and a prominent theme for elaborating the fully substituted carbon center at the BC ring fusion has been trapping of *N*-acylimium ion intermediates with electron-rich aryl rings.[6] It appeared to us to be highly desirable



Erythrina alkaloids

1; X or Z = O; R = Me



2; erysotramidine

to design a new, easily tunable strategy for the Erythrina alkaloids, that relied on a multicascade sequence of reactions. Tandem or cascade processes belong to a growing family of reactions that allow the regio- and stereocontrolled formation of several carbon−carbon bonds and/or ring systems in a single operation.[7] Important contributions to this area have been realized utilizing a combination of cationic, anionic, radical, carbenoid, or pericyclic processes.[8] Few reactions can compete with the Diels−Alder cycloaddition with respect to the degree of complexity that can be accomplished in a single synthetic step.[9] Carbon−carbon bond forming reactions involving *N*-acyliminium ions play an equally important role in the synthesis of nitrogen heterocycles

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(6) Tsuda, Y.; Sano, T. In *Studies in Natural Products Chemistry*; Rahman, A. U., Ed.; Elsevier: Amsterdam, 1989; Vol. 3, Part B, p 455.

(7) Ho, T. L. *Tandem Organic Reactions;* Wiley: New York, 1992. Tietze, L. F.; Beifuss, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 131. Waldmann, H. In *Domino Reaction in Organic Synthesis Highlights;* Waldmann, H., Ed.; VCH: Weinheim, 1995; pp 193−202. Wender, P. A., Ed. Frontiers in Organic Synthesis. *Chem. Rev.* **1996**, *96*, 1−600.

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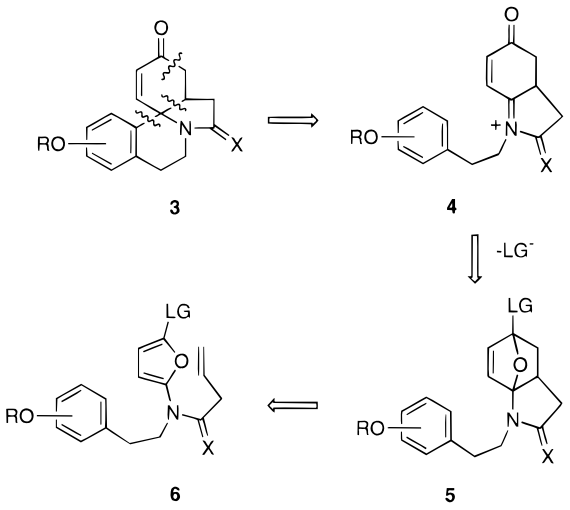
Scheme 1

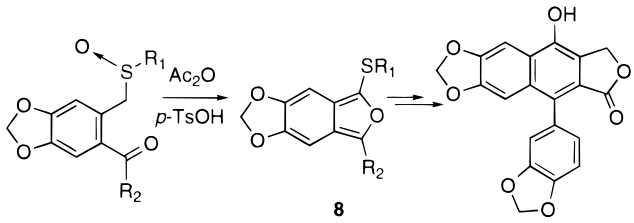


and alkaloidal target molecules.[10] A sequential combination of these two powerful synthetic methods would allow for the rapid, stereocontrolled synthesis of a variety of azapolycyclic products.

The retrosynthetic analysis to which we were attracted involved disconnection of the strategic bonds indicated by the wavy lines in Scheme 1. Disassembly of **3** in this fashion was expected to allow for a highly convergent synthesis of the Erythrina alkaloid ring system. The central feature of this approach involves using 2-amino-substituted furans such as **6** which contain both a suitable leaving group (LG) and an olefinic tether to allow for an intramolecular Diels−Alder reaction. The resulting cycloadduct **5** is expected to readily undergo ring-opening to generate a vinylogous *C*-acyliminium ion of type **4**. This sequence of reactions allows for a rapid entry into the erythrinane skeleton **3**, where the key ABC ring system is assembled in a single operation (**6** → **3**), and which also allows the oxygen functionality to be placed in the appropriate position. Reported herein are the complete details of our synthetic approach which culminated in a very concise, formal total synthesis of the Erythrina alkaloid, (±)-erysotramidine (**2**).[11]

Results and Discussion

There are only a few cases in the literature where Diels−Alder cycloadditions of 2-aminofurans have been described.[12−14] The paucity of examples is undoubtedly due to the inaccessibility and inherent instability of the 2-aminofuran ring system.[15−17] Recently, we reported on the Pummerer-induced cyclization of keto sulfoxides[18] as a method to prepare thio-substituted isobenzofurans of type **8**.[19] The α-thiocarbocation generated from the Pummerer reaction of an *o*-benzoyl-substituted sulfoxide (**7a**) was intercepted by the adjacent keto group to produce isobenzofuran **8**[20] as a transient intermediate which undergoes a subsequent Diels−Alder cycloaddition with an added dienophile. The resulting cycloadduct was subsequently converted to several types of arylnaphthalene lignans such as Taiwanin E (**9**).[21]



7a; R_2=Aryl
7b; R_2=NR_3R_4

We also found that *o*-amido-substituted sulfoxides (i.e., **7b**) can be used as precursors for generating 2-amino-substituted isobenzofurans (**8**; R_2=NR_3R_4) as reactive intermediates.[22] To test the viability of this pathway as an entry into the 3,4-benzoerythrinane skeleton, we decided to examine the Pummerer-induced reaction of *o*-imido sulfoxide **11** (Scheme 2). The construction of **11** was accomplished in four steps from the known carboxylic acid **10**.[22] Thus, treatment of **10** with thionyl chloride at 25 °C followed by reaction of the crude acid chloride with 3,4-dimethoxyphenethylamine provided the expected amide. Subsequent acylation with but-3-enoyl chloride followed by oxidation with sodium periodate furnished **11** in 69% overall yield. Slow addition of sulfoxide **11** to a refluxing mixture of *p*-xylene, acetic anhydride (10 equiv), and *p*-toluene sulfonic acid (5 mol

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(17) Freure, B. T.; Johnson, J. R. *J. Am. Chem. Soc.* **1931**, *53*, 3, 1142.

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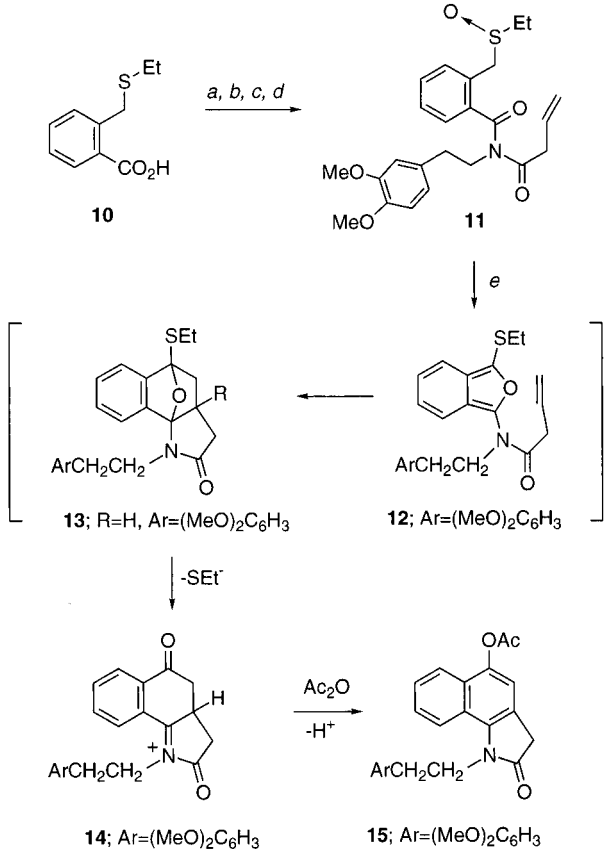
(22) Padwa, A.; Kappe, C. O.; Cochran, J. E.; Snyder, J. P. *J. Org. Chem.* **1997**, *62*, 2786.

Scheme 2

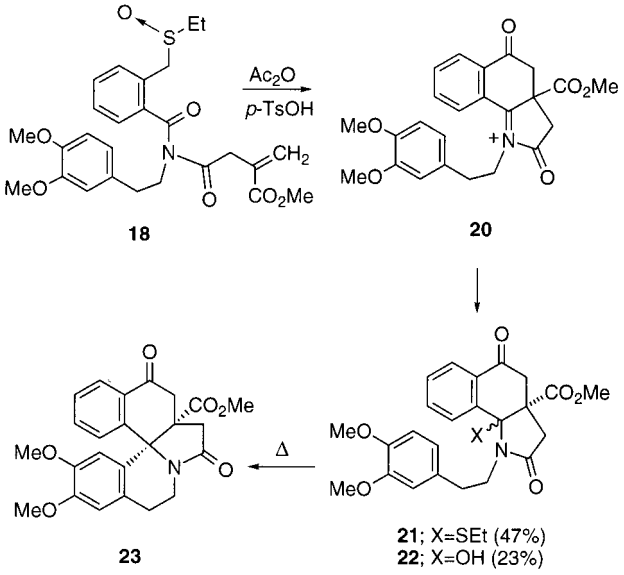


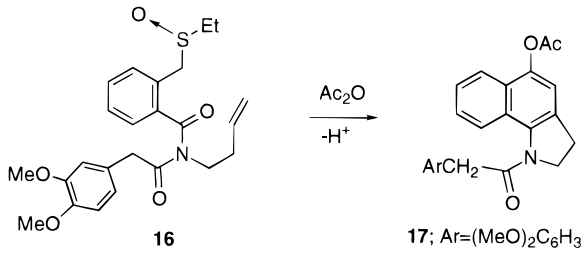
Reagents: (a) $SOCl_2$; (b) $(MeO)_2C_6H_3CH_2CH_2NH_2$; (c) $CH_2{=}CHCH_2COCl$; (d) $NaIO_4$; (e) Ac_2O, *p*-TsOH;

%)[23] did not lead to the desired benzoerythrinane derivative, but instead gave oxindole **15** in 76% yield. The isolation of **15** supports the proposed *cyclization−cycloaddition/ring opening/elimination* sequence **11** → **12** → **13** → **14** → **15**. With this system, the initially formed iminium ion **14** undergoes deprotonation followed by *O*-acetylation to afford the isolated oxindole **15** rather than the spirocyclization product. The driving force associated with the rapid deprotonation undoubtedly involves formation of the conjugated aromatic system present in **15**.

For comparison purposes, we have also investigated the chemistry of the closely related imido sulfoxide **16** where the carbonyl group has been switched from "*inside*" the tether to the "*outside*" position. In an earlier study we noted that incorporation of a C=O group α to nitrogen, either internal or external to the tether, promotes the intramolecular [4 + 2]-cycloaddition reaction of the isobenzofuran derivative across the tethered π-bond.[22] Removal of the C=O functionality significantly suppressed the Diels−Alder cycloaddition reaction. Density functional theory (DFT)[24] calculations suggested that the presence of an amido tether raises the energy of the intermediate isobenzofuran ground state and thereby reduces the intramolecular Diels−Alder activation barrier relative to the corresponding amine.[22] Indeed, we found that benzodihydroindole **17** was formed in 78% yield when **16** was subjected to the standard Pummerer conditions. Once again, deprotonation of the initially formed iminium ion proved much faster than spirocyclization.

Scheme 3





To avoid the deprotonation step, we prepared sulfoxides **18** and **19**, each possessing a carbomethoxy group attached to the olefin tether. This substituent was selected not only to prevent deprotonation, but also because the presence of an electron-withdrawing group on the double bond was expected to enhance the rate of intramolecular [4 + 2]-cycloaddition based on FMO considerations.[25] Subjection of **18** to the standard Pummerer conditions provided a 2:1 mixture of the N,S- and N,O-ketals **21** and **22**, respectively. These products are derived from bimolecular trapping of iminium ion **20** with a nucleophilic species present in the reaction medium (i.e., EtS^-; AcO^-/HO^-) (Scheme 3). Both ketals can be independently converted to the desired benzoerythrinane derivative **23** by heating each in toluene which contained 1.1 equiv of *p*-TsOH. We found it to be more convenient, however, to carry out the triple cascade sequence (**18** → **23**) in a one-pot fashion by first subjecting sulfoxide **18** to the Ac_2O/*p*-TsOH conditions, followed by treatment of the crude reaction mixture (after evaporation of the solvent and excess Ac_2O) with an additional quantity (1.1 equiv) of *p*-TsOH in refluxing toluene. By using this one-pot protocol, 3,4-benzoerythrinane **23** was obtained as a single diastereomer in 65−70% yield from sulfoxide **18**.

(23) Watanabe, M.; Nakamori, S.; Hasegawa, H.; Shirai, K.; Kumamoto, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 817.

(24) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Stevens, P. J.; Devlin, F. F.; Chablowski, C. F.; Frisch, M. J. *J. Chem. Phys.* **1994**, *99*, 11623. Wiest, O.; Black, K. A.; Houk, K. N. *J. Am. Chem. Soc.* **1994**, *116*, 10336.

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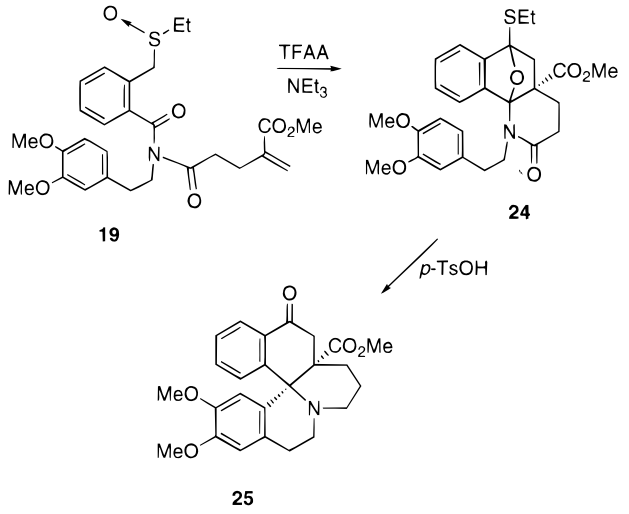
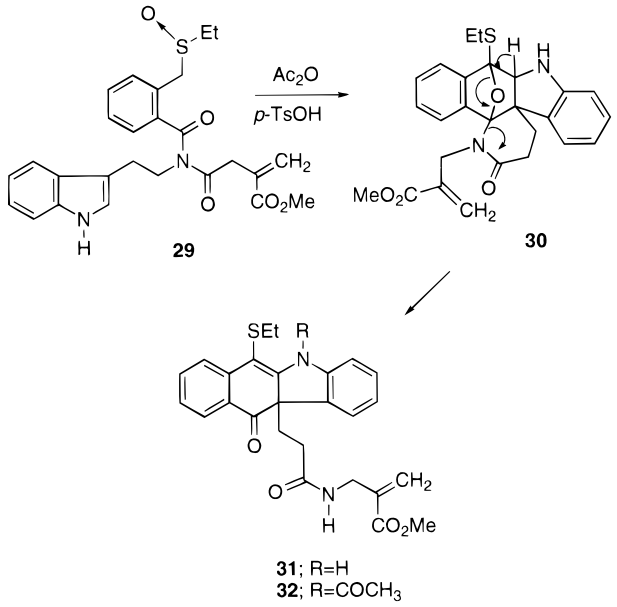
Alternatively, the tandem sequence could also be triggered at 0 °C by utilizing the more electrophilic trifluoroacetic anhydride as the Pummerer promoter (CH_2Cl_2, 2 equiv of Et_3N).[23] In this case, the isobenzofuran cycloadduct (i.e., **13**; R=CO_2Me) was isolated and was converted to **23** (70% overall) by exposure to *p*-TsOH (1.1 equiv) in refluxing toluene. The *cis*-stereochemistry of the A/B ring system of **23** is supported by a number of related iminium ion cyclizations reported in the literature[4,26] and by the distinct ^{1}H-chemical shift of the methyl ester.[27] Semiempirical calculations (AM1 or PM3) show that the ground-state energy of the cis A/B ring fusion present in **23** is ca. 15−18 kcal lower than the trans diastereomer and presumably some of this thermodynamic energy difference is reflected in the transition state for cyclization.

A similar one-pot sequence was successfully employed for the conversion of the homologous sulfoxide **19** to the homoerythrina analogue **25** in 66% yield. The triple cascade sequence of **19** was also carried out using trifluoroacetic anhydride at 0 °C with 2 equiv of triethylamine. Under these conditions, cycloadduct **24** was isolated and was subsequently transformed into **25** (65%) by exposure to 1.1 equiv of *p*-TsOH in refluxing toluene.



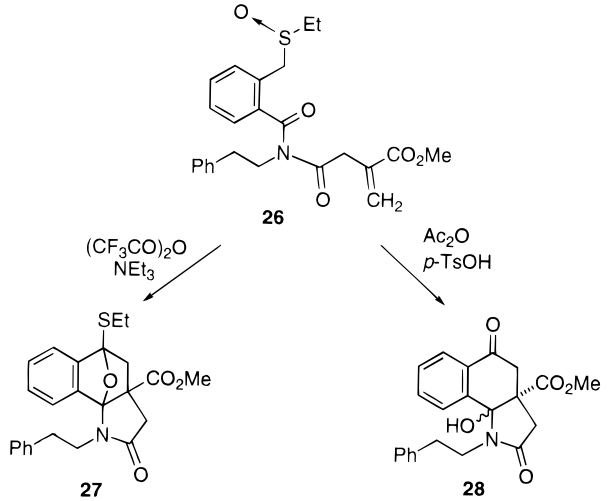
The versatility of acyliminium ions for the synthesis of a wide variety of nitrogenous materials underscores the need to find new methods for their preparation.[28] These reactive intermediates readily react with a wide assortment of π-nucleophiles to effect an overall α-amido alkylation.[29] The last step of our Pummerer-induced triple cascade reaction involves a Mannich cyclization of

Scheme 4



a *C*-acyliminium ion onto a highly activated aromatic π-bond. So that a cross section of additional information could be obtained in regard to the facility of the cyclization step, we needed to evaluate a series of amido sulfoxides containing different aromatic π-bonds. Compounds ranging from unsubstituted aromatics to indoles to simple alkenyl-tethered systems were considered. Ultimately, substrates **26** and **29** were studied as they contain a range of synthetically interesting and easily attainable functionalities.

The Pummerer-induced reaction of imido sulfoxide **26** using trifluoroacetic anhydride proceeded uneventfully and provided the expected isobenzofuran cycloadduct **27**



in 59% yield. When acetic anhydride was used as the Pummerer promoter, hydroxy lactam **28** was the only product (35%) isolated from the reaction mixture. All of our attempts to induce a further reaction of **27** or **28** using a variety of Lewis acids failed to give any characterizable products. The anticipated product of electrophilic aromatic substitution was not observed, thereby

(26) Wilkens, H. J.; Traxler, F. *Helv. Chim. Acta* **1975**, *58*, 1512.

(27) The high field chemical shift of the methyl ester (3.21 ppm for **23** vs 3.83 for sulfoxide **18**) is due to the fact that the ester functionality present in *cis*-**23** is situated directly above the plane of the aromatic D-ring of the erythrina skeleton. This particular stereochemical relationship is only realized in the *cis*-erythrina series and has been previously utilized to distinguish between the *cis*- and *trans*-ring fusion in erythrina derivatives.[26]

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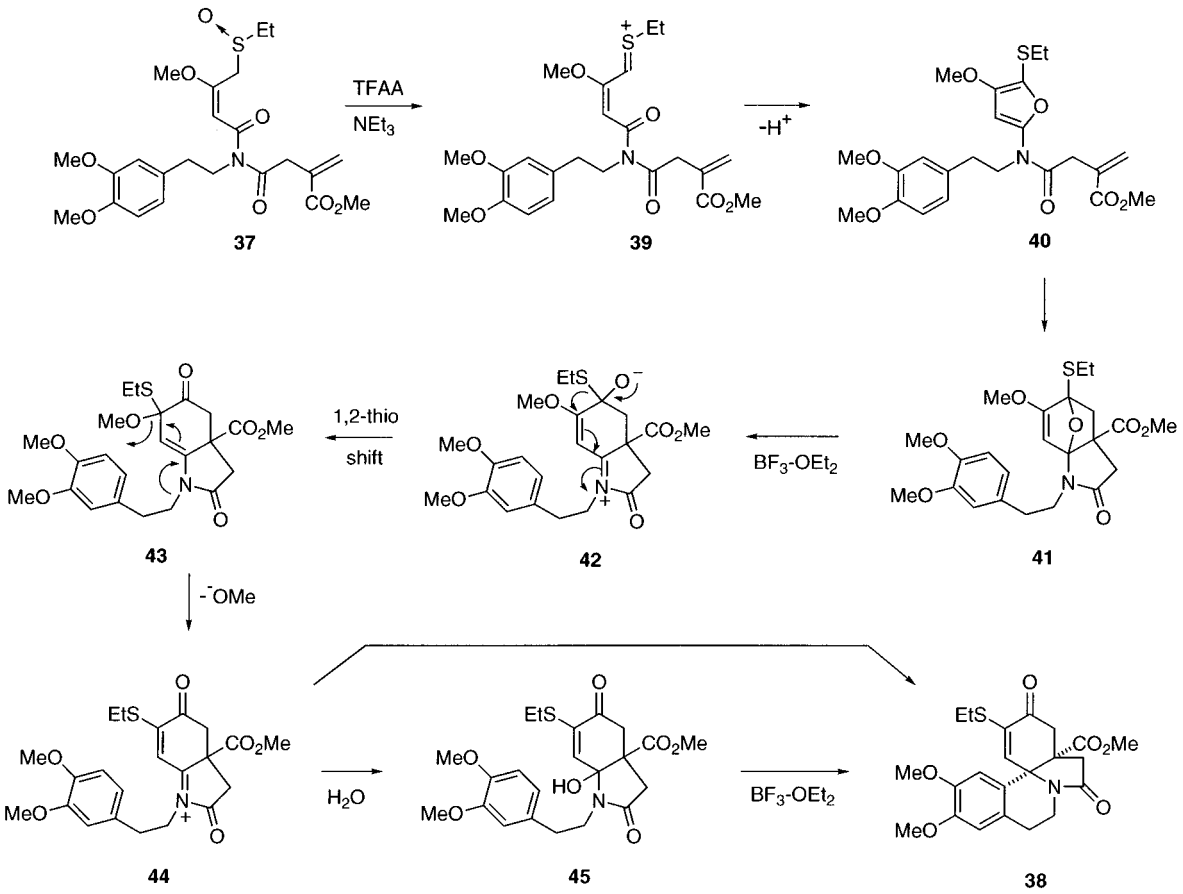
(30) Jones, G. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 2, p 438.

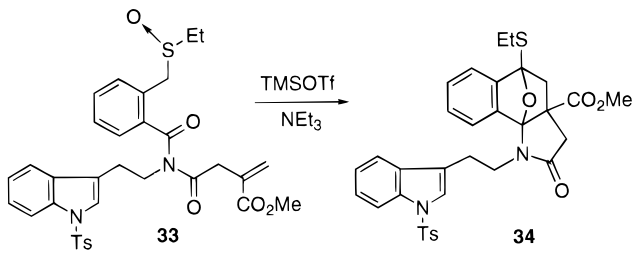
Scheme 5



suggesting that only highly activated aromatic rings are capable of undergoing the Mannich cyclization reaction.[30]

The synthesis of indoles bearing substituents at the 2- and 3-positions has been of interest for many years due to the large number of biologically active natural products having this substitution pattern.[31] Consequently, we decided to investigate the Pummerer reaction of imido sulfoxide **29** where an indolyl tether has been placed on the amide nitrogen as a method for generating highly functionalized indoles. Surprisingly, subjection of **29** to the standard Pummerer conditions failed to provide any product derived from an intramolecular cycloaddition across the acrylate π-bond. Instead, a 5:1-mixture of the unexpected tetracyclic fused indoles **31** (58%) and **32** (11%) was obtained. Indole **31** was readily converted to **32** upon heating in the presence of acetic anhydride. The mechanism of this unusual reaction has not been unequivocally established, but one possibility involves formation of the expected isobenzofuran derivative which undergoes preferential [4 + 2]-cycloaddition across the indole π-bond to give **30**. Cycloadduct **30** proceeds on to give **31**/**32** via oxabicyclic ring opening as outlined in Scheme 4. There are a few examples reported in the literature where the indole ring can function as a dienophile in intramolecular Diels–Alder chemistry,[32,33] thereby providing some precedent for the key step in this cycloaddition.

Interestingly, when the corresponding *N*-tosyl imido sulfoxide **33** was exposed to TMSOTf/NEt_3, cycloadduct **34** derived from the more traditional cyclization–cycloaddition pathway was isolated in 71% yield. The Pummerer reaction of **33** using Ac_2O/*p*-TsOH, however, led to a complex mixture of products which resisted



characterization. All of our attempts to convert **34** into a benzoerythrinane derivative were unsuccessful, and we abandoned further work with this system. At the moment, we have no satisfactory explanation to account for why the isobenzofuran derived from the NH-indole **29** prefers to react across the indole π-bond whereas the related *N*-tosyl amide **33** undergoes cycloaddition across

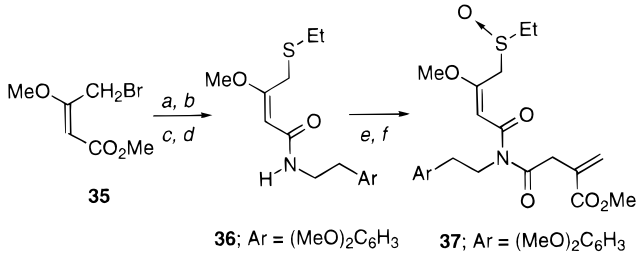
(31) Gilchrist, T. L. *Heterocyclic Chemistry*; Pitman: London, 1981.

(32) Kraus, G. A.; Raggon, J.; Thomas, P. J.; Bougie, D. *Tetrahedron Lett.* **1988**, *29*, 5605. Kraus, G. A.; Bougie, D.; Jacobsen, R. A.; Su, Y. *J. Org. Chem.* **1989**, *54*, 2425. Benson, S. C.; Li, J. H.; Snyder, J. K. *J. Org. Chem.* **1992**, *57*, 5285.

(33) Corsico Coda, A.; Grünanger, P.; Vernesi, G. *Tetrahedron Lett.* **1966**, 2911. Caramella, P.; Cellerino, G.; Corsico Coda, A.; Invernizzi, A. G.; Grünanger, P.; Houk, K. N.; Albini, F. M. *J. Org. Chem.* **1976**, *41*, 3349. Caramella, P. *Tetrahedron Lett.* **1968**, 743. Caramella, P.; Cellerino, G.; Grünanger, P.; Albini, F. M.; Cellerino, M. R. *Tetrahedron* **1978**, *34*, 3545. Caramella, P.; Cellerino, G.; Houk, K. N.; Albini, F. M.; Santiago, C. *J. Org. Chem.* **1978**, *43*, 3006. Caramella, P.; Corsico Coda, A.; Corsaro, A.; Monte, D. D.; Albini, F. M. *Tetrahedron* **1982**, *38*, 173. Hassner, A.; Murthy, K. S. K.; Padwa, A.; Chiacchio, U.; Dean, D. C.; Schoffstall, A. M. *J. Org. Chem.* **1989**, *54*, 5277. Dehaen, W.; Hassner, A. *J. Org. Chem.* **1991**, *56*, 896. Yin, H.; Franck, R. W.; Chen, S. L.; Quigley, G. J.; Todaro, L. *J. Org. Chem.* **1992**, *57*, 644.

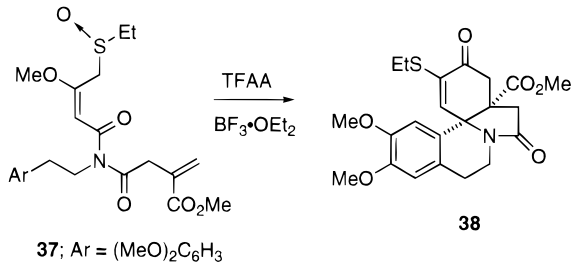
the acrylate π-bond. The insight gained from these experiments is that the last step of the triple cascade process is markedly dependent on the nature of the π-aromatic tethered onto the amide nitrogen atom.

At this point, we decided to undertake a synthesis of (±)-erysotramidine (**2**)[1] in order to test the viability of the triple cascade process as an entry into the erythrinane alkaloid family. The requisite starting imido sulfoxide **37**, possessing both a dienophilic and diactivated aromatic π-tether, was efficiently synthesized from the known allylic bromide **35**.[34] Displacement of the bromide with ethanethiol/KOH followed by ester hydrolysis and subsequent conversion of the resulting acid to amide **36** was accomplished in 54% overall yield. Standard acylation and oxidation steps furnished the desired sulfoxide **37** in 82% yield. We found it most effective to trigger the cyclization reaction by adding trifluoroacetic anhydride to a solution of sulfoxide **37** and 2 equiv of triethylamine at −78 °C. The starting sulfoxide was consumed immediately upon addition of the Pummerer promoter. After addition of 3 equiv of $BF_3 \cdot OEt_2$ and gradual warming of the reaction to reflux, compound **38** was obtained as a single diastereomer in 83% yield. The cis A/B ring fusion present in **38** was unequivocally established by an X-ray crystallographic analysis[35] and is identical to the stereochemical relationship found in the naturally occurring Erythrina alkaloids.[26]



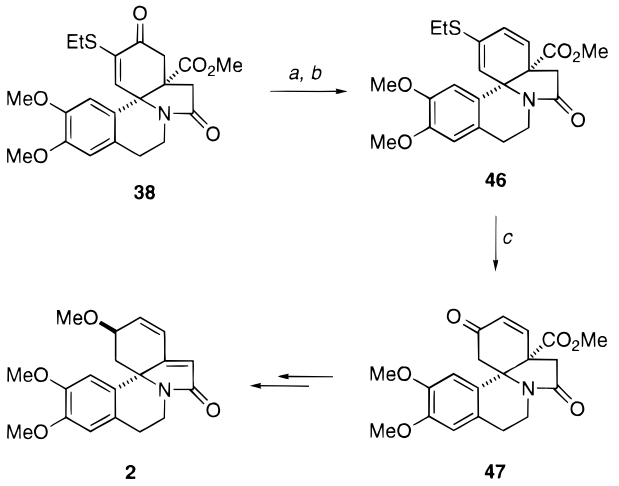
Reagents: (a) EtSH, KOH; (b) KOTMS; (c) 2 N HCl; (d) 1,1'-carbonyldiimidazole, $(MeO)_2C_6H_3CH_2CH_2NH_2$; (e) $ClCOCH_2C(CO_2Me)=CH_2$; (f) $NaIO_4$

The conversion of **37** into **38** is believed to follow the pathway outlined in Scheme 5. The initially formed α-thiocarbocation intermediate generated from the Pummerer reaction of **37** is intercepted by the adjacent imido carbonyl to produce the α-amido substituted furan **40**.



This transient intermediate undergoes a subsequent intramolecular Diels−Alder cycloaddition across the tethered π-bond to furnish cycloadduct **41**. Nitrogen-assisted ring opening of the oxabicyclic bridge results in the formation of zwitterionic intermediate **42** which undergoes a 1,2-thioethyl shift followed by methoxide ion ejection. Cyclization of the diactivated aromatic tether onto *N*-acyliminium ion **44** ultimately provides the tetracyclic amide **38**. By carrying out the reaction for shorter periods of time, it was possible to isolate N,O-ketal **45**. This compound arises by addition of water to iminium ion **44** and was independently converted to **38** when treated with $BF_3 \cdot OEt_2$.

With a supply of **38** in hand, this enone was converted into the corresponding vinyl triflate[36] which, in turn, was subjected to a palladium-catalyzed formate reduction to furnish diene **46**.[37] This thio-substituted diene was subsequently transformed into ketone **47** via a titanium-mediated hydrolysis.[38] The present sequence constitutes a formal synthesis of (±)-erysotramidine (**2**) based on the successful conversion of **47** into **2** by Tsuda and coworkers.[39]



Reagents: (a) KH, $PhNTf_2$, THF, 70%; (b) $(PPh_3)_2PdCl_2$, NEt_3, HCO_2H, DMF, 91%; (c) $TiCl_4$, AcOH, H_2O, 54%

In conclusion, the ready conversion of imido sulfoxide **37** into the azapolyheterocycle **38** represents an efficient and novel approach toward the erythrinane skeleton in which the spirocyclic ABC ring skeleton is assembled in a single operation. The key step in this transformation involves the generation of a vinylogous *C*-acyliminium ion intermediate by fragmentation of a suitable Diels−Alder cycloadduct. This triple cascade process is applicable toward the preparation of ring homologues of the Erythrina skeleton by simply varying the tether length of the starting sulfoxides. Further work in this area and the application of this methodology to other furano systems is in progress and will be reported at a later date.

Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Unless otherwise noted, all reactions were performed in flame-dried glassware under an atmosphere of dry nitrogen. Solutions were evaporated under reduced pressure with a rotary evaporator, and the

(34) Jones, R. C. F.; Bates, A. D. *Tetrahedron Lett.* **1986**, *27*, 5285.
(35) The authors have deposited coordinates for structure **38** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U. K.
(36) McCague, R. *Tetrahedron: Asymmetry* **1990**, *1*, 97.
(37) Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1984**, *42*, 4821.
(38) Mukaiyama, T.; Kamio, K.; Kobayashi, S.; Takei, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3723.

residue was chromatographed on a silica gel column using an ethyl acetate−hexane mixture as the eluent unless specified otherwise.

General Procedure for the Tandem Pummerer Cyclization Diels−Alder Cycloaddition Sequence. A mixture containing 10 mL of xylene, 0.5 mL of acetic anhydride, and 5 mg of *p*-toluenesulfonic acid was heated at reflux under argon. To this mixture was added dropwise a solution of 0.5 mmol of the appropriate sulfoxide in 3 mL of solvent via syringe over a 20 min period. After the addition was complete, the solution was heated at reflux for an additional 10 min until no sulfoxide was detected by TLC. The mixture was concentrated under reduced pressure, and the crude residue was purified by flash silica gel chromatography.

***N*-(3,4-Dimethoxyphenethyl)-2-[(ethylthio)methyl]-benzamide.** To a stirred suspension containing 4.9 g (25 mmol) of 2-[(ethylthio)methyl]benzoic acid (**10**) in 50 mL of benzene was added 6.0 g (50 mmol) of thionyl chloride. After stirring at rt for 1 h, the solution was concentrated under reduced pressure. The resulting oil was dissolved in 20 mL of CH_2Cl_2, and this mixture was added dropwise to a solution containing 13.6 g (75 mmol) of 3,4-dimethoxyphenylethylamine in 50 mL of CH_2Cl_2 at 0 °C under argon. After stirring at rt for 2 h, the mixture was washed successively with 5% HCl, a saturated $NaHCO_3$ solution, and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography and recrystallized from ethyl acetate/hexane to give 7.8 g (88%) of *N*-(3,4-dimethoxyphenethyl)-2-[(ethylthio)methyl]benzamide as a colorless solid, mp 96−97 °C; IR (KBr) 3317, 1633, 1543, 1515, 1262 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.22 (t, 3H, J = 7.5 Hz), 2.42 (q, 2H, J = 7.5 Hz), 2.91 (t, 2H, J = 7.0 Hz), 3.70 (dt, 2H, J = 7.0 and 7.0 Hz), 3.85 (s, 8H), 6.56 (brs, 1H), 6.79−6.83 (m, 3H), 7.23−7.44 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 25.8, 33.5, 35.0, 41.0, 55.7, 55.8, 111.3, 111.9, 120.6, 127.1, 128.1, 129.7, 130.5, 131.3, 135.8, 136.3, 147.5, 148.9, 169.2. Anal. Calcd for $C_{20}H_{25}NO_3S$: C, 66.82; H, 7.01; N, 3.90. Found: C, 66.68; H, 6.97; N, 3.84.

***N*-But-3-enoyl-*N*-(3,4-dimethoxyphenethyl)-2-[(ethylthio)methyl]benzamide.** A mixture containing 1.8 g (5 mmol) of the above amide, 0.78 g (7.5 mmol) of but-3-enoyl chloride, and 4.0 g of powdered molecular sieves (4 Å) in 30 mL of CH_2Cl_2 was stirred at rt for 24 h. The reaction mixture was filtered through a pad of silica gel, the solvent was removed under reduced pressure, and the resulting oil was purified by flash silica gel chromatography to give 1.8 g (82%) of *N*-but-3-enoyl-*N*-(3,4-dimethoxyphenethyl)-2-[(ethylthio)-methyl]benzamide as a colorless oil; IR (neat) 1691, 1654, 1515, 1354, 1258, 1141 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.20 (t, 3H, J = 7.5 Hz), 2.42 (q, 2H, J = 7.5 Hz), 2.86 (t, 2H, J = 7.0 Hz), 3.31 (d, 2H, J = 7.0 Hz), 3.79 (s, 3H), 3.83 (s, 3H), 3.83−3.89 (m, 2H), 3.86 (s, 2H), 5.02−5.16 (m, 2H), 5.88−6.01 (m, 1H), 6.56−6.76 (m, 3H), 7.13−7.42 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 25.6, 32.8, 34.1, 42.9, 47.8, 55.4, 55.5, 110.9, 111.7, 118.0, 120.6, 126.8, 127.5, 130.3, 130.5, 130.7, 135.1, 136.9, 147.3, 148.5, 172.9, 174.4; HRMS (FAB) Calcd for $C_{24}H_{30}NO_4S$ (M + H) 428.1896. Found: 428.1887.

***N*-But-3-enoyl-*N*-(3,4-dimethoxyphenethyl)-2-[(ethylsulfinyl)methyl]benzamide (11).** A 1.7 g (4 mmol) sample of the above sulfide was oxidized in the manner outlined previously[21] to give 1.8 g of sulfoxide **11** (95%) as a colorless oil; IR (neat) 1686, 1654, 1509, 1451, 1349, 1023 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.33 (t, 3H, J = 7.5 Hz), 2.60−2.92 (m, 4H), 3.38 (d, 2H, J = 7.0 Hz), 3.80 (s, 3H), 3.84 (s, 3H), 3.82−3.99 (m, 4H), 5.04−5.17 (m, 2H), 5.86−5.97 (m, 1H), 6.57−6.77 (m, 3H), 7.22−7.52 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 6.5, 34.2, 42.7, 45.4, 48.1, 55.0, 55.5, 55.6, 111.0, 112.0, 118.5, 120.8, 127.8, 127.9, 130.4, 130.7, 131.2, 132.2, 135.1, 147.7, 148.6, 172.8, 174.3; HRMS (FAB) Calcd for $C_{24}H_{30}NO_5S$ (M + H): 444.1845. Found: 444.1863.

5-Acetoxy-1-(3,4-dimethoxyphenethyl)-2,3-dihydro-1*H*-benzo[*g*]indol-2-one (15) was obtained from 217 mg (0.5 mmol) of sulfoxide **11** in 76% yield as a white solid, mp 168−169 °C (ethanol); IR (KBr) 1760, 1698, 1513, 1199, 1158 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.45 (s, 3H), 2.99 (t, 2H, J = 8.0 Hz), 3.56 (s, 2H), 3.82 (s, 3H), 3.83 (s, 3H), 4.41 (t, 2H, J = 8.0 Hz), 6.74−6.82 (m, 3H), 7.21 (s, 1H), 7.51−7.60 (m, 2H), 7.88 (dd, 1H, J = 8.0 and 1.0 Hz), 8.29 (dd, 1H, J = 8.0 and 1.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7, 34.5, 36.0, 43.4, 55.5, 55.6, 111.2, 111.8, 115.0, 119.9, 120.5, 120.9, 121.1, 122.3, 125.6, 126.2, 126.7, 130.0, 136.8, 141.8, 147.6, 148.7, 169.5, 175.8. Anal. Calcd for $C_{24}H_{23}NO_5$: C, 71.10; H, 5.72; N, 3.45. Found: C, 71.09; H, 5.71; N, 3.43.

***N*-But-3-enyl-2-[(ethylthio)methyl]benzamide.** To a stirred suspension containing 4.9 g (25 mmol) of 2-[(ethylthio)-methyl]benzoic acid (**10**) in 50 mL of benzene was added 6.0 g (50 mmol) of thionyl chloride. After stirring at rt for 1 h, the solution was concentrated under reduced pressure. The crude acid chloride was dissolved in 20 mL of CH_2Cl_2, and this mixture was added dropwise to a solution containing 5.3 g (75 mmol) of but-3-enylamine in 50 mL of CH_2Cl_2 at 0 °C under argon. After stirring at rt for 2 h, the mixture was washed successively with 5% HCl, a saturated $NaHCO_3$ solution, and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography and recrystallized from ethyl acetate/hexane to give 4.7 g (76%) of *N*-but-3-enyl-2-[(ethylthio)methyl]benzamide as a colorless solid, mp 48−49 °C; IR (KBr) 3291, 1637, 1537, 1317, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.26 (t, 3H, J = 7.5 Hz), 2.39 (dt, 2H, J = 7.0 and 7.0 Hz), 2.52 (q, 2H, J = 7.0 Hz), 3.54 (dt, 2H, J = 7.0 and 7.0 Hz), 3.92 (s, 2H), 5.09−5.19 (m, 2H), 5.78−5.91 (m, 1H), 6.53 (brs, 1H), 7.25−7.49 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 25.8, 33.5, 33.6, 38.9, 117.0, 127.0, 128.1, 129.6, 130.4, 135.2, 135.7, 136.4, 169.2. Anal. Calcd for $C_{14}H_{19}NOS$: C, 67.43; H, 7.68; N, 5.62. Found: C, 67.51; H, 7.75; N, 5.61.

***N*-But-3-enyl-*N*-(3,4-dimethoxyphenylacetyl)-2-[(ethylthio)methyl]benzamide.** A mixture of 1.3 g (5 mmol) of the above amide, 1.6 g (7.5 mmol) of 3,4-dimethoxyphenylacetyl chloride, and 4.0 g of powdered molecular sieves (4 Å) in 30 mL of CH_2Cl_2 was stirred at rt for 24 h. The reaction mixture was filtered through a pad of silica gel, the solvent was removed under reduced pressure, and the resulting crude oil was purified by flash silica gel chromatography to give 1.8 g (84%) of *N*-but-3-enyl-*N*-(3,4-dimethoxyphenylacetyl)-2-[(ethylthio)methyl]benzamide as a colorless oil; IR (neat) 1691, 1651, 1590, 1509, 1448 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.21 (t, 3H, J = 7.5 Hz), 2.31 (dt, 2H, J = 7.0 and 7.0 Hz), 2.45 (q, 2H, J = 7.5 Hz), 3.72 (t, 2H, J = 7.0 Hz), 3.83 (s, 2H), 3.85 (s, 6H), 3.92 (s, 2H), 4.97−5.03 (m, 2H), 5.60−5.74 (m, 1H), 6.70 (d, 1H, J = 8.0 Hz), 6.72 (s, 1H), 6.81 (d, 1H, J = 8.0 Hz), 7.15−7.42 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 25.9, 32.9, 33.0, 44.3, 45.8, 55.8, 55.9, 111.1, 112.6, 117.2, 121.6, 127.1, 127.9, 130.7, 130.9, 134.7, 135.4, 137.7, 148.0, 148.8, 173.4, 175.2; HRMS (FAB) Calcd for $C_{24}H_{29}NO_4S$: 427.1817. Found: 427.1809.

***N*-But-3-enyl-*N*-(3,4-dimethoxyphenylacetyl)-2-[(ethylsulfinyl)methyl]benzamide (16).** To a solution containing a 1.7 g (4 mmol) sample of the above sulfide in 20 mL of methanol was added 0.95 g (4.4 mmol) of sodium periodate at 0 °C. To this mixture was added 3 mL of water, and the solution was stirred for 5 h at rt. After the addition of water, the aqueous layer was extracted with CH_2Cl_2, and the combined organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash silica gel chromatography to give 1.7 g (95%) of sulfoxide **16** as a colorless oil; IR (neat) 1684, 1651, 1511, 1445, 1259 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.36 (t, 3H, J = 7.5 Hz), 2.34 (dt, 2H, J = 7.0 and 7.0 Hz), 2.61−2.85 (m, 2H), 3.72−3.79 (m, 2H), 3.82 (s, 3H), 3.83 (s, 2H), 3.85 (s, 3H), 3.99 (d, 1H, J = 13.0 Hz), 4.20 (d, 1H, 13.0 Hz), 4.99−5.05 (m, 2H), 5.61−5.74 (m, 1H), 6.67−6.79 (m, 3H), 7.17 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 6.8, 33.2, 44.3, 45.7, 45.9, 55.3, 55.8, 55.9, 111.1, 112.4, 117.5, 121.4, 126.6, 128.2, 128.3, 130.8, 131.6, 132.6, 134.5, 135.6, 148.1, 148.9, 173.3, 175.1; HRMS (FAB) Calcd for $C_{24}H_{30}NO_5S$ (M + H): 444.1845. Found: 444.1845.

5-Acetoxy-1-(3,4-dimethoxyphenylacetyl)-2,3-dihydro-1*H*-benzo[*g*]indole (17) was obtained from 217 mg (0.5

mmol) of sulfoxide **16** in 78% yield as a white solid upon treatment with Ac_2O, mp 178−179 °C (ethanol); IR (KBr) 1758, 1653, 1509, 1397, 1201 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.45 (s, 3H), 3.11 (brs, 2H), 3.85 (s, 3H), 3.87 (s, 3H), 3.91 (s, 2H), 4.25 (brs, 2H), 6.78−6.98 (m, 3H), 7.16 (s, 1H), 7.42−7.55 (m, 2H), 7.82−7.90 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 30.6, 43.2, 51.7, 55.9, 111.3, 111.8, 115.1, 120.9, 121.5, 125.3, 125.8, 125.9, 126.5, 127.3, 131.2, 136.6, 144.8, 148.0, 149.2, 169.6. Anal. Calcd for $C_{24}H_{23}NO_5$: C, 71.10; H, 5.72; N, 3.45. Found: C, 70.84; H, 5.75; N, 3.40.

***N*-(3,4-Dimethoxyphenethyl)-*N*-[3-(methoxycarbonyl)-but-3-enoyl]-2-[(ethylthio)methyl]benzamide.** A mixture containing 1.8 g (5.0 mmol) of *N*-(3,4-dimethoxyphenethyl)-2-[(ethylthio)methyl]benzamide, 1.2 g (7.5 mmol) of 3-(methoxycarbonyl)but-3-enoyl chloride (prepared from the corresponding carboxylic acid),[40] and 4.0 g of powdered molecular sieves (4 Å) in 30 mL of CH_2Cl_2 was stirred at rt for 24 h. The reaction mixture was filtered through a pad of silica gel, and the filtrate was washed with an aqueous $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 and was concentrated under reduced pressure. The crude oil was purified by flash silica gel chromatography to give 2.0 g (83%) of *N*-(3,4-dimethoxyphenethyl)-*N*-[3-(methoxycarbonyl)but-3-enoyl]-2-[(ethylthio)methyl]benzamide as a colorless oil; IR (neat) 1718, 1691, 1659, 1515, 1440, 1349 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.20 (t, 3H, J = 7.5 Hz), 2.44 (q, 2H, J = 7.5 Hz), 2.84 (t, 2H, J = 8.0 Hz), 3.72 (s, 2H), 3.78 (s, 6H), 3.81−3.88 (m, 2H), 3.83 (s, 3H), 3.85 (s, 2H), 5.67 (s, 1H), 6.32 (s, 1H), 6.54 (s, 1H), 6.58 (d, 1H, J = 8.0 Hz), 6.73 (d, 1H, J = 8.0 Hz), 7.20−7.42 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 25.9, 33.0, 34.2, 42.1, 48.4, 52.0, 55.7, 55.8, 111.1, 112.0, 120.8, 127.0, 127.6, 128.2, 130.5, 130.7, 130.8, 134.7, 135.1, 137.1, 147.5, 148.8, 166.6, 173.4, 173.7; HRMS (FAB) Calcd for $C_{26}H_{31}NO_6S$: 485.1872. Found: 485.1865.

***N*-(3,4-Dimethoxyphenethyl)-*N*-[3-(methoxycarbonyl)-but-3-enoyl]-2-[(ethylsulfinyl)methyl]benzamide (18).** A 1.9 g (4 mmol) sample of the above sulfide was oxidized in the manner previously outlined[21] to give sulfoxide **18** (93%) as a colorless oil; IR (neat) 1714, 1684, 1656, 1512, 1351, 1260, 1149 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.35 (t, 3H), 2.65−2.89 (m, 4H), 3.63 (s, 2H), 3.77 (s, 3H), 3.78 (s, 3H), 3.84 (s, 3H), 3.81−3.92 (m, 4H), 5.70 (s, 1H), 6.32 (s, 1H), 6.56 (s, 1H), 6.59 (d, 1H, J = 8.0 Hz), 6.74 (d, 1H, J = 8.0 Hz), 7.28−7.53 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 6.6, 34.3, 41.8, 45.5, 48.6, 51.9, 54.9, 55.6, 55.7, 111.1, 112.1, 120.9, 128.0, 128.1, 128.4, 130.5, 130.6, 131.3, 132.2, 134.4, 135.1, 147.6, 148.8, 166.6, 173.2, 173.6; HRMS (FAB) Calcd for $C_{26}H_{32}NO_7S$ (M + H): 502.1899. Found: 502.1892.

Methyl 1-(3,4-Dimethoxyphenethyl)-2,5-dioxo-9b-(ethylthio)-1,2,3,4,5,9b-hexahydrobenzo[*g*]indole-3a-carboxylate (21). The reaction of 251 mg (0.5 mmol) of sulfoxide **18** with acetic anhydride following the general procedure[21] afforded a 2:1-mixture of **21** and methyl 1-(3,4-dimethoxyphenethyl)-2,5-dioxo-9b-hydroxy-1,2,3,4,5,9*b*-hexahydrobenzo[*g*]indole-3*a*-carboxylate (**22**). The crude mixture was separated by flash silica gel chromatography to furnish 113 mg (47%) of N,S-ketal **21** and 50 mg (23%) of N,O-ketal **22**.

N,S-Ketal **21**: white solid, mp 149−150 °C (ethanol); IR (KBr) 1740, 1709, 1697, 1593, 1575, 1262 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.08 (t, 3H, J = 7.5 Hz), 2.08−2.41 (m, 4H), 2.63 (d, 1H, J = 16.5 Hz), 2.73 (d, 1H, J = 16.5 Hz), 3.31−3.52 (m, 2H), 3.57 (s, 3H), 3.73 (s, 3H), 3.77 (s, 3H), 3.78−3.89 (m, 2H), 6.24 (d, 1H, J = 8.0 Hz), 6.31 (s, 1H), 6.55 (d, 1H, J = 8.0 Hz), 7.55 (t, 1H, J = 7.5 Hz), 7.71 (t, 1H, J = 7.5 Hz), 8.11 (dd, 1H, J = 7.5 and 1.0 Hz), 8.22 (dd, 1H, J = 7.5 and 1.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 25.8, 33.8, 40.0, 41.0, 44.5, 52.7, 55.5, 55.8, 56.9, 76.4, 110.8, 111.5, 120.6, 127.2, 129.7, 130.1, 131.2, 132.6, 133.3, 135.5, 147.5, 148.5, 170.4, 171.9, 192.5. Anal. Calcd for $C_{26}H_{29}NO_6S$: C, 64.58; H, 6.04; N, 2.90. Found: C, 64.68; H, 6.07; N, 2.87.

N,O-Ketal **22**: white solid, mp 168−169 °C (ethanol); IR (KBr) 3360, 1740, 1698, 1685, 1515, 1397, 1256 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33−2.42 (m, 2H), 2.57 (d, 1H, J = 16.5 Hz), 2.97 (d, 1H, J = 16.5 Hz), 3.30−3.43 (m, 2H), 3.61 (s, 3H), 3.72 (s, 3H), 3.61−3.67 (m, 2H), 3.79 (s, 3H), 4.51 (s, 1H, exchangeable with D_2O), 6.29 (s, 1H), 6.30 (d, 1H, J = 8.0 Hz), 6.56 (d, 1H, J = 8.0 Hz), 7.54 (dd, 1H, J = 7.5 and 7.0 Hz), 7.72 (dd, 1H, J = 7.5 and 7.0 Hz), 7.94−8.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.0, 39.4, 40.6, 45.0, 53.0, 54.4, 55.5, 55.7, 88.6, 110.9, 111.4, 120.5, 126.8, 127.8, 129.6, 130.3, 130.9, 133.8, 138.8, 147.4, 148.5, 172.0, 173.4, 192.5. Anal. Calcd for $C_{24}H_{25}NO_7$: C, 65.59; H, 5.73; N, 3.19. Found: C, 65.43; H, 5.86; N, 3.15.

Methyl 15,16-Dimethoxy-2,8-dioxo-3,4-benzoerythrinane-6-carboxylate (23). A mixture containing 10 mL of toluene, 0.5 mL of acetic anhydride, and 1 mg of *p*-toluenesulfonic acid was heated at reflux under argon. To this mixture was added dropwise a solution of 251 mg (0.5 mmol) of sulfoxide **18** in 3 mL of toluene via syringe over a 15 min period. After the addition was complete, the solution was heated at reflux for an additional 5 min until no sulfoxide was detected by TLC. The mixture was concentrated under reduced pressure, and the residue was dissolved in 10 mL of toluene. To this solution was added 94 mg (0.55 mol) of *p*-TsOH, and the mixture was heated at reflux for 15 min. After removal of the solvent under reduced pressure, the crude residue was purified by flash silica gel chromatography and recrystallized from CH_2Cl_2/hexane to give 147 mg (70%) of **23** as a white solid; mp 257−258 °C; IR (KBr) 1730, 1697, 1690, 1592, 1515, 1413, 1248 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.54 (d, 1H, J = 16.5 Hz), 2.71−2.93 (m, 3H), 2.99 (d, 1H, J = 16.5 Hz), 3.21 (s, 3H), 3.28−3.40 (m, 1H), 3.61−3.65 (m, 1H), 3.64 (s, 3H), 3.87 (s, 3H), 4.52−4.59 (m, 1H), 6.30 (s, 1H), 6.65 (s, 1H), 7.22 (dd, 1H, J = 8.0 and 1.0 Hz), 7.43 (t, 1H, J = 8.0 Hz), 7.54 (t, 1H, J = 8.0 Hz), 8.06 (dd, 1H, J = 8.0 and 1.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.6, 36.2, 40.4, 41.1, 52.0, 53.5, 55.6, 56.0, 66.3, 110.6, 111.1, 125.9, 126.7, 127.2, 128.2, 128.8, 129.9, 134.9, 145.0, 147.8, 148.5, 171.0, 171.2, 194.8. Anal. Calcd for $C_{24}H_{23}NO_6$: C, 68.40; H, 5.50; N, 3.32. Found: C, 68.28; H, 5.58; N, 3.30.

The cyclization of **18** was also carried out using trifluoroacetic anhydride. To a solution of 250 mg (0.5 mmol) of sulfoxide **18** and 101 mg (1.0 mmol) of triethylamine in 20 mL of CH_2Cl_2 was added dropwise 116 mg (0.55 mmol) of trifluoroacetic anhydride at 0 °C. After stirring at rt for 10 min, the mixture was filtered through a plug of silica gel, and the solvent was removed under reduced pressure. The crude product was dissolved in 10 mL of toluene, and after addition of 94 mg (0.55 mmol) of *p*-TsOH, the solution was heated at reflux for 1 h. Removal of the solvent under reduced pressure followed by flash silica gel chromatography provided 147 mg (70%) of **23**. In addition, cycloadduct **13** (R═CO_2Me) was isolated as a colorless oil; IR (KBr) 1726, 1515, 1461, 1400, 1264, 1237 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, 3H, J = 7.5 Hz), 2.31 (d, 1H, J = 12.0 Hz), 2.64−3.07 (m, 7H), 3.31 (s, 3H), 3.57−3.67 (m, 1H), 3.84 (s, 3H), 3.85 (s, 3H), 3.91−4.01 (m, 1H), 6.72−6.80 (m, 3H), 6.98 (dd, 1H, J = 8.0 and 1.0 Hz), 7.27 (t, 1H, J = 8.0 Hz), 7.40 (t, 1H, J = 8.0 Hz), 7.45 (dd, 1H, J = 8.0 and 1.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.1, 24.1, 34.4, 40.8, 43.8, 44.4, 52.3, 55.7, 55.8, 56.7, 92.3, 105.0, 111.1, 112.1, 119.2, 120.7, 121.3, 127.6, 128.8, 131.2, 138.0, 144.3, 147.5, 148.7, 171.2, 176.1; HRMS (FAB) Calcd for $C_{26}H_{29}NO_6SLi$ (M + Li): 490.1876. Found: 490.1879.

***N*-(3,4-Dimethoxyphenethyl)-*N*-[4-(methoxycarbonyl)-pent-4-enoyl]-2-[(ethylthio)methyl]benzamide.** A mixture of 2.2 g (6.0 mmol) of *N*-(3,4-dimethoxyphenethyl)-2-[(ethylthio)methyl]benzamide, 1.6 g (9.0 mmol) of 4-(methoxycarbonyl)pent-4-enoyl chloride (prepared from the corresponding acid),[41] and 6.0 g of powdered molecular sieves (4 Å) in 40 mL of CH_2Cl_2 was stirred at rt for 24 h. The reaction mixture was filtered through a pad of silica gel, and the filtrate was washed with an aqueous $NaHCO_3$ solution. The organic layer

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was dried over Na_2SO_4 and was concentrated under reduced pressure. The crude residue was purified by flash silica gel chromatography to 2.3 g (76%) of *N*-(3,4-dimethoxyphenethyl)-*N*-[4-(methoxycarbonyl)pent-4-enoyl]-2-[(ethylthio)methyl]benzamide as a colorless oil; IR (neat) 1714, 1691, 1652, 1510, 1438, 1348 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.20 (t, 3H, J = 7.5 Hz), 2.44 (q, 2H, J = 7.5 Hz), 2.64 (q, 2H, J = 7.2 Hz), 2.78−2.88 (m, 4H), 3.73 (s, 2H), 3.80 (s, 3H), 3.81−3.88 (m, 2H), 3.84 (s, 6H), 5.52 (s, 1H), 6.12 (s, 1H), 6.57−6.63 (m, 2H), 6.75 (d, 1H, J = 8.1 Hz), 7.14−7.43 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 25.9, 27.4, 33.0, 34.4, 37.4, 48.0, 51.7, 55.7, 55.8, 111.1, 111.9, 120.8, 125.7, 127.0, 127.6, 130.4, 130.7, 130.8, 135.5, 137.1, 138.9, 147.5, 148.8, 167.0, 173.2, 175.5; HRMS Calcd for $C_{27}H_{33}NO_6S$: 499.2028. Found: 499.2027.

***N*-(3,4-Dimethoxyphenethyl)-*N*-[4-(methoxycarbonyl)-pent-4-enoyl]-2-[(ethylsulfinyl)methyl]benzamide (19).** A 1.7 g (3.4 mmol) sample of the above sulfide was oxidized in the standard manner[21] to give sulfoxide **19** (90%) as a colorless oil; IR (neat) 1713, 1691, 1656, 1512, 1445, 1351 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, 3H, J = 7.5 Hz), 2.61−2.89 (m, 8H), 3.74 (s, 3H), 3.80 (s, 3H), 3.84 (s, 3H), 3.86−3.96 (m, 4H), 5.56 (s, 1H), 6.17 (s, 1H), 6.58−6.64 (m, 2H), 6.75 (d, 1H, J = 8.1 Hz), 7.21−7.49 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 6.6, 27.6, 34.5, 37.1, 45.5, 48.2, 51.8, 55.2, 55.7, 55.8, 111.1, 112.1, 121.0, 126.0, 127.8, 128.0, 130.5, 130.6, 131.2, 132.3, 135.5, 138.7, 147.7, 148.8, 167.0, 173.0, 175.4; HRMS (FAB) Calcd for $C_{27}H_{33}NO_7SLi$ (M + Li): 522.2138. Found: 522.2159.

Pummerer-Induced Reaction of Sulfoxide 19. A mixture of 10 mL of toluene and 0.5 mL of acetic anhydride containing 5 mg of *p*-toluenesulfonic acid was heated at reflux under argon. To this solution was added dropwise a solution of 257 mg (0.5 mmol) of sulfoxide **19** in 3 mL of toluene via syringe over a 10 min period. After the addition was complete, the solution was heated at reflux for an additional 5 min until no sulfoxide was detected by TLC. The mixture was concentrated under reduced pressure, and the residue was dissolved in 10 mL of toluene and, after addition of 85 mg (0.5 mmol) of *p*-TsOH, was heated at reflux for 30 min. After evaporation of the solvent under reduced pressure, the crude residue was purified by flash silica gel chromatography and recrystallized from CH_2Cl_2/hexane to give 144 mg (66%) of **25** as a white solid, mp 170−171 °C; IR (neat) 1727, 1687, 1656, 1512, 1410, 1262 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.76 (t, 2H, J = 7.5 Hz), 2.45−2.64 (m, 3H), 2.71 (d, 1H, J = 18.6 Hz), 2.75−2.84 (m, 1H), 3.03−3.12 (m, 1H), 3.49 (s, 3H), 3.52 (s, 3H), 3.53 (d, 1H, J = 18.6 Hz), 3.86 (s, 3H), 5.32−5.39 (m, 1H), 6.16 (s, 1H), 6.66 (s, 1H). 7.31 (dd, 1H, J = 7.8 and 0.9 Hz), 7.48 (t, 1H, J = 7.8 Hz), 7.67 (t, 1H, J = 7.8 Hz), 8.15 (dd, 1H, J = 7.8 and 0.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.7, 29.1, 29.9, 40.8, 45.2, 52.4, 52.5, 55.8, 55.9, 66.1, 111.5, 113.0, 125.4, 125.9, 126.2, 128.5, 130.3, 131.9, 136.0, 145.8, 146.8, 148.2, 171.3, 172.1, 195.4. Anal. Calcd for $C_{25}H_{25}NO_6$: C, 68.95; H, 5.79; N, 3.22. Found: C, 69.00; H, 5.76; N, 3.16.

The Pummerer reaction of **19** was also carried out using trifluoroacetic anhydride. To a solution of 257 mg (0.5 mmol) of sulfoxide **19** and 0.1 g (1.0 mmol) of triethylamine in 10 mL of CH_2Cl_2 was added dropwise 146 mg (0.7 mmol) of trifluoroacetic anyhydride at 0 °C. After stirring at rt for 5 min, the mixture was filtered through a plug of silica gel, and the solvent removed under reduced pressure. The crude product was dissolved in 10 mL of toluene, and, after addition of 85 mg (0.5 mmol) of *p*-TsOH, the solution was heated at reflux for 1 h. Evaporation of the solvent under reduced pressure followed by flash silica gel chromatography provided 139 mg (64%) of **25**. In addition, cycloadduct **24** was isolated as a colorless oil; IR (neat) 1734, 1668, 1515, 1461, 1397, 1345 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, 3H, J = 7.5 Hz), 2.18 (d, 1H, J = 12 Hz), 2.20−2.58 (m, 2H), 2.47 (d, 1H, J = 12 Hz), 2.63−2.88 (m, 5H), 3.07 (dt, 1H, J = 12 and 5.1 Hz), 3.39 (dt, 1H, J = 12 and 5.1 Hz), 3.45 (s, 3H), 3.80 (s, 3H), 3.81 (s, 3H), 4.09−4.19 (m, 1H), 6.62−6.74 (m, 3H), 7.20−7.37 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.4, 24.1, 29.4, 30.2, 34.5, 47.2, 48.4, 51.9, 53.9, 55.6, 55.7, 89.9, 99.4, 111.0, 111.9, 119.7, 120.4, 122.4, 127.1, 128.4, 132.0, 140.1, 144.8, 147.2, 148.6, 170.8, 171.7; HRMS (FAB) Calcd for $C_{27}H_{31}NO_6SLi$ (M + Li): 504.2032. Found: 504.2049.

***N*-Phenethyl-2-[(ethylthio)methyl]benzamide.** To a stirred suspension containing 3.0 g (15.2 mmol) of 2-[(ethylthio)methyl]benzoic acid (**10**)[22] in 30 mL of benzene was added 5.4 g (45.4 mmol) of thionyl chloride. After stirring at rt for 2 h, the solution was concentrated under reduced pressure. The crude acid chloride was dissolved in 25 mL of CH_2Cl_2, and 3.86 g (31.9 mmol) of phenethylamine was added to the solution at 0 °C over a 10 min period. After stirring at rt for 2 h, the mixture was poured into water and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography and recrystallized from ethyl acetate/hexane to give 3.9 g (86%) of *N*-phenethyl-2-[(ethylthio)methyl]benzamide as a white solid, mp 79−80 °C; IR (neat) 3296, 1631, 1538, 1445, 1311 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.21 (t, 3H, J = 7.5 Hz), 2.43 (q, 2H, J = 7.5 Hz), 2.96 (t, 2H, J = 6.9 Hz), 3.72 (q, 2H, J = 6.9 Hz), 3.84 (s, 2H), 6.55 (brs, 1H), 7.21−7.42 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.4, 25.9, 33.6, 35.5, 41.0, 126.4, 127.2, 128.2, 128.5, 128.7, 129.8, 130.6, 135.8, 136.3, 138.8, 169.9. Anal. Calcd for $C_{18}H_{21}NOS$: C, 72.21; H, 7.08; N, 4.68. Found: C, 72.21; H, 7.09; N, 4.73.

***N*-Phenethyl-*N*-[3-(methoxycarbonyl)but-3-enoyl]-2-[(ethylthio)methyl]benzamide.** A mixture of 2.1 g (7.0 mmol) of the above amide, 1.7 g (10.5 mmol) of 3-(methoxycarbonyl)but-3-enoyl chloride,[40] and 5.5 g of powdered molecular sieves (4 Å) in 40 mL of CH_2Cl_2 was stirred at rt for 24 h. The reaction mixture was filtered through a pad of silica gel, and the filtrate was washed twice with an aqueous $NaHCO_3$ solution. The organic layer was dried over $MgSO_4$ and was concentrated under reduced pressure to give 2.1 g (69%) of *N*-phenethyl-*N*-[3-(methoxycarbonyl)but-3-enoyl]-2-[(ethylthio)methyl]benzamide as a colorless oil; IR (neat) 1721, 1692, 1660, 1441, 1350, 1207 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, 3H, J = 7.5 Hz), 2.42 (q, 2H, J = 7.5 Hz), 2.91 (t, 2H, J = 7.2 Hz), 3.71 (s, 2H), 3.77 (s, 3H), 3.81−3.85 (m, 4H), 5.66 (s, 1H), 6.32 (s, 1H), 7.05 (d, 2H, J = 6.6 Hz), 7.17−7.43 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 25.9, 33.0, 34.7, 42.1, 48.2, 52.0, 126.4, 127.1, 127.6, 128.2, 128.4, 128.8, 130.6, 130.7, 134.7, 135.1, 137.2, 138.3, 166.7, 173.4, 173.7; HRMS Calcd for $C_{24}H_{27}NO_4S$: 425.1661. Found: 425.1659.

***N*-Phenethyl-*N*-[3-(methoxycarbonyl)but-3-enoyl]-2-[(ethylsulfinyl)methyl]benzamide (26).** A 1.7 g (4.0 mmol) sample of the above sulfide was oxidized in the standard manner[21] to give sulfoxide **26** (91%) as a colorless oil; IR (neat) 1718, 1690, 1658, 1442, 1351, 1268 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, 3H, J = 7.5 Hz), 2.62−2.96 (m, 4H), 3.62 (s, 2H), 3.76 (s, 3H), 3.81−3.96 (m, 4H), 5.69 (s, 1H), 6.32 (s, 1H), 7.06 (d, 2H, J = 7.8 Hz), 7.19−7.50 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 6.7, 34.7, 41.8, 45.5, 48.4, 52.0, 55.0, 126.5, 128.0, 128.1, 128.5, 128.6, 129.0, 130.4, 131.3, 132.2, 134.4, 135.2, 138.1, 166.6, 173.2, 173.6; HRMS (FAB) Calcd for $C_{24}H_{27}NO_5SLi$ (M + Li): 448.1770. Found: 448.1790.

Pummerer-Induced Reaction of Sulfoxide 26. A mixture of 10 mL of toluene and 0.5 mL of acetic anhydride containing 5 mg of *p*-toluenesulfonic acid was heated to reflux under argon. To this mixture was added dropwise a solution of 0.21 g (0.47 mmol) of sulfoxide **26** in 3 mL of toluene via syringe over a 10 min period. After the addition was complete, the solution was heated at reflux for an additional 10 min until no sulfoxide was detected by TLC. The mixture was concentrated under reduced pressure, and the crude residue was purified by flash silica gel chromatography and recrystallized from CH_2Cl_2/hexane to afford 65 mg (36%) of N,O-ketal **28** as a white solid, mp 134−135 °C; IR (neat) 3322, 1741, 1688, 1403, 1291, 1205 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.40 (d, 1H, J = 16.5 Hz), 2.41−2.60 (m, 2H), 2.61 (d, 1H, J = 17.1 Hz), 3.01 (d, 1H, J = 17.1 Hz), 3.30 (d, 1H, J = 16.5 Hz), 3.41−3.65 (m, 2H), 3.66 (s, 3H), 4.20 (s, 1H), 6.84−6.87 (m, 2H), 7.11−7.13 (m, 3H), 7.56 (t, 1H, J = 7.8 Hz), 7.78 (t, 1H, J = 7.8 Hz), 7.98−8.05 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.5, 39.5, 40.7, 45.0, 53.2, 54.3, 88.6, 126.4, 127.1, 127.9, 128.4, 128.5, 129.8, 130.9, 134.2, 138.0, 139.0, 172.4, 173.2, 192.5.

Anal. Calcd for $C_{22}H_{21}NO_5$: C, 69.65; H, 5.58; N, 3.69. Found: C, 69.48; H, 5.61; N, 3.63.

The cyclization of **26** was also carried out using trifluoroacetic anhydride. To a solution of 255 mg (0.58 mmol) of sulfoxide **26** and 117 mg (1.16 mmol) of triethylamine in 10 mL of CH_2Cl_2 was added dropwise 180 mg (0.85 mmol) of trifluoroacetic anyhdride at 0 °C. After stirring at rt for 5 min, the solution was concentrated under reduced pressure. The crude residue was purified by flash silica gel chromatography and recrystallized from CH_2Cl_2/hexane to give 144 mg (59%) of cycloadduct **27** as a pale yellow solid, mp 86−87 °C; IR (neat) 1725, 1458, 1393, 1302, 1198 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, 3H, J = 7.5 Hz), 2.30 (d, 1H, J = 12.0 Hz), 2.66 (d, 1H, J = 12.0 Hz), 2.67−2.80 (m, 2H), 2.73 (d, 1H, J = 16.5 Hz), 2.98 (d, 1H, J = 16.5 Hz), 3.00−3.11 (m, 2H), 3.33 (s, 3H), 3.59−3.69 (m, 1H), 3.89−4.00 (m, 1H), 6.88 (d, 1H, J = 7.2 Hz), 7.20−7.45 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.2, 24.2, 34.9, 40.9, 43.8, 49.6, 52.4, 56.8, 92.4, 105.1, 119.3, 121.4, 126.4, 127.8, 128.4, 128.5, 128.9, 138.0, 138.8, 144.3, 171.4, 176.3. Anal. Calcd for $C_{24}H_{25}NO_4S$: C, 68.06; H, 5.95; N, 3.31. Found: C, 67.95; H, 5.94; N, 3.37.

***N*-[2-(1*H*-Indol-3-yl)ethyl]-2-[(ethylthio)methyl]benzamide.** To a stirred suspension containing 1.12 g (5.7 mmol) of 2-[(ethylthio)methyl]benzoic acid (**10**) in 20 mL of dry benzene was added 1.47 g (12 mmol) of thionyl chloride. After stirring at rt for 2 h, the solution was concentrated under reduced pressure. The crude acid chloride was dissolved in 20 mL of CH_2Cl_2, and 2.01 g (12.5 mmol) of tryptamine was added over a 10 min period at 0 °C. After stirring at rt for 2 h, the mixture was poured into water and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography and recrystallized from ethyl acetate/hexane to give 1.45 g (76%) of *N*-[2-(1*H*-indol-3-yl)ethyl]-2-[(ethylthio)methyl]benzamide as a white solid, mp 68−69 °C; IR (neat) 3404, 3296, 1640, 1528, 1457, 1309 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, 3H, J = 7.5 Hz), 2.36 (q, 2H, J = 7.5 Hz), 3.09 (t, 2H, J = 6.6 Hz), 3.79 (q, 2H, J = 6.6 Hz), 3.83 (s, 2H), 6.61 (brs, 1H), 7.02−7.64 (m, 9H), 8.36 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.4, 25.2, 26.0, 33.6, 40.1, 111.2, 112.7, 118.6, 119.3, 122.0, 122.2, 127.2, 127.3, 128.2, 129.8, 130.6, 135.8, 136.4, 169.4. Anal. Calcd for $C_{20}H_{22}N_2OS$: C, 70.97; H, 6.55; N, 8.28. Found: C, 70.86; H, 6.62; N, 8.27.

***N*-[2-(1*H*-Indol-3-yl)ethyl]-*N*-[(methoxycarbonyl)but-3-enoyl]-2-[(ethylthio)methyl]benzamide.** A mixture of 2.96 g (8.8 mmol) of the above amide, 2.15 g (13.2 mmol) of 3-(methoxycarbonyl)but-3-enoyl chloride,[40] and 8.5 g of powdered molecular sieves (4 Å) in 60 mL of CH_2Cl_2 was stirred at rt for 24 h. The reaction mixture was filtered through a pad of silica gel, and the filtrate was washed with an aqueous $NaHCO_3$ solution. The organic layer was dried over $MgSO_4$ and was concentrated under reduced pressure. The crude residue was purified by flash silica gel chromatography to give 2.54 g (63%) of *N*-[2-(1*H*-indol-3-yl)ethyl]-*N*-[(methoxycarbonyl)but-3-enoyl]-2-[(ethylthio)methyl]benzamide as a colorless oil; IR (neat) 3396, 1711, 1697, 1654, 1439, 1352, 1209 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, 3H, J = 7.5 Hz), 2.38 (q, 2H, J = 7.5 Hz), 3.05 (t, 2H, J = 7.2 Hz), 3.76 (s, 3H), 3.77 (s, 4H), 3.87 (t, 2H, J = 7.2 Hz), 5.66 (s, 1H), 6.33 (s, 1H), 6.90−7.41 (m, 9H), 8.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 24.4, 25.8, 32.9, 42.2, 47.4, 52.0, 111.0, 112.2, 118.6, 119.2, 121.9, 122.4, 127.1, 127.2, 127.7, 128.3, 130.5, 130.7, 134.8, 135.1, 136.1, 137.1, 166.8, 173.7, 173.9; HRMS Calcd for $C_{26}H_{28}N_2O_4S$: 464.1770. Found: 464.1774.

***N*-[2-(1*H*-Indol-3-yl)ethyl]-*N*-[3-(methoxycarbonyl)but-3-enoyl]-2-[(ethylsulfinyl)methyl]benzamide (29).** A 2.44 g (5.3 mmol) sample of the above sulfide was oxidized in the standard manner[21] to afford sulfoxide **29** (74%) as a clear oil: IR (neat) 3385, 1709, 1680, 1651, 1439, 1353, 1209 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.27 (t, 3H, J = 7.5 Hz), 2.52−2.70 (m, 2H), 2.99−3.11 (m, 2H), 3.50 (brs, 2H), 3.67 (s, 2H), 3.75 (s, 3H), 3.82−4.00 (m, 2H), 5.66 (s, 1H), 6.31 (s, 1H), 6.86−7.43 (m, 9H), 8.79 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 6.7, 24.4, 41.7, 45.2, 47.8, 52.0, 54.8, 111.2, 111.5, 118.3, 119.2, 121.7, 123.0, 127.0, 127.9, 128.0, 128.5, 130.5, 131.1, 132.0, 134.5, 134.8, 136.2, 166.7, 173.2, 173.7; HRMS (FAB) Calcd for $C_{26}H_{28}N_2O_5SLi$ (M + Li): 487.1879. Found: 487.1895.

2-[[[2-[6-(Ethylthio)-11-oxo-5,11-dihydrobenzo[*b*]carbazol-11a-yl]ethyl]carbamoyl]methyl]acrylic Acid Methyl Ester (31). The reaction of 190 mg (0.4 mmol) of sulfoxide **29** with acetic anhydride following the general procedure[21] gave rise to a 5:1 mixture of **31** and 2-[[[2-(5-acetyl-6-(ethylthio)-11-oxo-5,11-dihydrobenzo[*b*]carbazol-11*a*-yl)ethyl]carbamoyl]methyl]acrylic acid methyl ester (**32**) which were separated by silica gel chromatography.

Cycloadduct **31** (58%): IR (neat) 3318, 1721, 1676, 1456, 1331, 1213 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.20 (t, 3H, J = 7.5 Hz), 2.05 (q, 2H, J = 7.5 Hz), 2.61 (t, 2H, J = 7.2 Hz), 3.00 (s, 2H), 3.06−3.10 (m, 1H), 3.28−3.35 (m, 1H), 3.71 (s, 3H), 5.70 (s, 1H), 5.76 (brs, 1H, exchangeable with D_2O), 6.24 (s, 1H), 6.87 (d, 1H, J = 7.8 Hz), 7.00 (t, 1H, J = 7.8 Hz), 7.16−7.24 (m, 2H), 7.32 (brs, 1H), 7.56 (dt, 1H, J = 8.1 and 1.2 Hz), 7.76 (d, 1H, J = 8.1 Hz), 7.84 (d, 1H, J = 7.5 Hz), 7.90 (dd, 1H, J = 7.5 and 1.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.9, 28.0, 35.4, 39.8, 42.3, 52.1, 60.4, 93.4, 109.4, 120.8, 124.2, 124.7, 125.6, 126.0, 127.4, 128.5, 128.6, 129.0, 133.8, 134.8, 140.6, 144.3, 160.3, 167.0, 169.3, 199.4; HRMS (FAB) Calcd for $C_{26}H_{26}N_2O_4SLi$ (M + Li): 469.1773. Found: 469.1795.

Cycloadduct **32** (11%): IR (neat) 3310, 1717, 1681, 1654, 1453, 1332, 1268 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, 3H, J = 7.5 Hz), 1.99−2.05 (m, 2H), 2.41 (q, 2H, J = 7.5 Hz), 2.49 (s, 3H), 3.02 (s, 2H), 3.08−3.16 (m, 2H), 3.72 (s, 3H), 5.72 (s, 1H), 5.84 (brs, 1H, exchangeable with D_2O), 6.25 (s, 1H), 7.20 (t, 1H, J = 7.2 Hz), 7.33 (t, 1H, J = 7.8 Hz), 7.43 (t, 1H, J = 7.2 Hz), 7.71 (t, 1H, J = 7.8 Hz), 7.95−8.03 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 25.0, 28.0, 35.3, 39.9, 40.0, 52.2, 58.2, 116.3, 124.6, 125.1, 127.4, 127.6, 128.2, 128.5, 128.9, 129.1, 133.7, 135.0, 136.7, 143.2, 167.1, 169.4, 169.7, 197.6; HRMS Calcd for $C_{28}H_{28}N_2O_5S$: 504.1719. Found: 504.1741.

***N*-[2-(*N*-Tosylindol-3-yl)ethyl]-2-[(ethylthio)methyl]benzamide.** To a stirred solution of 0.5 g (1.5 mmol) of amide *N*-[2-(1*H*-indol-3-yl)ethyl]-2-[(ethylthio)methyl]benzamide and 51 mg (0.15 mmol) of tetrabutylammonium hydrogen sulfate in 15 mL of benzene was added 5 mL of a 50% aqueous NaOH solution. After stirring for 5 min, a solution of 0.35 g (1.84 mmol) of *p*-toluenesulfonyl chloride in 8 mL of benzene was added dropwise over a 10 min period. The mixture was stirred at rt for 1 h and washed with water, and the aqueous phase was extracted with benzene. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by flash silica gel chromatography to give 0.66 g (90%) of *N*-[2-(*N*-tosylindol-3-yl)ethyl]-2-[(ethylthio)-methyl]benzamide as a colorless oil; IR (neat) 3296, 1649, 1529, 1448, 1367, 1173 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, 3H, J = 7.5 Hz), 2.27 (s, 3H), 2.39 (q, 2H, J = 7.5 Hz), 3.01 (t, 2H, J = 6.9 Hz), 3.24 (q, 2H, J = 6.9 Hz), 3.82 (s, 2H), 6.68 (brs, 1H), 7.07 (d, 2H, J = 8.1 Hz), 7.20−7.42 (m, 6H), 7.46 (s, 1H), 7.53−7.71 (m, 3H), 7.98 (d, 1H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 21.4, 25.0, 25.9, 33.6, 39.1, 113.7, 119.4, 119.7, 123.1, 123.5, 124.8, 126.6, 127.2, 128.3, 129.7, 129.8, 130.5, 130.6, 135.0, 135.2, 135.9, 136.1, 144.7, 169.4; HRMS (FAB) Calcd for $C_{27}H_{29}N_2O_3S_2$ (M + H): 493.1620. Found: 493.1622.

***N*-[2-(*N*-Tosylindol-3-yl)ethyl]-*N*-[3-(methoxycarbonyl)but-3-enoyl]-2-[(ethylthio)methyl]benzamide.** A mixture of 1.3 g (2.6 mmol) of the above amide, 0.64 g (3.9 mmol) of 3-(methoxycarbonyl)but-3-enoyl chloride,[40] and 3.1 g of powdered molecular sieves (4 Å) in 20 mL of CH_2Cl_2 was stirred for 24 h at rt. The reaction mixture was filtered through a pad of silica gel, and the filtrate was washed with an aqueous $NaHCO_3$ solution. The organic layer was dried over $MgSO_4$ and was concentrated under reduced pressure. The resulting crude oil was purified by flash silica gel chromatography to give 1.3 g (77%) of *N*-[2-(*N*-tosylindol-3-yl)ethyl]-*N*-[3-(methoxycarbonyl)but-3-enoyl]-2-[(ethylthio)methyl]benzamide as a colorless oil; IR (neat) 1718, 1696, 1656, 1438, 1359, 1169 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, 3H, J = 7.5 Hz), 2.31 (s, 3H), 2.38 (q, 2H, J = 7.5 Hz), 2.98 (t, 2H, J = 7.2 Hz), 3.70 (s, 2H), 3.78 (s, 3H), 3.81−3.86 (m, 4H), 5.68 (s, 1H), 6.33 (s, 1H), 7.10−7.42 (m, 10H), 7.70 (d, 2H, J =

8.1 Hz), 7.92 (d, 1H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.4, 21.6, 24.3, 26.1, 33.2, 42.4, 46.5, 52.2, 113.7, 119.3, 119.7, 123.2, 123.8, 124.8, 126.9, 127.4, 127.8, 128.5, 129.9, 130.7, 130.8, 131.0, 134.9, 135.1, 135.2, 135.3, 137.6, 144.9, 166.9, 173.6, 174.1; HRMS (FAB) Calcd for $C_{33}H_{35}N_2O_6S_2$ (M + H): 619.1937. Found: 619.1930.

***N*-[2-(*N*-Tosylindol-3-yl)ethyl]-*N*-[3-(methoxycarbonyl-)but-3-enoyl]-2-[(ethylsulfinyl)methyl]benzamide (33).** A 0.93 g (1.50 mmol) sample of the above sulfide was oxidized in the standard manner[21] to give sulfoxide **33** as a colorless oil (78%); IR (neat) 1719, 1684, 1648, 1452, 1347, 1262 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, 3H, J = 7.5 Hz), 2.31 (s, 3H), 2.62−3.08 (m, 4H), 3.62 (s, 2H), 3.78 (s, 3H), 3.81−4.00 (m, 4H), 5.71 (s, 1H), 6.33 (s, 1H), 7.10−7.51 (m, 10H), 7.72 (d, 2H, J = 8.1 Hz), 7.94 (d, 1H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.0, 21.7, 24.4, 42.2, 45.9, 46.9, 52.3, 55.0, 113.8, 119.0, 119.6, 123.4, 124.2, 124.9, 127.0, 128.3, 128.4, 128.9, 130.1, 130.6, 131.0, 131.7, 132.7, 134.7, 135.0, 135.2, 135.3, 145.1, 166.9, 173.4, 174.1; HRMS (FAB) Calcd for $C_{33}H_{35}N_2O_7S_2$ (M + H): 635.1886. Found: 635.1914.

Pummerer-Induced Reaction of Sulfoxide 33. To a solution of 120 mg (0.19 mmol) of sulfoxide **33** and 60 μL (0.43 mmol) of triethylamine in 10 mL of CH_2Cl_2 was added dropwise 52 μL (0.29 mmol) of trimethylsilyl trifluoromethanesulfonate at 0 °C. After stirring at rt for 5 min, the solution was concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 83 mg (71%) of cycloadduct **34**; IR (neat) 1726, 1441, 1362, 1171 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (t, 3H, J = 7.5 Hz), 2.30 (s, 3H), 2.64−2.78 (m, 4H), 2.70 (d, 1H, J = 16.5 Hz), 2.95 (d, 1H, J = 16.5 Hz), 2.98−3.10 (m, 2H), 3.31 (s, 3H), 3.58−3.68 (m, 1H), 4.03−4.13 (m, 1H), 7.02 (d, 1H, J = 7.5 Hz), 7.13−7.45 (m, 9H), 7.71 (d, 2H, J = 8.1 Hz), 7.93 (d, 1H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.2, 21.5, 24.2, 24.3, 40.9, 41.4, 44.4, 52.4, 56.8, 92.5, 104.9, 113.6, 119.2, 119.4, 119.5, 121.5, 123.0, 123.2, 124.7, 126.7, 127.8, 129.0, 129.8, 130.6, 135.1, 135.2, 137.8, 144.3, 144.7, 171.3, 176.2; HRMS (FAB) Calcd for $C_{33}H_{33}N_2O_6S_2$ (M + H): 617.1776. Found: 617.1780.

***N*-[2-(3,4-Dimethoxyphenethyl)]-4-(ethylthio)-3-methoxy-2-butenamide (36).** To a solution containing 14.0 g (0.25 mol) of KOH in 60 mL of water was added 15 mL (0.20 mol) of ethanethiol at 0 °C. After stirring for 10 min, a solution of 37.6 g (0.18 mol) of methyl 4-bromo-3-methoxybut-2-enoate (**35**)[34] in 40 mL of ether was added, and the biphasic mixture was warmed to rt. After stirring vigorously at rt for 20 h, the organic layer was separated, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was distilled to give 30.4 g (89%) of methyl 4-(ethylthio)-3-methoxy-2-butenoate as a colorless liquid, bp 88−90 °C (0.2 mm); IR (neat) 1713, 1623 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27 (t, 3H, J = 7.5 Hz), 2.63 (q, 2H, J = 7.5 Hz), 3.69 (s, 6H), 3.85 (s, 2H), 5.08 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6, 26.3, 30.6, 50.9, 55.7, 91.1, 167.5, 172.7; HRMS Calcd for $C_8H_{14}O_3S$: 190.0664. Found: 190.0662.

A mixture containing 12.0 g (63 mmol) of the above ester, 9.3 g (65 mmol) of potassium trimethylsilanolate (ca. 90% purity, Aldrich), and 150 mL of ether was stirred for 16 h at rt. The white precipitate that formed was filtered, dissolved in 20 mL of water, and acidified with 2 N HCl. The aqueous solution was extracted with chloroform, and the organic layer was separated, dried over $MgSO_4$, and concentrated under reduced pressure to give 4-(ethylthio)-3-methoxy-2-butenoic acid as a yellow liquid which was used without purification in the next step; IR (neat) 1712, 1614 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.23 (t, 3H, J = 7.5 Hz), 2.55 (q, 2H, J = 7.5 Hz), 3.59 (s, 2H), 3.63 (s, 3H), 5.21 (s, 1H), 10.6 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 29.5, 37.3, 55.2, 92.9, 156.9, 176.2; HRMS Calcd for $C_7H_{12}O_3S$: 176.0507. Found: 176.0508.

To a solution containing 2.18 g (12.4 mmol) of the above carboxylic acid and 30 mL of CH_2Cl_2 was added 2.54 g (15.7 mmol) of 1,1′-carbonyldiimidazole. After stirring for 2 h at rt, 4.4 mL (26.0 mmol) of 3,4-dimethoxyphenethylamine was added, and the mixture was stirred for an additional 3 h. The solution was poured into water, washed with saturated NH_4Cl, and extracted with chloroform. The organic layer was separated, dried over $MgSO_4$, and concentrated under reduced pressure. The crude amide was purified by flash silica gel chromatography and recrystallized from CH_2Cl_2/hexane to give 2.9 g (68%) of amide **36** as a white solid, mp 72−73 °C; IR (neat) 3302, 1654, 1517, 1452, 1256, 1146 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.21 (t, 3H, J = 7.5 Hz), 2.52 (q, 2H, J = 7.5 Hz), 2.75 (t, 2H, J = 6.9 Hz), 3.39 (s, 2H), 3.49 (q, 2H, J = 6.9 Hz), 3.54 (s, 3H), 3.86 (s, 3H), 3.88 (s, 3H), 5.12 (s, 1H), 5.85 (brs, 1H), 6.71−6.82 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 29.5, 35.1, 39.9, 40.7, 55.1, 55.8, 55.9, 92.9, 111.3, 111.9, 120.6, 131.3, 147.6, 148.9, 157.7, 168.4. Anal. Calcd for $C_{17}H_{25}NO_4S$: C, 60.15; H, 7.42; N, 4.13. Found: C, 59.93; H, 7.36; N, 4.22.

Methyl 2-[2-[*N*-[2-(3,4-Dimethoxyphenethyl)-4-(ethylthio)-3-methoxybut-2-enoyl]amino]-2-oxoethyl]prop-2-enoate. A mixture containing 730 mg (2.15 mmol) of amide **36**, 525 mg (3.23 mmol) of 3-(methoxycarbonyl)but-3-enoyl chloride,[40] and 25 mL of benzene was heated at reflux for 24 h. After cooling, the reaction mixture was washed with a 10% NaOH solution, and the organic layer was separated, dried over $MgSO_4$, and concentrated under reduced pressure. The crude oil was purified by flash silica gel chromatography to give 902 mg (90%) of methyl 2-[2-[*N*-[2-(3,4-dimethoxyphenethyl)-4-(ethylthio)-3-methoxybut-2-enoyl]amino]-2-oxoethyl]-prop-2-enoate as a yellow oil; IR (neat) 1717, 1681, 1645, 1595, 1509, 1258 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.26 (t, 3H, J = 7.5 Hz), 2.63 (q, 2H, J = 7.5 Hz), 2.86 (t, 2H, J = 7.2 Hz), 3.59 (s, 3H), 3.69 (s, 2H), 3.72 (s, 2H), 3.76 (s, 3H), 3.85 (s, 3H), 3.87 (s, 3H), 3.91 (t, 2H, J = 7.2 Hz), 5.30 (s, 1H), 5.66 (s, 1H), 6.32 (s, 1H), 6.76−6.84 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6, 26.6, 31.5, 34.4, 41.8, 47.2, 51.9, 55.6, 55.7, 55.8, 94.1, 111.3, 112.3, 120.8, 128.0, 131.3, 134.9, 147.6, 149.0, 166.8, 169.5, 173.4, 174.1; HRMS (FAB) Calcd for $C_{23}H_{31}NO_7SLi$ (M + Li): 472.1981. Found: 472.2001.

Methyl 2-[2-[*N*-[2-(3,4-Dimethoxyphenethyl)-4-(ethylsulfinyl)-3-methoxybut-2-enoyl]amino]-2-oxoethyl]prop-2-enoate (37). A 698 mg (1.50 mmol) sample of the above sulfide was oxidized in the standard manner[21] to give sulfoxide **37** (92%) as a colorless oil; IR (neat) 1720, 1675, 1642, 1597, 1512, 1447 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.38 (t, 3H, J = 7.5 Hz), 2.79−2.89 (m, 4H), 3.61 (s, 3H), 3.67 (s, 2H), 3.77 (s, 3H), 3.86 (s, 3H), 3.87 (s, 3H), 3.92 (d, 1H, J = 12 Hz), 3.93 (m, 2H), 4.16 (d, 1H, J = 12 Hz), 5.55 (s, 1H), 5.66 (s, 1H), 6.33 (s, 1H), 6.76−6.84 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 6.5, 34.5, 41.8, 46.4, 47.2, 52.0, 55.1, 55.8, 55.9, 56.2, 97.6, 111.4, 112.4, 120.9, 128.3, 131.2, 134.7, 147.7, 149.0, 166.6, 166.8, 169.4, 173.5; HRMS (FAB) Calcd for $C_{23}H_{31}NO_8SLi$ (M + Li): 488.1950. Found: 488.1930.

Methyl 11-(Ethylthio)-7,8-dimethoxy-2,12-dioxo-1,4,5,12,13,13a-hexahydro-2*H*-indolo[7a,1-*a*]isoquinoline-13a-carboxylate (38). To a solution of 286 mg (0.59 mmol) of sulfoxide **37** and 120 mg (1.18 mmol) of triethylamine in 10 mL of CH_2Cl_2 was added dropwise 186 mg (0.89 mmol) of trifluoroacetic anhydride at −78 °C. After stirring for 10 min, 254 mg (1.79 mmol) of boron trifluoride etherate was added, and the mixture was warmed to rt. After stirring for 30 min at rt, the solution was heated to reflux for an additional 20 h. The reaction mixture was poured into water and extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure, and the crude product was purified by flash silica gel chromatography and recrystallized from CH_2Cl_2/hexane to give 211 mg (83%) of **38** as a white solid, mp 187−188 °C; IR (neat) 1730, 1687, 1509, 1346, 1260 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28 (t, 3H, J = 7.5 Hz), 2.54 (d, 1H, J = 16.5 Hz), 2.61−2.70 (m, 3H), 2.77 (d, 1H, J = 16.5 Hz), 2.81−2.85 (m, 1H), 2.92 (d, 1H, J = 17.7 Hz), 2.99−3.07 (m, 1H), 3.29 (s, 3H), 3.58 (d, 1H, J = 17.7 Hz), 3.82 (s, 3H), 3.87 (s, 3H), 4.46−4.52 (m, 1H), 6.15 (s, 1H), 6.59 (s, 1H), 6.63 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.9, 24.5, 28.1, 35.6, 40.7, 41.0, 52.2, 52.7, 55.9, 56.3, 64.8, 109.6, 111.9, 124.0, 127.7, 135.0, 135.2, 148.0, 149.0, 170.3, 171.0, 192.3. Anal. Calcd for $C_{22}H_{25}NO_6S$: C, 61.24; H, 5.84; N, 3.25. Found: C, 60.98; H, 5.86; N, 3.10.

When the above reaction was quenched before heating at reflux for 20 h, N,O-ketal **45** was isolated in 51% yield as a

white solid, mp 158−159 °C (CH_2Cl_2/hexane); IR (neat), 1738, 1672, 1510, 1260 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.35 (t, 3H, J = 7.5 Hz), 2.32 (d, 1H, J = 17.1 Hz), 2.51 (d, 1H, J = 16.2 Hz), 2.61−2.94 (m, 5H), 3.15 (d, 1H, J = 17.1 Hz), 3.48−3.69 (m, 2H), 3.75 (s, 3H), 3.85 (s, 3H), 3.87 (s, 3H), 3.92 (s, 1H, exchangeable with D_2O), 6.02 (s, 1H), 6.70−6.77 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.7, 24.4, 29.9, 34.8, 39.0, 41.2, 43.7, 53.2, 53.3, 55.8, 87.7, 111.2, 111.9, 120.7, 129.7, 130.7, 140.0, 147.8, 148.9, 171.7, 171.9, 191.1. Anal. Calcd for $C_{22}H_{27}NO_7S$: C, 58.78; H, 6.05; N, 3.12. Found: C, 58.72; H, 6.11; N, 3.07.

Methyl 11-(Ethylthio)-7,8-dimethoxy-2-oxo-12-[[(trifluoromethyl)sulfonyl]oxy]-1,4,5,13a-tetrahydro-2*H*-indolo[7a,1-*a*]isoquinoline-13a-carboxylate. To a solution of 100 mg (0.88 mmol) of KH (35% dispersion in mineral oil) in 5 mL of THF was added 187 mg (0.43 mmol) of enone **38** in 5 mL of THF at rt. After stirring for 20 min, a solution containing 315 mg (0.88 mmol) of *N*-phenyltrifluoromethanesulfonimide in 5 mL of THF was added, and stirring was continued for an additional 30 min. Water (3 mL) was added slowly to the mixture, and the aqueous layer was extracted with chloroform. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure, the crude product was purified by flash silica gel chromatography to yield 107 mg (70%) of methyl 11-(ethylthio)-7,8-dimethoxy-2-oxo-12-[[(trifluoromethyl)sulfonyl]oxy]-1,4,5,13a-tetrahydro-2*H*-indolo-[7a,1-*a*]isoquinoline-13a-carboxylate; IR (neat) 1733, 1698, 1510, 1420, 1211 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.28 (t, 3H, J = 7.5 Hz), 2.55−3.08 (m, 7H), 3.25 (s, 3H), 3.80 (s, 3H), 3.84 (s, 3H), 4.42−4.48 (m, 1H), 5.70 (s, 1H), 6.35 (s, 1H), 6.53 (s, 1H), 6.84 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.2, 26.5, 27.8, 35.7, 43.2, 52.3, 54.1, 55.7, 56.0, 66.1, 108.6, 111.0, 118.7, 125.0, 125.2, 125.8, 128.0, 143.8, 148.2, 149.0, 170.1, 170.5. Anal. Calcd for $C_{23}H_{24}F_3NO_8S_2$: C, 49.02; H, 4.29; N, 2.49. Found: C, 49.05; H, 4.33; N, 2.43.

Methyl 11-(Ethylthio)-7,8-dimethoxy-2-oxo-1,4,5,13a-tetrahydro-2*H*-indolo[7a,1-*a*]isoquinoline-13a-carboxylate (46). To a solution containing 94 mg (0.17 mmol) of the above triflate and 2 mL of DMF were added sequentially 51 mg (0.50 mmol) of triethylamine, 12 mg (0.017 mmol) of bis(triphenylphosphine)palladium(II) chloride, and 40 mg (0.87 mmol) of formic acid at rt. After heating the mixture at 60 °C for 15 min, ethyl acetate and water were added to the solution. The mixture was washed with water, and the organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography to give 64 mg (91%) of **46** as a clear oil; IR (neat) 1731, 1693, 1513, 1431, 1260 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.26 (t, 3H, J = 7.5 Hz), 2.56−3.09 (m, 7H), 3.22 (s, 3H), 3.77 (s, 3H), 3.84 (s, 3H), 4.39−4.45 (m, 1H), 5.45 (s, 1H), 5.97 (d, 1H, J = 10.2 Hz), 6.33 (d, 1H, J = 10.2 Hz), 6.51 (s, 1H), 6.79 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 25.2, 27.9, 35.5, 43.9, 51.8, 53.6, 55.8, 56.0, 66.4, 109.3, 110.8, 121.2, 123.3, 125.7, 127.0, 127.5, 128.7, 147.7, 148.6, 171.0, 172.2; HRMS Calcd for $C_{22}H_{25}NO_5S$: 415.1453. Found: 415.1440.

Methyl 7,8-Dimethoxy-2,11-dioxo-1,4,5,10,11,13a-hexahydro-2*H*-indolo[7a,1-*a*]isoquinoline-13a-carboxylate (47). To a solution containing 20 μL (0.18 mmol) of $TiCl_4$ in 3 mL of acetic acid was added 35 mg (0.08 mmol) of vinyl sulfide **46** in 1 mL of acetic acid. After stirring for 30 min at rt, 3 mL of water was added, and the mixture was stirred for an additional 24 h. The solution was washed with a saturated $NaHCO_3$ solution and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure, and the crude product was purified by flash silica gel chromatography to furnish 17 mg (54%) of **47** as a white solid, mp 203−204 °C (ethanol) (lit.[39] mp 206−207 °C); IR (neat) 1734, 1700, 1686, 1512, 1415, 1252 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.63−2.67 (m, 1H), 2.80 (d, 1H, J = 16.4 Hz), 2.81−2.83 (m, 1H), 2.86 (d, 1H, J = 15.6 Hz), 3.01 (d, 1H, J = 16.4 Hz), 3.04−3.07 (m, 1H), 3.16 (d, 1H, J = 15.6 Hz), 3.26 (s, 3H), 3.69 (s, 3H), 3.84 (s, 3H), 4.39−4.43 (m, 1H), 6.40 (d, 1H, J = 10.4 Hz), 6.50 (s, 1H), 6.56 (s, 1H), 7.25 (d, 1H, J = 10.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.0, 35.2, 41.7, 50.2, 52.3, 53.1, 55.7, 55.8, 66.4, 107.7, 111.6, 126.1, 127.7, 127.8, 147.2, 147.5, 148.4, 168.6, 171.2, 194.9.

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Supporting Information Available: ^1H NMR and ^{13}C NMR spectra for new compounds lacking analyses together with an ORTEP drawing for structure **38** (27 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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