Additive and Vinylogous Pummerer Reactions of Amido Sulfoxides and Their Use in the Preparation of Nitrogen Containing Heterocycles

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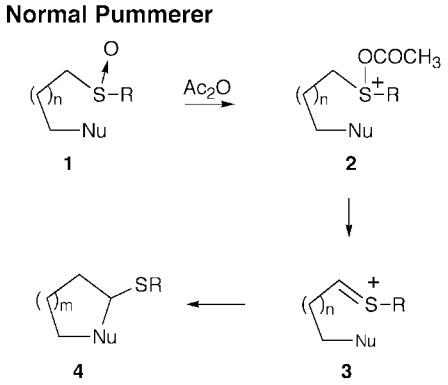
The α-thiocarbocation generated from the Pummerer reaction of *N*-methyl-*N*-phenyl-2-[2-(toluene-4-sulfinyl)phenyl]acetamide undergoes Friedel−Crafts reaction at the γ-carbon with the tethered aromatic ring. Reductive removal of the phenylthio group from the resulting product using Raney nickel occurs in high yield, and the overall reaction represents a new method for the synthesis of a variety of 3-phenyl-substituted oxindoles. Treatment of the related *N*-benzyl-*N*-alkyl amido sulfoxide system with trifluoroacetic anhydride affords tetrahydroisoquinolone derivatives. The product distribution encountered coincides with the rotamer population of the starting amide. When the *N*-benzyl-*N*-methyl amide is used, only the normal Pummerer product is formed. In this case, the thionium ion is generated in the wrong conformation for π-cyclization to occur. The corresponding *N*-*tert*-butyl amido system, however, exists in a geometric orientation which places the benzylic group in the crucial conformation necessary for π-cyclization, and consequently, the reaction proceeds smoothly. Related cyclization reactions occur in good yield with the corresponding furanyl and cyclohexenyl *N*-*tert*-butyl amido sulfoxides. The additive Pummerer reaction of 3-phenylsulfinyl-*N*-benzyl-*N*-*tert*-butylacrylamide gave products derived from both 5- and 6-*exo trig* cyclizations. Intramolecular electrophilic aromatic substitution via six-membered ring closure ultimately afforded a dihydropyridone. The competitive process involving *ipso* attack of the aromatic ring on the thionium ion generates a spiro cyclohexadienyl cation that undergoes fragmentation of the adjacent σ-bond. The resulting acyl iminium ion is converted to *N*-*tert*-butyl-2-phenyl-3-phenylsulfinylacrylamide upon aqueous workup. Only cyclizations leading to five-membered rings occur with the corresponding indolyl and alkenyl *N*-*tert*-butyl amido sulfoxides.

The Pummerer rearrangement of sulfoxides with acid anhydrides has been extensively utilized as a method for synthesizing α-substituted sulfides.[1−6] The initial step of the reaction involves acylation of the sulfoxide oxygen to form an acyloxysulfonium salt (**2**), thus converting this oxygen to a good leaving group. Removal of a proton from the α-carbon with elimination of the acyloxy group generates a thionium ion (**3**), which is trapped by one of the nucleophilic species present in the reaction medium (Scheme 1). The finding that thionium ions may serve as electrophiles in electrophilic substitution chemistry has greatly extended the synthetic range of the Pummerer reaction.[4] Thus, both inter-[7] and intramolecular[8] versions of the process have been used to prepare a wide assortment of compounds. Currently, Pummerer-based transformations are finding widespread application in carbo-[9] and heterocyclic syntheses[10] by reaction of the initially generated thionium ions with internally disposed nucleophiles (Scheme 1).[2]

Scheme 1



When α,β-unsaturated sulfoxides are used, the initially formed oxysulfonium ion (**6**) may undergo reaction via two different pathways (Scheme 2). In the *additive Pummerer* reaction,[11−17] nucleophilic attack occurs at the

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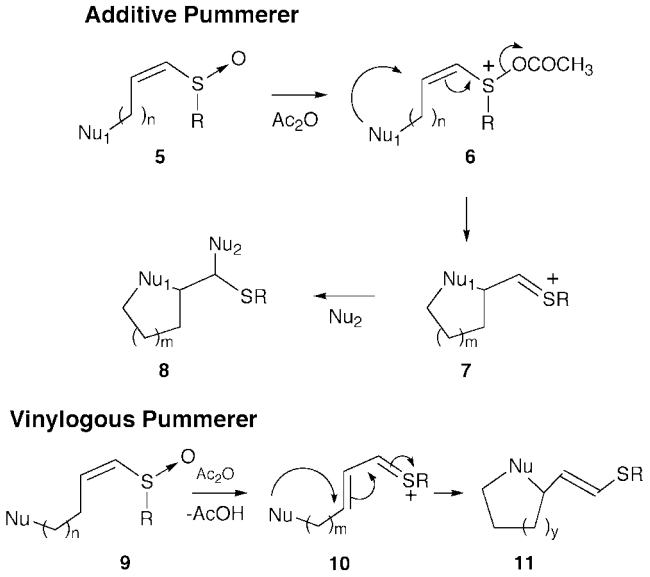
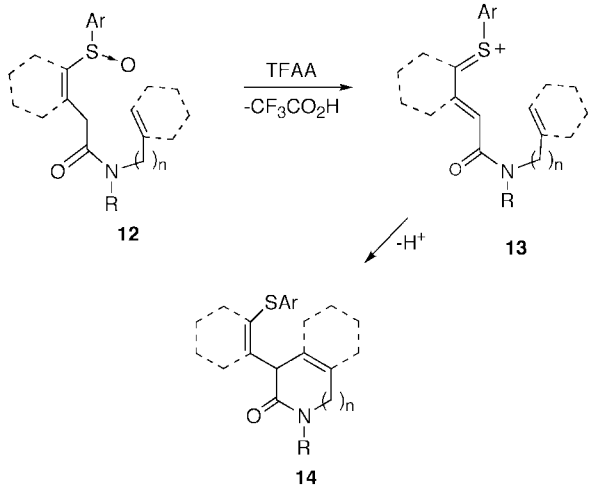
Scheme 2



Scheme 3



electrophilic β-carbon atom of the O-activated substrate producing a saturated β-functionalized thionium species (**7**). Trapping with a second nucleophilic agent affords a product (**8**) formally derived by the sequential attack of two nucleophiles on an α,β-dication. This sequence of reactions has been utilized in recent years for the formation of heteroatom−carbon and carbon−carbon bonds.[18−20] The second pathway corresponds to the related *vinylogous Pummerer* reaction of vinylic sulfoxides[21] which involves an electrophilic thionium ion intermediate formed by γ-proton loss followed by sulfoxide S−O bond scission. The resulting unsaturated thionium ion **10** is then intercepted by a nucleophile at the γ-position.

For the past several years we have been examining tandem Pummerer processes with the intention of assessing its viability as a general strategy for the synthesis of carbo- and heterocyclic ring systems.[22] We were particularly interested in determining whether activated vinyl sulfoxides such as **9** could be used as electrophilic reagents to trigger tandem carbon−heteroatom bond formation. In a preliminary communication, we described a novel vinylogous Pummerer reaction of aryl amido sulfoxides of type **12** (Scheme 3).[23] Electrophilic attack proceeded at the nucleophilic oxygen and was followed by proton loss to give the highly reactive intermediate **13** in which the γ-position was activated by the positively charged sulfur atom. Attack at the γ-carbon by a tethered π-bond resulted in an overall annulation leading to various heterocyclic systems (i.e., **14**). In this paper we report in full the results of our earlier investigations[23] that show that the Pummerer induced reaction of aryl amido sulfoxides with trifluoroacetic anhydride (TFAA) represents a convenient method for the synthesis of oxindoles and related heterocycles.

Results and Discussion

Our studies began with an investigation of the Pummerer reaction of amido sulfoxide **18**. Construction of **18** first involved the bis(bipyridyl)nickel(II)-catalyzed thioarylation of 2-iodophenylacetic acid with sodium *p*-thiocresolate.[24] Conversion of the resulting acid **17** to the corresponding amide was followed by sulfide oxidation to furnish the desired sulfoxide **18** (Scheme 4). When sodium periodate was used as the oxidant, elevated temperatures were necessary and this resulted in the formation of a significant amount of the corresponding sulfone. After considerable experimentation with a variety of oxidizing agents, we found that the best yields are obtained using the titanium(III)−hydrogen peroxide method of Oae.[25] This procedure was found to be particularly effective for the oxidation of highly hindered sulfides and resulted in the isolation of sulfoxide **18** in 81% overall yield from carboxylic acid **17**.

Treatment of **18** with trifluoroacetic anhydride (TFAA) in CH_2Cl_2 at 25 °C gave the 3-substituted oxindole **19** in 91% yield which could easily be reduced with Raney

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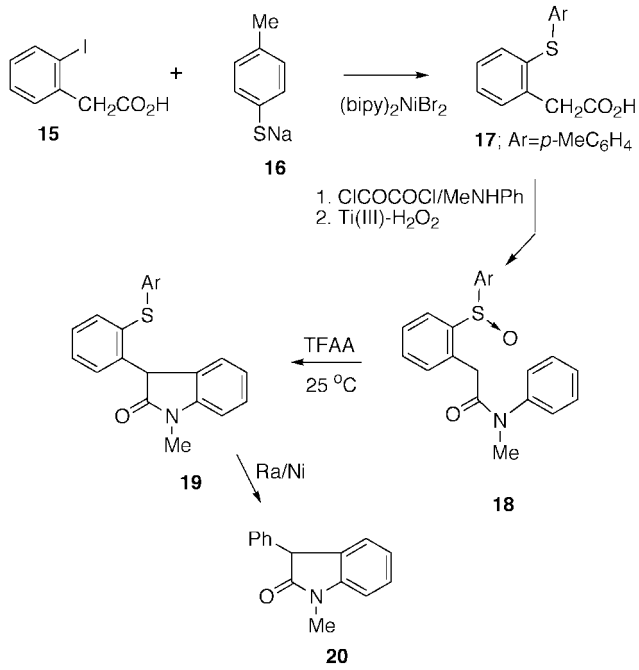
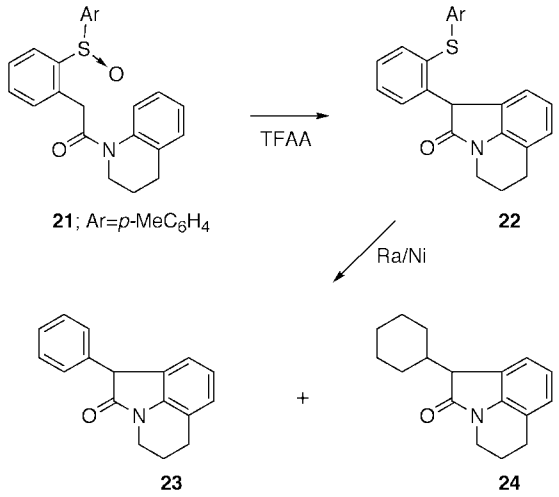
Scheme 4



Scheme 5

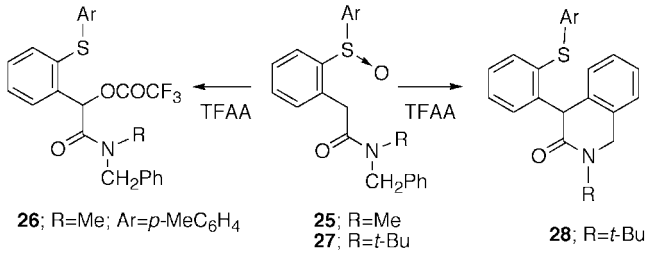


nickel to the known 3-phenyloxindole **20**.[26] We assume that the mechanism for the conversion of **18** to **19** proceeds by the sequential set of reactions outlined in Scheme 3 where the *N*-phenyl group effectively traps the Pummerer-generated thionium ion in a Friedel−Crafts fashion.[27]

In a like manner, sulfoxide **21** afforded the tetrahydroquinolone derivative **22** in 85% isolated yield when treated with TFAA at room temperature. In this case, reductive removal of the *p*-tolylthio group with Raney nickel in refluxing ethanol required 5 days and led to a 1:1 mixture of the 3-phenyl- and 3-cyclohexyl-substituted oxindoles **23** and **24** (Scheme 5).

Interestingly, treatment of the homologous *N*-benzyl-*N*-methylamido sulfoxide **25** with TFAA did not afford

Scheme 6



the product of internal cyclization on the aromatic ring. Instead, only the *normal Pummerer* product (i.e., α-trifluoroacetoxy sulfide **26**; 66%) was formed which readily hydrolyzed to the corresponding alcohol upon workup. On the other hand, when the related *tert*-butyl amide **27** was subjected to TFAA, the desired tetrahydroisoquinolone derivative **28** was obtained in 83% yield (Scheme 6). The product distribution encountered coincides with the rotamer population of the starting amide. It is well-known that rotation around the acyl carbon−nitrogen bond is restricted, leading to the existence of two geometric isomers which are usually not separable due to the relatively low barrier to rotation (ca. 20 kcal/mol).[28] The preference for unsymmetrical *N*,*N*-disubstituted amides to exist predominantly with the larger substituent on nitrogen *syn* to the carbonyl oxygen is well documented.[29] Due to the *N*-benzyl-*N*-methylamido sulfoxide **25** preferred *syn* (benzyl) geometry, the thionium ion is generated in an unfavorable conformation for π-cyclization and thus no cyclization occurs. Moreover, the failure to isolate the tetrahydroisoquinolone derivative from the Pummerer reaction of **25** implies that the amide linkage does not rotate during the lifetime of the thionium ion.[30] *N*-*tert*-Butylamides strongly favor the *Z*-rotamer,[28] thereby suggesting that amido sulfoxide **27** exists in the geometric orientation which places the benzylic group into the crucial conformation necessary for π-cyclization. This nicely accounts for the facility with which **27** is converted into tetrahydroisoquinolone **28**.

As an extension of these studies, amido sulfoxide **29** was prepared to evaluate the effect of an electron-rich aryl group on the efficiency and selectivity of the cyclization process. The *m*-methoxy aryl-substituted amido sulfoxide **29** was synthesized from acid **17** in 89% overall yield and was subjected to the TFAA reaction conditions. Although the presence of the activated aryl group seemed to facilitate the Pummerer reaction (94% yield), there was no discernible preference in the regiochemical mode of cyclization since a 1:1 mixture of *ortho*- and *para*-cyclized products was obtained (Scheme 7).

So that a cross-section of additional information could be obtained in regard to the *vinylogous Pummerer*/π-cyclization protocol, a series of different amido sulfoxides was needed to represent a variety of different π-bonds. Compounds ranging from substituted aromatics to simple

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(27) Jung and co-workers have described a related trapping of an α-ketosulfonium ion with an aromatic ring as a method for preparing biaryls. See: Jung, M. E.; Kim, C.; Bussche, L. V. D. *J. Org. Chem.* **1994**, *59*, 3248. Jung, M. E.; Jachiet, D.; Khan, S. I.; Kim, C. *Tetrahedron Lett.* **1995**, *36*, 361.

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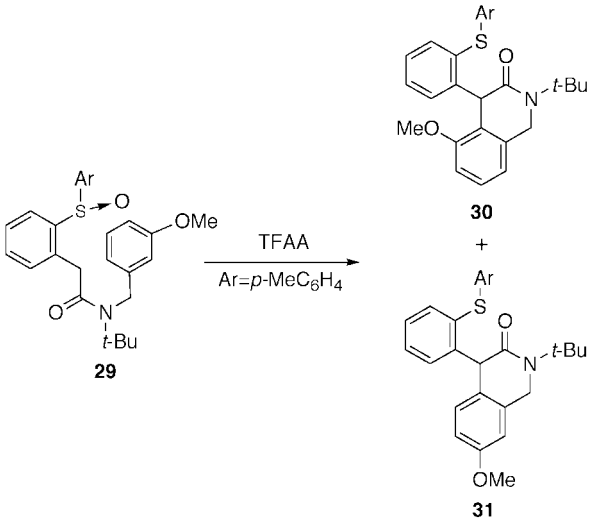
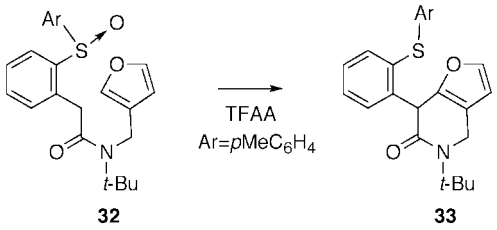
(30) The fact that no cyclization occurred with amide **25** even though ca. 30% of the rotamer population is in the correct conformation indicates that the product distribution is determined by Curtin−Hammett kinetics in a more complex fashion than indicated.

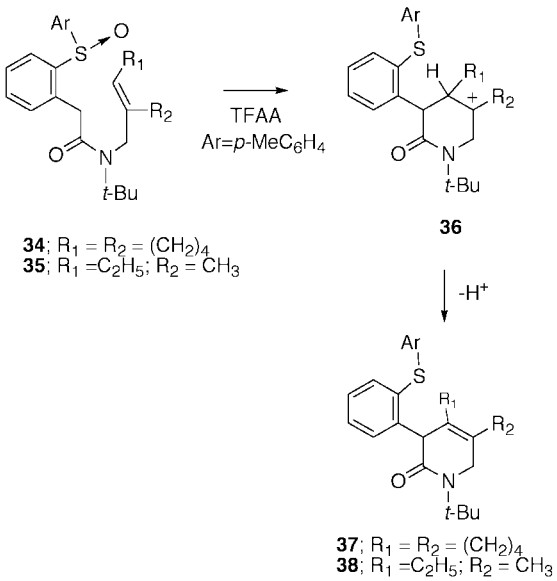
Scheme 7



Scheme 8



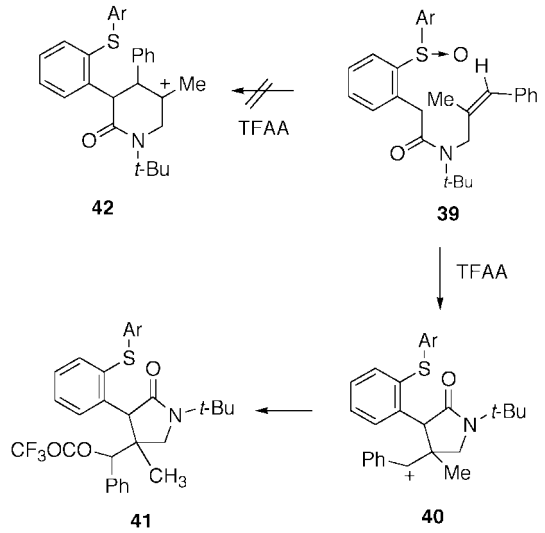
Scheme 9



alkenyl-tethered systems were considered. Ultimately, substrates **32**, **34**, and **35** were studied as they contain a range of synthetically interesting and easily attainable functionality. Exposure of the furanyl tethered amido sulfoxide **32** to TFAA in CH_2Cl_2 at 25 °C furnished **33** in 68% yield (Scheme 8). Similarly, reaction of *tert*-butylamido sulfoxides **34** and **35** with TFAA gave the cyclized dihydropyridones **37** and **38** in 67% and 54% yields (Scheme 9), thereby demonstrating that tethered alkenes can also be used in these Pummerer-induced cyclizations.

It is interesting to note that treatment of the related amido sulfoxide **39** under standard Pummerer reaction conditions led to pyrrolidone **41** as a mixture of diastereomers in 65% yield. The major stereoisomer was

Scheme 10



separated by fractional crystallization, and its structure was unequivocally established by an X-ray crystallographic study.[31] Formation of **41** can be attributed to preferential 5-*exo trig* cyclization which leads to the more stable benzylic cation **40** rather than 6-*endo trig* cyclization which would give the tertiary cation **42**. Interception of **40** by trifluoroacetate leads to the observed product **41** (Scheme 10).

The Lewis acid mediated addition of allylsilanes to electron deficient centers has proven to be a powerful method for the preparation of many different types of cyclic ring systems.[32] A wide variety of allylsilanes has been utilized, and the method has found significant use in organic synthesis.[33,34] There have been relatively few instances of cyclization involving the intramolecular addition of allylsilanes to thionium ions, despite the ongoing activity in this area.[35] The well-documented reactivity of allylsilanes toward electrophiles[32] suggested that the reaction of sulfoxide **43** with a Pummerer promoter should provide access to adduct **44** which possesses an exocyclic double bond. Surprisingly, when amido sulfoxide **43** was treated with TFAA, a 1:1 mixture of dihydropyridones **45** (45%) and **46** (45%) was obtained in high yield (Scheme 11). There was no evidence of the anticipated desilylated compound **44** in the crude reaction mixture. Evidently, the trifluoroacetoxy anion generated from the Pummerer reaction is not sufficiently nucleophilic to attack the trimethylsilyl group, and consequently, only products resulting from proton loss are observed. This example represents a rare case of an allylsilane cyclization where the trialkylsilyl group is retained in the final product.[36]

It occurred to us at this stage of our studies that the *additive Pummerer* reaction of vinyl amido sulfoxides of

(31) The authors have deposited atomic coordinates for structure **41** with the Cambridge Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, CB2 1EZ, U.K.

(32) Fleming, I.; Dunogues, J.; Smithers, R. The Electrophilic Substitution of Allylsilanes and Vinylsilanes. In *Organic Reactions*; Kende, A. S., Ed.; John Wiley and Sons: New York, 1989; Vol. 37, Chapter 2, p 57.

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(34) Heerding, D. A.; Hong, C. Y.; Kado, N.; Look, G. C.; Overman, L. E. *J. Org. Chem.* **1993**, *58*, 6947.

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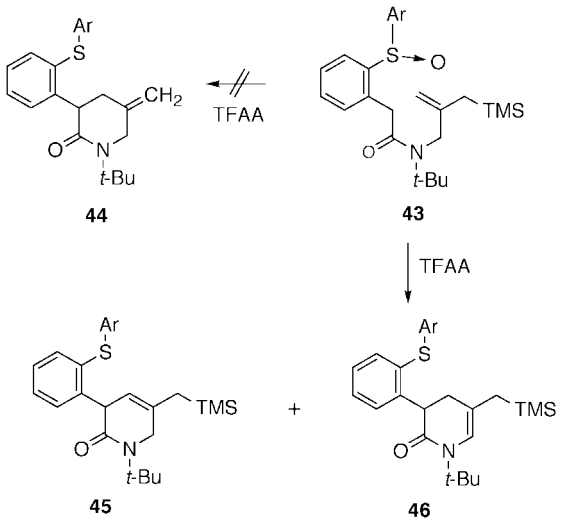
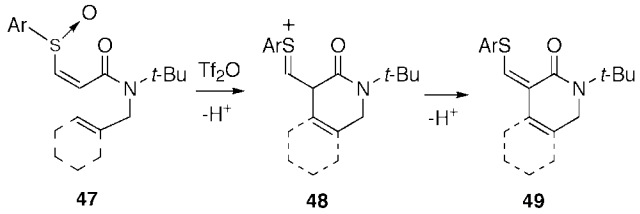
Scheme 11



Scheme 12

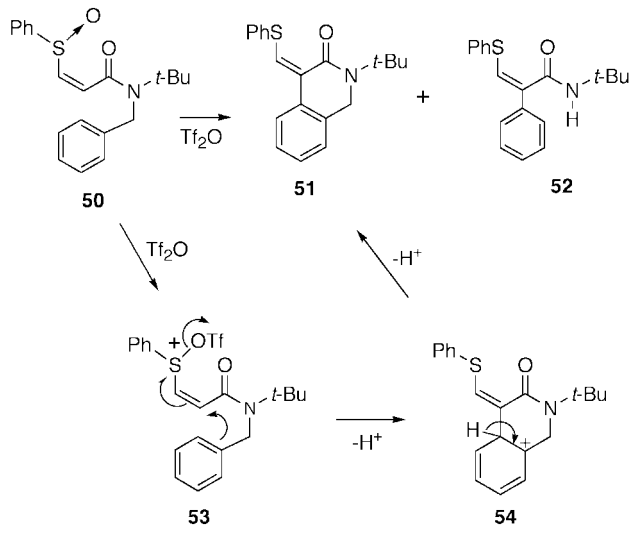


type **47** might proceed in a related fashion. We anticipated that activation of the vinylic sulfoxide C−C double bond by sulfoxide O-trifluoroacetylation would be followed by intramolecular cyclization via nucleophilic addition of the tethered π-bond. The resulting thionium ion **48** could then undergo deprotonation to furnish dihydropyridone **49** (Scheme 12).

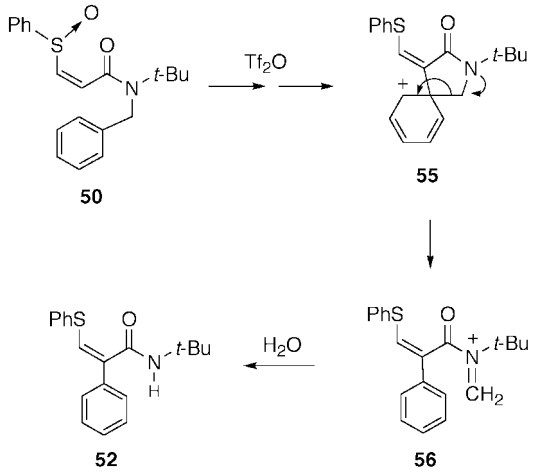
In this context, we prepared amido sulfoxide **50** in 76% overall yield from the reaction of 3-(phenylthio)acrylic acid with *tert*-butylbenzylamine followed by titanium(III)−H_2O_2 oxidation of the resulting sulfide. Extensive experimentation established that the best conditions to induce the *additive Pummerer* reaction involved treating **50** with 1.1 equiv of triflic anhydride in the presence of 2.2 equiv of triethylamine at −78 °C. The reaction of **50** under these Pummerer conditions gave rise to a mixture of dihydroisoquinoline **51** (32%) and the rearranged *N*-*tert*-butyl-2-phenyl-3-phenylsulfenyl acrylamide **52** (45%) (Scheme 13). The formation of **51** is perfectly consistent with the sequence of events proposed in Scheme 12. The critical step in this transformation involves a 6-*exo trig* cyclization of intermediate **53** to give **54** which is ultimately converted to **51** (Scheme 6). A plausible mechanism for the formation of the rearranged enamide **52** from amido sulfoxide **50** is outlined in Scheme 14. The first step involves *ipso* attack of the aromatic ring on the activated vinyl sulfoxide π-bond to produce the spiro-substituted cyclohexadienyl cation **55**. Nitrogen-assisted fragmentation of the C−C π-bond results in generation of acyl iminium ion **56** which is eventually converted to **52** on aqueous workup (Scheme 14).

In a further investigation of the *additive Pummerer* sequence, we examined the reaction of the related sulfoxides **57** and **60** with triflic anhydride. In the case of sulfoxide **57**, the reaction afforded a 1:4 mixture of

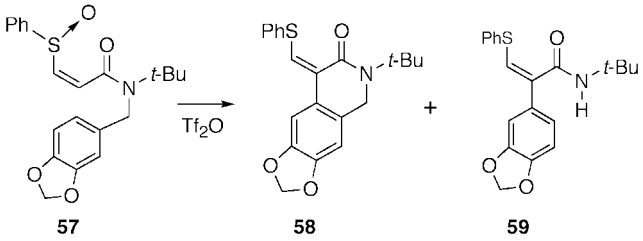
Scheme 13



Scheme 14

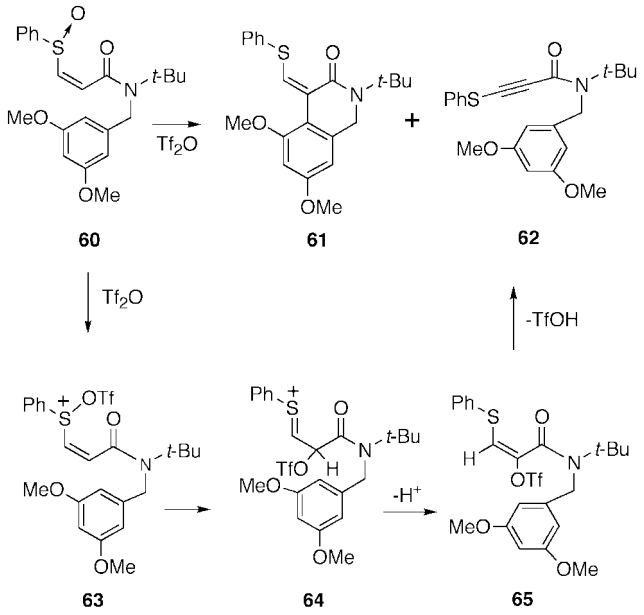


Scheme 15

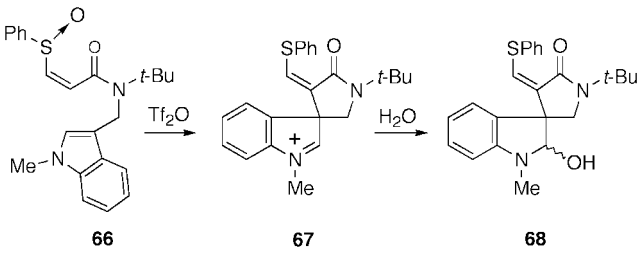


cyclized (**58**) and rearranged (**59**) amides (Scheme 15). The fact that **59** was the major product formed (60%) indicates that subtle electronic factors can influence the ratio of five-membered vs six-membered ring cyclization. With sulfinyl acrylamide **60**, the *meta* arrangement of substituents on the aromatic ring should preclude *ipso* attack. Indeed, stirring a sample of **60** with triflic anhydride afforded the expected dihydroisoquinolone **61** (63%) as the major product together with a small quantity of acetylene **62** (8%). No signs of a rearranged amide derived from five-membered ring cyclization (i.e., **55**) could be detected in the crude reaction mixture. More than likely, the formation of **62** involves attack of a triflate anion on the initially formed thionium ion followed by deprotonation and subsequent elimination of

Scheme 16



Scheme 17

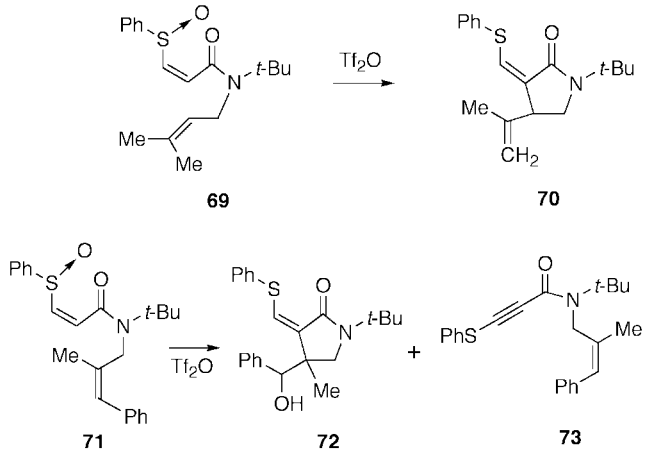


triflic acid (i.e., **60** → **63** → **64** → **65** → **62**) as shown in Scheme 16.[37–39]

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.[40] Consequently, we decided to investigate the additive Pummerer reaction where an indolyl methylene tether has been placed on the amide nitrogen as a method for generating highly functionalized indoles. Interestingly, the reaction of indoyl sulfoxide **66** with triflic anhydride produced spiro γ-lactam **68** in 51% yield as the only identifiable product. The reaction proceeds via a 5-*exo trig* cyclization to generate **67** as a transient cation which ultimately captures water (or its equivalent) to produce **68** (Scheme 17). In this case, preferential five-membered ring cyclization is probably related to the enhanced electron density at the β-position of the indole ring.[40]

The ability of simple π-bonds to participate as nucleophiles in *additive Pummerer* reactions was established by exposure of amido sulfoxides **69** and **71** to triflic anhydride at −78 °C which provided γ-lactams **70** and **72** in 57% and 40% isolated yields, respectively. The minor reaction product (14%) obtained from the reaction of **71** corresponded to acetylene **73** (Scheme 18). The formation of **70** and **72** nicely demonstrates that tethered alkenes can also be utilized in the cyclization step of these cascade reactions. Once again, all cyclization products are derived from a *5-exo trig* ring closure.

Scheme 18



In conclusion, the results presented here demonstrate the potential of both the *additive* and *vinylogous Pummerer* reactions for the synthesis of nitrogen heterocycles. The reaction sequence involves formation of an electrophilic thionium ion intermediate which is intercepted by a π-nucleophile tethered on the amide nitrogen. The overall transformations represent highly effective methods for converting relatively simple starting materials into complex nitrogen heterocycles. Further application of these sequences for the stereocontrolled synthesis of several alkaloids is under active investigation.

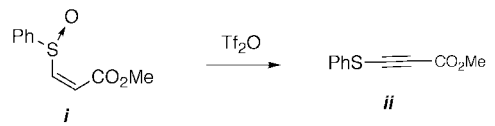
Experimental Section

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 argon. Solutions were evaporated under reduced pressure with a rotary evaporator, and the residue was chromatographed on a silica gel column using an ethyl acetate−hexane mixture as the eluent unless specified otherwise.

General Procedure for the Preparation of Secondary Allylic Amines. To a stirred solution of 50 mmol of the appropriate α,β-unsaturated aldehyde in 100 mL of $CHCl_3$ was added 5 g of $MgSO_4$ followed by an excess of *tert*-butylamine. The mixture was heated at reflux for 18 h, cooled to room temperature, and concentrated under reduced pressure. The crude imine was taken up in 100 mL of methanol and cooled to 0 °C, and 50 mmol of sodium borohydride was added over a period of 10 min. The mixture was stirred for an additional 2 h at room temperature, poured into 200 mL of water, and extracted with CH_2Cl_2. The solvent was removed under reduced pressure, and the crude product was purified by either distillation or silica gel column chromatography to give the pure amine.

General Procedure for the Preparation of Amido Sulfoxides Derived from 2-(*p*-Tolylsulfenylphenyl)acetic Acid (17). A solution containing 5.9 g (22.7 mmol) of 2-iodophenylacetic acid[41] and 4.6 g (31.7 mmol) of sodium *p*-thiocresolate in 40 mL of ethylene glycol was treated with 36

(37) Treatment of the known sulfoxide i[38] with triflic anhydride under the same experimental conditions used with **59** afforded acetylene ii,[39] thereby providing support for the proposed mechanism.



(38) Proust, S. M.; Ridley, D. D. *Aust. J. Chem.* **1984**, *37*, 1677.
(39) Gupta, I.; Yates, P. *J. Chem. Soc., Chem. Commun.* **1982**, 1227.
(40) Gilchrist, T. L. *Heterocyclic Chemistry*; Pitman: London, 1981.
(41) Sindelar, K.; Metysova, J.; Protiva, M. *Collect. Czech. Chem. Commun.* **1972**, *37*, 1734.

mg (0.068 mmol) of bis(bipyridine)−nickel(II) bromide.[24] The resulting mixture was heated at 150 °C for 3 h, acidified with 10% HCl, extracted with ether, and concentrated under reduced pressure. The residue was taken up in aqueous NaOH, washed with ether, and acidified with concentrated HCl. The aqueous solution was extracted with ether, and the organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The resulting solid was recrystallized from a benzene−hexane mixture to give 4.9 g (83%) of 2-(*p*-tolylsulfenylphenyl)acetic acid (**17**): mp 115−116 °C; IR (CCl_4) 3014, 2921, 1707, 1401, and 797 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.29 (s, 3H), 3.86 (s, 2H), 7.18 (m, 8H), and 10.95 (brs, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0, 39.3, 127.8, 128.3, 129.9, 130.6, 131.0, 132.0, 133.2, 135.0, 135.8, 136.9, and 177.6. Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46. Found: C, 69.75; H, 5.44.

To a solution of 1.3 g (5.0 mmol) of carboxylic acid **17** in 25 mL of benzene was added 1.3 g (10.1 mmol) of oxalyl chloride followed by one drop of DMF. After being stirred for 2 h at room temperature, the mixture was concentrated under reduced pressure, dissolved in 5 mL CH_2Cl_2, and added dropwise to a mixture of the appropriate secondary amine (11.6 mmol) in 50 mL of CH_2Cl_2. The solution was allowed to stir for 2 h and was quenched with water, extracted with CH_2Cl_2, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give the pure amide.

A mixture containing 1.0 mmol of the amido sulfide and 1.5 mmol of a 16% aqueous solution of titanium(III) chloride in 50 mL of acetonitrile/methanol (1:5) was stirred at room temperature. To this mixture was added 0.45 mL (4 mmol) of 30% hydrogen peroxide in 10 mL of methanol. After being stirred for 10 min at room temperature, the mixture was diluted with water, extracted with $CHCl_3$, and dried over $MgSO_4$. Concentration under reduced pressure followed by chromatography on silica gel afforded the pure sulfoxide.

***N*-Methyl-*N*-phenyl-2-(2-*p*-tolylsulfenylphenyl)acetamide.** A solution containing 4.2 g (16.3 mmol) of carboxylic acid **17** and 2.5 mL of triethylamine in 75 mL of CH_2Cl_2 was treated with 5.4 g (20.3 mmol) of phenyl *N*-phenylphosphoramidochloridate.[42] The mixture was stirred for 45 min under N_2, and then 3.5 g (32.5 mmol) of *N*-methylaniline was added dropwise via syringe. The solution was stirred an additional 1.5 h, acidified with 10% HCl, extracted with CH_2Cl_2, and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by flash silica gel chromatography afforded 4.9 g (87%) of *N*-methyl-*N*-phenyl-2-(2-*p*-tolylsulfenylphenyl)acetamide as a colorless solid: mp 93−94 °C; IR (CCl_4) 3053, 2918, 1659, 1374, and 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.26 (s, 3H), 3.24 (s, 3H), 3.61 (s, 2H), and 7.19 (m, 13H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.6, 37.1, 39.2, 126.9, 127.2, 127.3, 127.4, 129.3, 129.5, 129.9, 130.4, 132.1, 132.5, 134.6, 136.0, 137.1, 143.5, and 170.0. Anal. Calcd for $C_{22}H_{21}NOS$: C, 76.05; H, 6.09. Found: C, 76.03; H, 6.08.

***N*-Methyl-*N*-phenyl-2-(2-*p*-tolylsulfinylphenyl)acetamide (18).** Following the general procedure, a 2.7 g (7.8 mmol) sample of the above sulfide was oxidized to give 2.6 g (93%) of **18** as a colorless oil: IR (neat) 1652, 1588, 1488, 1367, and 1026 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.34 (s, 3H), 3.28 (s, 3H), 3.59 (d, 1H, J = 16.1 Hz), 3.66 (d, 1H, J = 16.1 Hz), 7.19 (d, 4H, J = 6.8 Hz), 7.37−7.46 (m, 8H), and 7.68−7.71 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.3, 37.6, 125.5, 125.6, 127.2, 128.1, 128.2, 129.7, 129.9, 130.7, 131.0, 134.2, 141.1, 141.2, 143.4, 144.1, and 169.5; HRMS calcd for $C_{22}H_{21}NO_2S$ 363.1293, found 363.1287.

1-Methyl-3-(2-*p*-tolylsulfenylphenyl)-1,3-dihydroindol-2-one (19). To a solution of 0.95 g (2.6 mmol) of **18** in 10 mL of CH_2Cl_2 was added 0.36 mL of triethyamine followed by 1.1 g (5.2 mmol) of trifluoroacetic anhydride. After being stirred for 10 min, the reaction mixture was diluted with CH_2Cl_2, washed with 10% HCl, saturated $NaHCO_3$, and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded 0.82 g (91%) of **19** as a white solid: mp 110−111 °C; IR (CCl_4) 3053, 2925, 1709, 1488, 1082, and 748 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.32 (s, 3H), 3.28 (s, 3H), 5.30 (brs, 1H), and 6.81−7.49 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0, 26.4, 49.9, 108.0, 122.5, 128.1, 128.2, 128.3, 128.4, 128.5, 129.9, 130.5, 130.6, 130.7, 130.8, 133.7, 136.3, 136.9, 144.3, and 176.0. Anal. Calcd for $C_{21}H_{19}NOS$: C, 76.49; H, 5.54. Found: C, 76.39; H, 5.51.

The structure of **19** was established by reduction to oxindole **20**. To a solution containing 100 mg (0.29 mmol) of **19** in 5 mL of ethanol was added 34 mg of W-2 Raney nickel. The mixture was heated at reflux for 24 h, filtered through Celite, and concentrated under reduced pressure. The residue was subjected to silica gel chromatography to give 63 mg (97%) of 1-methyl-3-phenyl-1,3-dihydroindole-2-one (**20**) as a colorless solid: mp 115−116 °C (lit.[26] mp 116−117 °C); ^1H NMR ($CDCl_3$, 300 MHz) δ 3.24 (s, 3H), 4.60 (s, 1H), 6.89 (d, 1H, J = 7.7 Hz), and 7.05−7.40 (m, 8H).

1-(3,4-Dihydro-2*H*-quinolin-1-yl)-2-(2-*p*-tolylsulfenylphenyl)ethanone. Following the general procedure, treatment of 1.0 g (3.8 mmol) of carboxylic acid **17** with 1.2 g (8.9 mmol) of 1,2,3,4-tetrahydroquinoline gave 1.4 g (99%) of 1-(3,4-dihydro-2*H*-quinolin-1-yl)-2-(2-*p*-tolylsulfenylphenyl)ethanone as a light yellow oil: IR (neat) 2938, 1644, 1484, 1372, and 749 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.88 (m, 2H), 2.25 (s, 3H), 2.66 (t, 2H, J = 6.7 Hz), 3.75 (m, 2H), 3.97 (s, 2H), 7.04 (s, 4H), and 7.12−7.33 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.8, 23.7, 26.5, 39.8, 43.2, 124.3, 125.0, 125.8, 127.5, 128.2, 129.6, 130.1, 130.5, 132.0, 132.8, 134.6, 136.4, 137.4, 138.8, and 170.0; HRMS calcd for $C_{24}H_{23}NOS$ 373.1500, found 373.1499.

1-(3,4-Dihydro-2*H*-quinolin-1-yl)-2-(2-*p*-tolylsulfinylphenyl)ethanone (21). Following the general procedure, treatment of 0.57 g (1.5 mmol) of the above sulfide with 2.2 mL of a 16% aqueous solution of $TiCl_3$ followed by 0.7 mL of 30% H_2O_2 afforded 0.56 g (95%) of **21** as a colorless oil: IR (neat) 2921, 1560, 1486, 1380, and 1032 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.94 (m, 2H), 2.31 (s, 3H), 2.74 (t, 2H, J = 6.7 Hz), 3.71 (m, 1H), 3.95 (m, 1H), 3.97 (s, 2H), 7.13−7.18 (m, 5H), 7.27−7.30 (m, 3H), 7.38−7.42 (m, 3H), and 7.78−7.81 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.1, 23.7, 26.6, 37.8, 43.1, 124.2, 125.2, 125.5, 125.8, 125.9, 126.1, 128.1, 128.5, 129.6, 130.9, 131.0, 134.1, 138.5, 140.8, 141.1, 143.4, and 169.1; HRMS calcd for $C_{24}H_{23}NO_2S$ 389.1449, found 389.1447.

1-(2-*p*-Tolylsulfenylphenyl)-1,4,5,6-tetrahydropyrrolo[3,2,1-*ij*]quinolin-2-one (22). To a solution of 0.29 g (0.76 mmol) of **21** in 25 mL of CH_2Cl_2 was added 0.12 mL of triethylamine followed by 0.32 g (1.5 mmol) of trifluoroacetic anhydride. After being stirred for 10 min, the reaction mixture was diluted with CH_2Cl_2, washed with 10% HCl and a saturated $NaHCO_3$ solution, and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by silica gel chromatography gave 0.24 g (85%) of **22** as a white solid: mp 166−167 °C; IR (CCl_4) 2947, 1701, 1474, 1353, and 784 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.03 (m, 2H), 2.31 (s, 3H), 2.80 (t, 2H, J = 5.9 Hz), 3.77 (m, 2H), 5.50 (brs, 1H), 6.87 (m, 3H), and 7.01−7.35 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0, 21.2, 24.5, 39.1, 50.8, 120.0, 121.9, 122.2, 126.8, 128.0, 128.2, 129.8, 130.5, 130.6, 130.7, 130.8, 132.7, 133.6, 136.3, 136.8, 140.1, and 174.9. Anal. Calcd for $C_{24}H_{21}NOS$: C, 77.60; H, 5.70. Found: C, 77.62; H, 5.75.

1-Phenyl-5,6-dihydro-1*H*,4*H*-pyrrolo[3,2,1-*ij*]quinolin-2-one (23). To a solution containing 0.9 g (2.4 mmol) of **22** in 50 mL of ethanol was added 0.5 g of W-2 Raney nickel. The mixture was heated at reflux for 5 days, filtered through Celite, and concentrated under reduced pressure. The residue was subjected to silica gel chromatography. The first product eluted from the column (0.14 g, 23% yield) was identified as **23**: mp 126−127 °C; IR (CCl_4) 2925, 1709, 1623, 1474, and 1346 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.00 (m, 2H), 2.78 (t, 2H, J = 6.0 Hz), 3.71 (m, 2H), 4.57 (s, 1H), 6.98 (m, 3H), and 7.27 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0, 24.4, 38.9, 52.7, 120.0, 121.9, 122.5, 126.9, 127.1, 127.2, 128.2, 128.6, 136.4, 140.1, and 174.6. Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.76; H, 6.09; N, 5.59.

(42) Mestres, R.; Palomo, C. *Synthesis* **1982**, 288.

1-Cyclohexyl-5,6-dihydro-1*H*,4*H*-pyrrolo[3,2,1-*ij*]quinolin-2-one (24). The second product isolated (0.14 g, 23% yield) was assigned as **24**; mp 104−105 °C; IR (CCl_4) 2925, 1702, 1481, 1353, and 784 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.02−1.51 (m, 6H), 1.63 (d, 2H, J = 10.6 Hz), 1.76 (d, 2H, J = 10.6 Hz), 1.98 (m, 2H), 2.14 (m, 1H), 2.75 (t, 2H, J = 6.0 Hz), 3.32 (d, 1H, J = 3.3 Hz), 3.71 (m, 2H), 6.91 (t, 1H, J = 7.5 Hz), 7.00 (d, 1H, J = 7.5 Hz), and 7.10 (d, 1H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 24.6, 26.1, 26.2, 26.6, 28.2, 30.7, 38.6, 40.4, 52.6, 119.7, 121.4, 122.3, 126.4, 126.5, 140.5, and 176.2. Anal. Calcd for $C_{15}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.77; H, 8.22; N, 5.44.

***N*-Benzyl-*N*-methyl-2-(2-*p*-tolylsulfenylphenyl)acetamide.** Following the general procedure, treatment of 1.7 g (6.6 mmol) of carboxylic acid **17** with 1.8 g (15.1 mmol) of *N*-benzylmethylamine afforded 1.6 g (67%) of *N*-benzyl-*N*-methyl-2-(2-*p*-tolylsulfenylphenyl)acetamide as a 1.4:1 mixture of rotamers in solution: IR (neat) 3057, 3022, 2924, 1644, 1491, 1106, 805, and 749 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) major rotamer δ 2.26 (s, 3H), 2.82 (s, 3H), 3.87 (s, 2H), 4.56 (s, 2H), and 7.0−7.35 (m, 13H); minor rotamer δ 2.23 (s, 3H), 2.89 (s, 3H), 3.89 (s, 2H), 4.44 (s, 2H), and 7.0−7.35 (m, 13H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.7, 33.6, 34.7, 38.2, 38.5, 50.7, 53.3, 126.3, 127.0, 127.2, 127.5, 127.6, 127.7, 127.8, 128.2, 128.5, 129.6, 129.7, 129.8, 129.9, 130.0, 131.9, 132.8, 132.9, 134.3, 134.4, 136.3, 136.4, 136.5, 136.7, 137.1, 170.4, and 170.7; HRMS calcd for $C_{23}H_{23}NOS$ 361.1500, found 361.1505.

***N*-Benzyl-*N*-methyl-2-(2-*p*-tolylsulfinylphenyl)acetamide (25).** Following the general procedure, treatment of 1.4 g (3.8 mmol) of the above sulfide with 5.6 mL of a 16% aqueous solution of $TiCl_3$ followed by reaction with 1.8 mL of 30% H_2O_2 gave 1.2 g (83%) of **25** as a 1.4:1 mixture of rotamers: IR (neat) 3050, 2917, 1644, 1071, 1029, and 721 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) major rotamer δ 2.30 (s, 3H), 2.88 (s, 3H), 3.85−4.06 (m, 2H), 4.56−4.64 (m, 2H), 7.12−7.54 (m, 12H), and 7.75−7.79 (m, 1H); minor rotamer δ 2.30 (s, 3H), 2.94 (s, 3H), 3.85−4.06 (m, 2H), 4.56−4.64 (m, 2H), 7.12−7.54 (m, 12H), and 7.75−7.79 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.3, 34.3, 35.0, 36.6, 37.1, 51.1, 53.6, 125.6, 126.2, 126.3, 126.5, 127.4, 127.7, 128.0, 128.3, 128.5, 128.9, 129.8, 130.4, 131.4, 131.5, 137.0, 141.3, 169.8, and 170.0; HRMS calcd for $C_{23}H_{23}NO_2S$ 377.1449, found 377.1446.

***N*-Benzyl-2-hydroxy-*N*-methyl-2-(2-*p*-tolylsulfenylphenyl)acetamide (26).** To a solution of 0.5 g (1.3 mmol) of **25** in 20 mL of CH_2Cl_2 was added 0.2 mL of triethylamine followed by 0.55 g (2.6 mmol) of trifluoroacetic anhydride. After being stirred for 10 min, the reaction was diluted with CH_2Cl_2, washed with 10% HCl and saturated $NaHCO_3$, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel to give **26** as 1.7:1 mixture of rotamers in solution: mp 103−104 °C; IR (CCl_4) 3402, 2925, 1645, 1488, 1381, and 1061 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) major rotamer δ 2.31 (s, 3H), 2.63 (s, 3H), 4.60 (d, 1H, J = 14.6 Hz), 4.70 (d, 1H, J = 6.1 Hz), 4.71 (d, 1H, J = 14.6 Hz), 5.89 (d, 1H, J = 6.1 Hz), 6.82 (m, 1H), and 6.99−7.37 (m, 12H); minor rotamer δ 2.26 (s, 3H), 2.92 (s, 3H), 4.27 (d, 1H, J = 16.1 Hz), 4.34 (d, 1H, J = 16.1 Hz), 4.77 (d, 1H, J = 6.3 Hz), 5.96 (d, 1H, J = 6.3 Hz), 6.82 (m, 1H), and 6.99−7.37 (m, 12H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 21.0, 33.6, 33.7, 51.9, 52.0, 68.2, 68.4, 126.7, 127.4, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.6, 129.2, 130.0, 130.1, 130.9, 131.3, 131.6, 132.2, 132.6, 135.1, 135.3, 135.9, 136.2, 137.4, 137.5, 139.1, 139.8, 172.8, and 173.0. Anal. Calcd for $C_{23}H_{23}NO_2S$: C, 73.18; H, 6.14. Found: C, 73.13; H, 6.19.

***N*-Benzyl-*N*-*tert*-butyl-2-(2-*p*-tolylsulfenylphenyl)acetamide.** Following the general procedure, treatment of 2.0 g (7.7 mmol) of carboxylic acid **17** with 2.9 g (17.8 mmol) of *N*-*tert*-butylbenzylamine afforded 2.7 g (86%) of *N*-benzyl-*N*-*tert*-butyl-2-(2-*p*-tolylsulfenylphenyl)acetamide as a colorless solid: mp 101−102 ×a1C; IR (CCl_4) 2908, 1630, 1488, 1196, and 784 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.43 (s, 9H), 2.27 (s, 3H), 3.77 (s, 2H), 4.59 (s, 2H), 7.05 (s, 3H), and 7.03−7.33 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0, 28.7, 41.6, 49.1, 58.0, 125.6, 126.8, 127.6, 127.8, 128.6, 129.8, 130.1, 132.5, 133.3, 134.9, 136.4, 137.8, 139.4, and 172.0. Anal. Calcd for $C_{26}H_{29}NOS$: C, 77.38; H, 7.24. Found: C, 77.35; H, 7.22.

***N*-Benzyl-*N*-*tert*-butyl-2-(2-*p*-tolylsulfinylphenyl)acetamide (27).** Following the general procedure, treatment of 2.9 g (7.3 mmol) of the above sulfide with 10.5 mL of a 16% aqueous solution of $TiCl_3$ followed by 3.3 mL of 30% H_2O_2 gave 2.7 g (89%) of **27** as a colorless solid: mp 158−159 °C; IR (CCl_4) 2954, 1645, 1381, 1026, and 748 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.45 (s, 9H), 2.32 (s, 3H), 3.73 (d, 1H, J = 16.3 Hz), 3.83 (d, 1H, J = 16.3 Hz), 4.59 (s, 2H), 7.15 (d, 2H, J = 7.9 Hz), 7.22−7.33 (m, 5H), 7.38−7.43 (m, 5H), and 7.76 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.3, 28.6, 39.6, 49.0, 58.2, 125.4, 125.6, 125.8, 127.1, 128.2, 128.9, 129.7, 130.1, 131.2, 134.4, 138.8, 141.0, 141.1, 144.1, and 171.0. Anal. Calcd for $C_{26}H_{29}NO_2S$: C, 74.43; H, 6.97. Found: C, 74.42; H, 6.98.

2-*tert*-Butyl-4-(2-*p*-tolylsufenylphenyl)-2,4-dihydro-1*H*-isoquinolin-3-one (28). To a solution of 2.6 g (6.1 mmol) of **27** in 50 mL of CH_2Cl_2 was added 0.9 mL of triethylamine followed by 2.6 g (12.3 mmol) of trifluoroacetic anhydride. After the mixture was stirred for 10 min, the reaction was diluted with CH_2Cl_2, washed with 10% HCl and a saturated $NaHCO_3$ solution, and dried over $MgSO_4$. Removal of the solvent under reduced pressure left a crude oil which was chromatographed on silica gel to give 2.04 g (83%) of **28** as a white foam: IR (CCl_4) 2970, 1647, 1489, 807, and 745 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.51 (s, 9H), 2.28 (s, 3H), 4.56 (d, 1H, J = 15.5 Hz), 4.72 (d, 1H, J = 15.5 Hz), 5.32 (brs, 1H), 6.74 (d, 1H, J = 7.5 Hz), 7.02 (d, 2H, J = 8.0 Hz), and 7.10−7.33 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0, 28.4, 47.1, 52.7, 57.8, 125.0, 126.3, 126.9, 127.3, 127.5, 127.8, 129.7, 131.0, 131.3, 132.1, 133.2, 133.6, 136.2, 136.4, 136.6, 141.4, and 170.1; HRMS calcd for $C_{26}H_{27}NOS$ 401.1813, found: 401.1812.

***N*-*tert*-Butyl-*N*-(3-methoxybenzyl)-2-(2-*p*-tolylsulfenylphenyl)acetamide.** Treatment of a 25 g (184 mmol) sample of *m*-anisaldehyde with excess *tert*-butylamine followed by reduction with sodium borohydride according to the general method gave 33.4 g (94%) of *tert*-butyl(3-methoxybenzyl)amine as a colorless liquid: bp 136 °C/15 mm; IR (neat) 3309, 1595, 1488, 1260, and 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.85 (brs, 1H), 1.15 (s, 9H), 3.68 (d, 2H, J = 5.7 Hz), 6.74 (m, 1H), 6.90 (m, 2H), and 7.19 (t, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.9, 47.0, 50.3, 54.8, 111.9, 113.5, 120.2, 129.1, 143.0, and 159.5.

Following the general procedure, treatment of 1.5 g (5.8 mmol) of carboxylic acid **17** with 2.6 g (13.4 mmol) of *tert*-butyl(3-methoxybenzyl)amine afforded 2.4 g (93%) of *N*-*tert*-butyl-*N*-(3-methoxybenzyl)-2-(2-*p*-tolylsulfenylphenyl)acetamide as a white solid: mp 88−89 °C; IR (CCl_4) 2959, 1637, 1393, 1036, and 777 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.44 (s, 9H), 2.28 (s, 3H), 3.78 (s, 5H), 4.57 (s, 2H), 6.77−6.85 (m, 3H), 6.99−7.06 (m, 3H), and 7.13−7.33 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0, 28.7, 41.6, 49.1, 55.2, 58.0, 111.2, 112.3, 117.9, 127.6, 127.7, 129.7, 129.8, 130.1, 130.3, 132.5, 133.1, 135.1, 136.5, 137.7, 141.2, 160.0, and 172.0. Anal. Calcd for $C_{26}H_{31}NO_2S$: C, 74.79; H, 7.21. Found: C, 74.65; H, 7.20.

***N*-*tert*-Butyl-*N*-(3-methoxybenzyl)-2-(2-*p*-tolylsulfinylphenyl)acetamide (29).** Treatment of 2.1 g (4.9 mmol) of the above sulfide with 7.1 mL of a 16% aqueous solution of $TiCl_3$ followed by reaction with 2.2 mL of 30% H_2O_2 gave 2.1 g (96%) of **29** as a colorless oil: IR (neat) 2961, 1645, 1595, 1033, and 727 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.45 (s, 9H), 2.31 (s, 3H), 3.75 (d, 1H, J = 16.3 Hz), 3.80 (s, 3H), 3.84 (d, 1H, J = 16.3 Hz), 4.56 (s, 2H), 6.83 (m, 3H), 7.15 (d, 2H, J = 7.8 Hz), 7.22−7.37 (m, 3H), 7.40 (m, 3H), and 7.76 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 28.5, 39.5, 48.8, 55.0, 58.1, 111.1, 112.3, 117.6, 125.5, 125.7, 128.1, 129.6, 129.9, 130.0, 131.1, 134.4, 140.5, 141.0, 141.1, 144.1, 160.0, and 170.9; HRMS calcd for $C_{26}H_{31}NO_3S$ 449.2025, found 449.2027.

2-*tert*-Butyl-5-methoxy-4-(2-*p*-tolysulfenylphenyl)-1,4-dihydro-2*H*-isoquinolin-3-one (30). To a solution containing 0.33 g (0.7 mmol) of **29** in 25 mL of CH_2Cl_2 was added 0.11 mL of triethylamine followed by 0.31 g (1.5 mmol) of trifluoroacetic anhydride. After 10 min of stirring, the reaction mixture was diluted with CH_2Cl_2, washed with 10% HCl and

a saturated $NaHCO_3$ solution, and dried over $MgSO_4$. Removal of the solvent under reduced pressure left a colorless oil which was subjected to silica gel chromatography. The first product eluted from the column (50% yield) contained a colorless oil whose structure was assigned as **30** on the basis of its spectral properties: IR (neat) 2966, 1637, 1463, 1260, and 728 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.47 (s, 9H), 2.32 (s, 3H), 3.60 (s, 3H), 4.67 (d, 1H, J = 17.0 Hz), 4.82 (d, 1H, J = 17.0 Hz), 5.77 (s, 1H), 6.69 (d, 1H, J = 8.2 Hz), 6.84 (m, 2H), 7.05 (m, 3H), 7.25 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.1, 28.1, 46.9, 47.7, 55.4, 57.7, 108.8, 117.3, 124.7, 126.6, 127.0, 127.7, 127.8, 129.6, 131.0, 131.3, 133.4, 135.0, 136.2, 137.5, 142.6, 156.3, and 169.9; HRMS calcd for $C_{26}H_{29}NO_2S$ 431.1919, found 431.1912.

2-*tert*-Butyl-7-methoxy-4-(2-*p*-tolylsulfenylphenyl)-1,4-dihydro-2*H*-isoquinolin-3-one (31). The second product eluted from the column (44% yield) was assigned as **31** on the basis of its spectral properties: IR (neat) 2963, 1647, 1500, 1458, and 1194 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.51 (s, 9H), 2.28 (s, 3H), 3.78 (s, 3H), 4.55 (d, 1H, J = 15.5 Hz), 4.69 (d, 1H, J = 15.5 Hz), 5.24 (s, 1H), 6.16 (m, 2H), 7.02 (d, 1H, J = 8.1 Hz), and 7.13−7.32 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0, 28.3, 47.3, 52.0, 55.3, 57.8, 110.0, 113.4, 127.4, 127.7, 128.1, 128.4, 129.7, 130.9, 131.1, 133.0, 133.2, 133.6, 136.0, 136.5, 141.9, 158.1, and 170.3; HRMS calcd for $C_{26}H_{29}NO_2S$ 431.1919, found 431.1918.

***N*-*tert*-Butyl-*N*-furan-3-ylmethyl-2-(2-*p*-tolylsulfenylphenyl)acetamide.** Treatment of 4.2 g (43.7 mmol) of 3-furancarboxaldehyde with an excess of *tert*-butylamine followed by reduction with sodium borohydride according to the general procedure afforded 5.6 g (85%) of *N*-*tert*-butyl-*N*-furan-3-ylmethylamine as a colorless liquid: bp 90−91 °C (27 mm); IR (neat) 3317, 1502, 1360, and 896 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.78 (brs, 1H), 1.14 (s, 9H), 3.57 (s, 2H), 6.36 (s, 1H), and 7.33 (s, 2H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 28.6, 37.3, 50.1, 110.1, 124.7, 139.0, and 142.5.

Following the general procedure, treatment of 1.3 g (5.03 mmol) of carboxylic acid **17** with 1.6 g (10.1 mmol) of *N*-*tert*-butyl-*N*-furan-3-ylmethylamine gave 1.5 g (75%) of *N*-*tert*-butyl-*N*-furan-3-ylmethyl-2-(2-*p*-tolylsulfenylphenyl)acetamide as a colorless solid: mp 104−105 °C; IR (CCl_4) 2968, 1652, 1488, 1381, 1189, 1018, and 869 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHZ) δ 1.44 (s, 9H), 2.28 (s, 3H), 3.85 (s, 2H), 4.36 (s, 2H), 6.28 (s, 1H), 7.05 (q, 4H, J = 8.5 Hz), 7.13−7.36 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9, 28.6, 41.2, 41.4, 57.7, 109.1, 124.6, 127.5, 127.8, 129.8, 129.9, 130.1, 132.4, 133.2, 134.8, 136.5, 137.7, 139.3, 143.3, and 171.4. Anal. Calcd for $C_{24}H_{27}NO_2S$: C, 73.25; H, 6.92. Found: C, 73.18; H, 6.90.

***N*-*tert*-Butyl-*N*-furan-3-ylmethyl-2-(2-*p*-tolylsulfinylphenyl)acetamide (32).** Treatment of 0.44 g (1.11 mmol) of the above sulfide with 1.6 mL of a 16% aqueous solution of $TiCl_3$ followed by reaction with 0.5 mL of 30% H_2O_2 afforded 0.44 g (96%) of **32** as a colorless oil: IR (neat) 2968, 1645, 1374, 1033, and 727 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.45 (s, 9H), 2.34 (s, 3H), 3.84 (d, 1H, J = 16.2 Hz), 3.93 (d, 1H, J = 16.2 Hz), 4.34 (s, 2H), 6.32 (s, 1H), 7.18−7.47 (m, 9H), and 7.73−7.76 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 28.5, 39.5, 41.3, 58.0, 108.9, 124.3, 125.5, 126.0, 128.2, 129.8, 130.0, 131.3, 134.6, 139.2, 140.9, 141.2, 143.7, 144.0, and 170.5; HRMS calcd for $C_{24}H_{27}NO_3S$ 409.1712, found 409.1702.

5-*tert*-Butyl-7-(2-*p*-tolylsulfenylphenyl)-5,7-dihydro-4*H*-furo[3,2-*c*]pyridin-6-one (33). To a solution of 0.37 g (0.9 mmol) of **32** in 25 mL of CH_2Cl_2 was added 0.14 mL of triethylamine followed by 0.34 g (1.8 mmol) of trifluoroacetic anhydride. After being stirred for 10 min, the reaction mixture was diluted with CH_2Cl_2, washed with 10% HCl and a saturated $NaHCO_3$ solution, and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by silica gel chromatography afforded 240 mg (68%) of **33** as a clear oil: IR (neat) 2965, 1641, 1463, and 1190 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.51 (s, 9H), 2.29 (s, 3H), 4.46 (d, 2H, J = 3.9 Hz), 5.33 (t, 1H, J = 3.9 Hz), 6.25 (d, 1H, J = 1.8 Hz), and 7.03−7.27 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0, 28.1, 42.4, 48.5, 58.5, 107.6, 112.3, 127.4, 128.2, 129.7, 131.1, 133.2, 133.5, 136.1, 136.6, 140.0, 143.0, 146.8, and 168.4; HRMS calcd for $C_{24}H_{25}NO_2S$ 391.1606, found 391.1602.

***N*-*tert*-Butyl-*N*-cyclohex-1-enylmethyl-2-(2-*p*-tolylsulfenylphenyl)acetamide.** Following the general procedure, treatment of 1.3 g (5.0 mmol) of carboxylic acid **17** with 1.9 g (11.6 mmol) of cyclohexenylamine[43] gave 1.8 g (88%) of *N*-*tert*-butyl-*N*-cyclohex-1-enylmethyl-2-(2-*p*-tolylsulfenylphenyl)acetamide as a colorless oil: IR (neat) 2925, 1645, 1488, 1196, and 748 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.43 (s, 9H), 1.55−1.63 (m, 4H), 1.80 (m, 2H), 2.00 (m, 2H), 2.29 (s, 3H), 3.67 (s, 2H), 3.74 (s, 2H), 5.64 (brs, 1H), 7.08 (q, 4H, J = 8.4 Hz), and 7.14−7.34 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0, 22.5, 24.8, 26.4, 28.4, 41.2, 50.6, 57.3, 121.2, 127.4, 127.7, 129.7, 129.8, 130.2, 132.5, 133.0, 134.7, 134.8, 136.5, 138.1, and 171.9; HRMS calcd for $C_{26}H_{33}NOS$ 407.2283, found 407.2282.

***N*-*tert*-Butyl-*N*-cyclohex-1-enylmethyl-2-(2-*p*-tolylsulfinylphenyl)acetamide (34).** Treatment of 0.23 g (0.56 mmol) of the above sulfide with 0.1 mL of a 16% aqueous solution of $TiCl_3$ followed by reaction with 0.25 mL of 30% H_2O_2 afforded 0.2 g (84%) of **34** as a clear oil: IR (neat) 2925, 1645, 1196, and 755 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.43 (s, 9H), 1.65 (m, 4H), 1.86 (m, 2H), 2.07 (m, 2H), 2.33 (s, 3H), 3.73 (s, 2H), 3.80 (s, 2H), 5.67 (brs, 1H), 7.21−7.29 (m, 3H), 7.37−7.42 (m, 2H), 7.52 (d, 2H, J = 8.2 Hz), and 7.74−7.77 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.1, 22.2, 22.3, 24.6, 26.2, 28.1, 39.1, 50.4, 57.4, 121.1, 125.3, 125.6, 127.9, 129.6, 129.8, 131.0, 134.4, 134.8, 140.9, 141.1, 143.9, and 170.6; HRMS calcd for $C_{26}H_{33}NO_2S$ 423.2232, found 423.2230.

2-*tert*-Butyl-4-(2-*p*-tolylsulfenylphenyl)-2,4,5,6,7,8-hexahydro-1*H*-isoquinolin-3-one (37). To a solution of 0.17 g (0.4 mmol) of **34** in 20 mL of CH_2Cl_2 was added 0.06 mL of triethylamine followed by 0.17 g (0.8 mmol) of trifluoroacetic anhydride. After being stirred for 10 min, the reaction mixture was diluted with CH_2Cl_2, washed with 10% HCl and a saturated $NaHCO_3$ solution, and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by silica gel chromatography afforded 110 mg (67%) of **37** as a colorless oil: IR (neat) 2918, 1637, 1196, and 741 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.38−1.58 (m, 4H), 1.44 (s, 9H), 1.68 (m, 2H), 1.88 (m, 2H), 2.30 (s, 3H), 3.85 (d, 1H, J = 16.3 Hz), 3.94 (d, 1H, J = 16.3 Hz), 4.53 (brs, 1H), and 7.05−7.25 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.1, 22.3, 22.4, 26.7, 26.8, 28.0, 49.8, 53.1, 57.2, 124.2, 124.4, 127.1, 127.7, 129.2, 129.8, 131.4, 133.0, 133.5, 136.4, 136.6, 142.1, and 169.6; HRMS calcd for $C_{26}H_{31}NOS$ 405.2126, found 405.2124.

***N*-*tert*-Butyl-*N*-(2-methylpent-2-enyl)-2-(2-*p*-tolylsulfenylphenyl)acetamide.** Treatment of a 10.0 g (102 mmol) sample of 2-methyl-2-pentenal with excess *tert*-butylamine followed by reduction with sodium borohydride according to the general procedure afforded 11.1 g (70%) of *N*-*tert*-butyl-(2-methylpent-2-enyl)amine: IR (neat) 3320, 2958, 1448, and 1225 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.70 (brs, 1H), 0.95 (t, 3H, J = 7.5 Hz), 1.11 (s, 9H), 1.65 (s, 3H), 2.02 (m, 2H), 3.06 (s, 2H), 5.29 (t, 1H, J = 1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.9, 14.9, 20.9, 28.9, 49.9, 50.5, 126.9, and 133.6.

Following the general procedure, treatment of 1.3 g (5.0 mmol) of carboxylic acid **17** with 1.7 g (11.1 mmol) of *N*-*tert*-butyl(2-methylpent-2-enyl)amine afforded 1.8 g (91%) of *N*-*tert*-butyl-*N*-(2-methylpent-2-enyl)-2-(2-*p*-tolylsulfenylphenyl)acetamide as a colorless solid: mp 61−62 °C; IR (CCl_4) 2961, 1645, 1388, 1196, 805, and 748 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.95 (t, 3H, J = 7.5 Hz), 1.43 (s, 9H), 1.54 (s, 3H), 2.06 (m, 2H), 2.91 (s, 3H), 3.70 (s, 2H), 3.72 (s, 2H), 5.41 (t, 1H, J = 7.0 Hz), 7.12 (m, 4H), and 7.27 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.1, 14.3, 20.8, 21.0, 28.4, 41.1, 51.5, 57.4, 126.0, 127.3, 127.6, 129.6, 129.8, 130.4, 131.0, 132.4, 132.8, 135.0, 136.5, 137.9, and 171.9. Anal. Calcd for $C_{25}H_{33}NOS$: C, 75.90; H, 8.41; N, 3.54. Found: C, 75.68; H, 8.31; N, 3.44.

***N*-*tert*-Butyl-*N*-(2-methylpent-2-enyl)-2-(2-*p*-tolylsulfinylphenyl)acetamide (35).** Treatment of a 0.89 g (2.3 mmol) sample of the above sulfide with 3.3 mL of a 16%

(43) De Kimpe, N.; Stanoeva, E.; Verhe, R.; Schamp, N. *Synthesis* **1988**, 587.

aqueous solution of $TiCl_3$ followed by reaction with 1.0 mL of 30% H_2O_2 gave 0.8 g (86%) of **35** as a colorless oil: IR (neat) 2961, 1645, 1388, 1189, and 1033 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.99 (t, 3H, J = 7.6 Hz), 1.43 (s, 9H), 1.56 (s, 3H), 2.12 (m, 2H), 2.34 (s, 3H), 3.75 (s, 2H), 3.78 (s, 2H), 5.41 (t, 1H, J = 7.0 Hz), 7.25 (m, 3H), 7.39 (m, 2H), 7.52 (d, 2H, J = 8.1 Hz), and 7.76 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.1, 14.3, 20.7, 21.2, 28.2, 28.3, 39.2, 51.3, 57.5, 125.5, 125.7, 126.0, 128.0, 129.7, 130.8, 131.1, 134.9, 141.0, 141.1, 144.0, and 170.7; HRMS calcd for $C_{25}H_{33}NO_2S$ 411.2232, found 411.2230.

1-*tert*-Butyl-4-ethyl-5-methyl-3-(2-*p*-tolylsulfenylphenyl)-3,6-dihydro-1*H*-pyridin-2-one (38). To a solution containing 0.72 g (1.7 mmol) of **35** in 35 mL of CH_2Cl_2 was added 0.3 mL of triethylamine followed by 0.74 g (3.5 mmol) of trifluoroacetic anhydride. After being stirred for 10 min, the reaction mixture was diluted with CH_2Cl_2, washed with 10% HCl and a saturated $NaHCO_3$ solution, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give 0.37 g (54%) of **38** as a colorless oil: IR (neat) 2961, 1645, 1460, 1203, and 748 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.84 (t, 3H, J = 7.6 Hz), 1.43 (s, 9H), 1.70 (s, 3H), 2.06 (m, 1H), 2.31 (s, 4H), 3.84 (d, 1H, J = 16.8 Hz), 4.01 (d, 1H, J = 16.8 Hz), 4.76 (s, 1H), 7.11 (m, 6H), and 7.25 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.3, 15.4, 21.0, 23.0, 27.9, 50.7, 50.8, 57.1, 121.6, 126.8, 127.4, 128.8, 129.8, 131.5, 131.6, 132.5, 133.3, 136.7, 136.9, 142.1, and 169.6; HRMS calcd for $C_{25}H_{31}NOS$ 393.2126, found 393.2125.

***N*-*tert*-Butyl-*N*-(2-methyl-3-phenylallyl)-2-(2-*p*-tolylsulfenylphenyl)acetamide.** Treatment of a 25.0 g (171 mmol) sample of α-methyl-*trans*-cinnamaldehyde with excess *tert*-butylamine followed by reduction with sodium borohydride according to the general procedure gave 27 g (78%) of *tert*-butyl(2-methyl-3-phenylallyl)amine as a colorless liquid: bp 151 °C (18 mm); IR (neat) 2961, 1445, 1225, and 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.78 (brs, 1H), 1.13 (s, 9H), 1.90 (s, 3H), 3.23 (s, 2H), 6.45 (s, 1H), and 7.22 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.9, 29.0, 50.1, 51.2, 124.7, 125.8, 127.8, 128.7, 138.0, and 138.1.

Following the general procedure, treatment of 1.3 g (5.0 mmol) of acid **17** with 2.5 g (12.1 mmol) of *tert*-butyl(2-methyl-3-phenylallyl)amine afforded 2.0 g (88%) of *N*-*tert*-butyl-*N*-(2-methyl-3-phenylallyl)-2-(2-*p*-tolylsulfenylphenyl)acetamide as a clear oil: IR (neat) 2966, 1644, 1484, 1386, 1190, and 742 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.49 (s, 9H), 1.80 (s, 3H), 2.26 (s, 3H), 3.81 (s, 2H), 3.90 (s, 2H), 6.54 (s, 1H), 7.00 (d, 2H, J = 8.3 Hz), 7.07 (d, 2H, J = 8.3 Hz), and 7.14−7.37 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz), δ 16.1, 20.9, 28.4, 41.3, 52.2, 57.5, 124.2, 126.3, 127.5, 127.8, 128.0, 128.7, 129.7, 129.8, 130.1, 132.4, 133.1, 134.8, 135.4, 136.4, 137.5, 137.8, and 172.0; HRMS calcd for $C_{29}H_{33}NOS$ 443.2283, found 443.2280.

***N*-*tert*-Butyl-*N*-(2-methyl-3-phenylallyl)-2-(2-*p*-tolylsulfinylphenyl)acetamide (39).** The reaction of a 1.9 g (4.4 mmol) sample of the above sulfide with 6.3 mL of a 16% aqueous solution of $TiCl_3$ followed by the addition of 2.0 mL of 30% H_2O_2 afforded 1.6 g (79%) of **39** as a white foam: IR (CCl_4) 2980, 1644, 1190, 1029, and 749 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.49 (s, 9H), 1.84 (s, 3H), 2.31 (s, 3H), 3.82 (s, 2H), 3.92 (s, 2H), 6.49 (s, 1H), 7.16 (d, 2H, J = 8.1 Hz), 7.22−7.48 (m, 10H), and 7.80 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.6, 20.7, 27.9, 38.8, 51.6, 57.2, 123.7, 125.1, 125.5, 126.0, 127.6, 127.7, 128.2, 129.3, 129.5, 130.8, 134.3, 134.9, 136.7, 140.6, 140.7, 143.6, and 170.4; HRMS calcd for $C_{29}H_{33}NO_2S$ 459.2232, found 459.2229.

Trifluoroacetic Acid [1-*tert*-Butyl-3-methyl-5-oxo-4-(2-*p*-tolylsulfenylphenylpyrrolidin-3-yl]phenyl Methyl Ester (41). To a solution containing 0.47 g (1.0 mmol) of a sample of **39** in 30 mL of CH_2Cl_2 was added 0.16 mL of triethylamine followed by 0.43 g (2.0 mmol) of trifluoroacetic anhydride. After being stirred for 10 min, the reaction mixture was diluted with CH_2Cl_2, washed with 10% HCl and a saturated $NaHCO_3$ solution, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue subjected to silica gel chromatography to afford **41** (65%) as a mixture of three diastereomers. One diastereomer was separated from the other two isomers and exhibited the following properties: mp 185−186 °C; IR (CCl_4) 2975, 1780, 1687, 1218, 1161, and 748 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22 (s, 3H), 1.54 (s, 9H), 2.33 (s, 3H), 3.21 (d, 1H, J = 10.4 Hz), 4.16 (d, 1H, J = 10.4 Hz), 4.19 (s, 1H), 5.85 (s, 1H), 7.05 (m, 2H), and 7.13−7.36 (m, 11H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.1, 27.0, 27.8, 42.9, 52.0, 54.7, 57.8, 81.5, 127.4, 127.5, 127.8, 128.3, 128.6, 128.9, 129.6, 130.2, 130.9, 131.5, 132.0, 135.7, 136.8, 137.5, 137.6, and 173.7. Anal. Calcd for $C_{31}H_{32}F_3NO_3S$: C, 67.01; H, 5.80; N, 2.52. Found: C, 66.84; H, 5.84; N, 2.48.

***N*-*tert*-Butyl-2-(2-*p*-tolylsulfenylphenyl)-*N*-(2-trimethylsilylmethylallyl)acetamide.** To a stirred solution containing 250 mL of *tert*-butylamine at room temperature was added dropwise 4.9 g (22.0 mmol) of 2-[(methylsulfonyloxy)methyl]-3-trimethylsilylprop-1-ene.[44] The resulting mixture was heated at reflux for 1.5 h and cooled to room temperature, and the solvent was removed under reduced pressure. The crude mixture was purified by flash silica gel chromatography to give 4.3 g (98%) of *tert*-butyl(2-trimethylsilylmethylallyl)amine: IR (neat) 2954, 1630, 1360, 1246, and 841 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.08 (s, 9H), 0.60 (brs, 1H), 1.00 (s, 9H), 1.48 (s, 2H), 2.95 (s, 2H), 4.49 (s, 1H), 4.70 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.20, 25.2, 29.0, 48.9, 49.9, 106.6, and 146.6.

To a solution containing 1.0 g (3.9 mmol) of carboxylic acid **17** in 40 mL of CH_2Cl_2 was added 0.69 g (4.3 mmol) of 1,1′-carbonyldiimidazole. After 1 h of stirring, 0.8 g (4.0 mmol) of the above amine was added and the mixture was heated at reflux for 5 days. The solution was concentrated under reduced pressure, and the residue was subjected to silica gel chromatography to give 0.85 g (50%) of *N*-*tert*-butyl-2-(2-*p*-tolylsulfenylphenyl)-*N*-(2-trimethylsilylmethylallyl)acetamide as a clear oil: IR (neat) 2954, 1652, 1381, and 833 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.05 (s, 9H), 1.48 (s, 11H), 2.31 (s, 3H), 3.76 (s, 2H), 3.78 (s, 2H), 4.83 (s, 1H), 5.01 (s, 1H), and 7.06−7.33 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.26, 20.9, 24.7, 28.4, 40.9, 51.6, 57.3, 107.9, 127.3, 127.5, 129.7, 129.8, 130.1, 132.5, 132.8, 134.9, 136.2, 137.9, 144.2, and 171.6; HRMS calcd for $C_{26}H_{37}NOSSi$ 439.2365, found 439.2366.

***N*-*tert*-Butyl-2-(2-*p*-tolylsulfinylphenyl)-*N*-(2-trimethylsilylmethylallyl)acetamide (43).** Treatment of a 0.53 g (1.2 mmol) sample of the above sulfide with 1.7 mL of a 16% aqueous solution of $TiCl_3$ followed by the addition of 0.55 mL of 30% H_2O_2 afforded 0.55 g (100%) of **43** as a colorless oil: IR (neat) 2961, 1652, 1388, 1246, and 833 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.06 (s, 9H), 1.43 (s, 9H), 1.52 (m, 2H), 2.30 (s, 3H), 3.78 (s, 2H), 3.87 (m, 2H), 4.87 (s, 1H), 4.98 (s, 1H), 7.20 (m, 3H), 7.34 (m, 2H), 7.55 (d, 2H, J = 7.8 Hz), and 7.72 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.5, 20.9, 24.4, 28.0, 38.8, 51.2, 57.2, 107.5, 125.2, 125.6, 127.8, 129.3, 129.8, 130.8, 134.6, 140.5, 140.9, 144.1, 144.2, and 170.3; HRMS calcd for $C_{26}H_{37}NO_2SSi$ 455.2314, found 455.2312.

1-*tert*-Butyl-3-(2-*p*-tolylsulfenylphenyl)-5-trimethylsilylmethyl-3,4-dihydro-1*H*-pyridin-2-one (45). To a solution containing 0.21 g (0.5 mmol) of **43** in 30 mL of CH_2Cl_2 was added 0.07 mL of triethylamine followed by 0.19 g (0.9 mmol) of trifluoroacetic anhydride. After being stirred for 10 min, the reaction mixture was diluted with CH_2Cl_2, washed with 10% HCl and a saturated $NaCO_3$ solution, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude oil was chromatographed on silica gel. The first product eluted from the column contained a colorless oil (45%) whose structure was assigned as **45**: IR (neat) 2954, 1659, 1211, and 848 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.01 (s, 9H), 1.49 (s, 2H), 1.52 (s, 9H), 2.15 (dd, 1H, J = 16.1 and 6.7 Hz), 2.33 (s, 3H), 2.46 (m, 1H), 4.32 (dd, 1H, J = 12.3 and 6.7 Hz), 6.05 (s, 1H), 7.09 (d, 2H, J = 8.2 Hz), 7.19 (m, 3H), and 7.31 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.5, 21.0, 24.7, 28.9, 34.1, 47.2, 57.5, 117.7, 119.9, 127.4, 127.9, 129.2, 129.8, 130.2, 133.3, 133.6, 134.8, 136.3, 142.1, and 169.8; HRMS calcd for $C_{26}H_{35}NOSSi$ 437.2209, found 437.2208.

1-*tert*-Butyl-3-(2-*p*-tolylsulfenylphenyl)-5-trimethylsilylmethyl-3,6-dihydro-1*H*-pyridin-2-one (46). A second

(44) Trost, B. M.; Vincent, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 5680.

product isolated (45% yield) was identified as **46**: IR (neat) 2954, 1645, 1246, and 841 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.6 (s, 9H), 1.44 (s, 2H), 1.46 (s, 9H), 2.30 (s, 3H), 3.88 (m, 2H), 4.76 (m, 1H), 5.18 (m, 1H), 7.08 (m, 3H), and 7.18 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.3, 21.0, 23.9, 28.0, 48.8, 50.2, 57.4, 119.0, 127.3, 127.5, 128.6, 129.7, 130.0, 130.9, 133.1, 133.3, 135.4, 136.4, 143.5, and 169.4; HRMS calcd for $C_{26}H_{35}NOSSi$ 437.2209, found 437.2200.

***N*-Benzyl-*N*-*tert*-butyl-3-phenylsulfenylacrylamide.** Following the general procedure, treatment of 2.5 g (13.8 mmol) of 3-(phenylthio)acrylic acid with 5.7 g (34.7 mmol) of *N*-(*tert*-butyl)benzylamine afforded 4.2 g (92%) of *N*-benzyl-*N*-*tert*-butyl-3-phenylsulfenylacrylamide as a white solid: mp 100−101 °C; IR (CCl_4) 2961, 1630, 1403, 1189, and 784 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.50 (s, 9H), 4.64 (s, 2H), 6.04 (d, 1H, J = 9.8 Hz), 7.02 (d, 1H, J = 9.8 Hz), 7.35 (m, 8H), and 7.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.7, 49.0, 57.7, 115.9, 125.7, 127.0, 127.6, 128.7, 129.1, 130.6, 137.9, 139.5, 145.8, and 168.9. Anal. Calcd for $C_{20}H_{23}NOS$: C, 73.81; H, 7.12; N, 4.30. Found: C, 73.83; H, 7.17; N, 4.27.

3-Benzenesulfinyl-*N*-benzyl-*N*-*tert*-butylacrylamide (50). Treatment of 1.2 g (3.5 mmol) of the above sulfide with 5.1 mL of a 16% aqueous solution of $TiCl_3$ followed by 1.6 mL of 30% H_2O_2 gave 1.0 g (83%) of **50** as a colorless solid: mp 129−130 °C; IR (CCl_4) 2982, 1637, 1403, 1196, and 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.48 (s, 9H), 4.66 (s, 2H), 6.41 (d, 1H, J = 9.9 Hz), 6.51 (d, 1H, J = 9.9 Hz), 7.24 (m, 3H), 7.34 (m, 2H), 7.47 (m, 3H), and 7.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.1, 49.7, 58.1, 124.8, 125.2, 127.1, 128.7, 128.8, 129.8, 130.4, 138.0, 143.9, 148.6, and 165.7. Anal. Calcd for $C_{20}H_{23}NO_2S$: C, 70.35; H, 6.79; N, 4.10. Found: C, 70.14; H, 6.77; N, 4.08.

2-*tert*-Butyl-4-phenylsulfenylmethylene-1,4-dihydro-2*H*-isoquinolin-3-one (51). To a solution of 0.51 g (1.5 mmol) of **49** in 30 mL of CH_2Cl_2 at −78 °C was added 0.33 g (3.3 mmol) of triethylamine followed by 0.44 g of triflic anhydride. After being stirred for 10 min, the reaction mixture was diluted with water, extracted with CH_2Cl_2, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography. The first product eluted from the column contained 0.15 g (32%) of 2-*tert*-butyl-4-phenylsulfenylmethylene-1,4-dihydro-2*H*-isoquinolin-3-one (**51**) as a white solid: mp 105−106 °C; IR (CCl_4) 2968, 1630, 1388, and 1196 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.43 (s, 9H), 4.91 (s, 2H), 7.22 (m, 4H), and 7.36 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.4, 51.0, 58.2, 94.5, 126.1, 126.7, 127.1, 127.2, 128.7, 129.3, 130.7, 139.0, and 155.3. Anal. Calcd for $C_{20}H_{21}NOS$: C, 74.27; H, 6.54; N, 4.33. Found: C, 74.10; H, 6.59; N, 4.22.

***N*-*tert*-Butyl-2-phenyl-3-(phenylsulfenyl)acrylamide (52).** The second product eluted from the column contained 210 mg (45%) of **52** as a white solid: mp 122−123 °C; IR (CCl_4) 3302, 2968, 1637, 1538, and 1218 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.00 (s, 9H), 4.79 (brs, 1H), 5.53 (s, 1H), and 7.41 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.2, 50.8, 120.8, 128.6, 128.9, 129.2, 129.3, 129.5, 130.4, 135.1, 136.4, 149.1, and 164.7. Anal. Calcd for $C_{19}H_{21}NOS$: C, 73.28; H, 6.80; N, 4.50. Found: C, 73.47; H, 6.82; N, 4.45.

***N*-Benzo[1,3]dioxol-5-ylmethyl-*N*-*tert*-butyl-3-(phenylsulfenyl)acrylamide.** Treatment of a 20 g (133 mmol) sample of piperonal with a 10-fold excess of *tert*-butylamine followed by reduction with sodium borohydride according to the general procedure gave 24.4 g (88%) of benzo[1,3]dioxol-5-ylmethyl-*tert*-butylamine as a colorless liquid: bp 110 °C/0.6 mm; IR (neat) 3317, 2961, 1488, 1246, and 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.91 (brs, 1H), 1.15 (s, 9H), 3.61 (s, 2H), 5.89 (s, 2H), 6.74 (m, 2H), and 6.84 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.0, 46.9, 50.4, 100.6, 107.9, 108.8, 121.0, 135.4, 146.2, and 147.5.

Following the general procedure, treatment of 2.5 g (13.9 mmol) of 3-(phenylthio)acrylic acid with 6.6 g (31.9 mmol) of the above amine afforded 4.4 g (85%) of *N*-benzo[1,3]dioxol-5-ylmethyl-*N*-*tert*-butyl-3-(phenylsulfenyl)acrylamide as a white solid: mp 97−98 °C; IR (CCl_4) 2968, 1630, 1488, 1232, 1189, and 1033 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.49 (s, 9H), 4.54 (s, 2H), 5.95 (s, 2H), 6.05 (d, 1H, J = 9.8 Hz), 6.73 (s, 2H), 6.79 (d, 1H, J = 7.8 Hz), 7.03 (d, 1H, J = 9.8 Hz), 7.31 (m, 3H), and 7.47 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.7, 48.7, 57.7, 101.1, 106.2, 108.4, 115.8, 118.7, 127.6, 129.1, 130.6, 133.4, 137.9, 145.9, 146.5, 148.1, and 168.8. Anal. Calcd for $C_{21}H_{23}NO_3S$: C, 68.27; H, 6.27; N, 3.79. Found: C, 68.00; H, 6.27; N, 3.72.

3-Benzenesulfinyl-*N*-benzo[1,3]dioxol-5-ylmethyl-*N*-*tert*-butylacrylamide (57). Treatment of 2.0 g (5.4 mmol) of the above sulfide with 7.8 mL of a 16% aqueous solution of $TiCl_3$ followed by 2.5 mL of 30% H_2O_2 gave 1.9 g (89%) of **57** as a white solid: mp 122−123 °C; IR (CCl_4) 2971, 1635, 1486, 1238, and 1032 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.48 (s, 9H), 4.57 (s, 2H), 5.92 (s, 2H), 6.43 (d, 1H, J = 9.9 Hz), 6.54 (d, 1H, J = 9.9 Hz), 6.68 (s, 2H), 6.78 (d, 1H, J = 7.7 Hz), 7.48 (m, 3H), and 7.97 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.0, 49.3, 58.0, 100.9, 105.7, 108.3, 118.2, 124.7, 128.7, 129.7, 130.3, 131.8, 143.8, 146.5, 148.0, 148.6, and 165.6. Anal. Calcd for $C_{21}H_{23}NO_4S$: C, 65.43; H, 6.01; N, 3.63. Found: C, 65.26; H, 6.07; N, 3.57.

6-*tert*-Butyl-8-phenylsulfenylmethylene-5,8-dihydro-6*H*-[1,3]dioxol[4,5-*g*]isoquinolin-7-one (58). To a stirred solution of 0.5 g (1.3 mmol) of **56** in 35 mL of CH_2Cl_2 at −78 °C was added 0.29 g of triethylamine followed by 0.38 g of triflic anhydride. After being stirred for 10 min, the reaction mixture was diluted with water, extracted with CH_2Cl_2, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography. The first product eluted from the column contained 67 mg (15%) of **58** as a white solid: mp 110−111 °C; IR (CCl_4) 2961, 1630, 1609, 1388, and 1246 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.43 (s, 9H), 4.81 (s, 2H), 5.97 (s, 2H), 6.78 (m, 3H), and 7.23 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.4, 50.7, 58.3, 94.5, 101.1, 106.7, 108.4, 119.3, 126.9, 127.2, 129.4, 130.7, 132.9, 146.7, 148.0, and 155.1. Anal. Calcd for $C_{21}H_{21}NO_3S$: C, 68.64; H, 5.76; N, 3.81. Found: C, 68.41; H, 5.79; N, 3.72.

2-Benzo[1,3]dioxol-5-yl-*N*-*tert*-butyl-3-(phenylsulfenyl)acrylamide (59). The second product eluted from the column contained 0.28 g (60%) of **59** as a white solid: mp 142−143 °C; IR (CCl_4) 3309, 1645, 1481, 1232, and 734 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.10 (s, 9H), 4.90 (brs, 1H), 5.49 (s, 1H), 5.98 (s, 2H), 6.81 (d, 1H, J = 7.9 Hz), 6.95 (m, 2H), 7.31 (m, 3H), 7.39 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.3, 50.9, 101.4, 108.4, 109.4, 120.5, 122.9, 129.2, 129.5, 129.9, 130.6, 134.8, 147.7, 148.4, 148.9, and 164.8. Anal. Calcd for $C_{20}H_{21}NO_3S$: C, 67.58; H, 5.96; N, 3.94. Found: C, 67.48; H, 5.92; N, 3.93.

***N*-*tert*-Butyl-*N*-(3,5-dimethoxybenzyl)-3-(phenylsulfenyl)acrylamide.** Treatment of a 6.0 g (36 mmol) sample of 3,5-dimethoxybenzaldehyde with a 10-fold excess of *tert*-butylamine followed by reduction with sodium borohydride according to the general procedure gave 7.7 g (96%) of *tert*-butyl(3,5-dimethoxybenzyl)amine as a colorless oil: IR (neat) 2954, 1595, 1460, 1203, and 1154 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.90 (brs, 1H), 1.16 (s, 9H), 3.67 (s, 2H), 3.77 (s, 6H), 6.33 (s, 1H), and 6.51 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.1, 47.3, 50.5, 55.1, 98.7, 106.0, 144.0, and 160.7.

Following the general procedure, treatment of 1.3 g (7.2 mmol) of 3-(phenylthio)acrylic acid with 3.5 g (15.9 mmol) of the above amine afforded 2.2 g (80%) of *N*-*tert*-butyl-*N*-(3,5-dimethoxybenzyl)-3-(phenylsulfenyl)acrylamide as a colorless oil: IR (neat) 2961, 1623, 1595, 1403, and 1196 cm^{-1}; 1H NMR ($CDCl_3$, 300 MHz) δ 1.51 (s, 9H), 3.77 (s, 6H), 4.56 (s, 2H), 6.04 (d, 1H, J = 9.8 Hz), 6.35 (s, 1H), 6.41 (s, 2H), 7.01 (d, 1H, J = 9.8 Hz), 7.36 (m, 3H), and 7.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.6, 49.1, 55.3, 57.7, 98.7, 103.7, 116.0, 127.5, 129.1, 130.6, 137.8, 142.3, 145.6, 161.2, and 168.9; HRMS calcd for $C_{22}H_{27}NO_3S$ 385.1711, found 385.1712.

3-Benzenesulfinyl-*N*-*tert*-butyl-*N*-(3,5-dimethoxybenzyl)acrylamide (60). Treatment of 2.2 g (5.7 mmol) of the above sulfide with 8.2 mL of a 16% aqueous solution of $TiCl_3$ followed by 2.6 mL of 30% H_2O_2 gave 2.1 g (90%) of **60** as a clear oil: IR (neat) 2961, 1637, 1595, 1403, 1203, and 1154 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.49 (s, 9H), 3.77 (s, 6H), 4.60 (s, 2H), 6.36 (s, 3H), 6.42 (d, 1H, J = 10.0 Hz), 6.54 (d,

1H, J = 10.0 Hz), 7.41 (m, 3H), and 7.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.1, 49.8, 55.1, 58.2, 98.7, 103.4, 124.8, 128.8, 130.0, 130.4, 140.8, 143.9, 148.4, 161.2, and 165.8. Anal. Calcd for $C_{22}H_{27}NO_4S$: C, 65.81; H, 6.78; N, 3.49. Found: C, 65.66; H, 6.79; N, 3.44.

2-*tert*-Butyl-5,7-dimethoxy-4-phenylsulfenylmethylene-1,4-dihydro-2*H*-isoquinolin-3-one (61). To a solution of 0.8 g (2.0 mmol) of **60** in 45 mL of CH_2Cl_2 at −78 °C was added 0.44 g (4.4 mmol) of triethylamine followed by 0.62 g (2.2 mmol) of triflic anhydride. After being stirred for 10 min, the reaction was diluted with water, extracted with CH_2Cl_2, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue purified by silica gel chromatography. The major product eluted from the column contained 0.48 g (63%) of **61** as a colorless solid: mp 165−166 °C; IR (CCl_4) 2968, 1623, 1388, 1324, and 1189 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.39 (s, 9H), 3.82 (s, 6H), 4.14 (d, 1H, J = 15.0 Hz), 4.31 (d, 1H, J = 15.0 Hz), 6.03 (s, 1H), 6.42 (d, 1H, J = 2.3 Hz), 6.46 (d, 1H, J = 2.3 Hz), 7.29 (m, 3H), and 7.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.9, 47.8, 55.3, 55.7, 57.5, 98.1, 104.0, 118.2, 126.1, 128.3, 129.2, 133.6, 134.5, 141.8, 143.8, 158.7, 160.9, and 166.7. Anal. Calcd for $C_{22}H_{25}NO_3S$: C, 68.90; H, 6.57; N, 3.65. Found: C, 68.87; H, 6.58; N, 3.62.

3-Phenylsulfenylpropynoic Acid *tert*-Butyl(3,5-dimethoxybenzyl)amide (62). The minor product eluted from the column contained 60 mg (8%) of **62** as a colorless oil: IR (neat) 2961, 2153, 1630, 1381, and 1196 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.45 (s, 9H), 3.79 (s, 6H), 4.84 (s, 2H), 6.39 (s, 1H), 6.44 (s, 2H), 7.17 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.2, 50.9, 55.2, 58.2, 79.6, 94.3, 98.9, 103.8, 126.5, 127.0, 129.2, 130.4, 141.5, 155.1, and 161.0; HRMS calcd for $C_{22}H_{25}NO_3S$ 383.1555, found 383.1553.

1′-*tert*-Butyl-2-hydroxy-1-methyl-4′-phenylsulfenylmethylene-1,2-dihydrospiro[indole-3,3′-pyrrolodin]-5′-one (68). Treatment of a 10 g (62.8 mmol) sample of 1-methylindole-3-carboxaldehyde with a 10-fold excess of *tert*-butylamine followed by reduction with sodium borohydride according to the general procedure gave 12.4 g (91%) of *tert*-butyl(1-methylindol-3-yl)methylamine as a white solid: mp 53−54 °C; IR (CCl_4) 3309, 2961, 1467, and 734 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.23 (s, 10H), 3.74 (s, 3H), 3.93 (s, 2H), 7.09 (m, 2H), 7.25 (m, 2H), and 7.63 (d, 1H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.1, 32.6, 37.7, 50.6, 109.2, 118.7, 118.8, 121.5, 127.1, and 127.4.

Following the general procedure, treatment of 0.25 g (1.4 mmol) of 3-(phenylthio)acrylic acid with the above amine gave 0.52 g (100%) of *N*-*tert*-butyl-*N*-(1-methyl-1*H*-indol-3-ylmethyl)-3-phenylsulfenylacrylamide which was used in the next step without further purification. To a solution of the above sulfide in 60 mL of CH_2Cl_2 at 0 °C was added 0.26 g (1.5 mmol) of *m*-chloroperbenzoic acid. After being stirred for 1 h, the reaction was diluted with water, extracted with $CHCl_3$, and dried over $MgSO_4$. Filtration of the extracts through a short pad of silica gel and removal of the solvent under reduced pressure afforded *N*-*tert*-butyl-*N*-(1-methyl-1*H*-indol-3-ylmethyl)-3-phenylsulfinylacrylamide (**66**) as a white foam which was immediately used in the next step without purification.

To a stirred solution of 0.54 g (1.4 mmol) of **66** at −78 °C was added 0.3 g (3.0 mmol) of triethylamine followed by 0.43 g (1.5 mmol) of triflic anhydride. After 10 min of stirring, the reaction was diluted with water, extracted with CH_2Cl_2, and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by silica gel chromatography gave 0.28 g (51%) of **68** as a white solid which consisted of an inseparable 2:1 mixture of diastereomers: mp 179−180 °C; IR (CCl_4) 3324, 2975, 1630, 1488, 1317, and 1203 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) major diastereomer δ 1.40 (s, 9H), 2.98 (s, 3H), 3.01 (d, 1H, J = 11.1 Hz) 3.38 (d, 1H, J = 12.8 Hz), 3.47 (d, 1H, J = 12.8 Hz), 5.14 (d, 1H, J = 11.1 Hz), 5.43 (s, 1H), 6.54 (m, 1H), 6.81 (m, 1H), 7.26 (m, 2H), 7.39 (m, 3H), and 7.50 (m, 2H); minor diastereomer δ 1.38 (s, 9H), 2.87 (s, 3H), 2.53 (brs, 1H), 3.58 (d, 1H, J = 12.7 Hz), 3.97 (d, 1H, J = 12.7 Hz), 5.27 (m, 1H), 5.43 (s, 1H), 6.54 (m, 1H), 6.81 (m, 1H), 7.26 (m, 2H), 7.39 (m, 3H), and 7.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.3, 28.5, 30.5, 31.5, 47.1, 51.3, 53.2, 54.3, 56.5, 56.8, 92.1, 95.4, 106.8, 106.9, 117.9, 118.3, 119.3, 122.2, 124.6, 125.7, 127.2, 128.9, 129.1, 129.7, 129.9, 130.1, 135.1, 135.6, 149.8, 150.1, 153.4, 157.3, and 164.7. Anal. Calcd for $C_{23}H_{26}N_2O_2S$: C, 70.02; H, 6.64; N, 7.10. Found: C, 69.91; H, 6.69; N, 6.99.

***N*-*tert*-Butyl-*N*-(3-methylbut-2-enyl)-3-phenylsulfenylacrylamide.** To a stirred solution of *tert*-butylamine was added dropwise 20 g (134 mmol) of 4-bromo-2-methyl-2-butene. The mixture was heated at reflux for 30 min, diluted with water, extracted with CH_2Cl_2, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the product distilled to give 10.6 g (56%) of *tert*-butyl(3-methylbut-2-enyl)amine as a colorless liquid: bp 63 °C (23 mm); IR (neat) 3302, 2962, 1438, 1353, and 1232 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.90 (brs, 1H), 1.12 (s, 9H), 1.65 (s, 3H), 1.70 (s, 3H), 3.15 (m, 2H), and 5.27 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.6, 25.6, 29.0, 40.1, 50.1, 123.7, and 133.4.

Following the general procedure, treatment of 1.5 g (8.3 mmol) of 3-(phenylthio)acrylic acid with 2.9 g (21 mmol) of the above amine gave 2.5 g (97%) of *N*-*tert*-butyl-*N*-(3-methylbut-2-enyl)-3-phenylsulfenylacrylamide as a clear oil: IR (CCl_4) 1H NMR ($CDCl_3$, 300 MHz) δ 1.49 (s, 9H), 1.64 (s, 3H), 1.72 (s, 3H), 3.94 (m, 2H), 5.12 (m, 1H), 6.15 (d, 1H, J = 9.8 Hz), 7.05 (d, 1H, J = 9.8 Hz), 7.32 (m, 3H), and 7.49 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9, 25.4, 28.9, 43.8, 57.1, 116.2, 124.0, 127.4, 129.0, 130.5, 132.7, 138.1, 144.6, and 168.0. Anal. Calcd for $C_{18}H_{25}NOS$: C, 71.24; H, 8.30; N, 4.62. Found: C, 70.95; H, 8.29; N, 4.68.

3-Benzenesulfinyl-*N*-*tert*-butyl-*N*-(3-methylbut-2-enyl)acrylamide (69). Treatment of 1.3 g (4.4 mmol) of the above sulfide with 6.4 mL of a 16% aqueous solution of $TiCl_3$ followed by 2.0 mL of 30% H_2O_2 afforded 0.95 g (67%) of **69** as a white foam: IR (neat) 2968, 1630, 1403, 1182, and 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.49 (s, 9H), 1.62 (s, 3H), 1.73 (s, 3H), 3.99 (brs, 2H), 5.10 (m, 1H), 6.41 (d, 1H, J = 10.0 Hz), 6.62 (d, 1H, J = 10.0 Hz), 7.48 (m, 3H), and 7.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9, 25.4, 28.4, 44.8, 57.6, 122.3, 124.8, 128.9, 130.4, 130.9, 134.0, 143.9, 146.3, and 165.1; HRMS calcd for $C_{18}H_{25}NO_2S$ 319.1606, found 319.1602.

5-*tert*-Butyl-3-isopropenyl-2-phenylsulfinylmethylenecyclopentanone (70). To a solution of 0.83 g (2.6 mmol) of **68** in 50 mL of CH_2Cl_2 at −78 °C was added 0.66 g (6.5 mmol) of triethylamine followed by 0.74 g (2.6 mmol) of triflic anhydride. After being stirred for 10 min, the reaction mixture was diluted with water, extracted with CH_2Cl_2, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue chromatographed on silica gel to give 0.45 g (57%) of **70** as a clear oil: IR (neat) 3075, 2968, 1673, 1451, and 1239 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.44 (s, 9H), 1.69 (s, 3H), 3.22 (dd, 1H, J = 10.0 and 2.6 Hz), 3.55 (m, 1H), 3.68 (m, 1H), 4.89 (s, 1H), 4.96 (s, 1H), 7.25 (m, 3H), and 7.40 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0, 27.3, 42.5, 48.2, 54.2, 113.4, 127.2, 128.9, 129.7, 130.6, 131.9, 134.4, 142.7, and 166.6; HRMS calcd for $C_{18}H_{23}NOS$ 301.1500, found 301.1498.

***N*-*tert*-Butyl-*N*-(2-methyl-3-phenylallyl)-3-phenylsulfenylacrylamide.** Following the general procedure, treatment of 1.5 g (8.3 mmol) of 3-(phenylthio)acrylic acid with 3.9 g (19 mmol) of *tert*-butyl(2-methyl-3-phenylallyl)amine afforded 2.9 g (96%) of *N*-*tert*-butyl-*N*-(2-methyl-3-phenylallyl)-3-phenylsulfenylacrylamide as a white solid, mp 117−118 °C; IR (CCl_4) 2968, 1630, 1559, 1403, and 1189 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.54 (s, 9H), 1.84 (s, 3H), 3.94 (s, 2H), 6.11 (d, 1H, J = 9.9 Hz), 6.46 (s, 1H), 7.03 (d, 1H, J = 9.9 Hz), 7.26 (m, 8H), and 7.46 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.8, 28.1, 51.9, 56.9, 115.9, 124.8, 126.1, 127.2, 127.8, 128.4, 128.8, 130.2, 135.1, 137.0, 137.6, 144.8, and 168.4. Anal. Calcd for $C_{23}H_{27}NOS$: C, 75.58; H, 7.45; N, 3.83. Found: C, 75.38; H, 7.47; N, 3.80.

3-Phenylsulfinyl-*N*-*tert*-Butyl-*N*-(2-methyl-3-phenylallyl)acrylamide (71). Treatment of 2.3 g (6.3 mmol) of the above sulfide with 9.1 mL of a 16% aqueous solution of $TiCl_3$ followed by 2.8 mL of 30% H_2O_2 gave 1.4 g (56%) of **71** as a colorless oil: IR (neat) 2975, 1637, 1403, 1189, and 1033 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.55 (s, 9H), 1.85 (s, 3H), 4.01 (s, 2H), 6.44 (s, 1H), 6.48 (d, 1H, J = 9.8 Hz), 6.61 (d, 1H, J = 9.8 Hz), 7.23 (d, 2H, J = 7.5 Hz), 7.31 (m, 2H), 7.48 (m, 4H),

7.97 (d, 2H, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.0, 28.1, 53.0, 57.9, 124.9, 125.1, 126.6, 128.2, 128.6, 129.0, 130.2, 130.6, 134.8, 136.8, 144.0, 148.5, and 165.9; HRMS calcd for $C_{23}H_{27}NO_2S$ 381.1762, found 381.1763.

1-*tert*-Butyl-4-(hydroxyphenylmethyl)-4-methyl-3-phenylsulfenylmethylenepyrrolidin-2-one (72). To a solution of 0.8 g (2.1 mmol) of **71** in 50 mL of CH_2Cl_2 at −78 °C was added 0.47 g (4.6 mmol) of triethylamine followed by 0.62 g (2.2 mmol) of triflic anhydride. After being stirred for 10 min, the reaction mixture was diluted with water, extracted with CH_2Cl_2, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by silica gel chromatography. The major product **72** isolated (0.32 g (40%)) as a colorless solid: mp 175−176 °C; IR (CCl_4) 3366, 2975, 1623, 1537, and 1317 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.21 (s, 3H), 1.42 (s, 9H), 2.35 (d, 1H, $J = 2.8$ Hz), 3.10 (d, 1H, $J = 12.4$ Hz), 3.89 (d, 1H, $J = 12.4$ Hz), 4.94 (d, 1H, $J = 2.8$ Hz), 5.09 (s, 1H), and 7.37 (m, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.4, 28.5, 45.3, 50.3, 56.4, 74.8, 119.2, 127.9, 128.0, 128.1, 128.4, 129.7, 135.6, 140.2, 158.9, and 164.6. Anal. Calcd for $C_{23}H_{27}NO_2S$: C, 72.41; H, 7.13; N, 3.67. Found: C, 72.44; H, 7.11; N, 3.65.

3-Phenylsulfenylpropynoic Acid *tert*-Butyl(2-methyl-3-phenyallyl)amide (73). The minor product **73** was isolated (0.11 g (14%)) as a colorless oil: IR (neat) 2968, 2143, 1623, 1374, and 1196 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.51 (s, 9H), 1.84 (s, 3H), 4.29 (s, 2H), 6.47 (s, 1H), 7.19−7.40 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.9, 28.2, 54.0, 58.0, 94.4, 103.2, 125.4, 126.5, 127.1, 127.3, 128.2, 128.8, 129.4, 135.5, 137.4, and 160.9; HRMS calcd for $C_{23}H_{25}NOS$ 363.1657, found 364.1531 $[M + H]^+$.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra for new compounds lacking analyses together with an ORTEP drawing for structure **41** (29 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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