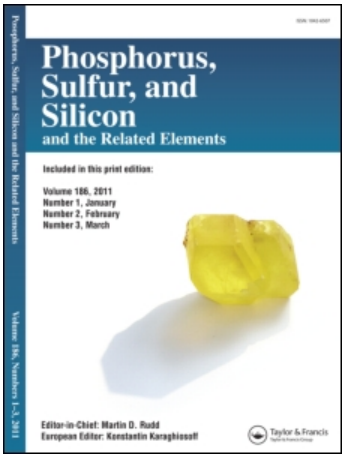

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STERICALLY HINDERED 4-AMINO-3,5-DIALKYLBENZENETHIOL DERIVATIVES: SYNTHESIS AND CHARACTERIZATION

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STERICALLY HINDERED 4-AMINO-3,5-DIALKYLBENZENETHIOL DERIVATIVES: SYNTHESIS AND CHARACTERIZATION

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The synthesis and characterization of a sterically hindered aminobenzenethiol **1** (4-NH_2-3-^{t}Bu-5-MeC_6H_2SH) is described. The addition of **1** to electron-deficient olefins as well as the Mannich-type reaction of **1** with formaldehyde and a *sec*-amine was investigated. Phosphorothiolate derivatives were prepared by the reaction of the corresponding sulfenyl chloride 4-NH_2-3-^{t}Bu-5-MeC_6H_2SCl with tricoordinate P(III) esters.

Keywords: 4;4′-thiobis(2;6-dialkylanilines); 4-amino-3;5-dialkylbenzenthiol; 4-aminobenzenesulfenyl chloride; phosphorothiolates; conjugate addition

Derivatives of 4-aminobenzenethiol are claimed in the patent literature as pesticides[1] and dye-fixation agents.[2] Anticholesteremic and hypolipemic activities have been found in 3;5-dialkyalkyl-4-amino-substituted arylthioalkanoic acids.[3] Sterically hindered derivatives are claimed as antioxidants.[4] Previously reported methodologies for the synthesis of alkylated aminobenzenethiol derivatives include the reaction of an alkylated aniline with thiocyanogen bromide followed by reduction;[5] and the Lewis-acid catalyzed reaction of aromatic amines with disulfides.[6] Our interest in the chemistry of hindered anilines; which resulted in the isolation of a stable N-aryl methanimine;[7] led to the development of a

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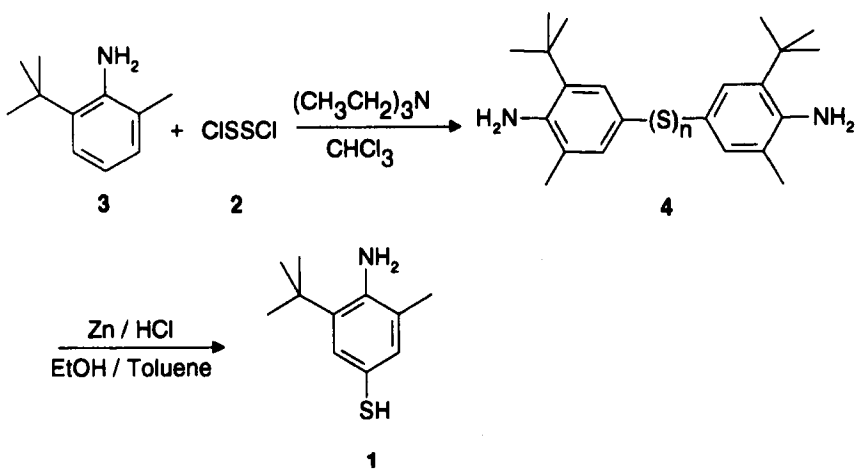
convenient thiolation-reduction method for the synthesis of the sterically hindered 4-aminobenzenethiol **1**.

RESULTS AND DISCUSSION

Orloff and Worrel reported that the reaction of 2,6-dialkylanilines with sulfur monochloride (S_2Cl_2), **2**, led to a mixture of 4,4′-polythiobis(2,6-dialkylanilines) from which the disulfide could be isolated.[8] More recently, Inamoto *et al.* reported that the reaction of 2,4-di-*tert*-butyl-6-methylaniline with **2** in chloroform using triethylamine as an acid acceptor gave the corresponding *N*-thiosufinylaniline in 80% yield, whereas replacement of the 6-methyl substituent by an isopropyl group led to a significant reduction in yield.[9] Significant differences in reactivity between the 2,4,6-trimethyl- and 2,4,6-tri-*tert*-butylanilines with **2** were observed.



A mixture of polysulfides **4** (n = 1,2,3,4) were obtained by the reaction of two equivalents of 2-*tert*-butyl-6-methylaniline **3** with one equivalent of **2** in the presence of two equivalents of triethylamine in chloroform solvent. Purification of the polysulfide mixture by recrystallization from nitromethane gave a yellow crystalline solid (47%) that was determined by mass spectral analysis to be predominately the disulfide **4** (n = 2).

Dissolving metal reductions of disulfides have been used in the preparation of thiols.[10–12] The hindered aminobenzenethiol **1** was obtained by the reduction of **4** (n = 2) with zinc in hydrochloric acid. In the ^{1}H NMR spectrum of **1**, distinct signals were observed for the protons bonded to sulfur and nitrogen at δ 3.29 and δ 3.82, respectively.

The base-catalyzed addition of thiols to electron-deficient olefins is well known.[13–15] Kinetic studies on the base-catalyzed addition of thiols to maleic anhydride have been reported.[16] The triethylamine-catalyzed addition of **1** to the acrylate esters **5a,b** gave the corresponding addition products **6a,b**. The diadduct **8** was obtained by the reaction of the diacrylate **7** with two equivalents of **1**. In the case of the reaction of **1** with **7**, a small quantity of the monoadduct **9** was isolated by preparative HPLC. No addition reaction was observed between **1** and the methacrylate ester **5c** when triethylamine was used as a catalyst. Kuwajima *et al.* reported that fluoride ion in aprotic media promoted the conjugate addition of thiols to substituted α,β-unsaturated carbonyl compounds.[17] Indeed, tetrabutylammonium fluoride ion was found to effectively catalyze the addition of **1** to **5c**.

The succinate derivative **11** was readily prepared by the reaction of **1** with di-*n*-butyl maleate catalyzed by triethylamine. Previously we reported base catalyzed addition of sterically hindered 4-hydroxybenzenethiols to maleimides.[18] In a similar manner, the pyrrolidine-2,5-dione derivatives **13a–c** were prepared by the base catalyzed addition of **1** to the maleimides **12a–c**.

A mechanistic study of the Mannich-type reaction of amines with hemimercaptals derived from sterically hindered 4-hydroxybenzenethiols has been reported.[19,20] Grillot and Schaffrath reported[21] that the reaction of thiophenols with formaldehyde and aryl amines gave aminomethyl aryl sulfides. The reaction of **1** with formaldehyde and the diarylamine **14** gave the sulfide **15** in 45% chromatographic yield.

Denney *et al.* have studied the mechanism of the reaction of phosphites with benzenesulfenyl chloride.[22] The stereochemical outcome of the reaction was consistent with a phosphonium ion intermediate formed by nucleophilic attack of the lone pair of electrons on phosphorus at sulfur.[22] The reaction of a sterically hindered 4-hydroxybenzenesulfenyl chloride with *sec*-amines led to an unexpected dimerization reaction.[23] The corresponding reaction with a trialkyl phosphite gave the expected Arbusov product.[24] Sulfenyl chlorides have been prepared by the reaction of a disulfide with elemental chlorine.[25] The sulfenyl chloride **16** was prepared *in situ* by reaction of the disufide **4** (n = 2) with chlorine gas at −40°C in toluene solution. The reaction of **16** with the phosphites **17a,b** gave the corresponding phosphorothiolates **18a,b**.

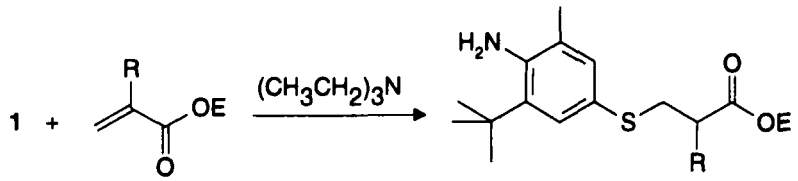
In summary, electrophilic aromatic substitution is observed in the reaction of **3** with **2** without significant competitive reaction at nitrogen. A reasonable explanation of this observation is that steric hindrance provided by the methyl and *tert*-butyl substitution *ortho* to the amino substituent of **3** minimizes the reactivity at nitrogen. This rational also provides an explanation for the observed reactivity of the aminobenzenethiol **1**. The *in situ* generation and subsequent reaction of the sulfenyl chloride **16** is noteworthy, particularly in light of the known propensity of hydroxyarenesulfenyl chlorides for rapid self-condensation.[26,27]

EXPERIMENTAL

All melting points were determined in open capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. MS were obtained on a Finnegan Model 8200 mass spectrometer. IR spectra were recorded on a Perkin-Elmer 1300 spectrophotometer, and reported peak absorptions are estimated to be accurate to ± 10 cm^{-1}. ^{1}H NMR (90 MHz) spectra were taken on a JEOL Model FX-90Q spectrometer. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. Significant ^{1}H NMR data are tabulated in the following order: multiplicity (m, multiplet; s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dq, doublet of quartets; dt, doublet of triplets), atom assignments, coupling constant in Hertz, and number of protons. Merck silica gel 60 (200–400 mesh) was used for column chromatography. Merck precoated (0.25 mm) silica gel F-254 plates were used for TLC. Reagents were purchased from commercial laboratory supply houses. A sample of 2-methyl-6-*tert*-butylaniline was kindly provided by Ethyl Corporation. Solvents were dried prior to use when necessary with appropriate drying agents. Reactions were carried out in flame-dried apparatus under a dry inert atmosphere of either nitrogen or argon. Elemental analyses were performed by the Analytical Research Department, Ciba-Geigy Corporation.

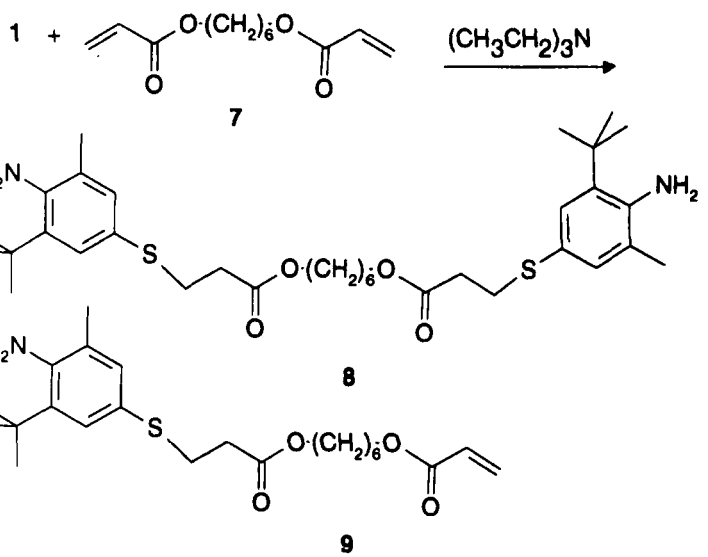
3-*tert*-Butyl-5-methyl-4-aminobenzenethiol, (1). To a solution of 35.0 g (214 mmol) of **3** and 29.6 mL of triethylamine (214 mmol) in 200 mL of chloroform at 10°C was added dropwise a solution of 8.6 mL (107 mmol) of **2** in 200 mL of chloroform.[28] The reaction mixture was stirred for 18 h at room temperature and then to the resultant mixture was added 200 mL of methylene chloride. The reaction mixture was washed sequentially once with a 5% aqueous sodium hydroxide solution (400 mL) followed by three times with water (3 × 300 mL). The organic phase was dried with anhydrous sodium sulfate and the volatiles removed *in vacuo*. The residue was recrystallized twice from ni-

tromethane to give 19.5 g (47%) of yellow crystals, **4** (n = 2), mp 119–120°C. ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 18 H), 2.18 (s, 6 H), 3.93 (s, NH_2, 4 H), 7.18 (d, 2 H), 7.27 (m, 2 H). The disulfide **4** (n = 2) was converted to **1** without further purification.



5
a. R = H; E = Me
b. R = H; E = *n*-$C_{18}H_{37}$
c. R = E = Me

6
a. R = H; E = Me
b. R = H; E = *n*-$C_{18}H_{37}$
c. R = E = Me



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8

9

To a stirred mixture of 5.0 g of **4** (n = 2), 75 g of zinc dust, 10 mL of ethanol, and 20 mL of toluene was added dropwise over a three hour period 40 mL of concentrated hydrochloric acid. The reaction mixture was stirred for 24 h at room temperature and then the acidic mixture was cautiously neutralized with 5% aqueous sodium hydroxide. The heterogeneous reaction mixture was extracted with diethyl ether and the extracts were dried over anhydrous sodium sulfate. The solvent was removed *in vacuo*. To the residue was added 20 mL of

heptane and the resultant solid[29] was removed by filtration. The heptane was removed *in vacuo* and the residue distilled to give 1.3 g (26%) of **1** as a colorless liquid, bp 170°C. (0.3 mm). ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 9 H), 2.13 (s, 3 H), 3.29 (s, SH, 1 H), 3.82 (broad s, NH_2, 2 H), 7.02 (d, 1 H), 7.16 (d, 1 H); IR (1% in CH_2Cl_2) ν 3510, 3420 (NH_2) and 2550 (SH) cm^{-1}. Anal. Calcd for $C_{11}H_{17}NS$: C, 67.6; H, 8.8; N, 7.2. Found: C, 67.6; H, 9.0; N, 7.3.

Methyl 3-(4-Amino-3-Tert-Butyl-5-Methylphenylthio)Propionate, (6a). To a stirred solution of 1.00 g (5.1 mmol) of **1** and 0.05 g (0.5 mmol) of triethylamine in 5 mL of toluene at −5°C was added dropwise a solution of 0.44 g (5.1 mmol) of **5a** in 5 mL of toluene. The reaction mixture was stirred for 24 h at room temperature. The solvent was removed *in vacuo* and the residue was purified by flash chromatography[30] (silica gel, 95.5, heptane:ethyl acetate eluent) to give 0.95 g (66%) of a colorless liquid. ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 9 H), 2.13 (s, 3 H), 2.56 (t, 2 H), 2.98 (t, 2 H), 3.67 (s, 3 H), 3.89 (exchangeable s, 2 H), 7.12 (m, 2 H); IR (1% in CH_2Cl_2) ν 3520, 3420 (NH_2), 1730 (C═O) cm^{-1}. Anal. Calcd for $C_{15}H_{23}NO_2S$: C, 64.0; H, 8.2; N, 5.0. Found: C, 64.0; H, 8.4; N, 5.1.

Octadecyl 3-(4-Amino-3-Tert-Butyl-5-Methylphenylthio)Propionate, (6b). The procedure for compound **6a** was repeated using 4.5 g (23 mmol) of **1**, 7.5 g (23 mmol) of **5b**, and 0.2 g (2 mmol) of triethylamine in 50 mL of toluene (50°C for 18 hrs). The solvent was removed in vacuo and the residue was purified by preparative HPLC (silica gel, 9:1, heptane:ethyl acetate eluent) to give 8.6 g (72%) of a colorless liquid. ^{1}H NMR ($CDC1_3$) δ 0.89 (t, 3 H), 1.24 (s. 32 H), 1.42 (s. 9 H), 2.13 (s, 3 H), 2.53 (t. 2 H), 3.00 (t. 2 H), 3.80 (exchangeable s, 2 H), 4.06 (t, 2 H), 7.12 (d, 1 H), 7.24 (d, 1 H). Anal. Calcd for $C_{32}H_{57}NO_2S$: C, 73.9; H, 11.0; N, 2.7. Found: C, 73.7; H, 11.2, N. 2.6.

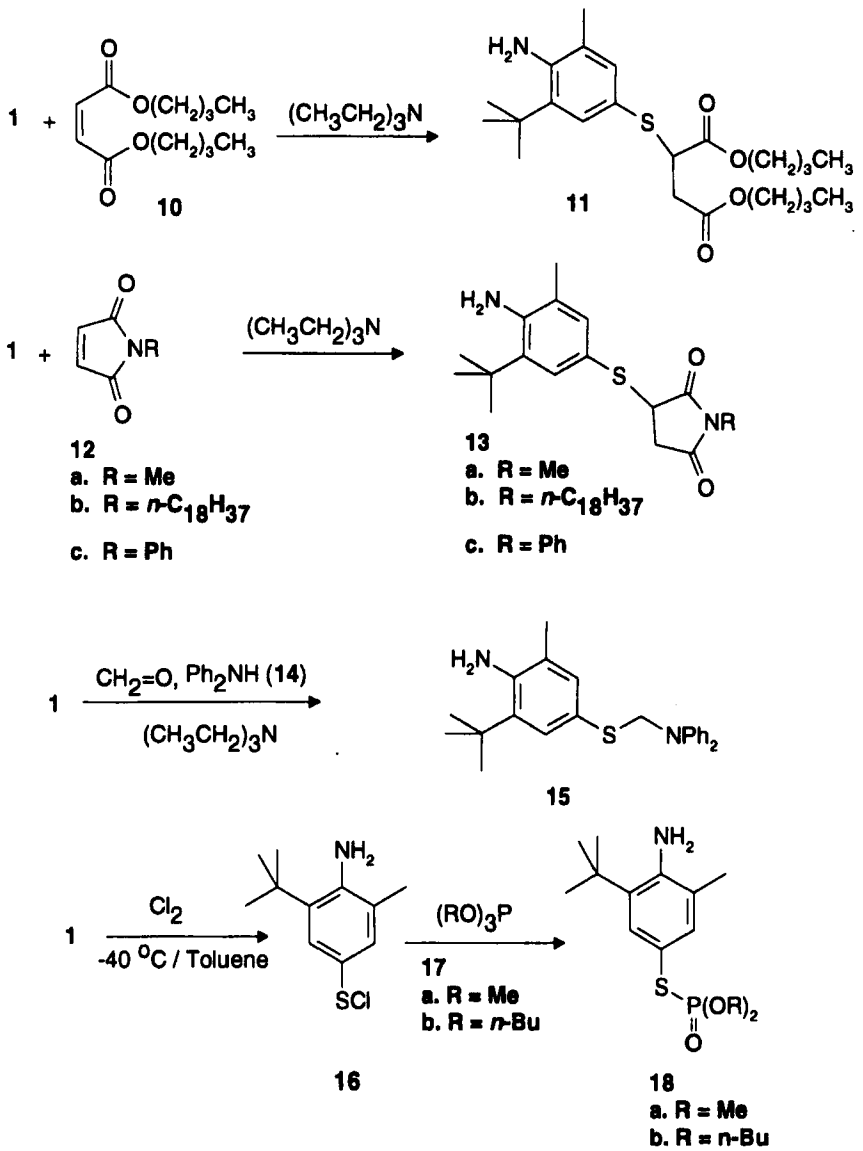
Methyl-3-(4-Amino-3-Tert-Butyl-5-Methylphenylthio)-2-Methylpropionate, (6c). To a stirred solution of 1.00 g (5.1 mmol) of **1** and 0.15 g (0.5 mmol) of tetra-butylammonium fluoride in 5 mL of toluene at −5°C was added dropwise a solution of 0.51 g (5.1 mmol) of **5c** in 5 mL of toluene. The reaction mixture was stirred for 24 hrs at rt. The reaction mixture was added to 50 mL of water, and the resultant phases separated. The organic phase was dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo* and the residue was purified by flash column chromatography[29] (silica gel, 4:1, heptane:ethyl acetate eluent) to give 0.28 g (18%) of a colorless liquid. ^{1}H NMR ($CDCL_3$) δ 1.24 (d, 3 H), 1.43 (s, 9 H), 2.18 (s, 3 H), 2.65 (m, 1 H), 2.77 (m, 1 H), 3.11 (m, 1 H) 3.68 (s, 3 H), 3.89 (exchangeable s, 2 H), 7.11 (d, 2 H), 7.29 (d, 1 H); IR (1% in CH_2Cl_2) ν 3520, 3420 (NH_2), 1730 (C═O) cm^{-1}. Anal. Calcd for $C_{16}H_{25}NO_2S$: C, 65.1; H, 8.5; N, 4.7. Found: C, 65.4; H, 8.6; N, 4.7.

1,6-Hexanediolbis(3-(4-Amino-3-Tert-Butyl-5-Methylphenylthio)Propionate), (8). The procedure for compound **5a** was repeated using 4.9 g (25 mmol) of **1**, 2.8 g (12 mmol) of **7** and 0.2 g (2 mmol) of triethylamine in 25 mL of toluene (50°C for 18 h). The solvent was removed *in vacuo* and the residue was purified by preparative HPLC (silica gel, 3:1, heptane:ethylacetate eluent) to give 3.4 g (44%) of a colorless liquid. ^{1}H NMR ($CDCl_3$) δ 1.41 (overlapping m, 8 H), 1.42 (s, 18 H), 2.13 (s, 6 H), 2.57 (t, 4 H), 3.02 (t, 4 H), 3.91 (exchangeable s, 4 H), 4.08 (t, 4 H), 7.11 (d, 2 H); 7.24 (d, 2 H); IR (1% in CH_2Cl_2) ν 3520, 3420 (NH_2), 1720 (C═O) cm^{-1}. Anal. Calcd for $C_{34}H_{52}N_2O_4S$: C, 66.2; H, 8.5: N, 4.5. Found: C, 66.2; H, 8.5; N, 4.4.

1-(4-Amino-3-Tert-Butyl-5-Methylphenylthio)-3,12-Dioxa-4,11-Dioxo-13-Tetradecene, (9). During the HPLC purification of **8**, 1.9 g of compound **9** was isolated by HPLC as a colorless liquid. ^{1}H NMR ($CDCl_3$) δ 1.41 (overlapping m, 8 H), 1.42 (s, 9 H), 2.13 (s, 3 H), 2.57 (t, 2 H), 3.02 (t, 2 H), 3.91 (exchangeable s, 2 H), 4.08 (overlapping m, 4 H), 6.13 (m, 3 H), 7,20 (m, 2 H); IR (1% in CH_2Cl_2) ν 3520, 3420 (NH_2), 1720 (C═O) cm^{-1}. Anal. Calcd for $C_{23}H_{35}NO_4S$: C, 65.5; H, 8.4: N, 3.3. Found: C, 65.7; H, 8.1; N, 3.6.

Di-n-butyl 2-(4-Amino-4-Tert-Butyl-5-Methylphenylthio)Succinate, (11). To a stirred solution of 1.00 g (5.1 mmol) of **1** and 0.05 g (0.5 mmol) of triethylamine in 5 mL of toluene at room temperature was added dropwise a solution of 1.16 g (5.1 mmol) of **10** in 5 mL of toluene. The reaction mixture was stirred for 18 h at rt. The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography (silica gel, 85:15, heptane:ethylacetate eluent) to give 0.60 g (28%) of a colorless liquid. ^{1}H NMR ($CDCL_3$) δ 0.91 (t, 6 H, 1.41 (overlapping m, 8 H), 1.42 (s, 9 H), 2.13 (s, 3 H), 2.64 (dd, $^3J_{HCCH}$ = 6.4 Hz, $^3J_{HCCH}$ = 8.8 Hz, 1 H), 2.93 (dd, $^3J_{HCCH}$ = 6.4 Hz, $^2J_{HCH}$ = 16.4 Hz, 1 H), 3.84 (dd, $^3J_{HCCH}$ = 8.8 Hz, $^2J_{HCH}$ = 16.4 Hz, 1 H), 4.08 (t, 4 H), 7.11 (d, 1 H); 7.24 (d, 1 H); IR (1% in CH_2Cl_2) ν 3520, 3420 (NH_2), 1730 (C═O) cm^{-1}. Anal. Calcd for $C_{23}H_{37}NO_4S$: C, 65.2; H, 8.8; N, 3.3. Found: C, 64.8, H, 8.7; N, 3.2.

3-(4-Amino-3-*Tert*-Butyl-5-Methylphenylthio)-N-Methylpyrrolidine-2,5-dione, (13a). The procedure for compound **11** was repeated using 1.0 g (5 mmol) of **1** 0.6 g (5 mmol) of **12a**, and 0.1 g (1 mmol) of triethylamine in 10 mL of toluene (50°C for 18 h). The solvent was removed *in vacuo* and the residue was purified by flash chromatography (silica gel, 3:2, heptane:ethyl acetate eluent) followed by recrystallization from a heptane:toluene solvent mixture to give 0.8 g (51%) of a white solid; m.p. 92–94°C. ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 9 H), 2.08 (s, 3 H), 2.66 (dd, 1 H), 2.80 (s, 3 H), 3.06 (dd, 1 H), 3.82 (dd, 1 H), 4.02 (exchangeable s, 2 H), 7.11 (d, 1 H); 7.24 (d, 1 H); IR (1% in CH_2Cl_2)



ν 3520, 3430 (NH_2), 1780, 1710 (C═O) cm^{-1}. Anal. Calcd for $C_{16}H_{22}N_2O_2S$: C, 62.7; H, 7.2; N, 9.1 Found: C, 62.6; H, 7.0; N, 9.0.

3-(4-Amino-3-T*ert*-Butyl-5-Methylphenylthio)-N-Octadecylpyrrolidine-2,5-Dione, (13b). The procedure for compound **11** was repeated using 2.8 g (14 mmol) of **1**, 5.0 g (14 mmol) of **12b**, and 0.1 g (1 mmol) of triethylamine in 50 mL of toluene (50° for 18 h). The solvent was removed *in vacuo* and the residue

was purified by preparative HPLC (silica gel, 4:1, heptane:ethyl acetate eluent) to give 4.3 g (55%) of a caramel-colored liquid. ^{1}H NMR ($CDCl_3$) δ 0.84 (t, 3 H), 1.20 (m, 32 H), 1.35 (s, 9 H), 2.08 (s, 3 H), 2.62 (dd, 1 H), 3.02 (dd, 1 H), 3.28 (t, 2 H) 3.77 (dd, 1 H) 3.95 (exchangeable s, 2 H), 7.11 (d, 1 H); 7.24 (d, 1 H); IR (1% in CH_2Cl_2) ν 3520, 3430 (NH_2), 1780, 1700 (C=O) cm^{-1}. Anal. Calcd for $C_{33}H_{56}N_2O_2S$: C, 72.7; H, 10.4; N, 5.1. Found: C, 72.3; H, 10.5; N, 5.1.

3-(4-Amino-3-*Tert*-Butyl-5-Methylphenylthio)-N-Phenylpyrrolidine-2,5-Dione, (13c). The procedure for compound **11** was repeated using 1.0 g (5 mmol) of **1**, 0.9 g (5 mmol) of **12c**, and 0.1 g (1 mmol) of triethylamine in 10 mL of toluene was heated at 50°C for 18 hrs. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, ethyl acetate eluent) to give 0.7 g (37%) of a white solid; m.p. 126–128°C. ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 9 H), 2.13 (s, 3 H), 2.93 (dd, 1 H), 3.33 (dd, 1 H), 2.97 (dd, 1 H), 4.06 (exchangeable (s, 2 H), 6.88–7.51 (overlapping m, 7 H); IR (1% in CH_2Cl_2) ν 3520, 3430 (NH_2), 1780, 1720 (C=O) cm^{-1}. Anal. Calcd for $C_{21}H_{24}N_2O_2S$: C, 68.5; H, 6.6; N, 7.6. Found: C, 68.3; H, 6.4; N, 7.5.

N-(4-Amino-3-*Tert*-Butyl-5-Methylphenylthiomethyl)-N,N-Diphenylamine, (15). To a stirred solution of 4.5 g (23 mmol) of **1** and 3.9 g (23 mmol) of diphenylamine in 30 mL of methanol at −5°C was added 0.9 g (23 mmol) of formaldehyde as a 37% aqueous solution (1.9 mL). The reaction mixture was stirred for 72 h at room temperature and then the mixture was heated for 5 hrs at 50–55°C. The solvent was removed *in vacuo* and the residue was purified by flash column chromatography (silica gel, 9:1, heptane:ethyl acetate eluent) to give 3.9 g (45%) of a colorless liquid. ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 9 H), 2.04 (s, 3 H), 3.84 (exchangeable s, 2 H), 5.11 (s, 2 H), 6.80–7.29 (overlapping m, 12 H), IR (1% in CH_2Cl_2) ν 3520, 3420 (NH_2) cm^{-1}. Anal. Calcd for $C_{24}H_{28}N_2S$: C, 76.6; H, 7.5; N, 7.4. Found: C, 76.3; H, 7.5; N, 7.3.

S-(4-Amino-3-*Tert*-Butyl-5-Methylphenyl)-0,0-Dimethylphosphorothiolate, (18a). To a stirred suspension of 15.5 g (40 mmol) of **4** (n = 2) in 50 mL of toluene at −40°C was introduced 3.4 g (48 mmol) of elemental chlorine through a gas inlet tube below the surface of the reaction mixture over a 15 to 20 min period. The reaction mixture was stirred for 15 min and then to it was added 10.9 g (88 mmol) of **17a**. The reaction mixture was stirred for 24 h at room temperature and then any precipitate was removed by filtration. The solvent was removed *in vacuo* and the residue was purified by preparative HPLC (silica gel, 1:1, heptane:ethyl acetate) followed by recrystallization from a heptane:toluene solvent mixture to give 2.6 g (27%) of a white solid; m.p. 85–88°C. ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 9 H), 2.13 (s, 3 H), 3.82 (d, 6 H), 4.00 (exchangeble s, 2 H), 7.15 (d, 1 H), 7.33 (d, 1 H); IR (1% in CH_2Cl_2) ν 3520,

3420 (NH_2) cm^{-1}. Anal. Calcd for $C_{13}H_{22}NO_3PS$: C, 51.5; H, 7.3; N, 4.6. Found: C, 51.1; H, 7.3; N, 4.6.

S-(4-Amino-3-*Tert*-Butyl-5-Methylphenyl)-0,0-Di-*N*-Butylphosphorothiolate, (18b). The procedure for compound **18a** was repeated using 15.5 g (40 mmol) of **4** (n = 2), 3.4 g (48 mmol) of elemental chlorine, and 22.0 g (88 mmol) of **17b** in 50 mL of toluene. The reaction mixture was stirred for 24 hrs at rt and then any precipitate was removed by filtration. The solvent was removed in vacuo from the filtrate and the residue was purified by preparative HPLC (silica gel, 7:3, heptane:ethyl acetate) to give 13.5 g (43%) of a colorless liquid. ^1H NMR ($CDCl_3$) δ 0.89 (m, 6 H), 1.41 (overlapping m, 8 H), 1.42 (s, 9 H), 2.13 (s, 3 H), 4.04 (dt, 4 H), 7.20 (m, 2 H); IR (1% in CH_2Cl_2) ν 3520, 3420 (NH_2) cm^{-1}. Anal. Calcd for $C_{19}H_{34}NO_3PS$: C, 58.9; H, 8.8; N, 3.6. Found: C, 58.8; H, 8.9: N, 3.6.

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