Reaction of (1,ω)-*N*-Acylamino Alcohols with Lawesson's Reagent: Synthesis of Sulfur-Containing Heterocycles

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Lawesson's reagent [LR: 2,4-bis(*p*-methoxyphenyl)-1,3,2,4-dithiaphosphetane 2,4-disulfide] is shown to be a valuable reagent for the ready access of sulfur-containing heterocycles: thiazolines **2** starting from the (1,2)-*N*-acylamino alcohols **1** and benzothiazines **14** from [2-(*N*-acylamino)phenyl]alkanols **12**. Treatment of (1,2)-*N*-acylamino secondary alcohols **1a**−**p** with LR gave the thiazolines **2a**−**p** via direct conversion of the alcohols to the respective thiols, and the subsequent thionation of the amide carbonyl, followed by cyclization with the elimination of hydrogen sulfide. However, reaction of (1,2)-*N*-acylamino tertiary alcohols **1q**−**u** with LR yielded the dehydration products **5**−**7** and **9**. Treatment of [2-(*N*-acylamino)phenyl]alkanols **12a**−**f** with a molar equivalent of LR yielded the 3,1-benzothiazines **14a**−**f**. In this reaction, the [2-(*N*-acylamino)phenyl]alkanethiols **13a**−**e** were isolated when the corresponding alcohols **12a**−**e** were treated with 0.5 equiv of LR. Further thionation of **13c** with LR also gave 3,1-benzothiazine **14c**.

2,4-Bis(*p*-methoxyphenyl)-1,3,2,4-dithiaphosphetane 2,4-disulfide, commonly known as Lawesson's reagent (LR), is one of the best known thionation reagents.[1] LR has also been utilized in the synthesis of five- and six-membered phosphorus heterocycles such as oxathiaphospholes,[2] oxathiazaphospholidine-2-thiones,[3] benzodioxaphospholane 2-sulfides,[4] oxazaphosphorine-4-thione 2-sulfides,[5] thiazaphosphorin-4-one 2-sulfides,[6] thiazaphosphorin-4-thione 2-sulfides,[6] benzoxathiaphosphorin-4-thione 2-sulfides and their oxo analogues,[7] and sulfur-containing heterocycles such as thienothiazine-4-thiones,[8] benzothiazine-4-thiones,[9] and benzothiazole-3-thiones and benzodithiol-3-imines.[10] Recently we reported the direct conversion of alcohols into thiols using LR[11] and novel routes to sulfur-containing heterocycles such as tetrahydrothiophen-2-imines, tetrahydrothiophene-2-thione, and tetrahydrothiopyran-2-thione by the reaction of the substrates containing two functional groups [*e.g.*, (1,ω)-amide alcohols] with LR.[12] This paper reports the synthesis of 1,3-thiazolines **2**, 3,1-benzothiazines **14**, and 3,1-benzoxazine **15** by the reaction of (1,ω)-*N*-acylamino alcohols with LR.

Results and Discussion

The reaction of the (1,2)-*N*-acylamino secondary alcohol, 2-(*N*-benzoylamino)-1-phenylethan-1-ol (**1a**), with an equimolar amount of LR in toluene at reflux temperature under argon for 30 min yielded 2,5-diphenylthiazoline (**2a**) in 56% yield. The yield of **2a** dropped to 31% when 0.5 equiv of LR was used in this reaction. Similar treatment of the (1,2)-*N*-acylamino alcohols **1b**−**p** with LR gave the corresponding thiazolines **2b**−**p** in reasonable to good yields. The 2-[*N*-(adamantanecarbonyl)-amino]-1-phenylalkan-1-ols **1h**−**i** were treated with LR to yield the 2-adamantylthiazolines **2h**−**i** and 2-[*N*-(adamantanecarbonyl)amino]-1-phenylalkane-1-thiols **3h**−**i** after purification by flash chromatography. Formation of these products was dependent on the molar ratios of the reactants. For example, treatment of **1h**−**i** with an equimolar amount of LR yielded the thiazolines **2h**−**i** exclusively. However, treating **1h**−**i** with 0.5 mol equiv of LR yielded the corresponding thiols **3h**−**i** and a small amount of the thiazolines **2h**−**i**. This result suggests that the hydroxy group is more reactive toward LR than the amide group. The thiol **3h** thus obtained underwent further thionation, followed by cyclization with the elimination of hydrogen sulfide, to yield the thiazoline **2h** when **3h** was treated with 0.5 equiv of LR under the same conditions as described above. The thiazolines **2j**−**m**, which are substituted with heterocycles such as furan and thiophene at the 2-position, are also produced in good yields from the 2-(*N*-furoylamino)alcohols **1j**−**k** and the 2-(*N*-thenoylamino)alcohols **1l**−**m**. 1-Phenyl-2-(*N*-thenoylamino)propane-1-thiol (**3m**) was also isolated as a byproduct but in low yield when **1m** was treated with LR. The structures of the thiazolines **2** and (1,2)-(*N*-acylamino)thiols **3** were elucidated on the basis of their spectroscopic properties and elemental analyses. The IR spectra of 2-(*N*-acylamino)alkane-1-thiols **3h**−**i**, **m** exhibit a characteristic thiol absorption around 2520−2565 cm^{-1}. On the other hand, reaction of acyclic (1,3)-*N*-acylamino secondary alcohols **1v**−**w** with LR in the same way leads to intractable mixtures.

On the treatment of (1,2)-*N*-acylamino tertiary alcohol, 2-(*N*-benzoylamino)-1,1-diphenylethan-1-ol (**1q**) with an equimolar amount of LR, the dehydration products, *N*-(2-phenylstyryl)thiobenzamide (**5q**) and *N*-(2-phenylstyryl)-benzamide (**6q**) were obtained in 40% and 13% yields, respectively. However, treatment of **1q** with 0.5 mol equiv of LR gave **5q** and **6q** in 7% and 42% yields,

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Scheme 1

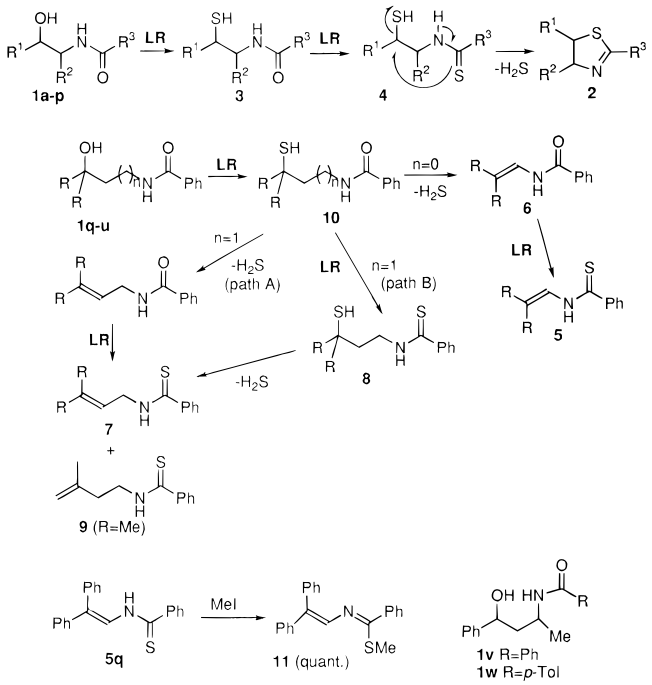


Table 1. Yields of Products 2 and 3 from (1,2)-*N*-acylamino Alcohols 1

	R^1	R^2	R^3	molar ratio LR/**1**	yield (%)[a] **2**	**3**
1a	Ph	H	Ph	1	56	
1a				0.5	31	
1b	Ph	Me	Ph	1	57	
1c	Ph	H	*p*-Tol	1	60	
1d	Ph	Me	*p*-Tol	1	62	
1e	Ph	H	α-naphthyl	1	80	
1f	Ph	H	$PhCH_2$	1	36	
1f				0.5	27	trace
1g	Ph	H	Bu^t	1	64	
1h	Ph	H	adamantyl	1	52	
1h				0.5	4	63
1i	Ph	Me	adamantyl	1	56	
1i				0.5	5	46
1j	Ph	H	2-furyl	1	71	
1k	Ph	Me	2-furyl	1	36	
1l	Ph	H	2-thienyl	1	61	
1m	Ph	Me	2-thienyl	1	55	8
1n	Me	H	Ph	1	11	
1o	Me	Me	Ph	1	17	
1p	Me	$PhCH_2$	Ph	1	22	

[a] Isolated yield.

respectively. On the basis of this result and our earlier findings,[10] it is suggested that **1q** is initially converted to *N*-acylaminothiol **10** (n = 0, R = Ph), which then dehydrates to **6q**, and a final thionation gives **5q** (Scheme 1). The treatment of (1,2)-*N*-acylamino tertiary alcohol **1r** with LR gives *N*-alkenylthioamide **5r** as the sole product. The structures of **5q**−**r** and **6q** were determined by elemental analyses as well as by their spectroscopic properties. *N*-(2-Styrylthio)benzamide **5q**, when treated with methyl iodide, yields 1-(methylthio)-1,4,4-triphenyl-2-aza-1,3-butadiene (**11**) in quantitative yield. (1,3)-*N*-Acylamino tertiary alcohols **1s**−**u** gives the dehydration products **7s**−**u** and **9u**. *N*-(3,3-Diphenyl-3-mercaptopropyl)thiobenzamide (**8**) was isolated as a byproduct when **1s** was treated with LR. The IR spectrum of **8** shows an absorption at 2550 cm^{-1} assignable to thiol, and the ^1H and ^{13}C NMR spectra of **8** show a singlet at δ 2.93 (1H, s) assignable to thiol and a singlet at δ 56.7 due to

Table 2. Yields of Products 5−9 from (1,ω)-*N*-Acylamino Alcohols 1

	R	n	molar ratio LR/**1**	yield (%)[a] **5**	**6**	**7**	**8**	**9**
1q	Ph	0	1	40	13			
1q			0.5	7	42			
1r	Me	0	1	47				
1s[b]	Ph	1	1			46	26	
1s			1			77	3	
1s			0.5			15	12	
1t	*p*-Tol	1	1			63		
1u	Me	1	1			27[c]		38[c]

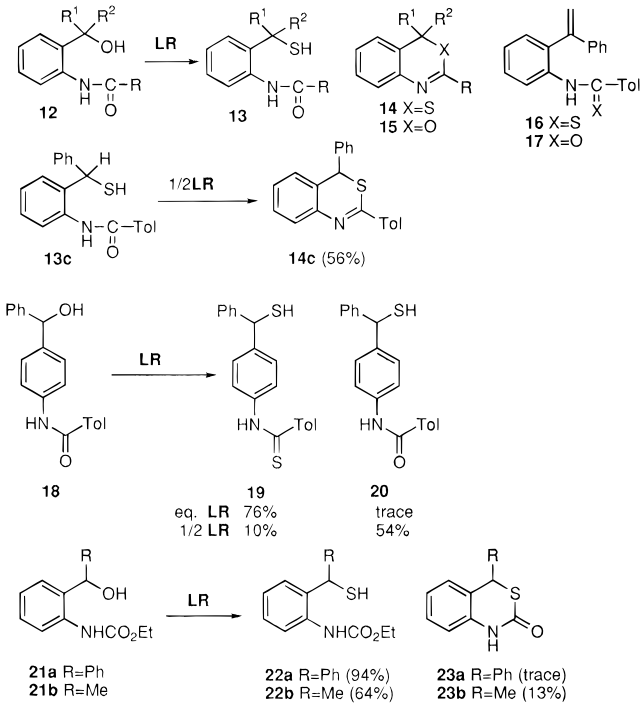
[a] Isolated yield. [b] Reflux for 15 min. [c] Two products were not separated, and yields were determined by NMR.

quaternary carbon at C-1, respectively. The dehydration product, *N*-allylthiobenzamide **7s**, was also produced when the *N*-thioacylamino thiol **8** thus obtained was refluxed in toluene in the presence of 0.5 mol equiv of LR. However, the *N*-thioacylamino thiol **8** was recovered quantitatively when refluxed in toluene in the absence of LR.

A reasonable mechanism for the formation of the thiazolines **2**, *N*-acylamino thiols **3**, *N*-thioacylamino thiol **8**, and dehydration products **5**−**7**, **9** is depicted in Scheme 1. On the basis of the above findings, the (1,2)-*N*-Acylamino alcohols **1a**−**p** are apparently converted to the *N*-acylamino thiols **3**, which then undergo further thionation to form the *N*-thioacylamino thiols **4**. Subsequent cyclization of **4** with the elimination of hydrogen sulfide yields thiazolines **2**. On the other hand, the elimination of hydrogen sulfide from (1,2)-*N*-acylamino thiols **10** (n = 0), initially derived from (1,2)-*N*-acylamino tertiary alcohols **1q**−**r** (n = 0) with LR, gives *N*-alkenylbenzamides **6**. Further thionation of **6** with LR yields the *N*-alkenylthiobenzamides **5**. The formation of *N*-thioacylamino thiols **8** can be understood in terms of the thionation of (1,3)-*N*-acylamino thiols **10** (n = 1). The formation of *N*-alkenylthiobenzamide **7** can be explained by a similar pathway as for the formation of **5**, which involves the elimination of hydrogen sulfide from *N*-benzoylamino thiols **10** (n = 1), followed by further thionation of *N*-alkenylbenzamides (path A). The pathway B, which involves the thionation of **10** (n = 1) and subsequent elimination of hydrogen sulfide leading to **7** would be also included.

The reaction described above provides a convenient method for the synthesis of five-membered sulfur-containing heterocycles such as thiazolines **2**. Consequently, we explored the reaction of the [2-(*N*-acylamino)-phenyl]alkanols **12** with LR in the hope of forming six-membered heterocycles such as benzothiazines and benzoxazines through the corresponding [2-(*N*-thioacylamino)phenyl]- or [2-(*N*-acylamino)phenyl]alkanethiols. [2-(*N*-Acylamino)phenyl]alkanols **12a**−**e** react with an equimolar amount of LR in toluene at the reflux temperature under argon for 30 min to give 3,1-benzothiazines **14a**−**e** in good yields and a small amount of [2-(*N*-acylamino)phenyl]alkanethiols **13a**−**e**. [2-(*N*-Acylamino)-phenyl]alkanethiols **13a**−**e** were predominantly produced when **12a**−**e** were treated with 0.5 equiv of LR under the same conditions. The [2-(*N*-toluoylamino)phenyl]-phenylmethanethiol (**13c**) thus obtained reacted with 0.5 mol equiv of LR to yield 4-phenyl-2-*p*-tolyl-3,1-benzothiazine (**14c**) in 56% yield with elimination of hydrogen sulfide. The formation of the 3,1-benzothiazines **14** can be understood in terms of a direct conversion of hydroxy

Scheme 2



to thiol groups, thionation of amide carbonyl, and then cyclization with loss of hydrogen sulfide analogous to the pathway for the formation of thiazolines from (1,2)-acylamino alcohols. The treatment of [2-(*N*-toluoylamino)pheny]diphenylcarbinol (**12f**) with LR under the similar conditions yields 4,4-diphenyl-2-*p*-tolyl-3,1-benzothiazine (**14f**) and 4,4-diphenyl-2-*p*-tolyl-3,1-benzoxazine (**15f**). The formation of these products, **14f** and **15f**, is not dependent on the molar ratios of the reactants, suggesting that [2-(*N*-acylamino)phenyl]methanethiol **13f** initially formed undergoes cyclization to give the benzoxazine **15f** in preference to further thionation of **13f** due to steric hindrance of the bulky phenyl groups. The treatment of 1-phenyl-1-[2-(*N*-toluoylamino)phenyl]ethanol (**12g**) with LR gives two isomeric dehydration products, **16g** and **17g**, whose formation is dependent on the molar ratios of the reactants. This reaction proceeds through a direct conversion of the hydroxy to thiol groups, elimination of hydrogen sulfide, and then further thionation. [4-(*N*-Toluoylamino)phenyl]phenylmethanol (**18**), in which there would be no appreciable interaction between hydroxy and amido groups, was treated with LR to afford different amounts of α-phenyl-α-[4-(*N*-thiotoluoylamino)phenyl]methanethiol (**19**) and α-phenyl-α-[4-(*N*-toluoylamino)phenyl]methanethiol (**20**) depending on the molar ratios of **18** and LR. [2-[*N*-(Ethoxycarbonyl)amino]-phenyl]alkan-1-ols **21** react with LR to yield [2-[*N*-(ethoxycarbonyl)amino]phenyl]alkane-1-thiols **22**, along with small amounts of the cyclized products, 3,1-benzothiazin-2-ones **23**, indicating that the hydroxy group is more reactive toward LR than the carbamate group.

The procedure described here represents a useful method for the prepararion of sulfur-containing five- or six-membered heterocycles such as thiazolines **2** and benzothiazines **14**.

Experimental Section

Melting and boiling points are uncorrected. NMR spectra were measured in $CDCl_3$ using TMS as the internal standard. *J* values are given in hertz.

Table 3. Yields of Products 13−17 from 2-(*N*-Acylamino)phenylalkanols 12

	R	R^1	R^2	molar ratio LR/**12**	yield (%)[a] **13**	**14**	**15**	**16**	**17**
12a	Me	Ph	H	1	tr	56			
12b	Bu^t	Ph	H	1	4	71			
12b				0.5	87	tr			
12c	*p*-Tol	Ph	H	1	tr	89			
12c				0.5	84	8			
12d	*p*-Tol	Me	H	1	tr	79			
12d				0.5	66	6			
12e	α-naphthyl	Me	H	1	15	67			
12e				0.5	59	10			
12f	*p*-Tol	Ph	Ph	1		25	52		
12f				0.5		19	55		
12g	*p*-Tol	Ph	Me	1				64	tr
12g				0.5				14	62

[a] Isolated yield.

Reactions of (1,ω)-*N*-Acylamino Alcohols 1 with LR. A solution of (1,ω)-*N*-acylamino alcohols **1** (2 mmol) and LR (1−2 mmol) in toluene (70 mL) was refluxed under argon for 15−30 min. After removal of the solvent, the residue was chromatographed with benzene−ethyl acetate (50:1−9:1) to give the products **2**, **3**, and **5**−**9**.

2,5-Diphenylthiazoline (2a): bp 170 °C (3 mmHg); ^{1}H NMR δ 4.63 (2H, A and B of ABX), 5.01 (1H, X of ABX), 7.17−7.53 (8H, m), 7.70−7.96 (2H, m); ^{13}C NMR δ 54.6 (d), 73.3 (t), 127.0 (d), 128.4 (d), 128.8 (d), 131.2 (d), 133.2 (s), 142.1 (s), 167.6 (s). Anal. Calcd for $C_{15}H_{13}NS$: C, 75.30; H, 5.47; N, 5.85. Found: C, 75.11; H, 5.48; N, 5.82.

2,5-Diphenyl-4-methylthiazoline (2b): bp 190 °C (3 mmHg) [lit.[13] 162−167 °C (0.55 mmHg)]; ^{1}H NMR δ 1.46 (3H, d, *J* = 6.6), 4.61 (1H, d, *J* = 6.3), 4.78−4.80 (1H, m), 7.20−7.48 (8H, m), 7.80−7.88 (2H, m); ^{13}C NMR δ 20.1 (q), 61.7 (d), 81.3 (d), 127.5 (d), 127.7 (d), 128.3 (d), 128.4 (d), 128.5 (d), 131.2 (d), 133.3 (s), 141.4 (s), 165.5 (s).

5-Phenyl-2-*p*-tolylthiazoline (2c): mp 82−83 °C; ^{1}H NMR δ 2.38 (3H, s), 4.66 (2H, t, *J* = 7.8), 5.00 (1H, dd, *J* = 7.8, 14.2), 7.16−7.37 (7H, m), 7.76 (2H, d, *J* = 7.8); ^{13}C NMR δ 21.4 (q), 54.5 (d), 73.3 (t), 127.0 (d), 127.7 (d), 128.3 (d), 128.8 (d), 129.2 (d), 130.5 (s), 141.6 (s), 142.1 (s), 167.4 (s). Anal. Calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.96; N, 5.52. Found: C, 75.71; H, 5.99; N, 5.61.

4-Methyl-5-phenyl-2-*p*-tolylthiazoline (2d): mp 34−35 °C; ^{1}H NMR δ 1.46 (3H, d, *J* = 6.6), 2.38 (3H, s), 4.59 (1H, d, *J* = 6.0), 4.70−4.81 (1H, m), 7.19−7.38 (7H, m), 7.75 (2H, d, *J* = 9.3); ^{13}C NMR δ 20.6 (q), 21.9 (q), 60.0 (d), 81.6 (d), 127.9 (d), 128.1 (d), 128.8 (d), 129.2 (d), 129.6 (d), 131.0 (s), 141.9 (s), 142.0 (s), 165.8 (s). Anal. Calcd for $C_{17}H_{17}NS$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.26; H, 6.36; N, 5.23.

2-α-Naphthyl-5-phenylthiazoline (2e): mp 62−63 °C; ^{1}H NMR δ 4.61−5.17 (3H, m), 7.21−7.68 (8H, m), 7.78−7.95 (3H, m), 8.76−8.93 (1H, m); ^{13}C NMR δ 54.4 (d), 74.3 (t), 124.7 (d), 125.9 (d), 126.3 (d), 127.0 (d), 127.3 (d), 127.7 (d), 128.3 (d), 128.9 (d), 130.5 (s), 131.2 (d), 133.8 (s), 142.3 (d), 167.2 (s). Anal. Calcd for $C_{19}H_{15}NS$: C, 78.55; H, 5.22; N, 4.82. Found: C, 78.76; H, 5.24; N, 4.88.

2-Benzyl-5-phenylthiazoline (2f): bp 175 °C (3 mmHg); ^{1}H NMR δ 3.86 (2H, br s), 4.25−4.58 (2H, A and B of ABX), 4.90 (1H, X of ABX, *J* = 6.4, 8.3), 7.08−7.39 (10H, m); ^{13}C NMR δ 40.7 (t), 55.1 (d), 72.7 (t), 126.8 (d), 127.0 (d), 127.5 (d), 128.5 (d), 128.6 (d), 129.0 (d), 135.9 (s), 141.9 (s), 169.6 (s). Anal. Calcd for $C_{16}H_{15}NS$: C, 75.86; H, 5.97; N, 5.53. Found: C, 75.63; H, 6.04; N, 5.46.

1-Phenyl-2-[*N*-(phenylacetyl)amino]ethane-1-thiol (3f): mp 81−82 °C; IR (KBr) 3260 (NH), 2540 (SH), 1640 (CO) cm^{-1}; ^{1}H NMR δ 1.86 (1H, d, *J* = 6.3), 3.49 (2H, s), 3.62 (2H, d, *J* = 6.4), 3.98−4.20 (1H, m), 5.74 (1H, br s), 7.00−7.49 (10H, m); ^{13}C NMR δ 42.9 (d), 43.7 (t), 47.3 (t), 127.1 (d), 127.3 (d), 127.7 (d), 128.0 (d), 128.8 (d), 128.9 (d), 129.3 (d), 134.6 (s), 140.9

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(s), 170.9 (s). Anal. Calcd for $C_{16}H_{17}NOS$: C, 70.82; H, 6.31; N, 5.16. Found: C, 70.79; H, 6.18; N, 5.15.

2-*tert*-Butyl-5-phenylthiazoline (2g): bp 140 °C (3 mmHg); ^{1}H NMR δ 1.30 (9H, s), 4.33 (1H, A of ABX, J = 6.3, 15.1), 4.60 (1H, B of ABX, J = 15.1), 4.88 (1H, X of ABX, J = 6.3, 8.3), 7.27 (5H, s); ^{13}C NMR δ 29.1 (q), 38.0 (s), 54.2 (d), 72.7 (t), 126.8 (d), 127.5 (d), 128.2 (d), 142.5 (s), 179.7 (s). Anal. Calcd for $C_{13}H_{17}NS$: C, 71.19; H, 7.81; N, 6.39. Found: 71.42; H, 7.94; N, 6.49.

2-Adamantyl-5-phenylthiazoline (2h): bp 210 °C (2 mmHg); ^{1}H NMR δ 1.62−2.14 (15H, m), 4.22−4.45 (2H, A and B of ABX), 4.65−4.89 (1H, X of ABX), 7.19−7.35 (5H, m). ^{13}C NMR δ 28.3 (d), 36.6 (t), 40.1 (s), 41.4 (t), 53.1 (d), 72.5 (t), 126.8 (d), 127.5 (d), 128.7 (d), 142.7 (s), 178.0 (s). Anal. Calcd for $C_{19}H_{23}NS$: C, 76.73; H, 7.80; N, 4.71. Found: C, 77.02; H, 8.03; N, 4.88.

2-[*N*-(Adamantanecarbonyl)amino]-1-phenylethane-1-thiol (3h): mp 130−131 °C; IR (KBr) 3380 (NH), 2520 (SH), 1625 (CO) cm^{-1}; ^{1}H NMR δ 1.60−2.10 (16H, m), 3.45−3.69 (2H, m), 4.07−4.29 (1H, m), 5.87 (1H, br s), 7.22-7.32 (5H, m); ^{13}C NMR δ 28.0 (d), 36.4 (t), 39.1 (t), 40.6 (s), 43.2 (d), 47.2 (t), 127.2 (d), 127.7 (d), 128.8 (d), 141.3 (s), 177.9 (s). Anal. Calcd for $C_{19}H_{25}NOS$: C, 72.34; H, 7.99; N, 4.44. Found: C, 72.01; H, 7.98; N, 4.39. A solution of **3h** (1 mmol) and LR (0.5 mmol) in toluene (50 mL) was refluxed under argon for 15 min. After purification by flash chromatography, **2h** was obtained in 20% yield.

2-Adamantyl-4-methyl-5-phenylthiazoline (2i): bp 220 °C (2 mmHg); ^{1}H NMR δ 1.33 (3H, d, J = 6.6), 1.70−1.80 (6H, m), 1.93−1.96 (6H, m), 2.06 (3H, br s), 4.34 (1H, d, J = 5.8), 4.50−4.60 (1H, m), 7.20−7.35 (5H, m); ^{13}C NMR δ 20.7 (d), 28.8 (q), 37.0 (t), 40.3 (s), 41.9 (t), 60.4 (d), 80.8 (d), 127.6 (d), 127.9 (d), 129.1 (d), 142.9 (s), 178.2 (s). Anal. Calcd for $C_{20}H_{25}NS$: C, 77.13; H, 8.09; N, 4.50. Found: C, 76.99; H, 8.04; N, 4.51.

2-[*N*-(Adamantanecarbonyl)amino]-1-phenylpropane-1-thiol (3i): mp 118−119 °C; IR (KBr) 3360 (NH), 2655 (SH), 1630 (CO) cm^{-1}; ^{1}H NMR δ 1.10 (3H, d, J = 6.9), 1.63−1.82 (11H, m), 1.96−2.02 (4H, m), 4.26−4.32 (1H, m), 4.35−4.46 (1H, m), 5.71 (1H, br d, J = 8.2), 7.21−7.41 (5H, m); ^{13}C NMR δ 16.2 (d), 27.9 (q), 36.3 (t), 39.0 (t), 40.4 (s), 49.0 (d), 49.7 (d), 127.3 (d), 127.7 (d), 128.3 (d), 140.6 (s), 177.0 (s). Anal. Calcd for $C_{20}H_{27}NOS$: C, 76.92; H, 8.26; N, 4.25. Found: C, 76.61; H, 8.39; N, 4.05.

2-Furyl-5-phenylthiazoline (2j): bp 210 °C (2 mmHg); ^{1}H NMR δ 4.57 (1H, dd, J = 5.6, 16.2), 4.73 (1H, dd, J = 8.6, 16.2), 5.04 (1H, dd, J = 5.6, 8.6), 6.49 (1H, dd, J = 1.6, 3.3), 6.93 (1H, d, J = 3.3), 7.21−7.34 (5H, m), 7.53 (1H, d, J = 1.6); ^{13}C NMR δ 54.3 (t), 72.6 (d), 111.8 (d), 114.0 (d), 126.9 (d), 127.7 (d), 128.8 (d), 141.4 (s), 144.9 (d), 147.5 (s), 151.2 (s). Anal. Calcd for $C_{13}H_{11}NOS$: C, 68.11; H, 4.84; N, 6.11. Found: C, 68.35; H, 4.90; N, 6.12.

2-Furyl-4-methyl-5-phenylthiazoline (2k): bp 250 °C (2 mmHg); ^{1}H NMR δ 1.47 (3H, d, J = 6.6), 4.61 (1H, d, J = 6.6), 4.69−4.80 (1H, m), 6.48 (1H, dd, J = 1.7, 3.3), 6.84 (1H, d, J = 3.3), 7.23−7.37 (5H, m), 7.53 (1H, br s); ^{13}C NMR δ 19.7 (q), 61.4 (d), 80.3 (d), 111.8 (d), 114.4 (d), 127.3 (d), 127.8 (d), 128.7 (d), 140.2 (s), 145.0 (d), 147.2 (s), 155.5 (s). Anal. Calcd for $C_{14}H_{13}NOS$: C, 69.12; H, 5.39; N, 5.75. Found: C, 68.96; H, 5.56; N, 5.65.

5-Phenyl-2-thienylthiazoline (2l): mp 77−78 °C; ^{1}H NMR δ 4.53 (1H, dd, J = 5.6, 15.8), 4.70 (1H, dd, J = 8.6, 15.8), 5.09 (1H, dd, J = 5.6, 8.6), 7.06 (1H, dd, J = 3.9, 5.0), 7.23−7.47 (7H, m); ^{13}C NMR δ 55.4 (t), 72.7 (d), 127.0 (d), 127.5 (d), 127.8 (d), 128.8 (d), 129.8 (d), 130.8 (d), 136.8 (s), 131.6 (s), 160.8 (s). Anal. Calcd for $C_{13}H_{11}NS_2$: C, 63.67; H, 4.52; N, 5.71. Found: C, 63.42; H, 4.48; N, 5.69.

4-Methyl-5-phenyl-2-thienylthiazoline (2m): bp 190 °C (2 mmHg); ^{1}H NMR δ 1.47 (3H, d, J = 6.9), 4.66 (1H, d, J = 6.6), 4.69−4.77 (1H, m), 7.05 (1H, dd, J = 3.6, 5.0), 7.23−7.49 (7H, m); ^{13}C NMR δ 19.9 (q), 62.3 (d), 80.7 (d), 127.4 (d), 127.8 (d), 128.5 (d), 129.6 (d), 130.6 (d), 136.9 (s), 140.9 (s), 158.5 (s). Anal. Calcd for $C_{14}H_{13}NS_2$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.92; H, 4.98; N, 5.41.

1-Phenyl-2-(*N*-thenoylamino)propane-1-thiol (3m): mp 145−146 °C; IR (KBr) 3325 (NH), 2565 (SH), 1620 (CO) cm^{-1}; ^{1}H NMR δ 1.19 (3H, d, J = 6.9), 1.88 (1H, d, J = 7.3), 4.46 (1H, dd, J = 4.6, 7.3), 4.55−4.67 (1H, m), 6.23 (1H, d, J = 7.9), 7.06 (1H, t, J = 4.0), 7.23−7.48 (7H, m); ^{13}C NMR δ 16.0 (q), 49.1 (d), 50.7 (d), 127.6 (d), 127.9 (d), 128.0 (d), 128.5 (d), 130.1 (d), 138.8 (s), 140.2 (s), 161.1 (s). Anal. Calcd for $C_{14}H_{15}NS_2$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.42; H, 5.45; N, 5.01.

5-Methyl-2-phenylthiazoline (2n): bp 150 °C (5 mmHg) [lit.[14] 86−91 °C (1 mmHg)]; ^{1}H NMR δ 1.34−1.42 (3H, m), 3.98−4.08 (1H, m), 4.13−4.24 (1H, m), 4.31−4.48 (1H, m), 7.35−7.46 (3H, m), 7.81−7.85 (2H, m); ^{13}C NMR δ 22.1 (q), 45.9 (d), 72.2 (t), 128.3 (d), 128.4 (d), 131.0 (d), 133.5 (s), 167.7 (s).

4,5-Dimethyl-2-phenylthiazoline (2o): This product was obtained as a 10:1 mixture of the *trans*- and *cis*-isomers: bp (a mixture of *trans*- and *cis*-isomers) 160 °C (5 mmHg) [lit. 129−130 °C (3 mmHg),[15] 281 °C (736 mmHg) for *trans*-isomer and 107 °C (2 mmHg) for *cis*-isomer[16]]; ^{1}H NMR δ (for *trans*-isomer) 1.34 (3H, d, J = 6.6), 1.40 (3H, d, J = 6.6), 3.54−3.64 (1H, m), 4.29−4.39 (1H, m), 7.34−7.46 (3H, m), 7.80−7.84 (2H, m); δ (for *cis*-isomer) 1.26 (3H, d, J 6.9), 1.45 (3H, d, J = 6.9), 3.84−3.98 (1H, m), 4.41−4.52 (1H, m), 7.34−7.46 (3H, m), 7.80−7.84 (2H, m); ^{13}C NMR δ (for *trans*-isomer) 19.0 (q), 21.4 (q), 52.1 (d), 79.3 (d), 128.1 (d), 128.3 (d), 130.9 (d), 133.4 (s), 165.6 (s); δ (for *cis*-isomer) 14.7 (q), 16.0 (q), 49.3 (d), 74.1 (d), 167.7 (s) in addition to aromatic carbon peaks.

4-Benzyl-5-methyl-2-phenylthiazoline (2p): bp 180 °C (3 mmHg); ^{1}H NMR δ 1.22 (3H, d, J = 6.8), 2.68 (1H, dd, J = 8.8, 13.7), 3.12 (1H, dd, J = 5.4, 13.7), 3.68 (1H, dq, J = 3.4, 6.8), 4.59 (1H, ddd, J = 3.4, 5.4, 8.8), 7.10−7.53 (8H, m), 7.75−7.94 (2H, m); ^{13}C NMR δ 22.7 (q), 39.0 (t), 48.5 (d), 85.2 (d), 126.3 (d), 128.3 (d), 129.2 (d), 130.9 (d), 133.5 (s), 138.3 (s), 166.0 (s). Anal. Calcd for $C_{17}H_{17}NS$: C, 76.36; H, 6.41; N, 5.23. Found: C, 76.12; H, 6.46; N, 5.28.

***N*-(2-Phenylstyryl)thiobenzamide (5q):** mp 160−161 °C; IR ($CHCl_3$) 3370 (NH), 1630 (C=C) cm^{-1}; ^{1}H NMR δ 7.24−7.54 (13H, m), 7.63 (2H, d, J = 7.3), 8.25 (1H, d, J = 10.6), 9.10 (1H, br d); ^{13}C NMR δ 124.0 (d), 126.6 (d), 127.3 (d), 127.8 (d), 128.5 (d), 128.7 (d), 129.5 (d), 129.7 (d), 130.2 (s), 131.5 (d), 136.9 (s), 139.2 (s), 141.1 (s), 193.6 (s). Anal. Calcd for $C_{21}H_{17}NS$: C, 79.96; H, 5.43; N, 4.44. Found: C, 80.04; H, 5.54; N, 4.40. To a solution of **5q** (0.5 mmol) in acetone (10 mL) in the presence of potassium carbonate (1 mmol) was added a solution of methyl iodide (2 mmol) in acetone (10 mL), and then the mixture was stirred at room temperature for 30 min. The usual workup gave **11** in quantitative yield.

1-(Methylthio)-1,4,4-triphenyl-2-azabuta-1,3-diene (11): mp 98−99 °C; ^{1}H NMR δ 2.34 (3H, s), 7.10−7.75 (16H, m). Anal. Calcd for $C_{22}H_{19}NS$: C, 80.22; H, 5.81; N, 4.25. Found: 79.94; H, 5.79; N, 4.19.

***N*-(2-Phenylstyryl)benzamide (6q):** mp 131−132 °C; IR (KBr) 3430 (NH), 1670 (CO), 1635 (C=C) cm^{-1}; ^{1}H NMR δ 7.16−7.73 (16H, m), 7.96 (1H, d, J = 11.6); ^{13}C NMR δ 119.8 (d), 125.2 (s), 126.7 (d), 128.0 (d), 128.3 (d), 128.6 (d), 129.3 (d), 129.7 (d), 131.9 (d), 133.2 (s), 137.3 (s), 139.8 (s), 163.7 (s). Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.67. Found: C, 84.34; H, 5.90; N, 4.62.

***N*-(2-Methypropenyl)thiobenzamide (5r):** bp 240 °C (1 mmHg); mp 32 °C; IR (KBr) 3150 (NH) cm^{-1}; ^{1}H NMR δ 1.76 (3H, s), 1.82 (3H, s), 7.19−7.49 (4H, m), 7.71−7.78 (2H, m), 8.77 (1H, br s); ^{13}C NMR δ 17.2 (q), 22.6 (q), 121.1 (d), 122.7 (s), 126.5 (d), 128.4 (d), 131.0 (d), 141.5 (s), 193.2 (s). Anal. Calcd for $C_{11}H_{13}NS$: C, 69.07; H, 6.84; N, 7.32. Found: C, 69.29; H, 7.01; N, 7.19.

***N*-(3,3-Diphenylallyl)thiobenzamide (7s):** oil; IR (film) 3230 (NH) cm^{-1}; ^{1}H NMR δ 4.48 (2H, dd, J = 5.3, 7.3), 6.22 (1H, t, J = 7.3), 7.16−7.43 (13H, m), 7.62−7.66 (2H, m); ^{13}C NMR δ 46.1 (t), 121.9 (d), 126.7 (d), 127.5 (d), 127.8 (d), 128.2 (d), 128.3 (d), 128.4 (d), 128.5 (d), 129.6 (d), 130.1 (d), 138.7 (s), 141.3 (s), 141.5 (s), 146.3 (s), 198.7 (s). Anal. Calcd for

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$C_{22}H_{19}NS$: C, 80.21; H, 5.81; N, 4.25. Found: C, 79.88; H, 6.07; N, 4.38.

***N*-(3,3-Diphenyl-3-mercaptopropyl)thiobenzamide (8)**: mp 140−141 °C; IR (KBr) 3270 (NH), 2550 (SH) cm^{-1}; ^1H NMR δ 2.93 (1H, s), 2.89 (2H, t, J = 6.8), 3.88 (2H, q, J = 6.6), 7.16−7.56 (15H, m); ^{13}C NMR δ 42.2 (t), 43.7 (t), 56.7 (s), 126.5 (d), 127.0 (d), 127.3 (d), 128.2 (d), 128.3 (d), 128.4 (d), 130.9 (d), 141.3 (s), 146.6 (s), 198.5 (s). Anal. Calcd for $C_{22}H_{21}NS_2$: C, 72.69; H, 5.82; N, 3.85. Found: C, 72.80; H, 5.82; N, 3.86. A solution of **8** (1 mmol) and LR (0.5mmol) in toluene (15 mL) was refluxed for 10 min. After purification by column chromatography, **7s** was obtained in 58% yield.

***N*-(3,3-Di-*p*-tolylallyl)thiobenzamide (7t):** mp 111−112 °C; IR (KBr) 3395 (NH) cm^{-1}; ^1H NMR δ 2.32 (3H, s), 2.37 (3H, s), 4.49 (2H, dd, J = 5.3, 6.9), 6.17 (1H, t, J = 6.9), 7.05−7.66 (14H, m); ^{13}C NMR δ 21.0 (q), 21.2 (q), 46.1 (t), 120.6 (d), 126.6 (d), 127.4 (d), 128.3 (d), 128.9 (d), 129.1 (d), 129.4 (d), 130.9 (d), 135.8 (s), 137.5 (s), 137.6 (s), 138.7 (s), 141.6 (s), 146.3 (s), 198.5 (s). Anal. Calcd for $C_{24}H_{23}NS$: C, 80.63; H, 6.48; N, 3.92. Found: C, 80.29; H, 6.66; N, 4.01.

***N*-(3-Methyl-2-butenyl)thiobenzamide (7u) and *N*-(3-methyl-3-butenyl)thiobenzamide (9)** could not completely separated: bp (a 5:7 mixture of **7u** and **9**) 260 °C (1 mmHg); IR (film) (a mixture of **7u** and **9**) 3320 (NH), 1645 (C=C) cm^{-1}; ^1H NMR δ (for **7u**) 1.79 (3H, s), 1.80 (3H, s), 4.35 (2H, t, J = 5.9), 5.37−5.44 (1H, m), 7.33−7.75 (5H, m); δ (for **9**) 1.80 (3H, s), 2.47 (2H, t, J = 6.6), 3.91 (2H, t, J = 6.6), 4.89 (2H, d, J = 16.5), 7.35−7.75 (5H, m); ^{13}C NMR δ (for **7u**) 18.2 (q), 25.7 (q), 45.2 (t), 117.9 (d), 141.8 (s), 198.5 (s) in addition to aromatic carbon peaks; δ (for **9**) 21.8 (q), 36.0 (t), 43.8 (t), 113.2 (t), 142.4 (s), 198.9 (s) in addition to aromatic carbon peaks. Anal. Calcd for $C_{12}H_{15}NS$: C, 70.20; H, 7.36; N, 6.82. Found (a mixture of **7u** and **9**): C, 70.43; H, 7.40; N, 6.85.

Reactions of [2-(*N*-Acylamino)phenyl]alkanols 12, [4-(*N*-acylamino)phenyl]alkanols 18, and [2-[*N*-(Ethoxycarbonyl)amino]phenyl]alkanols 21 with LR. A solution of **12** (or **18** or **21**) (2 mmol) and LR (1−2 mmol) in toluene (70 mL) was heated to reflux under argon for 15−30 min. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene−ethyl acetate (50:1−9:1) to yield the products **13**−**17**, **19**, **20, 22**, and **23**.

2-Methyl-4-phenyl-3,1-benzothiazine (14a): mp 64−65 °C; ^1H NMR δ 2.33 (3H, s), 5.23 (1H, s), 6.91−7.49 (9H, m); ^{13}C NMR δ 28.4 (q), 45.5 (d), 121.3 (s), 127.2 (d), 127.4 (d), 127.6 (d), 128.5 (d), 128.7 (d), 141.9 (s), 143.2 (s), 159.5 (s): Anal. Calcd for $C_{15}H_{13}NS$: C, 75.28; H, 5.47; N, 5.85. Found: C, 75.30; H, 5.48; N, 5.85.

α-[2-(*N*-Pivaloylamino)phenyl]-α-phenylmethanethiol (13b): mp 106−107 °C; IR (KBr) 3270 (NH), 1645 (CO) cm^{-1}; ^1H NMR δ 1.14 (9H, s), 2.32 (1H, d, J = 4.9), 5.51 (1H, d, J = 4.9), 6.99−7.40 (8H, m), 7.90−7.99 (2H, m); ^{13}C NMR δ 27.4 (q), 39.5 (s), 44.8 (d), 124.8 (d), 127.7 (d), 127.8 (d), 128.4 (d), 128.7 (d), 129.0 (d), 133.3 (s), 135.6 (s), 140.2 (s), 176.6 (s). Anal. Calcd for $C_{18}H_{21}NOS$: C, 72.20; H, 7.07; N, 4.67. Found: C, 72.34; H, 7.09; N, 4.68.

2-*tert*-Butyl-4-phenyl-3,1-benzothiazine (14b): mp 105−107 °C; ^1H NMR δ 1.18 (9H, s), 5.17 (1H, s), 6.94−7.51 (9H, m); ^{13}C NMR δ 27.7 (q), 41.9 (s), 44.8 (d), 122.5 (s), 127.1 (d), 127.2 (d), 127.5 (d), 128.3 (d), 128.4 (d), 141.4 (s), 143.6 (s), 170.9 (s). Anal Calcd for $C_{18}H_{19}NS$: C, 76.83; H, 6.80; N, 4.98. Found: C, 76.62; H, 7.07; N, 4.70.

α-Phenyl-α-[2-(*N*-*p*-toluoylamino)phenyl]methanethiol (13c): mp 123−124 °C; IR (KBr) 3290 (NH), 2540 (SH), 1635 (CO) cm^{-1}; ^1H NMR δ 2.34 (1H, d, J = 5.4), 2.39 (3H, s), 5.56 (1H, d, J = 5.4), 7.03−7.46 (10H, m), 7.61 (2H, d, J = 8.3), 8.02 (1H, d, J = 7.8), 8.45 (1H, br s); ^{13}C NMR δ 21.4 (q), 44.6 (d), 124.7 (d), 125.1 (d), 127.0 (d), 127.7 (d), 128.0 (d), 128.4 (d), 128.8 (d), 129.3 (d), 131.6 (s), 133.8 (s), 135.4 (s), 140.5 (s), 142.3 (s), 165.2 (s). Anal. Calcd for $C_{21}H_{19}NOS$: C, 75.64; H, 5.74; N, 4.20. Found: C, 75.75; H, 5.74; N, 4.20. A solution of **13c** (0.5 mmol) and LR (0.25 mmol) in toluene (50 mL) was refluxed under argon for 15 min. After purification by flash chromatography, **14c** was obtained in 56% yield.

4-Phenyl-2-*p*-tolyl-3,1-benzothiazine (14c): mp 125−126 °C; ^1H NMR δ 2.36 (3H, s), 5.33 (1H, s), 6.98−7.64 (11H, m), 7.98 (2H, d, J = 8.3); ^{13}C NMR δ 21.4 (q), 45.6 (d), 122.7 (s), 127.2 (d), 127.5 (d), 128.1 (d), 128.4 (d), 128.7 (d), 129.1 (d), 135.3 (s), 141.3 (s), 141.9 (s), 144.2 (s), 159.1 (s). Anal. Calcd for $C_{21}H_{17}NS$: C, 79.96; H, 5.43; N, 4.44. Found: C, 79.64; H, 5.43; N, 4.37.

[2-(*N*-*p*-Toluoylamino)phenyl]ethane-1-thiol (13d): mp 146−147 °C; IR (KBr) 3240 (NH), 2560 (SH), 1640 (CO) cm^{-1}; ^1H NMR δ 1.74 (3H, d, J = 6.8), 2.13 (1H, d, J = 5.4), 2.43 (3H, s), 4.19−4.47 (1H, m), 7.06−7.41 (5H, m), 7.80−7.99 (3H, m), 8.97 (1H, br s); ^{13}C NMR δ 21.4 (q), 23.9 (q), 35.2 (d), 125.0 (d), 125.3 (d), 126.0 (d), 127.2 (d), 128.1 (d), 129.4 (d), 131.6 (s), 135.3 (s), 135.4 (s), 142.3 (s), 165.3 (s). Anal. Calcd for $C_{16}H_{17}NOS$: C, 70.82; H, 6.31; N, 5.16. Found: C, 71.09; H, 6.31; N, 5.15.

4-Methyl-2-*p*-tolyl-3,1-benzothiazine (14d): bp 195 °C (3 mmHg); ^1H NMR δ 1.44 (3H, d, J = 6.8), 2.36 (3H, s), 4.12 (1H, q, J = 6.8), 7.04−7.55 (6H, m), 8.05 (2H, d, J = 8.3); ^{13}C NMR δ 21.4 (q), 23.2 (q), 37.2 (d), 125.4 (d), 125.6 (s), 127.4 (d), 127.5 (d), 128.7 (d), 129.1 (d), 135.7 (s), 141.7 (s), 143.2 (s), 159.0 (s). Anal. Calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.53. Found: C, 75.85; H, 5.92; N, 5.57.

1-[2-(*N*-α-Naphthoylamino)phenyl]ethane-1-thiol (13e): mp 124−125 °C; IR (KBr) 3260 (NH), 1640 (CO) cm^{-1}; ^1H NMR δ 1.73 (3H, d, J 6.8), 2.00 (1H, d, J = 5.9), 4.18−4.46 (1H, m), 7.05−7.63 (6H, m), 7.72−8.05 (4H, m), 8.40−8.68 (2H, m); ^{13}C NMR δ 24.3 (q), 34.6 (d), 124.8 (d), 125.1 (d), 125.4 (d), 126.0 (d), 126.5 (d), 127.4 (d), 128.1 (d), 128.4 (d), 130.3 (s), 131.2 (d), 133.9 (s), 134.1 (s), 135.0 (s), 136.0 (s), 167.7 (s). Anal. Calcd for $C_{19}H_{17}NOS$: C, 74.23; H, 5.57; N, 4.56. Found: C, 74.23; H, 5.50; N, 4.58.

4-Methyl-2-(α-naphthyl)-3,1-benzothiazine (14e): bp 230 °C (2 mmHg); ^1H NMR δ 1.56 (3H, d, J = 6.8), 4.19 (1H, q, J = 6.8), 7.11−7.68 (6H, m), 7.73−7.98 (4H, m), 8.54−8.68 (1H, m); ^{13}C NMR δ 23.8 (q), 37.9 (d), 124.7 (d), 125.3 (d), 125.7 (d), 126.1 (d), 127.0 (d), 127.4 (d), 128.1 (d), 129.0 (d), 130.8 (d), 133.9 (s), 136.1 (s), 142.5 (s), 160.3 (s). Anal. Calcd for $C_{19}H_{15}NS$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.61; H, 5.08; N, 4.78.

4,4-Diphenyl-2-*p*-tolyl-3,1-benzothiazine (14f): mp 199−200 °C; ^1H NMR δ 2.35 (3H, s), 6.72 (1H, dd, J = 1.0, 7.3), 7.11−7.65 (15H, m), 7.92 (2H, br d, J = 7.8); ^{13}C NMR δ 21.5 (q), 60.2 (s), 127.0 (d), 127.4 (d), 127.5 (d), 127.9 (d), 128.3 (d), 129.2 (d), 129.5 (d), 129.7 (s), 135.1 (s), 141.9 (s), 142.9 (s), 145.2 (s), 160.5 (s). Anal. Calcd for $C_{27}H_{21}NS$: C, 82.84; H, 5.41; N, 3.58. Found: C, 82.63; H, 5.36; N, 3.53.

4,4-Diphenyl-2-*p*-tolyl-3,1-benzoxazine (15f): mp 180−181 °C; ^1H NMR δ 2.37 (3H, s), 6.70 (1H, br d, J = 7.3), 7.03−7.42 (15H, m), 8.10 (2H, br d, J = 7.8); ^{13}C NMR δ 21.5 (q), 86.0 (s), 124.8 (d), 125.8 (d), 126.7 (d), 127.9 (d), 128.1 (d), 128.2 (d), 128.9 (d), 129.1 (d), 129.9 (d), 129.9 (s), 140.0 (s), 141.8 (s), 142.9 (s), 156.9 (s). Anal. Calcd for $C_{27}H_{21}NO$: C, 86.37; H, 5.64; N, 3.73. Found: C, 86.09; H, 5.88; N, 3.65.

1-Phenyl-1-[2-(*N*-*p*-thiotoluoylamino)phenyl]ethylene (16g): mp 127−128 °C; IR (KBr) 3350 (NH) cm^{-1}; ^1H NMR δ 2.30 (3H, s), 5.41 (1H, d, J = 1.0), 5.83 (1H, d, J = 1.0), 6.91−7.61 (13H, m), 8.70 (1H, br s); ^{13}C NMR δ 21.2 (q), 117.6 (t), 125.1 (d), 126.5 (d), 127.0 (d), 128.2 (d), 128.8 (d), 128.9 (d), 130.9 (d), 135.8 (s), 136.5 (s), 139.1 (s), 139.8 (s), 141.4 (s), 146.0 (s), 197.2 (s). Anal. Calcd for $C_{22}H_{19}NS$: C, 80.20; H, 5.81; N, 4.22. Found: C, 80.36; H, 5.74; N, 4.22.

1-Phenyl-1-[2-(*N*-*p*-toluoylamino)phenyl]ethylene (17g): mp 81−82 °C; IR (KBr) 3430 (NH), 1670 (CO), 1615 (C=C) cm^{-1}; ^1H NMR δ 2.26 (s), 5.35 (1H, d, J = 1.0), 5.83 (1H, d, J = 1.0), 6.97−7.62 (12H, m), 7.79 (1H, br s), 8.49 (1H, dd, J = 1.0, 8.3); ^{13}C NMR δ 21.1 (q), 117.4 (t), 120.8 (d), 123.4 (d), 126.4 (d), 128.5 (d), 128.7 (d), 128.8 (d), 130.3 (d), 131.4 (s), 131.7 (s), 135.3 (s), 138.7 (s), 141.7 (s), 146.2 (s), 164.6 (s). Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.46; H, 6.16; N, 4.49.

α-Phenyl-α-[4-(*N*-*p*-thiotoluoylamino)phenyl]-methanethiol (19): mp 77−78 °C; IR (KBr) 3400 (NH), 2540 (SH) cm^{-1}; ^1H NMR δ 2.28 (1H, d, J = 4.9), 2.36 (3H, s), 5.42 (1H, d, J = 4.9), 7.12−7.45 (10H, m), 7.52−7.78 (3H, m), 9.00 (1H, br s); ^{13}C NMR δ 21.4 (q), 47.3 (d), 123.5 (d), 126.8 (d), 127.3 (d), 127.7 (d), 128.3 (d), 128.6 (d), 129.1 (d), 137.9 (s), 140.1 (s), 142.9 (s), 198.0 (s). Anal. Calcd for $C_{21}H_{19}NS_2$: C, 72.16; H, 5.48; N, 4.01. Found: C, 71.97; H, 5.45; N, 4.05.

α-Phenyl-α-[4-(*N*-*p*-toluoylamino)phenyl]methanethiol (20): mp 130−132 °C; IR (KBr) 3350 (NH), 1640 (CO) cm^{-1}; ^1H NMR δ 2.25 (1H, d, J = 4.9), 2.38 (3H, s), 5.41 (1H, d, J = 4.9), 7.10−7.77 (13H, m), 7.98 (1H, br s); ^{13}C NMR δ 21.4 (q), 47.3 (d), 120.2 (d), 127.0 (d), 127.1 (d), 128.4 (d), 128.5 (d), 129.3 (d), 131.9 (s), 137.0 (s), 139.3 (s), 142.3 (s), 143.3 (s), 165.7 (s). Anal. Calcd for $C_{21}H_{19}NOS$: C, 75.64; H, 5.74; N, 4.20. Found: C, 75.32; H, 5.65; N, 4.07.

α-[2-[*N*-(Ethoxycarbonyl)amino]phenyl]-α-phenylmethanethiol (22a): bp 200 °C (3 mmHg); IR (film) 3320 (NH), 2550 (SH), 1720 (CO_2) cm^{-1}; ^1H NMR δ 1.27 (3H, t, J = 7.3), 2.26 (1H, d, J = 5.4), 4.18 (2H, q, J = 7.3 Hz), 5.53 (1H, d, J = 5.4), 6.97−7.46 (8H, m), 7.71 (1H, br d); ^{13}C NMR δ 14.5 (q), 43.7 (d), 61.3 (t), 124.1 (d), 124.8 (d), 127.4 (d), 128.0 (d), 128.2 (d), 128.6 (d), 131.2 (s), 135.0 (s), 141.1 (s), 154.2 (s). Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 67.05; H, 5.71; N, 4.95.

1-[2-[*N*-(Ethoxycarbonyl)amino]phenyl]ethane-1-thiol (22b): bp 165 °C (3 mmHg); IR (film) 3320 (NH), 2550 (SH), 1700 (CO_2) cm^{-1}; ^1H NMR δ 1.32 (3H, t, J = 7.3), 1.73 (3H, d, J = 6.8), 2.01 (1H, d, J = 5.9), 4.23 (2H, q, J = 7.3), 4.12−4.44 (1H, m), 7.01−7.39 (3H, m), 7.69 (1H, dd, J = 1.0, 8.3); ^{13}C NMR δ 14.5 (q), 24.3 (q), 34.1 (d), 61.3 (t), 123.9 (d), 124.9 (d), 125.8 (d), 127.9 (d), 134.9 (s), 135.4 (s), 154.2 (s). Anal. Calcd for $C_{11}H_{15}NO_2S$: C, 58.64; H, 6.71; N, 6.22. Found: C, 58.69; H, 6.58; N, 6.19.

4-Methyl-3,1-benzothiazin-2-one (23b): mp 159−161 °C; IR (KBr) 3180 (NH), 1620 (CO) cm^{-1}; ^1H NMR δ 1.76 (1H, d, J = 6.8), 5.55 (1H, q, J = 6.8), 6.98−7.40 (4H, m), 10.69 (1H, br s); ^{13}C NMR δ 19.9 (q), 77.2 (d), 114.0 (d), 122.7 (s), 123.8 (d), 125.3 (d), 129.3 (d), 132.3 (s), 185.0 (s). Anal. Calcd for C_9H_9NOS: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.31; H, 5.10; N, 7.78.

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