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A Facile Synthesis of 2-Cyano-4H-3,1-benzothiazines and 2-Cyano-4H-3,1-benzoxazines

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ABSTRACT

*Treatment of the hydrochloride salts of 4-chloro-5-(2-halomethylaryl-imino)-5H-1,2,3-dithiazoles (**2**) with sodium cyanoborohydride in THF at room temperature gave 2-cyano-4H-3,1-benzothiazines (**1**) in good to moderate yields. 2-Cyano-4H-3,1-benzoxazines (**4**) were obtained in good to moderate yields by refluxing of 4-chloro-5-(2-hydroxymethylarylimino)-5H-1,2,3-dithiazoles (**3**) with sodium hydride in THF. Intermolecular reaction of 5-(p-tolylimino)-5H-1,2,3-dithiazole (**12**) with benzyl alcohol under the same conditions gave the acyclic analog of **4**.*

INTRODUCTION

There are basically three different ways to prepare 2-substituted 4H-3,1-benzothiazines reported in the literature. First, reactions of o-aminobenzyl alcohols with carbon disulfide in ethanol in the presence of base give 2-mercapto-4H-3,1-benzothiazines [1,2]. However, the reactions of the same alcohols with thiourea at 180°C give 2-amino-4H-3,1-benzothiazines [2–4]. Second, heating of o-aminobenzyl bromide hydrobromide with ethyl thiocarbamate at 60°C gives 2-carbethoxy-4H-3,1-benzothiazine [3]. Third, o-(α-substituted methyl)phenylisothiocyanates react with certain nucleophiles, such as amines and phenoxide ions, to give 2-amino- and 2-phenoxy-4H-3,1-benzothiazines [5,6]. Other 2-substituted 4H-3,1-benzothiazines have been synthesized, mostly by using either 2-mercapto- or 2-amino-4H-3,1-benzothiazines as a starting material [1,3].

In spite of description of a variety of 2-substituted 4H-3,1-benzothiazines in the literature, there is only one report describing the synthesis of 2-cyano-4H-3,1-benzothiazine (**1h**). The compound **1h** was synthesized by dehydration of 2-carbamoyl-4H-3,1-benzothiazine, which, in turn, was prepared in two steps starting from *o*-aminobenzyl bromide hydrobromide [3].

In continuation of our efforts to develop the synthetic utility of 5-arylimino-4-chloro-5H-1,2,3-dithiazoles, [7] we have found that 4-chloro-5-(2-halomethylarylimino)-5H-1,2,3-dithiazoles (**2**) and 4-chloro-5-(2-hydroxymethylarylimino)-5H-1,2,3-dithiazoles (**3**) are promising precursors for 2-cyano-4H-3,1-benzothiazines (**1**) and 2-cyano-4H-3,1-benzoxazines (**4**), respectively. The details are described herein.

RESULTS AND DISCUSSION

The compounds **2** are readily synthesized by the reaction of 1-amino-2-halomethylarenes with 4,5-dichloro-1,2,3-dithiazolium chloride (Appel's salt) in methylene chloride at room temperature [8]. Treatment of the hydrochloride salts of **2**, generated *in situ* by bubbling hydrogen chloride gas into the solution of **2** in THF at room temperature, with a slight molar excess of sodium cyanoborohydride gave **1** in good to moderate yields along with 2-thiocarbamoyl-4H-3,1-benzothiazines (**5**). The yields of **1** and **5** are summarized in Table 1.

All of the compounds (**1a–1g**) are new ones except for **1h**. The mechanism of formation of **1** is proposed, as shown in Scheme 1.

Dedicated to Prof. James Cullen Martin on the occasion of his 65th birthday.

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TABLE 1 Yields of 2-Cyano-4H-3,1-benzothiazines (**1**) and 2-Thiocarbamoyl-4H-3,1-benzothiazines (**5**)

	2			Yield[a] (%)	
	X	R^1	R^2	1	5
(a)	Cl	H	Cl	64	8
(b)	Cl	H	Me	71	7
(c)	Cl	Me	H	68	
(d)	Cl	Me	Cl	54	
(e)	Cl	Me	Me	63	13
(f)	Cl	Ph	H	44	9
(g)	Cl	Ph	Cl	48	
(h)	Br	H	H	71	

[a]Isolated yields by column chromatography.

Hydrochloride salts (**6**) deposited by bubbling of hydrogen chloride gas into **2** in THF are attacked by hydride ion to form ring-opened intermediates (**7**), which rapidly lose hydrogen chloride and sulfur to give cyanothioformamide derivatives (**8**), followed by intramolecular cyclizations, yielding compounds **1**. The assumption of the formation of compounds **8** as intermediates was supported by the isolation of N-(p-tolyl)- and N-(p-nitrophenyl)cyanothioformamide [9] by the same treatment of 4-chloro-5-(p-tolylimino)- and 4-chloro-5-(p-nitrophenylimino)-5H-1,2,3-dithiazole, respectively.

On the other hand, refluxing of 4-chloro-5-(2-hydroxymethylarylimino)-5H-1,2,3-dithiazoles (**3**) with sodium hydride in THF led to **4**, **1**, and 4H-3,1-benzoxazine-2-thiones (**9**). The yields of these products are given in Table 2.

Although there have been a few reports of the synthesis of 2-aryl-4H-3,1-benzoxazines [10,11] and

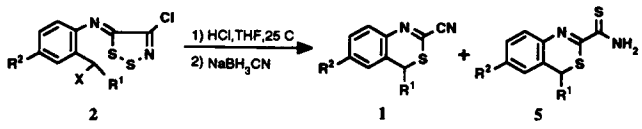
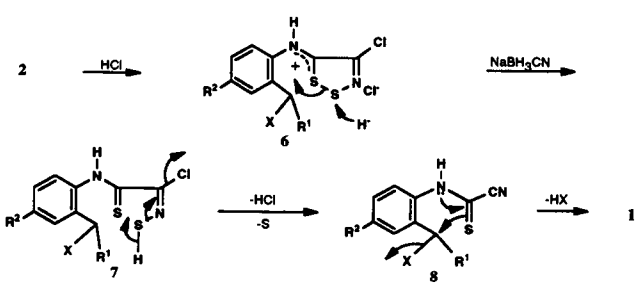


FIGURE 1



SCHEME 1

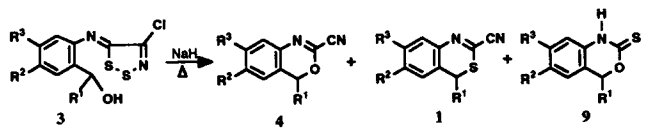


FIGURE 2

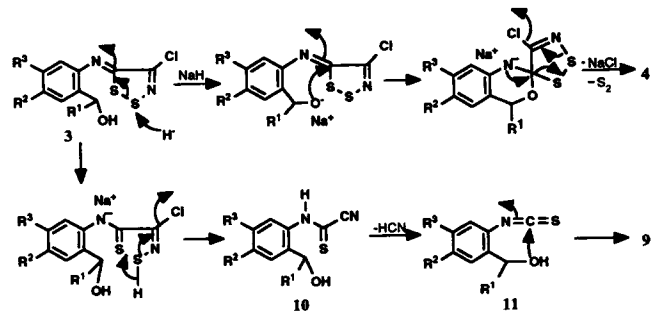
2-arylthio-4H-3,1-benzoxazines [1], no 2-cyano analogs, to our knowledge, have been reported.

The formation of compounds **4** can be rationalized by nucleophilic attack of alkoxide ion at the imino carbon, followed by extrusion of sulfur, as shown in Scheme 2. This is analogous to the mechanism of formation of 2-cyanobenzoxazole from 5-(o-hydroxyphenylimino)-5H-1,2,3-dithiazole [12]. On the other hand, nucleophilic attack of a hydride ion at the sulfur atom at the 2-position of a dithiazole ring, followed by ring opening, give an N-(2-hydroxymethylaryl)cyanothioformamide (**10**), which then loses hydrogen cyanide, yielding a 2-hydroxymethylarylisothiocyanate (**11**). Intramolecular cyclization of the isothiocyanate (**11**) gives **9**. It has been demonstrated that sodium hydride acts as the anion source in aprotic solvents [13,14]. However, the mechanism of formation of **1** from **3** is uncertain.

TABLE 2 Yields of 2-Cyano-4H-3,1-benzoxazines (**4**), 2-Cyano-4H-3,1-benzothiazines (**1**), and 4H-3,1-Benzoxazine-2-thiones (**9**)

	3			Yield[a] (%)		
	R^1	R^2	R^3	4	1	9
(a)	H	Cl	H	66	8	
(b)	H	Me	H	71	10	
(c)	Me	H	H	71	6	
(d)	Me	Cl	H	45	6	34
(e)	Me	Me	H	37	6	49
(f)	Ph	H	H	35	5	
(g)	Ph	Cl	H	54	8	
(i)	Ph	H	Me	29	6	

[a]Yields of **4** and **1** by column chromatography (a)–(c) and HPLC (d)–(i). Yields of **9** by column chromatography.



SCHEME 2

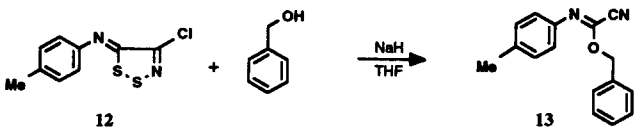


FIGURE 3

The intermolecular reaction of 4-chloro-5-(p-tolylimino)-5H-1,2,3-dithiazole (**12**) with benzyl alcohol under the same conditions gave only a 17% yield of N-(p-tolylimino)cyanomethyl benzyl ether (**13**), which was the acyclic analog of **4**.

EXPERIMENTAL

Sodium cyanoborohydride and sodium hydride were purchased from Aldrich Chemical Co., Inc. 1-(2-Aminophenyl)ethanol was prepared by reduction of o-aminoacetophenone with $NaBH_4$ [15]. 2-Amino-5-methylbenzaldehyde was prepared by oxidation of 2-amino-5-methylbenzyl alcohol with MnO_2 [16]. 2-Amino-4-methylbenzhydrol and 2-amino-5-chlorobenzhydrol were prepared by reduction of the corresponding benzophenone derivatives with $NaBH_4$ [15]. 1-(2-Amino-5-chlorophenyl)ethanol was prepared by a Grignard reaction of 2-amino-5-chlorobenzaldehyde. 4,5-Dichloro-1,2,3-dithiazolium chloride (Appel's salt) was prepared according to the literature method [8]. Column chromatography was performed using silica gel (Merck 7347, 70–230 mesh ASTM). The ^1H NMR spectra were measured on a Varian EM 360A NMR spectrometer, using tetramethylsilane as an internal standard unless otherwise specified, or a Brucker 80 MHz spectrometer. Infrared (IR) spectra were obtained using a Perkin-Elmer Model 283 spectrometer. HPLC was performed on a Waters Model 510 instrument. Mass spectra (MS) were obtained by use of a VG 12–250 mass spectrometer at 70 eV. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were obtained from the Korea Basic Science Center.

4-Chloro-5-(o-tolylimino)-5H-1,2,3-dithiazole [8]

The reaction of o-toluidine with Appel's salt [8] gave the title compound (70%): yellow crystals: mp 84–86°C (EtOH): ^1H NMR ($CDCl_3$) δ 2.31 (s, 3H, Me). 7.10–7.60 (m, 4H, ArH): IR (KBr) 1595, 1588, 1563, 1480, 1373, 1226, 1192, 1140, 1110, 1050, 863, 848, 794, 755, 718, 664 cm^{-1}. Anal. calcd for $C_9H_7ClN_2S_2$: C, 44.53; H, 2.91; N, 11.54; S, 26.42. Found: C, 44.65; H, 2.97; N, 11.43; S, 26.40.

5-(2-Bromomethylphenylimino)-4-chloro-5H-1,2,3-dithiazole (**2h**)

A solution of 4-chloro-5-(o-tolylimino)-5H-1,2,3-dithiazole (1.84 g, 7.58 mmol) and N-bromosuccinimide (1.35 g, 7.58 mmol) in carbon tetrachloride (60 mL) was irradiated with a 60 W tungsten lamp for 6 hours at reflux. The mixture was cooled to room temperature, followed by addition of water (100 mL), the mixture then being extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was dried ($MgSO_4$). Removal of the solvent *in vacuo* was followed by chromatography of the residue on silica gel (1.5 × 10 cm). Elution with a mixture of petroleum ether and CH_2Cl_2 (v:v, 9:1, 100 mL) gave 4-chloro-5-(o-tolylimino)-5H-1,2,3-dithiazole (527 mg, 2.17 mmol). After removal of unknown compounds, **2h** (803 mg, 2.50 mmol, 33%) was eluted using the same solvent mixture (300 mL). **2h**: red crystals: mp 92–93°C (petroleum ether-acetone): ^1H NMR ($CDCl_3$) δ 4.75 (s, 2H, CH_2). 7.20–8.00 (m, 4H, ArH): IR (KBr) 1591, 1580, 1560, 1550, 1478, 1420, 1220, 1194, 1148, 1130, 898, 870, 848, 800, 760, 665 cm^{-1}; MS *m/e* 322 (M^+ +2), 320 (M^+), 241 (M^+ −Br).

4-Chloro-5-(4-chloro-2-hydroxymethylphenylimino)-5H-1,2,3-dithiazole (**3a**)

The reaction of 4-chloro-2-hydroxymethylaniline with Appel's salt [8] gave **3a** (47%): yellow crystals: mp 108–112°C (petroleum ether-CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 4.30 (s, 1H, OH), 4.70 (s, 2H, CH_2), 7.20–8.00 (m, 3H, ArH): IR (KBr) 3240, 1590, 1180, 1148, 1090, 1035, 860, 810, 770, 681 cm^{-1}. Anal. calcd for $C_9H_6ClN_2OS_2$: C, 36.87; H, 2.06; N, 9.55; S, 21.87. Found: C, 36.92; H, 2.10; N, 9.43; S, 21.90.

4-Chloro-5-(4-chloro-2-chloromethylphenylimino)-5H-1,2,3-dithiazole (**2a**)

To a solution of **3a** (898 mg, 3.06 mmol) in CH_2Cl_2 (50 mL) was added a solution of $SOCl_2$ (0.25 mL, 3.4 mmol) in CH_2Cl_2 (5 mL), the new solution then being stirred for 10 minutes at room temperature, followed by addition of pyridine (0.28 mL, 3.5 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred for an additional 10 minutes and filtered. The filtrate was washed with water (3 × 10 mL) and dried ($MgSO_4$). Evaporation of the solvent gave **2a** (954 mg, 3.06 mmol, 100%): a red solid: mp 139–141°C (EtOH): ^1H NMR ($CDCl_3$) δ 4.73 (s, 2H, CH_2), 7.25–7.80 (m, 3H, ArH): IR (KBr) 1590, 1470, 1430, 1272, 1266, 1194, 1145, 1120, 1086, 860, 820, 768, 687, 668 cm^{-1}. Anal. calcd for $C_9H_5Cl_3N_2S_2$: C, 34.69; H, 1.62; N, 8.99; S, 20.58. Found: C, 34.82; H, 1.64; N, 8.89; S, 20.38.

4-Chloro-5-(2-hydroxymethyl-4-methylphenylimino)-5H-1,2,3-dithiazole (**3b**)

The reaction of 2-hydroxymethyl-4-methylaniline with Appel's salt [8] gave **3b** (53%): a yellow solid: mp 117–119°C (EtOH): ^1H NMR ($CDCl_3$) δ 2.45 (s,

3H, Me), 4.36 (s, 1H, OH), 4.73 (s, 2H, CH_2). 7.25–7.70 (m, 3H, ArH): IR (KBr) 3240, 1608, 1588, 1480, 1230, 1140, 1110, 1040, 1015, 860, 798, 772, 660 cm^{-1}. Anal. calcd for $C_{10}H_9ClN_2OS_2$: C, 44.03; H, 3.33; N, 10.27; S, 23.51. Found: C, 44.14; H, 3.35; N, 10.22; S, 23.44.

4-Chloro-5-(2-chloromethyl-4-methylphenylimino)-5H-1,2,3-dithiazole (**2b**)

By use of **3b** (2.040 g, 7.479 mmol), $SOCl_2$ (0.55 mL, 7.6 mmol), and pyridine (0.60 mL, 7.4 mmol) in CH_2Cl_2, as described in the synthesis of **2a**, these was obtained **2b** (2.168 g, 7.445 mmol, 100%): a red solid; mp 117–118°C (EtOH): ^1H NMR ($CDCl_3$) δ 2.45 (s, 3H, Me), 4.80 (s, 2H, CH_2), 7.30–7.66 (m, 3H, ArH): IR (KBr) 1560, 1485, 1265, 1225, 1160, 1140, 860, 820, 770, 730, 668 cm^{-1}. Anal. calcd for $C_{10}H_8Cl_2N_2S_2$: C, 41.25; H, 2.77; N, 9.62; S, 22.02. Found: C, 41.32; H, 2.81; N, 9.53; S, 21.95.

4-Chloro-5-[2-(1-hydroxyethyl)phenylimino]-5H-1,2,3-dithiazole (**3c**)

The reaction of 1-(2-aminophenyl)ethanol with Appel's salt [8] gave **3c** (98%): a yellow solid; mp 83.5–84.5°C (EtOH): ^1H NMR ($CDCl_3$) δ 1.50 (d, 3H, J = 7 Hz, Me), 3.83 (s, 1H, OH), 5.14 (q, 1H, J = 7 Hz, CH), 7.25–7.80 (m, 4H, ArH): IR (KBr) 3310, 1580, 1563, 1478, 1440, 1410, 1238, 1215, 1195, 1154, 1076, 1000, 885, 865, 788, 763, 738 cm^{-1}. Anal. calcd for $C_{10}H_9ClN_2OS_2$: C, 44.03; H, 3.33; N, 10.27; S, 23.51. Found: C, 44.10; H, 3.36; N, 10.16; S, 23.46.

4-Chloro-5-[2-(1-chloroethyl)phenylimino]-5H-1,2,3-dithiazole (**2c**)

By use of **3c** (1.708 g, 6.262 mmol), $SOCl_2$ (0.46 mL, 6.3 mmol), and pyridine (0.51 mL, 6.3 mmol) in CH_2Cl_2, as described in the synthesis of **2a**, there was obtained **2c** (1.614 g, 5.542 mmol, 89%): a brown oil: ^1H NMR ($CDCl_3$) δ 1.86 (d, 3H, J = 7 Hz, Me), 5.65 (q, 1H, J = 7 Hz, CH), 7.15–7.95 (m, 4H, ArH): IR (neat) 1588, 1570, 1480, 1225, 1148, 880, 853, 760, 663 cm^{-1}. Anal. calcd for $C_{10}H_8Cl_2N_2S_2$: C, 41.25; H, 2.77; N, 9.62; S, 22.02. Found: C, 41.37; H, 2.80; N, 9.56; S, 21.95.

4-Chloro-5-[4-chloro-2-(1-hydroxyethyl)phenylimino]-5H-1,2,3-dithiazole (**3d**)

The reaction of 4-chloro-2-(1-hydroxyethyl)aniline with Appel's salt [8] gave **3d** (90%): a brown oil; ^1H NMR ($CDCl_3$) δ 1.44 (d, 3H, J = 7 Hz, Me), 3.40 (s, 1H, OH), 4.95 (q, 1H, J = 7 Hz, CH), 7.12 (s, 1H, ArH), 7.34 (s, 2H, ArH): IR (neat) 3370, 1590, 1465, 1147, 1100, 1072, 866, 808, 768, 680 cm^{-1}. Anal. calcd for $C_{10}H_8Cl_2N_2OS_2$: C, 39.10; H, 2.62; N, 9.12; S, 20.87. Found: C, 39.18; H, 2.66; N, 9.06; S, 20.76.

4-Chloro-5-[4-chloro-2-(1-chloroethyl)phenylimino]-5H-1,2,3-dithiazole (**2d**)

By use of **3d** (1.25 g, 4.07 mmol), $SOCl_2$ (0.30 mL, 4.1 mmol), and pyridine (0.35 mL, 4.3 mmol) in CH_2Cl_2, as described in the synthesis of **2a**, there was obtained **2d** (1.20 g, 3.68 mmol, 90%): a brown oil; ^1H NMR ($CDCl_3$) δ 1.83 (d, 3H, J = 7 Hz, Me), 5.52 (q, 1H, J = 7 Hz, CH), 7.18 (d, 1H, J = 9 Hz, ArH), 7.44 (dd, 1H, J = 9, 3 Hz, ArH), 7.72 (d, 1H, J = 3 Hz, ArH); IR (neat) 1590, 1470, 1140, 1047, 860, 810, 763 cm^{-1}. Anal. calcd for $C_{10}H_7Cl_3N_2S_2$: C, 36.88; H, 2.17; N, 8.60; S, 19.69. Found: C, 36.96; H, 2.21; N, 8.53; S, 19.54.

4-Chloro-5-[2-(1-hydroxyethyl)-4-methylphenylimino]-5H-1,2,3-dithiazole (**3e**)

The reaction of o-(1-hydroxyethyl)-p-toluidine with Appel's salt [8] gave **3e** (96%): a brown oil; ^1H NMR ($CDCl_3$) δ 1.52 (d, 3H, J = 7 Hz, Me), 2.45 (s, 3H, Me), 3.83 (s, 1H, OH), 5.15 (q, 1H, J = 7 Hz, CH), 7.20–7.56 (m, 3H, ArH): IR (neat) 3370, 1580, 1482, 1217, 1150, 1123, 1075, 865, 825, 770 cm^{-1}. Anal. calcd for $C_{11}H_{11}ClN_2OS_2$: C, 46.07; H, 3.87; N, 9.77; S, 22.36. Found: C, 46.14; H, 3.91; N, 9.72; S, 22.27.

4-Chloro-5-[2-(1-chloroethyl)-4-methylphenylimino]-5H-1,2,3-dithiazole (**2e**)

By use of **3e** (1.097 g, 3.825 mmol), $SOCl_2$ (0.28 mL, 3.9 mmol), and pyridine (0.31 mL, 3.8 mmol) in CH_2Cl_2, as described in the synthesis of **2a**, there was obtained **2e** (1.024 g, 3.355 mmol, 88%): a brown oil: ^1H NMR ($CDCl_3$) δ 1.86 (d, 3H, J = 7 Hz, Me), 2.45 (s, 3H, Me), 5.72 (q, 1H, J = 7 Hz, CH), 7.15–7.76 (m, 3H, ArH): IR (neat) 1582, 1490, 1232, 1148, 865, 770 cm^{-1}. Anal. calcd for $C_{11}H_{10}Cl_2N_2S_2$: C, 43.28; H, 3.30; N, 9.18; S, 21.01. Found: C, 43.31; H, 3.32; N, 9.15; S, 20.95.

4-Chloro-5-[2-(1-hydroxy-1-phenylmethyl)phenylimino]-5H-1,2,3-dithiazole (**3f**)

The reaction of 2-aminobenzhydrol with Appel's salt [8] gave **3f** (76%): a yellow solid: mp 83.5–84.5°C (n-hexane); ^1H NMR ($CDCl_3$) δ 4.07 (s, 1H, OH), 6.00 (s, 1H, CH), 7.05–7.80 (m, 9H, ArH); IR (neat) 3390, 1585, 1569, 1475, 1448, 1148, 1020, 880, 860, 761, 735, 700, 668 cm^{-1}. Anal. calcd for $C_{15}H_{11}ClN_2OS_2$: C, 53.81; H, 3.31; N, 8.37; S, 19.15. Found: C, 53.90; H, 3.35; N, 8.29; S, 19.11.

4-Chloro-5-[2-(1-chloro-1-phenylmethyl)phenylimino]-5H-1,2,3-dithiazole (**2f**)

By use of **3f** (1.35 g, 4.03 mmol), $SOCl_2$ (0.32 mL, 4.4 mmol), and pyridine (0.35 mL, 4.3 mmol) in

CH_2Cl_2, as described in the synthesis of **2a**, there was obtained **2f** (605 mg, 1.71 mmol, 42%): a brown oil; ^1H NMR ($CDCl_3$) δ 6.56 (s, 1H, CH), 6.95–8.00 (m, 9H, ArH); IR (neat) 1584, 1568, 1475, 1445, 1145, 880, 858, 760, 745, 698, 666 cm^{-1}. Anal. calcd for $C_{15}H_{10}Cl_2N_2S_2$: C, 51.00; H, 2.85; N, 7.93; S, 18.15. Found: C, 51.04; H, 2.89; N, 7.86; S, 18.07.

4-Chloro-5-[4-chloro-2-(1-hydroxy-1-phenylmethyl)phenylimino]-5H-1,2,3-dithiazole (**3g**)

The reaction of 2-amino-5-chlorobenzhydrol with Appel's salt [8] gave **3g** (72%): a yellow solid; mp 32–34°C (n-hexane-CH_2Cl_2): ^1H NMR ($CDCl_3$) δ 3.22 (s, 1H, OH), 5.95 (s, 1H, CH), 7.00–7.55 (m, 7H, ArH), 7.67 (d, 1H, J = 2 Hz, ArH); IR (neat) 3380, 1590, 1468, 1150, 1090, 1022, 870, 782, 740, 702 cm^{-1}. Anal. calcd for $C_{15}H_{10}Cl_2N_2OS_2$: C, 48.79; H, 2.73; N, 7.59; S, 17.39. Found: C, 48.88; H, 2.79; N, 7.52; S, 17.33.

4-Chloro-5-[4-chloro-2-(1-chloro-1-phenylmethyl)phenylimino]-5H-1,2,3-dithiazole (**2g**)

By use of **3g** (802 mg, 2.17 mmol), $SOCl_2$ (0.16 mL, 2.2 mmol), and pyridine (0.18 mL, 2.2 mmol) in CH_2Cl_2, as described in the synthesis of **2a**, there was obtained **2g** (705 mg, 1.82 mmol, 84%): a red solid; mp 107–108°C (n-hexane-CH_2Cl_2): ^1H NMR ($CDCl_3$) δ 6.50 (s, 1H, CH), 6.95–7.55 (m, 7H, ArH), 7.70 (d, 1H, J = 2 Hz, ArH); IR (neat) 1592, 1468, 1145, 870, 780, 730, 700 cm^{-1}. Anal. calcd for $C_{15}H_9Cl_3N_2S_2$: C, 46.47; H, 2.34; N, 7.22; S, 16.54. Found: C, 46.52; H, 2.35; N, 7.19; S, 16.41.

4-Chloro-5-[2-(1-hydroxy-1-phenylmethyl)-5-methylphenylimino]-5H-1,2,3-dithiazole (**3i**)

The reaction of 2-amino-4-methylbenzhydrol with Appel's salt [8] gave **3i** (78%): a yellow solid; mp 102–104°C (n-hexane-CH_2Cl_2): ^1H NMR ($CDCl_3$) δ 2.37 (s, 3H, Me), 4.01 (d, 1H, J = 7 Hz, OH), 5.96 (d, 1H, J = 7 Hz, CH), 6.90–7.70 (m, 8H, ArH): IR (neat) 3340, 1588, 1488, 1452, 1039, 904, 870, 765, 750, 720, 700 cm^{-1}. Anal. calcd for $C_{16}H_{13}ClN_2OS_2$: C, 55.09; H, 3.76; N, 8.03; S, 18.38. Found: C, 55.17; H, 3.80; N, 8.01; S, 18.25.

General Procedure for the Synthesis of 2-Cyano-4H-3,1-benzothiazines (**1**)

Dry hydrogen chloride gas was bubbled into a solution of an appropriate amount of **2** in dry tetrahydrofuran (20 mL) until the hydrochloride salt of 2 precipitated. The mixture was stirred for an additional 10 minutes followed by addition of a solution of $NaBH_3CN$ in dry THF (10 mL). After the hydrochloride salt of **2** had disappeared, the mixture was stirred for an additional 10 minutes followed by addition of water (20 mL). Neutralization with saturated $NaHCO_3$, followed by removal of tetrahydrofuran *in vacuo*, gave a residue in aqueous solution, which was extracted with CH_2Cl_2 (3 × 20 mL). The combined extract was dried over $MgSO_4$. Removal of the solvent was followed by chromatography on silica gel (1.5 × 10 cm).

6-Chloro-2-cyano-4H-3,1-benzothiazine (**1a**)

From the reaction of hydrochloride salt of **2a** (514 mg, 1.65 mmol) with $NaBH_3CN$ (130 mg, 2.07 mmol) in THF were obtained sulfur (45 mg, 0.18 mmol) and **1a** (220 mg, 1.05 mmol, 64%) by elution with petroleum ether (100 mL) and a mixture of petroleum ether and CH_2Cl_2 (v:v, 2:3, 100 mL), respectively. **1a**: pale yellow crystals; mp 178–180°C (n-hexane-$CHCl_3$); ^1H NMR ($CDCl_3$) δ 4.11 (s, 2H, CH_2), 7.20–7.65 (m, 3H, ArH); IR (KBr) 2230, 1590, 1560, 1530, 1472, 1415, 1402, 1290, 1120, 1075, 909, 860, 840, 808, 760, 680 cm^{-1}; MS *m/e* 208 (M^+). Anal. calcd for $C_9H_5ClN_2S$: C, 51.81; H, 2.42; N, 13.43; S, 15.36. Found: C, 51.55; H, 2.51; N, 13.54; S, 15.45. Finally, elution with CH_2Cl_2 (60 mL) gave 6-chloro-2-thiocarbamoyl-4H-3,1-benzothiazine (**5a**) (31 mg, 0.13 mmol, 8%): yellow crystals: mp 180–182°C (n-hexane-$CHCl_3$); ^1H NMR ($CDCl_3$ + DMSO-d_6, 80 MHz) δ 3.90 (s, 2H, CH_2), 7.14–7.37 (m, 3H, ArH), 9.05 (s, 1H, NH), 9.60 (s, 1H, NH); IR (KBr) 3375, 3265, 1577, 1528, 1466, 1420, 1260, 1235, 1210, 1115, 1080, 1058, 874, 830, 780, 640 cm^{-1}; MS *m/e* 242 (M^+). Anal. calcd for $C_9H_7ClN_2S_2$: C, 44.53; H, 2.91; N, 11.54; S, 26.42. Found: C, 44.64; H, 2.97; N, 11.46; S, 26.45.

2-Cyano-6-methyl-4H-3,1-benzothiazine (**1b**)

From the reaction of the hydrochloride salt of **2b** (509 mg, 1.75 mmol) with $NaBH_3CN$ (135 mg, 2.15 mmol) in THF, there were obtained sulfur (29 mg, 0.11 mmol) and **1b** (236 mg, 1.25 mmol, 71%) by elution with petroleum ether (60 mL) and a mixture of petroleum ether and CH_2Cl_2 (v:v, 1:1, 150 mL), respectively. **1b**: pale yellow crystals: mp 105–106°C (n-hexane): ^1H NMR ($CDCl_3$) δ 2.43 (s, 3H, Me), 4.10 (s, 2H, CH_2), 7.05–7.63 (m, 3H, ArH): IR (KBr) 2222, 1603, 1570, 1539, 1532, 1300, 1160, 1124, 1080, 840, 815, 761 cm^{-1}; MS *m/e* 188 (M^+). Anal. calcd for $C_{10}H_8N_2S$: C, 63.80; H, 4.28; N, 14.88; S, 17.03. Found: C, 63.71; H, 4.25; N, 14.95; S, 17.09. Elution with CH_2Cl_2 (60 mL) gave 6-methyl-2-thiocarbamoyl-4H-3,1-benzothiazine (**5b**) (29 mg, 0.13 mmol, 7%): yellow crystals: mp 152–153°C (n-hexane-$CHCl_3$): ^1H NMR ($CDCl_3$ + DMSO-d_6, 80 MHz) δ 2.37 (s, 3H, Me), 3.88 (s, 2H, CH_2), 6.90–7.34 (m, 3H, ArH), 9.06 (s, 1H, NH), 9.51 (s, 1H, NH): IR (KBr) 3345, 3225, 1588, 1530, 1272, 1210, 1120, 1062, 890, 830, 783, 678, 652 cm^{-1}; MS *m/e* 222 (M^+). Anal. calcd for $C_{10}H_{10}N_2S_2$: C, 54.03; H, 4.53; N,

12.60; S, 28.84. Found: C, 53.91; H, 4.55; N, 12.65; S, 28.89.

2-Cyano-4-methyl-4H-3,1-benzothiazine (**1c**)

From the reaction of the hydrochloride salt of **2c** (570 mg, 1.96 mmol) with $NaBH_3CN$ (170 mg, 2.71 mmol) in THF at 0°C, there were obtained sulfur (15 mg, 0.058 mmol) and **2c** (21 mg, 0.072 mmol, 4%) by elution with n-hexane (100 mL) and a mixture of n-hexane and CH_2Cl_2 (v:v, 3:1, 80 mL), respectively. Continuous elution with the same solvent mixture gave **1c** (250 mg, 1.33 mmol, 68%): white crystals; mp 40–42°C (n-hexane); ^1H NMR ($CDCl_3$) δ 1.53 (d, 3H, J = 7 Hz, Me), 4.27 (q, 1H, J = 7 Hz), 7.15–7.71 (m, 4H, ArH); IR (KBr) 2230, 1570, 1530, 1478, 1444, 1372, 1118, 1085, 968, 868, 770, 750 cm^{-1}; MS m/e 188 (M^+). Anal. calcd for $C_{10}H_8N_2S$: C, 63.80; H, 4.28; N, 14.88; S, 17.03. Found: C, 63.75; H, 4.24; N, 14.85; S, 17.16.

6-Chloro-2-cyano-4-methyl-4H-3,1-benzothiazine (**1d**)

Hydrogen chloride gas was bubbled into a solution of **2d** (1.01 g, 3.10 mmol) in THF at 0°C. No precipitates were formed. After the solution had been stirred for 3 hours, $NaBH_3CN$ (260 mg, 4.14 mmol) in THF (10 mL) was added. From the reaction mixture were obtained sulfur (54 mg, 0.21 mmol) and **2d** (21 mg, 0.064 mmol, 2%) by the elution with petroleum ether (60 mL) and a mixture of petroleum ether and CH_2Cl_2 (v:v, 2:1, 60 mL), respectively. Elution with the same solvent mixture gave **1d** (375 mg, 1.68 mmol, 54%): white crystals: mp 134–136°C (n-hexane): ^1H NMR ($CDCl_3$) δ 1.57 (d, 3H, J = 7 Hz, Me), 4.31 (q, 1H, J = 7 Hz, CH), 7.30–7.80 (m, 3H, ArH); IR (KBr) 2235, 1590, 1525, 1470, 1450, 1408, 1375, 1289, 1262, 1236, 1129, 1090, 1065, 1042, 970, 888, 880, 848, 800, 750, 690, 670 cm^{-1}; MS m/e 222 (M^+). Anal. calcd for $C_{10}H_7ClN_2S$: C, 53.94; H, 3.17; N, 12.58; S, 14.40. Found: C, 53.71; H, 3.22; N, 12.49; S, 14.63.

2-Cyano-4,6-dimethyl-4H-3,1-benzothiazine (**1e**)

The hydrochloride salt of **2e** (830 mg, 2.72 mmol) was treated with $NaBH_3CN$ (210 mg, 3.34 mmol) in THF at 0°C with stirring for 30 minutes at room temperature and workup as before. From the reaction mixture were obtained sulfur (71 mg, 0.28 mmol) and **1e** (343 mg, 1.70 mmol, 63%) by elution with petroleum ether (80 mL) and a mixture of petroleum ether and CH_2Cl_2 (v:v, 1:2, 150 mL), respectively. **1e**: pale yellow crystals: mp 97–98°C (n-hexane-CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.55 (d, 3H, J = 7 Hz, Me), 2.47 (s, 3H, Me), 4.26 (q, 1H, J = 7 Hz, CH). 7.10–7.70 (m, 3H, ArH); IR (KBr) 2222, 1604, 1522, 1480, 1450, 1370, 1298, 1264, 1248, 1130, 1090, 1065, 1041, 972, 840, 819, 750, 668 cm^{-1}; MS m/e 202 (M^+). Anal. calcd for $C_{11}H_{10}N_2S$: C, 65.32; H, 4.98; N, 13.85; S, 15.85. Found: C, 65.05; H, 5.06; N, 13.94; S, 15.95. Elution with CH_2Cl_2 (40 mL) gave 4,6-dimethyl-2-thiocarbamoyl-4H-3,1-benzothiazine (**5e**) (86 mg, 0.36 mmol, 13%): yellow crystals; mp 149–151°C (petroleum ether-CH_2Cl_2); ^1H NMR ($CDCl_3$, 80 MHz) δ 1.43 (d, 3H, J = 7 Hz, Me), 2.39 (s, 3H, Me), 4.10 (q, 1H, J = 7 Hz, CH), 6.90–7.70 (m, 4H, ArH, NH), 8.99 (s, 1H, NH); IR (KBr) 3360, 3225, 1585, 1528, 1440, 1265, 1127, 1072, 1040, 890, 830, 782, 675, 645 cm^{-1}; MS m/e 236 (M^+). Anal. calcd for $C_{11}H_{12}N_2S_2$: C, 55.90; H, 5.12; N, 11.85; S, 27.13. Found: C, 56.05; H, 5.16; N, 11.74; S, 27.05.

2-Cyano-4-phenyl-4H-3,1-benzothiazine (**1f**)

From the reaction of the hydrochloride salt of **2f** (528 mg, 1.49 mmol) with $NaBH_3CN$ (135 mg, 2.15 mmol) in THF at 0°C, there were obtained sulfur (37 mg, 0.14 mmol) and **1f** (163 mg, 0.651 mmol, 44%) by the elution with petroleum ether (100 mL) and a mixture of petroleum ether and CH_2Cl_2 (v:v, 1:2, 70 mL), respectively. **1f**: a yellow solid; mp 94–95°C (n-hexane); ^1H NMR ($CDCl_3$) δ 5.50 (s, 1H, CH), 7.00–7.88 (m, 9H, ArH): IR (KBr) 2230, 1572, 1525, 1450, 1310, 1118, 1079, 778, 747, 722, 700, 678 cm^{-1}; MS m/e 250 (M^+). Anal. calcd for $C_{15}H_{10}N_2S$: C, 71.91; H, 4.03; N, 11.19; S, 12.81. Found: C, 72.05; H, 4.11; N, 11.15; S, 12.69. Next elution with CH_2Cl_2 (40 mL) gave 4-phenyl-2-thiocarbamoyl-4H-3,1-benzothiazine (**5f**) (40 mg, 0.14 mmol, 9%): a yellow crystal; mp 172–174°C (n-hexane-CH_2Cl_2); ^1H NMR ($CDCl_3$ + DMSO-d_6, 80 MHz) δ 5.36 (s, 1H, CH), 6.95–7.64 (m, 9H, ArH), 9.12 (s, 1H, NH), 9.70 (s, 1H, NH); IR (KBr) 3365, 3230, 1580, 1530, 1443, 1425, 1113, 1060, 910, 885, 769, 745, 720, 695, 674, 636, 610 cm^{-1}; MS m/e 284 (M^+). Anal. calcd for $C_{15}H_{12}N_2S_2$: C, 63.35; H, 4.25; N, 9.85; S, 22.55. Found: C, 63.51; H, 4.26; N, 9.78; S, 22.45.

6-Chloro-2-cyano-4-phenyl-4H-3,1-benzothiazine (**1g**)

From the reaction of the hydrochloride salt of **2g** (510 mg, 1.32 mmol) with $NaBH_3CN$ (120 mg, 1.91 mmol) in THF at 0°C, there were obtained sulfur (20 mg, 0.078 mmol) and **1g** (179 mg, 0.629 mmol, 48%) by elution with petroleum ether (100 mL) and a mixture of petroleum ether and CH_2Cl_2 (v:v, 1:1, 70 mL), respectively. **1g**: white crystals; mp 139–140°C (n-hexane-CH_2Cl_2): ^1H NMR ($CDCl_3$) δ 5.37 (s, 1H, CH), 6.95–7.63 (m, 8H, ArH); IR (KBr) 2225, 1590, 1523, 1490, 1469, 1452, 1208, 1122, 1090, 836, 740, 700, 680 cm^{-1}; MS m/e 284 (M^+). Anal. calcd for $C_{15}H_9ClN_2S$: C, 63.27; H, 3.19; N, 9.84; S, 11.26. Found: C, 63.51; H, 3.22; N, 9.50; S, 11.25.

2-Cyano-4H-3,1-benzothiazine (**1h**)

From the reaction of the hydrochloride salt of **2h** (300 mg, 0.933 mmol) with $NaBH_3CN$ (80 mg, 1.3 mmol) in THF, there were obtained sulfur (20 mg, 0.078 mmol) and **1h** (115 mg, 0.660 mmol, 71%) by elution with petroleum ether (60 mL) and a mixture of petroleum ether and CH_2Cl_2 (v:v, 1:1, 60 mL), respectively. **1h**: a pale yellow crystal: mp 82–83°C (n-hexane) (Ref. [3] 83–84°C); ^1H NMR ($CDCl_3$) δ 4.08 (s, 2H, CH_2), 7.10–7.70 (m, 4H, ArH), 4.08 (s, 2H, CH_2); IR(KBr) 2230, 1570, 1522, 1472, 1451, 1418, 1305, 1160, 1150, 1110, 1074, 862, 770, 750, 708 cm^{-1}; MS *m/e* 174 (M^+).

General Procedure for 2-Cyano-4H-3,1-benzoxazines (**4**)

To a solution of an appropriate amount of **3** in THF (15 mL) was added NaH, with subsequent refluxing for 90 minutes, followed by cooling to room temperature. Addition of water (10 mL) followed by removal of THF *in vacuo* gave an aqueous solution, which was extracted with CH_2Cl_2 (3 × 20 mL). The combined extract was dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel (1.5 × 10 cm). After removal of sulfur by use of petroleum ether, a mixture of **4** and **1** was eluted and pure **4** was obtained either by recrystallization or by HPLC techniques.

6-Chloro-2-cyano-4H-3,1-benzoxazine (**4a**)

From the reaction of **3a** (588 mg, 2.01 mmol) with NaH (60 mg, 2.5 mmol) in THF, there were obtained sulfur (83 mg, 0.32 mmol) and a mixture (290 mg) of **4a** (66%) and **1a** (8%, based on ^1H NMR analysis), recrystallized from MeOH to give **4a** (116 mg, 0.556 mmol): pale yellow: mp 158–160°C; ^1H NMR ($CDCl_3$) δ 5.46 (s, 2H, CH_2), 7.03–7.63 (m, 3H, ArH): IR (KBr) 2222, 1620, 1595, 1477, 1369, 1297, 1250, 1180, 1082, 1012, 884, 875, 846, 785 cm^{-1}; MS *m/e* 192 (M^+). Anal. calcd for $C_9H_5ClN_2O$: C, 56.13; H, 2.62; N, 14.54. Found: C, 56.45; H, 2.71; N, 14.45.

2-Cyano-6-methyl-4H-3,1-benzoxazine (**4b**)

From the reaction of **3b** (607 mg, 2.23 mmol) with NaH (78 mg, 3.3 mmol) in THF, there were obtained sulfur (104 mg, 0.405 mmol) and a mixture (314 mg) of **4b** (71%) and **1b** (10%, based on ^1H NMR analysis), recrystallized from n-hexane and $CHCl_3$ to give **4b** (202 mg, 1.17 mmol): pale yellow; mp 121–123°C; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3H, Me), 5.45 (s, 2H, CH_2), 6.83–7.34 (m, 3H, ArH); IR (KBr) 2220, 1628, 1597, 1490, 1460, 1370, 1274, 1230, 1200, 1140, 1021, 888, 848, 802, 746 cm^{-1}; MS *m/e* 172 (M^+). Anal. calcd for $C_{10}H_8N_2O$: C, 69.75; H, 4.68; N, 16.27. Found: C, 69.85; H, 4.66; N, 16.22.

2-Cyano-4-methyl-4H-3,1-benzoxazine (**4c**)

From the reaction of **3c** (540 mg, 1.98 mmol) with NaH (70 mg, 2.9 mmol) in THF, there were obtained sulfur (106 mg, 0.413 mmol) and a mixture (261 mg) of **4c** (71%) and **1c** (6%, based on ^1H NMR analysis), which was separated by HPLC to give **4c**: white; mp 31–32°C; ^1H NMR ($CDCl_3$) δ 1.68 (d, 3H, J = 7 Hz, Me), 5.70 (q, 1H, J = 7 Hz, CH), 6.98–7.63 (m, 4H, ArH); IR (KBr) 2241, 1620, 1600, 1482, 1446, 1350, 1240, 1192, 1058, 1030, 1010, 878, 770 cm^{-1}; MS *m/e* 172 (M^+). Anal. calcd for $C_{10}H_8N_2O$: C, 69.75; H, 4.68; N, 16.27. Found: C, 69.92; H, 4.65; N, 16.20.

6-Chloro-2-cyano-4-methyl-4H-3,1-benzoxazine (**4d**)

From the reaction of **3d** (876 mg, 2.85 mmol) with NaH (90 mg, 3.8 mmol) in THF, there were obtained sulfur (108 mg, 0.421 mmol) and a mixture (217 mg) of **4d** (45%) and **1d** (6%, based on HPLC analysis), which was separated by HPLC to give **4d**: white: mp 100–101°C; ^1H NMR ($CDCl_3$) δ 1.83 (d, 3H, J = 7 Hz, Me), 5.63 (q, 1H, J = 7 Hz, CH), 6.98–7.50 (m, 3H, ArH): IR (KBr) 2238, 1613, 1590, 1468, 1439, 1404, 1368, 1333, 1289, 1242, 1182, 1100, 1080, 1053, 1005, 892, 859, 828, 768 cm^{-1}: MS *m/e* 206 (M^+). Anal. calcd for $C_{10}H_7ClN_2O$: C, 58.13; H, 3.41; N, 13.56. Found: C, 58.20; H, 3.43; N, 13.40. Finally, elution with CH_2Cl_2 and EtOAc (v:v, 5:1, 40 mL) gave 6-chloro-4-methyl-4H-3,1-benzoxazine-2-thione (**9d**) (210 mg, 0.983 mmol, 34%): mp 193–194°C (petroleum ether-CH_2Cl_2); ^1H NMR ($CDCl_3$ + DMSO-d_6) δ 1.73 (d, 3H, J = 7 Hz, Me), 5.51 (q, 1H, J = 7 Hz, CH), 7.00–7.42 (m, 3H, ArH), 12.05 (s, 1H, NH); IR (neat) 3160, 1610, 1530–1508 (br), 1480, 1370, 1300, 1210, 1154, 1127, 1075, 1000, 930, 885, 868, 840, 823, 805, 724 cm^{-1}; MS *m/e* 213 (M^+). Anal. calcd for C_9H_8ClNOS: C, 50.59; H, 3.77; N, 6.55; S, 15.00. Found: C, 50.55; H, 3.78; N, 6.62; S, 14.91.

2-Cyano-4,6-dimethyl-4H-3,1-benzoxazine (**4e**)

From the reaction of **3e** (792 mg, 2.76 mmol) with NaH (65 mg, 2.7 mmol) in THF, there were obtained sulfur (73 mg, 0.28 mmol) and a mixture (261 mg) of **4e** (37%) and **1e** (6%, based on HPLC analysis), which was separated by HPLC to give **4e**: pale yellow: mp 59–61°C: ^1H NMR ($CDCl_3$) δ 1.67 (d, 3H, J = 7 Hz, Me), 2.41 (s, 3H, Me), 5.71 (q, 1H, J = 7 Hz, CH), 7.00 (s, 1H, ArH), 7.34 (s, 2H, ArH); IR (neat) 2240, 1625, 1598, 1490, 1445, 1348, 1260, 1230, 1210, 1100, 1060, 1018, 890, 862, 822 cm^{-1}; MS *m/e* 186 (M^+). Anal. calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 71.02; H, 5.42; N, 14.95. After **4e** and **1e** were eluted, further elution with ether (50 mL) gave 4,6-dimethyl-4H-3,1-benzoxazine-2-thione (**9e**) (259 mg, 1.34 mmol, 49%):

mp 180–183°C (petroleum ether-CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.81 (d, 3H, J = 7 Hz, Me), 2.42 (s, 3H, Me), 5.70 (q, 1H, J = 7 Hz, CH), 7.53–7.00 (m, 3H, ArH), 10.07 (s, 1H, NH); IR (neat) 3185, 1620, 1530, 1504, 1395, 1310, 1240, 1180, 1157, 1135, 1005, 940, 810, 733 cm^{-1}; MS *m/e* 193 (M^+), 178 (M^+-NH), 160 (M^+-SH), 149 (M^+-CS), 132 (M^+-CS-OH). Anal. calcd for $C_{10}H_{11}NOS$: C, 62.15; H, 5.74; N, 7.25; S, 16.59. Found: C, 62.27; H, 5.82; N, 7.17; S, 16.50.

2-Cyano-4-phenyl-4H-3,1-benzoxazine (**4f**)

A mixture of **3f** (950 mg, 2.84 mmol) and NaH (75 mg, 3.1 mmol) in THF was refluxed for 2 hours. After removal of sulfur (91 mg, 0.35 mmol), elution with petroleum ether and CH_2Cl_2 (v:v, 1:3, 80 mL) gave a mixture (271 mg) of **4f** (35%) and **1f** (5%, based on HPLC analysis), which was separated by HPLC to give **4f**: white; mp 31–32°C; ^1H NMR ($CDCl_3$) δ 6.54 (s, 1H, CH), 6.78–7.72 (m, 9H, ArH); IR (KBr) 2247, 1632, 1598, 1485, 1458, 1330, 1304, 1236, 1228, 1200, 1180, 985, 910, 772, 708, 610 cm^{-1}: MS *m/e* 234 (M^+). Anal. calcd for $C_{15}H_{10}N_2O$: C, 76.91; H, 4.30; N, 11.96. Found: C, 77.05; H, 4.35; N, 11.80.

6-Chloro-2-cyano-4-phenyl-4H-3,1-benzoxazine (**4g**)

From the reaction of **3g** (812 mg, 2.20 mmol) with NaH (70 mg, 2.9 mmol) in THF, there were obtained sulfur (80 mg, 0.31 mmol) and a mixture (378 mg) of **4g** (54%) and **1g** (8%, based on HPLC analysis), which was separated by HPLC to give **4g**: sticky oil; ^1H NMR ($CDCl_3$) δ 6.50 (s, 1H, CH), 6.90 (s, 1H, ArH), 7.20–7.70 (m, 7H, ArH); IR (KBr) 2248, 1620, 1478, 1235, 1200, 1175, 1087, 980, 845, 765, 702 cm^{-1}; MS *m/e* 268 (M^+). Anal. calcd for $C_{15}H_9ClN_2O$: C, 67.05; H, 3.38; N, 10.43. Found: C, 67.21; H, 3.40; N, 10.34.

2-Cyano-7-methyl-4-phenyl-4H-3,1-benzoxazine (**4i**)

A mixture of **3i** (606 mg, 1.74 mmol) and NaH (56 mg, 2.3 mmol) in THF was refluxed for 2 hours. After removal of sulfur (58 mg, 0.23 mmol), elution with petroleum ether and CH_2Cl_2 (v:v, 1:3, 70 mL) gave a mixture (378 mg) of **4i** (29%) and **1i** (6%, based on HPLC analysis), which was separated by HPLC to give **4i**: white; mp 83.5–84°C; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3H, Me), 6.53 (s, 1H, CH), 6.80 (d, 1H, J = 8 Hz, ArH), 7.10–7.70 (m, 7H, ArH); IR (KBr) 2244, 1630, 1608, 1500, 1452, 1326, 1296, 1245, 1228, 1200, 1188, 900, 830, 800, 758, 700 cm^{-1}; MS *m/e* 248 (M^+). Anal. calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.56; H, 4.88; N, 11.14. **1i**: sticky oil; ^1H NMR ($CDCl_3$) δ 2.46 (s, 3H, Me), 5.45 (s, 1H), 6.93–7.65 (m, 8H, ArH); IR (KBr) 2232, 1530, 1495, 1454, 1127, 1080, 822, 722, 690 cm^{-1}; MS *m/e* 264 (M^+). Anal. calcd for $C_{16}H_{12}N_2S$: C, 72.70; H, 4.58; N, 10.60; S, 12.13. Found: C, 72.56; H, 4.68; N, 10.64; S, 12.12.

N-(p-Tolyimino)cyanomethyl Benzyl Ether (**13**)

A mixture of 4-chloro-5-(p-tolylimino)-5H-1,2,3-dithiazole (**12**) (1.000 g, 4.12 mmol), benzyl alcohol (449 mg, 4.15 mmol), and NaH (100 mg, 4.17 mmol) in THF (20 mL) was refluxed for 90 minutes followed by chromatography. A petroleum ether fraction (80 mL) gave **13** (177 mg, 0.707 mmol, 17%): white crystals; mp 63–64°C (n-hexane); ^1H NMR ($CDCl_3$) δ 2.38 (s, 3H, Me), 5.40 (s, 2H, CH_2), 7.03 (d, 2H, J = 8 Hz, ArH), 7.33 (d, 2H, J = 8 Hz, ArH), 7.53 (s, 5H, Ph); IR (neat) 2222, 1665, 1455, 1378, 1278, 1220, 1113, 955, 912, 830, 759, 701 cm^{-1}; MS *m/e* 250 (M^+). Anal. calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 77.89; H, 5.68; N, 11.10.

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