Formal [3+2] Cycloaddition Reactions of 1-Methyl-2-[methylthio-(trimethylsilylmethylimino)methylimino]-1,2-dihydropyridine and Related Compound with Carbonyl Compounds Promoted by Fluoride Ion[1)]

Shinya KOHRA,*[,a] Kazuo UEDA,[a] and Yoshinori TOMINAGA[b]

Faculty of Liberal Arts,[a] Faculty of Pharmaceutical Sciences,[b] Nagasaki University, 1–14, Bunkyo-machi, Nagasaki 852, Japan. Received July 6, 1994; accepted September 27, 1994

Reaction of 1-methyl-2-[methylthio(trimethylsilylmethylimino)methylimino]-1,2-dihydropyridine (1), prepared from 2-amino-1-methyl-pyridinium iodide in 3 steps, with carbonyl compounds in the presence of 2 eq of cesium fluoride in acetonitrile afforded 2-(1-methyl-1,2-dihydropyridylidene)aminooxazoline derivatives (12), which correspond to formal [3+2] cycloadducts of the aminonitrile ylid. Further, compound 1 reacted with carbonyl compounds in the presence of a catalytic amount of tetra-*n*-butylammonium fluoride (TBAF) to give corresponding cycloadducts.

Key words desilylation; aminonitrile ylid; formal [3+2] cycloaddition; synthetic equivalent; 2-azaallyl anion; 2-aminooxazoline

Reaction of azomethine ylids with dipolarophiles is one of the most important reactions for constructing *N*-containing five-membered heterocycles.[2)] In 1984, Hosomi *et al.* reported the generation and 1,3-dipolar cycloaddition of nonstabilized azomethine ylids *via* 1,3-elimination of silylmethylamines.[3)] Numerous *N*-(silylmethyl)imines and related compounds have been reported as synthetic equivalents of azomethine ylids.[4)] During the course of our studies on the potential usefulness of polarized ethylenes and imines containing a methylthio group as the leaving group,[5)] we have reported that alkylideneazomethine ylids[6)] and iminoazomethine ylids[7)] can be generated by 1,3-elimination reaction of *N*-(trimethylsilylmethyl)-substituted ketene *N*,*S*-acetals and isothioureas promoted by fluoride ion and that [3+2] cycloadditions to a variety of dipolarophiles occur, giving N-containing 2-alkylidene- and 2-imino-heterocycles. In the present article, we show that 1-methyl-2-[methylthio-(trimethylsilylmethylimino)methylimino]-1,2-dihydropyridine (**1**) and a related compound (**2**), synthetic equivalents of aminonitrile ylids,[8)] react with carbonyl compounds under mild conditions to afford the corresponding oxazoline derivatives.

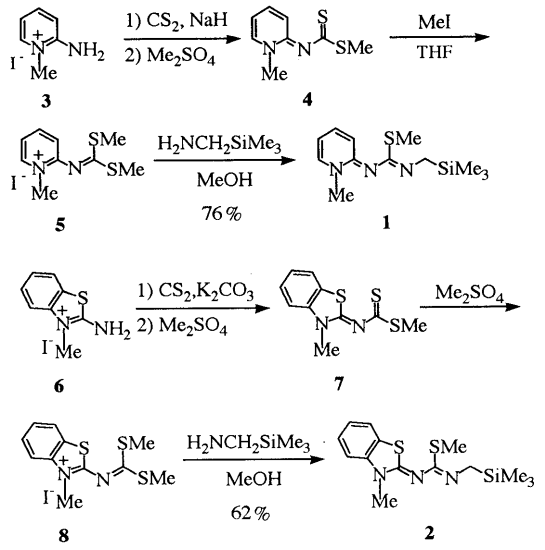


Chart 1

Compound **1** was prepared from 2-amino-1-methylpyridinium iodide (**3**) in 3 steps (Chart 1). 1-Methyl-2-[*N*-bis(methylthio)methylene]aminopyridinium iodide (**5**),[9)] readily prepared from **3**, was treated with aminomethyltrimethylsilane in methanol to afford the title compound (**1**) as a lemon-colored oily mixture of two isomers in 76% yield (Chart 1). The ratio of major and minor isomers was *ca.* 1.6 : 1 as determined from the proton nuclear magnetic resonance (^{1}H-NMR) spectrum. The isomers could not be separated. In a manner similar to that described for the preparation of **1**, 3-methyl-2-[methylthio(trimethylsilylmethylimino)methylimino]-2,3-dihydrobezothiazole (**2**) was synthesized from 2-amino-3-methylbenzothiazolium iodide (**6**). Reaction of 3-methyl-2-[*N*-bis(methylthio)-methylene]aminobenzothiazolium iodide (**8**)[9)] with aminomethyltrimethylsilane afforded compound **2** in 62% yield as pale yellow needles, mp 147—149 °C (ethanol).

It is well known that cesium fluoride and tetra-*n*-butylammonium fluoride (TBAF) are available as fluoride ion sources in organic synthesis using organosilicons.[10)] Compound **1** was treated with cesium fluoride in wet acetonitrile to give the desilylation product, 1-methyl-2-[methylthio(methylimino)methylimino]-1,2-dihydropyridine (**9**). Compound **2** could also be desilylated with cesium fluoride in wet *N*,*N*-dimethyl formamide (DMF) to give 3-methyl-2-[methylthio(methylimino)methylimino]-2,3-dihydrobenzothiazole (**10**).

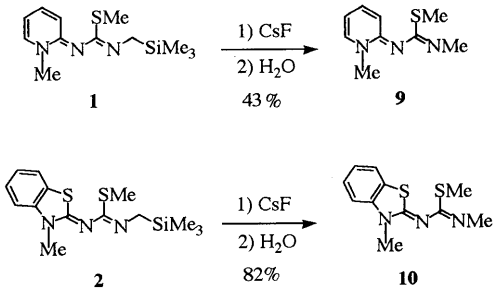
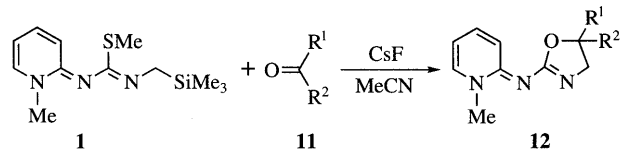
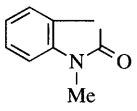


Chart 2

* To whom correspondence should be addressed.

TABLE I. Reaction of Organosilicon (**1**) and Carbonyl Compounds (**11**) in the Presence of Cesium Fluoride[a]



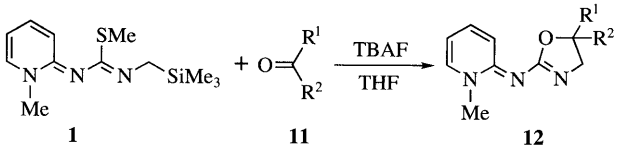
Entry	11			Yield (%) of 12[b]	
	R^1	R^2			
1	C_6H_5	H	(**11a**)	71	(**12a**)
2	4-$C_6H_5C_6H_4$	H	(**11b**)	73	(**12b**)
3	4-MeC_6H_4	H	(**11c**)	71	(**12c**)
4	4-$MeOC_6H_4$	H	(**11d**)	57	(**12d**)
5	4-ClC_6H_4	H	(**11e**)	73	(**12e**)
6	2,6-$Cl_2C_6H_3$	H	(**11f**)	77	(**12f**)
7	4-NCC_6H_4	H	(**11g**)	52	(**12g**)
8	1-Naphthyl	H	(**11h**)	55	(**12h**)
9	2-Thienyl	H	(**11i**)	44[c]	(**12i**)
10	3-Pyridyl	H	(**11j**)	43	(**12j**)
11	(*E*)-$C_6H_4CH=CH$	H	(**11k**)	38[d]	(**12k**)
12	C_6H_5	C_6H_5CO	(**11l**)	42	(**12l**)
13			(**11m**)	68	(**12m**)

a) All reactions were carried out using **1** (1.0 mmol) and **11** (1.0 mmol) in the presence of CsF (2.0 mmol) in MeCN (4 ml) at room temperature for 1 week, unless otherwise noted. *b*) Yield after isolation by column chromatography. *c*) Cesium fluoride (4.0 mmol) was used. *d*) Carbonyl compound (**11**) (2.0 mmol) was used.

The reaction of **1** with 1 eq of benzaldehyde (**11a**) in the presence of 2 eq of cesium fluoride proceeded in acetonitrile at room temperature for a week to afford the corresponding 2-(1-methyl-1,2-dihydropyridylidene)-amino-5-phenyloxazoline (**12a**), which corresponds to a formal [3+2] cycloadduct of an aminonitrile ylid, in 71% yield. As shown in Table I, a variety of aromatic aldehydes (**11b—j**) reacted with **1** in a similar manner to that described for **12a** to give the corresponding 5-substituted 2-(1-methyl-1,2-dihydropyridylidene)aminooxazoline derivatives (**12b—j**) in moderate yields. Cinnamaldehyde (**11k**), benzil (**11l**) and 1-methylisatin (**11m**) also reacted with **1** to give [3+2] cycloaddition products (**12k—m**). However, aliphatic aldehydes, simple ketones, and active alkenes such as dimethyl fumarate and *N*-methylmaleimide did not react under the present conditions. With 1 eq of TBAF instead of 2 eq of cesium fluoride as the fluoride ion source, the reaction of **1** and **11a** in tetrahydrofuran (THF) gave **12a** in 67% yield. In contrast, desilylation reaction of **1** did not proceed under acidic conditions,[4i-j] in the presence of trifluoroacetic acid without fluoride ion. It should be noted that **1** also reacted with carbonyl compounds in the presence of a catalytic amount of TBAF in THF, as shown in Table II. The reactions demonstrate that compound **1** can be viewed as a synthetic equivalent of a novel 1,3-dipolar reagent, an aminonitrile ylid.

On the other hand, compound **2** reacted in stages with carbonyl compounds. Reaction of **2** with **11a** in the presence of cesium fluoride in DMF gave a mixture of 3-methyl-2-[methylthio(2-hydroxy-2-phenylethylimino)-methylimino]-2,3-dihydrobenzothiazole (**13a**) and 3-

TABLE II. Reaction of Organosilicon (**1**) and Carbonyl Compounds (**11**) in the Presence of TBAF[a]



Entry	11			Equiv. of TBAF	Yield (%) of 12[b]	
	R^1	R^2				
1	C_6H_5	H	(**11a**)	1.0	67	(**12a**)
2	C_6H_5	H	(**11a**)	0.1	71	(**12a**)
3	4-$MeOC_6H_4$	H	(**11d**)	0.1	38	(**12d**)
4	4-ClC_6H_4	H	(**11e**)	0.1	76	(**12e**)
5	4-NCC_6H_4	H	(**11g**)	0.1	41	(**12g**)
6	C_6H_5	C_6H_5CO	(**11l**)	0.1	70	(**12l**)

a) All reactions were carried out using **1** (1.0 mmol) and **11** (1.0 mmol) in the presence of TBAF in THF (4 ml) at room temperature for a week. *b*) Yield after isolation by column chromatography.

methyl-2-(5-phenyloxazol-2-ylimino)-2,3-dihydrobenzothiazole (**14a**). A suspension of the mixture and aluminum oxide in methanol was stirred at room temperature for 12 h, resulting in the conversion of **13a** into **14a** in good yield. The cycloaddition product **14a** was obtained from **2** in 85% overall yield as pale yellow prisms, mp 125—126 °C (*n*-hexane–ethyl acetate). When 2,6-dichlorobenzaldehyde (**11f**) and 3-pyridinecarboxaldehyde (**11j**) was used instead of **11a**, the corresponding adducts **13b** and **13c** could be isolated in 86% and 82% yields. Compounds **13b** and **13c** were easily converted into the cycloadducts **14b** and **14c** in good yield, as shown in Table III. *n*-Butyraldehyde (**11n**), which did not react with **1**, reacted with **2** to give the cycloadduct **14e** in 36% yield (Table III, entry 5). The reaction of **2** with carbonyl compounds promoted by fluoride ion is also considered to be a formal [3+2] cycloaddition. In addition, compound **2** reacted with dimethyl fumarate (**15**) under the present conditions to give 3-methyl-2-[methylthio(2,3-bis(methoxycarbonyl)propylimino)methylimino]-2,3-dihydrobenzothiazole (**16**) in 35% yield as a pale yellow viscous oil.

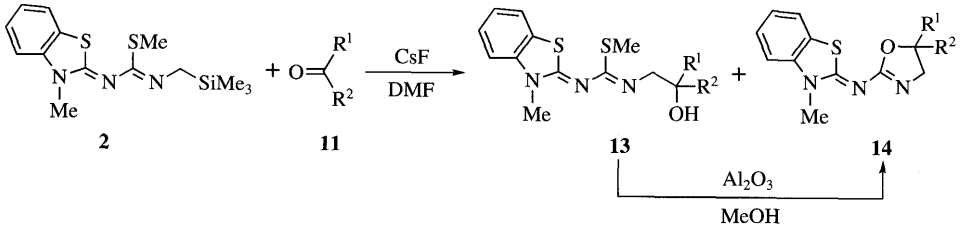
The results suggest that the reactions of **1** and **2** promoted by fluoride ion proceed *via* generation of 2-azaallyl anions.[4m]

In conclusion, we have shown that 1-methyl-2-[methylthio(trimethylsilylmethylimino)methylimino]-1,2-dihydropyridine (**1**) and a related compound (**2**), which are readily prepared, storable and easy to handle, are synthetic equivalents of aminonitrile ylids. The reactions of compound **1** and **2** with carbonyl compounds in the presence of fluoride ion are formal [3+2] cycloadditions between the carbon–oxygen double bond and aminonitrile ylids.

Experimental

All melting points were determined in a capillary tube without correction. Infrared (IR) spectra were recorded in potassium bromide pellets on a JASCO 810 spectrometer and ultraviolet (UV) absorption spectra were determined in 95% ethanol on a Hitachi UV-323 spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained on a JNM-FX-90Q (90 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra (MS) were recorded on a JEOL

TABLE III. Reaction of Organosilicon (**2**) and Carbonyl Compounds (**11**)[a]



Entry	11			Yield (%) of **13**[b]		Yield (%) of **14** from **2**[b]	
	R^1	R^2					
1	C_6H_5	H	(**11a**)	—	(**13a**)	85	(**14a**)
2	2,6-$Cl_2C_6H_3$	H	(**11f**)	86	(**13b**)	67	(**14b**)
3	3-Pyridyl	H	(**11j**)	82	(**13c**)	74	(**14c**)
4	C_6H_5	C_6H_5CO	(**11l**)	—	(**13d**)	44	(**14d**)
5	C_3H_7	H	(**11n**)			36	(**14e**)

a) All reactions were carried out using **2** (1.0 mmol) and **11** (1.0 mmol). *b*) Yield after isolation.

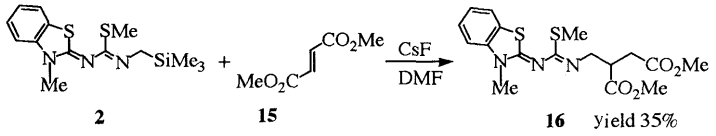


Chart 3

JMS-DX303 mass spectrometer. Elemental analyses were performed at the Microanalytical Laboratory of the Center for Instrumental Analysis in Nagasaki University.

1-Methyl-2-[methylthio(trimethylsilylmethylimino)methylimino]-1,2-dihydropyridine (1) A solution of **3** (20.4 g, 60 mmol) and aminomethyltrimethylsilane (6.2 g, 60 mmol) in methanol (200 ml) was refluxed for 3 h. The reaction mixture was concentrated to 80 ml *in vacuo*, and 10% sodium hydroxide (20 ml) was added. The basic solution was poured into 300 ml of water and extracted with ethyl acetate (3 × 100 ml). The combined organic layer was washed with water (2 × 100 ml) and brine (100 ml), and then dried over anhydrous $MgSO_4$. After removal of the solvent, the crude product was chromatographed on an alumina (Merck, Aluminum oxide 90 active, basic) column with dichloromethane to give 12.2 g (76%) of lemon-yellow oil. IR ν_{max}^{neat} cm^{-1}: 2950, 1640, 1600, 1550, 855. UV λ_{max}^{EtOH} nm (log ε): 336 (4.26), 275 (4.00). ^{1}H-NMR ($CDCl_3$) δ: major isomer: 0.04 (9H, s, $SiMe_3$), 2.34 (3H, s, SMe), 2.99 (2H, s, NCH_2Si), 3.48 (3H, s, NMe), 5.91 (1H, t, J=6.8 Hz, 5-H on pyridine ring), 6.45 (1H, d, J=8.8 Hz, 3-H on pyridine ring), 6.90—7.30 (2H, m, 4- and 6-H on pyridine ring); minor isomer: 0.13 (9H, s, $SiMe_3$), 2.30 (3H, s, SMe), 3.15 (2H, s, NCH_2Si), 3.51 (3H, s, NMe), 5.91 (1H, t, J=6.8 Hz, 5-H on pyridine ring), 6.45 (1H, d, J=8.8 Hz, 3-H on pyridine ring), 6.90—7.30 (2H, m, 4- and 6-H on pyridine ring) (major : minor = *ca.* 1.6 : 1). MS *m/z*: 268 (M^++1, 10), 267 (M^+, 49), 252 (11), 237 (17), 221 (21), 220 (100), 151 (43), 134 (16). *Anal.* Calcd for $C_{12}H_{21}N_3SSi$: C, 53.88; H, 7.92; N, 15.71. Found: C, 53.90; H, 7.83; N, 15.69.

3-Methyl-2-[methylthio(trimethylsilylmethylimino)methylimino]-2,3-dihydrobenzothiazole (2) This compound was synthesized from **8** and aminomethyltrimethylsilane in 62% yield in a manner similar to that described for the preparation of **1**. An analytical sample was recrystallized from ethanol to give pale yellow needles, mp 126—127 °C. IR ν_{max}^{KBr} cm^{-1}: 2950, 1560, 1540, 1470, 860. UV λ_{max}^{EtOH} nm (log ε): 320 (4.40), 262 (3.96), 226 (4.51). ^{1}H-NMR ($CDCl_3$) δ: 0.13 (9H, s, $SiMe_3$), 2.57 (3H, s, SMe), 3.21 (2H, s, NCH_2Si), 3.71 (3H, s, NMe), 7.00—7.65 (4H, m, aromatic-H). MS *m/z*: 323 (M^+, 100), 276 (69), 207 (35), 191 (57). *Anal.* Calcd for $C_{14}H_{21}N_3S_2Si$: C, 51.97; H, 6.54; N, 12.99. Found: C, 51.78; H, 6.39; N, 13.06.

1-Methyl-2-[methylthio(methylimino)methylimino]-1,2-dihydropyridine (9) A solution of **1** (267 mg, 1.0 mmol) and cesium fluoride (304 mg, 2.0 mmol) in wet acetonitrile (4 ml) was stirred at room temperature for a week. The reaction mixture was poured into water (50 ml) and extracted with ethyl acetate (50 ml). The organic layer was washed with water (2 × 30 ml) and brine (30 ml), and then dried over anhydrous $MgSO_4$. After removal of the solvent, the crude product was recrystallized from *n*-hexane to give 90 mg (46%) of pale yellow needles, mp 96—97 °C. IR ν_{max}^{KBr} cm^{-1}: 2900, 2850, 1640, 1610, 1555, 1380, 1120, 1050. UV λ_{max}^{EtOH} nm (log ε): 330 (4.23), 264 (3.92). ^{1}H-NMR ($CDCl_3$) δ: major isomer: 2.32 (3H, s, SMe), 2.95 (3H, s, NMe), 3.48 (3H, s, NMe), 5.91 (1H, t, J=6.6 Hz, 5-H on pyridine ring), 6.38 (1H, d, J=9.2 Hz, 3-H on pyridine ring), 6.90—7.30 (2H, m, 4- and 6-H on pyridine ring); minor isomer: 2.30 (3H, s, SMe), 3.13 (3H, s, NMe), 3.50 (3H, s, NMe), 5.91 (1H, t, J=6.6 Hz, 5-H on pyridine ring), 6.38 (1H, d, J=9.2 Hz, 3-H on pyridine ring), 6.90—7.30 (2H, m, 4 and 6-H on pyridine ring) (major : minor = *ca.* 2 : 1). MS *m/z*: 195 (M^+, 10), 148 (100). *Anal.* Calcd for $C_9H_{13}N_3S$: C, 53.88; H, 7.92; N, 15.71. Found: C, 53.90; H, 7.83; N, 15.69.

3-Methyl-2-[methylthio(methylimino)methylimino]-2,3-dihydrobenzothiazole (10) This compound was synthesized from **2** in 82% yield in a manner similar to that described for the preparation of **9** using DMF instead of acetonitrile. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give colorless needles, mp 82—84 °C. IR ν_{max}^{KBr} cm^{-1}: 2920, 2840, 1580, 1535, 1470, 1345. UV λ_{max}^{EtOH} nm (log ε): 316 (4.42), 273 (3.85), 224 (4.50). ^{1}H-NMR ($CDCl_3$) δ: 2.57 (3H, s, SMe), 3.27 (3H, s, NMe), 3.69 (3H, s, NMe), 7.00—7.56 (4H, m, aromatic-H). MS *m/z*: 251 (M^+, 14), 205 (13), 204 (100). *Anal.* Calcd for $C_{11}H_{13}N_3S_2$: C, 52.56; H, 5.21; N, 16.72. Found: C, 52.46; H, 5.03; N, 16.58.

General Method of Reaction of 1 and Carbonyl Compound (11) Under a nitrogen atmosphere, a solution of 1.0 mmol of **1** and 1.0 mmol of a carbonyl compound (**11**) in acetonitrile (4 ml) in the presence of 2.0 mmol of cesium fluoride was stirred at room temperature for a week. The solvent was evaporated, and the residue was diluted with water (50 ml), then extracted with ethyl acetate (2 × 30 ml). The combined organic layer was washed with water (2 × 30 ml) and brine (30 ml) and then dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* to give a crude product, which was purified by chromatography on alumina (Merck, Aluminum oxide 90 active, basic) column with *n*-hexane–ethyl acetate (1 : 4).

2-(1-Methyl-1,2-dihydropyridylidene)amino-5-phenyloxazoline (12a) Yield was 71%. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 109—110 °C. IR ν_{max}^{KBr} cm^{-1}: 3075, 2905, 2855, 1635, 1595, 1545, 1505, 1385, 1015. UV λ_{max}^{EtOH} nm (log ε): 320 (4.17), 265 (4.17), 205 (4.47). ^{1}H-NMR ($CDCl_3$) δ: 3.70 (3H, s, NMe), 3.87 (1H, dd, J=13.0, 7.9 Hz, 4-H on oxazoline ring), 4.36 (1H, dd, J=13.0, 9.4 Hz, 4-H on oxazoline ring), 5.4 (1H,

dd, $J=9.4$, 7.9 Hz, 5-H on oxazoline ring), 6.26 (1H, td, $J=6.6$, 1.3 Hz, 5′-H on pyridine ring), 7.12—7.47 (7H, m, 4′- and 6′-H on pyridine ring and phenyl-H), 8.19 (1H, dd, $J=9.7$, 1.3 Hz, 3′-H on pyridine ring). MS *m/z*: 253 (M^+, 76), 147 (100), 135 (60). *Anal.* Calcd for $C_{15}H_{15}N_3O$: C, 71.12; H, 5,97; N, 16.59. Found: C, 71.18; H, 6.03; N, 16.64.

2-(1-Methyl-1,2-dihydropyridylidene)amino-5-(4-biphenyl)oxazoline (12b) Yield was 73%. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 137—140 °C. IR ν_{max}^{KBr} cm^{-1}: 3010, 2905, 2850, 1635, 1595, 1540, 1520, 1445, 1380. UV λ_{max}^{EtOH} nm (log ε): 324 (4.07), 260 (4.48), 206 (4.64). ^{1}H-NMR ($CDCl_3$) δ: 3.70 (3H, s, NMe), 3.91 (1H, dd, $J=13.2$, 7.9 Hz, 4-H on oxazoline ring), 4.39 (1H, dd, $J=13.2$, 9.4 Hz, 4-H on oxazoline ring), 5.49 (1H, dd, $J=9.4$, 7.9 Hz, 5-H on oxazoline ring), 6.26 (1H, td, $J=6.7$, 1.5 Hz, 5′-H on pyridine ring), 7.21—7.64 (11H, m, 4′- and 6′-H on pyridine ring and phenyl-H), 8.18 (1H, dd, $J=9.7$, 1.3 Hz, 3′-H on pyridine ring). MS *m/z*: 329 (M^+, 14), 322 (17), 281 (100), 183 (48), 108 (44). *Anal.* Calcd for $C_{21}H_{19}N_3O$: C, 76.57; H, 5.81; N, 12.76. Found: C, 76.49; H, 5.90; N, 12.80.

2-(1-Methyl-1,2-dihydropyridylidene)amino-5-(4-methylphenyl)oxazoline (12c) Yield was 71%. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 95—97 °C. IR ν_{max}^{KBr} cm^{-1}: 2905, 2850, 1640, 1600, 1540, 1450, 1385. UV λ_{max}^{EtOH} nm (log ε): 323 (3.99), 269 (4.12). ^{1}H-NMR ($CDCl_3$) δ: 2.33 (3H, s, Me), 3.66 (3H, s, NMe), 3.82 (1H, dd, $J=13.2$, 7.9 Hz, 4-H on oxazoline ring), 4.23 (1H, dd, $J=13.2$, 9.4 Hz, 4-H on oxazoline ring), 5.46 (1H, dd, $J=9.4$, 7.9 Hz, 5-H on oxazoline ring), 6.23 (1H, td, $J=6.5$, 1.3 Hz, 5′-H on pyridine ring), 7.00—7.41(6H, m, 3′- and 4′-H on pyridine ring and phenyl-H), 8.10 (1H, dd, $J=9.7$, 1.3 Hz, 3′-H on pyridine ring). MS *m/z*: 267 (M^+, 14), 220 (20), 208 (10), 178 (14), 148 (23), 135 (41), 121 (100). *Anal.* Calcd for $C_{16}H_{17}N_3O_2$: C, 71.88; H, 6.41; N, 15.72. Found: C, 71.85; H, 6.44; N, 15.69.

2-(1-Methyl-1,2-dihydropyridylidene)amino-5-(4-methoxyphenyl)-oxazoline (12d) Yield was 57%. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 110—111 °C. IR ν_{max}^{KBr} cm^{-1}: 3075, 2900, 2850, 1635, 1595, 1545, 1505, 1015. UV λ_{max}^{EtOH} nm (log ε): 319 (4.26), 263 (4.22), 229 (4.17). ^{1}H-NMR ($CDCl_3$) δ: 3.68 (3H, s, NMe), 3.80 (3H, s, OMe), 3.87 (1H, dd, $J=13.2$, 8.1 Hz, 4-H on oxazoline ring), 4.32 (1H, dd, $J=13.2$, 9.4 Hz, 4-H on oxazoline ring), 5.46 (1H, dd, $J=9.4$, 8.1 Hz, 5-H on oxazoline ring), 6.25 (1H, td, $J=6.6$, 1.3 Hz, 5′-H on pyridine ring), 6.87 (2H, d, $J=8.8$ Hz, phenyl-H), 7.26—7.45 (4H, m, 4′- and 6′-H on pyridine ring and phenyl-H), 8.15 (1H, dd, $J=9.7$, 1.3 Hz, 3′-H on pyridine ring). MS *m/z*: 283 (M^+, 23), 253 (16), 147 (100), 135 (62), 119 (43). *Anal.* Calcd for $C_{16}H_{17}N_3O_2$: C, 67.87; H, 6.05; N, 14.83. Found: C, 67.69; H, 6.08; N, 14.75

2-(1-Methyl-1,2-dihydropyridylidene)amino-5-(4-chlorophenyl)oxazoline (12e) Yield was 73%. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 119—120 °C. IR ν_{max}^{KBr} cm^{-1}: 2945, 2860, 1640, 1600, 1540, 1385. UV λ_{max}^{EtOH} nm (log ε): 323 (4.06), 268 (4.98). ^{1}H-NMR ($CDCl_3$) δ: 3.72 (3H, s, NMe), 3.87 (1H, dd, $J=13.0$, 7.9 Hz, 4-H on oxazoline ring), 4.36 (1H, dd, $J=13.0$, 9.4 Hz, 4-H on oxazoline ring), 5.46 (1H, dd, $J=9.4$, 7.9 Hz, 5-H on oxazoline ring), 6.35 (1H, td, $J=6.6$, 1.3 Hz, 5′-H on pyridine ring), 7.15—7.51 (6H, m, 4′- and 6′-H on pyridine ring and phenyl-H), 8.10 (1H, dd, $J=9.7$, 1.3 Hz, 3′-H on pyridine ring). MS *m/z*: 287 (M^+, 34), 165 (23), 147 (47), 135 (100). *Anal.* Calcd for $C_{15}H_{14}ClN_3O$: C, 62.61; H, 4.90; N, 14.60. Found: C, 62.66; H, 4.95; N, 14.59.

2-(1-Methyl-1,2-dihydropyridylidene)amino-5-(2,6-dichlorophenyl)-oxazoline (12f) Yield was 77%. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 161—163 °C. IR ν_{max}^{KBr} cm^{-1}: 3075, 2925, 2860, 1635, 1600, 1540, 1505, 1385, 1300, 1220, 1010. UV λ_{max}^{EtOH} nm (log ε): 322 (4.10), 268 (4.17), 205 (4.66). ^{1}H-NMR ($CDCl_3$) δ: 3.67 (3H, s, NMe), 4.03 (1H, dd, $J=13.2$, 9.6 Hz, 4-H on oxazoline ring), 4.33 (1H, dd, $J=13.2$, 10.3 Hz, 4-H on oxazoline ring), 6.20 (1H, dd, $J=10.3$, 9.6 Hz, 5-H on oxazoline ring), 6.25 (1H, td, $J=6.6$, 1.4 Hz, 5′-H on pyridine ring), 7.10—7.45 (5H, m, 4′- and 6′-H on pyridine ring and phenyl-H), 8.16 (1H, dd, $J=9.8$, 1.3 Hz, 3′-H on pyridine ring). MS *m/z*: 323 ($M^+ + 2$, 9), 321 (M^+, 14), 199 (11), 187 (20), 185 (14), 177 (61), 176 (17), 175 (100). *Anal.* Calcd for $C_{15}H_{13}Cl_2N_3O$: C, 55.92; H, 4.07; N, 13.04. Found: C, 55.84; H, 4.09; N, 12.85.

2-(1-Methyl-1,2-dihydropyridylidene)amino-5-(4-cyanophenyl)oxazoline (12g) Yield was 52%. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 153—154 °C. IR ν_{max}^{KBr} cm^{-1}: 3100, 2950, 2855, 2210, 1640, 1595, 1540, 1520, 1380. UV λ_{max}^{EtOH} nm (log ε): 328 (4.02), 271 (4.18), 232 (4.30). ^{1}H-NMR ($CDCl_3$) δ: 3.72 (3H, s, NMe), 3.78 (1H, dd, $J=13.0$, 7.8 Hz, 4-H on oxazoline ring), 4.41 (1H, dd, $J=13.0$, 9.4 Hz, 4-H on oxazoline ring), 5.47 (1H, dd, $J=9.4$, 7.8 Hz, 5-H on oxazoline ring), 6.32 (1H, td, $J=6.6$, 1.3 Hz, 5′-H on pyridine ring), 7.16—7.75 (6H, m, 3′- and 4′-H on pyridine ring and phenyl-H), 8.22 (1H, dd, $J=9.7$, 1.3 Hz, 6′-H on pyridine ring). MS *m/z*: 278 (M^+, 11), 195 (11), 148 (100), 135 (36). *Anal.* Calcd for $C_{16}H_{14}N_4O$: C, 69.05; H, 5,07; N, 20.13. Found: C, 68.75; H, 5.21; N, 19.90.

2-(1-Methyl-1,2-dihydropyridylidene)amino-5-(1-naphthyl)oxazoline (12h) Yield was 55%. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 154—156 °C. IR ν_{max}^{KBr} cm^{-1}: 3075, 2905, 2855, 1635, 1595, 1545, 1505, 1385, 1015. UV λ_{max}^{EtOH} nm (log ε): 328 (3.94), 271 (4.15), 222 (4.85). ^{1}H-NMR ($CDCl_3$) δ: 3.70 (3H, s, NMe), 3.87 (1H, dd, $J=13.0$, 7.7 Hz, 4-H on oxazoline ring), 4.58 (1H, dd, $J=13.0$, 9.7 Hz, 4-H on oxazoline ring), 6.15 (1H, dd, $J=9.7$, 7.7 Hz, 5-H on oxazoline ring), 6.23 (1H, td, $J=6.8$, 1.3 Hz, 5′-H on pyridine ring), 7.12—8.24 (10H, m, 3′-, 4′-, and 6′-H on pyridine ring and naphthyl-H). MS *m/z*: 303 (M^+, 40), 196 (24), 157 (30), 147 (100). *Anal.* Calcd for $C_{19}H_{17}N_3O$: C, 75.22; H, 5.65; N, 13.85. Found: C, 74.95; H, 5.74; N, 13.67.

2-(1-Methyl-1,2-dihydropyridylidene)amino-5-(2-thienyl)oxazoline (12i) Yield was 44%. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 107—108 °C. IR ν_{max}^{KBr} cm^{-1}: 3080, 2845, 1635, 1600, 1550, 1510, 1390, 1295, 1015. UV λ_{max}^{EtOH} nm (log ε): 320 (4.20), 263 (4.13). ^{1}H-NMR ($CDCl_3$) δ: 3.67 (3H, s, NMe), 4.02 (1H, dd, $J=13.0$, 7.7 Hz, 4-H on oxazoline ring), 4.34 (1H, dd, $J=13.0$, 9.2 Hz, 4-H on oxazoline ring), 5.73 (1H, dd, $J=9.2$, 7.7 Hz, 5-H on oxazoline ring), 6.26 (1H, td, $J=6.6$, 1.3 Hz, 5′-H on pyridine ring), 6.80—7.51 (5H, m, 4′- and 6′-H on pyridine ring and thienyl-H), 8.08 (1H, dd, $J=9.7$, 1.3 Hz, 3′-H on pyridine ring). MS *m/z*: 259 (M^+, 57), 149 (14), 147 (100), 135 (82), 119 (52). *Anal.* Calcd for $C_{13}H_{13}N_3OS$: C, 60.21; H, 5.05; N, 10.20. Found: C, 60.12; H, 5.08; N, 16.03.

2-(1-Methyl-1,2-dihydropyridylidene)amino-5-(3-pyridyl)oxazoline (12j) Yield was 43%. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale brown prisms, mp 131—135 °C. IR ν_{max}^{KBr} cm^{-1}: 3080, 2905, 2855, 1635, 1595, 1545, 1505, 1385, 1300, 1215, 1015. UV λ_{max}^{EtOH} nm (log ε): 360 (3.61), 319 (4.19), 262 (4.22). ^{1}H-NMR ($CDCl_3$) δ: 3.72 (3H, s, NMe), 3.86 (1H, dd, $J=13.0$, 7.5 Hz, 4-H on oxazoline ring), 4.40 (1H, dd, $J=13.0$, 9.4 Hz, 4-H on oxazoline ring), 5.48 (1H, dd, $J=9.4$, 7.5 Hz, 5-H on oxazoline ring), 6.32 (1H, td, $J=6.8$, 1.3 Hz, 5″-H on pyridine ring), 7.12—7.80 (4H, m, 4′-, 5′-, 3″-, and 4″-H on pyridine ring), 8.20 (1H, dd, $J=9.8$, 1.3 Hz, 6″-H on pyridine ring), 8.54 (1H, dd, $J=4.5$, 1.5 Hz, 6′-H on pyridine ring), 8.63 (1H, d, $J=2.2$ Hz, 2′-H on pyridine ring). MS *m/z*: 254 (M^+, 49), 148 (22), 147 (89), 135 (98), 119 (58), 93 (100). *Anal.* HR-MS Calcd for $C_{14}H_{14}N_4O$ *m/z*: 254.1168. Found *m/z*: 254.1164.

2-(1-Methyl-1,2-dihydropyridylidene)amino-5-(2-phenylethenyl)oxazoline (12k) Yield was 38%. An analytical sample was chromatographed on an alumina (Merck, Aluminum oxide 90 active, basic) column with *n*-hexane–ethyl acetate (1 : 4) to give a pale brown viscous oil. IR ν_{max}^{film} cm^{-1}: 2910, 2855, 1635, 1595, 1540, 1520, 1505, 1450, 1385. UV λ_{max}^{EtOH} nm (log ε): 322 (4.11), 263 (4.32). ^{1}H-NMR ($CDCl_3$) δ: 3.65 (3H, s, NMe), 3.74 (1H, dd, $J=13.2$, 7.9 Hz, 4-H on oxazoline ring), 4.13 (1H, dd, $J=13.2$, 9.2 Hz, 4-H on oxazoline ring), 5.05 (1H, dd, $J=9.2$, 7.9 Hz, 5-H on oxazoline ring), 6.22 (1H, td, $J=6.7$, 1.4 Hz, 4′-H on pyridine ring), 6.30 (1H, dd, $J=15.8$, 7.4 Hz, –CH=CH–C_6H_5 and 5′-H on pyridine ring), 6.62 (1H, d, $J=15.8$ Hz, –CH=CH–C_6H_5), 7.15—7.40 (7H, m, 3′- and 4′-H on pyridine ring and phenyl-H), 8.12 (1H, dd, $J=9.8$, 1.4 Hz, 6′-H on pyridine ring). MS *m/z*: 279 (M^+, 41), 253 (21), 149 (23), 148 (80), 147 (60), 135 (100). *Anal.* HR-MS Calcd for $C_{17}H_{17}N_3O$ *m/z*: 279.1372. Found *m/z*: 279.1368.

2-(1-Methyl-1,2-dihydropyridylidene)amino-5-phenyl-5-benzoyloxazoline (12l) Yield was 42%. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 187—189 °C. IR ν_{max}^{KBr} cm^{-1}: 3040, 2905, 2855, 1635, 1595, 1540, 1520, 1505, 1385. UV λ_{max}^{EtOH} nm (log ε): 332 (4.04), 256 (4.29). ^{1}H-NMR ($CDCl_3$) δ: 3.60 (3H, s, NMe), 3.95 (1H, d, $J=13.8$ Hz, 4-H on oxazoline ring), 5.02 (1H, d, $J=13.8$ Hz, 4-H on oxazoline ring), 6.17 (1H, td, $J=6.6$, 1.3 Hz, 5″-H on pyridine ring), 7.00—7.55 (10H, m, 3″- and 4″-H on pyridine ring and phenyl-H), 7.84—8.03 (3H, m, 2′- and 6′-H on benzoyl and 6″-H on pyridine ring). MS *m/z*: 357 (M^+, 7), 252 (100), 148 (16), 135 (51). *Anal.* Calcd for $C_{22}H_{19}N_3O_2$: C, 73.93; H, 5.36; N, 11.76. Found: C,

73.67; H, 5.48; N, 11.59.

2-(1-Methyl-1,2-dihydropyridylidene)aminooxazoline-5-spiro-1′-methyl-2′-oxoindole (12m) Yield was 67%. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale brown prisms, mp 204—205 °C. IR ν_{max}^{KBr} cm^{-1}: 3075, 2905, 2855, 1725, 1640, 1615, 1545, 1530, 1460, 1360, 1235, 998. UV λ_{max}^{EtOH} nm (log ε): 335 (4.04), 270 (4.26), 212 (4.58), 201 (4.51). ^{1}H-NMR ($CDCl_3$) δ: 3.21 (3H, s, NMe), 3.70 (3H, s, NMe), 4.13 (1H, d, J=13.0 Hz, 4-H on oxazoline ring), 4.37 (1H, d, J=13.0 Hz, 4-H on oxazoline ring), 6.42 (1H, td, J=6.6, 1.3 Hz, 5′-H on pyridine ring), 7.12—7.47 (6H, m, 3′- and 4′-H on pyridine ring and phenyl-H), 8.10 (1H, dd, J=9.7, 1.3 Hz, 6′-H on pyridine ring). MS m/z: 308 (M^+, 21), 203 (49), 147 (49), 135 (100), 119 (25). *Anal.* Calcd for $C_{17}H_{16}N_4O_2$: C, 66.22; H, 5.23; N, 18.17. Found: C, 66.49; H, 5.32; N, 17.90.

Reaction of 1 with 11 in the Presence of TBAF Under a nitrogen atmosphere, 1 M TBAF in THF (0.1 ml, 0.1 mmol) was added to a solution of 1.0 mmol of **1** and 1.0 mmol of carbonyl compound (**11**) in THF (4 ml), and the reaction mixture was stirred at room temperature for a week. The solvent was evaporated, and the residue was diluted with water (50 ml), then extracted with ethyl acetate (2×30 ml). The combined organic layer was washed with water (2×30 ml) and brine (30 ml), and then dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* to give crude product, which were purified by chromatography on alumina (Merck, Aluminum oxide 90 active, basic) column with *n*-hexane–ethyl acetate (1 : 4).

Reaction of 2 with Benzaldehyde (11a) in the Presence of Cesium Fluoride in DMF Under a nitrogen atmosphere, a solution of **2** (323 mg, 1.0 mmol) and **11a** (106 mg, 1.0 mmol) in DMF (3 ml) in the presence of cesium fluoride (304 mg, 2.0 mmol) was stirred at room temperature for a week. The solvent was evaporated, and the residue was washed with water, then collected. The precipitate was a mixture of **13a** and **14a**. A suspension of this mixture and 0.3 g of Al_2O_3 in methanol (30 ml) was stirred at room temperature for 12 h. The solvent was removed *in vacuo*, and the resulting precipitate was recrystallized from *n*-hexane–ethyl acetate to give 267 mg (85%) of **14a** as pale yellow needles, mp 125—126 °C.

3-Methyl-2-[methylthio(2-hydroxy-2-phenylethylimino)methylimino]-2,3-dihydrobenzothiazole (13a) ^{1}H-NMR ($CDCl_3$) δ: 2.53 (3H, s, SMe), 3.30—3.76 (6H, m, NMe, CH_2, and OH), 5.05(1H, dd, J=8.6, 4.0, C<u>H</u>(OH)), 6.95—7.53 (9H, m, aromatic-H). FAB-MS m/z: 358 ($M^+ + 1$).

3-Methyl-2-(5-phenyloxazol-2-ylimino)-2,3-dihydrobenzothiazole (14a) Yield was 85%. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 125—126 °C. IR ν_{max}^{neat} cm^{-1}: 2920, 2860, 1615, 1540, 1470, 1410, 1300. UV λ_{max}^{EtOH} nm (log ε): 307 (4.49), 282 (4.07), 217 (4.61). ^{1}H-NMR ($CDCl_3$) δ: 3.75 (3H, s, NMe), 3.96 (1H, dd, J=13.3, 8.0 Hz, 4-H on oxazoline ring), 4.47 (1H, dd, J=13.3, 9.6 Hz, 4-H on oxazoline ring), 5.59 (1H, dd, J=9.6, 7.9 Hz, 5-H on oxazoline ring), 7.10—7.62 (9H, m, aromatic-H). MS m/z: 309 (M^+, 100), 250 (45), 191 (90). *Anal.* Calcd for $C_{17}H_{15}N_3OS_2$: C, 66.00; H, 4.89; N, 13.58. Found: C, 65.97; H, 4.96; N, 13.43.

3-Methyl-2-[methylthio(2-hydroxy-2-(2,6-dichlorophenyl)ethylimino)-methylimino]-2,3-dihydrobenzothiazole (13b) This compound was synthesized from **2** and **11f** in 86% yield in a manner similar to that described for the preparation of a mixture of **13a** and **14a**. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 135—138 °C. IR ν_{max}^{KBr} cm^{-1}: 2920, 1540, 1470, 1430, 1410, 1190. UV λ_{max}^{EtOH} nm (log ε): 316 (4.42), 274 (3.89), 260 (3.91), 222 (4.58). ^{1}H-NMR ($CDCl_3$) δ: 2.58 (3H, s, SMe), 3.39 (1H, br s, OH), 3.73 (1H, dd, J=14.0, 4.9 Hz, CH_2), 3.74 (3H, s, NMe), 4.09 (1H, dd, J=14.0, 9.7 Hz, CH_2), 5.78—5.88 (1H, m, C<u>H</u>(OH)), 7.11—7.56 (7H, m, aromatic-H). FAB-MS m/z: 426 (M^+). *Anal.* Calcd for $C_{18}H_{17}Cl_2N_3OS_2$: C, 50.70; H, 4.02; N, 9.86. Found: C, 50.80; H, 4.03; N, 10.12.

3-Methyl-2-[methylthio(2-hydroxy-2-(3-pyridyl)ethylimino)methylimino]-2,3-dihydrobenzothiazole (13c) This compound was synthesized from **2** and **11j** in 82% yield in a manner similar to that described for the preparation of a mixture of **13a** and **14a**. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 147—149 °C. IR ν_{max}^{neat} cm^{-1}: 2920, 2850, 1560, 1530, 1470, 1405, 1180. UV λ_{max}^{EtOH} nm (log ε): 310 (4.47), 281 (4.01), 269 (4.00), 263 (3.99), 218 (4.55). ^{1}H-NMR ($CDCl_3$) δ: 2.58 (3H, s, SMe), 3.50 (1H, dd, J=14.2, 8.6 Hz, CH_2), 3.62 (1H, br s, OH), 3.72 (1H, dd, J=14.2, 3.6 Hz, CH_2) 3.75 (3H, s, NMe), 5.04—5.13(1H, m, C<u>H</u>(OH)), 7.17—7.60 (5H, m, 5-H on pyridine ring and aromatic-H), 7.83 (1H, d, J=8.0 Hz, 4-H on pyridine ring), 8.53 (1H, dd, J=4.8, 1.7 Hz, 6-H on pyridine ring), 8.72 (1H, d, J=2.3 Hz, 2-H on pyridine ring). FAB-MS m/z: 359 ($M^+ + 1$). *Anal.* Calcd for $C_{17}H_{18}N_4OS_2$: C, 56.96; H, 5.06; N, 15.63. Found: C, 57.12; H, 5.04; N, 15.59.

3-Methyl-2-[methylthio(2-benzoyl-2-hydroxy-2-phenylethylimino)-methylimino]-2,3-dihydrobenzothiazole (13d) ^{1}H-NMR ($CDCl_3$) δ: 2.55 (3H, s, SMe), 3.56 (1H, d, J=14.0 Hz, CH_2), 3.69 (3H, s, NMe), 4.52 (1H, d, J=14.0 Hz, CH_2), 7.15—7.66 (12H, m, aromatic-H), 7.94 (2H, d, J=1.3 Hz, 2′- and 6′-H on benzoyl). FAB-MS m/z: 462 ($M^+ + 1$).

3-Methyl-2-[5-(2,6-dichlorophenyl)oxazol-2-ylimino]-2,3-dihydrobenzothiazole (14b) This compound was synthesized from **13b** in 78% yield in a manner similar to that described for the conversion of **13a** to **14a**. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 181—185 °C. IR ν_{max}^{neat} cm^{-1}: 3050, 2930, 2860, 1620, 1545, 1470, 1410, 1380, 1295. UV λ_{max}^{EtOH} nm (log ε): 351 (3.24), 307 (4.50), 282 (4.11), 219 (4.65), 203(4.74). ^{1}H-NMR ($CDCl_3$) δ: 3.72 (3H, s, NMe), 4.14 (1H, dd, J=13.3, 9.5 Hz, 4-H on oxazoline ring), 4.43 (1H, dd, J=13.3, 10.6 Hz, 4-H on oxazoline ring), 6.31 (1H, dd, J=10.6, 9.5 Hz, 5-H on oxazoline ring), 7.15—7.58 (7H, m, aromatic-H). MS m/z: 379 ($M^+ + 1$, 28), 378 (M^+, 9), 377 ($M^+ - 1$, 40), 203 (100), 191 (54), 175 (51). *Anal.* Calcd for $C_{17}H_{13}Cl_2N_3OS$: C, 53.98; H, 3.46; N, 11.11. Found: C, 53.96; H, 3.57; N, 11.15.

3-Methyl-2-[5-(3-pyridyl)oxazol-2-ylimino]-2,3-dihydrobenzothiazole (14c) This compound was synthesized from **13c** in 90% yield in a manner similar to that described for the conversion of **13a** to **14a**. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 168—170 °C. IR ν_{max}^{neat} cm^{-1}: 3050, 2930, 2860, 1615, 1540, 1470, 1410, 1300. UV λ_{max}^{EtOH} nm (log ε): 308 (4.48), 281 (4.05), 271 (3.98), 217 (4.56). ^{1}H-NMR ($CDCl_3$) δ: 3.75 (3H, s, NMe), 3.96 (1H, dd, J=13.5, 7.7 Hz, 4-H on oxazoline ring), 4.47 (1H, dd, J=13.5, 9.7 Hz, 4-H on oxazoline ring), 5.59 (1H, dd, J=9.7, 7.7 Hz, 5-H on oxazoline ring), 7.19—7.58 (5H, m, 5-H on pyridine ring and aromatic-H), 7.74 (1H, d, J=8.0 Hz, 4-H on pyridine ring), 8.56 (1H, dd, J=4.8, 1.7 Hz, 6-H on pyridine ring), 8.62 (1H, d, J=2.3 Hz, 2-H on pyridine ring). MS m/z: 310 (M^+, 73), 203 (100), 191 (56), 175 (67). *Anal.* Calcd for $C_{16}H_{14}N_4OS$: C, 61.91; H, 4.55; N, 18.05. Found: C, 61.83; H, 4.58; N, 17.86.

3-Methyl-2-(5-benzoyl-5-phenyloxazol-2-ylimino)-2,3-dihydrobenzothiazole (14d) This compound was synthesized from **2** and **11l** in 44% yield in a manner similar to that described for the preparation of **14a**. An analytical sample was recrystallized from *n*-hexane–ethyl acetate to give pale yellow prisms, mp 192—194 °C. IR ν_{max}^{KBr} cm^{-1}: 3050, 2910, 2860, 1680, 1620, 1540, 1470, 1410, 1300. UV λ_{max}^{EtOH} (insufficient solubility): 309, 280, 217. ^{1}H-NMR ($CDCl_3$) δ: 3.72 (3H, s, NMe), 4.05 (1H, d, J=13.3 Hz , 4-H on oxazoline ring), 5.17 (1H, d, J=13.3 Hz, 4-H on oxazoline ring), 7.15—7.66 (12H, m, aromatic-H), 8.03 (2H, d, J=1.3 Hz, 2′- and 6′-H on benzoyl). MS m/z: 413 (M^+, 8), 308 (100). *Anal.* Calcd for $C_{24}H_{19}N_3O_2S$: C, 69.71; H, 4.63; N, 10.16. Found: C, 69.46; H, 4.79; N, 10.09.

3-Methyl-2-(5-propyloxazol-2-ylimino)-2,3-dihydrobenzothiazole (14e) This compound was synthesized from **2** and **11n** in 36% yield in a manner similar to that described for the preparation of **14a**. An analytical sample was chromatographed on an alumina(Merck, Aluminum oxide 90 active, basic) column with *n*-hexane–ethyl acetate (1 : 3) to give a pale yellow viscous oil. IR ν_{max}^{film} cm^{-1}: 2955, 2940, 2860, 1610, 1550, 1475, 1415, 1300, 1230. UV λ_{max}^{EtOH} nm (log ε): 306 (4.39), 219 (4.45). ^{1}H-NMR ($CDCl_3$) δ: 0.94 (3H, t, J=7.2 Hz, –CH_2<u>Me</u>), 1.22—1.85 (4H, m, –$(CH_2)_2$–), 3.64 (1H, dd, J=13.2, 7.8 Hz, 4-H on oxazoline ring), 3.70 (3H, s, NMe), 4.09 (1H, dd, J=13.2, 9.2 Hz, 4-H on oxazoline ring), 4.54—4.66 (1H, m, 5-H on oxazoline ring), 7.14—7.55 (4H, m, aromatic-H). MS m/z: 275 (M^+, 25), 203 (12), 191 (100), 175 (20). *Anal.* HR-MS Calcd for $C_{14}H_{17}N_3OS$ m/z: 275.1093. Found m/z: 275.1097.

3-Methyl-2-[methylthio(2,3-bis(methoxycarbonyl)propylimino)methylimino]-2,3-dihydrobenzothiazole (16) This compound was obtained from **2** and dimethyl fumarate (**15**) in 35% yield in a similar manner to that described for a mixture of **13a** and **14a**. An analytical sample was chromatographed on a silica gel (Merck, Silica gel 60) column with *n*-hexane–ethyl acetate (3 : 1) to give a pale yellow viscous oil. IR ν_{max}^{film} cm^{-1}: 2950, 1735, 1570, 1530, 1475, 1435, 1415, 1350. UV λ_{max}^{EtOH} nm (log ε): 317 (4.48), 259 (3.95), 224 (4.51). ^{1}H-NMR ($CDCl_3$) δ: 2.57 (3H, s, SMe), 2.70—3.00 (2H, m, –CH_2–), 3.10—3.45 (2H, m, –CH_2–), 3.50—3.70 (1H, m, CH), 3.70 (6H, s, 2×CO_2Me), 3.73 (3H, s, NMe), 7.10—7.59 (4H, m, aromatic-H). MS m/z: 395 (M^+, 4), 279 (20), 251 (55), 204 (100). *Anal.* Calcd for $C_{17}H_{21}N_3O_4S_2$: C, 51.63; H, 5.35; N, 10.63. Found: C, 51.68; H, 5.26; N, 10.66.

References and Notes

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