Formal [3 + 2] Cycloaddition Reactions of 1-Methyl-2-[methylthio-(trimethylsilylmethylimino)methylimino]-1,2-dihydropyridine and Related Compound with Carbonyl Compounds Promoted by Fluoride Ion¹⁾

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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 ylids⁶⁾ and iminoazomethine ylids⁷⁾ can be generated by 1,3-elimination reaction of *N*-(trimethylsilylmethyl)-substituted ketene *N,S*-acetals and isothiouras 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.

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 (¹H-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-dihydrobenzothiazole (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 1

Chart 2

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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 ₆ H ₅	H	(11a) 71 (12a)
2	4-C ₆ H ₅ C ₆ H ₄	H	(11b) 73 (12b)
3	4-MeC ₆ H ₄	H	(11c) 71 (12c)
4	4-MeOC ₆ H ₄	H	(11d) 57 (12d)
5	4-ClC ₆ H ₄	H	(11e) 73 (12e)
6	2,6-Cl ₂ C ₆ H ₃	H	(11f) 77 (12f)
7	4-NCC ₆ H 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	(<i>E</i>)-C ₆ H ₄ CH=CH	H	(11k) 38 ^{d)} (12k)
12	C ₆ H ₅	C ₆ H ₅ CO	(11l) 42 (12l)
13			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)amino-oxazoline 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 ₆ H ₅	H	(11a) 1.0	67 (12a)
2	C ₆ H ₅	H	(11a) 0.1	71 (12a)
3	4-MeOC ₆ H ₄	H	(11d) 0.1	38 (12d)
4	4-ClC ₆ H ₄	H	(11e) 0.1	76 (12e)
5	4-NCC ₆ H ₄	H	(11g) 0.1	41 (12g)
6	C ₆ H ₅	C ₆ H ₅ CO	(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 ₆ H ₅	H	—	(13a)	85 (14a)
2	2,6-Cl ₂ C ₆ H ₃	H	86	(13b)	67 (14b)
3	3-Pyridyl	H	82	(13c)	74 (14c)
4	C ₆ H ₅	C ₆ H ₅ CO	—	(13d)	44 (14d)
5	C ₃ H ₇	H	—		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(trimethylsilyl)methylimino]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 MgSO₄. 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 $\nu_{\text{max}}^{\text{neat}}$ cm⁻¹: 2950, 1640, 1600, 1550, 855. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 336 (4.26), 275 (4.00). ¹H-NMR (CDCl₃) δ : major isomer: 0.04 (9H, s, SiMe₃), 2.34 (3H, s, SMe), 2.99 (2H, s, NCH₂Si), 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, SiMe₃), 2.30 (3H, s, SMe), 3.15 (2H, s, NCH₂Si), 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 C₁₂H₂₁N₃SSi: C, 53.88; H, 7.92; N, 15.71. Found: C, 53.90; H, 7.83; N, 15.69.

3-Methyl-2-[methylthio(trimethylsilyl)methylimino]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 $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 2950, 1560, 1540, 1470, 860. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 320 (4.40), 262 (3.96), 226 (4.51). ¹H-NMR (CDCl₃) δ : 0.13 (9H, s, SiMe₃), 2.57 (3H, s, SMe), 3.21 (2H, s, NCH₂Si), 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 C₁₄H₂₁N₃S₂Si: 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 MgSO₄. 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 $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 2900, 2850, 1640, 1610, 1555, 1380, 1120, 1050. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 330 (4.23), 264 (3.92). ¹H-NMR (CDCl₃) 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 C₉H₁₃N₃S: 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 $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 2920, 2840, 1580, 1535, 1470, 1345. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 316 (4.42), 273 (3.85), 224 (4.50). ¹H-NMR (CDCl₃) 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 C₁₁H₁₃N₃S₂: 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 MgSO₄. 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 $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3075, 2905, 2855, 1635, 1595, 1545, 1505, 1385, 1015. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 320 (4.17), 265 (4.17), 205 (4.47). ¹H-NMR (CDCl₃) 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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3010, 2905, 2850, 1635, 1595, 1540, 1520, 1445, 1380. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 324 (4.07), 260 (4.48), 206 (4.64). $^1\text{H-NMR}$ (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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2905, 2850, 1640, 1600, 1540, 1450, 1385. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 323 (3.99), 269 (4.12). $^1\text{H-NMR}$ (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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3075, 2900, 2850, 1635, 1595, 1545, 1505, 1015. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 319 (4.26), 263 (4.22), 229 (4.17). $^1\text{H-NMR}$ (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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2945, 2860, 1640, 1600, 1540, 1385. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 323 (4.06), 268 (4.98). $^1\text{H-NMR}$ (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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3075, 2925, 2860, 1635, 1600, 1540, 1505, 1385, 1300, 1220, 1010. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 322 (4.10), 268 (4.17), 205 (4.66). $^1\text{H-NMR}$ (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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3100, 2950, 2855, 2210, 1640, 1595, 1540, 1520, 1380. UV

$\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 328 (4.02), 271 (4.18), 232 (4.30). $^1\text{H-NMR}$ (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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3075, 2905, 2855, 1635, 1595, 1545, 1505, 1385, 1015. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 328 (3.94), 271 (4.15), 222 (4.85). $^1\text{H-NMR}$ (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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3080, 2845, 1635, 1600, 1550, 1510, 1390, 1295, 1015. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 320 (4.20), 263 (4.13). $^1\text{H-NMR}$ (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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3080, 2905, 2855, 1635, 1595, 1545, 1505, 1385, 1300, 1215, 1015. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 360 (3.61), 319 (4.19), 262 (4.22). $^1\text{H-NMR}$ (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 $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 2910, 2855, 1635, 1595, 1540, 1520, 1505, 1450, 1385. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 322 (4.11), 263 (4.32). $^1\text{H-NMR}$ (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, $-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$ and 5'-H on pyridine ring), 6.62 (1H, d, $J=15.8$ Hz, $-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$), 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 $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3040, 2905, 2855, 1635, 1595, 1540, 1520, 1505, 1385. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 332 (4.04), 256 (4.29). $^1\text{H-NMR}$ (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)aminoxazoline-5-spiro-1'-methyl-2'-oxindole (12m) Yield was 67%. An analytical sample was recrystallized from *n*-hexane-ethyl acetate to give pale brown prisms, mp 204–205 °C. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3075, 2905, 2855, 1725, 1640, 1615, 1545, 1530, 1460, 1360, 1235, 998. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 335 (4.04), 270 (4.26), 212 (4.58), 201 (4.51). ¹H-NMR (CDCl₃) 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 C₁₇H₁₆N₄O₂: 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 MgSO₄. 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 Al₂O₃ 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) ¹H-NMR (CDCl₃) δ : 2.53 (3H, s, SMe), 3.30–3.76 (6H, m, NMe, CH₂, and OH), 5.05 (1H, dd, J = 8.6, 4.0, CH(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 $\nu_{\text{max}}^{\text{neat}}$ cm⁻¹: 2920, 2860, 1615, 1540, 1470, 1410, 1300. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 307 (4.49), 282 (4.07), 217 (4.61). ¹H-NMR (CDCl₃) 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 C₁₇H₁₅N₃O₂S: 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 $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 2920, 1540, 1470, 1430, 1410, 1190. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 316 (4.42), 274 (3.89), 260 (3.91), 222 (4.58). ¹H-NMR (CDCl₃) δ : 2.58 (3H, s, SMe), 3.39 (1H, br s, OH), 3.73 (1H, dd, J = 14.0, 4.9 Hz, CH₂), 3.74 (3H, s, NMe), 4.09 (1H, dd, J = 14.0, 9.7 Hz, CH₂), 5.78–5.88 (1H, m, CH(OH)), 7.11–7.56 (7H, m, aromatic-H). FAB-MS m/z : 426 (M⁺). Anal. Calcd for C₁₈H₁₇Cl₂N₃O₂S: 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 $\nu_{\text{max}}^{\text{neat}}$ cm⁻¹: 2920, 2850, 1560, 1530, 1470, 1405, 1180. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 310 (4.47), 281 (4.01), 269 (4.00), 263 (3.99), 218 (4.55). ¹H-NMR (CDCl₃) δ : 2.58 (3H, s, SMe), 3.50 (1H, dd, J = 14.2, 8.6 Hz, CH₂), 3.62 (1H, br s, OH), 3.72 (1H, dd, J = 14.2, 3.6 Hz, CH₂), 3.75 (3H, s, NMe), 5.04–5.13 (1H, m, CH(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 C₁₇H₁₈N₄O₂S: 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) ¹H-NMR (CDCl₃) δ : 2.55 (3H, s, SMe), 3.56 (1H, d, J = 14.0 Hz, CH₂), 3.69 (3H, s, NMe), 4.52 (1H, d, J = 14.0 Hz, CH₂), 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 $\nu_{\text{max}}^{\text{neat}}$ cm⁻¹: 3050, 2930, 2860, 1620, 1545, 1470, 1410, 1380, 1295. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 351 (3.24), 307 (4.50), 282 (4.11), 219 (4.65), 203 (4.74). ¹H-NMR (CDCl₃) 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 C₁₇H₁₃Cl₂N₃O₂S: 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 $\nu_{\text{max}}^{\text{neat}}$ cm⁻¹: 3050, 2930, 2860, 1615, 1540, 1470, 1410, 1300. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 308 (4.48), 281 (4.05), 271 (3.98), 217 (4.56). ¹H-NMR (CDCl₃) 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 C₁₆H₁₄N₄O₂S: 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 **11i** 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 $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3050, 2910, 2860, 1680, 1620, 1540, 1470, 1410, 1300. UV $\lambda_{\text{max}}^{\text{EtOH}}$ (insufficient solubility): 309, 280, 217. ¹H-NMR (CDCl₃) 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 C₂₄H₁₉N₃O₂S: 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 $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 2955, 2940, 2860, 1610, 1550, 1475, 1415, 1300, 1230. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 306 (4.39), 219 (4.45). ¹H-NMR (CDCl₃) δ : 0.94 (3H, t, J = 7.2 Hz, -CH₂Me), 1.22–1.85 (4H, m, -(CH₂)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 C₁₄H₁₇N₃O₂S: 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 $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 2950, 1735, 1570, 1530, 1475, 1435, 1415, 1350. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 317 (4.48), 259 (3.95), 224 (4.51). ¹H-NMR (CDCl₃) δ : 2.57 (3H, s, SMe), 2.70–3.00 (2H, m, -CH₂-), 3.10–3.45 (2H, m, -CH₂-), 3.50–3.70 (1H, m, CH), 3.70 (6H, s, 2 × CO₂Me), 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 C₁₇H₂₁N₃O₄S₂: 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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