N-Bis(methylthio)methylene Derivatives. VII.[1,2] Syntheses and Reactions of Synthetic Equivalents of New 1,3-Dipolar Reagents Using *N*-Bis(methylthio)methylene Derivatives

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N-Cyano- or N-(p-toluenesulfonyl)-N′-(trimethylsilylmethyl)-S-methylisothioureas (3, 4), readily prepared by reactions of S,S′-dimethyl N-cyano- (1a) and S,S′-dimethyl N-(p-toluenesulfonyl)- (1b) carbonimidodithioates with trimethylsilylmethylamine (2a), followed by N-alkylation, have been found to provide synthetic equivalents of iminoazomethine ylide. Treatment of these compounds with cesium fluoride in the presence of reactive hetero-dipolarophiles such as carbonyl compounds afforded 1,3-dipolar cycloadducts, 4,5-dihydro-2-iminooxazoles and 4,5-dihydro-2-iminothiazoles, *via* the 1,3-elimination of (methylthio)trimethylsilane.

S-Methyl-S′-trimethylsilylmethyl N-cyano- (5a) and N-(p-toluene-sulfonyl)- (5b) carbonimidodithioates, also readily prepared from the corresponding 1a and 1b with (mercaptomethyl)trimethylsilane (2b), were used as new reagents for introducing a thioformaldehyde unit at a carbonyl carbon. Reactions of these compounds with aldehydes in the presence of cesium fluoride afforded thiiranes *via* the 1,3-dipolar cycloaddition of iminothiocarbonyl ylide to the C=O double bond. Reactions of 5 with dimethyl fumarate and maleate in the presence of cesium fluoride in acetonitrile gave 1,3-dipolar cycloadducts, dimethyl 2-(N-(p-toluenesulfonyl)imino)tetrahydrothiophene-3,4-dicarboxylates.

Key words iminoazomethine ylide; iminothiocarbonyl ylide; 1,3-dipolar cycloaddition; oxazole; thiirane; oxathiolane

The 1,3-dipolar cycloaddition reaction is very important from a synthetic point of view for obtaining five-membered heterocycles.[3] In this reaction, azomethine and thiocarbonyl ylides are widely used for the preparation of *N*- and *S*-containing five-membered heterocycles. Tailor-made alkylideneazomethine ylides were previously obtained by the 1,3-elimination reaction of *N*-(trimethylsilylmethyl)-substituted ketene *N*,*S*-acetals promoted by fluoride ion, and [3+2] cycloaddition to various dipolarophiles of azomethine ylides is possible by the addition–elimination reactions of trimethylsilylmethylamine with the corresponding ketene dithioacetals.[4] Our studies on the potential use of new silicon-based 1,3-dipolar synthons in 1,3-elimination reaction[5] have indicated that *N*-(silylmethyl)-substituted isothioureas (**3** and **4**), and *S*-methyl-*S′*-trimethylsilylmethyl *N*-cyano- (**5a**) and *N*-(*p*-toluenesulfonyl)- (**5b**) carbonimidodithioates are useful precursors for obtaining previously unknown and otherwise inaccessible imino azomethine and iminothiocarbonyl ylides. The present paper describes the preparation of *N*-(trimethylsilylmethyl)isothioureas (**3**, **4**), *S*-methyl-*S′*-trimethylsilylmethyl *N*-cyano- (**5a**) and *N*-(*p*-toluenesulfonyl)- (**5b**) carbonimidodithioates and 1,3-dipolar cycloaddition reactions with various dipolarophiles to give the corresponding heterocycles.

Preparation of Synthetic Equivalents of 1,3-Dipolar Reagents Dimethyl *N*-cyano- and *N*-(*p*-toluenesulfonyl)-carbonimidodithioates (**1a**[6] and **1b**[7]), readily available from the reaction of cyanamide or *p*-toluenesulfonamide and carbon disulfide, respectively, in the presence of sodium hydroxide followed by methylation with methyl iodide, are quite useful for the synthesis of heterocyclic compounds, like ketene dithioacetals.[8] Carbonimidodithioates **1a** and **b** smoothly react with various nucleophiles such as amines or active methylene compounds to give the corresponding displacement products of the methylthio group in good yields.

Reaction of **1a** with trimethylsilylmethylamine (**2a**) in methanol under reflux for 10 min gave the corresponding mono displacement product of a methylthio group, *N*-(trimethylsilylmethyl)isothiourea (**3a**), in 94% yield. Reaction of **1b** with trimethylsilylmethylamine (**2a**) gave the corresponding product, **3b**, in 95% yield.

The *N*-alkylation of **3a**, **b** with alkyl halides (methyl iodide and benzyl bromide) proceeded easily in the presence of potassium carbonate in acetone at room

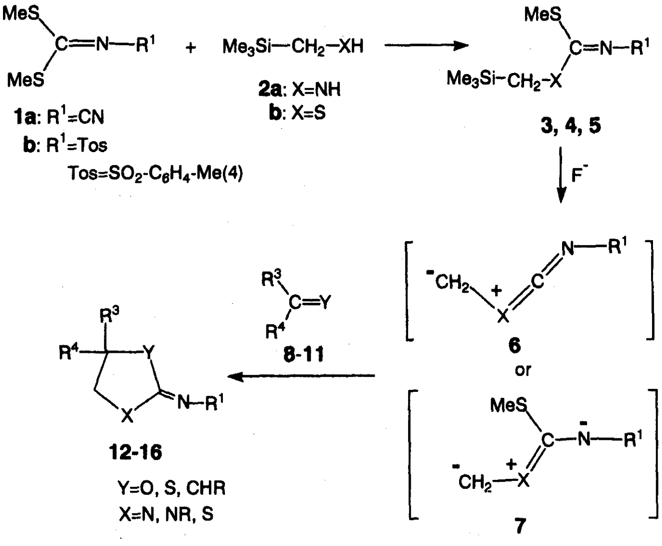

Chart 1

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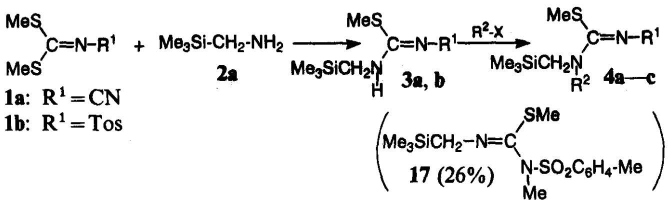
Table 1. Preparation of *N*-Cyano- or *N*-(*p*-toluenesulfonyl)-*N*′-(trimethylsilylmethyl)-*S*-methylisothiourea Derivatives **3** and **4**



No.	R^1	R^2X	Conditions	Yield (%)*a*)	mp (°C)
3a	CN	—	MeOH, r.t.—60 °C, 20 min	94	166
3b	Tos	—	MeOH, reflux, 30 min	95	63
4a	CN	MeI	Acetone, K_2CO_3, r.t., 48 h	91	—*b*)
4b	CN	$C_6H_5CH_2Br$	Acetone, K_2CO_3, r.t., 48 h	93	—*b*)
4c	Tos	MeI	Acetone, K_2CO_3, r.t., 7 d	50	—*b*)

a) Isolated yield. *b*) Colorless oil. r.t. = room temperature.

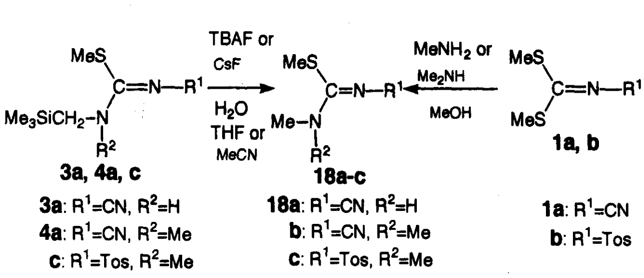


Chart 2

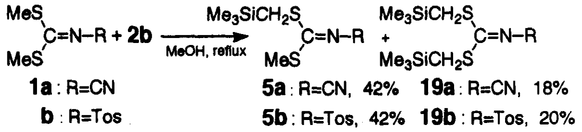
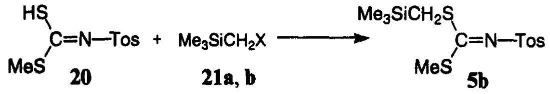


Chart 3

Table 2. Preparation of *S*-Methyl-*S*′-trimethylsilylmethyl *N*-(*p*-Toluenesulfonyl)carbonimidodithioate (**5b**)



Entry	X	Conditions	Yield (%)*a*)
1	Cl	NaH, THF, r.t., 45 h	0
2	I	NaH, THF, r.t., 20 h	0
3	Cl	NaH, THF, reflux, 15 h	0
4	Cl	NaOH, EtOH, reflux, 26 h	59
5	Cl	NaI, NaOH, EtOH, 70 °C, 20 h	71

a) Yield following isolation by silica gel column chromatography. r.t. = room temperature.

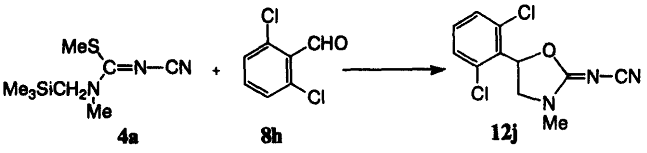
temperature to afford the corresponding *N*-alkylate derivatives (**4a**—**c**) in high yields. In the methylation of **3b** with methyl iodide, compound **17** was obtained along with **4c** in 26% yield. Treatment of **3a** with tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) gave the desilyl protonation product, **18a**, which was identical with *N*-cyano-*N*′,*S*-dimethylisothiourea prepared by the reaction of **1a** with methylamine. Compound **18b** was also prepared in good yield by treatment of **4a** with cesium fluoride in acetonitrile containing water. This desilyl protonation strongly suggests the formation of thiocarbanion species.

An attempt was made to prepare *S*-methyl-*S*′-trimethylsilylmethyl *N*-cyanocarbonimidodithioate (**5a**) by the addition–elimination reaction of (mercaptomethyl) trimethylsilane (**2b**) to *S*,*S*′-dimethyl *N*-cyanocarbonimidodithioate (**1a**). An alternative synthesis of **5a** from the corresponding *S*-methyl *N*-cyanocarbonimidodithioate and (chloromethyl)trimethylsilane could not be carried out successfully, different from the preparation of **5a** from *S*-methyl *N*-(*p*-toluenesulfonyl)carbonimidodithioate (**20**), owing to the considerable instability of the corresponding iminodithiocarbonate.

Reaction of **1a** with **2b** in methanol gave a separable mixture of *S*-methyl-*S*′-trimethylsilylmethyl *N*-cyanocarbonimidodithioate (**5a**) and *S*,*S*′-bis(trimethylsilylmethyl) *N*-cyanocarbonimidodithioate (**19a**) in 42 and 18% yields, respectively. This reaction of **1b** with **2b** in methanol gave an easily separable mixture of *S*-methyl-*S*′-trimethylsilylmethyl *N*-(*p*-toluenesulfonyl)carbonimidodithioate (**5b**) and *S*,*S*′-bis(trimethylsilylmethyl) *N*-(*p*-toluenesulfonyl)carbonimidodithioate (**19b**) in 42 and 20% yields, respectively. The desired **5b** was obtained alternatively and more conveniently by treatment of **20** with (chloromethyl)trimethylsilane (**21a**). At the start of the present study, reactions of **20** with **21a, b** were studied under various basic conditions and results are summarized in Table 2. Reaction of **20** with **21a** in the presence of sodium iodide and sodium hydroxide in ethanol at reflux temperature for 20 h gave the best results. The yield of **5a** in this reaction was 71%.

1,3-Dipolar Cycloaddition Reactions of Iminoazomethine Ylides Alkylideneazomethine ylides should be easily obtainable by the fluoride ion-promoted 1,3-elimination reaction of (trimethylsilyl)methyl sulfide under mild conditions, as well as various 1,3-dipolar reagents such as iminoazomethine ylides and related species. In this study, reactions of **4a** with 2,6-dichlorobenzaldehyde (**8h**) in the presence of various fluoride ions were conducted to obtain 2-cyanoimino-5-(2,6-dichlorophenyl)-4,5-dihydro-oxazole (**12j**). The results are shown in Table 3. Cesium fluoride as the fluoride ion source gave the best results in the reaction of **4a** with **8h** at room temperature in acetonitrile. Other fluoride ion sources such as TBAF also served well

Table 3. Reaction of *N*-Cyano-*N'*-methyl-*N'*-trimethylsilylmethylisothiourea (**4a**) with 2,6-Dichlorobenzaldehyde (**8h**)

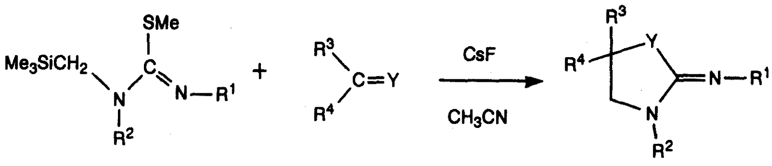


4a **8h** **12j**

Entry	**4a** (mmol)	**8h** (mmol)	Conditions	**12j** Yield (%)[a]
1	0.50	1.00	CsF(1.2 eq.), MeCN, r.t., 20 h	68
2	0.50	1.00	CsF(1.2 eq.), MeCN, 60 °C, 4 h	61
3	0.50	1.00	TBAF(1.0 eq.), THF, r.t., 20 h	40
4	0.50	1.00	TMSOTf(1.2 eq.), CH_2Cl_2, −55 °C, −r.t., 48 h	0
5	0.50	1.00	$BF_3 \cdot OEt_2$(1.2 eq.), CH_2Cl_2, −55 °C, −r.t., 48 h	0
6	0.50	1.00	TFAA(1.2 eq.), MeCN, r.t., 20 h	0
7	0.50	1.50	CsF(1.2 eq.), MeCN, r.t., 20 h	78
8	0.50	1.50	CsF(3.0 eq.), MeCN, r.t., 20 h	77

a) Yield following isolation by silica gel column chromatography. r.t. = room temperature.

Table 4. Reaction of *N*-Substituted *N'*-(Trimethylsilylmethyl)-*S*-methylisothiourea Derivatives with Carbonyl Compounds[a]



3a, b, 4a—c **8—10** **12a—q, 13a—d, 14**

Entry	R^1	R^2	R^3	R^4	Y	Product	mp (°C)	Yield (%)
1	CN	H	H	C_6H_5 (**8a**)	O	**12a**	127	41
2	CN	H	H	4-$C_6H_5C_6H_4$ (**8i**)	O	**12b**	202	62
3	CN	H	H	2,6-$Cl_2C_6H_3$ (**8h**)	O	**12c**	226	84
4	Tos	H	H	C_6H_5 (**8a**)	O	**12d**	169	42
5	Tos	H	H	4-$C_6H_5C_6H_4$ (**8i**)	O	**12e**	167	45
6	Tos	H	H	2,6-$Cl_2C_6H_3$ (**8h**)	O	**12f**	213	61
7	CN	Me	H	C_6H_5 (**8a**)	O	**12g**	133	77
8	CN	Me	H	4-ClC_6H_4 (**8g**)	O	**12h**	144	74
9	CN	Me	H	4-$MeOC_6H_4$ (**8f**)	O	**12i**	109	86
10	CN	Me	H	2,6-$Cl_2C_6H_3$ (**8h**)	O	**12j**	237	78
11	CN	Me	H	4-$C_6H_5C_6H_4$ (**8i**)	O	**12k**	193	81
12	CN	Me	H	4-$NO_2C_6H_4$ (**8l**)	O	**12l**	133	55
13	CN	Me	H	1-naphthyl (**8j**)	O	**12m**	133	63
14	CN	Me	H	(*E*)-$C_6H_5CH=CH$ (**8m**)	O	**12n**	165	60
15	CN	Me	H	$CH_3(CH_2)_3$ (**8n**)	O	**12o**	Oil	70
16	CN	$CH_2C_6H_5$	H	C_6H_5 (**8a**)	O	**12p**	Oil	66
17	Tos	Me	H	C_6H_5 (**8a**)	O	**12q**	178	52
18	CN	Me	C_6H_5	C_6H_5 (**9a**)	O	**13a**	168	40
19	CN	Me	C_6H_5	COC_6H_5 (**9b**)	O	**13b**	165	35
20	CN	$CH_2C_6H_5$	C_6H_5	C_6H_5 (**9a**)	O	**13c**	135	48
21	Tos	Me	C_6H_5	C_6H_5 (**9a**)	O	**13d**	179	34
22	CN	Me	4-$MeOC_6H_4$	2-Benzo[*b*]thienyl (**10**)	S	**14**	252	38

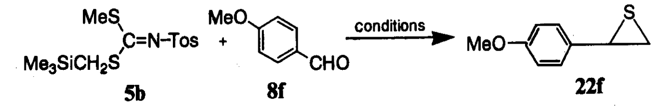
a) All reactions were carried out in a system of **3** or **4** (0.5 mmol), **8**, **9**, or **10** (1.5 mmol), and CsF (0.6 mmol) in MeCN. *b*) Yield following isolation by silica gel column chromatography.

as catalysts to give the corresponding **12j**, while lithium fluoride and silver fluoride were not effective for this 1,3-dipolar cycloaddition. Acids such as trimethylsilyl trifluoromethanesulfonate, iodotrimethylsilane, or trifluoroacetic acid did not promote the reaction. Thus, cesium fluoride was used as the main fluoride ion source in subsequent experiments.

The reaction of **4a** with two equivalents of **8h** proceeded smoothly in acetonitrile at room temperature for 20 h to afford the 4,5-dihydro-2-iminooxazole derivative (**12c**) in 68% yield. The reaction time could be shortened to 6 h without any decrease in yield at higher temperature (*ca.* 60 °C). Yields of cycloadducts were increased to 78% through the use of three equivalents of **8h** with respect to **4a**.

Not only *N*-substituted isothioureas (**4a—c**) but also *N*-unsubstituted isothioureas (**3a, b**) react effectively with aldehydes **8** and ketones **9**. As summarized in Table 4, isothioureas (**3a, b** and **4a—c**) react smoothly with aldehydes (**8**) in the presence of cesium fluoride to give

Table 5. Reaction of *S*-Methyl-*S*'-trimethylsilylmethyl *N*-*p*-Toluenesulfonylcarboimidodithioate (**5b**) with 4-Methoxybenzaldehyde (**8f**)



Entry	**5b** (mmol)	**8f** (mmol)	Conditions (eq)	Yield (%)[a]
1	0.50	0.50	CsF (1.2), MeCN, r.t., 43 h	19
2	0.50	1.00	CsF (1.2), MeCN, r.t., 43 h	18
3	0.50	1.50	CsF (1.2), MeCN, r.t., 43 h	75
4	0.50	1.50	CsF (1.2), r.t., 47 h	52
5	0.50	1.50	CsF (1.2), BF_3, Et_2O (1.0), MeCN, r.t., 43 h	36
6	0.50	1.50	TBAF (0.1), THF, r.t., 20 h	19
7	0.50	1.50	TBAF (1.0), THF, r.t., 20 h	0
8	0.50	1.50	AgF (1.2), MeCN, r.t., 43 h	0
9	0.50	1.50	TASF (1.0), THF, r.t., 22 h	30

a) Determined by NMR. r.t. = room temperature.

α-imino-substituted [3+2] cycloadducts (**12a**—**q**). Reaction of **4** with ketones (**9a, b**) was found in this study to give 5,5'-disubstituted 4,5-dihydro-2-iminooxazole derivatives (**13a**—**d**). Various aromatic aldehydes and ketones possessing electron-donating and electron-withdrawing substituents and α,β-unsaturated aldehyde reacted with **3** and **4** to give 4,5-dihydro-2-iminooxazoles **12** and **13**, respectively, in modest to high yields. The thioketone **10** was found to be a good acceptor in the present [3+2] cycloaddition to provide 4,5-dihydro-2-iminothiazole **14**.

Reaction of **3a, b** and **4a, b** with activated alkenes in the presence of fluoride ion gave in each case a mixture of the desired cycloadducts and many unknown products not separable by TLC or silica gel column chromatography.[9]

1,3-Dipolar Cycloaddition of Iminothiocarbonyl Ylides α-Thiocarbanion species were previously shown to be readily generated by the fluoride ion-promoted desilylation of trimethylsilyl-methyl sulfides under mild conditions, in contrast to the rather drastic conditions required in the deprotonation of alkyl sulfides, requiring a strong lithium base.[10] As in the case of alkylidene- and imino-azomethine ylides derived by fluoride ion-promoted reactions of *N*-(trimethylsilylmethyl)substituted ketene *N*,*S*-acetals and their aza analogs, the generation of iminothiocarbonyl ylides and reactions with dipolarophiles should be studied for potential application to the synthesis of sulfur-containing heterocycles.

Reaction conditions were optimized to augment the yield of the thiirane **22f**, as shown in Table 5. Reaction of **5b** with 1 eq amount of 4-methoxybenzaldehyde (**8f**), promoted by cesium fluoride, proceeded in acetonitrile at room temperature for 43 h to afford 2-(4-methoxyphenyl)thiirane (**22f**) (19% yield), instead of the expected 2-imino-1,3-oxathiolane. The yield of **22f** was increased to 75% through the use of 3 eq of **8f**. This reaction was also carried out without solvent at room temperature, but the yield was only 52%. As shown in Table 6, **5b** reacted smoothly with various aldehydes (**8a**—**j**) to give 2-substituted thiiranes (**22a**—**j**). When **5b** reacted with 2,6-dichlorobenzaldehyde (**8h**) under the same reaction conditions, 5-(2,6-dichlorophenyl)-4,5-dihydro-2-(*p*-toluenesulfonyl)iminooxazole (**15a**) was obtained in 18% yield along with the thiirane derivative **22h** (Chart 4).

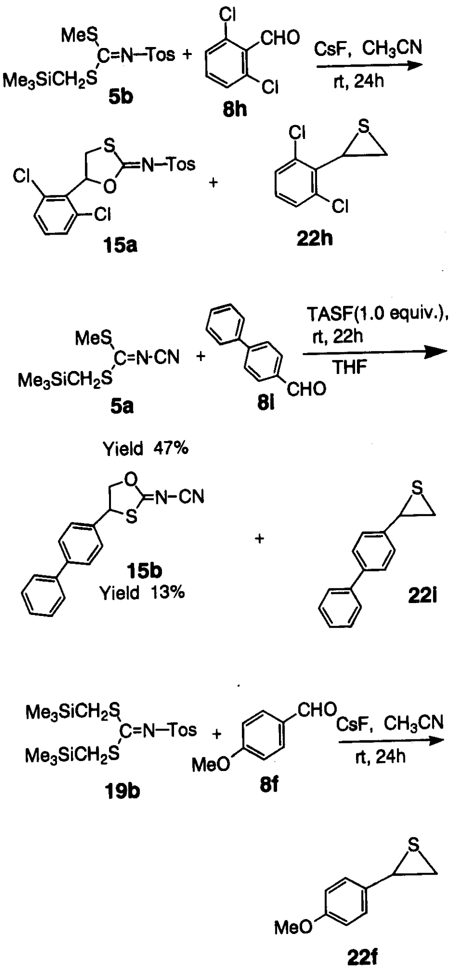


Chart 4

Thiiranes from **5b** appear quite likely to be formed *via* 1,3-dipolar [3+2] cycloaddition, as in the reactions of alkylidene- and iminoazomethine ylides with carbonyl compounds. Reaction of **5b** with 4-cyanobenzaldehyde (**8k**) gave 4-cyanostyrene (**23a**), in 35% yield, through desulfurization from a thiirane compound. In the reaction of **5b** with 4-nitrobenzaldehyde **8l**, the 4-nitrostyrene derivative (**23b**) was also obtained in 56% yield. The reaction pathway *via* **22** is proposed to be as shown in Chart 5.[11] Treatment of **5b** with fluoride ion generates

Reaction Pathway

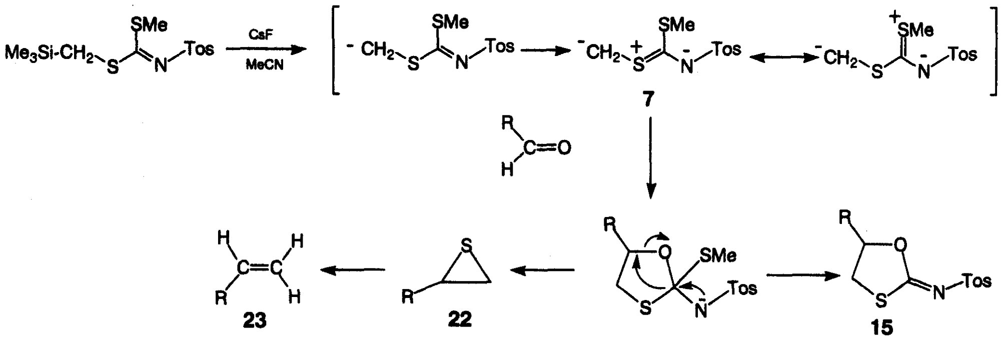
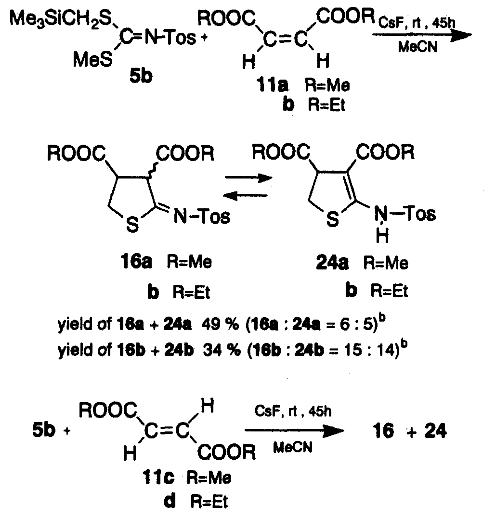


Chart 5



a) All reactions were carried out in a system of **5b**(1.0 mmol), **11** (3.0 mmol) and CsF(1.2 mmol) in MeCN(3 ml).
b) Determined by ^{1}H-NMR.

Chart 6

a novel 1,3-dipolar species (**7**) at the initial stage which adds to an aldehyde to form an anionic 1,3-oxathiolane intermediate. Ring construction of 1,3-oxathiolane gives the thiirane **22**, instead of a 4,5-dihydro-2-imino-1,3-oxathiolane **15**, *via* elimination of a methylthio group.

Compound **5a** reacted with various aldehydes (**8a, c, g, i, j**) to give thiirane derivatives **22a, c, g, i,** and **j** in 47—68% yields as shown in Table 6. Reaction of **5a** with **8k** gave 4-cyanostyrene (**23a**) in 56% yield. When **5a** reacted with **8i** in the presence of tris(dimethylamino)sulfur(trimethylsilyl)- difluoride (TASF) as the fluoride ion source, the oxathiolane derivative, **15b**, was obtained in 13% yield along with **22i**, in a manner similar to that noted for the preparation of **15a** from **5b** (Chart 4).

Compound **19b** bearing two trimethylsilylmethylthio groups was also of use as a 1,3-dipolar reagent in the reaction with the heterodipolarophile **8f** to give the thiirane **22f** in 32% yield.

Reaction of **5b** with activated alkenes in the presence of fluoride ion gave the corresponding [3+2] cycloadducts. To determine the stereo specificity of the reaction, the cycloaddition of **5b** with *cis* and *trans* disubstituted dipolarophiles was conducted. Thiocarbonyl ylides examined in the literature undergo stereospecific cycloaddition. Interestingly, treatment of **5b** with dimethyl maleate (**11a**) or dimethyl fumarate (**11c**) at room temperature for 20 h in the presence of cesium fluoride afforded the cycloadduct, dimethyl 2-*N*-(*p*-toluenesulfonyl)iminotetrahydrothiophene-3,4-dicarboxylate (**16a**), tautomeric with the 2-amino form **24a**, in this study. This tautomerism was nonstereospecific. Reaction of **5b** with diethyl maleate (**11b**) and diethyl fumarate (**11d**) gave cycloadducts **16b** and **24b** as shown in Chart 6.

N-(Silylmethyl)-substituted isothioureas (**3** and **4**) and *S*-methyl-*S*′-trimethylsilylmethyl *N*-cyano- (**5a**) and *N*-(*p*-toluenesulfonyl)- (**5b**) dithioiminocarbonate, readily prepared, storable and easy to handle, are shown by the present study to be not only useful as precursors of new 1,3-dipolar reagents and, previously inaccessible iminoazomethine and iminothiocarbonyl ylides, under mild conditions, but also applicable to the synthesis of five-membered ring sulfur- and nitrogen-containing heterocycles.

Experimental

All melting points were determined in a capillary tube and are uncorrected. Infrared (IR) spectra were recorded in potassium bromide pellets on, JASCO 810 or Shimadzu IR-460 spectrometer and ultraviolet (UV) absorption spectra were determined in 95% ethanol on a Hitachi 323 spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained on JEOLPS-100 (100 MHz), JEOLFX-90Q (90 MHz), JEOLPMX-60S1 (60 MHz), and JEOLGX-400 (400 MHz) spectrometers with tetramethylsilane as an internal standard. Mass spectra (MS) were recorded on JEOL-01SG and JEOL DX-303 mass spectrometers. Elemental analyses were performed at the Microanalytical Laboratory of the Center for Instrumental Analysis in Nagasaki University.

***N*-Cyano-*N*′-trimethylsilylmethyl-*S*-methylisothiourea (3a)** To a solution of 7.31 g (50.0 mmol) of *N*-cyanocarbonimidodithioate (**1a**) in 30 ml of MeOH was added 5.16 g (50.0 mmol) of trimethylsilylmethylamine (**2a**). The reaction started immediately with an increase of reaction temperature and evolution of methylmercaptan. This reaction mixture was refluxed for 20 min. After evaporation of the solvent, the residue was recrystallized from EtOH to give 9.44 g (46.9 mmol) of **3a** as colorless needles, mp 164—166 °C, in 94% yield. IR (KBr): 3240 (NH), 2195 (CN), 2170 (CN), 1560 (C=N), 1510, 1390, 1290, 1245 ($SiMe_3$), 1080, 860 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 246 (4.18). ^{1}H-NMR ($CDCl_3$) δ: 0.14 (9H, s, $SiMe_3$), 2.49 (3H, s, SMe), 2.88 (2H, near d, CH_2), 6.17 (1H, br s, NH). LR-MS *m/z* (%): 201 (M^+, 10), 186 (M^+-15, 35), 157 (20), 154 (38), 105 (17), 73 ($SiMe_3$, 100). *Anal.* Calcd for $C_7H_{15}N_3SSi$: C, 41.76; H, 7.51; N, 20.87. Found: C, 41.79; H, 7.21; N, 20.84.

***N*-*p*-Toluenesulfonyl-*N*′-trimethylsilylmethyl-*S*-methylisothiourea (3b)** This compound (4.70 g, 14.3 mmol) was synthesized in 95% yield from

1b (4.125 g, 15.0 mmol) and **2a** (1.55 g, 15.0 mmol) in a manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from EtOH to give colorless needles, mp 62—63 °C. IR (KBr): 3320 (NH), 1540 (C=N), 1480, 1390, 1280, 1265, 1250 ($SiMe_3$), 1145, 1090, 855 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 223 (4.16), 245 (4.26). ^1H-NMR ($CDCl_3$) δ: 0.05 (9H, s, $SiMe_3$), 2.41 (6H, s, SMe and Me), 2.90 (2H, d, J=5.3 Hz, CH_2), 7.36 (2H, d, J=8.4 Hz, aromatic-H), 7.73 (2H, d, J=8.4 Hz, aromatic-H), 7.80 (1H, br s, NH). LR-MS m/z (%): 330 (M^+, 5), 315 (M^+-15, 11), 299 (14), 283 (24), 91 (84), 73 ($SiMe_3$, 100). *Anal.* Calcd for $C_{13}H_{22}N_2O_2S_2Si$: C, 47.24; H, 6.71; N, 8.51. Found: C, 47.07; H, 6.52; N, 8.51.

***N*-Cyano-*N*′-methyl-*N*′-trimethylsilylmethyl-*S*-methylisothiourea (4a)** A 300-ml, three-necked flask was fitted with a stirring bar, a rubber stopper, a 20 ml pressure-equalizing dropping funnel, and a three-way stopcock equipped with a balloon of argon gas. The flask was charged with 4.02 g (20.0 mmol) of **3a**, K_2CO_3 (11.04 g, 80 mmol), and 100 ml of dry acetone. The dropping funnel was charged with methyl iodide (17.03 g, 120.0 mmol) in 20 ml of dry acetone, which was added dropwise over 20 min. After the addition was complete, the pale yellow solution was stirred for an additional 48 h at room temperature. After removal of precipitated inorganic compound by filtration and the solvent by evaporation, the residue was dissolved in 50 ml of CH_2Cl_2 and this solution was washed with 30 ml of water. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated to give a light-brown oil. The product was dissolved in 10 ml of CH_2Cl_2 and purified by chromatography on a column of silica gel with CH_2Cl_2 as an eluent to give 3.94 g (18.2 mmol, 91%) of **4a** as a colorless oil. IR (KBr): 2180 (CN), 1565 (C=N), 1550, 1430, 1405, 1250 ($SiMe_3$), 850 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 265 (4.39). ^1H-NMR ($CDCl_3$) δ: 0.13 (9H, s, $SiMe_3$), 2.78 (3H, s, SMe), 3.22 (3H, s, NMe), 3.24 (2H, s, CH_2). LR-MS m/z (%): 215 (M^+, 10), 200 (100), 168 (96), 157 (35), 105 (21), 73 (95). *Anal.* Calcd for $C_8H_{17}N_3SSi$: C, 44.61; H, 7.96; N, 19.51; S, 14.88. Found: C, 44.70; H, 7.74; N, 19.65; S, 14.87.

***N*-Cyano-*N*′-benzyl-*N*′-trimethylsilylmethyl-*S*-methylisothiourea (4b)** This compound (5.39 g, 18.5 mmol) was synthesized in 93% yield from **3a** (4.03 g, 20.0 mmol), benzyl bromide (3.59 g, 21.0 mmol), and K_2CO_3 (13.82 g, 100.0 mmol) in a manner similar to that described for the preparation of **4a**. An analytical sample was purified by chromatography on a column of silica gel with CH_2Cl_2 as an eluent to give a colorless oil. IR (KBr): 2180 (CN), 1550 (C=N), 1455, 1423, 1250 ($SiMe_3$), 700 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 266 (4.19). ^1H-NMR ($CDCl_3$) δ: 0.12 (9H, s, $SiMe_3$), 2.84 (3H, s, SMe), 3.16 (2H, s, CH_2), 4.84 (2H, s, $\underline{CH_2}$-Ph), 7.15—7.50 (5H, m, Ph). LR-MS m/z (%): 291 (M^+, 5), 276 (11), 244 (25), 127 (14), 91 (100), 73 (47), 61 (27). *Anal.* Calcd for $C_{14}H_{21}N_3SSi$: C, 57.69; H, 7.26; N, 14.42. Found: C, 57.76; H, 7.20; N, 14.53.

***N*-*p*-Toluenesulfonyl-*N*-methyl-*N*′-trimethylsilylmethyl-*S*-methylisothiourea (4c)** This compound (2.65 g, 7.68 mmol) was synthesized in 50% yield from **3b** (5.40 g, 15.3 mmol), methyl iodide (14.19 g, 100.0 mmol), and K_2CO_3 (11.04 g, 80.0 mmol) in a manner similar to that described for the preparation of **4a**. A mixture of products was separated by chromatography on a column of silica gel with a 1 : 1 mixture of cyclohexane and CH_2Cl_2 as an eluent to give **4c** as a colorless oil. IR (KBr): 1535 (C=N), 1410, 1280, 1250 ($SiMe_3$), 1140, 1090, 845, 670 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 0.08 (9H, s, $SiMe_3$), 2.38 (3H, s, Me), 2.52 (3H, s, SMe), 3.17 (2H, s, CH_2), 3.22 (3H, s, NMe), 7.21 (2H, d, J=8.1 Hz, aromatic-H), 7.80 (2H, d, J=8.1 Hz, aromatic-H). LR-MS m/z (%): 344 (M^+, 7), 329 (79), 299 (25), 297 (28), 228 (64), 207 (30), 189 (100), 180 (78), 73 ($SiMe_3$, 100). UV λ_{max}^{EtOH} nm (log ε): 226 (4.11), 259 (4.14). *Anal.* Calcd for $C_{14}H_{24}N_2O_2S_2Si$: C, 48.80; H, 7.02; N, 8.13. Found: C, 48.77; H, 6.82; N, 8.11.

Subsequent elution with CH_2Cl_2 gave *N*-trimethylsilyl-methyl-*N*′-(*p*-toluenesulfonyl)-*N*′,*S*-dimethylisothiourea (**17**) (1.38 g, 3.99 mmol) as colorless prisms in 26% yield. An analytical sample was recrystallized from iso-PrOH to give colorless prisms, mp 59 °C. IR (KBr): 1600 (C=N), 1350, 1250 ($SiMe_3$), 1165, 1020, 860, 665 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 232 (4.22). ^1H-NMR ($CDCl_3$) δ: 0.05 (9H, s, $SiMe_3$), 2.42 (6H, s, Me), 2.54 (3H, s, SMe), 2.96 (3H, s, NMe), 3.17 (2H, s, NCH_2), 7.27 (2H, d, J=8.4 Hz, aromatic-H), 7.80 (2H, d, J=8.4 Hz, aromatic-H). LR-MS m/z (%): 329 (M^+-15, 79), 297 (12), 189 (40), 155 (14), 88 (100), 180 (78), 73 ($SiMe_3$, 19). *Anal.* Calcd for $C_{14}H_{24}N_2O_2S_2Si$: C, 48.80; H, 7.02; N, 8.13. Found: C, 48.55; H, 6.81; N, 8.17.

Protiodesilylation of 3a, 4a, and b with Fluoride Ion *N*-Cyano-*N*′,*S*-dimethylisothiourea (18a) A solution of TBAF (1.0 ml of 1 M solution in THF) was added to a solution of **3a** (0.10 g, 0.5 mmol) of 5 ml of THF and the mixture was stirred for 24 h at room temperature (the proton presumably comes from the water present). After evaporation of the solvent, the residue was chromatographed on a silica gel column with benzene as an eluent to give colorless prisms. This compound was recrystallized from EtOH to give 0.05 g (91%) of colorless prisms, mp 202 °C (lit., 196 °C).[12] ^1H-NMR ($CDCl_3$) δ: 2.47 (3H, s, SMe), 3.03 (3H, s, NMe), 6.60 (1H, br s, NH).

***N*-Cyano-*N*′,*N*′,*S*-trimethylisothiourea (18b)** A mixture of 0.215 g (1.0 mmol) of **4a**, 0.30 g (2.0 mmol) of CsF, 0.2 ml of water, and 10 ml of acetonitrile was stirred at room temperature for 10 h. After evaporation of the solvent and water, the residue was chromatographed on a column of silica gel using ethyl acetate as an eluent to give a colorless oil. IR (KBr): 2170 (CN), 1565, 1422, 1440 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 2.78 (3H, s, SMe), 3.24 (6H, s, NMe_2). LR-MS m/z (%): 143 (M^+, 58), 103 (12), 96 (100), 71 (14). HR-MS Calcd for $C_5H_9N_3S$: 143.0517. Found: 143.0517.

***N*-(*p*-Toluenesulfonyl)-*N*′,*N*′,*S*-trimethylisothiourea (18c)** This compound (0.112 g, 4.12 mmol) was synthesized in 82% yield from 1.72 g (5 mmol) of **4c**, in a manner similar to that described for the preparation of **18a**, mp 66—69 °C. IR (KBr): 1570, 1425, 1362, 1265, 1140 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 2.40 (3H, s, *p*-Me), 2.43 (3H, s, SMe), 3.25 (6H, s, NMe_2), 7.24 (2H, d, J=8.1 Hz, phenyl-H), 7.82 (2H, d, J=8.1 Hz, phenyl-H). *Anal.* Calcd for $C_{11}H_{16}N_2O_2S_2$: C, 48.51; H, 5.92; N, 10.28; S, 23.54. Found: C, 48.55; H, 6.01; N, 10.22; S, 23.56.

***S*-Methyl-*S*′-trimethylsilylmethyl *N*-Cyanocarbonimidodithioate (5a) and *S*,*S*′-Bis(trimethylsilylmethyl) *N*-Cyanocarbonimidodithioate (19a)** A solution of **1a** (2.93 g, 20.0 mmol) and trimethylsilylmercaptan (**2b**) (2.41 g, 20.0 mmol) in 30 ml of methanol was refluxed for 60 h. After evaporation of the solvent, the residue was chromatographed on a column of silica gel with a 1 : 1 mixture of hexane and benzene as an eluent to give **5a** (1.83 g, 8.40 mmol) as colorless prisms in 42% yield. An analytical sample was recrystallized from EtOH to give colorless prisms, mp 61—62 °C. IR (KBr): 2950 (CH_2), 2190 (CN), 1485, 1250 ($SiMe_3$), 1020, 850 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 265 (4.24). ^1H-NMR ($CDCl_3$) δ: 0.23 (9H, s, $SiMe_3$), 2.35 (2H, s, CH_2), 2.63 (3H, s, SMe). LR-MS m/z (%): 203 (M^+-15, 76), 157 (52), 145 (21), 130 (36), 105 (36), 84 (38), 73 (Me_3Si, 100), 59 (59), 45 (80). *Anal.* Calcd for $C_7H_{14}N_2S_2Si$: C, 38.49; H, 6.46; N, 12.83. Found: C, 38.78; H, 6.31; N, 12.82.

Subsequent elution with a 2 : 3 mixture of hexane and benzene gave **19a** (1.07 g, 8.40 mmol) as colorless prisms in 18% yield. An analytical sample was recrystallized from EtOH to give colorless prisms, mp 63—64 °C. IR (KBr): 2950 (CH_2), 2190 (CN), 1495, 1380, 1250 ($SiMe_3$), 1135, 1005, 980, 845, 770 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 0.28 (18H, s, 2 × $SiMe_3$), 2.43 (4H, s, 2 × CH_2). LR-MS m/z (%): 275 (M^+-15, 58), 203 (35), 171 (33), 157 (41), 73 ($SiMe_3$, 100). UV λ_{max}^{EtOH} nm (log ε): 271 (4.28). *Anal.* Calcd for $C_{10}H_{22}N_2S_2Si_2$: C, 41.33; H, 7.63; N, 9.64. Found: C, 41.28; H, 7.40; N, 9.34.

***S*-Methyl-*S*′-trimethylsilylmethyl *N*-(*p*-Toluenesulfonyl)carbonimidodithioate (5b) and *S*,*S*′-Bis(trimethylsilylmethyl) *N*-(*p*-Toluenesulfonyl)carbonimidodithioate (19b)** A solution of **1b** (4.13 g, 15.0 mmol) and trimethylsilylmercaptan (**2b**) (1.93 g, 16.0 mmol) in 20 ml of methanol was refluxed for 60 h. After evaporation of the solvent, the residue was chromatographed on a column of silica gel with a 1 : 1 mixture of hexane and benzene as an eluent to give **5b** (2.28 g, 6.36 mmol) as colorless leaflets in 42% yield. An analytical sample was recrystallized from EtOH to give colorless leaflets, mp 86—87 °C. IR (KBr): 2950 (CH_2), 1470 (C=N), 1300, 1250, 1150, 1090, 950, 850, 810, 670 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 29 (4.00), 265 (4.31). ^1H-NMR ($CDCl_3$) δ: 0.13 (9H, s, $SiMe_3$), 2.31 (2H, s, CH_2), 2.42 (3H, s, Me), 2.49 (3H, s, SMe), 7.28 (2H, d, J=8.35 Hz, aromatic-H), 7.87 (2H, d, J=8.35 Hz, aromatic-H). LR-MS m/z (%): 347 (M^+, 1), 332 (M^+-15, 5), 228 (14), 155 (100), 91 (90), 73 (Me_3Si, 100), 59 (59), 45 (80). *Anal.* Calcd for $C_{13}H_{21}NO_2S_3Si$: C, 44.92; H, 6.09; N, 4.03. Found: C, 45.01; H, 5.92; N, 4.17.

Subsequent elution with a 2 : 3 mixture of hexane and benzene as an eluent gave **19b** (1.26 g, 3.0 mmol) as colorless needles in 20% yield. An analytical sample was recrystallized from EtOH to give colorless needles, mp 102—103 °C. IR (KBr): 2950 (CH_2), 1480, 1315, 1250 ($SiMe_3$), 1150, 1090, 950, 810, 770 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 229 (4.01), 268 (4.31). ^1H-NMR ($CDCl_3$) δ: 0.13 (18H, s, $SiMe_3$), 2.29 (4H, s, 2 × CH_2), 2.42 (3H, s, Me), 7.28 (2H, d, J=8.4 Hz, aromatic-H), 7.87 (2H, d, J=8.4 Hz, aromatic-H). *Anal.* Calcd for $C_{16}H_{29}NO_2S_3Si_2$: C, 45.78; H, 6.96; N, 3.34. Found: C, 45.72; H, 6.75; N, 3.40.

Alternative Synthesis of 5b A 500 ml, three-necked, round-bottomed flask was fitted with a magnetic stirrer, a reflux condenser attached to a nitrogen inlet, and a pressure-equalizing funnel. The flask was flushed with nitrogen and charged with methyl *N*-(*p*-toluenesulfonyl)dithiocarbamate (**20**) (8.08 g, 30.0 mmol), sodium iodide (4.49 g, 30.0 mmol), sodium hydroxide (1.28 g, 32.0 mmol), and 250 ml of absolute EtOH. The solution was warmed to 45—60 °C and 7.36 g (60.0 mmol) of (chloromethyl)trimethylsilane (**21a**) was added dropwise over 20 min. This mixture was refluxed for 20 h under stirring. The reaction solution was decanted and the remaining solid was washed twice with 30 ml of absolute EtOH. The organic phases were combined and concentrated under reduced pressure with a rotary evaporator. The product was purified by chromatography on a column of silica gel with a 1 : 1 mixture of hexane and CH_2Cl_2 as an eluent to give 7.45 g (21.4 mmol) of **5b** as colorless crystals in 71% yield. When compound **20** was allowed to react with **21a** without NaI, the yield was 59%. In the case of using NaH instead of NaOH, the reaction of **20** with **21a** or (iodidemethyl)-trimethylsilane (**21b**) did not afford the desired product (**5b**) from any reaction mixture.

1,3-Dipolar Cycloaddition Reaction of 3 or 4 with Heterodipolarophile General Method A: A 50 ml, two necked flask was fitted with a magnetic stirring bar and gas inlet tube. The flask was charged with 0.091 g (0.6 mmol) of CsF and was heated at 100—140 °C with a hot plate stirrer for 1 h. The apparatus was cooled under purging with nitrogen. A solution of an aldehyde (1.5 mmol) in 1 ml of dry acetonitrile was then added. A solution of 0.5 mmol of **3a, b** or **4a, b**, in 2 ml of acetonitrile was introduced *via* a syringe with stirring. When all reagents had been added, the reaction mixture was stirred for 20 h at room temperature. The solvent was removed under reduced pressure on a rotary evaporator to yield a residue. The residue was added to the top of a 20 g 60—200 mesh silica gel chromatography column and the column was eluted with a mixture of hexane and ethyl acetate. The solvent was removed from those fractions containing the product under reduced pressure on a rotary evaporator to afford the corresponding product as shown in Table 4. An analytical sample of each product was recrystallized from an appropriate solvent.

Method B: A 50 ml, two-necked flask was fitted with a magnetic stirring bar and gas inlet tube. To a solution of 0.50 mmol of **3** or **4** and 1.0 mmol of the corresponding aldehyde in 5 ml of absolute THF was added 1.0 mmol of TBAF. The mixture was stirred for 22 h at room temperature. After removal of the solvent by evaporation, the residue was added to the top of a 20 g, 60—200 mesh silica gel chromatography column and the column was eluted with a mixture of hexane and ethyl acetate. The solvent was removed from those fractions containing the product under reduced pressure on a rotary evaporator to afford the corresponding product. The results of a typical experiment in the case of synthesis of **12j** are shown in Table 3.

2-Cyanoimino-4,5-dihydro-5-phenyl-1,3-oxazole (12a) Yield 41%, colorless prisms (hexane–EtOH, 20 : 1), mp 126—127 °C. IR (KBr): 3155 (NH), 2190 (CN), 1650 (C=N), 1490, 1455, 1310, 1278, 1160, 960, 908, 720, 700 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 216 (4.34), 258 (2.55), 263 (2.52). ^{1}H-NMR ($CDCl_3$) δ: 2.76 (1H, dd, *J*=8.1, 9.9 Hz, CH_a), 4.18 (1H, dd, *J*=8.5, 9.9 Hz, CH_b), 5.83 (1H, dd, *J*=8.1, 8.5 Hz, CH-O), 7.39 (5H, s, phenyl-H), 8.32 (1H, br s, NH). LR-MS *m/z* (%): 187 (M^+, 100), 186 (M^+-1, 11), 131 (33), 119 (40), 118 (31), 110 (16), 92 (46), 91 (40), 77 (12), 42 (19). *Anal.* Calcd for $C_{10}H_9N_3O$: C, 64.16; H, 4.85; N, 22.45. Found: C, 64.20; H, 4.97; N, 22.50.

2-Cyanoimino-4,5-dihydro-5-(4-phenyl)phenyl-1,3-oxazole (12b) Yield 62%, colorless needles(EtOH), mp 200—202 °C. IR (KBr): 3160 (NH), 3040 (NH), 2195 (CN), 1655 (C=N), 1490, 1460, 1160, 1110, 985, 740. UV λ_{max}^{EtOH} nm (log ε): 255 (3.98). ^{1}H-NMR ($CDCl_3$) δ: 3.70 (1H, dd, *J*=7.9, 9.9 Hz, CH_a), 4.14 (1H, dd, *J*=8.8, 9.9 Hz, CH_b), 6.02 (1H, dd, *J*=7.9, 8.8 Hz, CH-O), 7.30—7.80 (9H, m, aromatic-H), 8.24 (1H, br s, NH). LR-MS *m/z* (%): 264 (M^++1, 21), 263 (M^+, 100), 261 (M^+-1, 21), 207 (40), 167 (25), 152 (15), 106 (31), 103 (68), 91 (45), 77 (25), 76 (26). *Anal.* Calcd for $C_{16}H_{13}N_3O$: C, 72.99; H, 4.98; N, 15.96. Found: C, 72.70; H, 5.08; N, 15.86.

2-Cyanoimino-4,5-dihydro-5-(2,6-dichlorophenyl)-1,3-oxazole (12c) Yield 84%, colorless prisms (EtOH), mp 225—226 °C. IR (KBr): 3180 (NH), 2200 (CN), 1660 (C=N), 1460, 1435, 1275, 1150, 960, 800 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 204 (4.54), 220 (4.22). ^{1}H-NMR ($CDCl_3$) δ: 4.08 (1H, dd, *J*=8.5, 9.7 Hz, CH_a), 4.27 (1H, dd, *J*=8.5, 10.1 Hz, CH_b), 6.78 (1H, dd, *J*=9.7, 10.1 Hz, CH-O), 7.30—7.50 (3H, m, phenyl-H), 7.91 (1H, br s, NH). *Anal.* Calcd for $C_{10}H_7C_{12}N_3O$: C, 54.44; H, 3.20; N, 19.04. Found: C, 54.43; H, 3.18; N, 19.11.

5-Phenyl-4,5-dihydro-2-(*p*-toluenesulfonyl)imino-1,3-oxazole (12d) Yield 42%, colorless prisms (EtOH), mp 168—169 °C. IR (KBr): 3100 (NH), 2975, 1650 (C=N), 1440, 1285, 1150, 1110, 1075, 875 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 230 (4.24), 258 (2.99). ^{1}H-NMR ($CDCl_3$) δ: 2.41 (3H, s, *p*-Me), 3.76 (1H, dd, *J*=8.1, 9.5 Hz, CH_a), 4.16 (1H, dd, *J*=8.6, 9.5 Hz, CH_b), 5.69 (1H, dd, *J*=8.1, 8.6 Hz, CH-O), 7.10—7.40 (7H, m, aromatic-H), 7.83 (2H, d, *J*=8.4 Hz, aromatic-H), 7.85 (1H, br s, NH). LR-MS *m/z* (%): 316 (M^+, 54), 252 (29), 209 (10), 133 (27), 119 (58), 118 (59), 91 (100), 65 (28). *Anal.* Calcd for $C_{16}H_{16}N_2O_3S$: C, 60.74; H, 5.10; N, 8.85; S, 10.13. Found: C, 60.65; H, 5.16; N, 8.78; S, 10.34.

5-(4-Phenyl)-4,5-dihydro-2-(*p*-toluenesulfonyl)imino-1,3-oxazole (12e) Yield 45%, colorless needles (iso-PrOH), mp 165—167 °C. IR (KBr): 3280 (NH), 3180 (NH), 1638 (C=N), 1420, 1302, 1285, 1160, 1108, 1075, 872, 580 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 236 (4.41), 254 (4.39). ^{1}H-NMR ($CDCl_3$) δ: 2.41 (3H, s, *p*-Me), 3.77 (1H, dd, *J*=8.1, 9.5 Hz, CH_a), 4.19 (1H, dd, *J*=8.6, 9.5 Hz, CH_b), 5.74 (1H, dd, *J*=8.1, 8.6 Hz, CH-O), 7.10—7.90 (14H, m, NH and aromatic-H). LR-MS *m/z* (%): 392 (M^+, 17), 221 (9), 195 (17), 171 (36), 155 (52), 91 (100). *Anal.* Calcd for $C_{22}H_{20}N_2O_3S$: C, 67.33; H, 5.14; N, 7.14; S, 8.17. Found: C, 67.22; H, 5.16; N, 7.09; S, 8.40.

5-(2,6-Dichlorophenyl)-4,5-dihydro-2-(*p*-toluenesulfonyl)imino-1,3-oxazole (12f) Yield 61%, colorless needles (iso-PrOH), mp 211—213 °C. IR (KBr): 3380 (NH), 3200, 1650 (C=N), 1615, 1428, 1280, 1070, 870 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 227 (4.37), 265 (2.95), 2690 (3.00), 275 (3.02), 285 (2.85). ^{1}H-NMR ($CDCl_3$) δ: 2.41 (3H, s, *p*-Me), 4.05 (2H, m, CH_2), 6.45 (1H, dd, *J*=9.2, 10.1 Hz, CH-O), 7.10—7.40 (5H, m, aromatic-H), 7.82 (2H, d, *J*=8.4 Hz, aromatic-H), 8.14 (1H, br s, NH). *Anal.* Calcd for $C_{16}H_{14}Cl_2N_2O_3S$: C, 49.88; H, 3.66; N, 7.27; S, 8.32. Found: C, 49.72; H, 3.64; N, 7.03; S, 8.34.

2-Cyanoimino-4,5-dihydro-3-methyl-5-phenyl-1,3-oxazole (12g) Yield 77%, colorless prisms (iso-PrOH), mp 132—133 °C. IR (KBr): 2195 (CN), 1665 (C=N), 1505, 1460, 1270, 1185, 945, 770, 706 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 218 (4.34). ^{1}H-NMR ($CDCl_3$) δ: 2.97 (3H, s, NMe), 3.67 (1H, dd, *J*=7.9, 9.4 Hz, CH_a), 4.13 (1H, dd, *J*=9.0, 9.4 Hz, CH_b), 5.74 (1H, dd, *J*=7.9, 9.0 Hz, CH-O), 7.37 (5H, s, phenyl-H). LR-MS *m/z* (%): 201 (M^+, 42), 132 (13), 124 (9), 104 (8), 91 (12), 44 (32), 40 (100). *Anal.* Calcd for $C_{11}H_{11}N_3O$: C, 65.66; H, 5.51; N, 20.88. Found: C, 65.57; H, 5.60; N, 20.77.

5-(4-Chlorophenyl)-2-cyanoimino-4,5-dihydro-3-methyl-1,3-oxazole (12h) Yield 74%, colorless needles (iso-PrOH), mp 142—144 °C. IR (KBr): 2195 (CN), 1670 (C=N), 1655, 1500, 1265, 1090, 945, 805, 770, 706 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 222 (4.51). ^{1}H-NMR ($CDCl_3$) δ: 3.01 (3H, s, NMe), 3.64 (1H, dd, *J*=7.9, 9.5 Hz, CH_a), 4.10 (1H, dd, *J*=8.8, 9.5 Hz, CH_b), 5.73 (1H, dd, *J*=7.9, 8.8 Hz, CH-O), 7.20—5.50 (4H, m, phenyl-H). LR-MS *m/z* (%): 237 (M^+, 29), 235 (M^+, 86), 201 (21), 167 (22), 124 (31), 83 (30), 42 (100). *Anal.* Calcd for $C_{11}H_{10}ClN_3O$: C, 56.06; H, 4.28; Cl, 15.06; N, 17.83. Found: C, 56.14; H, 4.28; Cl, 14.77; N, 17.84.

2-Cyanoimino-4,5-dihydro-3-methyl-5-(4-methoxyphenyl)-1,3-oxazole (12i) Yield 86%, colorless prisms (iso-PrOH), mp 108—109 °C. IR (KBr): 2195 (CN), 1660 (C=N), 1500, 1460, 1330, 1255, 1180, 1020, 955, 775 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 222 (4.34), 273 (3.40), 278 (3.42). ^{1}H-NMR ($CDCl_3$) δ: 2.97 (3H, s, NMe), 3.57 (1H, dd, *J*=7.5, 9.2 Hz, CH_a), 3.84 (3H, s, OMe), 4.17 (1H, dd, *J*=9.2, 9.2 Hz, CH_b), 5.88 (1H, dd, *J*=7.5, 9.2 Hz, CH-O), 6.93 (2H, d, *J*=7.5 Hz, phenyl-H), 7.33 (2H, d, *J*=7.5 Hz, phenyl-H). LR-MS *m/z* (%): 231 (M^+, 100), 213 (33), 162 (18), 132 (37), 91 (30), 42 (48). *Anal.* Calcd for $C_{12}H_{13}N_3O_2$: C, 62.33; H, 5.67; N, 18.77. Found: C, 62.33; H, 5.62; N, 18.24.

5-(2,6-Dichlorophenyl)-2-cyanoimino-4,5-dihydro-3-methyl-1,3-oxazole (12j) Yield 78%, colorless needles (EtOH), mp 235—237 °C. IR (KBr): 2200 (CN), 1645 (C=N), 1505, 1440, 1410, 1325, 1275, 1265, 1188, 1090, 1000, 960 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 220 (4.48), 277 (2.94), 285 (2.90). ^{1}H-NMR ($CDCl_3$) δ: 3.04 (3H, s, NMe), 3.87 (1H, dd, *J*=9.2, 9.2 Hz, CH_a), 4.11 (1H, dd, *J*=9.2, 10.1 Hz, CH_b), 6.52 (1H, dd, *J*=9.2, 10.1 Hz, CH-O), 7.1—7.40 (3H, m, phenyl-H). LR-MS *m/z* (%): 271 (M^+, 14), 269 (M^+, 21), 166 (11), 131 (9), 124 (18), 42 (100). *Anal.* Calcd for $C_{11}H_9Cl_2N_3O$: C, 48.91; H, 3.36; N, 15.56. Found: C, 49.00; H, 3.46; N, 15.48.

2-Cyanoimino-4,5-dihydro-3-methyl-5-(4-phenylphenyl)-1,3-oxazole (12k) Yield 81%, colorless needles (iso-PrOH), mp 192—193 °C. IR (KBr): 2190 (CN), 1640 (C=N), 1495, 770 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 255 (4.34). ^{1}H-NMR ($CDCl_3$) δ: 3.03 (3H, s, NMe), 3.72 (1H, dd, *J*=7.9, 9.2 Hz, CH_a), 4.12 (1H, dd, *J*=8.8, 9.2 Hz, CH_b), 5.79 (1H, dd, *J*=7.9, 8.8 Hz, CH-O), 7.30—7.70 (9H, m, phenyl-H). LR-MS *m/z* (%): 277 (M^+, 100), 208 (48), 183 (35), 181 (33), 152 (24), 44 (28), 91 (12), 42

(41). *Anal.* Calcd for $C_{17}H_{15}N_3O$: C, 69.13; H, 5.80; N, 14.23. Found: C, 69.16; H, 5.59; N, 14.24.

2-Cyanoimino-4,5-dihydro-3-methyl-5-(4-nitrophenyl)-1,3-oxazole (12l) Yield 55%, pale yellow crystals (iso-PrOH), mp 132—133 °C. IR (KBr): 2200 (CN), 1675 (C=N), 1675, 1655, 1525, 1500, 1350 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 217 (4.35), 262 (4.02). ^{1}H-NMR (CDCl$_3$) δ: 3.03 (3H, s, NMe), 3.71 (1H, dd, $J=7.9$, 9.7 Hz, CH$_a$), 4.28 (1H, dd, $J=9.0$, 9.7 Hz, CH$_b$), 5.95 (1H, dd, $J=7.9$, 9.0 Hz, CH-O), 7.59 (2H, d, $J=9.0$ Hz, phenyl-H), 8.25 (2H, d, $J=9.0$ Hz, phenyl-H). LR-MS m/z (%): 246 (M$^+$, 29), 201 (13), 152 (54), 82 (47), 77 (24), 57 (55), 43 (100). HR-MS Calcd for $C_{11}H_{10}N_4O_3$: 246.075. Found: 246.075.

2-Cyanoimino-4,5-dihydro-3-methyl-5-(1-naphthyl)-1,3-oxazole (12m) Yield 63%, colorless needles (iso-PrOH), mp 132—133 °C. IR (KBr): 2190 (CN), 1656 (C=N), 1640, 1493, 1410, 1268, 985, 810, 780 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 224 (5.02), 263 (3.63), 272 (3.82), 288 (3.72), 293 (3.74). ^{1}H-NMR (CDCl$_3$) δ: 2.97 (3H, s, NMe), 3.64 (1H, dd, $J=7.5$, 9.2 Hz, CH$_a$), 4.36 (1H, dd, $J=9.2$, 9.2 Hz, CH$_b$), 6.41 (1H, dd, $J=7.5$, 9.2 Hz, CH-O), 7.20—8.00 (7H, m, naphthyl-H). LR-MS m/z (%): 251 (M$^+$, 100), 182 (48), 167 (11), 152 (21), 142 (11), 141 (14), 76 (11), 44 (32). *Anal.* Calcd for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.21; N, 16.72. Found: C, 71.41; H, 5.32; N, 16.72.

2-Cyanoimino-4,5-dihydro-3-methyl-5-styryl-1,3-oxazole (12n) Yield 60%, colorless needles (iso-PrOH), mp 164—165 °C. IR (KBr): 2195 (CN), 1665 (C=N), 1655, 1495, 1265, 1180, 990, 850, 790, 700 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 210 (4.59), 216 (4.48), 255 (4.32), 283 (3.34), 293 (3.06). ^{1}H-NMR (CDCl$_3$) δ: 2.99 (3H, s, NMe), 3.56 (1H, dd, $J=7.7$, 9.2 Hz, CH$_a$), 3.94 (1H, dd, $J=8.6$, 9.2 Hz, CH$_b$), 5.35 (1H, m, CH-O), 6.19 (1H, dd, $J=7.5$, 15.8 Hz, Ph–CH=C$\underline{H}$–), 6.77 (1H, d, $J=15.8$ Hz, Ph–C$\underline{H}$=CH), 7.20—7.50 (5H, m, phenyl-H). LR-MS m/z (%): 227 (M$^+$, 32), 143 (42), 105 (27), 103 (28), 96 (100), 91 (33), 77 (23), 45 (81). *Anal.* Calcd for $C_{13}H_{13}N_3O \cdot 1/5H_2O$: C, 67.63; H, 5.85; N, 18.20. Found: C, 67.63; H, 5.86; N, 18.05.

5-Butyl-2-cyanoimino-4,5-dihydro-3-methyl-1,3-oxazole (12o) Yield 70%, colorless oil. IR (KBr): 2960, 2940, 2870, 2200 (CN), 1660 (C=N), 1570, 1505, 1460, 1415, 1270, 990 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 220 (4.11), 249 (3.67), 255 (4.32), 283 (3.34), 293 (3.06). ^{1}H-NMR (CDCl$_3$) δ: 0.8—2.0 (9H, m, Bu), 2.96 (3H, s, NMe), 3.39 (1H, dd, $J=7.7$, 9.2 Hz, CH$_a$), 3.85 (1H, dd, $J=8.6$, 9.2 Hz, CH$_b$), 4.80 (1H, m, CH-O). LR-MS m/z (%): 181 (M$^+$, 49), 152 (29), 138 (100), 124 (54), 98 (19), 83 (26), 70 (41), 55 (40), 44 (77), 42 (80). HR-MS Calcd for $C_9H_{15}N_3O$: 181.122. Found: 181.121.

3-Benzyl-2-cyanoimino-4,5-dihydro-5-phenyl-1,3-oxazole (12p) Yield 66%, colorless oil. IR (KBr): 2200 (CN), 1645 (C=N), 1495, 1455, 1260, 955, 700 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 208 (4.49), 2224 (4.39, shoulder), 257 (2.77). ^{1}H-NMR (CDCl$_3$) δ: 3.49 (1H, dd, $J=8.1$, 9.7 Hz, CH$_a$), 3.96 (1H, dd, $J=8.8$, 9.0 Hz, CH$_b$), 4.50 (2H, s, PhCH$_2$), 5.67 (1H, dd, $J=8.1$, 8.8 Hz, CH-O), 7.10—7.40 (10H, m, phenyl-H). LR-MS m/z (%): 227 (M$^+$, 27), 149 (39), 104 (69), 91 (100), 57 (20). HR-MS Calcd for $C_{17}H_{15}N_3O$: 277.125. Found: 277.122.

4,5-Dihydro-3-methyl-5-phenyl-2-(*p*-toluenesulfonyl)imino-1,3-oxazole (12q) Yield 52%, colorless needles (EtOH), mp 177—178 °C. IR (KBr): 1622 (C=N), 1488, 1445, 1308, 1297, 1283, 1150, 900, 883, 582 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 202 (4.53), 230 (4.26). ^{1}H-NMR (CDCl$_3$) δ: 2.39 (3H, s, Me), 2.98 (3H, s, NMe), 3.46 (1H, dd, $J=7.0$, 9.2 Hz, CH$_a$), 3.99 (1H, dd, $J=9.0$, 9.2 Hz, CH$_b$), 5.70 (1H, dd, $J=7.0$, 9.0 Hz, CH-O), 7.20—7.40 (7H, m, aromatic-H), 7.86 (2H, d, $J=8.1$ Hz, aromatic-H). LR-MS m/z (%): 330 (M$^+$, 10), 329 (M$^+-1$, 44), 266 (24), 175 (33), 132 (63), 104 (100), 91 (79), 83 (32), 69 (62), 57 (48), 55 (51), 42 (65). *Anal.* Calcd for $C_{17}H_{18}N_2O_3S$: C, 61.80; H, 5.49; N, 8.48. Found: C, 61.82; H, 5.51; N, 8.45.

2-Cyanoimino-4,5-dihydro-3-methyl-5,5-diphenyl-1,3-oxazole (13a) Yield 40%, colorless needles (iso-PrOH), mp 167—168 °C. IR (KBr): 2200 (CN), 1660 (C=N), 1640, 1493, 1448, 1282, 1262, 1227, 962, 755, 700 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 219 (4.41, shoulder). ^{1}H-NMR (CDCl$_3$) δ: 2.99 (3H, s, NMe), 4.32 (2H, s, CH$_2$), 7.37 (10H, s, phenyl-H). LR-MS m/z (%): 277 (M$^+$, 25), 106 (50), 103 (100), 91 (70), 76 (31), 57 (20), 40 (56). *Anal.* Calcd for $C_{17}H_{15}N_3O$: C, 73.63; H, 5.45; N, 15.15. Found: C, 73.39; H, 5.61; N, 15.12.

5-Benzoyl-2-cyanoimino-4,5-dihydro-3-methyl-5-phenyl-1,3-oxazole (13b) Yield 35%, pale yellow needles (iso-PrOH), mp 164—165 °C. IR (KBr): 2200 (CN), 1690 (C=N), 1665, 1505, 1450, 1410, 1315, 1265 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 255 (4.08). ^{1}H-NMR (CDCl$_3$) δ: 2.95 (3H, s, NMe), 3.69 (1H, d, $J=9.9$ Hz, CH$_a$), 4.92 (1H, d, $J=9.9$ Hz, CH$_b$), 7.20—7.60 (8H, m, phenyl-H), 7.80—8.12 (2H, m, phenyl-H). LR-MS m/z (%): 305 (M$^+$, 23), 237 (11), 236 (16), 105 (100), 77 (37). HR-MS Calcd for $C_{18}H_{15}N_3O_2$: 305.116. Found: 305.116.

3-Benzyl-2-cyanoimino-4,5-dihydro-1-methyl-5,5-diphenyl-1,3-oxazole (13c) Yield 48%, colorless needles (iso-PrOH), mp 134—135 °C. IR (KBr): 2200 (CN), 1650 (C=N), 1495, 1450, 1285, 960, 755, 705 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 219 (4.42, shoulder). ^{1}H-NMR (CDCl$_3$) δ: 4.11 (2H, s, CH$_2$), 4.51 (2H, s, PhCH$_2$), 7.00—7.40 (15H, m, phenyl-H). LR-MS m/z (%): 353 (M$^+$, 18), 194 (12), 180 (100), 165 (22), 106 (22), 103 (45), 91 (92), 44 (48). *Anal.* Calcd for $C_{23}H_{19}N_3O$: C, 78.17; H, 5.42; N, 11.89. Found: C, 77.90; H, 5.50; N, 11.74.

3-Methyl-4,5-dihydro-5,5-diphenyl-2-*p*-toluenesulfonylimino-1,3-oxazole (13d) Yield 34%, colorless needles (EtOH), mp 178—179 °C. IR (KBr): 1624 (C=N), 1485, 1443, 1308, 1297, 1283, 1150, 897, 595 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 202 (4.70), 231 (4.30). ^{1}H-NMR (CDCl$_3$) δ: 2.39 (3H, s, Me), 2.94 (3H, s, NMe), 4.14 (2H, s, CH$_2$), 7.00—7.30 (12H, m, aromatic-H), 7.90 (2H, d, $J=8.4$ Hz, aromatic-H). LR-MS m/z (%): 406 (M$^+$, 6), 405 (M$^+-1$, 22), 368 (7), 342 (8), 251 (22), 236 (25), 209 (38), 208 (48), 180 (55), 165 (28), 103 (93), 97 (43), 91 (98), 83 (46), 77 (35), 69 (100), 59 (66), 57 (65), 43 (67). *Anal.* Calcd for $C_{23}H_{22}N_2O_3S$: C, 67.96; H, 5.45; N, 6.89, S, 7.89. Found: C, 67.68; H, 5.46; N, 6.92; S, 7.89.

5-(2-Benzo[*b*]thienyl)-2-cyanoimino-4,5-dihydro-3-methyl-1,3-oxazole (14) Yield 38%, colorless prisms (iso-PrOH), mp 250—252 °C. IR (KBr): 2190 (CN), 1605 (C=N), 1515, 1260, 1180, 1035, 825, 760 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 3.05 (3H, s, NMe), 3.69 (3H, s, OMe), 4.45 (2H, d, $J=6.2$ Hz, CH$_2$), 6.78 (2H, d, $J=9.0$ Hz, aromatic-H), 7.15—7.31 (2H, m, aromatic-H), 7.29 (2H, d, $J=9.0$ Hz, aromatic-H), 7.44 (1H, s, 3′-H), 7.58—7.71 (2H, m, aromatic-H). LR-MS m/z (%): 379 (M$^+$, 54), 298 (19), 106 (55), 104 (51), 91 (100), 57 (32), 44 (54). HR-MS Calcd for $C_{20}H_{17}N_3OS_2$: 379.505. Found: 379.501.

2-Phenylthiirane (22a)[11a] A 50-ml, two necked flask was fitted with a magnetic stirring bar and gas inlet tube. The flask was charged with 0.091 g (0.6 mmol) of CsF and was heated at *ca.* 140 °C with a hot plate stirrer for 1 h. The apparatus was cooled under purging with nitrogen. A solution of benzaldehyde (**8a**) (0.159 g, 1.5 mmol) in 1 ml of dry acetonitrile was then added. A solution of **5b** (0.174 g, 0.5 mmol) in 2 ml of acetonitrile was introduced *via* a syringe with stirring. When all reagents had been added, the reaction mixture was stirred for 45 h at room temperature. After evaporation of the solvent, the residue was chromatographed on silica gel column with a mixture of 10 : 1 hexane and ethyl acetate as an eluent to give 0.030 g (0.221 mmol, 44%) of colorless oil. This compound was alternatively prepared from **5a** and **8a** under the same reaction conditions in 68% yield. ^{1}H-NMR (CDCl$_3$) δ: 2.62 (1H, dd, $J=1.5$, 5.5 Hz, CH$_a$), 2.84 (1H, dd, $J=1.5$, 6.5 Hz, CH$_b$), 3.87 (1H, dd, $J=5.5$, 6.5 Hz, CH), 7.26 (5H, s, Ph-H). LR-MS m/z (%): 136 (M$^+$, 29), 135 (34), 104 (11), 103 (12), 91 (28), 86 (61), 84 (100), 77 (14), 47 (35). HR-MS Calcd for C_7H_8S: 136.035. Found: 136.035.

2-(2-Methylphenyl)thiirane (22b) This compound (0.048 g, 0.320 mmol) was prepared in 64% yield from 2-methylbenzaldehyde (**8b**) (0.180 g, 1.5 mmol), **5b** (0.174 g, 0.5 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **22a**. IR (KBr): 2914, 1711, 1491, 1461, 732 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 2.46 (3H, s, 2-Me), 2.70 (1H, dd, $J=1.4$, 5.8 Hz, CH$_a$), 2.83 (1H, dd, $J=1.4$, 6.6 Hz, CH$_b$), 3.98 (1H, dd, $J=5.8$, 6.6 Hz, CH), 7.14 (4H, m, phenyl-H). LR-MS m/z (%): 150 (M$^+$, 36), 135 (33), 117 (21), 115 (13), 91 (11), 32 (25), 28 (100). HR-MS Calcd for $C_9H_{10}S$: 150.050. Found: 150.050.

2-(4-Methylphenyl)thiirane (22c) This compound (0.035 g, 0.235 mmol) was prepared in 47% yield from 4-methylbenzaldehyde (**8c**) (0.180 g, 1.5 mmol), **5b** (0.174 g, 0.5 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **22a**. This compound was alternatively prepared from **5a** and **8c** under the same reaction conditions in 63% yield. IR (KBr): 2922, 1517, 1491, 1022, 820, 617 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 2.31 (3H, s, 2-Me), 2.61 (1H, dd, $J=1.5$, 5.7 Hz, CH$_a$), 2.82 (1H, dd, $J=1.5$, 6.6 Hz, CH$_b$), 3.85 (1H, dd, $J=5.7$, 6.6 Hz, CH), 7.12 (4H, m, phenyl-H). LR-MS m/z (%): 150 (M$^+$, 83), 135 (100), 118 (21), 105 (39), 91 (29), 28 (60). HR-MS Calcd for $C_9H_{10}S$: 150.050. Found: 150.052.

2-(2-Methoxyphenyl)thiirane (22d) This compound (0.061 g, 0.365 mmol) was prepared in 73% yield from 2-methoxybenzaldehyde (**8d**) (0.204 g, 1.5 mmol), **5b** (0.174 g, 0.5 mmol) and CsF (0.091 g, 0.06 mmol) in a manner similar to that described for the preparation of **22a**. IR (KBr): 2924, 1600, 1496, 1243, 1025, 758 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 2.63 (1H, dd, $J=1.3$, 5.9 Hz, CH$_a$), 2.81 (1H, dd, $J=1.3$, 6.6 Hz, CH$_b$), 3.88 (3H, s, OMe), 4.25 (1H, dd, $J=5.9$, 6.6 Hz, CH), 6.80—7.20 (4H, m, phenyl-H). LR-MS m/z (%): 166 (M$^+$, 32), 135 (20), 119 (15), 91

(28), 84 (100), 47 (25), 28 (15). HR-MS Calcd for $C_9H_{10}OS$: 166.045. Found: 166.045.

2-(3-Methoxyphenyl)thiirane (22e) This compound (0.054 g, 0.325 mmol) was prepared in 65% yield from 3-methoxybenzaldehyde (**8e**) (0.204 g, 1.5 mmol), **5b** (0.174 g, 0.5 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **22a**. IR (KBr): 2957, 1600, 1260, 1044, 640 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.61 (1H, dd, $J=1.5$, 5.5 Hz, CH_a), 2.83 (1H, dd, $J=1.5$, 6.6 Hz, CH_b), 3.77 (3H, s, OMe), 3.85 (1H, dd, $J=5.5$, 6.6 Hz, CH), 6.70—7.30 (4H, m, phenyl-H). LR-MS m/z (%): 166 (M^+, 51), 155 (22), 135 (31), 123 (29), 84 (100), 47 (24). HR-MS Calcd for $C_9H_{10}OS$: 166.045. Found: 166.046.

2-(4-Methoxyphenyl)thiirane (22f) This compound (0.062 g, 0.375 mmol) was prepared in 75% yield from 4-methoxybenzaldehyde (**8f**) (0.204 g, 1.5 mmol), **5b** (0.174 g, 0.5 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **22a**. Compound **22f** was alternatively synthesized from **5b** and **8f** using TBAF or TASF as the fluoride ion source in 19% or 30% yield, respectively. IR (KBr) : 2925, 1508, 1242, 1020, 598 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.61 (1H, dd, $J=1.5$, 5.7 Hz, CH_a), 2.82 (1H, dd, $J=1.5$, 6.6 Hz, CH_b), 3.78 (3H, s, OMe), 3.83 (1H, dd, $J=5.7$, 6.6 Hz, CH), 6.81 (2H, d, $J=8.9$ Hz, phenyl-H), 7.19 (2H, d, $J=8.9$ Hz, phenyl-H). LR-MS m/z (%): 166 (M^+, 37), 151 (6), 135 (19), 134 (26), 103 (26), 28 (100). HR-MS Calcd for $C_9H_{10}OS$: 166.045. Found: 166.045.

2-(4-Chlorophenyl)thiirane (22g) This compound (0.023 g, 0.135 mmol) was prepared in 27% yield from 4-chlorobenzaldehyde (**8g**) (0.210 g, 1.5 mmol), **5b** (0.174 g, 0.5 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **22a**. This compound was also prepared from **5a** and **8g** under the same reaction conditions in 52% yield. ^{1}H-NMR ($CDCl_3$) δ: 2.57 (1H, dd, $J=1.5$, 5.5 Hz, CH_a), 2.85 (1H, dd, $J=1.5$, 6.6 Hz, CH_b), 3.83 (1H, dd, $J=5.5$, 6.6 Hz, CH), 6.90—7.30 (4H, m, phenyl-H). IR (KBr): 2920, 1704, 1490, 1405, 1090, 830 cm^{-1}. LR-MS m/z (%): 172 (M^+, 18), 170 (M^+, 48), 135 (100), 125 (31), 67 (15), 40 (16). HR-MS Calcd for C_8H_7ClS: 169.996. Found: 169.992.

2-(2,6-Dichlorophenyl)thiirane (22h) This compound (0.030 g, 0.145 mmol) was prepared in 29% yield from 2,6-dichlorobenzaldehyde (**8h**) (0.263 g, 1.5 mol), **5b** (0.174 g, 0.5 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **22a**. IR (KBr): 2957, 1558, 1432, 11198, 1098, 778 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.01 (1H, d, $J=5.9$ Hz, CH_a), 3.01 (1H, d, $J=6.4$ Hz, CH_b), 3.78 (1H, dd, $J=5.9$, 6.6 Hz, CH), 67.10—7.40 (3H, m, phenyl-H). LR-MS m/z (%): 206 (M^+, 57), 204 (M^+, 82), 169 (100), 159 (25), 134 (78), 84 (16), 45 (9). HR-MS Calcd for $C_8H_6Cl_2S$: 203.957. Found: 203.957.

2-(4-Phenylphenyl)thiirane (22i) This compound (0.061 g, 0.290 mmol) was prepared in 58% yield from 4-phenylbenzaldehyde (**8i**) (0.273 g, 1.5 mmol), **5b** (0.174 g, 0.5 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **22a**. This compound was alternatively prepared from **5a** and **8i** under the same reaction conditions in 63% yield. IR (KBr): 1483, 839, 760, 687, 600 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.69 (1H, dd, $J=1.5$, 5.5 Hz, CH_a), 2.89 (1H, dd, $J=1.5$, 6.6 Hz, CH_b), 3.93 (1H, dd, $J=5.5$, 6.6 Hz, CH), 6.70—7.30 (9H, m, phenyl-H). LR-MS m/z (%): 212 (M^+, 14), 188 (7), 180 (100), 165 (16), 152 (17), 76 (9). HR-MS Calcd for $C_{14}H_{12}S$: 212.066. Found: 212.066.

2-(1-Naphthyl)thiirane (22j) This compound (0.045 g, 0.240 mmol) was prepared in 48% yield from 1-naphthylaldehyde (**8j**) (0.234 g, 1.5 mmol), **5b** (0.174 g, 0.5 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **22a**. This compound was alternatively prepared from **5a** and **8j** under the same reaction conditions in 47% yield. IR (KBr): 1483, 839, 760, 687, 600 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.83 (1H, dd, $J=1.3$, 5.9 Hz, CH_a), 2.96 (1H, dd, $J=1.3$, 6.4 Hz, CH_b), 4.45 (1H, dd, $J=5.9$, 6.4 Hz, CH), 7.20—8.30 (7H, m, naphthyl-H). LR-MS m/z (%): 186 (M^+, 50), 171 (10), 153 (77), 141 (14), 32 (26), 28 (100). HR-MS Calcd for $C_{12}H_{10}S$: 186.049. Found: 186.049.

4-Cyanostyrene (23a)[13] This compound (0.023 g, 0.175 mmol) was prepared in 35% yield from 4-cyanobenzaldehyde (**8k**) (0.197 g, 1.5 mmol), **5b** (0.174 g, 0.5 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **22a**. This compound was also prepared in 56% yield from **5a** and **8k**. IR (KBr): 2217 (CN), 1608, 1404, 992, 923, 847 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 5.44 (1H, dd, $J=0.7$, 10.8 Hz, $=CH_a$), 5.85 (1H, dd, $J=0.7$, 17.6 Hz, $=CH_b$), 6.73 (1H, dd, $J=10.8$, 17.6 Hz, =CH–), 7.30—7.70 (4H, m, phenyl-H). LR-MS m/z (%): 129 (M^+, 22), 103 (53), 91 (14), 76 (18), 32 (29), 28 (100). HR-MS Calcd for C_9H_7N: 129.058. Found: 129.058.

4-Nitrostyrene (23b)[13] This compound (0.042 g, 0.280 mmol) was prepared in 56% yield from 4-nitrobenzaldehyde (**8l**) (0.227 g, 1.5 mmol), **5b** (0.174 g, 0.5 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **22a**. ^{1}H-NMR ($CDCl_3$) δ: 5.49 (2H, ddd, $J=0.4$, 10.8, 10.8 Hz, $CH=C\underline{H}_2$), 6.79 (1H, dd, $J=10.8$, 17.6 Hz, =CH–), 7.51 (2H, d, $J=8.8$ Hz, 2′, 6′-H), 8.18 (2H, d, $J=8.8$ Hz, 3′, 5′-H).

4-(2,6-Dichlorophenyl)-2-(*p*-toluenesulfonyl)imino-1,3-oxathiolane (15a) A solution of 0.263 g (1.5 mmol) of 2,6-dichlorobenzaldehyde (**8h**), 0.174 g (0.5 mmol) of **5b**, and 0.091 g (0.6 mmol) of CsF in 10 ml of dry acetonitrile was stirred at room temperature for 43 h under an argon atmosphere. Water was added with stirring, and the mixture was extracted with three 20 ml portions of ether. The organic extracts were combined and washed with 30 ml of saturated sodium chloride solution, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was chromatographed on a silica gel column (20 g) using a mixture of hexane and ethyl acetate (10 : 1) as an eluent to give 0.030 g (0.146 mmol, 29% yield) of **22h** as a pale yellow oil.

Subsequent elution with hexane–ethyl acetate (1 : 1) as an eluent gave 0.037 g (0.092 mmol, 18% yield) of colorless prisms, **15a**, mp 154—155 °C. IR (KBr): 1520, 1300, 1150, 830, 558 cm^{-1}. UV λ_{max}^{EtOH} nm (log ε): 220 (4.33, shoulder), 270 (4.34). ^{1}H-NMR ($CDCl_3$) δ: 2.44 (3H, s, Me), 3.45 (1H, m, CH_a), 4.40 (1H, m, CH_b), 6.20 (1H, dd, $J=5.9$, 12.7 Hz, CH-O), 7.10—7.40 (5H, m, aromatic-H), 7.87 (2H, d, $J=8.1$ Hz, aromatic-H). *Anal.* Calcd for $C_{16}H_{13}C_{12}NO_3S_2$: C, 47.77; H, 3.26; N, 3.48. Found: C, 47.78; H, 3.25; N, 3.52.

Reaction of 5a with 4-Phenylbenzaldehyde (8i) in the Presence of TASF: 2-Cyanoimino-4-(4-phenylphenyl)-1,3-oxathiolane (15b) A 50 ml, two necked flask was fitted with a magnetic stirring bar and gas inlet tube. To a solution of 0.218 g (1.0 mmol) of **19b** and 0.558 (3 mmol) of 4-phenylbenzaldehyde (**8i**) in 2 ml of absolute THF was added 1.0 ml of TASF (1.0 mmol, 1 M). The mixture was stirred for **22h** at room temperature. After removal of the solvent by evaporation, the residue was chromatographed on a silica gel column (20 g) with a 10% ethyl acetate–hexane mixture as an eluent to give 0.099 g (0.469 mmol, 47%) of **22i** as a pale yellow oil.

Subsequent elution with a 50% ethyl acetate–hexane mixture as an eluent gave 0.036 g (0.13 mmol, 13%) of a pale yellow oil (**15b**). IR (KBr): 2185 (CN), 1583, 1484, 1027, 944 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.85 (2H, m, CH_2), 6.01 (1H, dd, $J=6.8$, 9.8 Hz, CH), 7.30—7.70 (9H, m, aromatic-H). LR-MS m/z (%): 280 (M^+, 10), 209 (100), 192 (33), 180 (56), 152 (39). HR-MS Calcd for $C_{16}H_{12}N_2OS$: 280.067. Found: 280.068.

The reaction of 19b with 4-methoxybenzaldehyde (8f) This reaction was carried out using 0.420 g (1.0 mmol) of **19b**, 0.136 g (1.0 mmol) of 4-methoxybenzaldehyde (**8f**), and 0.334 g (2.2 mmol) of CsF. Work-up in the usual manner followed by silica gel chromatography afforded 0.044 g (0.32 mmol, 32%) of **22f** as a colorless oil.

Reaction of 5b with Active Alkenes: Dimethyl 2-(*p*-Toluenesulfonyl)iminotetrahydrothiophene-3,4-dicarboxylate (16a) and Dimethyl 5-(*p*-Toluenesulfonylamino)-2,3-dihydrothiophene-3,4-dicarboxylate (24a) A 50 ml, two necked flask was fitted with a magnetic stirring bar and gas inlet tube. The flask was charged with 0.182 g (1.2 mmol) of CsF and was heated at 100—140 °C with hot plate stirrer for 1 h. The apparatus was cooled under purging with nitrogen. A solution of methyl maleate (0.288 g, 2.0 mmol) in 1 ml of dry acetonitrile was then added. A solution of **5b** (0.347 g, 1.0 mmol) in 2 ml of acetonitrile was introduced *via* a syringe with stirring. When all reagents had been added, the reaction mixture was stirred for 24 h at room temperature. The solvent was removed under reduced pressure on a rotary evaporator to yield a residue. The residue was added to the top of a 20 g, 60—200 mesh silica gel chromatography column and the column was eluted with 90% CH_2Cl_2–10% ethyl acetate solvent mixture. The solvent was removed from those fractions containing the product under reduced pressure on a rotary evaporator to afford 0.182 g (0.49 mmol, 49%) of a white product, which was a 1 : 1 mixture of **16a** and **24a**. A mixture of **16a** and **24a** (0.197 g, 0.53 mmol) was also prepared from **5b** (0.347 g, 1.0 mmol) and dimethyl fumarate (0.288 g, 2.0 mmol) under the same conditions in 53% yield. An analytical sample was recrystallized from iso-PrOH, mp 115—123 °C. IR (KBr): 3440 (NH), 1740 (CO), 1555, 1320, 1165, 1080, 760, 670, 560 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.43 (3H, s, *p*-Me), 3.30—3.50 (m), 3.50—3.70 (m), 3.69 (3H, s, OMe), 3.71 (3H, m, OMe), 3.75 (OMe), 4.01 (m), 4.18 (d, $J=8.4$ Hz, phenyl-H), 7.29—7.33 (m, aromatic-H), 7.80—

7.86 (m, aromatic-H), 10.8 (1/2H, br s, NH). ^{13}C-NMR (100 MHz, CDCl$_3$): 21.6, 33.8, 35.6, 46.3, 48.6, 51.6, 52.5, 53.1, 60.3, 100.1, 127.5, 127.6, 129.6, 129.8, 136.2, 136.4, 144.4, 144.6, 157.5, 166.0, 167.7, 170.0, 172.6, 184.4. LR-MS *m/z* (%): 370 (M$^+$ − 1, 14), 311 (83), 184 (19), 103 (31), 91 (100), 45 (42). *Anal.* Calcd for $C_{15}H_{17}NO_6S_2$: C, 48.51; H, 4.61; N, 3.77; S, 17.27. Found: C, 48.29; H, 4.49; N, 3.76; S, 17.02.

Diethyl 2-(*p*-Toluenesulfonyl)iminotetrahydrothiophene-3,4-dicarboxylate (16b) and Diethyl 5-(*p*-Toluenesulfonylamino)-2,3-dihydrothiophene-3,4-dicarboxylate (24b) These compounds (0.196 g, 0.49 mmol) were prepared in 49% yield from diethyl maleate (0.516 g, 3.0 mmol), **5b** (0.345 g, 1.0 mmol), and CsF (0.182 g, 1.2 mmol) in a manner similar to that described for the preparation of a mixture of **16a** and **24a**, as a pale yellow caramel oil. A mixture of **16b** and **24b** (0.151 g, 0.38 mmol) was also prepared from **5b** (0.345 g, 1.0 mmol) and diethyl fumarate (0.516 g, 3.0 mmol) under the same conditions in 38% yield. IR (KBr): 3440 (NH), 1735 (CO), 1555, 1320, 1155, 815, 775, 550 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.10—1.30 (6H, m, CH$_2$C$\underline{H}_3$), 2.43 (3H, s, Me), 3.40 (2H, dd, J = 6.4, 7.6 Hz, S-CH$_2$), 3.50—3.80 (2H, m, CH–CH), 3.90—4.30 (4H, m, C$\underline{H}_2$–CH$_3$), 7.29 (2H, d, J = 8.6 Hz, aromatic-H), 7.81 (2H, d, J = 8.6 Hz, aromatic-H), 10.90 (1/2H, br s, NH). LR-MS *m/z* (%): 399 (M$^+$, 16), 326 (97), 172 (19), 155 (68), 91 (100), 65 (21). HR-MS: Calcd for $C_{17}H_{21}NO_6S_2$: 399.081. Found: 399.081.

References and Notes

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9) The reaction of **4a** with dimethyl fumarate (**11c**) in the presence of cesium fluoride in acetonitrile gave a mixture of the desired cycloadduct, dimethyl 1-methyl-2-cyanoiminopyrrolidine-*trans*-3,4-dicarboxylate and an unidentified product in 37 and 37% yields, respectively. This unknown product was obtained as pale yellow crystals and its molecular formula was $C_{16}H_{21}N_3O_8 = 383$ which showed that it is the cycloadduct of 2 eq of dimethyl fumarate with 1 eq of iminoazomethine ylide.

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