1,3-Dipolar Cycloaddition Reaction of 2-[(Trimethylsilylmethylamino)(methylthio)]methylene-1,3-indandione and 2-[(Trimethylsilylmethylthio)(methylthio)]methylene-1,3-indandione: Synthetic Equivalents of Cyclic Dicarbonyl Alkylideneazomethine and Alkylidenethiocarbonyl Ylides as Novel 1,3-Dipolar Reagents¹⁾

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2-[(Trimethylsilylmethylamino)(methylthio)]methylene- and 2-[(trimethylsilylmethylthio)(methylthio)]methylene-1,3-indandiones (**1a**, **b**), which are readily prepared by reaction of the corresponding 2-bis(methylthio)methylene-1,3-indandione (**12**) with trimethylsilylmethylamine (**13a**) and trimethylsilylmethylmercaptan (**13b**), were found to be synthetic equivalents of carbonyl alkylidene-azomethine and alkylidene-thiocarbonyl ylides. Reaction of **1a**, **b** with reactive hetero-dipolarophiles such as aldehydes and ketones and reactive alkenes in the presence of cesium fluoride gave 1,3-dipolar cycloadducts, 4,5-dihydro-2-(1,3-dioxindan-2-ylidene)-1,3-oxazoles (**6a–f**, **7a–c**), 4,5-dihydro-2-(1,3-dioxindan-2-ylidene)pyrroles (**8a–c**), 2-alkylidene-1,3-oxathiolanes (**9a–k**, **10a**, **b**), and 2-alkylidenethiophenes (**11a–c**), via formation of the counterpart of the carbonyl-substituted intermediate with concomitant desilylation.

Key words 1,3-dipolar cycloaddition reaction; azomethine ylide; thiocarbonyl ylide; ketene dithioacetal; 4,5-dihydro-1,3-oxazole; 1,3-oxathiolane

Azomethine and thiocarbonyl ylides are the most important classes of 1,3-dipolar reagents for the construction of nitrogen or sulfur-containing five-membered heterocycles such as pyrrolidine, 4,5-dihydro-1,3-oxazole, thiophene, 1,3-oxathiolane, and 4,5-dihydro-1,3-thiazole derivatives.²⁾ Among them, alkylidene-azomethine or thiocarbonyl ylides are also synthetically useful reagents for the preparation of *N*- or *S*-containing five-membered heterocycles bearing an active methylene group at the α -position.³⁾ It has been reported that alkylidene-azomethine ylides can be generated by the 1,3-elimination reaction of *N*-(trimethylsilylmethyl) substituted ketene *N,S*-acetals or ketene dithioacetals promoted by fluoride ion. On the other hand, α -oxoketene *N,S*-acetals are also synthetically useful reagents, and numerous preparation methods and synthetic reactions have been reported.⁴⁾ As an extension of the use of ketene dithioacetals for synthesis of heterocycles, we wish to report here the preparation of α -oxoketene *N,S*-acetal and ketene dithioacetal, 2-[(trimethylsilylmethylamino)(methylthio)]methylene-1,3-indandione (**1a**) and 2-[(trimethylsilylmethylthio)(methylthio)]methylene-1,3-indandione (**1b**) as new synthetic equivalents of carbonyl alkylidene-azomethine and -thiocarbonyl ylides. We also describe a novel synthesis of cyclic α -oxoketene *N,O*-acetals and 2-carbonyl alkylidene-

pyrrolidines via the 1,3-dipolar cycloaddition to carbonyl compounds and reactive alkenes.

2-Bis(methylthio)methylene-1,3-indandione (**12**),⁵⁾ readily available from 1,3-indandione by reaction with carbon disulfide in the presence of sodium hydroxide followed by methylation with methyl iodide, was treated with trimethylsilylmethylamine (**13a**) in methanol under reflux for 30 min to afford a separable mixture of **1a**⁶⁾ and 2-bis(trimethylsilylmethylamino)methylene-1,3-indandione (**14a**) in 51 and 23% yields, respectively.

2-[(Trimethylsilylmethylthio)(methylthio)]methylene-1,3-indandione (**1b**) was also prepared by the addition-elimination reaction of trimethylsilylmethylmercaptan (**13b**) with **12**. This reaction in tetrahydrofuran (THF) gave a separable mixture of **1b** and 2-bis(trimethylsilylmethylthio)methylene-1,3-indandione (**14b**) in 54 and 20% yields, respectively.

It was previously shown that the synthesis of 2-alkylidene-1,3-oxazolidines from alkylidene-azomethine ylides and carbonyl compounds as hetero 1,3-dipolarophiles could be effectively conducted by using a stoichiometric amount of cesium fluoride.³⁾ At the start of this study, the reaction of **1a** with benzaldehyde (**3a**) was attempted in the presence of cesium fluoride in acetonitrile at room temperature for 45 h. The reaction proceeded

Chart 1

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smoothly to afford the corresponding 4,5-dihydro-2-(1,3-dioxindan-2-ylidene)-4-phenyl-1,3-oxazole (**6a**) in 42% yield. Compound **1a** also reacted with various aromatic aldehydes (**3b–f**) to give the corresponding 4,5-dihydro-2-(1,3-dioxindan-2-ylidene)-1,3-oxazoles (**6b–f**) in the yields shown in Table 1. The reaction of **1a** with ketones (**4a–c**) proceeded smoothly to give the corresponding 4,4-disubstituted 2-oxazole derivatives (**7a–c**) in 11–59% yields.

In order to ascertain the stereospecificity of the reaction, we studied the cycloaddition of **1a** with *cis* and *trans*-disubstituted dipolarophiles. The azomethine ylides examined so far in the literature²⁾ have been shown to undergo stereospecific cycloaddition. Interestingly, treatment of **1a** with either dimethyl fumarate (**5a**) or dimethyl maleate (**5b**) at room temperature for 20 h in the presence of cesium fluoride afforded a 9:1 mixture of *trans* and *cis* cycloadducts, dimethyl 4,5-dihydro-2-(1,3-dioxindan-2-ylidene)pyrrole-3,4-dicarboxylate (**8a, a'**) as the exclusive product, without stereocontrolled. Similarly, reaction of **1a** with diethyl fumarate (**5c**) and diethyl maleate (**5d**) gave the corresponding 1,3-dipolar cycloadducts (**8b, b'**) in 22 and 24% yields, respectively. Initially, exposure of compound **1a** to cesium fluoride promotes a metal-assisted ionization of the carbonyl group of indandione and a concomitant desilylation to form the stabilized 1,3-dipole (**15**). The 1,3-dipolar cycloaddition of **15** with active

alkenes occurs, followed by elimination of the methylthio group and hydrolysis of cesium salts (**16**) to yield the corresponding final products (**8a, b**). The reaction as shown in Chart 3, involving the intermediates (**16**), is proposed.

We also examined the regioselectivity of the cycloaddition reaction using an unsymmetrically substituted dipolarophile. When methyl acrylate (**5e**) was used as the dipolarophile, cycloadduct (**8c**) was the exclusive product. The structure of **8c** was established by ¹H-NMR, IR, and MS analyses.

α -Thiocarbanions should be readily generated by the fluoride ion-promoted desilylation of trimethylsilylmethyl sulfide under mild conditions and should be conveniently applicable for obtaining various 1,3-dipolar reagents, such as thiocarbonyl ylides and related species.⁷⁾ At the start of the present study, reaction of **1b** with 2,6-dichlorobenzaldehyde (**3d**) in the presence of various fluoride ions was conducted to afford the 2-(1,3-oxazolidin-2-ylidene)-1,3-indandione derivative (**9f**). The results are summarized in Table 2. Cesium fluoride as a fluoride ion source gave the best results in the reaction of **1b** with **3d** at room temperature in acetonitrile. Other fluoride ion sources such as TBAF and TASF also served well as catalysts to give the corresponding **9f**, but lithium fluoride and silver fluoride were not effective. Thus, cesium fluoride was mainly used as the fluoride ion source. As shown in Table 3, **1b** reacted smoothly with various aromatic, α,β -unsaturated and aliphatic aldehydes and ketones bearing electron-donating and electron-withdrawing substituents.

To determine the stereospecificity of the reaction, the cycloaddition of **1b** with *cis*- and *trans*-disubstituted dipolarophiles was carried out. The thiocarbonyl ylides examined so far in the literature have been shown to undergo stereospecific cycloaddition. Interestingly, treatment of **1b** with dimethyl fumarate (**5a**) or dimethyl maleate (**5b**) at room temperature for 20 h in the presence of cesium fluoride afforded the cycloadduct, dimethyl 2-(1,3-dioxindan-2-ylidene)-4,5-dihydrothiophene-*trans*-3,4-dicarboxylate (**11a**) as the exclusive product without stereocontrol. Exposure of this compound to cesium

Table 1. Reaction of 2-[(Trimethylsilylmethylamino)(methylthio)]methylene-1,3-indandione (**1a**) with Carbonyl Compounds (**3** and **4**)

Entry	R ¹ , R ² , (3)		Product	mp (°C)	Yield (%)
1	R ¹ = C ₆ H ₅	R ² = H (3a)	6a	245–247	42
2	R ¹ = 4-MeC ₆ H ₄	R ² = H (3b)	6b	255–258	51
3	R ¹ = 4-C ₆ H ₅ C ₆ H ₄	R ² = H (3c)	6c	222–225	47
4	R ¹ = 2,6-Cl ₂ C ₆ H ₃	R ² = H (3d)	6d	318–321	74
5	R ¹ = 4-NO ₂ C ₆ H ₄	R ² = H (3e)	6e	271–273	54
6	R ¹ = 1-Naphthyl	R ² = H (3f)	6f	252–256	62
7	R ¹ = C ₆ H ₅	R ² = C ₆ H ₅ (4a)	7a	213–219	11
8	R ¹ = C ₆ H ₅	R ² = C ₆ H ₅ -CO (4b)	7b	265–268	33
9	R ¹ = COOEt	R ² = COOEt (4c)	7c	178–179	59

rt, room temp.

Chart 3

Table 2. Reaction of 2-[(Trimethylsilylmethylthio)(methylthio)methylene]-1,3-indandione (**1b**) with 2,6-Dichlorobenzaldehyde (**3d**) in the Presence of Fluoride Ion

Entry	1b (mmol)	3d (mmol)	Activator	Conditions	Yield (%) of 9f ^{a)}
1	0.5	1.0	TASF (1.0 eq)	THF, r.t., 2.5 h	52
2	0.5	1.0	TBAF (0.1 eq)	THF, r.t., 20 h	50
3	0.5	1.0	TBAF (0.5 eq)	THF, r.t., 20 h	45
4	0.5	1.0	CsF (1.2 eq)	MeCN, r.t., 20 h	66
5	0.5	1.5	CsF (1.2 eq)	MeCN, r.t., 20 h	59
6	0.5	1.0	LiF (1.2 eq)	MeCN, r.t., 20 h	0
7	0.5	1.0	AgF (1.2 eq)	MeCN, r.t., 20 h	0

a) Isolated yield. TASF=Tris(dimethylamino)sulfur(trimethylsilyl) difluoride ($(\text{Me}_3\text{N})_3\text{S}(\text{Me}_3\text{SiF}_2)$). TBAF=Tetrabutylammonium fluoride $[\text{Me}(\text{CH}_2)_3]_4\text{NF}$.

fluoride promotes a metal-assisted ionization of the carbonyl group of indandione and concomitant desilylation to form the stabilized 1,3-dipole (**17**) as shown in Chart 4. In these reactions, compound **18** could be isolated as a stable cesium salt of **11** from the reaction mixture and was converted to the corresponding mixture of expected *cis* and *trans* alkylidenethiophene-3,4-dicarboxylates, **11a** and **b** (ratio of *cis* and *trans*: 10:1 from the ^1H -NMR spectrum).

The cycloaddition behavior of an unsymmetrically substituted dipolarophile was studied to determine the regioselectivity of the reaction. When methyl acrylate (**5e**) was used as a dipolarophile, the cycloadduct **11c** was obtained exclusively. The structure of **11c** was established by ^1H -NMR, IR, and MS analyses.

It is evident from the present data that the new ketene

N,S-acetal (**1a**) and ketene dithioacetal (**1b**) are synthetic equivalents of alkylidene-azomethine and -thiocarbonyl ylides. The reaction shows complete regioselectivity in cycloaddition with heterodipolarophiles and monosubstituted olefins.

Experimental

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

2-[(Trimethylsilylmethylamino)(methylthio)methylene]-1,3-indandione

Table 3. Reaction of 2-[(Trimethylsilylmethylthio)(methylthio)methylene]-1,3-indandione (**1b**) with Aldehydes (**3**) and Ketones (**4**) in the Presence of Fluoride Ion

Entry	R ¹	R ²	Product	Yield (%)	mp (°C)
1	C ₆ H ₅	H (3a)	9a	71	216
2	4-MeC ₆ H ₄	H (3b)	9b	44	237
3	4-MeOC ₆ H ₄	H (3g)	9c	21	215
4	3-MeOC ₆ H ₄	H (3h)	9d	33	142
5	4-ClC ₆ H ₄	H (3i)	9e	66	226
6	2,6-Cl ₂ C ₆ H ₃	H (3d)	9f	64	288
7	4-C ₆ H ₅ C ₆ H ₄	H (3c)	9g	45	237
8	4-NCC ₆ H ₄	H (3j)	9h	51	237
9	2-NO ₂ C ₆ H ₄	H (3e)	9i	54	223
10	1-Naphthyl	H (3f)	9j	78	176
11	CH=CH-C ₆ H ₅	H (3k)	9k	44	170
12	COOEt	COOEt (4c)	10a	89	131
13	4-NO ₂ C ₆ H ₄	Me (4d)	10b	36	231

Chart 4

(1a) and 2-Bis(trimethylsilylmethylamino)methylene-1,3-indandione (14a)
A solution of 5.06 g (20 mmol) of 2-bis(methylthio)methylene-1,3-indandione (**12**) and 2.48 g (24.0 mmol) of trimethylsilylmethylamine (**13a**) in 40 ml of absolute methanol was refluxed for 30 min. After evaporation of the solvent, the residue was chromatographed on a column of silica gel using a 6:1 mixture of hexane and ethyl acetate as an eluent to give **1a** (3.11 g, 10.2 mmol) as yellow needles in 51% yield. An analytical sample was recrystallized from methanol to give yellow needles, mp 72–73 °C. IR (KBr) ν cm⁻¹: 3030(NH), 1675, 1655 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 222 (4.40), 244 (4.17), 282 (4.68), 301 (3.96), 312 (4.15), 325 (4.18). ¹H-NMR (CDCl₃) δ : 0.20 (9H, s, SiMe₃), 2.69 (3H, s, SMe), 3.23 (2H, d, J =6.1 Hz, N-CH₂-), 7.46–7.71 (4H, m, aromatic-H), 8.91 (1H, br s, NH). Low resolution (LR-MS) m/z (%): 305 (M⁺, 100), 73 (25), 60 (18). High resolution (HR-MS) Calcd for C₁₅H₁₈NO₂SSi₂=305.090. Found: 305.091.

Subsequent elution using a 3:1 mixture of hexane–ethyl acetate as an eluent gave **14a** (1.66 g, 4.6 mmol) as yellow crystals, mp 125–127 °C, in 23% yield. IR (KBr) ν cm⁻¹: 3200, 2950 (NH), 1655, 1640 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 213 (4.16), 230 (4.47), 299 (4.22), 348 (4.44). ¹H-NMR (CDCl₃) δ : 0.23 (18H, s, SiMe₃), 3.02 (4H, d, J =4.8 Hz, N-CH₂-), 7.37–7.60 (4H, m, aromatic-H), 8.04 (1H, br s, NH), 8.90 (1H, br s, NH). LR-MS m/z (%): 360 (M⁺, 91), 345 (75), 73 (85), 60 (100). Anal. Calcd for C₁₈H₂₈N₂O₂SSi₂=360.592; C, 59.95; H, 7.83; N, 7.77. Found:

C, 59.98; H, 7.65; N, 7.57.

4,5-Dihydro-4-phenyl-2-(1,3-dioxindan-2-ylidene)-1,3-oxazole (6a)
This compound (0.061 g, 0.209 mmol) was prepared in 42% yield from **1a** (0.153 g, 0.5 mmol), benzaldehyde (**3a**) (0.106 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **6b**. An analytical sample was recrystallized from methanol to give yellow needles, mp 245–247 °C. IR (KBr) ν cm⁻¹: 3280 (NH), 1700, 1690, 1655 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 226 (4.50), 244 (4.19), 273 (4.54), 282 (4.81), 304 (4.29), 316 (4.28). ¹H-NMR (CDCl₃) δ : 3.86 (1H, dd, J =7.9, 9.9 Hz, N-CH_a-), 4.28 (1H, dd, J =9.1, 9.9 Hz, N-CH_b-), 6.01 (1H, dd, J =7.9, 9.1 Hz, O-CH), 7.42 (5H, s, phenyl-H), 7.57–9.97 (4H, m, aromatic-H), 9.21 (1H, br s, NH). LR-MS m/z (%): 291 (M⁺, 77), 173 (43), 119 (100), 92 (16), 91 (17). Anal. Calcd for C₁₈H₁₃NO₃=291.309; C, 74.22; H, 4.50; N, 4.81. Found: C, 74.03; H, 4.66; N, 4.77.

4,5-Dihydro-4-(4-methylphenyl)-2-(1,3-dioxindan-2-ylidene)-1,3-oxazole (6b)
A 50 ml, two-necked flask was fitted with a magnetic stirring bar and a gas inlet tube. The flask was charged with 0.091 g (0.6 mmol) of CsF and was heated at 100–140 °C under reduced pressure with a hot plate stirrer for 1 h. The apparatus was cooled under purging with nitrogen. A solution of a 4-methylbenzaldehyde (**3b**) (1.5 mmol) in 1 ml of dry acetonitrile was then added. A solution of 0.5 mmol of **1a** in 2 ml of acetonitrile was introduced *via* a syringe with stirring. When these reagents had been added, the mixture was stirred for 45 h at

room temperature, then poured into 50 ml of ice-water and acidified with 10% hydrochloric acid. The mixture was extracted with two 30 ml portions of ethyl acetate. The combined organic layer and extracts were washed once with aqueous saturated sodium chloride, dried over magnesium sulfate, filtered into a 200 ml round-bottomed flask and concentrated with a rotary evaporator. The residue was chromatographed on a silica gel column (50 g) with a 25% ethyl acetate-hexane mixture (ca. 100 ml) as the eluent to give 0.077 g (0.250 mmol) of **6b** as yellow crystals in 51% yield. An analytical sample was recrystallized from methanol to give yellow needles, mp 255–258 °C. IR (KBr) ν cm⁻¹: 3260 (NH), 1700, 1645 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 205 (4.59), 213 (4.60), 227 (4.67), 245 (4.29), 273 (4.63), 282 (4.92), 305 (4.38), 316 (4.39). ¹H-NMR (CDCl₃) δ : 2.36 (3H, s, Me), 3.81 (1H, dd, J =7.9, 9.9 Hz, N-CH₂-), 4.23 (1H, dd, J =9.0, 9.9 Hz, N-CH₂-), 5.94 (1H, dd, J =7.9, 9.0 Hz, O-CH), 7.14–7.79 (8H, m, aromatic-H), 9.19 (1H, br s, NH). LR-MS m/z (%): 305 (M⁺, 60), 173 (23), 133 (100). Anal. Calcd for C₁₉H₁₅NO₃=305.317: C, 74.74; H, 4.95; N, 4.59. Found: C, 74.57; H, 5.04; N, 4.69.

4,5-Dihydro-4-(4-biphenyl)-2-(1,3-dioxindan-2-ylidene)-1,3-oxazole (6c) This compound (0.086 g, 0.234 mmol) was prepared in 47% yield from **1a** (0.153 g, 0.5 mmol), 4-phenylbenzaldehyde (**3c**) (0.182 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **6b**. An analytical sample was recrystallized from methanol to give yellow needles, mp 222–225 °C. IR (KBr) ν cm⁻¹: 3310 (NH), 1730, 1690, 1655 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 202 (4.83), 227 (4.60), 248 (4.56), 274 (4.68), 283 (4.92), 305 (4.38), 316 (4.38). ¹H-NMR (CDCl₃) δ : 3.88 (1H, dd, J =7.9, 10.0 Hz, N-CH₂-), 4.30 (1H, dd, J =9.7, 10.0 Hz, N-CH₂-), 6.03 (1H, dd, J =7.9, 9.7 Hz, O-CH), 7.35–7.88 (13H, m, aromatic-H), 9.22 (1H, br s, NH). LR-MS m/z (%): 367 (M⁺, 40), 195 (47), 44 (100). Anal. Calcd for C₂₄H₁₇NO₃=367.387: C, 78.46; H, 4.67; N, 3.81. Found: C, 78.38; H, 4.79; N, 3.77.

4,5-Dihydro-4-(2,6-dichlorophenyl)-2-(1,3-dioxindan-2-ylidene)-1,3-oxazole (6d) This compound (0.133 g, 0.37 mmol) was prepared in 74% yield from **1a** (0.153 g, 0.5 mmol), 2,6-dichlorobenzaldehyde (**3d**) (0.175 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **6b**. An analytical sample was recrystallized from methanol to give yellow needles, mp 318–321 °C. IR (KBr) ν cm⁻¹: 3255 (NH), 1700, 1645 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 226, 244, 273, 282, 304, 316; λ min nm: 218, 220, 220, 278, 300, 312. ¹H-NMR (CDCl₃) δ : 3.87 (1H, dd, J =10.6, 10.7 Hz, N-CH₂-), 4.29 (1H, dd, J =10.7, 10.6 Hz, N-CH₂-), 6.69 (1H, dd, J =10.7, 10.6 Hz, O-CH), 7.50–7.59 (10H, m, aromatic-H), 9.80 (1H, br s, NH). LR-MS m/z (%): 361 (M⁺, 38), 359 (M⁺, 55), 173 (42), 44 (100). Anal. Calcd for C₁₃H₁₁Cl₂NO₃=360.187: C, 60.02; H, 3.08; Cl, 19.69; N, 3.87. Found: C, 60.17; H, 3.30; Cl, 19.87; N, 3.85.

4,5-Dihydro-4-(4-nitrophenyl)-2-(1,3-dioxindan-2-ylidene)-1,3-oxazole (6e) This compound (0.091 g, 0.270 mmol) was prepared in 54% yield from **1a** (0.153 g, 0.5 mmol), 4-nitrobenzaldehyde (**3e**) (0.151 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **6b**. An analytical sample was recrystallized from methanol to give tan needles, mp 271–273 °C. IR (KBr) ν cm⁻¹: 3280 (NH), 1700, 1690, 1655 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 246 (4.49), 275 (4.59), 305 (4.34), 316 (4.31), 349 (3.27). ¹H-NMR (CDCl₃) δ : 3.81 (1H, dd, J =9.2, 9.9 Hz, N-CH₂-), 4.43 (1H, dd, J =9.5, 9.9 Hz, N-CH₂-), 6.08 (1H, dd, J =9.2, 9.9 Hz, O-CH), 7.54–8.34 (13H, m, aromatic-H), 9.19 (1H, br s, NH). LR-MS m/z (%): 336 (M⁺, 100), 173 (83), 164 (59). HR-MS Calcd for C₂₄H₁₇NO₃=336.074. Found: 336.074.

4,5-Dihydro-4-(1-naphthyl)-2-(1,3-dioxindan-2-ylidene)-1,3-oxazole (6f) This compound (0.105 g, 0.305 mmol) was prepared in 62% yield from **1a** (0.153 g, 0.5 mmol), 1-naphthylbenzaldehyde (**3f**) (0.156 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **6b**. An analytical sample was recrystallized from methanol to give yellow needles, mp 252–256 °C. IR (KBr) ν cm⁻¹: 3280 (NH), 1695, 1690, 1645 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 223 (5.04), 245 (4.24), 274 (4.58), 283 (4.81), 305 (4.36), 316 (4.35). ¹H-NMR (CDCl₃) δ : 3.88 (1H, dd, J =7.5, 9.7 Hz, N-CH₂-), 4.49 (1H, dd, J =9.5, 9.7 Hz, N-CH₂-), 6.03 (1H, dd, J =7.5, 9.5 Hz, O-CH), 7.25–7.97 (13H, m, aromatic-H), 9.23 (1H, br s, NH). LR-MS m/z (%): 341 (M⁺, 77), 169 (100), 141 (22). Anal. Calcd for C₂₄H₁₇NO₃=341.347: C, 77.40; H, 4.43; N, 4.10. Found: C, 77.14; H, 4.60; N, 4.09.

4,5-Dihydro-4,4-diphenyl-2-(1,3-dioxindan-2-ylidene)-1,3-oxazole (7a) This compound (0.050 g, 0.055 mmol) was prepared in 11% yield from **1a** (0.153 g, 0.5 mmol), benzophenone (**4a**) (0.182 g, 1.0 mmol) and

CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **6b**. An analytical sample was recrystallized from methanol to give colorless needles, mp 213–219 °C. IR (KBr) ν cm⁻¹: 3290 (NH), 1695, 1690, 1650 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 227 (4.58), 245 (4.21), 274 (4.54), 283 (4.83), 305 (4.35), 316 (4.38). ¹H-NMR (CDCl₃) δ : 4.46 (2H, s, N-CH₂-), 7.25–7.81 (14H, m, aromatic-H), 9.10 (1H, br s, NH). LR-MS m/z (%): 367 (M⁺, 40), 195 (42), 44 (100). Anal. Calcd for C₂₄H₁₇NO₃=367.387: C, 78.46; H, 4.67; N, 3.81. Found: C, 78.34; H, 4.79; N, 3.81.

4-Benzoyl-4,5-dihydro-4-phenyl-2-(1,3-dioxindan-2-ylidene)-1,3-oxazole (7b) This compound (0.065 g, 0.165 mmol) was prepared in 33% yield from **1a** (0.153 g, 0.5 mmol), acetophenone (**4b**) (0.165 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **6b**. An analytical sample was recrystallized from methanol to give yellow needles, mp 265–268 °C. IR (KBr) ν cm⁻¹: 3280 (NH), 1700, 1685, 1655 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 229 (4.61), 247 (4.48), 275 (4.56), 284 (4.79), 305 (4.37), 317 (4.39). ¹H-NMR (CDCl₃) δ : 3.90 (1H, d, J =10.3 Hz, N-CH₂-), 5.06 (1H, d, J =10.3 Hz, N-CH₂-), 7.33–8.31 (14H, m, aromatic-H), 9.55 (1H, br s, NH). LR-MS m/z (%): 395 (M⁺, 71), 290 (93), 105 (100). Anal. Calcd for C₂₅H₁₇NO₃=395.397: C, 75.94; H, 4.33; N, 3.54. Found: C, 75.91; H, 4.52; N, 3.55.

4,4-Bis(ethoxycarbonyl)-4,5-dihydro-2-(1,3-dioxindan-2-ylidene)-1,3-oxazole (7c) This compound (0.106 g, 0.295 mmol) was prepared in 59% yield from **1a** (0.153 g, 0.5 mmol), diethyl ketomalonate (**4c**) (0.174 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **6b**. An analytical sample was recrystallized from ethanol to give colorless needles, mp 178–179 °C. IR (KBr) ν cm⁻¹: 3250 (NH), 1700, 1650 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 228 (4.37), 244 (4.22), 283 (4.75), 304 (4.28), 316 (4.30). ¹H-NMR (CDCl₃) δ : 1.35 (6H, t, J =7.2 Hz, O-CH₂-CH₃), 4.38 (4H, q, J =7.2 Hz, O-CH₂-), 4.33 (2H, s, N-CH₂-), 7.56–7.82 (4H, m, aromatic-H), 9.12 (1H, br s, NH). LR-MS m/z (%): 359 (M⁺, 100), 286 (47), 174 (57). Anal. Calcd for C₁₈H₁₇NO₇=359.327: C, 60.16; H, 4.77; N, 3.90. Found: C, 59.90; H, 4.75; N, 3.85.

Dimethyl 4,5-Dihydro-2-(1,3-dioxindan-2-ylidene)pyrrole-trans and cis 3,4-Dicarboxylate (8a, 8a') 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 dimethyl maleate (**5b**) (0.288 g, 2.0 mmol) in 1 ml of dry acetonitrile was then added. A solution of **1a** (0.306 g, 2.0 mmol) in 2 ml of dry acetonitrile was introduced via a syringe with stirring. When these reagents had been added, the reaction mixture was stirred for 20 h at room temperature. The solvent was removed under reduced pressure with a rotary evaporator to yield a residue. The residue was added to the top of 20 g of 60–200 mesh silica gel in a column and the column was eluted with a 90% CH₂Cl₂-ethyl acetate solvent mixture. The solvent was removed from the fractions containing the product under reduced pressure with a rotary evaporator to afford 0.229 g (0.63 mmol, 63%) of a white product, which was a 9:1 mixture of **8a** and **8a'**. A mixture of **8a** and **8a'** (0.236 g, 0.65 mmol) was also prepared from **1a** and dimethyl fumarate (**5a**) (0.288 g, 2.0 mmol) under the same conditions in 65% yield. An analytical sample was recrystallized from methanol to give colorless crystals, mp 180–185 °C. IR (KBr) ν cm⁻¹: 3280 (NH), 1740, 1670 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 237 (4.45), 283 (4.24), 294 (4.56), 320 (4.44), 330 (4.59). ¹H-NMR (CDCl₃) δ : 3.47 (9H, m, OMe, N-CH₂-CH), 4.92 (1H, d, J =3.7 Hz, N-C-CH of **8a**), 5.10 (1H, d, J =6.2 Hz, N-C-CH of **8a'**), 7.49–7.76 (4H, m, aromatic-H), 9.44 (1H, br s, NH 30%), 9.54 (1H, br s, NH 70%), 4.33 (2H, s, N-CH₂-), 7.56–7.82 (4H, m, aromatic-H), 9.12 (1H, br s, NH). LR-MS m/z (%): 329 (36), 298 (6), 270 (34), 238 (100), 210 (36). HR-MS: Calcd for C₁₇H₁₅NO₆=329.090. Found: 329.090.

Diethyl 4,5-Dihydro-2-(1,3-dioxindan-2-ylidene)pyrrole-trans and cis 3,4-Dicarboxylate (8b, 8b') These compounds (0.085 g, 0.24 mmol) were prepared in 24% yield from diethyl maleate (**5d**) (0.172 g, 1.0 mmol), **1a** (0.153 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 **8b** and **8b'**, as yellow crystals in 24% yield. These compounds (**8b**, **b'**) were also prepared in 22% yield from **1a** and diethyl fumarate (**5c**) in a manner similar to that described for preparation of **8a**. An analytical sample was recrystallized from ethanol to give yellow crystals, mp 142–145 °C. IR (KBr) ν cm⁻¹: 3270 (NH), 1730, 1690, 1655 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 236 (4.42), 283 (4.23), 293 (4.56), 318 (4.42), 330 (4.58). ¹H-NMR (DMSO-*d*₆) δ :

1.11—1.29 (6H, m, $\text{CH}_2\text{—CH}_3$), 3.44—3.57 (1H, m, $\text{N—CH}_2\text{—}$), 3.61—4.28 (6H, m, $\text{N—CH}_2\text{—}$, $2 \times \text{O—CH}_2\text{—}$), 4.72 (1H, d, $J=3.7$ Hz, $\text{N—CH}_2\text{—CH—}$), 7.52—7.64 (4H, m, aromatic-H), 9.25 (1H, brs, NH). LR-MS m/z (%): 357 (M^+ , 53), 238 (100), 44 (43). *Anal.* Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_6$: 357.347; C, 63.86; H, 5.36; N, 3.72. Found: C, 63.74; H, 5.37; N, 3.86.

Methyl 4,5-Dihydro-2-(1,3-dioxoindan-2-ylidene)pyrrole-3-dicarboxylate (8c) This compound (0.038 g, 0.140 mmol) was prepared in 28% yield from methyl acrylate (**5e**) (0.086 g, 1.0 mmol), **1a** (0.153 g, 1.0 mmol), and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of a mixture of **8a** and **8a'**, as yellow crystals. An analytical sample was recrystallized from methanol to give yellow crystals, mp 272—273 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 3290 (NH), 1718, 1695, 1650 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 226 (4.37), 235 (4.39), 282 (4.24), 292 (4.56), 317 (4.41), 329 (4.57). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$) δ : 2.05 (2H, m, 4-H), 3.49—3.76 (2H, m, 5-H), 3.64 (3H, s, OMe), 4.47 (1H, dd, $J=7.6$, 10.1 Hz, 3-H), 7.62 (4H, m, aromatic-H), 10.00 (1H, brs, NH). LR-MS m/z (%): 271 (M^+ , 100), 212 (68), 40 (50). *Anal.* Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_4$: 271.257; C, 66.41; H, 4.83; N, 5.16. Found: C, 66.09; H, 4.88; N, 5.06.

2-[(Trimethylsilylmethylthio)(methylthio)methylene-1,3-indandione (1b) and 2-Bis(trimethylsilylmethylthio)methylene-1,3-indandione (14b)] A solution of 1.00 g (4 mmol) of 2-bis(methylthio)methylene-1,3-indandione (**12**) and 0.57 g (4.80 mmol) of trimethylsilylmethylmercaptan (**13b**) in 30 ml of absolute THF was refluxed for 1 h. After evaporation of the solvent, the residue was chromatographed on a column of silica gel using a 6:1 mixture of hexane and ethyl acetate as an eluent to give **1b** (0.322 g, 2.16 mmol) as yellow needles in 54% yield. An analytical sample was recrystallized from methanol to give yellow needles, mp 71—75 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 2950, 1675, 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 236 (4.84), 309 (4.34), 367 (4.78), 400 (4.69). $^1\text{H-NMR}$ (CDCl_3) δ : 0.16 (9H, s, SiMe_3), 2.45 (2H, s, CH_2), 2.63 (3H, s, SMe), 7.59—7.88 (4H, m, aromatic-H). LR-MS m/z (%): 322 (M^+ , 46), 261 (36), 189 (35). *Anal.* Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2\text{S}_2\text{Si}$: 322.498; C, 55.86; H, 5.62; S, 19.88. Found: C, 55.72; H, 5.58; S, 19.75.

Subsequent elution using a 3:1 mixture of hexane—ethyl acetate as an eluent gave **14b** (0.70 g, 0.806 mol) as yellow crystals in 20% yield, mp 94—95 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 237 (4.41), 310 (3.88), 369 (4.33), 401 (4.26). $^1\text{H-NMR}$ (CDCl_3) δ : 0.15 (18H, s, SiMe_3), 2.44 (4H, s, $\text{S—CH}_2\text{—}$), 7.59—7.88 (4H, m, aromatic-H). LR-MS m/z (%): 394 (M^+ , 35), 189 (29), 73 (100). *Anal.* Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_2\text{S}_2\text{Si}_2$: 394.356; C, 54.82; H, 6.65; S, 14.24. Found: C, 54.68; H, 6.55; S, 14.18.

4-Phenyl-2-(1,3-dioxoindan-2-ylidene)-1,3-oxathiolane (9a) 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 under reduced pressure with a hot plate stirrer for 1 h. The apparatus was cooled while being purged with nitrogen. A solution of benzaldehyde (**3a**) (1.5 mmol) in 1 ml of dry acetonitrile was then added. A solution of 0.5 mmol of **1b** in 2 ml of acetonitrile was introduced via a syringe with stirring. When these reagents had been added, the mixture was stirred for 20 h at room temperature, then poured into 50 ml of ice-water and acidified with 10% hydrochloric acid. The mixture was extracted with two 30 ml portions of ethyl acetate. The combined organic layer and extracts were washed once with aqueous saturated sodium chloride, dried over magnesium sulfate, filtered into a 200 ml round-bottomed flask and concentrated with a rotary evaporator. The residue was chromatographed on a silica gel column (50 g) using a 25% ethyl acetate—hexane mixture (*ca.* 100 ml) as the eluent to give 0.110 g (0.357 mmol) of **9a** as colorless crystals in 71% yield. An analytical sample was recrystallized from methanol to give colorless needles, mp 215—216 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 1700, 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 239 (4.51), 273 (3.64), 287 (3.99), 297 (4.34), 332 (4.53). $^1\text{H-NMR}$ (CDCl_3) δ : 3.42 (1H, dd, $J=8.8$, 11.3 Hz, $\text{S—CH}_a\text{—}$), 3.69 (1H, dd, $J=7.0$, 11.3 Hz, $\text{S—CH}_b\text{—}$), 6.02 (1H, $J=7.0$, 8.8 Hz, O—CH—), 7.42—7.91 (8H, m, aromatic-H). LR-MS m/z (%): 308 (M^+ , 37), 136 (100), 91 (28). *Anal.* Calcd for $\text{C}_{18}\text{H}_{12}\text{O}_3\text{S}$: 308.920; C, 69.98; H, 3.92; S, 10.38. Found: C, 69.98; H, 4.09; S, 10.20.

Method B: A 50 ml, two-necked flask was fitted with a magnetic stirring bar and a gas inlet tube. TBAF (1.0 mmol) was added to a solution of 0.50 mmol of **3** or **4** and 1.0 mmol of the corresponding aldehyde **3a** in 5 ml of absolute THF, and the mixture was stirred for 20 h at room temperature. After removal of the solvent by evaporation, the residue was placed on the top of 20 g of 60—200 mesh silica gel in a column and the column was eluted with a 25% mixture of ethyl acetate—hexane.

The solvent was removed from the fractions containing the product under reduced pressure with a rotary evaporator to afford 0.052 g (0.25 mmol) of **9a** in 50% yield.

4-(4-Methylphenyl)-2-(1,3-dioxoindan-2-ylidene)-1,3-oxathiolane (9b) This compound (0.075 g, 0.222 mmol) was prepared in 44% yield from **1b** (0.161 g, 0.5 mmol), 4-methylbenzaldehyde (**3b**) (0.120 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized from ethanol to give colorless needles, mp 237—238 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 1705, 1665 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 239 (4.57), 287 (4.06), 297 (4.40), 332 (4.59). $^1\text{H-NMR}$ (CDCl_3) δ : 2.37 (3H, s, Me), 3.40 (1H, dd, $J=8.8$, 11.3 Hz, $\text{S—CH}_a\text{—}$), 3.69 (1H, dd, $J=7.0$, 11.3 Hz, $\text{S—CH}_b\text{—}$), 5.97 (1H, dd, $J=7.0$, 8.8 Hz, O—CH—), 7.21—7.87 (8H, m, aromatic-H). LR-MS m/z (%): 322 (M^+ , 35), 150 (97), 135 (100). *Anal.* Calcd for $\text{C}_{19}\text{H}_{14}\text{O}_3\text{S}$: 322.364; C, 70.79; H, 4.38; S, 9.93. Found: C, 70.79; H, 4.47; S, 9.90.

4-(4-Methoxyphenyl)-2-(1,3-dioxoindan-2-ylidene)-1,3-oxathiolane (9c) This compound (0.091 g, 0.10 mmol) was prepared in 20% yield from **1b** (0.161 g, 0.5 mmol), 4-methoxybenzaldehyde (**3g**) (0.136 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized from ethanol to give colorless needles, mp 214—215 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 1700, 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 239 (5.01), 272 (4.51), 286 (4.43), 298 (4.67), 332 (4.85). $^1\text{H-NMR}$ (CDCl_3) δ : 3.40 (1H, dd, $J=8.6$, 11.4 Hz, $\text{S—CH}_a\text{—}$), 3.61—3.81 (4H, m, O—Me, $\text{S—CH}_b\text{—}$), 5.97 (1H, dd, $J=8.6$, 8.8 Hz, O—CH—), 6.87—7.90 (8H, m, aromatic-H). LR-MS m/z (%): 338 (M^+ , 25), 166 (100), 135 (36). *Anal.* Calcd for $\text{C}_{19}\text{H}_{14}\text{O}_4\text{S}$: 338.364; C, 67.44; H, 4.17; S, 9.48. Found: C, 67.31; H, 4.23; S, 9.53.

4-(3-Methoxyphenyl)-2-(1,3-dioxoindan-2-ylidene)-1,3-oxathiolane (9d) This compound (0.055 g, 0.155 mmol) was prepared in 33% yield from **1b** (0.161 g, 0.5 mmol), 3-methoxybenzaldehyde (**3h**) (0.120 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized from ethanol to give colorless needles, mp 141—142 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 1700, 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 239 (4.48), 286 (3.99), 297 (4.32), 331 (4.53). $^1\text{H-NMR}$ (CDCl_3) δ : 3.41 (1H, dd, $J=8.6$, 11.4 Hz, $\text{S—CH}_a\text{—}$), 3.76 (1H, dd, $J=7.0$, 11.4 Hz, $\text{S—CH}_b\text{—}$), 3.80 (3H, s, OMe), 5.99 (1H, dd, $J=7.0$, 8.6 Hz, O—CH—), 6.84—7.91 (8H, m, aromatic-H). LR-MS m/z (%): 338 (M^+ , 28), 166 (100), 135 (42). *Anal.* Calcd for $\text{C}_{19}\text{H}_{14}\text{O}_4\text{S}$: 338.364; C, 67.44; H, 4.17; S, 9.48. Found: C, 67.31; H, 4.23; S, 9.53.

4-(4-Chlorophenyl)-2-(1,3-dioxoindan-2-ylidene)-1,3-oxathiolane (9e) This compound (0.110 g, 0.330 mmol) was prepared in 66% yield from **1b** (0.161 g, 0.5 mmol), 4-chlorobenzaldehyde (**3i**) (0.140 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized from ethanol to give colorless needles, mp 225—226 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 1705, 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 239 (4.58), 273 (3.83), 286 (4.07), 297 (4.40), 332 (4.58). $^1\text{H-NMR}$ (CDCl_3) δ : 3.37 (1H, dd, $J=8.6$, 11.3 Hz, $\text{S—CH}_a\text{—}$), 3.77 (1H, dd, $J=6.8$, 11.3 Hz, $\text{S—CH}_b\text{—}$), 5.99 (1H, dd, $J=6.8$, 8.6 Hz, O—CH—), 7.39—7.88 (12H, m, aromatic-H). LR-MS m/z (%): 344 (M^+ , 13), 342 (M^+ , 34), 172 (22), 170 (46), 138 (20), 135 (100). *Anal.* Calcd for $\text{C}_{19}\text{H}_{11}\text{ClO}_3\text{S}$: 342.787; C, 63.07; H, 3.24; Cl, 10.34; S, 9.35. Found: C, 53.04; H, 3.40; Cl, 10.60; S, 9.49.

4-(2,6-Dichlorophenyl)-2-(1,3-dioxoindan-2-ylidene)-1,3-oxathiolane (9f) This compound (0.123 g, 0.320 mmol) was prepared in 64% yield from **1b** (0.161 g, 0.5 mmol), 2,6-dichlorobenzaldehyde (**3d**) (0.175 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized from ethanol to give colorless needles, mp 287—288 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 1705, 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 239 (4.57), 273 (3.91), 285 (4.10), 297 (4.42), 331 (4.58). $^1\text{H-NMR}$ (CDCl_3) δ : 3.70 (2H, d, $J=9.9$ Hz, $\text{S—CH}_2\text{—}$), 6.61 (1H, dd, $J=9.9$, 9.9 Hz, O—CH—), 7.26—7.89 (7H, m, aromatic-H). LR-MS m/z (%): 378 (M^+ , 30), 376 (M^+ , 45), 204 (48), 169 (100), 134 (39). *Anal.* Calcd for $\text{C}_{18}\text{H}_{10}\text{Cl}_2\text{O}_3\text{S}$: 377.234; C, 57.31; H, 2.67; Cl, 18.80; S, 8.50. Found: C, 57.40; H, 2.86; Cl, 10.06; S, 8.47.

4-(4-Biphenyl)-2-(1,3-dioxoindan-2-ylidene)-1,3-oxathiolane (9g) This compound (0.089 g, 0.225 mmol) was prepared in 45% yield from **1b** (0.161 g, 0.5 mmol), 4-phenylbenzaldehyde (**3c**) (0.182 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized from ethanol to give colorless needles, mp 235—237 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 1700, 1660

(CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 239, 243, 285, 297, 332. $^1\text{H-NMR}$ (CDCl_3) δ : 3.46 (1H, dd, $J=8.6, 11.3$ Hz, S-CH_2), 3.80 (1H, dd, $J=6.8, 11.3$ Hz, S-CH_2), 6.07 (1H, dd, $J=6.8, 8.6$ Hz, O-CH), 7.35–7.88 (13H, m, aromatic-H). LR-MS m/z (%): 383 ($\text{M}^+ - 1$, 18), 212 (100), 180 (48). *Anal.* Calcd for $\text{C}_{24}\text{H}_{16}\text{O}_3\text{S}$ = 384.434: C, 74.98; H, 4.20; S, 8.34. Found: C, 75.01; H, 4.35; S, 8.24.

4-(4-Cyanophenyl)-2-(1,3-dioxindan-2-ylidene)-1,3-oxathiolane (9h) This compound (0.085 g, 0.255 mmol) was prepared in 51% yield from **1b** (0.161 g, 0.5 mmol), 4-cyanobenzaldehyde (**3j**) (0.131 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized from ethanol to give colorless needles, mp 237–238 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 2210 (CN), 1700, 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 239 (4.74), 273 (3.87), 286 (4.10), 297 (4.43), 332 (4.62). $^1\text{H-NMR}$ (CDCl_3) δ : 3.37 (1H, dd, $J=8.1, 11.4$ Hz, S-CH_2), 3.83 (1H, dd, $J=7.0, 11.4$ Hz, S-CH_2), 6.06 (1H, dd, $J=7.0, 8.1$ Hz, O-CH), 7.26–7.93 (8H, m, aromatic-H). LR-MS m/z (%): 333 (M^+ , 39), 161 (100), 129 (22). *Anal.* Calcd for $\text{C}_{19}\text{H}_{11}\text{NO}_3\text{S}$ = 333.351: C, 68.45; H, 3.33; N, 4.20; S, 9.62. Found: C, 68.25; H, 3.55; N, 4.16; S, 8.24.

4-(2-Nitrophenyl)-2-(1,3-dioxindan-2-ylidene)-1,3-oxathiolane (9i) This compound (0.095 g, 0.270 mmol) was prepared in 54% yield from **1b** (0.161 g, 0.5 mmol), 4-nitrobenzaldehyde (**3e**) (0.151 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized from ethanol to give colorless needles, mp 221–223 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 1700, 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 241 (4.58), 286 (4.07), 297 (4.40), 332 (4.58). $^1\text{H-NMR}$ (CDCl_3) δ : 3.34 (1H, dd, $J=7.3, 11.2$ Hz, S-CH_2), 4.18 (1H, dd, $J=7.5, 11.2$ Hz, S-CH_2), 6.71 (1H, dd, $J=7.3, 7.5$ Hz, O-CH), 7.53–8.28 (8H, m, aromatic-H). LR-MS m/z (%): 353 (M^+ , 47), 132 (100), 104 (44), 91 (33). *Anal.* Calcd for $\text{C}_{18}\text{H}_{11}\text{NO}_5\text{S}$ = 353.341: C, 61.18; H, 3.14; N, 3.96; S, 9.07. Found: C, 61.12; H, 3.28; N, 3.94; S, 9.00.

4-(1-Naphthyl)-2-(1,3-dioxindan-2-ylidene)-1,3-oxathiolane (9j) This compound (0.140 g, 0.390 mmol) was prepared in 78% yield from **1b** (0.161 g, 0.5 mmol), 1-naphthylaldehyde (**3f**) (0.156 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized from ethanol to give colorless needles, mp 174–176 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 1710, 1665 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 239 (4.55), 273 (4.03), 286 (4.19), 297 (4.41), 332 (4.57). $^1\text{H-NMR}$ (CDCl_3) δ : 3.47 (1H, dd, $J=8.1, 11.3$ Hz, S-CH_2), 3.96 (1H, dd, $J=7.3, 11.3$ Hz, S-CH_2), 6.69 (1H, dd, $J=7.3, 8.1$ Hz, O-CH), 7.30–7.93 (11H, m, aromatic-H). LR-MS m/z (%): 358 (M^+ , 10), 186 (100), 153 (69). HR-MS: Calcd for $\text{C}_{22}\text{H}_{14}\text{O}_3\text{S}$ = 358.066. Found: 358.066.

4-Styryl-2-(1,3-dioxindan-2-ylidene)-1,3-oxathiolane (9k) This compound (0.075 g, 0.222 mmol) was prepared in 44% yield from **1b** (0.161 g, 0.5 mmol), cinnamaldehyde (**3k**) (0.132 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized from ethanol to give colorless needles, mp 168–170 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 1705, 1665 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 241, 285, 297, 332. $^1\text{H-NMR}$ (CDCl_3) δ : 3.30 (1H, dd, $J=8.1, 11.3$ Hz, S-CH_2), 3.59 (1H, dd, $J=6.8, 11.3$ Hz, S-CH_2), 5.65 (1H, dd, $J=6.8, 8.1$ Hz, O-CH), 6.33 (1H, dd, $J=7.3, 16.2$ Hz, PhCH=CH), 6.87 (1H, d, $J=16.2$ Hz, PhCH=CH), 7.26–7.87 (9H, m, aromatic-H). LR-MS m/z (%): 334 (M^+ , 10), 306 (100), 162 (84). HR-MS Calcd for $\text{C}_{20}\text{H}_{14}\text{O}_3\text{S}$ = 334.066. Found: 334.066.

Diethyl 2-(1,3-dioxindan-2-ylidene)-1,3-oxathiolane-4,4-dicarboxylate (10a) This compound (0.168 g, 0.445 mmol) was prepared in 89% yield from **1b** (0.161 g, 0.5 mmol), diethyl ketomalonate (**4c**) (0.174 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized from ethanol to give colorless needles, mp 131–132 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 1740, 1680 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 239 (4.57), 287 (4.06), 297 (4.37), 330 (4.55). $^1\text{H-NMR}$ (CDCl_3) δ : 1.33 (6H, t, $J=7.3$ Hz, $2 \times \text{O-CH}_2\text{-CH}_3$), 3.91 (2H, s, S-CH_2), 4.35 (4H, q, $J=7.3$ Hz, O-CH_2), 7.76–7.94 (8H, m, aromatic-H). LR-MS m/z (%): 376 (M^+ , 90), 303 (73), 204 (76), 189 (51), 173 (100), 158 (77), 104 (39), 76 (29). *Anal.* Calcd for $\text{C}_{18}\text{H}_{16}\text{O}_7\text{S}$ = 376.374: C, 57.44; H, 4.29; S, 8.52. Found: C, 57.27; H, 4.28; S, 8.39.

4-Methyl-4-nitrophenyl-2-(1,3-dioxindan-2-ylidene)-1,3-oxathiolane (10b) This compound (0.067 g, 0.180 mmol) was prepared in 36% yield from **1b** (0.161 g, 0.5 mmol), 4-nitroacetophenone (**4d**) (0.165 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized from ethanol to give colorless needles, mp 229–231 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$:

1685, 1670 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 245, 350, 458; λ_{min} nm: 235, 320, 395. $^1\text{H-NMR}$ (CDCl_3) δ : 2.46 (3H, s, Me), 5.21 (2H, s, S-CH_2), 7.74–8.45 (8H, m, aromatic-H). LR-MS m/z (%): 367 (M^+ , 42), 352 (28), 320 (90), 217 (33), 150 (100), 104 (43), 76 (20). HR-MS Calcd for $\text{C}_{19}\text{H}_{13}\text{NO}_5\text{S}$ = 367.051. Found: 367.051.

Dimethyl 2-(1,3-Dioxindan-2-ylidene)tetrahydrothiophene-3,4-dicarboxylate (11a) This compound (0.135 g, 0.370 mmol) was prepared in 76% yield from **1b** (0.161 g, 0.5 mmol), methyl fumarate (**5a**) (0.144 g, 1.0 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **8**. An analytical sample was recrystallized from ethanol to give tan needles, mp 167–170 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 1730, 1670 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 246, 294, 306, 352; λ_{min} nm: 236, 290, 302, 318. $^1\text{H-NMR}$ (CDCl_3) δ : 3.41 (1H, q, $J=6.2$ Hz, $\text{S-CH}_2\text{-CH}$), 3.72 (3H, s, OMe), 3.74 (3H, s, OMe), 3.80–3.90 (2H, m, S-CH_2), 5.70 (1H, d, $J=6.0$ Hz, 3-H of **11a**), 5.81 (1H, d, $J=1.0$ Hz, 3-H of **11b**), 7.66–7.95 (4H, m, aromatic-H). LR-MS m/z (%): 364 (M^+ , 20), 255 (32), 71 (39). *Anal.* Calcd for $\text{C}_{17}\text{H}_{14}\text{O}_6\text{S}$ = 346.354: C, 58.95; H, 4.07; S, 9.26. Found: C, 58.77; H, 4.07; S, 9.27.

Cesium 2-(3,4-Bismethoxycarbonyl-4,5-dihydrothien-2-yl)-3-oxoindan-1-olate (18) A 50 ml, two-necked flask was fitted with a magnetic stirring bar and a gas inlet tube. The flask was charged with 0.091 g (0.6 mmol) of CsF and heated at 100–140 °C with a hotplate stirrer for 1 h. The apparatus was cooled under purging with nitrogen. A solution of dimethyl fumarate (**5a**) (0.144 g, 1.0 mmol) in 1 ml of acetonitrile was then added. A solution of **1b** (0.161 g, 0.5 mmol) in 2 ml of dry acetonitrile was introduced via a syringe with stirring. When these reagents had been added, the reaction mixture was stirred for 15 min. The products were collected by filtration and recrystallized from methanol to give 0.045 g (0.130 mmol) of tan crystals, mp 266–269 °C, in 26% yield. IR (KBr) $\nu_{\text{cm}^{-1}}$: 3430 (OH), 1728, 1660, (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 253 (4.19), 222 (4.40), 306 (3.95), 359 (4.12). $^1\text{H-NMR}$ (CDCl_3) δ : 2.90–3.28 (2H, m, S-CH_2), 3.41 (3H, s, OMe), 3.59 (3H, s, OMe), 4.04 (1H, dd, $J=7.3, 9.3$ Hz, CH-COOMe), 7.11–7.34 (4H, m, aromatic-H). FAB-MS m/z 479 ($\text{M}^+ + 1$, 84).

Methyl 2-(1,3-Dioxindan-2-ylidene)tetrahydrothiophene-4-carboxylate (11c) This compound (0.048 g, 0.165 mmol) was prepared in 33% yield from **1b** (0.161 g, 0.5 mmol), methyl acrylate (**5e**) (0.130 g, 1.5 mmol) and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of **8**. An analytical sample was recrystallized from ethanol to give tan needles, mp 137–140 °C. IR (KBr) $\nu_{\text{cm}^{-1}}$: 1670, 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 246 (4.25), 306 (3.74), 356 (4.25). $^1\text{H-NMR}$ (CDCl_3) δ : 2.36 (1H, m, 4a-H), 2.80 (1H, m, 4b-H), 3.28 (2H, m, 5-H), 3.73 (3H, s, OMe), 5.24 (1H, dd, $J=1.9, 7.8$ Hz, 3-H), 7.34–7.94 (4H, m, aromatic-H). LR-MS m/z (%): 288 (M^+ , 23), 250 (100), 189 (80). HR-MS Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_4\text{S}$ = 288.05. Found: 288.045.

References and Notes

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- 6) Protiodesilylation of **1a** in the presence of fluoride ion in acetonitrile (the proton presumably comes from the water present) gave the corresponding 2-[(dimethylamino)(methylthio)]methylene-1,3-indandione, which was alternatively prepared by the displacement reaction of **12** with dimethylamine in methanol in good yield. Tetrabutylammonium fluoride (TBAF) can be used as a source of fluoride ion in the present reaction. In the reaction of **1a** with **3d**, the desired product (**6d**) was obtained in 57% yield.
- 7) a) Hosomi A., Ogata K., Hoashi K., Kohra S., Tominaga Y., *Chem. Pharm. Bull.*, **36**, 3736—3738 (1988); b) Hosomi A., Ogata K., Ohkuma M., Hojo M., *Synlett.*, **3**, 557—558 (1991); c) Kohra S., Ueda H., Tominaga Y., *Heterocycles*, **36**, 1497—1500 (1993).