Photoaddition Reactions of Benzoxazole-2(3*H*)-thiones to Cycloalkenes and Heteroaromatics

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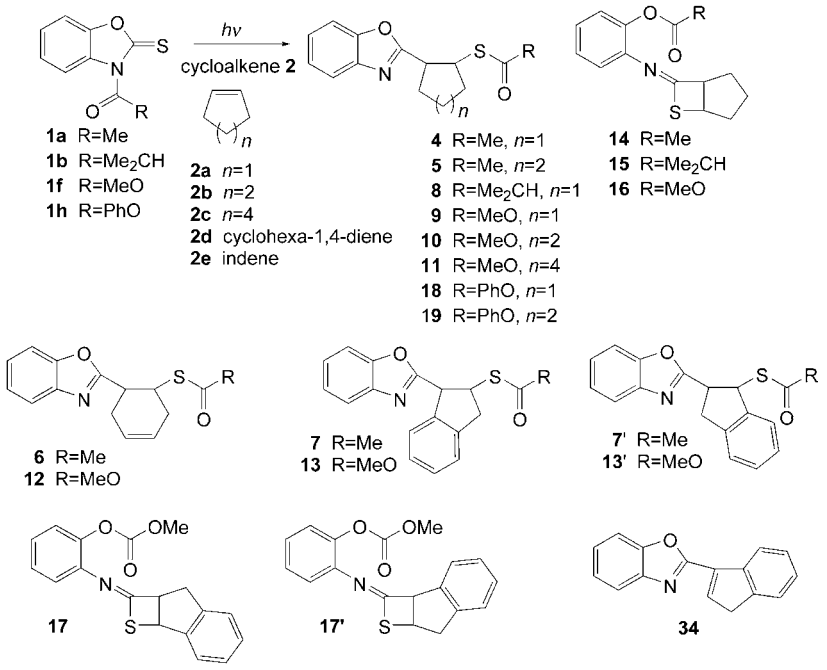
Photoaddition reactions of benzoxazole-2-thiones **1** with cycloalkenes **2** and heteroaromatics **3** were examined. Irradiation of *N*-acylbenzoxazole-2-thiones **1a** and **1b**, and 3-(methoxycarbonyl)- and 3-(phenoxycarbonyl)benzoxazole-2(3*H*)-thiones (**1f** and **1h**, resp.) in the presence of cycloalkenes **2a**–**2c**, cyclohexa-1,4-diene (**2d**), and indene (**2e**) yielded 2-substituted benzoxazoles **4**–**13**, **18** and **19**, and iminothietanes **14**–**17**, by intramolecular trapping of the acyl or MeOCO and PhOCO groups by thiolate anion of the zwitterionic intermediate **I** and by the phenolate anion of the zwitterionic intermediate **II**, respectively, derived from the spirocyclic amino-thietanes **AT** formed by [2+2] cycloaddition of the C=S bond of **1** and C=C bond of **2**. Irradiation of **1** in the presence of heteroaromatics **3** gave the 2-substituted benzoxazoles **20**–**33** exclusively.

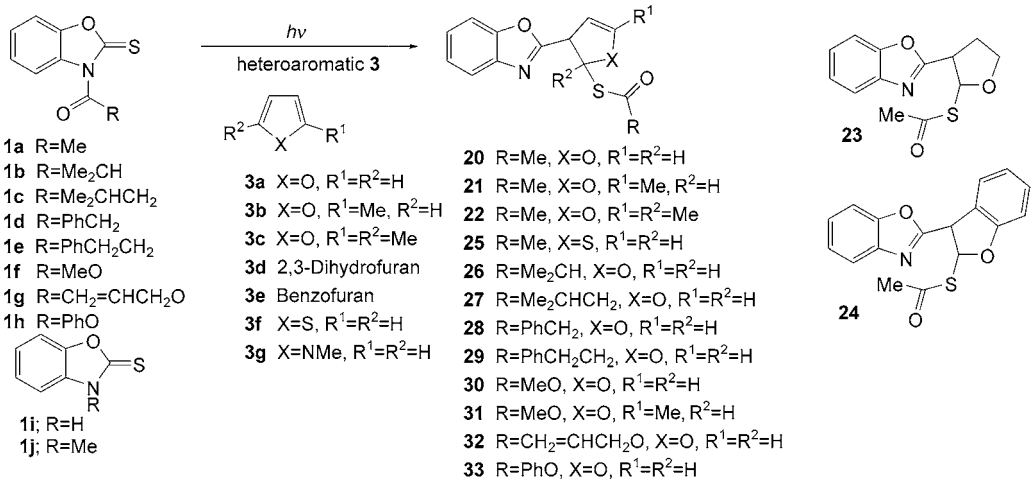
1. Introduction. – The photochemistry of thiocarbonyl compounds such as thioketones [1a–c][1e,f], thioimides, and thioamides [1d][1g–m] has been of considerable synthetic and mechanistic interest. These compounds behave like carbonyl compounds in many respects. In the course of our studies on the photochemistry of cyclic conjugated nitrogen-thiocarbonyl systems [1j–m][2][3], we have reported the photoaddition reactions of the benzoxazole-2-thiones [2] and benzothiazole-2-thiones [3] with alkenes. For example, irradiation of *N*-acylbenzoxazole-2-thiones, in the presence of alkenes gave 2-alkylated benzoxazoles and/or iminothietanes, *via* the [2+2] cycloaddition intermediates, spirocyclic amino-thietanes [2b], depending on the nature of substituents present in the alkenes, while that of *N*-(alkoxycarbonyl)- and *N*-(aryloxycarbonyl)-benzoxazole-2-thiones, in the presence of alkenes, gave [2+2] cycloadducts, spirocyclic amino-thietanes [2c]. To investigate the scope and limitation of the photocycloaddition of benzoxazole-2(3*H*)-thiones **1** and alkenes, we examined the photoreactions of **1** and cycloalkenes **2a**–**2c**, cyclohexa-1,4-diene (**2d**) and indene (**2e**), and heteroaromatics **3**, and our results are described in this paper (*Schemes 1* and *2*).

2. Results and Discussion. – When a solution of 3-acetylbenzoxazole-2(3*H*)-thione (**1a**) in MeOH was irradiated in the presence of cyclopentene (**2a**) with a high-pressure Hg lamp through a *Pyrex* filter under Ar at room temperature, 2-substituted benzoxazole, *S*-[2-(benzoxazol-2-yl)cyclopentyl] thioacetate (**4**), and iminothietane, 2-[(6-thiabicyclo[3.2.0]heptan-7-ylidene)amino]phenyl acetate (**14**), were obtained, which were 1:1 adducts of **1a** and **2a**, in 34 and 25% isolated yields, respectively. A similar result was obtained when benzene was used as solvent. The structures of photoproducts **4** and **14** were elucidated on the basis of spectral data and elemental

Scheme 1. *Photoaddition of Benzoxazole-2(3*H*)-thiones* **1a**, **1b**, **1f**, *and* **1h**, *and Cyclic Alkenes* **2**



Scheme 2. *Photoaddition of Benzoxazole-2(3*H*)-thiones* **1a**–**1h** *and Heteroaromatics* **3**



analyses. The *cis* relationship between the two substituents, benzoxazolyl and thioacetyl groups at C(2) and C(1), repectively, of the cyclopentane ring in **4** was established by an X-ray structure determination (*Fig.*). The configuration of the cyclopentane ring in **4** is predictable on the basis of mechanistic considerations, where are initially formed

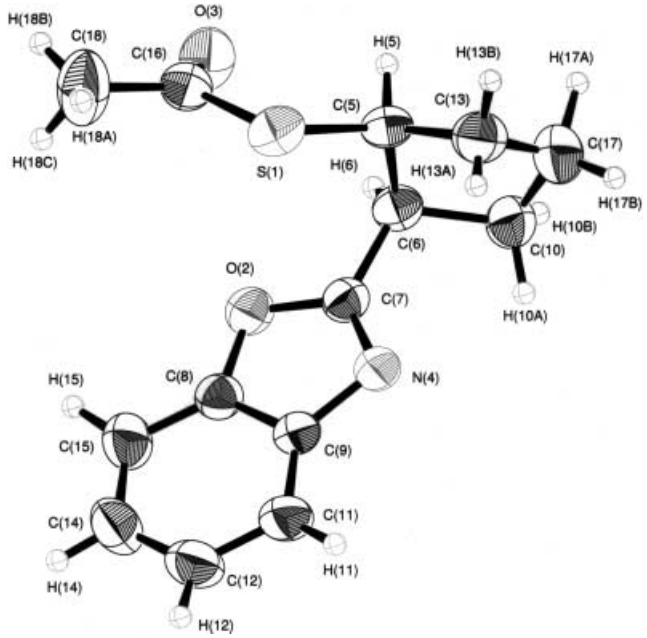


Figure. *ORTEP View of* S-*[2-(benzoxazol-2-yl)cyclopentyl] thioacetate* (**4**) *with crystallographic numbering scheme*

amino-thietane **AT** by [2 + 2] cycloaddition of the C=S bond of **1a** and C=C bond of **2a** (*cf. Scheme 4*). Irradiation of **1b** and **1f** in the presence of cyclopentene (**2a**), and **1f** in the presence of indene (**2e**) gave 2-substituted benzoxazoles **8** and **9**, **13**, respectively, and iminothietanes **15**–**17**. Irradiation of **1a**, **1f**, and **1h** in the presence of cyclic alkenes **2b** and **2c**, cyclohexa-1,4-diene (**2d**), and indene (**2e**) afforded 2-substituted benzoxazoles **5**–**7**, **10**–**12**, and **18** and **19**, respectively, as the sole products (*Table 1*). For the

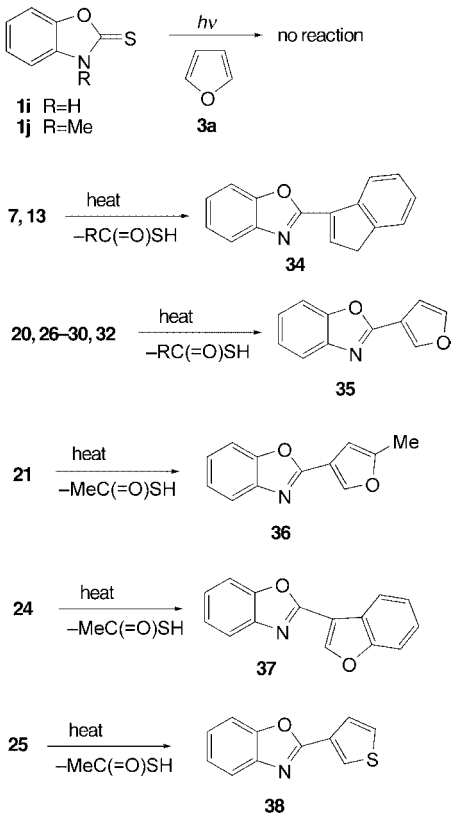
Table 1. *Yields of the Photoproducts* **4**–**19**

	R	Cycloalkene	Solvent	Product (Yield [%][a]))
1a	Me	**2a**	MeOH	**4** (34), **14** (25)
1a	Me	**2b**	MeOH	**5** (84)
1a	Me	**2d**	MeOH	**6** (37)
1a	Me	**2e**	Benzene	**7** (63)
1a	Me	**2e**	Benzene[b])	**7** (trace)
1a	Me	**2e**	MeOH	**7** (91)
1b	Me_2CH	**2a**	MeOH	**8** (32), **15** (46), **1i** (20)
1f	MeO	**2a**	Benzene	**9** (61), **16** (trace)
1f	MeO	**2b**	MeOH	**10** (78)
1f	MeO	**2c**	MeOH	**11** (52)
1f	MeO	**2d**	MeOH	**12** (43)
1f	MeO	**2e**	MeOH	**13** (43), **17** (21)
1h	PhO	**2a**	MeOH	**18** (69)
1h	PhO	**2b**	MeOH	**19** (67)

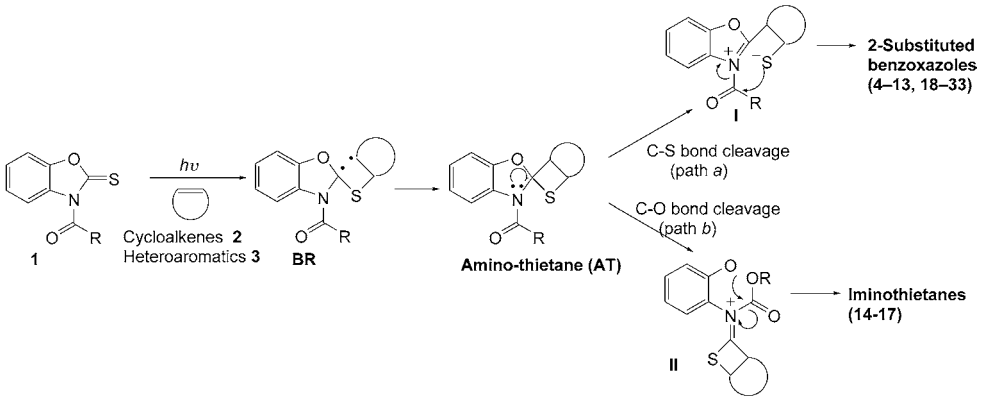
[a]) Isolated yield. [b]) Under an O_2 atmosphere

1:1 adducts, 2-substituted benzoxazoles derived from **1a** and **1f** and indene **2e**, and imino-thietane derived from **1f** and **2e**, the formation of two regioisomers (*i.e.*, **7** and **7′**, **13** and **13′**, and **17** and **17′**) is to be expected, in principle. The regioisomers of these photoproducts could not be determined from their spectral data. However, the structures of these compounds were tentatively assigned as **7**, **13**, and **17** from the following evidence. 2-Substituted benzoxazole **7** was converted gradually at room temperature or easily on distillation to 2-(1*H*-inden-3-yl)benzoxazole (**34**) by the elimination of MeCOSH (*Scheme 3*). 2-Substituted benzoxazole **13** was also heated to reflux in toluene for 10 h to yield **34** in 50% yield. In the ^{1}H-NMR spectrum of **34**, the signal of the CH_2 H-atoms appeared as *doublet* with a coupling constant of 2.3 Hz [4], indicating that the compound **34** is to be 3-substituted 1*H*-indene. The regiochemistry of **7**, **13**, and **17** is reasonably explained by a mechanism in that the photoexcited thioamide **1** initially attacks the C(2)-atom of indene (**2e**) to give the stabilized intermediate biradical **BR** (*cf. Scheme 4*). The two modes of cleavage in this reaction intermediate **AT** might be explained in terms of the stability of zwitterions **I** and **II** affected by a ring-size effect [2b]. In the photoreaction of 3-isobutyrylbenzoxazole-2(3*H*)-thione **1b** and **2a**, the deacylation product, benzoxazole-2(3*H*)-thione **1i**, was

Scheme 3



Scheme 4



obtained in 20% yield, accompanied by 2-substituted benzoxazole **8** (32%) and iminothietane **15** (46%). Probably, compound **1i** arises from the γ-H abstraction by the excited thioamide S-atom, followed by elimination of ketene. Analogous γ-H abstractions were observed in the photolysis of *N*-acylthiazolidine-2-thiones [5] and *N*-acylindoline-2-thiones [6]. The 1:1 adduct **7** was not formed when a benzene solution of **1a** and indene **2e** was irradiated under an O_2 atmosphere.

Irradiation of *N*-acylbenzoxazole-2-thiones **1a**–**1e** in the presence of heteroaromatics such as furan derivatives **3a**–**3e** and thiophene (**3f**) in MeOH (or benzene) under the same conditions as described above gave 1:1 adducts of **1** and **3**, 2-substituted benzoxazoles **20**–**29**, along with a deacylation product, benzoxazole-2(3*H*)-thione (**1i**; *Scheme 2* and *Table 2*).

Table 2. *Yields of the Products* **20**–**33**

	R	Heteroaromatic	Solvent	Product (Yield [%][a]))
1a	Me	**3a**	MeOH	**20** (75)
1a	Me	**3a**	MeOH[b])	**20** (6)
1a	Me	**3b**	MeOH	**21** (20) **1i** (27)
1a	Me	**3c**	Benzene	**22** (47)
1a	Me	**3d**	MeOH	**23** (30)
1a	Me	**3e**	Benzene	**24** (35)
1a	Me	**3f**	MeOH	**25** (20)
1a	Me	**3g**	Benzene	–[c])
1b	Me_2CH	**3a**	MeOH	**26** (55) **1i** (40)
1c	Me_2CHCH_2	**3a**	Benzene	**27** (67) **1i** (30)
1d	$PhCH_2$	**3a**	Benzene	**28** (13) **1i** (50)
1e	$PhCH_2CH_2$	**3a**	Benzene	**29** (65) **1i** (25)
1f	MeO	**3a**	MeOH	**30** (69)
1f	MeO	**3b**	MeOH	**31** (39)
1g	CH_2=$CHCH_2O$	**3a**	Benzene	**32** (53)
1h	PhO	**3a**	MeOH	**33** (59)

[a]) Isolated yield. [b]) Under an O_2 atmosphere. [c]) No reaction.

The formation of **1i** can be explained in terms of the pathway involving γ-H abstraction by the excited thioamide S-atom as already described above. In contrast, when a benzene solution of **1a** and an excess of 1-methyl-1*H*-pyrrole (**3g**) was irradiated, no photoproducts were obtained, and unchanged starting material **1a** was recovered quantitatively. Irradiation of 3-(alkoxycarbonyl)- and 3-(aryloxycarbonyl)-benzoxazole-2(3*H*)-thiones (**1f**–**1h**) gave in the presence of furans **3a** and **3b** 1:1 adducts of **1** and **3**, 2-substituted benzoxazoles **30**–**33**. Irradiation of **1a** and furan **3a** in MeOH under an O_2 atmosphere gave the 1:1 adduct **20** (6%), but in low yield. The structures of photoproducts **20**–**33** were elucidated on the basis of their spectral properties and chemical evidence (see *Exper. Part*). The 1:1 adducts **20** and **21**, **24**–**30**, and **32** are not stable and converted gradually at room temperature and easily on distillation into 2-(furan-3-yl)benzoxazole derivatives **35**–**37**, and 2-(thiophen-3-yl)benzoxazole **38** by elimination of the corresponding alkanethioic *S*-acid or *O*-alkyl hydrogen thiocarbonate (*Scheme 3*). Irradiation of the parent benzoxazole-2(3*H*)-thione (**1i**) and 3-methylbenzoxazole-2(3*H*)-thione (**1j**) in benzene in the presence of furan (**3a**) resulted in recovery of unchanged starting materials **1i** and **1j**.

The mechanism for the formation of 2-substituted benzoxazoles **4**–**13**, **18**–**33**, and iminothietane derivatives **14**–**17** in the photoaddition reaction of 3-acylbenzoxazole-2(3*H*)-thiones (**1a**–**1e**), and 3-(alkoxycarbonyl)- and 3-(aryloxycarbonyl)benzoxazole-2(3*H*)-thiones (**1f**–**1h**, resp.) with cycloalkenes **2a**–**2c**, cyclohexa-1,4-diene (**2d**), and indene (**2e**), and heteroaromatics **3** could be understood in terms of the pathways shown in *Scheme 4*, which we had proposed for the photoreactions of thioamides and alkenes [2][3][5]. The spirocyclic amino-thietanes **AT** were formed initially through the regioselective [2+2] photocycloaddition of the C=S bond of **1** and C=C bond of **2** or **3**. The regiochemistry of the addition of **1** to heteroaromatics **3** could be explained by the thietane formation in the first step, where the photo-excited **1** initially attacks C(2) of the heteroaromatics **3**. This addition mechanism is similar to that proposed by *Oda* and *Machida* for the photoaddition reaction of arenecarbothioamides and furans [7]. The chemoselectivity in the addition of **1** to **3** seems to reflect the steric effect of an α-substituent on an unsymmetrically substituted furan **3b** [7]. Amino-thietane **AT** then underwent C–S bond cleavage of the thietane ring or C–O bond cleavage of oxazole ring assisted by the lone-pair electrons on the N-atom to yield the zwitterions **I** or **II**. Intramolecular trapping of acyl group by the thiolate (path *a*) or phenolate moiety (path *b*) of the zwitterions gave the 2-substituted benzoxazoles **3**–**13**, **18**–**33**, and iminothietanes **14**–**17** [2c].

Experimental Part

General. M.p. and b.p.: *Yanako* micro melting-point apparatus (*MP-3J*) and a *Shibata* glass-tube oven-distillation apparatus (*GTO-350RD*), resp.; uncorrected. Flash chromatography (FC): silica gel *Wakogel C-300* and *Merck 60*. IR Spectra: *JASCO FT/IR-300* spectrophotometer, in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *JEOL-JNM-EX270* (270 MHz) spectrometer; in $CDCl_3$, with Me_4Si as internal standard; δ in ppm, *J* in Hz. Irradiation: *Eikosha HALos* (500 W) high-pressure Hg lamp.

*General Procedure for the Photochemical Reactions of the Benzoxazole-2(3*H*)-thiones* **1** *and Cycloalkenes* **2** *or Heteroaromatics* **3**. A soln. of **1** (1 mmol) and **2** (or **3**) (*ca.* 0.5 ml) in MeOH (or benzene) (70 ml) was irradiated in a *Pyrex* vessel with the high-pressure Hg lamp under Ar for 5–15 h at r. t. After removal of the solvent, the residual oil was chromatographed on a silica-gel column with toluene/AcOEt 50:1–9:1 to yield the 2-substituted benzoxazoles **4**–**13**, **18**–**33**, and iminothietanes **14**–**17**. For yields, *cf. Tables 1* and *2*.

S-*[2-(Benzoxazol-2-yl)cyclopentyl] Thioacetate* (**4**). M.p. 55–56°. IR ($CHCl_3$): 1685, 1610. ^{1}H-NMR: 1.76–2.34 (*m*, 6 H); 2.17 (*s*, 3 H); 3.87 (*dd*, *J* = 7.6, 14.9, 1 H); 4.23 (*dd*, *J* = 7.6, 14.9, 1 H); 7.27–7.34 (*m*, 2 H); 7.45–7.52 (*m*, 1 H); 7.66–7.73 (*m*, 1 H). ^{13}C-NMR: 23.3; 29.4; 30.5; 32.4; 42.8; 46.6; 110.4; 119.8; 124.1; 124.6; 141.0; 150.6; 167.3; 195.2. Anal. calc. for $C_{14}H_{15}NO_2S$ (261.27): C 64.36, H 5.79, N 5.36; found: C 64.49, H 5.82, N 5.33.

2-[(6-Thiabicyclo[3.2.0]heptan-7-ylidene)amino]phenyl Acetate (**14**). B.p. 200°/3 Torr. IR ($CHCl_3$): 1760, 1670. ^{1}H-NMR: 1.58–2.38 (*m*, 6 H); 2.29 (*s*, 3 H); 4.00 (*t*, *J* = 5.9, 1 H); 4.39 (*dd*, *J* = 5.9, 8.6, 1 H); 6.98–7.26 (*m*, 4 H). ^{13}C-NMR: 20.7; 23.0; 31.4; 32.8; 41.3; 63.6; 120.4; 122.8; 125.6; 126.5; 140.3; 142.8; 168.4; 168.9. Anal. calc. for $C_{14}H_{15}NO_2S$ (261.27): C 64.36, H 5.79, N 5.36; found C 64.25, H 5.85, N 5.63.

S-*[2-(Benzoxazol-2yl)cyclohexyl] Thioacetate* (**5**). M.p. 62–63°. IR ($CHCl_3$): 1690, 1610. ^{1}H-NMR: 1.43–1.54 (*m*, 1 H); 1.63–2.18 (*m*, 7 H); 2.17 (*s*, 3 H); 3.42–3.49 (*m*, 1 H); 4.21–4.38 (*m*, 1 H); 7.26–7.33 (*m*, 2 H); 7.46–7.51 (*m*, 1 H); 7.56–7.73 (*m*, 1 H). ^{13}C-NMR: 23.2; 23.7; 30.7; 31.2; 40.9; 44.2; 110.4; 119.9; 124.0; 124.7; 141.0; 150.5; 167.0; 194.5. Anal. calc. for $C_{15}H_{17}NO_2S$ (275.29): C 65.44, H 6.22, N 5.09; found C 65.29, H 6.27 N 4.97.

S-*[6-(Benzoxazol-2yl)cyclohex-3-enyl] Thioacetate* (**6**). M.p. 107–108°. IR (KBr): 1685. ^{1}H-NMR: 2.21 (*s*, 3 H); 2.41–2.85 (*m*, 4 H); 3.58–3.65 (*m*, 1 H); 4.45–4.55 (*m*, 1 H); 5.70–5.85 (*m*, 2 H); 7.26–7.34 (*m*, 2 H); 7.48–7.53 (*m*, 1 H); 7.68–7.73 (*m*, 1 H). ^{13}C-NMR: 26.5; 30.7; 31.7; 37.4; 41.0; 110.4; 119.9; 124.1; 124.7; 125.1; 141.0; 150.8; 166.5; 194.9.

S-*[1-(Benzoxazol-2-yl)-2,3-dihydro-1*H*-inden-3-yl] Thioacetate* (**7**). B.p. >250°/2 Torr (dec.). IR ($CHCl_3$): 1690. ^{1}H-NMR: 2.22 (*s*, 3 H); 3.37–3.45 (*m*, 2 H); 4.73 (*dd*, *J* = 8.3, 17.5, 1 H); 5.06 (*d*, *J* = 8.3, 1 H); 7.17–7.34 (*m*, 6 H); 7.40–7.46 (*m*, 1 H); 7.67–7.72 (*m*, 1 H). ^{13}C-NMR: 30.4; 38.1; 45.7; 48.8; 110.5; 120.0; 124.2; 124.8; 125.1; 127.2; 128.3; 140.1; 140.9; 141.8; 150.7; 165.4; 195.1. The photoproduct **7** was gradually converted to **34** at r.t.

*2-(1*H*-Inden-3-yl)benzoxazole* (**34**). M.p. 93–94°. IR: 1630, 1515, 1450, 1380, 1240, 1145, 985, 955, 745. ^{1}H-NMR: 3.63 (*d*, *J* = 2.3, 2 H); 7.28–7.59 (*m*, 7 H); 7.78–7.84 (*m*, 1 H); 8.47 (*d*, *J* = 7.6, 1 H). ^{13}C-NMR: 38.9; 110.3; 120.3; 122.6; 123.8; 124.4; 125.3; 125.8; 126.7; 132.1; 139.3; 140.5; 141.9; 143.5; 150.0; 159.6. Anal. calc. for $C_{16}H_{11}NO$ (233.26): C 82.38, H 4.75, N 6.01; found C 82.44, H 4.84, N 5.73.

S-*[2-(Benzoxazol-2-yl)cyclopentyl] 2-Methylpropanethioate* (**8**). B.p. 205°/2 Torr. IR ($CHCl_3$): 1680, 1615. ^{1}H-NMR: 0.96 (*d*, *J* = 6.9, 3 H); 1.04 (*d*, *J* = 6.9, 3 H); 1.70–2.42 (*m*, 6 H); 2.53 (*sept.*, *J* = 6.9, 1 H); 3.86 (*dd*, *J* = 7.6, 14.8, 1 H); 4.22 (*dd*, *J* = 7.6, 14.8, 1 H); 7.25–7.35 (*m*, 2 H); 7.43–7.53 (*m*, 1 H); 7.65–7.74 (*m*, 1 H). ^{13}C-NMR: 19.1; 19.2; 22.8; 29.3; 32.3; 42.9; 46.0; 110.3; 119.7; 124.0; 141.0; 150.6; 167.4; 203.4. Anal. calc. for $C_{16}H_{19}NO_2S$ (289.32): C 66.41, H 6.62, N 4.84; found C 66.02, H 6.29, N 4.62.

2-[(6-Thiabicyclo[3.2.0]heptan-7-ylidene)amino]phenyl 2-Methylpropanoate (**15**). B.p. 200°/3 Torr. IR (film): 1755, 1670. ^{1}H-NMR: 1.32 (*d*, *J* = 6.9, 6 H); 1.54–2.37 (*m*, 6 H); 2.84 (*sept.*, *J* = 6.9, 1 H); 3.97 (*t*, *J* = 5.9, 1 H); 4.32–4.39 (*m*, 1 H); 6.99–7.20 (*m*, 4 H). ^{13}C-NMR: 19.0; 19.1; 22.9; 31.3; 32.8; 33.9; 41.1; 63.6; 120.3; 122.8; 125.6; 126.3; 140.3; 142.9; 168.0; 174.8. Anal. calc. for $C_{16}H_{19}NO_2S$ (289.32): C 66.41, H 6.62, N 4.84; found C 66.26, H 6.73, N 4.84.

S-*[2-(Benzoxazol-2-yl)cyclopentyl]* O-*Methyl Thiocarbonate* (**9**) *and Methyl 2-[(6-Thiabicyclo[3.2.0]heptan-7-ylidene)amino]phenyl Carbonate* (**16**). Compounds **9** and **16** could not be separated completely. B.p. (a mixture of **9** and **16**) 200°/3 Torr. IR (film; a mixture of **9** and **16**): 1750, 1705, 1605. ^{1}H-NMR of **9**: 1.76–1.88 (*m*, 1 H); 2.01–2.38 (*m*, 5 H); 3.70 (*s*, 3 H); 3.85 (*dd*, *J* = 7.3, 14.2, 1 H); 4.12 (*dd*, *J* = 7.3, 14.2, 1 H); 7.26–7.32 (*m*, 2 H); 7.45–7.51 (*m*, 1 H); 7.66–7.72 (*m*, 1 H). ^{13}C-NMR of **9**: 23.1; 29.3; 32.4; 43.1; 48.6; 54.0; 110.4; 119.8; 124.1; 124.6; 141.0; 150.7; 167.0; 170.8. ^{1}H-NMR of **16**: 1.68–2.35 (*m*, 6 H); 3.31–3.40 (*m*, 1 H); 3.68–3.77 (*m*, 1 H); 3.75 (*s*, 3 H); 7.04–7.09 (*m*, 1 H); 7.23–7.36 (*m*, 2 H); 8.12–8.16 (*m*, 1 H). ^{13}C-NMR of **16**: 22.8; 26.5; 36.6; 41.3; 51.3; 52.4; 154.0; 171.2 in addition to the signals of aromatic C-atoms. Anal. calc. for $C_{14}H_{15}NO_3S$ (277.27; a mixture of **9** and **16**): C 60.63, H 5.45, N 5.05; found C 60.29, H 5.45, N 5.10.

S-*[2-(Benzoxazol-2-yl)cyclohexyl]* O-*Methyl Carbonate* (**10**). M.p. 74–75°. IR ($CHCl_3$): 1710. ^{1}H-NMR: 1.41–1.59 (*m*, 1 H); 1.61–1.85 (*m*, 3 H); 1.93–2.27 (*m*, 4 H); 3.47–3.55 (*m*, 1 H); 3.65 (*s*, 3 H); 4.19–4.25 (*m*, 1 H); 7.26–7.36 (*m*, 2 H); 7.45–7.53 (*m*, 1 H); 7.63–7.73 (*m*, 1 H). ^{13}C NMR: 23.0; 23.7; 27.1; 31.3; 41.1; 46.7; 54.0; 110.4; 119.9; 124.1; 124.7; 141.1; 150.6; 166.8; 170.7. Anal. calc. for $C_{15}H_{17}NO_3S$ (291.29): C 61.85, H 5.88, N 4.81; found C 61.45, H 5.90, N 4.75.

S-*[2-(Benzoxazol-2-yl)cyclooctyl]* O-*Methyl Carbonate* (**11**). B.p. 210°/3 Torr. IR (film): 1730, 1610. ^{1}H-NMR: 1.55–2.25 (*m*, 12 H); 3.26–3.33 (*m*, 1 H); 3.67–3.74 (*m*, 1 H); 3.75 (*s*, 3 H); 7.05 (*d*, *J* = 4.3, 1 H); 7.13–7.27 (*m*, 1 H); 7.42 (br. *s*, 1 H); 8.12 (br. *d*, *J* = 8.3, 1 H). ^{13}C-NMR: 24.1; 25.9; 26.4; 27.6; 35.8; 40.8; 47.9; 52.4; 120.5; 122.2; 123.3; 126.7; 130.6; 139.9; 154.0; 172.4. Anal. calc. for $C_{17}H_{21}NO_3S$ (319.35): C 63.93, H 6.63, N 4.39; found C 64.16, H 6.76, N, 4.12.

S-*[6-(Benzoxazol-2-yl)cyclohex-3-enyl]* O-*Methyl Carbonate* (**12**). B.p. 220°/3 Torr. IR (film): 1710, 1615. ^{1}H-NMR: 2.52–2.81 (*m*, 3 H); 3.65 (*s*, 3 H); 4.30–4.36 (*m*, 1 H); 5.71–5.90 (*m*, 2 H); 7.26–7.33 (*m*, 2 H); 7.46–7.51 (*m*, 1 H); 7.68–7.72 (*m*, 1 H). ^{13}C-NMR: 23.6; 31.8; 37.7; 43.3; 54.0; 110.4; 119.9; 124.1; 124.7; 124.8; 125.0; 141.1; 150.7; 166.7; 170.8. Anal. calc. for $C_{15}H_{15}NO_3S$ (289.28): C 62.28, H 5.23, H 4.84; found C 62.22, H 5.28, N 4.82.

S-*[2-(Benzoxazol-2-yl)-2,3-dihydro-1*H*-inden-1-yl]* O-*Methyl Thiocarbonate* (**13**). Oil. IR ($CHCl_3$): 1710. ^{1}H-NMR: 3.39–3.51 (*m*, 2 H); 3.76 (*s*, 3 H); 4.63 (*dd*, *J* = 8.3, 17.8, 1 H); 5.11 (*d*, *J* = 7.9, 1 H); 7.20–7.47 (*m*, 7 H); 7.66–7.71 (*m*, 1 H). ^{13}C-NMR: 30.3; 47.5; 49.1; 57.4; 110.4; 122.0; 124.2; 124.8; 125.1; 127.3; 128.4; 140.1; 141.6; 150.8; 165.2; 170.5. Anal. calc. for $C_{18}H_{15}NO_3S$ (325.31): C 66.45, H 4.65, N 4.32; found C 66.75, H 4.81, N 4.03.

*Methyl 2-[(1,2a,3,7b-Tetrahydroindeno[2,1-*b*]thiet-1-yl)amino]phenyl Carbonate* (**17**). M.p. 129–130°. IR ($CHCl_3$): 1735, 1615. ^{1}H-NMR: 2.18 (*d*, *J* = 9.2, 1 H); 3.26 (*dd*, *J* = 7.6, 15.8, 1 H); 3.75 (*s*, 3 H); 4.06 (*dd*, *J* = 7.6, 18.9, 1 H); 4.51 (*d*, *J* = 7.6, 1 H); 7.02–7.08 (*m*, 2 H); 7.18–7.30 (*m*, 5 H); 7.70 (br. *d*, *J* = 3.3, 1 H). ^{13}C-NMR: 40.8; 42.6; 52.1; 57.4; 122.1; 123.1; 124.8; 125.3; 126.8; 127.4; 128.5; 130.5; 138.3; 142.2; 153.8; 169.1. Anal. calc. for $C_{18}H_{15}NO_3S$ (325.31): C 66.45, H 4.65, N 4.32; found C 66.24, H 4.61, N 4.08.

S-*[2-(Benzoxazol-2-yl)cyclopentyl]* O-*Phenyl Thiocarbonate* (**18**). B.p. 220°/3 Torr. IR (film): 1725. ^{1}H-NMR: 1.80–2.47 (*m*, 6 H); 3.92 (*dd*, *J* = 7.3, 14.2, 1 H); 4.18 (*dd*, *J* = 7.3, 14.2, 1 H); 6.95–7.00 (*m*, 2 H); 7.21–7.36 (*m*, 5 H); 7.47–7.54 (*m*, 1 H); 7.72–7.77 (*m*, 1 H). ^{13}C-NMR: 23.3; 29.2; 32.2; 43.1; 48.9; 110.5; 119.9; 121.2; 124.2; 124.7; 128.3; 129.4; 141.1; 151.1; 167.0. Anal. calc. for $C_{19}H_{17}NO_3S$ (339.33): C 67.25, H 5.05, N 4.13; found C 67.08, H 5.34, N 4.41.

S-*[2-(Benzoxazol-2-yl)cyclohexyl]* O-*Phenyl Thiocarbonate* (**19**). M.p. 97–98°. IR (KBr): 1720, 1615. ^{1}H-NMR: 1.39–1.59 (*m*, 1 H); 1.62–1.85 (*m*, 3 H); 1.93–2.15 (*m*, 3 H); 2.23–2.35 (*m*, 1 H); 3.50–3.57 (*m*, 1 H); 4.24–4.30 (*m*, 1 H); 6.88–6.95 (*m*, 2 H); 7.11–7.34 (*m*, 5 H); 7.45–7.52 (*m*, 1 H); 7.70–7.77 (*m*, 1 H). ^{13}C-NMR: 23.2; 23.6; 27.1; 31.1; 41.0; 47.1; 110.5; 119.9; 121.1; 124.1; 124.7; 125.9; 128.3; 129.3; 141.1; 151.1; 166.7. Anal. calc. for $C_{20}H_{19}NO_3S$ (353.36): C 67.98, H 5.42, N 3.96; found C 67.67, H 5.49, N 3.85.

2-*[2-(Acetylsulfanyl)-2,3-dihydrofuran-3-yl]benzoxazole* (**20**). B.p. 175–180°/3 Torr (dec.). IR (film): 1695, 1605. ^{1}H-NMR: 2.24 (*s*, 3 H); 4.95 (*dt*, *J* = 2.3, 9.9, 1 H); 5.40 (*dd*, *J* = 2.3, 2.6, 1 H); 6.63 (*t*, *J* = 2.6, 1 H); 6.73 (*d*, *J* = 9.9, 1 H); 7.32–7.40 (*m*, 2 H); 7.51–7.56 (*m*, 1 H); 7.73–7.77 (*m*, 1 H). ^{13}C-NMR: 31.0; 46.4, 86.0; 101.0; 110.8; 120.3; 124.6; 125.4; 140.9; 147.8; 150.8; 163.5; 192.9. Anal. calc. for $C_{13}H_{11}NO_3S$ (261.23): C 59.77, H 4.24, N 5.36; found C 60.08, H 4.04, N 5.44. The photoadduct **20** was unstable at r.t. and converted gradually or easily on distillation (175–180°/3 Torr) to **35**.

2-*(Furan-3-yl)benzoxazole* (**35**). M.p. 88–89°. IR ($CHCl_3$): 1645. ^{1}H-NMR: 7.03 (*dd*, *J* = 1.0, 2.0, 1 H); 7.26–7.36 (*m*, 2 H); 7.40–7.56 (*m*, 2 H); 8.22 (*dd*, *J* = 1.0, 1.7, 1 H). ^{13}C-NMR: 108.8; 110.2; 115.2; 119.5; 124.3; 124.7; 141.6; 144.1; 150.0; 158.1. Anal. calc. for $C_{11}H_7NO_2$ (185.17): C 71.35, H 3.81, N 7.56; found C 71.36, H 3.71, N 7.52.

2-*[2-(Acetylsulfanyl)-2,3-dihydro-5-methylfuran-3-yl]benzoxazole* (**21**). B.p. 185°/3 Torr (dec.). IR ($CHCl_3$): 1715. ^{1}H-NMR: 1.95 (*s*, 3 H); 2.23 (*s*, 3 H); 4.96 (*dt*, *J* = 2.0, 9.9, 1 H); 5.02 (*dd*, *J* = 1.3, 2.0, 1 H); 6.27 (*d*, *J* = 9.9, 1 H); 7.31–7.39 (*m*, 2 H); 7.49–7.55 (*m*, 1 H); 7.73–7.77 (*m*, 1 H). ^{13}C-NMR: 13.7; 30.9; 47.4; 85.9; 95.7; 110.7; 120.2; 124.5; 125.2; 140.8; 150.8; 157.6; 164.2; 193.1. The photoadduct **21** was unstable at r.t. and converted gradually or easily on distillation (185–190°/3 Torr) to **36**.

2-*(5-Methylfuran-3-yl)benzoxazole* (**36**). M.p. 75–76°. IR ($CHCl_3$): 1645. ^{1}H-NMR: 2.34 (*d*, *J* = 1.0, 3 H); 6.59 (*t*, *J* = 1.0, 1 H); 7.25–7.32 (*m*, 2 H); 7.44–7.52 (*m*, 1 H); 7.65–7.77 (*m*, 1 H); 8.05 (*d*, *J* = 0.7, 1 H). ^{13}C-NMR: 13.3; 104.6; 110.2; 115.8; 119.4; 124.3; 124.6; 141.7; 142.7; 150.0; 154.1; 158.5. Anal. calc. for $C_{12}H_9NO_2$ (199.20): C 72.35, H 4.55, N 7.03; found C 72.39, H 4.51, N 6.93.

2-*[2-(Acetylsulfanyl)-2,3-dihydro-2,5-dimethylfuran-3-yl]benzoxazole* (**22**). M.p. 72–73°. IR (film): 1695, 1610. ^{1}H-NMR: 1.94 (*d*, *J* = 2.0, 3 H); 2.07 (*s*, 3 H); 2.32 (*s*, 3 H); 4.60 (*q*, *J* = 2.0, 1 H); 5.06 (*s*, 1 H); 7.28–7.38 (*m*, 2 H); 7.52–7.56 (*m*, 1 H); 7.73–7.78 (*m*, 1 H). ^{13}C-NMR: 14.0; 27.6; 31.3; 56.1; 96.1; 99.0; 110.7; 120.2; 124.5; 125.0; 141.0; 150.8; 156.6; 163.5; 193.5. Anal. calc. for $C_{15}H_{15}NO_3S$ (289.28): C 62.28, H 5.23, N 4.84; found C 62.14, H 5.21, N 4.75.

2-*[2-(Acetylsulfanyl)-2,3,4,5-tetrahydrofuran-3-yl]benzoxazole* (**23**). B.p. 19°/3 Torr. IR ($CHCl_3$): 1695, 1615. ^{1}H-NMR: 2.21 (*s*, 3 H); 2.33–2.56 (*m*, 2 H); 4.08 (*dd*, *J* = 8.2, 15.2, 1 H); 4.35–4.44 (*m*, 2 H); 5.52 (*d*, *J* = 7.3, 1 H); 7.29–7.36 (*m*, 2 H); 7.50–7.55 (*m*, 1 H); 7.71–7.76 (*m*, 1 H). ^{13}C-NMR: 30.2; 31.2; 44.0; 68.1; 76.0; 110.7; 120.3; 124.3; 125.2; 140.5; 150.3; 163.7; 194.2. Anal. calc. for $C_{13}H_{13}NO_3S$ (263.24): C 59.31, H 4.98, N 5.32; found C 59.08, H 4.99, N 5.36.

2-*[2-(Acetylsulfanyl)-2,3-dihydrobenzofuran-3-yl]benzoxazole* (**24**). Oil. IR ($CHCl_3$): 1705. ^{1}H-NMR: 2.25 (*s*, 3 H); 5.45 (*d*, *J* = 9.2, 1 H); 6.94–7.05 (*m*, 3 H); 7.24–7.40 (*m*, 4 H); 7.50–7.54 (*m*, 1 H); 7.74–7.99 (*m*, 1 H).

^{13}C-NMR: 30.3; 46.2; 87.4; 110.9; 120.4; 122.3; 124.1; 124.6; 125.5; 125.6; 130.0; 140.8; 150.9; 158.4; 162.5; 192.8. The photoadduct **24** was unstable at r.t. and gradually converted to **37**.

2-(Benzofuran-3-yl)benzoxazole (**37**). M.p. 128–130°. IR ($CHCl_3$): 1645. ^{1}H-NMR: 7.26–7.47 (*m*, 4 H); 7.53–7.59 (*m*, 2 H); 7.75–7.83 (*m*, 1 H); 8.35–8.43 (*m*, 2 H). ^{13}C-NMR: 110.3; 111.1; 111.7; 119.8; 122.2; 124.1; 124.5 125.0; 125.6; 141.9; 147.0; 150.0; 155.6; 158.0. Anal. calc. for $C_{15}H_9NO_2$ (235.23): C 75.58, H 3.86, N 5.95; found C, 75.89, H 3.78, N 5.88.

2-[2-(Acetylsulfanyl)-2,3-dihydrothiophen-3-yl]benzoxazole (**25**). Oil. ^{1}H-NMR: 2.15 (*s*, 3 H); 4.95 (*td*, *J* = 2.3, 7.9, 1 H); 5.81 (*d*, *J* = 7.9, 1 H); 6.03 (*dd*, *J* = 2.3, 6.3, 1 H); 6.58 (*dd*, *J* = 3.0, 6.3, 1 H); 7.31–7.39 (*m*, 3 H); 7.51–7.56 (*m*, 1 H); 7.73–7.81 (*m*, 2 H). ^{13}C-NMR: 30.5; 51.8; 55.3; 110.7; 120.2; 120.4; 124.6; 125.4; 129.0; 140.8; 150.8; 163.0; 193.9. The photoadduct **25** was unstable at r.t. and converted to **38**.

2-(Thiophen-3-yl)benzoxazole (**38**). M.p. 139–140°. IR (KBr): 1620. ^{1}H-NMR: 7.29–7.37 (*m*, 2 H); 7.41–7.45 (*m*, 1 H); 7.50–7.56 (*m*, 1 H); 7.72–7.80 (*m*, 2 H); 8.17–8.20 (*m*, 1 H). ^{13}C-NMR: 110.4; 119.9; 124.5; 125.0; 126.6; 127.0; 128.0; 129.2; 141.9; 150.3; 159.7. Anal. calc. for $C_{11}H_7NOS$ (201.17): C 65.67, H 3.51, N 6.96; found C 65.67, H 3.46, N 6.87.

2-{2,3-Dihydro-2-[(2-methylpropanoyl)sulfanyl]furan-3-yl}benzoxazole (**26**). B.p. 175°/3 Torr (dec.). IR ($CHCl_3$): 1695, 1620. ^{1}H-NMR: 1.02 (*d*, *J* = 6.9, 3 H); 1.09 (*d*, *J* = 6.9, 3 H); 2.56 (*sept.*, *J* = 6.9, 1 H); 4.97 (*td*, *J* = 2.3, 9.9, 1 H); 5.40 (*t*, *J* = 2.3, 1 H); 6.64 (*t*, *J* = 2.6, 1 H); 6.71 (*d*, *J* = 9.9, 1 H); 7.31–7.39 (*m*, 2 H); 7.49–7.55 (*m*, 1 H); 7.72–7.77 (*m*, 1 H). ^{13}C-NMR: 18.9; 19.0; 43.5; 46.6; 85.7; 100.9; 110.7; 120.2; 124.5; 125.2; 140.8; 147.8; 150.8; 163.6; 201.1. Anal. calc. for $C_{15}H_{15}NO_3S$ (289.28): C 62.28, H 5.23, N 4.84; found 62.49, H 4.94, N 4.66. The photoadduct **26** was unstable at r.t. and converted to **35**.

2-{2,3-Dihydro-2-[(3-methylbutanoyl)sulfanyl]furan-3-yl}benzoxazole (**27**). B.p. 180°/3 Torr (dec.). IR ($CHCl_3$): 1700, 1620, 1610. ^{1}H-NMR: 0.82 (*d*, *J* = 6.6, 3 H); 0.86 (*d*, *J* = 6.6, 3 H); 1.95–2.09 (*m*, 1 H); 2.23–2.39 (*m*, 2 H); 4.96 (*td*, *J* = 2.3, 9.9, 1 H); 5.36–5.41 (*m*, 1 H); 6.63 (*t*, *J* = 2.3, 1 H); 6.74 (*d*, *J* = 9.9, 1 H); 7.31–7.39 (*m*, 2 H); 7.48–7.56 (*m*, 1 H); 7.70–7.76 (*m*, 1 H). ^{13}C-NMR: 22.0, 22.1; 26.1; 46.6; 53.1; 85.8; 100.9; 110.7; 120.3; 124.5; 125.2; 140.9; 147.8; 150.8; 163.6; 195.9. The photoadduct **27** was unstable at r.t. and converted gradually or easily on distillation (175–180°/3 Torr) to **35**.

2-{2,3-Dihydro-2-[(2-phenylethanoyl)sulfanyl]furan-3-yl}benzoxazole (**28**). Oil. IR ($CHCl_3$): 1700, 1645, 1610. ^{1}H-NMR: 3.67 (*s*, 2 H); 4.97 (*td*, *J* = 2.3, 9.9, 1 H); 5.37 (*t*, *J* = 2.3, 1 H); 6.59 (*t*, *J* = 2.6, 1 H); 6.70 (*d*, *J* = 9.9, 1 H); 7.01–9.07 (*m*, 2 H); 7.12–7.19 (*m*, 2 H); 7.26–7.41 (*m*, 3 H); 7.44–7.52 (*m*, 1 H); 7.69–7.78 (*m*, 1 H). ^{13}C-NMR: 46.6; 50.5; 86.0; 100.9; 110.7; 120.2; 124.5; 152.2; 127.4; 128.5; 129.4; 132.3; 140.7; 147.7; 150.7; 163.4; 194.5. The photoadduct **28** was unstable at r.t. and converted gradually or easily on distillation (175–180°/3 Torr) to **35**.

2-{2,3-Dihydro-2-[(3-phenylpropanoyl)sulfanyl]furan-3-yl}benzoxazole (**29**). Oil. IR ($CHCl_3$): 1700, 1645. ^{1}H-NMR: 2.63–3.05 (*m*, 4 H); 4.95 (*td*, *J* = 2.3, 9.9, 1 H); 5.39 (*t*, *J* = 2.3, 1 H); 6.62 (*t*, *J* = 2.5, 1 H); 6.76 (*d*, *J* = 9.9, 1 H); 7.02–7.40 (*m*, 4 H); 7.48–7.55 (*m*, 1 H); 7.69–7.78 (*m*, 1 H). ^{13}C-NMR: 30.8, 45.8; 46.5; 85.8; 101.0; 110.7; 120.3; 124.5; 125.3; 126.3; 128.1; 128.4; 139.5; 140.8; 147.7; 150.8; 163.5; 195.6. The photoadduct **29** was unstable at r.t. and converted gradually or easily on distillation (175–180°/3 Torr) to **35**.

S-*[3-(Benzoxazol-2-yl)-2,3-dihydrofuran-2-yl]* O-*Methyl Thiocarbonate* (**30**). Oil. IR ($CHCl_3$): 1720, 1610. ^{1}H-NMR: 3.78 (*s*, 3 H); 4.98 (*dt*, *J* = 2.3, 9.6, 1 H); 5.41 (*t*, *J* = 2.3, 1 H); 6.63 (*t*, *J* = 2.3, 1 H); 6.70 (*d*, *J* = 9.6, 1 H); 7.27–7.39 (*m*, 2 H); 7.51–7.55 (*m*, 1 H); 7.70–7.76 (*m*, 1 H). ^{13}C-NMR: 46.4; 54.6; 88.3; 101.1; 110.7; 120.2; 124.5; 125.3; 140.7; 147.5; 150.7; 163.0; 168.8. The photoadduct **30** was unstable at r.t. and converted gradually or easily on distillation (175–100°/3 Torr) to **35**.

S-*[3-(Benzoxazol-2-yl)-2,3-dihydro-5-methylfuran-2-yl]* O-*Methyl Thiocarbonate* (**31**). B.p. 190°/3 Torr (dec.). IR ($CHCl_3$): 1720, 1610. ^{1}H-NMR: 1.95 (*dd*, *J* = 1.3, 2.3, 3 H); 2.35 (*s*, 3 H); 3.62 (*s*, 3 H); 4.63 (*t*, *J* = 2.3, 1 H); 5.09 (br. *s*, 1 H); 7.28–7.37 (*m*, 2 H); 7.49–7.55 (*m*, 1 H); 7.72–7.76 (*m*, 1 H). ^{13}C-NMR: 13.9; 27.9; 53.5; 55.9; 96.2; 98.7; 110.6; 120.1; 124.4; 125.2; 140.8; 150.7; 156.5; 163.0; 167.9. The result of the elemental analysis of **31** was not in agreement with the calculated values, since **31** decomposed on distillation.

S-*[3-(Benzoxazol-2-yl)-2,3-dihydrofuran-2-yl]* O-*(Prop-2-enyl) Thiocarbonate* (**32**). Oil. IR ($CHCl_3$): 1720, 1610. ^{1}H-NMR: 4.66 (*m*, 2 H); 4.98 (*td*, *J* = 2.3, 9.9, 1 H); 5.20–5.31 (*m*, 2 H); 5.41 (*t*, *J* = 2.3, 1 H); 5.76–5.91 (*m*, 1 H); 6.63 (*t*, *J* = 2.6, 1 H); 6.69 (*d*, *J* = 9.9, 1 H); 7.30–7.40 (*m*, 2 H); 7.48–7.55 (*m*, 1 H); 7.72–7.77 (*m*, 1 H). ^{13}C NMR: 46.5; 68.4; 88.3; 101.2; 110.7; 119.5; 120.3; 124.6; 125.4; 130.9; 140.8; 147.5; 150.8; 163.1; 168.1. The photoadduct **32** was unstable at r.t. and converted gradually or easily on distillation (175–180°/3 Torr) to **35**.

S-*[3-(Benzoxazol-2-yl)-2,3-dihydrofuran-2-yl]* O-*Phenyl Thiocarbonate* (**33**). M.p. 112–113°. IR (KBr): 1725, 1625, 1610. ^{1}H-NMR: 5.03 (*dt*, *J* = 2.3, 9.9, 1 H); 5.44 (*t*, *J* = 3.0, 1 H); 6.65 (*t*, *J* = 3.0, 1 H); 6.74 (*d*, *J* = 9.9, 1 H); 7.02–7.08 (*m*, 2 H); 7.17–7.41 (*m*, 5 H); 7.53–7.58 (*m*, 1 H); 7.73–7.80 (*m*, 1 H). ^{13}C-NMR: 46.7; 88.5;

101.3; 110.8; 120.4; 121.0; 124.7; 125.6; 126.4; 128.3; 129.5; 140.8; 147.6; 150.9; 163.0; 167.5. Anal. calc. for $C_{18}H_{13}NO_4S$ (339.29): C 63.72, H 3.86, N 4.13; found C 63.95, H 3.71, N 4.10.

X-Ray Crystal-Structure Determination of **4**. The crystal of **4** from $CHCl_3$/hexane (approximate dimensions of $0.30 \times 0.35 \times 0.20$ mm) was mounted on a glass fiber and used for the X-ray study.

Crystal Data. $C_{14}H_{15}NO_2S$, M_r 261.343, monoclinic, space group $P21/c$, $a = 12.054(3)$, $b = 5.564(2)$, $c = 20.413(5)$ Å, $\alpha = 90.00°$, $\beta = 104.36(2)°$, $\gamma = 90.00°$, $V = 1326.2(7)$ Å^3, $Z = 4$, $D_x = 1.309$ g cm^{-3}, colorless rod, $F(000) = 552$, $\mu(CuK_\alpha) = 2.12$ mm^{-1}.

Data Collection, Structure Solution, and Refinement. The intensity data were collected in a *Mac Science MXC 18* diffractometer with graphite-monochromated CuK_α radiation (λ 1.54 Å) by means of ω-2θ scan technique in the range $2\theta < 70.00°$. Out of 2892 total reflections, 2274 reflections with intensities greater than 3.0 $\sigma(I)$ were used, but no absorption correction was made. The structure was solved by direct methods with maXus. Least-squares refinement including anisotropic thermal parameters for non-H-atoms and isotropic refinement of H-atoms located in difference *Fourier* synthesis terminated at R 0.055 and R_W 0.265 (F^2).

Tables of crystal data are available as supplementary data. Atomic coordinates, bond lengths and angles, and thermal parameters of X-ray crystal structure of **4** (CCDC-208836) have been deposited with *Cambridge Crystallographic Data Centre*. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223/336-033; e-mail: deposit@ccdc.scan.ac.uk).

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