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Photochemical Synthesis of s-Triazolo[3,4-*b*]benzothiazole and Mechanistic Studies on Benzothiazole Formation

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A general photochemical synthesis of *s*-triazolo[3,4-*b*]benzothiazoles from 4,5-disubstituted 1,2,4-triazole-3-thione is described. Steady photolysis, quantum yield determination, and laser flash photolysis experiments have been carried out. An intramolecular electron transfer mechanism has been proposed.

Introduction

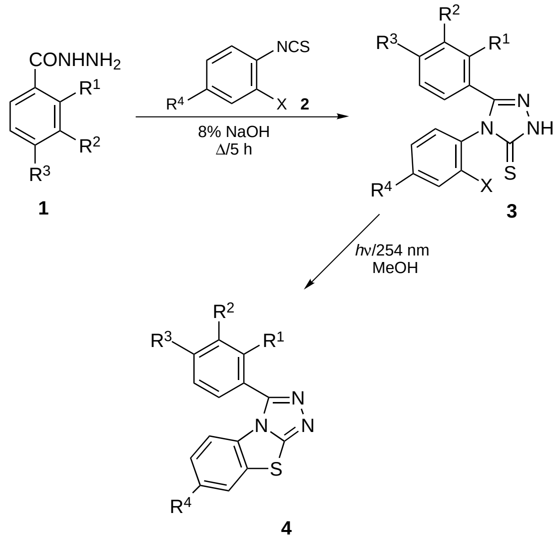
The photochemical synthesis of heterocycles has been of interest in achieving the synthesis of various heterocyclic systems which in some cases proceed very efficiently. Oxidative photocyclization of *cis*-stilbenes to phenanthrenes is well known.[1] The closely related cyclizations of systems containing heteroatoms, such as Schiff bases,[2] diphenylamines,[3] and anilides,[4] as well as some nonoxidative processes[5−8] have also been reported.

The photochemistry of compounds containing *o*-haloaryl groups in the structure has given rise to many heterocyclic systems. Irradiation of *o*-halobenzoic acid anilides as well as *N*-(2-haloaryl)benzamides has been reported to give phenanthridine derivatives.[9,10] The syntheses of condensed thienoquinoline ring systems have been reported by the irradiation of suitable haloacid amides.[11,12]

The formation of benzothiazole ring system has been reported by oxidative photocyclization of thiobenzanilide[2] as well as *N*-phenylthiourethane.[13] We have first reported the formation of 2-methylbenzothiazole by the irradiation of *o*-halothioacetanilide.[14] Subsequently the irradiation studies were carried out with a variety of substituted aniline derivatives in methanol or benzene medium.[15] The studies were extended to get naphtho[1,2-*d*]thiazole and naphtho[2,1-*d*]thiazole,[16] 2-(indol-1-yl)benzothiazole,[17] benzothiazolo[2,3-*b*]quinazolin-12-one.[18]

Results and Discussion

In continuation of our earlier work,[14−18] we report herein the synthesis of s-triazolo[3,4-*b*]benzothiazole. The required 4-(2′-haloaryl)-5-aryl-s-triazole-3-thione **3** was prepared from the respective acid hydrazide **1** and appropriate 2-halophenyl isothiocyanate **2**. Irradiation of **3** furnished the s-triazolo[3,4-*b*] benzothiazole **4** in 30−60% yields. The products were characterized by IR, NMR, MS, and elemental analysis (Table-1).



Mechanistic Studies. Benzothiazoles have been prepared[19,20] under basic conditions from *o*-halothioacetanilides; *N*-(3-iodophenyl)benzamide also gave 2-phen-

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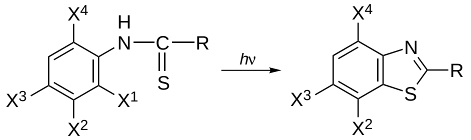
Table I. Substituted s-Triazolo [3,4-*b*]benzothiazoles

3 → 4	R^1	R^2	R^3	R^4	X	irradiation time (h)	yield (%)
a	H	H	H	H	Cl	15	41
b	H	H	CH_3	H	Cl	15	40
c	CH_3	H	H	H	Cl	25	38
d	H	H	OCH_3	H	Cl	20	56
e	CH_3	H	H	CH_3	Br	24	48
f	H	H	CH_3	CH_3	Br	18	47
g	-CH=CHCH=CH-		H	H	Cl	5	34

Table 2. 2-Substituted Benzothiazoles

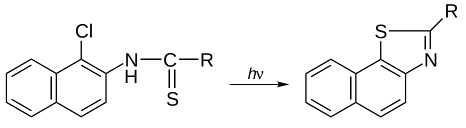
5 → 6	R	X^1	X^2	X^3	X^4	irradiation time (h)
a	CH_3	Cl	Cl	–	–	42
b	CH_3	Cl	Cl	Br	–	24
c	CH_3	Br	Cl	Br	CH_3	18
d	CH_3	Br	CH_3	Br	CH_3	8
e	$CH_2C_6H_5$	Cl	Cl	–	–	42
f	C_6H_5	Cl	Cl	–	–	72
g	Indol-1-yl	Cl	Cl	–	–	35
h	1,3-Dioxocyclohexan-2-yl	Cl	Cl	–	–	40
i	5,5-Dimethyl-1,3-dioxocyclohexan-2-yl	Cl	Cl	–	–	42

ylbenzothiazole; hence a benzyne intermediate has been proposed. Under photochemical conditions, photoinduced elimination of HX resulting in a benzyne intermediate followed by cyclization can be contemplated.



5 **6**

The enol nature of the thioacetanilides was supported[15] by the ^{1}H-NMR signals in the region δ 2.2–2.5 due to the SH proton in some cases. However, the benzyne mechanism can be ruled out, because *N*-(2,3-dihaloaryl)-thioamides **5** (Table 2) as well as the naphthyl system **7** undergo facile photocyclization.



7 **8**

a, R = phenyl
b, R = indol-1-yl
c, R = 1,3-dioxocyclohexan-2-yl
d, R = 5,5-dimethyl-1,3-dioxocyclohexan-2-yl
e, R = C_6H_5CONH-
f, R = methyl

A number of reports of photocyclization accompanied by elimination of HCl or HBr have appeared in the literature, although the details of the mechanism have not been discussed clearly.[21] The actual mechanism of the photocyclization reaction, thus, cannot be unequivocally putforth on the basis of the products present in the irradiated solution and the various reactions with different substrates. In order to elucidate the mechanism for the above photocyclization, studies involving quantum yield of the products and flash photolysis identification of intermediates were carried out in the present work.

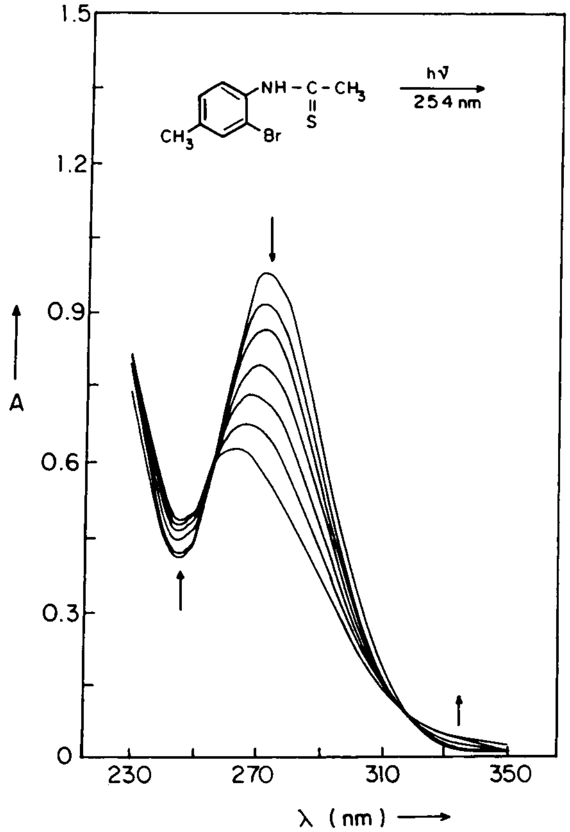


Figure 1. Absorption spectral changes during the photolysis of *N*-(2-bromo-4-methylphenyl)thioacetamide in nitrogen-saturated methanol. Each spectrum recorded after 25 irradiation.

Steady Photolysis. Steady photolyses were carried out for selected substrates (qualitatively) using a low-pressure mercury pen-ray lamp which emits light of wavelength 254 nm. Absorption spectra of the compounds in the ultraviolet region were taken after each specified duration of irradiation. Absorption spectral changes accompanying the 254 nm photolysis of *N*-(2-bromo-4-methylphenyl)thioacetamide in methanol showed the isosbestic points at 255 and 316 nm during conversion to the product (Figure 1); *N*-(2-chlorophenyl)thiobenzamide showed the isosbestic points at 239 and 267 nm;

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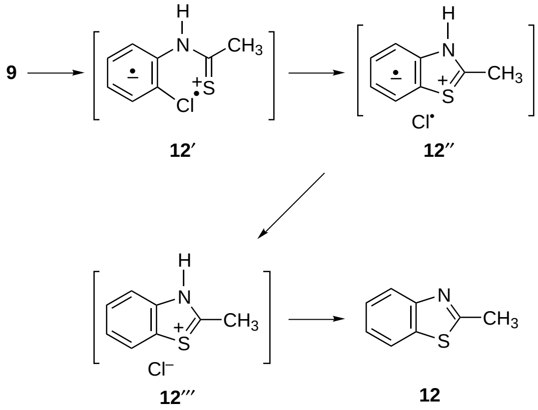
N-(2,5-dichlorophenyl)indolethiocarboxamide showed the isosbestic point at 242 nm, which disappeared, and the reappearance of isosbestic points has been observed at 275 and 300 nm until the product spectrum was obtained; 3-(2-chlorophenyl)-2-thioxo-1,2-dihydro-4(3*H*)quinazolinone showed an isosbestic point initially at 285 nm which disappeared and reappeared again at 270 and 316 nm, until the product spectrum was obtained. The changes indicate that the reaction is a multi-step process in nature. 2-(Indol-1-yl)benzothiazole, 7-chloro-2-(indol-1-yl)benzothiazole, and 12*H*-benzothiazolo[2,3-*b*]quinazolin-12-one were separately irradiated using pen-ray lamp; recording of the UV spectrum at frequent intervals showed that all the above benzothiazoles undergo secondary photolysis on further irradiation.

The quantum yield determination was carried out for the formation of 2-phenylbenzothiazole from *N*-(2-chlorophenyl)thiobenzamide. Light intensity was measured by ferrioxalate actinometry.[22] The quantum yield (ϕ) for the formation of product was found to be 0.037 ± 0.003.

Laser Flash Photolysis. A set of experiments were designed to establish the cleavage of aryl−halogen bond. The compounds chosen for this study were (a) *N*-(2-chlorophenyl)thioacetamide (**9**), (b) *N*-(3-chlorophenyl)thioacetamide (**10**), and (c) *N*-(2-chlorophenyl)acetamide (**11**).

The laser flash photolysis of **9** with pulses (266 nm) from the fourth harmonic of Nd/YAG laser was carried out. Chlorine atoms are not readily detectable in experiments of this type. In order to make chlorine atoms detectable, tetraethylammonium chloride was added to generate $Cl_2^{\bullet-}$ which is known to absorb strongly at λ_{max} $\sim$ 345 nm;[23] significant absorption from $Cl_2^{\bullet-}$ was noted. The laser flash photolysis experiments carried out with **10** and **11** showed very weak transient absorption spectra for $Cl_2^{\bullet-}$, thus supporting the absence of product formation during the irradiation (Figures 2 and 3). The signal observed in the case of **10** may be due to a similar electron transfer and elimination of $Cl^{\bullet}$, but to a small extent. In addition, loss or shift of hydrogen from the *ortho* position must also occur to give benzothiazole, which was not observed. In the case of **11**, the electron transfer from oxygen can be expected to be weaker than from sulfur, resulting in a weak signal for $Cl_2^{\bullet-}$. Thus the above experiment suggests the elimination of chlorine radical.



As suggested in the S$_{\mathrm{RN}}$1 mechanism,[24] the formation of radical anion by intramolecular electron transfer reaction might be expected to give **12′**. The expected initial homolysis of the Ar−Cl bond probably does not occur since no dehalogenated thioamide or amine was detected. The driving force for the homolysis may emanate from the favorable formation of aryl−sulfur bond. The detection of HCl in some of the experiments[15]

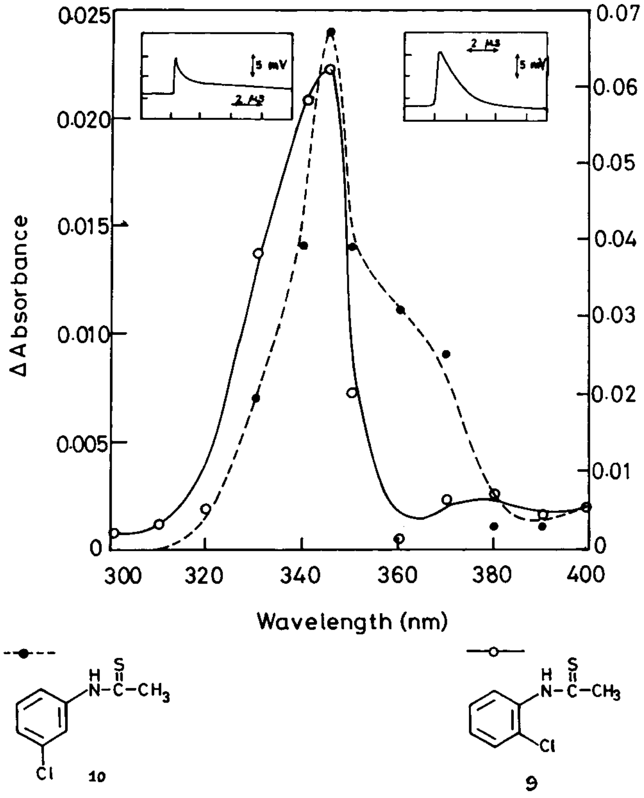


Figure 2. Transient absorption spectra recorded 2 μs after a 266 nm laser pulse in argon-saturated acetonitrile solution for *N*-(2-chlorophenyl)thioacetamide (**9**) and *N*-(3-chlorophenyl)thioacetamide (**10**). Insert left: Transient decay of **10** at the absorption maximum. Inset right: Transient decay of **9** at the absorption maximum.

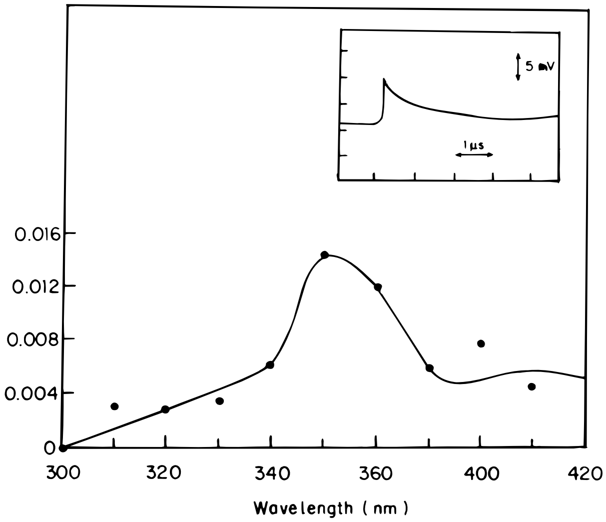


Figure 3. Transient absorption spectrum of *N*-(2-chlorophenyl)acetamide (**11**) in argon-saturated acetonitrile solution. Inset: Transient decay at the absorption maximum.

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is also experimental evidence for the above mechanism.

A mechanism involving intramolecular $S_{RN}1$ substitution has been proposed earlier for the formation of benzothiazole from *o*-halothioacetanilide, which was, however, based on the irradiation studies on the thioamide anion.[25] In the electron transfer reactions, amines are known to participate as inter- and intramolecular electron donors.[26–28] So far, there appear to be no report of any electron transfer from an amide nitrogen. In the present work, the thioamides being the substrates, the electron transfer may be expected to occur from sulfur rather than from nitrogen. A mechanism involving nucleophilic displacement[29] by the thiolate anion has been proposed for the base catalyzed cyclization of triazole-3-thiols to yield s-triazolo[3,4-*b*]benzothiazole ruling out the benzyne mechanism.

Conclusion

Substituted s-triazolo[3,4-*b*]benzothiazoles were prepared from the respective triazole-3-thiones by photochemical method. In order to establish the mechanism, steady photolysis experiments were carried out. The changes in the isosbestic points indicate a multistep nature and secondary photolysis. Laser flash photolysis experiments indicate the expulsion of halogen as radical. An intramolecular electron transfer mechanism has been proposed.

Experimental Section

All the melting points are uncorrected. The reactions were monitored by TLC. IR spectra were recorded for the samples as KBr pellets. ^{1}H NMR spectra were recorded on 60, 90, and 400 MHz instruments, and the shifts are reported in ppm downfield from TMS. Mass spectra were determined at an ionizing voltage of 70 eV. The photochemical reactions were carried out in a quartz vessel in an Applied Photophysics reactor (254 nm) and a Hanovia medium-pressure immersion reactor.

4-(2-Chlorophenyl)-5-phenyl-1,2,4-triazole-3-thione (3a). A mixture of benzhydrazide (1.4 g, 0.01 mol) and 2-chlorophenyl isothiocyanate (1.7 g, 0.01 mol) was refluxed in NaOH solution (30 mL; 8%) for 5 h, cooled, and filtered and the filtrate washed with ether. The aqueous layer was acidified with cold, dilute HCl. The separated solid was filtered and washed with water to give **3a**: yield 59%; mp 222–224 °C (EtOH); IR (KBr, cm^{-1}) 3090 (NH), 1620 (C=N); ^{1}H NMR (90 MHz, DMSO-d_6) δ 7.40–8.25 (m, 9H, ArH); MS *m/z* (relative intensity) 287 (M$^+$, 18), [289, M + 2], 252 (100), 149 (85). Anal. Calcd for $C_{14}H_{10}ClN_3S$: C, 58.43; H, 3.50; N, 14.60. Found: C, 58.53; H, 3.48; N, 14.63.

4-(2-Chlorophenyl)-5-(4-methylphenyl)-1,2,4-triazole-3-thione (3b). Thione **3b** was prepared using *p*-toluic hydrazide (4.0 g, 0.027 mol) and 2-chlorophenyl isothiocyanate (4.5 g, 0.027 mol): yield 87%; mp 238–240 °C; IR (KBr, cm^{-1}) 3070 (NH), 1606 (C=N); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.30 (s, 3H, ArMe), 7.05–7.55 (m, 8H, ArH); MS *m/z* (relative intensity) 301 (M$^+$, 17), [303, M + 2], 266 (100), 149 (80). Anal. Calcd for $C_{15}H_{12}ClN_3S$: C, 59.69; H, 4.00; N, 13.92. Found: C, 59.51; H, 3.94; N, 13.71.

4-(2-Chlorophenyl)-5-(2-methylphenyl)-1,2,4-triazole-3-thione (3c). From *o*-toluic hydrazide (1.3 g, 0.009 mol) and 2-chlorophenyl isothiocyanate (1.5 g, 0.009 mol) was obtained **3c**: yield 45%; mp 244–246 °C; IR (KBr, cm^{-1}) 3090 (NH), 1605 (C=N); ^{1}H NMR (60 MHz; acetone-d_6) δ 2.45 (s, 3H, ArMe), 7.20–7.80 (m, 8H, ArH); MS *m/z* (relative intensity) 301 (M$^+$, 14), [303, M + 2], 266 (100), 149 (73). Anal. Calcd for $C_{15}H_{12}ClN_3S$: C, 59.69; H, 4.00; N, 13.92. Found: C, 59.80; H, 3.98; N, 13.95.

4-(2-Chlorophenyl)-5-(4-methoxyphenyl)-1,2,4-triazole-3-thione (3d). Thione **3d** was prepared using *p*-anisic hydrazide (1.0 g, 0.006 mol) and 2-chlorophenyl isothiocyanate (1.0 g, 0.006 mol): yield 41%; mp 240–242 °C; IR (KBr, cm^{-1}) 3090 (NH), 1610 (C=N), 1020, 1250 (=COC); ^{1}H NMR (60 MHz, acetone-d_6) δ 3.90 (s, 3H, OMe), 7.10–8.00 (m, 8H, ArH); MS *m/z* (relative intensity) 317 (M$^+$, 21), [319, M + 2], 282 (100), 149 (88). Anal. Calcd for $C_{15}H_{12}ClN_3OS$: C, 56.69; H, 3.80; N, 13.22. Found: C, 56.78; H, 3.78; N, 13.24.

4-(2-Bromo-4-methylphenyl)-5-(2-methylphenyl)-1,2,4-triazole-3-thione (3e). Thione **3e** was prepared from *o*-toluic hydrazide (1.5 g, 0.01 mol) and 2-bromo-4-methylphenyl isothiocyanate (2.3 g, 0.01 mol): yield 42%; mp 221–223 °C; IR (KBr, cm^{-1}) 3080 (NH), 1590 (C=N); ^{1}H NMR (60 MHz, acetone-d_6) δ 2.35 (s, 3H, ArMe), 2.50 (s, 3H, ArMe), 7.15–7.70 (m, 7H, ArH); MS *m/z* (relative intensity) 359 (M$^+$, 8), [361, M + 2], 280 (100), 163 (75). Anal. Calcd for $C_{16}H_{14}BrN_3S$: C, 53.34; H, 3.91; N, 11.66. Found: C, 53.48; H, 3.89; N, 11.69.

4-(2-Bromo-4-methylphenyl)-5-(4-methylphenyl)-1,2,4-triazole-3-thione (3f). Reaction of *p*-toluic hydrazide (1.5 g, 0.01 mol) with 2-bromo-4-methylphenyl isothiocyanate (2.3g, 0.01 mol) gave **3f**: yield 86%; mp 270–272 °C; IR (KBr, cm^{-1}) 3080 (NH), 1600 (C=N); ^{1}H NMR (400 MHz, acetone-d_6) δ 2.30 (s, 3H, ArMe), 2.40 (s, 3H, ArMe), 7.15–7.60 (m, 7H, ArH); MS *m/z* (relative intensity) 359 (M$^+$, 31), [361, M + 2], 280 (100), 163(77).

4-(2-Chlorophenyl)-5-(1-naphthyl)-1,2,4-triazole-3-thione (3g). Reaction of 1-naphthoic hydrazide (2.8 g, 0.015 mol) with 2-chlorophenyl isothiocyanate (2.55 g, 0.015 mol) furnished **3g**: yield 69%; mp 262–264 °C; IR (KBr, cm^{-1}) 3060 (NH), 1580 (C=N). ^{1}H NMR (60 MHz, acetone-d_6) δ 7.20–8.50 (m, 11H, ArH); MS *m/z* (relative intensity) 337 (M$^+$, 14), [339, M + 2], 302 (100), 149 (98).

Irradiation. A solution of **3a** (0.7 g, 0.0024 mol) in absolute methanol (150 mL) was flushed with nitrogen for 1 h and irradiated for 15 h, monitoring by TLC. After removal of solvent, the residue was chromatographed over a column of silica gel. Elution with ethyl acetate–petroleum ether mixture (1:6) furnished 3-phenyl-s-triazolo[3,4-*b*]benzothiazole **4a**: yield 41%; mp 144–146 °C (EtOH); (lit.[30] mp 153 °C); IR (KBr, cm^{-1}) 1610 (C=N); ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.4–8.0 (m, 9H, ArH); MS *m/z* (relative intensity) 251 (M$^+$, 14), 148 (92). Anal. Calcd for $C_{14}H_9N_3S$: C, 66.91; H, 3.60; N, 16.72. Found: C, 66.73; H, 3.42; N, 16.70.

3-(4-Methylphenyl)-s-triazolo[3,4-*b*]benzothiazole (4b): yield 40% from 0.6 g of **3b**; mp 154–156 °C (EtOH); IR (KBr, cm^{-1}) 1590 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.3 (s, 3H, ArMe), 7.0–7.7 (m, 8H, ArH); MS *m/z* (relative intensity) 265 (M$^+$, 85), 148 (100). Anal. Calcd for $C_{15}H_{11}N_3S$: C, 67.90; H, 4.17; N, 15.83. Found: C, 67.84; H, 4.02; N, 15.81.

3-(2-Methylphenyl)-s-triazolo[3,4-*b*]benzothiazole (4c): yield 38% from 0.3 g of **3c**; mp 110–112 °C (EtOH); IR (KBr, cm^{-1}); 1585 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.3 (s, 3H, ArMe), 7.0–7.7 (m, 8H, ArH); MS *m/z* (relative intensity) 265 (M$^+$, 82), 148 (45). Anal. Calcd for $C_{15}H_{11}N_3S$: C, 67.90; H, 4.17; N, 15.83. Found: C, 67.84; H, 4.43; N, 15.56.

3-(4-Methoxyphenyl)-s-triazolo[3,4-*b*]benzothiazole (4d): yield 56% from 0.2 g of **3d**; mp 140–142 °C (EtOH); (lit.[31] mp 145–146 °C); IR (KBr, cm^{-1}) 1610 (C=N), 1020, 1250 (=COC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.9 (s, 3H, OMe), 7.1–7.8 (m, 8H, ArH); MS *m/z* (relative intensity) 281 (M$^+$, 100), 148 (84).

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Anal. Calcd for $C_{15}H_{11}N_3OS$: C, 64.04; H, 3.94; N, 14.93. Found: C, 64.35; H, 4.12; N, 15.00.

3-(2-Methylphenyl)-7-methyl-s-triazolo[3,4-*b*]benzothiazole (4e): yield 48% from 0.4 g of **3e**; mp 120−122 °C (EtOH); IR (KBr, cm^{-1}) 1600 (C═N); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.3 (s, 3H, ArMe), 2.45 (s, 3H, ArMe), 6.8−7.5 (m, 7H, ArH); MS *m/z* (relative intensity) 279 (M^+, 85), 162 (50). Anal. Calcd for $C_{16}H_{13}N_3S$: C, 68.79; H, 4.69; N, 15.04. Found: C, 68.50; H, 4.83; N, 14.79.

3-(4-Methylphenyl)-7-methyl-s-triazolo[3,4-−*b*]benzothiazole (4f): yield 57% from 0.25 g of **3f**: mp 182−184 °C (EtOH); IR (KBr, cm^{-1}) 1610 (C═N); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H, ArMe), 2.5 (s, 3H, ArMe), 7.1−7.7 (m, 7H, ArH); MS *m/z* (relative intensity) 279 (M^+, 78), 162 (100). Anal. Calcd for $C_{16}H_{13}N_3S$: C, 68.79; H, 4.69; N, 15.04. Found: C, 68.61; H, 4.72; N, 15.04.

3-(1-Naphthyl)-s-triazolo[3,4-*b*]benzothiazole (4g): yield 34% obtained by Immersion type photolysis from 0.5 g of **3g**: mp 154−156 °C (EtOH); IR (KBr, cm^{-1}) 1580 (C═N); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.6−8.2 (m, 11H, ArH); MS *m/z* (relative intensity) 301 (M^+, 62), 148 (57). Anal. Calcd for $C_{18}H_{11}N_3S$: C, 71.74; H, 4.01; N, 13.94. Found: C, 71.81; H, 3.86; N, 13.84.

In steady photolysis experiments, a low pressure mercury pen-ray quartz lamp (254 nm) was used. Absorption spectra of samples were recorded initially and after each specified duration of irradiation in a standard 1 cm quartz cell.

N-(2-Chlorophenyl)thiobenzamide (4.1×10^{-4} mol/L) in methanol was used for the quantum yield determination, which had an absorbance of more than 4.0 at 254 nm to absorb the entire light; the solution was irradiated using a pen-ray lamp for a specified time (2 min), and the absorbance was monitored at 290 and 300 nm. Three separate irradiation experiments were carried out for each run, and the absorbance was determined with three independent solutions.

Laser flash photolysis experiments of the samples were carried out in argon-saturated acetonitrile solutions using a Quanta Ray GCR-2(10) Nd-YAG Laser using the fourth harmonics output of 266 nm with a pulse width of 8 ns. The signals were detected using a 250 W pulsed Xenon lamp, Czerny Turner monochromator, and R-928 PMT and captured using a Hewlett-Packard 54201A digital storage oscilloscope.

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