29. Synthesis of Indole Derivatives by [2 + 2] Photocycloaddition of Indoline-2-thiones with Alkenes and Photodesulfurization of Indoline-2-thiones

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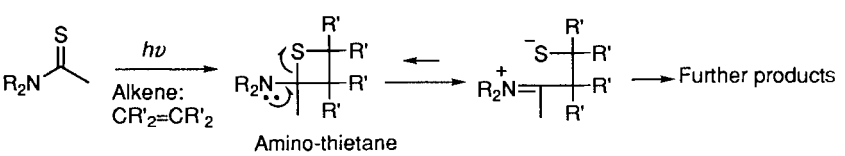
The photochemical synthesis of indole derivatives starting from the indoline-2-thiones **1** is described. Irradiation of indoline-2-thiones **1** in the presence of alkenes **3** gave 2-alkyl-3*H*-indoles **4**–**7** or 2-alkylindoles **8**–**22** through the ring cleavage of the intermediates, spirocyclic amino-thietanes, initially derived by [2 + 2] cycloaddition of the C=S bond of **1** and the C=C bond of **3**. Irradiation of **1** in the presence of trialkylamines **26** gave desulfurization products **27**–**32** and unexpected 3-alkylindoles **33**–**40**. *N*-Acylindoline-2-thiones **1i**–**p** yielded the deacylated products, indoline-2-thiones **1a**–**b**, and ethyl esters **43** through γ-H abstraction by the excited thioamide S-atom when irradiated in $CDCl_3$/EtOH or benzene/EtOH. Oxygen analogues **2a**–**d** also underwent intramolecular H abstraction to give the indolin-2-ones **2e**–**f** and ethyl esters **43** in a similar way.

1. Introduction. – In recent years, there has been great interest in the photochemistry of thioamide compounds from both synthetic and mechanistic view points [1]. In particular, they undergo [2 + 2] photocycloadditions with alkenes to yield amino-thietanes as primary products, which are usually unstable and are transformed into fragmentation products (*Scheme 1*). This may be ascribed to the participation of the lone-pair electrons on the N-atom, which facilitate the C–S bond cleavage of the thietane ring leading to zwitterions, and then they undergo further reactions [1c–d]. In the course of our studies of the photochemical reactions of cyclic conjugated nitrogen-thiocarbonyl systems [2], we found that photochemically induced addition of thioamides to alkenes provided a convenient method for the C–C bond formation of N-containing heterocycles [2a–d, g, j–k, m]. We recently reported that photodesulfurization reactions of indoline-2-thiones and 3,3-disubstituted indoline-2-thiones to indoles [2e] and indolines [2f], respectively, and [2 + 2] photocycloaddition reaction of 3,3-disubstituted indoline-2-thiones with electron-poor alkenes leading to 2-alkylideneindolines [2g]. *Das* and coworkers have shown that indoline-2-thiones undergo photoinduced addition to electron-poor alkene, methyl methacrylate, to give a mixture of isomeric 2-substituted indoles [3]. To see the scope and limitation of the photoaddition of indoline-2-thiones **1** and alkenes, we examined the photoreactions of **1** with a variety of alkenes **3** including electron-rich ones and related photoreactions of **1** (*Table 1*).

Scheme 1



Scheme 2

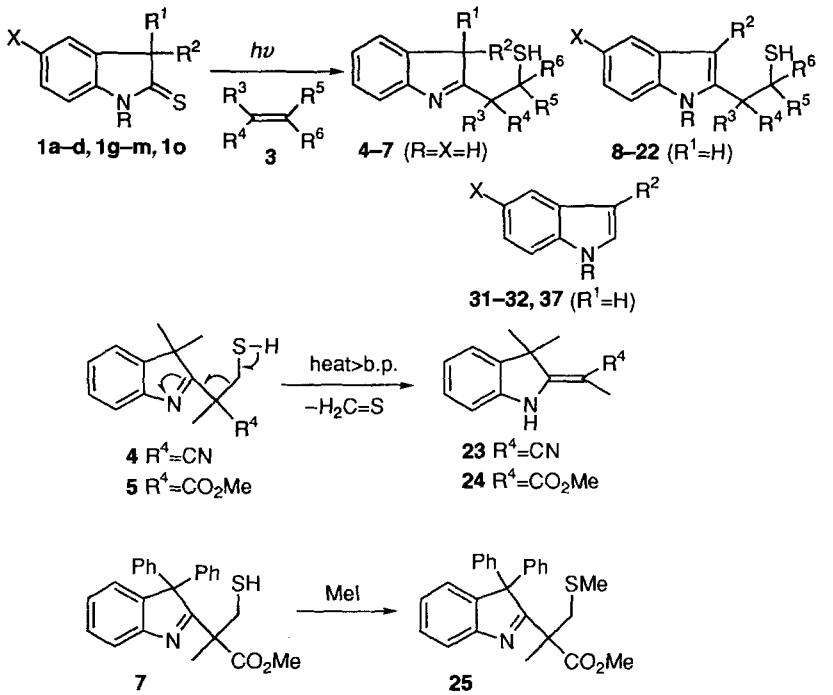


Table 1. *Yield of 3H-Indoles* **4**–**7** *and 2-Alkylindoles* **8**–**22**

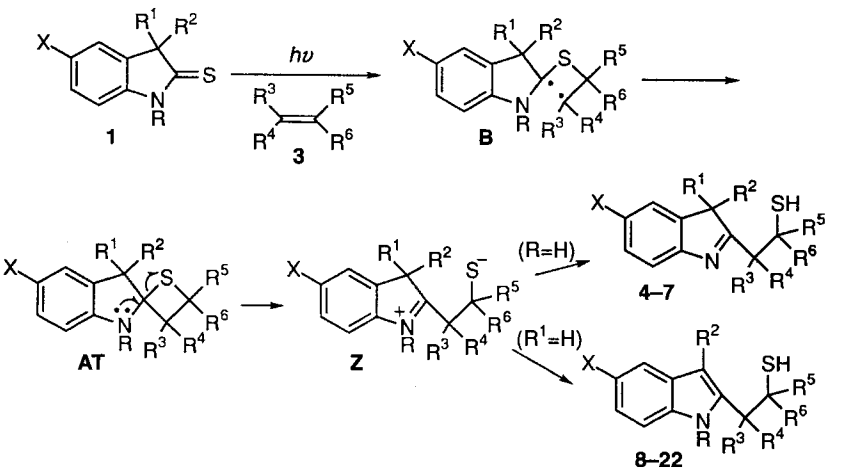
	R	R^1	R^2	X		R^3	R^4	R^5	R^6	Product (Yield [%][a]))	
1a	H	Me	Me	H	**3a**	Me	CN	H	H	**4** (98)	
1a	H	Me	Me	H	**3b**	Me	CO_2Me	H	H	**5** (70)	
1b	H	Ph	Ph	H	**3a**	Me	CN	H	H	**6** (82)	
1b	H	Ph	Ph	H	**3b**	Me	CO_2Me	H	H	**7** (52)	
1c	H	H	H	H	**3a**	Me	CN	H	H	**8** (76)	
1c	H	H	H	H	**3d**	Me	Me	H	H	**9** (54)	
1c	H	H	H	H	**3e**	Me	Me	Me	Me	**10** (72)	
1d	$PhCH_2$	H	H	H	**3b**	Me	CO_2Me	H	H	**11** (48)	
1g	Me	Ph	H	H	**3b**	Me	CO_2Me	H	H	**12** (53)	
1h	Ph	H	H	H	**3a**	Me	CN	H	H	**13** (94)	
1h	Ph	H	H	H	**3b**	Me	CO_2Me	H	H	**14** (61)	
1h	Ph	H	H	H	**3c**	Me	CO_2Me	Me	H	**15** (48)	**31** (20)
1h	Ph	H	H	H	**3d**	Me	Me	H	H	**16** (72)	**31** (9)
1h	Ph	H	H	H	**3e**	Me	Me	Me	Me	**17** (16)	**31** (24)
1h	Ph	H	H	H	**3f**	EtO	H	H	H	**18** (21)	**31** (5)
1i	*p*-Tol	H	H	Me	**3b**	Me	CO_2Me	H	H	**19** (65)	**32** (11)
1j	Ph	H	Me	H	**3b**	Me	CO_2Me	H	H	**20** (54)	
1j	Ph	H	Me	H	**3d**	Me	Me	H	H	**21** (69)	
1k	Ph	H	Et	H	**3b**	Me	CO_2Me	H	H	**22** (75)	**37** (20)
1l	MeCO	Me	Me	H	**3a**	Me	CN	H	H	**4** (17)	
1m	Pr^iCO	Me	Me	H	**3a**	Me	CN	H	H	**4** (78)	
1o	Ph_2CHCO	Me	Me	H	**3a**	Me	CN	H	H	**4** (49)	
1p	MeCO	Ph	Ph	H	**3a**	Me	CN	H	H	[b])	

[a]) Isolated yield. [b]) **1l** was recovered in > 85%.

2. Results and Discussion. – 2.1. *Photoaddition of the Indoline-2-thiones* **1a–d, g–m, o–p** *and Alkenes* **3**. When a benzene solution of the 3,3-disubstituted indoline-2-thiones **1a–b** was irradiated with a high-pressure Hg lamp through a *Pyrex* filter under Ar, the unchanged starting materials were recovered quantitatively (*Scheme 2*). However, the 2-(mercaptoalkyl)-3*H*-indoles **4–7** were produced as one isomer, when indoline-2-thiones **1a–b** were irradiated in benzene in the presence of a large excess of the electron-poor alkenes such as methacrylonitrile **3a** and methyl methacrylate **3b**. The structures of these photoproducts were elucidated on the basis of their spectroscopic properties (IR: 2550–2580 cm^{-1} (SH), ^{1}H-NMR: *ABX* pattern for CH_2SH) and microanalyses, the latter indicating that they were 1:1 adducts of indoline-2-thiones **1** and alkenes **3**. Treatment of the 2-(mercaptoalkyl)-3*H*-indole **7** with MeI yielded the methylthio-ester **25** in 65% yield. 2-(Mercaptoalkyl)-3*H*-indoles **4–5** was heated at a higher temperature than their boiling points to yield 2-alkylideneindoles **23–24** with a loss of thioformaldehyde. Irradiation of the indoline-2-thione **1a** in the presence of electron-rich alkenes such as 2-methylprop-2-ene (**3d**), 2,3-dimethylbut-2-ene (**3e**), and ethyl vinyl ether (**3f**) under the same conditions resulted in recovery of the unchanged thione **1a**. In contrast, the indoline-2-thiones **1c–d, g–k**, which have at least one H-atom at C(3), undergo [2 + 2] photocycloaddition with both electron-poor and electron-rich alkenes to give 2-(mercapto)alkylindoles **8–22** in moderate-to-good yields. In the cases of 1-phenylindoline-2-thione (**1h**) and electron-poor trisubstituted alkene **3c** and electron-rich alkenes **3d–f**, 5-methyl-1-(*p*-tolyl)indoline-2-thione (**1i**) and electron-poor alkene **3b**, and 3-ethyl-1-phenylindoline-2-thione (**1k**) and **3b**, the desulfurization products, indoles **31–32** and **37**, were obtained as by-products. The formation of the desulfurization products **31–32** and **37** was already observed in the photolysis of the corresponding indoline-2-thiones in benzene [2e]. The photoaddition reaction of 1-phenylindoline-2-thione **1h** and methacrylonitrile **3a** was quenched by the addition of a triplet quencher such as 2,5-dimethylhexa-2,4-diene and cyclooctatetraene, and it proceeded by the addition of triplet sensitizer xanthone when irradiated at 366 nm light, and also proceeded when irradiated in the n-π^* region with a halogen lamp ($\lambda > 400$ nm). These facts suggested that the photocycloaddition proceeded *via* the excited n-π^* triplet state of **1h**. A reasonable mechanism for the formation of 2-(mercaptoalkyl)-3*H*-indoles **4–7** and 2-(mercaptoalkyl)indoles **8–22** can be best explained by the intermediacy of a spirocyclic amino-thietane **AT**, which was formed by regioselective [2 + 2] photocycloaddition of the C=S bond of indoline-2-thiones **1** and the C=C bond of alkenes **3** through the more stable biradical intermediate **B** [1c, d] [2]. Subsequent heterolytic cleavage of the C–S bond of the amino-thietane **AT** due to the participation of the lone-pair electrons on the N-atom afforded the zwitterion **Z**. 1,5-H Transfer from the N- to the S-atom gave 2-(mercaptoalkyl)-3*H*-indoles **4–7**, while H transfer from C(3) to the S-atom gave 2-alkylindoles **8–22** (*Scheme 3*).

Irradiation of 1-acylindoline-2-thiones **1l–m** and **1o** in the presence of methacrylonitrile **3a** also gave the 2-(mercaptoalkyl)-3*H*-indole **4**, which is the same product derived from **1a** and **3a**. 1-Acylindoline-2-thione **1p** was inert to the photoaddition with **3a**. The formation of **4** is considered to arise by photocycloaddition of **1a**, which is formed by γ-H abstraction by the excited thioamide S-atom of 1-acylindoline-2-thiones **1l–m** and **o**, to **3a** (see *Sect. 2.3*).

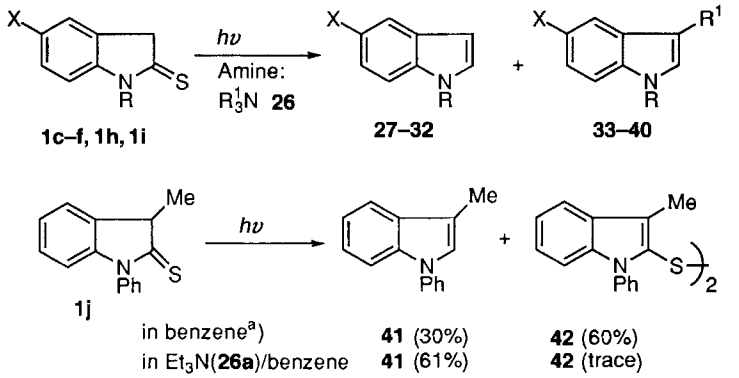
Scheme 3



2.2. *Photochemical Reactions of the Indoline-2-thiones* **1c–f** *and* **h–j** *in the Presence of Trialkylamines* **26.** We recently reported that irradiation of 3,3-disubstituted indoline-2-thiones in the presence of Et_3N affords the desulfurization products, indolines, *via* a sequential electron/proton-transfer mechanism [2f]. We now carried out the photolysis of the indoline-2-thiones **1c–f** and **h–j**, which have no substituents at C(3), in the presence of trialkylamine **26** and observed the formation of unexpected products, 3-alkylindoles **33–40**, along with desulfurization products, indoles **27–32** (*Scheme 4* and *Table 2*). Irradiation of indoline-2-thiones **1c–f**, **1h**, and **1i** in benzene in the presence of an excess of Et_3N (**26a**) under the similar conditions as described above gave the desulfurization products, indoles **27–32**, and unexpected products, 3-ethylindoles **33–37** and **40** in 11–41 and 23–61% yields, respectively. The structure of these photoproducts was confirmed by direct comparison of their IR and NMR spectra with those of authentic materials [2e] or on the basis of their spectral and analytical data. Both products, indole **31** and 3-alkylindoles **38** and **39** were obtained, when the indoline-2-thione **1h** was irradiated in the presence of trialkylamines such as Pr_3N (**26b**) and Bu_3N (**26c**) but in low yields, while the sole product, indole **31**, was obtained when **1h** was irradiated in the presence of amines such as Me_3N (**26d**), $(PhCH_2)_3N$ (**26e**), *N*,*N*-dimethylaniline, and Et_2NH. However, irradiation of 3-substituted indoline-2-thiones, 1-phenyl-3-methylindoline-2-thione **1j**, in the presence of Et_3N (**26a**) gave the corresponding indole **41** (61%) and the disulfide **42** (trace). This result is similar to that obtained in the photolysis of **1j** alone in benzene [2e]. 3-Ethylindole (**37**) was not produced, when 1-phenylindole (**31**) was irradiated in the presence of Et_3N (**26a**) in benzene. The mechanism for the formation of 3-alkylindoles **33–40** is not clear at present, but we tentatively postulate that the formation of **33–40** involves intermediates, anion radicals, resulting from electron transfer from the amine to the excited indoline-2-thiones **1**, analogous to the photodesulfurization of indoline-2-thiones **1** with amines [1f].

2.3. *γ-H Abstraction Reaction of 1-Acylindoline-2-thiones* **1l–p** *and Their Oxo Analogues* **2a–d.** As described briefly in *Sect. 2.1*, irradiation of 1-acylindoline-2-thiones

Scheme 4



[a]) *Cf.* [1e].

Table 2. *Yields of Indoles* **27**–**32** *and 2-Alkylindoles* **33**–**40**

Indoline-2-thiones			Amine **26**		Products (Yield [%][a]))	
	R	X		R^1		
1c	H	H	**26a**	Et	**27** (41)	**33** (52)
1d	$PhCH_2$	H	**26a**	Et	**28** (12)	**34** (41)
1e	Bu	H	**26a**	Et	**29** (18)	**35** (61)
1f	Me	H	**26a**	Et	**30** (11)	**36** (26)
1h	Ph	H	**26a**	Et	**31** (34)	**37** (34)
1h	Ph	H	**26b**	Pr	**31** (44)	**38** (4)
1h	Ph	H	**26c**	Bu	**31** (64)	**39** (9)
1h	Ph	H	**26d**	Me	**31** (32)	[b])
1h	Ph	H	**26e**	$PhCH_2$	**31** (8)	[b])
1h	Ph	H	Et_2NH		**31** (21)	[b])
1h	Ph	H	$PhNMe_2$		**31** (38)	[b])
1i	*p*-Tol	Me	**26a**	Et	**32** (34)	**40** (23)

[a]) Isolated yield. [b]) Not detected.

1l–**o** in the presence of alkene **3a** gave the unexpected product, 2-(mercaptoalkyl)-3*H*-indolenine **4**, suggesting that γ-H abstraction by the excited thioamide S-atom would be involved in this reaction yielding deacylation product, indoline-2-thione **1a**. We carried out the photoreaction of 1-acylindoline-2-thiones **1l**–**p** and their oxo analogues **2a**–**d**. Irradiation of **1l**–**p** in $CDCl_3$ containing a small amount of EtOH in a NMR tube or benzene/EtOH (preparative scale) gave the parent indoline-2-thione **1a** and the corresponding ethyl esters **43a**–**d** with an efficiency depending on the nature of the substituents at C(1) (*Scheme 5* and *Table 3*). Similar deacylation was observed in the photolysis of 1-acylindolin-2-ones **2a**–**d**. The formation of esters **43a**–**d** can be explained in terms of the pathway involving γ-H abstraction by the excited thioamide S-atom or amide O-atom: removal of a H-atom from the C-atom α to the acyl function by the S-atom of the thiones **1l**–**p** or the O-atom of amides **2** leads to a diradical, which subsequently collapse to ketenes **44** and indoline-2-thiones **1a**–**b**, or indolin-2-ones

Scheme 5

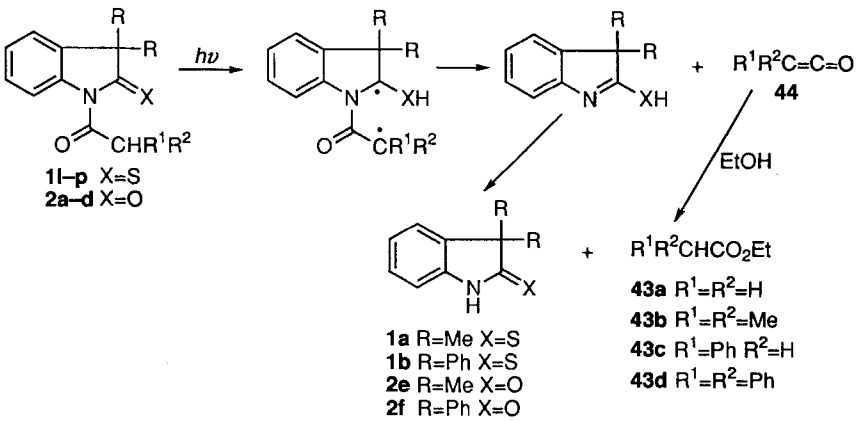


Table 3. *Yields of Indoline-2-thiones* **1a–b**, *Indolin-2-ones* **2e–f**, *and Esters* **43**

					Products (Yield [%])	
	R	R^1	R^2	X	**1** or **2**	Ester **43**
1l	Me	H	H	S	**1a** (trace)	**43a** trace
1m	Me	Me	Me	S	**1a** (90)	**43b** (90)
1m[a])	Me	Me	Me	S	**1a** (97)	**43b** (95)
1n[a])	Me	Ph	H	S	**1a** (88)	**43c** (85)
1o[a])	Me	Ph	Ph	S	**1a** (97)	**43d** (89)
1p	Ph	H	H	S	**1b** (29)	**43a** (29)
2a	Me	H	H	O	**2e** (95)	**43a** (95)
2b	Me	Me	Me	O	**2e** (41)	**43b** (38)
2c	Me	Ph	H	O	**2e** (86)	**43c** (86)
2d	Ph	H	H	O	**2f** (95)	**43a** (95)

[a]) Photolysis was carried out in benzene/EtOH.

2e–f. Ketenes **44** thus produced reacted with EtOH to yield ethyl esters **43a–d**. Analogous γ-H abstractions were observed by *Barton* and *White* in the photolysis of *N*-acyl-2-thionothiazolidines [4].

Experimental Part

General. Chromatography: silica gel *Merck 60* and *Wakogel C-300* for flash chromatography (FC). M.p. and b.p.: uncorrected. IR Spectra: *Hitachi-260-30* or *Jasco FT/IR-300* photospectrometers, in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Jeol FX-100* (100 MHz) or *Jeol JNM-EX-270* (270 MHz) spectrometers; in $CDCl_3$ using Me_4Si as an internal standard; δ in ppm, J in Hz.

Photoaddition of Indoline-2-thiones **1** *and Alkenes* **3**. *General Procedure.* A soln. of **1** (1 mmol) in benzene (70 ml) in the presence of an excess of alkene **3** (*ca.* 1 ml) in a *Pyrex* vessel under Ar was irradiated with a high-pressure Hg lamp (*Halos EHP 500 W, Eikosha*) for 10–20 h at r.t. After removal of the solvent, the residue was chromatographed (silica gel, benzene/hexane 1:4 to 4:1) to yield products **4–22**, **31–32**, and **37** (*Table 1*). The structures of **31–32** and **37** were confirmed by comparison of their spectral data with those of previously described samples [2e].

*2-(3,3-Dimethyl-3*H*-indol-2-yl)-3-mercapto-2-methylpropanenitrile* (**4**). B.p. 150°/1 Torr (dec.). IR (film): 2550, 2230, 1545, 770, 755, 710. ^{1}H-NMR: 1.59 (*s*, 3H); 1.62 (*s*, 3H); 1.80 (*s*, 3H); 1.83 (*t*, *J* = 9.2, 1H); 3.03 (*A* of *ABX*, *J* = 9.2, 13.9, 1H); 3.47 (*B* of *ABX*, *J* = 9.2, 13.9, 1H); 7.28–7.36 (*m*, 3H); 7.45–7.58 (*m*, 1H). ^{13}C-NMR: 22.1(*q*); 22.7(*q*); 27.7(*q*); 34.8(*t*); 43.8(*s*); 55.1(*s*); 120.8(*d*); 121.0(*d*); 121.1(*s*); 126.6(*d*); 127.7(*d*); 146.0(*s*); 151.4(*s*); 183.4(*s*). This product decomposed when heated at higher temperature than b.p. yielding *2-(2,3-dihydro-3,3-dimethyl-1*H*-indol-2-ylidene)propanenitrile* (**23**). M.p. 204–205°. IR (KBr): 3270, 2190, 1615, 1470, 1455, 1225, 1205, 745. ^{1}H-NMR: 1.63 (*s*, 6H); 1.87 (*s*, 3H); 6.70–6.95 (*m*, 2H); 7.10–7.16 (*m*, 2H). ^{13}C-NMR: 14.6(*q*); 26.0(*q*); 46.8(*s*); 68.3(*s*); 108.4(*d*); 121.3(*d*); 122.2(*d*); 122.7(*s*); 127.8(*d*); 137.9(*s*); 141.8(*s*); 166.8(*s*). Anal. calc. for $C_{13}H_{14}N_2$ (198.26): C 78.75, H 7.12, N 14.13; found: C 78.93, H 7.04, N 13.82.

*Methyl 2-(3,3-Dimethyl-3*H*-indol-2-yl)-3-mercapto-2-methylpropanecarboxylate* (**5**). B.p. 180°/2 Torr (dec.). IR (film): 2550, 1725, 1640, 1545, 1370, 1355, 1285, 1230, 1200, 775, 755. ^{1}H-NMR: 1.35 (*s*, 3H); 1.43 (*s*, 3H); 1.55 (*dd*, *J* = 7.8, 16.5, 1H); 1.73 (*s*, 3H); 3.29–3.37 (*m*, 2H); 3.72 (*s*, 3H); 7.19–7.35 (*m*, 3H); 7.59 (*d*, *J* = 7.6, 1H). ^{13}C-NMR: 20.7(*q*); 23.6(*q*); 24.6(*q*); 33.3(*t*); 52.3(*q*); 53.8(*s*); 55.4(*s*); 120.7(*d*); 120.8(*d*); 126.2(*d*); 127.6(*d*); 146.7(*s*); 151.6(*s*); 172.9(*s*); 186.8(*s*). This product decomposed by distillation to yield *methyl-2-(2,3-dihydro-3,3-dimethyl-1*H*-indol-2-ylidene)propanecarboxylate* (**24**). B.p. 170°/2 Torr. IR (film): 3320, 1655, 1590, 1480, 1280, 1250, 1235, 1195, 1160, 780, 740. ^{1}H-NMR: 1.57 (*s*, 6H); 2.02 (*s*, 3H); 3.74 (*s*, 3H); 6.71–6.75 (*m*, 1H); 6.86–6.90 (*m*, 1H); 7.08–7.14 (*m*, 2H); 10.46 (*br s*, 1H). ^{13}C-NMR: 11.7(*q*); 25.4(*q*); 47.8(*s*); 51.0(*q*); 89.3(*s*); 108.3(*d*); 120.4(*d*); 121.6(*d*); 127.7(*d*); 138.4(*s*); 142,5(*s*); 166.4(*s*); 171.6(*s*). Anal. calc. for $C_{14}H_{17}NO_2$ (231.28): C 72.70, H 7.41, N 6.06; found: C 72.59, H 7.24, N 5.79.

*2-(3,3-diphenyl-3*H*-indol-2-yl)-3-mercapto-2-methylpropanenitrile* (**6**). M.p. 117–118°. IR (KBr): 2570, 2230, 1595, 1550, 1485, 1445, 755, 700. ^{1}H-NMR: 1.32 (*s*, 3H); 1.90 (*dd*, *J* = 8.9, 9.9, 1H); 2.78 (*dd*, *J* = 9.9, 13.9, 1H); 3.01 (*dd*, *J* = 8.9, 13.9, 1H); 7.01–7.23 (*m*, 2H); 7.28–7.44 (*m*, 11H); 7.67 (*d*, *J* = 7.9, 1H). ^{13}C-NMR: 26.4(*q*); 35.1(*t*); 44.0(*s*); 73.4(*s*); 120.2(*s*); 121.3(*d*); 123.8(*d*); 127.7(*d*); 128.2(*d*); 128.8(*d*); 128.9(*d*); 138.4(*s*); 146.8(*s*); 152.1(*s*); 182.4(*s*). Anal. calc. for $C_{24}H_{20}N_2S$ (368.42): C 78.22, H 5.47, N 7.60; found: C 78.09, H 5.60, N 7.61.

*Methyl 2-(3,3-Diphenyl-3*H*-indol-2-yl)-3-mercapto-2-methylpropanecarboxylate* (**7**). M.p. 101–102°. IR ($CHCl_3$): 2580, 1730, 1585, 1545, 1455, 1280, 1230, 1200, 750. ^{1}H-NMR: 1.43 (*s*, 3H); 1.68 (*t*, *J* = 8.9, 1H); 2.98–3.05 (*m*, 2H); 3.31 (*s*, 3H); 6.93 (*d*, *J* = 7.4, 1H); 7.08–7.15 (*m*, 1H); 7.22–7.38 (*m*, 11H); 7.70 (*d*, *J* = 7.6, 1H). ^{13}C-NMR: 20.6(*q*); 33.7(*t*); 52.2(*q*); 54.7(*s*); 73.2(*s*); 121.3(*d*); 123.4(*d*); 127.1(*d*); 127.5(*d*); 127.6(*d*); 127.7(*d*); 128.1(*d*); 128.4(*d*); 128.9(*d*); 129.2(*d*); 137.7(*s*); 139.0(*s*); 148.1(*s*); 152.2(*s*); 172.2(*s*); 184.6(*s*). Anal. calc. for $C_{25}H_{23}NO_2S$ (401.44): C 74.78, H 5.77, N 3.49; found: C 74.79, H 6.05, N 3.32.

A soln. of **7** (0.5 mmol) and MeI (3 mmol) in acetone (30 ml) in the presence of K_2CO_3 (2 mmol) was stirred for 5 h under Ar at r.t. A usual workup gave the sulfide **25** (65%).

*Methyl 2-(3,3-Diphenyl-3*H*-indol-2-yl)-2-methyl-3-(methylthio)propanecarboxylate* (**25**). M.p. 101–102°. IR ($CHCl_3$): 1735, 1600, 1490, 1455, 1205, 1110, 775, 745, 730, 700. ^{1}H-NMR: 1.44 (*s*, 3H); 2.04 (*s*, 3H); 2.99 (*d*, *J* = 13.2, 1H); 3.19 (*d*, *J* = 13.2, 1H); 3.32 (*s*, 3H); 6.93 (*d*, *J* = 7.6, 1H); 7.08–7.14 (*m*, 1H); 7.24–7.36 (*m*, 11H); 7.67 (*d*, *J* = 7.6, 1H). ^{13}C-NMR: 18.2(*q*); 21.2(*q*); 44.1(*t*); 52.1(*q*); 54.8(*s*); 73.3(*s*); 121.3(*d*); 123.4(*d*); 127.0(*d*); 127.5(*d*); 127.7(*d*); 128.3(*d*); 128.4(*d*); 128.6(*d*); 129.2(*d*); 137.7(*s*); 139.1(*s*); 148.2(*s*); 152.2(*s*); 172.4(*s*); 185.4(*s*).

*2-(1*H*-Indol-2-yl)-3-mercapto-2-methylpropanitrile* (**8**). B.p. 170°/2 Torr. IR ($CHCl_3$): 2575, 2240, 1455, 1415, 1295, 1230, 775, 765, 730. ^{1}H-NMR: 1.68 (*t*, *J* = 9.2, 1H); 1.87 (*s*, 3H); 2.97 (*dd*, *J* = 9.2, 14.2, 1H); 3.07 (*dd*, *J* = 9.2. 14.2, 1H); 6.46 (br. *s*, 1H); 7.09–7.22 (*m*, 2H); 7.37 (*d*, *J* = 8.2, 1H); 7.58 (*d*, *J* = 7.9, 1H); 8.64 (br. *s*, 1H). ^{13}C-NMR: 24.2(*q*); 35.5(*t*); 40.5(*s*); 100.5(*d*); 111.2(*d*); 120.5(*d*); 120.7(*d*); 121.2(*s*); 122.9(*d*); 127.6(*s*); 135.0(*s*); 136.1(*s*).

*2-(1*H*-Indol-2-yl)-2-methylpropane-1-thiol* (**9**). B.p. 180°/2 Torr. IR (film): 3415, 2565, 1615, 1455, 1410, 1335, 1295, 1010, 790, 745, 690. ^{1}H-NMR: 1.22 (*t*, *J* = 8.6, 1H); 1.43 (*s*, 6H); 2.73 (*d*, *J* = 8.6, 2H); 6.29 (*dd*, *J* = 0.7, 2.3, 1H); 7.07–7.19 (*m*, 2H); 7.29–7.32 (*m*, 1H); 7.53–7.57 (*m*, 1H); 8.11 (br. *s*, 1H). ^{13}C-NMR: 26.7(*q*); 36.5(*s*); 38.1(*t*); 98.9(*d*); 110.6(*d*); 119.7(*d*); 120.1(*d*); 121.4(*d*); 128.2(*s*); 135.8(*s*); 145.0(*s*).

*3-(1*H*-Indol-2-yl)-2,3-dimethylbutane-2-thiol* (**10**). B.p. > 250°/2 Torr. IR ($CHCl_3$): 3480, 2520, 1455, 1375, 1290, 1145, 755, 740. ^{1}H-NMR: 1.39 (*s*, 6H); 1.51 (*s*, 6H); 1.76 (*s*, 1H); 6.34 (*dd*, *J* = 1.0, 2.0, 1H); 7.06–7.17 (*m*, 2H); 7.33 (*d*, *J* = 1.0, 1H); 7.54–7.58 (*m*, 1H); 8.70 (br. *s*, 1H). ^{13}C-NMR: 24.5(*q*); 29.4(*q*); 42.7(*s*); 52.1(*s*); 100.1(*d*); 110.6(*d*); 119.5(*d*); 119.9(*d*); 121.2(*d*); 127.6(*s*); 135.3(*s*); 144.7(*s*).

*Methyl 2-(1-Benzyl-1*H*-indol-2-yl)-3-mercapto-2-methylpropanecarbonylate* (**11**). B.p. 155°/2 Torr. IR (film): 2555, 1715, 1600, 1490, 1465, 1345, 1240, 1120, 1095, 740, 730, 700, 696. ^{1}H-NMR: 1.17 (*dd*, *J* = 7.8, 10.3, 1H); 1.74 (*s*, 3H); 3.22 (*s*, 3H); 2.93–3.38 (*m*, 2H); 5.30 (*s*, 2H); 6.58 (*s*, 1H); 6.75–6.91 (*m*, 2H); 7.00–7.37 (*m*, 6H); 7.67–7.70 (*m*, 1H). ^{13}C-NMR: 23.0(*q*); 32.8(*t*); 47.4(*t*); 48.3(*s*); 52.1(*q*); 102.0(*d*); 120.0(*d*); 120.6(*d*); 122.2(*d*); 125.6(*d*); 126.9(*s*); 127.0(*d*); 128.5(*d*); 136.8(*s*); 138.2(*s*); 139.8(*s*); 174.4(*s*). Anal. calc. for $C_{20}H_{21}NO_2S$ (339.38): C 70.76, H 6.24, N 4.13; found: C 70.91, H 5.98, N 3.96.

Methyl 2-(1-Methyl-3-phenyl-1H-indol-2-yl)-3-mercapto-2-methylpropanecarboxylate (**12**). M.p. 135–137°. IR (KBr): 2540, 1720, 1605, 1465, 1235, 1105, 825, 760, 740, 710, 700. ^{1}H-NMR: 1.13 (*dd*, *J* = 7.8, 9.3, 1 H); 1.52 (*s*, 3 H); 3.01–3.15 (*m*, 2 H); 3.65 (*s*, 3 H); 3.69 (*s*, 3 H); 6.98–7.43 (*m*,9 H). ^{13}C-NMR: 24.5(*q*); 31.2(*q*); 33.8(*t*); 50.3(*s*); 52.6(*q*); 108.6(*d*); 117.8(*s*); 119.6(*d*); 122.4(*d*); 126.9(*d*); 127.8(*d*); 129.3(*s*); 131.5(*d*); 133.9(*s*); 136.4(*s*); 136.7(*s*); 175.3(*s*). Anal. calc. for $C_{20}H_{21}NO_2S$ (339.38): C 70.76, H 6.24, N 4.13; found: C 70.66, H 6.27, N 4.09.

2-(1-Phenyl-1H-indol-2-yl)-3-mercapto-2-methylpropanenitrile (**13**). B.p. 165°/2 Torr. IR (film): 2550, 2220, 1590, 1495, 750, 700. ^{1}H-NMR: 1.41 (*t*, *J* = 8.8, 1 H); 1.77 (*s*, 3 H); 2.72 (*A* of *ABX*, *J* = 8.8, 13.7, 1 H); 2.90 (*B* of *ABX*, *J* = 8.8, 13.7, 1 H); 6.65-6.85 (*m*, 1 H); 7.00–7.20 (*m*, 2 H); 7.29–7.69 (*m*, 7 H). ^{13}C-NMR: 24.8(*q*); 33.7(*t*); 39.5(*s*); 104.3(*d*); 110.5(*d*); 120.5(*d*); 120.6(*d*); 121.2(*s*); 125.9(*s*); 129.5(*d*); 129.7(*d*); 130.3(*d*); 135.5(*s*); 137.1(*s*); 140.8(*s*). Anal. calc. for $C_{18}H_{16}N_2S$ (292.32): C 73.93, H 5.51, N 9.58; found: C 73.91, H 5.58, N 9.46.

Methyl 2-(1-Phenyl-1H-indol-2-yl)-3-mercapto-2-methylpropanecarboxylate (**14**). B.p. 150°/2 Torr. IR (film): 2550, 1725, 1595, 1495, 1285, 1230, 1125, 1100, 745, 695. ^{1}H-NMR: 1.03 (*t*, *J* = 8.3, 1 H); 1.68 (*s*, 3 H); 2.89 (*d*, *J* = 8.3, 2 H); 3.49 (*s*, 3 H); 6.64 (*s*, 1 H); 6.60–6.77 (*m*, 1 H); 6.98–7.19 (*m*, 3 H); 7.21–7.66 (*m*, 5 H). ^{13}C-NMR: 22.3(*q*); 32.1(*t*); 48.4(*s*); 52.1(*q*); 103.5(*d*); 110.2(*d*); 120.1(*d*); 120.2(*d*); 126.5(*s*); 128.2(*s*); 129.1(*d*); 129.3(*d*); 129.6(*d*); 137.6(*s*); 140.2(*s*); 174.2(*s*). Anal. calc. for $C_{19}H_{19}NO_2S$ (325.35): C 70.12, H 5.89, N 4.30; found: C 70.17, H 5.90, N 4.25.

2-(1-Phenyl-1H-indol-2-yl)-3-mercapto-2-methylbutanecarboxylate (**15**). M.p. 114–115°. IR (KBr): 2520, 1720, 1595, 1490, 1445, 1220, 1195, 1175, 1165, 810, 780, 760, 740, 700. ^{1}H-NMR: 1.31 (*d*, *J* = 2.9, 3 H); 1.33 (*d*, *J* = 6.8, 1 H); 1.61 (*s*, 3 H); 3.51 (*s*, 3 H); 3.64–3.89 (*m*, 1 H); 6.69 (*s*, 1 H); 6.64–6.74 (*m*, 1 H); 6.92–7.20 (*m*, 3 H); 7.34–7.71 (*m*, 5 H). ^{13}C-NMR: 18.0(*q*); 20.7(*q*); 40.1(*d*); 51.5(*s*); 52.0(*q*); 103.6(*d*); 110.4(*d*); 120.3(*d*); 122.2(*d*); 126.3(*s*); 129.1(*d*); 129.3(*d*); 129.5(*d*); 129.8(*d*); 138.0(*s*); 140.4(*s*); 141.8(*s*); 173.1(*s*). Anal. calc. for $C_{20}H_{21}NO_2S$ (339.38): C 70.76, H 6.24, N 4.13; found: C 70.55, H 6.27, N 4.05.

2-Methyl-2-(1-phenyl-1H-indol-2-yl)propane-1-thiol (**16**). M.p. 83–84°. IR ($CHCl_3$): 2560, 1595, 1500, 1455, 1225, 1115, 745, 700. ^{1}H-NMR: 1.11 (*t*, *J* = 8.3, 1 H); 1.36 (*s*, 6 H); 2.58 (*d*, *J* = 8.3, 2 H); 6.62 (br. *s*, 1 H); 7.01–7.12 (*m*, 2 H); 7.35–7.68 (*m*, 7 H). ^{13}C-NMR: 28.3(*q*); 36.5(*t*); 38.4(*s*); 102.5(*d*); 110.3(*d*); 119.8(*d*); 121.6(*d*); 126.6(*s*); 129.1(*d*); 129.3(*d*); 130.1(*d*); 139.7(*s*); 141.0(*s*); 145.8(*s*). Anal. calc. for $C_{18}H_{19}NS$ (281.34): C 76.81, H 6.81,N 4.98; found: C 76.70, H 6.82, N 4.93.

2,3-Dimethyl-3-(1-phenyl-1H-indol-2-yl)butane-2-thiol (**17**). M.p. 118–120°. IR (KBr): 2565, 1595, 1495, 1455, 1375, 1210, 1100, 750, 700. ^{1}H-NMR: 1.35 (*s*, 6 H); 1.42 (*s*, 6 H); 1.65 (*s*, 1 H); 6.67 (*dd*, *J* = 1.0, 3.3, 1 H); 6.98–7.12 (*m*, 2 H); 7.32–7.60 (*m*, 7 H). ^{13}C-NMR: 27.2(*q*); 30.2(*q*); 45.5(*s*); 52.8(*s*); 105.3(*d*); 110.9(*d*); 119.5(*d*); 120.0(*d*); 121.4(*d*); 126.3(*s*); 128.4(*d*); 128.7(*d*); 130.8(*d*); 140.7(*s*); 141.0(*s*); 145.2(*s*). Anal. calc. for $C_{20}H_{23}NS$ (309.39): C 77.76, H 7.49, N 4.53; found: C 77.50, H 7.55, N 4.58.

2-Ethoxy-2-(1-phenyl-1H-indol-2-yl)ethane-1-thiol (**18**). B.p. 155°/2 Torr. IR (film): 2555, 1595, 1495, 1455, 1215, 1075, 1015, 745, 700. ^{1}H-NMR: 1.11 (*t*, *J* = 6.9, 3 H); 1.58 (*t*, *J* = 8.6, 1 H); 2.69–2.91 (*m*, 2 H); 3.29–3.47 (*m*, 2 H); 4.44 (*t*, *J* = 6.9, 1 H); 6.67 (*s*, 1 H); 7.02–7.19 (*m*, 3 H); 7.33–7.68 (*m*, 6 H). ^{13}C-NMR: 15.2(*q*); 29.1(*t*); 64.3(*t*); 75.9(*d*); 101.6(*d*); 110.5(*d*); 120.4(*d*); 120.6(*d*); 122.2(*d*); 127.4(*s*); 128.4(*d*); 129.5(*d*); 137.4(*s*); 138.8(*s*); 139.4(*s*).

Methyl 2-[5-Methyl-1-(p-tolyl)-1H-indol-2-yl]-3-mercapto-2-methylpropanecarboxylate (**19**). B.p. 180°/2 Torr. IR (film): 2550, 1720, 1505, 1370, 1230, 1100, 840, 790. ^{1}H-NMR: 1.05 (*dd*, *J* = 1.5, 9.2, 1 H); 1.68 (*s*, 3 H); 2.42 (*s*, 6 H); 2.87 (br. *d*, *J* = 9.2, 2 H); 3.51 (*s*, 3 H); 6.59 (*s*, 1 H); 6.46–6.68 (*m*, 1 H); 6.78–7.68 (*m*, 6 H). ^{13}C-NMR: 21.3(*q*); 23.4(*q*); 32.1(*d*); 48.4(*s*); 52.1(*q*); 103.0(*d*); 110.0(*d*); 119.9(*d*); 123.7(*d*); 126.7(*s*); 129.3(*s*); 129.3(*d*); 129.8(*t*); 130.0(*d*); 135.2(*s*); 139.0(*s*); 140.3(*s*); 174.5(*s*). Anal. calc. for $C_{21}H_{23}NO_2S$ (252.21): C 71.35, H 6.55, N 3.96; found: C 71.53, H 6.62, N 3.93.

Methyl 2-(3-Methyl-1-phenyl-1H-indol-2-yl)-3-mercapto-2-methylpropanecarboxylate (**20**). M.p. 64–65°. IR (KBr): 2550, 1725, 1590, 1495, 1445, 1360, 1225, 1105, 820, 740, 700. ^{1}H-NMR: 1.15 (*dd*, *J* = 6.8, 10.3, 1 H); 1.67 (*s*, 3 H); 2.45 (*s*, 3 H); 2.82 (*dd*, *J* = 10.3, 13.7, 1 H); 3.14 (*dd*, *J* = 6.8, 13.7, 1 H); 3.52 (*s*, 3 H); 6.45–6.71 (*m*, 1 H); 6.95–7.66 (*m*, 8 H). ^{13}C-NMR: 10.6(*q*); 24.2(*q*); 33.8(*t*); 50.5(*s*); 52.1(*q*); 110.2(*d*); 111.6(*s*); 118.1(*d*); 119.6(*d*); 122.4(*d*); 128.4(*s*); 129.2(*d*); 130.0(*d*); 130.2(*d*); 134.3(*s*); 138.9(*s*); 139.3(*s*); 174.7(*s*). Anal. calc. for $C_{20}H_{21}NO_2S$ (339.38): C 70.76, H 6.24, N 4.13; found: C 70.49, H 6.16, N 4.02.

2-Methyl-2-(3-methyl-1-phenyl-1H-indol-2-yl)propane-1-thiol (**21**). B.p. 180°/2 Torr. IR ($CHCl_3$): 2565, 1595, 1500, 1475, 1460, 1355, 1270, 750, 740, 700. ^{1}H-NMR: 1.16 (*t*, *J* = 8,2, 1 H); 1.37 (*s*, 6 H); 2.53 (*s*, 3 H); 2.72 (*d*, *J* = 8.2, 2 H); 7.00–7.15 (*m*, 2 H); 7.35–7.69 (*m*, 7 H). ^{13}C-NMR: 11.6(*q*); 29.6(*q*); 38.2(*t*); 40.6(*s*); 110.3(*d*); 117.7(*d*); 119.4(*d*); 121.8(*d*); 128.4(*d*); 128.9(*s*); 139.9(*s*); 141.1(*s*). Anal. calc. for $C_{19}H_{21}NS$ (295.37): C 77.26, H 7.17, N 4.74; found: C 76.90, H 6.98, N 4.75.

*Methyl 2-(3-Ethyl-1-phenyl-1*H*-indol-2-yl)-3-mercapto-2-methylpropanecarboxylate* (**22**). M.p. 106–107°. IR (KBr): 2550, 1725, 1595, 1495, 1475, 1380, 1220, 1105, 760, 745, 700. ^{1}H-NMR: 1.14 (*X* of *ABX*, *J* = 7.3, 10.4, 1H); 1.35 (*t*, *J* = 7.3, 3H); 2.86 (*A* of *ABX*, *J* = 10.4, 14.2, 1H); 2.93 (*q*, *J* = 7.3, 2H); 3.14 (*B* of *ABX*, *J* = 7.3, 14.2, 1H); 3.55 (*s*, 3H); 6.54–6.71 (*m*, 1H); 6.96–7.69 (*m*, 8H). ^{13}C-NMR: 15.7(*q*); 18.5(*t*); 24.1(*q*); 33.9(*t*); 50.6(*s*); 52.2(*q*); 110.4(*d*); 118.4(*d*); 119.6(*d*); 122.3(*d*); 127.6(*s*); 129.9(*d*); 129.1(*d*); 130.0(*d*); 130.2(*d*); 133.7(*s*); 139.1(*s*); 139.7(*s*); 174.9(*s*). Anal. calc. for $C_{21}H_{23}NO_2S$ (353.40): C 71.37, H 6.56, N 3.96; found: C 71.40, H 6.64, N 3.94.

Photochemical Reactions of Indoline-2-thiones **1** *in the Presence of Amines* **26.** *General Procedure.* A soln. of **1** (1 mmol) in benzene (70 ml) in the presence of an excess of **26** (*ca.* 1 ml) was irradiated under the same conditions as described above for 5 h. After purification by FC, indole derivatives **27**–**40** were obtained. (*Table 2*). The structures of **27**–**32** and **37** were confirmed by direct comparison of their spectral data with those of commercially available or previously described samples [2e].

*3-Ethyl-1*H*-indole* (**33**). B.p. 120°/2 Torr ([5]: 144–5°/13–4 Torr). IR ($CHCl_3$): 3480, 1615, 1485, 1455, 1415, 1340, 1235, 1090, 1035, 1010, 755. ^{1}H-NMR: 1.32 (*t*, *J* = 7.6, 3H); 2.76 (*q*, *J* = 7.6, 2H); 6.89 (*t*, *J* = 1.0, 1H); 7.07–7.41 (*m*, 3H); 7.60 (*d*, *J* = 7.6, 1H); 7.70 (br. *s*, 1H). ^{13}C-NMR: 14.4(*q*); 18.3(*t*); 111.0(*d*); 118.7(*s*); 119.0(*d*); 120.4(*d*); 121.8(*d*); 127.3(*s*); 128.3(*d*); 136.3(*s*).

*1-Benzyl-3-ethyl-1*H*-indole* (**34**). B.p. 155°/2 Torr. IR (film): 1610, 1495, 1480, 1465, 1450, 1355, 1175, 805, 735, 695. ^{1}H-NMR: 1.30 (*t*, *J* = 7.3, 3H); 2.77 (*q*, *J* = 7.3, 2H); 5.16 (*s*, 2H); 6.83 (*s*, 1H); 6.98–7.30 (*m*, 8H); 7.52–7.67 (*m*, 1H). ^{13}C-NMR: 14.6(*q*); 18.3(*t*); 49.7(*t*); 109.4(*d*); 117.9(*s*); 118.7(*d*); 119.0(*d*); 121.5(*d*); 124.6(*d*); 126.6(*d*); 127.3(*d*); 128.0(*s*); 128.6(*d*); 136.7(*s*); 137.8(*s*). Anal. calc. for $C_{17}H_{17}N$ (235.31): C 86.77, H 7.28, N 5.95; found: C 86.53, H 7.30, N 5.83.

*1-Butyl-3-ethyl-1*H*-indole* (**35**). B.p. 150°/2 Torr. IR (film): 1610, 1480, 1465, 1365, 1185, 735. ^{1}H-NMR: 0.91 (*t*, *J* = 6.3, 1H); 1.31 (*t*, *J* = 7.3, 3H); 1.41–1.65 (*m*, 2H); 1.70–1.92 (*m*, 2H); 2.77 (*q*, *J* = 7.3, 2H); 4.02 (*t*, *J* = 6.8, 2H); 6.83 (*s*, 1H); 6.97–7.34 (*m*, 3H); 7.53–7.63 (*m*, 1H). ^{13}C-NMR: 13.7(*q*); 14.6(*q*); 18.3(*t*); 20.6(*t*); 32.4(*t*); 45.8(*t*); 109.1(*d*); 117.1(*s*); 118.2(*d*); 119.0(*d*); 121.2(*d*); 124.2(*d*); 127.9(*s*); 136.4(*s*). Anal. calc. for $C_{14}H_{19}N$ (201.30): C 83.53, H 9.51, N 6.96; found: C 83.59, H 9.48, N 6.88.

*3-Ethyl-1-methyl-1*H*-indole* (**36**). B.p. 145°/2 Torr ([6]: 74–6°/0.3–0.4 Torr). IR ($CHCl_3$): 1615, 1555, 1485, 1470, 1375, 1330, 1240, 910, 770, 755, 735. ^{1}H-NMR: 1.32 (*t*, *J* = 7.3, 3H); 2.77 (*q*, *J* = 7.3, 2H); 3.71 (*s*, 3H); 6.81 (*s*, 1H); 7.05–7.20 (*m*, 3H); 7.57–7.61 (*m*, 1H). ^{13}C-NMR: 14.7(*q*); 18.2(*t*); 32.5(*q*); 109.0(*d*); 117.3(*s*); 118.4(*d*); 119.0(*d*); 121.4(*d*); 125.4(*d*); 127.7(*s*); 137.1(*s*).

*1-Phenyl-3-propyl-1*H*-indole* (**38**). Oil. IR ($CHCl_3$): 1595, 1500, 1455, 1380, 1235, 770, 755, 695. ^{1}H-NMR: 1.03 (*t*, *J* = 7.3, 3H); 1.71–1.85 (*m*, 2H); 2.78 (*t*, *J* = 7.3, 2H); 7.13–7.66 (*m*, 10H). ^{13}C-NMR: 14.2(*q*); 23.2(*t*); 27.2(*t*); 110.4(*d*); 118.0(*s*); 119.3(*d*); 119.7(*d*); 122.2(*d*); 124.0(*d*); 125.0(*d*); 125.9(*d*); 129.2(*s*); 129.5(*d*); 136.0(*s*); 140.0(*s*).

*3-Butyl-1-phenyl-1*H*-indole* (**39**). Oil. IR ($CHCl_3$): 1595, 1500, 1455, 1375, 1230, 740, 695. ^{1}H-NMR: 0.97 (*t*, *J* = 7.3, 3H); 1.39–1.54 (*m*, 2H); 1.68–1.80 (*m*, 2H); 2.81 (*t*, *J* = 7.3, 2H); 7.13–7.35 (*m*, 4H); 7.48–7.67 (*m*, 6H).

*3-Ethyl-5-methyl-1-(*p*-tolyl)-1*H*-indole* (**40**). B.p. 165°/2 Torr. IR (film): 1605, 1515, 1475, 1455, 1380, 1220, 825, 795. ^{1}H-NMR: 1.35 (*t*, *J* = 7.3, 3H); 2.38 (*s*, 3H); 2.47 (*s*, 3H); 2.80 (*q*, *J* = 7.3, 2H); 6.95–7.05 (*m*, 2H); 7.14–7.45 (*m*, 6H). ^{13}C-NMR: 14.4(*q*); 18.3(*t*); 20.9(*q*); 21.4(*q*); 110.1(*d*); 118.8(*d*); 118.9(*s*); 123.2(*d*); 124.5(*d*); 128.2(*d*); 128.7(*s*); 129.0(*s*); 129.9(*d*); 134.5(*s*); 135.3(*s*); 137.7(*s*). Anal. calc. for $C_{18}H_{19}N$ (249.34): C 86.70, H 7.68, N 5.62; found: C 86.41, H 7.63, N 5.36.

Photolysis of 1-Acylindoline-2-thiones **11**–**p** *and 1-Acylindolin-2-ones* **2***: General Procedure.* A soln. of **1** or **2** (50 mg) in $CDCl_3$ (0.5 ml) containing 2 drops of EtOH in a NMR tube was irradiated under the same conditions for 2–10 h, and then products and yields were confirmed by NMR. A prep. scale photolysis of **1** or **2** (1 mmol) in benzene (70 ml) containing EtOH (1 ml) was carried out under the same conditions, and similar results were obtained (*Table 3*).

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