37. Photocycloaddition of Quinoxaline-2(1*H*)-thiones to Alkenes

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Dedicated to Prof. Dr. *O. Jeger*

(6.1.92)

A synthetically useful C–C bond formation involving the photochemical addition of quinoxaline-2(1*H*)-thiones to alkenes is described. Irradiation of the quinoxaline-2(1*H*)-thiones **1–4** in the presence of the alkenes **7** gave the 2-(2′-mercaptoalkyl)quinoxalines **8–11** in moderate-to-good yields *via* ring cleavage of an intermediate aminothietane with aromatization of the quinoxaline ring. The latter was formed by [2 + 2] photocycloaddition of the C=S bond of the quinoxaline-2(1*H*)-thione and the C=C bond of the alkene.

1. Introduction. – Photochemical reactions of thiocarbonyl compounds received much attention [1–5]. As a result of differences in chemical reactivity and thermodynamic properties, the photoreactions of thiocarbonyl compounds often follow a different course from those of analogous carbonyl compounds. Some reports dealt with the photochemical reactions involving the C=S group of thioamides [6]. The reactions of thioamides are [2 + 2] photocycloadditions with alkenes. The formed aminothietanes are usually unstable, probably due to the conjugation of lone-pair electrons at the N-atom, which facilitate the C–S bond cleavage of the thietane ring yielding fragmentation products[1]). On the contrary, thioimides, cross-conjugated thiocarbonyl systems involving an N-atom, gave thietanes by photochemical cycloaddition with alkenes [7]. In continuation of our work on the photochemistry of cyclic conjugated N-containing thiocarbonyl systems, we found that photoinduced addition of these thiones to alkenes provided a novel method for C–C bond formation in heterocyclic compounds [6l–o]. We now report the photochemical reactions of quinoxaline-2(1*H*)-thiones **1–4** and alkenes, which have potential in the synthesis of 2-substituted quinoxalines[2]).

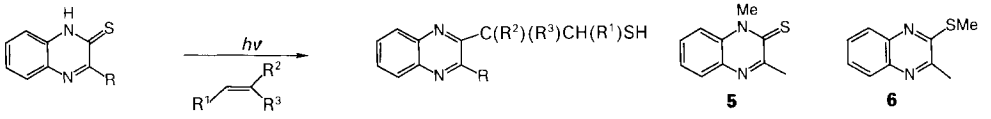
2. Results and Discussion. – The quinoxaline-2(1*H*)-thiones **1–4** are readily accessible by direct sulfurization of their oxo analogues using the dimer of (4-methoxyphenyl)-thionophosphine (*Lawesson*'s reagent). Two tautomeric forms of *N*-unsubstituted quinoxaline-2(1*H*)-thiones, the thione and thiol form, are possible. For identification, the UV and ^{13}C-NMR spectra of 3-methylquinoxaline-2(1*H*)-thione (**2**) were compared with

[1]) Quite recently, we succeeded in the first isolation, though in low yield, of an aminothietane derived from the photochemical [2 + 2] cycloaddition of 1,3,3-trimethyl-1*H*-indole-2(3*H*)-thione with 2-methylprop-1-ene [6n].

[2]) Part of this work was reported in preliminary form [8].

those of the *N*-methylated 1,3-dimethylquinoxaline-2(1*H*)-thione (**5**; thione form) and the *S*-methylated 3-methyl-2-(methylthio)quinoxaline (**6**; thiol form). Thus, 3-methylquinoxaline-2(1*H*)-thione (**2**) in solution exists predominantly in the thione form.

Scheme 1



5 **6**

1 R = H
2 R = Me
3 R = $Me_2CH(CH_2)_2$
4 R = Ph

	R^1	R^2	R^3
7a	H	Me	CN
b	H	Me	CO_2Me
c	H	H	CO_2Me
d	$-(CH_2)_4-$		H
e	H	Me	Me
f	H	H	EtO
g	H	Me	Ph
h	H	H	Ph

8 R = H
9 R = Me
10 R = $Me_2CH(CH_2)_2$
11 R = Ph

The UV spectrum of **2** (λ_{max} 218, 275, 392 nm) was similar to that of **5** (λ_{max} 218, 278, 398 nm), but different from that of **6** (λ_{max} 212, 232, 260, 342, 351 nm). The ^{13}C-NMR spectrum of **2** showed a *s* at 175.1 ppm for a thioamide C-atom (C(2)) and no signal around 155 ppm, while a *s* at 177.5 and 156.5 ppm was observed for C(2) of **5** and **6**, respectively (see *Exper. Part*).

Irradiation of quinoxaline-2(1*H*)-thiones **1–4** in 1,2-dimethoxyethane in the presence of a large excess of electron-poor alkenes **7** such as methacrylonitrile (**7a**), methyl methacrylate (**7b**), and methyl acrylate (**7c**) with a high-pressure mercury lamp under an Ar atmosphere at room temperature gave 2-(2′-mercaptoethyl)quinoxalines **8a,b**, **9a–c**, **10a,b**, **11a,b**, respectively, as the sole product in moderate to good yields (see *Table*). The structures of these photoproducts were established by spectroscopic data (IR: 2525–2575 cm^{-1} (SH), no NH; ^{1}H-NMR; *ABX* pattern for CH_2SH) and microanalysis, the latter indicating that they were 1:1 adducts of quinoxaline-2(1*H*)-thiones and alkenes.

Table. *Yield of Photoproducts* **8–11**

	R	R^1	R^2	R^3	Yield [%][a])		R	R^1	R^2	R^3	Yield [%][a])
8a	H	H	Me	CN	35	**9f**	Me	H	H	EtO	55
8b	H	H	Me	CO_2Me	63	**9g**	Me	H	Me	Ph	21
8d	H	$-(CH_2)_4-$		H	43	**9h**	Me	H	H	Ph	47
8f	H	H	H	EtO	42	**10a**	$Me_2CH(CH_2)_2$	H	Me	CN	64
9a	Me	H	Me	CN	54	**10b**	$Me_2CH(CH_2)_2$	H	Me	CO_2Me	87
9b	Me	H	Me	CO_2Me	59	**10f**	$Me_2CH(CH_2)_2$	H	H	EtO	71
9c	Me	H	H	CO_2Me	34	**11a**	Ph	H	Me	CN	35
9d	Me	$-(CH_2)_4-$		H	48	**11b**	Ph	H	Me	CO_2Me	35
9e	Me	H	Me	Me	44	**11d**	Ph	$-(CH_2)_4-$		H	50

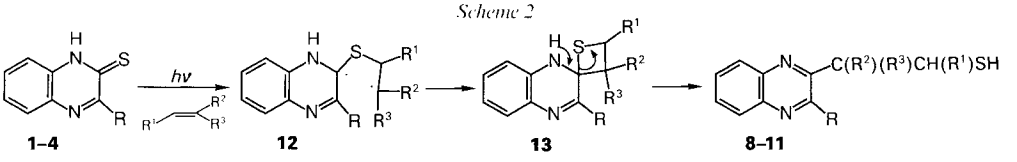
[a]) Isolated yield.

Photocycloadditions of **1–4** to electron-rich alkenes such as cyclohexene (**7d**), 2-methylprop-1-ene (**7e**), and ethyl vinyl ether (**7f**) and to arylalkenes such as α-methylstyrene (**7g**) and styrene (**7h**) gave the corresponding 2-mercaptoalkylated quinoxalines

8d,f, **9d–h**, **10f**, and **11d** in 21–71% yield (see *Table*). By contrast, irradiation of 1,3-dimethylquinoxaline-2(1*H*)-thione (**5**) in the presence of alkenes **7** resulted in recovery of the unchanged starting thione.

The formation of the 2-mercaptoalkylated quinoxalines **8–11** from **1–4** and **7** can be best explained through the intermediacy of a spirocyclic aminothietane **13**, which is formed *via* **12** by the photochemical [2 + 2] cycloaddition of the C=S bond of the quinoxaline-2(1*H*)-thione and the C=C bond of the alkene (*Scheme 2*). Then **13** undergoes thietane-ring cleavage with concomittant 1,3-H shift (NH→SH). This [2 + 2] photocycloaddition of thioamides to alkenes proceeds in a regiospecific manner since 2-mercaptoalkylated quinoxalines derived from the alternate spirocyclic aminothietane could not be detected. This is in accord with previously published work on thioamide photochemistry [6a–c, l–n]. The observed regiospecificity is that expected, with the formation of the more stable diradical intermediate **12**.

Scheme 2



The described regiospecific photoreaction of quinoxaline-2(1*H*)-thiones **1–4** with alkenes **7** represents a ready mode of C–C bond formation and provides an efficient and novel method for alkylation of the quinoxaline ring.

Experimental Part

General. Chromatography: silica gel *Merck 60* and *Wakogel C-300* for flash chromatography. M.p. and b.p.: uncorrected. UV Spectra: *Jasco-UVIDEC-505* photospectrometer; λ_{max} (ε) in nm. IR Spectra: *Hitachi-260-30* photospectrometer, in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *JEOL FX-100* (100 MHz) spectrometer; in $CDCl_3$ using TMS as an internal standard unless otherwise stated; δ in ppm, J in Hz. Mass spectra: *Hitachi-M-80* spectrometer.

*Quinoxaline-2(1*H*)-thiones* **1–5**. A soln. of the quinoxalin-2(1*H*)-one (10 mmol) and *Lawesson*'s reagent (5.5 mmol) in dimethoxyethane (50 ml) was refluxed for 0.5–3 h. After removal of the solvent, the residue was chromatographed with benzene/AcOEt 50:1→19:1 to yield the corresponding quinoxaline-2(1*H*)-thiones **1–5**.

*Quinoxaline-2(1*H*)-thione* (**1**): M.p. 198–200° ([9]: 204–205°). UV (EtOH): 217 (22000), 285 (15800), 405 (8400). IR (KBr): 1610, 1600, 1565, 1140, 1110. ^1H-NMR ((D_6)DMSO): 7.33–7.93 (*m*, 4 H); 8.61 (*s*, 1 H); 14.50 (br. *s*, 1 H). ^{13}C-NMR: 116.2 (*d*); 125.7 (*d*); 128.8 (*d*); 131.4 (*d*); 131.7 (*s*); 135.3 (*s*); 155.9 (*d*); 170.5 (*s*).

*3-Methylquinoxaline-2(1*H*)-thione* (**2**): M.p. 246° (subl., [10]: 250–251°). UV (EtOH): 218 (16800), 275 (9800), 392 (6200). IR (KBr): 1610, 1575, 1218, 1138. ^1H-NMR ((D_6)DMSO): 2.74 (*s*, 3 H); 7.42–7.71 (*m*, 3 H); 7.84–7.92 (*m*, 1 H); 14.45 (br. *s*, 1 H). ^{13}C-NMR: 24.7 (*q*); 115.7 (*d*); 125.6 (*d*); 128.0 (*d*); 130.1 (*d*); 131.6 (*s*); 134.9 (*s*); 161.4 (*s*); 175.1 (*s*).

*3-(3-Methylbutyl)quinoxaline-2(1*H*)-thione* (**3**): M.p. 177–178°. UV (EtOH): 219 (17600), 278 (17600), 397 (11900). IR (KBr): 1610, 1570, 1138. ^1H-NMR ((D_6)DMSO): 1.01 (*d*, J = 5.9, 6 H); 1.53–1.88 (*m*, 3 H); 3.19 (br. *t*, 2 H); 7.41–7.67 (*m*, 3 H); 7.89 (br. *d*, 1 H); 14.44 (br. *s*, 1 H). ^{13}C-NMR: 22.5 (*q*); 27.7 (*d*); 34.0 (*t*); 35.8 (*t*); 115.7 (*d*); 125.7 (*d*); 128.2 (*d*); 130.2 (*d*); 131.4 (*s*); 135.1 (*s*); 164.3 (*s*); 174.9 (*s*). Anal. calc. for $C_{13}H_{16}N_2S$: C 67.20, H 6.94, N 12.05; found: C 66.98, H 6.89, N 12.04.

*3-Phenylquinoxaline-2(1*H*)-thione* (**4**): M.p. 226–228°. UV (EtOH): 227 (42000), 294 (21500), 383 (9000), 417 (8800). IR (KBr): 1615, 1575, 1220, 1140. ^1H-NMR ((D_6)DMSO): 7.30–8.03 (*m*, 8 H); 8.38–8.48 (*m*, 1 H); 14.59 (br. *s*, 1 H). Anal. calc. for $C_{14}H_{10}N_2S$: C 70.56, H 4.22, N 11.75; found: C 70.19, H 4.33, N 12.03.

*1,3-Dimethylquinoxaline-2(1*H*)-thione* (**5**): M.p. 145–147° ([10]: 146–147°). UV (EtOH): 218 (33100), 278

(18000), 398 (11700). IR (KBr): 1590, 1545, 1218, 1149. ^{1}H-NMR: 2.83 (*s*, 3 H); 4.22 (*s*, 3 H); 7.32–7.68 (*m*, 3 H); 7.80–7.90 (*m*, 1 H). ^{13}C-NMR: 27.1 (*q*); 37.8 (*q*); 114.5 (*d*); 125.5 (*d*); 129.7 (*d*); 129.9 (*d*); 133.3 (*s*); 135.0 (*s*); 161.9 (*s*); 177.5 (*s*).

3-Methyl-2-(methylthio)quinoxaline (**6**) was prepared according to the literature procedure [10]. M.p. 54–55° ([10]: 55–56°). UV (EtOH): 212 (21400), 232 (13900), 260 (15300), 342 (9500), 351 (9400). IR (KBr): 1550, 1055, 750. ^{1}H-NMR: 2.67 (*s*, 3 H); 2.68 (*s*, 3 H); 7.56–7.68 (*m*, 2 H); 7.88–8.00 (*m*, 2 H). ^{13}C-NMR: 12.8 (*q*); 22.1 (*q*); 127.4 (*d*); 127.7 (*d*); 128.3 (*d*); 128.9 (*d*); 139.1 (*s*); 141.4 (*s*); 151.9 (*s*); 156.5 (*s*).

Photocycloaddition of Quinoxaline-2(1H)-thiones **1–4** *to Alkenes* **7**: *General Procedure*. A soln. of the quinoxaline-2(1*H*)-thione **1–4** (200 mg) in 1,2-dimethoxyethane (70 ml) in the presence of an excess of the alkene **7** (*ca.* 1 ml for 7**a–f**; 2 mol-equiv. for **7g–h**) in a *Pyrex* vessel under Ar was irradiated with a high-pressure mercury lamp (*HAlos EHP 300 W, Eikosha*) for 10–12 h at r.t. After removal of the solvent, the residue was chromatographed (silica-gel column, benzene/AcOEt 19:1→4:1) to yield products **8–11**.

3-Mercapto-2-methyl-2-(quinoxalin-2-yl)propanenitrile (**8a**): B.p. 150°/3 Torr. IR (film): 2555 (SH), 2240 (CN). ^{1}H-NMR: 1.77 (*t*, *J* = 9.3, 1 H); 1.96 (*s*, 3 H); 3.18 (*dd*, *J* = 9.3, 14.2, 1 H); 3.47 (*dd*, *J* = 9.3, 14.2, 1 H); 7.67–7.89 (*m*, 2 H); 8.00–8.23 (*m*, 2 H); 9.21 (*s*, 1 H). ^{13}C-NMR: 25.5 (*q*); 34.1 (*t*); 46.2 (*s*); 120.9 (*s*); 129.0 (*d*); 130.4 (*d*); 130.6 (*d*); 131.3 (*s*); 141.8 (*s*); 142.8 (*d*); 151.8 (*s*). Anal. calc. for $C_{12}H_{11}N_3S$: C 62.85, H 4.83, N 18.32; found: C 62.65, H 4.82, N 18.48.

Methyl 3-Mercapto-2-methyl-2-(quinoxalin-2-yl)propanoate (**8b**): B.p. 185°/2 Torr. IR (film): 2570 (SH), 1735 (C=O). ^{1}H-NMR: 1.61 (*t*, *J* = 8.8, 1 H); 1.86 (*s*, 3 H); 3.38 (*d*, *J* = 8.8, 2 H); 3.77 (*s*, 3 H); 7.55–7.82 (*m*, 2 H); 7.98–8.15 (*m*, 2 H); 8.89 (*s*, 1 H). ^{13}C-NMR: 22.0 (*q*); 32.3 (*t*); 52.5 (*q*); 54.3 (*s*); 128.8 (*d*); 129.2 (*d*); 129.7 (*d*); 129.9 (*d*); 141.0 (*s*); 141.1 (*s*); 144.0 (*d*); 155.5 (*s*); 173.6 (*s*). Anal. calc. for $C_{13}H_{14}N_2O_2S$: C 59.52, H 5.37, N 10.67; found: C 59.79, H 5.43, N 10.68.

2-(Quinoxalin-2-yl)cyclohexane-1-thiol (**8d**): B.p. 145°/2 Torr. IR (film): 2540 (SH). ^{1}H-NMR: 1.33 (*d*, *J* = 7.3, 1 H); 1.14–2.48 (*m*, 8 H); 3.38 (*td*, *J* = 3.4, 11.7, 1 H); 3.87 (*dd*, *J* = 3.4, 7.3, 1 H); 7.48–7.79 (*m*, 2 H); 8.00–8.18 (*m*, 2 H); 8.79 (*s*, 1 H). ^{13}C-NMR: 20.2 (*t*); 23.9 (*t*); 25.4 (*t*); 34.6 (*t*); 41.7 (*d*); 48.0 (*d*); 128.8 (*d*); 128.9 (*d*); 129.0 (*d*); 141.2 (*s*); 141.7 (*s*); 144.6 (*d*); 157.9 (*s*). CI-MS: 235 ([*M* + 1]$^+$), 211. Anal. calc. for $C_{14}H_{16}N_2S$: C 68.82, H 6.60, N 11.46; found: C 68.58, H 6.57, N 11.48.

2-Ethoxy-2-(quinoxalin-2-yl)ethanethiol (**8f**): B.p. 140°/2 Torr. IR (film): 2560 (SH). ^{1}H-NMR: 1.29 (*t*, *J* = 6.8, 3 H); 1.78 (*t*, *J* = 7.8, 1 H); 3.50–3.59 (*m*, 2 H); 3.62 (*dq*, *J* = 2.0, 6.8, 2 H); 4.76 (*t*, *J* = 5.9, 1 H); 7.66–7.83 (*m*, 2 H); 7.99–8.18 (*m*, 2 H); 9.05 (*s*, 1 H). ^{13}C-NMR: 15.2 (*q*); 29.8 (*t*); 65.6 (*t*); 82.5 (*d*); 128.9 (*d*); 129.2 (*d*); 129.6 (*d*); 130.0 (*d*); 141.5 (*s*); 142.0 (*s*); 143.7 (*d*); 155.4 (*s*). Anal. calc. for $C_{12}H_{14}N_2OS$: C 61.51, H 6.02, N 11.95; found: C 61.59, H 5.96, N 11.99.

3-Mercapto-2-methyl-2-(3-methylquinoxalin-2-yl)propanenitrile (**9a**): M.p. 74–75°. IR (KBr): 2570 (SH), 2230 (CN). ^{1}H-NMR: 1.90 (*s*, 3 H); 1.97 (*dd*, *J* = 8.3, 10.3, 1 H); 3.08 (*s*, 3 H); 3.15 (*dd*, *J* = 10.3, 14.2, 1 H); 3.73 (*dd*, *J* = 8.3, 14.2, 1 H); 7.69–7.83 (*m*, 2 H); 7.95–8.08 (*m*, 2 H). ^{13}C-NMR: 24.2 (*q*); 25.0 (*q*); 33.6 (*t*); 45.4 (*s*); 121.2 (*s*); 128.2 (*d*); 128.9 (*d*); 129.6 (*d*); 130.6 (*d*); 139.7 (*s*); 141.1 (*s*); 150.1 (*s*); 152.0 (*s*). Anal. calc. for $C_{13}H_{13}N_3S$: C 64.16, H 5.38, N 17.26; found: C 64.14, H 5.37, N 17.26.

Methyl 3-Mercapto-2-methyl-2-(3-methylquinoxalin-2-yl)propanoate (**9b**): B.p. 155°/Torr. IR (film): 2570 (SH), 1735 (C=O), ^{1}H-NMR: 1.48 (*t*, *J* = 8.8, 1 H); 1.76 (*s*, 3 H); 2.65 (*s*, 3 H); 3.46 (*d*, *J* = 8.8, 2 H); 3.75 (*s*, 3 H); 7.59–7.78 (*m*, 2 H); 7.91–8.08 (*m*, 2 H). ^{13}C-NMR: 21.8 (*q*); 23.2 (*q*); 33.2 (*t*); 52.5 (*q*); 54.2 (*s*); 127.9 (*d*); 128.9 (*d*); 129.7 (*d*); 139.6 (*s*); 140.6 (*s*); 152.2 (*s*); 154.8 (*s*); 174.4 (*s*). Anal. calc. for $C_{14}H_{16}N_2O_2S$: C 60.84, H 5.83, N 10.13; found: C 60.62, H 5.88, N 9.96.

Methyl 3-Mercapto-2-(3-methylquinoxalin-2-yl)propanoate (**9c**): B.p. 150°/2 Torr. IR (film): 2570 (SH), 1740 (C=O). ^{1}H-NMR: 1.71 (*t*, *J* = 8.8, 1 H); 2.85 (*s*, 3 H); 3.37 (br. *t*, 2 H); 3.69 (*s*, 3 H); 4.42 (*t*, *J* = 7.3, 1 H); 7.56–7.78 (*m*, 2 H); 7.93–8.09 (*m*, 2 H). ^{13}C-NMR: 22.8 (*q*); 24.8 (*t*); 52.4 (*q*); 53.4 (*d*); 128.2 (*d*); 128.9 (*d*); 129.0 (*d*); 129.8 (*d*); 140.7 (*s*); 141.0 (*s*); 151.4 (*s*); 153.1 (*s*); 170.6 (*s*). Anal. calc. for $C_{13}H_{14}N_2O_2S$: C 59.52, H 5.33, N 10.67; found: C 59.25, H 5.53, N 10.34.

2-(3-Methylquinoxalin-2-yl)cyclohexane-1-thiol (**9d**): M.p. 101–102°. IR (KBr): 2555 (SH). ^{1}H-NMR: 1.25–2.62 (*m*, 8 H); 1.60 (*d*, *J* = 5.9, 1 H); 2.75 (*s*, 3 H); 3.39–3.73 (*m*, 2 H); 7.45–7.71 (*m*, 2 H); 7.88–8.13 (*m*, 2 H). ^{13}C-NMR: 21.1 (*t*); 22.5 (*q*); 24.6 (*t*); 25.2 (*t*); 34.5 (*t*); 40.0 (*d*); 45.3 (*d*); 128.0 (*d*); 128.5 (*d*); 128.9 (*d*); 140.3 (*s*); 140.4 (*s*); 152.3 (*s*); 156.9 (*s*). CI-MS: 259 ([*M* + 1]$^+$), 225. Anal. calc. for $C_{15}H_{18}N_2S$: C 69.74, H 7.02, N 10.85; found: C 69.76, H 7.08, N 10.67.

2-(3-Methylquinoxalin-2-yl)cyclohexane-1-thiol (**9d**): B.p. 145°/2 Torr. IR (film): 2560 (SH). ^{1}H-NMR: 1.52 (*t*, *J* = 8.0, 1 H); 1.58 (*s*, 6 H); 2.91 (*s*, 3 H); 3.15 (*dd*, *J* = 8.0, 18.3, 2 H); 7.56–7.73 (*m*, 2 H); 7.88–8.06 (*m*, 2 H). ^{13}C-NMR: 26.0 (*q*); 26.3 (*q*); 37.7 (*t*); 43.3 (*s*); 127.8 (*d*); 128.7 (*d*); 126.8 (*d*); 129.2 (*d*); 129.6 (*d*); 139.6 (*s*); 140.0 (*s*); 152.4 (*s*); 159.1 (*s*). Anal. calc. for $C_{13}H_{16}N_2S$: C 67.20, H 6.94, N 12.05; found: C 67.16, H 6.91, N 11.96.

2-Ethoxy-2-(3-methylquinoxalin-2-yl)ethanethiol (**9f**): B.p. 150°/2 Torr. IR (film): 2560 (SH). ^{1}H-NMR: 1.24 (*t*, *J* = 6.8, 3 H); 1.74 (*t*, *J* = 8.3, 1 H); 2.87 (*s*, 3 H); 3.15 (*dd*, *J* = 6.8, 8.3, 1 H); 3.57 (*dq*, *J* = 2.0, 6.8, 2 H); 4.88 (*t*, *J* = 6.8, 1 H); 7.60–7.80 (*m*, 2 H); 7.94–8.14 (*m*, 2 H). ^{13}C-NMR: 15.3 (*q*); 22.5 (*q*); 26.8 (*t*); 65.1 (*t*); 82.1 (*s*); 128.2 (*d*); 129.0 (*d*); 129.9 (*d*); 140.5 (*s*); 141.3 (*s*); 153.1 (*s*). Anal. calc. for $C_{13}H_{16}N_2OS$: C 62.87, H 6.49, N 11.28; found: C 62.54, H 6.46, N 11.18.

2-Phenyl-2-(3-methylquinoxalin-2-yl)propanethiol (**9g**): B.p. 185°/2 Torr. IR (film): 2570 (SH). ^{1}H-NMR: 1.29 (*dd*, *J* = 7.8, 9.3, 1 H); 1.92 (*s*, 3 H); 2.19 (*s*, 3 H); 3.29 (*dd*, *J* = 7.8, 13.7, 1 H); 3.63 (*dd*, *J* = 9.3, 13.7, 1 H); 7.05–7.35 (*m*, 5 H); 7.51–7.77 (*m*, 2 H); 7.89–8.15 (*m*, 2 H). ^{13}C-NMR: 22.1 (*q*); 24.2 (*q*); 38.7 (*t*); 50.1 (*s*); 126.8 (*d*); 127.9 (*d*); 128.5 (*d*); 128.8 (*d*); 128.9 (*d*); 129.3 (*d*); 139.3 (*s*); 140.4 (*s*); 144.2 (*s*); 153.5 (*s*); 159.6 (*s*). Anal. calc. for $C_{18}H_{18}N_2S$: C 73.42, H 6.18, N 9.51; found: C 73.28, H 6.14, N 9.52.

2-Phenyl-2-(3-methylquinoxalin-2-yl)ethanethiol (**9h**): B.p. 195°/2 Torr. IR (film): 2560 (SH). ^{1}H-NMR: 1.64 (*dd*, *J* = 8.3, 9.3, 1 H); 2.60 (*s*, 3 H); 2.94–3.23 (*m*, 1 H); 3.58–3.90 (*m*, 1 H); 4.52 (*dd*, *J* = 5.9, 8.3, 1 H); 7.23 (br. *s*, 5 H); 7.60–7.74 (*m*, 2 H); 7.93–8.22 (*m*, 2 H). ^{13}C-NMR: 22.7 (*q*); 29.7 (*t*); 54.0 (*d*); 127.2 (*d*); 128.2 (*d*); 128.3 (*d*); 128.6 (*d*); 128.9 (*s*); 129.2 (*d*); 140.6 (*s*); 140.7 (*s*); 153.6 (*s*); 155.2 (*s*). Anal. calc. for $C_{17}H_{16}N_2S$: C 77.82, H 5.75, N 9.99; found: C 72.63, H 5.75, N 9.90.

3-Mercapto-2-methyl-2-[3-(3-methylbutyl)quinoxalin-2-yl]propanenitrile (**10a**): B.p. 175°/2 Torr. IR (film): 2560 (SH), 2230 (CN). ^{1}H-NMR: 1.05 (*d*, *J* = 6.4, 6 H); 1.16–2.00 (*m*, 3 H); 1.91 (*s*, 3 H); 1.98 (*dd*, *J* = 8.3, 10.3, 1 H); 3.14 (*dd*, *J* = 10.3, 13.7, 1 H); 3.06–3.40 (*m*, 2 H); 3.73 (*dd*, *J* = 8.3, 13.7, 1 H); 7.60–7.85 (*m*, 2 H); 7.91–8.10 (*m*, 2 H). ^{13}C-NMR: 22.4 (*q*); 25.4 (*q*); 28.4 (*d*); 33.6 (*t*); 33.9 (*t*); 38.1 (*t*); 45.1 (*s*); 121.5 (*d*); 128.3 (*d*); 128.8 (*d*); 129.4 (*d*); 130.4 (*d*); 139.4 (*s*); 141.3 (*s*); 149.9 (*s*); 156.1 (*s*). Anal. calc. for $C_{16}H_{21}N_3S$: C 68.19, H 7.06, N 14.03; found: C 68.25, H 7.05, N 14.19.

Methyl 3-Mercapto-2-methyl-2-[3-(3-methylbutyl)quinoxalin-2-yl]propanoate (**10b**): B.p. 170°/2 Torr. IR (film): 2570 (SH), 1730 (C=O). ^{1}H-NMR: 1.00 (*d*, *J* = 6.3, 6 H); 1.59 (*t*, *J* = 8.8, 1 H); 1.76 (*s*, 3 H); 1.59–1.87 (*m*, 3 H); 2.66–2.88 (*m*, 2 H); 2.35 (*dd*, *J* = 2.0, 8.8, 2 H); 3.74 (*s*, 3 H); 7.55–7.77 (*m*, 2 H); 7.91–8.08 (*m*, 2 H). ^{13}C-NMR: 22.5 (*q*); 28.4 (*d*); 32.8 (*t*); 33.4 (*t*); 37.8 (*t*); 52.3 (*q*); 54.0 (*s*); 128.1 (*d*); 128.8 (*d*); 128.9 (*d*); 129.5 (*d*); 139.3 (*s*); 140.8 (*s*); 154.3 (*s*); 156.3 (*s*); 174.6 (*s*). Anal. calc. for $C_{18}H_{24}N_2O_2S$: C 65.02, H 7.27, N 8.42; found: C 65.06, H 7.26, N 8.45.

2-Ethoxy-2-[3-(3-methylbutyl)quinoxalin-2-yl]ethanethiol (**10f**): B.p. 170°/2 Torr. IR (film): 2575 (SH). ^{1}H-NMR: 1.03 (*d*, *J* = 5.9, 6 H); 1.25 (*s*, 3 H); 1.50–1.88 (*m*, 4 H); 3.05–3.26 (*m*, 4 H); 3.59 (*dq*, *J* = 2.0, 6.8, 2 H); 4.92 (*q*, *J* = 6.8, 2 H); 7.59–7.80 (*m*, 2 H); 7.96–8.15 (*m*, 2 H). ^{13}C-NMR: 15.3 (*q*); 22.4 (*q*); 26.9 (*t*); 28.3 (*d*); 32.7 (*t*); 38.0 (*t*); 65.0 (*t*); 81.3 (*d*); 128.8 (*d*); 128.4 (*d*); 129.1 (*d*); 129.7 (*d*); 140.4 (*s*); 141.5 (*s*); 152.7 (*s*); 157.0 (*s*). Anal. calc. for $C_{17}H_{24}N_2OS$: C 67.06, H 7.94, N 9.20; found: C 67.37, H 7.93, N 9.38.

3-Mercapto-2-methyl-2-(3-phenylquinoxalin-2-yl)propanenitrile (**11a**): M.p. 118–119°. IR (KBr): 2525 (SH), 2225 (CN). ^{1}H-NMR: 1.71 (*t*, *J* = 9.3, 1 H); 1.84 (*s*, 3 H); 3.10 (*dd*, *J* = 9.3, 13.7, 1 H); 3.46 (*dd*, *J* = 9.3, 13.7, 1 H); 7.56 (*s*, 5 H); 7.72–7.88 (*m*, 2 H); 8.06–8.24 (*m*, 2 H). ^{13}C-NMR: 26.6 (*q*); 34.8 (*t*); 46.6 (*s*); 121.0 (*d*); 128.5 (*d*); 129.0 (*d*); 129.2 (*d*); 129.5 (*d*); 130.6 (*d*); 131.0 (*d*); 138.4 (*s*); 140.3 (*s*); 140.5 (*s*); 150.0 (*s*); 154.1 (*s*). Anal. calc. for $C_{18}H_{15}N_3S$: C 70.79, H 4.95, N 13.76; found: C 70.91, H 4.90, N 13.63.

Methyl 3-Mercapto-2-methyl-2-(3-phenylquinoxalin-2-yl)propanoate (**11b**): B.p. 190°/2 Torr. IR (film): 2570 (SH), 1725 (C=O). ^{1}H-NMR: 1.32 (*t*, *J* = 8.8, 1 H); 1.68 (*s*, 3 H); 3.24 (*dd*, *J* = 7.8, 8.8, 2 H); 7.32–7.50 (*m*, 4 H); 7.55–7.81 (*m*, 2 H); 8.01–8.23 (*m*, 2 H). Anal. calc. for $C_{19}H_{18}N_2O_2S$: C 67.43, H 5.36, N 8.27; found: C 67.22, H 5.41, N 8.07.

2-(3-Phenylquinoxalin-2-yl)cyclohexane-1-thiol (**11d**): M.p. 113–114°. IR (KBr): 2530 (SH). ^{1}H-NMR: 1.48 (*d*, *J* = 6.3, 1 H); 1.15–2.55 (*m*, 8 H); 3.28–3.42 (*m*, 1 H); 3.65–3.83 (*m*, 1 H); 7.32–7.81 (*m*, 7 H); 8.01–8.22 (*m*, 2 H). ^{13}C-NMR: 21.0 (*t*); 24.4 (*t*); 25.3 (*t*); 34.4 (*t*); 40.3 (*d*); 44.9 (*d*); 128.3 (*d*); 128.5 (*d*); 128.6 (*d*); 128.9 (*d*); 129.2 (*d*); 129.3 (*d*); 139.0 (*s*); 140.1 (*s*); 140.7 (*s*). CI-MS: 321 ($[M + 1]^+$), 287. Anal. calc. for $C_{20}H_{20}N_2S$: C 74.96, H 6.29, N 8.74; found: C 74.82, H 6.33, N 8.48.

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