# Copper-Catalyzed Synthesis of 2*H*-Thiopyran Derivatives from Alkynes, Sulfonyl Azides, Carbon Disulfide, and Malononitrile

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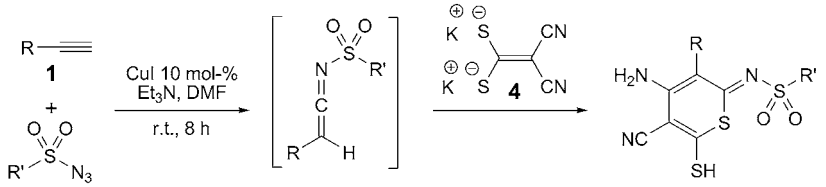
A one-pot synthesis of functionalized thiopyran derivatives *via* a Cu-catalyzed multicomponent reaction of sulfonyl azides, arylacetylenes and dipotassium 2,2-dicyanoethylene-1,1-dithiolate, generated from malononitrile and $CS_2$, has been developed. When alkylacetylenes were used as the terminal alkynes, *N*-(alkanethioyl)-*N*-(2,2-dicyanoethanethioyl)methanesulfonamides were obtained in good yields.

**Introduction.** – Ketenimines [1], as useful intermediates, have attracted much attention due to their diverse chemistry and relative reactivity [2–4]. Perhaps, the most attractive method for generation of ketenimines is the Cu-catalyzed azide–alkyne cycloaddition (*Scheme 1*), established by *Sharpless* and co-workers [5]. This method is well-suited for multicomponent reactions (MCRs) [6]. Herein, we report a simple and efficient procedure for the synthesis of 4-amino-6-[alkyl(aryl)sulfonylimino]-5-aryl-2-sulfanyl-6*H*-thiopyran-3-carbonitriles *via* the Cu-catalyzed four-component coupling reaction of malononitrile, $CS_2$, sulfonyl azides, and terminal alkynes (*Scheme 1*).

*Scheme 1*

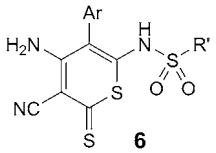



| | R | R' | Yield [%] |
|---|---|---|---|
| **5a** | Ph | 4-Me–$C_6H_4$ | 83 |
| **5b** | Ph | Ph | 87 |
| **5c** | Ph | Me | 79 |
| **5d** | 4-pentyl–$C_6H_4$ | 4-Me–$C_6H_4$ | 75 |
| **5e** | 4-pentyl–$C_6H_4$ | Ph | 72 |
| **5f** | 4-pentyl–$C_6H_4$ | Me | 69 |

**Results and Discussion.** – The ketenimine intermediates **3**, generated *in situ* from arylacetylenes **1** and sulfonyl azides **2**, undergo with dipotassium 2,2-dicyanoethylene-1,1-dithiolate (**4**), a nucleophilic addition/cyclization reaction to afford 4-amino-3-aryl-6-sulfanyl-2-(sulfonylimino)-2*H*-thiopyran-5-carbonitriles **5** in good yields. Several catalysts such as CuI, CuBr, CuCl, $Cu_2O$, and Cu powder were tested, with CuI and CuBr giving the best results. Among several solvents screened, DMF was the best. Thus, the optimized reaction conditions used were 10 mol-% of CuI, 1 mmol of alkyne, 1.2 mmol of azide, 1 mmol of malononitrile, and 1.5 mmol of $CS_2$ in DMF at room temperature. Aryl- and alkylsulfonyl azides reacted efficiently, and the corresponding products were obtained in good yields.

The structures of compound **5a**–**5f** were deduced from IR, $^1$H- and $^{13}$C-NMR, and MS data. The $^1$H-NMR spectrum of **5a** exhibited three *singlet*s for SH ($\delta$ 2.19), Me ($\delta$ 2.69), and $NH_2$ ($\delta$ 4.71), respectively, along with characteristic *multiplet*s for the phenyl groups. The $^{13}$C-NMR spectrum of **5a** exhibited 15 signals in agreement with the proposed structure. The MS of **5a** displayed the molecular-ion peak at *m*/*z* 413.

Although the hemi-thioketone acetal structures **5** are rather unusual, their tautomeric form (*Fig.*), namely, 2-thioxo-2*H*-thiopyrane **6**, is ruled out on the basis of the following observations: *a*) the H-atom of the sulfonamido group in **6** is expected to appear at $\delta$ 7–8, and not at $\delta$ 2.5, *b*) the C=S group in **6** is expected to resonate at *ca.* $\delta$(C) 200. The most downfield signal in the $^{13}$C-NMR spectra of compounds **5** appears, however, at *ca.* 164 ppm.




**6**

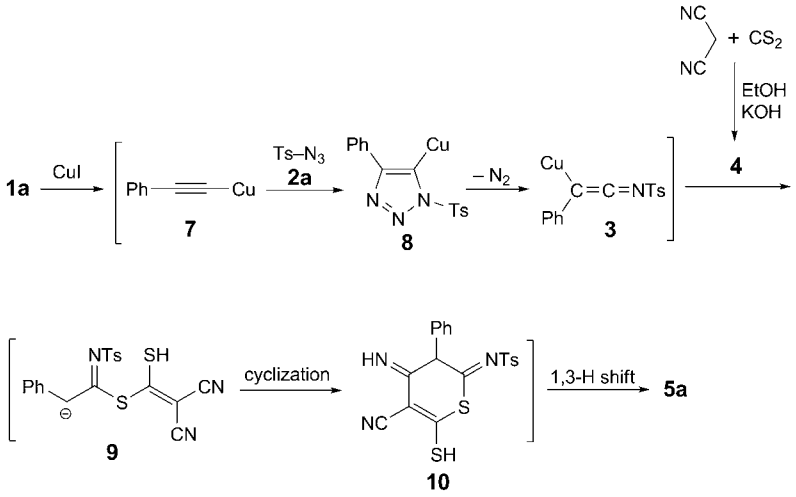
Figure. *Tautomeric form* **6** *of the rather unusual hemi-thioketone acetal structures* **5**

A plausible mechanism for the formation of compound **5a** is proposed in *Scheme 2*. The yellow Cu acetylide **7**, formed from **1** and CuI, undergoes a 1,3-dipolar cycloaddition with sulfonyl azide **2** to generate the triazole derivative **8** [7][8]. This intermediate can then be converted into the ketenimine derivative **3** [5][9], which is attacked by dipotassium 2,2-dicyanoethylene-1,1-dithiolate (**4**) to give intermediate **9**. This intermediate undergoes cyclization to afford **10**, which is converted to **5a** by tautomerization.

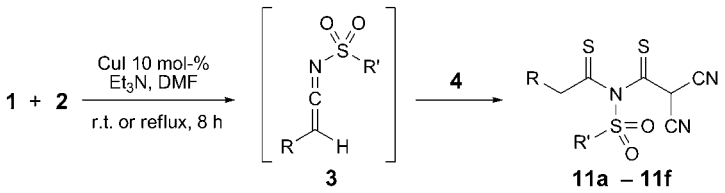
To extend our knowledge on this transformation, we also examined aliphatic terminal acetylenes such as hex-1-yne and pent-1-yne (*Scheme 3*). These reactions afforded the substituted malononitrile derivatives **11**, rather than the thiopyrans **5**, neither at room temperature nor under reflux conditions. This behavior can be attributed to the relatively high reactivity of intermediate **9**, which undergoes protonation rather than cyclization. Compounds **11** are again fully characterized by their IR, and $^1$H- and $^{13}$C-NMR spectra.

Formation of the acyclic product **11** can be explained by protonation of the intermediate **9** to afford **12**, which is then converted to **13** by tautomerization.

*Scheme 2*




*Scheme 3*

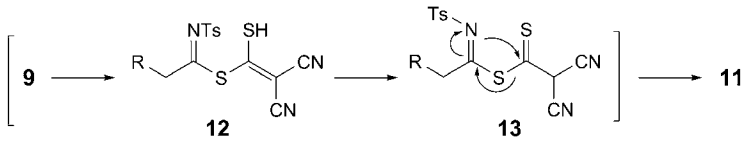



| | R | R′ | Yield [%] |
|---|---|---|---|
| **11a** | Pr | 4-Me–$C_6H_4$ | 72 |
| **11b** | Pr | Ph | 70 |
| **11c** | Pr | Me | 65 |
| **11d** | Bu | 4-Me–$C_6H_4$ | 71 |
| **11e** | Bu | Ph | 73 |
| **11f** | Bu | Me | 65 |

Intermediate **13** is transformed to the substituted malononitrile derivatives **11** (*Scheme 4*) by a well-documented rearrangement [10–12].

In conclusion, ketenimine intermediates generated by addition of Cu acetylides to tosyl azides are trapped by the dipotassium salt of 2,2-dicyanoethylene-1,1-dithiolate. Aromatic acetylenes afforded thiopyran derivatives, but aliphatic acetylenes furnished substituted malononitrile derivatives.

*Scheme 4*



## Experimental Part

*General.* All chemicals were obtained commercially and used without further purification. M.p.: *Electrothermal-9100* apparatus. IR Spectra: *Shimadzu-IR-460* spectrometer; $\tilde{\nu}$ in $cm^{-1}$. $^1H$- and $^{13}C$-NMR Spectra: *Bruker DRX-500 Avance* instrument at 500.1 and 125.7 MHz, resp.; $\delta$ in ppm, $J$ in Hz. MS: *Finnigan-MAT-8430EI-MS* mass spectrometer; at 70 eV; in *m/z* (rel. %). Elemental analyses: *Vario EL III CHNOS* elemental analyzer.

*General Procedure for Preparation of Compounds* **5** *and* **11**. To a mixture of the sulfonyl azide **2** (1.2 mmol), terminal alkyne **1** (1 mmol), CuI (0.1 mmol), and $Et_3N$ (1 mmol) in DMF (2 ml) was slowly added dipotassium 2,2-dicyanoethylene-1,1-dithiolate (**4**; prepared from malononitrile (1 mmol), $CS_2$ (1.5 mmol), and KOH (2 mmol) in EtOH at r.t. in 15 min). The mixture was stirred at r.t. under $N_2$. After completion of the reaction (*ca.* 8 h; TLC (AcOEt/hexane 1:5) monitoring), the mixture was diluted with $CH_2Cl_2$ (2 ml) and aq. $NH_4Cl$ soln. (3 ml), stirred for 30 min, and the layers were separated. The aq. layer was extracted with $CH_2Cl_2$ ($3 \times 3$ ml), and the combined org. fractions were dried ($Na_2SO_4$) and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel (230–400 mesh, *Merck*); hexane/AcOEt 5:1) to give the product.

N-*(4-Amino-5-cyano-3-phenyl-6-sulfanyl-2*H-*thiopyran-2-ylidene)-4-methylbenzenesulfonamide* (**5a**). Yield: 0.34 g (83%). Cream powder. M.p. 102–105°. IR (KBr): 3436, 3371, 2199, 1623, 1319, 1158, 1021. $^1H$-NMR: 2.19 (*s*, SH); 2.69 (*s*, Me); 4.71 (*s*, $NH_2$); 7.05 (*t*, $^3J = 7.4$, 2 arom. H); 7.22 (*d*, $^3J = 7.4$, 2 arom. H); 7.42 (*t*, $^3J = 7.4$, 1 arom. H); 7.93 (*d*, $^3J = 7.9$, 2 arom. H); 8.02 (*d*, $^3J = 7.9$, 2 arom. H). $^{13}C$-NMR: 33.2 (Me); 101.6 (C); 115.1 (CN); 120.1 (C); 123.3 (2 CH); 123.5 (2 CH); 124.8 (C); 126.8 (2 CH); 129.9 (2 CH); 130.8 (CH); 136.0 (C); 136.5 (C); 140.2 (C); 147.4 (C); 163.5 (C). MS: 413 ($M^+$, 2), 397 (10), 321 (30), 259 (16), 155 (100), 91 (70), 77 (54). Anal. calc. for $C_{19}H_{15}N_3O_2S_3$ (413.03): C 55.18, H 3.66, N 10.16; found: C 55.49, H 3.70, N 10.22.

N-*(4-Amino-5-cyano-3-phenyl-6-sulfanyl-2*H-*thiopyran-2-ylidene)benzenesulfonamide* (**5b**). Yield: 0.35 g (87%). Cream powder. M.p. 110–113°. IR (KBr): 3362, 3213, 2163, 1631, 1370, 1105, 1027. $^1H$-NMR: 2.17 (*s*, SH); 4.80 (*s*, $NH_2$); 6.98 (*t*, $^3J = 7.2$, 1 arom. H); 7.32 (*t*, $^3J = 7.2$, 2 arom. H); 7.38 (*d*, $^3J = 7.2$, 2 arom. H); 7.45 (*t*, $^3J = 8.0$, 2 arom. H); 7.65 (*t*, $^3J = 8.0$, 1 arom. H); 7.81 (*d*, $^3J = 8.0$, 2 arom. H). $^{13}C$-NMR: 102.0 (C); 115.6 (CN); 119.3 (C); 122.1 (2 CH); 123.1 (2 CH); 128.5 (CH); 128.8 (2 CH); 129.4 (CH); 129.8 (2 CH); 131.0 (C); 131.9 (C); 143.4 (C); 148.5 (C); 164.6 (C). MS: 399 ($M^+$, 1), 383 (6), 321 (10), 259 (18), 141 (100), 115 (48), 77 (52). Anal. calc. for $C_{18}H_{13}N_3O_2S_3$ (399.02): C 54.11, H 3.28, N 10.52; found: C 54.43, H 3.35, N 10.41.

N-*(4-Amino-5-cyano-3-phenyl-6-sulfanyl-2*H-*thiopyran-2-ylidene)methanesulfonamide* (**5c**). Yield: 0.27 g (79%). Cream powder. M.p. 85–89°. IR (KBr): 3360, 3214, 2169, 1632, 1373, 1105, 1026. $^1H$-NMR: 2.15 (*s*, SH); 2.50 (*s*, Me); 4.70 (*s*, $NH_2$); 7.58 (*t*, $^3J = 7.3$, 1 arom. H); 7.79 (*t*, $^3J = 7.3$, 2 arom. H); 7.87 (*d*, $^3J = 7.3$, 2 arom. H). $^{13}C$-NMR: 29.6 (Me); 101.5 (C); 115.5 (CN); 120.0 (C); 128.2 (2 CH); 128.8 (2 CH); 133.0 (CH); 135.6 (C); 140.5 (C); 147.5 (C); 164.5 (C). MS: 337 ($M^+$, 2), 321 (8), 259 (11), 115 (34), 79 (100), 77 (70). Anal. calc. for $C_{13}H_{11}N_3O_2S_3$ (337.02): C 46.27, H 3.29, N 12.45; found: C 46.52, H 3.35, N 12.37.

N-*[4-Amino-5-cyano-3-(4-pentylphenyl)-6-sulfanyl-2*H-*thiopyran-2-ylidene]-4-methylbenzenesulfonamide* (**5d**). Yield: 0.36 g (75%). Pale-yellow oil. IR (KBr): 3430, 3361, 2198, 1620, 1481, 1310, 1151, 1029. $^1H$-NMR: 0.93 (*t*, $^3J = 6.8$, Me); 1.36–1.48 (*m*, 3 $CH_2$); 2.18 (*s*, SH); 2.65 (*t*, $^3J = 6.8$, $CH_2$); 2.70 (*s*, Me); 4.69 (*s*, $NH_2$); 7.27 (*d*, $^3J = 7.3$, 2 arom. H); 7.40 (*d*, $^3J = 7.3$, 2 arom. H); 7.83 (*d*, $^3J = 7.8$, 2 arom. H); 8.00 (*d*, $^3J = 7.8$, 2 arom. H). $^{13}C$-NMR: 14.0 (Me); 22.2 ($CH_2$); 30.0 (2 $CH_2$); 34.2 ($CH_2$); 35.0 (Me); 102.3 (C); 115.4 (CN); 119.9 (C); 123.0 (2 CH); 123.8 (2 CH); 124.8 (C); 126.0 (2 CH); 129.1 (2 CH); 131.9 (C); 134.4 (C); 135.9 (C); 143.7 (C); 149.2 (C); 164.6 (C). MS: 483 ($M^+$, 1), 467 (7), 369 (20), 155 (100), 147 (22), 91 (70), 71 (50). Anal. calc. for $C_{24}H_{25}N_3O_2S_3$ (483.11): C 59.60, H 5.21, N 8.69; found: C 59.29, H 5.30, N 8.76.

N-*[4-Amino-5-cyano-3-(4-pentylphenyl)-6-sulfanyl-2*H-*thiopyran-2-ylidene]benzenesulfonamide* (**5e**). Yield: 0.34 g (72%). Pale-yellow oil. IR (KBr): 3359, 3232, 2173, 1634, 1374, 1102, 1026. $^1H$-NMR: 0.95 (*t*, $^3J = 6.9$, Me); 1.35–1.49 (*m*, 3 $CH_2$); 2.18 (*s*, SH); 2.66 (*t*, $^3J = 6.9$, $CH_2$); 4.68 (*s*, $NH_2$); 7.20 (*d*, $^3J = 7.3$, 2 arom. H); 7.34 (*d*, $^3J = 7.3$, 2 arom. H); 7.42 (*t*, $^3J = 7.9$, 2 arom. H); 7.60 (*t*, $^3J = 7.9$, 1 arom. H); 7.80 (*d*, $^3J = 7.9$, 2 arom. H). $^{13}C$-NMR: 14.4 (Me); 21.2 ($CH_2$); 30.8 (2 $CH_2$); 34.7 ($CH_2$); 102.2 (C); 115.0

(CN); 119.8 (C); 123.6 (2 CH); 123.9 (2 CH); 124.6 (C); 126.6 (2 CH); 129.9 (2 CH); 132.2 (CH); 134.8 (C); 135.8 (C); 144.7 (C); 148.2 (C); 163.3 (C). MS: 469 ($M^+$, 1), 453 (7), 321 (22), 147 (20), 141 (100), 77 (63), 71 (55). Anal. calc. for $C_{23}H_{23}N_3O_2S_3$ (469.09): C 58.82, H 4.94, N 8.95; found: C 58.51, H 4.88, N 8.89.

N-*[4-Amino-5-cyano-3-(4-pentylphenyl)-6-sulfanyl-2*H-*thiopyran-2-ylidene]methanesulfonamide* (**5f**). Yield: 0.28 g (69%). Pale-yellow oil. IR (KBr): 3361, 3213, 2170, 1630, 1372, 1100, 1022. $^1$H-NMR: 0.92 (*t*, $^3J$ = 6.8, Me); 1.32 – 1.47 (*m*, 6 H, $CH_2$); 2.17 (*s*, SH); 2.51 (*s*, Me); 2.64 (*t*, $^3J$ = 6.8, $CH_2$); 4.69 (*s*, $NH_2$); 7.22 (*d*, $^3J$ = 7.3, 2 arom. H); 7.35 (*d*, $^3J$ = 7.3, 2 arom. H). $^{13}$C-NMR: 14.2 (Me); 21.5 ($CH_2$); 30.0 (2 $CH_2$); 30.4 (Me); 34.9 ($CH_2$); 102.4 (C); 115.9 (CN); 120.0 (C); 123.5 (2 CH); 123.9 (2 CH); 126.8 (C); 130.2 (C); 143.3 (C); 148.5 (C); 164.3 (C). MS: 407 ($M^+$, 1), 391 (9), 259 (14), 147 (25), 114 (43), 79 (100), 71 (65). Anal. calc. for $C_{18}H_{21}N_3O_2S_3$ (407.08): C 53.04, H 5.19, N 10.31; found: C 53.40, H 5.30, N 10.23.

N-*(2,2-Dicyano-1-thioxoethyl)*-N-*[(4-methylphenyl)sulfonyl]pentanethioamide* (**11a**). Yield: 0.27 g (72%). Pale-yellow oil. IR (KBr): 2209, 2083, 1485, 1362, 1262, 1023. $^1$H-NMR: 0.88 (*t*, $^3J$ = 6.9, Me); 1.26 – 1.31 (*m*, $CH_2$); 1.53 – 1.57 (*m*, $CH_2$); 2.23 (*t*, $^3J$ = 6.9, $CH_2$); 2.69 (*s*, Me); 3.55 (*s*, CH); 7.82 (*d*, $^3J$ = 7.9, 2 arom. H); 7.93 (*d*, $^3J$ = 7.9, 2 arom. H). $^{13}$C-NMR: 14.7 (Me); 19.3 ($CH_2$); 21.7 ($CH_2$); 31.7 ($CH_2$); 33.0 (Me); 42.1 (CH); 114.6 (CN); 115.0 (CN); 126.5 (2 CH); 128.4 (2 CH); 129.5 (C); 129.7 (C); 200.7 (C=S); 204.1 (C=S). MS: 379 ($M^+$, 1), 321 (8), 314 (11), 155 (100), 101 (50), 91 (42), 65 (44), 57 (45). Anal. calc. for $C_{16}H_{17}N_3O_2S_3$ (379.05): C 50.64, H 4.51, N 11.07; found: C 50.37, H 4.60, N 11.16.

N-*(2,2-Dicyano-1-thioxoethyl)*-N-*(phenylsulfonyl)pentanethioamide* (**11b**). Yield: 0.25 g (70%). Pale-yellow oil. IR (KBr): 2208, 2086, 1485, 1361, 1261, 1026. $^1$H-NMR: 0.89 (*t*, $^3J$ = 6.9, Me); 1.22 – 1.29 (*m*, $CH_2$); 1.47 – 1.51 (*m*, $CH_2$); 2.20 (*t*, $^3J$ = 6.9, $CH_2$); 3.57 (*s*, CH); 7.47 (*t*, $^3J$ = 7.9, 2 arom. H); 7.83 (*t*, $^3J$ = 7.9, 1 arom. H); 7.98 (*d*, $^3J$ = 7.9, 2 arom. H). $^{13}$C-NMR: 14.1 (Me); 19.2 ($CH_2$); 22.7 ($CH_2$); 31.6 ($CH_2$); 42.4 (CH); 114.5 (CN); 115.7 (CN); 126.1 (2 CH); 128.7 (2 CH); 128.9 (CH); 130.0 (C); 200.8 (C=S); 203.0 (C=S). MS: 365 ($M^+$, 2), 307 (11), 141 (100), 101 (33), 77 (47), 65 (42), 57 (43). Anal. calc. for $C_{15}H_{15}N_3O_2S_3$ (365.03): C 49.29, H 4.14, N 11.50; found: C 49.52, H 4.21, N 11.42.

N-*(2,2-Dicyano-1-thioxoethyl)*-N-*(methylsulfonyl)pentanethioamide* (**11c**). Yield: 0.20 g (65%). Pale-yellow oil. IR (KBr): 2205, 2094, 1478, 1319, 1252, 1018. $^1$H-NMR: 0.89 (*t*, $^3J$ = 6.9, Me); 1.23 – 1.29 (*m*, $CH_2$); 1.39 – 1.45 (*m*, $CH_2$); 2.24 (*t*, $^3J$ = 6.9, $CH_2$); 2.49 (*s*, Me); 3.58 (*s*, CH). $^{13}$C-NMR: 14.2 (Me); 20.0 ($CH_2$); 23.7 ($CH_2$); 30.5 ($CH_2$); 31.0 (Me); 42.8 (CH); 114.3 (CN); 115.1 (CN); 201.7 (C=S); 204.4 (C=S). MS: 303 ($M^+$, 2), 101 (30), 79 (100), 65 (65), 57 (40). Anal. calc. for $C_{10}H_{13}N_3O_2S_3$ (303.02): C 39.58, H 4.32, N 13.85; found: C 40.00, H 4.38, N 13.77.

N-*(2,2-Dicyano-1-thioxoethyl)*-N-*[(4-methylphenyl)sulfonyl]hexanethioamide* (**11d**). Yield: 0.28 g (71%). Pale-yellow oil. IR (KBr): 2208, 2085, 1568, 1457, 1269, 1019. $^1$H-NMR: 0.90 (*t*, $^3J$ = 6.8, Me); 1.19 – 1.25 (*m*, $CH_2$); 1.33 – 1.40 (*m*, $CH_2$); 1.67 – 1.72 (*m*, $CH_2$); 2.10 (*t*, $^3J$ = 6.8, $CH_2$); 2.65 (*s*, Me); 3.56 (*s*, CH); 7.65 (*d*, $^3J$ = 7.9, 2 arom. H); 7.78 (*d*, $^3J$ = 7.9, 2 arom. H). $^{13}$C-NMR: 14.8 (Me); 19.6 ($CH_2$); 23.0 ($CH_2$); 26.6 ($CH_2$); 30.0 ($CH_2$); 33.5 (Me); 42.5 (CH); 114.4 (CN); 115.7 (CN); 128.2 (2 CH); 128.8 (2 CH); 130.0 (C); 131.1 (C); 200.8 (C=S); 204.0 (C=S). MS: 393 ($M^+$, 2), 155 (100), 91 (60), 71 (76), 65 (35). Anal. calc. for $C_{17}H_{19}N_3O_2S_3$ (393.06): C 51.88, H 4.87, N 10.68; found: C 51.53, H 4.79, N 10.76.

N-*(2,2-Dicyano-1-thioxoethyl)*-N-*(phenylsulfonyl)hexanethioamide* (**11e**). Yield: 0.28 g (73%). Pale-yellow oil. IR (KBr): 2201, 2072, 1514, 1368, 1264, 1023. $^1$H-NMR: 0.88 (*t*, $^3J$ = 6.8, Me); 1.11 – 1.19 (*m*, $CH_2$); 1.20 – 1.29 (*m*, $CH_2$); 1.33 – 1.42 (*m*, $CH_2$); 2.15 (*t*, $^3J$ = 6.8, $CH_2$); 3.54 (*s*, CH); 7.41 (*t*, $^3J$ = 7.9, 2 arom. H); 7.50 (*t*, $^3J$ = 7.9, 1 arom. H); 7.97 (*d*, $^3J$ = 7.9, 2 arom. H). $^{13}$C-NMR: 14.1 (Me); 19.9 ($CH_2$); 23.7 ($CH_2$); 25.8 ($CH_2$); 33.8 ($CH_2$); 43.1 (CH); 114.0 (CN); 115.3 (CN); 127.5 (2 CH); 128.4 (2 CH); 128.6 (CH); 129.1 (C); 201.3 (C=S); 204.4 (C=S). MS: 379 ($M^+$, 3), 307 (10), 141 (26), 115 (100), 71 (70), 65 (35). Anal. calc. for $C_{16}H_{17}N_3O_2S_3$ (379.05): C 50.64, H 4.51, N 11.07; found: C 51.03, H 4.59, N 11.16.

N-*(2,2-Dicyano-1-thioxoethyl)*-N-*(methylsulfonyl)hexanethioamide* (**11f**). Yield: 0.21 g (65%). Pale-yellow oil. IR (KBr): 2205, 2090, 1524, 1446, 1265, 1026. $^1$H-NMR : 0.90 (*t*, $^3J$ = 6.9, Me); 1.22 – 1.27 (*m*, $CH_2$); 1.34 – 1.37 (*m*, $CH_2$); 1.65 – 1.73 (*m*, $CH_2$); 2.38 (*t*, $^3J$ = 6.9, $CH_2$); 2.48 (*s*, Me); 3.58 (*s*, CH). $^{13}$C-NMR: 14.3 (Me); 19.1 ($CH_2$); 23.4 ($CH_2$); 26.8 ($CH_2$); 30.1 ($CH_2$); 31.1 (Me); 42.7 (CH); 114.2 (CN); 115.2 (CN); 201.9 (C=S); 204.8 (C=S). MS: 317 ($M^+$, 1), 115 (17), 79 (100), 71 (40), 65 (33). Anal. calc. for $C_{11}H_{15}N_3O_2S_3$ (317.03): C 41.62, H 4.76, N 13.24; found: C 41.92, H 4.84, N 13.15.

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