Towards Functionalised Quasi-planar Dithiadiazafulvalenes: Synthesis of Various Precursors

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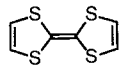
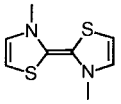
Abstract: The synthesis of 1,2-bis(2-thioxo-2,3-dihydrothiazol-3-yl)benzenes and 1,2-bis(2-selenoxo-2,3-dihydrothiazol-3-yl)benzenes, precursors of quasi-planar dithiadiazafulvalenes, is described. Functionalisation of these derivatives via lithiation is also reported.

Key words: lithiation, bis(thiazole-2(3*H*)-selone), aza-TTF precusors, DTDAF

Very little work has been realised on dithiadiazafulvalenes (DTDAF)[1] compared to the investigations carried out on tetrathiafulvalenes (TTF) derivatives.[2] Several modifications of the TTF framework have been studied with the aim of discovering novel organic materials.[3] Actually, DTDAFs due to their strong donating ability have the disadvantage of being air sensitive except when they are substituted by electron-withdrawing groups.[1] Therefore, the introduction of functional groups on the formed DTDAF core is difficult, as attempts to isolate these donors result in the formation of oxidation products.[4] On the other hand, DTDAFs can be trapped in situ by organic[4] or inorganic acceptors and form molecular materials.[5] In order to functionalise this excellent π-donor and to extend the range of available building blocks, we have prepared several precursors. In this paper we report the synthesis of these derivatives as well as the chemical modifications which have been realised leading to promising precursors of new functionalised quasi-planar DTDAF.



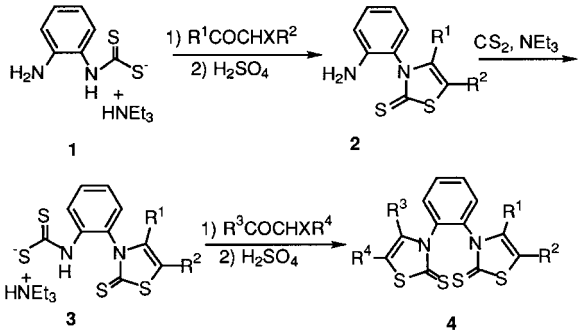
Tetrathiafulvalene (TTF)



Dithiadiazafulvalene (DTDAF)

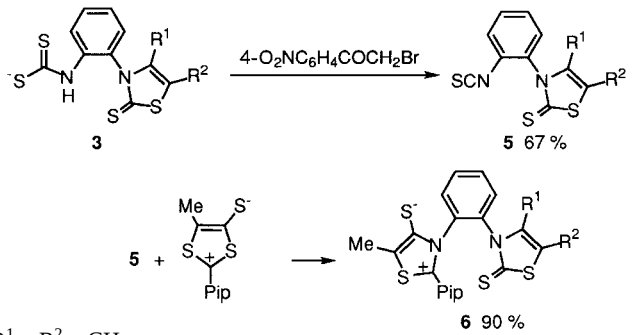
Alkylation of the mono-dithiocarbamate salt **1** with an α-halogenated ketone followed by cyclisation and dehydration with sulfuric acid gives thiazole-2(3*H*)-thione **2**.[6] Dithiocarbamate salt **3** is obtained by refluxing **2** in CS_2 with NEt_3. Then alkylation of dithiocarbamate salt **3** with an α-halogenated ketone followed by acid treatment affords bis(thiazole-2(3*H*)-thione) **4** (Scheme 1). This strategy is interesting as we can either use the same α-halogenated ketone in the second alkylation step for synthesising symmetrically substituted precursors of DTDAF, or we can use a different α-halogenated ketone for preparing the unsymmetrical one.

In the case of electron-withdrawing substituents such as *p*-$NO_2C_6H_4$ **2e** or $COCH_3$ **2d** on the thiazole ring, the remaining amino group is deactivated and the dithiocarbamate salt **3** is not obtained even by modifying the experimental conditions. An interesting reaction occurs when 2-bromo-4'-nitroacetophenone is used in the second alkylation step. The presence of this α-halogenated ketone induces the formation of isothiocyanate **5** (Scheme 2). Aryl isothiocyanates have previously been used in our laboratory to convert mesoionic dithiole derivatives into mesoionic thiazole derivatives,[7] precursors of DTDAF.[8] Taking advantage of this possibility to form aryl isothiocyanate **5** from **3a** in good yields, we applied this methodology and **5** is readily transformed into the mesoionic thiazolium 4-thiolate **6**, by simply refluxing **5** with the mesoionic 5-methyl-1,3-dithiolium 4-thiolate.



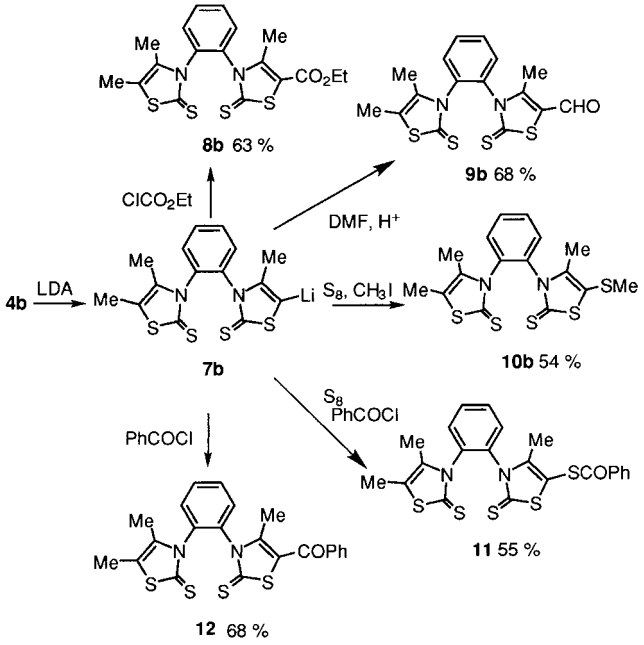
2/4	R^1	R^2	Yield (%) of **2**	R^3	R^4	Yield (%) of **4**
a	CH_3	CH_3	71	CH_3	CH_3	54
b	CH_3	H	76	CH_3	CH_3	56
c	H	H	29	CH_3	CH_3	63
d	CH_3	$COCH_3$	59			
e	H	4-$NO_2C_6H_4$	37			
f	CH_3	H		CH_3	H	56

Scheme 1



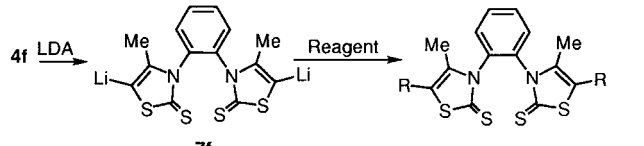
$R^1 = R^2 = CH_3$
Pip = piperidino
Scheme 2

Lithiation of the TTF core is a very useful route for the preparation of a wide variety of mono- and multisubstituted TTF derivatives.[9] In analogy with this synthetic strategy, we have performed metallation of the thiazole-2(3*H*)-thione ring on the 5 position **4b** with butyllithium or lithium diisopropylamide. It is noteworthy that the reactivity of a thiazole ring is similar to the dithiole one towards these strong bases. Then, the corresponding lithium salt **7b** can react with a range of electrophiles.



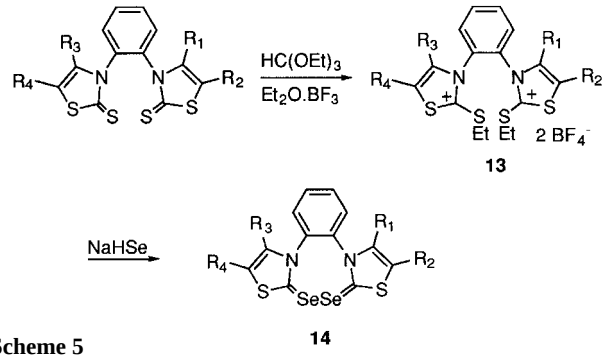
Scheme 3

As shown in Scheme 3, reaction with ethyl chloroformate or dimethylformamide gives the monocarboxylate **8b** and the monocarbaldehyde **9b.** Addition of sulfur to the lithium salt **7b** prior to the addition of the halogenated derivative yields the sulfide **10b**. The thiolate intermediate can also be protected by using benzoyl chloride, the thioester **11** can be stored as a precursor for further work. This strategy was often used in the case of dithiole chemistry such as, for example, the synthesis of 2-thioxo-1,3-dithiole-4,5-dithiolate.[10] Benzoyl chloride reacts also directly with the lithium salt **7b** to yield the ketone derivative **12**. The disubstituted derivatives can also be prepared in a similar way. Metallation of **4f** yields the dilithium salt **7f**, which reacts like the monolithiated intermediate; the synthesis of dicarboxylate **8f**, dicarbaldehyde **9f** and bis(methylthio) **10f** can be performed (Scheme 4).



Reagent	Product	yield (%)
$ClCO_2Et$	R = CO_2Et, **8f**	50
DMF	R = CHO, **9f**	42
S_8,CH_3I	R = SMe, **10f**	24

Scheme 4



Scheme 5

Bis(thiazole-2(3*H*)-thiones) in the presence of phosphorus derivatives do not yield DTDAF by intramolecular coupling. In order to overcome this problem the bis(thiazole-2(3*H*)-thiones) are converted into bis(thiazole-2(3*H*)-selones) **14** (Scheme 5).[5] Unlike thiazole-2(3*H*)-thione, thiazole-2(3*H*)-selone can be coupled in the presence of triethyl phosphite.[1, 5] Lithiation of the thiazole ring can also be realised on the bis(thiazole-2(3*H*)-selone) **14** using the same experimental procedure as described for bis(thiazole-2(3*H*)-thione) **4**. Treatment of bis(thiazole-2(3*H*)-selone) **14** with two equivalents of a trivalent phosphorus derivative gives the corresponding DTDAF, which can be trapped by adding a solution of an acceptor.[5]

In conclusion, we have described the synthesis of various stable precursors of quasi-planar dithiadiazafulvalenes together with the possibility of functionalising these derivatives via the metallation procedure. This methodology in the case of tetrathiafulvalenes chemistry has been, and still is, used for supramolecular assemblies.[11] Compared to their sulfur analogues, DTDAF are super π-donors and these precursors should allow the access to new generation of materials containing DTDAF.

^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz on Bruker AM 300 spectrometer with TMS as internal reference. MS were determined with a Varian Mat 311 spectrometer (Centre de Mesures Physiques de l'Ouest). Mps were measured using a Kofler hot stage apparatus and are uncorrected. Elemental analysis results were obtained from the Laboratoire Central de Microanalyse du CNRS (Lyon). Column chromatography was performed on Merck silica gel 60 (0.040–0.063 mm).

3-(2-Aminophenyl)thiazole-2(3*H*)-thiones 2a–e; General Procedure:

To a suspension of 1,2-phenylenediamine (7.0 g, 64 mmol) in CS_2 (150 mL) was added NEt_3 (17 mL). After stirring for 2 h, the yellow dithiocarbamate salt **1** was filtered off, washed with anhyd Et_2O and used without further purification. To a suspension of **1** (17.0 g, 60 mmol) in MeCN (150 mL) was added α-halogenated ketone $R^1COCHXR^2$ (60 mmol). After stirring for 12 h at r.t., the solvent was removed in vacuo and 98% H_2SO_4 (5 mL) was slowly added under vigorous stirring. The mixture was left stirring for 15 min, then the solution was hydrolysed (H_2O, 100 mL). The mixture was extracted with CH_2Cl_2 (3 × 100 mL), the organic phase was washed with water (3 × 100 mL), dried ($MgSO_4$) and evaporated. Column chromatography of the residue (silica gel, 90 g, CH_2Cl_2) afforded **2**.

2a $R^1 = CH_3$, $R^2 = CH_3$: white powder; yield: 10.07 g (71%); mp 139–140 °C; R_f = 0.22.
^{1}H NMR ($CDCl_3$): δ = 1.85 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 3.72 (s, 2H, NH_2), 6.85–7.31 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 12.36, 13.55, 118.00, 118.61, 119.81, 124.97, 128.90, 131.12, 135.88, 143.43, 187.12.
Anal. Calcd for $C_{11}H_{12}N_2S_2$: C, 55.90; H, 5.12; N, 11.85; S, 27.13. Found C, 56.12; H, 5.18; N, 12.16; S, 27.08.

2b $R^1 = CH_3$, $R^2 = H$; white powder; yield: 10.14 g (76%); mp 184 °C; R_f = 0.22.
^{1}H NMR ($CDCl_3$): δ = 1.96 (s, 3H, CH_3), 3.68 (s, 2H, NH_2), 6.37 (s, 1H, =CH), 6.88–7.33 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 16.28, 107.28, 118.33, 120.28 124.36, 129.21, 131.56, 141.40, 143.69, 189.67.
Anal. Calcd for $C_{10}H_{10}N_2S_2$: C, 54.03; H, 4.53; N, 12.60; S, 28.84 Found C, 54.01; H, 4.53; N, 12.62; S, 28.93.

2c $R^1 = H$, $R^2 = H$; white powder; yield: 4.15 g (29%); mp 85 °C; R_f = 0.25.
^{1}H NMR ($CDCl_3$): δ = 3.91 (s, 2H, NH_2), 6.63 (d, 1H, =CH, J = 4.5 Hz), 6.90 (d, 1H, =CH, J = 4.5 Hz), 6.70–7.19 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 112.50, 117.66, 118.74, 124.68, 127.45, 130.50, 133.11, 142.40, 187.12.

2d $R^1 = CH_3$, $R^2 = COCH_3$; pale brown powder; yield: 9.36 g (59%); mp 197 °C; R_f = 0.12.
^{1}H NMR (DMSO-d_6): δ = 2.24 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 5.26 (s,, 2H, NH_2), 6.62–7.23 (m, 4H, Ar).
^{13}C NMR (DMSO-d_6): δ = 15.20, 29.72, 116.14, 116.26, 121.08, 122.48, 128.91, 130.46, 144.49, 147.71, 188.29, 188.78.
Anal. Calcd for $C_{12}H_{12}ON_2S_2$: C, 54.52; H, 4.58; N, 10.60; S, 24.25. Found C, 54.56; H, 4.60; N, 10.51; S, 24.26.

2e $R^1 = H$, $R^2 = 4\text{-}NO_2C_6H_4$; orange powder; yield: 7.31 g (37%); mp 251 °C; R_f = 0.34.
^{1}H NMR ($CDCl_3$): δ = 5.30 (s, 2H, NH_2), 6.49–6.90 (m, 4H, Ar), 7.48 (s, 1H, =CH), 7.54–8.19 (m, 4H, Ar).
Anal. Calcd for $C_{15}H_{11}O_2N_3S_2$: C, 54.70; H, 3.36; N, 12.77; S, 19.47. Found C, 54.61; H, 3.45; N, 12.67; S, 19.40.

1,2-Bis(2-thioxo-2,3-dihydrothiazol-3-yl)benzene 4a–f; General Procedure:
A suspension of **2** (11 mmol) and NEt_3 (15 mL) in CS_2 (100 mL) was refluxed for 1 h and then stirred at r.t. for 10 h. The yellow dithiocarbamate salt **3** was filtered off, washed with anhyd Et_2O and used without further purification. To a suspension of **3** (10 mmol) in MeCN (150 mL) was added the α-halogenated ketone $R^3COCHXR^4$ (10 mmol). The mixture was stirred overnight. MeCN was removed in vacuo and 98% H_2SO_4 (1 mL) was slowly added under stirring to the resulting oil. After 15 min, water (100 mL) was added and the mixture was extracted with CH_2Cl_2 (2 × 100 mL), the organic phase was washed with water (3 × 100 mL), dried ($MgSO_4$) and evaporated. The residue was column chromatographed (silica gel, 90 g, CH_2Cl_2) to afford **4**.

4a $R^1 = CH_3$, $R^2 = CH_3$, $R^3 = CH_3$, $R^4 = CH_3$; white powder; yield: 1.97 g (54%); mp 234–235 °C; R_f = 0.44.
^{1}H NMR ($CDCl_3$): δ = 2.09 (s, 6H, CH_3), 2.13 (s, 6H, CH_3), 7.30–7.68 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 12.42, 15.85, 119.00, 130.71, 130.97, 136.40, 136.70, 187.36.
Anal. Calcd for $C_{16}H_{16}N_2S_4$: C, 52.72; H, 4.42; N, 7.68; S, 35.18. Found C, 52.84; H, 4.49; N, 7.71; S, 35.03.

4b $R^1 = CH_3$, $R^2 = H$, $R^3 = CH_3$, $R^4 = CH_3$; white powder; yield: 1.96 g (56%); mp 203 °C; R_f = 0.38.
^{1}H NMR ($CDCl_3$): δ = 2.08 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.21 (d, 3H, CH_3, J = 1.0 Hz), 6.31 (q, 1H, =CH, J = 1.0 Hz), 7.31–7.68 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 12.05, 15.46, 17.91, 107.82, 118.80, 130.40, 130.51, 130.55, 130.67, 135.21, 135.98, 136.27, 141.56, 186.96, 189.08.
Anal. Calcd for $C_{15}H_{14}N_2S_4$: C, 51.40; H, 4.03; N, 7.99; S, 36.58. Found C, 51.44; H, 4.06; N, 8.15; S, 36.61.

4c $R^1 = H$, $R^2 = H$, $R^3 = CH_3$, $R^4 = CH_3$; white powder; yield: 2.12 g (63%); mp 178 °C; R_f = 0.50.
^{1}H NMR ($CDCl_3$): δ = 1.97 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 6.54 (d, 1H, =CH, J = 4.7 Hz), 7.71 (d, 1H, =CH, J = 4.7 Hz), 7.35–7.81 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 12.39, 14.27, 111.41, 118.98, 131.23, 131.31, 131.59, 133.23, 134.94, 136.30, 189.07, 189.59.
Anal. Calcd for $C_{14}H_{12}N_2S_4$: C, 49.97; H, 3.59; N, 8.33; S, 38.11. Found C, 50.07; H, 3.43; N, 8.31; S, 38.36.

4f $R^1 = CH_3$, $R^2 = H$, $R^3 = CH_3$, $R^4 = H$; white powder; yield: 1.88 g (56%); mp >260 °C; R_f = 0.40.
^{1}H NMR ($CDCl_3$): δ = 2.22 (d, 6H, CH_3, J = 1.1 Hz), 6.30 (q, 2H, =CH, J = 1.1 Hz), 7.34–7.72 (m, 4H, Ar).
Anal. Calcd for $C_{14}H_{12}N_2S_4$: C, 49.97; H, 3.59; N, 8.33; S, 38.11. Found C, 49.75; H, 3.54; N, 8.31; S, 38.33.

3-(2-Thiocyanatophenyl)thiazole-2(3*H*)-thione (5):
To a suspension of dithiocarbamate salt **3a** (4.3 g, 10.4 mmol) in MeCN (150 mL) was added 2-bromo-4'-nitroacetophenone (2.55 g, 10.4 mmol). The solution was stirred at r.t. for 12 h. MeCN was removed in vacuo, CH_2Cl_2 (100 mL) was added to the mixture and the extract was washed with water (3 × 50 mL), dried ($MgSO_4$) and evaporated. The residue was column chromatographed (silica gel, 80 g, CH_2Cl_2) to afford **5** as a beige powder: yield: 1.93 g (67%); mp 138 °C; R_f = 0.56.
^{1}H NMR ($CDCl_3$): δ = 1.85 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 7.29–7.55 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 12.44, 13.58, 119.19, 126.68, 128.78, 130.47, 131.39, 131.45, 134.93, 135.71, 142.14, 189.05.
Anal. Calcd for $C_{12}H_{10}N_2S_3$: C, 51.77; H, 3.62; N, 10.06; S, 34.55. Found C, 51.51; H, 3.55; N, 10.02; S, 34.46.

3-[2-(4,5-Dimethyl-2-thioxo-2,3-dihydrothiazol-3-yl)phenyl]-5-methyl-2-piperidino-4-sulfidothiazol-2-ium (6):
Isothiocyanate **5** (1.5 g, 5.4 mmol) and mesoionic 5-methyl-2-piperidino-4-sulfido-1,3-dithiol-2-ium (1.25 g, 5.4 mmol) were refluxed in benzene (60 mL) for 36 h. The solvent was removed in vacuo, the solid was filtered and washed with anhyd Et_2O. **6** was obtained as an orange powder; yield: 2.1 g (90%); mp 142 °C.
^{1}H NMR ($CDCl_3$): δ = 1.56 (m, 6H, CH_2), 1.98 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.29 (s. 3H, CH_3), 3.29–3.60 (m, 4H, CH_2), 7.52–8.09 (m, 4H, Ar).
HRMS ($C_{20}H_{23}N_3S_4$, M^+): calcd 433.0775, found 433.0776.

Ethyl 3-[2-(4,5-Dimethyl-2-thioxo-2,3-dihydrothiazol-3-yl)phenyl]-4-methyl-2-thioxo-2,3-dihydrothiazole-5-carboxylate (8b):
To a solution of the 1,2-*bis*(2-thioxo-2,3-dihydrothiazol-3-yl)benzene **4b** (1.0 g, 2.85 mmol) in anhyd THF (100 mL) was added 1.6 M BuLi in hexane (2.7 mL, 4.3 mmol) at –80 °C under argon. After stirring for 0.5 h, ethyl chloroformate (0.5 mL, 4.3 mmol) was added and the solution was stirred for 0.5 h at –80 °C. The temperature was slowly allowed to reach r.t. and the mixture was stirred for 5 h. Solvent was evaporated and CH_2Cl_2 (60 mL) was added to the resulting oil. The organic phase was washed with water (3 × 100mL), dried (Na_2SO_4) and the solvent was evaporated. The residue was column chromatographed (silica gel, 80 g, CH_2Cl_2) to afford **8b** as a yellow powder; yield: 0.76 g (63%); mp 149–150 °C; R_f = 0.48.

^{1}H NMR ($CDCl_3$): δ = 1.33 (t, 3H, CH_3, J = 7.1 Hz), 2.04 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 4.27 (q, 2H, CH_2, J = 7.1 Hz), 7.31–7.71 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 12.44, 14.69, 15.77, 18.26, 61.96, 114.02, 119.51, 130.84, 131.10, 131.16, 131.30, 135.16, 136.32, 136.49, 150.72, 160.24, 187.39, 189.64.
Anal. Calcd for $C_{18}H_{18}N_2O_2S_4$: C, 51.16; H, 4.29; N, 6.63; S, 30.35. Found C, 51.28; H, 4.38; N, 6.49; S, 30.53.

1,2-Bis(5-ethoxycarbonyl-4-methyl-2-thioxo-2,3-dihydrothiazol-3-yl)benzene (8f):
Using the same procedure as for **8b** with **4f** (0.96 g, 2.85 mmol), 1.6 M BuLi in hexane (5.4 mL, 8.6 mmol) and ethyl chloroformate (1 mL, 8.6 mmol) gave **8f** as a yellow powder; yield: 0.68 g (50%); mp 190–191 °C; R_f = 0.58 (CH_2Cl_2).
^{1}H NMR ($CDCl_3$): δ = 1.32 (t, 6H, CH_3, J = 7.1 Hz), 2.48 (s, 6H, CH_3), 4.26 (q, 4H, CH_2, J = 7.1 Hz), 7.32–7.73 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 14.74, 18.71, 62.15, 115.15, 131.37, 131.50, 135.27, 150.34, 160.25, 189.63.
Anal. Calcd for $C_{20}H_{20}N_2O_4S_4$: C, 49.98; H, 4.19; N, 5.83; S, 26.68. Found C, 50.25; H, 4.24; N, 5.82; S, 26.96.

3-[2-(4,5-Dimethyl-2-thioxo-2,3-dihydrothiazol-3-yl)phenyl]-4-methyl-2-thioxo-2,3-dihydrothiazole-5-carbaldehyde (9b):
To a solution of **4b** (1.0 g, 2.85 mmol) in anhyd THF (100 mL) was added 1.6 M BuLi in hexane (2.7 mL, 4.3 mmol) at –80 °C under argon. After stirring for 0.5 h, anhyd DMF (0.3 mL, 4.3 mmol) was added and the solution was stirred for another 0.5 h at –80 °C. The temperature was slowly allowed to reach r.t., the mixture was stirred for 5 h and the solution was hydrolysed with 2 N H_2SO_4 (50 mL). The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 100 mL). The THF solution was concentrated in vacuo and CH_2Cl_2 (2 × 100 mL) was added to the resulting oil. The combined organic phases were washed with water (3 × 100 mL), dried (Na_2SO_4) and the solvent evaporated. The residue was column chromatographed (silica gel, 80 g, CH_2Cl_2) to afford **9b** as a yellow powder; yield: 0.73 g (68%); mp 208 °C; R_f = 0.25.
^{1}H NMR ($CDCl_3$): δ = 2.01 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 7.34–7.74 (m, 4H, Ar), 9.74 (s, 1H, CHO).
^{13}C NMR ($CDCl_3$): δ = 12.55, 15.82, 17.24, 120.12, 125.32, 130.97, 131.13, 131.39, 131.75, 134.49, 136.35, 136.57, 153.16, 179.50, 187.48, 191.26.
Anal. Calcd for $C_{16}H_{14}N_2OS_4$: C, 50.77; H, 3.73; N, 7.40; S, 33.88. Found C, 51.00; H, 3.70; N, 7.43; S, 34.16.

1,2-Bis(5-formyl-4-methyl-2-thioxo-2,3-dihydrothiazol-3-yl)benzene (9f):
Using the same procedure as for **9b** with **4f** (0.96 g, 2.85 mmol), 1.6 M BuLi in hexane (5.4 mL, 8.6 mmol), and DMF (0.6 mL, 8.6 mmol) gave **9f** as a pale yellow powder; yield: 0.47 g (42%); mp >260 °C; R_f = 0.24 (CH_2Cl_2).
^{1}H NMR ($CDCl_3$): δ = 2.53 (s, 6H, CH_3), 7.41–7.83 (m, 4H, Ar), 9.80 (s, 1H, CHO).
Anal. Calcd for $C_{16}H_{12}N_2O_2S_4$: C, 48.96; H, 3.08; N, 7.14; S, 32.67. Found C, 48.74; H, 3.16; N, 7.03; S, 32.78.

1-(4,5-Dimethyl-2-thioxo-2,3-dihydrothiazol-3-yl)-2-(4-methyl-5-methylthio-2-thioxo-2,3-dihydrothiazol-3-yl)benzene (10b):
To a solution of thione **4b** (1.0 g, 2.85 mmol) in anhyd THF (100 mL) was added LDA, prepared from diisopropylamine (0.4 mL, 2.85 mmol) and 2.5 M BuLi in hexane (1.14 mL, 2.85 mmol) at –80 °C under N_2. After stirring for 0.5 h, sulfur (92 mg, 2.85 mmol) was added and the solution was stirred for 0.5 h at –80 °C. The temperature was slowly allowed to rise to –30 °C and iodomethane (0.4 mL, 6.4 mmol) was added. The cooling bath was removed, the temperature was allowed to warm to r.t. and the mixture stirred overnight. Solvent was evaporated and CH_2Cl_2 (150 mL) was added to the resulting oil. The organic solution was washed with water (3 × 100 mL), dried (Na_2SO_4) and the solvent was evaporated. The residue was column chromatographed (silica gel, 40 g, CH_2Cl_2) to afford thione **10b** as a yellow powder; yield: 0.60 g (54%); mp 182 °C; R_f = 0.69.
^{1}H NMR ($CDCl_3$): δ = 2.05 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 7.30–7.69 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 12.49, 15.86, 17.22, 21.02, 116.59, 119.34, 130.87, 130.93, 131.00, 131.09, 136.19, 136.35, 136.54, 145.81, 187.47, 189.81.
Anal. Calcd for $C_{16}H_{16}N_2S_5$: C, 48.45; H, 4.07; N, 7.06; found C, 48.54; H, 4.09; N, 7.09.

1,2-Bis(4-methyl-5-methylthio-2-thioxo-2,3-dihydrothiazol-3-yl)benzene (10f):
Using the same procedure as for **10b** with **4f** (0.96 g, 2.85 mmol), LDA prepared from diisopropylamine (0.8 mL, 5.7 mmol) and 2.5 M BuLi in hexane (2.28 mL, 5.7 mmol), sulfur (185 mg, 5.7 mmol), and iodomethane (0.8 mL, 12.8 mmol) gave **10f** as a yellow powder; yield: 0.29 g (24%); mp 166–167 °C; R_f = 0.80 (CH_2Cl_2).
^{1}H NMR ($CDCl_3$): δ = 2.22 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 7.32–7.69 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 17.17, 21.06, 116.99, 131.00, 131.12, 136.05, 145.58, 189.82.
Anal. Calcd for $C_{16}H_{16}N_2S_6$: C, 44.83; H, 3.76; N, 6.54; S, 44.87; found C, 44.95; H, 3.65; N, 6.52; S, 45.13.

1-(5-Benzoylthio-4-methyl-2-thioxo-2,3-dihydrothiazol-3-yl)-2-(4,5-dimethyl-2-thioxo-2,3-dihydrothiazol-3-yl)benzene (11):
To a solution of thione **4b** (1.0 g, 2.85 mmol) in anhyd THF was added 1.6 M BuLi in hexane (2.7 mL, 4.3 mmol) at –80 °C. After stirring for 0.5 h, sulfur (92 mg, 2.85 mmol) was added and the solution was stirred for 0.5 h at –80 °C. The temperature was slowly allowed to warm to –30 °C and benzoyl chloride (0.5 mL, 4.3 mmol) was added. The temperature was allowed to rise to r.t. and the mixture was stirred overnight. Solvent was evaporated and CH_2Cl_2 (100 mL) was added to the resulting oil. The organic solution was washed with water (3 × 100 mL), dried (Na_2SO_4) and the solvent evaporated. The residue was column chromatographed (silica gel, 80 g, CH_2Cl_2) to afford **11** as a yellow powder; yield: 0.76 g (55%); mp 100 °C (dec); R_f = 0.59.
^{1}H NMR ($CDCl_3$): δ = 2.07 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.23 (s, 3H, CH_3) 7.32–7.99 (m, 9H, Ar).
^{13}C NMR ($CDCl_3$): δ = 12.54, 15.88, 17.56, 106.10, 119.51, 128.28, 129.56, 131.02, 131.24, 134.96, 135.93, 136.07, 136.43, 136.53, 148.99, 187.65, 188.16, 191.07.
Anal. Calcd for $C_{22}H_{18}N_2OS_5$: C, 54.29; H, 3.73; N, 5.76; S, 32.94. Found C, 54.43; H, 3.70; N, 5.72; S, 32.65.

1-(5-Benzoyl-4-methyl-2-thioxo-2,3-dihydrothiazol-3-yl)-2-(4,5-dimethyl-2-thioxo-2,3-dihydrothiazol-3-yl)benzene (12):
To a solution of thione **4b** (1.0 g, 2.85 mmol) in anhyd THF was added 1.6 M BuLi in hexane (2.7 mL, 4.3 mmol) at –80 °C. After stirring for 0.5 h, benzoyl chloride (0.5 mL, 4.3 mmol) was added. The temperature was slowly allowed to warm to r.t., solvent was evaporated and CH_2Cl_2 was added to the resulting oil. The organic solution was washed several times with water, dried (Na_2SO_4) and the solvent was evaporated. The residue was column chromatographed (silica gel, 80 g, CH_2Cl_2) to afford **12** as pale yellow powder; yield: 0.88g (68%); mp 215 °C; R_f = 0.43.
^{1}H NMR ($CDCl_3$): δ = 2.04 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 7.34–7.83 (m, 4H, Ar).

^{13}C NMR ($CDCl_3$): δ = 12.59, 15.90, 19.54, 119.80, 123.32, 129.27, 129.52, 131.03, 131.28, 131.36, 131.48, 133.59, 135.32, 136.59, 136.64, 138.85, 149.35, 187.13, 187.58, 189.69.

Anal. Calcd for $C_{22}H_{18}N_2OS_4$: C, 58.12; H, 3.99; N, 6.16; S, 28.21; found C, 58.18; H, 3.92; N, 5.96; S, 28.42.

1,2-Bis(2-selenoxo-2,3-dihydrothiazol-3-yl)benzene 14; General Procedure:

To a solution of 1,2-bis(2-thioxo-2,3-dihydrothiazol-3-yl)benzene (1.5 mmol) in $CHCl_3$ (20 mL) was added $HC(OEt)_3$ (2 mL, 12 mmol) and $Et_2O{\cdot}BF_3$ (2 mL, 16 mmol). The mixture was refluxed for 15 min and stirred at r.t. overnight. Anhyd Et_2O (25 mL) was added to the solution, the resulting oil was washed several times with Et_2O, and **13** precipitated with the addition of EtOH. The salt was dried under vacuum and used without further purification. A solution of thiazolium salt **13** in anhyd MeCN (15 mL) was slowly added to a mixture of $NaBH_4$ (250 mg, 6.6 mmol) and selenium powder (475 mg, 6 mmol) in degassed abs EtOH (100 mL). After stirring for 30 min, the mixture was poured into 2% AcOH (100 mL). The red precipitate was filtered off and washed with CH_2Cl_2 several times. The aqueous layer was separated from the filtrate and extracted with CH_2Cl_2 (2 × 75 mL). The combined organic phases were washed with water (3 × 100mL), dried ($MgSO_4$) and the solvent was evaporated. The residue was column chromatographed (silica gel, 80 g, CH_2Cl_2) to yield **14** as yellow powder.

14a $R^1 = CH_3$, $R^2 = CH_3$, $R^3 = CH_3$, $R^4 = CH_3$; yield: 0.58 g (84%), mp 252 °C (dec); R_f = 0.26.
^{1}H NMR ($CDCl_3$): δ = 2.13 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 7.37–7.73 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 12.55, 17.33, 123.90, 131.05, 131.38, 136.85, 140.00, 180.24.
Anal. Calcd for $C_{16}H_{16}N_2S_2Se_2$: C, 41.93; H, 3.52; N, 6.11; S, 13.99. Found C, 42.21; H, 3.54; N, 6.26; S, 14.41.

14b $R^1 = CH_3$, $R^2 = H$, $R^3 = CH_3$, $R^4 = CH_3$; yield: 0.30 g (45%), mp 212 °C; R_f = 0.25.
^{1}H NMR ($CDCl_3$): δ = 2.08 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.29 (d, 3H, CH_3, J = 1.0 Hz), 6.51 (d, 1H, =CH, J = 1.0 Hz), 7.34–7.70 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 12.51, 17.06, 19.15, 112.77, 123.76, 130.93, 131.04, 131.16, 131.31, 135.83, 136.63, 139.79, 144.94, 180.07, 182.68.
Anal. Calcd for $C_{15}H_{14}N_2S_2Se_2$: C, 40.55; H, 3.18; N, 6.30. Found C, 40.74; H, 3.23; N, 6.26.

14c $R^1 = H$, $R^2 = H$, $R^3 = CH_3$, $R^4 = CH_3$; yield: 0.54 g (83%); mp 245 °C (dec); R_f = 0.38.
^{1}H NMR ($CDCl_3$): δ = 2.12 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 6.77 (d, 1H, =CH, J = 4.5 Hz), 7.45–7.99 (m, 4H, Ar), 8.16 (d, 1H, =CH, J = 4.5 Hz).
^{13}C NMR ($CDCl_3$): δ = 12.55, 15.10, 115.94, 123.53, 131.44, 131.51, 131.84, 132.17, 135.42, 135.75, 136.61, 139.17, 182.40, 183.25.
Anal. Calcd for $C_{14}H_{12}N_2S_2Se_2$: C, 39.08; H, 2.81; N, 6.51; S, 14.90. Found C, 39.18; H, 2.72; N, 6.50; S, 15.18.

14f $R^1 = CH_3$, $R^2 = H$, $R^3 = CH_3$, $R^4 = H$; yield: 0.28 g (44%), mp 200 °C (dec); R_f = 0.25.
^{1}H NMR ($CDCl_3$): δ = 2.35 (d, 6H, CH_3, J = 1.0 Hz), 6.53 (d, 2H, =CH, J = 1.0 Hz), 7.41–7.77 (m, 4H, Ar).
Anal. Calcd for $C_{14}H_{12}N_2S_2Se_2$: C, 39.08; H, 2.81; N, 6.51; S, 14.90. Found C, 38.53; H, 2.76; N, 6.42; S, 14.50.

14g $R^1 = CH_3$, $R^2 = CO_2Et$, $R^3 = CH_3$, $R^4 = CH_3$; yield: 0.29 g (37%), mp 172 °C; R_f = 0.40.
^{1}H NMR ($CDCl_3$): δ = 1.34 (t, 3H, CH_3, J = 7.1 Hz), 2.14 (s, 3H, CH_3), 2.65 (s, 6H, CH_3), 4.29 (q, 2H, CH_2, J = 7.1 Hz), 7.36–7.76 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 12.61, 14.71, 17.08, 19.45, 62.20, 118.65, 124.26, 131.06, 131.38, 131.41, 131.50, 135.12, 136.89, 139.54, 152.83, 159.97, 180.23, 184.72.
Anal. Calcd for $C_{18}H_{18}N_2O_2S_2Se_2$: C, 41.87; H, 3.51; N, 5.42. Found C, 41.50; H, 3.46; N, 5.48.

14h $R^1 = CH_3$, $R^2 = CO_2Et$, $R^3 = CH_3$, $R^4 = CO_2Et$; yield: 0.68 g (79%); mp 209–210 °C; R_f = 0.43.
^{1}H NMR ($CDCl_3$): δ = 1.35 (t, 6H, CH_3, J = 7.1 Hz), 2.61 (s, 6H, CH_3), 4.30 (q, 4H, CH_2, J = 7.1 Hz), 7.39–7.80 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$): δ = 14.21, 18.81, 61.82, 118.51, 131.05, 131.09, 135.27, 151.94, 159.45, 184.23.
Anal. Calcd for $C_{20}H_{20}N_2O_4S_2Se_2$: C, 41.82; H, 3.51; N, 4.88; S, 11.16. Found C, 41.49; H, 3.42; N, 4.87; S, 11.02.

14i $R^1 = CH_3$, $R^2 = SCH_3$, $R^3 = CH_3$, $R^4 = CH_3$; yield: 0.40 g (54%); mp 200 °C; R_f = 0.50.
^{1}H NMR ($CDCl_3$) δ = 2.10 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 7.33–7.71 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$) δ = 12.59, 17.11, 18.41, 20.77, 121.21, 124.02, 131.05, 131.14, 131.16, 131.29, 136.49, 136.62, 139.73, 148.16, 180.13, 183.57.
Anal. Calcd for $C_{16}H_{16}N_2S_3Se_2$: C, 39.19; H, 3.29; N, 5.71. Found C, 38.69; H, 3.31; N, 5.66.

14j $R^1 = CH_3$, $R^2 = SCH_3$, $R^3 = CH_3$, $R^4 = SCH_3$; yield: 0.20 g (26%); mp 192 °C (dec); R_f = 0.70.
^{1}H NMR ($CDCl_3$) δ = 2.32 (s, 6H, CH_3), 2.33 (s, 6H, CH_3), 7.37–7.73 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$) δ = 18.36, 20.81, 121.50, 131.14, 131.25, 136.37, 147.95, 183.55.
Anal. Calcd for $C_{16}H_{16}N_2S_4Se_2$: C, 36.78; H, 3.08; N, 5.36; S, 24.54; found C, 36.24; H, 2.93; N, 5.27; S, 24.37.

DTDAF; General Procedure:

A suspension of bis(thiazole-2(3*H*)-selone) **14** (0.1 mmol) in degassed toluene (2 mL) and $P(OEt)_3$ (34 µL, 0.2 mmol), freshly distilled, was heated to 110 °C under argon for 30 min. After cooling to r.t., the DTDAF generated in the medium can be trapped in situ by adding a solution of an acceptor.[5]

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