Supporting Information

4H-Dithieno[2,3-b:3',2'-e][1,4]thiazines – synthesis and electronic properties of a novel class of electron rich redox systems

Catherine Dostert\textsuperscript{a}, Claudia Wanstrath\textsuperscript{a}, Prof. Dr. Walter Frank\textsuperscript{b}, and Prof. Dr. Thomas J. J. Müller\textsuperscript{a,*}

\textsuperscript{a}Institut für Organische und Makromolekulare Chemie
\textsuperscript{b}Institut für Anorganische und Strukturchemie
Heinrich-Heine-Universität Düsseldorf
Universitätsstr. 1, D-40225 Düsseldorf, Germany
E-Mail: ThomasJJ.Mueller@uni-duesseldorf.de
Fax: (+)49 (0)211-8114324
1 General considerations

All cross coupling reactions of the oilbath experiments were carried out on oven dried Schlenk glassware using septa and syringes under nitrogen atmosphere. All cross coupling reactions under microwave irradiation were performed in 10 mL microwave vials under nitrogen atmosphere. The dielectric heating was performed with Dicover Labmate microwave reactor by CEM. Toluene was refluxed under nitrogen atmosphere over sodium, destilled and stored in a Schlenk flask over molecular sieve 4 Å under nitrogen atmosphere.

Commercial grade reagents were used as supplied without further purification and were purchased from abcr GmbH & Co. KG, Acros Organics, Alfa Aesar GmbH & Co. KG, Avocado Research Chemicals Ltd., Chempur Feinchemikalien GmbH, Merck KGaA, Riedel-de Haën GmbH, Sigma-Aldrich Chemie GmbH, VWR International GmbH.

The purification of dithienothiazines was performed on silica gel 60 M (0.04-0.063 mm) from Macherey-Nagel GmbH & Co. KG using flash technique under pressure of 2 bar. The crude mixtures were adsorbed on Celite® 545 from Carl Roth GmbH Co. KG before chromatographic purification.

The reaction progress was monitored qualitatively using TLC Silica gel 60 F254 aluminium sheets obtained from Merck KGaA, Darmstadt. The spots were detected with UV light at 254 nm and using iodine chamber.

$^1$H, $^{13}$C, and 135-DEPT $^{13}$C NMR spectra were recorded on Bruker Advanced DRX 500 and Bruker AVIII-300. Acetone-d$_6$, CDCl$_3$, DMSO-d$_6$ with CS$_2$, CD$_2$Cl$_2$ and C$_6$D$_6$ were used as deuterated solvents. The resonances of the solvents were locked as internal standards (acetone-d$_6$: $^1$H δ 2.05, $^{13}$C δ 29.9; CDCl$_3$: $^1$H δ 7.24, $^{13}$C δ 77.2; DMSO-d$_6$: $^1$H δ 2.50, $^{13}$C δ 39.5; CD$_2$Cl$_2$: $^1$H δ 5.32, $^{13}$C δ 54.0; C$_6$D$_6$: $^1$H δ 7.16, $^{13}$C δ 128.4). The multiplicities of the signals were abbreviated as follows:

s: singlet; d: doublet; dd: doublet of doublets; t: triplet; m: multiplet. The type of carbon atoms was determined on the basis of 135-DEPT $^{13}$C NMR spectra. For the description of the $^{13}$C NMR spectra primary carbon atoms are abbreviated with CH$_3$, secondary carbon atoms with CH$_2$, tertiary carbon atoms with CH and quaternary carbon atoms with C$_{quat}$.

EI mass spectra were measured on Finnigan MAT 8200 spectrometer.
IR spectra were obtained on Shimadzu IRAffinity-1 which works with the attenuated total reflection (ATR) method. The intensity of signals is abbreviated as follows: s (strong), m (medium), w (weak).

The melting points (uncorrected) were measured on Reichert Thermovar.

UV/Vis spectra were recorded on 84252 Diode Array spectrometer by Hewlett Packard in dichloromethane at T = 293 K.

Cyclic voltammetry experiments were performed with 263A E&G Princeton Applied Research as potentiostatic instrumentation under argon in dry and degassed dichloromethane at T = 293 K and at scan rates of 100, 250, 500 and 1000 mVs⁻¹.

The electrolyte was tetrabutylammonium hexafluorophosphate at a concentration of c = 0.025 molL⁻¹. The working electrode was a 1 mm platinum disk, the counter electrode was a platinum wire and the reference electrode was a silver/silverchloride electrode filled with aqueous saturated sodium chloride solution. The potentials were calibrated using [FeCp*₂]/[FeCp*₂⁺] as an internal potential standard. The absolute potential of this standard was determined against [FeCp]/[FeCp₂⁺⁺] (E₀⁰⁺⁺ = 450 mV). This procedure provided a value of E₀⁺⁺⁺ = -95 mV for [FeCp*₂]/[FeCp*₂⁺⁺].

Combustion analyses were carried out on Perkin Elmer Series II Analyser 2400 in the micro analytical laboratory of the Institut für Pharmazeutische und Medizinische Chemie der Heinrich-Heine-Universität Düsseldorf.

2 Preparation of starting materials

2.1 Preparation of Bis(phenylsulfonyl)sulfide (6)[2]

41.1 g (250 mmol) of sodium benzenesulfinate were suspended in 300 mL of dry diethyl ether before a solution of 12.9 g (125 mmol) of sulfur dichloride[3] in 50 mL of diethyl ether was added dropwise. The mixture was stirred for 2 h at 40 °C in a preheated oil bath and was allowed to come to room temperature. Afterwards water was added and the insoluble product was filtered off. Recrystallisation from acetone gave 28.3 g (90 mmol, 72 %) of large, colorless crystals.

Mp 130 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.56 (t, \(J = 8.0\) Hz, 4 H), 7.68 (t, \(J = 7.5\) Hz, 2 H), 7.99 (dd, \(J = 8.4\) Hz, 0.9 Hz, 4 H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 128.3 (CH), 129.6 (CH), 135.1 (CH), 144.5 (C\text{quat}). Anal. calcd. for C\(_{12}\)H\(_{10}\)O\(_4\)S\(_3\) (314.4): C 45.96, H 2.92. Found: C 45.71, H 2.92.

Data reported in literature:[4]

Mp 125-130 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.60 (dd, \(J = 7\) Hz, 7.5 Hz, 2 H), 7.72 (t, \(J = 7\) Hz, 1 H), 7.87 (d, \(J = 7.5\) Hz, 1 H), 8.02 (d, \(J = 7.5\) Hz, 1 H).

2.2 Preparation of 3,3’-Dibromo-2,2'-dithienylsulfide (3)\[^4\]

Initially a LDA solution was prepared. For this purpose a solution of 6.48 g (64 mmol) of diisopropylamine in 60 mL of dry toluene was placed under nitrogen atmosphere in a dry Schlenk vessel with septum. Afterwards the solution was cooled to 0 °C and 38.1 mL of \(^6\)BuLi (1.6 M in hexane, 61 mmol) were added before stirring 2 h at 0 °C. During this time another solution of 10.0 g (61.3 mmol) of 3-bromothiophene in 50 mL of dry toluene was prepared and precooled to 0 °C. Then, the LDA solution was transferred to 3-bromothiophene and the mixture was stirred 3 h at 0 °C. After cooling to -78°C, 9.17 g (29.2 mmol) of bis(phenylsulfonyl)sulfide (6) were added and stirring was continued for another 4 h. At -78°C the reaction mixture was quenched with 50 mL of water and the mixture was extracted with diethyl ether (3 x 30 mL). The combined organic layers were dried with anhydrous magnesium sulfate and the desiccant was removed by filtration. After removal of the solvents in vacuum the residue was adsorbed on Celite\textsuperscript{®} and purified chromatographically on silica gel with hexane to give 6.3 g (18 mmol, 62 %) of compound 3 as a colorless solid.

\[
\begin{align*}
\text{Br} & \quad \text{S} & \quad \text{Br} \\
\text{S} & \quad \text{Br} & \quad \text{S} & \quad \text{Br}
\end{align*}
\]

Initial LDA solution preparation:
\[
\begin{align*}
\text{1. LDA} & \quad \text{2. 0.5 \text{aq}.$\text{Li}_2\text{CO}_3$}
\end{align*}
\]

\[
\begin{align*}
\text{Br} & \quad \text{S} & \quad \text{Br} & \quad \text{S} & \quad \text{Br}
\end{align*}
\]

\[
\text{3}
\]

\[
\begin{align*}
\text{Br} & \quad \text{S} & \quad \text{Br} & \quad \text{S} & \quad \text{Br}
\end{align*}
\]

\[
\text{3}
\]

Mp 55.2°C. \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta 6.98 \ (d, J = 5.5 \text{ Hz}, 2 \text{ H}), 7.32 \ (d, J = 5.5 \text{ Hz}, 2 \text{ H})\). \(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta 118.1 \ (C_{\text{quat}}), 130.0 \ (2 \times \text{CH}), 131.0 \ (C_{\text{quat}})\).

EI + MS (70 eV, m/z (%)): 358 ([C\textsubscript{8}H\textsubscript{4}\textsuperscript{32}S\textsuperscript{32}S\textsuperscript{81}Br\textsubscript{2}]\textsuperscript{+}, 11), 356 ([C\textsubscript{8}H\textsubscript{4}\textsuperscript{32}S\textsuperscript{32}S\textsuperscript{79}Br\textsuperscript{81}Br\textsuperscript{+}, 18), 354 ([C\textsubscript{8}H\textsubscript{4}\textsuperscript{32}S\textsuperscript{32}S\textsuperscript{79}Br\textsubscript{2}]\textsuperscript{+}, 9), 198 (13), 197 (11), 196 (100).

Data reported in literature\[^5\]:

Mp 54-55 °C. \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 6.998 \ (\text{AB}, J = 5.6 \text{ Hz}, 2 \text{ H}), 7.346 \ (\text{AB}, J = 5.6 \text{ Hz}, 2 \text{ H})\).

3 Preparation of Dithienothiazines

3 Preparation of N-substituted 4H-Dithieno[2,3-b:3',2'-e][1,4]thiazines

3.1 General procedure

3.1.1 Method A (oil bath experiment)

3 mL Dry toluene were placed under nitrogen atmosphere in a screw-cap Schlenk vessel. Then, 178 mg (0.5 mmol) of 3,3'-dibromo-2,2'-dithienylsulfide (3), 0.58 mmol (1.15 equivs.) of amine (4), 22 mg (7.5 mol%) of bis(dibenzylideneacetone)palladium, 42 mg (15 mol%) of 1,1'-bis(diphenylphosphino)ferrocene, and 144 mg (1.5 mmol) of sodium tert-butoxide were added to the solvent. The mixture was stirred for 30 h at 100 °C in a preheated oil bath and was allowed to come to room temperature. After complete conversion (product monitored by TLC) 20 mL of water were added and the mixture was extracted with dichloromethane (3 x 30 mL). The combined organic layers were dried with anhydrous magnesium sulfate and the desiccant was removed by filtration. After removal of the solvents in vacuum the residue was adsorbed on Celite® and purified chromatographically on silica gel with hexane/ethyl acetate with 2.5 % triethylamine to give N-substituted 4H-dithieno[2,3-b:3',2'-e][1,4]thiazines 5.

3.1.2 Method B (microwave experiment)

178 mg (0.5 mmol) of 3,3'-dibromo-2,2'-dithienylsulfide (3), 0.58 mmol (1.15 equivs.) of amine (4), 22 mg (7.5 mol%) of bis(dibenzylideneacetone)palladium, 42 mg (15 mol%) of 1,1'-bis(diphenylphosphino)ferrocene, 144 mg (1.5 mmol) of sodium tert-butoxide, and 3 mL of toluene were added to a 10 mL microwave vial under nitrogen atmosphere. The mixture was heated at 160 °C (fixed temperature) under microwave irradiation. After that procedure 20 mL of water were added and the mixture was extracted with dichloromethane (3 x 30 mL). The combined organic layers were dried with anhydrous magnesium sulfate and the desiccant was removed by filtration. After removal of the solvents in vacuum the residue was adsorbed on Celite® and purified chromatographically on silica gel with hexane/ethyl acetate with 2.5 % triethylamine to give N-substituted 4H-dithieno[2,3-b:3',2'-e][1,4]thiazines 5.
The experimental details for the synthesis of $N$-substituted $4H$-dithienothiazines $5$ are given in table 1.

**Table 1: Experimental details for the synthesis of $N$-substituted $4H$-dithieno[2,3-$b$:3',2'-e][1,4]thiazines $5$**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine $4$ (0.58 mmol)</th>
<th>$N$-Substituted $4H$-dithieno[2,3-$b$:3',2'-e][1,4]thiazine $5$ (isolated yield)</th>
<th>Chromatographic purification</th>
<th>Recrystallisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$N,N$-Dimethyl-$p$-phenylenediamine (85 %) (Acros Organics) $4a$ 93 mg</td>
<td>$5a$ 123 mg (0.37 mmol) 74 %</td>
<td>$n$-Hexane/EtOAc/NET$_3$ = 40:4:1</td>
<td>$R_f$ ($n$-Hexane/EtOAc 20:1) = 0.26 EtOH (Recryst.)</td>
</tr>
<tr>
<td>2</td>
<td>$p$-Anisidine (Acros Organics) $4b$ 71 mg</td>
<td>$5b$ 149 mg (0.47 mmol) 94 %</td>
<td>$n$-Hexane/NET$_3$ = 40:1</td>
<td>$R_f$ ($n$-Hexane) = 0.09</td>
</tr>
<tr>
<td>3</td>
<td>4-$t$-Butylaniline (Acros Organics) $4c$ 86 mg</td>
<td>$5c$ 108 mg (0.31 mmol) 63 %</td>
<td>$n$-Hexane/NET$_3$ = 40:1</td>
<td>$R_f$ ($n$-Hexane) = 0.2 EtOH (Recryst.)</td>
</tr>
<tr>
<td>4</td>
<td>$p$-Toluidine (Acros Organics) $4d$ 62 mg</td>
<td>$5d$ 92 mg (0.31 mmol) 61 %</td>
<td>$n$-Hexane/NET$_3$ = 40:1</td>
<td>$R_f$ ($n$-Hexane) = 0.17 $n$-Hexane (Recryst.)</td>
</tr>
</tbody>
</table>
### Table 1 (continued).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>N-Substituted 4H-dithieno[2,3-b:3',2'-e][1,4]thiazine 5 (isolated yield)</th>
<th>Chromatographic purification</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Aniline (VWR) (4e) 54 mg</td>
<td>118 mg (0.41 mmol) 82%</td>
<td>n-Hexane/NEt₃ = 40:1 Rₛ (n-Hexane) = 0.26</td>
</tr>
<tr>
<td>6</td>
<td>4-Fluoroaniline (98 %) (Acros Organics) (4f) 66 mg</td>
<td>133 mg (0.44 mmol) 87%</td>
<td>n-Hexane/NEt₃ = 40:1 Rₛ (n-Hexane) = 0.19 n-Hexane (Recryst.)</td>
</tr>
<tr>
<td>7</td>
<td>2-Chloroaniline (98 %) (Sigma Aldrich) (4g) 75 mg</td>
<td>127 mg (0.40 mmol) 79%</td>
<td>n-Hexane/NEt₃ = 40:1 Rₛ (n-Hexane) = 0.18</td>
</tr>
<tr>
<td>8</td>
<td>3-Chloroaniline (98 %) (Merck) (4h) 75 mg</td>
<td>106 mg (0.33 mmol) 66%</td>
<td>n-Hexane/NEt₃ = 40:1 Rₛ (n-Hexane) = 0.23</td>
</tr>
<tr>
<td>9</td>
<td>4-Chloroaniline (98 %) (Acros Organics) (4i) 75 mg</td>
<td>142 mg (0.44 mmol) 88%</td>
<td>n-Hexane/NEt₃ = 40:1 Rₛ (n-Hexane) = 0.24</td>
</tr>
</tbody>
</table>
Table 1 (continued).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>N-Substituted 4H-dithieno[2,3-b:3',2'-e][1,4]thiazine 5 (isolated yield)</th>
<th>Chromatographic purification R&lt;sub&gt;f&lt;/sub&gt; (eluent)</th>
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<tr>
<td>10</td>
<td>4-Bromoaniline (Avocado) (4j) 100 mg</td>
<td>n-Hexane/NEt&lt;sub&gt;3&lt;/sub&gt; = 40:1</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>R&lt;sub&gt;f&lt;/sub&gt; (n-Hexane) = 0.30</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>n-Hexane (Recryst.)</td>
</tr>
<tr>
<td></td>
<td>37 mg (0.10 mmol)</td>
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<tr>
<td>11&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Methyl-4-aminobenzoate (98 %) (Sigma Aldrich) (4k) 89 mg</td>
<td>n-Hexane/EtOAc/NEt&lt;sub&gt;3&lt;/sub&gt; = 40:4:1</td>
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<td></td>
<td></td>
<td></td>
<td>R&lt;sub&gt;f&lt;/sub&gt; (n-Hexane/EtOAc 10:1) = 0.21</td>
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<tr>
<td></td>
<td>143 mg (0.41 mmol)</td>
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<tr>
<td>12</td>
<td>4-Aminobenzotrifluoride (98 %) (abcr) (4l) 95 mg</td>
<td>n-Hexane/NEt&lt;sub&gt;3&lt;/sub&gt; = 40:1</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>R&lt;sub&gt;f&lt;/sub&gt; (n-Hexane) = 0.19</td>
</tr>
<tr>
<td></td>
<td>96 mg (0.27 mmol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13&lt;sup&gt;c,d&lt;/sup&gt;</td>
<td>4-Aminobenzenitrile (98 %) (Sigma Aldrich) (4m) 70 mg</td>
<td>n-Hexane/EtOAc/NEt&lt;sub&gt;3&lt;/sub&gt; = 40:4:1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R&lt;sub&gt;f&lt;/sub&gt; (n-Hexane/EtOAc 10:1) = 0.16</td>
</tr>
<tr>
<td></td>
<td>39 mg (0.12 mmol)</td>
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<tr>
<td></td>
<td>75 mg (0.24 mmol)</td>
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</table>
### Table 1 (continued).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>(N)-Substituted (4H)-dithieno[2,3-b:3',2'-e][1,4]thiazine 5 (isolated yield)</th>
<th>Chromatographic purification</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.58 mmol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14[^{[d]}]</td>
<td>4-Nitroaniline (Acros Organics) (4n) 80 mg</td>
<td><img src="image" alt="Image" /> 5n R_f (eluent) = 0.18 EtOH (Recryst.)</td>
<td>n-Hexane/EtOAc/NEt_3 = 40:4:1</td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>rr</td>
<td>40 mg (0.12 mmol) 24 %[^{[d]}]</td>
</tr>
<tr>
<td>15</td>
<td>n-Butylamine (Riedel-de Haén) (4o) 42 mg</td>
<td><img src="image" alt="Image" /> 5o</td>
<td>n-Hexane/NEt_3 = 40:1 R_f (n-Hexane) = 0.17</td>
</tr>
<tr>
<td>16</td>
<td>Benzylamine (Merck) (4p) 62 mg</td>
<td><img src="image" alt="Image" /> 5p</td>
<td>n-Hexane/EtOAc/NEt_3 = 40:4:1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>116 mg (0.38 mmol) 77 %</td>
</tr>
</tbody>
</table>

[b] Cs_2CO_3 (3 equivs) was used as base.
[c] Conventional heating at 100°C for 30 h.
[d] Dielectric heating at 160 °C for 2 h.
3 Preparation of Dithienothiazines

3.2 Spectroscopic data of compounds 5

3.2.1 4-(4H-Dithieno[2,3-b:3',2'-e][1,4]thiazin-4-yl)-N,N-dimethylaniline (5a)

Using method A 123 mg (0.37 mmol, 74 %) of the desired product were obtained as yellow crystals. Mp 196 °C. 1H NMR (500 MHz, CD2Cl2): δ 2.99 (s, 6 H), 6.06 (d, 3J = 5.5 Hz, 2 H), 6.76-6.81 (m, 2 H), 6.93 (d, 3J = 5.5 Hz, 2 H), 7.17-7.21 (m, 2 H). 13C NMR (125 MHz, CD2Cl2): δ 40.9 (CH3), 101.4 (Cquat), 113.7 (CH), 120.1 (CH), 123.3 (CH), 130.2 (CH), 132.8 (Cquat), 145.8 (Cquat), 150.6 (Cquat). EI + MS (70 eV, m/z (%)): 332 ([C16H14N234S32S2]+, 13), 331 (18), 330 ([C16H14N232S3]+, 82), 314 ([C15H8N234S32S2]+, 23), 313 (24), 312 ([C15H8N232S3]+, 100), 297 (16), 281 (10), 280 (16), 279 (34), 235 (34), 212 ([C9H4N34S32S2]+, 12), 211 (11), 210 ([C9H4N32S3]+, 86), 202 (18), 166 (12), 164 (14), 152 (15), 134 ([C7H4N32S3]+, 28). IR (ATR): ν̃ = 613 cm⁻¹ (w), 625 (s), 644 (w), 700 (s), 708 (s), 762 (m), 804 (m), 822 (s), 849 (w), 947 (w), 993 (m), 1034 (w), 1065 (w), 1099 (w), 1117 (w), 1180 (m), 1223 (m), 1263 (w), 1275 (m), 1354 (m), 1377 (m), 1387 (m), 1443 (w), 1481 (w), 1512 (s), 1555 (w), 1605 (w), 2342 (w), 2359 (w), 2801 (w), 2855 (w), 2882 (w), 2980 (w), 3084 (w), 3103 (w). UV/Vis (CH2Cl2): λmax (ε) 254 nm (35500), 318 (8300). Anal. calcd. for C16H14N2S3 (330.5): C 58.15, H 4.27, N 8.48. Found: C 58.33, H 4.53, N 8.46.
3.2.2 4-(4-Methoxyphenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5b)

Using method A 149 mg (0.47 mmol, 94 %) of the desired product were obtained as yellow crystals. Mp 120 °C. $^1$H NMR (500 MHz, acetone-d$_6$): $\delta$ = 3.87 (s, 3 H), 6.07 (d, $^3$J = 5.5 Hz, 2 H), 7.12-7.08 (m, 2 H), 7.18 (d, $^3$J = 5.5 Hz, 2 H), 7.35-7.30 (m, 2 H). $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta$ = 55.9 (CH$_3$), 102.0 (C$_{quat}$), 116.3 (CH), 120.4 (CH), 124.6 (CH), 131.1 (CH), 137.3 (C$_{quat}$), 145.5 (C$_{quat}$), 160.2 (C$_{quat}$). EI + MS (70 eV, m/z (%)): 319 ([C$_{15}$H$_{11}$ON$_3$S$_3$]$^+$, 14), 318 (19), 317 ([C$_{15}$H$_{11}$ON$_3$S$_3$]$^+$, 100), 285 (12), 284 (31), 210 ([C$_8$H$_4$N$_3$S$_3$]$^+$, 35), 134 ([C$_7$H$_4$N$_3$S]$^+$, 12). IR (ATR): $\tilde{\nu}$ = 615 cm$^{-1}$ (w), 629 (m), 642 (w), 673 (m), 714 (s), 762 (m), 816 (w), 829 (m), 847 (m), 934 (w), 995 (m), 1022 (w), 1036 (m), 1092 (w), 1103 (m), 1165 (m), 1179 (m), 1223 (m), 1234 (m), 1244 (s), 1273 (w), 1300 (w), 1333 (w), 1375 (m), 1389 (m), 1400 (m), 1441 (w), 1456 (w), 1506 (s), 1555 (m), 1888 (w), 2056 (w), 2361 (w), 2774 (w), 2832 (w), 2903 (w), 2945 (w), 3009 (w), 3096 (w). UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (ε) 242 nm (19000), 317 (4400). Anal. calcd. for C$_{15}$H$_{11}$ON$_3$S$_3$ (317.5): C 56.75, H 3.49, N 4.41. Found: C 56.75, H 3.62, N 4.27.
3.2.3 4-(4-(tert-Butyl)phenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5c)

Using method A 108 mg (0.31 mmol, 63 %) of the desired product were obtained as yellow crystals. Mp 210 °C. \(^1\)H NMR (500 MHz, DMSO-d\(_6\)): \(\delta = 1.34\) (s, 9 H), 6.18 (d, \(^3\)J = 5.3 Hz, 2 H), 7.36-7.30 (m, 4 H), 7.53 (d, \(^3\)J = 8.1 Hz, 2 H). \(^{13}\)C NMR (125 MHz, DMSO-d\(_6\)): \(\delta = 31.0\) (C quat), 103.2 (C quat), 119.8 (C quat), 124.8 (CH), 126.88 (CH), 126.9 (CH), 140.6 (C quat), 143.5 (CH), 149.6 (CH). EI + MS (70 eV, m/z (%)): 345 ([C\(_{18}\)H\(_{17}\)N\(_{34}\)S\(_3\)\(_2\)]\(^+\), 16), 344 (22), 343 ([C\(_{18}\)H\(_{17}\)N\(_{32}\)S\(_3\)]\(^+\), 100), 328 ([C\(_{17}\)H\(_{14}\)N\(_{32}\)S\(_3\)]\(^+\), 28), 210 ([C\(_8\)H\(_4\)N\(_{32}\)S\(_3\)]\(^+\), 31), 150 (17), 134 ([C\(_7\)H\(_4\)N\(_{32}\)S\(_3\)]\(^+\), 10). IR (ATR): \(\tilde{\nu} = 627\) cm\(^{-1}\) (m), 644 (w), 704 (s), 719 (m), 770 (w), 800 (m), 829 (m), 856 (m), 924 (w), 997 (m), 1013 (w), 1032 (m), 1096 (w), 1109 (m), 1182 (w), 1202 (w), 1223 (m), 1263 (m), 1279 (m), 1362 (w), 1377 (m), 1391 (m), 1400 (m), 1460 (w), 1472 (w), 1504 (m), 1512 (s), 1557 (m), 1915 (w), 2864 (w), 2901 (w), 2959 (w), 3084 (w), 3094 (w). UV/Vis (CH\(_2\)Cl\(_2\)): \(\lambda_{max} (\epsilon) = 244\) nm (43400), 318 (12200). Anal. calcd. for C\(_{18}\)H\(_{17}\)NS\(_3\) (343.5): C 62.93, H 4.99, N 4.08. Found: C 62.87, N 5.06, H 3.81.
3.2.4 4-(p-Tolyl)-4H-dithieno[2,3-b:3’,2’-e][1,4]thiazine (5d)

Using method A 92 mg (0.31 mmol, 61 %) of the desired product were obtained as yellow crystals. Mp 113 °C. $^1$H NMR (500 MHz, acetone-$d_6$): $\delta = 2.65-2.23$ (m, 3 H), 6.22-6.02 (m, 2 H), 7.24-7.11 (m, 2 H), 7.32-7.23 (m, 2 H), 7.37- 7.34 (m, 2 H). $^{13}$C NMR (125 MHz, acetone-$d_6$): $\delta = 21.2$ (CH$_3$), 103.3 (C$_{quat}$), 120.7 (CH), 124.8 (CH), 129.2 (CH), 131.8 (CH), 138.5 (C$_{quat}$), 142.2 (C$_{quat}$), 145.2 (C$_{quat}$). EI + MS (70 eV, m/z (%)): 303 ([C$_{15}$H$_{11}$N$_3$S$_3$]+, 14), 302 (20), 301 ([C$_{15}$H$_{11}$N$_3$S$_2$]+, 100), 300 (10), 269 (16), 268 (51), 224 (14), 210 ([C$_8$H$_4$NS$_3$]+, 46), 134 ([C$_7$H$_4$N$_2$S]+, 16). IR (ATR): $\tilde{\nu} = 617$ cm$^{-1}$ (m), 644 (m), 675 (m), 702 (s), 750 (m), 812 (m), 824 (m), 854 (w), 941 (w), 993 (m), 1030 (w), 1043 (w), 1101 (m), 1171 (w), 1207 (w), 1267 (m), 1377 (m), 1402 (m), 1447 (w), 1506 (m), 1558 (m), 2357 (w), 2920 (w), 3026 (w), 3092 (w). UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ ($\varepsilon$) 247 nm (21300), 318 (5700). Anal. calcd. for C$_{15}$H$_{11}$N$_3$S$_3$ (301.5): C 59.76, H 3.68, N 4.65. Found: C 59.59, H 3.93, N 4.49.
3.2.5 4-Phenyl-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5e)

![Chemical Structure](image)

C₁₄H₉NS₃ 287.42

Using method A 118 mg (0.41 mmol, 82 %) of the desired product were obtained as yellow crystals. Mp 93 °C. ¹H NMR (500 MHz, acetone-d₆): δ = 6.19 (d, ²J = 5.5 Hz, 2 H), 7.23 (d, ²J = 5.5 Hz, 2 H), 7.38-7.43 (m, 3 H), 7.53-7.57 (m, 2 H). ¹³C NMR (125 MHz, acetone-d₆): δ = 104.9 (C quat), 121.0 (CH), 125.0 (CH), 128.3 (CH), 128.7 (CH), 131.2 (CH), 144.9 (2 x C quat). EI + MS (70 eV, m/z (%)): 287 ([C₁₄H₉NS₃⁺], 6), 198 (30), 197 (16), 196 (100), 153 (13), 152 (23), 151 (10), 120 (14). IR (ATR): ν = 513 cm⁻¹ (m), 521 (w), 533 (w), 606 (m), 629 (m), 683 (s), 687 (s), 722 (m), 795 (m), 835 (m), 853 (m), 916 (w), 993 (s), 1007 (w), 1072 (w), 1098 (m), 1221 (m), 1275 (m), 1375 (m), 1398 (m), 1444 (w), 1487 (s), 1512 (m), 1555 (m), 2852 (w), 2924 (w), 3119 (w). UV/Vis (CH₂Cl₂): λ_max (ε) 248 nm (19400), 319 nm (5650). Anal. calcd. for C₁₄H₉NS₃ (287.4): C 58.50, H 3.16, N 4.87. Found: C 58.55, H 3.33, N 4.59.
3.2.6 4-(4-Fluorophenyl)-4\textit{H}-dithieno[2,3-b:3',2'-e][1,4]thiazine (5f)

\[
\begin{array}{c}
\text{C}_{14}\text{H}_{8}\text{FNS}_{3} \\
305.41
\end{array}
\]

Using method A 133 mg (0.44 mmol, 87 \%) of the desired product were obtained as yellow crystals. Mp 81 °C. \textsuperscript{1}H NMR (500 MHz, acetone-d\textsubscript{6}): \(\delta = 6.15\) (d, \(^3J = 5.5\) Hz, 2 H), 7.23 (d, \(^3J = 5.5\) Hz, 2 H), 7.36-7.29 (m, 2 H), 7.50-7.44 (m, 2 H). \textsuperscript{13}C NMR (125 MHz, acetone-d\textsubscript{6}): \(\delta = 103.9\) (C\textsubscript{quat}), 118.0 (CH, d, \(^2J = 22.8\) Hz), 120.6 (CH), 125.0 (CH), 131.6 (CH, d, \(^3J = 8.8\) Hz), 141.0 (C\textsubscript{quat}, d, \(^4J = 3.1\) Hz), 144.9 (C\textsubscript{quat}), 162.6 (C\textsubscript{quat}, d, \(^1J = 245.5\)). EI + MS (70 eV, m/z (%)): 307 ([C\textsubscript{14}H\textsubscript{8}FN\textsuperscript{34}S\textsuperscript{32}SS\textsuperscript{2}]\textsuperscript{+}, 15), 306 (18), 305 ([C\textsubscript{14}H\textsubscript{8}FN\textsuperscript{32}SS\textsuperscript{3}]\textsuperscript{+}, 100), 273 ([C\textsubscript{14}H\textsubscript{8}FN\textsuperscript{32}SS\textsuperscript{2}]\textsuperscript{+}, 32), 228 (29), 210 ([C\textsubscript{8}H\textsubscript{4}N\textsuperscript{32}SS\textsuperscript{3}]\textsuperscript{+}, 46), 152 (13), 134 ([C\textsubscript{7}H\textsubscript{4}N\textsuperscript{32}S\textsuperscript{1}]\textsuperscript{+}, 17). IR (ATR): \(\tilde{\nu} = 619\) cm\textsuperscript{-1} (m), 640 (m), 673 (m), 698 (s), 708 (s), 762 (m), 772 (m), 831 (s), 849 (m), 883 (w), 937 (m), 957 (w), 968 (w), 993 (m), 1028 (w), 1045 (w), 1086 (m), 1148 (m), 1213 (m), 1242 (w), 1265 (w), 1287 (w), 1339 (w), 1377 (m), 1404 (m), 1464 (w), 1472 (w), 1503 (s), 1514 (m), 1558 (w), 1597 (w), 2330 (w), 2361 (w), 2886 (w), 2930 (w), 2970 (m), 2980 (m), 3647 (w). UV/Vis (CH\textsubscript{2}Cl\textsubscript{2}): \(\lambda_{\text{max}}\) (\(\varepsilon\)) 248 nm (20600), 315 (5500).

Anal. calcd. for C\textsubscript{14}H\textsubscript{8}FNS\textsubscript{3} (305.4): C 55.06, H 2.64, N 4.59. Found: C 54.80, H 2.78, N 4.48.
3.2.7 4-(2-Chlorophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5g)

Using method A 127 mg (0.40 mmol, 79 %) of the desired product were obtained as a yellow oil (solidified upon storage in refrigerator). Mp 66 °C. $^1$H NMR (500 MHz, acetone-d$_6$): δ 5.99 (d, $^3$J = 5.5 Hz, 2 H), 7.21 (d, $^3$J = 5.5 Hz, 2 H), 7.51-7.64 (m, 3 H), 7.67-7.73 (m, 1 H). $^{13}$C NMR (125 MHz, acetone-d$_6$): δ 102.3 (C$_{quat}$), 119.8 (CH), 124.9 (CH), 130.1 (CH), 131.2 (CH), 132.2 (CH), 133.2 (CH), 135.3 (C$_{quat}$), 140.8 (C$_{quat}$), 143.2 (C$_{quat}$). EI + MS (70 eV, m/z (%)): 324 (1), 323 ([M]$^+$, 3), 322 (1), 212 ([C$_8$H$_4$N$_3$S$_2$]$^+$, 1), 211, (1), 201 (m/ z), (C$_8$H$_4$N$_3$S$_2$)$^+$, 7), 100 (12), 57 (100). IR (ATR): $\tilde{\nu}$ = 610 cm$^{-1}$ (m), 625 (m), 673 (s), 694 (s), 706 (s), 750 (s), 791 (m), 812 (w), 853 (m), 869 (w), 993 (s), 1034 (m), 1042 (m), 1070 (m), 1105 (m), 1187 (w), 1223 (m), 1244 (w), 1285 (m); 1377 (m), 1396 (s), 1437 (m), 1472 (m), 1518 (s), 1553 (m), 3105 (w). UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (ε) 248 nm (10700), 316 (2900). Anal. calcd. for C$_{14}$H$_8$ClNS$_3$ (321.9): C 52.24, H 2.51, N 4.35. Found: C 52.01, H 2.77, N 4.26.
Using method A 106 mg (0.33 mmol, 66 %) of the desired product were obtained as a yellow oil. \( ^1H \) NMR (500 MHz, acetone-\( d_6 \)): \( \delta \) 6.49 (d, \( ^3J = 5.5 \) Hz, 2 H), 7.31-7.37 (m, 4 H), 7.39 (t, \( ^3J = 2.0 \) Hz, 1 H), 7.50 (t, \( ^3J = 8.0 \) Hz, 1 H). \( ^{13}C \) NMR (125 MHz, acetone-\( d_6 \)): \( \delta \) 110.9 (C\( _{quat} \)), 122.2 (CH), 124.5 (CH), 125.8 (CH), 125.9 (CH), 126.9 (CH), 132.4 (CH), 135.9 (C\( _{quat} \)), 144.2 (C\( _{quat} \)), 146.7 (C\( _{quat} \)). El + MS (70 eV, m/z (%)): 323 ([C\(_{14}\)H\(_8\)\(^{37}\)Cl\(^{32}\)S\(_3\)]\(^+\), 45), 322 ([C\(_{14}\)H\(_8\)\(^{37}\)Cl\(^{33}\)S\(^{32}\)S\(_2\)]\(^+\), 20), 321 ([C\(_{14}\)H\(_8\)\(^{35}\)Cl\(^{32}\)S\(_3\)]\(^+\), 95), 290 (14), 289 (14), 288 ([C\(_{14}\)H\(_8\)N\(^{33}\)S\(^{32}\)S\(_2\)]\(^+\), 29), 210 ([C\(_8\)H\(_4\)N\(^{32}\)S\(_3\)]\(^+\), 76), 198 ([C\(_8\)H\(_4\)\(^{33}\)S\(^{32}\)S\(_2\)]\(^+\), 14), 197 (17), 196 ([C\(_8\)H\(_4\)\(^{32}\)S\(_3\)]\(^+\), 100), 182 (14), 152 (10), 134 ([C\(_7\)H\(_4\)N\(^{32}\)S\(_2\)]\(^+\), 13), 105 (20). IR (ATR): \( \tilde{\nu} \) = 627 (m), 652 (m), 691 (s), 695 (s), 721 (m), 748 (m), 768 (m), 797 (m), 813 (m), 824 (m), 830 (m), 871 (w), 995 (s), 1022 (w), 1036 (m), 1072 (m), 1090 (m), 1221 (m), 1246 (m), 1265 (m), 1283 (m), 1298 (m), 1375 (s), 1396 (m), 1474 (s), 1516 (s), 1557 (m), 1587 (m), 2324 (w), 2359 (w), 3067 (w), 3103 (w). UV/Vis (CH\(_2\)Cl\(_2\)): \( \lambda_{\text{max}} (\varepsilon) \) 249 nm (19000), 315 (6900). Anal. calcd. for C\(_{14}\)H\(_8\)ClN\(_3\)S\(_3\) (321.9): C 52.24, H 2.51, N 4.35. Found: C 52.30, H 2.77, N 4.22.
3.2.9 4-(4-Chlorophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5i)

Using method A 142 mg (0.44 mmol, 88 %) of the desired product were obtained as yellow crystals. Mp 102 °C. $^1$H NMR (500 MHz, acetone-d$_6$): $\delta$ 6.32 (d, $^3$J = 5.5 Hz, 2 H), 7.29 (d, $^3$J = 5.5 Hz, 2 H), 7.39-7.45 (m, 2 H), 7.52-7.58 (m, 2 H). $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta$ 107.3 (C$_{quat}$), 121.4 (CH), 125.4 (CH), 129.5 (CH), 131.2 (CH), 132.7 (C$_{quat}$), 143.9 (C$_{quat}$), 144.4 (C$_{quat}$). El + MS (70 eV, m/z (%)): 323 (57), 322 (22), 321 ([C$_{14}$H$_8$ClNS$_3$]$^+$, 100), 290 (19), 289 (17), 288 ([C$_{14}$H$_8$ClNS$_2$]$^+$, 41), 212 (10), 211 (12), 210 ([C$_8$H$_4$NS$_3$]$^+$, 84), 166 (12), 134 ([C$_7$H$_4$NS$_2$]$^+$, 28), 106 (26), 105 (11). IR (ATR): $\tilde{\nu}$ = 513 cm$^{-1}$ (m), 518 (m), 534 (w), 617 (m), 638 (w), 658 (w), 692 (s), 719 (m), 756 (m), 802 (w), 827 (s), 849 (m), 941 (w), 993 (s), 1013 (m), 1026 (w), 1086 (m), 1165 (w), 1219 (w), 1263 (m), 1375 (s), 1398 (m), 1464 (w), 1485 (s), 1516 (m), 1557 (m), 1584 (w), 2776 (w), 3100 (w), 3105 (w). UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (Ɛ) 249 nm (21000), 318 (7300). Anal. calcd. for C$_{14}$H$_8$ClNS$_3$ (321.9): C 52.24, H 2.51, N 4.35. Found: C 52.38, H 2.33, N 4.36.
3.2.10 4-(4-Bromophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5j)

Using method A 37 mg (0.10 mmol, 20 %) of the desired product were obtained as yellow crystals. Mp 95 °C. \(^1\)H NMR (500 MHz, acetone-d\(_6\)): \(\delta = 6.63 \ (d, \ ^3J = 5.5 \ Hz, \ 2 \ H), \ 7.30 \ (d, \ ^3J = 5.5 \ Hz, \ 2 \ H), \ 7.37-7.33 \ (m, \ 2 \ H), \ 7.70-7.67 \ (m, \ 2 \ H). \ \ ^{13}\)C NMR (125 MHz, acetone-d\(_6\)): \(\delta = 108.0 \ (C_{quat}), \ 120.4 \ (C_{quat}), \ 121.6 \ (CH), \ 125.6 \ (CH), \ 129.4 \ (CH), \ 134.2 \ (CH), \ 144.4 \ (2 \times C_{quat}). \ \)EI + MS (70 eV, m/z (%)): 369 \([(C_{14}H_9BrN^3S_2S_2)^+, 11]\), 368 (15), 367 \([(C_{14}H_9BrN^3S_3)^+, 84]\), 366 (18), 365 (74), 335 (10), 334 (26), 332 (22), 287 (11), 212 \([(C_8H_4N^3S_2S_2)^+, 11]\), 211 (12), 210 \([(C_8H_4N^3S_3)^+, 100]\), 166 (11), 134 \([(C_7H_6N^3S)^+, 28]\). IR (ATR): \(\tilde{\nu} = 617 \ cm^{-1} \ (m), \ 635 \ (m), \ 694 \ (s), \ 708 \ (s), \ 752 \ (m), \ 795 \ (m), \ 827 \ (s), \ 851 \ (m), \ 941 \ (w), \ 991 \ (m), \ 1011 \ (m), \ 1067 \ (m), \ 1099 \ (m), \ 1124 \ (w), \ 1219 \ (m), \ 1261 \ (m), \ 1375 \ (m), \ 1418 \ (w), \ 1458 \ (w), \ 1483 \ (m), \ 1516 \ (m), \ 1558 \ (m), \ 1724 \ (w), \ 2359 \ (w), \ 2853 \ (w), \ 2924 \ (w), \ 2955 \ (w), \ 3096 \ (w). \ UV/Vis (CH\(_2\)Cl\(_2\)): \(\lambda_{max} (\varepsilon) = 249 \ nm (14300), \ 318 \ nm (4700). \) Anal. calcd. for C\(_{14}\)H\(_9\)BrNS\(_3\) (366.3): C 45.90, H 2.20, N 3.82. Found: C 46.06, H 2.46, N 3.90.
3.2.11 Methyl 4-(4\(H\)-dithieno[2,3-b:3'2'-e][1,4]thiazin-4-y]benzoate (5k)

Using method A and 489 mg (1.5 mmol) caesium carbonate as base 143 mg (0.41 mmol, 82 %) of the desired product were obtained as yellow crystals. Mp 112 °C. \(^1\)H NMR (500 MHz, acetone-\(d_6\)): \(\delta\) 3.86 (s, 3 H), 6.90 (d, \(^3\)J = 5.5 Hz, 2 H), 7.33-7.37 (m, 2 H), 7.49 (d, \(^3\)J = 5.5 Hz, 2 H), 7.98-8.03 (m, 2 H). \(^13\)C NMR (125 MHz, acetone-\(d_6\)): \(\delta\) 52.2 (CH\(_3\)), 119.7 (C\(_{\text{quat}}\)), 120.1 (CH), 124.0 (CH), 125.6 (C\(_{\text{quat}}\)), 127.0 (CH), 132.1 (CH), 143.9 (C\(_{\text{quat}}\)), 149.6 (C\(_{\text{quat}}\)), 166.8 (C=O). El + MS (70 eV, m/z (%)): 347 ([C\(_{16}\)H\(_{11}\)NO\(_2\)S\(_3^2\)S\(_2^2\)]\(+\), 14), 346 (20), 345 ([C\(_{16}\)H\(_{11}\)NO\(_2\)S\(_3^2\)S\(_3^2\)]\(+\), 100); 313 ([C\(_{16}\)H\(_{11}\)NO\(_2\)S\(_2^2\)]\(+\), 11), 312 ([C\(_{16}\)H\(_{10}\)NO\(_2\)S\(_2^2\)]\(+\), 27), 286 (10), 210 ([C\(_8\)H\(_4\)N\(_{32}\)S\(_3^2\)]\(+\), 66), 157 (12), 134 ([C\(_7\)H\(_4\)N\(_{32}\)S\(_3^2\)]\(+\), 20). IR (ATR): \(\tilde{\nu}\) = 621 cm\(^{-1}\) (w), 648 (m), 696 (m), 725 (m), 738 (s), 750 (m), 795 (s), 843 (m), 860 (m), 874 (m), 945 (w), 1018 (w), 1049 (w), 1061 (w), 1074 (w), 1099 (m), 1111 (m), 1146 (s), 1175 (m), 1194 (m), 1238 (m), 1252 (m), 1271 (m), 1285 (w), 1304 (w), 1350 (m), 1373 (m), 1398 (m), 1452 (s), 1485 (w), 1508 (w), 1570 (w), 1585 (w), 1603 (w), 2222 (w), 2845 (w), 2920 (w), 2965 (w). UV/Vis (CH\(_2\)Cl\(_2\)): \(\lambda_{\text{max}}\) (\(\varepsilon\)) 250 nm (13100), 328 nm (15100). Anal. calcd. for C\(_{16}\)H\(_{11}\)NO\(_2\)S\(_3\) (345.5): C 55.63, H 3.21, N 4.05. Found: C 55.71, H 3.32, N 4.00.
3.2.12 4-(4-(Trifluoromethyl)phenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5l)

![Chemical structure](image)

Using method A 96 mg (0.27 mmol, 54 %) of the desired product were obtained as yellow crystals. Mp 109 °C. $^1$H NMR (500 MHz, acetone-$d_6$): $\delta$ 6.85 (d, $^3J = 5.5$ Hz, 2 H), 7.43-7.51 (m, 4 H), 7.72 (d, $^3J = 5.5$ Hz, 2 H). $^{13}$C NMR (75 MHz, acetone-$d_6$): $\delta$ 118.7 (C$_{quat}$), 121.5 (CH), 123.8 (CH), 125.6, (q, $^2J = 32.6$ Hz, C$_{quat}$), 125.7 (q, $^1J = 169.0$ Hz, C$_{quat}$), 126.9 (CH), 127.9 (q, $^3J = 3.8$ Hz, CH), 143.9 (C$_{quat}$), 149.0 (C$_{quat}$).

EI + MS (70 eV, m/z (%)): 357 ([C$_{15}$H$_8$F$_3$N$_3$S$_3$]+, 15), 356 (19), 355 ([C$_{15}$H$_8$F$_3$N$_3$S$_2$]+, 100), 323 ([C$_{15}$H$_7$F$_3$N$_3$S$_2$]+, 11), 322 (26), 278 (11), 210 ([C$_8$H$_4$N$_3$S$_3$]+, 47). IR (ATR): $\tilde{v}$ = 619 cm$^{-1}$ (s), 640 (m), 687 (s), 704 (s), 773 (m), 808 (w), 831 (s), 856 (m), 957 (m), 997 (s), 1016 (m), 1028 (m), 1065 (s), 1099 (s), 1119 (s), 1165 (s), 1223 (w), 1265 (m), 1281 (m), 1319 (s), 1379 (m), 1400 (m), 1514 (s), 1558 (m), 1611 (m), 2928 (w), 2963 (w), 3109 (w). UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (e) 253 nm (30000), 315 nm (15700). Anal. calcd. for C$_{15}$H$_8$F$_3$NS$_3$ (355.4): C 50.69, H 2.27, N 3.94. Found: C 50.82, H 2.42, N 4.06.
3.2.13 4-(4H-Dithieno[2,3-b:3',2'-e][1,4]thiazin-4-yl)benzonitrile (5m)

Using method A 39 mg (0.12 mmol, 25%) of the desired product were obtained as colorless crystals. Using method B 75 mg (0.24 mmol, 48%) of the desired product were obtained as colorless crystals. Mp 184 °C. $^1$H NMR (500 MHz, acetone-d$_6$): $\delta = 7.10$ (d, $^3J = 5.5$ Hz, 2 H), 7.36 (d, $^3J = 8.8$ Hz, 2 H), 7.58 (d, $^3J = 5.5$ Hz, 2 H), 7.71 (d, $^3J = 8.8$ Hz, 2 H). $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta = 105.4$ (C$_{quat}$), 118.4 (CH), 119.7 (C$_{quat}$), 124.3 (C$_{quat}$), 124.8 (CH), 127.7 (CH), 134.6 (CH), 143.4 (C$_{quat}$), 149.4 (C$_{quat}$). E.I + MS (70 eV, m/z (%)): 314 ([C$_{15}$H$_8$N$_2$S$_3^{34}$S$_2$]$^+$, 16), 313 (22), 312 ([C$_{15}$H$_8$N$_2$S$_3^3$]$^+$, 100), 280 ([C$_{15}$H$_8$N$_2$S$_2^{34}$]$^+$, 15), 279 (33), 235 (31), 210 ([C$_8$H$_4$NS$_3^+$, 58), 134 ([C$_7$H$_4$N$_3^{34}$S]$^+$, 18). IR (ATR): $\tilde{\nu} = 611$ cm$^{-1}$ (m), 648 (s), 667 (s), 704 (s), 723 (s), 750 (m), 799 (m), 822 (s), 854 (w), 887 (m), 943 (m), 997 (m), 1043 (w), 1090 (m), 1109 (w), 1138 (m), 1177 (m), 1211 (w), 1248 (w), 1262 (m), 1292 (s), 1373 (m), 1504 (s), 1573 (m), 1595 (m), 1884 (w), 2099 (w), 2210 (m), 2259 (w), 2318 (w), 2355 (w), 2585 (w), 2679 (w), 2716 (w), 2963 (w), 3088 (w), 3107 (w). UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (\varepsilon) 256 nm (17200), 325 (21400). Anal. calcd. for C$_{15}$H$_8$N$_2$S$_3$ (312.4): C 57.66, H 2.58, N 8.97. Found: C 57.66, H 2.59, N 8.84.
3.2.14 4-(4-Nitrophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5n)

Using method B 40 mg (0.12 mmol, 24 %) of the desired product were obtained as orange crystals. Mp 161 °C. $^1$H NMR (500 MHz, acetone-d$_6$): $\delta$ 7.25 (d, $^3J = 5.5$ Hz, 2 H), 7.32-7.37 (m, 2 H), 7.64 (d, $^3J = 5.5$ Hz, 2 H), 8.17-8.22 (m, 2 H). $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta$ 116.1 (CH), 125.2 (CH), 126.5 (CH), 127.1 (Cquat), 128.2 (CH), 142.2 (Cquat), 143.2 (Cquat), 151.1 (Cquat). EI + MS (70 eV, m/z (%)): 334 ([C$_{14}$H$_8$N$_2$O$_2$S$_3$]$,^+$, 14), 333 (18), 332 ([C$_{14}$H$_8$N$_2$O$_2$S$_3$]$^+$, 100), 286 (38), 210 ([C$_8$H$_4$N$_3$S$_3$]$^+$, 34). IR (ATR): $\tilde{\nu}$ = 623 cm$^{-1}$ (m), 642 (s), 658 (m), 691 (s), 714 (m), 731 (s), 745 (s), 795 (m), 835 (s), 862 (w), 881 (w), 957 (m), 1001 (m), 1022 (m), 1076 (m), 1109 (s), 1124 (m), 1188 (m), 1215 (m), 1260 (m), 1296 (s), 1344 (m), 1372 (s), 1441 (m), 1493 (s), 1531 (m), 1589 (m), 1713 (w), 2363 (w), 2924 (w), 2961 (w), 3086 (w), 3105 (w). UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (ε) 249 nm (10500), 299 nm (5000), 391 (10800). Anal. calcd. for C$_{14}$H$_8$N$_2$O$_2$S$_3$ (332.4): C 50.58, H 2.43, N 8.43. Found: C 50.34, H 2.49, N 8.24.
3.2.15 4-Butyl-4\textit{H}-dithieno[2,3-\textit{b}:3',2'-\textit{e}][1,4]thiazine (5o)

\[
\text{C}_{12}\text{H}_{13}\text{NS}_{3}
\]

Using method A 91 mg (0.34 mmol, 68 \%) of the desired product were obtained as a yellow solid. Mp 36 °C. \textit{\textit{H}} NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}): \(\delta\) 0.71 (t, \(^3J = 7.4\ \text{Hz}, 3\ \text{H})\), 1.06-1.13 (m, 2 H), 1.29-1.35 (m, 2 H), 3.06-3.11 (m, 2 H), 6.16 (d, \(^3J = 5.5\ \text{Hz}, 2\ \text{H})\), 6.53 (d, \(^3J = 5.5\ \text{Hz}, 2\ \text{H})\). \textit{\textit{C}} NMR (125 MHz, C\textsubscript{6}D\textsubscript{6}): 14.2 (CH\textsubscript{3}), 20.4 (CH\textsubscript{2}), 30.2 (CH\textsubscript{2}), 49.9 (CH\textsubscript{2}), 105.3 (C\textsubscript{quat}), 118.2 (CH), 124.3 (CH), 145.5 (C\textsubscript{quat}). EI + MS (70 eV, m/z (%)): 267 ([M]\textsuperscript{+}, 28), 212 (10), 210 ([C\textsubscript{8}H\textsubscript{4}N\textsuperscript{32}S\textsubscript{3}]\textsuperscript{+}, 68), 155 (27), 134 ([C\textsubscript{7}H\textsubscript{4}N\textsuperscript{32}S]\textsuperscript{+}, 11), 113 (13), 112 (92), 111 (10), 57 (100). IR (ATR): \(\tilde{\nu} = 628\ \text{cm}^{-1}\) (s), 649 (w), 689 (s), 704 (s), 712 (s), 756 (w), 787 (w), 831 (s), 862 (s), 908 (w), 943 (m), 961 (w), 989 (s), 1037 (w), 1059 (w), 1090 (s), 1194 (m), 1231 (s), 1254 (w), 1315 (w), 1337 (w), 1366 (m), 1374 (m), 1416 (s), 1458 (m), 1467 (m), 1512 (s), 1557 (m), 2857 (w), 2924 (w), 2955 (m), 3028 (w), 3109 (w). UV/Vis (CH\textsubscript{2}Cl\textsubscript{2}): \(\lambda_{\text{max}} (\varepsilon)\) 248 nm (16000), 327 nm (3700). Anal. calcd. for C\textsubscript{12}H\textsubscript{13}NS\textsubscript{3} (267.4): C 53.89, H 4.90, N 5.24. Found: C 53.67, H 4.97, N 5.15.
3.2.16 4-Benzyl-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5p)

Using method A 116 mg (0.38 mmol, 77%) of the desired product were obtained as yellow crystals. Mp 99 °C. $^1$H NMR (500 MHz, acetone-d$_6$): $\delta$ 4.97 (s, 2 H), 6.64 (d, $^3$$J$ = 5.5 Hz, 2 H), 7.23-7.27 (m, 3 H), 7.31-7.38 (m, 4H). $^{13}$C NMR (125 MHz, acetone- d$_6$): $\delta$ 53.5 (CH$_2$), 103.9 (C$_{quat}$), 119.6 (CH), 125.4 (CH), 127.5 (CH), 128.0 (CH), 129.6 (CH), 139.1 (C$_{quat}$), 145.9 (C$_{quat}$). EI + MS (70 eV, m/z (%)): 301 ([M]$^+$, 12), 212 (14), 211 (11.5), 210 ([C$_8$H$_4$NS$_3$]$^+$, 100), 134 ([C$_7$H$_4$NS]$^+$, 12). IR (ATR): $\tilde{\nu}$ = 611 cm$^{-1}$ (m), 619 (m), 687 (s), 737 (s), 787 (w), 833 (m), 862 (w), 920 (w), 953 (m), 1016 (w), 1076 (w), 1096 (w), 1219 (w), 1240 (m), 1306 (w), 1333 (w), 1350 (w), 1381 (w), 1418 (m), 1450 (m), 1493 (m), 1516 (s), 1562 (w), 2361 (w), 2926 (w), 3028 (w), 3090 (w), 3107 (w). UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ ($\varepsilon$) 245 nm (22300), 328 nm (4500).

Anal. calcd. for C$_{15}$H$_{11}$NS$_3$ (301.5): C 59.76, H 3.68, N 4.65. Found: C 59.86, H 3.78, N 4.60.
4 $^1$H and $^{13}$C NMR spectra of N-substituted 4H-dithieno[2,3-b:3',2'-e][1,4]thiazines 5

4.1 4-(4H-Dithieno[2,3-b:3',2'-e][1,4]thiazin-4-yl)-N,N-dimethylaniline (5a)

$^1$H NMR (500 MHz) of 5a (20mg) in CD$_2$Cl$_2$ at 298 K ($\delta$ in ppm).
$^1$H and $^{13}$C NMR spectra of dithienothiazines 5

$^{13}$C NMR (125 MHz) of 5a (20 mg) in CD$_2$Cl$_2$ at 298 K ($\delta$ in ppm).

$^{13}$C DEPT 135-NMR (125 MHz) of 5a (20 mg) in CD$_2$Cl$_2$ at 298 K ($\delta$ in ppm).
4.2 4-(4-Methoxyphenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5b)

$^1$H NMR (500 MHz) of 5b (20mg) in acetone-d$_6$ at 298 K (δ in ppm).
$^1$H und $^{13}$C NMR spectra of dithienothiazines $5$

$^{13}$C NMR (125 MHz) of $5b$ (20 mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).

$^{13}$C DEPT 135-NMR (125 MHz) of $5b$ (20 mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).
4.3 4-(4-(tert-Butyl)phenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5c)

$^1$H NMR (500 MHz) of 5c (20 mg) in DMSO-d$_6$ with 10% CS$_2$ at 298 K ($\delta$ in ppm).
$^1$H und $^{13}$C NMR spectra of dithienothiazines 5

$^{13}$C NMR (125 MHz) of 5c (20 mg) in DMSO-$d_6$ with 10% CS$_2$ at 298 K ($\delta$ in ppm).

$^{13}$C DEPT 135-NMR (125 MHz) of 5c (20 mg) in DMSO-$d_6$ with 10% CS$_2$ at 298 K ($\delta$ in ppm).
4.4 4-(p-Tolyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5d)

\[ \text{\textsuperscript{13}C NMR (125 MHz) of 5d (20 mg) in acetone-d}_6 \text{ at 298 K (\textit{\delta} in ppm).} \]
$^1$H und $^{13}$C NMR spectra of dithienothiazines 5

$^{13}$C NMR (125 MHz) of 5d (20 mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).

$^{13}$C DEPT 135-NMR (125 MHz) of 5d (20 mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).
4.5 4-Phenyl-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5e)

$^{13}$C NMR (125 MHz) of 5e (20 mg) in acetone-$d_6$ at 298 K (δ in ppm).
4 $^1$H und $^{13}$C NMR spectra of dithienothiazines 5

$^{13}$C NMR (125 MHz) of 5e (20 mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).

$^{13}$C DEPT 135-NMR (125 MHz) of 5e (20 mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).
4.6 4-(4-Fluorophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5f)

$^1$H NMR (500 MHz) of 5f (20mg) in acetone-$_d_6$ at 298 K (δ in ppm).

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$^1$H and $^{13}$C NMR spectra of dithienothiazines 5

$^{13}$C NMR (125 MHz) of 5f (20 mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).

$^{13}$C DEPT 135-NMR (125 MHz) of 5f (20 mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).
4.7 4-(2-Chlorophenyl)-4\textsubscript{H}-dithieno[2,3-\textsubscript{b}:3',2'\textsubscript{-e}][1,4]thiazine (5g)

\textsuperscript{1}H NMR (500 MHz) of 5g (20mg) in acetone-d\textsubscript{6} at 298 K (\textdelta in ppm). *Impurities from residual solvents.
$^1$H und $^{13}$C NMR spectra of dithienothiazines 5

$^{13}$C NMR (125 MHz) of 5g (20 mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).

$^{13}$C DEPT 135-NMR (125 MHz) of 5g (20 mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).
4.8 4-(3-Chlorophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5h)

$^1$H NMR (500 MHz) of 5h (20mg) in acetone-d$_6$ at 298 K ($\delta$ in ppm). *Impurities from residual solvents.
$^1$H and $^{13}$C NMR spectra of dithienothiazines 5

$^{13}$C NMR (125 MHz) of 5h (20 mg) in acetone-$d_6$ at 298 K (δ in ppm).

$^{13}$C DEPT 135-NMR (125 MHz) of 5h (20 mg) in acetone-$d_6$ at 298 K (δ in ppm).
4.9 4-(4-Chlorophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5i)

\[\begin{align*}
\text{H} & \quad 7.28 \\
\text{H} & \quad 6.33 \\
\text{H} & \quad 6.32 \\
\text{H} & \quad 6.00 \\
\text{H} & \quad 1.98 \\
\text{H} & \quad 1.99 \\
\text{H} & \quad 2.01 \\
\text{H} & \quad 2.00 \\
\text{H} & \quad 2.05 \\
\text{H} & \quad 0.00 \\
\text{H} & \quad 0.50 \\
\text{H} & \quad 1.00 \\
\text{H} & \quad 1.50 \\
\text{H} & \quad 2.00 \\
\text{H} & \quad 2.50 \\
\text{H} & \quad 3.00 \\
\text{H} & \quad 3.50 \\
\text{H} & \quad 4.00 \\
\text{H} & \quad 4.50 \\
\text{H} & \quad 5.00 \\
\text{H} & \quad 5.50 \\
\text{H} & \quad 6.00 \\
\text{H} & \quad 6.50 \\
\text{H} & \quad 7.00 \\
\text{H} & \quad 7.50 \\
\text{H} & \quad 8.00 \\
\text{H} & \quad 8.50 \\
\text{H} & \quad f_{1} (\text{ppm})
\end{align*}\]

\[\text{H} \text{NMR (500 MHz) of 5i (20mg) in acetone-d}_6 \text{ at 298 K (}\delta\text{ in ppm). *Impurities from residual solvents.}\]
$^1$H und $^{13}$C NMR spectra of dithienothiazines 5.

$^{13}$C NMR (125 MHz) of 5i (20 mg) in acetone-d$_6$ at 298 K ($\delta$ in ppm).

$^{13}$C DEPT 135-NMR (125 MHz) of 5i (20 mg) in acetone-d$_6$ at 298 K ($\delta$ in ppm).
4.10 4-(4-Bromophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5j)

$^1$H NMR (500 MHz) of 5j (20mg) in acetone-d$_6$ at 298 K ($\delta$ in ppm).
$^1$H and $^{13}$C NMR spectra of dithienothiazines 5

$^{13}$C NMR (125 MHz) of 5j (20 mg) in acetone-d$_6$ at 298 K ($\delta$ in ppm).

$^{13}$C DEPT 135-NMR (125 MHz) of 5j (20 mg) in acetone-d$_6$ at 298 K ($\delta$ in ppm).
4.11 Methyl 4-(4H-dithieno[2,3-b:3',2'-e][1,4]thiazin-4-yl)benzoate (5k)

$^1$H NMR (500 MHz) of 5k (20mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).
$^1$H and $^{13}$C NMR spectra of dithienothiazines 5

$^{13}$C NMR (125 MHz) of 5k (20 mg) in acetone-d$_6$ at 298 K ($\delta$ in ppm).

$^{13}$C DEPT 135-NMR (125 MHz) of 5k (20 mg) in acetone-d$_6$ at 298 K ($\delta$ in ppm).
4.12 4-(4-(Trifluoromethyl)phenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5l)

$^1$H NMR (500 MHz) of 5l (20mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).
$^1$H und $^{13}$C NMR spectra of dithienothiazines 5

$^{13}$C NMR (75 MHz) of 5l (20 mg) in acetone-$d_6$ at 298 K (δ in ppm).

$^{13}$C DEPT 135-NMR (75 MHz) of 5l (20 mg) in acetone-$d_6$ at 298 K (δ in ppm).
4.13 4-(4H-Dithieno[2,3-b:3',2'-e][1,4]thiazin-4-yl)benzonitrile (5m)

$^1$H NMR (500 MHz) of 5m (20mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).
$^1$H and $^{13}$C NMR spectra of dithienothiazines 5

$^{13}$C NMR (125 MHz) of 5m (20 mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).

$^{13}$C DEPT 135-NMR (125 MHz) of 5m (20 mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).
4.14 4-(4-Nitrophenyl)-4H-dithieno[2,3-b:3',2'e][1,4]thiazine (5n)

$^1$H NMR (500 MHz) of 5n (20mg) in acetone-d$_6$ at 298 K (δ in ppm). *Impurities from residual solvents.
$^1$H und $^{13}$C NMR spectra of dithienothiazines 5

$^{13}$C NMR (125 MHz) of 5n (20 mg) in acetone-$d_6$ at 298 K (δ in ppm).

$^{13}$C NMR (125 MHz) of 5n (20 mg) in acetone-$d_6$ at 298 K (δ in ppm).
4.15 4-Butyl-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5o)

$^1$H NMR (500 MHz) of 5o (20mg) in C$_6$D$_6$ at 298 K ($\delta$ in ppm).
$^1$H und $^{13}$C NMR spectra of dithienothiazines 5

$^{13}$C NMR (125 MHz) of 5o (20 mg) in C$_6$D$_6$ at 298 K ($\delta$ in ppm).

$^{13}$C DEPT 135-NMR (125 MHz) of 5o (20 mg) in C$_6$D$_6$ at 298 K ($\delta$ in ppm).
4.16 4-Benzyl-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5p)

$^1$H NMR (500 MHz) of 5p (20mg) in acetone-$d_6$ at 298 K ($\delta$ in ppm).
$^1$H und $^{13}$C NMR spectra of dithienothiazines 5

$^{13}$C NMR (125 MHz) of 5p (20 mg) in acetone-$d_6$ at 298 K (δ in ppm).

$^{13}$C DEPT 135-NMR (125 MHz) of 5p (20 mg) in acetone-$d_6$ at 298 K (δ in ppm).
5 UV spectra of dithienothiazines 5a-5p

5 UV spectra of \(N\)-substituted 4\(H\)-dithieno[2,3-\(b\):3',2'-e][1,4]thiazines 5

5.1 4-(4\(H\)-Dithieno[2,3-\(b\):3',2'-e][1,4]thiazin-4-yl)-\(N\),\(N\)-dimethylaniline (5a)

UV spectrum of 5a in dichloromethane at 298 K.

5.2 4-(4-Methoxyphenyl)-4\(H\)-dithieno[2,3-\(b\):3',2'-e][1,4]thiazine (5b)

UV spectrum of 5b in dichloromethane at 298 K.
5.3 4-(4-( tert-Butyl)phenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5c)

UV spectrum of 5c in dichloromethane at 298 K.

5.4 4-(p-Tolyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5d)

UV spectrum of 5d in dichloromethane at 298 K.
5.5 4-Phenyl-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5e)

UV spectrum of 5e in dichloromethane at 298 K.

5.6 4-(4-Fluorophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5f)

UV spectrum of 5f in dichloromethane at 298 K.
5.7 4-(2-Chlorophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5g)

UV spectrum of 5g in dichloromethane at 298 K.

5.8 4-(3-Chlorophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5h)

UV spectrum of 5h in dichloromethane at 298 K.
5.9 4-(4-Chlorophenyl)-4H-dithieno[2,3-b:2',3'-e][1,4]thiazine (5i)

UV spectrum of 5i in dichloromethane at 298 K.

5.10 4-(4-Bromophenyl)-4H-dithieno[2,3-b:2',3'-e][1,4]thiazine (5j)

UV spectrum of 5j in dichloromethane at 298 K.
5 UV spectra of dithienothiazines 5a-5p

5.11 Methyl 4-(4H-dithieno[2,3-b:3',2'-e][1,4]thiazin-4-yl)benzoate (5k)

UV spectrum of 5k in dichloromethane at 298 K.

5.12 4-(4-(Trifluoromethyl)phenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5l)

UV spectrum of 5l in dichloromethane at 298 K.
5 UV spectra of dithienothiazines 5a-5p

5.13 4-(4H-Dithieno[2,3-b:3',2'-e][1,4]thiazin-4-yl)benzonitrile (5m)

UV spectrum of 5m in dichloromethane at 298 K.

5.14 4-(4-Nitrophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5n)

UV spectrum of 5n in dichloromethane at 298 K.
5.15 4-Butyl-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5o)

UV spectrum of 5o in dichloromethane at 298 K.

5.16 4-Benzyl-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5p)

UV spectrum of 5p in dichloromethane at 298 K.
6 Cyclic voltammograms of dithienothiazines 5

6.1 4-(4H-Dithieno[2,3-b:3',2'-e][1,4]thiazin-4-yl)-N,N-dimethylaniline (5a)

Cyclic voltammogram of 5a recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [Bu₄N][PF₆], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

6.2 4-(4-Methoxyphenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5b)

Cyclic voltammogram of 5b recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [Bu₄N][PF₆], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.
6 Cyclic voltammograms of dithienothiazines 5

reference electrode.

6.3 4-(4-(tert-Butyl)phenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5c)

Cyclic voltammogram of 5c recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [nBu_{4}N^+]\[PF_6^-], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

6.4 4-(p-Tolyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5d)

Cyclic voltammogram of 5d recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [nBu_{4}N^+]\[PF_6^-], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.
6 Cyclic voltammograms of dithienothiazines 5

6.5 4-Phenyl-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5e)

Cyclic voltammogram of 5e recorded in dichloromethane, T = 298 K, \( \nu = 100 \text{ mV/s} \), 0.1 M electrolyte \([\text{"Bu}_4\text{N}^+][\text{PF}_6^-]\), Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

6.6 4-(4-Fluorophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5f)

Cyclic voltammogram of 5f recorded in dichloromethane, T = 298 K, \( \nu = 100 \text{ mV/s} \), 0.1 M electrolyte \([\text{"Bu}_4\text{N}^+][\text{PF}_6^-]\), Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.
6.7 4-(2-Chlorophenyl)-4\textsubscript{H}-dithieno[2,3-b:3',2'-e][1,4]thiazine (5g)

Cyclic voltammogram of 5g recorded in dichloromethane, \( T = 298 \text{ K} \), \( \nu = 100 \text{ mV/s} \), 0.1 M electrolyte \([\text{nBu}_4\text{N}^+][\text{PF}_6^-]\), Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

6.8 4-(3-Chlorophenyl)-4\textsubscript{H}-dithieno[2,3-b:3',2'-e][1,4]thiazine (5h)

Cyclic voltammogram of 5h recorded in dichloromethane, \( T = 298 \text{ K} \), \( \nu = 100 \text{ mV/s} \), 0.1 M electrolyte \([\text{nBu}_4\text{N}^+][\text{PF}_6^-]\), Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.
6.9 4-(4-Chlorophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5i)

Cyclic voltammogram of 5i recorded in dichloromethane, T = 298 K, \( \nu = 100 \text{ mV/s} \), 0.1 M electrolyte \([\text{"Bu}_4\text{N}^+][\text{PF}_6^-]\), Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

6.10 4-(4-Bromophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5j)

Cyclic voltammogram of 5j recorded in dichloromethane, T = 298 K, \( \nu = 100 \text{ mV/s} \), 0.1 M electrolyte \([\text{"Bu}_4\text{N}^+][\text{PF}_6^-]\), Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.
6.11 Methyl 4-(4H-dithieno[2,3-b:3',2'-e][1,4]thiazin-4-yl)benzoate (5k)

Cyclic voltammogram of 5k recorded in dichloromethane, T = 298 K, \( \nu = 100 \text{ mV/s} \), 0.1 M electrolyte \([n\text{Bu}_4\text{N}^+]\)[PF6], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

6.12 4-(4-(Trifluoromethyl)phenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5l)

Cyclic voltammogram of 5l recorded in dichloromethane, T = 298 K, \( \nu = 100 \text{ mV/s} \), 0.1 M electrolyte \([n\text{Bu}_4\text{N}^+]\)[PF6], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.
6.13 4-(4H-Dithieno[2,3-b:3',2'-e][1,4]thiazin-4-yl)benzonitrile (5m)

Cyclic voltammogram of 5m recorded in dichloromethane, T = 298 K, ν = 100 mV/s, 0.1 M electrolyte [nBu₄N][PF₆], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

6.14 4-(4-Nitrophenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5n)

Cyclic voltammogram of 5n recorded in dichloromethane, T = 298 K, ν = 100 mV/s, 0.1 M electrolyte [nBu₄N][PF₆], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.
6.15 4-Butyl-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5o)

Cyclic voltammogram of 5o recorded in dichloromethane, T = 298 K, ν = 100 mV/s, 0.1 M electrolyte ["Bu4N+][PF6−], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

6.16 4-Benzyl-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (5p)

Cyclic voltammogram of 5p recorded in dichloromethane, T = 298 K, ν = 100 mV/s, 0.1 M electrolyte ["Bu4N+][PF6−], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.
### 7 Crystallographic data of 4-(4H-Dithieno[2,3-b:3',2'-e][1,4]thiazin-4-yl)benzonitrile (5m)

#### 7.1 Crystal data and structure refinement for 5m.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Identification code</td>
<td>5m (no_68)</td>
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<tr>
<td>Empirical formula</td>
<td>C15 H8 N2 S3</td>
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<tr>
<td>Formula weight</td>
<td>312.44</td>
</tr>
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<td>Temperature</td>
<td>291(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
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<tr>
<td>Space group</td>
<td>P 21/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 12.1083(8) Å, α = 90°</td>
</tr>
<tr>
<td></td>
<td>b = 8.4579(4) Å, β = 90.114(5)°</td>
</tr>
<tr>
<td></td>
<td>c = 13.1468(9) Å, γ = 90°</td>
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<tr>
<td>Volume</td>
<td>1346.37(14) Å³</td>
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<tr>
<td>Z</td>
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</tr>
<tr>
<td>Density (calculated)</td>
<td>1.541 Mg/m³</td>
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<tr>
<td>Absorption coefficient</td>
<td>0.539 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>640</td>
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<tr>
<td>Crystal size</td>
<td>0.43 x 0.41 x 0.26 mm³</td>
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<tr>
<td>Theta range for data collection</td>
<td>2.28 to 25.00°</td>
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<tr>
<td>Index ranges</td>
<td>-14&lt;=h&lt;=14, -10&lt;=k&lt;=8, -15&lt;=l&lt;=15</td>
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<tr>
<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
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<td>Completeness to theta = 25.00°</td>
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<td>Absorption correction</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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<tr>
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<tr>
<td>R indices (all data)</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.320 and -0.309 eÅ⁻³</td>
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</table>
7 Crystallographic data of dithienothiazine 5m

### 7.2 Bond lengths [Å] and angles [*°*] for 5m.

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<th>Bond</th>
<th>Length/Angle</th>
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<tr>
<td>S(2)-C(1)</td>
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<td>S(3)-C(4)</td>
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<tr>
<td>S(3)-C(7)</td>
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<td>N(1)-C(9)</td>
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<td>N(1)-C(3)</td>
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<td>N(1)-C(2)</td>
<td>1.396(3)</td>
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<tr>
<td>N(2)-C(15)</td>
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<td>C(1)-C(2)</td>
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<tr>
<td>C(2)-C(6)</td>
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<td>C(5)-C(6)</td>
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<td>C(6)-H(51)</td>
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<td>C(7)-C(8)</td>
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<td>C(9)-N(1)-C(3)</td>
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<td>C(3)-N(1)-C(2)</td>
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<td>C(4)-S(1)-C(1)</td>
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<td>C(9)-N(1)-C(3)</td>
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<td>C(11)-C(12)-C(15)</td>
<td>120.2(2)</td>
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<td>C(13)-C(12)-C(15)</td>
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</table>
Crystallographic data of dithienothiazine 5m

C(14)-C(13)-C(12) 120.5(2)
C(14)-C(13)-H(131) 119.8
C(12)-C(13)-H(131) 119.8
C(13)-C(14)-C(9) 120.9(2)
C(13)-C(14)-H(141) 119.5
C(9)-C(14)-H(141) 119.5
N(2)-C(15)-C(12) 179.0(3)

Symmetry transformations used to generate equivalent atoms:

7.3 Torsion angles [°] for 5m.

C(5)-S(2)-C(1)-C(2) -0.50(17)
C(5)-S(2)-C(1)-S(1) -174.58(15)
C(4)-S(1)-C(1)-C(2) -31.8(2)
C(4)-S(1)-C(1)-S(2) 141.55(14)
S(2)-C(1)-C(2)-C(6) -0.7(2)
S(1)-C(1)-C(2)-C(6) 173.41(15)
S(2)-C(1)-C(2)-N(1) -173.75(15)
S(1)-C(1)-C(2)-N(1) 0.4(3)
C(9)-N(1)-C(2)-C(1) -124.0(2)
C(3)-N(1)-C(2)-C(1) 40.2(3)
C(9)-N(1)-C(2)-C(6) 64.0(3)
C(3)-N(1)-C(2)-C(6) -131.8(2)
C(9)-N(1)-C(3)-C(4) 124.1(2)
C(2)-N(1)-C(3)-C(4) -40.3(3)
C(9)-N(1)-C(3)-C(8) -63.0(3)
C(2)-N(1)-C(3)-C(8) 132.6(2)
C(8)-C(3)-C(4)-S(3) -1.1(2)
N(1)-C(3)-C(4)-S(3) 172.68(16)
C(8)-C(3)-C(4)-S(1) -173.91(16)
N(1)-C(3)-C(4)-S(1) -0.2(3)
C(7)-S(3)-C(4)-C(3) 1.80(17)
C(7)-S(3)-C(4)-S(1) 174.59(15)
C(1)-S(1)-C(4)-C(3) 31.8(2)
C(1)-S(1)-C(4)-S(3) -140.14(14)
C(1)-S(2)-C(5)-C(6) 1.64(18)
S(2)-C(5)-C(6)-C(2) -2.3(2)
C(1)-C(2)-C(6)-C(5) 1.9(3)
N(1)-C(2)-C(6)-C(5) 174.53(19)
C(4)-S(3)-C(7)-C(8) -2.15(19)
S(3)-C(7)-C(8)-C(3) 1.9(3)
C(4)-C(3)-C(8)-C(7) -0.5(3)
N(1)-C(3)-C(8)-C(7) -173.9(2)
C(3)-N(1)-C(9)-C(10) -1.2(3)
C(2)-N(1)-C(9)-C(10) 161.81(19)
C(3)-N(1)-C(9)-C(14) -179.8(2)
C(2)-N(1)-C(9)-C(14) -16.8(3)
N(1)-C(9)-C(10)-C(11) -177.2(2)
C(14)-C(9)-C(10)-C(11) 1.5(3)
C(9)-C(10)-C(11)-C(12) -1.6(3)
C(10)-C(11)-C(12)-C(13) 0.4(3)
C(10)-C(11)-C(12)-C(15) 177.6(2)
C(11)-C(12)-C(13)-C(14) 1.0(3)
C(15)-C(12)-C(13)-C(14) -176.3(2)
C(12)-C(13)-C(14)-C(9) -1.1(4)
N(1)-C(9)-C(14)-C(13) 178.5(2)
C(10)-C(9)-C(14)-C(13) -0.1(3)
C(11)-C(12)-C(15)-N(2) -65(14)
C(13)-C(12)-C(15)-N(2) 112(14)

Symmetry transformations used to generate equivalent atoms.
8 Molecular modeling coordinates and FMO energies of compounds 1, 2a-d and 5m

8.1 XYZ-Coordinates of the \( S_0 \) (Gaussian03, B3LYP/6-311G\*) of compound 1:

N  -0.018993  -1.123397  -0.717554
S  -0.013533   1.872328  -0.410900  
C  1.211221  -0.525467  -1.029858
C  -1.245530  -0.520508  -1.034391
C   1.348031   0.871254  -0.991632
C  -1.377102   0.876762  -0.996374
C  -2.354490  -1.295478  -1.387119
C   2.318381  -1.304942  -1.378184
C   3.543408  -0.708876  -1.664590
C  -3.576145  -0.694601  -1.677758
C  -3.697774   0.691817  -1.655797
C  -2.590456   1.473201  -1.328951
C   3.670301   0.677057  -1.642684
C   2.564882   1.462877  -1.319996
H  -2.257419  -2.377346  -1.427778
H  -4.428253  -1.315015  -1.934812
H  -4.643278  -1.161163  -1.894534
H  -2.669593   2.555327  -1.315791
H   2.648335   2.544674  -1.306767
H   4.618492   1.147634  -1.878199
H   4.394059  -1.332655  -1.918311
H   2.217164  -2.386419  -1.418796
H  -0.020952  -2.130114  -0.792184

SCF Done: E (RB + HF-LYP) = -915.775433742 A. U. after 8 cycles
Sum of electronic and zero-point Energies = -915.597983
Sum of electronic and thermal Energies = -915.587622
Sum of electronic and thermal Enthalpies = -915.586678
Sum of electronic and thermal Free Energies = -915.634189

LUMO+1 = -0.500 eV
LUMO = -0.686 eV
HOMO = -5.238 eV
HOMO-1 = -6.335 eV

8.2 XYZ-Coordinates of the \( S_0 \) (Gaussian03, B3LYP/6-311G\*) of compound 2a:

N  0.000394  -1.239861  -0.615532
S  0.000164   1.867425  -0.271129
C  1.201091  -0.563430  -0.907615
C  -1.200432  -0.563618  -0.907522
C   1.304250   0.802668  -0.841785
C  -1.303800   0.802464  -0.841684
C  -2.412231  -1.183054  -1.341313
C   2.412953  -1.182676  -1.341499
C   3.403477  -0.279848  -1.593835
C  -3.402915  -0.280380  -1.593573
8 Molecular modelling coordinates and FMO energies of compounds 1, 2a-d and 5m

| S      | 2.877196 | 1.353411 | -1.342060 |
| S      | -2.876870 | 1.352961 | -1.341838 |
| H      | 2.537356  | -2.253887 | -1.452842 |
| H      | -2.536475 | -2.254284 | -1.452646 |
| H      | 4.416406  | -0.472992 | -1.913918 |
| H      | -4.415839 | -0.473682 | -1.913578 |
| H      | 0.000460  | -2.217342 | -0.865615 |

SCF Done: E (RB + HF-LYP) = -1557.28554537 A. U. after 8 cycles
Sum of electronic and zero-point Energies = -1557.174864
Sum of electronic and thermal Energies = -1557.164923
Sum of electronic and thermal Enthalpies = -1557.163979
Sum of electronic and thermal Free Energies = -1557.211054

LUMO+1 = -0.525 eV
LUMO = -0.834 eV
HOMO = -4.993 eV
HOMO-1 = -6.487 eV

8.3 XYZ-Coordinates of the S0 (Gaussian03, B3LYP/6-311G*) of compound 2b:

| S      | -2.858635 | 1.370641 | -1.488452 |
| C      | -1.306149 | 0.815446 | -0.933718 |
| C      | -1.252381 | -0.553335 | -0.888127 |
| C      | -2.478299 | -1.170638 | -1.279070 |
| C      | -3.438481 | -0.259885 | -1.609518 |
| S      | 0.035166  | 1.880652 | -0.460909 |
| C      | 1.330276  | 0.736226 | -0.932895 |
| C      | 1.135822  | -0.616209 | -0.852857 |
| N      | -0.071727 | -1.235133 | -0.520933 |
| C      | 2.641007  | 1.088870 | -1.375243 |
| C      | 3.429662  | 0.005444 | -1.610126 |
| S      | 2.567034  | -1.489649 | -1.341717 |
| H      | -2.635617 | -2.242896 | -1.304798 |
| H      | -4.456156 | -0.445481 | -1.918530 |
| H      | -0.102185 | -2.238170 | -0.618212 |
| H      | 4.467785  | -0.027699 | -1.902913 |
| H      | 2.979253  | 2.111174 | -1.489111 |

SCF Done: E (RB + HF-LYP) = -1557.28470227 A. U. after 8 cycles
Sum of electronic and zero-point Energies = -1557.174270
Sum of electronic and thermal Energies = -1557.164224
Sum of electronic and thermal Enthalpies = -1557.163280
Sum of electronic and thermal Free Energies = -1557.210553

LUMO+1 = -0.366 eV
LUMO = -0.897 eV
HOMO = -4.997 eV
HOMO-1 = 6.412 eV
8 Molecular modelling coordinates and FMO energies of compounds 1, 2a-d and 5m

8.4 XYZ-Coordinates of the S₀ (Gaussian03, B3LYP/6-311G*) of compound 2c:

N  0.022854  -1.220440  -0.390378
S  -0.008208   1.866700  -0.599781
C   1.205912  -0.597550  -0.795612
C  -1.173304  -0.621304  -0.792943
C   1.336513   0.750092  -0.990362
C  -1.331222   0.723453  -0.987388
S  -2.604492  -1.507589  -1.260785
S   2.653438  -1.455095  -1.266709
C    3.446202   0.047659  -1.668121
C  -3.427938  -0.020985  -1.660563
C   2.619727   1.115636  -1.497971
C  -2.622618   1.063299  -1.492095
H  -4.461286  -0.055734  -1.970121
H   4.479355   0.033541  -1.979951
H  -2.914022  -2.137829  -1.700271
H  -2.937702   2.079404  -1.693745
H   0.032949  -2.213494  -0.226096

SCF Done: E (RB+HF-LYP)    = -1557.28335003 A. U. after 8 cycles
Sum of electronic and zero-point Energies = -1557.173375
Sum of electronic and thermal Energies  = -1557.163067
Sum of electronic and thermal Enthalpies = -1557.162123
Sum of electronic and thermal Free Energies = -1557.209936

LUMO+1   = -0.494 eV
LUMO      = -0.844 eV
HOMO      = -5.018 eV
HOMO-1    = -6.489 eV

8.5 XYZ-Coordinates of the S₀ (Gaussian03, B3LYP/6-311G*) of compound 2d:

N   0.009166   -1.203159  -0.602416
S   0.002596    1.934971  -0.560135
C   1.225412  -0.582911  -0.904876
C  -1.210359  -0.588047  -0.902150
C   1.348347   0.847588  -0.969133
C  -1.339469   0.841921  -0.966124
C  -2.396531  -1.223959  -1.146687
C   2.417004  -1.213816  -1.152071
S    3.698513  -0.080929  -1.445420
S  -3.686762  -0.096501  -1.437144
C   2.613999   1.257604  -1.266519
C  -2.607502   1.246594  -1.260676
H   2.611027  -2.275399  -1.178420
H  -2.589434  -2.286364  -1.172599
H    0.011238  -2.210399  -0.648469
H   -2.972061   2.256899  -1.368361
H    2.974053   2.269436  -1.375015

SCF Done: E (RB + HF-LYP)   = -1557.29432111 A. U. after 8 cycles
Sum of electronic and zero-point Energies = -1557.183683
Sum of electronic and thermal Energies  = -1557.173791
8 Molecular modelling coordinates and FMO energies of compounds 1, 2a-d and 5m

Sum of electronic and thermal Enthalpies = -1557.172847
Sum of electronic and thermal Free Energies = -1557.219773

LUMO+1 = -0.575 eV
LUMO = -0.575 eV
HOMO = -5.327 eV
HOMO-1 = -5.888 eV

8.6 XYZ-Coordinates of the S0 (Gaussian03, B3LYP/6-311G*) of compound 5m:

<table>
<thead>
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Sum of electronic and zero-point Energies = -1880.454838
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Sum of electronic and thermal Enthalpies = -1880.437633
Sum of electronic and thermal Free Energies = -1880.500032

LUMO+2 = -1.049 eV
LUMO+1 = -1.233 eV
LUMO = -1.478 eV
HOMO = -5.846 eV
HOMO-1 = -6.622 eV
HOMO-2 = -7.108 eV
8 Molecular modelling coordinates and FMO energies of compounds 1, 2a-d and 5m

8.7 Results of the TD-DFT calculation of compound 5m

Excitation energies and oscillator strengths:

| Excited State 1: Singlet-A, 3.8086 eV, 325.54 nm, f=0.2109 |
|-----------------|-----------------|
| 78 -> 82        | 0.10263         |
| 80 -> 81        | 0.64713         |
| 80 -> 83        | -0.17007        |

| Excited State 2: Singlet-A, 3.8099 eV, 325.43 nm, f=0.0132 |
|-----------------|-----------------|
| 80 -> 82        | 0.68559         |

| Excited State 3: Singlet-A, 4.2668 eV, 290.58 nm, f=0.1399 |
|-----------------|-----------------|
| 79 -> 81        | -0.20717        |
| 80 -> 81        | 0.14581         |
| 80 -> 83        | 0.63057         |

| Excited State 4: Singlet-A, 4.2970 eV, 288.54 nm, f=0.0055 |
|-----------------|-----------------|
| 75 -> 81        | -0.14032        |
| 75 -> 83        | -0.10695        |
| 80 -> 84        | 0.67381         |

| Excited State 5: Singlet-A, 4.5713 eV, 271.23 nm, f=0.1945 |
|-----------------|-----------------|
| 78 -> 82        | -0.11734        |
| 79 -> 81        | 0.62521         |
| 79 -> 83        | -0.15497        |
| 80 -> 83        | 0.14454         |

| Excited State 6: Singlet-A, 4.6670 eV, 265.66 nm, f=0.0303 |
|-----------------|-----------------|
| 79 -> 82        | -0.37066        |
| 79 -> 85        | -0.15125        |
| 80 -> 85        | 0.53871         |
| 80 -> 88        | 0.13965         |

| Excited State 7: Singlet-A, 4.7632 eV, 260.30 nm, f=0.0533 |
|-----------------|-----------------|
| 78 -> 81        | -0.13326        |
| 79 -> 82        | 0.55082         |
| 80 -> 85        | 0.38933         |

| Excited State 8: Singlet-A, 4.9018 eV, 252.94 nm, f=0.0021 |
|-----------------|-----------------|
| 79 -> 86        | -0.11143        |
| 80 -> 86        | 0.67337         |

| Excited State 9: Singlet-A, 5.0015 eV, 247.89 nm, f=0.0688 |
|-----------------|-----------------|
| 79 -> 81        | 0.13036         |
| 79 -> 83        | 0.51597         |
| 80 -> 87        | 0.42553         |

| Excited State 10: Singlet-A, 5.0073 eV, 247.61 nm, f=0.0200 |
|-----------------|-----------------|
| 78 -> 81        | 0.63838         |
| 79 -> 84        | -0.14361        |
| 80 -> 88        | -0.11932        |
9 Preparation and characterization of 10-Phenyl-10H-phenothiazine 7

9.1 Preparation of 10-Phenyl-10H-phenothiazine (7)

20 mL dry 1,4-dioxane were placed under nitrogen atmosphere in a screw-cap Schlenk vessel. Then, 658 mg (3.3 mmol) of 10H-phenothiazine, 471 mg (3.0 mmol) of bromobenzene, 104 mg (6.0 mol%) of bis(dibenzylideneacetone)palladium, 44 mg (5 mol%) of tri-tert-butylphosphine tetrafluoroborate, and 332 mg (3.5 mmol) of sodium tert-butoxide were added to the solvent. The mixture was stirred for 15 h at 100 °C in a preheated oil bath and was allowed to come to room temperature. After complete conversion (product monitored by TLC) 20 mL water were added and the mixture was extracted with dichloromethane (3 x 30 mL). The combined organic phases were dried with anhydrous magnesium sulfate and the desiccant was removed by filtration. After removal of the solvents in vacuum the residue was adsorbed on Celite® and purified chromatographically on silica gel with hexane to give 607 mg (2.2 mmol, 73 %)

$^1$H NMR (500 MHz, acetone-d$_6$): δ 6.23 (dd, $J = 8.2$ Hz, 1.2 Hz, 2 H), 6.85 (dt, $J = 7.4$ Hz, 1.3 Hz, 2 H), 6.88-6.93 (m, 2 H), 7.04 (dd, $J = 7.5$ Hz, 1.6 Hz, 2 H), 7.40-7.45 (m, 2 H), 7.55 (t, $J = 7.5$ Hz, 1 H), 7.68 (t, $J = 7.8$ Hz, 2 H). $^{13}$C NMR (125 MHz, acetone-d$_6$): δ 117.2 (CH), 121.1 (C$_{quat}$), 123.6 (CH), 127.5 (CH), 128.0 (CH), 129.3 (CH), 131.6 (CH), 131.9 (CH), 142.0 (C$_{quat}$), 145.2 (C$_{quat}$). Anal. calcd. for C$_{18}$H$_{13}$NS (275.4): C 78.51, H 4.76, N 5.09. Found: C 78.59, H 4.87, N: 5.00.

Data reported in literature$^5$:

$^1$H NMR (500 MHz, DMSO-d$_6$): δ 6.17 (dd, $J = 8.0$ Hz, 0.94 Hz, 2 H), 6.86 (ddd, $J = 8.00$ Hz, 7.07 Hz, 0.94 Hz, 2 H), 6.93 (ddd, $J = 8.1$ Hz, 8.0 Hz, 1.42 Hz, 2 H), 7.07 (dd, $J = 7.07$ Hz, 1.42 Hz, 2 H), 7.41 (d, $J = 7.54$ Hz, 2 H), 7.54 (broad t, $J = 7.53$ Hz, 2 H), 7.67 (dd, $J = 7.54$ Hz, 7.53 Hz, 2H).
9.2 UV spectrum of 10-Phenyl-10H-phenothiazine (7)

UV spectrum of 7 in dichloromethane at 298 K.

9.3 Cyclic voltammogram of 10-Phenyl-10H-phenothiazine (7)

Cyclic voltammogram of 7 recorded in dichloromethane, \( T = 298 \) K, \( v = 100 \) mV/s, 0.1 M electrolyte \([\text{Bu}_4\text{N}^+]\text{[PF}_6^-\text{]}\), Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.