Exploiting amphiphilicity: Facile metal free access to thianthrenes and related sulphur heterocycles

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Supplementary information

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General experimental

All solvents were distilled before use unless otherwise stated. Air and moisture sensitive reactions were carried out in oven-dried or flame-dried glassware, septum-capped under atmospheric pressure of argon. Commercially available compounds were used without further purification unless otherwise stated.

Proton ($^1$H) and carbon ($^{13}$C) NMR spectra were recorded on a 300, 400 or 600 MHz instrument using the residual signals from tetramethylsilane (TMS) $\delta = 0.00$ ppm, as internal references for $^1$H and $^{13}$C chemical shifts, respectively. Assignments of the respective signals were made by combination of H,H-COSY, HSQC and HMBC experiments. EI-HRMS mass spectrometry was carried out on JOEL AccuTOF GC JMS-T100GC instrument. ESI-HRMs mass spectrometry was carried out on a FTICR instrument. IR spectra were measured on an ATR spectrometer. UV spectra were measured with a common photometer.

The following aryne precursors and alkynes were applied in this manuscript.
**General procedure for aryne reaction (GP1)**

A mixture of dithioloimine 1 (1.0 equiv.), KF (3.0 equiv.) and 18-Crown-6 (3.0 equiv.) was pre-stirred in MeCN (0.05 M) for 2 min. Afterwards aryne precursor 2 (1.5 equiv.) was added and the reaction was further stirred at room temperature for additional 16 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel to obtain the corresponding thianthrene.

**General procedure for EWG-alkyne reaction (GP2)**

A mixture of dithioloimine 1 (1.0 equiv.), KF (3.0 equiv.) and 18-Crown-6 (3.0 equiv.) was pre-stirred in MeCN (0.1 M) for 2 min. Afterwards alkyne 4 (1.5 equiv.) was added dropwise at room temperature and the reaction was stirred for additional 5 min. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel to obtain the title compound.

**General procedure for EWG-alkyne reaction (GP3)**

A mixture of dithioloimine 1 (1.0 equiv.) and Cs$_2$CO$_3$ (3.0 equiv.) was pre-stirred in MeCN (0.1 M) for 2 min. Afterwards alkyne 4 (1.5 equiv.) was added dropwise at room temperature and the reaction was stirred for additional 5 min. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel to obtain the title compound.
1,2-Dithiocyanatobenzene (6a)

![Structure of 1,2-Dithiocyanatobenzene](image)

Benzene-1,2-thiol (500 mg, 3.51 mmol, 1.00 equiv.) in CH\textsubscript{2}Cl\textsubscript{2} (10 mL) was treated with trimethylamine (5 drops) and then the SO\textsubscript{2}Cl\textsubscript{2} (1.04 g, 7.72 mmol, 2.20 equiv.) was added dropwise at 0 °C. Stirring of the solution at 0 °C for 30 min was accompanied by the evolution of HCl gas. CH\textsubscript{2}Cl\textsubscript{2} was removed by evaporation and replaced with MeCN (10 mL), followed by the slow addition of TMSCN (776 mg, 7.72 mmol, 2.20 equiv.). The resulting brown solution was stirred at rt for 1 h. Evaporation of the solvent and purification of the crude residue by column chromatography on silica gel (pentane:EtOAc = 15:1) gave the title compound 6a as a colorless solid (641 mg, 3.33 mmol, 95%).

\textsuperscript{1}H-NMR (600 MHz, CDCl\textsubscript{3}): \( \delta = 7.55–7.59 \) (m, 2 H), 7.81–7.85 (m, 2 H) ppm.

\textsuperscript{13}C-NMR (150 MHz, CDCl\textsubscript{3}): \( \delta = 108.1, 126.6, 131.6, 132.9 \) ppm.

m.p.: 91 °C.

IR (ATR): \( \tilde{\nu} \) (cm\textsuperscript{-1}) = 3081, 2161, 1567, 1448, 1431.

UV (CH\textsubscript{3}CN): \( \lambda_{\text{max}} \) (lg \( \varepsilon \)) = 279 nm (3.08), 236 (3.96), 207 (4.21).

HRMS-EI: C\textsubscript{8}H\textsubscript{4}N\textsubscript{4}S\textsubscript{2} calcd for [M]\textsuperscript{+}: 191.9816 , found: 191.9827.
4-Methyl-1,2-dithiocyanatobenzene (6b)

4-Methylbenzene-1,2-dithiol (600 mg, 3.84 mmol, 1.00 equiv.) in CH₂Cl₂ (10 mL) was treated with trimethylamine (5 drops) and then SO₂Cl₂ (1.14 g, 8.45 mmol, 2.20 equiv.) was added dropwise at 0 °C. Stirring of the solution at 0 °C for 30 min was accompanied by the evolution of HCl gas. CH₂Cl₂ was removed by evaporation and replaced with MeCN (10 mL), followed by the slow addition of TMSCN (838 mg, 8.45 mmol, 2.20 equiv.). The resulting brown solution was stirred at rt for 1 h. Evaporation of the solvent and purification of the crude residue by column chromatography on silica gel (pentane:EtOAc = 15:1) gave the title compound 6b as a colorless solid (614 mg, 2.98 mmol, 78%).

¹H-NMR (600 MHz, CDCl₃): δ = 2.45 (s, 3 H), 7.34 (dd, J = 8.1, 1.7, 0.7 Hz, 1 H), 7.63–7.64 m, 1 H) 7.68 (d, J = 8.1 Hz, 1 H) ppm.

¹³C-NMR (150 MHz, CDCl₃): δ = 21.2, 108.6, 108.6, 121.8, 127.8, 132.4, 132.8, 134.0, 143.5 ppm.

m.p.: 96 °C.

IR (ATR): ν (cm⁻¹) = 2160, 1582, 1461, 1386, 1386, 1270.

UV (CH₃CN): λ_max (lg ε) = 277 nm (3.02), 236 (3.98), 213 (4.26).

Benzo[d][1,3]dithiolo-2-imine (1a)

To a solution of 1,2-dithiocyanatobenzene 6a (600 mg, 3.13 mmol, 1.0 equiv.) and CsF (710 mg, 4.70 mmol, 1.5 equiv.) in MeCN (30 mL) was added PPh₃ (900 mg, 3.44 mmol, 1.1 equiv.) and stirred at room temperature until TLC shows full conversion. Afterwards the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (pentane:EtOAc = 10:1→5:1) to obtain title compound 1a (481 mg, 2.88 mmol, 92%) as a white solid.

¹H-NMR (600 MHz, CDCl₃): δ = 7.16–7.34 (m, 4 H), 8.83 (s, 1 H) ppm.

¹³C-NMR (150 MHz, CDCl₃): δ = 121.6, 122.0, 126.0, 126.2, 134.4, 134.7, 172.5 ppm.

m.p.: 122 °C.

IR (ATR): ν (cm⁻¹) = 3176, 1700, 1550, 1431, 1236.

UV (CH₃CN): λ_max (lg ε) = 333 nm (2.31), 292 (3.40), 259 (3.85), 223 (4.60).

5-Methylbenzo[\textit{d}][1,3]dithiol-2-imine (1\textit{b})

To a solution of \textit{6b} (300 mg, 1.46 mmol, 1.0 equiv.) and CsF (331 mg, 2.19 mmol, 1.5 equiv.) in MeCN (15 mL) was added PPh$_3$ (420 mg, 1.60 mmol, 1.1 equiv.) and stirred at room temperature until TLC shows full conversion. Afterwards the solvent was removed \textit{in vacuo} and the residue was purified by column chromatography on silica gel (pentane:EtOAc = 10:1→5:1) to obtain the title compound \textit{1b} (240 mg, 1.33 mmol, 91%) as a pale orange solid.

\textsuperscript{1}H-NMR (300 MHz, CDCl$_3$): $\delta$ = 2.32 (d, $J = 0.3$ Hz, 3 H), 2.43 (s, 3 H), 6.99 (ddd, $J = 8.1$, 1.7, 0.7 Hz, 1 H), 7.07–7.16 (m, 2 H), 7.25 (ddd, $J = 8.1$, 1.7, 0.7 Hz, 1 H), 7.38–7.39 (m, 1 H), 7.44 (d, $J = 8.2$ Hz, 1 H), 8.79 (s, 1 H) ppm.

\textsuperscript{13}C-NMR (75 MHz, CDCl$_3$): $\delta$ = 21.0, 21.2, 113.8, 121.7, 121.7, 122.4, 122.4, 123.0, 123.5, 127.3, 127.1, 129.1, 131.3, 134.6, 136.5, 173.2 ppm.

m.p.: 94 °C.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3194, 2913, 2186, 1558, 1490, 1234.

UV (CH$_3$CN): $\lambda_{\text{max}}$ (lg $\epsilon$) = 323 nm (3.41), 303 (3.50), 261 (3.80), 248 (3.80), 223 (4.59).

6,7-Diphenyl-[1,3]dithiolo[4,5-g]quinoxalin-2-imine (1c)

To a solution of 2,3-diphenylbenzo[5,6][1,4]dithiino[2,3-g]quinoxaline 6c[1] (269 mg, 654 µmol, 1.0 equiv.) and CsF (150 mg, 981 µmol, 1.5 equiv.) in MeCN (20 mL) was added PPh₃ (188 mg, 719 mmol, 1.1 equiv.) and stirred at room temperature until TLC shows full conversion. Afterwards the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (pentane:EtOAc = 5:1→2:1) to obtain title compound 1c (131 mg, 353 µmol, 54%) as a pale orange solid.

¹H-NMR (300 MHz, DMSO-d₆): δ = 7.32-7.41 (m, 6 H), 7.43-7.47 (m, 4 H), 8.31 (S, 2 H), 11.00 (s, 1 H) ppm.

¹³C-NMR (75 MHz, DMSO-d₆): δ = 120.9, 128.1, 128.9, 128.9, 129.7, 138.5, 139.5, 152.8, 166.3 ppm.

m.p.: 220 °C (decomposition).

IR (ATR): ν (cm⁻¹) = 3167, 3063, 1577, 1344, 1225, 1100.

UV (CH₃CN): λₑₓₙ (lg ε) = 478 nm (2.68), 388 (4.33), 274 (4.64), 244 (4.47), 232 (4.47).

[1,3]Dithiolo[4',5':4,5]benzo[1,2-c][1,2,5]thiadiazol-6-imine (1d)

To a solution of 5,6-dithiocyanatobenzo[c][1,2,5]thiadiazole 6d[2] (250 mg, 1.00 mmol, 1.0 equiv.) and CsF (228 mg, 1.50 µmol, 1.5 equiv.) in MeCN (40 mL) was added PPh3 (288 mg, 1.50 mmol, 1.1 equiv.) and stirred at room temperature until TLC shows full conversion. Afterwards the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (pentane:EtOAc = 3:1→1:1) to obtain title compound 1d (97.4 mg, 433 µmol, 43%) as a brown solid.

1H-NMR, 13C-NMR: Decomposition in DMSO and insoluble in other solvents.

m.p.: 90-100 °C (decomposition).

IR (ATR): ν (cm\(^{-1}\)) = 3208, 3063, 1574, 1431, 1213, 1078.

UV (CH\(_3\)CN): \(\lambda_{\text{max}}\) (lg ε) = 483 nm (2.46), 368 (4.09), 358 (4.10), 226 (4.48).

HRMS-ESI: C\(_7\)H\(_4\)N\(_3\)S\(_3\) calcd for [M+H]\(^+\): 225.9562, found: 225.9563.
2-Ethyl-5-thiocyanatopyrrole (8b)

To a mixture of 2-ethylpyrrole (200 mg, 2.10 mmol, 1.0 equiv.) and KSCN (613 mg, 6.32 mmol, 3.0 equiv.) in MeCN (10 mL) was added bis(acetoxy)iodobenzene (744 mg, 2.31 mmol, 1.1 equiv.) at 0 °C. The mixture was slowly warmed up to room temperature over 1 h. Afterwards, the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (pentane:EtOAc = 30:1) to obtain the title compound 8b (285 mg, 189 mmol, 89%) as a colorless solid.

\[ ^1\text{H-NMR} \ (400 \text{ MHz, CDCl}_3): \delta = 1.24 \ (t, \ J = 7.6 \text{ Hz, } 3 \text{ H}), \ 2.63 \ (q, \ J = 7.6 \text{ Hz, } 2 \text{ H}), \ 5.98 \ (ddt, \ J = 3.5, 2.7, 0.8 \text{ Hz, } 1 \text{ H}), \ 6.54 \ (dd, \ J = 3.6, 2.7 \text{ Hz, } 1 \text{ H}), \ 8.41 \ (s, \ 1 \text{ H}) \text{ ppm.} \]

\[ ^{13}\text{C-NMR} \ (100 \text{ MHz, CDCl}_3): \delta = 13.1, 21.1, 100.2, 107.9, 111.0, 120.8, 141.3 \text{ ppm.} \]

m.p.: 52 °C.

IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 3337, 3138, 2976, 2150, 1564, 1137.

UV (CH\(_3\)CN): \( \lambda_{\text{max}} \ (lg \varepsilon) = 242 \text{ nm (3.91).} \]

HRMS-EI: C\(_7\)H\(_8\)N\(_2\)S \quad \text{calcd for } [\text{M+Na}^+]^+: 175.0300, \text{ found: 175.0302.} \]
Thianthrene (3aa)

Dithioloimine 1a (8.3 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2a (22.3 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3aa (10.3 mg, 47.7 µmol, 95%) was obtained as a white solid.

The analytical data were in accordance with the reported ones.[3]

Procedure for aryne reaction starting from dithiocyanate to thianthrene (3aa)

To a mixture of dithioloimine 1a (8.3 mg, 50.0 µmol, 1.0 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (2 mL) was added aryne precursor 2a (22.3 mg, 75.0 µmol, 1.5 equiv.) and PPh₃ (6.6 mg, 25 µmol, 50 mol%). The reaction was stirred at room temperature for 16 h. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (pentane) to obtain thianthrene (3aa) (7.0 mg, 32.4 µmol, 65%) as a white solid.

The analytical data were in accordance with the reported ones.[3]
Dithioloimine 1a (8.3 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2b (23.4 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3ab (8.9 mg, 38.6 µmol, 77%) was obtained as a white solid.

**Column:** pentane

$^1$H-NMR (600 MHz, CDCl₃): $\delta = 2.32$ (s, 3 H), 7.04 (ddd, $J = 7.9$, 1.8, 0.7 Hz, 1 H), 7.20–7.24 (m, 2 H), 7.31 (dd, $J = 1.2$, 0.5 Hz, 1 H), 7.36 (d, $J = 7.9$ Hz, 1 H), 7.45–7.49 (m, 2 H) ppm.

$^{13}$C-NMR (150 MHz, CDCl₃): $\delta = 20.9$, 127.5, 127.6, 128.5, 128.6, 128.7, 129.3, 132.0, 135.4, 135.7, 135.9, 137.9 ppm.

**m.p.:** 76 °C.

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3051, 2918, 1440, 1425, 1256.

**UV** (CH$_3$CN): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 256 nm (4.54), 243 (4.24).

**HRMS-EI:** C$_{13}$H$_{10}$S$_2$ calcd for [M]$^+$: 230.0224, found: 230.0236.
1-Methylthianthrene (3ac)

Dithioloimine 1a (8.3 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2c (23.4 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3ac (9.1 mg, 39.6 µmol, 79%) was obtained as a white solid.

**Column**: pentane

$^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ = 2.50 (s, 3 H), 7.11–7.15 (m, 2 H), 7.21–7.26 (m, 2 H), 7.33–7.36 (m, 1 H), 7.46–7.50 (m, 1 H), 7.50–7.53 (m, 1 H) ppm.

$^{13}$C-NMR (150 MHz, CDCl$_3$): $\delta$ = 21.0, 126.6, 127.1, 127.5, 127.8, 128.5, 128.9, 129.0, 135.0, 135.4, 135.4, 136.0, 137.4 ppm.

**m.p.**: 72 °C.

**IR** (ATR): $\bar{\nu}$ (cm$^{-1}$) = 3055, 1442, 1426, 1248, 1109.

**UV** (CH$_3$CN): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 278 nm (3.38), 257 (4.52), 241 (4.16).

**HRMS-EI**: C$_{13}$H$_{10}$S$_{2}$ calcd for [M]$^+$: 230.0224 , found: 230.0219.
Dithiolouimine 1a (8.3 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2d (26.1 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3ad (7.4 mg, 28.9 µmol, 58%) was obtained as a white solid.

**Column:** pentane

$^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 2.07$ (q, $J = 7.4$ Hz, 2 H), 2.86 (t, $J = 7.4$ Hz, 4 H), 7.19–7.23 (m, 2 H), 7.35 (s, 2 H), 7.46–7.49 (m, 2 H) ppm.

$^{13}$C-NMR (150 MHz, CDCl$_3$): $\delta = 25.7, 32.4, 124.6, 127.5, 128.7, 133.0, 136.3, 144.7$ ppm.

**m.p.:** 94 °C.

**IR (ATR):** $\tilde{\nu}$ (cm$^{-1}$) = 2954, 2916, 2842, 1440, 1426, 1096.

**UV (CH$_3$CN):** $\lambda_{\text{max}}$ (lg $\varepsilon$) = 286 nm (3.25), 258 (4.52), 242 (4.22), 196 (4.64).

**HRMS-EI:** C$_{15}$H$_{12}$S$_2$ calcd for [M]$^+: 256.0380$, found: 256.0388.
Benzo[b]thianthrene (3ae)

Dithioloimine 1a (8.3 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2e (26.1 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3ae (9.7 mg, 36.4 µmol, 73%) was obtained as a white solid.

**Column:** pentane

**1H-NMR** (600 MHz, CDCl$_3$): $\delta$ = 7.24–7.27 (m, 2 H), 7.43–7.47 (m, 2 H), 7.51–7.54 (m, 2 H), 7.72–7.76 (m, 2 H), 7.97 (S, 2 H) ppm.

**13C-NMR** (150 MHz, CDCl$_3$): $\delta$ = 126.6, 127.1, 127.2, 127.7, 128.9, 132.7, 133.2, 135.6 ppm.

**m.p.:** 166 °C.

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3051, 2924, 1577, 1445, 1423, 1099.

**UV** (CH$_3$CN): $\lambda_{max}$ (lg $\varepsilon$) = 326 nm (2.98), 274 (4.43), 259 (4.43), 230 (4.64), 214 (4.61).

**HRMS-EI:** C$_{16}$H$_{10}$S$_2$ calcd for [M]$^+$: 266.0224, found: 266.0244.
Dithioloimine 1a (8.3 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2f (26.1 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3af (11.6 mg, 43.6 µmol, 87%) was obtained as a white solid.

**Column:** pentane

**$^1$H-NMR** (600 MHz, CDCl$_3$): $\delta$ = 7.24–7.29 (m, 2 H), 7.48–7.51 (m, 1 H), 7.52–7.55 (m, 2 H), 7.57–7.62 (m, 2 H), 7.72 (d, $J$ = 8.5 Hz, 1 H), 7.82 (d, $J$ = 8.1 Hz, 1 H), 8.46 (d, $J$ = 8.5 Hz, 1 H) ppm.

**$^{13}$C-NMR** (150 MHz, CDCl$_3$): $\delta$ = 124.3, 126.3, 126.3, 127.1, 127.7, 127.7, 127.9, 128.4, 128.5, 129.1, 132.1, 132.5, 132.8, 133.7, 135.2, 136.9 ppm.

**m.p.:** 85 °C.

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3050, 2924, 1906, 1550, 1445, 1108.

**UV** (CH$_3$CN): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 315 nm (3.38), 266 (4.53), 224 (4.66).

**HRMS-EI:** C$_{16}$H$_{10}$S$_2$ calcd for [M]$^+$: 266.0224, found: 266.0225.
2-Chlorothianthrene (3ag)

Dithioloimine 1a (8.3 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2g (24.9 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3ag (8.6 mg, 34.3 µmol, 69%) was obtained as a white solid.

**Column:** pentane

$^1$H-NMR (600 MHz, CDCl$_3$): δ = 7.21 (ddd, J = 8.3, 2.2, 0.4 Hz, 1 H), 7.24–7.27 (m, 2 H), 7.38 (d, J = 8.3 Hz, 1 H), 7.46–7.49 (m, 3 H) ppm.

$^{13}$C-NMR (150 MHz, CDCl$_3$): δ = 127.8, 127.9, 128.0, 128.4, 128.8, 128.8, 129.4, 133.6, 134.1, 134.8, 135.3, 137.5 ppm.

m.p.: 90 °C.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3070, 2925, 1545, 1439, 1426, 1091.

UV (CH$_3$CN): $\lambda_{\text{max}}$ (lg ε) = 258 nm (4.60), 243 (4.24), 196 (4.66).

HRMS-EI: C$_{12}$H$_7$ClS$_2$ calcd for [M]$^+$: 249.9678, found: 249.9696.
2,3-Difluorothianthrene (3ah)

Dithioloaime 1a (8.3 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2h (25.1 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3ah (9.3 mg, 36.9 µmol, 74%) was obtained as a white solid.

**Column:** pentane

1H-NMR (600 MHz, CDCl₃): δ = 7.26–7.29 (m, 2 H), 7.31 (t, J = 8.6 Hz, 2 H), 7.47–7.50 (m, 2 H) ppm.

13C-NMR (150 MHz, CDCl₃): δ = 117.4 (dd, J = 14.3, 6.0 Hz), 128.1, 128.9, 131.9 (dd, J = 4.9 Hz), 134.9, 149.8 (dd, J = 253.3 Hz) ppm.

19F-NMR (376 MHz, CDCl₃): –138.4 ppm.

m.p.: 109 °C.

IR (ATR): ν (cm⁻¹) = 3052, 2923, 1594, 1565, 1475, 1275.

UV (CH₃CN): λ max (lg ε) = 286 nm (3.13), 254 (4.44), 241 (4.18).

1,3-Dibromothianthrene (3ai)

Dithioloimine 1a (8.3 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2i (103 mg, 2.25 µmol, 4.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3ai (8.3 mg, 22.2 µmol, 44%) was obtained as a white solid.

**Column**: pentane

**1H-NMR** (600 MHz, CDCl₃): δ = 7.27–7.29 (m, 2 H), 7.46-7.48 (m, 1 H), 7.53–7.55 (m, 1 H), 7.57 (d, J = 1.9 Hz, 1 H), 7.66 (d, J = 1.9 Hz, 1 H) ppm.

**13C-NMR** (150 MHz, CDCl₃): δ = 120.9, 123.2, 128.2, 128.4, 128.5, 129.1, 130.3, 133.8, 134.6, 134.7, 136.5, 138.2 ppm.

**m.p.**: 108 °C.

**IR** (ATR): ν (cm⁻¹) = 3082, 3057, 2922, 1530, 1378, 1248.

**UV** (CH₃CN): λ_max (lg ε) = 264 nm (4.30), 244 (4.13), 205 (4.56).

1-Methoxythianthrene (3aj)

Dithioloimine 1a (8.3 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2j (24.6 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3aj (11.8 mg, 48.0 µmol, 96%) was obtained as a white solid.

Column: pentane:EtOAc = 100:1

$^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 3.92$ (s, 3 H), 6.81 (dd, $J = 8.2$, 1.0 Hz, 1 H), 7.09 (dd, $J = 7.8$, 1.1 Hz, 1 H) 7.19 (d, $J = 8.0$ Hz, 1 H) 7.20–7.25 (m, 2 H), 7.43–7.46 (m, 1 H), 7.52–7.55 (m, 1 H) ppm.

$^{13}$C-NMR (150 MHz, CDCl$_3$): $\delta = 56.2$, 109.4, 121.2, 123.9, 127.6, 127.7, 128.1, 128.5, 129.0, 135.0, 135.5, 136.2, 156.8 ppm.

m.p.: 83 °C.

IR (ATR): $\bar{\nu}$ (cm$^{-1}$) = 3059, 3007, 2833, 1570, 1557, 1453, 1425, 1260.

UV (CH$_3$CN): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 292 nm (3.67), 257 (4.41), 242 (4.20).

HRMS-EI: C$_{13}$H$_{10}$OS$_2$ calcd for [M]$^+$: 246.0173, found: 246.0177.
2,3-Dimethoxythianthrene (3ak)

Dithiolouimine 1a (8.3 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2k (26.9 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3ak (8.8 mg, 31.9 µmol, 64%) was obtained as a white solid.

**Column**: pentane:EtOAc = 40:1

**$^1$H-NMR** (600 MHz, CDCl$_3$): $\delta$ = 3.87 (s, 6 H), 7.00 (s, 2 H), 7.22–7.25 (m, 2 H), 7.47–7.51 (m, 2 H) ppm.

**$^{13}$C-NMR** (150 MHz, CDCl$_3$): $\delta$ = 56.2, 111.8, 126.8, 127.6, 128.7, 136.3, 148.9 ppm.

**m.p.**: 113 °C.

**IR (ATR)**: $\tilde{\nu}$ (cm$^{-1}$) = 3003, 2932, 2840, 1584, 1427, 1251.

**UV (CH$_3$CN)**: $\lambda_{\text{max}}$ (lg $\varepsilon$) = 300 nm (3.44), 259 (4.37), 240 (4.36), 226 (4.32), 201 (4.56).

**HRMS-EI**: C$_{14}$H$_{12}$O$_2$S$_2$ calcd for [M]$^+$: 276.0279, found: 276.0294.
Dithioloimine 1a (8.3 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2l (37.3 mg, 125 µmol, 2.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3al (8.1 mg, 37.3 µmol, 75%) was obtained as a purple solid.

**Column:** pentane:EtOAc = 25:1

$^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.27$–$7.31$ (m, 2 H), 7.37 (dd, $J = 5.1$, 0.6 Hz, 1 H), 7.45–7.48 (m, 1 H), 7.48–7.52 (m, 1 H), 8.40 (d, $J = 5.1$ Hz, 1 H), 8.60 (s, 1 H) ppm.

$^{13}$C-NMR (150 MHz, CDCl$_3$): $\delta = 122.8$, 128.2, 128.4, 128.9, 129.2, 131.8, 133.3, 133.9, 146.5, 147.9, 148.0 ppm.

**m.p.:** 78 °C.

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3051, 2921, 2851, 1545, 1443, 1389, 1266, 1107.

**UV** (CH$_3$CN): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 276 nm (3.41), 257 (4.17), 239 (4.00).

**HRMS-EI:** C$_{11}$H$_7$N$_1$S$_2$ calcd for [M]$^+$: 217.0020, found: 217.0037.
2-Methylthianthrene (3ba) = (3ab)

Dithioloimine 1b (9.1 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2a (22.4 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3ba (8.2 mg, 35.6 µmol, 71%) was obtained as a white solid.

Analytical data were identical with compound 3ab.
2-Methylbenzo[b]thianthrene (3be)

Dithiololimine 1b (9.1 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2e (26.1 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.00 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.00 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3be (7.7 mg, 27.5 µmol, 55%) was obtained as a white solid.

Column: pentane

$^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ = 2.33 (s, 3 H), 7.06 (ddd, $J$ = 7.9, 1.8, 0.7 Hz, 1 H), 7.35 (dd, $J$ = 1.1, 0.3 Hz, 1 H), 7.40 (d, $J$ = 7.9 Hz, 1 H), 7.43–7.50 (m, 2 H), 7.72–7.75 (m, 2 H), 7.96 (s, 2 H) ppm.

$^{13}$C-NMR (150 MHz, CDCl$_3$): $\delta$ = 20.9, 126.5, 126.6, 127.0, 127.2, 127.2, 128.6, 128.6, 129.5, 132.0, 132.6, 132.6, 133.4, 133.6, 135.4, 137.9 ppm.

m.p.: 145 °C.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3034, 2915, 1567, 1487, 1463, 1104.

UV (CH$_3$CN): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 344 nm (2.91), 276 (4.41), 258 (4.49), 232 (4.63), 215 (4.62), 196 (4.43).

HRMS-EI: C$_{17}$H$_{12}$S$_2$ calcd for [M]$^+$: 280.0380, found: 280.0394.
2,3-Difluoro-7-methylthianthrene (3bh)

Dithioloimine 1b (9.1 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2h (25.1 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3bh (8.2 mg, 30.8 µmol, 62%) was obtained as a white solid.

**Column:** pentane

**1H-NMR** (600 MHz, CDCl$_3$): $\delta$ = 2.33 (s, 3 H), 7.08 (ddd, $J = 7.9, 1.8, 0.7$ Hz, 1 H), 7.28–7.32 (m, 3 H), 7.35 (d, $J = 7.9$ Hz, 1 H) ppm.

**13C-NMR** (150 MHz, CDCl$_3$): $\delta$ = 20.9, 117.3–117.3 (m), 117.3–117.5 (m), 128.6, 129.0, 129.4, 131.4, 132.1 (dd, $J = 5.8, 3.8$ Hz), 132.3 (dd, $J = 5.8, 4.0$ Hz), 134.8, 138.4, 148.9 (dd, $J = 15.3, 1.7$ Hz), 150.5 (dd, $J = 15.2, 1.3$ Hz) ppm.

**19F-NMR** (376 MHz, CDCl$_3$): $\delta$ = -138.6, -138.6 ppm.

**m.p.:** 82 °C.

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3036, 2926, 1593, 1478, 1277.

**UV** (CH$_3$CN): $\lambda_{max}$ (lg $\varepsilon$) = 255 nm (4.41), 242 (4.19).

**HRMS-EI:** C$_{13}$H$_8$F$_2$S$_2$ calcd for [M]$^+$: 266.0030, found: 266.0036.
2,3-Dimethoxy-7-methylthianthrene (3bk)

Dithioloimine 1b (9.1 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2k (26.9 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3bk (10.2 mg, 35.1 µmol, 70%) was obtained as a white solid.

**Column**: pentane:EtOAc = 40:1

**^1H-NMR** (600 MHz, CDCl₃): δ = 2.32 (s, 3 H), 3.87 (s, 6 H), 7.00 (s, 2 H), 7.03–7.06 (m, 1 H), 7.31–7.33 (m, 1 H), 7.36 (d, J = 7.9 Hz, 1 H) ppm.

**^13C-NMR** (150 MHz, CDCl₃): δ = 20.7, 55.9, 111.5, 111.5, 126.7, 127.0, 128.2, 128.2, 129.0, 132.5, 135.9, 137.5, 148.6, 148.6 ppm.

**m.p.**: 87 °C.

**IR** (ATR): ν (cm⁻¹) = 3048, 2918, 1443, 1121, 1035.

**UV** (CH₃CN): λ_max (lg ε) = 258 nm (4.61), 242 (4.27).

2,3-Diphenylbenzo[5,6][1,4]dithiino[2,3-g]quinoxaline (3ca)

Dithioloimine 1c (18.6 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2a (22.4 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (2 mL) were reacted as described in the GP1. Compound 3ca (14.4 mg, 34.3 µmol, 69%) was obtained as a yellow solid.

**Column:** pentane:EtOAc = 10:1

**$^1$H-NMR** (300 MHz, CDCl$_3$): $\delta = 7.28$–7.38 (m, 8 H), 7.47–7.52 (m, 4 H), 7.55 (dd, $J = 5.8$, 3.3 Hz, 2 H), 8.25 (s, 2 H) ppm.

**$^{13}$C-NMR** (75 MHz, CDCl$_3$): $\delta = 127.4$, 128.1, 128.3, 128.9, 129.0, 129.8, 134.4, 138.1, 138.7, 140.6, 153.8 ppm.

**m.p.:** 144 °C.

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3055, 2922, 1431, 1338, 1075.

**UV** (CH$_3$CN): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 386 nm (4.11), 287 (4.57), 256 (4.50), 207 (4.61).

**HRMS-ESI:** C$_{26}$H$_{16}$N$_2$S$_2$ calcd for [M+H]$^+$: 421.0828, found: 421.0828.
1,7-Dimethylthianthrene (3bc) and 1,8-Dimethylthianthrene (3bc')

Dithioloimine 1b (9.1 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2c (23.4 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3bj and 3bj' (7.8 mg, 32.0 µmol, 64%) were obtained as a colorless oil as inseparable mixture of regioisomers (ratio of 1:1).

Column: pentane

$^1$H-NMR (600 MHz, CDCl$_3$): δ = 2.32 (s, 6 H), 2.49 (s, 6 H), 7.01–7.07 (m, 2 H), 7.10–7.14 (m, 4 H), 7.29–7.41 (m, 6 H) ppm.

$^{13}$C-NMR (150 MHz, CDCl$_3$): δ = 20.9, 21.0, 21.0, 126.6, 126.6, 127.0, 127.0, 128.2, 128.4, 128.6, 128.9, 129.1, 129.5, 131.9, 132.5, 135.2, 135.3, 135.5, 135.6, 135.8, 135.9, 137.3, 137.4, 137.7, 137.9 ppm.

HRMS-EI: C$_{14}$H$_{12}$S$_2$ calcd for [M]$^+$: 244.0375, found: 244.0381.
1-Methoxy-7-methylthianthrene (3bj) and 1-Methoxy-8-methylthianthrene (3bj′)

Dithiolooimine 1b (9.1 mg, 50.0 µmol, 1.0 equiv.), aryne precursor 2j (24.6 mg, 75.0 µmol, 1.5 equiv.), KF (8.7 mg, 150 µmol, 3.0 equiv.) and 18-Crown-6 (39.6 mg, 150 µmol, 3.0 equiv.) in MeCN (1 mL) were reacted as described in the GP1. Compound 3bj and 3bj′ (10.3 mg, 39.6 µmol, 79%) were obtained as a colorless oil as inseparable mixture of regioisomers (ratio of 2:1).

**Column:** pentane

**1H-NMR** (600 MHz, CDCl$_3$): δ = 2.30 (s, 3 H), 2.31 (s, 3 H), 3.91 (s, 3 H), 6.79–6.81 (m, 2 H), 7.01–7.05 (m, 2 H), 7.07–7.10 (m, 2 H), 7.16–7.20 (m, 2 H), 7.27–7.28 (m, 1 H), 7.32 (d, $J = 7.7$ Hz, 1 H), 7.36–7.37 (m, 1 H), 7.41 (d, $J = 7.9$ Hz, 1 H) ppm.

**13C-NMR** (150 MHz, CDCl$_3$): δ = 20.9, 20.9, 56.2, 56.2, 109.3, 109.3, 121.2, 121.2, 124.0, 124.3, 128.0, 128.0, 128.3, 128.5, 128.6, 128.7, 129.1, 129.6, 131.4, 132.0, 134.9, 135.4, 136.3, 136.7, 137.7, 137.9, 156.7, 156.8 ppm.

**HRMS-EI:** C$_{14}$H$_{12}$OS$_2$ calcd for [M]$^+$: 260.0330, found: 260.0340.
Dimethyl benzo[b][1,4]dithiine-2,3-dicarboxylate (7aa)

Dithioloiimine 1a (33.2 mg, 200 µmol, 1.0 equiv.), KF (34.8 mg, 600 µmol, 3.0 equiv.), 18-Crown-6 (158 mg, 600 µmol, 3.0 equiv.) and acetylene dicarboxylic acid dimethylester (4a) (42.6 mg, 300 µmol, 1.5 equiv.) in MeCN (2 mL) were reacted as described in the GP2. Compound 7aa (46.2 mg, 149 µmol, 75%) was obtained as a yellow solid.

**Column**: pentane:EtOAc = 50:1

**\(^{1}\)H-NMR** (300 MHz, CDCl\(_3\)): \(\delta = 3.85\) (s, 6 H), 7.25–7.32 (m, 2 H), 7.37–7.44 (m, 2 H) ppm.

**\(^{13}\)C-NMR** (75 MHz, CDCl\(_3\)): \(\delta = 53.7, 129.0, 129.1, 133.4, 135.8, 163.4\) ppm.

**m.p.:** 62 °C.

**IR** (ATR): \(\tilde{\nu}\) (cm\(^{-1}\)) = 2951, 1718, 1579, 1451, 1235.

**UV** (CH\(_3\)CN): \(\lambda_{\text{max}}\) (lg \(\varepsilon\)) = 355 nm (2.97), 270 (3.96), 234 (4.15).

**HRMS-ESI**: C\(_{12}\)H\(_{10}\)O\(_4\)S\(_2\) calcd for [M+Na]\(^+\): 304.9913, found: 304.9915.
2-Methylbenzo[b]thianthrene (7ab)

Dithioloimine 1a (83.5 mg, 500 µmol, 1.0 equiv.), KF (87.2 mg, 1.50 mmol, 3.0 equiv.), 18-Crown-6 (396 mg, 1.50 mmol, 3.0 equiv.) and ethyl propynoate (4b) (106 mg, 750 µmol, 1.5 equiv.) in MeCN (5 mL) were reacted as described in the GP2. Compound 7ab (67.4 mg, 283 µmol, 57%) was obtained as a yellow oil.

Column: pentane:EtOAc:toluene = 250:1:0.1

\[ ^1H-NMR \ (300 \text{ MHz, CDCl}_3): \delta = 1.33 \ (t, J = 7.1 \text{ Hz, } 3 \text{ H}), \ 4.28 \ (q, J = 7.1 \text{ Hz, } 2 \text{ H}), \ 7.18–7.23 \ (m, 3 \text{ H}), \ 7.26–7.38 \ (m, 1 \text{ H}), \ 7.59 \ (s, 1 \text{ H}) \text{ ppm.} \]

\[ ^{13}C-NMR \ (75 \text{ MHz, CDCl}_3): \delta = 14.2, 62.0, 127.6, 128.1, 128.1, 128.4, 128.7, 131.5, 132.2, 135.4, 161.3 \text{ ppm.} \]

IR (ATR): \( \tilde{\nu} \ (\text{cm}^{-1}) = 2980, 1705, 1575, 1451, 1220. \)

UV (CH\textsubscript{3}CN): \( \lambda_{\text{max}} \ (\text{lg } \varepsilon) = 356 \text{ nm (2.96), 256 (4.17).} \)

HRMS-EI: C\textsubscript{11}H\textsubscript{10}O\textsubscript{2}S\textsubscript{2} calcd for [M]\textsuperscript{+}: 238.0117, found: 238.0130.
1-(Benzo[b][1,4]dithiin-2-yl)ethanone (7ac)

Dithioloiimine 1a (33.2 mg, 200 µmol, 1.0 equiv.), Cs$_2$CO$_3$ (90.6 mg, 600 µmol, 3.0 equiv.) and but-3-yn-2-one (4ac) (20.4 mg, 300 µmol, 1.5 equiv.) in MeCN (2 mL) were reacted as described in the GP3. Compound 7ac (29.7 mg, 143 µmol, 72%) was obtained as a yellow oil.

**Column:** pentane:EtOAc = 100:1

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 2.43 (s, 3 H), 7.19–7.24 (m, 3 H), 7.28–7.32 (m, 1 H), 7.51 (s, 1 H) ppm.

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 26.3, 127.5, 128.1, 128.6, 128.9, 131.3, 132.1, 135.9, 137.6, 190.2 ppm.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3038, 1666, 1542, 1452, 1358, 1222.

UV (CH$_3$CN): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 374 nm (3.03), 269 (4.13), 232 (4.10).

1-(3-Phenylbenzo[b][1,4]dithiin-2-yl)ethanone (7ad)

Dithioloimine 1a (33.2 mg, 200 µmol, 1.0 equiv.), Cs$_2$CO$_3$ (90.6 mg, 600 µmol, 3.0 equiv.) and 4-phenyl-3-butyne-2-one (4ad) (43.2 mg, 300 µmol, 1.5 equiv.) in MeCN (2 mL) were reacted as described in the GP3. Compound 7ad (43.9 mg, 154 µmol, 77%) was obtained as a yellow oil.

**Column:** pentane:EtOAc = 80:1 → 30:1

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 1.84 (s, 3 H), 7.25–7.32 (m, 2 H), 7.37–7.49 (m, 7 H) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 29.7, 127.5, 127.9, 128.4, 128.6, 128.8, 129.8, 130.2, 131.2, 135.1, 135.4, 136.6, 149.5, 196.9 ppm.

**IR (ATR):** $\tilde{\nu}$ (cm$^{-1}$) = 359 nm (3.22), 264 (4.14), 242 nm (4.29).

**UV (CH$_3$CN):** $\lambda_{\text{max}}$ (lg $\varepsilon$) = 3055, 1667, 1570, 1426, 1239, 1196.

**HRMS-ESI:** C$_{16}$H$_{12}$OS$_2$ calcd for [M+Na]$^+$: 307.0222, found: 307.0225.
Dimethyl 6-methylbenzo[b][1,4]dithiine-2,3-dicarboxylate (7ba)

Dithioloimine 1b (90.5 mg, 500 µmol, 1.0 equiv.), KF (87.2 mg, 1.50 mmol, 3.0 equiv.), 18-Crown-6 (396 mg, 1.50 mmol, 3.0 equiv.) and acetylene dicarboxylic acid dimethylester (4a) (106 mg, 750 µmol, 1.5 equiv.) in MeCN (5 mL) were reacted as described in the GP2. Compound 7ba (106 mg, 358 µmol, 72%) was obtained as a yellow solid.

**Column:** pentane:EtOAc = 50:1

1H-NMR (400 MHz, CDCl₃): δ = 2.31 (s, 3 H), 3.84 (s, 6 H), 7.08 (ddd, J = 8.0, 1.7, 0.7 Hz, 1 H), 7.20–7.22 (m, 1 H), 7.25–7.27 (m, 1 H) ppm.

13C-NMR (100 MHz, CDCl₃): δ = 20.7, 53.2, 128.2, 129.1, 129.4, 129.5, 132.9, 135.3, 135.7, 139.0, 163.0 ppm.

m.p.: 65 °C.

IR (ATR): ν (cm⁻¹) = 2952, 1720, 1575, 1432, 1240, 1012.

UV (CH₃CN): λ_max (lg ε) = 354 nm (2.94), 271 (3.93), 235 (4.21).

Dimethyl 7,8-diphenyl-[1,4]dithiino[2,3-g]quinoxaline-2,3-dicarboxylate (7ca)

Dithioloimine 1c (26.0 mg, 70 µmol, 1.0 equiv.), KF (12.2 mg, 210 µmol, 3.0 equiv.) and 18-Crown-6 (55.4 mg, 210 µmol, 3.0 equiv.) and acetylene dicarboxylic acid dimethylester (4a) (14.9 mg, 105 µmol, 1.5 equiv.) in MeCN (1.4 mL) were reacted as described in the GP2. Compound 7ca (25.6 mg, 52.6 µmol, 75%) was obtained as a yellow solid.

**Column:** pentane:EtOAc = 20:1

**1H-NMR** (400 MHz, CDCl₃): δ = 3.89 (s, 6 H), 7.30–7.40 (m, 6 H), 7.47–7.50 (m, 4 H), 8.12 (s, 2 H) ppm.

**13C-NMR** (100 MHz, CDCl₃): δ = 53.5, 127.6, 128.3, 129.2, 129.8, 134.3, 134.8, 138.4, 140.9, 154.4, 162.8 ppm.

**m.p.:** 151 °C.

**IR** (ATR): v (cm⁻¹) = 2954, 1719, 1577, 1434, 1248.

**UV** (CH₃CN): λ_max (lg ε) = 384 nm (4.12), 288 (4.46), 238 (4.57).

**Dimethyl [1,4]dithiino[2',3':4,5]benzo[1,2-c][1,2,5]thiadiazole-6,7-dicarboxylate (7da)**

![Chemical Structure](attachment:structure.png)

Dithioloimine **1d** (22.4 mg, 100 µmol, 1.0 equiv.), KF (17.5 mg, 300 µmol, 3.0 equiv.), 18-Crown-6 (79 mg, 300 µmol, 3.0 equiv.) and acetylene dicarboxylic acid dimethylester (**4a**) (21.3 mg, 150 µmol, 1.5 equiv.) in MeCN (2 mL) were reacted as described in the **GP2**. Compound **7da** (22.5 mg, 66.2 µmol, 66%) was obtained as a yellow solid.

**Column:** pentane:EtOAc = 20:1

**1H-NMR** (400 MHz, CDCl3): δ = 3.89 (s, 6 H), 8.02 (s, 2 H) ppm.

**13C-NMR** (100 MHz, CDCl3): δ = 53.5, 119.3, 134.4, 135.7, 154.3, 162.7 ppm.

**m.p.:** 92 °C.

**IR (ATR):** ν (cm⁻¹) = 2958, 1709, 1569, 1427, 1224, 1075.

**UV** (CH₃CN): λₘₐₓ (lg ε) = 366 nm (3.95), 294 (3.84), 281 (3.90), 231 (4.42).

2-Methylbenzo[b]thianthrene (9)

![Chemical structure of 2-Methylbenzo[b]thianthrene (9)]

To a stirred solution of 2-thiocyanatopyrrole (8a)\textsuperscript{[4]} (12.4 mg, 100 µmol, 1.0 equiv.) and aryne precursor 2a (44.7 mg, 1.50 mmol, 1.5 equiv.) in THF (4 mL) at 50 °C was added in one portion TBAF (1 M in THF, 600 µL, 600 µmol, 6.0 equiv.) and stirred for addition 10 min. After cooling to room temperature the solvent was removed \textit{in vacuo} and the residue was purified by column chromatography on basic alumina oxide (pentane:EtOAc = 200:1) to obtain the title compound 9 (7.8 mg, 45.1 µmol, 45%) as a white solid.

The analytical data were in accordance with the reported ones.\textsuperscript{[5]}
1-(3-Phenylpyrrolo[2,1-b]thiazol-2-yl)ethanone (10ad)

To a solution of 4-phenyl-3-butyne-2-one (4d) (576 mg, 4.00 mmol, 20 equiv.) and Cs₂CO₃ (98 mg, 300 µmol, 1.5 equiv.) in MeCN (2 mL) was added dropwise 2-thiocyanatopyrrole (8a) (24.8 mg, 200 µmol, 1.0 equiv.) dissolved in MeCN (1 mL) over 10 min at room temperature. Afterwards, the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (pentane:EtOAc = 50:1→30:1) to obtain the title compound 10ad (24.3 mg, 101 µmol, 50%) as a brown oil.

**¹H-NMR** (300 MHz, CDCl₃): δ = 2.02 (s, 3 H), 6.23 (dd, J = 3.6, 1.2 Hz, 1 H), 6.59 (dd, J = 3.6, 3.0 Hz, 1 H), 6.72 (dd, J = 3.0, 1.2 Hz, 1 H), 7.47–7.59 (m, 2 H) 7.58–7.62 (m, 3 H) ppm.

**¹³C-NMR** (75 MHz, CDCl₃): δ = 28.8, 98.5, 111.2, 117.1, 128.7, 129.0, 129.4, 129.6, 129.7, 130.7, 137.9, 191.3 ppm.

**IR (ATR):** ν (cm⁻¹) = 3058, 1646, 1563, 1449, 1330, 1195.

**UV (CH₃CN):** λmax (lg ε) = 369 nm (3.46), 294 (4.04), 227 (4.17).

Dimethyl 5-ethylpyrrolo[2,1-b]thiazole-2,3-dicarboxylate (10ba)

To a solution of acetylene dicarboxylic acid dimethylester (4a) (568 mg, 4.00 mmol, 20 equiv.) and Cs₂CO₃ (98 mg, 300 µmol, 1.5 equiv.) in MeCN (2 mL) was added dropwise thiocyanatopyrrole 8b (33.5 mg, 200 µmol, 1.0 equiv.) dissolved in MeCN (1 mL) over 10 min at room temperature. Afterwards, the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (pentane:EtOAc = 50:1). Afterwards, drying in high vacuo to remove volatile impurities, the title compound 11ba (33.9 mg, 128 µmol, 63%) was obtained as a yellow solid.

¹H-NMR (400 MHz, CDCl₃): δ = 1.27 (t, J = 7.4 Hz, 3 H), 2.64 (qd, J = 7.4, 1.0 Hz, 2 H), 3.87 (s, 3 H), 4.04 (s, 3 H), 6.16 (d, J = 3.7 Hz, 1 H), 6.37 (dt, J = 3.7, 1.0 Hz, 1 H) ppm.

¹³C-NMR (100 MHz, CDCl₃): δ = 12.3, 19.4, 52.7, 53.6, 97.7, 114.0, 117.5, 128.5, 130.4, 161.5, 161.8 ppm.

m.p.: 78 °C.

IR (ATR): v (cm⁻¹) = 2950, 1735, 1708, 1581, 1316, 1236.

UV (CH₃CN): λ max (lg ε) = 369 nm (3.24), 285 (3.99), 228 (4.13).

Ethyl 5-ethylpyrrolo[2,1-b]thiazole-2-carboxylate (10bb)

To a solution of ethyl propynoate (4b) (392 mg, 4.00 mmol, 20 equiv.) and Cs₂CO₃ (98 mg, 300 µmol, 1.5 equiv.) in MeCN (2 mL) was added dropwise thiocyanatopyrrole 8b (33.5 mg, 200 µmol, 1.0 equiv.) dissolved in MeCN (1 mL) over 10 min at room temperature. Afterwards, the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (pentane:EtOAc = 70:1). Afterwards, drying in high vacuo to remove volatile impurities, the title compound 10bb (27.1 mg, 122 µmol, 61%) was obtained as a yellow oil.

¹H-NMR (300 MHz, CDCl₃): δ = 1.31 (t, J = 7.5 Hz, 3 H), 1.38 (t, J = 7.1 Hz, 3 H), 2.78 (qd, J = 7.5, 0.9 Hz, 2 H), 4.36 (q, J = 7.1 Hz, 2 H), 6.10 (dd, J = 3.6, 0.7 Hz, 1 H), 6.33 (dt, J = 3.6, 1.0 Hz, 1 H), 7.98 (d, J = 0.7 Hz, 1 H) ppm.

¹³C-NMR (75 MHz, CDCl₃): δ = 12.6, 14.3, 19.9, 61.5, 97.2, 112.8, 120.0, 124.6, 127.3, 128.8, 162.2 ppm.

IR (ATR): ν (cm⁻¹) = 3112, 2938, 1706, 1582, 1225.

UV (CH₃CN): λmax (lg ε) = 354 nm (3.30), 282 (4.02), 229 (4.08).

Observed side products to support the mechanistic scenario

Phenyl(2-thiocyanatophenyl)sulfane (12a)

\[ \text{Ph} = \text{N} \quad \text{S} \quad \text{N} \]

1H-NMR (600 MHz, CDCl₃): \( \delta = 7.19–7.22 \) (m, 2 H), 7.26–7.28 (m, 1 H), 7.29–7.34 (m, 2 H), 7.34–7.36 (m, 1 H), 7.43–7.48 (m, 2 H), 7.76 (ddd, \( J = 8.0, 1.3, 0.4 \) Hz, 1 H) ppm.

13C-NMR (150 MHz, CDCl₃): \( \delta = 110.4, 127.4, 128.7, 129.4, 129.5, 129.6, 130.2, 131.0, 133.0, 134.2, 135.3 \) ppm.

GCMS-EI: C₁₃H₉NS₂  found: 243.1.

In the case of the thianthrene synthesis starting from aryne precursor 2a and benzodithioiloimine 1a traces of compound 12a were isolated.

(E)-Ethyl 3-((2-thiocyanatophenyl)thio)acrylate (13b)

\[ \text{Ph} = \text{N} \quad \text{S} \quad \text{CO₂Et} \]

GCMS-EI: C₁₂H₁₁NO₂S₂  found: 243.1.

In the case of the benzo[b][1,4]dithiine synthesis the side product 13b could not be isolated and was just observed by GC-MS.

Because of the observation of these side products which are protonated species of the proposed intermediates A and B in Scheme 4, the proposed mechanistic scenarios seem to be plausible.
1,2-Dithiocyanatobenzene (6a)

\[ \text{H-NMR (600 MHz, CDCl}_3\text{)} \]

\[ \text{\textsuperscript{13}C-NMR (150 MHz, CDCl}_3\text{)} \]
4-Methyl-1,2-dithiocyanatobenzene (6b)

\[ \text{H-NMR (600 MHz, CDCl}_3 \text{)} \]

\[ \text{C-NMR (150 MHz, CDCl}_3 \text{)} \]

\[ ^{1} \text{H-NMR (600 MHz, CDCl}_3 \text{)} \]

\[ ^{13} \text{C-NMR (150 MHz, CDCl}_3 \text{)} \]
Benzo[d][1,3]dithiol-2-imine (1a)
5-methylbenzo[d][1,3]dithiol-2-imine (1b)

$^1$H-NMR (300 MHz, CDCl$_3$)

$^{13}$C-NMR (75 MHz, CDCl$_3$)
6,7-Diphenyl-[1,3]dithiolo[4,5-g]quinoxalin-2-imine (1c)

$^1$H-NMR (300 MHz, $d_6$-DMSO)

$^{13}$C-NMR (75 MHz, $d_6$-DMSO)
2-Ethyl-5-thiocyanato-1H-pyrrole (8b)

$^{1}$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
2-Methylthianthrene (3ab)

$^1$H-NMR (600 MHz, CDCl$_3$)

$^{13}$C-NMR (150 MHz, CDCl$_3$)
1-Methylthianthrene (3ac)

$^{1}H$-NMR (600 MHz, CDCl$_3$)

$^{13}C$-NMR (150 MHz, CDCl$_3$)
2,3-Dihydro-1H-cyclopenta[b]thianthrene (3ad)
Benzo[b]thianthrene (3ae)

^1H-NMR (600 MHz, CDCl$_3$)

$^{13}$C-NMR (150 MHz, CDCl$_3$)
Benzo[a]thianthrene (3af)

$^{1}H$-NMR (600 MHz, CDCl$_3$)

$^{13}C$-NMR (150 MHz, CDCl$_3$)
2-Chlorothianthrene (3ag)

$^1$H-NMR (600 MHz, CDCl$_3$)

$^{13}$C-NMR (150 MHz, CDCl$_3$)
2,3-Difluorothianthrene (3ah)

$\text{H-NMR (600 MHz, CDCl}_3$)

$\text{C-NMR (150 MHz, CDCl}_3$)

$\text{H-NMR (600 MHz, CDCl}_3$)

$\text{C-NMR (150 MHz, CDCl}_3$)
$^{19}$F-NMR (376 MHz, CDCl$_3$)
1,3-Dibromothianthrene (3ai)

$^1$H-NMR (600 MHz, CDCl$_3$)

$^{13}$C-NMR (150 MHz, CDCl$_3$)
1-Methoxythianthrene (3aj)

$^1$H-NMR (600 MHz, CDCl$_3$)

$^{13}$C-NMR (150 MHz, CDCl$_3$)
2,3-Dimethoxythianthrene (3ak)

$\text{H-NMR (600 MHz, CDCl}_3\text{)}$

$\text{C-NMR (150 MHz, CDCl}_3\text{)}$
Benzo[5,6][1,4]dithiino[2,3-c]pyridine (3ai)

1H-NMR (600 MHz, CDCl₃)

13C-NMR (150 MHz, CDCl₃)
2-Methylbenzo[b]thianthrene (3be)

\[\text{H-NMR (600 MHz, CDCl}_3\text{)}\]

\[\text{\textsuperscript{13}C-NMR (150 MHz, CDCl}_3\text{)}\]
2,3-difluoro-7-methylthianthrene (3bh)

\[
\text{H-NMR (600 MHz, CDCl}_3\text{)}
\]

\[
\text{C-NMR (150 MHz, CDCl}_3\text{)}
\]
$^{19}$F-NMR (376 MHz, CDCl$_3$)
2,3-dimethoxy-7-methylthianthrene (3bk)

$^1$H-NMR (600 MHz, CDCl$_3$)

$^{13}$C-NMR (150 MHz, CDCl$_3$)
2,3-Diphenylbenzo[5,6][1,4]dithiino[2,3-g]quinoxaline (3ca)

$\mathrm{^1H-NMR\ (300\ MHz,\ CDCl_3)}$

$\mathrm{^{13}C-NMR\ (75\ MHz,\ CDCl_3)}$
1-Methoxy-7-methylthianthrene (3bj) and 1-Methoxy-8-methylthianthrene (3bj')

\[ \text{H-NMR (600 MHz, CDCl}_3\text{)} \]

\[ \text{C-NMR (150 MHz, CDCl}_3\text{)} \]
1,7-dimethylthianthrene (3bc) and 1,8-dimethylthianthrene (3bc′)

$^{1}H$-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
Dimethyl benzo[b][1,4]dithiine-2,3-dicarboxylate (7aa)
2-Methylbenzo[b]thianthrene (7ab)

\(^1\)H-NMR (300 MHz, CDCl\(_3\))

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\))
1-(Benzo[b][1,4]dithiin-2-yl)ethanone (7ac)
1-(3-Phenylbenzo[\(b\)][1,4]dithiin-2-yl)ethanone (7ad)

\[ \text{\(^1H-NMR (300 MHz, CDCl}_3\)} \]

\[ \text{\(^{13}C-NMR (75 MHz, CDCl}_3\)} \]
Dimethyl 6-methylbenzo[b][1,4]dithiine-2,3-dicarboxylate (7ba)

$\text{^1H-NMR (400 MHz, CDCl}_3\text{)}$

$\text{^13C-NMR (100 MHz, CDCl}_3\text{)}$
Dimethyl 7,8-diphenyl-[1,4]dithiino[2,3-g]quinoxaline-2,3-dicarboxylate (7ca)
Dimethyl [1,4]dithiino[2',3':4,5]benzo[1,2-c][1,2,5]thiadiazole-6,7-dicarboxylate (7da)
1-(3-Phenylpyrrolo[2,1-\(b\)]thiazol-2-yl)ethanone (10ad)

\(^1\)H-NMR (300 MHz, CDCl\(_3\))

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\))
Dimethyl 5-ethylpyrrolo[2,1-b]thiazole-2,3-dicarboxylate (10ba)

$\text{H-NMR (400 MHz, CDCl}_3\text{)}$

$\text{C-NMR (100 MHz, CDCl}_3\text{)}$
Ethyl 5-ethylpyrrolo[2,1-b]thiazole-2-carboxylate (10bb)

$\text{H-NMR (300 MHz, CDCl}_3$)

$\text{C-NMR (75 MHz, CDCl}_3$)
Phenyl(2-thiocyanatophenyl)sulfane (12a)

$^1$H-NMR (600 MHz, CDCl$_3$)

$^{13}$C-NMR (150 MHz, CDCl$_3$)
Literature:


