Electronic Supplementary Material (ESI) for ChemComm.

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

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Supplementary information

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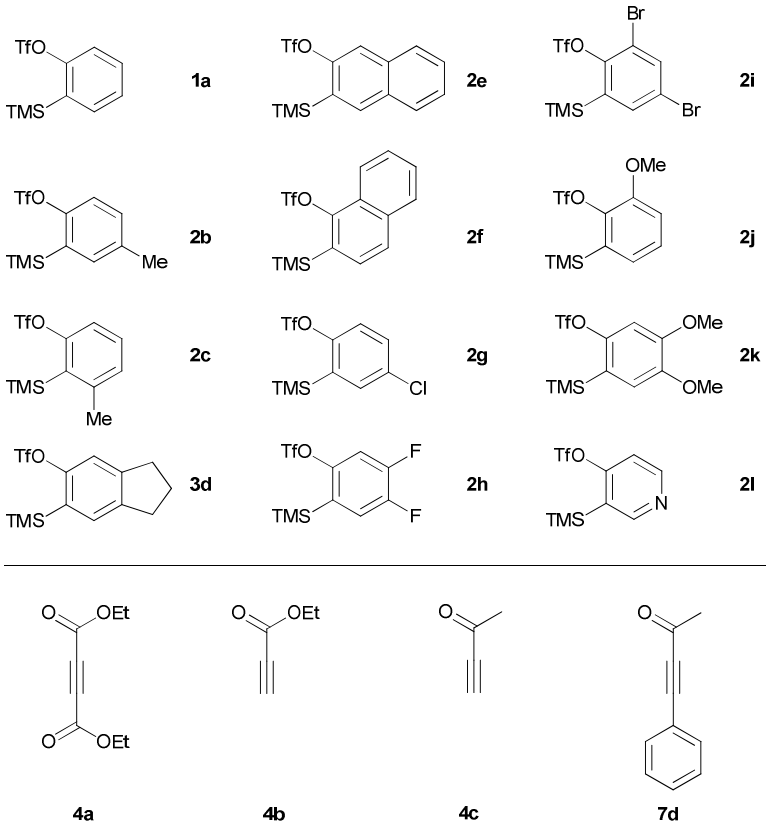
General experimental

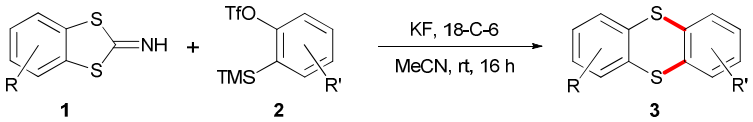
All solvents were distilled before use unless otherwise stated. Air and moisture sensitive reactions were carried out in oven-dried or flame-dried glassware, septum-capped under atmospheric pressure of argon. Commercially available compounds were used without further purification unless otherwise stated.

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) δ = 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)

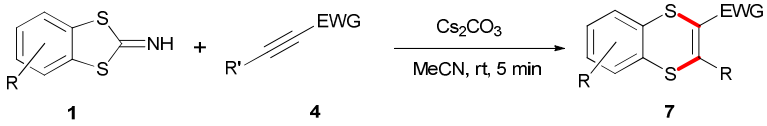


A mixture of dithioloimine **1** (1.0 equiv.), KF (3.0 equiv.) and 18-Crown-6 (3.0 equiv.) was prestirred in MeCN (0.05 M) for 2 min. Afterwards aryne precursor **2** (1.5 equiv.) was added and the reaction was further stirred at room temperature for additional 16 h. The solvent was removed *in vacuo*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

General procedure for EWG-alkyne reaction (GP2)

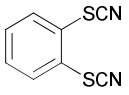
A mixture of dithioloimine **1** (1.0 equiv.), KF (3.0 equiv.) and 18-Crown-6 (3.0 equiv.) was prestirred in MeCN (0.1 M) for 2 min. Afterwards alkyne **4** (1.5 equiv.) was added dropwise at room temperature and the reaction was stirred for additional 5 min. The solvent was removed *in vacuo* and the 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_2CO_3 (3.0 equiv.) was prestirred 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.

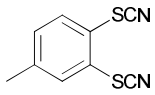
1,2-Dithiocyanatobenzene (6a)



Benzene-1,2-thiol (500 mg, 3.51 mmol, 1.00 equiv.) in CH_2Cl_2 (10 mL) was treated with trimethylamine (5 drops) and then the SO_2Cl_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_2Cl_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%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.55–7.59 (m, 2 H), 7.81–7.85 (m, 2 H) ppm.
^{13}C-NMR (150 MHz, $CDCl_3$): δ = 108.1, 126.6, 131.6, 132.9 ppm.
m.p.: 91 °C.
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3081, 2161, 1567, 1448, 1431.
UV (CH_3CN): λ_{max} (lg ε) = 279 nm (3.08), 236 (3.96), 207 (4.21).
HRMS-EI: $C_8H_4N_4S_2$ calcd for $[M]^+$: 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 CH_2Cl_2 (10 mL) was treated with trimethylamine (5 drops) and then SO_2Cl_2 (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. CH_2Cl_2 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%).

^{1}H-NMR (600 MHz, $CDCl_3$): 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.

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 21.2, 108.6, 108.6, 121.8, 127.8, 132.4, 132.8, 134.0, 143.5 ppm.

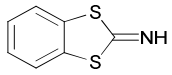
m.p.: 96 °C.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2160, 1582, 1461, 1386, 1386, 1270.

UV (CH_3CN): λ_{max} (lg ε) = 277 nm (3.02), 236 (3.98), 213 (4.26).

HRMS-EI: $C_9H_6N_2S_2$ calcd for $[M]^+$: 205.9972 , found: 205.9986.

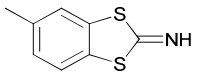
Benzo[*d*][1,3]dithiolo-2-imine (1a)



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 PPh_3 (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.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.16–7.34 (m, 4 H), 8.83 (s, 1 H) ppm.
^{13}C-NMR (150 MHz, $CDCl_3$): δ = 121.6, 122.0, 126.0, 126.2, 134.4, 134.7, 172.5 ppm.
m.p.: 122 °C.
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3176, 1700, 1550, 1431, 1236.
UV (CH_3CN): λ_{max} (lg ε) = 333 nm (2.31), 292 (3.40), 259 (3.85), 223 (4.60).
HRMS-ESI: $C_7H_5NS_2$ calcd for $[M+Na]^+$: 189,9756, found: 189.9756.

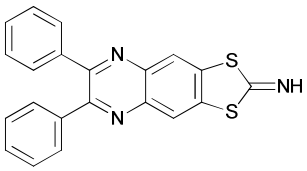
5-Methylbenzo[*d*][1,3]dithiol-2-imine (1b)



To a solution of **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 *in vacuo* and the residue was purified by column chromatography on silica gel (pentane:EtOAc = 10:1→5:1) to obtain the title compound **1b** (240 mg, 1.33 mmol, 91%) as a pale orange solid.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 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.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 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_3CN): λ_{max} (lg ε) = 323 nm (3.41), 303 (3.50), 261 (3.80), 248 (3.80), 223 (4.59).
HRMS-ESI: $C_8H_7NS_2$ calcd for $[M+H]^+$: 182.0093, found: 182.0094.

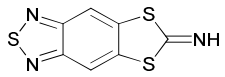
6,7-Diphenyl-[1,3]dithiolo[4,5-*g*]quinoxalin-2-imine (1c)



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 PPh_3 (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.

^{1}H-NMR (300 MHz, $DMSO_{d-6}$): 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.
^{13}C-NMR (75 MHz, $DMSO_{d-6}$): 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): $\tilde{\nu}$ (cm^{-1}) = 3167, 3063, 1577, 1344, 1225, 1100.
UV (CH_3CN): λ_{max} (lg ε) = 478 nm (2.68), 388 (4.33), 274 (4.64), 244 (4.47), 232 (4.47).
HRMS-ESI: $C_{21}H_{14}N_3S_2$ calcd for $[M+H]^+$: 372.0624, found: 372.0623.

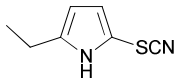
[1,3]Dithiolo[4',5':4,5]benzo[1,2-*c*][1,2,5]thiadiazol-6-imine (1d)



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 PPh_3 (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.

^{1}H-NMR, ^{13}C-NMR: Decomposition in DMSO and insoluble in other solvents.
m.p.: 90-100 °C (decomposition).
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3208, 3063, 1574, 1431, 1213, 1078.
UV (CH_3CN): λ_{max} (lg ε) = 483 nm (2.46), 368 (4.09), 358 (4.10), 226 (4.48).
HRMS-ESI: $C_7H_4N_3S_3$ calcd for $[M+H]^+$: 225.9562, found: 225.9563.

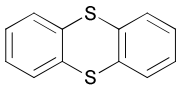
2-Ethyl-5-thiocyanatopyrrole (8b)



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}H-NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 7.6 Hz, 3 H), 2.63 (q, *J* = 7.6 Hz, 2 H), 5.98 (ddt, *J* = 3.5, 2.7, 0.8 Hz, 1 H), 6.54 (dd, *J* = 3.6, 2.7 Hz, 1 H), 8.41 (s, 1 H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 13.1, 21.1, 100.2, 107.9, 111.0, 120.8, 141.3 ppm.
m.p.: 52 °C.
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3337, 3138, 2976, 2150, 1564, 1137.
UV (CH_3CN): λ_{max} (lg ε) = 242 nm (3.91).
HRMS-EI: $C_7H_8N_2S$ calcd for $[M+Na]^+$: 175.0300, found: 175.0302.

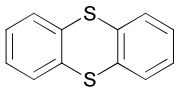
Thianthrene (3aa)



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]

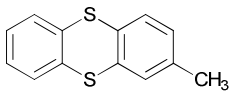
Precedure for aryne reaction starting from dithiocyanate to thianthrene (3aa)



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 PPh_3 (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]

2-Methylthianthrene (3ab)



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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 20.9, 127.5, 127.6, 128.5, 128.6, 128.7, 128.7, 129.3, 132.0, 135.4, 135.7, 135.9, 137.9 ppm.

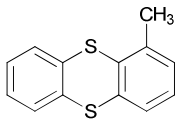
m.p.: 76 °C.

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

UV (CH_3CN): λ_{max} (lg ε) = 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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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.

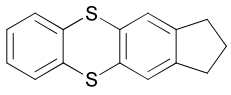
m.p.: 72 °C.

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

UV (CH_3CN): λ_{max} (lg ε) = 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.

2,3-Dihydro-1*H*-cyclopenta[*b*]thianthrene (3ad)



Dithioloimine **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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 25.7, 32.4, 124.6, 127.5, 128.7, 133.0, 136.3, 144.7 ppm.

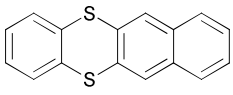
m.p.: 94 °C.

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

UV (CH_3CN): λ_{max} (lg ε) = 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

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 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.

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 126.6, 127.1, 127.2, 127.7, 128.9, 132.7, 133.2, 135.6 ppm.

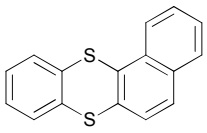
m.p.: 166 °C.

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

UV (CH_3CN): λ_{max} (lg ε) = 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.

Benzo[*a*]thianthrene (3af)



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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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.

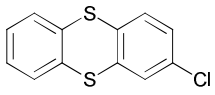
m.p.: 85 °C.

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

UV (CH_3CN): λ_{max} (lg ε) = 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.

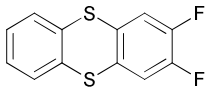
m.p.: 90 °C.

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

UV (CH_3CN): λ_{max} (lg ε) = 258 nm (4.60), 243 (4.24), 196 (4.66).

HRMS-EI: $C_{12}H_7ClS_2$ calcd for $[M]^+$: 249.9678, found: 249.9696.

2,3-Difluorothianthrene (3ah)



Dithioloimine **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

^{1}H-NMR (600 MHz, $CDCl_3$): 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.

^{13}C-NMR (150 MHz, $CDCl_3$): 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.

^{19}F-NMR (376 MHz, $CDCl_3$): –138.4 ppm.

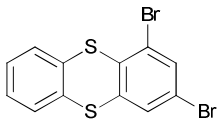
m.p.: 109 °C.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3052, 2923, 1594, 1565, 1475, 1275.

UV (CH_3CN): λ_{max} (lg ε) = 286 nm (3.13), 254 (4.44), 241 (4.18).

HRMS-EI: $C_{12}H_6F_2S_2$ calcd for $[M]^+$: 251.9879, found: 251.9876.

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

^{1}H-NMR (600 MHz, $CDCl_3$): 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.

^{13}C-NMR (150 MHz, $CDCl_3$): 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.

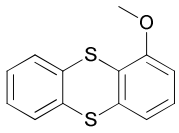
m.p.: 108 °C.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3082, 3057, 2922, 1530, 1378, 1248.

UV (CH_3CN): λ_{max} (lg ε) = 264 nm (4.30), 244 (4.13), 205 (4.56).

HRMS-EI: $C_{12}H_6Br_2S_2$ calcd for $[M]^+$: 371.8278, found: 371.8284.

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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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.

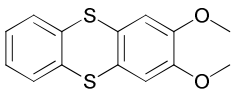
m.p.: 83 °C.

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

UV (CH_3CN): λ_{max} (lg ε) = 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)



Dithioloimine **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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 56.2, 111.8, 126.8, 127.6, 128.7, 136.3, 148.9 ppm.

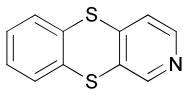
m.p.: 113 °C.

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

UV (CH_3CN): λ_{max} (lg ε) = 300 nm (3.44), 259 (4.37), 240 (4.36), 226 (4.32), 201 (4.56).

HRMS-EI: $C_{14}H_{12}O_2S_2$ calcd for $[M]^+$: 276.0279, found: 276.0294.

Benzo[5,6][1,4]dithiino[2,3-*c*]pyridine (3al)



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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 122.8, 128.2, 128.4, 128.9, 129.2, 131.8, 133.3, 133.9, 146.5, 147.9, 148.0 ppm.

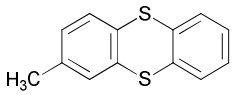
m.p.: 78 °C.

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

UV (CH_3CN): λ_{max} (lg ε) = 276 nm (3.41), 257 (4.17), 239 (4.00).

HRMS-EI: $C_{11}H_7N_1S_2$ calcd for $[M]^+$: 217.0020, found: 217.0037.

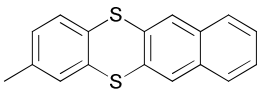
2-Methylthianthrene (3ba) = (3ab)



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)



Dithioloimine **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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 20.9, 126.5, 126.6, 127.0 127.0, 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.

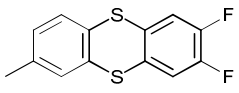
m.p.: 145 °C.

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

UV (CH_3CN): λ_{max} (lg ε) = 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

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 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.

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 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.

^{19}F-NMR (376 MHz, $CDCl_3$): δ = -138.6, -138.6 ppm.

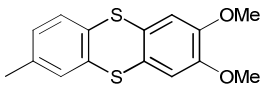
m.p.: 82 °C.

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

UV (CH_3CN): λ_{max} (lg ε) = 255 nm (4.41), 242 (4.19).

HRMS-EI: $C_{13}H_8F_2S_2$ 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

^{1}H-NMR (600 MHz, $CDCl_3$): 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.

^{13}C-NMR (150 MHz, $CDCl_3$): 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.

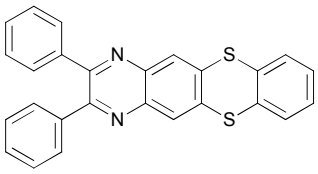
m.p.: 87 °C.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3048, 2918, 1443, 1121, 1035.

UV (CH_3CN): λ_{max} (lg ε) = 258 nm (4.61), 242 (4.27).

HRMS-EI: $C_{15}H_{14}O_2S_2$ calcd for $[M]^+$: 290.0430, found: 290.0443.

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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 127.4, 128.1, 128.3, 128.9, 129.0, 129.8, 134.4, 138.1, 138.7, 140.6, 153.8 ppm.

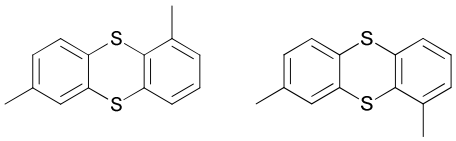
m.p.: 144 °C.

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

UV (CH_3CN): λ_{max} (lg ε) = 386 nm (4.11), 287 (4.57), 256 (4.50), 207 (4.61).

HRMS-ESI: $C_{26}H_{16}N_2S_2$ 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).

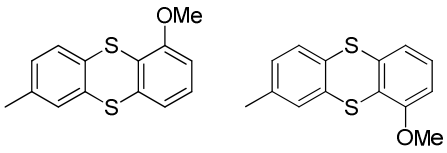
Column: pentane

^{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')



Dithioloimine **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).

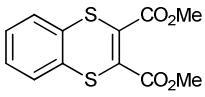
Column: pentane

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 2.31 (s, 3 H), 3.91 (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.

^{13}C-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)



Dithioloimine **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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 53.7, 129.0, 129.1, 133.4, 135.8, 163.4 ppm.

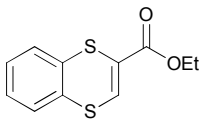
m.p.: 62 °C.

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

UV (CH_3CN): λ_{max} (lg ε) = 355 nm (2.97), 270 (3.96), 234 (4.15).

HRMS-ESI: $C_{12}H_{10}O_4S_2$ 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)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.1 Hz, 3 H), 4.28 (q, *J* = 7.1 Hz, 2 H), 7.18–7.23 (m, 3 H), 7.26–7.38 (m, 1 H), 7.59 (s, 1 H) ppm.

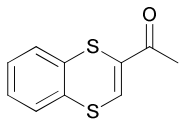
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.2, 62.0, 127.6, 128.1, 128.1, 128.4, 128.7, 131.5, 132.2, 135.4, 161.3 ppm.

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

UV (CH_3CN): λ_{max} (lg ε) = 356 nm (2.96), 256 (4.17).

HRMS-EI: $C_{11}H_{10}O_2S_2$ calcd for $[M]^+$: 238.0117, found: 238.0130.

1-(Benzo[*b*][1,4]dithiin-2-yl)ethanone (7ac)



Dithioloimine **1a** (33.2 mg, 200 µmol, 1.0 equiv.), Cs_2CO_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, $CDCl_3$): δ = 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.

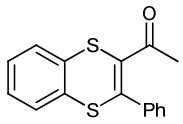
^{13}C-NMR (100 MHz, $CDCl_3$): δ =26.3, 127.5, 128.1, 128.6, 128.9, 131.3, 132.1, 135.9, 137.6, 190.2 ppm.

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

UV (CH_3CN): λ_{max} (lg ε) = 374 nm (3.03), 269 (4.13), 232 (4.10).

HRMS-EI: $C_{10}H_8OS_2$ calcd for $[M]^+$: 230.9909, found: 230.9910.

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



Dithioloimine **1a** (33.2 mg, 200 µmol, 1.0 equiv.), Cs_2CO_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, $CDCl_3$): δ = 1.84 (s, 3 H), 7.25–7.32 (m, 2 H), 7.37–7.49 (m, 7 H) ppm.

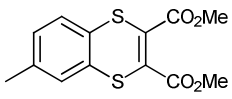
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 29.7, 127.5, 127.9, 128.4, 128.6, 128.8, 129.8, 130.2, 131.2, 135.1, 135.4, 136.6, 149.5, 196.9 ppm.

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

UV (CH_3CN): λ_{max} (lg ε) = 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

^{1}H-NMR (400 MHz, $CDCl_3$): 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.

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.7, 53.2, 128.2, 129.1, 129.4, 129.5, 132.9, 135.3, 135.7, 139.0, 163.0 ppm.

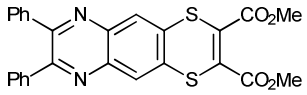
m.p.: 65 °C.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2952, 1720, 1575, 1432, 1240, 1012.

UV (CH_3CN): λ_{max} (lg ε) = 354 nm (2.94), 271 (3.93), 235 (4.21).

HRMS-ESI: $C_{13}H_{12}O_4S_2$ calcd for $[M+Na]^+$: 319.0069, found: 319.0071.

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

^{1}H-NMR (400 MHz, $CDCl_3$): 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.

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 53.5, 127.6, 128.3, 129.2, 129.8, 134.3, 134.8, 138.4, 140.9, 154.4, 162.8 ppm.

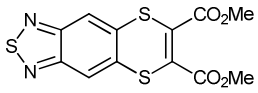
m.p.: 151 °C.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2954, 1719, 1577, 1434, 1248.

UV (CH_3CN): λ_{max} (lg ε) = 384 nm (4.12), 288 (4.46), 238 (4.57).

HRMS-ESI: $C_{26}H_{18}N_2O_4S_2$ calcd for $[M+Na]^+$: 509.0600, found: 509.0600.

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



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

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.89 (s, 6 H), 8.02 (s, 2 H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 53.5, 119.3, 134.4, 135.7, 154.3, 162.7 ppm.

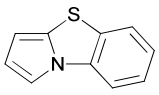
m.p.: 92 °C.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2958, 1709, 1569, 1427, 1224, 1075.

UV (CH_3CN): λ_{max} (lg ε) = 366 nm (3.95), 294 (3.84), 281 (3.90), 231 (4.42).

HRMS-ESI: $C_{12}H_8N_2O_4S_3$ calcd for $[M+Na]^+$: 362.9538, found: 362.9541.

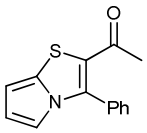
2-Methylbenzo[*b*]thianthrene (9)



To a stirred solution of 2-thiocyanatopyrrole (**8a**)[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 *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.[5]

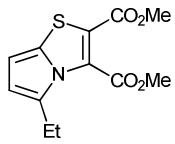
1-(3-Phenylpyrrolo[2,1-*b*]thiazol-2-yl)ethanone (10ad)



To a solution of 4-phenyl-3-butyne-2-one (**4d**)[4] (576 mg, 4.00 mmol, 20 equiv.) and Cs_2CO_3 (98 mg, 300 µmol, 1.5 equiv.) in MeCN (2 mL) was added dropwise 2-thiocyanatopyrrole[4] (**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.

^{1}H-NMR (300 MHz, $CDCl_3$): 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.
^{13}C-NMR (75 MHz, $CDCl_3$): 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): $\tilde{\nu}$ (cm^{-1}) = 3058, 1646, 1563, 1449, 1330, 1195.
UV (CH_3CN): λ_{max} (lg ε) = 369 nm (3.46), 294 (4.04), 227 (4.17).
HRMS-ESI: $C_{14}H_{11}NOS$ calcd for $[M+Na]^+$: 264.0454, found: 264.0455.

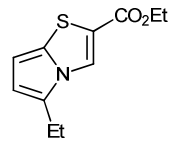
Dimethyl 5-ethylpyrrolo[2,1-*b*]thiazole-2,3-dicarboxylate (10ba)



To a solution of acetylene dicarboxylic acid dimethylester (**4a**) (568 mg, 4.00 mmol, 20 equiv.) and Cs_2CO_3 (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.

^{1}H-NMR (400 MHz, $CDCl_3$): 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.
^{13}C-NMR (100 MHz, $CDCl_3$): 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): $\tilde{\nu}$ (cm^{-1}) = 2950, 1735, 1708, 1581, 1316, 1236.
UV (CH_3CN): λ_{max} (lg ε) = 369 nm (3.24), 285 (3.99), 228 (4.13).
HRMS-ESI: $C_{12}H_{13}NO_4S$ calcd for $[M+Na]^+$: 290.0457, found: 290.0460.

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

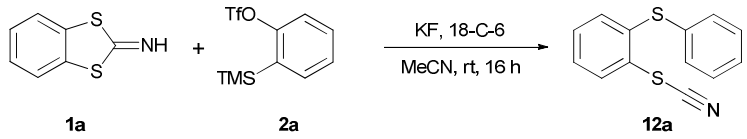


To a solution of ethyl propynoate (**4b**) (392 mg, 4.00 mmol, 20 equiv.) and Cs_2CO_3 (98 mg, 300 µmol, 1.5 equiv.) in MeCN (2 mL) was added dropwise thiocyanatopyrrole **8b** (33.5 mg, 200 µmol, 1.0 equiv.) dissolved in MeCN (1 mL) over 10 min at room temperature. Afterwards, the solvent was removed *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.

^{1}H-NMR (300 MHz, $CDCl_3$): 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.
^{13}C-NMR (75 MHz, $CDCl_3$): 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): $\tilde{\nu}$ (cm^{-1}) = 3112, 2938, 1706, 1582, 1225.
UV (CH_3CN): λ_{max} (lg ε) = 354 nm (3.30), 282 (4.02), 229 (4.08).
HRMS-ESI: $C_{11}H_{13}NO_2S$ calcd for $[M+Na]^+$: 246.0559, found: 246.0561.

Observed side products to support the mechanistic scenario

Phenyl(2-thiocyanatophenyl)sulfane(12a)



1a **2a** **12a**

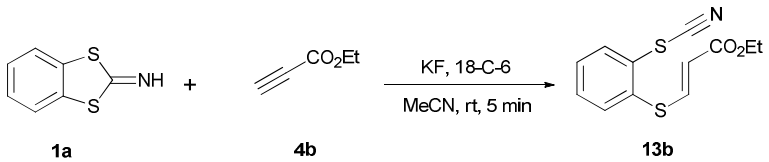
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.19–7.22 (m, 2 H), 7.26–7.28 (m, 1 H), 7.29–7.34 (m, 2 H), 7.34–7.36 (m, 1 H), 7.43–7.48 (m, 2 H), 7.76 (ddd, *J* = 8.0, 1.3, 0.4 Hz, 1 H) ppm.

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 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: $C_{13}H_9NS_2$ found: 243.1.

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

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



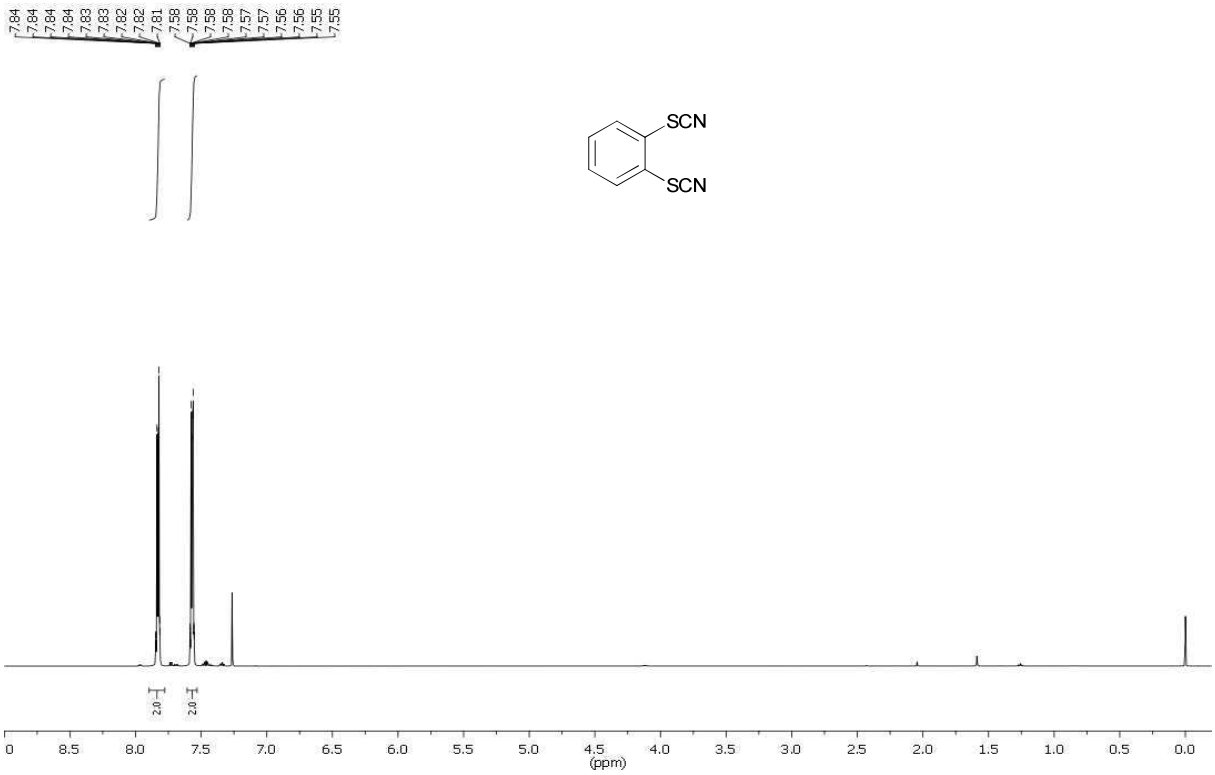
1a **4b** **13b**

GCMS-EI: $C_{12}H_{11}NO_2S_2$ found: 243.1.

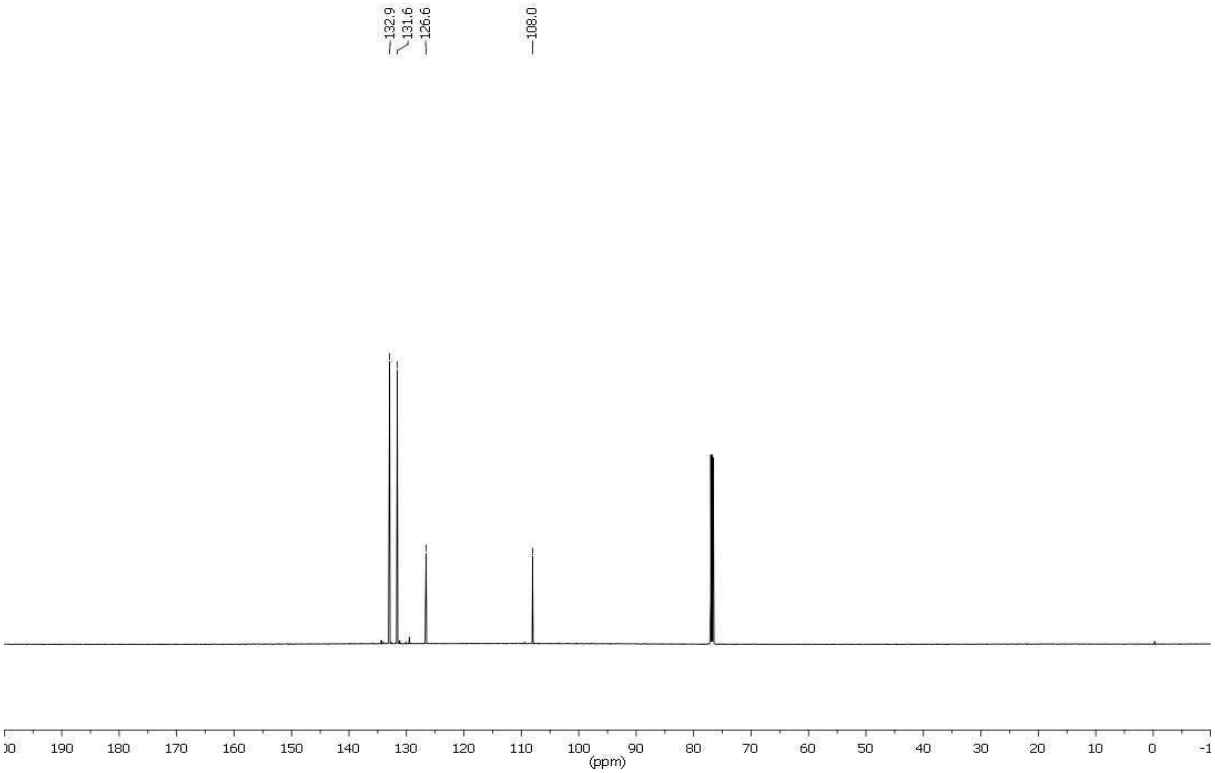
In the case of the benzo[b][1,4]dithiine synthesis the side product **13b** could not be isolated and was just observed by GC-MS.

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)

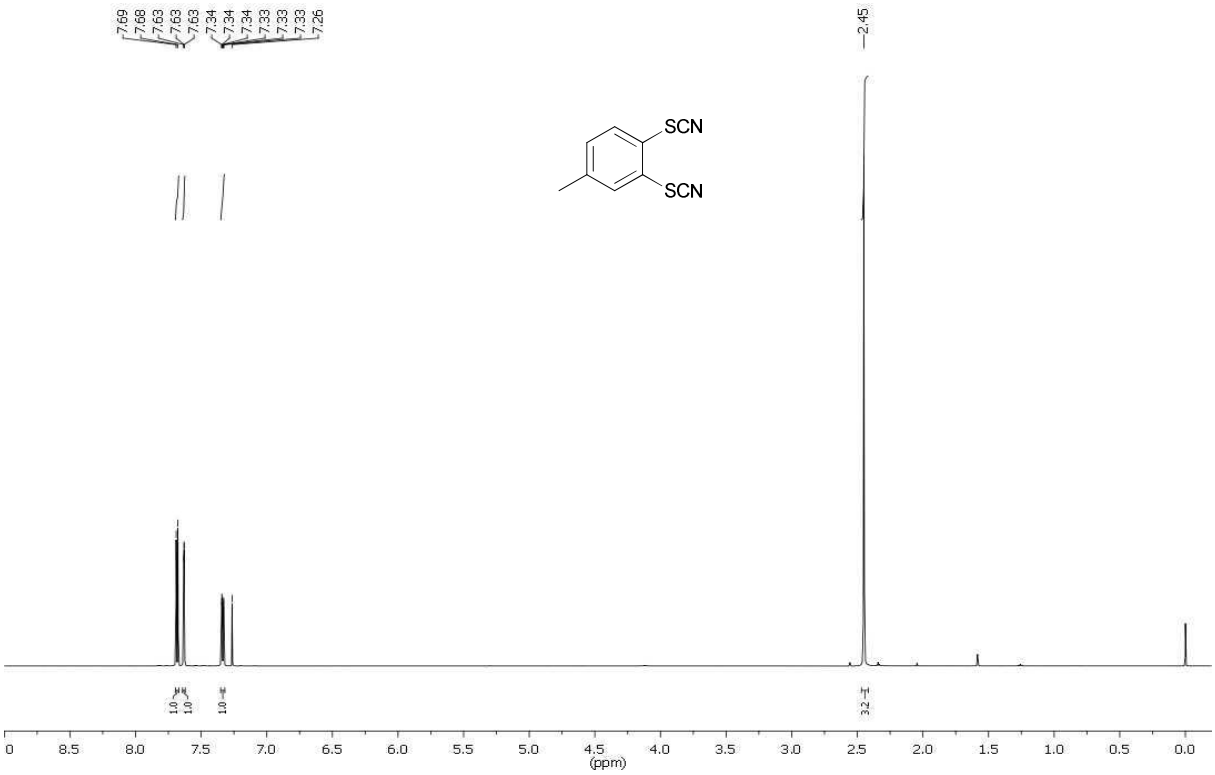


^{1}H-NMR (600 MHz, $CDCl_3$)

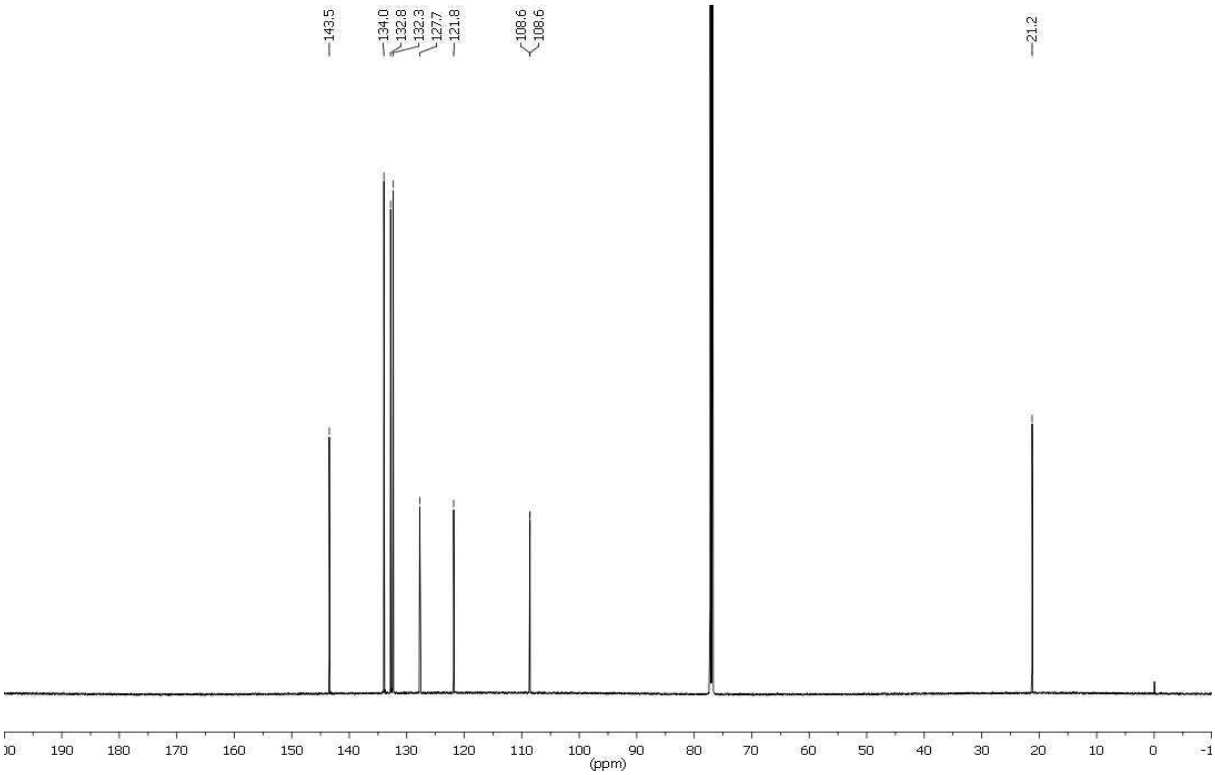


^{13}C-NMR (150 MHz, $CDCl_3$)

4-Methyl-1,2-dithiocyanatobenzene (6b)

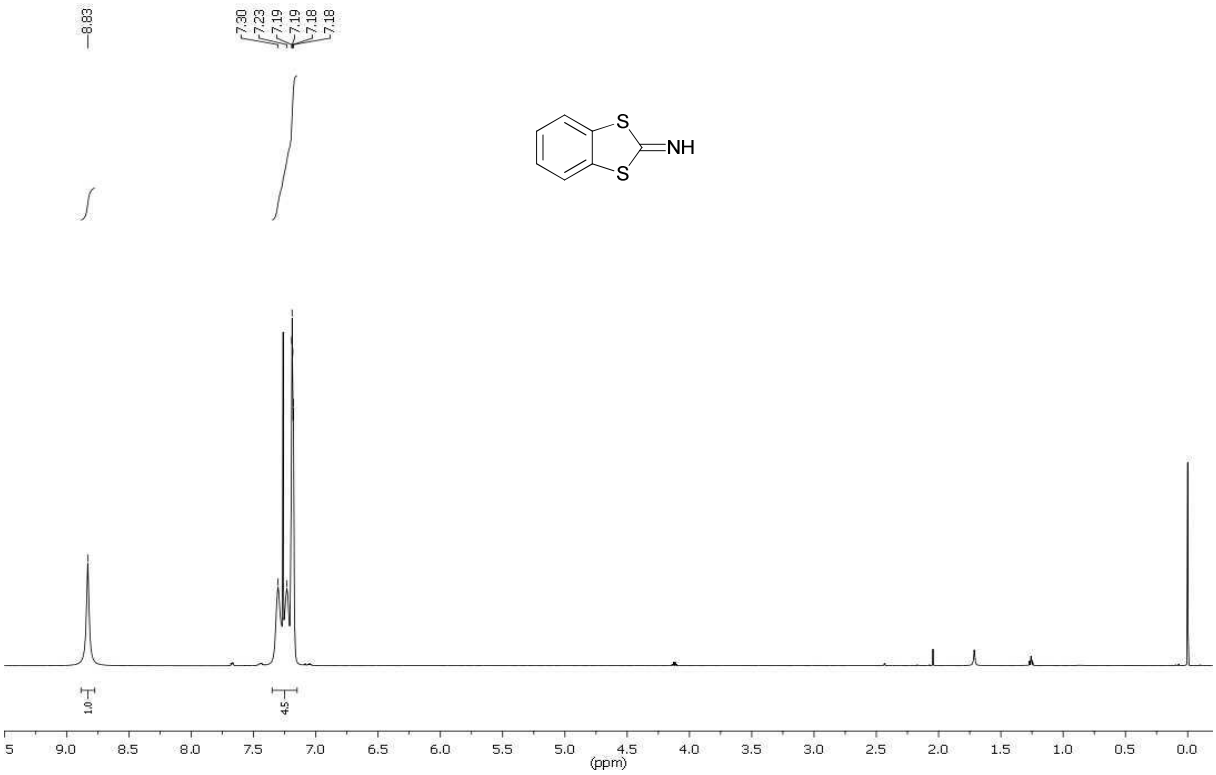


^{1}H-NMR (600 MHz, $CDCl_3$)

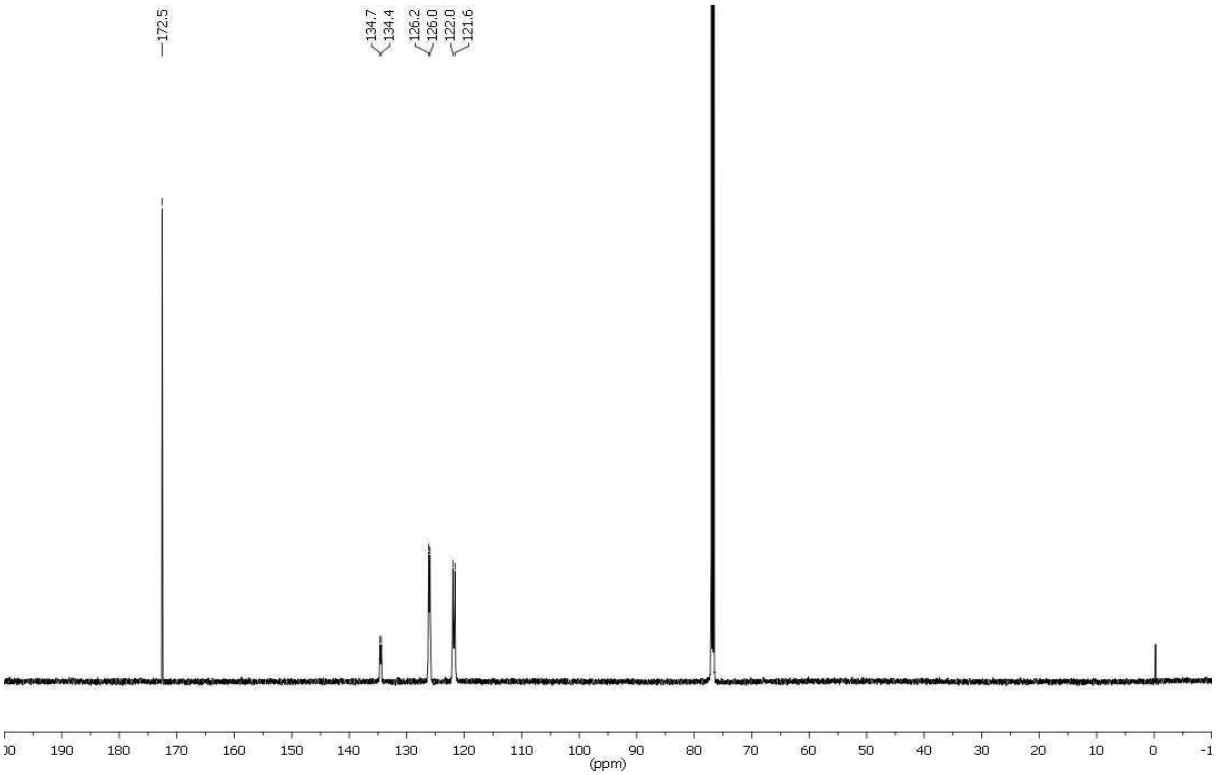


^{13}C-NMR (150 MHz, $CDCl_3$)

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

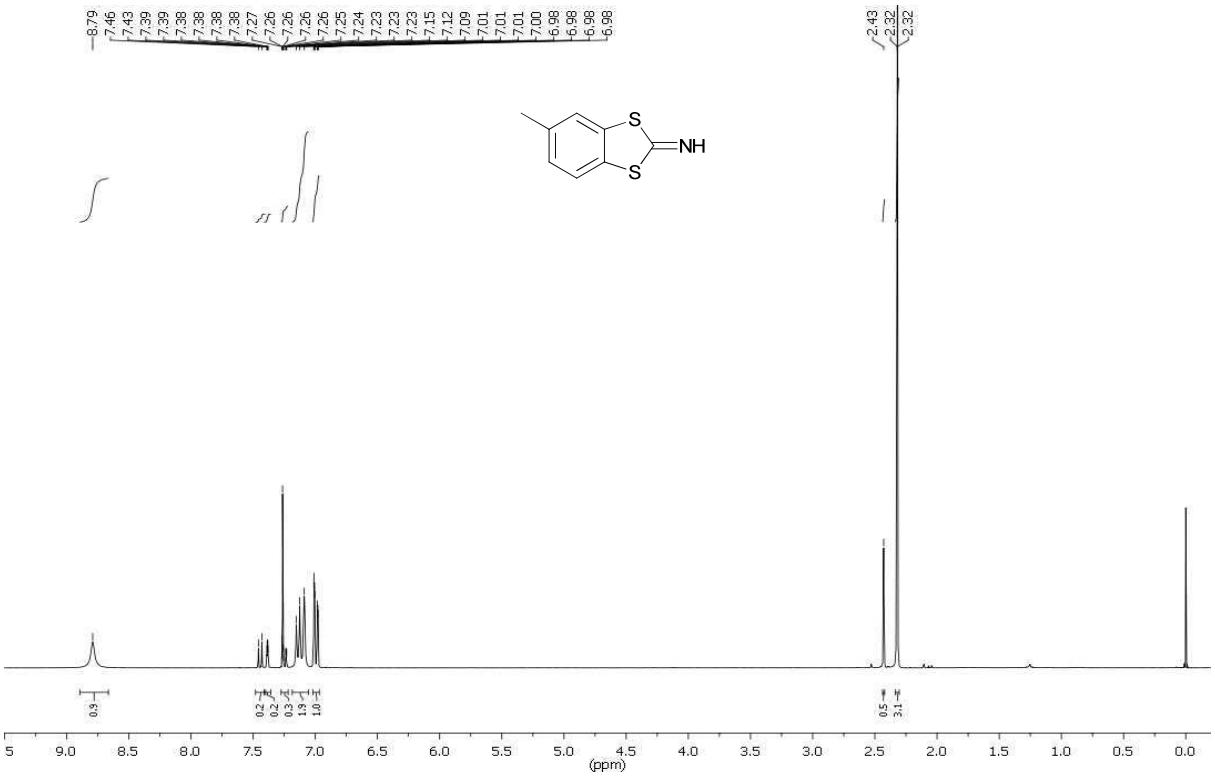


^{1}H-NMR (600 MHz, $CDCl_3$)

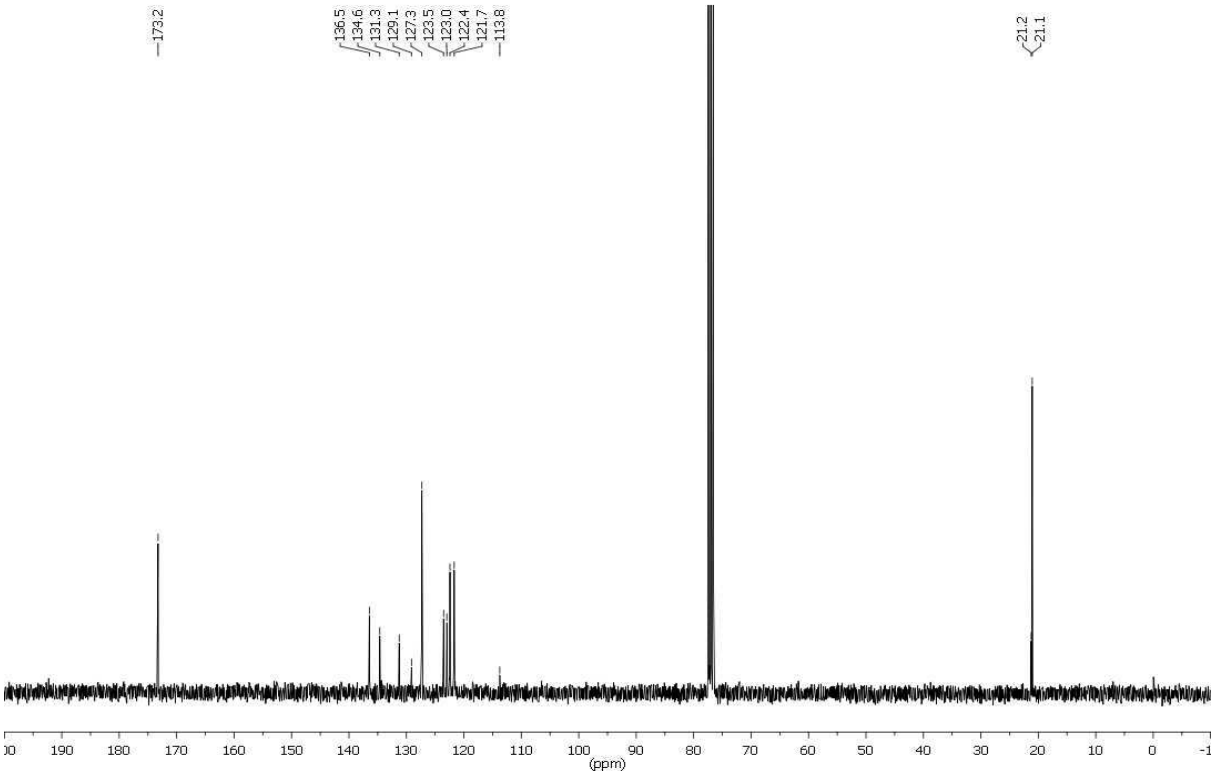


^{13}C-NMR (150 MHz, $CDCl_3$)

5-methylbenzo[*d*][1,3]dithiol-2-imine (1b)

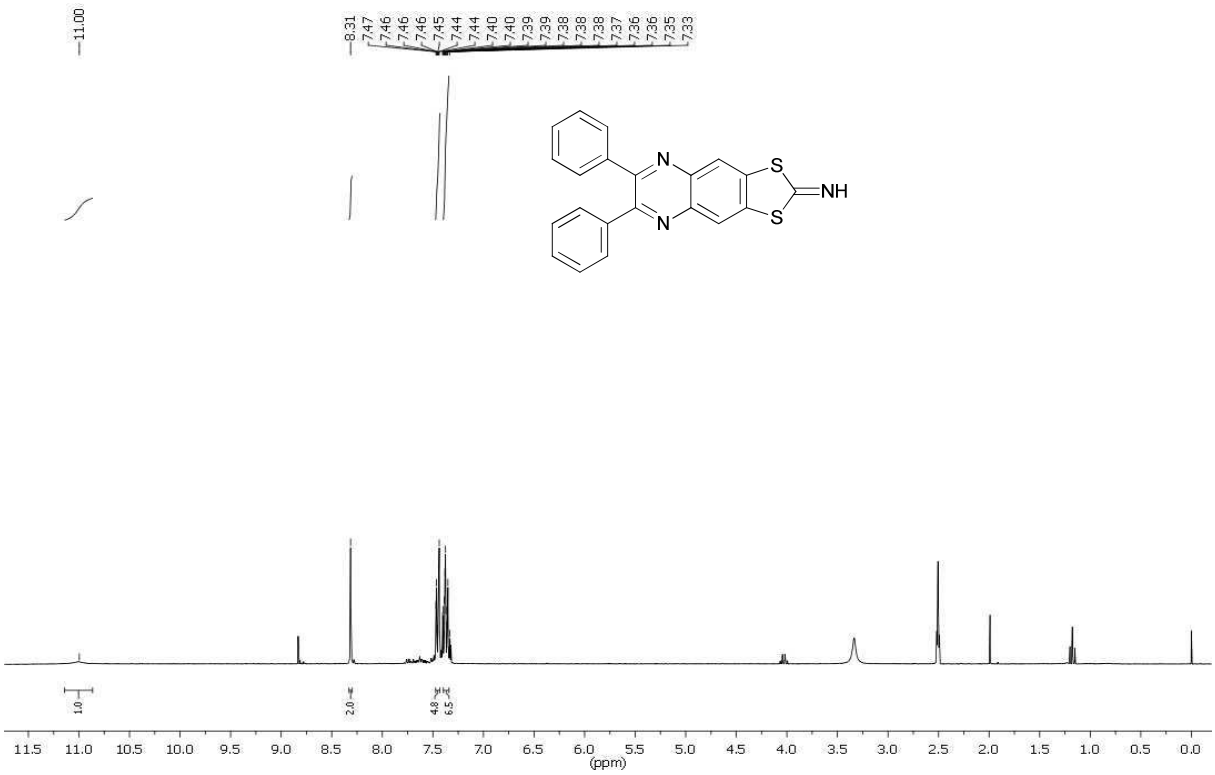


^{1}H-NMR (300 MHz, $CDCl_3$)

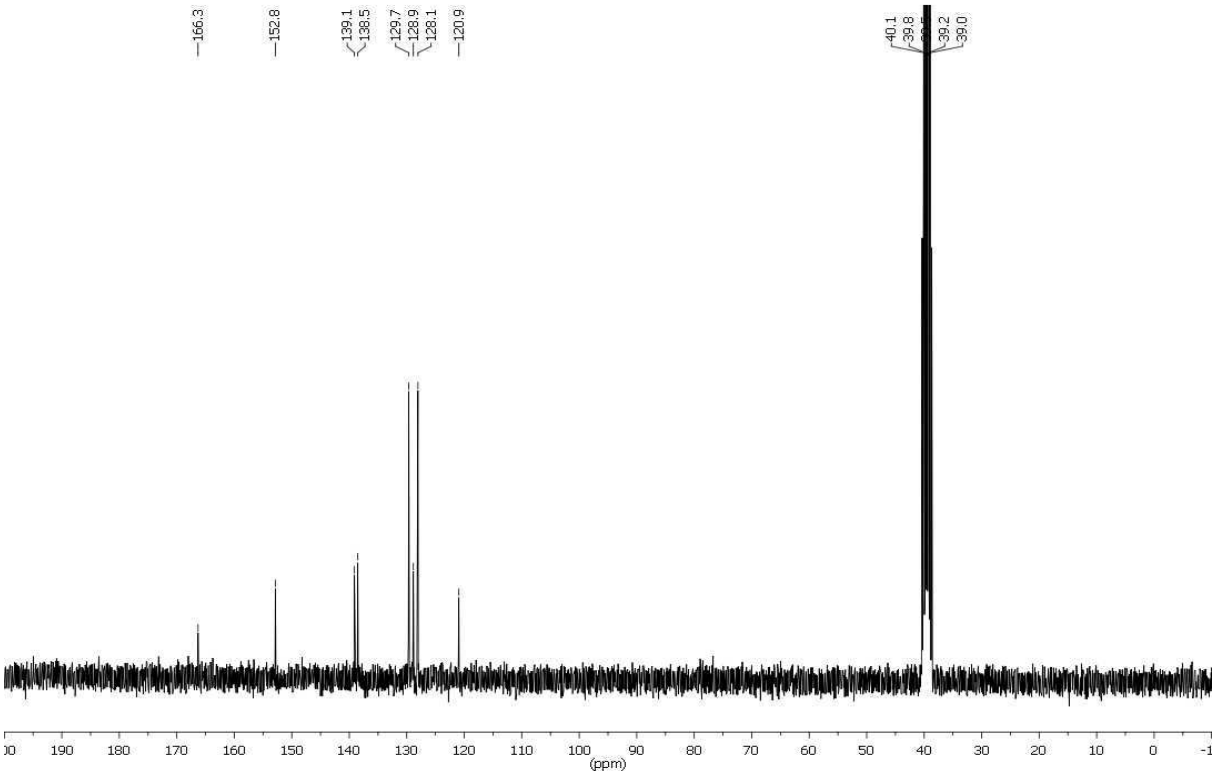


^{13}C-NMR (75 MHz, $CDCl_3$)

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

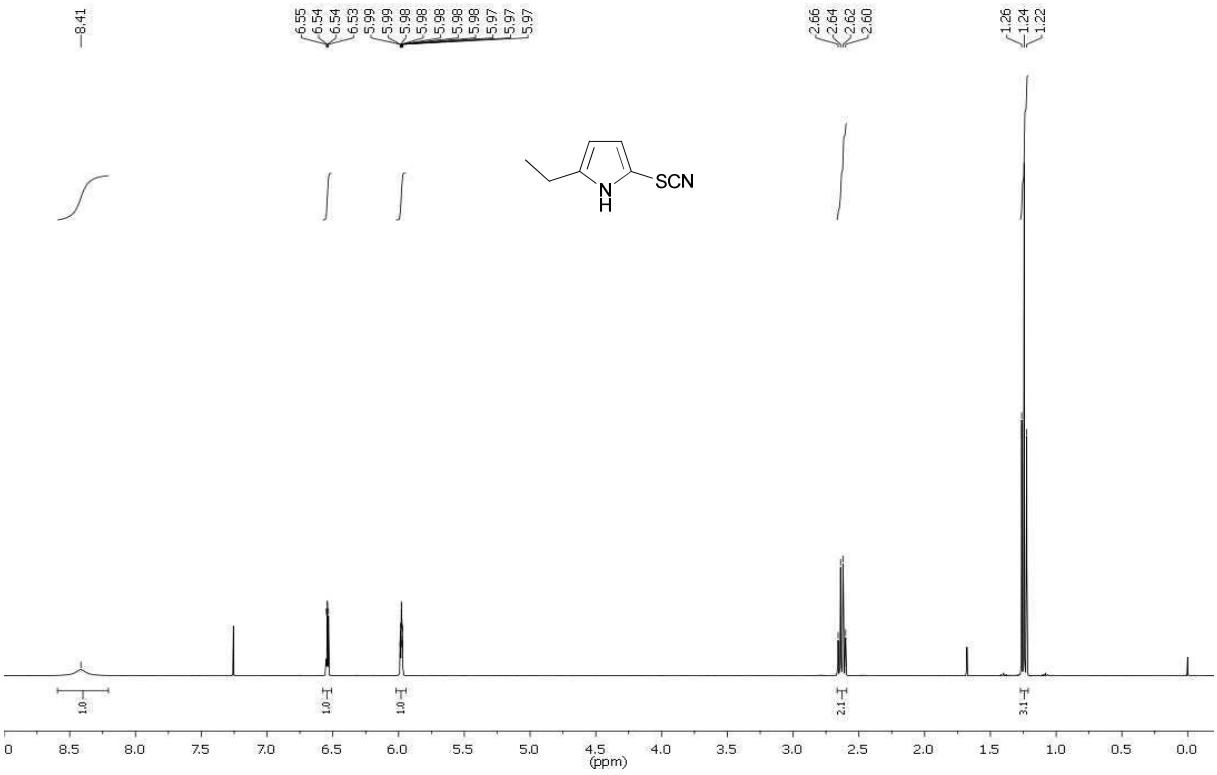


^{1}H-NMR (300 MHz, d_6-DMSO)

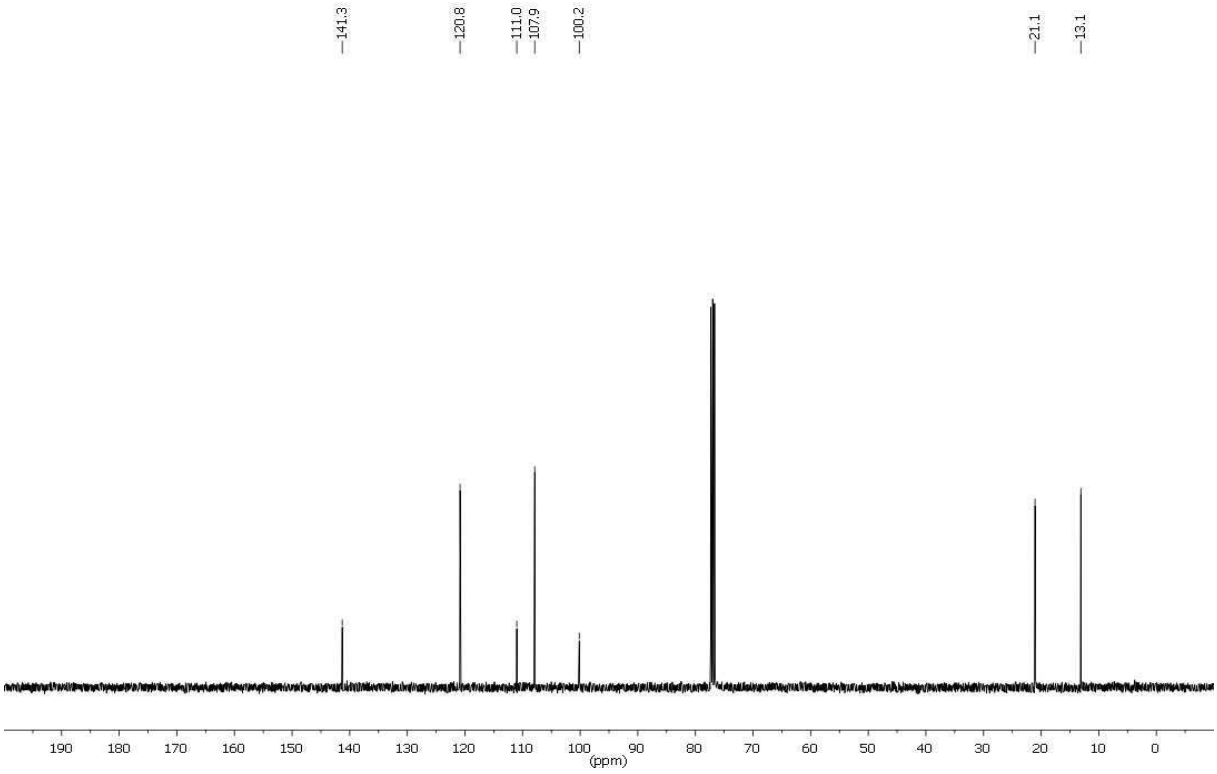


^{13}C-NMR (75 MHz, d_6-DMSO)

2-Ethyl-5-thiocyanato-1*H*-pyrrole (8b)

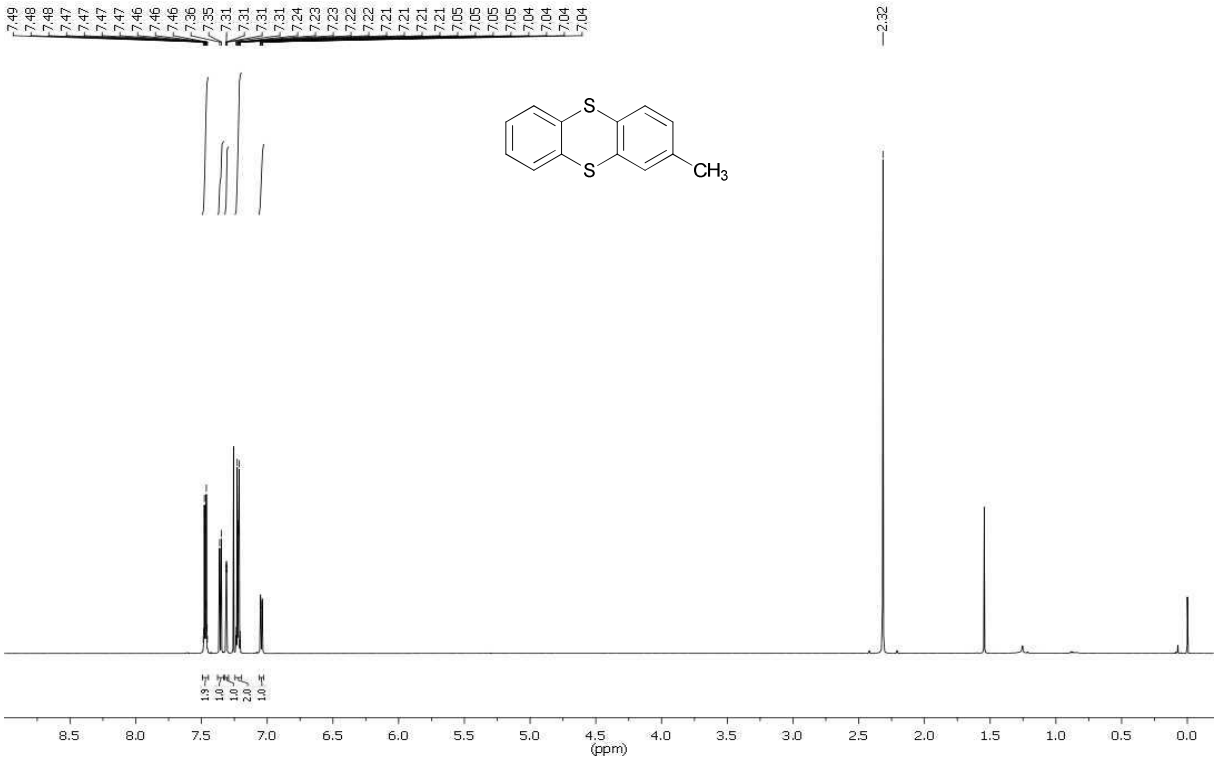


^{1}H-NMR (400 MHz, $CDCl_3$)

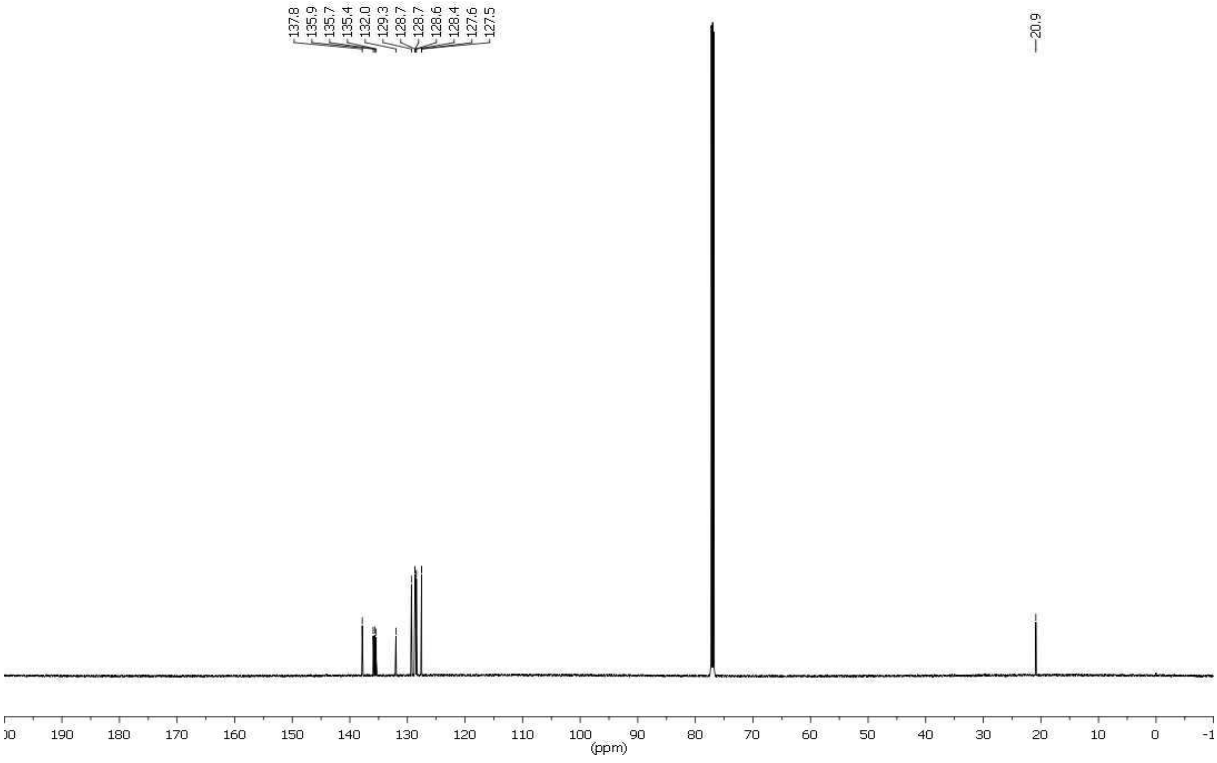


^{13}C-NMR (100 MHz, $CDCl_3$)

2-Methylthianthrene (3ab)

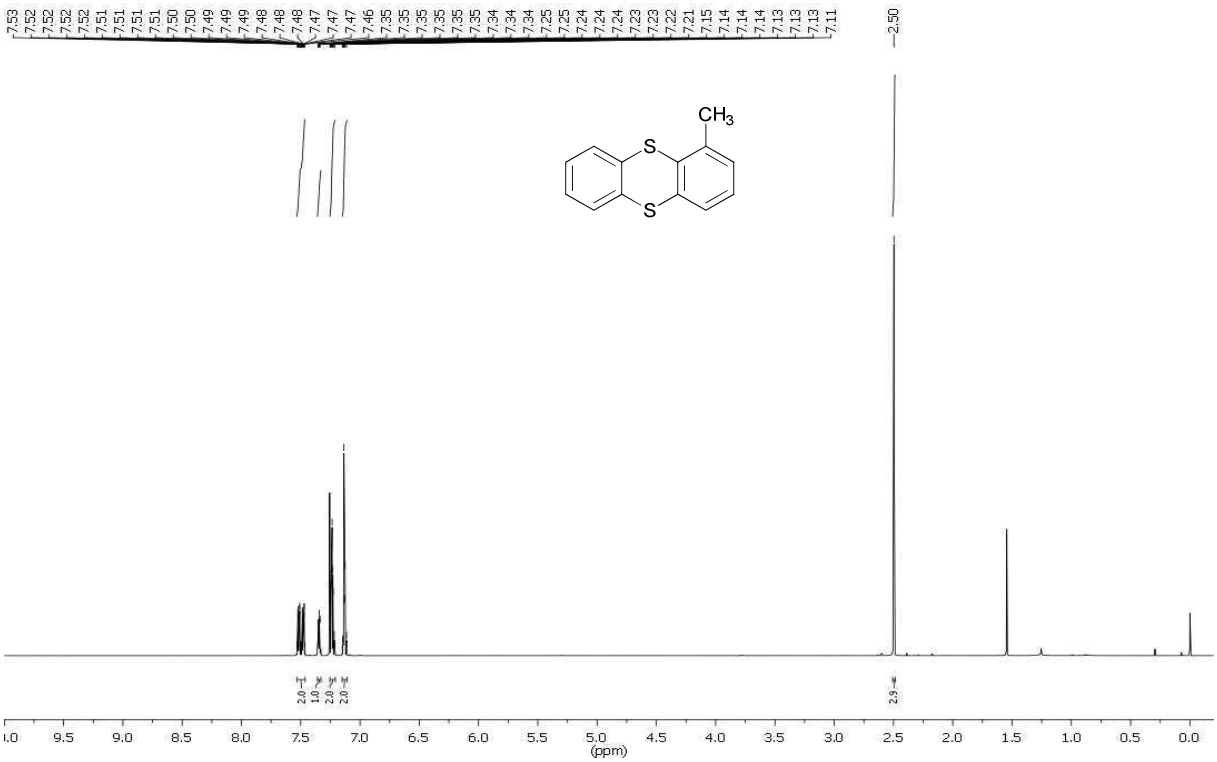


^{1}H-NMR (600 MHz, $CDCl_3$)

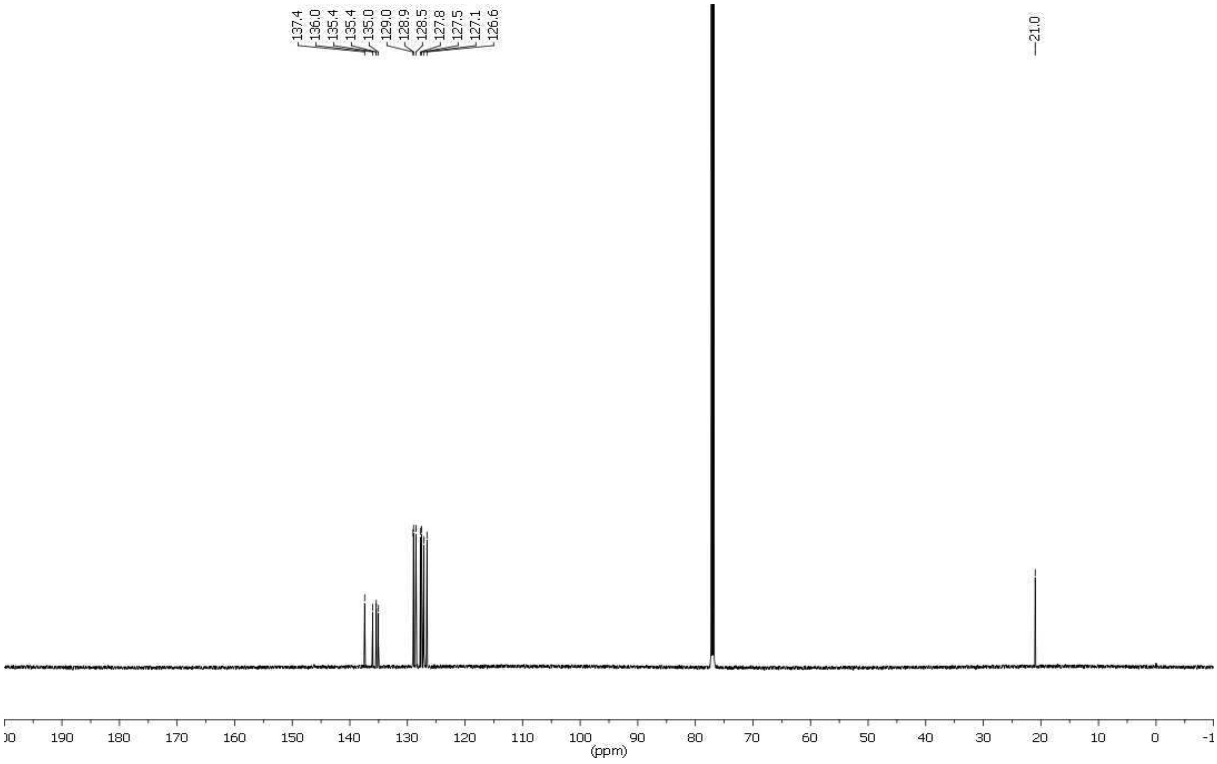


^{13}C-NMR (150 MHz, $CDCl_3$)

1-Methylthianthrene (3ac)

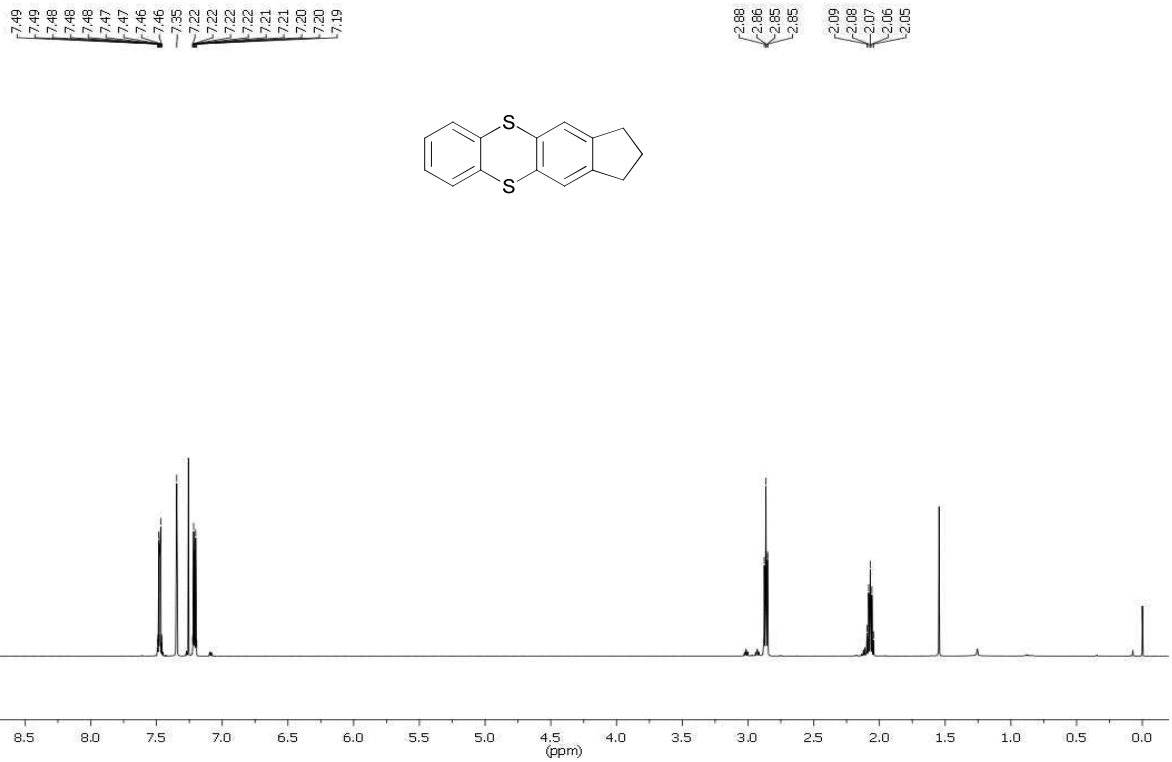


^{1}H-NMR (600 MHz, $CDCl_3$)

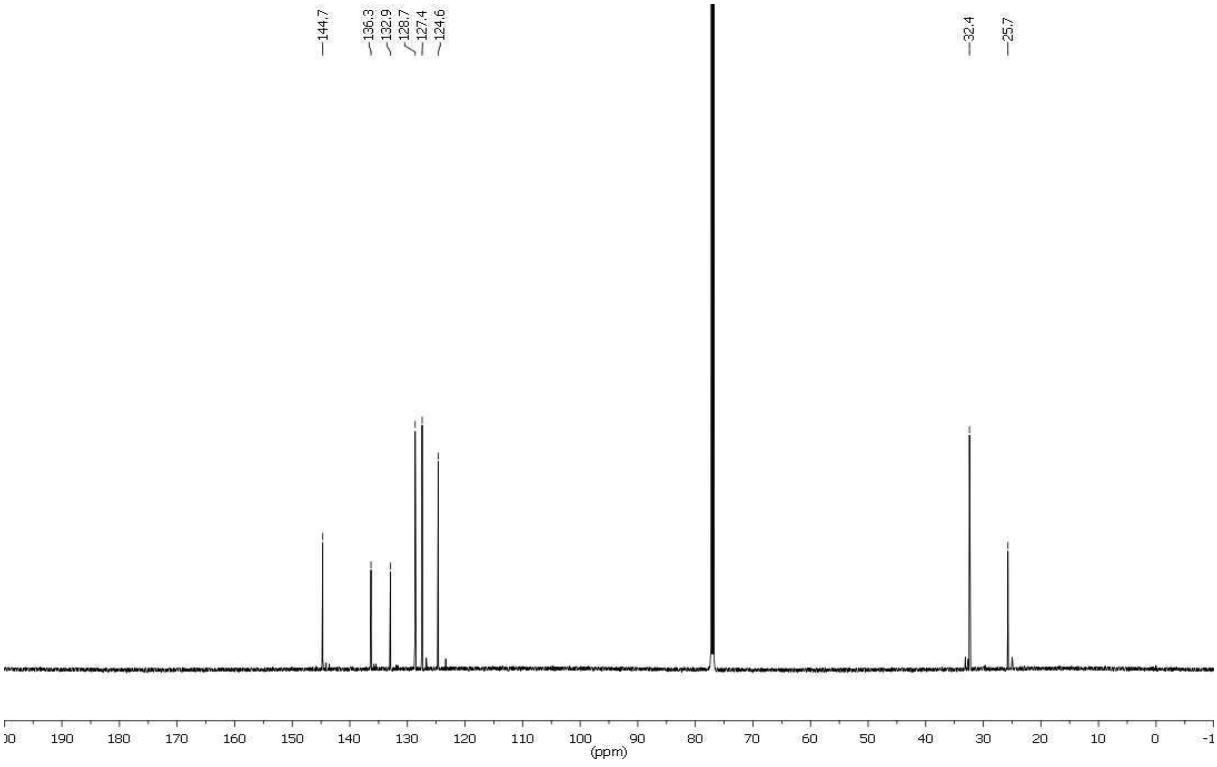


^{13}C-NMR (150 MHz, $CDCl_3$)

2,3-Dihydro-1*H*-cyclopenta[*b*]thianthrene (3ad)

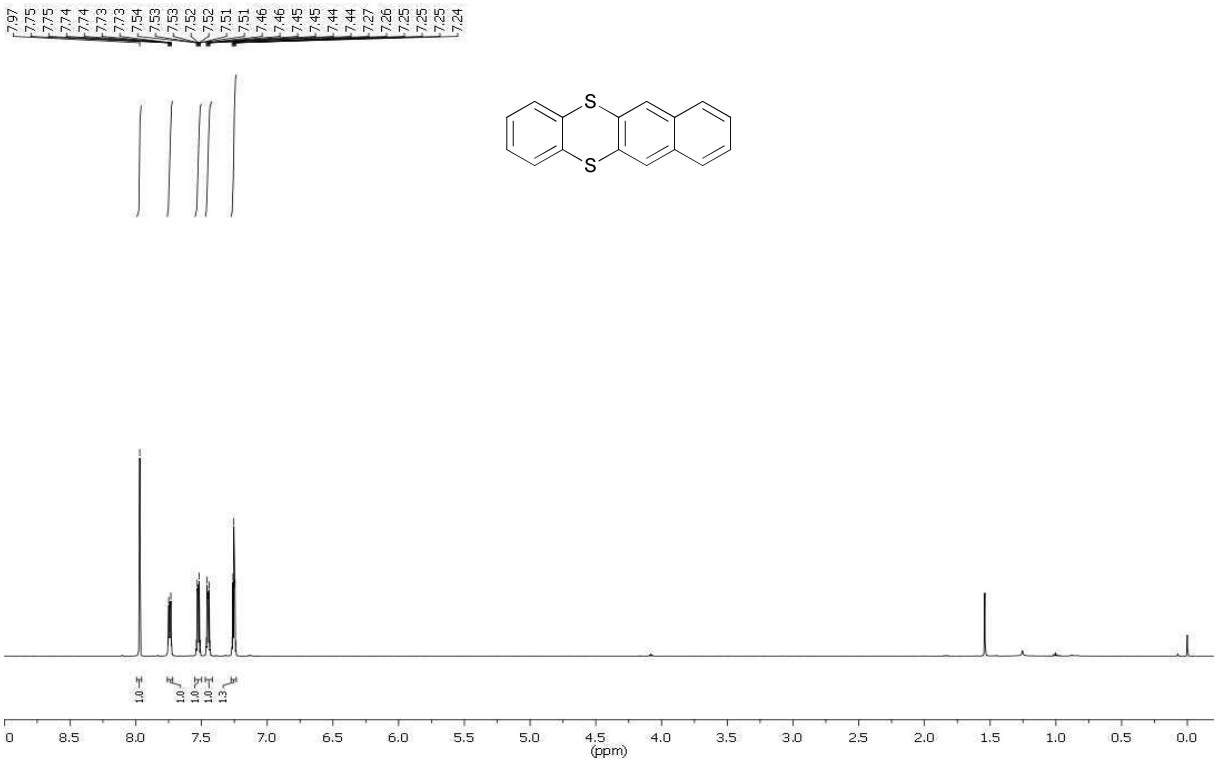


^{1}H-NMR (600 MHz, $CDCl_3$)

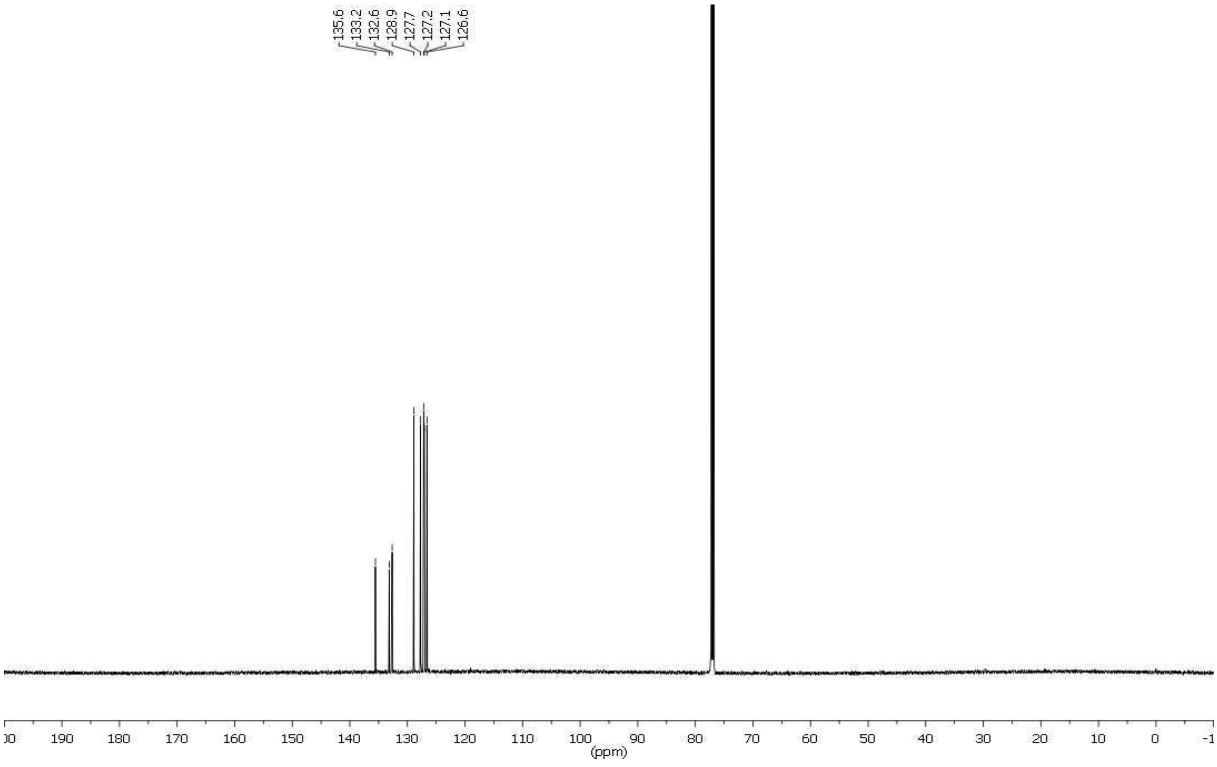


^{13}C-NMR (150 MHz, $CDCl_3$)

Benzo[*b*]thianthrene (3ae)

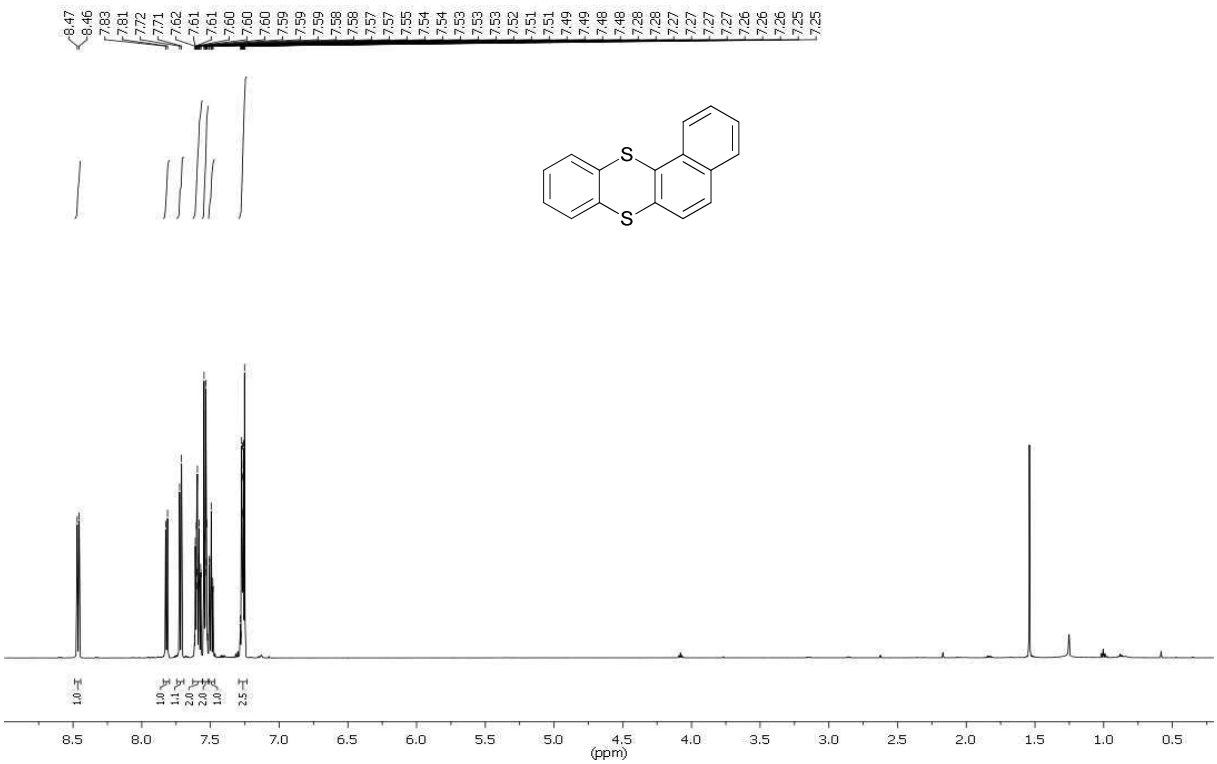


^{1}H-NMR (600 MHz, $CDCl_3$)

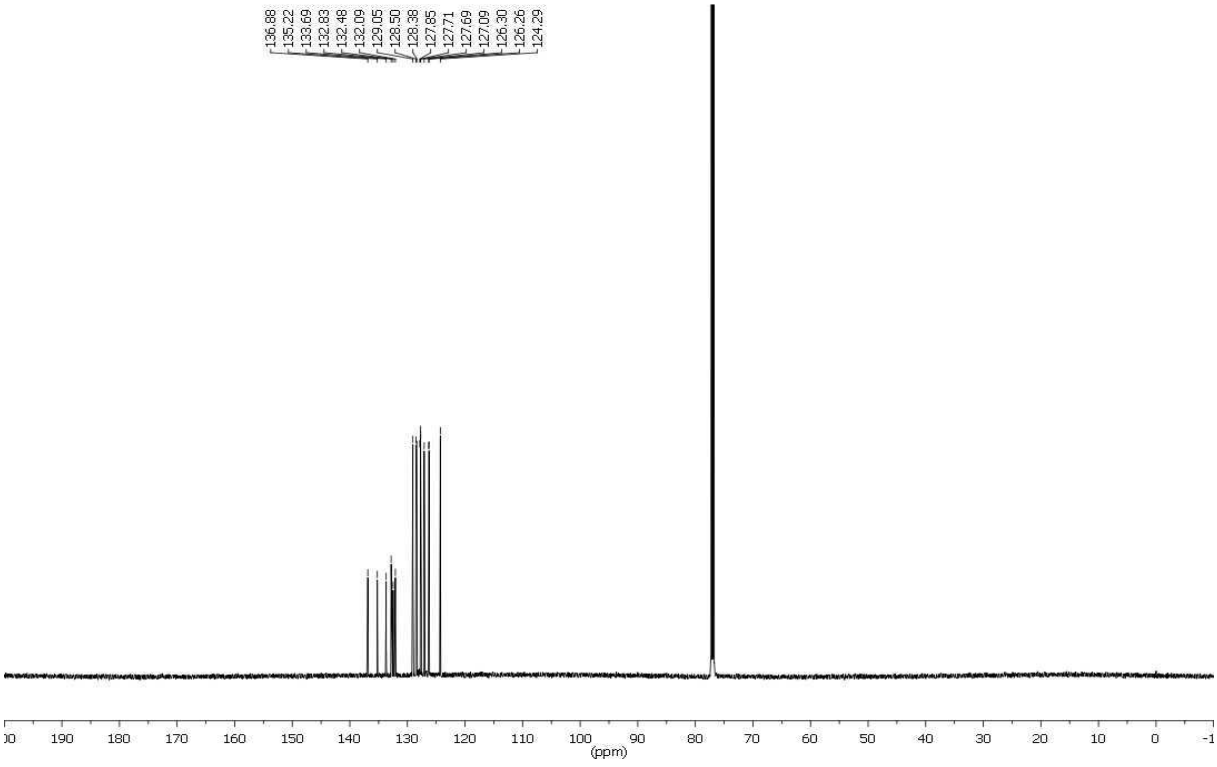


^{13}C-NMR (150 MHz, $CDCl_3$)

Benzo[*a*]thianthrene (3af)



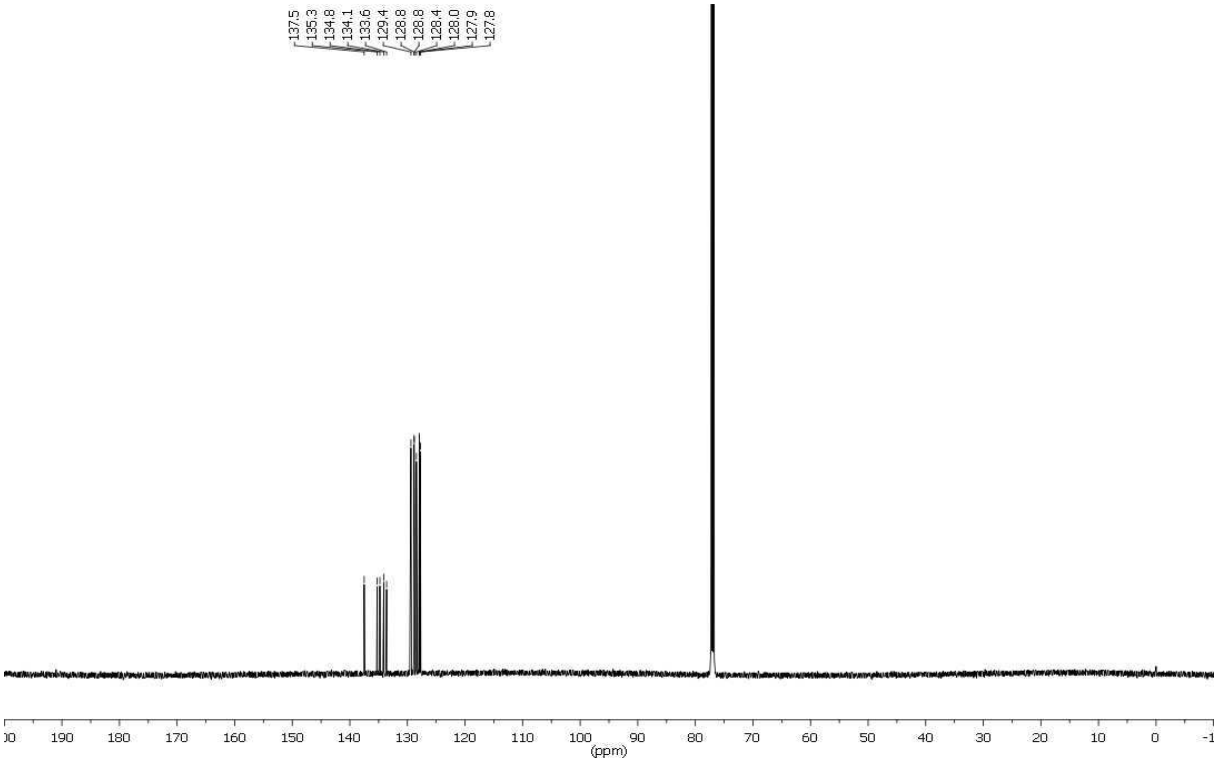
^{1}H-NMR (600 MHz, $CDCl_3$)



^{13}C-NMR (150 MHz, $CDCl_3$)

2-Chlorothianthrene (3ag)

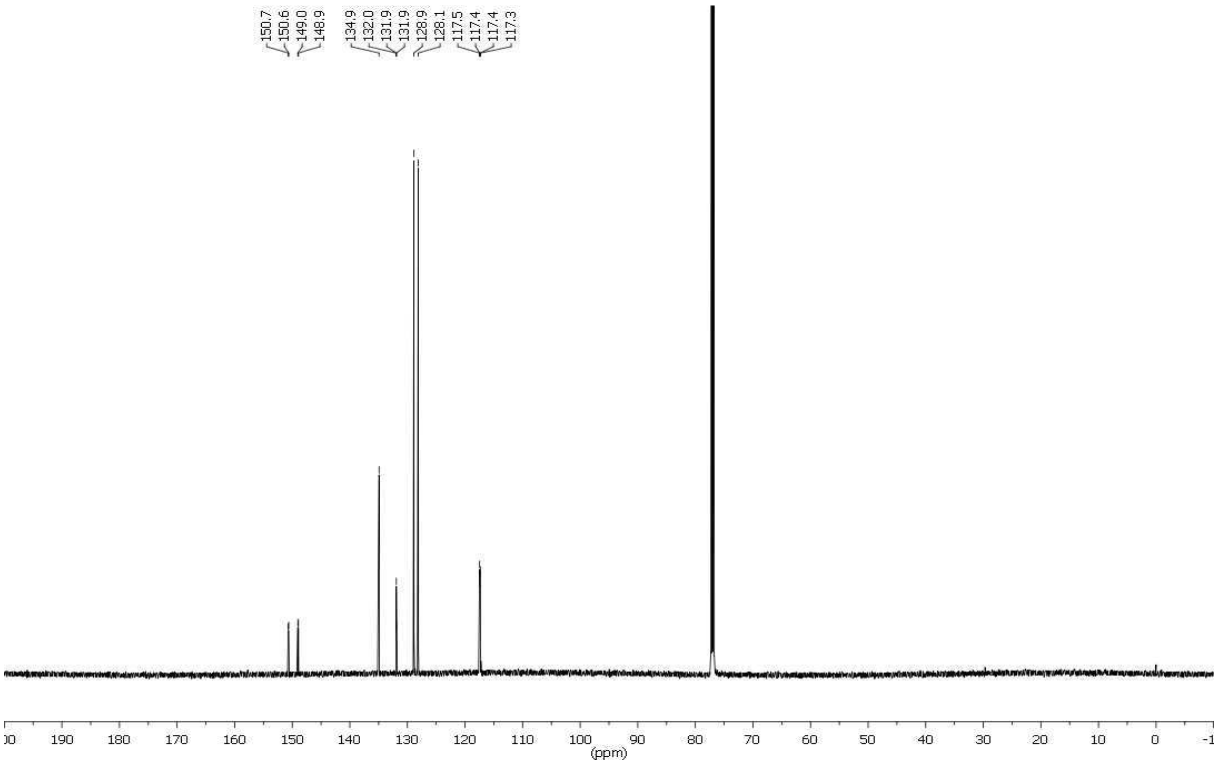
^{1}H-NMR (600 MHz, $CDCl_3$)



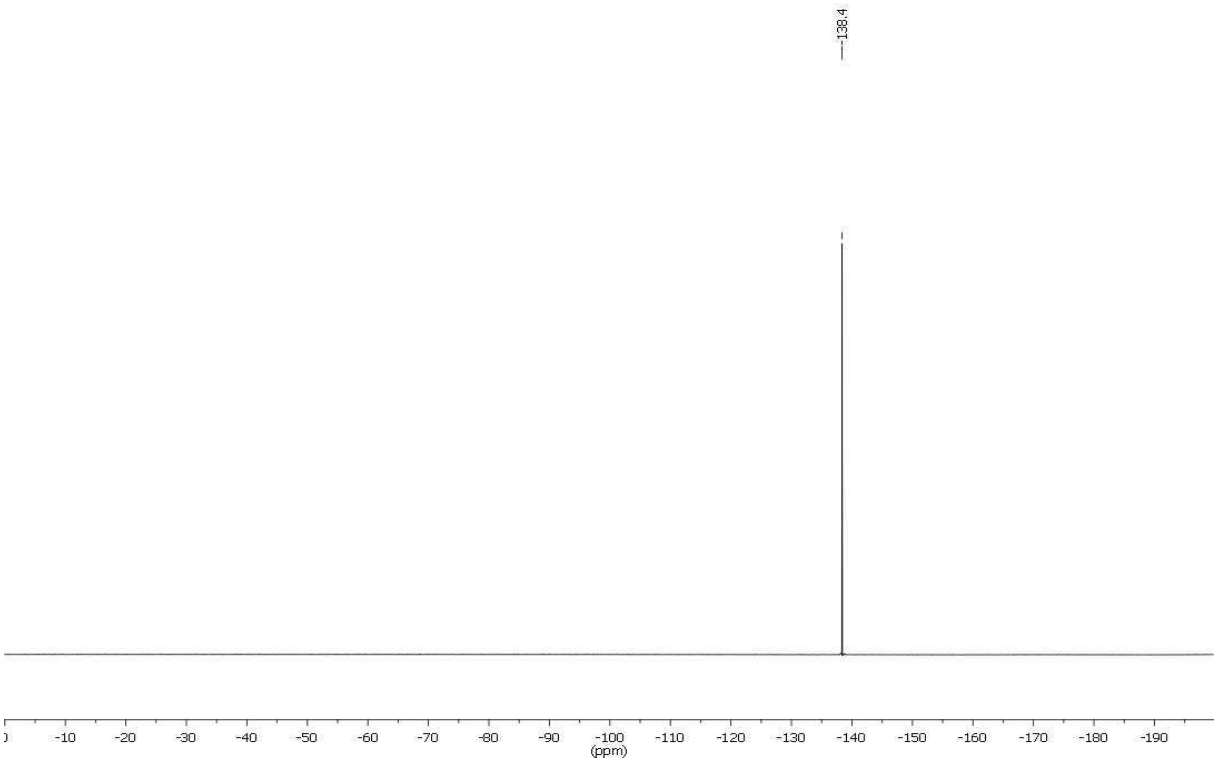
^{13}C-NMR (150 MHz, $CDCl_3$)

2,3-Difluorothianthrene (3ah)

^{1}H-NMR (600 MHz, $CDCl_3$)

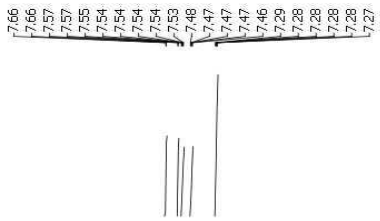


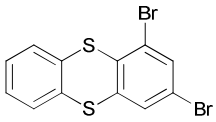
^{13}C-NMR (150 MHz, $CDCl_3$)

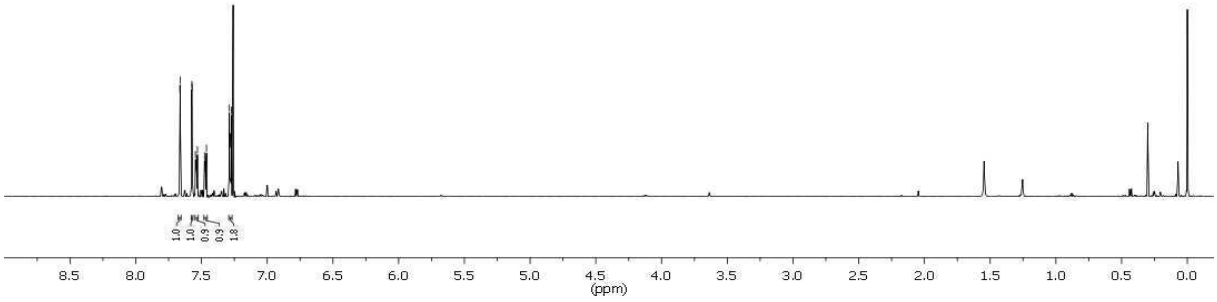


^{19}F-NMR (376 MHz, $CDCl_3$)

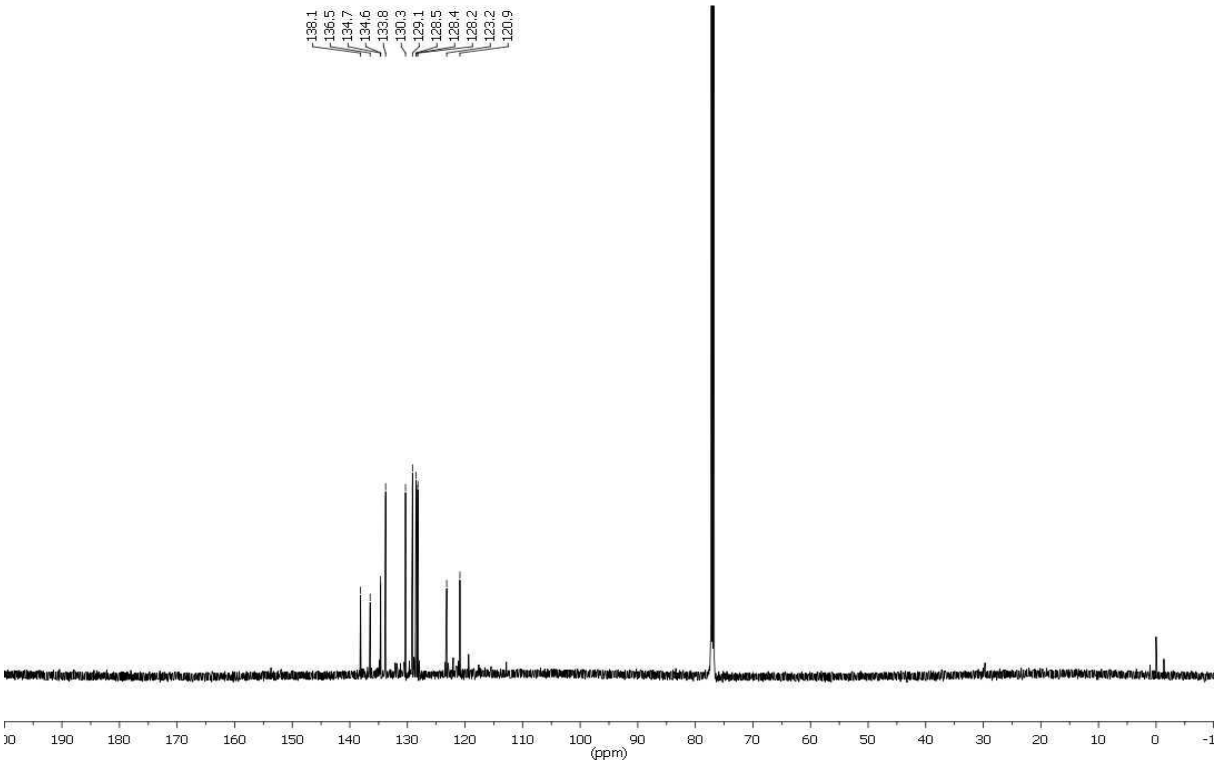
1,3-Dibromothianthrene (3ai)





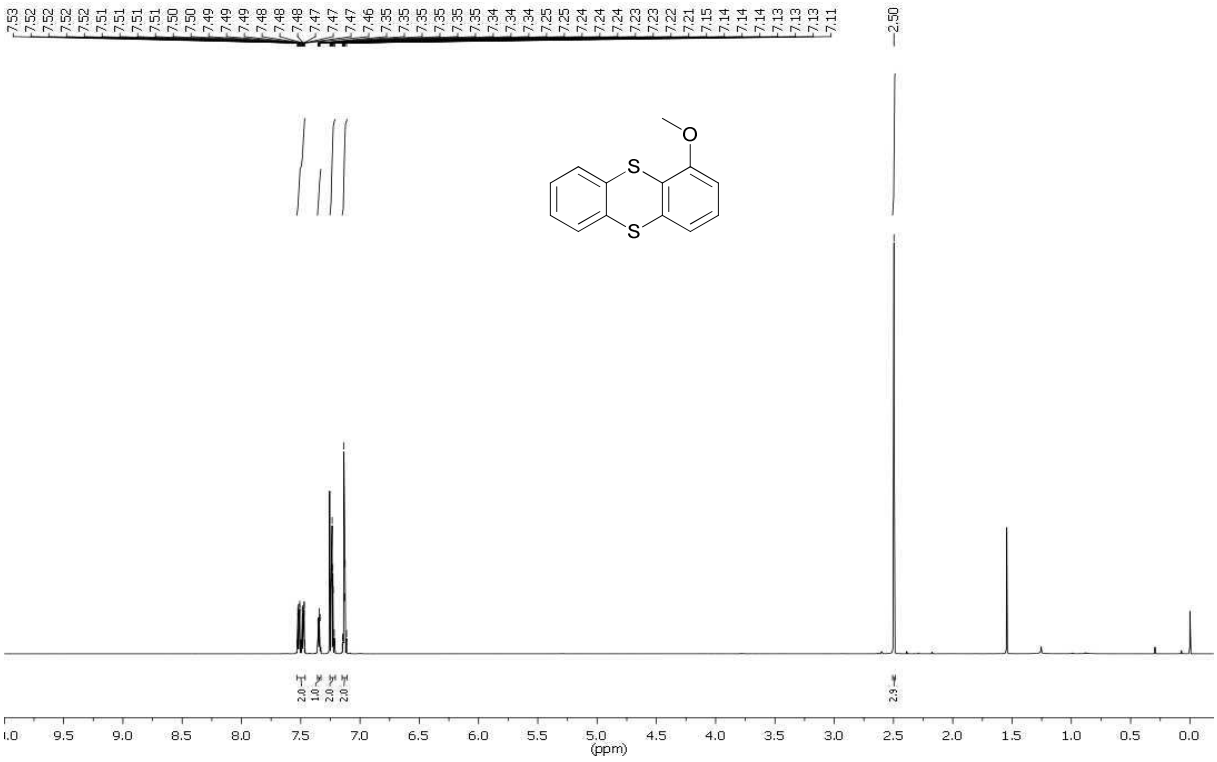


^{1}H-NMR (600 MHz, $CDCl_3$)

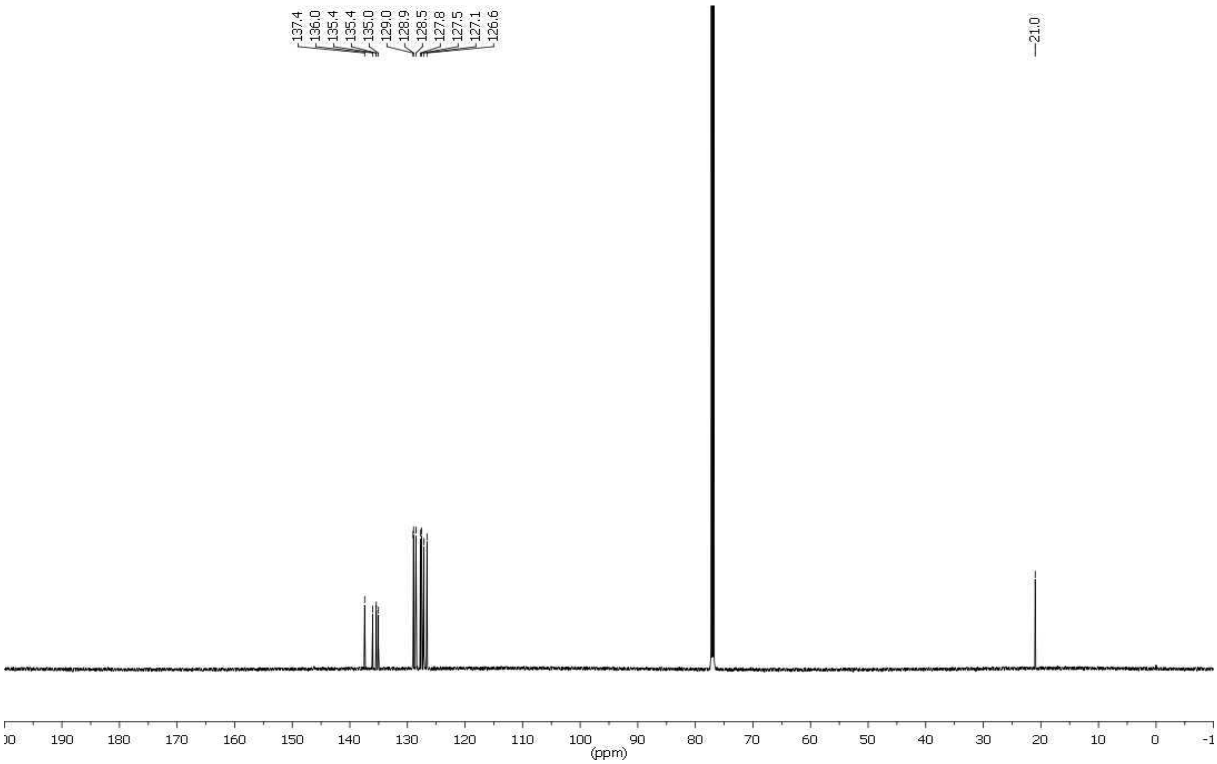


^{13}C-NMR (150 MHz, $CDCl_3$)

1-Methoxythianthrene (3aj)

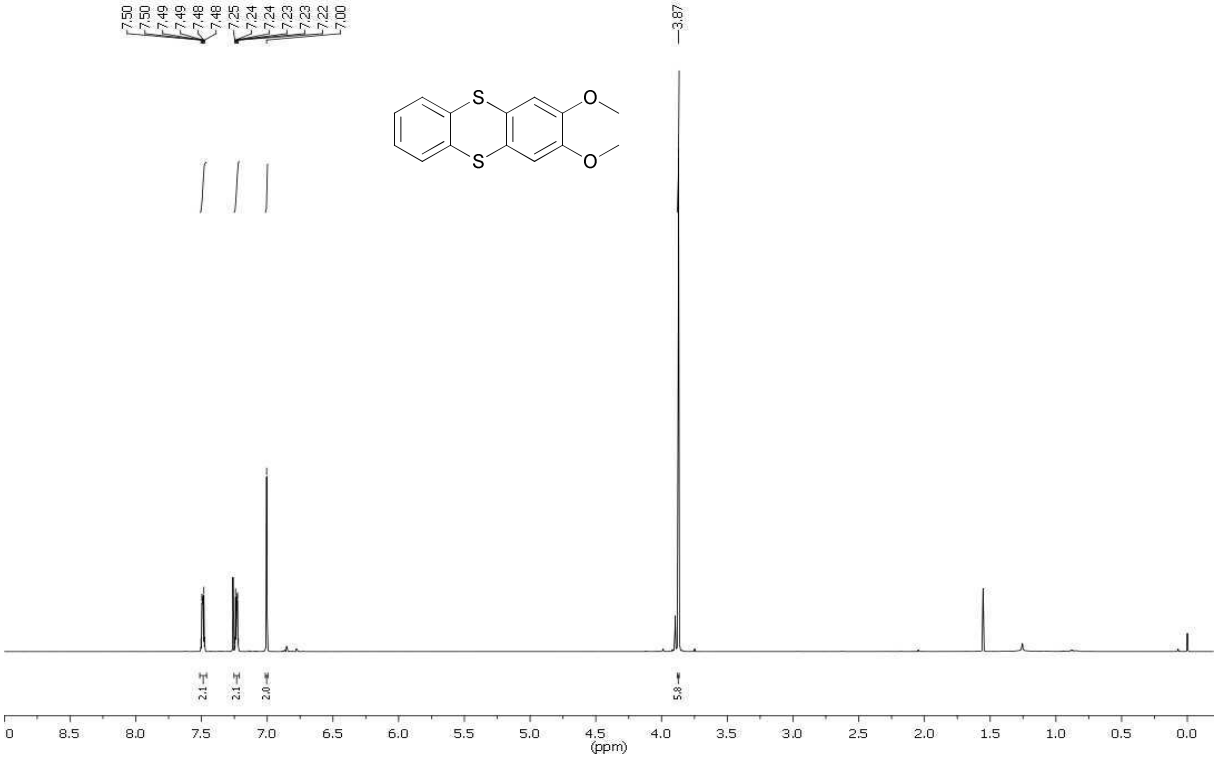


^{1}H-NMR (600 MHz, $CDCl_3$)

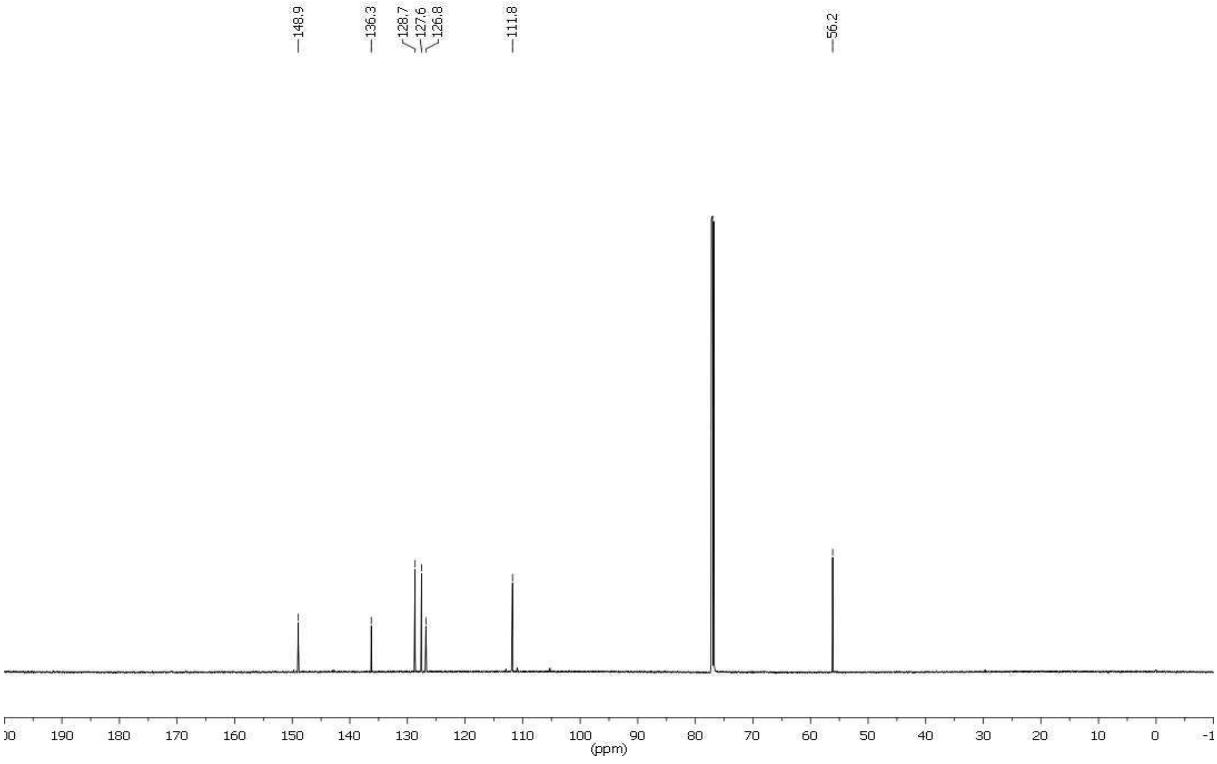


^{13}C-NMR (150 MHz, $CDCl_3$)

2,3-Dimethoxythianthrene (3ak)

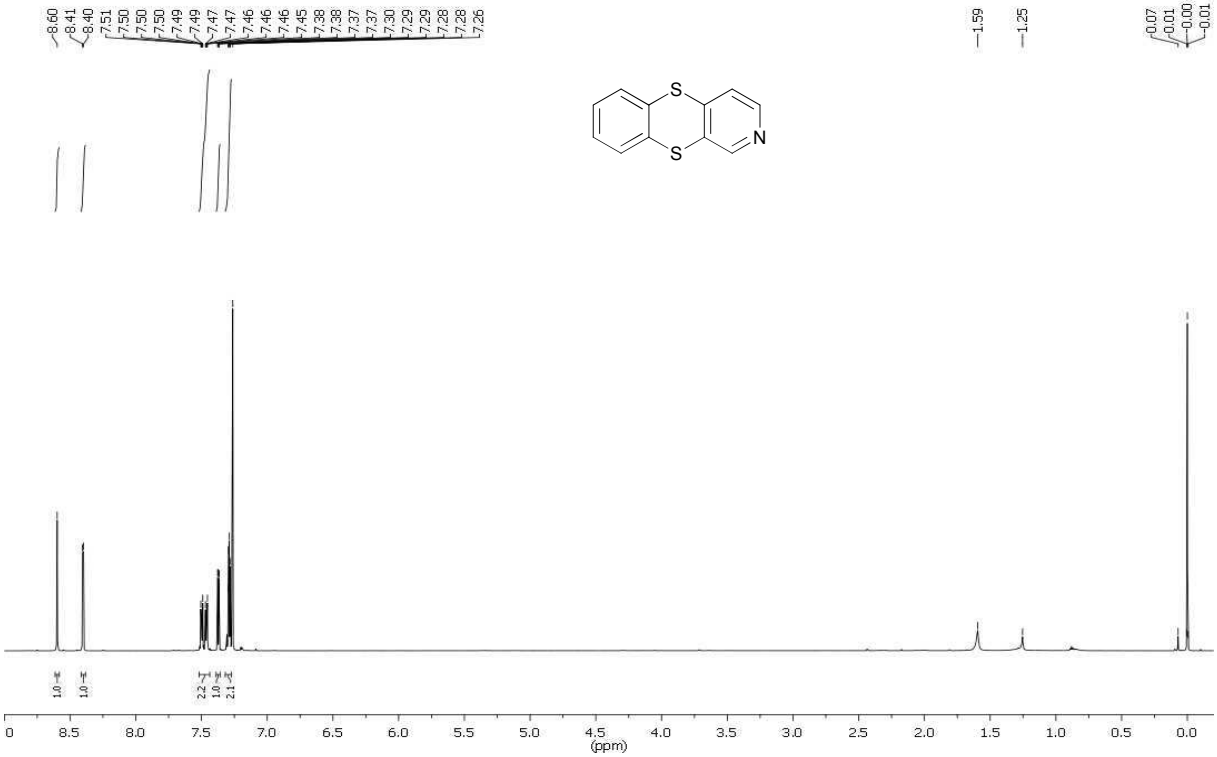


^{1}H-NMR (600 MHz, $CDCl_3$)

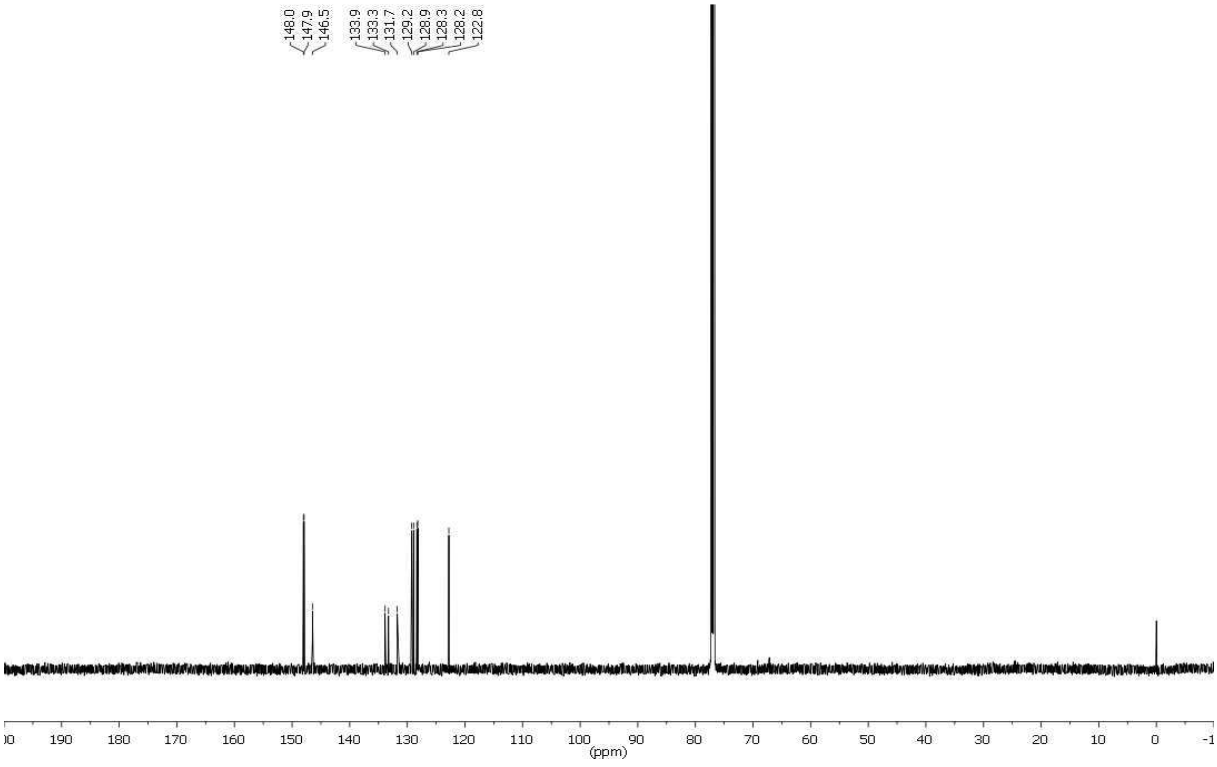


^{13}C-NMR (150 MHz, $CDCl_3$)

Benzo[5,6][1,4]dithiino[2,3-*c*]pyridine (3ai)

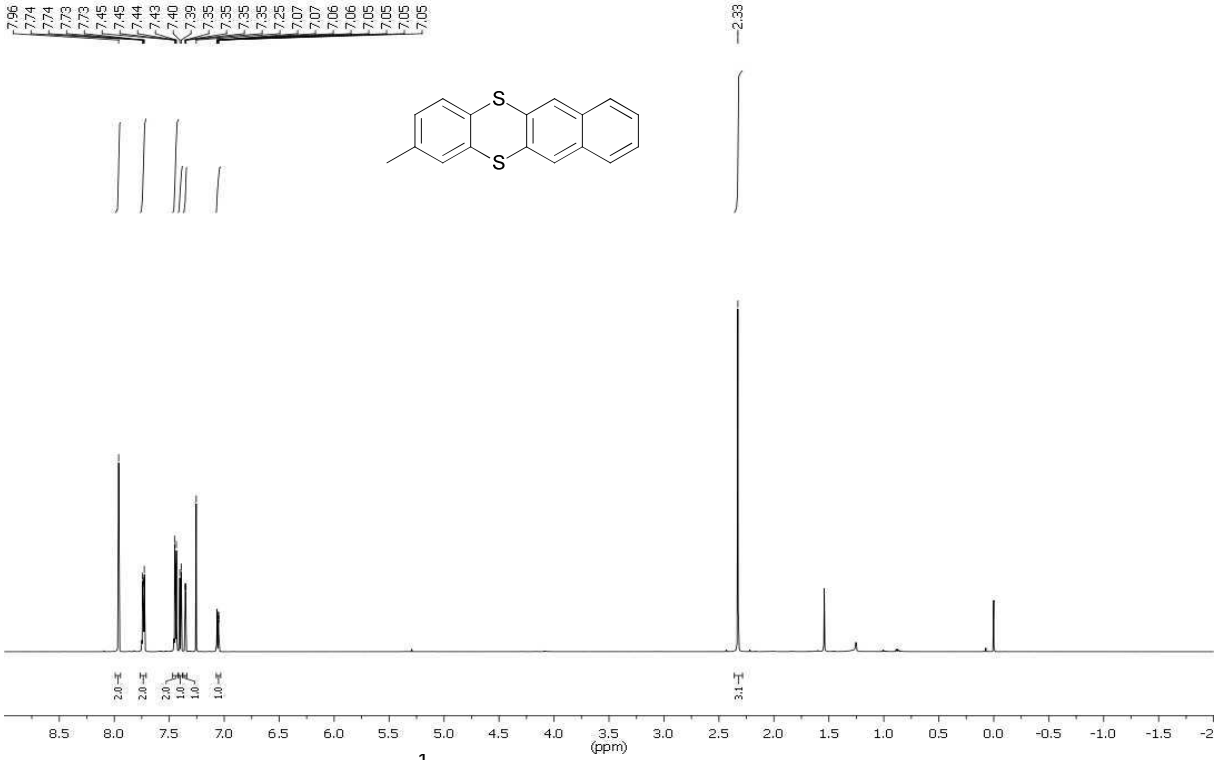


^{1}H-NMR (600 MHz, $CDCl_3$)

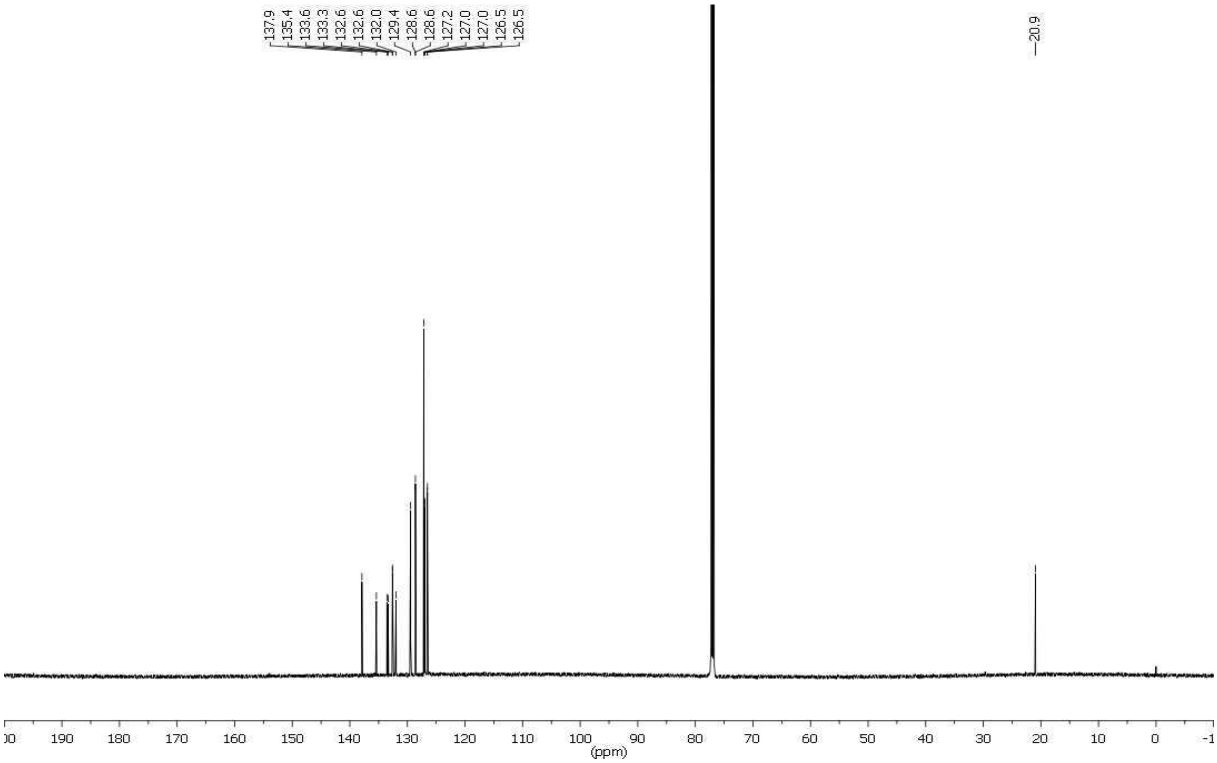


^{13}C-NMR (150 MHz, $CDCl_3$)

2-Methylbenzo[*b*]thianthrene (3be)

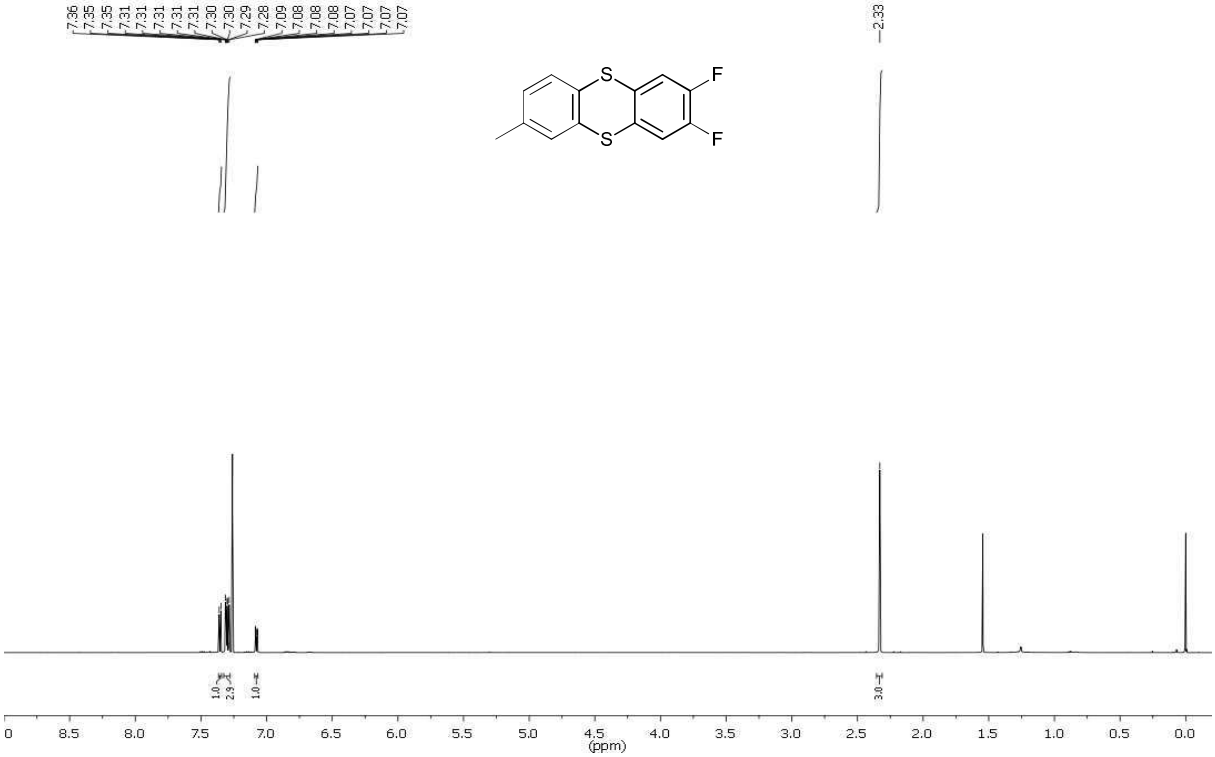


^{1}H-NMR (600 MHz, $CDCl_3$)

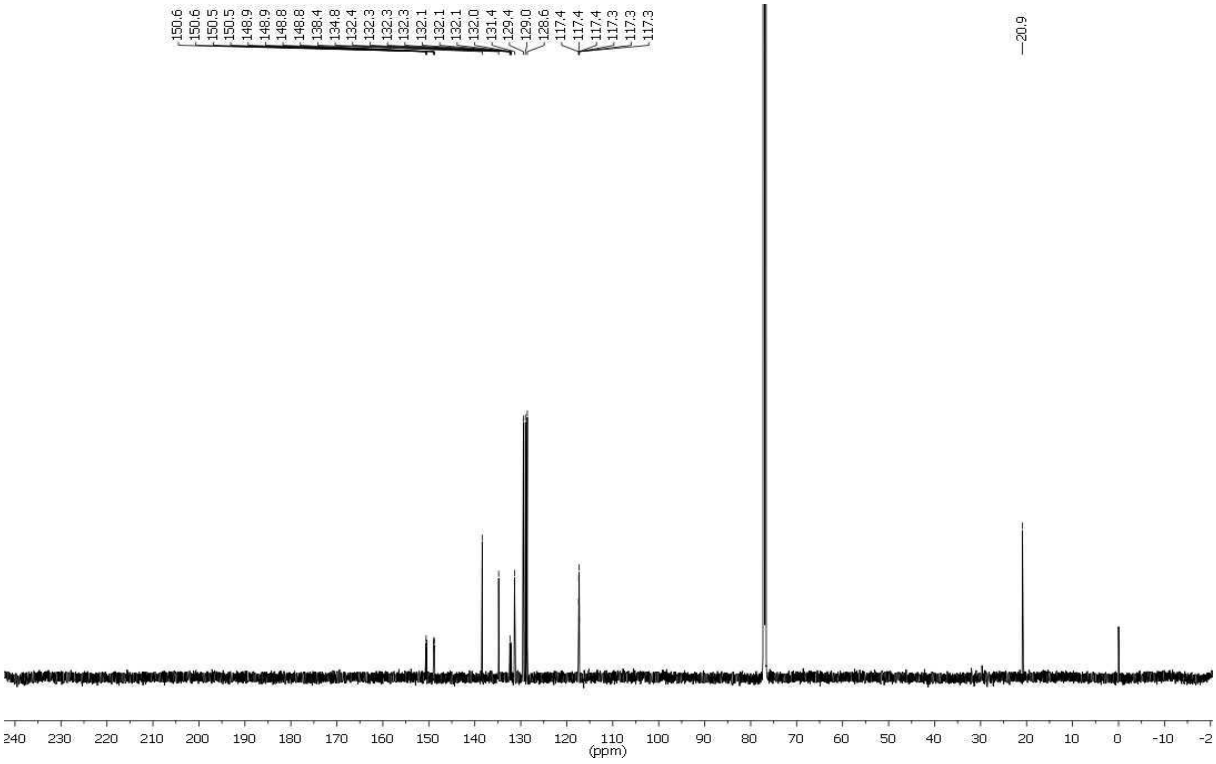


^{13}C-NMR (150 MHz, $CDCl_3$)

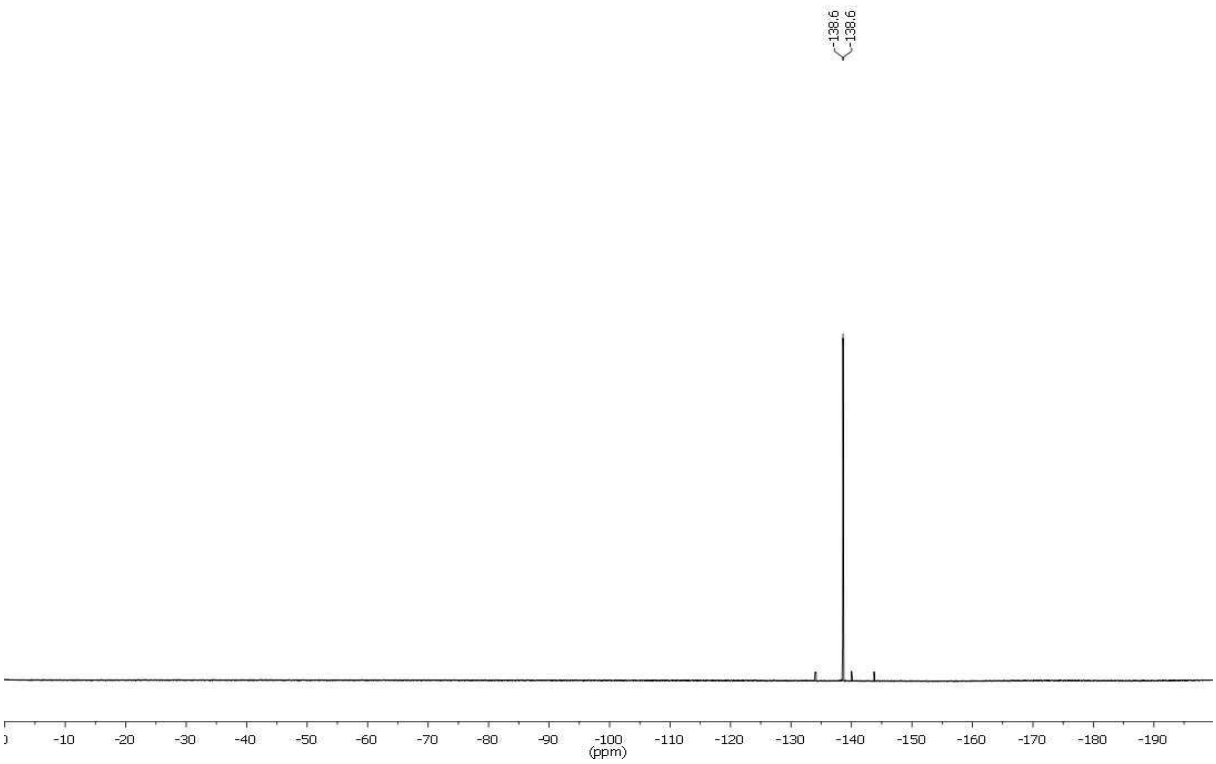
2,3-difluoro-7-methylthianthrene (3bh)



^{1}H-NMR (600 MHz, $CDCl_3$)

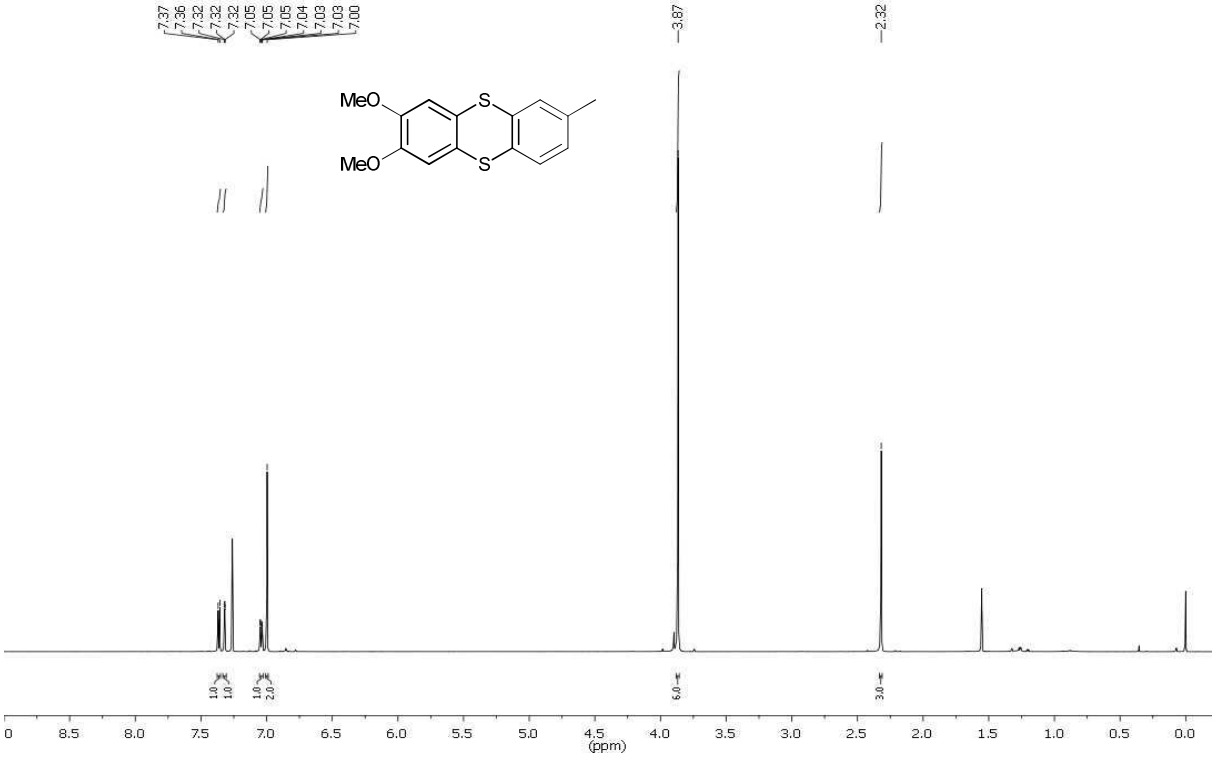


^{13}C-NMR (150 MHz, $CDCl_3$)

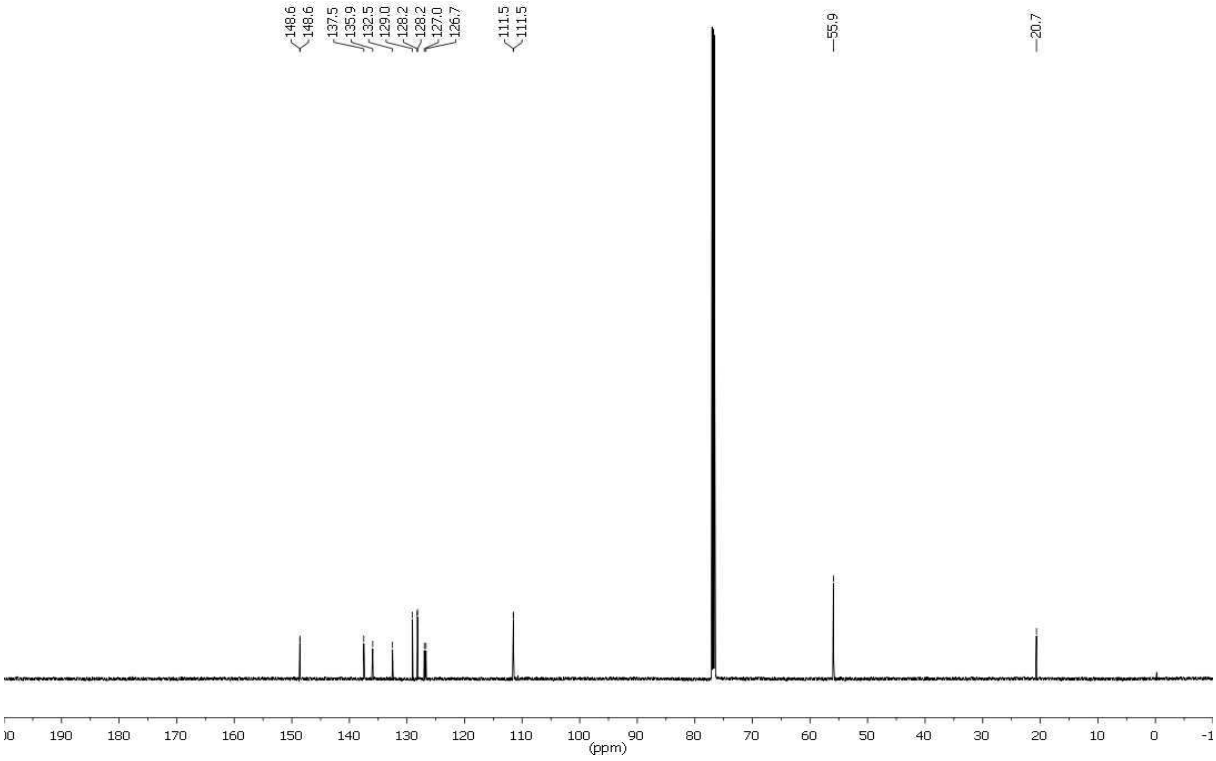


^{19}F-NMR (376 MHz, $CDCl_3$)

2,3-dimethoxy-7-methylthianthrene (3bk)

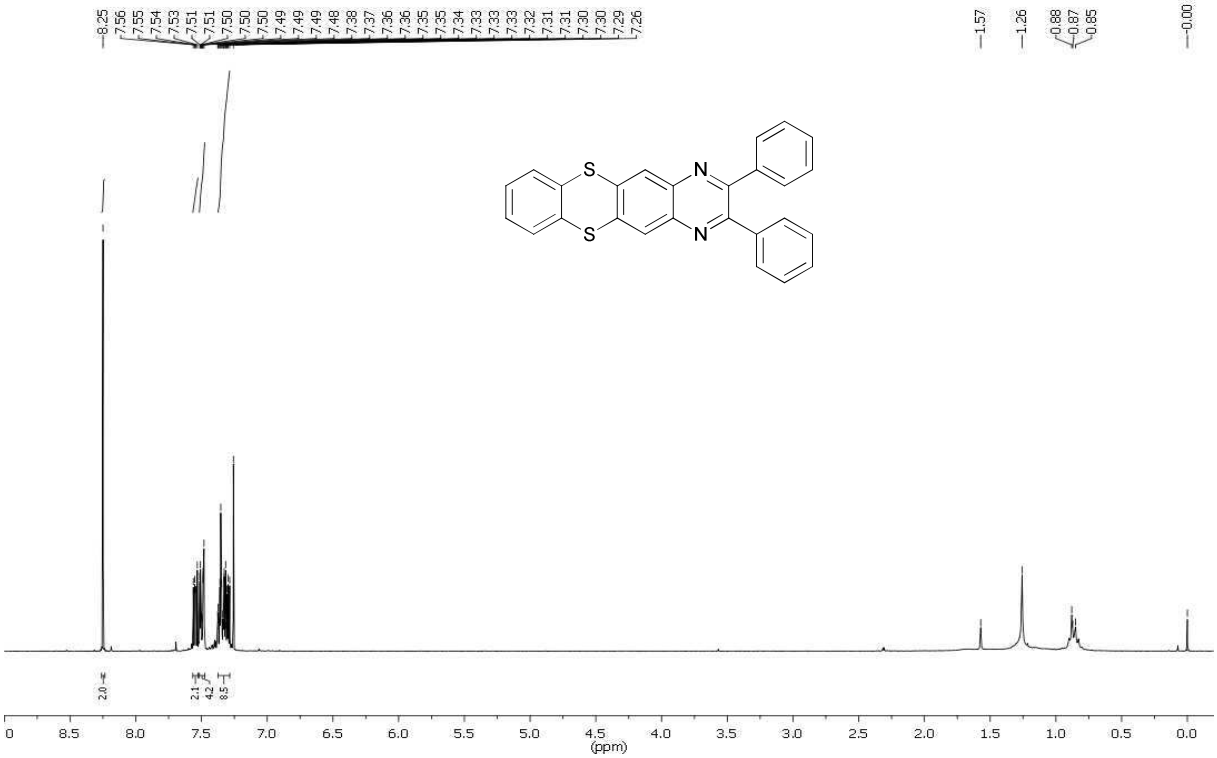


^{1}H-NMR (600 MHz, $CDCl_3$)

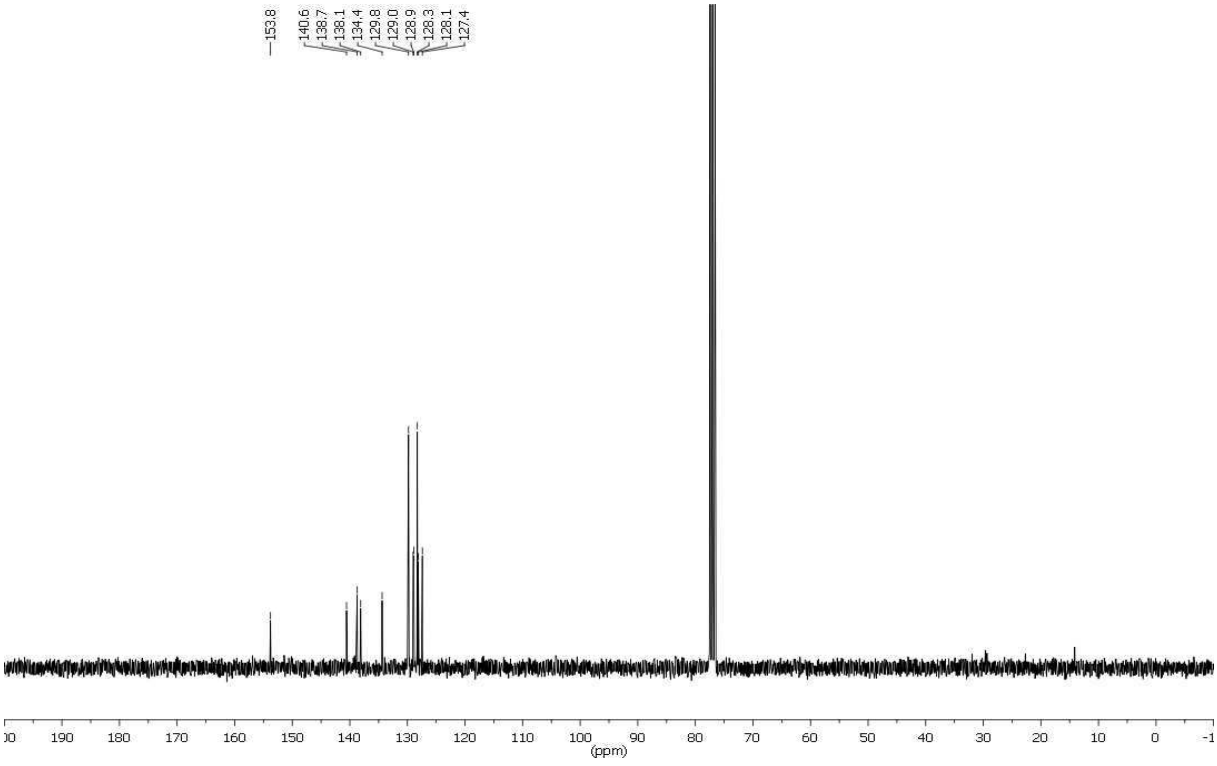


^{13}C-NMR (150 MHz, $CDCl_3$)

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

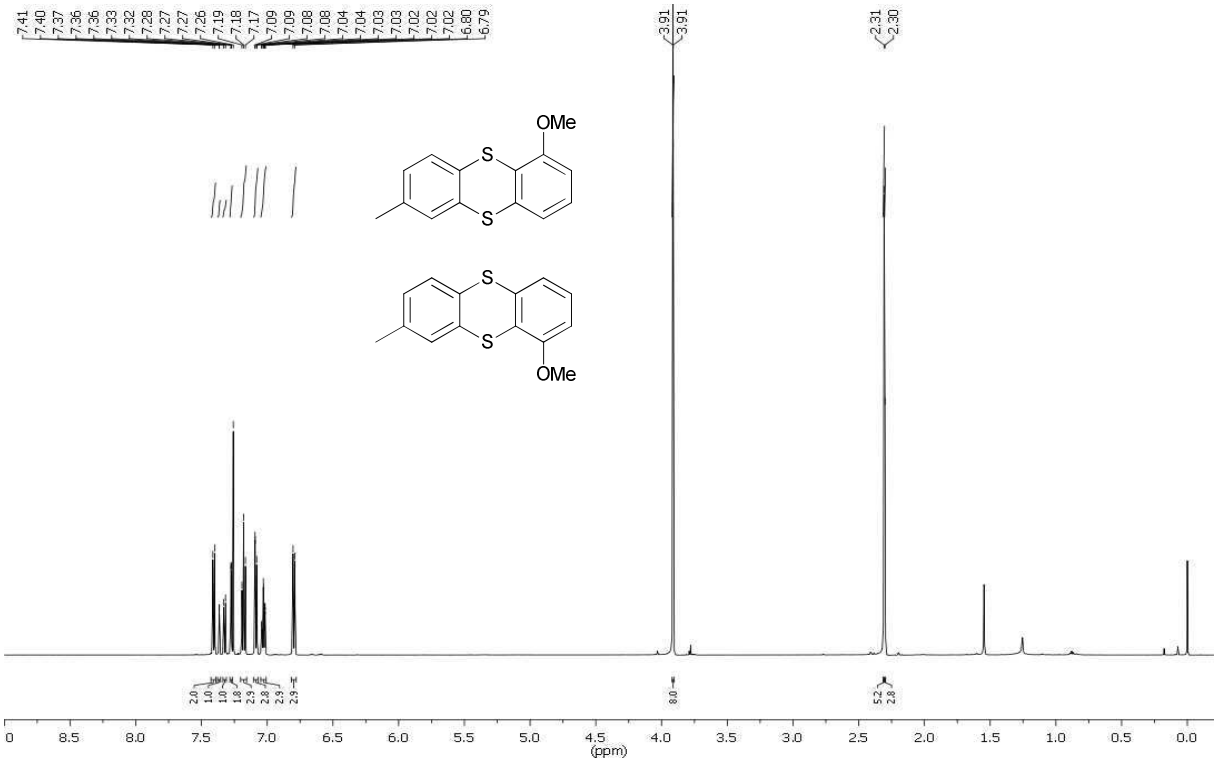


^{1}H-NMR (300 MHz, $CDCl_3$)

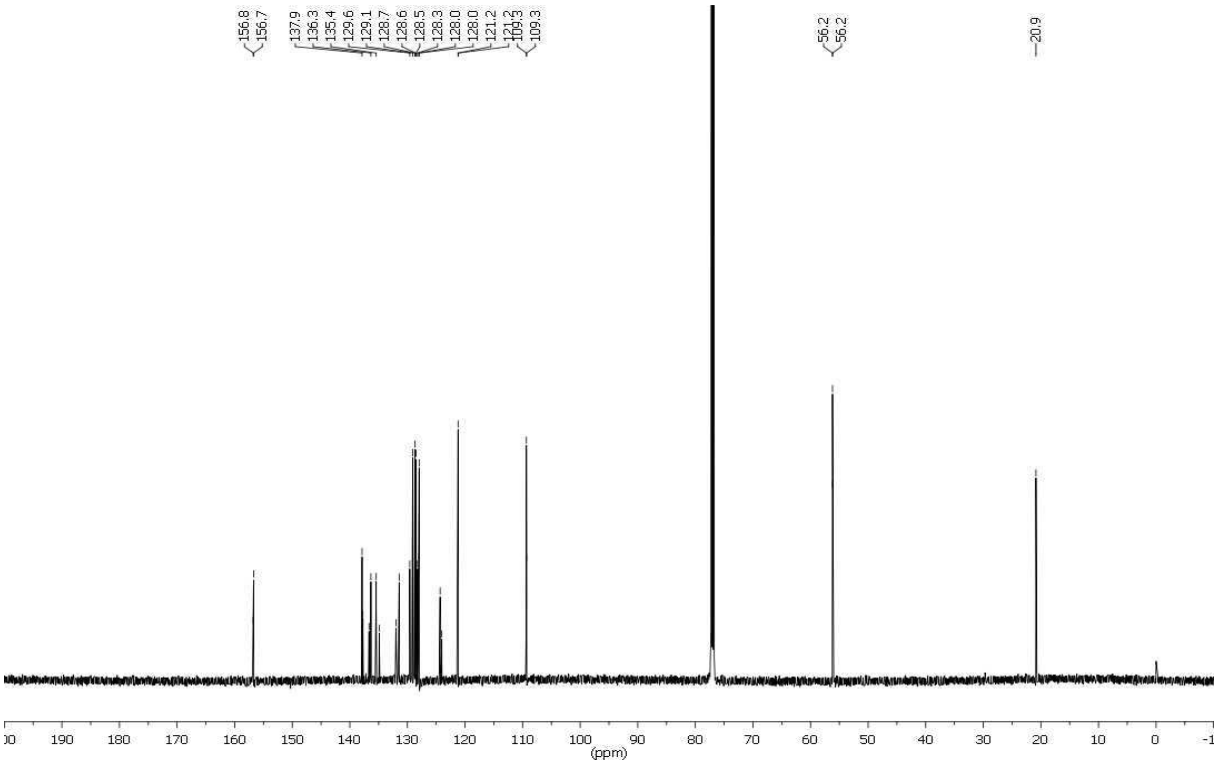


^{13}C-NMR (75 MHz, $CDCl_3$)

1-Methoxy-7-methylthianthrene (3bj) and 1-Methoxy-8-methylthianthrene (3bj')

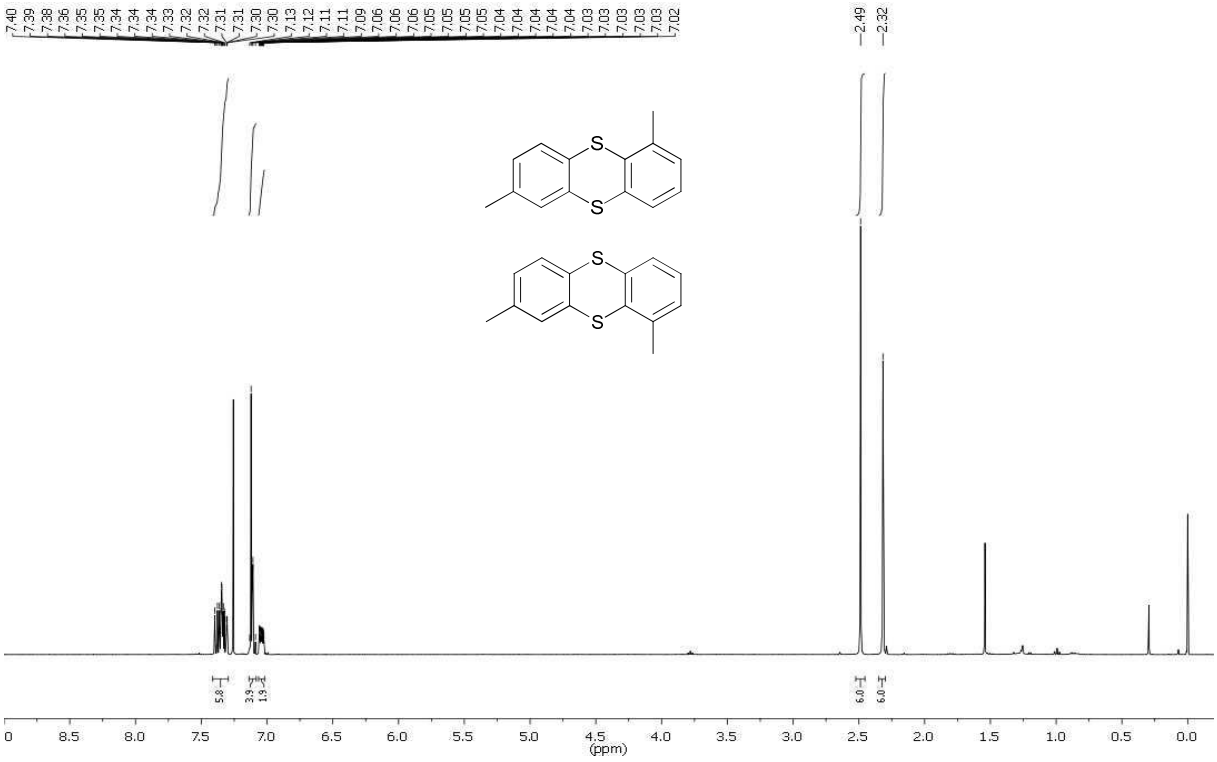


^{1}H-NMR (600 MHz, $CDCl_3$)

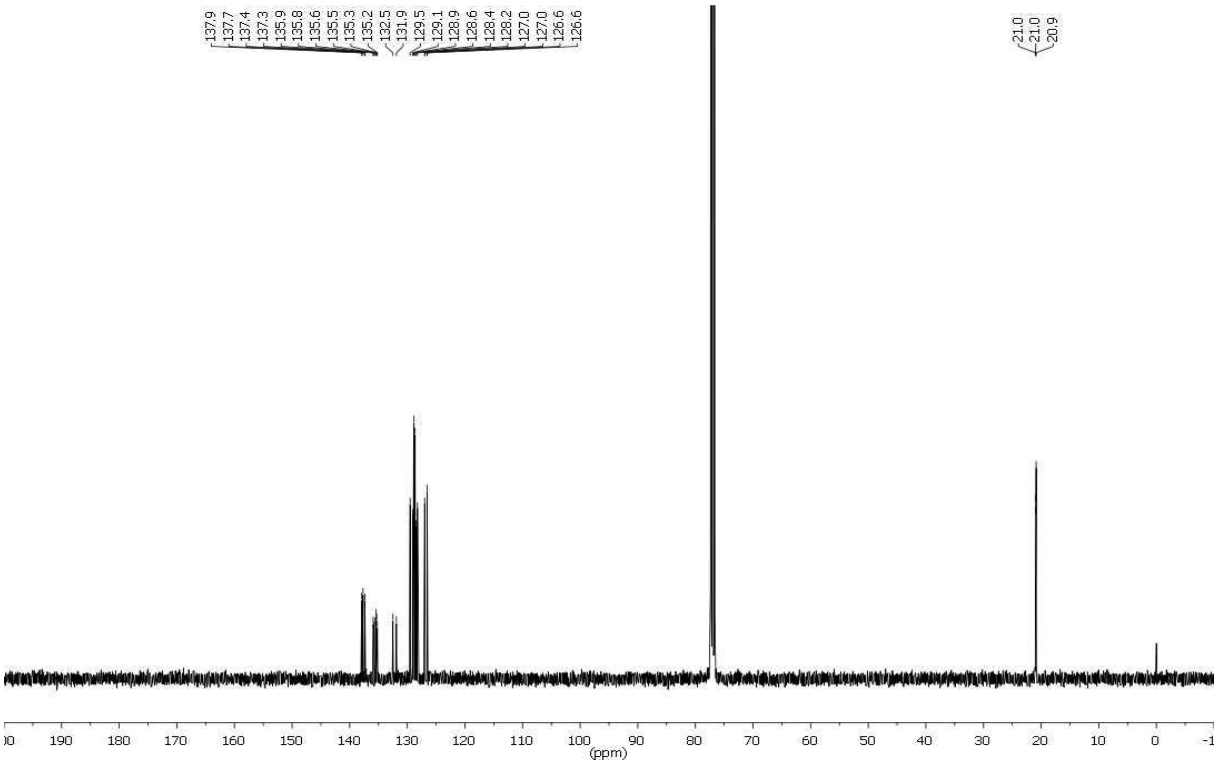


^{13}C-NMR (150 MHz, $CDCl_3$)

1,7-dimethylthianthrene (3bc) and 1,8-dimethylthianthrene (3bc')

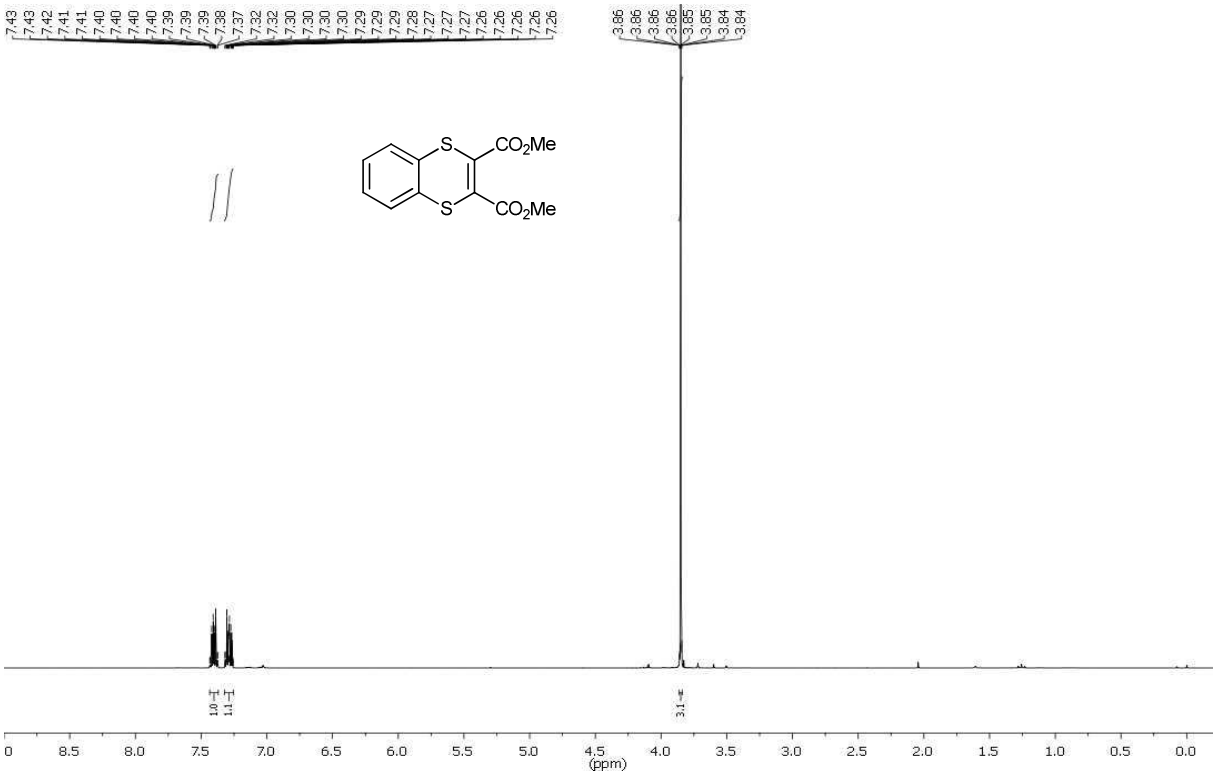


^{1}H-NMR (400 MHz, $CDCl_3$)

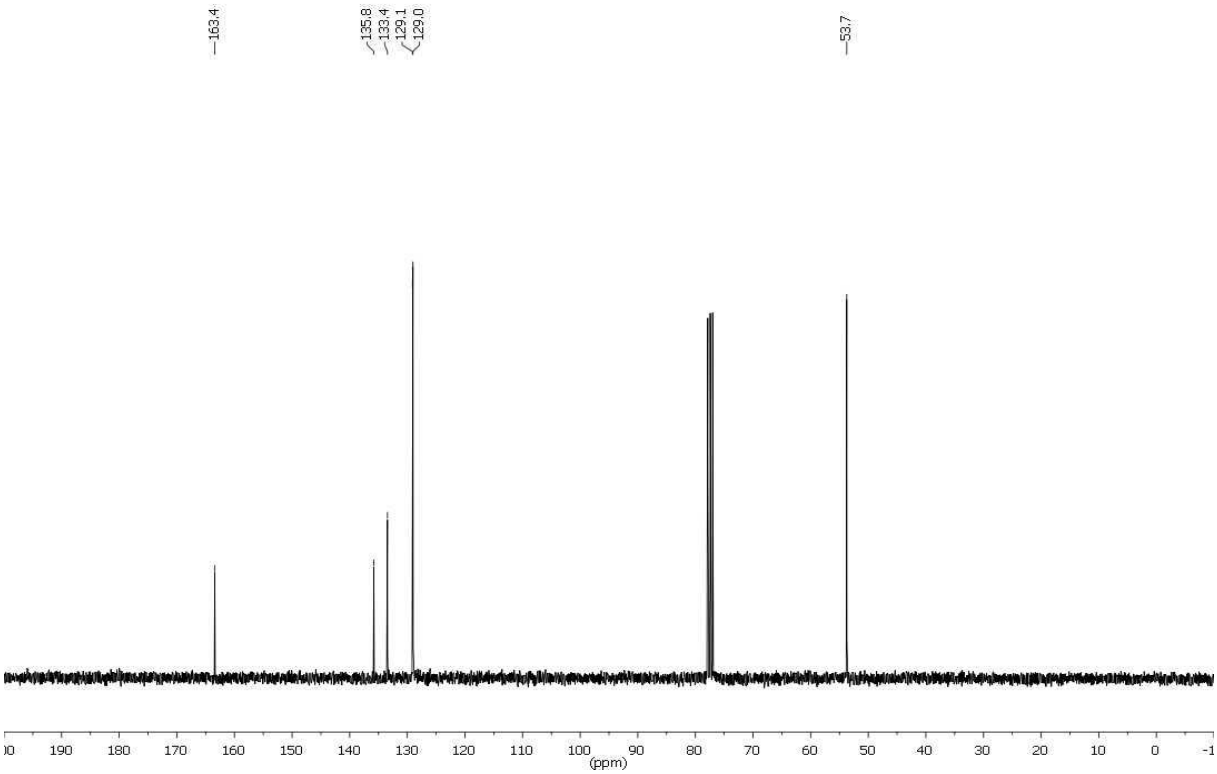


^{13}C-NMR (100 MHz, $CDCl_3$)

Dimethyl benzo[*b*][1,4]dithiine-2,3-dicarboxylate (7aa)

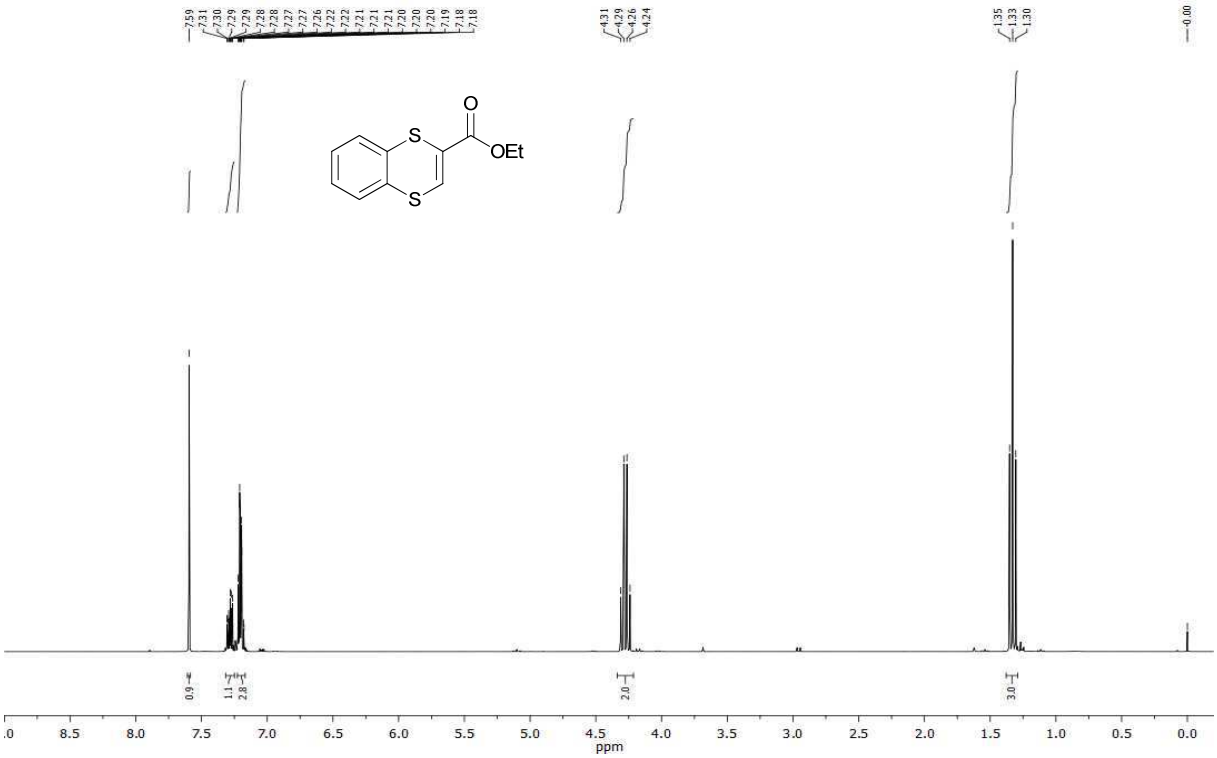


^{1}H-NMR (300 MHz, $CDCl_3$)

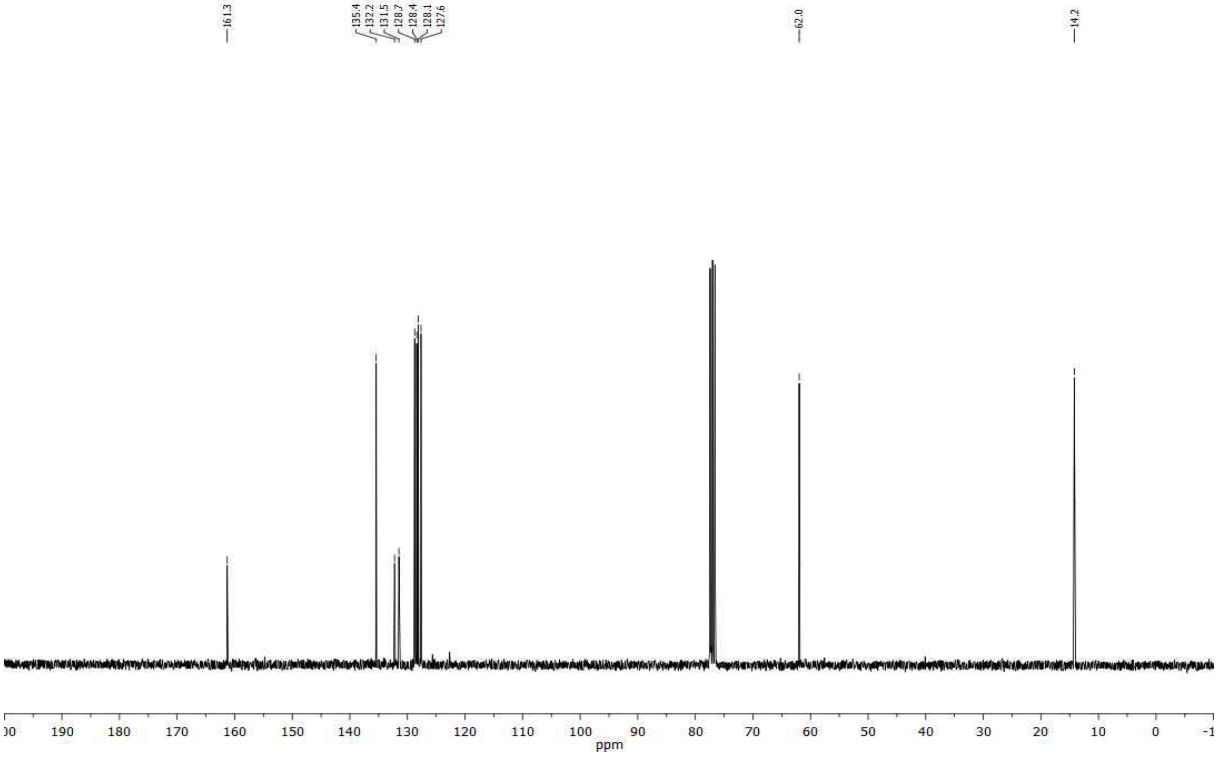


^{13}C-NMR (75 MHz, $CDCl_3$)

2-Methylbenzo[*b*]thianthrene (7ab)

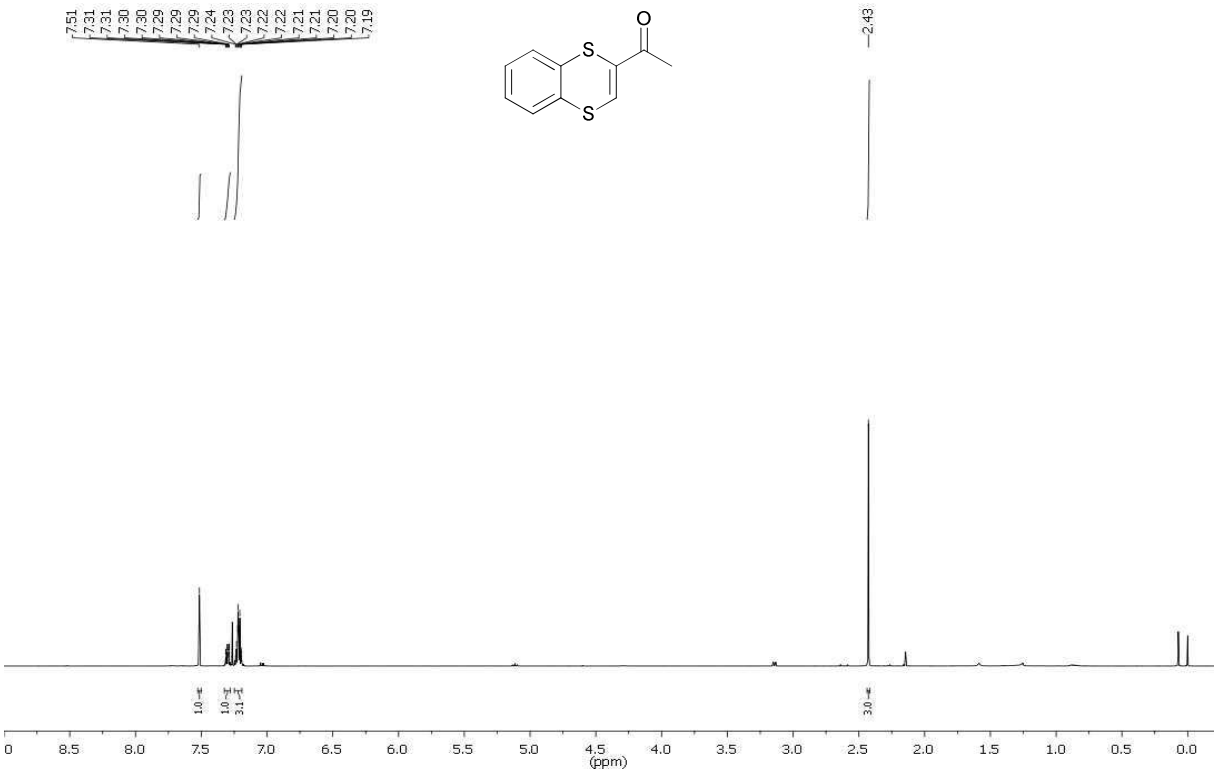


^{1}H-NMR (300 MHz, $CDCl_3$)

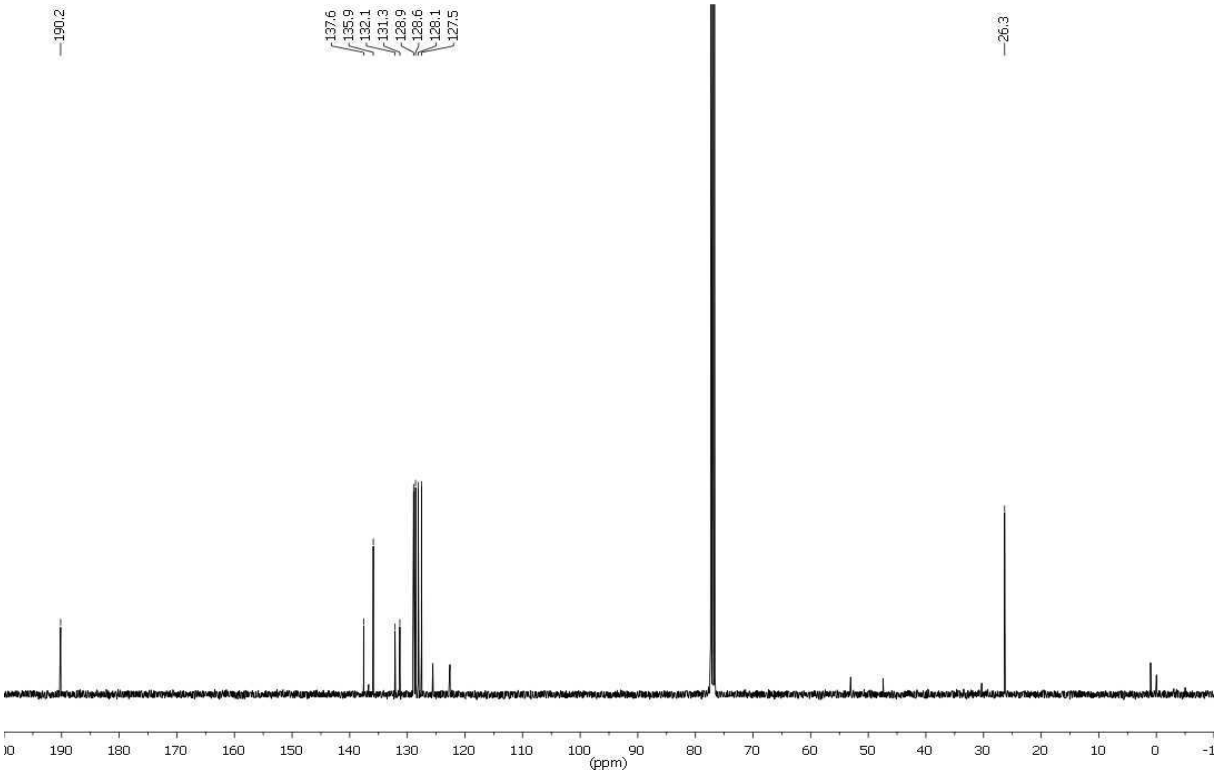


^{13}C-NMR (75 MHz, $CDCl_3$)

1-(Benzo[*b*][1,4]dithiin-2-yl)ethanone (7ac)

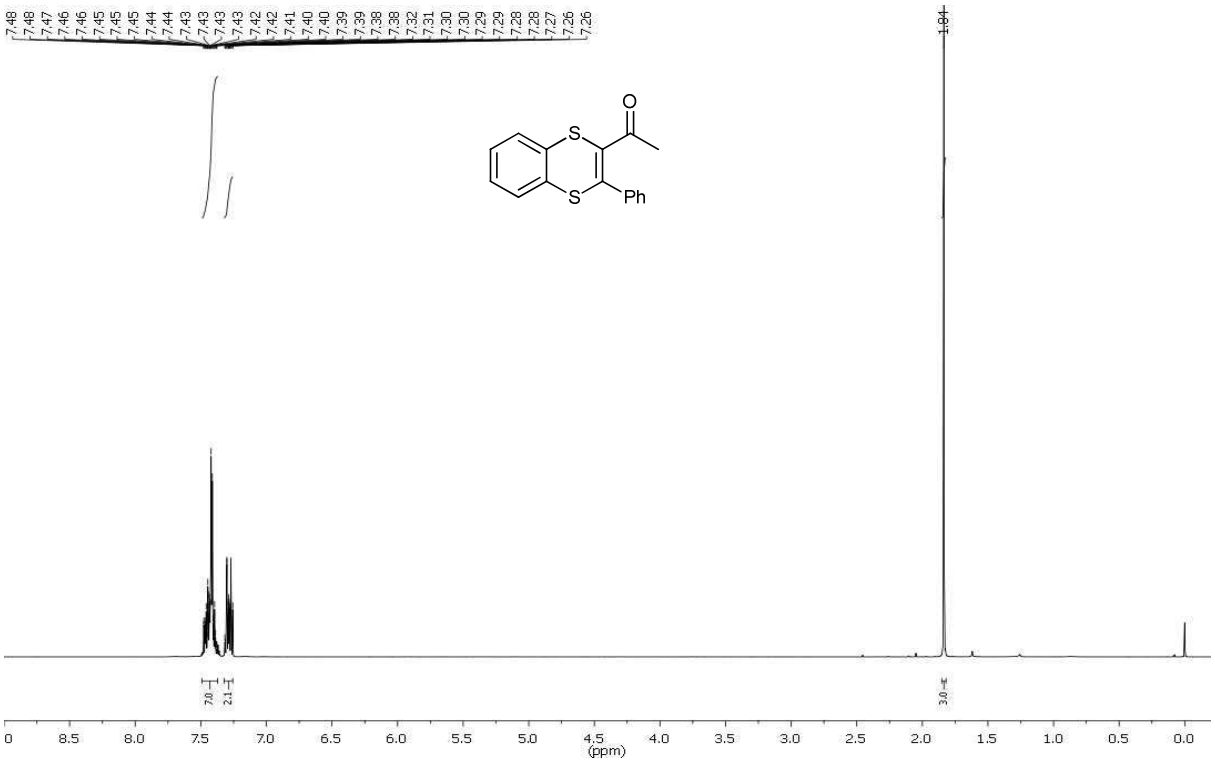


^{1}H-NMR (400 MHz, $CDCl_3$)

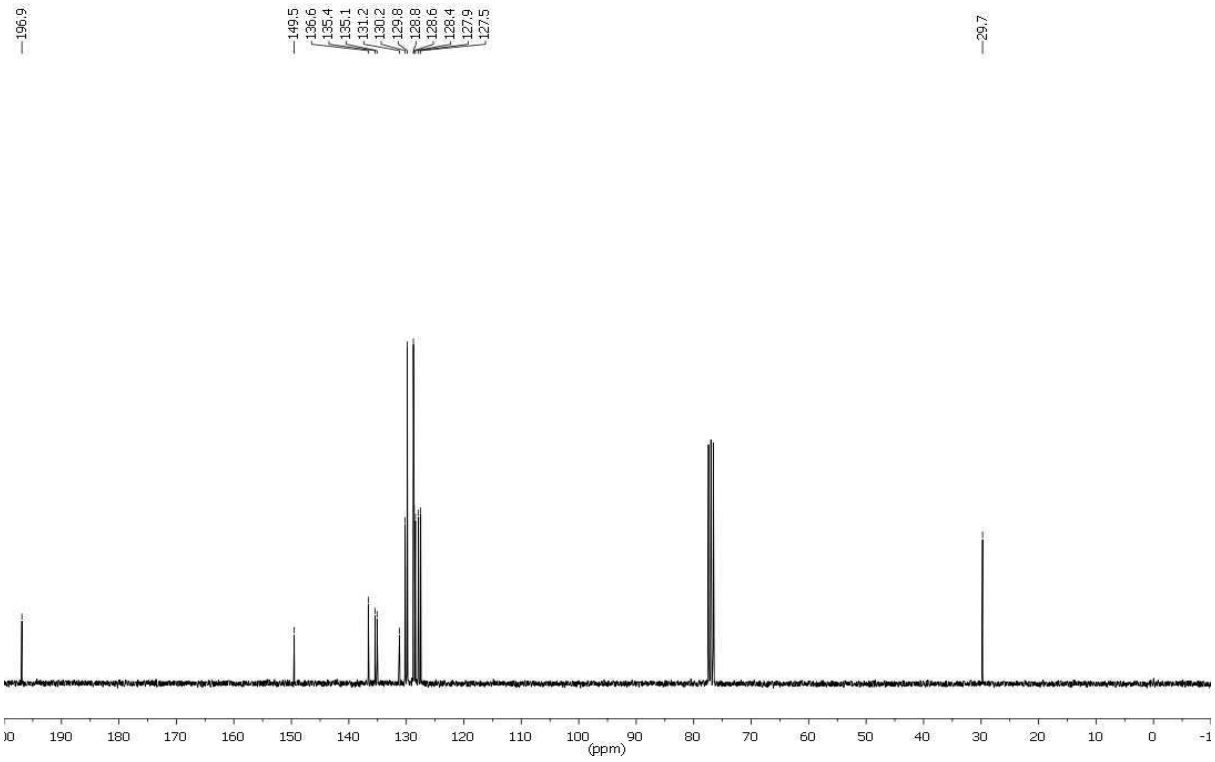


^{13}C-NMR (100 MHz, $CDCl_3$)

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

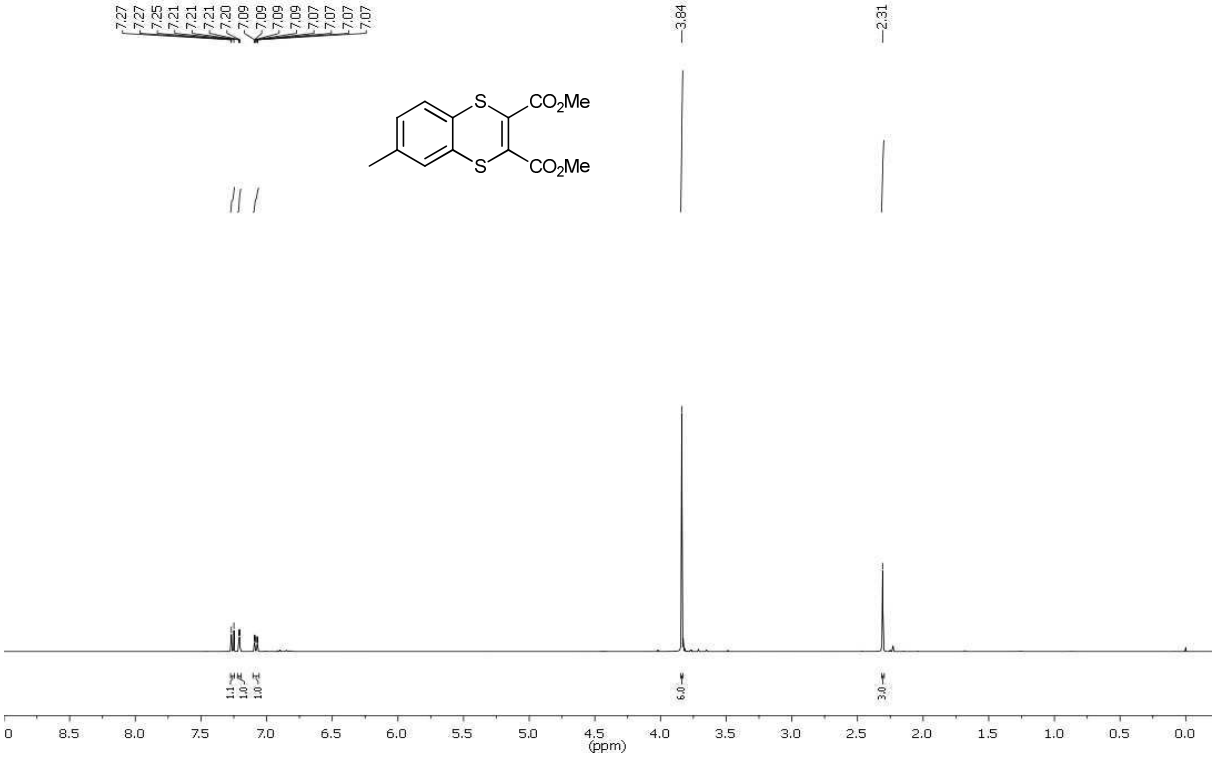


^{1}H-NMR (300 MHz, $CDCl_3$)

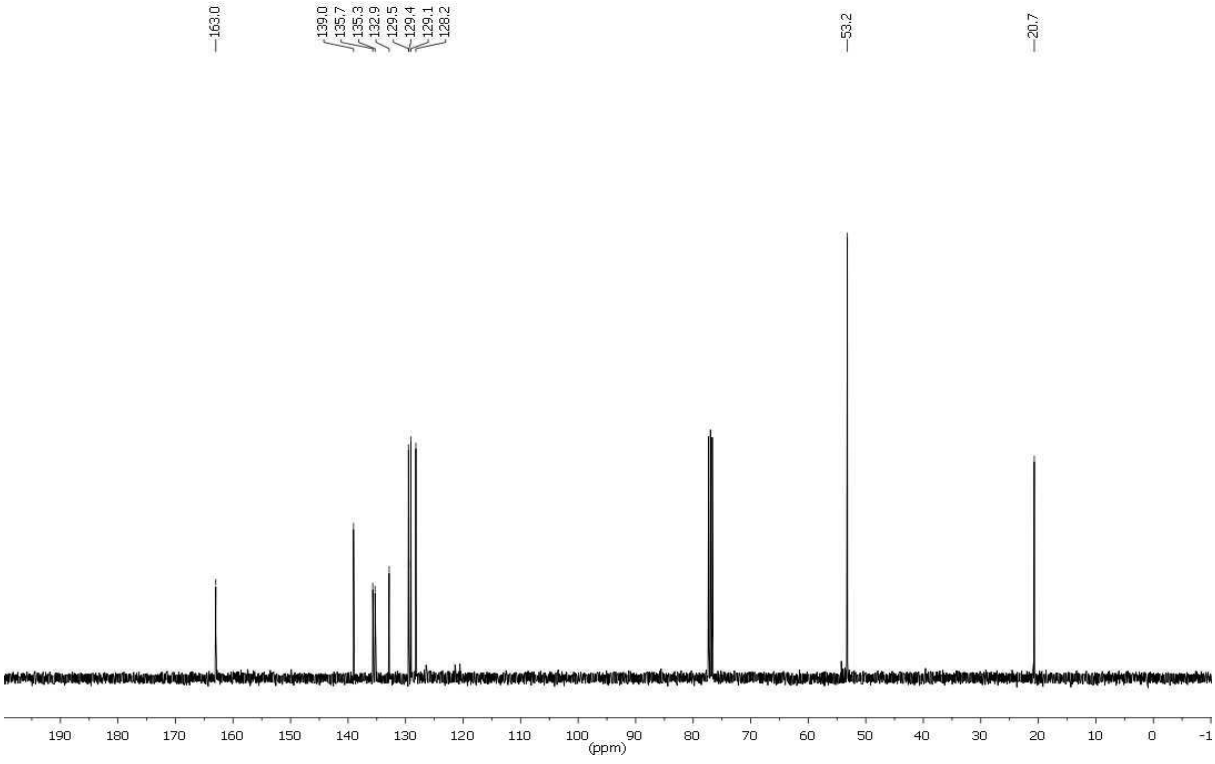


^{13}C-NMR (75 MHz, $CDCl_3$)

Dimethyl 6-methylbenzo[*b*][1,4]dithiine-2,3-dicarboxylate (7ba)

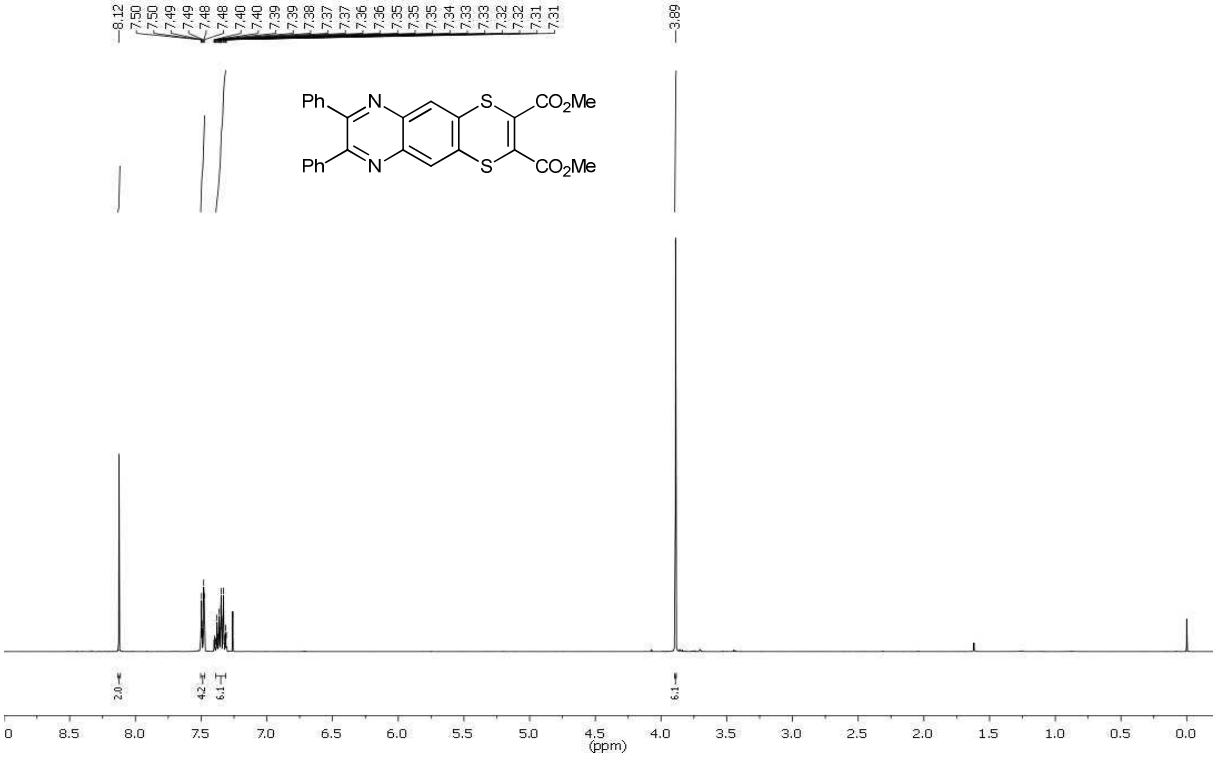


^{1}H-NMR (400 MHz, $CDCl_3$)

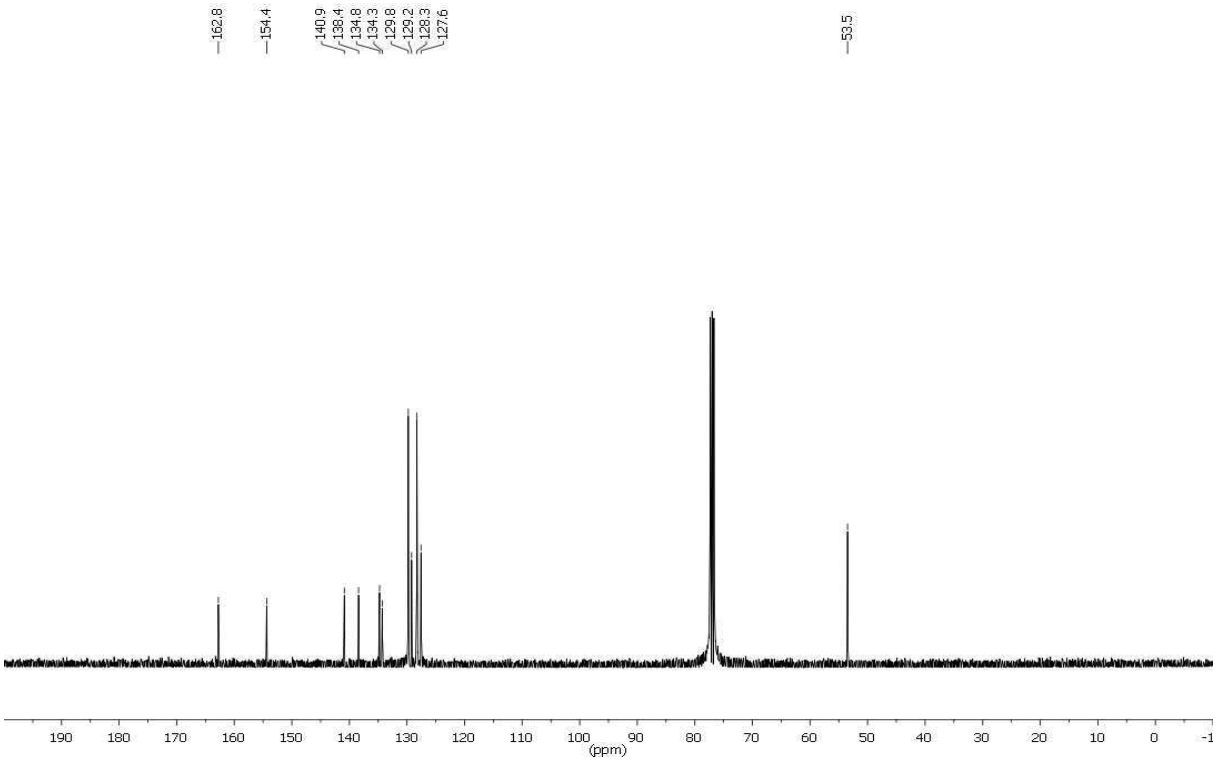


^{13}C-NMR (100 MHz, $CDCl_3$)

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

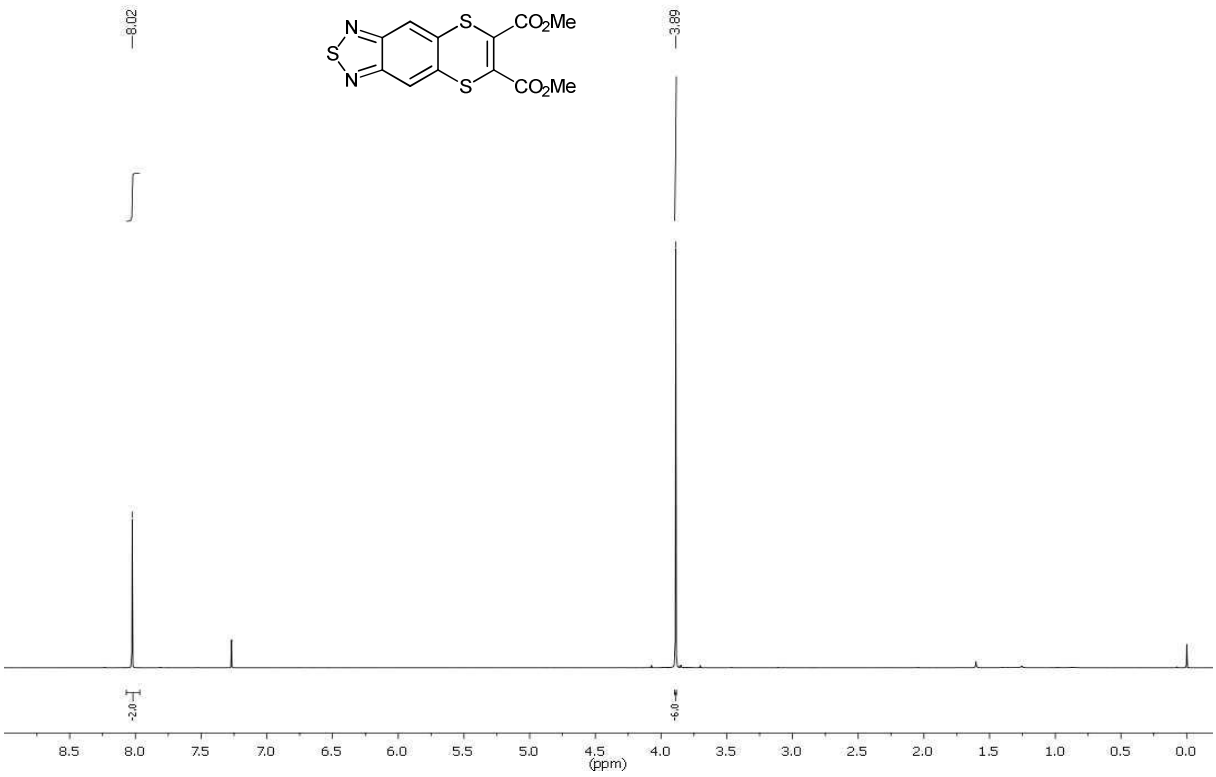


^{1}H-NMR (400 MHz, $CDCl_3$)

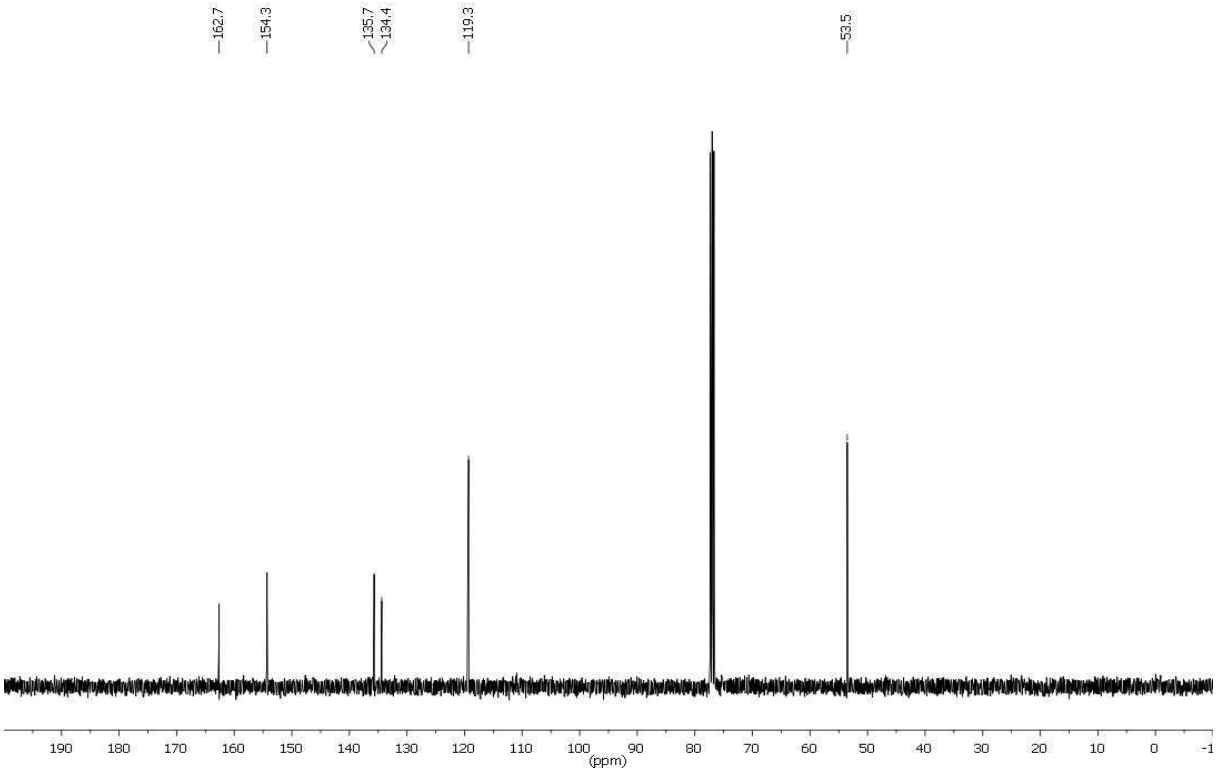


^{13}C-NMR (100 MHz, $CDCl_3$)

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

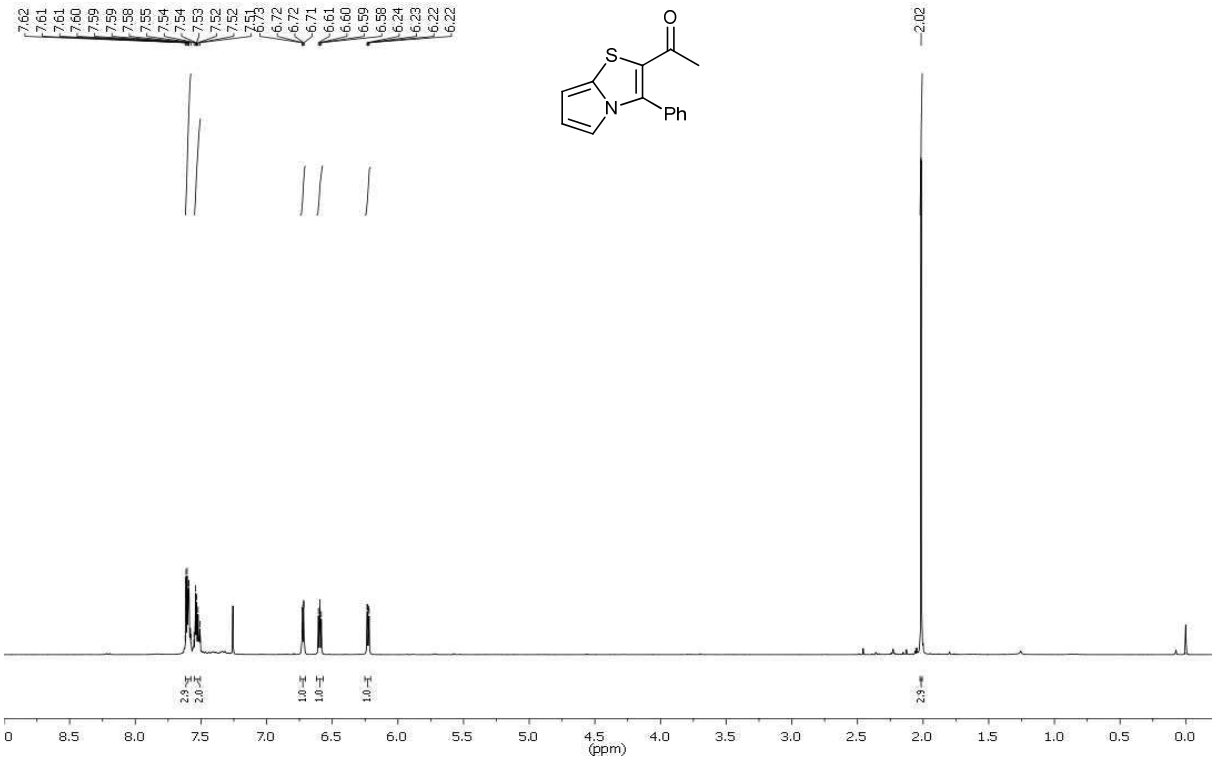


^{1}H-NMR (400 MHz, $CDCl_3$)

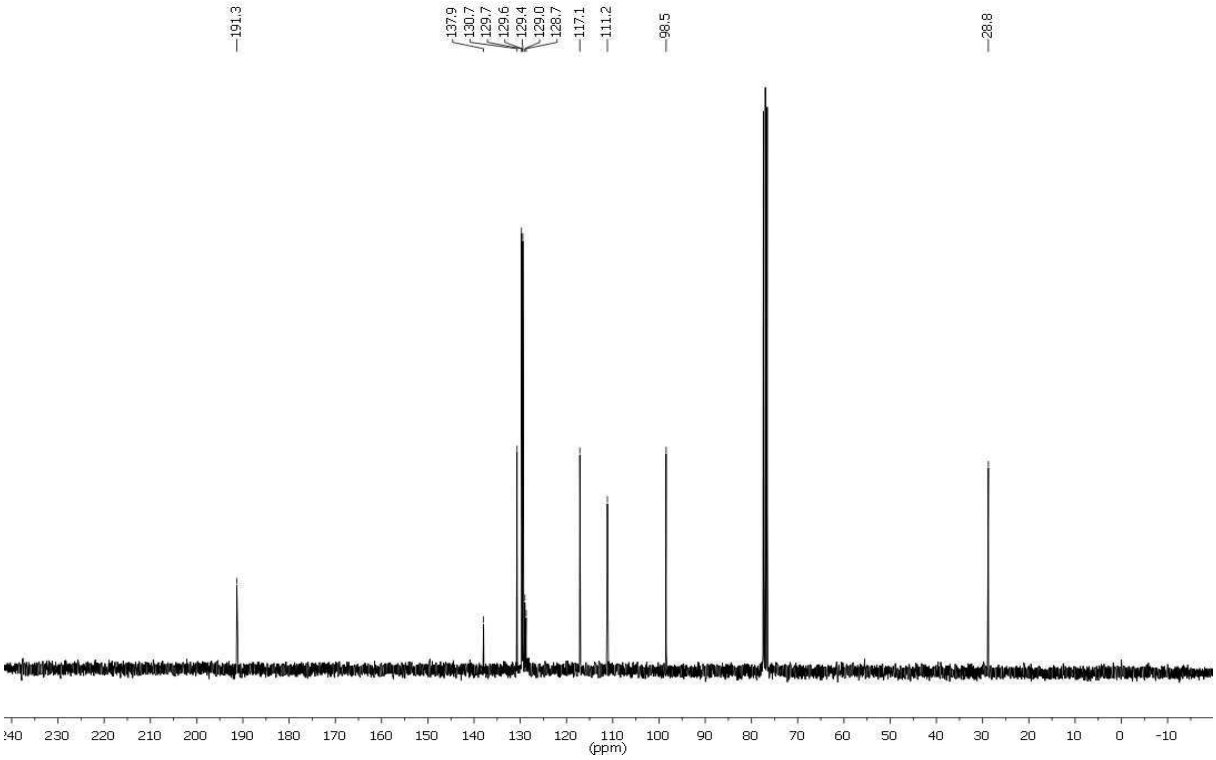


^{13}C-NMR (100 MHz, $CDCl_3$)

1-(3-Phenylpyrrolo[2,1-*b*]thiazol-2-yl)ethanone (10ad)

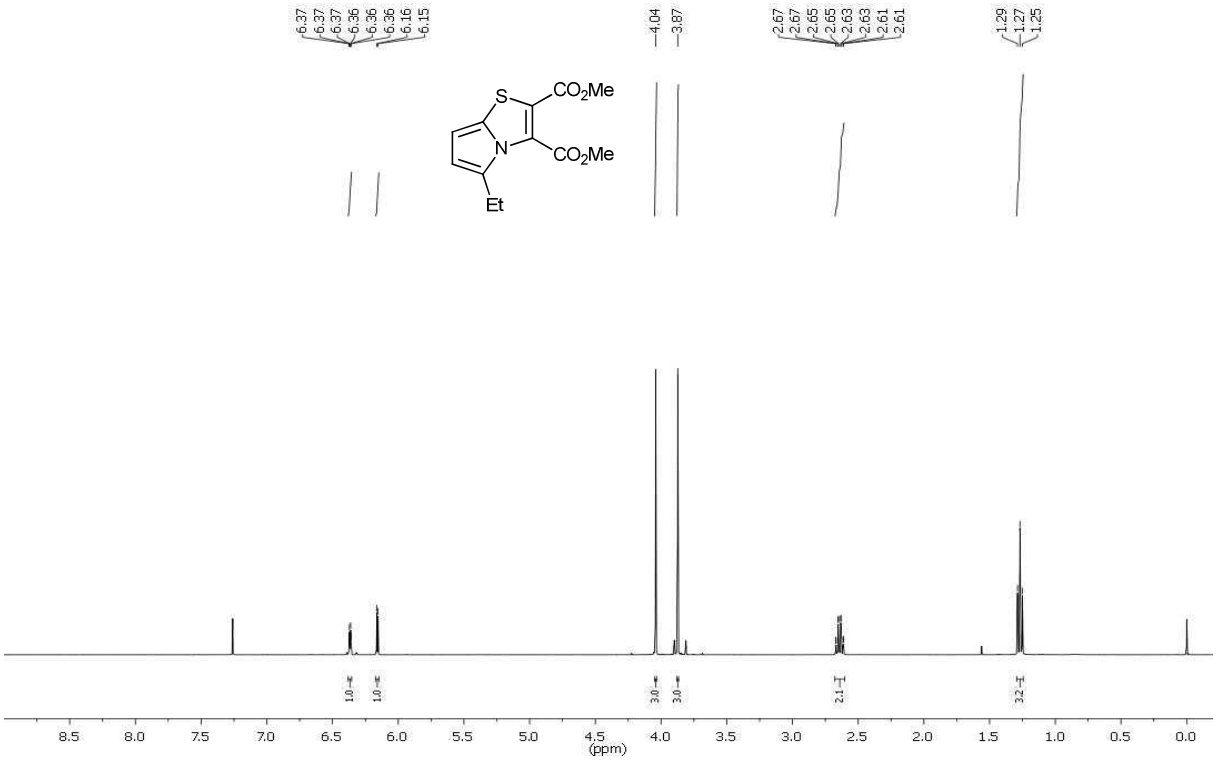


^{1}H-NMR (300 MHz, $CDCl_3$)

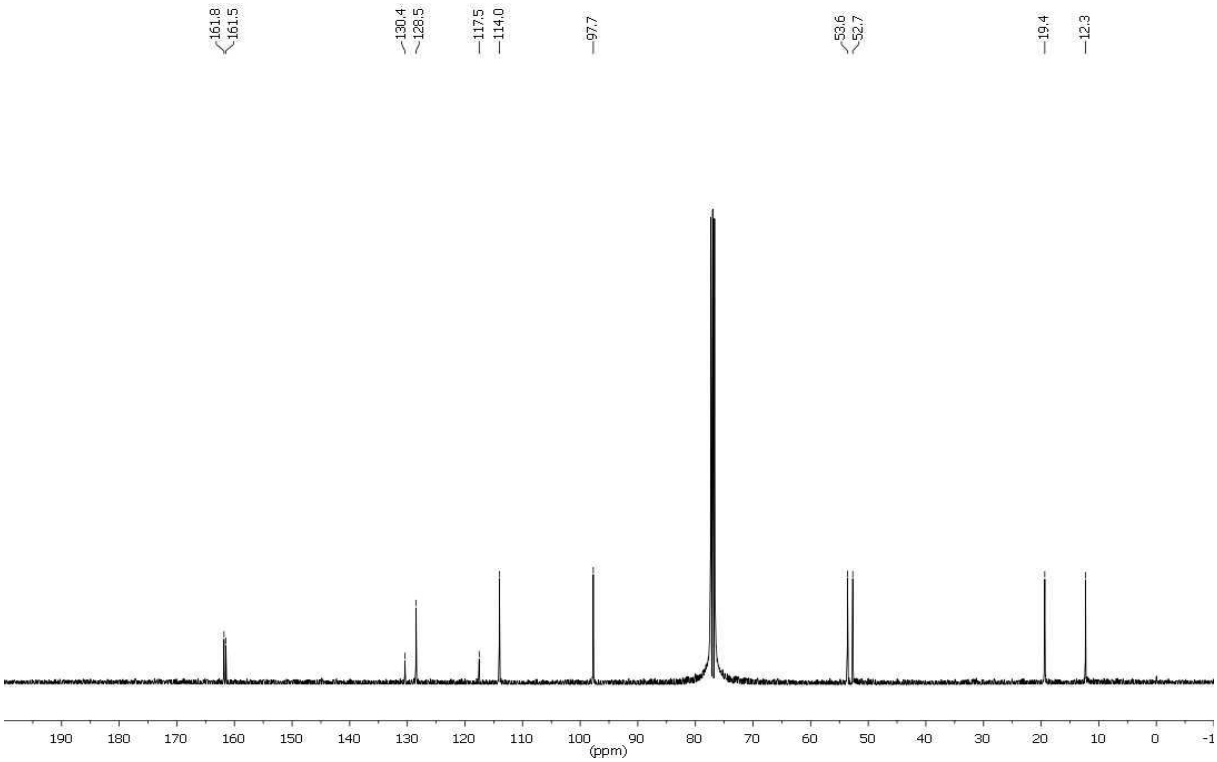


^{13}C-NMR (75 MHz, $CDCl_3$)

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

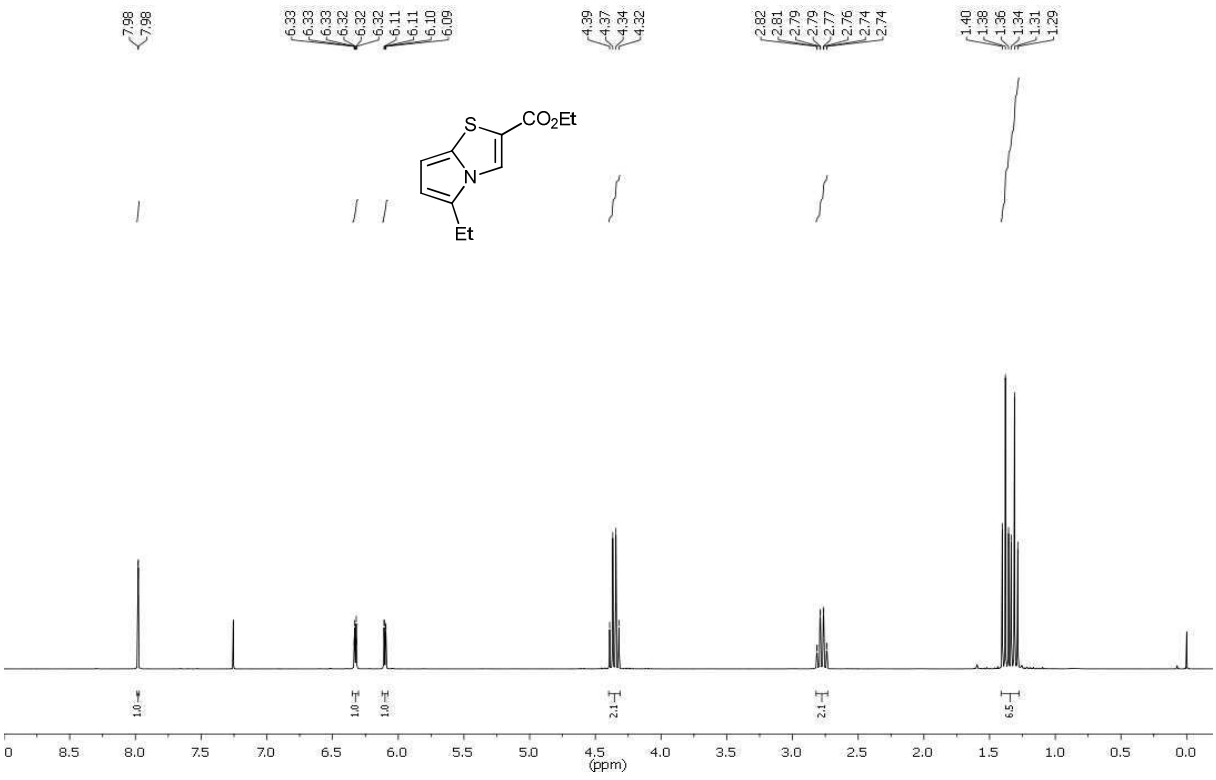


^{1}H-NMR (400 MHz, $CDCl_3$)

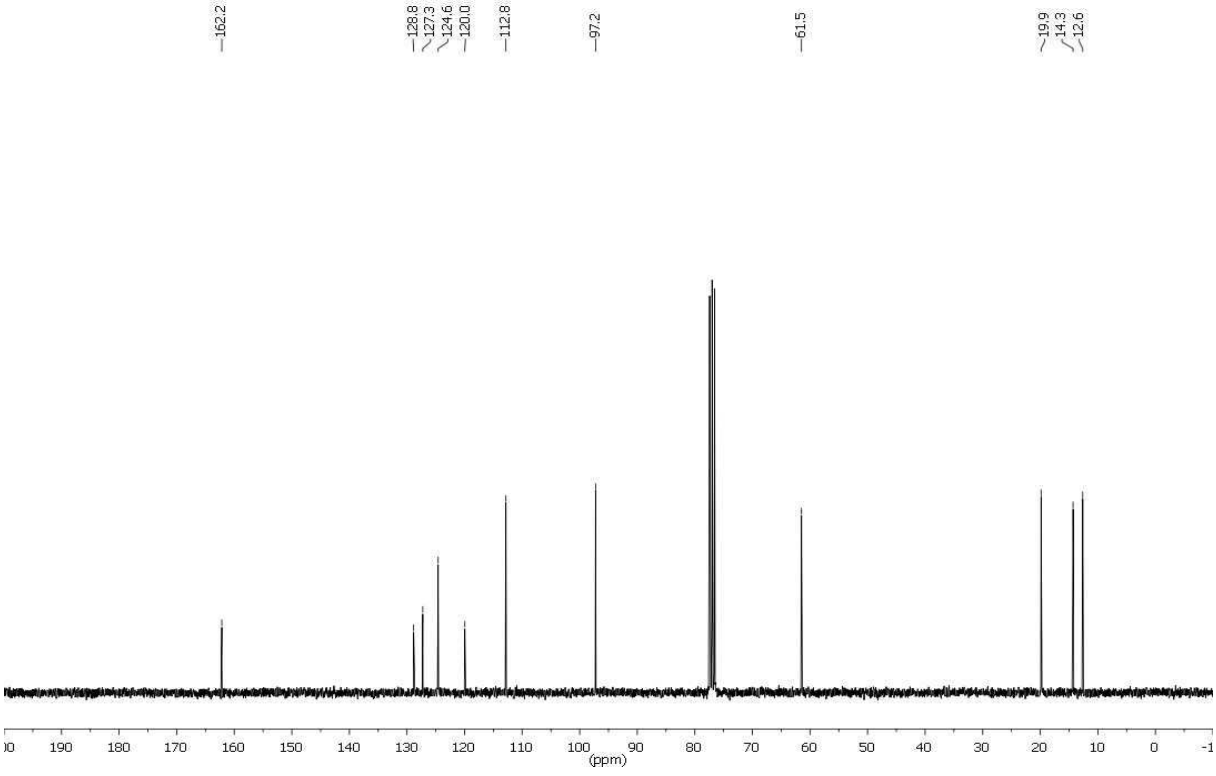


^{13}C-NMR (100 MHz, $CDCl_3$)

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

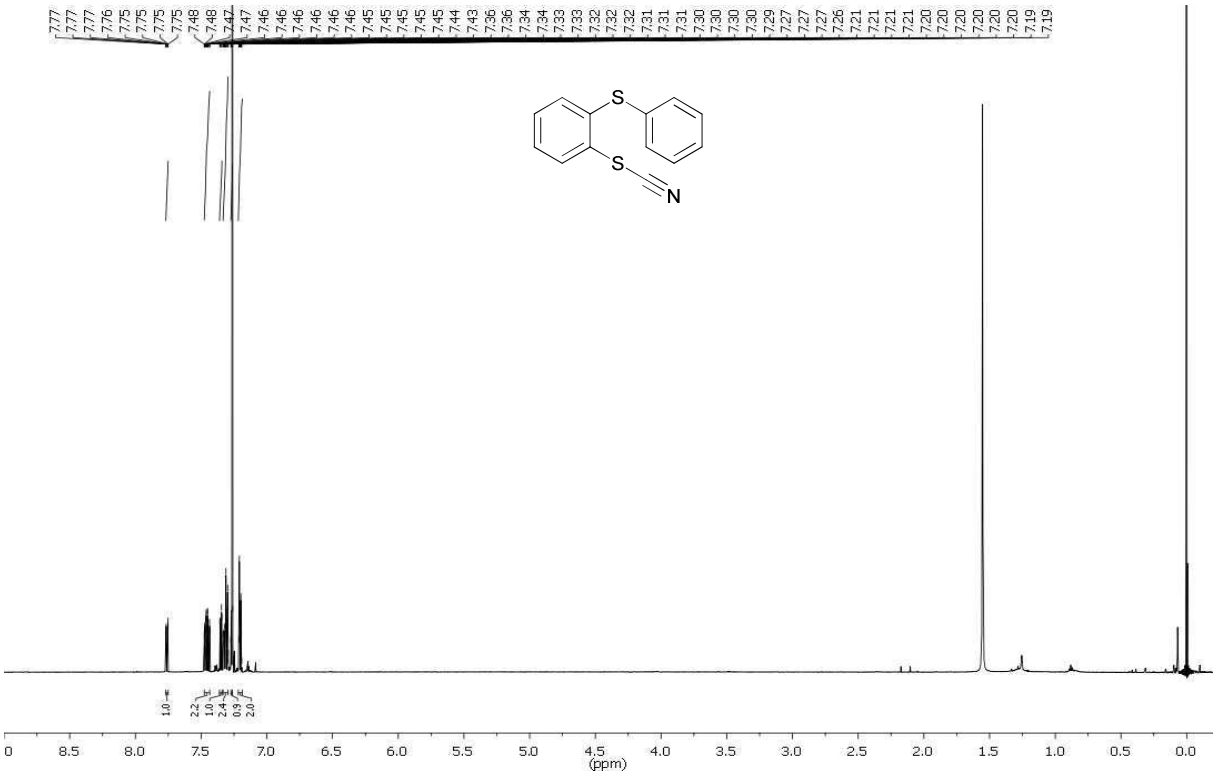


^{1}H-NMR (300 MHz, $CDCl_3$)

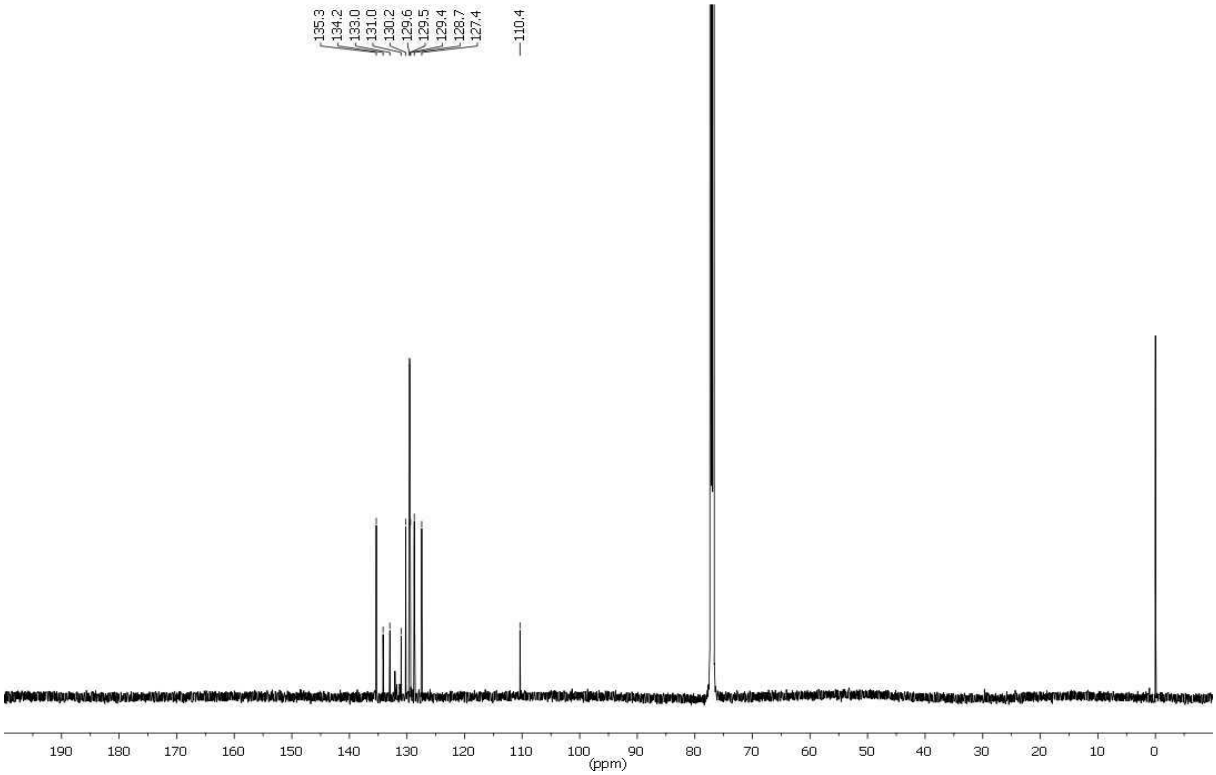


^{13}C-NMR (75 MHz, $CDCl_3$)

Phenyl(2-thiocyanatophenyl)sulfane (12a)



^{1}H-NMR (600 MHz, $CDCl_3$)



^{13}C-NMR (150 MHz, $CDCl_3$)

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[1] G. Durgaprasad, R. Bolligarla and S. K. Das, *J. Organomet. Chem.,* 2012, **706-707**, 37.

[2] J. L. Brusso, O. P. Clements, R. C. Haddon, M. E. Itkis, A. A. Leitch, R. T. Oakley, R. W. Reed and J. F. Richardson, *J. Am. Chem. Soc*., 2004, **126**, 8256.

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