Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

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

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1 General considerations

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

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

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

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

^{1}H, ^{13}C, and 135-DEPT ^{13}C NMR spectra were recorded on Bruker Advanced DRX 500 and Bruker AVIII-300. Acetone-d_6, $CDCl_3$, DMSO-d_6 with CS_2, CD_2Cl_2 and C_6D_6 were used as deuterated solvents. The resonances of the solvents were locked as internal standards (acetone-d_6: ^{1}H δ 2.05, ^{13}C δ 29.9; $CDCl_3$: ^{1}H δ 7.24, ^{13}C δ 77.2; DMSO-d_6: ^{1}H δ 2.50, ^{13}C δ 39.5; CD_2Cl_2: ^{1}H δ 5.32, ^{13}C δ 54.0; C_6D_6: ^{1}H δ 7.16, ^{13}C δ 128.4). The muliplicities of the signals were abbreviated as follows:

s: singlet; d: doublet; dd: doublet of doublets; t: triplet; m: muliplet. The type of carbon atoms was determined on the basis of 135-DEPT ^{13}C NMR spectra. For the description of the ^{13}C NMR spectra primary carbon atoms are abbreviated with CH_3, secondary carbon atoms with CH_2, tertiary carbon atoms with CH and quaternary carbon atoms with C_{quat}.

EI mass spectra were measuresd on Finnigan MAT 8200 spectrometer.

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

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

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

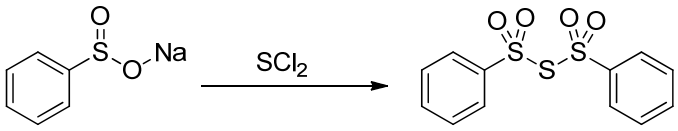
Cyclic voltammetry experiments were performed with 263A E&G Princeton Applied Research as potentiostatic instrumentation under argon in dry and degassed dichloromethane at T = 293 K and at scan rates of 100, 250, 500 and 1000 mVs^{-1}. The electrolyte was tetrabutylammonium hexafluorophosphate at a concentration of c = 0.025 $molL^{-1}$. The working electrode was a 1 mm platinum disk, the counter electrode was a platinum wire and the reference electrode was a silver/silverchloride electrode filled with aqueous saturated sodium chloride solution. The potentials were calibrated using $[FeCp^*_2]/[FeCp^*_2]^+$ as an internal potential standard. The absolute potential of this standard was determined against $[FeCp]/[FeCp_2]^+$ ($E_0^{0/+1}$ = 450 mV).[1] This procedure provided a value of $E_0^{0/+1}$ = -95 mV for $[FeCp^*_2]/[FeCp^*_2]^+$.

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

[1] P. Zanello in *Ferrocenes* (Eds.: A. Togni, T. Hayashi), VHC, Weinheim, 1995, pp. 317.

2 Preparation of starting materials

2 1 Preparation of Bis(phenylsulfonyl)sulfide (6)[2]



6

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

Mp 130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (t, J = 8.0 Hz, 4 H), 7.68 (t, J = 7.5 Hz, 2 H), 7.99 (dd, J = 8.4 Hz, 0.9 Hz, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 128.3 (CH), 129.6 (CH), 135.1 (CH), 144.5 (C_{quat}). Anal. calcd. for $C_{12}H_{10}O_4S_3$ (314.4): C 45.96, H 2.92. Found: C 45.71, H 2.92.

Data reported in literature:[4]

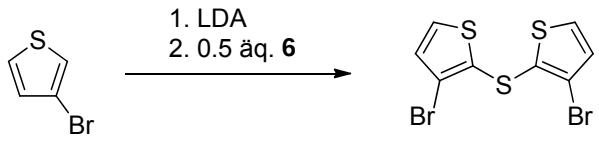
Mp 125-130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (dd, J = 7 Hz, 7.5 Hz, 2 H), 7.72 (t, J = 7 Hz, 1 H), 7.87 (d, J = 7.5 Hz, 1 H), 8.02 (d, J = 7.5 Hz, 1 H).

[2] F. Allared, J. Hellberg, T. Remonen, *Tetrahedron Lett.*, 2002, **43**, 1553.

[3] Synthesized according to: G. Brauer (ed.): *Handbuch der Präparativen Anorganischen Chemie*, Stuttgart: Ferdinand-Enke Verlag, 3rd revised edition 1954, p. 280.

[4] S. Inaoka, D. M. Collard, *J. Mater. Chem.*, 1999, **9**, 1719.

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



3

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

Mp 55.2°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.98 (d, J= 5.5 Hz, 2 H), 7.32 (d, J = 5.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 118.1 (C_{quat}), 130.0 (2 x CH), 131.0 (C_{quat}). EI + MS (70 eV, m/z (%)): 358 ($[C_8H_4{}^{32}S_3{}^{81}Br_2]^+$, 11), 356 ($[C_8H_4{}^{32}S_3{}^{79}Br{}^{81}Br]^+$, 18), 354 ($[C_8H_4{}^{32}S_3{}^{79}Br_2]^+$, 9), 198 (13), 197 (11), 196 (100).

Data reported in literature[5]:

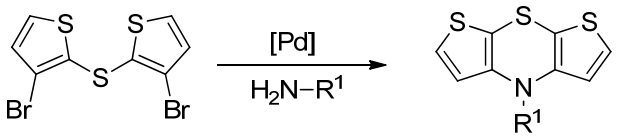
Mp 54-55 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.998 (AB, J = 5.6 Hz, 2 H), 7.346 (AB, J = 5.6 Hz, 2H).

[5] M. Miyasaka, A. Rajca, *J. Org. Chem.*, 2006, **71**, 3264.

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

3.1 General procedure

3.1.1 Method A (oil bath experiment)



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

3.1.2 Method B (microwave experiment)

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

The experimental details for the synthesis of *N*-substituted 4*H*-dithienothiazines **5** are given in table 1.

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

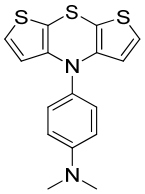
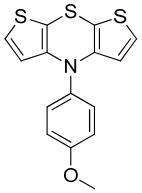
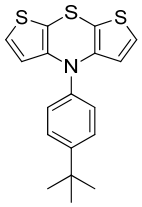
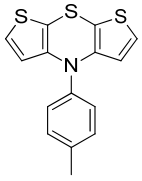
Entry	Amine **4** (0.58 mmol)	*N*-Substituted 4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine **5** (isolated yield)	Chromatographic purification R_f (eluent) Recrystallisation
1	*N,N*-Dimethyl-*p*-phenylenediamine (85 %) (*Acros Organics*) (**4a**) 93 mg	 **5a** 123 mg (0.37 mmol) 74 %	*n*-Hexane/EtOAc/NEt_3 = 40:4:1 R_f (*n*-Hexane/EtOAc 20:1) = 0.26 EtOH (Recryst.)
2	*p*-Anisidine (*Acros Organics*) (**4b**) 71 mg	 **5b** 149 mg (0.47 mmol) 94 %	*n*-Hexane/NEt_3 = 40:1 R_f (*n*-Hexane) = 0.09
3	4-*tert*-Butylaniline (*Acros Organics*) (**4c**) 86 mg	 **5c** 108 mg (0.31 mmol) 63 %	*n*-Hexane/NEt_3 = 40:1 R_f (*n*-Hexane) = 0.2 EtOH (Recryst.)
4	*p*-Toluidine (*Acros Organics*) (**4d**) 62 mg	 **5d** 92 mg (0.31 mmol) 61 %	*n*-Hexane/NEt_3 = 40:1 R_f (*n*-Hexane) = 0.17 *n*-Hexane (Recryst.)

Table 1 (continued).

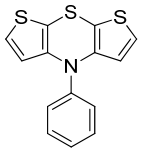
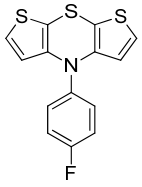
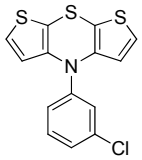
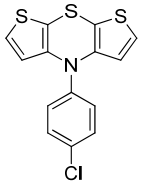
Entry	Amine **4** (0.58 mmol)	*N*-Substituted 4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine **5** (isolated yield)	Chromatographic purification R_f (eluent)
5	Aniline (*VWR*) (**4e**) 54 mg	 **5e** 118 mg (0.41 mmol) 82 %	*n*-Hexane/NEt_3 = 40:1 R_f (*n*-Hexane) = 0.26
6	4-Fluoroaniline (98 %) (*Acros Organics*) (**4f**) 66 mg	 **5f** 133 mg (0.44 mmol) 87 %	*n*-Hexane/NEt_3 = 40:1 R_f (*n*-Hexane) = 0.19 *n*-Hexane (Recryst.)
7	2-Chloroaniline (98 %) (*Sigma Aldrich*) (**4g**) 75 mg	 **5g** 127 mg (0.40 mmol) 79 %	*n*-Hexane/NEt_3 = 40:1 R_f (*n*-Hexane) = 0.18
8	3-Chloroaniline (98 %) (*Merck*) (**4h**) 75 mg	 **5h** 106 mg (0.33 mmol) 66 %	*n*-Hexane/NEt_3 = 40:1 R_f (*n*-Hexane) = 0.23
9	4-Chloroaniline (98 %) (*Acros Organics*) (**4i**) 75 mg	 **5i** 142 mg (0.44 mmol) 88 %	*n*-Hexane/NEt_3 = 40:1 R_f (*n*-Hexane) = 0.24

Table 1 (continued).

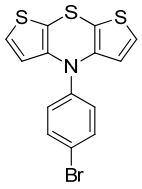
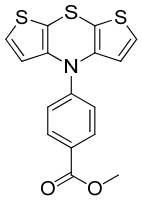
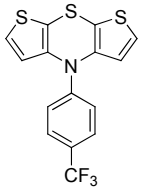
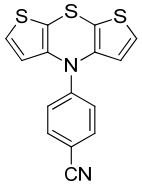
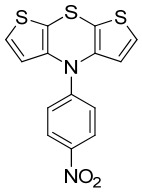
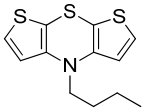
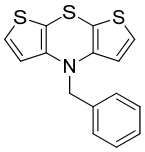
Entry	Amine **4** (0.58 mmol)	*N*-Substituted 4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine **5** (isolated yield)	Chromatographic purification R_f (eluent)
10	4-Bromoaniline (*Avocado*) (**4j**) 100 mg	 **5j** 37 mg (0.10 mmol) 20 %	*n*-Hexane/NEt_3 = 40:1 R_f (*n*-Hexane) = 0.30 *n*-Hexane (Recryst.)
11[b]	Methyl-4-aminobenzoate (98 %) (*Sigma Aldrich*) (**4k**) 89 mg	 **5k** 143 mg (0.41 mmol) 82 %	*n*-Hexane/EtOAc/NEt_3 = 40:4:1 R_f (*n*-Hexane/EtOAc 10:1) = 0.21
12	4-Aminobenzotrifluoride (98 %) (*abcr*) (**4l**) 95 mg	 **5l** 96 mg (0.27 mmol) 54 %	*n*-Hexane/NEt_3 = 40:1 R_f (*n*-Hexane) = 0.19 *n*-Hexane (Recryst.)
13[c,d]	4-Aminobenzonitrile (98 %) (*Sigma Aldrich*) (**4m**) 70 mg	 **5m** 39 mg (0.12 mmol) 25 %[c] 75 mg (0.24 mmol) 48 %[d]	*n*-Hexane/EtOAc/NEt_3 = 40:4:1 R_f (*n*-Hexane/EtOAc 10:1) = 0.16 EtOH (Recryst.)

Table 1 (continued).

Entry	Amine **4** (0.58 mmol)	*N*-Substituted 4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine **5** (isolated yield)	Chromatographic purification R_f (eluent)
14[d]	4-Nitroaniline (*Acros Organics*) (**4n**) 80 mg	 **5n** 40 mg (0.12 mmol) 24 %[d]	*n*-Hexane/EtOAc/NEt_3 = 40:4:1 R_f (*n*-Hexane/EtOAc 10:1) = 0.18 EtOH (Recryst.)
15	*n*-Butylamine (Riedel-de Haën) (**4o**) 42 mg	 **5o** 91 mg (0.34 mmol) 68 %	*n*-Hexane/NEt_3 = 40:1 R_f (*n*-Hexane) = 0.17
16	Benzylamine (*Merck*) (**4p**) 62 mg	 **5p** 116 mg (0.38 mmol) 77 %	*n*-Hexane/EtOAc/ NEt_3 = 40:4:1 R_f (*n*-Hexane/EtOAc 10:1) = 0.49 *n*-Hexane (Recryst.)

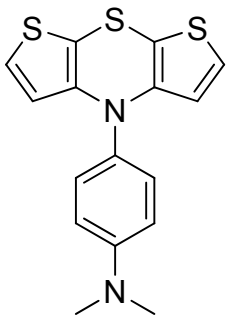
[b] Cs_2CO_3 (3 equivs) was used as base.

[c] Conventional heating at 100°C for 30 h.

[d] Dielectric heating at 160 °C for 2 h.

3.2 Spectroscopic data of compounds 5

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

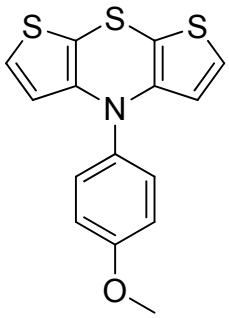


$C_{16}H_{14}N_2S_3$

330.49

Using method A 123 mg (0.37 mmol, 74 %) of the desired product were obtained as yellow crystals. Mp 196 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.99 (s, 6 H), 6.06 (d, ^3J = 5.5 Hz, 2 H), 6.76-6.81 (m, 2 H), 6.93 (d, ^3J = 5.5 Hz, 2 H), 7.17-7.21 (m, 2 H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 40.9 (CH_3), 101.4 (C_{quat}), 113.7 (CH), 120.1 (CH), 123.3 (CH), 130.2 (CH), 132.8 (C_{quat}), 145.8 (C_{quat}), 150.6 (C_{quat}). EI + MS (70 eV, m/z (%)): 332 ($[C_{16}H_{14}N_2{}^{34}S^{32}S_2]^+$, 13), 331 (18), 330 ($[C_{16}H_{14}N_2{}^{32}S_3]^+$, 82), 314 ($[C_{15}H_8N_2{}^{34}S^{32}S_2]^+$, 23), 313 (24), 312 ($[C_{15}H_8N_2{}^{32}S_3]^+$, 100), 297 (16), 281 (10), 280 (16), 279 (34), 235 (34), 212 ($[C_8H_4N^{34}S^{32}S_2]^+$, 12), 211 (11), 210 ($[C_8H_4N^{32}S_3]^+$, 86), 202 (18), 166 (12), 164 (14), 152 (15), 134 ($[C_7H_4N^{32}S]^+$, 28). IR (ATR): $\tilde{\nu}$ = 613 cm^{-1} (w), 625 (s), 644 (w), 700 (s), 708 (s), 762 (m), 804 (m), 822 (s), 849 (w), 947 (w), 993 (m), 1034 (w), 1065 (w), 1099 (w), 1117 (w), 1180 (m), 1223 (m), 1263 (w), 1275 (m), 1354 (m), 1377 (m), 1387 (m), 1443 (w), 1481 (w), 1512 (s), 1555 (w), 1605 (w), 2342 (w), 2359 (w), 2801 (w), 2855 (w), 2882 (w), 2980 (w), 3084 (w), 3103 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 254 nm (35500), 318 (8300). Anal. calcd. for $C_{16}H_{14}N_2S_3$ (330.5): C 58.15, H 4.27, N 8.48. Found: C 58.33, H 4.53, N 8.46.

3.2.2 4-(4-Methoxyphenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5b)

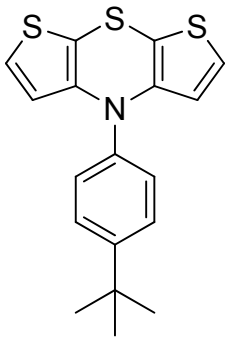


$C_{15}H_{11}ONS_3$

317.45

Using method A 149 mg (0.47 mmol, 94 %) of the desired product were obtained as yellow crystals. Mp 120 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ = 3.87 (s, 3 H), 6.07 (d, ^3J = 5.5 Hz, 2 H), 7.12-7.08 (m, 2 H), 7.18 (d, ^3J = 5.5 Hz, 2 H), 7.35-7.30 (m, 2 H). ^{13}C NMR (125 MHz, acetone-d_6): δ = 55.9 (CH_3), 102.0 (C_{quat}), 116.3 (CH), 120.4 (CH), 124.6 (CH), 131.1 (CH), 137.3 (C_{quat}), 145.5 (C_{quat}), 160.2 (C_{quat}). EI + MS (70 eV, m/z (%)): 319 ([$C_{15}H_{11}ON^{34}S^{32}S_2$]$^+$, 14), 318 (19), 317 ([$C_{15}H_{11}ON^{32}S_3$]$^+$, 100), 285 (12), 284 (31), 210 ([$C_8H_4N^{32}S_3$]$^+$, 35), 134 ([$C_7H_4N^{32}S$]$^+$, 12). IR (ATR): $\tilde{\nu}$ = 615 cm^{-1} (w), 629 (m), 642 (w), 673 (m), 714 (s), 762 (m), 816 (w), 829 (m), 847 (m), 934 (w), 995 (m), 1022 (w), 1036 (m), 1092 (w), 1103 (m), 1165 (m), 1179 (m), 1223 (m), 1234 (m), 1244 (s), 1273 (w), 1300 (w), 1333 (w), 1375 (m), 1389 (m), 1400 (m), 1441 (w), 1456 (w), 1506 (s), 1555 (m), 1888 (w), 2056 (w), 2361 (w), 2774 (w), 2832 (w), 2903 (w), 2945 (w), 3009 (w), 3096 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 242 nm (19000), 317 (4400). Anal. calcd. for $C_{15}H_{11}ONS_3$ (317.5): C 56.75, H 3.49, N 4.41. Found: C 56.75, H 3.62, N 4.27.

3.2.3 4-(4-(*tert*-Butyl)phenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5c)

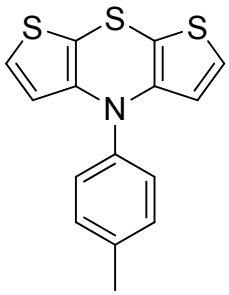


$C_{18}H_{17}NS_3$

343.53

Using method A 108 mg (0.31 mmol, 63 %) of the desired product were obtained as yellow crystals. Mp 210 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.34 (s, 9 H), 6.18 (d, ^{3}J = 5.3 Hz, 2 H), 7.36-7.30 (m, 4 H), 7.53 (d, ^{3}J = 8.1 Hz, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 31.0 (C_{quat}), 103.2 (C_{quat}), 119.8 (C_{quat}), 124.8 (CH), 126.88 (CH), 126.9 (CH), 140.6 (C_{quat}), 143.5 (CH), 149.6 (CH). EI + MS (70 eV, m/z (%)): 345 ($[C_{18}H_{17}N^{34}S^{32}S_2]^+$, 16), 344 (22), 343 ($[C_{18}H_{17}N^{32}S_3]^+$, 100), 328 ($[C_{17}H_{14}N^{32}S_3]^+$, 28), 210 ($[C_8H_4N^{32}S_3]^+$, 31), 150 (17), 134 ($[C_7H_4N^{32}S]^+$, 10). IR (ATR): $\tilde{\nu}$ = 627 cm^{-1} (m), 644 (w), 704 (s), 719 (m), 770 (w), 800 (m), 829 (m), 856 (m), 924 (w), 997 (m), 1013 (w), 1032 (m), 1096 (w), 1109 (m), 1182 (w), 1202 (w), 1223 (m), 1263 (m), 1279 (m), 1362 (w), 1377 (m), 1391 (m), 1400 (m), 1460 (w), 1472 (w), 1504 (m), 1512 (s), 1557 (m), 1915 (w), 2864 (w), 2901 (w), 2959 (w), 3084 (w), 3094 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 244 nm (43400), 318 (12200). Anal. calcd. for $C_{18}H_{17}NS_3$ (343.5): C 62.93, H 4.99, N 4.08. Found: C 62.87, N 5.06, H 3.81.

3.2.4 4-(*p*-Tolyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5d)

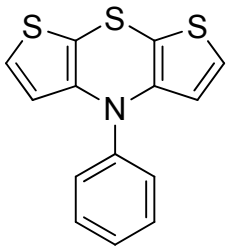


$C_{15}H_{11}NS_3$

301.45

Using method A 92 mg (0.31 mmol, 61 %) of the desired product were obtained as yellow crystals. Mp 113 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ = 2.65-2.23 (m, 3 H), 6.22-6.02 (m, 2 H), 7.24-7.11 (m, 2 H), 7.32-7.23 (m, 2 H), 7.37- 7.34 (m, 2 H). ^{13}C NMR (125 MHz, acetone-d_6): δ = 21.2 (CH_3), 103.3 (C_{quat}), 120.7 (CH), 124.8 (CH), 129.2 (CH), 131.8 (CH), 138.5 (C_{quat}), 142.2 (C_{quat}), 145.2 (C_{quat}). EI + MS (70 eV, m/z (%)): 303 ($[C_{15}H_{11}N^{34}S^{32}S_2]^+$, 14), 302 (20), 301 ($[C_{15}H_{11}N^{32}S_3]^+$, 100), 300 (10), 269 (16), 268 (51), 224 (14), 210 ($[C_8H_4NS_3]^+$, 46), 134 ($[C_7H_4N^{32}S]^+$, 16). IR (ATR): $\tilde{\nu}$ = 617 cm^{-1} (m), 644 (m), 675 (m), 702 (s), 750 (m), 812 (m), 824 (m), 854 (w), 941 (w), 993 (m), 1030 (w), 1043 (w), 1101 (m), 1171 (w), 1207 (w), 1267 (m), 1377 (m), 1402 (m), 1447 (w), 1506 (m), 1558 (m), 2357 (w), 2920 (w), 3026 (w), 3092 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 247 nm (21300), 318 (5700). Anal. calcd. for $C_{15}H_{11}NS_3$ (301.5): C 59.76, H 3.68, N 4.65. Found: C 59.59, H 3.93, N 4.49.

3.2.5 4-Phenyl-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5e)

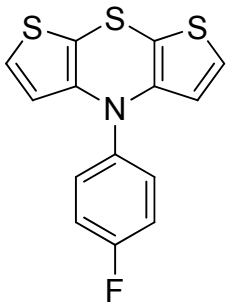


$C_{14}H_9NS_3$

287.42

Using method A 118 mg (0.41 mmol, 82 %) of the desired product were obtained as yellow crystals. Mp 93 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ = 6.19 (d, ^3J = 5.5 Hz, 2 H), 7.23 (d, ^3J = 5.5 Hz, 2 H), 7.38-7.43 (m, 3 H), 7.53-7.57 (m, 2 H). ^{13}C NMR (125 MHz, acetone-d_6): δ = 104.9 (C_{quat}), 121.0 (CH), 125.0 (CH), 128.3 (CH), 128.7 (CH), 131.2 (CH), 144.9 (2 x C_{quat}). EI + MS (70 eV, m/z (%)): 287 ([$C_{14}H_9NS_3$]$^+$, 6), 198 (30), 197 (16), 196 (100), 153 (13), 152 (23), 151 (10), 120 (14). IR (ATR): $\tilde{\nu}$ = 513 cm^{-1} (m), 521 (w), 533 (w), 606 (m), 629 (m), 683 (s), 687 (s), 722 (m), 795 (m), 835 (m), 853 (m), 916 (w), 993 (s), 1007 (w), 1072 (w), 1098 (m), 1221 (m), 1275 (m), 1375 (m), 1398 (m), 1444 (w), 1487 (s), 1512 (m), 1555 (m), 2852 (w), 2924 (w), 3119 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 248 nm (19400), 319 nm (5650). Anal. calcd. for $C_{14}H_9NS_3$ (287.4): C 58.50, H 3.16, N 4.87. Found: C 58.55, H 3.33, N 4.59.

3.2.6 4-(4-Fluorophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5f)

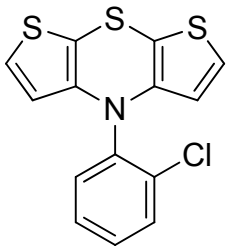


$C_{14}H_8FNS_3$

305.41

Using method A 133 mg (0.44 mmol, 87 %) of the desired product were obtained as yellow crystals. Mp 81 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ = 6.15 (d, ^3J = 5.5 Hz, 2 H), 7.23 (d, ^3J = 5.5 Hz, 2 H), 7.36-7.29 (m, 2 H), 7.50-7.44 (m, 2 H). ^{13}C NMR (125 MHz, acetone-d_6): δ = 103.9 (C_{quat}), 118.0 (CH, d, ^2J = 22.8 Hz), 120.6 (CH), 125.0 (CH), 131.6 (CH, d, ^3J = 8.8 Hz), 141.0 (C_{quat}, d, ^4J = 3.1 Hz), 144.9 (C_{quat}), 162.6 (C_{quat}, d, ^1J = 245.5). EI + MS (70 eV, m/z (%)): 307 ($[C_{14}H_8FN^{34}S^{32}S_2]^+$, 15), 306 (18), 305 ($[C_{14}H_8FN^{32}S_3]^+$, 100), 273 ($[C_{14}H_8FN^{32}S_2]^+$, 32), 228 (29), 210 ($[C_8H_4N^{32}S_3]^+$, 46), 152 (13), 134 ($[C_7H_4N^{32}S]^+$, 17). IR (ATR): $\tilde{\nu}$ = 619 cm^{-1} (m), 640 (m), 673 (m), 698 (s), 708 (s), 762 (m), 772 (m), 831 (s), 849 (m), 883 (w), 937 (m), 957 (w), 968 (w), 993 (m), 1028 (w), 1045 (w), 1086 (m), 1148 (m), 1213 (m), 1242 (w), 1265 (w), 1287 (w), 1339 (w), 1377 (m), 1404 (m), 1464 (w), 1472 (w), 1503 (s), 1514 (m), 1558 (w), 1597 (w), 2330 (w), 2361 (w), 2886 (w), 2930 (w), 2970 (m), 2980 (m), 3647 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 248 nm (20600), 315 (5500). Anal. calcd. for $C_{14}H_8FNS_3$ (305.4): C 55.06, H 2.64, N 4.59. Found: C 54.80, H 2.78, N 4.48.

3.2.7 4-(2-Chlorophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5g)

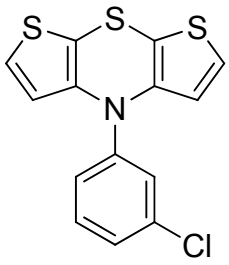


$C_{14}H_8ClNS_3$

321.87

Using method A 127 mg (0.40 mmol, 79 %) of the desired product were obtained as a yellow oil (solidified upon storage in refrigerator). Mp 66 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 5.99 (d, ^3J = 5.5 Hz, 2 H), 7.21 (d, ^3J = 5.5 Hz, 2 H), 7.51-7.64 (m, 3 H), 7.67-7.73 (m, 1 H). ^{13}C NMR (125 MHz, acetone-d_6): δ 102.3 (C_{quat}), 119.8 (CH), 124.9 (CH), 130.1 (CH), 131.2 (CH), 132.2 (CH), 133.2 (CH), 135.3 (C_{quat}), 140.8 (C_{quat}), 143.2 (C_{quat}). EI + MS (70 eV, m/z (%)): 324 (1), 323 ([M]$^+$, 3), 322 (1), 212 ([$C_8H_4N^{34}S^{32}S_2$]$^+$, 1), 211, (1), 210 ([$C_8H_4N^{32}S_3$]$^+$, 7), 100 (12), 57 (100). IR (ATR): $\tilde{\nu}$ = 610 cm^{-1} (m), 625 (m), 673 (s), 694 (s), 706 (s), 750 (s), 791 (m), 812 (w), 853 (m), 869 (w), 993 (s), 1034 (m), 1042 (m), 1070 (m), 1105 (m), 1187 (w), 1223 (m), 1244 (w), 1285 (m); 1377 (m), 1396 (s), 1437 (m), 1472 (m), 1518 (s), 1553 (m), 3105 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 248 nm (10700), 316 (2900). Anal. calcd. for $C_{14}H_8ClNS_3$ (321.9): C 52.24, H 2.51, N 4.35. Found: C 52.01, H 2.77, N 4.26.

3.2.8 4-(3-Chlorophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5h)

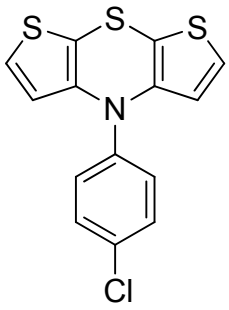


$C_{14}H_8ClNS_3$

321.87

Using method A 106 mg (0.33 mmol, 66 %) of the desired product were obtained as a yellow oil. ^{1}H NMR (500 MHz, acetone-d_6): δ 6.49 (d, ^3J = 5.5 Hz, 2 H), 7.31-7.37 (m, 4 H), 7.39 (t, ^3J = 2.0 Hz, 1 H), 7.50 (t, ^3J = 8.0 Hz, 1 H). ^{13}C NMR (125 MHz, acetone-d_6): δ 110.9 (C_{quat}), 122.2 (CH), 124.5 (CH), 125.8 (CH), 125.9 (CH), 126.9 (CH), 132.4 (CH), 135.9 (C_{quat}), 144.2 (C_{quat}), 146.7 (C_{quat}). EI + MS (70 eV, m/z (%)): 323 ($[C_{14}H_8{}^{37}ClN^{32}S_3]^+$, 45), 322 ($[C_{14}H_8{}^{37}ClN^{33}S^{32}S_2]^+$, 20), 321 ($[C_{14}H_8{}^{35}ClN^{32}S_3]^+$, 95), 290 (14), 289 (14), 288 ($[C_{14}H_8N^{33}S^{32}S_2]^+$, 29), 210 ($[C_8H_4N^{32}S_3]^+$, 76), 198 ($[C_8H_4{}^{33}S^{32}S_2]^+$, 14), 197 (17), 196 ($[C_8H_4{}^{32}S_3]^+$, 100), 182 (14), 152 (10), 134 ($[C_7H_4N^{32}S]^+$, 13), 105 (20). IR (ATR): $\tilde{\nu}$ = 627 (m), 652 (m), 691 (s), 695 (s), 721 (m), 748 (m), 768 (m), 797 (m), 813 (m), 824 (m), 830 (m), 871 (w), 995 (s), 1022 (w), 1036 (m), 1072 (m), 1090 (m), 1221 (m), 1246 (m), 1265 (m), 1283 (m), 1298 (m), 1375 (s), 1396 (m), 1474 (s), 1516 (s), 1557 (m), 1587 (m), 2324 (w), 2359 (w), 3067 (w), 3103 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 249 nm (19000), 315 (6900). Anal. calcd. for $C_{14}H_8ClNS_3$ (321.9): C 52.24, H 2.51, N 4.35. Found: C 52.30, H 2.77, N 4.22.

3.2.9 4-(4-Chlorophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5i)

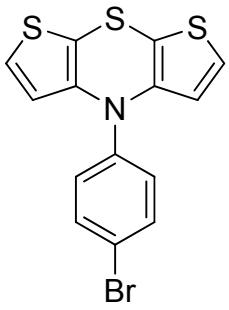


$C_{14}H_8ClNS_3$

321.87

Using method A 142 mg (0.44 mmol, 88 %) of the desired product were obtained as yellow crystals. Mp 102 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 6.32 (d, ^3J = 5.5 Hz, 2 H), 7.29 (d, ^3J = 5.5 Hz, 2 H), 7.39-7.45 (m, 2 H), 7.52-7.58 (m, 2 H). ^{13}C NMR (125 MHz, acetone-d_6): δ 107.3 (C_{quat}), 121.4 (CH), 125.4 (CH), 129.5 (CH), 131.2 (CH), 132.7 (C_{quat}), 143.9 (C_{quat}), 144.4 (C_{quat}). EI + MS (70 eV, m/z (%)): 323 (57), 322 (22), 321 ($[C_{14}H_8{}^{35}ClNS_3]^+$, 100), 290 (19), 289 (17), 288 ($[C_{14}H_8ClNS_2]^+$, 41), 212 (10), 211 (12), 210 ($[C_8H_4NS_3]^+$, 84), 166 (12), 134 ($[C_7H_4NS_2]^+$, 28), 106 (26), 105 (11). IR (ATR): $\tilde{\nu}$ = 513 cm^{-1} (m), 518 (m), 534 (w), 617 (m), 638 (w), 658 (w), 692 (s), 719 (m), 756 (m), 802 (w), 827 (s), 849 (m), 941 (w), 993 (s), 1013 (m), 1026 (w), 1086 (m), 1165 (w), 1219 (w), 1263 (m), 1375 (s), 1398 (m), 1464 (w), 1485 (s), 1516 (m), 1557 (m), 1584 (w), 2776 (w), 3100 (w), 3105 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 249 nm (21000), 318 (7300). Anal. calcd. for $C_{14}H_8ClNS_3$ (321.9): C 52.24, H 2.51, N 4.35. Found: C 52.38, H 2.33, N 4.36.

3.2.10 4-(4-Bromophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5j)

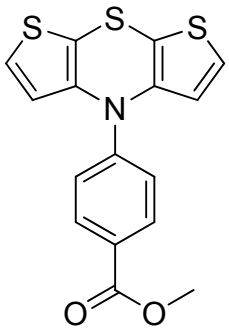


$C_{14}H_8BrNS_3$

366.32

Using method A 37 mg (0.10 mmol, 20 %) of the desired product were obtained as yellow crystals. Mp 95 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ = 6.63 (d, ^3J = 5.5 Hz, 2 H), 7.30 (d, ^3J = 5.5 Hz, 2 H), 7.37-7.33 (m, 2 H), 7.70-7.67 (m, 2 H). ^{13}C NMR (125 MHz, acetone-d_6): δ = 108.0 (C_{quat}), 120.4 (C_{quat}), 121.6 (CH), 125.6 (CH), 129.4 (CH), 134.2 (CH), 144.4 (2 x C_{quat}). EI + MS (70 eV, m/z (%)): 369 ([$C_{14}H_8BrN^{34}S^{32}S_2$]$^+$, 11), 368 (15), 367 ([$C_{14}H_8BrN^{34}S_3$]$^+$, 84), 366 (18), 365 (74), 335 (10), 334 (26), 332 (22), 287 (11), 212 ([$C_8H_4N^{34}S^{32}S_2$]$^+$,11), 211 (12), 210 ([$C_8H_4N^{32}S_3$]$^+$, 100), 166 (11), 134 ([$C_7H_4N^{32}S$]$^+$, 28). IR (ATR): $\tilde{\nu}$ = 617 cm^{-1} (m), 635 (m), 694 (s), 708 (s), 752 (m), 795 (m), 827 (s), 851 (m), 941 (w), 991 (m), 1011 (m), 1067 (m), 1099 (m), 1124 (w), 1219 (m), 1261 (m), 1375 (m), 1418 (w), 1458 (w), 1483 (m), 1516 (m), 1558 (m), 1724 (w), 2359 (w), 2853 (w), 2924 (w), 2955 (w), 3096 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 249 nm (14300), 318 nm (4700). Anal. calcd. for $C_{14}H_8BrNS_3$ (366.3): C 45.90, H 2.20, N 3.82. Found: C 46.06, H 2.46, N 3.90.

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

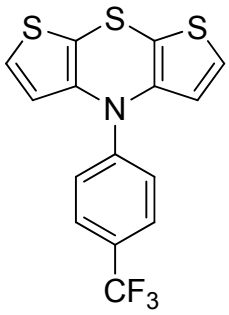


$C_{16}H_{11}NO_2S_3$

345.46

Using method A and 489 mg (1.5 mmol) caesium carbonate as base 143 mg (0.41 mmol, 82 %) of the desired product were obtained as yellow crystals. Mp 112 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 3.86 (s, 3 H), 6.90 (d, ^3J = 5.5 Hz, 2 H), 7.33-7.37 (m, 2 H), 7.49 (d, ^3J = 5.5 Hz, 2 H), 7.98-8.03 (m, 2 H). ^{13}C NMR (125 MHz, acetone-d_6): δ 52.2 (CH_3), 119.7 (C_{quat}), 120.1 (CH), 124.0 (CH), 125.6 (C_{quat}), 127.0 (CH), 132.1 (CH), 143.9 (C_{quat}), 149.6 (C_{quat}), 166.8 (C=O). EI + MS (70 eV, m/z (%)): 347 ([$C_{16}H_{11}NO_2{}^{34}S^{32}S_2$]$^+$, 14), 346 (20), 345 ([$C_{16}H_{11}NO_2S^{32}S_3$]$^+$, 100); 313 ([$C_{16}H_{11}NO_2{}^{32}S_2$]$^+$, 11), 312 ([$C_{16}H_{10}NO_2{}^{32}S_2$]$^+$, 27), 286 (10), 210 ([$C_8H_4N^{32}S_3$]$^+$, 66), 157 (12), 134 ([$C_7H_4N^{32}S$]$^+$, 20). IR (ATR): $\tilde{\nu}$ = 621 cm^{-1} (w), 648 (m), 696 (m), 725 (m), 738 (s), 750 (m), 795 (s), 843 (m), 860 (m), 874 (m), 945 (w), 1018 (w), 1049 (w), 1061 (w), 1074 (w), 1099 (m), 1111 (m), 1146 (s), 1175 (m), 1194 (m), 1238 (m), 1252 (m), 1271 (m), 1285 (w), 1304 (w), 1350 (m), 1373 (m), 1398 (m), 1452 (s), 1485 (w), 1508 (w), 1570 (w), 1585 (w), 1603 (w), 2222 (w), 2845 (w), 2920 (w), 2965 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 250 nm (13100), 328 nm (15100). Anal. calcd. for $C_{16}H_{11}NO_2S_3$ (345.5): C 55.63, H 3.21, N 4.05. Found: C 55.71, H 3.32, N 4.00.

3.2.12 4-(4-(Trifluoromethyl)phenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5l)

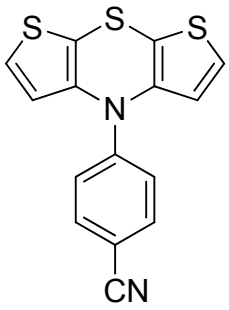


$C_{15}H_8F_3NS_3$

355.42

Using method A 96 mg (0.27 mmol, 54 %) of the desired product were obtained as yellow crystals. Mp 109 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 6.85 (d, ^3J = 5.5 Hz, 2 H), 7.43-7.51 (m, 4 H), 7.72 (d, ^3J = 5.5 Hz, 2 H). ^{13}C NMR (75 MHz, acetone-d_6): δ 118.7 (C_{quat}), 121.5 (CH), 123.8 (CH), 125.6, (q, ^2J = 32.6 Hz, C_{quat}), 125.7 (q, ^1J = 169.0 Hz, C_{quat}), 126.9 (CH), 127.9 (q, ^3J = 3.8 Hz, CH), 143.9 (C_{quat}), 149.0 (C_{quat}). EI + MS (70 eV, m/z (%)): 357 ($[C_{15}H_8F_3N^{34}S^{32}S_2]^+$, 15), 356 (19), 355 ($[C_{15}H_8F_3N^{32}S_3]^+$, 100), 323 ($[C_{15}H_7F_3N^{32}S_2]^+$, 11), 322 (26), 278 (11), 210 ($[C_8H_4N^{32}S_3]^+$, 47). IR (ATR): $\tilde{\nu}$ = 619 cm^{-1} (s), 640 (m), 687 (s), 704 (s), 773 (m), 808 (w), 831 (s),856 (m), 957 (m), 997 (s), 1016 (m), 1028 (m), 1065 (s), 1099 (s), 1119 (s), 1165 (s), 1223 (w), 1265 (m), 1281 (m), 1319 (s), 1379 (m), 1400 (m), 1514 (s), 1558 (m), 1611 (m), 2928 (w), 2963 (w), 3109 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 253 nm (30000), 315 nm (15700). Anal. calcd. for $C_{15}H_8F_3NS_3$ (355.4): C 50.69, H 2.27, N 3.94. Found: C 50.82, H 2.42, N 4.06.

3.2.13 4-(4*H*-Dithieno[2,3-*b*:3',2'-*e*][1,4]thiazin-4-yl)benzonitrile (5m)

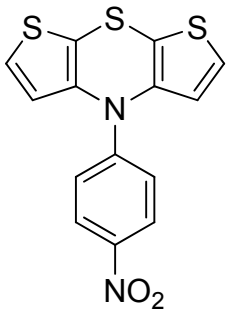


$C_{15}H_8N_2S_3$

312.43

Using method A 39 mg (0.12 mmol, 25 %) of the desired product were obtained as colorless crystals. Using method B 75 mg (0.24 mmol, 48 %) of the desired product were obtained as colorless crystals. Mp 184 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ = 7.10 (d, ^3J = 5.5 Hz, 2 H), 7.36 (d, ^3J = 8.8 Hz, 2 H), 7.58 (d, ^3J = 5.5 Hz, 2 H), 7.71 (d, ^3J = 8.8 Hz, 2 H). ^{13}C NMR (125 MHz, acetone-d_6): δ = 105.4 (C_{quat}), 118.4 (CH), 119.7 (C_{quat}), 124.3 (C_{quat}), 124.8 (CH), 127.7 (CH), 134.6 (CH), 143.4 (C_{quat}), 149.4 (C_{quat}). EI + MS (70 eV, m/z (%)): 314 ($[C_{15}H_8N_2{}^{34}S^{32}S_2]^+$, 16), 313 (22), 312 ($[C_{15}H_8N^{32}S_3]^+$, 100), 280 ($[C_{15}H_8N_2{}^{32}S_2]^+$, 15), 279 (33), 235 (31), 210 ($[C_8H_4NS_3]^+$, 58), 134 ($[C_7H_4N^{32}S]^+$, 18). IR (ATR): $\tilde{\nu}$ = 611 cm^{-1} (m), 648 (s), 667 (s), 704 (s), 723 (s), 750 (m), 799 (m), 822 (s), 854 (w), 887 (m), 943 (m), 997 (m), 1043 (w), 1090 (m), 1109 (w), 1138 (w), 1177 (m), 1211 (w), 1248 (w), 1262 (m), 1292 (s), 1373 (m), 1504 (s), 1573 (m), 1595 (m), 1884 (w), 2099 (w), 2210 (m), 2259 (w), 2318 (w), 2355 (w), 2585 (w), 2679 (w), 2716 (w), 2963 (w), 3088 (w), 3107 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 256 nm (17200), 325 (21400). Anal. calcd. for $C_{15}H_8N_2S_3$ (312.4): C 57.66, H 2.58, N 8.97. Found: C 57.66, H 2.59, N 8.84.

3.2.14 4-(4-Nitrophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5n)

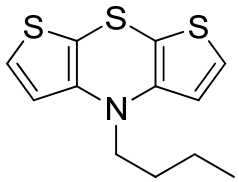


$C_{14}H_8N_2O_2S_3$

332.42

Using method B 40 mg (0.12 mmol, 24 %) of the desired product were obtained as orange crystals. Mp 161 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 7.25 (d, ^3J = 5.5 Hz, 2 H), 7.32-7.37 (m, 2 H), 7.64 (d, ^3J = 5.5 Hz, 2 H), 8.17-8.22 (m, 2 H). ^{13}C NMR (125 MHz, acetone-d_6): δ 116.1 (CH), 125.2 (CH), 126.5 (CH), 127.1 (C_{quat}), 128.2 (CH), 142.2 (C_{quat}), 143.2 (C_{quat}), 151.1 (C_{quat}). EI + MS (70 eV, m/z (%)): 334 ([$C_{14}H_8N_2O_2{}^{34}S^{32}S_2$], 14), 333 (18), 332 ([$C_{14}H_8N_2O_2{}^{32}S_3$]$^+$, 100), 286 (38), 210 ([$C_8H_4N^{32}S_3$]$^+$, 34). IR (ATR): $\tilde{\nu}$ = 623 cm^{-1} (m), 642 (s), 658 (m), 691 (s), 714 (m), 731 (s), 745 (s), 795 (m), 835 (s), 862 (w), 881 (w), 957 (m), 1001 (m), 1022 (m), 1076 (m), 1109 (s), 1124 (m), 1188 (m), 1215 (m), 1260 (m), 1296 (s), 1344 (m), 1372 (s), 1441 (m), 1493 (s), 1531 (m), 1589 (m), 1713 (w), 2363 (w), 2924 (w), 2961 (w), 3086 (w), 3105 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 249 nm (10500), 299 nm (5000), 391 (10800). Anal. calcd. for $C_{14}H_8N_2O_2S_3$ (332.4): C 50.58, H 2.43, N 8.43. Found: C 50.34, H 2.49, N 8.24.

3.2.15 4-Butyl-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5o)

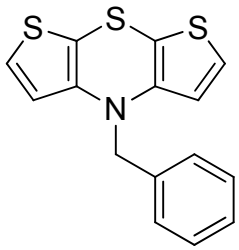


$C_{12}H_{13}NS_3$

[267.43]

Using method A 91 mg (0.34 mmol, 68 %) of the desired product were obtained as a yellow solid. Mp 36 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 0.71 (t, ^{3}J = 7.4 Hz, 3 H), 1.06-1.13 (m, 2 H), 1.29-1.35 (m, 2 H), 3.06-3.11 (m, 2 H), 6.16 (d, ^{3}J = 5.5 Hz, 2 H), 6.53 (d, ^{3}J = 5.5 Hz, 2 H). ^{13}C NMR (125 MHz, C_6D_6): 14.2 (CH_3), 20.4 (CH_2), 30.2 (CH_2), 49.9 (CH_2), 105.3 (C_{quat}), 118.2 (CH), 124.3 (CH), 145.5 (C_{quat}). EI + MS (70 eV, m/z (%)): 267 ($[M]^+$, 28), 212 (10), 210 ($[C_8H_4N^{32}S_3]^+$, 68), 155 (27), 134 ($[C_7H_4N^{32}S]^+$, 11), 113 (13), 112 (92), 111 (10), 57 (100). IR (ATR): $\tilde{\nu}$ = 628 cm^{-1} (s), 649 (w), 689 (s), 704 (s), 712 (s), 756 (w), 787 (w), 831 (s), 862 (s), 908 (w), 943 (m), 961 (w), 989 (s), 1037 (w), 1059 (w), 1090 (s), 1194 (m), 1231 (s), 1254 (w), 1315 (w), 1337 (w), 1366 (m), 1374 (m), 1416 (s), 1458 (m), 1467 (m), 1512 (s), 1557 (m), 2857 (w), 2924 (w), 2955 (m), 3028 (w), 3109 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 248 nm (19600), 327 nm (3700). Anal. calcd. for $C_{12}H_{13}NS_3$ (267.4): C 53.89, H 4.90, N 5.24. Found: C 53.67, H 4.97, N 5.15.

3.2.16 4-Benzyl-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5p)



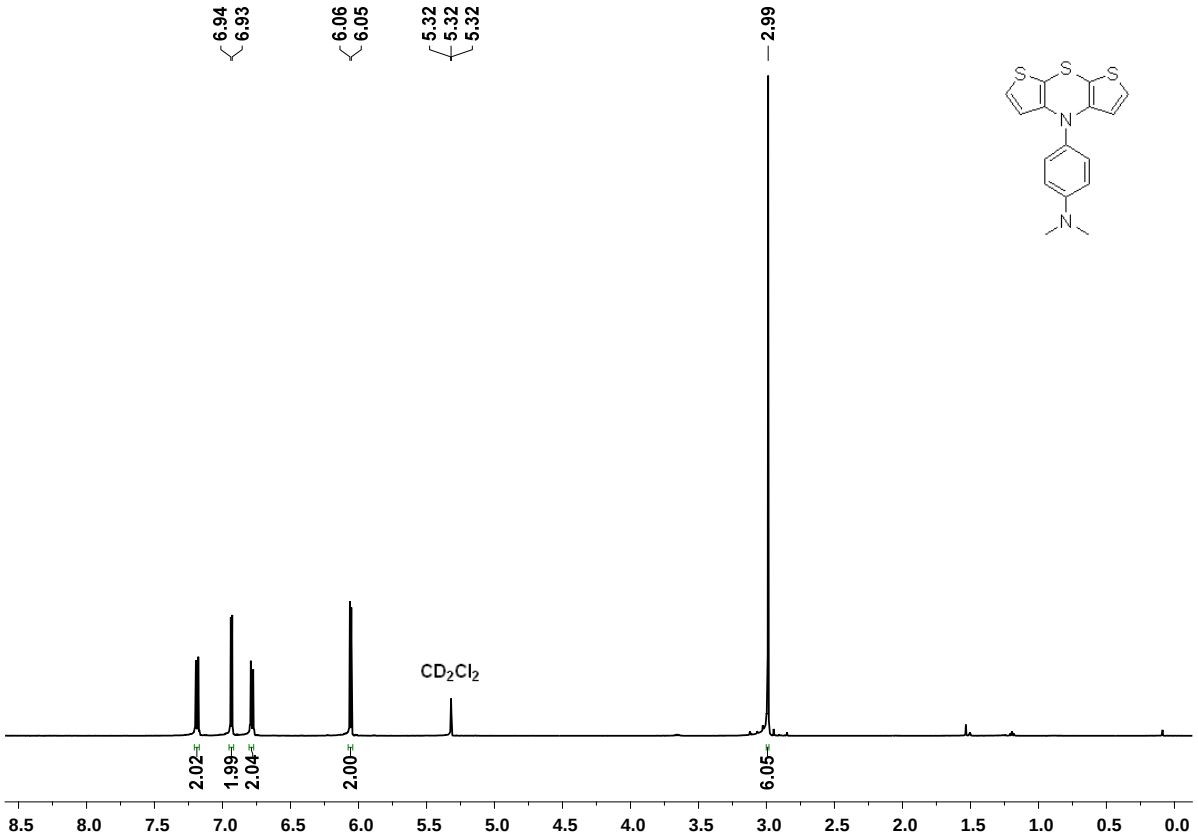
$C_{15}H_{11}NS_3$

301.45

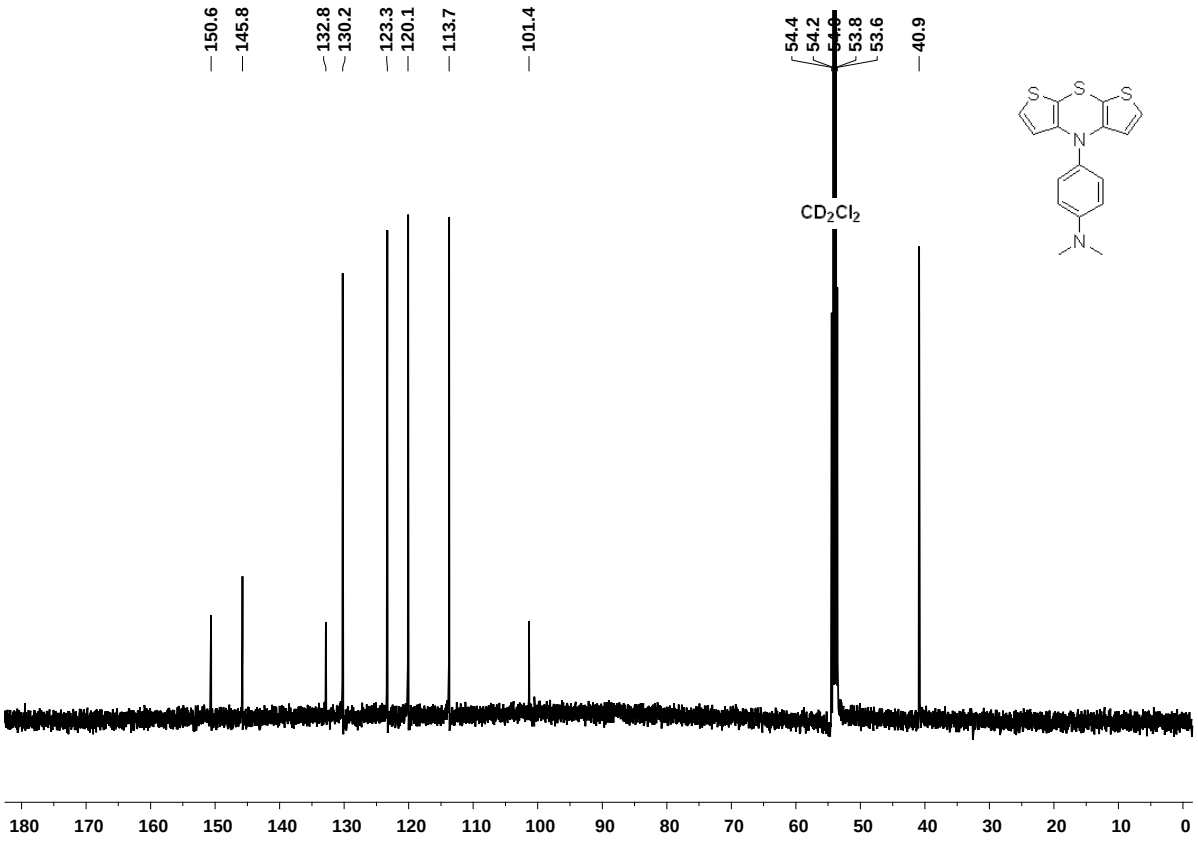
Using method A 116 mg (0.38 mmol, 77 %) of the desired product were obtained as yellow crystals. Mp 99 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 4.97 (s, 2 H), 6.64 (d, ^3J = 5.5 Hz, 2 H), 7.23-7.27 (m, 3 H), 7.31-7.38 (m, 4H). ^{13}C NMR (125 MHz, acetone-d_6): δ 53.5 (CH_2), 103.9 (C_{quat}), 119.6 (CH), 125.4 (CH), 127.5 (CH), 128.0 (CH), 129.6 (CH), 139.1 (C_{quat}), 145.9 (C_{quat}). EI + MS (70 eV, m/z (%)): 301 ([M]$^+$, 12), 212 (14), 211 (11.5), 210 ([$C_8H_4NS_3$]$^+$, 100), 134 ([C_7H_4NS]$^+$, 12). IR (ATR): $\tilde{\nu}$ = 611 cm^{-1} (m), 619 (m), 687 (s), 737 (s), 787 (w), 833 (m), 862 (w), 920 (w), 953 (m), 1016 (w), 1076 (w), 1096 (w), 1219 (w), 1240 (m), 1306 (w), 1333 (w), 1350 (w), 1381 (w), 1418 (m), 1450 (m), 1493 (m), 1516 (s), 1562 (w), 2361 (w), 2926 (w), 3028 (w), 3090 (w), 3107 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 245 nm (22300), 328 nm (4500). Anal. calcd. for $C_{15}H_{11}NS_3$ (301.5): C 59.76, H 3.68, N 4.65. Found: C 59.86, H 3.78, N 4.60.

4 ^{1}H and ^{13}C NMR spectra of *N*-substituted 4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazines 5

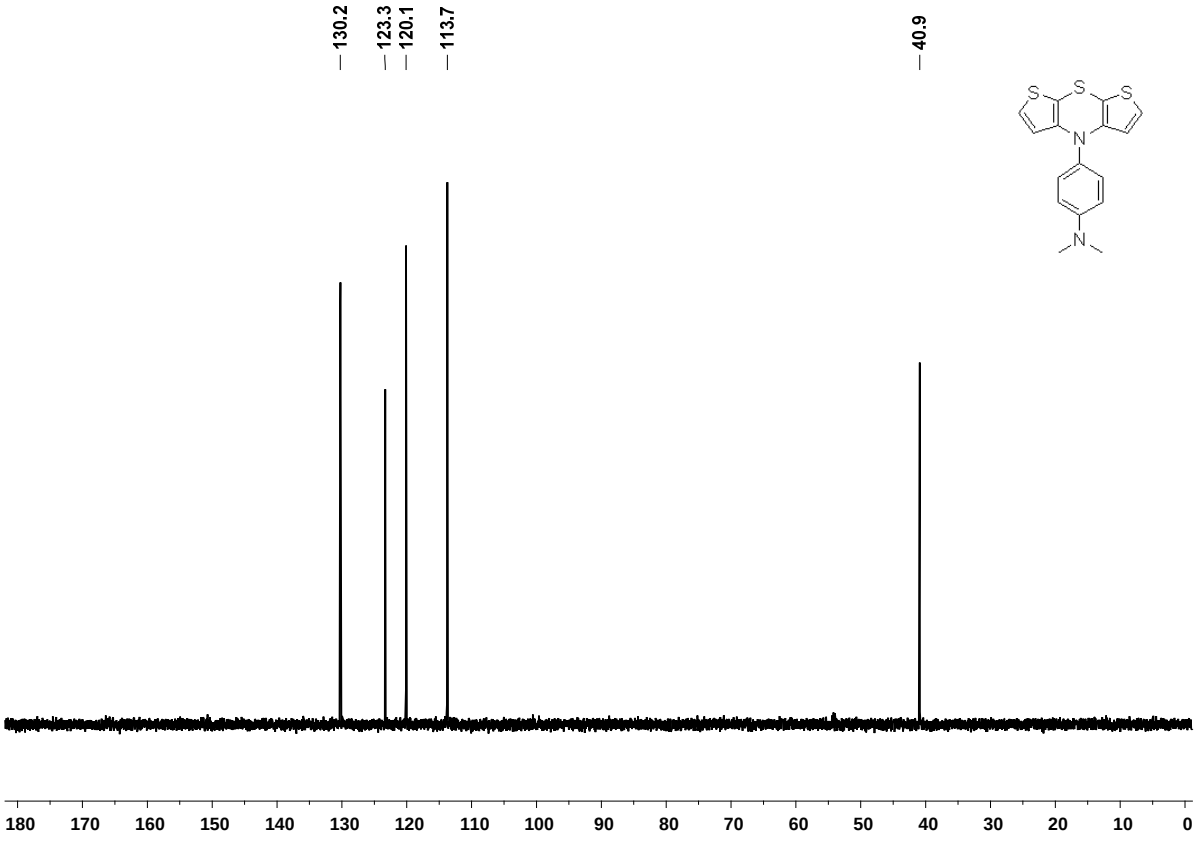
4.1 4-(4*H*-Dithieno[2,3-*b*:3',2'-*e*][1,4]thiazin-4-yl)-*N*,*N*-dimethylaniline (5a)



^{1}H NMR (500 MHz) of **5a** (20mg) in CD_2Cl_2 at 298 K (δ in ppm).

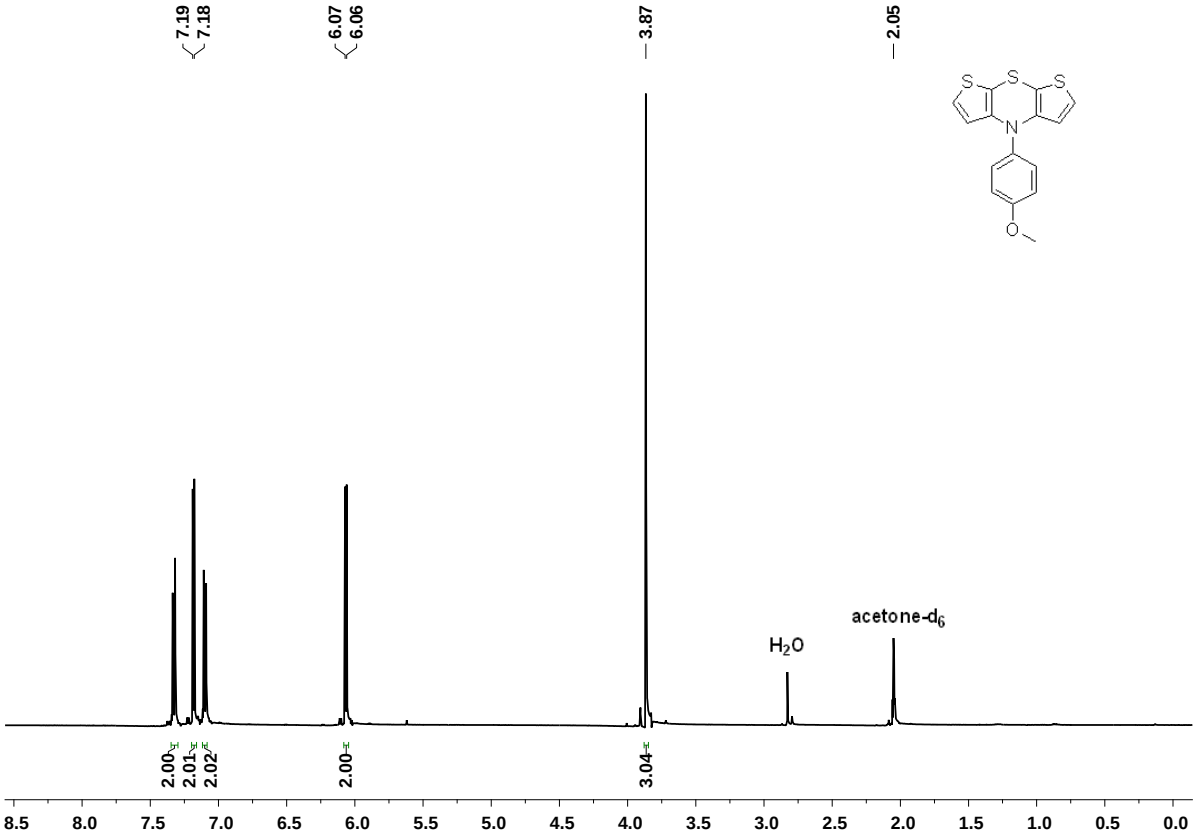


^{13}C NMR (125 MHz) of **5a** (20 mg) in CD_2Cl_2 at 298 K (δ in ppm).

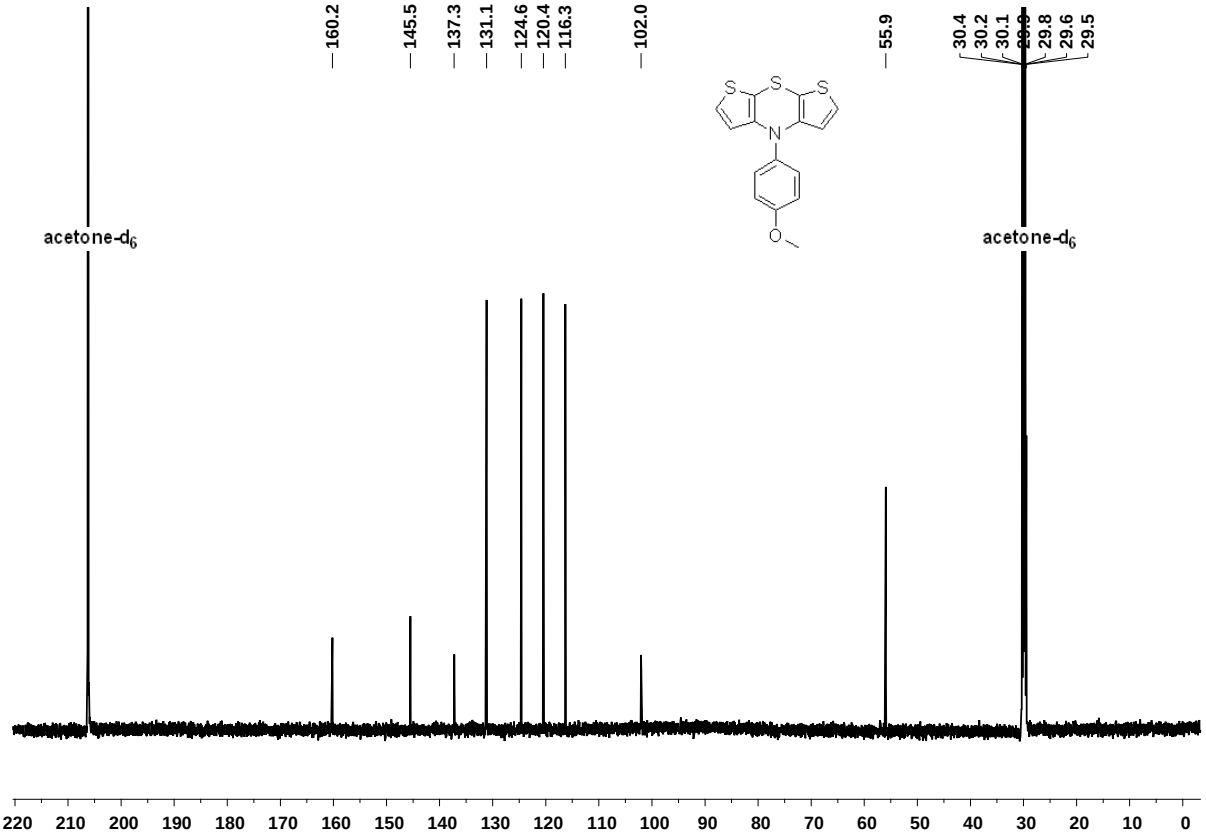


^{13}C DEPT 135-NMR (125 MHz) of **5a** (20 mg) in CD_2Cl_2 at 298 K (δ in ppm).

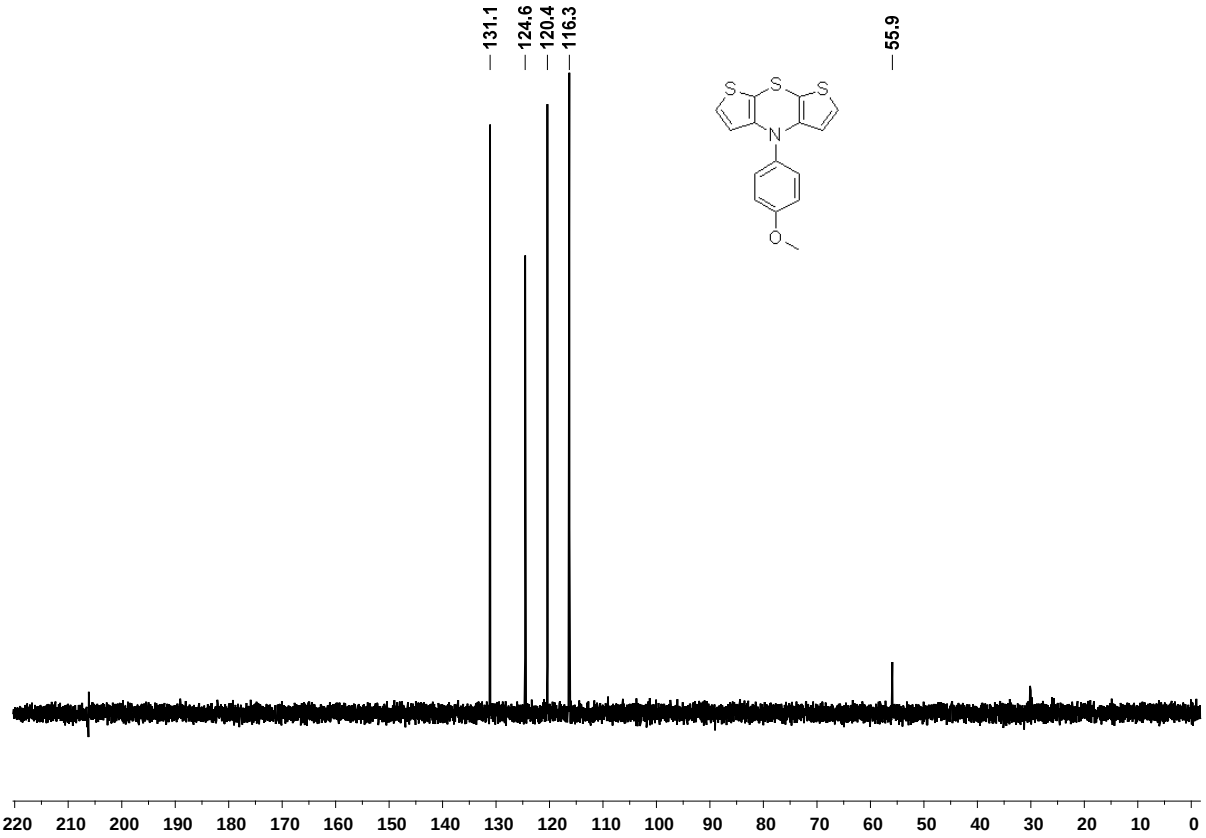
4.2 4-(4-Methoxyphenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5b)



^{1}H NMR (500 MHz) of **5b** (20mg) in acetone-d_6 at 298 K (δ in ppm).

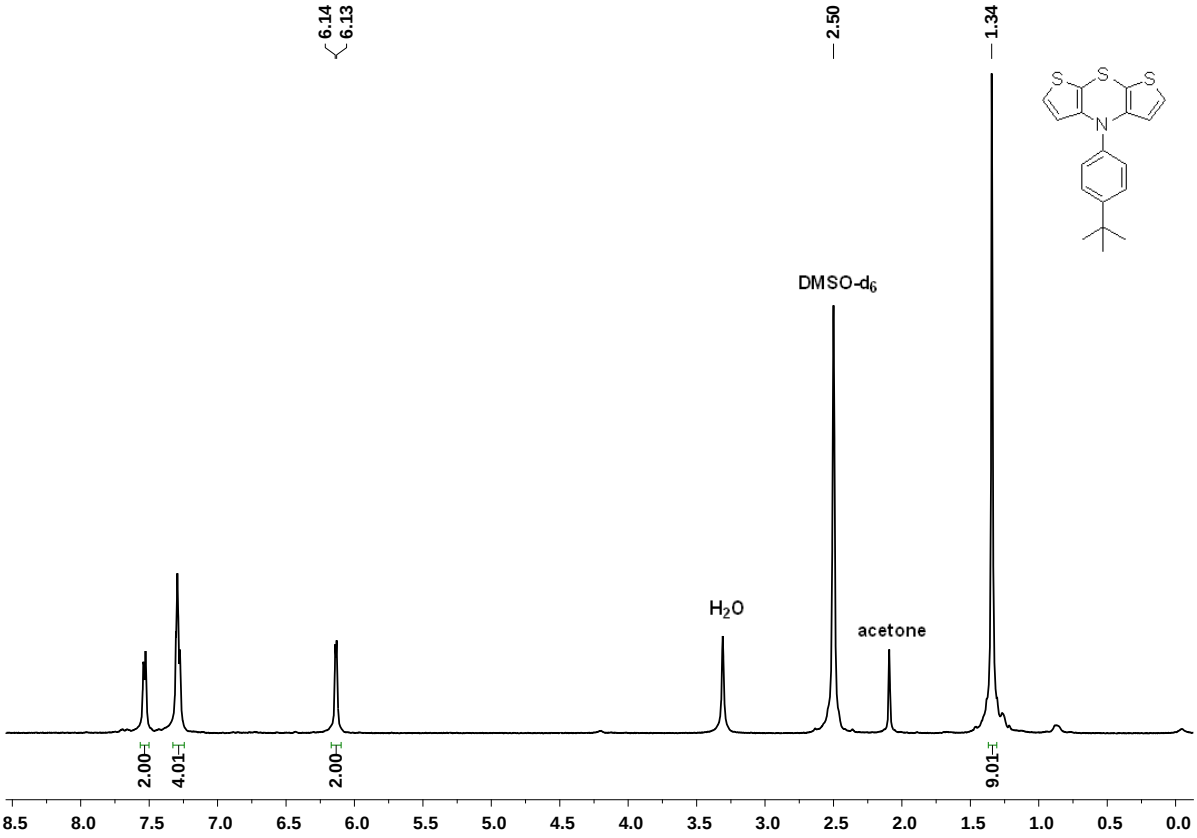


^{13}C NMR (125 MHz) of **5b** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

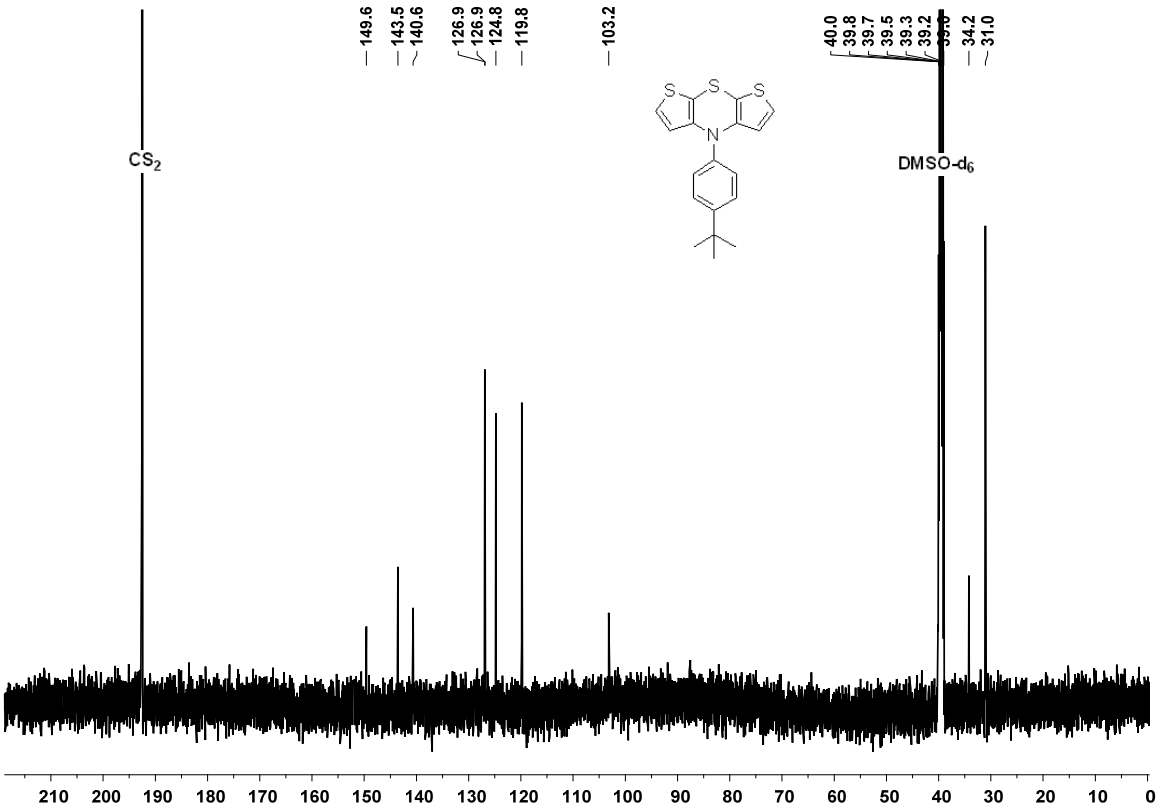


^{13}C DEPT 135-NMR (125 MHz) of **5b** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

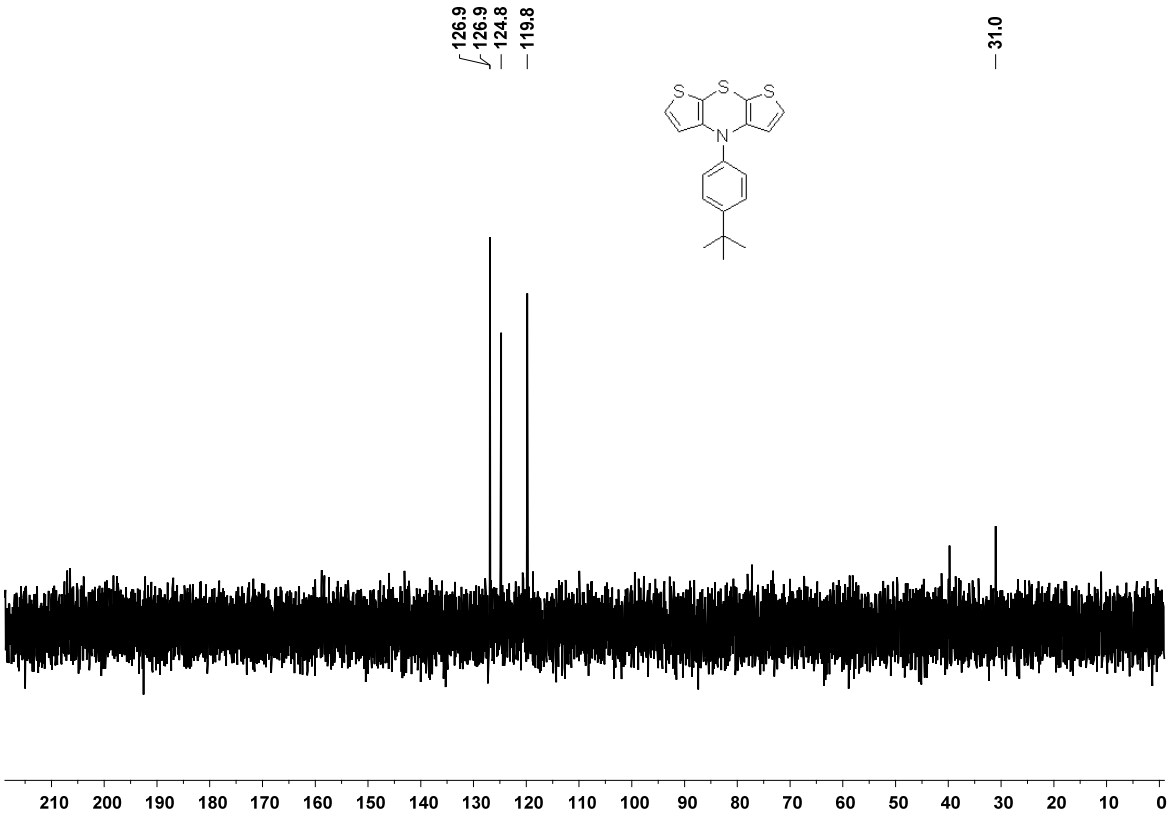
4.3 4-(4-(*tert*-Butyl)phenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5c)



^{1}H NMR (500 MHz) of **5c** (20 mg) in DMSO-d_6 with 10% CS_2 at 298 K (δ in ppm).

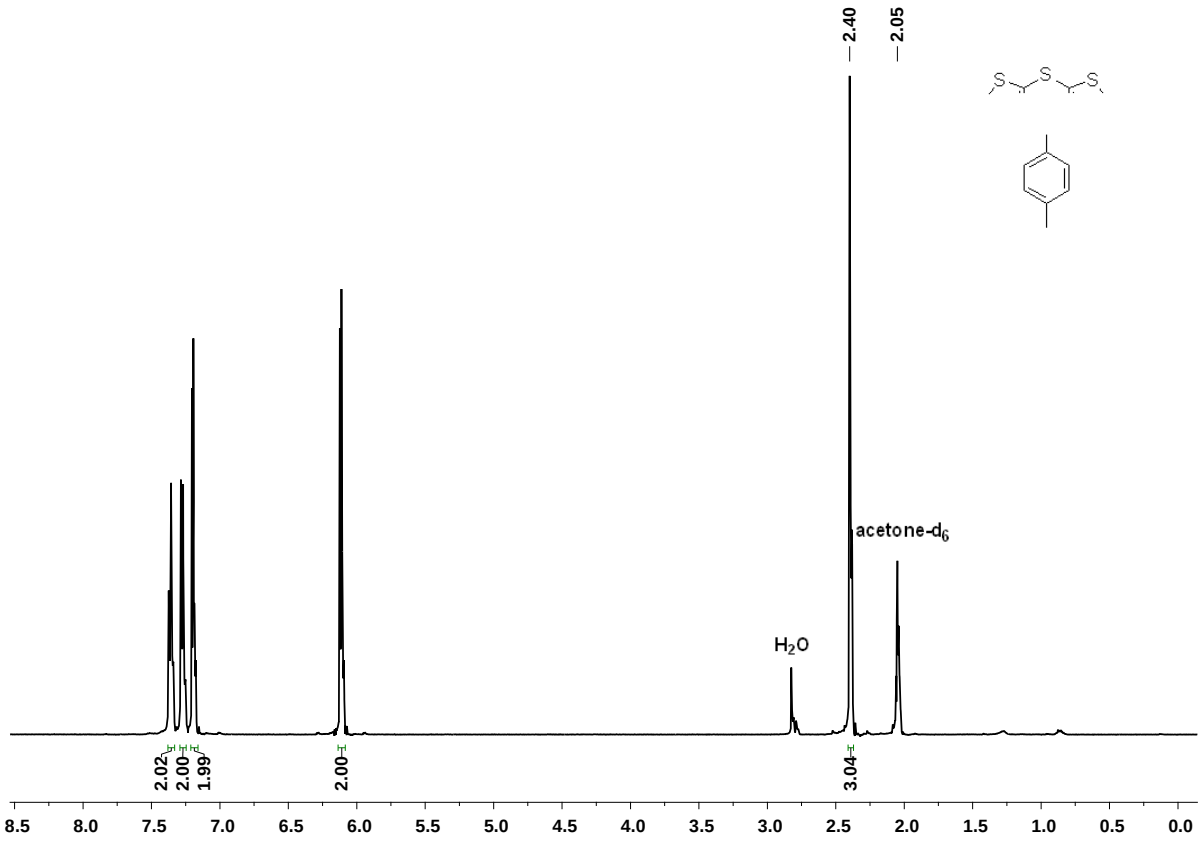


^{13}C NMR (125 MHz) of **5c** (20 mg) in DMSO-d_6 with 10% CS_2 at 298 K (δ in ppm).

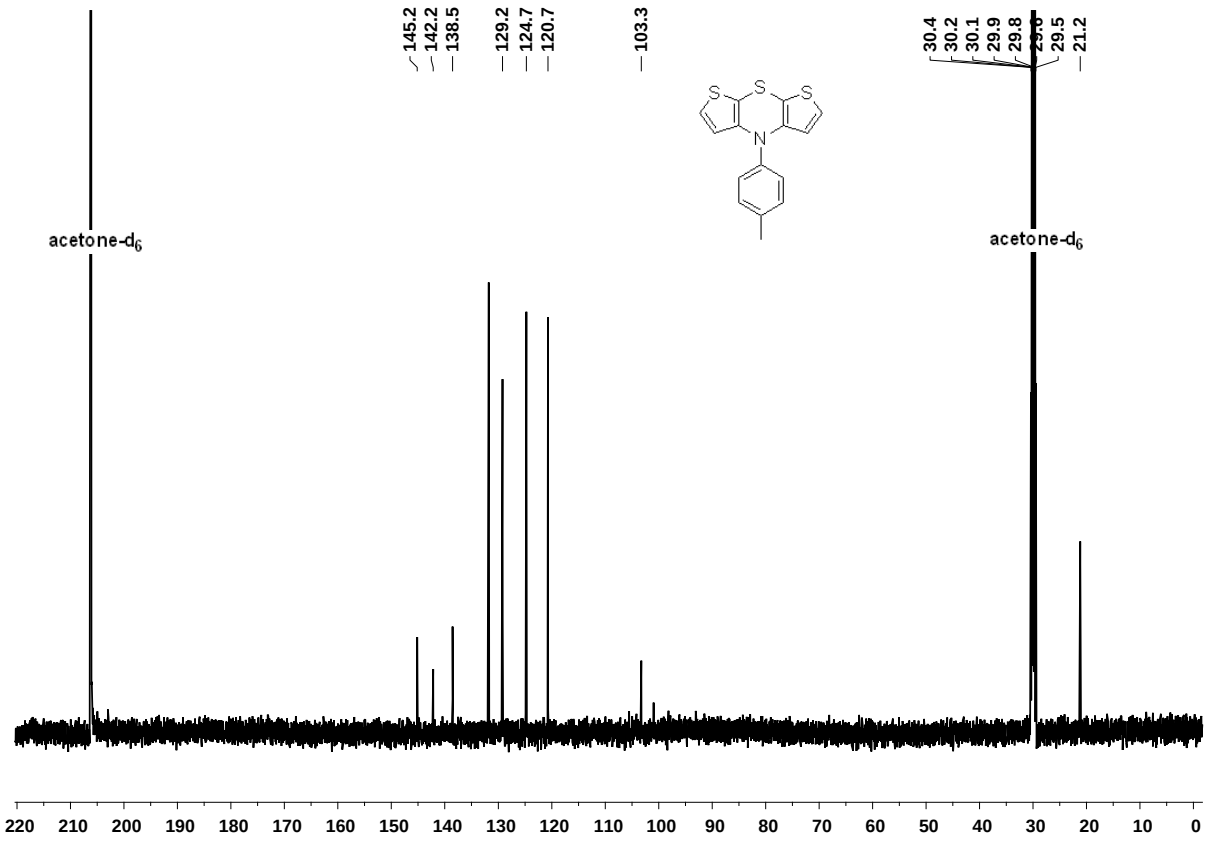


^{13}C DEPT 135-NMR (125 MHz) of **5c** (20 mg) in DMSO-d_6 with 10% CS_2 at 298 K (δ in ppm).

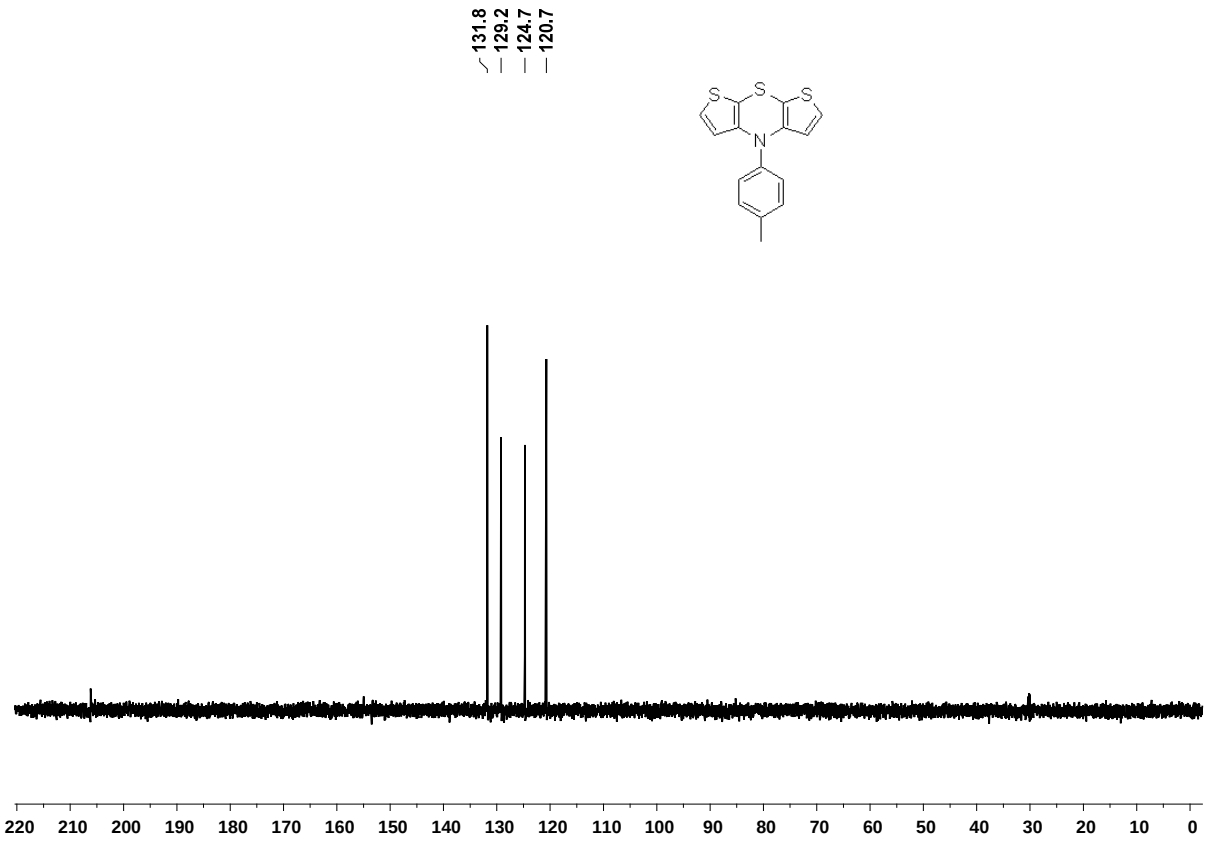
4.4 4-(*p*-Tolyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5d)



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

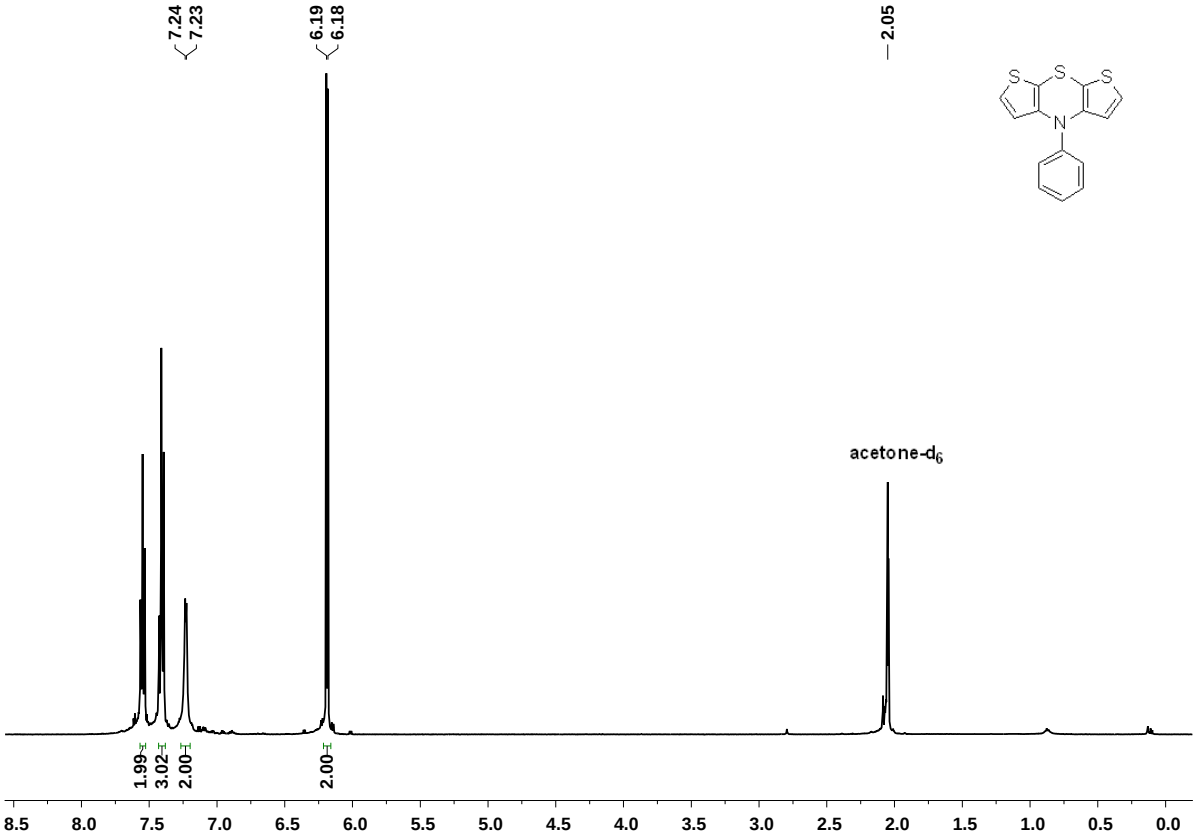


^{13}C NMR (125 MHz) of **5d** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

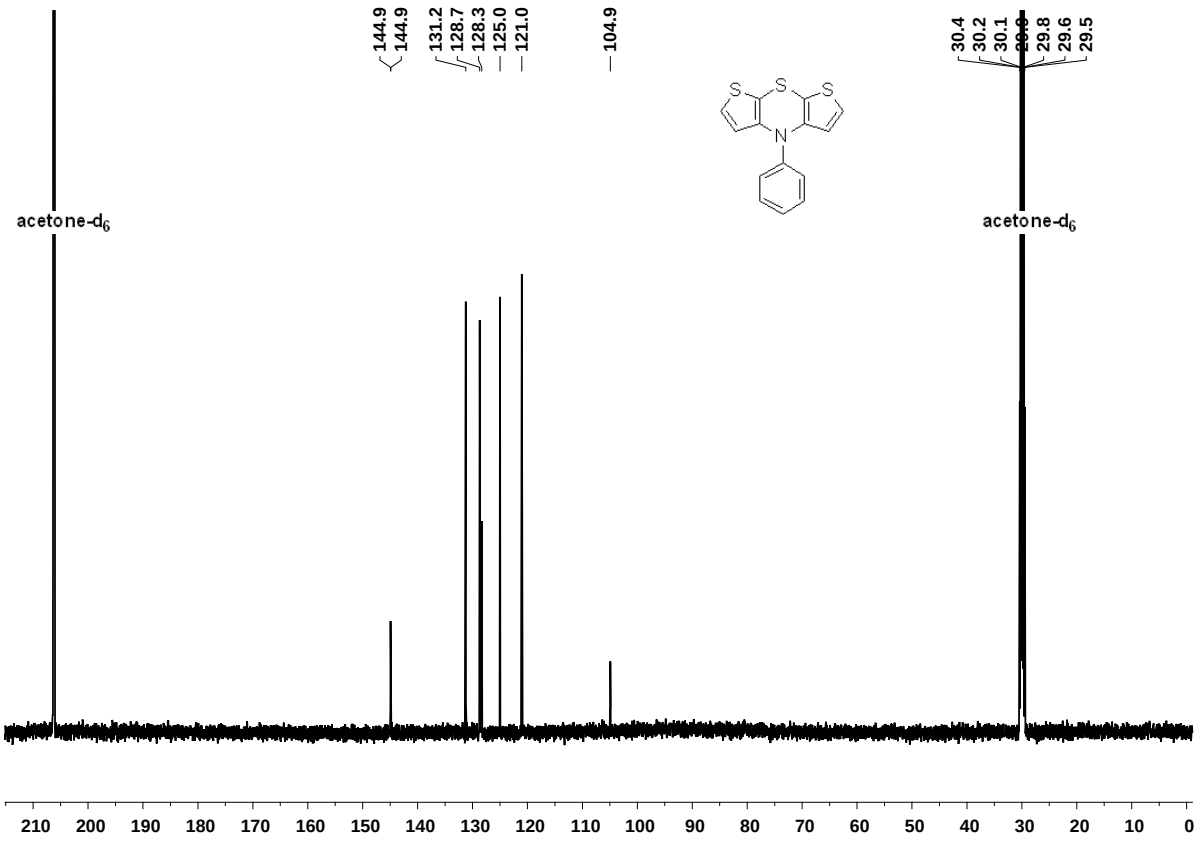


^{13}C DEPT 135-NMR (125 MHz) of **5d** (20mg) in acetone-d_6 at 298 K (δ in ppm).

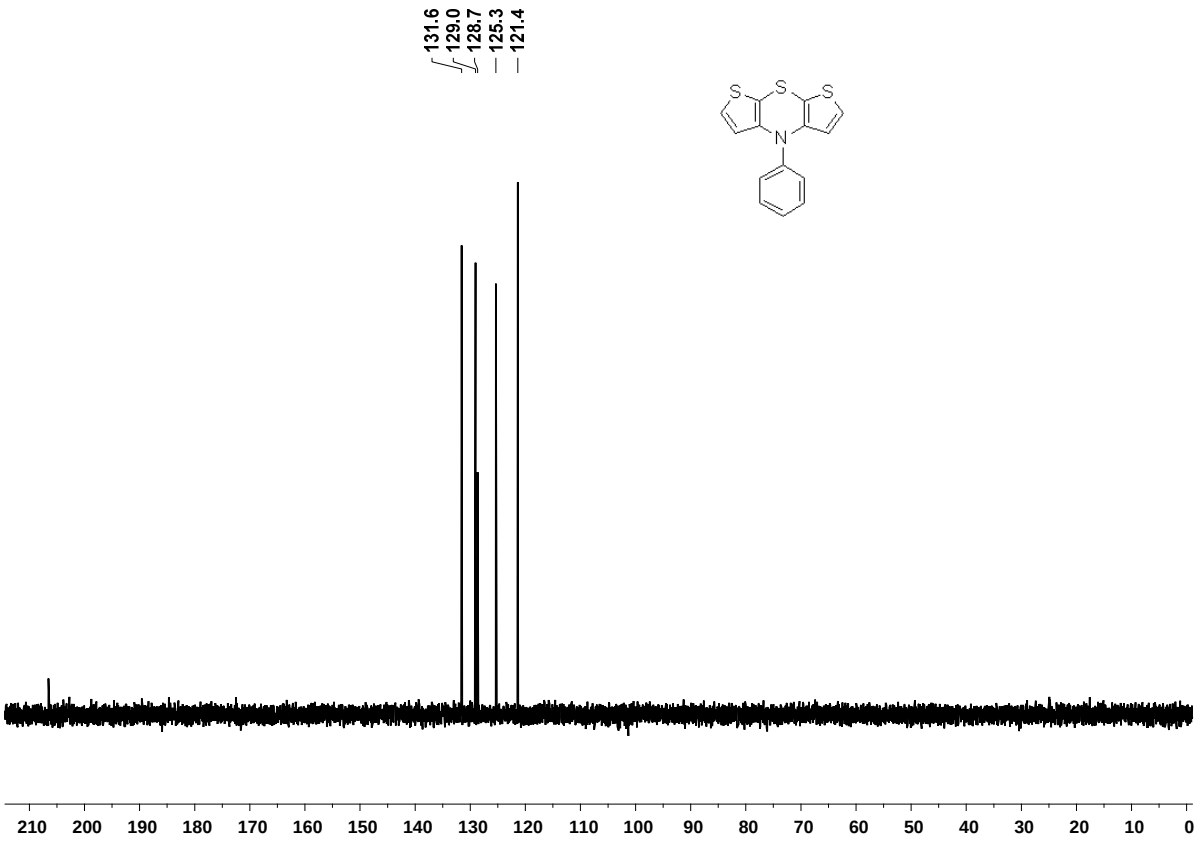
4.5 4-Phenyl-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5e)



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

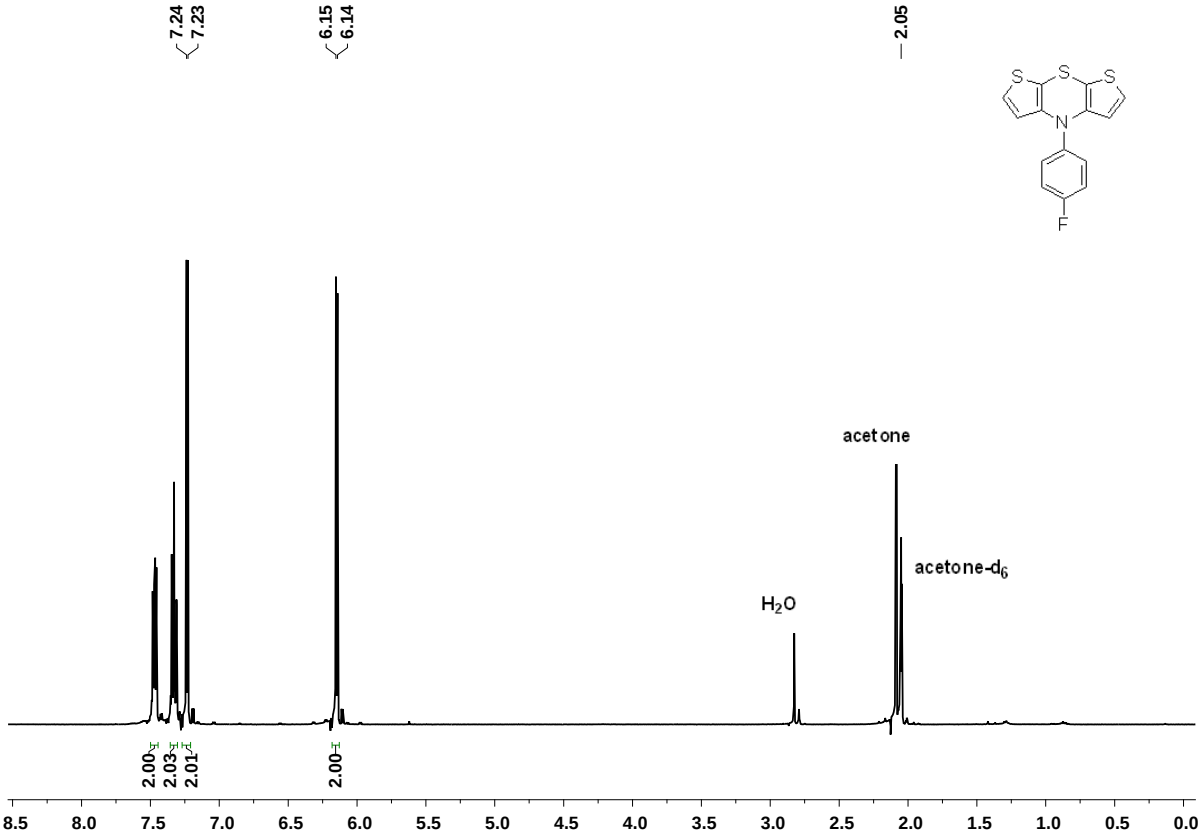


^{13}C NMR (125 MHz) of **5e** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

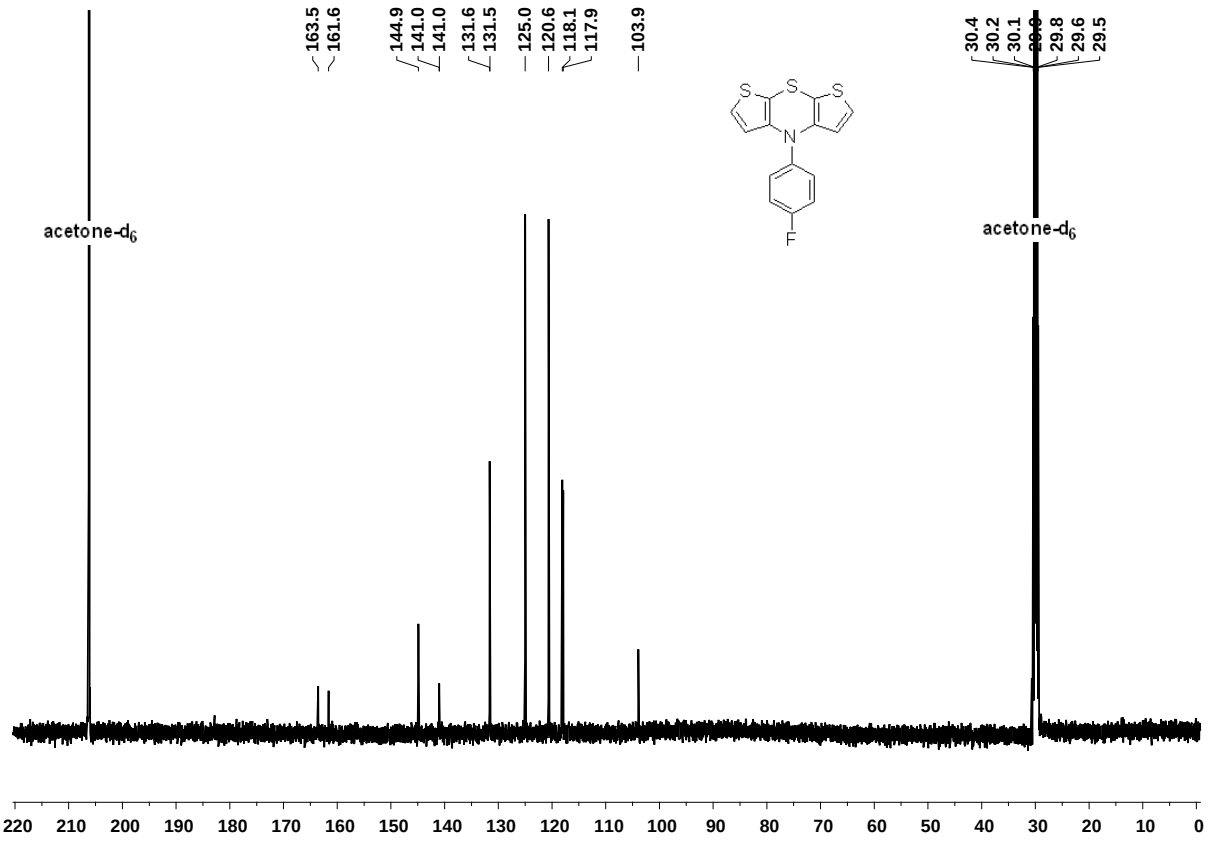


^{13}C DEPT 135-NMR (125 MHz) of **5e** (20mg) in acetone-d_6 at 298 K (δ in ppm).

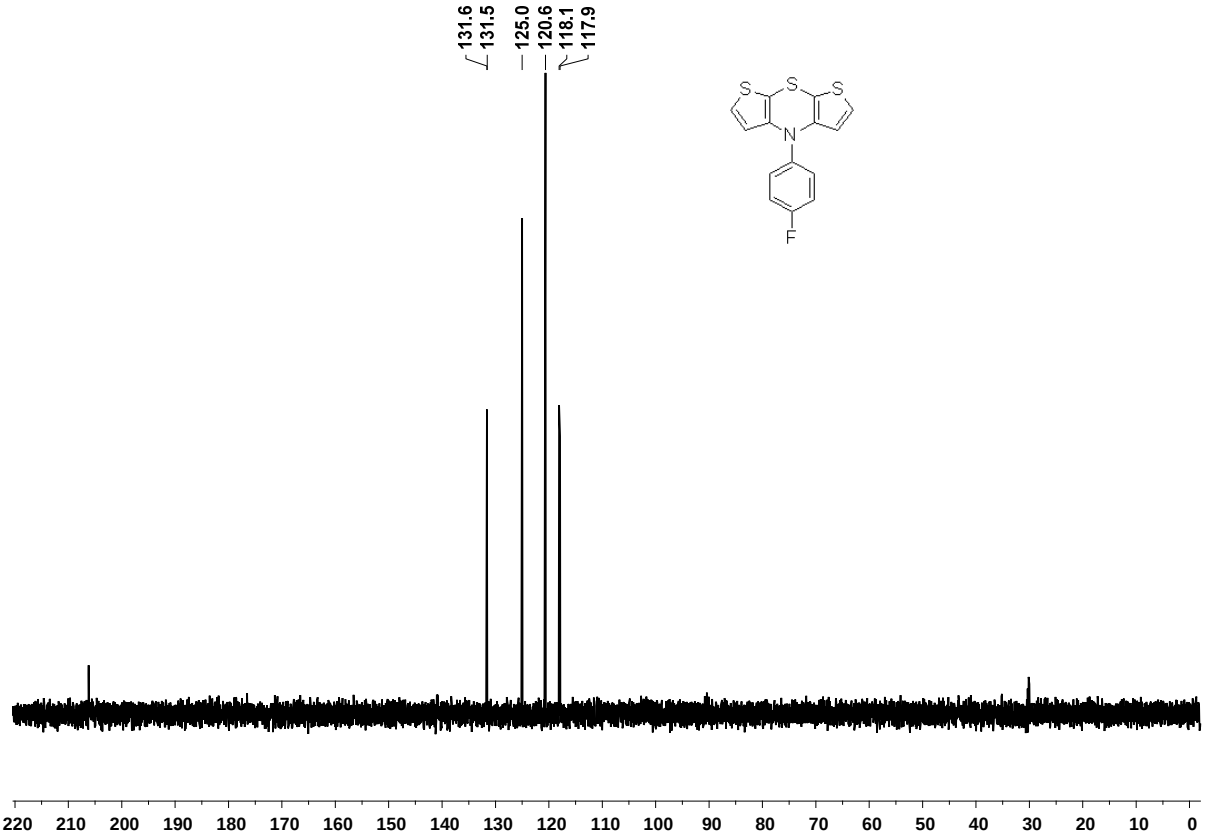
4.6 4-(4-Fluorophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5f)



^{1}H NMR (500 MHz) of **5f** (20mg) in acetone-d_6 at 298 K (δ in ppm).

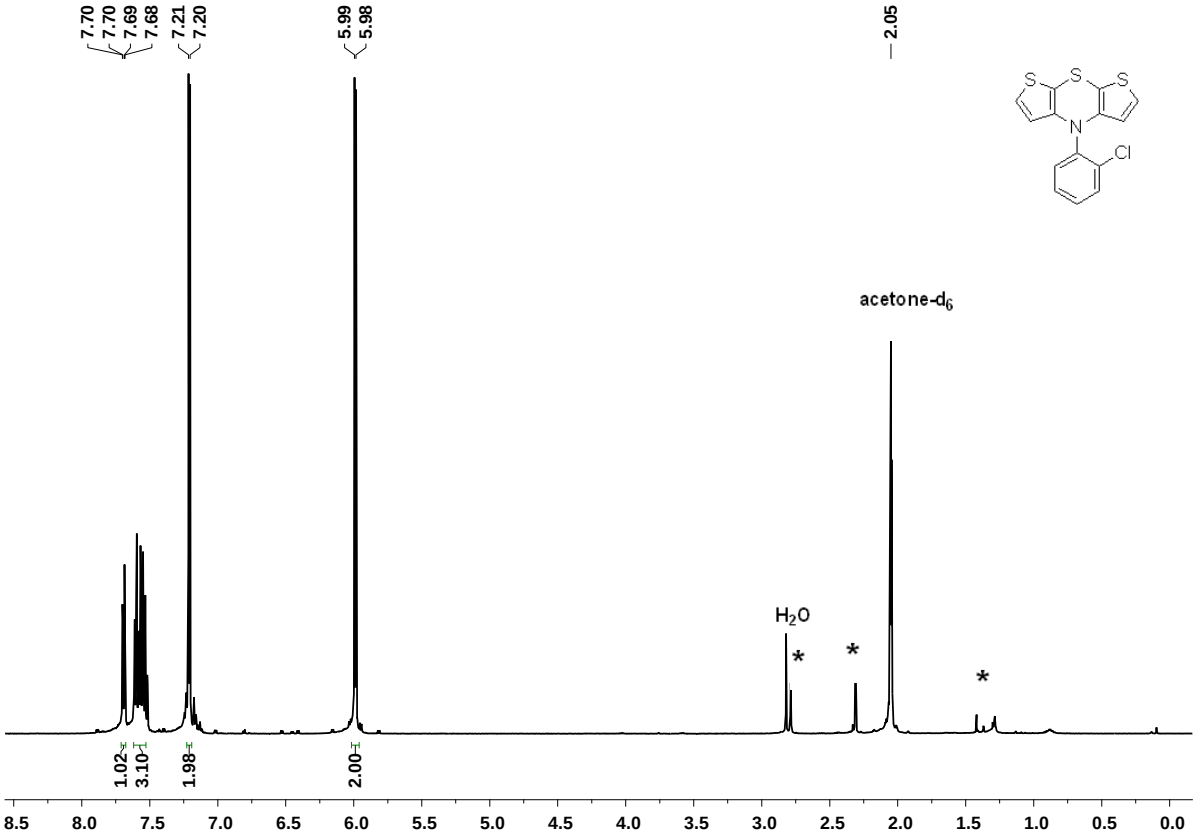


^{13}C NMR (125 MHz) of **5f** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

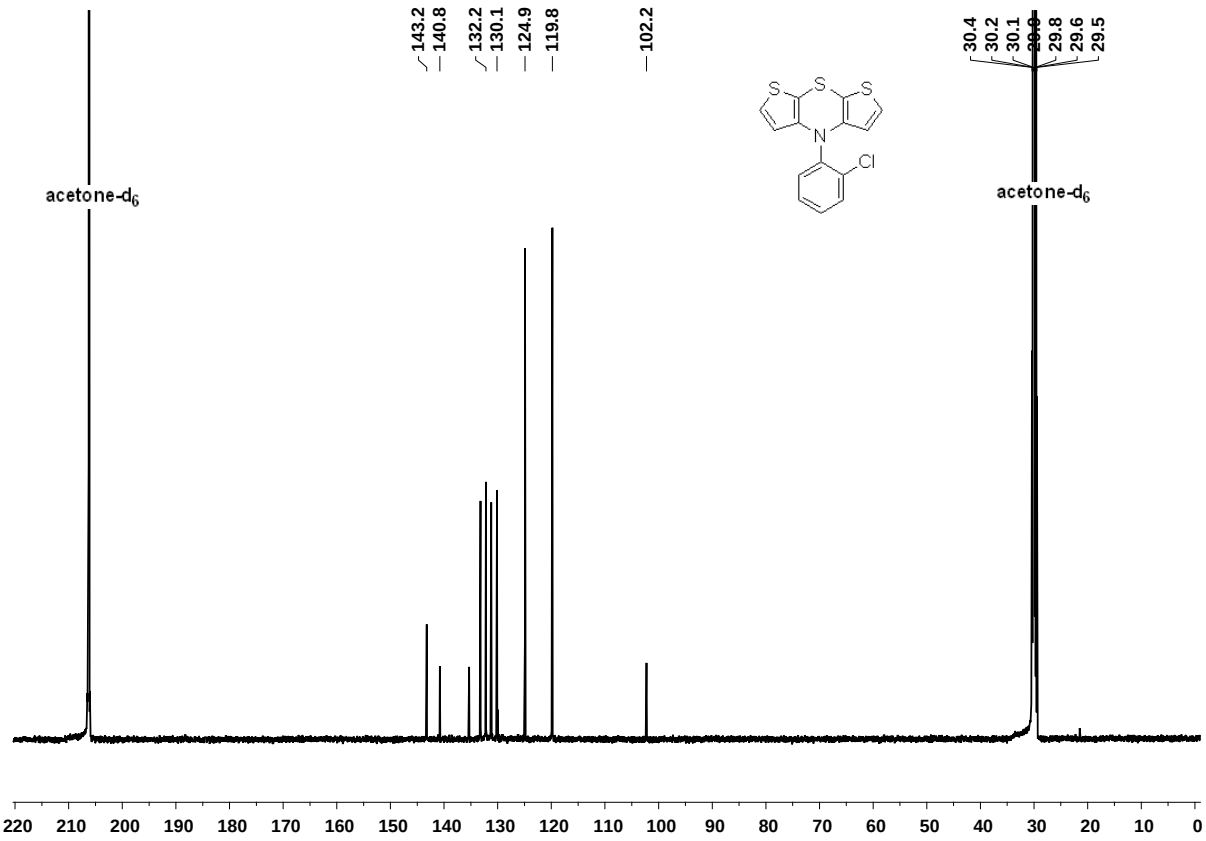


^{13}C DEPT 135-NMR (125 MHz) of **5f** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

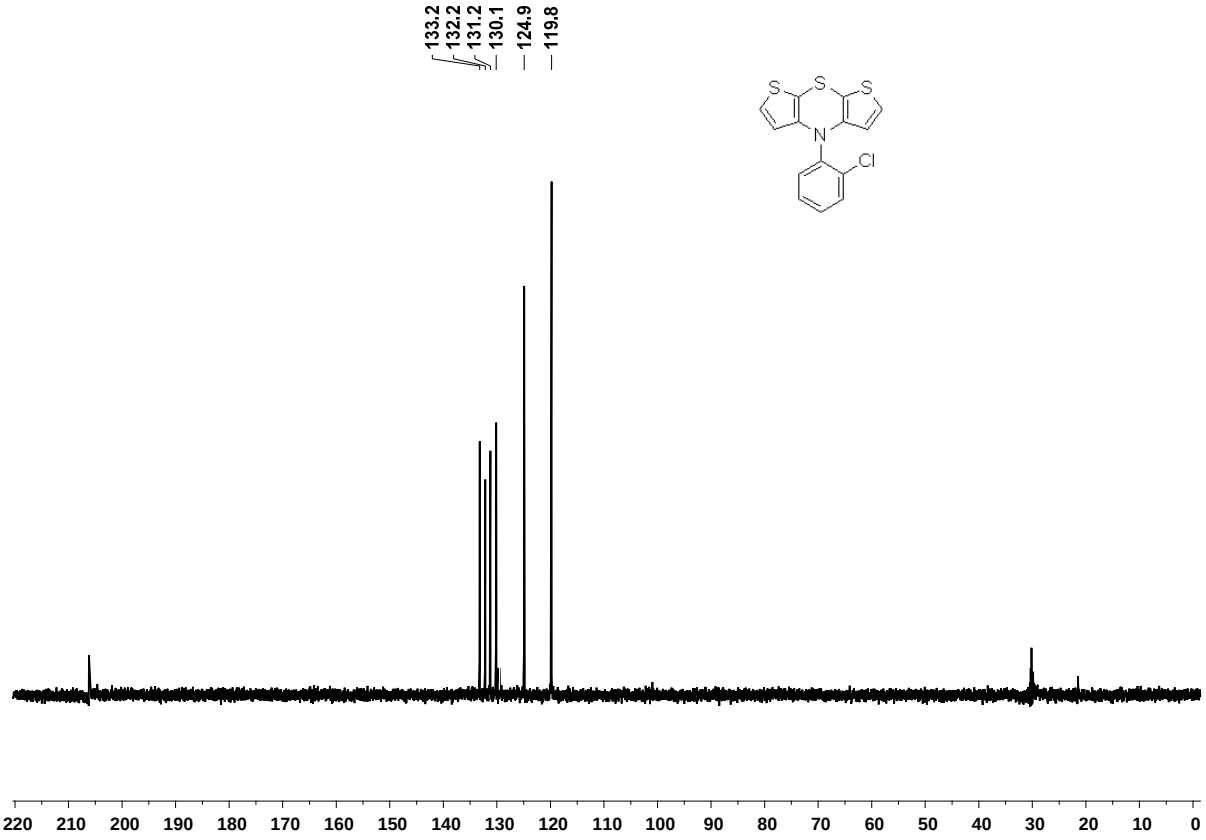
4.7 4-(2-Chlorophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5g)



^{1}H NMR (500 MHz) of **5g** (20mg) in acetone-d_6 at 298 K (δ in ppm). *Impurities from residual solvents.

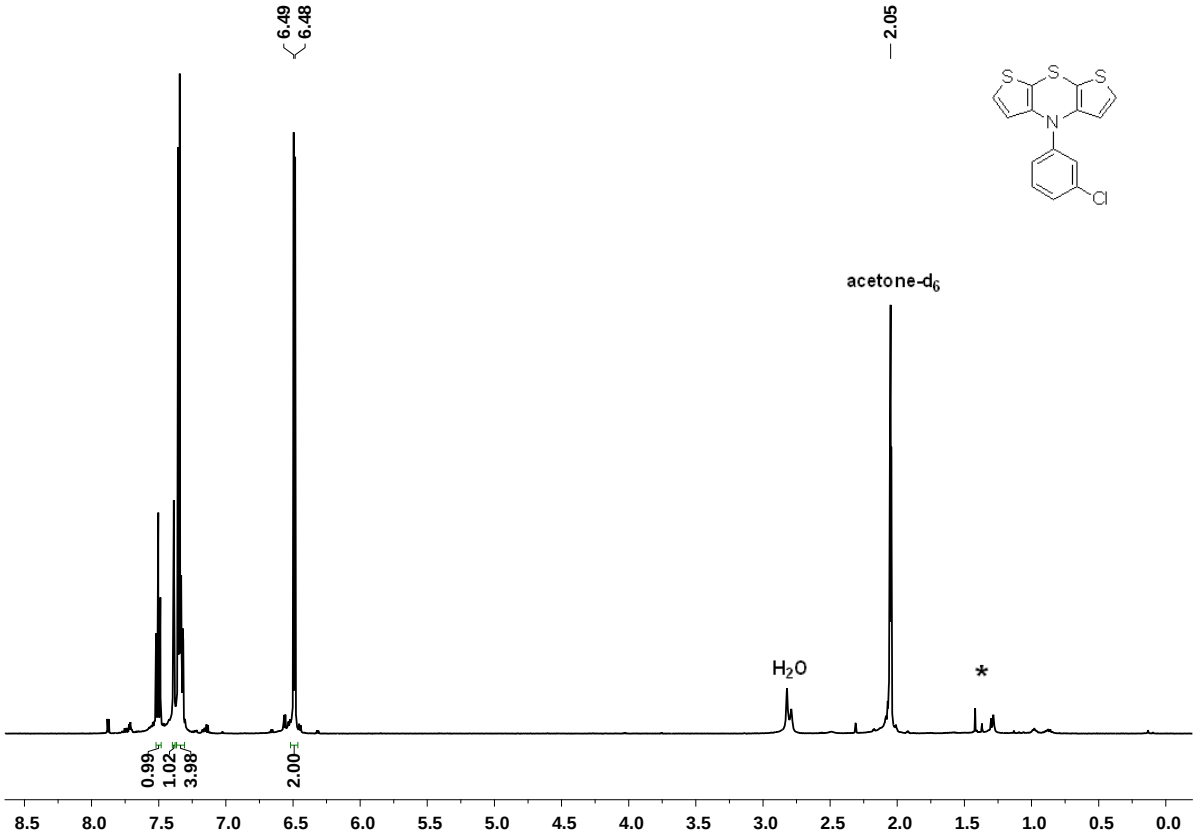


^{13}C NMR (125 MHz) of **5g** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

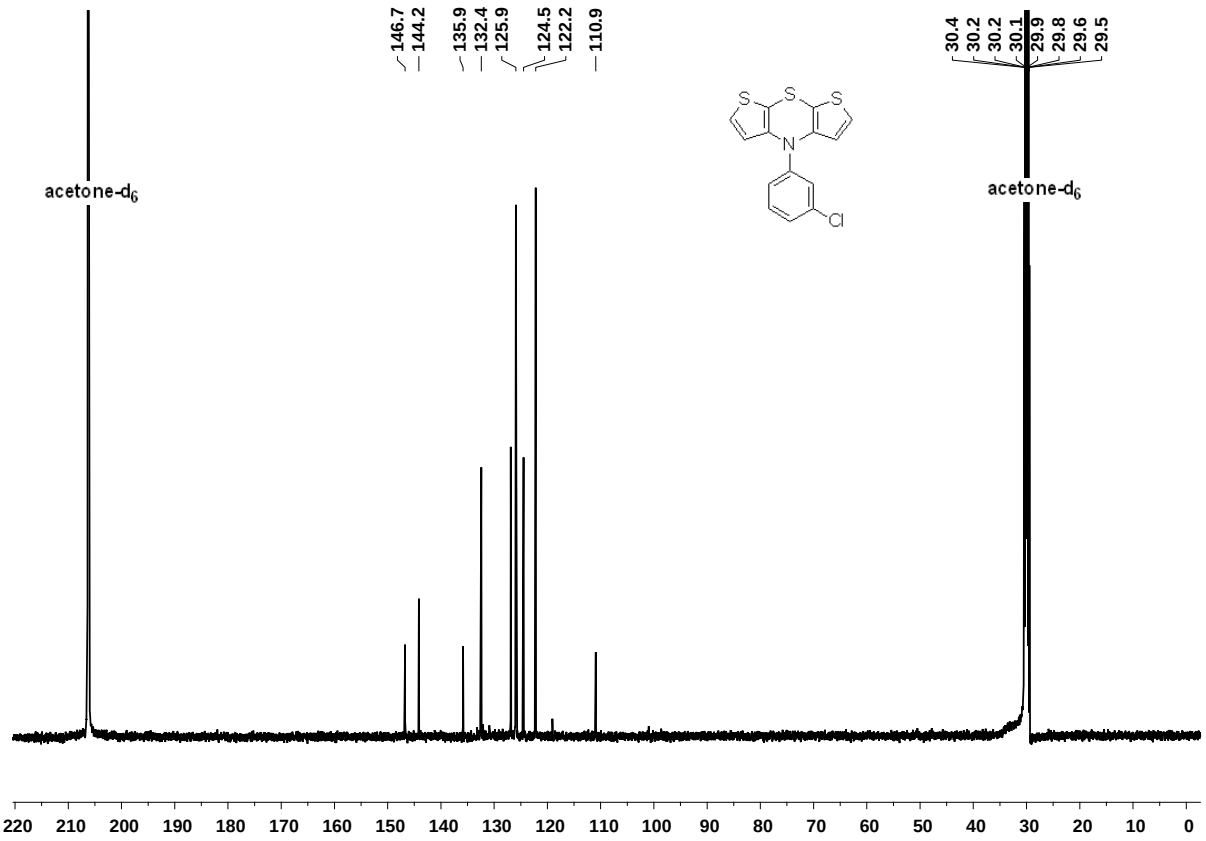


^{13}C DEPT 135-NMR (125 MHz) of **5g** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

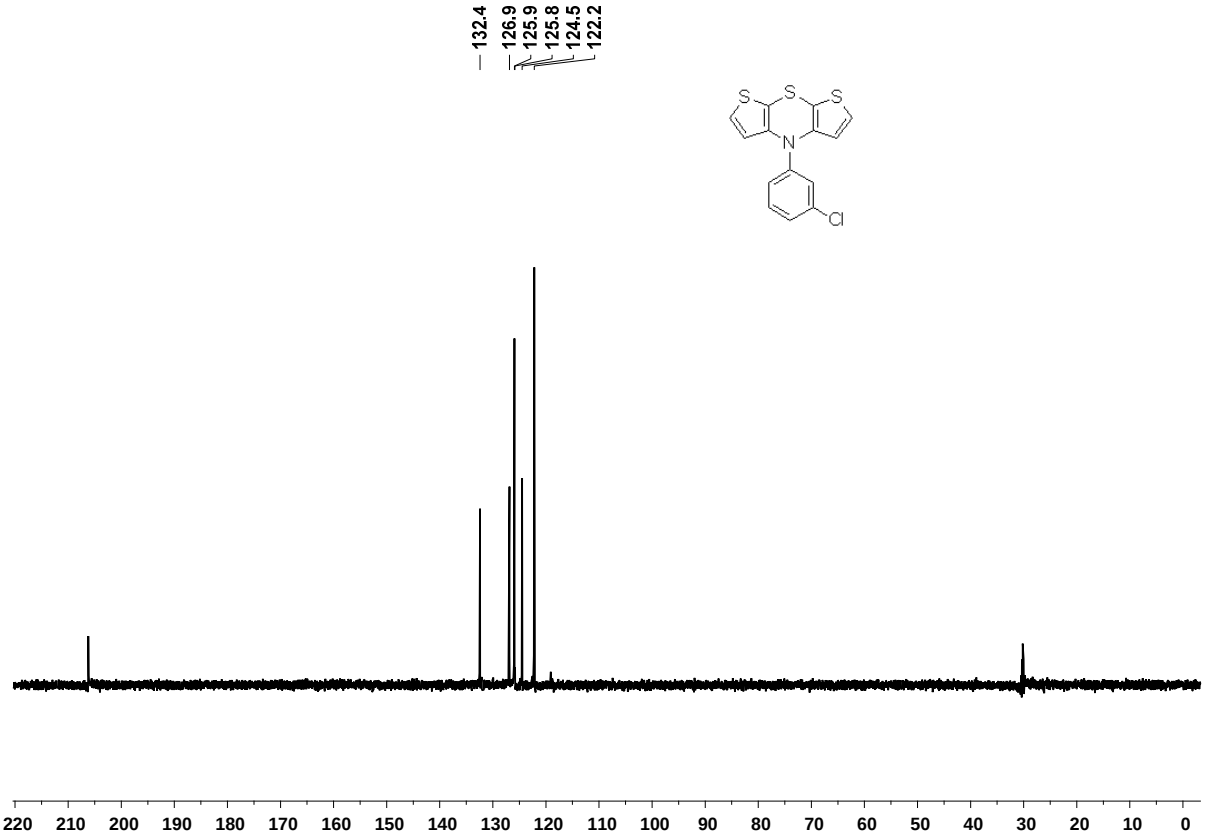
4.8 4-(3-Chlorophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5h)



^{1}H NMR (500 MHz) of **5h** (20mg) in acetone-d_6 at 298 K (δ in ppm). *Impurities from residual solvents.

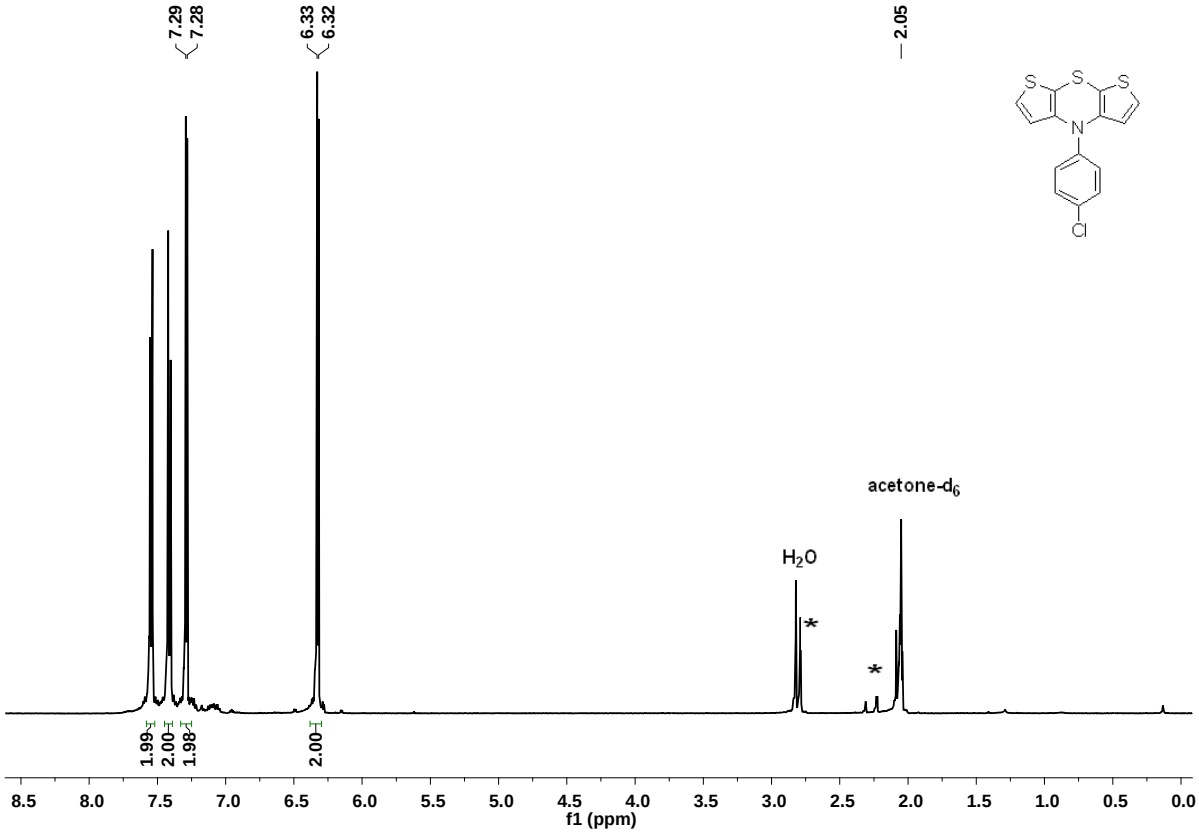


^{13}C NMR (125 MHz) of **5h** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

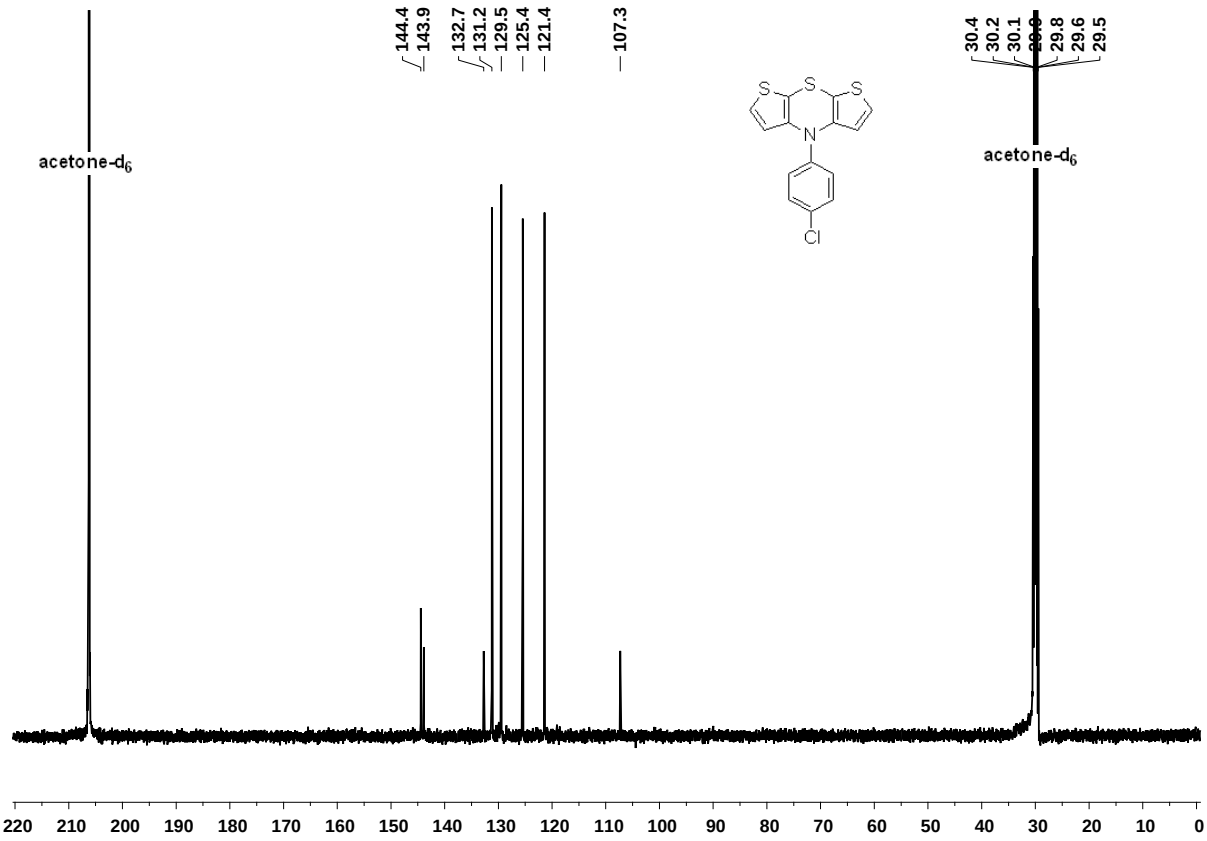


^{13}C DEPT 135-NMR (125 MHz) of **5h** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

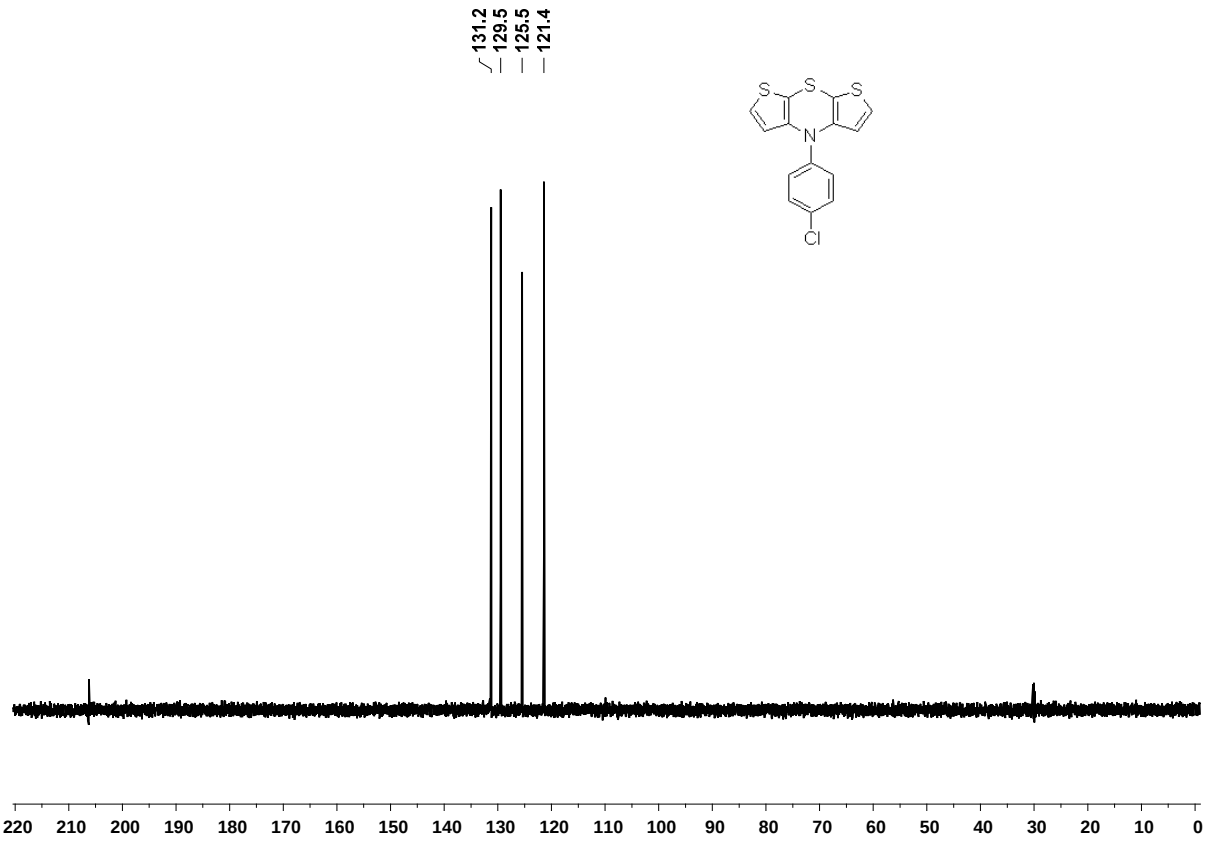
4.9 4-(4-Chlorophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5i)



^{1}H NMR (500 MHz) of **5i** (20mg) in acetone-d_6 at 298 K (δ in ppm). *Impurities from residual solvents.

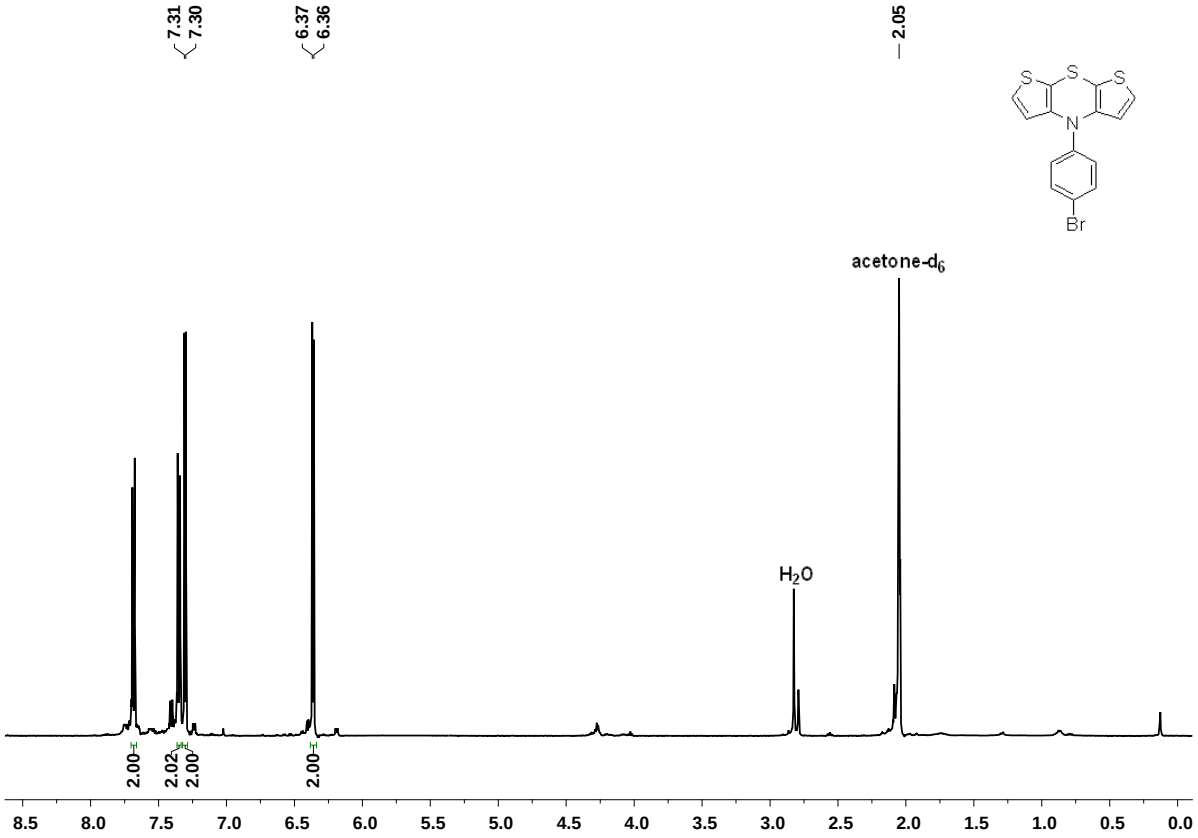


^{13}C NMR (125 MHz) of **5i** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

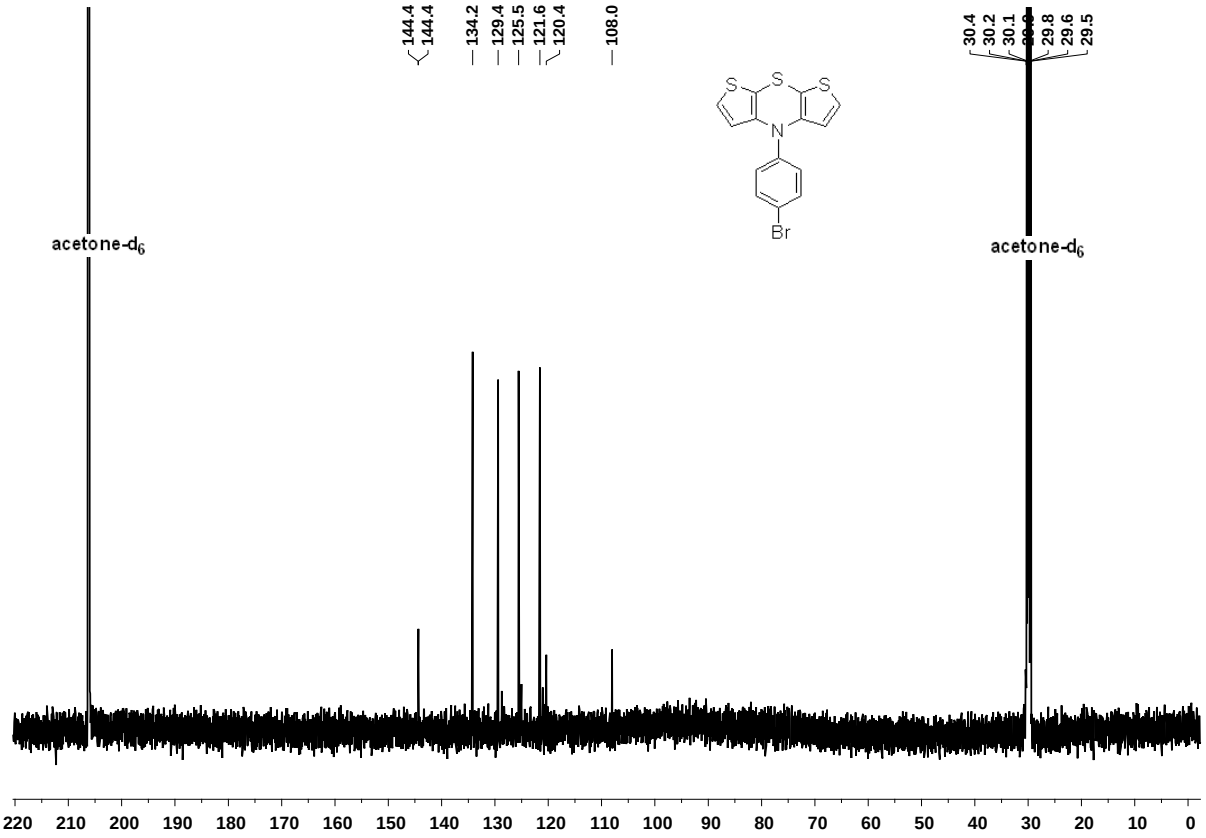


^{13}C DEPT 135-NMR (125 MHz) of **5i** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

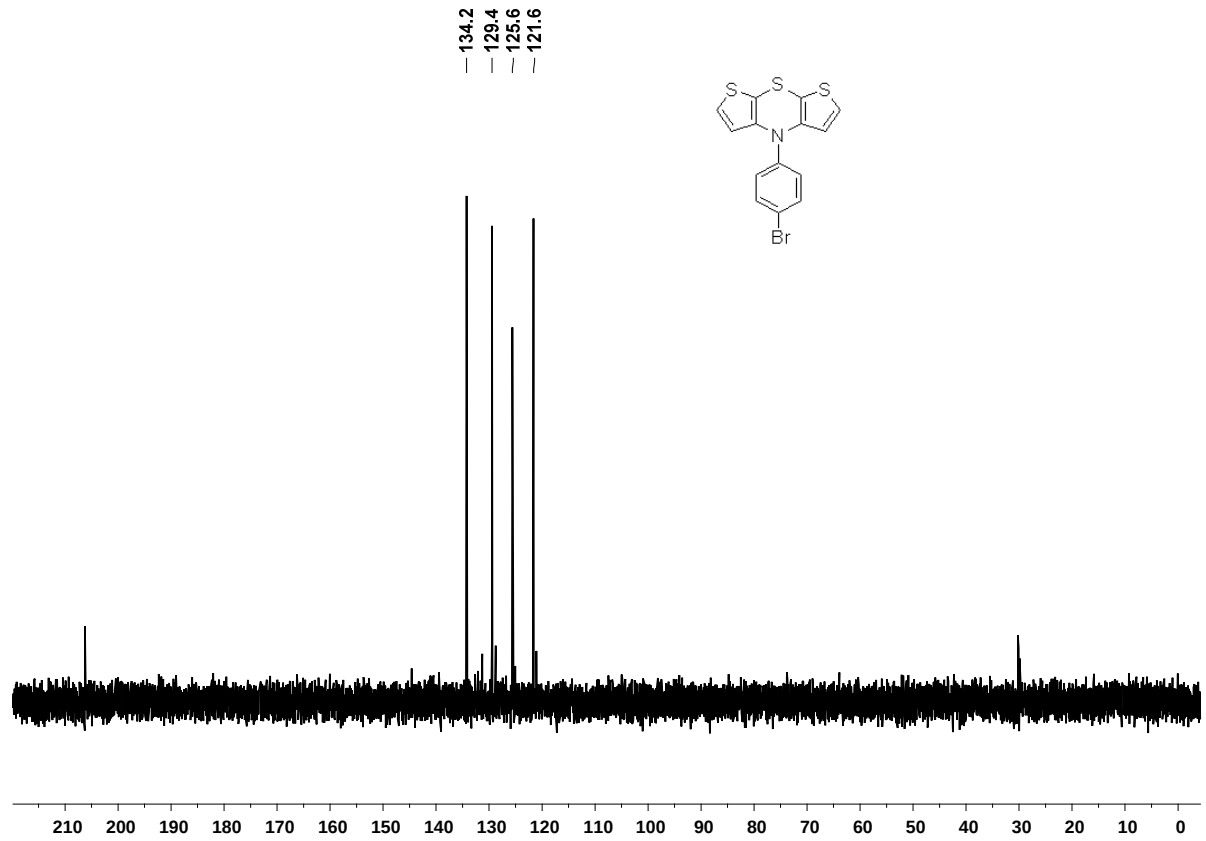
4.10 4-(4-Bromophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5j)



^{1}H NMR (500 MHz) of **5j** (20mg) in acetone-d_6 at 298 K (δ in ppm).

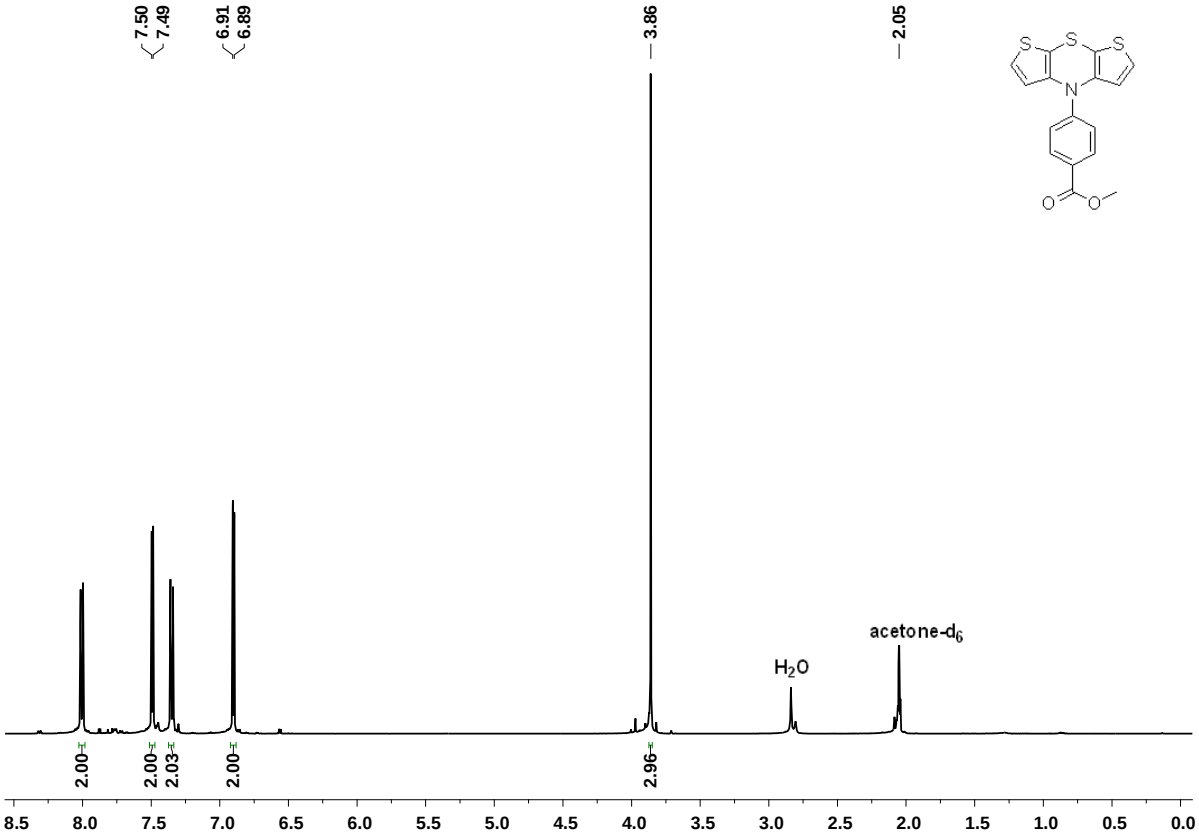


^{13}C NMR (125 MHz) of **5j** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

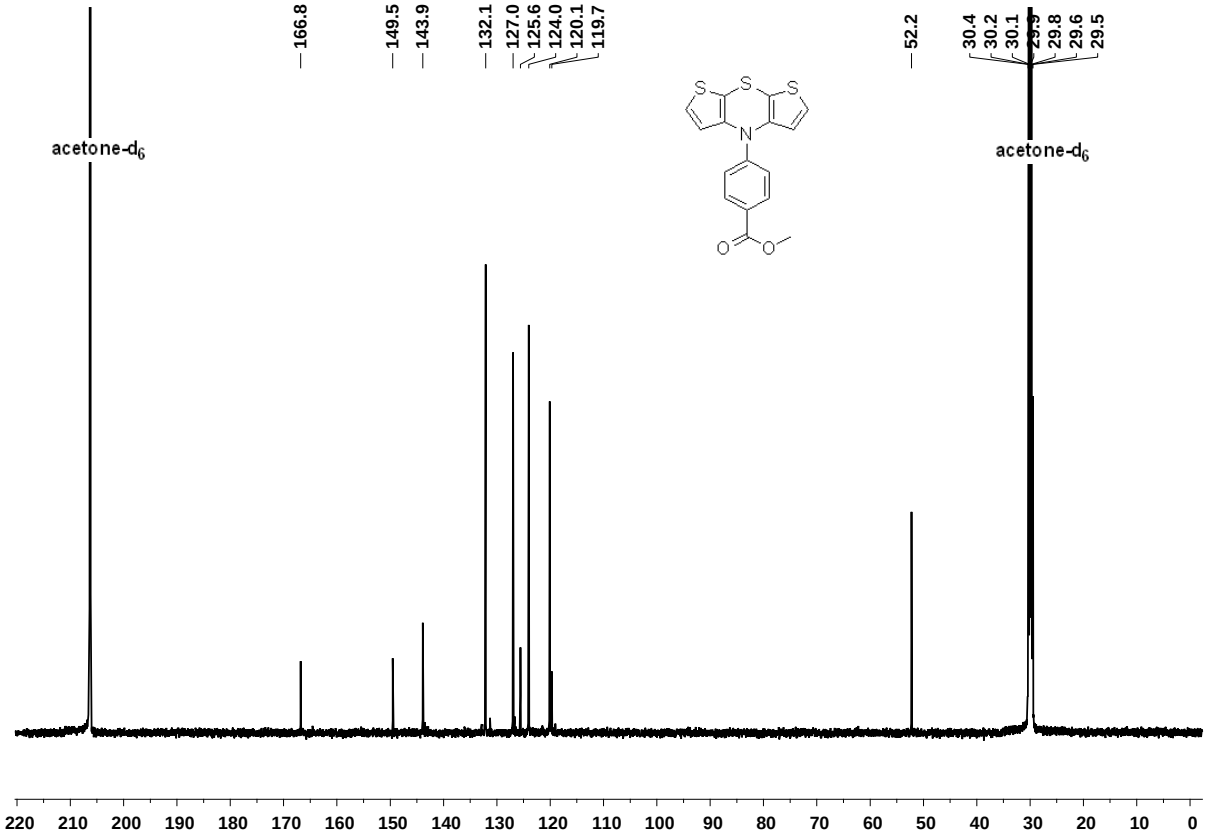


^{13}C DEPT 135-NMR (125 MHz) of **5j** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

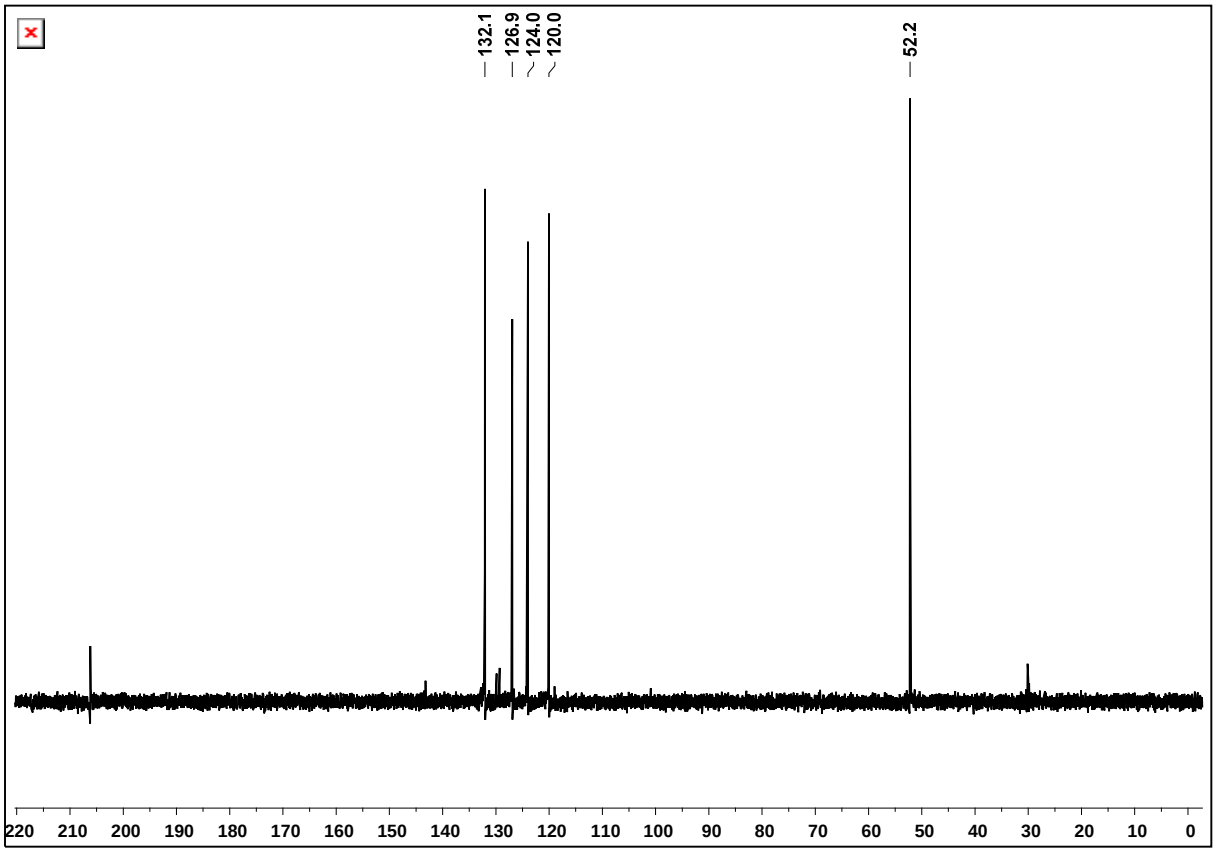
4.11 Methyl 4-(4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazin-4-yl)benzoate (5k)



^{1}H NMR (500 MHz) of **5k** (20mg) in acetone-d_6 at 298 K (δ in ppm).

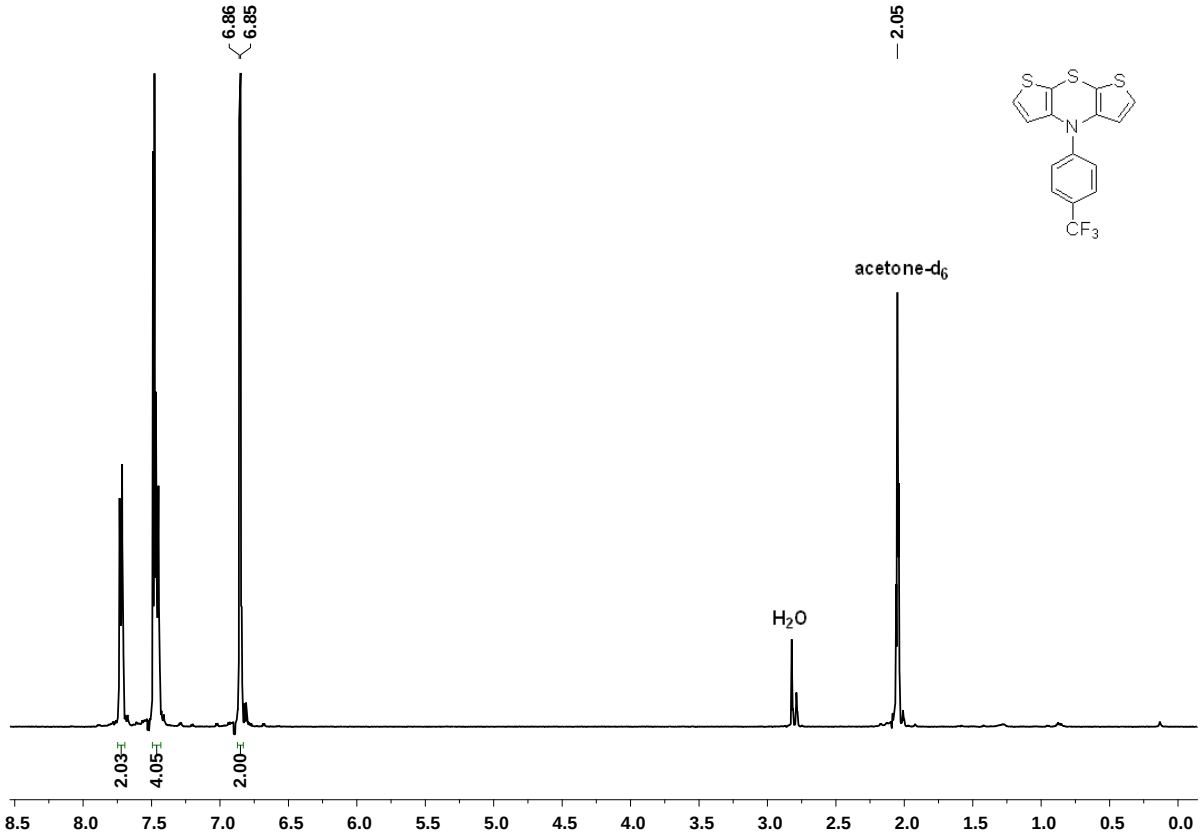


^{13}C NMR (125 MHz) of **5k** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

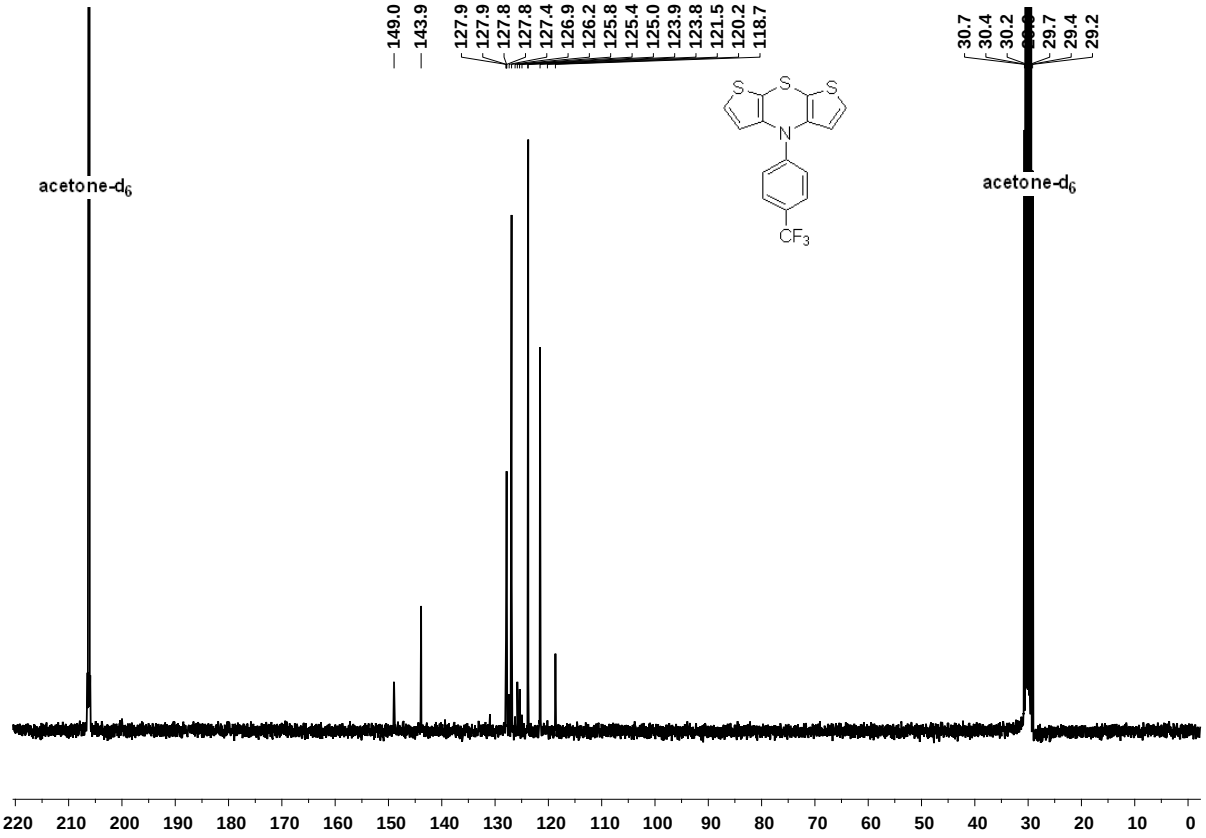


^{13}C DEPT 135-NMR (125 MHz) of **5k** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

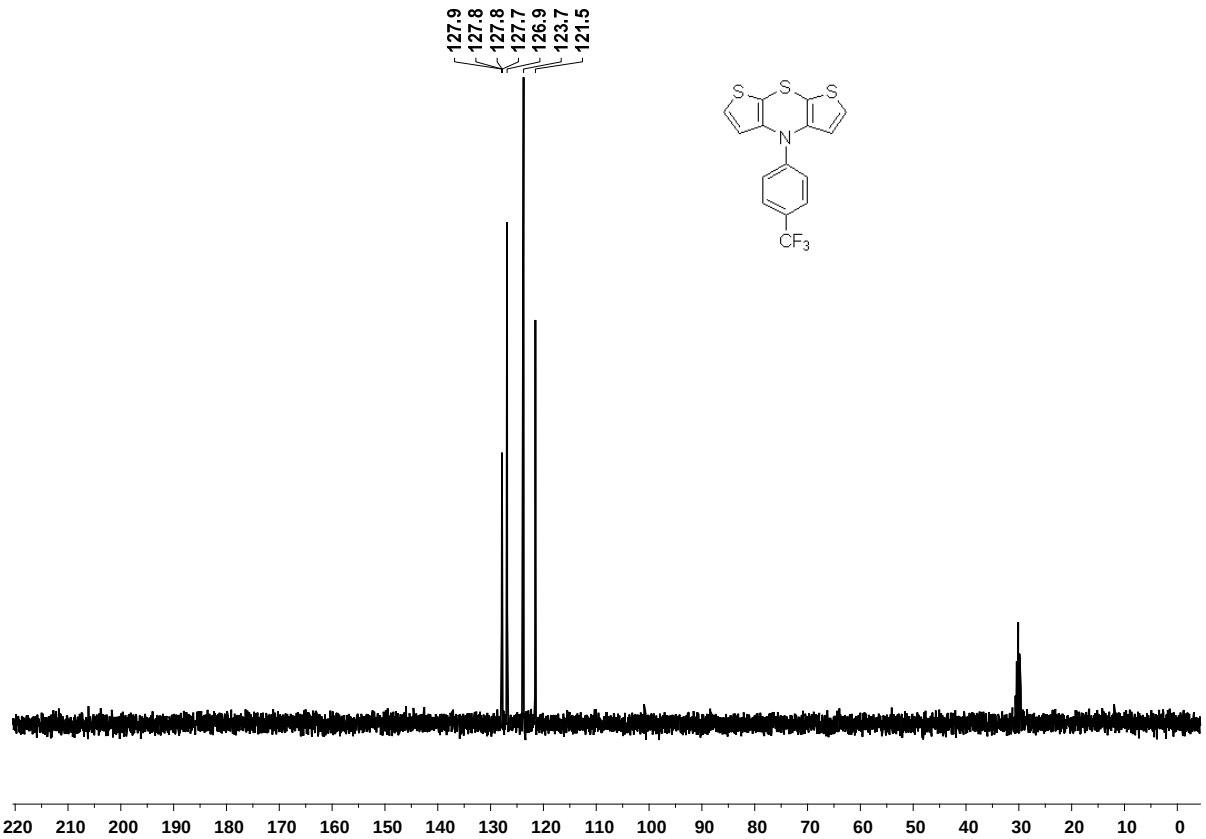
4.12 4-(4-(Trifluoromethyl)phenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5l)



^{1}H NMR (500 MHz) of **5l** (20mg) in acetone-d_6 at 298 K (δ in ppm).

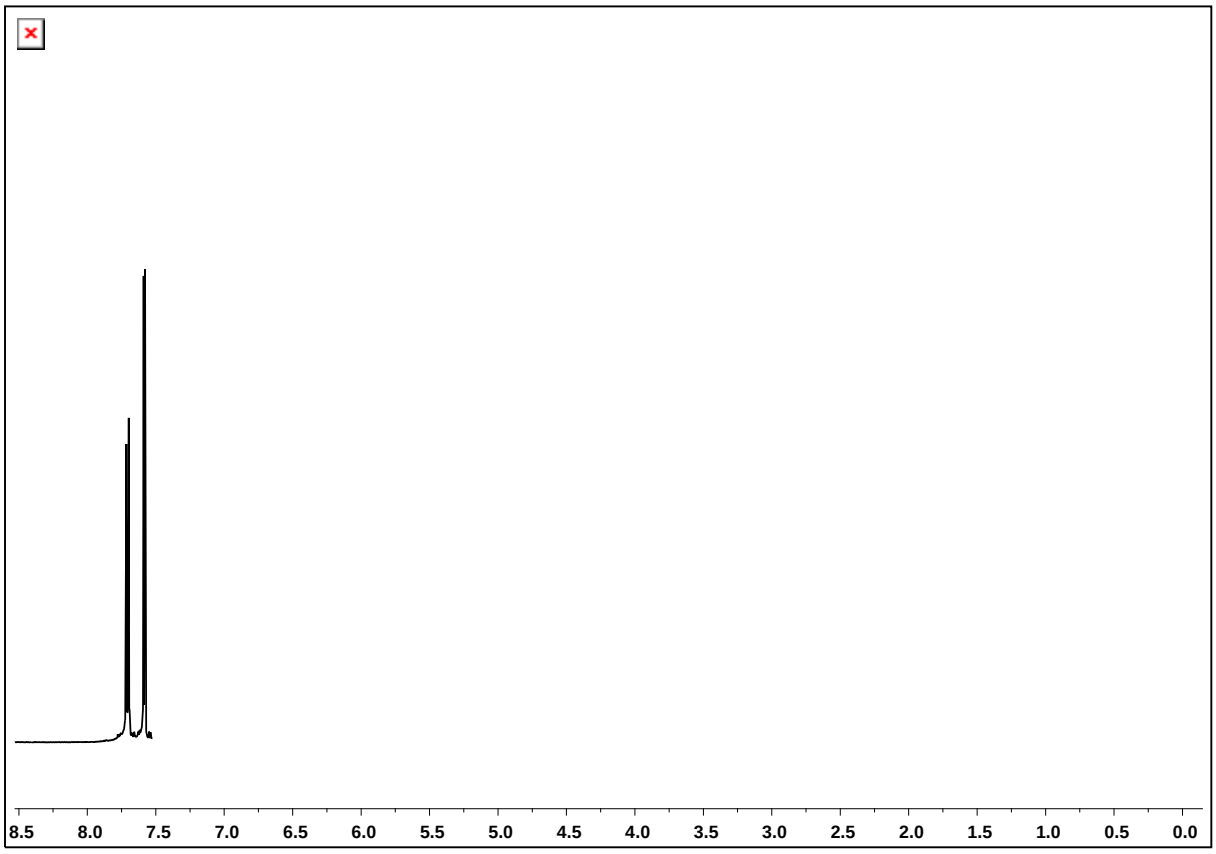


^{13}C NMR (75 MHz) of **5l** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

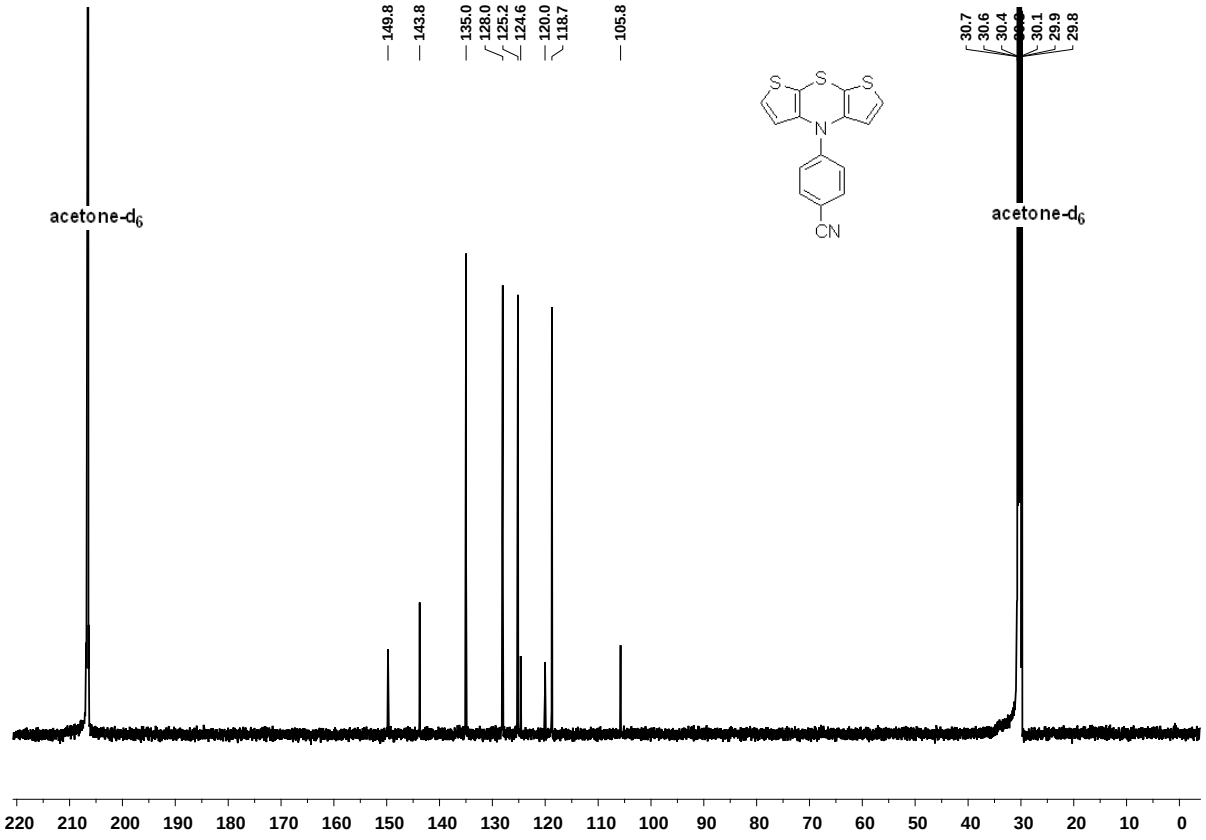


^{13}C DEPT 135-NMR (75 MHz) of **5l** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

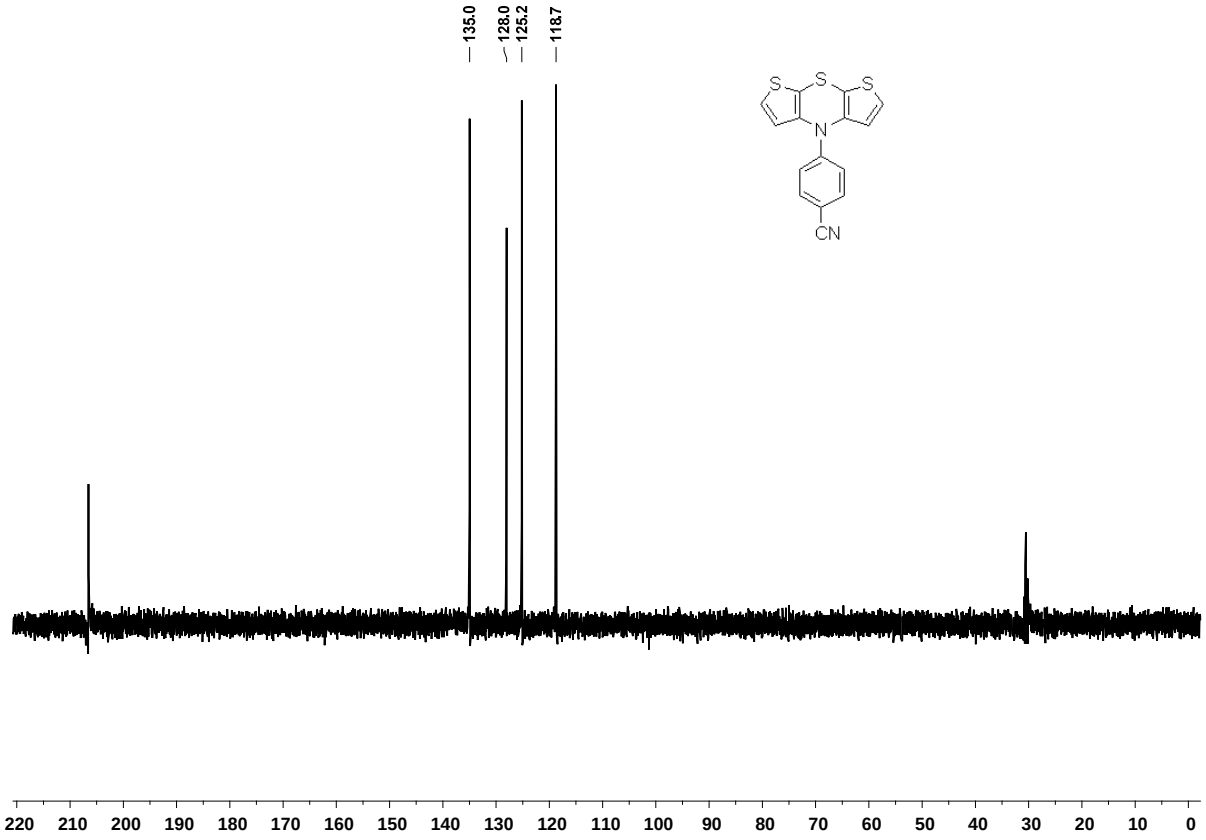
4.13 4-(4*H*-Dithieno[2,3-*b*:3',2'-*e*][1,4]thiazin-4-yl)benzonitrile (5m)



^{1}H NMR (500 MHz) of **5m** (20mg) in acetone-d_6 at 298 K (δ in ppm).

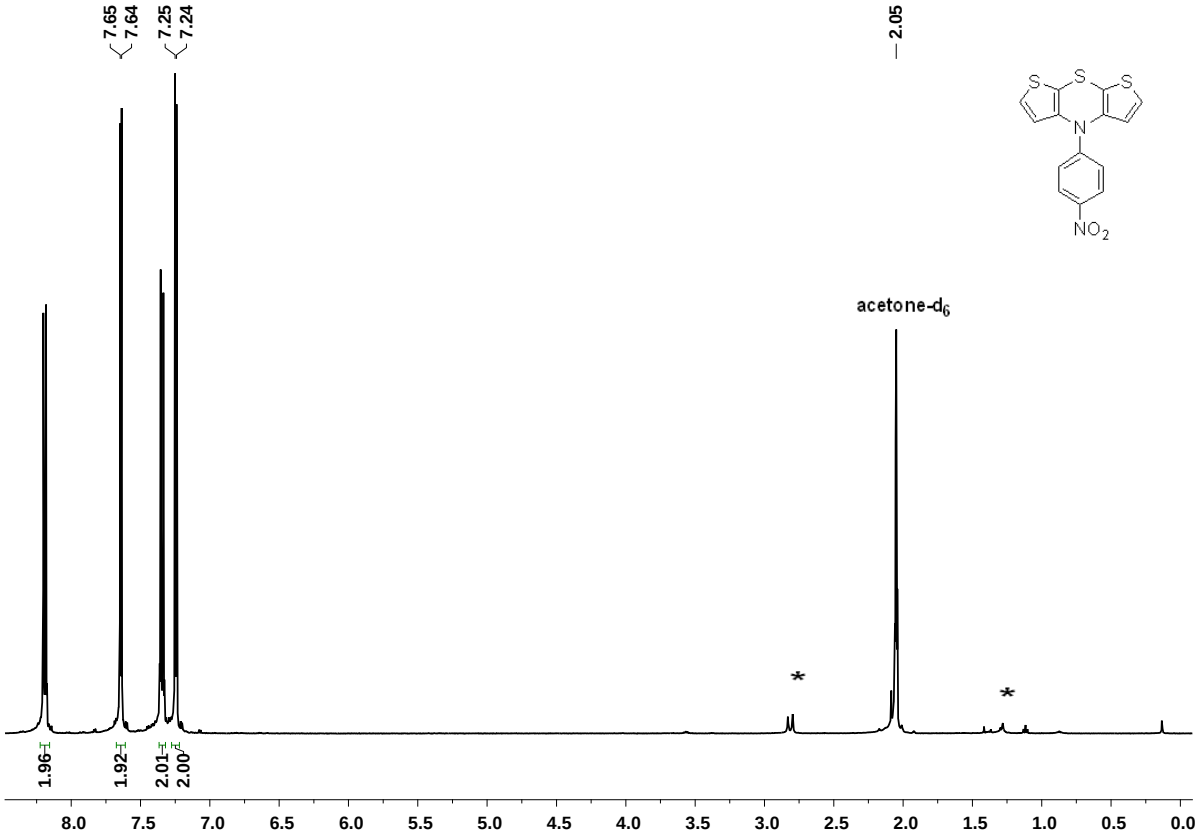


^{13}C NMR (125 MHz) of **5m** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

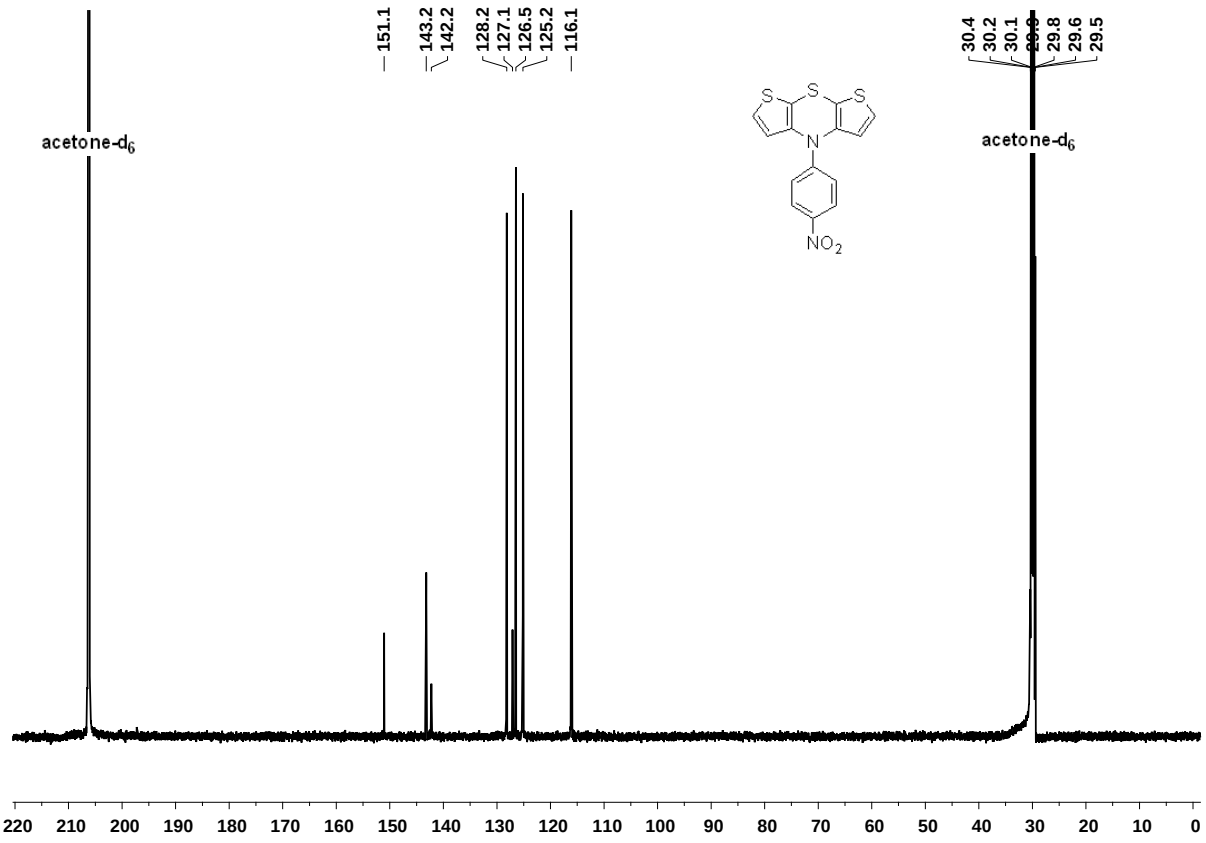


^{13}C DEPT 135-NMR (125 MHz) of **5m** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

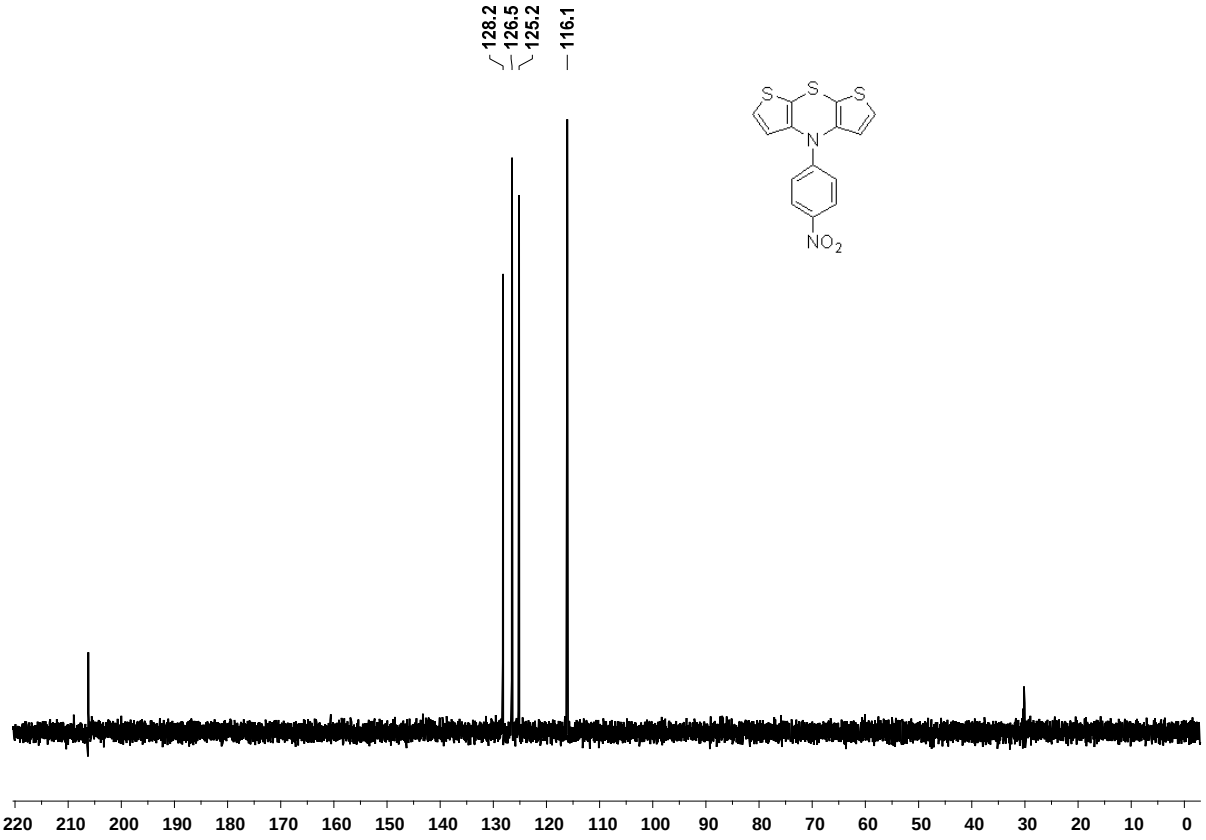
4.14 4-(4-Nitrophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5n)



^{1}H NMR (500 MHz) of **5n** (20mg) in acetone-d_6 at 298 K (δ in ppm). *Impurities from residual solvents.

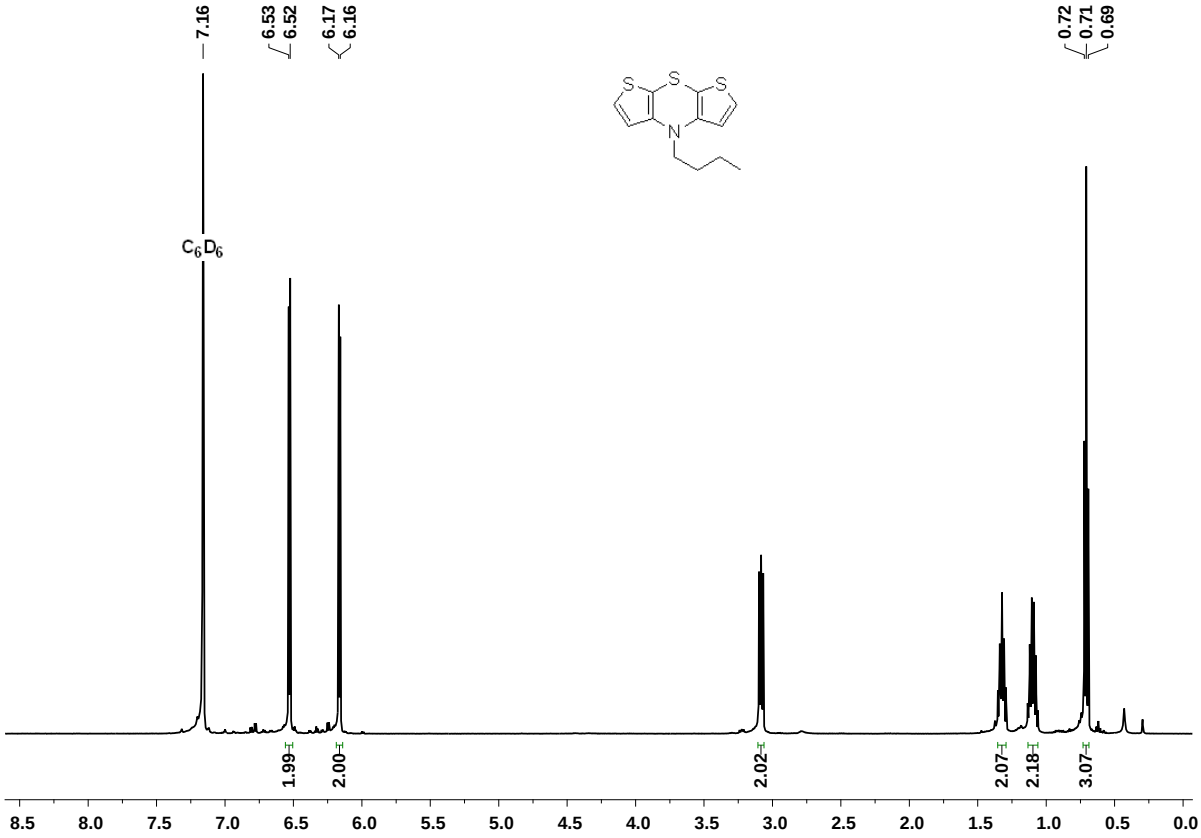


^{13}C NMR (125 MHz) of **5n** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

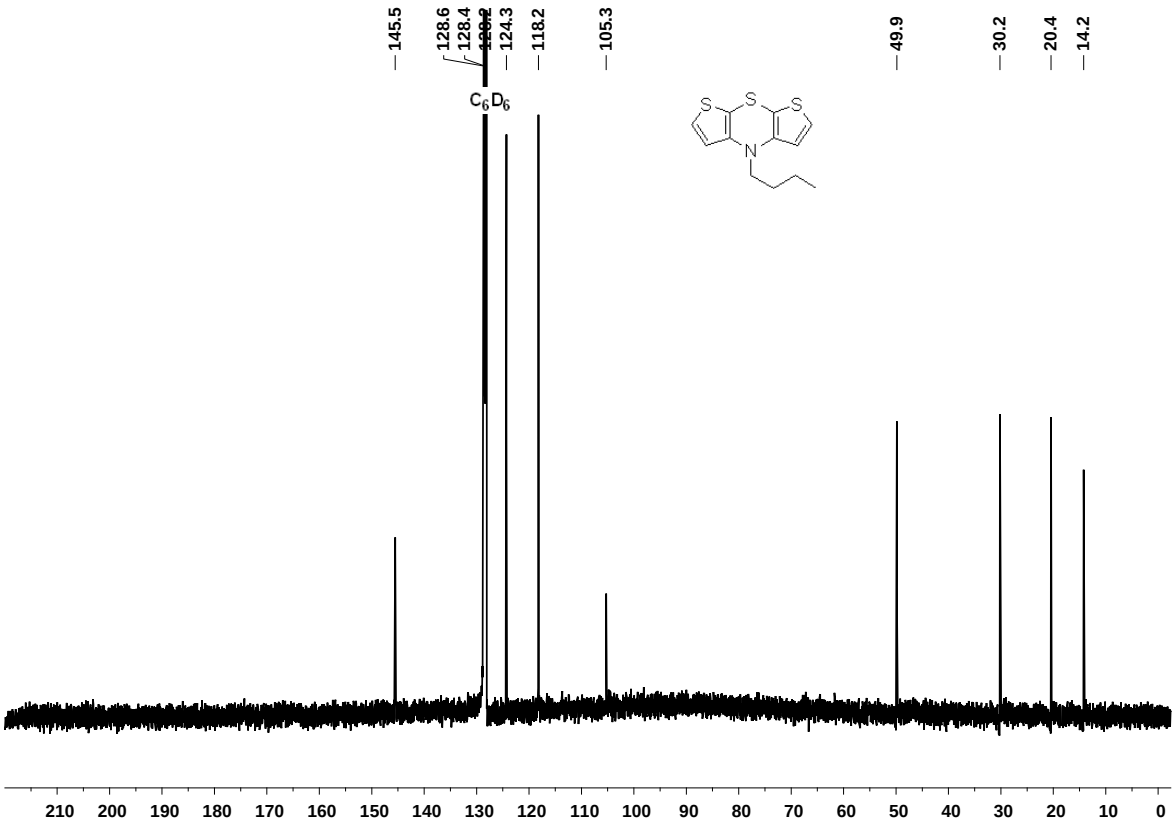


^{13}C NMR (125 MHz) of **5n** (20 mg) in acetone-d_6 at 298 K (δ in ppm).

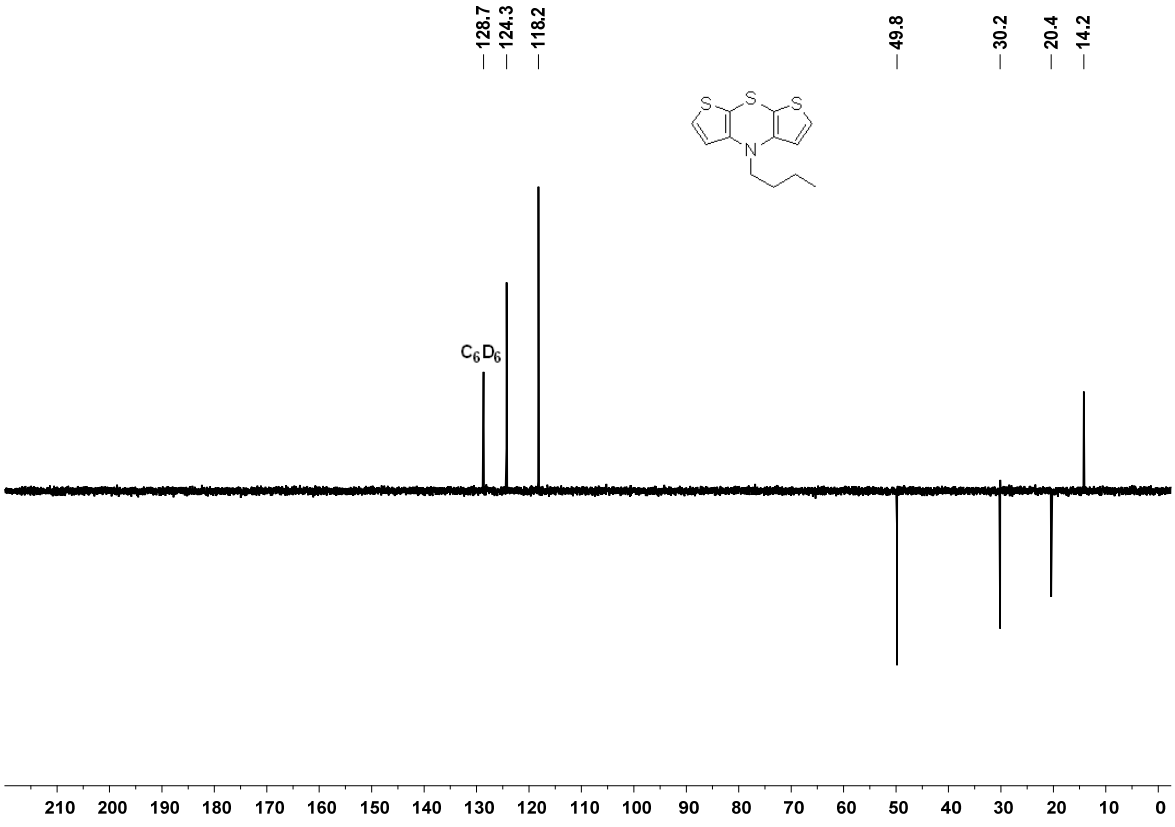
4.15 4-Butyl-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5o)



^{1}H NMR (500 MHz) of **5o** (20mg) in C_6D_6 at 298 K (δ in ppm).

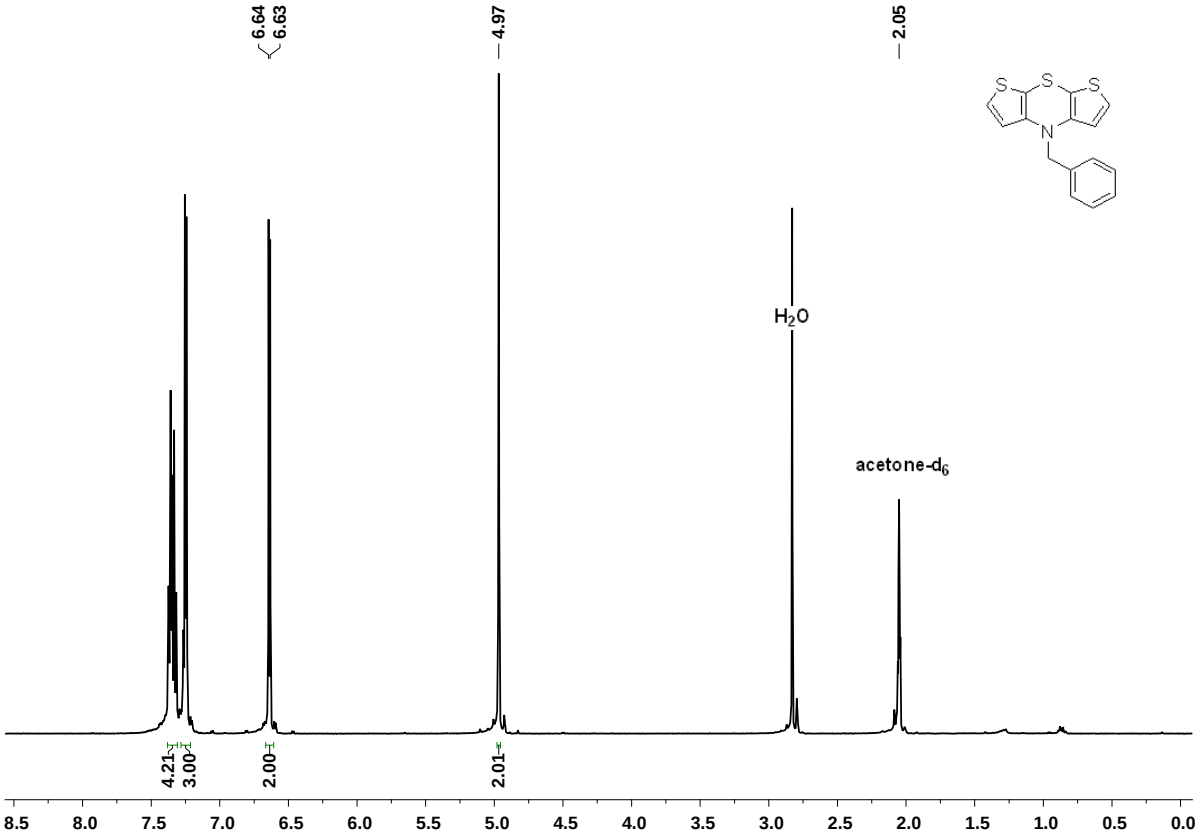


^{13}C NMR (125 MHz) of **5o** (20 mg) in C_6D_6 at 298 K (δ in ppm).

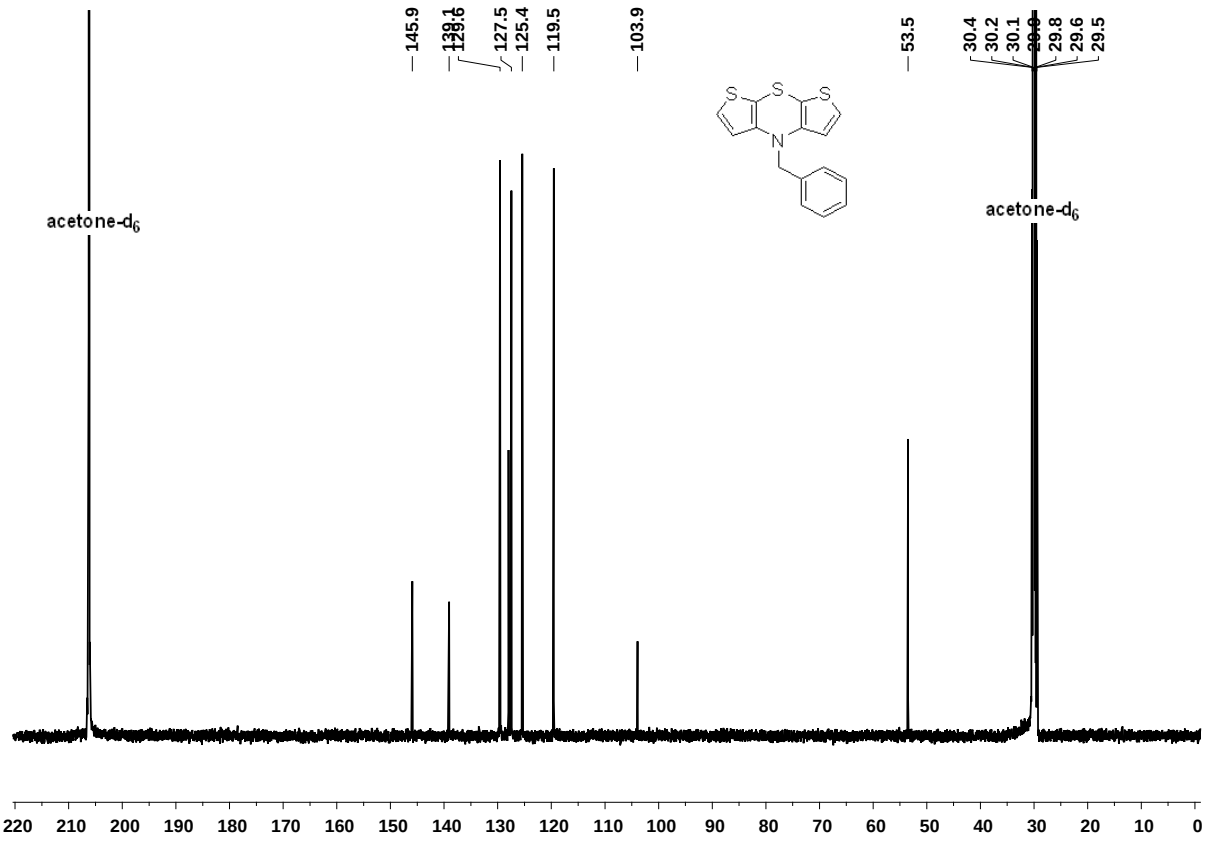


^{13}C DEPT 135-NMR (125 MHz) of **5o** (20 mg) in C_6D_6 at 298 K (δ in ppm).

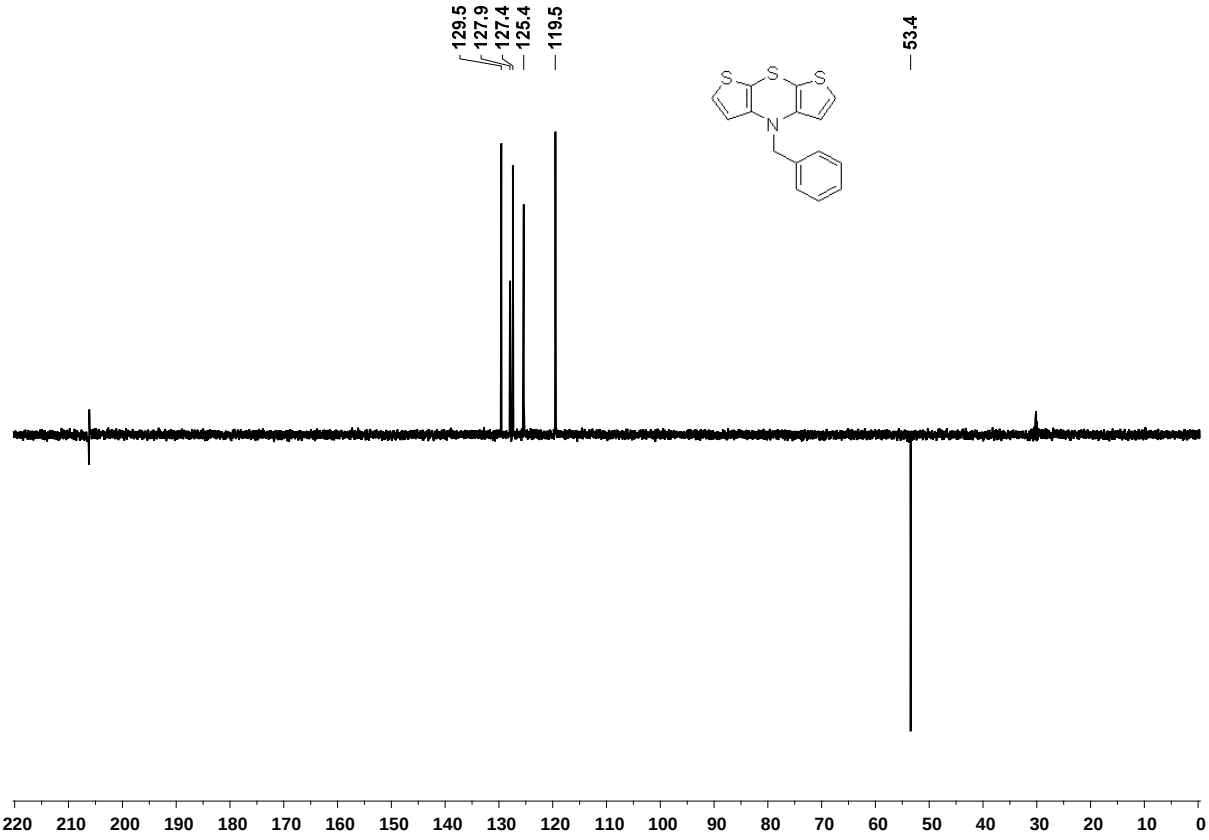
4.16 4-Benzyl-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5p)



^{1}H NMR (500 MHz) of **5p** (20mg) in acetone-d_6 at 298 K (δ in ppm).



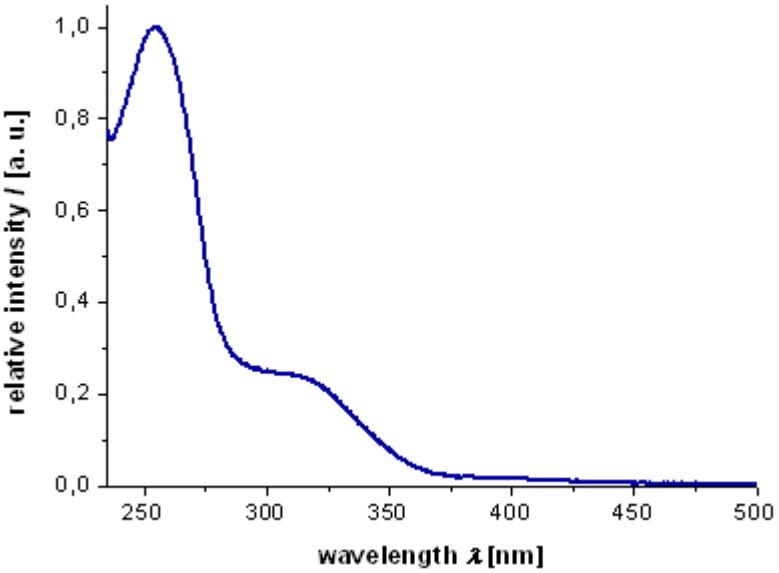
^{13}C NMR (125 MHz) of **5p** (20 mg) in acetone-d_6 at 298 K (δ in ppm).



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

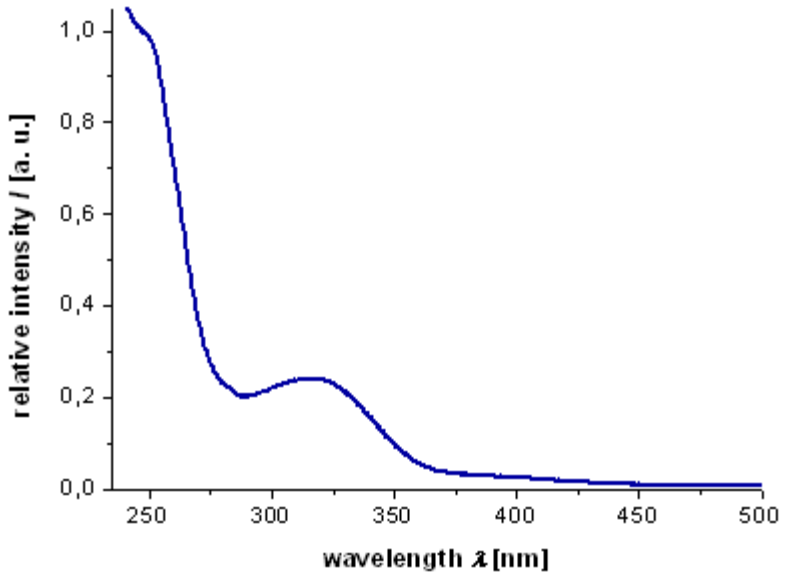
5 UV spectra of *N*-substituted 4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazines **5**

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



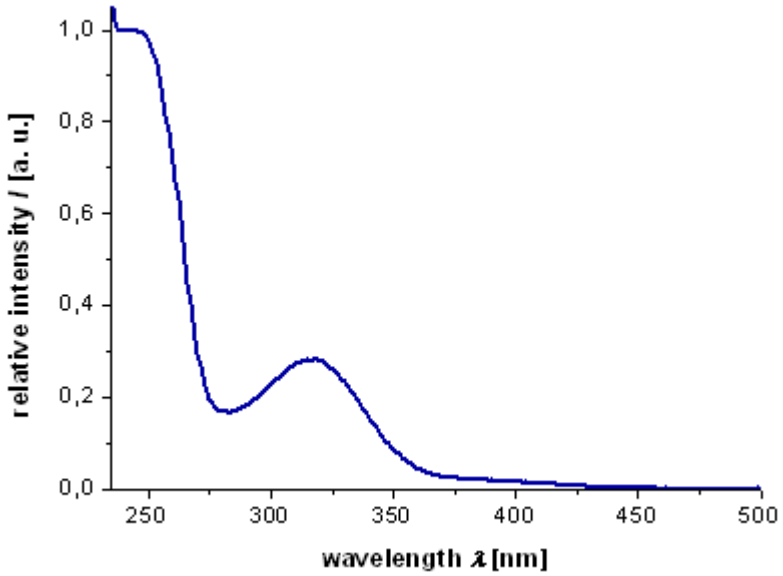
UV spectrum of **5a** in dichloromethane at 298 K.

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



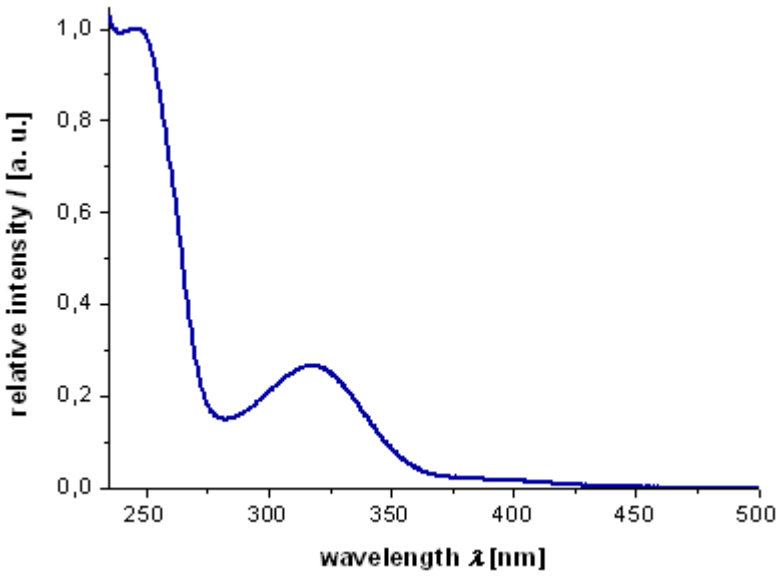
UV spectrum of **5b** in dichloromethane at 298 K.

5.3 4-(4-(*tert*-Butyl)phenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5c)



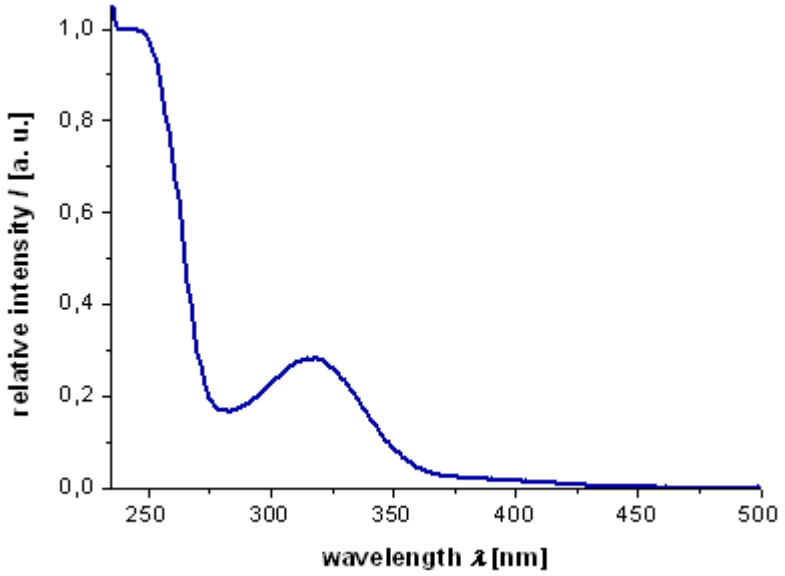
UV spectrum of **5c** in dichloromethane at 298 K.

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



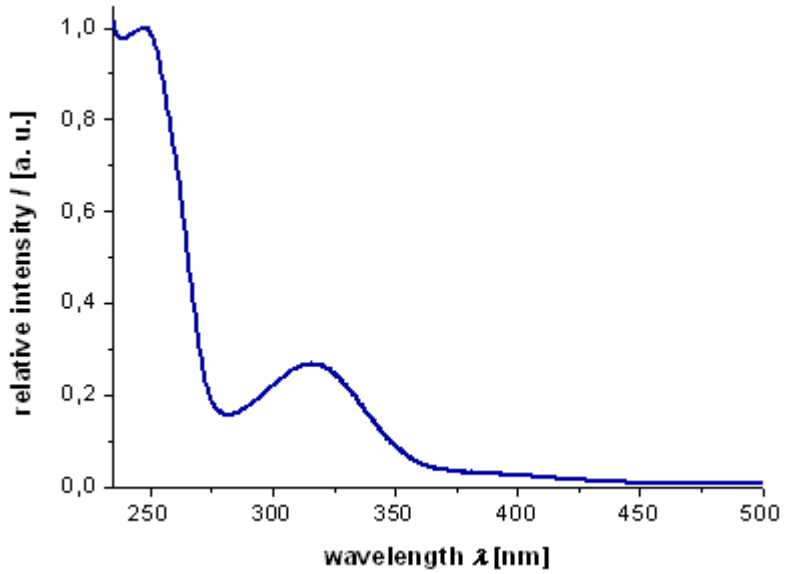
UV spectrum of **5d** in dichloromethane at 298 K.

5.5 4-Phenyl-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5e)



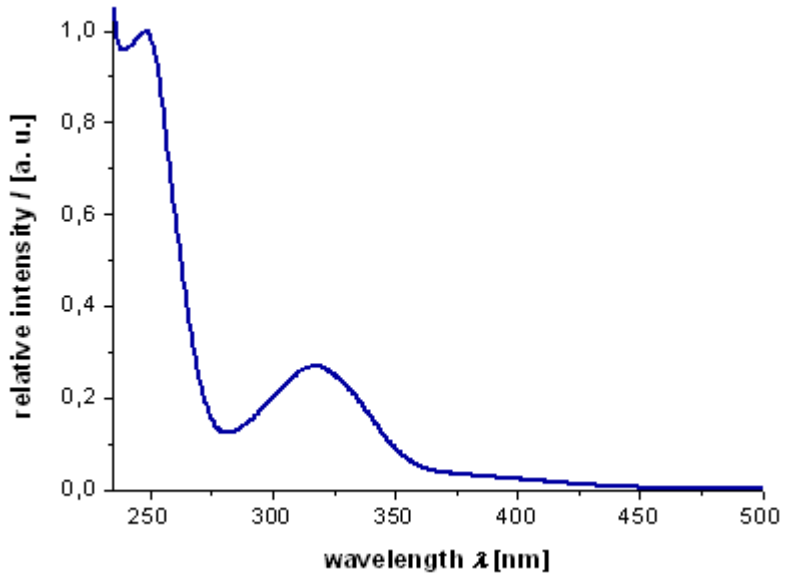
UV spectrum of **5e** in dichloromethane at 298 K.

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



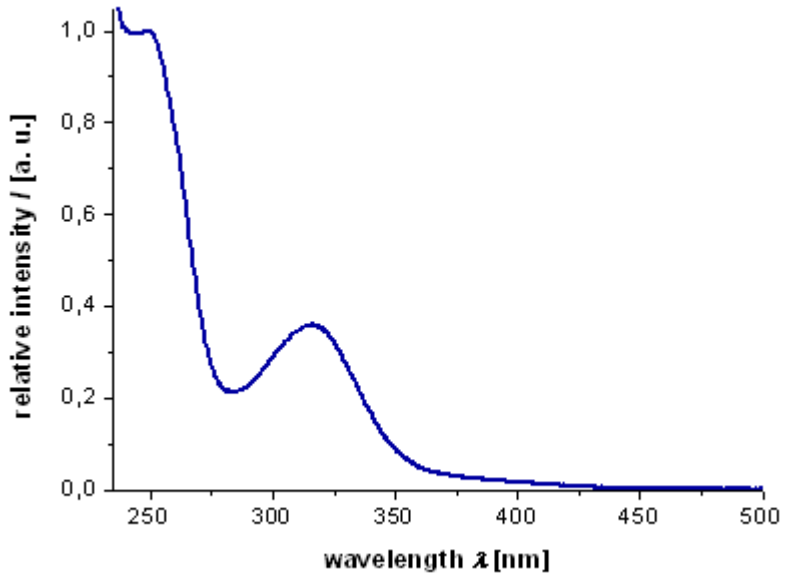
UV spectrum of **5f** in dichloromethane at 298 K.

5.7 4-(2-Chlorophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5g)



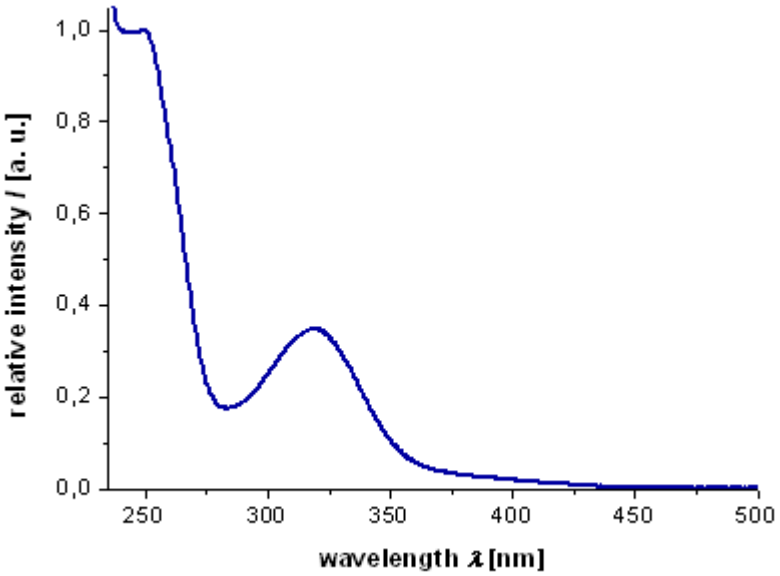
UV spectrum of **5g** in dichloromethane at 298 K.

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



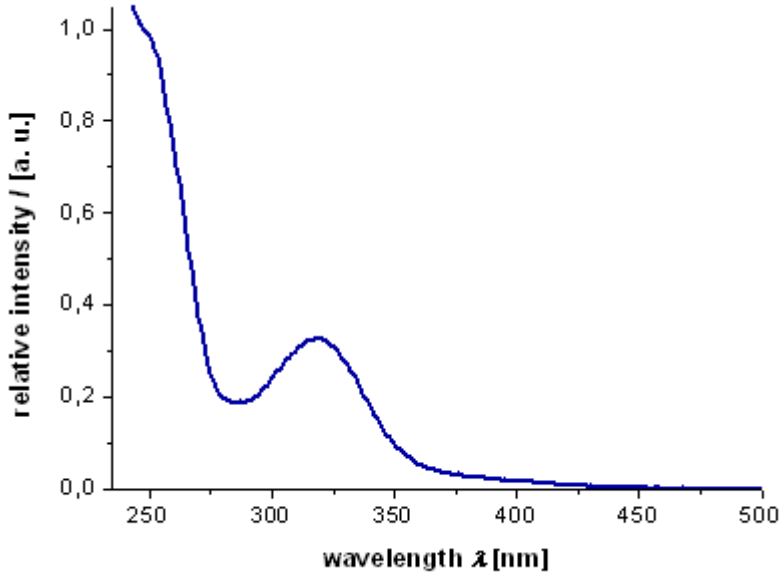
UV spectrum of **5h** in dichloromethane at 298 K.

5.9 4-(4-Chlorophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5i)



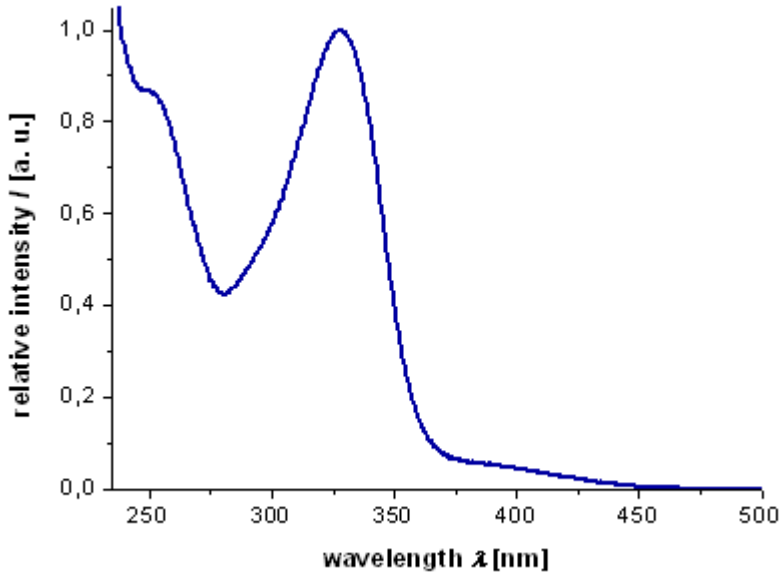
UV spectrum of **5i** in dichloromethane at 298 K.

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



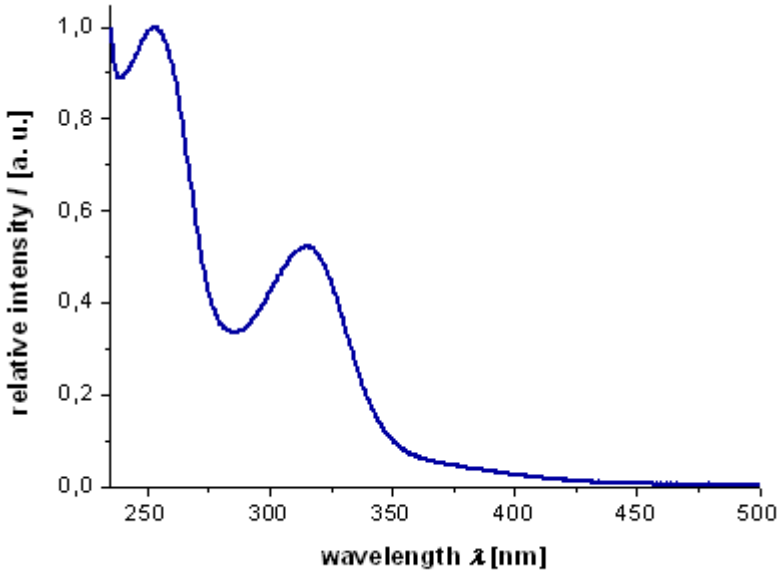
UV spectrum of **5j** in dichloromethane at 298 K.

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



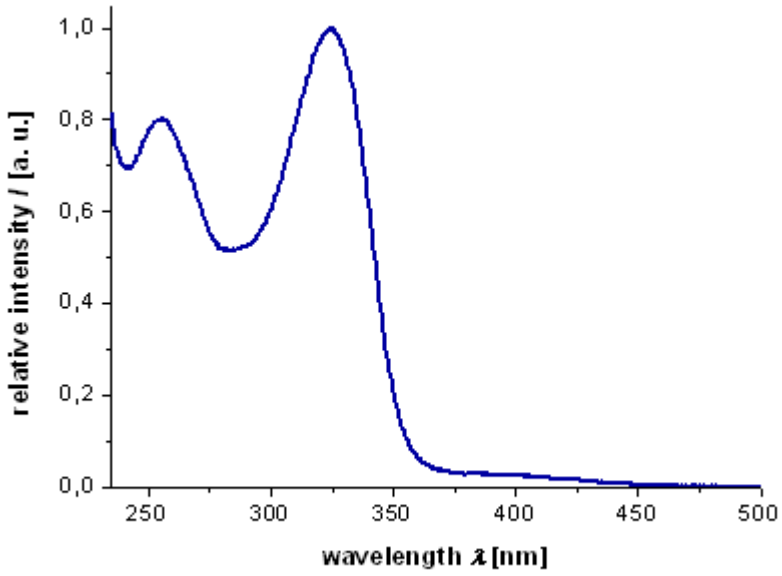
UV spectrum of **5k** in dichloromethane at 298 K.

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



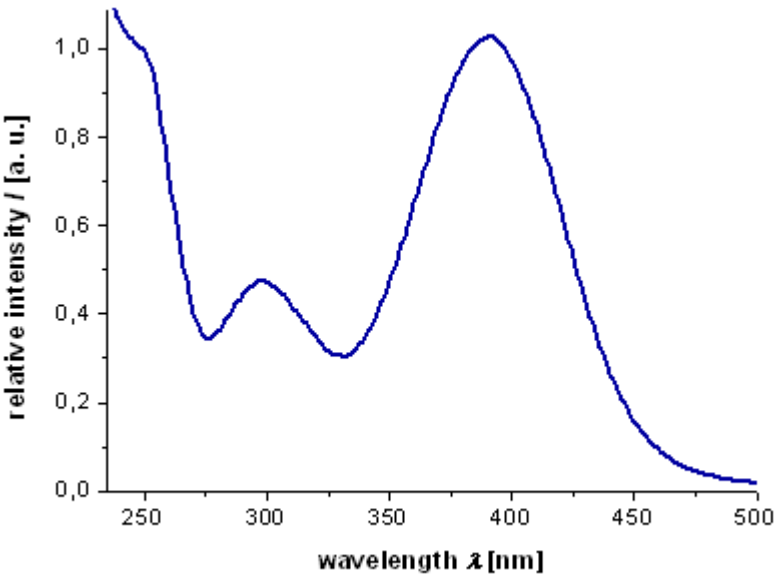
UV spectrum of **5l** in dichloromethane at 298 K.

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



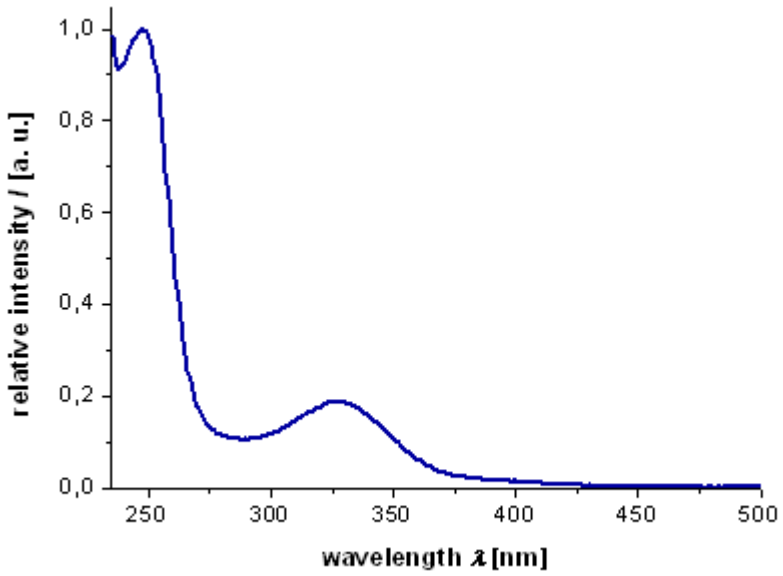
UV spectrum of **5m** in dichloromethane at 298 K.

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



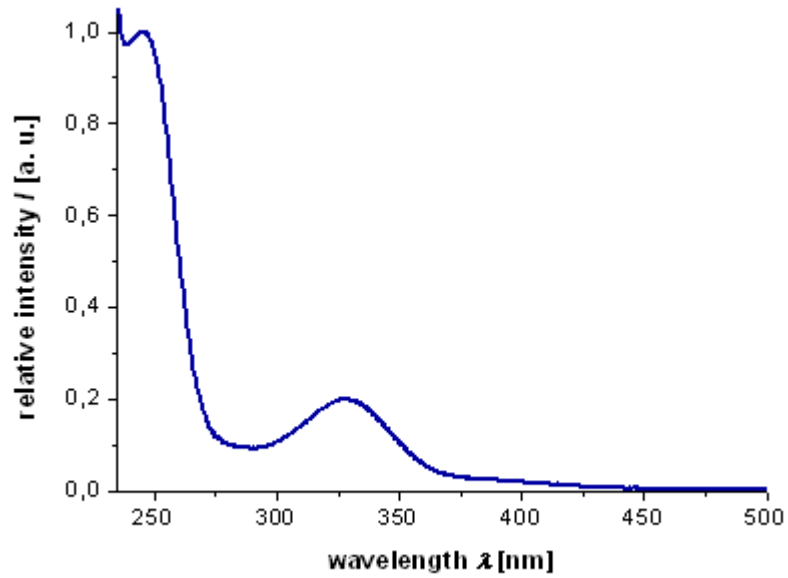
UV spectrum of **5n** in dichloromethane at 298 K.

5.15 4-Butyl-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5o)



UV spectrum of **5o** in dichloromethane at 298 K.

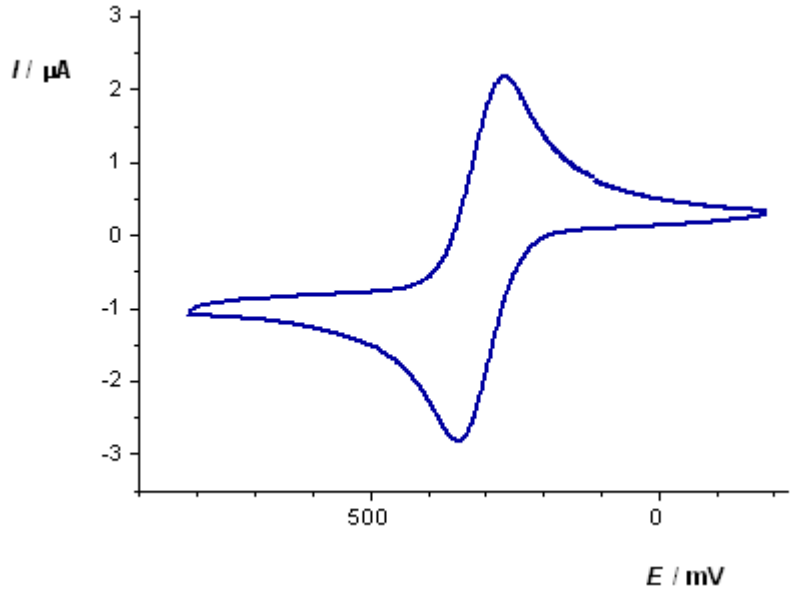
5.16 4-Benzyl-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5p)



UV spectrum of **5p** in dichloromethane at 298 K.

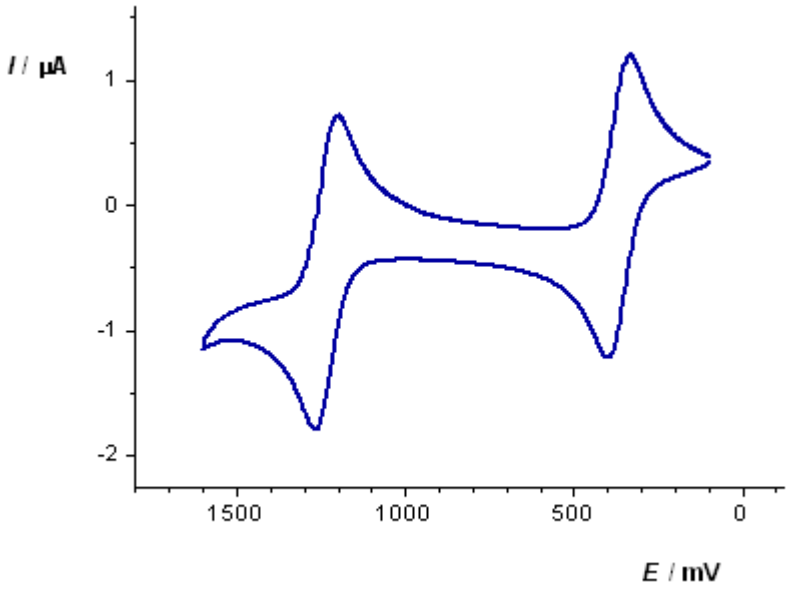
6 Cyclic voltammograms of *N*-substituted 4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazines 5

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



Cyclic voltammogram of **5a** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [^{n}Bu$_4$N$^+$][PF$_6^-$], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

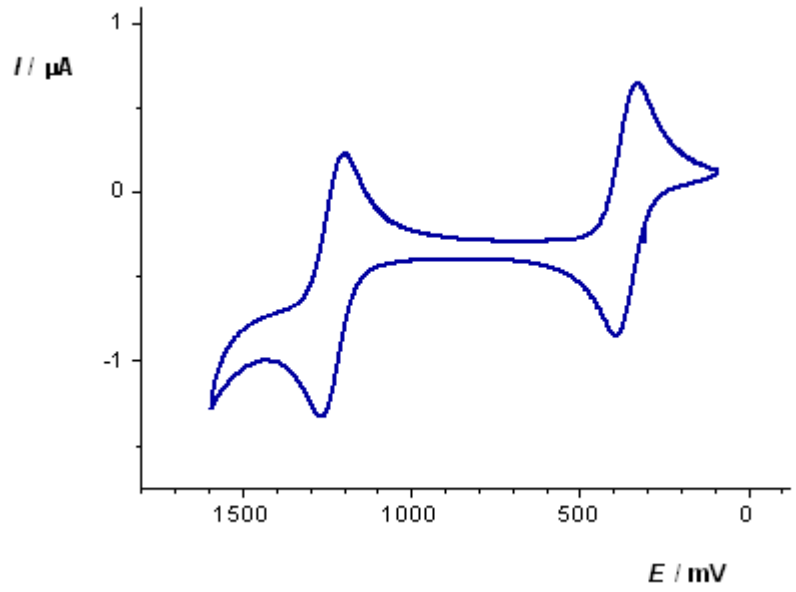
6.2 4-(4-Methoxyphenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5b)



Cyclic voltammogram of **5b** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [^{n}Bu$_4$N$^+$][PF$_6^-$], Pt working electrode, Pt counter electrode, Ag/AgCl

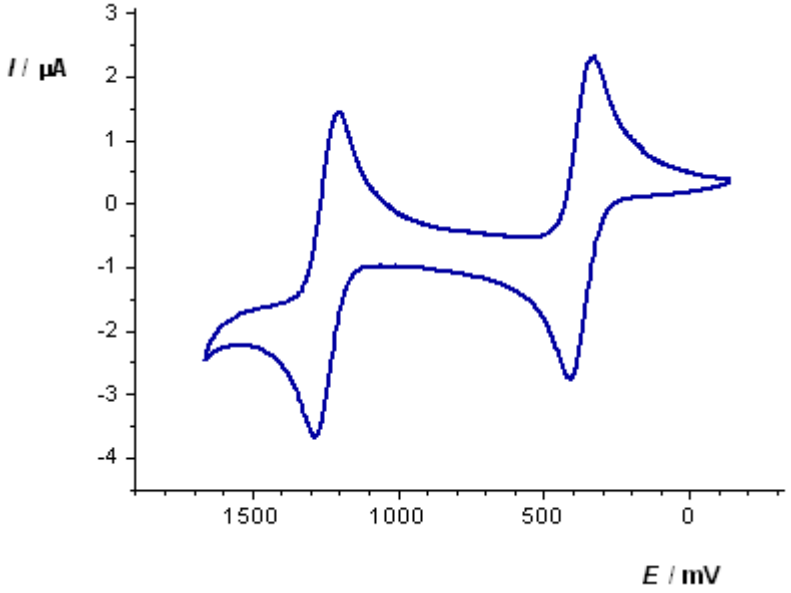
reference electrode.

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



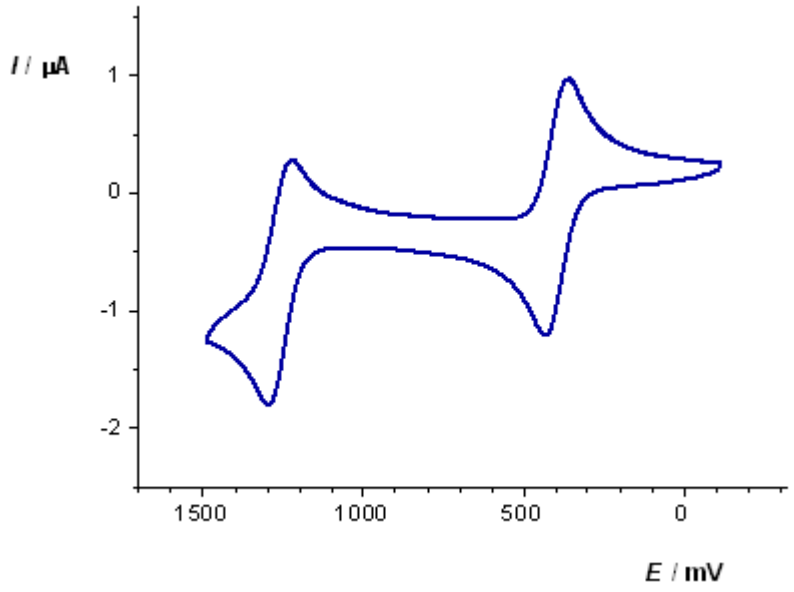
Cyclic voltammogram of **5c** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^{+}$][PF_6^{-}], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

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



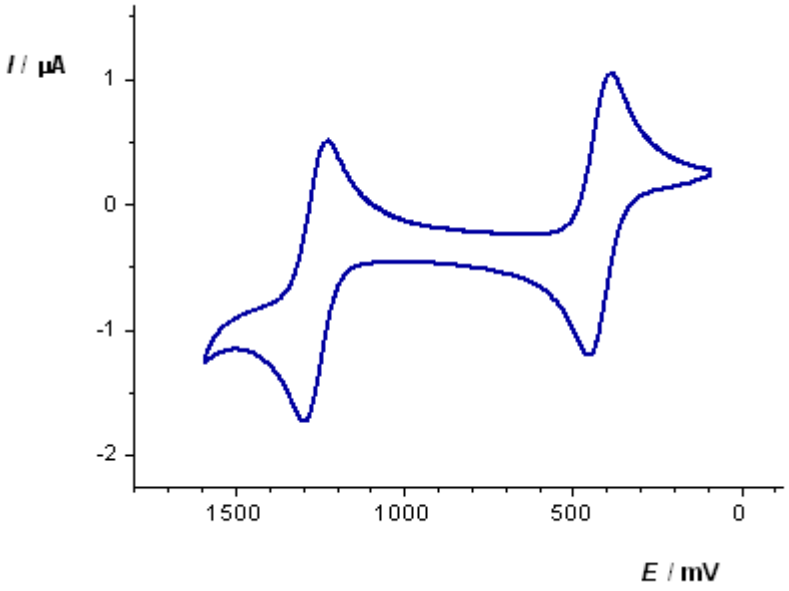
Cyclic voltammogram of **5d** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^{+}$][PF_6^{-}], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

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



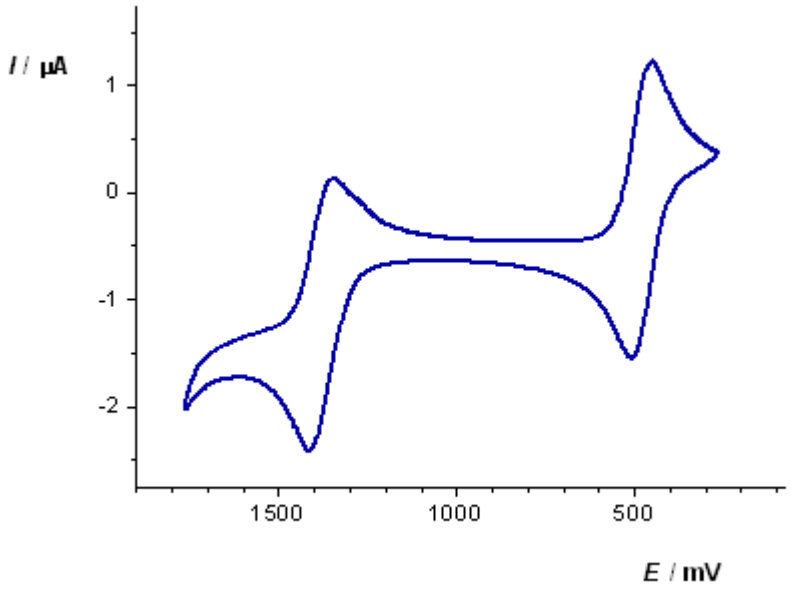
Cyclic voltammogram of **5e** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^+$][PF_6^-], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

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



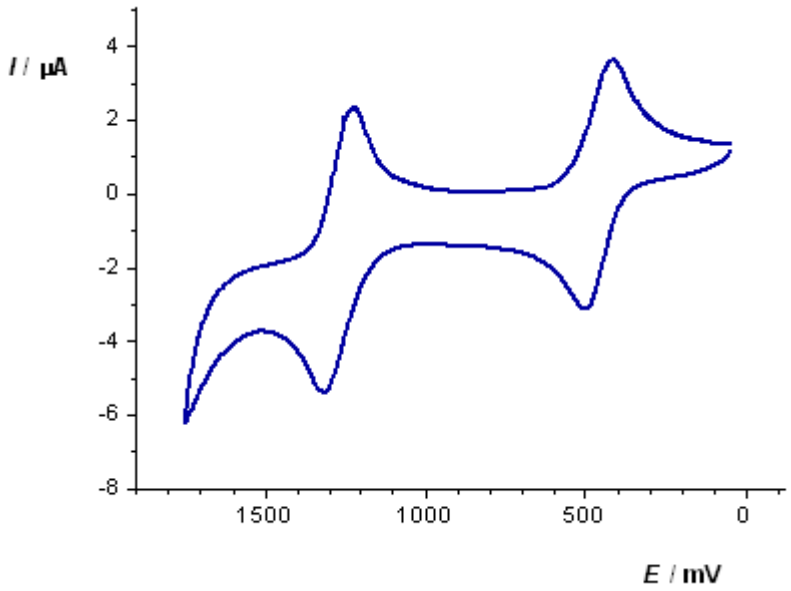
Cyclic voltammogram of **5f** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^+$][PF_6^-], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

6.7 4-(2-Chlorophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5g)



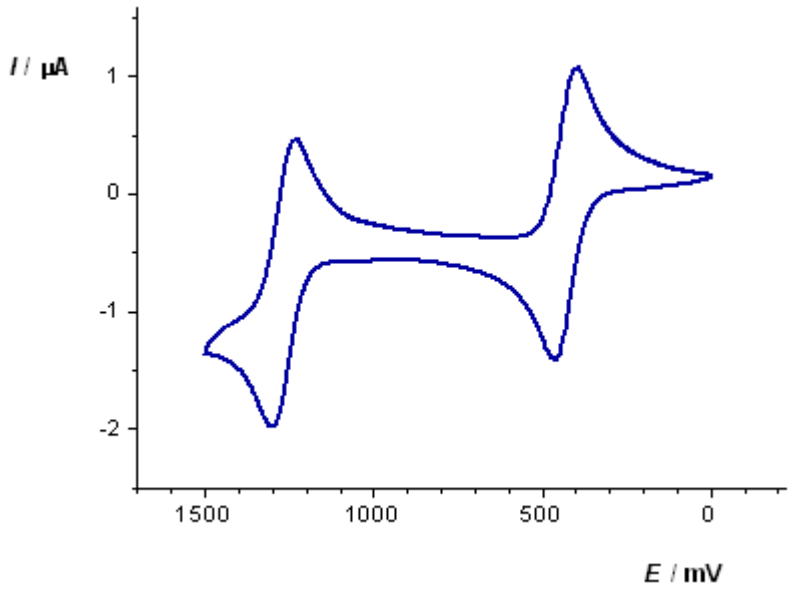
Cyclic voltammogram of **5g** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^{+}$][PF_6^{-}], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

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



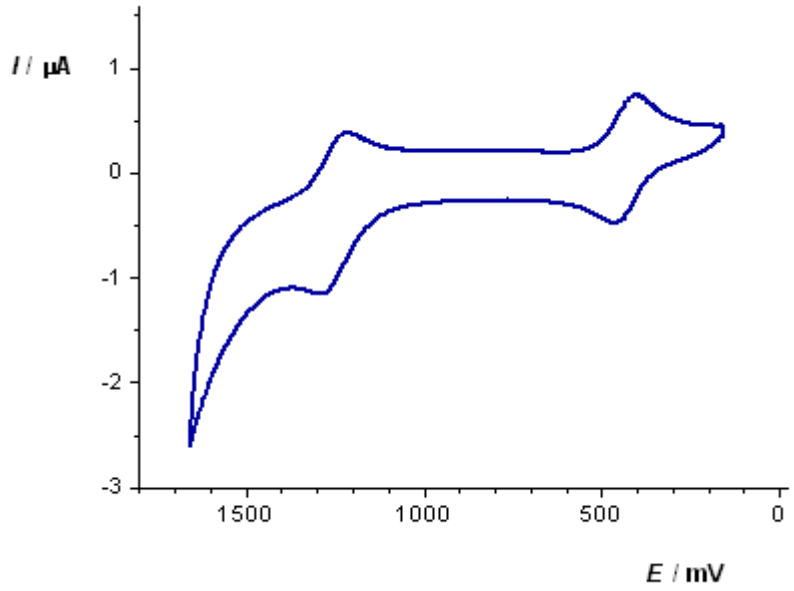
Cyclic voltammogram of **5h** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^{+}$][PF_6^{-}], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

6.9 4-(4-Chlorophenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5i)



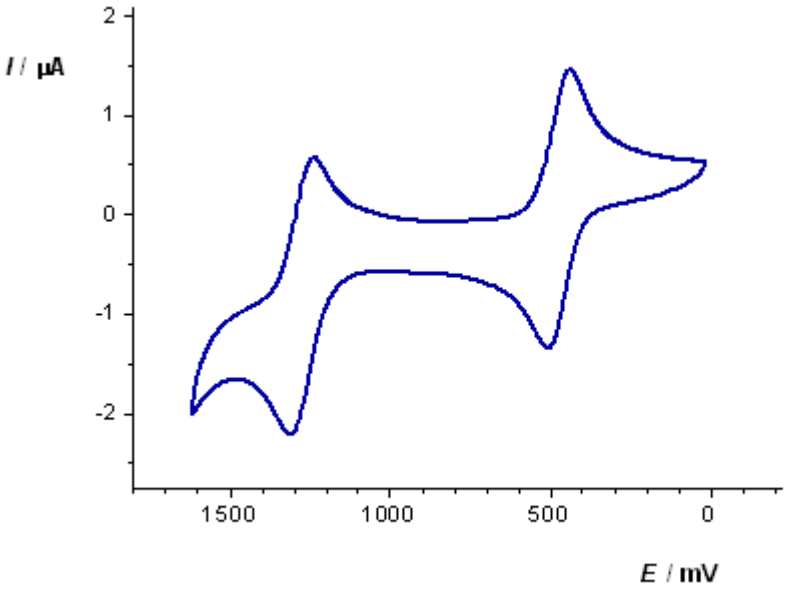
Cyclic voltammogram of **5i** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^{+}$][PF_6^{-}], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

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



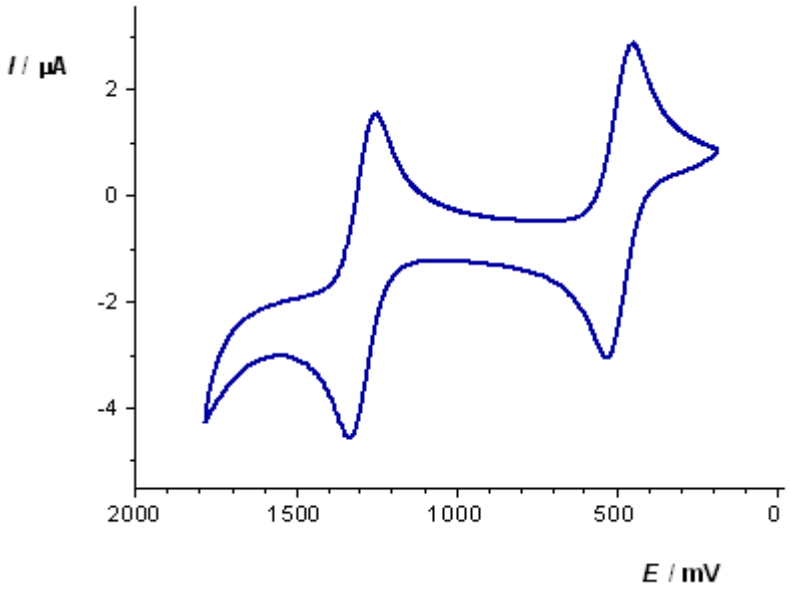
Cyclic voltammogram of **5j** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^{+}$][PF_6^{-}], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

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



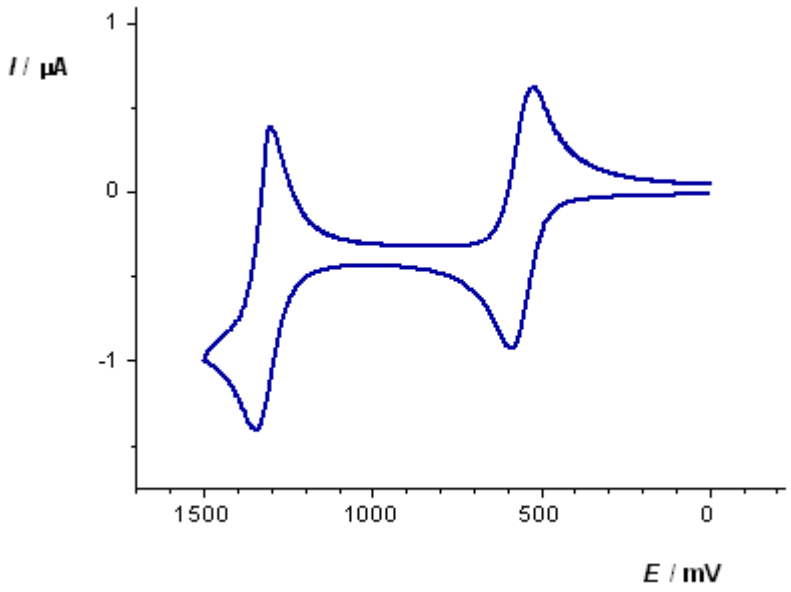
Cyclic voltammogram of **5k** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^{+}$][PF_6^{-}], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

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



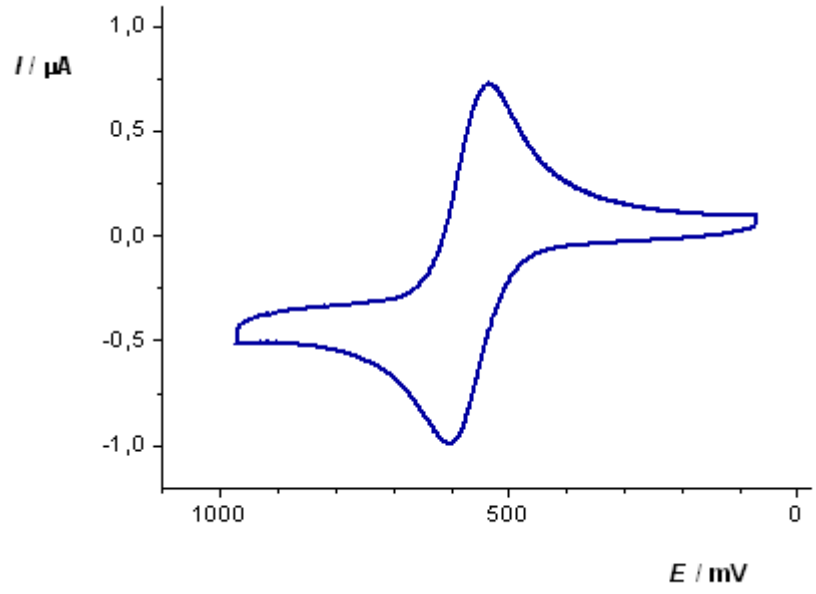
Cyclic voltammogram of **5l** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^{+}$][PF_6^{-}], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

6.13 4-(4*H*-Dithieno[2,3-*b*:3',2'-*e*][1,4]thiazin-4-yl)benzonitrile (5m)



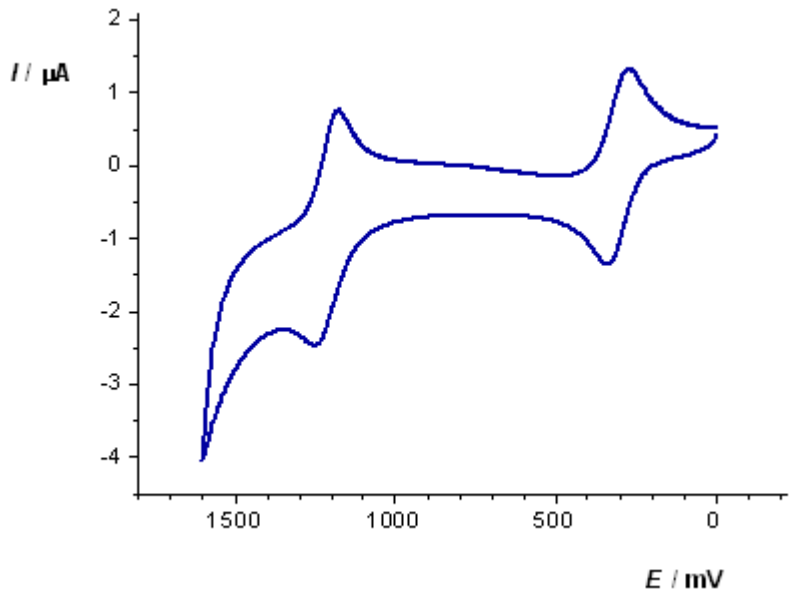
Cyclic voltammogram of **5m** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^+$][PF_6^-], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

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



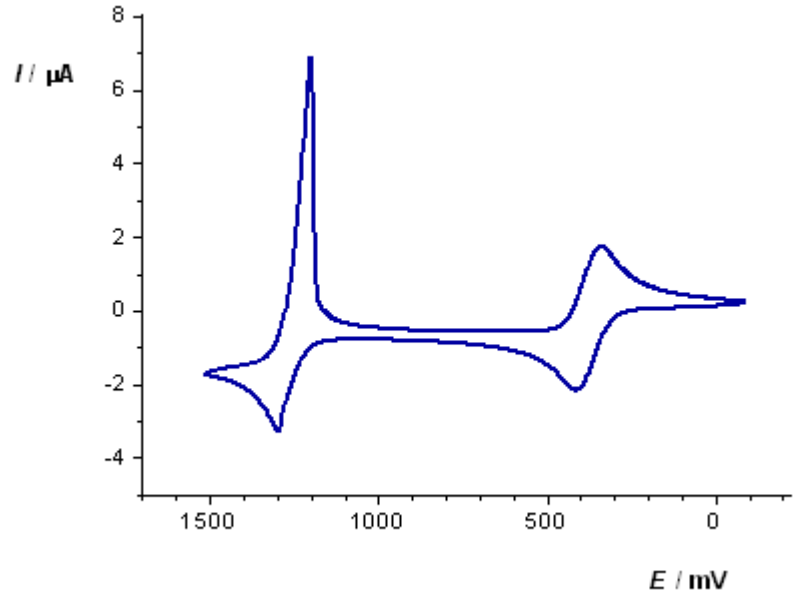
Cyclic voltammogram of **5n** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^+$][PF_6^-], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

6.15 4-Butyl-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (5o)



Cyclic voltammogram of **5o** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^+$][PF_6^-], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

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



Cyclic voltammogram of **5p** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^+$][PF_6^-], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

7 Crystallographic data of 4-(4*H*-Dithieno[2,3-*b*:3',2'-*e*][1,4]thiazin-4-yl)benzonitrile (5m)

7.1 Crystal data and structure refinement for 5m.

Identification code	**5m** (no_68)	
Empirical formula	C15 H8 N2 S3	
Formula weight	312.44	
Temperature	291(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.1083(8) Å	α = 90°.
	b = 8.4579(4) Å	β = 90.114(5)°.
	c = 13.1468(9) Å	γ = 90°.
Volume	1346.37(14) $Å^3$	
Z	4	
Density (calculated)	1.541 Mg/m^3	
Absorption coefficient	0.539 mm^{-1}	
F(000)	640	
Crystal size	0.43 x 0.41 x 0.26 mm^3	
Theta range for data collection	2.28 to 25.00°.	
Index ranges	-14<=h<=14, -10<=k<=8, -15<=l<=15	
Reflections collected	9624	
Independent reflections	2357 [R(int) = 0.0399]	
Completeness to theta = 25.00°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2357 / 0 / 181	
Goodness-of-fit on F^2	0.993	
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.1027	
R indices (all data)	R1 = 0.0392, wR2 = 0.1050	
Largest diff. peak and hole	0.320 and -0.309 $e.Å^{-3}$	

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

S(1)-C(4)	1.757(2)	C(9)-N(1)-C(2)	122.63(16)
S(1)-C(1)	1.759(2)	C(3)-N(1)-C(2)	113.68(16)
S(2)-C(5)	1.713(2)	C(2)-C(1)-S(2)	111.92(15)
S(2)-C(1)	1.720(2)	C(2)-C(1)-S(1)	123.74(16)
S(3)-C(4)	1.723(2)	S(2)-C(1)-S(1)	124.05(12)
S(3)-C(7)	1.715(3)	C(1)-C(2)-C(6)	112.31(18)
N(1)-C(9)	1.396(3)	C(1)-C(2)-N(1)	120.86(18)
N(1)-C(3)	1.429(2)	C(6)-C(2)-N(1)	126.41(18)
N(1)-C(2)	1.431(2)	C(4)-C(3)-C(8)	113.08(19)
N(2)-C(15)	1.137(3)	C(4)-C(3)-N(1)	120.71(18)
C(1)-C(2)	1.358(3)	C(8)-C(3)-N(1)	125.88(19)
C(2)-C(6)	1.426(3)	C(3)-C(4)-S(3)	111.37(16)
C(3)-C(4)	1.361(3)	C(3)-C(4)-S(1)	123.88(15)
C(3)-C(8)	1.419(3)	S(3)-C(4)-S(1)	124.33(12)
C(5)-C(6)	1.354(3)	C(6)-C(5)-S(2)	112.48(16)
C(5)-H(51)	0.9300	C(6)-C(5)-H(51)	123.8
C(6)-H(61)	0.9300	S(2)-C(5)-H(51)	123.8
C(7)-C(8)	1.348(3)	C(5)-C(6)-C(2)	112.10(19)
C(7)-H(71)	0.9300	C(5)-C(6)-H(61)	123.9
C(8)-H(81)	0.9300	C(2)-C(6)-H(61)	123.9
C(9)-C(10)	1.400(3)	C(8)-C(7)-S(3)	113.03(19)
C(9)-C(14)	1.402(3)	C(8)-C(7)-H(71)	123.5
C(10)-C(11)	1.371(3)	S(3)-C(7)-H(71)	123.5
C(10)-H(101)	0.9300	C(7)-C(8)-C(3)	111.6(2)
C(11)-C(12)	1.388(3)	C(7)-C(8)-H(81)	124.2
C(11)-H(111)	0.9300	C(3)-C(8)-H(81)	124.2
C(12)-C(13)	1.392(3)	N(1)-C(9)-C(10)	120.61(18)
C(12)-C(15)	1.443(3)	N(1)-C(9)-C(14)	121.51(18)
C(13)-C(14)	1.377(3)	C(10)-C(9)-C(14)	117.86(19)
C(13)-H(131)	0.9300	C(11)-C(10)-C(9)	120.9(2)
C(14)-H(141)	0.9300	C(11)-C(10)-H(101)	119.5
		C(9)-C(10)-H(101)	119.5
C(4)-S(1)-C(1)	94.63(10)	C(10)-C(11)-C(12)	120.9(2)
C(5)-S(2)-C(1)	91.14(10)	C(10)-C(11)-H(111)	119.5
C(4)-S(3)-C(7)	90.87(11)	C(12)-C(11)-H(111)	119.5
C(9)-N(1)-C(3)	121.71(17)	C(11)-C(12)-C(13)	118.9(2)
C(11)-C(12)-C(15)	120.2(2)		
C(13)-C(12)-C(15)	120.9(2)		

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

Symmetry transformations used to generate equivalent atoms:

7.3 Torsion angles [°] for 5m.

C(5)-S(2)-C(1)-C(2)	-0.50(17)
C(5)-S(2)-C(1)-S(1)	-174.58(15)
C(4)-S(1)-C(1)-C(2)	-31.8(2)
C(4)-S(1)-C(1)-S(2)	141.55(14)
S(2)-C(1)-C(2)-C(6)	-0.7(2)
S(1)-C(1)-C(2)-C(6)	173.41(15)
S(2)-C(1)-C(2)-N(1)	-173.75(15)
S(1)-C(1)-C(2)-N(1)	0.4(3)
C(9)-N(1)-C(2)-C(1)	-124.0(2)
C(3)-N(1)-C(2)-C(1)	40.2(3)
C(9)-N(1)-C(2)-C(6)	64.0(3)
C(3)-N(1)-C(2)-C(6)	-131.8(2)
C(9)-N(1)-C(3)-C(4)	124.1(2)
C(2)-N(1)-C(3)-C(4)	-40.3(3)
C(9)-N(1)-C(3)-C(8)	-63.0(3)
C(2)-N(1)-C(3)-C(8)	132.6(2)
C(8)-C(3)-C(4)-S(3)	-1.1(2)
N(1)-C(3)-C(4)-S(3)	172.68(16)
C(8)-C(3)-C(4)-S(1)	-173.91(16)
N(1)-C(3)-C(4)-S(1)	-0.2(3)
C(7)-S(3)-C(4)-C(3)	1.80(17)
C(7)-S(3)-C(4)-S(1)	174.59(15)
C(1)-S(1)-C(4)-C(3)	31.8(2)
C(1)-S(1)-C(4)-S(3)	-140.14(14)
C(1)-S(2)-C(5)-C(6)	1.64(18)
S(2)-C(5)-C(6)-C(2)	-2.3(2)
C(1)-C(2)-C(6)-C(5)	1.9(3)

N(1)-C(2)-C(6)-C(5)	174.53(19)
C(4)-S(3)-C(7)-C(8)	-2.15(19)
S(3)-C(7)-C(8)-C(3)	1.9(3)
C(4)-C(3)-C(8)-C(7)	-0.5(3)
N(1)-C(3)-C(8)-C(7)	-173.9(2)
C(3)-N(1)-C(9)-C(10)	-1.2(3)
C(2)-N(1)-C(9)-C(10)	161.81(19)
C(3)-N(1)-C(9)-C(14)	-179.8(2)
C(2)-N(1)-C(9)-C(14)	-16.8(3)
N(1)-C(9)-C(10)-C(11)	-177.2(2)
C(14)-C(9)-C(10)-C(11)	1.5(3)
C(9)-C(10)-C(11)-C(12)	-1.6(3)
C(10)-C(11)-C(12)-C(13)	0.4(3)
C(10)-C(11)-C(12)-C(15)	177.6(2)
C(11)-C(12)-C(13)-C(14)	1.0(3)
C(15)-C(12)-C(13)-C(14)	-176.3(2)
C(12)-C(13)-C(14)-C(9)	-1.1(4)
N(1)-C(9)-C(14)-C(13)	178.5(2)
C(10)-C(9)-C(14)-C(13)	-0.1(3)
C(11)-C(12)-C(15)-N(2)	-65(14)
C(13)-C(12)-C(15)-N(2)	112(14)

Symmetry transformations used to generate equivalent atoms.

8 Molecular modeling coordinates and FMO energies of compounds 1, 2a-d and 5m

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

N	-0.018993	-1.123397	-0.717554
S	-0.013533	1.872328	-0.410900
C	1.211221	-0.525467	-1.029858
C	-1.245530	-0.520508	-1.034391
C	1.348031	0.871254	-0.991632
C	-1.377102	0.876762	-0.996374
C	-2.354490	-1.295478	-1.387119
C	2.318381	-1.304942	-1.378184
C	3.543408	-0.708876	-1.664590
C	-3.576145	-0.694601	-1.677758
C	-3.697774	0.691817	-1.655797
C	-2.590456	1.473201	-1.328951
C	3.670301	0.677057	-1.642684
C	2.564882	1.462877	-1.319996
H	-2.257419	-2.377346	-1.427778
H	-4.428253	-1.315015	-1.934812
H	-4.643278	1.166163	-1.894534
H	-2.669593	2.555327	-1.315791
H	2.648335	2.544674	-1.306767
H	4.618492	1.147634	-1.878199
H	4.394059	-1.332655	-1.918311
H	2.217164	-2.386419	-1.418796
H	-0.020952	-2.130114	-0.792184

SCF Done: E (RB + HF-LYP) = -915.775433742 A. U. after 8 cycles

Sum of electronic and zero-point Energies = -915.597983
Sum of electronic and thermal Energies = -915.587622
Sum of electronic and thermal Enthalpies = -915.586678
Sum of electronic and thermal Free Energies = -915.634189

LUMO+1 = -0.500 eV

LUMO = -0.686 eV

HOMO = -5.238 eV

HOMO-1 = -6.335 eV

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

N	0.000394	-1.239861	-0.615532
S	0.000164	1.867425	-0.271129
C	1.201091	-0.563430	-0.907615
C	-1.200432	-0.563618	-0.907522
C	1.304250	0.802668	-0.841785
C	-1.303800	0.802464	-0.841684
C	-2.412231	-1.183054	-1.341313
C	2.412953	-1.182676	-1.341499
C	3.403477	-0.279848	-1.593835
C	-3.402915	-0.280380	-1.593573

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

SCF Done: E (RB + HF-LYP) = -1557.28554537 A. U. after 8 cycles

Sum of electronic and zero-point Energies = -1557.174864
Sum of electronic and thermal Energies = -1557.164923
Sum of electronic and thermal Enthalpies = -1557.163979
Sum of electronic and thermal Free Energies = -1557.211054

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

8.3 XYZ-Coordinates of the S_0 (Gaussian03, B3LYP/6-311G*) of compound 2b:

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

SCF Done: E (RB + HF-LYP) = -1557.28470227 A. U. after 8 cycles

Sum of electronic and zero-point Energies = -1557.174270
Sum of electronic and thermal Energies = -1557.164224
Sum of electronic and thermal Enthalpies = -1557.163280
Sum of electronic and thermal Free Energies = -1557.210553

LUMO+1 = -0.366 eV
LUMO = -0.897 eV
HOMO = -4.997 eV
HOMO-1 = 6.412 eV

8.4 XYZ-Coordinates of the S_0 (Gaussian03, B3LYP/6-311G*) of compound 2c:

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

SCF Done: E (RB+HF-LYP) = -1557.28335003 A. U. after 8 cycles

Sum of electronic and zero-point Energies = -1557.173375
Sum of electronic and thermal Energies = -1557.163067
Sum of electronic and thermal Enthalpies = -1557.162123
Sum of electronic and thermal Free Energies = -1557.209936

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

8.5 XYZ-Coordinates of the S_0 (Gaussian03, B3LYP/6-311G*) of compound 2d:

N	0.009166	-1.203159	-0.602416
S	0.002596	1.934971	-0.560135
C	1.225412	-0.582911	-0.904876
C	-1.210359	-0.588047	-0.902150
C	1.348347	0.847588	-0.969133
C	-1.339469	0.841921	-0.966124
C	-2.396531	-1.223959	-1.146687
C	2.413704	-1.213816	-1.152071
S	3.698513	-0.080929	-1.445420
S	-3.686762	-0.096501	-1.437144
C	2.613999	1.257604	-1.266519
C	-2.607502	1.246594	-1.260676
H	2.611027	-2.275399	-1.178420
H	-2.589434	-2.286364	-1.172599
H	0.011238	-2.210399	-0.648469
H	-2.972061	2.256899	-1.368361
H	2.974053	2.269436	-1.375015

SCF Done: E (RB + HF-LYP) = -1557.29432111 A. U. after 8 cycles

Sum of electronic and zero-point Energies = -1557.183683
Sum of electronic and thermal Energies = -1557.173791

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

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

8.6 XYZ-Coordinates of the S_0 (Gaussian03, B3LYP/6-311G*) of compound 5m:

N	0.049786	-1.147300	-0.230799
S	-0.186486	1.913197	-0.282449
C	1.219775	-0.444085	-0.643388
C	-1.155208	-0.629954	-0.791107
C	1.226679	0.926606	-0.698480
C	-1.367543	0.723573	-0.859930
C	-2.187688	-1.382384	-1.433696
C	2.427434	-1.021255	-1.146920
C	3.328157	-0.078069	-1.540802
C	-3.168226	-0.586392	-1.944578
S	2.706735	1.536937	-1.377168
S	-2.829402	1.103762	-1.721308
H	2.605989	-2.087010	-1.205388
H	-2.190527	-2.462328	-1.503355
H	4.327521	-0.225837	-1.922429
H	-4.077953	-0.883545	-2.444873
C	0.045947	-1.990955	0.891461
C	1.244655	-2.331591	1.547770
C	-1.157190	-2.518745	1.398850
C	-1.155029	-3.375153	2.486552
C	1.241125	-3.188409	2.635120
C	0.043775	-3.734732	3.118735
H	-2.103507	-2.241867	0.954896
H	2.184144	-1.907732	1.220704
H	-2.095055	-3.765874	2.859438
H	2.177218	-3.432991	3.124277
C	0.043705	-4.622601	4.235340
N	0.043757	-5.343342	5.139484

SCF Done: E (RB + HF-LYP) = -1880.6444500 A. U. after 18 cycles

Sum of electronic and zero-point Energies = -1880.454838
Sum of electronic and thermal Energies = -1880.438577
Sum of electronic and thermal Enthalpies = -1880.437633
Sum of electronic and thermal Free Energies = -1880.500032

LUMO+2 = -1.049 eV
LUMO+1 = -1.233 eV
LUMO = -1.478 eV
HOMO = -5.846 eV
HOMO-1 = -6.622 eV
HOMO-2 = -7.108 eV

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

Excitation energies and oscillator strengths:

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

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

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

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

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

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

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

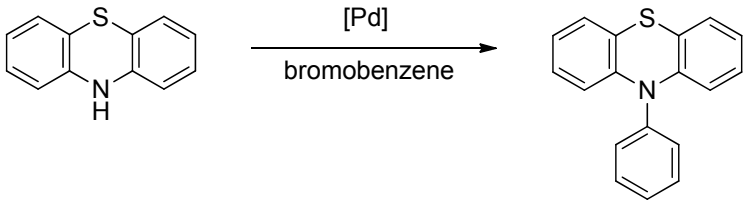
Excited State 8: Singlet-A, 4.9018 eV, 252.94 nm, f=0.0021
79 -> 86 -0.11143
80 -> 86 0.67337

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

Excited State 10: Singlet-A, 5.0073 eV, 247.61 nm, f=0.0200
78 -> 81 0.63838
79 -> 84 -0.14361
80 -> 88 -0.11932

9 Preparation and characterization of 10-Phenyl-10H-phenothiazine (7)

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



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

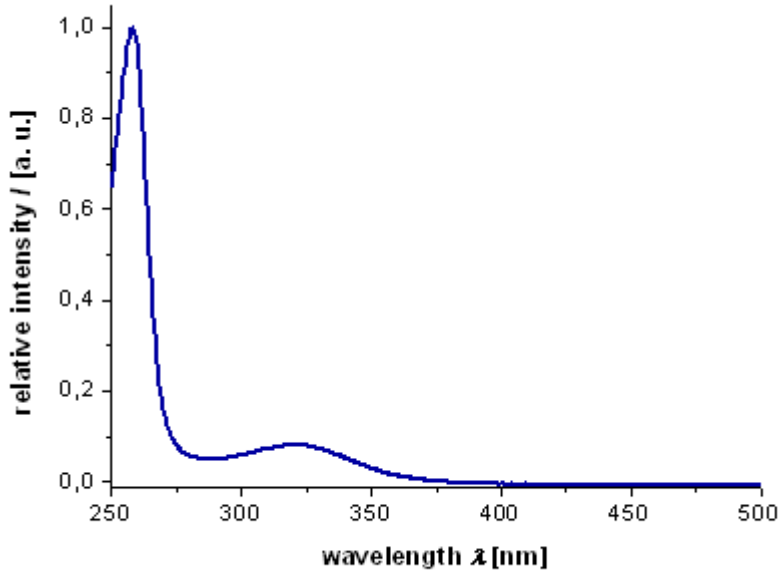
^{1}H NMR (500 MHz, acetone-d_6): δ 6.23 (dd, J = 8.2 Hz, 1.2 Hz, 2 H), 6.85 (dt, J = 7.4 Hz, 1.3 Hz, 2 H), 6.88-6.93 (m, 2 H), 7.04 (dd, J = 7.5 Hz, 1.6 Hz, 2 H), 7.40-7.45 (m, 2 H), 7.55 (t, J = 7.5 Hz, 1 H), 7.68 (t, J = 7.8 Hz, 2 H). ^{13}C NMR (125 MHz, acetone-d_6): δ 117.2 (CH), 121.1 (C_{quat}), 123.6 (CH), 127.5 (CH), 128.0 (CH), 129.3 (CH), 131.6 (CH), 131.9 (CH), 142.0 (C_{quat}), 145.2 (C_{quat}). Anal. calcd. for $C_{18}H_{13}NS$ (275.4): C 78.51, H 4.76, N 5.09. Found: C 78.59, H 4.87, N: 5.00.

Data reported in literature[5]:

^{1}H NMR (500 MHz, DMSO-d_6): δ 6.17 (dd, J = 8.0 Hz, 0.94 Hz, 2 H), 6.86 (ddd, J = 8.00 Hz, 7.07 Hz, 0.94 Hz, 2 H), 6.93 (ddd, J = 8.1 Hz, 8.0 Hz, 1.42 Hz, 2 H), 7.07 (dd, J = 7.07 Hz, 1.42 Hz, 2 H), 7.41 (d, J = 7.54 Hz, 2 H), 7.54 (broad t, J = 7.53 Hz, 2 H), 7.67 (dd, J = 7.54 Hz, 7.53 Hz, 2H).

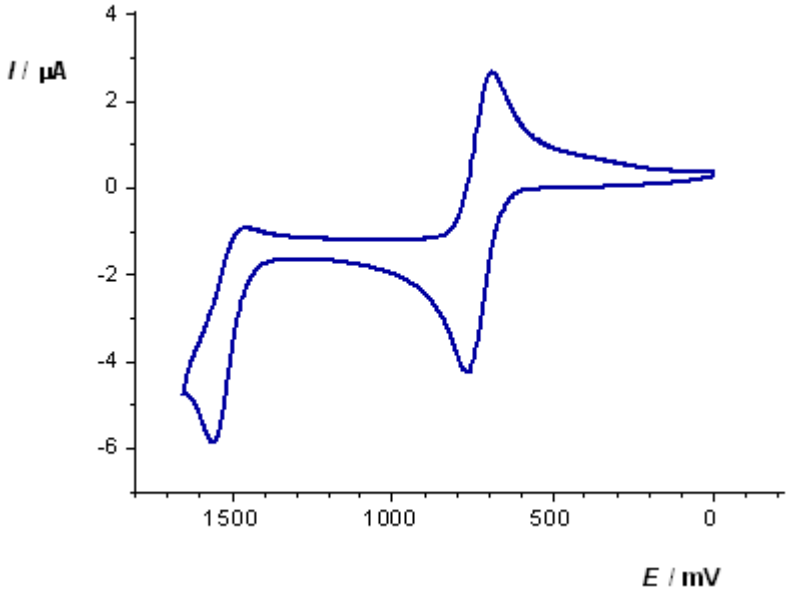
[5] T. Dahl, C. W. Tornøe, B. Bang-Andersen, P. Nielsen, M. Jørgensen, *Angew. Chem. Int. Ed.*, 2008, **47**, 1726.

9.2 UV spectrum of 10-Phenyl-10*H*-phenothiazine (7)



UV spectrum of **7** in dichloromethane at 298 K.

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



Cyclic voltammogram of **7** recorded in dichloromethane, T = 298 K, v = 100 mV/s, 0.1 M electrolyte [$^{n}Bu_4N^+$][PF_6^-], Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.