SUPPORTING INFORMATION OF:

A push-pull bithienyl chromophore with an unusual transverse path of conjugation

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General Experimental.

^{1}H and ^{13}C NMR spectra were obtained using on Varian VXR-400 MHz and Bruker-400 MHz FT spectrometer in $CDCl_3$ with TMS as an internal standard. Chemical shifts are reported in ppm. GCMS analyses were performed with an Finnigan SSQ 7000 Mass Spectrometer connected to a Varian 3400 GC, equipped with a DB-5MS column (30 m, 0.2 mm of internal diameter), electron impact (EI) at 70 eV and He was used as the carrier gas. Merck $60F_{254}$ plates were used for analytical (TLC) chromatography. Column chromatography was performed on silica gel (63–200 mesh, Merck). All new compounds gave satisfactory 400 MHz ^{1}H- and 100 MHz ^{13}C-NMR spectral data. Diffraction intensities of single crystal were collected at 293° K on a Enraf Nonius CAD4 diffractometer (Mo Kα, 0.71073 Å). Melting points are uncorrected. All starting materials are commercially available from Sigma-Aldrich or Acros Organics. All operations were carried out under atmosphere of dry argon if otherwise stated.

3,3'-[Methylenebis(thio)]dithiophene (2). To a solution of 3-bromothiophene (81.5 g, 46.8 mL, 0.50 mol) in ether (800 mL) *t*-butyllithium (687.0 mL, 1.03 mol, 1.5 M in *n*-pentanes) was added dropwise at -80°C. The resulting mixture was stirred at this temperature for 15 min. After warming to -40°C, sulfur powder (15.8 g, 0.493 mol) was added in one portion keeping the temperature below –30°C. The cooling bath was removed and the mixture was allowed to warm to r.t. for 1.5 h. Solvent was removed in vacuo. The residue was dissolved in DMF (500 mL) and dibromomethane (42.6 g, 17.2 mL, 0.245 mol) was added dropwise. After heating for 4 h at 60°C the mixture was passed through a short column (silica gel; DMF). The solvent was removed by rotary evaporation, and the residue was dissolved in CH_2Cl_2 (500 mL), washed with water (200 mL), dried over K_2CO_3 and finally evaporated. Distillation in portion (not more than 0.05 mol, b.p. 137º/10^{-1}Torr) afforded 50.9 g of **2** (yield 85%) as an yellow oil, R_f (Hexane/AcOEt = 4:1) = 0.63. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.31 (m, 4H), 7.04 (t, *J* = 3.2 Hz, 2H), 4.15 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.33, 130.12, 126.39, 126.20, 43.18. MS (EI, 70 eV); *m/z* (%): 244 (29) [M^+], 129 (100) [M^+-$C_4H_3S_2$]. Anal. Calcd for $C_9H_8S_4$: C, 44.22; H, 3.30. Found: C, 43.96; H, 3.35.

2,2'-[Methylenebis(thio)]bis(3-bromothiophene) (3a). To a solution of diisopropylamine (60.7 g, 84.1 mL, 0.600 mol) in ether (800 mL) n-butyllithium (206.0 mL, 0.515 mol, 2.5 M in *n*-hexanes) was

added dropwise at -30°C. The mixture was allowed to warm to 0°C for 15 min and recooled to –30°C. To the above solution, 3-bromothiophene (81.5 g, 46.8 mL, 0.500 mol) was added in one portion. The mixture was allowed to warm to 0°C for 1.5 h and was stirred at this temperature for 3 h. The solution was recooled to –40°C and sulfur powder (15.8 g, 0.493 mol) was added in one portion keeping the temperature below –30°C. After this addition, the cooling bath was removed and the mixture was allowed to warm to r.t. for 1.5 h. The solvent was removed in vacuo and the residue was dissolved in DMF (500 mL). At this solution dibromomethane (85.2 g, 34.4 mL, 0.490 mol) was added dropwise. After heating for 3 h at 100°C the mixture was allowed to cool to 80°C and poured into water (1000 mL). The precipitated product was filtered off, washed with water (2x200 mL), dissolved in toluene (500 mL), dried over K_2CO_3 and passed through a short column (silica gel; toluene). The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography (silica gel; hot (60°C) *n*-hexane/toluene, 2:1). The crude product (84 g) was dissolved in mixture ether/hexane (1:2, 600 mL); the resulting solution was concentrated to 200 mL volume. White crystals precipitated and were filtered off after cooling to 0°C, washed with hexane and dried to give 63.5 g (yield 65%) of **3a**, R_f (Hexane/AcOEt = 4:1) = 0.43. Mp 74.5-76°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 5.6 Hz, 2H), 7.04 (d, *J* = 5.6 Hz, 2H), 4.15 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.94, 130.15, 128.21, 119.48, 45.18. MS (EI, 70 eV); *m/z* (%): 402 (7) [M^+], 323 (16) [M^+-Br], 242 (3) [M^+-Br-Br], 209, 207 (95, 100) [M^+-$C_4H_2BrS_2$], 128 (42) [M^+-$C_4H_2BrS_2$-Br]. Anal. Calcd for $C_9H_6Br_2S_4$: C, 26.88; H, 1.50. Found: C, 26.59; H, 1.54.

3,3'-[Methylenebis(thio)]bis(2-bromothiophene) (3b). To a stirred solution of **2** (74.0 g, 0.303 mol) in $CHCl_3$ (1000 mL) was added NBS (107.8 g, 0.606 mol) over 30 min. The mixture was stirred for 24 h at r.t., then H_2O (1000 mL) was added and the product was extracted with CH_2Cl_2 (100 mL). The organic layer was washed with water (3*150 mL) and aq Na_2CO_3 then dried over K_2CO_3. The solvent was removed by rotary evaporation, and the crude product was purified by flash chromatography (silica gel; *n*-hexane/AcOEt, 50:1) to afford 109.6 g of **3** (yield 90%) as a yellow oil (unstable at r.t. and should be used immediately in next step but could be stored at -30°C for about month). After standing for about month at -30°C, the resulting oil solidified to give yellow crystals, R_f (Hexane/AcOEt = 4:1) = 0.43. Mp 44-46°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 5.9 Hz, 2H), 7.00 (d, *J* = 5.9 Hz, 2H), 4.20 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.00, 126.04, 116.58, 107.59, 41.24. MS (EI, 70 eV); *m/z* (%):

402 (1) [M^+], 323 (42) [M^+-Br], 242 (53) [M^+-Br-Br], 209, 207 (100, 95) [M^+-$C_4H_2BrS_2$], 128 (68) [M^+-$C_4H_2BrS_2$-Br]. Anal. Calcd for $C_9H_6Br_2S_4$: C, 26.88; H, 1.50. Found: C, 26.85; H, 1.55.

10*H*-Bisthieno[2,3-*d*:3',2'-*g*][1,3]dithiocin-10-one (4a). Compound **3a** (63.3 g, 0.157 mol) was dissolved in dry ether (3400 mL) and cooled to -78°C; then *t*-BuLi (420 mL, 0.630 mol, 1.5 M in *n*-pentane) was added dropwise (see Figure S1). The resulting mixture was stirred for 1 h during which time, the temperature was allowed to rise to -40°C. The yellow solution thus obtained was cooled to -50°C and solution of ethyl *N*,*N*'-dimethylcarbamate (64.5 g, 0.551 mol) in dry ether (100 mL) was added dropwise over 1 to 2 min. The mixture was allowed to warm to -40°C, then stirred for 4 h at temperatures between -40 to -30°C. After standing overnight at r.t., the solvent was evaporated in vacuo and the residue was dissolved in hot (60°C) $CHCl_3$ (1000 mL), washed with water (200 mL), dried over K_2CO_3 and passed through a short column (silica gel; $CHCl_3$). The solvent was removed by rotary evaporation, and the crude product (34 g) was purified by column chromatography (silica gel; eluted with a 2-10% AcOEt in *n*-hexane gradient) to afford 27.65 g of **4a** (yield 65%) as an orange oil. After standing for a long time at r.t., the resulting oil solidified to give orange crystals, R_f (Hexane/AcOEt = 4:1) = 0.40. Mp 63.0-64.0°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 5.6 Hz, 2H), 7.43 (d, *J* = 5.6 Hz, 2H), 3.83 (s, 2H). ^{13}C NMR ($CDCl_3$): δ = 183.01, 148.63, 132.41, 130.77, 130.03, 48.93. MS (EI, 70 eV); *m/z* (%): 270 (100) [M^+], 224 (68) [M^+-CH_2S], 142 (71) [M^+-$C_5H_4S_2$]. Anal. Calcd for $C_{10}H_6OS_4$: C, 44.42; H, 2.24. Found: C, 44.49; H, 2.42.

10*H*-Bisthieno[3,2-*d*:2',3'-*g*][1,3]dithiocin-10-one (4b). Compound **3b** (31.7 g, 0.079 mol) was dissolved in dry ether (1700 mL) and cooled to -78°C; then *t*-BuLi (210 mL, 0.315 mol, 1.5 M in *n*-pentane) was added dropwise. The resulting mixture was stirred for 1 h during which time, the temperature was allowed to rise to -40°C. The yellow solution thus obtained was cooled to -50°C and solution of *N*,*N*'-dimethylcarbamyl chloride (4.3 g, 0.040 mol) in dry ether (50 mL) was added dropwise over 1 to 2 min. The mixture was allowed to warm to -40°C, then stirred for 4 h at temperatures between -40 to -30°C. After standing overnight at r.t., the solvent was evaporated in vacuo and the residue was dissolved in hot (60°C) $CHCl_3$ (1000 mL), washed with water (200 mL), dried over K_2CO_3 and passed through a short column (silica gel; $CHCl_3$). The solvent was removed by rotary evaporation, and the crude product (20 g) was purified by column chromatography (silica gel; eluted with a 2-10% AcOEt in

n-hexane gradient) afforded 13.8 g of **4b** (yield 65%) as an yellow crystals, R_f (Hexane/AcOEt = 4:1) = 0.40. Mp 131.5º-133.0ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 5.0 Hz, 2H), 7.13 (d, *J* = 5.0 Hz, 2H), 3.91 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.19, 149.94, 135.37, 132.66, 130.00, 46.81. MS (EI, 70 eV); *m/z* (%): 270 (84) [M^+], 224 (100) [M^+-CH_2S], 142 (34) [M^+-$C_5H_4S_2$]. Anal. Calcd for $C_{10}H_6OS_4$: C, 44.42; H, 2.24. Found: C, 44.52; H, 2.36.

10*H*-Bisthieno[2,3-*d*:3',2'-*g*][1,3]dithiocin-10-ylidenemalononitrile (1a). To a solution of **4a** (0.365 g, 1.35 mmol) and malononitrile (0.100 g, 1.5 mmol) in dry CH_2Cl_2 (80 mL) at 0 °C were successively added dry pyridine (1.022 g, 1.0 mL, 13.0 mmol) and $TiCl_4$ (0.420 g, 0.725 mL, 2.2 mmol). The resulting mixture was refluxed for 24 h. The reaction mixture was cooled to r.t. and poured in water. The organic layer was extracted three times with CH_2Cl_2, washed with water, and dried over K_2CO_3. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (silica gel; eluted with a 5-10% AcOEt in *n*-hexane gradient) afforded 0.387 g of **1a** (yield 90%) as yellow crystals, R_f (Hexane/AcOEt = 4:1) = 0.30. Mp 196.5º-198.0ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 5.7 Hz, 2H), 7.62 (d, *J* = 5.7 Hz, 2H), 3.79 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.76, 136.67, 136.25, 134.93, 131.67, 113.56, 83.94, 46.81. MS (EI, 70 eV); *m/z* (%): 318 (55) [M^+], 272 (100) [M^+-CH_2S]. Anal. Calcd for $C_{13}H_6N_2S_4$: C, 49.03; H, 1.90. Found: C, 48.95; H, 1.85.

10*H*-Bisthieno[3,2-*d*:2',3'-*d*][1,3]dithiocin-10-ylidenemalononitrile (1b). To a solution of **4b** (0.365 g, 1.35 mmol) and malononitrile (0.100 g, 1.5 mmol) in dry CH_2Cl_2 (80 mL) at 0 °C were successively added dry pyridine (1.022 g, 1.0 mL, 13.0 mmol) and $TiCl_4$ (0.420 g, 0.725 mL, 2.2 mmol). The resulting mixture was refluxed for 24 h. The reaction mixture was cooled to r.t. and poured in water. The organic layer was extracted three times with CH_2Cl_2, washed with water, and dried over K_2CO_3. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (silica gel; eluted with a 5-10% AcOEt in *n*-hexane gradient) afforded 0.258 g of **1b** (yield 60%) as orange crystals and recovered 0.128 g of **4b** (yield 35%), R_f (Hexane/AcOEt = 4:1) = 0.30. Mp 162.5º-165.0ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 4.3 Hz, 2H), 7.14 (d, *J* = 4.3 Hz, 2H), 4.00 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.76, 136.67, 136.25, 134.93, 131.67, 113.56, 83.94, 46.81. MS (EI, 70 eV); *m/z* (%): 318 (45) [M^+], 272 (100) [M^+-CH_2S]. Anal. Calcd for $C_{13}H_6N_2S_4$: C, 49.03; H, 1.90. Found: C, 49.13; H, 1.95.

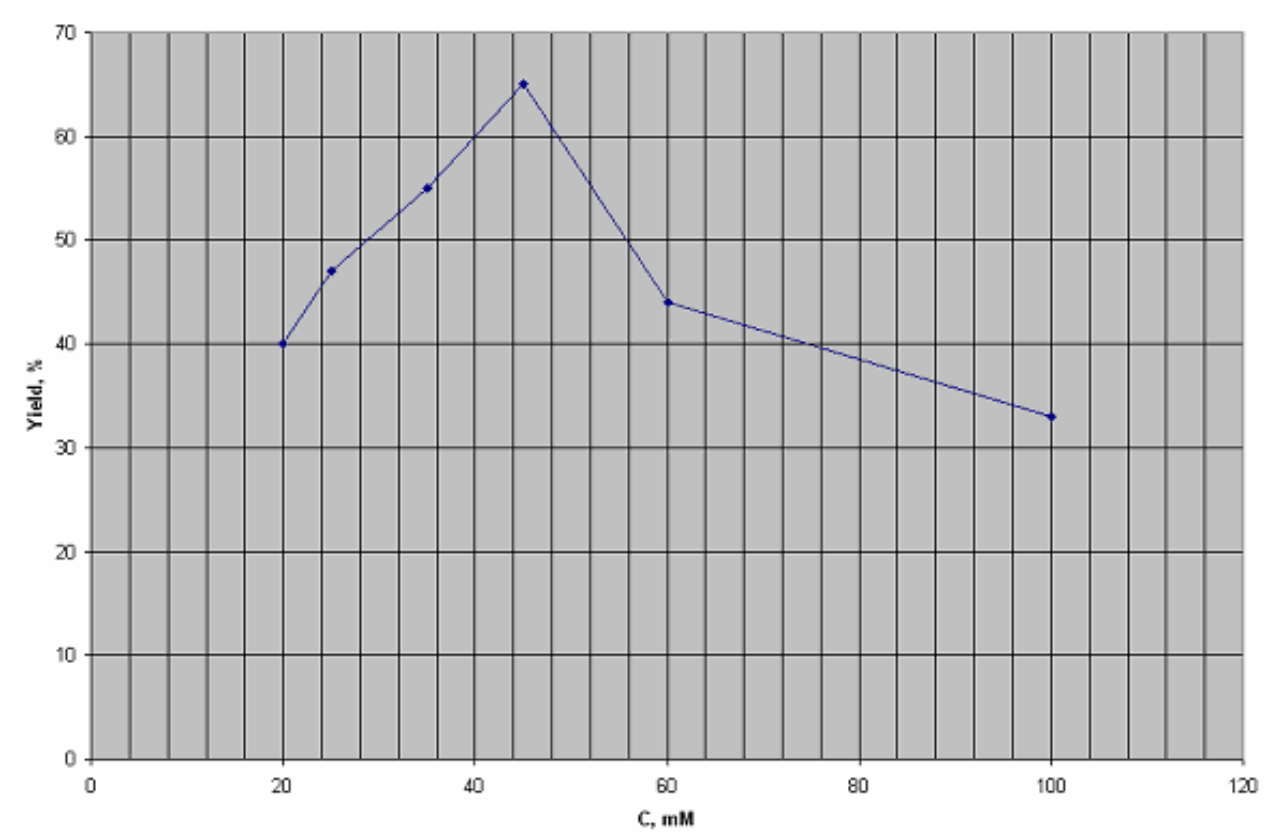


Figure S1: Optimization of the reaction conditions for the synthesis of 4a.

X-Ray structure of compound 1a:

Table S1. Crystal data and structure refinement for bal12.

Identification code	bal12	
Empirical formula	$C_{13}H_6N_2S_4$	
Formula weight	318.44	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, C2/c	
Unit cell dimensions	a = 17.264(3) Å	α = 90º.
	b = 9.878(2) Å	β = 91.45(3)º.
	c = 24.127(5) Å	γ = 90º.
Volume	4113.2(14) $Å^3$	
Z, Calculated density	12, 1.543 Mg/m^3	
Diffractometer	ENRAF NONIUS CAD4	
Collection method	theta/2theta	
Radiation type	MoK\a	
Radiation monochromator	beta filter	
Standards number	3	
Standards interval time	100 min	
Standards interval count	?	
Standards decay	0.8 %	
Theta range for data collection	2.36 to 24.49 deg.	
Limiting indices	$0 \leq h \leq 20$, $0 \leq k \leq 11$, $-28 \leq l \leq 28$	
Reflections collected/unique	3539/3417 [R(int) = 0.0154]	
Completeness to theta = 24.49	99.7 %	
Absorption correction	None	
Absorption coefficient	0.677 mm^{-1}	
F(000)	1944	
Crystal description	prism	

Crystal colour	yellow
Crystal size	0.32 x 0.13 x 0.11 mm^3
Max. and min. transmission	0.9293 and 0.8125
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3417/0/262
Goodness-of-fit on F^2	0.846
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.0933
R indices (all data)	R1 = 0.1388, wR2 = 0.0993
Largest diff. peak and hole	0.382 and -0.329 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for bal12. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
S(1)	4816(1)	2065(1)	969(1)	62(1)
S(2)	4457(1)	-726(1)	1319(1)	68(1)
S(3)	3952(1)	-1521(1)	149(1)	63(1)
S(4)	2967(1)	-3604(1)	691(1)	71(1)
N(1)	1775(2)	3581(3)	1020(2)	72(1)
N(2)	683(2)	-68(3)	633(2)	68(1)
C(1)	3427(2)	1190(3)	829(1)	36(1)
C(2)	3472(2)	2516(3)	591(1)	47(1)
C(3)	4171(2)	3091(4)	634(2)	57(1)
C(4)	4138(2)	812(4)	1050(1)	50(1)
C(5)	4726(2)	-1547(5)	679(2)	76(1)
C(6)	3177(2)	-1940(3)	562(1)	48(1)
C(7)	2252(3)	-3189(3)	1133(2)	66(1)
C(8)	2172(2)	-1845(3)	1179(1)	51(1)
C(9)	2701(2)	-1089(3)	853(1)	38(1)
C(10)	2706(2)	405(3)	836(1)	33(1)
C(11)	2008(2)	1051(3)	835(1)	35(1)
C(12)	1901(2)	2465(3)	936(1)	45(1)
C(13)	1279(2)	379(3)	732(1)	43(1)
S(1A)	6852(1)	5698(1)	2363(1)	87(1)
S(2A)	5269(1)	6326(1)	1905(1)	83(1)
N(1A)	6187(2)	415(3)	2326(2)	71(1)
C(1A)	5747(2)	4017(3)	2511(1)	44(1)
C(2A)	6417(2)	3529(4)	2810(1)	58(1)
C(3A)	7040(3)	4325(5)	2758(2)	77(1)

C(4A)	5912(2)	5222(4)	2247(1)	60(1)
C(5A1)	5021(16)	7315(10)	2415(6)	28(3)
C(5A2)	4663(9)	7345(14)	2427(7)	34(3)
C(6A)	5000	3297(4)	2500	37(1)
C(7A)	5000	1935(4)	2500	36(1)
C(8A)	5677(2)	1109(3)	2410(1)	44(1)

Table S3. Bond lengths [Å] and angles [º] for bal12.

S(1)-C(3)	1.695(4)
S(1)-C(4)	1.717(4)
S(2)-C(4)	1.736(4)
S(2)-C(5)	1.815(4)
S(3)-C(6)	1.738(4)
S(3)-C(5)	1.825(4)
S(4)-C(7)	1.702(4)
S(4)-C(6)	1.712(3)
N(1)-C(12)	1.143(4)
N(2)-C(13)	1.140(4)
C(1)-C(4)	1.378(4)
C(1)-C(2)	1.434(4)
C(1)-C(10)	1.467(4)
C(2)-C(3)	1.335(5)
C(6)-C(9)	1.379(4)
C(7)-C(8)	1.340(5)
C(8)-C(9)	1.430(4)
C(9)-C(10)	1.477(4)
C(10)-C(11)	1.364(4)
C(11)-C(12)	1.430(4)
C(11)-C(13)	1.438(5)
S(1A)-C(3A)	1.685(5)
S(1A)-C(4A)	1.706(4)
S(2A)-C(5A1)	1.635(13)
S(2A)-C(4A)	1.749(4)
S(2A)-C(5A2)#1	1.901(17)
S(2A)-C(5A2)	1.938(17)
S(2A)-C(5A1)#1	1.985(13)

N(1A)-C(8A)	1.139(4)
C(1A)-C(4A)	1.382(5)
C(1A)-C(2A)	1.432(5)
C(1A)-C(6A)	1.472(4)
C(2A)-C(3A)	1.341(5)
C(5A1)-C(5A1)#1	0.42(3)
C(5A1)-C(5A2)	0.62(3)
C(5A1)-C(5A2)#1	0.66(3)
C(5A1)-S(2A)#1	1.985(13)
C(5A2)-C(5A1)#1	0.66(3)
C(5A2)-C(5A2)#1	1.21(3)
C(5A2)-S(2A)#1	1.901(17)
C(6A)-C(7A)	1.345(6)
C(6A)-C(1A)#1	1.472(4)
C(7A)-C(8A)#1	1.446(4)
C(7A)-C(8A)	1.446(4)

C(3)-S(1)-C(4)	92.54(17)
C(4)-S(2)-C(5)	99.14(19)
C(6)-S(3)-C(5)	98.94(18)
C(7)-S(4)-C(6)	92.46(17)
C(4)-C(1)-C(2)	110.2(3)
C(4)-C(1)-C(10)	126.9(3)
C(2)-C(1)-C(10)	122.8(3)
C(3)-C(2)-C(1)	114.5(3)
C(2)-C(3)-S(1)	111.4(3)
C(1)-C(4)-S(1)	111.3(3)
C(1)-C(4)-S(2)	130.8(3)
S(1)-C(4)-S(2)	117.6(2)
S(2)-C(5)-S(3)	113.0(2)

C(9)-C(6)-S(4)	111.2(3)
C(9)-C(6)-S(3)	128.6(3)
S(4)-C(6)-S(3)	120.13(19)
C(8)-C(7)-S(4)	111.6(3)
C(7)-C(8)-C(9)	113.8(3)
C(6)-C(9)-C(8)	111.0(3)
C(6)-C(9)-C(10)	126.2(3)
C(8)-C(9)-C(10)	122.7(3)
C(11)-C(10)-C(1)	120.2(3)
C(11)-C(10)-C(9)	117.5(3)
C(1)-C(10)-C(9)	122.3(3)
C(10)-C(11)-C(12)	125.0(3)
C(10)-C(11)-C(13)	123.6(3)
C(12)-C(11)-C(13)	111.4(3)
N(1)-C(12)-C(11)	176.3(4)
N(2)-C(13)-C(11)	175.0(4)
C(3A)-S(1A)-C(4A)	92.25(19)
C(5A1)-S(2A)-C(4A)	101.1(8)
C(5A1)-S(2A)-C(5A2)#1	19.7(11)
C(4A)-S(2A)-C(5A2)#1	84.6(5)
C(5A1)-S(2A)-C(5A2)	17.5(12)
C(4A)-S(2A)-C(5A2)	111.3(5)
C(5A2)#1-S(2A)-C(5A2)	36.6(9)
C(5A1)-S(2A)-C(5A1)#1	7.4(6)
C(4A)-S(2A)-C(5A1)#1	95.0(6)
C(5A2)#1-S(2A)-C(5A1)#1	18.2(8)
C(5A2)-S(2A)-C(5A1)#1	19.3(7)
C(4A)-C(1A)-C(2A)	110.4(3)
C(4A)-C(1A)-C(6A)	126.7(3)
C(2A)-C(1A)-C(6A)	122.9(3)

C(3A)-C(2A)-C(1A)	113.2(4)
C(2A)-C(3A)-S(1A)	112.5(3)
C(1A)-C(4A)-S(1A)	111.6(3)
C(1A)-C(4A)-S(2A)	128.2(3)
S(1A)-C(4A)-S(2A)#1	19.7(2)
C(5A1)#1-C(5A1)-C(5A2)	76(6)
C(5A1)#1-C(5A1)-C(5A2)#1	66(6)
C(5A2)-C(5A1)-C(5A2)#1	141(3)
C(5A1)#1-C(5A1)-S(2A)	142.4(19)
C(5A2)-C(5A1)-S(2A)	110(3)
C(5A2)#1-C(5A1)-S(2A)	104(3)
C(5A1)#1-C(5A1)-S(2A)#1	30.2(15)
C(5A2)-C(5A1)-S(2A)#1	73.3(19)
C(5A2)#1-C(5A1)-S(2A)#1	76.4(19)
S(2A)-C(5A1)-S(2A)#1	113.8(6)
C(5A1)-C(5A2)-C(5A1)#1	38(3)
C(5A1)-C(5A2)-C(5A2)#1	19.9(15)
C(5A1)#1-C(5A2)-C(5A2)#1	18.7(15)
C(5A1)-C(5A2)-S(2A)#1	89(2)
C(5A1)#1-C(5A2)-S(2A)#1	57(2)
C(5A2)#1-C(5A2)-S(2A)#1	73.3(14)
C(5A1)-C(5A2)-S(2A)	52(2)
C(5A1)#1-C(5A2)-S(2A)	84(2)
C(5A2)#1-C(5A2)-S(2A)	70.0(13)
S(2A)#1-C(5A2)-S(2A)	104.6(7)
C(7A)-C(6A)-C(1A)#1	118.9(2)
C(7A)-C(6A)-C(1A)	118.9(2)
C(1A)#1-C(6A)-C(1A)	122.2(4)
C(6A)-C(7A)-C(8A)#1	124.36(19)
C(6A)-C(7A)-C(8A)	124.36(19)

C(8A)#1-C(7A)-C(8A)	111.3(4)
N(1A)-C(8A)-C(7A)	176.8(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

Table S4. Anisotropic displacement parameters ($Å^2$ x 10^3) for bal12. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2} U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	34(1)	90(1)	64(1)	-12(1)	0(1)	-13(1)
S(2)	68(1)	73(1)	63(1)	-2(1)	-22(1)	27(1)
S(3)	62(1)	74(1)	54(1)	-12(1)	10(1)	17(1)
S(4)	105(1)	32(1)	74(1)	-8(1)	-6(1)	17(1)
N(1)	67(2)	30(2)	118(3)	-7(2)	9(2)	-1(2)
N(2)	43(2)	56(2)	106(3)	-6(2)	3(2)	-15(2)
C(1)	32(2)	37(2)	38(2)	-3(1)	1(1)	-1(1)
C(2)	38(2)	48(2)	55(2)	3(2)	3(2)	-11(2)
C(3)	41(2)	66(2)	64(2)	1(2)	4(2)	-18(2)
C(4)	43(2)	58(2)	48(2)	-4(2)	-1(2)	4(2)
C(5)	50(2)	78(3)	100(3)	-12(3)	2(2)	30(2)
C(6)	63(2)	36(2)	43(2)	-8(2)	-5(2)	10(2)
C(7)	98(3)	32(2)	69(2)	8(2)	2(2)	-6(2)
C(8)	64(2)	36(2)	54(2)	3(2)	9(2)	-2(2)
C(9)	47(2)	32(2)	36(2)	1(1)	-2(1)	0(1)
C(10)	36(2)	35(2)	29(2)	3(1)	-1(1)	-1(1)
C(11)	34(2)	26(2)	47(2)	-1(1)	1(1)	-6(1)
C(12)	32(2)	38(2)	65(2)	-2(2)	0(2)	-6(2)
C(13)	38(2)	33(2)	57(2)	1(2)	6(2)	0(2)
S(1A)	119(1)	79(1)	65(1)	-5(1)	15(1)	-66(1)
S(2A)	159(1)	38(1)	52(1)	13(1)	32(1)	14(1)
N(1A)	43(2)	61(2)	110(3)	0(2)	4(2)	15(2)
C(1A)	56(2)	39(2)	37(2)	-2(1)	3(2)	-11(2)
C(2A)	51(2)	71(3)	50(2)	2(2)	-4(2)	-29(2)

C(3A)	71(3)	94(3)	65(3)	-6(2)	-4(2)	-49(3)
C(4A)	95(3)	43(2)	42(2)	-5(2)	16(2)	-23(2)
C(6A)	42(3)	37(3)	33(2)	0	-2(2)	0
C(7A)	25(2)	33(2)	49(3)	0	-3(2)	0
C(8A)	5(2)	38(2)	61(2)	4 (2)	2(2)	-3(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for bal12.

	x	y	z	U_{eq}
H(2)	3016	2920	417	80
H(3)	4368	3994	484	80
H(51)	4794	-2482	801	80
H(52)	5186	-1235	538	80
H(7)	1962	-3818	1284	80
H(8)	1853	-1477	1432	80
H(2A)	6387	2688	3035	80
H(3A)	7527	4320	2911	80
H(511)	4593	7880	2311	80
H(512)	5448	7908	2522	80
H(521)	4117	7464	2296	80
H(522)	4857	8281	2479	80

X-Ray structure of compound 1b:

Table S6. Crystal data and structure refinement for bal10.

Identification code	bal10	
Empirical formula	$C_{13}H_6N_2S_4$	
Formula weight	318.44	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, C2/c	
Unit cell dimensions	a = 16.357(3) Å	α = 90º.
	b = 9.943(2) Å	β = 123.73(3)º.
	c = 10.168(2) Å	γ = 90º.
Volume	1375.3(5) $Å^3$	
Z, Calculated density	4, 1.538 Mg/m^3	
Diffractometer	Enraf Nonius CAD4	
Collection method	theta/2theta	
Radiation type	MoK\a	
Radiation monochromator	beta filter	
Standards number	3	
Standards interval time	100 min	
Standards interval count	?	
Standards decay	0.4 %	
Theta range for data collection	2.54 to 27.97 deg.	
Limiting indices	$-21 \leq h \leq 0$, $-13 \leq k \leq 0$, $-11 \leq l \leq 13$	
Reflections collected/unique	1712/1658 [R(int) = 0.0364]	
Completeness to theta = 27.97	99.9 %	
Absorption correction	None	
Absorption coefficient	0.675 mm^{-1}	
F(000)	648	
Crystal description	prism	

Crystal colour	yellow
Crystal size	0.31 x 0.22 x 0.12 mm^3
Max. and min. transmission	0.9234 and 0.8181
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1658/0/101
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0308, wR2 = 0.0919
R indices (all data)	R1 = 0.0592, wR2 = 0.0963
Extinction coefficient	0.0044(13)
Largest diff. peak and hole	0.200 and -0.254 e.$Å^{-3}$

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for bal10. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
S(1)	6183(1)	1493(1)	5749(1)	59(1)
S(2)	5923(1)	4406(1)	2473(1)	83(1)
N(1)	6410(1)	-1528(2)	4468(2)	73(1)
C(1)	5751(1)	2133(1)	3897(2)	40(1)
C(2)	6947(2)	2812(2)	6670(2)	71(1)
C(3)	6895(1)	3694(2)	5634(3)	69(1)
C(4)	6206(1)	3343(2)	4044(2)	53(1)
C(5)	5000	5404(3)	2500	97(1)
C(6)	5000	1408(2)	2500	35(1)
C(7)	5000	22(2)	2500	39(1)
C(8)	5809(1)	-791(2)	3653(2)	47(1)

Table S8. Bond lengths [Å] and angles [º] for bal10.

S(1)-C(2)	1.691(2)
S(1)-C(1)	1.7247(15)
S(2)-C(4)	1.7492(19)
S(2)-C(5)	1.8202(19)
N(1)-C(8)	1.134(2)
C(1)-C(4)	1.379(2)
C(1)-C(6)	1.4518(17)
C(2)-C(3)	1.336(3)
C(3)-C(4)	1.408(3)
C(5)-S(2)#1	1.8202(19)
C(6)-C(7)	1.378(3)
C(6)-C(1)#1	1.4518(17)
C(7)-C(8)#1	1.4339(18)
C(7)-C(8)	1.4339(18)
C(2)-S(1)-C(1)	92.67(10)
C(4)-S(2)-C(5)	96.73(8)
C(4)-C(1)-C(6)	130.70(14)
C(4)-C(1)-S(1)	109.55(12)
C(6)-C(1)-S(1)	119.73(11)
C(3)-C(2)-S(1)	111.66(15)
C(2)-C(3)-C(4)	113.74(18)
C(1)-C(4)-C(3)	112.36(17)
C(1)-C(4)-S(2)	125.09(13)
C(3)-C(4)-S(2)	122.42(15)
S(2)#1-C(5)-S(2)	113.87(17)
C(7)-C(6)-C(1)	119.76(9)
C(7)-C(6)-C(1)#1	119.76(9)

C(1)-C(6)-C(1)#1	120.47(17)
C(6)-C(7)-C(8)#1	124.33(9)
C(6)-C(7)-C(8)	124.33(9)
C(8)#1-C(7)-C(8)	111.34(17)
N(1)-C(8)-C(7)	173.71(17)

Symmetry transformations used to generate equivalent atoms:

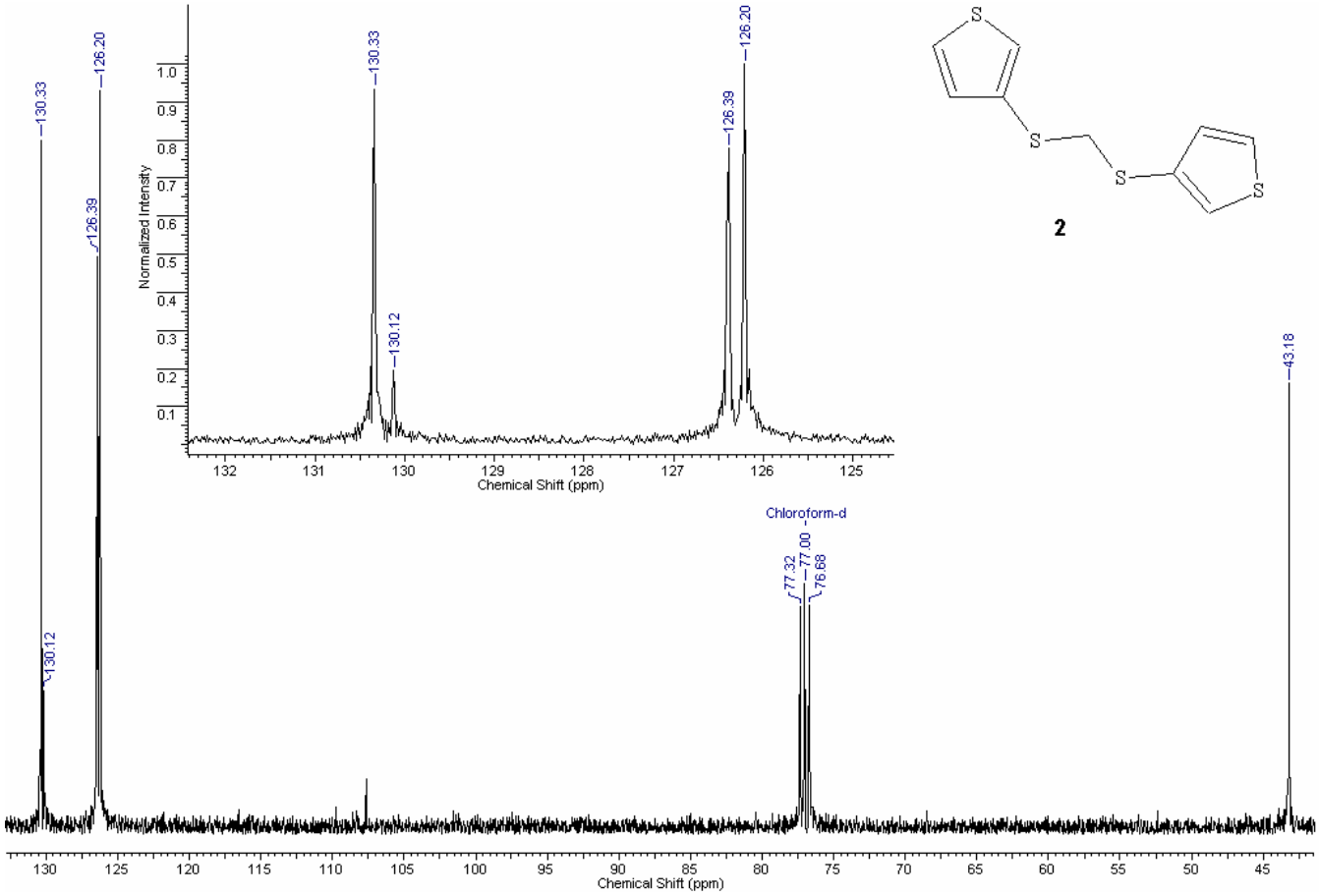
#1 -x+1,y,-z+1/2

Table S9. Anisotropic displacement parameters ($Å^2$ x 10^3) for bal10. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2} U^{11}$ + ... + 2 h k a* b* U^{12}]

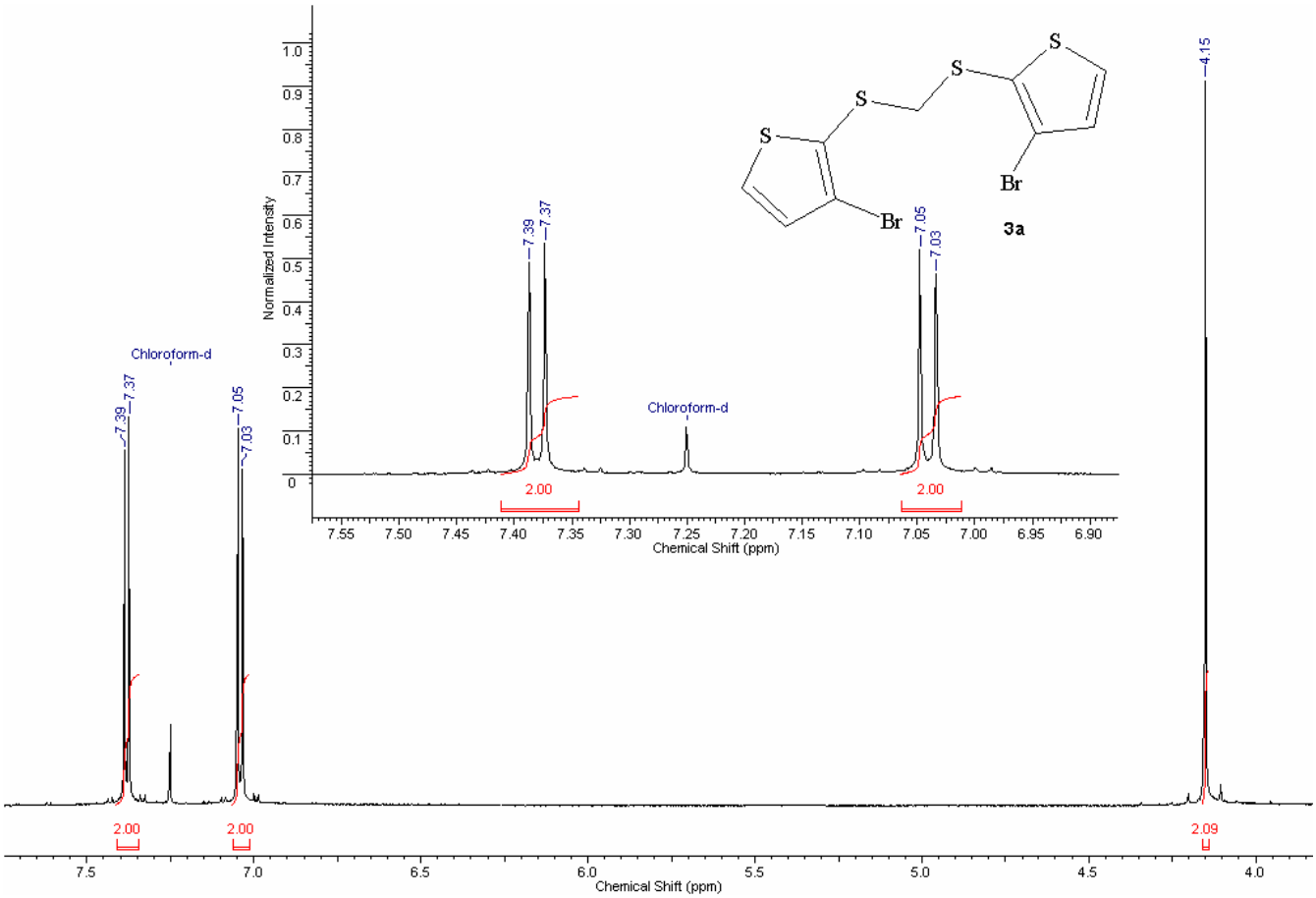
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	70(1)	64(1)	31(1)	-8(1)	20(1)	-5(1)
S(2)	107(1)	60(1)	99(1)	1(1)	69(1)	-29(1)
N(1)	68(1)	60(1)	51(1)	4(1)	8(1)	17(1)
C(1)	40(1)	42(1)	36(1)	-5(1)	21(1)	-2(1)
C(2)	60(1)	83(1)	51(1)	-32(1)	18(1)	-4(1)
C(3)	56(1)	66(1)	79(1)	-36(1)	35(1)	-19(1)
C(4)	56(1)	47(1)	64(1)	-14(1)	39(1)	-13(1)
C(5)	123(3)	40(2)	119(3)	0	62(3)	0
C(6)	39(1)	37(1)	30(1)	0	20(1)	0
C(7)	39(1)	37(1)	30(1)	0	12(1)	0
C(8)	49(1)	40(1)	37(1)	-2(1)	13(1)	-1(1)

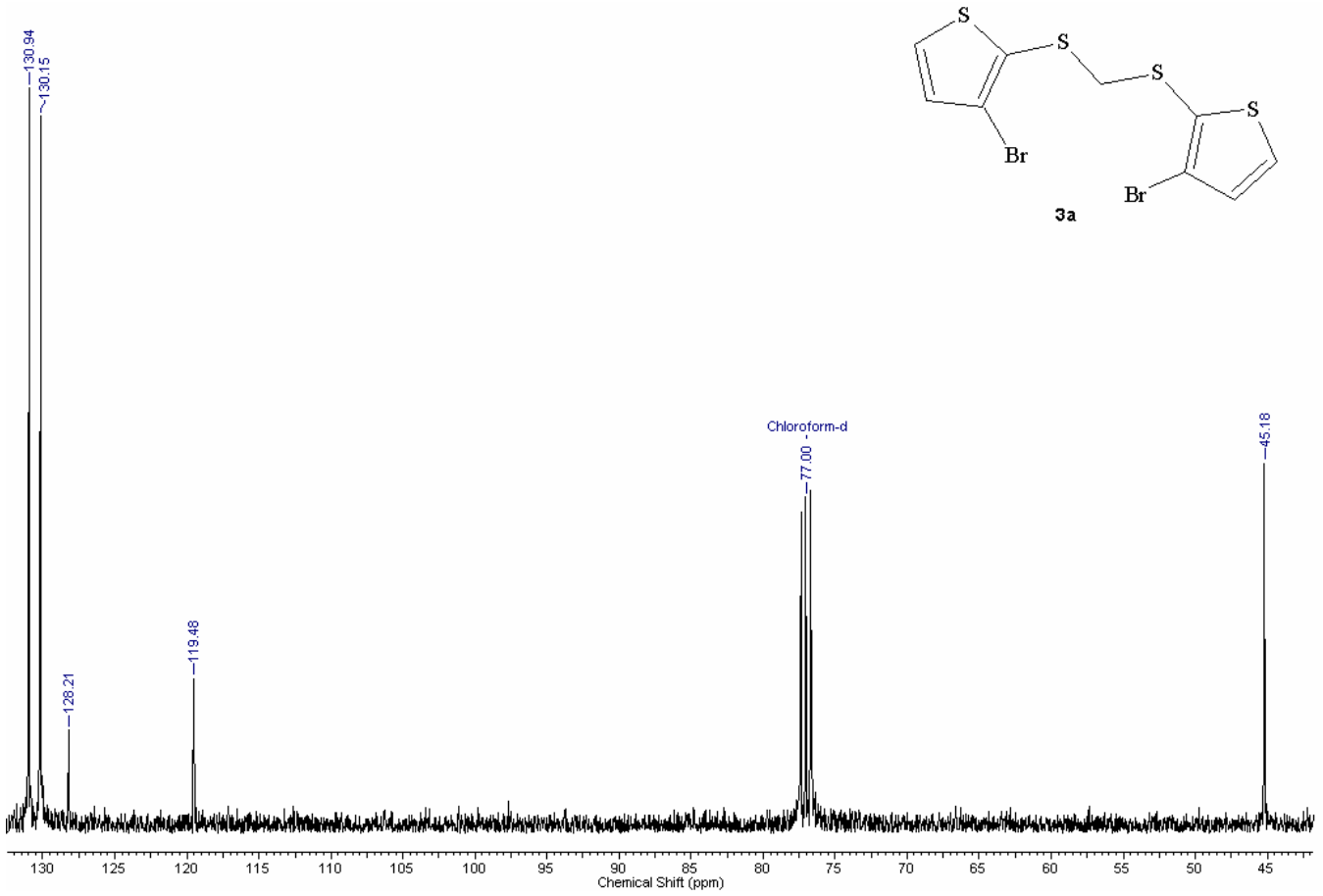
Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for bal10.

	x	y	z	U_{eq}
H(2)	7287(18)	2810(30)	7780(30)	105(9)
H(3)	7240(20)	4470(30)	5900(40)	106(9)
H(5)	4551(18)	5900(30)	1540(30)	97(8)

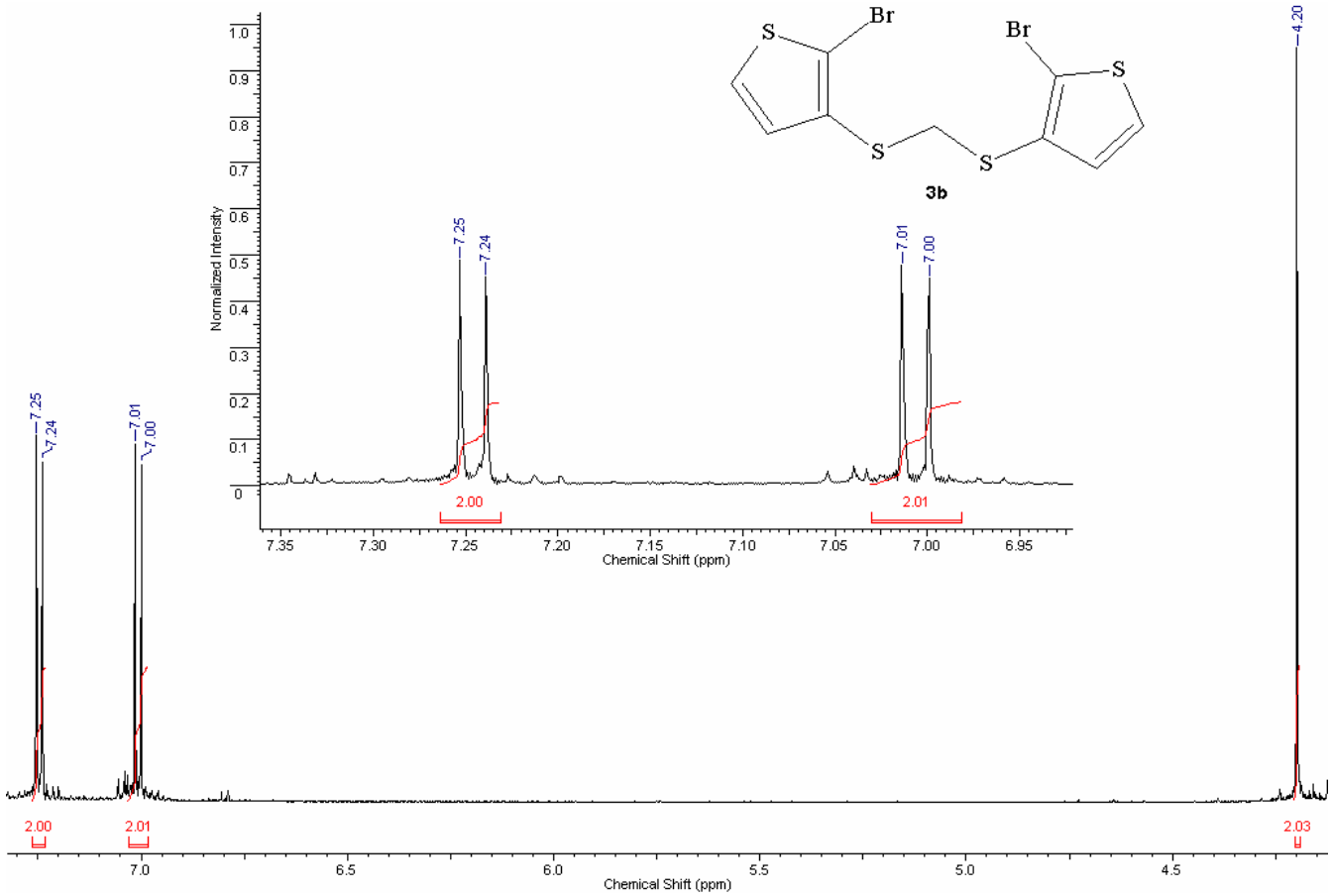

130.33
126.20
126.39
130.12
43.18
Chloroform-d
77.32
77.00
76.68
Chemical Shift (ppm)
Normalized Intensity
S
S
S
S

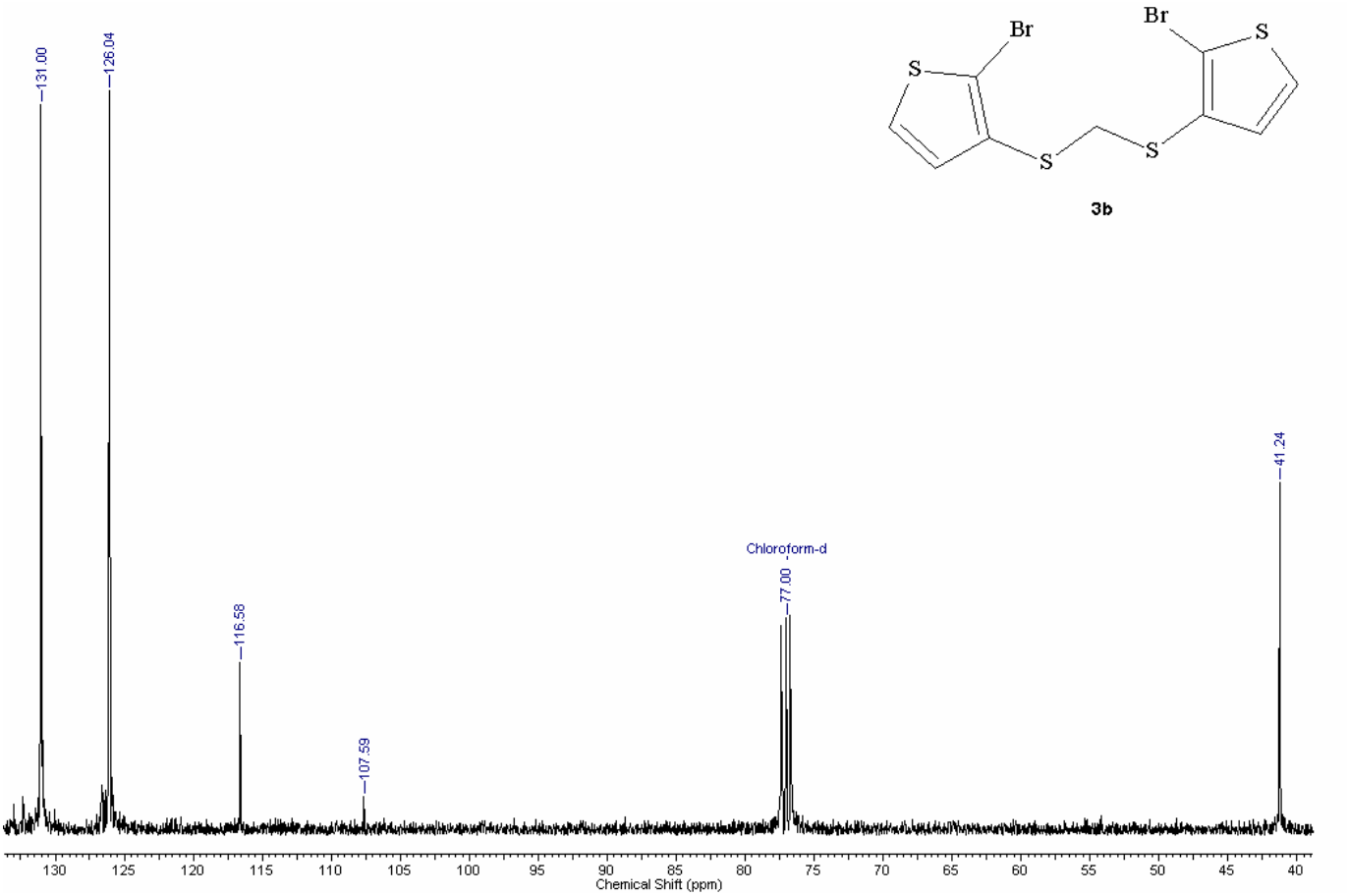
2


Chloroform-d
7.39
7.37
7.05
7.03
4.15
2.00
2.00
2.09
Chemical Shift (ppm)
Normalized Intensity
Chloroform-d
2.00
2.00
Chemical Shift (ppm)
S
S
S
S
Br
Br
3a


130.94
130.15
128.21
119.48
Chloroform-d
77.00
45.18
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
Chemical Shift (ppm)
S
S
S
S
Br
Br

3a


Br
S
Br
S
S
S
3b
Normalized Intensity
7.25
7.24
7.01
7.00
2.00
2.01
Chemical Shift (ppm)
4.20
2.03


Br
Br
S
S
S
S
3b
131.00
126.04
116.58
107.59
Chloroform-d
77.00
41.24
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
Chemical Shift (ppm)

FW 270.418	Formula $C_{10}H_6OS_4$				
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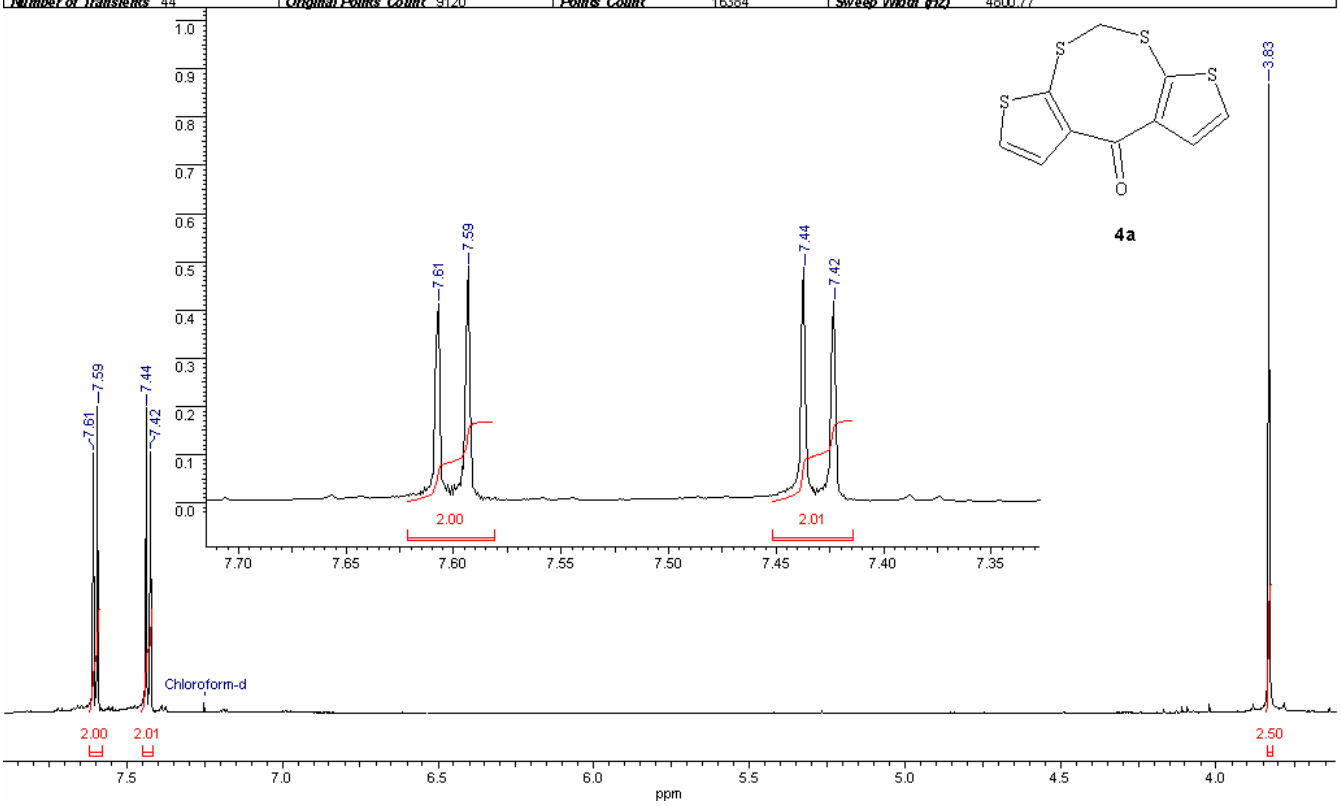
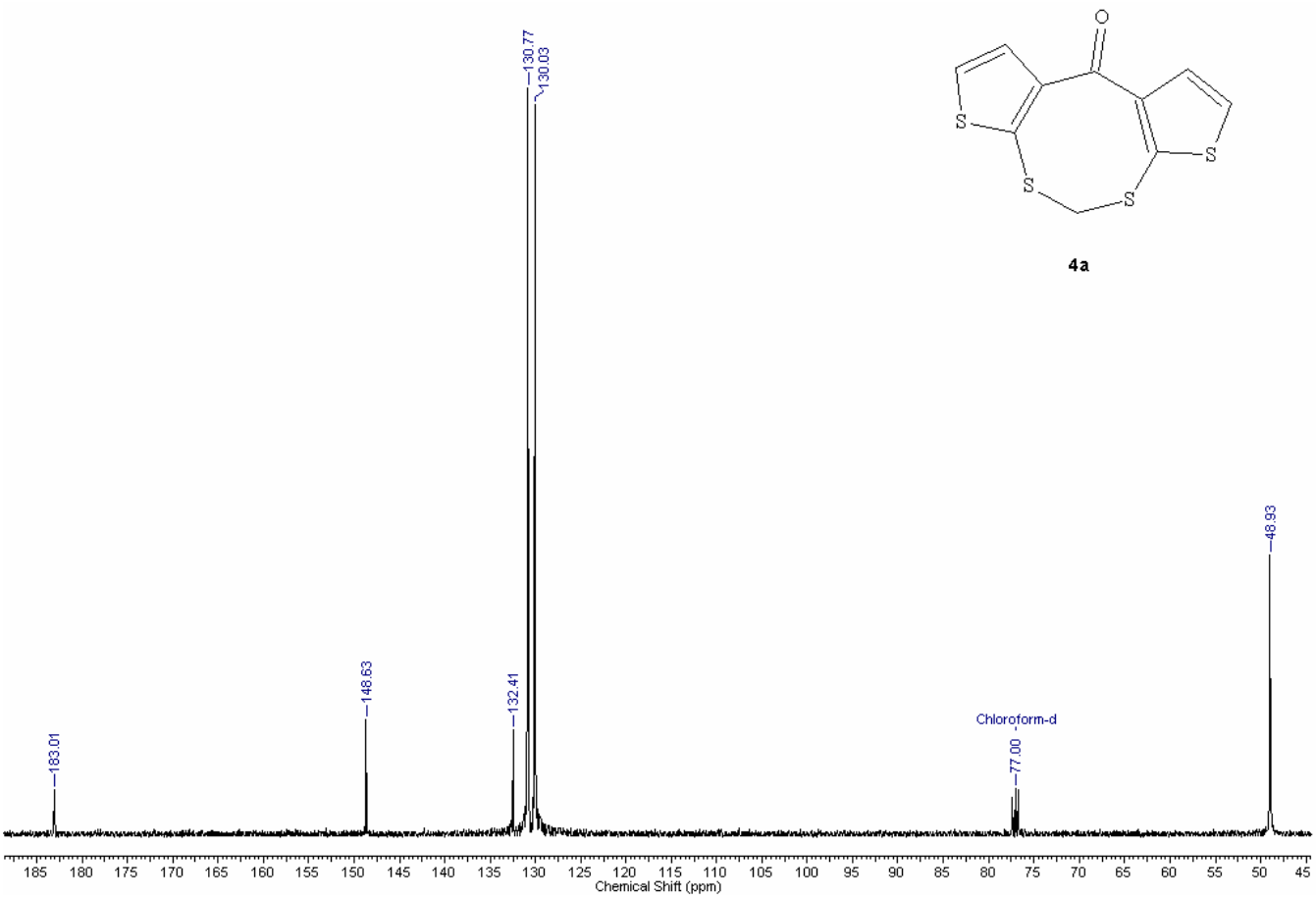
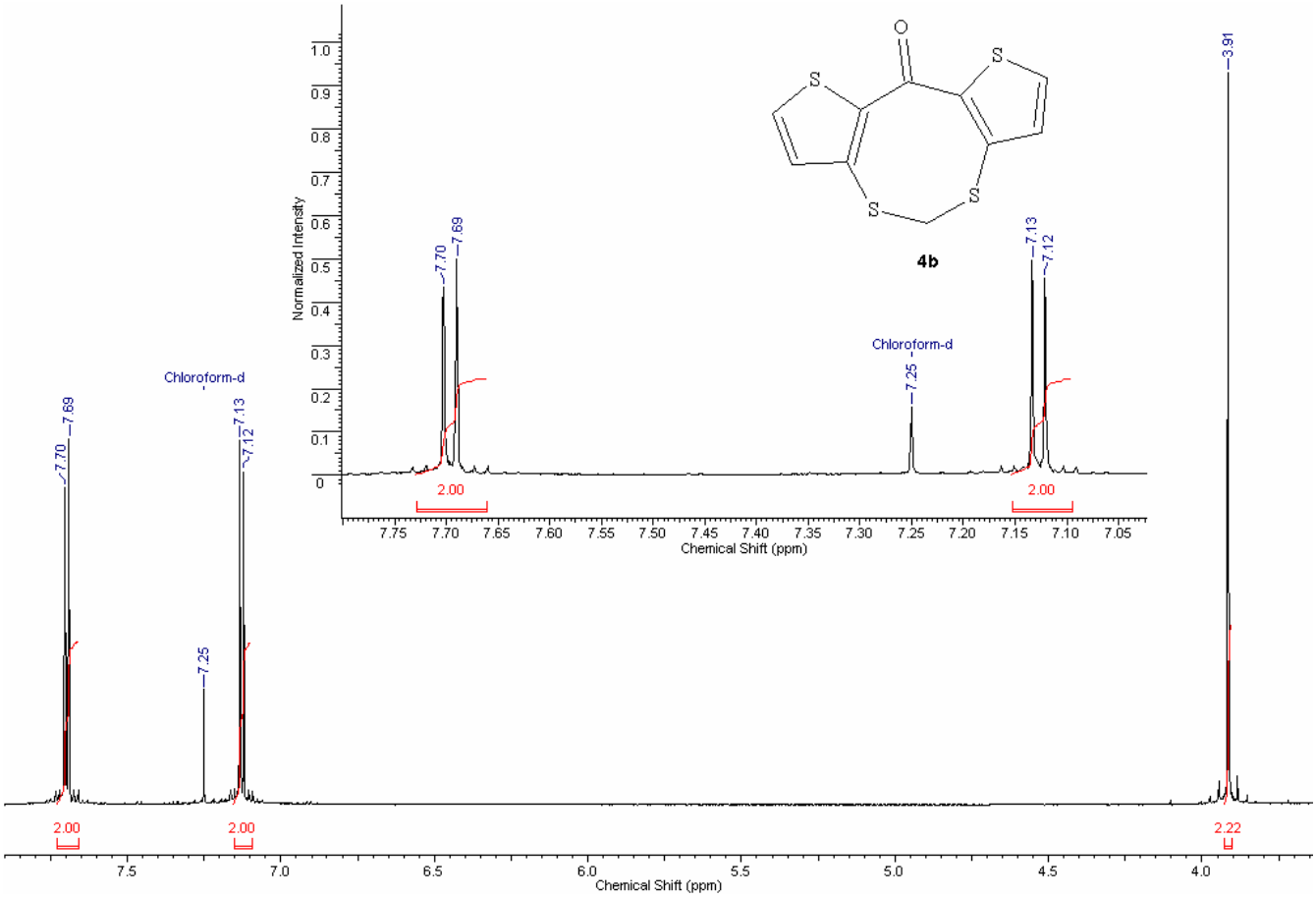
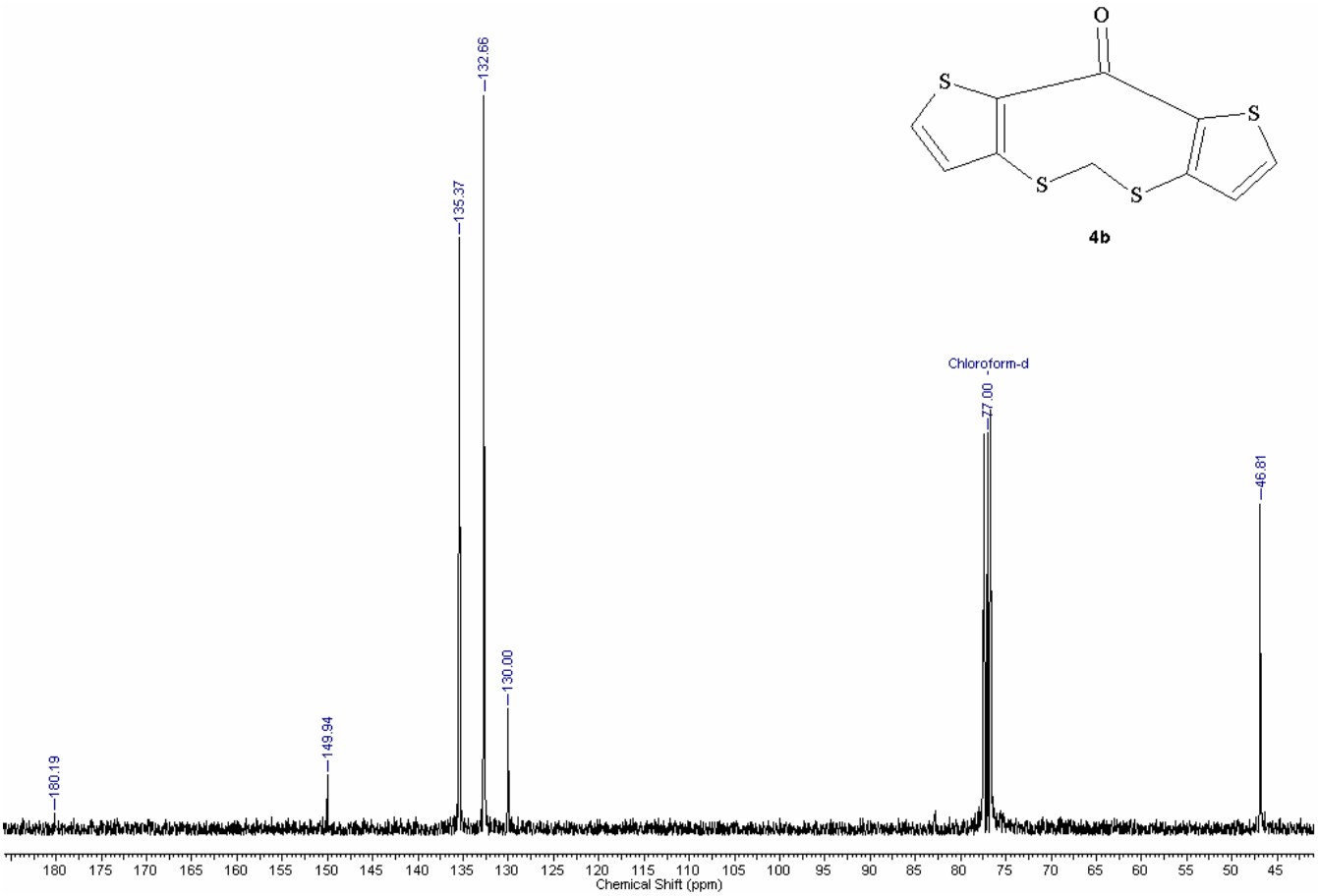



O
S
S
S
S
4a
130.77
130.03
148.63
132.41
183.01
Chloroform-d
77.00
48.93
185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45
Chemical Shift (ppm)


4b
Normalized Intensity
Chemical Shift (ppm)
Chloroform-d
7.70
7.69
7.25
7.13
7.12
3.91
2.00
2.22


O
S
S
S
S
4b
180.19
149.94
135.37
132.66
130.00
Chloroform-d
77.00
46.81
180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45
Chemical Shift (ppm)

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Nucleus	1H		
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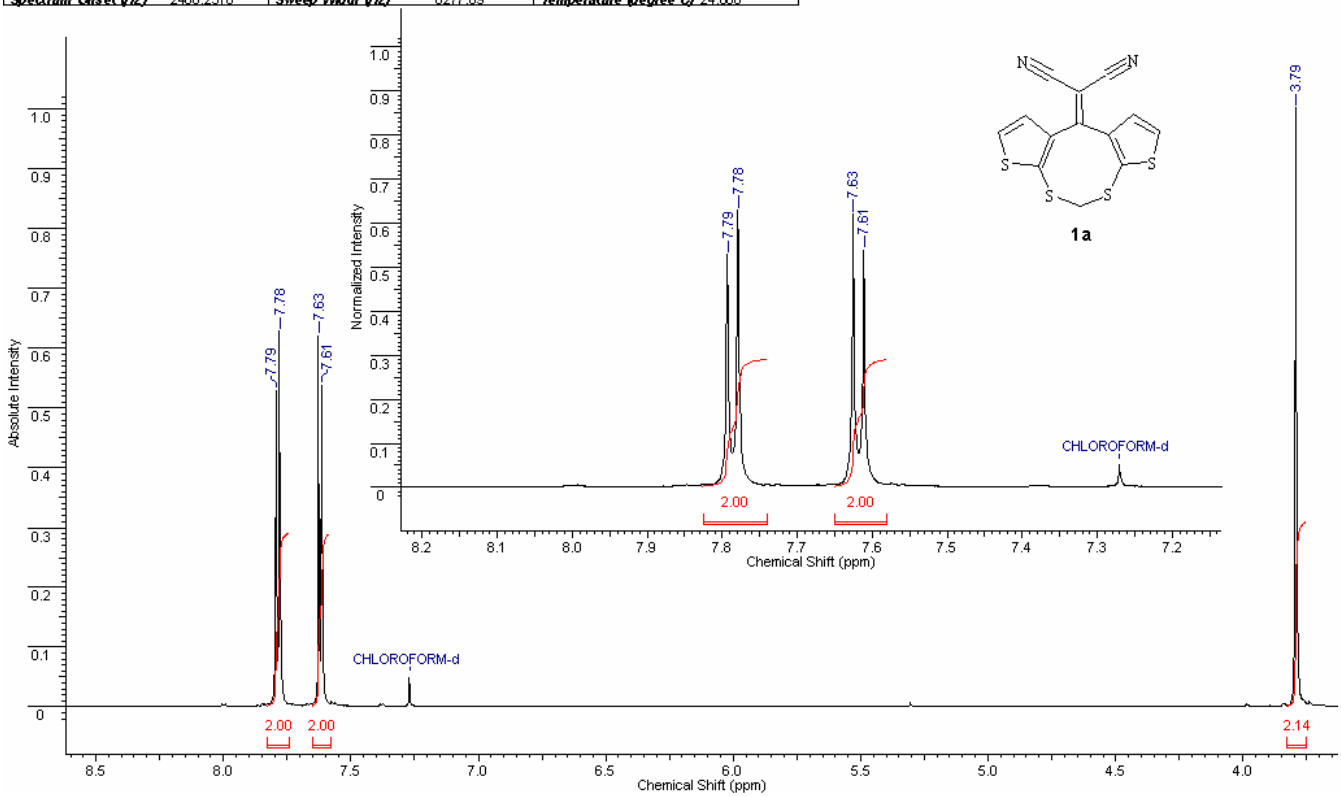

18.06.2005 11:47

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Pulse Sequence	zgpg30	***Receiver Gain***	161.30	***SW(cyclical) (Hz)***	23980.81	***Solvent***	CHLOROFORM-d
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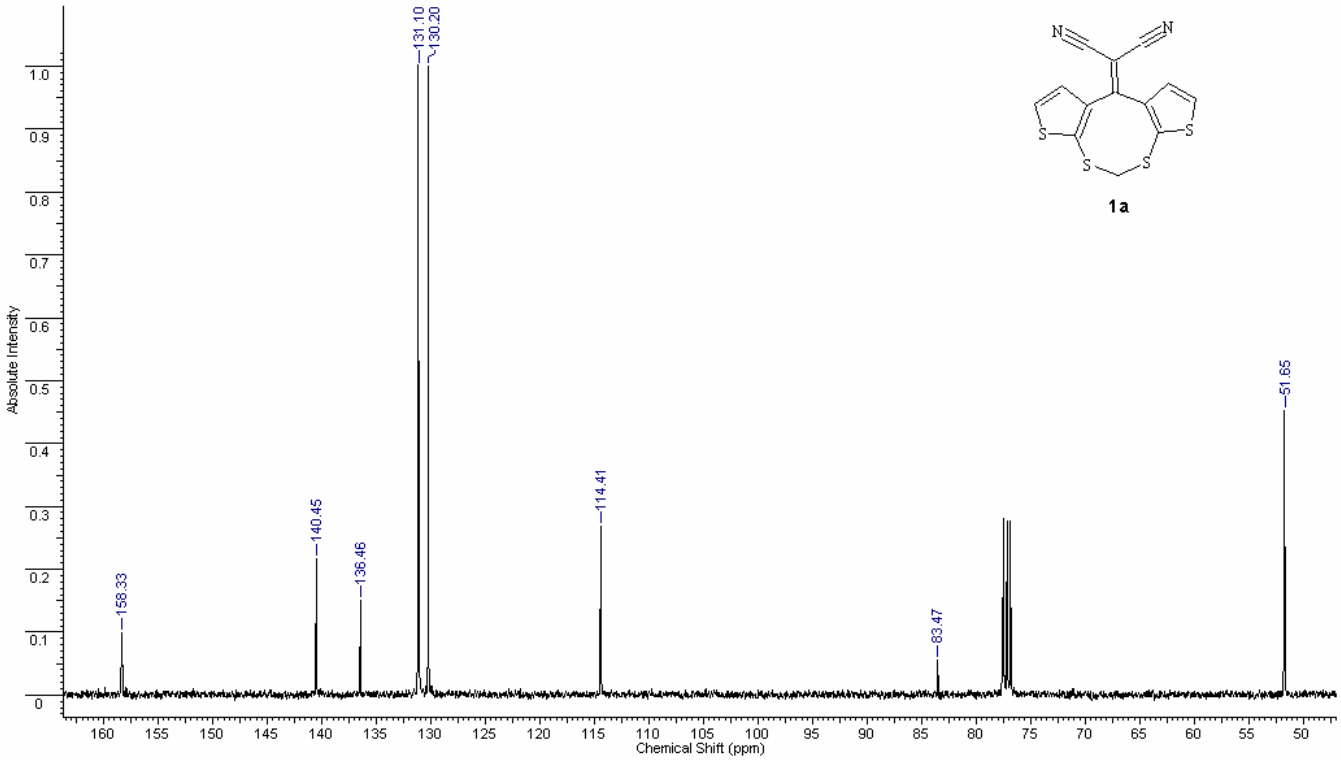

1a

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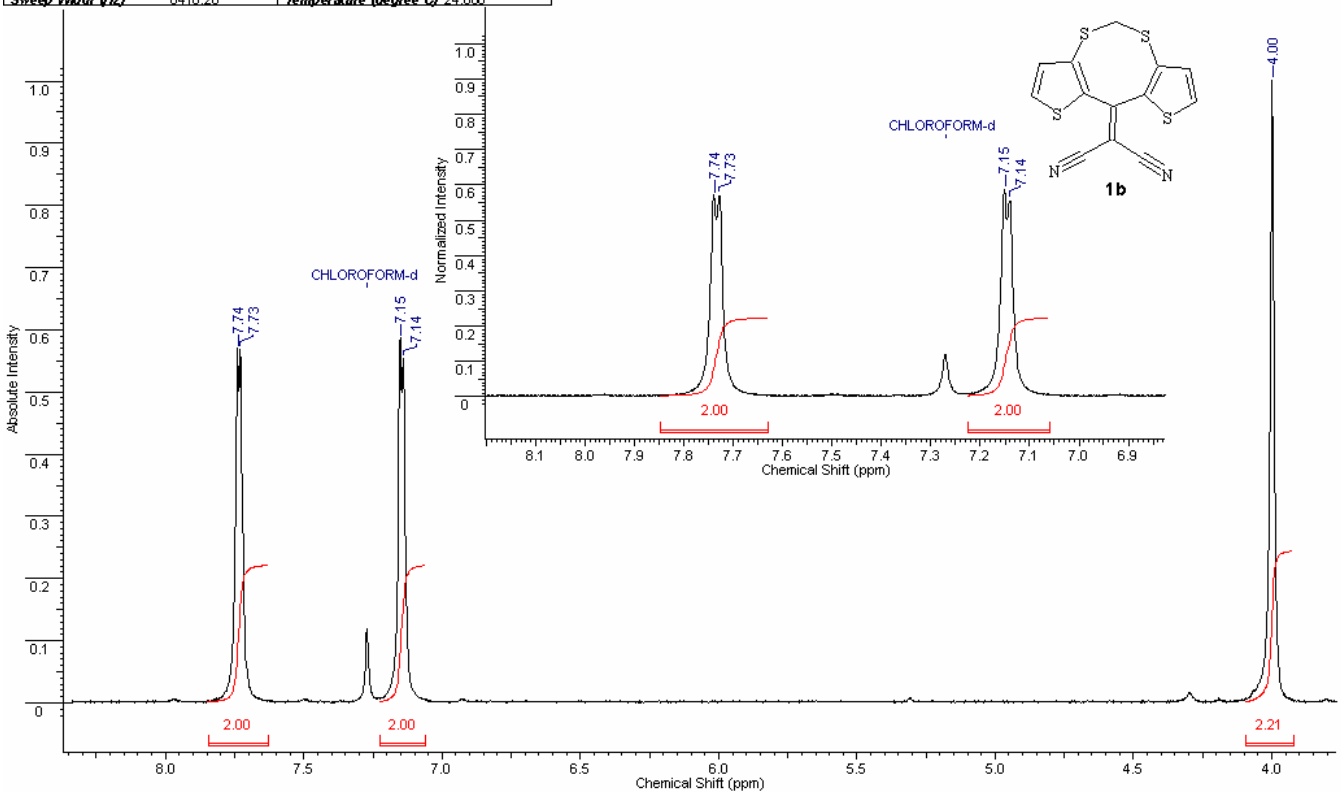

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Pulse Sequence	zgpg30	***Solvent***	CHLOROFORM-d			***Spectrum Offset (Hz)***	10055.5791
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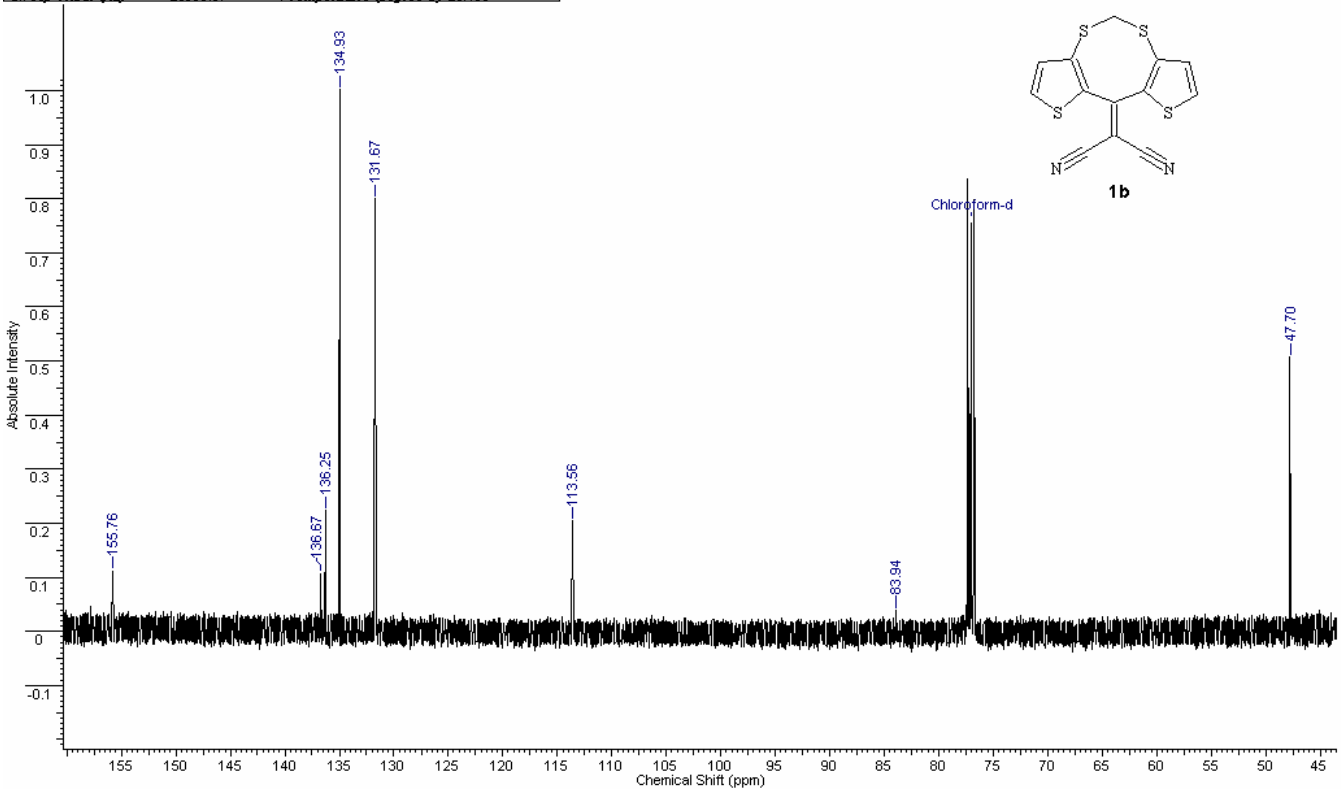

Full authors lists

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