Supporting information for:

A New Route to Annulated Oligothiophenes

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General Experimental. ^1H NMR and ^{13}C spectra were obtained using on Varian VXR-400 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 60F₂₅₄ 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 ^1H - and 100 MHz ^{13}C -NMR spectral data. Melting points are uncorrected. All starting materials are commercially available.

3-[[[(Thien-3-ylthio)methyl]thio]thiophene (3). 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. The solvent was removed in vacuo and the residue was dissolved in DMF (500 mL). At this solution 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. After distillation in portion (not more 0.05 mol, b.p. $137^\circ/10^{-1}\text{Torr}$) afforded 50.9 g of **3** (yield 85%) as an yellow oil, R_f (Hexane/AcOEt = 4:1) = 0.63. ^1H 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) [$\text{M}^+ - \text{C}_4\text{H}_3\text{S}_2$]. Anal. Calcd for $\text{C}_9\text{H}_8\text{S}_4$: C, 44.22; H, 3.30. Found: C, 43.96; H, 3.35.

3-Bromo-2-([[(3-bromothieryl-2-yl)thio]methyl]thio)thiophene (4a). 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 (2*200 mL), dissolved in toluene (500 mL), dried over K₂CO₃ 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 **4a**, *R*_f (Hexane/AcOEt = 4:1) = 0.43. Mp 74.5-76°C. ¹H NMR (400 MHz, CDCl₃): δ = 7.38 (d, *J* = 5.6 Hz, 2H), 7.04 (d, *J* = 5.6 Hz, 2H), 4.15 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): 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⁺-C₄H₂BrS₂], 128 (42) [M⁺-C₄H₂BrS₂-Br]. Anal. Calcd for C₉H₆Br₂S₄: C, 26.88; H, 1.50. Found: C, 26.59; H, 1.54.

2-Bromo-3-([[(2-bromothien-3-yl)thio]methyl]thio)thiophene (4b). To a stirred solution of **3** (74.0 g, 0.303 mol) in CHCl₃ (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 H₂O (1000 mL) was added and the product was extracted with CH₂Cl₂ (100 mL). The organic layer was washed with water (3*150 mL), aq Na₂CO₃ and dried over K₂CO₃. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (silica gel; *n*-hexane/AcOEt, 50:1) to afford 109.6 g of **4b** (yield 90%) as a yellow oil (unstable and should be used immediately in next step), *R*_f (Hexane/AcOEt = 4:1) = 0.43. ¹H NMR (400 MHz, CDCl₃): δ = 7.25 (d, *J* = 5.9 Hz, 2H), 7.00 (d, *J* = 5.9 Hz, 2H), 4.20 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): 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.

10H-Bisthieno[2,3-*d*:3',2'-*g*][1,3]dithiocin-10-one (5a). Compound **4a** (63.3 g, 0.157 mol) was dissolved in dry ether (4000 mL) and cooled to -78°C ; then *t*-BuLi (420 mL, 0.630 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 ethyl *N,N'*-dimethylcarbamate (64.5 g, 0.551 mol) 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 **5a** (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 . ^1H 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) $[M^+-\text{CH}_2\text{S}]$, 142 (71) $[M^+-\text{C}_5\text{H}_4\text{S}_2]$. Anal. Calcd for $\text{C}_{10}\text{H}_6\text{OS}_4$: C, 44.42; H, 2.24. Found: C, 44.49; H, 2.42.

10H-Bisthieno[2,3-*g*:3',2'-*d*][1,3]dithiocin-10-one (5b). Compound **4b** (31.7 g, 0.079 mol) was dissolved in dry ether (2000 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 ethyl *N,N'*-dimethylcarbamate (32.3 g, 0.275 mol) 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; CHCl₃). 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) to afford 13.8 g of **5b** (yield 65%) as an yellow crystals, *R*_f (Hexane/AcOEt = 4:1) = 0.40. Mp 131.5°-133.0°C. ¹H NMR (400 MHz, CDCl₃): δ = 7.70 (d, *J* = 5.0 Hz, 2H), 7.13 (d, *J* = 5.0 Hz, 2H), 3.91 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): 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⁺-CH₂S], 142 (34) [M⁺-C₅H₄S₂]. Anal. Calcd for C₁₀H₆OS₄: C, 44.42; H, 2.24. Found: C, 44.52; H, 2.36.

Intramolecular Coupling of 5a and 5b. Compound **5a** (2.705 g, 10.0 mmol) was dissolved in mixture ether/HMPA (9:1, 1000 mL) and cooled to -78°C; *t*-BuLi (6.67 mL, 10.0 mmol, 1.5 M in *n*-pentane,) was then added dropwise. The resulting mixture was stirred for 2 h at this temperature, then at r.t. overnight and quenched by addition of water (50 mL). The ether was removed by rotary evaporation (20°C) and the residue was heating for 1 h at 150-200°C. The HMPA was removed in vacuo (100°C/ 7 torr) then water was added and the product was extracted twice with CHCl₃ (50 mL). The combined organic layers were washed with water (3*25 mL), dried over K₂CO₃ and concentrated in vacuo. The crude product (1.50 g) was passed through a short column (silica gel; hexane/CHCl₃, 2:1) to afford 1.36 g of **1a** (yield 54%) after evaporation of solvent and crystallization from hexane/CHCl₃ (2:1). A similar reaction of **5b** produced **5a** in 50% yield.

Thieno[2,3-*b*]thieno[3',2':4,5]thieno[3,2-*d*]thiophene (1a). *R*_f (Hexane/AcOEt = 4:1) = 0.51. Mp 159.5-161.0°C. ¹H NMR (400 MHz, DMSO-*d*⁶): δ = 7.79 (B part of an AB system, *J* = 5.1 Hz, 2H), 7.71 (A part of an AB system, *J* = 5.1 Hz, 2H). ¹³C NMR (100 MHz, DMSO-*d*⁶): δ = 140.91, 138.54, 137.26, 129.15, 118.90, 115.32. MS (EI, 70 eV); *m/z* (%): 252 (100) [M⁺]. Anal. Calcd for C₁₀H₄S₄: C, 47.59; H, 1.60. Found: C, 47.68; H, 1.75.

Thieno[3,2-*b*]thieno[2',3':4,5]thieno[3,2-*d*]thiophene (1b). *R*_f (Hexane/AcOEt = 4:1) = 0.51. Mp 169.5-171.0°C. ¹H NMR (400 MHz, DMSO-*d*⁶): δ = 7.76 (d, *J* = 5.1 Hz, 2H), 7.56 (d, *J* = 5.1 Hz, 2H). ¹³C NMR (100 MHz, DMSO-*d*⁶): δ = 141.70, 141.10, 128.31, 127.21, 121.45, 115.32. MS (EI, 70 eV); *m/z* (%): 252 (100) [M⁺]. Anal. Calcd for C₁₀H₄S₄: C, 47.59; H, 1.60. Found: C, 47.65; H, 1.91.

X-Ray structure of compound 1a:

Table 1. Crystal data and structure refinement for bal02.

Identification code	bal02
Empirical formula	C ₁₀ H ₄ S ₄
Formula weight	252.37
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, C222(1)
Unit cell dimensions	a = 4.776(1) Å α = 90 deg. b = 13.918(3) Å β = 90 deg. c = 14.700(3) Å γ = 90 deg.
Volume	977.1(4) Å ³
Z, Calculated density	4, 1.716 Mg/m ³
Diffractometer	CAD4
Collection method	$\theta/2\theta$
Radiation type	MoK α
Radiation	monochromator filter
Standards number	3
Standards interval time	100 min
Standards interval count	?
Standards decay	0.3 %

Theta range for data collection	2.77 to 25.97 deg.
Limiting indices	$-5 \leq h \leq 0$, $-16 \leq k \leq 0$, $-18 \leq l \leq 18$
Reflections collected / unique	1105 / 958 [R(int) = 0.0356]
Completeness to theta = 25.97	100.0 %
Absorption correction	None
Absorption coefficient	0.919 mm ⁻¹
F(000)	512
Crystal description	plate
Crystal colour	colorless
Crystal size	0.41 x 0.38 x 0.02 mm
Max. and min. transmission	0.9818 and 0.7044
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	958 / 0 / 74
Goodness-of-fit on	F ² 1.012
Final R indices [I > 2sigma(I)]	R1 = 0.0270, wR2 = 0.0671
R indices (all data)	R1 = 0.0350, wR2 = 0.0686
Absolute structure parameter	-0.17(13)
Extinction coefficient	0.0019(17)
Largest diff. peak and hole	0.292 and -0.268 e.A ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for bal02.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	5409(1)	3854(1)	4477(1)	45(1)
S(2)	2084(2)	5403(1)	3335(1)	49(1)
C(1)	2790(5)	2605(2)	3482(2)	40(1)
C(2)	1850(4)	3523(2)	3183(2)	36(1)
C(3)	0	3896(2)	2500	35(1)
C(4)	4710(5)	2683(2)	4165(2)	45(1)
C(5)	3100(5)	4261(2)	3671(2)	40(1)
C(6)	0	4888(2)	2500	43(1)

Table 3. Bond lengths [Å] and angles [deg] for bal02.

S(1)-C(5)	1.715(2)
S(1)-C(4)	1.727(3)
S(2)-C(5)	1.733(2)
S(2)-C(6)	1.7353(15)
C(1)-C(4)	1.364(4)
C(1)-C(2)	1.424(3)
C(2)-C(5)	1.388(3)
C(2)-C(3)	1.435(3)
C(3)-C(6)	1.381(5)
C(3)-C(2)#1	1.435(3)
C(6)-S(2)#1	1.7353(15)
C(5)-S(1)-C(4)	90.24(12)
C(5)-S(2)-C(6)	89.07(12)
C(4)-C(1)-C(2)	111.6(2)
C(5)-C(2)-C(1)	111.6(2)
C(5)-C(2)-C(3)	111.0(2)
C(1)-C(2)-C(3)	137.3(2)
C(6)-C(3)-C(2)#1	111.22(15)

C(6)-C(3)-C(2)	111.22(15)
C(2)#1-C(3)-C(2)	137.6(3)
C(1)-C(4)-S(1)	113.57(19)
C(2)-C(5)-S(1)	112.91(18)
C(2)-C(5)-S(2)	114.26(18)
S(1)-C(5)-S(2)	132.81(15)
C(3)-C(6)-S(2)	114.38(10)
C(3)-C(6)-S(2)#1	114.38(10)
S(2)-C(6)-S(2)#1	131.2(2)

Symmetry transformations used to generate equivalent atoms:

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

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for bal02.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
S(1)	43(1)	48(1)	43(1)	-6(1)	-3(1)	2(1)
S(2)	57(1)	33(1)	56(1)	-5(1)	-7(1)	-2(1)
C(1)	44(1)	35(1)	42(1)	-2(1)	4(1)	3(1)
C(2)	32(1)	37(1)	40(1)	-2(1)	5(1)	1(1)
C(3)	36(1)	33(1)	36(1)	0	5(1)	0
C(4)	48(1)	43(1)	43(1)	-3(1)	-1(1)	6(1)
C(5)	38(1)	38(1)	43(1)	-1(1)	1(1)	0(1)
C(6)	48(2)	34(2)	46(2)	0	-1(1)	0

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for bal02.

	x	y	z	U(eq)
H(1)	2120(60)	2001(18)	3212(18)	41(7)
H(4)	5740(60)	2200(20)	4520(20)	56(8)

FW 270.418 Formula C₁₄H₆OS₄

Acquisition Time (sec) 1.8997

Comment

File Name

Frequency (MHz)

399.95

Nucleus

1H

Number of Transients 44

Original Points Count 9120

Points Count 16384

Sweep Width (Hz)

4800.77