Supporting Information

Perthio- and Perseleno-1,3-butadienes, -but-1-ene-3-yne and -[3]-cumulenes: One Step Syntheses from 1,4-Dilithio-1,3-butadiyne

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4c: Elemental analysis (%) calcd for $C_{16}H_{28}S_4$: C 55.12, H 8.09; found: C 54.94, H 7.82.

6a: Elemental analysis (%) calcd for $C_{10}H_{18}S_6$: C 36.32, H 5.49; found C 36.27, H 5.39.

7a: Elemental analysis (%) calcd for $C_{10}H_{18}Se_6$: C 19.63, H 2.96; found C 19.76, H 2.90.

9c: Elemental analysis (%) calcd for $C_{16}H_{28}Se_4$: C 35.84, H 5.26; found C 36.00, H 5.36.

3g: *t*BuSeSe*t*Bu was prepared in 8% yield by reaction of *t*BuBr with K_2Se_2 (from reaction of Se with $N_2H_4 \cdot H_2O$, KOH, and H_2O at 60-70 °C). From 3 eq *t*BuSeSe*t*Bu a yellow solid was obtained in 61% yield after chromatography on a column (hexane: ethyl acetate 20:1, 1% Et_3N) and using a Chromatotron (hexane, 1% Et_3N); mp 58 °C; 1H NMR (300 MHz) δ 1.55 (s); ^{13}C NMR (75 MHz) δ 31.9 (CH_3), 48.8 (CMe_3), 66.5, 89.5 ($C\equiv C$); ^{77}Se NMR (57 MHz) δ 392; LC-MS (70 eV) m/z 322 [M^+ for both ^{80}Se]; UV (CH_2Cl_2) λ_{max} 234, 272, 402 nm (ϵ 1200, 1102, 334); FT-IR (KBr) ν 2061 cm^{-1} ($C\equiv C$); elemental analysis (%) calcd for $C_{12}H_{18}Se_2$: C 45.01, H 5.67; found C 45.15, H 5.78.

4a: From 2 eq MeSSMe a yellow oil was obtained in 81% yield after chromatography on a column (hexane: ethyl acetate 20:1, 1% Et_3N) and using a Chromatotron (hexane, 1% Et_3N); 1H NMR (300 MHz) δ 2.39 (s); ^{13}C NMR (75 MHz) δ 18.0 (CH_3), 110.0, 146.1 ($C=C$); GC-MS (70 eV) m/z 236 [M^+]; UV (CH_2Cl_2) λ_{max} 232, 282, 352, 388 nm; FT-IR (KBr) ν 2028, 1566 cm^{-1} .

4b: From 2 eq EtSSEt a yellow oil was obtained in 78% yield after chromatography on a column (hexane: ethyl acetate 20:1, 1% Et_3N) and using a Chromatotron (hexane, 1% Et_3N); 1H NMR (300 MHz) δ 1.31 (t, J = 7.4, 12H, CH_3), 2.87 (q, J = 7.4, 8H, CH_2); ^{13}C NMR (75 MHz) δ 14.5 (CH_3), 29.0 (CH_2), 107.3, 146.6 ($C=C$); GC-MS (70 eV) m/z 292 [M^+]; UV (CH_2Cl_2) λ_{max} 232, 284, 352, 388 nm (ϵ 1447, 1282, 2129, 3768); FT-IR (KBr) ν 2029, 1561 cm^{-1} .

4d/8d: From 2 eq *i*PrSS*i*Pr a yellow oil was obtained which after chromatography on a column (hexane: ethyl acetate 20:1, 1% Et₃N) and using a Chromatotron (hexane, 1% Et₃N) gave **4d** (67%) and **8d** (17%) as yellow oils. **4d:** ¹H NMR (300 MHz) δ 1.30 (d, *J* = 6.6, 24H, CH₃), 3.39 (septet, *J* = 6.6, 4H, CHMe₂); ¹³C NMR (75 MHz) δ 22.7 (CH₃), 39.1 (CHMe₂), 107.5, 147.9 (C=C); GC-MS (70 eV) *m/z* 348 [M⁺]; UV (CH₂Cl₂): λ_{max} 232, 284, 352, 390 nm; FT-IR (KBr) ν 2032, 1562 cm⁻¹; elemental analysis (%) calcd for C₁₆H₂₈S₄: C 55.12, H 8.09; found C 54.96, H 7.83. **8d:** ¹H NMR (300 MHz) δ 1.23 (d, *J* = 6.3, 6H, CH₃), 1.25 (d, *J* = 6.6, 6H, CH₃), 1.41 (d, *J* = 6.9, 12H, CH₃), 3.18-3.60 (m, 4H, CHMe₂); ¹³C NMR (75 MHz) δ 22.8, 22.9, 23.2, 23.3 (CH₃), 38.1, 39.0, 39.3, 40.6 (CHMe₂), 88.2, 113.3 (C≡C), 126.6, 134.3 (C=C); FT-IR (KBr) ν 2032 (C≡C), 1562 (C=C) cm⁻¹; elemental analysis (%) calcd for C₁₆H₂₈S₄: C 55.12, H 8.09; found C 55.38, H 8.39.

4e: From 3 eq *n*BuSS*n*Bu a yellow oil was obtained in 67% yield after column chromatography (hexane: ethyl acetate 20:1, 1% Et₃N); ¹H NMR (300 MHz) δ 0.90 (t, *J* = 7.3, 12H, CH₃), 1.42 (m, 8H, CH₂), 1.62 (m, 8H, CH₂), 2.86 (t, *J* = 7.3, 8H, CH₂Pr); ¹³C NMR (75 MHz) δ 13.6 (CH₃), 21.8, 31.2, 34.5 (CH₂), 107.9, 146.8 (C=C); GC-MS (70 eV) *m/z* 404 [M⁺]; UV (CH₂Cl₂) λ_{max} 232, 282, 352, 388 nm (ε 1370, 1176, 2152, 3536); FT-IR (KBr) ν 2032, 1562 cm⁻¹.

6b: From 3 eq EtSSEt after 12 h at reflux, a yellow oil was obtained in 61% yield after chromatography on a column (hexane: ethyl acetate 40:1, 1% Et₃N) and using a Chromatotron (hexane, 1% Et₃N); ¹H NMR (300 MHz) δ 1.16 (t, *J* = 7.2, 6H, CH₃), 1.19 (t, *J* = 7.2, 6H, CH₃), 1.29 (t, *J* = 7.2, 6H, CH₃), 2.59-2.93 (m, 12H, CH₂); ¹³C NMR (75 MHz) δ 13.6, 14.9, 15.4 (CH₃), 26.6, 28.0, 28.3 (CH₂), 129.8, 141.5 (C=C); LC-MS (70 eV) *m/z* 414 [M⁺], 354 (M – Et); UV (CH₂Cl₂) λ_{max} 238, 272, 314, 354 nm (ε 2179, 2171, 2492, 2114); FT-IR (KBr) ν 1684, 1654 cm⁻¹.

6f/8f: From 3 eq PhSSPh column chromatography of the product (hexane: ethyl acetate 20:1, 1% Et₃N) gave **6f** (42%) and **8f** (4%) as yellow solids. **6f:** mp 132-134 °C; ¹H NMR (300 MHz) δ 6.80-7.81 (m); ¹³C NMR (75 MHz) δ 126.8, 127.1, 127.9, 128.1, 128.4, 128.9, 131.4, 132.2, 132.5, 133.2, 133.3, 134.5, 135.0, 138.7; GC-MS (70 eV) *m/z* 703 [M⁺], 593 (M-SPh); UV (CH₂Cl₂) λ_{max} 214, 220, 262, 316, 384 (ε 614, 598, 1247, 1284, 1234); FT-IR (KBr) ν 1655,

1580, 745, 730 cm^{-1} ; elemental analysis (%) calcd for $\text{C}_{40}\text{H}_{30}\text{S}_6$: C 68.33, H 4.30; found C 68.19, H 4.26. **8f**: mp 80-81 $^{\circ}\text{C}$; ^1H NMR (300 MHz) δ 7.07-7.57 (m); ^{13}C NMR (75 MHz) δ 87.6, 94.9 (C $\equiv$ C), 126.2, 126.5, 126.8, 127.3, 127.6, 128.4, 128.6, 128.7, 128.9, 129.1, 131.2, 131.7, 132.1, 133.0, 133.2, 133.5, 134.1, 135.5; GC-MS (70 eV) m/z 484 [M^+]; UV (CH_2Cl_2) λ_{max} 214, 264, 318, 388 (ϵ 419, 983, 1043, 1284, 1010); FT-IR (KBr) ν 2148 (C $\equiv$ C), 1652, 1589 (C=C), 798 (Ph) cm^{-1} .

7b: EtSeSeEt was prepared in 66% yield by reaction of EtBr with K_2Se_2 (from reaction of Se with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, KOH, and H_2O at 60-70 $^{\circ}\text{C}$). From 3 eq EtSeSeEt a yellow solid was obtained in 63% yield after chromatography on a column (hexane: ethyl acetate 40:1, 1% Et_3N) and using a Chromatotron (hexane, 1% Et_3N); mp 48-49 $^{\circ}\text{C}$; ^1H NMR (300 MHz) δ 1.35 (t, $J = 7.5$, 6H, CH_3), 1.38 (t, $J = 7.5$, 6H, CH_3), 1.52 (t, $J = 7.5$, 6H, CH_3), 2.72 (q, $J = 7.5$, 4H, CH_2), 2.75 (q, $J = 7.5$, 4H, CH_2), 2.82 (q, $J = 7.5$, 4H, CH_2); ^{13}C NMR (75 MHz) δ 14.1, 15.8, 16.1 (CH_3), 22.1, 23.9, 24.3 (CH_2), 115.4, 141.5 (C=C); ^{77}Se NMR (57 MHz) δ 320, 392, 409; GC-MS (70 eV) m/z 592 [$\text{M}^+ - \text{SeEt}$; for all ^{80}Se]; UV (CH_2Cl_2) λ_{max} 236, 318, 356, 362 nm (ϵ 1886, 2143, 1847, 1845); FT-IR (KBr) ν 1654 (C=C), 1449, 1374, 1228, 1094, 966 cm^{-1} ; elemental analysis (%) calcd for $\text{C}_{16}\text{H}_{30}\text{Se}_6$: C 27.60, H 4.34; found C 27.69, H 4.30.

7c: From 3 eq $n\text{PrSeSenPr}$ a yellow oil was obtained in 62% yield after chromatography on a column (hexane: ethyl acetate 40:1, 1% Et_3N) and using a Chromatotron (hexane, 1% Et_3N); ^1H NMR (300 MHz) δ 0.95 (t, $J = 7.2$, 6H, CH_3), 0.97 (t, $J = 7.2$, 6H, CH_3), 1.00 (t, $J = 7.2$, 6H, CH_3), 1.58-1.91 (m, 12H, CH_2), 2.61-2.95 (m, 12H, CH_2); ^{13}C NMR (75 MHz) δ 14.6, 14.7, 14.8 (CH_3), 22.8, 24.0, 24.1, 30.5, 32.4, 32.7 (CH_2), 115.8, 141.0 (C=C); ^{77}Se NMR (57 MHz) δ 286, 359, 387; LC-MS (70 eV) m/z 780 [M^+ for all ^{80}Se]; UV (CH_2Cl_2) λ_{max} 236, 320, 368 nm (ϵ 839, 895, 839); FT-IR (KBr) ν 1636, 1653 (C=C) cm^{-1} .

7f/9f: From 3 eq PhSeSePh column chromatography of the product (hexane: toluene 40:1, 1% Et_3N) gave **7f** (34%) as a yellow solid and **9f** (11%) as a brown oil. **7f**: mp 106-108 $^{\circ}\text{C}$; ^1H NMR (300 MHz) δ 6.96-7.91 (m); ^{13}C NMR (75 MHz) δ 122.8, 140.8 (olefinic), 127.1, 127.6, 127.7, 128.2, 128.4, 128.8, 128.9, 129.2, 130.0, 131.1, 131.3, 131.5 (aromatic); ^{77}Se NMR (57 MHz) δ 467, 530, 542; UV (CH_2Cl_2) λ_{max} 268, 318, 366 nm (ϵ 2750, 2964, 2760); FT-IR (KBr) ν 1576

(C=C), 733 (Ph) cm^{-1} ; elemental analysis (%) calcd for $\text{C}_{40}\text{H}_{30}\text{Se}_6$: C 48.80, H 3.07; found C 49.00, H 3.10. **9f**: ^1H NMR (300 MHz) δ 7.10-7.69 (m); ^{13}C NMR (75 MHz) δ 83.1, 101.1 (C $\equiv$ C), 126.9, 127.6, 127.7, 128.5, 128.6, 128.7, 128.9, 129.0, 129.1, 129.2, 129.4, 129.7, 130.7, 131.3, 131.5, 133.1, 133.9, 136.0; ^{77}Se NMR (57 MHz) δ 287, 482, 542, 563; UV (CH_2Cl_2) λ_{max} 266, 314, 380 nm (ϵ 3138, 3382, 3173); FT-IR (KBr) ν 2121 (C $\equiv$ C), 1698, 1632, 1576 (C=C), 733, 688, 667 (Ph) cm^{-1} ; elemental analysis (%) calcd for $\text{C}_{28}\text{H}_{20}\text{Se}_4$: C 50.02, H 3.00; found C 50.03, H 3.09.

STRUCTURE DETERMINATION SUMMARY for hexa(methylthio)-1,3-butadieneCrystal Data

Empirical Formula	$C_{10}H_{18}S_6$
Color; Habit	Pale Yellow Prism
Crystal size (mm)	0.40x0.55x0.60
Crystal System	Triclinic
Space Group	$P(-1)$
Unit Cell Dimensions	$a = 7.227(2) \text{ \AA}$ $b = 9.298(3) \text{ \AA}$ $c = 13.294(5) \text{ \AA}$ $\alpha = 110.00(3)^\circ$ $\beta = 112.39(3)^\circ$ $\gamma = 105.93(3)^\circ$
Volume	$791.0(5) \text{ \AA}^3$
Z	2
Formula weight	330.6
Density(calc.)	1.388 g/cm^3
Absorption Coefficient	8.39 cm^{-1}
$F(000)$	348

Data Collection

Diffractometer Used	Siemens (Bruker) R3m
Radiation	MoK α ($\lambda = 0.71073 \text{ \AA}$)
Temperature (K)	296
Monochromator	Highly oriented graphite crystal
2 θ Range	3.0 to 50.0 $^\circ$
Scan Type	$\omega/2\theta$
Scan Speed ω	Variable; 3.08 to 19.53 $^\circ$ /min. in ω
Scan Range (ω)	1.75 $^\circ$
Background Measurement stationary	Stationary crystal and counter at beginning and end of scan, each for 50% of total scan time
Standard Reflections	2 measured every 200 reflections
Index Ranges $l \leq 15$	$-8 \leq h \leq 8, \quad -11 \leq k \leq 10, \quad 0 \leq$
Reflections Collected	2913
Independent Reflections	2781 ($R_{\text{int}} = 3.65\%$)
Observed Reflections	2368 ($F' > 4.0\sigma(F')$)
Absorption Correction ($T_{\text{min}}/T_{\text{max}}$)	0.839/0.923

Solution and Refinement

System Used Version)	Siemens SHELXTL PLUS (PC
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o - F_c)^2$
Absolute Structure	N/A
Extinction Correction	N/A
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$
Number of Parameters Refined	145
Final R Indices (obs. data)	R = 3.87 %, wR = 5.94 %
R Indices (all data)	R = 4.63 %, wR = 6.47 %
Goodness-of-Fit	1.54
Largest and Mean Δ/σ	0.000, 0.000
Data-to-Parameter Ratio	16.3:1
Largest Difference Peak	0.44 eÅ ⁻³
Largest Difference Hole	-0.26 eÅ ⁻³

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for hexa(methylthio)-1,3-butadiene

	x	y	z	U(eq) *
S (1)	4887 (1)	8083 (1)	3718 (1)	46 (1)
S (2)	2684 (1)	5551 (1)	4533 (1)	48 (1)
S (3)	3082 (1)	5781 (1)	1341 (1)	54 (1)
S (4)	-1586 (1)	3536 (1)	1735 (1)	53 (1)
S (5)	-746 (1)	358 (1)	1510 (1)	52 (1)
S (6)	3606 (1)	2225 (1)	2389 (1)	51 (1)
C (1)	3255 (4)	6135 (3)	3442 (2)	35 (1)
C (2)	2427 (4)	5142 (3)	2407 (2)	34 (1)
C (3)	848 (4)	3570 (3)	2101 (2)	35 (1)
C (4)	1191 (4)	2206 (3)	2018 (2)	37 (1)
C (5)	6827 (4)	8336 (4)	4766 (3)	57 (1)
C (6)	2173 (5)	7268 (4)	5444 (3)	55 (1)
C (7)	2319 (6)	3959 (4)	158 (3)	73 (2)
C (8)	-1606 (5)	5446 (4)	2621 (3)	67 (2)
C (9)	-450 (6)	-435 (4)	2542 (3)	73 (2)
C (10)	3742 (5)	419 (4)	1372 (3)	69 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table S2. Bond lengths (Å) for hexa(methylthio)-1,3-butadiene

S(1)-C(1)	1.762 (3)	S(1)-C(5)	1.794 (4)
S(2)-C(1)	1.758 (3)	S(2)-C(6)	1.797 (4)
S(3)-C(2)	1.767 (3)	S(3)-C(7)	1.778 (3)
S(4)-C(3)	1.773 (3)	S(4)-C(8)	1.768 (4)
S(5)-C(4)	1.758 (2)	S(5)-C(9)	1.788 (5)
S(6)-C(4)	1.766 (3)	S(6)-C(10)	1.794 (4)
C(1)-C(2)	1.338 (3)	C(2)-C(3)	1.484 (3)
C(3)-C(4)	1.329 (4)		

Table S3. Bond angles ($^{\circ}$) for hexa(methylthio)-1,3-butadiene

C(1)-S(1)-C(5)	103.5(2)	C(1)-S(2)-C(6)	102.6(2)
C(2)-S(3)-C(7)	104.1(2)	C(3)-S(4)-C(8)	103.6(1)
C(4)-S(5)-C(9)	102.3(2)	C(4)-S(6)-C(10)	104.0(1)
S(1)-C(1)-S(2)	119.4(1)	S(1)-C(1)-C(2)	119.5(2)
S(2)-C(1)-C(2)	121.0(2)	S(3)-C(2)-C(1)	119.1(2)
S(3)-C(2)-C(3)	117.3(2)	C(1)-C(2)-C(3)	123.3(3)
S(4)-C(3)-C(2)	116.7(2)	S(4)-C(3)-C(4)	119.8(2)
C(2)-C(3)-C(4)	123.3(3)	S(5)-C(4)-S(6)	119.4(2)
S(5)-C(4)-C(3)	120.3(2)	S(6)-C(4)-C(3)	120.3(2)

Table S4. Anisotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for hexa(methylthio)-1,3-butadiene

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	49(1)	29(1)	49(1)	0(1)	3(1)	14(1)
S(2)	64(1)	38(1)	43(1)	10(1)	10(1)	20(1)
S(3)	72(1)	42(1)	41(1)	2(1)	14(1)	17(1)
S(4)	35(1)	43(1)	73(1)	12(1)	1(1)	14(1)
S(5)	42(1)	31(1)	69(1)	-1(1)	-8(1)	16(1)
S(6)	37(1)	39(1)	63(1)	12(1)	-5(1)	9(1)
C(1)	35(1)	29(1)	41(2)	6(1)	10(1)	16(1)
C(2)	36(1)	28(1)	38(1)	7(1)	8(1)	12(1)
C(3)	32(1)	30(1)	38(1)	4(1)	4(1)	12(1)
C(4)	32(1)	33(1)	38(1)	6(1)	1(1)	10(1)
C(5)	43(2)	51(2)	58(2)	5(1)	-3(1)	9(2)
C(6)	63(2)	53(2)	46(2)	17(2)	19(2)	13(1)
C(7)	95(3)	60(2)	42(2)	0(2)	17(2)	12(2)
C(8)	58(2)	53(2)	93(3)	34(2)	8(2)	19(2)
C(9)	82(3)	55(2)	78(3)	1(2)	23(2)	36(2)
C(10)	49(2)	57(2)	88(3)	23(2)	15(2)	7(2)

The anisotropic displacement exponent takes the form:

$$-2\pi^2 (h^2 a^{*2} U_{11} + \dots + 2hka^*b^*U_{12})$$

Table S5. H-Atom coordinates ($\times 10^4$) and isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for hexa(methylthio)-1,3-butadiene

	x	y	z	U
H(5A)	7800	9379	4974	80
H(5B)	7415	7508	4491	80
H(5C)	6303	8250	5390	80
H(6A)	1836	7071	6079	80
H(6B)	1096	7439	5079	80
H(6C)	3314	8212	5661	80
H(7A)	2622	4194	-470	80
H(7B)	930	3444	47	80
H(7C)	2998	3251	262	80
H(8A)	-2887	5533	2476	80
H(8B)	-651	6286	2500	80
H(8C)	-1295	5554	3365	80
H(9A)	-1452	-1463	2339	80
H(9B)	-571	300	3225	80
H(9C)	818	-570	2615	80
H(10A)	5025	334	1514	80
H(10B)	3504	467	664	80
H(10C)	2772	-508	1391	80

STRUCTURE DETERMINATION SUMMARY for hexa(phenylthio)-1,3-butadieneCrystal Data

Empirical Formula	$C_{40}H_{30}S_6$
Color; Habit	Pale Yellow Prism
Crystal size (mm)	0.50x0.55x0.80
Crystal System	Monoclinic
Space Group	$P2(1)/n$
Unit Cell Dimensions	$a = 16.071(3) \text{ \AA}$ $b = 11.203(2) \text{ \AA}$ $c = 19.730(4) \text{ \AA}$ $\beta = 92.34(1)^\circ$
Volume	$3549.3(11) \text{ \AA}^3$
Z	4
Formula weight	703.0
Density(calc.)	1.316 g/cm^3
Absorption Coefficient	4.14 cm^{-1}
$F(000)$	1464

Data Collection

Diffractometer Used	Siemens (Bruker) R3m
Radiation	MoK α (λ = 0.71073 Å)
Temperature (K)	296
Monochromator	Highly oriented graphite crystal
2 θ Range	3.0 to 50.0°
Scan Type	$\omega/2\theta$
Scan Speed	Variable; 3.08 to 19.53°/min. in ω
Scan Range (ω)	1.00°
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 50% of total scan time
Standard Reflections	2 measured every 200 reflections
Index Ranges $l \leq 23$	$-19 \leq h \leq 19, \quad 0 \leq k \leq 13, \quad 0 \leq$
Reflections Collected	6413
Independent Reflections	6220 ($R_{\text{int}} = 1.50\%$)
Observed Reflections	3902 ($F > 4.0\sigma(F)$)
Absorption Correction ($T_{\text{min}}/T_{\text{max}}$)	0.856/0.878

Solution and Refinement

System Used	Siemens SHELXTL PLUS (PC Version)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o - F_c)^2$
Absolute Structure	N/A
Extinction Correction	N/A
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0005F^2$
Number of Parameters Refined	415
Final R Indices (obs. data)	R = 4.67 %, wR = 5.28 %
R Indices (all data)	R = 8.10 %, wR = 5.87 %
Goodness-of-Fit	1.43
Largest and Mean Δ/σ	0.000, 0.000
Data-to-Parameter Ratio	9.4:1
Largest Difference Peak	0.54 eÅ ⁻³
Largest Difference Hole	-0.43 eÅ ⁻³

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coeff. ($\text{\AA}^2 \times 10^3$) for hexa(phenylthio)-1,3-butadiene

	x	y	z	U(eq) *
S (1)	4343 (1)	369 (1)	2533 (1)	60 (1)
S (2)	4920 (1)	942 (1)	1102 (1)	73 (1)
S (3)	4524 (1)	3649 (1)	1360 (1)	69 (1)
S (4)	3334 (1)	3818 (1)	2734 (1)	101 (1)
S (5)	5755 (1)	2275 (1)	3289 (1)	62 (1)
S (6)	4519 (1)	3914 (1)	3954 (1)	76 (1)
C (1)	4583 (2)	1400 (3)	1895 (2)	50 (1)
C (2)	4510 (2)	2574 (3)	2021 (2)	51 (1)
C (3)	4302 (2)	3067 (3)	2688 (2)	56 (1)
C (4)	4806 (2)	3068 (3)	3249 (2)	56 (1)
C (5)	4971 (2)	-896 (3)	2379 (2)	50 (1)
C (6)	5820 (3)	-816 (4)	2316 (2)	65 (1)
C (7)	6272 (3)	-1827 (4)	2202 (2)	77 (2)
C (8)	5890 (4)	-2919 (4)	2167 (2)	86 (2)
C (9)	5053 (3)	-3002 (4)	2242 (2)	79 (2)
C (10)	4589 (3)	-1991 (3)	2345 (2)	64 (1)
C (11)	4337 (3)	-353 (3)	903 (2)	59 (1)
C (12)	4746 (3)	-1283 (4)	613 (2)	72 (2)
C (13)	4307 (5)	-2263 (4)	394 (2)	100 (2)
C (14)	3485 (5)	-2349 (5)	483 (3)	119 (3)
C (15)	3069 (3)	-1422 (5)	777 (2)	106 (2)
C (16)	3491 (3)	-424 (4)	979 (2)	82 (2)
C (17)	5576 (2)	3993 (3)	1243 (2)	52 (1)
C (18)	5697 (3)	4948 (3)	815 (2)	74 (2)
C (19)	6486 (3)	5282 (4)	667 (3)	96 (2)
C (20)	7156 (3)	4714 (4)	942 (3)	98 (2)
C (21)	7039 (3)	3765 (4)	1360 (2)	87 (2)
C (22)	6257 (3)	3399 (4)	1512 (2)	71 (2)
C (23)	2736 (2)	3331 (4)	2021 (2)	65 (1)
C (24)	2438 (3)	2182 (4)	1962 (2)	76 (2)
C (25)	1911 (3)	1879 (5)	1425 (3)	99 (2)
C (26)	1683 (4)	2716 (8)	966 (3)	122 (3)
C (27)	1969 (4)	3848 (8)	1023 (3)	128 (3)
C (28)	2497 (3)	4148 (4)	1547 (3)	95 (2)
C (29)	6464 (2)	3367 (3)	3616 (2)	58 (1)
C (30)	6973 (3)	3084 (4)	4163 (2)	80 (2)
C (31)	7547 (3)	3891 (6)	4408 (3)	108 (2)
C (32)	7625 (3)	4976 (6)	4107 (3)	108 (3)
C (33)	7131 (3)	5248 (4)	3559 (3)	105 (2)
C (34)	6550 (3)	4460 (4)	3312 (2)	86 (2)
C (35)	4441 (2)	2892 (4)	4624 (2)	66 (1)
C (36)	4307 (3)	1690 (5)	4552 (2)	96 (2)
C (37)	4247 (4)	984 (5)	5109 (3)	120 (3)
C (38)	4295 (3)	1444 (7)	5739 (3)	113 (3)
C (39)	4426 (3)	2598 (7)	5820 (3)	120 (3)
C (40)	4482 (3)	3329 (5)	5269 (2)	98 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table S7. Bond lengths (Å) for hexa(phenylthio)-1,3-butadiene

S(1)-C(1)	1.761 (3)	S(1)-C(5)	1.772 (4)
S(2)-C(1)	1.754 (3)	S(2)-C(11)	1.762 (4)
S(3)-C(2)	1.776 (3)	S(3)-C(17)	1.758 (4)
S(4)-C(3)	1.775 (4)	S(4)-C(23)	1.758 (4)
S(5)-C(4)	1.763 (4)	S(5)-C(29)	1.776 (4)
S(6)-C(4)	1.761 (4)	S(6)-C(35)	1.756 (4)
C(1)-C(2)	1.345 (5)	C(2)-C(3)	1.479 (5)
C(3)-C(4)	1.344 (5)	C(5)-C(6)	1.378 (6)
C(5)-C(10)	1.373 (5)	C(6)-C(7)	1.370 (6)
C(7)-C(8)	1.369 (7)	C(8)-C(9)	1.362 (8)
C(9)-C(10)	1.375 (6)	C(11)-C(12)	1.369 (5)
C(11)-C(16)	1.377 (6)	C(12)-C(13)	1.366 (7)
C(13)-C(14)	1.344 (11)	C(14)-C(15)	1.375 (9)
C(15)-C(16)	1.359 (8)	C(17)-C(18)	1.381 (5)
C(17)-C(22)	1.370 (5)	C(18)-C(19)	1.365 (7)
C(19)-C(20)	1.345 (7)	C(20)-C(21)	1.363 (7)
C(21)-C(22)	1.368 (6)	C(23)-C(24)	1.377 (6)
C(23)-C(28)	1.353 (7)	C(24)-C(25)	1.371 (7)
C(25)-C(26)	1.343 (9)	C(26)-C(27)	1.352 (12)
C(27)-C(28)	1.352 (8)	C(29)-C(30)	1.365 (5)
C(29)-C(34)	1.373 (6)	C(30)-C(31)	1.366 (7)
C(31)-C(32)	1.362 (9)	C(32)-C(33)	1.351 (8)
C(33)-C(34)	1.361 (7)	C(35)-C(36)	1.370 (7)
C(35)-C(40)	1.363 (6)	C(36)-C(37)	1.360 (7)
C(37)-C(38)	1.345 (8)	C(38)-C(39)	1.319 (11)
C(39)-C(40)	1.367 (8)		

Table S8. Bond angles ($^{\circ}$) for hexa(phenylthio)-1,3-butadiene

C(1)-S(1)-C(5)	105.0(2)	C(1)-S(2)-C(11)	105.0(2)
C(2)-S(3)-C(17)	106.7(2)	C(3)-S(4)-C(23)	105.3(2)
C(4)-S(5)-C(29)	102.2(2)	C(4)-S(6)-C(35)	105.8(2)
S(1)-C(1)-S(2)	122.0(2)	S(1)-C(1)-C(2)	119.1(2)
S(2)-C(1)-C(2)	118.9(3)	S(3)-C(2)-C(1)	121.6(2)
S(3)-C(2)-C(3)	114.2(2)	C(1)-C(2)-C(3)	123.7(3)
S(4)-C(3)-C(2)	116.9(2)	S(4)-C(3)-C(4)	117.3(3)
C(2)-C(3)-C(4)	125.6(3)	S(5)-C(4)-S(6)	119.3(2)
S(5)-C(4)-C(3)	121.8(3)	S(6)-C(4)-C(3)	118.8(3)
S(1)-C(5)-C(6)	122.4(3)	S(1)-C(5)-C(10)	117.9(3)
C(6)-C(5)-C(10)	119.7(3)	C(5)-C(6)-C(7)	119.7(4)
C(6)-C(7)-C(8)	120.4(4)	C(7)-C(8)-C(9)	120.0(5)
C(8)-C(9)-C(10)	120.2(4)	C(5)-C(10)-C(9)	120.0(4)
S(2)-C(11)-C(12)	117.4(3)	S(2)-C(11)-C(16)	122.8(3)
C(12)-C(11)-C(16)	119.6(4)	C(11)-C(12)-C(13)	119.6(5)
C(12)-C(13)-C(14)	120.9(5)	C(13)-C(14)-C(15)	119.9(6)
C(14)-C(15)-C(16)	120.0(5)	C(11)-C(16)-C(15)	119.9(4)
S(3)-C(17)-C(18)	114.3(3)	S(3)-C(17)-C(22)	126.9(3)
C(18)-C(17)-C(22)	118.9(4)	C(17)-C(18)-C(19)	119.9(4)
C(18)-C(19)-C(20)	121.3(4)	C(19)-C(20)-C(21)	119.0(5)
C(20)-C(21)-C(22)	121.1(4)	C(17)-C(22)-C(21)	119.8(4)
S(4)-C(23)-C(24)	122.3(3)	S(4)-C(23)-C(28)	118.3(4)
C(24)-C(23)-C(28)	119.1(4)	C(23)-C(24)-C(25)	119.9(4)
C(24)-C(25)-C(26)	119.4(5)	C(25)-C(26)-C(27)	121.1(6)
C(26)-C(27)-C(28)	119.8(6)	C(23)-C(28)-C(27)	120.8(5)
S(5)-C(29)-C(30)	118.9(3)	S(5)-C(29)-C(34)	122.0(3)
C(30)-C(29)-C(34)	119.1(4)	C(29)-C(30)-C(31)	120.0(4)
C(30)-C(31)-C(32)	120.6(5)	C(31)-C(32)-C(33)	119.3(5)
C(32)-C(33)-C(34)	120.9(5)	C(29)-C(34)-C(33)	120.1(4)
S(6)-C(35)-C(36)	125.4(3)	S(6)-C(35)-C(40)	117.8(3)
C(36)-C(35)-C(40)	116.7(4)	C(35)-C(36)-C(37)	120.3(4)
C(36)-C(37)-C(38)	121.3(6)	C(37)-C(38)-C(39)	119.4(6)
C(38)-C(39)-C(40)	120.4(5)	C(35)-C(40)-C(39)	121.7(5)

Table S9. Anisotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for hexa(phenylthio)-1,3-butadiene

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S (1)	78 (1)	56 (1)	48 (1)	-4 (1)	24 (1)	-5 (1)
S (2)	105 (1)	69 (1)	48 (1)	-7 (1)	30 (1)	-8 (1)
S (3)	64 (1)	65 (1)	77 (1)	5 (1)	3 (1)	14 (1)
S (4)	74 (1)	134 (1)	93 (1)	34 (1)	-11 (1)	-59 (1)
S (5)	70 (1)	51 (1)	64 (1)	4 (1)	-6 (1)	-8 (1)
S (6)	92 (1)	67 (1)	68 (1)	10 (1)	-7 (1)	-31 (1)
C (1)	57 (2)	55 (2)	39 (2)	-2 (2)	8 (2)	-7 (2)
C (2)	52 (2)	55 (2)	47 (2)	0 (2)	6 (2)	-4 (2)
C (3)	58 (2)	54 (2)	57 (2)	1 (2)	1 (2)	-15 (2)
C (4)	64 (2)	47 (2)	58 (2)	-5 (2)	4 (2)	-13 (2)
C (5)	64 (2)	52 (2)	35 (2)	-5 (2)	11 (2)	2 (2)
C (6)	73 (3)	69 (3)	53 (2)	-7 (2)	5 (2)	-5 (2)
C (7)	72 (3)	94 (3)	64 (3)	15 (3)	5 (2)	1 (2)
C (8)	118 (4)	75 (3)	65 (3)	31 (3)	4 (3)	0 (2)
C (9)	118 (4)	51 (2)	68 (3)	-2 (3)	6 (3)	0 (2)
C (10)	80 (3)	63 (3)	50 (2)	-9 (2)	9 (2)	2 (2)
C (11)	85 (3)	60 (2)	31 (2)	15 (2)	7 (2)	-3 (2)
C (12)	106 (3)	66 (3)	43 (2)	21 (2)	9 (2)	-5 (2)
C (13)	180 (6)	62 (3)	58 (3)	16 (4)	10 (3)	-6 (2)
C (14)	198 (7)	94 (4)	63 (3)	-52 (5)	-3 (4)	-19 (3)
C (15)	100 (4)	143 (5)	75 (3)	-32 (4)	-6 (3)	-29 (3)
C (16)	85 (3)	98 (3)	64 (3)	17 (3)	1 (2)	-26 (2)
C (17)	64 (2)	43 (2)	51 (2)	1 (2)	4 (2)	-5 (2)
C (18)	82 (3)	60 (2)	81 (3)	1 (2)	4 (2)	9 (2)
C (19)	109 (4)	77 (3)	105 (4)	-8 (3)	26 (3)	27 (3)
C (20)	75 (3)	96 (4)	124 (4)	-15 (3)	24 (3)	16 (3)
C (21)	69 (3)	94 (3)	98 (3)	2 (3)	6 (3)	18 (3)
C (22)	70 (3)	72 (3)	71 (3)	1 (2)	10 (2)	14 (2)
C (23)	49 (2)	83 (3)	62 (2)	17 (2)	4 (2)	-15 (2)
C (24)	65 (3)	84 (3)	81 (3)	16 (2)	6 (2)	0 (2)
C (25)	70 (3)	103 (4)	123 (4)	-5 (3)	8 (3)	-44 (4)
C (26)	82 (4)	202 (8)	80 (4)	30 (5)	-19 (3)	-43 (5)
C (27)	109 (5)	187 (7)	87 (4)	61 (5)	-13 (4)	24 (5)
C (28)	87 (4)	91 (3)	107 (4)	25 (3)	1 (3)	6 (3)
C (29)	60 (2)	58 (2)	54 (2)	5 (2)	-3 (2)	-8 (2)
C (30)	81 (3)	87 (3)	70 (3)	-6 (3)	-8 (2)	-1 (2)
C (31)	88 (4)	147 (5)	86 (4)	-14 (4)	-26 (3)	-19 (4)
C (32)	83 (4)	124 (5)	117 (5)	-36 (4)	6 (3)	-50 (4)
C (33)	112 (4)	74 (3)	128 (5)	-24 (3)	5 (4)	-12 (3)
C (34)	92 (3)	68 (3)	94 (3)	-7 (3)	-22 (3)	3 (3)
C (35)	55 (2)	84 (3)	58 (2)	0 (2)	-1 (2)	-25 (2)
C (36)	126 (4)	110 (4)	54 (3)	-35 (3)	11 (3)	-19 (3)
C (37)	150 (5)	122 (4)	90 (4)	-54 (4)	22 (4)	-2 (4)
C (38)	95 (4)	184 (7)	61 (3)	-26 (4)	14 (3)	4 (4)
C (39)	113 (4)	195 (7)	51 (3)	-8 (5)	-4 (3)	-41 (4)
C (40)	112 (4)	117 (4)	64 (3)	2 (3)	-12 (3)	-43 (3)

The anisotropic displacement exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12})$

Table S10. H-Atom coordinates ($\times 10^4$) and isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for hexa(phenylthio)-1,3-butadiene

	x	y	z	U
H(6)	6093	-55	2351	80
H(7)	6862	-1775	2147	80
H(8)	6211	-3624	2088	80
H(9)	4786	-3769	2224	80
H(10)	3999	-2053	2397	80
H(12)	5337	-1245	564	80
H(13)	4592	-2899	173	80
H(14)	3189	-3059	346	80
H(15)	2481	-1479	837	80
H(16)	3198	232	1172	80
H(18)	5226	5373	621	80
H(19)	6565	5937	363	80
H(20)	7709	4971	847	80
H(21)	7512	3341	1550	80
H(22)	6183	2729	1806	80
H(24)	2601	1594	2296	80
H(25)	1707	1076	1380	80
H(26)	1309	2507	593	80
H(27)	1802	4434	690	80
H(28)	2703	4950	1584	80
H(30)	6927	2319	4378	80
H(31)	7904	3689	4793	80
H(32)	8027	5544	4282	80
H(33)	7185	6011	3343	80
H(34)	6202	4666	2922	80
H(36)	4261	1346	4107	80
H(37)	4170	140	5050	80
H(38)	4233	938	6126	80
H(39)	4482	2926	6269	80
H(40)	4552	4171	5340	80