### **Electronic Supplementary Information**

#### Highly Selective Synthesis of Bis-sulfanyl Substituted Conjugated Dienes by Copper-Palladium Cooperative Catalysis

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Empirical formula	C <sub>32</sub> H <sub>30</sub> S <sub>2</sub> ( <b>CCDC</b> : 2023253)
Formula weight	478.70
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	$a = 8.7800(10) \text{ Å} \qquad \alpha = 90^{\circ}$
	$b = 12.5320(8) \text{ Å}$ $\beta = 92.22(2)^{\circ}$
	$c = 11.4990(6) \text{ Å} \qquad \gamma = 90^{\circ}$
Volume	1264.30(18) Å <sup>3</sup>
Ζ	2
Density (calculated)	$1.257 \text{ mg/m}^3$
Absorption coefficient	$0.229 \text{ mm}^{-1}$
F(000)	508
Crystal size	$0.29 \times 0.25 \times 0.22 \text{ mm}^3$
Theta range for data collection	2.32 to 25.00 °
Index ranges	-10<=h<=10, -7<=k<=14, -13<=l<=13
Reflections collected	6150
Independent reflections	2225 [R(int) = 0.0719]
Completeness to theta = $25.00^{\circ}$	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9512 and 0.9364
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2223 / 0 / 154
Goodness-of-fit on F <sup>2</sup>	1.089
Final R indices [I>2sigma(I)]	$R_1 = 0.0550, wR_2 = 0.1021$
R indices (all data)	$R_1 = 0.0969, wR_2 = 0.1109$
Largest diff. peak and hole	0.334 and -0.231 e.Å <sup>-3</sup>

## 1. Crystal data of compound 4b

# 2. <sup>1</sup>H and <sup>13</sup>C NMR Spectra of 4



Figure S-1<sup>1</sup>H NMR spectrum of compound 4a (300 MHz, CDCl<sub>3</sub>)



Figure S-2<sup>13</sup>C NMR spectrum of compound 4a (75 MHz, CDCl<sub>3</sub>)



Figure S-3 <sup>1</sup>H NMR spectrum of compound 4a' (300 MHz, CDCl<sub>3</sub>)





Figure S-5 <sup>1</sup>H NMR spectrum of compound 4b (300 MHz, CDCl<sub>3</sub>)











Figure S-9 <sup>1</sup>H NMR spectrum of compound 4d (300 MHz, CDCl<sub>3</sub>)





Figure S-11 <sup>1</sup>H NMR spectrum of compound 4e (300 MHz, CDCl<sub>3</sub>)





Figure S-13 <sup>1</sup>H NMR spectrum of compound 4f (300 MHz, CDCl<sub>3</sub>)



Figure S-14 <sup>13</sup>C NMR spectrum of compound 4f (75 MHz, CDCl<sub>3</sub>)



Figure S-15 <sup>1</sup>H NMR spectrum of compound 4g (300 MHz, CDCl<sub>3</sub>)





Figure S-17<sup>1</sup>H NMR spectrum of compound 4h (300 MHz, CDCl<sub>3</sub>)





Figure S-19<sup>1</sup>H NMR spectrum of compound 4i (300 MHz, CDCl<sub>3</sub>)





Figure S-21 <sup>1</sup>H NMR spectrum of compound 4j (300 MHz, CDCl<sub>3</sub>)





Figure S-23 <sup>1</sup>H NMR spectrum of compound 4k (300 MHz, CDCl<sub>3</sub>)



Figure S-24<sup>13</sup>C NMR spectrum of compound 4k (75 MHz, CDCl<sub>3</sub>)



Figure S-25 <sup>1</sup>H NMR spectrum of compound 4l (300 MHz, CDCl<sub>3</sub>)



Figure S-26<sup>13</sup>C NMR spectrum of compound 4l (75 MHz, CDCl<sub>3</sub>)



Figure S-27 <sup>1</sup>H NMR spectrum of compound 4m (300 MHz, CDCl<sub>3</sub>)





**Figure S-29** <sup>1</sup>H NMR spectrum of compound **4n** (300 MHz, CDCl<sub>3</sub>)



Figure S-30<sup>13</sup>C NMR spectrum of compound 4n (75 MHz, CDCl<sub>3</sub>)



Figure S-31 <sup>1</sup>H NMR spectrum of compound 40 (300 MHz, CDCl<sub>3</sub>)





Figure S-33 <sup>1</sup>H NMR spectrum of compound 4p (300 MHz, CDCl<sub>3</sub>)





Figure S-35 <sup>1</sup>H NMR spectrum of compound 4q (300 MHz, CDCl<sub>3</sub>)





Figure S-37 <sup>1</sup>H NMR spectrum of compound 4r (300 MHz, CDCl<sub>3</sub>)





Figure S-39 <sup>1</sup>H NMR spectrum of compound 4s (300 MHz, CDCl<sub>3</sub>)





Figure S-41 <sup>1</sup>H NMR spectrum of compound 4t (300 MHz, CDCl<sub>3</sub>)





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Figure S-45 <sup>1</sup>H NMR spectrum of compound 4v (300 MHz, CDCl<sub>3</sub>)

