

SUPPORTING INFORMATION

Pyrrolo[2,3-*d*:5,4-*d'*]bisthiazoles: Alternate Synthetic Routes and a Comparative Study to Analogous Fused-ring Bithiophenes

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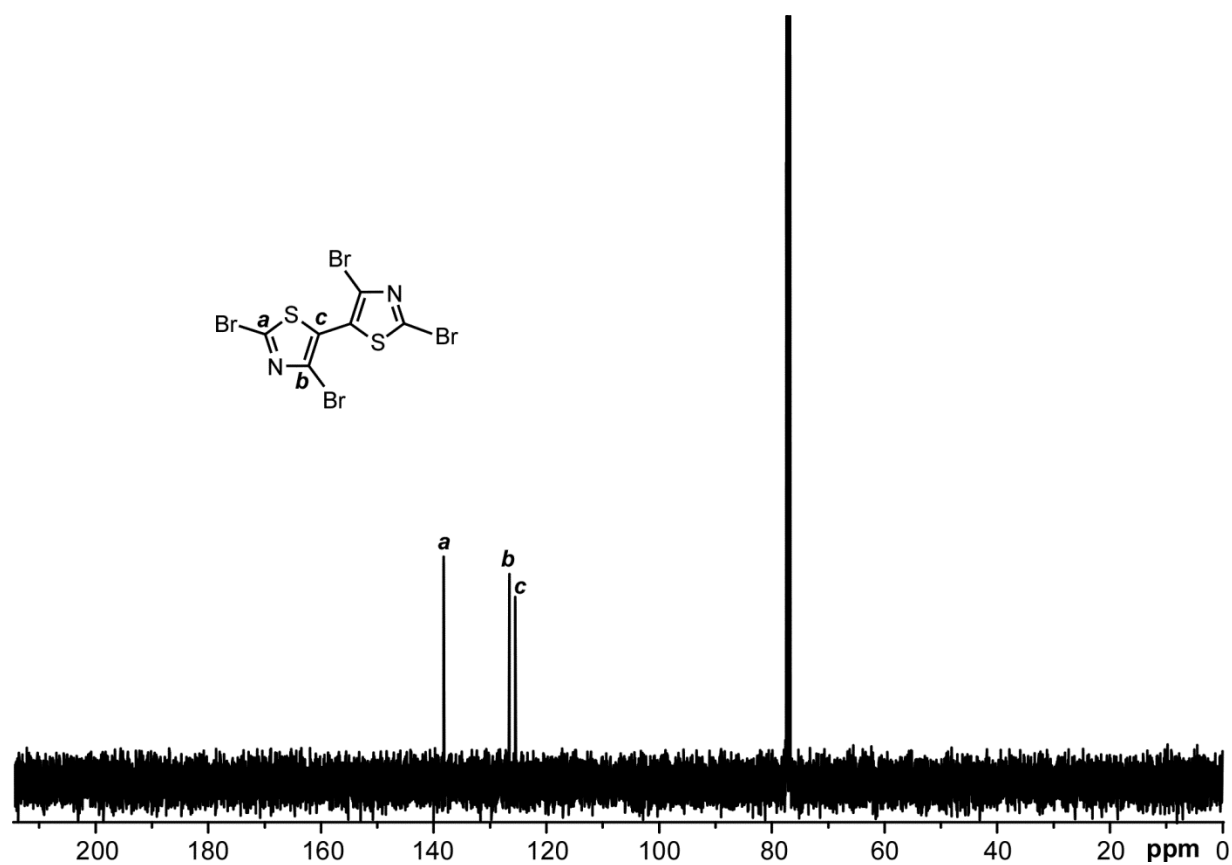


Figure S1. ^{13}C NMR spectrum of 2

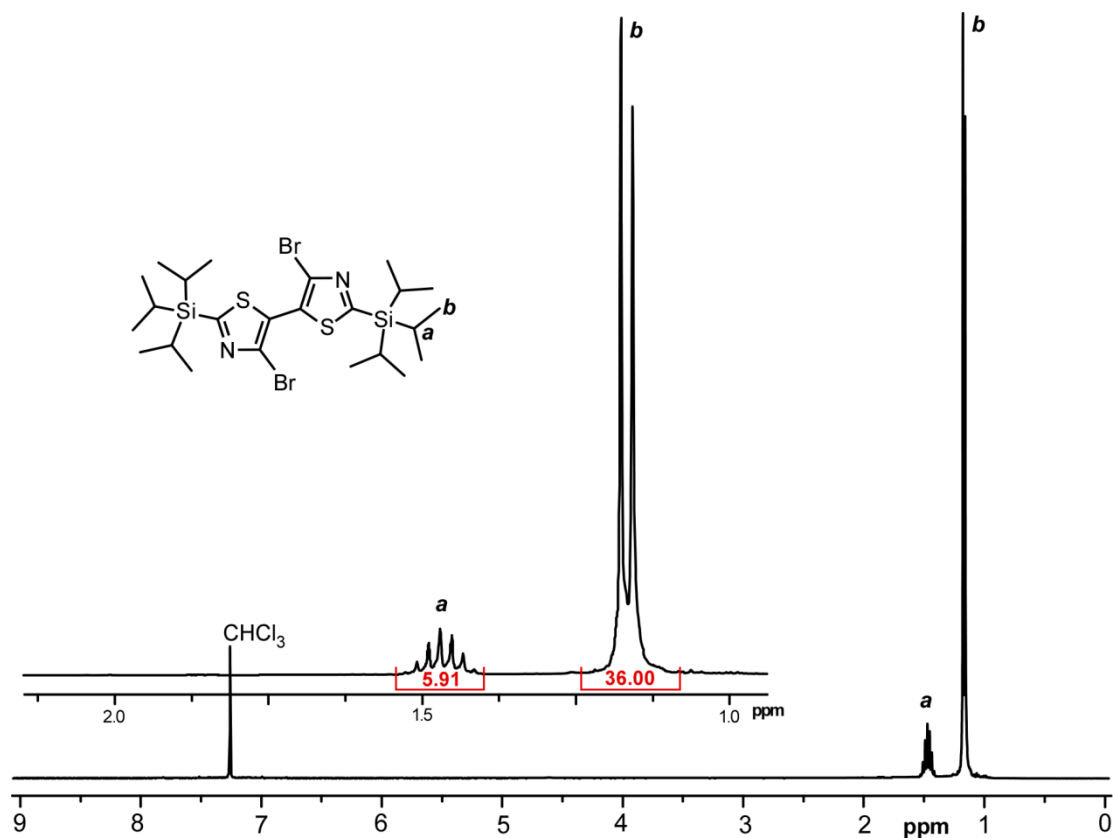


Figure S2. ^1H NMR spectrum of 3

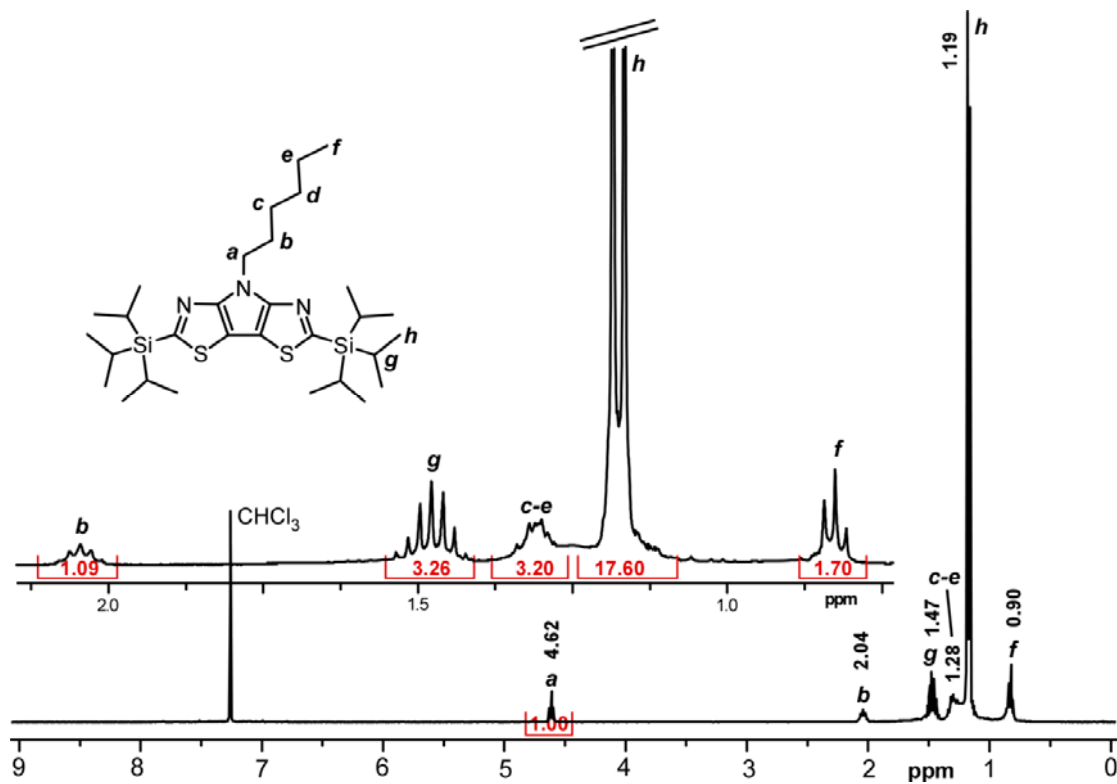


Figure S3. ^1H NMR spectrum of **4a**

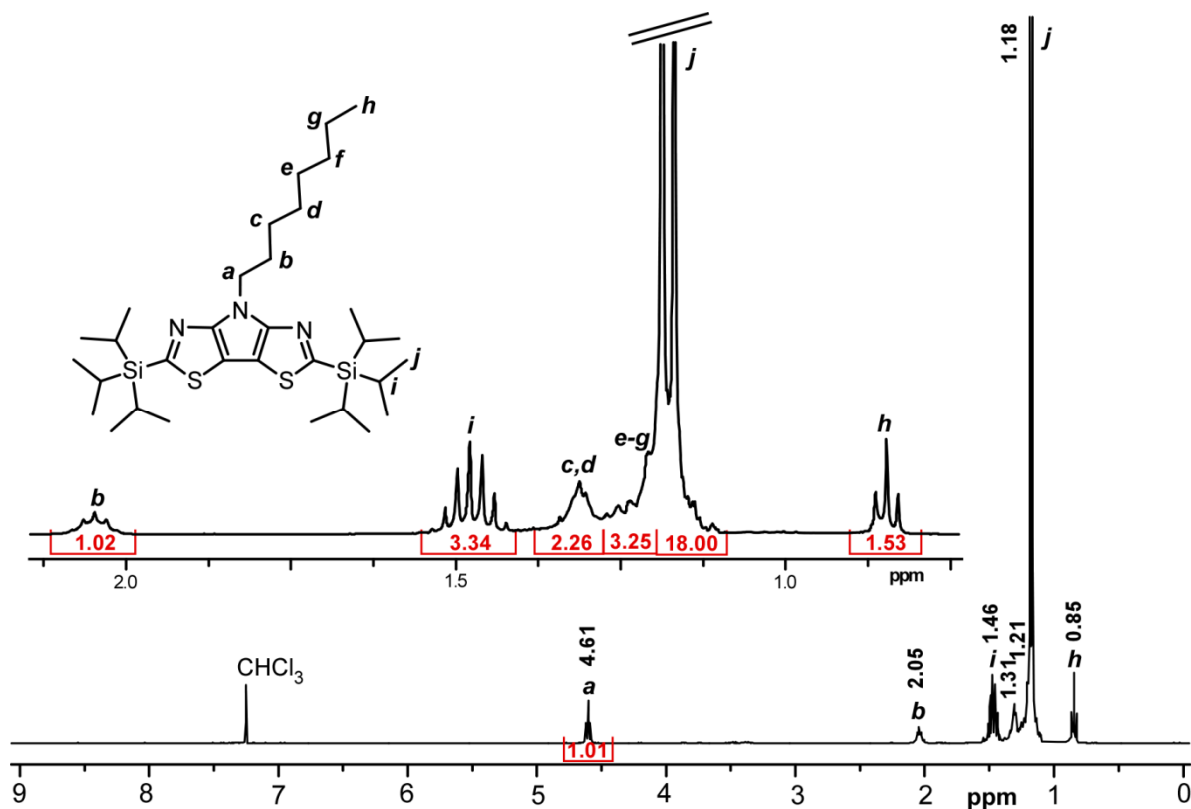


Figure S4. ^1H NMR spectrum of **4b**

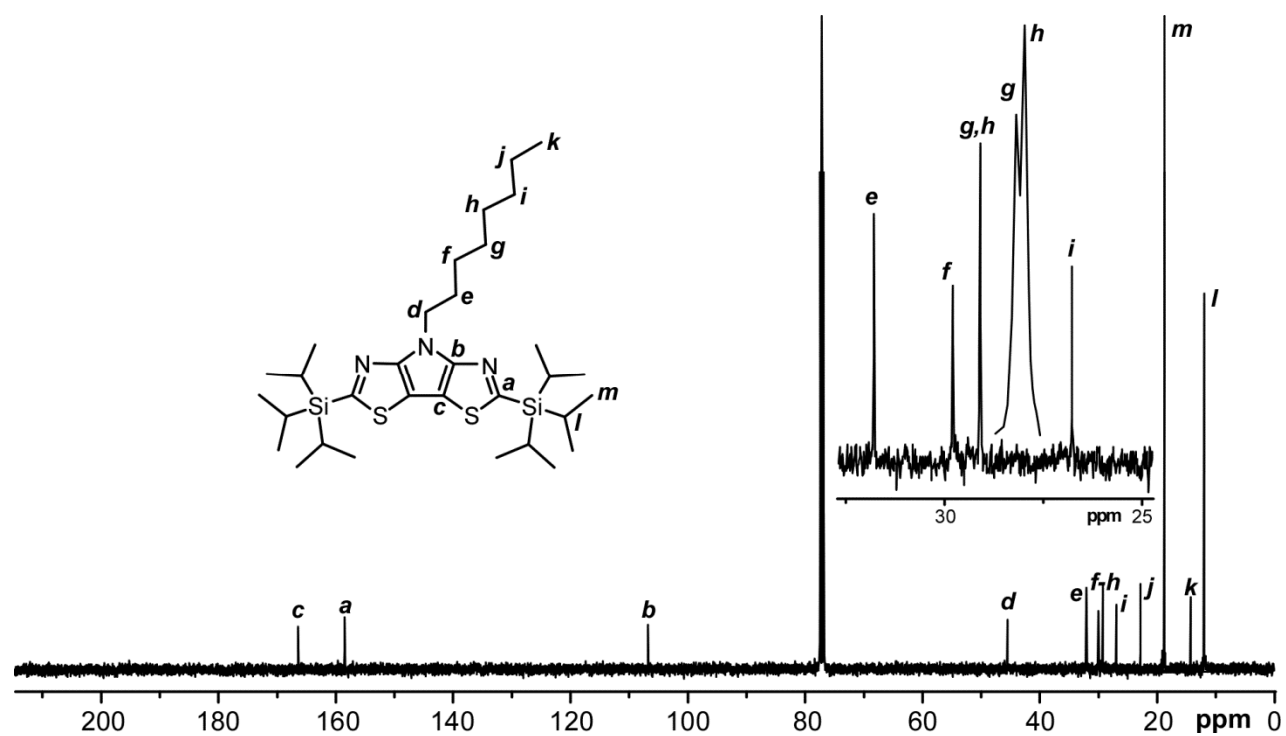


Figure S5. ¹³C NMR spectrum of **4b**

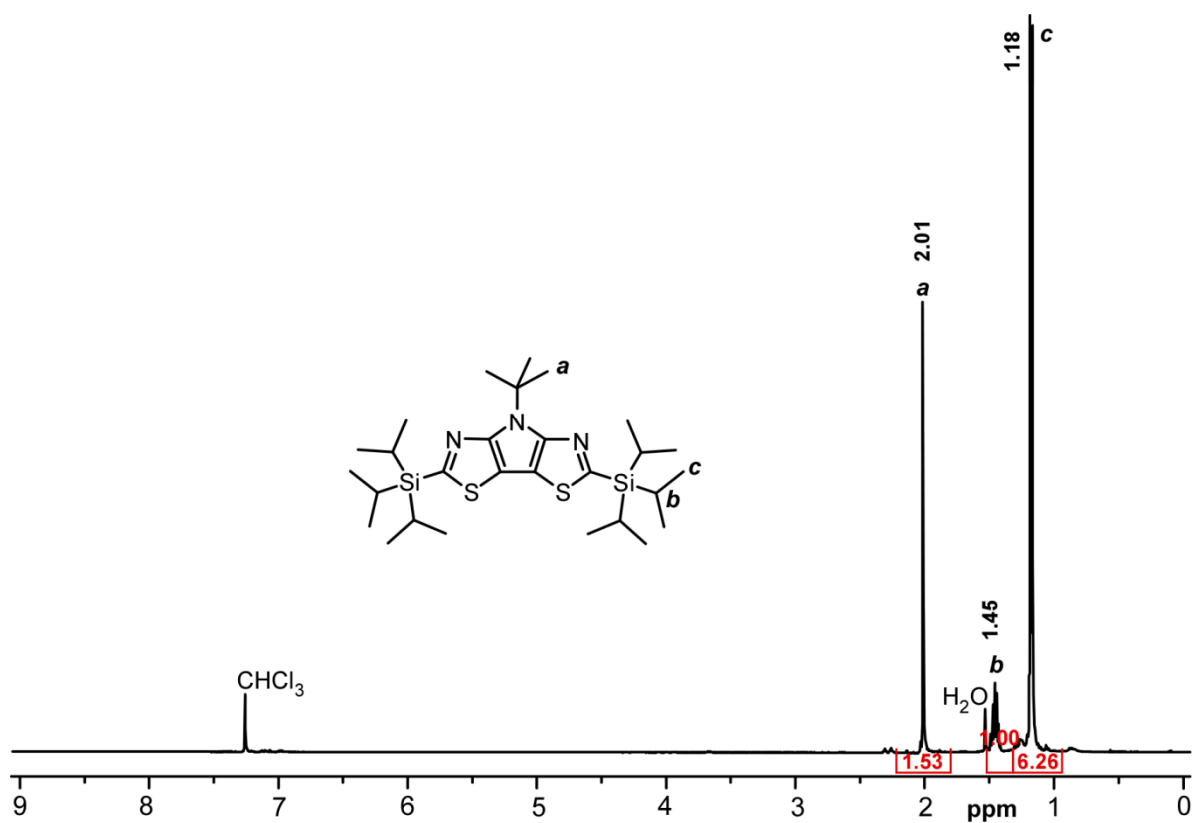


Figure S6. ¹H NMR spectrum of **4d**

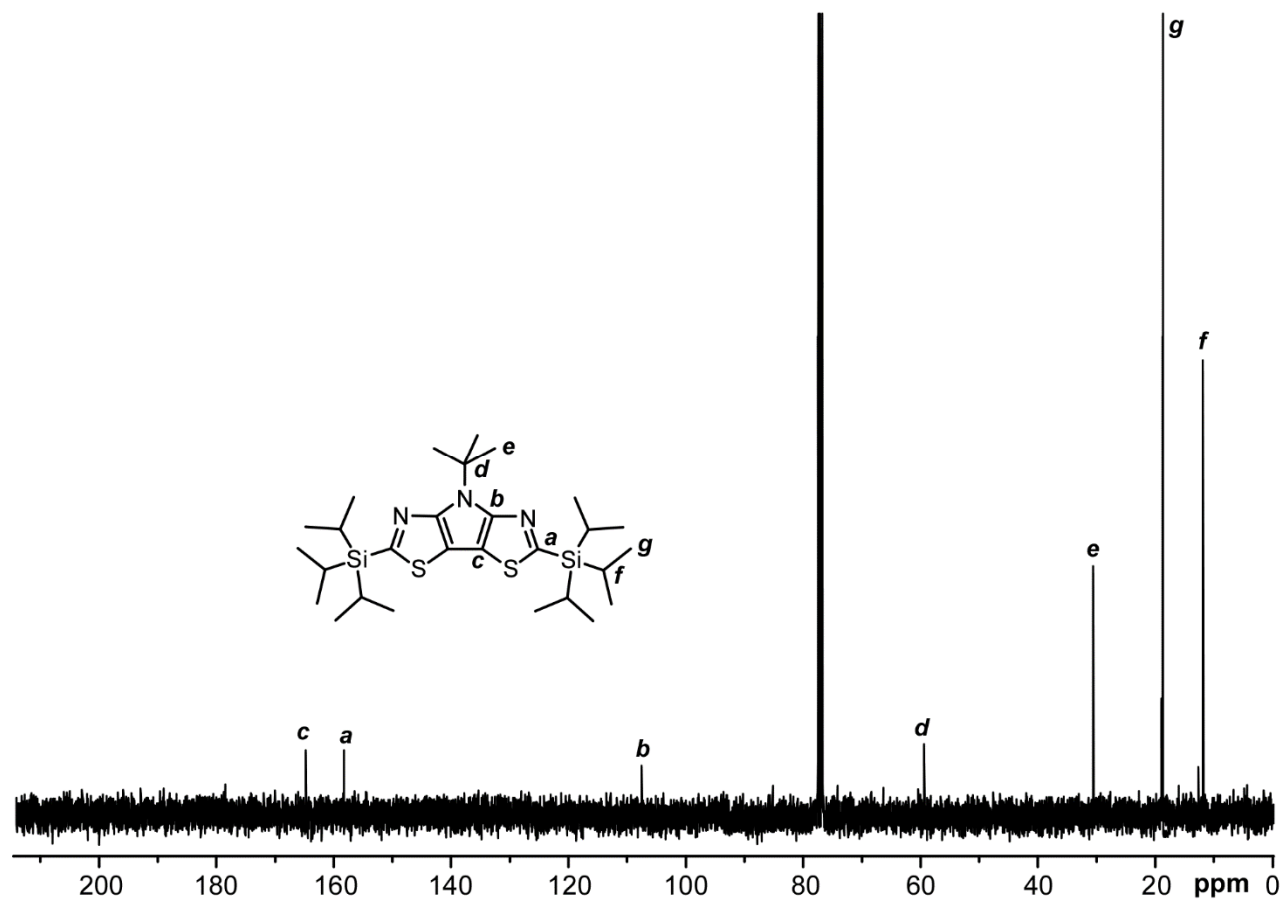


Figure S7. ^{13}C NMR spectrum of **4d**

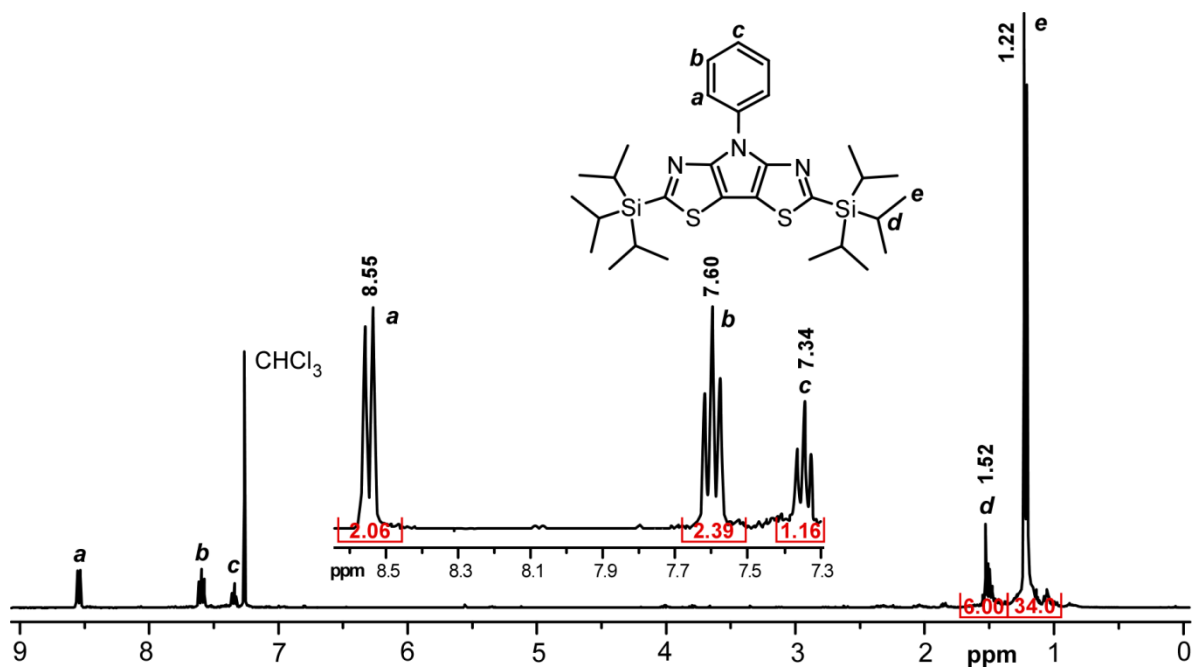


Figure S8. ^1H NMR spectrum of **4e**

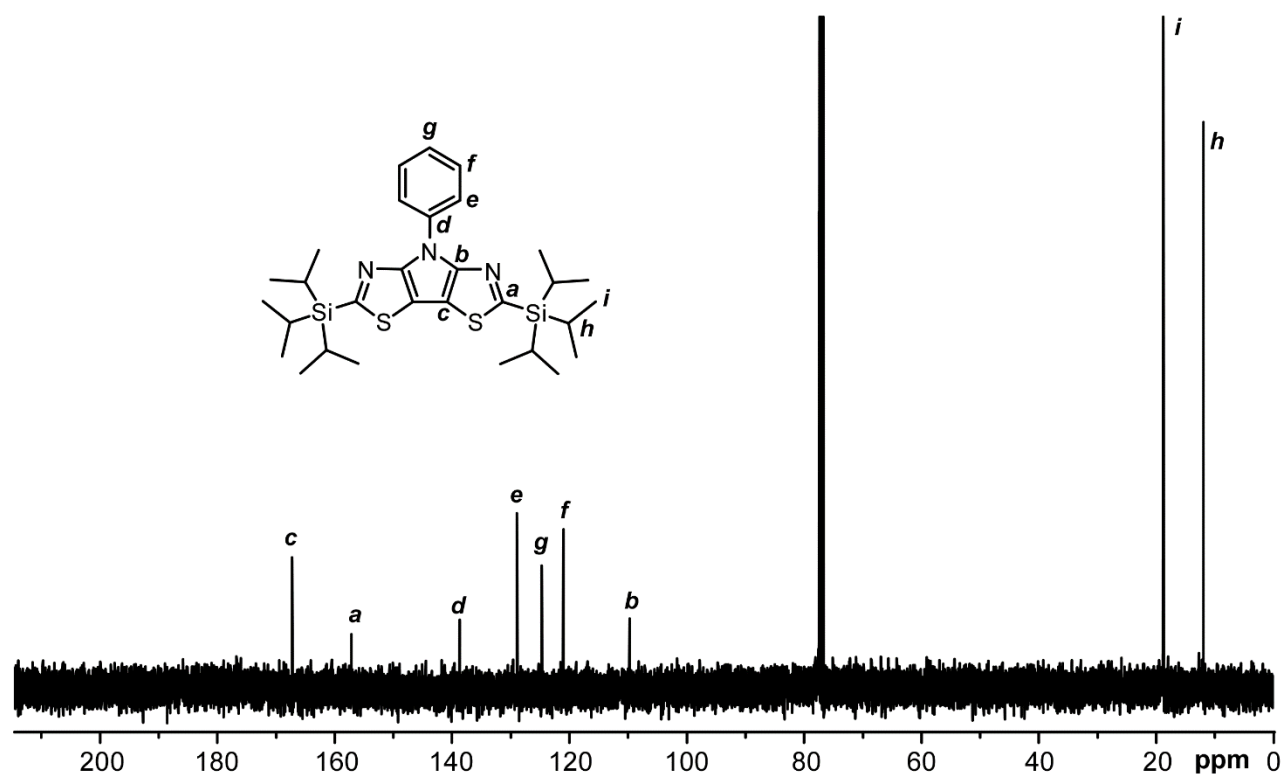


Figure S9. ^{13}C NMR spectrum of **4e**

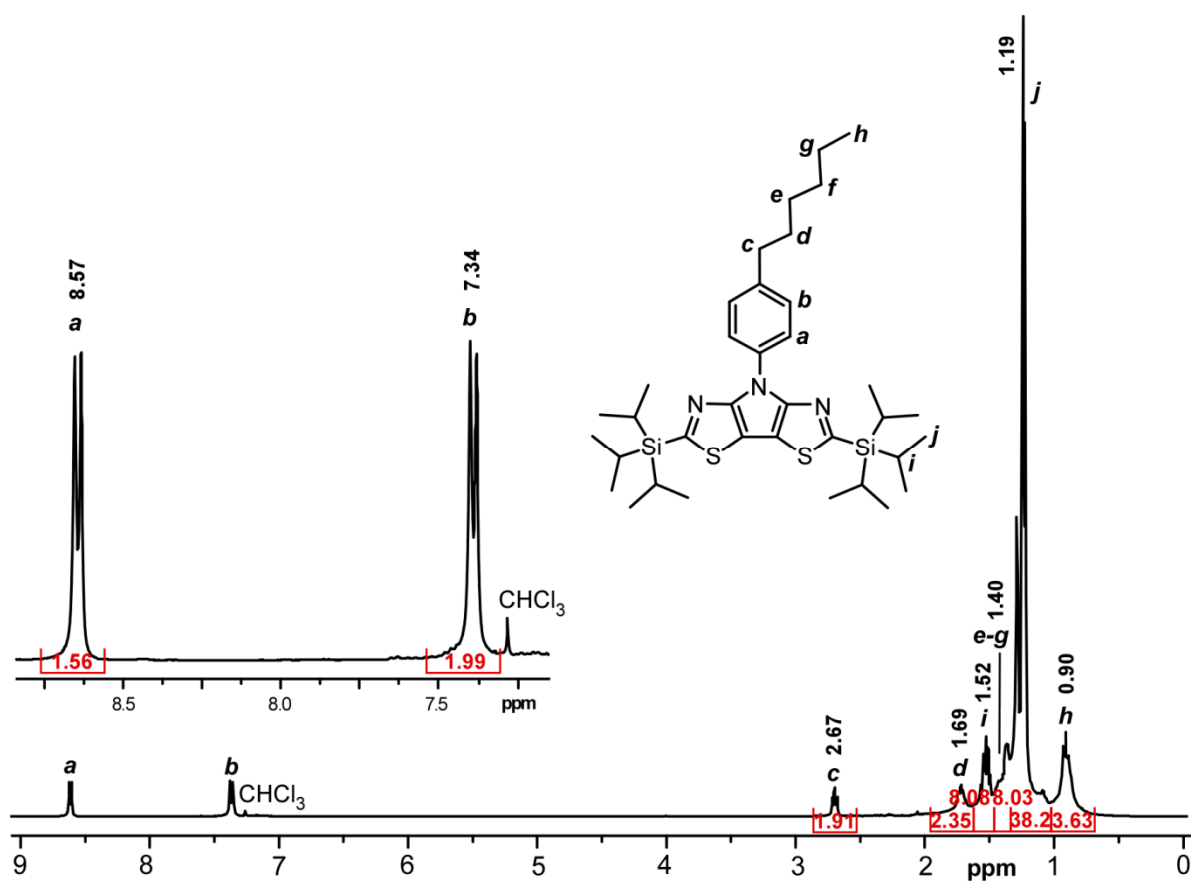


Figure S10. ^1H NMR spectrum of **4f**

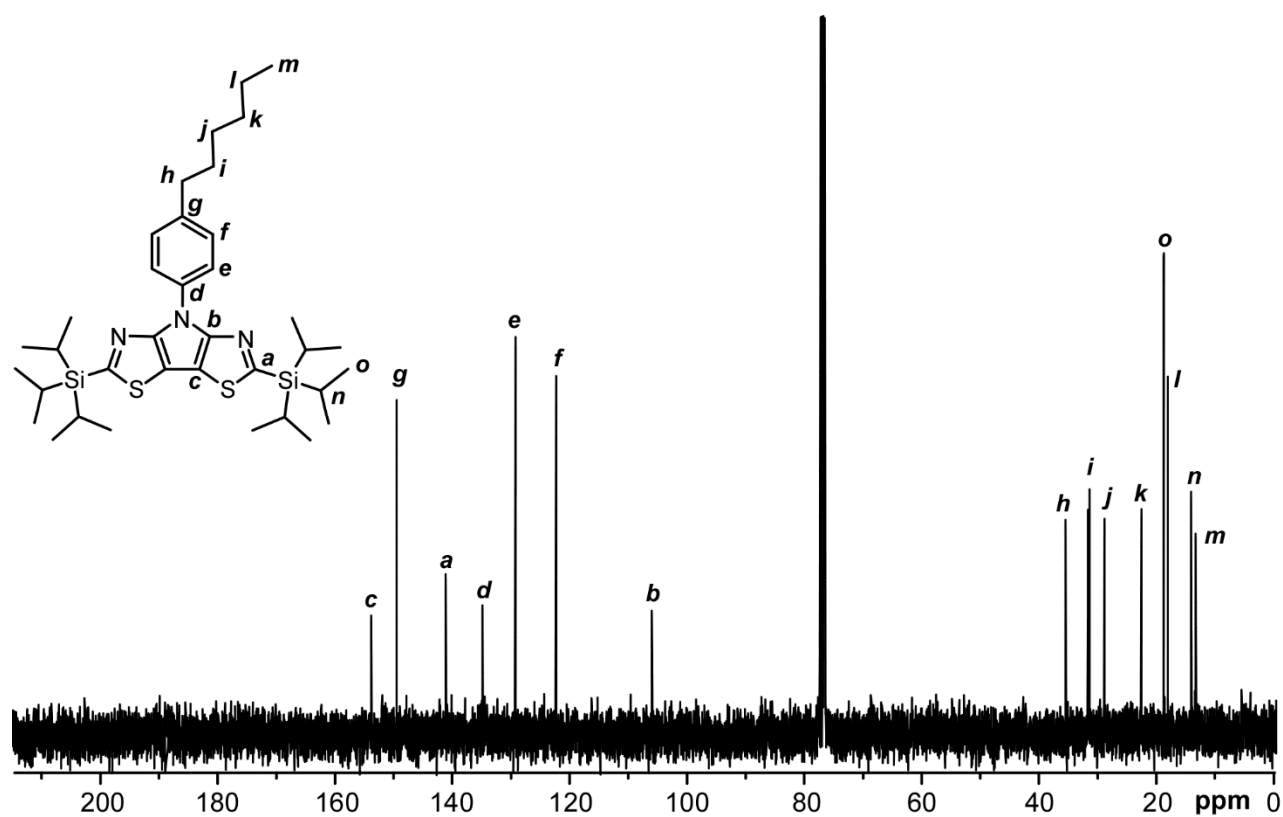


Figure S11. ^{13}C NMR spectrum of **4f**

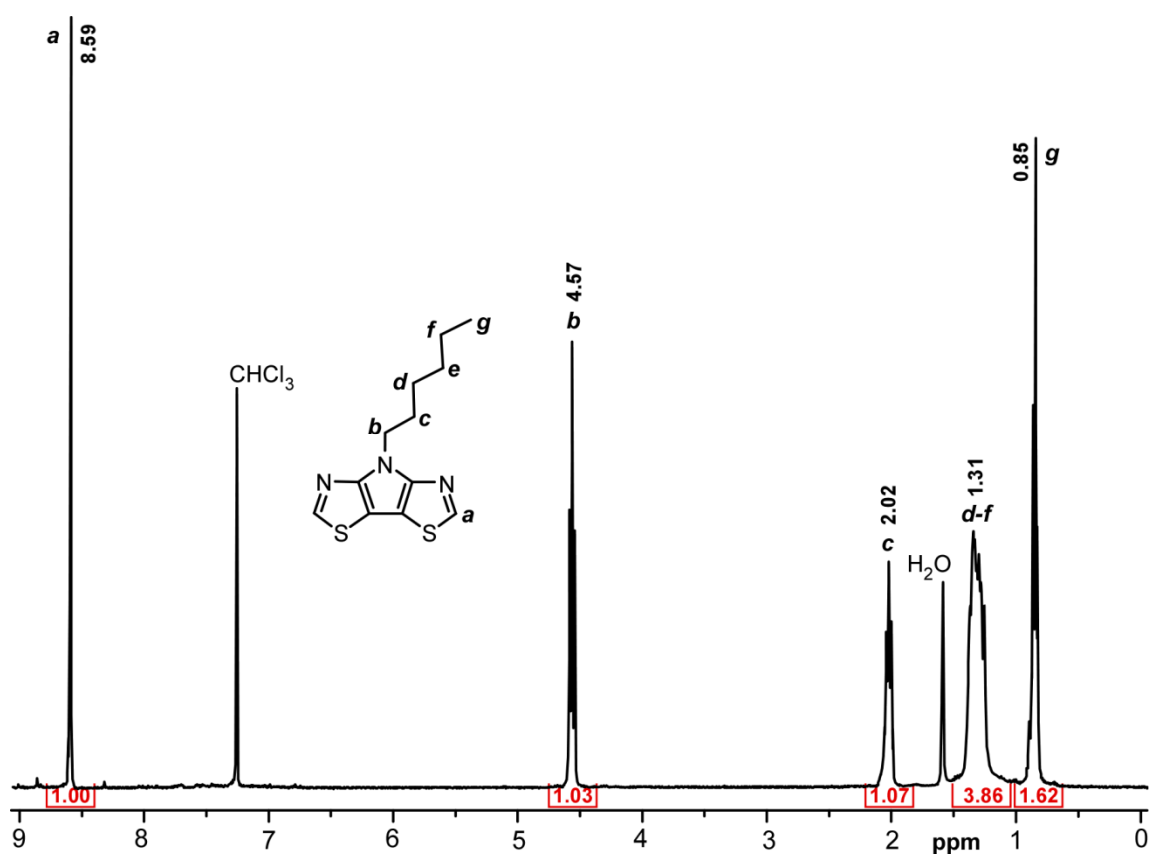


Figure S12. ^1H NMR spectrum of **5a**

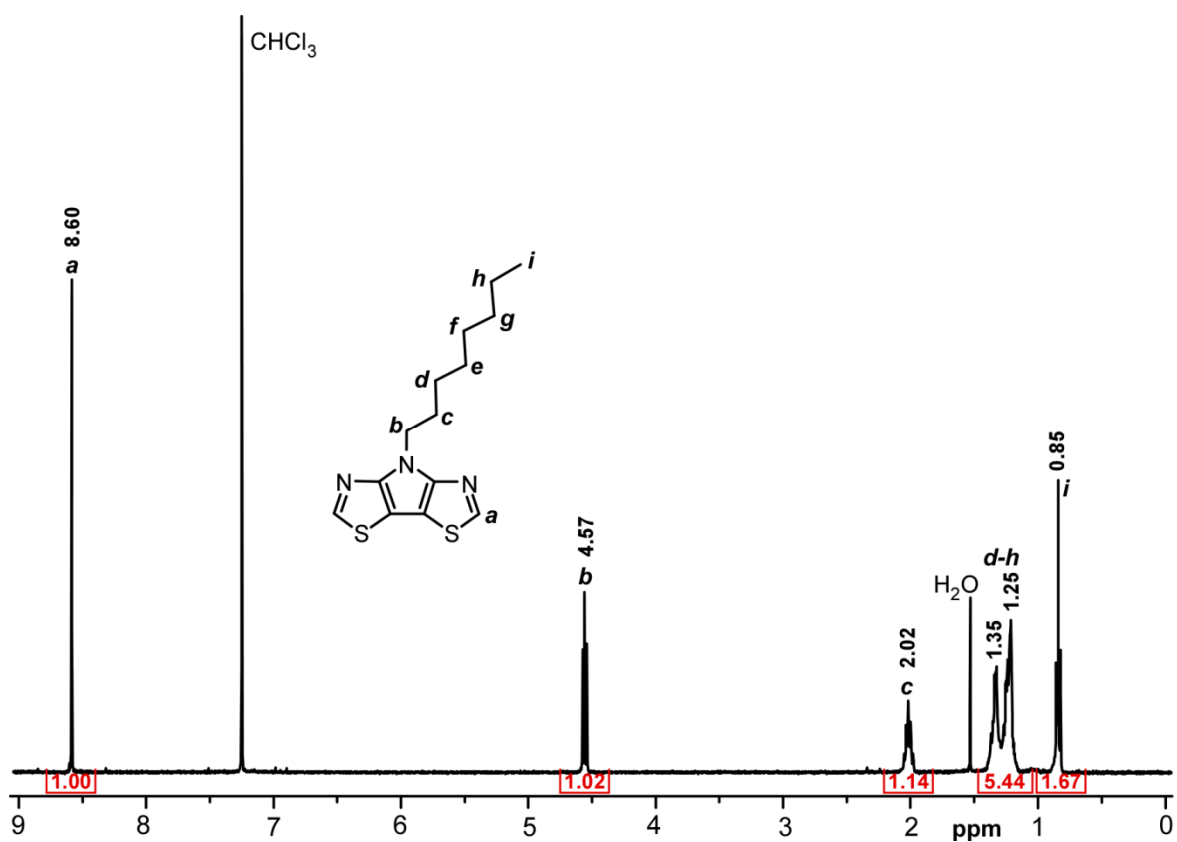


Figure S13. ¹H NMR spectrum of **5b**

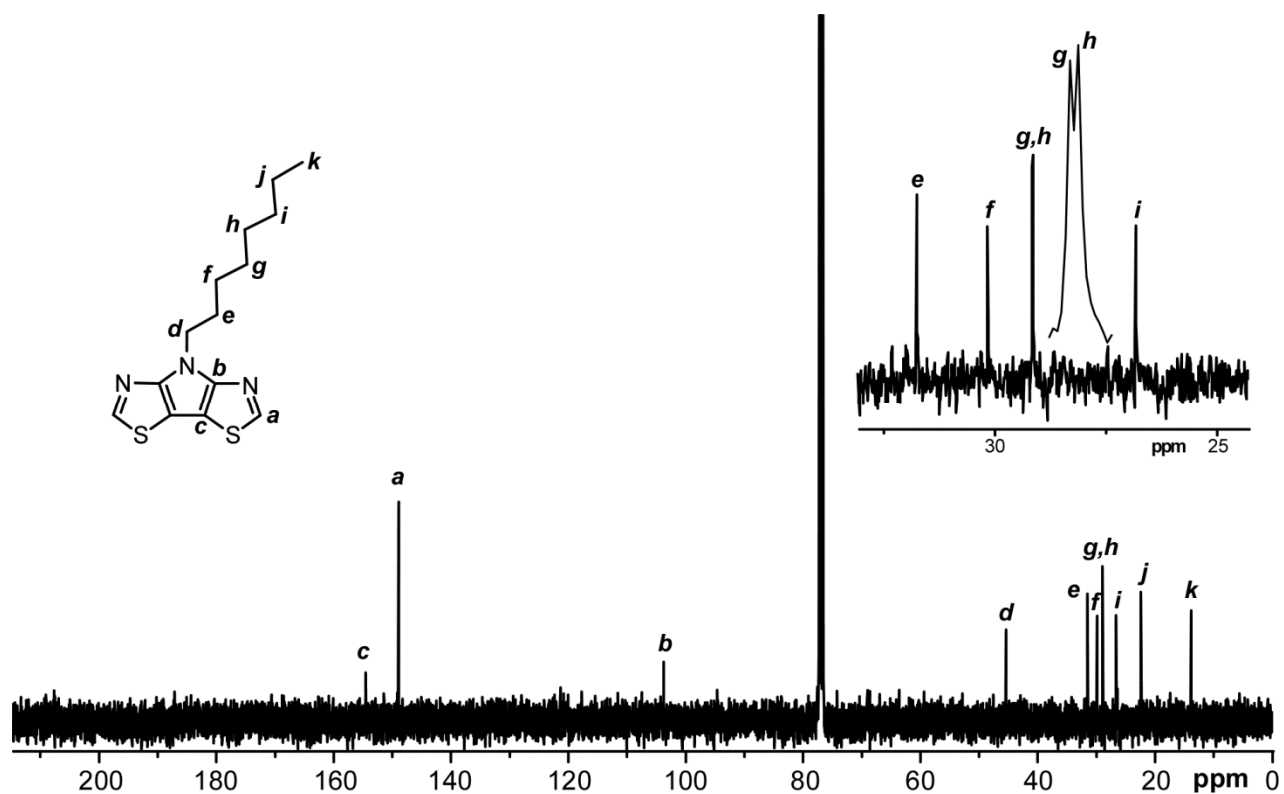


Figure S14. ¹³C NMR spectrum of **5b**

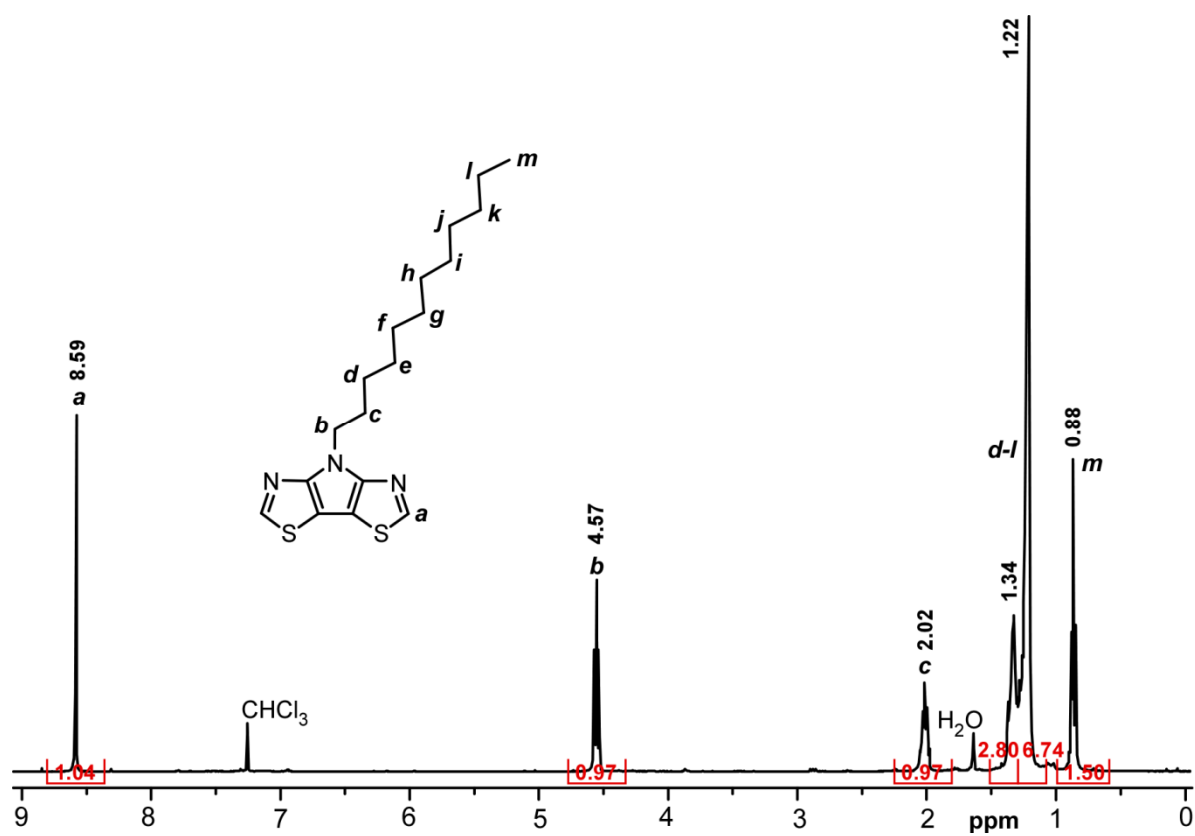


Figure S15. ¹H NMR spectrum of 5c

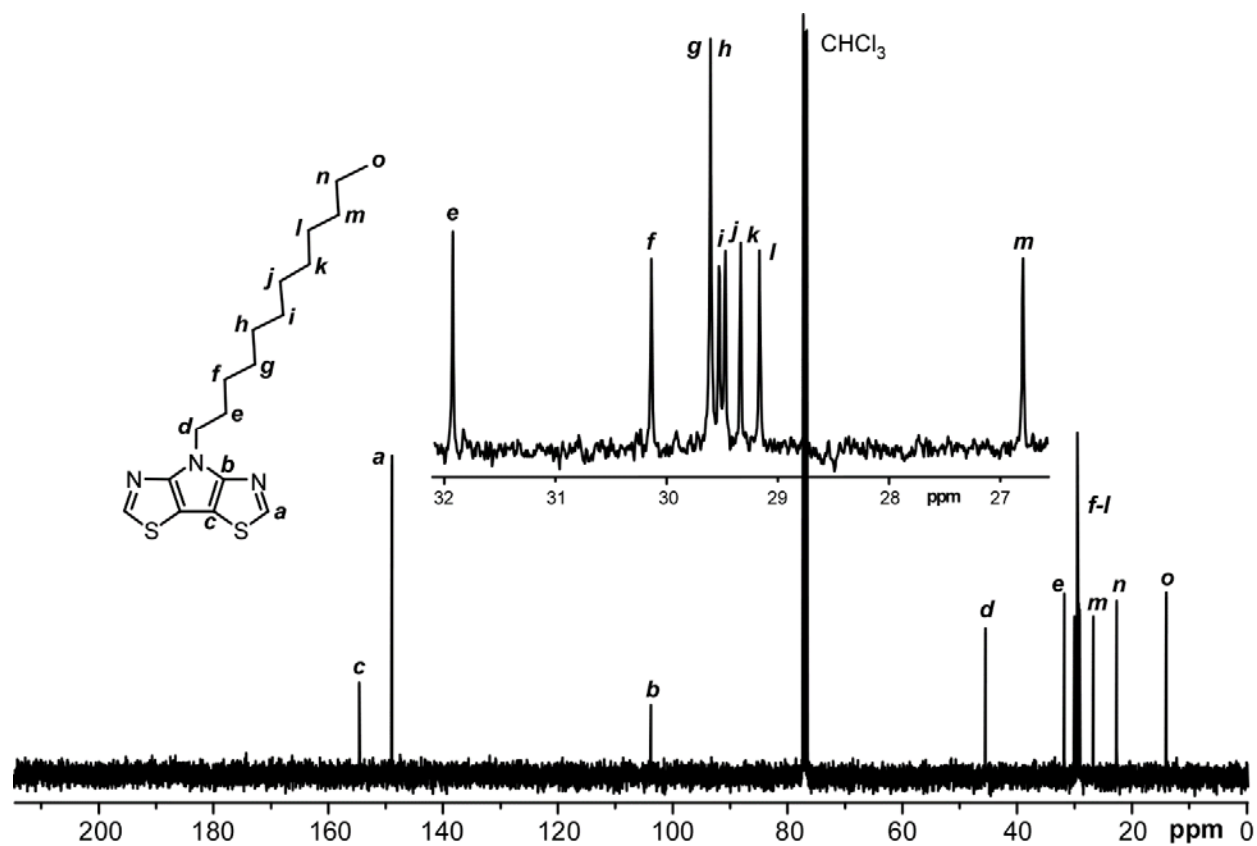


Figure S16. ¹³C NMR spectrum of 5c

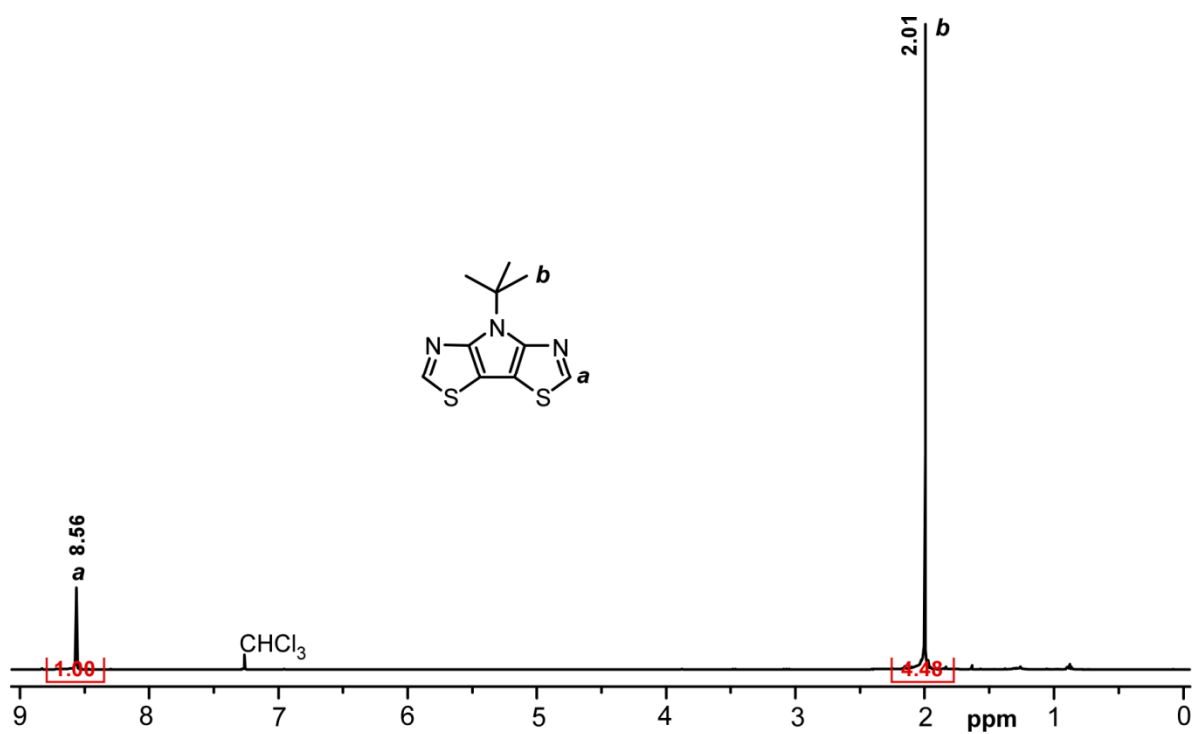


Figure S17. ¹H NMR spectrum of **5d**

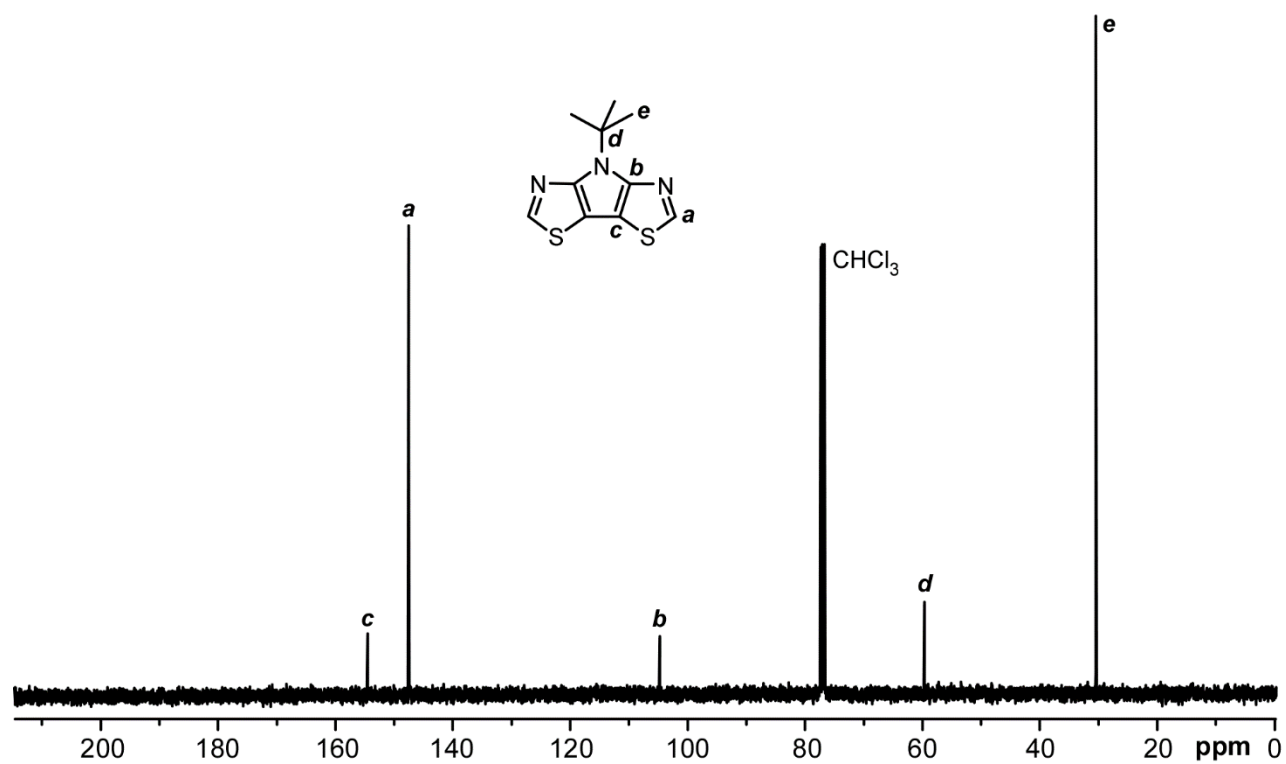
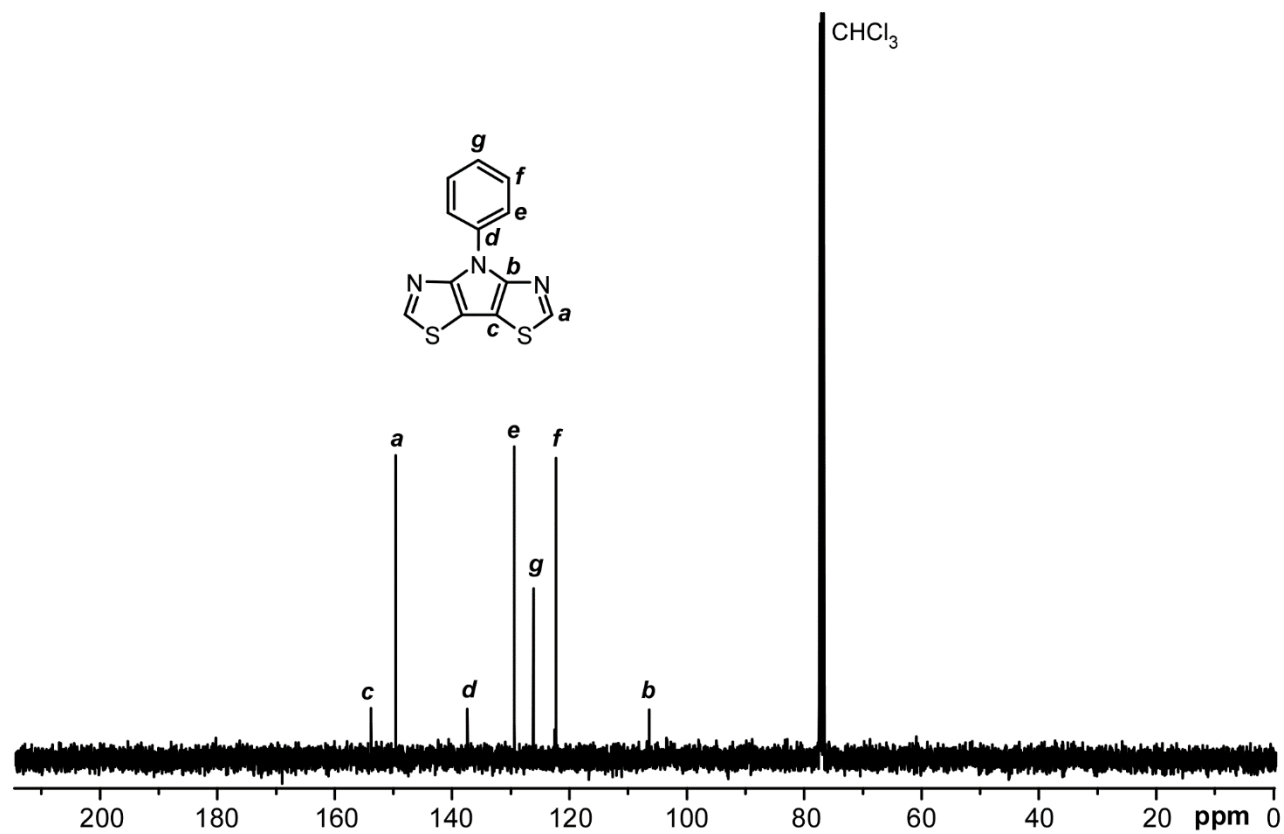
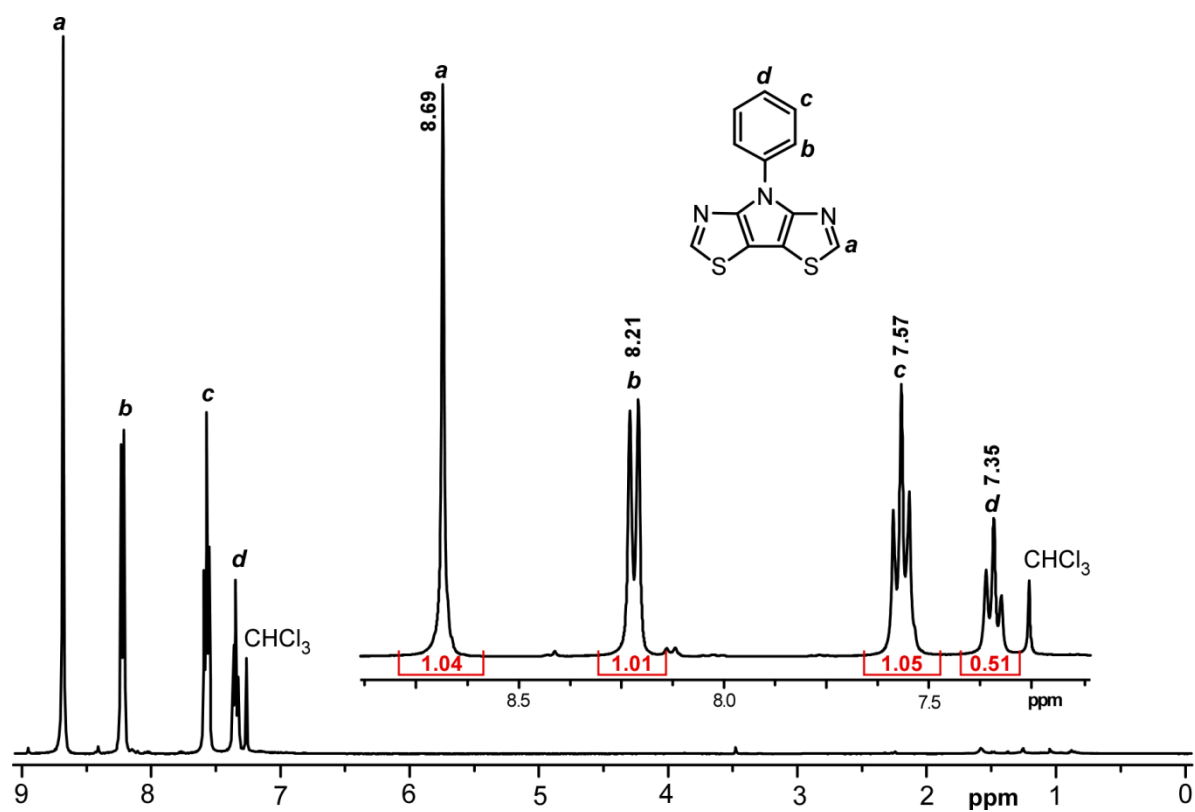


Figure S18. ¹³C NMR spectrum of **5d**



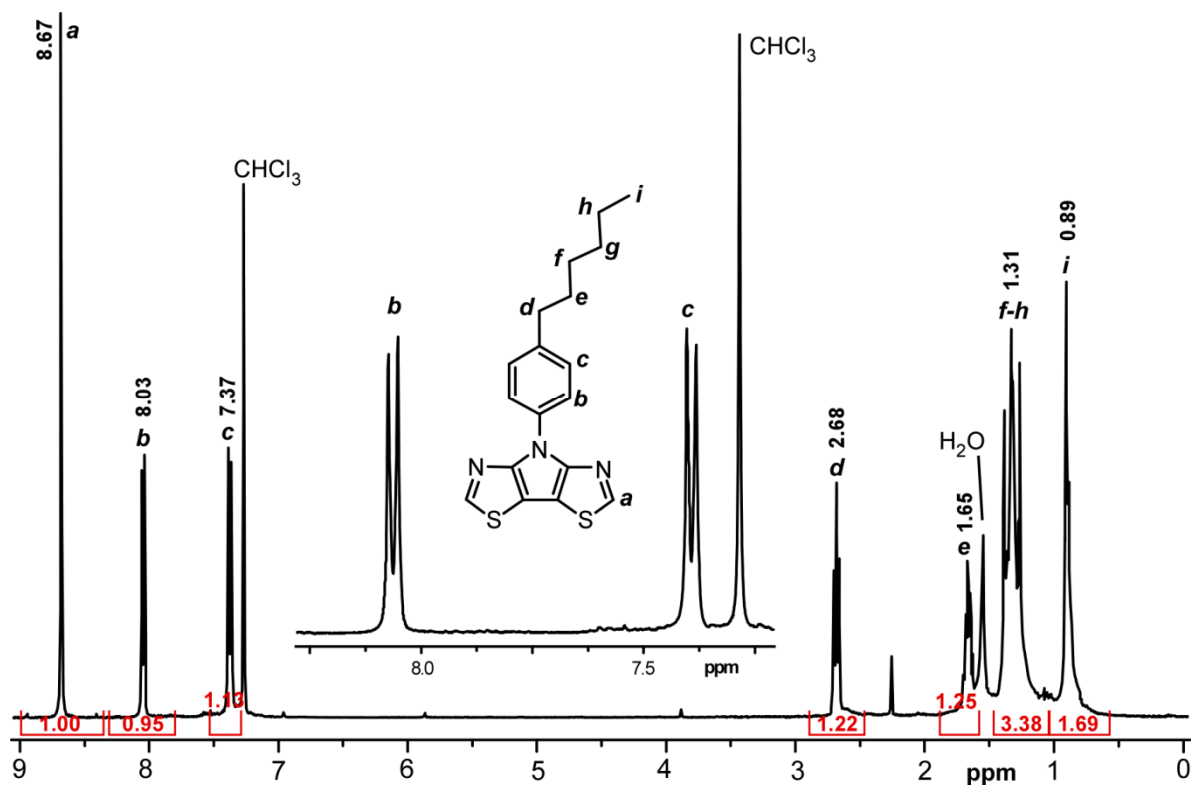


Figure S21. ¹H NMR spectrum of 5f

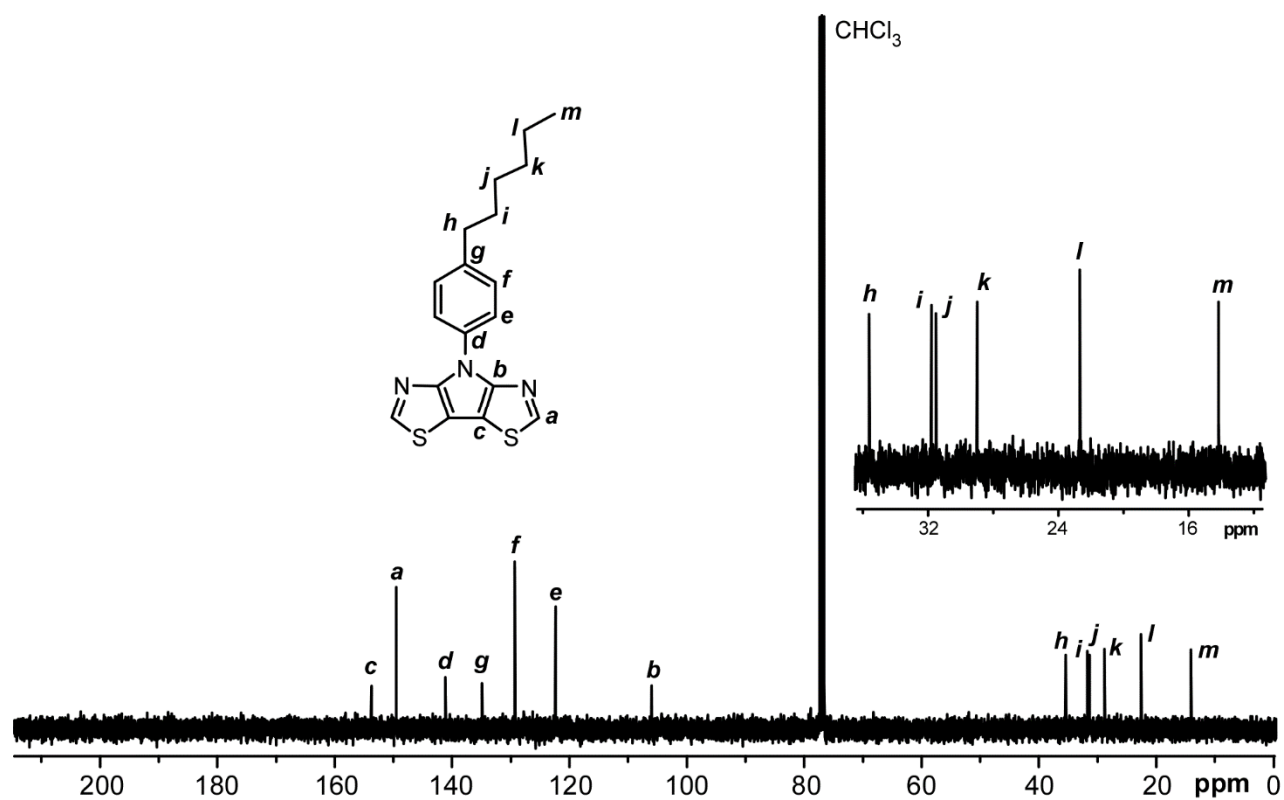


Figure S22. ¹³C NMR spectrum of 5f

X-ray Crystallography. X-ray quality crystals of **4d** and **6** were grown by slow evaporation of diethyl ether solutions, while crystals of **5a** were grown from cooling of molten samples. The X-ray intensity data of the crystals were measured at 100 K on a CCD-based X-ray diffractometer system equipped with a Cu X-ray tube ($\lambda = 1.54178 \text{ \AA}$) operated at 2000 W of power. The detector was placed at a distance of 5.047 cm from the crystal. Frames were collected with a scan width of 0.3° in ω and exposure time of 10 s/frame and then integrated with the Bruker SAINT software package using an arrow-frame integration algorithm. The unit cell was determined and refined by least-squares upon the refinement of XYZ-centeroids of reflections above $20\sigma(I)$. The structure was refined using the Bruker SHELXTL (Version 5.1) Software Package. The crystal data, data collection parameters, and refinement statistics are listed in Table S1. Full crystallography data for compounds 4,4'-dibromo-5,5'-bisthiazole, **5f**, and **6** are attached as a separate CIF file.

Table S1. Crystallographic data for compounds **4d**, **5a**, and **6**.

	4d	5a	6
Chemical Formula	C ₂₈ H ₅₁ N ₃ S ₂ Si ₂	C ₁₂ H ₁₅ N ₃ S ₂	C ₂₇ H ₃₈ N ₃ S ₂ Si
Formula Weight	550.01	265.39	496.81
Temperature (K)	100(2)	100(2)	100(2)
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	P12 ₁ /n1	C1c1	P12 ₁ /c1
<i>a</i> (Å)	27.9822(5)	11.4255(9)	14.8601(4)
<i>b</i> (Å)	15.7268(3)	11.8733(7)	17.8661(5)
<i>c</i> (Å)	30.7786(6)	9.8260(7)	9.9880(4)
α (°)	90.00	90.00	90.00
β (°)	108.1750(10)	107.618(6)	96.505(3)
γ (°)	90.00	90.00	90.00
<i>V</i> (Å ³)	12869.0(4)	1270.46(16)	2634.66(15)
<i>Z</i>	16	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.136	1.387	1.252
μ (mm ⁻¹)	2.356	3.636	2.411
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0472 <i>wR</i> ₂ = 0.1139	<i>R</i> ₁ = 0.0531 <i>wR</i> ₂ = 0.1368	<i>R</i> ₁ = 0.0514 <i>wR</i> ₂ = 0.1234
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.0624 <i>wR</i> ₂ = 0.1214	<i>R</i> ₁ = 0.0616 <i>wR</i> ₂ = 0.1422	<i>R</i> ₁ = 0.0854 <i>wR</i> ₂ = 0.1391

$$^a R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|, wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(F_o^2)^2]^{1/2}$$

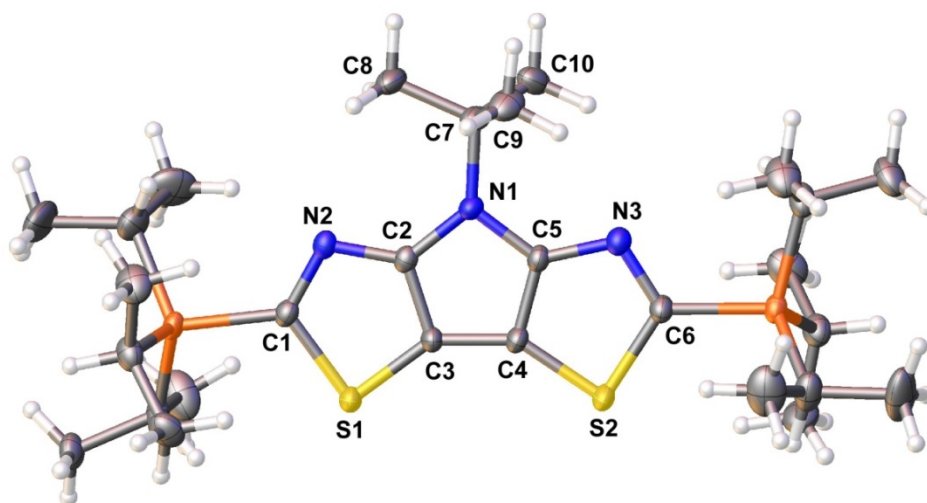


Figure S23. Ellipsoid Plot of **4d** at the 50% probability level.

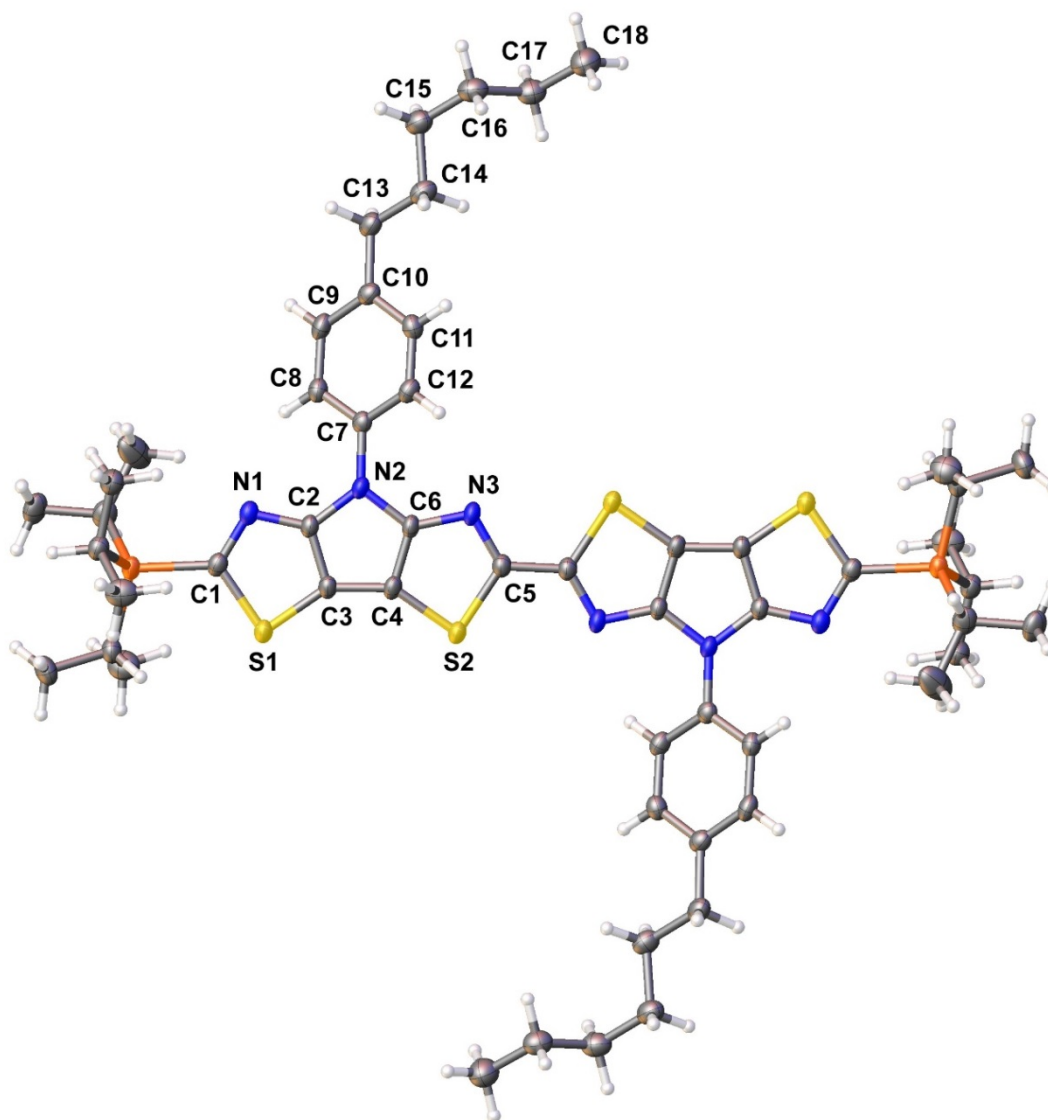


Figure S24. Ellipsoid Plot of **6** at the 50% probability level.

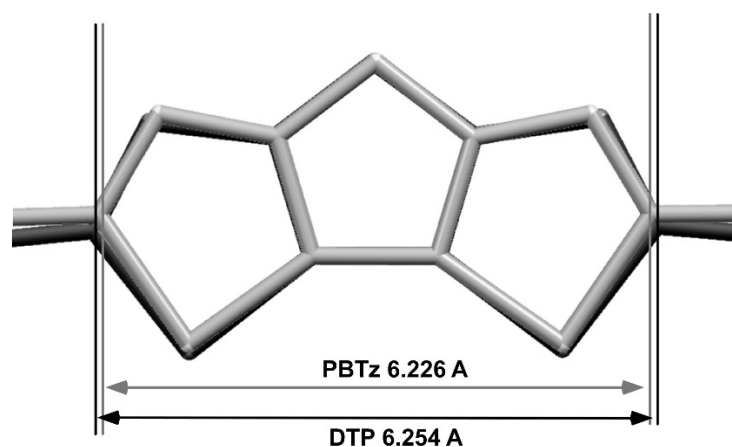


Figure S25. Overlay of PBTz and DTP structures.

Table S2. Electrochemical Data for TIPS-protected PBTz^a

Compound	R	$E_{1/2}$ (V)	ΔE (mV)
4a	C ₆ H ₁₃	0.78	140
4b	C ₈ H ₁₇	0.78	120
4c	C ₁₂ H ₂₅	0.78	100
4d	^t Bu	0.76	120
4e	Ph	0.89	100
4f	C ₆ H ₁₃ Ph	0.88	100

^aAll potentials vs. Fc/Fc⁺.

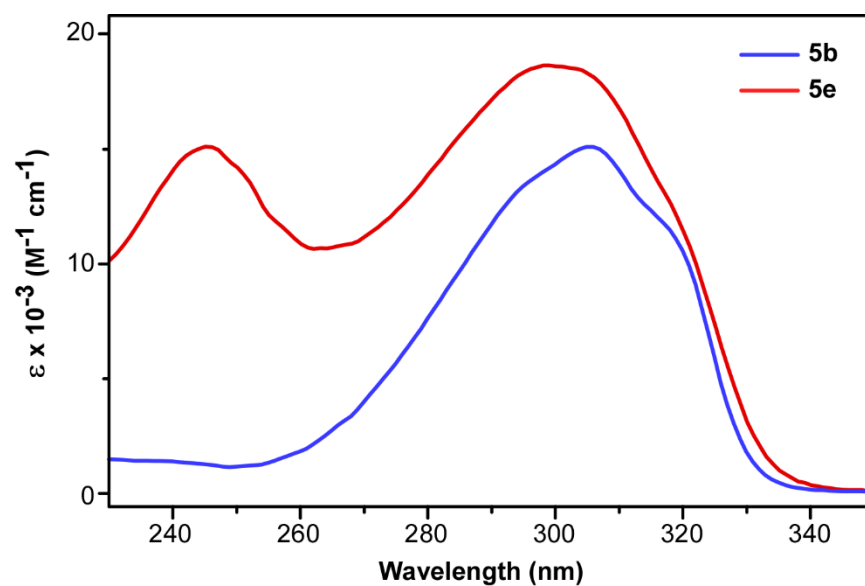


Figure S26. UV-vis spectra of **5a** and **5e**

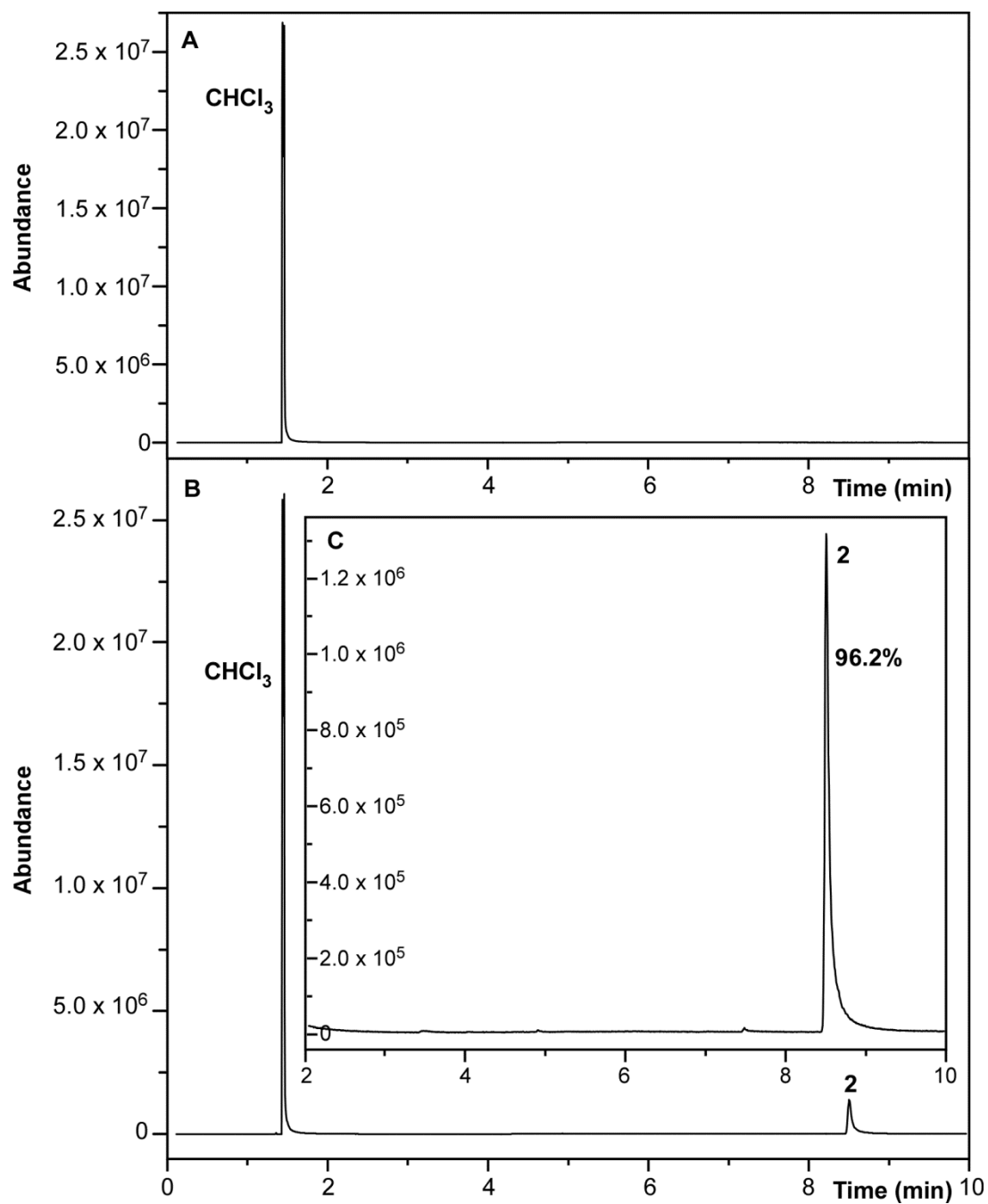


Figure S27. GC Analysis of 2: (A) GC of pure CHCl_3 , (B) GC of 1 mg/mL of 2 in CHCl_3 , (C) GC of 2 with solvent delay