Supporting Information for

Synthesis and Characterization of Optical and Redox Properties of Bithiophene-Functionalized Diketopyrrolopyrrole Chromophores

Hannah Bürckstümmer, Annike Weißenstein, David Bialas, and Frank Würthner*

Universität Würzburg, Institut für Organische Chemie, Am Hubland, 97074 Würzburg, Germany

wuerthner@chemie.uni-wuerzburg.de

Table of Contents

1. Materials and methods S2
2. Fluorescence spectra of DPPs **7a** and **7c–f** S3
3. References S3
4. ^{1}H and ^{13}C spectra S4

1. Materials and methods

Solvents and common reagents were obtained from commercial suppliers and purified and dried according to standard procedures.[S1] $ZnCl_2$ was first dried under vacuum at 100 °C and then stored in a glovebox.

Column chromatography was performed with commercial glass columns using silica gel (particle size 0.063–0.2 mm) as stationary phase. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C using residual solvent peaks as internal standard. High resolution ESI mass spectrometry was carried out in positive mode with MeCN or $CHCl_3$ as solvent. UV/vis spectra were measured using a conventional quartz cell (light path 1cm) with temperature control. Fluorescence spectra were taken using quartz cell (light path 1 cm) and corrected after the measurement. The solvents for spectroscopic studies were of spectroscopic grade and used as received. The fluorescence quantum yields in CH_2Cl_2 were determined by the optically dilute method[S2] using *N*,*N*'-bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylen-3,4,9,10-tetracarboxylic acid bisimide (Φ_{fl} = 0.96 in $CHCl_3$)[S3] as a reference. The given quantum yields were averaged from values obtained at three excitation wavelengths with a standard deviation σ of less than 3%.

CV measurements were performed on a standard commercial electrochemical analyzer in a three-electrode single-compartment cell under argon. Working electrode: Pt disc; reference electrode: Ag/AgCl; auxiliary electrode: Pt wire. Dichloromethane (HPLC grade) obtained from commercial sources was dried over calcium hydride and degassed prior to use. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was synthesized according to literature,[S4] recrystallized from ethanol/water and dried in high vacuum. The measurements were carried out under exclusion of air and moisture at a concentration of 10^{-4} M with ferrocene as internal standard for the calibration of the potential.

2. Fluorescence spectra of DPPs 7a and 7c–f

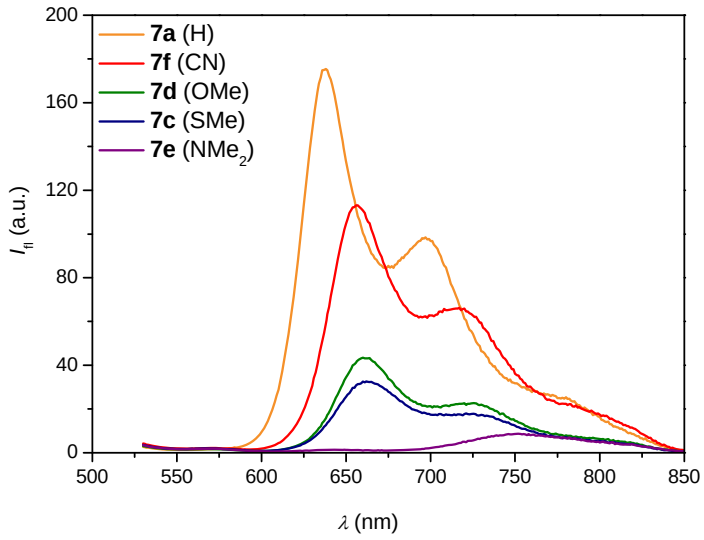

Figure S1. Emission spectra (excitation at 520 nm) of DPP **7a** and **7c–f** in dichloromethane at 20 °C.

3. References

(S1) Amarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals;* Elsevier, Burlington, 5th Ed., 2003.

(S2) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, *2nd ed.*; Kluwer Academic/ Plenum Publishers: New York, 1999; pp. 52–53.

(S3) Gvishi, R.; Reisfeld, R.; Burshstein, Z. *Chem. Phys. Lett.* **1993**, *213*, 338–344.

(S4) Fry, A. J. in *Laboratory Techniques in Electroanalytical Chemistry* (Eds. Kessing, P. T.; Heineman, W. R.), Marcel Dekker Ltd, New York, 2nd Ed., 1996, p. 481.

4. ^{1}H and ^{13}C NMR spectra

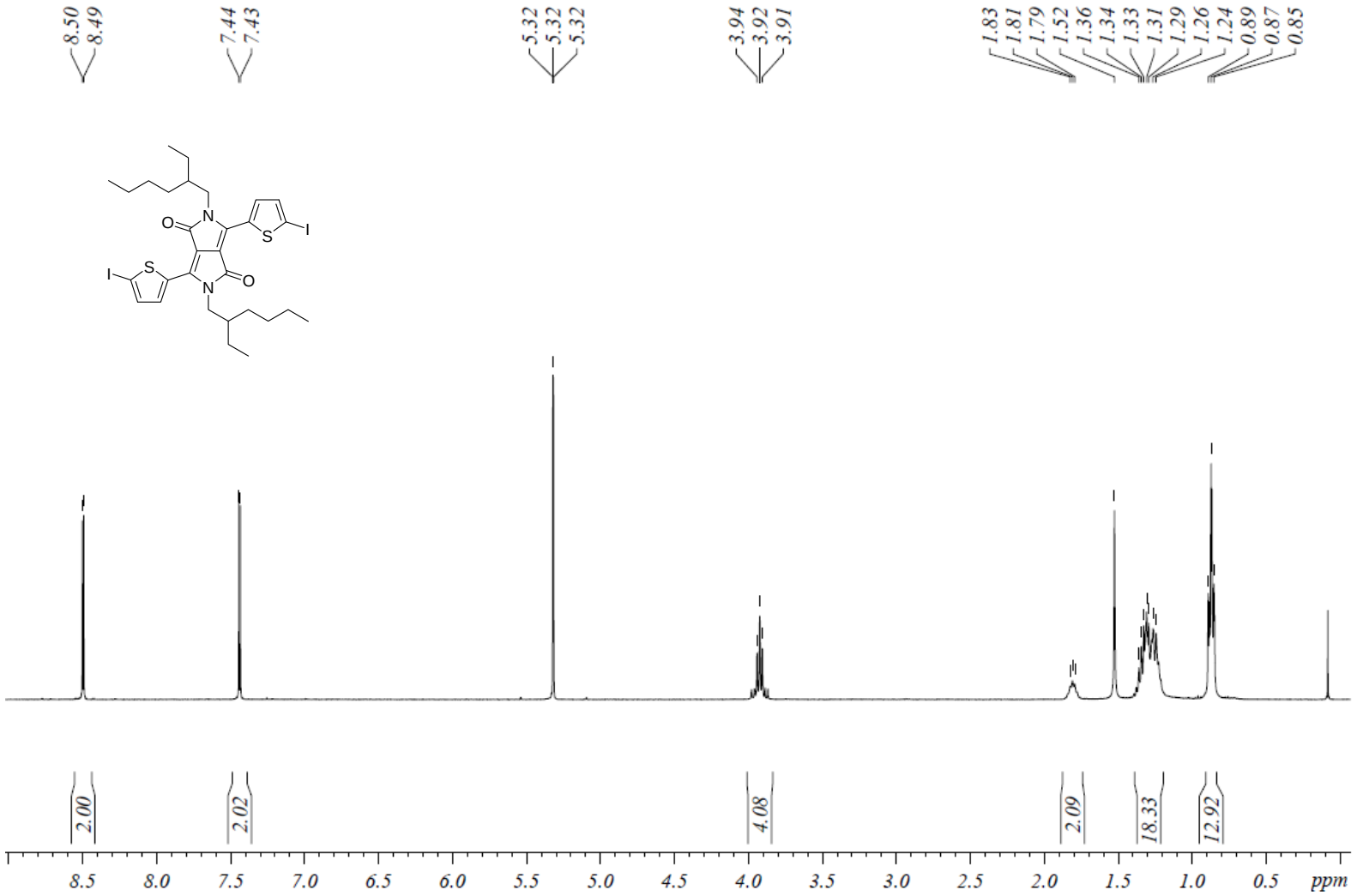

Figure S2. ^{1}H NMR spectrum of 2,5-bis(2-ethylhexyl)-3,6-bis(5-iodo-thiophen-2-yl)-2,5-dihydro-pyrrolo[3,4-*c*]-pyrrole-1,4-dione (**2**) in CD_2Cl_2.

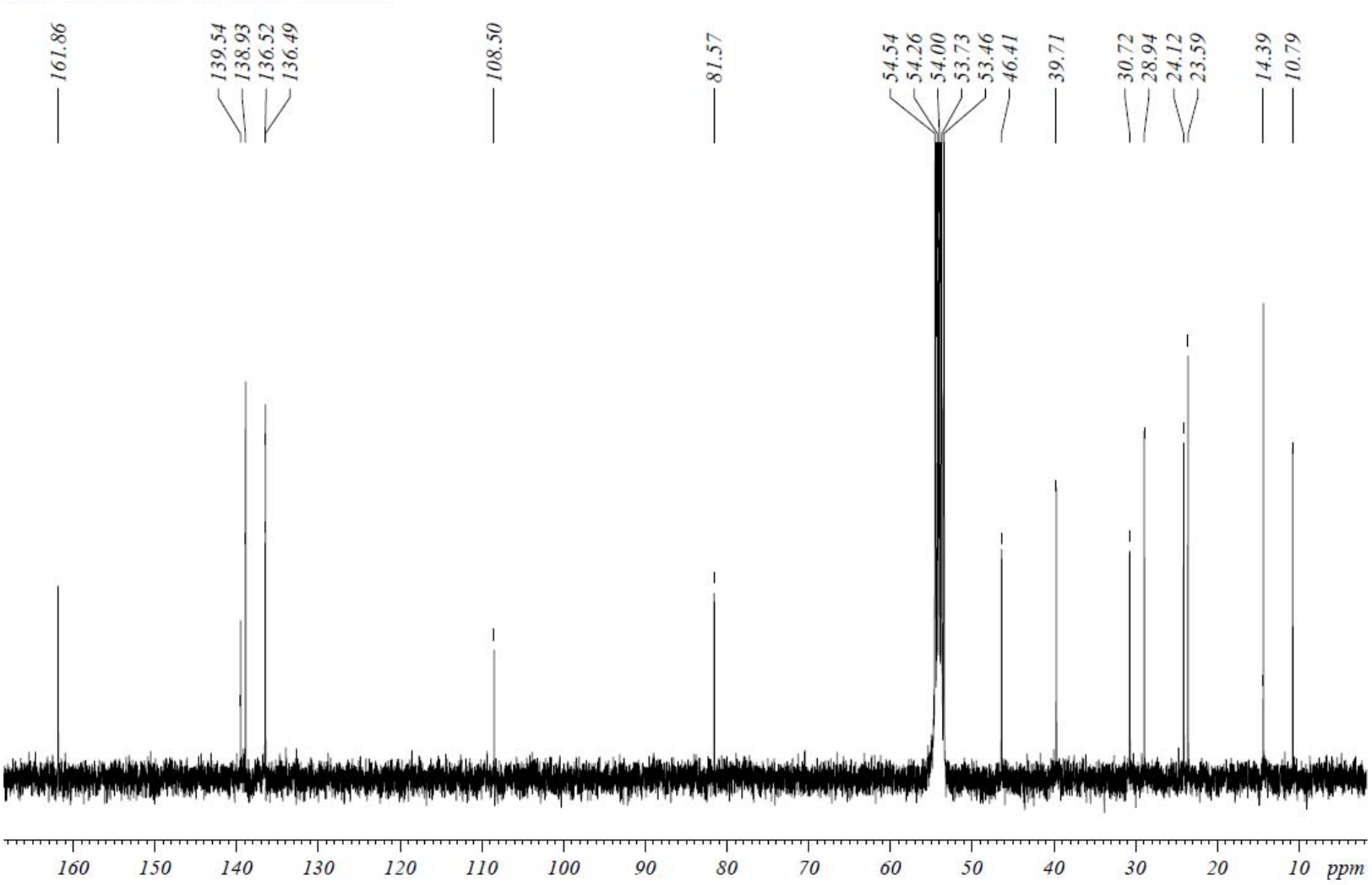

Figure S3. ^{13}C NMR spectrum of 2,5-bis(2-ethylhexyl)-3,6-bis(5-iodo-thiophen-2-yl)-2,5-dihydro-pyrrolo[3,4-*c*]-pyrrole-1,4-dione (**2**) in CD_2Cl_2.

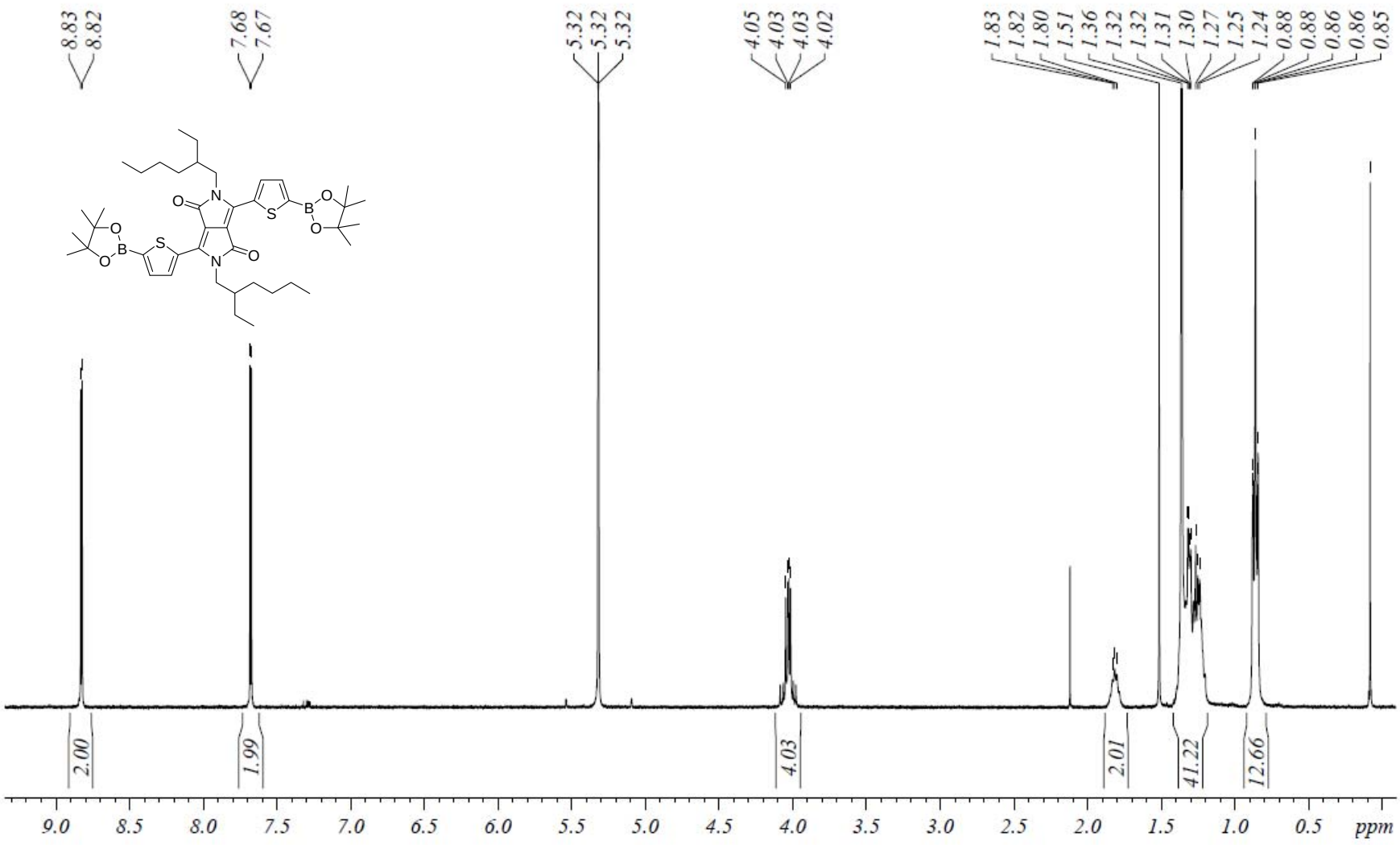

Figure S4. ^{1}H NMR spectrum of 2,5-bis(2-ethylhexyl)-3,6-bis[5-(4,4,5,5-tetramethyl-(1,3,2)dioxoborolan-2-yl)-thiophen-2-yl]-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**3**) in CD_2Cl_2.

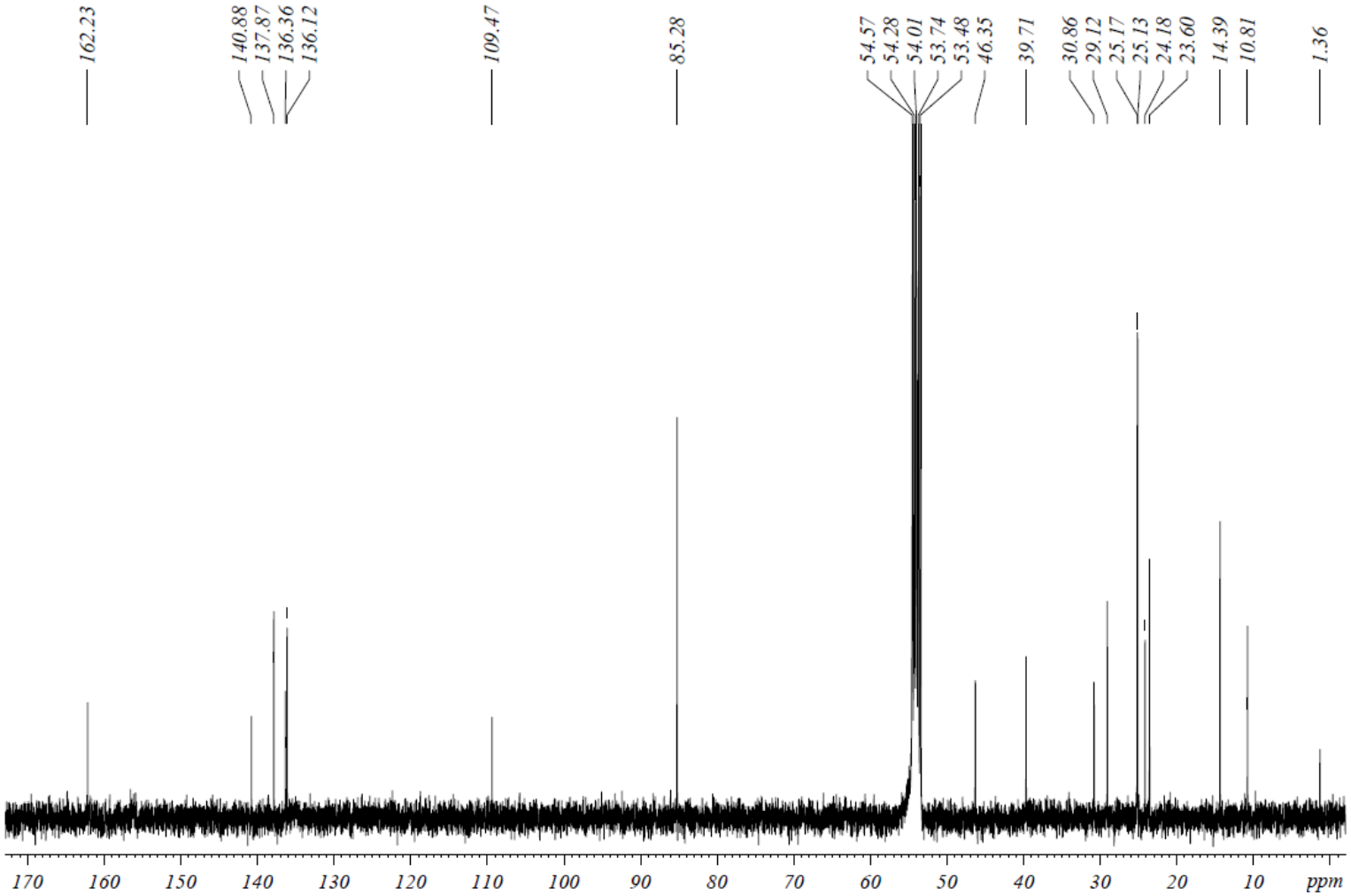

Figure S5. ^{13}C NMR spectrum of 2,5-bis(2-ethylhexyl)-3,6-bis[5-(4,4,5,5-tetramethyl-(1,3,2)dioxoborolan-2-yl)-thiophen-2-yl]-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**3**) in CD_2Cl_2.

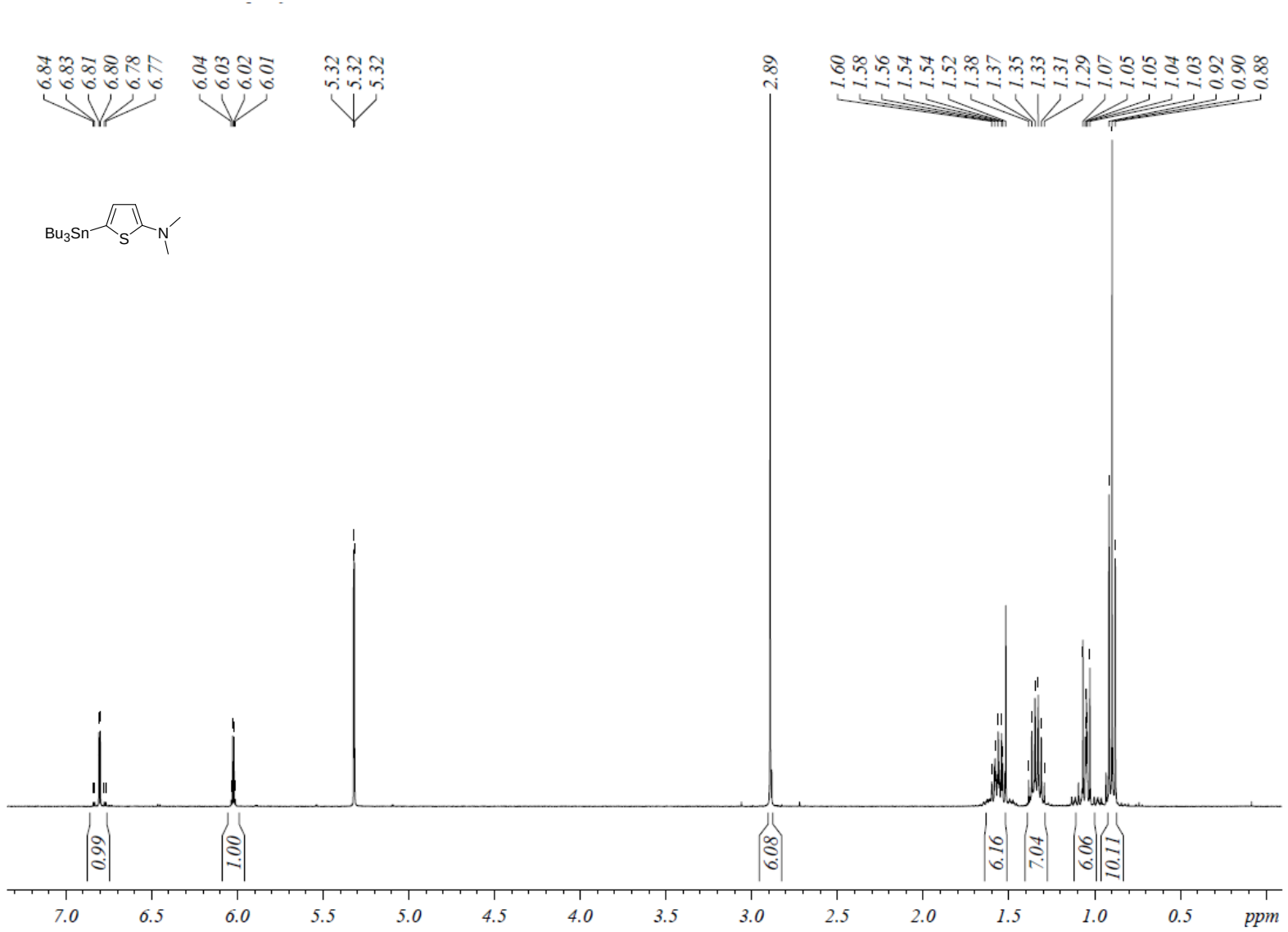

Figure S6. ^{1}H NMR spectrum of dimethyl-(5-tributylstannanyl-thiophen-2-yl)amine (**4e**) in CD_2Cl_2.

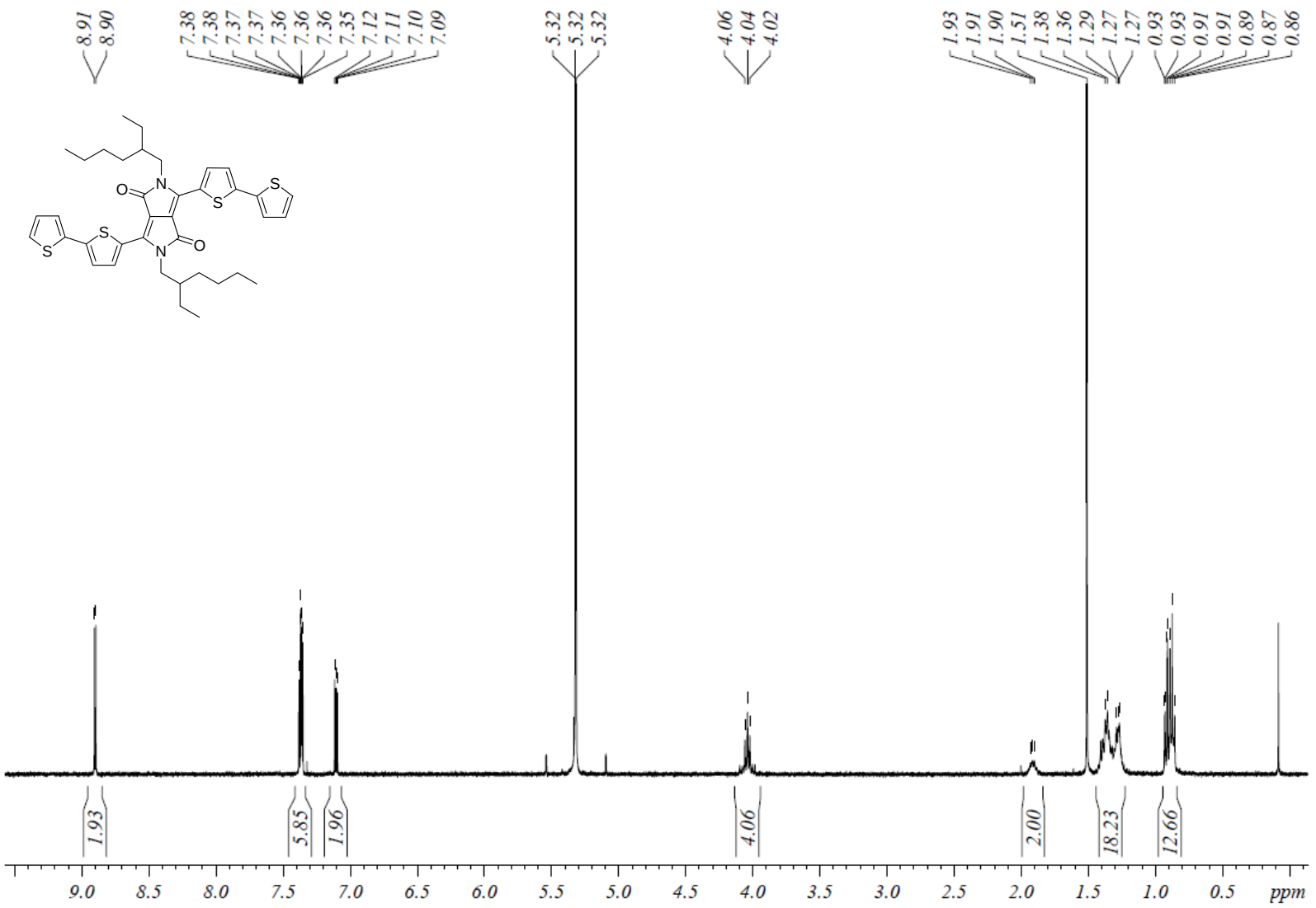

Figure S7. ^{1}H NMR spectrum of 3,6-bis(2,2'-bithiophenyl-5-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**7a**) in CD_2Cl_2.

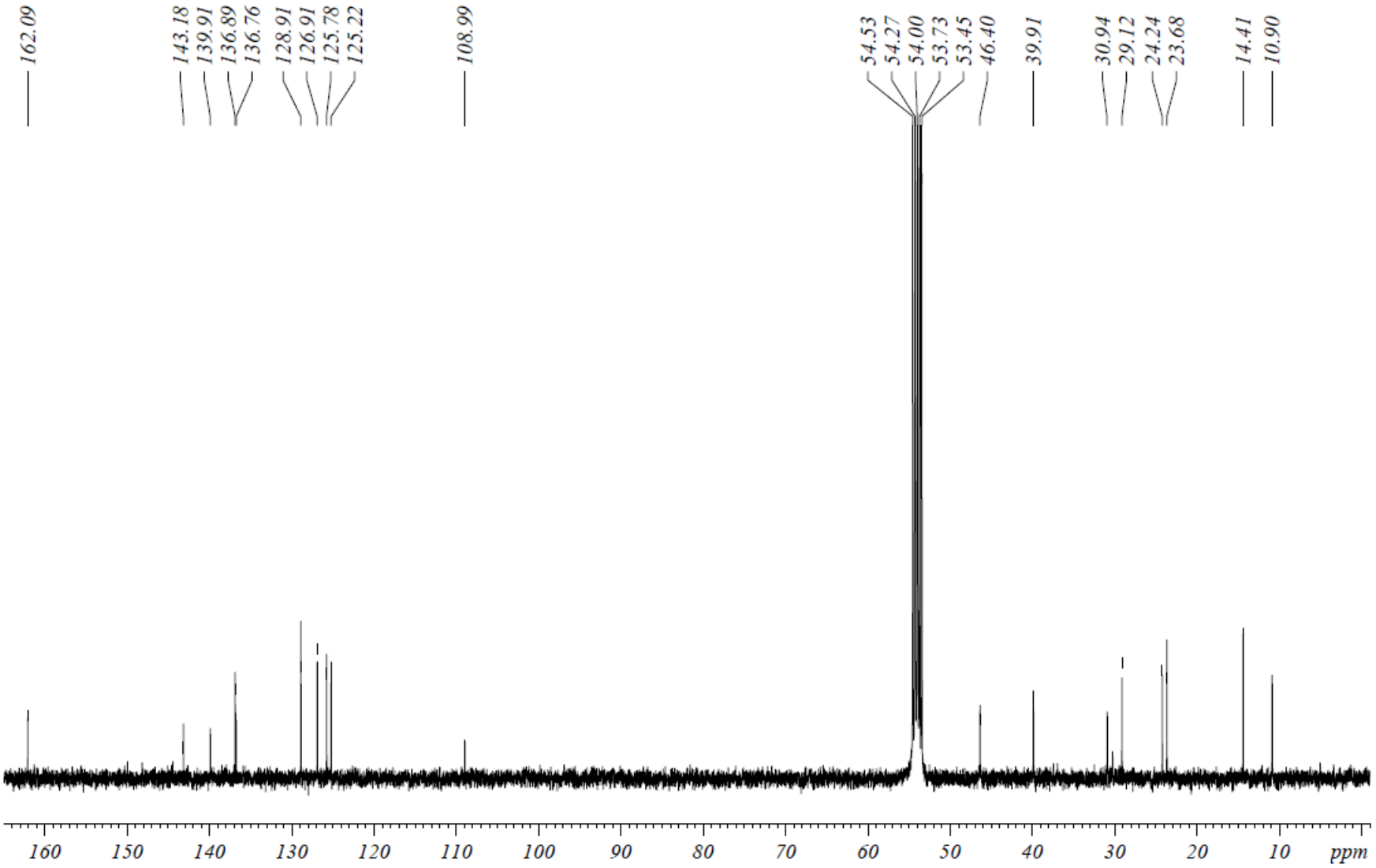

Figure S8. ^{13}C NMR spectrum of 3,6-bis(2,2'-bithiophenyl-5-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**7a**) in CD_2Cl_2.

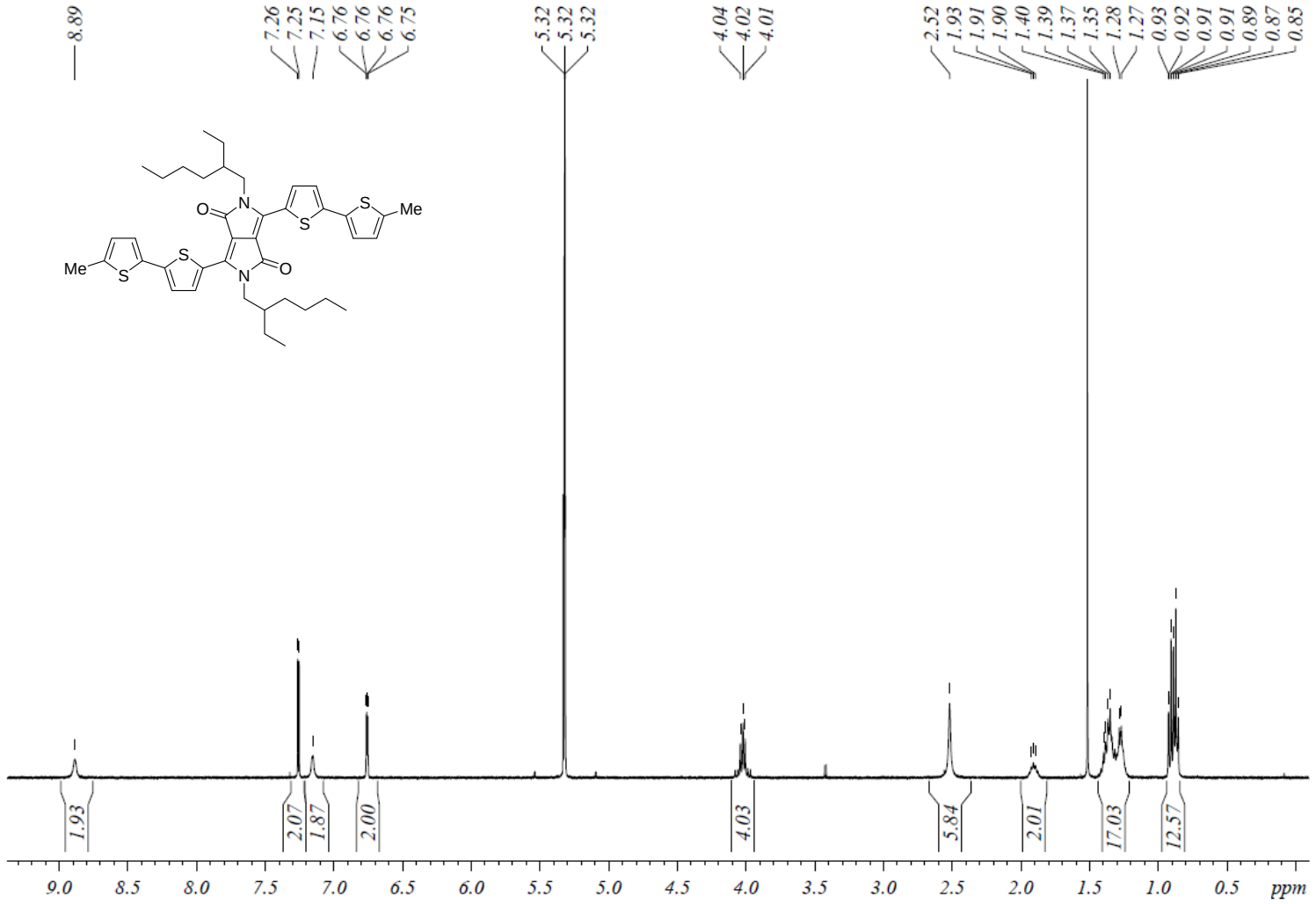

Figure S9. ^{1}H NMR spectrum of 2,5-bis(2-ethylhexyl)-3,6-bis(5'-methyl-(2,2'-bithiophenyl-5-yl)-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**7b**) in CD_2Cl_2.

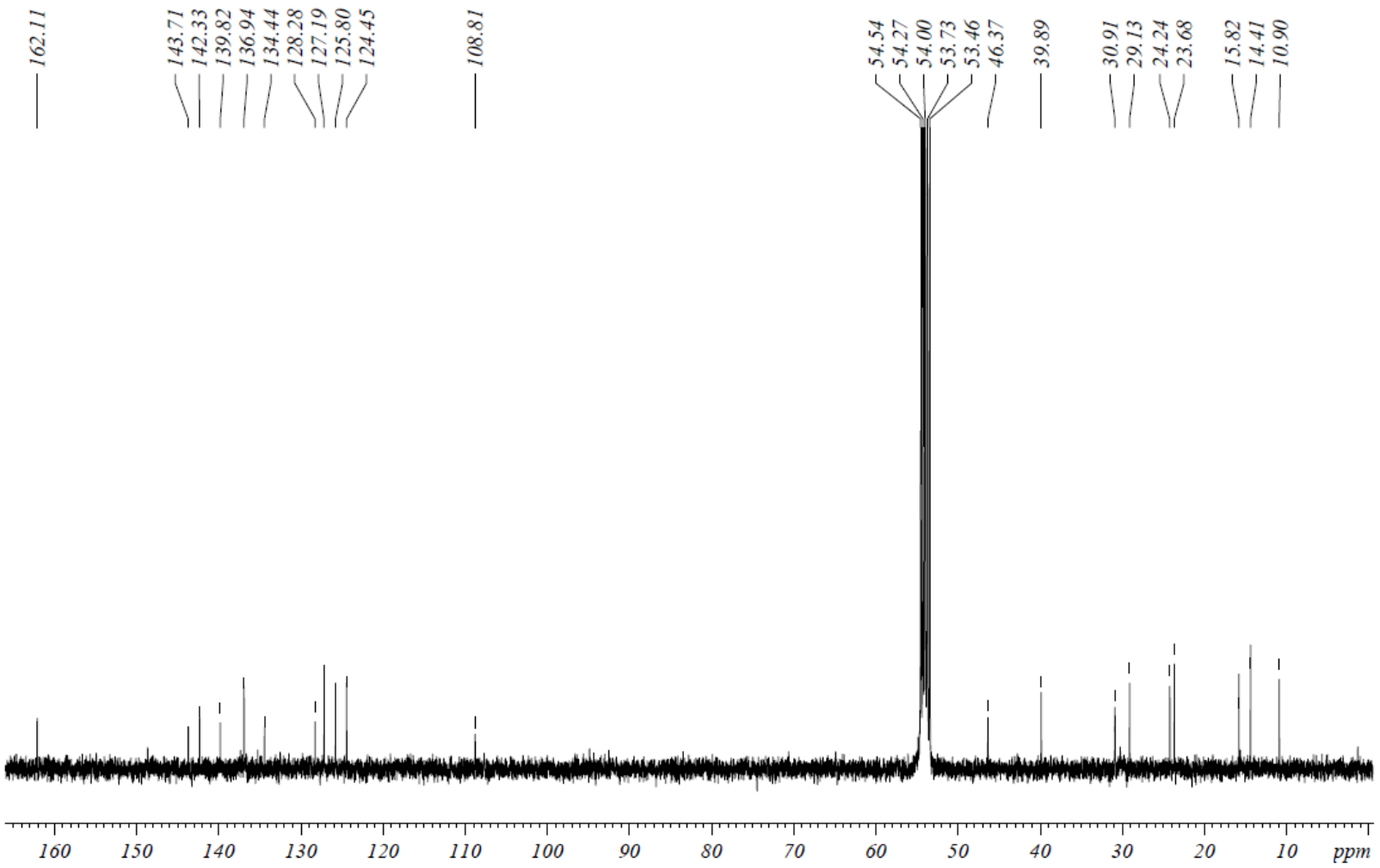

Figure S10. ^{13}C NMR spectrum of 2,5-bis(2-ethylhexyl)-3,6-bis(5'-methyl-(2,2'-bithiophenyl-5-yl)-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**7b**) in CD_2Cl_2.

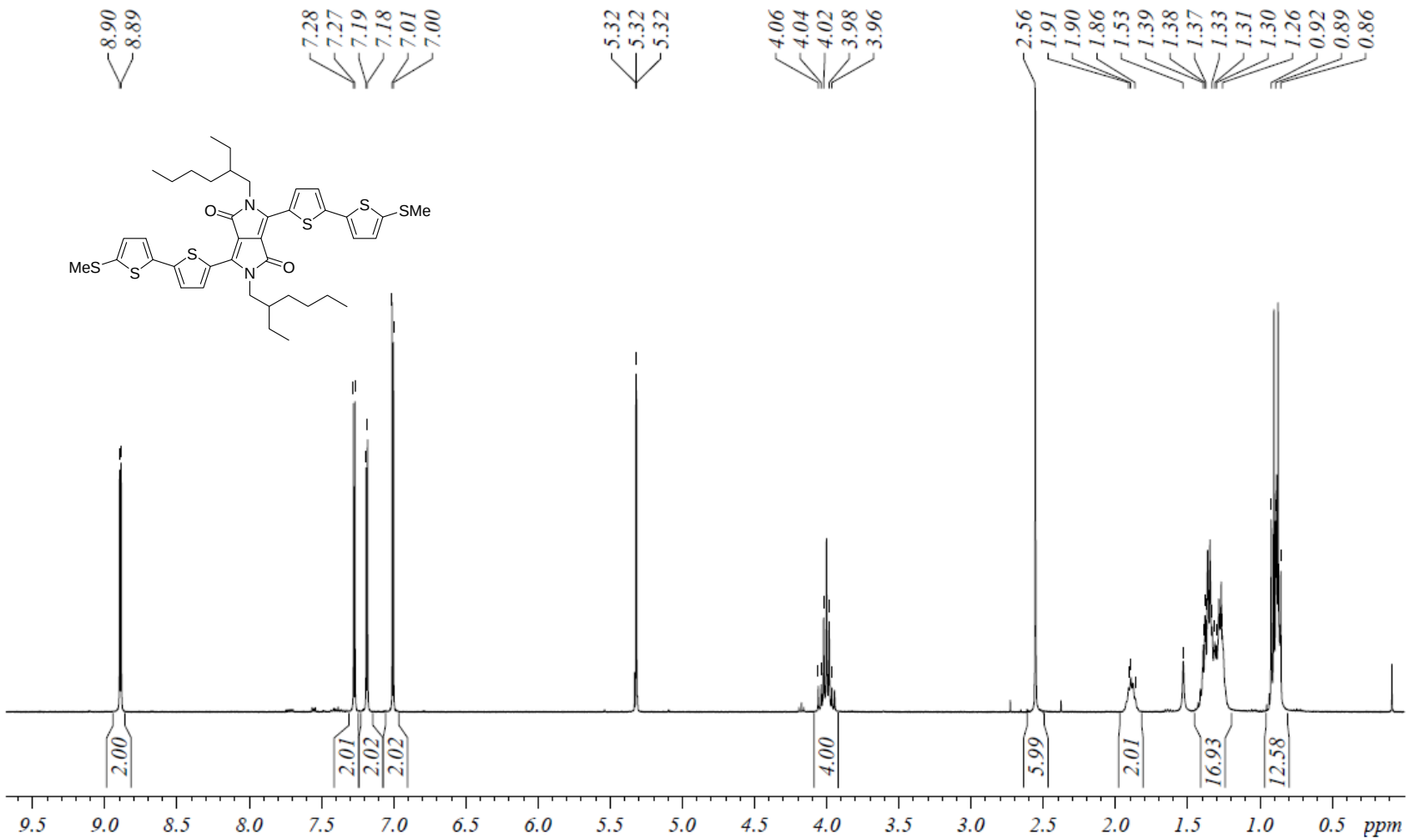

Figure S11. ^{1}H NMR spectrum of 2,5-bis(2-ethylhexyl)-3,6-bis(5'-methylsulfanyl-(2,2'-bithiophenyl-5-yl)-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**7c**) in CD_2Cl_2.

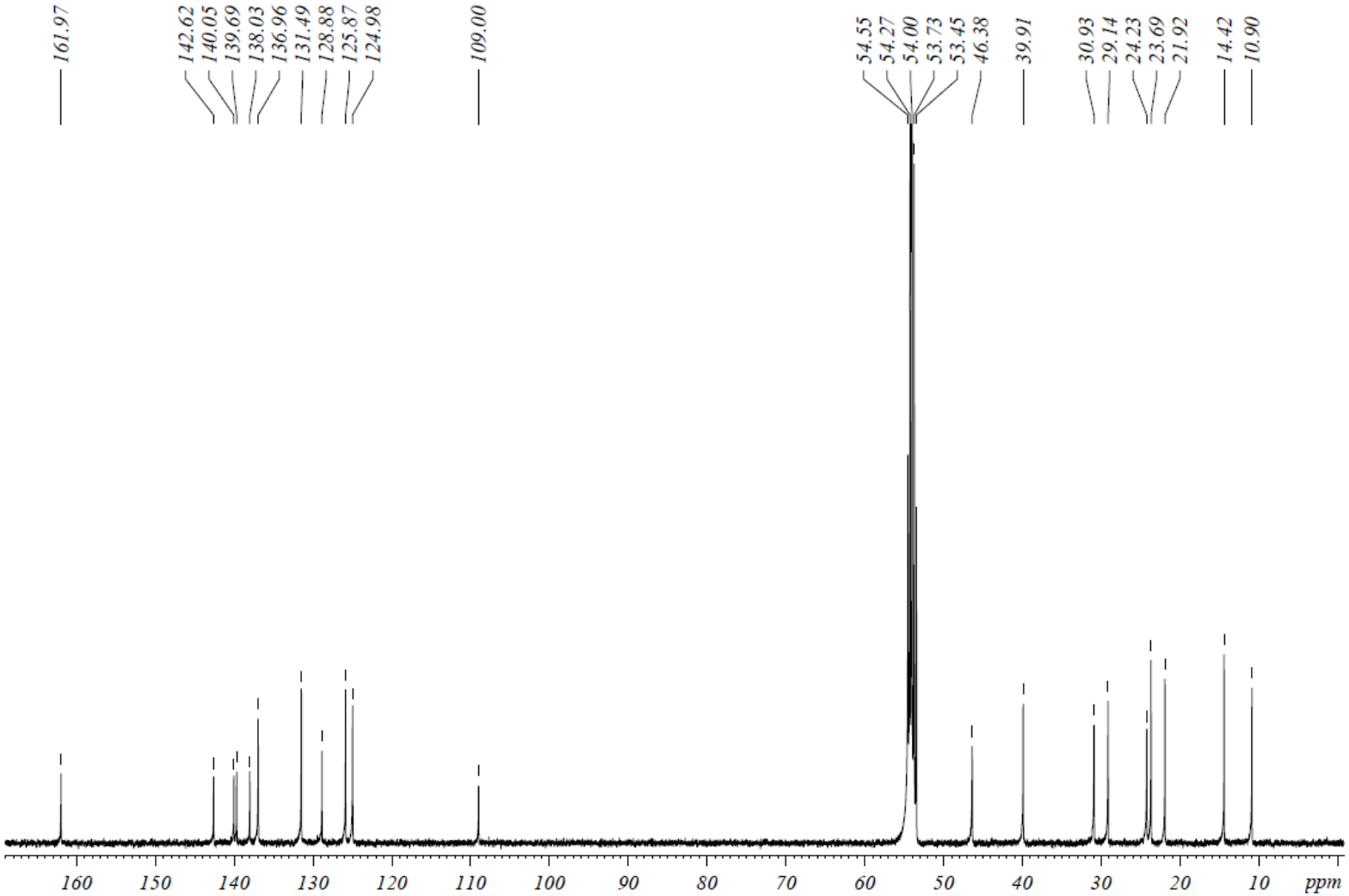

Figure S12. ^{13}C NMR spectrum of 2,5-bis(2-ethylhexyl)-3,6-bis(5'-methylsulfanyl-(2,2'-bithiophenyl-5-yl)-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**7c**) in CD_2Cl_2.

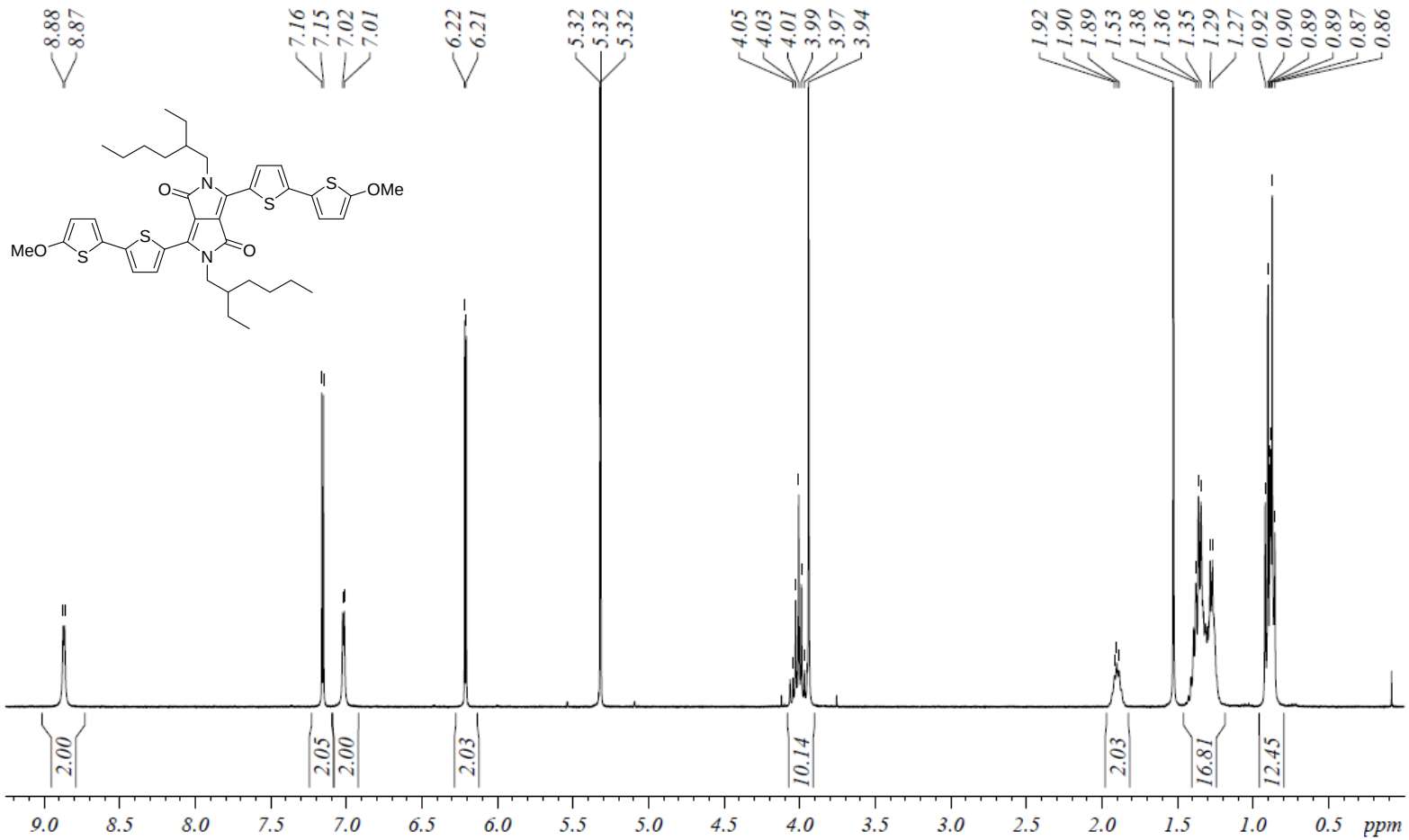

Figure S13. ^{1}H NMR spectrum of 2,5-bis(2-ethylhexyl)-3,6-bis(5'-methoxy-(2,2'-bithiophenyl-5-yl)-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**7d**) in CD_2Cl_2.

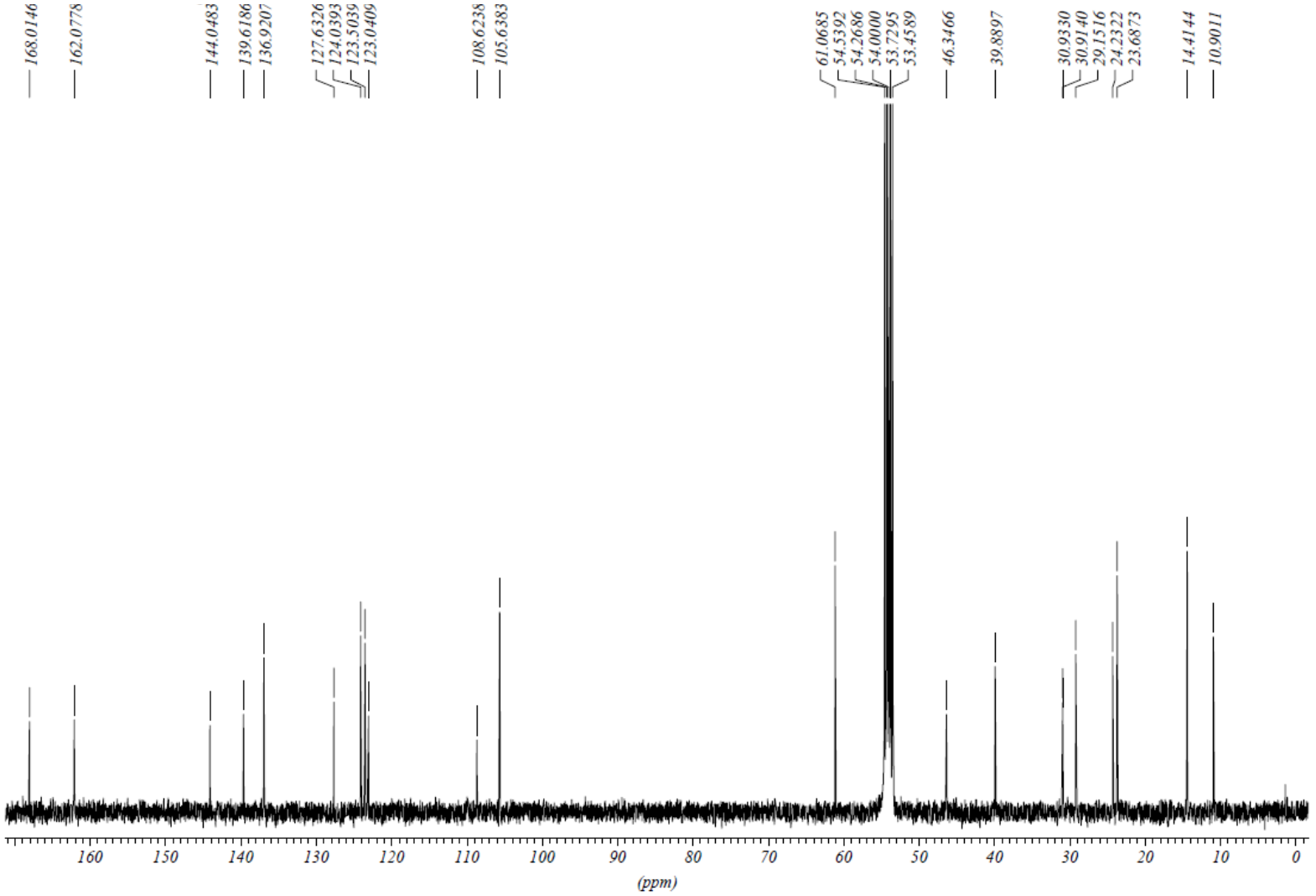

Figure S14. ^{13}C NMR spectrum of 2,5-bis(2-ethylhexyl)-3,6-bis(5'-methoxy-(2,2'-bithiophenyl-5-yl)-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**7d**) in CD_2Cl_2.

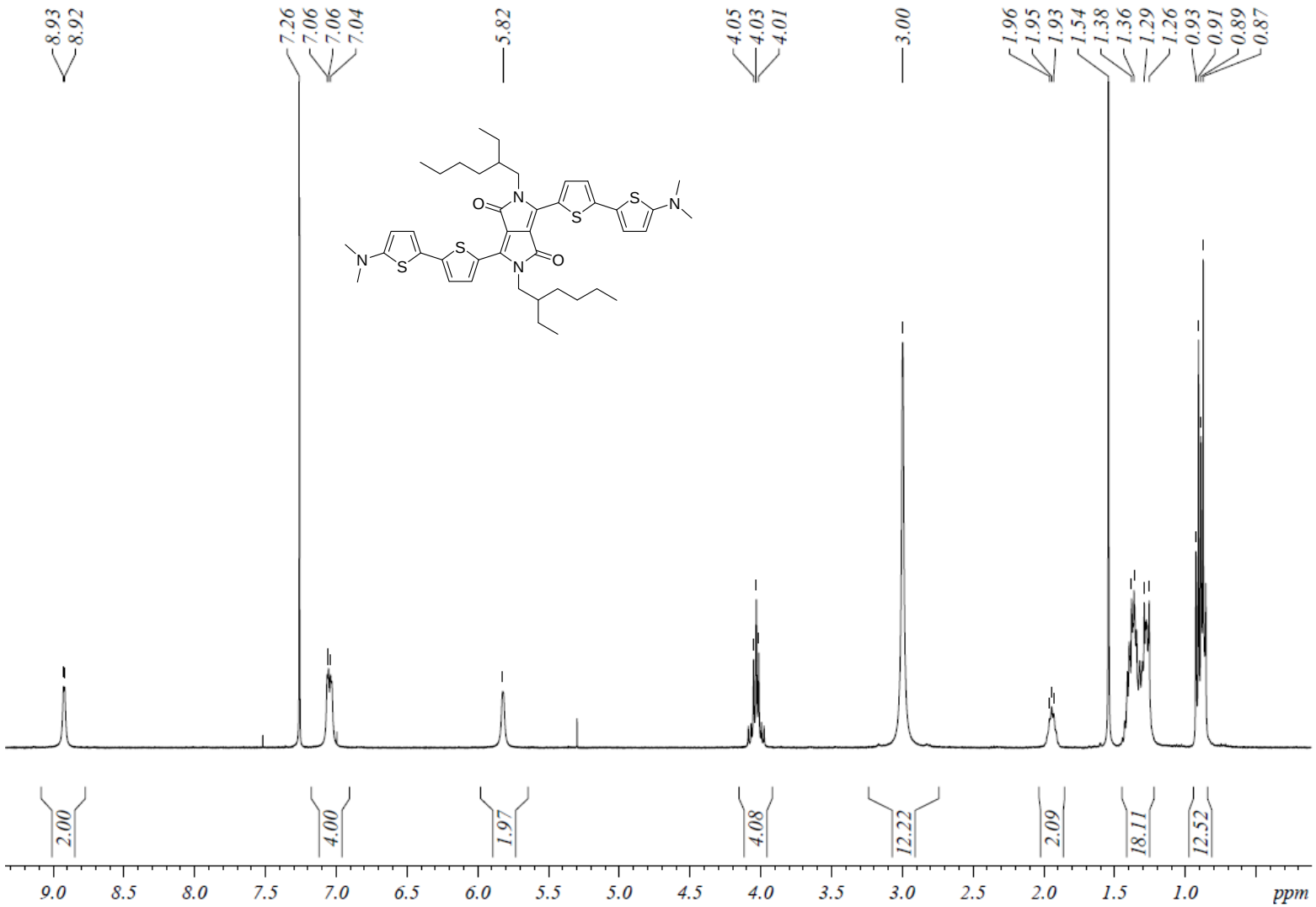

Figure S15. ^{1}H NMR spectrum of 2,5-bis(2-ethylhexyl)-3,6-bis(5'-dimethylamino-(2,2'-bithiophenyl-5-yl)-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**7e**) in CD_2Cl_2.

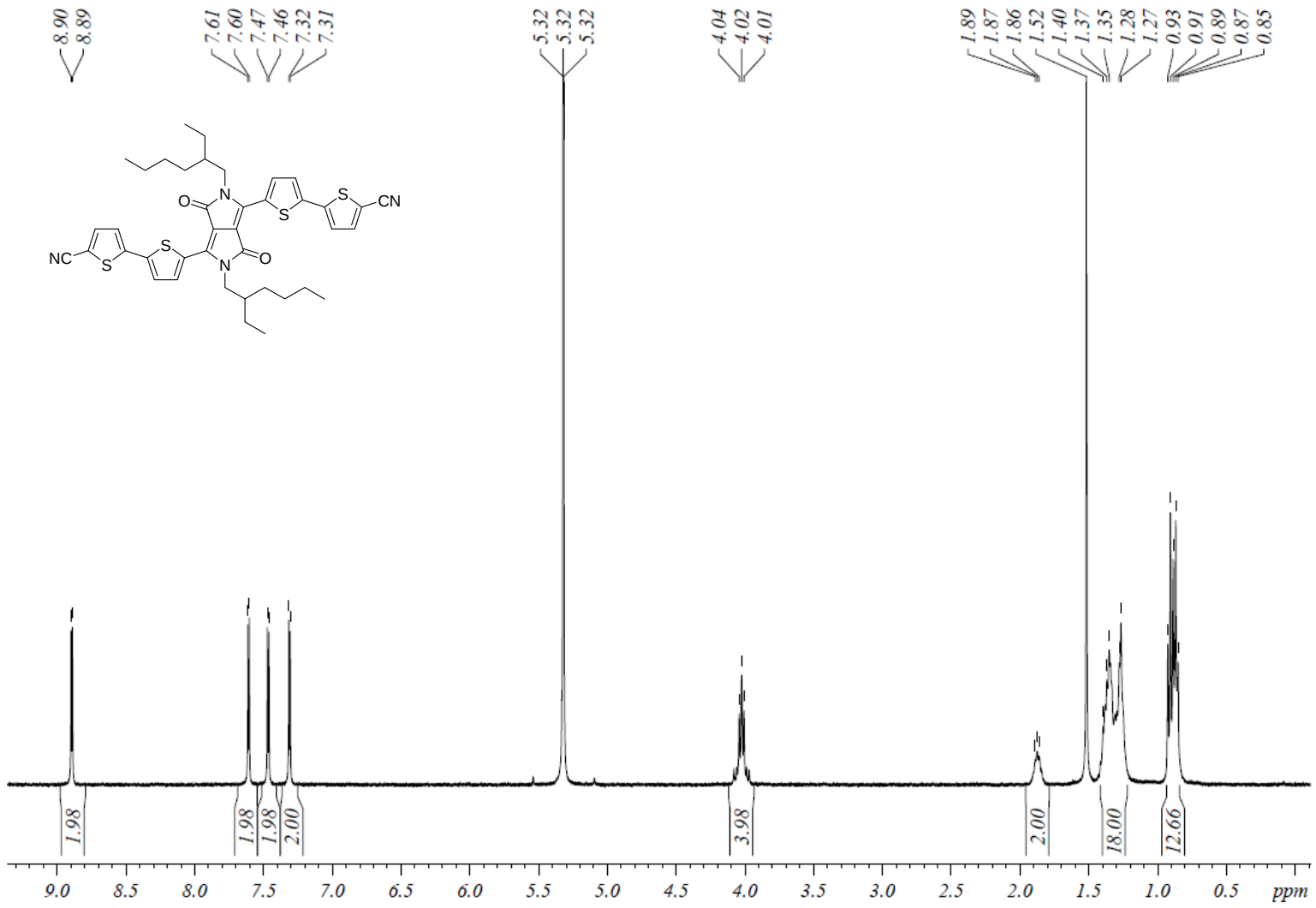

Figure S16. ^{1}H NMR spectrum of 2,5-bis(2-ethylhexyl)-3,6-bis(5'-dicarbonitrile-(2,2'-bithiophenyl-5-yl)-2,5-dihydro-pyrrolo [3,4-*c*]pyrrole-1,4-dione (**7f**) in CD_2Cl_2.

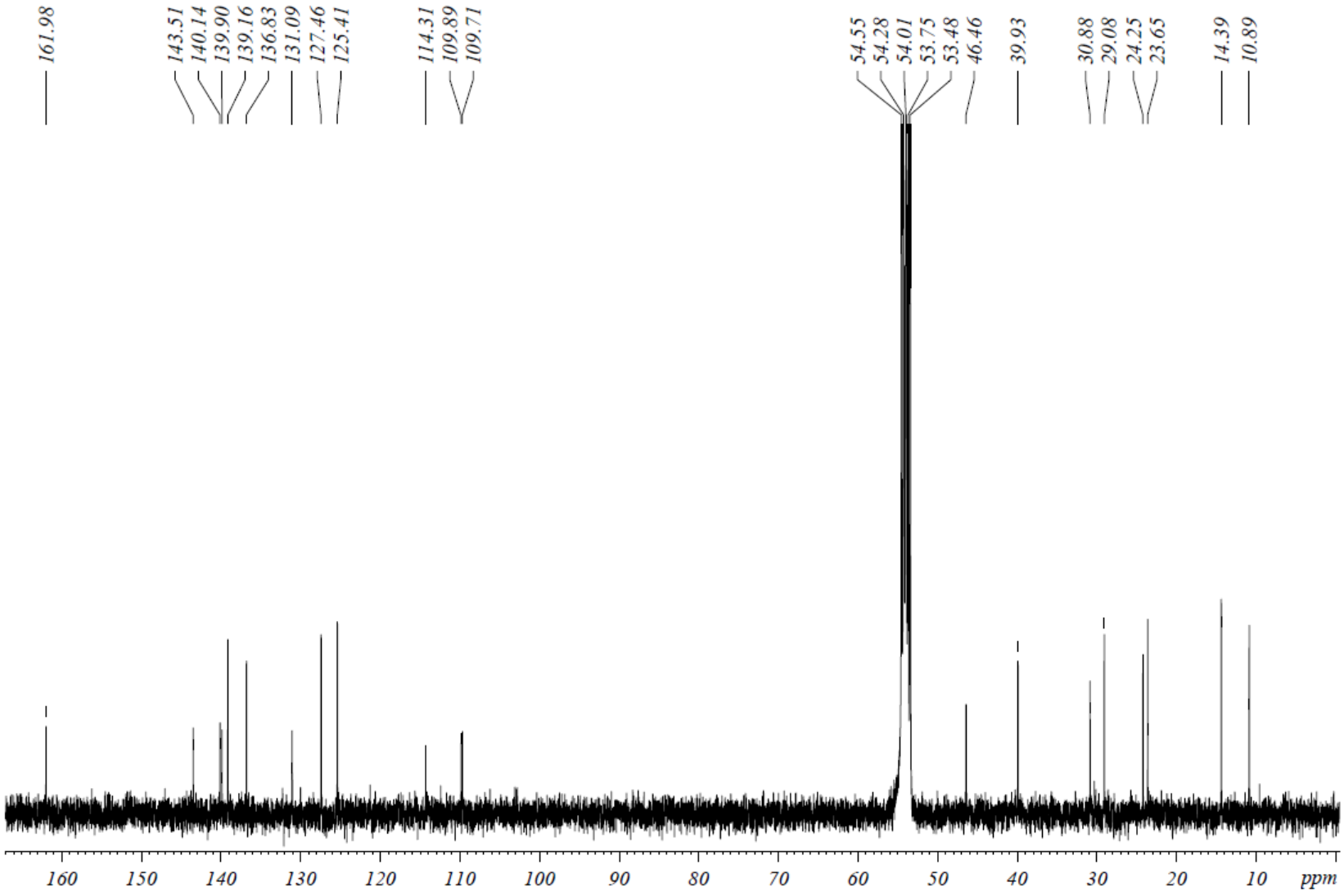

Figure S17. ^{13}C NMR spectrum of 2,5-bis(2-ethylhexyl)-3,6-bis(5'-dicarbonitrile-(2,2'-bithiophenyl-5-yl)-2,5-dihydro-pyrrolo [3,4-*c*]pyrrole-1,4-dione (**7f**) in CD_2Cl_2.