Electronic Supplementary Information

Highly π–extended tetrathiafulvalene analogues derived from pentacene–5,7,12,14–tetraone

*Eyad A. Younes and Yuming Zhao**

Department of Chemistry, Memorial University, St. John’s, NL, Canada A1B 3X7

Email: yuming@mun.ca

Table of Content

1. Experimental

1.1. *General*

Chemicals and reagents were purchased from commercial suppliers and used directly without purification. All reactions were conducted in standard, dry glassware and under an inert atmosphere of nitrogen unless otherwise noted. Evaporation and concentration were carried out with a water-aspirator. Flash column chromatography was performed with silica gel 60 (240-400 mesh). Thin-layer chromatography (TLC) was carried out with silica gel F254 covered on plastic sheets and visualized by UV light. ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance III 300 MHz multinuclear spectrometer. Chemical shifts (δ) are reported in ppm downfield relative to the signal of the internal reference $SiMe_4$. Coupling constants (*J*) are given in Hz. Infrared spectra (IR) were recorded on a Bruker Alfa spectrometer. HRMS analyses were performed on an Agilent 6230 TOF LC/MS instrument using an APPI ionizer. UV-Vis absorption spectra were measured on a Cary 6000i spectrophotometer. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) were carried out in a standard three-electrode setup controlled by a BASi epsilon workstation. Pentacene-5,7,12,14-tetraone **3**,[1] thione **4**,[2] and *S*-methyl phosphonate **6**[3] were prepared according to literature procedures with suitable modifications.

---

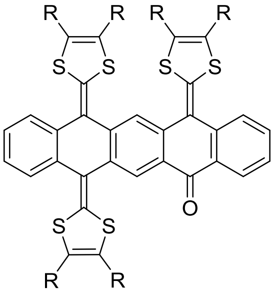
(1) N. Vets, H. Diliën, S. Toppet and W. Dehaen, *Synlett*, 2006, 1359-1362.

(2) (a) G. Steimecke, H. J. Sieler, R. Kirmse and E. Hoyer, *Phosphor. Sulf.*, 1979, **7**, 49-55; (b) M. R. Bryce and A. J. Moore, *Synthesis*, 1991, 26-28.

(3) A. J. Moore and M. R. Bryce, *Tetrahedron Lett.,* 1992, **33**, 1373-1376.

1.2 Synthetic procedures

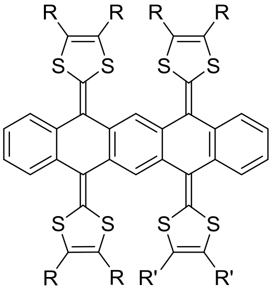
Compound 5



5 R = $SC_{10}H_{21}$

Pentacene–5,7,12,14–tetraone **3** (0.051 g, 0.15 mmol) and thione **4** (0.43 g, 0.90 mmol) were mixed in $P(OCH_3)_3$ (40 mL), and the mixture was heated to 130 °C for 3 h. The unreacted $P(OCH_3)_3$ was then removed under reduced pressure. The resulting crude product was subjected silica flash column chromatography (CH_2Cl_2/hexanes, 1:1) to yield pure compound **5** (0.10 g, 0.061 mmol, 41%) as a dark red semisolid. IR (neat): 2953, 2921, 2851, 1655, 1596, 1522, 1489, 1462, 1259, 758 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.29 (d, *J* = 9.0 Hz, 1H), 8.08 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.69-7.60 (m, 3H), 7.48-7.44 (m, 1H), 7.37-7.33 (m, 3H), 2.86-2.78 (m, 12H), 1.66-1.59 (m, 12H), 1.40-1.22 (m, 84H), 0.89-0.83 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.6, 140.5, 139.0, 137.9, 136.5, 134.6, 134.4, 134.2, 133.3, 132.6, 131.5, 130.9, 128.2, 128.2, 127.8, 127.6, 127.0, 126.7, 126.6, 126.5, 126.2, 125.6, 125.5, 125.2, 123.8, 122.1, 122.1, 121.7, 118.6, 37.0, 36.9, 36.8, 36.5, 36.4, 31.9, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 28.6, 28.5, 22.7, 14.2. HRMS (APCI, positive) *m/z* calcd for $C_{96}H_{137}OS_{12}$ ($[M + H]^+$) 1629.7318, found 1629.7266.

Compound 2b



2b R = $C_{10}H_{21}$, R' = CH_3

To a solution of *S*-methyl phosphonate **6** (0.025 g, 0.086 mmol) in dry THF (15 mL) at -78 °C was added *n*-BuLi (0.034 mL, 2.5M, 0.086 mmol). After stirring for 15 min, a solution of compound **5** (0.070 g, 0.043 mmol) in dry THF (5 mL) was added to the reaction mixture through a syringe. The resulting mixture was allowed to warm to rt and kept stirring overnight. Then the solvent was removed under reduced pressure, and the residue was diluted with CH_2Cl_2. The solution was collected and washed with brine and H_2O sequentially, and the organic phase was dried over $MgSO_4$ and then concentrated under vacuum, affording the crude product of **2b** which was purified by silica flash column chromatography (CH_2Cl_2/hexanes, 1:4) to yield compound **2b** (0.051 g, 0.028 mmol, 65%) as a yellow semisolid. IR (neat): 2953, 2921, 2851, 1732, 1539, 1455, 1260, 1092, 1021, 851, 772, 653 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.57(m, 5H), 7.42-7.33 (m, 5H), 2.90-2.78 (m, 12H), 2.46 (s, 3H), 2.42 (s, 3H), 1.68-158 (m, 12H), 1.41-1.25 (m, 84H), 0.89- 0.85 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.5, 134.5, 134.4, 132.8, 132.5, 131.2, 130.9, 130.8, 130.1, 127.1, 126.8, 126.7, 126.3, 126.3, 126.1, 125.4, 125.3, 124.7, 124.0, 122.8, 122.7, 121.5, 121.4, 36.7, 36.3, 31.9, 29.9, 29.8, 29.7, 29.6, 29.5, 29.3, 29.3, 29.2, 28.7, 28.6, 28.60, 22.7, 19.5, 19.3, 14.1. HRMS (APCI, positive) *m/z* calcd for $C_{96}H_{143}S_{16}$ ($[M + H]^+$) 1807.6721, found 1807.6629.

1.3 Oxidative UV-Vis titration experiments

Titration of 5: A solution of **5** in THF (7.38×10^{-6} M) was prepared and then titrated with a mixture solution of $PhI(OAc)_2$/ CF_3SO_3H, (1: 4 molar ratio, $[PhI(OAc)_2] = 2.60 \times 10^{-2}$ M) using a microsyringe. In each step of titrations, *ca.* 1 molar equivalent of oxidant was added. The mixture solution was allowed to stand for *ca.* 5 min before a UV-Vis absorption spectrum of the solution was recorded.

Titration of 2b: A solution of **2b** in THF (8.29×10^{-6} M) was prepared, and then titrated with a mixture solution of $PhI(OAc)_2$/ CF_3SO_3H, (1: 4 molar ratio, $[PhI(OAc)_2] = 2.57 \times 10^{-2}$ M) using a microsyringe. In each step of titrations, *ca.* 0.5 molar equivalent of oxidant was added. The mixture solution was allowed to stand for *ca.* 5

min before a UV-Vis absorption spectrum of the solution was recorded.

2. NMR spectra of compounds 5 and 2b

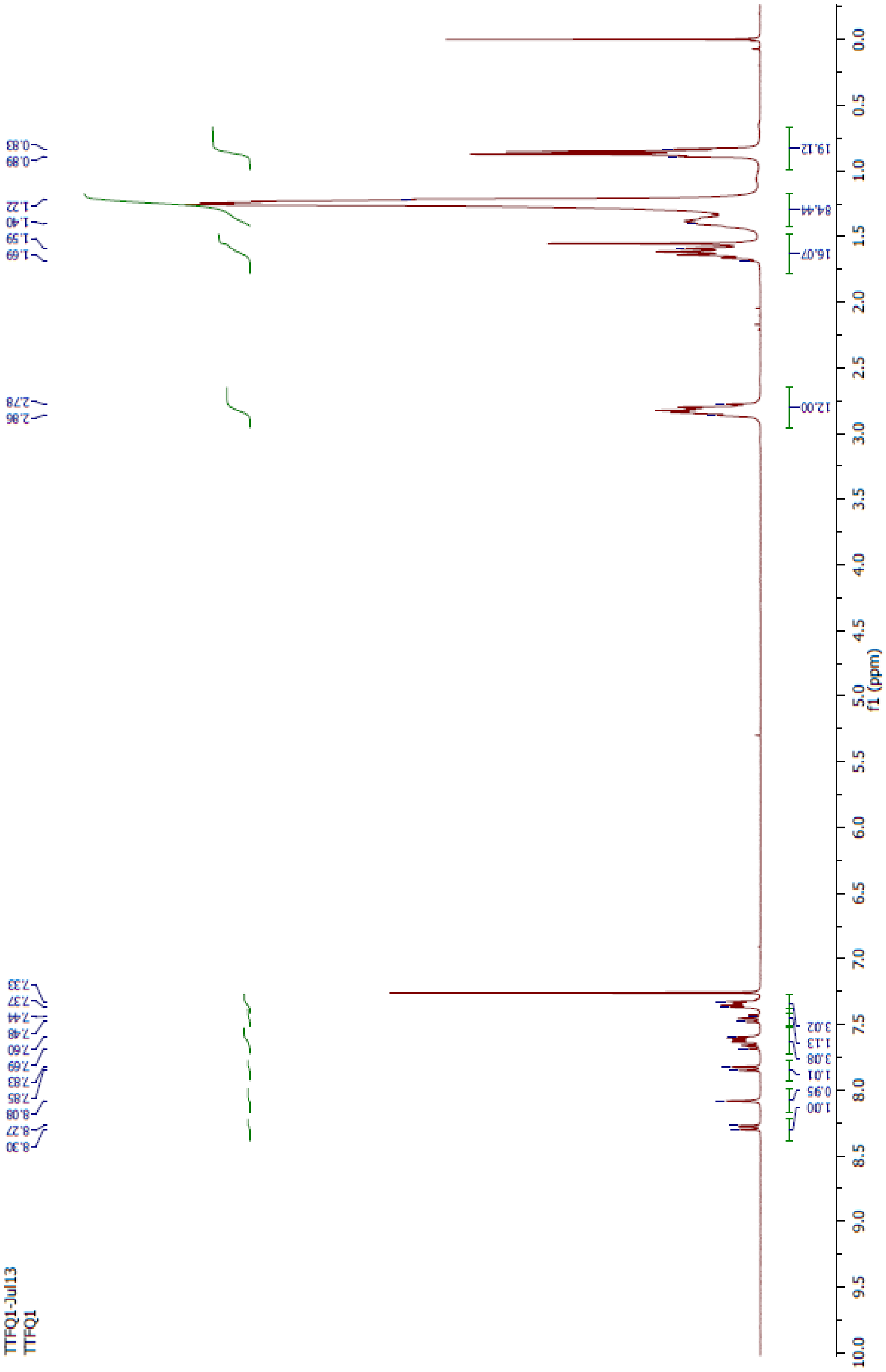


Fig. S-1 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **5**.

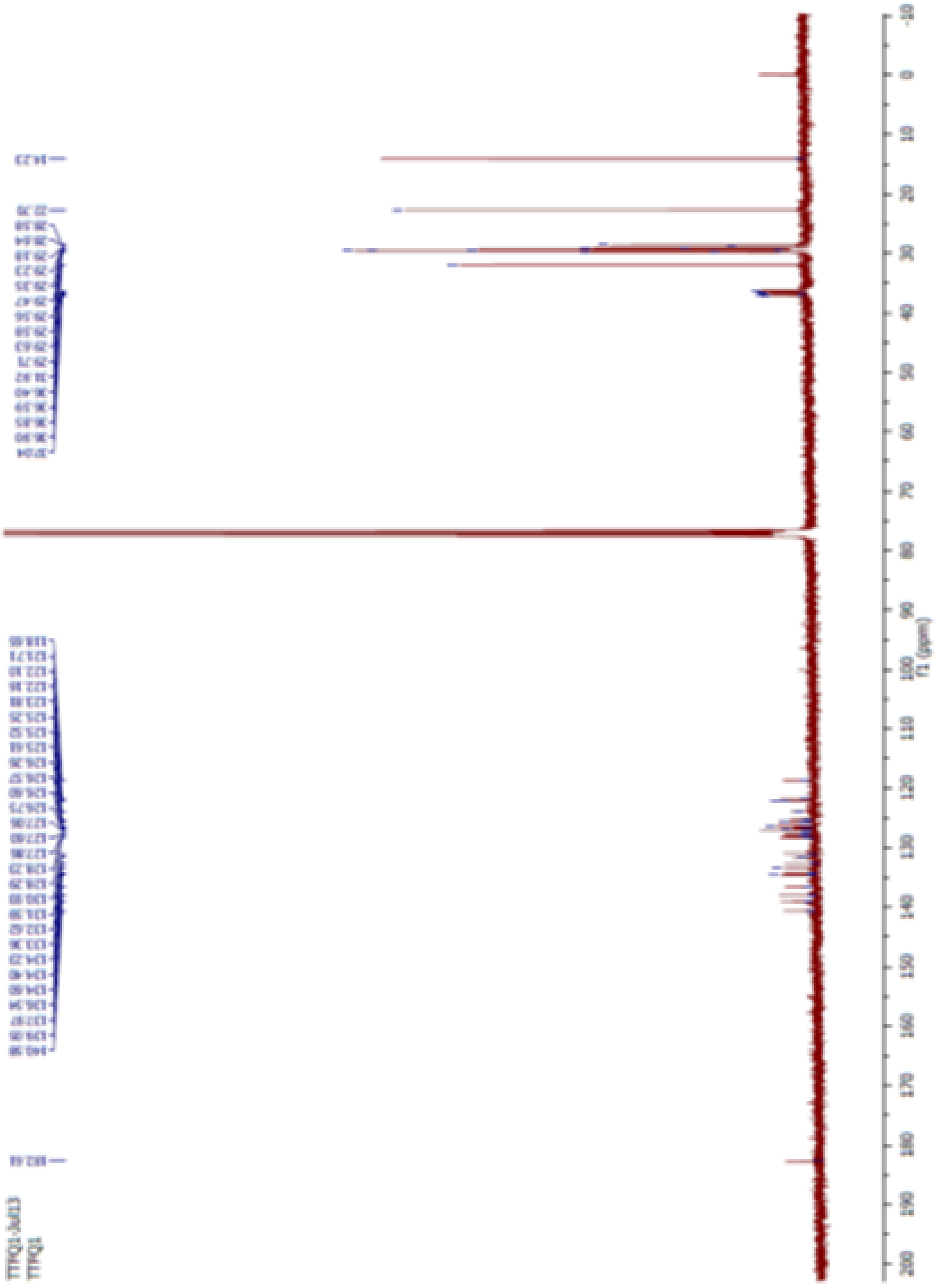


Fig. S-2 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **5**.

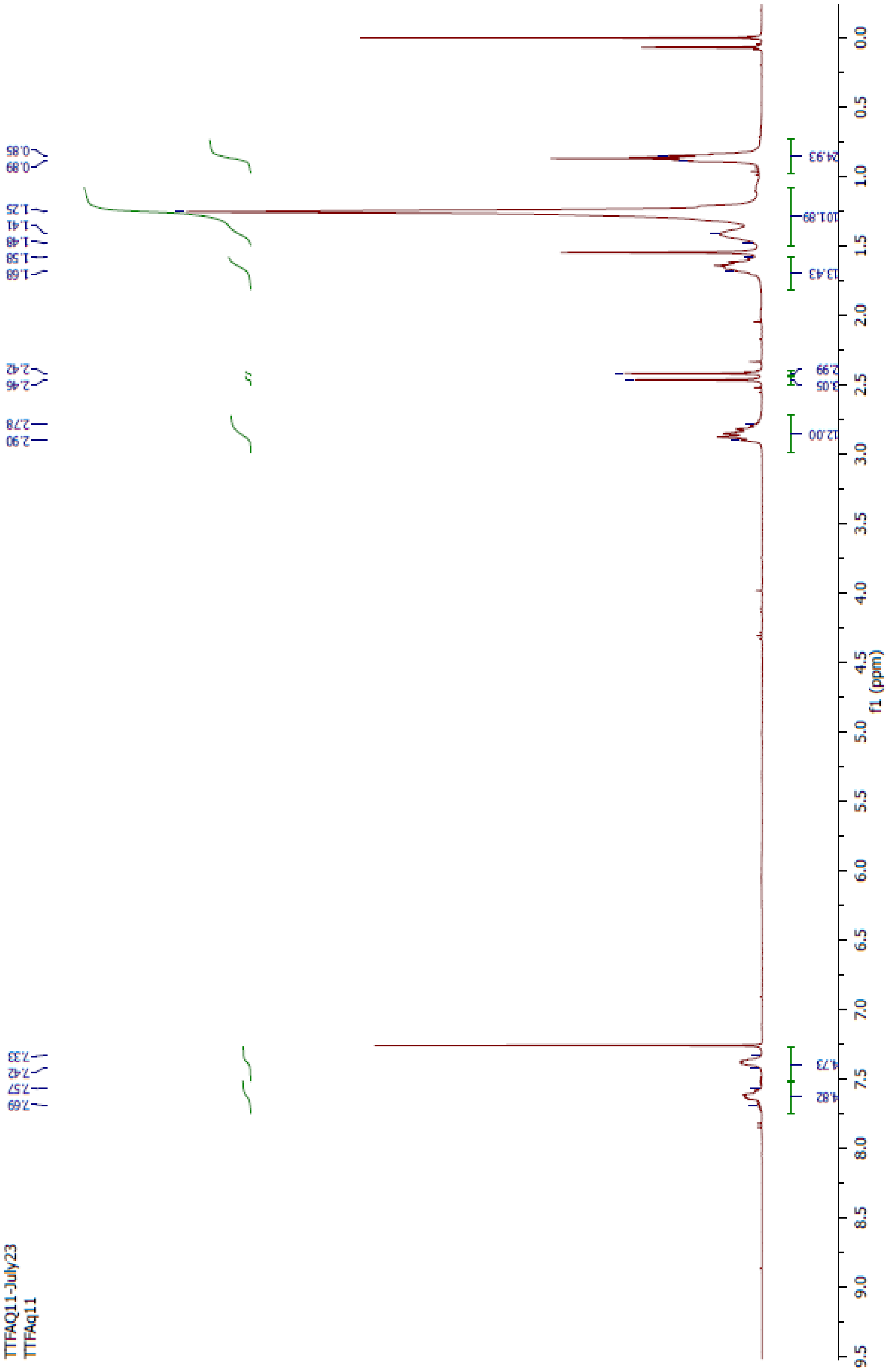


Fig. S-3 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **2b**.

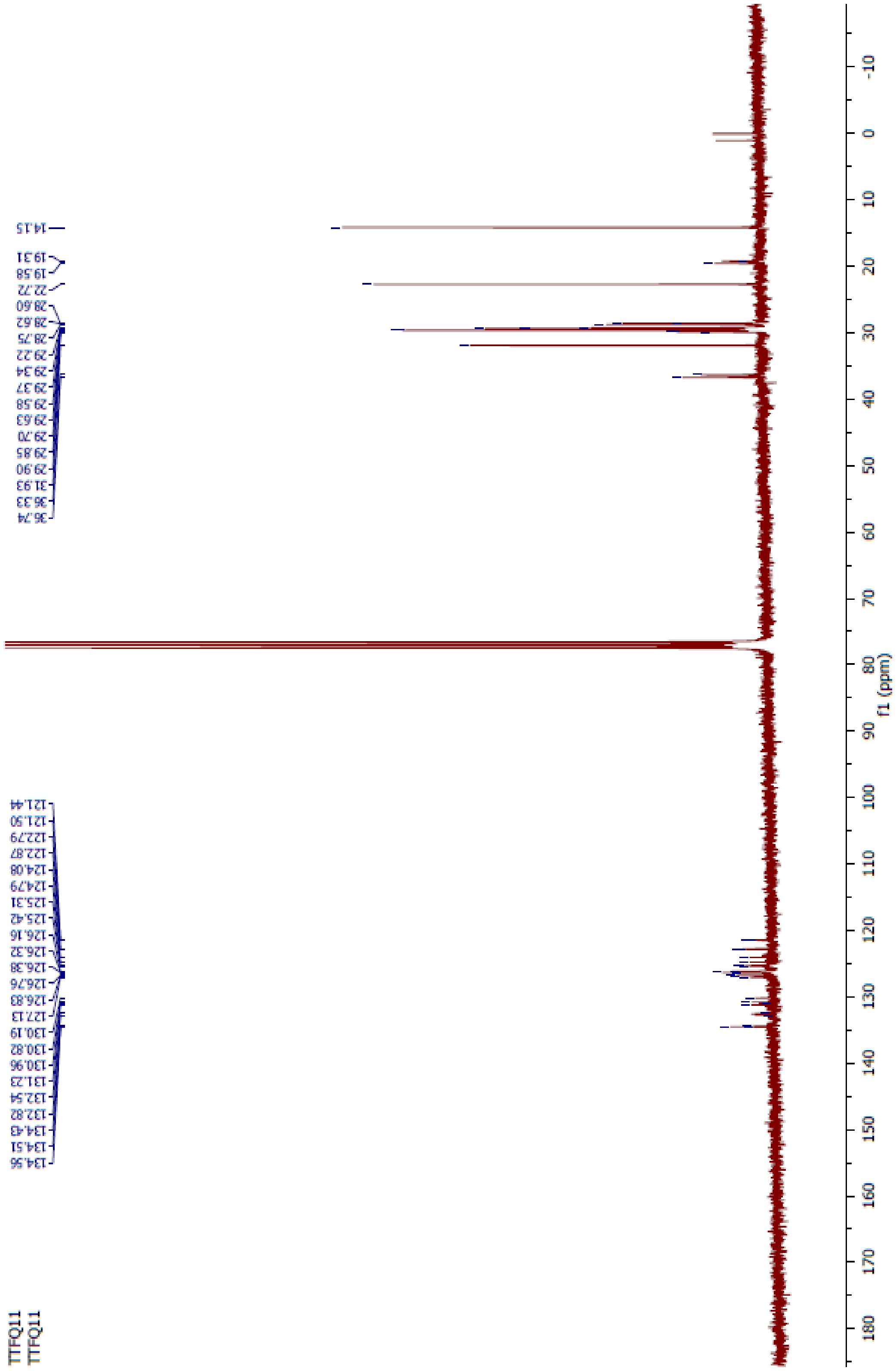


Fig. S-4 ^{13}C NMR (75 MHz, CDCl$_3$) spectrum of compound **2b**.

3. DFT Calculations on Compound 2a

The structural and frontier molecular orbital (FMO) properties of compound **2a** in different oxidation states were investigated by density functional theory (DFT) calculations using the Gaussain 09 software package.[4] The molecular geometries were optimized at the B3LYP/6-31G(d) level and visualized with CYLview, while the FMO plots were visualized with Gaussview 5.[5]

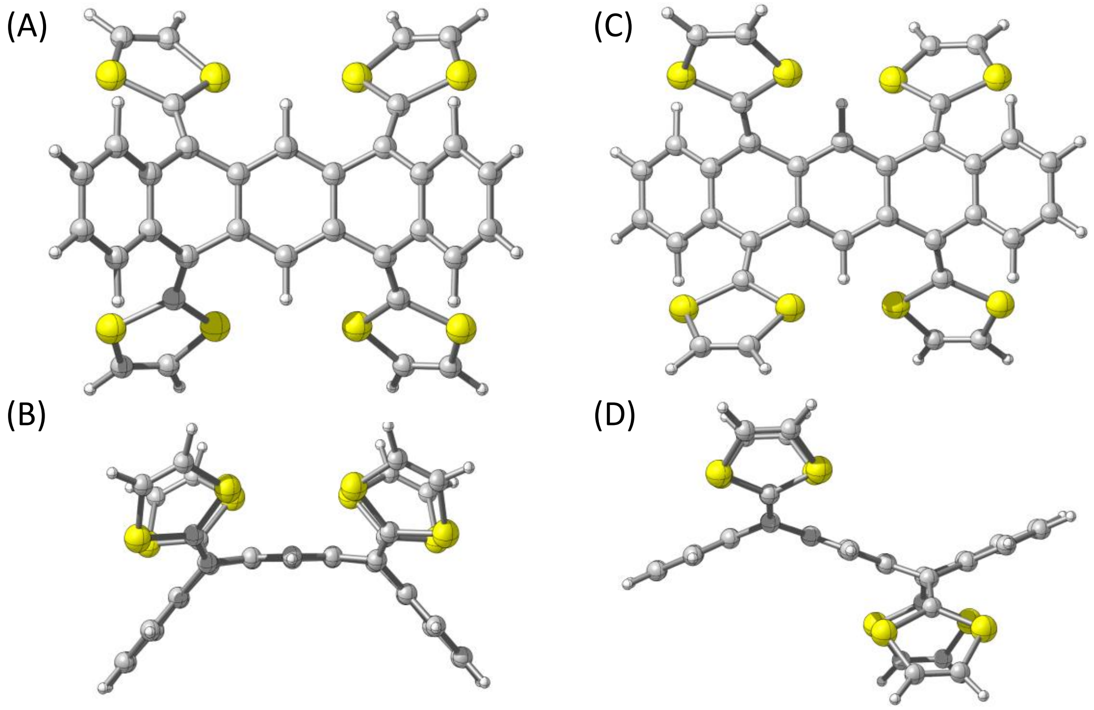


Fig. S-5 Optimized geometries of compound **2a** in the neutral state. (A) and (B): *cis* conformer (*E*(RB3LYP) = -4491.86093507 au, dipole moment = 3.1984 Debye), (C)

---

(4) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

(5) GaussView, Version 5, Roy Dennington, Todd Keith, and John Millam, Semichem Inc., Shawnee Mission, KS, 2009.

and (D) *trans* conformer (*E*(RB3LYP) = -4491.86251228 au, dipole moment = 0 Debye).

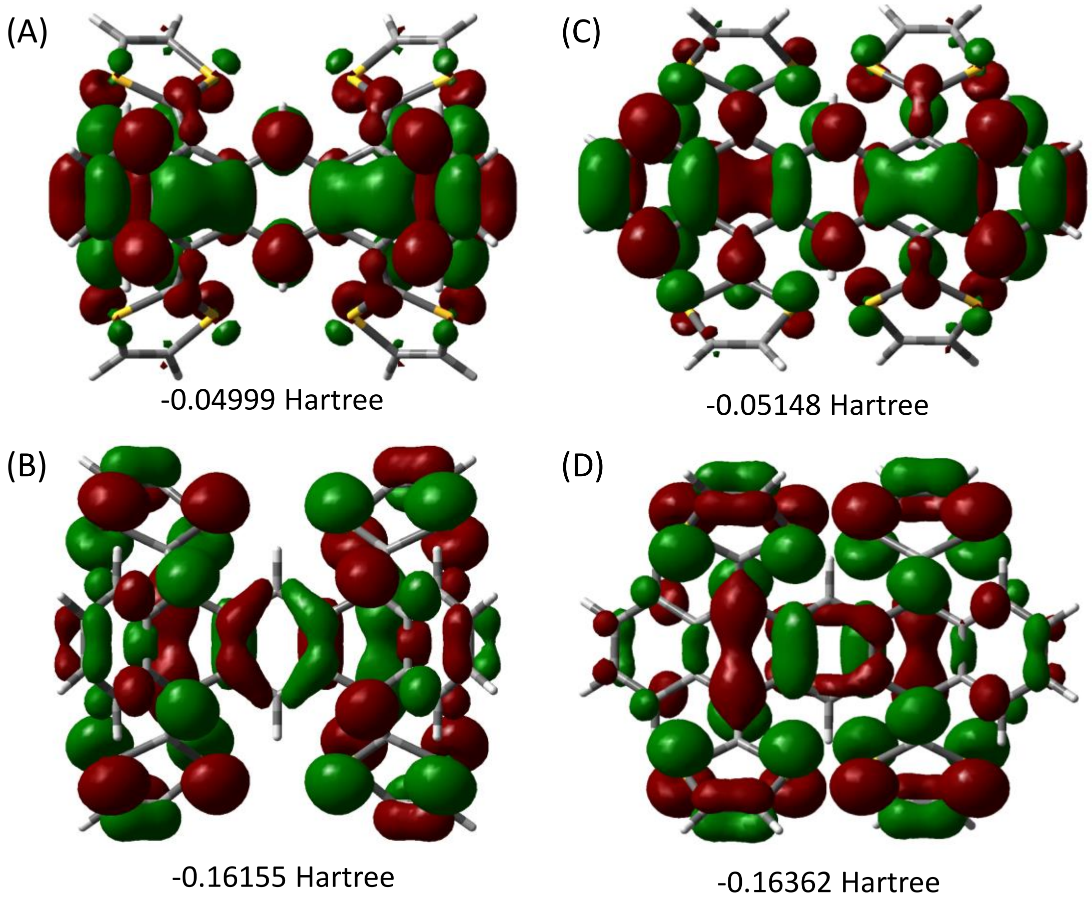


Fig. S-6 Plots and energies of FMOs for compound **2a** in the neutral state. (A) LUMO of *cis* conformer, (B) HOMO of *cis* conformer, (C) LUMO of *trans* conformer, and (D) HOMO of *trans* conformer.

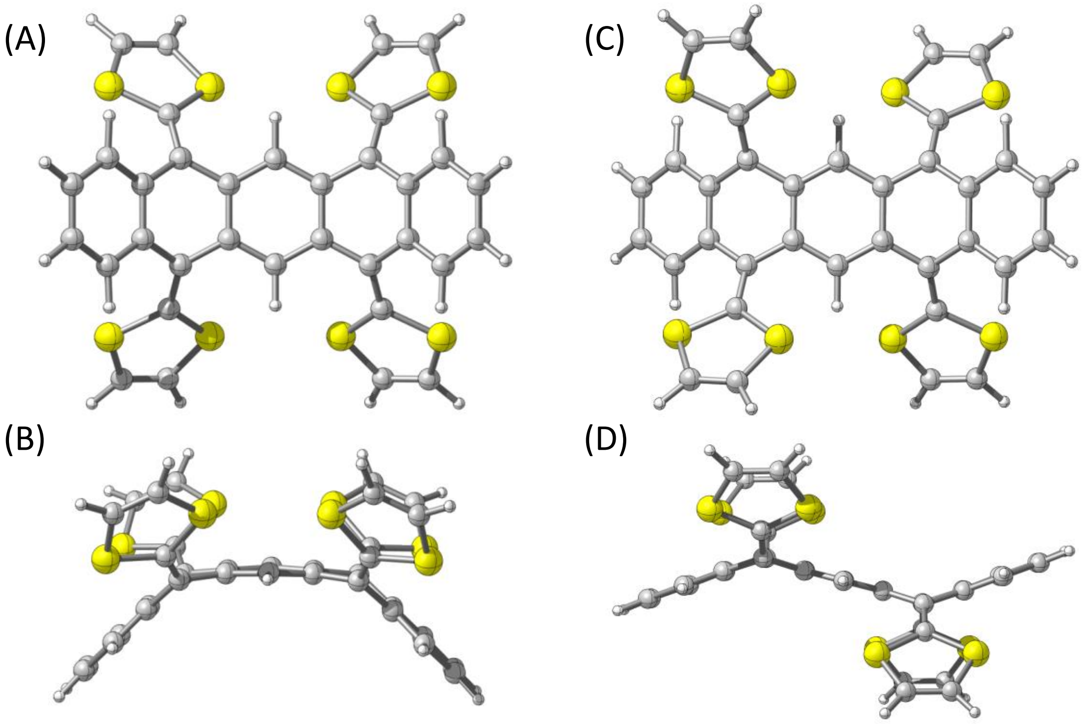


Fig. S-7 Optimized geometries of compound **2a** in the singlet dicationic state. (A) and (B): *cis* conformer (*E*(UB3LYP) = -4491.36838584 au, dipole moment = 4.8715 Debye), (C) and (D) *trans* conformer (*E* (UB3LYP) = -4491.36742237 au, dipole moment = 0 Debye).

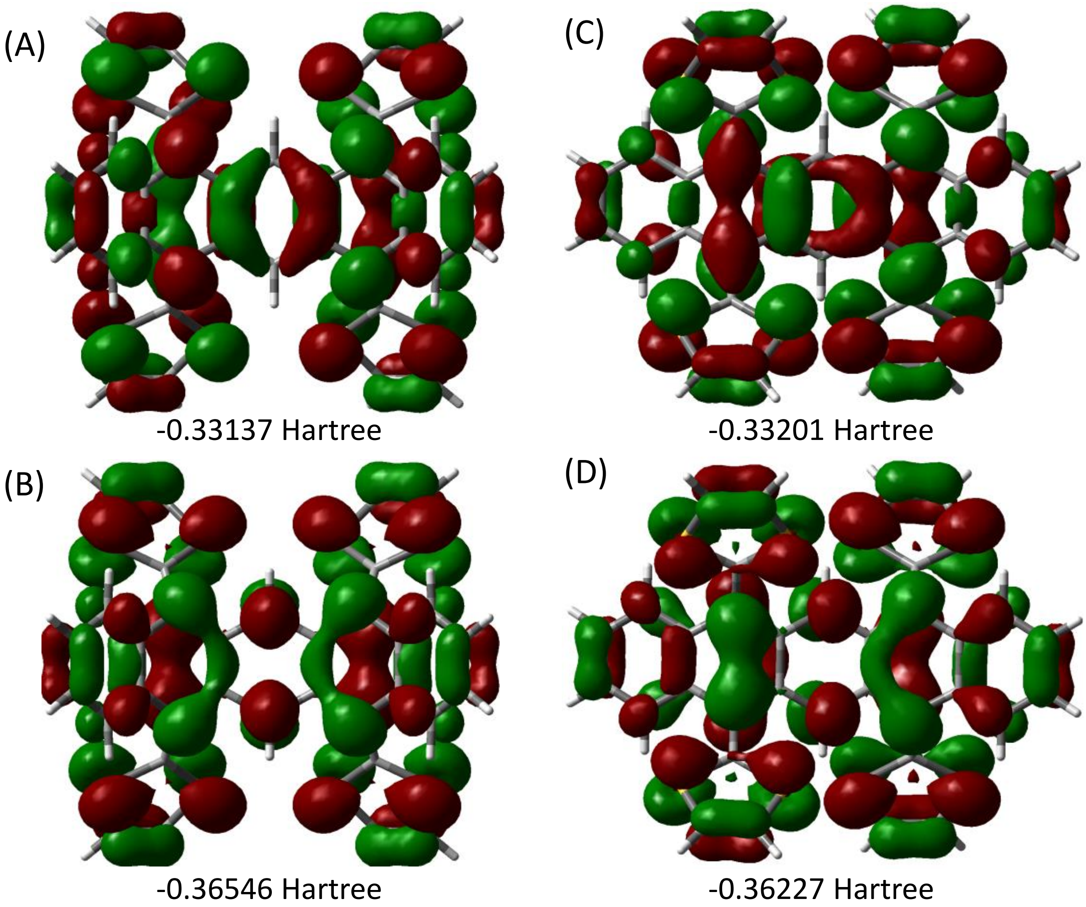


Fig. S-8 Plots and energies of FMOs for compound **2a** in the singlet dicationic state. (A) LUMO of *cis* conformer, (B) HOMO of *cis* conformer, (C) LUMO of *trans* conformer, and (D) HOMO of *trans* conformer.

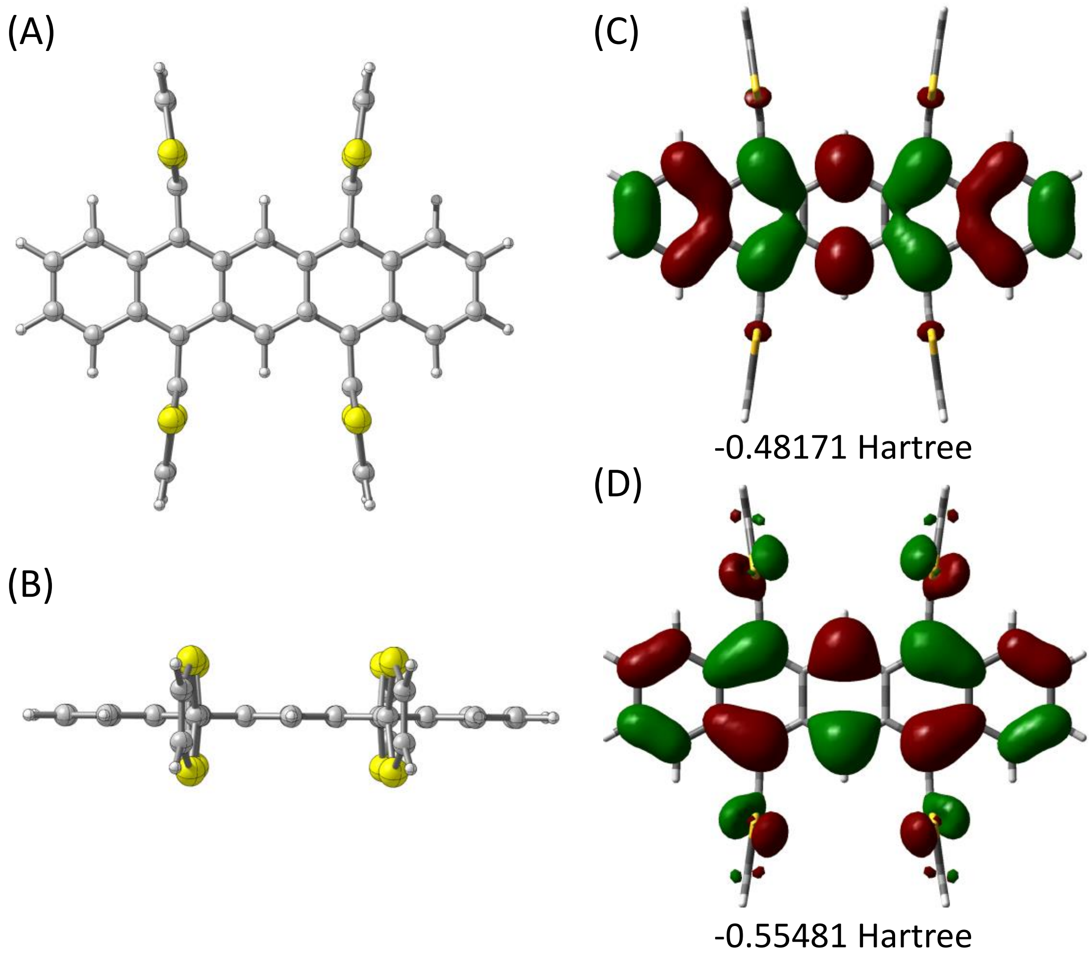


Fig. S-9 Optimized geometries of compound **2a** in the singlet tetracationic state (*E*(RB3LYP) = -4490.50168326 au, dipole moment = 0.0024 Debye). (A) Front view, (B) side view. Plots and energies of FMOs for compound **2a** in the singlet tetracationic state. (C) LUMO and (D) HOMO.

4. VT-NMR Results for Compound 2b

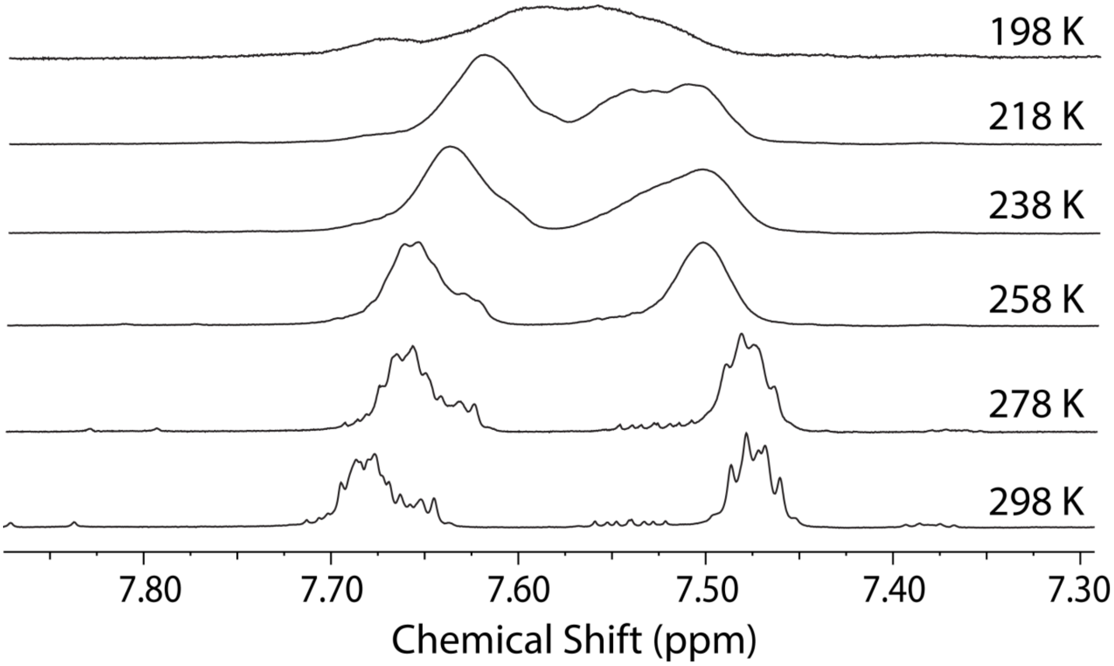


Fig. S-10 Partial VT ^{1}H NMR (CD_2Cl_2, 500 MHz) spectra of **2b** showing the aromatic region.