Straightforward access to aryl-substituted tetrathiafulvalenes by palladium-catalyzed direct C–H arylation and their photophysical and electrochemical properties

Yukihiro Mitamura, Hideki Yorimitsu,* Koichiro Oshima* and Atsuhiro Osuka

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Instrumentation and Chemicals

All reagents were of commercial reagent grade and were used without further purification unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL delta-600 spectrometer, and chemical shifts were reported as the δ scale in ppm relative to an internal standard $CDCl_3$ (δ = 7.26 ppm for ^{1}H, 77.23 ppm for ^{13}C). Spectroscopic grade solvents were used for all spectroscopic studies without further purification. UV/visible absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. UV/visible/NIR absorption spectra were recorded on a Shimadzu UV-3150 spectrometer. ESI-TOF-MS spectra were recorded on a Bruker Daltonics micro TOF LC instrument using a positive-ion mode. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Redox potentials were measured by the cyclic voltammetry method on an ALS electrochemical analyzer model 660, and the conditions were the following: 0.1 M Bu_4NPF_6 in benzonitrile, Ag/Ag^+ reference electrode, Pt working electrode, and Pt counter electrode, $50mVs^{-1}$, Fc/Fc^+ (0.16 V referred to Ag/Ag^+). Preparative separations were performed by silica gel chromatography (Wako gel C-200) or gel permeation chromatography (GPC) (Bio-Rad Bio-Beads S-X1, packed with $CHCl_3$ in a 6 × 40 cm gravity column). Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University. Single-crystal diffraction analysis data for compound **1a** were collected at –150 °C with a Rigaku RAXIS-RAPID diffraction by using graphite monochromated Mo-*K*α radiation (λ = 0.71073 Å). The structure was solved by the direct method (SHELXS-97). DFT calculations were performed at the B3LYP/6-31G*[1] level by using Gaussian 09 package.[2]

[1] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[2] *Gaussian 09, Revision A.02*. 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

Experimental Procedure

Typical procedure for palladium-catalyzed monoarylation reactions (1a–c, 1i): $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $PtBu_3$•HBF_4 (8.7 mg, 0.03 mmol), and Cs_2CO_3 (195.5 mg, 0.60 mmol) were placed in a 20-mL reaction flask under nitrogen. THF (0.5 mL) was added and the mixture was stirred for 10 min with heating. A solution of tetrathiafulvalene (102.2 mg, 0.50 mmol) and 4-bromotoluene (34.2 mg, 0.20 mmol) in THF (0.5 mL) was added. The mixture was heated at reflux for 3 h. The organic compounds were extracted with dichloromethane three times. The combined organic part was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by gel permeation chromatography with chloroform as an eluent to afford 2-(4-methylphenyl)tetrathiafulvalene (**1a**) as a yellow solid (30.0 mg, 0.10 mmol, 50%).

Synthesis of 1d–h, 1j, and 1k: Although the synthetic protocol is the same, purification was performed by silica gel column chromatography with a mixture of hexane/dichloromethane as an eluent, for instance, to yield 2-(4-methoxyphenyl)tetrathiafulvalene (**1d**) as a yellow solid (29.8 mg, 0.096 mmol, 48%).

Typical procedure for palladium-catalyzed tetraarylation reactions (2a–c, f–m): $Pd(OAc)_2$ (8.4 mg, 0.038 mmol), $PtBu_3$•HBF_4 (32.6 mg, 0.11 mmol), and Cs_2CO_3 (244.4 mg, 0.75 mmol) were placed in a 20-mL reaction flask under nitrogen. THF (1.0 mL) was added and the mixture was stirred for 10 min with heating. A solution of tetrathiafulvalene (30.7 mg, 0.15 mmol) and 4-bromotoluene (128.3 mg, 0.75 mmol) in THF (1.0 mL) was added. The mixture was heated at reflux for 15 h. The organic compounds were extracted with chloroform three times. The combined organic part was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Chromatographic purification on silica gel by using hexane/dichloromethane (or chloroform) as an eluent afforded 2,3,6,7-tetra(4-methylphenyl)tetrathiafulvalene (**2a**) (84.3 mg, 0.15 mmol, 100%) as a red solid.

Purification of 2d, 2e, and 2n: Purification of 2,3,6,7-tetra(4-methoxyphenyl)tetrathiafulvalene (**2d**) and 2,3,6,7-tetrakis(4-dimethylaminophenyl)tetrathiafulvalene (**2e**) were performed by reprecipitation from chloroform/methanol to provide orange solids in 78% (79.7 mg, 0.12 mmol) and 60% (56.6 mg, 0.09 mmol) yields, respectively. 2,3,6,7-Tetrakis(4-biphenylyl)tetrathiafulvalene (**2n**) was obtained from recrystallization from chloroform/methanol as red needles (109.8 mg, 0.14 mmol, 90%).

Characterization Data

2-(4-Methylphenyl)tetrathiafulvalene (1a): ^{1}H NMR ($CDCl_3$) δ = 2.35 (s, 3H), 6.33 (s, 2H), 6.43 (s, 1H), 7.16 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 21.42, 109.70, 111.41, 112.57, 119.21, 119.27, 126.36, 129.67, 129.94, 136.33, 138.68; HR-ESI TOF-MS: Observed (m/z) = 293.9659 (Δ = –0.34 ppm). Calcd for $C_{13}H_{10}S_4$ = 293.9660[M]; CV (in benzonitrile) E_1 = –0.08 V, E_2 = 0.37 V (vs. Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 277(16100) and 397(3100).

2-(2-Naphthyl)tetrathiafulvalene (1b): ^{1}H NMR ($CDCl_3$): δ = 6.35 (s, 2H), 6.62 (s, 1H), 7.47–7.52 (m, 2H), 7.55 (dd, J = 8.5, 1.4 Hz, 1H), 7.77 (s, 1H), 7.80–7.84 (m, 3H); ^{13}C NMR ($CDCl_3$): δ = 109.27, 112.04, 114.29, 119.27, 119.31, 123.62, 126.02, 126.78, 127.02, 127.88, 128.37, 128.69, 129.90, 133.16, 133.53, 136.39; HR-ESI TOF-MS: Observed (m/z) = 329.9662 (Δ = 0.61 ppm). Calcd for $C_{16}H_{10}S_4$ = 329.9660[M]; CV (in benzonitrile) E_1 = –0.07 V, E_2 = 0.38 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 297(42500) and 415(7500).

2-(4-Fluorophenyl)tetrathiafulvalene (1c): ^{1}H NMR ($CDCl_3$): δ = 6.34 (s, 2H), 6.42 (s, 1H), 7.03–7.07 (m, 2H), 7.37–7.40 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 109.10, 112.20, 113.57, 116.01, 116.15, 119.29, 128.26 (d, $J_{C\text{-}F}$ = 8.6 Hz), 129.00 (d, $J_{C\text{-}F}$ = 2.9 Hz), 135.09, 162.78 (d, $J_{C\text{-}F}$ = 248.5 Hz); HR-ESI TOF-MS: Observed (m/z) = 297.9416 (Δ = 2.35 ppm). Calcd for $C_{12}H_7FS_4$ = 297.9409[M]; CV (in benzonitrile) E_1 = –0.03 V, E_2 = 0.40 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 280(20000) and 395(1600).

2-(4-Methoxyphenyl)tetrathiafulvalene (1d): ^{1}H NMR ($CDCl_3$): δ = 3.82 (s, 3H), 6.33 (s, 2H), 6.35 (s, 1H), 6.87 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 55.59, 109.77, 111.39, 111.41, 111.50, 114.41, 119.26, 125.56, 127.85, 135.98, 159.95; HR-ESI TOF-MS: Observed (m/z) = 309.9606 (Δ = –0.97 ppm). Calcd for $C_{13}H_{10}OS_4$ = 309.9609[M]; CV (in benzonitrile) E_1 = –0.10 V, E_2 = 0.35 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 283(22900) and 392(4000).

2-(4-Dimethylaminophenyl)tetrathiafulvalene (1e): ^{1}H NMR ($CDCl_3$): δ = 2.98 (s, 6H), 6.25 (s, 1H), 6.32 (s, 2H), 6.66 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 40.52, 109.03, 110.44, 110.45, 110.62, 112.26, 119.26, 120.99, 127.57, 136.76, 150.59; HR-ESI TOF-MS: Observed (m/z) = 322.9922 (Δ = –0.93 ppm). Calcd for $C_{14}H_{13}NS_4$ = 322.9925[M]; CV (in benzonitrile) E_1 = –0.14 V, E_2 = 0.28 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 318(28800) and 386(5400).

2-(4-Ethoxycarbonylphenyl)tetrathiafulvalene (1f): ^{1}H NMR ($CDCl_3$): δ = 1.40 (t, J = 6.8 Hz, 3H), 4.38 (q, J = 6.8 Hz, 2H), 6.35 (s, 2H), 6.67 (s, 1H), 7.45 (dt J = 8.7, 1.8 Hz, 2H), 8.02 (dt, J = 8.7, 1.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 14.53, 61.33, 108.40, 112.74, 116.40, 119.24, 119.30, 126.12, 130.18, 130.30, 135.34, 136.52, 166.11; HR-ESI TOF-MS: Observed (m/z) = 351.9706 (Δ = –2.56 ppm). Calcd for $C_{15}H_{12}O_2S_4$ = 351.9720[M]; CV (in benzonitrile) E_1 = –0.04 V, E_2 = 0.40 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 296(23700) and 443(3460).

2-(4-Nitrophenyl)tetrathiafulvalene (1g): ^{1}H NMR ($CDCl_3$) δ = 6.36 (s, 2H), 6.79 (s, 1H), 7.53 (d, J = 8.7 Hz, 2H), 8.22 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 107.24, 114.21, 118.99, 119.29, 119.33, 124.51, 126.84, 134.14, 138.40, 147.23; HR-ESI TOF-MS: Observed (m/z) = 324.9361 (Δ = 2.20 ppm). Calcd for $C_{12}H_7NO_2S_4$ = 324.9354[M]; CV (in benzonitrile) E_1 = –0.01 V, E_2 = 0.42 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 324(31400) and 522(4700).

2-(3-Methoxyphenyl)tetrathiafulvalene (1h): ^{1}H NMR ($CDCl_3$): δ = 4.83 (s, 3H), 6.34 (s, 2H),

6.45 (s, 1H), 6.85 (dd, J = 8.3, 2.8 Hz, 1H), 6.93 (t, J = 2.8 Hz, 1H), 7.01 (m, 1H), 7.27 (t, J = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 55.57, 109.34, 111.67, 112.12, 113.91, 114.30, 119.01, 119.24, 119.30, 130.07, 133.97, 136.18, 160.04; HR-ESI TOF-MS: Observed (m/z) = 309.9614 (Δ = 1.61 ppm). Calcd for $C_{13}H_{10}OS_4$ = 309.9609[M]; CV (in benzonitrile) E_1 = –0.07 V, E_2 = 0.38 V (vs Fc/Fc$^+$); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 279(18600) and 402(3600).

2-(3-Trifluoromethylphenyl)tetrathiafulvalene (1i): ^{1}H NMR ($CDCl_3$): δ = 6.35 (s, 2H), 6.62 (s, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H), 7.65 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 108.31, 113.07, 115.87, 119.25, 119.31, 123.13 (q, $J_{C\text{-}F}$ = 2.9 Hz), 124.00 (q, $J_{C\text{-}F}$ = 271.4 Hz), 125.14 (d, $J_{C\text{-}F}$ = 2.9 Hz), 129.63 (two signals merge), 133.50, 134.75; HR-ESI TOF-MS: Observed (m/z) = 347.9375 (Δ = –0.57 ppm). Calcd for $C_{13}H_7F_3S_4$ = 347.9377[M]; CV (in benzonitrile) E_1 = –0.03 V, E_2 = 0.41 V (vs Fc/Fc$^+$); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 283(20000) and 414(3200).

2-(4-Acetylphenyl)tetrathiafulvalene (1j): ^{1}H NMR ($CDCl_3$): δ = 2.60 (s, 3H), 6.35 (s, 2H), 6.70 (s, 1H), 7.48 (d, J = 8.3 Hz, 2H), 7.94 (d, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 26.81, 108.23, 112.97, 116.75, 119.26, 119.31, 126.37, 129.15, 135.24, 136.62, 136.74, 197.27; HR-ESI TOF-MS: Observed (m/z) = 321.9600 (Δ = –2.80 ppm). Calcd for $C_{14}H_{10}OS_4$ = 321.9609[M]; CV (in benzonitrile) E_1 = –0.04 V, E_2 = 0.40 V (vs Fc/Fc$^+$); UV-Vis (in $CHCl_3$) λ [nm] (ε [M^{-1} cm^{-1}]) 305(32400) and 456(4840).

2-(4-Cyanophenyl)tetrathiafulvalene (1k): ^{1}H NMR ($CDCl_3$): δ = 6.35 (s, 2H), 6.71 (s, 1H), 7.48 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 107.46, 111.78, 113.85, 118.00, 118.63, 119.29, 119.33, 126.77, 132.87, 134.47, 136.63; HR-ESI TOF-MS: Observed (m/z) = 304.9460 (Δ = 1.31 ppm). Calcd for $C_{13}H_7NS_4$ = 304.9456[M]; CV (in benzonitrile) E_1 = –0.02 V, E_2 = 0.42 V (vs Fc/Fc$^+$); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 297(18500) and 455(3000).

2,3,6,7-Tetra(4-methylphenyl)tetrathiafulvalene (2a): ^{1}H NMR ($CDCl_3$): δ = 2.30 (s, 12H), 7.03 (d, J = 7.8 Hz, 8H), 7.11 (d, J = 7.8 Hz, 8H); ^{13}C NMR ($CDCl_3$): δ = 21.50, 108.33, 128.70, 129.19, 129.46, 130.15, 138.38; HR-ESI TOF-MS: Observed (m/z) = 564.1053 (Δ = –2.66 ppm). Calcd for $C_{34}H_{28}S_4$ = 564.1068[M]; CV (in benzonitrile) E_1 = –0.08 V, E_2 = 0.37 V (vs Fc/Fc$^+$); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 277(26300) and 399(4700).

2,3,6,7-Tetra(2-naphthyl)tetrathiafulvalene (2b): ^{1}H NMR ($CDCl_3$): δ = 7.23 (d, J = 1.9 Hz, 2H), 7.24 (d, J = 1.9 Hz, 2H), 7.44–7.49 (m, 8H), 7.61 (d, J = 8.7 Hz, 4H), 7.71–7.76 (m, 8H), 7.89 (s, 4H); ^{13}C NMR ($CDCl_3$): δ = 108.77, 126.73, 126.82, 126.92, 127.90, 128.37, 128.42, 128.88, 129.62, 130.48, 133.18, 133.44; HR-ESI TOF-MS: Observed (m/z) = 708.1050 (Δ = –2.54 ppm). Calcd for $C_{46}H_{28}S_4$ = 708.1068[M]; CV (in benzonitrile) E_1 = –0.02 V, E_2 = 0.40 V (vs Fc/Fc$^+$). It was impossible to determine λ and ε because the maximum absorption were not observed within the range of 250 to 900 nm.

2,3,6,7-Tetra(4-fluorophenyl)tetrathiafulvalene (2c): ^{1}H NMR ($CDCl_3$): δ = 6.94 (tt, J = 8.2, 2.6 Hz, 8H), 7.16–7.19 (m, 8H); ^{13}C NMR ($CDCl_3$): δ = 108.47, 116.09 (d, $J_{C\text{–}F}$ = 21.6 Hz), 128.36, 128.62 (d, $J_{C\text{–}F}$ = 2.9 Hz), 131.20 (d, $J_{C\text{–}F}$ = 8.6 Hz), 162.71 (d, $J_{C\text{–}F}$ = 247.0 Hz); HR-ESI TOF-MS: Observed (m/z) = 580.0050 (Δ = –2.59 ppm). Calcd for $C_{30}H_{16}F_4S_4$ = 580.0065[M]; CV (in benzonitrile) E_1 = 0.01 V, E_2 = 0.43 V (vs Fc/Fc$^+$); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 303(20100) and 402(4000).

2,3,6,7-Tetra(4-methoxyphenyl)tetrathiafulvalene (2d): ^{1}H NMR ($CDCl_3$): δ = 3.77 (s, 12H), 6.75 (dt, J = 8.7, 2.3 Hz, 8H), 7.15 (dt, J = 8.7, 2.3 Hz, 8H); ^{13}C NMR ($CDCl_3$): δ = 55.45, 108.19, 114.19, 125.45, 127.85, 130.63, 159.57; HR-ESI TOF-MS: Observed (m/z) = 628.0851 (Δ = –2.23

ppm). Calcd for $C_{34}H_{28}O_4S_4$ = 628.0865[*M*]; CV (in benzonitrile) E_1 = –0.11 V, E_2 = 0.34 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 262(37500) and 390(5500).

2,3,6,7-Tetrakis(4-dimethlyaminophenyl)tetrathiafulvalene (2e): ^{1}H NMR ($CDCl_3$): δ = 2.93 (s, 24H), 6.55 (d, *J* = 8.3 Hz, 8H), 7.11 (d, *J* = 8.3 Hz, 8H); ^{13}C NMR ($CDCl_3$): δ = 40.49, 112.12, 112.30, 114.33, 127.01, 130.19, 149.98; HR-ESI TOF-MS: Observed (*m/z*) = 680.2109 (Δ = –3.09 ppm). Calcd for $C_{38}H_{40}N_4S_4$ = 680.2130[*M*]; CV (in benzonitrile) E_1 = –0.24 V, E_2 = 0.15 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 314(80100).

2,3,6,7-Tetra(4-ethoxycarbonylphenyl)tetrathiafulvalene (2f): ^{1}H NMR ($CDCl_3$): δ = 1.37 (t, *J* = 7.1 Hz, 12H), 4.36 (q, *J* = 7.1 Hz, 8H), 7.25–7.27 (m, 8H), 7.91 (dt, *J* = 8.7, 1.8 Hz, 8H); ^{13}C NMR ($CDCl_3$): δ = 14.51, 61.42, 108.92, 129.27, 130.06, 130.19, 130.80, 136.82, 166.02; Elemental Analysis: Found: C, 62.99; H, 4.38%. Calcd for $C_{42}H_{36}O_8S_4$: C, 63.29; H, 4.55%; CV (in benzonitrile) E_1 = 0.07 V, E_2 = 0.48 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 307(51600) and 443(4400).

2,3,6,7-Tetra(4-nitrophenyl)tetrathiafulvalene (2g): ^{1}H NMR ($CDCl_3$): δ = 7.38 (d, *J* = 7.8 Hz, 8H), 8.15 (d, *J* = 7.8 Hz, 8H);^{13}C NMR ($CDCl_3$): δ = 109.18, 124.58, 130.22, 130.29, 138.19, 148.06; HR-ESI TOF-MS: Observed (*m/z*) = 687.9829 (Δ = –2.33 ppm). Calcd for $C_{30}H_{16}N_4O_8S_4$ = 687.9845[*M*]; CV (in benzonitrile) E_1 = 0.17 V, E_2 = 0.54 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 318(53000) and 499(5800).

2,3,6,7-Tetrakis(4-trifluoromethylphenyl)tetrathiafulvalene (2h): ^{1}H NMR ($CDCl_3$): δ = 7.32 (d, *J* = 8.2 Hz, 8H), 7.53 (d, *J* = 8.2 Hz, 8H); ^{13}C NMR ($CDCl_3$): δ = 108.91, 123.86 (q, $J_{C–F}$ = 270.0 Hz), 126.13 (d, $J_{C–F}$ = 2.9 Hz), 129.67, 131.07 (q, $J_{C–F}$ = 31.6 Hz), 135.81; Elemental Analysis: Found: C, 52.04; H, 2.11%. Calcd for $C_{34}H_{16}F_{12}S_4$: C, 52.31; H, 2.07%; CV (in benzonitrile) E_1 = 0.10 V, E_2 = 0.50 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 297(25200) and 429(2600).

2,3,6,7-Tetrakis(3-trifluoromethylphenyl)tetrathiafulvalene (2i): ^{1}H NMR ($CDCl_3$): δ = 7.36–7.41 (m, 8H), 7.45 (s, 4H), 7.54 (d, *J* = 7.4 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 108.88, 123.71 (q, $J_{C–F}$ = 271.4 Hz), 125.79 (q, $J_{C–F}$ = 4.3 Hz), 126.16 (q, $J_{C–F}$ = 4.3 Hz), 129.42, 129.69, 131.64 (q, $J_{C–F}$ = 31.6 Hz), 132.53, 133.00; Elemental Analysis: Found: C, 52.32; H, 2.32%. Calcd for $C_{34}H_{16}F_{12}S_4$: C, 52.31; H, 2.07%; CV (in benzonitrile) E_1 = 0.11 V, E_2 = 0.50 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 288(17000) and 420(2800).

2,3,6,7-Tetra(3-methoxyphenyl)tetrathiafulvalene (2j): ^{1}H NMR ($CDCl_3$): δ = 3.65 (s, 12H), 6.75–6.77 (m, 4H), 6.79 (dm, *J* = 8.7 Hz, 4H), 6.83 (dm, *J* = 6.8 Hz, 4H), 7.14 (t, *J* = 7.8 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 55.39, 108.55, 114.35, 114.88, 121.80, 129.25, 129.84, 134.10, 159.74; HR-ESI TOF-MS: Observed (*m/z*) = 628.0854 (Δ = –1.75 ppm). Calcd for $C_{34}H_{28}O_4S_4$ = 628.0865[*M*]; CV (in benzonitrile) E_1 = –0.03 V, E_2 = 0.40 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 296(24300) and 409(3600).

2,3,6,7-Tetrakis(3,5-dimethoxyphenyl)tetrathiafulvalene (2k): ^{1}H NMR ($CDCl_3$): δ = 3.65 (s, 24H), 6.34 (t, *J* = 2.3 Hz, 4H), 6.41 (d, *J* = 2.3 Hz, 8H); ^{13}C NMR ($CDCl_3$): δ = 55.57, 101.33, 107.27, 108.57, 129.31, 134.53, 160.90; HR-ESI TOF-MS: Observed (*m/z*) = 748.1271 (Δ = –2.27 ppm). Calcd for $C_{38}H_{36}O_8S_4$ = 748.1288[*M*]; CV (in benzonitrile) E_1 = –0.04 V, E_2 = 0.39 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 294(26600) and 404(3800).

2,3,6,7-Tetra(4-cyanophenyl)tetrathiafulvalene (2l): ^{1}H NMR ($CDCl_3$): δ = 7.29 (d, *J* = 8.3 Hz, 8H), 7.57 (d, *J* = 8.3 Hz, 8H); ^{13}C NMR ($CDCl_3$): δ = 108.99, 113.12, 118.08, 129.90, 130.10,

132.96, 136.44; HR-ESI TOF-MS: Observed (*m*/*z*) = 608.0254 (Δ = 0.33 ppm). Calcd for $C_{34}H_{16}N_4S_4$ = 608.0252[*M*]; CV (in benzonitrile) E_1 = 0.15 V, E_2 = 0.52 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 257(49500) and 429(2600).

2,3,6,7-Tetra(3-pyridyl)tetrathiafulvalene (2m): ^{1}H NMR ($CDCl_3$): δ = 7.22 (dd, *J* = 7.8, 5.0 Hz, 4H), 7.54 (dt, *J* = 7.8, 2.3 Hz, 4H), 8.46 (dm, *J* = 2.3 Hz, 4H), 8.52 (broad d, *J* = 5.0 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 109.18, 123.78, 127.97, 128.48, 136.59, 149.97, 150.09; HR-ESI TOF-MS: Observed (*m*/*z*) = 512.0240 (Δ = –2.34 ppm). Calcd for $C_{26}H_{16}N_4S_4$ = 512.0252[*M*]; CV (in benzonitrile) E_1 = 0.11 V, E_2 = 0.50 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 265(28900) and 415(4200).

2,3,6,7-Tetrakis(4-biphenylyl)tetrathiafulvalene (2n): ^{1}H NMR ($CDCl_3$): δ = 7.33–7.36 (m, 12H), 7.41–7.44 (m, 8H), 7.49–7.51 (m, 8H), 7.56–7.59 (m, 8H); ^{13}C NMR ($CDCl_3$): δ = 108.62, 127.19, 127.48, 127.85, 129.06, 129.15, 129.79, 131.91, 140.39, 141.32; HR-ESI TOF-MS: Observed (*m*/*z*) = 812.1685 (Δ = –1.11 ppm). Calcd for $C_{54}H_{36}S_4$ = 812.1694[*M*]; CV (in benzonitrile) E_1 = –0.03 V, E_2 = 0.40 V (vs Fc/Fc^+); UV-Vis (in $CHCl_3$) λ[nm] (ε [M^{-1} cm^{-1}]) 276(70400) and 402(5900).

NMR Spectra

Figure S1-1. ^{1}H NMR Spectrum of **1a**

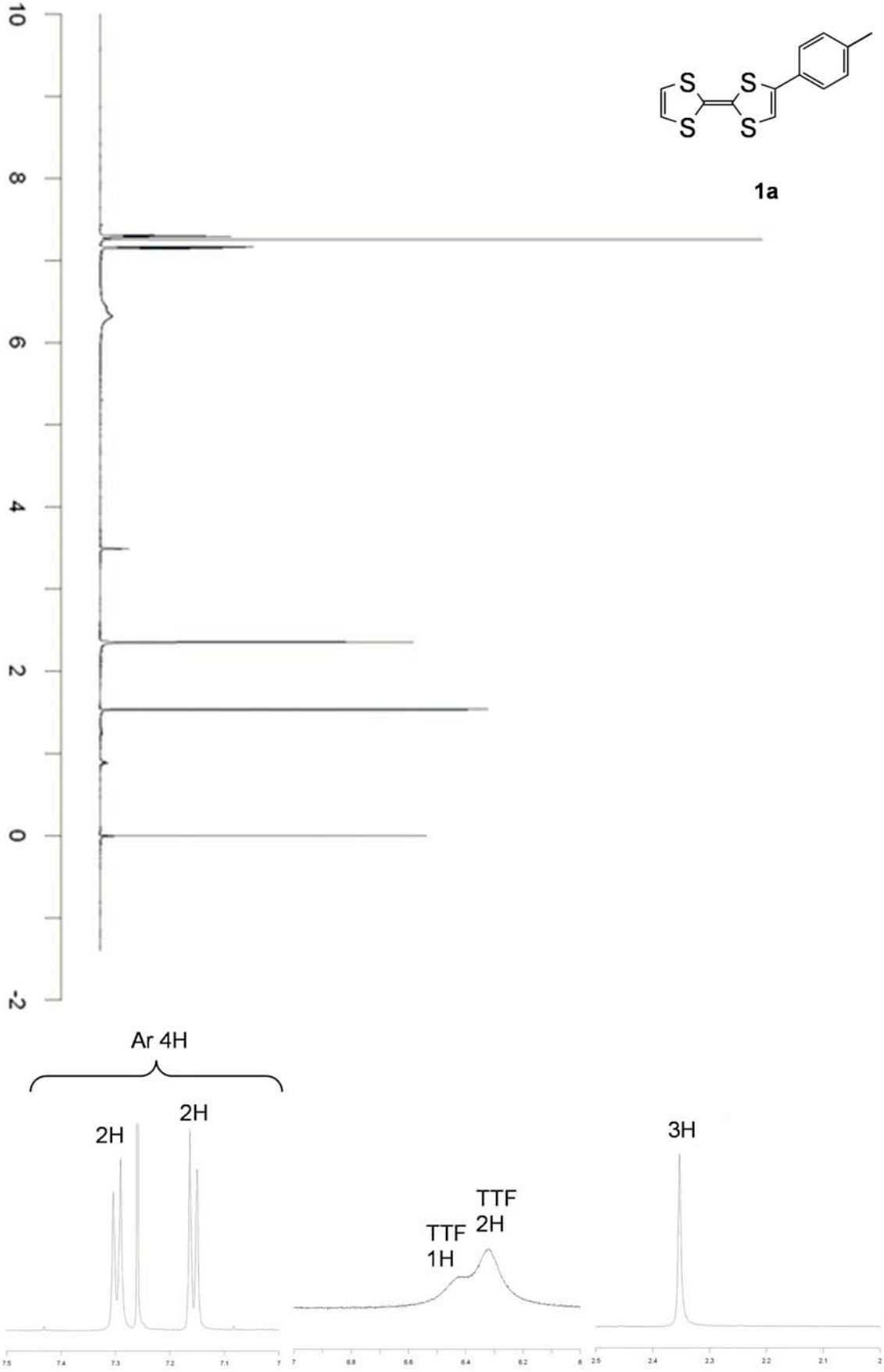


Figure S1-2. ^{13}C NMR Spectrum of **1a**

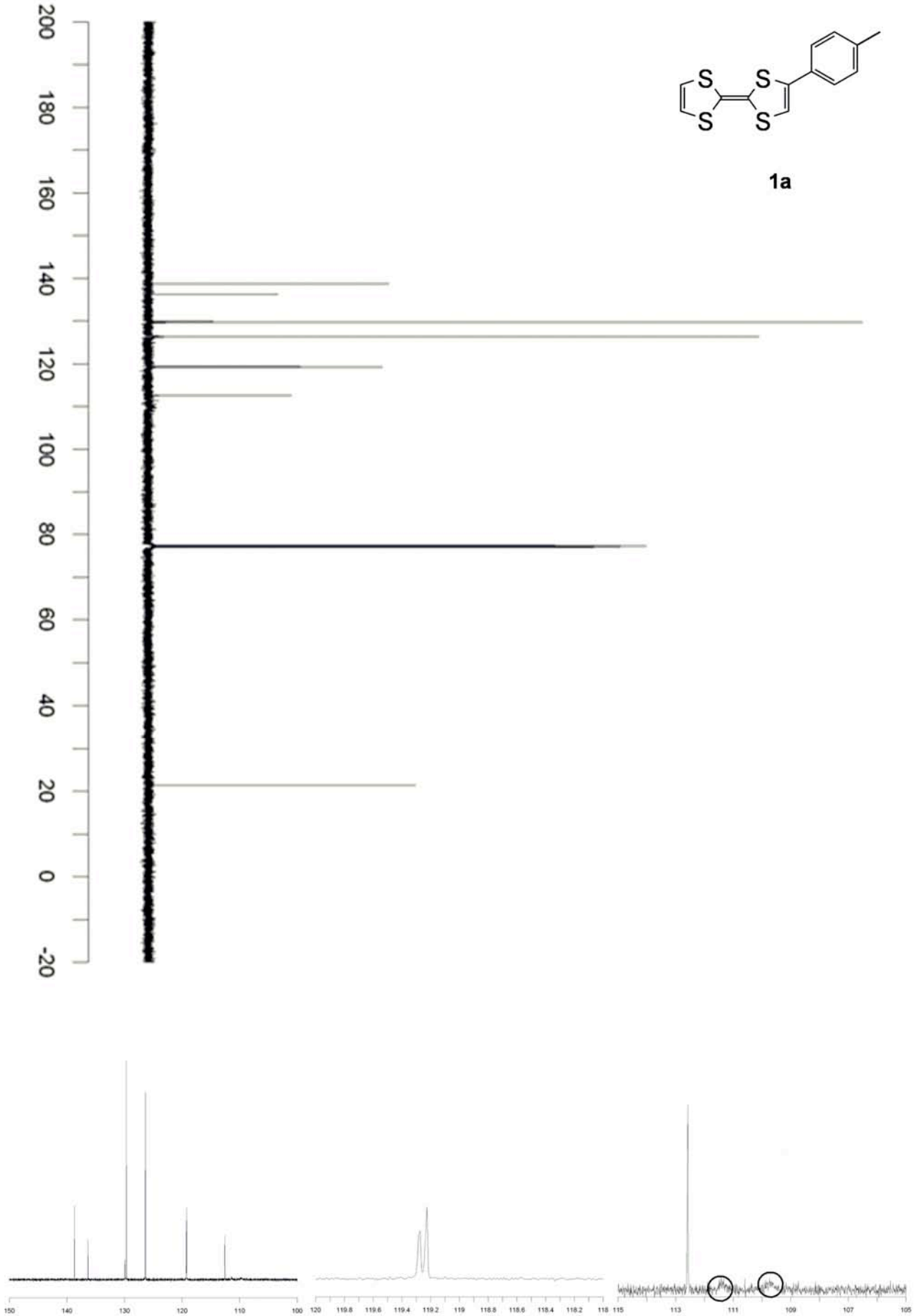


Figure S2-1. ^{1}H NMR Spectrum of **1b**

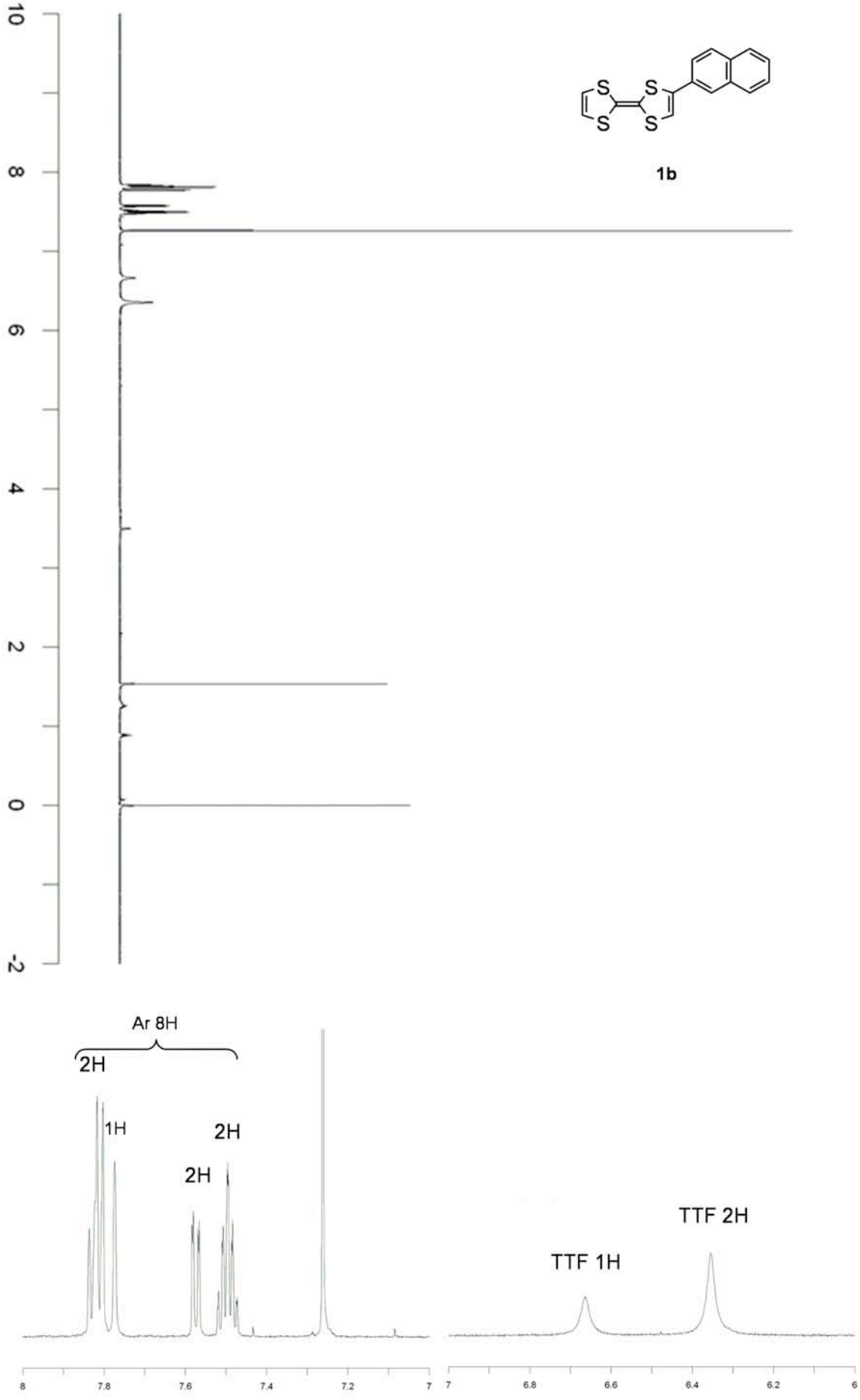


Figure S2-2. ^{13}C NMR Spectrum of **1b**

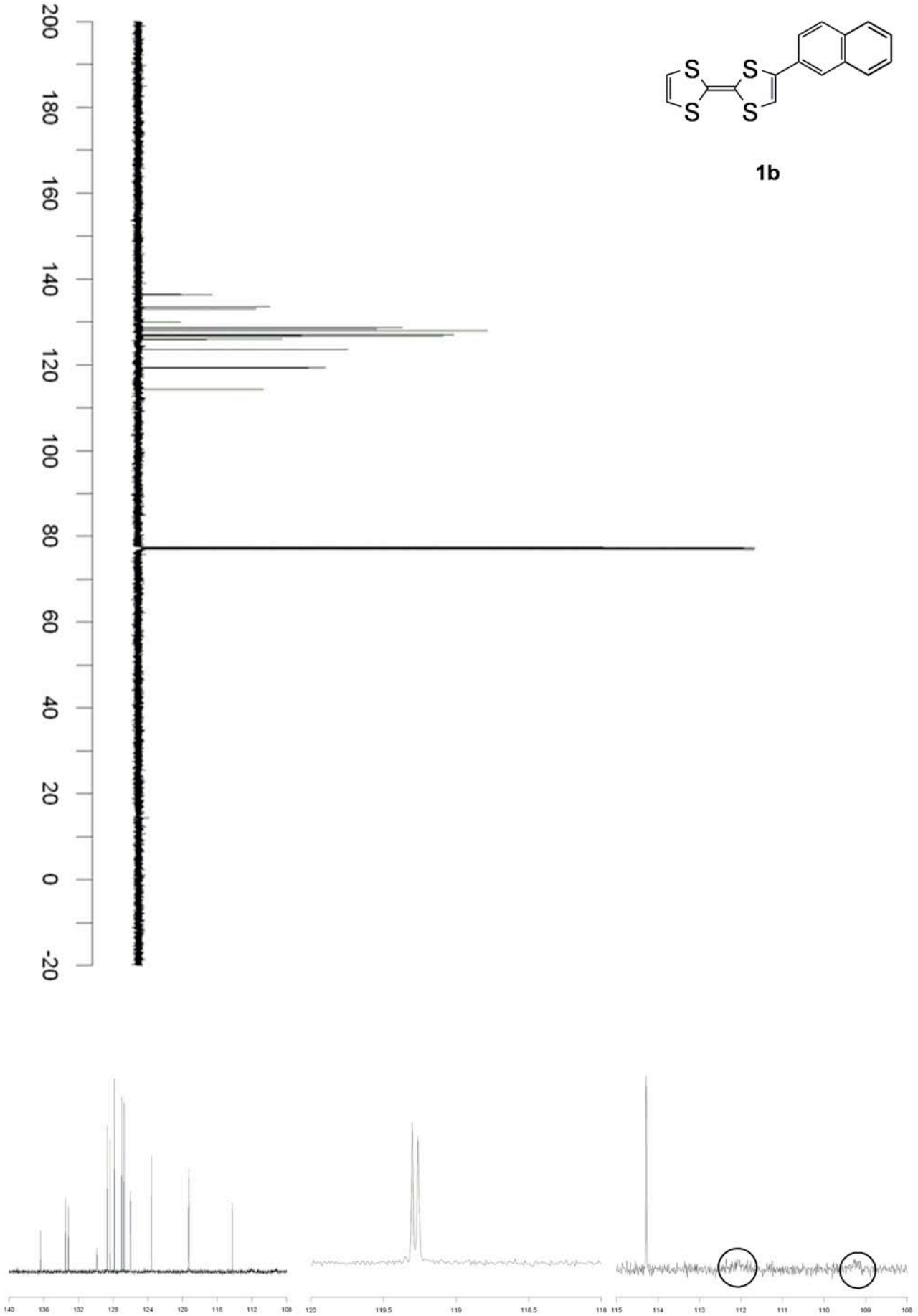


Figure S3-1. ^{1}H NMR Spectrum of **1c**

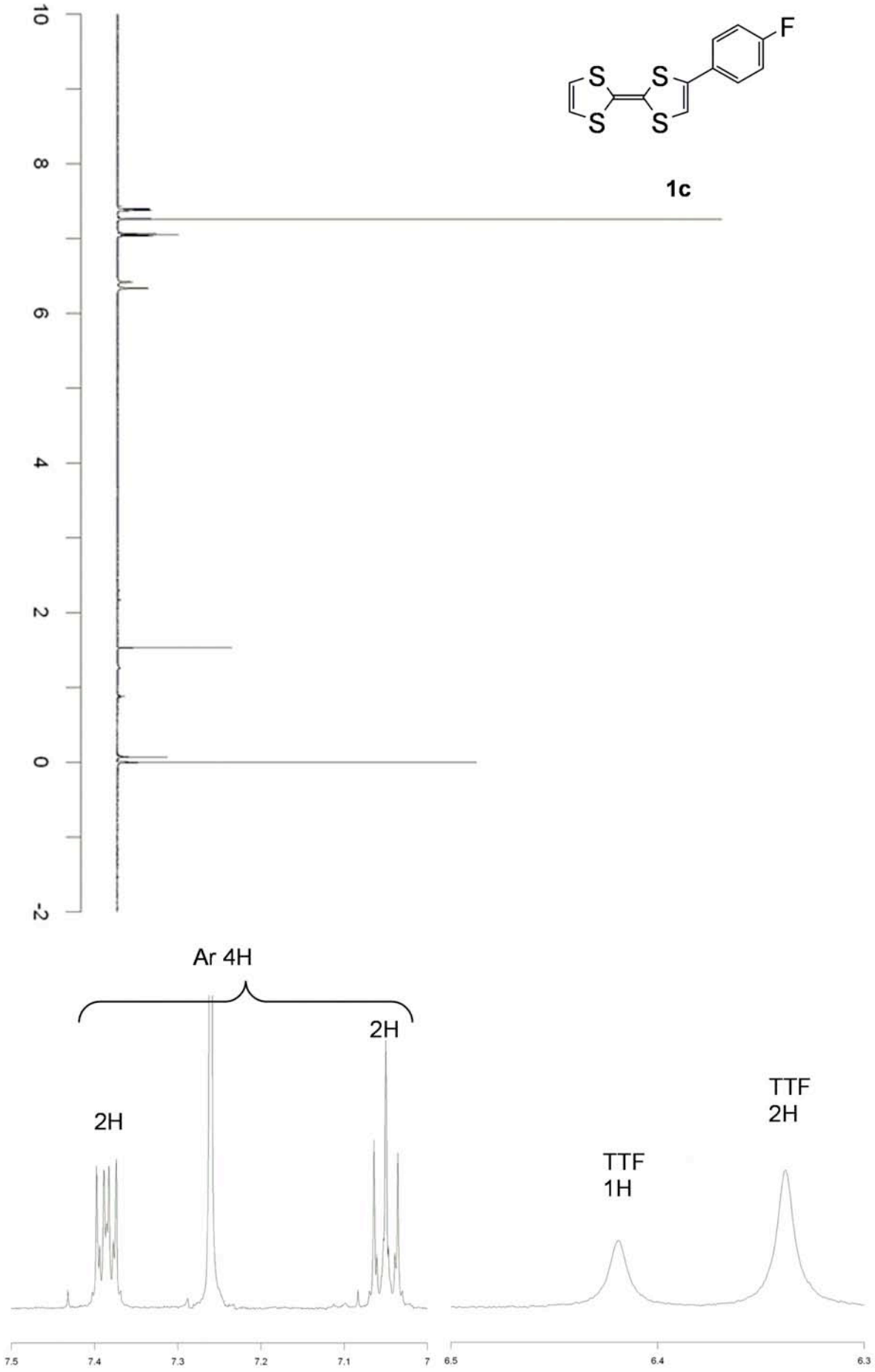


Figure S3-2. ^{13}C NMR Spectrum of **1c**

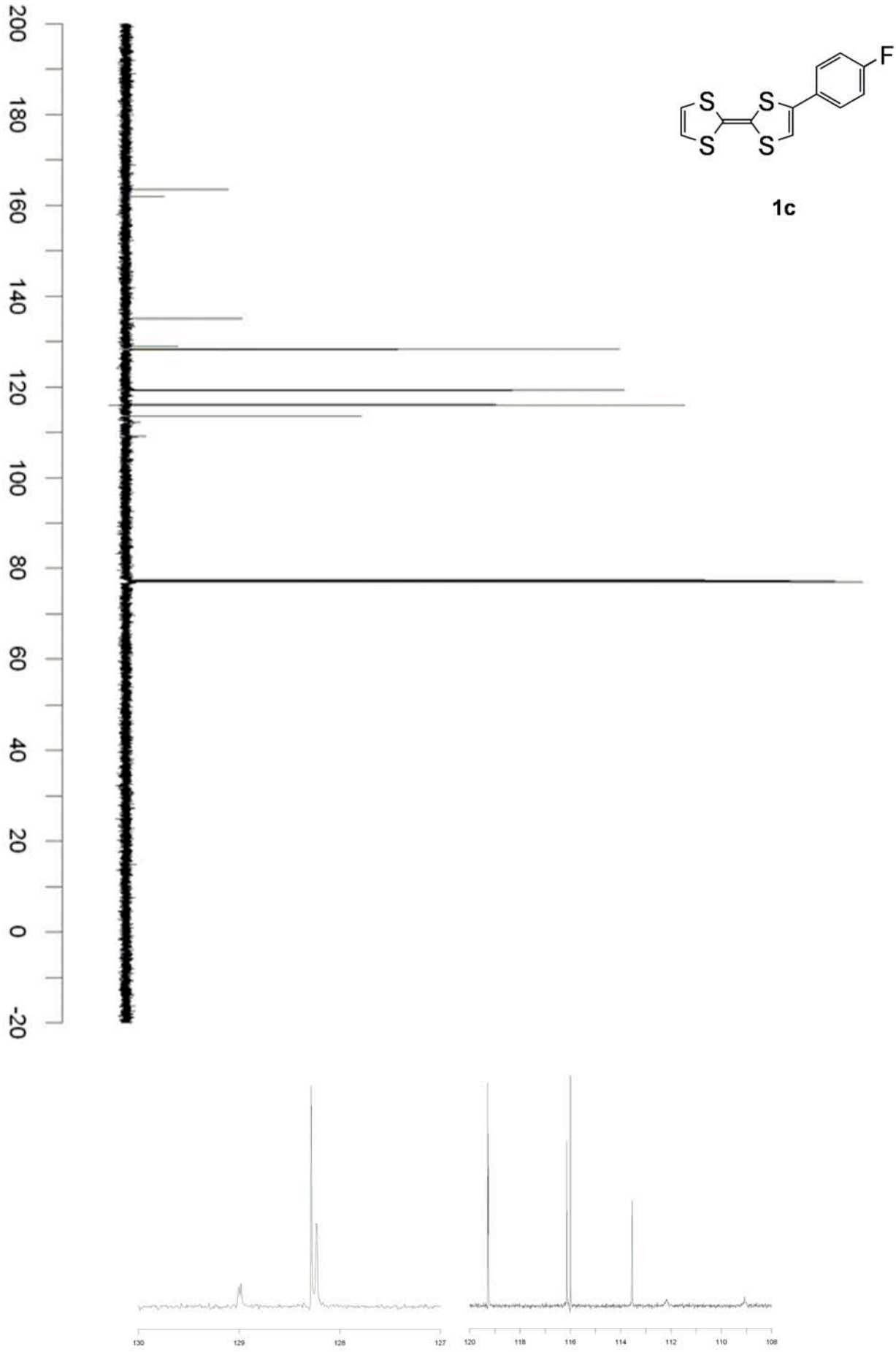


Figure S4-1. ^{1}H NMR Spectrum of **1d**

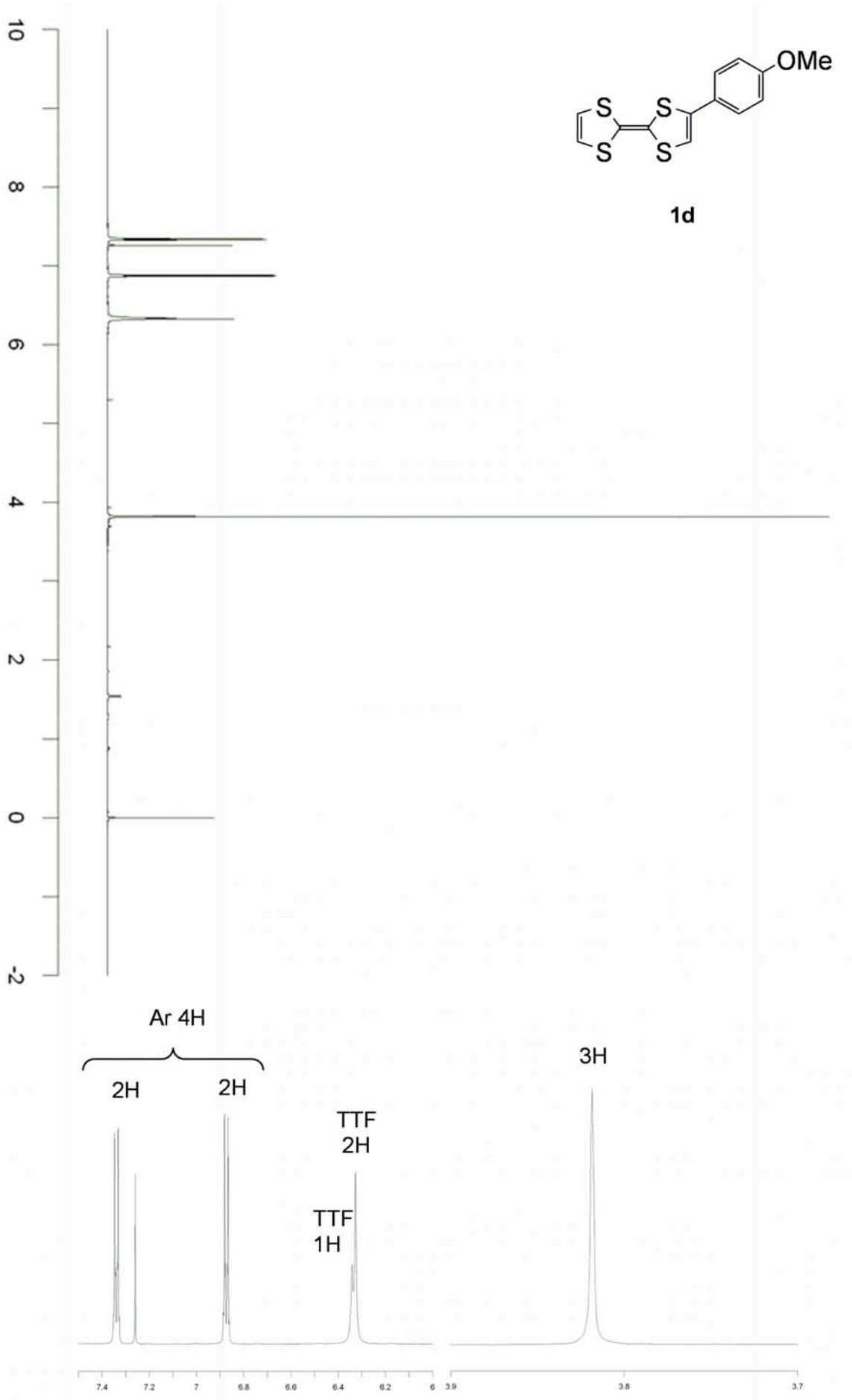


Figure S4-2. ^{13}C NMR Spectrum of **1d**

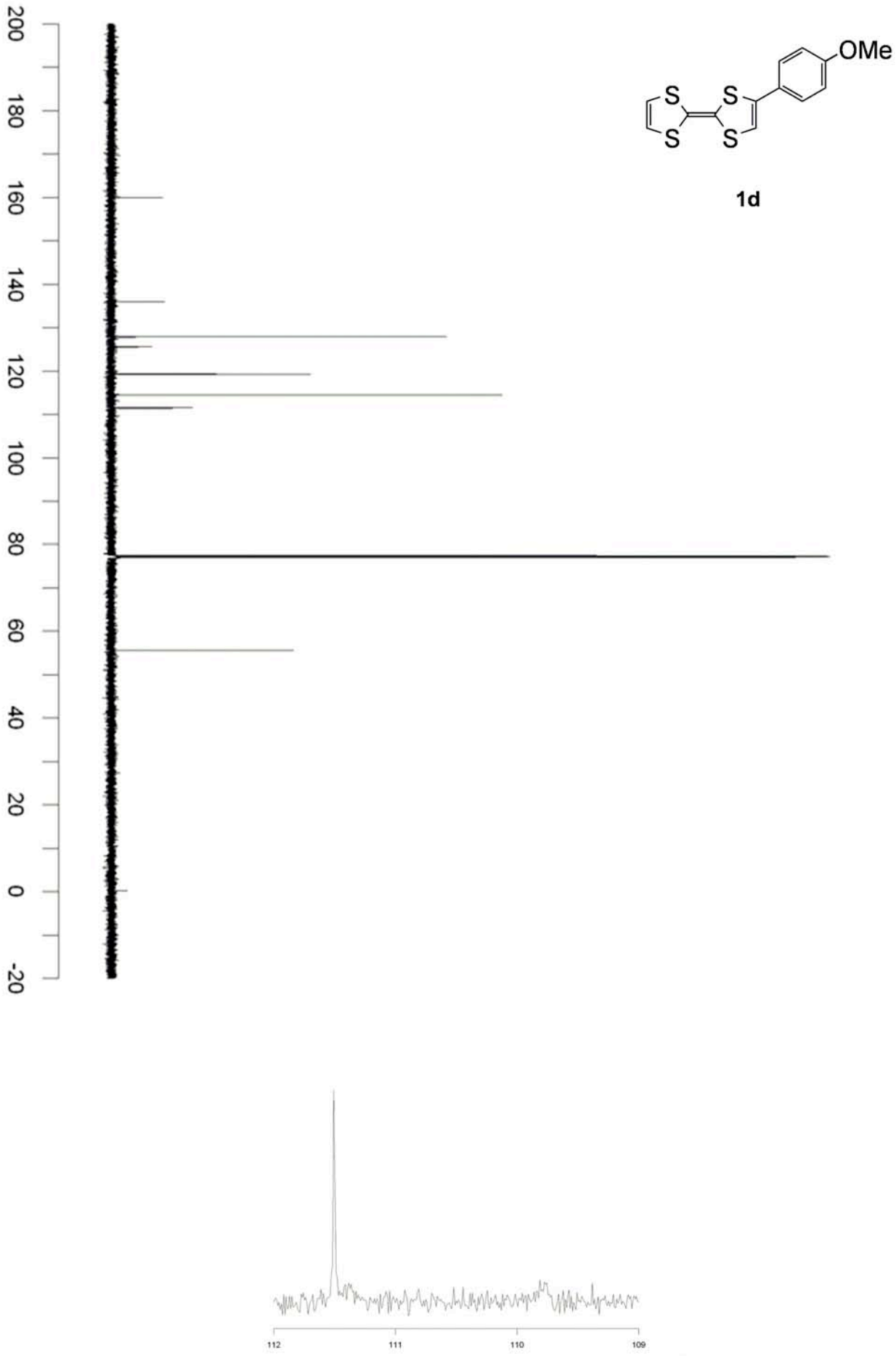


Figure S5-1. ^{1}H NMR Spectrum of **1e**

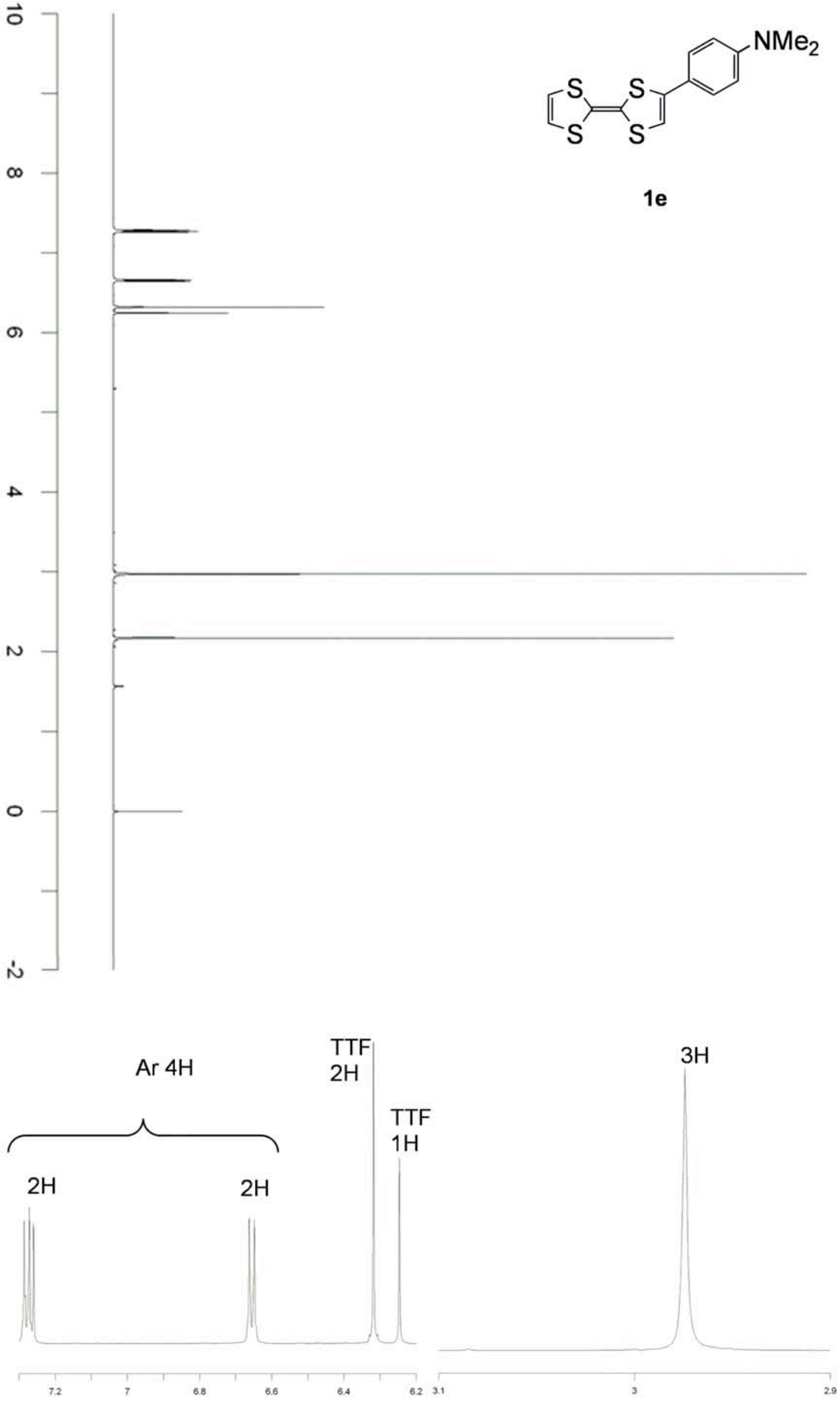


Figure S5-2. ^{13}C NMR Spectrum of **1e**

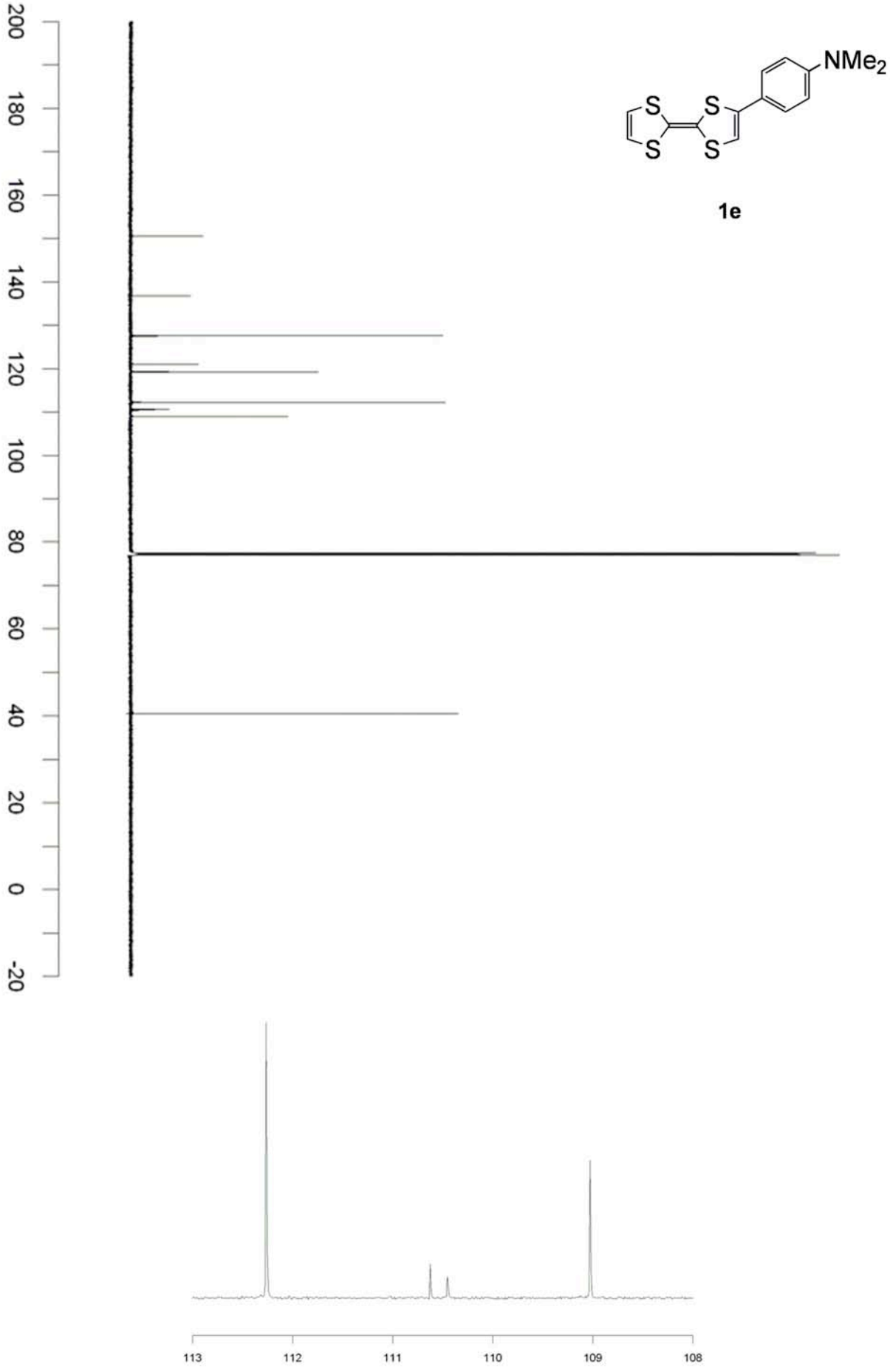


Figure S6-1. ^{1}H NMR Spectrum **of 1f**

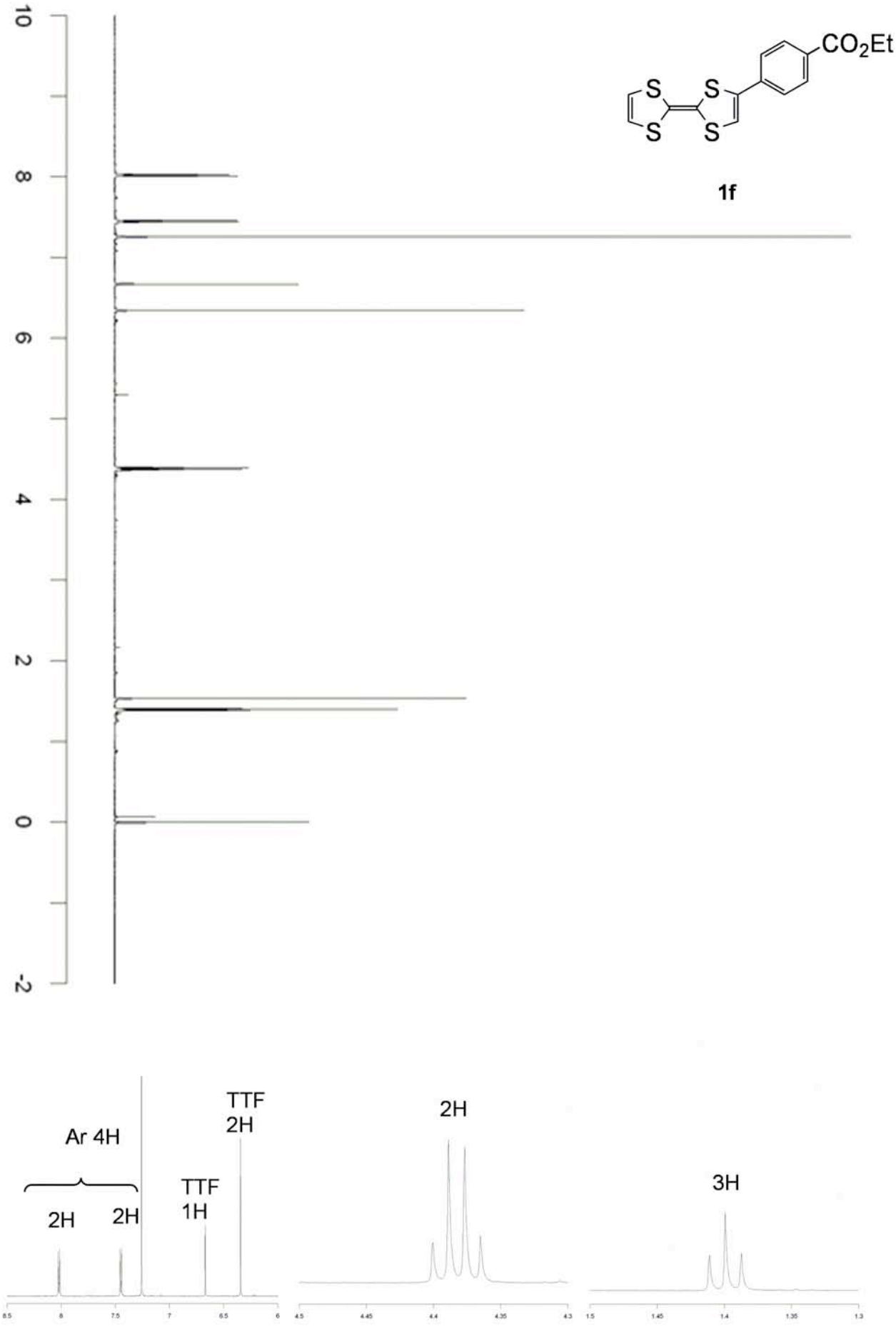


Figure S6-2. ^{13}C NMR Spectrum **of 1f**

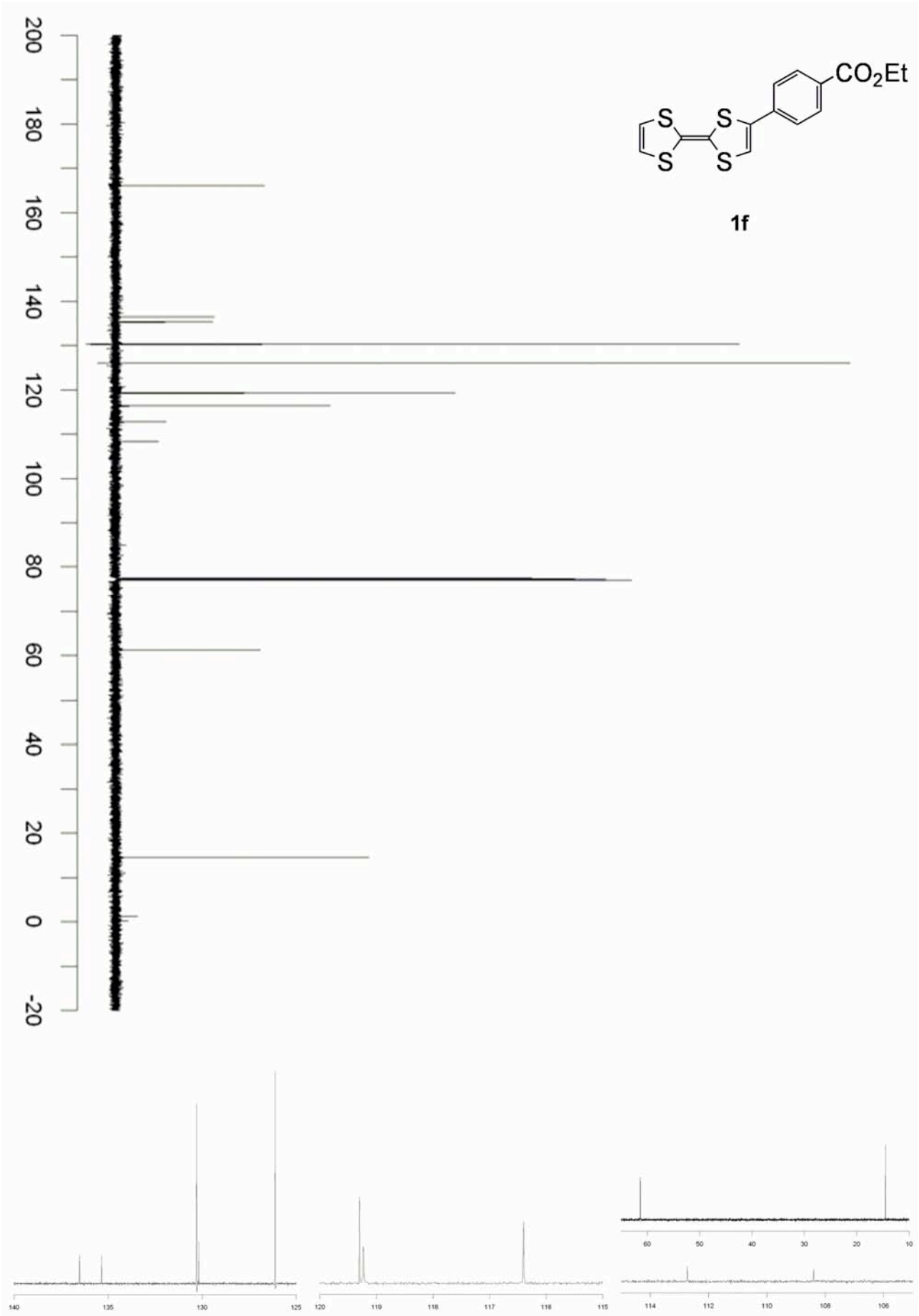


Figure S7-1. ^{1}H NMR Spectrum of **1g**

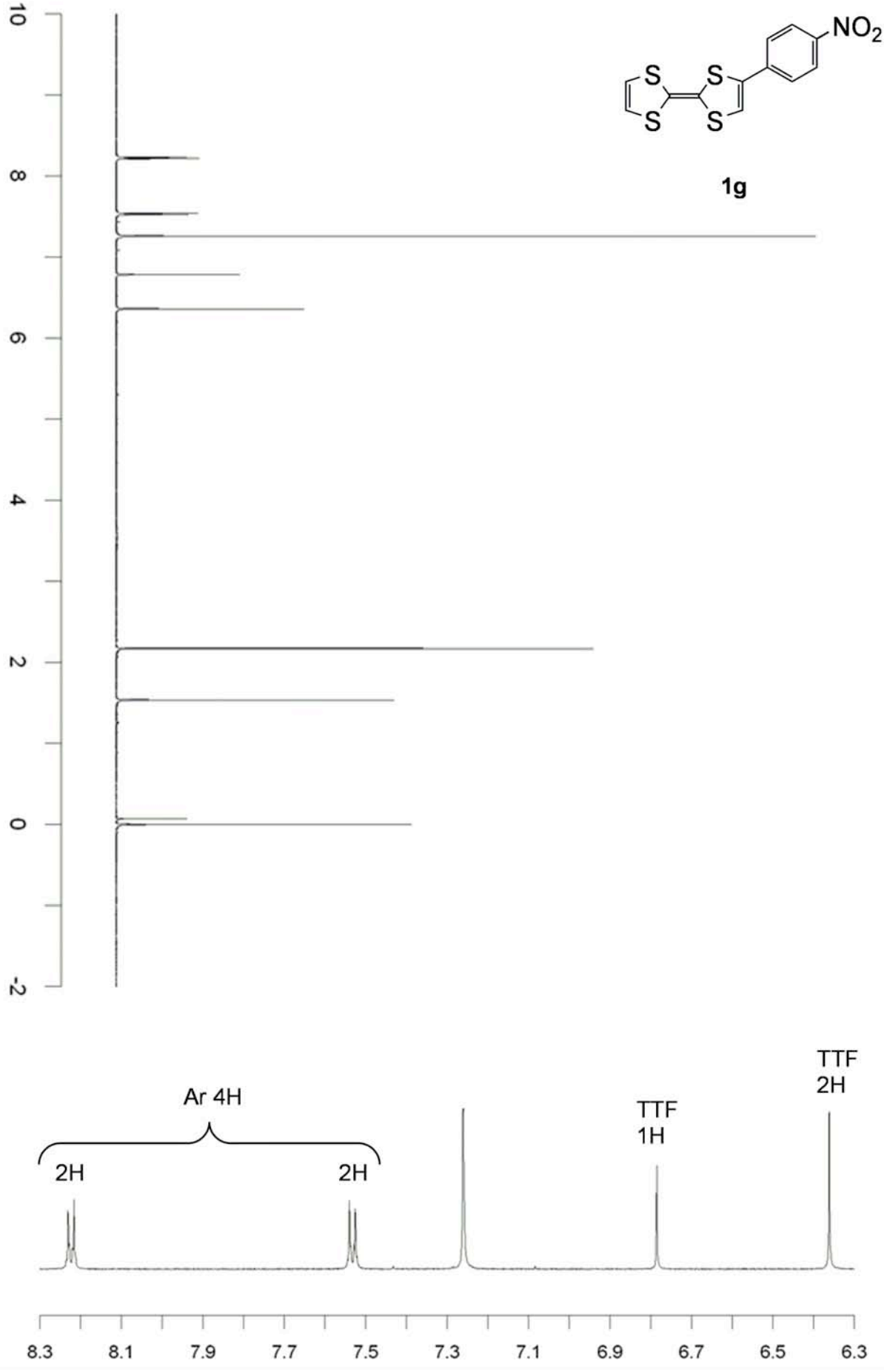


Figure S7-2. ^{13}C NMR Spectrum of **1g**

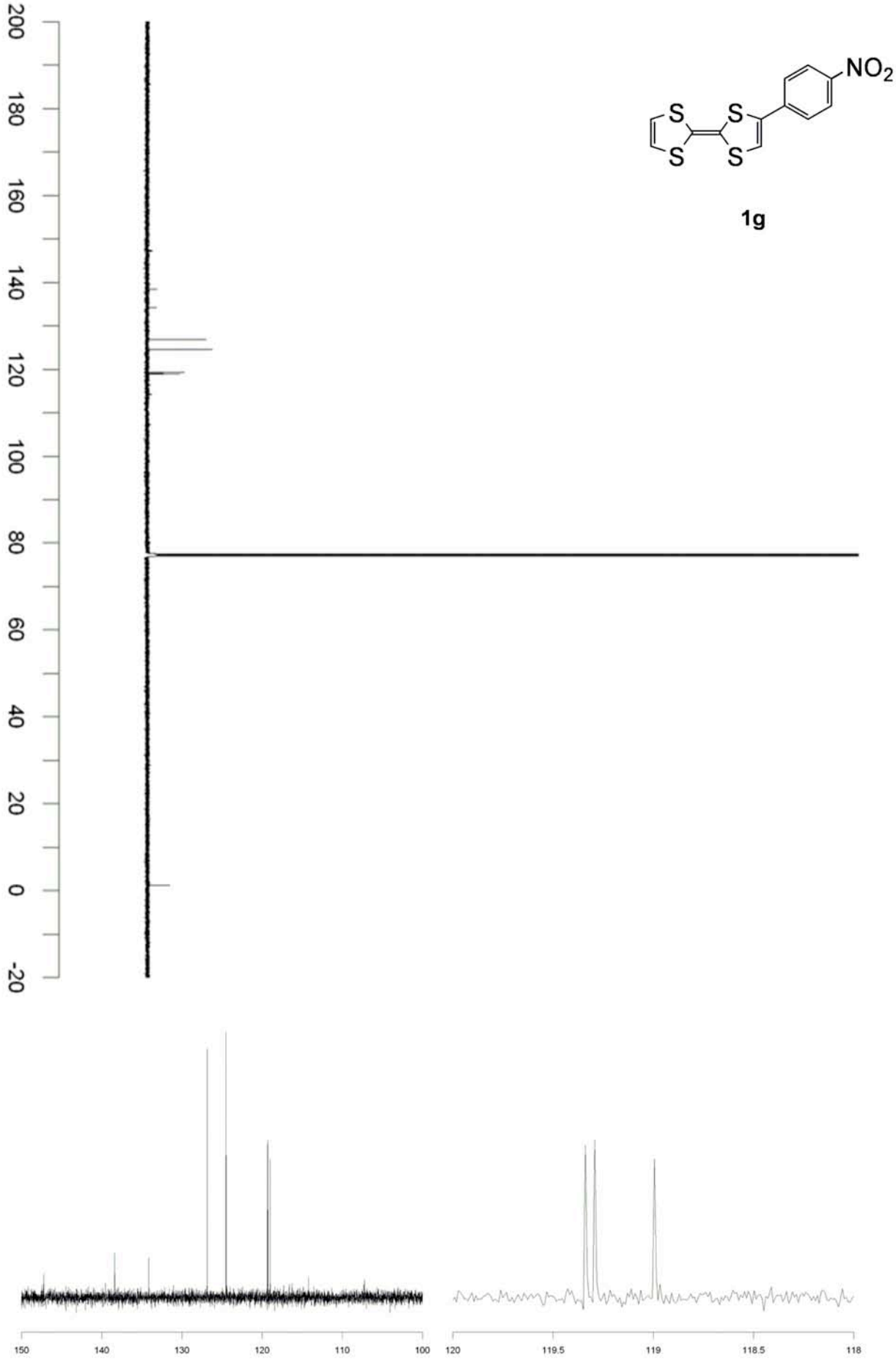


Figure S8-1. ^{1}H NMR Spectrum **of 1h**

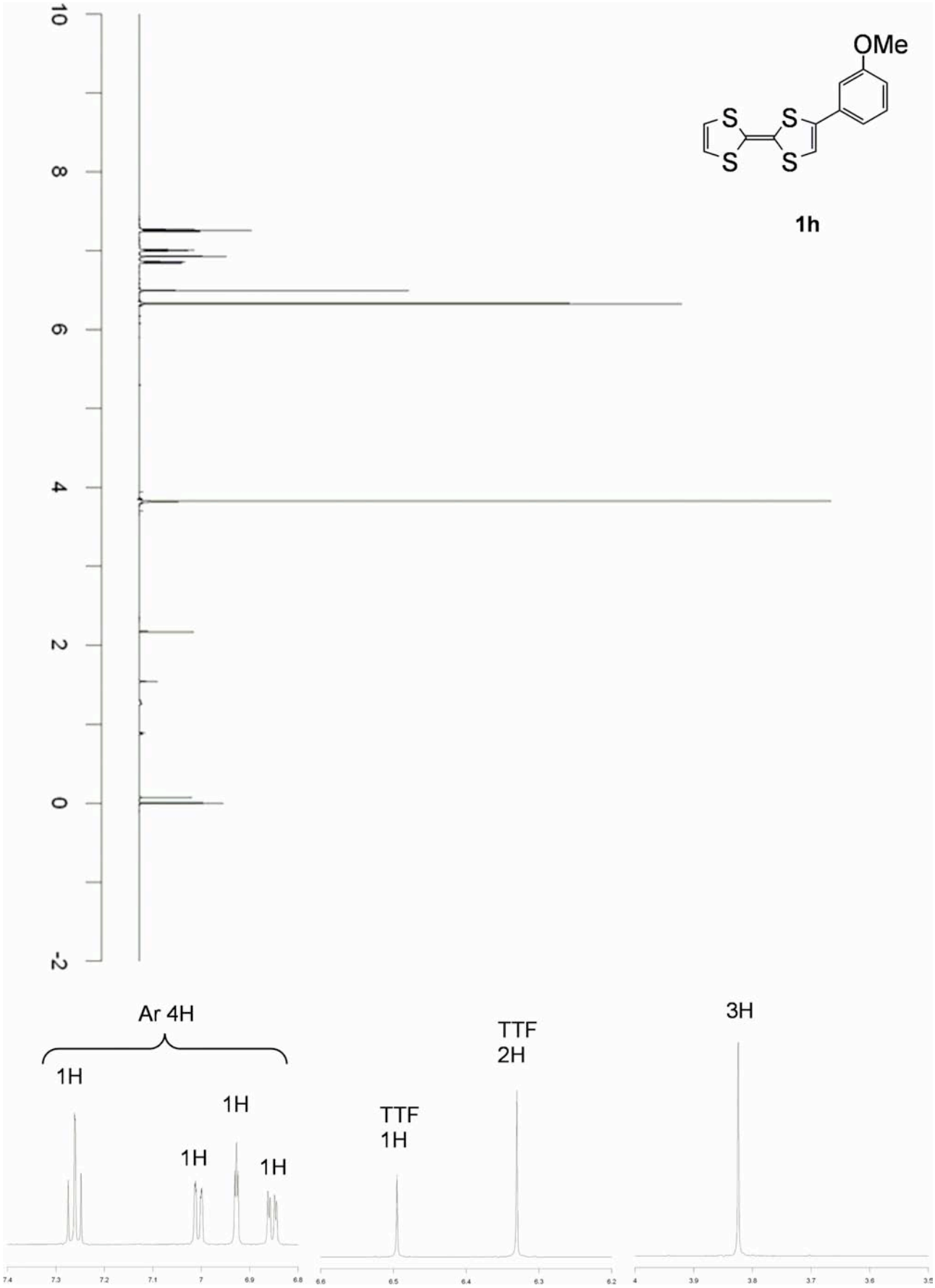


Figure S8-2. ^{13}C NMR Spectrum of **1h**

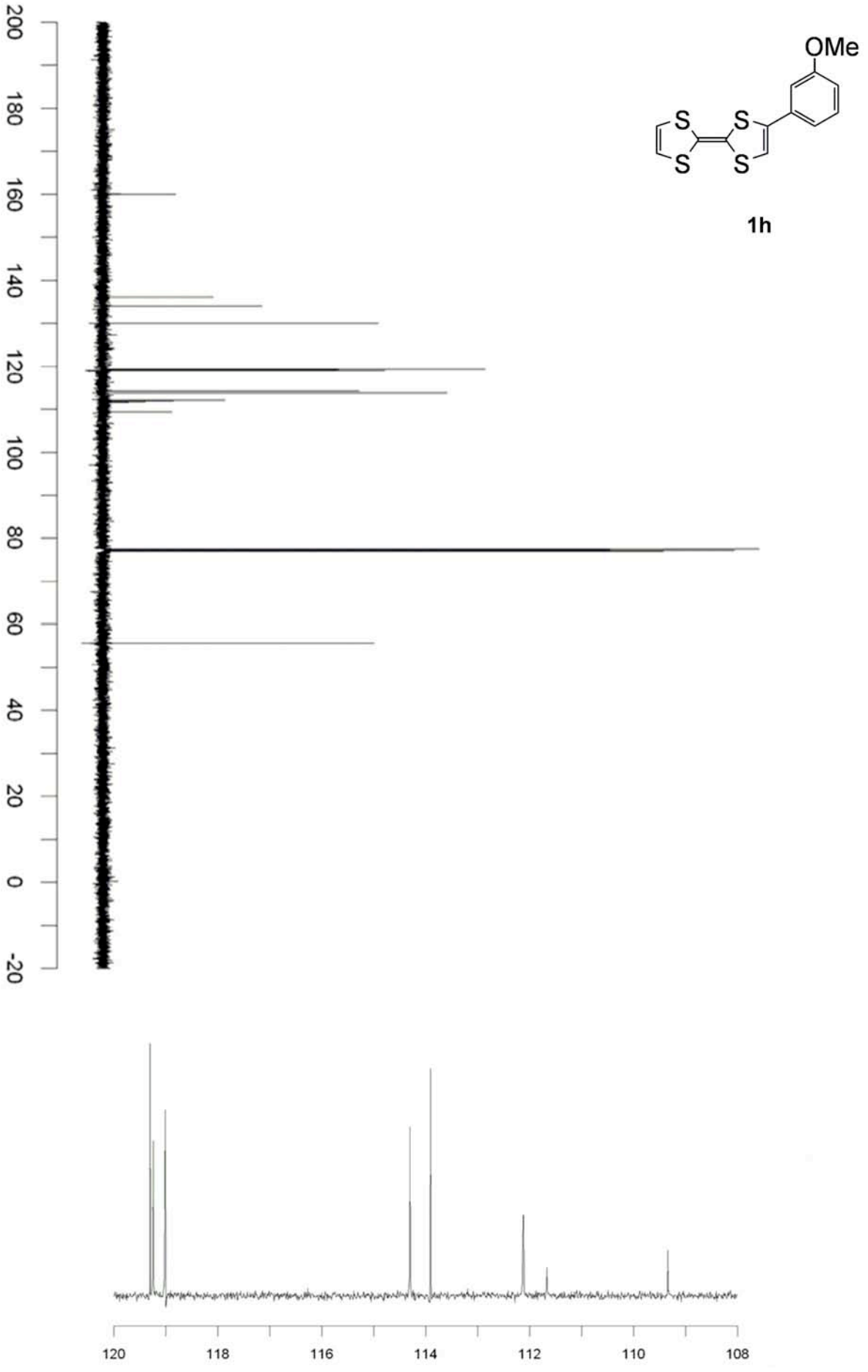


Figure S9-1. ^{1}H NMR Spectrum of **1i**

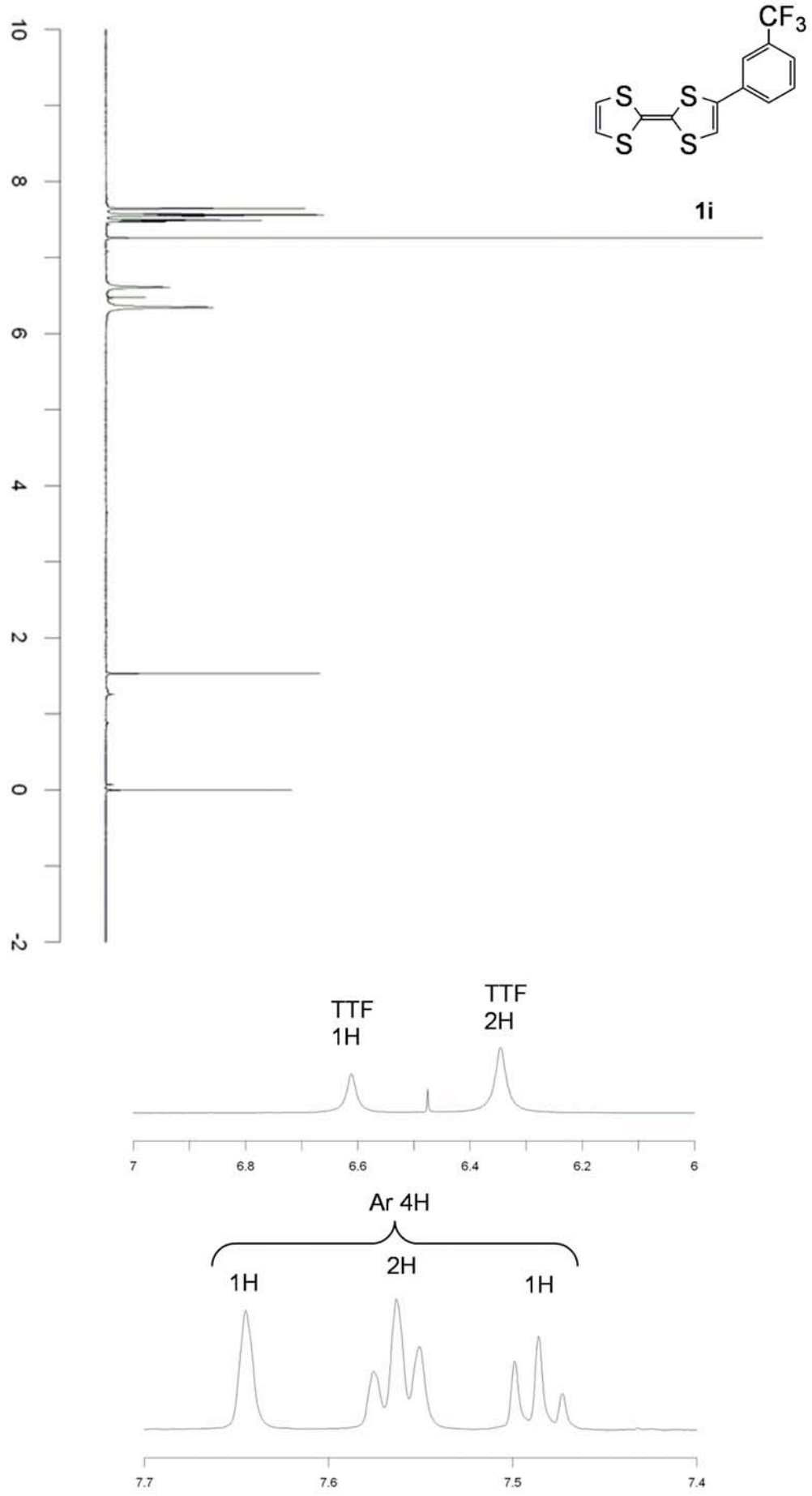


Figure S9-2. ^{13}C NMR Spectrum of **1i**

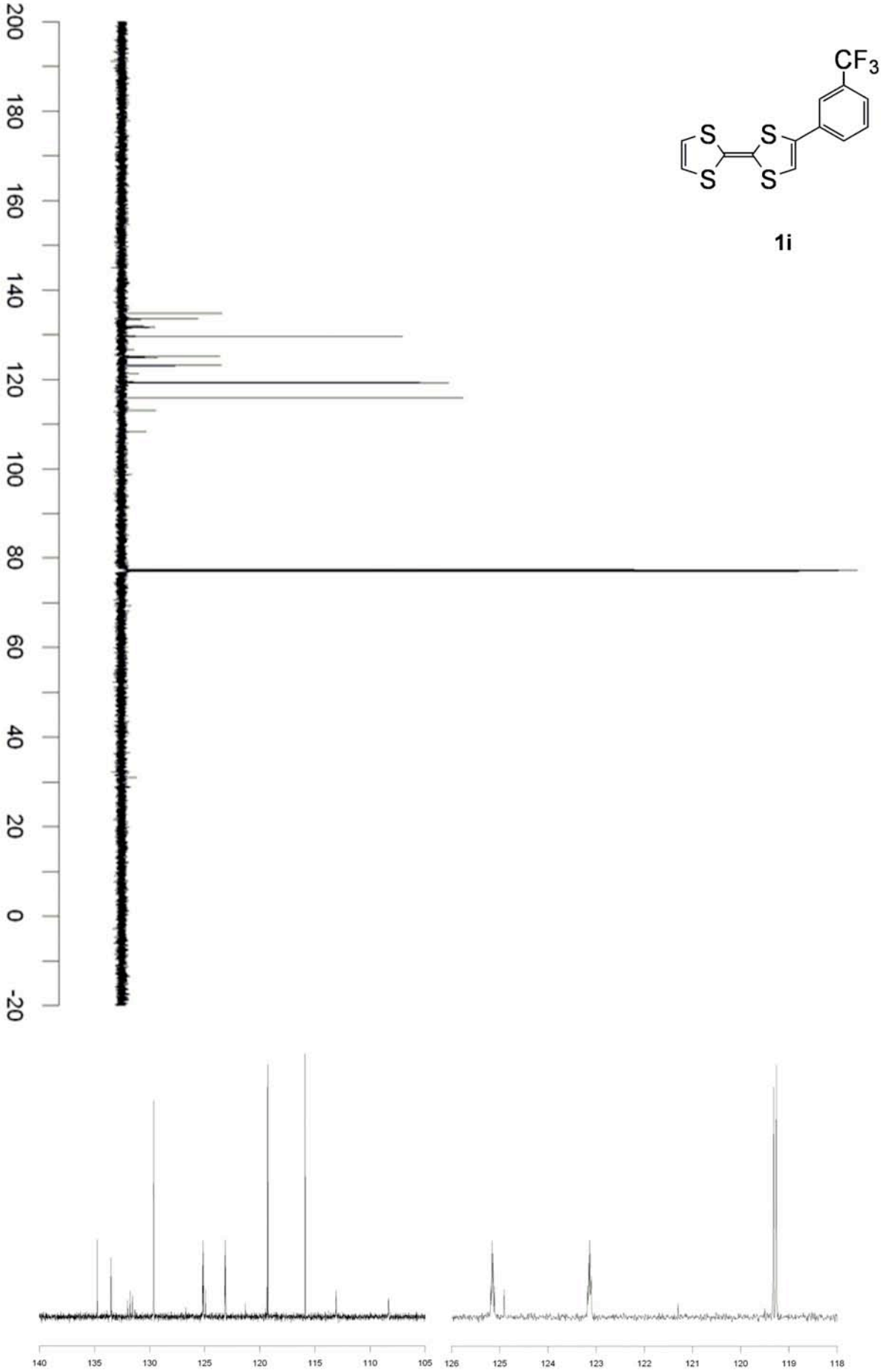


Figure S10-1. ^{1}H NMR Spectrum of **1j**

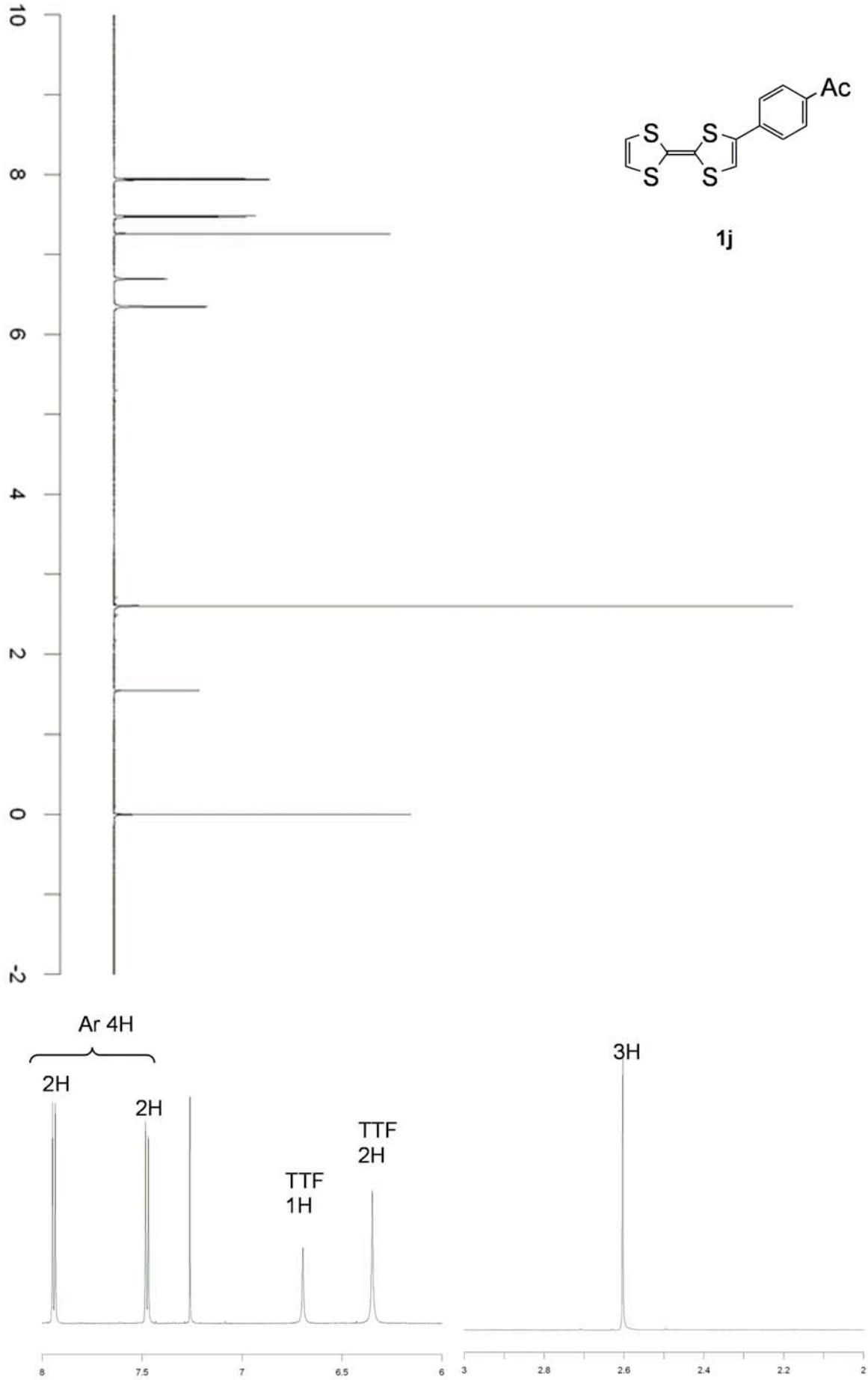


Figure S10-2. ^{13}C NMR Spectrum of **1j**

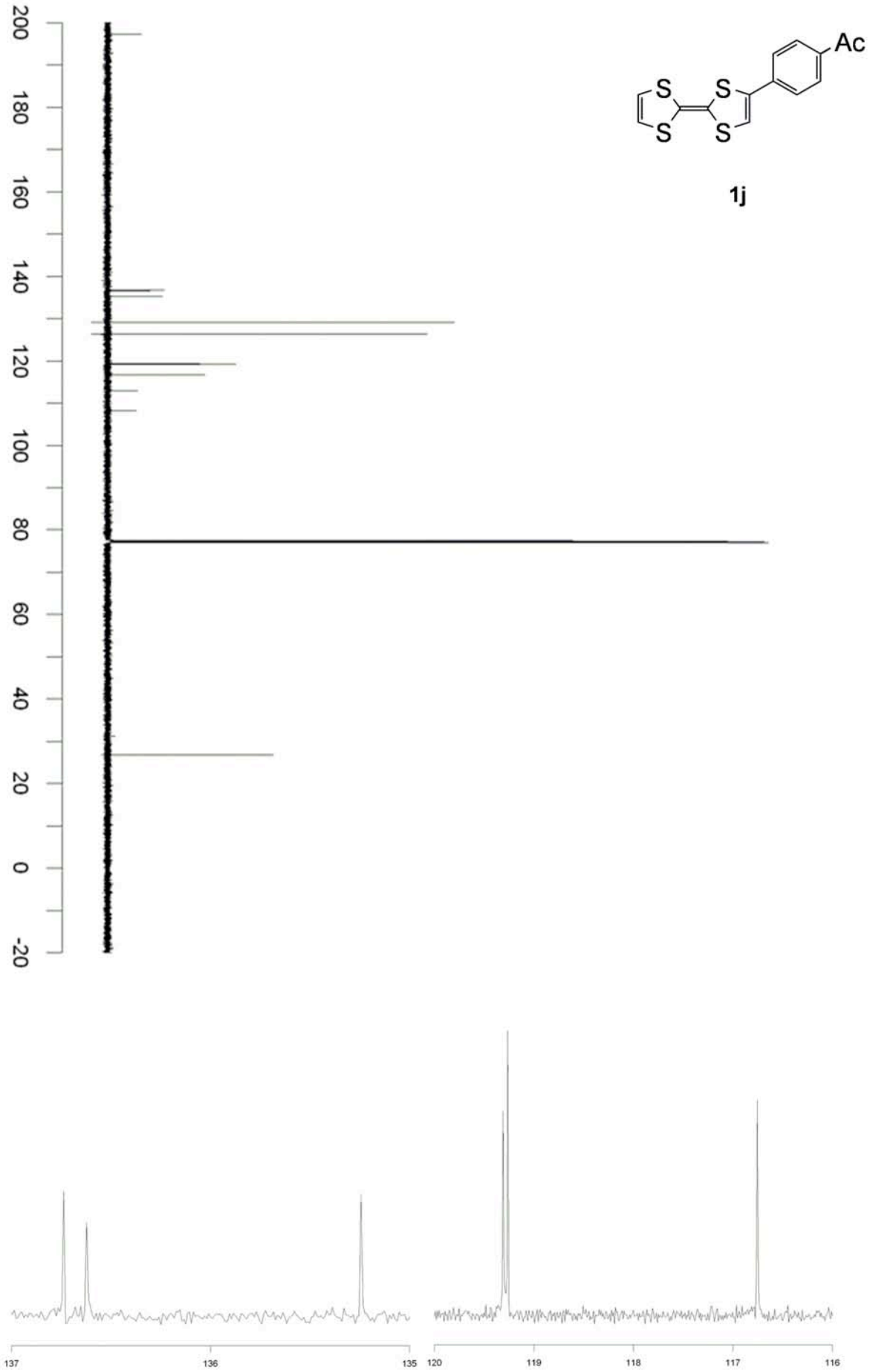


Figure S11-1. ^{1}H NMR Spectrum of **1k**

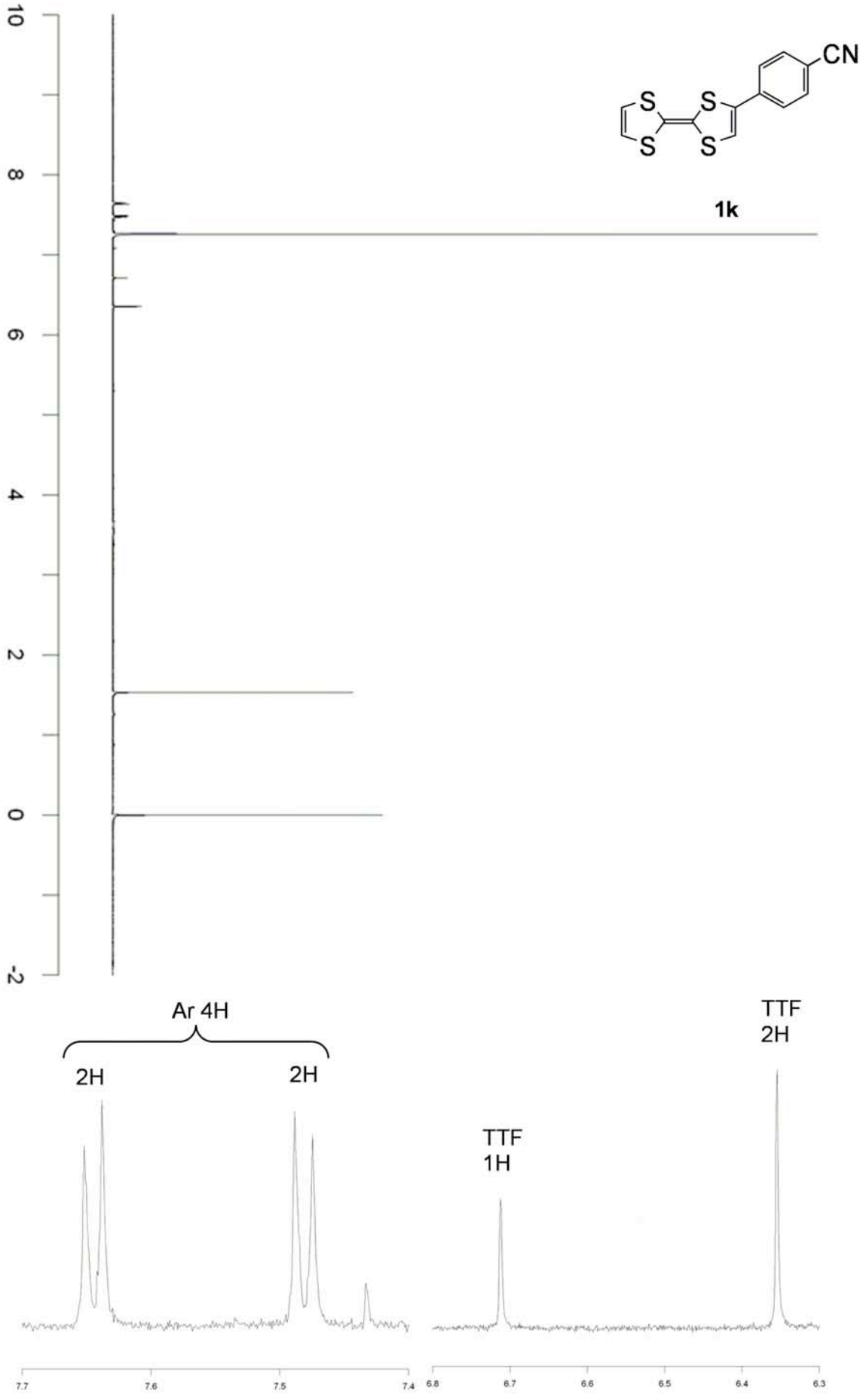


Figure S11-2. ^{13}C NMR Spectrum of **1k**

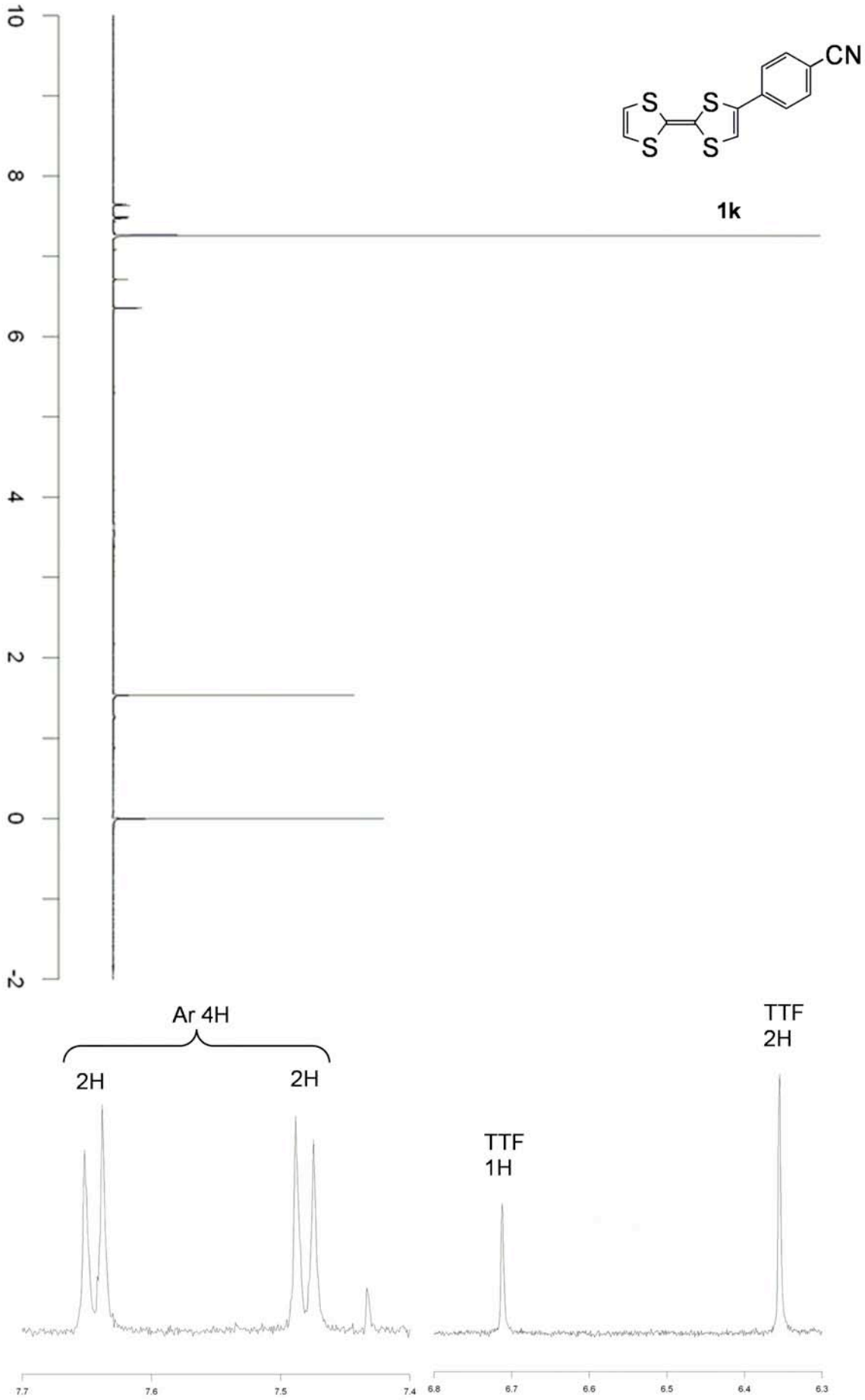


Figure S12-1. ^{1}H NMR Spectrum of **2a**

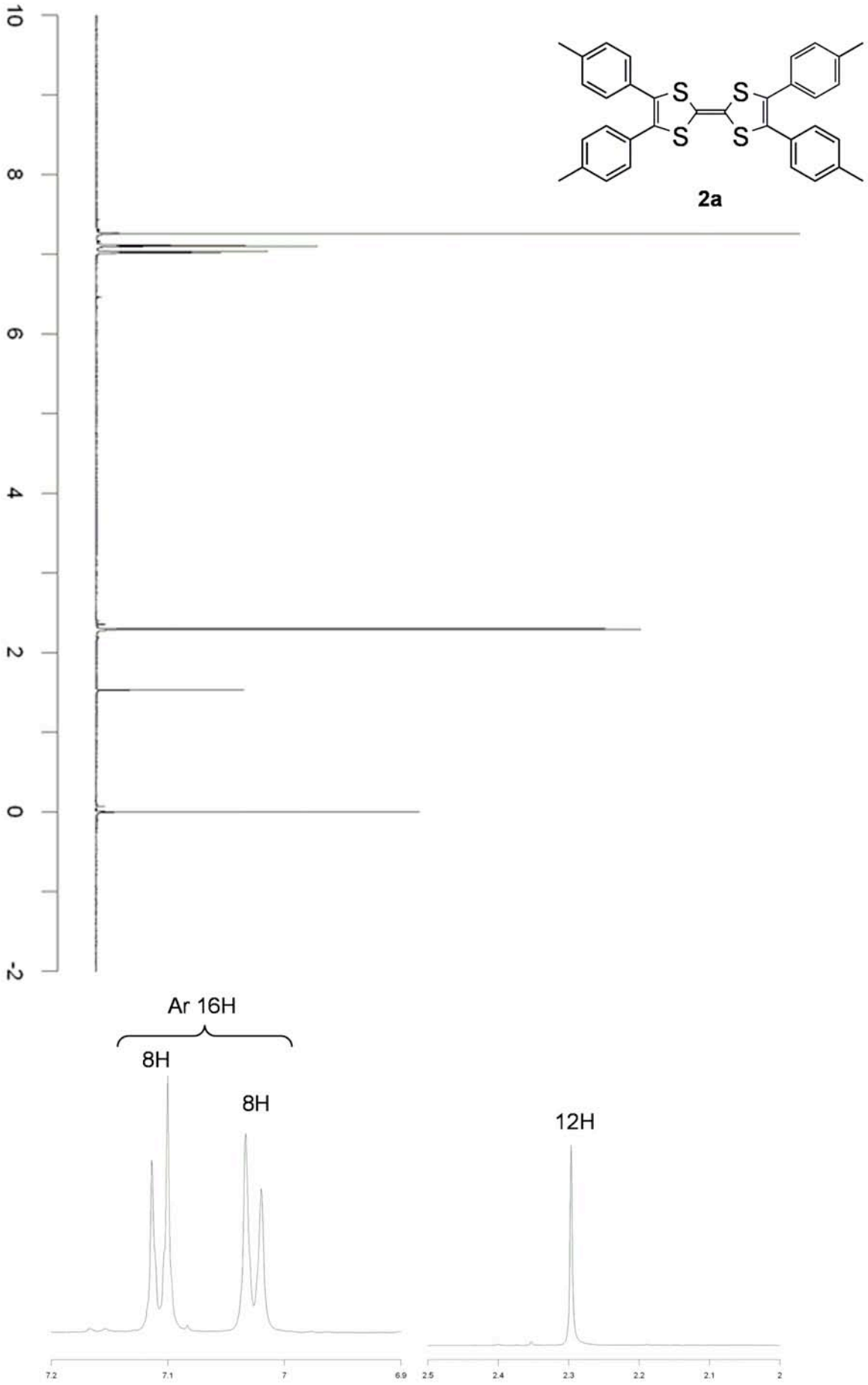


Figure S12-2. ^{13}C NMR Spectrum of **2a**

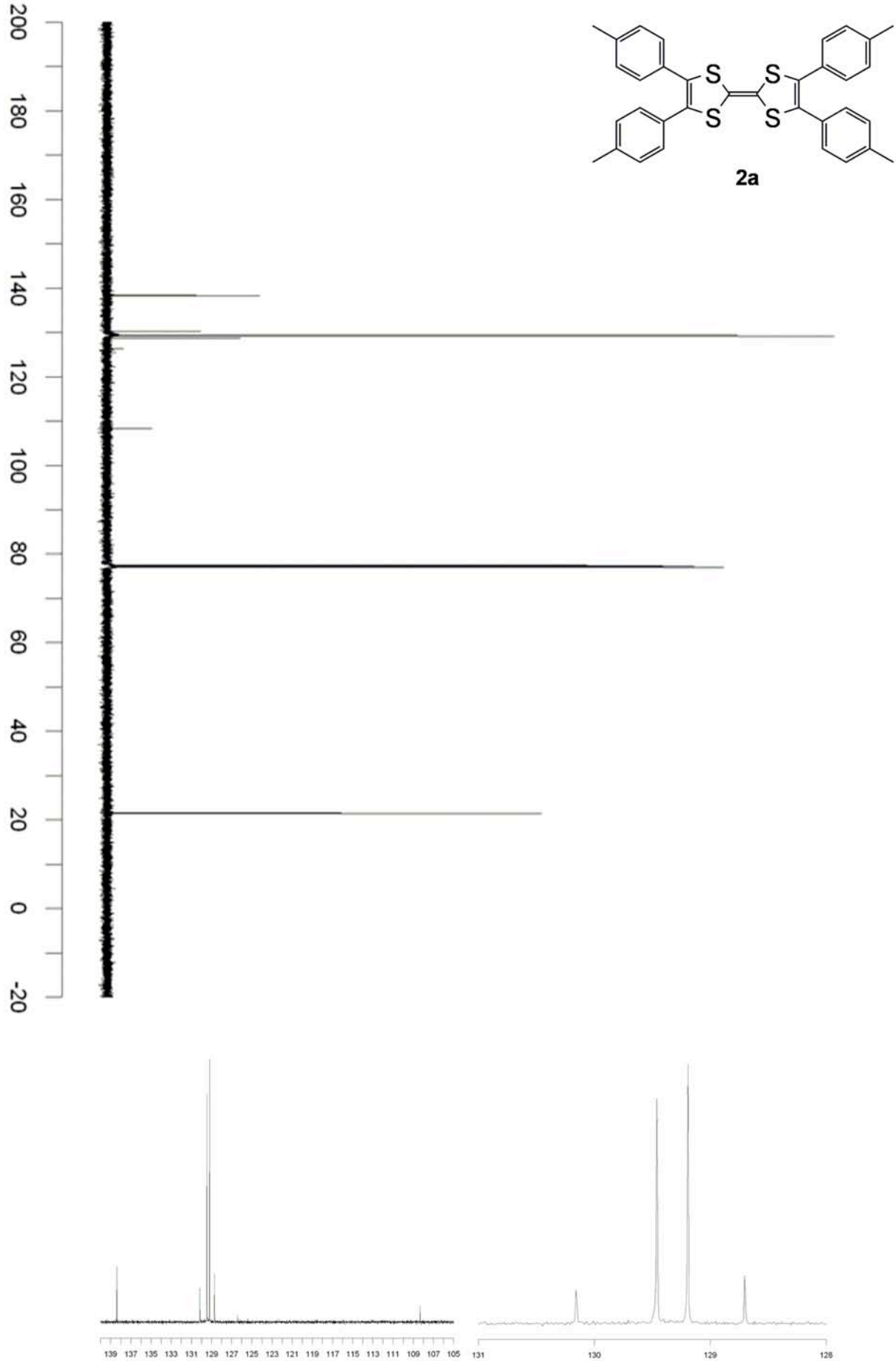


Figure S13-1. ^{1}H NMR Spectrum of **2b**

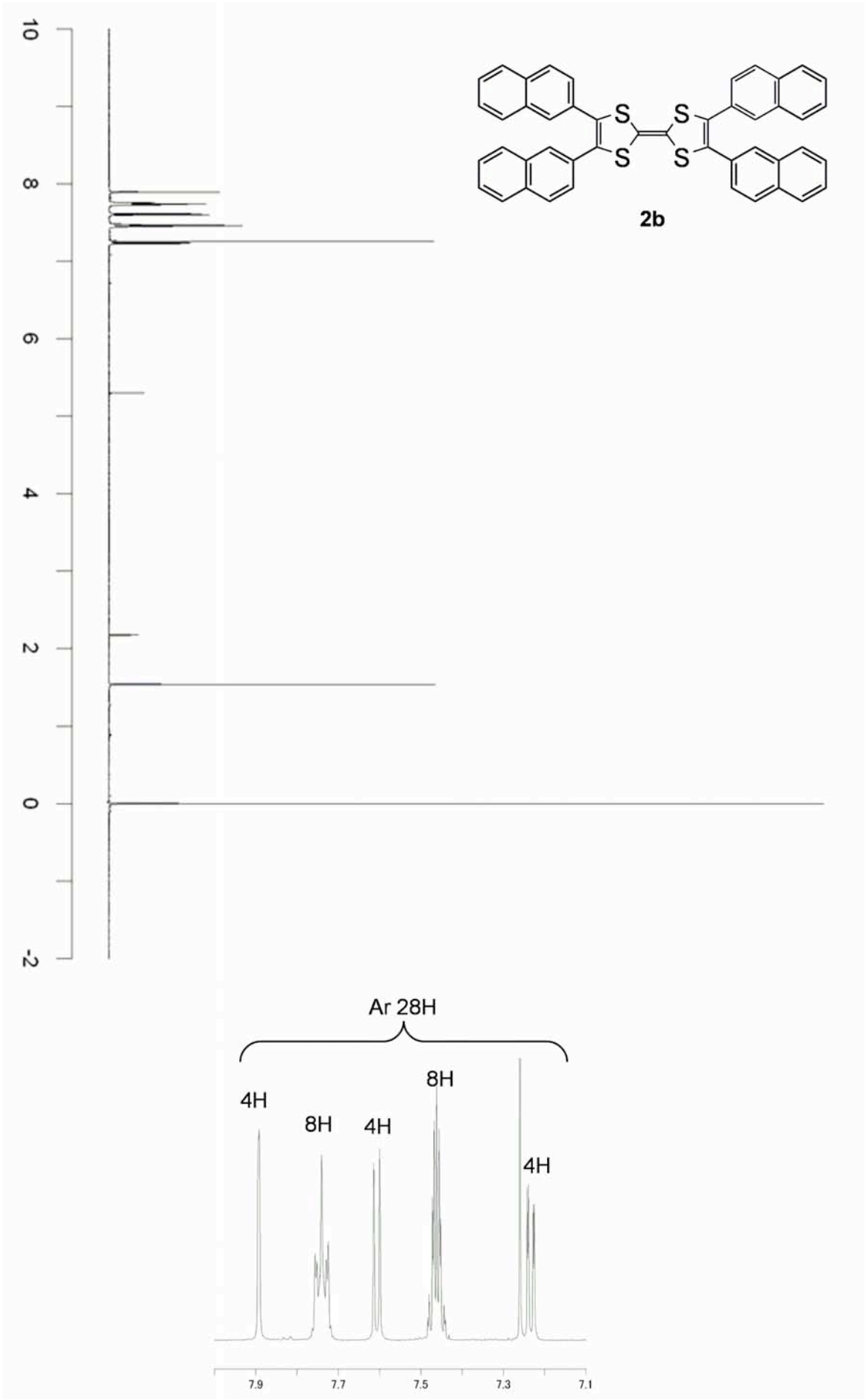


Figure S13-2. ^{13}C NMR Spectrum of **2b**

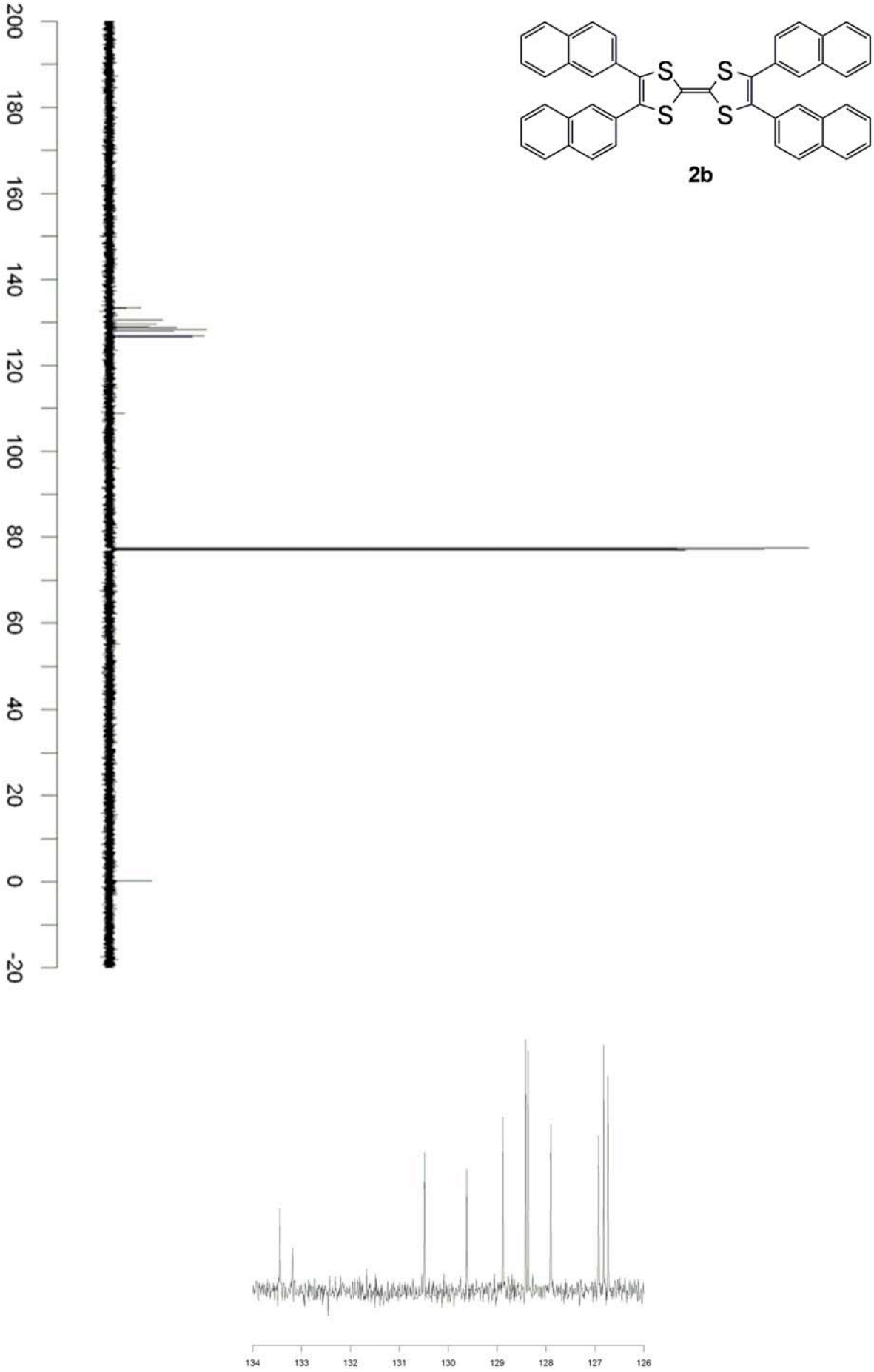


Figure S14-1. ^{1}H NMR Spectrum of **2c**

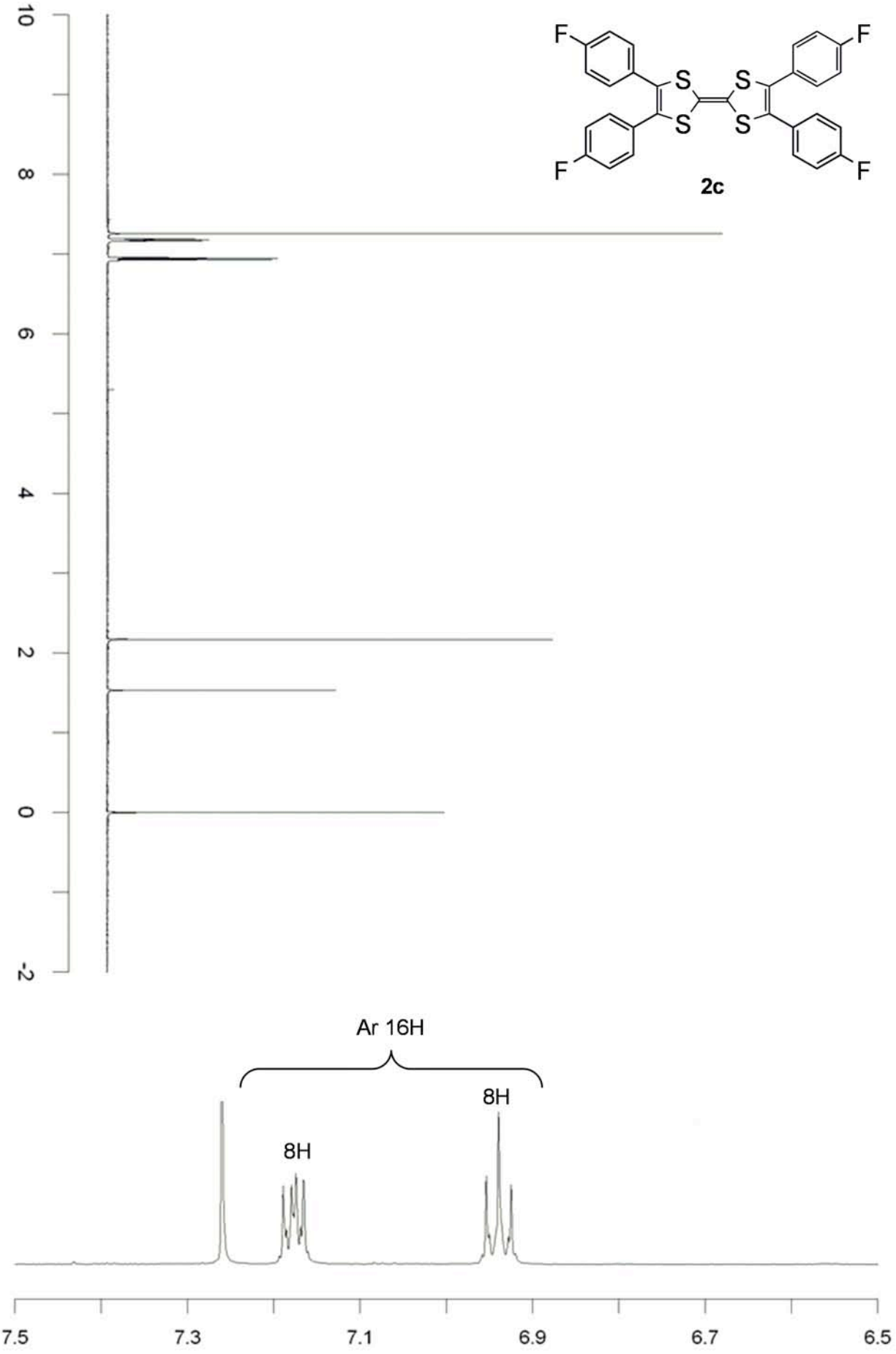


Figure S14-2. ^{13}C NMR Spectrum of **2c**

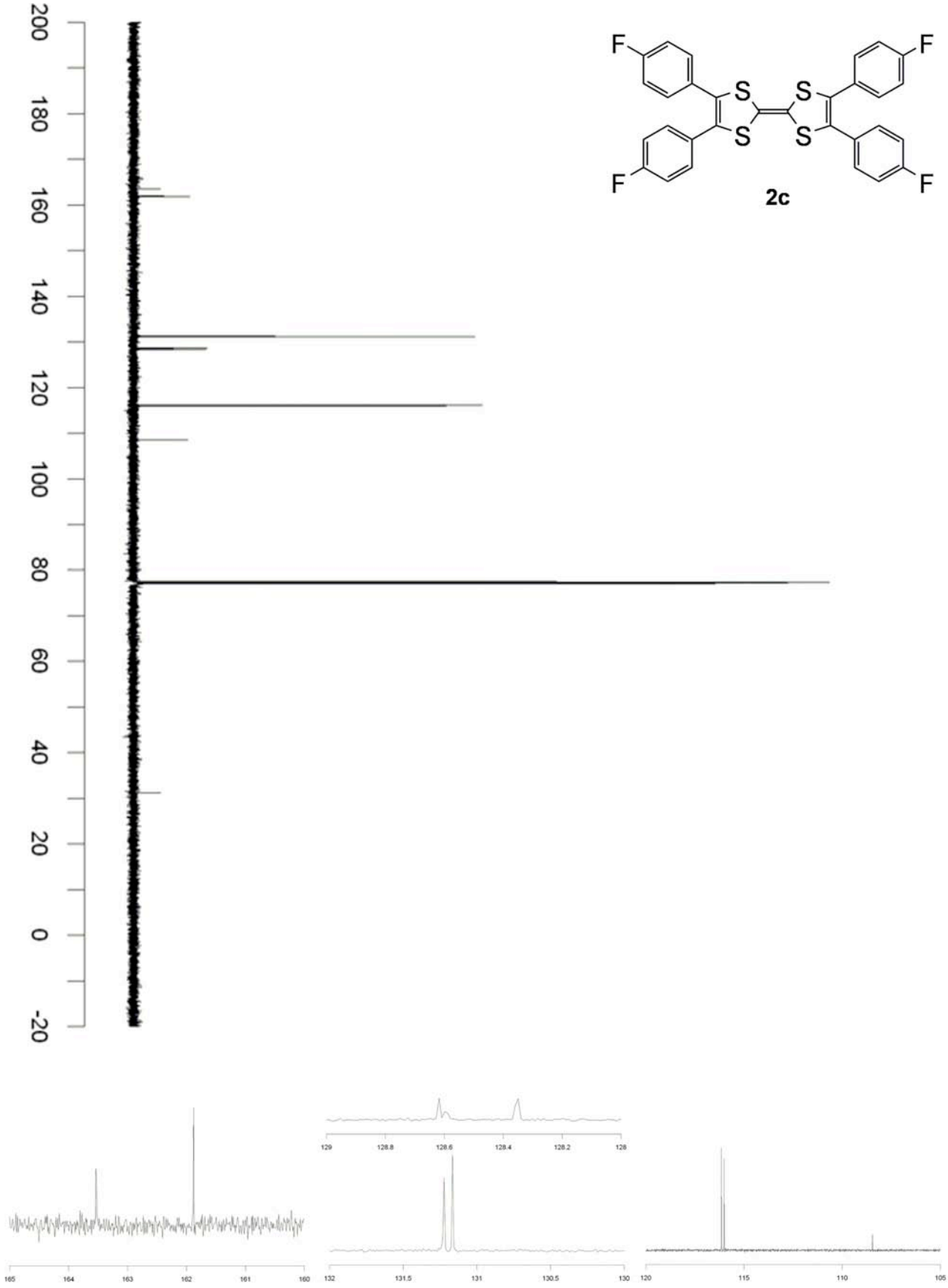


Figure S15-1. ^{1}H NMR Spectrum of **2d**

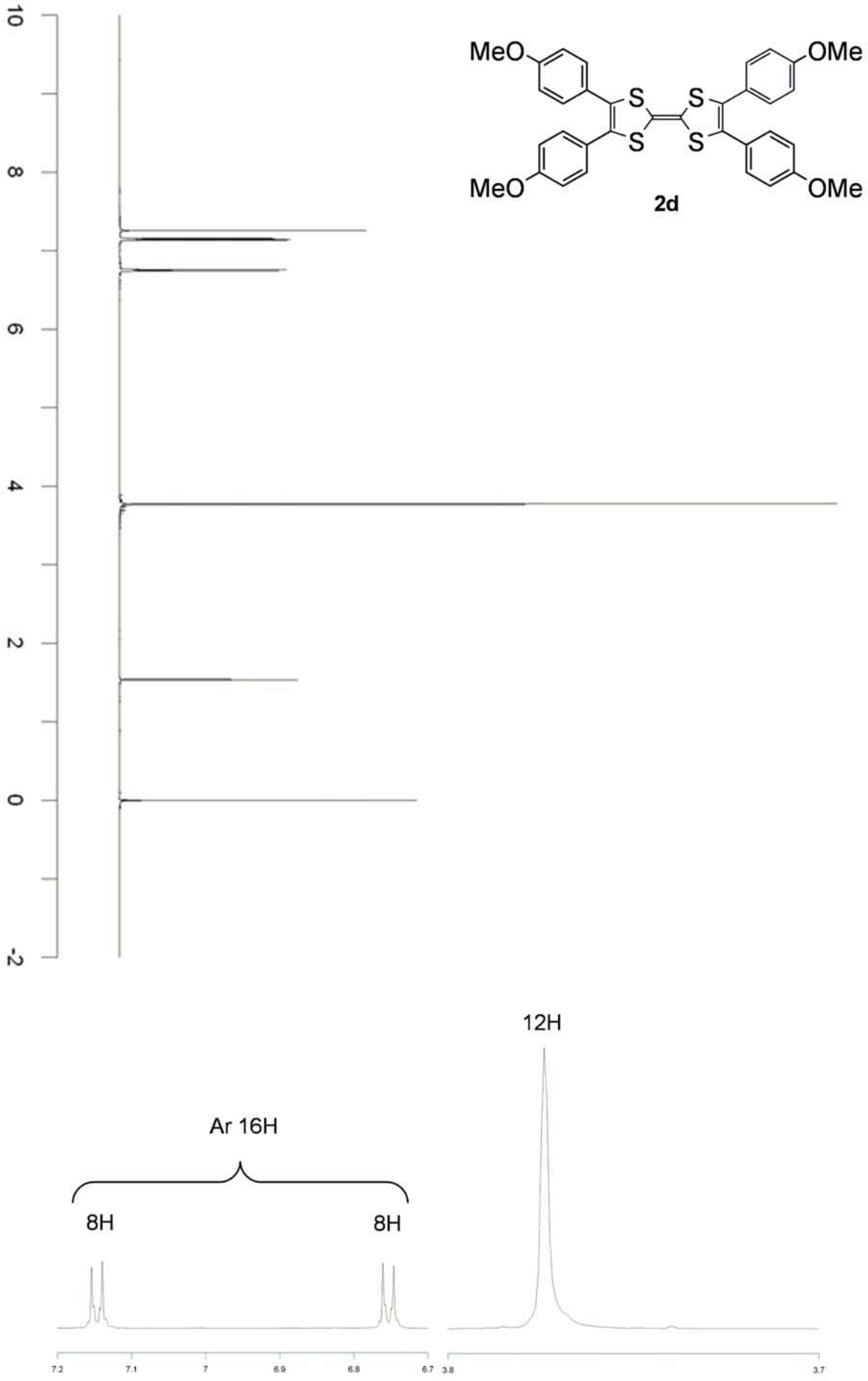


Figure S15-2. ^{13}C NMR Spectrum of **2d**

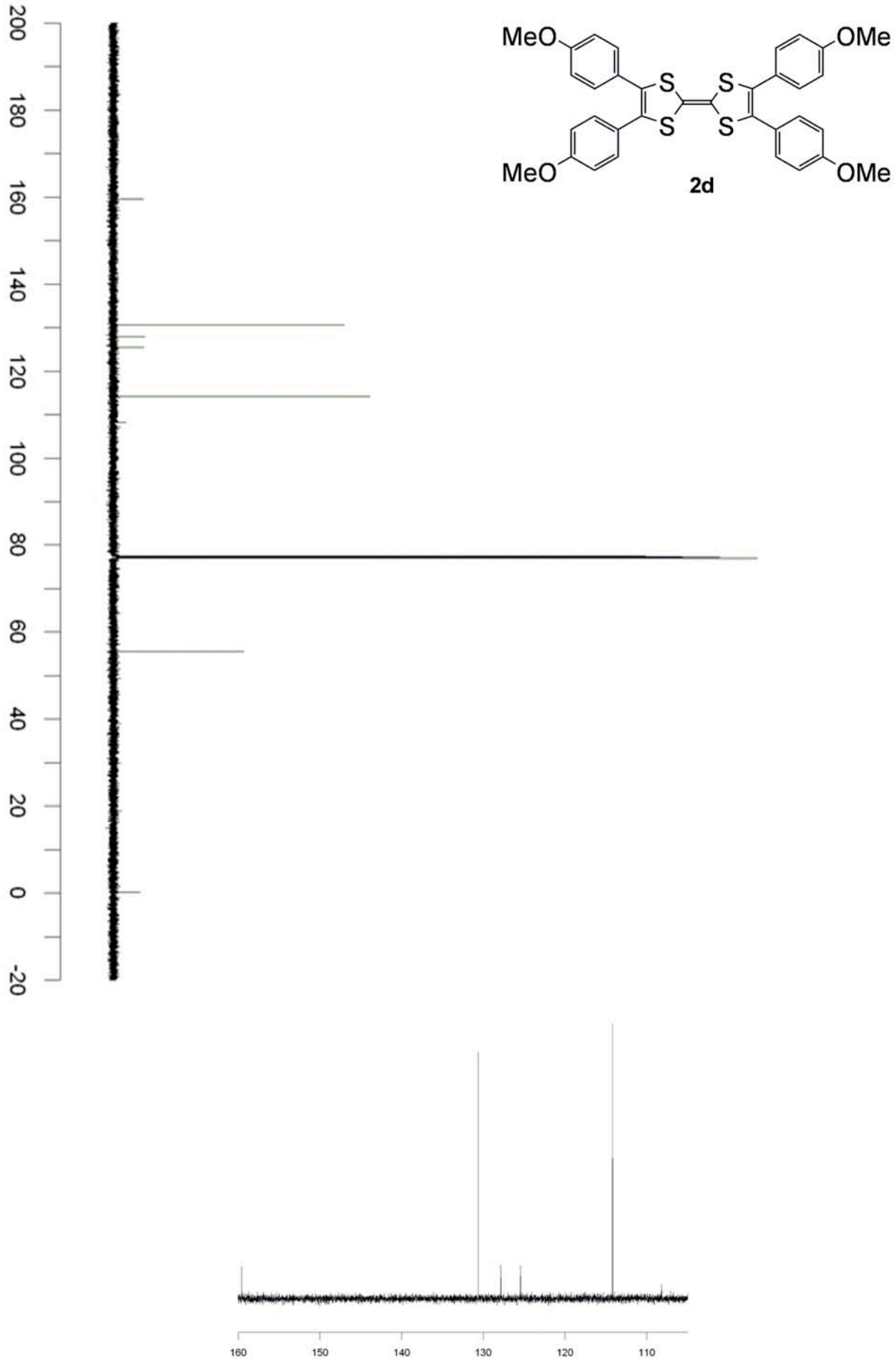


Figure S16-1. ^{1}H NMR Spectrum of **2e**

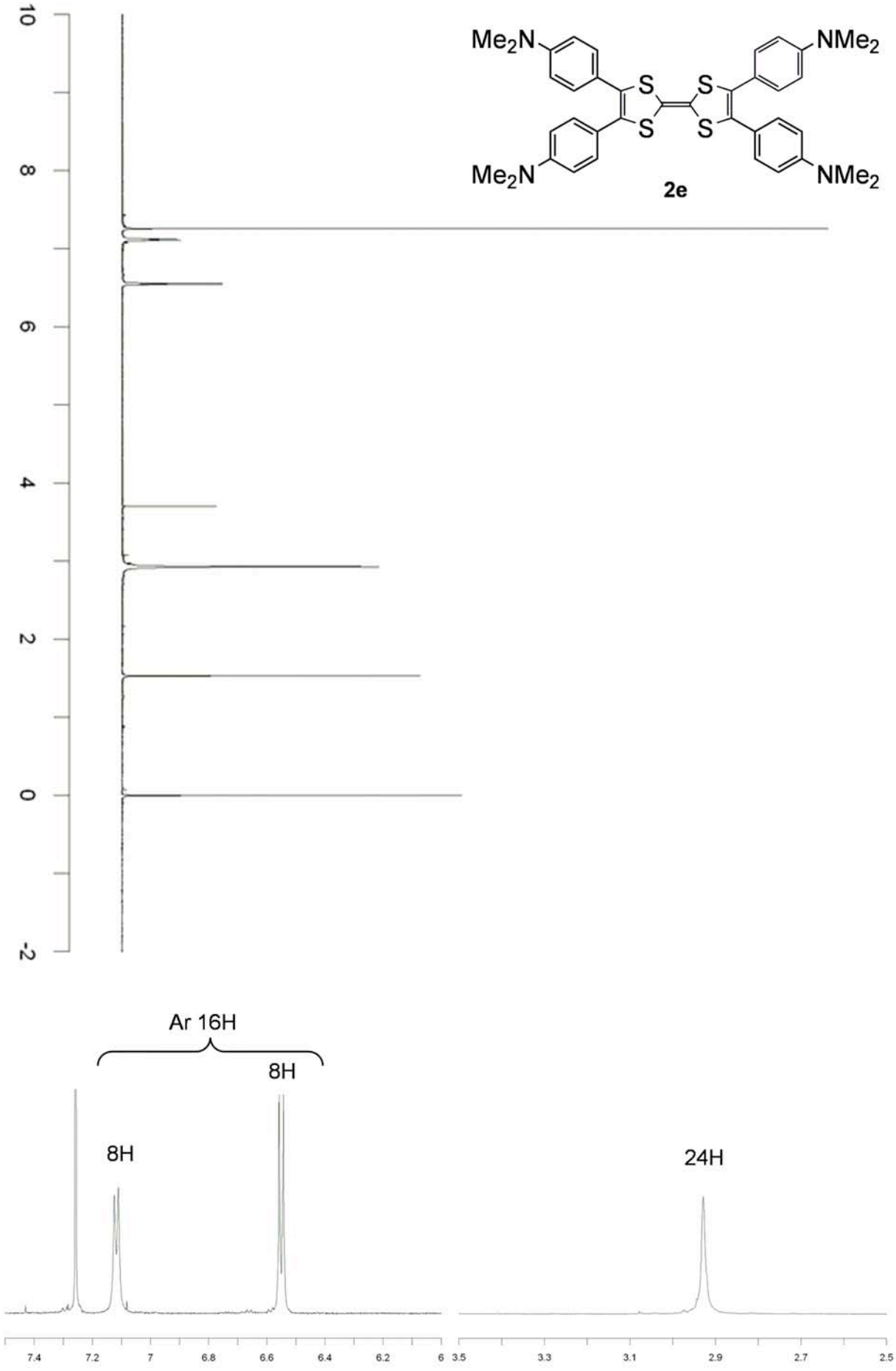


Figure S16-2. ^{13}C NMR Spectrum of **2e**

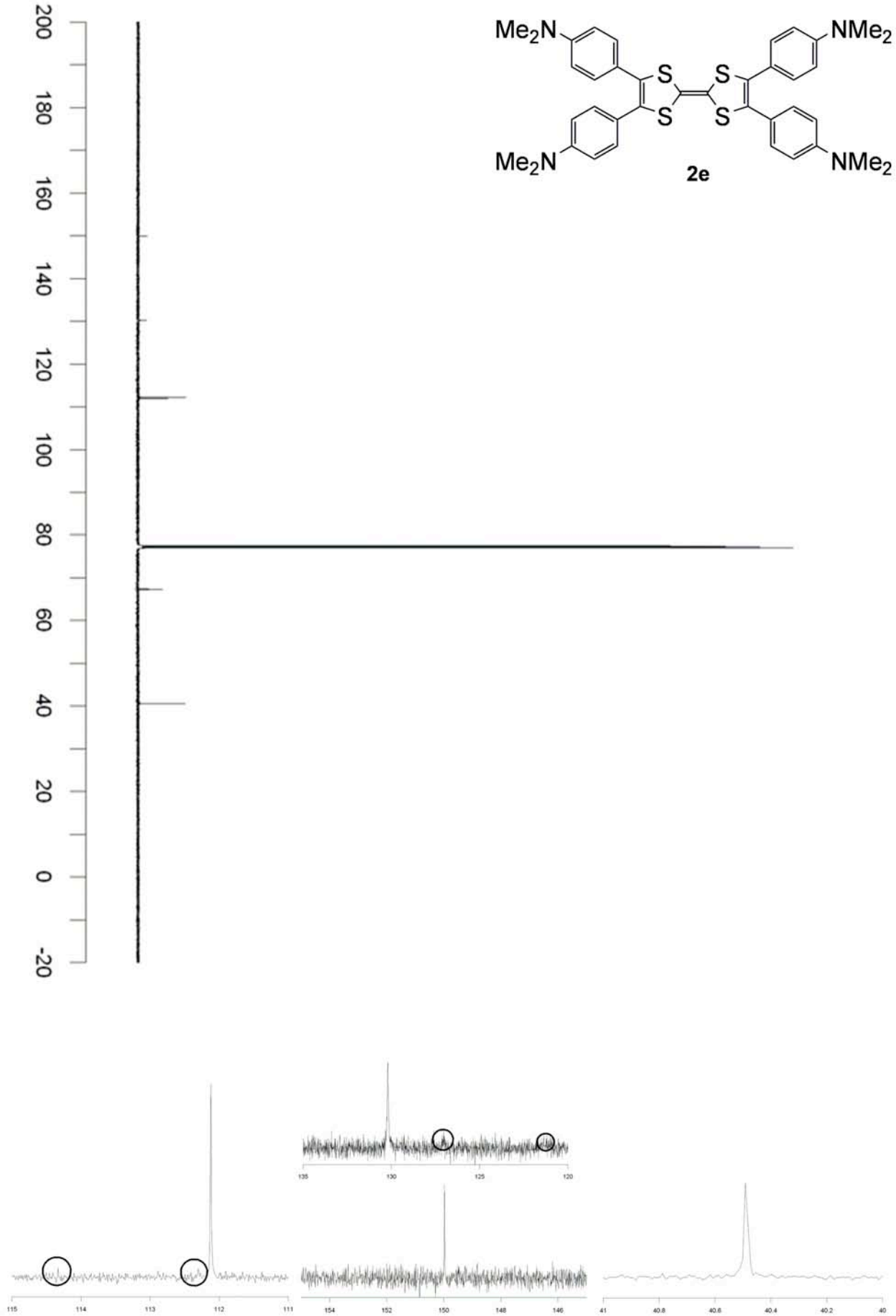


Figure S17-1. ^{1}H NMR Spectrum of **2f**

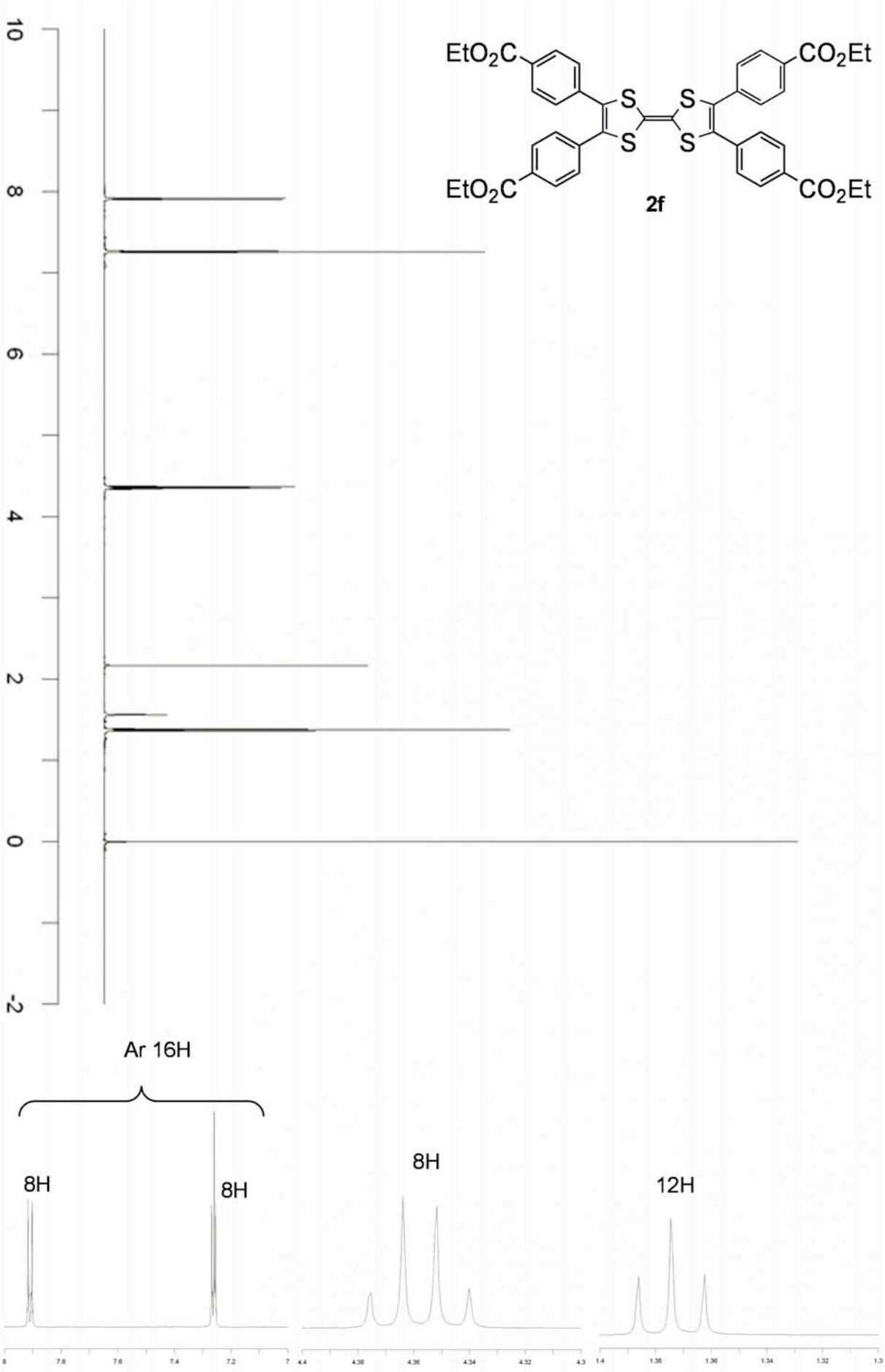


Figure S17-2. ^{13}C NMR Spectrum of **2f**

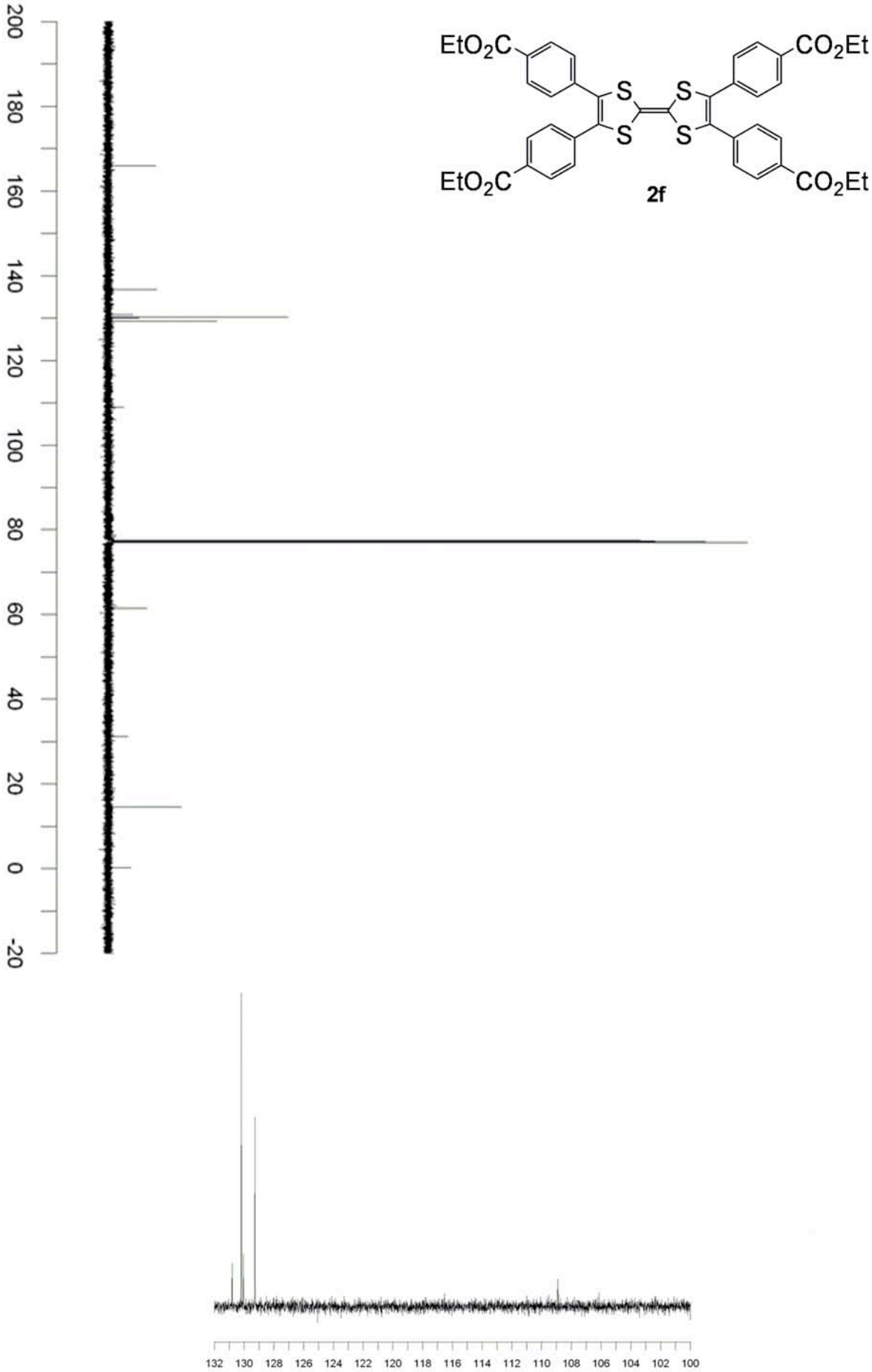


Figure S18-1. ^{1}H NMR Spectrum of **2g**

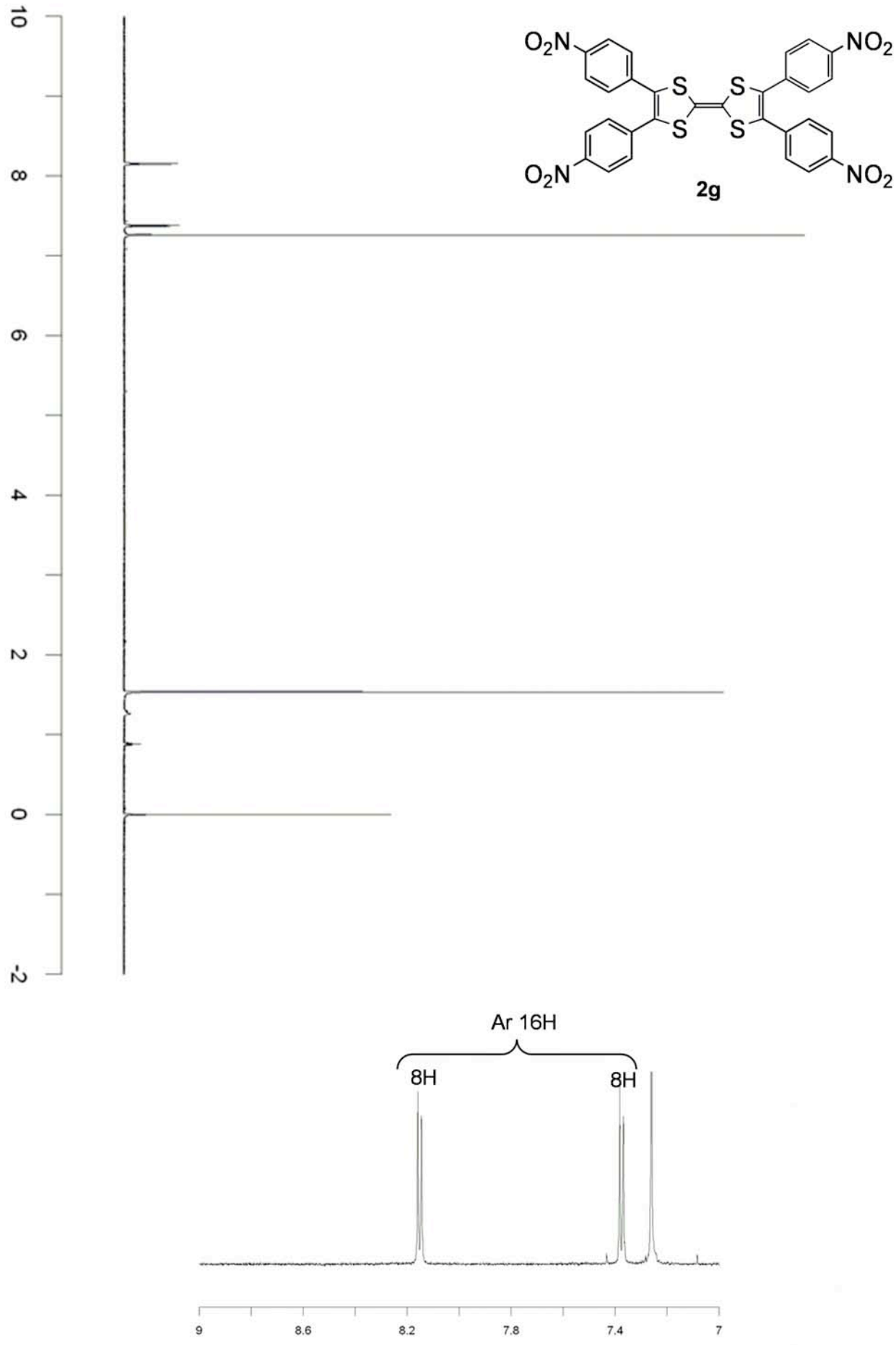


Figure S18-2. ^{13}C NMR Spectrum of **2g**

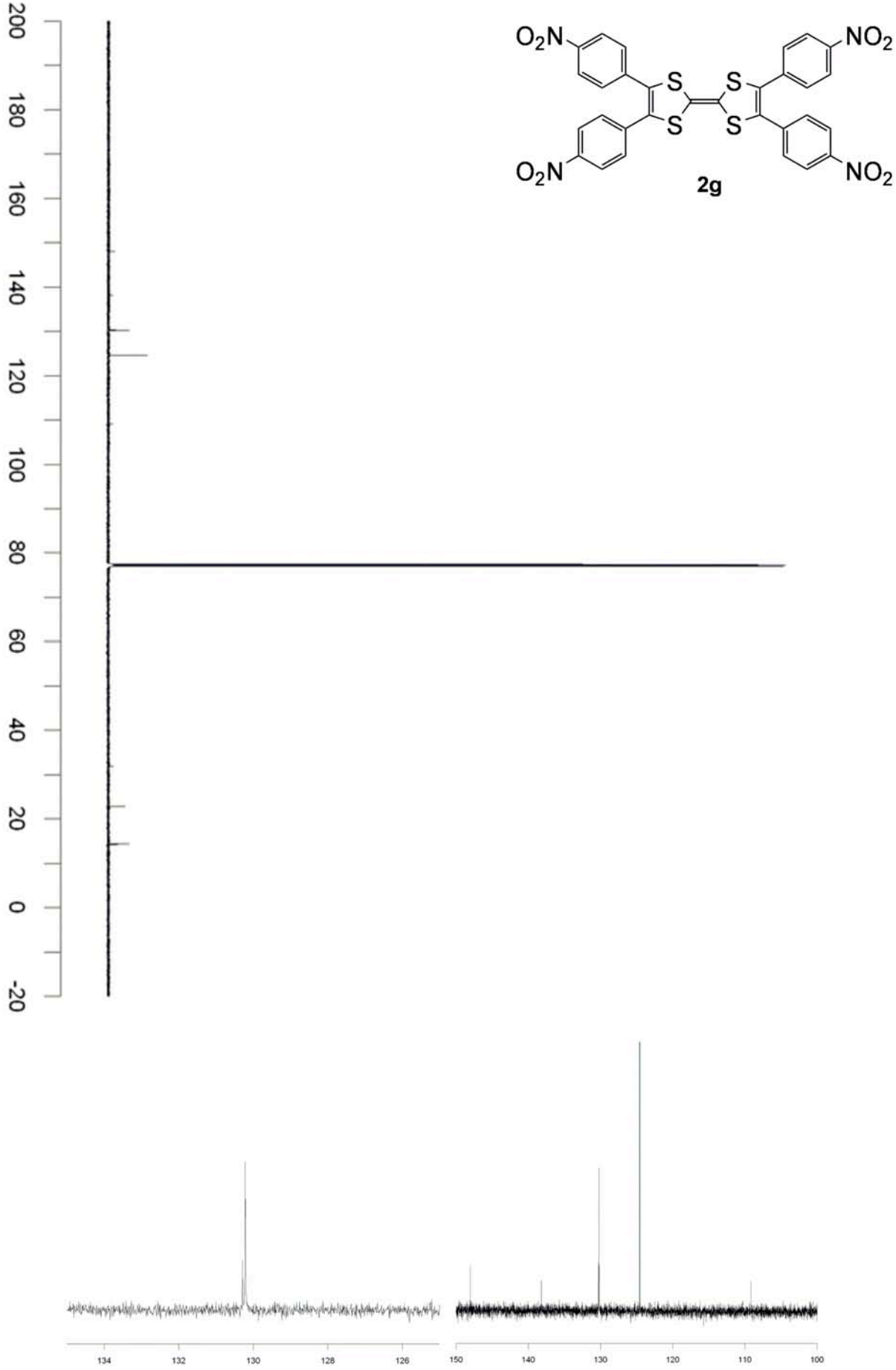


Figure S19-1. ^{1}H NMR Spectrum of **2h**

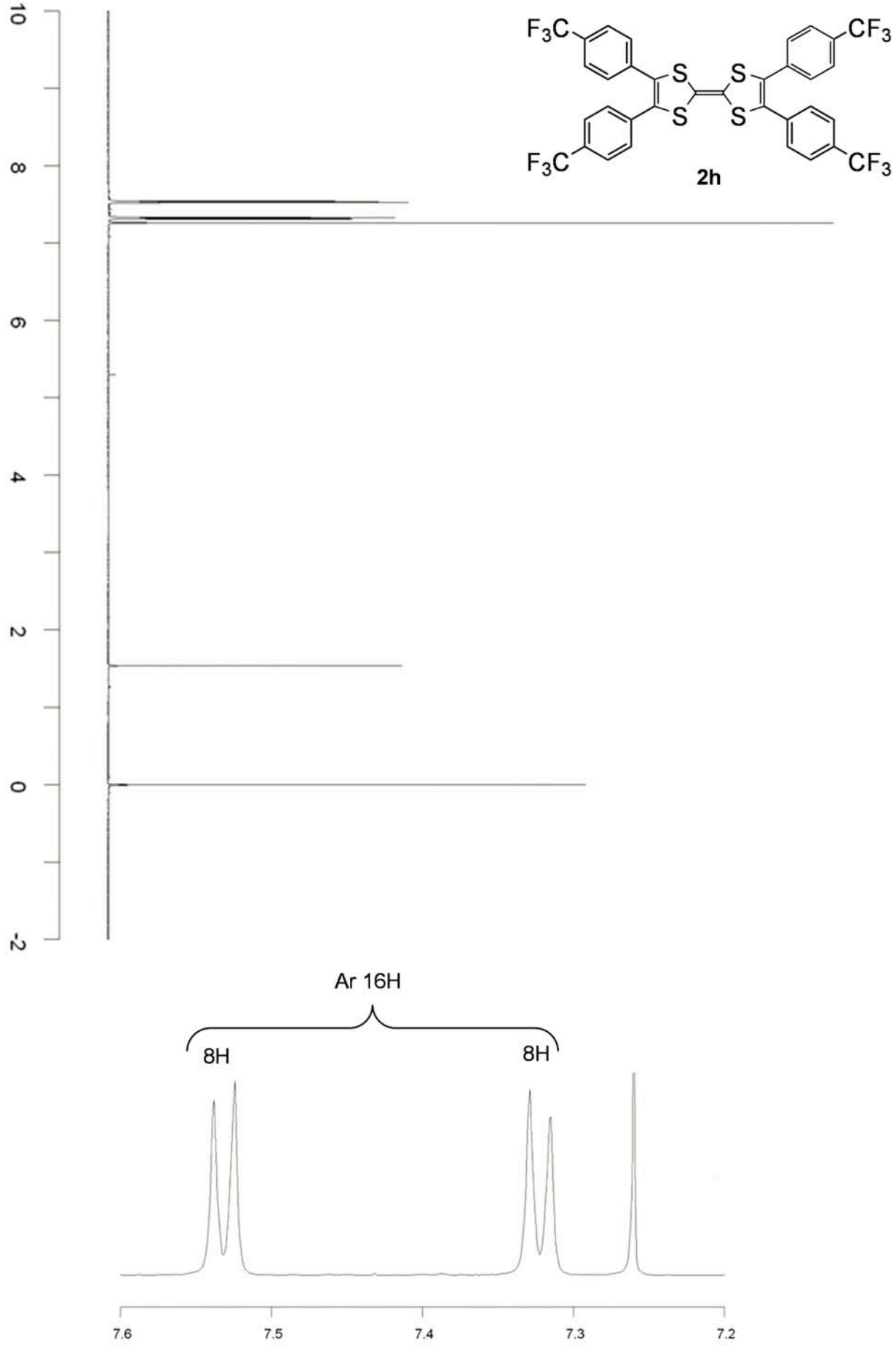


Figure S19-2. ^{13}C NMR Spectrum of **2h**

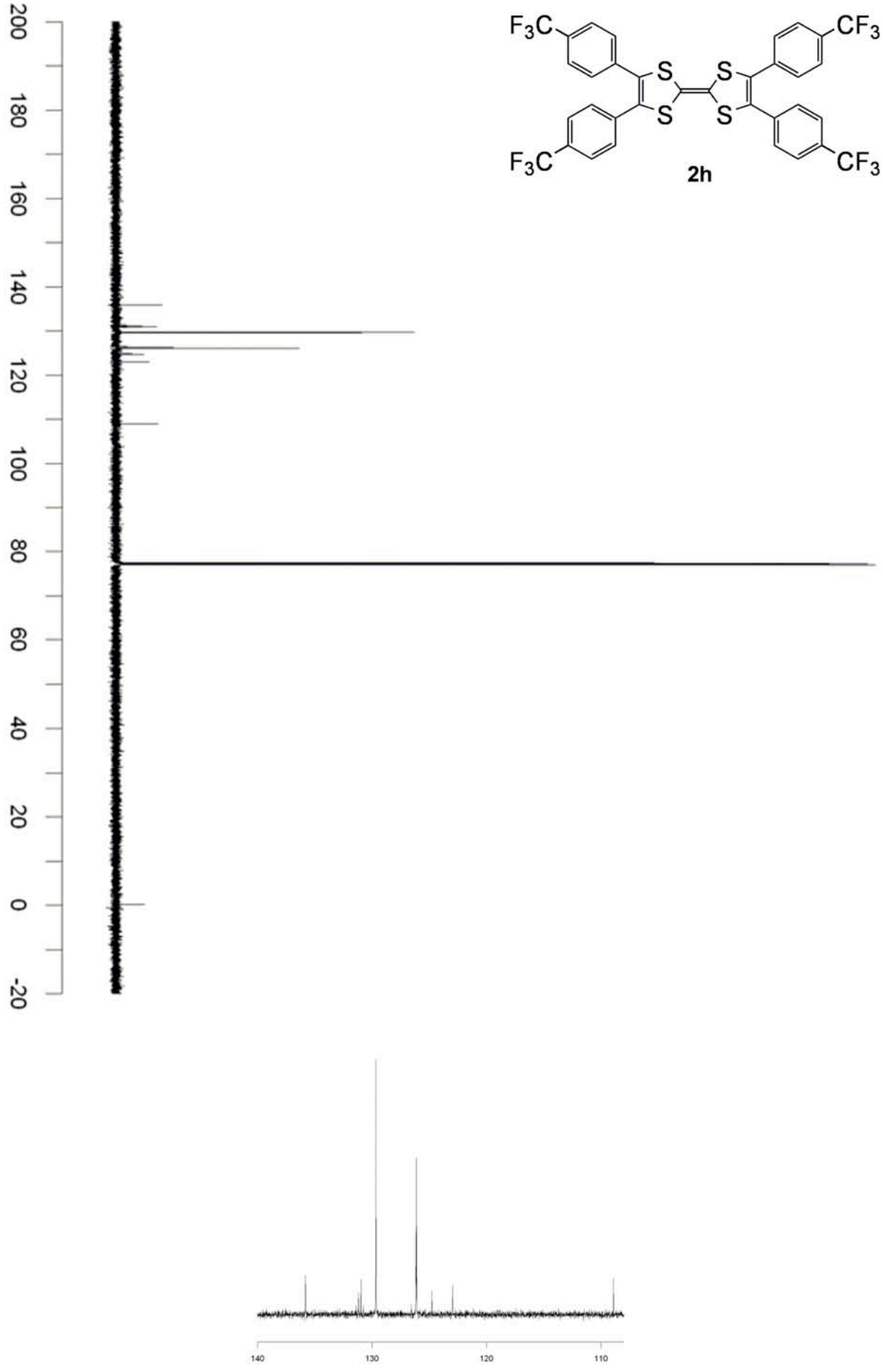


Figure S20-1. ^{1}H NMR Spectrum of **2i**

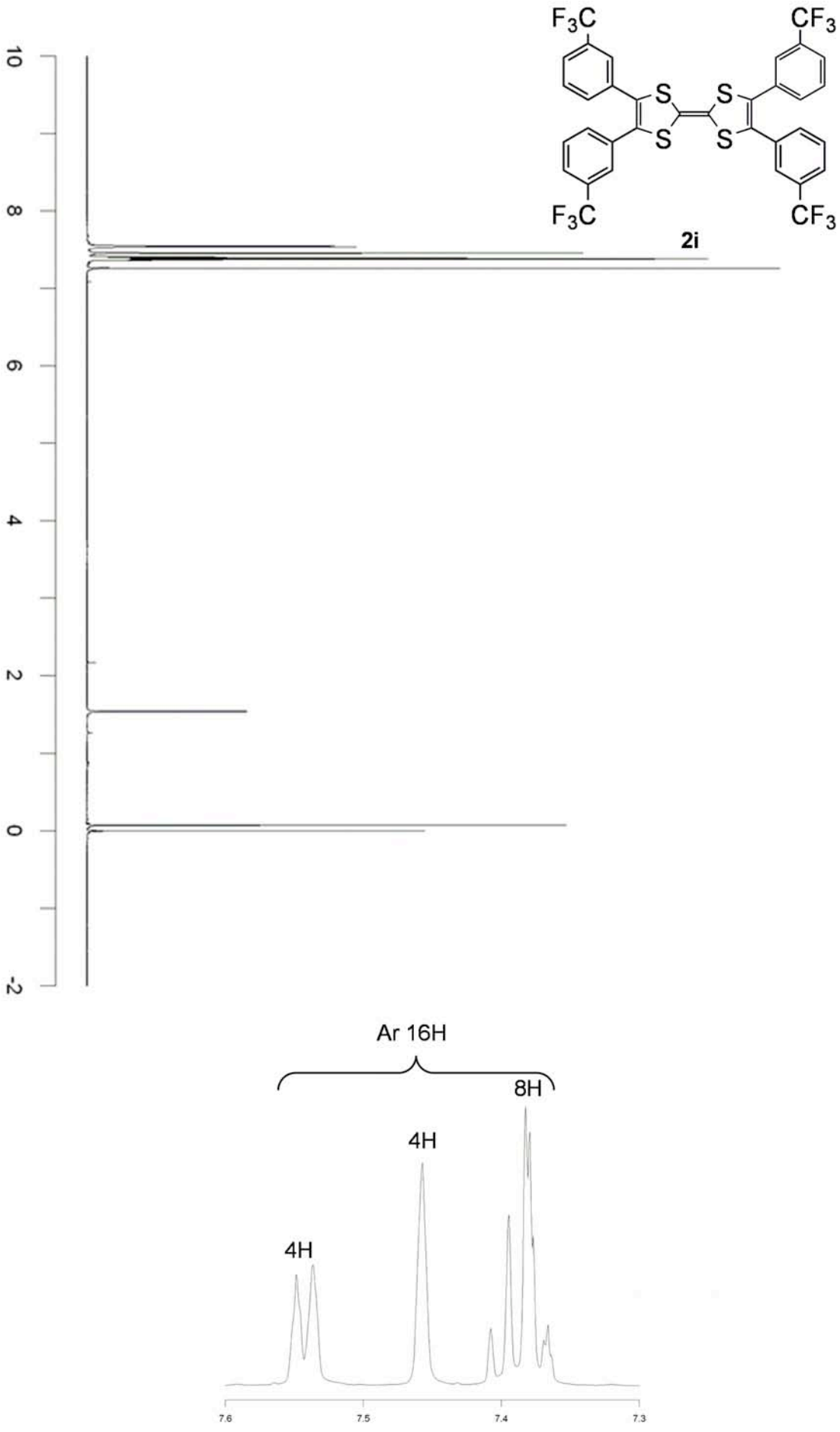


Figure S20-2. ^{13}C NMR Spectrum of **2i**

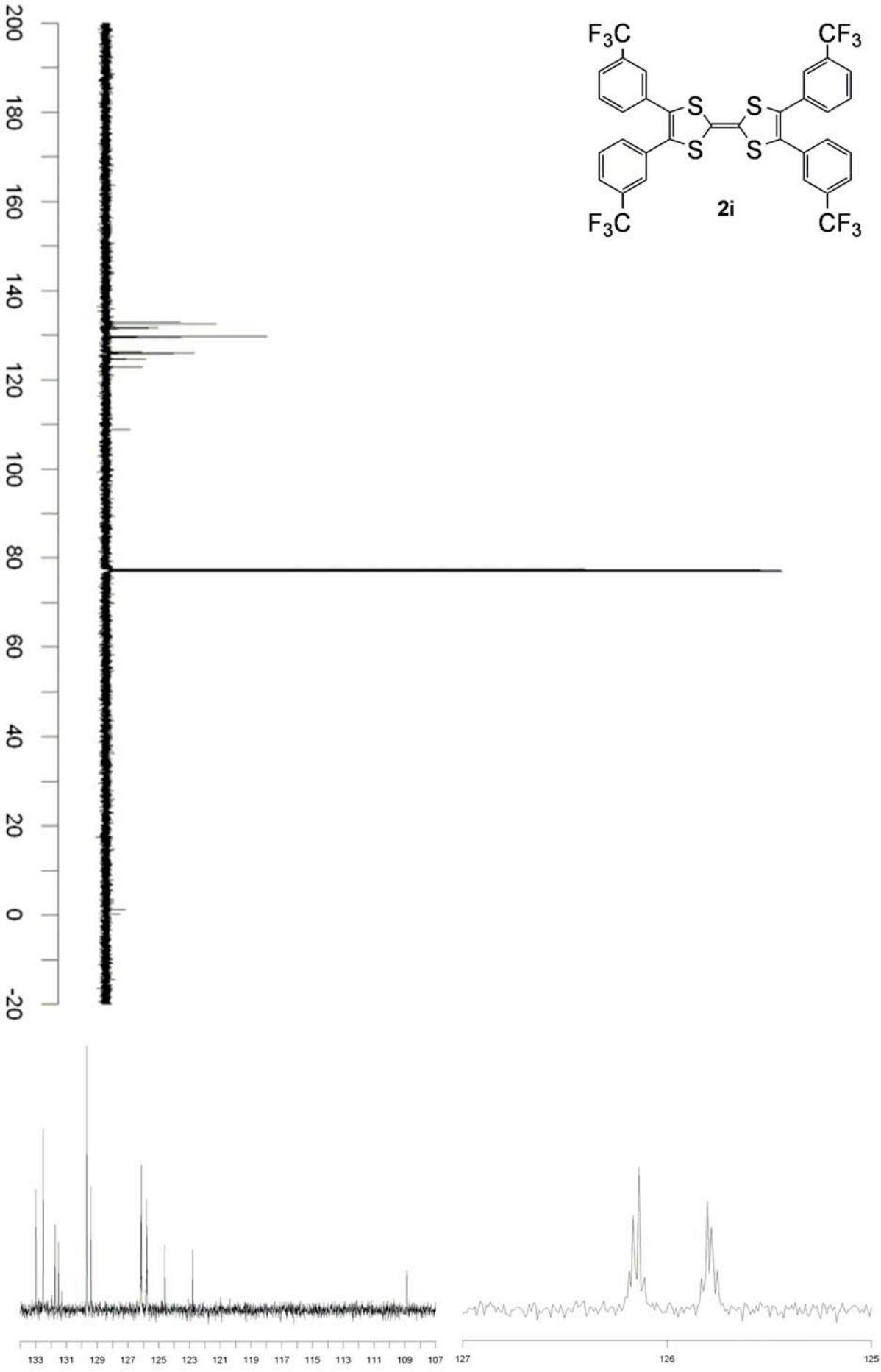


Figure S21-1. ^{1}H NMR Spectrum of **2j**

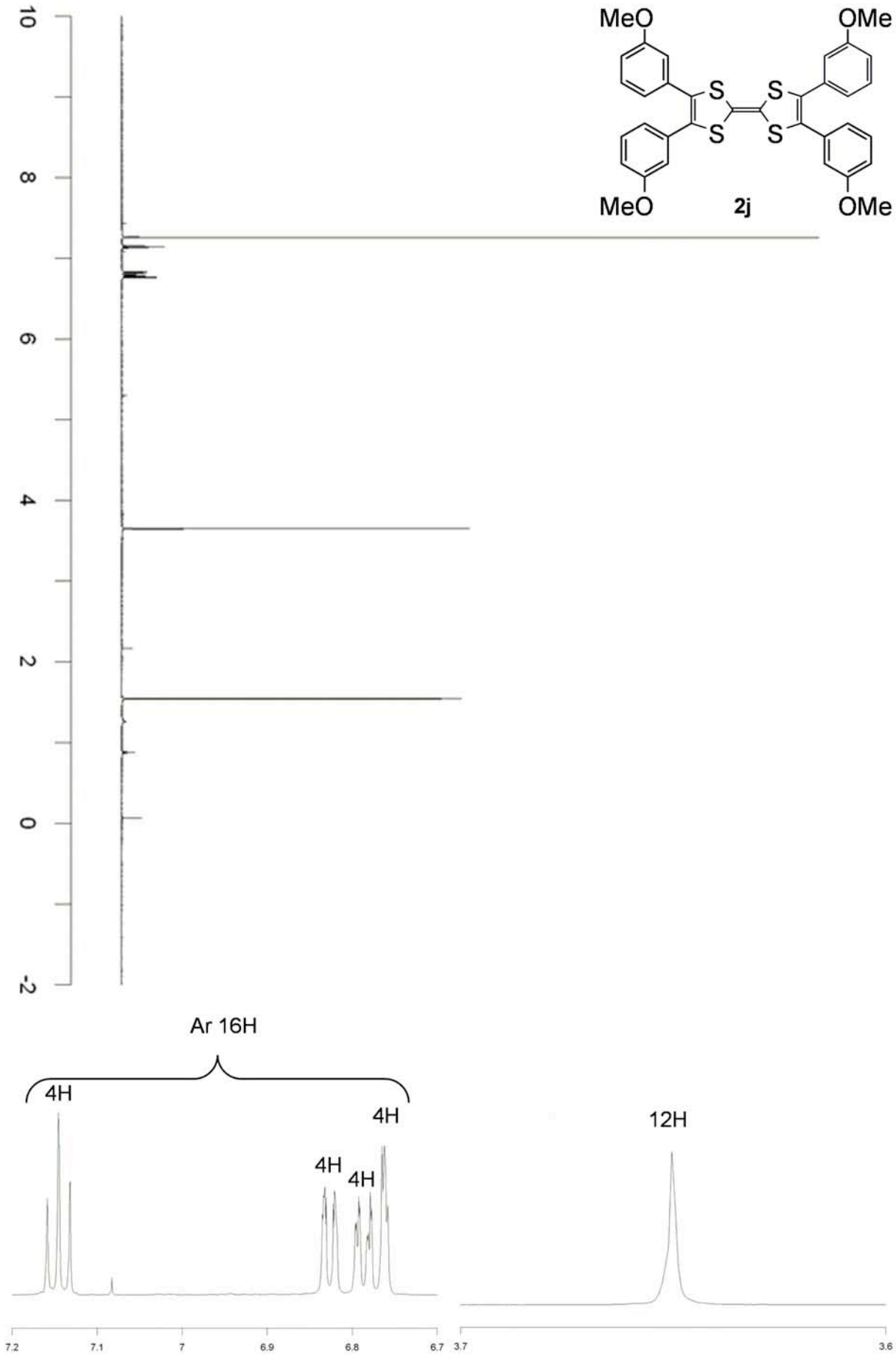


Figure S21-2. ^{13}C NMR Spectrum of **2j**

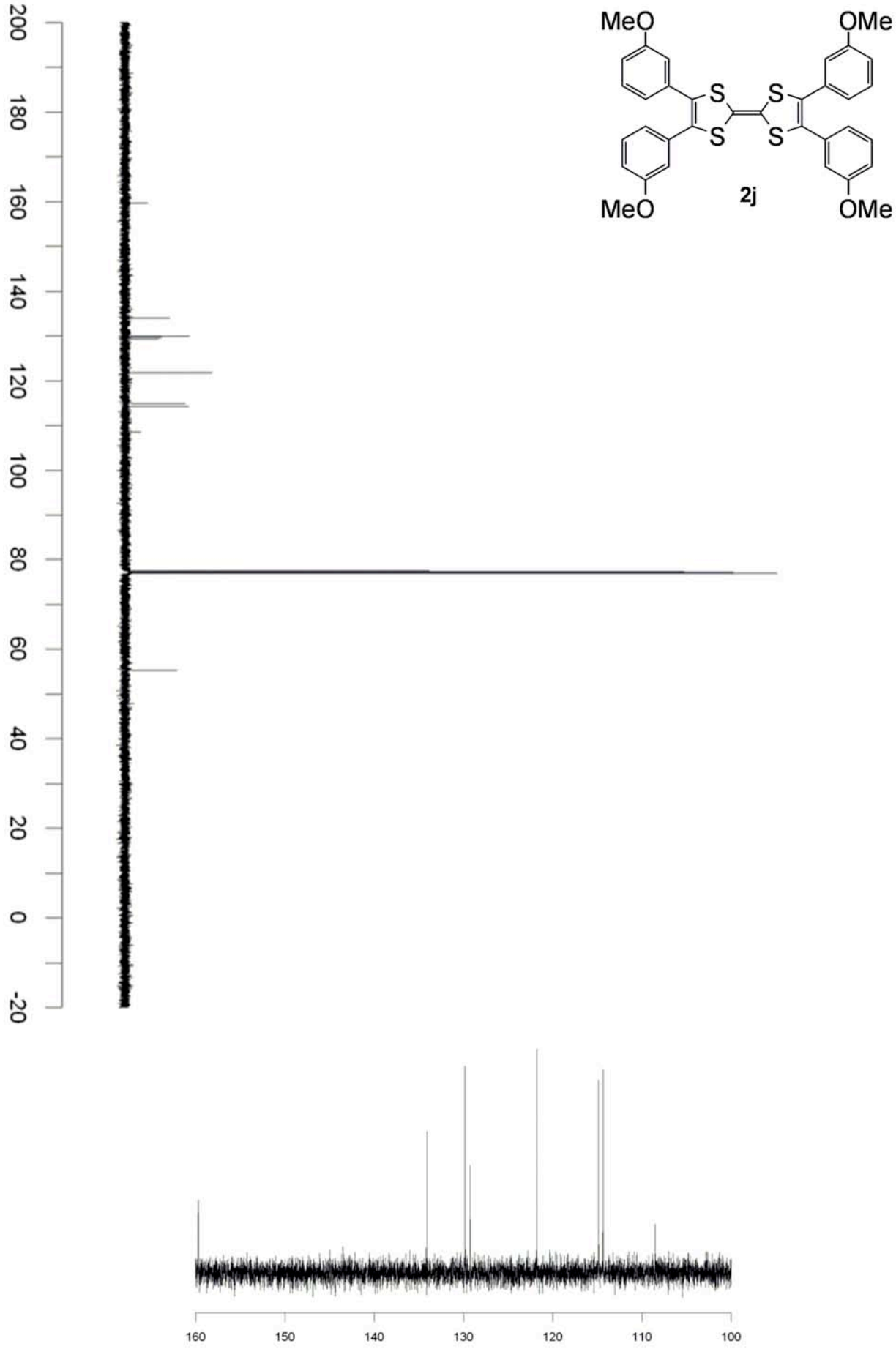


Figure S22-1. ^{1}H NMR Spectrum of **2k**

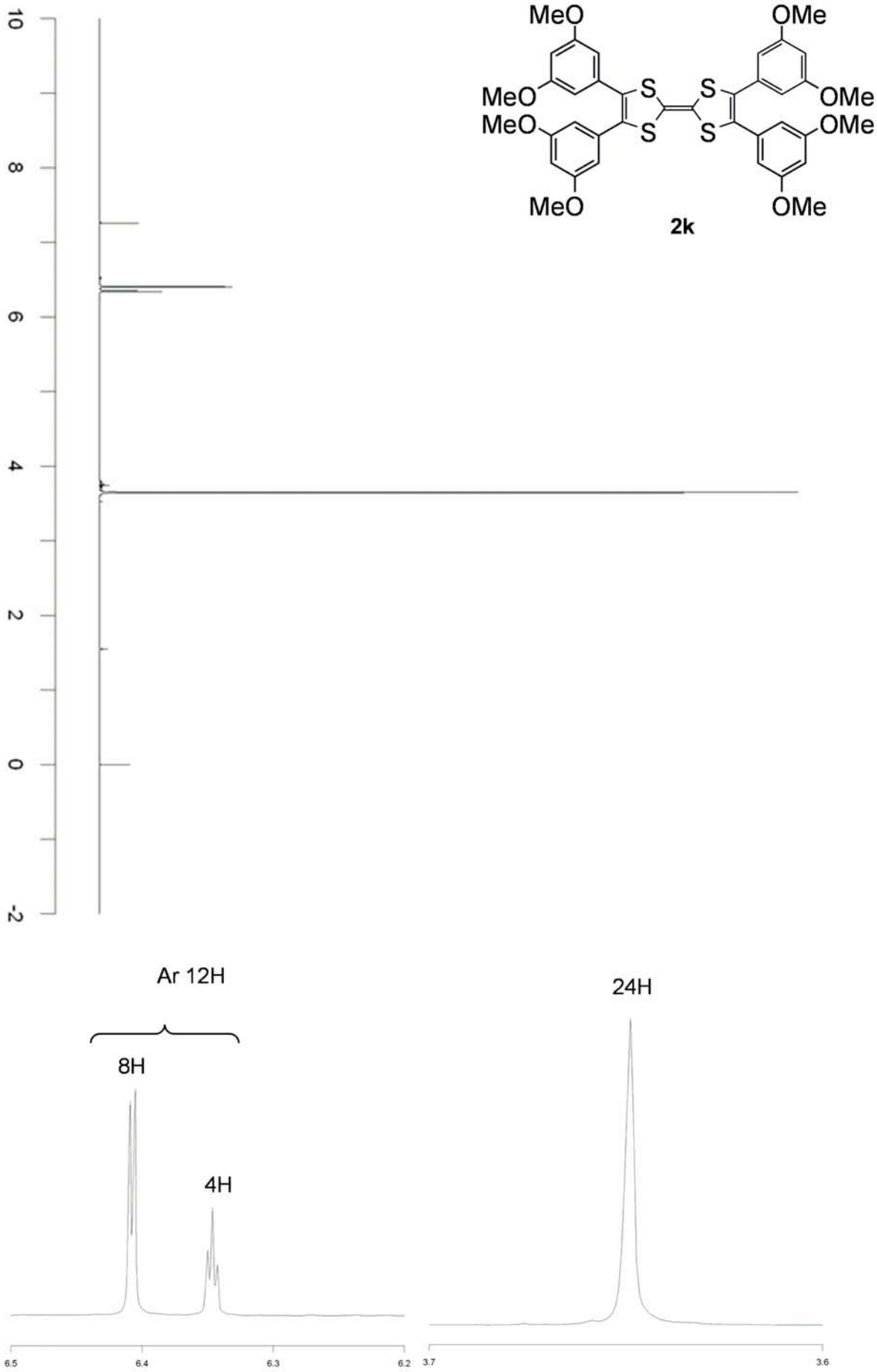


Figure S22-2. ^{13}C NMR Spectrum of **2k**

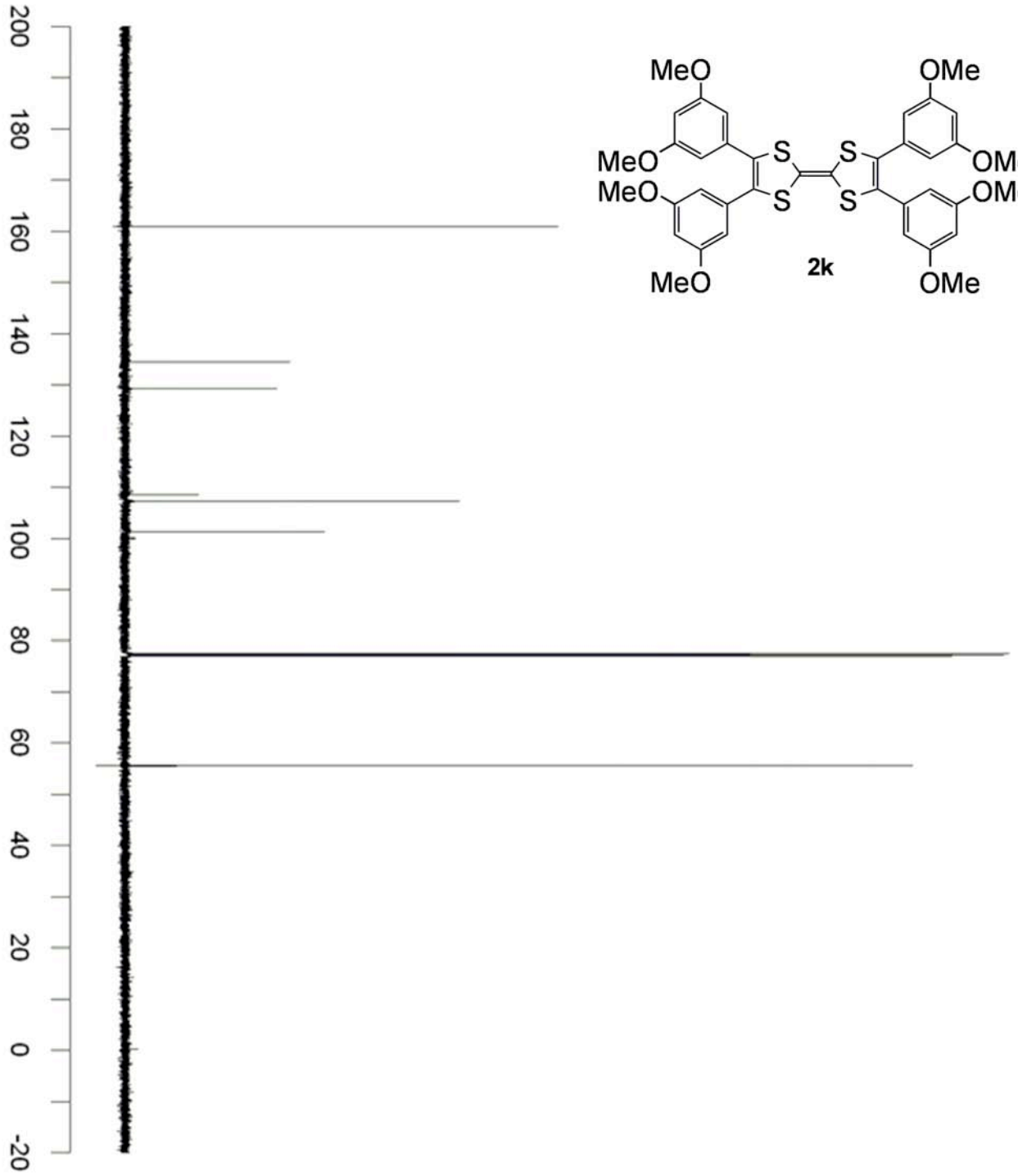


Figure S23-1. ^{1}H NMR Spectrum of **2l**

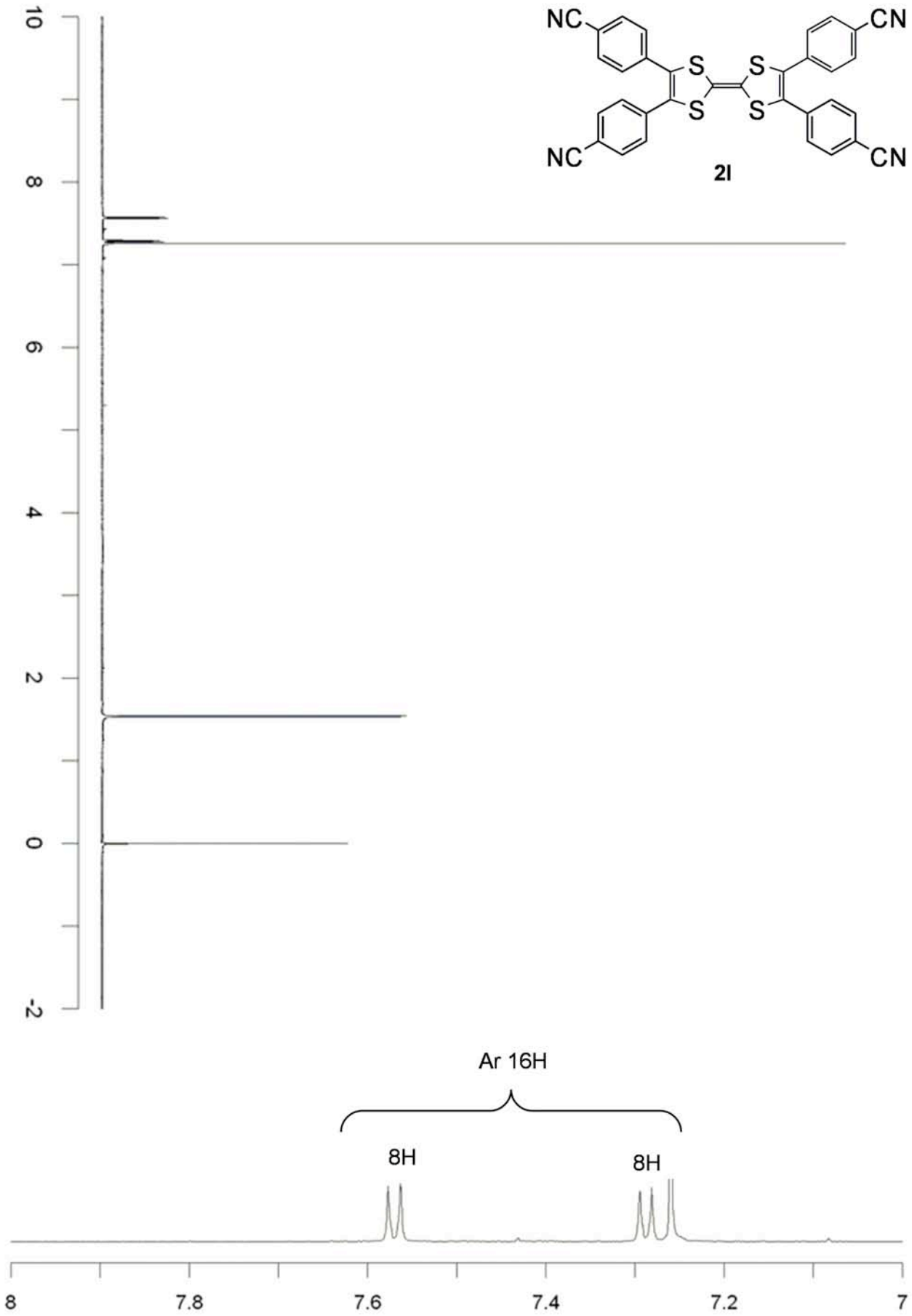


Figure S23-2. ^{13}C NMR Spectrum of **2l**

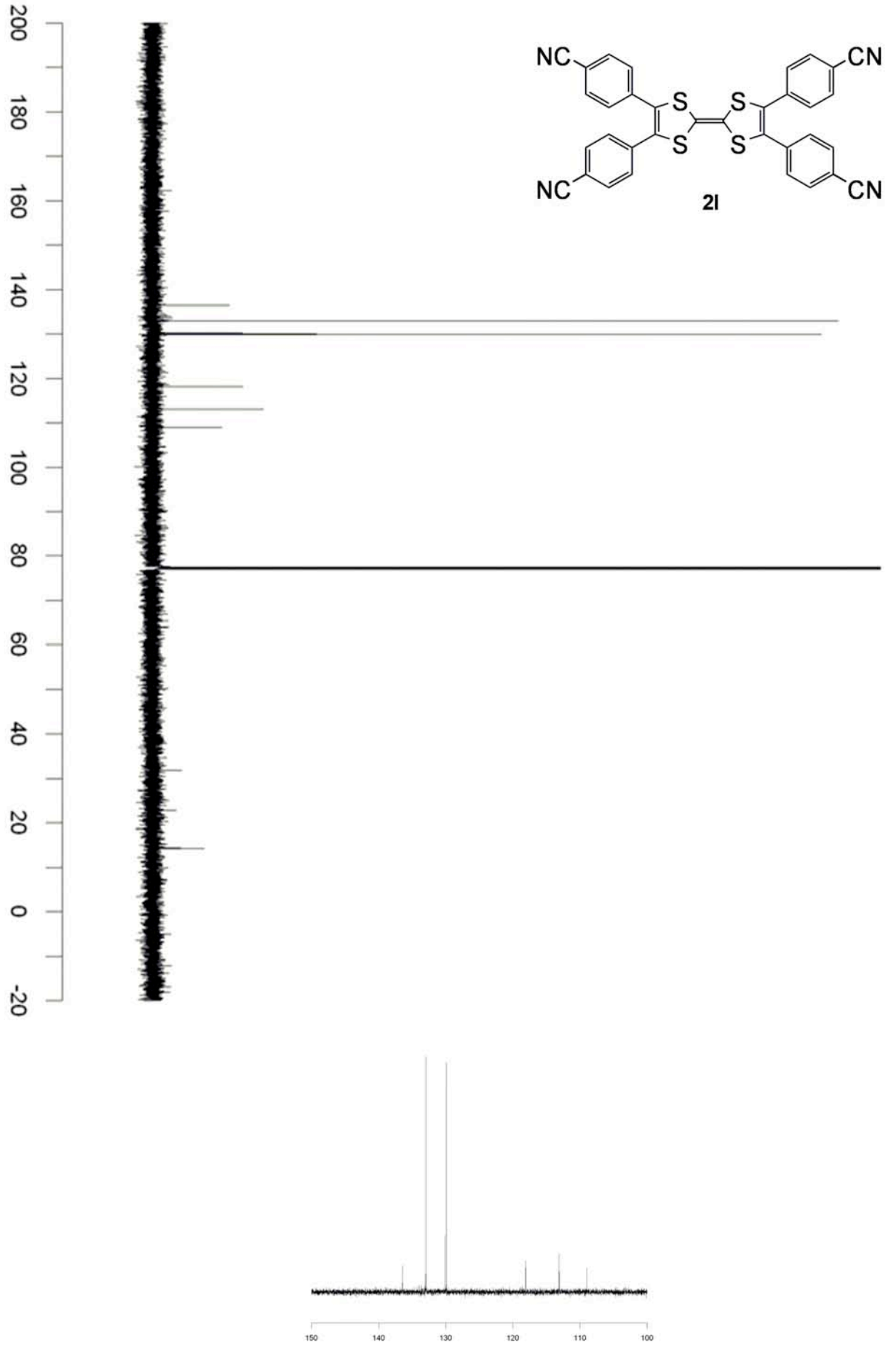


Figure S24-1. ^{1}H NMR Spectrum of **2m**

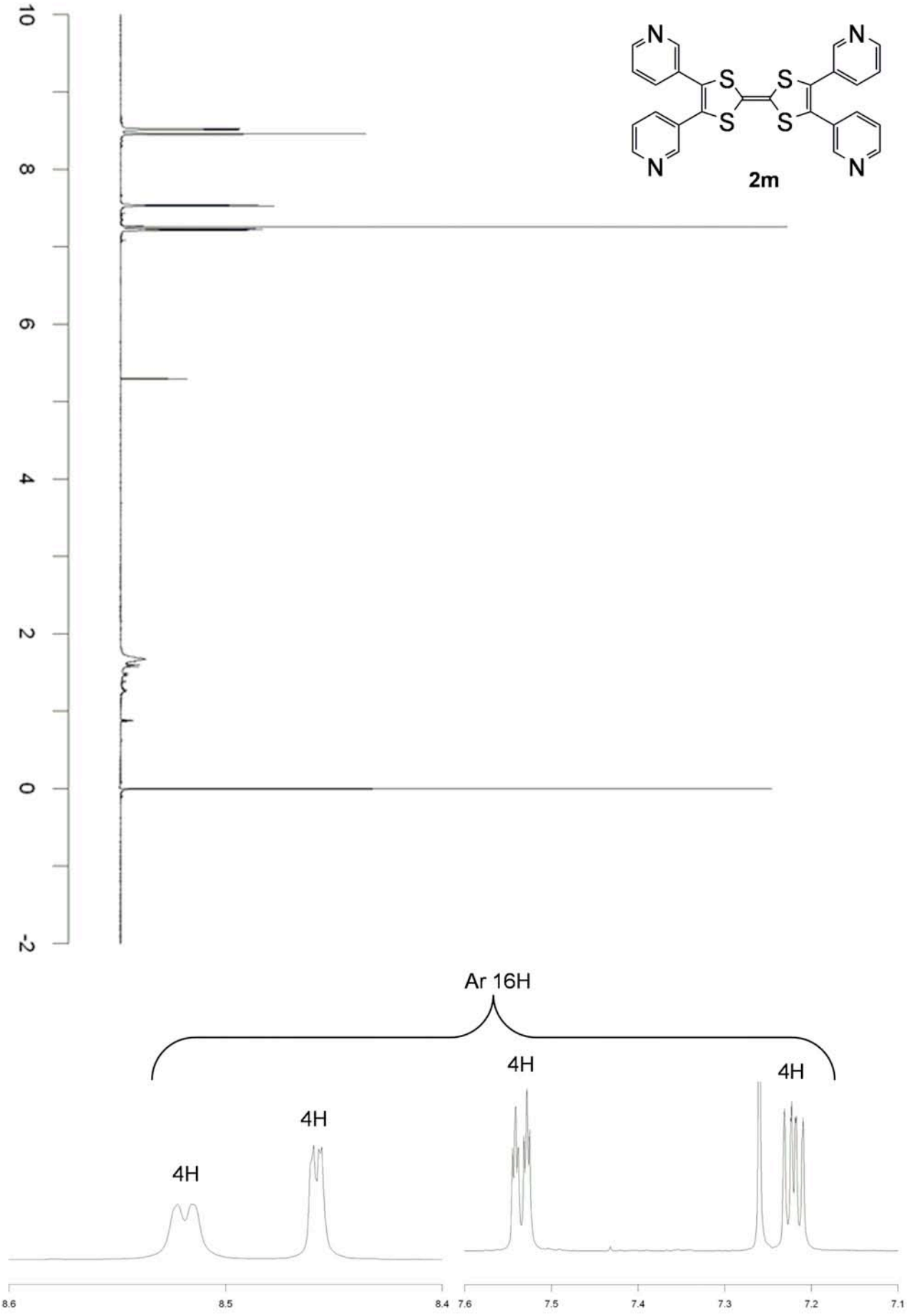


Figure S24-2. ^{13}C NMR Spectrum of **2m**

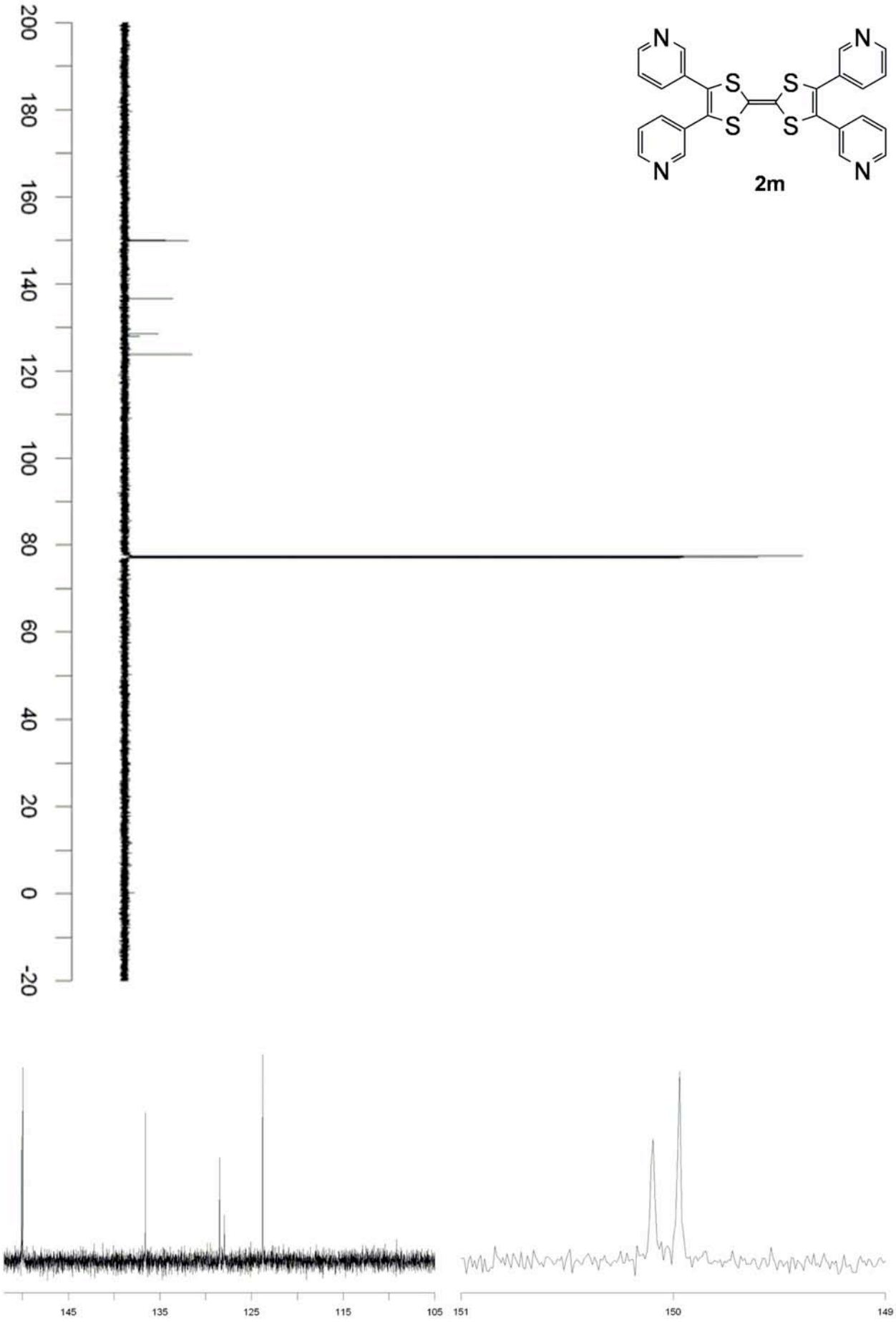


Figure S25-1. ^{1}H NMR Spectrum of **2n**

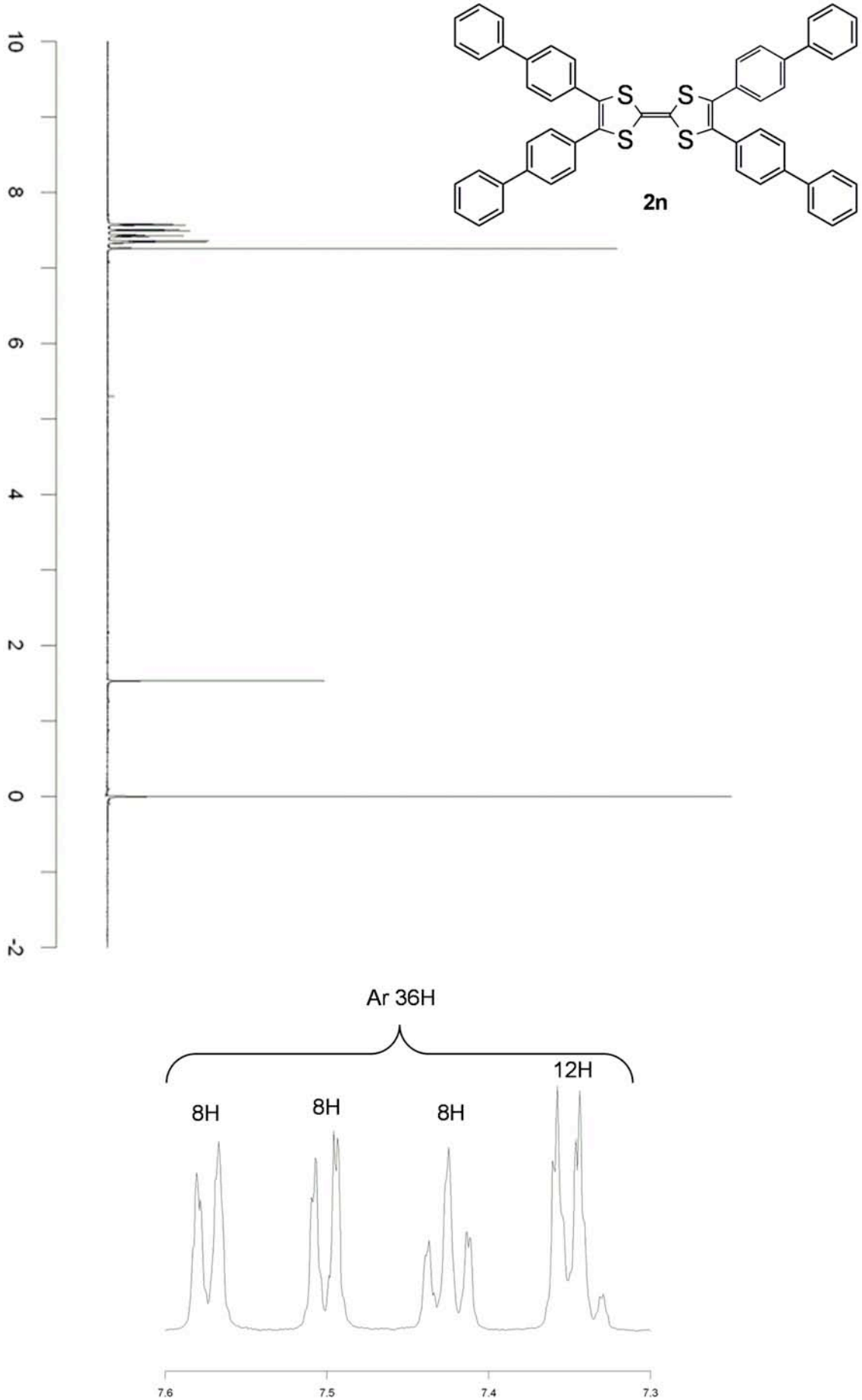
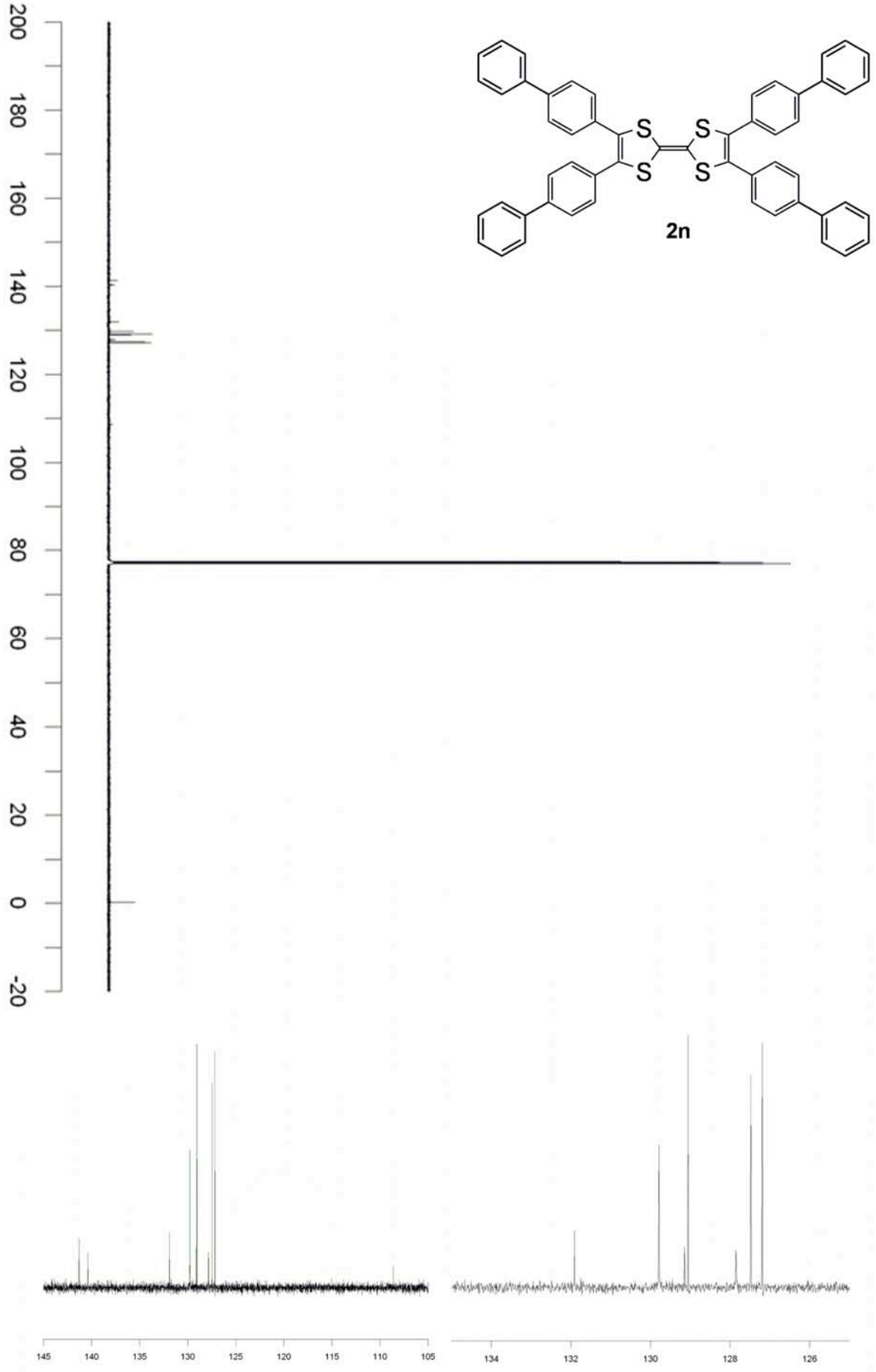


Figure S25-2. ^{13}C NMR Spectrum of **2n**



X-ray Diffraction Analysis

Crystallographic Data for 2a: $C_{34}H_{28}S_4$, Mw = 564.85, triclinic, P-1, a = 9.217(5) Å, b = 11.524(4) Å, c = 15.597(6) Å, α = 100.750(14)°, β = 105.128(17)°, γ = 110.659(17)°, V = 1423.6(10) Å^3, T = 123 K, Z = 2, R_1 = 0.0342, wR_2 = 0.0948, GOF = 1.007. CCDC No.: 818657.

Figure S26. Selected Bond Lengths of **2a**

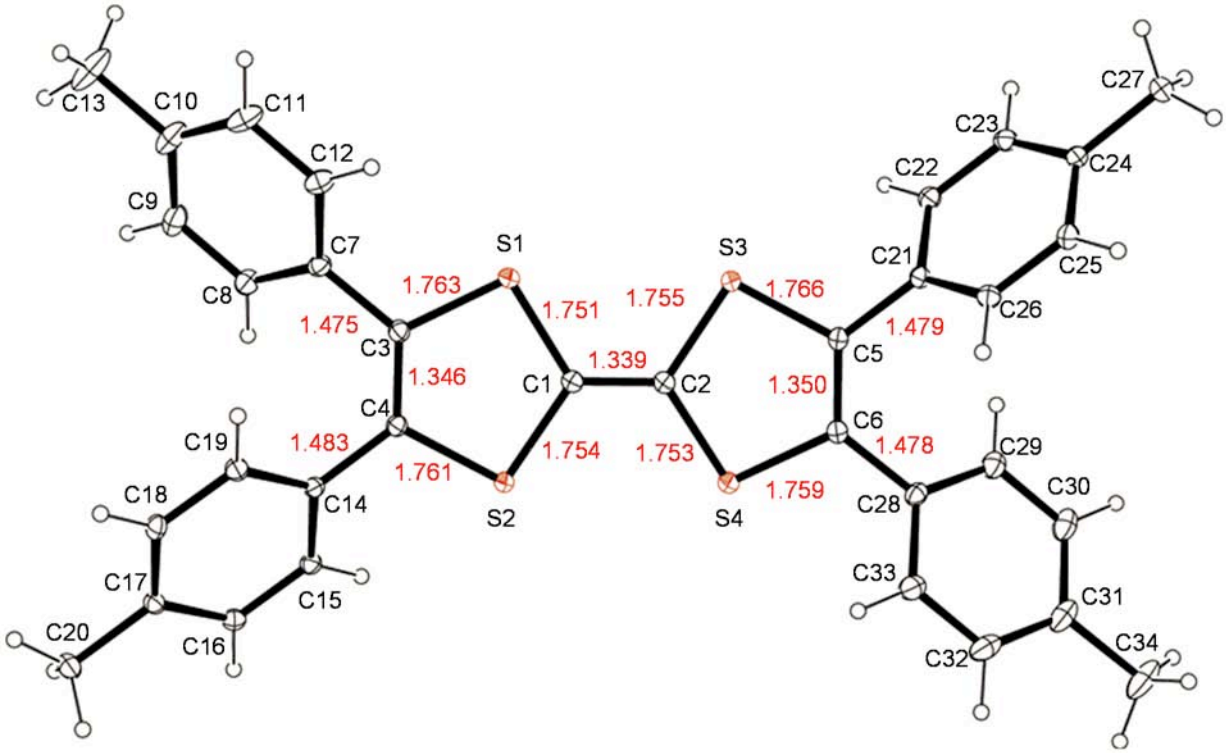


Figure S27. Selected Bond Angles of **2a**

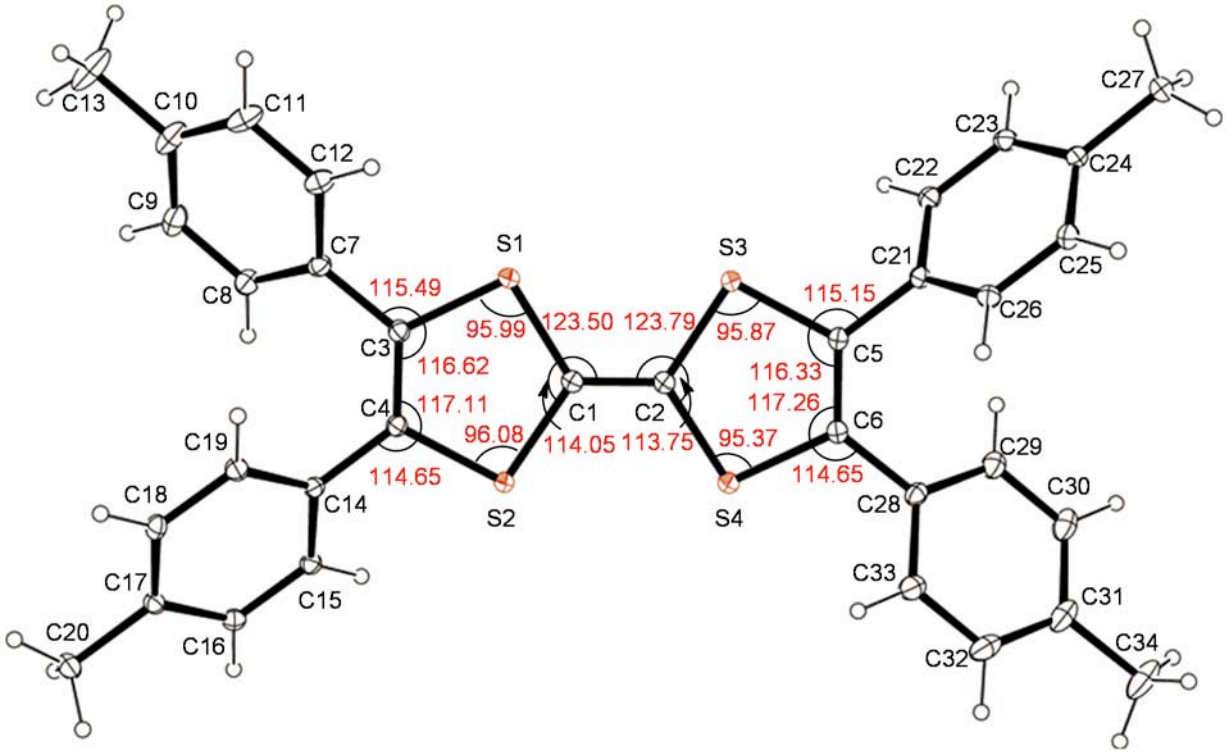
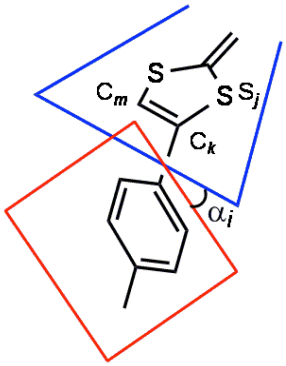


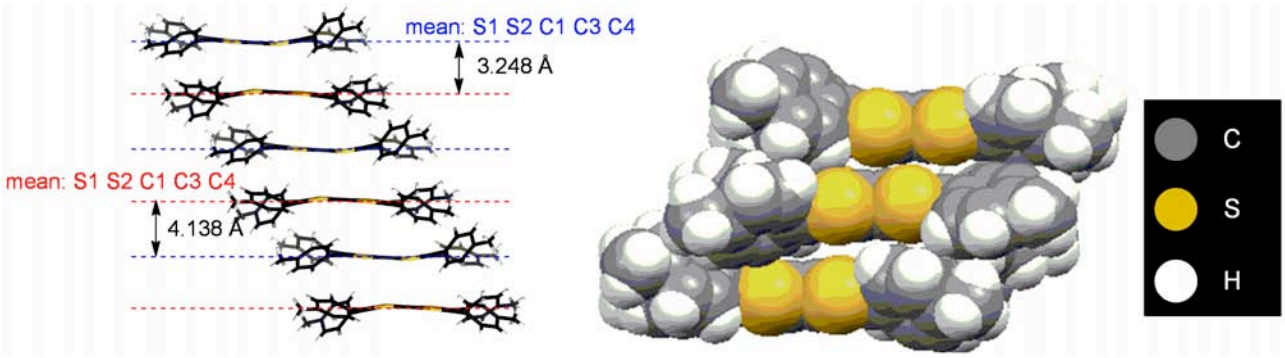
Figure S28. Dihedral Angles between TTF Moiety with Aryl Ring (Angles α_i (i = 1, 2, 3, 4) are defined by the dihedral angle between the plane of S_j-C_k-C_m and the mean plane of 4-methylphenyl ring)



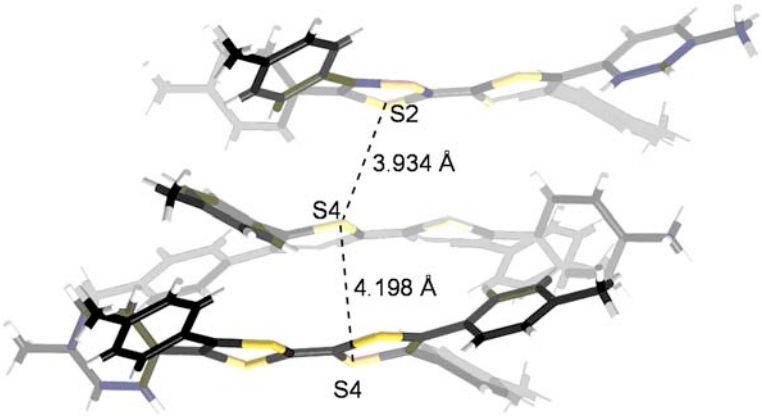
j	k	m	α_i
1	3	4	38.8
2	4	3	42.8
3	5	6	36.3
4	6	5	49.7

Figure S29. Packing Structure of **2a** (a) Distances between two planes and space filling model. (b) S-S distances. (c) Side view and top view.

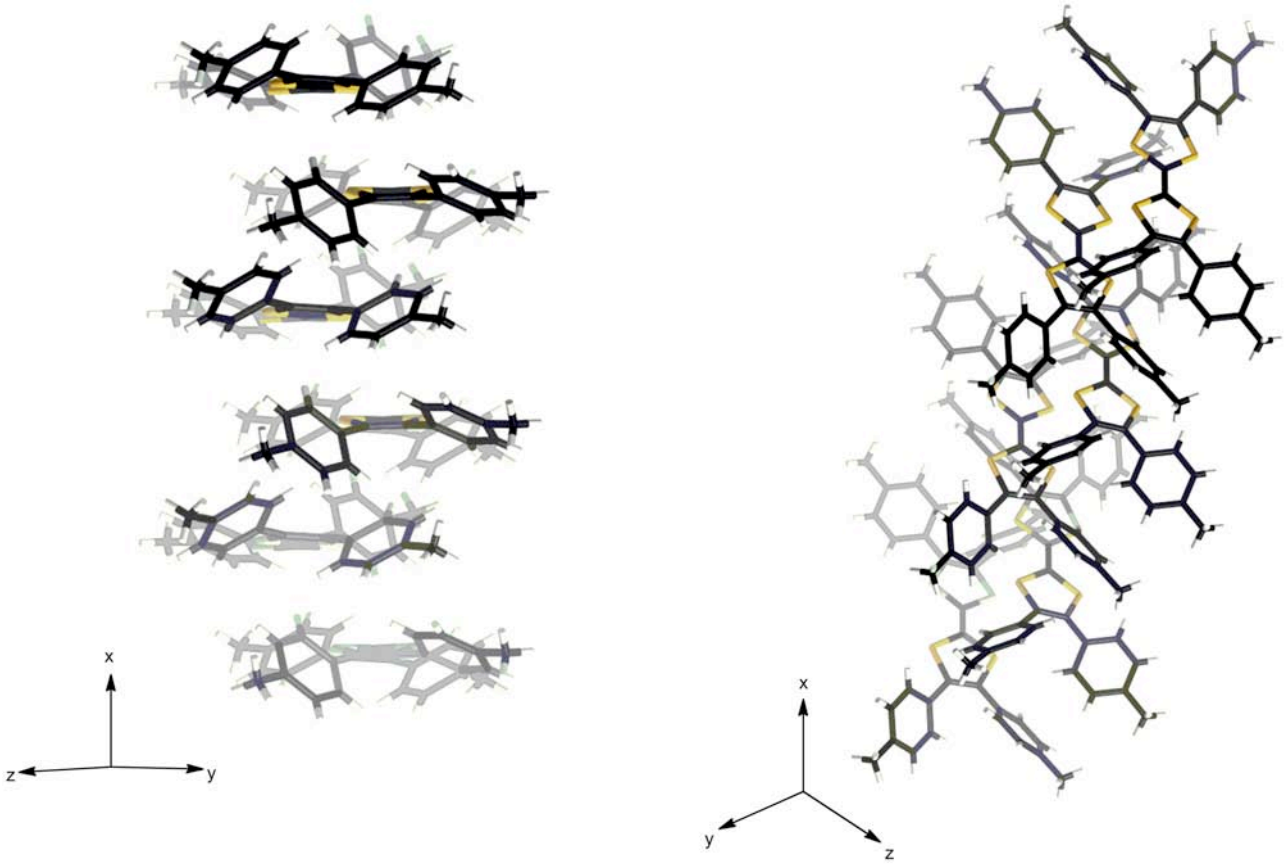
(a)



(b)



(c)



DFT Calculations

Figure S30. Energy Diagram of Kohn-Sham Orbitals of Monoaryl TTFs
(Gaussian 09, B3LYP/6-31G(d))

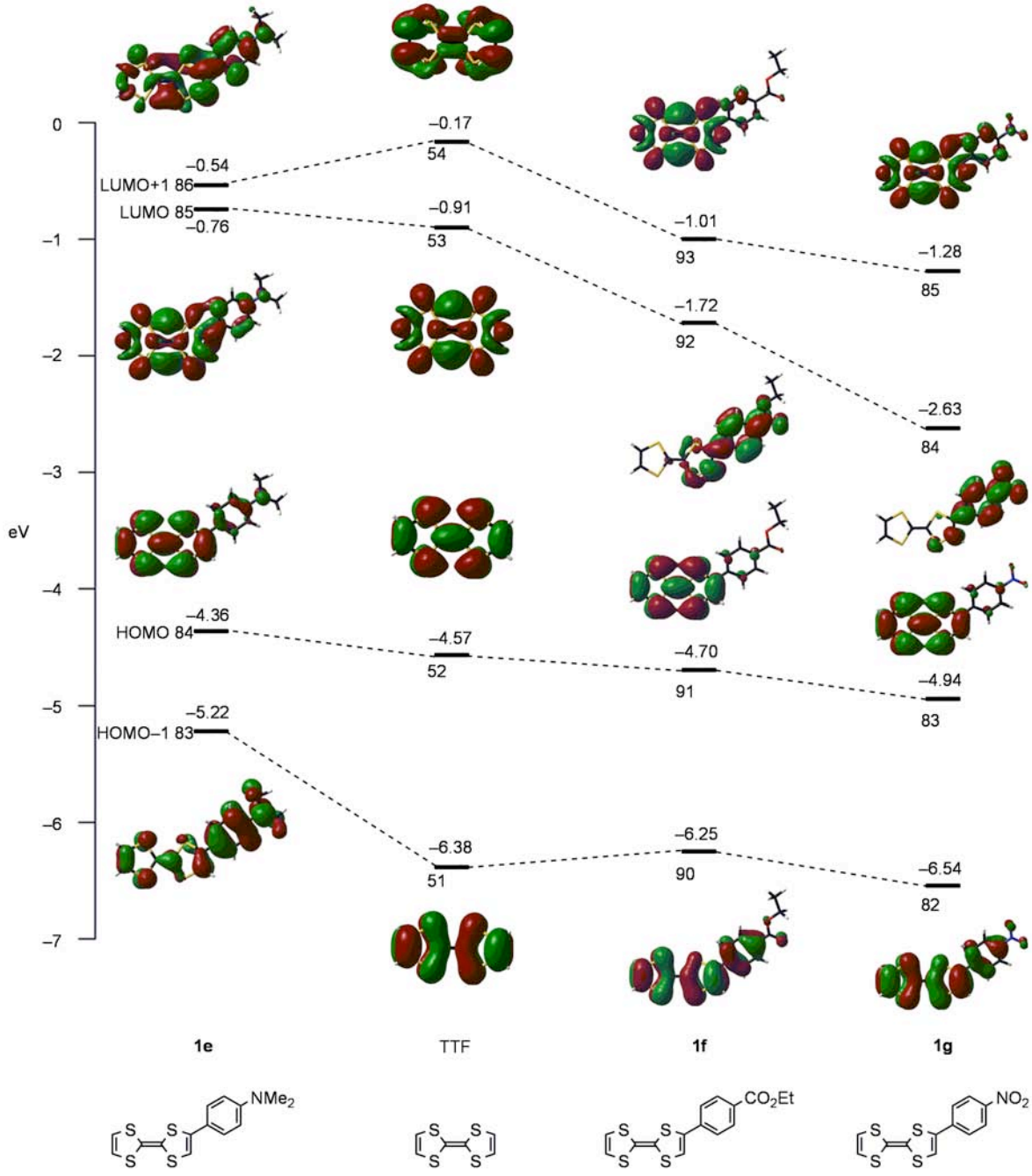


Figure S31. Energy Diagram of Kohn-Sham Orbitals of Radical Cations of Monoaryl TTFs (Gaussian 09, UB3LYP/6-31G(d))

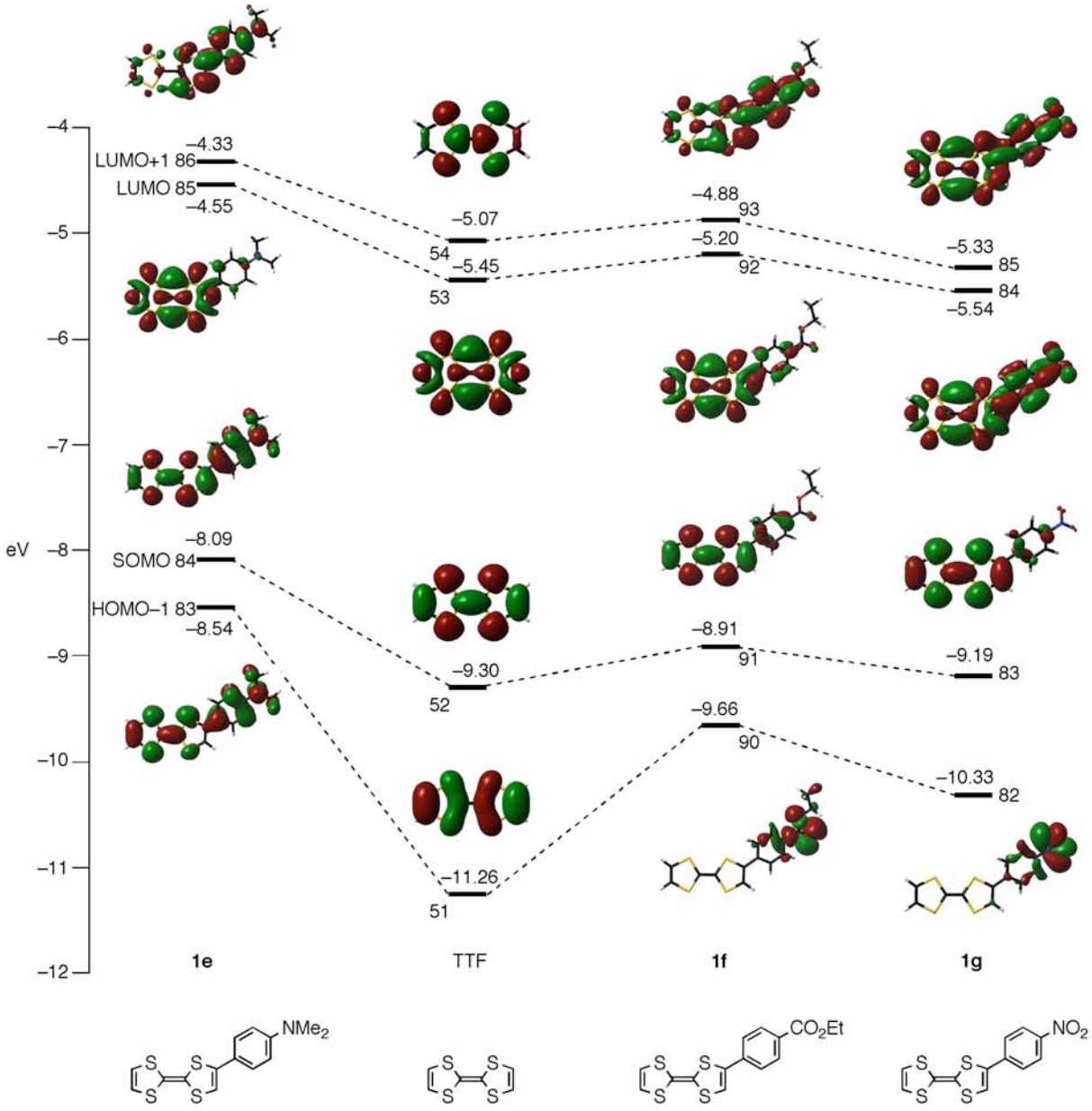


Figure S32. Energy Diagram of Kohn-Sham Orbitals of Tetraaryl TTF

(Gaussian 09, B3LYP/6-31G(d))

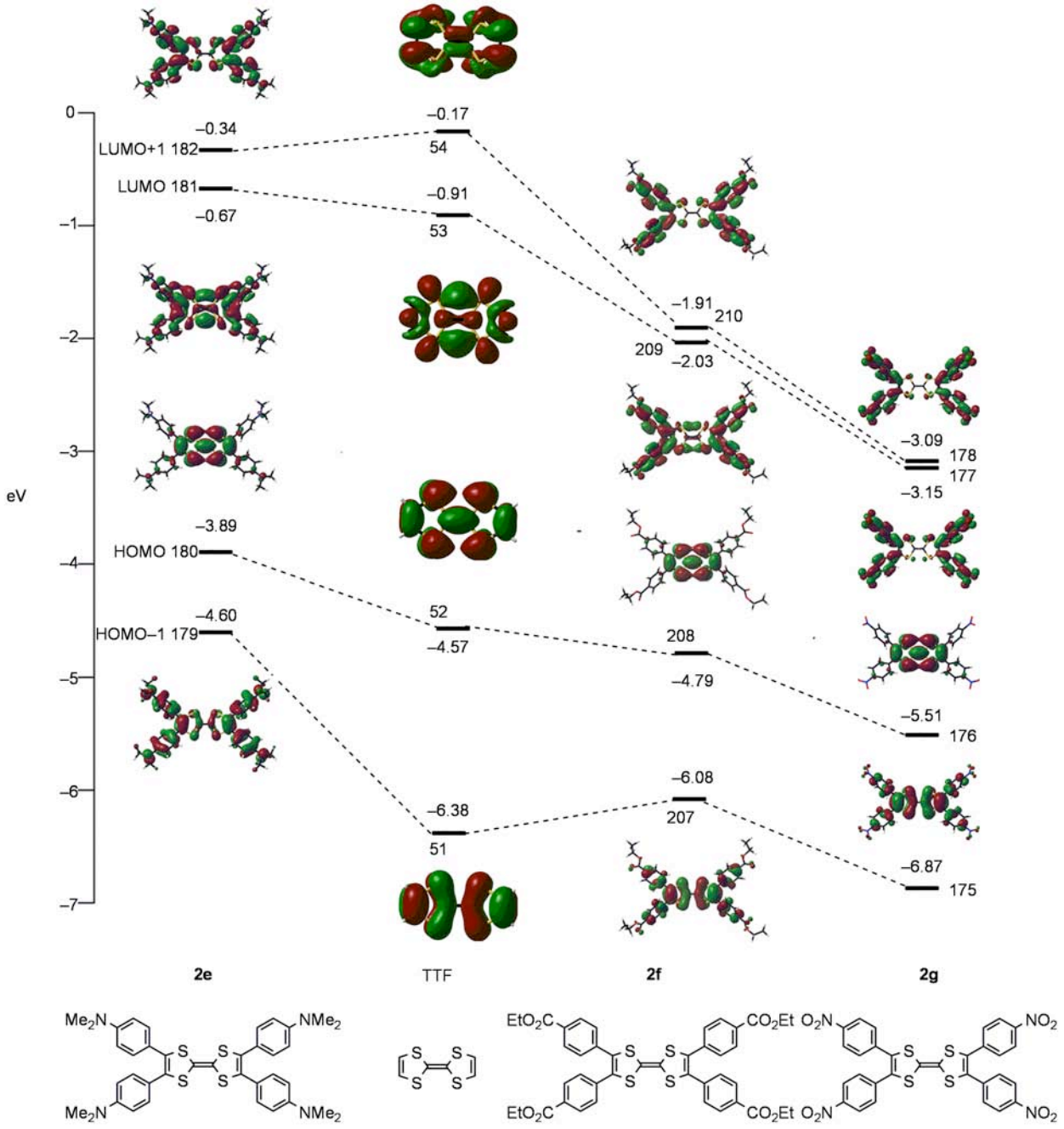


Figure S33. Energy Diagram of Kohn-Sham Orbitals of Radical Cations of Tetraaryl TTFs
(Gaussian 09, UB3LYP/6-31G(d))