Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 523–526

New thieno[3,2-*b*]indole conjugates with 5-(methylene)rhodanine-3-acetic acid in dye-sensitized solar cells

Alexander S. Steparuk, Roman A. Irgashev, Ekaterina F. Zhilina, Viktor V. Emets, Vitaly A. Grinberg, Ekaterina V. Tekshina, Ekaterina V. Belova, Petr I. Lazarenko, Nikita M. Tolkach, Gennady L. Rusinov and Sergey A. Kozyukhin

Table of contents

1. Experimental section

1.1. Materials

All chemicals were purchased from commercial sources and used without further purification. All solvents were dried and distilled according to standard procedures. 1-Methyl-3-propylimidazolium iodide was prepared as described.[S1] Compounds **1a,b** were synthesized by the reaction of [2,2'-bithiophen]-4(5*H*)-one with phenylhydrazine or naphthalen-1-ylhydrazine, respectively, according to our previously described procedure.[S2]

1.2. Characterizations

^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-400 (400 MHz) and Bruker AVANCE-500 (500 MHz), tetramethylsilane was an internal standard for ^{1}H NMR spectra and residual signals of deuterated solvent DMSO-d_6 (δ 39.5) or $CDCl_3$ (δ 77.2) were references for ^{13}C NMR spectra. Melting points were determined on a Boetius apparatus. Elemental analysis was carried out on a CHN PE 2400 Series II Perkin Elmer Instrument automated analyzer. High-resolution mass spectra were studied on a Bruker maXis Impact HD spectrometer. Electronic absorption spectra were obtained on a Shimadzu UV-2401PC dual-beam spectrophotometer and Cary 5000 UV-Vis-NIR spectrophotometer. Emission spectra were recorded on a Cary Eclipse spectrofluorometer. All measurements were performed at room temperature (20 ± 2 °C).

Thermogravimetric analysis was performed using a NETZSCH TG 209 F1 Iris in a temperature range 35-500°C. A sample in an Al_2O_3 crucible was heated with a constant heating rate, 10 K min^{-1}, in a dynamic atmosphere of air (gas flow 30 ml min^{-1}). The protective flow of argon was 20 ml min^{-1}. The evolved gas was analyzed by QMS 403C Aëolos mass-spectrometric unit coupled with the thermobalances. The ionization electron energy was 70 eV; the ion currents were registered for mass numbers (the mass-to-charge ratio) in the range from 1 to 299 a.m.u.

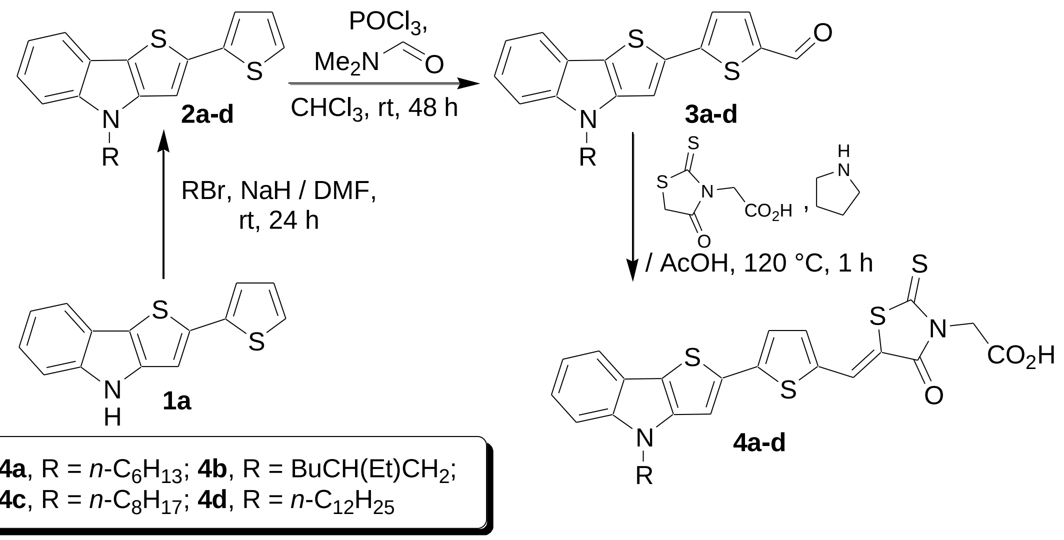
Electrochemical studies of synthesized dyes were carried out using the PAR (Princeton Applied Research) 273 potentiostat/galvanostat. The standard three-electrode cell equipped with a SU-2000 glassy carbon disc (0.0078 cm^2) pressed into Teflon as a working electrode, Ag quasi-reference electrode, and a platinum grid (1 cm^2) as a counter electrode was employed. The cyclic voltammograms (CVs) were registered in anhydrous CH_2Cl_2 with $(0.3\div0.8)\cdot10^{-3}$ M of analyzed compound and 0.1M Bu_4NPF_6as supporting electrolyte under high purity argon atmosphere at a scan rate in the range from 0.05 to 1.0 V s^{-1}. The HOMO energy values were estimated from the onset potentials of the first independent oxidation and reduction process, respectively, according to the following equations: E_{HOMO} (eV) = – [$E_{ox}^{onset} – E_{1/2}(Fc/Fc^+) + 4.8$],

where $E_{1/2}(Fc/Fc^+)$ is the half-wave potential of the Fc/Fc+ couple (in this work experimentally estimated as 0.14 V) against the Ag electrode.

The current-voltage characteristics of solar cells were determined under irradiation (100 mW cm^{-2}) using a Newport 67005 Arc lamp light source with a Xe lamp. The current density - voltage (*J/V*) characteristics were measured using a Keithley 2450 source meter by applying voltage and measuring current. The action spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for solar cell were performed by using a SCS10-PEC Photoelectrochemistry Measurement System. All measurements were performed at room temperature (20 ± 2 °C).

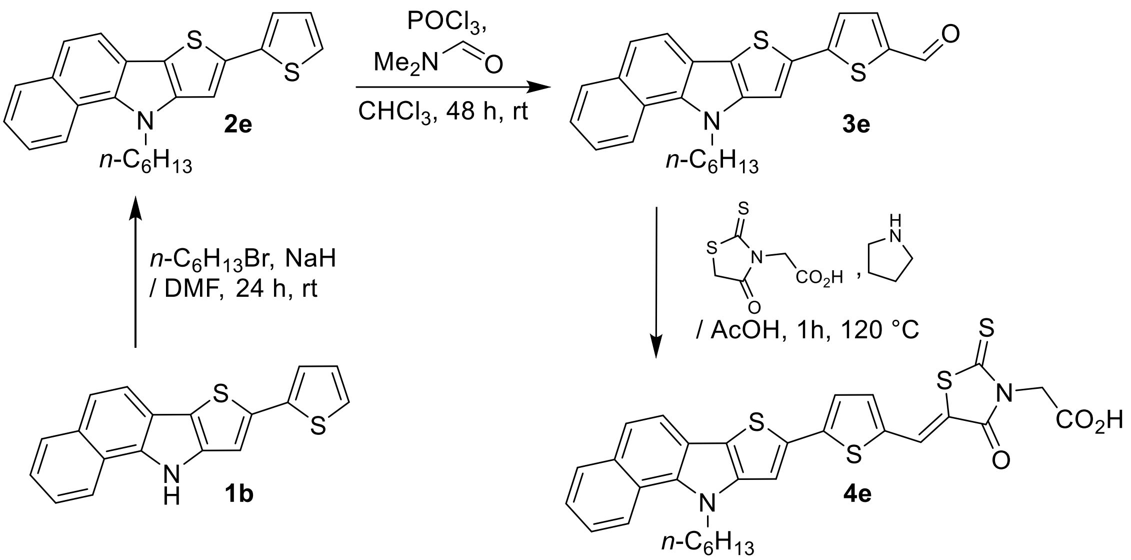
*1.3. Synthesis of dyes **4a-e***

The construction of new D-π-A dyes **4a-d** bearing thieno[3,2-*b*]indole ring-system as an electron-donating part, thiophene unit as π-linker and5-(methylene)rhodanine-3-acetic acid (MRAA) as an electron-accepting part was performed in three steps staring from compound**1a**, similar to dyes IS series, described in our recent work.[3] To this end, substrate **1a** was treated with alkyl (*n*-hexyl, 2-ethylhexyl, *n*-octyl, *n*-dodecyl) bromides in the presence of NaH in dry DMF to form *N*-substituted thieno[3,2-*b*]indoles **2a-d**. Then, their Vilsmeier-Haack-Arnold formylation was carried out by treatment them with $POCl_3$-DMF complex to afford thiophene-2-carbaldehydes **3a-d**. Finally, dyes **4a-d**were obtained by the Knoevenagel condensation of carbaldehydes **3a-d** with rhodanine-3-acetic acid (Scheme S1).



Scheme S1 Synthesis of thieno[3,2-*b*]indole / MRAA based dyes **4a-d**

We have also able to perform the construction of dye **4e**, having benzo[*g*]thieno[3,2-*b*]indole ring-system as an electron donating part of its D-π-A structure. To this end, the formylation of *N*-hexyl derivative **2e**, obtained by alkylation of compound **1b**, was performed using the Vilsmeier-Haack-Arnold reaction in the same manner as for derivatives **2a-d**, and the desired dye was readily formed by the condensation of carbaldehyde **3e** with rhodanine-3-acetic acid (Scheme S2).



Scheme S2 Synthesis of benzo[*g*]thieno[3,2-*b*]indole / MRAA based dye **4e**.

1.4. General procedure for synthesis of compounds ***2a-e***

Sodium hydride (0.100 g, 4.2 mmol) was added to a solution of thieno[3,2-*b*]indole **1a** or benzo[*g*]thieno[3,2-*b*]indole **1b** (2 mmol) in dry DMF (7 ml). The system was purged with argon, and the corresponding alkyl bromide (2.15 mmol) was added after 30 min. The reaction mixture was kept at ~20 °C for 24 h, diluted with water (5 ml) and extracted with $CHCl_3$ (10 ml), the extract was washed with water (2×10 ml). The organic layer was dried with $CaCl_2$ and concentrated under reduced pressure to afford crude compounds **2a-e**, which were further used for the next step without additional purification.

4-Hexyl-2-(thiophen-2-yl)-4*H*-thieno[3,2-*b*]indole (2a). Dark yellow oil, yield 0.582 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.23 (dd, J = 5.1, 1.0 Hz, 1H), 7.19 – 7.12 (m, 1H), 7.05 (dd, J = 5.1, 3.6 Hz, 1H), 4.24 (t, J = 7.2 Hz, 2H), 1.97 – 1.75 (m, 2H), 1.54 – 1.09 (m, 6H), 0.87 (t, J = 7.0 Hz, 3H).

4-(2-Ethylhexyl)-2-(thiophen-2-yl)-4*H*-thieno[3,2-*b*]indole (2b). Yellow oil, yield 0.693 g (94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.56 (s, 1H), 7.54 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.39 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.12 (dt, *J* = 11.5, 4.6 Hz, 2H), 4.23 (d, *J* = 7.5 Hz, 2H), 2.03 – 1.89 (m, 1H), 1.40 – 1.09 (m, 8H), 0.85 (t, *J* = 7.4 Hz, 3H), 0.79 (t, *J* = 7.1 Hz, 3H).

4-Octyl-2-(thiophen-2-yl)-4*H*-thieno[3,2-*b*]indole (2c). Yellow oil, yield 0.680 g (93%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.28 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.25 (d, *J* = 1.1 Hz, 1H), 7.23 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.19 – 7.12 (m, 2H), 7.04 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.24 (t, *J* = 7.2 Hz, 2H), 1.93 – 1.81 (m, 2H), 1.34 – 1.24 (m, 10H), 0.86 (t, *J* = 7.5 Hz, 3H).

4-Dodecyl-2-(thiophen-2-yl)-4*H*-thieno[3,2-*b*]indole (2d). Beige powder, yield 0.718 g (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.26 – 7.24 (m, 1H), 7.23 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.19 – 7.11 (m, 2H), 7.04 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.23 (t, *J* = 7.1 Hz, 2H), 1.92 – 1.81 (m, 2H), 1.33 – 1.23 (m, 18H), 0.87 (t, *J* = 6.9 Hz, 3H).

10-Hexyl-8-(thiophen-2-yl)-10*H*-benzo[*g*]thieno[3,2-*b*]indole (2e). Dark yellow oil, yield 0.700 g (90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.49 – 7.43 (m, 1H), 7.27 (dd, *J* = 3.6, 0.9 Hz, 1H), 7.24 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.22 (s, 1H), 7.05 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.72 – 4.66 (m, 2H), 2.09 – 2.00 (m, 2H), 1.54 – 1.45 (m, 2H), 1.37 (t, *J* = 7.5 Hz, 2H), 0.88 (t, *J* = 7.1 Hz, 3H).

*1.5. General procedure for synthesis of aldehydes **3a-e***

The agent $POCl_3$ (0.42 ml, 4.5 mmol) was added dropwise to dry DMF (0.35 ml, 4.5 mmol) with cooling, followed by the addition of a solution of compounds **2a-e** (1.5 mmol) in dry $CHCl_3$ (5 ml). The reaction mixture was allowed to stand at ~20 °C for 48 h, poured into saturated aqueous sodium hydrogen carbonate, extracted with $CHCl_3$, and washed with dilute sulfuric acid (20 ml) and water (3×10 ml). The organic layer was separated and dried with $CaCl_2$. Before evaporation of the solvent in a vacuum, the extract was passed through a short layer of silica gel (2×2 cm), eluting with $CHCl_3$ (2×5 ml), thus obtaining a pure product.

5-(4-Hexyl-4*H*-thieno[3,2-*b*]indol-2-yl)thiophene-2-carbaldehyde (3a). Yellow powder, m.p. 130-131 °C, yield 0.412 g (75%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.66 (s, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.20 – 7.15 (m, 1H), 4.23 (t, *J* = 7.2 Hz, 2H), 1.91 – 1.81 (m, 2H), 1.39 – 1.27 (m, 6H), 0.86 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.5, 148.8, 145.1, 141.7, 141.4, 137.6, 136.6, 123.8, 123.7, 121.5, 119.7, 119.5, 117.5, 110.2, 109.2, 45.4, 31.6, 29.8, 26.9, 22.7, 14.1. HRMS (ESI) m/z calcd for $C_{21}H_{22}NOS_2$ $[M+H]^+$: 368.1137, found: 368.1143.

5-[4-(2-Ethylhexyl)-4*H*-thieno[3,2-b]indol-2-yl]thiophene-2-carbaldehyde (3b). Dark yellow powder, m.p. 132-133 °C, yield 0.525 g (88%).^1H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 4.0 Hz, 1H), 7.39 – 7.28 (m, 4H), 7.21 – 7.15 (m, 1H), 4.19 – 4.04 (m, 2H), 2.10 – 1.94 (m, 1H), 1.42 – 1.24 (m, 8H), 0.95 – 0.84 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.4, 148.7, 145.5, 142.0, 141.3, 137.6, 136.5, 123.8, 123.6, 121.4, 119.6, 119.4, 117.4, 110.4, 109.2, 49.5, 40.0, 30.9, 28.8, 24.3, 23.1, 14.1, 10.9. HRMS (ESI) m/z calcd for $C_{23}H_{26}NOS_2$ $[M+H]^+$: 396.1450, found: 396.1450.

5-(4-Octyl-4*H*-thieno[3,2-*b*]indol-2-yl)thiophene-2-carbaldehyde (3c). Dark yellow powder, m.p. 122-123 °C, yield 0.482 g (82%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 4.0 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.22 – 7.15 (m, 1H), 4.24 (t, *J* = 7.1 Hz, 2H), 1.93 – 1.81 (m, 2H), 1.32 – 1.17 (m, 10H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.5, 148.8, 145.1, 141.7, 141.4, 137.6, 136.6, 123.8, 123.7, 121.5, 119.7, 119.5, 117.5, 110.2, 109.1, 45.4, 31.9, 29.9, 29.4, 29.3, 27.3, 22.7, 14.2. HRMS (ESI) m/z calcd for $C_{23}H_{26}NOS_2$ $[M+H]^+$: 396.1450, found: 396.1455.

5-(4-Dodecyl-4*H*-thieno[3,2-*b*]indol-2-yl)thiophene-2-carbaldehyde (3d). Yellow powder, m.p. 110-111 °C, yield 0.392 g (66%).^1H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 4.0 Hz, 1H), 7.40 – 7.29 (m, 4H), 7.21 – 7.14 (m, 1H), 4.24 (t, *J* = 7.1 Hz, 2H), 1.91 – 1.82 (m, 2H), 1.29 – 1.19 (m, 18H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.5, 148.8, 145.1, 141.7, 141.4, 137.6, 136.5, 123.8, 123.7, 121.5, 119.7, 119.5, 117.5, 110.2, 109.1, 45.4, 32.0, 29.9, 29.7, 29.7, 29.6, 29.4, 27.3, 22.8, 14.3 (2C was not observed).HRMS (ESI) m/z calcd for $C_{27}H_{34}NOS_2$ $[M+H]^+$: 452.2076, found: 452.2073.

5-(10-Hexyl-10*H*-benzo[*g*]thieno[3,2-*b*]indol-8-yl)thiophene-2-carbaldehyde (3e). Brown powder, m.p. 162-163 °C, yield 0.419 g (67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 4.0 Hz, 1H), 7.56 (dd, *J* = 11.7, 4.7 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.34 (s, 1H), 7.28 (d, *J* = 3.9 Hz, 1H), 4.63 (t, *J* = 7.5 Hz, 2H), 2.07 – 1.94 (m, 2H), 1.51 – 1.41 (m, 2H), 1.39 – 1.22 (m, 5H), 0.88 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 182.4, 148.8, 145.1, 141.2, 137.6, 135.4, 135.0, 132.2, 129.8, 125.9, 124.3, 123.6, 123.2, 121.7, 121.1, 118.9, 118.5, 118.5, 109.3, 48.9, 31.6, 30.4, 26.7, 22.6, 14.1. HRMS (ESI) m/z calcd for $C_{25}H_{24}NOS_2$ $[M+H]^+$: 418.1294, found: 418.1293.

*1.6. General procedure for synthesis of dyes **4a-e***

Rhodanine-3-acetic acid (0.287 g, 1.5 mmol) and pyrrolidine (0.1 ml) were added to a solution of an appropriate compound **3a-e** (1 mmol) in glacial acetic acid (7 ml) at continuous stirring at ambient temperature. Then, the reaction mixture was stirred and heated at 120 °C for 1 h. The formed precipitate was collected by filtration, washed with aqueous methanol, and dried to constant mass in air.

2-(5-{[5-(4-Hexyl-4*H*-thieno[3,2-*b*]indol-2-yl)thiophen-2-yl]methylene}-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (4a). Dark burgundy powder, m.p. 261-262 °C, yield 0.356 g (66%).^{1}H NMR (400 MHz, DMSO-d_6)δ 13.49 (s, 1H), 8.12 (s, 1H), 7.92 (s, 1H), 7.80 – 7.72 (m, 2H), 7.62 – 7.52 (m, 2H), 7.34 – 7.26 (m, 1H), 7.18 – 7.10 (m, 1H), 4.68 (s, 2H), 4.37 (t, *J* = 6.9 Hz, 2H), 1.87 – 1.69 (m, 2H), 1.33 – 1.20 (m, 6H), 0.82 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 191.5, 167.3, 165.8, 146.8, 145.2, 141.2, 138.1, 135.7, 135.5, 126.6, 125.2, 123.5, 120.6, 119.4, 119.1, 118.0, 115.6, 110.7, 110.2, 45.1, 44.4, 30.9, 29.2, 26.0, 22.1, 13.9.HRMS (ESI) m/z calcd for $C_{26}H_{23}N_2O_3S_4$ $[M-H]^+$: 539.0597, found: 539.0594. Anal. calcd for$C_{26}H_{24}N_2O_3S_4$: C, 57.75; H, 4.47, N, 5.18. Found: C, 57.87; H, 4.44, N, 5.25.

2-[5-({5-[4-(2-Ethylhexyl)-4*H*-thieno[3,2-*b*]indol-2-yl]thiophen-2-yl}methylene)-4-oxo-2-thioxothiazolidin-3-yl]acetic acid (4b). Dark burgundy crystals, m.p. 235-236 °C, yield 0.435 g (77%).^{1}H NMR (500 MHz, DMSO-d_6)δ 13.47 (s, 1H), 8.14 (s, 1H), 7.88 (s, 1H), 7.81 – 7.75 (m, 2H), 7.58 (d, *J* = 4.0 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.16 – 7.11 (m, 1H), 4.70 (s, 2H), 4.26 (d, *J* = 7.6 Hz, 2H), 1.33 – 1.18 (m, 7H), 0.86 (t, *J* = 7.4 Hz, 3H), 0.81 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (126 MHz, DMSO-d_6) δ 191.5, 167.3, 165.8, 146.7, 145.6, 141.4, 138.1, 135.7, 135.5, 126.6, 125.3, 123.5, 120.6, 119.4, 119.1, 118.0, 115.6, 110.8, 110.2, 48.5, 45.1, 29.9, 27.8, 23.5, 22.6, 13.9, 10.6 (1C was not observed). HRMS (ESI) m/z calcd for

$C_{28}H_{27}N_2O_3S_4$ $[M-H]^+$: 567.0910, found: 567.0910. Anal. calcd for $C_{28}H_{28}N_2O_3S_4$: C, 59.13; H, 4.96, N, 4.93. Found: C, 58.86; H, 4.83, N, 5.21.

2-(5-{[5-(4-Octyl-4*H*-thieno[3,2-*b*]indol-2-yl)thiophen-2-yl]methylene}-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (4c). Burgundy powder, m.p. 234-235 °C, yield 0.444 g (78%).^{1}H NMR (500 MHz, DMSO-*d*$_6$)δ 13.43 (s, 1H), 8.14 (s, 1H), 7.92 (s, 1H), 7.83 – 7.73 (m, 2H), 7.62 – 7.54 (m, 2H), 7.34 – 7.26 (m, 1H), 7.18 – 7.10 (m, 1H), 4.69 (s, 2H), 4.37 (t, *J* = 6.9 Hz, 2H), 1.85 – 1.73 (m, 2H), 1.30 – 1.16 (m, 10H), 0.81 (t, *J* = 6.9 Hz, 3H).^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 191.5, 167.3, 165.8, 146.8, 145.2, 141.2, 138.1, 135.7, 135.5, 126.6, 125.2, 123.4, 120.6, 119.4, 119.1, 118.0, 115.6, 110.7, 110.2, 45.1, 44.3, 31.2, 29.2, 28.6, 28.6, 26.3, 22.0, 13.9. HRMS (ESI) m/z calcd for $C_{28}H_{27}N_2O_3S_4$ $[M-H]^+$: 567.0910, found: 567.0907. Anal. calcd for $C_{28}H_{28}N_2O_3S_4$: C, 59.13; H, 4.96, N, 4.93. Found: C, 58.89; H, 4.79, N, 4.88.

2-(5-{[5-(4-Dodecyl-4*H*-thieno[3,2-*b*]indol-2-yl)thiophen-2-yl]methylene}-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (4d). Dark burgundy crystals, m.p. 226-227 °C, yield 0.440 g (70%).^{1}H NMR (500 MHz, DMSO-*d*$_6$)δ 13.55 (s, 1H), 8.13 (s, 1H), 7.92 (s, 1H), 7.82 – 7.73 (m, 2H), 7.63 – 7.54 (m, 2H), 7.34 – 7.26 (m, 1H), 7.16 – 7.10 (m, 1H), 4.67 (s, 2H), 4.37 (t, *J* = 6.9 Hz, 2H), 1.86 – 1.74 (m, 2H), 1.27 – 1.16 (m, 18H), 0.82 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 191.5, 167.2, 165.9, 146.8, 145.2, 141.2, 138.1, 135.7, 135.5, 126.5, 125.2, 123.4, 120.6, 119.4, 119.1, 118.1, 115.6, 110.7, 110.3, 45.3, 44.3, 31.3, 29.1, 29.0, 29.0, 28.9, 28.9, 28.7, 28.6, 26.2, 22.1, 13.9. HRMS (ESI) m/z calcd for $C_{32}H_{37}N_2O_3S_4$ $[M+H]^+$: 625.1682, found: 625.1677. Anal. calcd for $C_{32}H_{36}N_2O_3S_4$: C, 61.51; H, 5.81, N, 4.48. Found: C, 61.29; H, 5.86, N, 4.78.

2-(5-{[5-(10-Hexyl-10*H*-benzo[*g*]thieno[3,2-*b*]indol-8-yl)thiophen-2-yl]methylene}-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (4e). Burgundy powder, m.p. 270-271 °C, yield 0.533 g (90%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$)δ 13.45 (s, 1H), 8.42 (d, *J* = 8.8 Hz, 1H), 8.13 (s, 1H), 8.09 – 8.01 (m, 2H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 4.2 Hz, 1H), 7.69 – 7.48 (m, 4H), 4.91 – 4.79 (m, 2H), 4.68 (s, 2H), 1.96 – 1.84 (m, 2H), 1.47 – 1.35 (m, 2H), 1.33 – 1.21 (m, 4H), 0.83 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 191.5, 167.2, 165.8, 146.9, 145.5, 138.1, 135.3, 134.6, 134.1, 131.5, 129.3, 126.5, 126.0, 125.1, 124.3, 122.5, 121.7, 121.1, 118.8, 117.9, 117.9, 116.7, 110.7, 47.9, 45.0, 30.8, 29.7, 25.6, 21.9, 13.8. HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2O_3S_4$ $[M-H]^+$: 589.0754, found: 589.0744. Anal. calcd for $C_{30}H_{26}N_2O_3S_4$: C, 60.99; H, 4.44, N, 4.74. Found: C, 60.72; H, 4.31, N, 4.93.

Table S1 Photos of dyes **4a-e**

<table>
<tr><td>4a
</td><td>4b
</td></tr>
<tr><td>4c
</td><td>4d
</td></tr>
<tr><td colspan="2">4e
</td></tr>
</table>

1.7. Manufacture of DSSCs

Prior to adsorption of the dyes, the TiO_2 photoanodes (0.36 cm^2 active area, from Ti-Nanoxide T/SP covered by a reflective layer of Ti-Nanoxide R/SP, Solaronix) were heated at 450 °C for 30 min. When the electrodes cooled to 50 °C they were immersed in a 0.5 mM $CHCl_3$ solution of the sensitizing dyes **4a-e** for 24 h in the dark. The sensitized films were rinsed with isopropyl alcohol to remove excess dyes remaining on the surface and then dried at 50 °C for 10 min. The Pt-counter electrode (Solaronix) and dye-covered TiO_2 electrode were assembled into a sandwich type cell using Meltonix 1170-60 (Solaronix) in a thermal press (Carver) at 100 °C for 3 min. The solar cell was filled with electrolyte through a hole in the cathode. A mixture of in 3-propyl-1-methylimidazolium iodide (PMII, 0.6 M), lithium iodide (LiI, 0.1 M), iodine (I_2, 0.05 M), and 4-*tert*-butylpyridine (TBP, 0.5 M) in 3-methoxypropionitrile was used as the electrolyte.The hole was sealed with thin glass (0.5 mm thickness).

*1.8. Experimental data of synthesized dyes **4a-e***

Table S2 Characteristics of thermal degradation of the dyes **4a-e** in air at HR 10 K min^{-1}

Dye	T_d, °C (5 % mass loss)	Ions in MS (M/z) – all substances
4a	313	**Major products** $[H_2O]^+$ (18), $[CO_2]^+$ (44), $[SO_2]^+$(64), $[SO]^+$(48), $[C_3N]^+$ (50), $[C_4H_2]^+$ (50), $[C_4N]^+$(62), $[CS_2]^+$(76), $[C_6H_4]^+$(76), $[C_6H_6]^+$(78), $[CH_3COOH]^+$ (60), $[C_5H_{5-6}]^+$(65-66) **Small amounts in 4b-d** $[CNS]^+$(58), $[CH_2COOH]^+$ (59), $[C_4H_{2-10}]^+$ (50-55), $[C_3H_3N]^+$ (52), $[C_5H_{7-12}]^+$ (67-70)
4b	322	
4c	328	
4d	328	
4e	318	

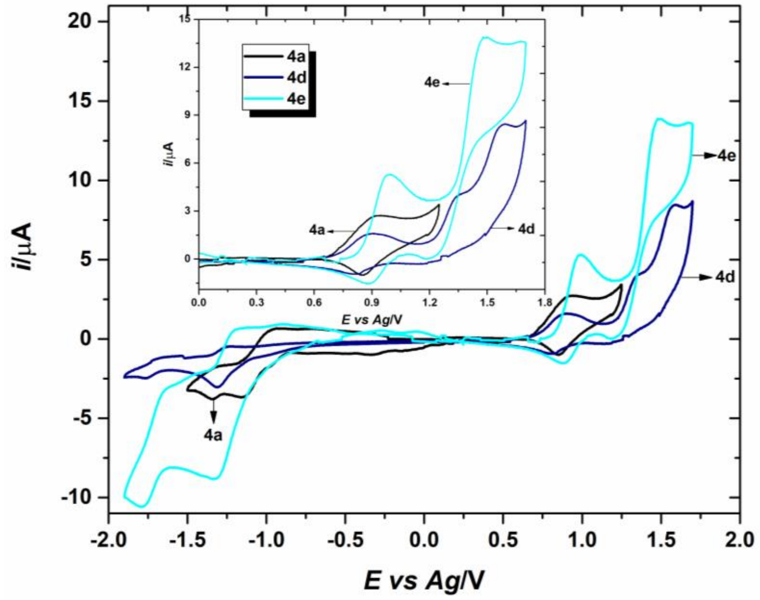


Figure S1 Cyclic voltammograms on **GC** electrode for **4a** and **4d-e**.

2. References

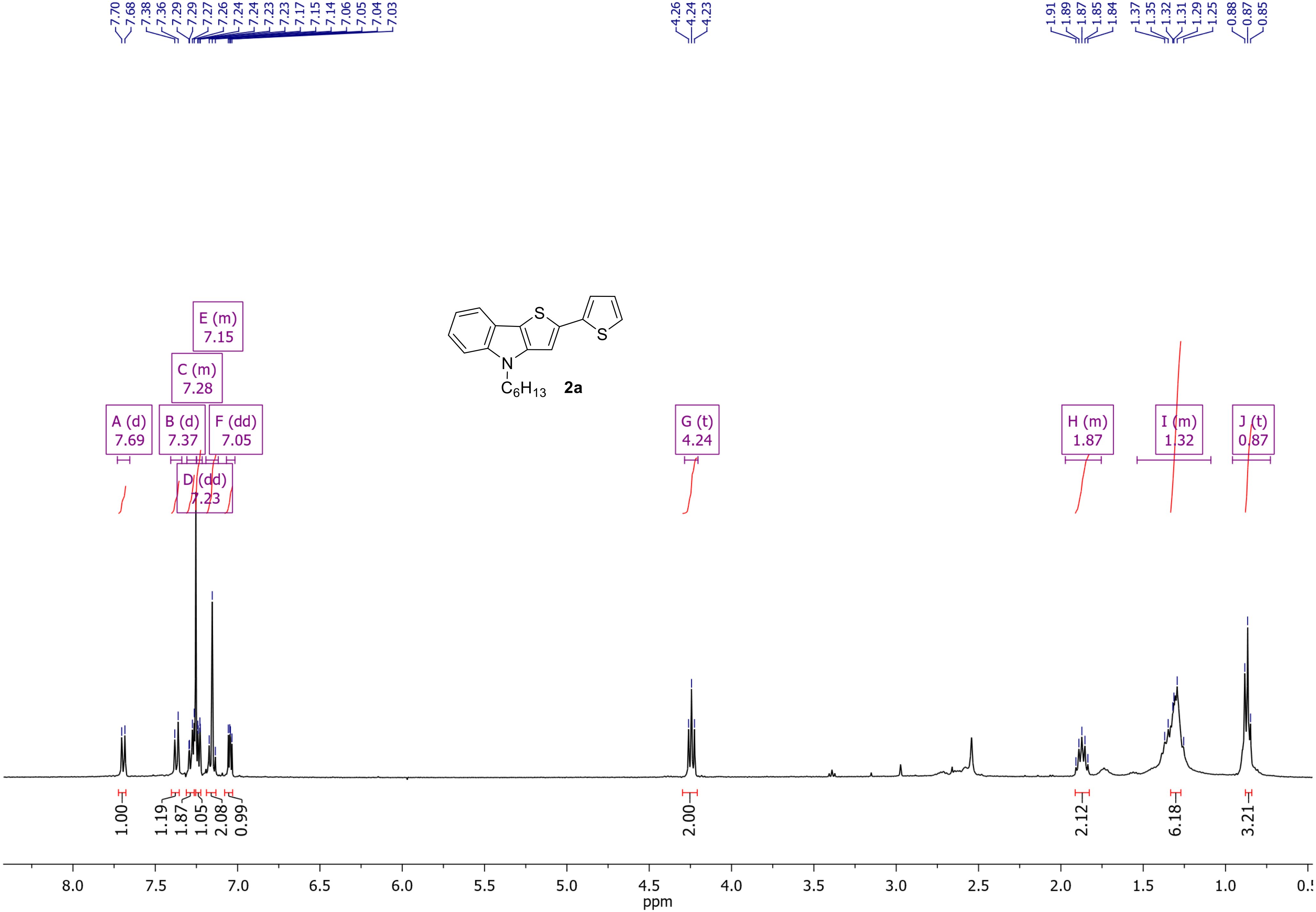
S1. N. E. Leadbeater, H. M. Torenius, H. Tye, *Tetrahedron*, 2003, **59**, 2253–2258.

S2. R. A. Irgashev, A. S. Steparuk, G. L. Rusinov, *Org. Biomol. Chem.*, 2018, **16**, 4821–4832.

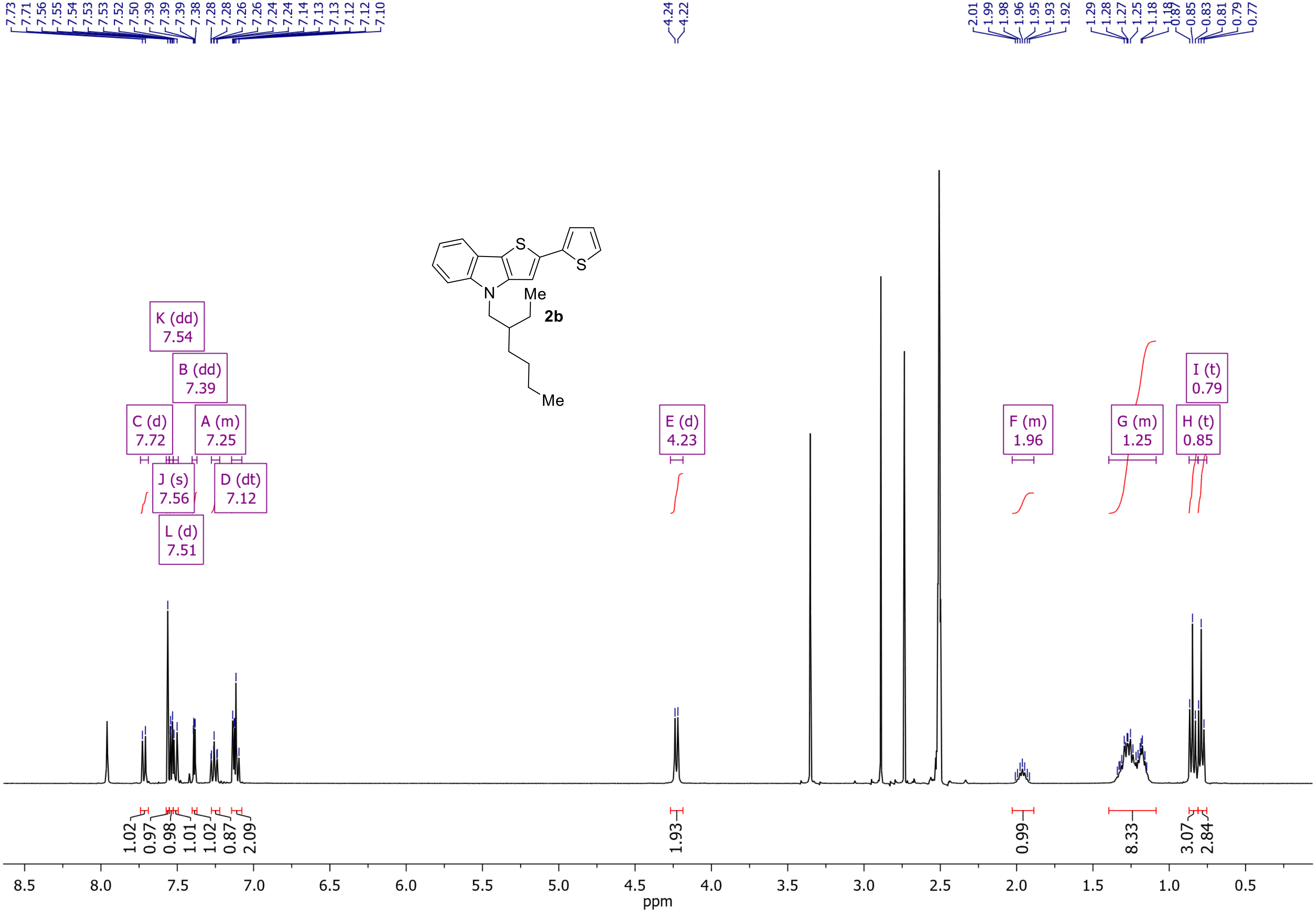
S3. A. S. Steparuk, R. A. Irgashev, G. L. Rusinov, E. V. Krivogina, P. I. Lazarenko, S. A. Kozyukhin, *Russ. Chem. Bull.*, 2019, **68**, 1208–1212.

3. Copies of ^{1}H and ^{13}C NMR spectra

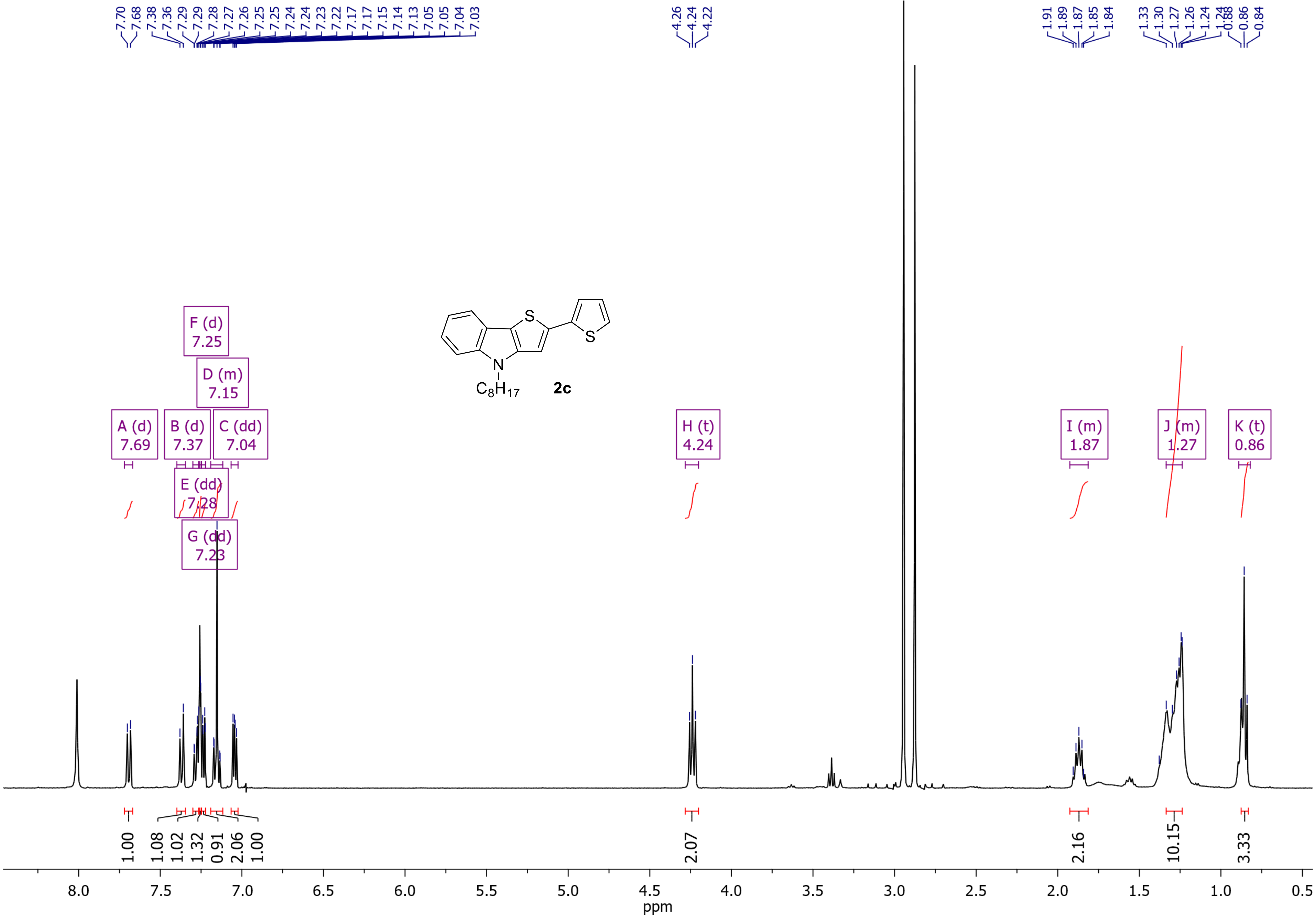
^{1}H NMR (solvent: $CDCl_3$)



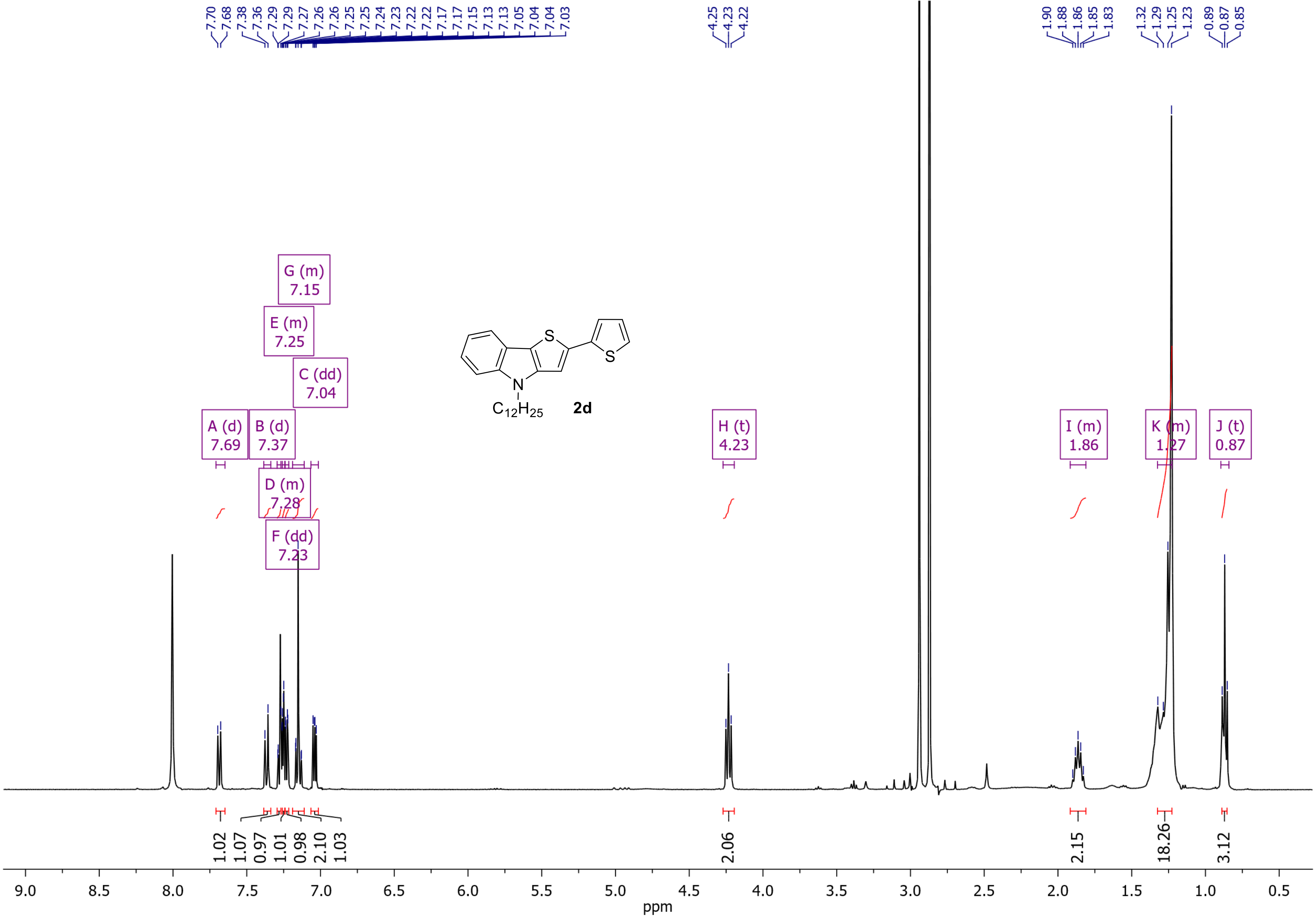
^{1}**H NMR** (solvent: DMSO-d_6)



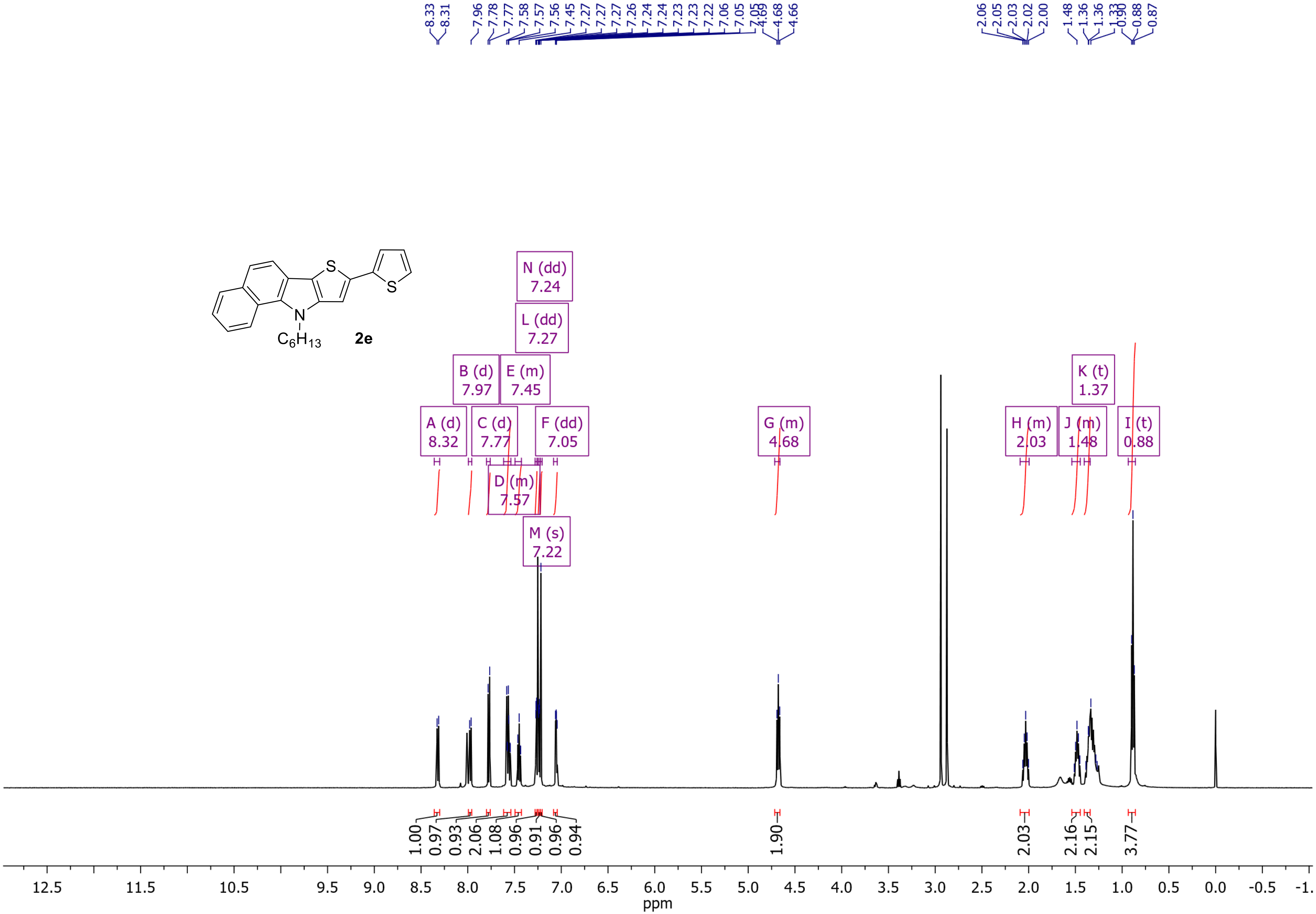
^{1}H NMR (solvent: $CDCl_3$)



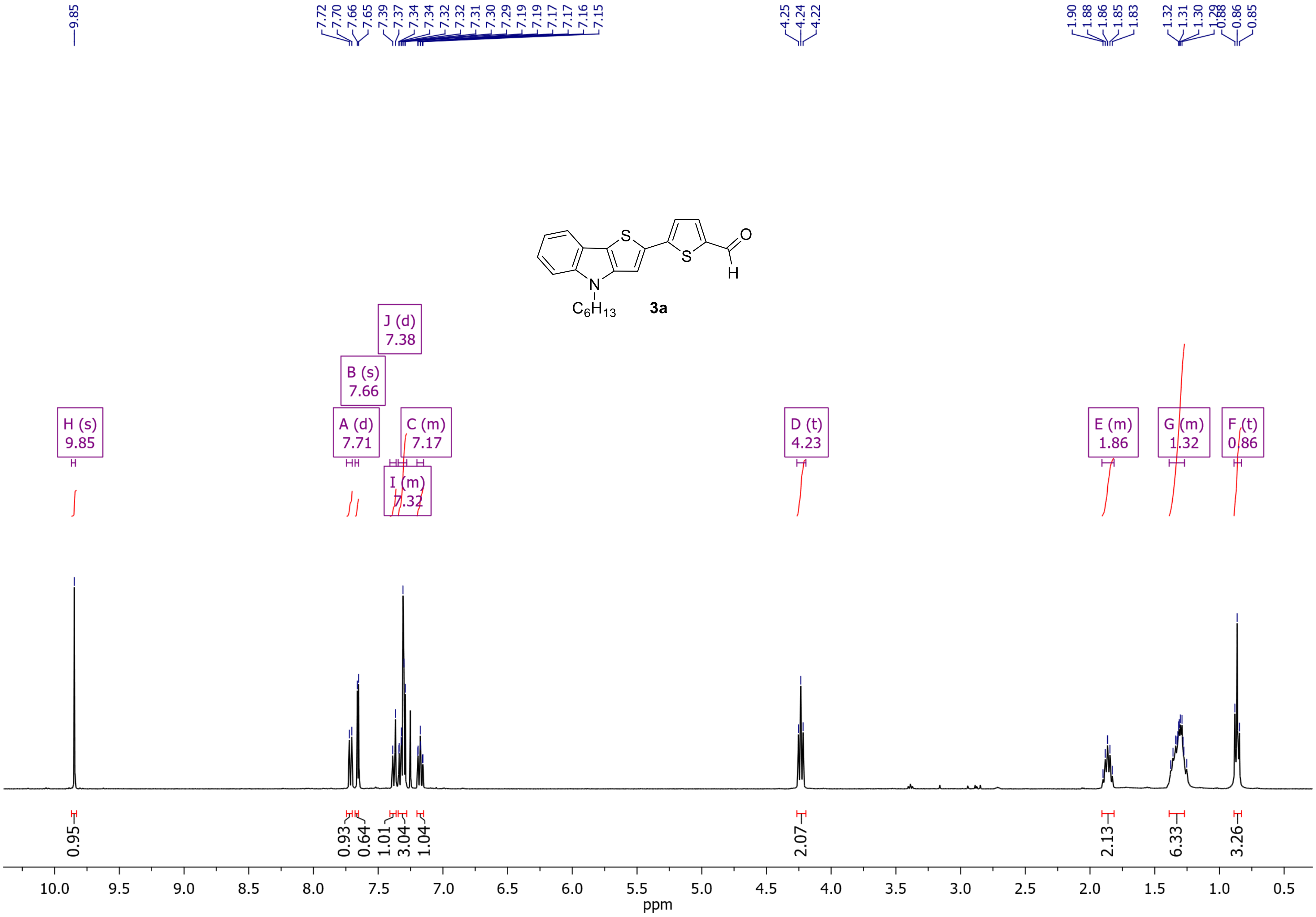
^{1}H NMR (solvent: $CDCl_3$)



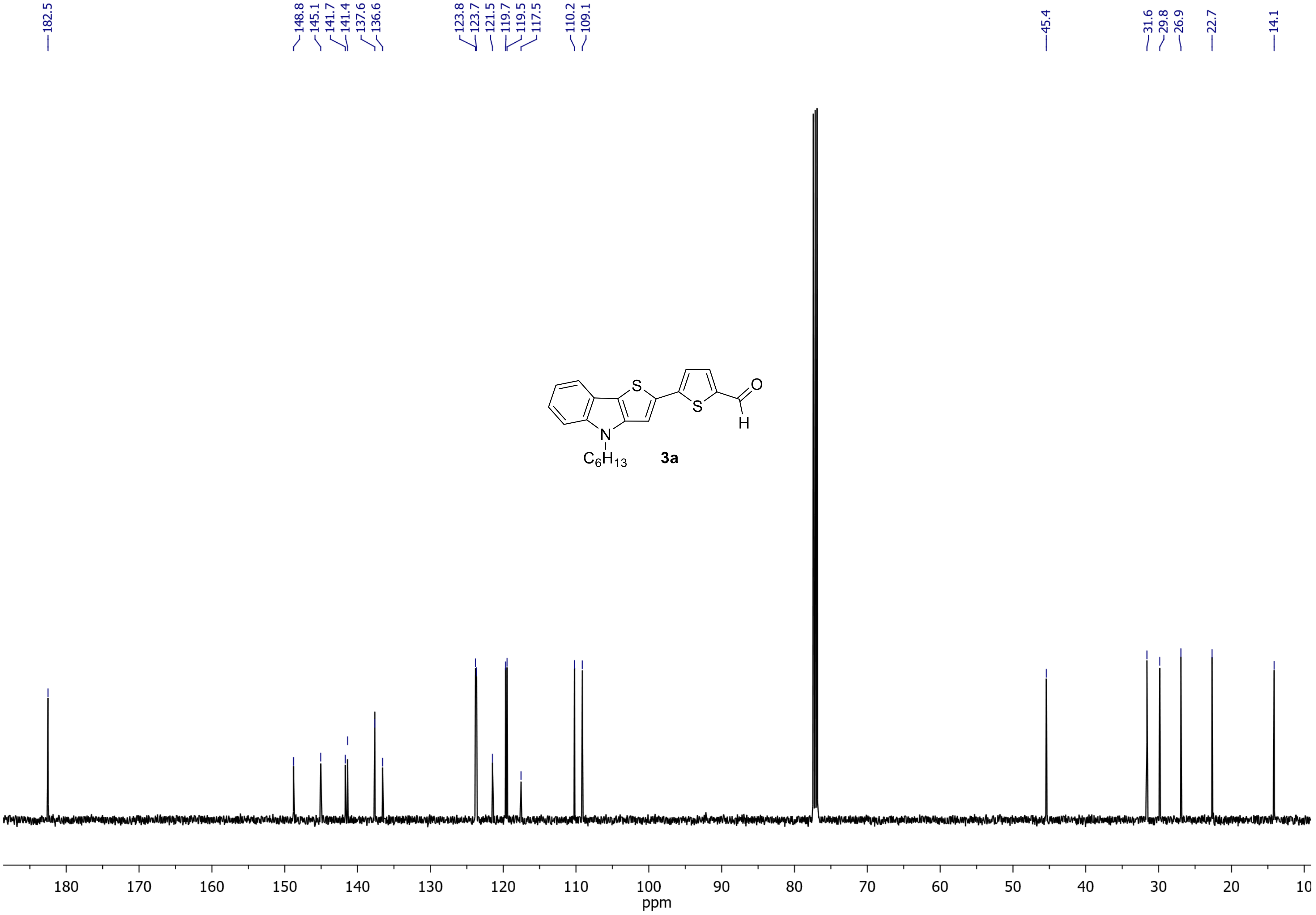
^{1}**H NMR** (solvent: $CDCl_3$)



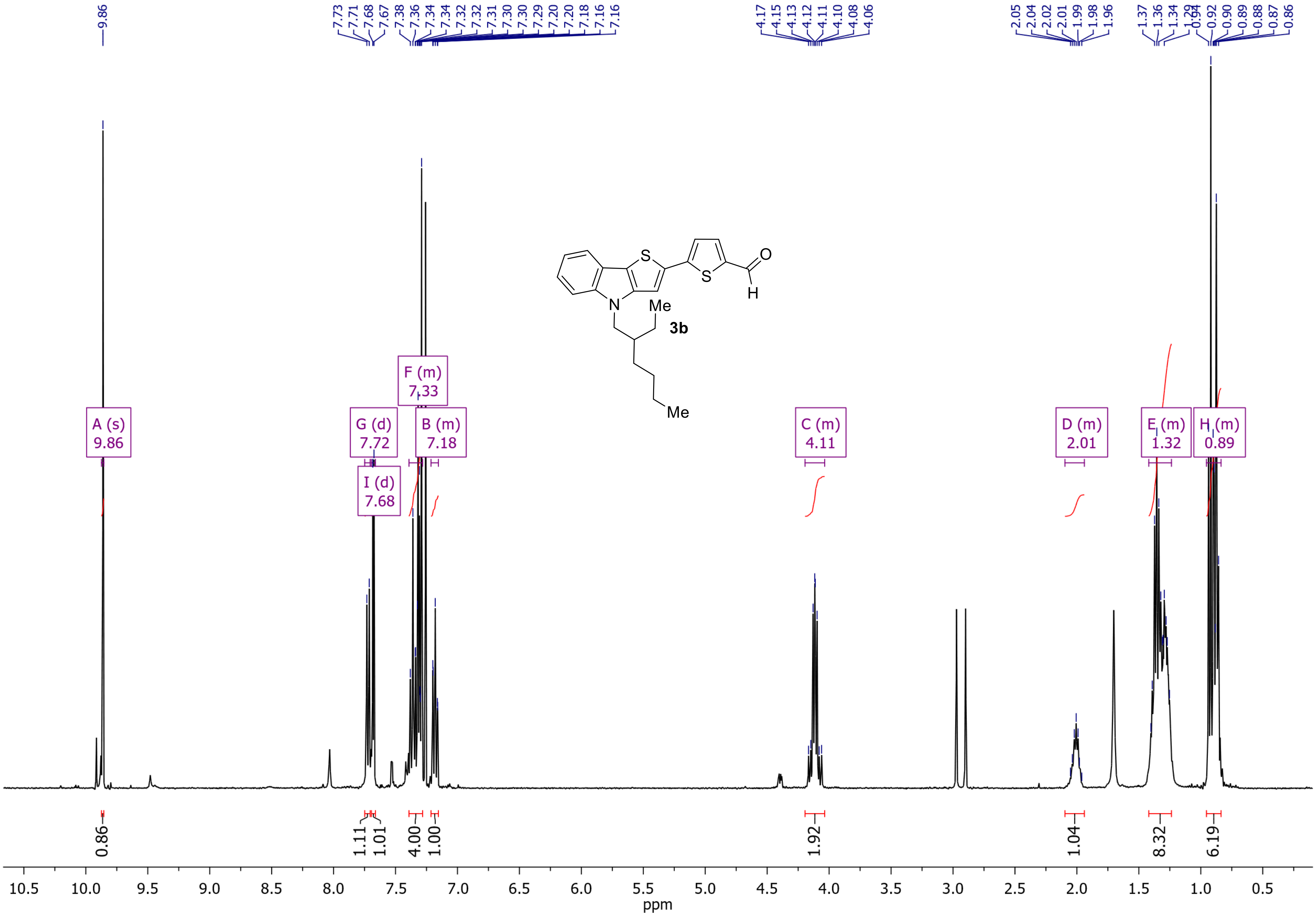
^{1}H NMR (solvent: $CDCl_3$)



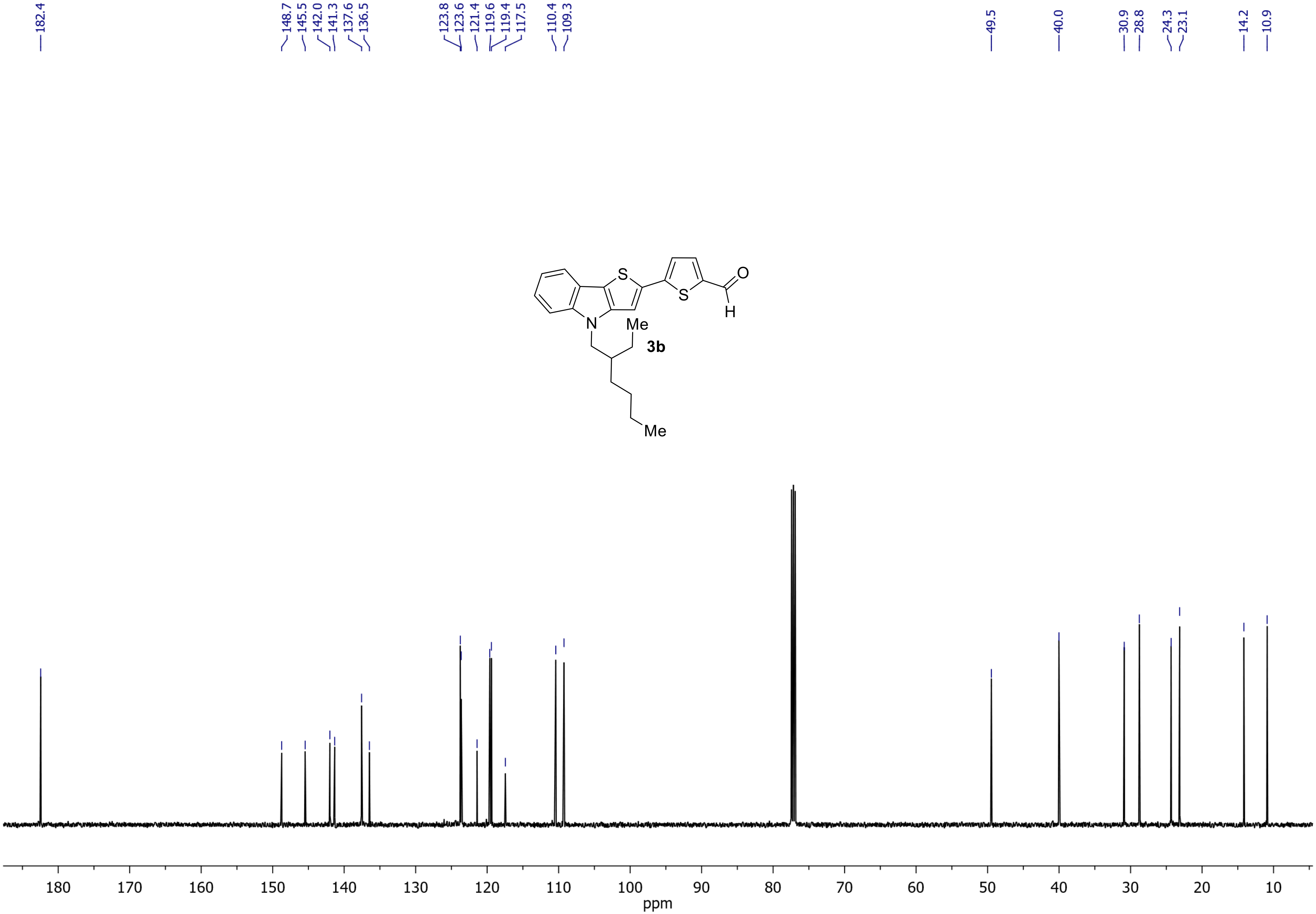
^{13}C NMR (solvent: $CDCl_3$)



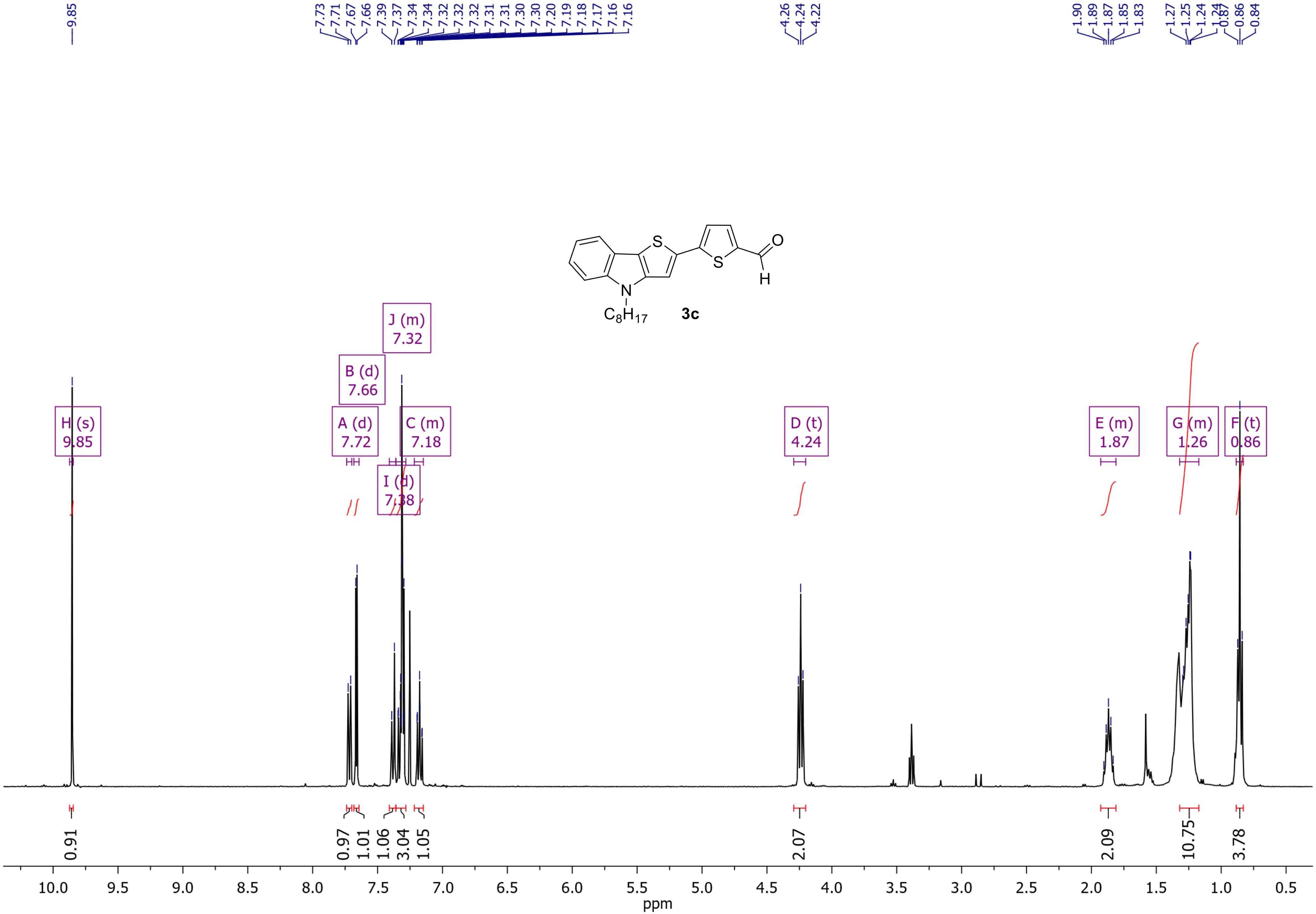
^{1}H NMR (solvent: CDCl$_3$)



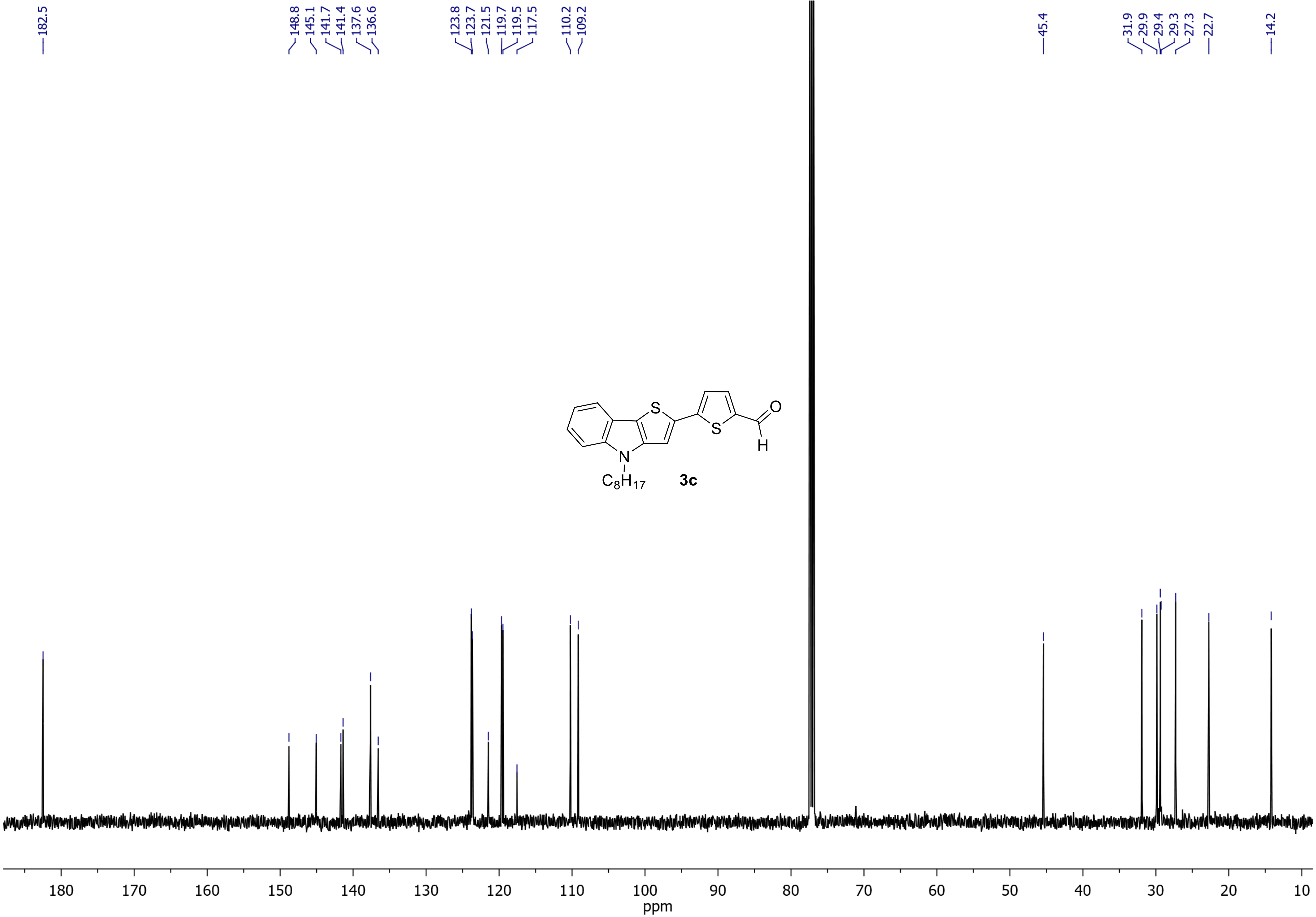
^{13}C NMR (solvent: $CDCl_3$)



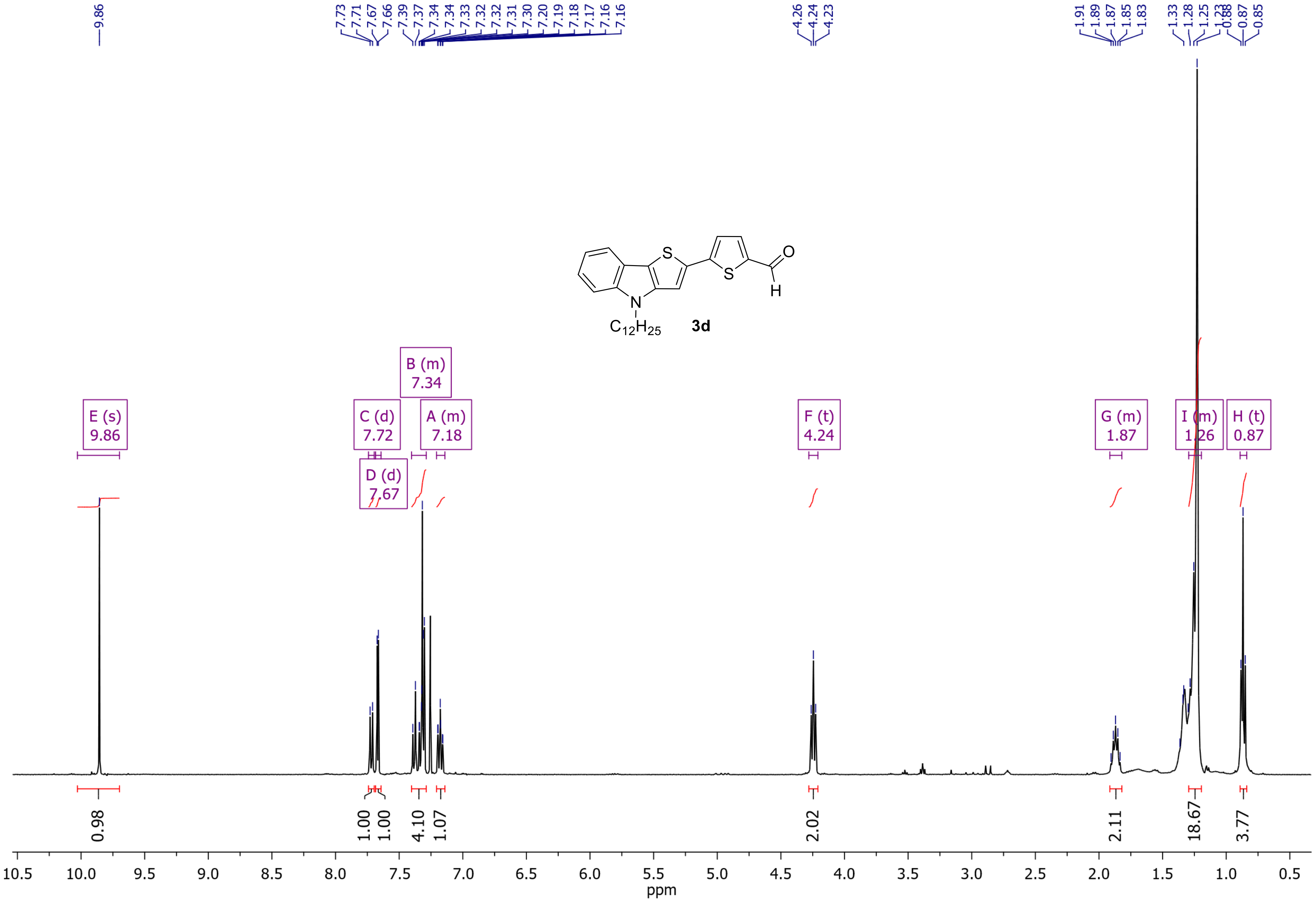
^{1}**H NMR** (solvent: $CDCl_3$)



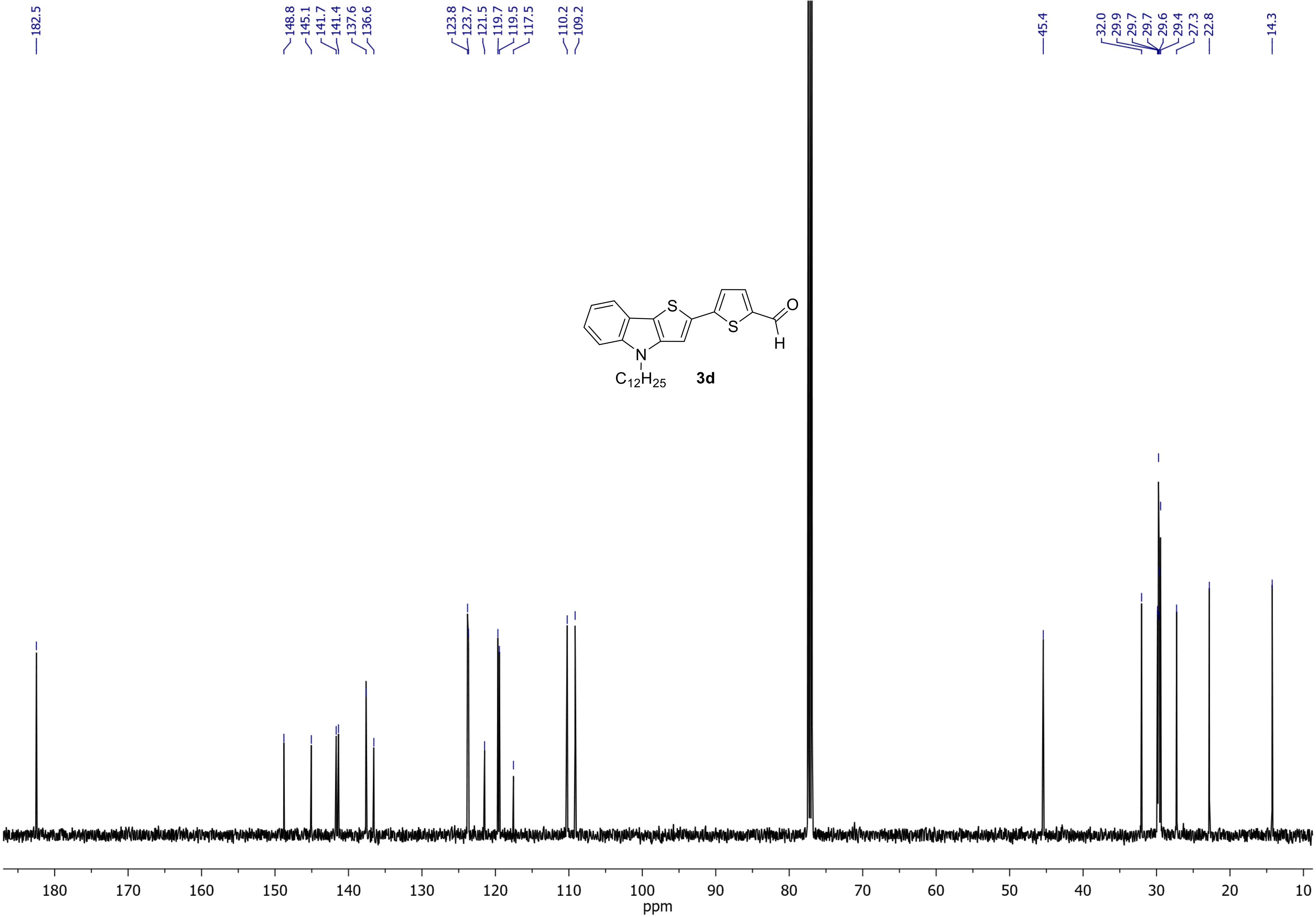
^{13}C NMR (solvent: $CDCl_3$)



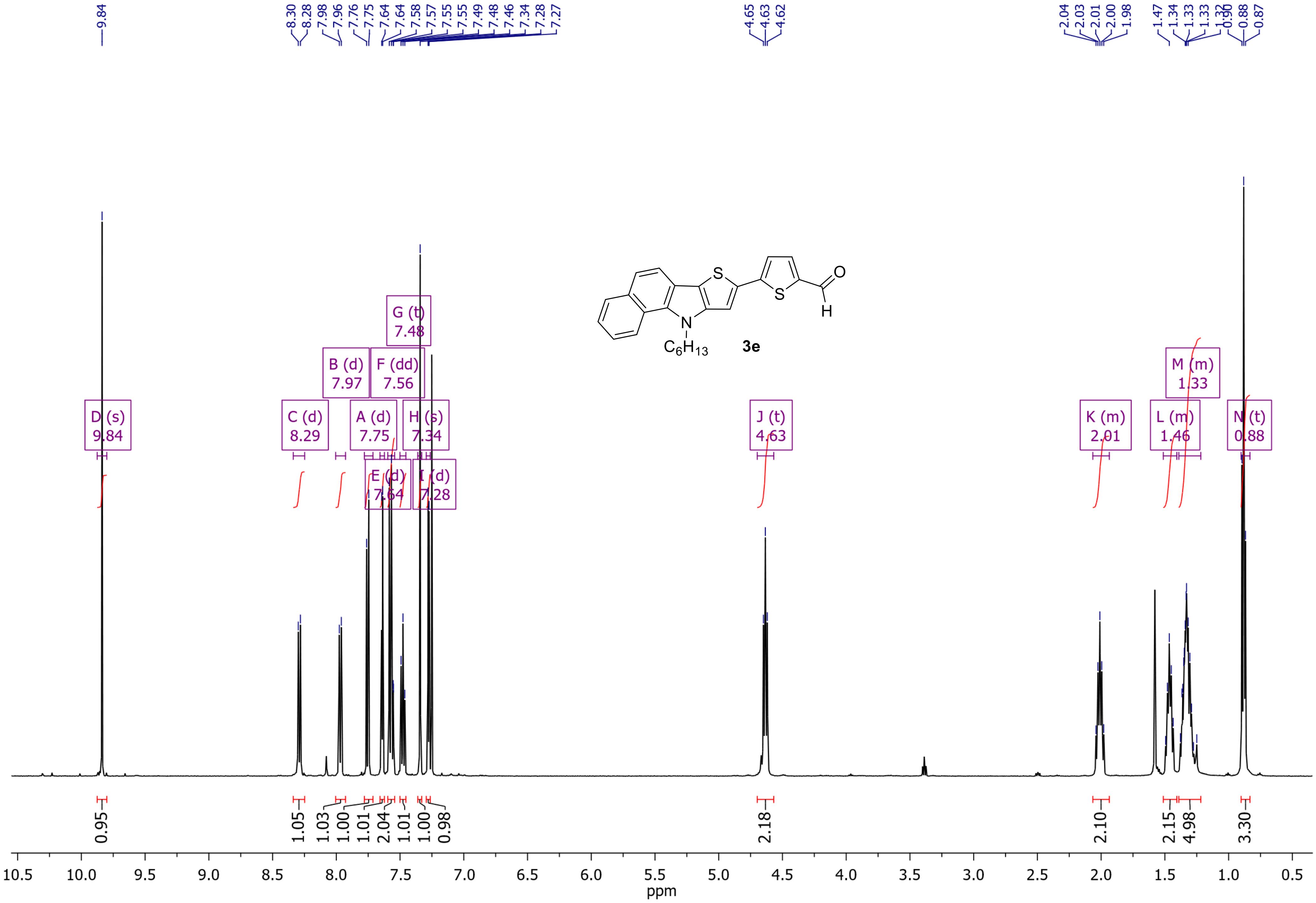
^{1}**H NMR** (solvent: $CDCl_3$)



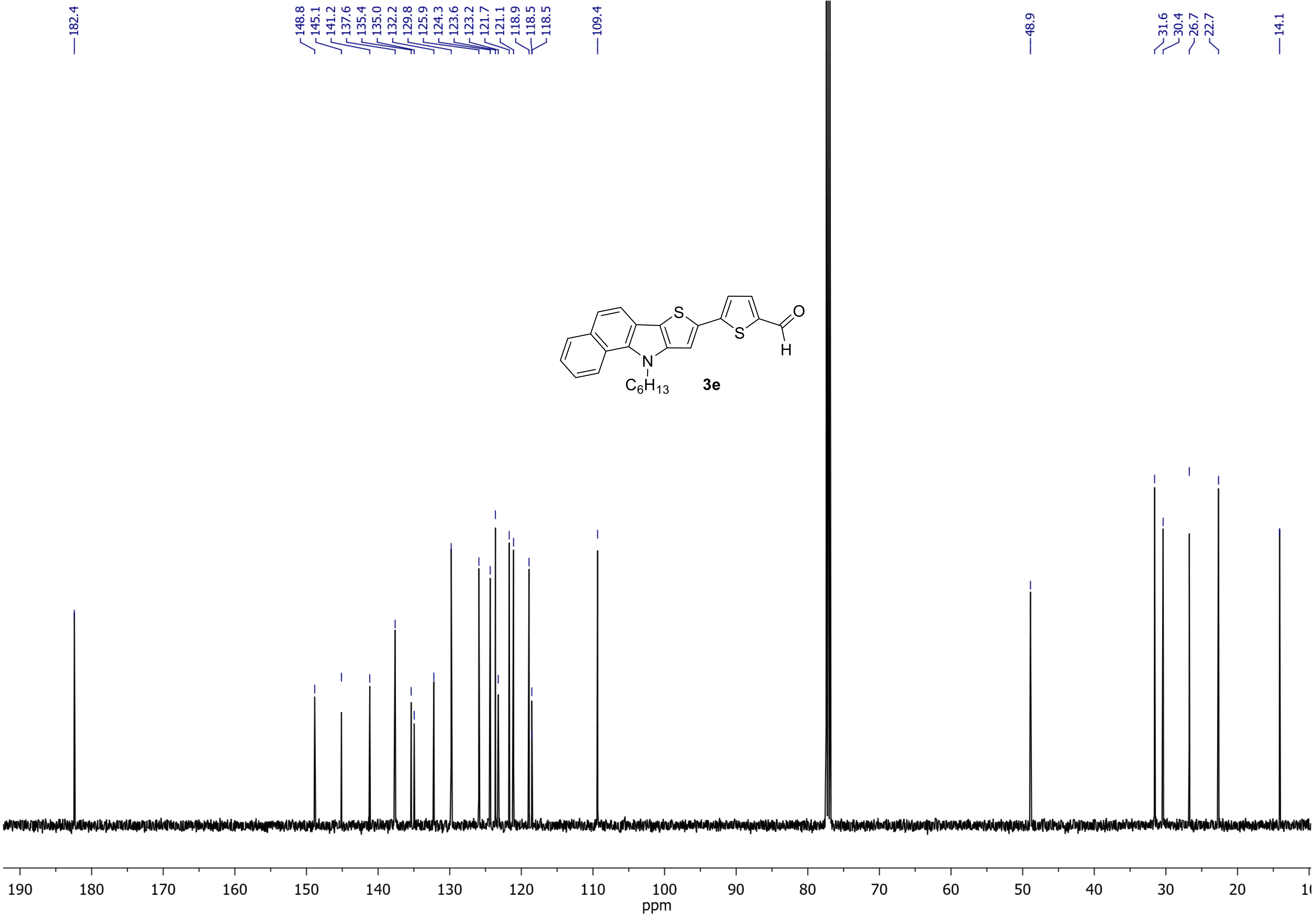
^{13}C NMR (solvent: $CDCl_3$)



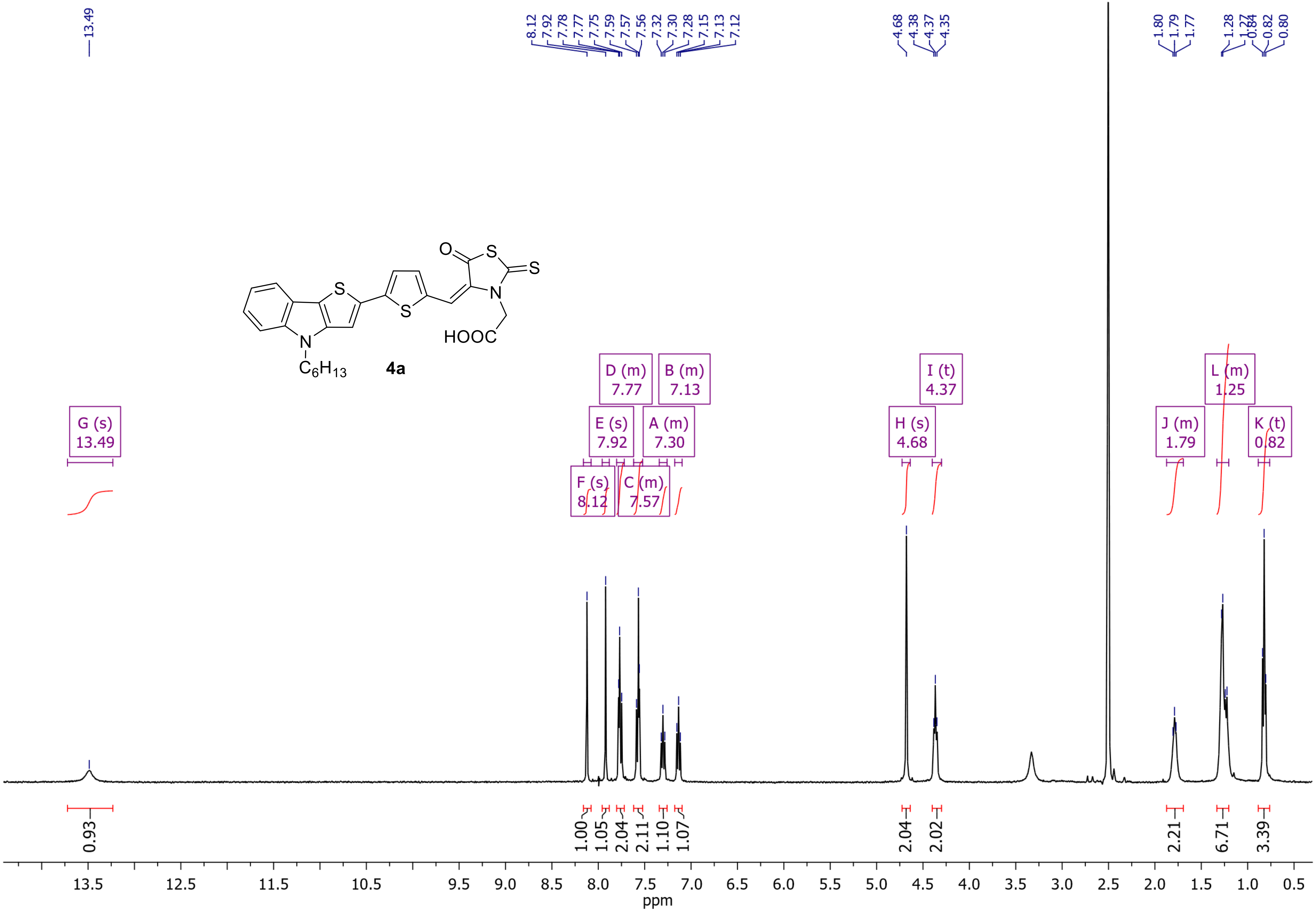
^{1}H NMR (solvent: CDCl$_3$)



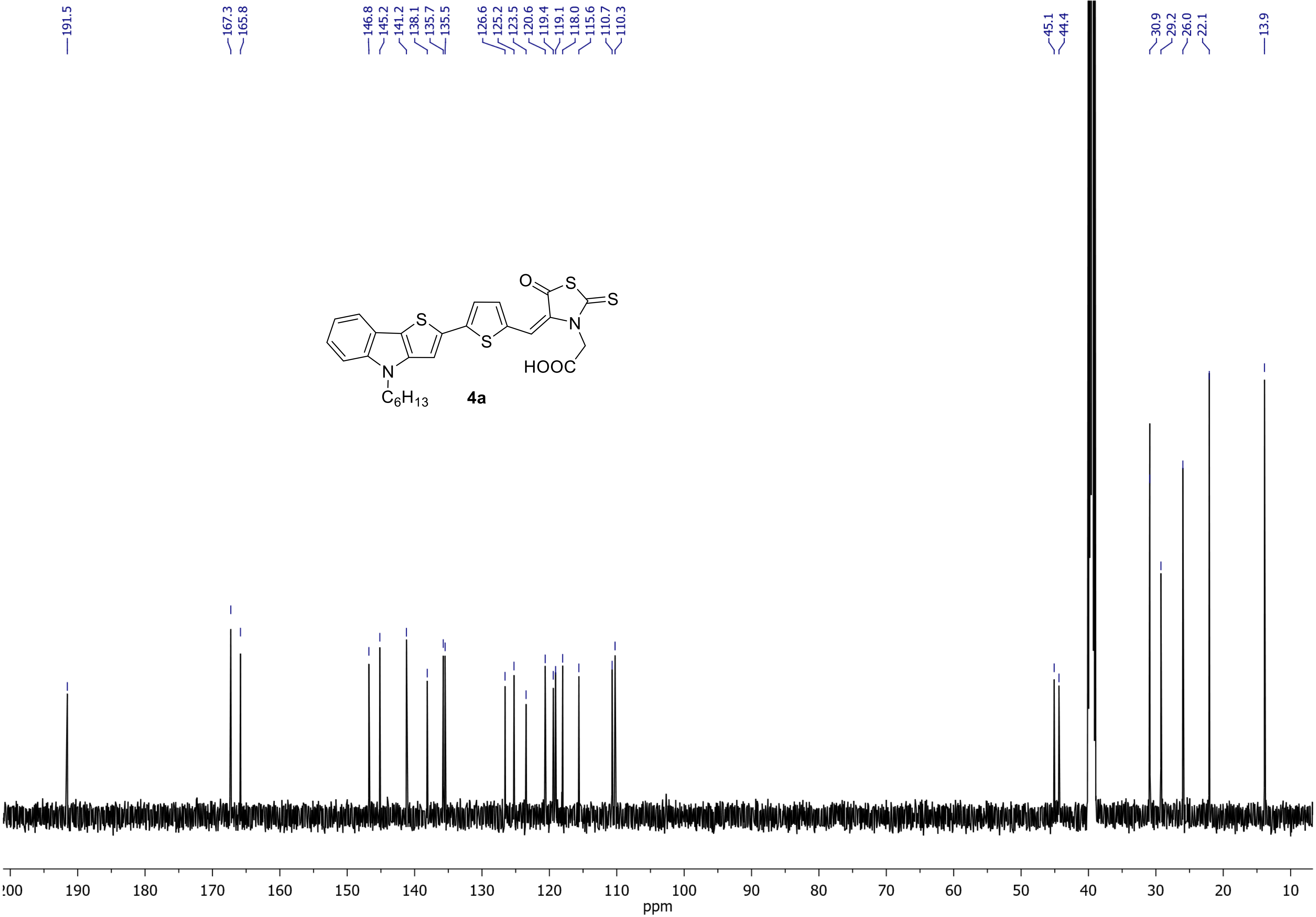
^{13}**C NMR** (solvent: $CDCl_3$)



^{1}**H NMR** (solvent: DMSO-d_6)

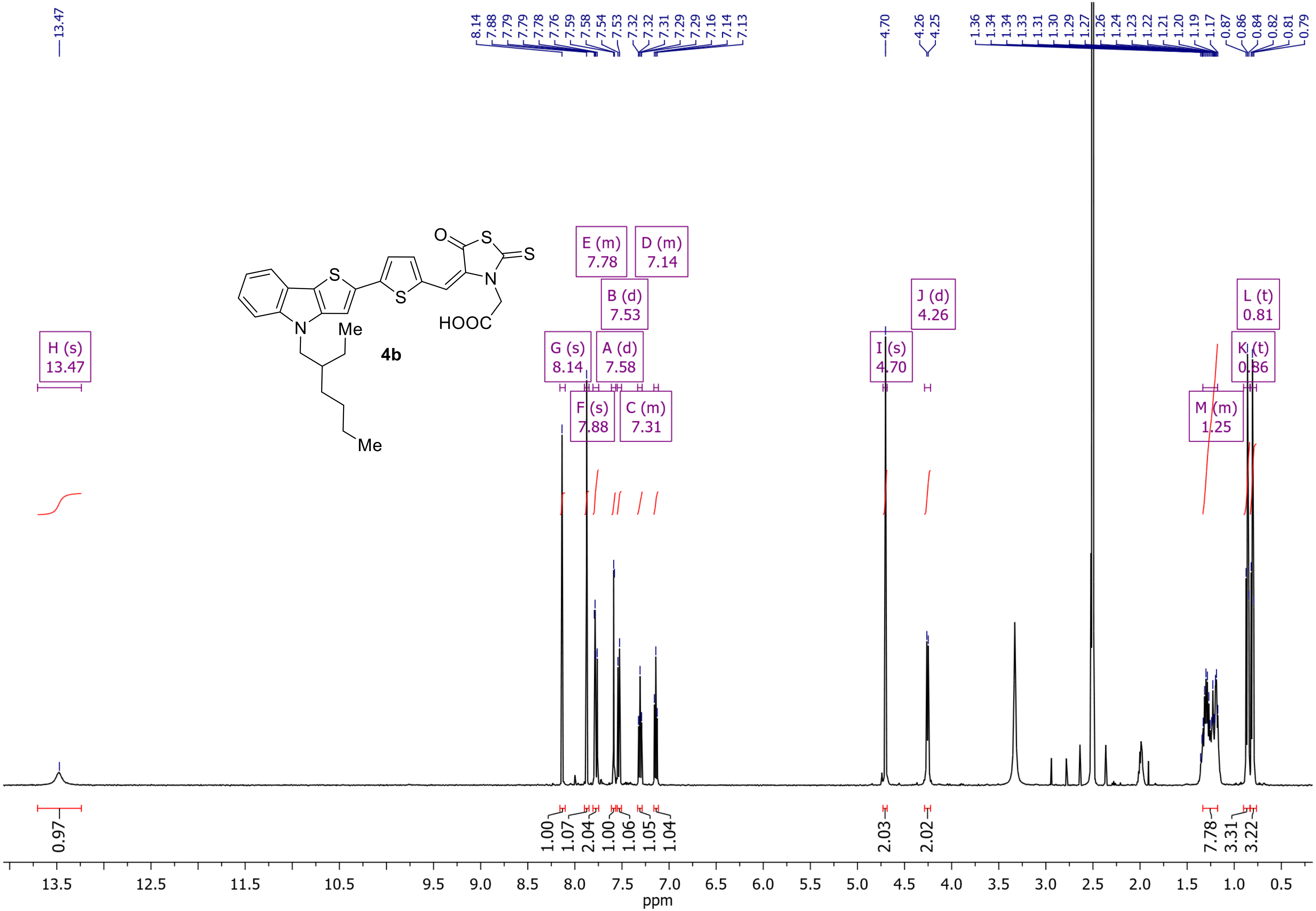


^{13}C NMR (solvent: DMSO-d_6)

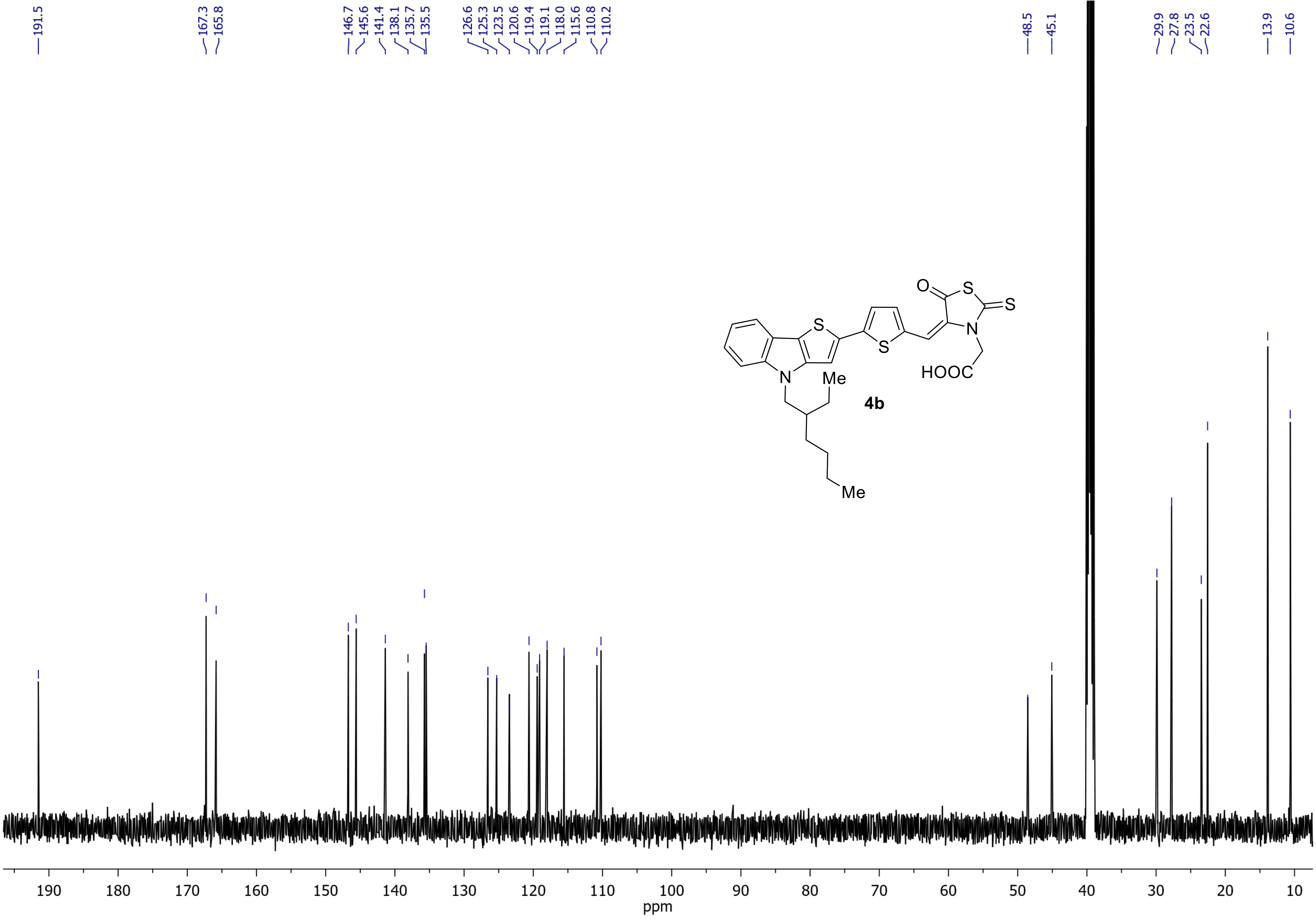


4a

^{1}**H NMR** (solvent: DMSO-d_6)

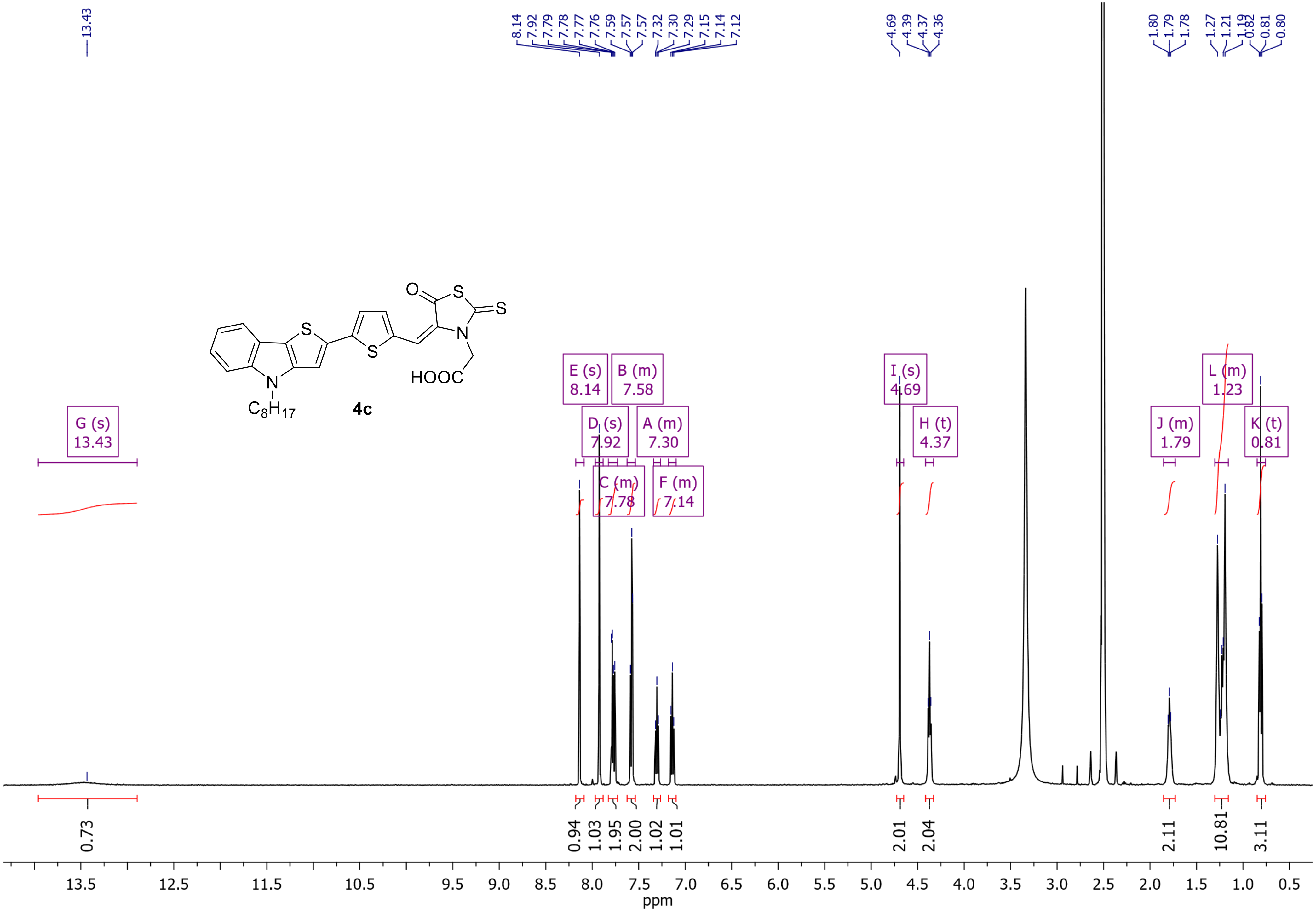


^{13}C NMR (solvent: DMSO-d_6)

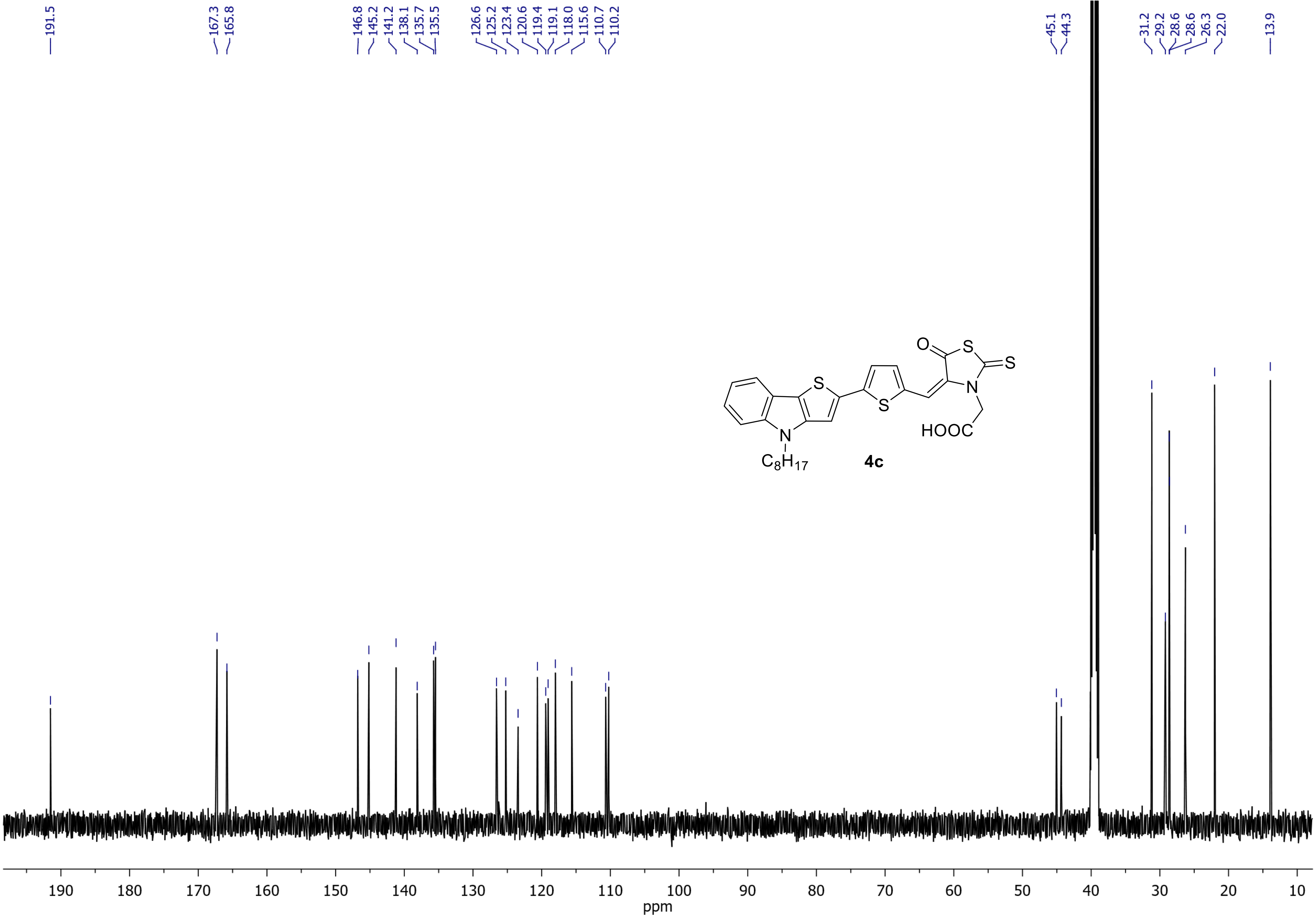


4b

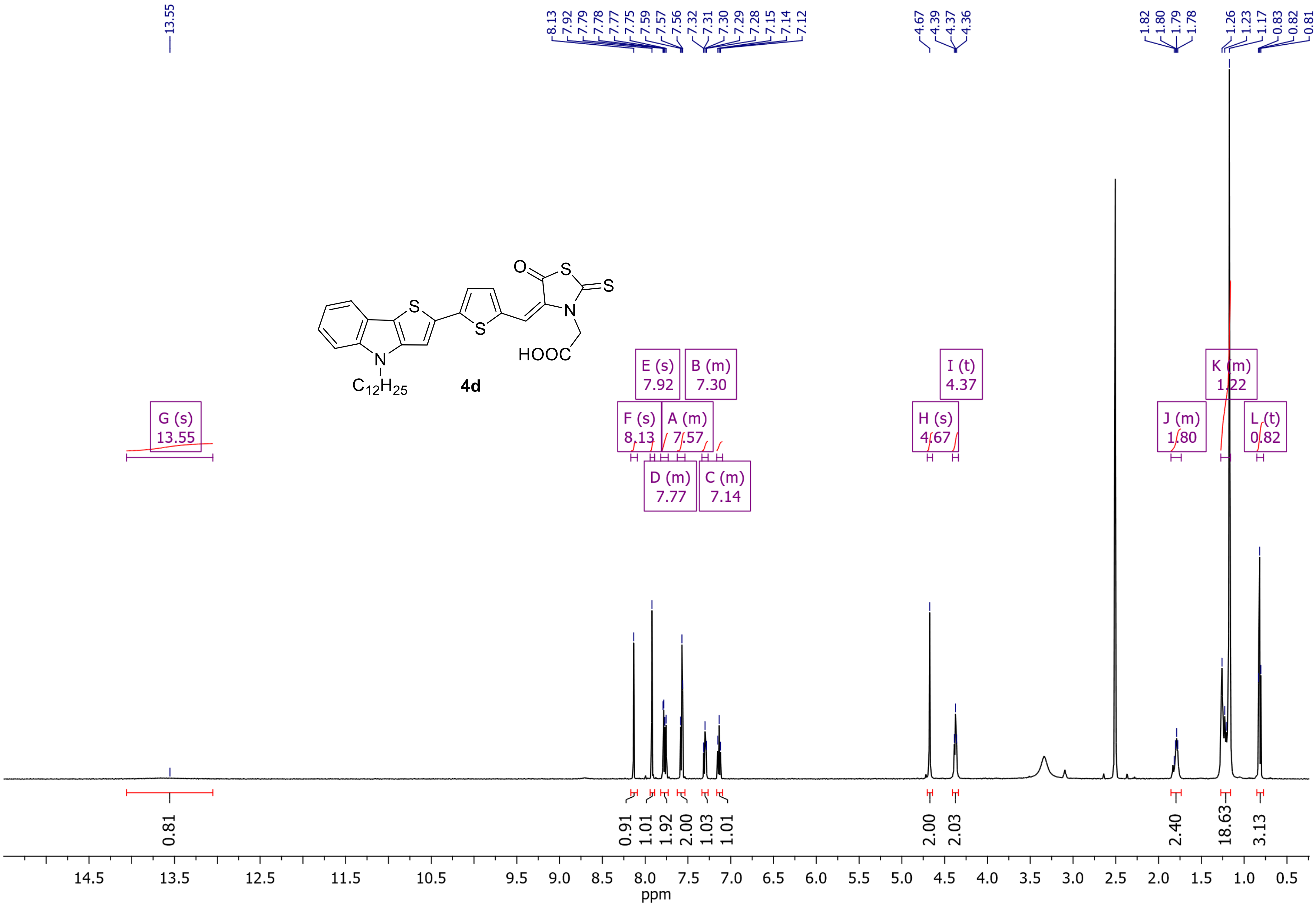
^{1}**H NMR** (solvent: DMSO-d_6)



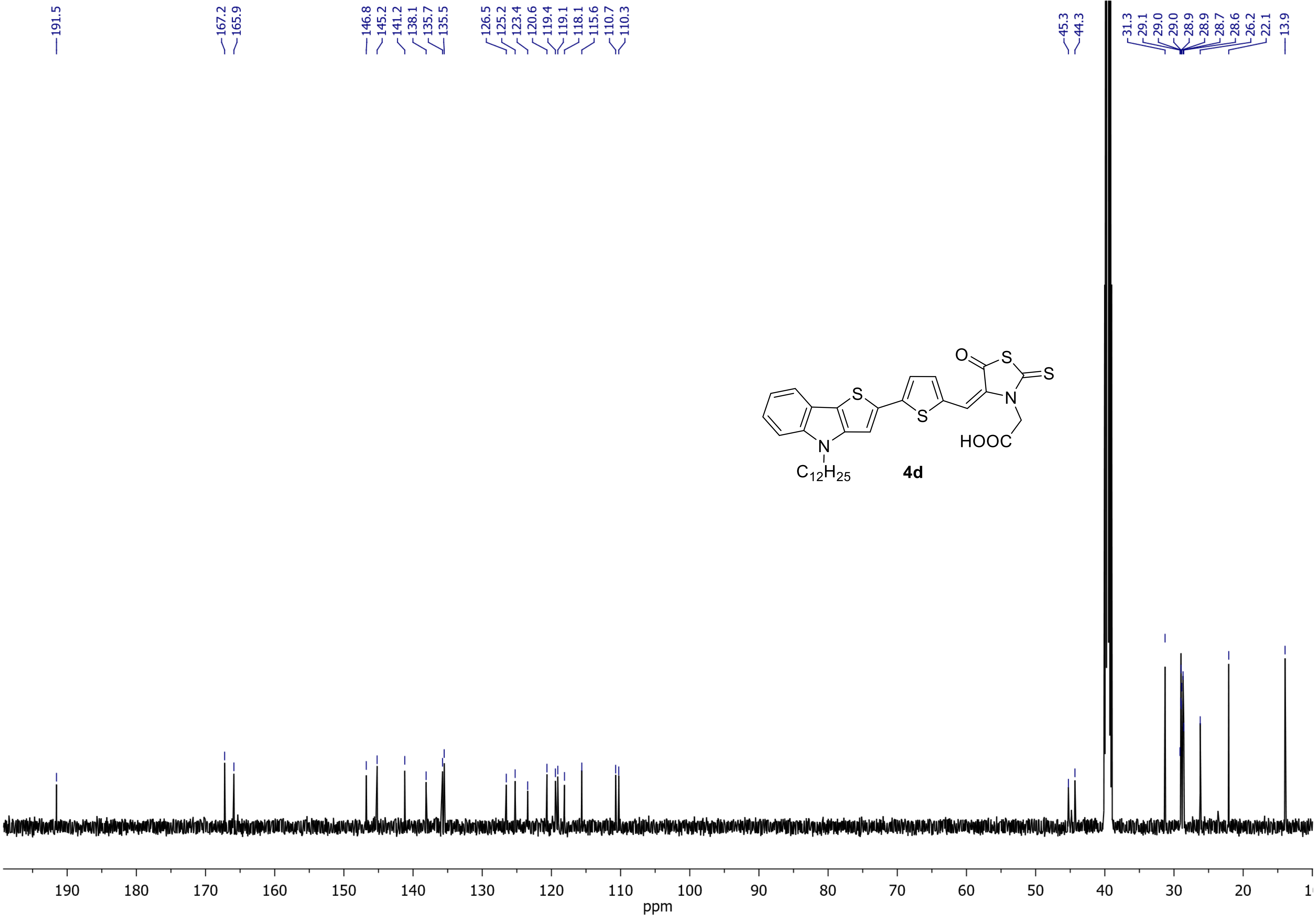
^{13}C NMR (solvent: DMSO-d_6)



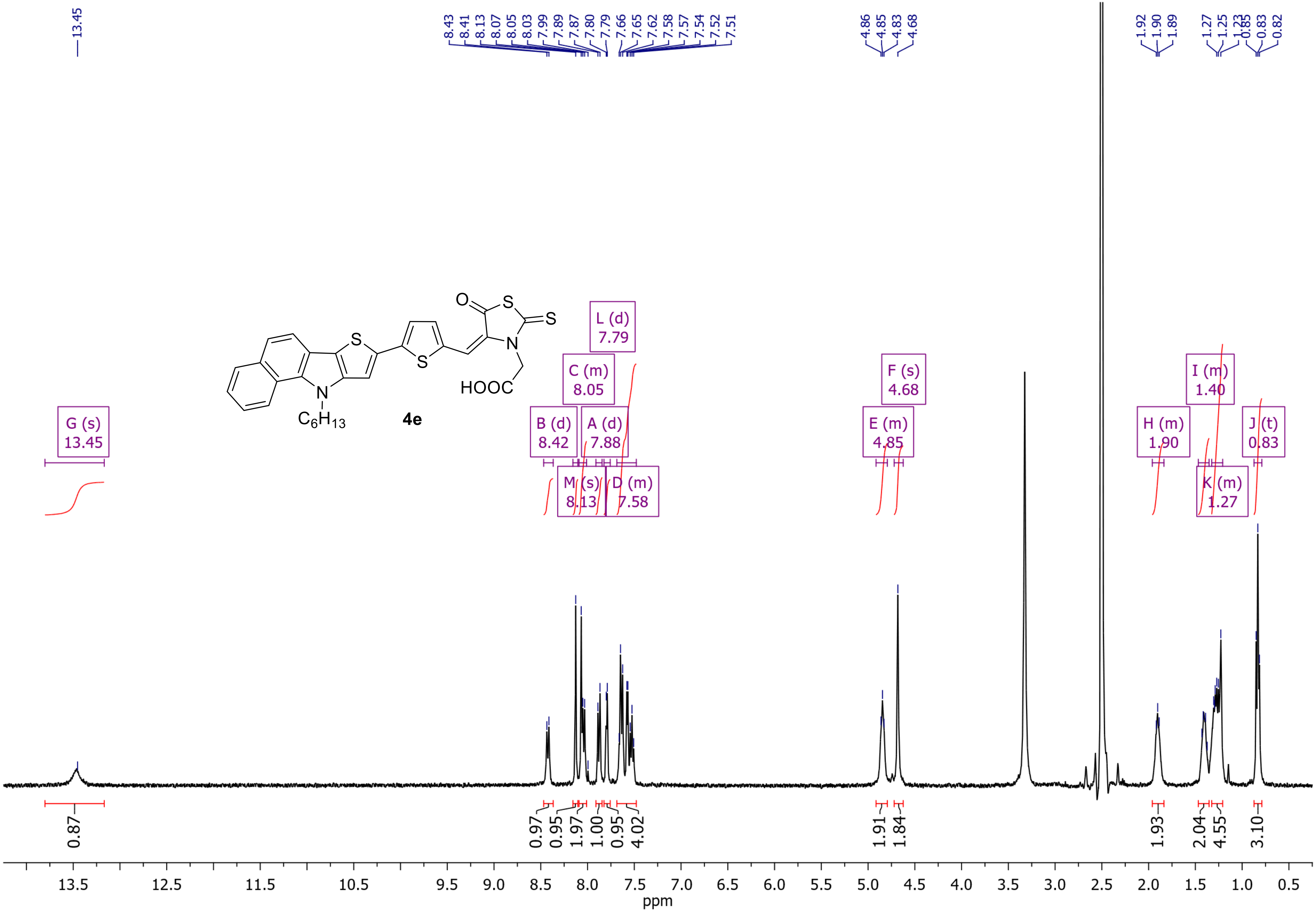
^{1}**H NMR** (solvent: DMSO-d_6)



^{13}C NMR (solvent: DMSO-d_6)



^{1}**H NMR** (solvent: DMSO-d_6)



^{13}C NMR (solvent: DMSO-d_6)