Thieno[3,2-*b*]indole - benzo[*b*]thieno[2,3-*d*]thiophen-3(2*H*)-one based D-π-A molecules as electron transport materials for perovskite solar cells

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1. Experimental Section

1.1. Materials

All chemicals were used without further purification and purchased from commercial sources. Silica gel 0.040–0.063 mm (230–400 mesh) was used to purify compounds. All solvents were dried and distilled according to standard procedures.

*1.2. General procedure for synthesis of compounds **2a-d***

NaH (0.100 g, 4.2 mmol) was added to a solution of thieno[3,2-*b*]indole **1** (2 mmol, 0.511 g) in dry DMF (7 mL). The system was purged with argon, and an appropriate alkyl bromide (2.15 mmol) was added after 30 min. The reaction mixture was maintained at room temperature 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-d**, which were further used for the next step without additional purification.

4-Ethyl-2-(thiophen-2-yl)-4*H*-thieno[3,2-*b*]indole (2a). Beige powder, yield 0.516 g (91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.24 (m, 3H), 7.24 (dd, *J* = 5.1, 1.2 Hz, 2H), 7.21 – 7.13 (m, 4H), 7.05 (dd, *J* = 5.1, 3.6 Hz, 2H), 4.33 (q, *J* = 7.2 Hz, 4H), 1.48 (t, *J* = 7.2 Hz, 6H).

4-Butyl-2-(thiophen-2-yl)-4*H*-thieno[3,2-*b*]indole (2b). Yellow oil, yield 0.536 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.24 – 7.21 (m, 1H), 7.18 – 7.13 (m, 2H), 7.04 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.24 (t, *J* = 7.1 Hz, 2H), 1.91 – 1.80 (m, 2H), 1.43 – 1.32 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

4-(2-Ethylhexyl)-2-(thiophen-2-yl)-4*H*-thieno[3,2-*b*]indole (2c). 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-Pentadecyl-2-(thiophen-2-yl)-4*H*-thieno[3,2-*b*]indole (2d). Beige powder, yield 0.652 g (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.24 (dd, *J* = 5.2, 1.0 Hz, 2H), 7.18 – 7.13 (m, 2H), 7.05 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.25 (t, *J* = 7.1 Hz, 2H), 1.92 – 1.83 (m, 2H), 1.41 – 1.16 (m, 24H), 0.88 (t, *J* = 6.9 Hz, 3H).

*1.3. General procedure for synthesis of aldehydes **3a-d***

$POCl_3$ (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 room temperature for 48 h, poured into saturated aqueous sodium hydrogen carbonate, extracted with $CHCl_3$, and the extract was 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-Ethyl-4*H*-thieno[3,2-*b*]indol-2-yl)thiophene-2-carbaldehyde (3a). Orange powder, m.p. 168-169 °C, yield 0.336 g (72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 4.0 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.29 (m, 3H), 7.22 – 7.16 (m, 1H), 4.33 (q, *J* = 7.3 Hz, 2H), 1.48 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.5, 148.7, 144.6, 141.4, 141.2, 137.6, 136.6, 123.8, 123.8, 123.7, 121.6, 119.7, 119.5, 117.7, 110.0, 109.0, 40.0, 14.9. HRMS (ESI) calcd for $C_{17}H_{14}NOS_2$ m/z 312.0511 $[M+H]^+$, found m/z 312.0513 $[M+H]^+$.

5-(4-Butyl-4*H*-thieno[3,2-*b*]indol-2-yl)thiophene-2-carbaldehyde (3b). Dark ginger powder, m.p. 150-151 °C, yield 0.448 g (88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 4.0 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.30 (m, 3H), 7.21 – 7.15 (m, 1H), 4.27 (t, *J* = 7.1 Hz, 2H), 1.93 – 1.81 (m, 2H), 1.44 – 1.33 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.3, 148.6, 144.9, 141.5, 141.2, 137.4, 136.4, 123.6, 123.5, 121.3, 119.5, 119.3, 117.4, 110.1, 109.0, 45.0, 31.8, 20.4, 13.8. HRMS (APCI) calcd for $C_{19}H_{18}NOS_2$ m/z 340.0824 $[M+H]^+$, found m/z 340.0824 $[M+H]^+$.

5-[4-(2-Ethylhexyl)-4*H*-thieno[3,2-*b*]indol-2-yl]thiophene-2-carbaldehyde (3c). Dark yellow powder, m.p. 132-133 °C, yield 0.522 g (88%). ^{1}H 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 (APCI) m/z calcd for $C_{23}H_{26}NOS_2$ $[M+H]^+$: 396.1450, found: 396.1450.

5-(4-Pentadecyl-4*H*-thieno[3,2-*b*]indol-2-yl)thiophene-2-carbaldehyde (3d). Yellow powder, m.p. 113-114 °C, yield 0.718 g (97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.73 (dd, *J* =

7.9, 0.7 Hz, 1H), 7.69 (d, *J* = 4.0 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.30 (m, 3H), 7.21 – 7.15 (m, 1H), 4.26 (t, *J* = 7.1 Hz, 2H), 1.93 – 1.83 (m, 2H), 1.37 – 1.19 (m, 24H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.3, 148.6, 144.9, 141.5, 141.2, 137.4, 136.4, 123.6, 123.5, 121.3, 119.5, 119.3, 117.4, 110.1, 109.0, 45.3, 31.9, 29.73, 29.69, 29.67, 29.65, 29.61, 29.57, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1. HRMS (APCI) calcd for $C_{30}H_{40}NOS_2$ m/z 494.2546 $[M+H]^+$, found m/z 494.2545 $[M+H]^+$.

*1.4. General procedure for synthesis of D-π-A molecules **ISC 1-4***

Benzo[*b*]thieno[2,3-*d*]thiophen-3(2*H*)-one (0.23 g, 1.1 mmol) and pyrrolidine (0.1 mL) were added to a solution of 5-(4-alkyl-4*H*-thieno[3,2-*b*]-indol-2-yl)thiophene-2-carbaldehyde **3a-d** (1 mmol) in glacial acetic acid (7 mL) with stirring at room temperature. Then, the reaction mixture was heated to 120 °C and maintained at this temperature for 1.5 h. The formed precipitate was collected by filtration, washed with aqueous methanol, and dried to constant mass in air.

2-{[5-(4-Ethyl-4*H*-thieno[3,2-*b*]indol-2-yl)thiophen-2-yl]methylene}benzo[*b*]thieno[2,3-*d*]thiophen-3(2*H*)-one (ISC 1). Dark claret powder, m.p. 263-264 °C, yield 0.475 g (95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.95 – 7.88 (m, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.59 – 7.47 (m, 3H), 7.48 – 7.43 (m, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.38 – 7.30 (m, 2H), 7.22 – 7.16 (m, 1H), 4.36 (q, *J* = 7.3 Hz, 2H), 1.51 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.1, 148.6, 146.6, 146.3, 144.7, 141.1, 137.0, 136.6, 136.2, 132.6, 131.5, 131.1, 128.8, 128.5, 125.5, 124.7, 124.5, 123.4, 123.3, 121.6, 119.6, 119.3, 117.1, 109.9, 108.1, 39.9, 14.9. HRMS (ESI) m/z calcd for $C_{27}H_{18}NOS_4$ $[M+H]^+$: 500.0266, found: 500.0263. Anal. calcd for $C_{27}H_{17}NOS_4 \cdot 0.5CH_3COOH$: C, 63.49; H, 3.62, N, 2.64. Found: C, 63.68; H, 3.55, N, 2.80.

2-{[5-(4-Butyl-4*H*-thieno[3,2-*b*]indol-2-yl)thiophen-2-yl]methylene}benzo[*b*]thieno[2,3-*d*]thiophen-3(2*H*)-one (ISC 2). Claret powder, m.p. 244-245 °C, yield 0.507 g (96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.95 – 7.87 (m, 2H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.44 (d, *J* = 3.9 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.20 – 7.16 (m, 1H), 4.28 (t, *J* = 7.1 Hz, 2H), 1.95 – 1.83 (m, 2H), 1.47 – 1.36 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.2, 148.7, 146.7, 146.5, 145.2, 141.7, 137.1, 136.7, 136.3, 132.7, 131.6, 131.2, 128.9, 128.6, 125.6, 124.8, 124.6, 123.5, 123.4, 121.6, 119.7, 119.4, 117.0, 110.2, 108.3, 45.2, 32.1, 20.6, 14.0. HRMS (APCI) m/z calcd for $C_{29}H_{22}NOS_4$ $[M+H]^+$: 528.0579, found: 528.0575. Anal. calcd for $C_{29}H_{21}NOS_4 \cdot 0.2CH_3COOH$: C, 65.42; H, 4.07, N, 2.60. Found: C, 65.44; H, 3.92, N, 2.72.

2-{[5-(4-(2-Ethylhexyl)-4*H*-thieno[3,2-*b*]indol-2-yl)thiophen-2-yl]methylene}benzo[*b*]thieno[2,3-*d*]thiophen-3(2*H*)-one (ISC 3). Claret powder, m.p. 197-198 °C, yield 0.486 g (83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.87 – 7.80 (m, 2H), 7.68 (d, J = 7.8 Hz, 1H), 7.50 – 7.39 (m, 2H), 7.36 – 7.27 (m, 3H), 7.24 – 7.11 (m, 3H), 4.14 – 3.99 (m, 2H), 2.06 – 1.96 (m, 1H), 1.45 – 1.23 (m, 8H), 0.98 – 0.85 (m, 6H). ^{13}C NMR (126 MHz, $CDCl^3$) δ 180.9, 148.6, 146.5, 146.4, 145.6, 141.9, 137.0, 136.6, 136.2, 132.5, 131.5, 131.0, 128.7, 128.4, 125.4, 124.6, 124.4, 123.4, 123.2, 121.5, 119.6, 119.3, 116.9, 110.3, 108.2, 49.5, 40.0, 30.9, 28.8, 24.5, 23.2, 14.2, 11.0. HRMS (ESI) m/z calcd for $C_{33}H_{30}NOS_4$ $[M+H]^+$: 584.1205, found: 584.1203. Anal. calcd for $C_{33}H_{29}NOS_4\cdot 0.3CH_3COOH$: C, 67.05; H, 5.06, N, 2.33. Found: C, 66.86; H, 4.75, N, 2.42.

2-{[5-(4-Pentadecyl-4*H*-thieno[3,2-*b*]indol-2-yl)thiophen-2-yl]methylene}benzo[*b*]thieno[2,3-*d*]thiophen-3(2*H*)-one (ISC 4). Dark claret powder, m.p. 154-155 °C, yield 0.655 g (96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.89 – 7.81 (m, 2H), 7.69 (d, J = 7.8 Hz, 1H), 7.55 – 7.41 (m, 2H), 7.39 – 7.33 (m, 2H), 7.31 (d, J = 6.9 Hz, 1H), 7.20 – 7.13 (m, 1H), 4.23 (t, J = 7.0 Hz, 2H), 1.95 – 1.81 (m, 2H), 1.40 – 1.15 (m, J = 48.8 Hz, 26H), 0.86 (t, J = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.0, 148.6, 146.6, 146.5, 145.2, 141.6, 137.1, 136.6, 136.2, 132.6, 131.6, 131.1, 128.8, 128.5, 125.5, 124.7, 124.4, 123.4, 123.3, 121.6, 119.6, 119.3, 117.0, 110.1, 108.2, 45.4, 32.1, 29.9, 29.84, 29.82, 29.80, 29.79, 29.78, 29.74, 29.67, 29.5, 27.3, 22.8, 14.3. HRMS (APCI) m/z calcd for $C_{40}H_{44}NOS_4$ $[M+H]^+$: 682.2300, found: 682.2295. Anal. calcd for $C_{40}H_{43}NOS_4\cdot 0.3CH_3COOH$: C, 69.66; H, 6.36, N, 2.00. Found: C, 69.37; H, 6.13, N, 2.12.

Table S1 Photos of D-π-A compounds **ISC 1-4**

 **ISC 1**	 **ISC 2**
 **ISC 3**	 **ISC 4**

1.5. 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 deuterosolvents $CDCl_3$ (δ_C 77.2) were references for ^{13}C NMR spectra. Melting points were determined on a Boetius apparatus. High-resolution mass spectra were studied on a Bruker maXis Impact HD spectrometer. Elemental analysis was carried out on a CHN PE 2400 Series II Perkin Elmer Instrument automated analyzer. Thermogravimetric studies were performed on a Mettler Toledo TGA / DSC 1 device under air (30 ml/min) with a heating rate of 10 °C/min in the range of 30-800 °C.

The frontier molecular orbitals of the **ISC 1-4** were calculated using density functional theory. Computing was carried out in the Orca 4.0.1 software package using the DFT B3LYP, 6-311G* method. Electronic absorption and emission spectra of solutions of D-π-A molecules **ISC 1-4** were obtained on a Shimadzu UV-2401PC dual-beam spectrophotometer and a Cary Eclipse spectrofluorimeter. A Shimadzu UV-3101PC dual-beam spectrophotometer was used for thin layers. For the UPS measurements, an UV (He I, 21.21 eV) light source and an AXIS Ultra DLD spectrometer (Kratos Analytical) were employed.

All measurements of the surface relief were carried out on a Solver Next (Nt-MDT) scanning probe microscope using the semicontact method. The X-ray diffraction patterns of thin films were collected on a D8 ADVANCE Bruker x-ray diffractometer in air at room temperature (Cu-Kα radiation). Micrographs of thin films **ISC 4** were obtained using a Nikon LV 100 optical inspection microscope.

The carrier mobility was determined by the MIS-CELIV method using sandwich-type samples prepared as follows. A glassy substrate was coated with an ITO (mixture of In_2O_3 and SnO_2) conductive layer and then with a 70-nm SiO_2 layer. Then, it was successively coated with a layer of the compound under study (layer thickness d = 100 nm) and with an Al layer (d = 80 nm) as a counterelectrode. The SiO_2 insulating layer played the role of the blocking layer for both types of charge carriers, i.e., it precluded injection of the charge carriers from ITO. When measuring the transient hole current, a positive potential linearly increasing at a rate of $A = 5 \cdot 10^4$ V/s was applied to ITO; this was accompanied by the extraction of holes at the Al electrode. To measure the electron mobility, the polarity of the potential applied to the electrode was reversed. The characteristic time (t_{max}) corresponding to the maximum transient conduction current was determined using the current signal detected at the load resistor of a DL-Analog Discovery (Digilent Co.) oscilloscope. The carrier mobility was calculated using the expression $\mu = 2d^2/(At^2_{\mathrm{max}})$.[1]

The current–voltage characteristics of photovoltaic cells were measured using Labview program, Keithley 2400 source measurement unit and Oriel 9600 solar simulator (Newport Corp.) at intensity 100 mW/cm^2 (AM 1.5G conditions) in a glove-box with dry atmosphere of argon.

1.6. Device fabrication

Perovskite solar cells with inverted planar architecture ITO/NiO (10 nm)/$MAPbI_3$ (400 nm)/**ISC 1-3 (20 nm)**/BCP (8 nm)/Al (80 nm) were fabricated under dry argon atmosphere in a glovebox. Sequential deposition of layers of nickel oxide NiO, methylammonium lead iodide $MAPbI_3$ and **$PC_{60}BM$** (for reference devices) onto a transparent conductive base sheet (ITO/glass from Kaivo) was carried out according to the method described in the literature.[2] A layer **ISC 1-3** with 20 nm thickness was deposited from $CHCl_3$ solution (~10 mg/L) using spin-coating technique at a speed of 3000 rpm (45 s) or thermal vacuum evaporation in case **ISC 1**. Then the resulting films were annealed at a temperature of 90 °C for 15 minutes. The next layers of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine, BCP) (8 nm) and Al electrode (80 nm) were deposited sequentially by thermal vacuum evaporation.

1.7. Experimental data of D-π-A molecules ***ISC 1-4***

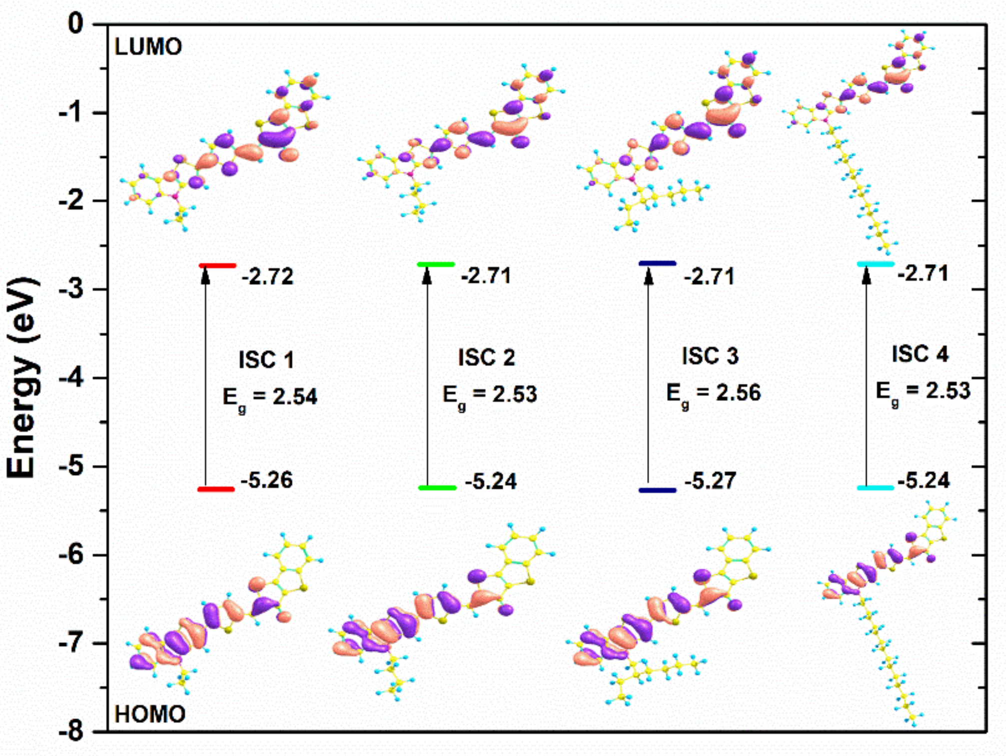

Fig. S1 Frontier HOMO and LUMO orbitals of the **ISC 1-4**.

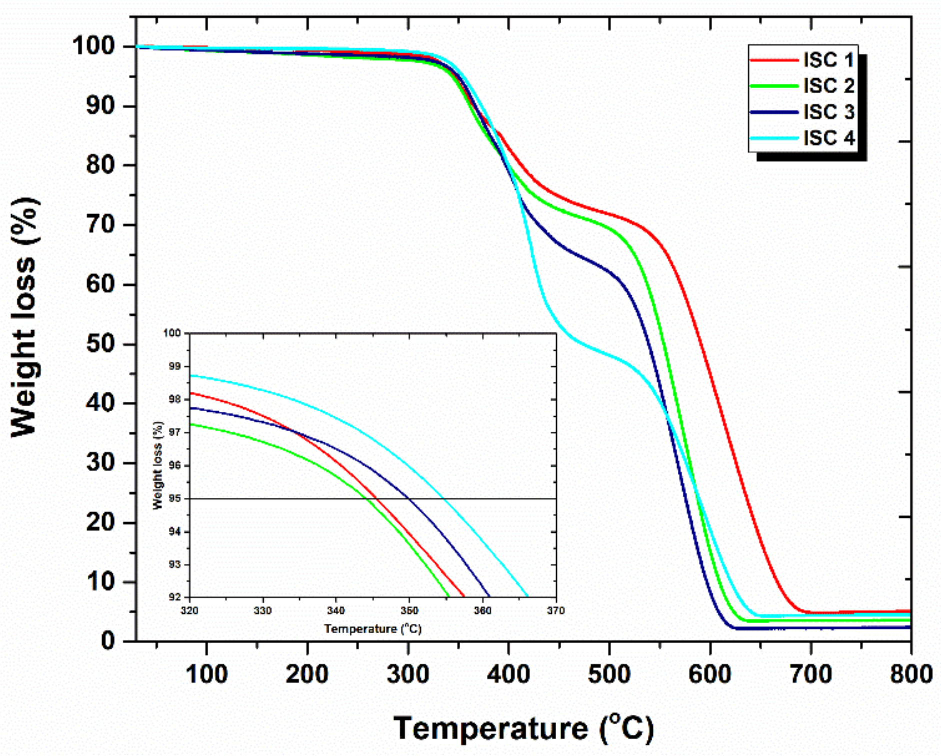

Fig. S2 Thermogravimetric analysis of the **ISC 1-4**.

Indexing was performed in the DICVOL06[3] and TOPAS[4] programs - the result is identical. Structureless refinement was performed in the TOPAS program.[4]

Table S2 Parameters of the unit cell of the powder sample **ISC 1**

SG	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
P-1	14.936	19.181	27.737	93.04	105.97	72.03

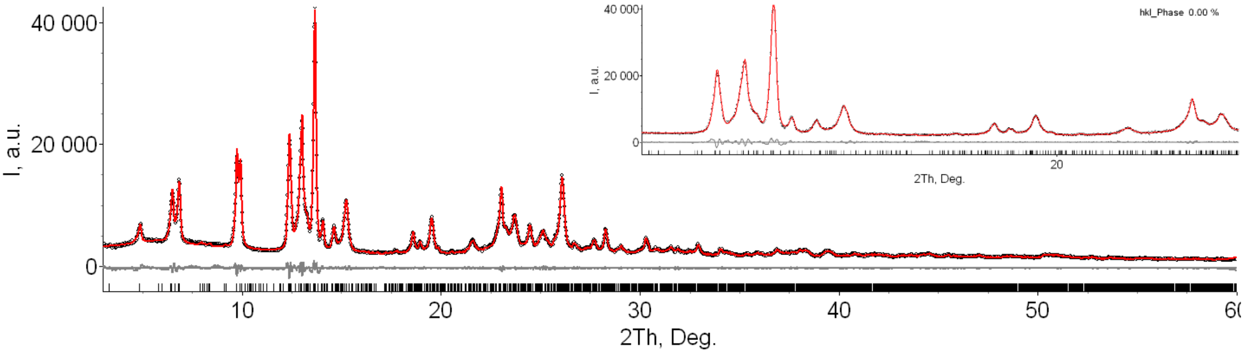

Fig. S3 The results of a structureless full-profile refinement of the diffraction pattern of the sample **ISC 1** with the found unit cell parameters (Rwp=3.9%, Rb=0.122). The inset shows an enlarged fragment.

Table S3 Parameters of the unit cell of the powder sample **ISC 2**

SG	a (Å)	b (Å)	c (Å)	β (°)
P21/m	38.345	14.413	15.418	112.4186

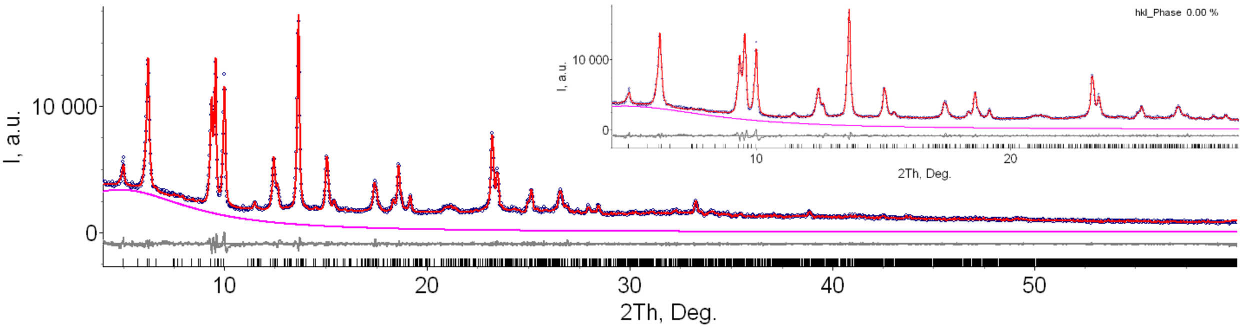

Fig. S4 The results of a structureless full-profile refinement of the diffraction pattern of the sample **ISC 2** with the found unit cell parameters (R_{wp}=3.6%, R_b=0.113). The inset shows an enlarged fragment.

Table S4 Parameters of the unit cell of the powder sample **ISC 3**

SG	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
P-1	17.603	24.443	35.467	82.01	75.67	75.631

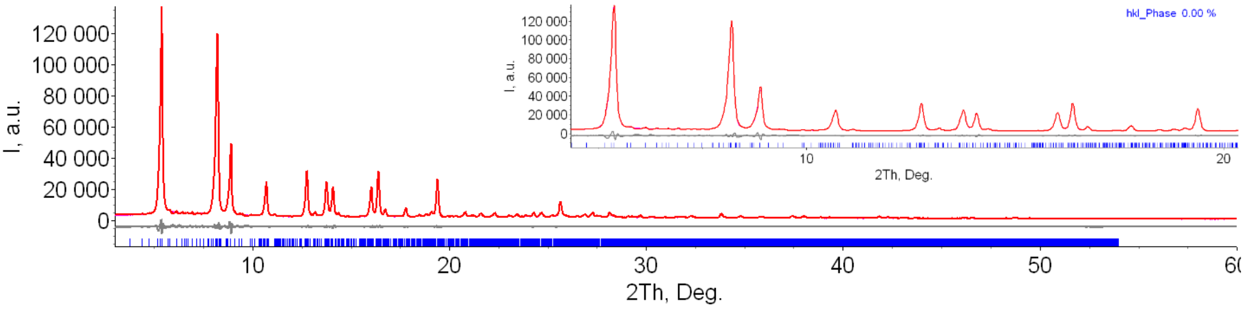

Fig. S5 The results of a structureless full-profile refinement of the diffraction pattern of the sample **ISC 3** with the found unit cell parameters (R_{wp}=4.9%, R_b=0.177). The inset shows an enlarged fragment.

Table S5 Parameters of the unit cell of the powder sample **ISC 4**

SG	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
P-1	32.190	28.372	40.121	128.57	124.473	36.30

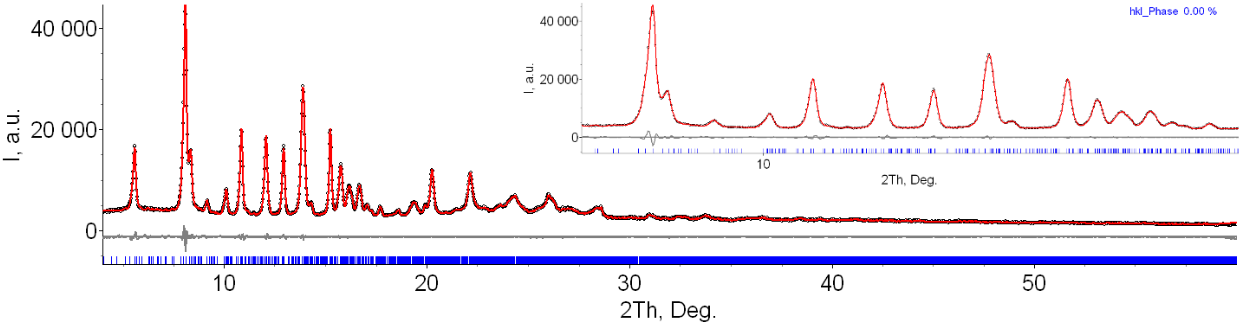

Fig. S6 The results of a structureless full-profile refinement of the diffraction pattern of the sample **ISC 4** with the found unit cell parameters (R_{wp}=3.2%, R_b=0.071). The inset shows an enlarged fragment.

1.7. Photovoltaic performance of the PSCs with ETL based on ***ISC 1***

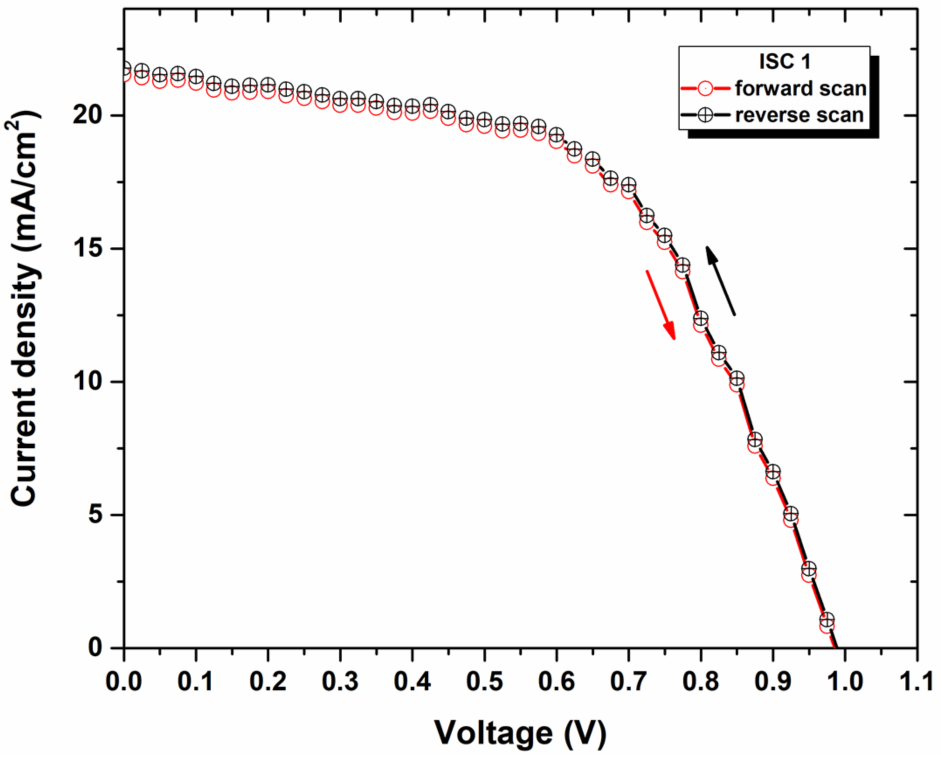

Fig. S7 Forward and reverse scan *J-V* curves for best performing PSCs with ETL based on **ISC 1**

2. References

1. V. V. Malov, T. Ghosh, V. C. Nair, M. M. Maslov, K. P. Katin, K. N. Narayanan Unni, A. R. Tameev, *Mendeleev Communications*, 2019, **29**, 218–219.

2. D.S. Saranin, V. N. Mazov, L. O. Luchnikov, D. A. Lypenko, P. A. Gostishev, D. S. Muratov, D. A. Podgorny, D. M. Migunov, S. I. Didenko, M. N. Orlova, D. V. Kuznetsov, A. R. Tameev, A. Di Carlo, *Journal of Materials Chemistry C,* 2018, **6**, 6179–6186.

3. DIFFRACPlus: TOPAS Bruker AXS GmbH, Ostliche. Rheinbruckenstraße 50, D-76187, Karlsruhe, Germany. 2008

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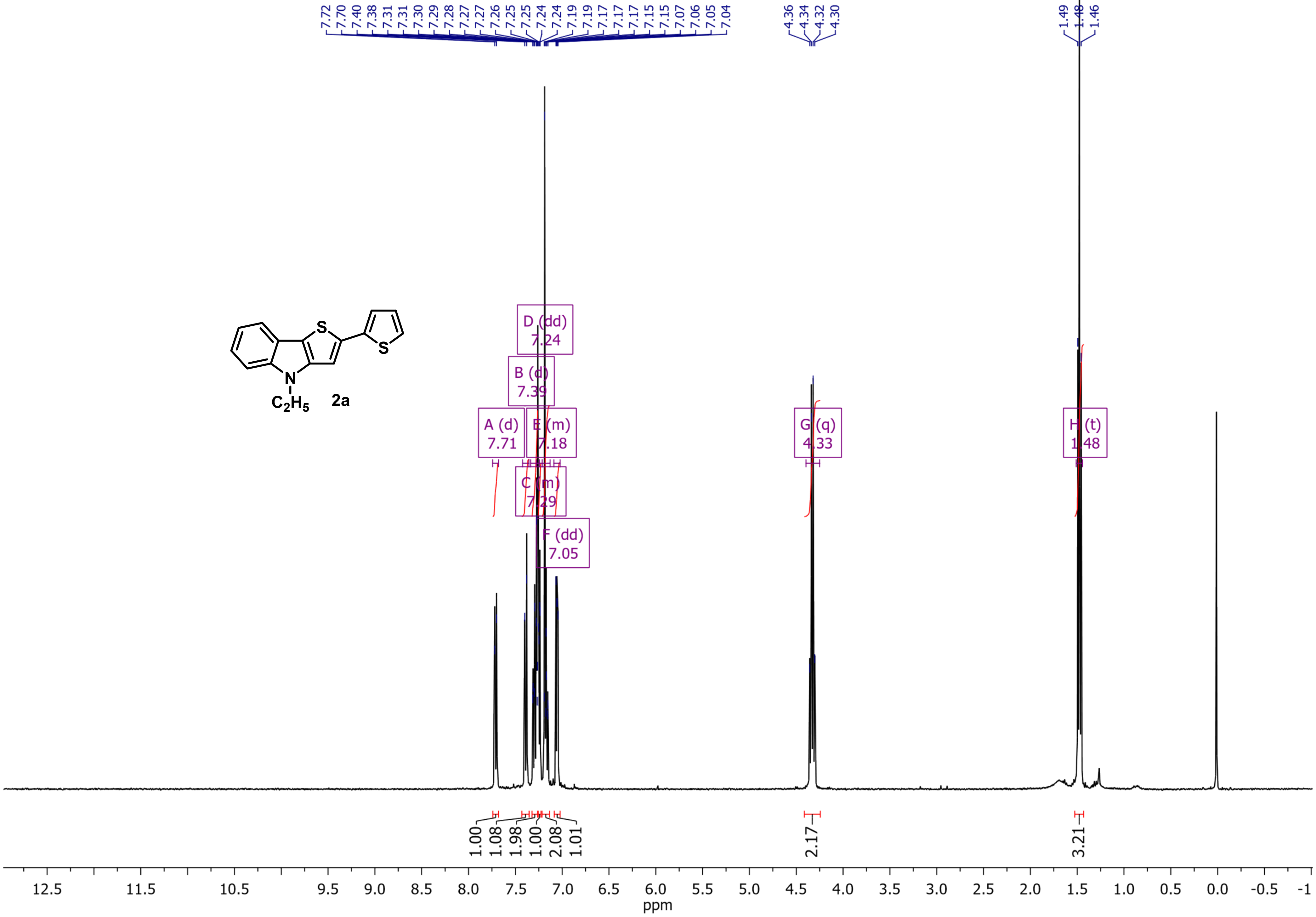
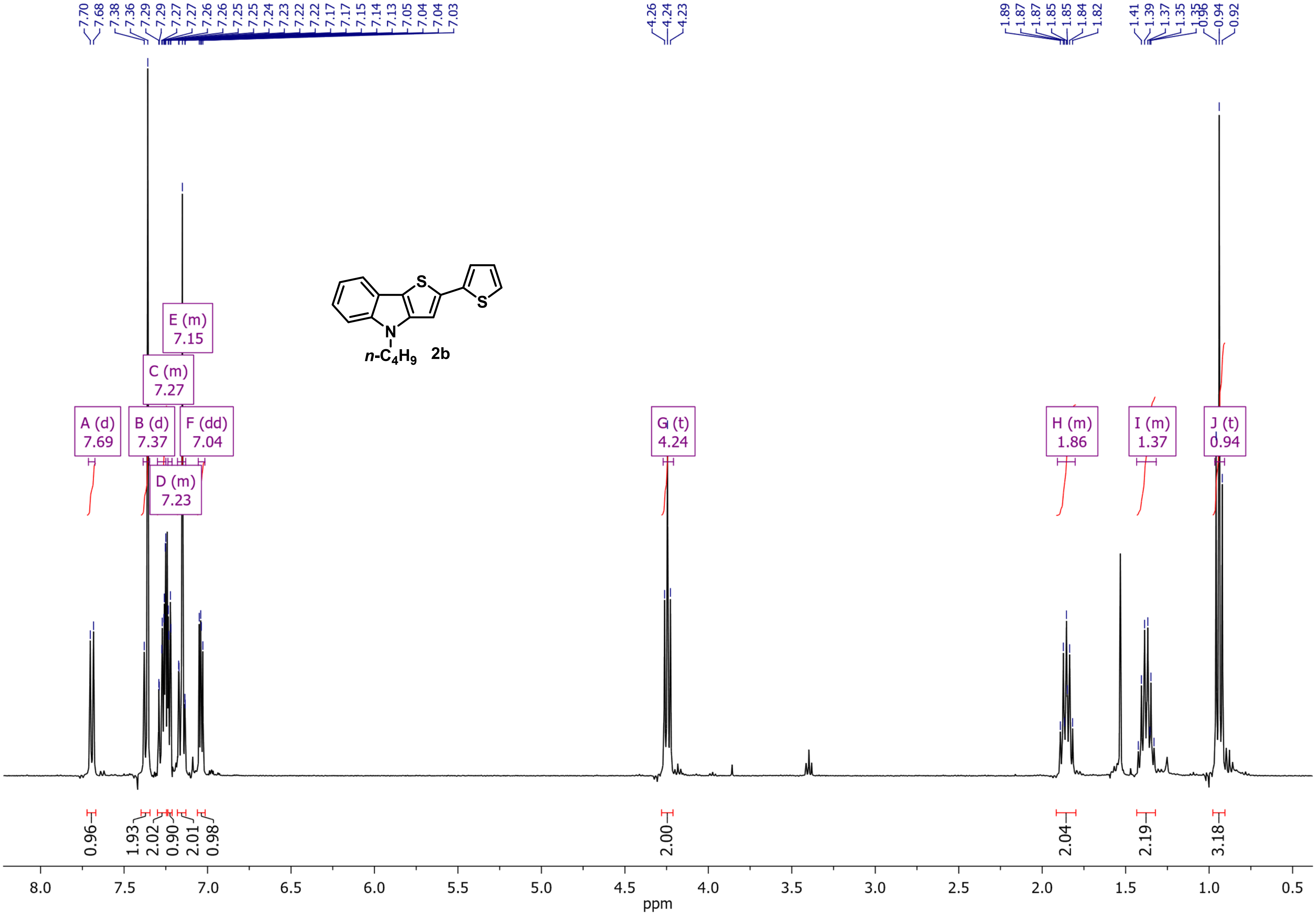
3. Copies of ^{1}H and ^{13}C NMR spectra

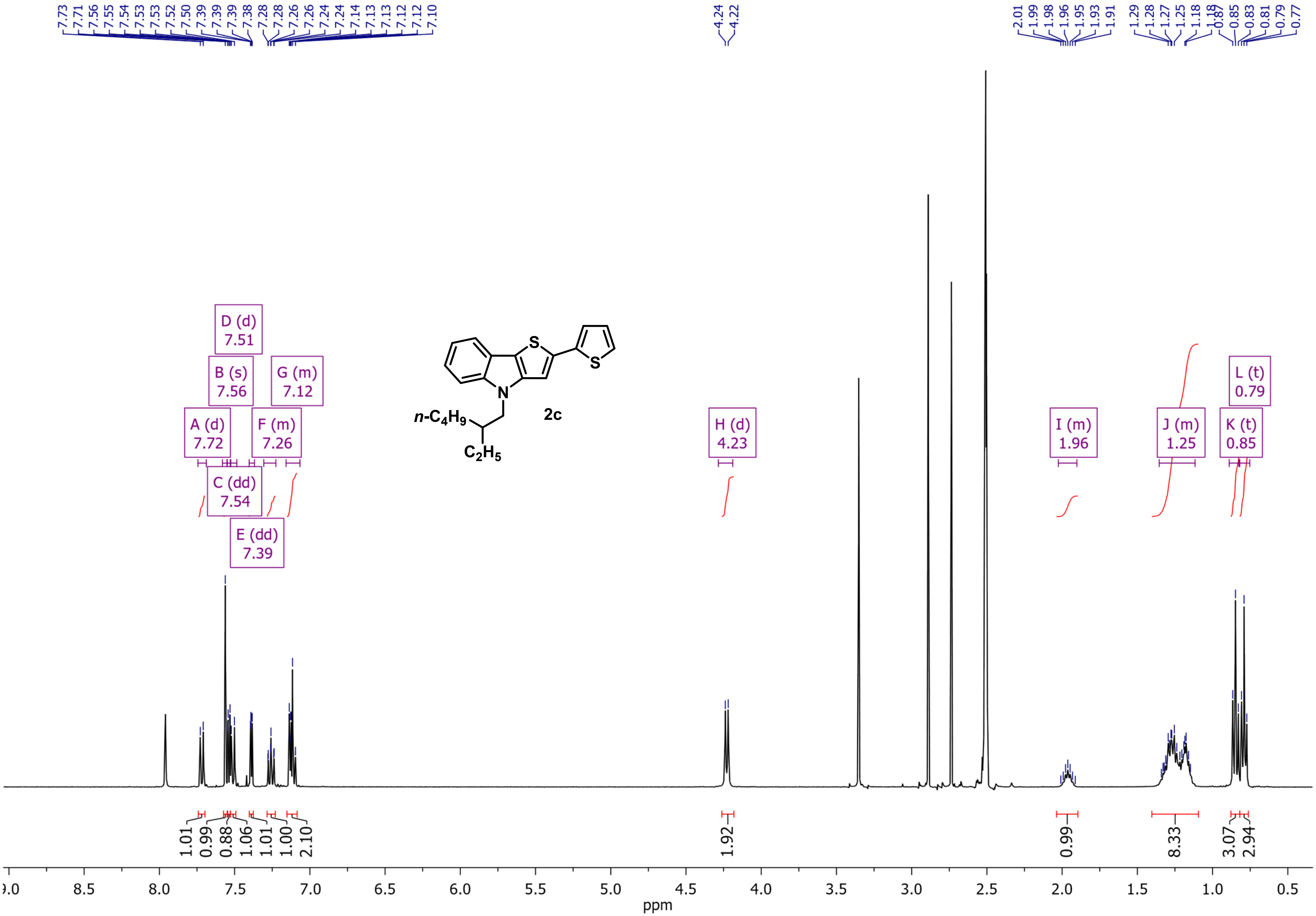
^{1}H NMR (solvent: $CDCl_3$) [a crude sample of compound **2a**]



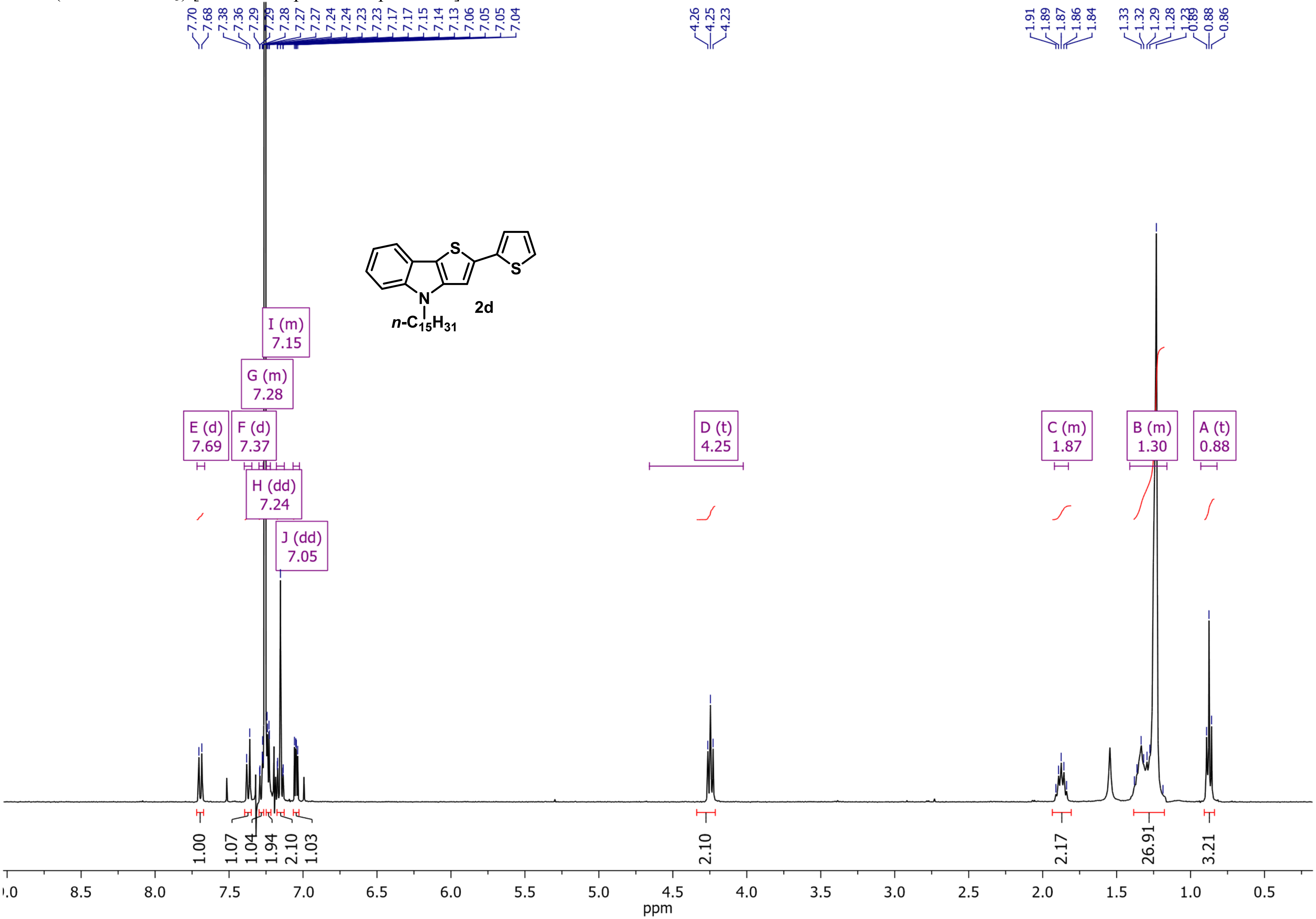
^{1}**H NMR** (solvent: $CDCl_3$) [a crude sample of compound **2b**]



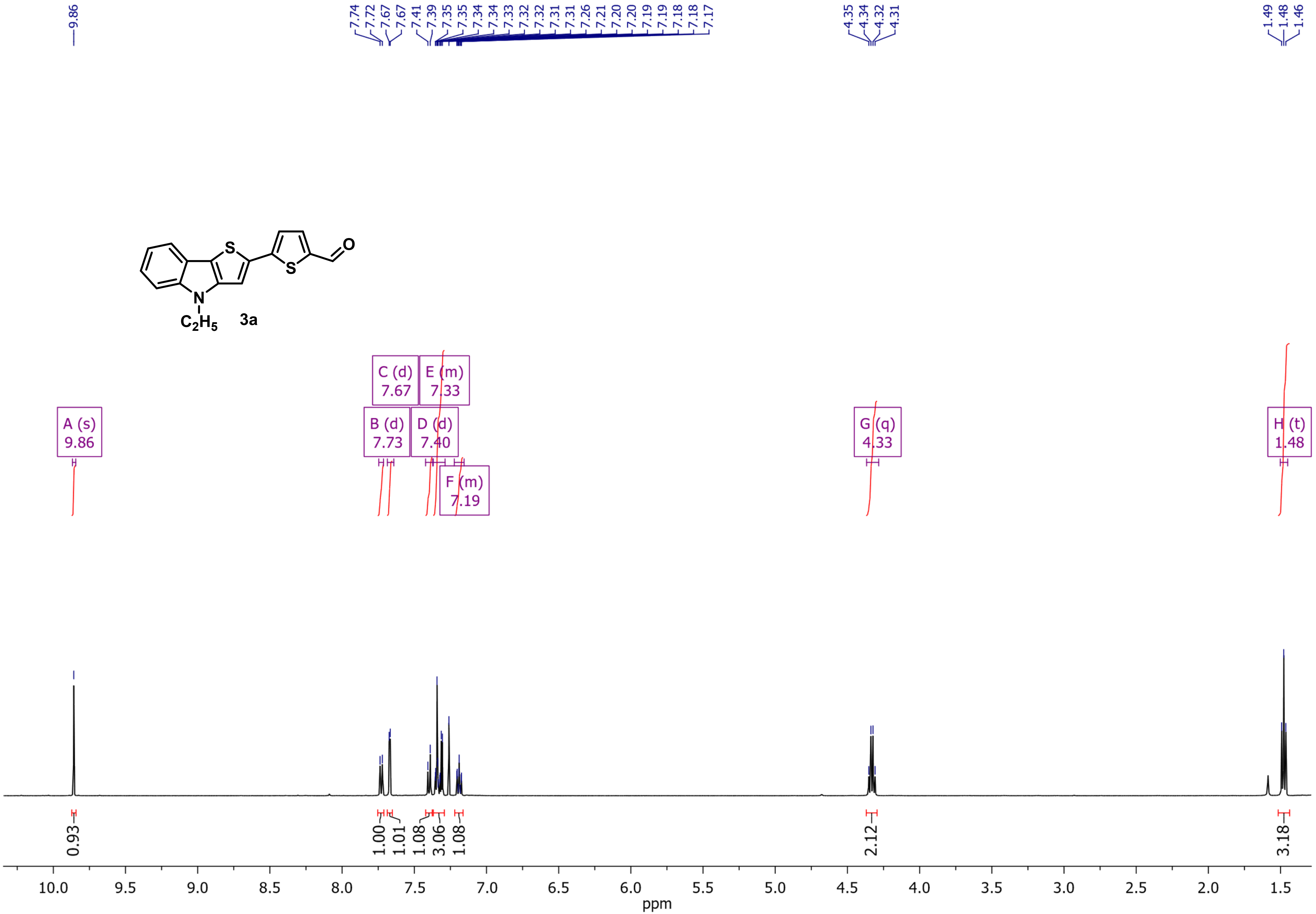
^{1}H NMR (solvent: $CDCl_3$) [a crude sample of compound **2c**]



^{1}H NMR (solvent: CDCl$_3$) [a crude sample of compound **2d**]

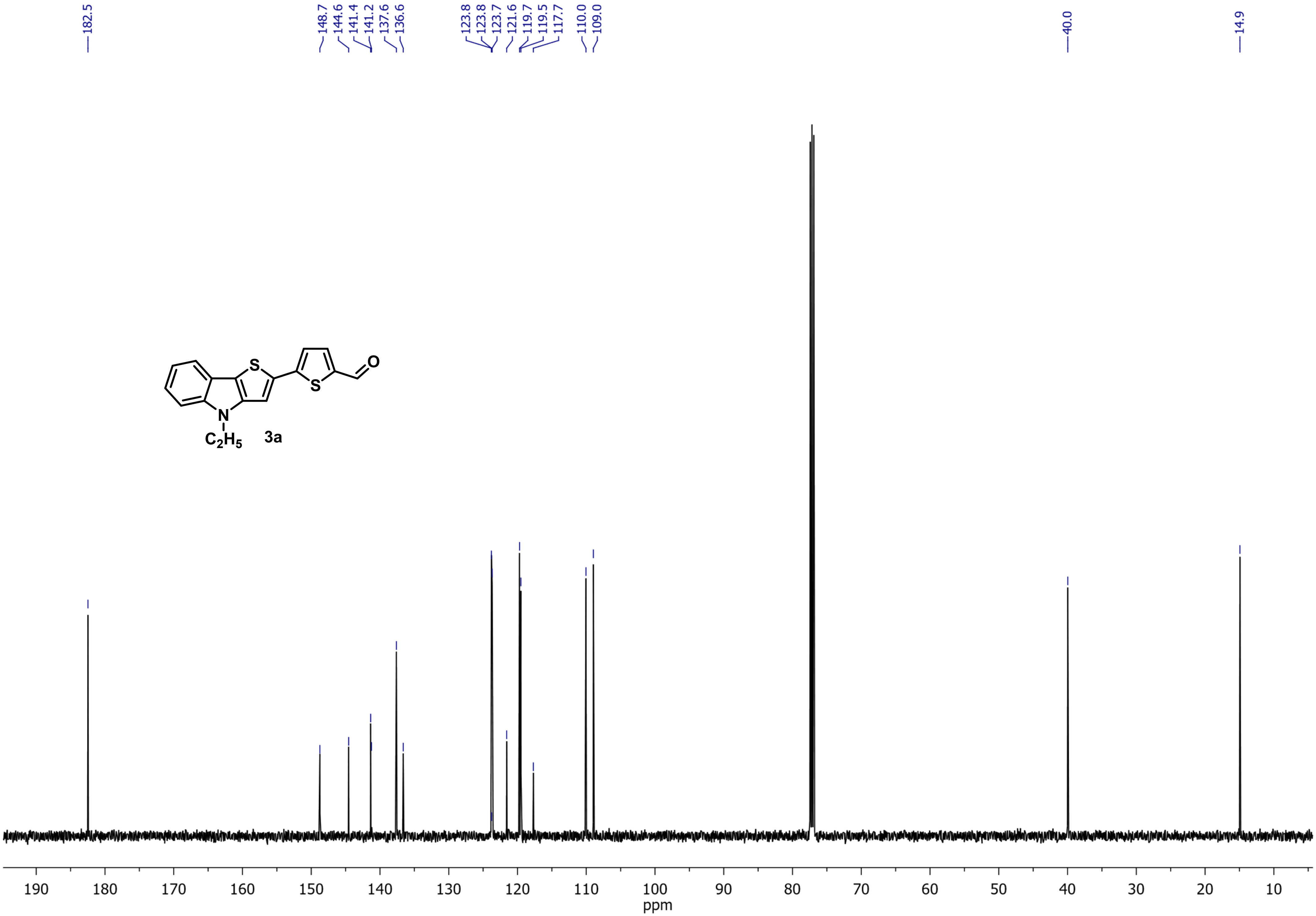


^{1}**H NMR** (solvent: $CDCl_3$)

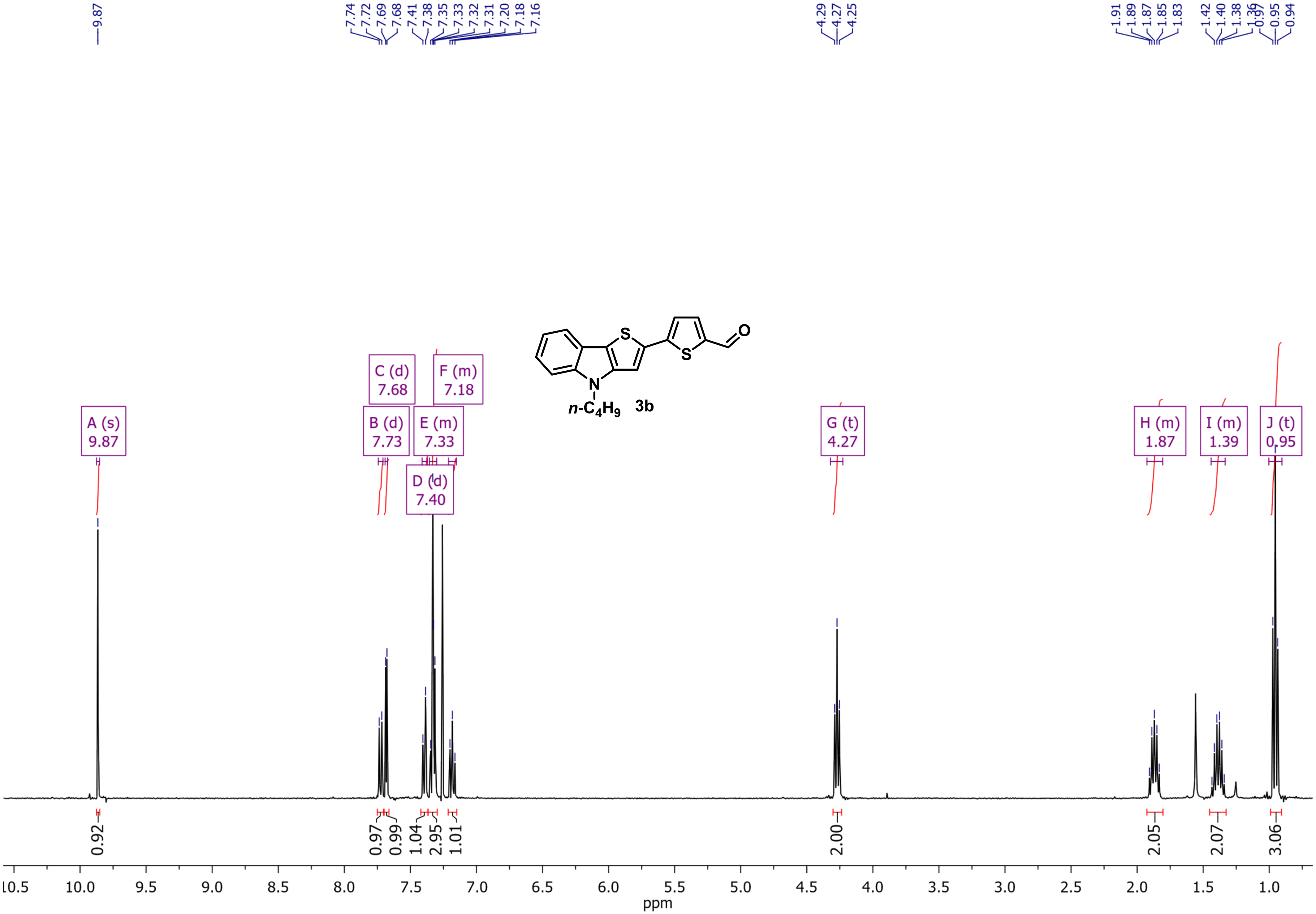


3a

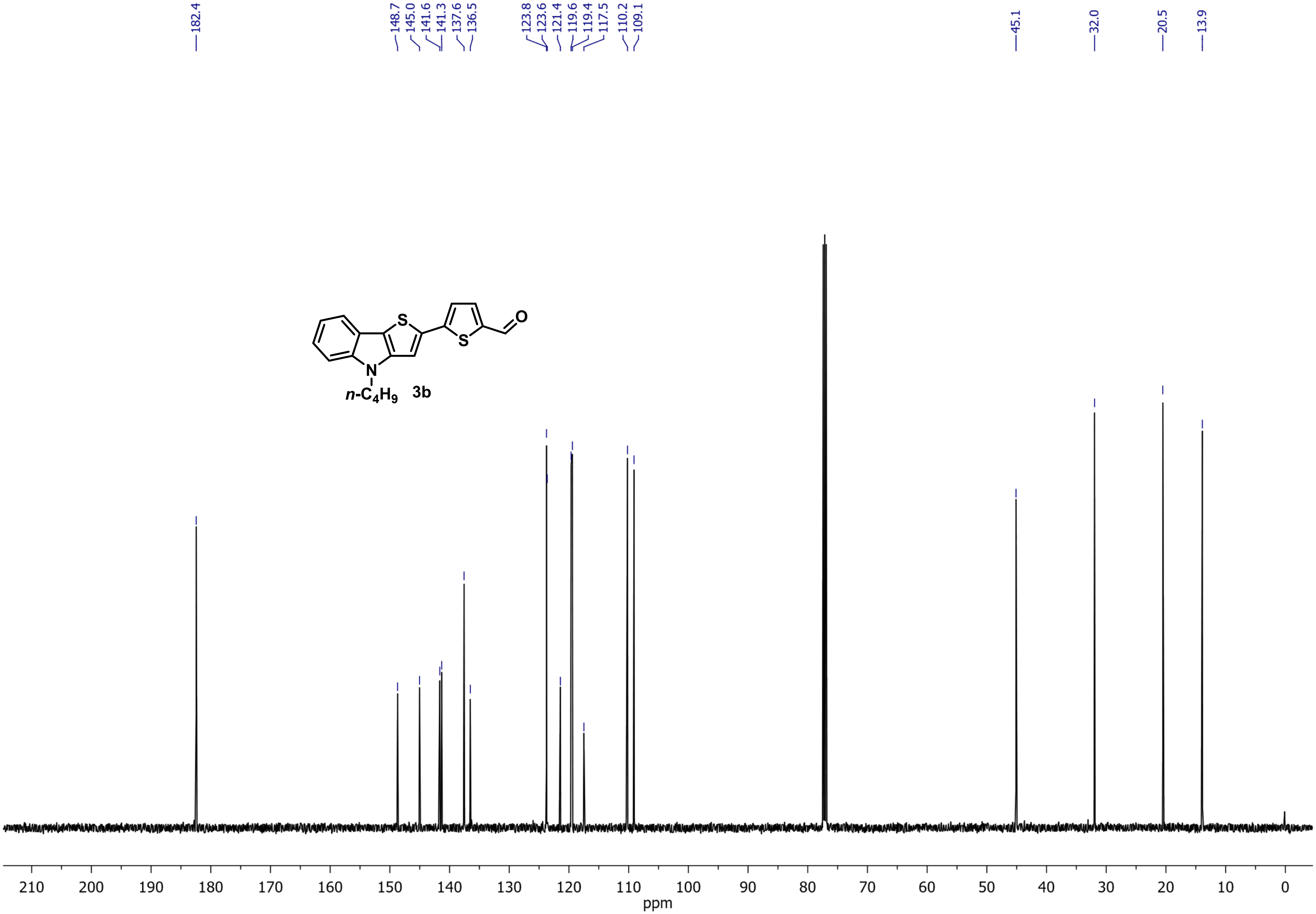
^{13}**C NMR** (solvent: $CDCl_3$)



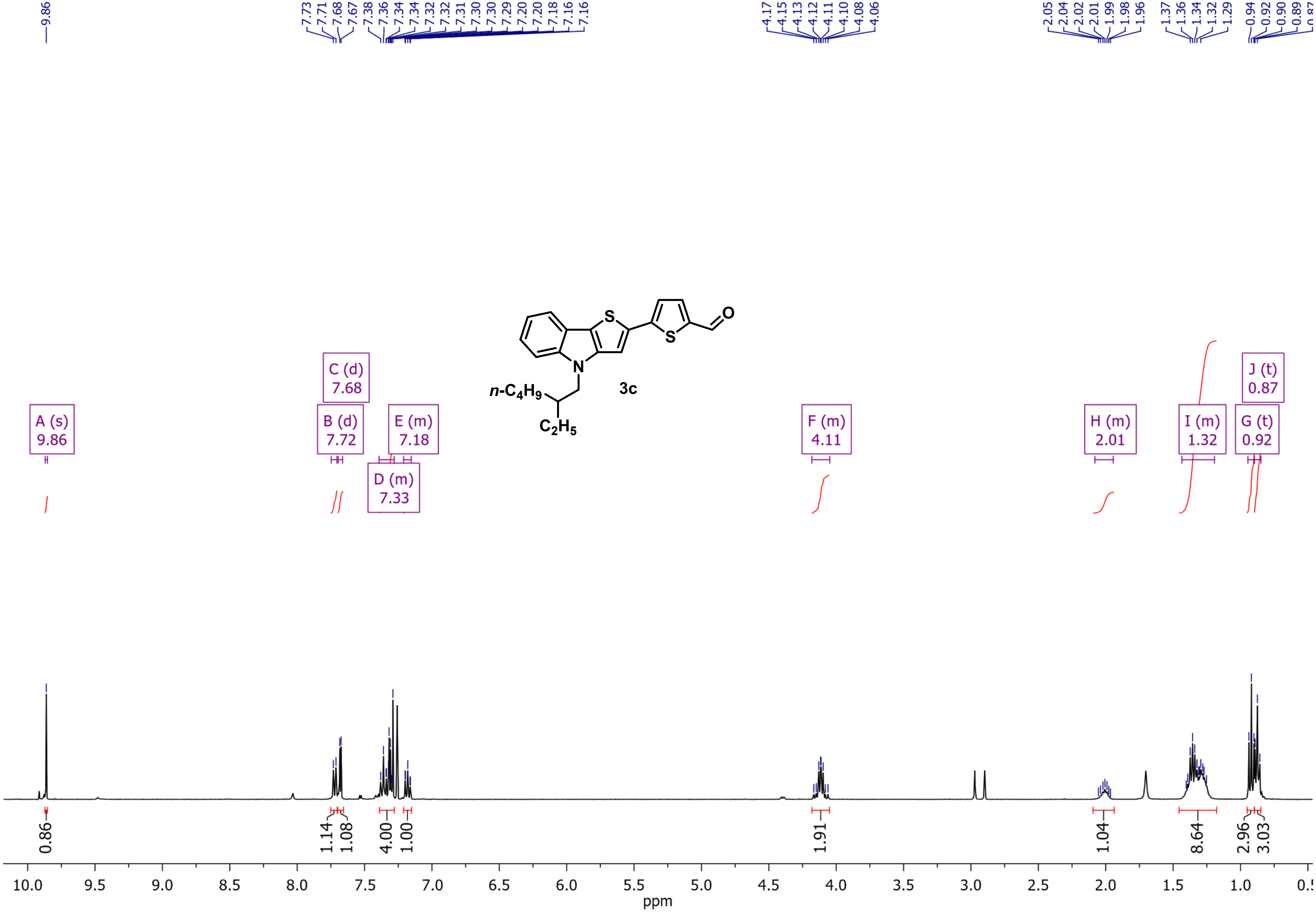
^{1}**H NMR** (solvent: $CDCl_3$)



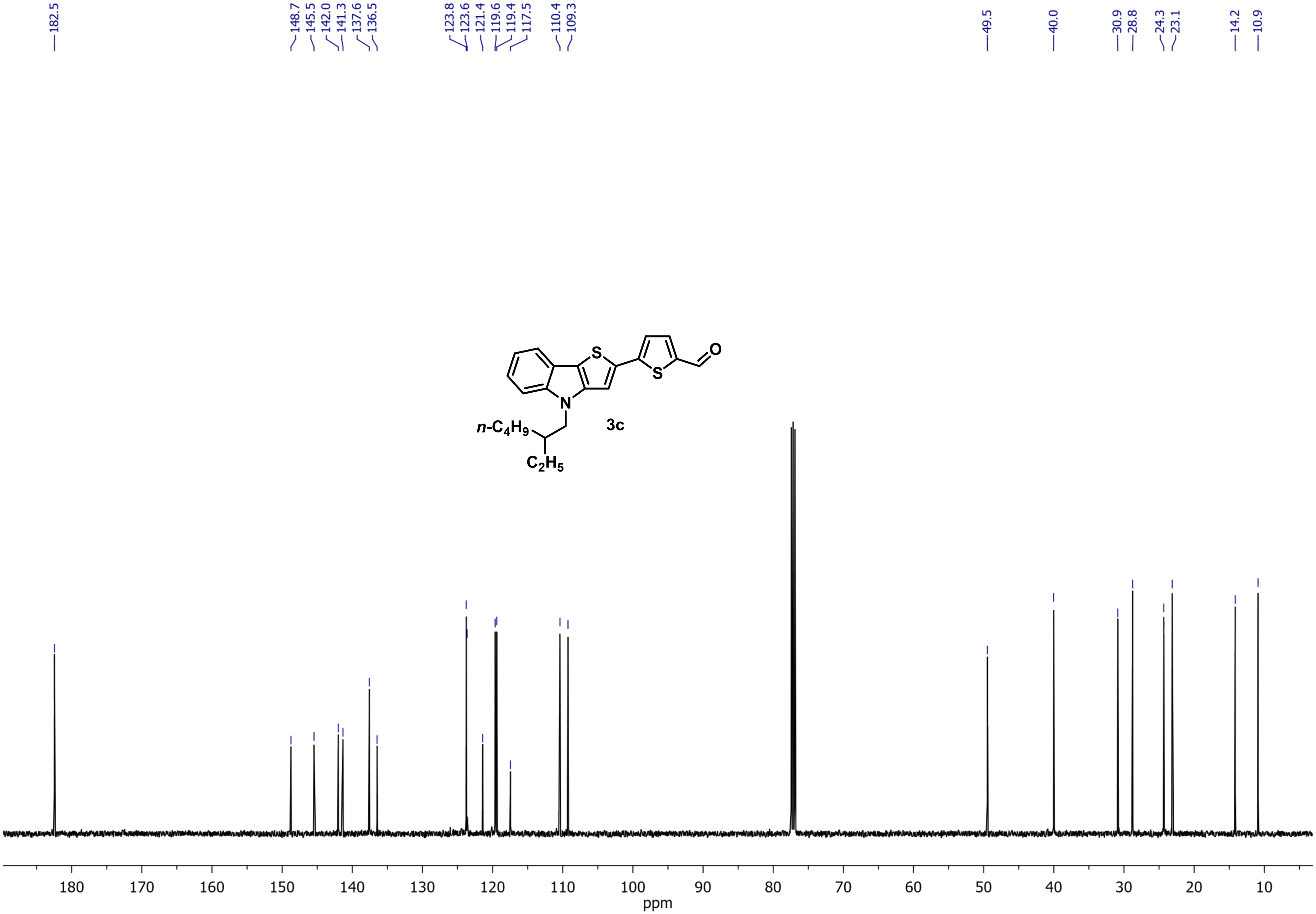
^{13}**C NMR** (solvent: $CDCl_3$)



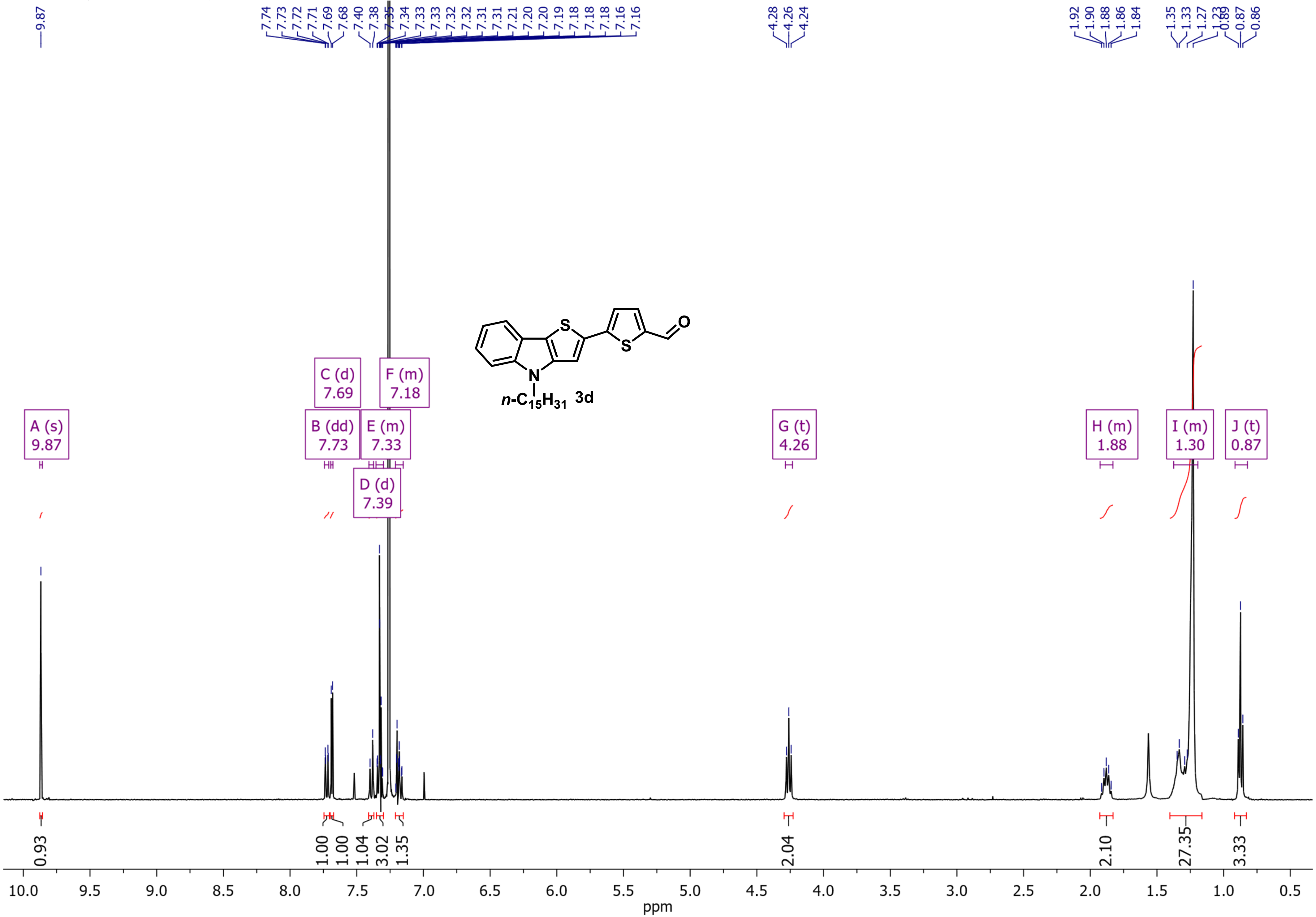
^{1}H NMR (solvent: $CDCl_3$)



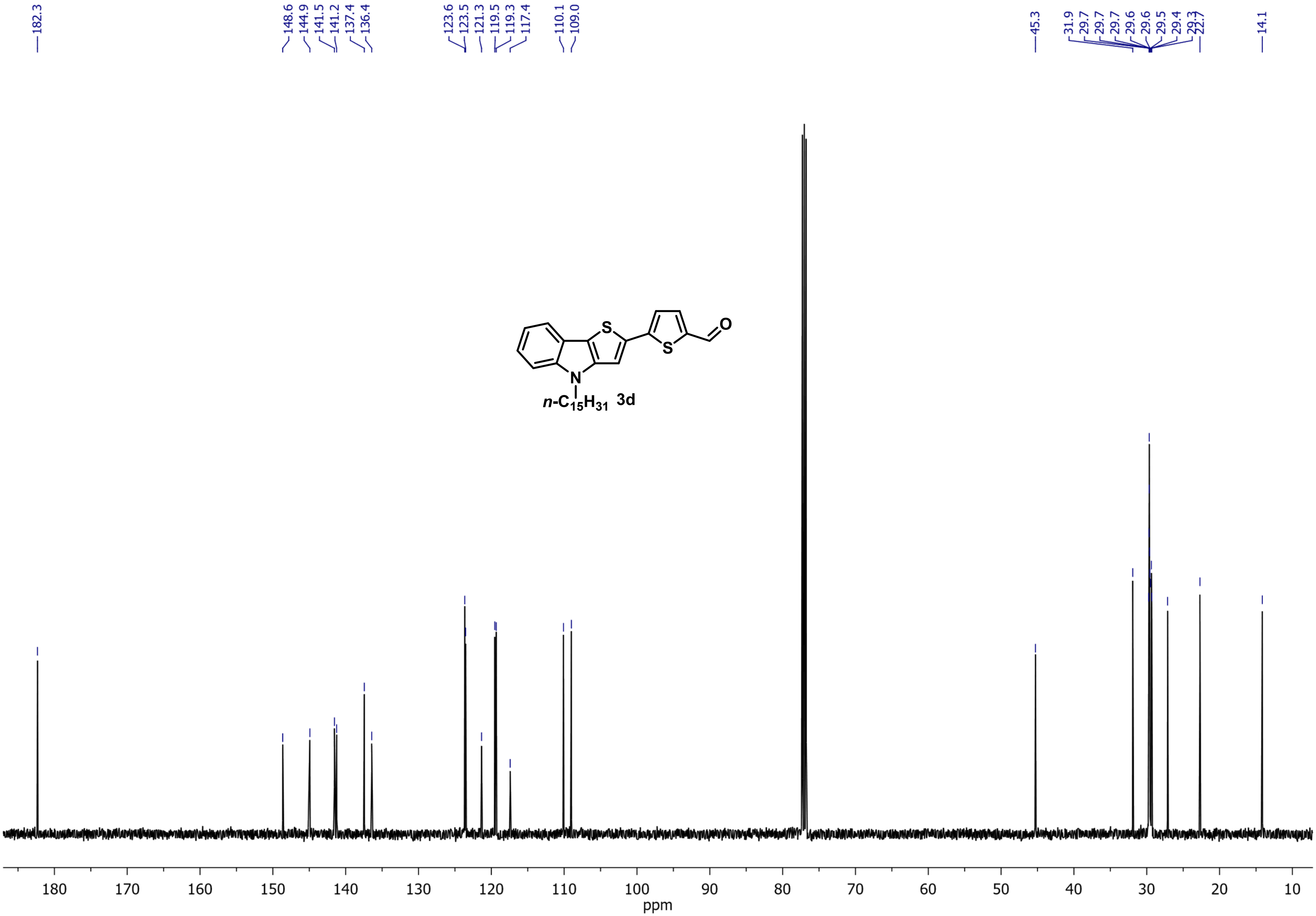
^{13}C NMR (solvent: $CDCl_3$)



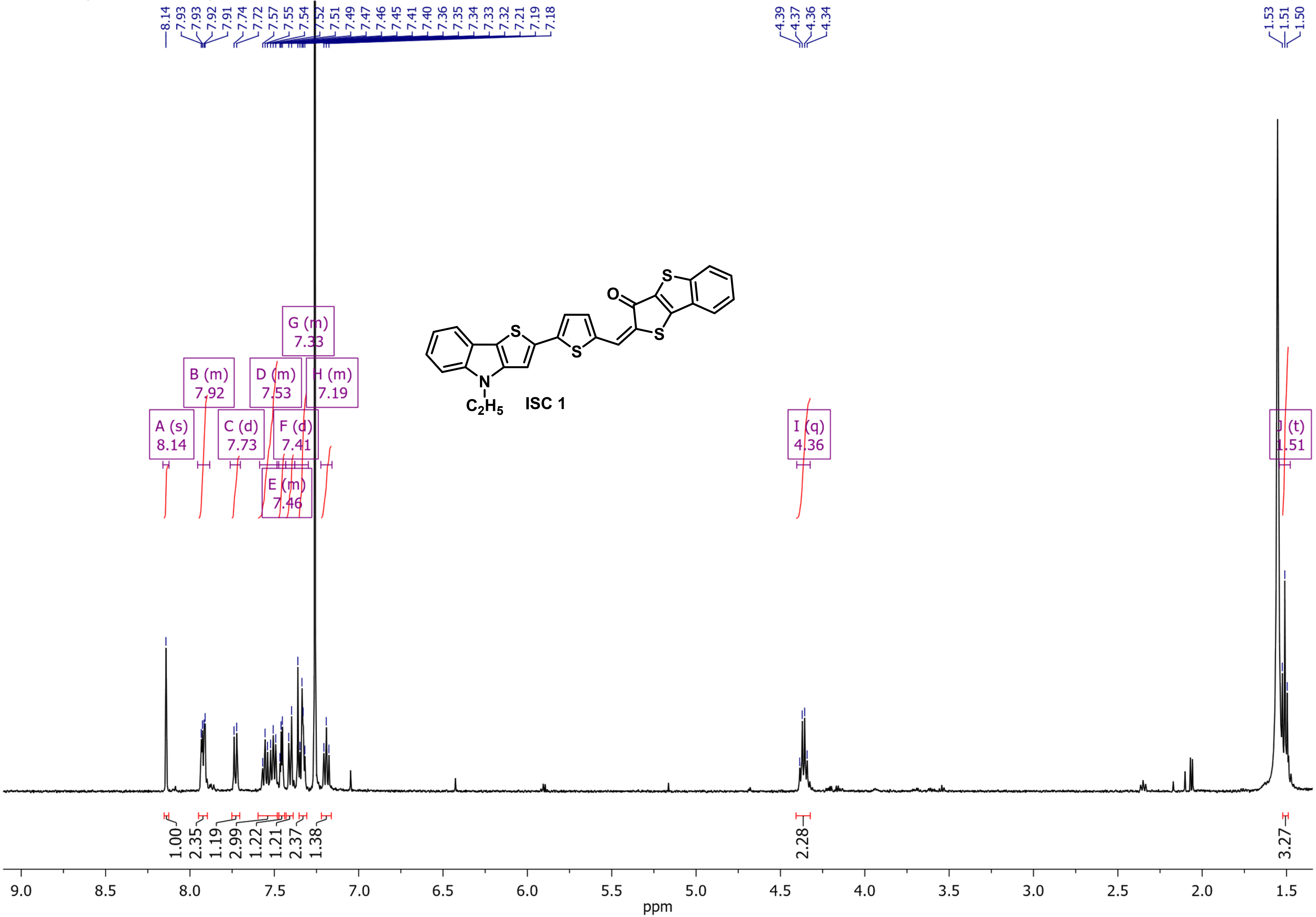
^{1}**H NMR** (solvent: $CDCl_3$)



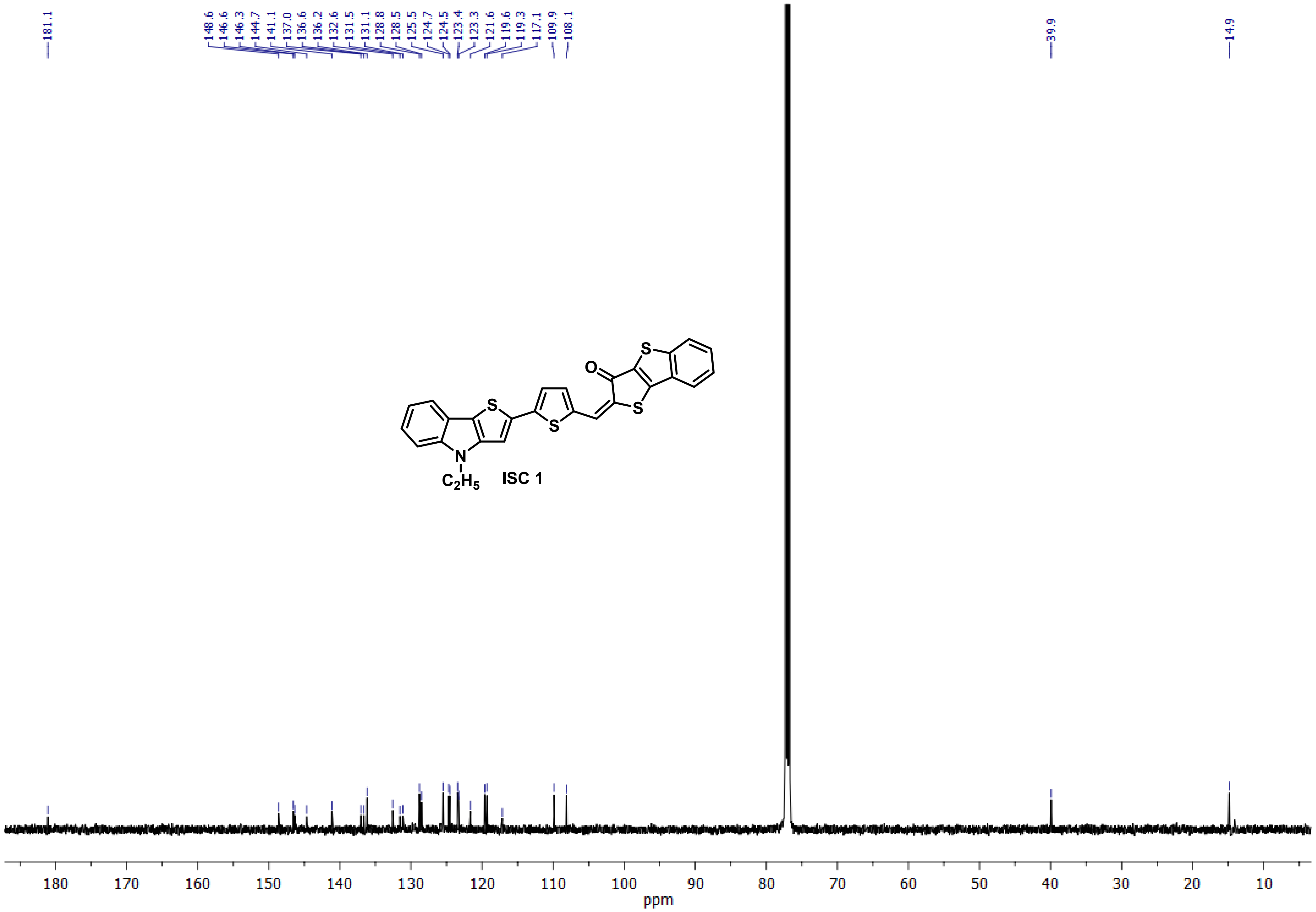
^{13}**C NMR** (solvent: $CDCl_3$)



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

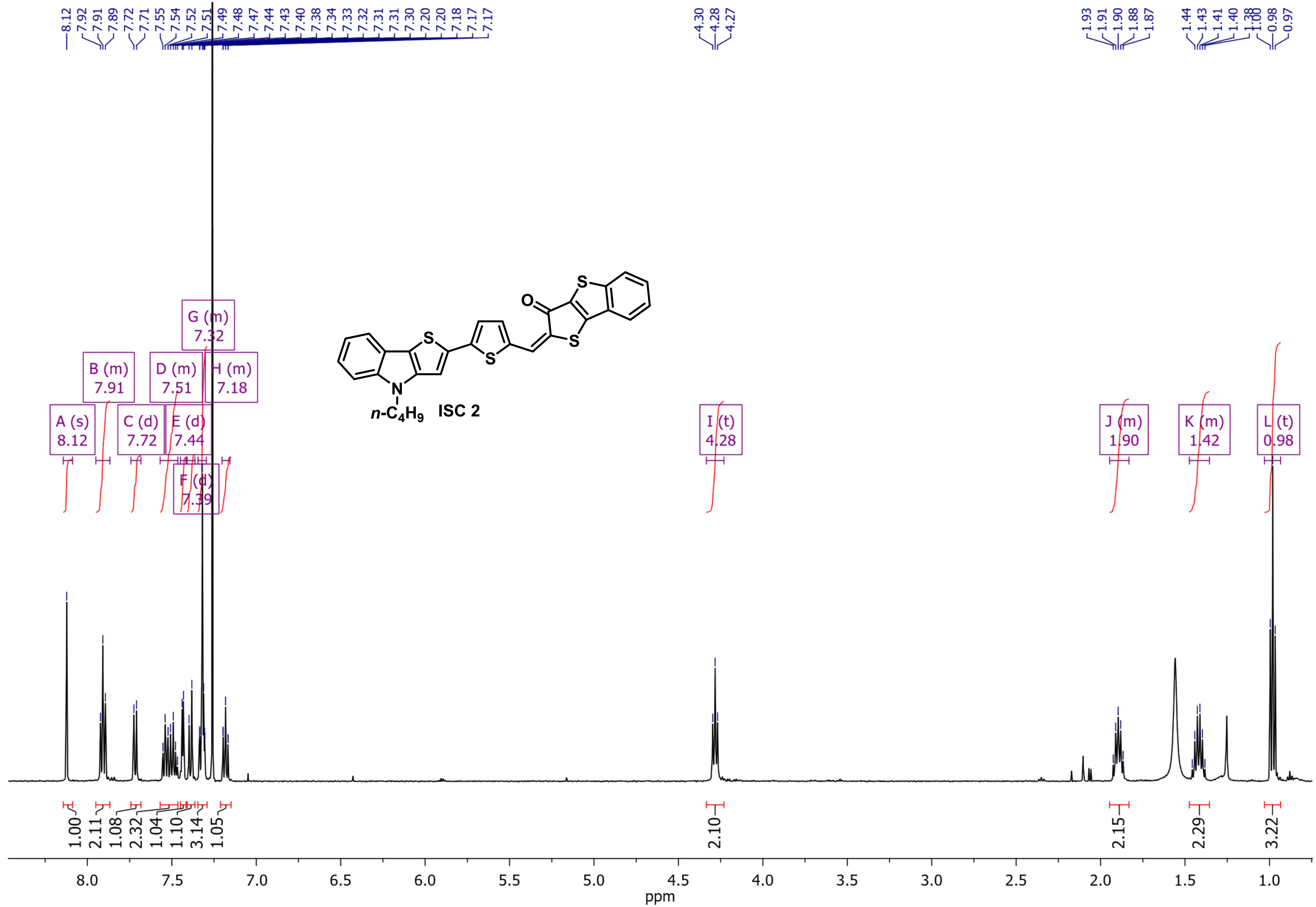


^{13}C NMR (solvent: $CDCl_3$)

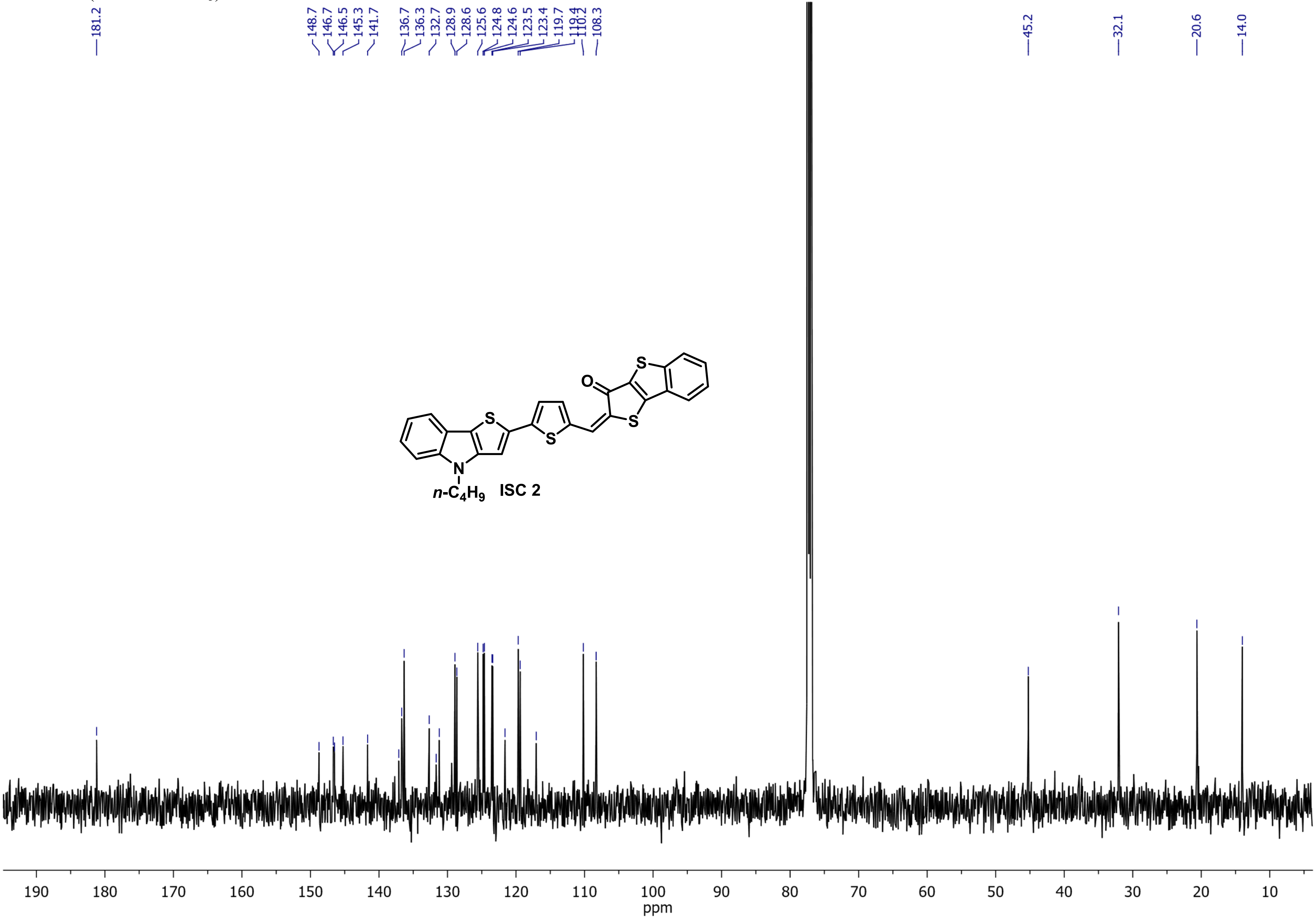


ISC 1

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

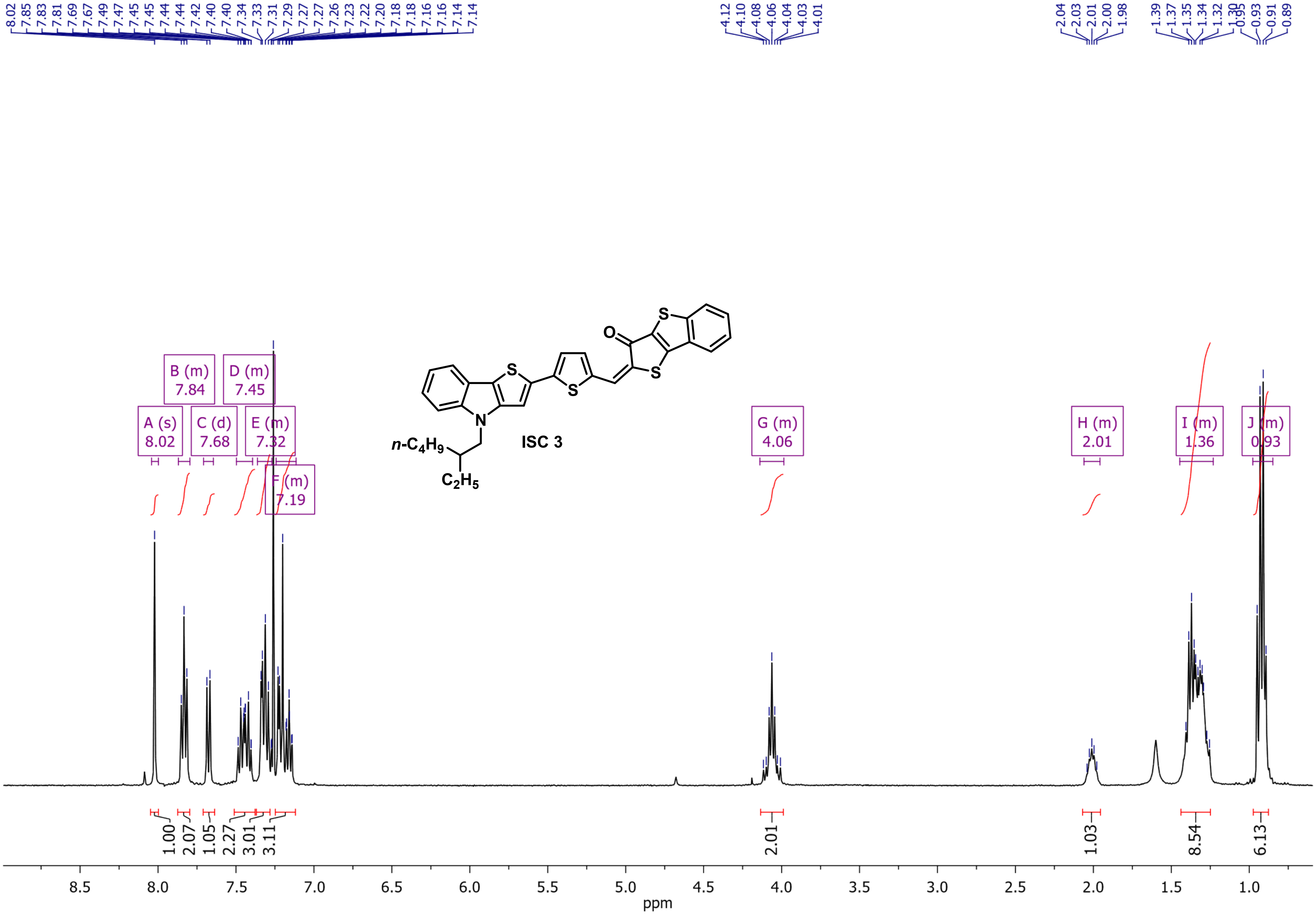


^{13}C NMR (solvent: $CDCl_3$)

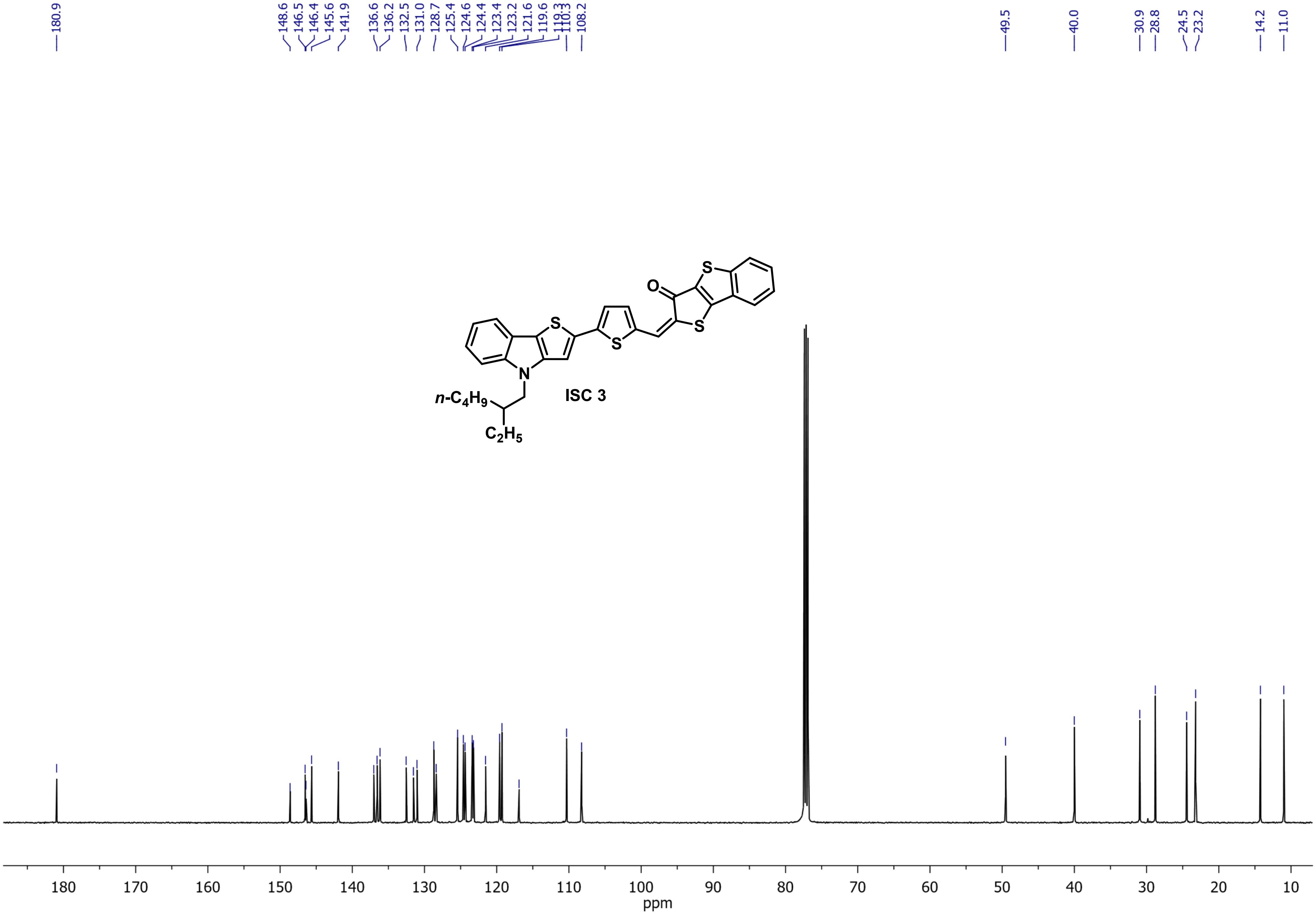


ISC 2

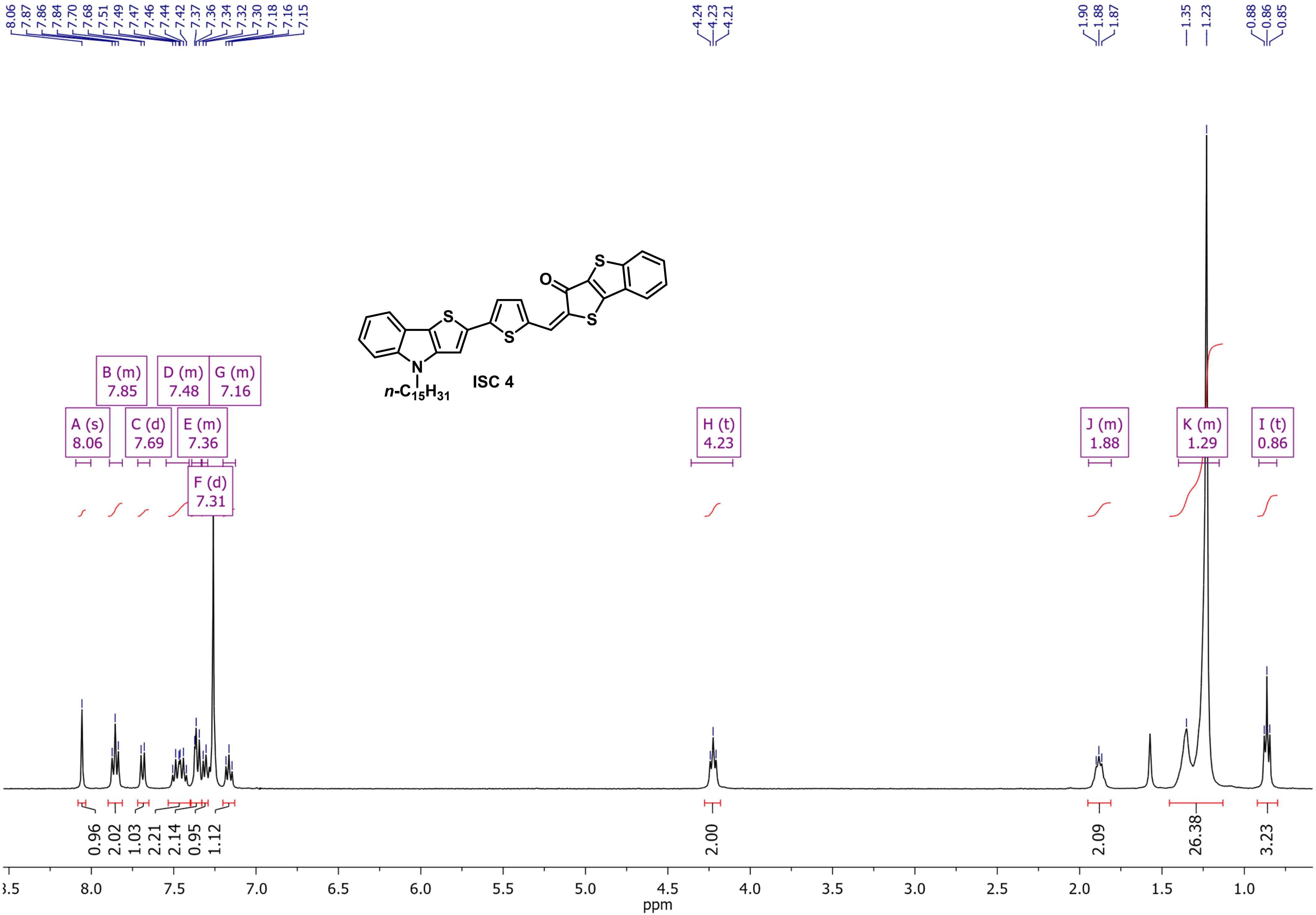
^{1}**H NMR** (solvent: $CDCl_3$)



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



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



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