

Supporting Information

Syntheses via direct arylation method of push-pull molecules based on Triphenylamine and 3-cyano-4-hexyloxythiophene moieties

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Crystallographic structure of compound II

Single crystals of **II** suitable for X-ray diffraction analysis were obtained by slow evaporation of a mixture of ethanol- chloroform solution. The compound crystallizes in the triclinic P-1 space group. X-ray single-crystal diffraction data were collected at 150 K on a BRUKER-NONIUS KappaCCD diffractometer, equipped with a graphite monochromator utilizing Mo K α radiation. The structure was solved by direct methods and refined on F² by the full-matrix least-squares method using the SHELX97 package. All non-H atoms were refined anisotropically and the H atoms were included in the calculation without refinement. The absorption was corrected by the SADABS program..

Empirical formula	C ₃₃ H ₂₈ N ₄ O S
Formula weight	528.65
Wavelength	1.54184 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 10.5659(3) Å alpha = 84.956(2) deg. b = 13.3660(4) Å beta = 76.050(2) deg. c = 20.8146(4) Å gamma = 77.060(2) deg.
Volume	2778.58(13) Å ³
Z, Calculated density	4, 1.264 Mg/m ³
Absorption coefficient	1.289 mm ⁻¹
F(000)	1112
Crystal size	0.3759 x 0.0840 x 0.0157 mm
Theta range for data collection	3.39 to 76.84 deg.
Limiting indices	-12 ≤ h ≤ 13, -16 ≤ k ≤ 16, -22 ≤ l ≤ 26
Reflections collected / unique	27539 / 11378 [R(int) = 0.0388]
Completeness to theta = 72.00	99.0 %

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.87281
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11378 / 0 / 705
Goodness-of-fit on F ²	1.074
Final R indices [I > 2σ(I)]	R1 = 0.0538, wR2 = 0.1434 [9534 Fo]
R indices (all data)	R1 = 0.0653, wR2 = 0.1554
Largest diff. peak and hole	0.488 and -0.383 e.Å ⁻³

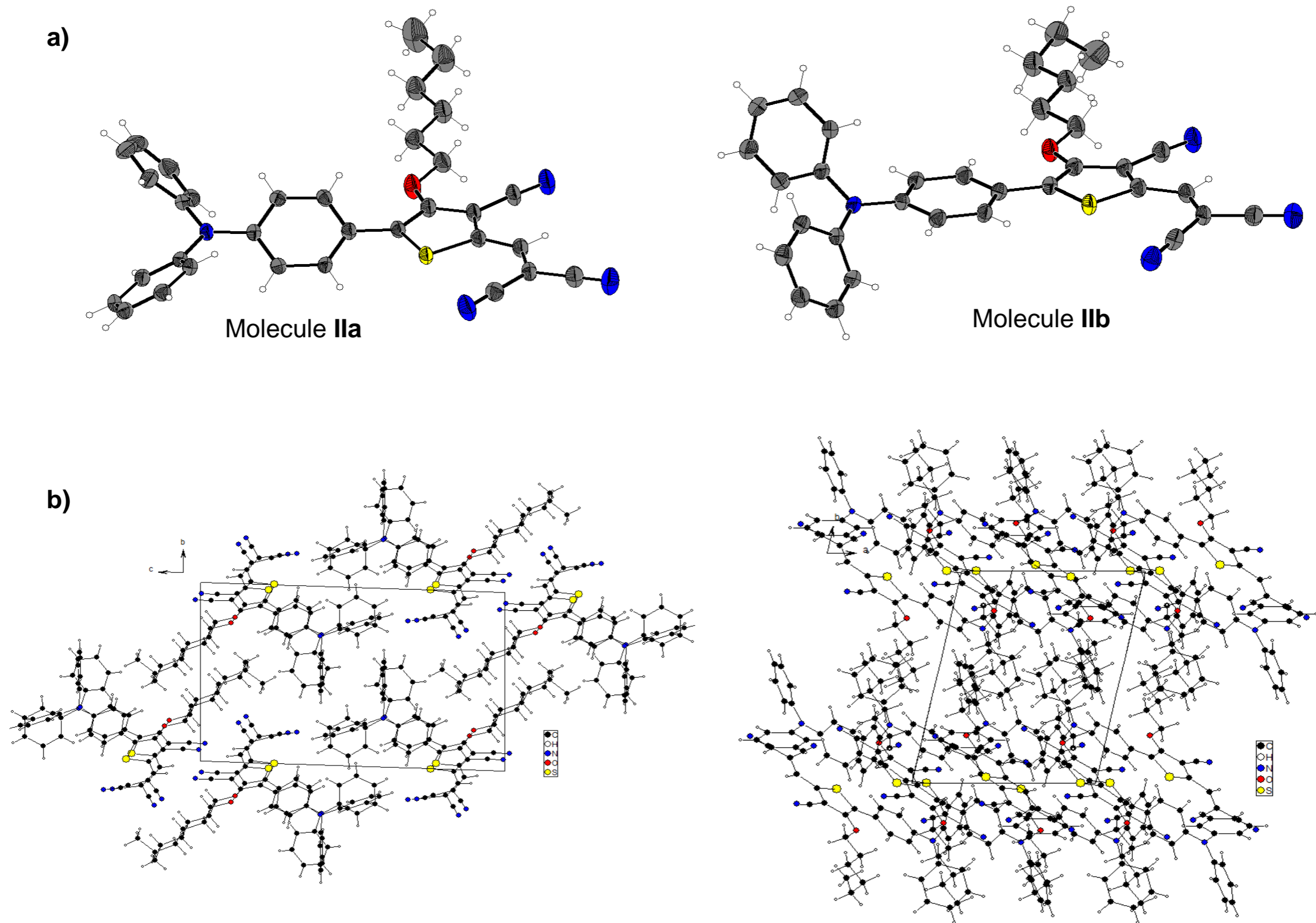


Figure S1: X-Ray structure of compound II.

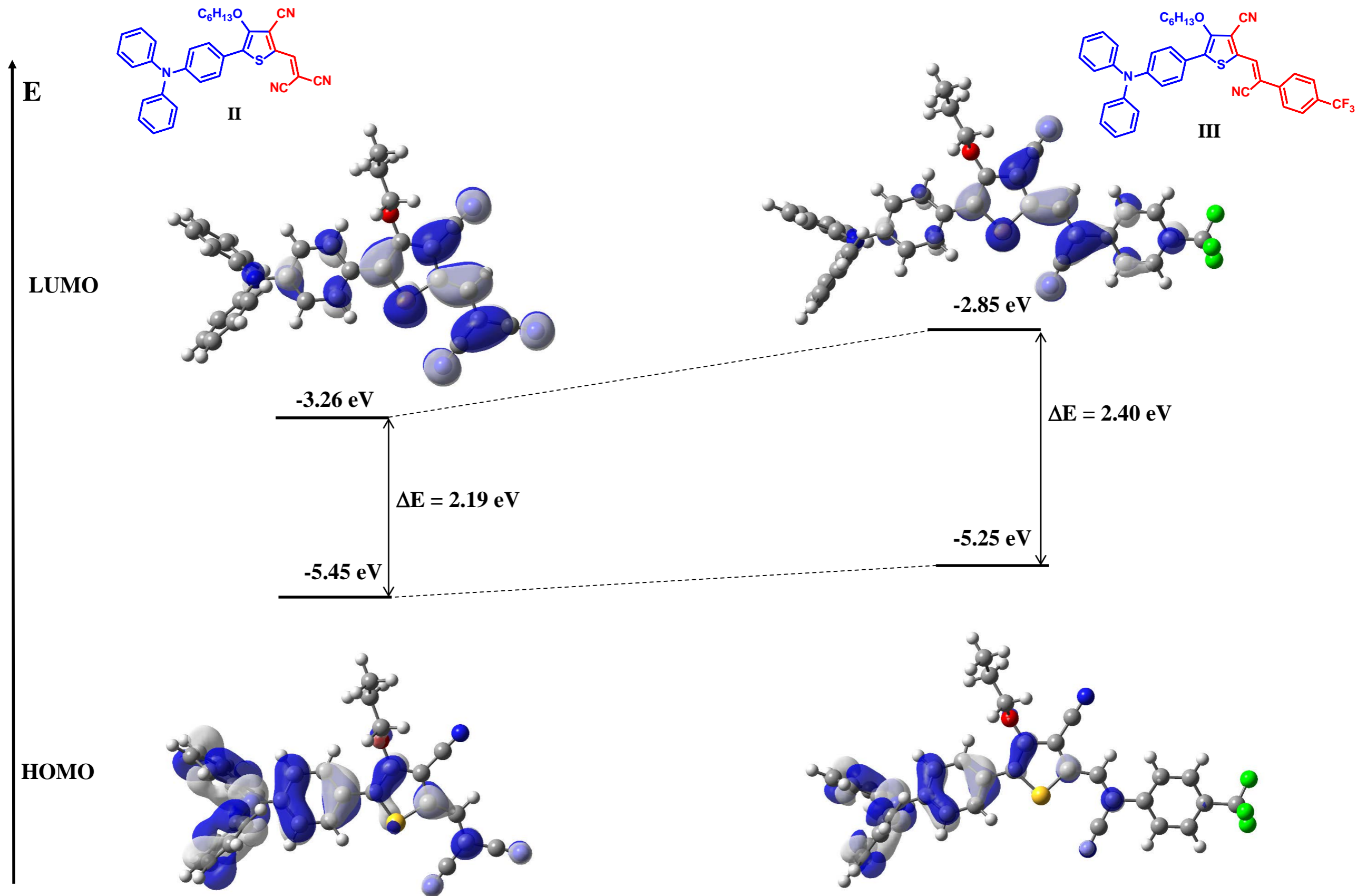


Figure S2: Calculated HOMOs and LUMOs (Gaussian 09, B3LYP – 6.31G (d,p)) and schematic representation of the energy levels for **II** and **III**.

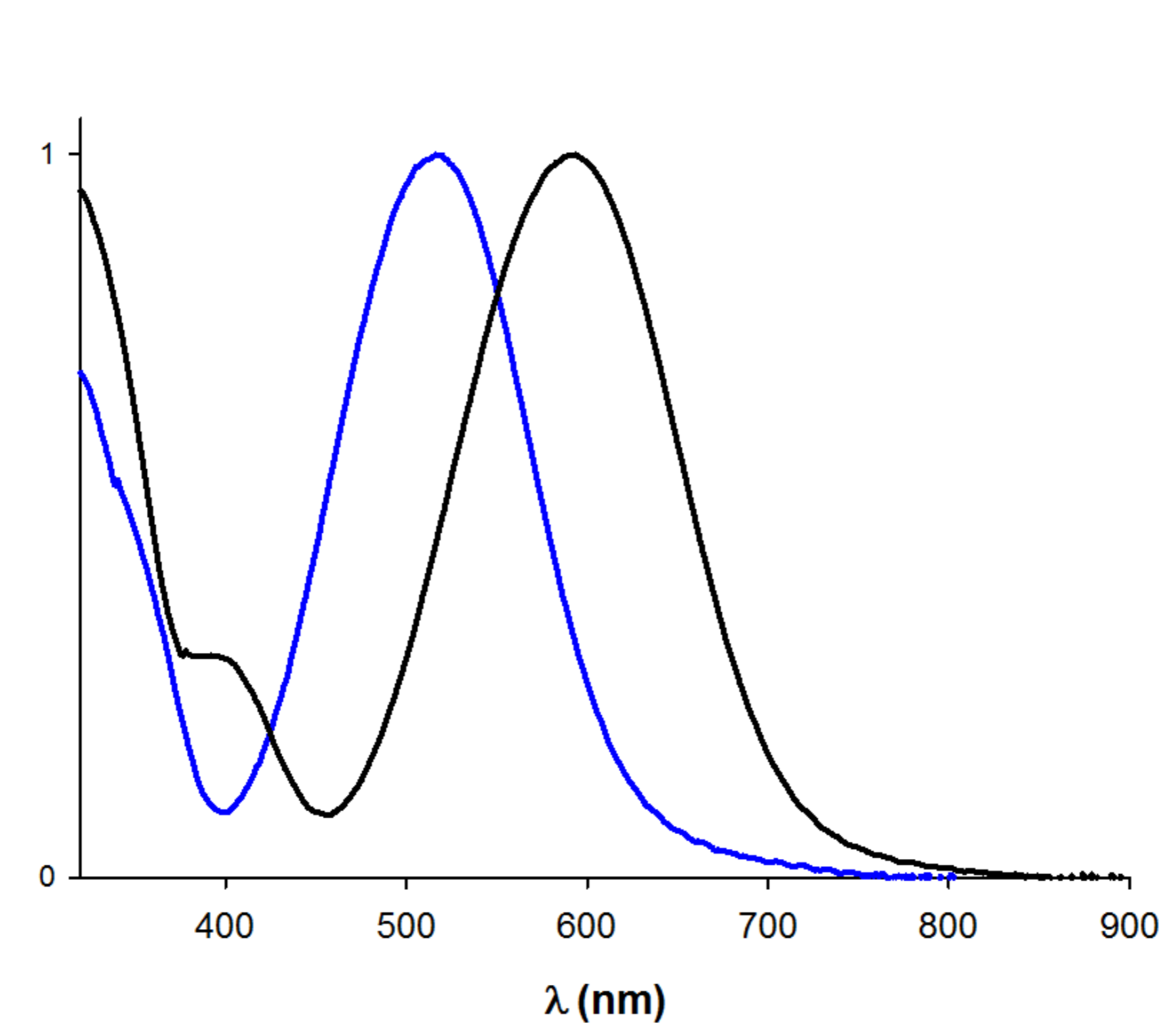
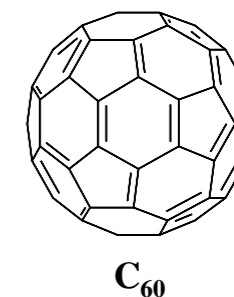
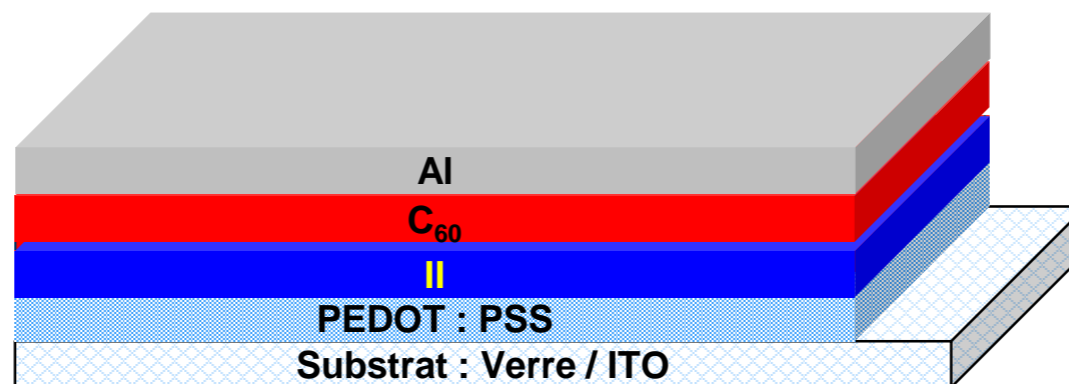
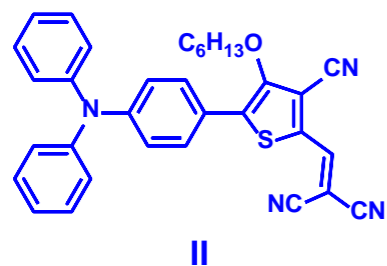


Figure S3: Normalized UV-vis absorption spectra of spin coated films of **II** (black) and **III** (blue)

Bilayer heterojunction cells (BLJ)

Preparation of the solar cells

Indium-tin oxide coated glass slides of $24 \times 25 \times 1.1$ mm with a sheet resistance of $RS = 10 \Omega/\text{sq}$ were purchased from VisionTek Systems Ltd. The substrates were scrubbed using dishwashing soap before being cleaned by a series of ultrasonic treatments for 15 min in distilled water, acetone, and isopropanol. Once dried under a steam of nitrogen, a UV-ozone plasma treatment (UV/Ozone ProCleaner Plus, Bioforce Nanosciences) was performed for 15 min. A filtered aqueous solution of poly(3,4-ethylenedioxy-thiophene)-poly(styrenesulfonate) (PEDOT:PSS; Clevios P VP. AI 4083) through a $0.45 \mu\text{m}$ RC membrane (Millex®) was spun-cast onto the patterned ITO surface at 5000 rpm for 40 s before being baked at 115°C for 15 min. The best devices were obtained with films spun-cast from chloroform solutions at 6000 rpm for **DA1**, **DA2** and Blend containing 10 mg/mL of material(s). Finally, OSCs were completed by the successive thermal deposition of C_{60} (30 nm) and aluminum (80 nm) at a pressure of 10^{-6} Torr through a shadow mask defining two cells of 27 mm^2 each. J vs V curves were recorded in the dark and under illumination using a Keithley 236 source-measure unit and a home-made acquisition program. The light source is an AM1.5 Solar Constant 575 PV simulator (Steuernagel Lichttechnik, equipped with a metal halogen lamp). The light intensity was measured by a broad-band power meter (13PEM001, Melles Griot). EQE was recorded under ambient atmosphere using a halogen lamp (Osram) with an Action Spectra Pro 150 monochromator, a lock-in amplifier (Perkin-Elmer 7225) and a S2281 photodiode (Hamamatsu).



Results of BLJ cells

Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)
0,70	4,96	29	1.22 (max = 1,23)

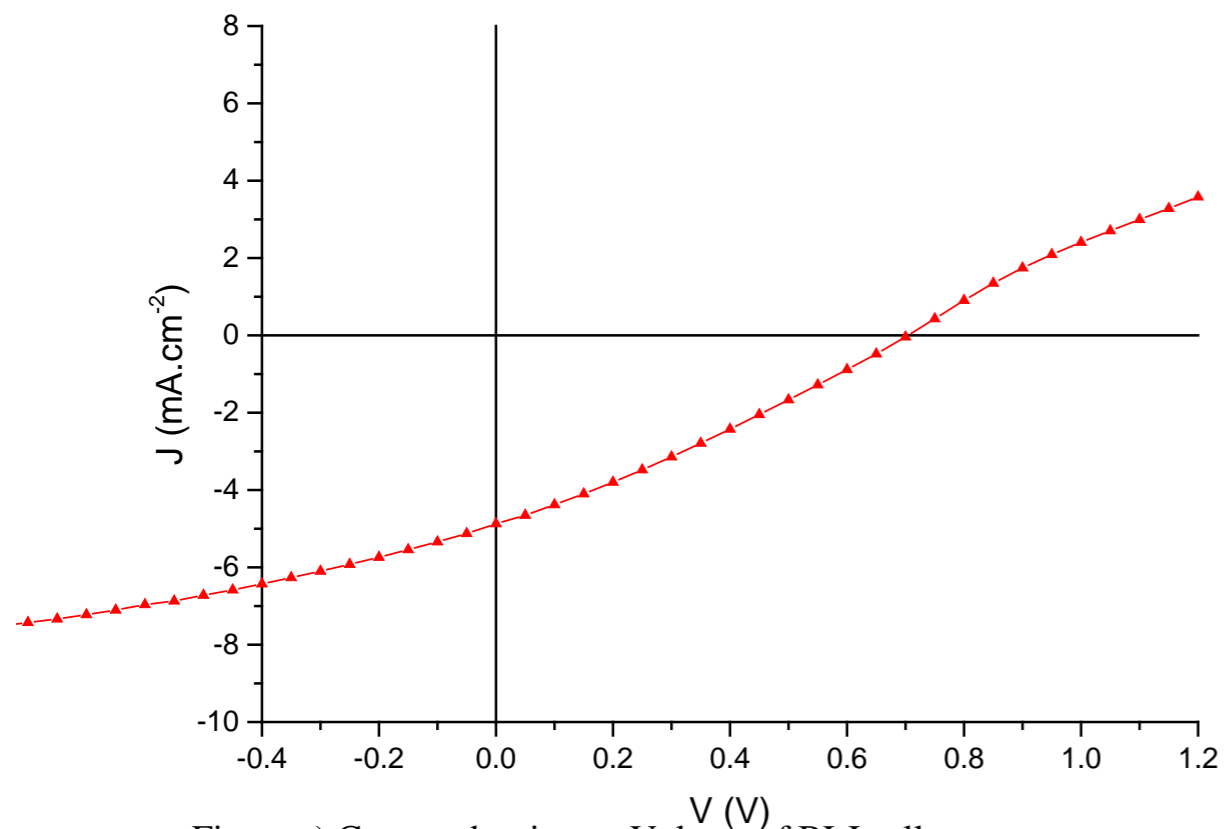


Figure a) Current density vs. Voltage of BLJ cells

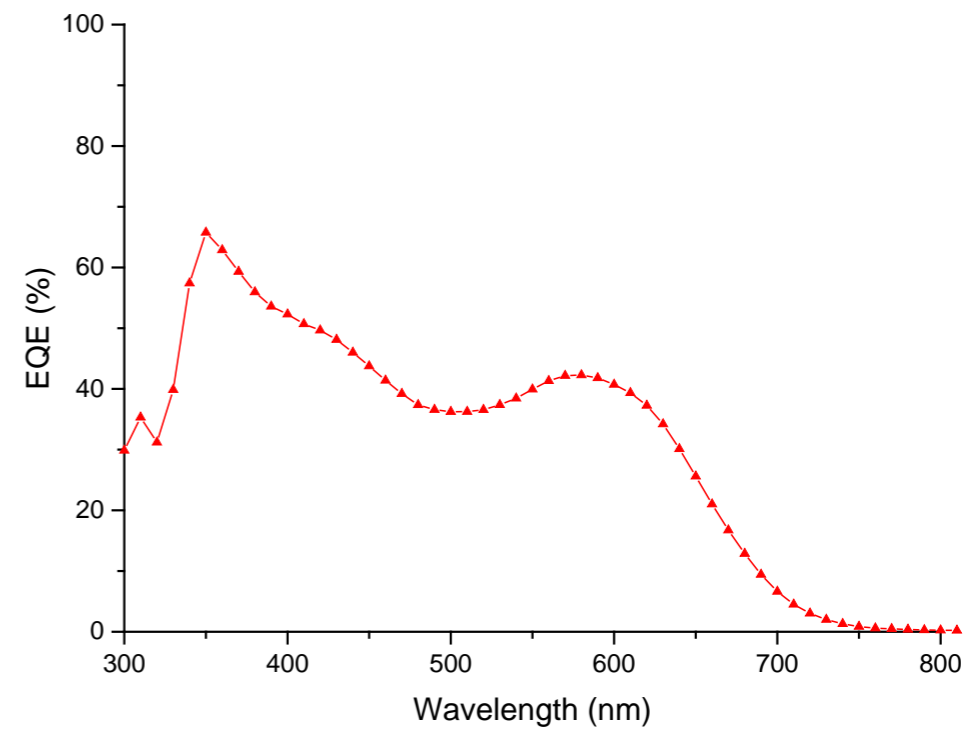


Figure b) EQE spectra of BLJ cells

Figure S4 : Photovoltaic characteristic of BLJ devices based on compound **II** as donor material and C₆₀ as acceptor material

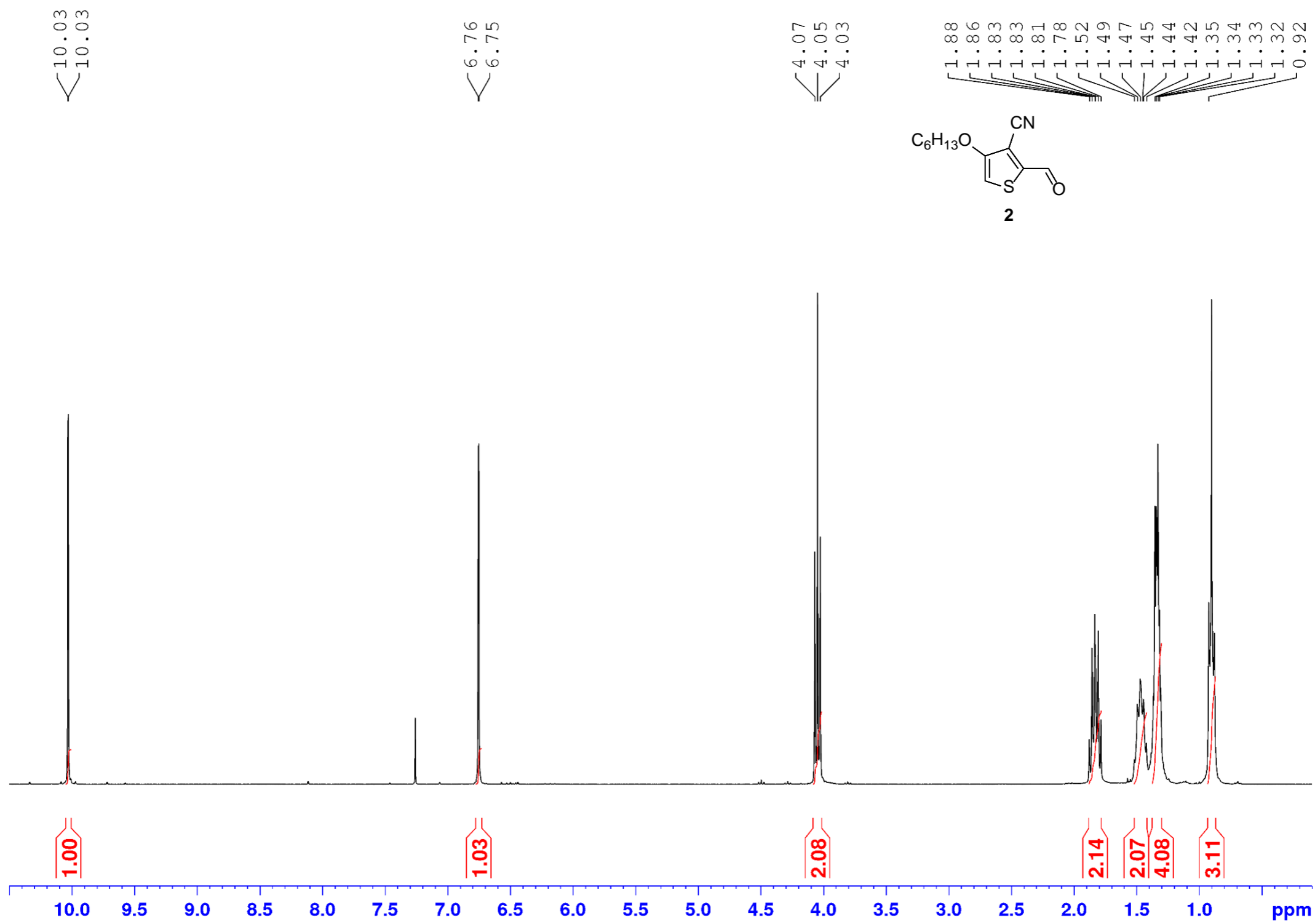


Figure S5 : ¹H NMR spectra in CDCl₃ of **2**

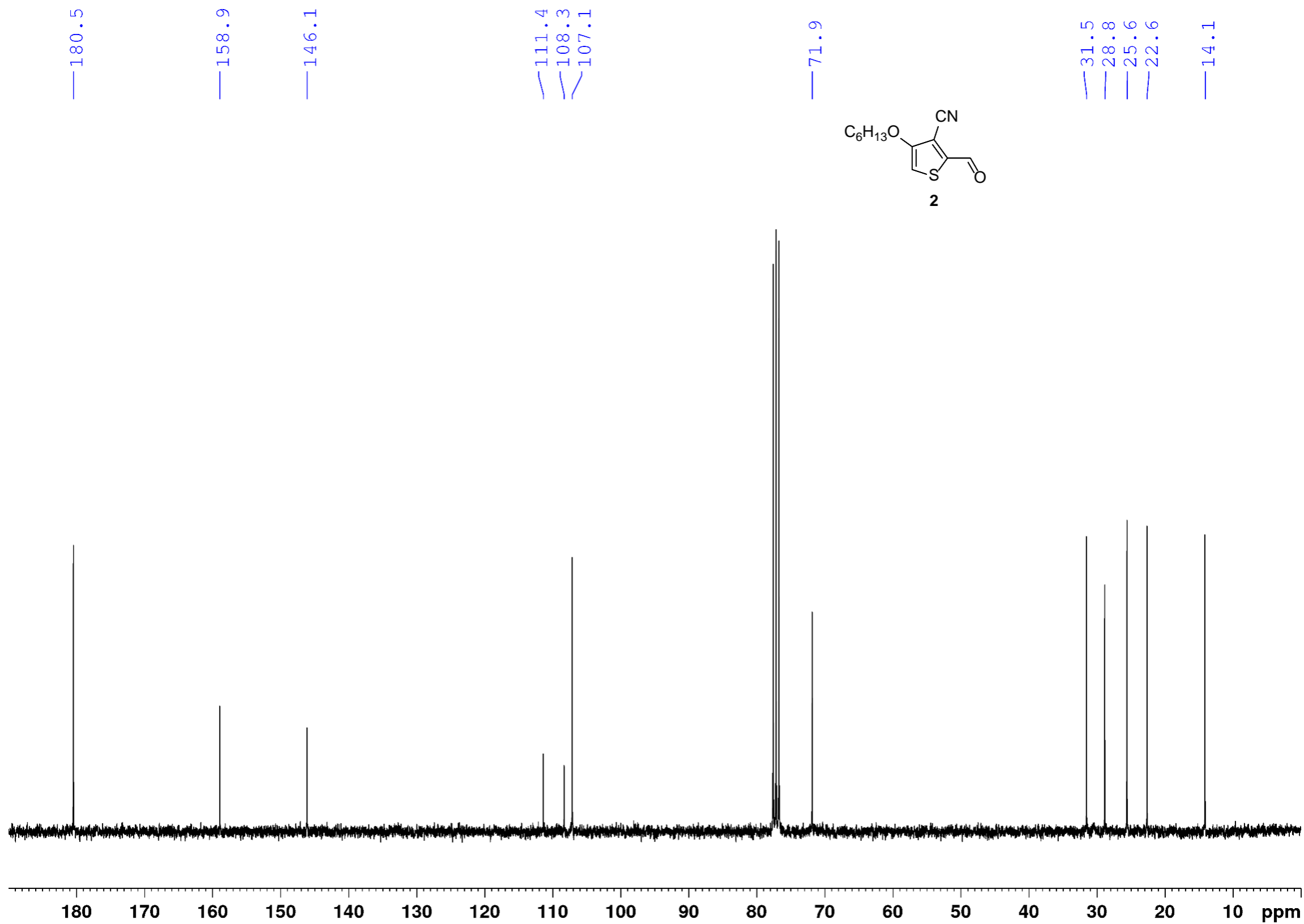


Figure S6 : ¹³C NMR spectra in CDCl₃ of **2**

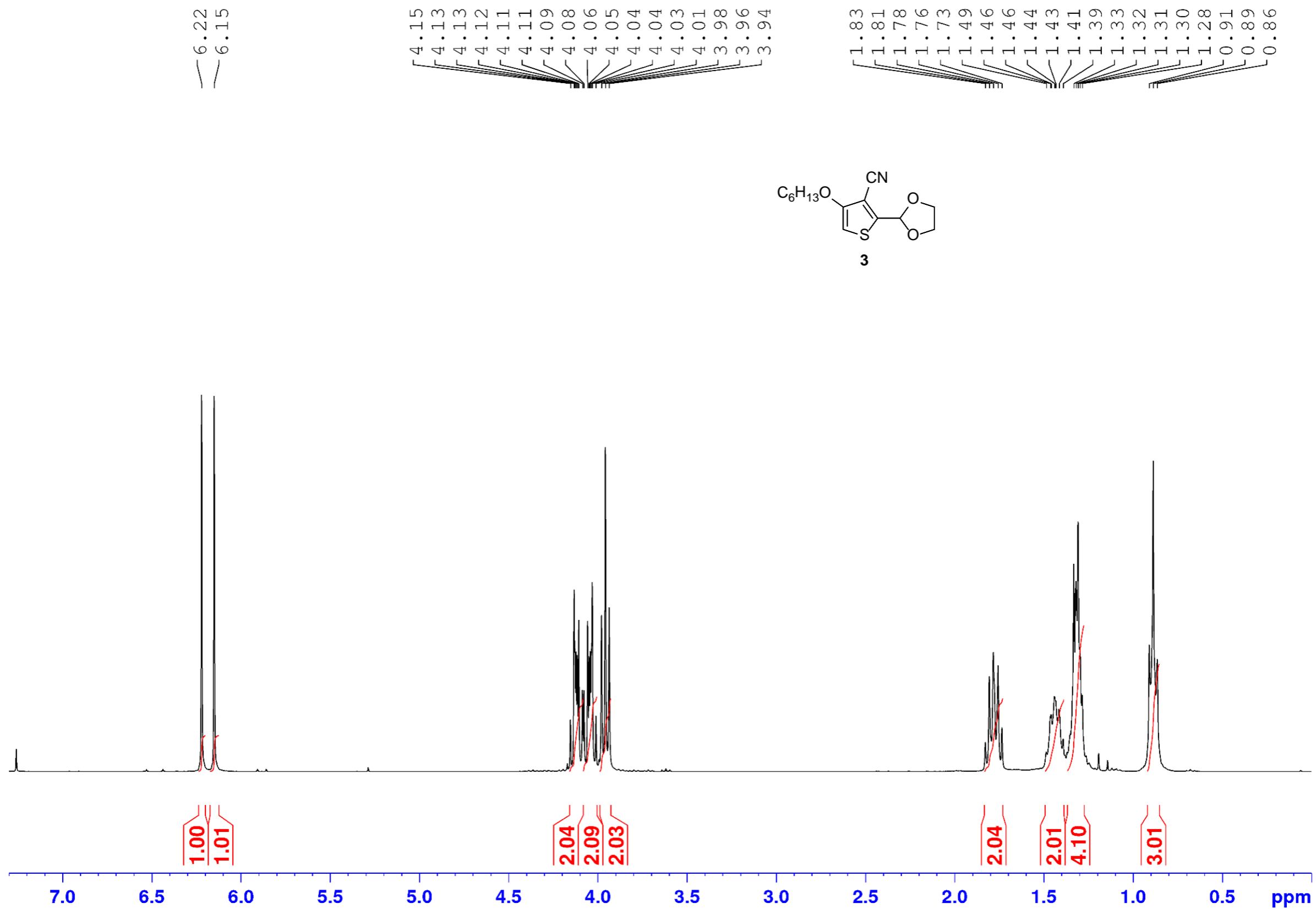


Figure S7 : ^1H NMR spectra in CDCl_3 of **3**

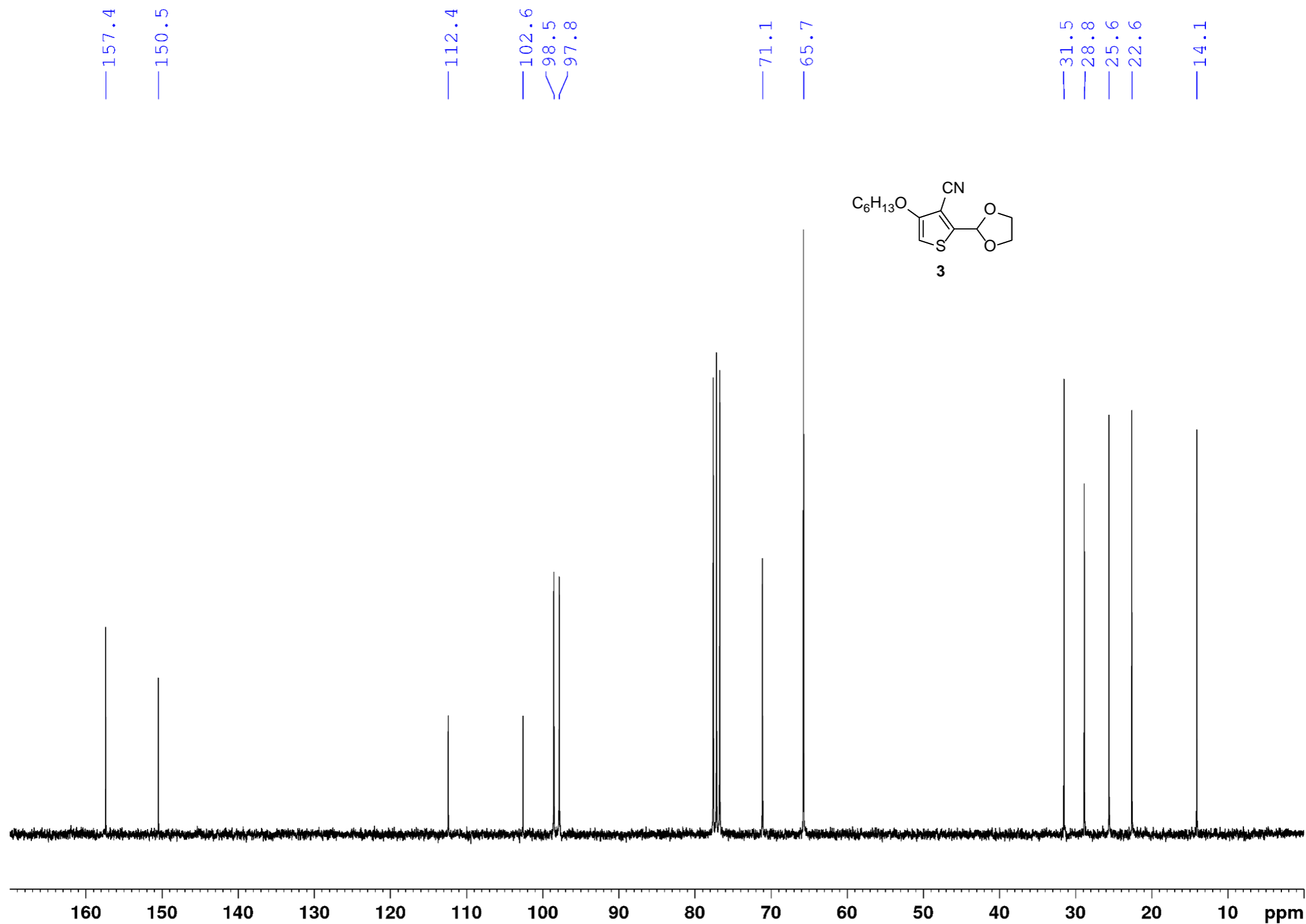


Figure S8: ^{13}C NMR spectra in CDCl_3 of **3**

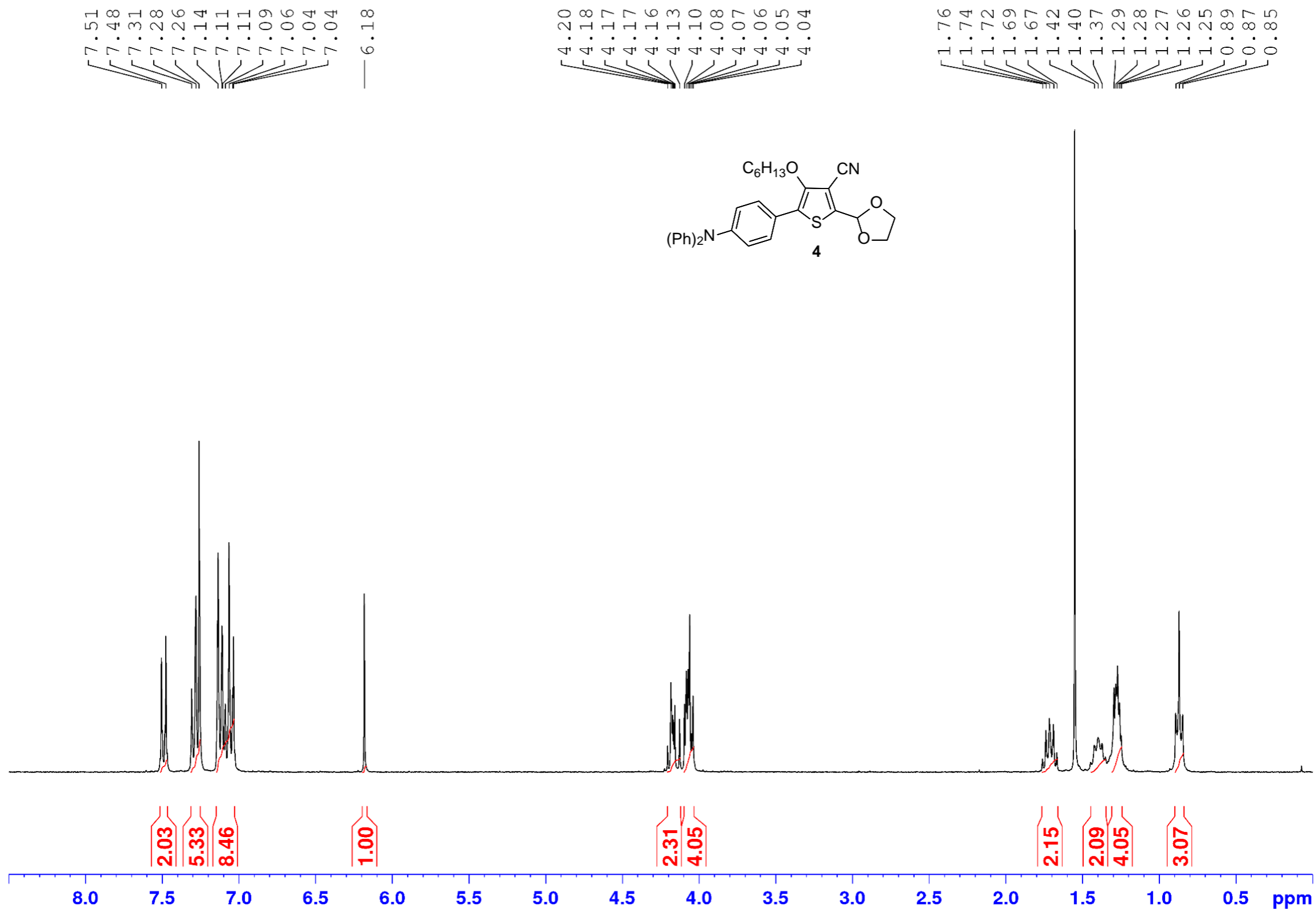


Figure S9 : ¹H NMR spectra in CDCl₃ of **4**

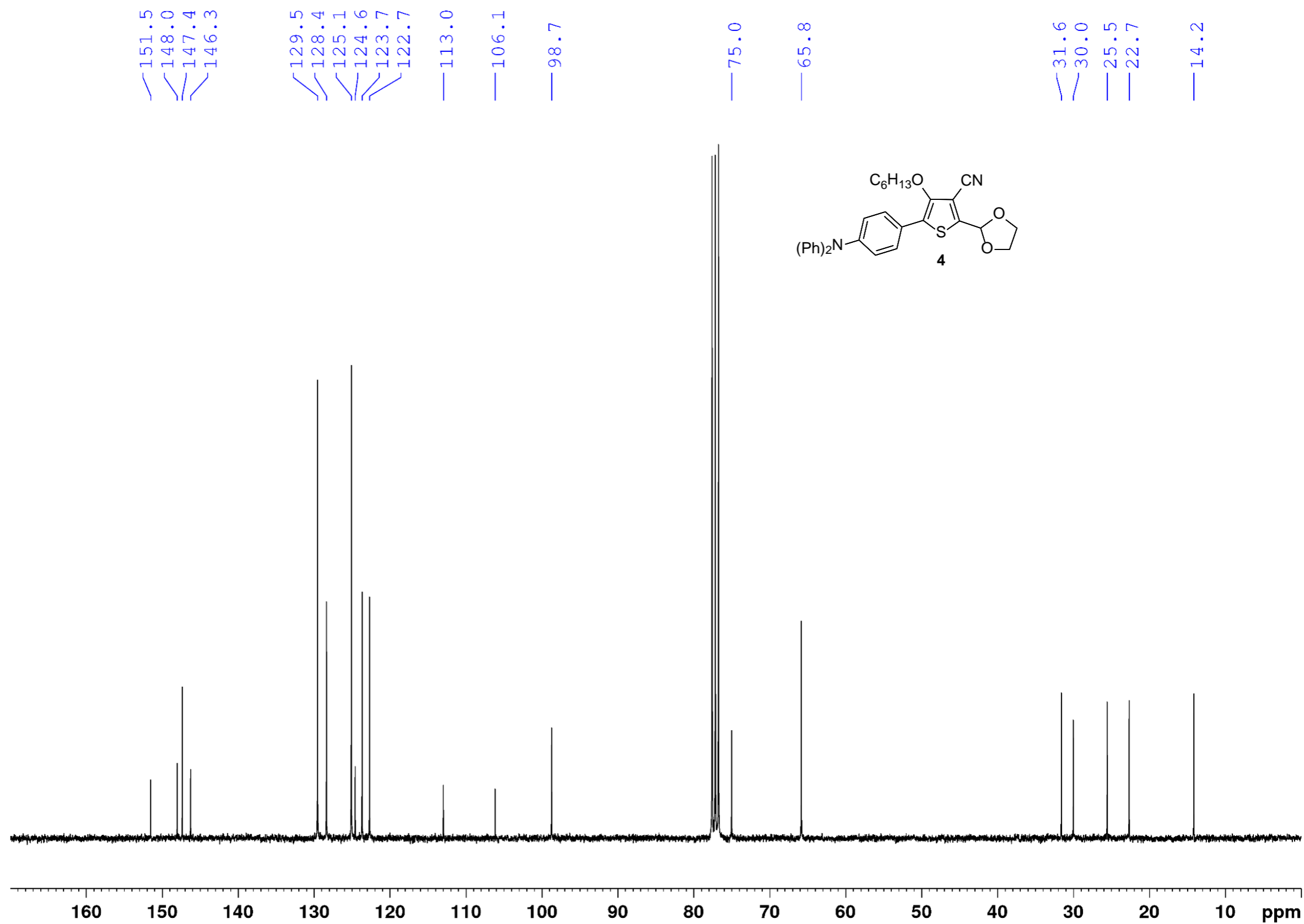


Figure S10 : ¹³C NMR spectra in CDCl₃ of **4**

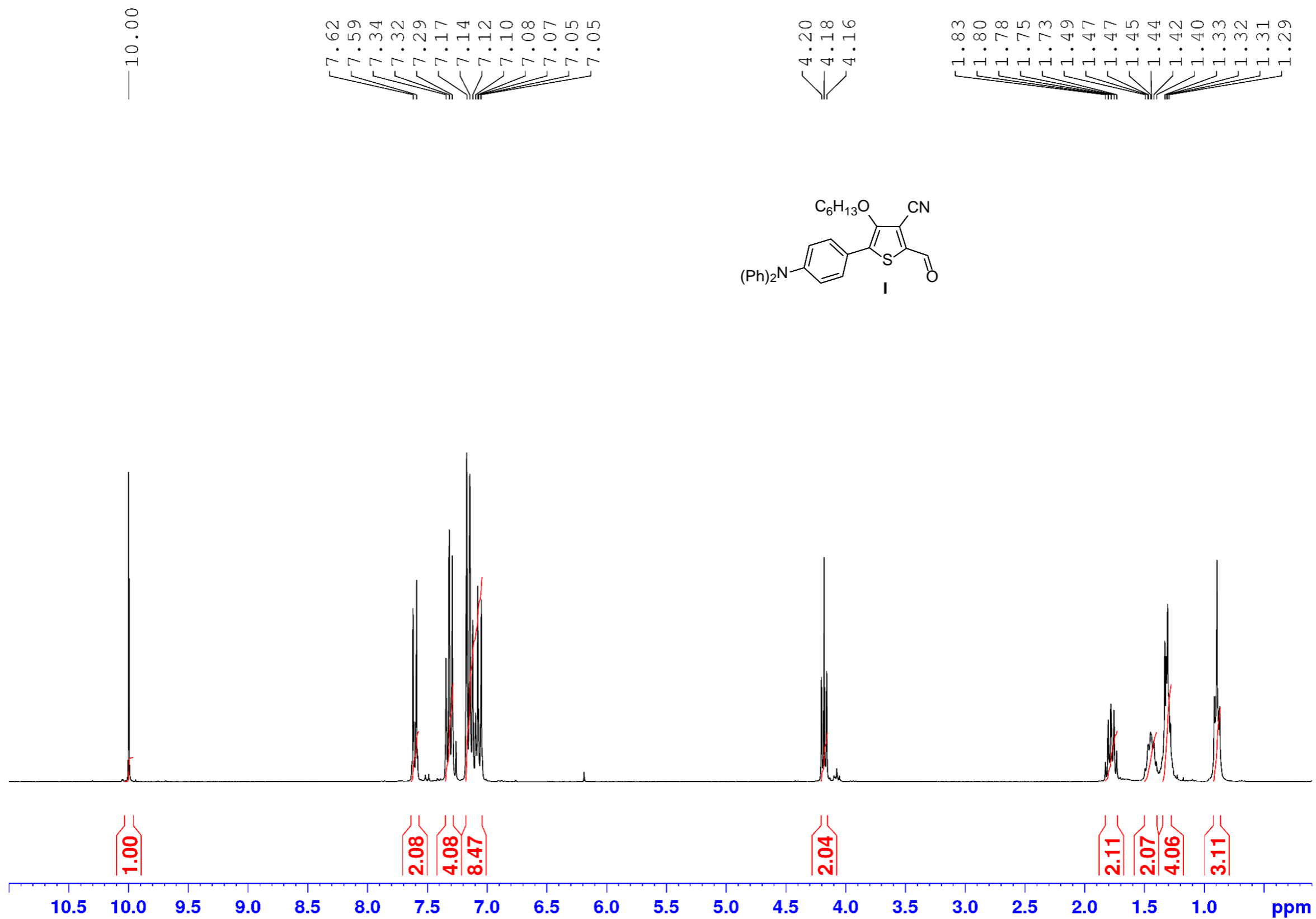


Figure S11 : ^1H NMR spectra in CDCl_3 of **I**

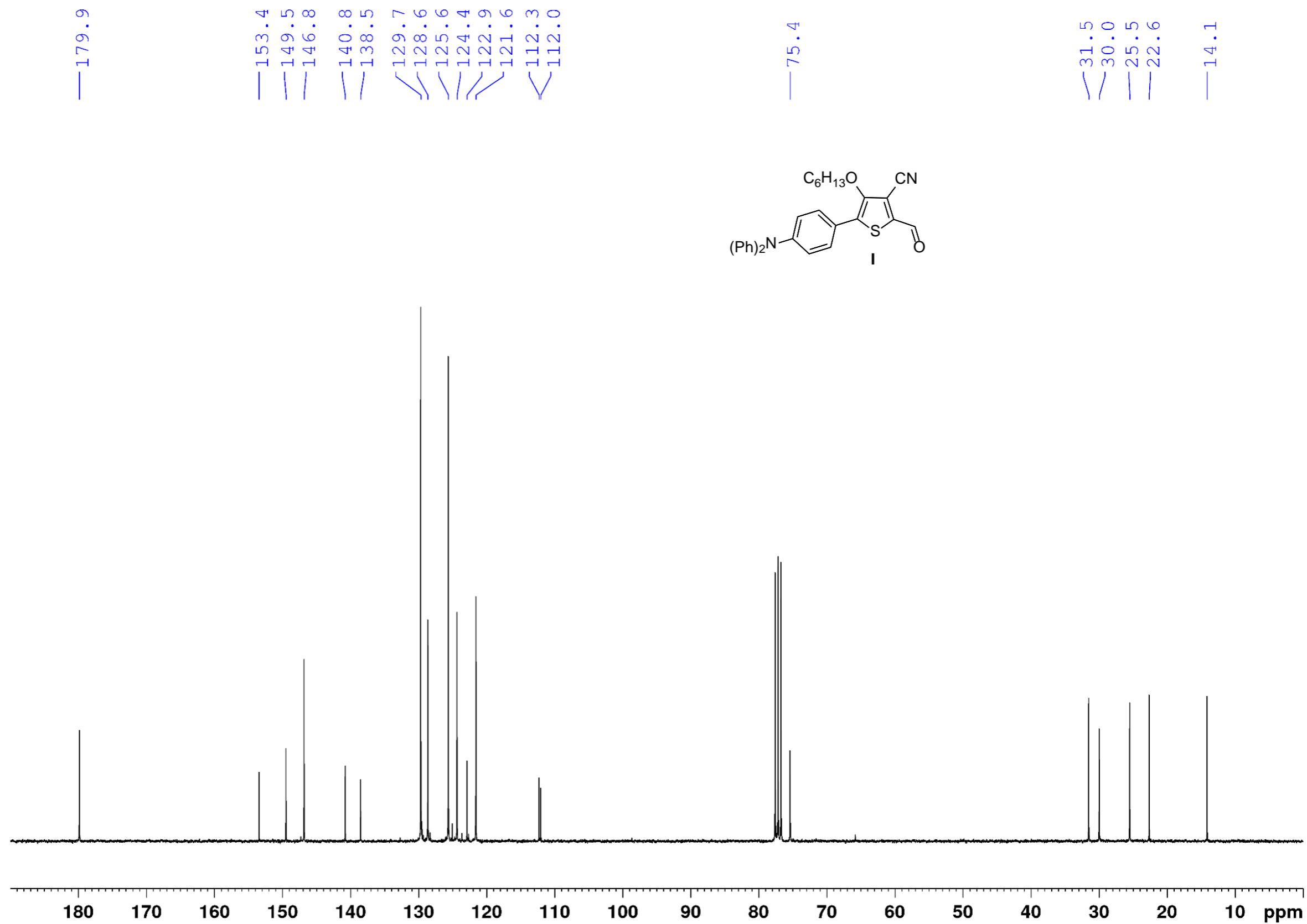


Figure S12 : ¹³C NMR spectra in CDCl₃ of I

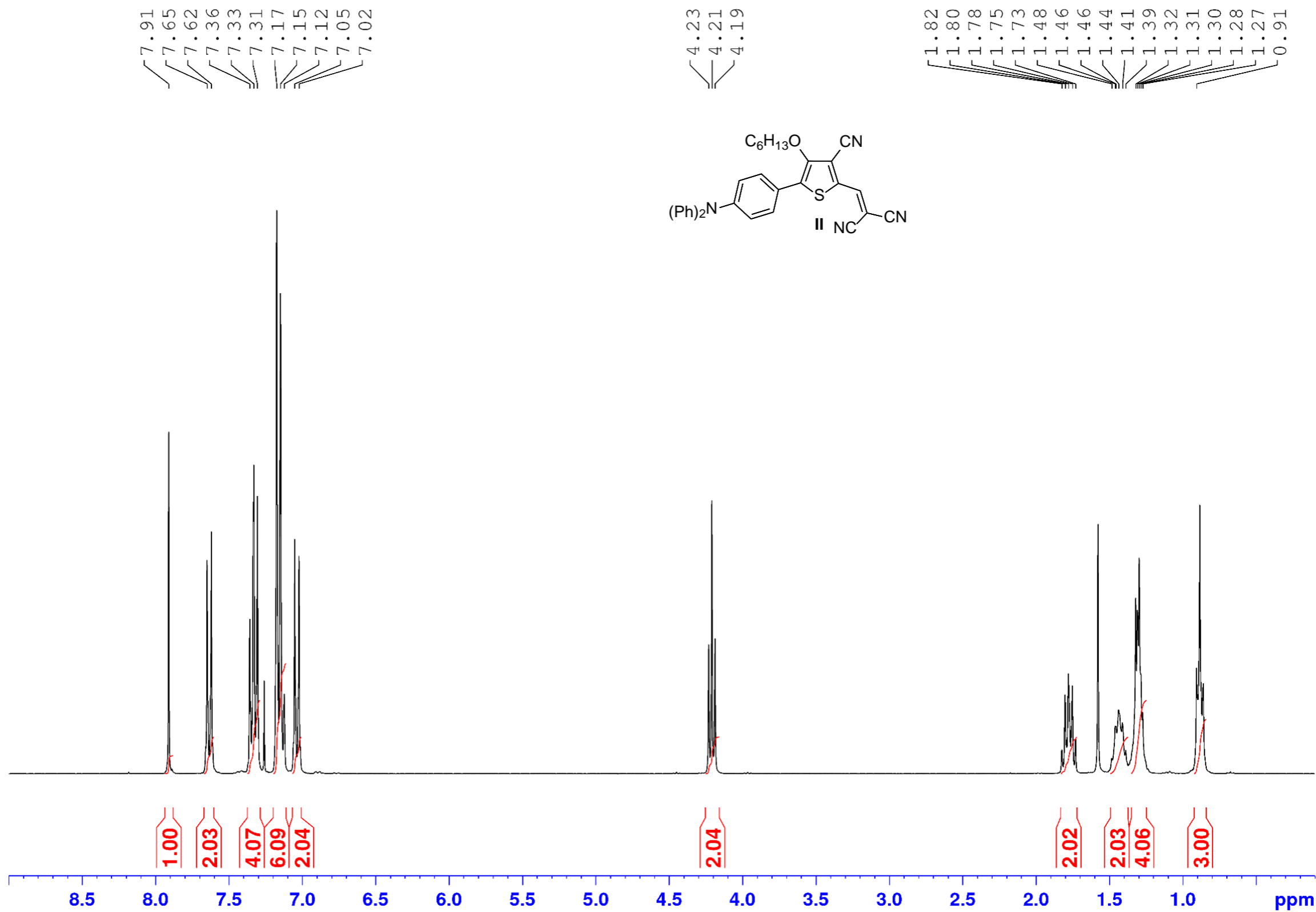


Figure S13 : ^1H NMR spectra in CDCl_3 of II

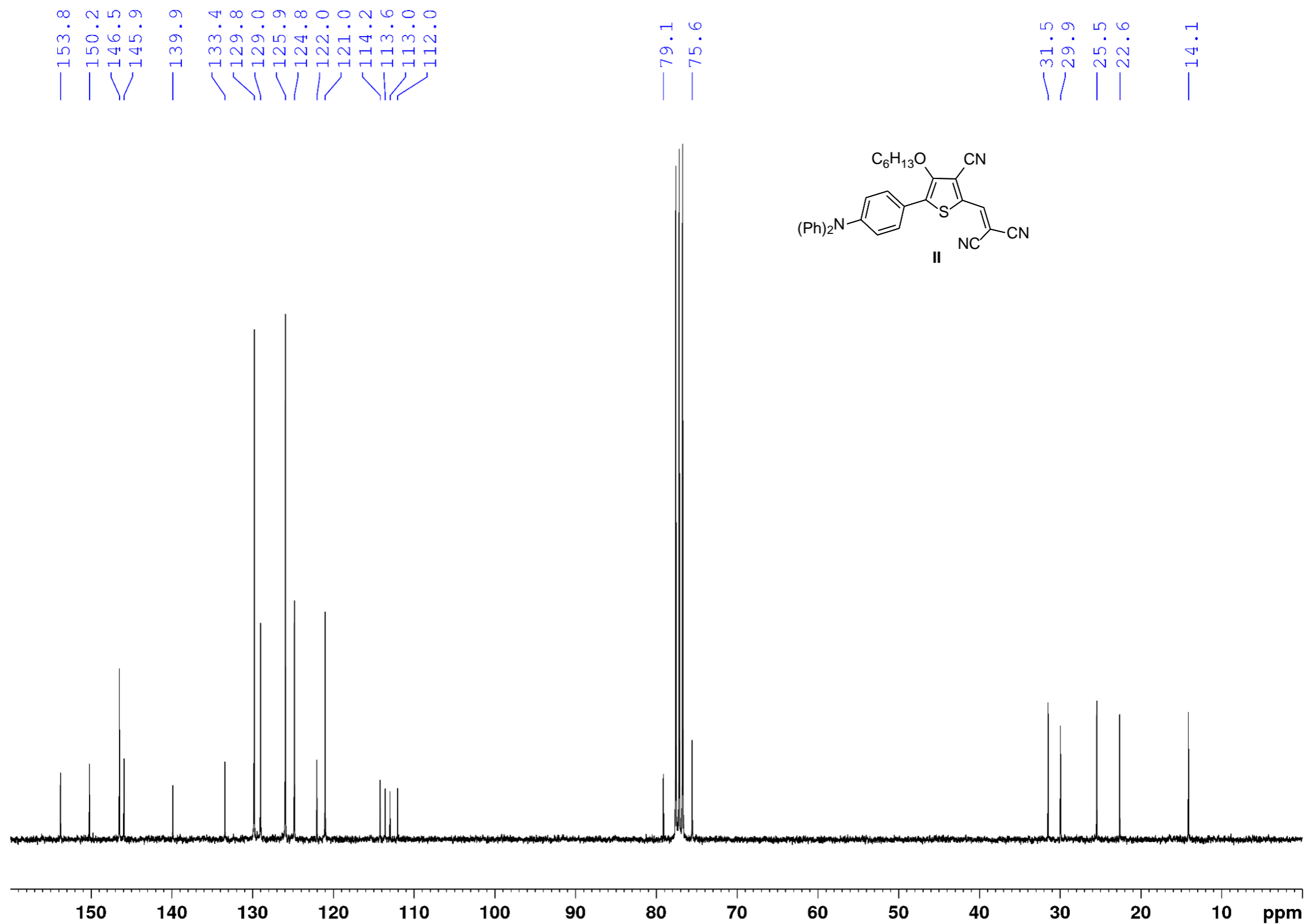


Figure S14 : ^{13}C NMR spectra in CDCl_3 of **II**

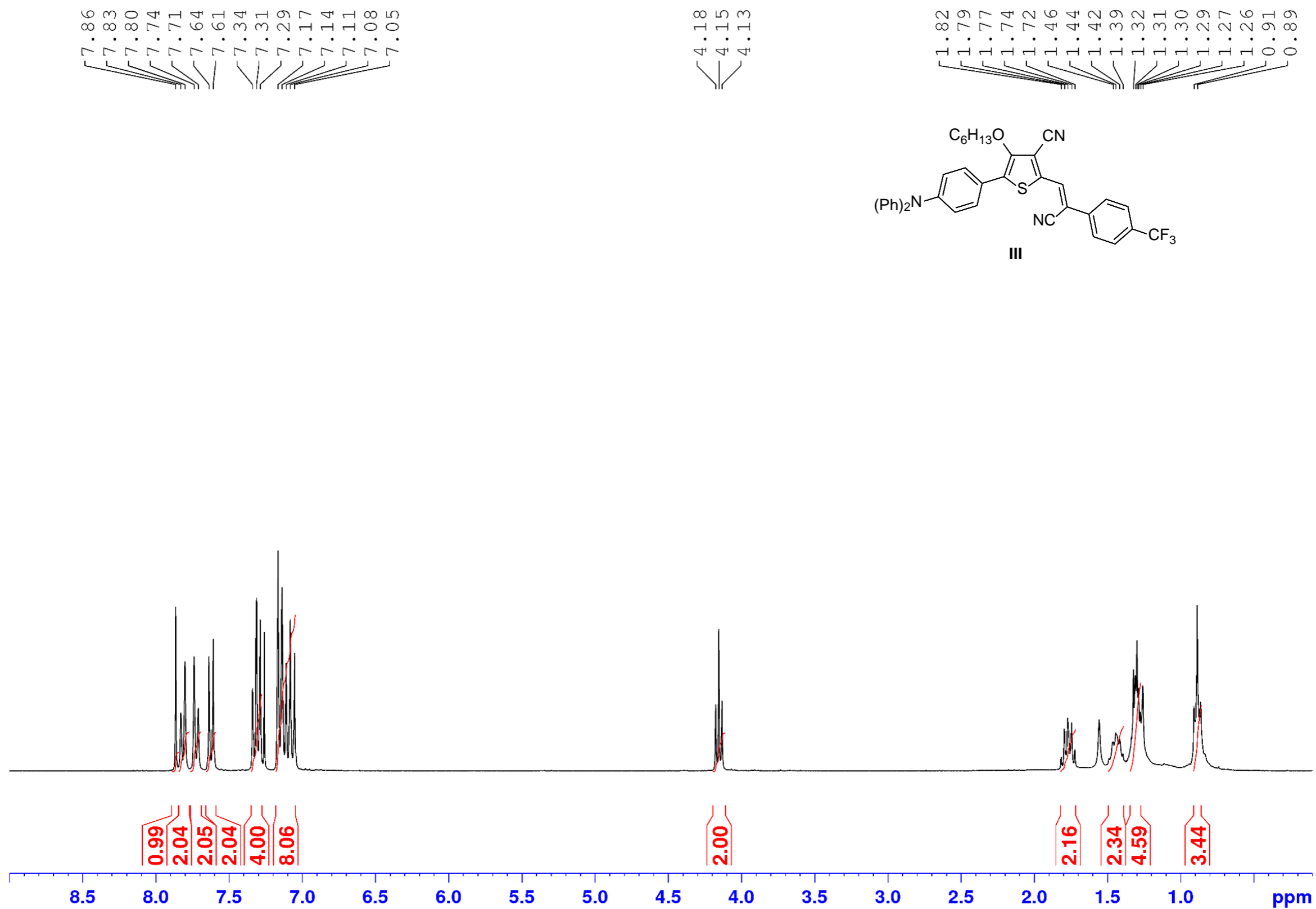


Figure S10 : 1H NMR spectra in $CDCl_3$ of **III**

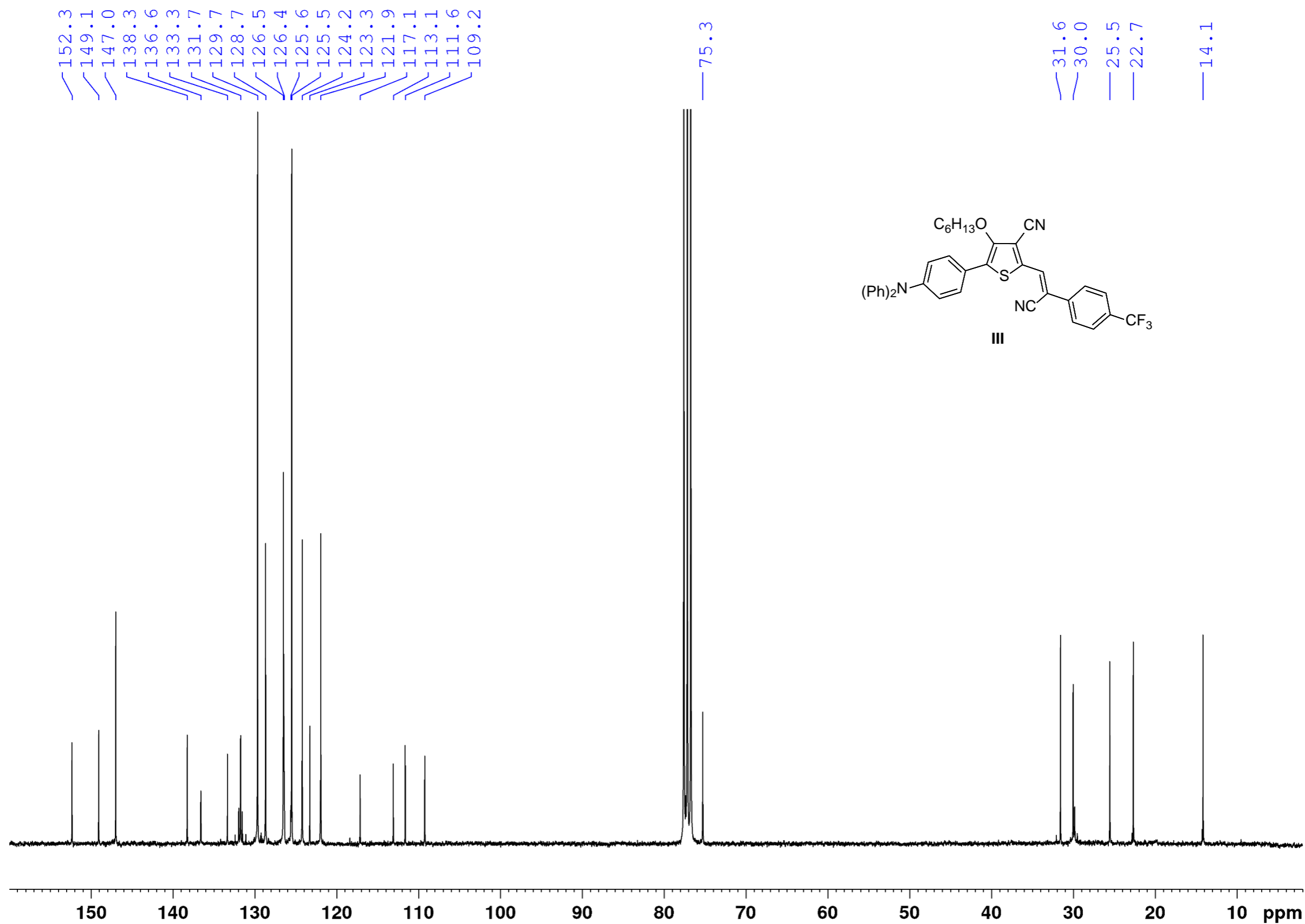


Figure S15 : ^{13}C NMR spectra in CDCl_3 of **III**

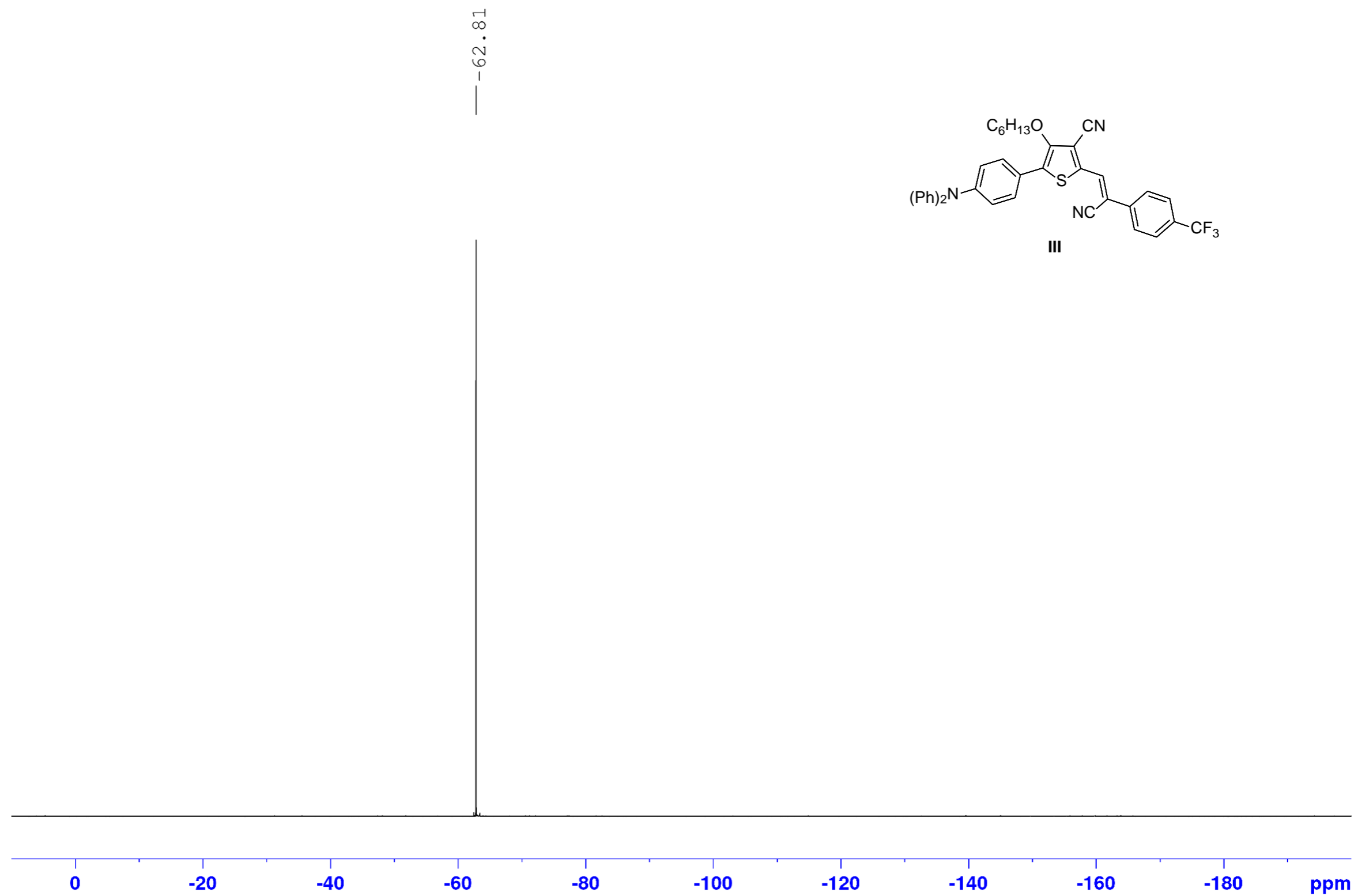


Figure S16 : ^{19}F NMR spectra in CDCl_3 of **III**