

Supplementary Materials:

Synthesis of novel 3,6-dithienyl diketopyrrolopyrrole dyes by direct C–H arylation

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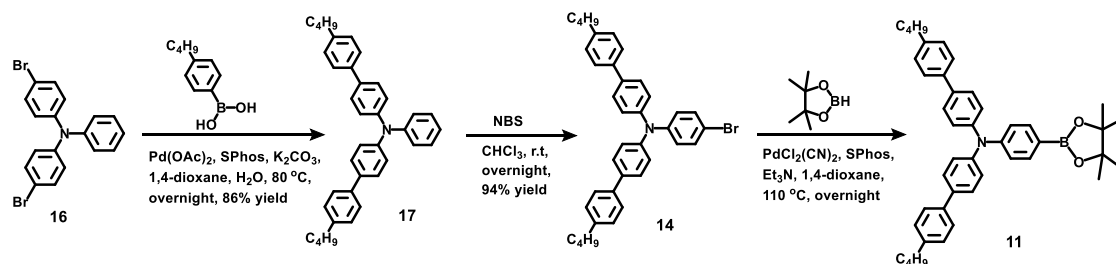
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Synthesis of building blocks **11** and **14**



Scheme S1: Synthesis route to **11**.

4'-Butyl-N-(4'-butyl-[1,1'-biphenyl]-4-yl)-N-phenyl-[1,1'-biphenyl]-4-amine (17).

Compound **16** (500 mg, 1.24 mmol, 1.0 eq.), (4-butylphenyl)boronic acid (550 mg, 3.10 mmol, 2.5 eq.), Pd(OAc)₂ (11.0 mg, 0.050 mmol, 4 mol%), SPhos (41.0 mg, 0.099 mmol, 8 mol%), and K₂CO₃ (0.68 g, 4.96 mmol, 4.0 eq.) were added before the flask was evacuated and nitrogen atmosphere established. Then 1,4-dioxane (4.5 mL) and degassed deionized water (4.5 mL) add and stirred for overnight at 80 °C. After cooling to r.t the reaction mixture was quenched by aqueous NaOH (1M, 10 mL). The aqueous layer was extracted with DCM (3x15 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography using (gradient: 0–50% DCM in hexane) leading to compound **17** (550 mg, 1.08 mmol, 86%) as a colorless sticky oil. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.50–7.47 (m, 8H), 7.30–7.22 (m, 6H), 7.18–7.15 (m, 6H), 7.04 (t, *J* = 7.3 Hz, 1H), 2.66–2.62 (m, 4H), 1.67–1.59 (m, 4H), 1.43–1.34 (m, 4H), 0.98 (t, *J* = 7.3 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 147.6, 146.7, 141.6, 137.9, 135.3, 129.2, 128.8, 127.6, 126.5, 124.4, 124.1, 122.9, 35.2, 33.6, 22.4, 13.9. HRMS (TOF ASAP+, *m/z*): observed 510.3160, calculated for C₃₈H₄₀N [M+H]⁺ 510.3155.

N-(4-Bromophenyl)-4'-butyl-N-(4'-butyl-[1,1'-biphenyl]-4-yl)-[1,1'-biphenyl]-4-amine (14).

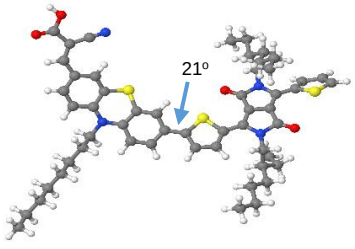
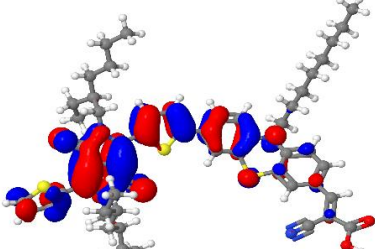
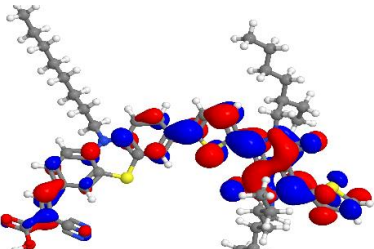
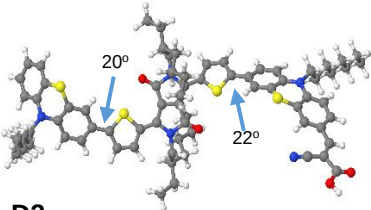
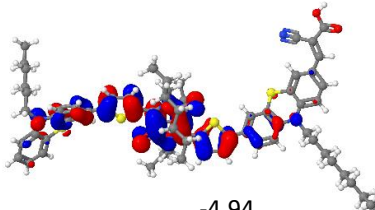
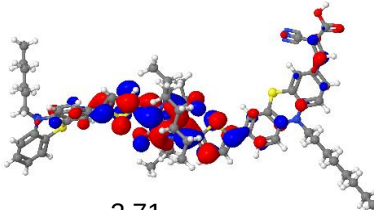
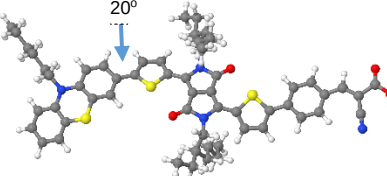
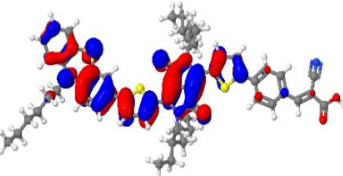
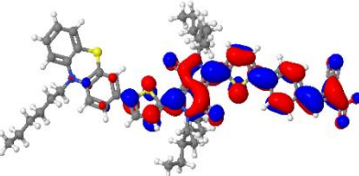
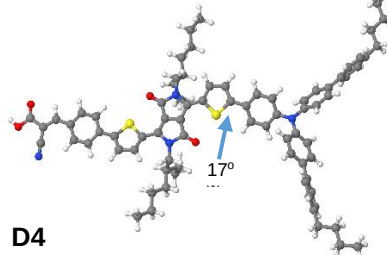
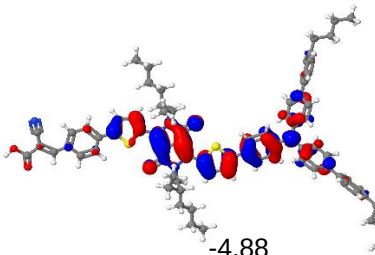
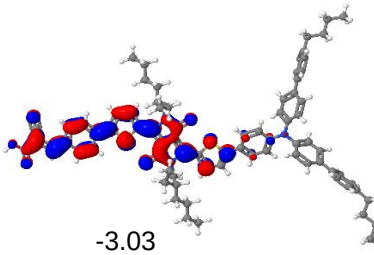
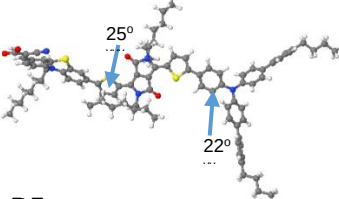
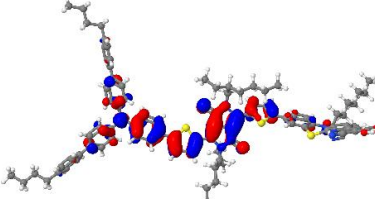
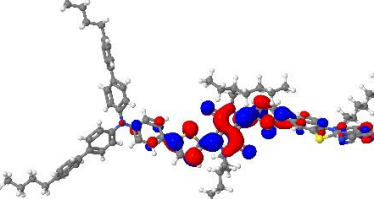
Compound **17** (100 mg, 0.196 mmol, 1.0 eq.) was dissolved in chloroform (10 mL) and NBS (34.9 mg, 0.196 mmol, 1.0 eq.) was added in one batch at r.t. After stirring overnight the reaction mixture was concentrated in vacuo then loaded directly on silica gel column chromatography eluted using DCM:hexane (1:3) leading to compound **14** (108 mg, 0.183 mmol, 94%) as a colorless sticky oil. ¹H NMR (600 MHz, CDCl₃, 298 K): δ 7.49–7.47 (m, 8H), 7.36 (d, *J* = 8.7 Hz, 1H), 7.29–7.22 (m, 6H), 7.18–7.14 (m, 4H), 7.03 (d, *J* = 8.8 Hz, 1H), 2.64 (t, *J* = 7.7 Hz, 4H), 1.66–1.61 (m, 4H), 1.42–1.36 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H). ¹³C NMR

(150 MHz, CDCl₃, 298 K): δ 147.64, 146.74, 141.6, 138.0, 136.0, 129.3, 128.8, 127.64, 126.5, 124.5, 124.2, 123.0, 35.3, 33.7, 22.4, 14.0. HRMS (TOF ASAP+, m/z): observed 588.2271, calculated for C₃₈H₃₉BrN [M+H]⁺ 588.2260.

4'-Butyl-N-(4'-butyl-[1,1'-biphenyl]-4-yl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1'-biphenyl]-4-amine (11). In a Schlenk tube compound **14** (300 mg, 0.510 mmol, 1.0 eq.), PdCl₂(CN)₂ (3.89 mg, 0.015 mmol, 3 mol%), and SPhos (12.3 mg, 0.030 mmol, 6 mol%) were added then evacuated and nitrogen atmosphere established. Then dry 1,4-dioxane (2 mL) was add and stirred at r.t before adding 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.155 mL, 137 mg, 1.07 mmol, 2.1 eq.) and Et₃N (0.220 mL, 160 mg, 1.58 mmol, 4.0 eq.). The reaction mixture was stirred for overnight at 110 °C. After cooling to r.t the reaction mixture was poured into water (100 mL). The aqueous layer was extracted with DCM (3x15 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated under reduced pressure to give crude compound **11**, which was used without further purification.

DFT calculations

Table S1. Optimized structure and electron distribution in HOMO and LUMO levels of **D1** to **D5** dyes. Optimization of the ground-state geometry at the density functional theory (DFT) level was carried out using the B3LYP functional and the 6-31G(d,p) basis set [1-4]. Solvent effects were introduced by using the polarized continuum model[5]. A subsequent vibrational frequency calculation was performed to ensure that the structure obtained in the first step is a true minimum. The lowest 5 excited states were then computed time-dependent density functional theory (TD-DFT) using the range-separated CAM-B3LYP functional and the 6-31G(d,p) atomic basis set[6]. All calculations were carried out using the Gaussian 09 software[7].

Structure	HOMO (eV)	LUMO (eV)
D1 	 -5.05	 -2.72
D2 	 -4.94	 -2.71
D3 	 -4.91	 -3.01
D4 	 -4.88	 -3.03
D5 	 -4.85	 -2.69

Absorption and emission spectra of the dyes D1–D5

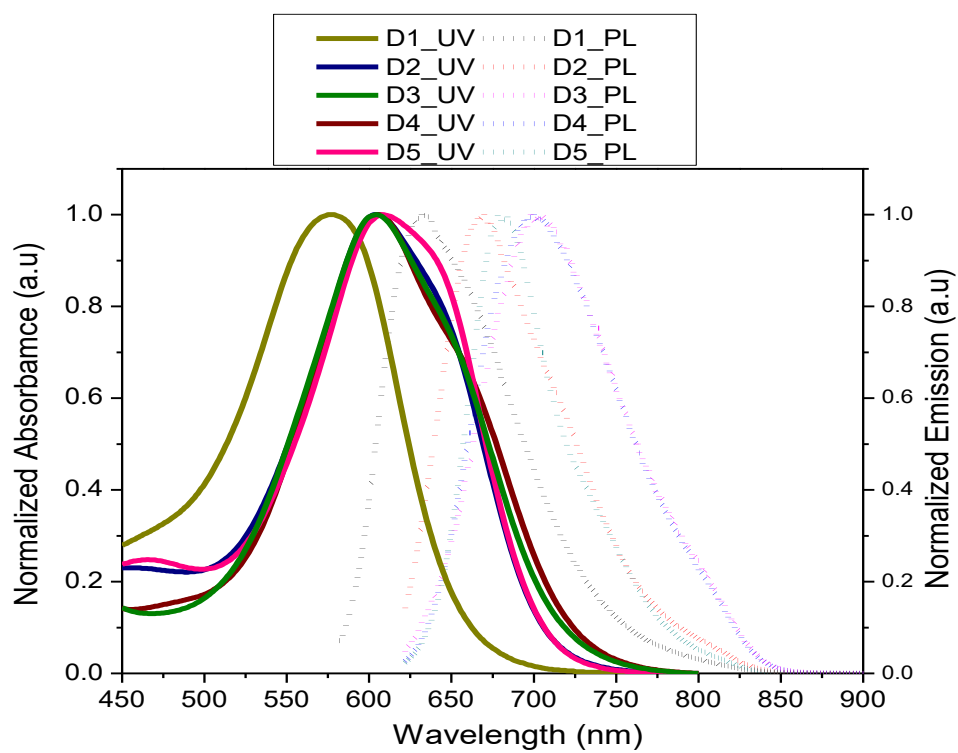


Figure S1. Normalized absorption and emission spectra of the dyes **D1–D5** in DCM solution.

Cyclic voltammogram of dyes D1–D5

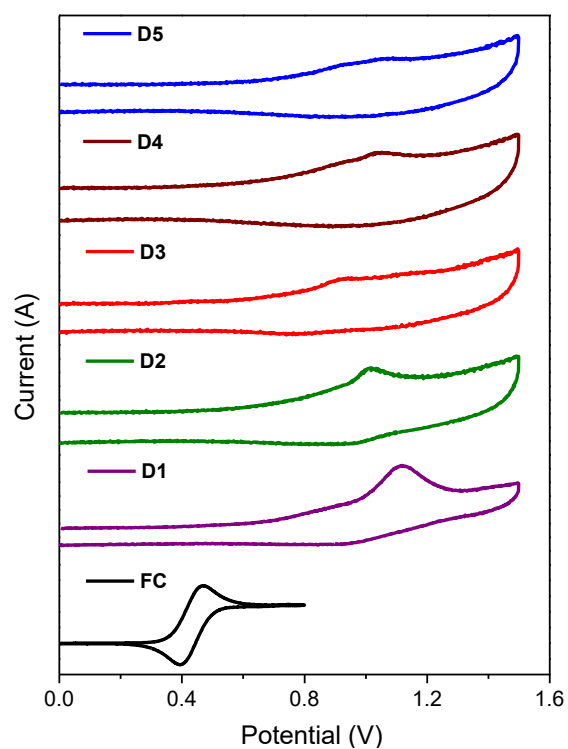


Figure S2. Cyclic voltammogram of dyes **D1–D5**. All measurements were done in solution with TBAPF₆ as supporting electrolyte (0.1 M in acetonitrile) at Scan rate 50 mV/s.

¹H and ¹³C NMR spectra of key building blocks and dyes

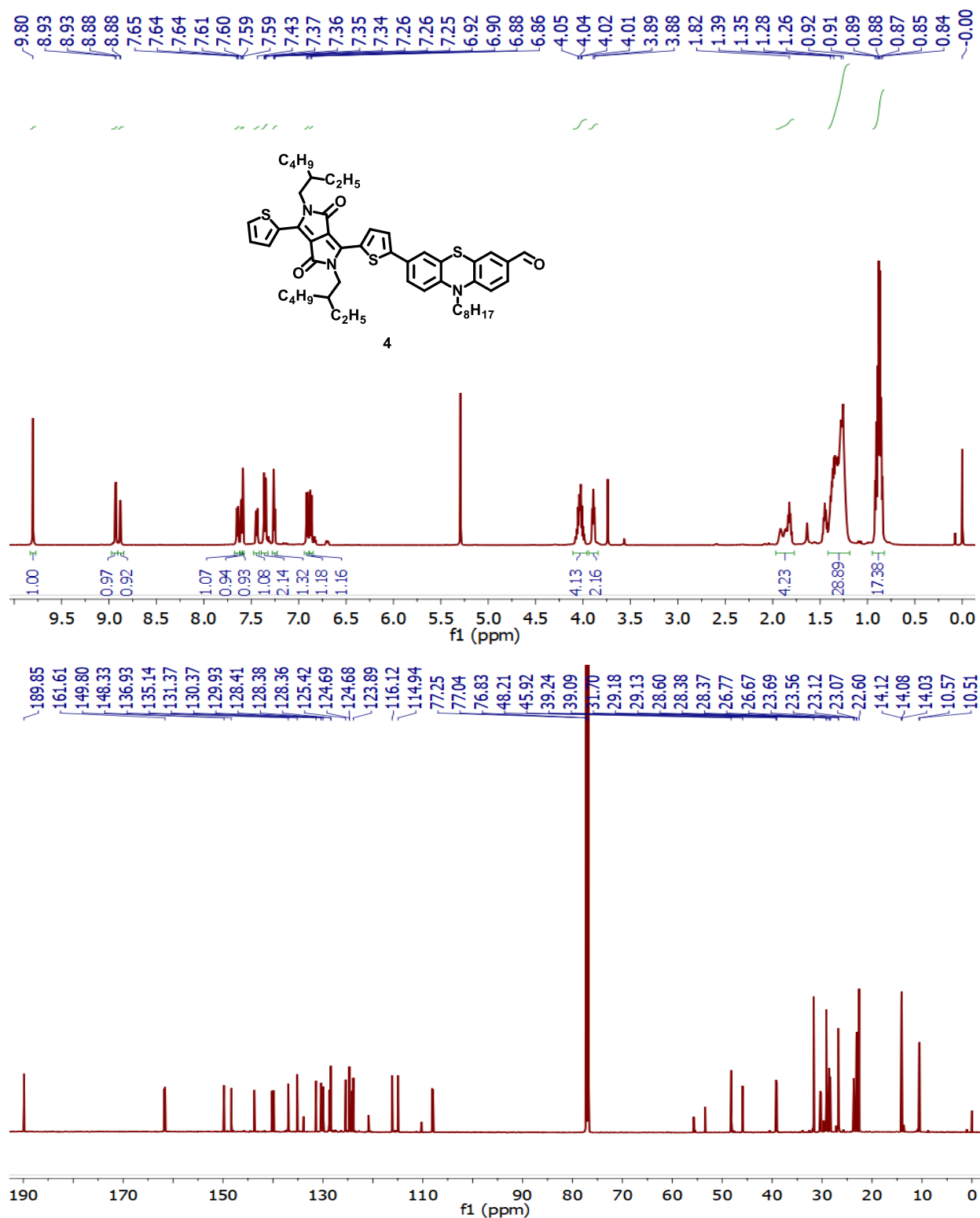
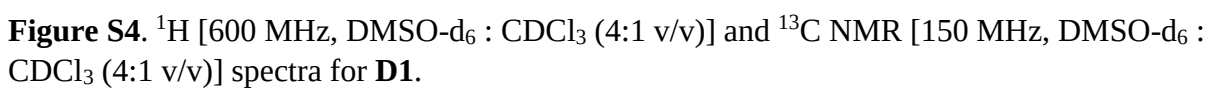


Figure S3. ¹H (600 MHz, CDCl₃) and ¹³C NMR (150 MHz, CDCl₃) spectra for **4**.



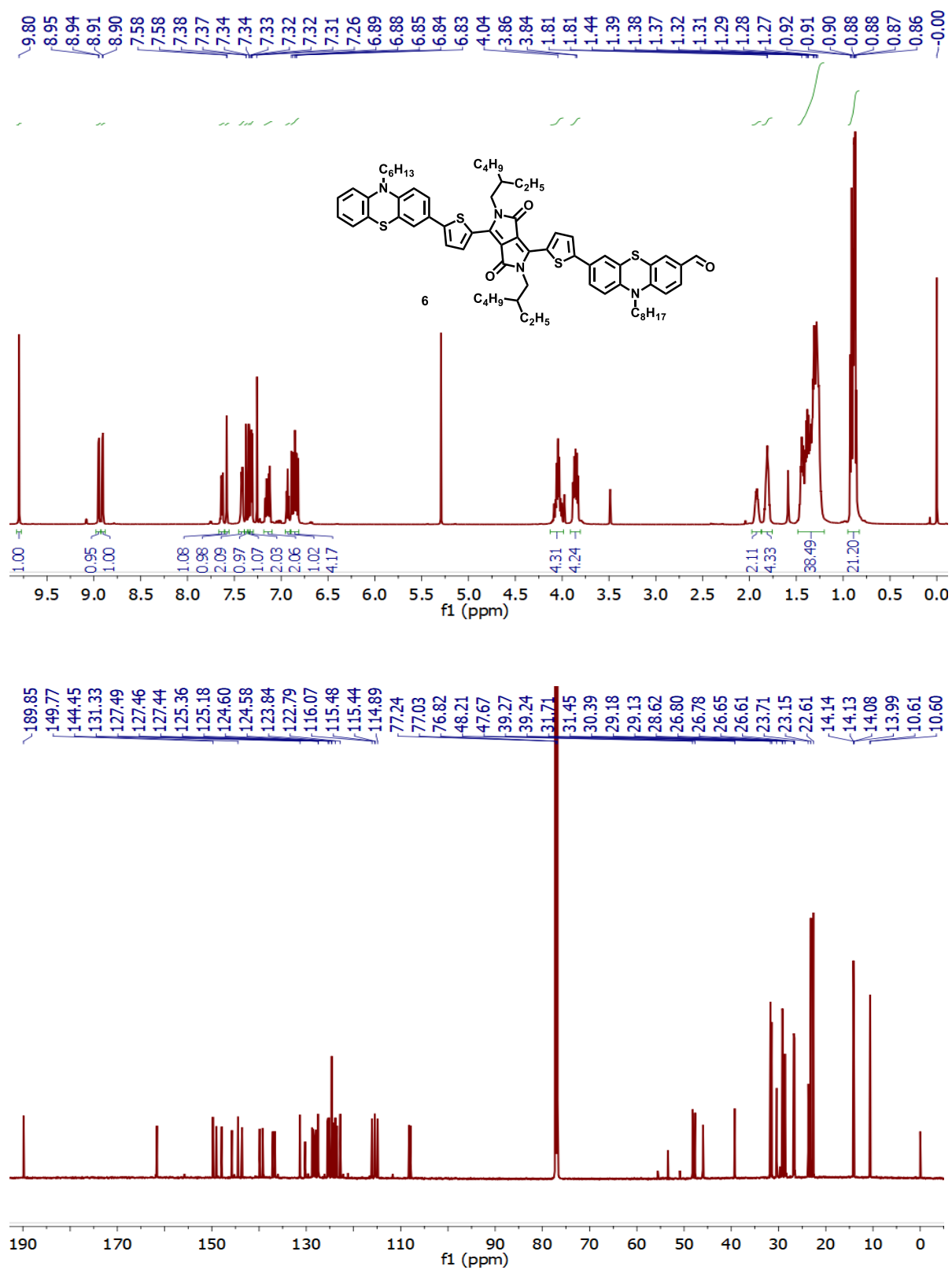


Figure S5. ¹H (600 MHz, CDCl₃) and ¹³C NMR (150 MHz, CDCl₃) spectra for **6**.

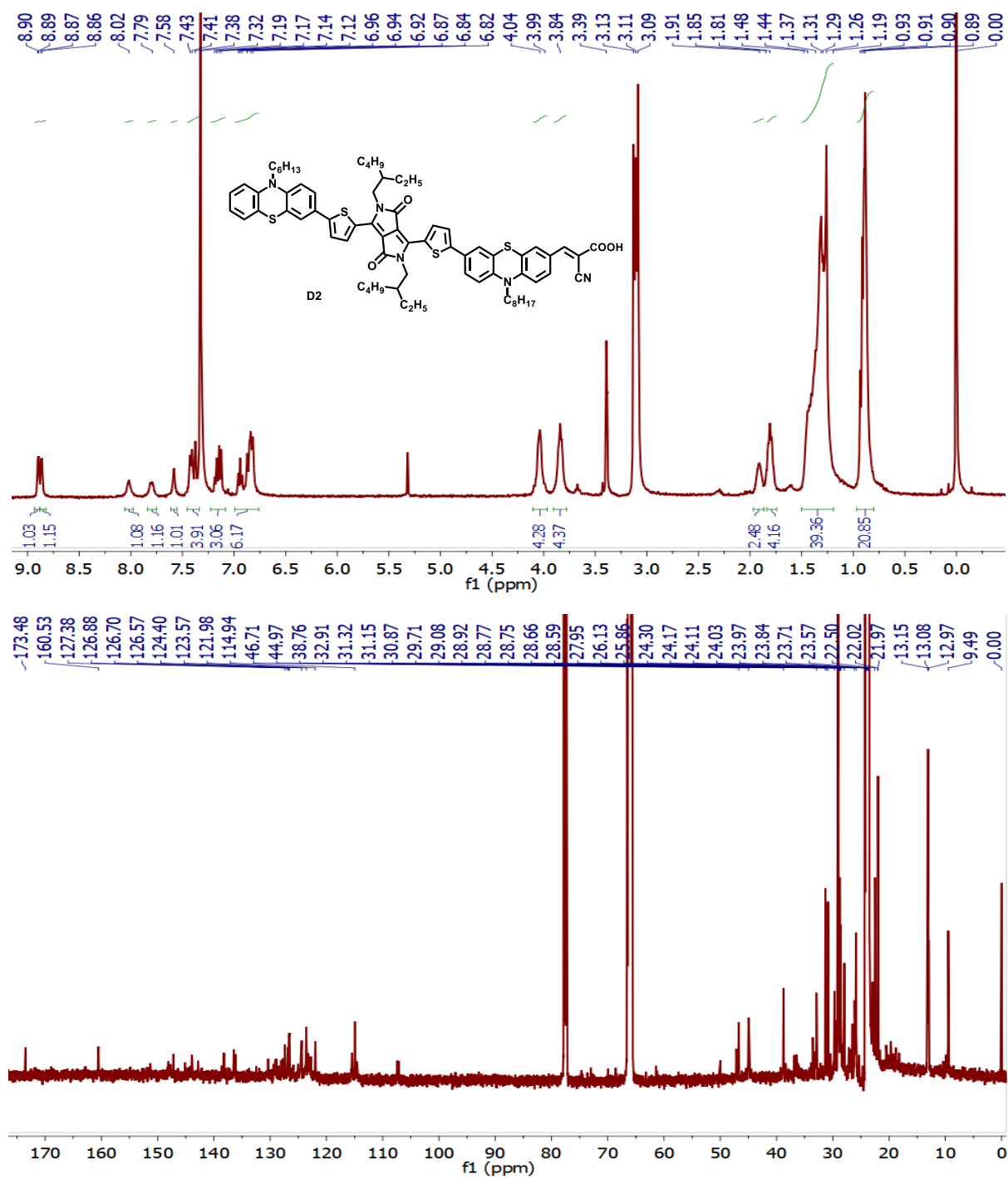


Figure S6. ¹H [400 MHz, CDCl₃ : CD₃OD (4:1 v/v)] and ¹³C NMR [150 MHz, DMSO-d₆ : CDCl₃ (4:1 v/v)] spectra for **D2**.

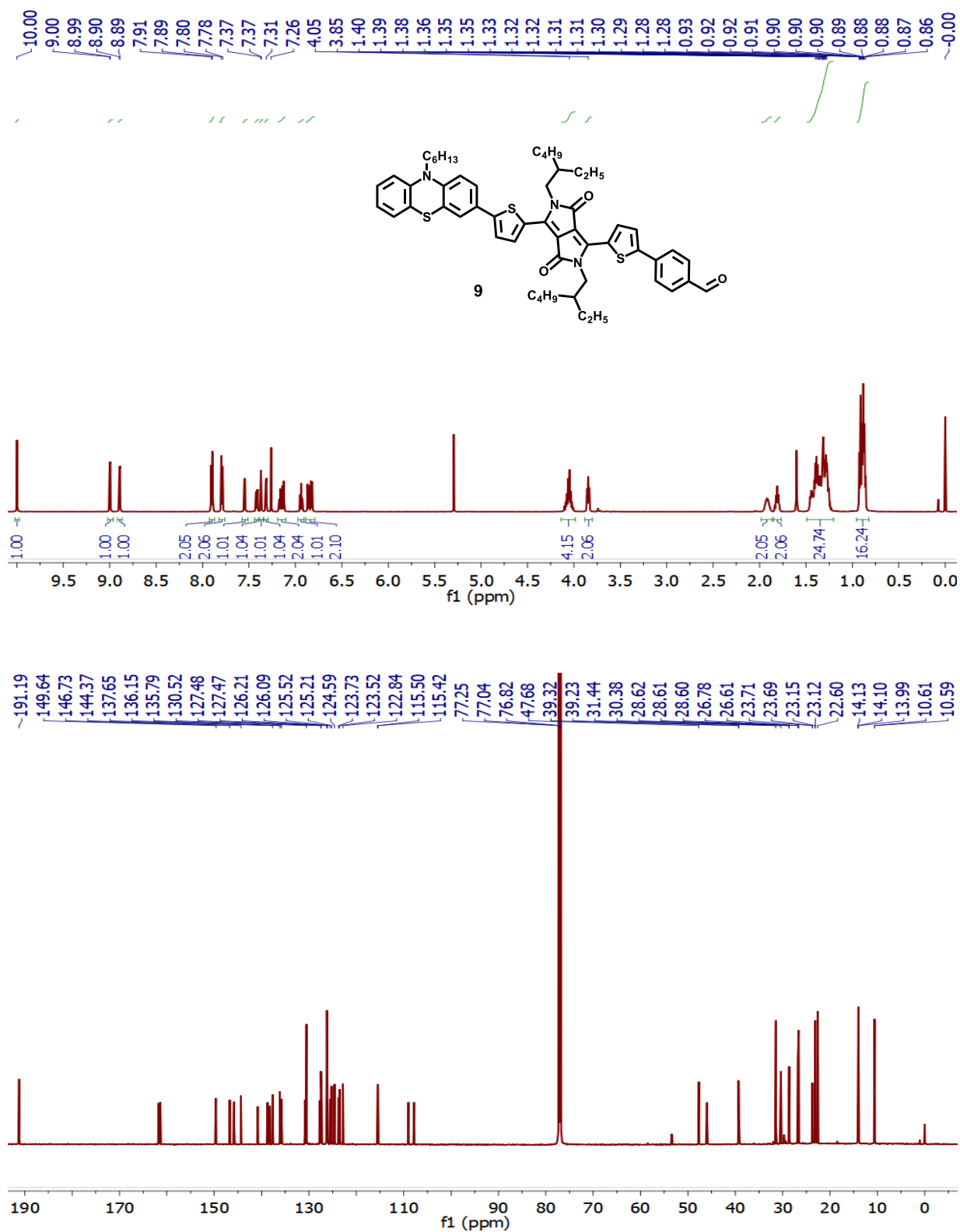


Figure S7. ¹H (600 MHz, CDCl₃) and ¹³C NMR (150 MHz, CDCl₃) spectra for **9**.

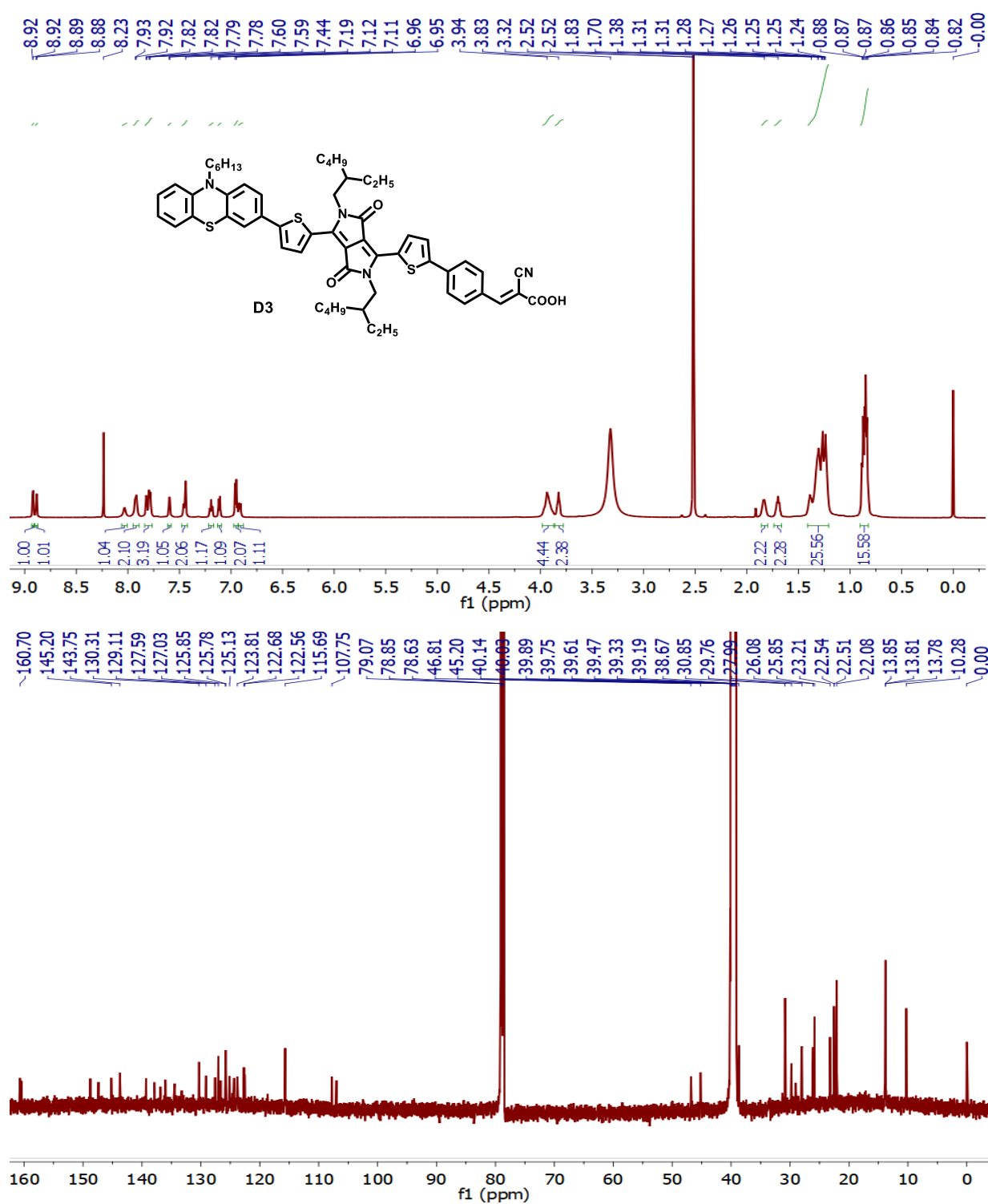


Figure S8. ¹H [600 MHz, DMSO-d₆ : CDCl₃ (4:1 v/v)] and ¹³C NMR [150 MHz, DMSO-d₆ : CDCl₃ (4:1 v/v)] spectra for **D3**.

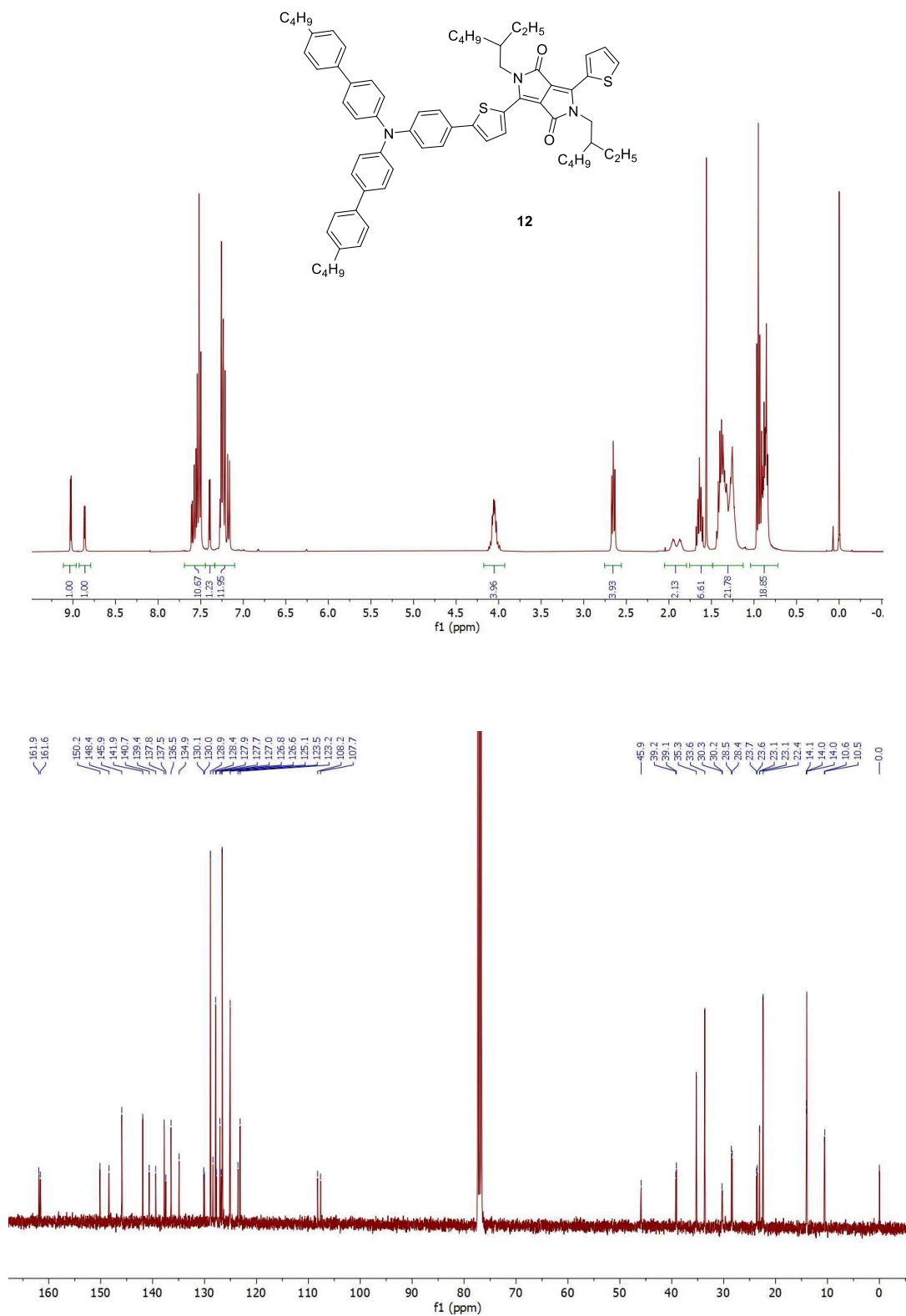


Figure S9. ^1H (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for **12**.

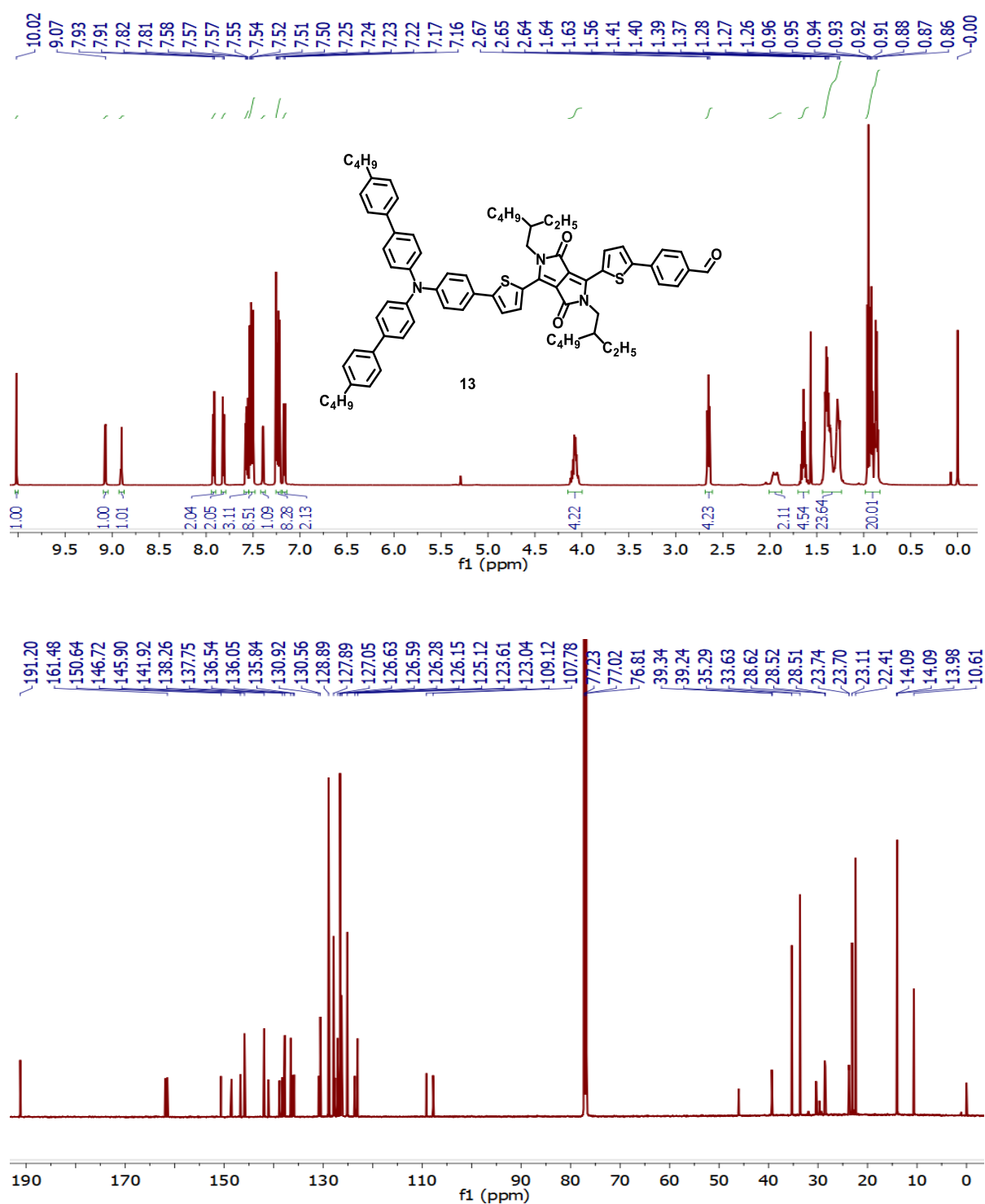


Figure S10. ¹H (600 MHz, CDCl₃) and ¹³C NMR (150 MHz, CDCl₃) spectra for **13**.

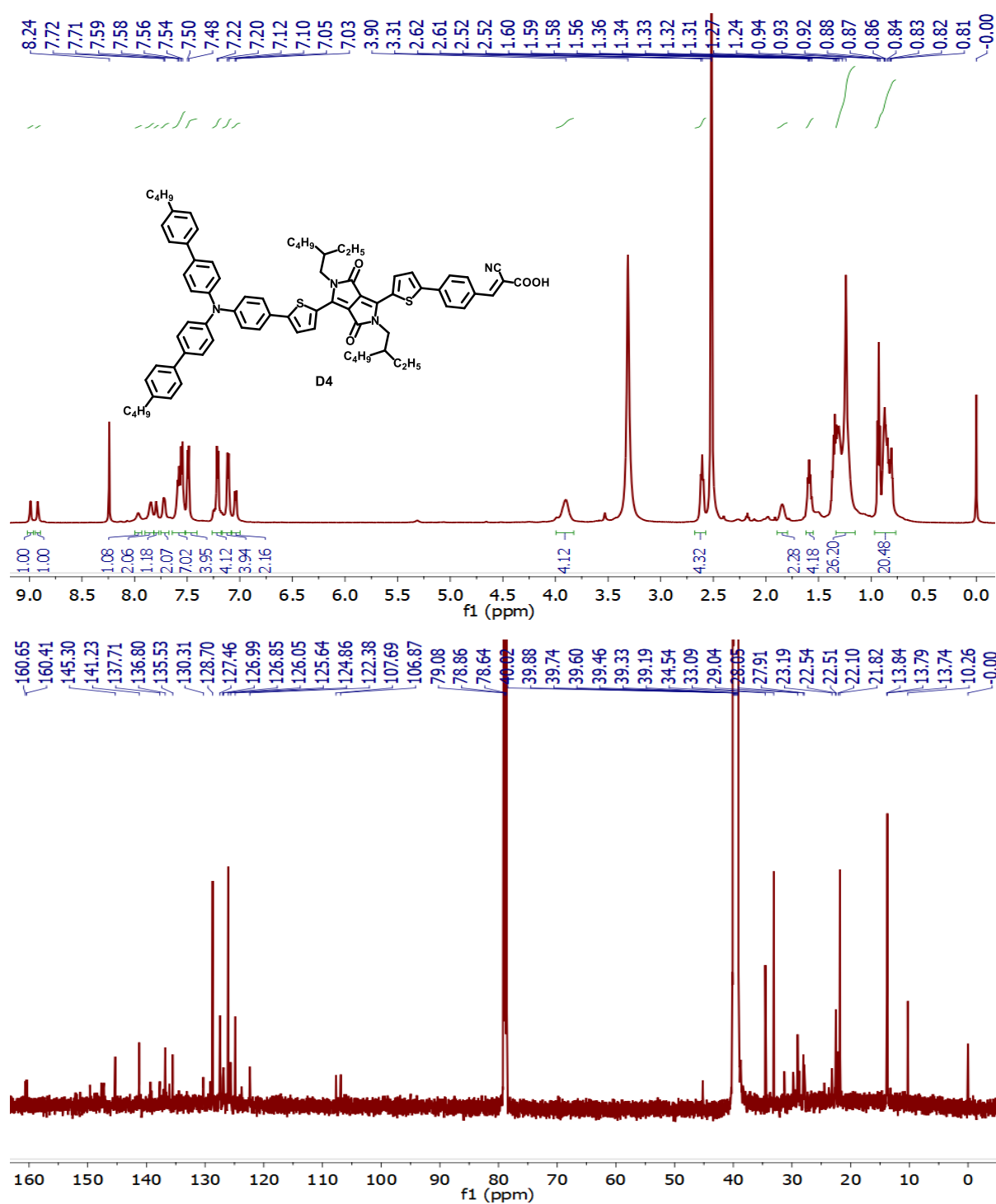


Figure S11. ¹H [600 MHz, DMSO-d₆: CDCl₃ (4:1 v/v)] and ¹³C NMR [150 MHz, DMSO-d₆: CDCl₃ (4:1 v/v)] spectra for **D4**.

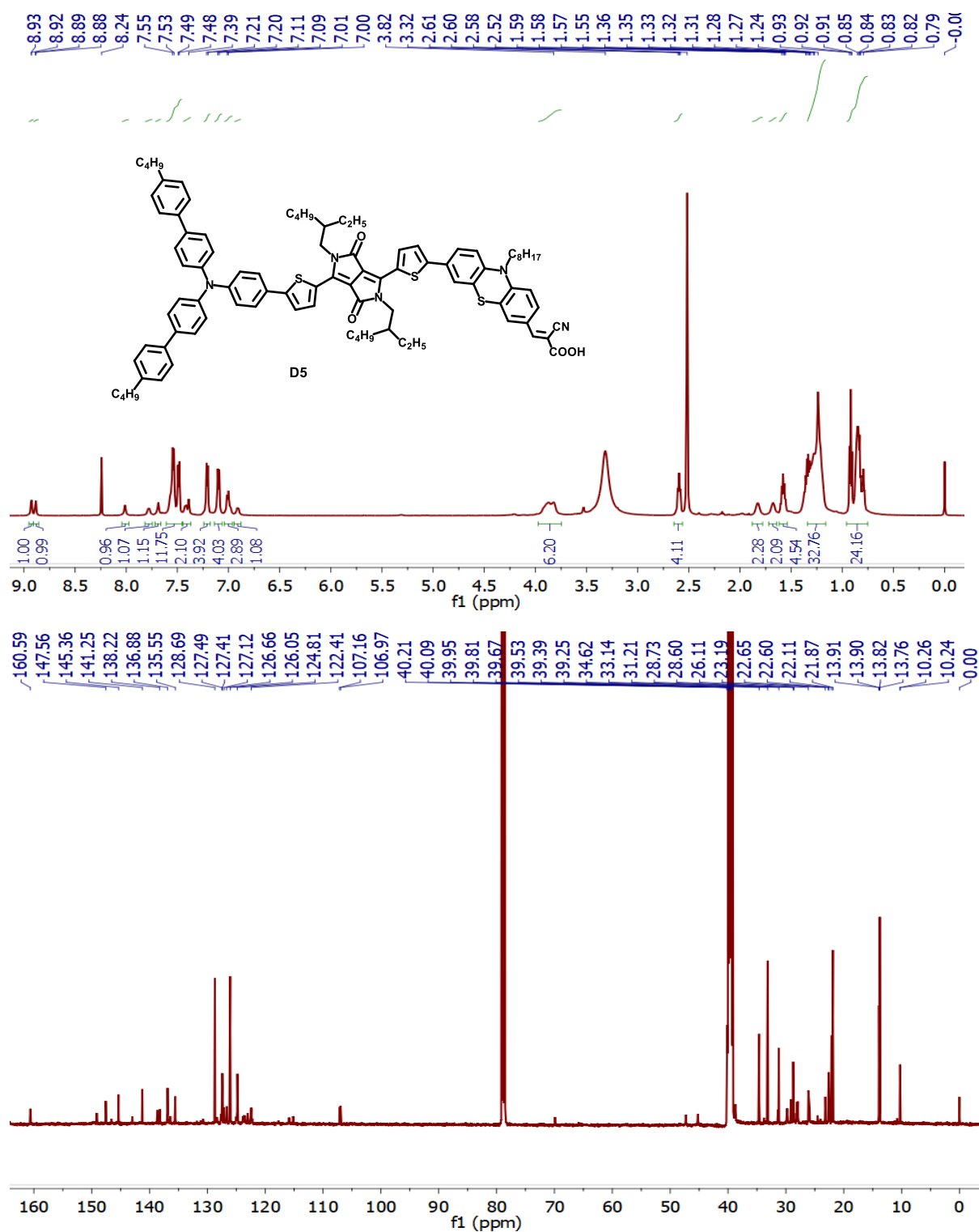


Figure S13. ¹H [600 MHz, DMSO-d₆; CDCl₃ (4:1 v/v)] and ¹³C NMR [150 MHz, DMSO-d₆; CDCl₃ (4:1 v/v)] spectra for **D5**.

References

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