Supporting Information

Enhancement of Photovoltaic Efficiency by Light Triggered Self Assembly

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Experimental

Synthetic Chemistry

Dry tetrahydrofuran (THF), CH_2Cl_2, and toluene were obtained by passing these solvents through activated alumina columns. All reagents were purchased from Sigma-Aldrich and used as received. Analytical thin layer chromatography (TLC) was conducted on Sigma-Aldrich silica gel coated aluminium sheets and visualised with UV. Flash chromatography was carried out using Merck Kieselgel 60 (230-400 mesh; particle size 0.04-0.63 mm) silica gel.

Analytical Chemistry

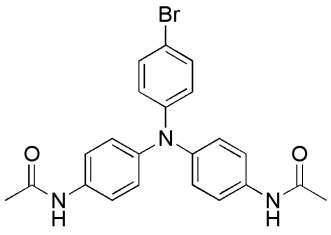
^{1}H and ^{13}C NMR spectra were recorded on a Bruker Av400 spectrometer at 400 MHz and 100.6 MHz respectively. Chemical shifts (δ) are measured in ppm and referenced internally to the residual solvent signal. Melting points were recorded on an Electrothermal IA9300 digital melting point apparatus. Positive ion EI mass spectra were run on a ThermoQuest MAT95XL mass spectrometer using an ionization energy of 70 eV. Accurate mass measurements were obtained with a resolution of 5000-10000 using perfluorokerosene as the reference compound. Microanalyses were performed by Chemical and MicroAnalytical Services Pty. Ltd. Belmont, 3216, Australia. Illumination of samples was conducted using a 100W Tungsten light source. EPR spectra was obtained using a Bruker CW ELGXYS E500 spectrometer at room temperature. The AFM samples were prepared by drop casting compounds (1 mg/ml in chloroform) on a Silicon substrate. Tapping-mode AFM (NanoScope II, Dimension, Digital Instrument Inc.) was carried out with commercially available tapping mode tips.

Device Fabrication

Bulk-heterojunction (BHJ) solar cells were fabricated by the spin coating of 30-nm-thick layers of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; Baytron AI 4083 from HC Starck) on patterned glass substrates which were washed by acetone, and 2-propanol in an ultrasonication bath and UV/ozone-treated. The PEDOT:PSS films were baked at 140 °C for 10 min in air. An active layer of the device consisting of the blend of organic donor molecule and $PC_{60}BM$ (99.5% pure, Solenne BV) with a ratio of 1:1 was then spin coated from chloroform solvent with a thickness of ~ 80 nm. A thin layer of ZnO nanopaticle was deposited on the active layer by spin-coating (3000 rpm) to form 25nm of ZnO layer. The films were transferred to a metal evaporation chamber and aluminum (100 nm) were deposited through a shadow mask (active area was 0.06 cm^2) at approximately 1 $x10^{-6}$ torr. Film thickness was determined by Veeco Dektak 150+Surface Profiler. The current density-voltage measurements of the devices were carried out using a 1 kW Oriel solar simulator with an AM 1.5G filter as the light source in conjunction with a Keithley 2400 source measurement unit. Solar measurements were carried out under 1000 W/m^2 AM 1.5G illumination conditions. For accurate measurement, the light intensity was calibrated using a reference silicon solar cell (PVmeasurements Inc.) certified by the National Renewable Energy Laboratory. Device fabrication and characterizations were performed in an ambient environment without any encapsulation.

Synthesis

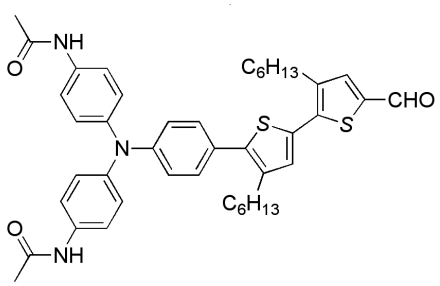
N,N′-*(((4-bromophenyl)azanediyl)bis(4,1-phenylene))diacetamide* (**2**)



To a solution of acetic anhydride (100 mL) and 4-bromotriphenylamine (1.4 g, 4 mmol) under inert atmosphere was added $Cu(NO_3)_2.2.5H_2O$ (920 mg, 4 mmol) and

the solution heated at 50 ^{o}C with stirring for 4 h. Water (200 mL) and $CHCl_3$ (100 mL) were then added to the reaction mixture, followed by careful addition of saturated $NaHCO_3$ solution until no further CO_2 was produced. The aqueous layer was then extracted with $CHCl_3$ (3 x 100 mL) and the combined organic layers were dried ($MgSO_4$) and evaporated *in vacuo* to give the crude dinitro compound as an orange solid. In a separate flask, crystalline $SnCl_2$ (28.0 g, 0.14 mol) was treated with Ac_2O (35 mL, caution: exothermic) for 10 min. After the dehydration was complete, the crude dinitro compound was added and the reaction was then heated at 70 ^{o}C for 4 h until a clear yellow solution was obtained. The Ac_2O was removed *in vacuo* and the crude residue was treated with water (80 mL) and briefly heated to 80 ^{o}C with agitation. The solution was then allowed to cool to room temperature, filtered and the aqueous filtrate was extracted with dichloromethane (3 x 100 mL). The combined organic extracts were combined with the solid product and dried ($MgSO_4$), and the solvent removed in vacuo. The crude residue was purified by column chromatography (SiO_2, 5% CH_3OH, CH_2Cl_2) yielding the product as a light yellow powder (1.2 g, 67 %). m.p. 241 – 243 ºC; R_f 0.07 (CH_2Cl_2, 5% CH_3OH); IR (neat, cm^{-1}) 1653, 1597, 1533,1502, 1484, 1411, 1400,1371, 1307, 1267, 1071, 1006, 827, 766, 710, 671, 605; ^{1}H NMR (400 MHz, DMSO-d6) δ 9.92 (s, 2H), 7.56 – 7.47 (m, 4H), 7.40 – 7.31 (m, 2H), 7.02 – 6.93 (m, 4H), 6.82 – 6.73 (m, 2H), 2.02 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d6) δ 167.9, 147.1, 141.6, 135.4, 131.9, 125.1, 122.6, 120.3, 112.2, 23.8; HRMS (ESI) Calcd for $C_{22}H_{20}{}^{79}BrN_3O_2Na$: 460.06311 $[M+Na]^+$, found 460.06305.

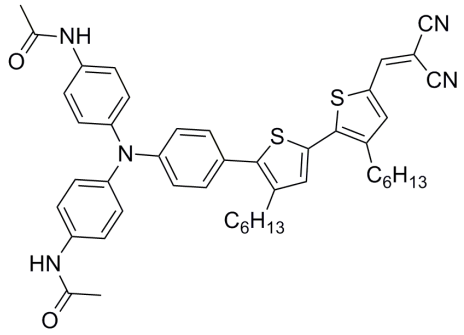
N,N'-*(((4-(5'-formyl-3',4-dihexyl-[2,2'-bithiophen]-5-yl)phenyl)azanediyl)bis(4,1-phenylene))diacetamide* (**3**)



To a degassed solution of **2** (0.25 g, 0.56 mmol), 3,4'-dihexyl-5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[2,2'-bithiophene]-5-carbaldehyde (0.25 g, 0.51 mmol) and Cs_2CO_3 (0.50 g, 1.5 mmol) was added $Pd(PPh_3)_4$ (0.059 g, 0.051 mmol) and the resulting suspension was heated to reflux for 16 h. The reaction mixture was cooled to

room temperature, diluted with *n*-heptane, filtered and concentrated in vacuo. The crude residue was then purified by flash chromatography (SiO_2, 5% CH_3OH, CH_2Cl_2) to give **3** (0.19 g, 0.26 mmol, 52%) as an orange solid. m.p. 151 – 153 ºC; R_f 0.35 (10% CH_3OH/CH_2Cl_2); IR (neat, cm^{-1}) 3303, 3275, 2954, 2927, 2856, 1664, 1601, 1533, 1506, 1456, 1421, 1406, 1370, 1313, 1284, 1261, 1252, 1180, 1156, 831, 737, 731, 724, 681, 674, 669, 661, 638, 625, 614, 609, 602; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.81 (s, 2H), 7.58 (s, 1H), 7.45 – 7.34 (m, 4H), 7.26 – 7.21 (m, 2H), 7.13 (s, 1H), 7.08 – 6.97 (m, 6H), 2.87 – 2.73 (m, 2H), 2.72 – 2.58 (m, 2H), 2.16 (s, 6H), 1.74 – 1.55 (m, 4H), 1.45 – 1.19 (m, 12H), 0.91 – 0.81 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.7, 168.6, 147.5, 143.6, 142.1, 140.4, 140.0, 139.8, 139.4, 139.2, 133.7, 132.3, 130.2, 129.9, 127.1, 125.4, 122.2, 121.6, 31.7, 31.0, 30.4, 29.5, 29.3, 29.2, 28.9, 24.5, 22.7, 14.20, 14.18. LRMS (EI): *m/z* (%): 240 (11), 719 (100), 720 (50), 721 (22); HRMS (EI) Calcd for $C_{43}H_{49}N_3O_3{}^{32}S_2$: 719.3215 $[M]^{+\bullet}$, found 719.3224.

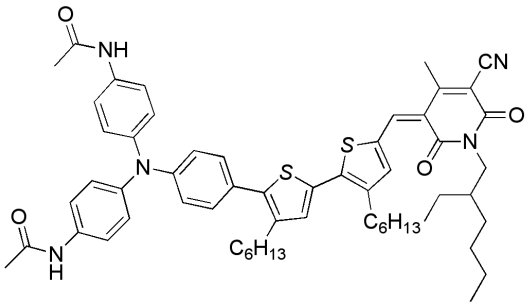
*N,N'-(((4-(5'-(2,2-dicyanovinyl)-3',4-dihexyl-[2,2'-bithiophen]-5-yl)phenyl)azanediyl)bis(4,1-phenylene))diacetamide (**4**)*



To a solution of malononitrile (9.6 mg, 0.15 mmol) and **3** (35 mg, 0.05 mmol) in chloroform (5 mL) was added pyridine (20 μL, 0.25 mmol) at room temperature. The resulting solution was then heated to 70 °C and stirred for 4 h. The resulting solution was cooled to room temperature and concentrated *in vacuo*. The crude residue was purified by column chromatography (SiO_2, 10% CH_3OH/CH_2Cl_2) to give titled compound **4** (25 mg, 0.03 mmol, 67%) as a red solid. m.p. 159 – 162 ºC; R_f 0.38 (CH_2Cl_2, 5% CH_3OH); IR (neat, cm^{-1}) 3301, 3040, 2927, 2856, 2221, 1665, 1601, 1569, 1536, 1506, 1433, 1418, 1371, 1314, 1282, 1181, 1090, 1017, 918, 830, 728; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.51 (s, 1H), 7.47 (s, 2H), 7.40 (d, *J* = 8.6 Hz, 4H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.23 (s, 1H), 7.06 (d, *J* = 8.6 Hz, 4H), 7.02 (d, *J* = 8.6 Hz, 2H), 2.86 – 2.77 (m, 2H), 2.71 – 2.59 (m, 2H), 2.17 (s, 6H), 1.72 – 1.57 (m,

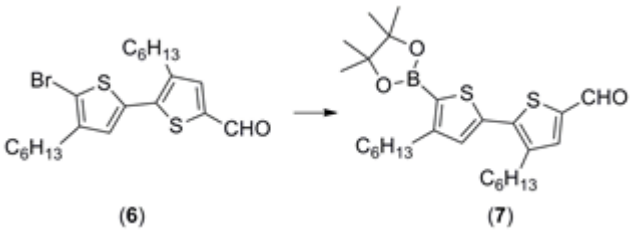
4H), 1.43 – 1.22 (m, 12H), 0.95 – 0.78 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 150.1, 147.7, 145.0, 143.5, 142.14, 142.06, 140.4, 139.7, 133.7, 131.8, 131.4, 131.3, 129.9, 126.7, 125.5, 122.0, 121.5, 114.7, 113.9, 75.3, 31.7, 31.7, 31.1, 30.1, 29.4, 29.3, 29.3, 28.9, 24.6, 22.72, 22.70, 14.23, 14.20; LRMS (ESI) *m/z* (%): 791 (100), 848 (12); HRMS Calcd for $C_{46}H_{49}N_5O_2{}^{32}S_2$: 790.3225 $[M+Na]^+$, found 790.3223; elemental analysis calcd (%) for $C_{46}H_{49}N_5O_2{}^{32}S_2$ C 71.9, H 6.4, N 9.1; found C 71.7, H 6.6, N 9.0.

(Z)-N,N'-*((((4-(5'-((5-cyano-1-(2-ethylhexyl)-4-methyl-2,6-dioxo-1,6-dihydropyridin-3(2H)-ylidene)methyl)-3',4-dihexyl-[2,2'-bithiophen]-5-yl)phenyl)azanediyl)bis(4,1-phenylene))diacetamide* (**5**)



A solution of **3** (62 mg, 86 µmol) and 1-(2-ethylhexyl)-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (23 mg, 86 µmol) was refluxed in EtOH (10 mL) for 2 h. The resulting suspension was cooled to room temperature and the solid that was formed in the reaction was collected by filtration to give **5** (63 mg, 65 µmol, 76 %) as a dark purple solid. m.p. 246 – 249 ºC; R_f 0.15 (CH_2Cl_2, 5% CH_3OH); IR (neat, cm^{-1}) 3335, 3318, 2955, 2927, 2868, 2857, 2222, 1669, 1642, 1600, 1576, 1534, 1507, 1449, 1429, 1410, 1380, 1355, 1292, 1231, 1219, 1178, 1110, 1092, 1016, 1007, 830, 785, 727, 635; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.59 (s, 1H), 7.47 – 7.37 (m, 5H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.18 (s, 2H), 7.09 (d, *J* = 8.4 Hz, 4H), 7.05 (d, *J* = 8.4 Hz, 2H), 4.03 – 3.88 (m, 2H), 2.86 (m, 2H), 2.69 (m, 2H), 2.63 (s, 3H), 2.18 (s, 6H), 1.93 – 1.81 (m, 1H), 1.77 – 1.60 (m, 4H), 1.51 – 1.18 (m, 20H), 0.97 – 0.82 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 163.4, 161.2, 158.3, 148.8, 147.8, 144.1, 143.6, 140.4, 139.8, 134.5, 133.7, 132.5, 131.4, 129.9, 127.0, 125.6, 122.1, 121.4, 116.1, 115.4, 110.8, 44.1, 37.6, 31.8, 31.1, 30.7, 30.1, 29.5, 29.4, 29.3, 28.9, 28.6, 24.7, 24.1, 23.3, 22.7, 19.1, 14.3, 14.2, 10.8; HRMS (ESI) Calcd for $C_{58}H_{69}N_5O_4{}^{32}S_2$: 963.47855 $[M+H]^+$, found 963.4787.

3,4'-dihexyl-5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[2,2'-bithiophene]-5-carbaldehyde (**7**)



(**6**) (**7**)

To a degassed solution of 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (1.2 g, 4.6 mmol), 5'-bromo-3,4'-dihexyl-[2,2'-bithiophene]-5-carbaldehyde (1.7 g, 3.9 mmol) and KOAc (0.76 g, 7.7 mmol) was added Pd(dppf) (0.12 g, 0.164 mmol) and the resulting solution was heated to 70 ºC for 16 h. The solution was then cooled to room temperature, diluted with *n*-heptane, filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography (SiO_2, 5% EtOAc/*n*-heptane) to give **7** (0.30 g, 0.61 mmol, 16%) as a yellow oil. R_f 0.25 (*n*-heptane, 5% EtOAc); IR (neat, cm^{-1}) 2975, 2954, 2925, 2856, 1667, 1525, 1466, 1428, 1396, 1391, 1379, 1371, 1337, 1271, 1241, 1214, 1200, 1141, 1111, 1096, 1047, 959, 854, 826, 671, 647; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.58 (s, 1H), 7.18 (s, 1H), 2.90 – 2.77 (m, 4H), 1.72 – 1.55 (m, 4H), 1.43 – 1.26 (m, 24H), 0.94 – 0.84 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.7, 155.2, 141.7, 140.8, 140.5, 140.3, 139.0, 130.8, 84.0, 31.79, 31.76, 30.33, 30.27, 29.4, 29.2, 29.1, 24.9, 22.74, 22.71, 14.24, 14.19; LRMS (EI): *m/z* (%): 83 (13), 417 (15), 418 (44), 419 (12), 487 (25), 488 (100), 489 (33), 490 (15); HRMS (EI) Calcd for $C_{27}H_{41}BO_3{}^{32}S_2$: 488.2590 $[M]^{+\bullet}$, found 488.2580.

Synthesis of ZnO Nanoparticles:

Zinc oxide (ZnO) nano-particles were synthesized as reported[1] by a sol-gel method using precursors of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $(CH_3)_4NOH$ (TMAH). In a typical process, ZnO nano-particles are synthesized by drop-wise addition of 0.4 M TMAH dissolved in ethanol to 0.1 M $Zn(CH_3COO)_2 \cdot 2H_2O$ dissolved in dimethyl sulfoxide (DMSO). The resulting ZnO nano-particles are washed and dispersed in ethanol at 25 mg/mL.

[1] G. Sarasqueta, K. R. Choudhury, J. Subbiah, F. So. Adv. Funct. Mater., **21** (2011), 167–171

Figures

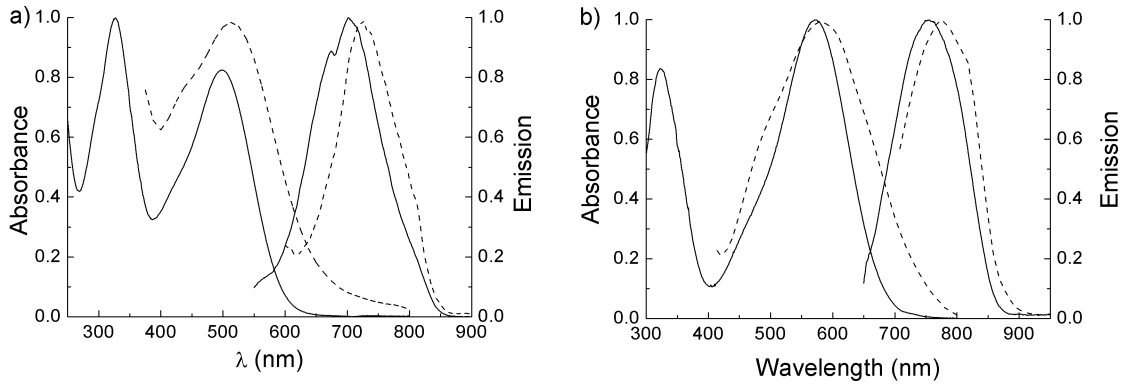


Figure S1: Absorption and Emission spectra of compounds **4** (a) and **5** (b) in $CHCl_3$ (solid line) and as a neat film (dashed line). Both the solution and film were freshly prepared in the dark.

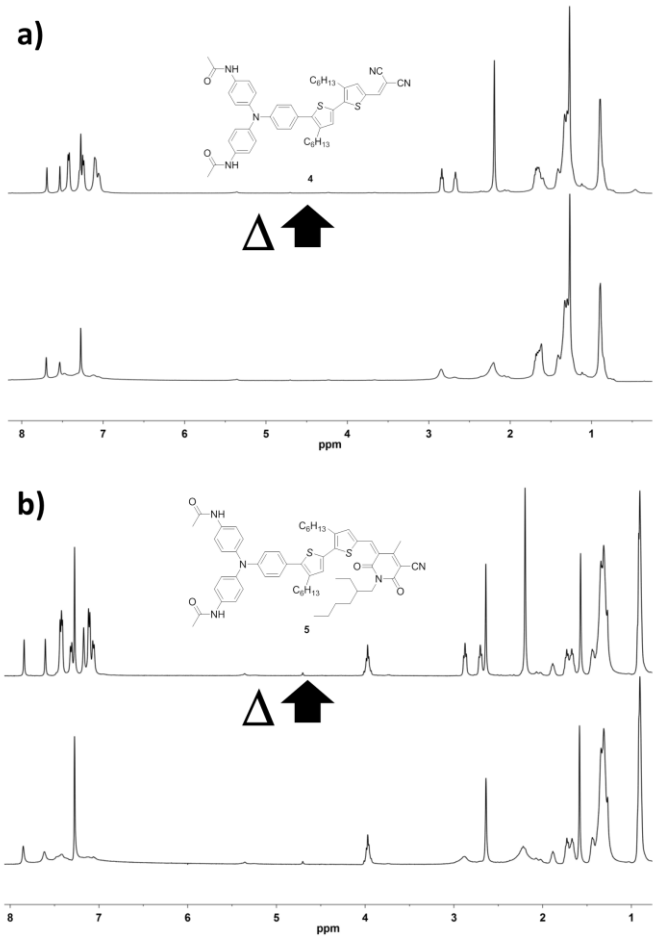


Figure S2: Recovery of ^{1}H-NMR signal upon heating $CDCl_3$ solutions of a) compound **4** and b) compound **5** at 60 °C for 48 h.

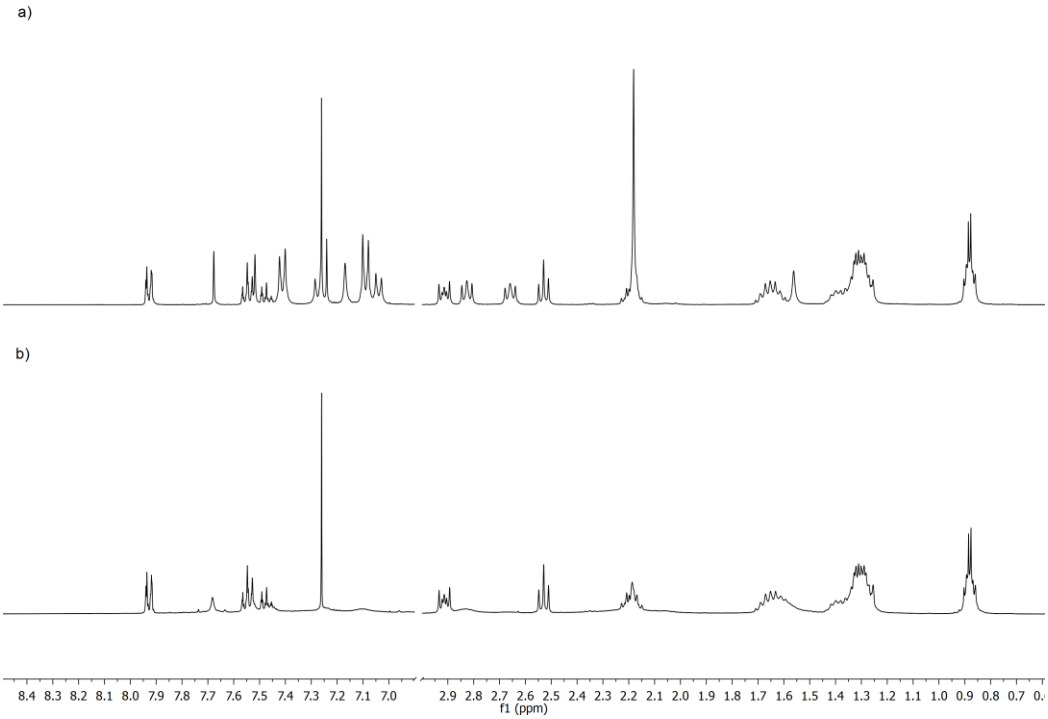


Figure S3:[1]H-NMR Spectra of a solution of **5** and PCBM (1:1 w/w) a) after 2 h in the dark and b) after white light irradiation for 2 h.

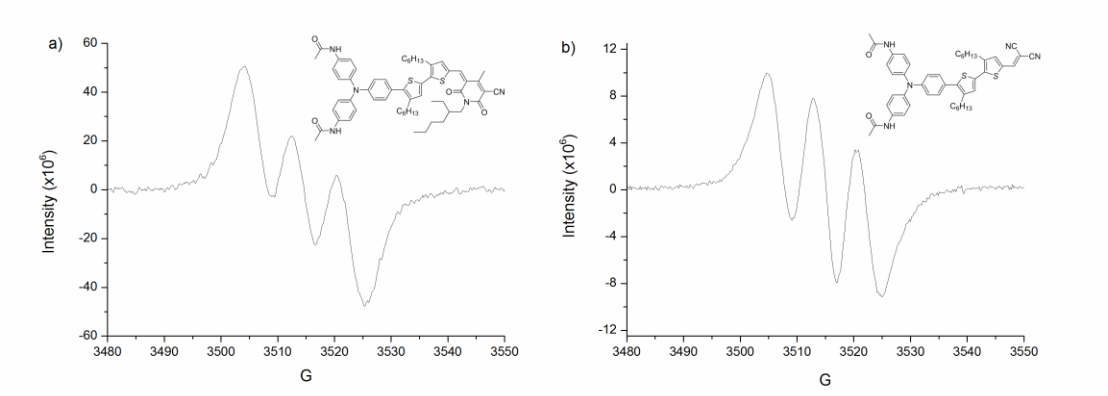


Figure S4: EPR Spectra of an irradiated (tungsten source) 5 mM $CHCl_3$ solution of compound a) **4** and b) **5**.

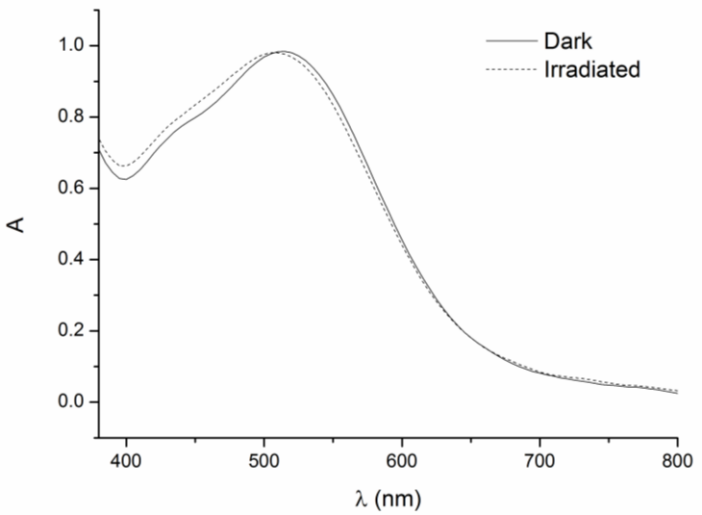


Figure S5: Effect of Irradiation on the absorption spectra of **5**.

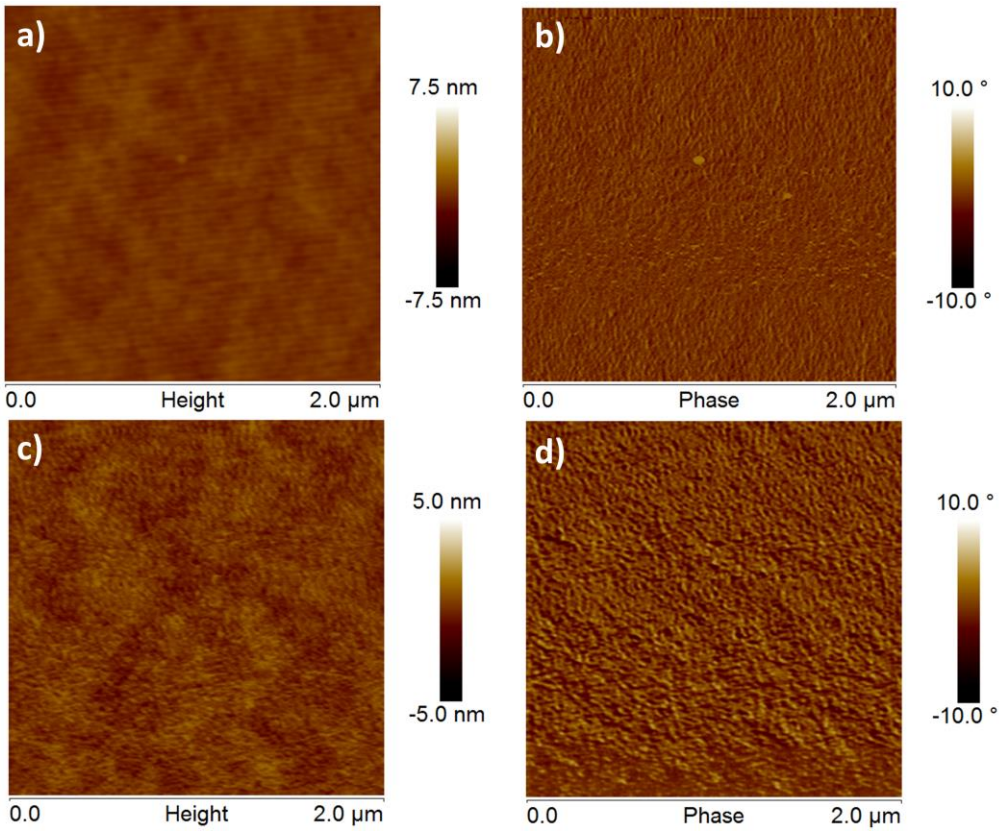


Figure S6: Height and phase AFM images of blended films of **4** (6 mg/mL) and $PC_{61}BM$ (6 mg/mL) spin coated from $CHCl_3$. Images a) and b) are have not been irradiated and images c) and d) were irradiated for 2 h using a tungsten white light source.

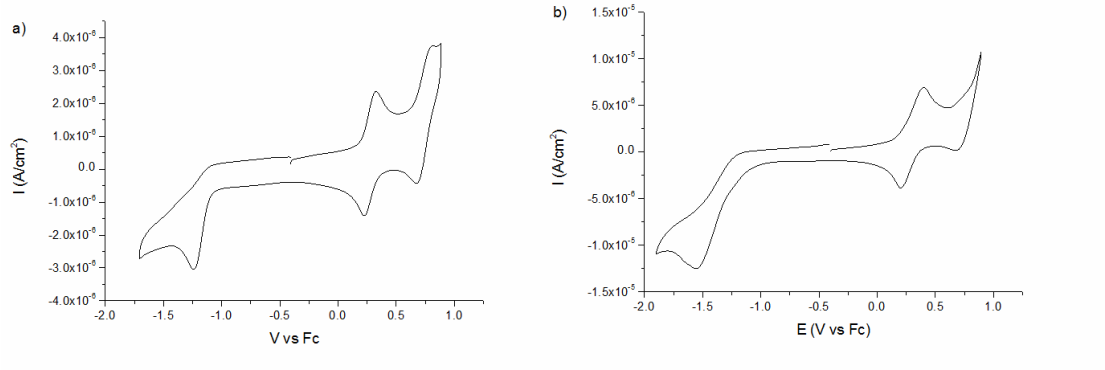


Figure S7: Cyclic voltammetry plots of a) compound **4** and b) compound **5**.

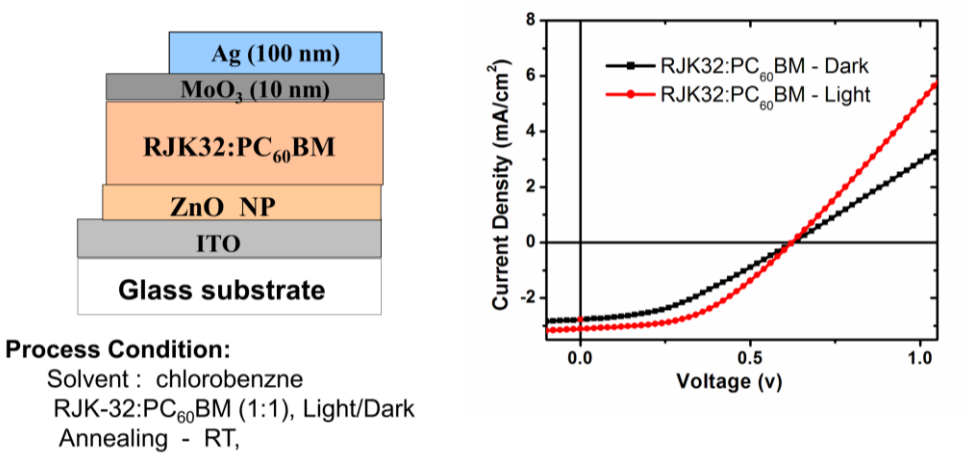


Figure S8: J/V Plots and Device Architecture for compound **4**.

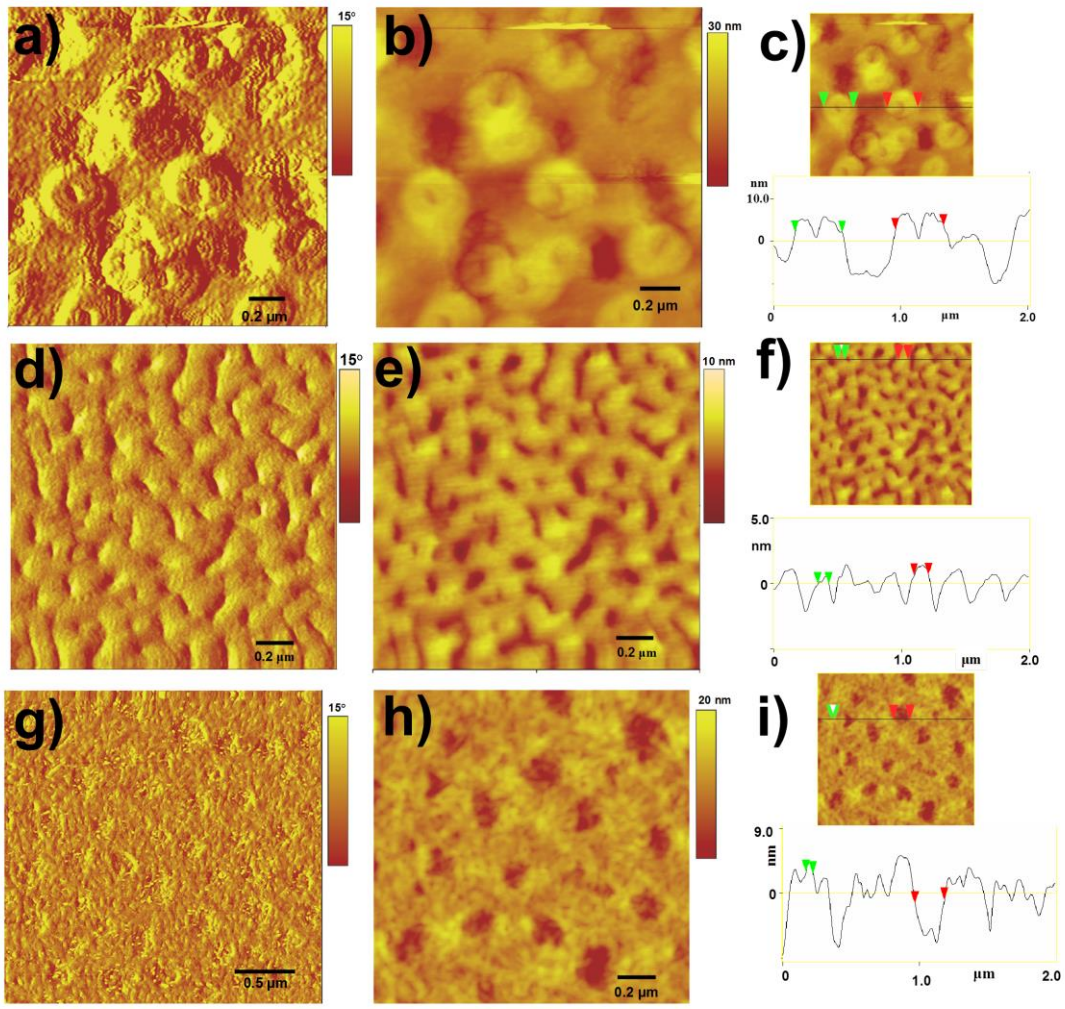


Figure S9: AFM images of drop-cast films deposited from the following solutions: 1 mg/mL **5** in chloroform dark condition a) phase image, b) height image and c) line scan; 1 mg/mL **5** in chloroform light condition d) phase image, e) height image and f) line scan; 5 mg/mL **5** and 5 mg/mL PCBM light condition g) phase image, h) height image and i) line scan.

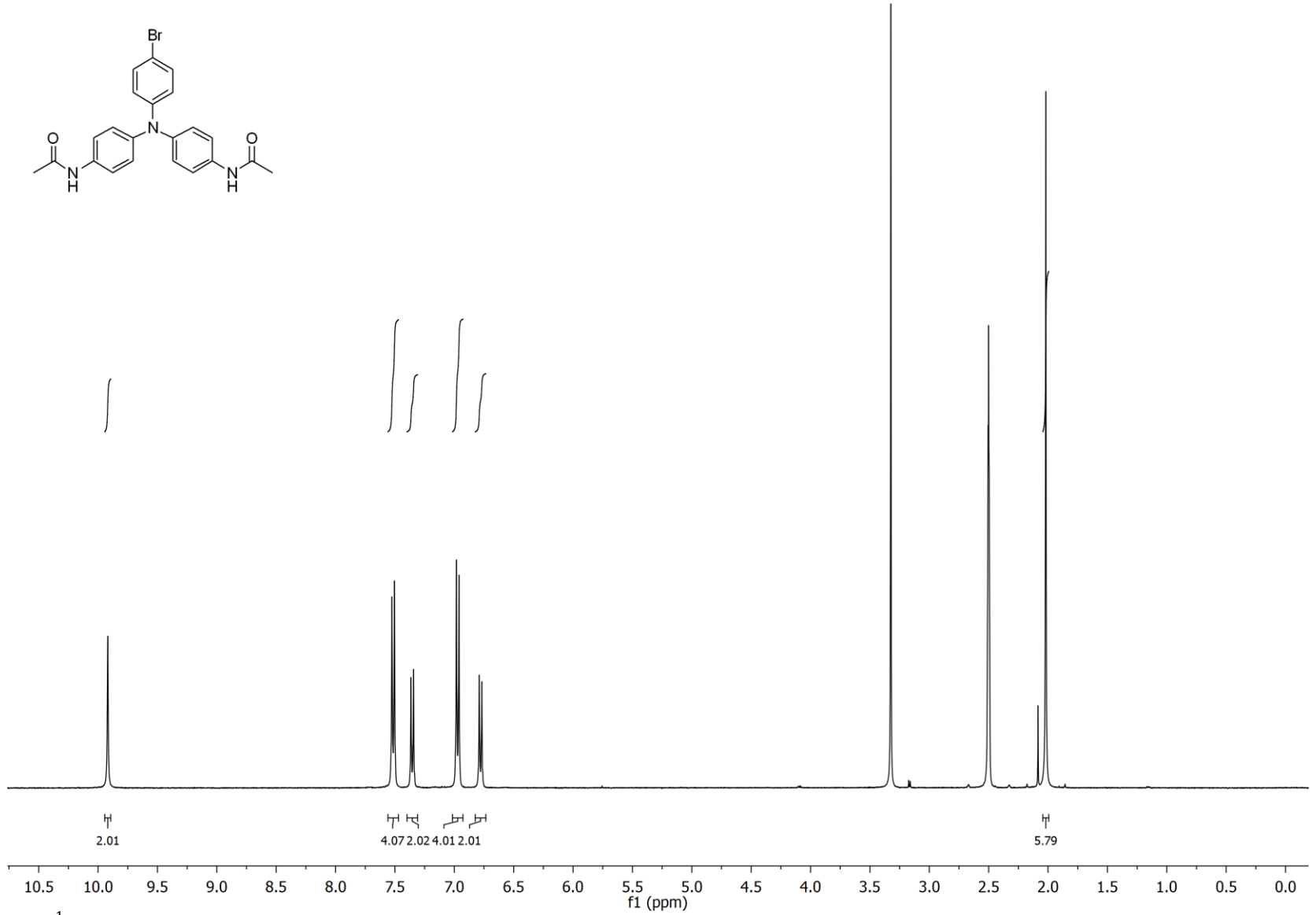


Figure S10: ^{1}H NMR of **2** in DMSO-d6.

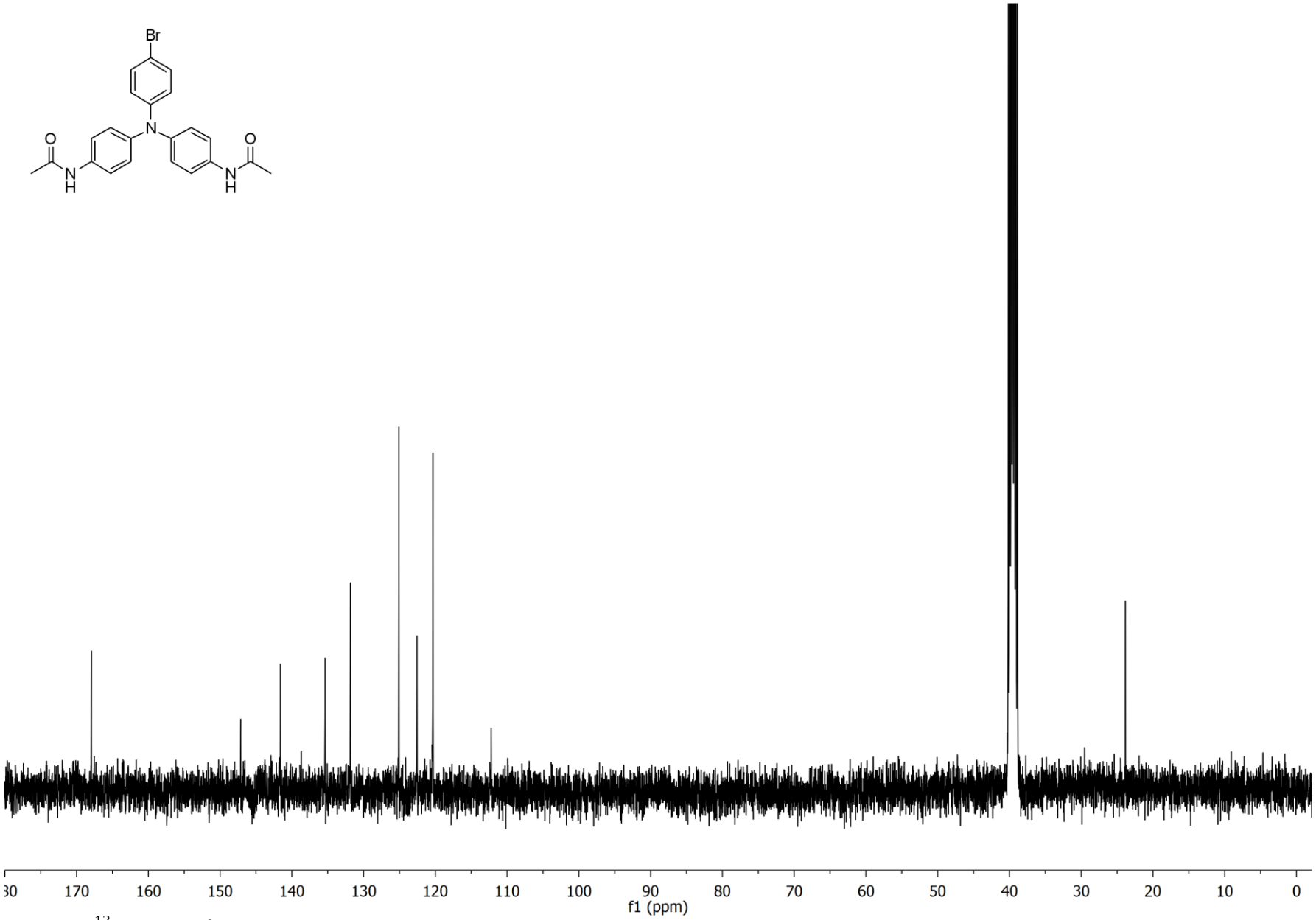


Figure S11: ^{13}C NMR of **2** in DMSO-d6.

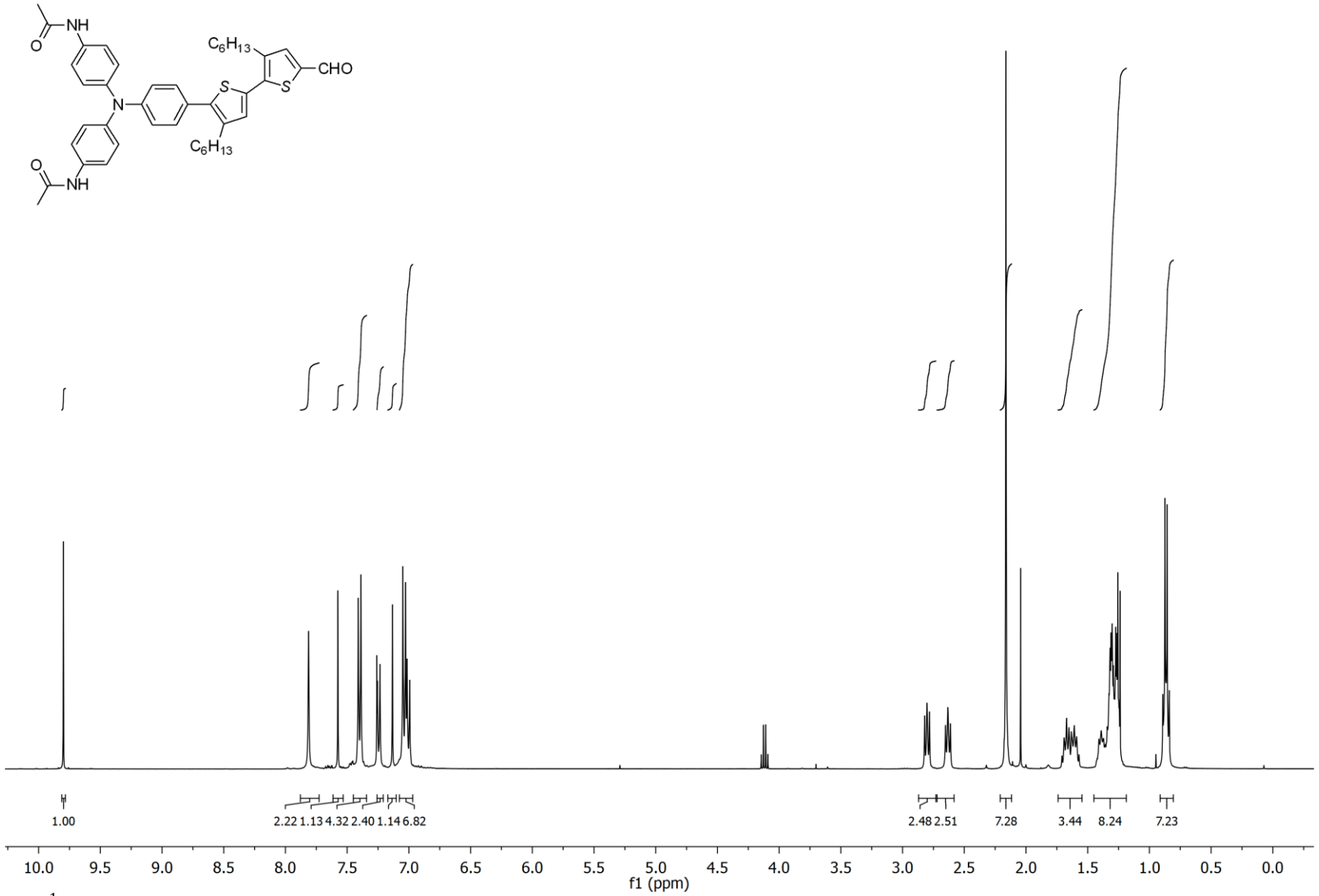


Figure S12:[1]H NMR of **3** in $CDCl_3$.

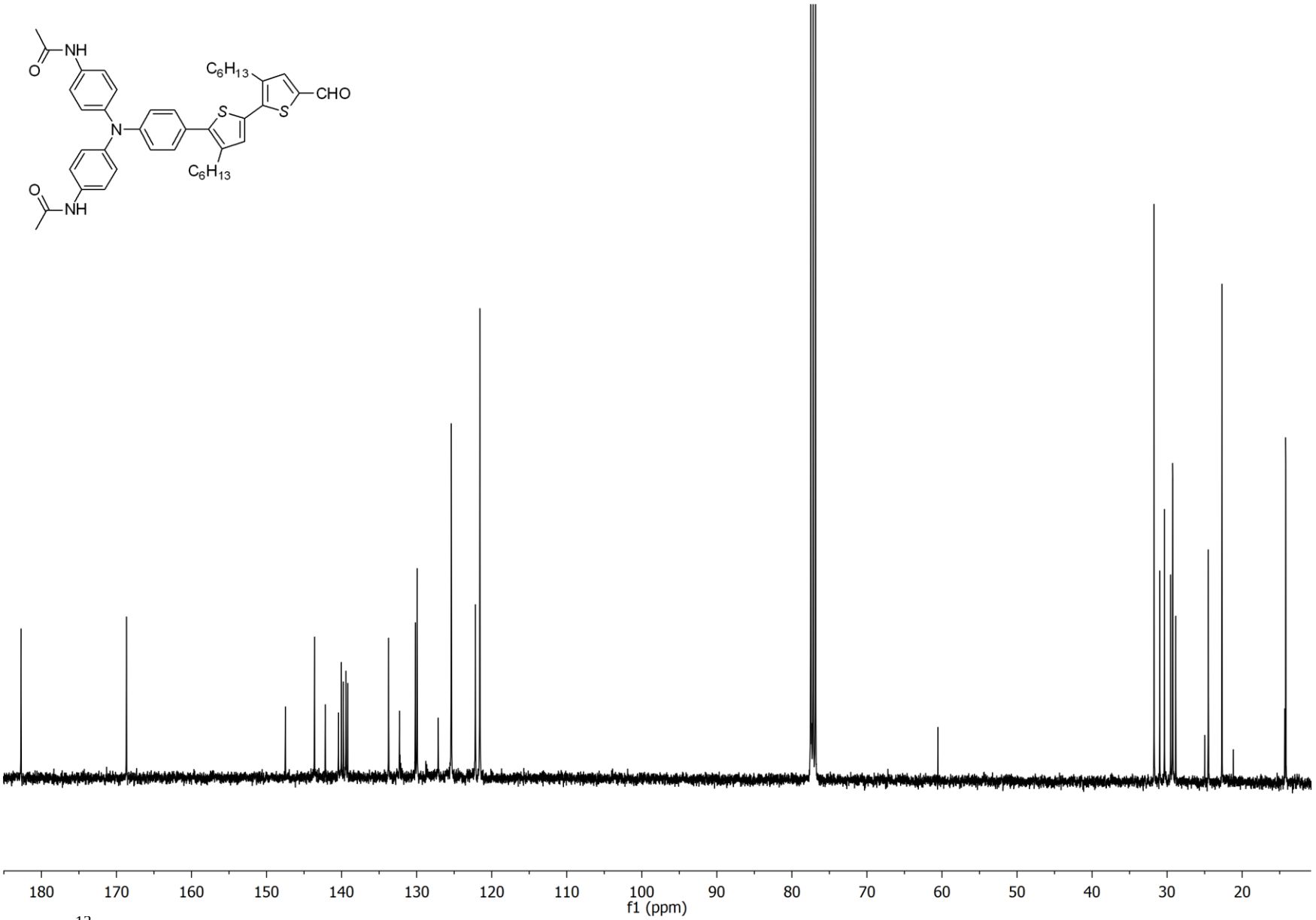


Figure S13:^{13}C NMR of **3** in CDCl3.

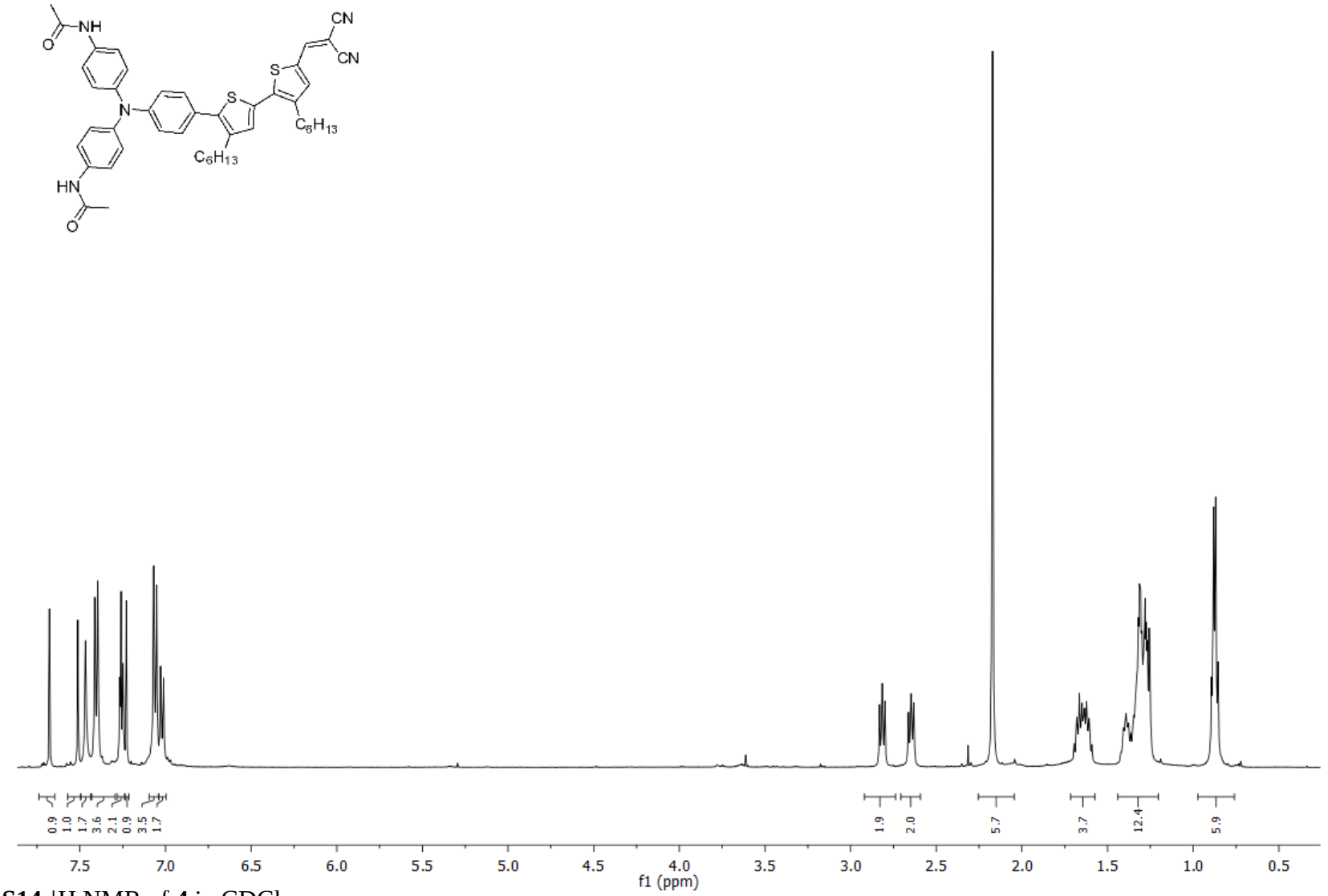


Figure S14: ^{1}H NMR of **4** in $CDCl_3$.

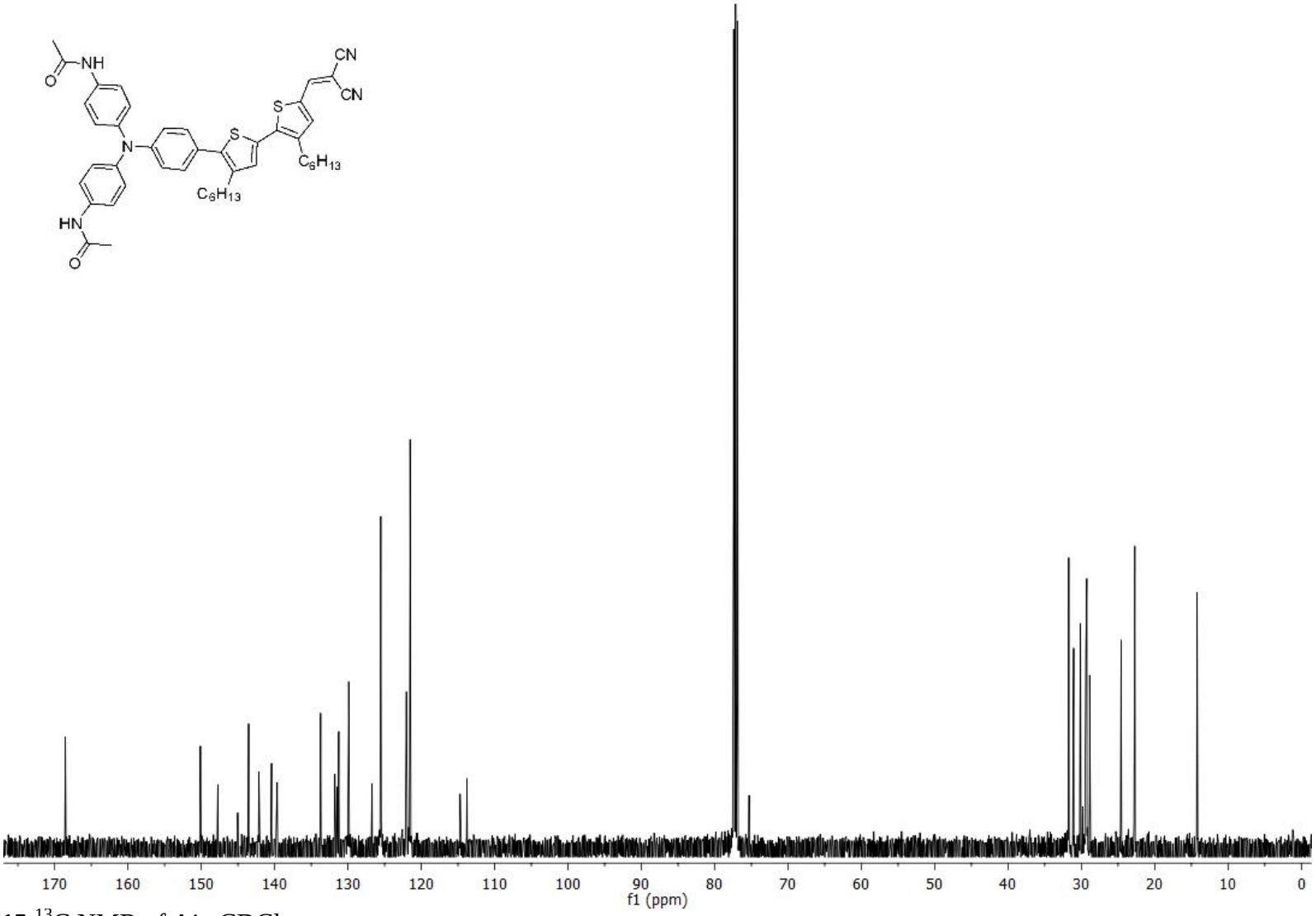


Figure S15:^{13}C NMR of **4** in $CDCl_3$

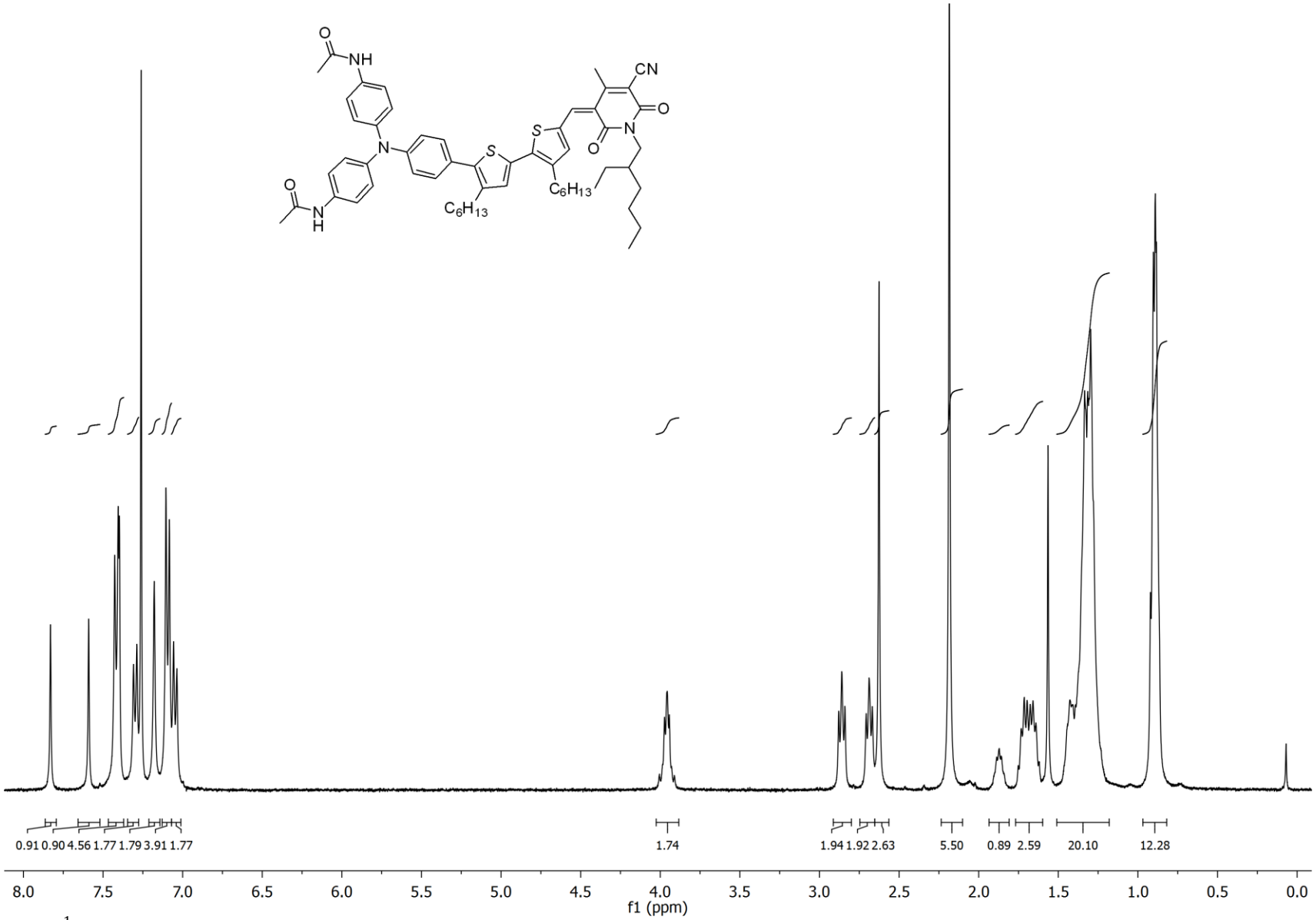


Figure S16: ^{1}H NMR of **5** in $CDCl_3$.

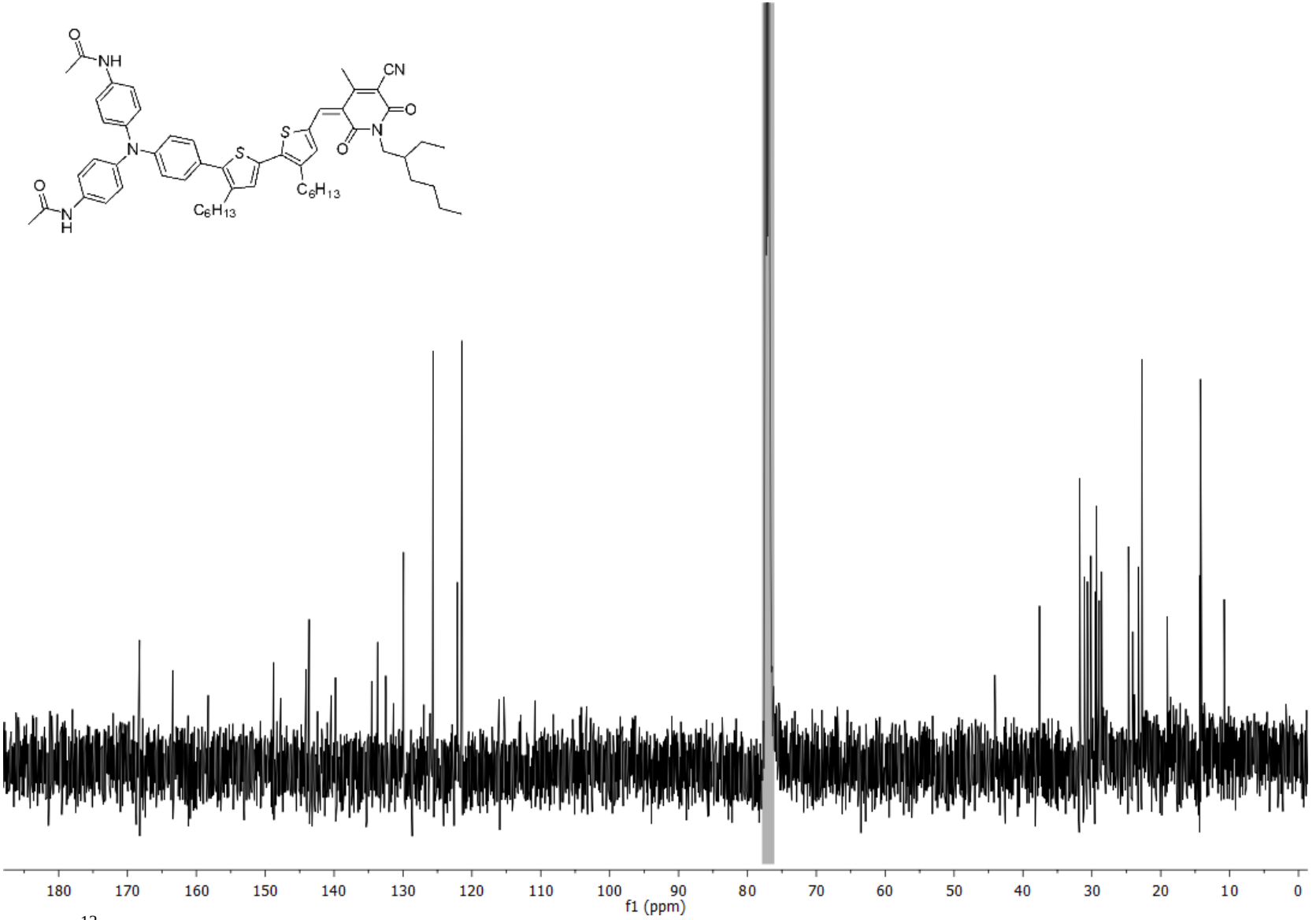


Figure S17: ^{13}C NMR of **5** in $CDCl_3$

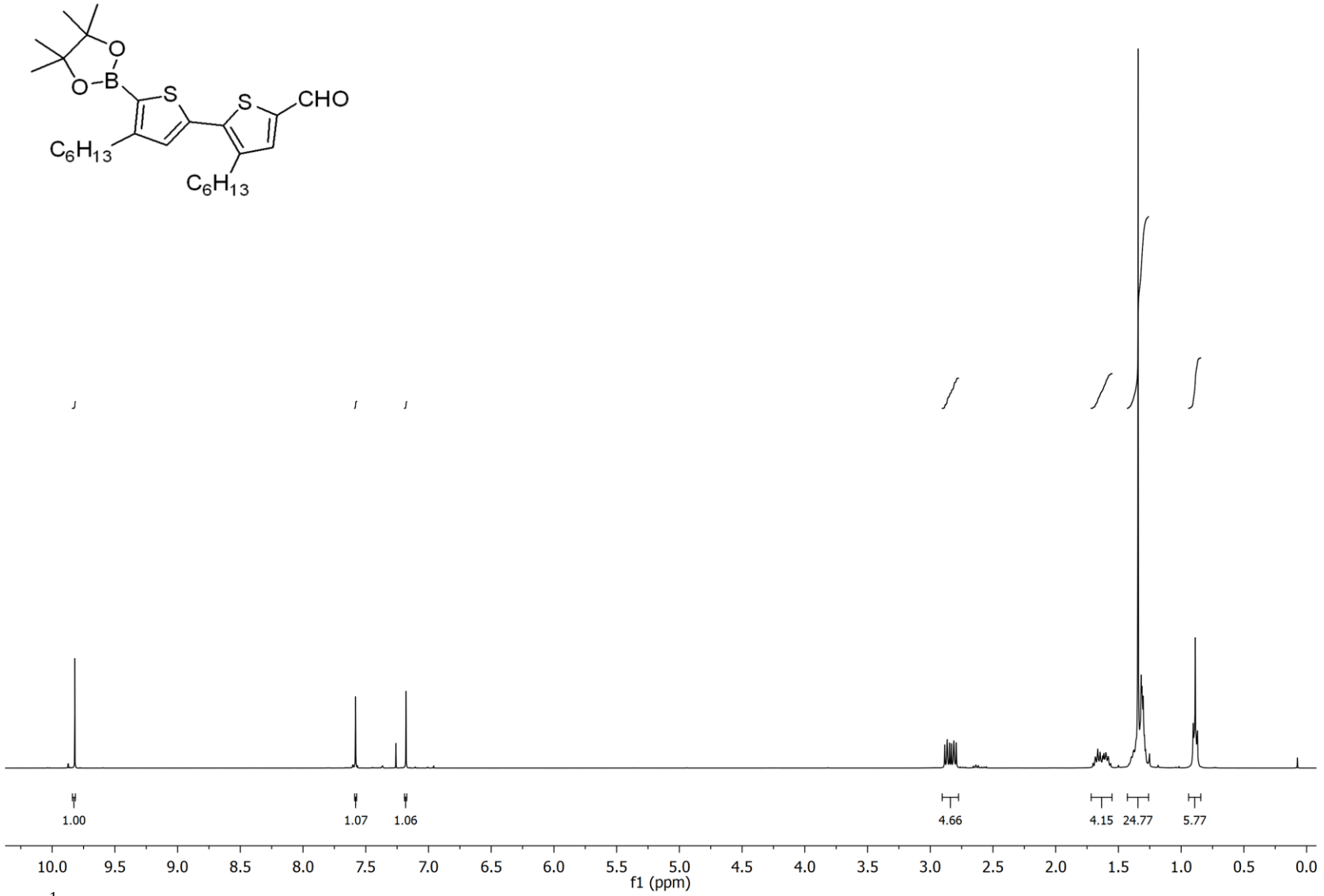


Figure S18: ^{1}H NMR of **7** in $CDCl_3$.

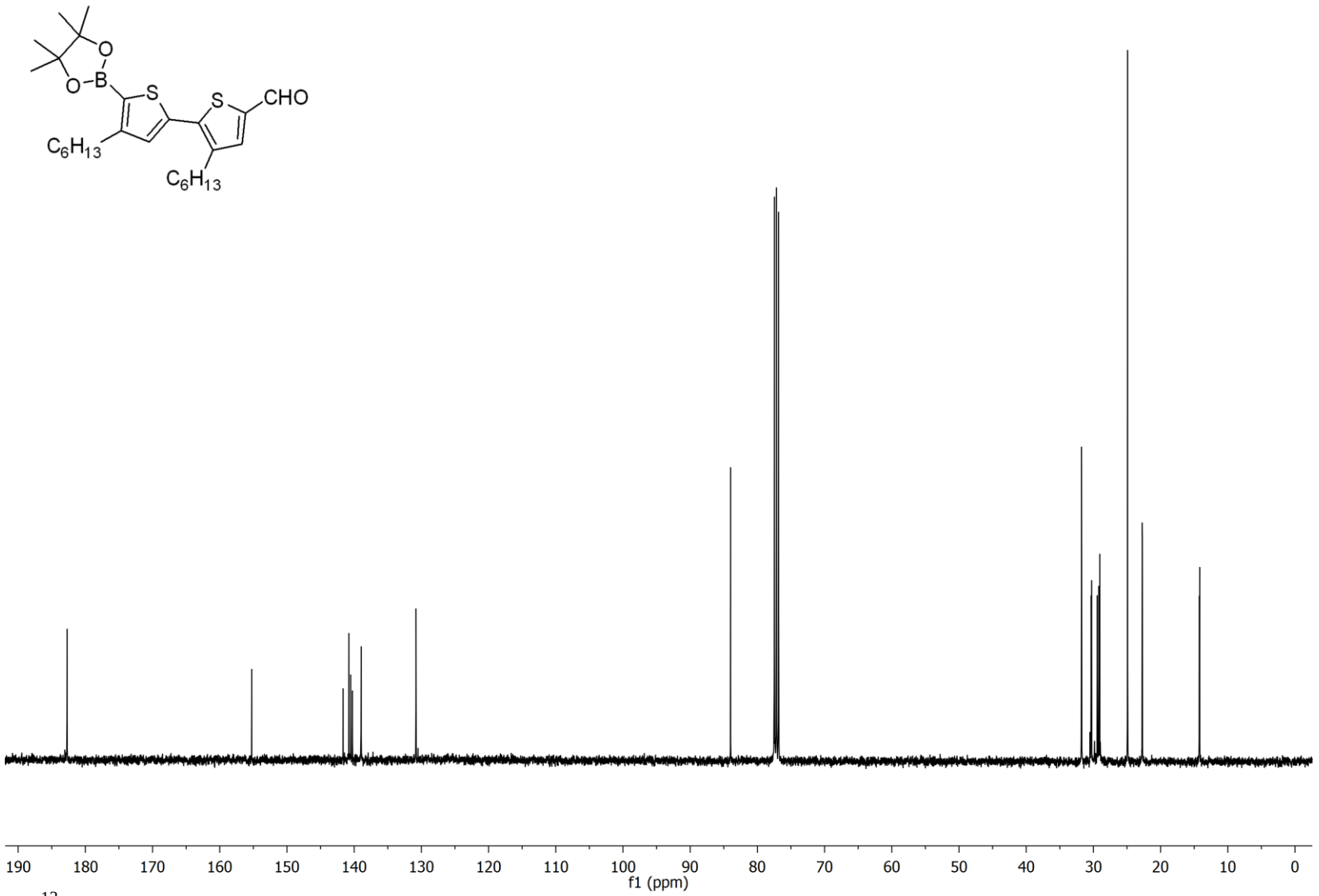


Figure S19:^{13}C NMR of **7** in $CDCl_3$.