

## Supporting information

### Vacuum-processed small molecule solar cells based on terminal acceptor-substituted low-band gap oligothiophenes

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#### General remarks:

NMR spectra were recorded on a *Bruker AMX 500* (<sup>1</sup>H NMR: 500 MHz, <sup>13</sup>C NMR: 125 MHz) or an *Avance 400* spectrometer (<sup>1</sup>H NMR: 400 MHz, <sup>13</sup>C NMR: 100 MHz), unless mentioned otherwise at 25 °C. Chemical shift values (δ) are expressed in parts per million using residual solvent protons (<sup>1</sup>H NMR, δ<sub>H</sub> = 7.26 for CDCl<sub>3</sub>, δ<sub>H</sub> = 5.32 for CD<sub>2</sub>Cl<sub>2</sub>, δ<sub>H</sub> = 2.5 for DMSO-d<sub>6</sub>; <sup>13</sup>C NMR, δ<sub>C</sub> = 77.0 for CDCl<sub>3</sub>, δ<sub>C</sub> = 53.5 for CD<sub>2</sub>Cl<sub>2</sub>, δ<sub>C</sub> = 39.4 for DMSO-d<sub>6</sub>) as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet) and m (multiplet). The assignments are Ar-H (H-atoms of aromatic systems) and Th-H (H-atoms of thiophene rings). Melting points were determined using a *Büchi B-545* apparatus and were not corrected. Elemental analyses were performed on an *Elementar Vario EL* (University of Ulm) and a *Carlo Erba 1104* (University of Stuttgart). Thin layer chromatography was carried out on aluminum plates, pre-coated with silica gel, *Merck Si60 F<sub>254</sub>*. Preparative column chromatography was performed on glass columns packed with silica gel, *Merck Silica 60*, particle size 40 – 43 μm. EI mass spectra were recorded on a *Varian Saturn 2000* GC-MS, High resolution MALDI-MS experiments were performed using a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer *solariX* (*Bruker Daltonik GmbH*, Bremen, Germany) equipped with a 7.0 T superconducting magnet and interfaced to an Apollo II Dual ESI/MALDI source. UV/Vis absorption spectra were recorded in 1 cm cuvettes with *Merck Uvasol* grade solvents on a *Perkin Elmer Lambda 19* spectrometer. Cyclic voltammetry experiments were performed with a computer-controlled *Autolab PGSTAT30* potentiostat in a three-electrode single-compartment cell with a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl

reference electrode. All potentials were internally referenced to the ferrocene / ferrocenium couple. Tetrahydrofuran (*Merck*) was dried under reflux over sodium/benzophenone (*Merck*) and dichloromethane (*Merck*) over calcium hydride (*Merck*). All synthetic steps were carried out under argon atmosphere. *N*-Bromo succinimide (NBS), NaOH and K<sub>2</sub>CO<sub>3</sub> were purchased from *Merck*, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, trifurylphosphine (TFP) and *n*BuLi (1.6 mol/L in hexane) from *Acros*, tri-*n*-butyltin chloride and tri-*n*-methyltin chloride from *Aldrich*.

**Vacuum processed solar cells:** N,N'-di(naphthalen-1-yl)-N,N'-diphenyl-benzidine (Di-NPB) and zinc phthalocyanine (ZnPc), doped with proprietary compounds NDP2 or NDP9 of *Novald GmbH* (Dresden) were used as p-doped hole transport layers. Doping concentrations of Di-NPB was 5 wt%. C<sub>60</sub> has been provided by *Alfa Aesar* and Di-NPB by *Sensient Imaging Technologies*. Except the oligothiophenes, all materials were cleaned at least twice by thermal gradient sublimation before evaporation. The organic layers and metal contacts were thermally deposited in an ultra high vacuum system ("UFO", *Bestec GmbH*) at 10<sup>-8</sup> to 10<sup>-7</sup> mbar through shadow masks onto semitransparent indium tin oxide (ITO) coated glass substrates (*Thin Film Devices Inc.*, sheet resistance < 30 Ω / sq) without breaking the vacuum. Ceramic or graphite crucibles were used as sublimation sources (*Creaphys GmbH*, *Reinhardtsgrimma*), temperatures were set by a *Eurotherm* controller and film thicknesses were determined by quartz crystal monitors (*Leybold Inficon Inc.*). Substrates were cleaned using detergent, acetone, and ethanol. The active area of the cells had an average size of 4 – 7 mm<sup>2</sup>. *J-V* characteristics were measured using a Source Measurement Unit 236 SMU (*Keithley*) in an N<sub>2</sub>-filled glovebox without exposing the samples to air. Illumination was provided by a sun simulator SOL 1200 (*Hoehnle*) with an intensity of 127 mW cm<sup>-2</sup>, which was calibrated using an outdoor reference cell provided by the *Fraunhofer Institute for Solar Energy Systems* (Freiburg). External quantum efficiency (EQE) spectra were recorded using a homemade setup based on a xenon lamp (*ILC-Technologies*) and a grating monochromator. Calibration was done using a *Newport Corporation* powermeter or a *Hamamatsu Photonics* photo diode. Organic films for spectral analysis were vapor deposited onto quartz substrates under ultra high vacuum with deposition rates of about 0.1 Å s<sup>-1</sup>. A commercial *Shimadzu* UV-2101/3101 spectrophotometer was used for absorption measurements. Luminescence spectra were recorded using a *Spex FluoroMAX* with separated monochromators for excitation and luminescence light.

## Synthesis:

**5,5''-Bis(tributylstannyl)-3',4'-dibutyl-2,2':5'2''-terthiophene (4a).** 3',4'-Dibutyl-2,2':5'2''-terthiophene (1.00 g, 2.77 mmol, 1.0 eq.) was dissolved under argon atmosphere in dry THF (20 mL). A solution of *n*-BuLi in *n*-hexane (2.5M, 6.93 mmol, 2.50 eq.) was added drop wise at -50 °C. Stirring was then continued for 30 minutes at around -25 °C. The solution was stirred for another hour at 0 °C and then again cooled down to -15 °C. Tributyltin chloride (1.92 mL, 7.07 mmol, 2.55 eq.) was added, the cooling bath removed and the reaction mixture was stirred over night at ambient temperature. The crude product was washed with water and extracted with dichloromethane, dried over Na<sub>2</sub>SO<sub>4</sub>. The solvents were removed under reduced pressure and the crude product (2.00 g, 2.13 mmol) was obtained as yellow-brown oil in a yield of 77% as confirmed by <sup>1</sup>H-NMR and was used without further purification. Product **4a** was confirmed by the absence of terminal α-proton of the terthiophene in the aromatic region. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ ppm: 7.25 (d, 2H, *J* = 3.34 Hz, Th-H), 7.10 (d, 2H, *J* = 3.38 Hz, Th-H), 2.72 (t, 4H, Th-CH<sub>2</sub>), 1.63-1.55 (m, 12H, CH<sub>2</sub> overlapped), 1.49-1.41 (m, 8H, Th-CH<sub>2</sub>-CH<sub>2</sub>), 1.4-1.3 (m, 12H, CH<sub>2</sub> overlapped) 1.16-1.09 (m, 12H, CH<sub>2</sub> overlapped), 0.95 (t, 6H, CH<sub>3</sub>), 0.91 (t, 18H, CH<sub>3</sub> overlapped). Overlapped NMR signal is due to the excess of stannyl reagent in the mixture. MS (MALDI-TOF): *m/z* 932.4 [M]<sup>+</sup> (calc. for C<sub>44</sub>H<sub>76</sub>S<sub>3</sub>Sn<sub>2</sub>: 940.3).

**5,5''-Bis(trimethylstannyl)-3',4'-dibutyl-2,2':5'2''-terthiophene (4b)**

3',4'-Dibutyl-2,2':5'2''-terthiophene (177 mg, 0.49 mmol, 1.00 eq.) was dissolved under argon atmosphere in dry THF (2 mL) and TMEDA (0.16 mL, 1.08 mmol, 2.20 eq.) was added. At -50 °C a solution of *n*BuLi in *n*-hexane (1.6M, 0.718 mL, 1.15 mmol, 2.34 eq.) was added drop wise. The cooling bath was removed and stirring was continued for 30 minutes. The reaction mixture was then heated to 30 °C for another 20 minutes, after which it was again cooled below -50 °C. A solution of trimethyltin chloride (229 mg, 1.15 mmol, 2.34 eq.) in THF (1.5 mL) was added, the cooling bath removed and the mixture stirred over night at room temperature. The mixture was then poured into ice cold aq. NH<sub>4</sub>Cl solution (25 mL) and extracted with diethyl ether. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. Recrystallization from methanol afforded the desired compound **4b** (160 mg, 0.23 mmol, 48%) as yellow solid. The product was used in subsequent syntheses without further purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ ppm: 7.24 (d, 2H, *J* = 3.39 Hz, Th-H), 7.13 (d, 2H, *J* = 3.39 Hz, Th-H), 2.75-2.67 (m, 4H, Th-CH<sub>2</sub>), 1.61-1.54 (m, 4H, CH<sub>2</sub>), 1.50-1.39 (m, 4H, CH<sub>2</sub>), 0.96 (t, 6H, *J* = 7.28 Hz, CH<sub>3</sub>), 0.39 (s, 18H, Sn-CH<sub>3</sub>).

**5,5''-Di(benzo[*c*][1,2,5]thiadiazol-4-yl)-3',4'-dibutyl-2,2':5'2''-terthiophene (1, BTDA3T).**

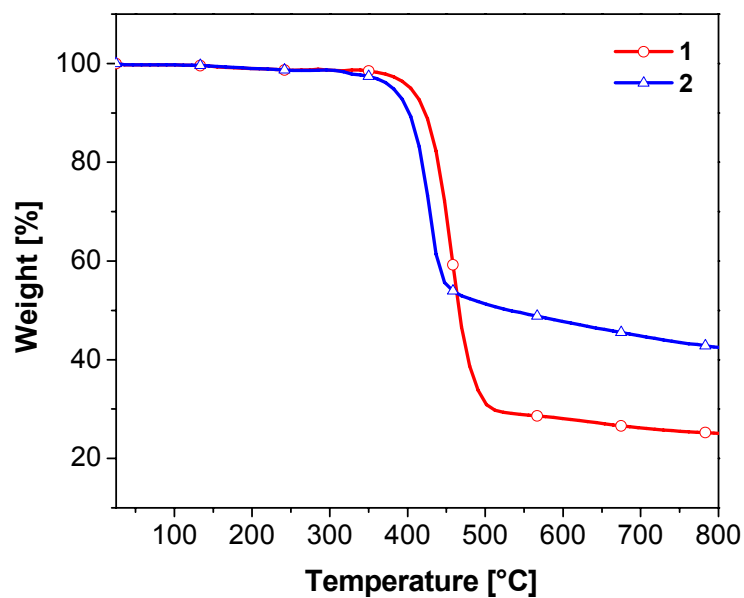
Stannylated terthiophene **4a** (362 mg, 0.39 mmol, 1.0 eq.), 4-bromobenzo[*c*][1,2,5]thiadiazole (290 mg, 1.35 mmol, 3.5 eq.), CsF (351 mg, 2.31 mmol, 6.0 eq.) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (27 mg, 40 μmol, 0.1 eq.) were dissolved in DMF (5 mL) and 1,2-dichloroethane (2 mL) under argon

atmosphere. The mixture was irradiated by microwave for 4 h at 100 °C. The formed dark red, gel like mixture was further extracted with dichloromethane and water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed by rotary evaporation. Title compound **1** (50 mg, 0.08 mmol) was purified by column chromatography (SiO<sub>2</sub>, gradient eluent from DCM:*n*-hexane (7:3) → pure DCM) as red-brown powder in a yield of 21%. M.p.: 141 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz) δ ppm: 8.12 (d, 2H, *J* = 3.85 Hz, Th-H), 7.92 (dd, 2H, *J* = 0.88 Hz, *J* = 8.67 Hz, Ar-H), 7.88 (dd, 2H, *J* = 0.90 Hz, *J* = 7.06 Hz, Ar-H), 7.65 (dd, 2H, *J* = 7.09 Hz, *J* = 8.67 Hz, Ar-H), 7.28 (d, 2H, *J* = 3.90 Hz, Th-H), 2.85 (t, 4H, Th-CH<sub>2</sub>-), 1.68-1.59 (m, 4H, CH<sub>2</sub>), 1.56-1.46 (m, 4H, CH<sub>2</sub>), 1.01 (t, 6H, *J* = 7.28 Hz, -CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz) δ ppm: 155.63, 140.96, 138.89, 137.65, 131.99, 130.12, 129.68, 128.34, 127.09, 126.46, 124.97, 120.03, 32.85, 28.05, 23.10, 13.71. HR-MS (MALDI): *m/z* 628.0909 [M]<sup>+</sup> (calc. for C<sub>32</sub>H<sub>28</sub>N<sub>4</sub>S<sub>5</sub>: 628.0912). Elemental analysis: calc. (%) for C<sub>32</sub>H<sub>28</sub>N<sub>4</sub>S<sub>5</sub> C: 61.11; H: 4.49; N: 8.91; S: 25.49; found: C: 60.88; H: 4.50; N: 8.85. S: 25.67.

**4-Chloro-[1,2,5]thiadiazolo[3,4-*c*]pyridine (6).** 2-Bromopyridine-3,4-diamine (285 mg, 1.52 mmol) was dissolved in thionyl chloride (8.3 mL, 13.5 g, 0.11 mol) and the mixture was refluxed for 5 h. Excess thionyl chloride was distilled off under reduced pressure and the crude product was neutralized carefully with saturated solution of aq. NaHCO<sub>3</sub>. The crude product was washed with water and extracted with dichloromethane, dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporator. Recrystallization from methanol furnished product **6** (50 mg, 0.29 mmol, 19%) as orange-brown needles. M.p. 109-112 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ ppm: 8.44 (d, 1H, Ar-H), 8.10 (d, 1H, Ar-H). MS (EI): *m/z* = 171 ([M]<sup>+</sup>, 100), 136 (50). (Due to instability of compound **6** under air and moisture <sup>13</sup>C NMR and elemental analysis were not measured).

**5,5''-Di([1,2,5]thiadiazolo[3,4-*c*]pyridin-4-yl)-3',4'-dibutyl-2,2':5'2''-terthiophene (2, TDAPy-3T).** Bis-stannylated terthiophene **4b** (120 mg, 0.17 mmol, 1.0 eq.), thiadiazolo-pyridine **6** (63 mg, 0.37 mmol, 2.1 eq.) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (6.14 mg, 8.74 μmol, 5 mol-%) were dissolved in DMF (2 mL) under argon atmosphere. The mixture was heated under microwave conditions for 2 h at 90 °C. After washed with water and extraction with DCM, the organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. Title compound **4** (53 mg, 0.08 mmol) was purified by gradient column chromatography (SiO<sub>2</sub>: pure DCM → DCM:ethyl acetate (97:3)) as deep red powder in a yield of 48%. M.p.: 167-169 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ ppm: 8.70 (d, 2H, *J* = 4.01 Hz, Ar-H), 8.54 (d, 2H, *J* = 6.21 Hz, Ar-H), 7.72 (d, 2H, *J* = 6.18 Hz, Ar-H), 7.34 (d, 2H, *J* = 4.03 Hz, Ar-H), 2.88 (t, 4H, Th-CH<sub>2</sub>-), 1.70 (m, 4H, CH<sub>2</sub>), 1.57-1.48 (m, 4H, CH<sub>2</sub>), 1.00 (t, 6H, *J* = 7.28 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ ppm: 157.77, 148.42, 148.06, 144.93, 141.63, 141.46, 140.94, 133.10, 130.85, 127.40, 112.85, 32.68, 28.17, 23.03, 13.90. HR-MS (MALDI): *m/z*

630.0814 [M]<sup>+</sup> (calc. for C<sub>30</sub>H<sub>26</sub>N<sub>6</sub>S<sub>5</sub>: 630.0817). Elemental analysis: calc. (%) for C<sub>30</sub>H<sub>26</sub>N<sub>6</sub>S<sub>5</sub> C: 57.11; H: 4.15; N: 13.32; S: 25.41; found: C: 57.05; H: 4.31; N: 13.26; S: 25.28.



**Figure S1.** TGA thermograms of compounds **1** and **2** measured under N<sub>2</sub>. Conditions: N<sub>2</sub> flow, 50 mL/min; heating rate, 10 °C/min.

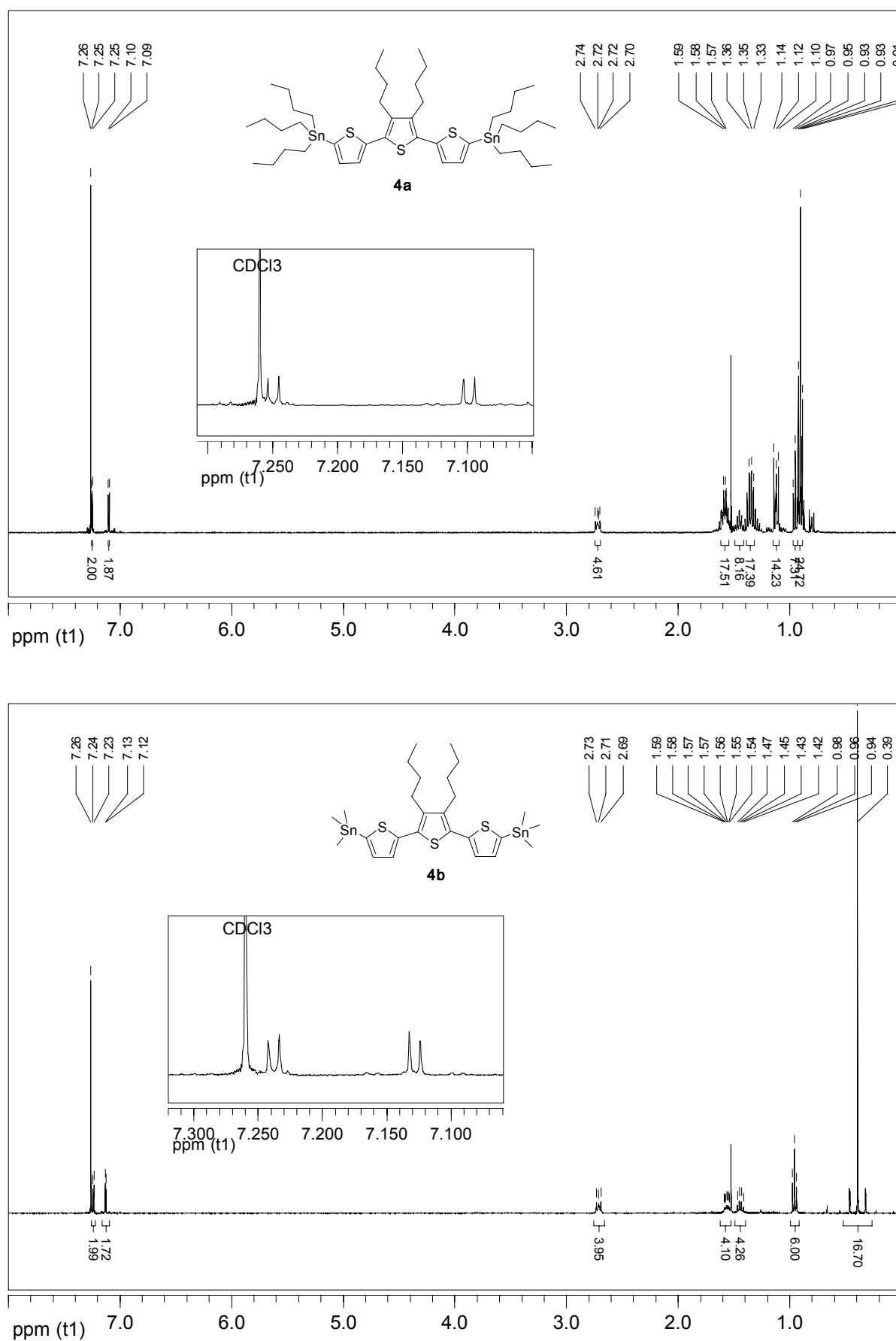


Figure S1.  $^1\text{H}$  NMR of bis(tributylstannyl)- **4a** and bis(trimethylstannyl)-terthiophenes **4b** in  $\text{CDCl}_3$ . (\*) water in  $\text{CDCl}_3$ .

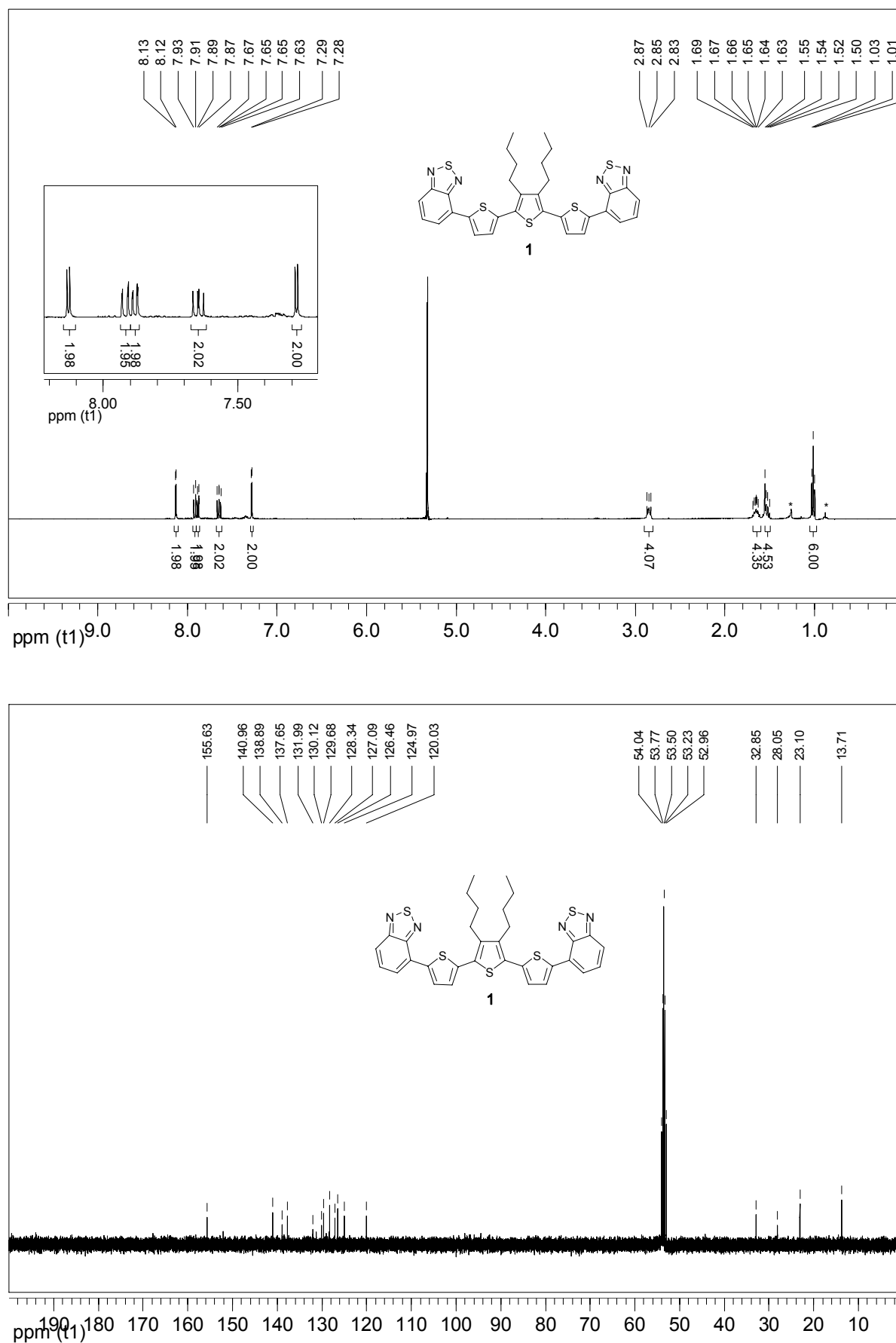


Figure S2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR of BTDA derivative **1** measured in  $\text{CD}_2\text{Cl}_2$ . (\*) solvent impurity.

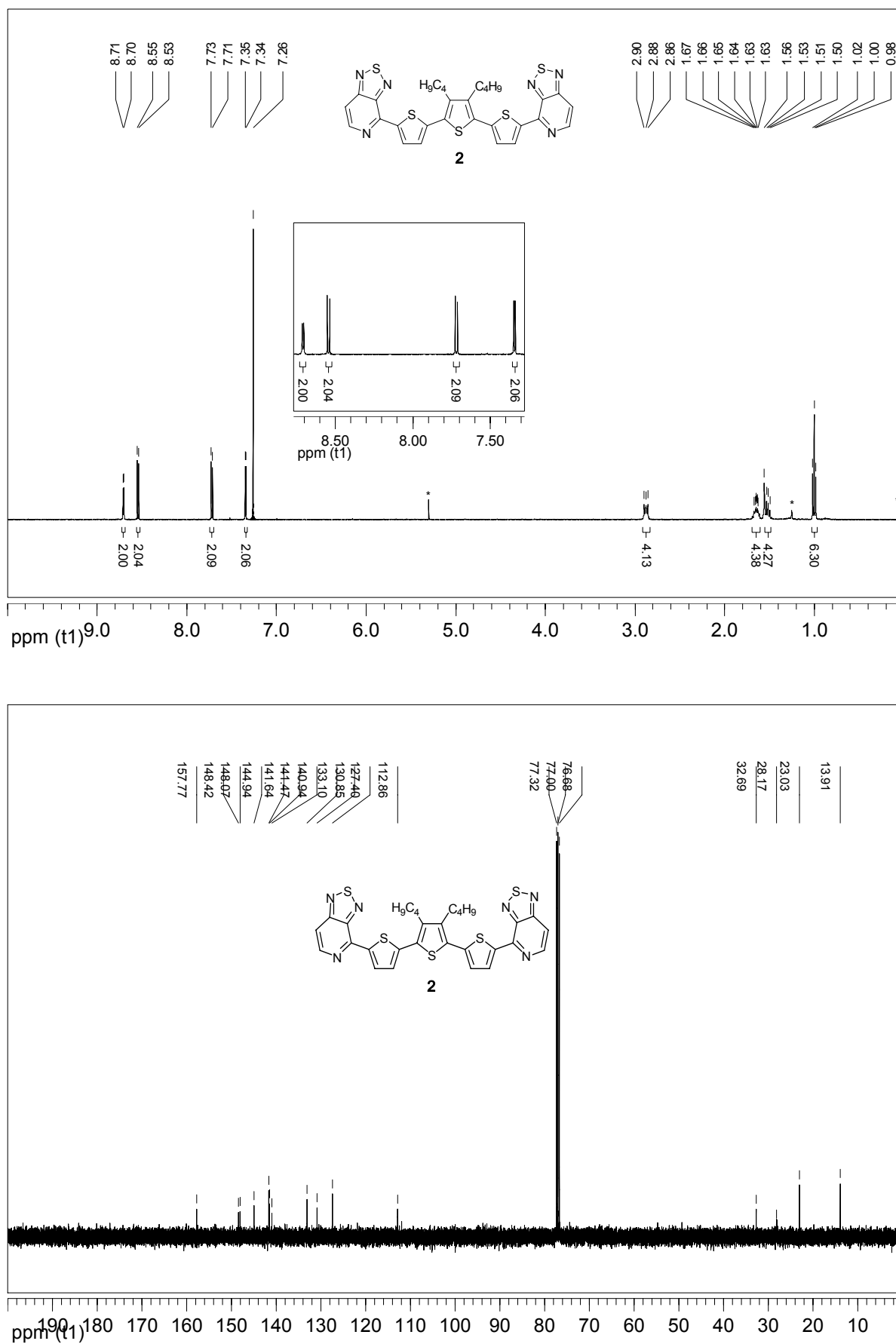


Figure S3.  $^1\text{H}$  and  $^{13}\text{C}$  NMR of TDAPy derivative **2** measured in  $\text{CDCl}_3$ . (\*) solvent impurity.