Supporting information

A-D-A-D-A-Type Oligothiophenes for Vacuum-Deposited Organic Solar Cells

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Instrument and Measurements:

NMR spectra were recorded on a *Bruker* AMX 500 (^{1}H NMR: 500 MHz, ^{13}C NMR: 125 MHz) or an *Avance* 400 spectrometer (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz), unless mentioned otherwise at 25 °C. Chemical shift values (δ) are expressed in parts per million using residual solvent protons (^{1}H NMR, δ_H = 7.26 for $CDCl_3$, δ_H = 5.32 for CD_2Cl_2, δ_H = 5.93 for CD_2Cl_4; ^{13}C NMR, δ_C = 77.0 for $CDCl_3$, δ_C = 53.8 for CD_2Cl_2, δ_C = 74.2 for CD_2Cl_4) as internal standard. The splitting patterns are designated as follows: s (singulet), 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_{254}. Preparative column chromatography was performed on glass columns packed with silica gel, *Merck* Silica 60, particle size 40 – 43 µm. CI and EI mass spectra were recorded on a *Finnigan* MAT SSQ-7000 or a *Varian Saturn* 2000 GC-MS, MALDI-TOF on a *Bruker* Daltonics Reflex III. 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. Tetrahydrofurane (*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_2CO_3 were purchased from *Merck*, $Pd(PPh_3)_2Cl_2$, trifurylphosphine (TFP) and *n*BuLi (1.6 mol/L in hexane) from *Acro*s, tri-*n*-butyltin chloride and tri-*n*-methyltin chloride from *Aldrich*. Thermogravimetric analysis (TGA) was conducted on a *Mettler Toledo* TGA/SDTA851^e instrument with a heating rate of 10 ^oC/min under a nitrogen at a flow rate of 50 cm^3/min.

Vacuum processed solar cells: N-9,9-bis(4-[di-(p-biphenyl)aminophenyl])fluorine (BPAPF) and zinc phthalocyanine (ZnPc), doped with proprietary compounds NDP9 of *Novaled GmbH* (Dresden) were used as p-doped hole transport layers. Doping concentrations of BPAPF and ZnPc were 2 – 5 wt%. C_{60} and ZnPc have been provided by *Alfa Aesar* and Di-NPB by *Sensient Imaging Technologies*. Except the oligothiophenes, all materials were purified 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^{-8} to 10^{-7} 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^2. *J-V* characteristics were measured using a Source Measurement Unit 236 SMU (*Keithley*) in an N_2-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^{-2}, 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^{-1}. A commercial *Shimadzu* UV-2101/3101 spectrophotometer was used for absorption measurements. Luminescence spectra were recorded using a *Spex* FluoroMAX spectrofluorometer.

Synthesis:

Tributyl-(3,4-diethyl-thien-2-yl)-stannane (5a): Under argon atmosphere, 3,4-diethylthiophene (40.0 g, 285 mmol) was dissolved in dried THF (400 ml). The solution was cooled down to -10°C using an ice/sodium chloride bath and then *n*-BuLi (178 ml, 285 mmol, 1.6M solution in *n*-hexane) was added dropwise under vigorous stirring. The internal temperature was maintained at -10 °C for 30 min, then was slowly brings to ambient temperature for a period of 90 min. The reaction mixture was further cool down to -10 °C and tri-*n*-butyltin chloride (77.4 ml, 92.8 g, 285 mmol) was added dropwise. The reaction mixture was slowly warm to room temperature and stirred for 12 h. After diluting the reaction mixture with dethyl ether at 0 ^{o}C, was added cold aqueous saturated $NaHCO_3$ solution under vigorous stirring. The organic phase was separated, and the water phase was extracted with diethyl ether (2 × 100 mL). The combined organic extracts were dried ($MgSO_4$) and filtered, and then the solvent was removed by rotary evaporation. The crude product was purified by distillation under high vacuum (148 ^{o}C, 4 × 10^{-3} mbar) to yield **5a** (106.8 g, 249 mmol, 87%) as a colorless viscous liquid. ^{1}H NMR ($CDCl_3$, δ ppm) 7.21 (s, 1H, Th-H), 2.59 (dq, ^3J = 7.45 Hz, ^4J = 0.96 Hz, 2H, CH_2), 2.57 (q, ^3J = 7.53 Hz, 2H, CH_2), 1.61-1.5 (m, 6H, CH_2), 1.34 (m, 6H, CH_2), 1.30 (t, ^3J = 7.47 Hz 3H, CH_3), 1.12-1.06 (m, 9H, CH_2), 0.90 (t, ^3J = 7.3 Hz, 9H, CH_3); ^{13}C NMR ($CDCl_3$, δ ppm) 150.7, 144.6, 131.6, 125.6, 29.1, 27.3, 24.5, 21.9, 16.2, 14.1, 13.6, 10.8; MS (EI): m/z = 430 (M^+, 2%), 373 (M^+ - C_4H_9, 100%); elemental analysis for $C_{20}H_{38}SSn$: calcd. C, 55.96; H, 8.92; S, 7.47%; found C, 55.71; H, 8.82; S, 7.27%.

4,7-Bis(3,4-diethylthien-2-yl)benzo[*c*][1,2,5]thiadiazole (**6a**)

4,7-Dibromobenzothiadiazole **4** (1.0 g, 3.40 mmol, 1 eq.), palladium(II)bis(triphenylphosphine) dichloride (0.2 mmol, 6 mol%) and tributyl(3,4-diethylthiophen-2-yl)stannane (3.65 g, 8.50 mmol, 2.5 eq.) were dissolved in freshly dried THF (50 ml). The reaction mixture was heated to reflux and stirred for 48 h. The progress was monitored by TLC (silica, DCM:*n*-hexane = 1 : 1). After cooling to ambient temperature, the reaction mixture was extracted with DCM (150 ml). The organic phase was then washed with saturated aqueous solution of NH_4Cl and finally with water. After drying with Na_2SO_4, the solvent was removed under reduced pressure and the product was isolated by column chromatography (SiO_2, DCM:*n*-hexane = 1 : 1) to obtain **6a** (970 mg, 2.35 mmol, 69%) as yellow crystals. M.p.: 117-118 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 7.65 (s, 2H, Ar-H), 7.13 (t, 2H, *J* = 1.0Hz, Th-H), 2.71 (dq, 4H, *J* = 7.48 Hz, *J* = 1.1 Hz, CH_2), 2.64 (q, 4H, *J* = 7.45 Hz, CH_2), 1.37 (t, 6H, *J* = 7.46 Hz, CH_3), 1.30 (t, 6H, *J* = 7.54 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm: 154.4, 144.2, 141.7, 132.5, 129.9, 128.1, 120.5, 22.3, 21.0, 15.0,

13.7. MS (CI): *m/z* 413 ([M]$^+$, 100). Elemental analysis: calc. (%) for $C_{22}H_{24}N_2S_3$ C: 64.04; H: 5.86; N: 6.79; found: C: 64.20; H: 5.84; N: 6.78.

4,7-Bis(5-bromo-3,4-diethylthien-2-yl)benzo[*c*][1,2,5]thiadiazole (**7a**)

Benzo[*c*][1,2,5]thiadiazole **6a** (199 mg, 0.48 mmol, 1 eq.) was dissolved in chloroform (30 ml). The solution was stirred at room temperature and NBS (182 mg, 1.02 mmol, 2.12 eq.) was slowly added. Stirring was continued for 48 h under argon atmosphere, after which the reaction mixture was extracted with DCM. The organic phase was then washed with water, dried over Na_2SO_4. After removal of the solvent by rotary evaporator the compound was purified by column chromatography (SiO_2, DCM:*n*-hexane = 1:1) to yield **7a** (180 mg, 0.32 mmol) as yellow-orange crystals in 65% yield. M.p.: 111-112 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 7.63 (s, 2H, Ar-H), 2.70 (q, 4H, *J* = 7.58 Hz, CH_2), 2.66 (q, 4H, *J* = 7.51 Hz, CH_2), 1.25 (t, 6H, *J* = 7.56 Hz, CH_3), 1.12 (t, 6H, *J* = 7.54 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm: 154.1, 143.0, 141.8, 132.5, 129.7, 127.3, 111.0, 21.9, 21.7, 15.4, 14.1. MS (CI): *m/z* 567.9 ([M]$^+$, 100). Elemental analysis: calc. (%) for $C_{22}H_{22}Br_2N_2S_3$ C: 46.32; H: 3.89; N: 4.91; found: C: 46.60; H: 4.00; N: 4.91.

4,7-Bis(3,4-diethyl-2,2'-bithien-5-yl)benzo[*c*][1,2,5]thiadiazole (**8a**)

BTDA derivative **7a** (296 mg, 0.52 mmol, 1 eq.) was dissolved in 1,2-dichloroethane (50 ml). $Pd(PPh_3)_2Cl_2$ (36 mg, 52 µmol, 10 mol-%) and 2-(tributylstannyl)-thiophene (484 mg, 0.41 ml, 1.3 mmol, 2.5 eq.) were added and the mixture was irradiated by microwave in a closed vessel for 4 h at 100 °C. After extracting the orange mixture with DCM, the organic layer was washed with water, dried over Na_2SO_4 and the solvent was removed under reduced pressure. After column chromatography (SiO_2, DCM:n-hexane = 1:1) product **8a** (230 mg, 0.40 mmol) was obtained as orange-red powder in 77% yield. M.p.: 142-144 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 7.71 (s, 2H, Ar-H), 7.34 (dd, 2H, *J* = 5.16 Hz, *J* = 1.17 Hz, Th-H), 7.22 (dd, 2H, *J* = 3.59 Hz, *J* = 1.17 Hz, Th-H), 7.09 (dd, 2H, *J* = 5.15 Hz, *J* = 3.59 Hz, Th-H), 2.86 (q, 4H, *J* = 7.53 Hz, CH_2), 2.71 (q, 4H, *J* = 7.53 Hz, CH_2), 1.29 (t, 6H, *J* = 7.54 Hz, CH_3), 1.14 (t, 6H, *J* = 7.53 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm: 154.2, 143.1, 140.8, 136.1, 132.1, 131.6, 129.9, 127.6, 127.3, 126.2, 125.5, 21.3, 21.1, 15.5, 15.4. MS (CI): *m/z* 576.0 ([M]$^+$, 100). Elemental analysis: calc. (%) for $C_{30}H_{28}N_2S_5$ C: 62.46; H: 4.89; N: 4.86; found: C: 62.66; H: 4.99; N: 4.89.

1,1'-(5',5''-(Benzo[*c*][1,2,5]thiadiazole-4,7-diyl)bis(3',4'-diethyl-2,2'-bithien-5',5-diyl))bis(2,2,2-trifluoroethanone) (**1**)

Pentamer **8a** (107 mg, 0.19 mmol, 1 eq.) was dissolved in 1,2-dichloroethane (4 ml) at around 60 °C. Trifluoroacetic anhydride (2.92 g, 13.91 mmol, 75 eq.) was added and the resulting

mixture irradiated under microwave conditions in a closed vessel for 8 h at 100 °C. After extracting the deep orange solution with DCM, the organic layer was washed with water, dried over Na_2SO_4. The organic solvent was removed under reduced pressure. Title compound **1** (86 mg, 0.11 mmol) was isolated by column chromatography (SiO_2, DCM:n-hexane, 1:1) as orange powder in 60% yield. M.p.: 138-140 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 7.94-7.91 (m, 2H, Th-H), 7.75 (s, 2H, Ar-H), 7.33 (d, 2H, *J* = 4.24 Hz, Th-H), 2.97 (q, 4H, *J* = 7.52 Hz, CH_2), 2.72 (q, 4H, *J* = 7.51 Hz, CH_2), 1.34 (t, 6H, *J* = 7.55 Hz, CH_3), 1.15 (t, 6H, *J* = 7.54 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm: 154.0, 144.3, 143.9, 134.8, 134.5, 130.7, 130.0, 127.4, 127.0, 21.4, 21.2, 15.4, 14.9. MS (MALDI-TOF): *m/z* 768.2 $[M]^+$ (calc. for $C_{34}H_{26}F_6N_2O_2S_5$: 768.1). Elemental analysis: calc. (%) for $C_{34}H_{26}F_6N_2O_2S_5$ C: 53.11; H: 3.41; N: 3.64; found: C: 53.16; H: 3.70; N: 3.57.

4,7-Bis-(4-butyl-thien-2-yl)-benzo[*c*][1,2,5]thiadiazole (**6b**)

4,7-dibromobenzo[*c*][1,2,5]thiadiazole (768 mg, 2.67 mmol, 1.0 eq.), tributyl-(4-butyl-thiophen-2-yl)-stannane (2.87 g, 6.68 mmol, 2.5 eq.) and $Pd(PPh_3)_2Cl_2$ (188 mg, 0.27 mmol, 10 mol%) were dissolved in 1,2-dichloroethane (30 ml). CsF(1.62 g, 10.7 mmol, 4.0 eq.) was added and the resulting mixture heated to 110 °C under microwave irradiation. Only the desired product was observed by TLC (silica, DCM:n-hexane = 1:1) after irradiating for 3.5 h. The mixture was extracted with DCM, and the organic layer washed with saturated aqueous solution of NH_4Cl and then with water. After drying the organic phase with Na_2SO_4, the solvent was removed under reduced pressure and purified by column chromatography (SiO_2, DCM:n-hexane = 1:1) to yield **6b** (451 mg, 1.1 mmol) as yellow crystals in 41% yield. M.p.: 77 - 78 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 7.97 (d, 2H, *J* = 1.37 Hz, Th-H), 7.79 (s, 2H, Ar-H), 7.03 (d, 2H, *J* = 1.16 Hz, Th-H), 2.71 (t, 4H, *J* = 7.78 Hz, CH_2), 1.76-1.66 (m, 4H, CH_2), 1.48-1.40 (m, 4H, CH_2), 0.98 (t, 6H, *J* = 7.36 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm: 152.5, 144.2, 138.9, 128.9, 125.9, 125.4, 121.4, 32.6, 30.3, 22.4, 13.9. MS (CI): *m/z* 413 ($[M]^+$, 100). Elemental analysis: calc. (%) for $C_{22}H_{24}N_2S_3$ C: 64.04; H: 5.86; N: 6.79; found: C: 64.23; H: 5.96; N: 6.53.

4,7-Bis-(5-bromo-4-butyl-thien-2-yl)-benzo[*c*][1,2,5]thiadiazole (**7b**)

NBS (403 mg, 2.27 mmol, 2.05 eq.) was dissolved in chloroform (35 ml) and the solution was added drop wise at 0 °C to a stirred solution of benzothiadiazole **6b** (456 mg, 1.11 mmol, 1 eq.) in chloroform (35 ml). The cooling bath was removed and the mixture was stirred at room temperature for 2 h under argon atmosphere. The reaction mixture was extracted with DCM, washed with water, dried over Na_2SO_4. The solvent was removed by rotary evaporator and then purified by column chromatography (SiO_2, DCM:n-hexane = 1:1) followed by recrystallization

from n-hexane afforded **7b** (450 mg, 0.79 mmol) as yellow-orange solid in 71% yield. M.p.: 114-115 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 7.77 (s, 2H, Th-H), 7.73 (s, 2H, Ar-H), 2.65 (t, 4H, CH_2), 1.72-1.61 (m, 4H, *J* = 7.59 Hz, CH_2), 1.49-1.38 (m, 4H, CH_2), 0.98 (t, 6H, *J* = 7.34 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm: 152.2, 143.0, 138.5, 128.1, 125.3, 124.8, 111.6, 31.9, 29.4, 22.4, 13.9. MS (CI): *m/z* 567.9 ($[M]^+$, 100). Elemental analysis: calc. (%) for $C_{22}H_{22}Br_2N_2S_3$ C: 46.32; H: 3.89; N: 4.91; found: C: 46.26; H: 3.82; N: 4.88.

4,7-Bis-(3-butyl-[2,2']bithien-5-yl)-benzo[*c*][1,2,5]thiadiazole (**8b**)

Benzothiadiazole **7b** (190 mg, 0.33 mmol, 1.0 eq.), 2-(tributylstannyl)-thiophene (0.264 ml, 0.83 mmol, 2.5 eq.) and $Pd(PPh_3)_2Cl_2$ (23 mg, 0.03 mmol, 10mol%) were dissolved in 1,2-dichloroethane (25 ml). CsF (304 mg, 2.00 mmol, 6.0 eq.) was added and the mixture was irradiated by microwave for 4 h at 100 °C. After extracting the deep red solution with DCM, the organic phase was washed with water, dried over Na_2SO_4. The solvent was removed under reduced pressure and then passed through a short SiO_2 column (DCM:n-hexane = 1:1). The crude product was further purified by recrystallization from n-hexane to obtain **8b** (127 mg, 0.22 mmol) as deep red powder in 66% yield. M.p.: 108 - 111 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 7.99 (s, 2H, Th-H), 7.83 (s, 2H, Ar-H), 7.35 (dd, 2H, *J* = 5.16 Hz, *J* = 1.16 Hz, Th-H), 7.24 (dd, 2H, *J* = 3.60 Hz, *J* = 1.17 Hz, Th-H), 7.11 (dd, 2H, *J* = 5.15 Hz, *J* = 3.60 Hz, Th-H), 2.85 (t, 4H, *J* = 7.79 Hz, CH_2), 1.79-1.68 (m, 4H, CH_2), 1.53-1.41 (m, 4H, CH_2), 0.97 (t, 6H, *J* = 7.35 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm: 152.5, 140.4, 136.9, 136.0, 132.3, 130.5, 127.4, 126.0, 125.5, 125.4, 125.2, 32.8, 29.2, 22.7, 13.9. MS (CI): *m/z* 576.1 ($[M]^+$, 100). Elemental analysis: calc. (%) for $C_{30}H_{28}N_2S_5$ C: 62.46; H: 4.89; N: 4.86; found: C: 62.52; H: 4.97; N: 4.82.

1-(3'-Butyl-5'-(7-[3-butyl-5'-(2,2,2-trifluoro-acetyl)-[2,2']bithiophenyl-5-yl]-benzo[*c*][1,2,5]-thiadiazol-4-yl)-[2,2']bithien-5-yl)-2,2,2-trifluoro-ethanone (**2**)

Pentamer **8b** (127 mg, 0.22 mmol, 1 eq.) was dissolved in 1,2-dichloroethane (20 ml) at around 60 °C and after cooling down to room temperature, trifluoroacetic anhydride (4.62 g, 22 mmol, 100 eq.) was added. The resulting mixture was irradiated under microwave conditions for 5 h at 100 °C. The solvent was then removed under reduced pressure and the product isolated by column chromatography (SiO_2, gradiential eluention from DCM:n-hexane = 7:3 to pure DCM). Further recrystallization from n-hexane using a Soxhlet apparatus afforded title compound **3** (116 mg, 0.15 mmol) as deep red powder in 69% yield. M.p.: (DSC): 190 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 7.99 (s, 2H, Th-H), 7.92 (m, 2H, Th-H), 7.86 (s, 2H, Ar-H), 7.35 (d, 2H, *J* = 4.21 Hz, Th-H), 2.91 (t, 4H, *J* = 7.7 Hz, CH_2), 1.82-1.70 (m, 4H, CH_2), 1.57-1.45 (m, 4H, CH_2), 1.01 (t, 6H, *J* = 7.35 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm: 152.2, 149.1, 143.9, 139.5, 136.9, 134.6,

131.1, 131.0, 126.7, 125.5, 125.3, 32.3, 29.8, 22.7, 14.0. MS (MALDI-TOF): *m/z* 768.2 $[M]^+$ (calc. for $C_{34}H_{26}F_6N_2O_2S_5$: 768.1). Elemental analysis: calc. (%) for $C_{34}H_{26}F_6N_2O_2S_5$ C: 53.11; H: 3.41; N: 3.64; found: C: 53.26; H:3.53; N: 3.60.

4,7-Bis-[2,2']bithien-5-yl-benzo[*c*][1,2,5]thiadiazole (**9**)

4,7-dibromobenzo[*c*][1,2,5]thiadiazole (208 mg, 0.71 mmol), [2,2']Bithiophenyl-5-yl-tributyl-stannane (743 mg, 1.63 mmol, 2.3 eq.), CsF (593 mg, 3.90 mmol, 5.5 eq.) and Pd(dppp)Cl_2 (50 mg, 0.07 mmol, 10mol%) were dissolved in dry DMF (30 ml) under argon atmosphere. The reaction mixture was irradiated in a closed vessel by microwave for 3 h at 100 °C. The resulting deep red solution was then extracted with DCM and washed with water. The organic phase was dried over Na_2SO_4 and removed by rotary evaporator. Column chromatography (SiO_2, 1. DCM, 2. DCM:n-hexane = 1:1) and successive recrystallization from ethanol afforded the desired product **9** (201 mg, 0.43 mmol) as deep red powder in a yield of 61%. M.p.: 189-191 °C. ^{1}H NMR (CD_2Cl_4, 500 MHz, 100 °C) δ ppm: 8.00 (d, 2H, *J* = 3.89 Hz, Th-H), 7.80 (s, 2H, Ar-H), 7.25 (dd, 2H, *J* = 3.58 Hz, *J* = 1.1 Hz, Th-H), 7.24 – 7.21 (m, 4H, Th-H), 7.05 (dd, 2H, *J* = 5.11 Hz, *J* = 3.59 Hz, Th-H). ^{13}C NMR (CD_2Cl_4, 125 MHz, 100 °C) δ ppm: 152.8, 139.1, 138.5, 137.4, 128.6, 128.1, 126.0, 125.4, 125.1, 124.9, 124.4. MS (CI): *m/z* 464.0 ($[M]^+$, 100). Elemental analysis: calc. (%) for $C_{22}H_{12}N_2S_5$ C: 56.87; H: 2.60; N: 6.03; found: C: 56.81; H: 2.82; N: 5.74.

2,2,2-Trifluoro-1-(5'-(7-[5'-(2,2,2-trifluoro-acetyl)-[2,2']bithiophenyl-5-yl]-benzo[*c*][1,2,5]thiadiazol-4-yl)-[2,2']bithien-5-yl)-ethanone (**3**)

Pentamer **9** (143 mg, 0.31 mmol) was dissolved in 1,2-dichloroethane (18 ml) at ca. 60 °C. Then trifluoroacetic anhydride (4.3 ml, 30.8 mmol, 100 eq.) was added and the resulting mixture heated to 110 °C under microwave irradiation conditions. Only the desired product was observed by TLC (DCM:n-hexane = 7:3) after irradiating for 15 h. The solvent was removed under reduced pressure and the insoluble solid was then adsorbed on flash silica gel before subjecting to column chromatography (SiO_2, DCM:n-hexane = 7:3). Title compound **3** (135 mg, 0.20 mmol) was obtained as deep red powder in 67% yield. M.p.: 258 - 260 °C. ^{1}H NMR (CD_2Cl_4, 500 MHz, 100 °C) δ ppm: 8.08 (d, 2H, J = 4.0 Hz, Th-H), 7.90 (s, 2H, Ar-H), 7.86 - 7.84 (m, 2H, Th-H), 7.48 (d, 2H, J = 3.98 Hz, Th-H), 7.36 (d, 2H, J = 4.16 Hz, Th-H). ^{13}C NMR (CD_2Cl_4, 125 MHz, 100 °C) δ ppm: 152.5, 149.9, 142.0, 137.6, 137.5, 137.1, 134.7, 129.2, 128.0, 126.1, 126.0, 125.5. MS (CI): *m/z* 656.1 ($[M]^+$, 100). Elemental analysis: calc. (%) for $C_{26}H_{10}F_6N_2O_2S_5$ C: 47.55; H: 1.53; N: 4.27; found: C: 47.27; H: 1.69; N: 4.09.

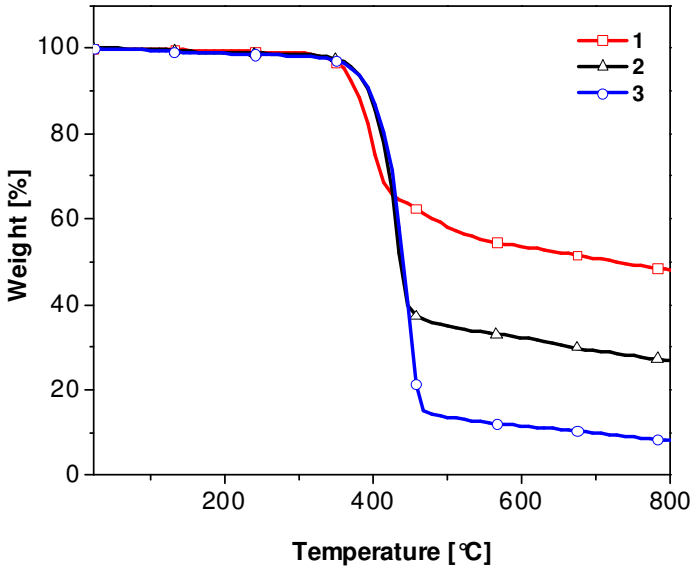


Figure S1. TGA thermograms of compounds **1**-**3** measured under N_2. Conditions: N_2 flow, 50 mL/min; heating rate, 10 °C/min.

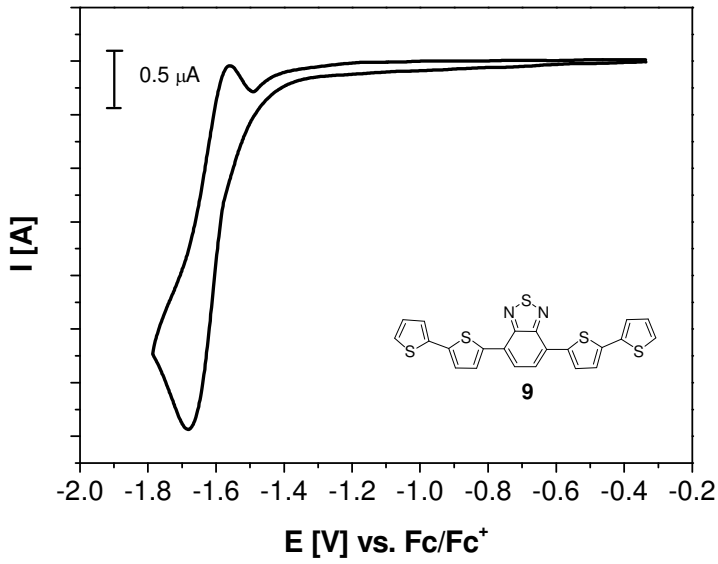
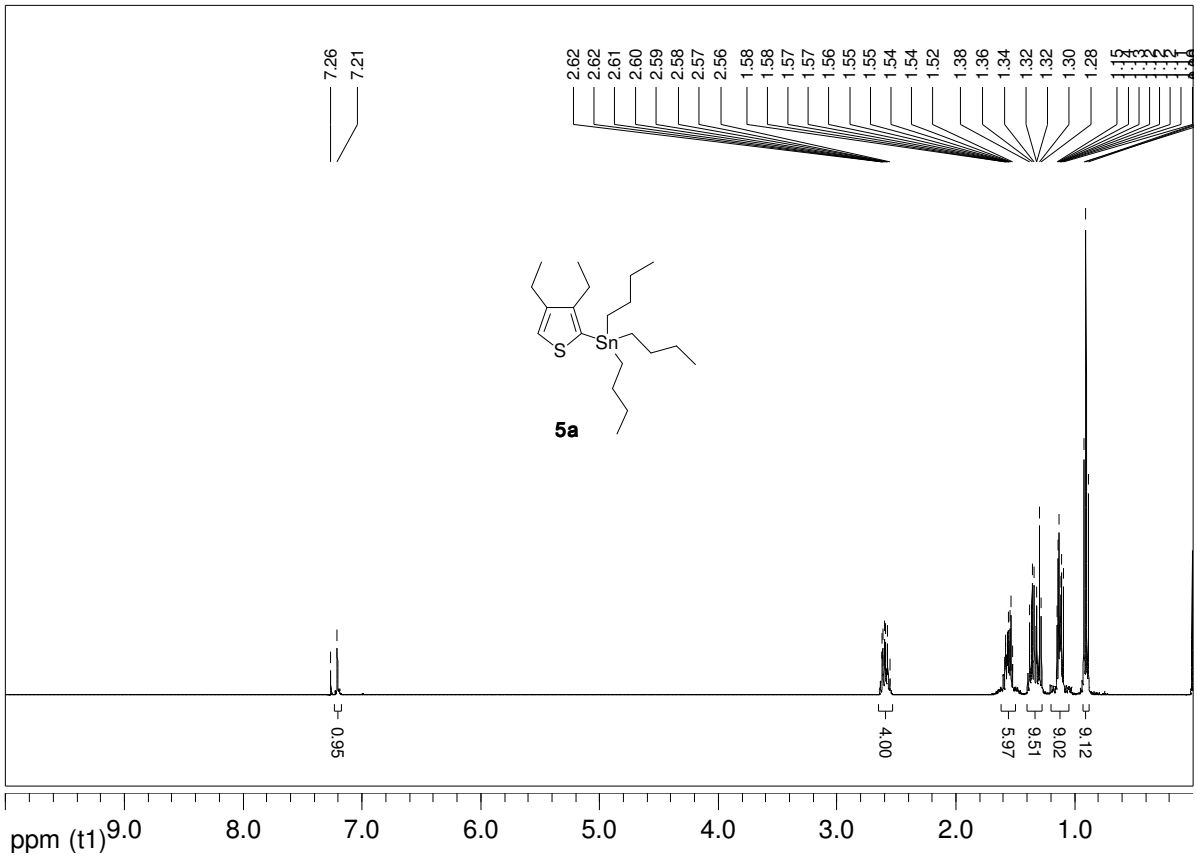


Figure S2. Electrochemical characterization of BTDA-oligomers **9** in dichloromethane–$TBAPF_6$ (0.1 M), scan speed 100 mV/s. Fc/Fc^+ was used as external reference. The LUMO energy was calculated from the onset of reduction wave. E^0_{red} = -1.62 V, LUMO = -3.57 eV.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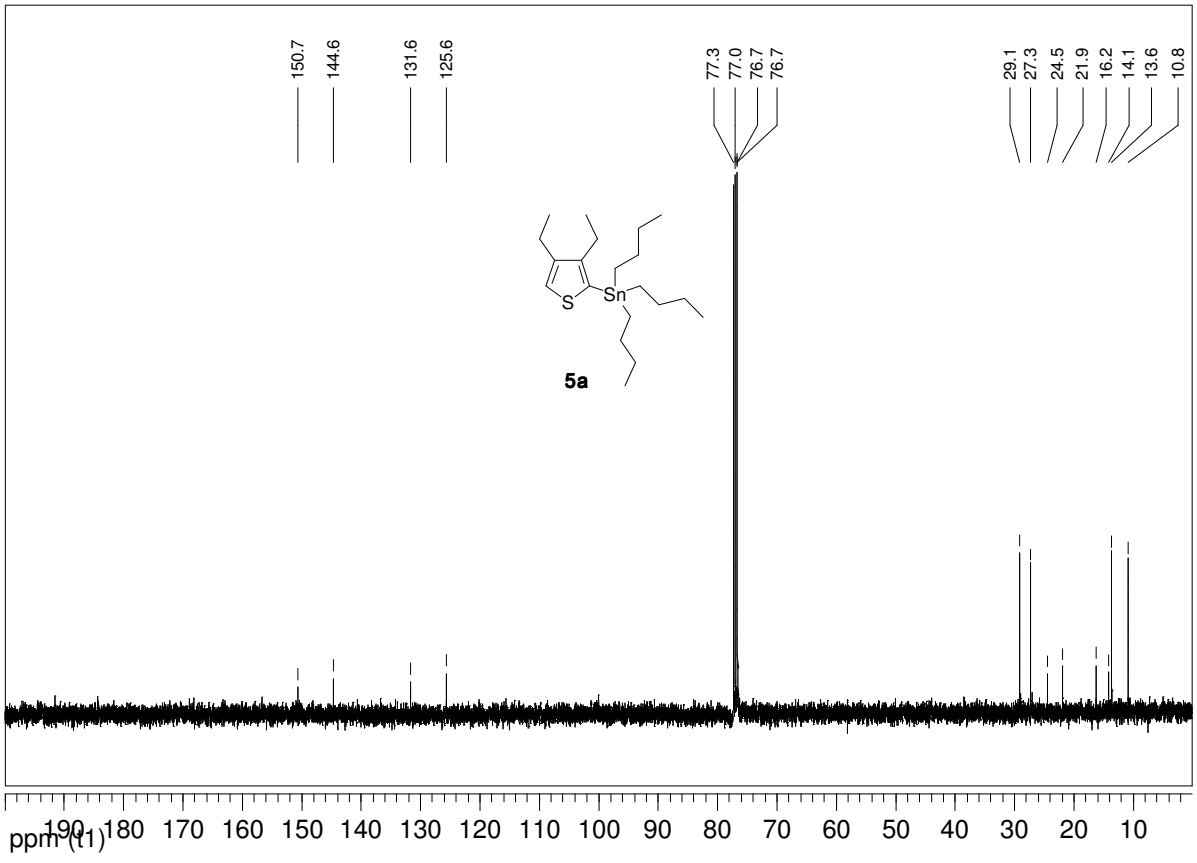
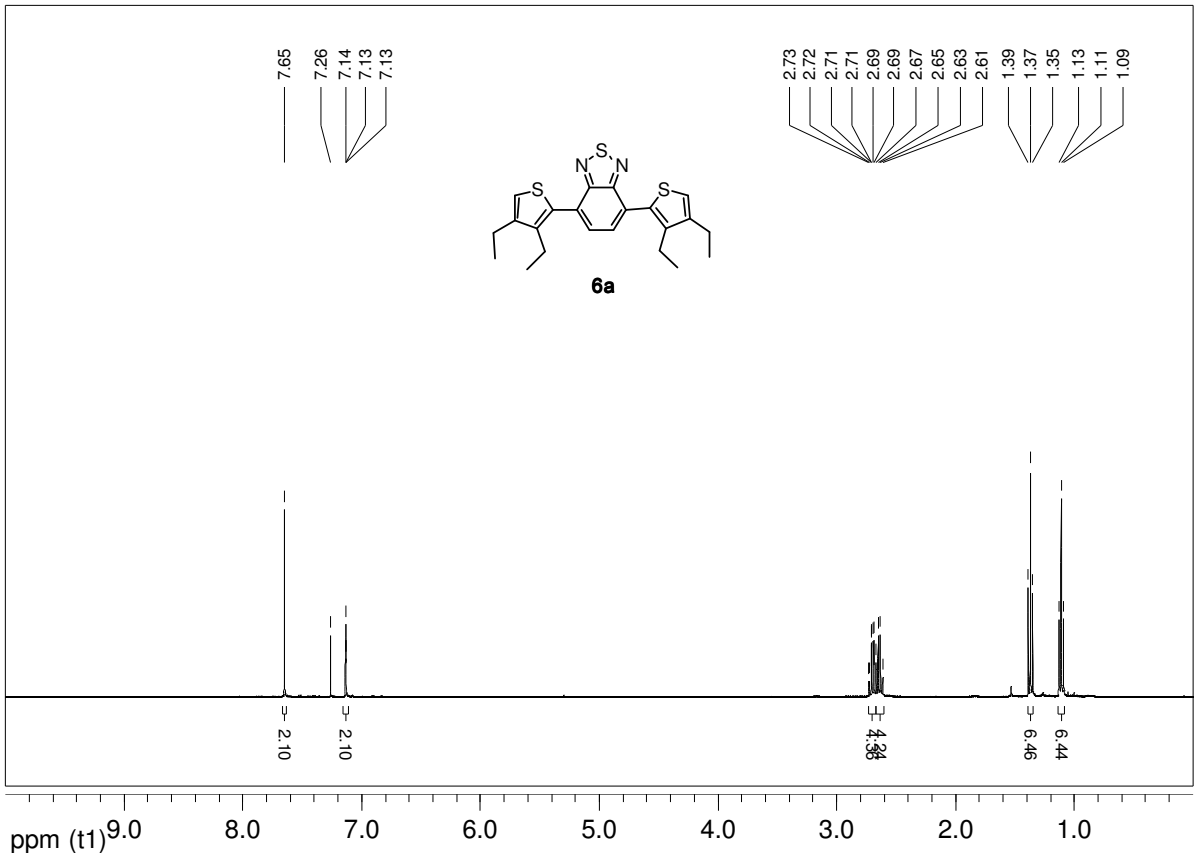
7.21
2.62
2.62
2.61
2.60
2.59
2.58
2.57
2.56
1.58
1.58
1.57
1.57
1.56
1.55
1.55
1.54
1.54
1.52
1.38
1.36
1.34
1.32
1.32
1.30
1.28
S
Sn
5a
0.96
4.00
5.97
9.51
9.02
9.12
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


150.7
144.6
131.6
125.6
77.3
77.0
76.7
76.7
29.1
27.3
24.5
21.9
16.2
14.1
13.6
10.8
S
Sn
5a
ppm (t1)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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7.26
7.14
7.13
7.13
2.73
2.72
2.71
2.71
2.69
2.69
2.67
2.65
2.63
2.61
1.39
1.37
1.35
1.13
1.11
1.09
6a
2.10
2.10
6.46
6.44
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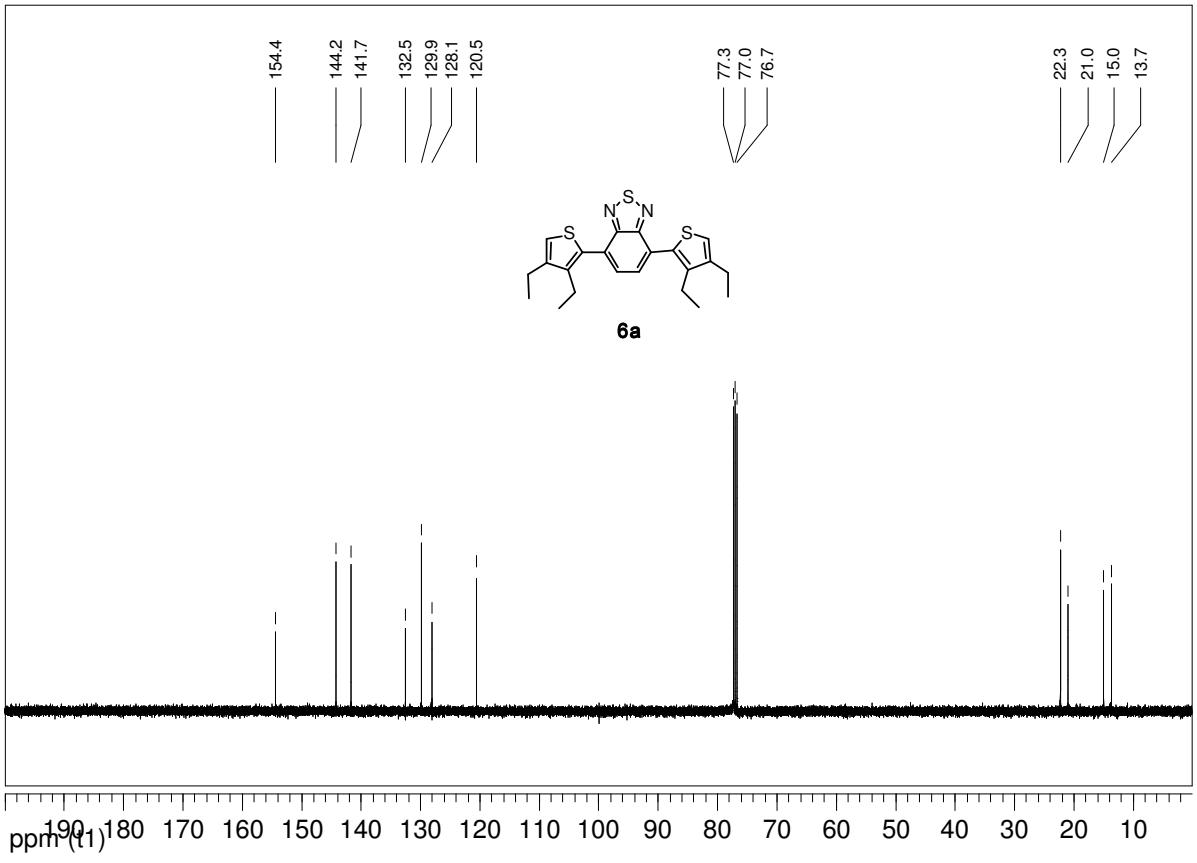
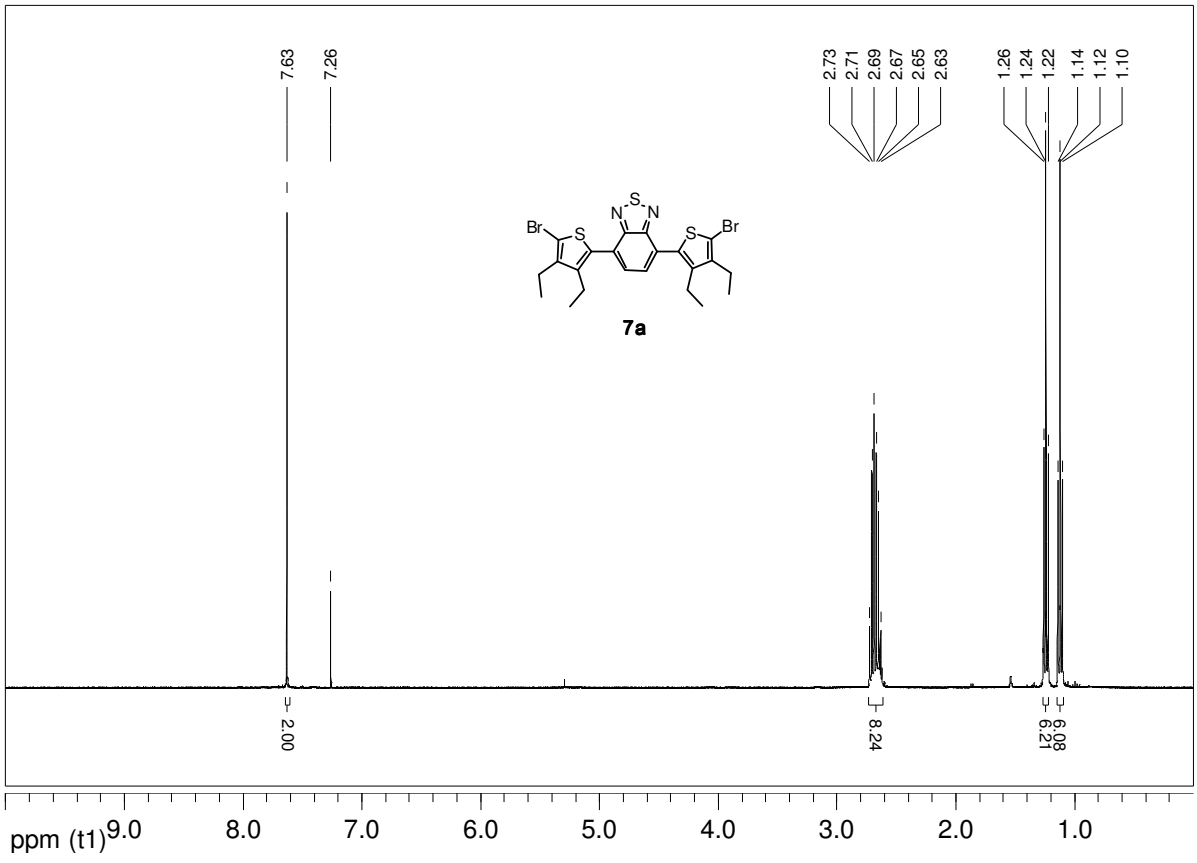
7.0
6.0
5.0
4.0
3.0
2.0
1.0


154.4
144.2
141.7
132.5
129.9
128.1
120.5
77.3
77.0
76.7
22.3
21.0
15.0
13.7
6a
ppm (t1)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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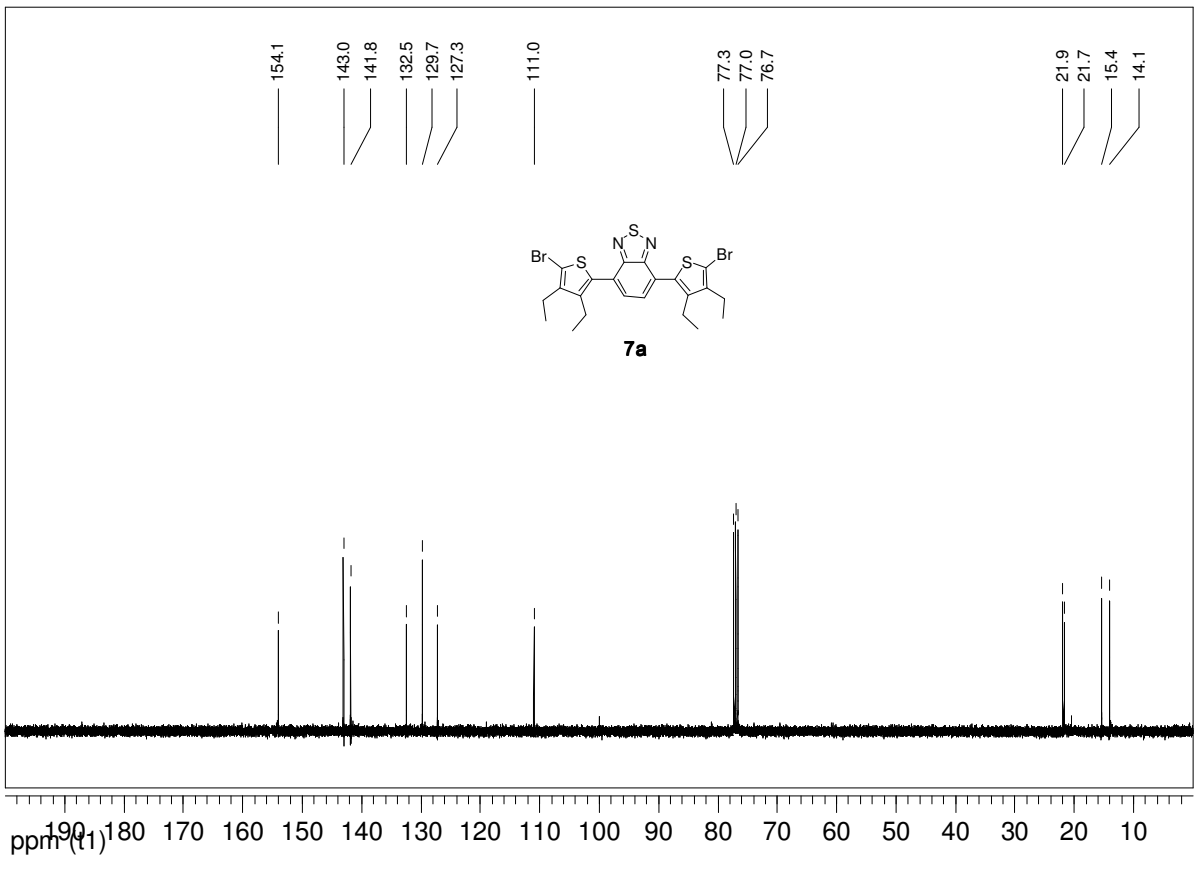
7.26
2.73
2.71
2.69
2.67
2.65
2.63
1.26
1.24
1.22
1.14
1.12
1.10
Br
S
N
S
N
S
Br
7a
2.00
8.24
6.08
6.21
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0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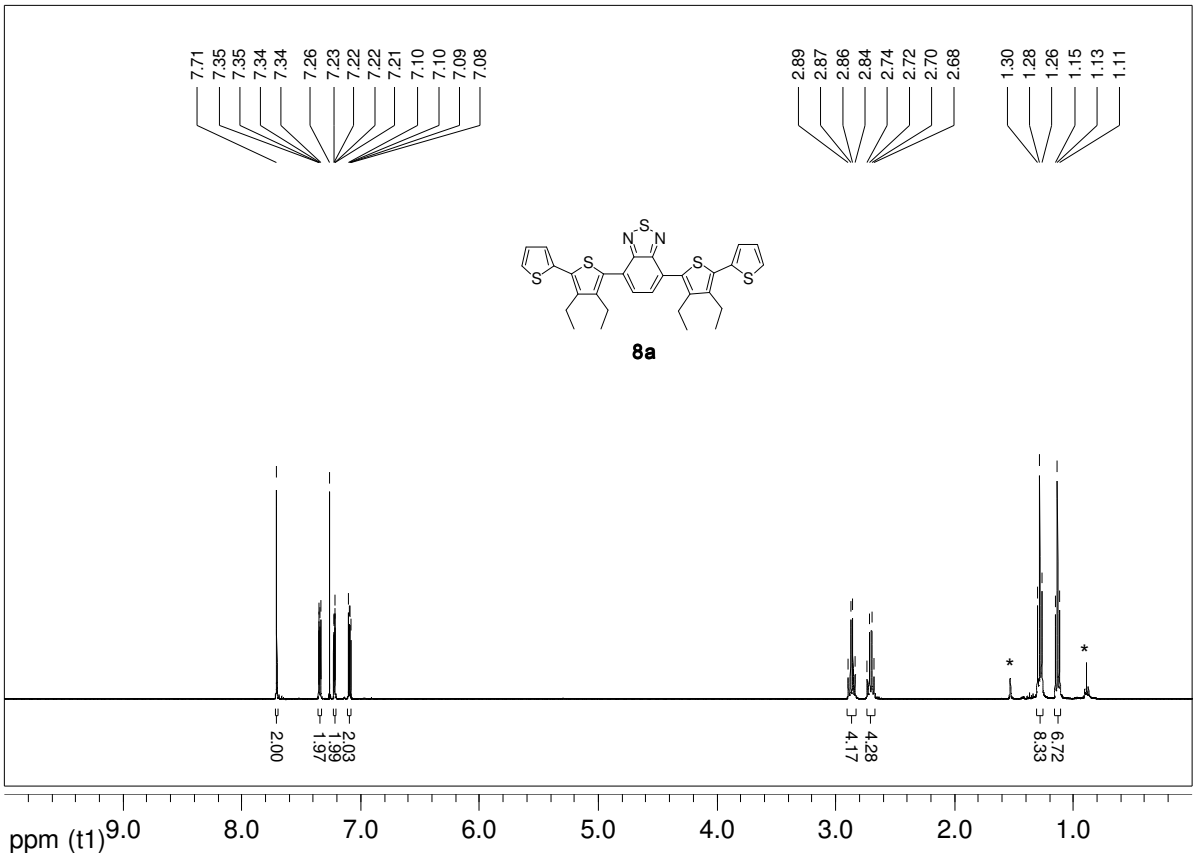
141.8
132.5
129.7
127.3
111.0
77.3
77.0
76.7
21.9
21.7
15.4
14.1
Br
S
N
S
N
S
Br
7a
ppm (t1)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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7.35
7.34
7.34
7.26
7.23
7.22
7.22
7.21
7.10
7.10
7.09
7.08
2.89
2.87
2.86
2.84
2.74
2.72
2.70
2.68
1.30
1.28
1.26
1.15
1.13
1.11
8a
2.00
1.97
1.99
2.03
4.17
4.28
8.33
6.72
ppm (t1)
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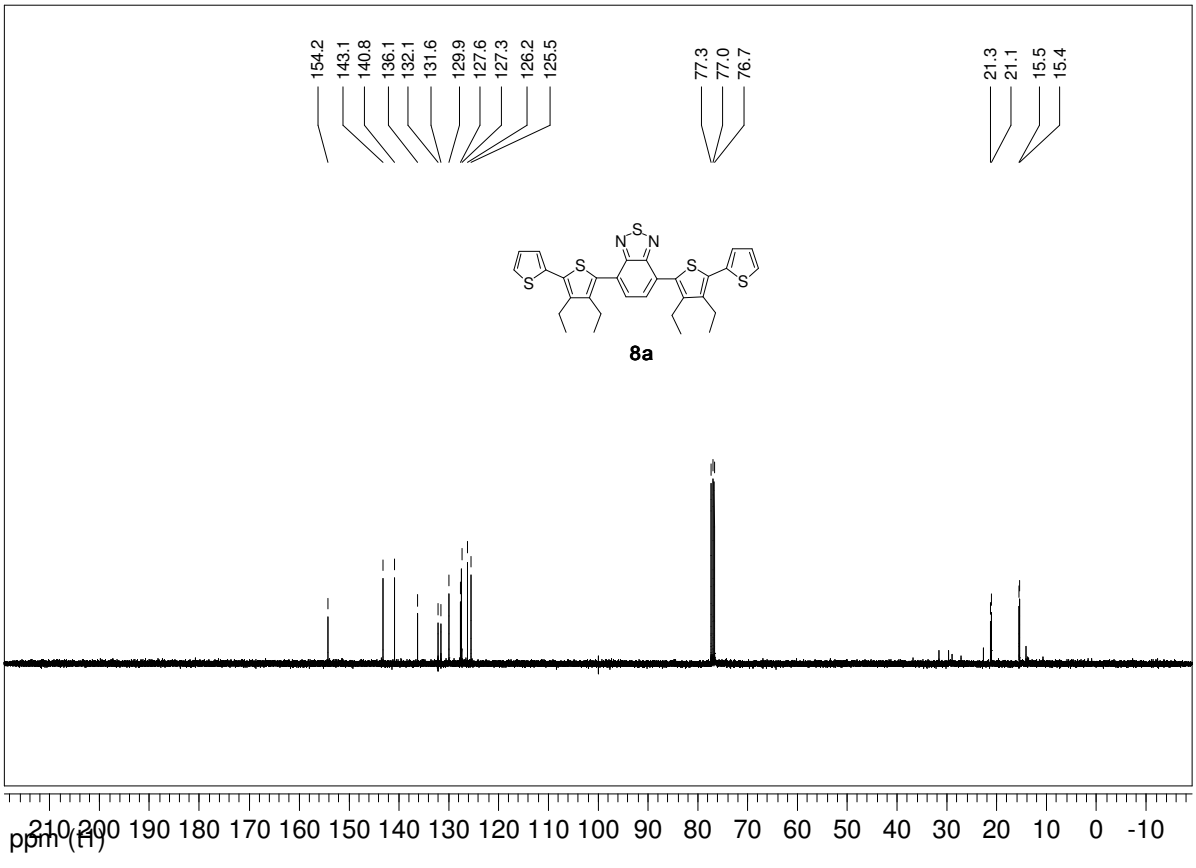
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0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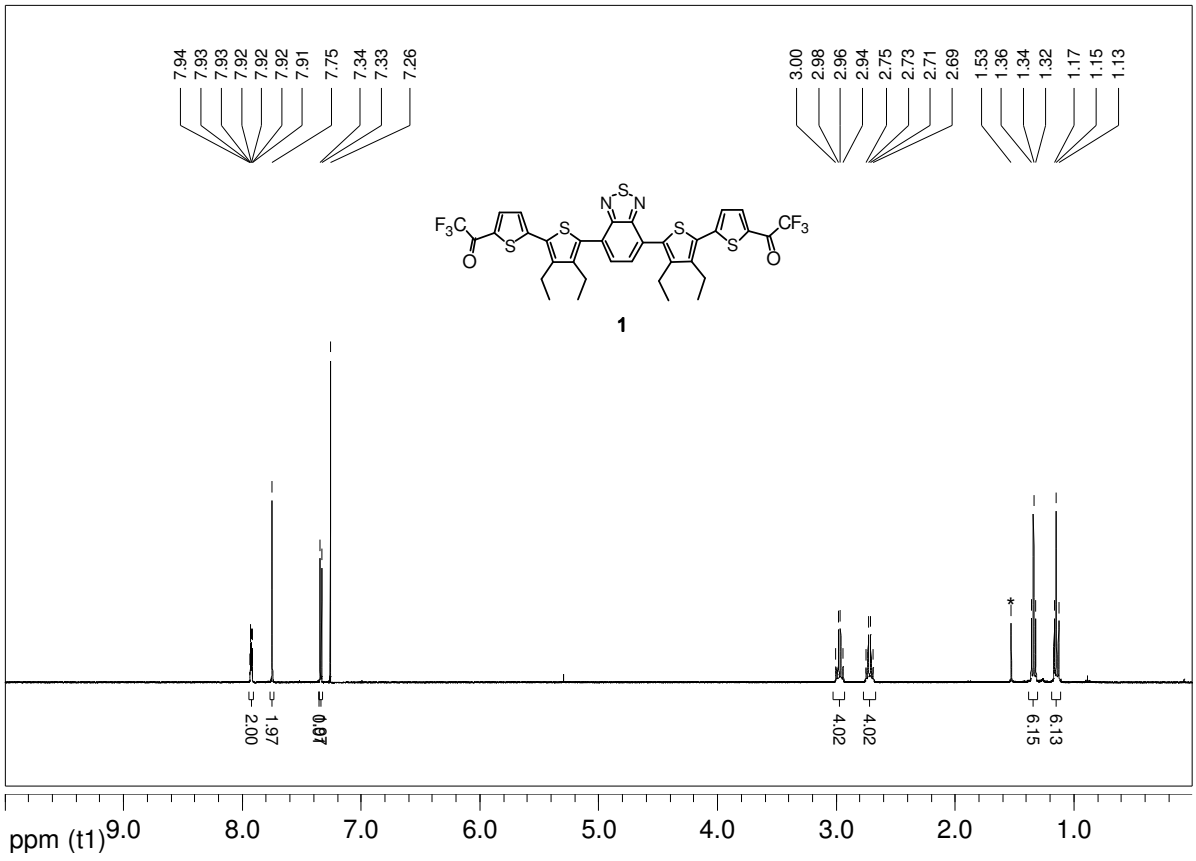
140.8
136.1
132.1
131.6
129.9
127.6
127.3
126.2
125.5
77.3
77.0
76.7
21.3
21.1
15.5
15.4
8a
ppm (t1)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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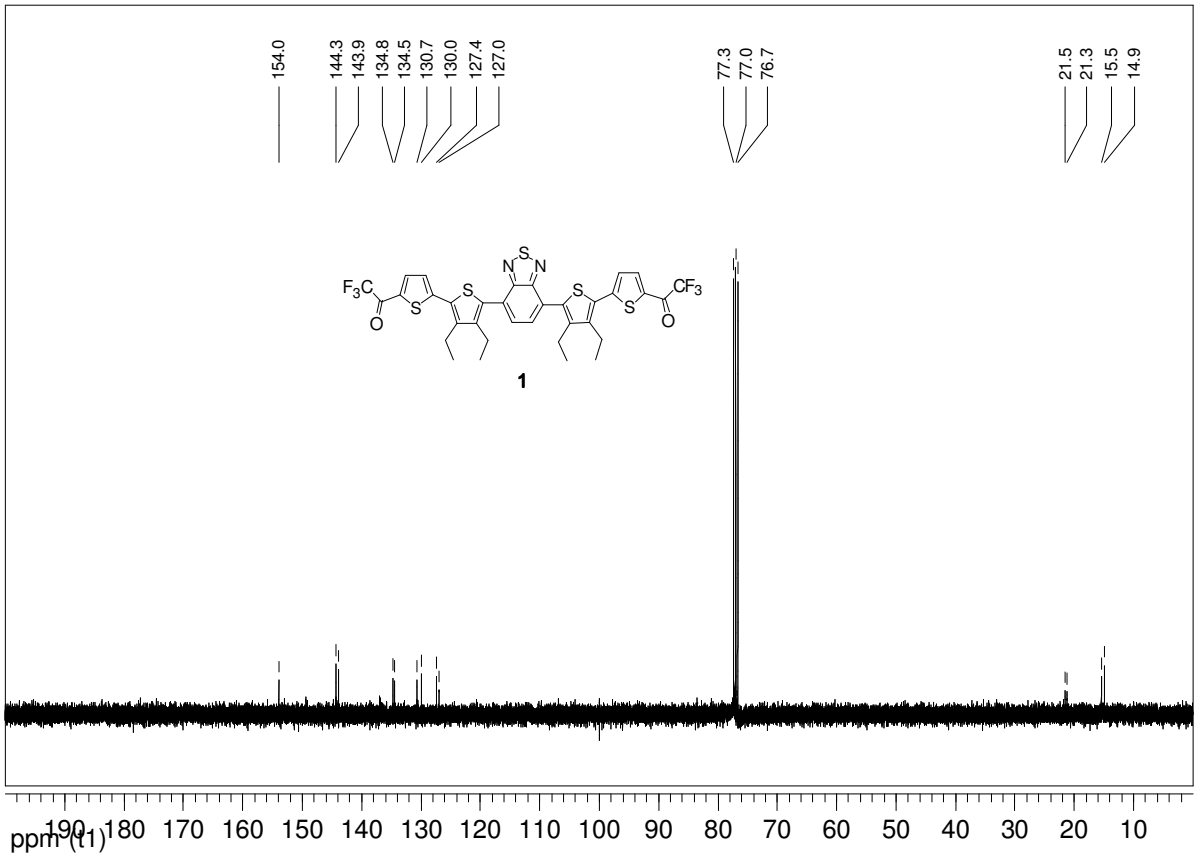
7.93
7.93
7.92
7.92
7.92
7.91
7.75
7.34
7.33
7.26
3.00
2.98
2.96
2.94
2.75
2.73
2.71
2.69
1.53
1.36
1.34
1.32
1.17
1.15
1.13
1
2.00
1.97
4.02
4.02
6.15
6.13
ppm (t1)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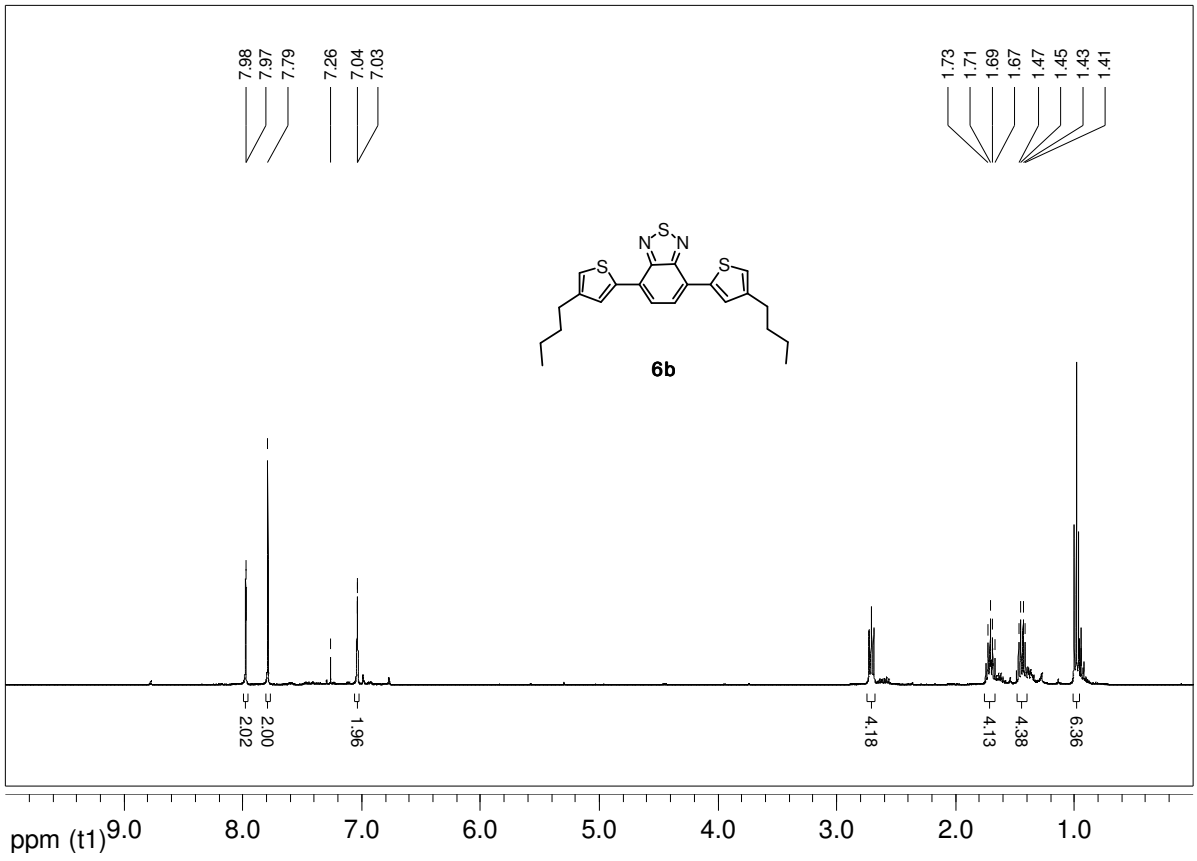
143.9
134.8
134.5
130.7
130.0
127.4
127.0
77.3
77.0
76.7
21.5
21.3
15.5
14.9
1
ppm (t1)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7.79
7.26
7.04
7.03
1.73
1.71
1.69
1.67
1.47
1.45
1.43
1.41
6b
2.02
2.00
1.96
4.18
4.13
4.38
6.36
ppm (t1)
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8.0
7.0
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5.0
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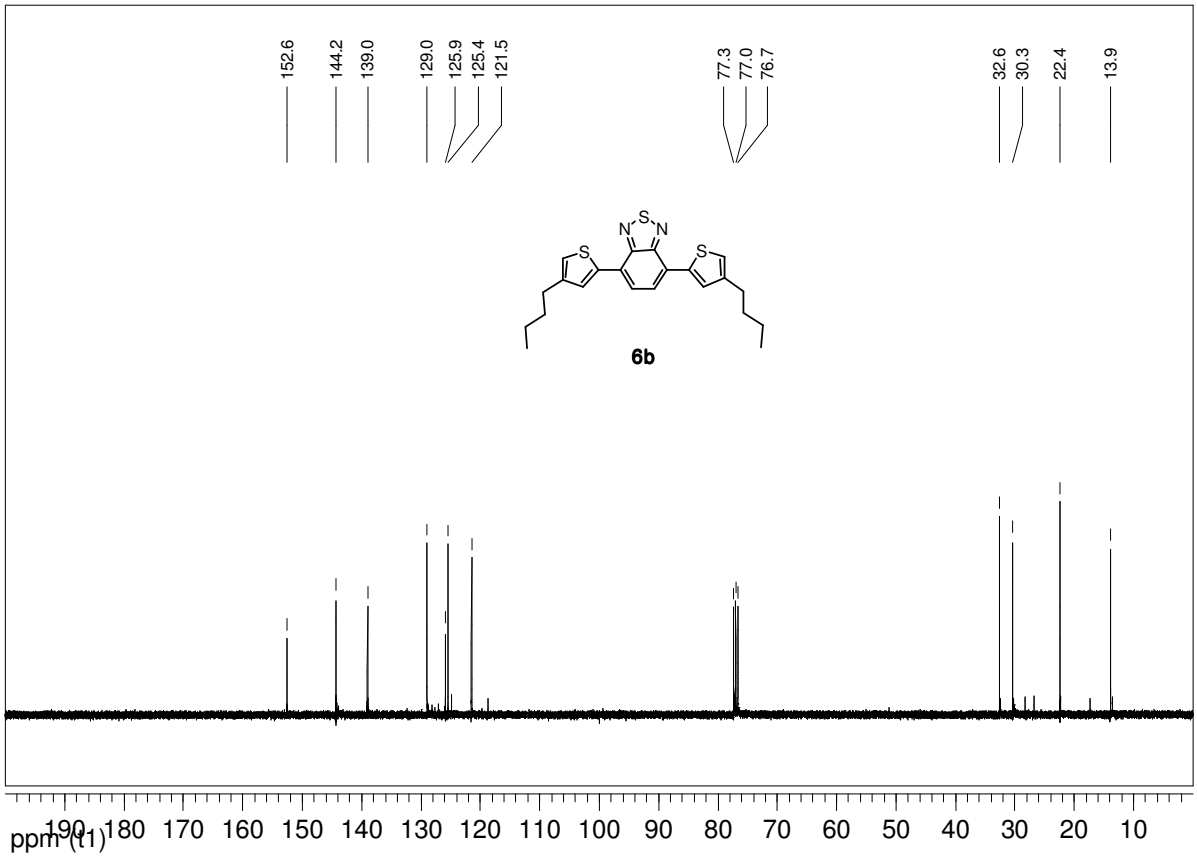
3.0
2.0
1.0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129.0
125.9
125.4
121.5
77.3
77.0
76.7
32.6
30.3
22.4
13.9
6b
ppm (t1)
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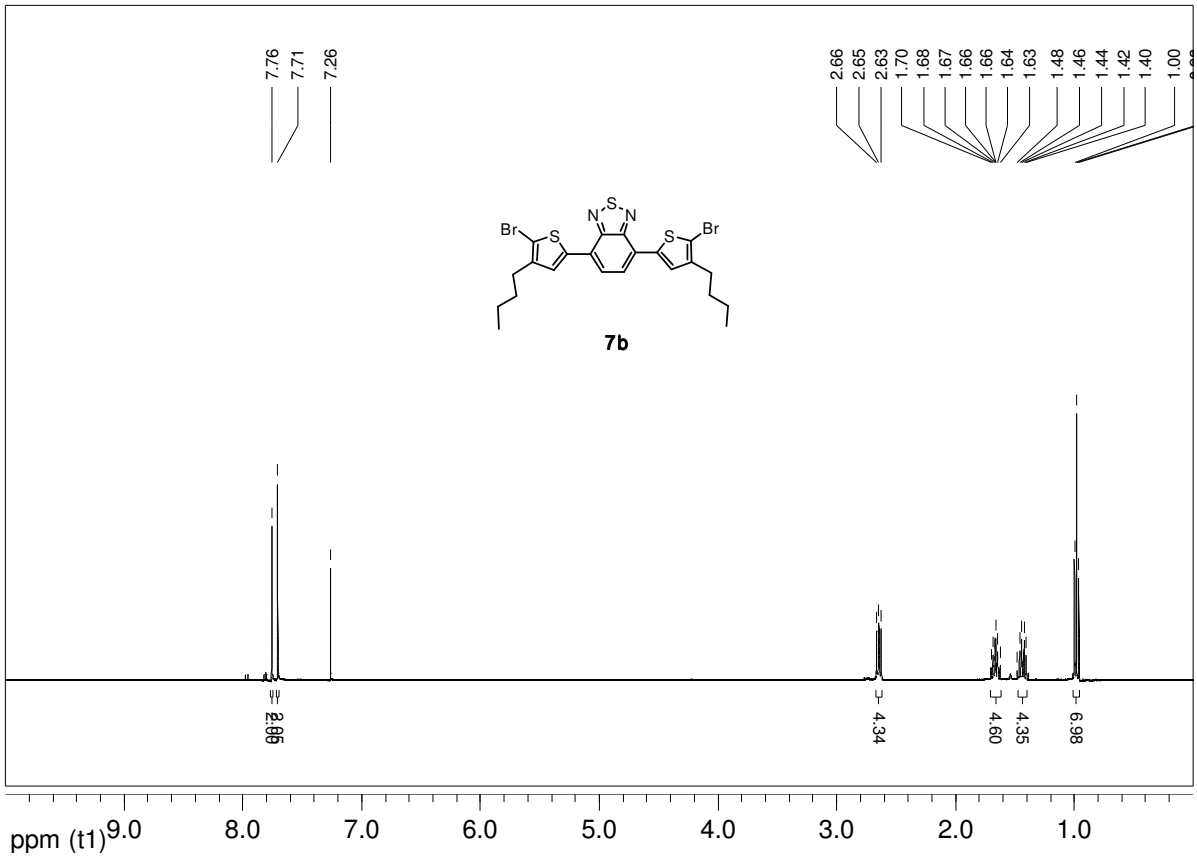
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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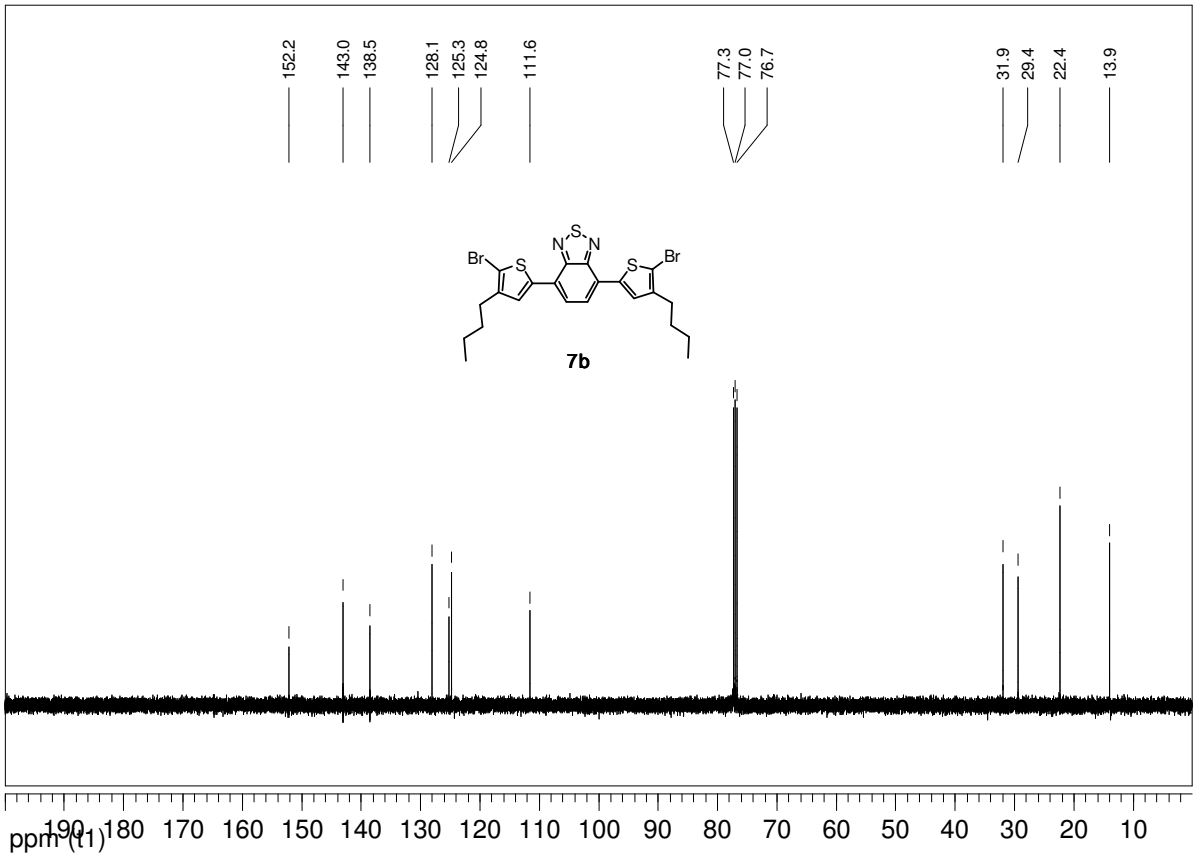
1.67
1.66
1.66
1.64
1.63
1.48
1.46
1.44
1.42
1.40
1.00
Br
S
N
S
N
S
Br
7b
2.00
2.00
4.34
4.00
4.35
6.98
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0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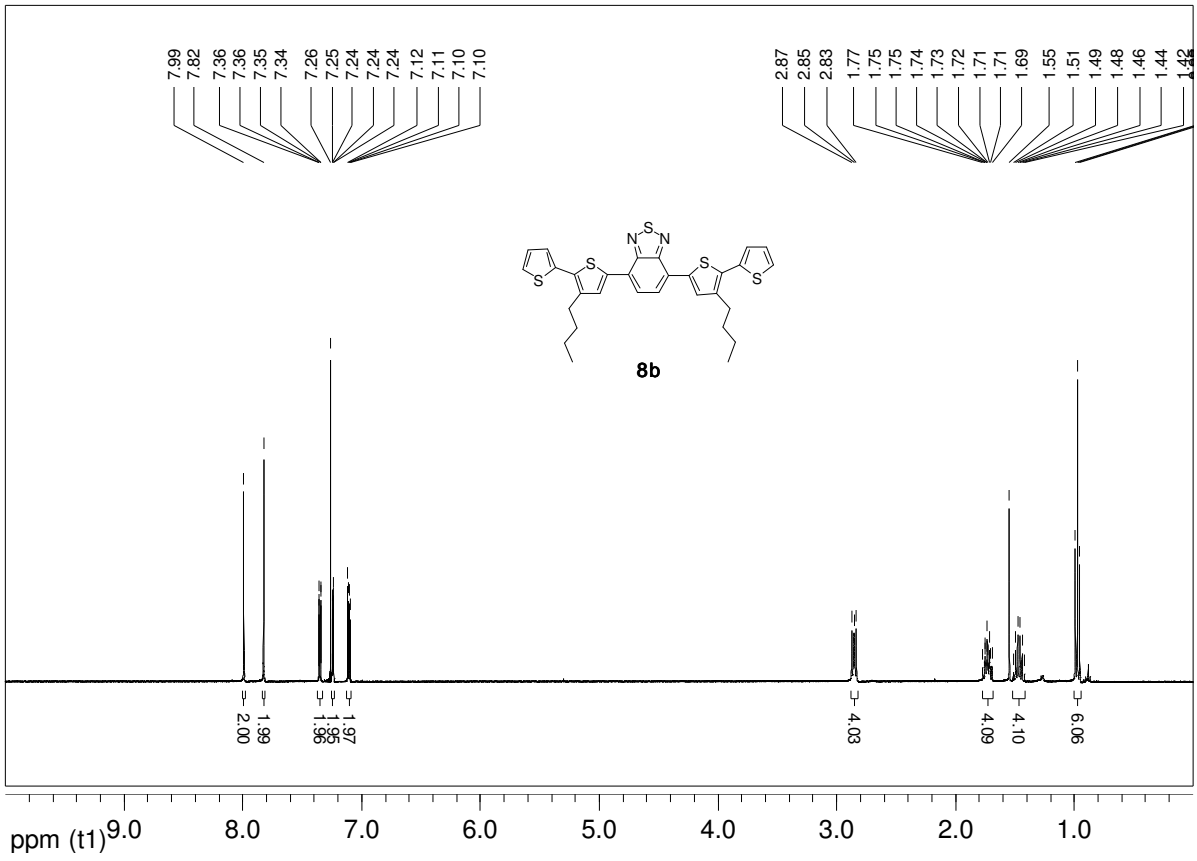
138.5
128.1
125.3
124.8
111.6
77.3
77.0
76.7
31.9
29.4
22.4
13.9
Br
S
N
S
N
S
Br
7b
ppm (t1)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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7.34
7.26
7.25
7.24
7.24
7.24
7.12
7.11
7.10
7.10
2.87
2.85
2.83
1.77
1.75
1.75
1.74
1.73
1.72
1.71
1.71
1.69
1.55
1.51
1.49
1.48
1.46
1.44
8b
2.00
1.99
1.96
1.96
1.97
4.03
4.09
4.10
6.06
ppm (t1)
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8.0
7.0
6.0
5.0
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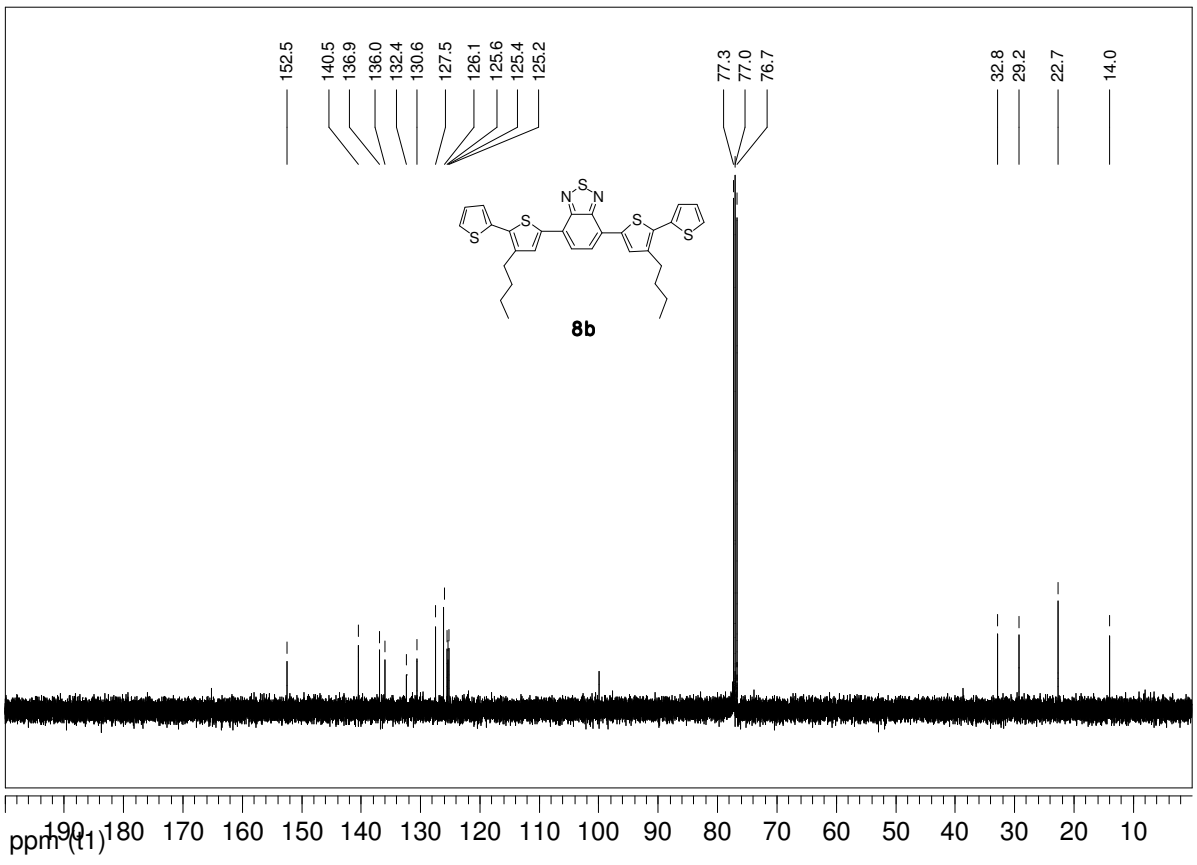
2.0
1.0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126.1
125.6
125.4
125.2
77.3
77.0
76.7
32.8
29.2
22.7
14.0
8b
ppm (t1)
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180
170
160
150
140
130
120
110
100
90
80
70
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40
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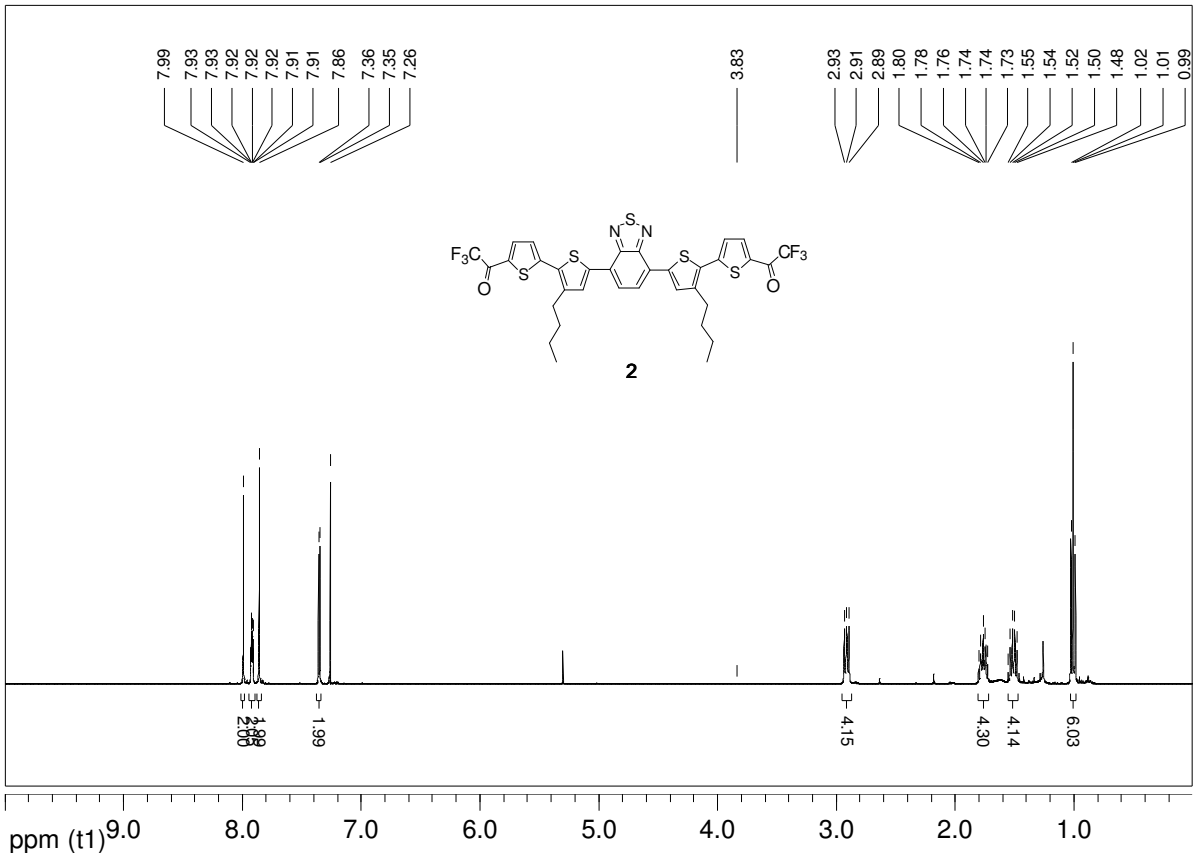
20
10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7.26
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2.91
2.89
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1.78
1.76
1.74
1.74
1.73
1.55
1.54
1.52
1.50
1.48
1.02
1.01
0.99
F3C
O
S
N
S
N
S
S
CF3
O
2
2.00
2.00
1.99
4.15
4.30
4.14
6.03
ppm (t1)
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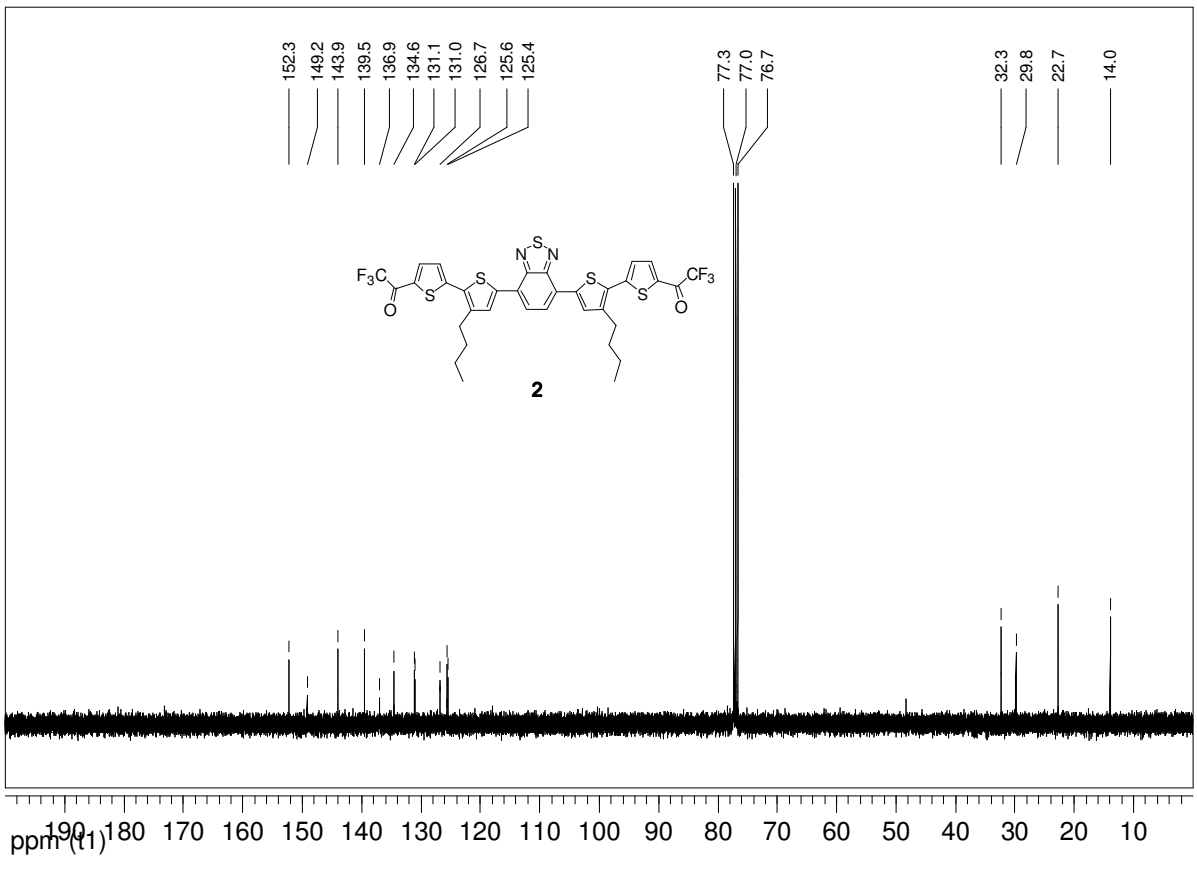
5.0
4.0
3.0
2.0
1.0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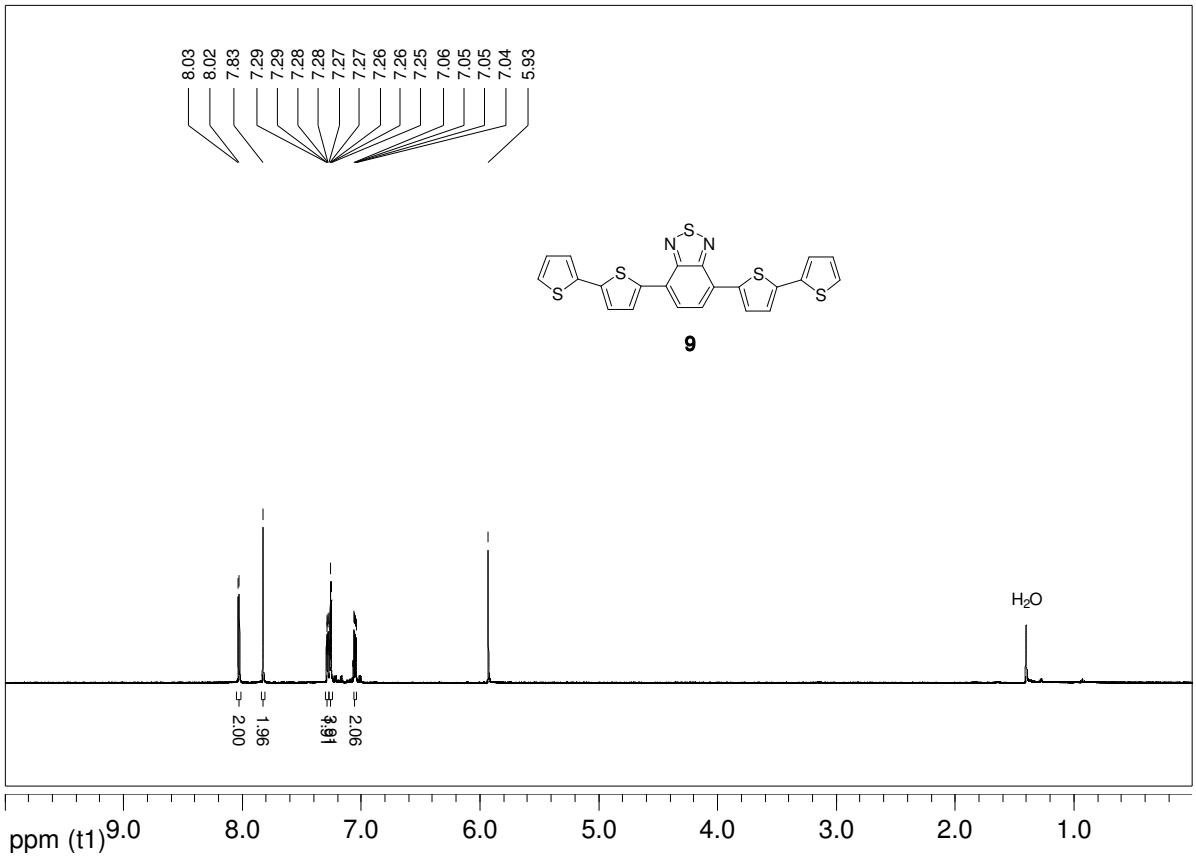
136.9
134.6
131.1
131.0
126.7
125.6
125.4
77.3
77.0
76.7
32.3
29.8
22.7
14.0
F3C
O
S
N
S
N
S
S
CF3
O
2
ppm (t1)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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7.29
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7.26
7.25
7.06
7.05
7.05
7.04
5.93
9
H2O
2.00
1.96
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5.0
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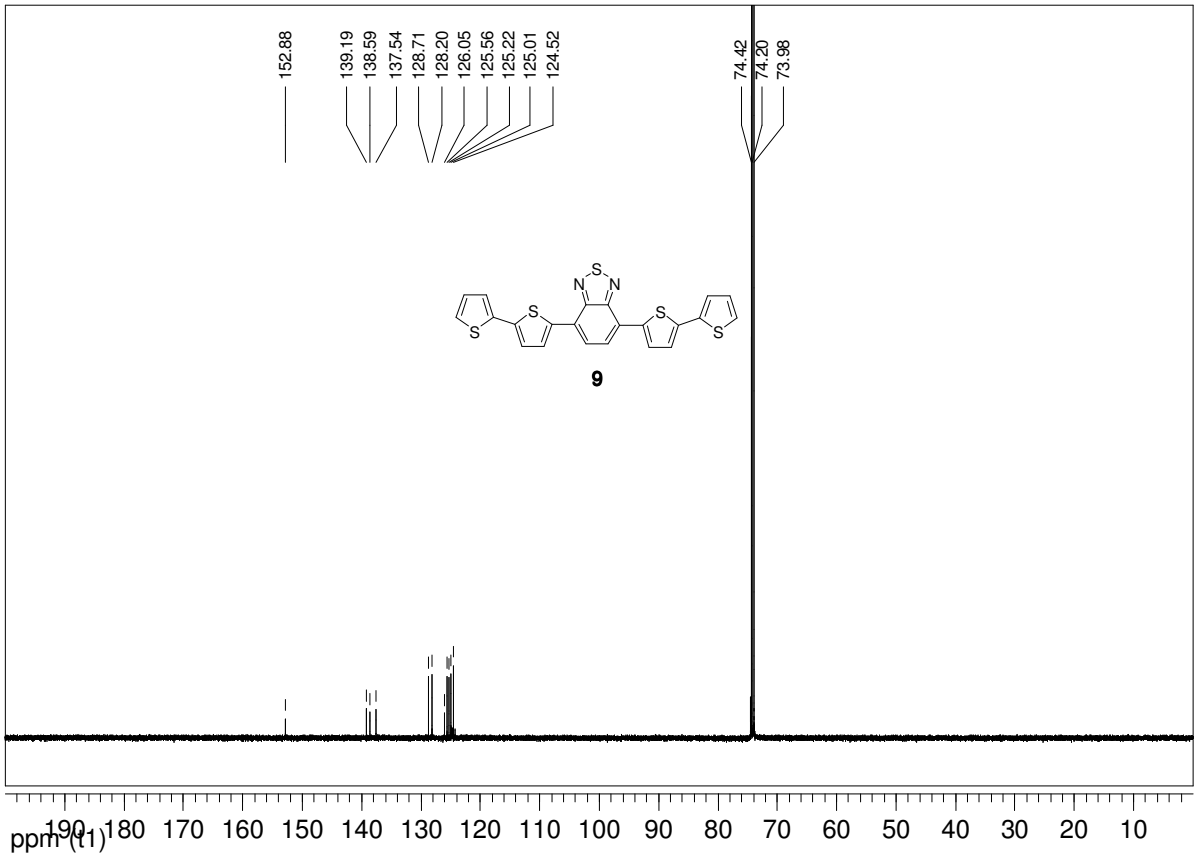
1.0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126.05
125.56
125.22
125.01
124.52
74.42
74.20
73.98
9
ppm (t1)
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180
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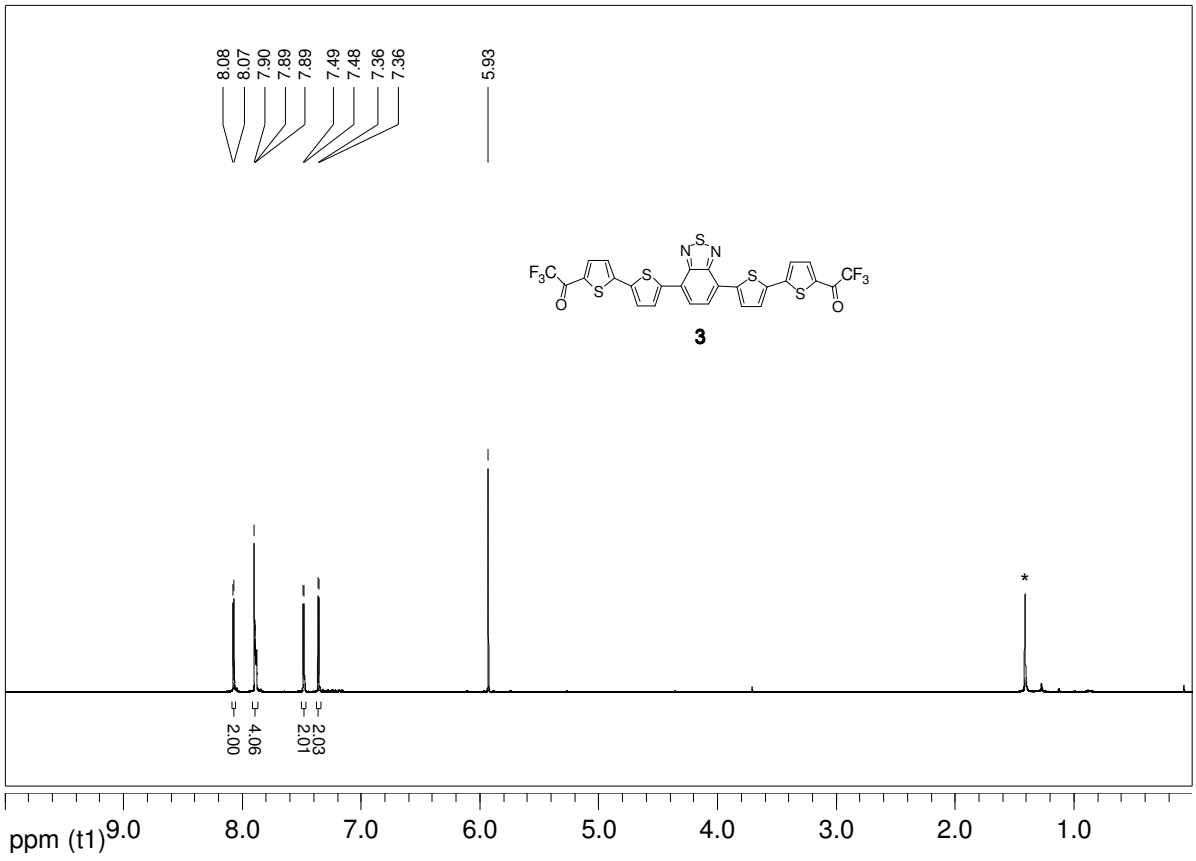
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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7.49
7.48
7.36
7.36
5.93
3
2.00
4.06
2.01
2.03
*
ppm (t1)
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7.0
6.0
5.0
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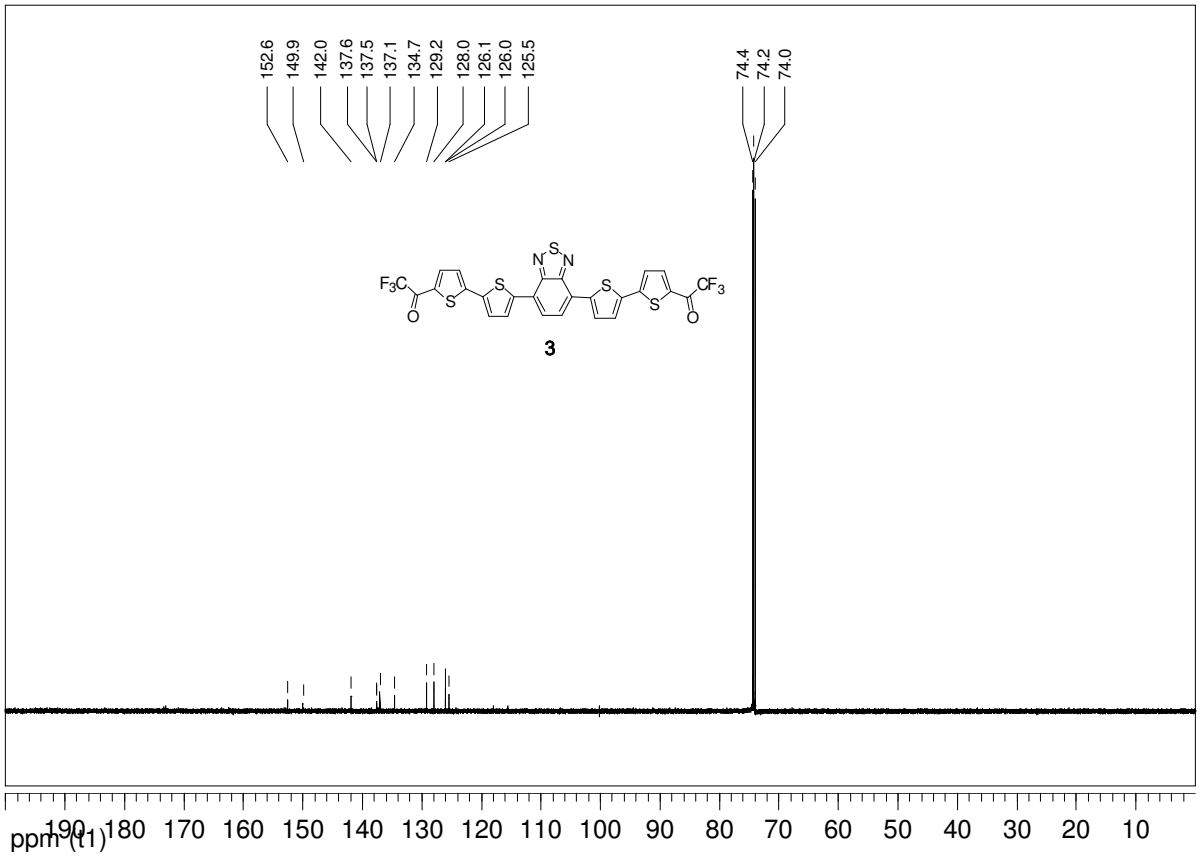
1.0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149.9
142.0
137.6
137.5
137.1
134.7
129.2
128.0
126.1
126.0
125.5
74.4
74.2
74.0
3
ppm (t1)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10