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New perylene diimide electron acceptors for organic electronics: synthesis, optoelectronic properties and performance in perovskite solar cells

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Content

Experimental Part

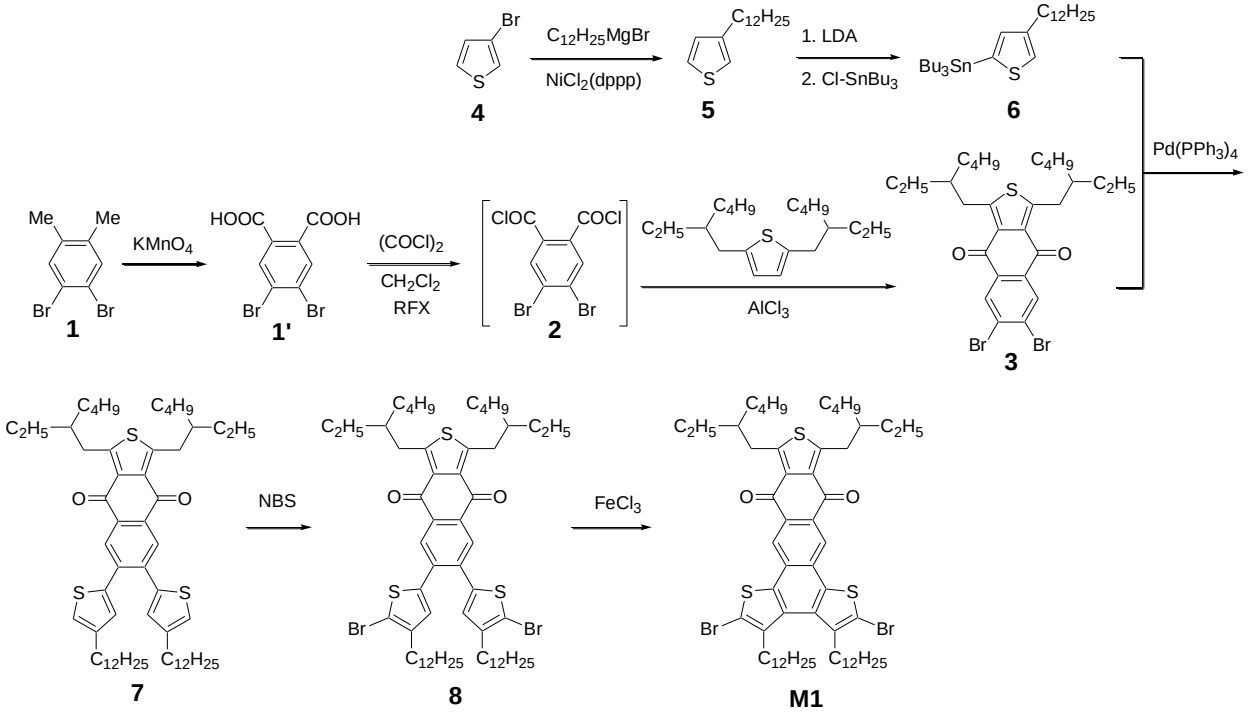
Instruments

^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker Avance III 400 (400 MHz) or an Agilent 600 MHz DD2 nuclear magnetic resonance (NMR) spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Oxidation and reduction potentials of the compounds were determined by cyclic voltammetry (CV) experiments on a computer controlled potentiostat "Autolab type III" at a scan rate of 100 mVs^{-1}. A platinum working electrode, $Ag/AgNO_3$ (0.1 M in anhydrous acetonitrile), and a platinum wire were used as the working electrode, reference electrode and counter electrode, respectively, in a nitrogen-saturated tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution (0.1 M in anhydrous acetonitrile). Electrospray ionization high resolution mass spectrometry was carried out with Bruker microTOF II instrument operating in positive (capillary voltage of 4500 V) and negative (capillary voltage of 3200 V) ion modes. Quantum calculations were performed using Gaussian 16 program package and Multiwfn visualization software, on B3LYP/6-311++g(d,p) level of theory. MALDI-TOF mass-spectra were recorded using a Shimadzu Biotech Axima Confidence spectrometer in positive ions mode using trihydroxyacetophenone as a matrix.

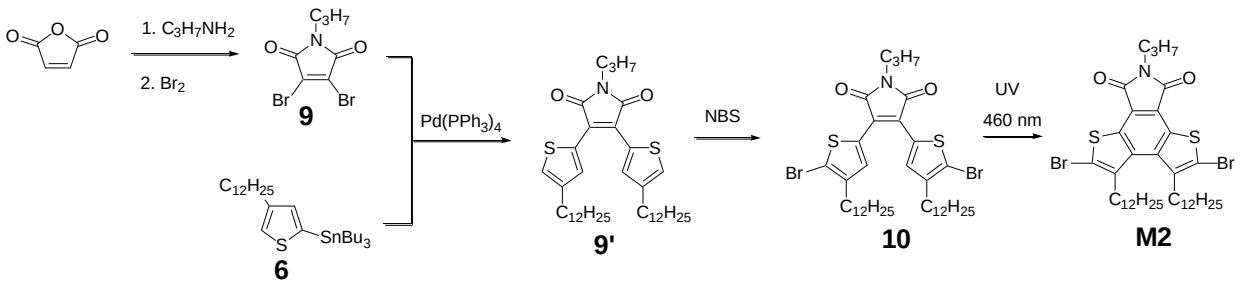
Perovskite solar cells (PSC) were made in the following way. A hole-transport layer of poly(bis(4-phenyl)(4'-methylphenyl)amine) (PTA) was deposited on thoroughly cleaned glass substrates with an electrically conductive ITO layer using spin-coating, and then dried at 110°C.

After drying, a light-absorbing $MAPbI_3$ perovskite layer was applied over the PTA by a two-step method with toluene as an anti-solvent to initiate crystallization of the perovskite layer. After treatment with toluene, the $MAPbI_3$ layer was dried at 55°C for 15 minutes, then slowly heated to 80°C, and kept at this temperature for 5 minutes. After cooling, a layer of **NFA-1** or **NFA-2** was applied at the surface of the perovskite layer by spin-coating, followed by a hole-blocking layer deposition by thermal evaporation in high vacuum (6×10^{-6} mbar). At the final stage, thermal deposition of electrode materials, Mg (5 nm) and Al (100 nm), was carried out.

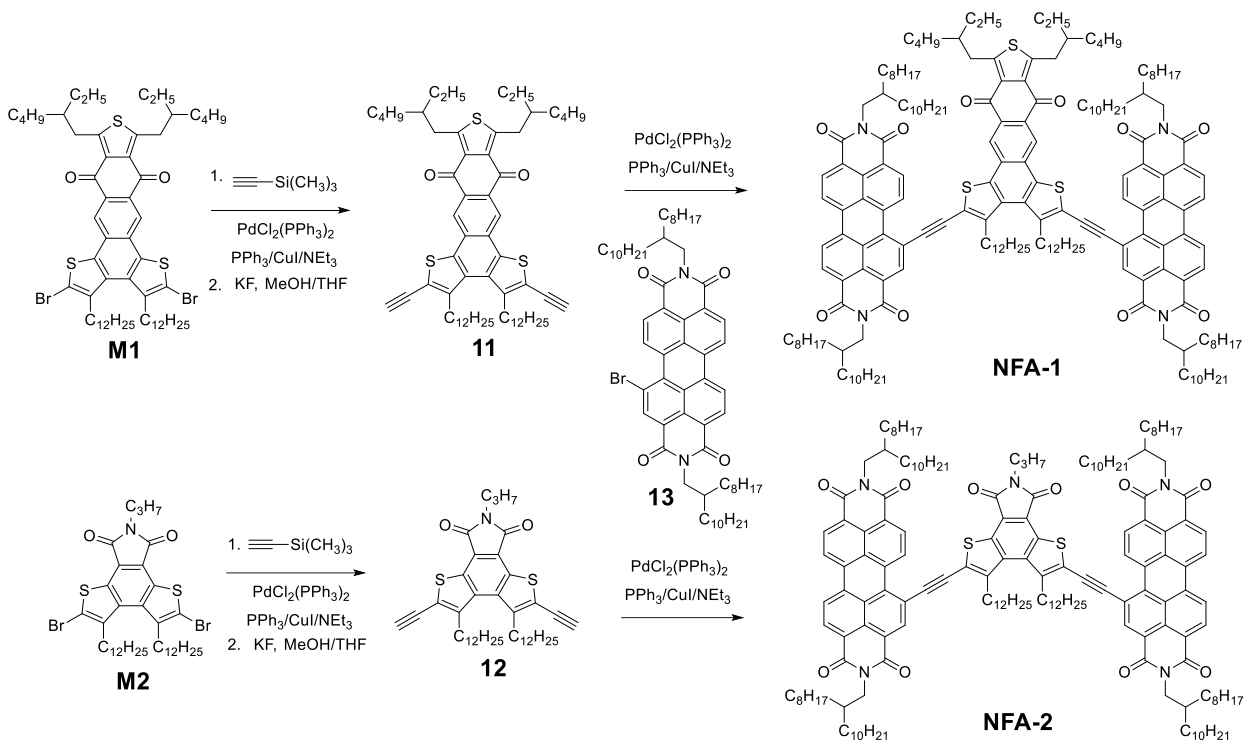
Synthesis of the compounds



Scheme S1 Synthetic pathway to the compound **M1**.

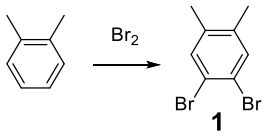


Scheme S2 Synthetic pathway to the compound **M2**.



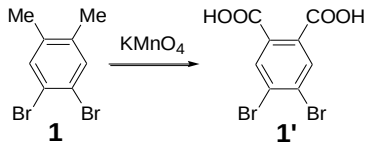
Scheme S3 Synthetic pathway to the acceptor PDI derivatives **NFA-1** and **NFA-2**.

1,2-Dibromo-4,5-dimethylbenzene (1).



Bromine (40.5 ml, 121.9 g, 0.763 mol) was added dropwise to a mixture of *o*-xylene (46 ml, 40.48 g, 0.381 mol) and iodine (0.503 g, 2 mmol) for 4 h at 0°C and with good stirring. Then the mixture was left overnight at room temperature. Then the mixture was dissolved in CH_2Cl_2 (150 ml) and washed with 2 M NaOH solution (2×100 ml). The organic phase was separated, the water phase was extracted with CH_2Cl_2 (2×100 ml). The combined organics were washed with water (300 ml), dried with $MgSO_4$, then the solvent was evaporated. The oily residue was dissolved in boiling MeOH (250–300 ml) and cooled to –15°C. White product was filtrated, washed with cold MeOH and dried. The title compound was obtained as white solid with the yield of 81 g (80.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 2H), 2.18 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.78, 134.33, 131.07, 121.23, 19.23.

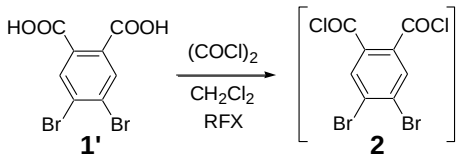
4,5-Dibromophthalic acid (1').



1 **1'**

A suspension of 1,2-dibromo-4,5-dimethylbenzene **1** (13 g, 49.25 mmol) and $KMnO_4$ (31.12 g, 197 mmol) in water (300 ml) was refluxed for 6 h. After cooling the excess of permanganate was inactivated by addition of ethanol (25 ml) and then solid KOH (15 g) was added. The warm suspension was filtered and excess of hydrochloric acid (12M) was slowly added, and the mixture was cooled to 0°C. The precipitate was filtered and dried. The title compound (12.8 g, 80%) was obtained as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (s, 2H), 3.45 (br.s, 3H, COOH + traces of H_2O in DMSO-d_6). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.72, 135.13, 134.47, 127.05.

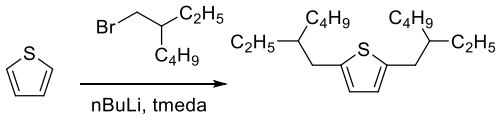
4,5-Dibromophthaloyl dichloride (2).



1' **2**

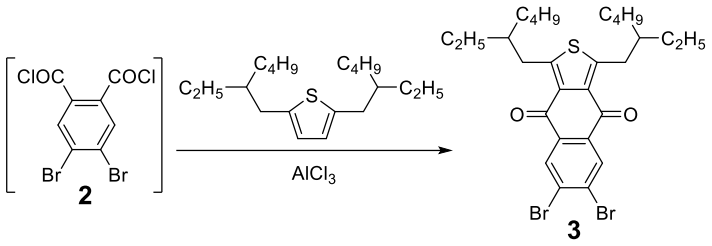
To a suspension of 4,5-dibromophthalic acid **1'** (3 g, 9.26 mmol) in dry CH_2Cl_2 (120 ml), oxalyl chloride (4 ml, 5.88 g, 46.31 mmol) and dry DMF (0.04 ml) were added at 0°C with stirring. The mixture was warmed to 25°C during 30 min and then refluxed for 24 h. After cooling the solvents were removed in vacuum and the residue was used in the next stage without further purification.

2,5-Bis(2-ethylhexyl)thiophene.



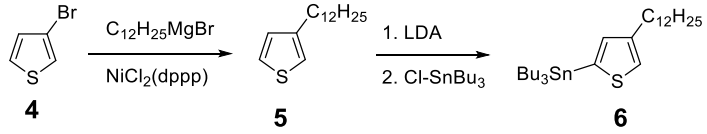
This compound was prepared according to the literature method [*Synthesis*, 2018, 51, 859] from thiophene (13.50 g, 160.45 mmol), Bu^{n}Li (1.6 M, 250 ml, 401 mmol), TMEDA (37.29 g, 321 mmol) and 2-ethylhexyl bromide (77.47 g, 401 mmol) in dry THF (1000 ml) with the yield of 25 g (50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (s, 1H), 2.70 (d, J = 6.7 Hz, 2H), 1.55 (m, 1H), 1.46 – 1.22 (m, 8H), 0.89 (t, J = 7.3 Hz, 6H).

6,7-Dibromo-1,3-bis(2-ethylhexyl)naphtho[2,3-*c*]thiophene-4,9-dione (3).



The 4,5-dibromophthaloyl dichloride **2** (from the previous stage) was dissolved in dry CH_2Cl_2 (150 ml), and 2,5-bis(2-ethylhexyl)thiophene (2.86 g, 9.26 mmol) was added to the solution. The mixture was cooled to 0°C, and $AlCl_3$ (6.17 g, 46.28 mmol) was added by small portions with good stirring. After the addition was completed, the mixture was stirred at 0°C for additional 30 min and then 24 h at 25°C. Then this was poured onto ice (100 g), the organic phase was separated and the water layer was extracted with CH_2Cl_2 (1×120 ml). The combined organic phase was dried with $MgSO_4$, filtrated and evaporated to dryness. The residue was purified on SiO_2 column using gradient mixture of hexane/CH_2Cl_2 (100:0 to 85:15) as an eluent. After evaporating and drying the title compound was obtained as yellowish oil (2.2 g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 2H), 3.29 (ddd, *J* = 12.1, 8.3, 2.3 Hz, 4H), 1.87 – 1.69 (m, 2H), 1.54–1.17 (m, 16H), 1.09–0.73 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.92, 155.77, 134.70, 132.65, 131.42, 131.17, 41.09, 34.06, 32.75, 28.77, 26.01, 23.15, 14.22, 10.82.

Tributyl(4-dodecylthiophen-2-yl)stannane (6).



1-st stage: **3-Dodecylthiophene (5)**. To a suspension of Mg (12.62 g, 0.519 mmol) in dry THF (100 ml), a small portion of $C_{12}H_{25}Br$ (3 ml) was added to initiate the reaction. After several minutes the dropwise addition of a solution of $C_{12}H_{25}Br$ (86.3 g, 346.26 mmol) in dry THF (600 ml) was started. After completion of the addition, the reaction mixture was refluxed for 4 h, then cooled and left at room temperature overnight. Then the Grignard solution was transferred to a dropping funnel *via* teflon tubing and added slowly for 2 h to a cooled (0°C) solution of 3-bromothiophene (**4,** 56.46 g, 346.3 mmol) and $NiCl_2$(dppp) (1.88 g, 3.36 mmol) in dry THF (500 ml) with good stirring. After completion of the addition, the mixture was refluxed overnight. After cooling, water (200 ml) was added, the organic phase was separated and evaporated. The residue was dissolved in petroleum ether (300 ml), washed with 1 M HCl (1×300 ml), dried with $MgSO_4$, filtrated and evaporated. The residue was distilled in vacuum, the title compound was collected at 185–192°C (1 Torr). The yield is 75 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 –

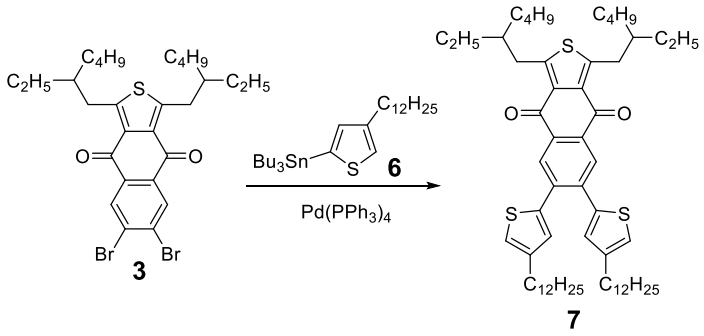
7.21 (m, 1H), 6.97 (m, 2H), 2.67 (t, *J* = 7.7 Hz, 2H), 1.74 – 1.57 (m, 2H), 1.33 (m, 18H), 0.93 (t, *J* = 6.6 Hz, 3H).

2-nd stage: **Tributyl(4-dodecylthiophen-2-yl)stannane (6)**.

To a 3-necked flask (500 ml) charged with dry THF (200 ml) and $Pr^{i}_{2}NH$ (23 ml, 16.67 g, 165 mmol), a $Bu^{n}Li$ solution (97 ml, 154.5 mmol, 1.6 M in hexanes) was added dropwise at -80°C with stirring. After completion of the addition, the cooling bath was removed and the reaction was warmed to -10°C during 30 min. Then it was cooled to -80°C again.

Another 3-necked flask (1000 ml) was charged with dry THF (600 ml) and 3-dodecylthiophene (**5,** 26 g, 103 mmol) and cooled to -80°C. Then to this mixture the previously prepared cold solution of LDA was quickly added from the first flask *via* teflon tubing with septa with good stirring. After the addition of LDA was completed, the resulting mixture was warmed to 0°C during 1 h, then cooled to -80°C again, and a solution of $ClSnBu_3$ (53.64 g, 164.8 mmol) in dry THF (50 ml) was added dropwise. The cooling was removed, and the mixture was stirred at room temperature overnight. Then water (350 ml) was added, the organic phase was separated and evaporated. The residue was dissolved in petroleum ether (300 ml), washed with water (1×300 ml), dried with $MgSO_4$, filtrated and evaporated. The residue was distilled in vacuum, the title compound was collected at 260–290°C (1 Torr). The yield is 49 g (90.5%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 1H), 7.08 – 6.93 (m, 1H), 2.74 – 2.62 (m, 2H), 1.78 – 1.49 (m, 8H), 1.47 – 1.22 (m, 28H), 1.22 – 1.01 (m, 6H), 1.01 – 0.85 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.47, 136.98, 136.89, 136.79, 136.27, 125.55, 125.50, 125.46, 31.96, 30.75, 30.01, 29.73, 29.72, 29.69, 29.66, 29.54, 29.51, 29.40, 29.13, 29.07, 29.03, 28.99, 28.90, 27.88, 27.52, 27.36, 27.28, 27.06, 27.05, 26.88, 22.73, 17.53, 14.15, 13.69, 13.63, 12.18, 12.12, 10.89, 10.85, 10.76, 9.41, 9.35.

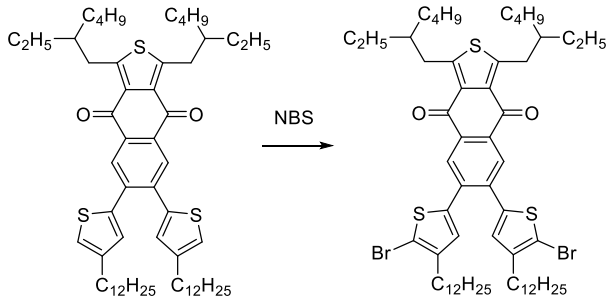
6,7-Bis(4-dodecylthiophen-2-yl)-1,3-bis(2-ethylhexyl)naphtho[2,3-*c*]thiophene-4,9-dione (7).



A solution of compound **3** (2.2 g, 3.69 mmol) and compound **6** (5g, 9.22 mmol) in dry toluene (100 ml) was purged with argon for 45 min. Then $Pd(PPh_3)_4$ (213 mg, 0.1844 mmol) was added, and the purging with argon was continued for additional 20 min. The solution was refluxed for

24 h. After cooling the solvent was removed in vacuum, and the residue was purified on SiO_2 column using gradient mixture of hexane/CH_2Cl_2 (100:0 to 90:10) as an eluent. After evaporation of the eluate, the title compound was obtained as yellow oil (3.36 g, 97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 2H), 6.94 (d, *J* = 1.4 Hz, 2H), 6.90 (d, *J* = 1.4 Hz, 2H), 3.34 (ddd, *J* = 9.3, 7.2, 2.6 Hz, 4H), 2.55 (m, *J* = 7.6 Hz, 4H), 1.90 – 1.76 (m, 2H), 1.57 (m, 4H), 1.50 – 1.18 (m, 57H), 1.04 – 0.91 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.47, 154.76, 143.62, 140.70, 139.02, 133.83, 131.84, 129.78, 129.72, 122.27, 41.11, 34.05, 32.74, 32.08, 30.67, 30.56, 29.87, 29.82, 29.78, 29.64, 29.53, 29.40, 28.79, 26.02, 23.18, 22.84, 14.27, 14.24, 10.84

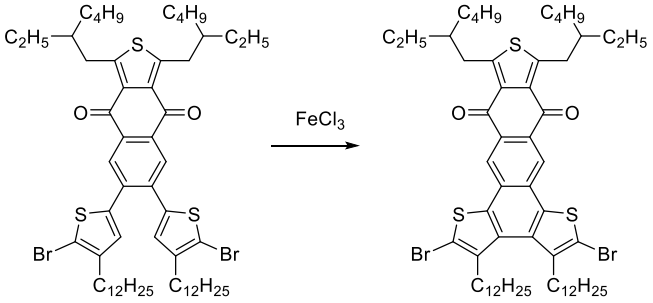
6,7-Bis(5-bromo-4-dodecylthiophen-2-yl)-1,3-bis(2-ethylhexyl)naphtho[2,3-*c*]thiophene-4,9-dione (8).



7 **8**

Compound **7** (3.36 g, 3.58 mmol) was dissolved in a mixture of CH_2Cl_2 (75 ml) and AcOH (25 ml), and the solution was cooled to 0°C. Then NBS (1.40 g, 7.88 mmol) was added by small portions for 20 min, the cooling bath was removed, and the mixture was stirred at 25°C for 24 h. Then the reaction mixture was poured onto ice, neutralized with $NaHCO_3$ and extracted with CH_2Cl_2 (2×100 ml). The combined organic phase was washed with water (1×250 ml), dried with $MgSO_4$ and evaporated. The residue was purified on SiO_2 column using gradient mixture of hexane/CH_2Cl_2 (100:0 to 90:10) as an eluent. The title compound was obtained as yellow oil (solidified at RT within 10 – 15 h) with the yield of 2.8 g (71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 2H), 6.81 (s, 2H), 3.33 (ddd, *J* = 9.4, 7.2, 2.7 Hz, 4H), 2.60–2.50 (t, *J* = 6.9 Hz, 4H), 1.90–1.75 (m, 2H), 1.65–1.50 (m, 4H), 1.49–1.18 (m, 54H), 1.04–0.81 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.12, 155.10, 142.63, 140.03, 137.86, 134.14, 131.70, 129.58, 111.62, 41.13, 34.07, 32.75, 32.09, 29.89, 29.87, 29.86, 29.82, 29.74, 29.60, 29.53, 29.31, 28.79, 26.02, 23.17, 22.85, 14.27, 14.24, 10.84.

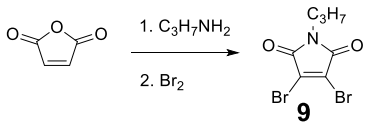
2,5-Dibromo-3,4-didodecyl-9,11-bis(2-ethylhexyl)anthra[1,2-b:4,3-b':6,7-c'']trithiophene-8,12-dione (M1).



8 **M1**

To a solution of compound **8** (500 mg, 0.4556 mmol) in a mixture of CH_2Cl_2 (60 ml) and $MeNO_2$ (15 ml), anhydrous $FeCl_3$ (370 mg, 2.28 mmol) was added in one portion, then the mixture was refluxed for 5 h. After that another portion of $FeCl_3$ (370 mg, 2.28 mmol) was added, and refluxing was continued for additional 5 h. After cooling water (50 ml) was added, the organic phase was separated, and water phase was extracted with CH_2Cl_2 (2×70 ml). The combined organic layers were washed with H_2O (1×250 ml), dried with $MgSO_4$ and evaporated. The residue was purified on SiO_2 column using gradient mixture of hexane/CH_2Cl_2 (100:0 to 90:10) as an eluent. After evaporation the title compound **M1** was obtained as yellow oil (solidified on standing) with the yield of 300 mg (60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 2H), 3.35 (m, 4H), 3.15 (t, *J* = 7.9 Hz, 4H), 1.84 (m, 2H), 1.63 – 1.52 (m, 4H), 1.50 – 1.12 (m, 30H), 1.00 – 0.84 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.04, 154.90, 139.28, 138.69, 133.17, 132.33, 132.09, 128.08, 124.10, 116.09, 41.05, 34.20, 32.75, 32.06, 31.28, 29.80, 29.78, 29.72, 29.63, 29.50, 29.44, 29.23, 28.78, 26.03, 23.22, 22.83, 14.26, 10.85. HRMS: $C_{60}H_{86}Br_2O_2S_3$, *m/z*: 1095.4224 (M^+). Calcd. 1095.4216. Anal. Calcd for $C_{60}H_{86}Br_2O_2S_3$: C, 65.79%; H, 7.91%; S, 8.78%. Found: C, 66.01%; H, 7.74%; S, 8.46%.

3,4-Dibromo-1-propyl-1*H*-pyrrole-2,5-dione (9).

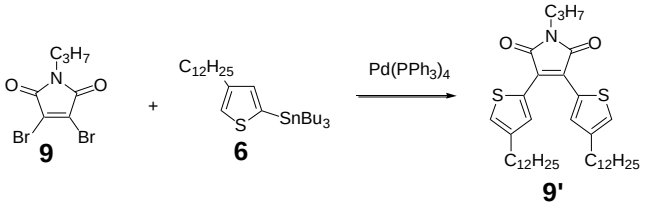


9

To a cooled (0…+5°C) solution of propylamine (50 ml, 0.589 mol) in abs. THF (150 ml), was added dropwise a solution of maleic anhydride (55 g, 0.561 mol) in abs. THF (300 ml). After the addition was completed, the cooling bath was removed and the mixture was stirred at RT for 1 h. Solid potassium acetate (55 g, 0.561 mol) was added with good stirring and then propionic anhydride (130 ml) was added dropwise, and the yellow solution was stirred at RT overnight. The mixture was evaporated to dryness in vacuum at heating (60-80°C), then $CHCl_3$ (400 ml) and H_2O (400 ml) were added to the residue, and solid $NaHCO_3$ was added by small portions

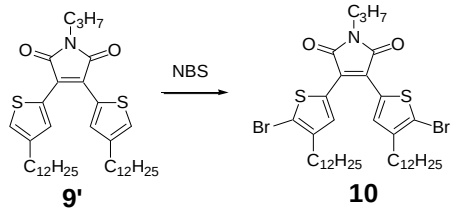
until the neutralization was completed. The organic phase was separated, washed with water, dried with $MgSO_4$ and evaporated. The dark brown residue (60 g) was dissolved in AcOH (250 ml) and to this solution potassium acetate (112 g, 1.143 mol) was added. Then bromine (45 ml, 0.873 mol) was added dropwise with good stirring at room temperature (cooling bath is necessary). After completion of the addition the reaction mixture was heated at 80°C overnight. After cooling the mixture was poured into 1 L of water/ice mixture and stirred. The product was filtered, washed with water and dried. The yield is 66 g (40%) of light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.57 (t, 2H, *J* = 7.96 Hz), 1.63 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, C_6D_6) δ 164.13, 129.44, 41.50, 21.92, 11.27.

3,4-Bis(4-dodecylthiophen-2-yl)-1-propyl-1*H*-pyrrole-2,5-dione (9')



3,4-Dibromo-1-propyl-1*H*-pyrrole-2,5-dione (**9**) (6.65 g, 22.39 mmol) and tributyl(4-dodecylthiophen-2-yl)stannane (**6,** 29.2 g, 53.75 mmol) were dissolved in dry toluene (300 ml) and the solution was purged with Ar. Then $Pd(PPh_3)_4$ (259 mg, 0.224 mmol) was added, and the mixture was refluxed overnight. After cooling, reaction mixture was evaporated to dryness, the residue was purified by column chromatography on SiO_2 using hexane/CH_2Cl_2 = 100:30 mixture as eluent. After evaporation of the eluate the residue was dissolved in hexane and cooled. After filtration the title product was obtained with 10.7 g (75%) yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 1.2 Hz, 2H), 7.15 (d, *J* = 0.8 Hz, 2H), 3.61 – 3.56 (t, *J* = 7.4 Hz, 2H), 2.62 – 2.57 (t, *J* = 7.66 Hz, 4H), 1.72 – 1.64 (m, 2H), 1.60 (m, 5H), 1.37 – 1.20 (m, 39H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.61, 143.99, 132.57, 129.69, 127.21, 126.08, 40.27, 32.07, 30.69, 30.37, 29.84, 29.80, 29.76, 29.61, 29.51, 29.40, 22.84, 21.99, 14.27, 11.48.

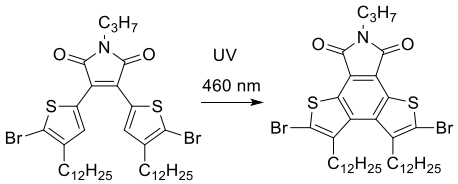
3,4-Bis(5-bromo-4-dodecylthiophen-2-yl)-1-propyl-1*H*-pyrrole-2,5-dione (10).



To a cooled solution of 3,4-bis(4-dodecylthiophen-2-yl)-1-propyl-1*H*-pyrrole-2,5-dione (**9'**) (4.278 g, 6.68 mmol) in dry DCM (70 ml) and AcOH (35 ml), NBS (2.62 g,14.70 mmol) was

added by small portions at 0°C. Then the cooling bath was removed, and the mixture was stirred at RT overnight. Then the mixture was washed with water three times, neutralized with $NaHCO_3$, dried with $MgSO_4$ and evaporated. The residue was purified by column chromatography on SiO_2, with hexane/DCM = 4:1 mixture as an eluent. The title compound was obtained as red solid with 5.0 g (94%) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 2H), 3.56 (t, *J* = 7.2 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 4H), 1.76 – 1.49 (m, 6H), 1.45 – 1.16 (m, 38H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.17, 143.01, 132.26, 129.58, 125.97, 116.73, 40.38, 32.07, 29.89, 29.82, 29.80, 29.72, 29.57, 29.51, 29.33, 22.84, 21.94, 14.27, 11.46.

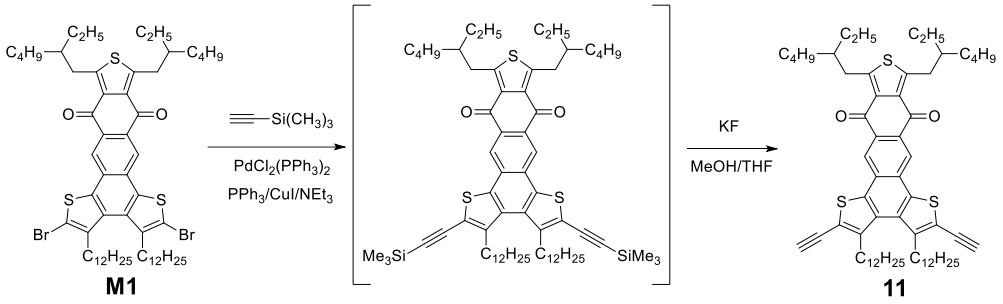
2,5-Dibromo-3,4-didodecyl-8-propyl-7*H*-dithieno[2,3-*e*:3',2'-*g*]isoindole-7,9(8*H*)-dione (M2).



10 **M2**

A solution of bis(5-bromo-4-dodecylthiophen-2-yl)-1-propyl-1*H*-pyrrole-2,5-dione (**10,** 500 mg, 0.6267 mmol) and molecular iodine (80 mg, 0.315 mmol) in dry toluene (100 ml) was irradiated with UV light (465 nm) for 6 h with continuous purging with air through the solution. The reaction was controlled by TLC. After the completion of the process, the solvent was removed in vacuum, the residue was purified by column chromatography on SiO_2 with hexane/DCM = 4:1 mixture as an eluent. The title compound was obtained after evaporation of light-yellow band with the yield of 298 mg (60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.68 (t, *J* = 7.2 Hz, 2H), 3.21 (t, *J* = 7.54 Hz, 4H), 1.79 – 1.71 (m, 2H), 1.56 – 1.45 (m, 4H), 1.26 (m, 38H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.20, 137.64, 137.32, 132.60, 122.06, 121.68, 40.05, 32.06, 31.04, 29.77, 29.69, 29.59, 29.47, 29.42, 29.08, 22.83, 22.18, 14.26, 11.49. Anal. Calcd for $C_{39}H_{57}Br_2NO_2S_2$: C, 58.86%; H, 7.22%; N, 1.76%; S, 8.06%. Found: C, 59.34%; H, 7.34%; N, 1.76%; S, 7.85%. HRMS: $C_{39}H_{52}Br_2NO_2S_2Na$, *m/z*: 818.2044 $(M+Na)^+$. Calcd. 818.2072.

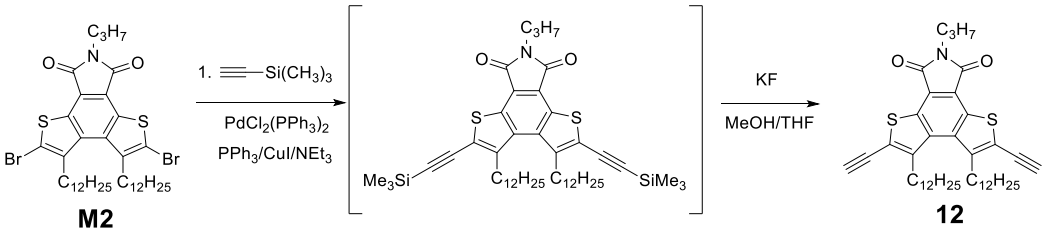
3,4-Didodecyl-9,11-bis(2-ethylhexyl)-2,5-diethynylanthra[1,2-*b*:4,3-*b*':6,7-*c*'']trithiophene-8,12-dione (11).



A solution of 2,5-dibromo-3,4-didodecyl-9,11-bis(2-ethylhexyl)anthra[1,2-*b*:4,3-*b*':6,7-*c*'']-trithiophene-8,12-dione (**M1**) (2.27 g, 2.07 mmol) and trimethylsilylacetylene (1.48 ml, 10.36 mmol) in abs. THF (30 ml) and abs. NEt_3 (30 ml) was purged with argon for 20 min, then CuI (197 mg, 0.623 mmol), PPh_3 (163 mg, 0.623 mmol) and $PdCl_2(PPh_3)_2$ (145 mg, 0.207 mmol) were added in sequence, and the mixture was refluxed for 20 h. After cooling, the solvents were evaporated, the residue was dissolved in hexane and passed through SiO_2 pad (5 cm), the SiO_2 was washed with hexane and then with hexane/CH_2Cl_2 = 5:1 for several times. The eluate was evaporated and the title product was obtained with 2.33 g (99%) yield, and was used in the next stage without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 3.47 – 3.20 (m, 4H), 1.86 (m, 1H), 1.70 – 1.56 (m, 2H), 1.52 – 1.20 (m, 30H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 180.07, 154.71, 145.80, 138.49, 133.72, 132.45, 132.01, 129.25, 124.34, 121.63, 105.17, 98.05, 40.94, 34.04, 32.64, 31.93, 31.16, 29.90, 29.68, 29.66, 29.61, 29.60, 29.36, 29.29, 29.18, 28.66, 25.92, 23.08, 22.69, 14.12, 10.73, -0.09, -0.50.

To a solution of bis-TMS intermediate (2.39 g, 2.11 mmol) in 100 ml of dry THF, was added a solution of KF (1.23 g, 21.12 mmol) in 15 ml of MeOH, and this was stirred for 3 h at RT. After the reaction was completed, the solution was evaporated to dryness, the residue was dissolved in CH_2Cl_2 (150 ml), washed with water (150 ml), dried with $MgSO_4$ and evaporated. The solid residue was suspended in cold hexane, filtrated and dried. The yield of title compound is of 1.78 g (85.5%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (s, 1H), 3.73 (s, 1H), 3.47 – 3.23 (m, 4H), 1.91 – 1.79 (m, 1H), 1.65 – 1.53 (m, 2H), 1.50 – 1.09 (m, 28H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.11, 154.97, 146.30, 138.88, 133.65, 132.68, 132.10, 129.32, 124.46, 120.53, 86.97, 77.52, 77.41, 77.16, 76.91, 41.06, 34.20, 32.75, 32.06, 31.33, 30.00, 29.80, 29.78, 29.72, 29.63, 29.49, 29.41, 29.25, 28.78, 26.04, 23.21, 22.83, 14.26, 10.85. Anal. Calcd for $C_{64}H_{88}O_2S_3$: C, 77.99; H, 9.00; S, 9.76. Found: C, 77.92; H, 8.98; S, 9.75. %. HRMS: $C_{64}H_{88}O_2S_3$, *m/z*: 985.6005 (M^+). Calcd. 985.6019.

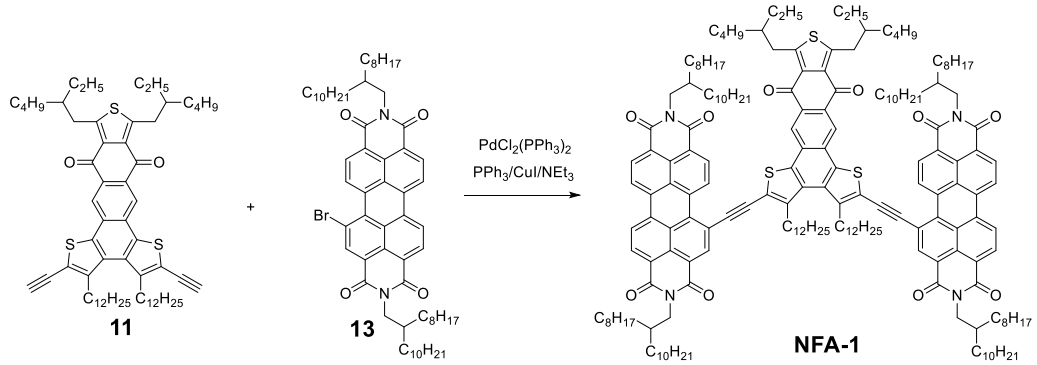
3,4-Didodecyl-2,5-diethynyl-8-propyl-7*H*-dithieno[2,3-*e*:3',2'-*g*]isoindole-7,9(8*H*)-dione (12).



A solution of 2,5-dibromo-3,4-didodecyl-8-propyl-7*H*-dithieno[2,3-*e*:3',2'-*g*]isoindole-7,9(8*H*)-dione (**M2**) (2.84 g, 3.57 mmol) and trimethylsilylacetylene (2.55 ml, 17.84 mmol) in abs. THF (40 ml) and abs. NEt_3 (40 ml) was purged with argon for 20 min, then CuI (227 mg, 0.714 mmol), PPh_3 (187 mg, 0.714 mmol) and $PdCl_2(PPh_3)_2$ (250 mg, 0.357 mmol) were added in sequence, and the mixture was refluxed for 20 h. After cooling, the solvents were evaporated, the residue was dissolved in hexane and passed through SiO_2 pad (5 cm), the SiO_2 was washed with hexane and then with hexane/CH_2Cl_2 = 5:1 for several times. The eluate was evaporated, and the title product was obtained with 2.89 g (99%) yield, and was used in the next stage without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.72 – 3.69 (t, *J* = 7.7 Hz, 2H), 3.36 – 3.32 (t, *J* = 7.7 Hz, 4H), 1.82 – 1.72 (m, 2H), 1.59 (m, 4H), 1.38 – 1.18 (m, 37H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 6H), 0.37 – 0.33 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.19, 144.06, 138.34, 132.02, 126.48, 122.95, 107.29, 97.94, 39.85, 31.92, 30.87, 29.92, 29.66, 29.65, 29.59, 29.35, 29.28, 29.04, 22.69, 22.08, 14.12, 11.37, -0.20.

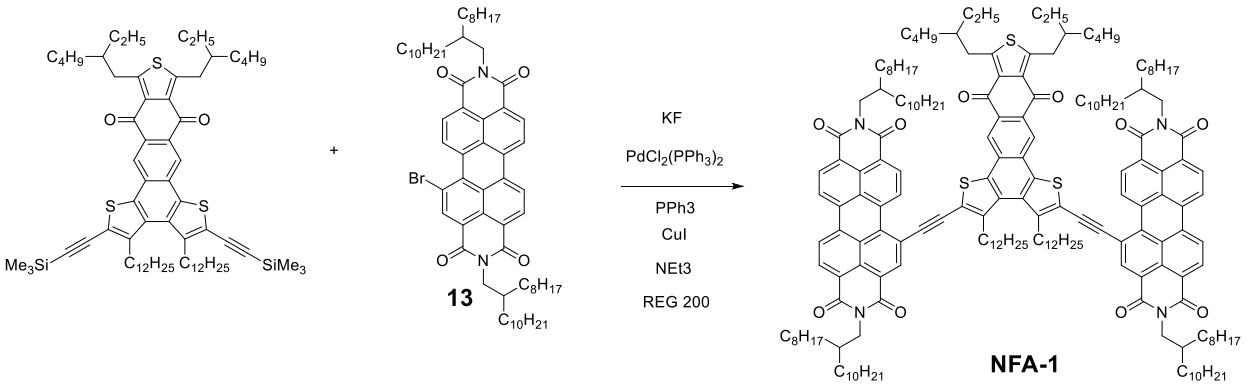
To a solution of bis-TMS intermediate (3.00 g, 3.61 mmol) in dry THF (220 ml), was added a solution of KF (2.1 g, 36.13 mmol) in MeOH (20 ml), and the solution was stirred for 3 h ad RT. After the reaction was completed, the solution was evaporated to dryness, the residue was dissolved in CH_2Cl_2 (150 ml), washed with water (150 ml), dried with $MgSO_4$ and evaporated. The solid residue was suspended in cold hexane, filtrated and dried. The yield of title compound is of 2.00 g (80.6%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (s, 2H), 3.69 (t, *J* = 7.39 Hz, 2H), 3.34 (t, *J* = 7.46 Hz, 4H), 1.79 – 1.69 (m, 2H), 1.52 (m, 4H), 1.32 – 1.16 (m, 38H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.25, 144.68, 138.38, 132.26, 125.46, 123.29, 88.73, 77.44, 40.03, 32.05, 31.04, 30.00, 29.77, 29.76, 29.70, 29.60, 29.48, 29.41, 29.11, 22.83, 22.19, 14.26, 11.50. Anal. Calcd for $C_{43}H_{59}NO_2S_2$: C, 75.28; H, 8.67; N, 2.04; S, 9.35. Found: C, 75.30; H, 8.66; N, 2.16; S, 9.24. HRMS: $C_{43}H_{59}NO_2S_2$, *m/z*: 686.4060 (M^+). Calcd. 686.4060.

5,5'-((3,4-Didodecyl-9,11-bis(2-ethylhexyl)-8,12-dioxo-8,12-dihydroanthra[1,2-*b*:4,3-*b*':6,7-*c*'']-trithiophene-2,5-diyl)bis(ethyne-2,1-diyl))bis(*N*,*N*'-di(2-octyldodecyl)perylene-3,4,9,10-tetracarboxybisimide) (NFA-1).



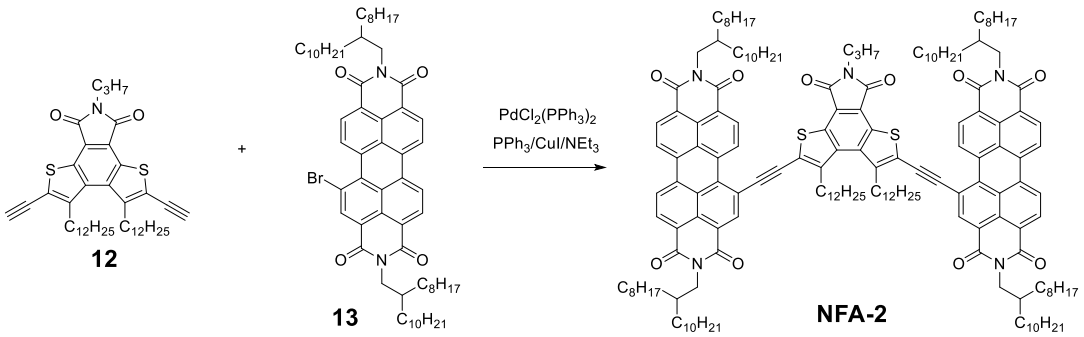
A solution of 3,4-didodecyl-9,11-bis(2-ethylhexyl)-2,5-diethynylanthra[1,2-*b*:4,3-*b*':6,7-*c*'']-trithiophene-8,12-dione (**11**) (1 g, 1.01 mmol) and 1-bromo-*N*,*N*'-bis(2-octyldodecyl)perylene-3,4,9,10-tetracarboxybisimide (**13**) (2.61 g, 2.54 mmol) in a mixture of dry THF (100 ml) and NEt_3 (40 ml) was purged with argon for 20 min, then CuI (55 mg, 0.284 mmol), PPh_3 (75 mg, 0.284 mmol) and $PdCl_2(PPh_3)_2$ (100 mg, 0.142 mmol) were added in sequence, and the solution was refluxed for 20 h. After cooling the reaction mixture was evaporated, and the residue was purified by column chromatography on SiO_2 using CH_2Cl_2/EtOAc = 100:5 as an eluent. The yield is 1.85 g (63.1 %) . ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.10 (br.s, 1H), 8.18 – 9.08 (br.m, 7H), 4.18 (s, 2H), 4.08 (s, 2H), 3.47 (br.s, 4H), 0.47 – 2.22 (m, 121 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.61, 163.30, 162.96, 162.26, 154.74, 140.49, 137.76, 134.06, 133.59, 133.37, 131.53, 130.66, 128.80, 128.11, 126.79, 126.12, 123.88, 123.68, 123.44, 122.90, 122.79, 121.96, 120.87, 119.20, 101.66, 96.40, 44.93, 40.96, 36.84, 36.71, 34.26, 32.71, 32.06, 31.94, 31.88, 30.31, 30.28, 30.12, 30.05, 29.98, 29.87, 29.81, 29.78, 29.64, 29.52, 28.80, 26.76, 26.71, 26.07, 23.29, 22.81, 22.77, 14.32, 14.23, 14.14, 10.94. MALDI-TOF: $C_{192}H_{265}N_4O_{10}S_3$, *m/z*: 2885.57 $[M+H]^+$. Calcd. 2884.96; $C_{192}H_{264}NaN_4O_{10}S_3$, *m/z*: 2907.66 $[M+Na]^+$. Calcd. 2906.94. Anal. Calcd for $C_{192}H_{264}N_4O_{10}S_3$: C, 79.95; H, 9.23; N, 1.94; S, 3.33. Found: C, 79.85; H, 9.53; N, 1.91; S, 3.71.

Alternative one-pot method for preparation of **NFA-1**.



To a solution of bis-TMS intermediate (1.13 g, 1.00 mmol) in a solvent mixture of THF (30 ml) / NEt_3 (10 ml) 1-bromo-*N*,*N'*-bis(2-octyldodecyl)perylene-3,4,9,10-tetracarboxybisimide **13**, 2.62 g, 2.54 mmol) was added, then the solution was purged with argon for 20 min. Then CuI (11.4 mg, 0.06 mmol), PPh_3 (15.7 mg, 0.06 mmol), $(PPh_3)_2PdCl_2$ (21 mg, 0.03 mmol), 1.13 ml PEG 200MW and H_2O (0.51 ml) were added in sequence. The purging with argon was continued for additional 15 min, then KF (232 mg, 4 ммоль) was added, and the mixture was refluxed for 20 h. The conversion was controlled by TLC ($CHCl_3$). After the reaction was completed, the mixture was evaporated and the residue was purified by column chromatography on SiO_2 using CH_2Cl_2/EtOAc = 100:5 as an eluent. The yield is 1.54 g (53.4 %). The spectroscopic data were identical with the sample prepared by conventional two-stage method (see above).

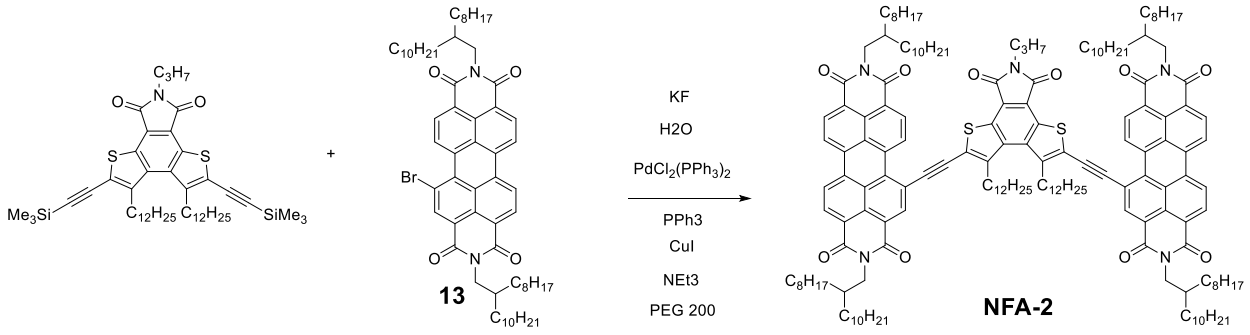
5,5'-((3,4-Didodecyl-7,9-dioxo-8-propyl-8,9-dihydro-7*H*-dithieno[2,3-*e*:3',2'-*g*]isoindole-2,5-diyl)bis(ethyne-2,1-diyl))bis(*N*,*N*'-di(2-octyldodecyl)perylene-3,4,9,10-tetracarboxybisimide) (NFA-2).



A solution of 3,4-didodecyl-2,5-diethynyl-8-propyl-7*H*-dithieno[2,3-*e*:3',2'-*g*]isoindole-7,9(8*H*)-dione (**12**, 0.68 g, 0.991 mmol) and 1-bromo-*N*,*N'*-bis(2-octyldodecyl)perylene-3,4,9,10-tetracarboxybisimide (**13**, 2.55 g, 2.48 mmol) in a mixture of dry THF (100 ml) and NEt_3 (40 ml) was purged with argon for 20 min, then CuI (55 mg, 0.284 mmol), PPh_3 (75 mg, 0.284 mmol) and $PdCl_2(PPh_3)_2$ (100 mg, 0.142 mmol) were added in sequence, and the solution was refluxed for 20 h. After cooling, the reaction mixture was evaporated, and the residue was purified by column chromatography on SiO_2 using CH_2Cl_2/EtOAc = 100:5 as an eluent. The yield is 1.94 g

(75.8 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.03 (d, *J* = 7.6 Hz, 1H), 8.68 (d, *J* = 7.6 Hz, 1H), 8.63 (s, 1H), 8.57 (d, *J* = 7.7 Hz, 1H), 8.49 (d, *J* = 7.5 Hz, 1H), 8.39 – 8.33 (m, 2H), 4.16 (d, *J* = 5.5 Hz, 2H), 4.07 (d, *J* = 4.9 Hz, 2H), 3.93 (s, 1H), 3.51 (s, 2H), 2.07 – 1.92 (m, 5H), 1.62 (s, 2H), 1.50 – 1.03 (m, 96H), 0.85 (m, 12H), 0.75 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.58, 163.55, 163.13, 162.85, 162.31, 145.50, 138.14, 137.63, 134.07, 133.55, 133.47, 133.35, 133.18, 131.18, 130.70, 128.84, 128.24, 126.95, 126.86, 126.15, 125.82, 123.89, 123.63, 123.52, 123.35, 122.90, 122.78, 122.18, 118.82, 103.33, 94.20, 44.90, 40.46, 36.82, 36.72, 32.07, 31.93, 31.54, 30.30, 30.28, 30.06, 29.99, 29.95, 29.88, 29.83, 29.78, 29.63, 29.53, 26.74, 26.71, 22.83, 22.82, 22.79, 22.24, 14.25, 14.24, 14.17, 11.70. MALDI-TOF: $C_{171}H_{236}N_5O_{10}S_3$, *m/z*: 2584.75 $[M+H]^+$. Calcd. 2584.76; $C_{171}H_{235}NaN_5O_{10}S_3$, *m/z*: 2607.77 $[M+Na]^+$. Calcd. 2607.74; $C_{171}H_{235}KN_5O_{10}S_3$, *m/z*: 2624.79 $[M+K]^+$. Calcd. 2622.72. Anal. Calcd for $C_{171}H_{235}N_5O_{10}S_2$: C, 79.46; H, 9.16; N, 2.71; S, 2.48. Found: C, 79.56; H, 9.29; N, 2.66; S, 2.68.

Alternative one-pot method for preparation of **NFA-2**.



To a solution of bis-TMS intermediate (0.81 g, 0.975 mmol) in a solvent mixture of THF (30 ml) / NEt_3 (10 ml) 1-bromo-*N*,*N*'-bis(2-octyldodecyl)perylene-3,4,9,10-tetracarboxybisimide (**13**, 2.55 g, 2.48 mmol) was added, then the solution was purged with argon for 20 min. Then CuI (11.2 mg, 0.058 mmol), PPh_3 (15.3 mg, 0.058 mmol), $(PPh_3)_2PdCl_2$ (20 mg, 0.029 mmol), 0.85 ml PEG 200MW and 0.4 ml H_2O were added in sequence. The purging with argon was continued for additional 15 min, then KF (226 mg, 3.9 mmol) was added and the reaction mixture was refluxed for 20 h. The conversion was controlled by TLC ($CHCl_3$). After the reaction was completed, the mixture was evaporated and the residue was purified by column chromatography on SiO_2 using CH_2Cl_2/EtOAc = 100:5 as an eluent. The yield is 1.48 g (58.7 %). The spectroscopic data were identical with the sample prepared by conventional two-stage method (see above).

Mass-spectra characterization

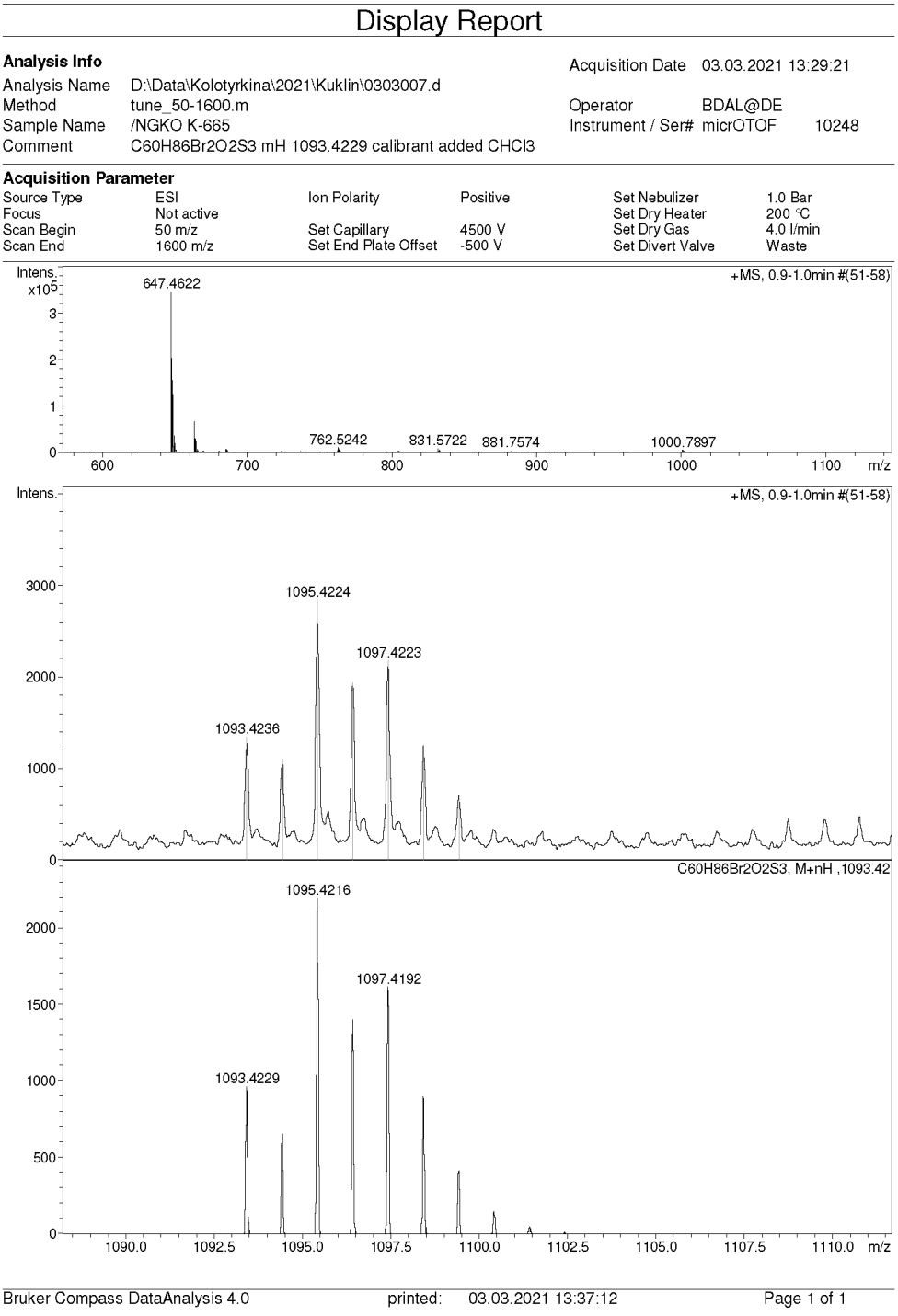


Figure S1 – Experimental and simulated high resolution mass spectrum of compound **M1**.

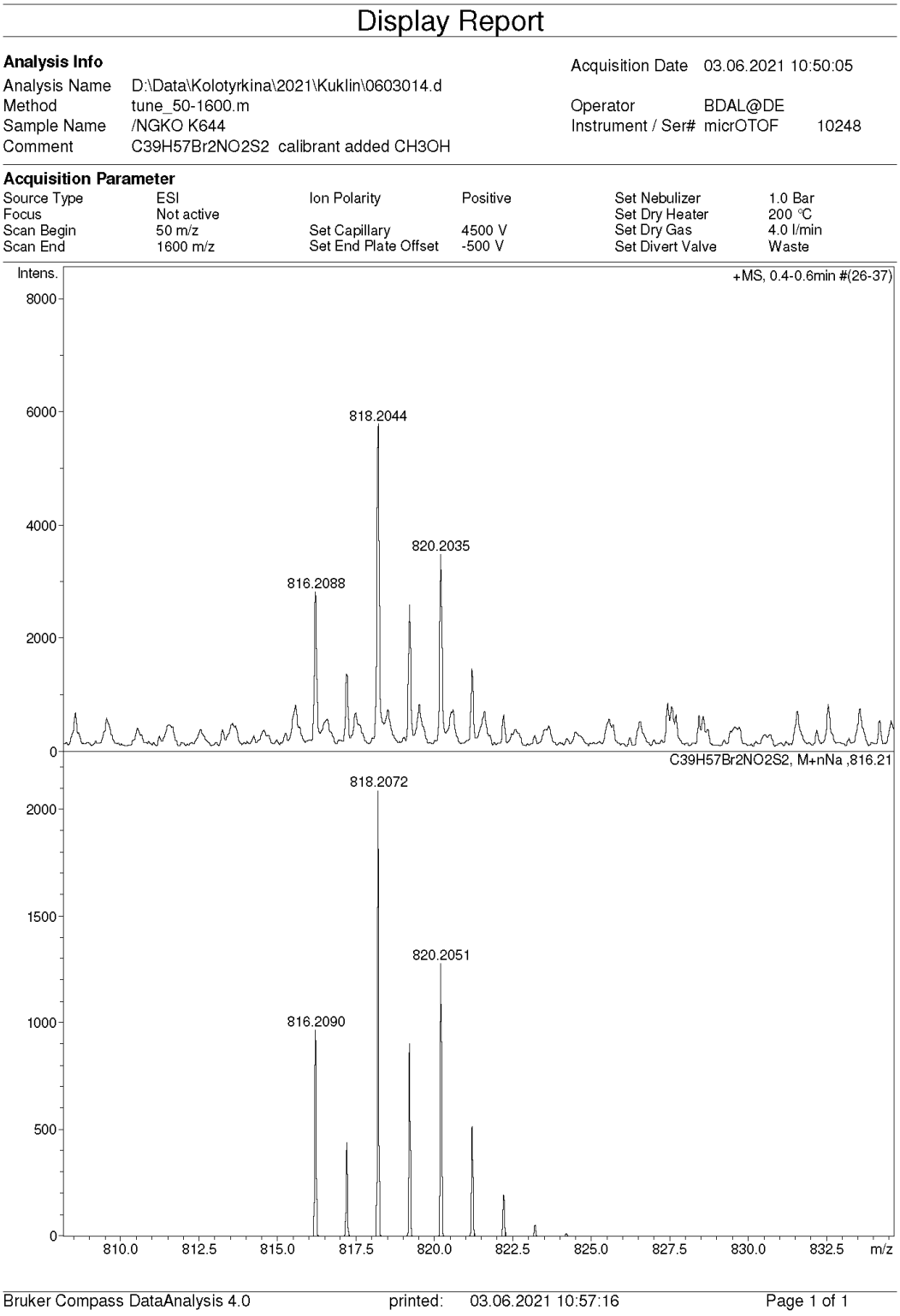


Figure S2 – Experimental and simulated high resolution mass spectrum of compound **M2.**

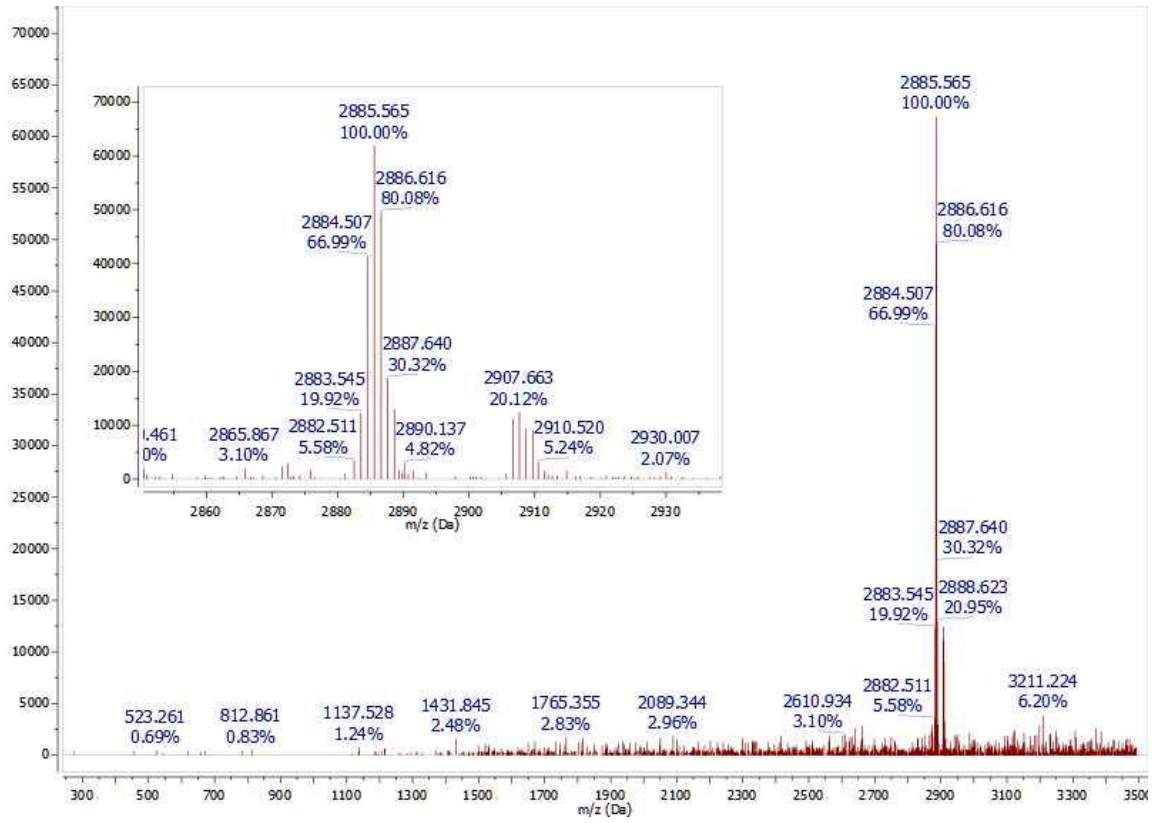


Figure S3 – MALDI mass spectrum of compound **NFA-1**.

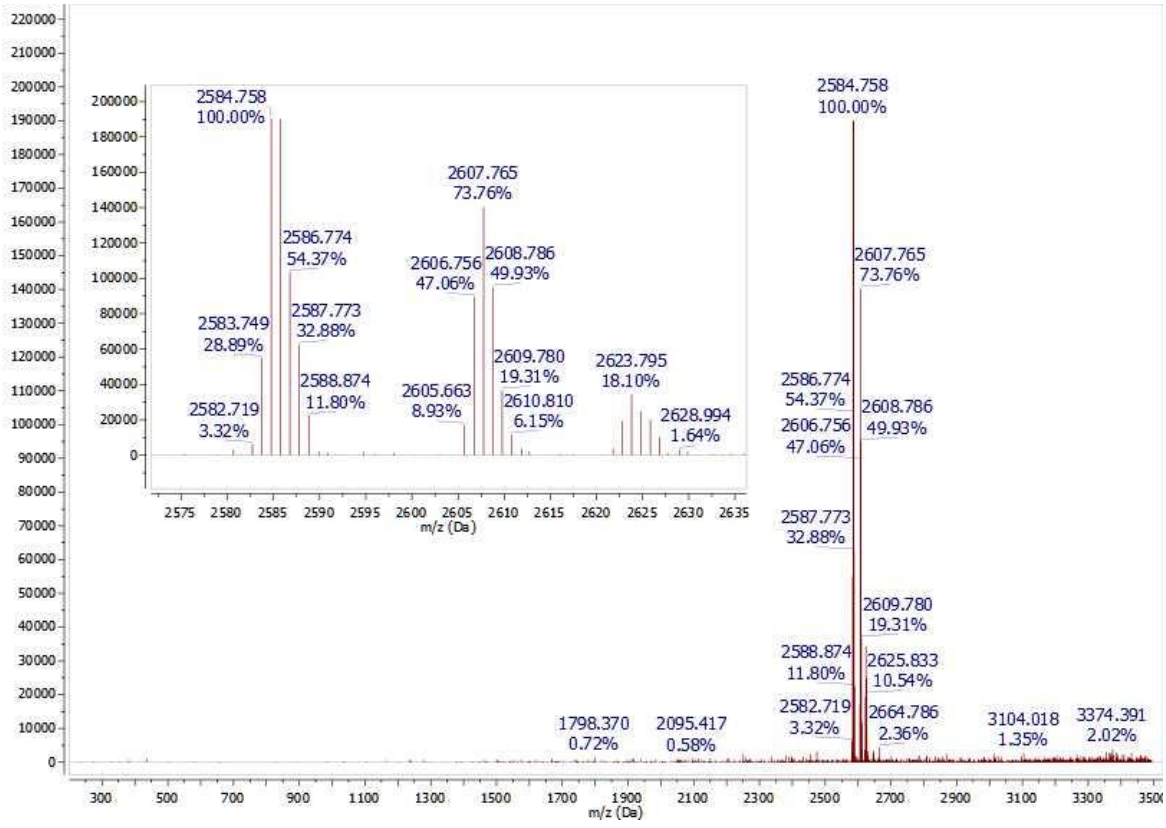


Figure S4 – MALDI mass spectrum of compound **NFA-2**.

Optical and electronic properties of acceptor molecules NFA-1, NFA-2

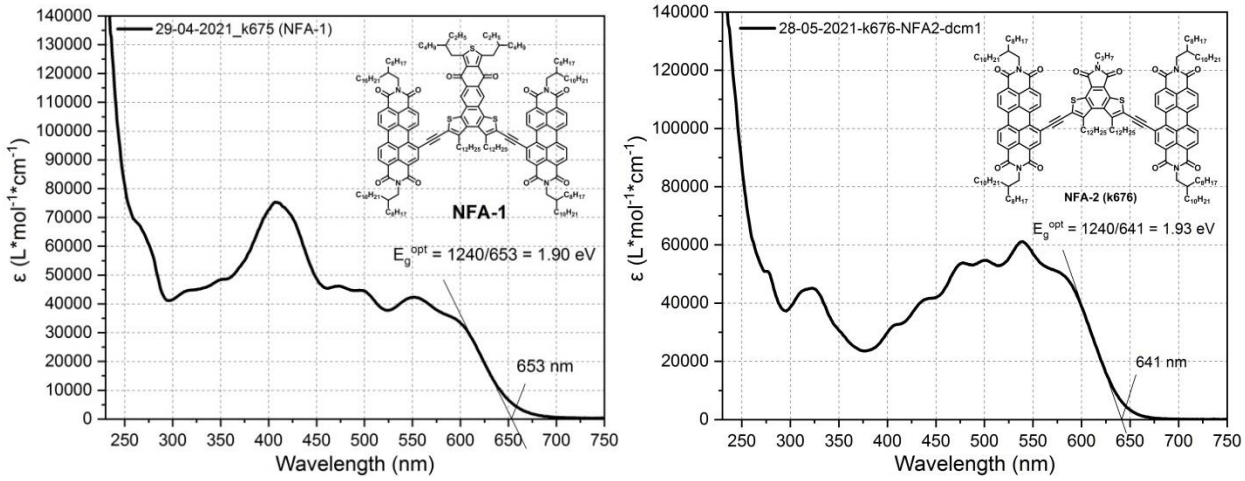
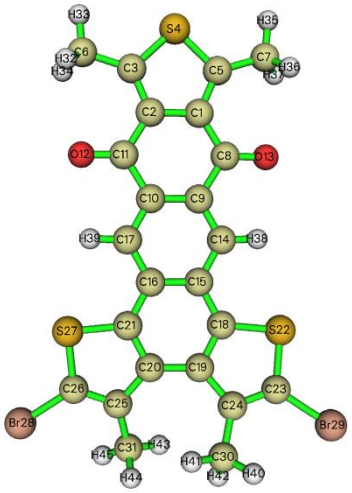
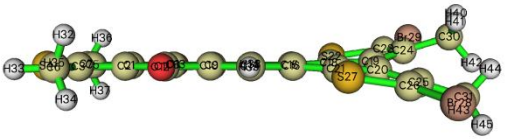


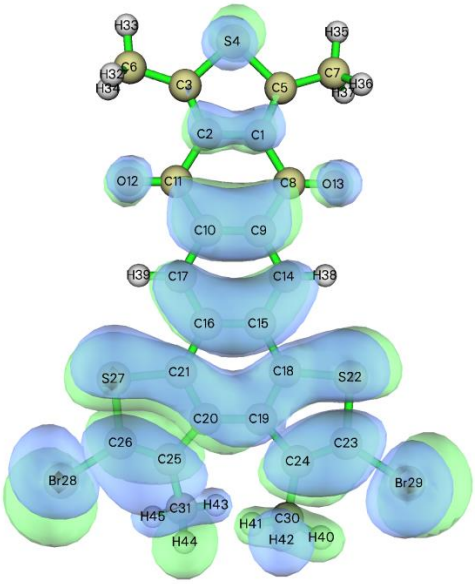
Figure S5 – UV spectra of novel non-fullerene acceptors **NFA-1** and **NFA-2** in DCM.

Theoretical calculations

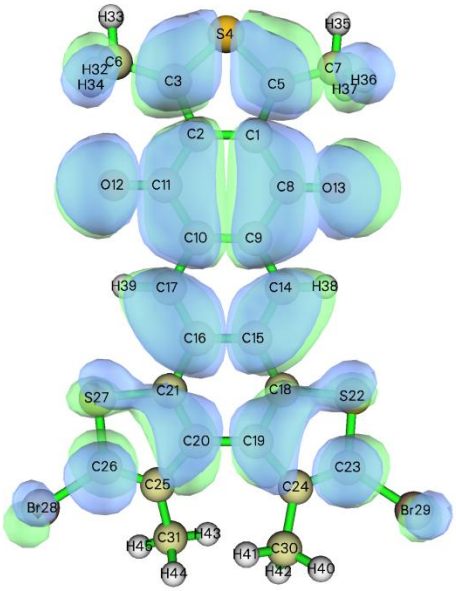
Theoretical calculations for M1







HOMO



LUMO

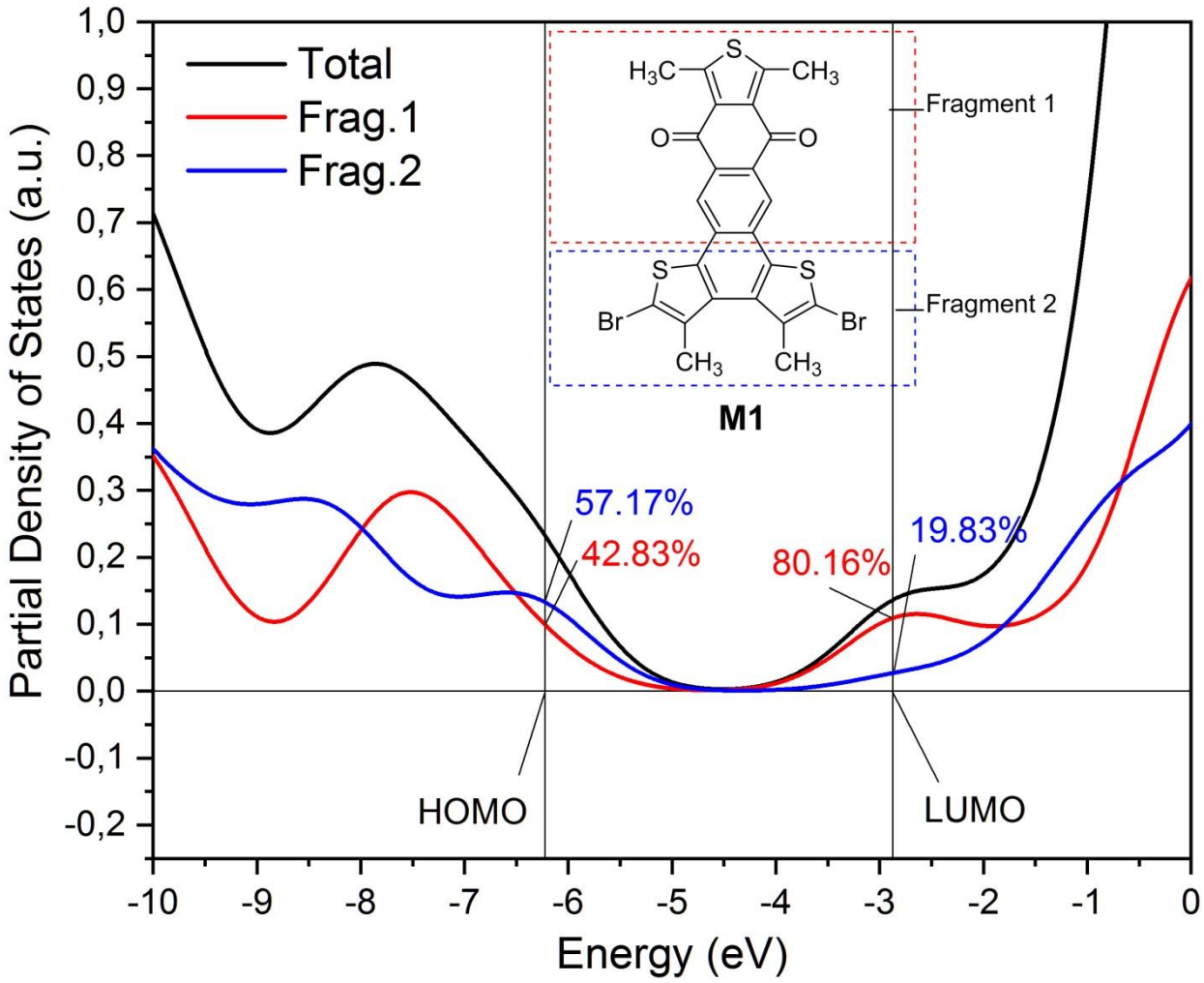


Figure S6 – Front and side views, HOMO/LUMO distributions, and PDOS curves for **M1** molecule.

Atomic coordinates for optimized structure M1:

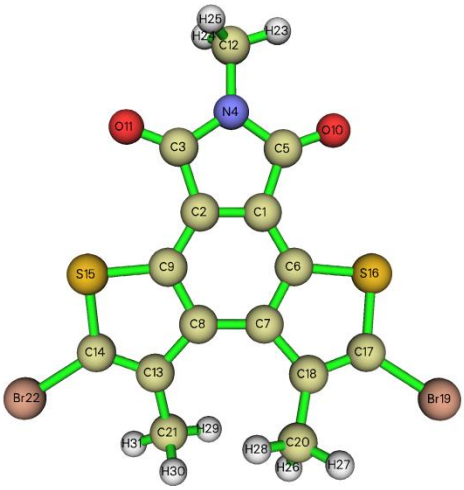
Standard orientation:

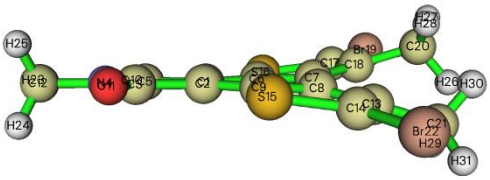
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.059974	0.712070	-0.121476
2	6	0	-5.059973	-0.712073	0.121479
3	6	0	-6.325276	-1.251701	0.212637
4	16	0	-7.511894	-0.000003	0.000002
5	6	0	-6.325277	1.251697	-0.212633
6	6	0	-6.755962	-2.663918	0.453469
7	6	0	-6.755965	2.663913	-0.453465
8	6	0	-3.815153	1.479082	-0.254059
9	6	0	-2.545901	0.701570	-0.119648
10	6	0	-2.545900	-0.701571	0.119646
11	6	0	-3.815151	-1.479084	0.254061
12	8	0	-3.799293	-2.690192	0.463858
13	8	0	-3.799296	2.690190	-0.463858

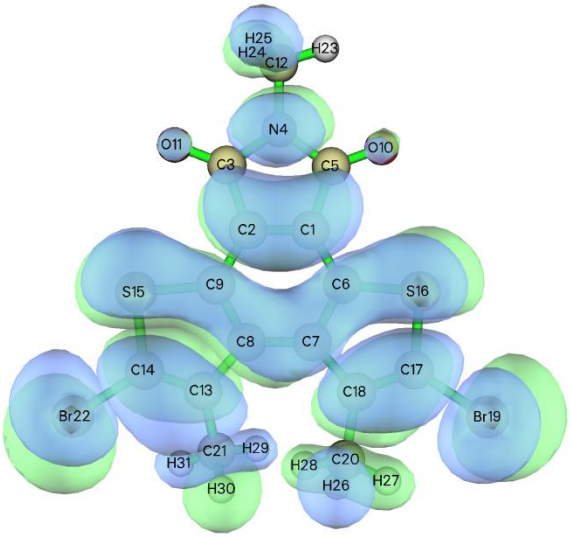
14	6	0	-1.342302	1.373243	-0.228133
15	6	0	-0.108524	0.704740	-0.111504
16	6	0	-0.108523	-0.704740	0.111497
17	6	0	-1.342300	-1.373243	0.228128
18	6	0	1.154933	1.368792	-0.146917
19	6	0	2.394173	0.726821	0.001023
20	6	0	2.394173	-0.726819	-0.001040
21	6	0	1.154935	-1.368791	0.146906
22	16	0	1.318815	3.105935	-0.233644
23	6	0	3.026215	2.956608	0.043573
24	6	0	3.480684	1.675615	0.194551
25	6	0	3.480685	-1.675613	-0.194563
26	6	0	3.026219	-2.956606	-0.043574
27	16	0	1.318817	-3.105934	0.233630
28	35	0	4.050771	-4.541608	-0.194925
29	35	0	4.050763	4.541611	0.194939
30	6	0	4.872566	1.381126	0.683864
31	6	0	4.872569	-1.381125	-0.683873
32	1	0	-6.381012	-3.020726	1.415830
33	1	0	-7.843244	-2.753234	0.447607
34	1	0	-6.344906	-3.326137	-0.311924
35	1	0	-7.843247	2.753228	-0.447602
36	1	0	-6.344909	3.326132	0.311928
37	1	0	-6.381016	3.020721	-1.415826
38	1	0	-1.373452	2.442428	-0.401543
39	1	0	-1.373449	-2.442429	0.401538
40	1	0	5.214739	2.195435	1.323842
41	1	0	4.889509	0.466936	1.275083
42	1	0	5.597069	1.279945	-0.126686
43	1	0	4.889512	-0.466942	-1.275102
44	1	0	5.597068	-1.279934	0.126679
45	1	0	5.214747	-2.195440	-1.323841

E(RB3LYP) = -7416.67411141 a.u; nuclear repulsion energy 4408.7140214870 Hartrees

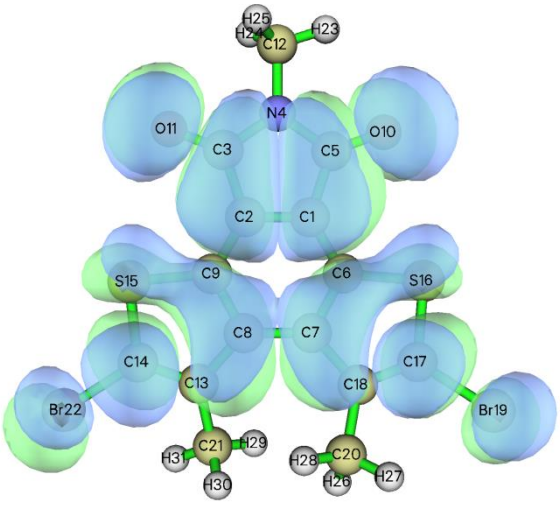
Theoretical calculations for M2







HOMO



LUMO

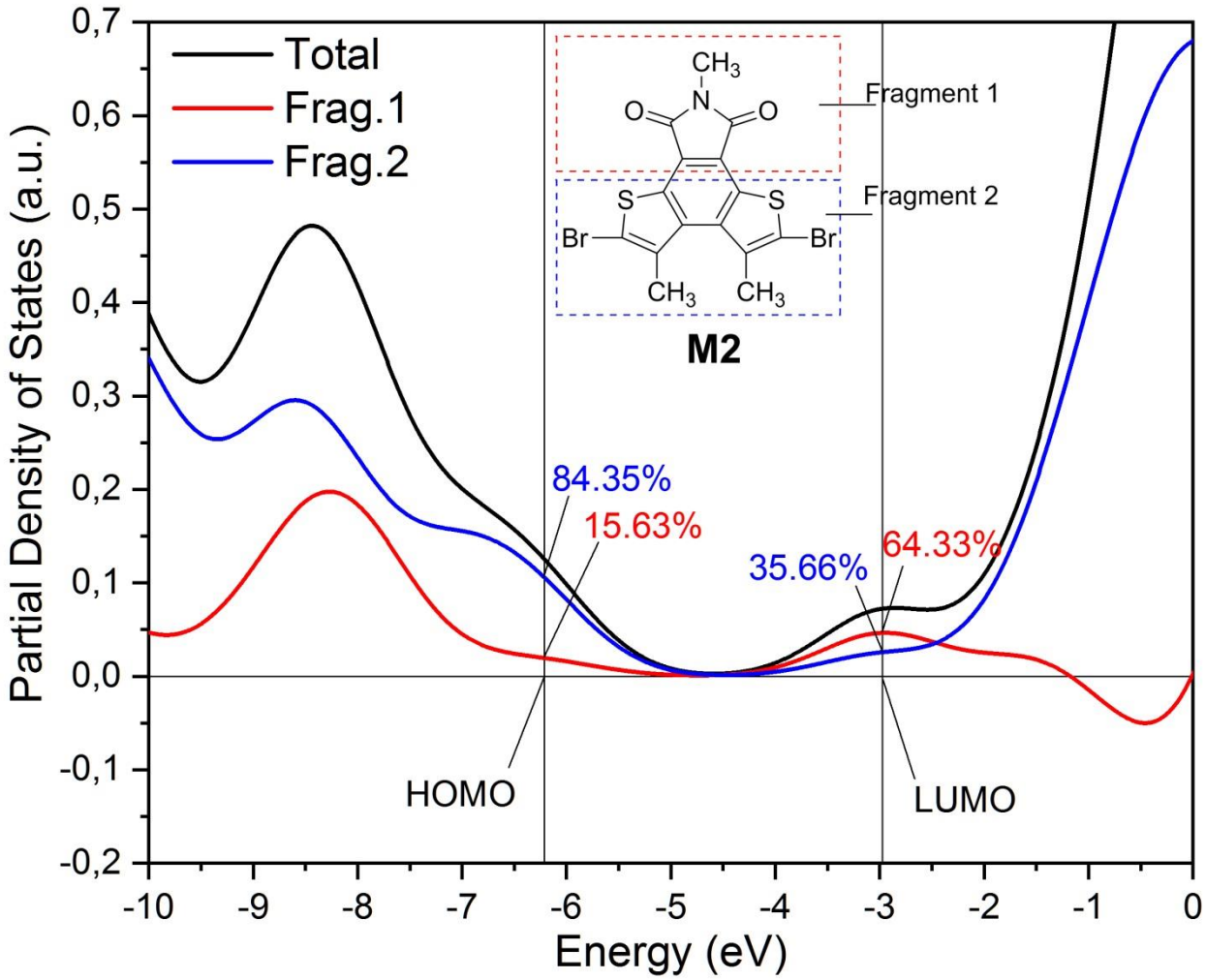


Figure S7 – Front and side views, HOMO/LUMO distributions, and PDOS curves for **M2** molecule.

Atomic coordinates for optimized structure M2:

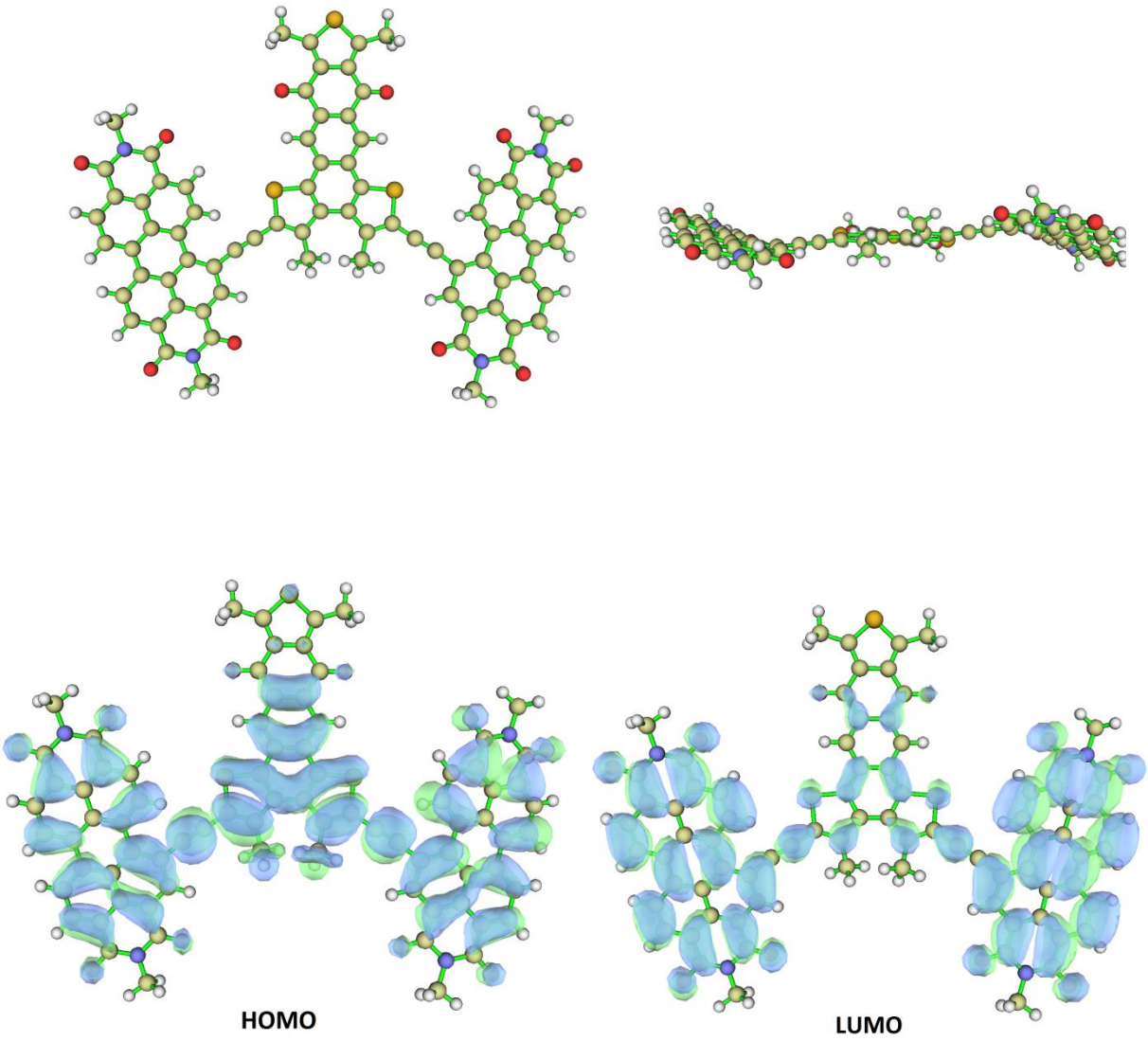
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.682589	2.002270	-0.100236
2	6	0	-0.685009	2.001431	0.100073
3	6	0	-1.144073	3.412192	0.171143
4	7	0	-0.002419	4.199700	-0.000476
5	6	0	1.142787	3.412805	-0.171706
6	6	0	1.383459	0.803395	-0.150222
7	6	0	0.720580	-0.451698	-0.009085
8	6	0	-0.719870	-0.452594	0.009125
9	6	0	-1.384193	0.801733	0.150208
10	8	0	2.269889	3.830531	-0.341598
11	8	0	-2.269500	3.835893	0.341287
12	6	0	-0.013155	5.655209	0.000751
13	6	0	-1.683141	-1.535265	-0.146832
14	6	0	-2.957606	-1.071326	0.023106

15	16	0	-3.115941	0.645709	0.280854
16	16	0	3.115338	0.649355	-0.280801
17	6	0	2.959000	-1.067899	-0.022959
18	6	0	1.685125	-1.533263	0.147139
19	35	0	4.548896	-2.087920	0.085561
20	6	0	1.412580	-2.935181	0.619820
21	6	0	-1.409006	-2.936798	-0.619758
22	35	0	-4.546259	-2.093237	-0.085483
23	1	0	1.008532	5.995708	-0.155562
24	1	0	-0.649216	6.030255	-0.802316
25	1	0	-0.380518	6.031054	0.956769
26	1	0	1.276386	-3.642420	-0.200508
27	1	0	2.253501	-3.289656	1.216740
28	1	0	0.524927	-2.964115	1.249633
29	1	0	-0.521313	-2.964568	-1.249567
30	1	0	-1.272017	-3.644054	0.200421
31	1	0	-2.249509	-3.292107	-1.216769

E(RB3LYP) = -6727.17740423 a.u.; nuclear repulsion energy 2944.5970472088 Hartrees.

Theoretical calculations for NFA-1



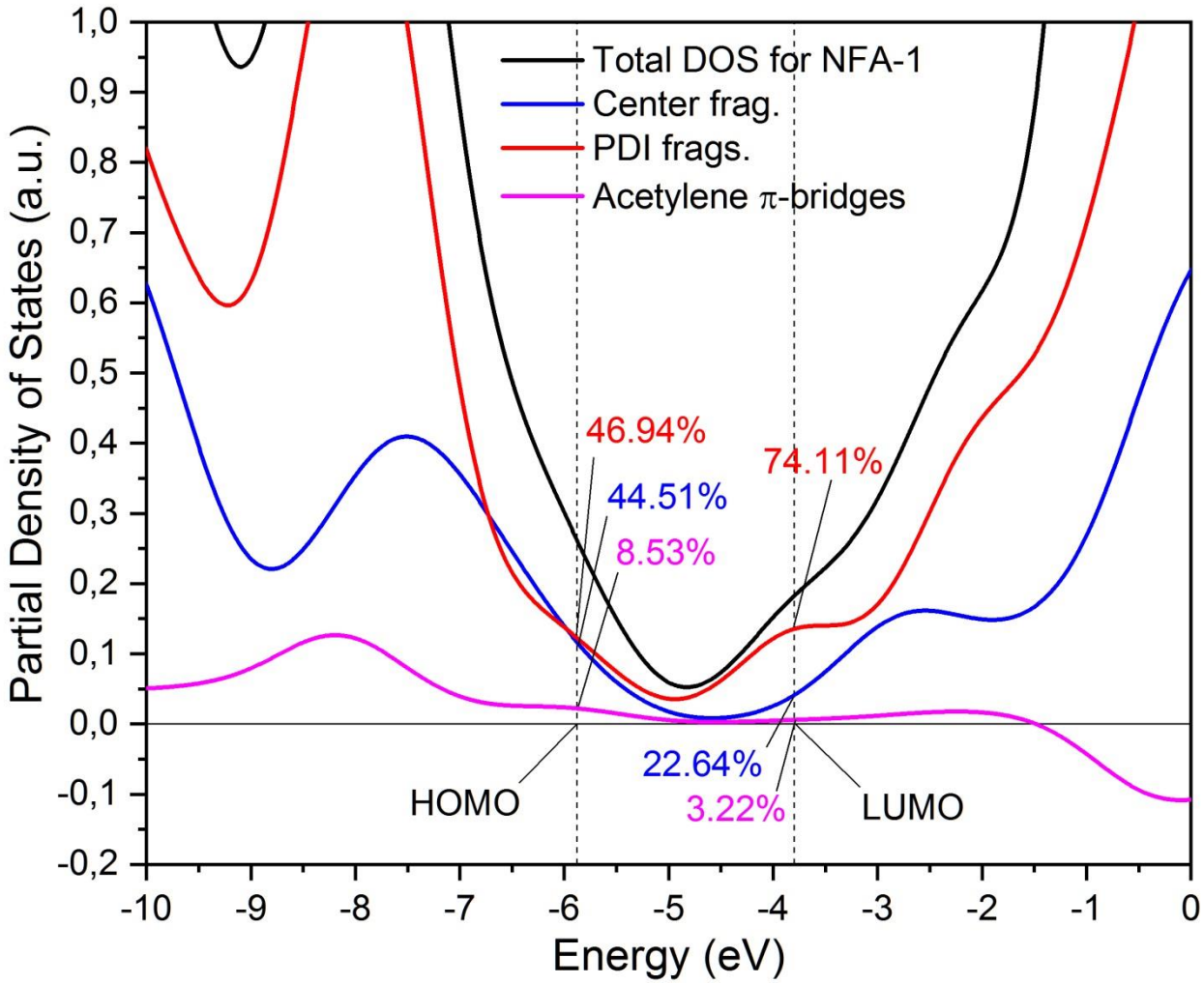


Figure S8 – Front and side views, HOMO/LUMO distributions, and PDOS curves for **NFA-1** molecule.

Atomic coordinates for optimized structure NFA-1:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.715152	7.730107	-0.102302
2	6	0	-0.715097	7.730112	0.102229
3	6	0	-1.256948	8.995545	0.178883
4	16	0	0.000054	10.182036	0.000095
5	6	0	1.257020	8.995536	-0.178892
6	6	0	1.485383	6.485959	-0.214550
7	6	0	0.704020	5.215786	-0.100813
8	6	0	-0.703994	5.215791	0.100667
9	6	0	-1.485353	6.485969	0.214368
10	6	0	1.378943	4.012043	-0.191091
11	6	0	0.707250	2.779027	-0.092606
12	6	0	-0.707233	2.779032	0.092514
13	6	0	-1.378922	4.012053	0.190970

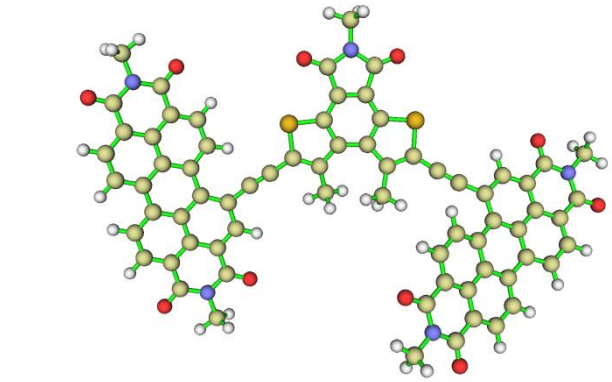
14	6	0	1.376166	1.516034	-0.111833
15	6	0	0.728645	0.273636	0.018293
16	6	0	-0.728640	0.273639	-0.018336
17	6	0	-1.376156	1.516043	0.111767
18	6	0	-2.675149	9.425612	0.381881
19	6	0	2.675219	9.425595	-0.381921
20	8	0	2.701171	6.468017	-0.392340
21	8	0	-2.701125	6.468036	0.392267
22	6	0	-1.669326	-0.798104	-0.235546
23	6	0	-2.980975	-0.362453	-0.132659
24	16	0	-3.108514	1.363449	0.149271
25	16	0	3.108522	1.363429	-0.149352
26	6	0	2.980977	-0.362453	0.132696
27	6	0	1.669324	-0.798100	0.235568
28	6	0	1.381317	-2.201360	0.692118
29	6	0	-1.381331	-2.201393	-0.692016
30	6	0	-4.144191	-1.127052	-0.279284
31	6	0	4.144188	-1.127042	0.279412
32	6	0	5.180814	-1.749356	0.401879
33	6	0	-5.180823	-1.749366	-0.401705
34	6	0	6.289274	-2.625931	0.506393
35	6	0	-6.289285	-2.625931	-0.506286
36	6	0	-7.652910	-2.257104	-0.383854
37	6	0	-8.628853	-3.304332	-0.298799
38	6	0	-8.245090	-4.663463	-0.506349
39	6	0	-6.884508	-4.981027	-0.731192
40	6	0	-5.939497	-3.987943	-0.697690
41	6	0	-9.996314	-3.027426	0.015824
42	6	0	-10.914459	-4.078437	0.030093
43	6	0	-10.531532	-5.394096	-0.222029
44	6	0	-9.204455	-5.697210	-0.478499
45	6	0	-8.814467	-7.105182	-0.717777
46	7	0	-7.455730	-7.357328	-0.952276
47	6	0	-6.459712	-6.380448	-0.962834
48	6	0	-8.125502	-0.867506	-0.333068
49	6	0	-9.467585	-0.600715	0.088681
50	6	0	-10.399076	-1.652953	0.321587
51	6	0	-7.330568	0.217535	-0.705861
52	6	0	-7.773473	1.537147	-0.584219
53	6	0	-9.028535	1.817272	-0.077338
54	6	0	-9.896540	0.750840	0.254053
55	6	0	-11.196748	1.028004	0.734386
56	6	0	-12.060286	-0.015064	1.022051
57	6	0	-11.668811	-1.336815	0.806842
58	6	0	-9.455917	3.224489	0.083859
59	7	0	-10.744507	3.438355	0.589808
60	6	0	-11.643724	2.423268	0.928168
61	6	0	-11.210267	4.819169	0.783750
62	8	0	-8.728639	4.164718	-0.204899
63	8	0	-12.751323	2.708916	1.363865
64	8	0	-9.630098	-8.015880	-0.714882
65	8	0	-5.293826	-6.693302	-1.159202
66	6	0	-7.021335	-8.740852	-1.195193
67	6	0	5.939479	-3.987942	0.697784
68	6	0	6.884479	-4.981039	0.731232
69	6	0	8.245056	-4.663486	0.506344
70	6	0	8.628827	-3.304356	0.298804
71	6	0	7.652899	-2.257117	0.383910

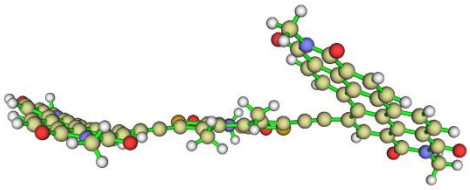
72	6	0	9.204407	-5.697244	0.478440
73	6	0	10.531479	-5.394142	0.221930
74	6	0	10.914412	-4.078482	-0.030182
75	6	0	9.996281	-3.027460	-0.015860
76	6	0	10.399050	-1.652987	-0.321611
77	6	0	9.467578	-0.600741	-0.088661
78	6	0	8.125504	-0.867524	0.333127
79	6	0	9.896543	0.750811	-0.254027
80	6	0	9.028560	1.817248	0.077405
81	6	0	7.773511	1.537131	0.584319
82	6	0	7.330594	0.217522	0.705957
83	6	0	11.668774	-1.336855	-0.806897
84	6	0	12.060258	-0.015106	-1.022099
85	6	0	11.196740	1.027968	-0.734395
86	6	0	11.643725	2.423229	-0.928173
87	7	0	10.744530	3.438322	-0.589773
88	6	0	9.455956	3.224463	-0.083780
89	6	0	6.459674	-6.380458	0.962865
90	7	0	7.455680	-7.357350	0.952254
91	6	0	8.814410	-7.105217	0.717702
92	6	0	11.210297	4.819133	-0.783718
93	8	0	12.751313	2.708870	-1.363901
94	8	0	8.728692	4.164696	0.205000
95	6	0	7.021279	-8.740871	1.195174
96	8	0	5.293793	-6.693301	1.159278
97	8	0	9.630034	-8.015921	0.714781
98	1	0	2.452232	4.043423	-0.335965
99	1	0	-2.452211	4.043440	0.335841
100	1	0	-3.056555	9.052417	1.335483
101	1	0	-2.765164	10.512745	0.371331
102	1	0	-3.316850	9.012174	-0.399522
103	1	0	2.765257	10.512725	-0.371269
104	1	0	3.316950	9.012067	0.399409
105	1	0	3.056570	9.052485	-1.335579
106	1	0	2.226985	-2.577725	1.268927
107	1	0	0.500612	-2.230419	1.333420
108	1	0	1.222254	-2.892328	-0.137778
109	1	0	-0.500645	-2.230492	-1.333344
110	1	0	-1.222240	-2.892309	0.137918
111	1	0	-2.227016	-2.577795	-1.268774
112	1	0	-4.896463	-4.248128	-0.818733
113	1	0	-11.957599	-3.884989	0.235840
114	1	0	-11.265084	-6.189614	-0.209704
115	1	0	-6.344861	0.052547	-1.107823
116	1	0	-7.126647	2.353660	-0.878360
117	1	0	-13.049700	0.206053	1.401130
118	1	0	-12.381361	-2.119172	1.026832
119	1	0	-10.409525	5.488665	0.488723
120	1	0	-12.095180	4.999688	0.173425
121	1	0	-11.466938	4.977114	1.831100
122	1	0	-7.901252	-9.374938	-1.193852
123	1	0	-6.513426	-8.801542	-2.157237
124	1	0	-6.331236	-9.054881	-0.411827
125	1	0	4.896447	-4.248118	0.818863
126	1	0	11.265021	-6.189668	0.209562
127	1	0	11.957548	-3.885043	-0.235963
128	1	0	7.126702	2.353647	0.878491
129	1	0	6.344898	0.052541	1.107946

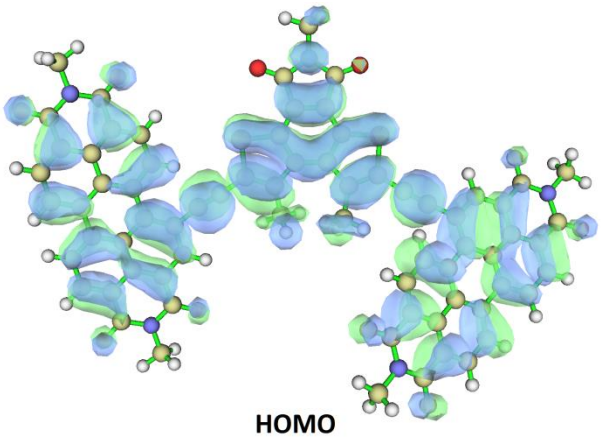
130	1	0	12.381310	-2.119217	-1.026919
131	1	0	13.049663	0.206005	-1.401204
132	1	0	10.409570	5.488634	-0.488661
133	1	0	12.095229	4.999639	-0.173418
134	1	0	11.466938	4.977083	-1.831075
135	1	0	7.901189	-9.374968	1.193790
136	1	0	6.513410	-8.801566	2.157239
137	1	0	6.331145	-9.054884	0.411834

E(RB3LYP) = -5239.76167879 A.U.; nuclear repulsion energy 15861.1218142017 Hartrees.

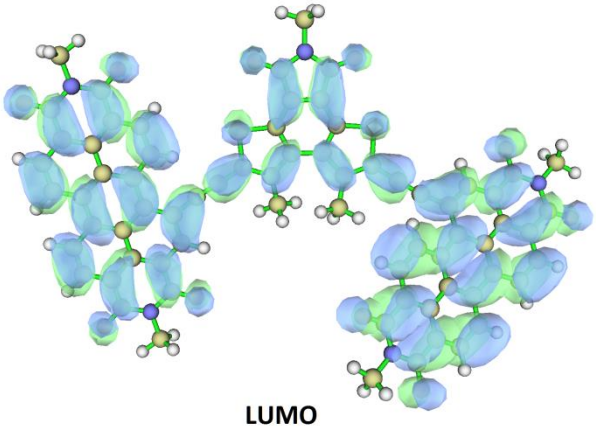
Theoretical calculations for NFA-2







HOMO



LUMO

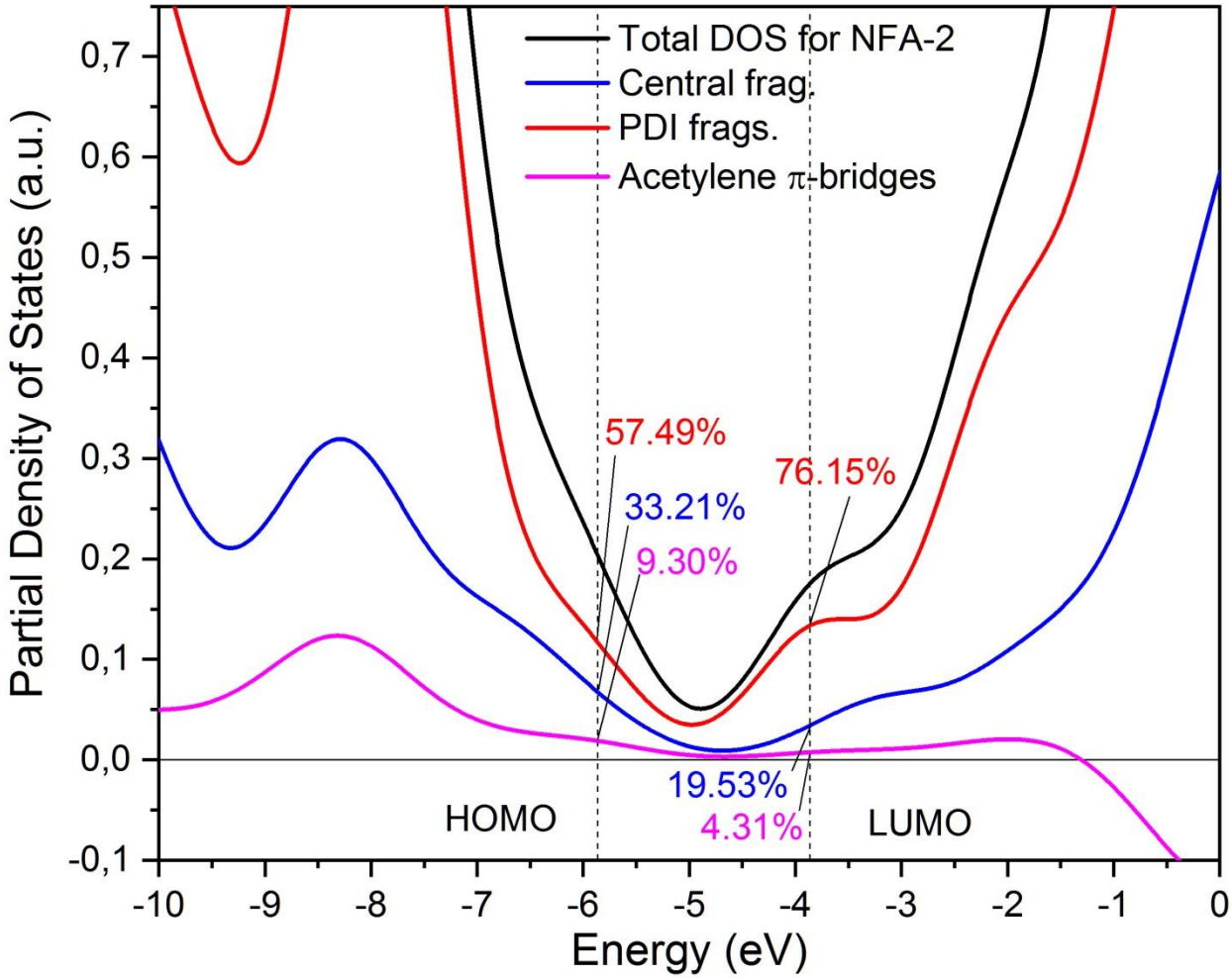


Figure S9 – Front and side views, HOMO/LUMO distributions, and PDOS curves for **NFA-2** molecule.

Atomic coordinates for optimized structure NFA-2:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.707254	-6.914269	0.706816
2	6	0	1.680931	-5.908802	0.700508
3	6	0	0.956491	-4.642151	0.418668
4	6	0	-0.387017	-4.932909	0.276461
5	6	0	-0.566158	-6.397238	0.455697
6	6	0	1.416700	-3.341790	0.246429
7	6	0	0.522944	-2.272132	-0.070648
8	6	0	-0.897714	-2.548698	-0.038819
9	6	0	-1.307626	-3.914685	0.056979
10	8	0	-1.589757	-7.048403	0.401956
11	8	0	2.868490	-6.071866	0.891064
12	6	0	0.977840	-8.325505	0.940138
13	6	0	-2.047274	-1.672190	-0.019104
14	6	0	-3.239027	-2.376602	-0.033832

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92	1	0	0.383522	0.902639	-0.358878
93	1	0	1.546585	0.640633	-1.649337
94	1	0	-0.064811	-0.060255	-1.772093
95	1	0	-1.285042	0.148562	0.832996
96	1	0	-1.941577	0.353058	-0.795363
97	1	0	-3.025592	0.128864	0.566117
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103	1	0	6.029171	-1.169209	-1.199176
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109	1	0	10.889971	-5.579820	1.156295
110	1	0	12.477073	-4.850423	0.798576
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E(RB3LYP) = -4550.26314109 A.U.; nuclear repulsion energy 13581.9958501262 Hartrees.

NMR characterization

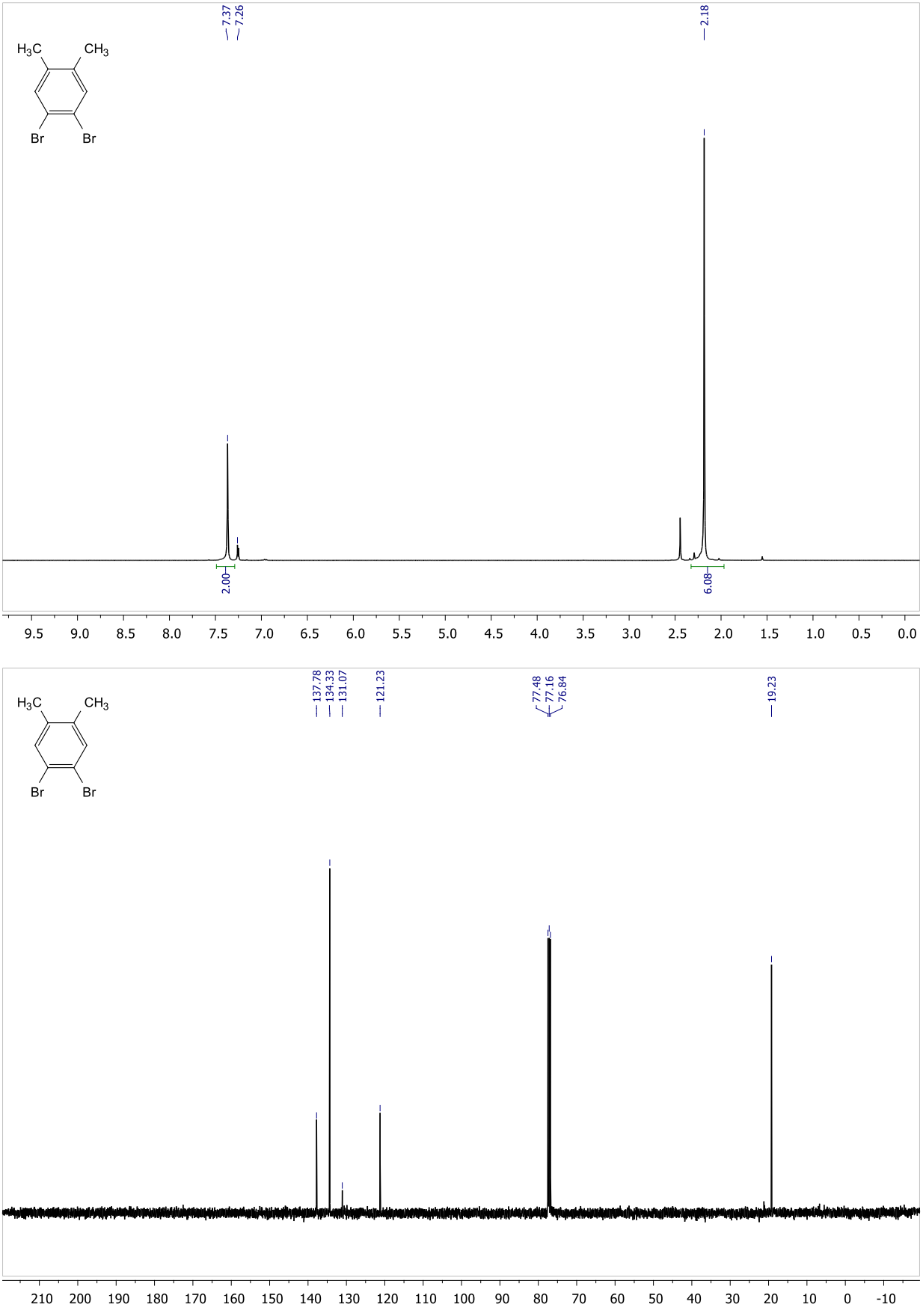

Figure S10 – ^{1}H and ^{13}C NMR spectra of 1,2-Dibromo-4,5-dimethylbenzene (**1**) in $CDCl_3$.

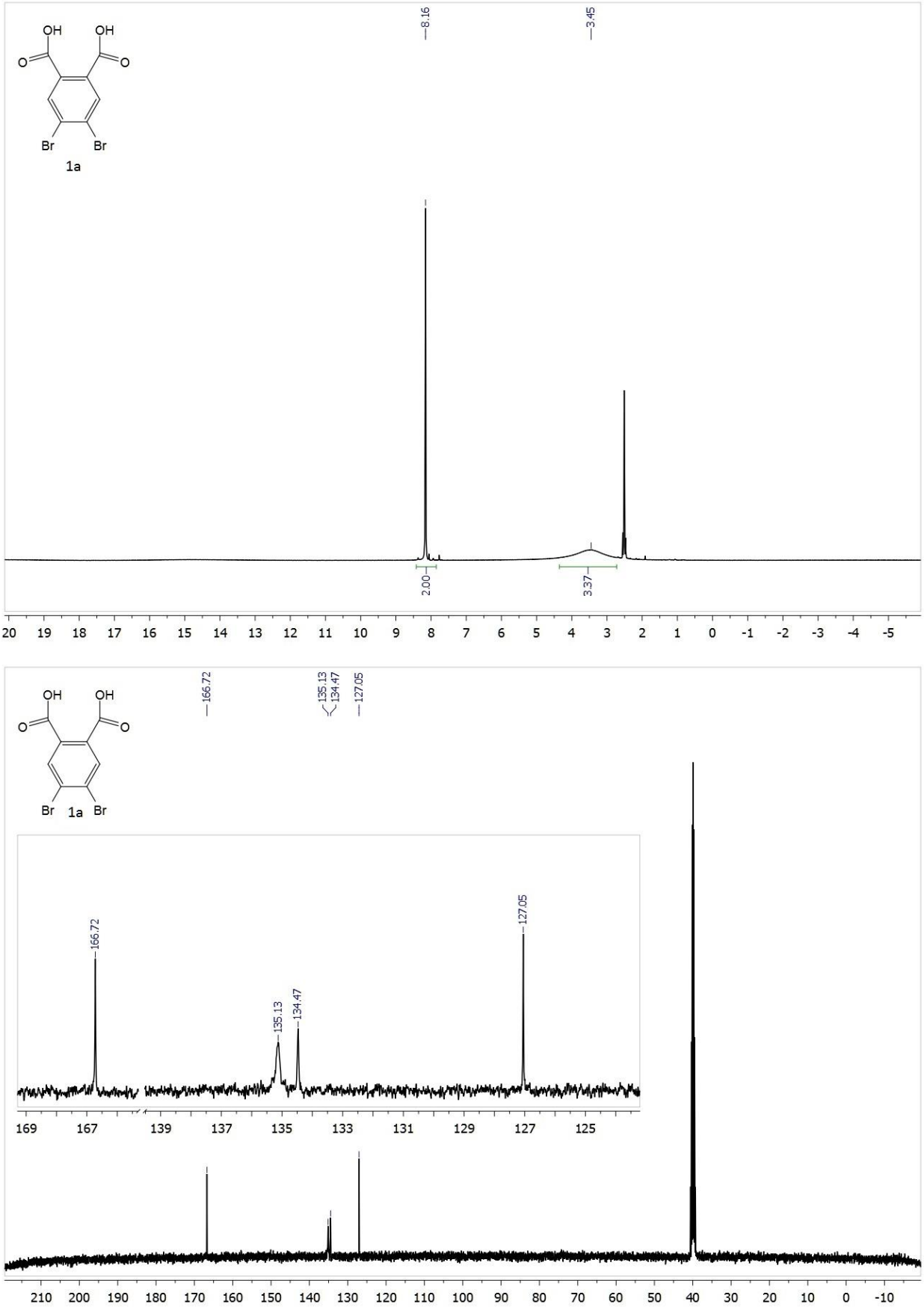

Figure S11 – ^{1}H and ^{13}C NMR spectra of 4,5-Dibromophthalic acid (**1'**) in $CDCl_3$.

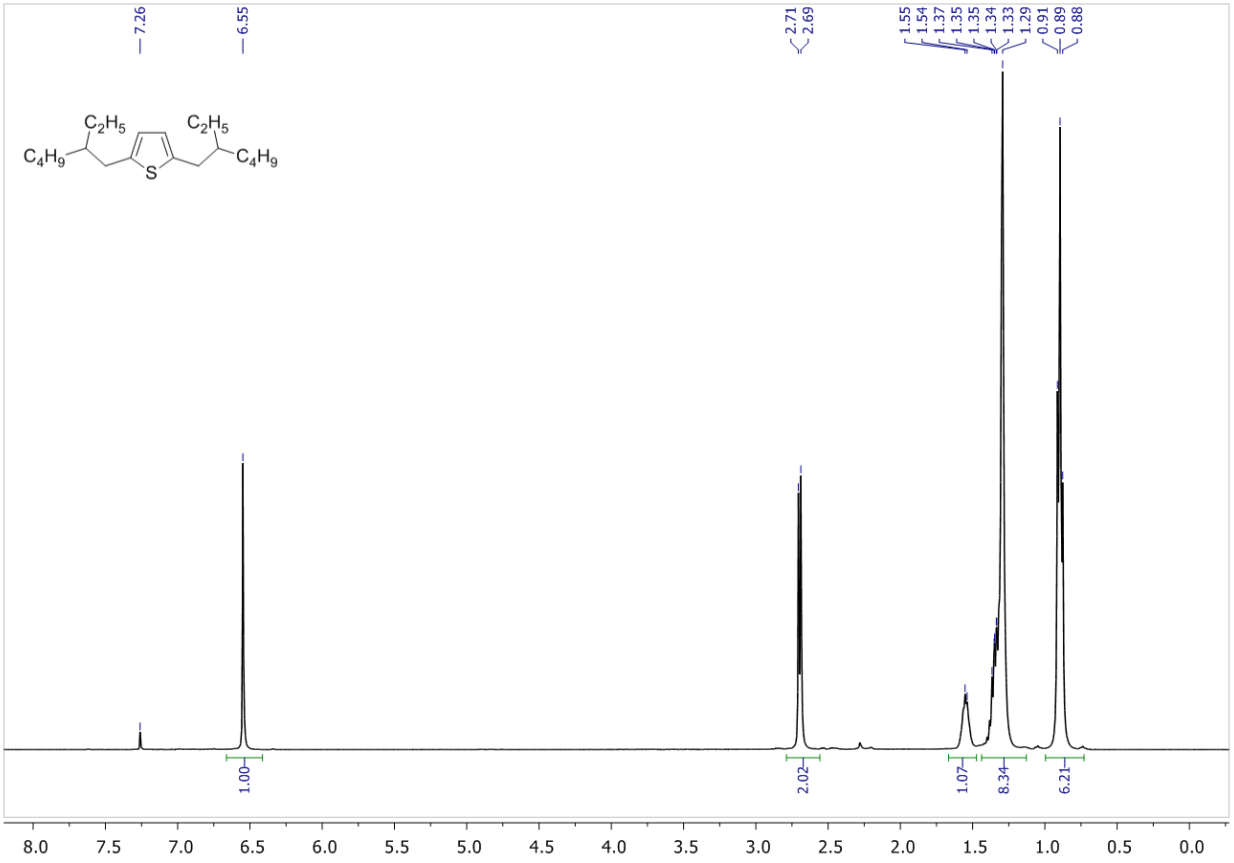

Figure S12 – ^{1}H NMR spectrum of 2,5-Bis(2-ethylhexyl)thiophene in $CDCl_3$.

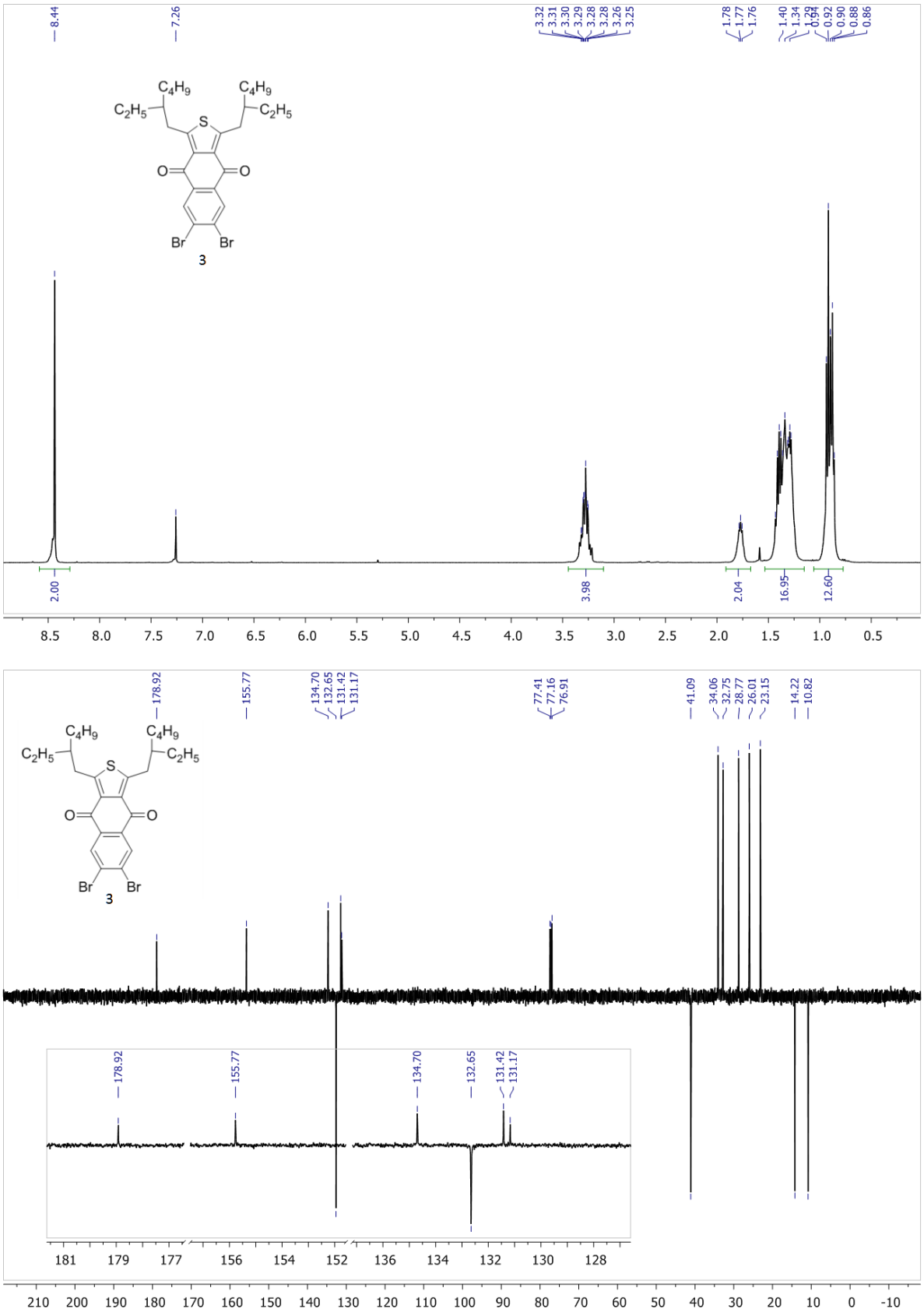

Figure S13 – ^{1}H and ^{13}C NMR spectra of 6,7-Dibromo-1,3-bis(2-ethylhexyl)naphtho-[2,3-*c*]thiophene-4,9-dione (**3**) in $CDCl_3$.

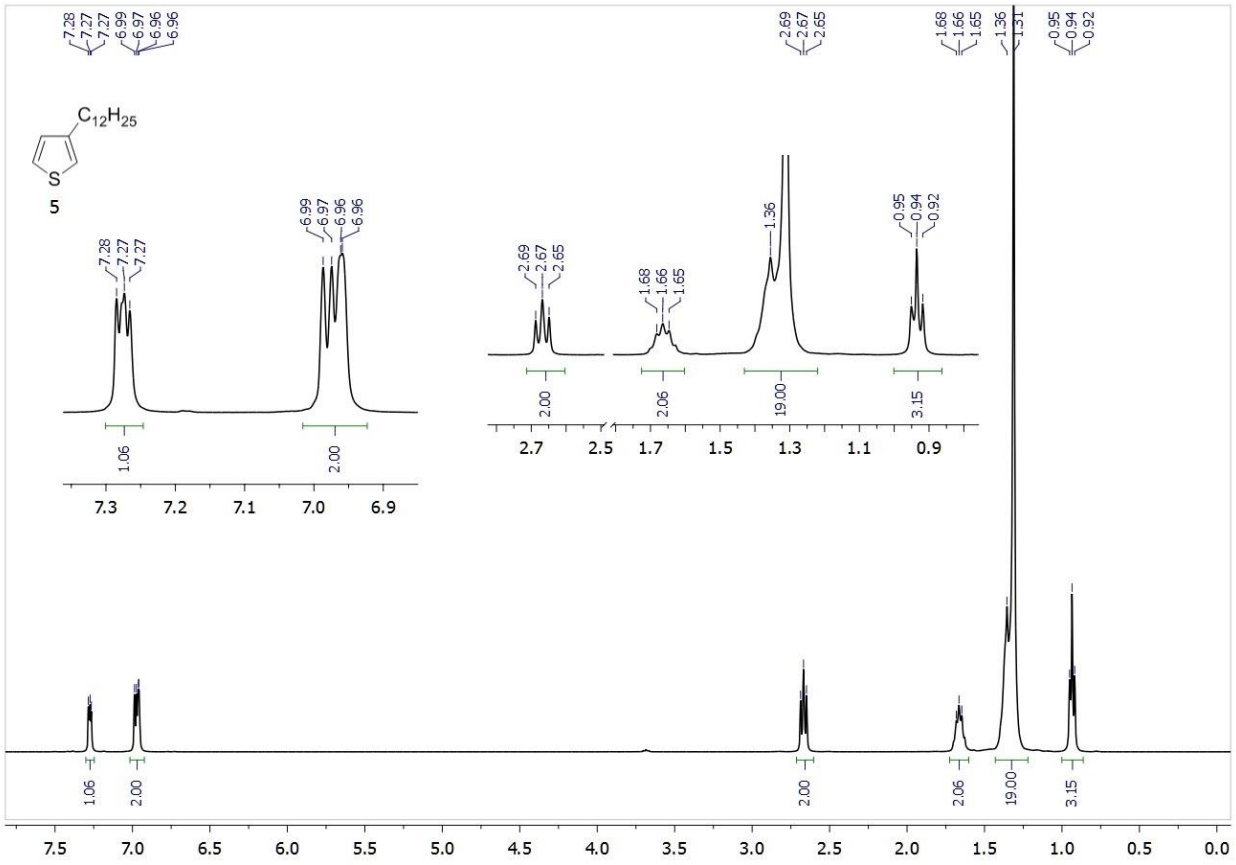

Figure S14 – ^{1}H NMR spectrum of 3-Dodecylthiophene (**5**) in $CDCl_3$.

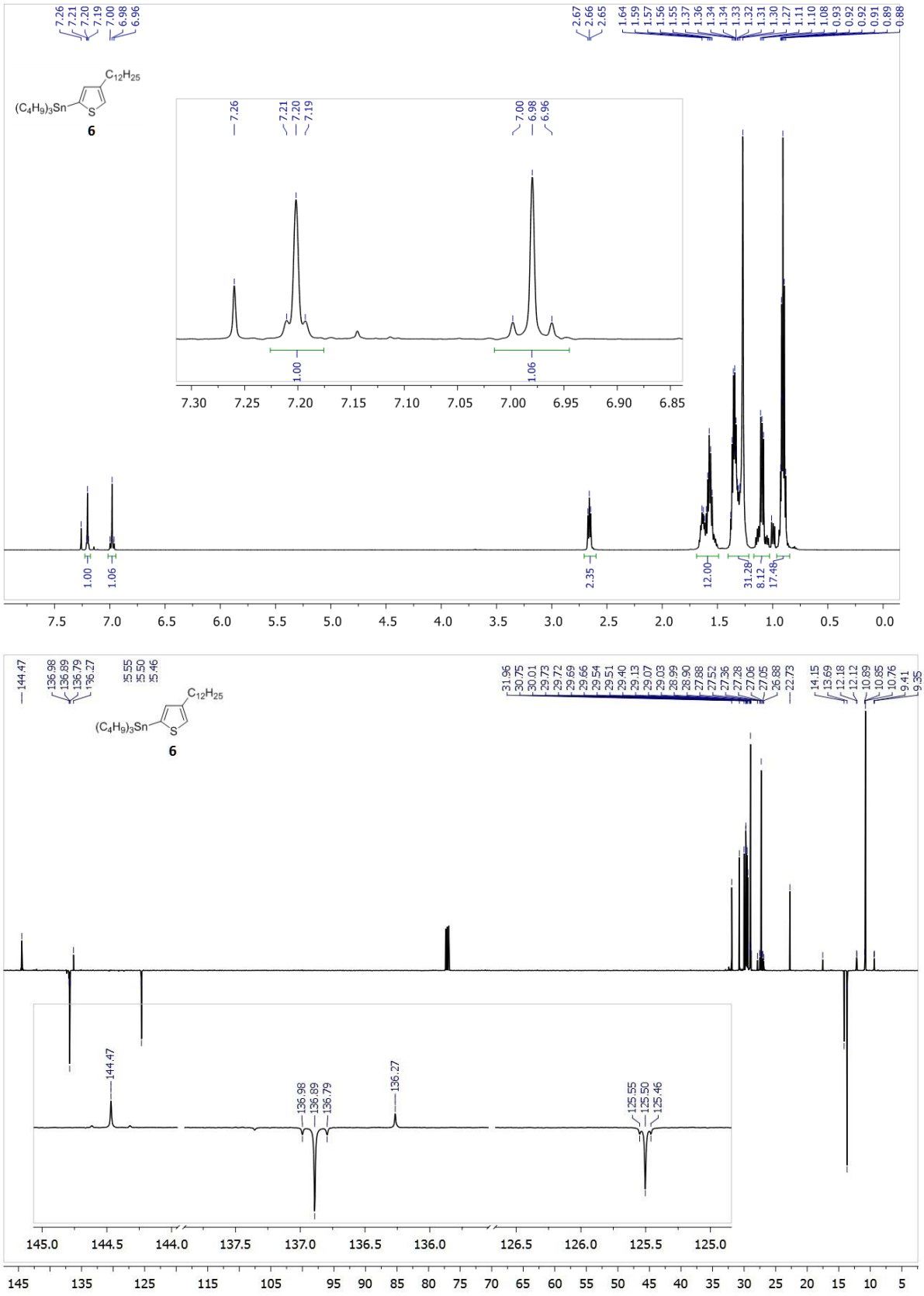

Figure S15 – ^{1}H and ^{13}C NMR spectra of Tributyl(4-dodecylthiophen-2-yl)stannane (**6**) in $CDCl_3$.

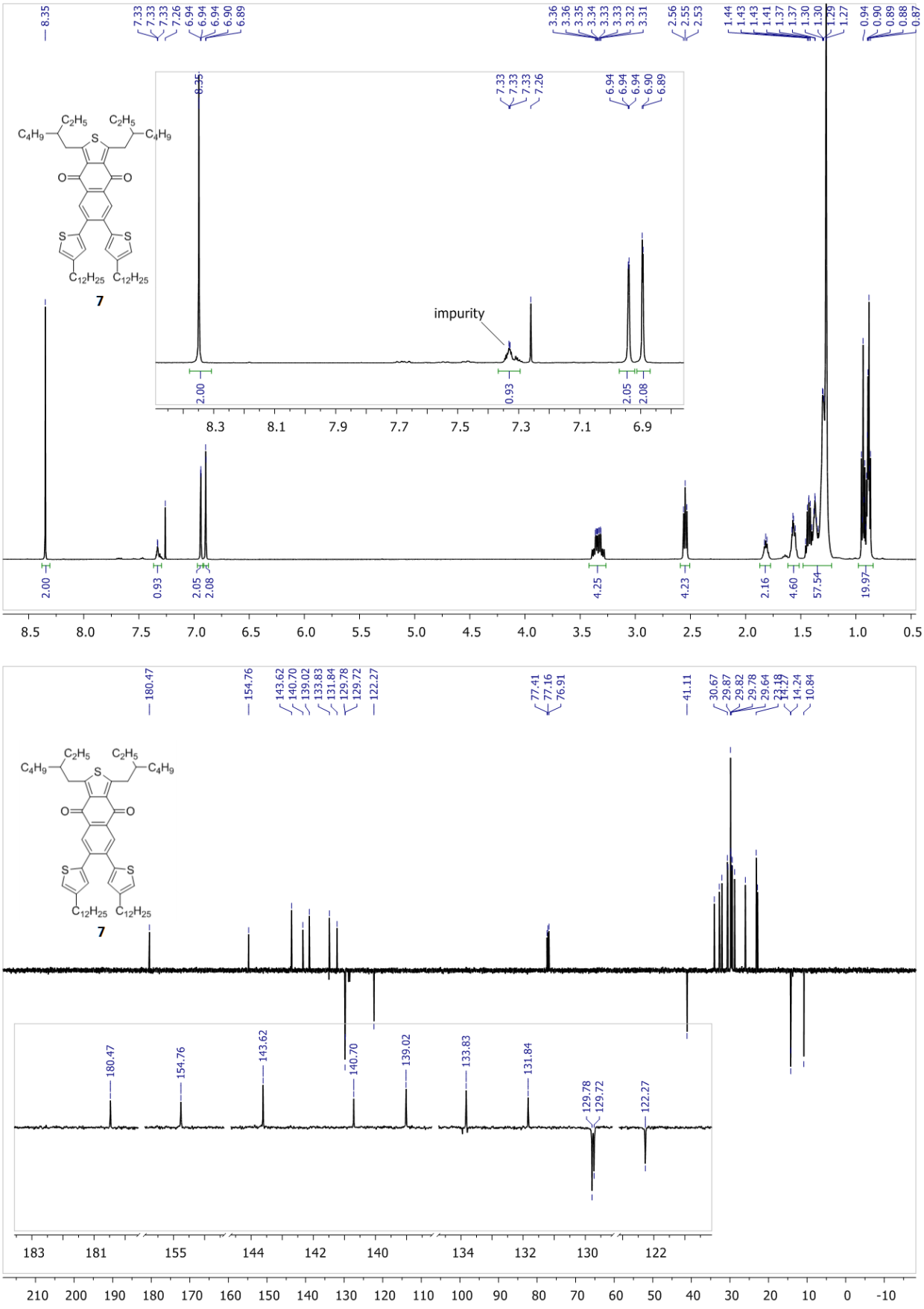

Figure S16 – ^{1}H and ^{13}C NMR spectra of 6,7-Bis(4-dodecylthiophen-2-yl)-1,3-bis(2-ethylhexyl)naphtho[2,3-*c*]thiophene-4,9-dione (**7**) in $CDCl_3$.

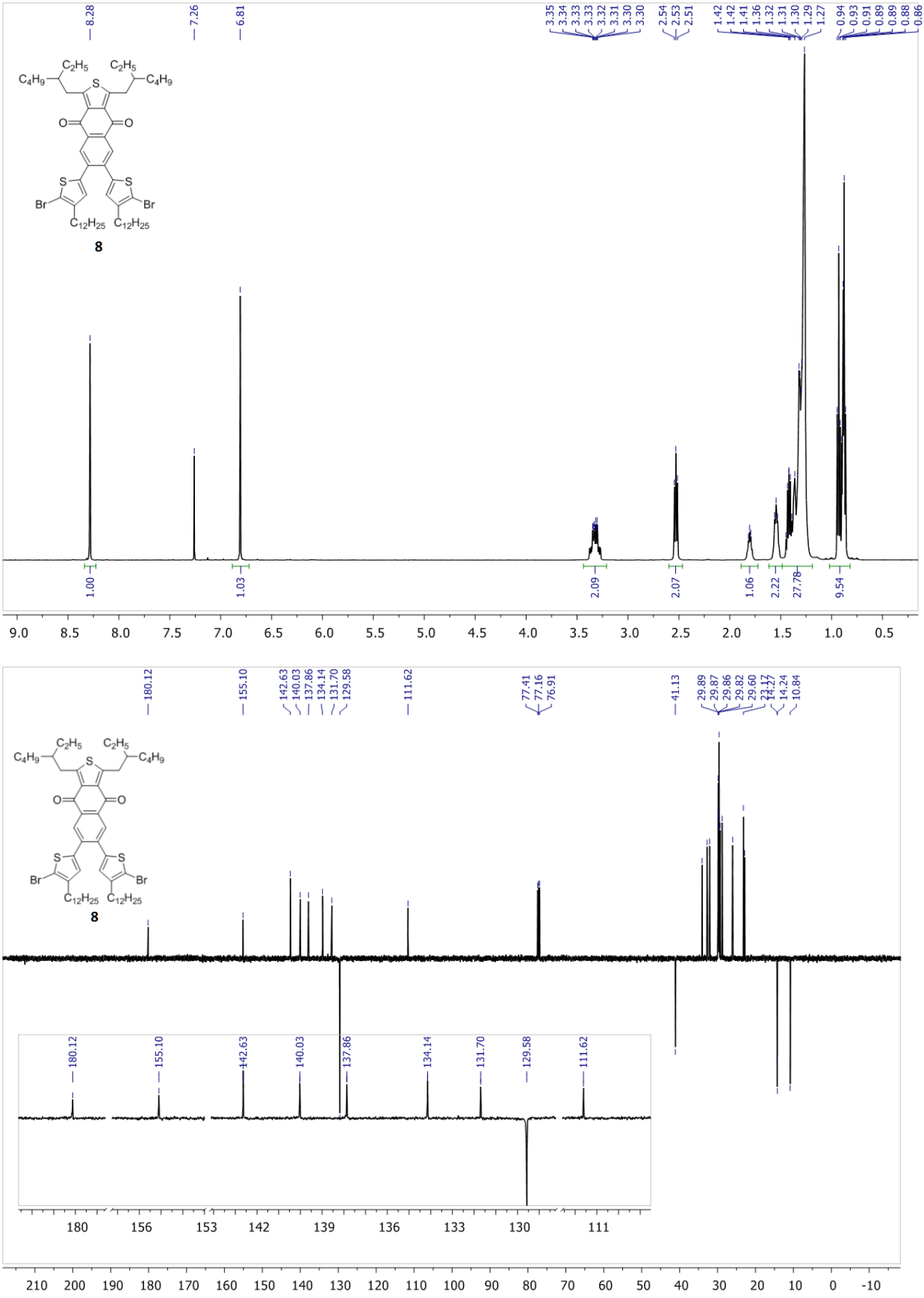

Figure S17 – ^{1}H and ^{13}C NMR spectra of 6,7-Bis(5-bromo-4-dodecylthiophen-2-yl)-1,3-bis(2-ethylhexyl)naphtho[2,3-*c*]thiophene-4,9-dione (**8**) in $CDCl_3$.

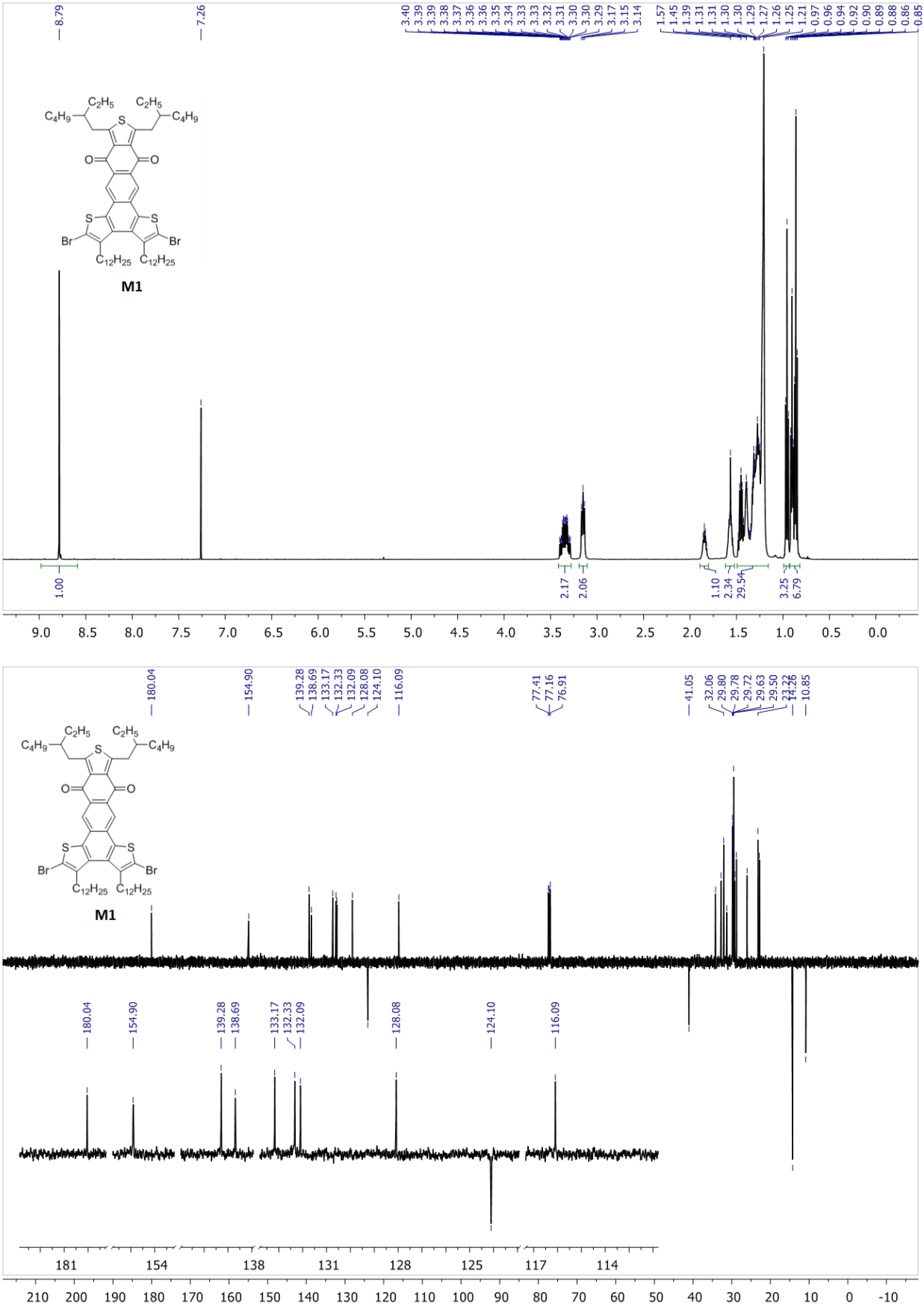

Figure S18 – ^{1}H and ^{13}C NMR spectra of 2,5-Dibromo-3,4-didodecyl-9,11-bis(2-ethylhexyl)anthra[1,2-*b*:4,3-*b*':6,7-*c*'']trithiophene-8,12-dione (**M1**) in $CDCl_3$.

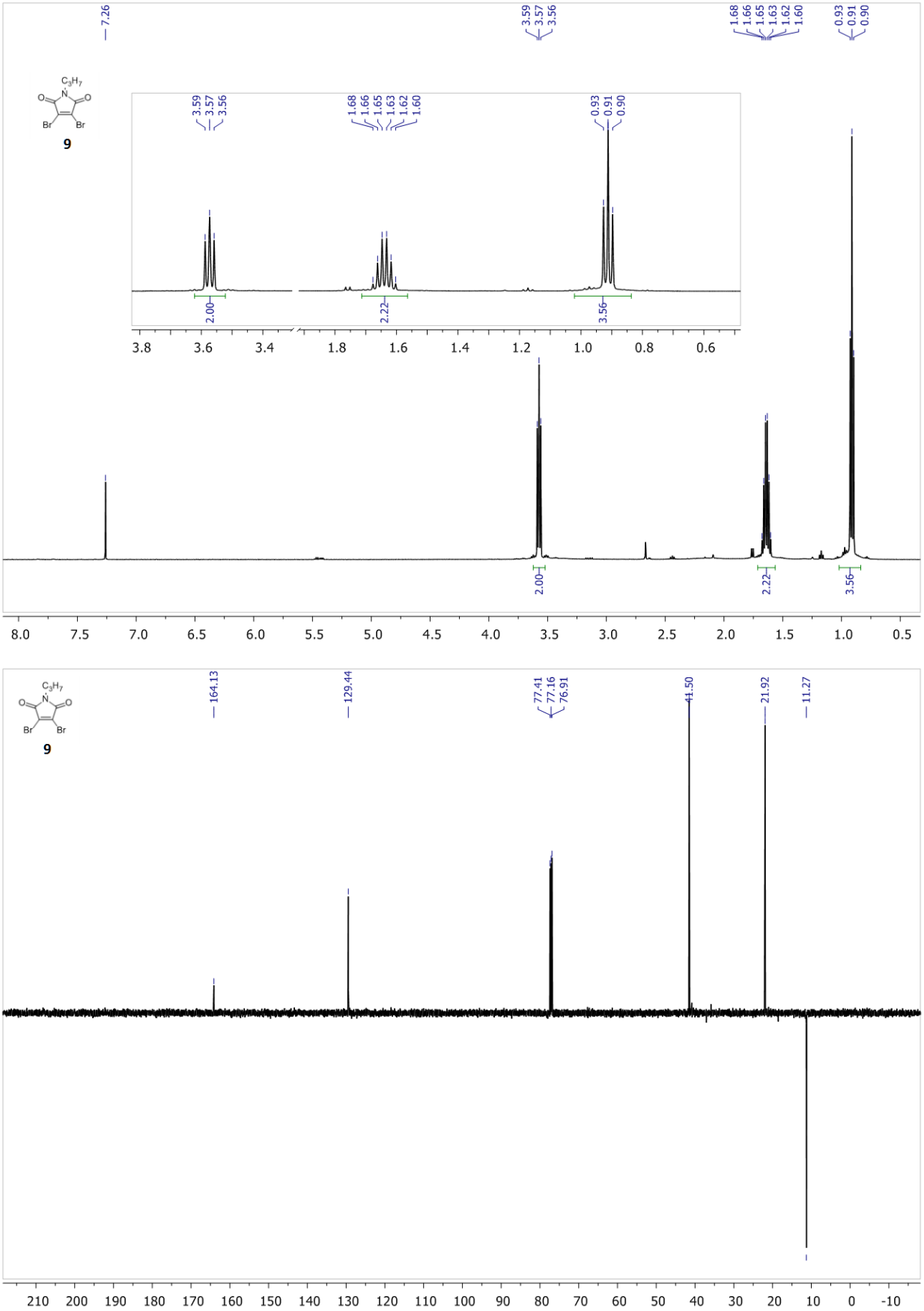

Figure S19 – ^{1}H and ^{13}C NMR spectra of 3,4-Dibromo-1-propyl-1*H*-pyrrole-2,5-dione (**9**) in $CDCl_3$.

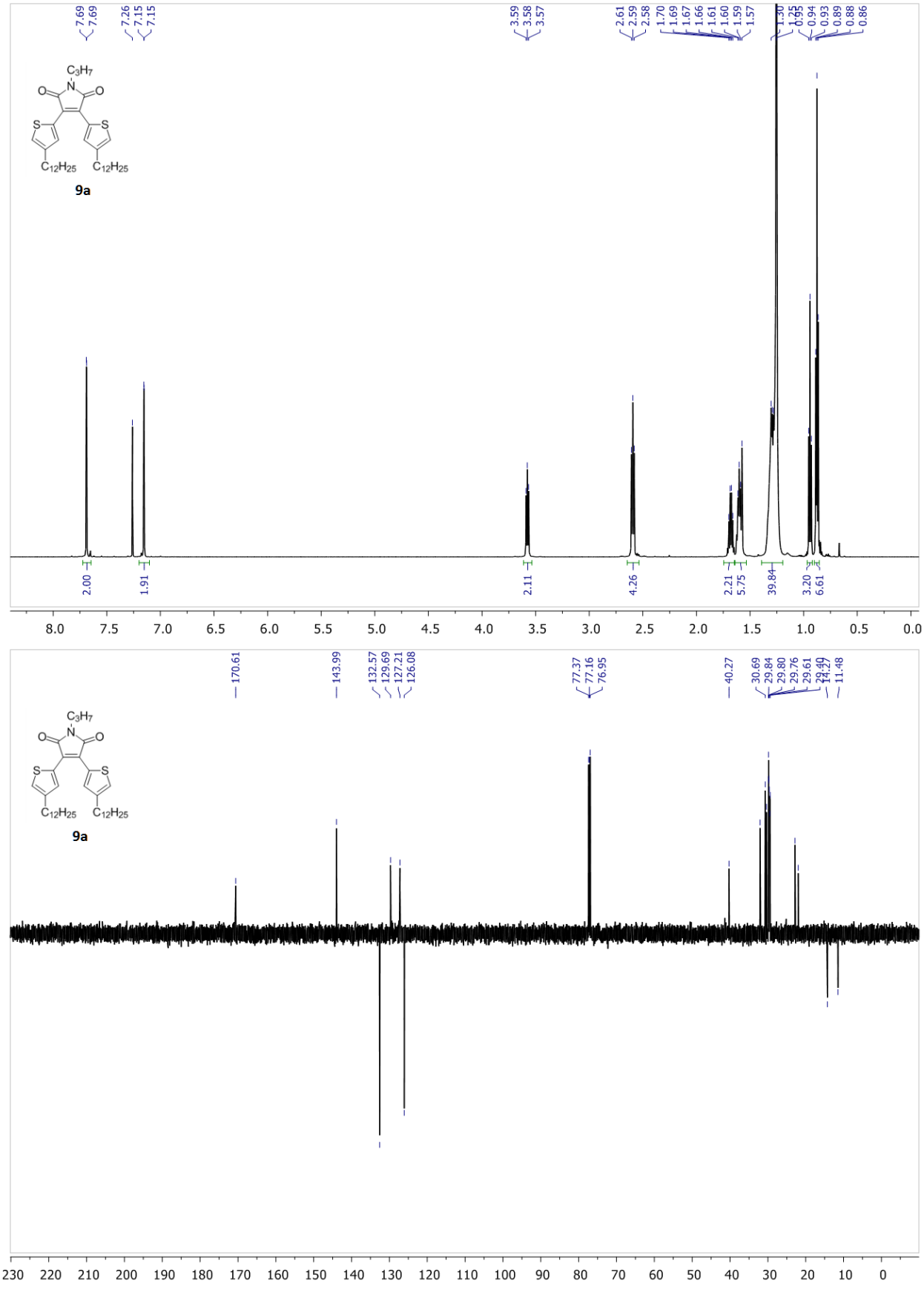

Figure S20 – ^{1}H and ^{13}C NMR spectra of 3,4-Bis(4-dodecylthiophen-2-yl)-1-propyl-1*H*-pyrrole-2,5-dione (**9'**) in $CDCl_3$.

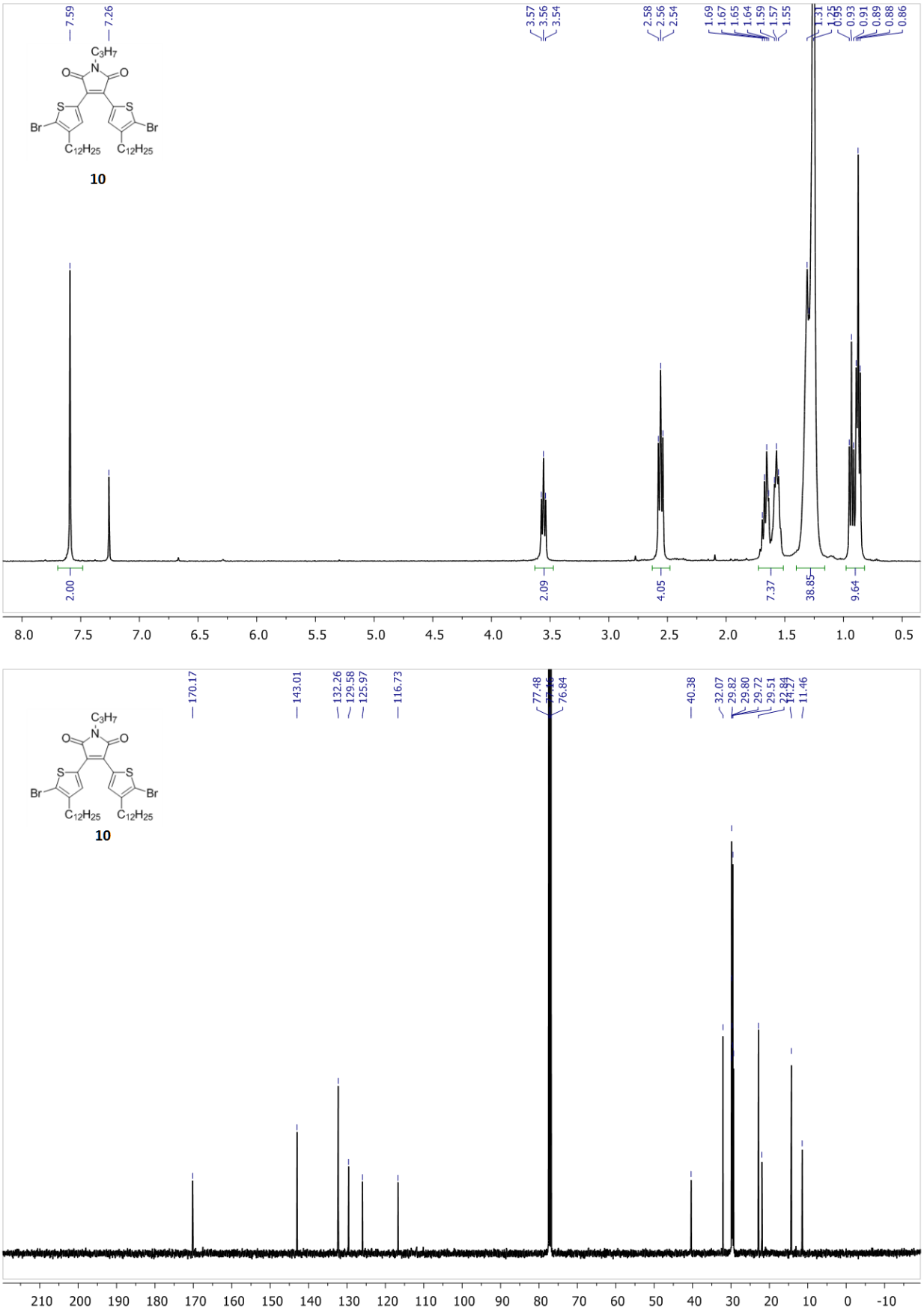

Figure S21 – ^{1}H and ^{13}C NMR spectra of 3,4-Bis(5-bromo-4-dodecylthiophen-2-yl)-1-propyl-1*H*-pyrrole-2,5-dione (**10**) in $CDCl_3$.

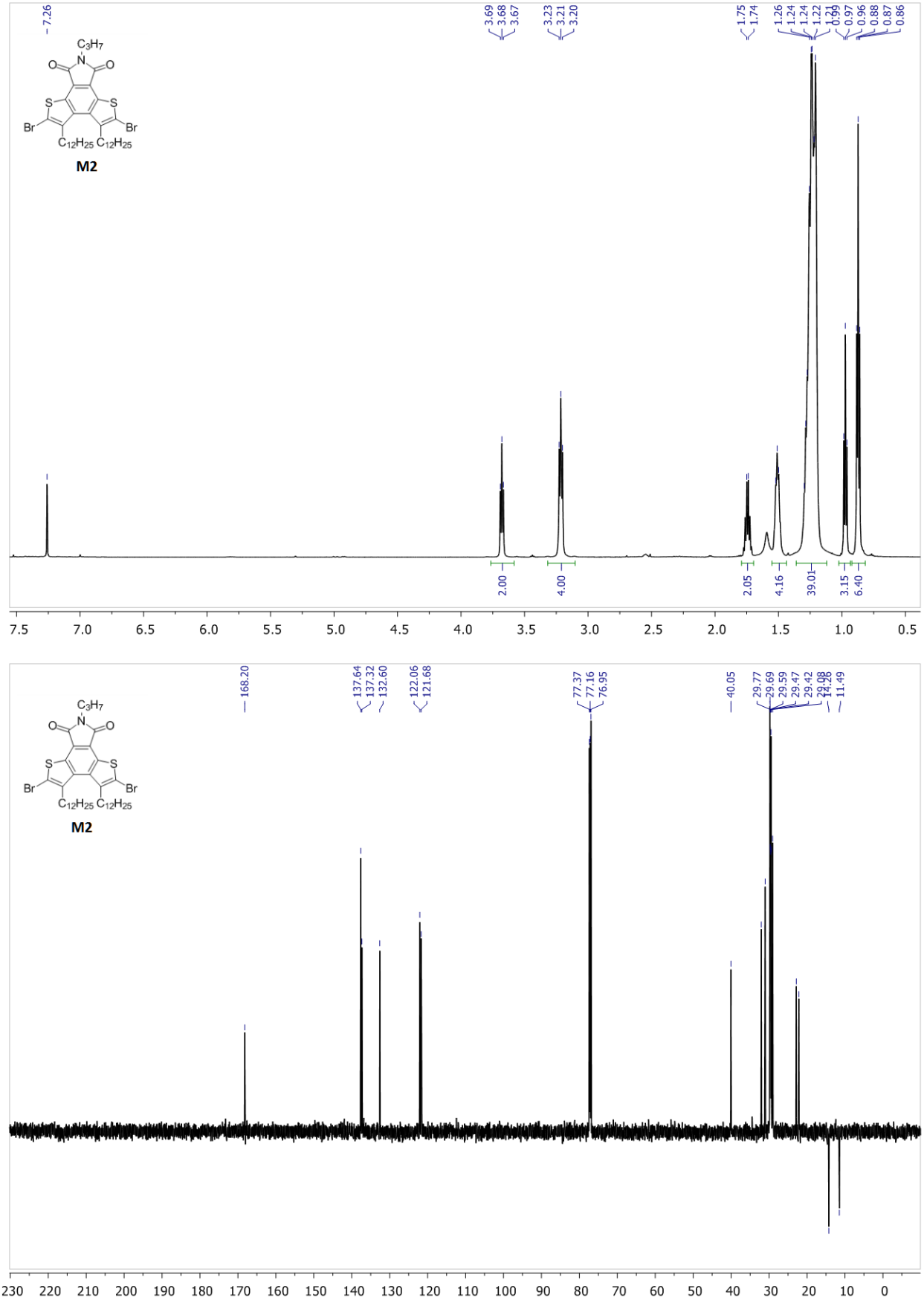

Figure S22 – ^{1}H and ^{13}C NMR spectra of 2,5-dibromo-3,4-didodecyl-8-propyl-7*H*-dithieno-[2,3-*e*:3',2'-*g*]isoindole-7,9(8*H*)-dione (**M2**) in $CDCl_3$.

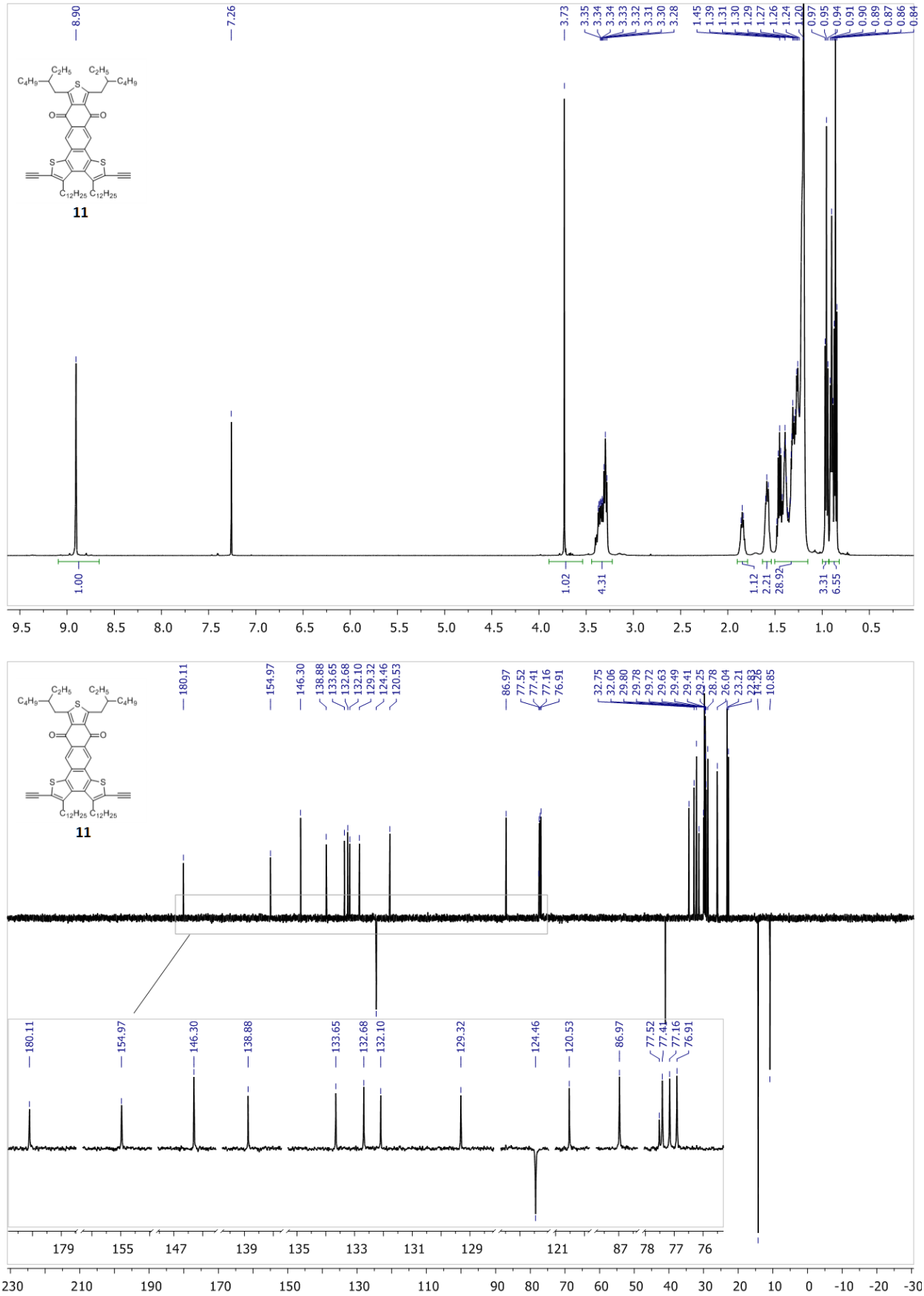

Figure S23 – ^{1}H and ^{13}C NMR spectra of 3,4-didodecyl-9,11-bis(2-ethylhexyl)-2,5-diethynylanthra[1,2-*b*:4,3-*b*':6,7-*c*"]trithiophene-8,12-dione (**11**) in $CDCl_3$.

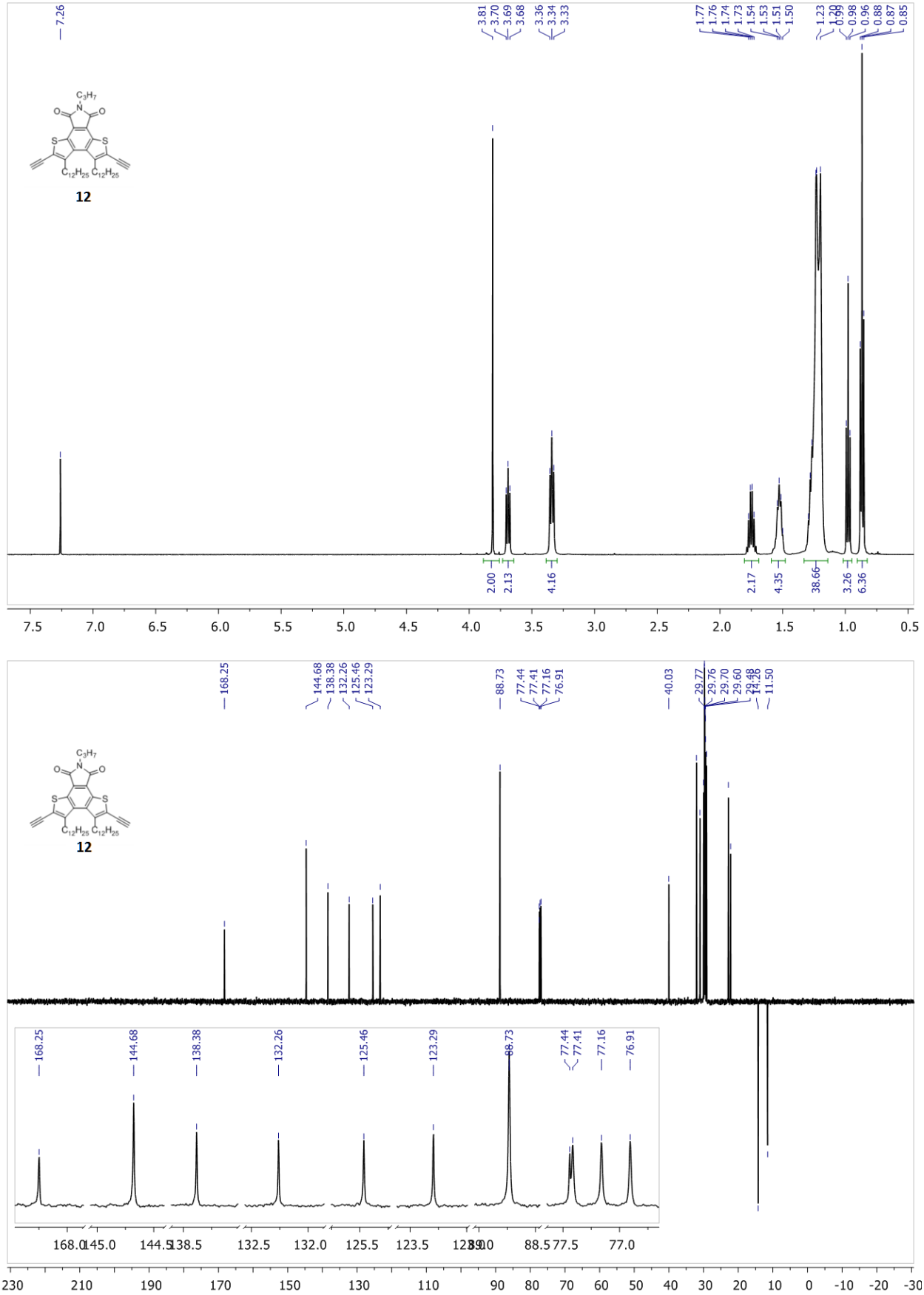

Figure S24 – ^{1}H and ^{13}C NMR spectra of 3,4-didodecyl-2,5-diethynyl-8-propyl-7*H*-dithieno-[2,3-*e*:3',2'-*g*]isoindole-7,9(8*H*)-dione (**12**) in $CDCl_3$.

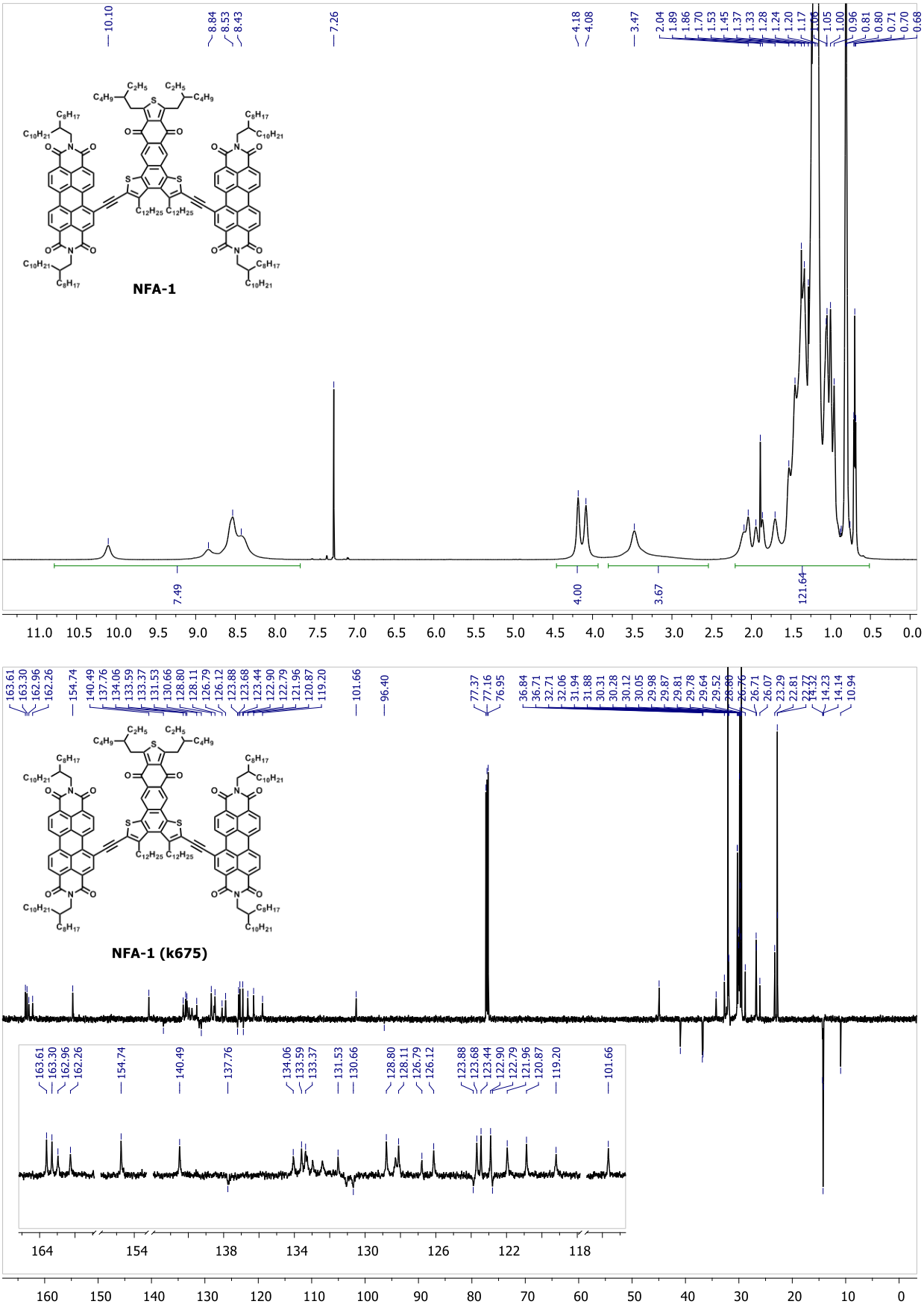

Figure S25 – ^{1}H and ^{13}C NMR spectra of non-fullerene acceptor **NFA-1** in $CDCl_3$.

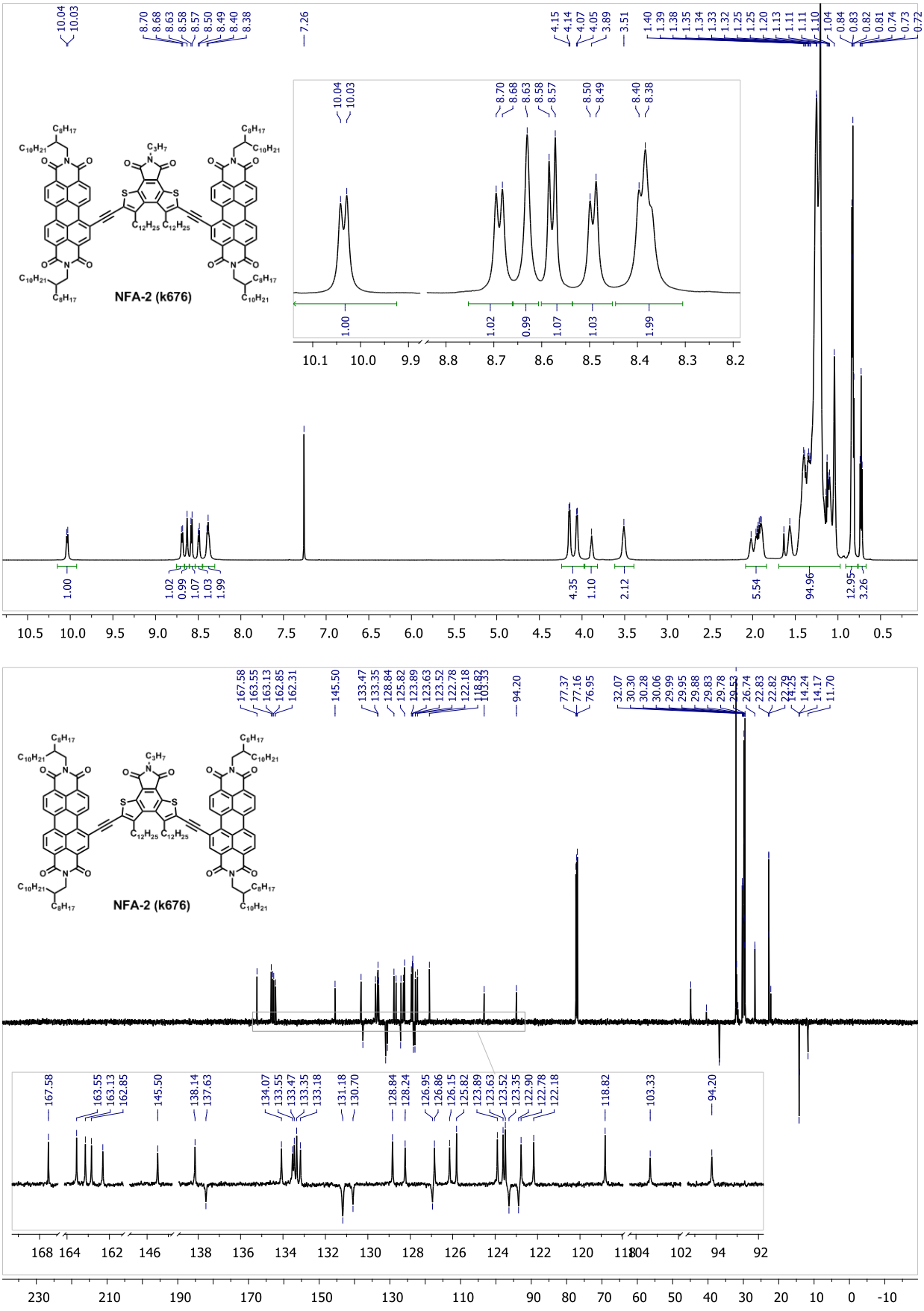

Figure S26 – ^{1}H and ^{13}C NMR spectra of non-fullerene acceptor **NFA-2** in $CDCl_3$.