Supplementary Information

for

Incorporation of Polycyclic Azaborine Compounds into Polythiophene-Type Conjugated Polymers for Organic Field-Effect Transistors

Xiao-Ye Wang, Fang-Dong Zhuang, Jie-Yu Wang, and Jian Pei**

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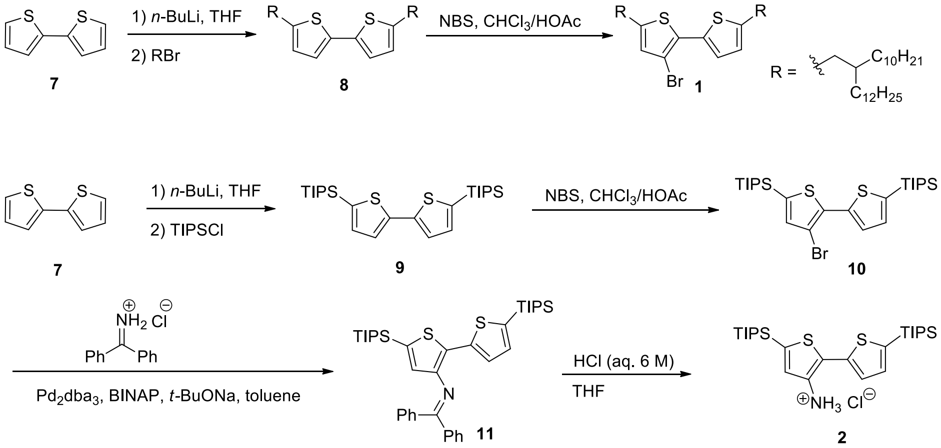
1. Experimental Section

General. All commercially available chemicals were used without further purification unless otherwise noted. CYTOP was purchased from Asahi Glass Co., Ltd. including the polymer solution CTL809M and the solvent CT-solv180. P3HT was bought from Sigma Aldrich with an average M_n of 15 ~ 45 kDa. Column chromatography was performed with silica gel. All yields given referred to isolated yields. Nuclear Magnetic Resonance (NMR) spectra were recorded on 400 or 500 MHz Bruker AVANCE III spectrometers. Chemical shifts were reported in ppm. Coupling constants (J values) were reported in Hertz. ^{1}H NMR chemical shifts were referenced to TMS (0 ppm). ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.00 ppm). ^{11}B NMR chemical shifts were referenced to the external standard boron signal of $BF_3 \cdot Et_2O$ (0 ppm). MALDI-TOF mass spectroscopy was performed on a Bruker BIFLEX III Mass Spectrometer or a Varian 7.0T FTMS Mass Spectrometer (Agilent Technologies, Santa Clara, CA). Elemental analyses were carried out on a German Vario EL III elemental analyzer.

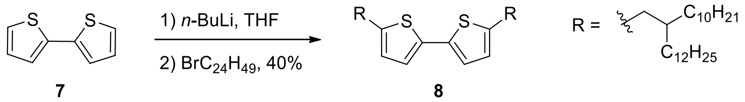
Absorption spectra were recorded on PerkinElmer Lambda 750 UV-*vis* Spectrometer. Cyclic voltammetry was performed on BASi Epsilon workstation and thin film measurements were carried out in acetonitrile containing 0.1 M n-Bu_4NPF_6 as the supporting electrolyte (scan rate: 100 mV s^{-1}.). Glassy carbon electrode was used as the working electrode, a platinum sheet as the counter electrode and Ag/AgCl as the reference electrode. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q600 analyzer under N_2 (10 ℃ min^{-1}). Differential scanning calorimetry (DSC) was performed on a METTLER TOLEDO Instrument DSC822e calorimeter under N_2. Gel permeation chromatography (GPC) was carried out on Polymer Laboratories PL-GPC220 at 150 ℃ with 1,2,4-tricholorobenzene (TCB) as the eluent and polystyrene (PS) as the standard. Photoelectron spectroscopy (PES) was performed on AC-2 photoelectron spectrometer (Riken-Keiki Co.). AFM images were recorded on Bruker Dimension Icon. The X-ray diffraction data were obtained at beamline BL14B1 of Shanghai Synchrotron Radiation Facility (SSRF) with a wavelength of 1.2398 Å.

Device Fabrication and Characterization. Top-gate/bottom-contact FET devices were fabricated using n^{++}-Si/SiO_2 (300 nm) substrates. The gold source and drain bottom electrodes (with Ti as the adhesion layer) were patterned by photolithography on the SiO_2 surface. The substrates were subjected to cleaning using ultrasonication in acetone, cleaning reagent, deionized water (twice), and *iso*-propanol. The cleaned substrates were dried under vacuum at 80 ℃ for 1 h. Then a thin film of the polymer was deposited on the treated substrates by spin-coating a polymer solution (4 mg/mL in 1,2-dichlorobenzene) at 1800 rpm for 40 s and annealed at 150 ℃ for 10 min. After polymer thin film deposition, a CYTOP solution (CTL809M : CT-solv180 = 3:1) was spin-coated onto the semiconducting layer at 2000 rpm for 90 s, resulting in a dielectric layer of 500 nm thick. The CYTOP layer was then baked at 100 ℃ for 1 h. Gate electrodes comprising a layer of Al (50 nm) were then thermally evaporated through a shadow mask onto the dielectric layer. The OTFT devices had a channel length (L) of 10 μm and a channel width (W) of 200 μm. Characteristics of the OFET devices were measured under ambient conditions on a probe stage using a Keithley 4200 SCS as the parameter analyzer. The carrier mobility (μ) was calculated in the saturated regime according to the equation $I_{SD} = C_i(W/2L)\mu(V_G - V_T)^2$, where I_{SD} is the source-drain current in the saturated regime, and V_G and V_T are the gate and threshold voltage, respectively. W and L are the semiconductor channel width and length, respectively. C_i (C_i = 3.7 nF) is the capacitance per unit area of the dielectric layer.

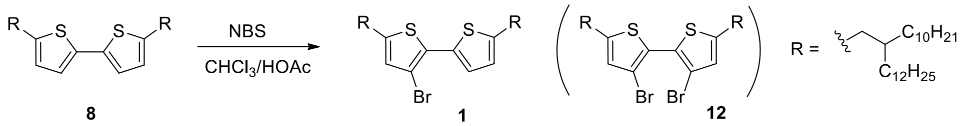
Synthetic Procedures.



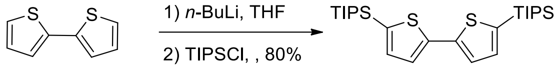
Scheme S1. Synthetic routes to bithiophene derivatives **1** and **2**.



5,5'-bis(2-decyltetradecyl)-2,2'-bithiophene (8). To a stirred solution of compound **7** (3.34 g, 20.1 mmol) in THF (200 mL) was added *n*-BuLi (1.6 M in hexane, 27.7 mL, 44.3 mmol) at 0 ℃. The mixture was stirred at this temperature for 1 h before 11-(bromomethyl)tricosane (21.0 g, 50.3 mmol) was added. Then the reaction mixture was heated at 70 ℃ for 8 h. After cooled down to room temperature, the reaction was quenched by aqueous NH_4Cl and extracted with hexane for three times. The combined organic layer was washed with water and then dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel (eluent: petroleum ether) to give 10.79 g (40%) of compound **8** as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ 6.89 (d, J = 3.5 Hz, 2H), 6.60 (d, J = 3.5 Hz, 2H), 2.70 (d, J = 6.6 Hz, 4H), 1.61 (m, 2H), 1.27 (m, 80H), 0.88 (t, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 298K, ppm): δ 143.1, 135.6, 125.6, 122.4, 39.9, 34.5, 33.2, 32.0, 30.0, 29.72, 29.71, 29.68, 29.4, 26.6, 22.7, 14.1; HRMS (MALDI) *m/z*: Calcd for $C_{56}H_{102}S_2$: 838.7417; Found: 838.7421 $[M]^+$.

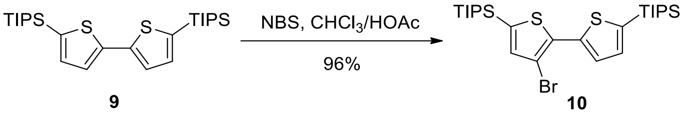


3-bromo-5,5'-bis(2-decyltetradecyl)-2,2'-bithiophene (1). *N*-Bromosuccinimide (1.25 g, 7.0 mmol) was added slowly to a solution of compound **8** (5.88 g, 7.0 mmol) in $CHCl_3$/HOAc (120 mL/60 mL) at 0 ℃ during 1 h. The reaction mixture was warmed to room temperature and stirred for another 1 h. The organic layer was washed with water and aqueous Na_2CO_3, and then dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel (eluent: petroleum ether) to give the crude product, which contained trace dibrominated compound **12** and unreacted compound **8**. This mixture could not be separated and was thus used directly for the next step.



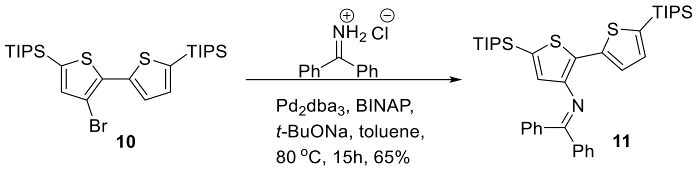
7 9

5,5'-bis(triisopropylsilyl)-2,2'-bithiophene (9). To a stirred solution of compound **7** (5.00 g, 30.1 mmol) in THF (200 mL) was added *n*-BuLi (1.6 M in hexane, 41.4 mL 66.2 mmol) at 0 ℃. The reaction mixture was stirred at this temperature for 1 h before TIPSCl (14.5 g, 75.2 mmol) was added. The mixture was stirred for another 8 h at room temperature and then quenched by aqueous NH_4Cl. The organic layer was extracted with hexane for three times and then dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel (eluent: petroleum ether) to give 11.45 g (80%) of compound **9** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ 7.29 (d, J = 3.5 Hz, 2H), 7.15 (d, J = 3.5 Hz, 2H), 1.32 (m, 6H), 1.12 (d, J = 7.4 Hz, 36H); ^{13}C NMR (100 MHz, $CDCl_3$, 298K, ppm): δ 142.4, 136.4, 135.6, 124.7, 18.6, 11.8; HRMS (MALDI) *m/z*: Calcd for $C_{26}H_{46}S_2Si_2$: 478.2574; Found: 478.2573 $[M]^+$.

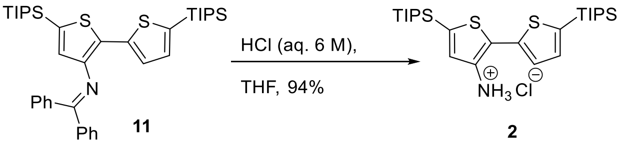


9 10

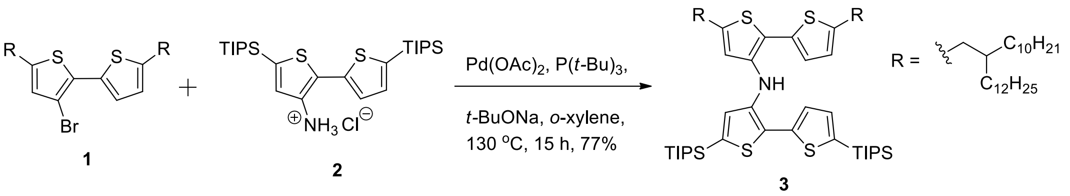
3-bromo-5,5'-bis(triisopropylsilyl)-2,2'-bithiophene (10). *N*-Bromosuccinimide (9.29 g, 52.2 mmol) was added slowly to a stirred solution of compound **9** (25.0 g, 52.5 mmol) in $CHCl_3$/HOAc (300 mL/150 mL) at 0 ℃ during 1 h. The reaction mixture was warmed to room temperature and stirred for another 1 h. The organic layer was washed with water and aqueous Na_2CO_3, and then dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel (eluent: petroleum ether) and recrystallization from $CHCl_3$/EtOH to give 5.82 g (96%) of compound **10** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ 7.60 (d, J = 3.6 Hz, 1H), 7.22 (d, J = 3.6 Hz, 1H), 7.10 (s, 1H), 1.34 (m, 6H), 1.12 (m, 36H); ^{13}C NMR (100 MHz, $CDCl_3$, 298K, ppm): δ 139.7, 139.6, 137.2, 135.8, 135.3, 133.8, 127.1, 108.4, 18.6, 18.5, 11.8, 11.6; HRMS (MALDI) *m/z*: Calcd for $C_{26}H_{45}BrS_2Si_2$: 556.1679; Found: 556.1674 $[M]^+$.



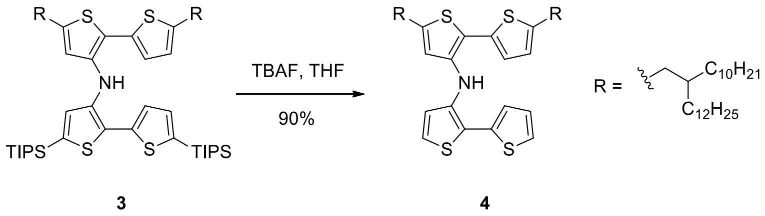
N-(5,5'-bis(triisopropylsilyl)-[2,2'-bithiophen]-3-yl)-1,1-diphenylmethanimine (11). A mixture of compound **10** (10.22 g, 18.3 mmol), diphenylmethanimine hydrochloride (7.98 g, 36.7 mmol), Pd_2dba_3 (167 mg, 0.183 mmol), BINAP (342 mg, 0.552 mmol), and *t*-BuONa (7.046 g, 73.4 mmol) in toluene (60 mL) was heated at 80 °C for 15 h. After filtration, the filtrate was concentrated under reduced pressure and the residue was purified by column chromatography over silica gel (eluent: petroleum ether/CH_2Cl_2 = 5 : 1) to give 7.87 g (65%) of compound **11** as a reddish solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ 7.94 (d, J = 7.2 Hz, 2H), 7.37 (m, 7H), 7.17 (m, 3H), 6.20 (s, 1H), 1.28 (m, 3H), 1.12 (m, 21H), 0.95 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298K, ppm): δ 167.4, 145.5, 141.1, 139.1, 137.2, 135.7, 134.2, 131.2, 130.7, 130.6, 130.2, 129.6, 128.7, 128.5, 128.3, 128.0, 124.8, 18.6, 18.5, 11.8, 11.5; HRMS (MALDI) m/z: Calcd for $C_{39}H_{56}NS_2Si_2$: 658.3387; Found: 658.3388 $[M+H]^+$.



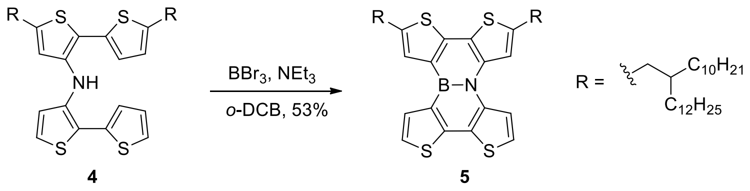
5,5'-bis(triisopropylsilyl)-[2,2'-bithiophen]-3-aminium chloride (2). To a stirred solution of compound **11** (2.43 g, 3.69 mmol) in THF (30 mL) was added 6 M aqueous HCl (30 mL). The reaction mixture was stirred at room temperature for 10 min and then concentrated under reduced pressure. The residue was washed with hexane to give 1.84 g (94%) of compound **2** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ 10.66 (br, 3H), 7.69 (d, J = 3.4 Hz, 1H), 7.57 (s, 1H), 6.99 (d, J = 3.3 Hz, 1H), 1.28 (m, 6H), 1.12 (d, J = 7.4 Hz, 18H), 1.03 (d, J = 7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298K, ppm): *δ* 137.1, 136.7, 136.3, 135.2, 131.9, 127.6, 123.3, 18.5, 11.7, 11.6; HRMS (MALDI) *m/z*: Calcd for $C_{26}H_{47}NS_2Si_2$: 493.2683; Found: 493.2687 $[M - HCl]^+$.



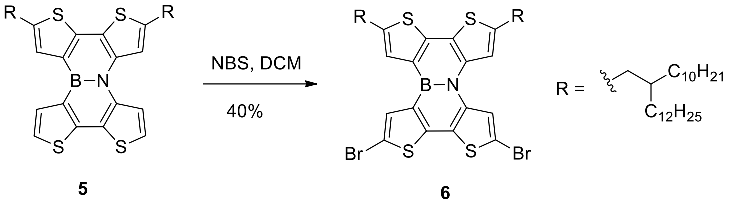
***N*-(5,5'-bis(2-decyltetradecyl)-[2,2'-bithiophen]-3-yl)-5,5'-bis(triisopropylsilyl)-[2,2'-bithiophen]-3-amine (3)**. A mixture of compound **1** (2.39 g, 4.51 mmol), compound **2** (4.40 g, 4.79 mmol), $Pd(OAc)_2$ (50 mg, 0.22 mmol), P(*t*-Bu)$_3$ (50 mg, 0.25 mmol), and *t*-BuONa (1.34g, 13.9 mmol) in *o*-xylene (50 mL) was heated at 150 ℃ for 20 h. The reaction mixture was extracted with hexane and washed with aqueous NaCl, and then dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel (eluent: petroleum ether) to give 4.60 g (77%) of compound **3** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): *δ* 7.30 (d, *J* = 3.5, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 7.04 (s, 1H), 6.95 (d, *J* = 3.5 Hz, 1H), 6.63 (d, *J* = 3.5 Hz, 1H), 6.57 (s, 1H), 6.20 (s, 1H), 2.69 (d, *J* = 6.6 Hz, 2H), 2.59 (d, *J* = 6.6 Hz, 2H), 1.55 (m, 2H), 1.32 (m, 86H), 1.11 (m, 36H), 0.87 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 298K, ppm): *δ* 143.0, 141.6, 140.7, 139.5, 137.6, 136.1, 133.5, 132.7, 131.5, 131.1, 125.4, 124.6, 123.0, 122.5, 120.3, 113.7, 39.9, 39.8, 35.0, 34.5, 33.2, 33.1, 31.9, 30.00, 29.96, 29.72, 29.69, 29.67, 29.64, 29.37, 29.35, 29.33, 26.7, 26.6, 22.7, 18.61, 18.59, 14.1, 11.8, 11.7; HRMS (MALDI) *m/z*: Calcd for $C_{82}H_{147}NS_4Si_2$: 1329.9949; Found: 1329.9943 $[M]^+$.



***N*-([2,2'-bithiophen]-3-yl)-5,5'-bis(2-decyltetradecyl)-[2,2'-bithiophen]-3-amine (4)**. To a stirred solution of compound **3** (505 mg, 0.373 mmol) in THF (30 mL) was added TBAF (2.0 mL, 1.0 M in THF). The reaction mixture was stirred at room temperature for 1 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel (eluent: petroleum ether) to give 227 mg (90%) of compound **4** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ 7.23 (dd, ^3J = 5.1 Hz, ^4J = 1.1 Hz, 1H), 7.18 (dd, ^3J = 3.6 Hz, ^4J = 1.1 Hz, 1H), 7.09 (d, J = 5.4 Hz, 1H), 7.03 (dd, ^3J = 5.1 Hz, ^4J = 3.6 Hz, 1H), 6.91 (d, J = 3.5 Hz, 1H), 6.84 (d, J = 5. 4 Hz, 1H), 6.63 (d, J = 3.6 Hz, 1H), 6.52 (s, 1H), 5.97 (s, 1H), 2.69 (d, J = 6.6 Hz, 2H), 2.61 (d, J = 6.6 Hz, 2H), 1.58 (m, 2H), 1.25 (m, 80H), 0.88 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 298K, ppm): δ 143.2, 141.5, 139.3, 137.0, 135.4, 133.3, 127.4, 125.4, 124.4, 124.3, 123.1, 123.0, 122.6, 121.1, 116.1, 116.0, 39.9, 39.7, 34.8, 34.5, 33.1, 31.9, 30.0, 29.7, 29.65, 29.63, 29.4, 29.34, 29.32, 26.6, 22.7, 14.1; HRMS (MALDI) *m/z*: Calcd for $C_{64}H_{108}NS_4$: 1018.7359; Found: 1018.7355 [M + H]$^+$.



2,13-bis(2-decyltetradecyl)dithieno[3',2':3,4;2'',3'':5,6][1,2]azaborinino[1,2-a]dithieno[3,2-c:2',3'-e][1,2]azaborinine (5). To a solution of compound **4** (1.29 g, 1.27 mmol) and triethylamine (257 mg, 2.54 mmol) in *o*-dichlorobenzene (20 mL) was added BBr_3 (476 mg, 1.90 mmol). The reaction mixture was heated at 180 ℃ for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel (eluent: petroleum ether) to give 682 mg (53%) of compound **5** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ 8.06 (d, J = 5.1 Hz, 1H), 7.93 (d, J = 5.6 Hz, 1H), 7.67 (s, 1H), 7.60 (s, 1H), 7.35 (m, 4H), 2.90 (d, J = 6.6 Hz, 2H), 2.82 (d, J = 6.6 Hz, 2H), 1.73 (m, 2H), 1.29 (m, 80H), 0.85 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 298K, ppm): δ 144.1, 143.8, 142.2, 141.3, 138.6, 137.3, 136.8, 136.0, 131.3, 128.8, 122.9, 122.7, 121.9, 121.71, 121.66, 119.8, 40.1, 40.0, 35.4, 34.9, 33.3, 33.2, 31.9, 30.0, 29.71, 29.67, 29.4, 26.67, 26.66, 22.7, 14.1; ^{11}B NMR (160 MHz, $CDCl_3$, 298K, ppm): δ 26.6; MALDI-TOF MS *m/z*: 1025.7 (100%) $[M]^+$; Elemental Anal. Calcd for $C_{64}H_{104}BNS_4$: C, 74.88; H, 10.21; N, 1.36; Found: C, 74.77; H, 10.15; N, 1.30.



2,13-dibromo-6,9-bis(2-decyltetradecyl)dithieno[3',2':3,4;2'',3'':5,6][1,2]azaborinino[1,2-a]dithieno[3,2-c:2',3'-e][1,2]azaborinine (6). To a stirred solution of compound **5** (190 mg, 0.185 mmol) in dichloromethane was slowly added *N*-bromosuccinimide (49.4 mg 0.278 mmol) during 10 min. The reaction mixture was stirred for another 1 h. The organic layer was washed with water and aqueous Na_2CO_3, and then dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel (eluent: petroleum ether) to give 88 mg (40%) of compound **6** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ 7.66 (s, 2H), 7.31 (s, 1H), 7.27 (s, 1H), 2.86 (d, J = 6.6 Hz, 2H), 2.80 (d, J = 6.6 Hz, 2H), 1.72 (m, 2H), 1.29 (m, 80H), 0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 298K, ppm): δ 143.8, 143.5, 142.5, 141.6, 137.3, 137.0, 136.3, 135.2, 133.6, 128.3, 124.3, 122.7, 122.2, 119.2, 111.1, 110.6, 40.2, 40.0, 25.3, 35.0, 33.3, 33.2, 32.0, 30.1, 29.8, 29.73, 29.69, 29.4, 26.7, 22.7, 14.1; ^{11}B NMR (160 MHz, $CDCl_3$, 298K, ppm): δ 27.0; HRMS (MALDI) *m/z*: Calcd for $C_{64}H_{101}BBr_2NS_4$: 1182.5267; Found: 1182.5269 $[M - H]^+$; Elemental Anal. Calcd for $C_{64}H_{102}BBr_2NS_4$: C, 64.90; H, 8.68; N, 1.18; Found: C, 64.92; H, 8.71; N, 1.08.

General Procedures for Stille Polymerization and Polymer Purification.

P1: To a Schlenk tube were added compound **6** (88 mg, 0.074 mmol), 2,5-bis(trimethylstannyl)thiophene (30.2 mg, 0.074 mmol), $Pd_2(dba)_3$ (2.8 mg, 4 mol%.), P(*o*-tol)$_3$ (3.6 mg, 16 mol%), and 10 mL of toluene. The tube was charged with nitrogen through a freeze-pump-thaw cycle for three times. The mixture was stirred at 110 ℃ for 48 h. *N,N'*-Diethylphenylazothioformamide (10 mg) was then added and the mixture was stirred for 1 h to remove any residual catalyst before being precipitated into methanol (200 mL). The precipitate was filtered through a nylon filter and purified via Soxhlet extraction for 12 h with methanol, 12 h with acetone, 12 h with hexane, and finally was collected with chloroform. The chloroform solution was then concentrated and precipitated into methanol (200 mL), and filtered off to afford a dark solid (66 mg). Yield: 81%, M_n: 14.0 kDa, M_w: 33.6 kDa, PDI: 2.40; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 366 K, ppm): δ 8.32 – 6.61 (m, 6H), 3.25 – 2.50 (m, 4H), 1.92 – 1.61 (m, 2H), 1.61 – 0.91 (m, 80H), 0.91 – 0.60 (m, 12H); Elemental Anal. Calcd for $(C_{68}H_{104}BNS_5)_n$: C, 73.80; H, 9.47; N, 1.27; Found: C, 73.32; H, 9.49; N, 1.12.

P2: The synthetic procedure is similar to that of P**1**. Yield: 82%, M_n: 18.4 kDa, M_w: 43.4 kDa, PDI: 2.36; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 366 K, ppm): δ 8.12 – 6.41 (m, 8H), 3.25 – 2.50 (m, 4H), 1.92 – 1.61 (m, 2H), 1.61 – 0.91 (m, 80H), 0.91 – 0.60 (m, 12H); Elemental Anal. Calcd for $(C_{72}H_{106}BNS_6)_n$: C, 72.74; H, 8.99; N, 1.18; Found: C, 71.50; H, 9.02; N, 1.10.

2. Gel Permeation Chromatography (GPC)

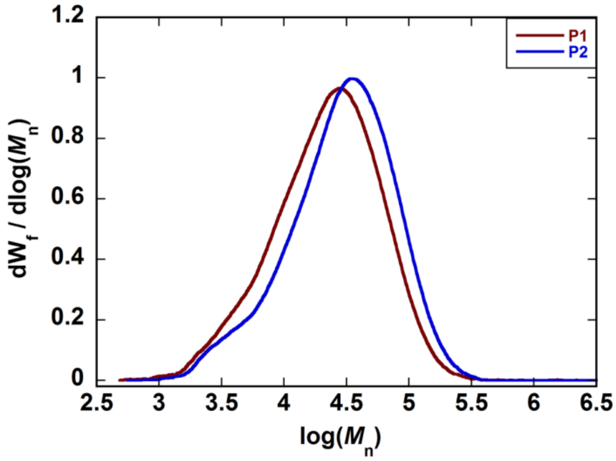


Fig. S1 GPC traces of **P1** and **P2** measured at 150 ℃ in 1,2,4-trichlorobenzene.

3. Thermal Properties (TGA and DSC)

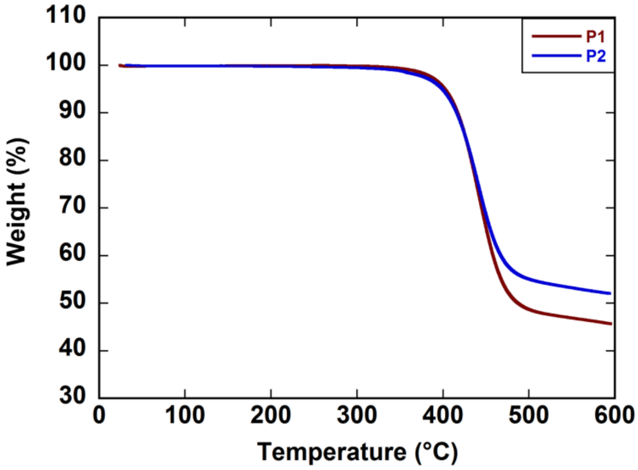


Fig. S2 TGA curves of **P1** and **P2**. T_d with 5% weight loss: 402 ℃ (**P1**), 399 ℃ (**P2**).

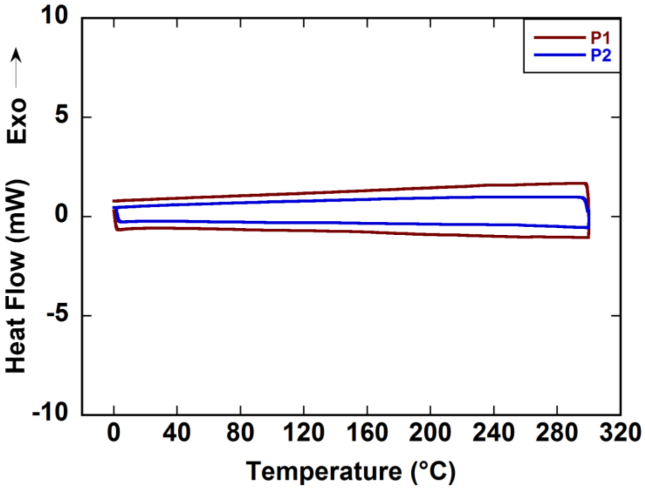


Fig. S3 DSC traces of polymers **P1** and **P2**.

4. Absorption Spectra

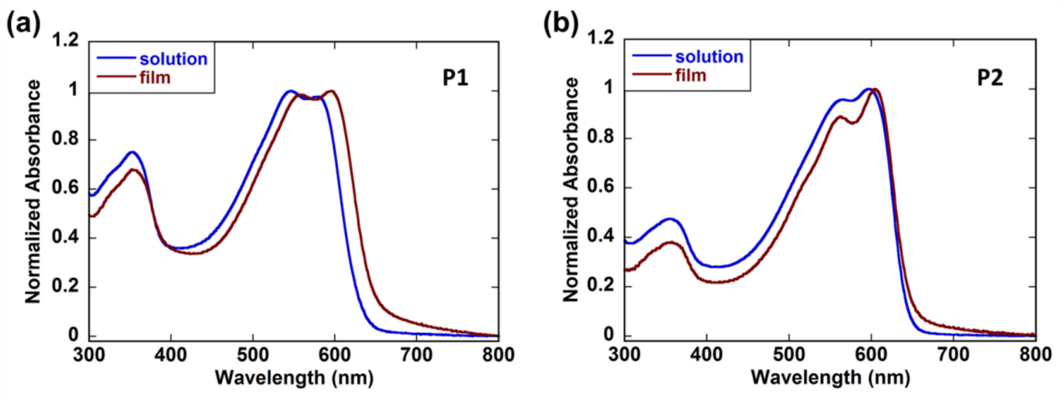


Fig. S4 Absorption spectra of (a) **P1** and (b) **P2** both in $CHCl_3$ (1×10^{-5} M) solutions solution and in spin-coated thin films.

5. Cyclic Voltammogram (CV)

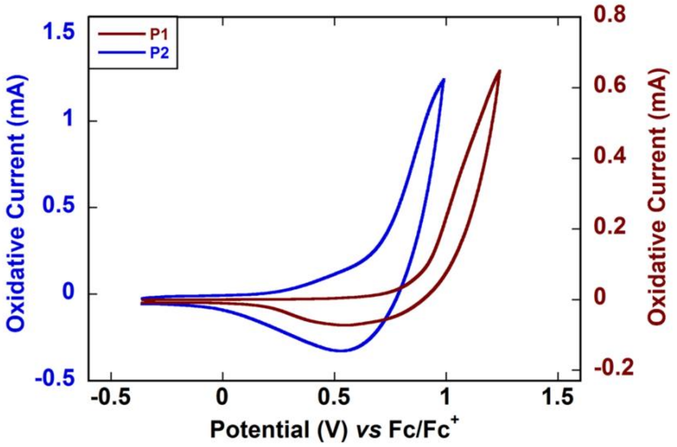


Fig. S5 Cyclic voltammograms of drop-casted films of **P1** and **P2** in acetonitrile containing 0.1 M *n*-Bu_4NPF_6 as the supporting electrolyte. Ferrocene was used as an external standard. The HOMO energy levels were estimated from the equation HOMO $= -4.80 - E_{ox}$ based on the oxidation onsets.

6. Photoelectron Spectroscopy (PES)

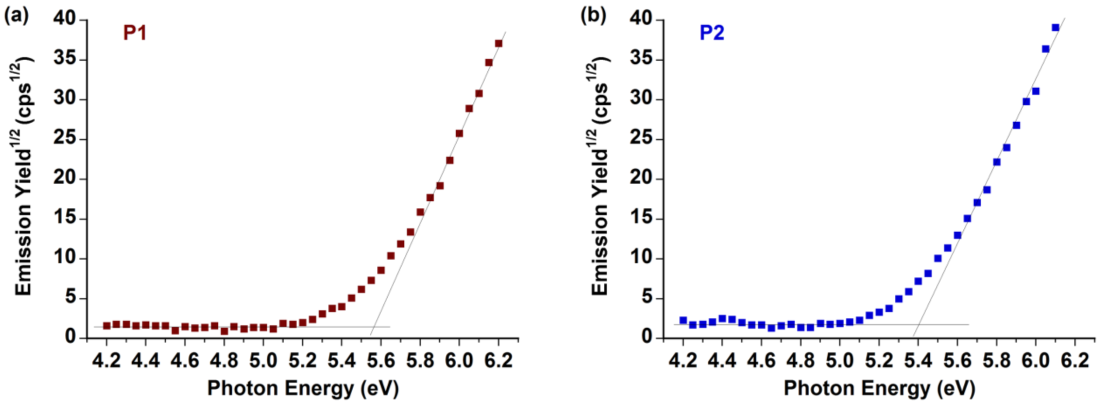


Fig. S6 PES spectra of **P1** and **P2** in thin films (work function: **P1**, –5.57 eV; **P2**, 5.40 eV).

7. Atomic Force Microscopy (AFM)

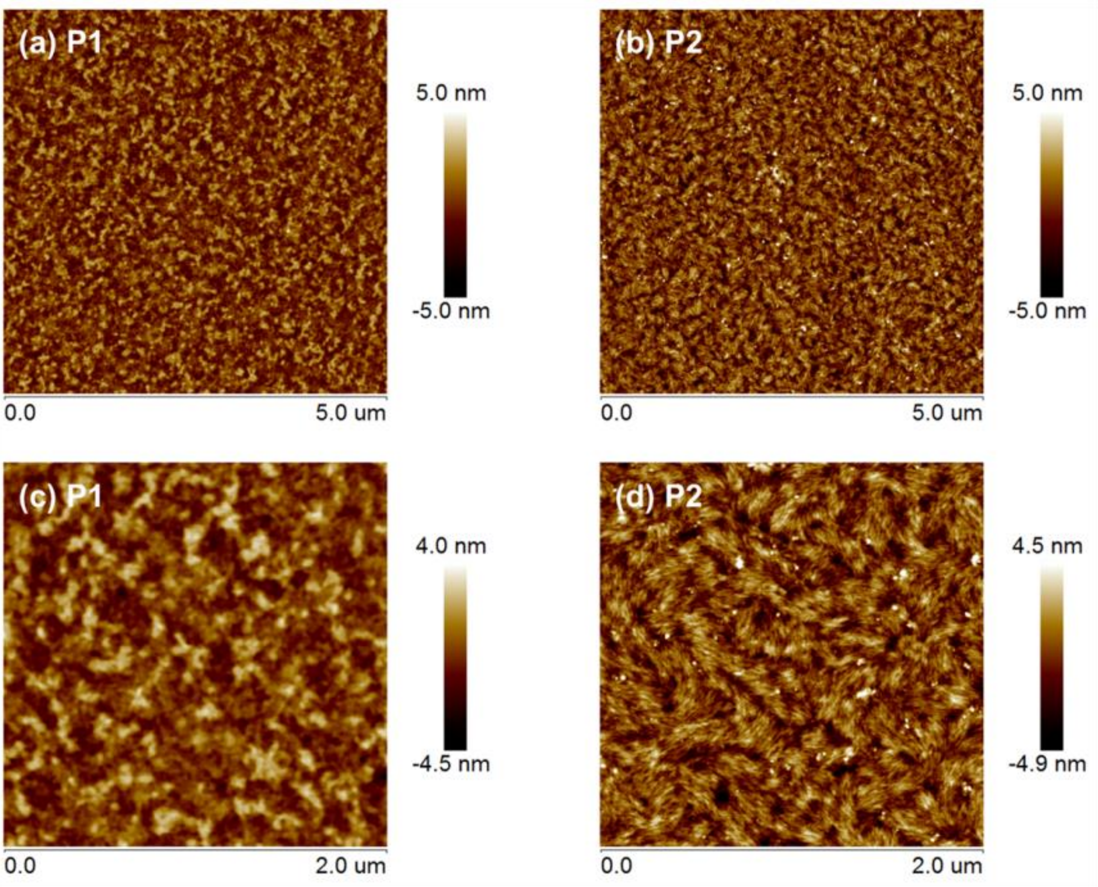


Fig. S7 AFM height images of **P1** and **P2** films.

8. X-Ray Diffraction (XRD)

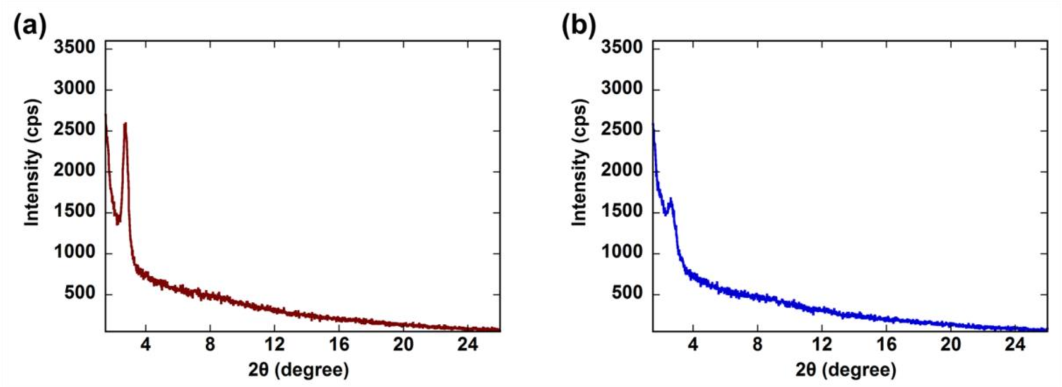


Fig. S8 Out-of-plane XRD patterns of (a) **P1** and (b) **P2** thin films.

9. Computational Studies

Calculations were performed using the Gaussian 09 software package.[1] The geometries and energies were calculated at the B3LYP/6-31G* level.

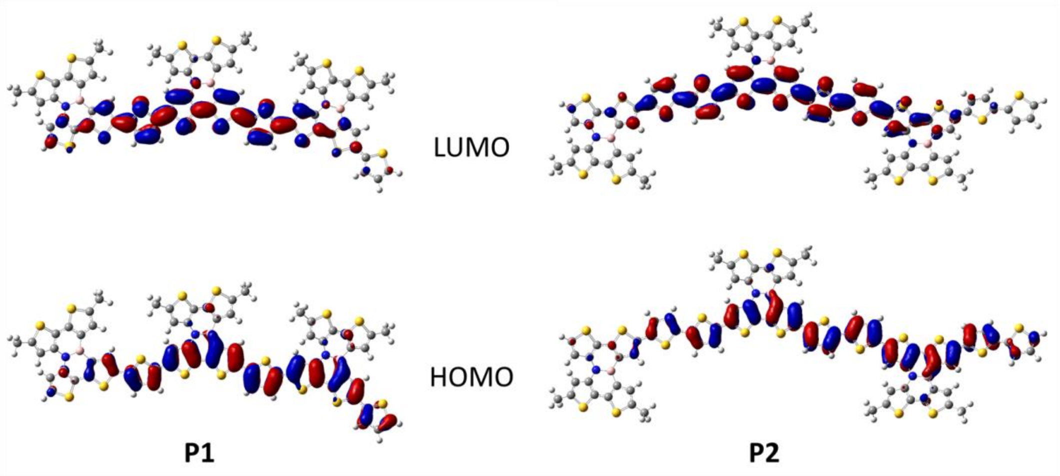


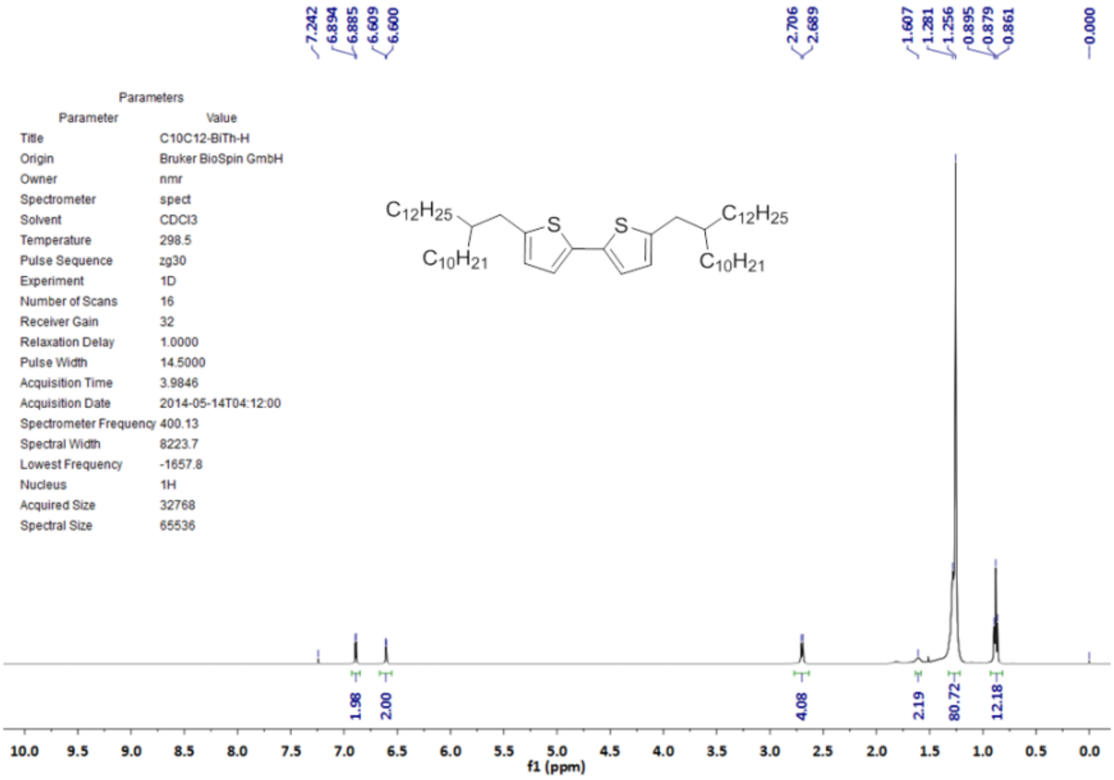
Fig. S9 DFT-calculated molecular orbitals of the trimers of **P1** and **P2**. Alkyl chains were replaced with methyl groups to simplify the calculations. The HOMO and LUMO of both polymers are delocalized over the conjugated main chain, similar to the electronic structure of polythiophenes.[2]

Reference:

(1) Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.;Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2010.

(2) Z. Fei, P. Boufflet, S. Wood, J. Wade, J. Moriarty, E. Gann, E. L. Ratcliff, C. R. McNeill, H. Sirringhaus, J.-S. Kim and M. Heeney, *J. Am. Chem. Soc.*, **2015**, *137*, 6866.

10. NMR Spectra



Parameters

Parameter	Value
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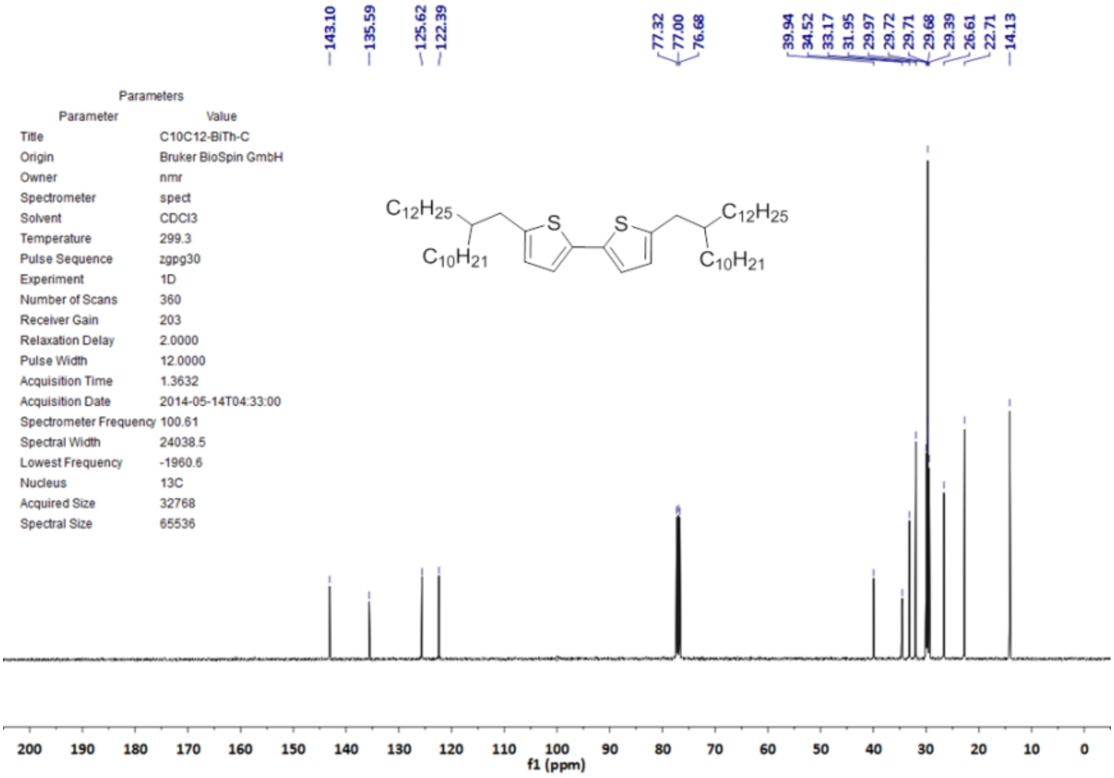
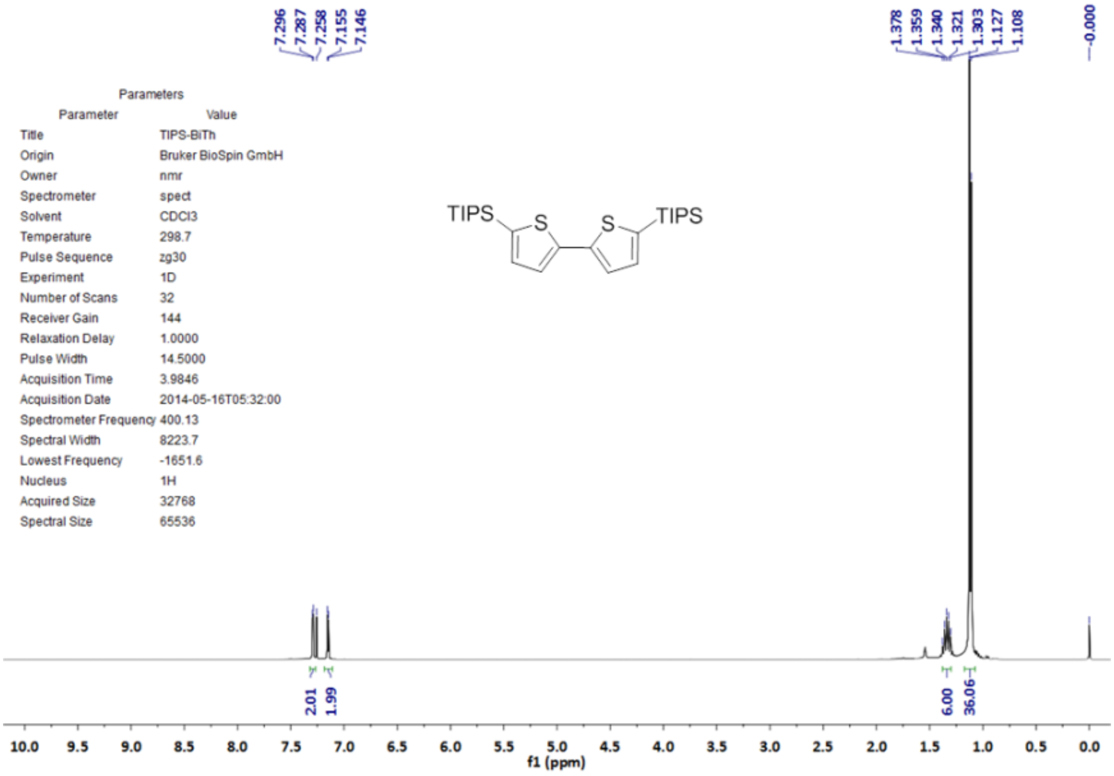
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	298.5
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9846
Acquisition Date	2014-05-14T04:12:00
Spectrometer Frequency	400.13
Spectral Width	8223.7
Lowest Frequency	-1657.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
Title	C10C12-BiTh-C
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	299.3
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	360
Receiver Gain	203
Relaxation Delay	2.0000
Pulse Width	12.0000
Acquisition Time	1.3632
Acquisition Date	2014-05-14T04:33:00
Spectrometer Frequency	100.61
Spectral Width	24038.5
Lowest Frequency	-1960.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
Title	TIPS-BiTh
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	298.7
Pulse Sequence	zg30
Experiment	1D
Number of Scans	32
Receiver Gain	144
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9846
Acquisition Date	2014-05-16T05:32:00
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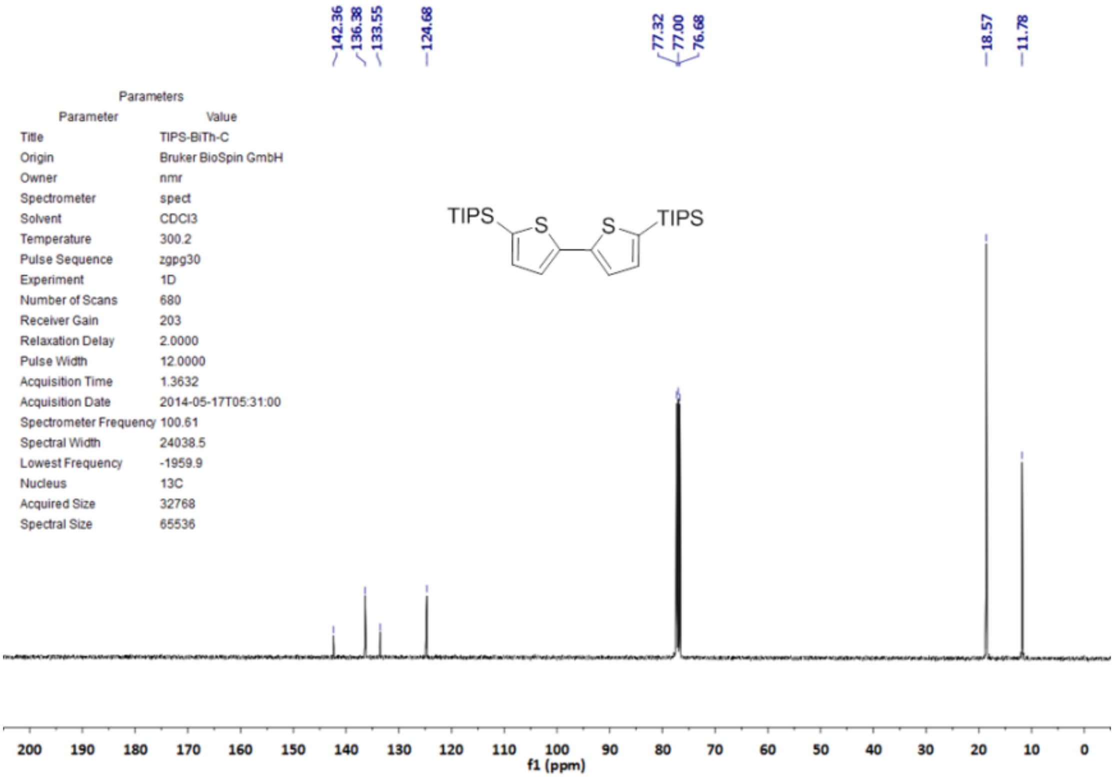
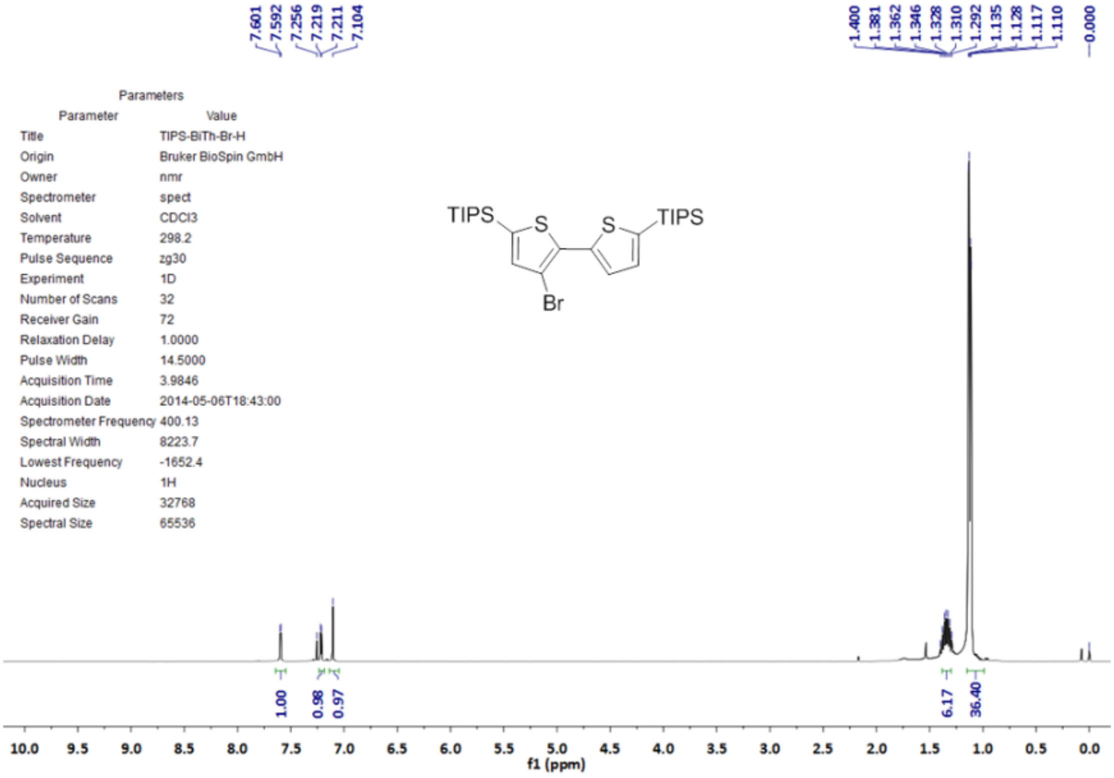
Spectral Width	8223.7
Lowest Frequency	-1651.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



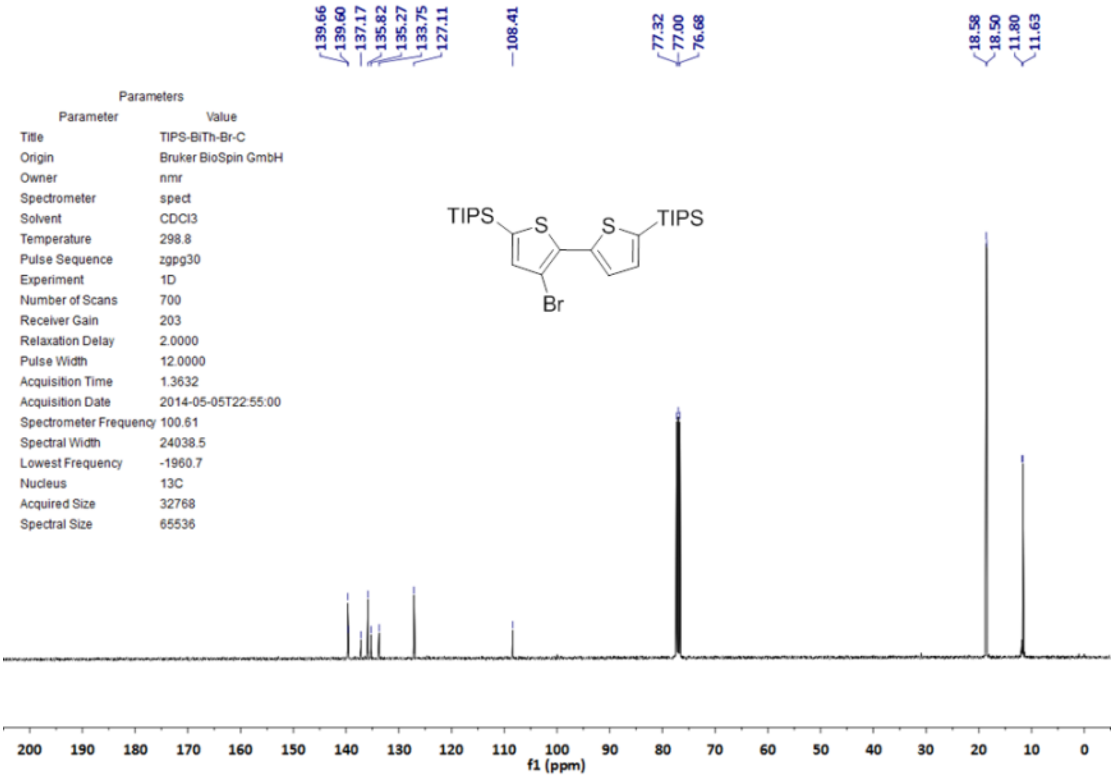
Parameters

Parameter	Value
Title	TIPS-BiTh-C
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	300.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	680
Receiver Gain	203
Relaxation Delay	2.0000
Pulse Width	12.0000
Acquisition Time	1.3632
Acquisition Date	2014-05-17T05:31:00
Spectrometer Frequency	100.61
Spectral Width	24038.5
Lowest Frequency	-1959.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
Title	TIPS-BiTh-Br-H
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	32
Receiver Gain	72
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9846
Acquisition Date	2014-05-06T18:43:00
Spectrometer Frequency	400.13
Spectral Width	8223.7
Lowest Frequency	-1652.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
Title	TIPS-BiTh-Br-C
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	298.8
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	700
Receiver Gain	203
Relaxation Delay	2.0000
Pulse Width	12.0000
Acquisition Time	1.3632
Acquisition Date	2014-05-05T22:55:00
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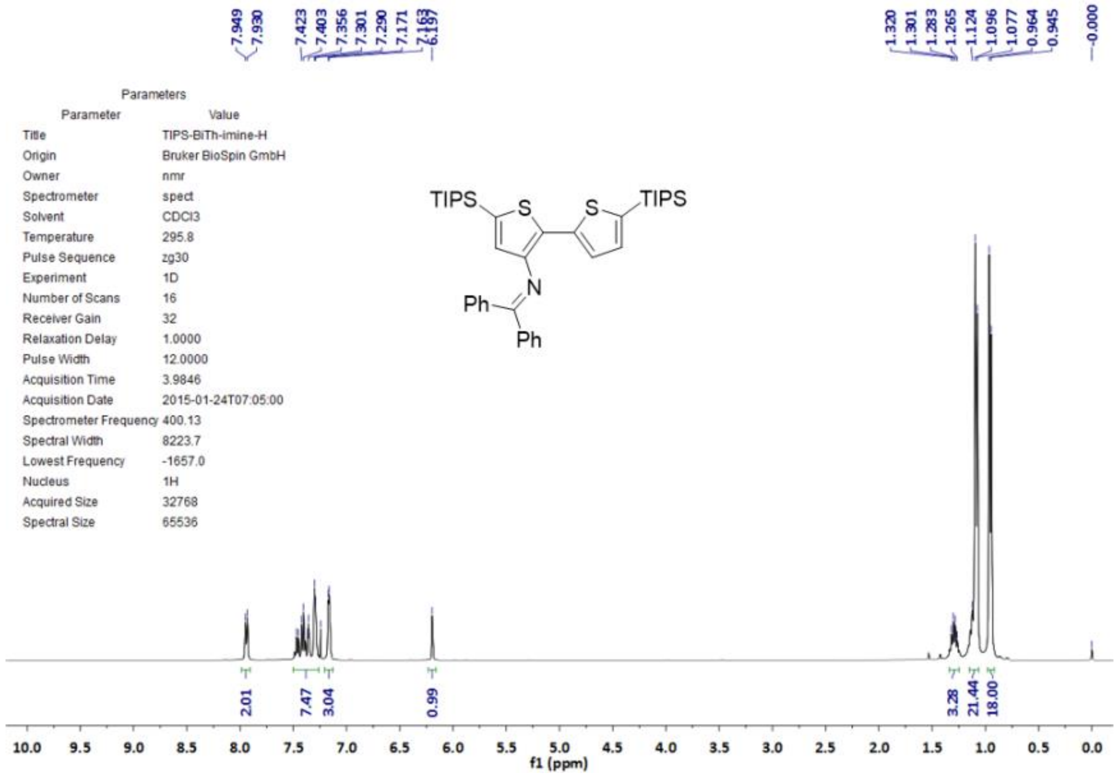
Spectral Width	24038.5
Lowest Frequency	-1960.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
Title	TIPS-BiTh-imine-H
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	295.8
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	12.0000
Acquisition Time	3.9846
Acquisition Date	2015-01-24T07:05:00
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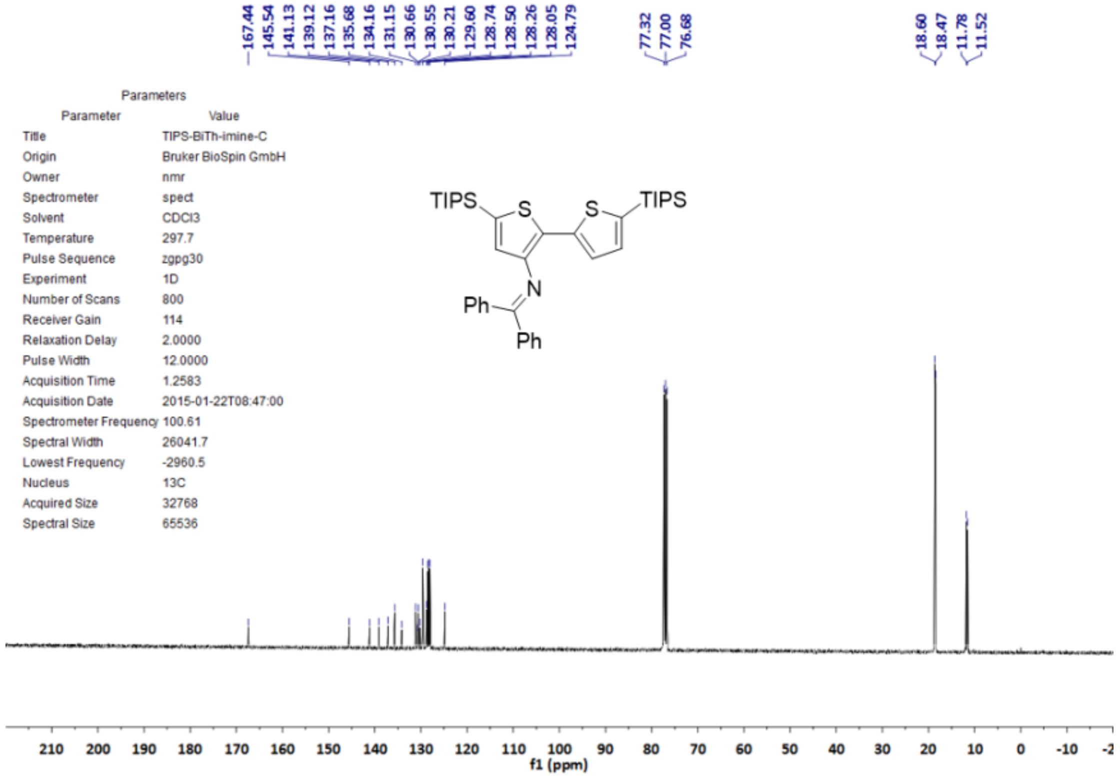
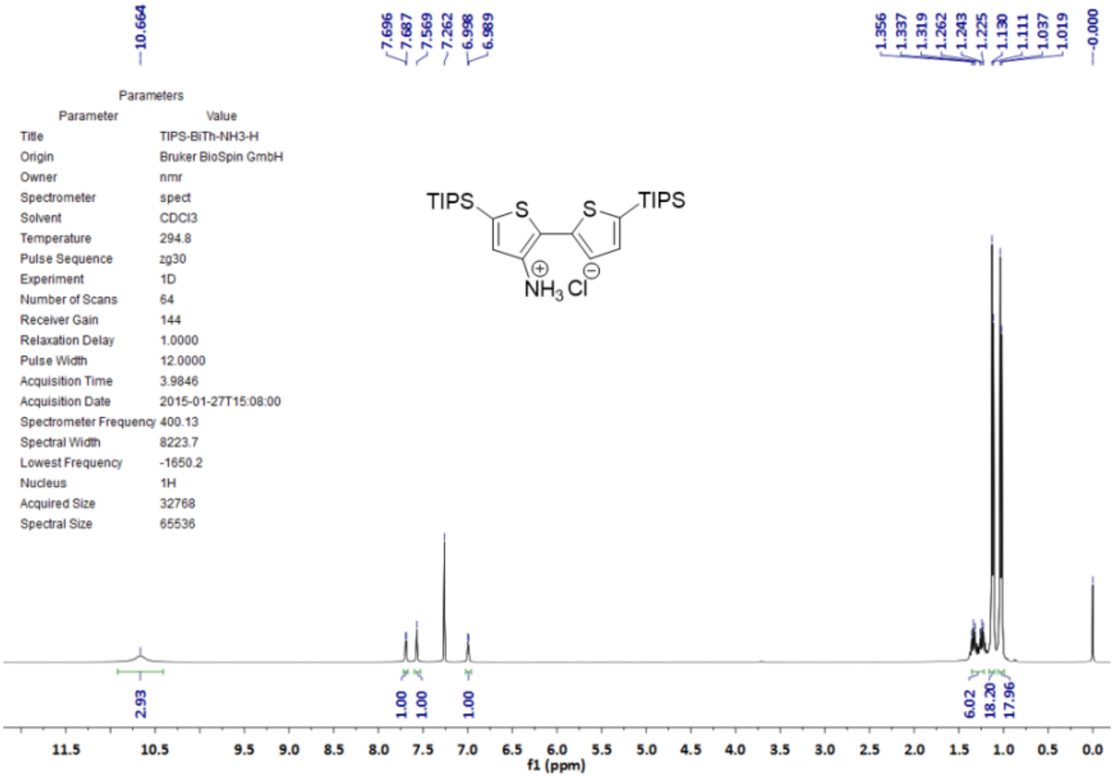
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
Title	TIPS-BiTh-imine-C
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	297.7
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	800
Receiver Gain	114
Relaxation Delay	2.0000
Pulse Width	12.0000
Acquisition Time	1.2583
Acquisition Date	2015-01-22T08:47:00
Spectrometer Frequency	100.61
Spectral Width	26041.7
Lowest Frequency	-2960.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
Title	TIPS-BiTh-NH3-H
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	294.8
Pulse Sequence	zg30
Experiment	1D
Number of Scans	64
Receiver Gain	144
Relaxation Delay	1.0000
Pulse Width	12.0000
Acquisition Time	3.9846
Acquisition Date	2015-01-27T15:08:00
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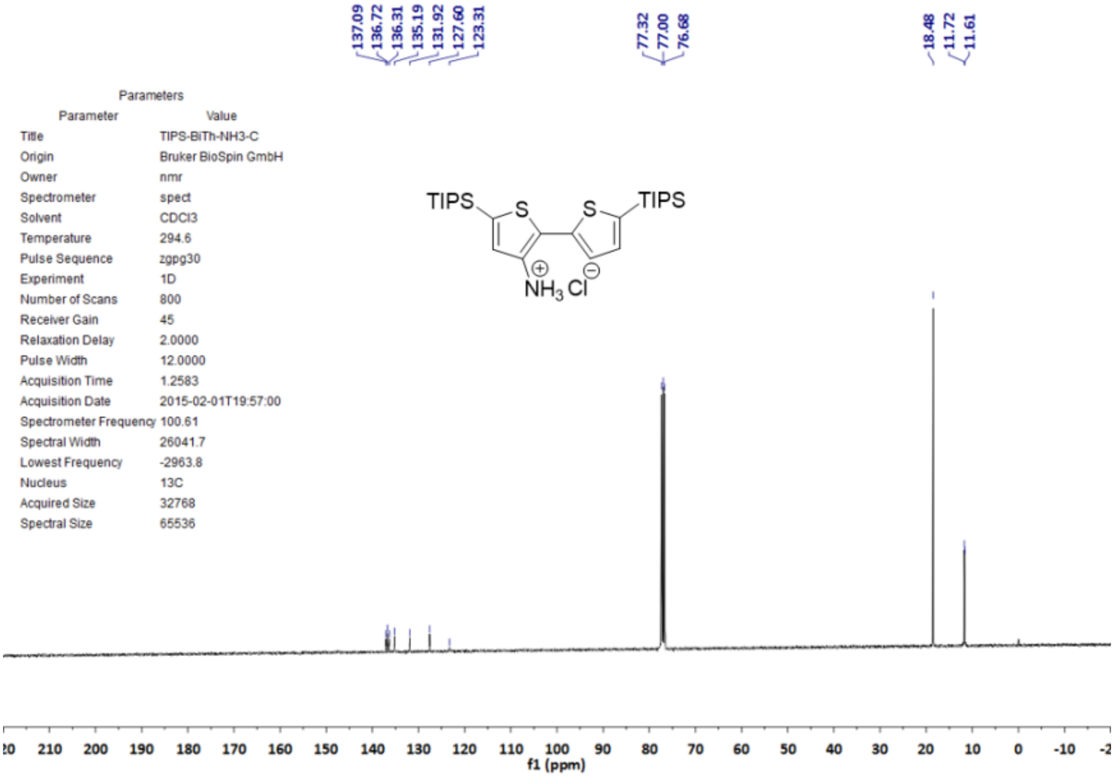
Lowest Frequency	-1650.2
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
Title	TIPS-BiTh-NH3-C
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	294.6
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	800
Receiver Gain	45
Relaxation Delay	2.0000
Pulse Width	12.0000
Acquisition Time	1.2583
Acquisition Date	2015-02-01T19:57:00
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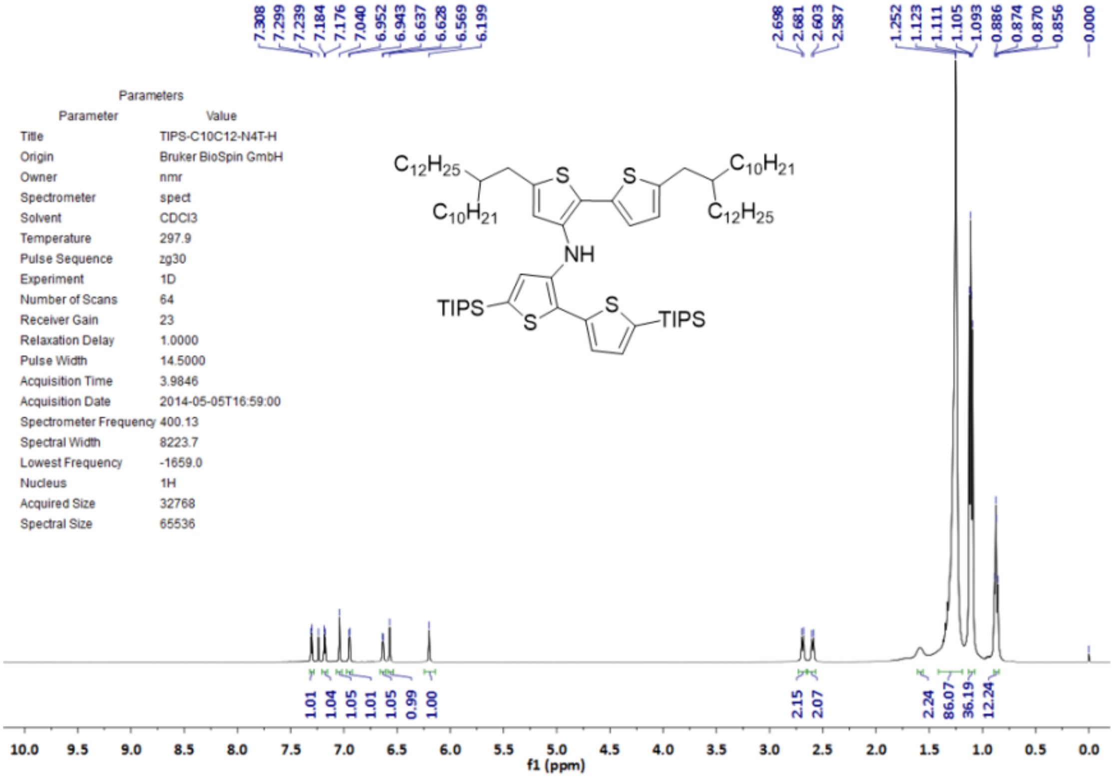
Spectral Width	26041.7
Lowest Frequency	-2963.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
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Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	297.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	64
Receiver Gain	23
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9846
Acquisition Date	2014-05-05T16:59:00
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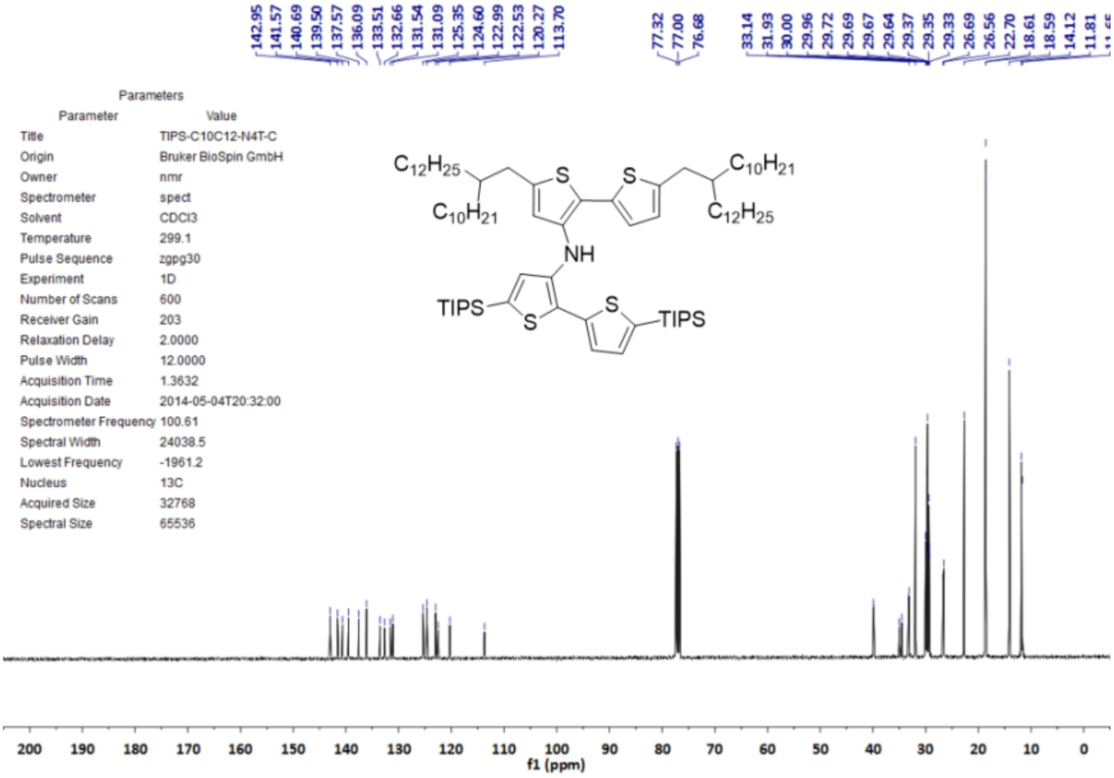
Spectral Width	8223.7
Lowest Frequency	-1659.0
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
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Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	299.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	600
Receiver Gain	203
Relaxation Delay	2.0000
Pulse Width	12.0000
Acquisition Time	1.3632
Acquisition Date	2014-05-04T20:32:00
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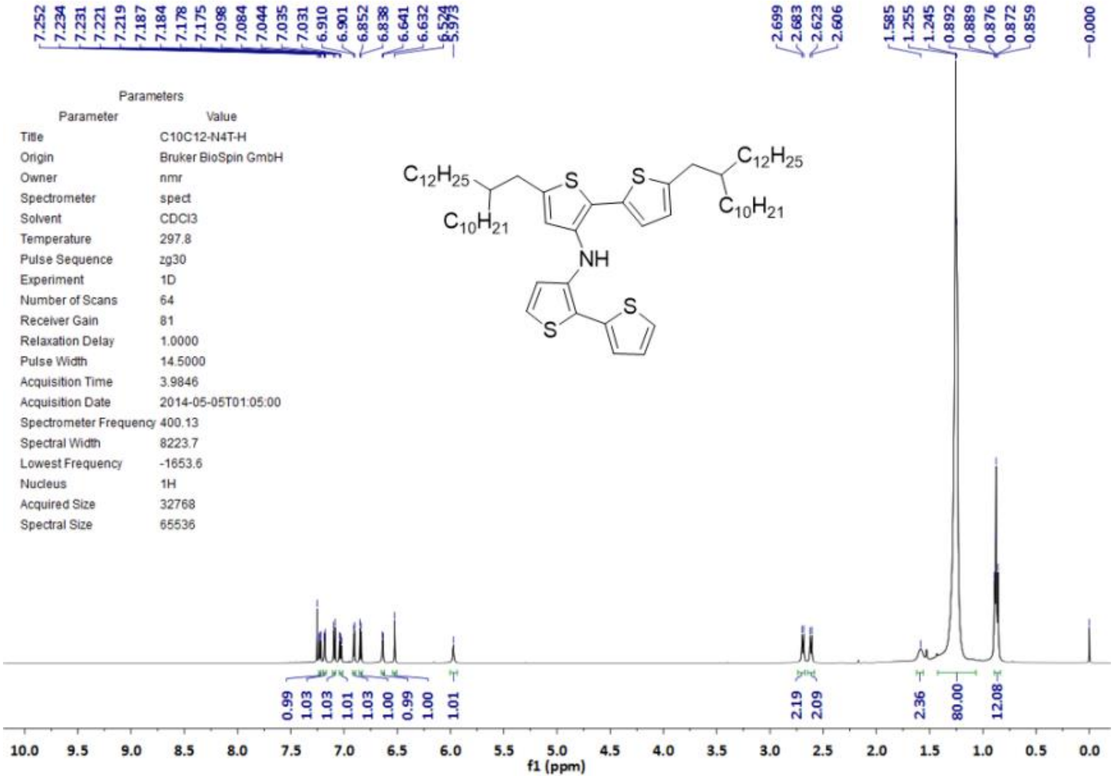
Spectral Width	24038.5
Lowest Frequency	-1961.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
Title	C10C12-N4T-H
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	297.8
Pulse Sequence	zg30
Experiment	1D
Number of Scans	64
Receiver Gain	81
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9846
Acquisition Date	2014-05-05T01:05:00
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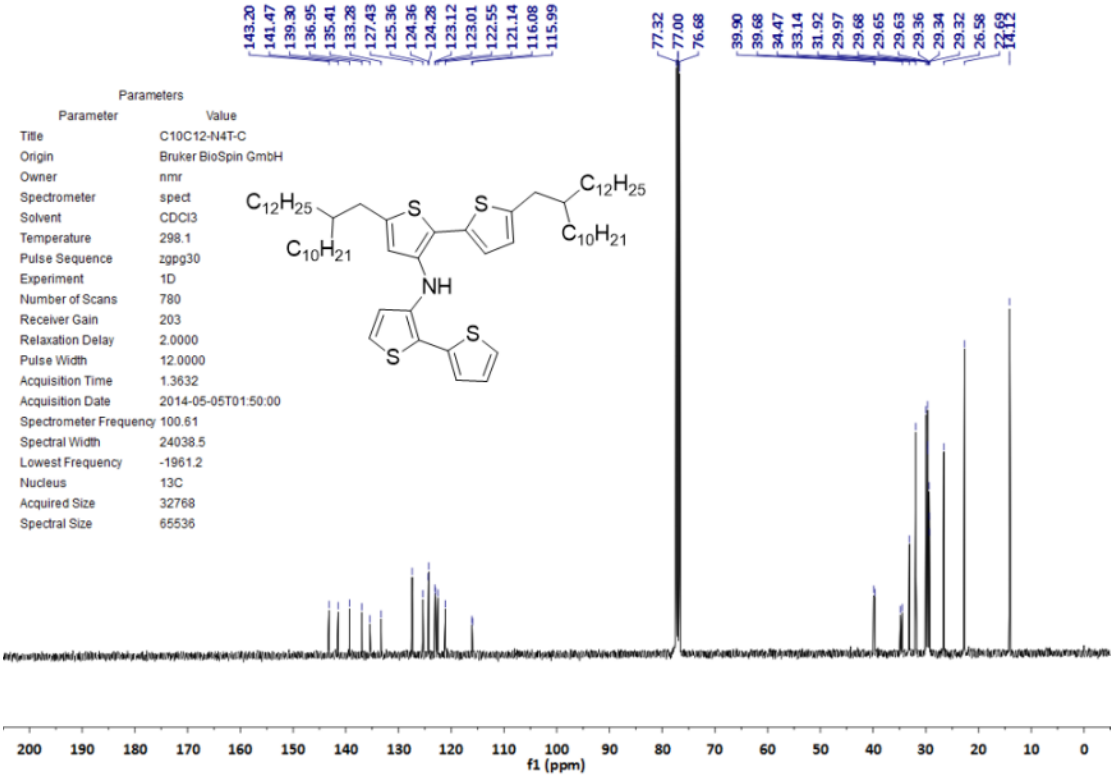
Spectral Width	8223.7
Lowest Frequency	-1653.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
Title	C10C12-N4T-C
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	780
Receiver Gain	203
Relaxation Delay	2.0000
Pulse Width	12.0000
Acquisition Time	1.3632
Acquisition Date	2014-05-05T01:50:00
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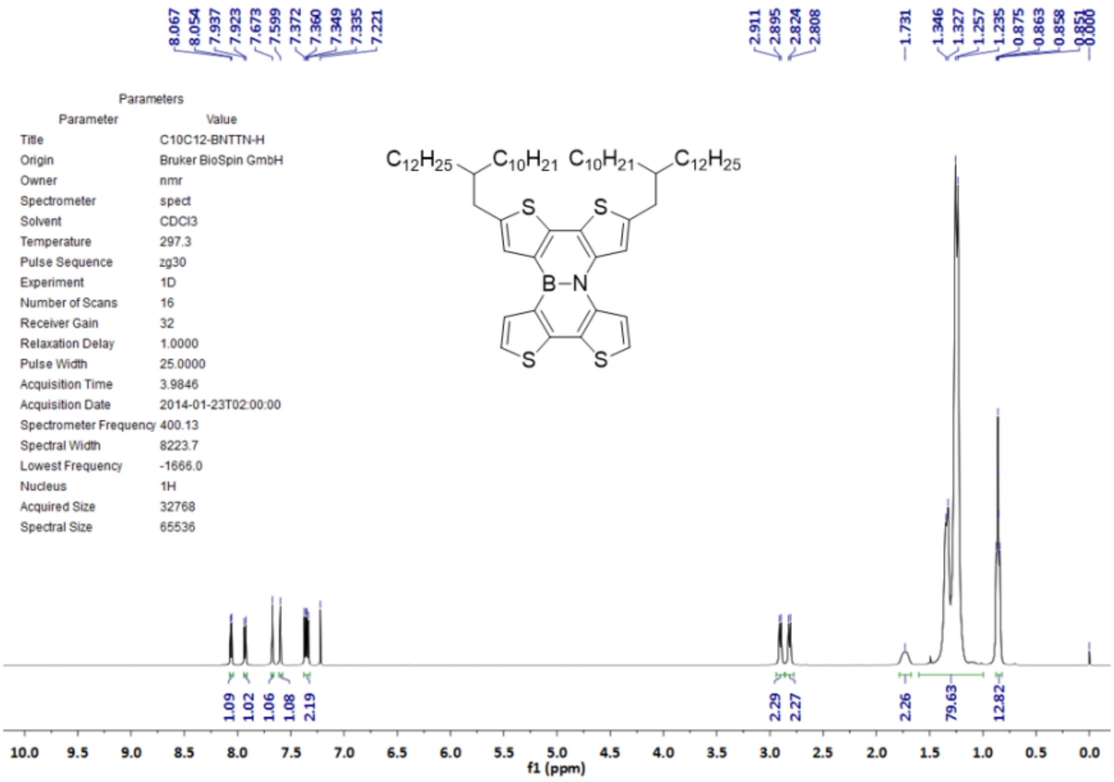
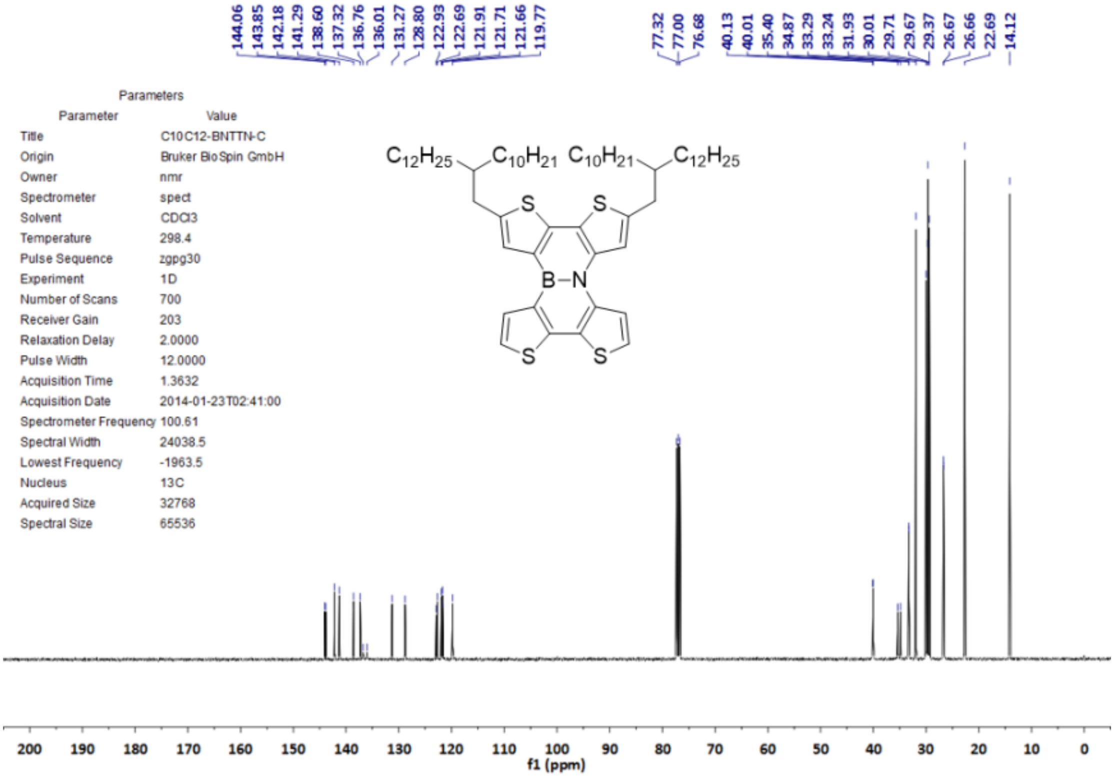
Spectral Width	24038.5
Lowest Frequency	-1961.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
Title	C10C12-BNTTN-H
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	297.3
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	25.0000
Acquisition Time	3.9846
Acquisition Date	2014-01-23T02:00:00
Spectrometer Frequency	400.13
Spectral Width	8223.7
Lowest Frequency	-1666.0
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
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Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	298.4
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	700
Receiver Gain	203
Relaxation Delay	2.0000
Pulse Width	12.0000
Acquisition Time	1.3632
Acquisition Date	2014-01-23T02:41:00
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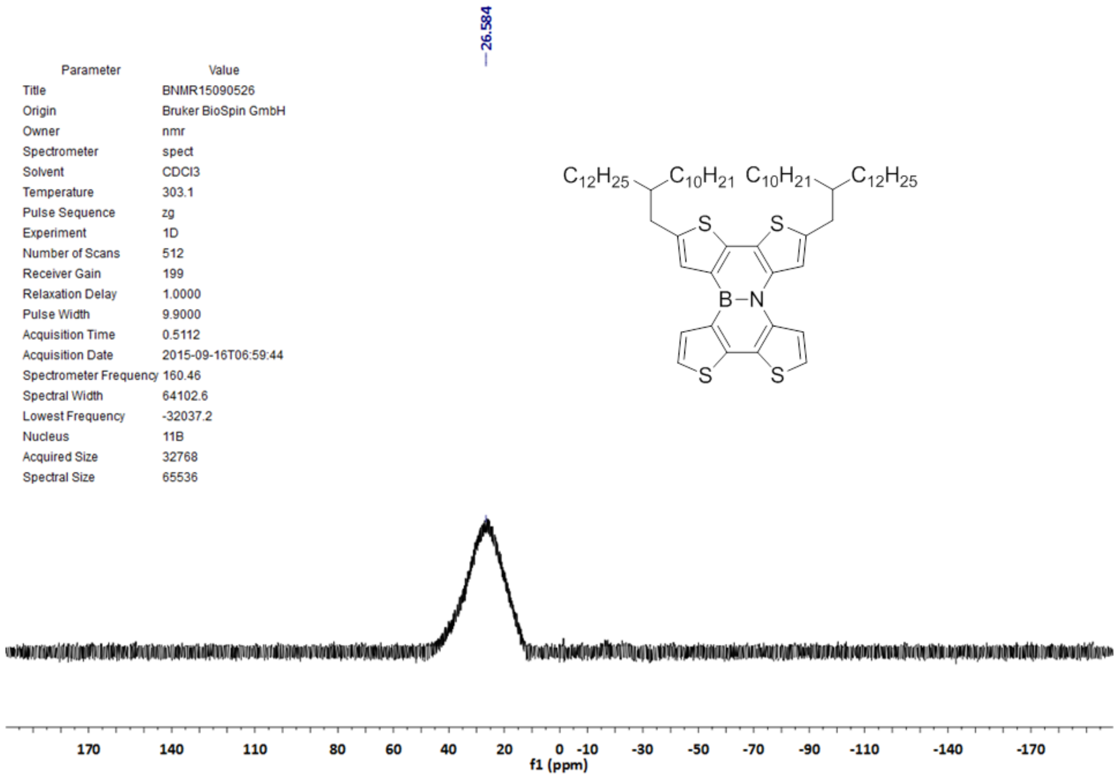
Spectral Width	24038.5
Lowest Frequency	-1963.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



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Title	BNMR15090526
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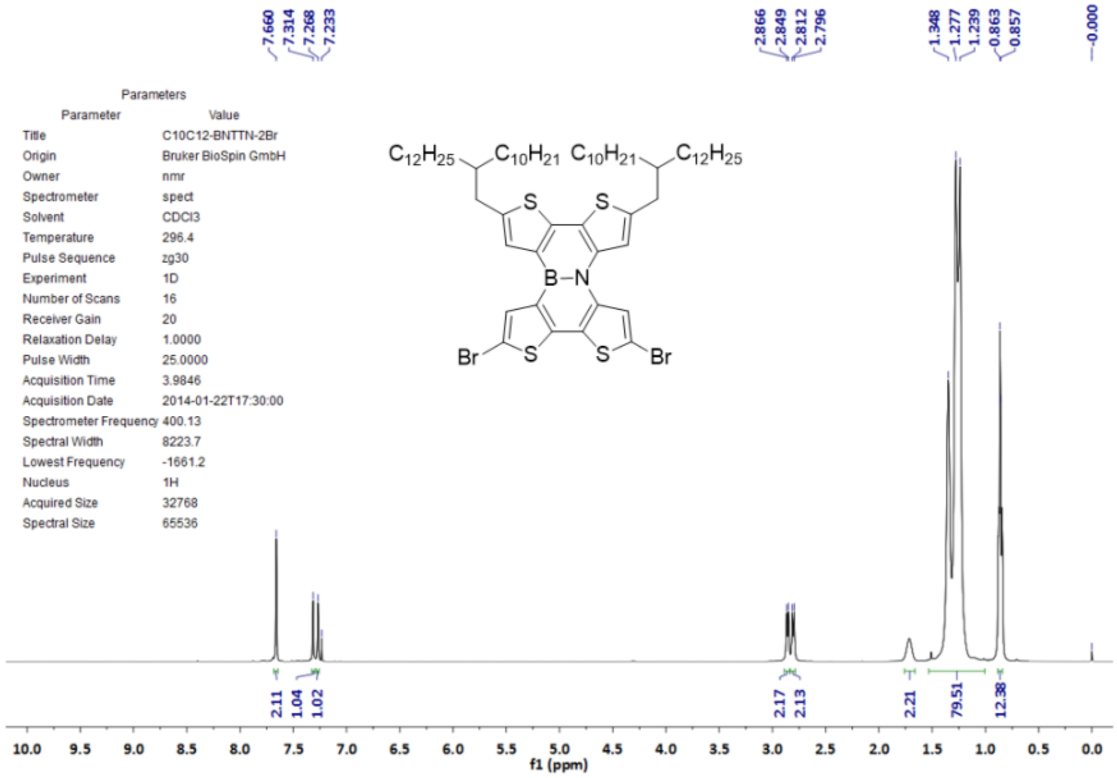
Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	303.1
Pulse Sequence	zg
Experiment	1D
Number of Scans	512
Receiver Gain	199
Relaxation Delay	1.0000
Pulse Width	9.9000
Acquisition Time	0.5112
Acquisition Date	2015-09-16T06:59:44
Spectrometer Frequency	160.46
Spectral Width	64102.6
Lowest Frequency	-32037.2
Nucleus	11B
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
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Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	296.4
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	20
Relaxation Delay	1.0000
Pulse Width	25.0000
Acquisition Time	3.9846
Acquisition Date	2014-01-22T17:30:00
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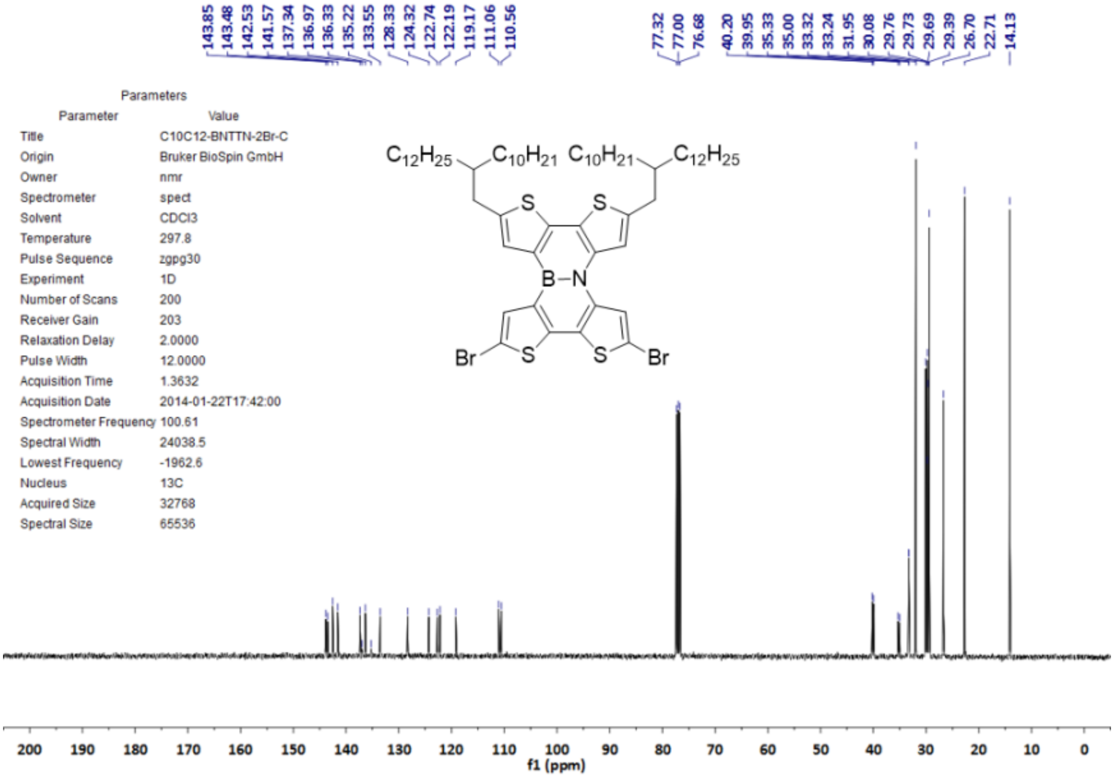
Spectral Width	8223.7
Lowest Frequency	-1661.2
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



Parameters

Parameter	Value
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Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	297.8
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	200
Receiver Gain	203
Relaxation Delay	2.0000
Pulse Width	12.0000
Acquisition Time	1.3632
Acquisition Date	2014-01-22T17:42:00
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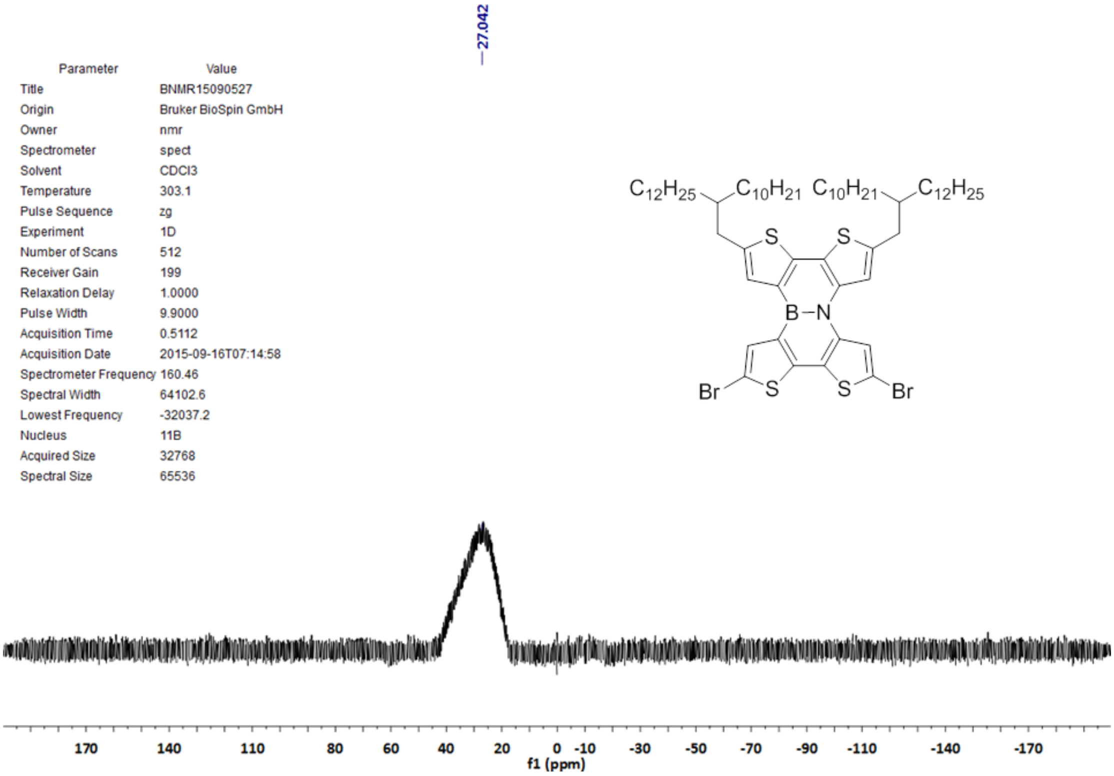
Spectral Width	24038.5
Lowest Frequency	-1962.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Title	BNMR15090527
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Owner	nmr
Spectrometer	spect
Solvent	CDCl3
Temperature	303.1
Pulse Sequence	zg
Experiment	1D
Number of Scans	512
Receiver Gain	199
Relaxation Delay	1.0000
Pulse Width	9.9000
Acquisition Time	0.5112
Acquisition Date	2015-09-16T07:14:58
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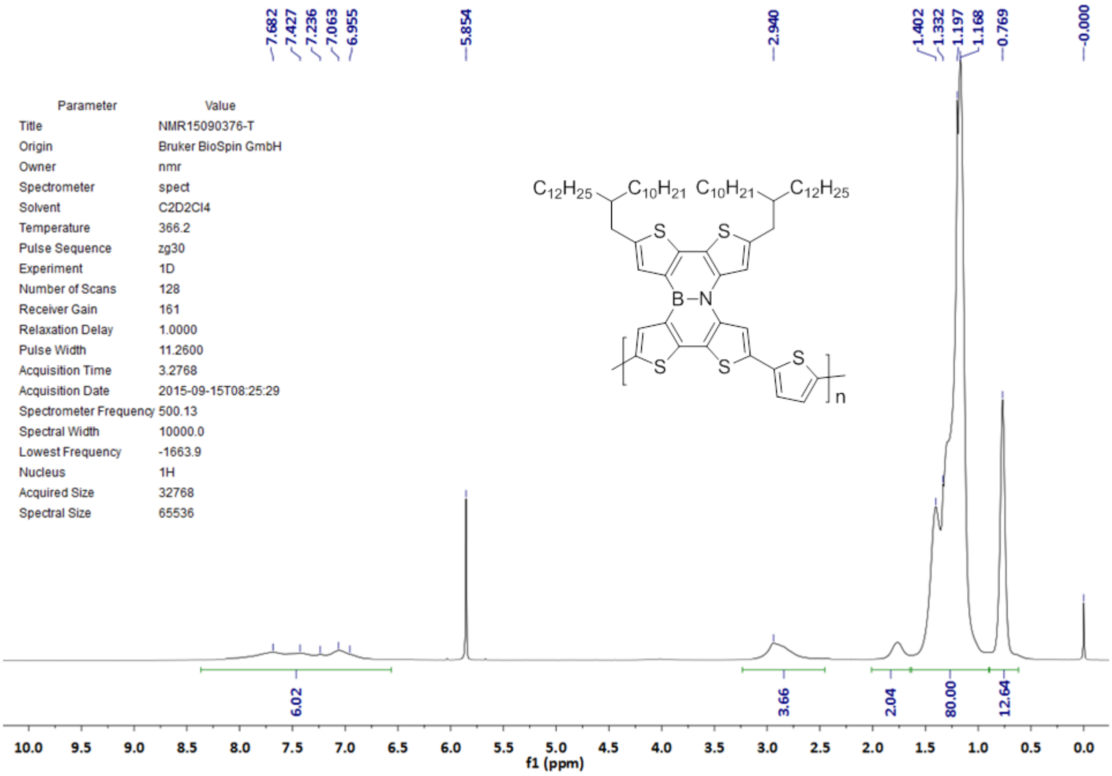
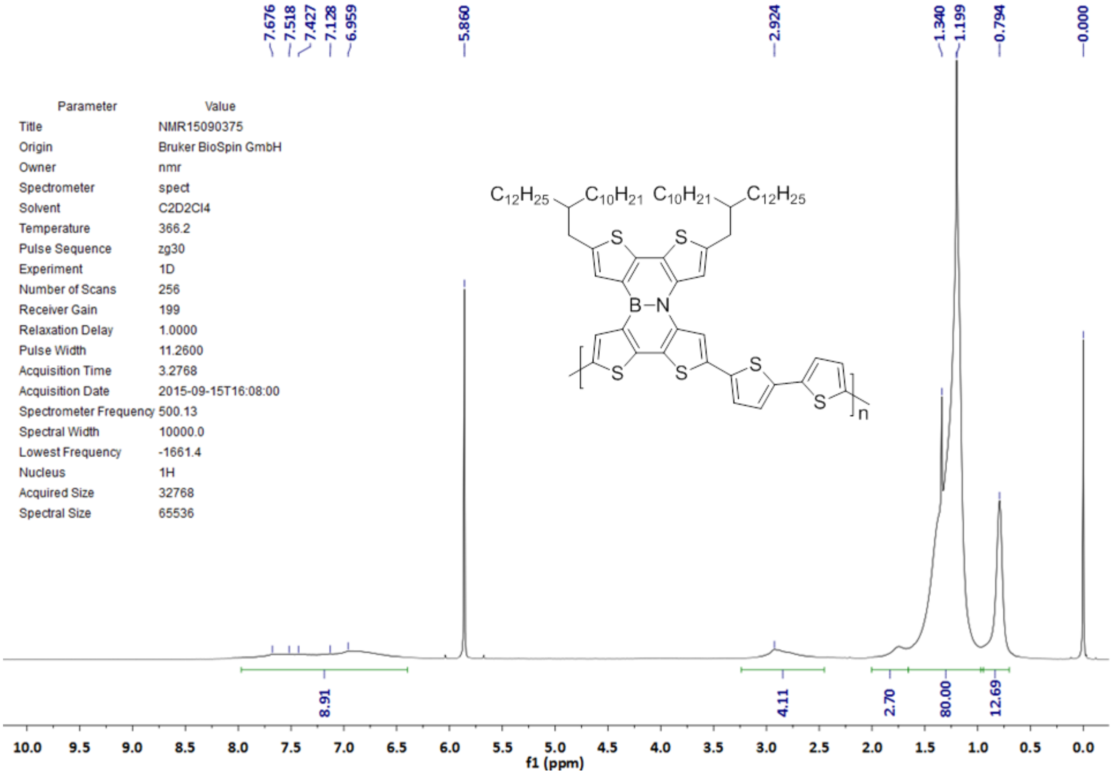


Parameter	Value
Title	NMR15090376-T
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	C2D2Cl4
Temperature	366.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	128
Receiver Gain	161
Relaxation Delay	1.0000
Pulse Width	11.2600
Acquisition Time	3.2768
Acquisition Date	2015-09-15T08:25:29
Spectrometer Frequency	500.13
Spectral Width	10000.0
Lowest Frequency	-1663.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Title	NMR15090375
Origin	Bruker BioSpin GmbH
Owner	nmr
Spectrometer	spect
Solvent	C2D2Cl4
Temperature	366.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	256
Receiver Gain	199
Relaxation Delay	1.0000
Pulse Width	11.2600
Acquisition Time	3.2768
Acquisition Date	2015-09-15T16:08:00
Spectrometer Frequency	500.13
Spectral Width	10000.0
Lowest Frequency	-1661.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536