Supporting Information

Modulation of charge transport through single-molecule bilactam junctions by the tuning of hydrogen bond

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Abstract: The charge transport through single-molecule junctions highly depends on the intramolecular coupling determined by the twisting angles between molecular building blocks. However, elaborate control of twisting angle in the complex conjugated system to tune the charge transport through single-molecule junctions remained unexplored. In this work, we have synthesized and characterized their single-molecule conductance of a series of bilactam derivatives to investigate the twisting angle tuning effect induced by the intramolecular hydrogen bond on the charge transport through their single-molecules junctions. We found that the bilactam derivatives with strong intramolecular hydrogen bonds exhibited twice higher conductance because of the reduced dihedral twisting, which was reversible for at least three cycles with the addition of hydrogen bond destroy solvent. The combined DFT calculations reveal that the presence of intramolecular hydrogen bonds promotes the planarization of the molecular structure without additional transmission channels. Our findings offer a novel strategy for the control of molecular switches via tuning the molecular twisting.

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1. Synthesis Information

1.1 Synthesis Information

Materials and Characterization Techniques.

We carried out all reactions and operations under argon (Ar) atmosphere with the use of standard Schlenk techniques. Unless otherwise specified, all chemicals were purchased from commercial resources (Adamas or other) and used as received. The purification of dichloromethane and triethylamine were distillated with calcium hydride. Anhydrous tetrahydrofuran is obtained by distilling water away from sodium metal, using benzophenone as an indicator. N-hexylthiophen-3-amine was synthesized as procedure previously reported.[1-3] The ^{1}H NMR and the ^{13}C NMR spectra were collected on a Bruker AVANCE III HD 400 spectrometer operating at 400 MHz in deuterated chloroform solution with TMS as reference, respectively. High-resolution mass spectroscopy (HRMS) measurements were carried out on a Shimadzu LCMS-IT-TOF. The UV-Vis spectra were measured by using a Shimadzu UV-3600 spectrophotometer.

1.2 Synthetic Experiments

Synthesis steps of N1,N4-dihexyl-N1,N4-di(thiophen-3-yl)succinamide (DTSA)

Oxalyl chloride (10.35 mL, 121 mmol) and 3 drops of DMF were added to a solution of succinic acid (2.87 g, 24.3 mmol) in chloroform (50 mL), and stirred for 6 hours at room temperature. The dichloride was obtained by removing the solvent under vacuum and used in the next step without further purification. A solution of dichloride in dry CH_2Cl_2 (40 mL) was slowly added to the solution of N-hexylthiophen-3-amine (9.91 g, 54.0 mmol) and dry triethylamine (8 mL) in dry CH_2Cl_2 (60 mL) at 0 °C and stirred at room temperature overnight. After that, the mixture was dissolved in water and extracted three times with CH_2Cl_2. After removing the solvent of the organic layer by anhydrous Na_2SO_4, the crude product was washed with hexane to give a white solid (7.03 g, 64%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.31 (dd, *J* = 5.1, 3.2 Hz, 2H), 7.12 (d, *J* = 2.9 Hz, 2H), 6.94 (d, *J* = 4.9 Hz, 2H), 3.58 (t, 4H), 2.34 (s, 4H), 1.50-1.43 (m, 4H), 1.32-1.17 (m, 12H), 0.84 (t, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 171.9, 141.0, 126.6, 125.8, 121.4, 48.9, 31.5, 29.5, 27.8, 26.4, 22.5, 14.0. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{24}H_{36}N_2O_2S_2$, 471.2110; found, 471.2107.

Synthesis steps of 4,4'-dihexyl-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTP)

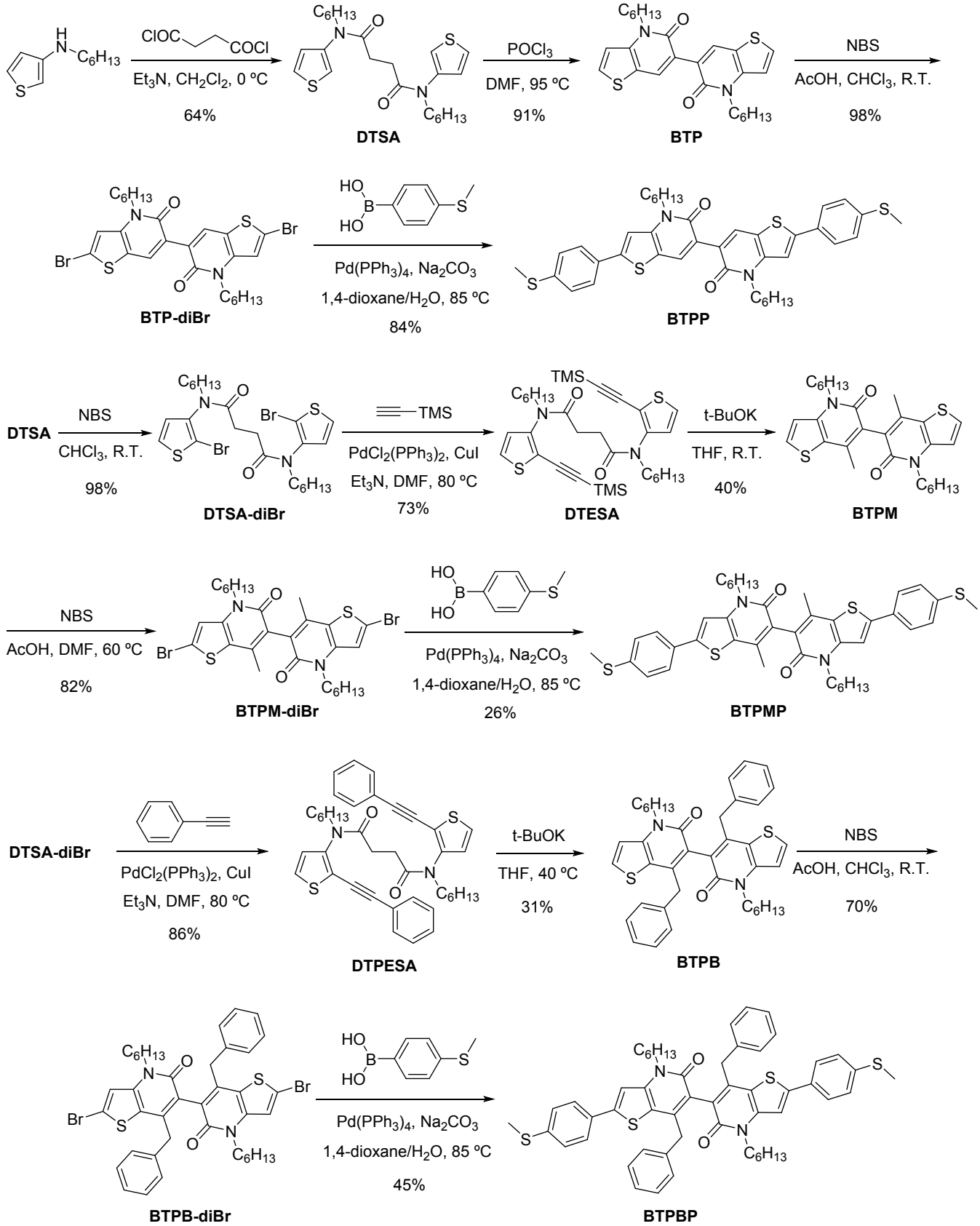
Phosphorus oxychloride (0.52 mL, 5.58 mmol) was added dropwise to dry DMF (10 mL) at 0 °C. The resulting solution was stirred at room temperature for 30 minutes, then added DTSA (500 mg, 1.12 mmol) and heated the stirred mixture to 95 °C for 90 minutes. After cooling, the mixture was poured into crushed ice and the resulting suspension was treated with an excess of saturated aqueous solution NaOAc and stirred at room temperature for 1 hour. Then, the mixture was extracted with CH_2Cl_2 three times. After removing the solvent of the organic layer by anhydrous Na_2SO_4, the crude product was purified with a mixture of petroleum/ethyl acetate (50:1) as eluent through a silica gel column to give a yellow solid (477 mg, 91%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.57 (s, 2H), 7.57 (d, *J* = 5.5 Hz, 2H), 7.03 (d, *J* = 5.4 Hz, 2H), 4.26 (t, 4H), 1.82-1.74 (m, 4H), 1.51-1.23 (m, 12H), 0.88 (t, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.7, 142.8, 133.6, 130.1, 122.2, 118.5, 116.0, 46.1, 31.5, 28.1, 26.8, 22.5, 14.0. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{26}H_{32}N_2O_2S_2$, 491.1797; found, 491.1796.

Synthesis steps of 2,2'-dibromo-4,4'-dihexyl-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTP-diBr)

To a solution of BTP (149 mg, 0.318 mmol) in chloroform (10 mL) were added N-bromosuccinimide (70 mg, 0.954 mmol) and a catalytic amount of acetic acid, and the mixture was stirred overnight at room temperature. The mixture was dissolved in water and extracted three times with CH_2Cl_2. After removing the solvent of the organic layer by anhydrous Na_2SO_4, the crude product was purified with a mixture of petroleum/ethyl acetate (20:1) as eluent through a silica gel column to give a yellow solid (197 mg, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.49 (s, 2H), 7.04 (s, 2H), 4.17 (t, 4H), 1.78-1.71 (m, 4H), 1.48-1.39 (m, 4H), 1.37-1.30 (m, 8H), 0.89 (t, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.3, 142.1, 132.6, 121.9, 119.7, 119.5, 119.2, 46.3, 31.5, 28.1, 26.7, 22.5, 14.0. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{26}H_{30}Br_2N_2O_2S_2$, 647.0008; found, 647.0004.

Synthesis steps of 4,4'-dihexyl-2,2'-bis(4-(methylthio)phenyl)-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTPP-SMe)

To a solution of BTP-diBr (50 mg, 0.0798 mmol), (4-(methylthio)phenyl)boronic acid (54 mg, 0.319 mmol) and anhydrous sodium carbonate (42 mg, 0.399 mmol) in a mixture of 1,4-dioxane (10 mL) and water (2 mL) was added $Pd(PPh_3)_4$ (9 mg, 7.98 μmol), then heated to 85 °C for 24 hours. The mixture was poured into water and extracted three times with CH_2Cl_2 after cooling to room temperature. After removing the solvent of the organic layer by anhydrous Na_2SO_4, the crude product was purified with a mixture of petroleum/CH_2Cl_2/ethyl acetate (5:5:1) as eluent through a silica gel column and then recrystallized from chloroform/methanol to give an orange solid (48 mg, 84 %). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.61 (s, 2H), 7.59 (d, *J* = 8.4 Hz, 4H), 7.30 (d, *J* = 8.4 Hz, 4H), 7.17 (s, 2H), 4.29 (t, 4H), 2.53 (s, 6H), 1.86-1.78 (m, 4H), 1.52-1.45 (m, 4H), 1.42-1.31 (m, 8H), 0.90 (t, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.7, 148.0, 143.3, 140.1, 133.2, 130.1, 126.5, 126.3, 121.7, 118.0, 111.0, 46.0, 31.6, 28.1, 26.8, 22.6, 15.5, 14.0. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{40}H_{44}N_2O_2S_4$, 735.2178; found, 735.2197.



Scheme S1. Synthetic routs to molecules used in conductance measurements.

Synthesis steps of N^1,N^4-bis(2-bromothiophen-3-yl)-N^1,N^4-dihexylsuccinamide (DTSA-diBr)

To a solution of DTSA (535 mg, 1.19 mmol) in chloroform (20 mL) was added N-bromosuccinimide (637 mg, 3.58 mmol). The mixture was stirred overnight at room temperature, and then was poured into water and extracted three times with CH_2Cl_2. After removing the solvent of the organic layer by anhydrous Na_2SO_4, the crude product was purified with a mixture of petroleum/ethyl acetate (8:1) as eluent through a silica gel column to give a white solid (707 mg, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.32 (d, *J* = 5.7 Hz, 2H), 6.87 (dd, *J* = 5.7, 5.7 Hz, 2H), 3.73-3.66 (m, 2H), 3.49-3.42 (m, 2H), 2.55-2.11 (m, 4H), 1.48-1.43 (m, 4H), 1.35-1.19 (m, 12H), 0.85 (t, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 171.8, 140.4, 140.2, 127.3, 127.0, 126.0, 111.2, 48.2, 31.6, 29.3, 27.9, 26.5, 22.5, 14.0. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{24}H_{34}Br_2N_2O_2S_2$, 627.0321; found, 627.0301.

Synthesis steps of N^1,N^4-dihexyl-N^1,N^4-bis(2-((trimethylsilyl)ethynyl)thiophen-3-yl)succinamide (DTESA)

To a solution of DTSA-diBr (458 mg, 0.755 mmol) in a mixture of dry DMF (5 mL) and dry triethylamine (5 mL) were added trimethylsilylacetylene (0.32 mL, 2.27 mmol), $PdCl_2(PPh_3)_2$ (26 mg, 0.0378 mmol) and CuI (7 mg, 0.0378 mmol). The mixture was heated to 80 °C for 4 hours. Then the mixture was poured into water and extracted three times with ethyl acetate after cooling to room temperature. After removing the solvent of the organic layer by anhydrous Na_2SO_4, the crude product was purified with a mixture of petroleum/ethyl acetate (8:1) as eluent through a silica gel column to give a yellow oil (351 mg, 73%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.18 (d, *J* = 5.3 Hz, 2H), 6.86 (d, *J* = 5.3 Hz, 2H), 3.59 (s, 4H), 2.39 (s, 4H), 1.47-1.42 (m, 4H), 1.29-1.16 (m, 12H), 0.82 (t, 6H), 0.16 (s, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 171.6, 144.9, 126.7, 126.1, 119.4, 104.1, 94.9, 48.6, 31.5, 29.2, 27.9, 26.4, 22.5, 13.9, -0.4. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{34}H_{52}N_2O_2S_2Si_2$, 641.3081; found, 641.3100.

Synthesis steps of 4,4'-dihexyl-7,7'-dimethyl-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTPM)

To a solution of DTESA (147 mg, 0.229 mmol) in dry tetrahydrofuran (10 mL) was added t-BuOK (103 mg, 0.917 mmol). The reaction mixture was stirred for 1 hour at room temperature, and then was poured into water and extracted three times with CH_2Cl_2. After removing the solvent of the organic layer by anhydrous Na_2SO_4, the crude product was purified with a mixture of petroleum/ethyl acetate (1:1) as eluent through a silica gel column to give a yellow oil (45 mg, 40%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.53 (d, *J* = 5.4 Hz, 2H), 7.07 (d, *J* = 5.5 Hz, 2H), 4.37-4.30 (m, 2H), 4.13-4.06 (m, 2H), 2.24 (s, 6H), 1.80-1.72 (m, 4H), 1.36-1.24 (m, 12H), 0.86 (t, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ160.6, 142.6, 141.8, 128.0, 122.8, 121.0, 116.6, 45.7, 31.5, 28.3, 26.7, 22.6, 18.4, 14.0 HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{28}H_{36}N_2O_2S_2$, 497.2291; found, 497.2304.

Synthesis steps of 2,2'-dibromo-4,4'-dihexyl-7,7'-dimethyl-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTPM-diBr)

To a solution of BTPM (60 mg, 0.123 mmol) in a mixture of dry DMF (5 mL) and acetic acid (5 mL) was added N-bromosuccinimide (66 mg, 0.368 mmol), and the reaction mixture was heated to 60 °C for 10 hours. Then, the mixture was poured into water, extracted with CH_2Cl_2 three times and washed with $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified through a silica gel column with a mixture of petroleum/ethyl acetate (2:1) as eluent to give a light brown solid (66 mg, 82%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.08 (s, 2H), 4.29-4.21 (m, 2H), 4.05-3.97 (m, 2H), 2.15 (s, 6H), 1.76-1.69 (m, 4H), 1.45-1.25 (m, 12H), 0.87 (t, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.0, 141.9, 141.1, 122.6, 122.0, 119.7, 117.5, 45.8, 31.4, 28.2, 26.6, 22.5, 18.3, 14.0. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{28}H_{34}Br_2N_2O_2S_2$, 653.0501; found, 653.0512.

Synthesis steps of 4,4'-dihexyl-7,7'-dimethyl-2,2'-bis(4-(methylthio)phenyl)-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTPMP)

To a solution of BTPM-diBr (50 mg, 0.0764 mmol), (4-(methylthio)phenyl)boronic acid (51mg, 0.306 mmol) and anhydrous sodium carbonate (40 mg, 0.382 mmol) in a mixture of 1,4-dioxane (10 mL) and water (2 mL) was added $Pd(PPh_3)_4$ (9 mg, 7.64 μmol), and then heated to 85 °C for 14 hours. The mixture was poured into water and extracted three times with CH_2Cl_2 after cooling to room temperature. After removing the solvent of the organic layer by Na_2SO_4, the crude product was purified with a mixture of petroleum /ethyl acetate (1:1) as eluent through a silica gel column and then recrystallized from chloroform/methanol to give a yellow solid (15 mg, 26 %). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.61 (d, *J* = 8.5 Hz, 4H), 7.31 (d, *J* = 8.4 Hz, 4H), 7.21 (s, 2H), 4.40-4.33 (m, 2H), 4.16-4.09 (m, 2H), 2.54 (s, 6H), 2.25 (s, 6H), 1.84-1.76 (m, 4H), 1.49-1.41 (m, 4H), 1.38-1.30 (m, 8H), 0.88 (t, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.5, 145.8, 142.5, 142.4, 139.9, 130.3, 126.7, 126.3, 122.6, 120.3, 111.6, 45.6, 31.5, 28.3, 26.7, 22.6, 18.4, 15.6, 14.0. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{42}H_{48}N_2O_2S_4$, 741.2671; found, 741.2648.

Synthesis steps of N^1,N^4-dihexyl-N^1,N^4-bis(2-(phenylethynyl)thiophen-3-yl)succinamide (DTPESA)

To a solution of DTSA-diBr (219 mg, 0.361 mmol) in a mixture of dry DMF (5 mL) and dry triethylamine (5 mL) were added phenylacetylene (0.12 mL, 1.08 mmol), $PdCl_2(PPh_3)_2$ (13 mg, 0.0181 mmol) and CuI (3 mg, 0.0181 mmol), and then heated to 80 °C for 4 hours. The mixture was poured into water and extracted with three times ethyl acetate after cooling to room temperature. After removing the solvent of the organic layer by anhydrous Na_2SO_4, the crude product was purified with a mixture of petroleum/ethyl acetate (5:1) as eluent through a silica gel column to give a yellow oil (201 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.45-7.38 (m, 4H), 7.35-7.29 (m, 6H), 7.19 (d, *J* = 5.3 Hz, 2H), 6.88 (d, *J* = 5.4 Hz, 2H), 3.67 (s, 4H), 2.49 (s, 4H), 1.55-1.47 (m, 4H), 1.33-1.16 (m, 12H), 0.84-0.75 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 172.0, 144.0, 131.4, 128.7, 128.3, 126.8, 126.2, 122.3, 119.6, 97.7, 80.0, 48.7, 31.6, 29.7, 28.0, 26.6, 22.5, 14.0. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{40}H_{44}N_2O_2S_2$, 649.2917; found, 649.2927.

Synthesis steps of 7,7'-dibenzyl-4,4'-dihexyl-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTPB)

To a solution of DTPESA (336 mg, 0.518 mmol) in dry tetrahydrofuran (10 mL) was added t-BuOK (232 mg, 2.07 mmol), and then was heated to 40 °C for 3 hours. The mixture was then poured into water and extracted three times with CH_2Cl_2. After removing the solvent of the organic layer by anhydrous Na_2SO_4, the crude product was purified with a mixture of petroleum/ethyl acetate (1:1) as eluent

through a silica gel column to give a white solid (105 mg, 31%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.43 (d, *J* = 5.5 Hz, 2H), 7.17-7.14 (m, 10H), 7.00 (d, *J* = 5.5 Hz, 2H), 4.36-4.29 (m, 2H), 4.16-4.08 (m, 2H), 3.99 (d, *J* = 15.6 Hz, 2H), 3.64 (d, *J* = 15.7 Hz, 2H), 1.82-1.71 (m, 4H), 1.43-1.38 (m, 4H), 1.35-1.26 (m, 8H), 0.86 (t, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.7, 145.3, 142.6, 137.4, 129.5, 129.2, 128.4, 126.5, 123.6, 120.2, 115.9, 45.8, 39.0, 31.5, 28.2, 26.7, 22.5, 14.0. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{40}H_{44}N_2O_2S_2$, 649.2917; found, 649.2930.

Synthesis steps of 7,7'-dibenzyl-2,2'-dibromo-4,4'-dihexyl-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTPB-diBr)

To a solution of BTPB (69 mg, 0.106 mmol) in a mixture of chloroform (10 mL) and acetic acid (5 mL) was added N-bromosuccinimide (57 mg, 0.319 mmol), and then stirred overnight at room temperature. The mixture was then poured into water, extracted three times with CH_2Cl_2 and washed with $NaHCO_3$. After removing the solvent of the organic layer by anhydrous Na_2SO_4, the crude product was purified with a mixture of petroleum/ethyl acetate (2:1) as eluent through a silica gel column to give a white solid (60 mg, 70%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.20-7.18 (m, 6H), 7.11-7.09 (m, 4H), 7.00 (s, 2H), 4.27-4.20 (m, 2H), 4.08-4.01 (m, 2H), 3.89 (d, *J* = 15.8 Hz, 2H), 3.56 (d, *J* = 15.8 Hz, 2H), 1.80-1.66 (m, 4H), 1.43-1.36 (m, 4H), 1.34-1.24 (m, 8H), 0.86 (t, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.2, 144.8, 142.0, 136.7, 129.5, 128.6, 126.9, 123.5, 121.2, 119.0, 118.9, 45.9, 38.9, 31.4, 28.2, 26.6, 22.5, 14.0. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{40}H_{42}Br_2N_2O_2S_2$, 805.1127; found, 805.1142.

Synthesis steps of 7,7'-dibenzyl-4,4'-dihexyl-2,2'-bis(4-(methylthio)phenyl)-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTPBP)

To a solution of BTPB-diBr (40 mg, 0.0496 mmol), (4-(methylthio)phenyl)boronic acid (33 mg, 0.198 mmol) and anhydrous sodium carbonate (26 mg, 0.248 mmol) in a mixture of 1,4-dioxane (10 mL) and water (2 mL) was added $Pd(PPh_3)_4$ (6 mg, 4.96 μmol), and then heated to 85 °C for 21 hours. The mixture was poured into water and extracted three times with CH_2Cl_2 after cooling to room temperature. After removing the solvent of the organic layer by anhydrous Na_2SO_4, the crude product was purified with a mixture of petroleum/ethyl acetate (1:1) as eluent through a silica gel column and then recrystallized from chloroform/methanol to give a yellow solid (20 mg, 45 %). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.49 (d, *J* = 8.5 Hz, 4H), 7.24 (d, *J* = 8.3 Hz, 4H), 7.18-7.16 (m, 10H), 7.14 (s, 2H), 4.39-4.32 (m, 2H), 4.18-4.11 (m, 2H), 3.98 (d, *J* = 15.7 Hz, 2H), 3.62 (d, *J* = 15.7 Hz, 2H), 2.50 (s, 6H), 1.83-1.76 (m, 4H), 1.48-1.41 (m, 4H), 1.37-1.27 (m, 8H), 0.87 (t, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.7, 146.8, 145.2, 143.3, 139.8, 137.3, 130.2, 129.4, 128.4, 126.5, 126.3, 123.4, 119.6, 111.0, 45.7, 39.0, 31.5, 28.2, 26.7, 22.5, 15.6, 14.0. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{54}H_{56}N_2O_2S_4$, 893.3297; found, 893.3285.

Elemental Analysis

BTPP: Elemental Analysis calcd. for $C_{40}H_{44}N_2O_2S_4$: C, 67.38; H, 6.22; N, 3.93, found: C, 66.52; H, 6.51; N, 3.70

BTPMP: Elemental Analysis calcd. for $C_{42}H_{48}N_2O_2S_4$: C, 68.07; H, 6.53; N, 3.78, found: C, 67.53; H, 6.78; N, 3.59

BTPBP: Elemental Analysis calcd. for $C_{54}H_{56}N_2O_2S_4$: C, 72.61; H, 6.32; N, 3.14, found: C, 72.37; H, 6.38; N, 2.96

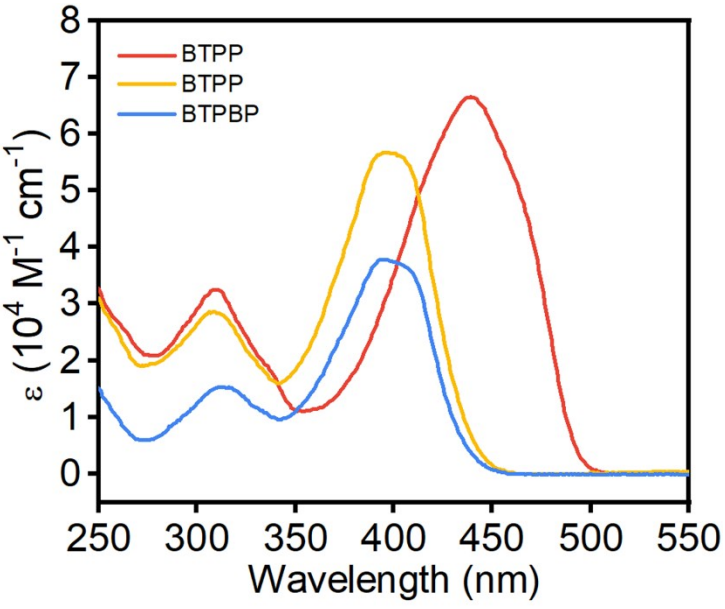


Figure S1. The UV-Vis spectra of **BTPP** (red), **BTPMP** (yellow) and **BTPBP** (blue).

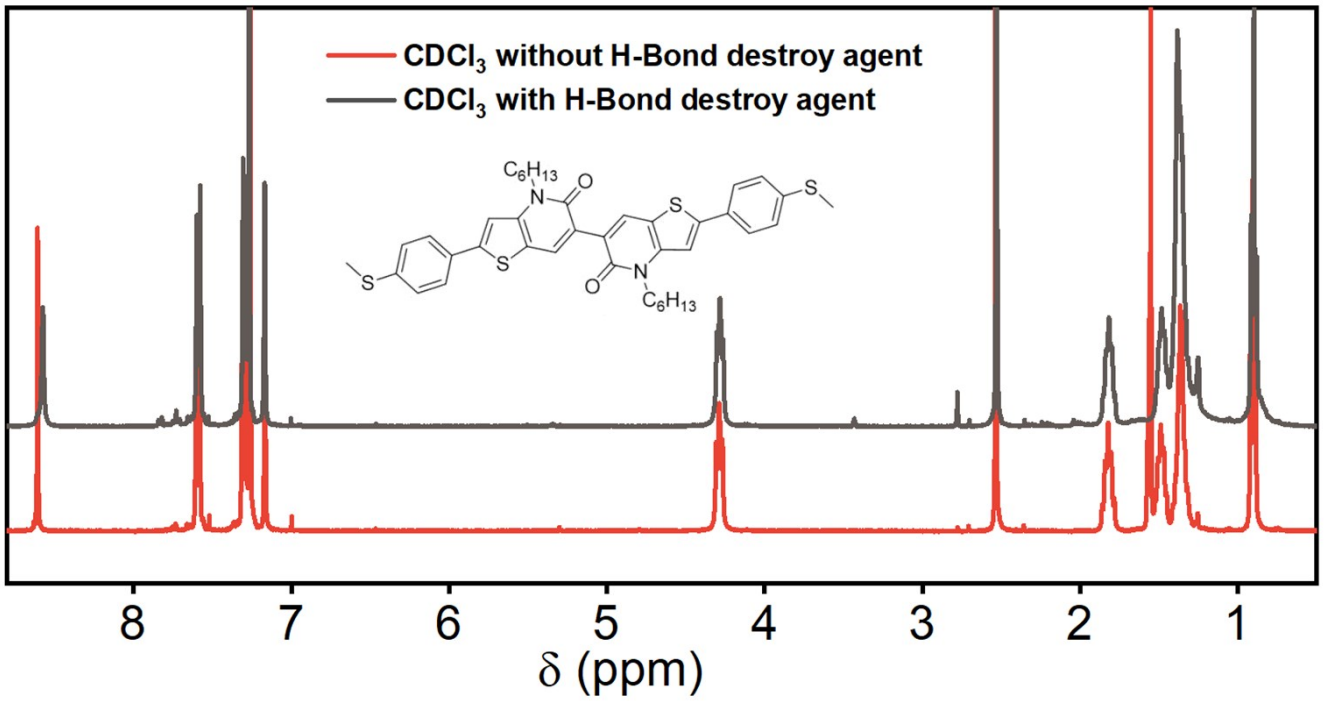


Figure S2. The ^{1}H NMR comparison spectra of **BTPP**.

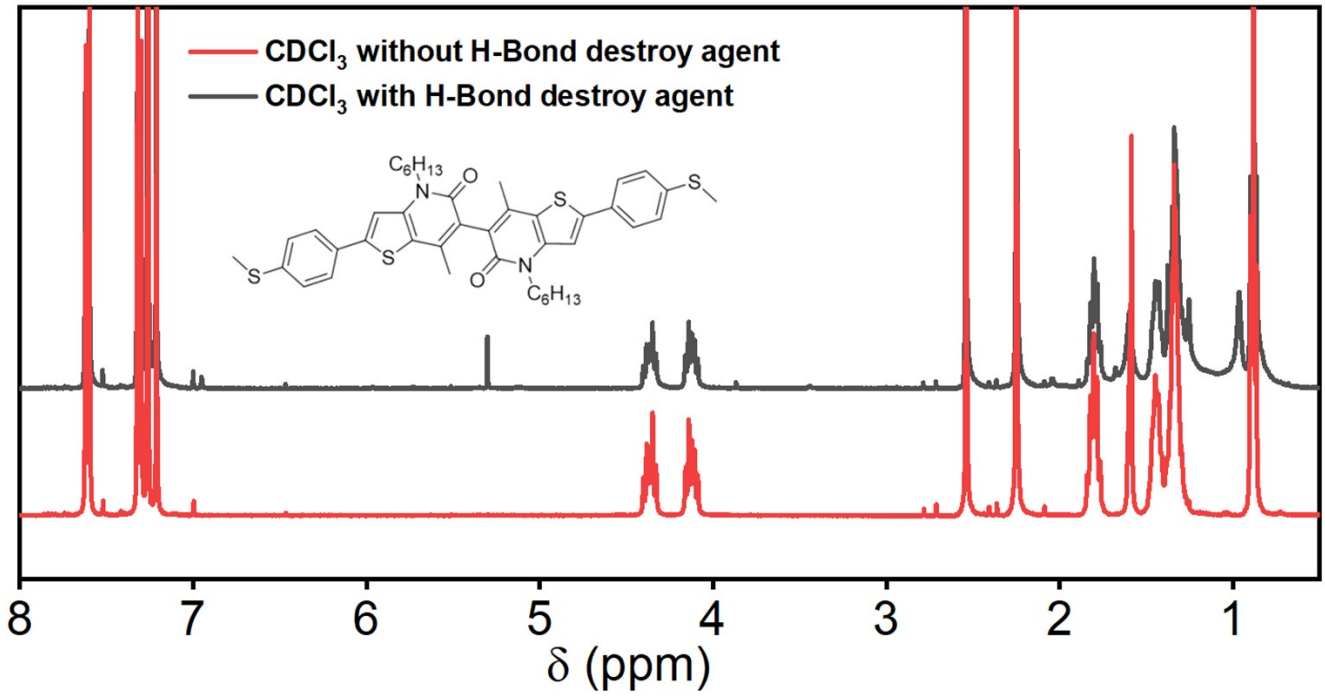


Figure S3. The ^{1}H NMR comparison spectra of **BTPMP**.

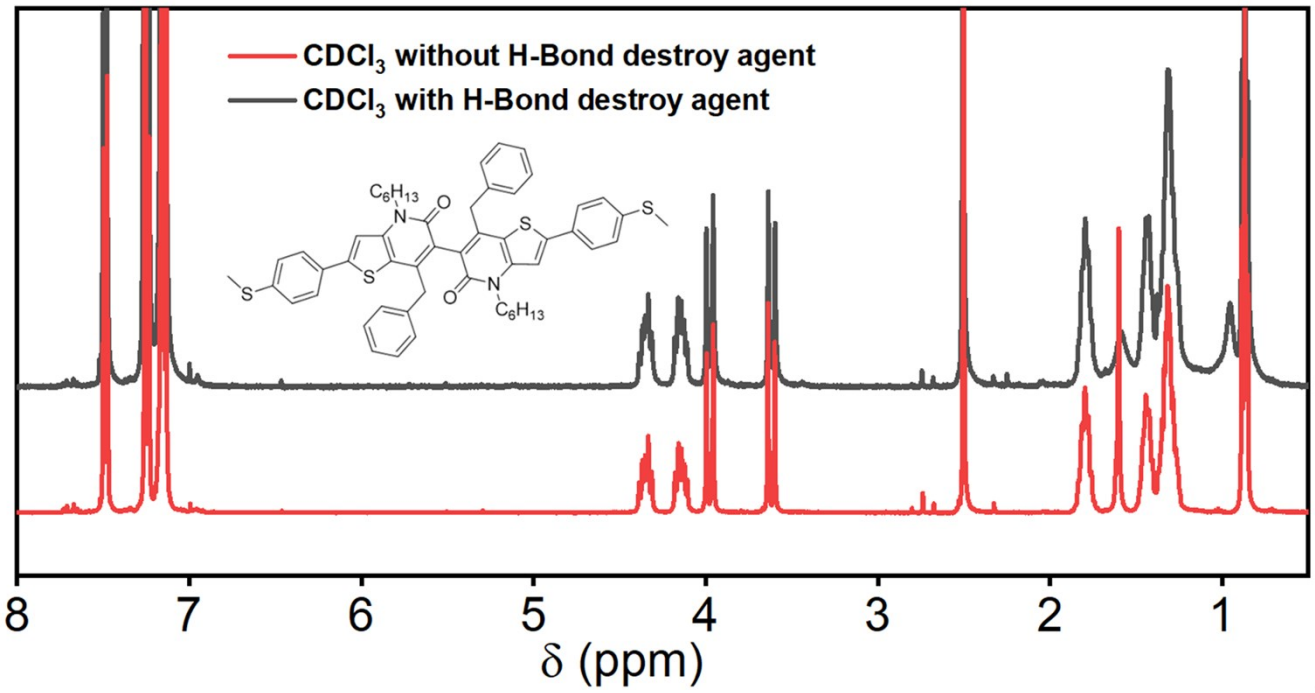


Figure S4. The ^{1}H NMR comparison spectra of **BTPBP**.

2. Single-molecule Junction Measurements

In this work, we used a home-built scanning tunneling microscope break junction (STM-BJ) set-up to perform the single-molecule conductance measurement. A piece of gold wire (99.99%, 0.25 mm in diameter, Jiaming, Beijing) with one end burned into a bead is used as a tip, which is fixed onto a piezo, while the piezo is adhered to the bottom of a stepping motor. A gold-evaporated silicon wafer, which was pre-washed by piranha solution (V (H_2SO_4): V(H_2O_2) = 3:1 CAUTION! piranha solution is extremely corrosive) and rinsed with fresh deionized water, is placed below the tip. Then, 50 μL 1,2,4-trichlorobenezen (TCB) solution containing 0.1 mmol target molecule was dripped on the substrate, and the tip was also immersed in the solution. In the text, both the tip and the substrate are connected with the external current amplifier and the controller, and a 100 mV bias voltage is applied between them. Using the current between the two electrodes as feedback, the tip was controlled to pull up and down to repeatedly contact/leave the substrate. Molecular junctions can be formed during the break junction process so that the single-molecule conductance can be detected. The construction method of 1D/2D conductance and PSD analysis histogram can refer to some of our recent work.[4, 5]

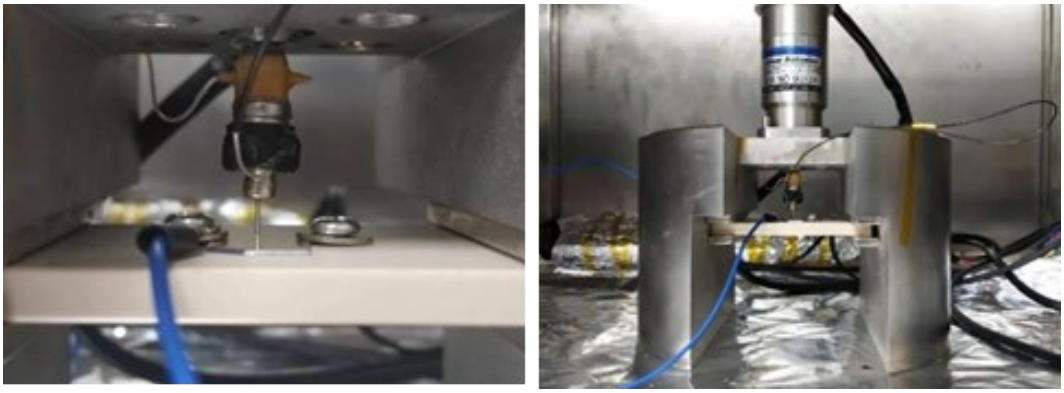


Figure S5. The photos of home-built STM setup.

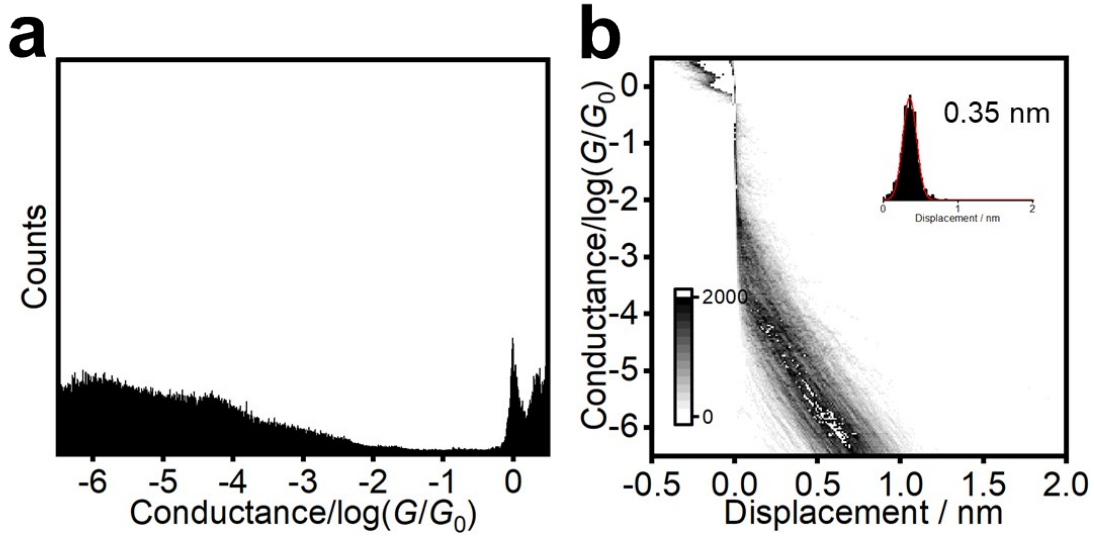


Figure S6. (a) 1D conductance histogram and (b) 2D conductance versus relative displacement histogram of the pure TCB.

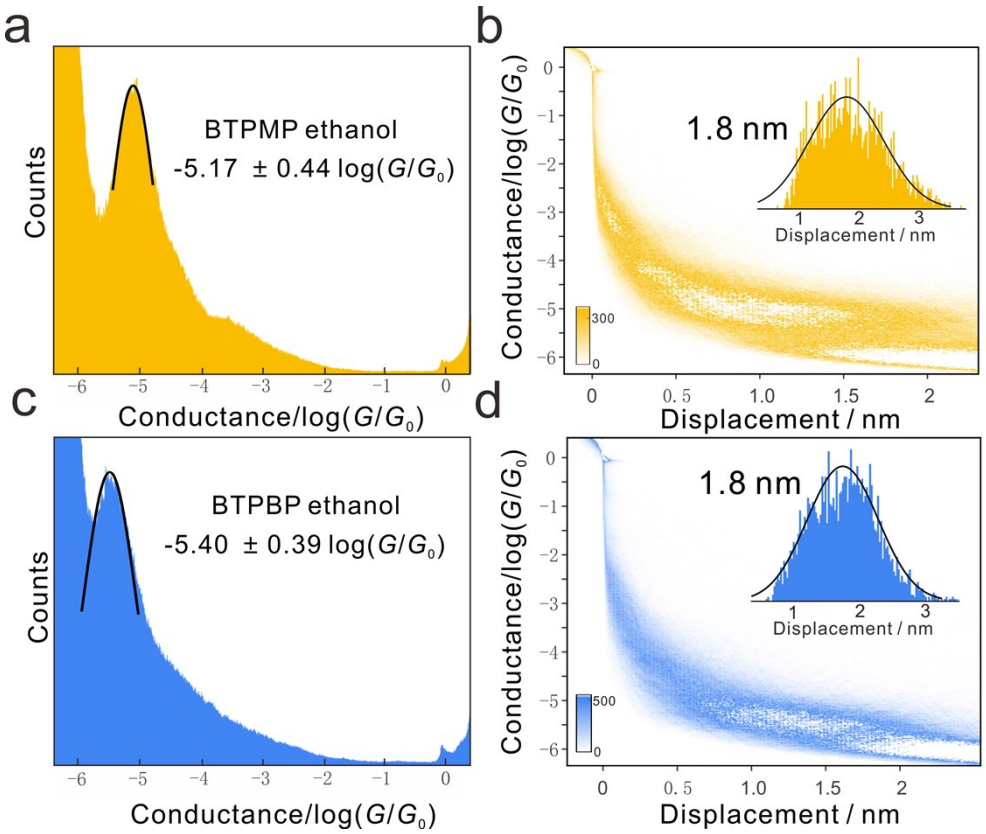


Figure S7. Results of single-molecule conductance by STM-BJ measurement. (a) The one-dimensional (1D) conductance histogram comparisons of target molecules of **BTPMP**$_{ethanol}$ and **BTPBP**$_{ethanol}$. (b) Two-dimensional (2D) conductance histogram versus relative displacement and relative distance distributions (inset) of **BTPMP**$_{ethanol}$ (yellow) and **BTPBP**$_{ethanol}$ (blue). According to the relative distance distributions, the conductance ranges are confirmed to be $10^{-0.3}$ G_0 ~ $10^{-6.0}$ G_0.

The solvent switching cycle measurements were carried out as follows:
We first assembled the substrate and the tip according to the above method. A solution of 0.1 mM **BTPP** concentration with pure TCB was added onto the substrate to carry out the measurement. Then, ethanol was introduced into the solution by in-situ addition (V (ethanol): V(TCB) = 1:9), and the experiment is tested at the first time after adding ethanol. After that, the gold tip was elevated by motor to aspirate the solution and TCB was added to switch the solvent environment. The switching cycle was obtained by repeating these procedures. Since the switching behavior do not occur as shown in Figure S3, we did not proceed further the solvent switching cycle measurements of **BTPMP** and **BTPBP**.

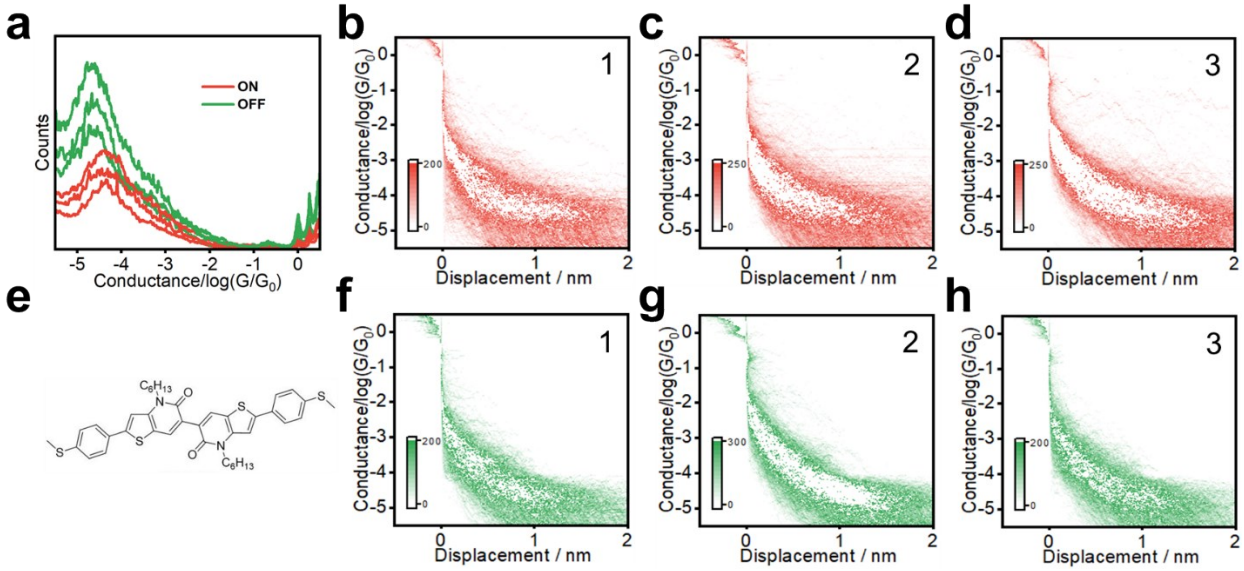


Figure S8. The solvent switching cycle measurements and molecular structure. (a) 1D conductance histogram of **BTPP** with different solvent. ON state represents the TCB solvent (red), and OFF state represents the solvent mixed with TCB and ethanol (green). 2D conductance histogram of ON state (b-d) and OFF state (f-h) for **BTPP**. Molecular structure as shown in (e).

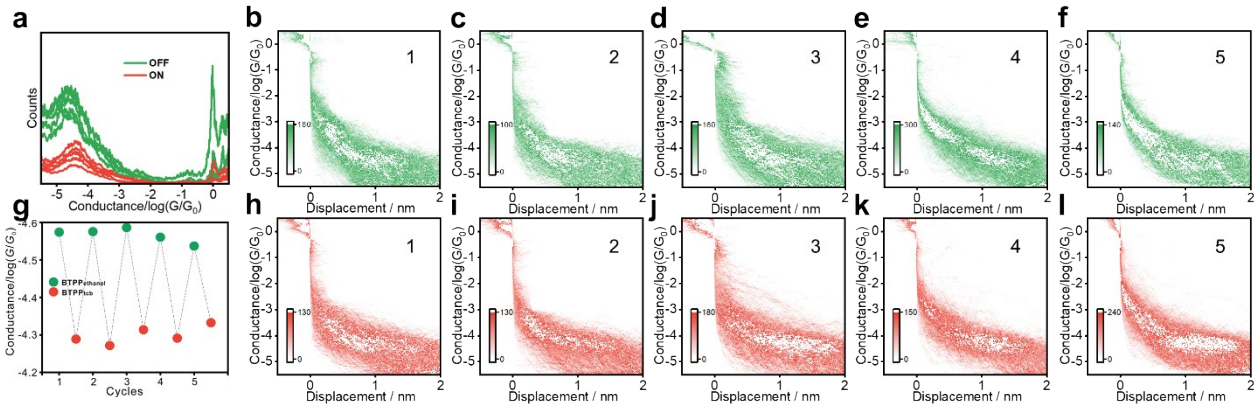


Figure S8. The solvent switching cycle measurements. (a) 1D conductance histogram of **BTPP** with different solvent. ON state represents the TCB solvent (red), and OFF state represents the solvent mixed with TCB and ethanol (green). 2D conductance histogram of ON state (b-f) and OFF state (h-l) for **BTPP**. Switch cycles as shown in (g).

We analyzed the noise of conductance traces by flicker noise analysis methods and plotted the noise histogram to distinguish different ways of transport. Two-dimensional flicker noise histogram is used to analyze suspended traces. We suspended the retracting process of the tip for 150 ms to collect suspended traces. Then, we calculated the noise power from 100 Hz to 1000 Hz signals by fast Fourier transform. The noise power was normalized by the average conductance of each sampling. All noise points were further analyzed by two-dimensional Gaussian fitting to distinguish two different flicker noise signals well. Finally, in order to evaluate the transport of molecules, we tested a series of value *n* from 1 to 2 in the movement of 0.1. The noise power scales with exponent of conductance G_0^n, and the *n* is determined when we get the minimum of the correlation between noise power and conductance.

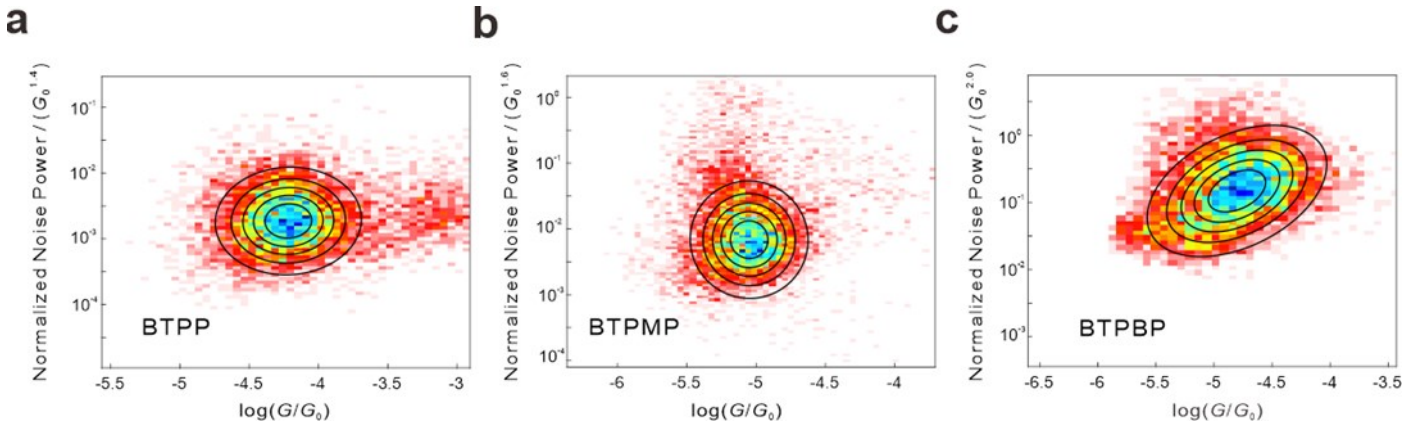


Figure S9. Two-dimensional histogram of normalized conductance change versus normalized noise power for **BTPP** (a), **BTPMP** (b) and **BTPBP** (c).

3. Theoretical Calculations

All molecular structures were optimized by Gaussian 16 software package.[6] The B3LYP/6-31G(d) basis set with empirical dispersion = gd3 used for geometry optimization in the gas phase at 298 K.[7-9] The transmission functions of the single-molecule device were performed with the combination of density functional theory (DFT) and the non-equilibrium Green's function (NEGF) method by using the Atomic Tool Kit (ATK) package.[10-12] For constructing such single-molecule device models, all the molecules were optimized by Gaussian 16 as mentioned above. Then, target molecules were attached to the gold atoms at both the right side and left side of electrodes respectively to fabricate the typical gold-molecule-gold model. The initial Au-S distance is 2.65 Å and C-S-Au angle of 115 degrees. For structural optimization, the geometry of entire scattering region is relaxed until all residual forces on each atom are less than 0.05 eV/Å. The GGA-PBE exchange correlation functional with the double-ζ polarized (DZP) basis set for the molecules and the single-ζ polarized (SZP) basis set for Au atoms were adopted in the calculation.[13] The k-points sampling was set as 1×1×200 (for x, y and z direction, respectively) with mesh cut-off energy of 75 Hartree.

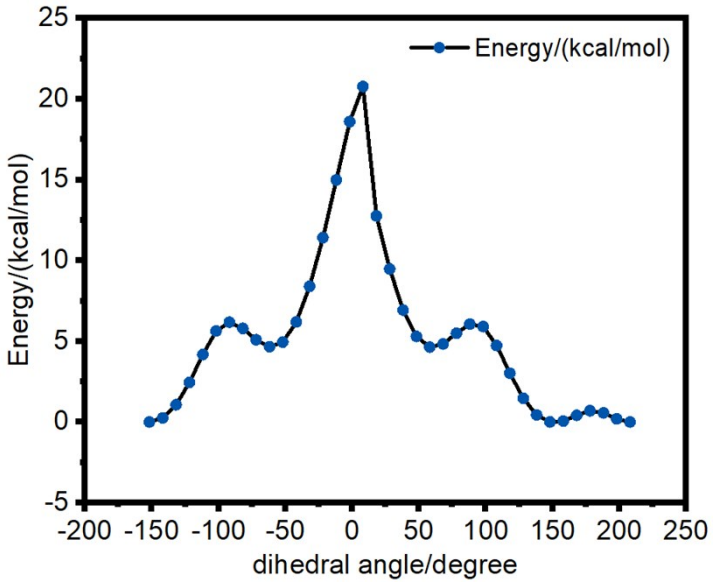


Figure S10. The scanned potential energy of **BTPP** with 10° per step.

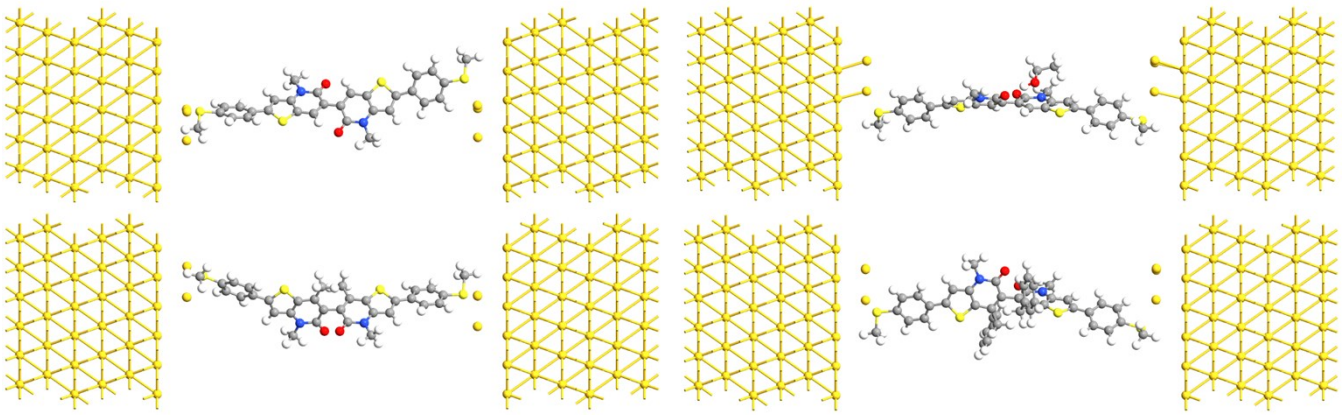


Figure S11. The optimized molecular device structures of **BTPP**, **BTPP**$_{ethanol}$, **BTPMP** and **BTPBP**.

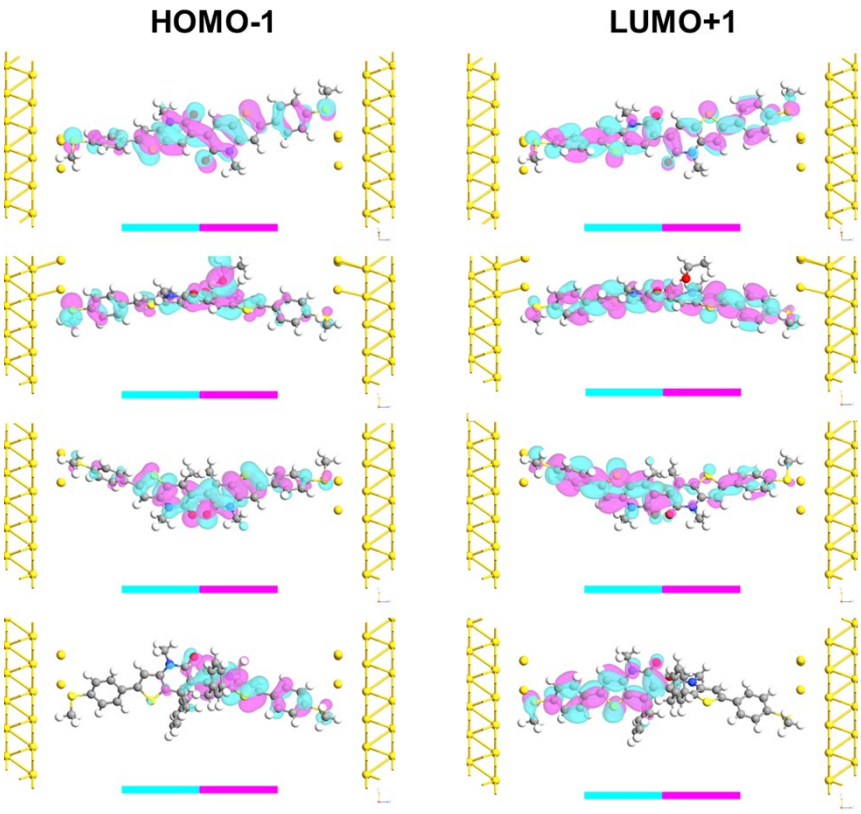


Figure S12. The spatial distribution of orbital levels of **BTPP$_{tcb}$**, **BTPP$_{ethanol}$**, **BTPMP$_{tcb}$** and **BTPBP$_{tcb}$** related to the HOMO-1 and LUMO+1, from up to the down.

4. References

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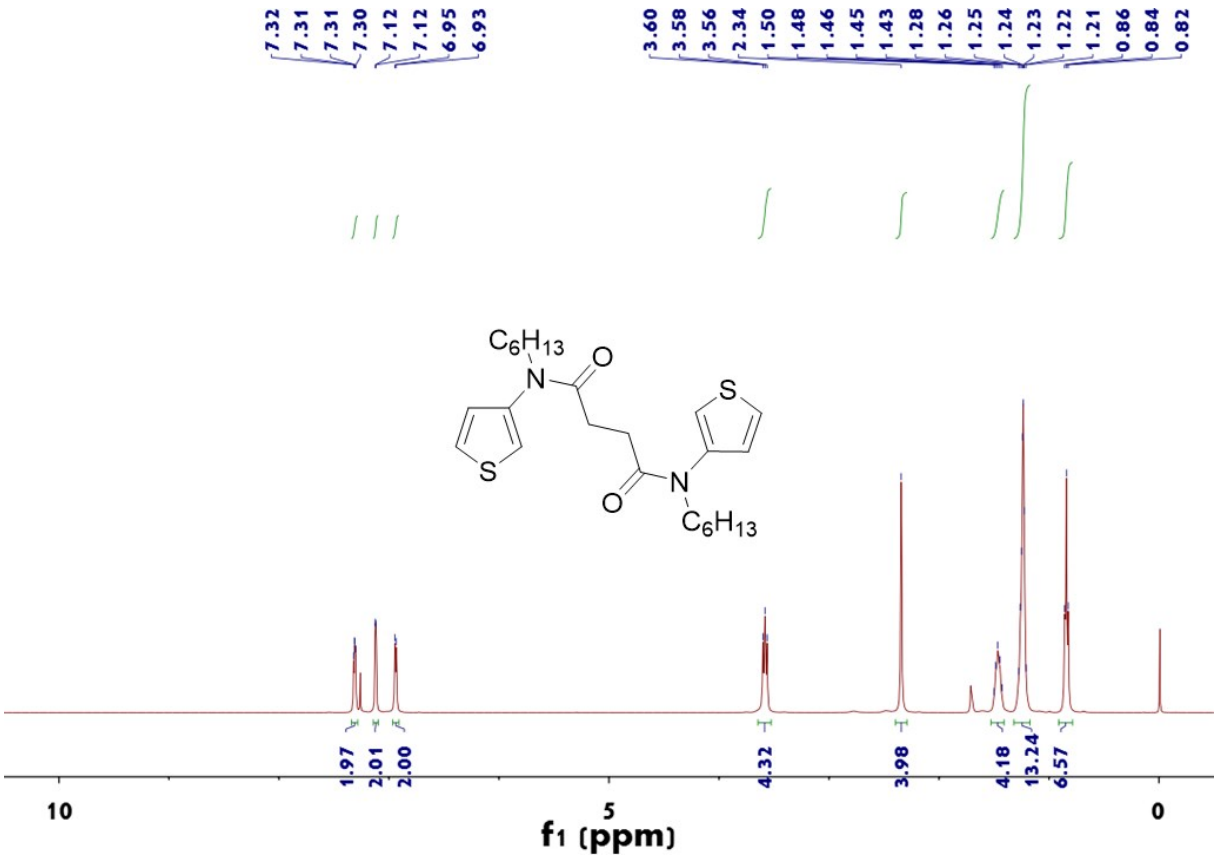

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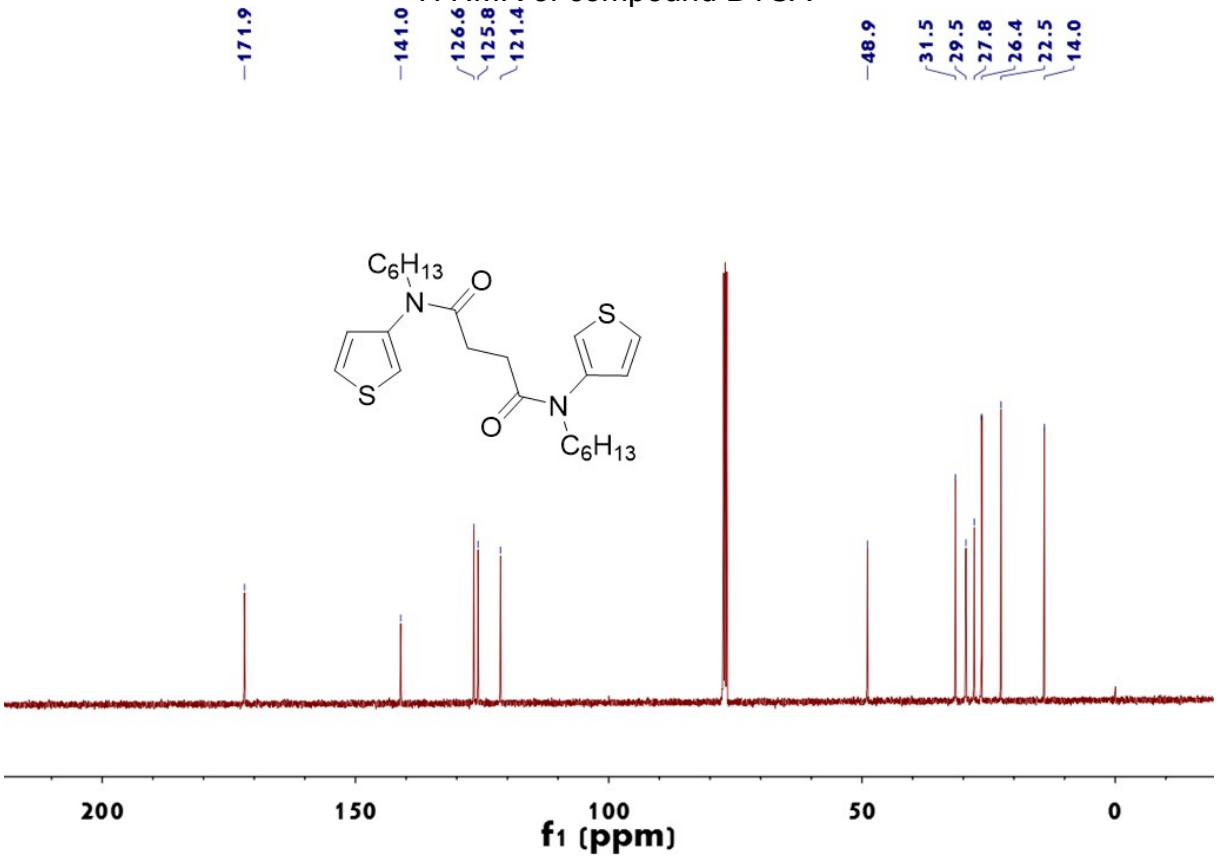

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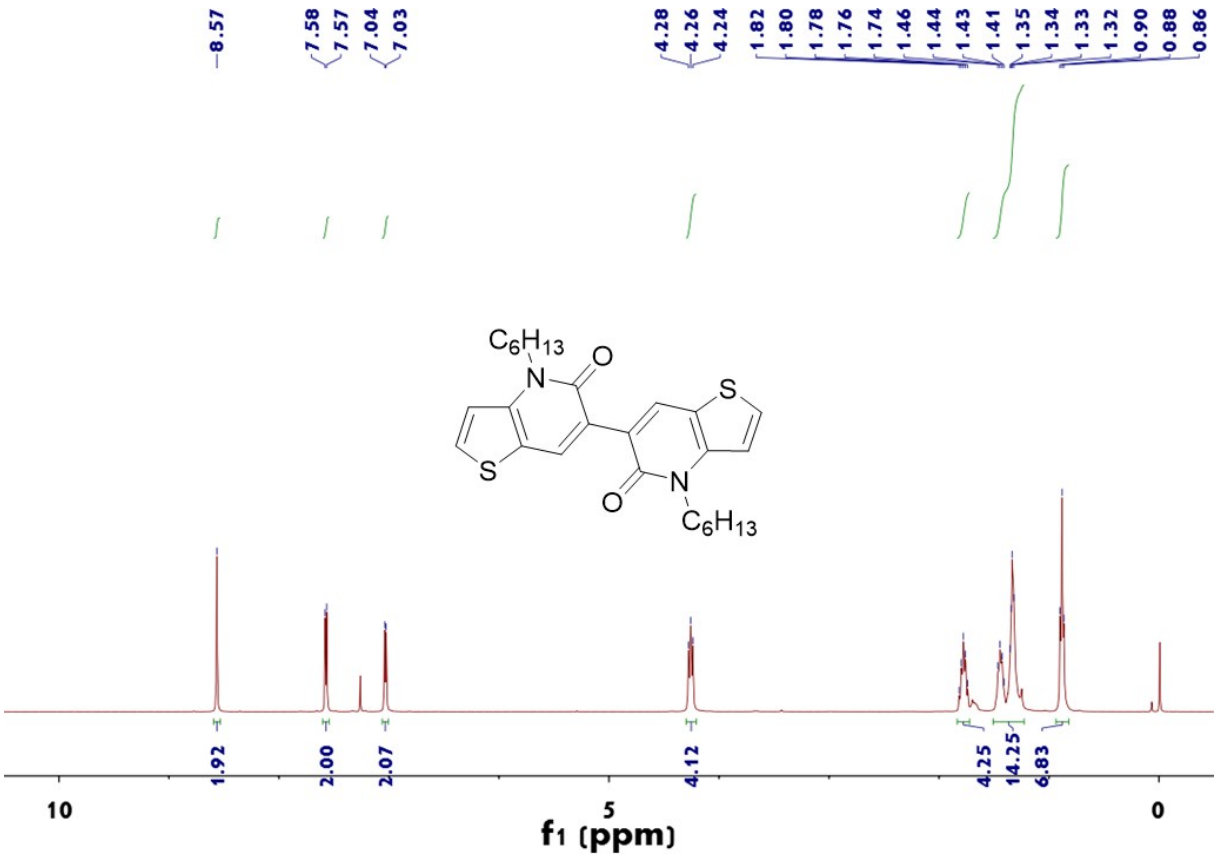

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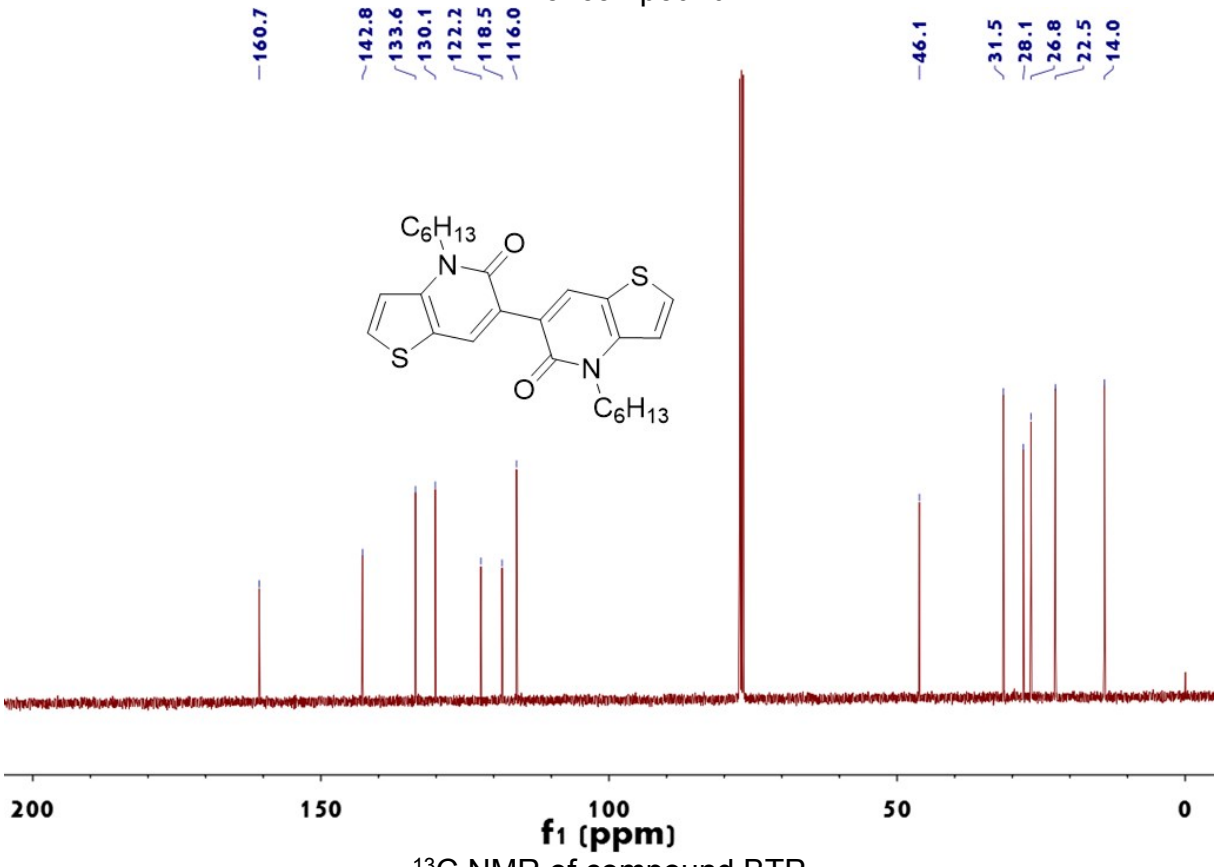

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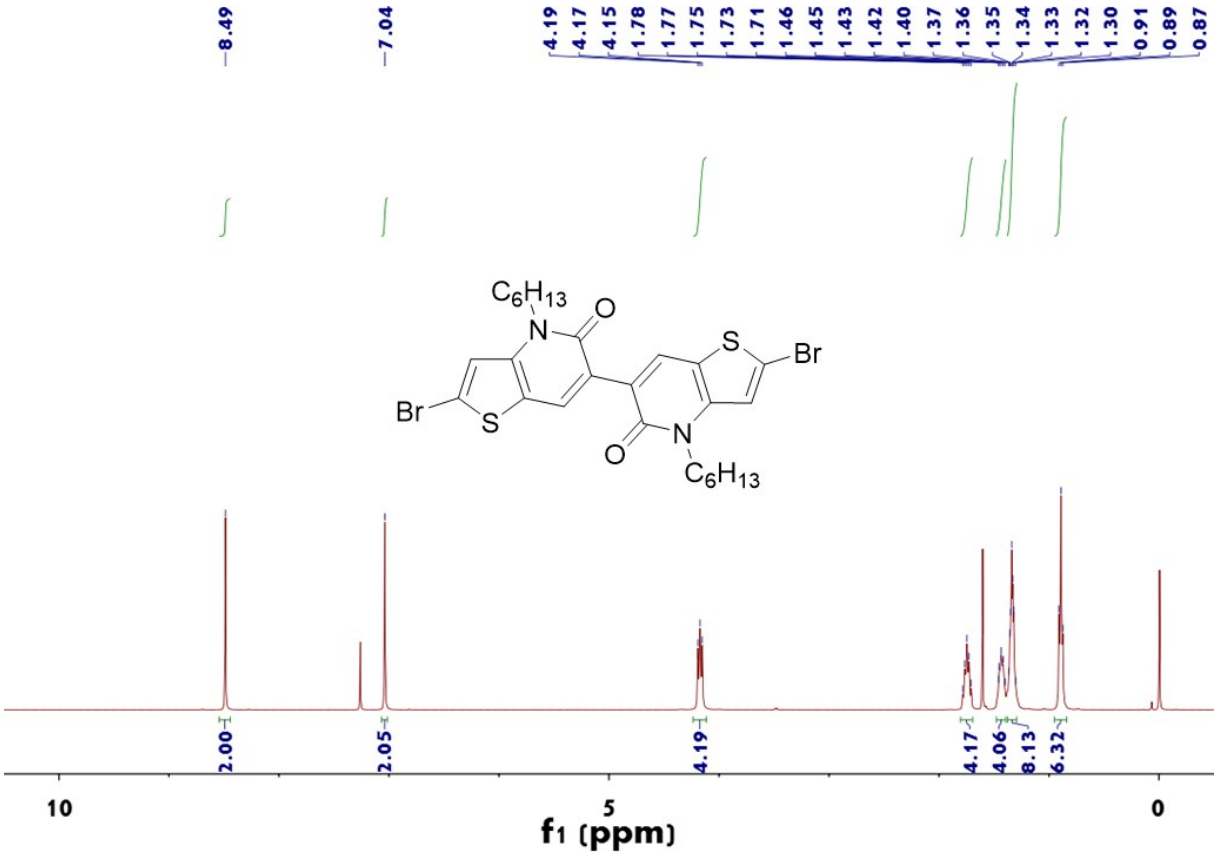

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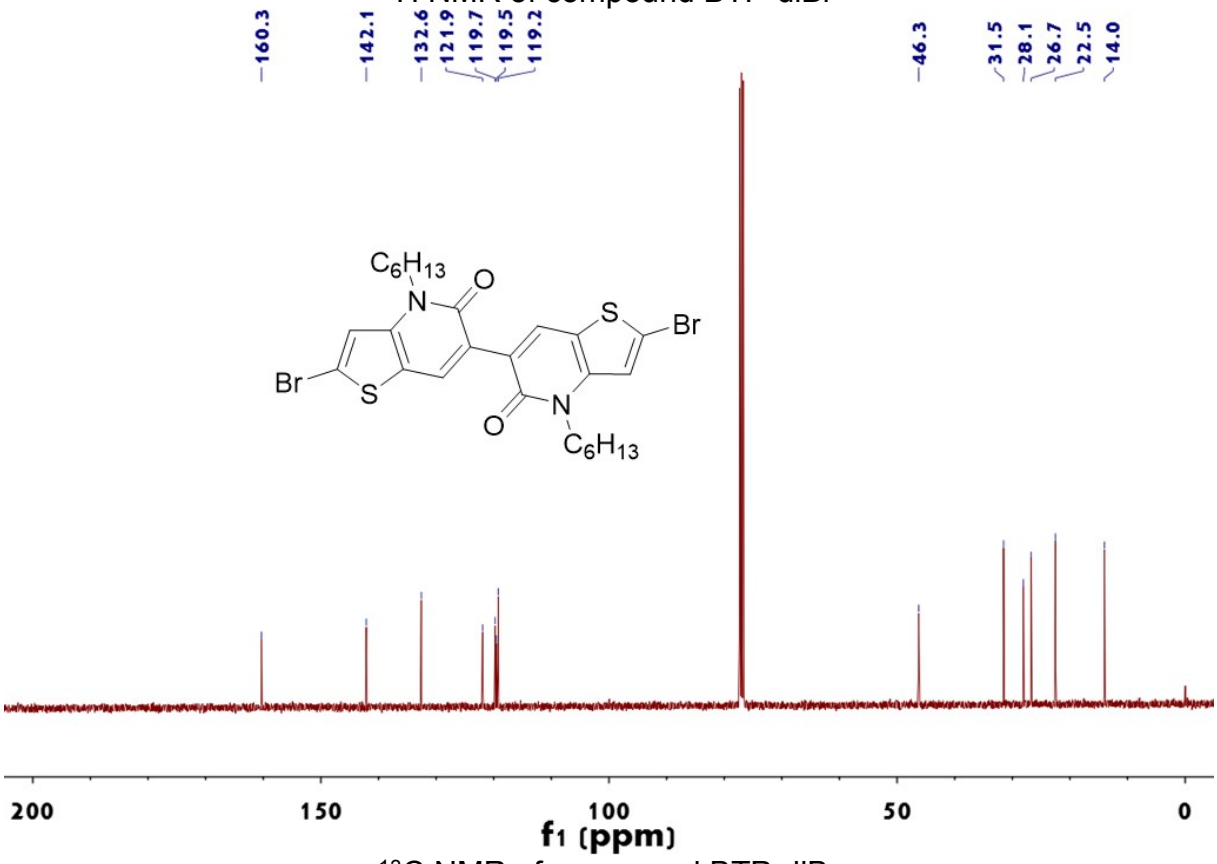

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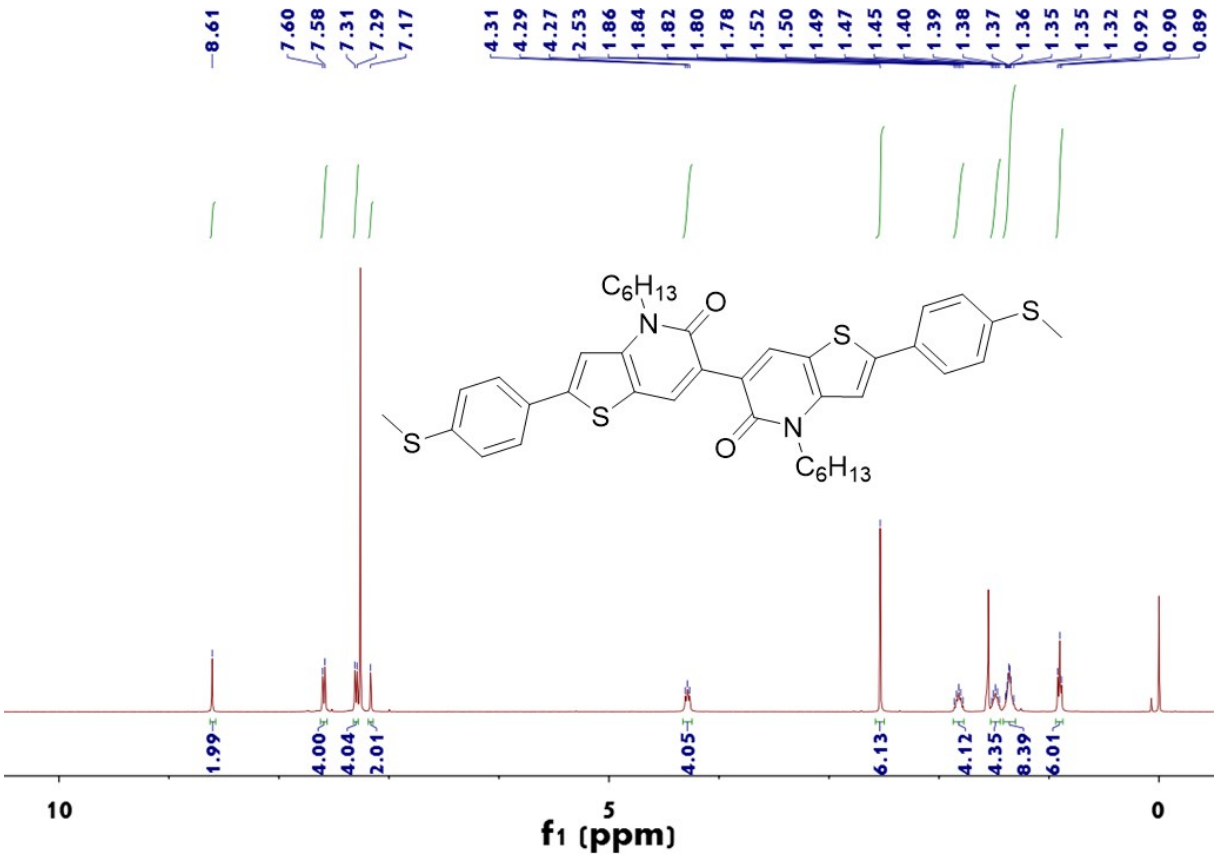

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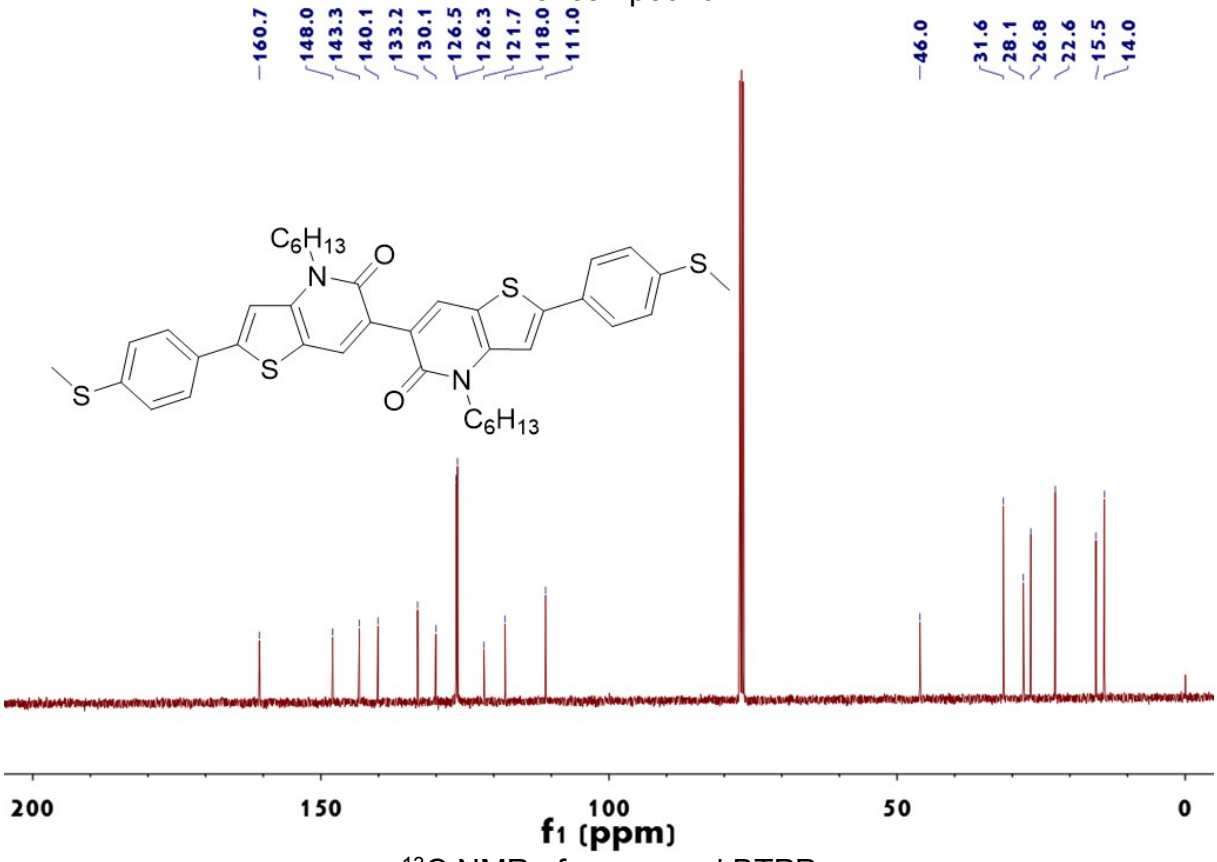

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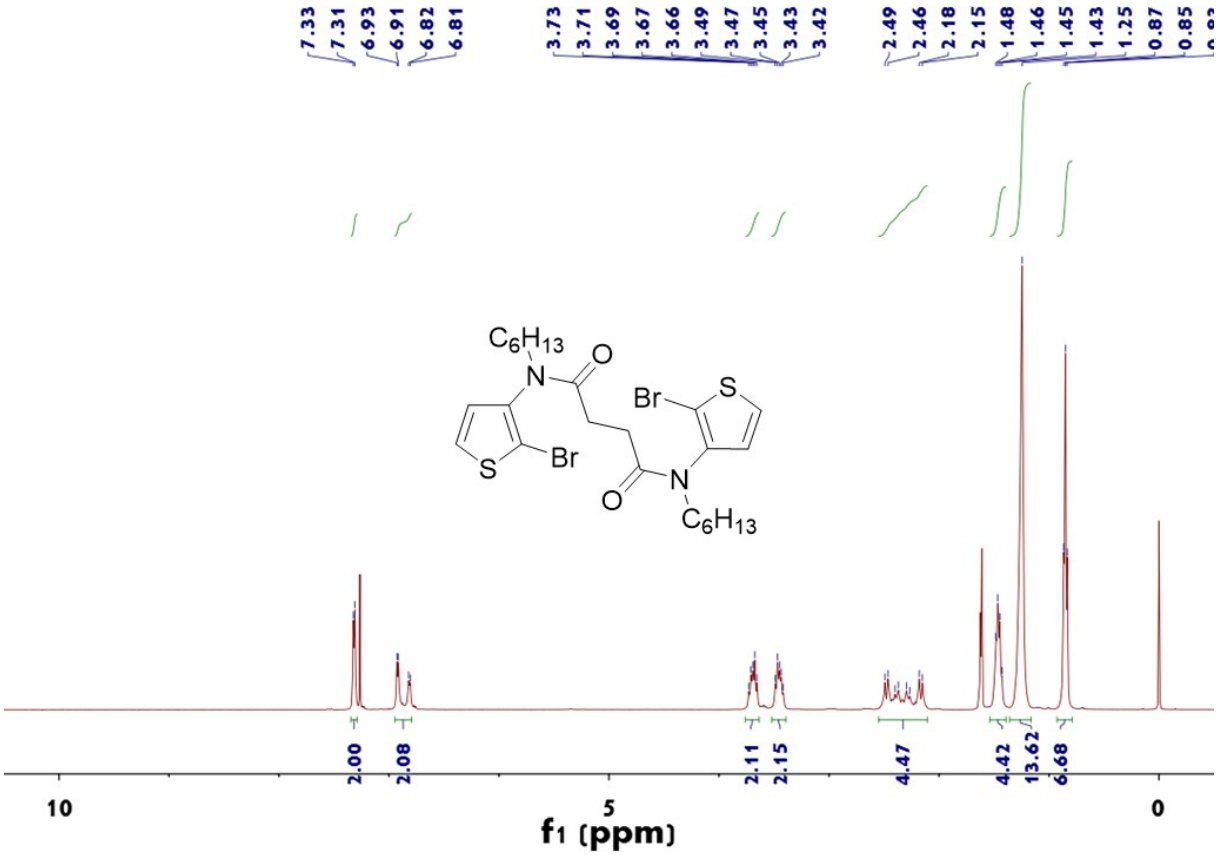

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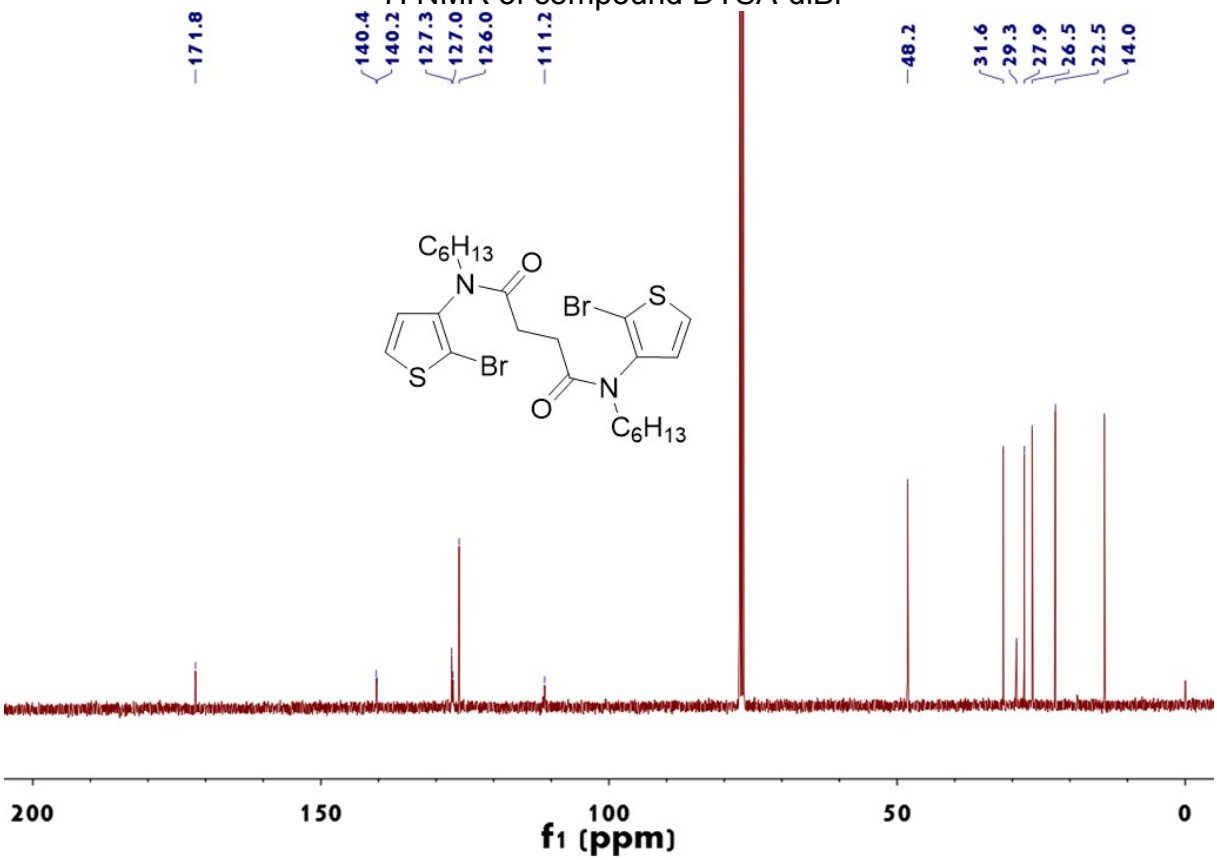

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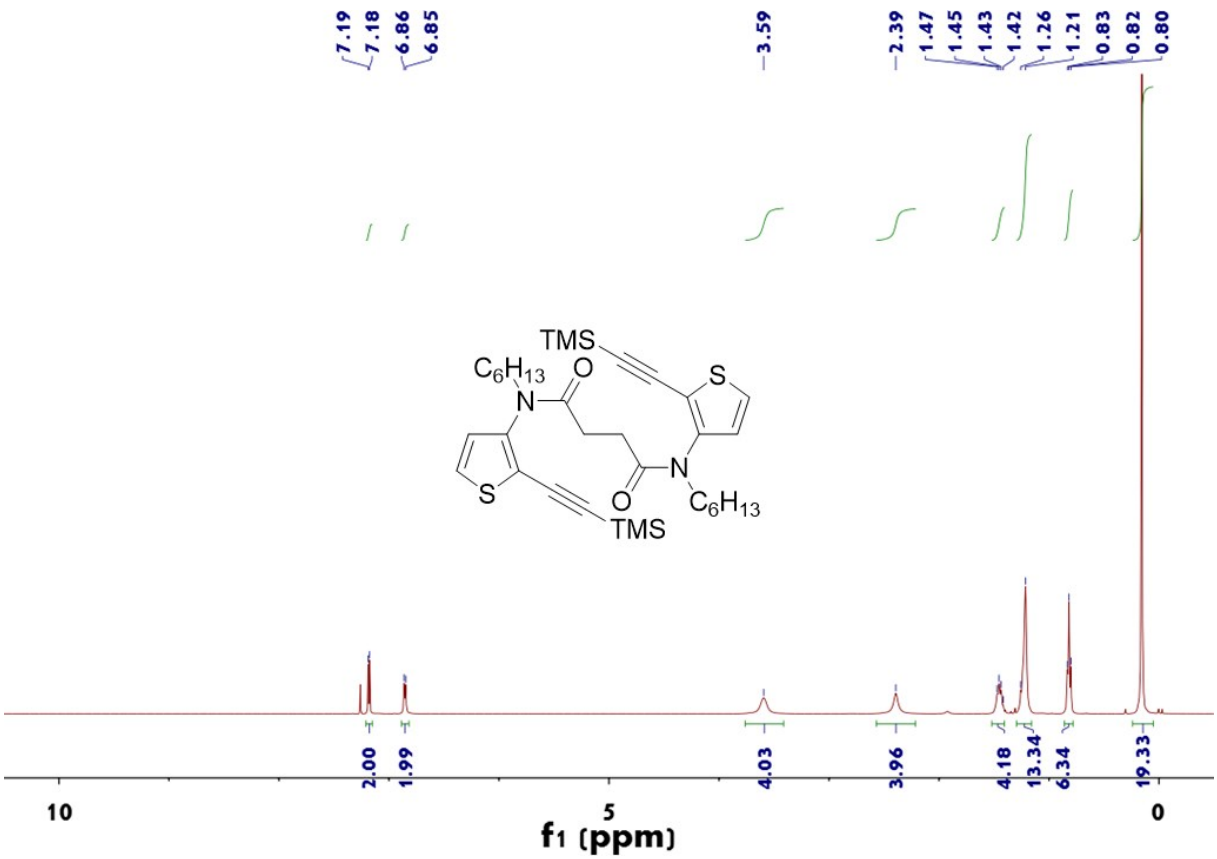

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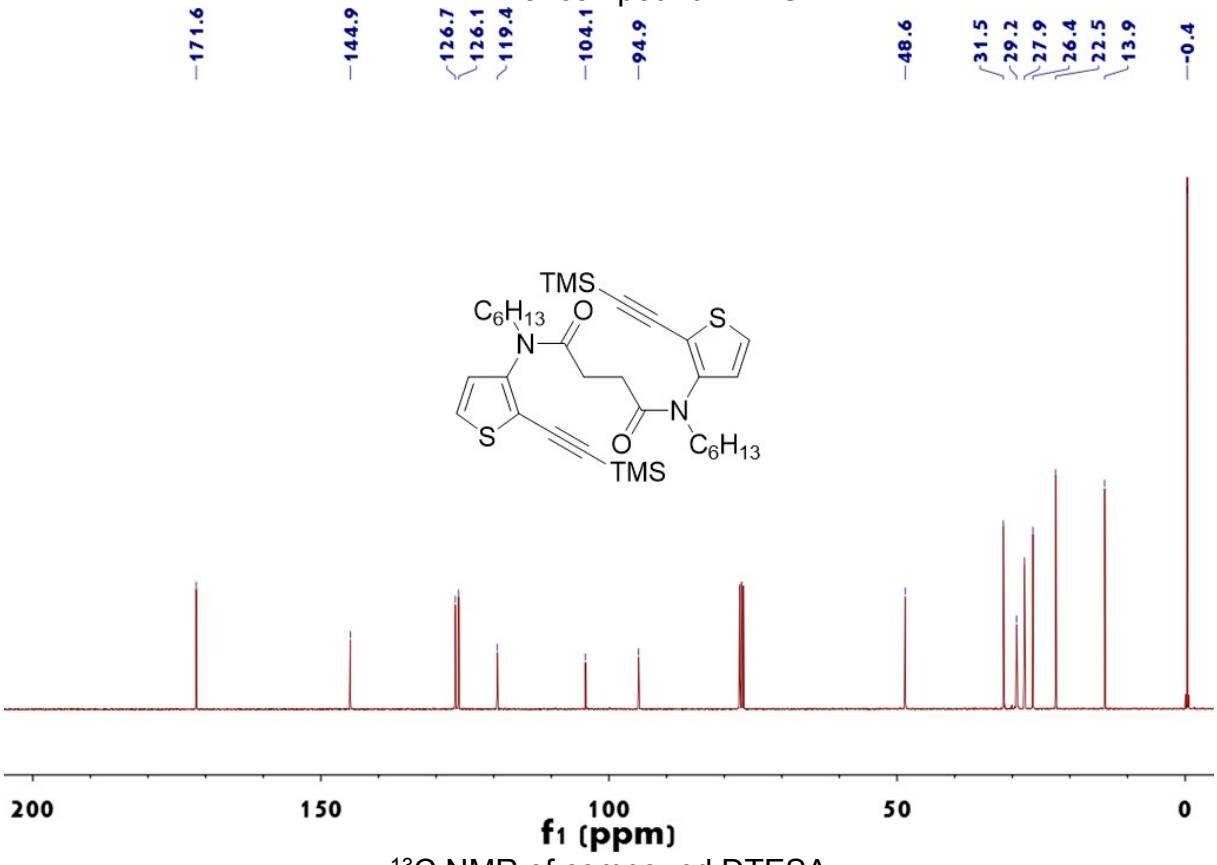

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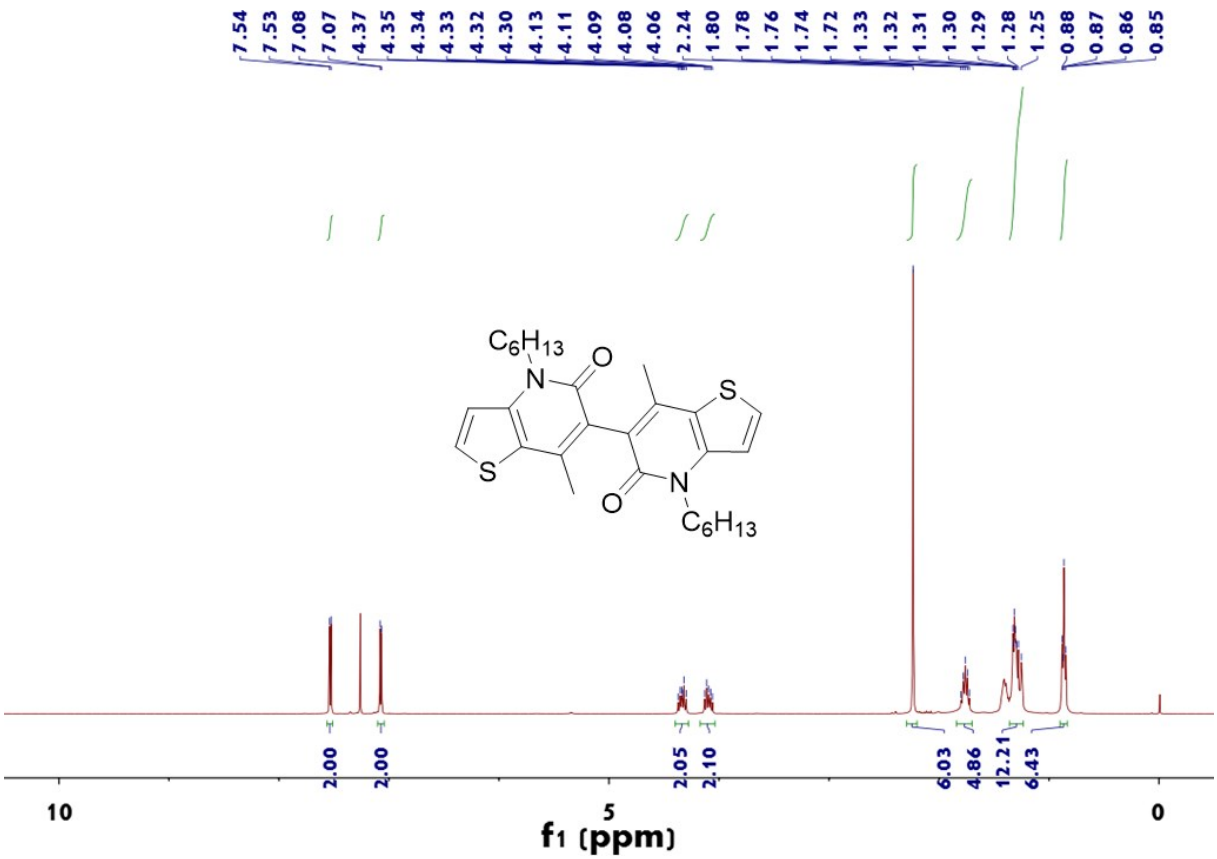

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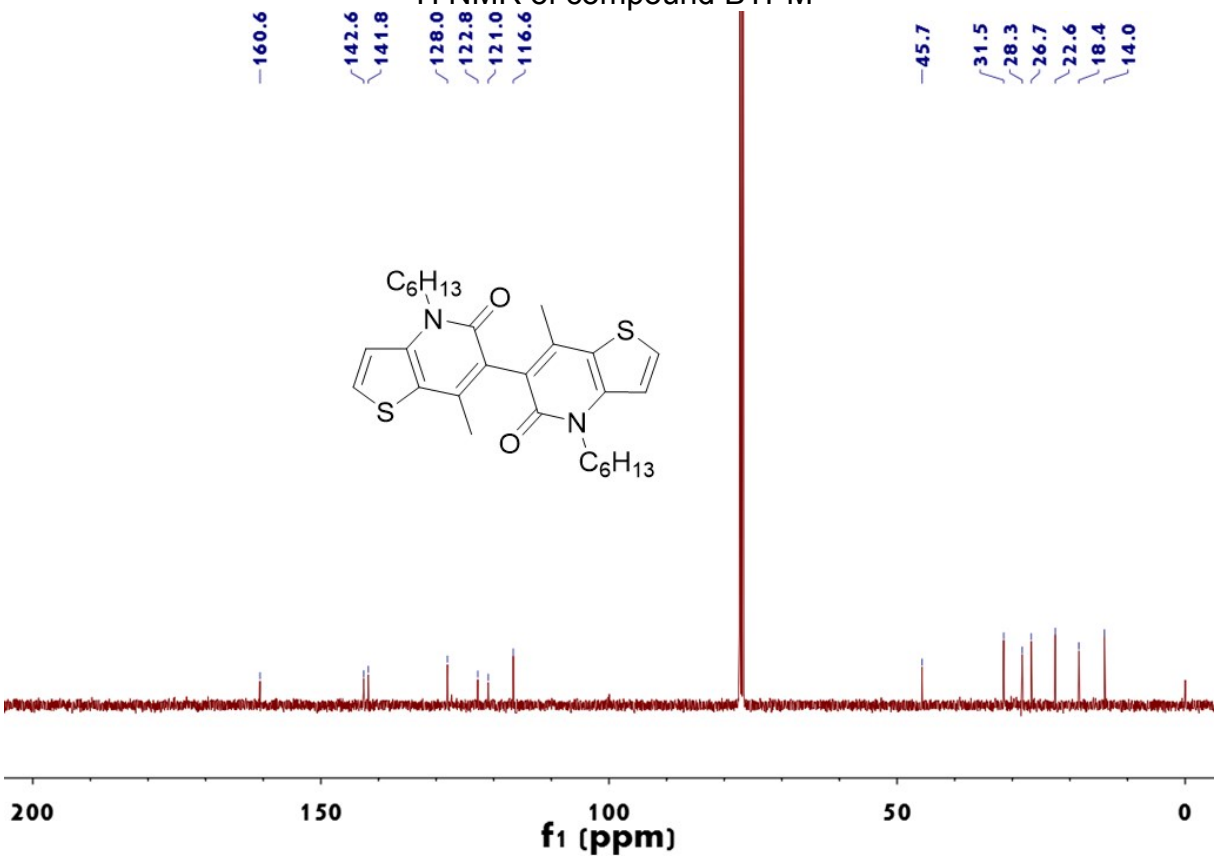

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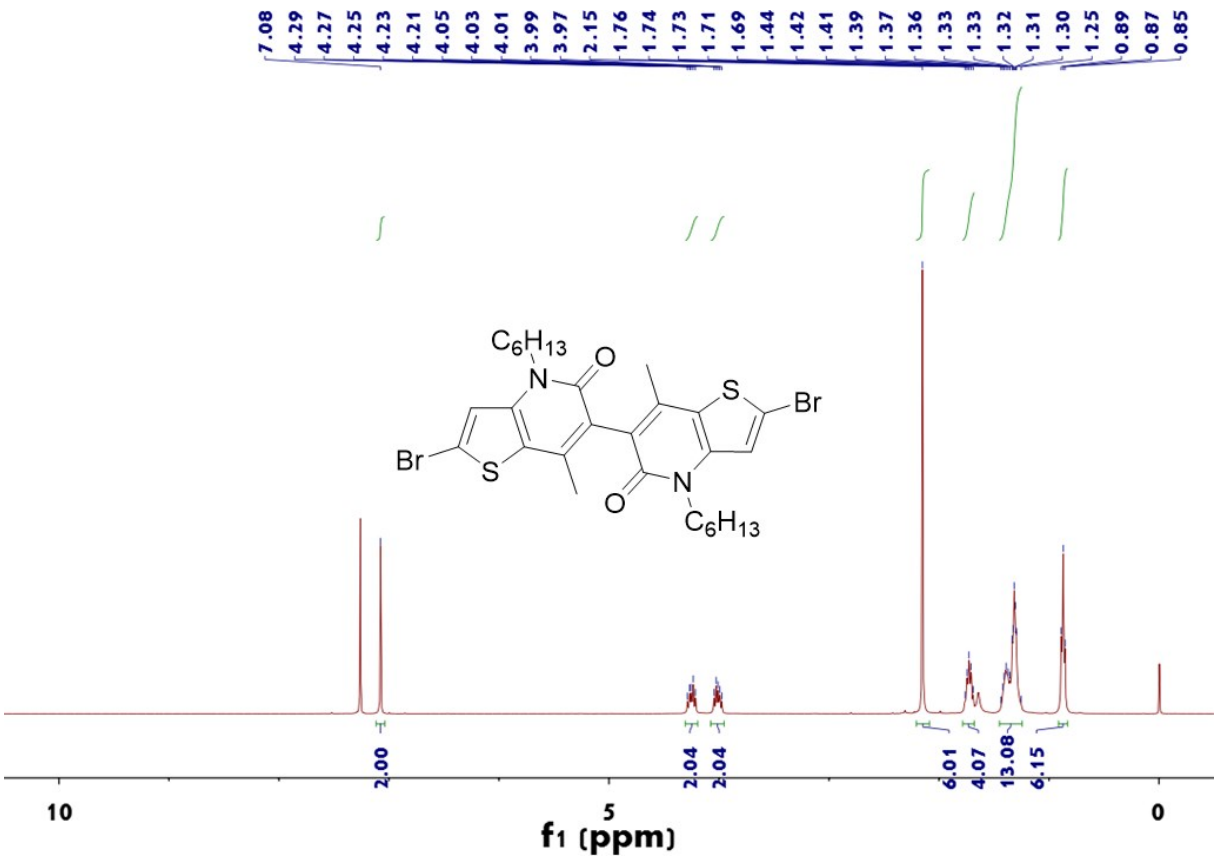

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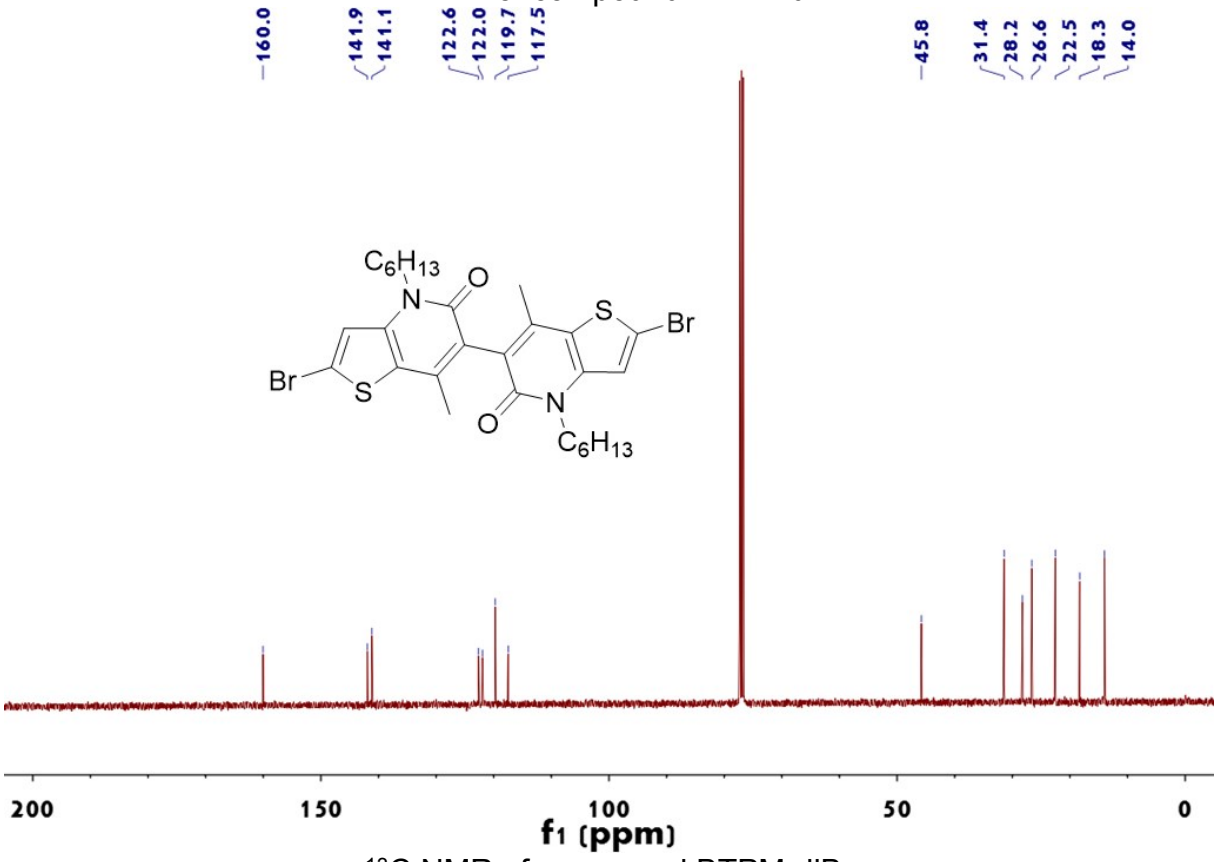

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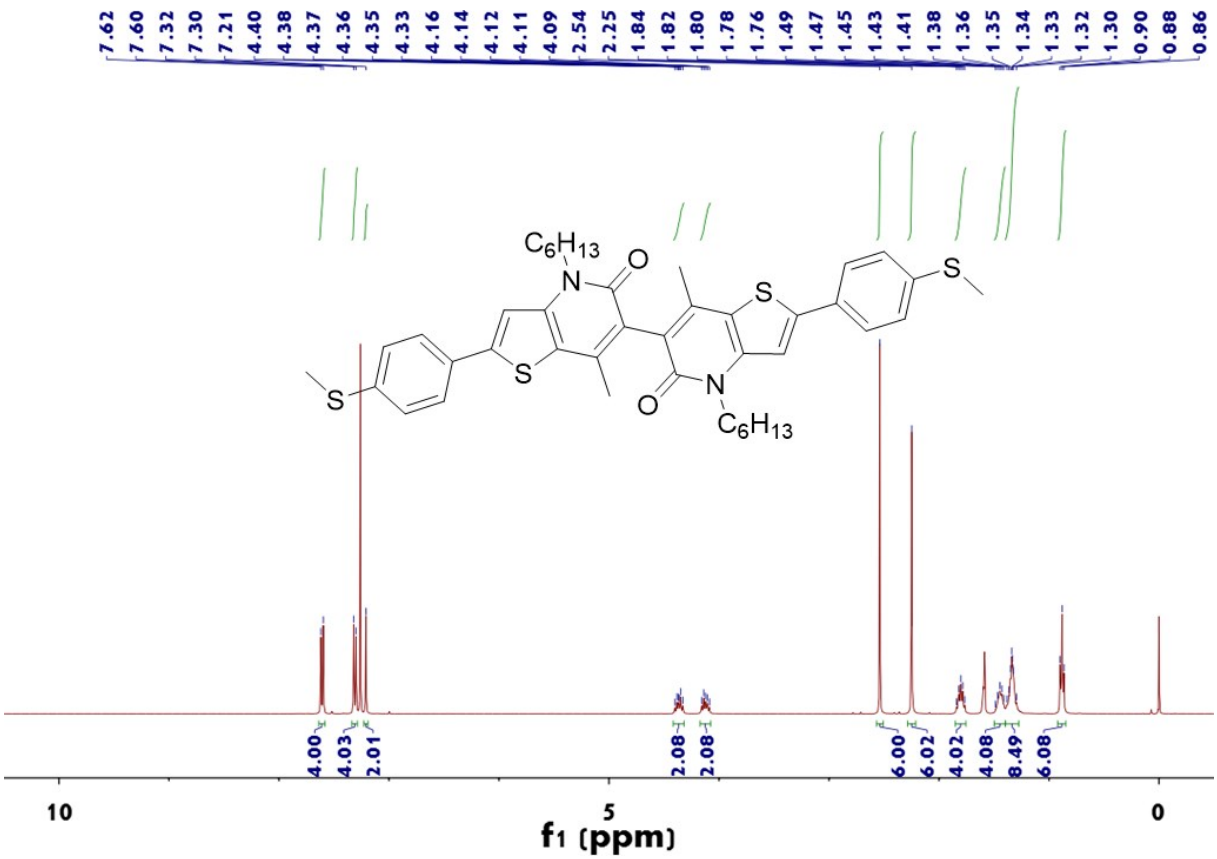

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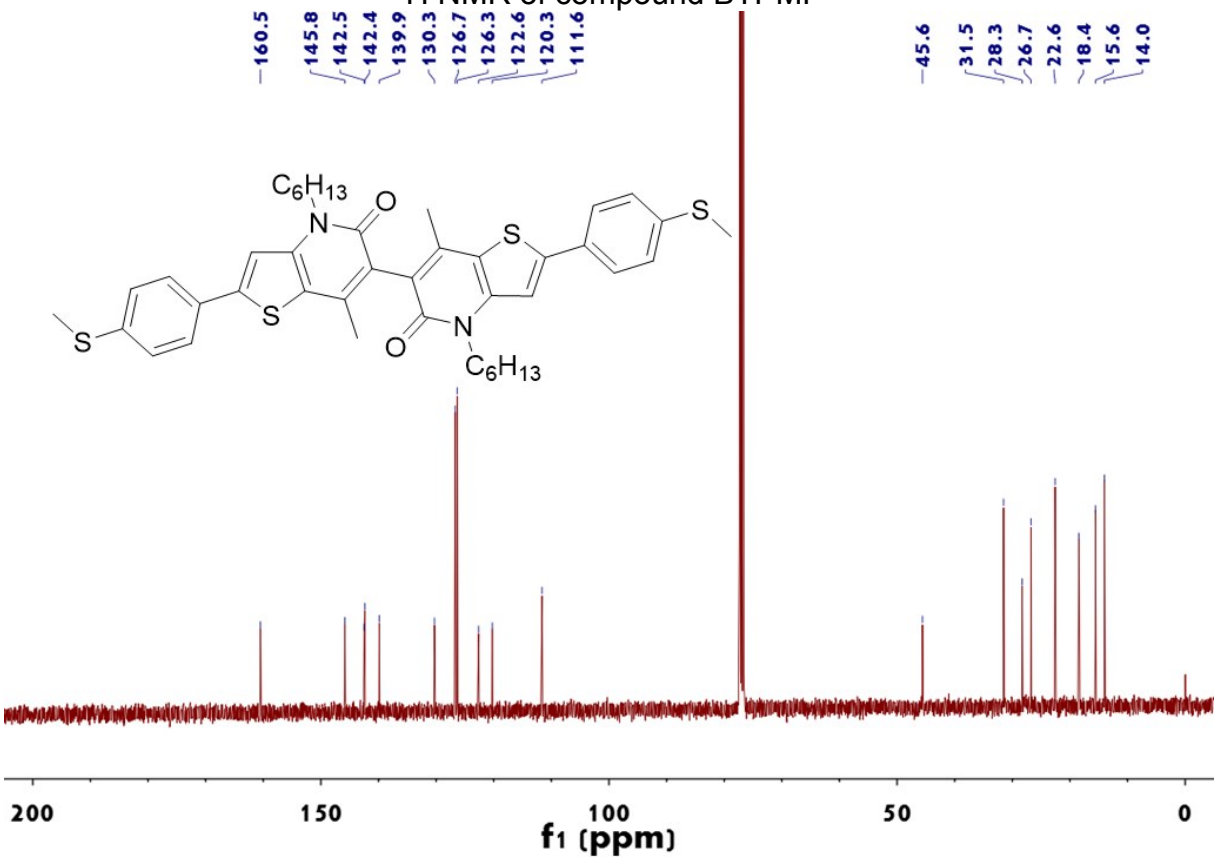

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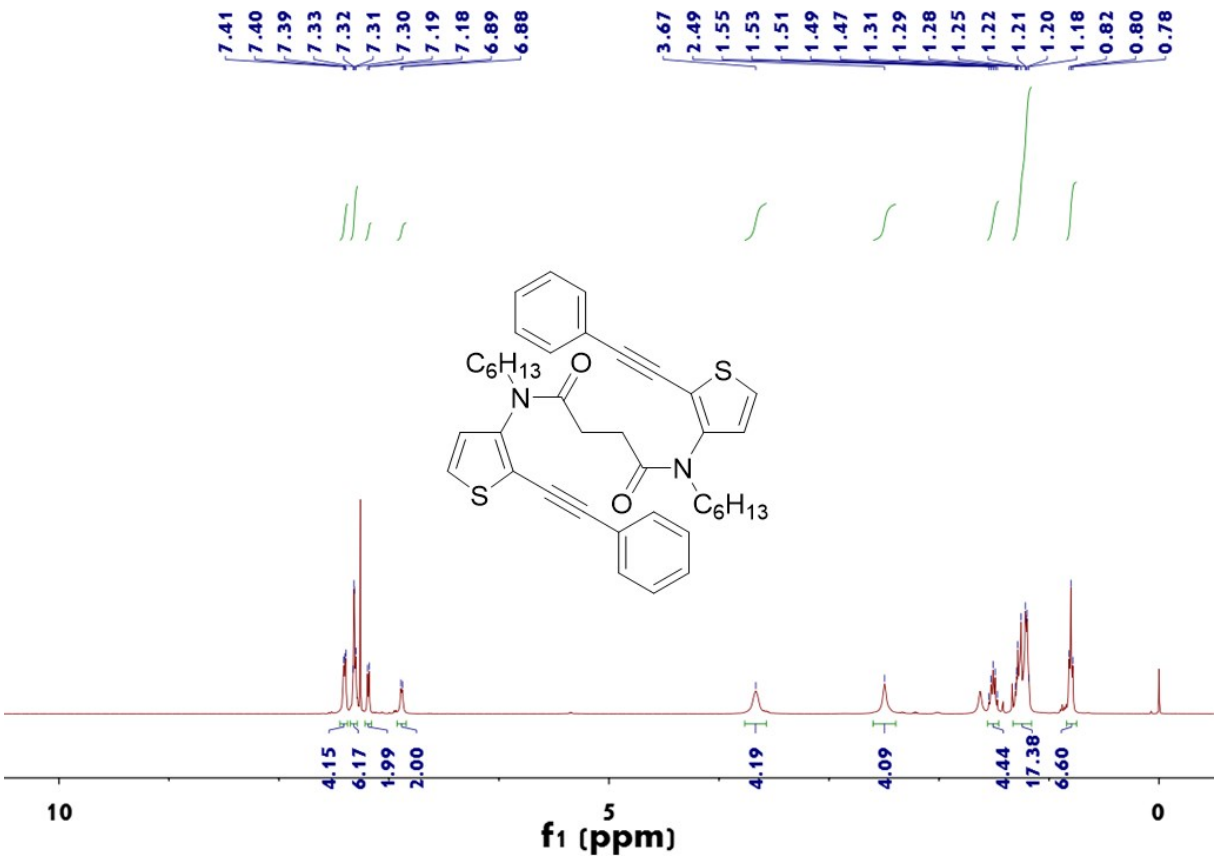

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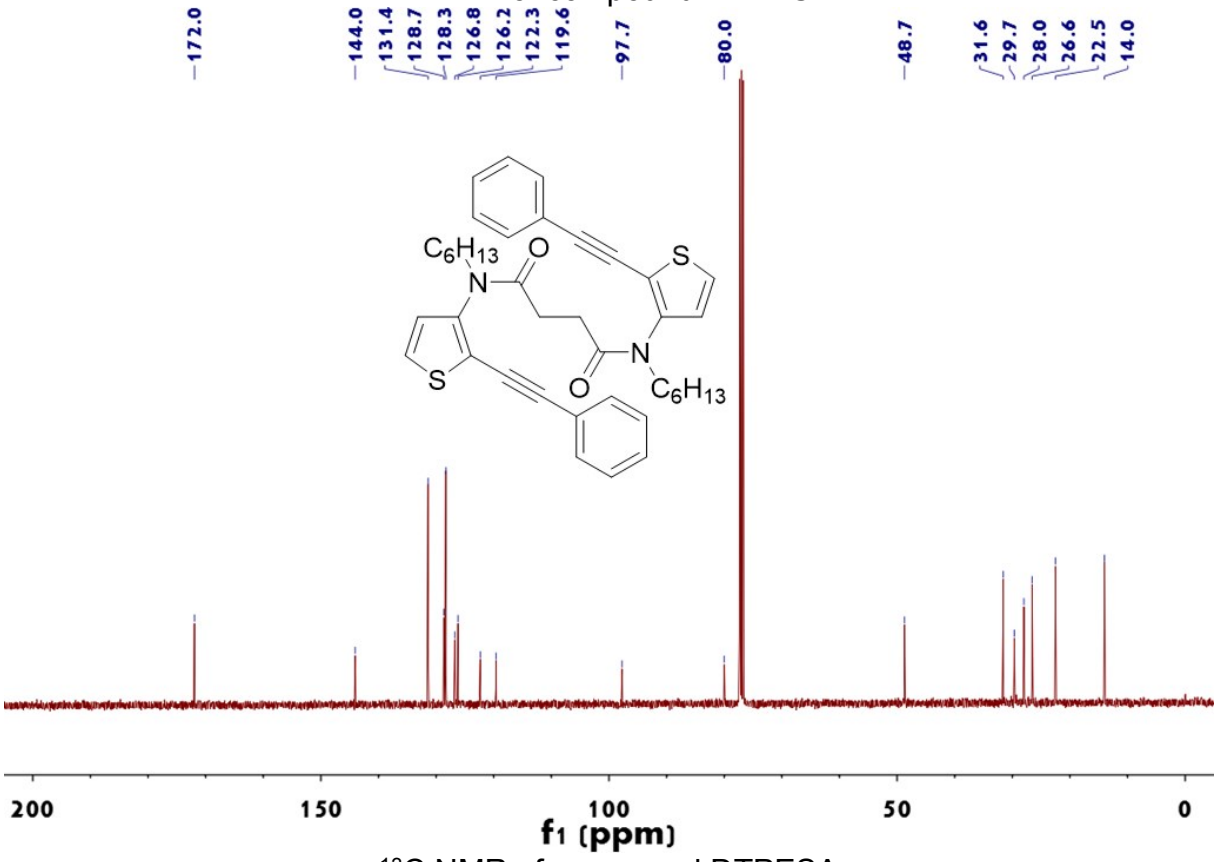

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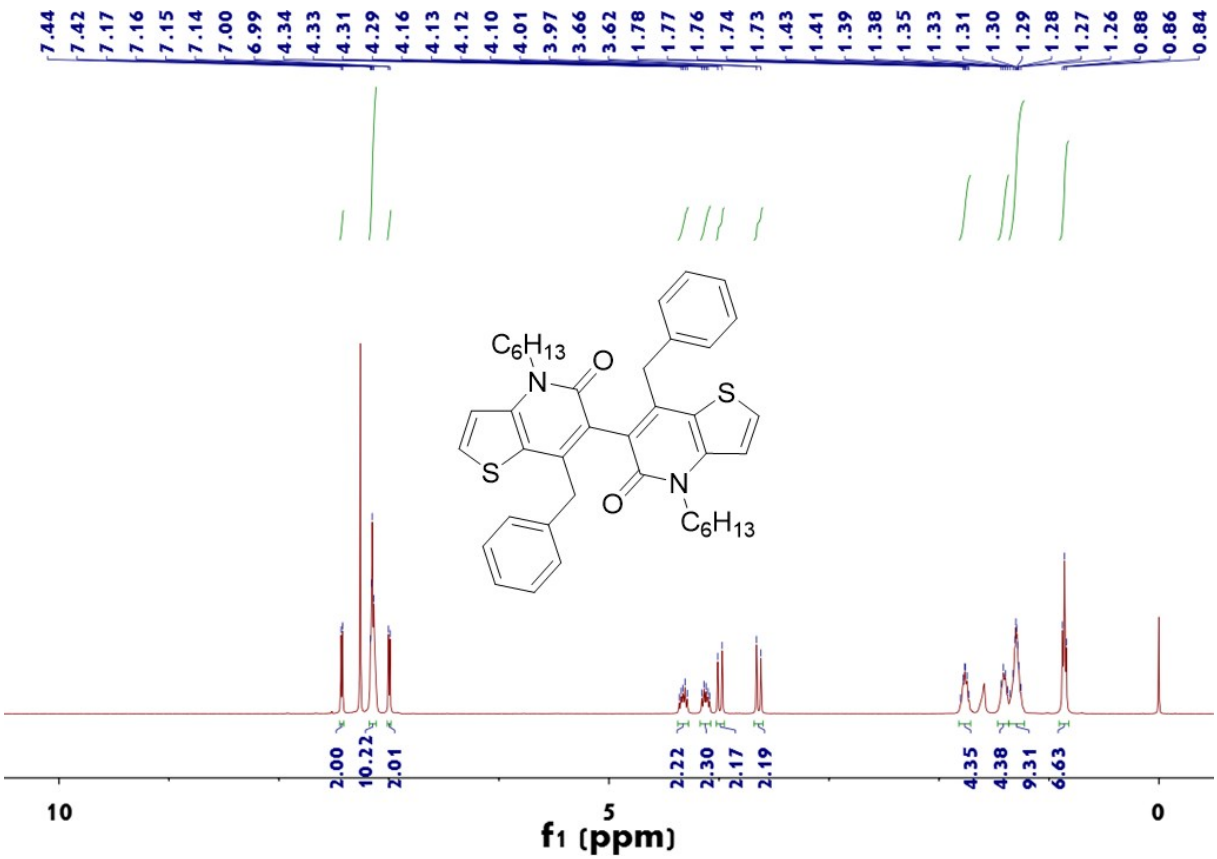

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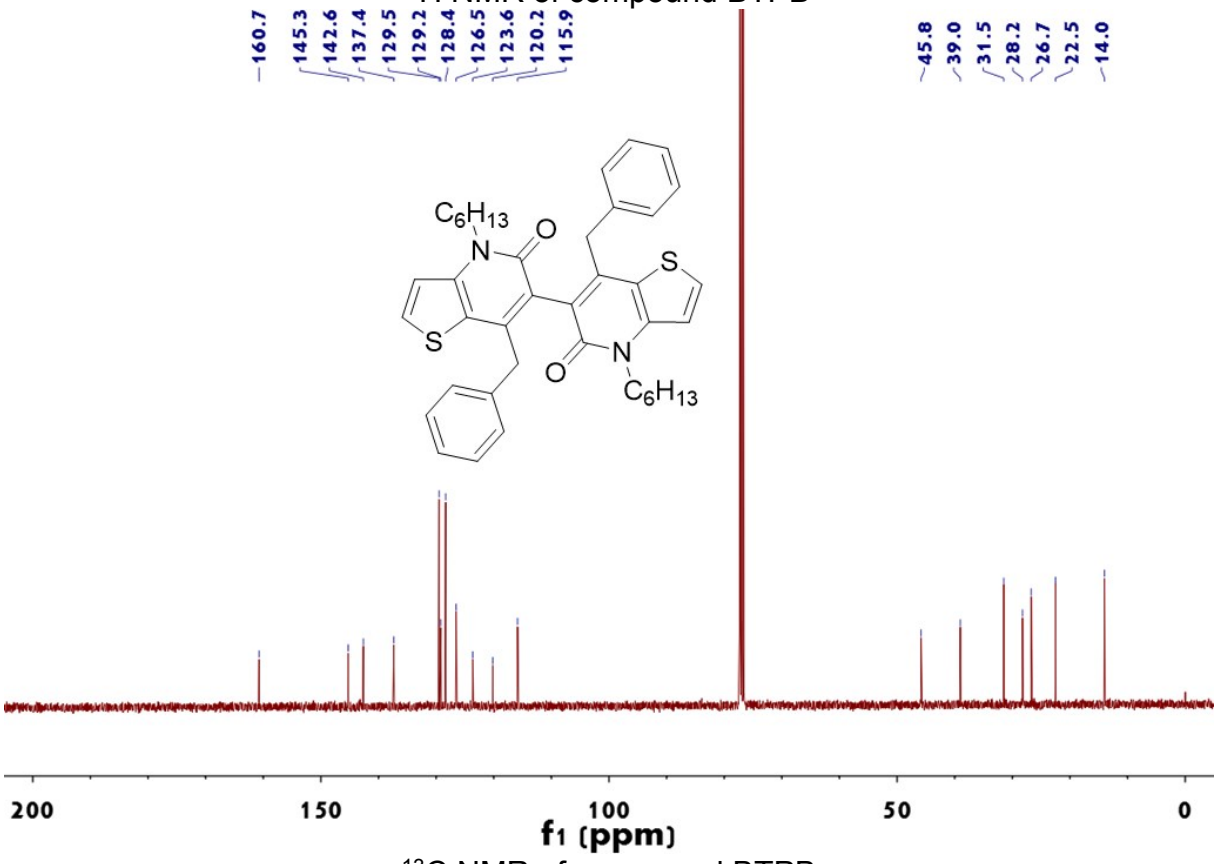

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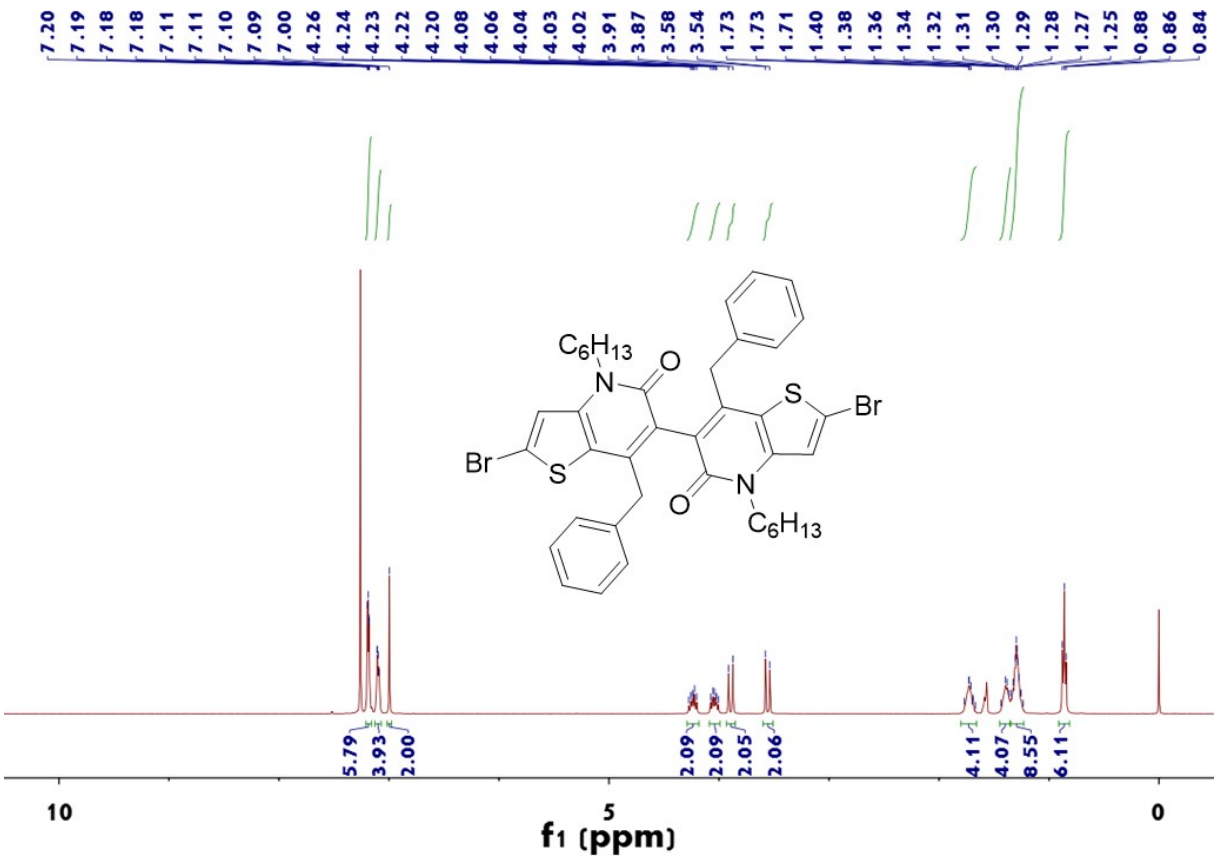

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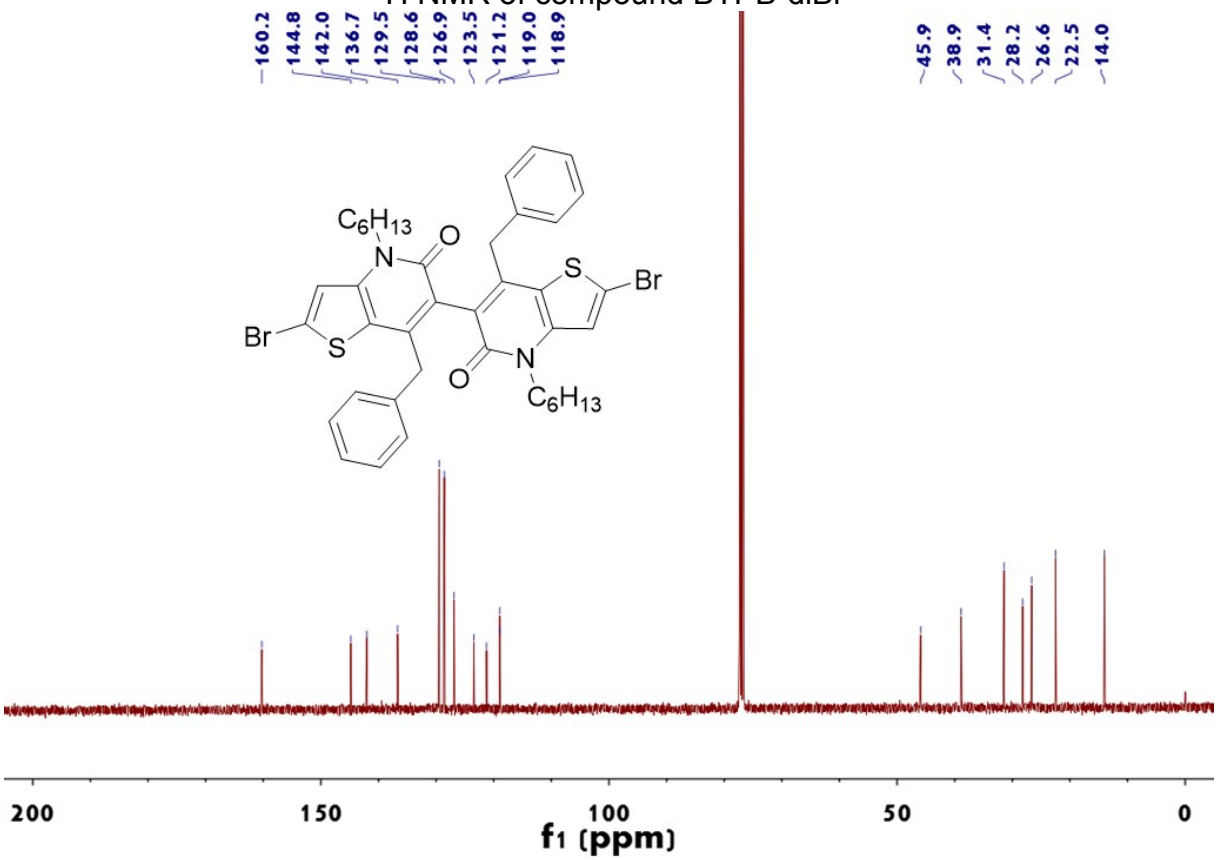

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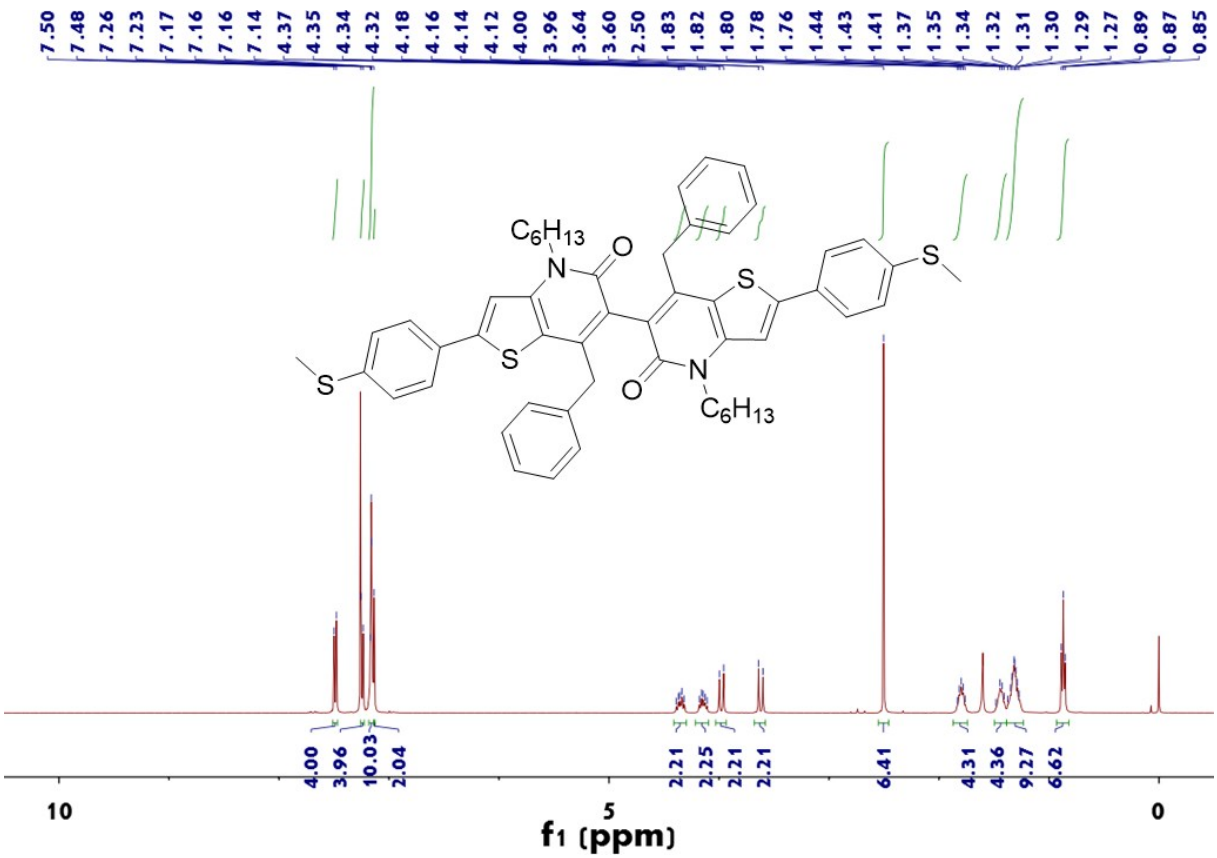

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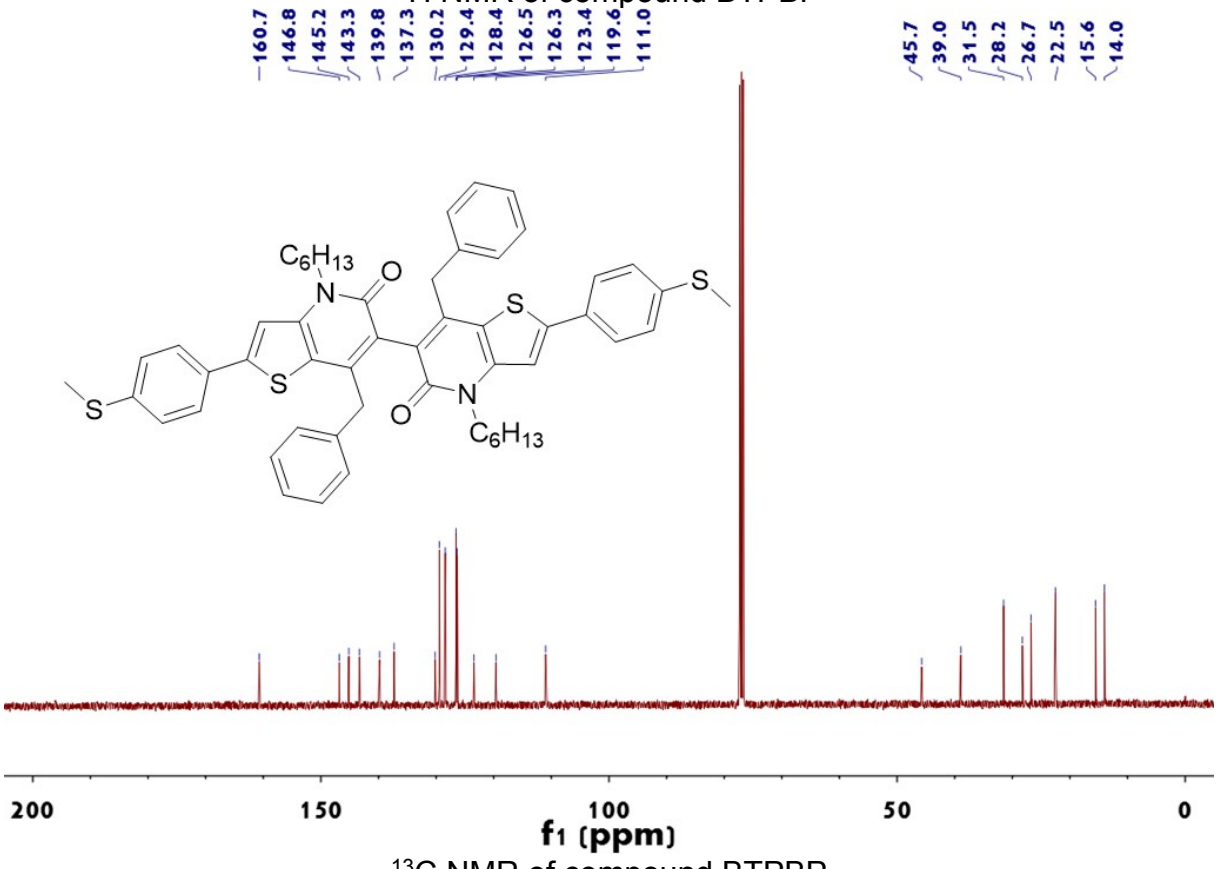

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