Electronic Supporting Information for:

Predictably Tuning the Frontier Molecular Orbital Energy Levels of Panchromatic Low Bandgap BODIPY-based Conjugated Polymers

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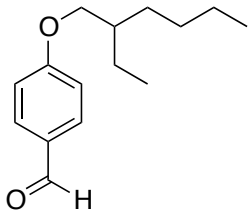
Detailed Synthetic Procedures

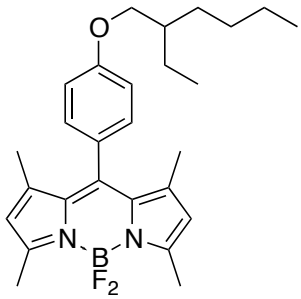
4-(2'-ethyl)hexyloxybenzaldehyde



1

4-hydroxybenzaldehyde (10.0 g, 82 mmol) was dissolved in acetone (500 mL). Activated potassium carbonate (22 g, 164 mmol) and 18-crown-6 (2.2 g, 8.2 mmol) were added to the flask. 2-ethylhexyl bromide (17.4 g, 90 mmol) was added to the flask via a syringe. The reaction mixture was stirred vigorously under reflux for 48 h. After cooling the flask and its contents to room temperature, the solvent was evaporated under reduced pressure. The slurry was suspended in ethyl acetate and repeatedly washed with water followed by brine. The organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was then purified by silica gel chromatography using Combiflash Rf-200 automated flash chromatograph with hexanes-ethyl acetate as the eluents. The solvents were evaporated *in vacuo* to give the final product as a colorless oil (18.5 g, yield 88%). ^{1}H-NMR (400 MHz; CDCl3): δ 9.88 (s, 1H), 7.82 (d, J = 8.9 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 3.93 (dd, J = 5.7, 1.0 Hz, 2H), 1.77-1.73 (m, 1H), 1.48-1.44 (m, 4H), 1.34-1.30 (m, 4H), 0.95-0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 164.5, 132.0, 129.7, 114.8, 70.9, 39.3, 30.5, 29.1, 23.8, 23.0, 14.1, 11.1, 1.1. EI-MS: M^+ ($C_{15}H_{22}O_2$) Calcd m/z = 234.33, Found m/z = 234.23.

BODIPY

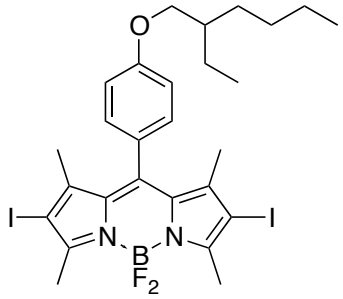


2

4-(2'-ethyl)hexyloxybenzaldehyde (2.5 g, 10.5 mmol) was dissolved in anhydrous dichloromethane (800 mL). To this solution 2,4-dimethylpyrrole (2.0 g, 21 mmol) was added and the contents were degassed for 5 minutes by purging argon. Trifluoroacetic acid (0.2 mL) was added and the reaction was allowed to proceed at room temperature for 1.5 h. The solution color gradually changed from yellow to deep wine red over the course of the reaction. The reaction mixture was then washed with 2N NaOH solution (200 mL) and then with water (200 mL). The organic layer was dried over anhydrous sodium sulfate, concentrated under reduced pressure to yield viscous dark brown oil. This was then dissolved in toluene (50 mL) and DDQ (2.7 g, 11.7 mmol) was added. After 5 minutes of stirring under argon flow, triethylamine (8 mL) and borontrifluoride etherate (7 mL) were added and the reaction was allowed to proceed at room temperature for 1.5 h. The reaction mixture was then diluted with ethyl ether and repeatedly washed with water. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was then purified by silica gel chromatography

using Combiflash Rf-200 automated flash chromatograph with hexanes-ethyl ether as the eluents. The solvents were evaporated *in vacuo* to give the final product as a bright orange solid with a metallic luster (1.2 g, yield 25%). ^{1}H NMR (400 MHz; CDCl3): δ 7.14 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 5.97 (s, 2H), 3.89 (d, J = 5.9 Hz, 2H), 2.55 (s, 6H), 1.80-1.74 (m, 1H), 1.54-1.50 (m, 4H), 1.44 (s, 6H), 1.38-1.33 (m, 4H), 0.98-0.94 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 155.2, 143.2, 142.1, 131.9, 129.1, 126.7, 121.1, 115.2, 70.9, 39.4, 30.6, 29.2, 23.9, 23.1, 14.6, 14.6, 14.1, 11.2. EI-MS: M^+ ($C_{27}H_{35}BF_2N_2O$) Calcd m/z = 452.39, Found m/z = 452.30.

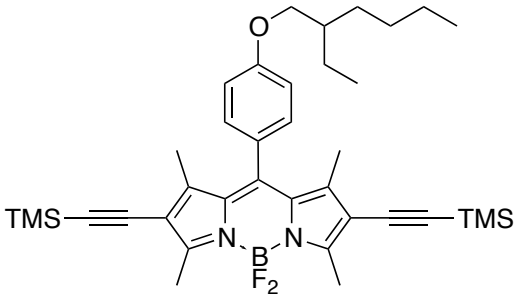
2,6-diiodoBODIPY



3

BODIPY (2) (1.2 g, 2.7 mmol) was dissolved in dichloromethane (36 mL) and the flask was purged with argon. A solution of *N*-iodosuccinimide in anhydrous and degassed DMF (12 mL) was slowly added to the flask via a syringe. The reaction mixture was vigorously stirred for 24 h at room temperature. After 24 h, dichloromethane was evaporated under reduced pressure. The residue was dissolved in ethyl ether and repeatedly extracted with water. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was then purified by silica gel chromatography using Combiflash Rf-200 automated flash chromatograph with hexanes-dichloromethane as the eluents. The solvents were evaporated *in vacuo* to give the final product as a deep red solid (1.5 g, yield 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 3.91 (d, J = 5.9 Hz, 2H), 2.64 (s, 6H), 1.80-1.74 (m, 1H), 1.54-1.50 (m, 4H), 1.45 (s, 6H), 1.38-1.33 (m, 4H), 0.98-0.94 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 156.5, 145.4, 141.8, 131.8, 129.0, 126.4, 115.5, 70.9, 39.4, 30.5, 29.1, 23.9, 23.0, 17.2, 16.0, 14.1, 11.2. EI-MS: M^+ ($C_{27}H_{33}BF_2I_2N_2O$) Calcd m/z = 704.18, Found m/z = 704.20.

2,6-bis(trimethylsilylethynyl)BODIPY

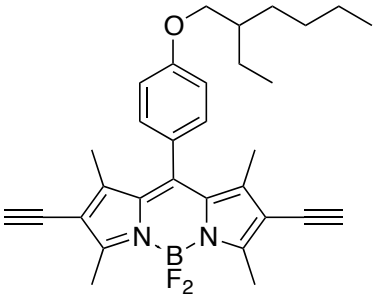


4

2,6-diiodoBODIPY (3) (1.1 g, 1.56 mmol) was placed in a round bottom flask equipped with a magnetic stirrer. The flask and its contents were transferred to a glove box under inert atmosphere. $Pd(PPh_2)Cl_2$ (109 mg, 10 mol%) and CuI (59 mg, 20 mol%) were added to the flask under nitrogen. The flask was sealed and taken out of the glove box. Freshly distilled diisopropylamine (50 mL) and trimethylsilylacetylene (0.6 g, 6.25 mmol) were then added to the flask and the reaction was carried out at 90 °C for 2 h. After cooling the reaction mixture to room temperature, the solvent was removed under reduced pressure. The crude product directly purified by silica gel chromatography using Combiflash Rf-200 automated flash chromatograph with hexanes-dichloromethane as the eluents. The solvents were

evaporated *in vacuo* to give the final product as a deep red solid (900 mg, yield 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H), 3.90 (d, J = 5.8 Hz, 2H), 2.63 (s, 6H), 1.80-1.74 (m, 1H), 1.56-1.54 (m, 2H), 1.52 (s, 6H), 1.40-1.34 (m, 6H), 0.98-0.92 (m, 6H), 0.20 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 158.5, 145.0, 143.1, 131.5, 129.0, 126.1, 116.1, 115.3, 101.6, 97.2, 70.9, 39.4, 30.5, 29.1, 23.9, 23.1, 14.1, 13.6, 11.2, 0.1. EI-MS: M^+ ($C_{37}H_{51}BF_2N_2OSi_2$) Calcd m/z = 644.79, Found m/z = 644.50.

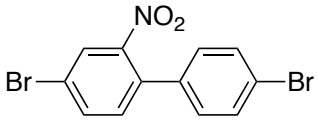
2,6-diethynylBODIPY



5

2,6-bis(trimethylsilylethynyl)BODIPY (4) (900 mg, 1.4 mmol) was dissolved in freshly distilled THF (20 mL), purged with argon and the solution was cooled to –70 °C. A solution of TBAF in THF (1M) (8.7 mL, 8.7 mmol) was added dropwise via a syringe over 30 minutes. The reaction mixture was then removed from the cooling bath and stirred at room temperature for 3h. The reaction was then quenched with dilute acetic acid (pH 4) and the crude product was extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was then purified by silica gel chromatography using Combiflash Rf-200 automated flash chromatograph with hexanes-dichloromethane as the eluents. The solvents were evaporated *in vacuo* to give the final product as a deep red solid (560 mg, yield 70%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.12 (d, J = 7.4 Hz, 2H), 7.03 (d, J = 7.5 Hz, 2H), 3.91 (d, J = 5.3 Hz, 2H), 3.31 (s, 2H), 2.64 (s, 6H), 1.77 (m, 1H), 1.53 (s, 6H), 1.45 (m, 4H), 1.35 (m, 4H), 0.95 (m, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 158.6, 145.6, 143.5, 131.3, 128.9, 125.9, 115.4, 114.9, 84.0, 76.0, 70.9, 39.3, 30.5, 29.1, 23.9, 23.0, 14.1, 13.5, 11.2. EI-MS: M^+ ($C_{31}H_{35}BF_2N_2O$) Calcd m/z = 500.43, Found m/z = 500.30.

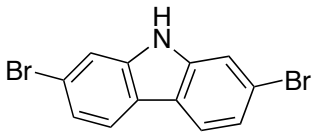
4,4'-Dibromo-2-nitrobiphenyl



6

To a solution of 4,4'dibromobiphenyl (10.0 g, 32 mmol) in glacial acetic acid (150 mL) was added fuming nitric acid (50 mL). The reaction mixture was stirred at 100ºC for 30 min. After cooling to room temperature a few pieces of ice were added to the reaction mixture carefully to induce precipitation. A voluminous yellow precipitate resulted that was then filtered off. The residue was then crystallized from boiling ethanol, filtered and dried in vacuum to give a pale yellow solid (10.9 g, 95%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.03 (d, J = 3.2 Hz, 1H), 7.75 (dd, J = 9.0, 3.0 Hz, 1H), 7.56 (d, J = 6.9 Hz, 2H), 7.29 (d, J = 8.2 Hz, 1H), 7.16 (d, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 149.4, 135.7, 135.4, 134.2, 133.2, 132.2, 129.5, 127.4, 123.2, 122.0. EI-MS: M^+ ($C_{12}H_7Br_2NO_2$) Calcd m/z = 357.00, Found m/z = 356.90.

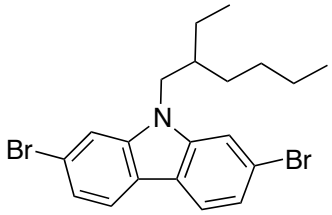
2,7-Dibromo-9*H*-carbazole



7

To a 100 mL two-necked round bottom flask was added 4,4'-Dibromo-2-nitrobiphenyl (10.0 g, 28 mmol) and triethylphosphite (40 mL). The mixture was stirred under reflux for 24 h under argon. The excess triethylphosphite was distilled under reduced pressure and the residue was purified by silica gel chromatography using Combiflash Rf-200 automated flash chromatograph with hexanes-ethyl acetate as the eluents. The solvents were evaporated *in vacuo* to give the final product as a pale yellow solid (5.5 g, 60%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.04 (s, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.58 (dd, J = 1.7, 0.4 Hz, 2H), 7.36 (dd, J = 8.3, 1.7 Hz, 2H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 140.3, 123.3, 121.8, 121.5, 119.8, 113.8. EI-MS: M^+ ($C_{12}H_7Br_2N$) Calcd m/z = 325.00, Found m/z = 324.90.

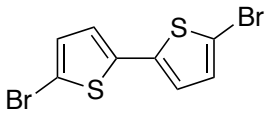
2,7-Dibromo-9-(2-ethylhexyl)-9*H*-Carbazole



8

To a 100 ml Schlenk flask was added 2,7-dibromo-9*H*-carbazole (2.0 g, 6.15 mmol) and sodium hydride (220 mg, 9.2 mmol) inside a nitrogen filled glove box. Anhydrous DMF (100 mL) was then added to the flask and the suspension was stirred at room temperature under argon for 30 min. 2-ethylhexyl bromide (1.5 g, 8.0 mmol) was syringed into the flask and the reaction mixture was stirred at room temperature for additional 18 h. The reaction was quenched with water and the crude product was extracted with ether. The organic fractions were washed with copious amounts of water, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was then purified by silica gel chromatography using Combiflash Rf-200 automated flash chromatograph with hexanes and ethyl acetate as the eluents. ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.89 (dd, J = 8.3, 0.4 Hz, 2H), 7.51 (d, J = 1.4 Hz, 2H), 7.34 (dd, J = 8.3, 1.7 Hz, 2H), 4.12-4.02 (m, 2H), 2.05-1.99 (m, 1H), 1.41-1.26 (m, 8H), 0.90 (dt, J = 16.8, 7.3 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 141.8, 122.5, 121.4, 121.2, 119.7, 112.2, 47.6, 39.1, 30.8, 28.6, 24.4, 23.1, 14.1, 10.9. EI-MS: M^+ ($C_{20}H_{23}Br_2N$) Calcd m/z = 437.21, Found m/z = 437.10.

5,5'-dibromo-2,2'-bithiophene

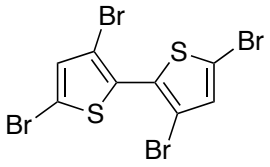


9

2,2'-bithiophene (500 mg, 3.0 mmol) was dissolved in dichloromethane and *N*-bromosuccinimide (1.12 g, 6.3 mmol) was added at room temperature and the reaction mixture was stirred under argon for 12 h. The reaction mixture was then washed with water and brine. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was then purified by silica gel chromatography using Combiflash Rf-200 automated flash chromatograph with hexanes as the eluents. The solvent was evaporated *in vacuo* to give the final product as a white powder (1.8 g,

90%) ^{1}H NMR (400 MHz; $CDCl_3$): δ 6.96 (d, J = 3.8 Hz, 1H), 6.85 (d, J = 3.8 Hz, 1H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.8, 130.7, 124.1, 111.5. EI-MS: M^+ ($C_8H_4Br_2S_2$) Calcd m/z = 324.06, Found m/z = 324.0.

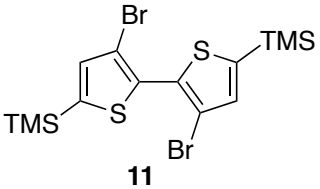
3,3',5,5'-tetrabromo-2,2'-bithiophene



10

2,2'-bithiophene (5.0 g, 30.1 mmol) was dissolved in chloroform (60 mL) and glacial acetic acid (30 mL). The solution was cooled with an ice-water bath. Bromine (6.2 mL, 120.3 mmol) was added as a solution in chloroform (30 mL) dropwise over three to four hours. The reaction mixture was slowly allowed to warm to room temperature and stirred overnight. After completion, HBr was driven off by passing a gentle stream of air through the flask. The solvents were removed *in vacuo*. The crude solid was washed with ether (4 x 100 mL) to yield a light green solid (9.7 g, 67%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.05 (s, 2H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 133.0, 129.5, 114.8, 112.1. EI-MS: M^+ ($C_8H_2Br_4S_2$) Calcd m/z = 481.85, Found m/z = 481.70.

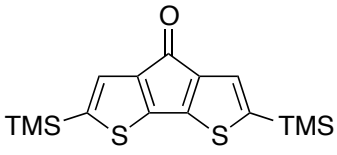
3,3'-dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene



11

In a three-neck round bottom flask equipped with an addition funnel, 3,3',5,5'-tetrabromo-2,2'-bithiophene (8.55 g, 17.7 mmol) was dissolved in dry tetrahydrofuran (150 ml). The solution was cooled to -78°C using a dry ice/acetone bath. A 2.5M butyllithium solution (14.0 ml, 35.0 mmol) was added dropwise over 15 min and the reaction was stirred at -78°C for 15 min. Chlorotrimethylsilane (5.60 ml, 44.1 mmol) was added to the reaction mixture by syringe at once. The reaction mixture was raised to room temperature. Deionoized water was added, followed by extraction with diethyl ether (2 x 50 ml). The combined organic layer was dried over sodium sulfate and purified by silica gel column chromatography (hexanes). The collected viscous oil was then dried under vacuum and used for the following step without further purification. ^{1}H NMR (400 MHz; CDCl3): δ 7.15 (s, 2H), 0.34 (s, 18H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 143.1, 137.2, 134.1, 113.1, -0.2. EI-MS: M^+ ($C_{14}H_{20}Br_2S_2Si_2$) Calcd m/z = 468.42, Found m/z = 468.00.

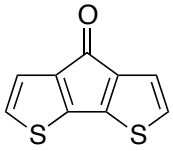
2,6-Bis(trimethylsilyl)cyclopenta[2,1-*b*:3,4-*b*']dithiophen-4-one



12

To a 250 mL two-necked round bottom flask was added 3,3'-dibromo-5,5'-(bis)trimethylsiyl-2,2'-bithiophene (7.5 g, 16.1 mmol) in 60 mL freshly distilled THF. Under argon atmosphere, *n*BuLi (12.9 mL, 32.2 mmol) was added dropwise using a pressure equalized addition funnel to the stirring reaction mixture at –78°C. After stirring for 15 min at this temperature, *N*,*N*-dimethylcarbamyl chloride (1.5 mL, 16.1 mmol) dissolved in 15 mL freshly distilled THF was added dropwise to the reaction mixture. After addition, the reaction mixture was warmed to 0°C and maintained at that temperature for an additional 2 h. The reaction mixture was then quenched with 60 mL saturated NH_4Cl solution and the aqueous layer was separated and washed with hexanes. The combined organic fractions were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was then quickly purified by silica gel chromatography using Combiflash Rf-200 automated flash chromatograph with hexanes as the eluents. The solvent was evaporated *in vacuo* to give the final product as a deep red semisolid (2.78 g), which was used as such for the next reaction without further purification. ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.07 (s, 2H), 0.31 (s, 18H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 183.3, 154.5, 145.1, 144.3, 128.1, -0.1. EI-MS: M^+ ($C_{15}H_{20}OS_2Si_2$) Calcd *m*/*z* = 336.62, Found *m*/*z* = 366.10.

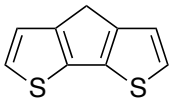
4*H*-Cyclopenta[2,1-*b*:3,4-*b*']dithiophen-4-one



13

2,6-Bis(trimethylsilyl)cyclopenta[2,1-*b*;3,4-*b*']dithiophen-4-one (2. 8 g, 8.3 mmol) was dissolved in THF (10 mL) and MeOH (10 mL). Potassium carbonate (5.7 g, 41.5 mmol) was added to the flask and the reaction mixture was stirred at room temperature for 5 h. After quenching the reaction with water (150 mL), the crude product was extracted with ether (50 mL). The aqueous layer was washed with ether (3 x 50 mL). The combined organic fractions were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was then purified by silica gel chromatography using Combiflash Rf-200 automated flash chromatograph with hexanes and dichloromethane as the eluents. The solvent was evaporated *in vacuo* to give the final product as a deep red solid (943 mg, 60%). Analytical samples were prepared by recrystallization from ether to give deep red needles. ^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.04 (d, J = 4.9 Hz, 2H), 7.00 (d, J = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.9, 149.4, 142.6, 127.3, 121.9. EI-MS: M^+ ($C_9H_4OS_2$) Calcd *m*/*z* = 192.26, Found *m*/*z* = 192.00.

4*H*-Cyclopenta[2,1-*b*:3,4-*b*']dithiophene

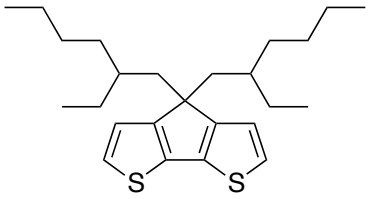


14

4*H*-Cyclopenta[2,1-*b*:3,4-*b*']dithiophen-4-one (943 mg, 4.9 mmol) and powdered KOH (950 mg, 17 mmol) were suspended in tetraethylene glycol (100 mL). Hydrazine monohydrate (6 mL) was added via a syringe at room temperature and the mixture was gradually heated to 180°C and stirred at that temperature for 7 h. After cooling the reaction mixture to room temperature water (100 mL) was added and the crude product was extracted into ether (50 ml). The organic layer was then washed with saturated NH_4Cl solution (2 x 100 mL) and then water (2 x 100 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was then purified by silica gel

chromatography using Combiflash Rf-200 automated flash chromatograph with hexanes the eluents. The solvent was evaporated *in vacuo* to give the final product as an off-white solid (530 mg, 61%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.18 (d, J = 4.9 Hz, 2H), 7.09 (d, J = 4.9 Hz, 2H), 3.54 (d, J = 2.2 Hz, 2H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 149.8, 138.8, 124.6, 123.1, 31.9. EI-MS: M^+ ($C_9H_6S_2$) Calcd m/z = 178.27, Found m/z = 178.10.

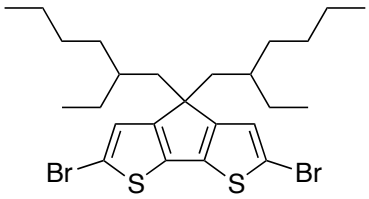
4,4-bis(2-ethylhexyl)-4*H*-Cyclopenta[2,1-*b*:3,4-*b*']dithiophene



15

To a 25 mL round-bottom flask was added 4*H*-Cyclopenta[2,1-*b*:3,4-*b*']dithiophene (530 mg, 2.9 mmol) dissolved in DMSO (10 mL). KOH (530 mg, 9.5 mmol) was added to the flask followed by the successive addition of a catalytic amount of KI (10 mg) and 2-ethylhexyl bromide (1.2 g, 6.2 mmol). The reaction mixture turned deep green and was allowed to stir under argon for 20 h at room temperature. The reaction was then quenched with water and the crude product was extracted into ether (50 mL). The organic layer was washed with saturated NH_4Cl solution (2 x 100 mL) and water (2 x 100 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was then purified by silica gel chromatography using Combiflash Rf-200 automated flash chromatograph with hexanes as the eluents. The solvent was evaporated *in vacuo* to give the final product as a pale yellow oil (990 mg, 83%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.11 (d, J = 4.9 Hz, 2H), 6.93-6.91 (m, 2H), 1.91-1.81 (m, 4H), 1.30-1.27 (m, 2H), 0.98-0.87 (m, 16H), 0.75 (t, J = 6.8 Hz, 6H), 0.60-0.57 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 136.9, 124.1, 122.4, 53.4, 43.4, 35.1, 34.3, 32.0, 28.7, 22.9, 14.2, 10.8. EI-MS: M^+ ($C_{25}H_{38}S_2$) Calcd m/z = 402.24, Found m/z = 402.20.

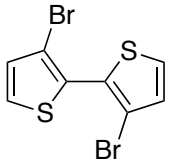
2,6-Dibromo-4,4-bis(2-ethylhexyl)-4*H*-Cyclopenta[2,1-*b*:3,4-*b*']dithiophene



16

To a solution of 4,4-bis(2-ethylhexyl)-4*H*-Cyclopenta[2,1-*b*:3,4-*b*']dithiophene (990 mg, 2.5 mmol) in DMF (20 mL) was added a solution of *N*-bromosuccinimide (1.25 g, 6.5 mmol) in DMF (10 mL). The reaction flask was covered with aluminum foil and the reaction was allowed to proceed at room temperature for 12 h. The reaction was then quenched with water (150 mL) and the crude product was extracted into ether (2 x 75 mL). The organic fraction was washed with copious amount of water, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was then purified by silica gel chromatography using Combiflash Rf-200 automated flash chromatograph with hexanes as the eluents. The solvent was evaporated *in vacuo* to give the final product as a discolored oil (1.01 g, 73%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 6.93 (t, J = 3.8 Hz, 2H), 1.84-1.76 (m, 4H), 1.03-0.89 (m, 18H), 0.78 (t, J = 7.0 Hz, 6H), 0.62 (td, J = 7.4, 1.7 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 155.6, 136.6, 125.3, 125.2, 125.1, 110.7, 54.9, 43.1, 35.1, 34.1, 28.57, 27.4, 22.8, 14.1, 10.7. EI-MS: M^+ ($C_{25}H_{36}Br_2S_2$) Calcd m/z = 560.49, Found m/z = 560.20.

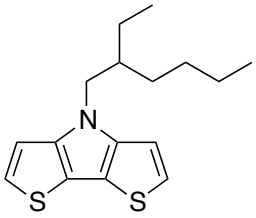
3,3'-dibromo-2,2'-bithiophene



17

To a round bottom flask equipped with a reflux condenser were added 3,3',5,5'-tetrabromo-2,2'-bithiophene (5.0 g, 10.4 mmol), glacial acetic acid (40 mL) and ethanol (80 mL). To this suspension was added concentrated hydrochloric acid (5 mL) and water (5 mL) followed by zinc dust (8 g). The reaction mixture was stirred under reflux overnight. After cooling to room temperature, the reaction mixture was decanted to remove excess zinc. Solvents were removed *in vacuo*. The crude product was dissolved in dichloromethane and the organic layer was washed with water (2 x 250 mL) and a saturated aqueous sodium bicarbonate solution (1 x 250 mL). The organic fraction was dried over anhydrous sodium sulfate and concentrated to yield light green solid (3 g, 88%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.40 (d, J = 5.4 Hz, 2H), 7.09 (d, J = 5.4 Hz, 2H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 130.9, 129.0, 127.6, 112.7. EI-MS: M^+ ($C_8H_4Br_2S_2$) Calcd m/z = 323.81, Found m/z = 323.90.

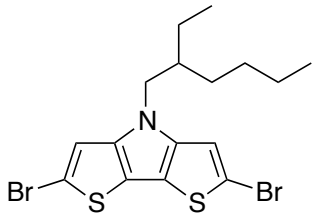
4-(2-ethylhexyl)-4*H*-Dithieno[3,2-*b*:2',3'-*d*]pyrrole



18

A 50 mL Schlenk flask was dried in an oven overnight and was equipped with a magnetic stirrer. The side arm was sealed with a rubber septum. 3,3'-dibromo-2,2'-bithiophene (3.5 g, 10.8 mmol), NaO*t*Bu (2.6 g, 27 mmol) and BINAP (0.7 g, 1.08 mmol, 10 mol%) were weighed out in ambient. The flask was then taken inside a glove box maintained under nitrogen. Pd_2dba_3 (197 mg, 0.2 mmol, 2 mol%) was then added to the flask. Once outside, a reflux condenser was attached to the open end of the flask under positive argon pressure (the exposure to ambient was kept as short as possible). The entire assembly was then evacuated and backfilled with argon. Degassed toluene (20 mL) was then added to the flask and the reaction mixture was purged by bubbling argon for 30 min. 2-ethylhexyl amine (1.4 g, 10.8 mmol) was added via a syringe and the flask was lowered in an oil bath maintained at 120ºC. The reaction mixture was stirred under reflux for 12 h. The reaction mixture turned brown and remained so until the end of the reaction. After cooling to room temperature, the reaction mixture was added to water (175 mL) and the organic layer was separated. The aqueous layer was washed with ether (3 x 50 mL) and the combined organic fractions were dried over anhydrous sodium sulfate and concentrated *in vacuo*. The crude product was purified by silica gel chromatography using Combiflash Rf-200 automated flash chromatograph with hexanes-dichloromethane as the eluents. The solvents were evaporated *in vacuo* to yield a pale yellow oil that solidified upon cooling (2.6 g, 67%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.12 (d, J = 5.3 Hz, 2H), 6.99 (d, J = 5.3 Hz, 2H), 4.11-4.01 (m, 2H), 1.98-1.92 (m, 1H), 1.38-1.26 (m, 8H), 0.92-0.85 (m, 6H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 145.3, 122.7, 114.6, 111.2, 51.4, 40.5, 30.7, 28.7, 24.1, 23.1, 14.1, 10.8. EI-MS: M^+ ($C_{16}H_{21}NS_2$) Calcd m/z = 291.47, Found m/z = 291.20.

2,6-dibromo-4-(2-ethylhexyl)-4*H*-Dithieno[3,2-*b*:2',3'-*d*]pyrrol



19

4-(2-ethylhexyl)-4*H*-Dithieno[3,2-b:2',3'-d]pyrrole (1.0 g, 3.4 mmol) was dissolved in glacial acetic acid (45 mL) and dry chloroform (45 mL). The flask was covered with aluminum foil and lowered in an ice-water bath. *N*-bromosuccinimide (1.5 g, 8.6 mmol) was added to the flask and the reaction mixture was stirred at 0ºC for 1 h under a gentle argon flow. After 1 h, the reaction mixture was warmed to room temperature and stirred for an additional 1 h. The reaction mixture was then diluted with dichloromethane (90 mL) and washed with water (3 x 130 mL) and then with saturated aqueous sodium bicarbonate solution (3 x 130 mL). The organic fractions were dried over anhydrous sodium sulfate and solvents were evaporated *in vacuo* without heating. The crude product was then mixed with silica gel and quickly purified by silica gel chromatography using Combiflash Rf-200 automated flash chromatograph with hexanes as the eluents. The solvents were evaporated *in vacuo* to yield a pale yellow solid (1.45 g, 67%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 6.99 (s, 2H), 4.00-3.89 (m, 2H), 1.90-1.83 (m, 1H), 1.33-1.25 (m, 8H), 0.88 (m, 6H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 141.8, 114.6, 114.3, 109.7, 51.5, 40.4, 30.6, 28.6, 24.0, 23.0, 14.0, 10.7. EI-MS: M^+ ($C_{16}H_{19}Br_2NS_2$) Calcd *m/z* = 449.27, Found *m/z* = 448.9.

NMR Spectra

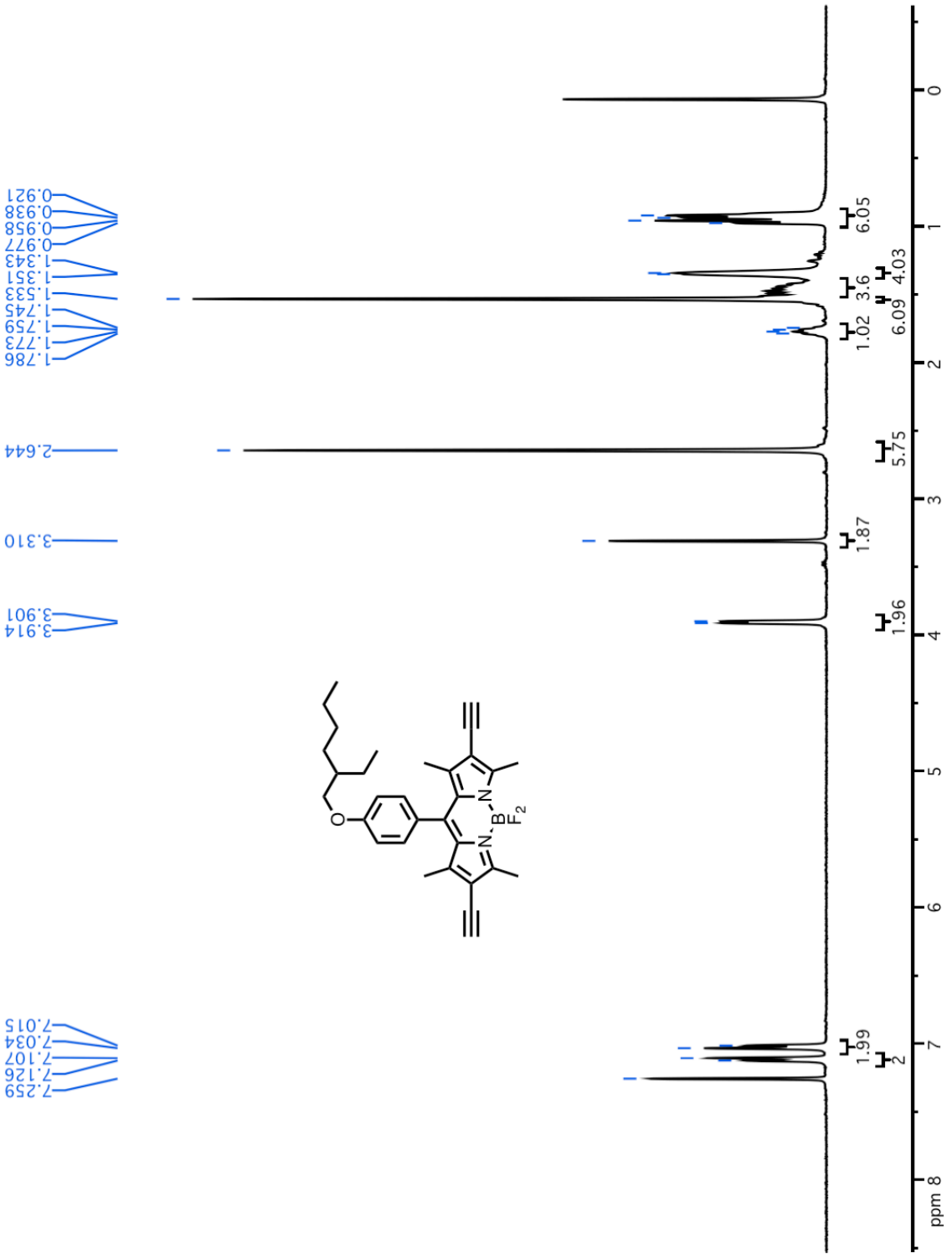


Figure S1. ^{1}H NMR Spectrum for 2,6-diethynyl BODIPY

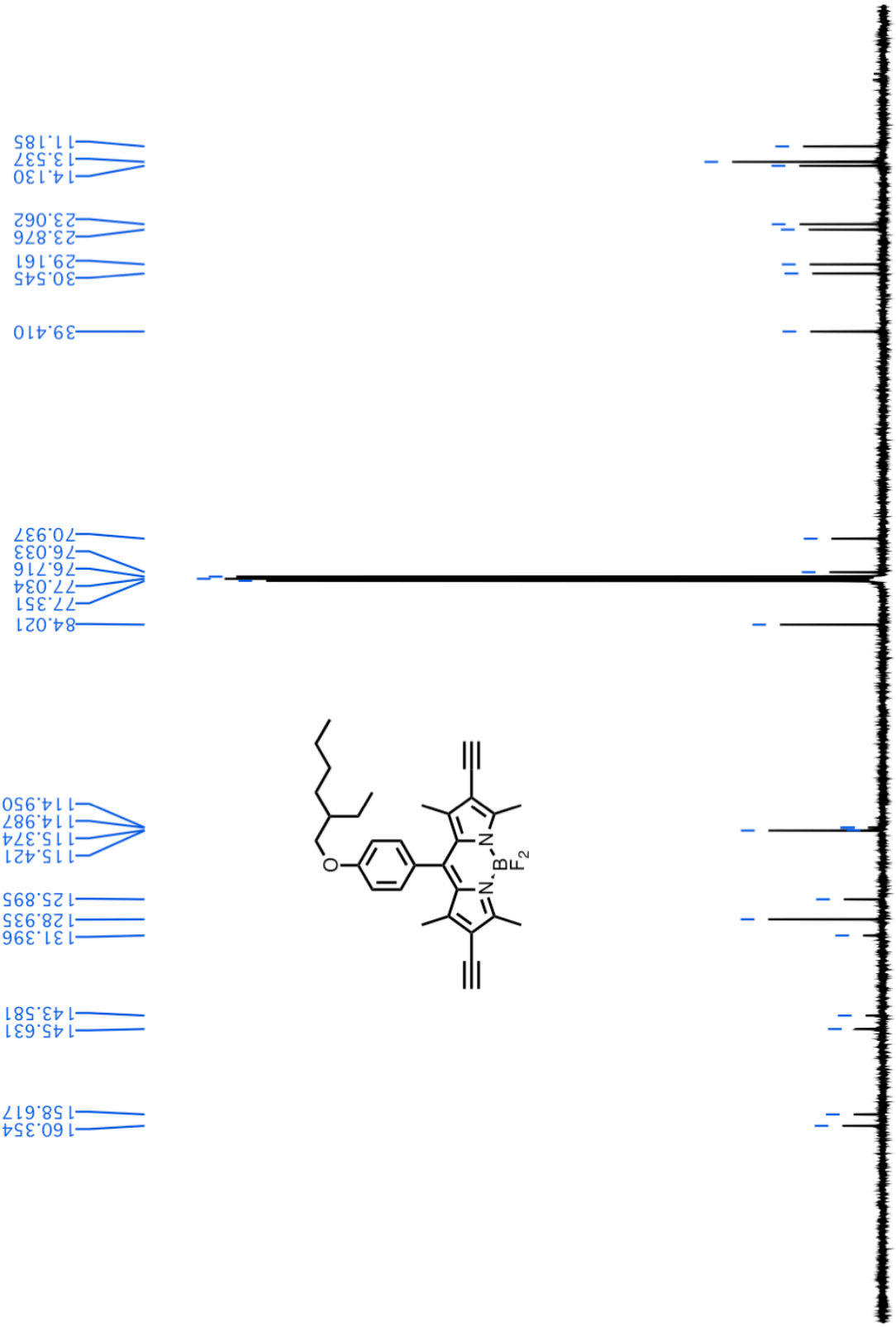


Figure S2. ^{13}C NMR Spectrum for 2,6-diethynyl BODIPY

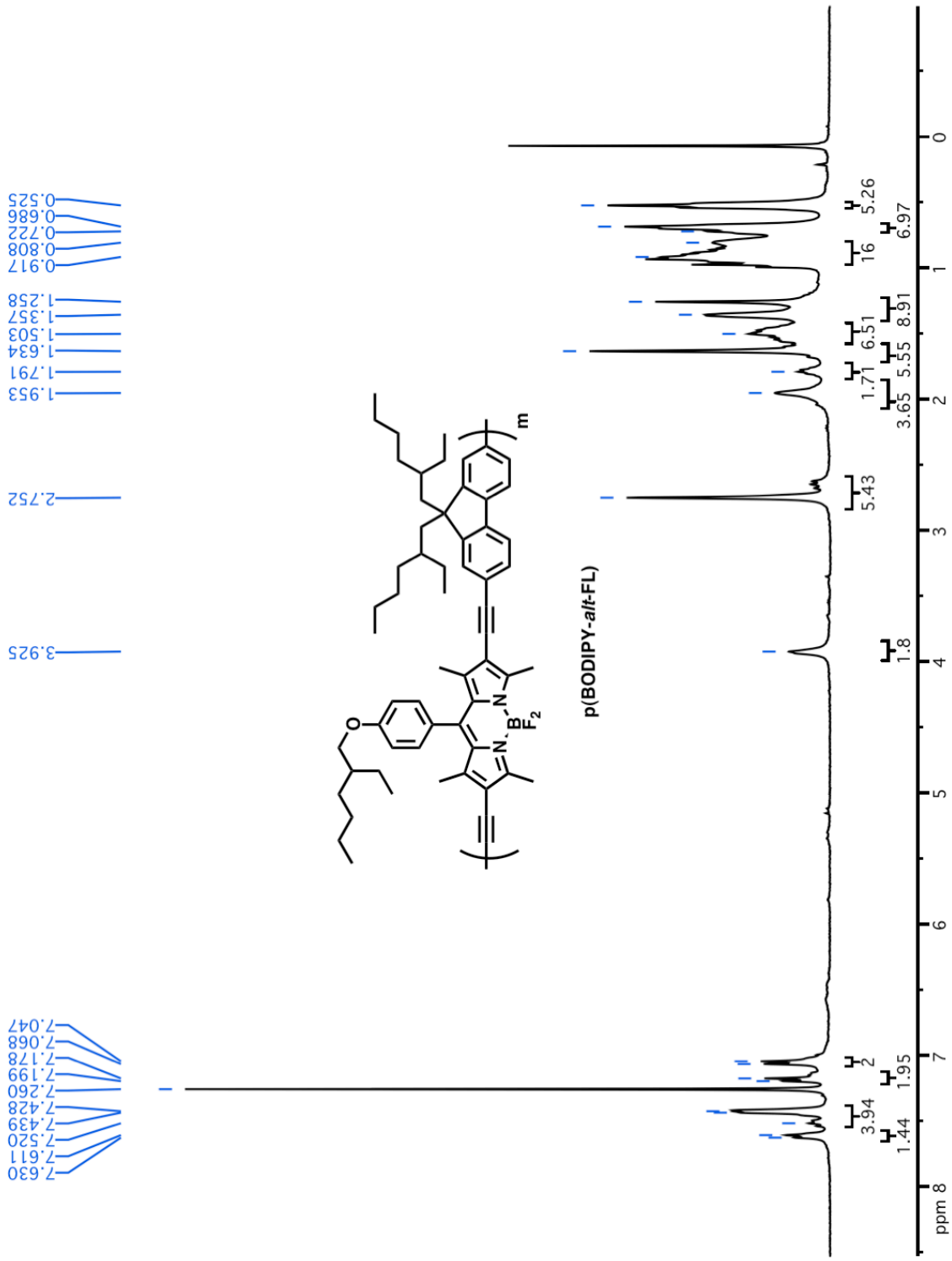


Figure S3. ^{1}H NMR Spectrum for p(BODIPY-*alt*-FL)

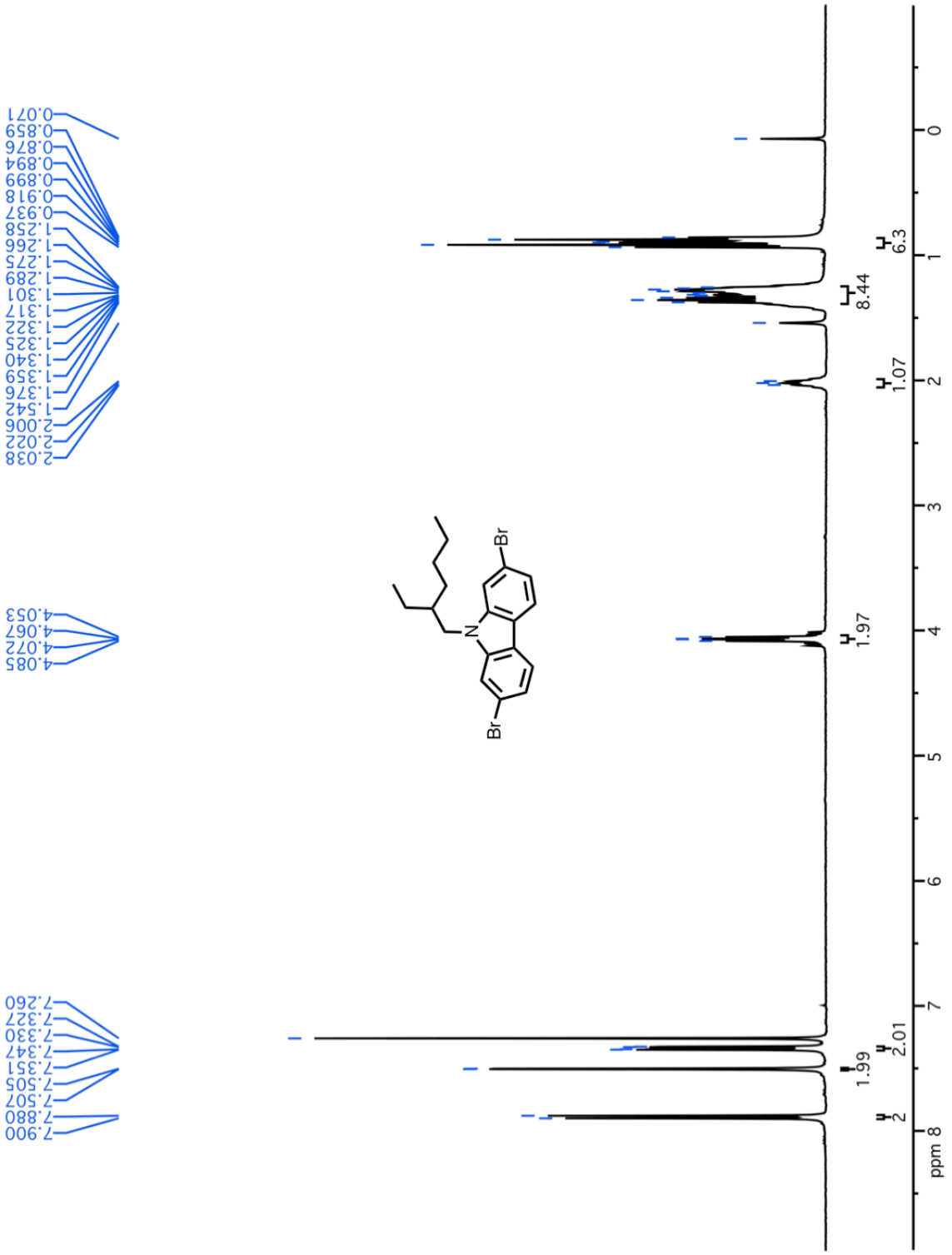


Figure S4. ^{1}H NMR Spectrum for 2,7-Dibromo-9-(2-ethylhexyl)-9*H*-Carbazole

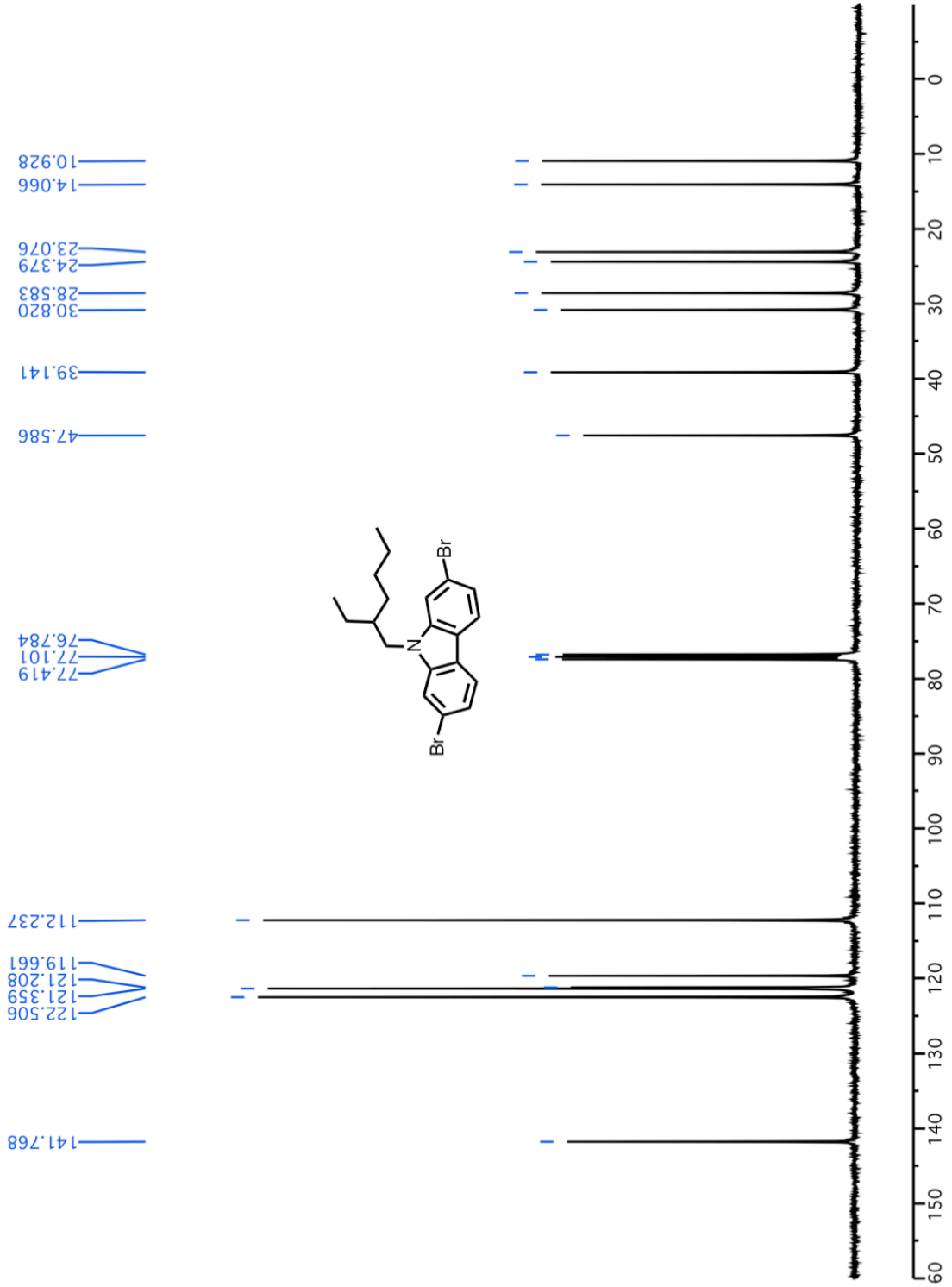


Figure S5. ^{13}C NMR Spectrum for 2,7-Dibromo-9-(2-ethylhexyl)-9*H*-Carbazole

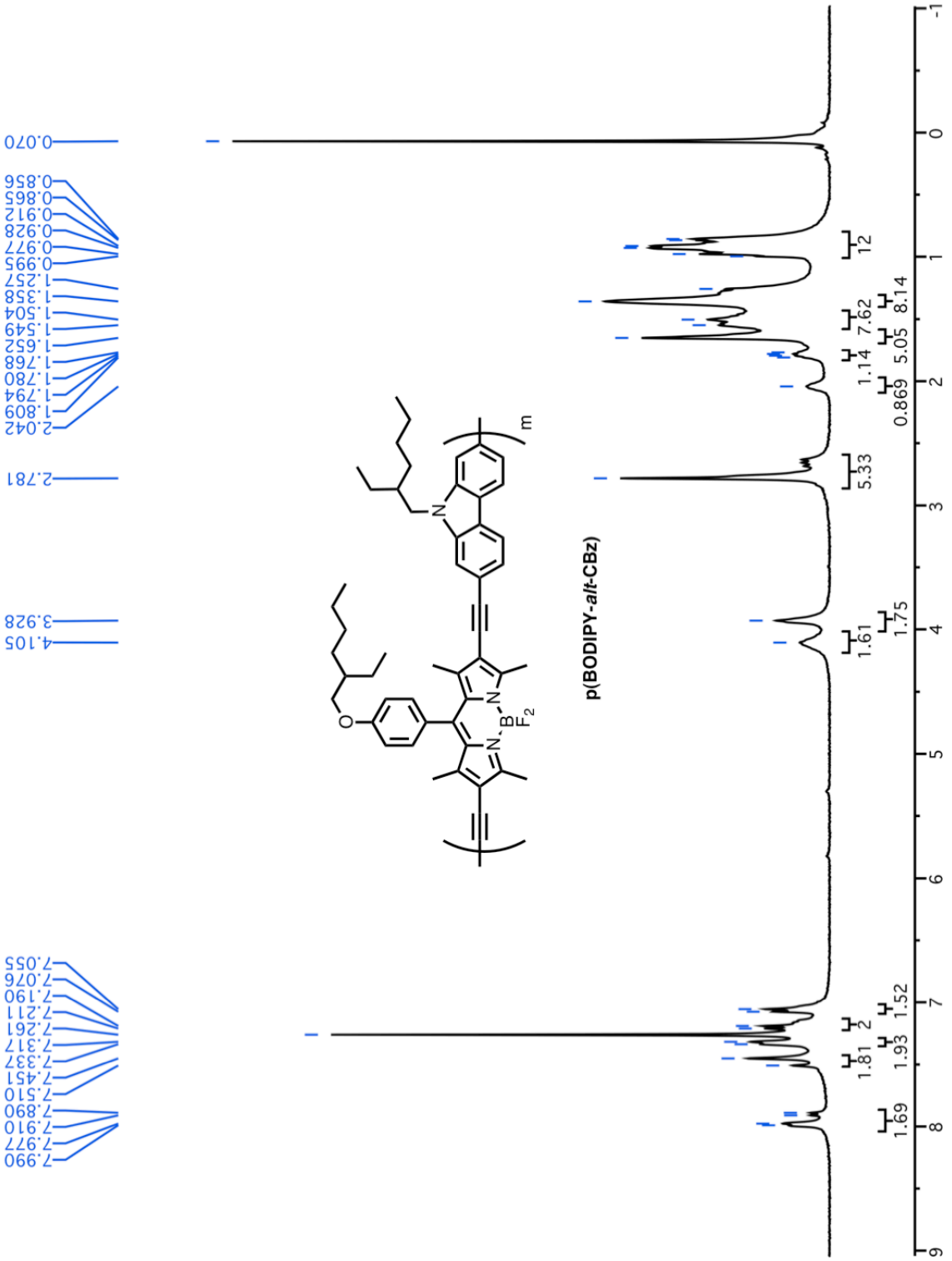


Figure S6. ^{1}H NMR Spectrum for p(BODIPY-*alt*-CBz)

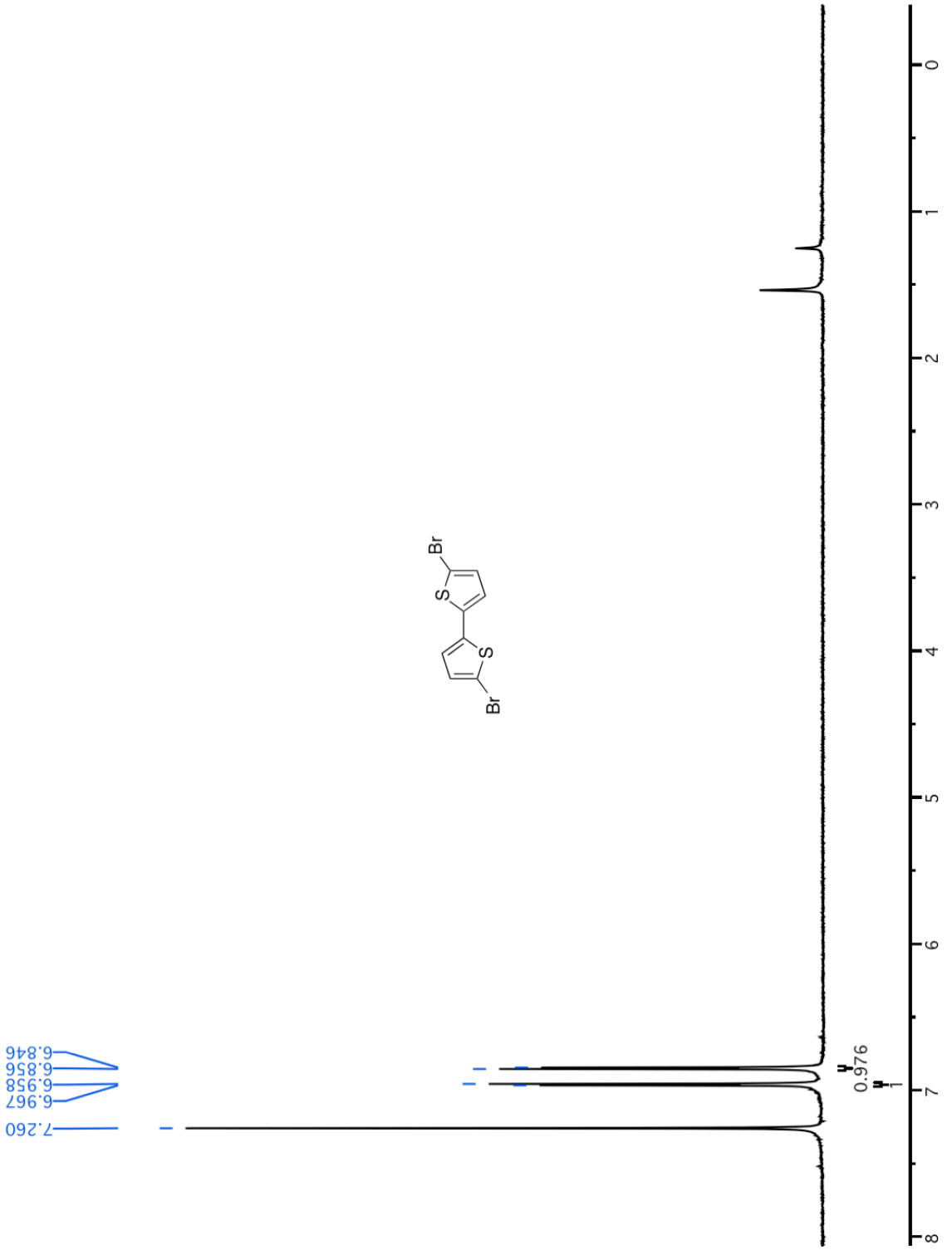


Figure S7. ^{1}H NMR Spectrum for 5,5’-dibromo-2,2’-bithiophene

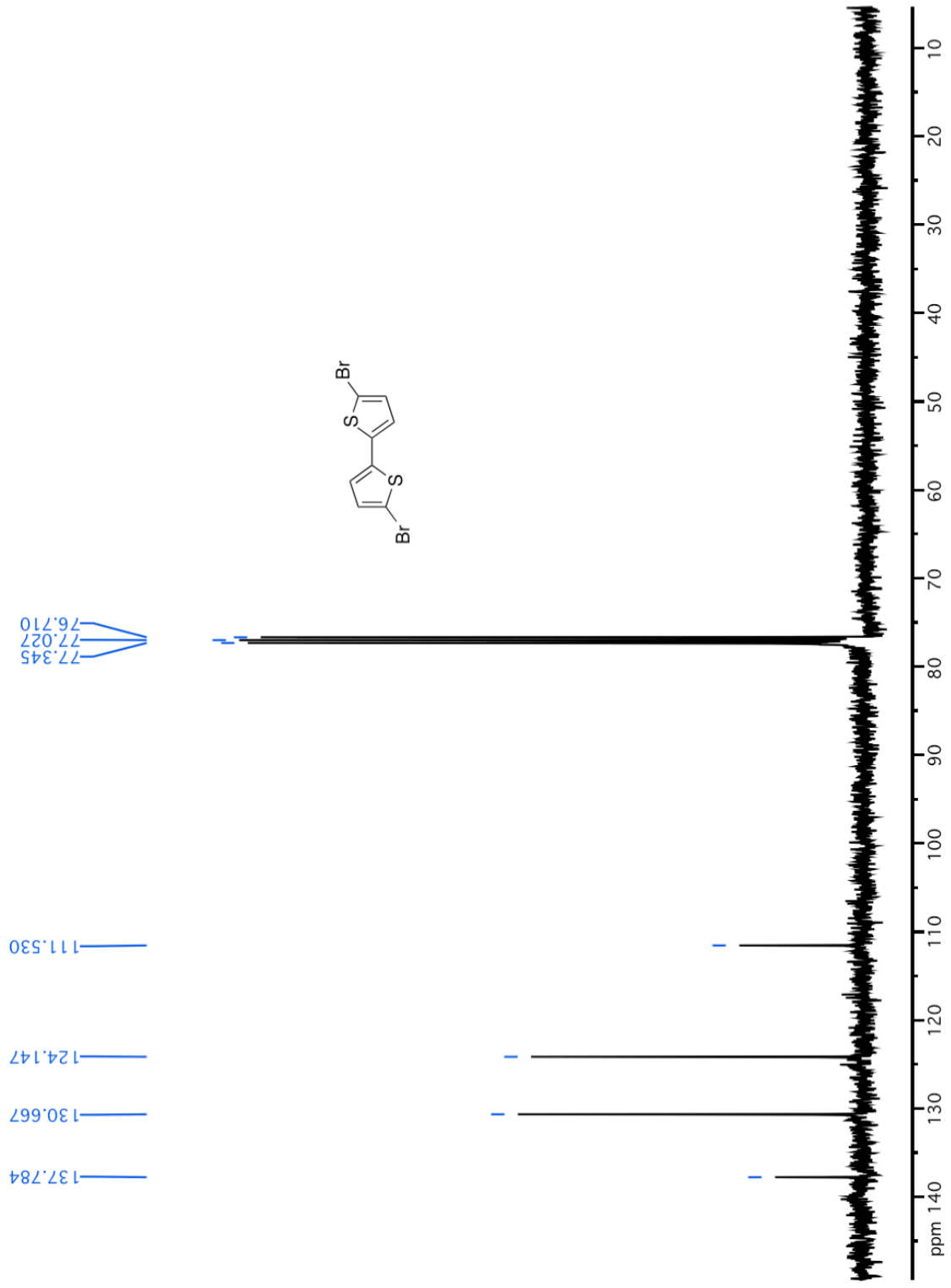


Figure S8. ^{13}C NMR Spectrum for 5,5’-dibromo-2,2’-bithiophene

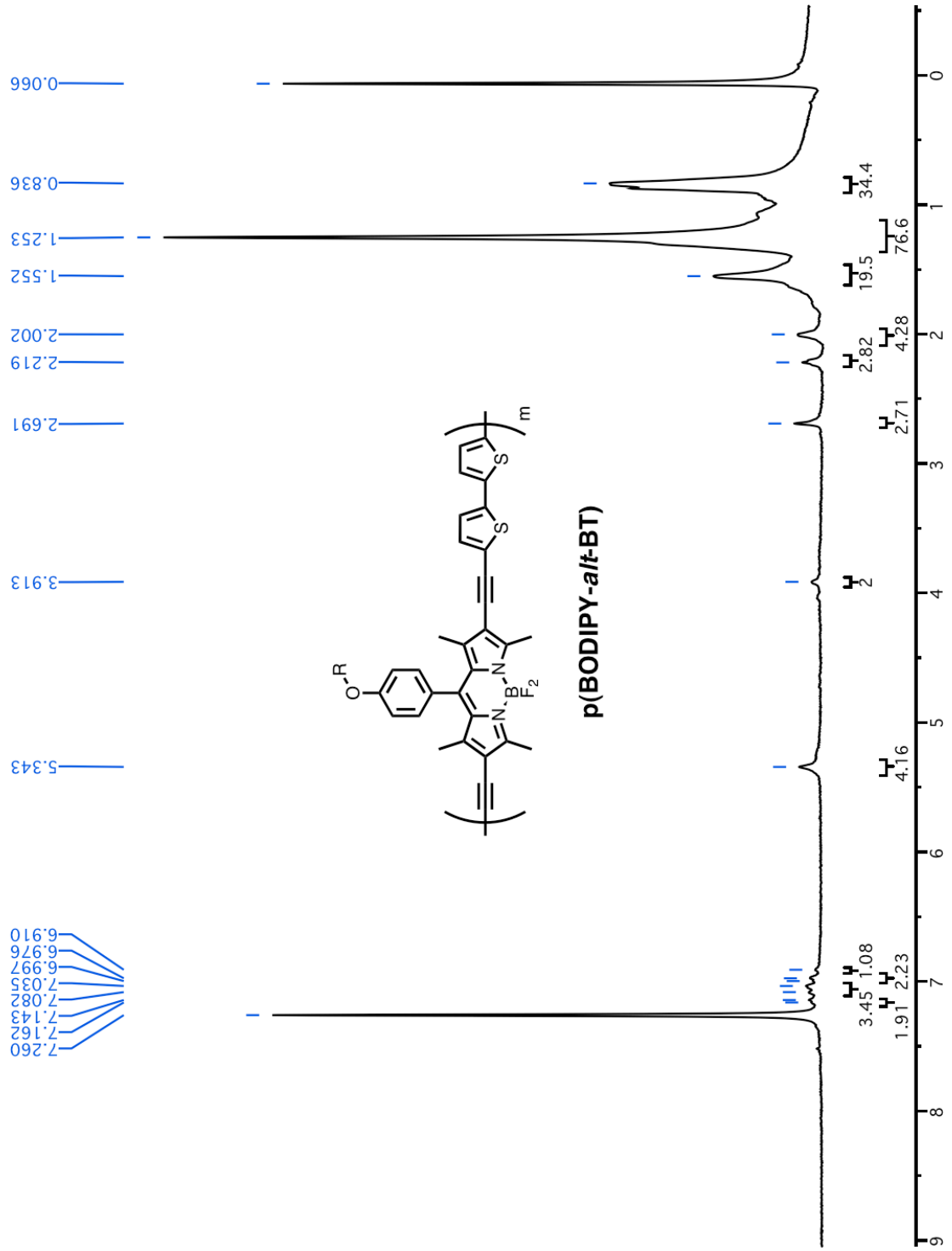


Figure S9. ^{1}H NMR Spectrum for p(BODIPY-*alt*-BT)

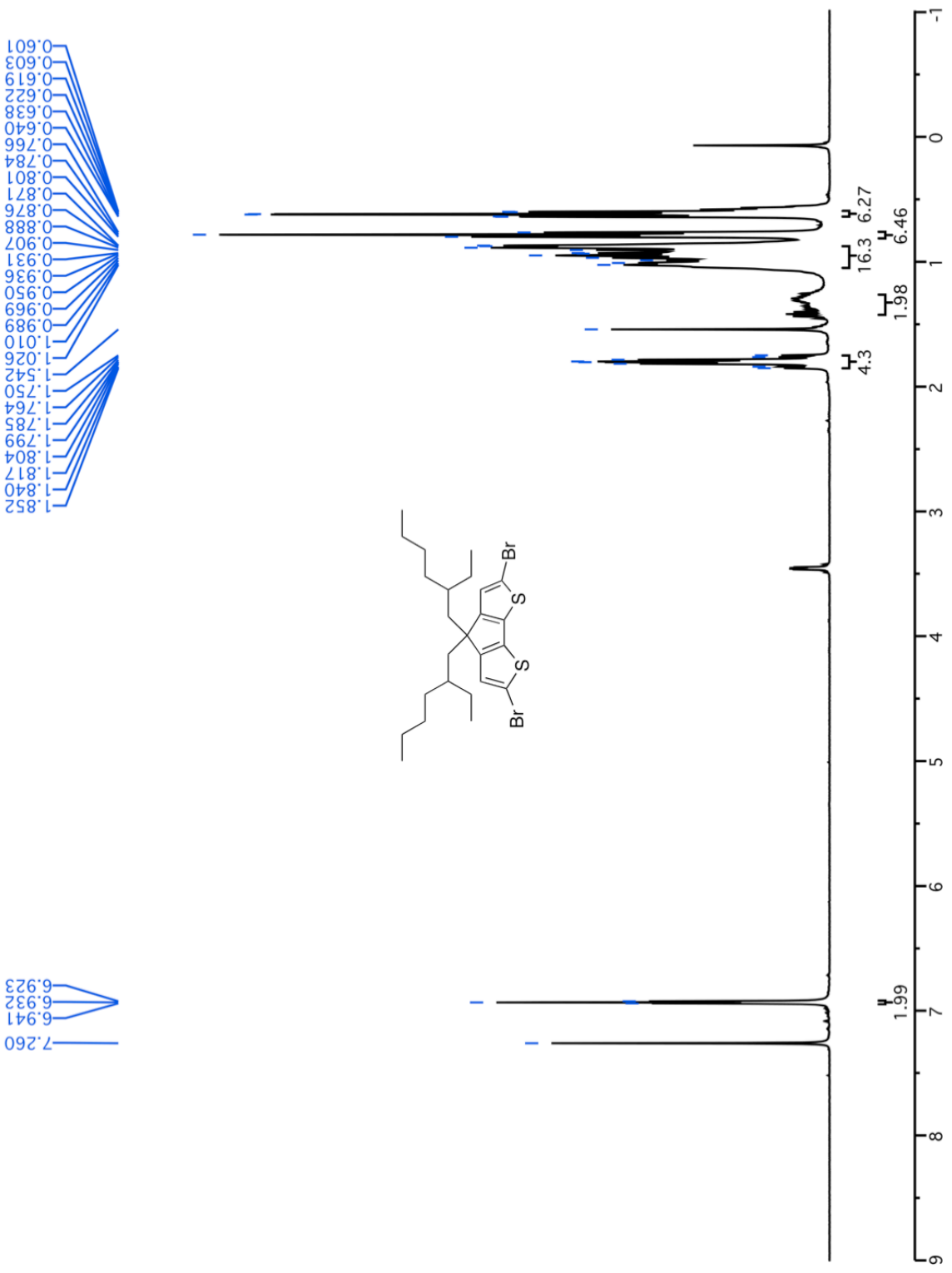


Figure S10. ^{1}H NMR Spectrum for 2,6-Dibromo-4,4-bis(2-ethylhexyl)-4*H*-Cyclopenta[2,1-*b*:3,4-*b*']dithiophene

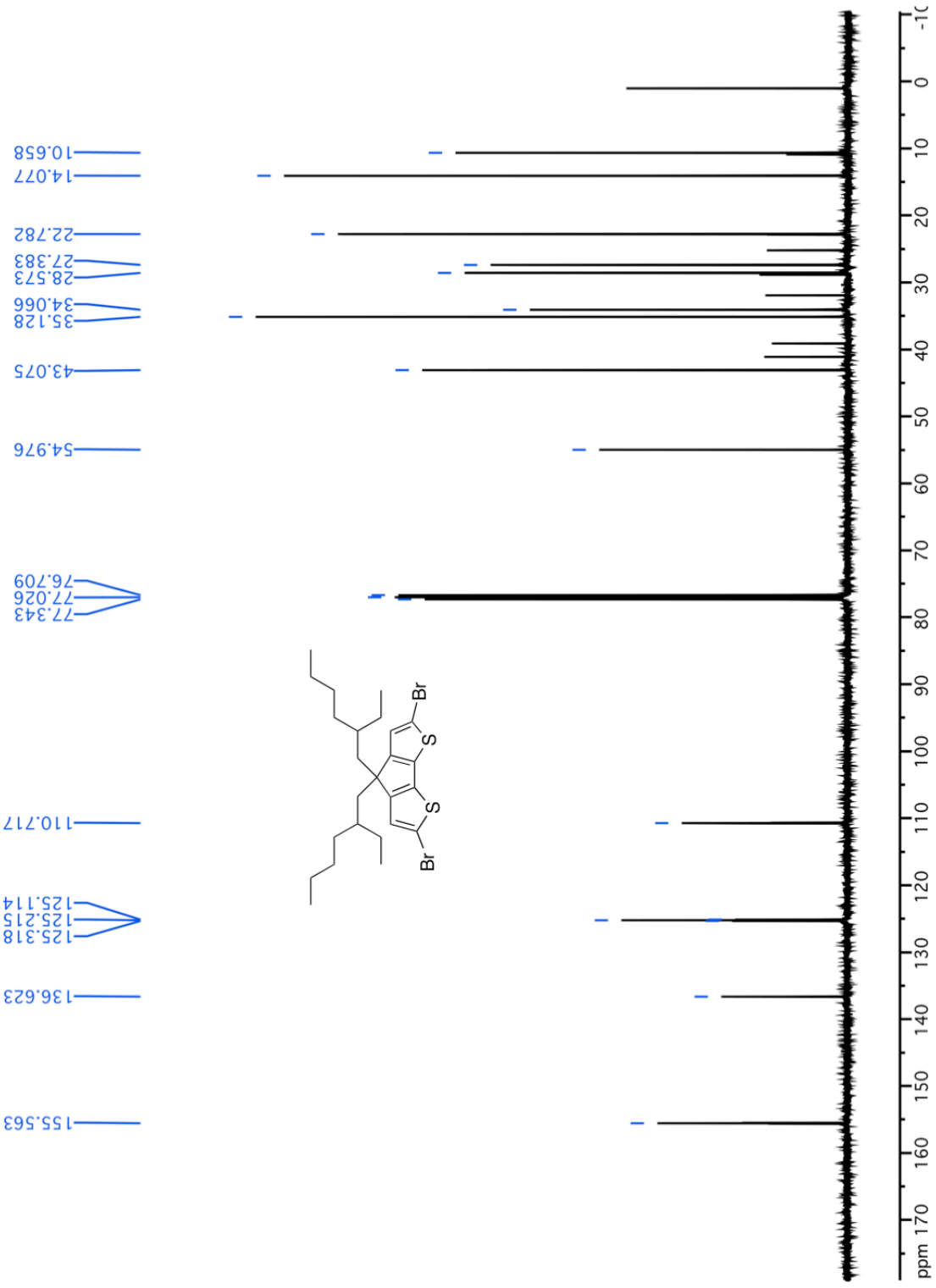


Figure S11. ^{13}C NMR Spectrum for 2,6-Dibromo-4,4-bis(2-ethylhexyl)-4*H*-Cyclopenta[2,1-*b*:3,4-*b*']dithiophene

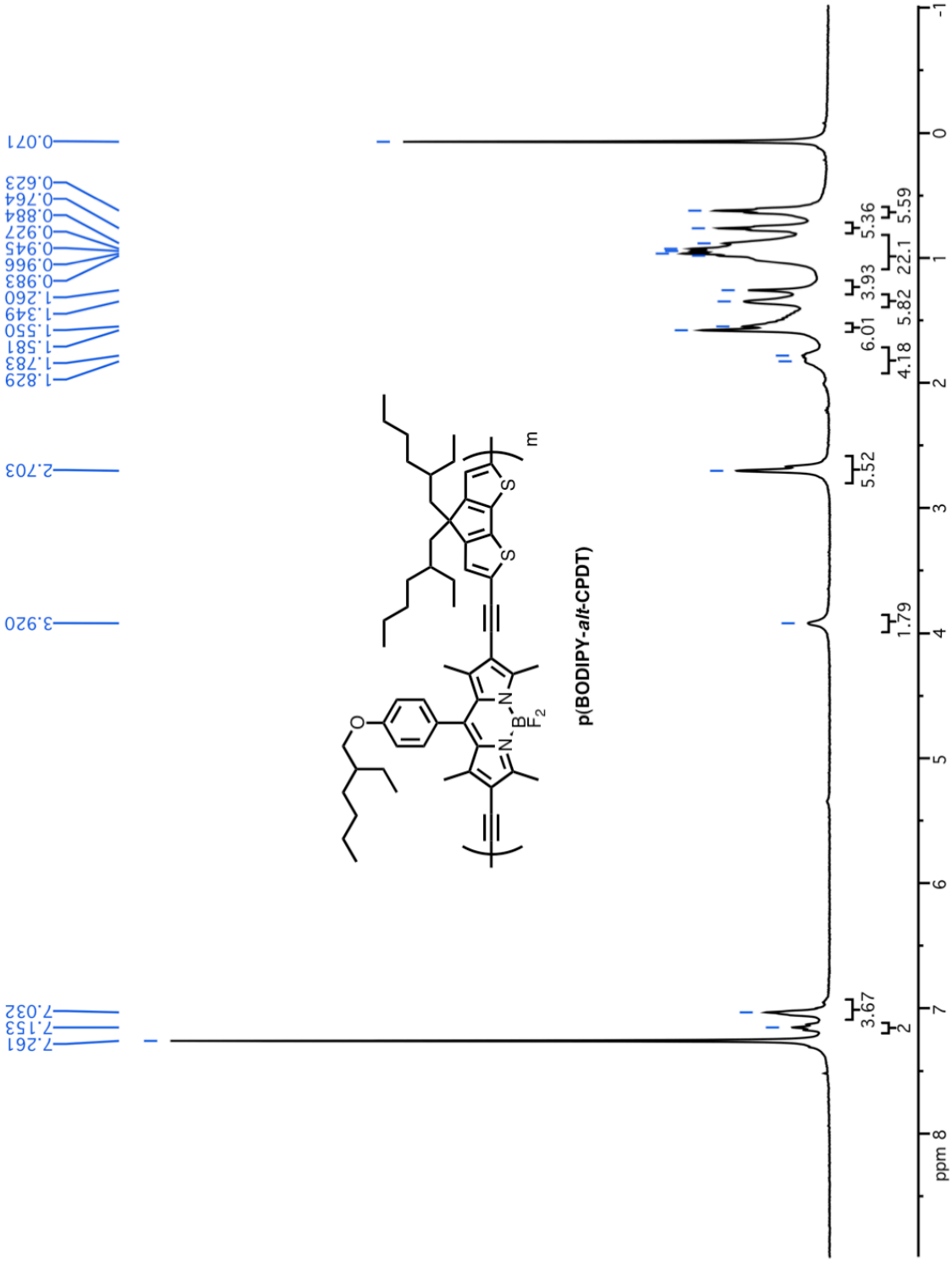


Figure S12. ^{1}H NMR Spectrum for p(BODIPY-*alt*-CPDT)

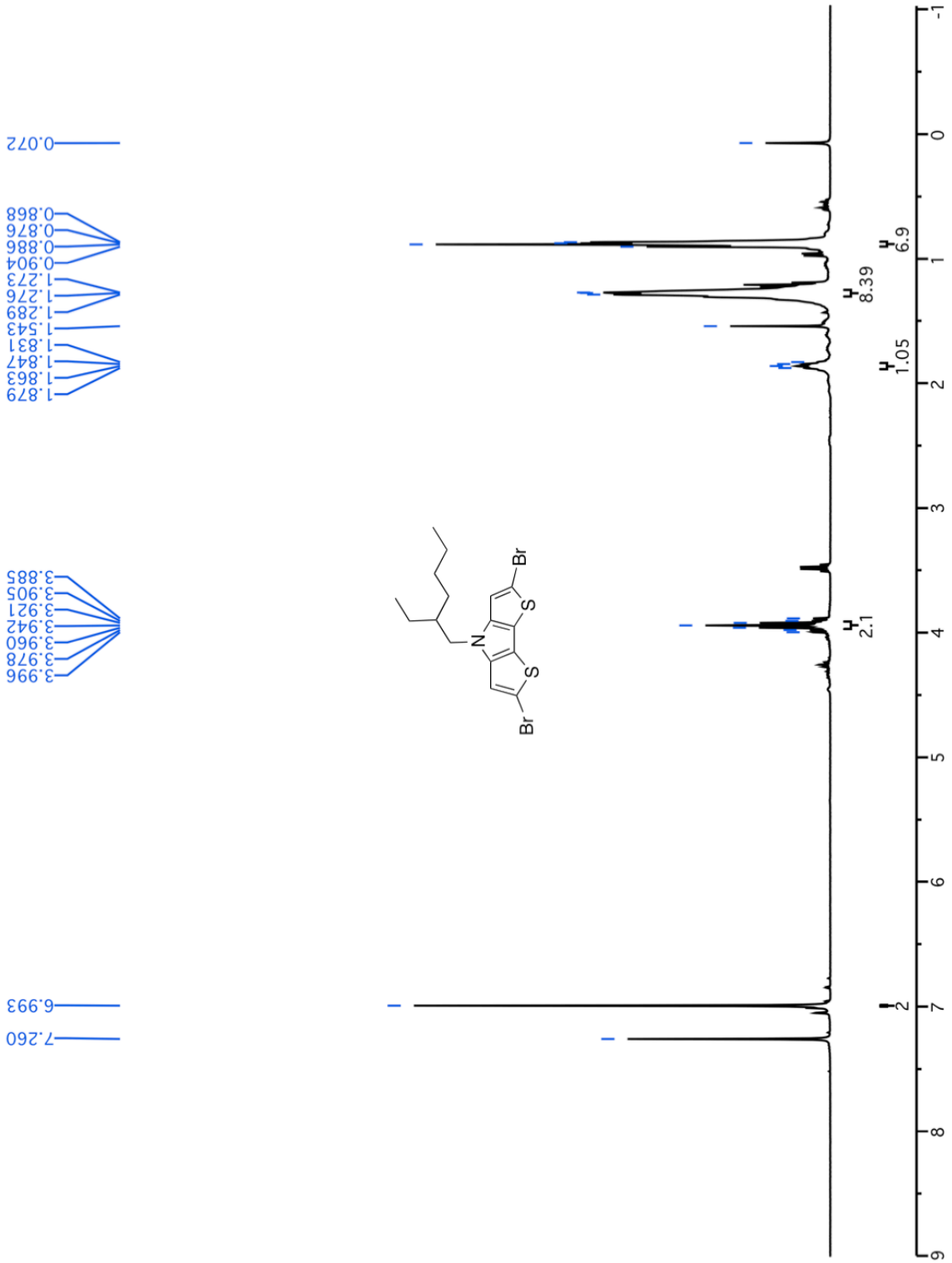


Figure S13. ^{1}H NMR Spectrum for 2,6-dibromo-4-(2-ethylhexyl)-4*H*-Dithieno[3,2-*b*:2',3'-*d*]pyrrole

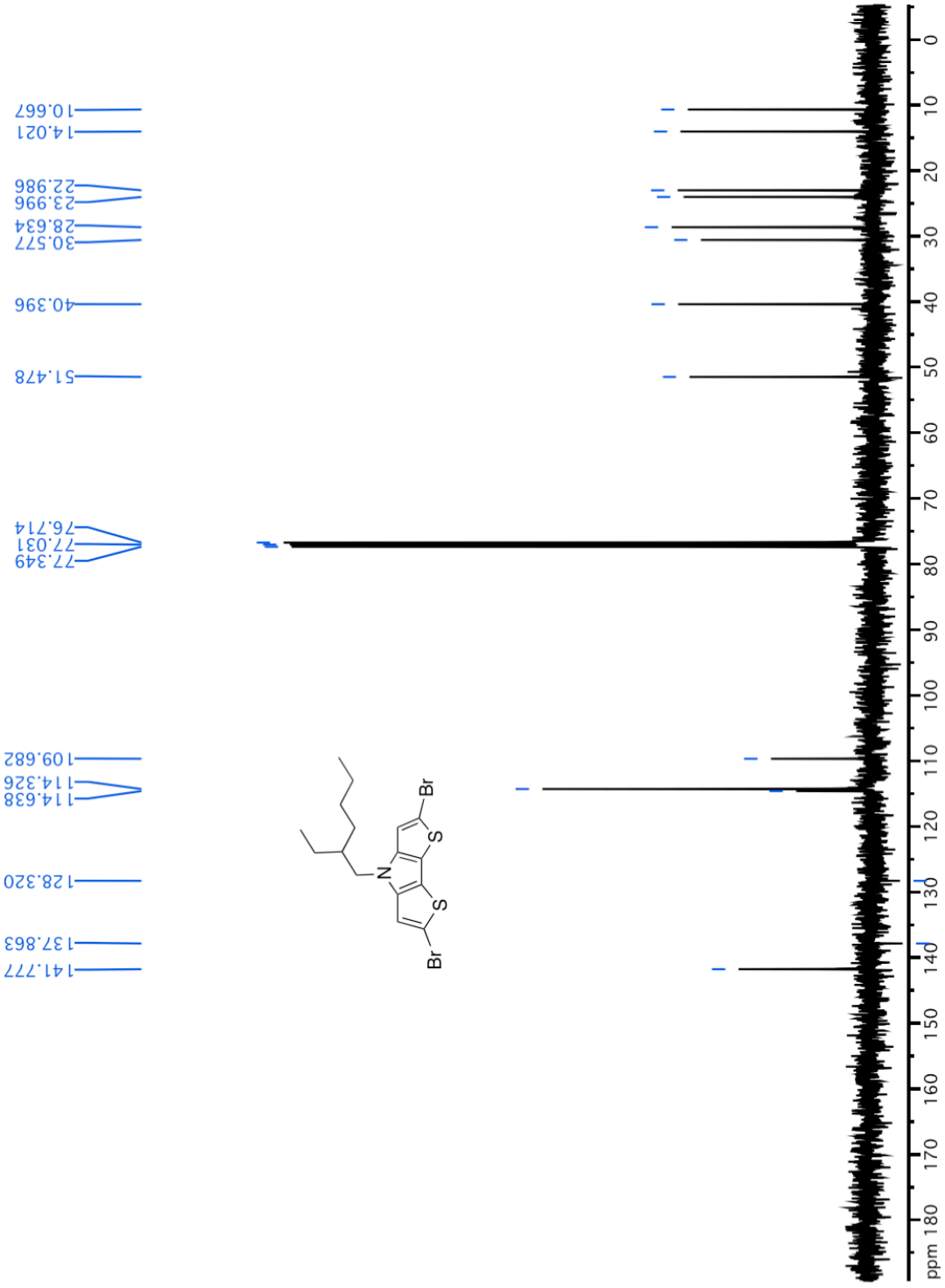


Figure S14. ^{1}H NMR Spectrum for 2,6-dibromo-4-(2-ethylhexyl)-4*H*-Dithieno[3,2-*b*:2',3'-*d*]pyrrole

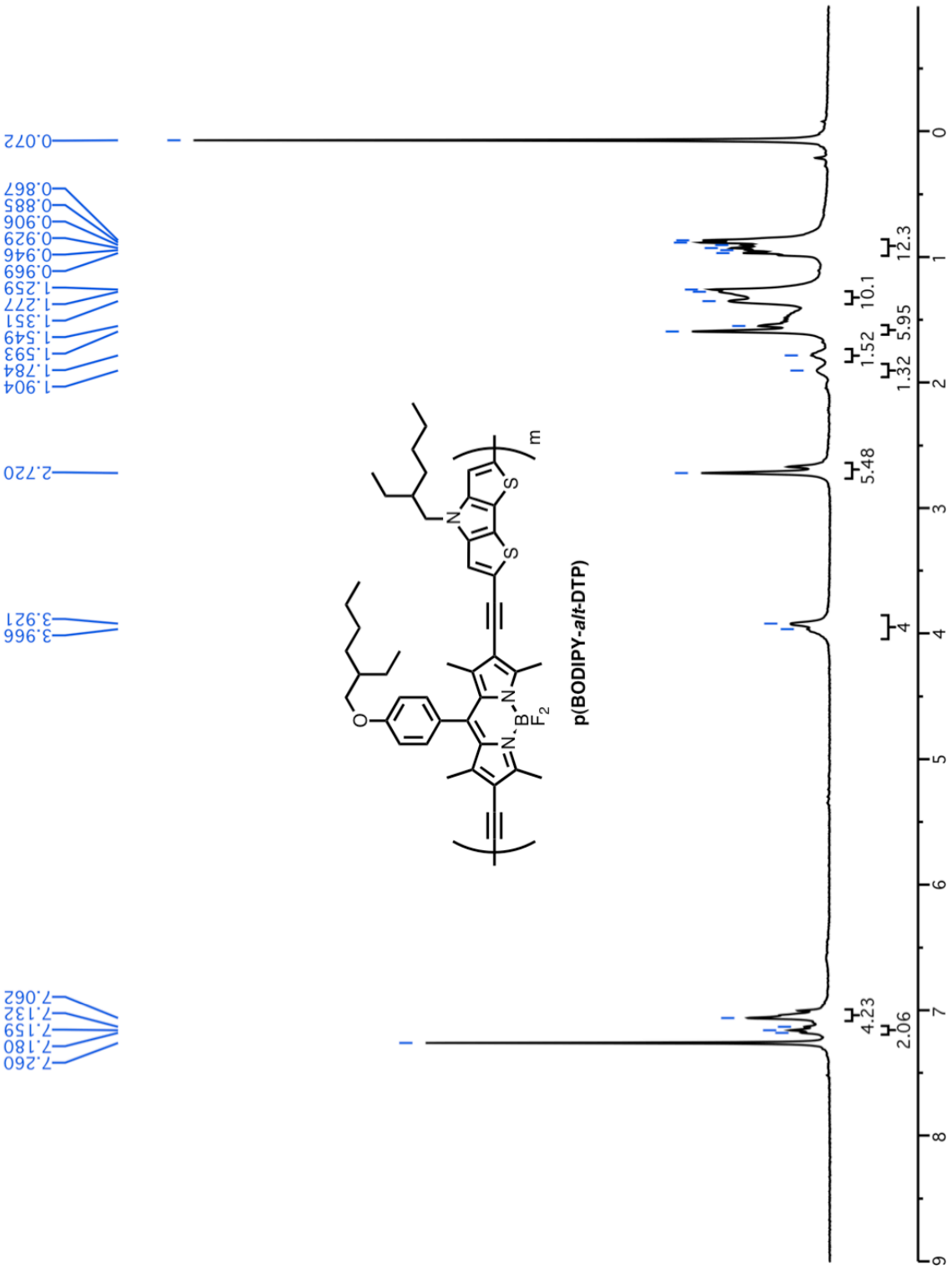


Figure S15. ^{1}H NMR Spectrum for p(BODIPY-*alt*-DTP)

Figure S16. Representative cyclic voltammograms of Fc/Fc^+ redox couple (1 mg/mL) in anhydrous acetonitrile (solid line) and anhydrous dichloromethane (dashed line). The scans were recorded in degassed solvents with a Pt disk electrode as a working electrode and a Pt wire as the auxiliary electrode. The potentials were measured against Ag/Ag^+ reference electrode at a scan rate of 50 mV/s. Anodic (E^{pa}) and the cathodic (E^{pc}) peak potentials are denoted on each voltammogram. $E_{1/2}$ values for Fc/Fc^+ couple in each solvent were calculated according to the equation: $E_{1/2} = E^{pa} - (\Delta E^p)/2$, where $\Delta E^p = E^{pa} - E^{pc}$.

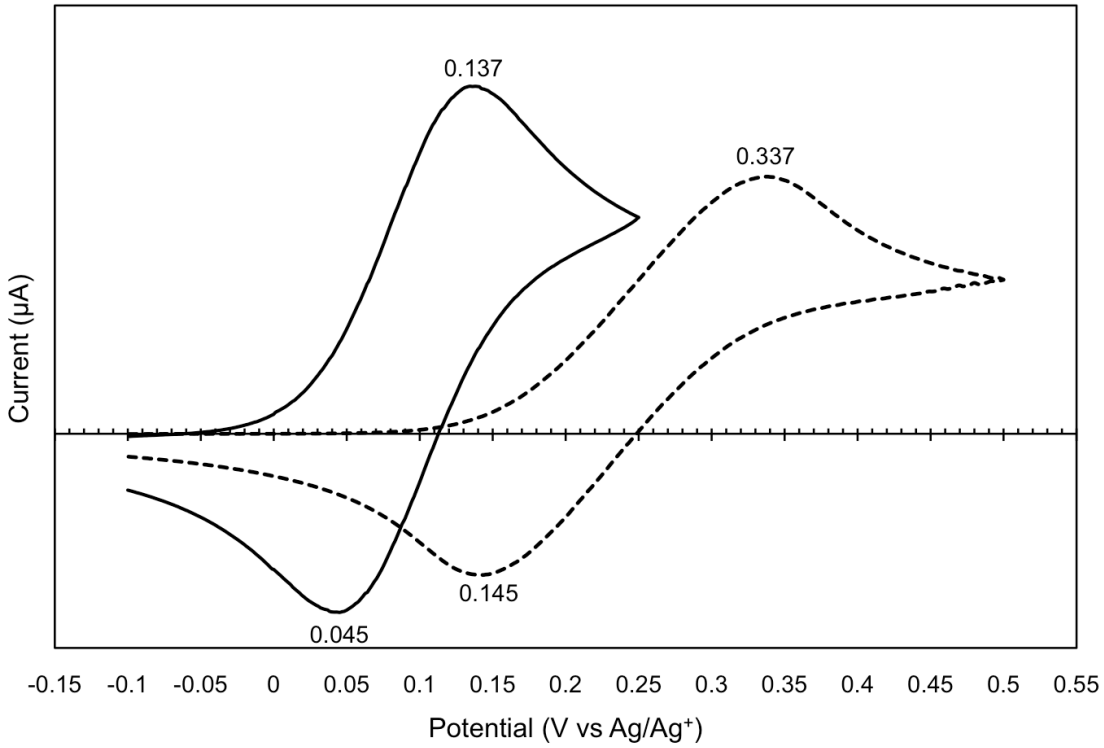


Table S1. Redox Potentials for Fc/Fc^+ in Acetonitrile and Dichloromethane

Solvent	E^{pa} **[V]**	E^{pc} **[V]**	ΔE^p **[V]**	$E_{1/2}$ **[V]**
Acetonitrile	0.137	0.045	0.092	0.091
Dichloromethane	0.337	0.145	0.192	0.241

Reference 11 from Main Text

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada,

M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. *Gaussian 03* **2004**, *revision C.02*, Gaussian, Inc.: Wallingford, CT.

Figure S17. Chemical Structures and HOMO-LUMO plots for the comonomers used; the alkyl chains have been replaced by isopropyl groups for smaller computational time.

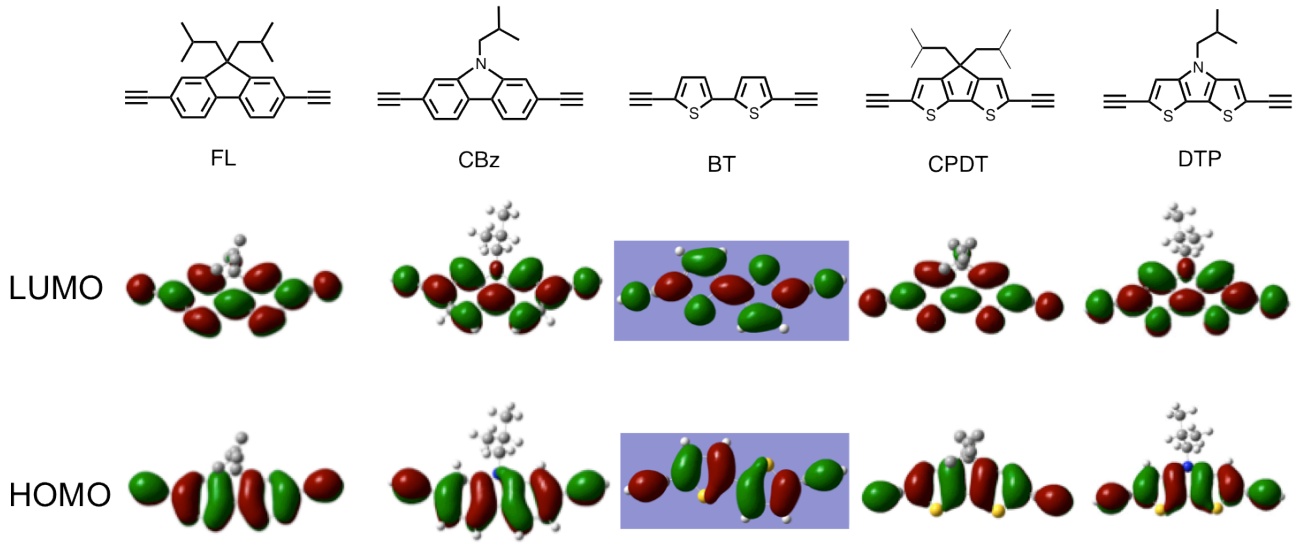


Figure S18. Chemical Structures of BODIPY-Donor Model Compounds