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SUPPORTING INFORMATION

Consequences of Hydrogen Bonding on Molecular Organization and Charge Transport in Molecular Organic Photovoltaic Materials

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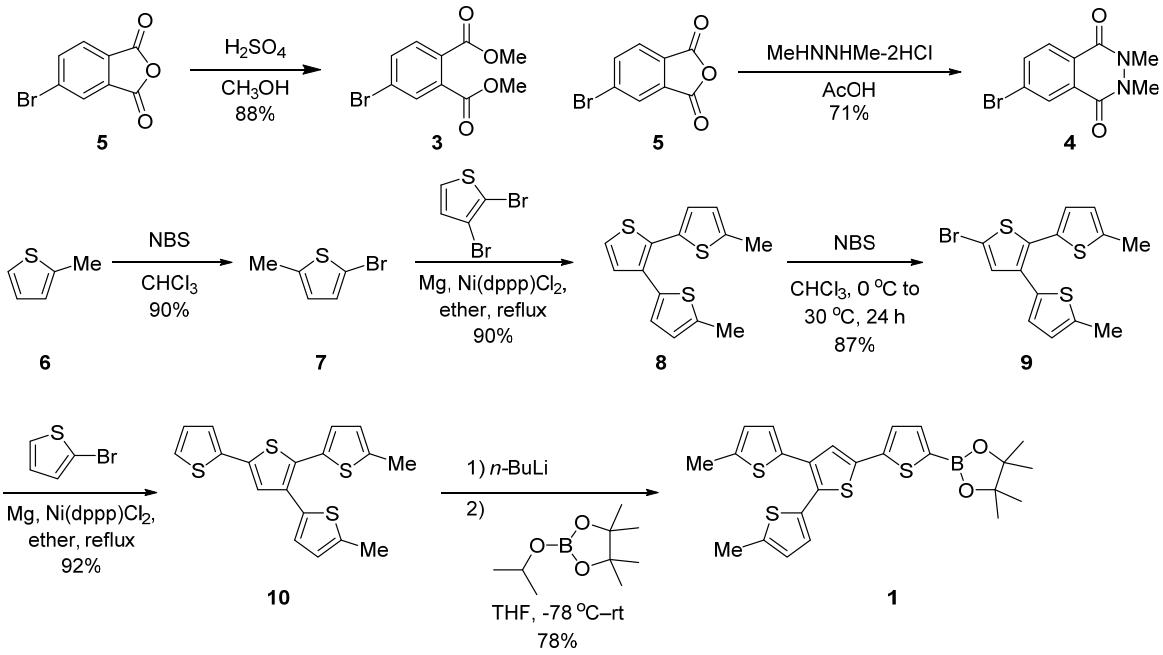
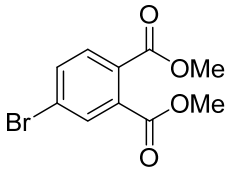
Synthetic Details

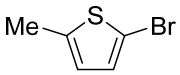
Reported below are the full synthetic details for the preparation of **MeBQPME**, **HexBQPME**, and **MeBQPNMe**. Complete synthetic details for the **HexBQP** family will be reported elsewhere, although the full characterization data for the target compounds is provided here.



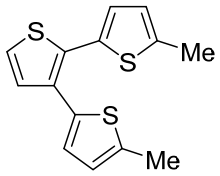
Scheme S1. Synthesis of **3**, **4**, and **1** (see Scheme 1 in main text).



Dimethyl-4-bromophthalate (3). To a solution of 4-bromophthalic anhydride (**5**) (1.14 g, 5.00 mmol) in methanol (10 mL), concentrated H_2SO_4 (18 M, 0.5 mL) was added dropwise and the reaction mixture was heated to reflux for 24 h. After cooling, the organic substance was extracted with methylene chloride (150 mL), followed by washing with saturated $NaHCO_4$ solution (50 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The product was obtained without further purification as white solid in 88% yield (1.2 g): ^{1}H NMR ($CDCl_3$): δ 7.84 (d, J = 1.7 Hz, 1H), 7.69 (dd, J = 8.2, 1.8 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 3.91 (d, J = 3.8 Hz, 6H) ppm; ^{13}C NMR ($CDCl_3$): δ 167.5, 167.3, 134.6, 134.5, 132.4, 131.1, 130.8, 126.3, 53.5, 53.3 ppm. The ^{1}H and ^{13}C NMR data match that found in the literature.[1]

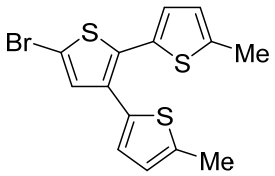


2-Bromo-5-methylthiophene (7). In the absence of light, 2-methylthiophene (**6**) (1.00 mL, 10.3 mmol) was added to a solution of *N*-bromosuccinimide (2.07 g, 11.4 mmol) in chloroform/acetic acid (10 mL of a 1:1 solution). The resulting solution was stirred at 0 °C for 1 h. The mixture was then allowed to warm to room temperature and stirred for an additional 12 h. The reaction was quenched with aqueous NaOH. The organic layer was separated, washed with water, and dried over $MgSO_4$. The product was distilled under reduced pressure and obtained as a pale yellow oil in 75% yield (1.4 g): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.82 (d, J = 3.6 Hz, 1H), 6.51 (d, J = 3.6, 1H), 2.42 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 141.5, 129.7, 125.6, 108.7, 15.6 ppm. The ^{1}H and ^{13}C NMR data match that found in the literature.[2]

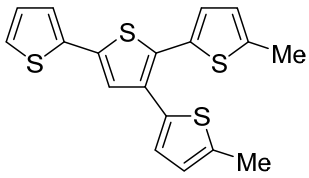


5,5''-Dimethyl-2,2':3',2''-terthiophene (8). Under argon, 2-bromo-5-methylthiophene (**7**) (3.97 g, 22.4 mmol) was added dropwise to a suspension of iodine and magnesium turnings (0.63 g, 26 mmol) in dry diethyl ether (20 mL) to form the Grignard reagent. The resulting solution was heated to reflux for 1 h. After cooling to room temperature, the Grignard reagent was then slowly added to a mixture of 2,3-dibromothiophene (2.85 mL, 25.2 mmol) and [1,3-bis(diphenylphosphino)propane]dichloronickel(II) ($Ni(dppp)_2Cl_2$, 160 mg, 0.30 mmol) in diethyl ether (100 mL) at 0 °C under argon. The resulting mixture was heated to reflux for 24 h and then quenched with 1 M HCl (10 mL). The mixture was extracted with diethyl ether (300 mL). The organic layers were combined, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by flash column chromatography (petroleum ether) and obtained as a green oil in 90% yield (5.52 g): ^{1}H NMR

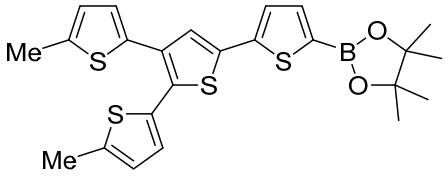
($CDCl_3$, 300 MHz): δ 7.22 (d, J = 5.2 Hz, 1H), 7.13 (d, J = 5.2 Hz, 1H), 6.95 (d, J = 3.2 Hz, 1H), 6.88 (d, J = 3.2 Hz, 1H), 6.68 (dd, J = 2.4 Hz, J = 2.4 Hz, 2H), 2.49 (s, 6H) ppm. The ^{1}H NMR data matches that found in the literature.[3]



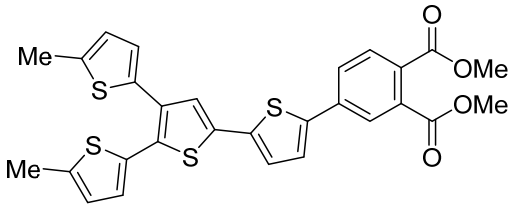
5'-Bromo-5,5''-dimethyl-2,2':3',2''-terthiophene (9). In the absence of light, 5,5''-dimethyl-2,2':3',2''-terthiophene (**8**) (1.45 g, 5.25 mmol) was added to a solution of *N*-bromosuccinimide (1.01 g, 5.67 mmol) in chloroform, and the resulting solution was stirred at 0 °C for 1 h. The mixture was allowed to warm to room temperature and stirred for 12 h. The mixture was then warmed to 30 °C and allowed to react for an additional 24 h. The reaction was quenched with aqueous NaOH. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The product was then purified by flash column chromatography (hexanes) and obtained as a green oil in 88% yield (1.64 g): ^{1}H NMR ($CDCl_3$): δ 7.07 (s, 1H), 6.89 (d, J = 3.4 Hz, 1H), 6.82 (d, J = 3.4 Hz, 1H), 6.66 (d, J = 2.5 Hz, 1H), 6.63 (d, J = 2.4 Hz, 1H), 2.46 (s, 3H), 2.45 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 500 MHz, determined via gHMBC): δ 142.6, 141.7, 140.1, 138.9, 133.6, 132.0, 131.0, 128.1, 126.2, 125.8, 125.6, 105.0, 16.5, 15.4 ppm; HRMS (MALDI-TOF) calculated 354.9100 for $C_{14}H_{10}S_3Br$ $(M-H)^+$, found 354.9106.



5,5''-Dimethyl-5'-(thiophen-2-yl)-2,2',3',2''-terthiophene (10). Under argon, 2-bromothiophene (10.3 g, 63.3 mmol) was added dropwise to a suspension of iodine and magnesium (1.52 g, 63.3 mmol) in dry diethyl ether (20 mL) to form the Grignard reagent. The resulting solution was heated to reflux for 1 h. After cooling to room temperature, the Grignard reagent was slowly added to a mixture of 5'-bromo-5,5''-dimethyl-2,2':3',2''-terthiophene (**9**) (13 g, 37 mmol) and [1,3-bis(diphenylphosphino)propane]dichloronickel(II) ($Ni(dppp)_2Cl_2$, 198 mg, 0.36mmol) in dry diethyl ether (100 mL) at 0 °C under argon. The resulting mixture was heated to reflux for 24 h and quenched with dilute 1 M HCl (10 mL). The mixture was extracted with diethyl ether (300 mL). The organic layers were combined, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The product was then purified by flash column chromatography (hexanes) and obtained as a yellow liquid in 92% yield (12 g): ^{1}H NMR ($CDCl_3$): δ 7.40 (s, 1H), 7.35 (m, 2H), 7.17 (m, 3H), 6.86 (m, 2H), 2.65 (dd, J = 7.7, 1.1Hz, 6H) ppm; ^{13}C NMR ($CDCl_3$): δ 141.3, 140.0, 136.6, 135.2, 134.8, 132.4, 132.3, 130.3, 127.9, 127.8, 126.7, 126.1, 125.5, 125.4, 124.6, 123.9, 15.31, 15.28 ppm; HRMS (APCI-TOF) calculated 359.0051 for $C_{18}H_{14}S_4$ $(M+H)^+$, found 359.0065.

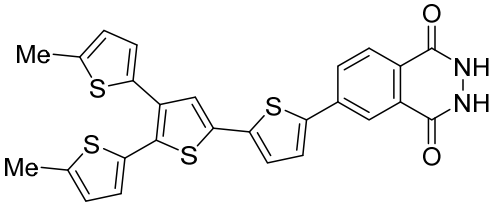


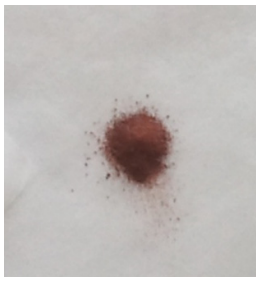
4,4,5,5-Tetramethyl-2-(5''-methyl-5'-(5-methylthiophen-2-yl)-[2,2':4',2''-terthiophen]-5-yl)-1,3,2-dioxaborolane (1). Under argon, *n*-butyllithium in hexane (2.5 M, 4.4 mL, 11 mmol) was added to a solution of 5,5''-dimethyl-5'-(thiophen-2-yl)-2,2',3',2''-terthiophene (**10**) (3.9 g, 10 mmol) in dry THF (150 mL) at –78 °C and the mixture was stirred at this temperature for 2 h. 2-Isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (2.2 mL, 11 mmol) was added, and the reaction mixture was warmed to room temperature and stirred for an additional 12 h. The reaction was then quenched with brine (50 mL) and the product was extracted with diethyl ether. The organic layers were combined, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by gradient flash column chromatography (0–20% dichloromethane in hexane) to give the product as a green liquid in 79% yield (3.8 g): ^{1}H NMR ($CDCl_3$): δ 7.58 (d, J = 4.0 Hz, 1H), 7.28 (s, 1H), 6.99 (d, J = 3.2 Hz, 1H), 6.93 (d, J = 3.3 Hz, 1H), 6.70 (d, J = 2.5 Hz, 2H), 2.52 (d, J = 4.0 Hz, 6H), 1.39 (s, 12H) ppm; ^{13}C NMR ($CDCl_3$): δ 143.1, 141.3, 140.0, 137.7, 134.8, 134.5, 132.2, 132.0, 130.8, 127.6, 126.5, 126.4, 125.3, 125.1, 124.8, 83.9, 24.5, 15.2, 15.1 ppm; HRMS (APCI-TOF) calculated 485.0908 for $C_{24}H_{25}BO_2S_4$ $(M+H)^+$, found 485.0908.



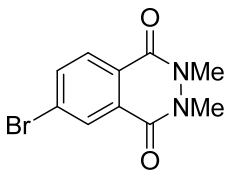
Dimethyl-4-(5''-methyl-5'-(5-methylthiophen-2-yl)-[2,2':4',2''-terthiophen]-5-yl)phthalate (MeBQPME). Under argon, degassed toluene (15 mL) was added to a suspension of 4,4,5,5-tetramethyl-2-(5''-methyl-5'-(5-methylthiophen-2-yl)-[2,2':4',2''-terthiophen]-5-yl)-1,3,2-dioxaborolane (**1**) (1.5 g, 3.1 mmol), potassium phosphate tribasic (K_3PO_4, 2 M aqueous solution, 10 mL), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, 21 mg), tri-*tert*-butylphosphonium tetrafluoroborate ($(tBu)_3P$-HBF_4, 27 mg) and dimethyl-4-bromophthalate (**3**) (1.3 g , 4.5 mmol). The solution was heated to reflux for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with methylene chloride. The organic layers were combined, washed with water, dried over

$MgSO_4$, and concentrated under reduced pressure. The product was purified by flash column chromatography (petroleum ether/CH_2Cl_2, 1:1) and obtained as a yellow solid in 61% yield (1.04 g): ^{1}H NMR ($CDCl_3$): δ 7.86 (d, J = 1.7 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.72 (dd, J = 8.1, 1.8 Hz, 1H), 7.35 (d, J = 3.9 Hz, 1H), 7.20 (s, 1H), 7.17 (d, J = 3.9 Hz, 1H), 6.96 (d, J = 3.6 Hz, 1H), 6.91 (d, J = 3.5 Hz, 1H), 6.68 (d, J = 3.2 Hz, 2H), 3.95 (d, J = 9.9 Hz, 6H), 2.49 (d, J = 5.0 Hz, 6H) ppm; ^{13}C NMR ($CDCl_3$): δ 168.2, 167.1, 141.6, 140.4, 140.3, 137.9, 137.1, 134.6, 134.5, 133.7, 132.4, 132.2, 131.1, 130.1, 129.2, 127.9, 127.0, 126.9, 126.6, 125.8, 125.6, 125.4, 125.1, 124.9, 52.8, 52.6, 15.42, 15.38 ppm; HRMS (ESI-TOF) calculated 551.0474 for $C_{28}H_{22}O_4S_4$ $(M+H)^+$, found 551.0491; elemental analysis calculated C: 61.07; H: 4.03 and found C: 61.13; H: 3.74.

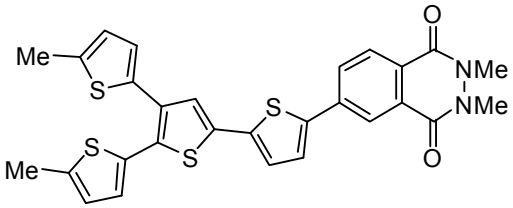




6-(5''-Methyl-5'-(5-methylthiophen-2-yl)-[2,2':4',2''-terthiophen]-5-yl)-2,3-dihydrophthalazine-1,4-dione (MeBQPH). Under argon, anhydrous hydrazine (2.42 mL, 50 mmol) was added to a solution of dimethyl-4-(5''-methyl-5'-(5-methylthiophen-2-yl)-[2,2':4',2''-terthiophen]-5-yl)phthalate (**MeBQPME**) (0.55 g, 1.0 mmol) in DMF (40 mL). The reaction mixture was heated at 80 °C for 24 h. The mixture was then cooled to 0 °C and ethanol (40 mL) was added. The yellow precipitate formed was isolated by filtration. The precipitate was recrystallized from DMF–ethanol (1:1) to yield the product as a dark orange solid in 31% yield (400 mg): ^{1}H NMR (DMSO-d_6): δ 11.61 (s, 2H), 8.22 (d, J = 8.8 Hz, 2H), 8.09 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 3.9 Hz, 1H), 7.54 (s, 1H), 7.48 (d, J = 3.8 Hz, 1H), 7.09 (d, J = 3.5 Hz, 1H), 7.04 (d, J = 3.5 Hz, 1H), 6.81 (m, 2H), 2.44 (d, J = 5.2 Hz, 6H) ppm; ^{13}C NMR (DMSO-d_6): δ 162.3, 141.8, 140.7, 140.2, 136.8, 136.7, 134.2, 133.5, 132.6, 130.8, 129.6, 129.1, 128.7, 127.4, 127.2, 126.5, 126.2, 126.1, 125.7, 120.6, 15.0, 14.9 ppm; HRMS (DART-TOF) calculated 519.0324 for $C_{26}H_{18}N_2O_2S_4$ $(M+H)^+$, found 519.0321; elemental analysis calculated N: 5.40; C: 60.21; H: 3.50 and found N: 5.50; C: 59.95; H: 3.76.

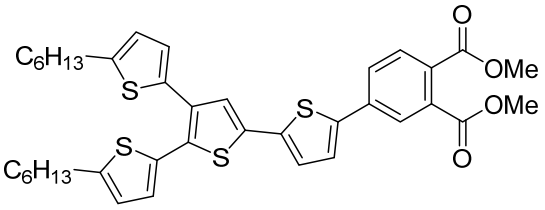


6-Bromo-2,3-dimethyl-2,3-dihydrophthalazine-1,4-dione (4). To a solution of 4-bromophthalic anhydride (**5**) (1.03 g, 4.54 mmol) in glacial acetic acid (50 mL) was added *N*,*N*'-dimethylhydrazine dihydrochloride (1.13 g, 9.86 mmol) and the reaction mixture heated at reflux for 18 h. The reaction mixture was then cooled, and poured into deionized water. The mixture was extracted with methylene chloride (300 mL). The organic layers were combined, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by flash column chromatography (methylene chloride and ethyl acetate, 1:1) and obtained as a white solid in 71% yield (0.86 g): ^{1}H NMR ($CDCl_3$): δ 8.45 (s, 1H), 8.19 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 3.74 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$): δ 157.3, 156.6, 136.7, 130.6, 130.3, 129.5, 128.7, 127.7, 33.5, 33.4 ppm; HRMS (DIP-CI-DSQ) calculated 268.9926 for $C_{10}H_{10}O_2N_2Br$ $(M+H)^+$, found 268.9931.

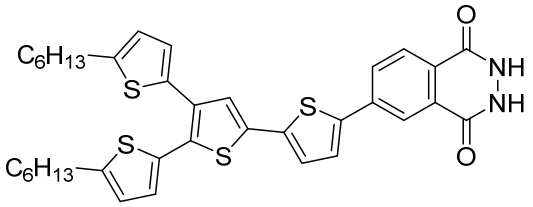


6-(5''-Methyl-5'-(5-methylthiophen-2-yl)-[2,2':4',2''-terthiophen]-5-yl)-2,3-dimethyl-2,3-dihydrophthalazine-1,4-dione (MeBQPNMe). Under argon, degassed toluene (15 mL) was added to a suspension of 4,4,5,5-tetramethyl-2-(5''-methyl-5'-(5-methylthiophen-2-yl)-[2,2':4',2''-terthiophen]-5-yl)-1,3,2-dioxaborolane (**10**) (0.8 g, 2 mmol), potassium phosphate tribasic (K_3PO_4, 2 M aqueous solution, 5 mL), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, 11 mg), tri-*tert*-butylphosphonium tetrafluoroborate ((tBu)$_3$P-HBF_4, 15 mg) and 6-bromo-2,3-dimethyl-2,3-dihydrophthalazine-1,4-dione (**4**) (0.83 g, 3.1 mmol). The solution was heated to reflux for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with methylene chloride. The organic layers were combined, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by flash column chromatography (ethyl acetate/methylene chloride, 3:7) followed by recrystallization from chloroform–ethanol (1:1) to get the product as an orange solid in 30% yield (0.262 g): ^{1}H NMR (DMSO-d_6): δ 8.32 (d, J = 1.7 Hz, 1H), 8.23 (dd, J = 8.1,1.7 Hz, 1H), 8.19 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 3.9 Hz, 1H), 7.58 (s, 1H), 7.50 (d, J = 3.9 Hz, 1H), 7.11 (d, J = 3.6 Hz, 1H), 7.07 (d, J = 3.5 Hz, 1H), 6.83 (d, J = 3.2 Hz, 1H), 6.80 (d, J = 3.2 Hz, 1H), 3.69 (s, 3H), 3.67 (s, 3H), 2.46 (s, 3H); 2.44 (s, 3H) ppm; ^{13}C NMR (DMSO-d_6): δ 156.5, 156.5, 142.3, 140.7, 140.7, 138.0, 137.4, 134.6, 134.0, 133.1, 131.3, 130.1, 130.0, 129.8, 129.2, 128.7, 128.0, 127.9, 127.6, 127.1, 126.7, 126.6, 126.2, 122.8, 33.4, 33.2, 15.5, 15.4 ppm; HRMS (DART-TOF) calculated 547.0637 for $C_{28}H_{23}N_2O_2S_4$ $(M+H)^+$, found 547.0642; elemental analysis calculated N: 5.12; C: 61.51; H: 4.06 and found N: 4.99; C: 61.53; H: 3.90.

*The complete synthetic details for the synthesis of the **HexBQP** family will be reported elsewhere. The general procedure follows that reported in Scheme S1 and Scheme 1.*



Dimethyl-4-(5''-hexyl-5'-(5-hexylthiophen-2-yl)-[2,2':4',2''-terthiophen]-5-yl) phthalate (HexBQPME). Under argon, degassed toluene (15 mL) was added to a suspension of 4,4,5,5-tetramethyl-2-(5''-hexyl-5'-(5-hexylthiophen-2-yl)-[2,2':4',2''-terthiophen]-5-yl)-1,3,2-dioxaborolane (0.624 g, 1.00 mmol), potassium phosphate tribasic (K_3PO_4, 2 M aqueous solution, 10 mL), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, 7 mg), tri-*tert*-butylphosphonium tetrafluoroborate ((tBu)$_3$P-HBF$_4$, 9 mg) and dimethyl-4-bromophthalate **3** (0.409 g , 1.50 mmol). The solution was heated to reflux for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with methylene chloride (3 × 100 mL). The organic layers were combined, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by flash column chromatography (petroleum ether/CH_2Cl_2, 1:1) and obtained as a yellow solid in 61% yield (0.418 g): ^{1}H NMR ($CDCl_3$): δ 7.81 (d, J = 1.8 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.60 (dd, J = 8.0, 1.8 Hz, 1H), 7.22 (d, J = 3.7 Hz, 1H), 7.17 (s, 1H), 7.05 (d, J = 4.1 Hz, 1H), 6.94 (d, J = 3.6 Hz, 1H), 6.90 (d, J = 3.6 Hz, 1H), 6.67 (dd, J = 9.1, 3.6 Hz, 2H), 3.94 (d, J = 9.9 Hz, 6H), 2.80 (m, 4H), 1.69 (m, 4H), 1.40 (m, 12H), 0.92 (t, 6H) ppm; ^{13}C NMR ($CDCl_3$): δ 168.1, 167.0, 147.6, 146.4, 140.3, 138.0, 137.0, 134.4, 134.3, 133.7, 132.3, 132.0, 131.2, 130.0, 129.1, 127.5, 126.9, 126.5, 125.7, 125.0, 124.8, 124.3, 124.1, 52.7, 52.5, 31.6, 31.62, 31.61, 31.60, 31.5, 30.2, 28.8, 22.7, 14.1; HRMS (APCI) calculated 690.1960 for $C_{38}H_{42}O_4S_4$ $(M+H)^+$, found 691.2073; elemental analysis calculated C: 66.05; H: 6.13 and found C: 65.68; H: 6.03.



6-(5''-Hexyl-5'-(5-hexylthiophen-2-yl)-[2,2':4',2''-terthiophen]-5-yl)-2,3-dihydrophthalazine-1,4-dione (HexBQPH). Under argon, anhydrous hydrazine (1.75 mL, 36 mmol) was added to a solution of dimethyl-4-(5''-hexyl-5'-(5-hexylthiophen-2-yl)-[2,2':4',2''-terthiophen]-5-yl) phthalate (**HexBQPME**) (0.50 g, 0.72 mmol) in DMF (40 mL). The reaction mixture was heated at 80 °C for 24 h. The reaction mixture was then cooled to 0 °C and ethanol (40 ml) was added. The yellow precipitate formed was isolated by filtration. The precipitate was recrystallized from DMF–ethanol (20 mL/20 mL) to obtain the product as an orange solid in 36% yield

(169 mg); ^{1}H NMR (DMSO-d_6): δ 11.38 (s, 2H), 7.97 (m, 2H), 7.85 (s, 1H), 7.56 (d, J = 4.1 Hz, 1H), 7.30 (s, 1H), 7.23 (d, J = 4.1 Hz, 1H), 6.84 (d, J = 3.6 Hz, 1H), 6.80 (d, J = 3.6 Hz, 1H), 6.57 (dd, J = 11.8, 3.6 Hz, 2H), 2.28 (m, *4*H), 1.35 (m, 4H), 1.08 (m, 12H), 0.63 (t, 6H) ppm; ^{13}C NMR (DMSO-d_6): δ 148.3, 146.8, 141.3, 137.5, 134.8, 134.0, 133.4, 131.4, 130.4, 129.8, 129.1, 127.9, 127.8, 127.2, 127.1, 126.9, 126.8, 125.7, 125.2, 31.8, 31.7, 31.6, 31.6, 30.0, 29.99, 28.7, 28.70, 22.7, 14.6 ppm; HRMS (APCI-TOF) calculated 659.1889 for $C_{36}H_{39}N_2O_2S_4$ $(M+H)^+$, found 659.1890; elemental analysis calculated N: 4.25; C: 65.55; H: 5.77 and found N: 4.20; C: 65.76; H: 5.85.

UV-Vis Absorbance Spectra in DMF

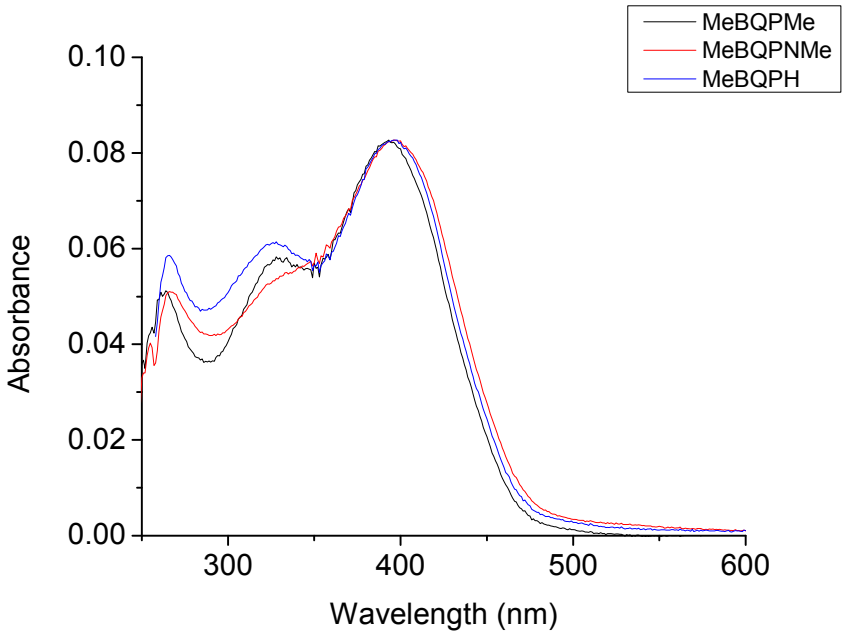


Figure S1. UV-Vis absorbance spectra for **MeBQPNMe**, **MeBQPME**, and **MeBQPH** in DMF (room temperature, 100 μM).

Table S1. UV-Vis absorbance data for **MeBQPNMe**, **MeBQPME**, and **MeBQPH** in DMF (room temperature, 100 μM).

	λ_{max} (nm)	λ_{onset} (nm)	$E_{g\text{-}opt}$ (eV)
MeBQPME	392	464	2.67
MeBQPNMe	397	470	2.64
MeBQPH	396	467	2.65

Cyclic Voltammetry/Differential Pulse Voltammetry

Table S2. Electrochemical potentials, electrochemical energy gaps, and corresponding HOMO/LUMO energies for **MeBQPME**, **MeBQPH**, and **MeBQPNMe** based on DPV peak onsets. Representative DPV and CV data are shown on the following pages.

	$E_{ox\text{-}onset}$ (V)[c]	$E_{red\text{-}onset}$ (V)[c]	E_g (V)[c]	E_{HOMO} (eV)[d]	E_{LUMO} (eV)[d]
MeBQPME[a]	0.511 (±0.011)	-1.86 (±0.05)	2.37 (±0.05)	-5.61 (±0.01)	-3.25 (±0.06)
	0.524	-1.84	2.36	-5.62	-3.29
	0.506	-1.91	2.42	-5.61	-3.19
	0.504	-1.82	2.32	-5.60	-3.28
MeBQPNMe[b]	0.532 (±0.028)	-1.80 (±0.04)	2.31 (±0.04)	-5.63 (±0.03)	-3.30 (±0.04)
	0.512	-1.77	2.28	-5.61	-3.33
	0.551	-1.83	2.34	-5.61	-3.27
MeBQPH[a,e]	0.525 (±0.027)	–	–	-5.63 (±0.03)	–
	0.513	–	–	-5.61	–
	0.556	–	–	-5.66	–
	0.505	–	–	-5.61	–

[a]Values reported are the average of three DPV runs from two different sample preparations. [b]Values reported are the average of two DPV runs from one sample preparation. [c]Oxidation ($E_{ox\text{-}onset}$) and reduction ($E_{red\text{-}onset}$) potentials are reported vs. Fc/Fc^+. [d]HOMO and LUMO levels were calculated from $E_{ox\text{-}onset}$ and $E_{red\text{-}onset}$, respectively, considering that Fc/Fc^+ is 5.1 eV relative to vacuum (see reference[4]). [e] The compound is not readily soluble in DMF and additionally has not given reproducible data at negative potentials.

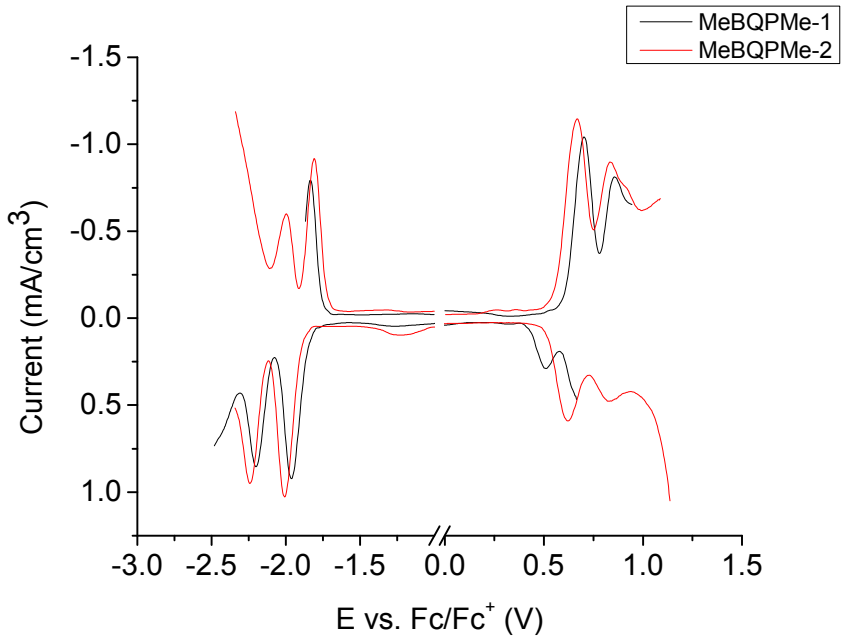


Figure S2. DPV scans of **MeBQPME**.

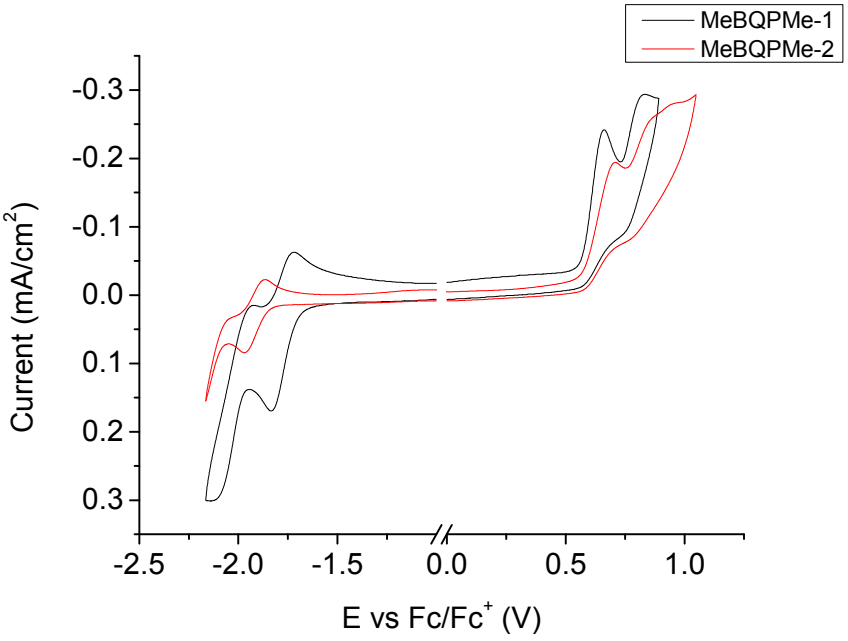


Figure S3. CV scans of **MeBQPME**.

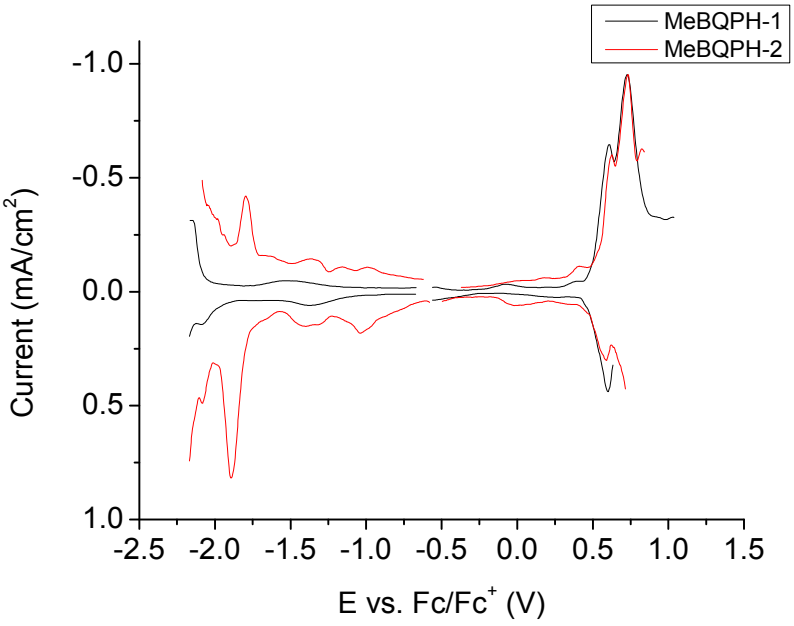


Figure S4. DPV scans of **MeBQPH**.

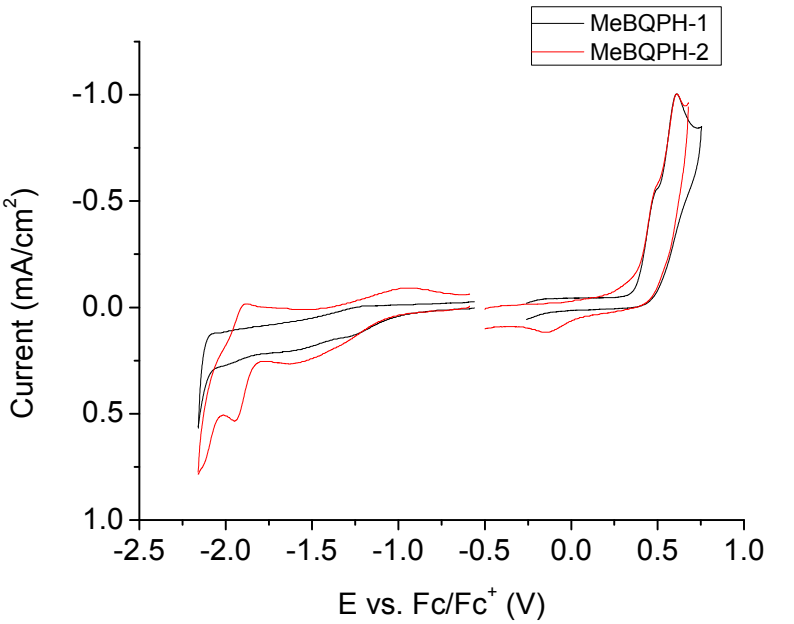


Figure S5. CV scans of **MeBQPH**.

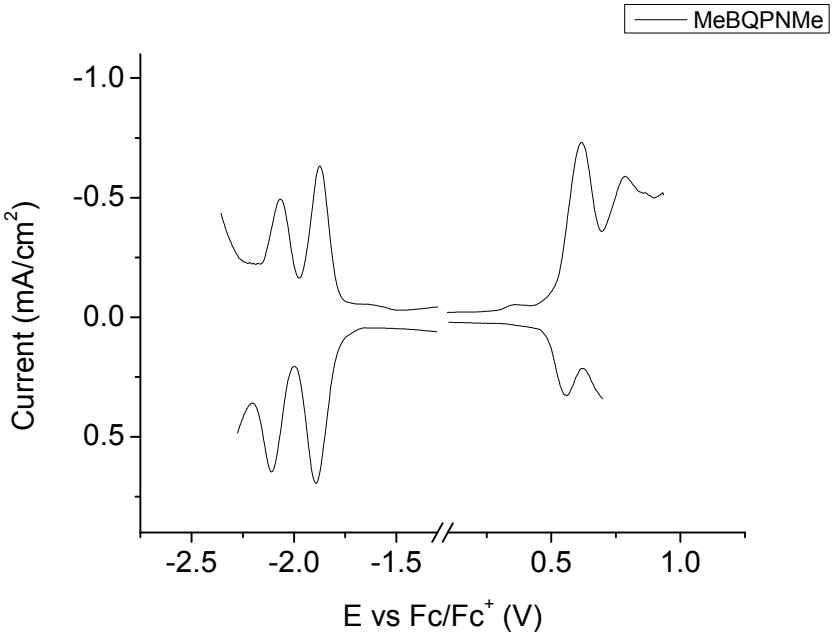


Figure S6. DPV scan of **MeBQPNMe**.

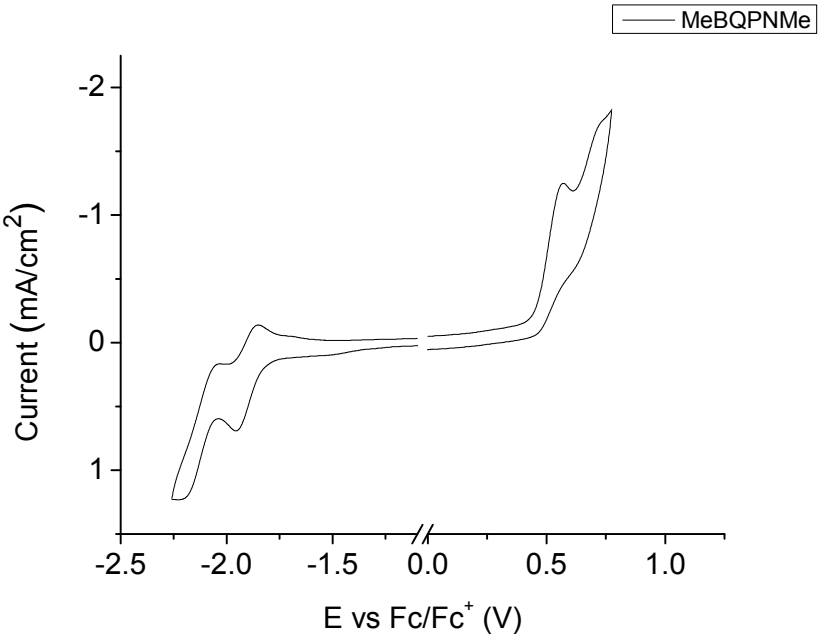


Figure S7. CV scan of **MeBQPNMe**.

Variable-Temperature ^{1}H NMR of HexBQPH (full spectra)

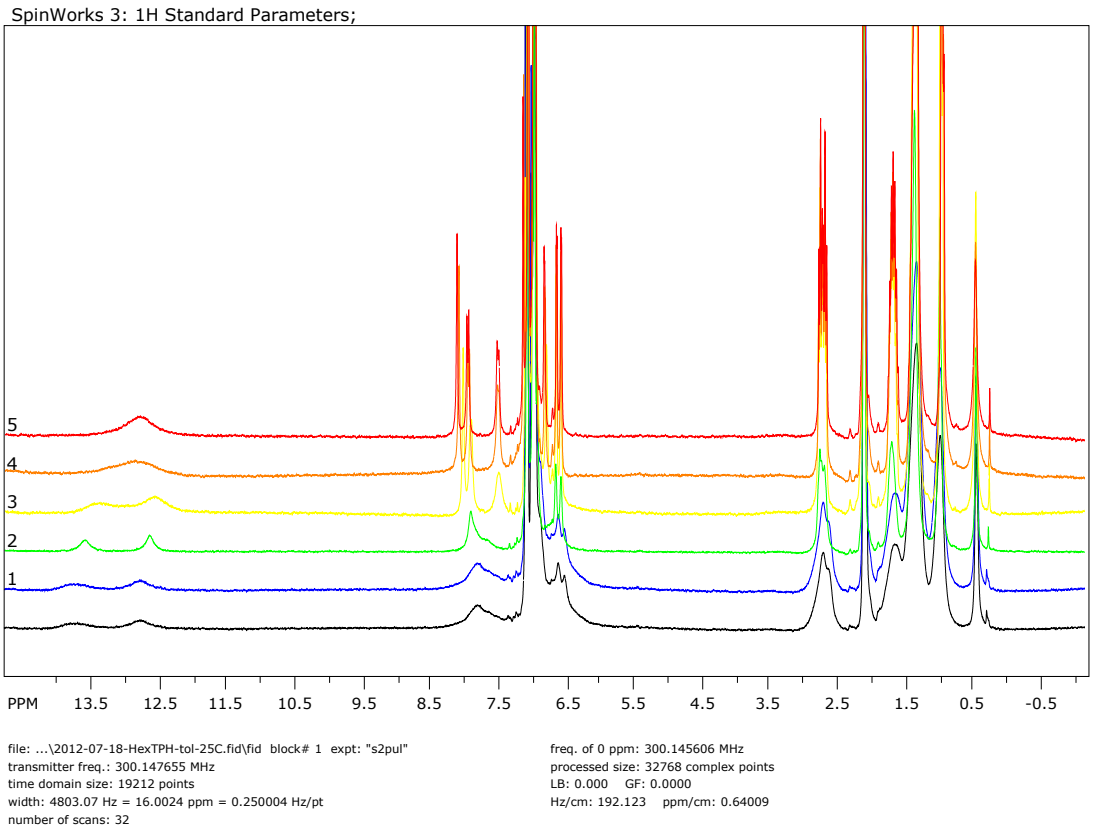


Figure S8. VT-NMR spectra (300 MHz, toluene-d_8, 10 mM) of **HexBQPH** collected at 27 (1), 55 (2), 75 (3), 85 (4), and 90 °C (5).

Thermogravimetric Analysis

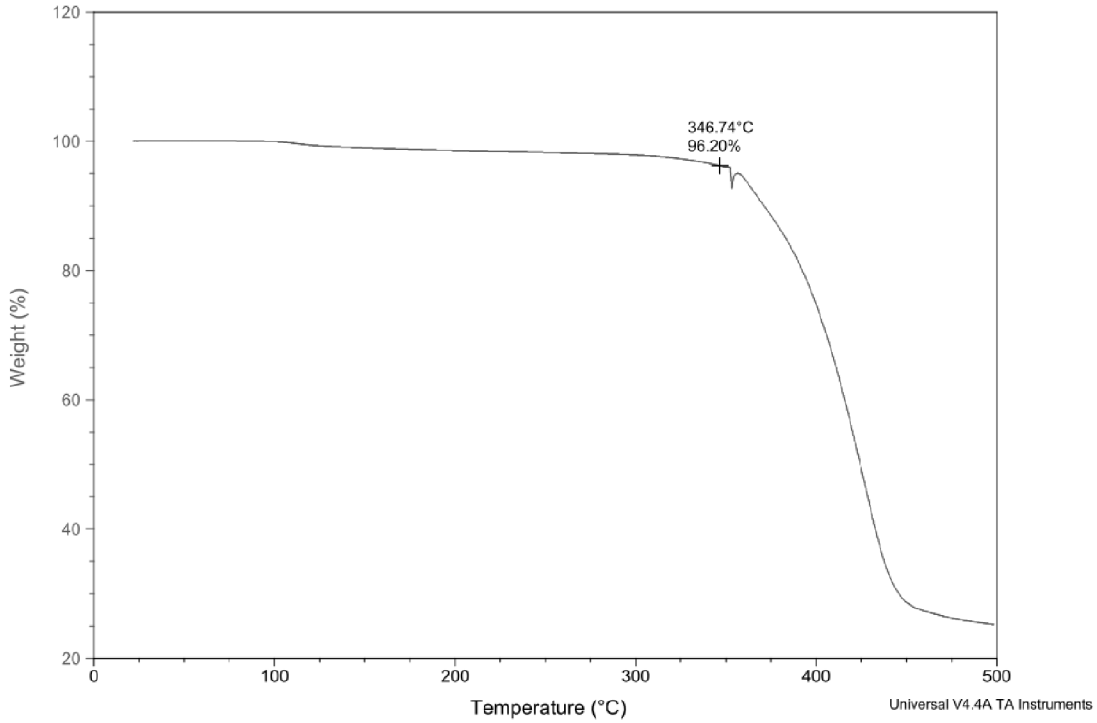


Figure S9. TGA scan of **MeBQPME**.

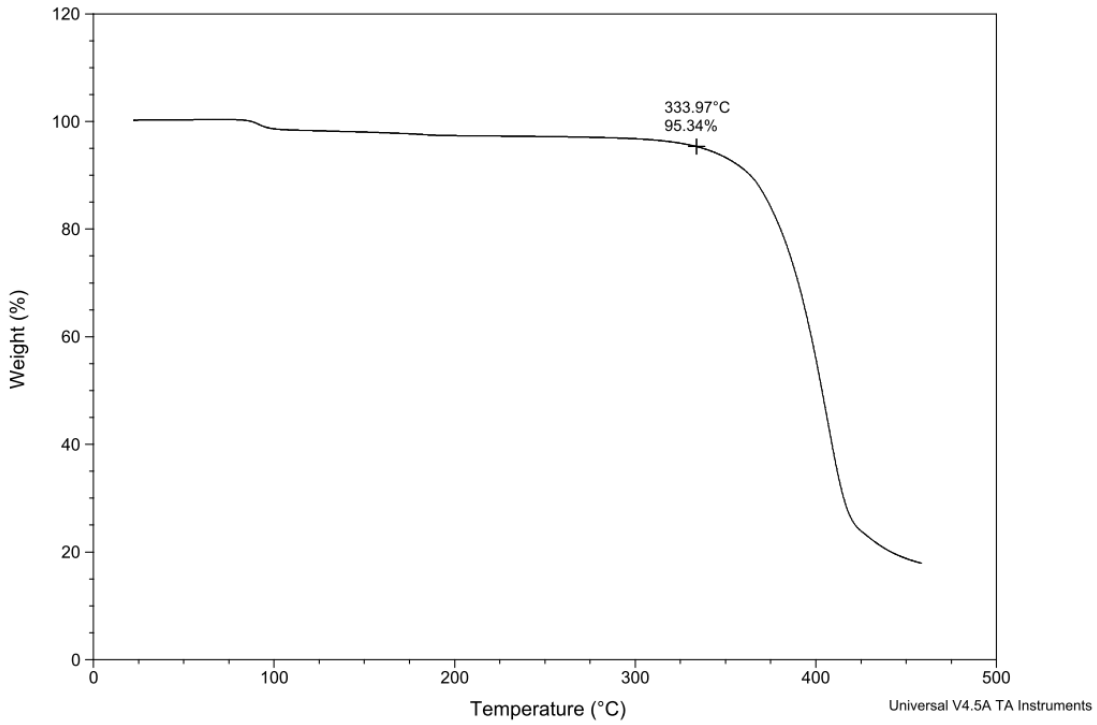


Figure S10. TGA scan of **MeBQPNMe**.

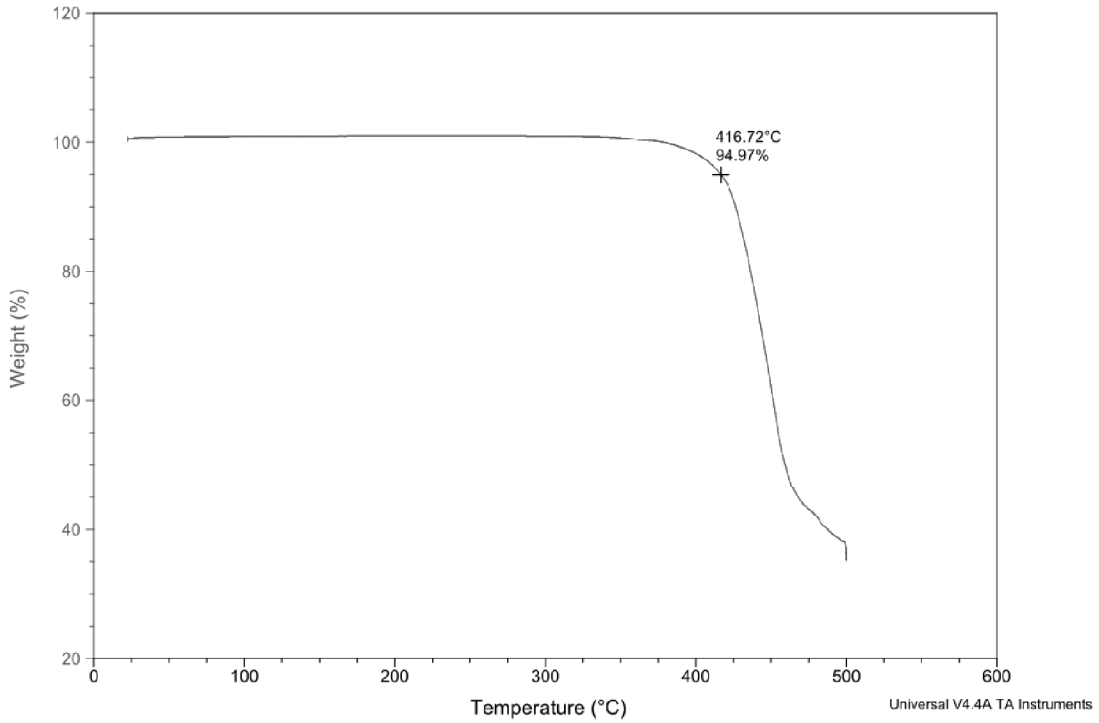


Figure S11. TGA scan of **MeBQPH**.

Differential Scanning Calorimetry

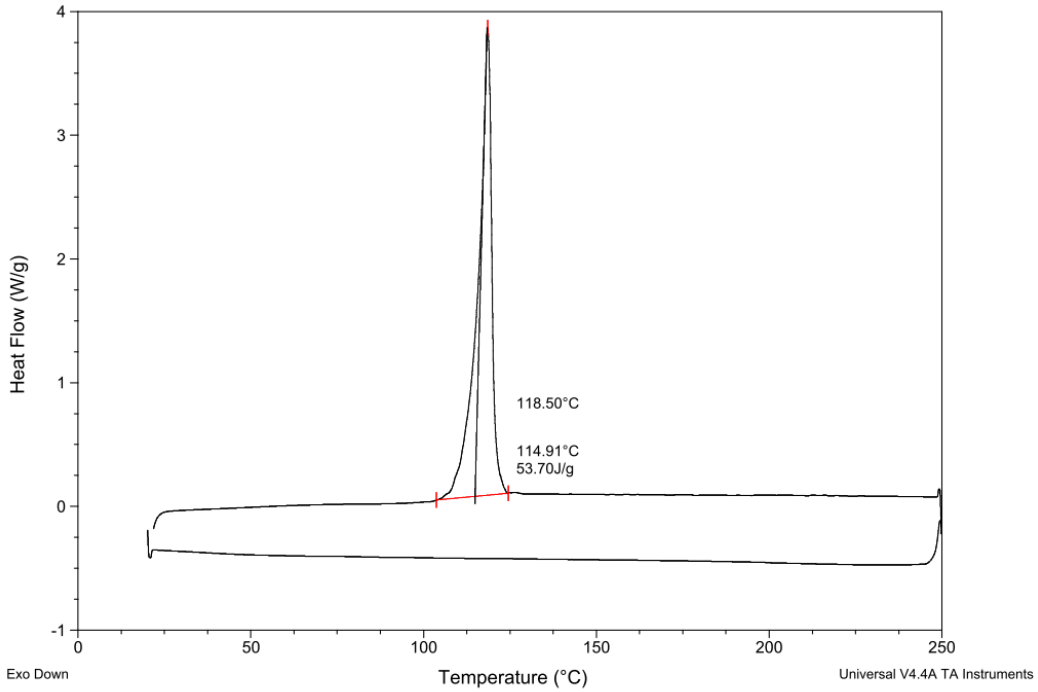


Figure S12. DSC trace of **MeBQPME** with peak labels.

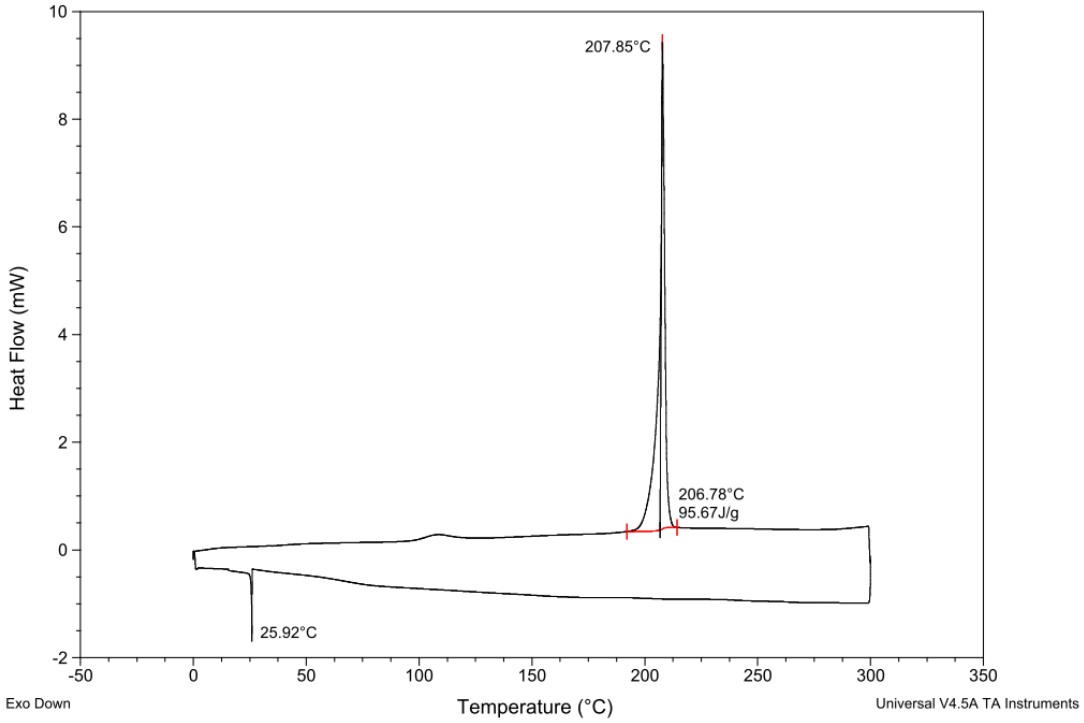


Figure S13. DSC trace of **MeBQPNMe** with peak labels.

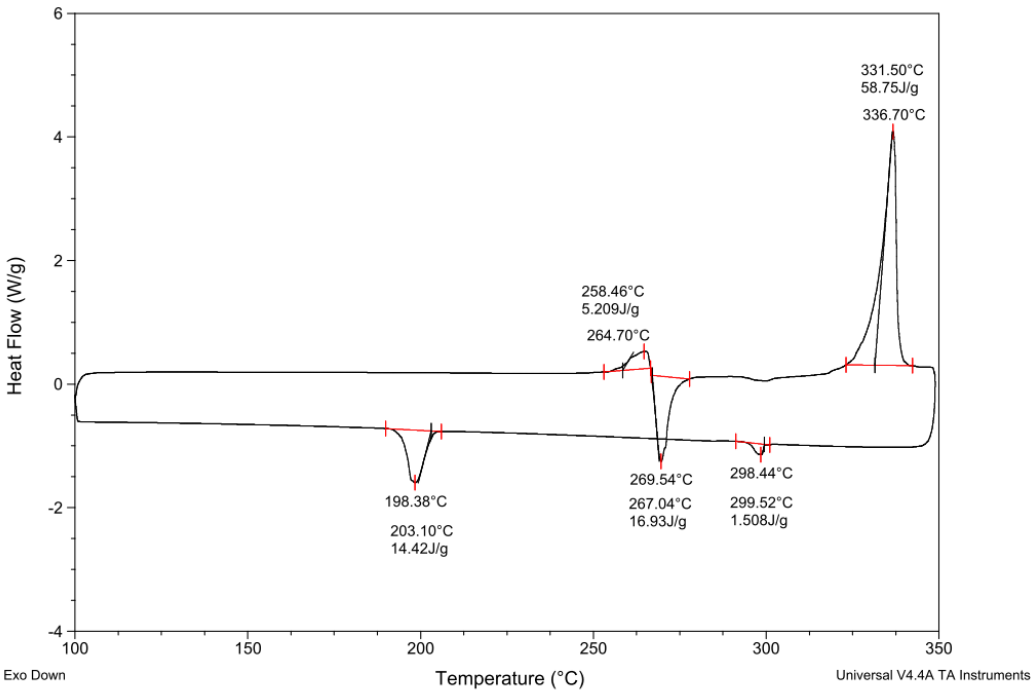


Figure S14. DSC trace of **MeBQPH** with peak labels; in this particular experiment, two cycles of heating and subsequent cooling were performed, however, for clarity, only the second run is shown.

Thin Film FT-IR Spectroscopy (expansions and peak labels)

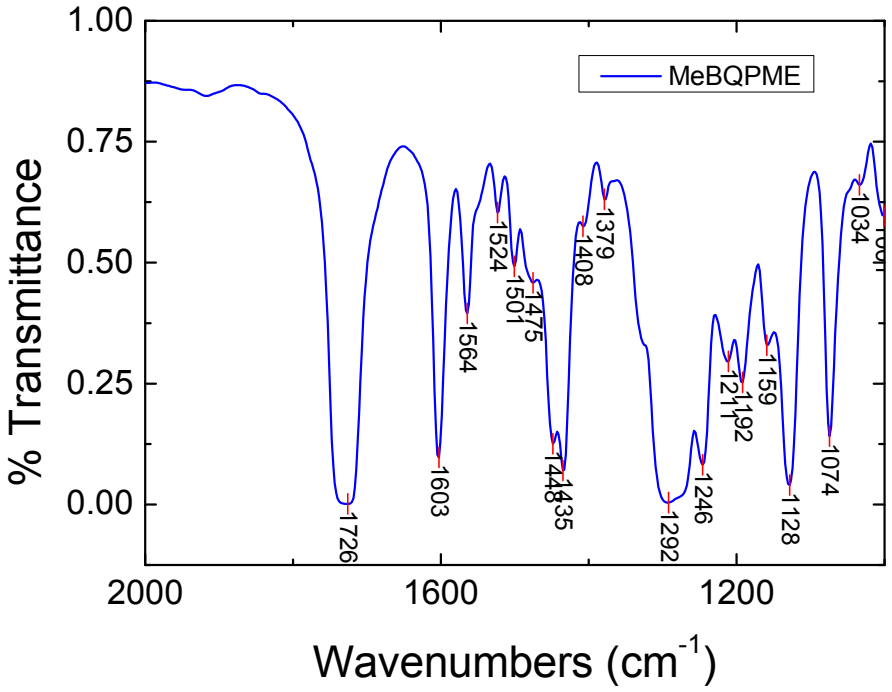


Figure S15. Expanded FT-IR spectra for a thick film (~ 2.5 μm) of **MeBQPME**.

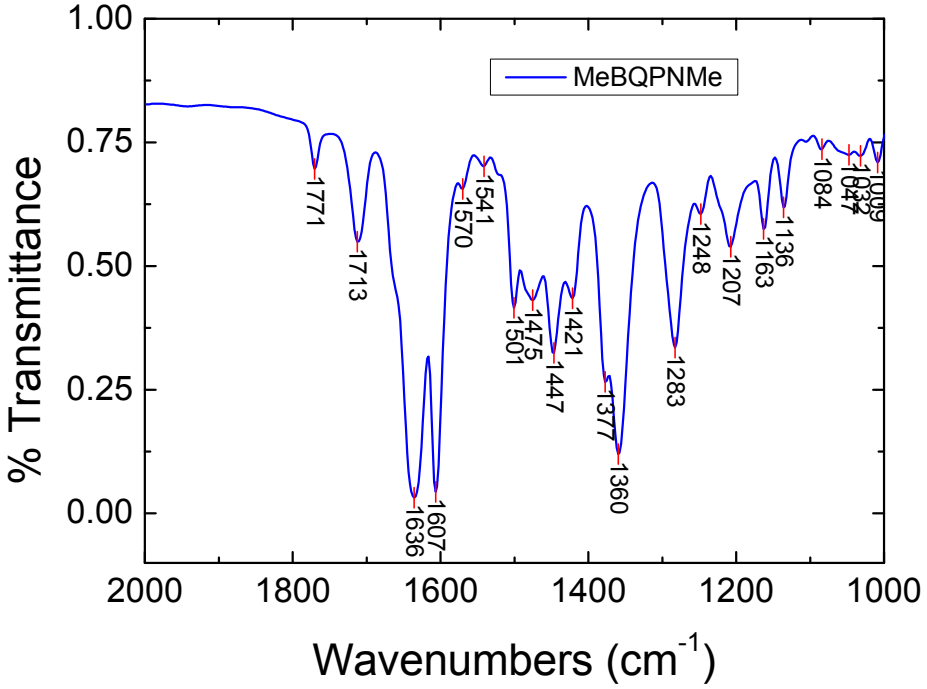


Figure S16. Expanded FT-IR spectra for a thick film (~ 2.5 μm) of **MeBQPNMe**.

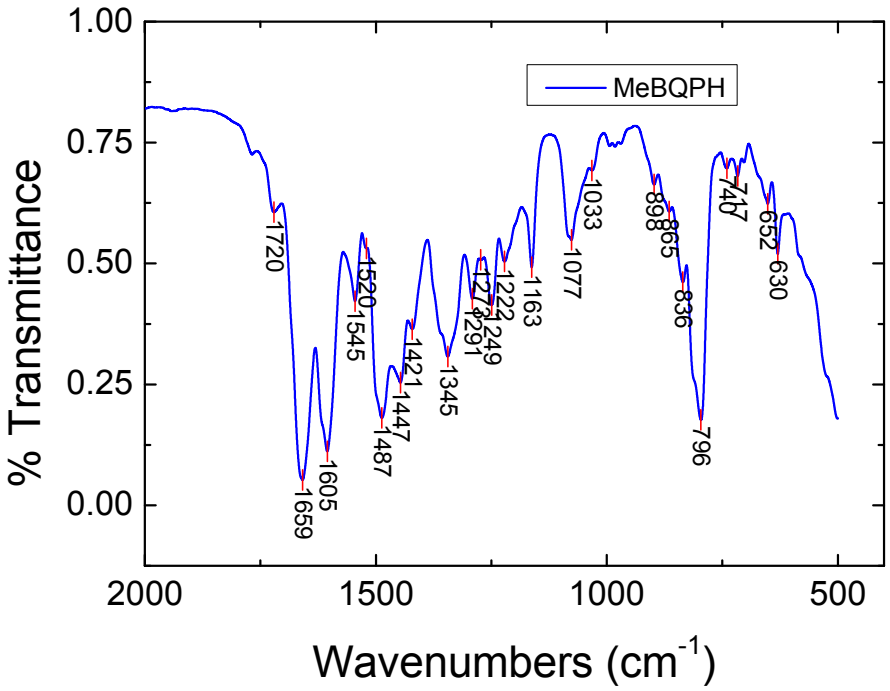
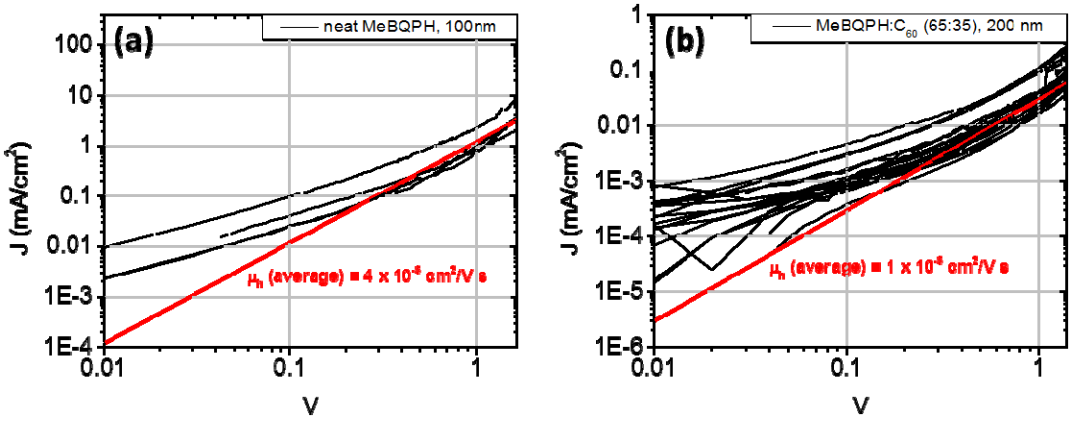


Figure S17. Expanded FT-IR spectra for a thick film (~ 2.5 μm) of **MeBQPH**.

Thin Film Morphology and Charge Transport Properties



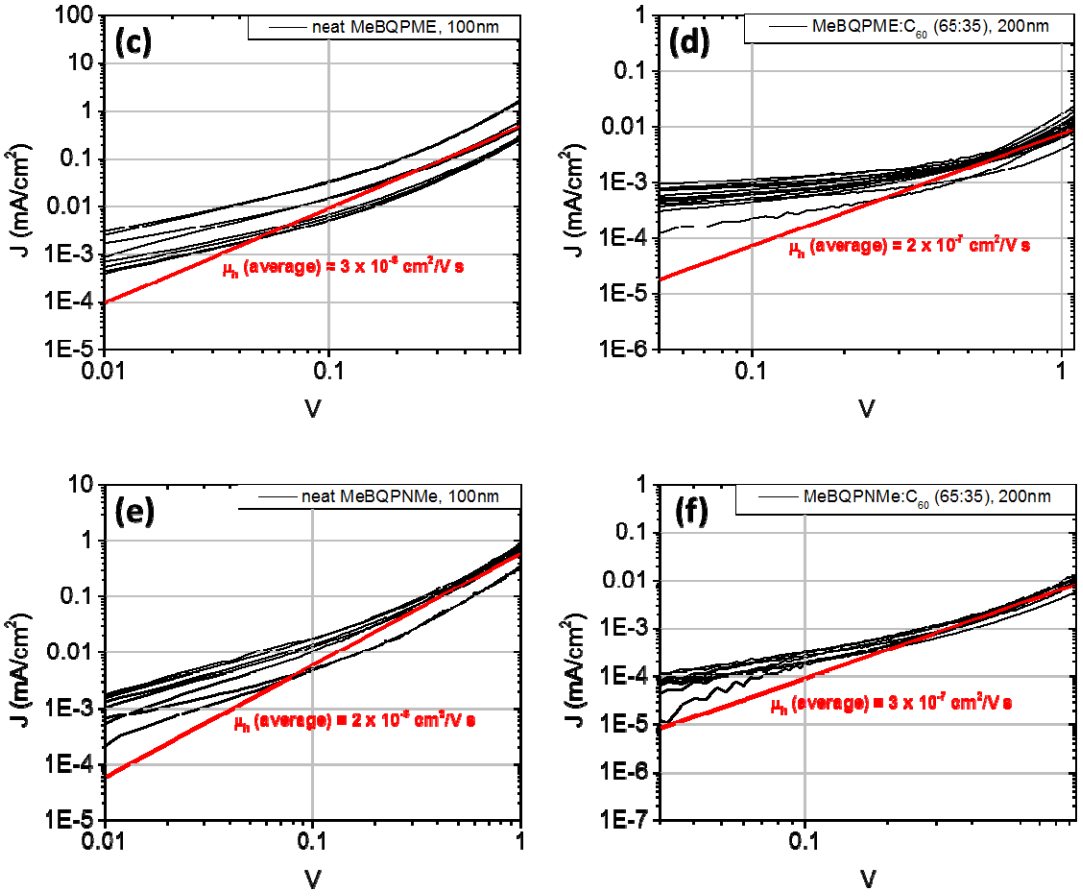


Figure S18. Space-charge-limited hole mobility fits for neat films (a,c,e) and blends with C_{60} (b,d,f) from **MeBQPH** (a,b), **MeBQPME** (c,d) and **MeBQPNMe** (e,f). In all cases the device structure was Au (60 nm)/MoOx (5 nm)/organic/MoOx (5 nm)/Au (60 nm) with device areas of ~0.25 mm^2. Black lines are data from multiple devices, while the bold red lines are produced from Child's law using the average fitted mobility value from individual fits performed on each curve. Devices transitioned from ohmic (slope = 1) to space-charge-limited (slope = 2) current at around 0.2 - 0.5 V applied bias.

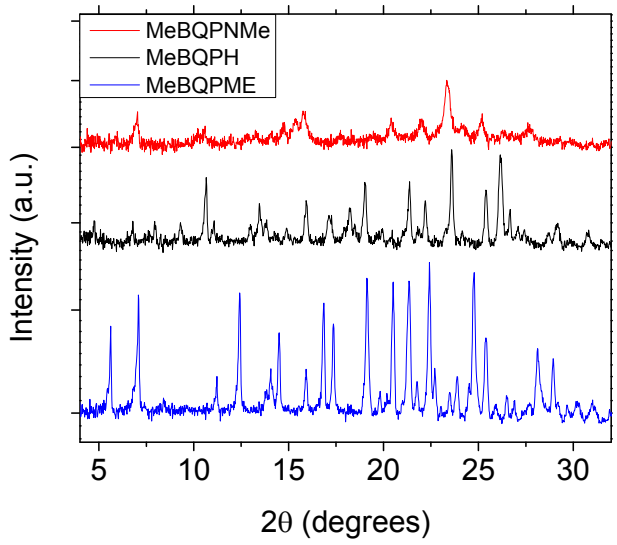


Figure S19. Powder XRD spectra for **MeBQPNMe**, **MeBQPH** and **MeBQPME**.

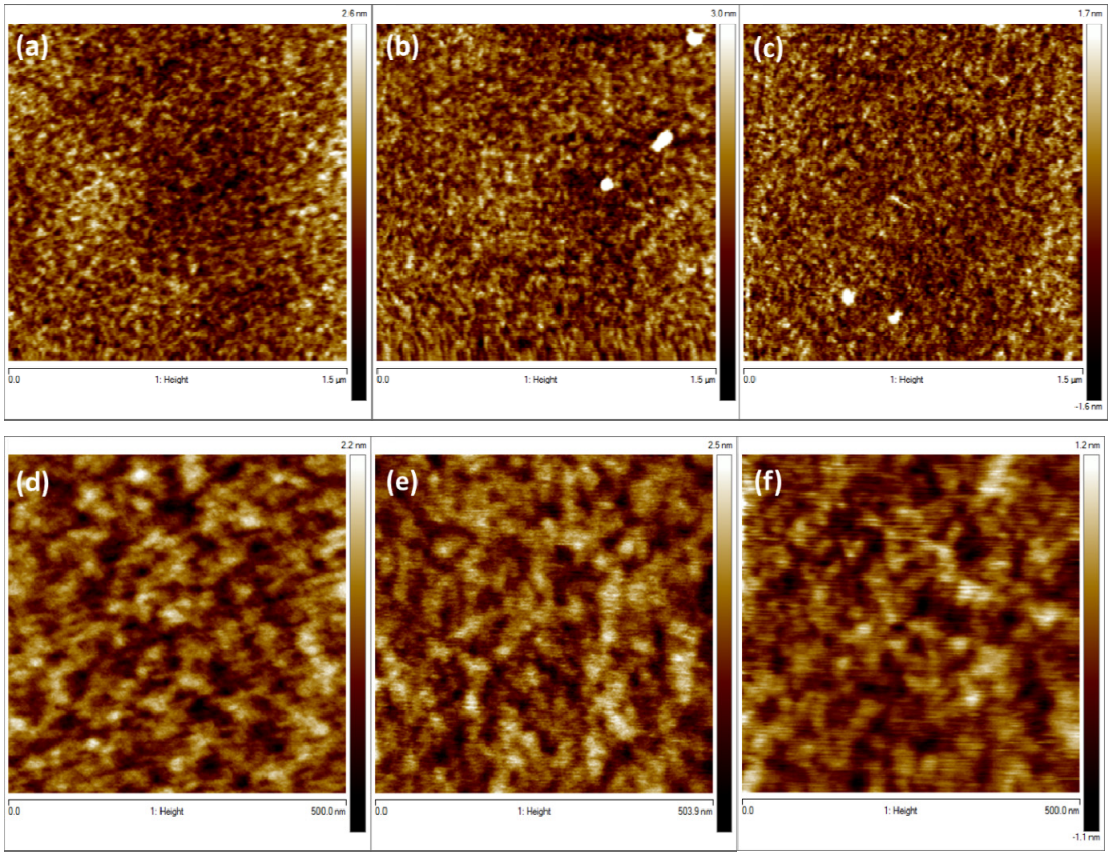


Figure S20. AFM images of 1:1 by weight, 40 nm thick blend films thermally evaporated on silicon/MoOx (5nm). (a,d) **MeBQPH**:C_{60}, (b,e) **MeBQPME**:C_{60}, and (c,f) **MeBQPNMe**:C_{60} with a scan area of 1.5x1.5 µm (a-c) and 500x500 nm (d-f).

Annealed Device Performance

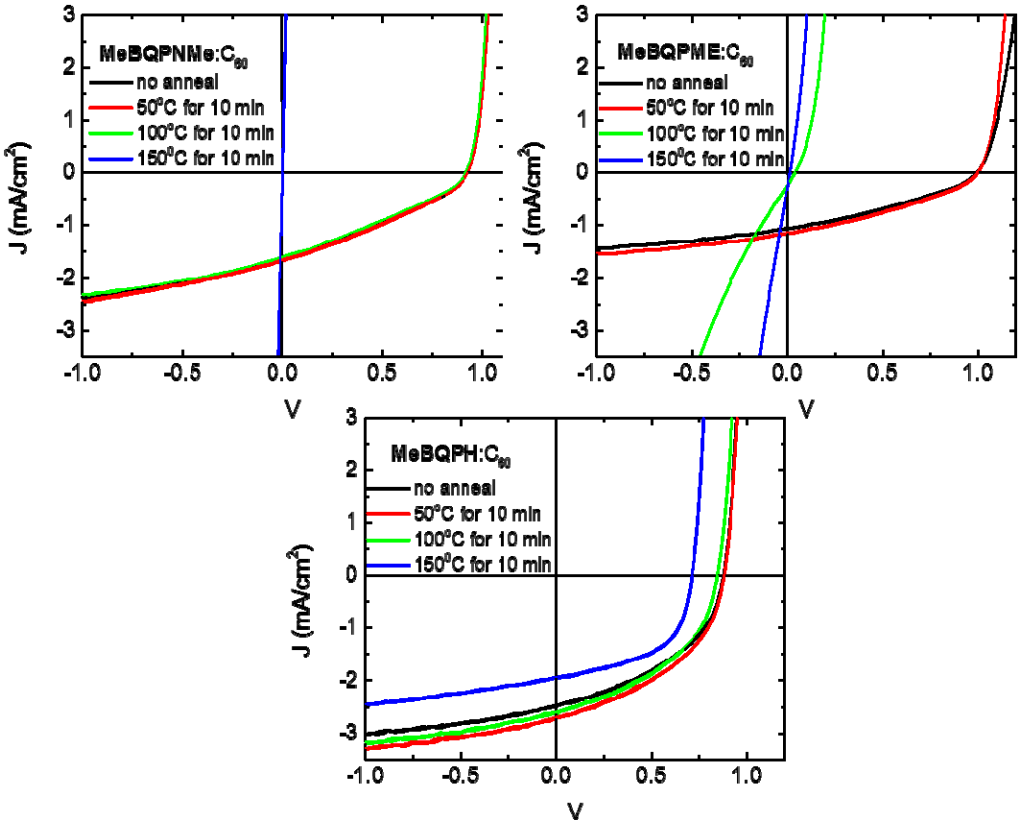


Figure S21. Current density vs. voltage characteristics under simulated 1 sun AM1.5G illumination for annealed devices at 50, 100, and 150˚C. Device structures are the same as those reported in the paper.

Charge Collection Length Fitting

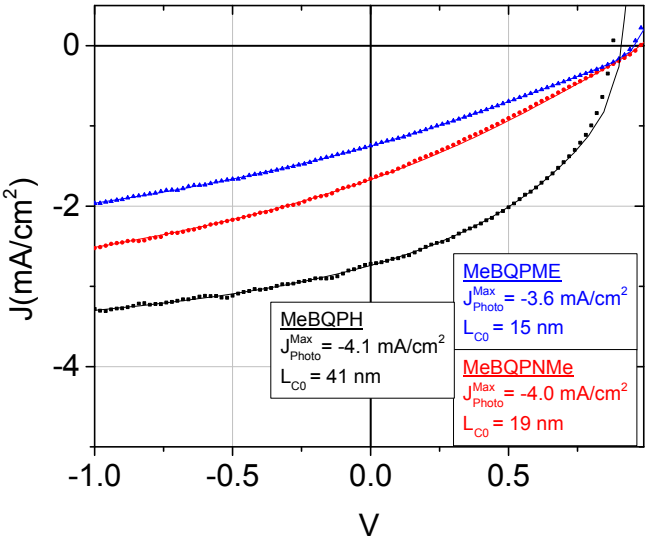


Figure S22. Curve fitting for the determination of the charge collection length at short-circuit (symbols: experimental data; solid lines: fitted data). The current density-voltage characteristics of the bulk heterojunction organic photovoltaic cells were fitting according to a charge collection model[5,6] using $J = J_{Dark} + J_{Photo}^{Max} * \eta_{CC}(V)$ where $\eta_{CC}(V) = \frac{L_C}{d_m}(1 - \exp\left(\frac{-d_m}{L_C}\right))$ and $L_C = L_{C0} * (\frac{V_{BI}-V}{V_{BI}})$. J_{Dark} is the current density in the dark, J_{Photo}^{Max} is the maximum photocurrent achieved at high reverse bias, L_C is the charge collection length (L_{C0} is the charge collection length at 0V or short circuit), V_{BI} is the build-in voltage, and d_m is the mixed layer thickness.

Cartesian Coordinates and Energies for Optimized Structures

MeBQPH (lactam tautomer)

Energy: -2854.29973519 a.u.

XYZ file generated by gabedit : coordinates in Angstrom

C	6.2511580000	0.5698260000	0.2612830000
C	7.2026640000	-0.3679160000	-0.1742210000
C	6.7697930000	-1.6225120000	-0.6225420000
C	5.4201390000	-1.9344510000	-0.6248250000
C	4.4500640000	-1.0082850000	-0.1711750000
C	4.8946400000	0.2470800000	0.2715180000
C	8.6431880000	-0.0359110000	-0.2113530000
N	8.9831320000	1.1814400000	0.3607080000
O	9.5126000000	-0.7570680000	-0.6857100000
C	6.6739080000	1.9008420000	0.7647690000
N	8.0204740000	2.1850100000	0.6159590000
O	5.9196830000	2.7250890000	1.2661800000
C	3.0325660000	-1.3655430000	-0.1693750000
C	2.4618000000	-2.6205740000	-0.2257130000
C	1.0477440000	-2.6108780000	-0.1954870000
C	0.5034880000	-1.3430630000	-0.1176550000
S	1.7783920000	-0.1400870000	-0.0832850000
C	-0.8871690000	-0.9538290000	-0.0662530000
C	-1.4310530000	0.3103880000	-0.0269640000
C	-2.8580510000	0.3469120000	-0.0198910000
C	-3.4181640000	-0.9250040000	-0.0448170000
S	-2.1656690000	-2.1536180000	-0.0713640000
C	-4.8024280000	-1.3620410000	0.0162110000
C	-5.3807930000	-2.4241310000	-0.6436700000
C	-6.7423700000	-2.6397780000	-0.2929180000
C	-7.2182010000	-1.7547130000	0.6401110000
S	-5.9690440000	-0.6287550000	1.1099290000
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C	-3.3943160000	2.7038530000	0.7925000000
C	-4.2081410000	3.8266240000	0.4611090000
C	-5.0190290000	3.6184510000	-0.6234170000
S	-4.7818590000	2.0085530000	-1.2596400000
C	-6.0025360000	4.5647250000	-1.2456440000
C	-8.5975570000	-1.6717450000	1.2229320000
H	7.5126550000	-2.3305520000	-0.9748230000
H	5.1001450000	-2.9017460000	-0.9988410000
H	4.2021540000	0.9936820000	0.6473000000
H	9.8573210000	1.5588110000	0.0098180000
H	8.3554630000	2.8976030000	1.2558540000

H	3.0443150000	-3.5344430000	-0.2607110000
H	0.4439700000	-3.5117380000	-0.2242960000
H	-0.8341360000	1.2159430000	-0.0436970000
H	-4.8440610000	-3.0183820000	-1.3758360000
H	-7.3582440000	-3.4207940000	-0.7275510000
H	-2.6976680000	2.6867610000	1.6243060000
H	-4.1970940000	4.7610300000	1.0136350000
H	-5.7634150000	4.7745540000	-2.2954670000
H	-7.0259660000	4.1710280000	-1.2155010000
H	-5.9933050000	5.5159280000	-0.7040590000
H	-9.2231900000	-2.4672950000	0.8061570000
H	-8.5901390000	-1.7871310000	2.3137350000
H	-9.0797850000	-0.7123620000	0.9986500000

MeBQPH (lactim-lactam 1)

Energy: -2854.30217968 a.u.

XYZ file generated by gabedit : coordinates in Angstrom

C	-6.2711780000	0.5740620000	-0.2345710000
C	-7.2127870000	-0.3803470000	0.2008650000
C	-6.7693480000	-1.6467600000	0.6056430000
C	-5.4207040000	-1.9526490000	0.5796380000
C	-4.4602640000	-1.0086760000	0.1346900000
C	-4.9070500000	0.2550370000	-0.2702820000
C	-8.6487310000	-0.0487100000	0.2346470000
N	-8.9200890000	1.2389590000	-0.1943130000
O	-9.5461440000	-0.8042970000	0.5973200000
C	-6.7898400000	1.8660050000	-0.6416330000
N	-8.0402000000	2.1914550000	-0.6267380000
O	-5.8869410000	2.7860800000	-1.0643970000
C	-3.0417920000	-1.3669120000	0.1051150000
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^{1}H and ^{13}C NMR SPECTRA

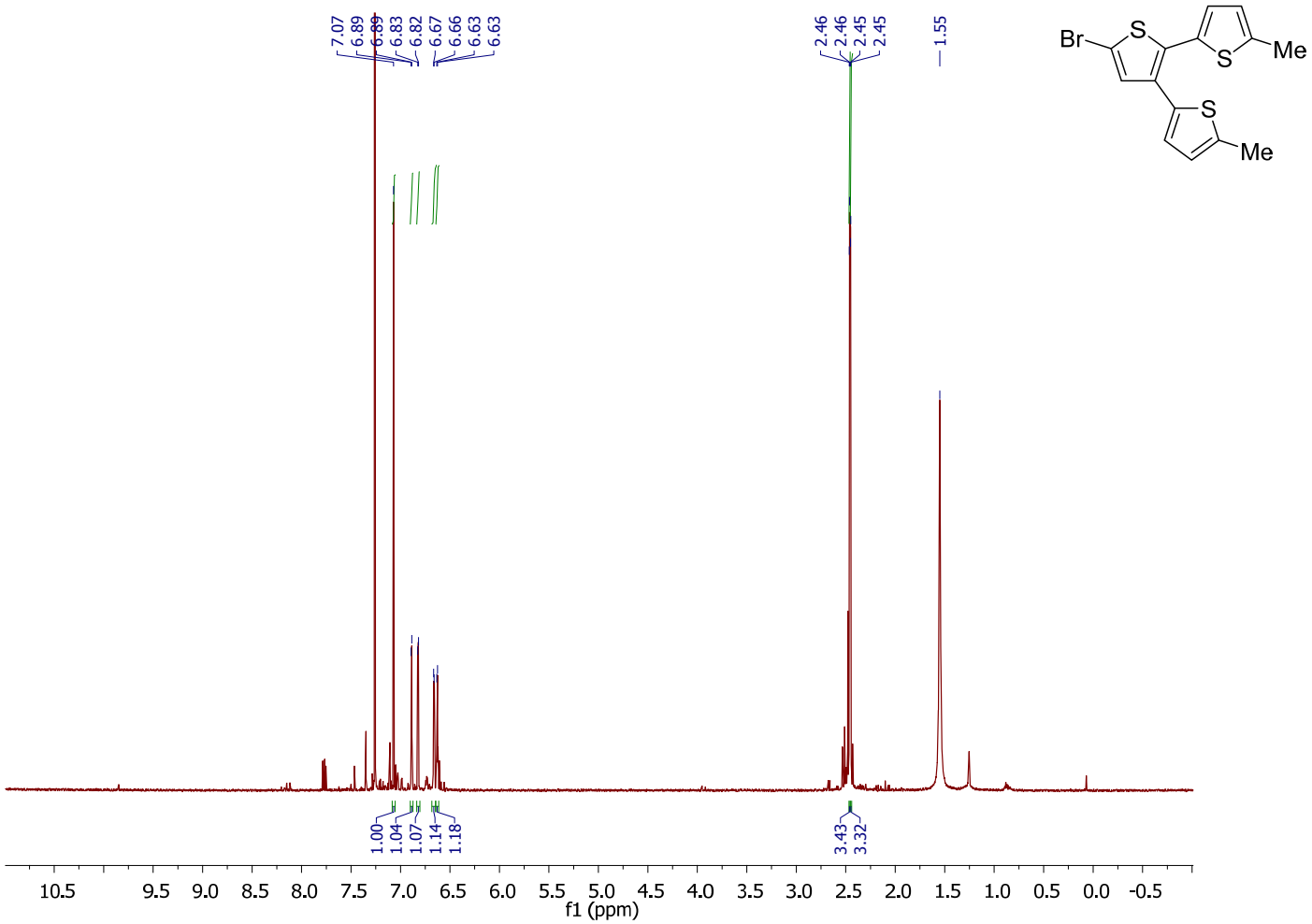

Figure S23. ^{1}H NMR spectrum of compound **7** (300 MHz, $CDCl_3$).

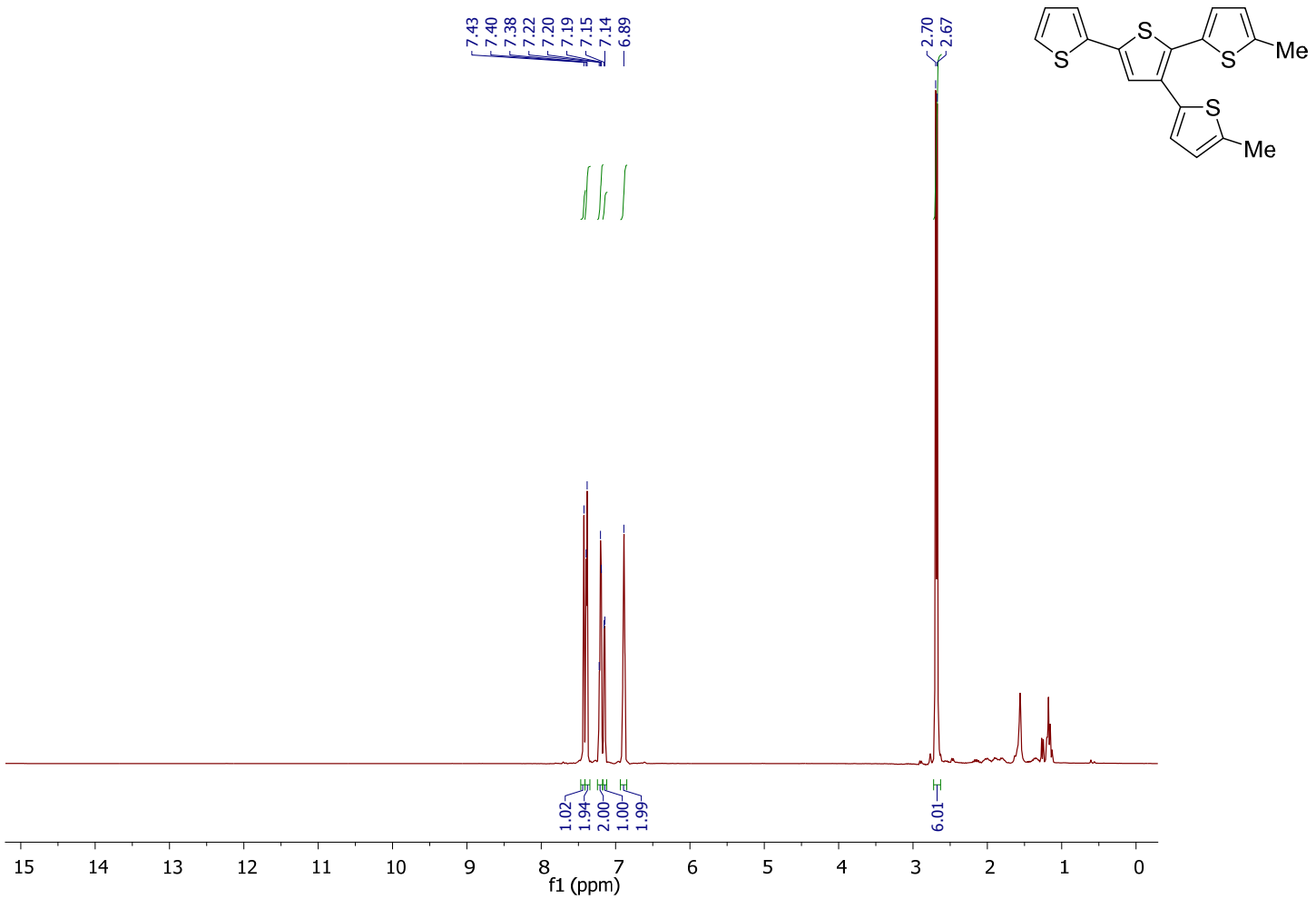

Figure S24. ^{1}H NMR spectrum of compound **7** (300 MHz, $CDCl_3$).

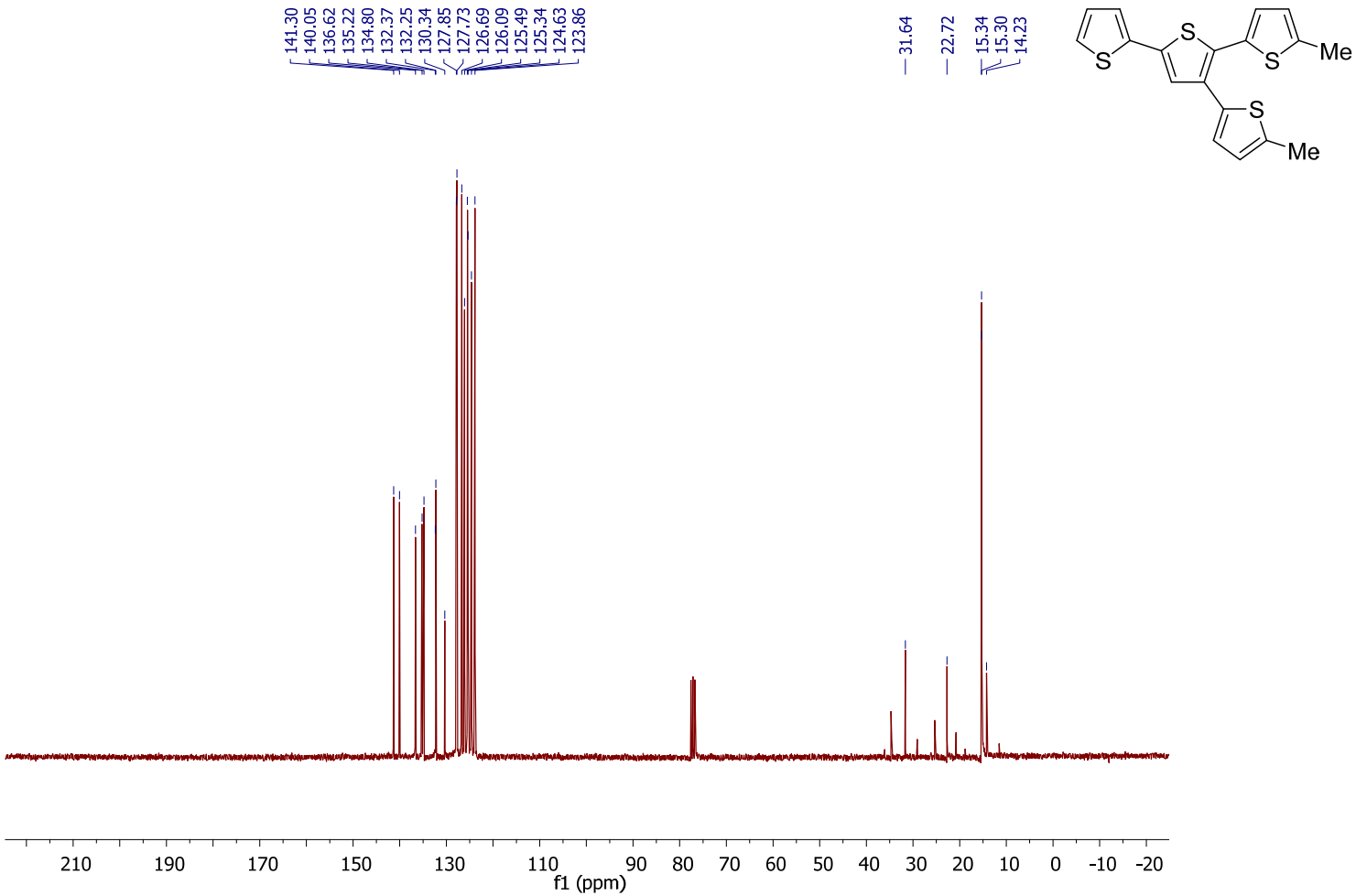

Figure S25. ^{13}C NMR spectrum of compound **7** (75 MHz, $CDCl_3$).

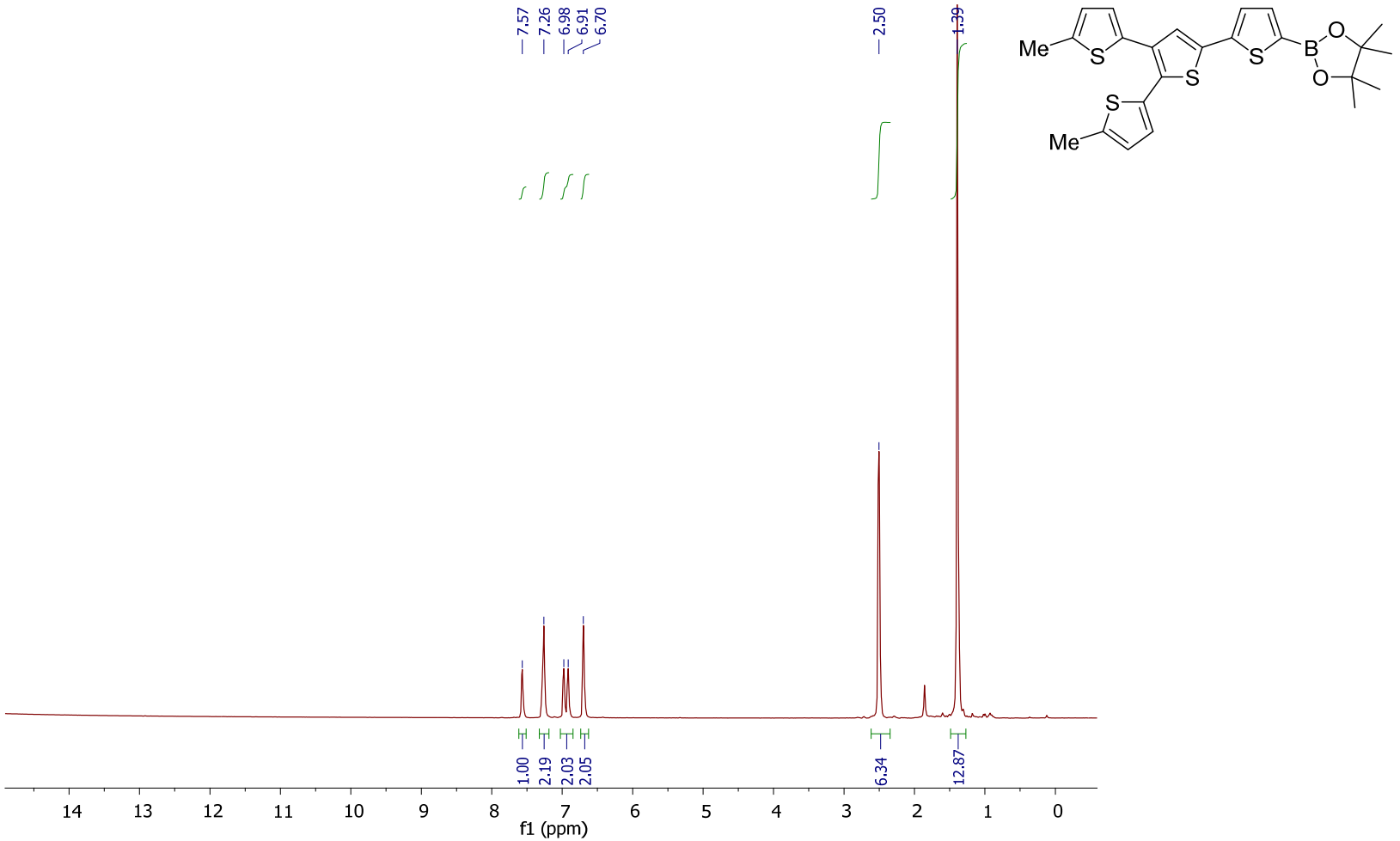

Figure S26. ^{1}H NMR spectrum of compound **8** (300 MHz, $CDCl_3$).

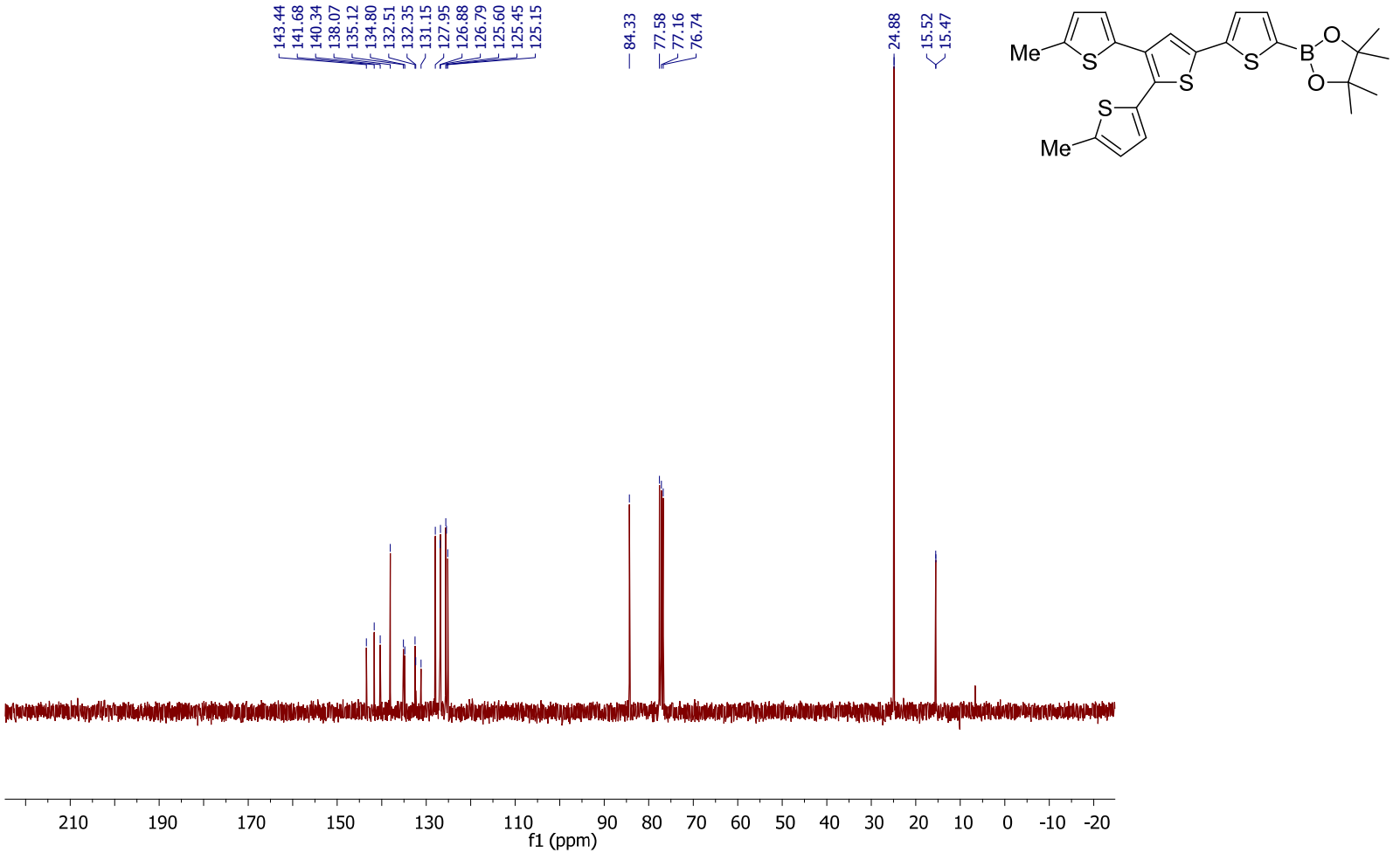

Figure S27. ^{13}C NMR spectrum of compound **8** (75 MHz, $CDCl_3$).

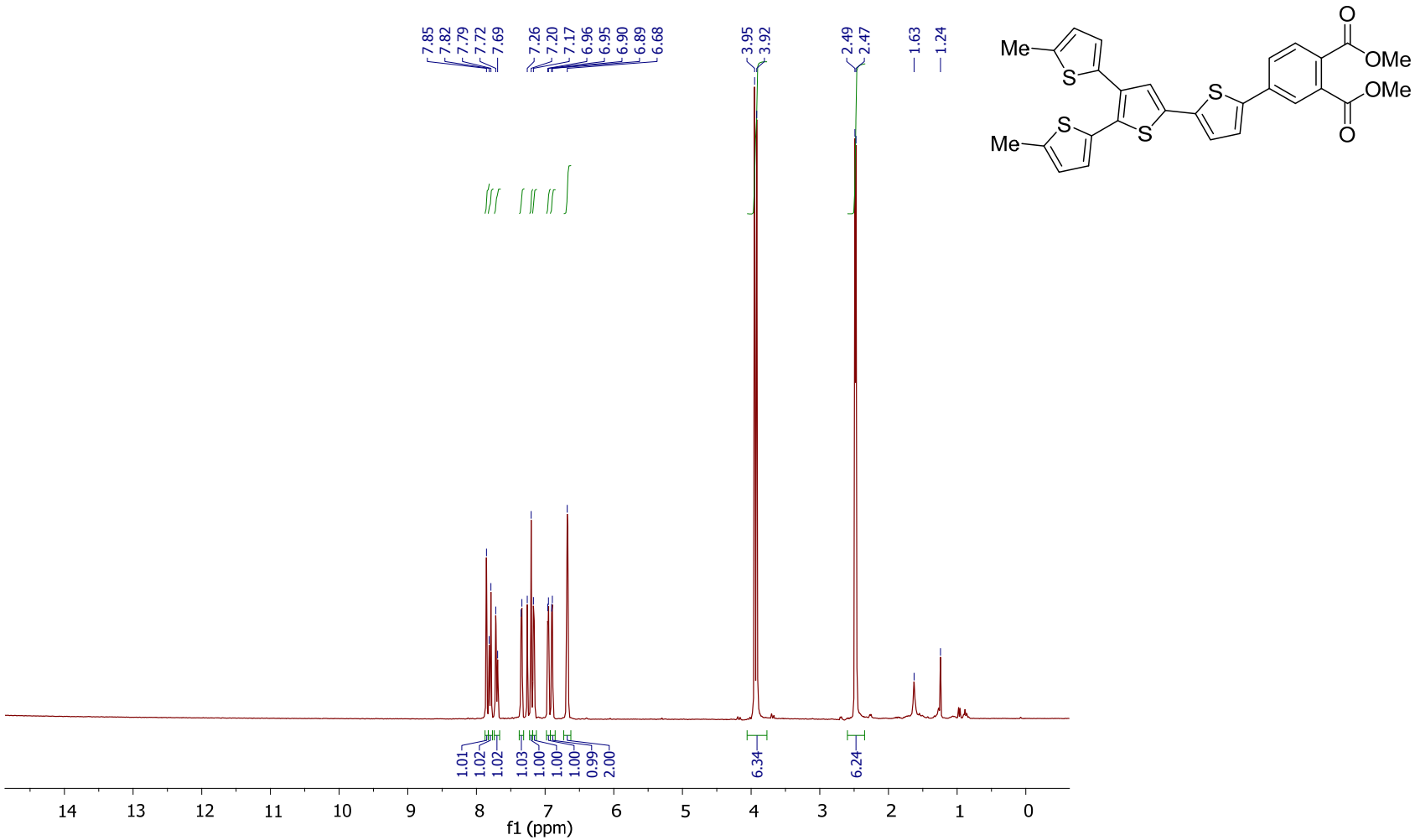

Figure S28. ^{1}H NMR spectrum of compound **9** (300 MHz, $CDCl_3$).

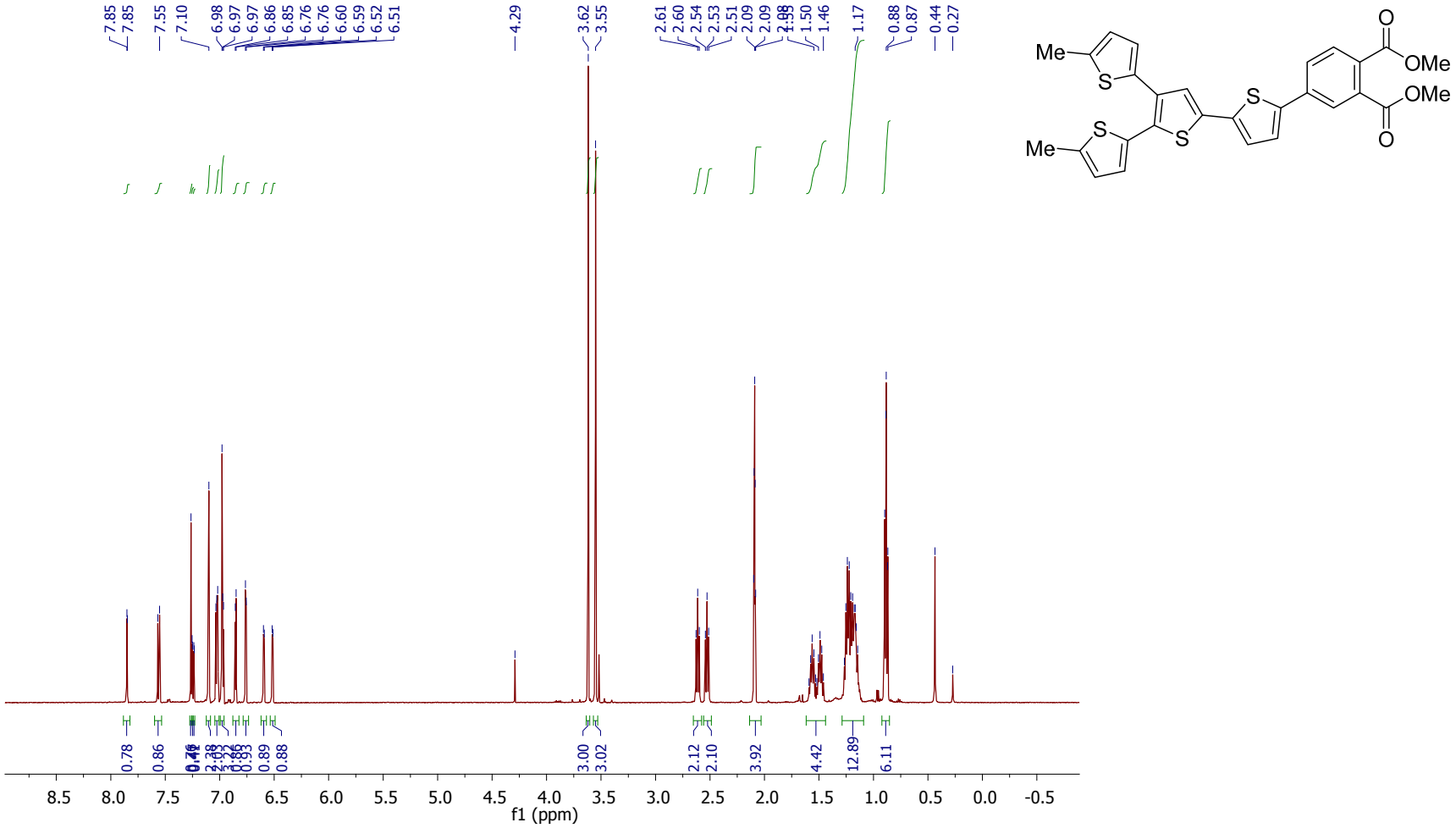

Figure S29. ^{1}H NMR spectrum of compound **9** (500 MHz, toluene-d_8, room temperature).

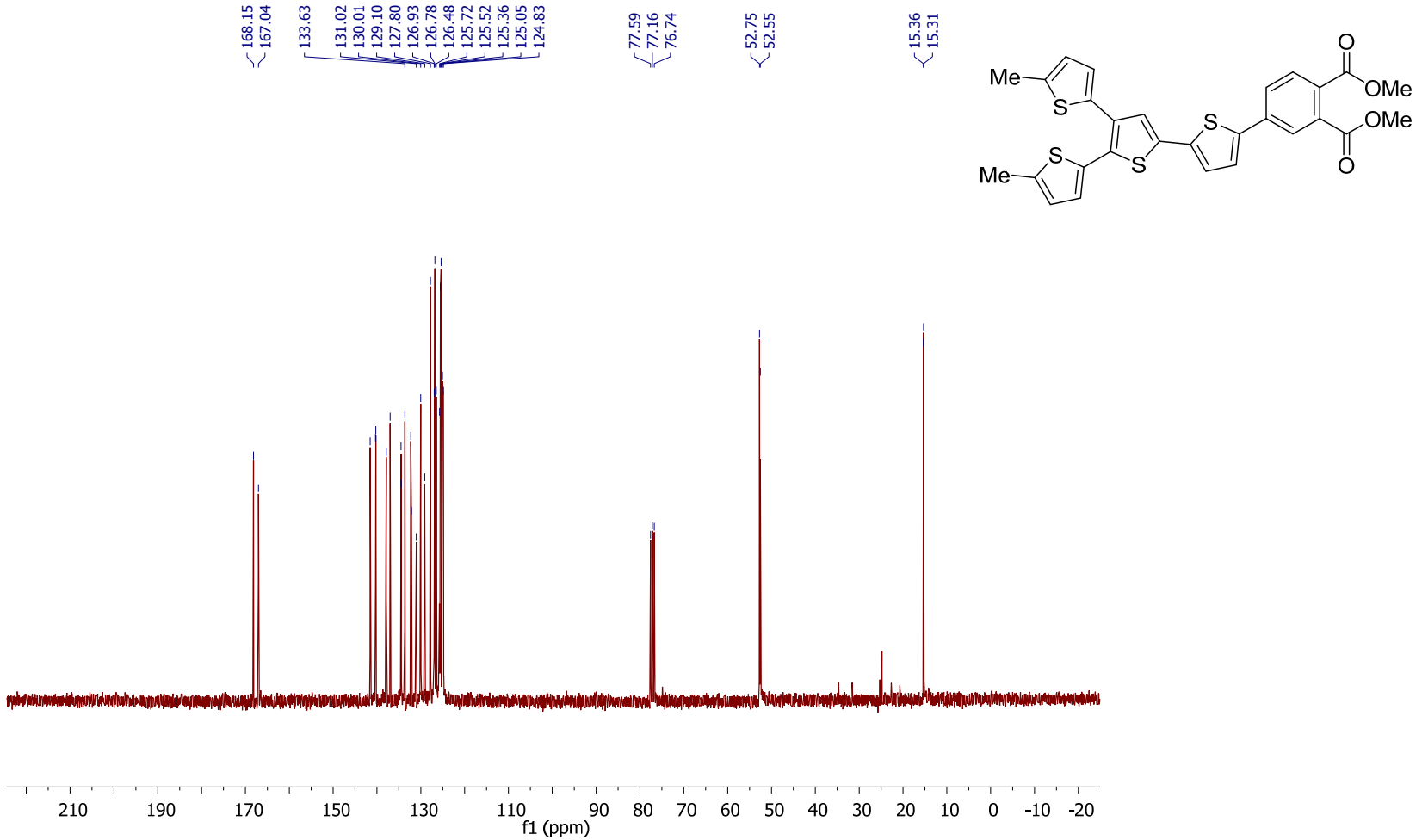

Figure S30. ^{13}C NMR spectrum of compound **9** (75 MHz, $CDCl_3$).

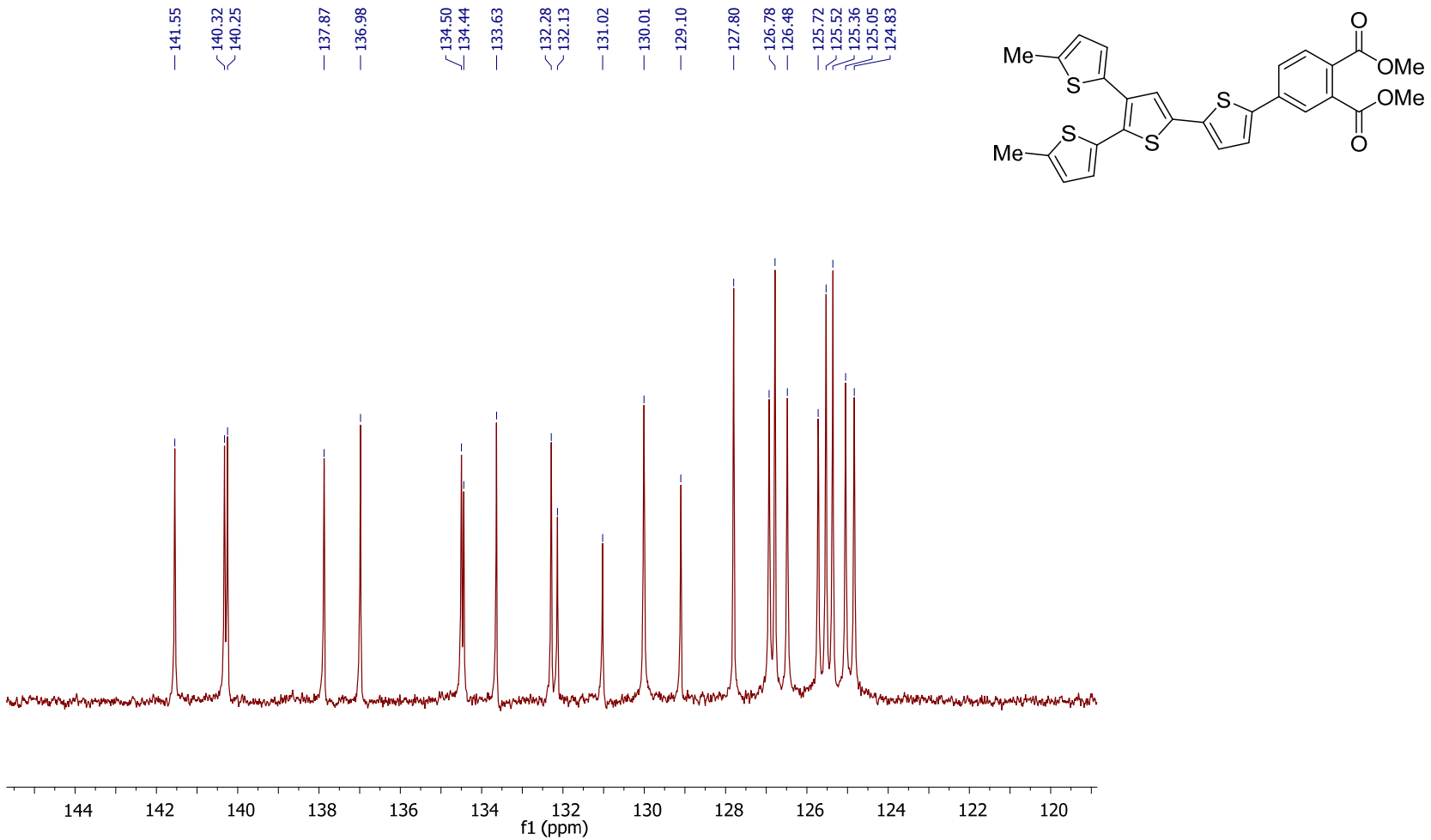

Figure S31. Expanded ^{13}C NMR spectrum of compound **9** (75 MHz, $CDCl_3$) of the aryl region.

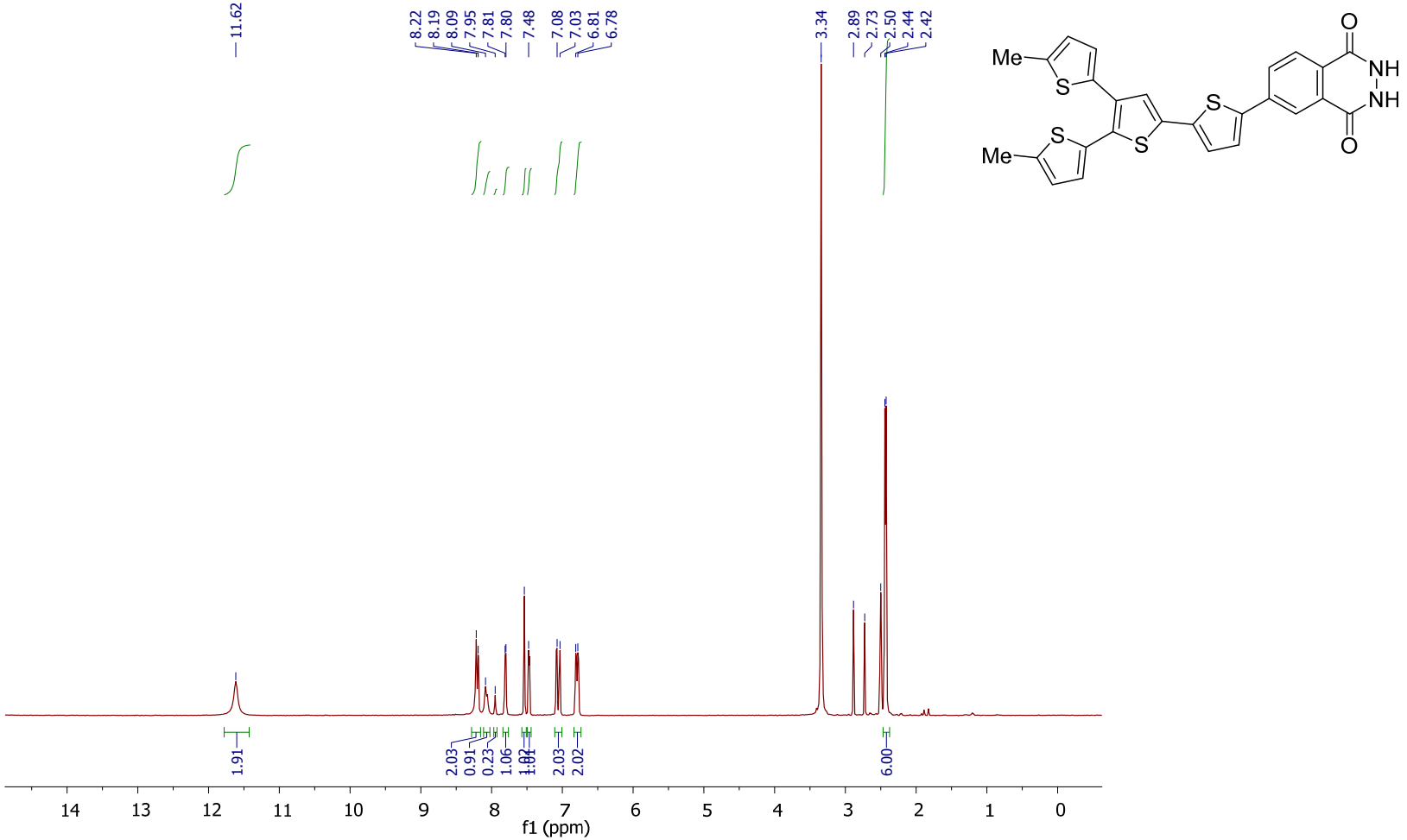

Figure S32. ^{1}H NMR spectrum of compound **10** (300 MHz, DMSO-d_6).

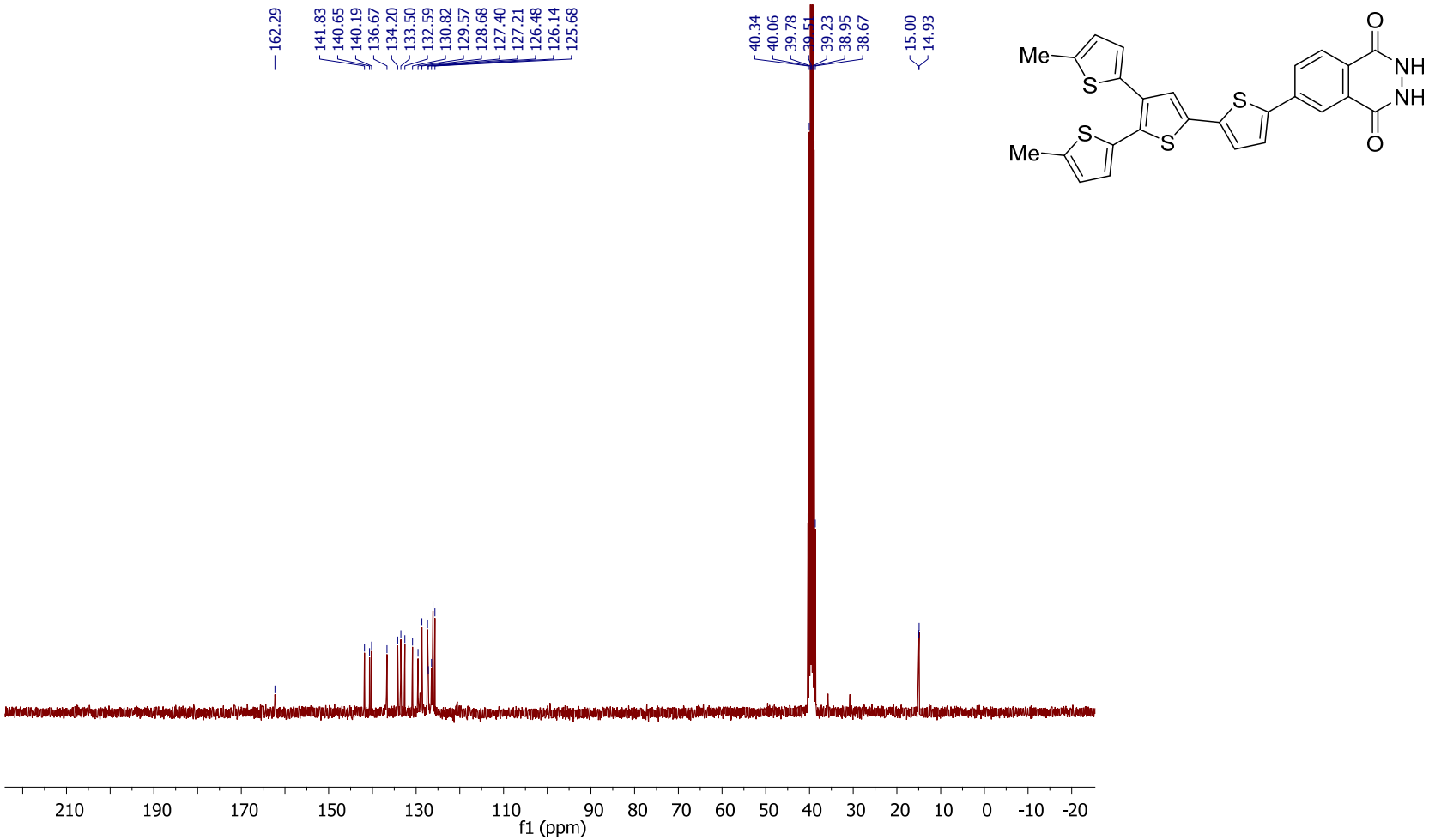

Figure S33. ^{13}C NMR spectrum of compound **10** (75 MHz, DMSO-d_6).

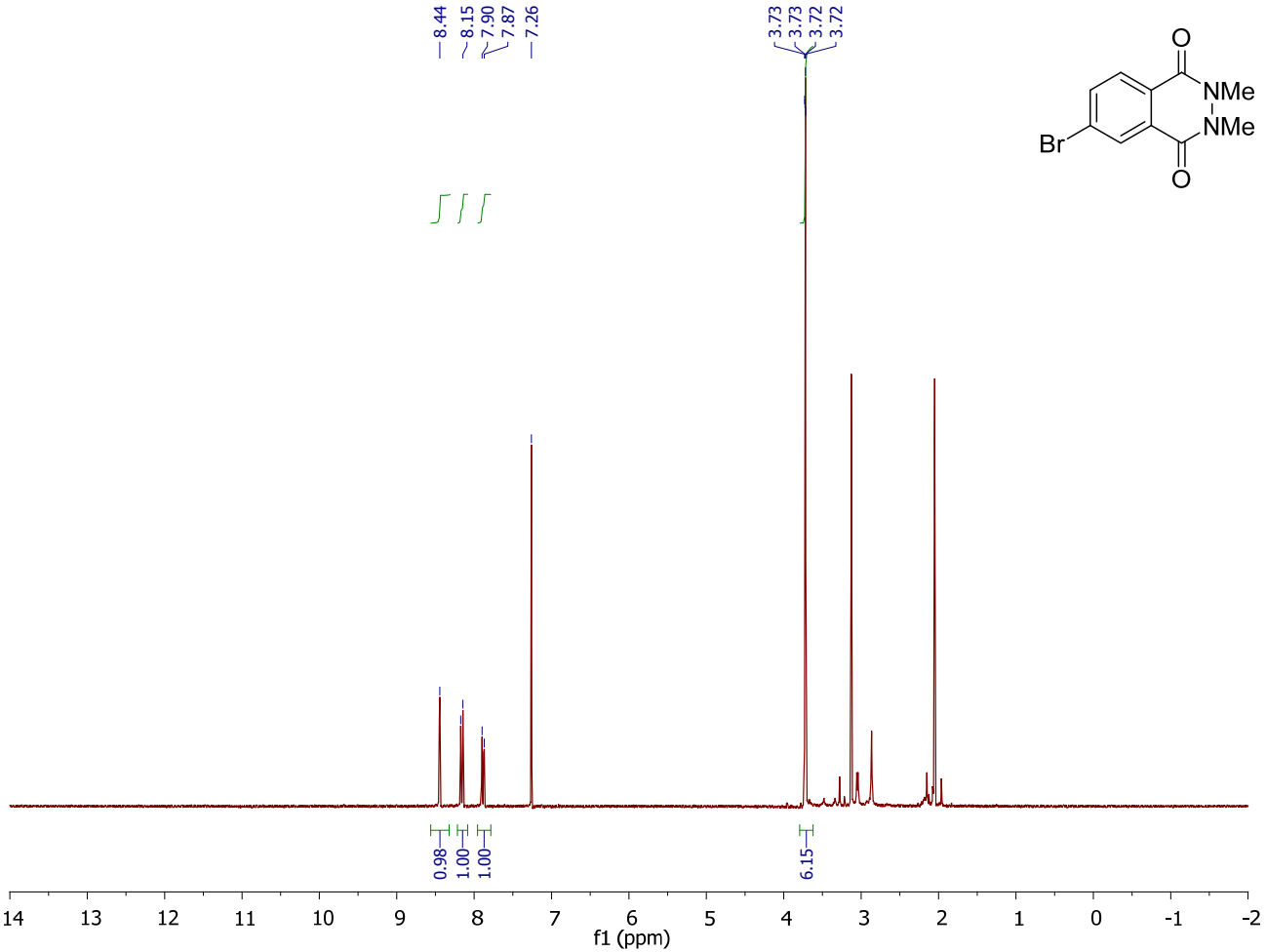

Figure S34. ^{1}H NMR spectrum of compound **12** (300 MHz, $CDCl_3$).

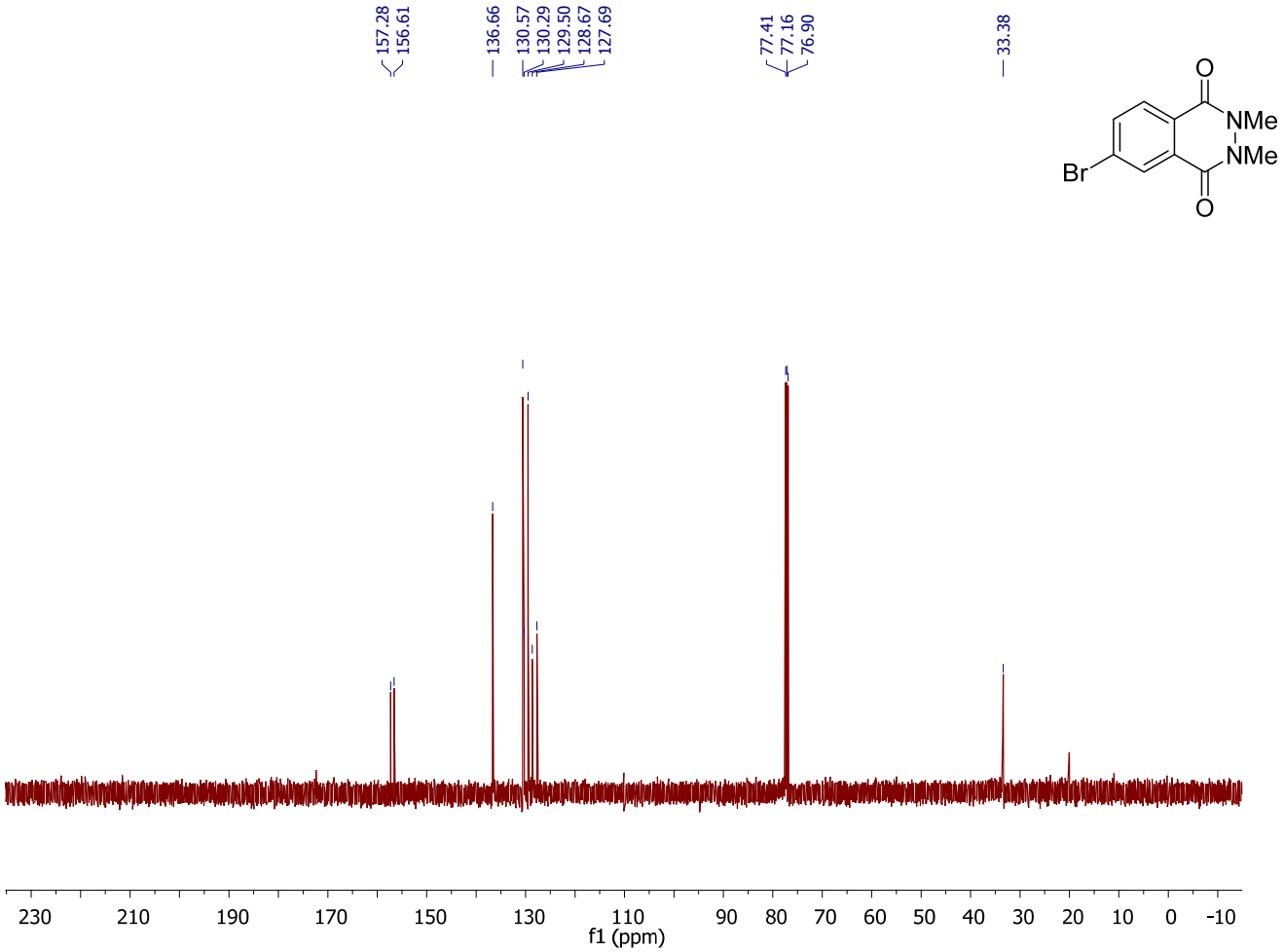

Figure S35. ^{13}C NMR spectrum of compound **12** (75 MHz, $CDCl_3$).

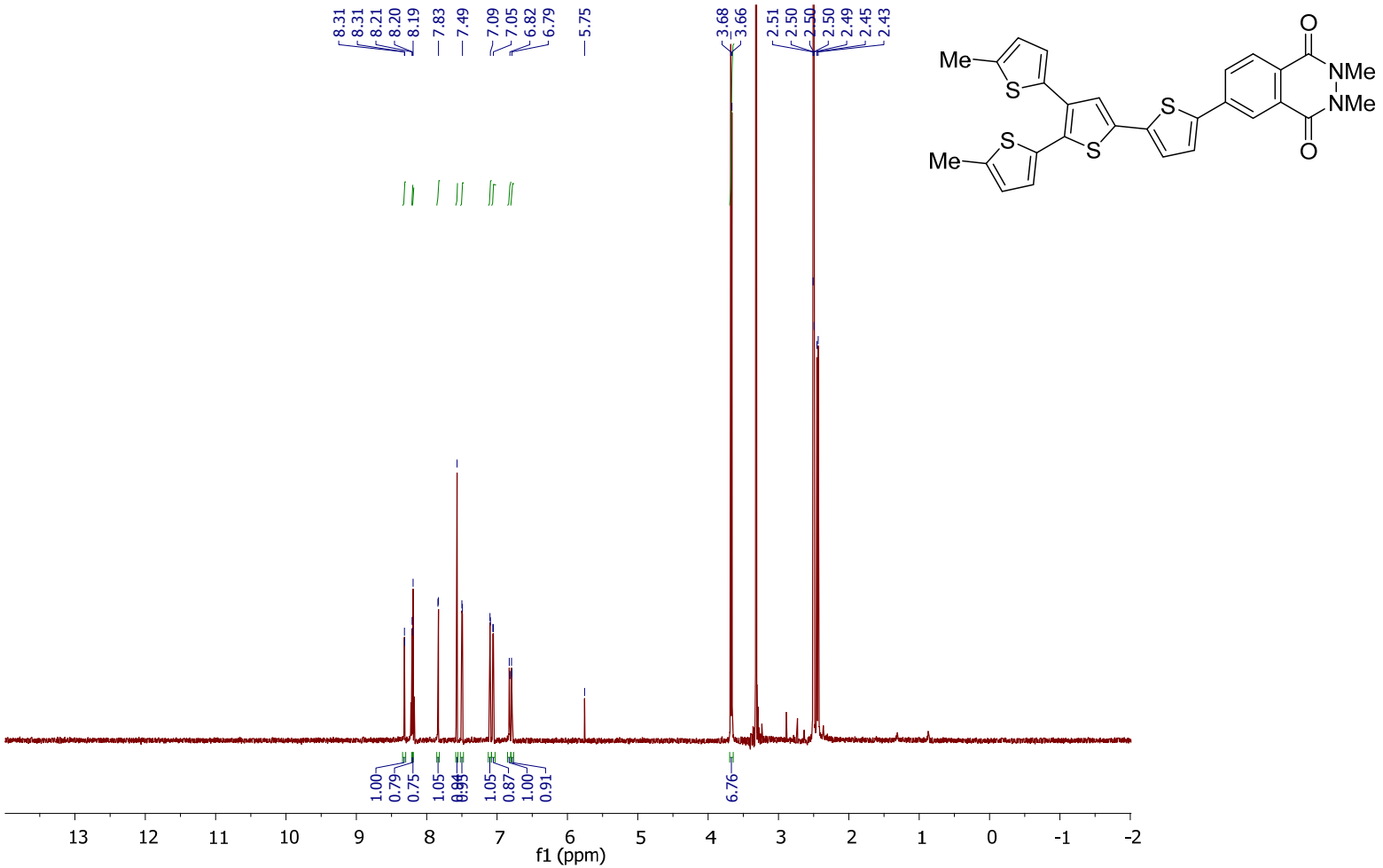

Figure S36. ^{1}H NMR spectrum of compound **13** (500 MHz, DMSO-d_6).

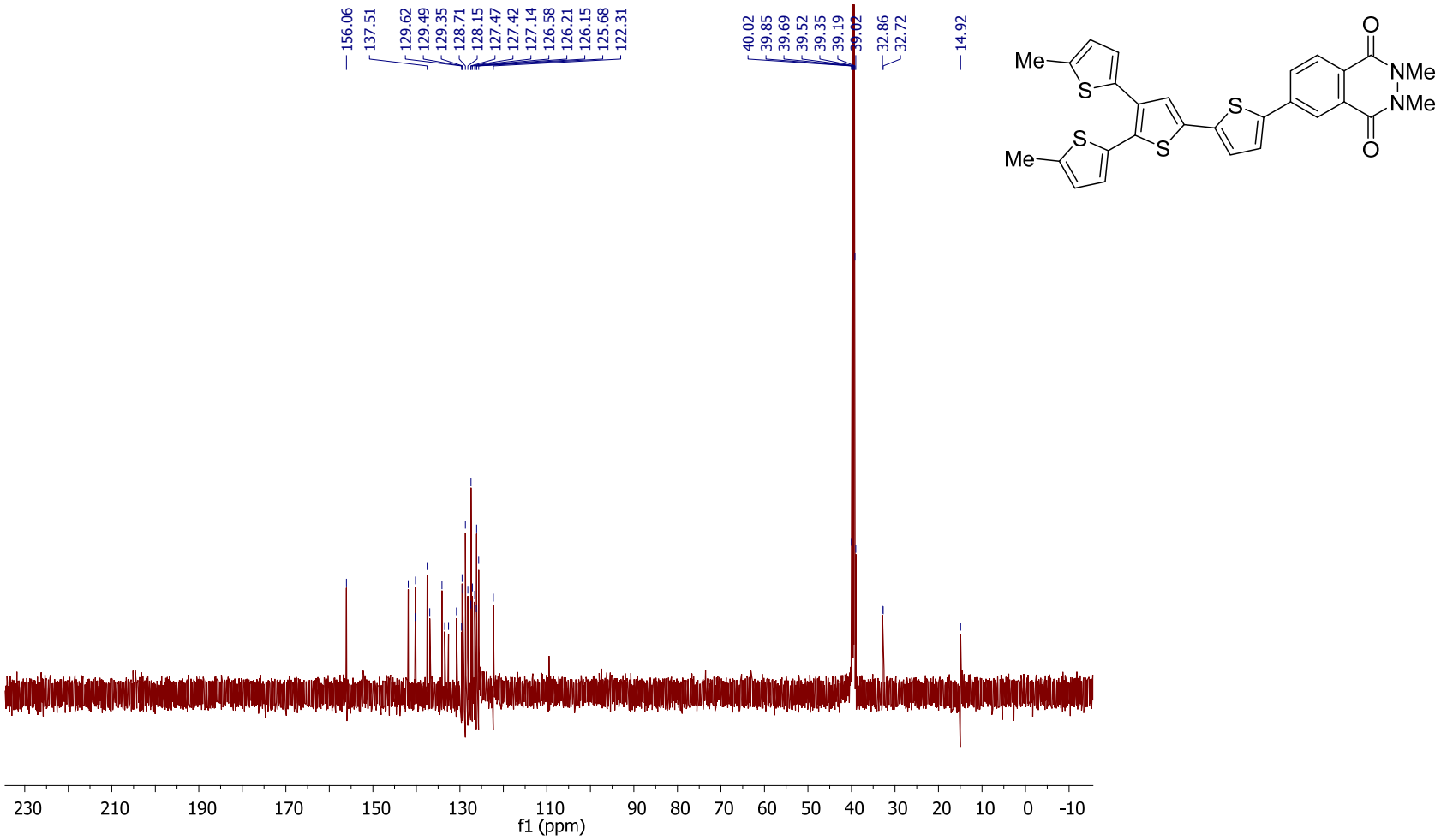

Figure S37. ^{13}C NMR spectrum of compound **13** (125 MHz, DMSO-d_6).