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Unsymmetrical donor–acceptor oligothiophenes end-capped with triphenylamine and phenyldicyanovinyl units

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CONTENTS

1. Experimental Section

1.1 Materials

n-Butyllithium (1.6 *M* solution in hexane), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (IPTMDOB), tetrakis(triphenylphosphine)palladium(0) $Pd(PPh_3)_4$, malononitrile, *p*-toluenesulfonic acid (TsOH), 2,2-dimethylpropane-1,3-diol, 2-bromothiophene, 2-benzoylthiophene **1** were obtained from Sigma–Aldrich Co. and used without further purification. Benzene, toluene, THF pyridine were dried and purified according to the known techniques. 5,5-Dimethyl-2-phenyl-2-[5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithien-5-yl]-1,3-dioxane **4** was prepared as described in reference [S1]. (4-Bromophenyl)diphenylamine was obtained as described in reference [S2]. All reactions, unless stated otherwise, were carried out under an inert atmosphere.

1.2 Characterization

^{1}H NMR spectra were recorded at a Bruker WP-250 SY spectrometer, working at a frequency of 250.13 MHz and using $CDCl_3$ signal (7.25 ppm) and DMSO-d_6 (2.50 ppm) as the internal standard. ^{13}C NMR spectra were recorded using a Bruker Avance II 300 spectrometer at 75 MHz. In the case of ^{1}H NMR spectroscopy, the compounds to be analyzed were taken in the form of 1% solutions in $CDCl_3$ or DMSO-d_6. In the case of ^{13}C NMR spectroscopy, the compounds to be analyzed were taken in the form of 5% solutions in $CDCl_3$ or DMSO-d_6. The spectra were then processed on the computer using the ACD Labs software.

Mass-spectra (MALDI) were registered on the Autoflex II Bruker (resolution FWHM 18000), equipped with a nitrogen laser (work wavelength 337 nm) and time-of-flight mass-detector working in reflections mode. The accelerating voltage was 20 kV. Samples were applied to a polished stainless steel substrate. Spectrum was recorded in the positive ion mode. The resulting spectrum was the sum of 300 spectra obtained at different points of sample. 2,5-Dihydroxybenzoic acid (DHB) (Acros, 99%) and α-cyano-4-hydroxycinnamic acid (HCCA) (Acros, 99%) were used as matrices.

Elemental analysis of C, N and H elements was carried out using CHN automatic analyzer CE 1106 (Italy). The settling titration using $BaCl_2$ was applied to analyze sulfur. Experimental error for elemental analysis is 0.30-0.50%. The Knövenagel condensation was carried out in the microwave “Discovery”, (CEM corporation, USA), using a standard method with the open vessel option, 50 watts. In the case of column chromatography, silica gel 60 (“Merck”) was taken. Absorption profiles were recorded with a Shimadzu UV 2501 PC absorption spectrometer from

350 to 1100. All measurements were carried out at room temperature in diluted solutions (10^{-5} M) of THF. Films were cast from THF solutions on quartz substrate.

Cyclic voltammetry measurements were carried out using solid compact layers of the oligomers, which in turn were made by electrostatically rubbing the materials onto a glassy carbon electrode. Measurements were made in MeCN - *o*-$Cl_2C_6H_4$ (1:4) solution using 0.1 *M* Bu_4NPF_6 as supporting electrolyte and using IPC-Pro M potentiostat. The sweep rate was 200 mV s^{-1}. The glassy carbon electrode was used as a working electrode. Potentials were measured relative to a saturated calomel electrode (SCE). The HOMO and LUMO energy levels were calculated using the first standard formal oxidation and reduction potentials obtained from CV experiments in films according to the following equations: LUMO=e(φ_{red}+4.40) (eV) and HOMO=-e(φ_{ox}+4.40) (eV) [S3,S4].

DSC analysis of the samples was carried out by a DSC-822e (Mettler-Toledo, Switzerland) at a heating rate 10 ^oC min^{-1} in argon. TGA was done by a Derivatograph-C instrument (MOM, Hungary), at a heating rate 10 ^oC min^{-1} in air and argon.

Solubility of oligomers was measured using its saturated solution in ODCB, which was prepared by stirring of an excess of solid material in the solvent. For this purpose, materials were added in small portions to 1 ml of pure solvent. As prepared, the saturated solutions were filtered through 0.25-mm PTFE syringe filters and the solvent was evaporated using a rotary evaporator. Afterwards the residue was dried in vacuum at 130°C until it achieved constant weight, which was used to calculate the exact solubility value.

1.3 Synthesis of the oligomers

5,5-Dimethyl-2-phenyl-2-(2-thienyl)-1,3-dioxane 2. 2-Benzoylthiophene **1** (7.5 g, 39.8 mmol) was dissolved in dry benzene (150 ml). After complete dissolution, 2,2-dimethylpropane-1,3-diol (20.75 g, 199.2 mmol) and TsOH (1.52 g, 8.0 mmol) were added. Afterwards, the mixture was stirred at reflux for 14 hours using a Dean – Stark water separator. After that, the mixture was extracted with toluene and washed with distilled water. The combined organic phases were dried over sodium sulfate and filtered. The solvent was evaporated and the residue was dried at 1 Torr. This crude product was purified by column chromatography on silica gel (eluent hexane) to give pure product (10.93 g, 73%) as a white solid. M.p.: 64-65^oC. ^1H NMR (250 MHz, $CDCl_3$, δ, ppm): 0.86 (s, 3H), 1.16 (s, 3H), 3.60 (d, 2H, *J* = 11.0 Hz), 3.68 (d, 2H, *J* = 11.0 Hz), 6.73 (dd, 1H, J_1 = 3.4 Hz, J_2 = 1.2 Hz), 6.87 (dd, 1H, J_1 = 5.2 Hz, J_2 = 3.7 Hz), 7.26 (dd, 1H, J_1 = 4.9 Hz, J_2 = 1.2 Hz), 7.29-7.43 (overlapping peaks, 3H), 7.52-7.61 (overlapping peaks, 2H). ^{13}C NMR (125 MHz,

$CDCl_3$): δ [ppm] 22.23, 22.70, 30.05, 72.40, 99.67, 126.01, 126.09, 126.33, 126.97, 128.28, 128.42, 128.48, 140.24, 147.35. Calcd (%) for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61; S, 11.69. Found: C, 70.21; H, 6.73; S, 11.47.

5,5-Dimethyl-2-phenyl-2-[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thienyl]-1,3-dioxane 3. n-Butyllithium (1.6 *M* hexane solution, 17.54 ml, 28.0 mmol) was added dropwise to a solution of compound **2** (7.70 g, 28.0 mmol) in dry THF (154 ml) at -78ºC. The reaction mixture was stirred for 60 min at -78ºC, and then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (IPTMDOB, 5.38 g, 29.0 mmol) was added in one portion. The mixture was stirred for 1 h at –78ºC, then the cooling bath was removed, and the stirring was continued for 1 h. After completion of the reaction, freshly distilled diethyl ether (300 ml), distilled water (100 ml) and 1 *M* HCl (28 ml) were added. The organic phase was separated, washed with water, dried over sodium sulfate, and filtered. The solvent was evaporated to give 10.4 g (93%) of pure product as a pale pink solid. M.p.: 141-143ºC. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 0.91 (s, 3H), 1.06 (s, 3H), 1.30 (s, 12H), 3.58 (d, 2H, *J* = 11.0 Hz), 3.69 (d, 2H, *J* = 11.0 Hz), 6.91 (d, 1H, *J* = 3.7 Hz), 7.26-7.39 (overlapping peaks, 3H), 7.41 (d, 1H, *J* = 3.7 Hz), 7.52-7.59 (overlapping peaks, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] 22.33, 22.57, 24.71, 30.04, 72.38, 84.04, 99.58, 126.60, 127.29, 128.20, 128.41, 136.69, 140.88, 154.08. Calcd (%) for $C_{22}H_{29}BO_4S$: C, 66.00; H, 7.30; S, 8.01. Found: C, 66.41; H, 7.53; S, 7.72.

5,5-Dimethyl-2-phenyl-2-(2,2':5',2''-terthien-5-yl)-1,3-dioxane 5. In an inert atmosphere, deaerated solutions of 2-bromothiopene (3.16 g, 19 mmol) and compound **4** (7.2 g, 15 mmol) in toluene/ethanol mixture (105 and 11 ml correspondingly) and 2 *M* aqueous solution of Na_2CO_3 (10 ml) were added to $Pd(PPh_3)_4$ (430 mg, 0.4 mmol). The mixture was stirred under reflux for 19 h, and then it was cooled to room temperature and poured into water (100 ml) and toluene (100 ml). The organic phase was separated, washed with water, dried over sodium sulfate and filtered. The solvent was evaporated and the residue was dried at 1 Torr. The product was purified by column chromatography on silica gel (eluent toluene) to give pure compound **5** (4.72 g, 72%) as yellow solid. M.p.: 206-207ºC. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 0.87 (s, 3H), 1.17 (s, 3H), 3.60 (d, 2H, *J* = 11.0 Hz), 3.70 (d, 2H, *J* = 11.0 Hz), 6.64 (d, 1H, *J* = 3.7 Hz), 6.92 (d, 1H, *J* = 3.7 Hz), 6.96–7.10 (overlapping peaks, 3H), 7.11–7.21 (overlapping peaks, 2H), 7.30–7.45 (overlapping peaks, 3H), 7.53–7.63 (overlapping peaks, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] 22.24, 22.69, 30.04, 72.46, 99.60, 122.98, 123.66, 124.25, 124.29, 124.39, 126.63, 126.86, 127.77, 128.30, 128.45, 136.34, 136.35, 137.19, 137.64, 140.29, 146.51. Calcd (%) for $C_{24}H_{22}O_2S_3$: C, 65.72; H, 5.06; S, 21.93. Found: C, 65.31; H, 5.27; S, 21.42. MALDI-MS: found m/z 437.93; calculated for [M]+ 438.63

5,5-Dimethyl-2-phenyl-2-[5''-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2':5',2''-terthien-5-yl]-1,3-dioxane 6. Compound **6** was obtained analogously to the procudure described above for compound **3** using **5** (4.70 g, 11.0 mmol), 1.6 *M* hexane solution of *n*-butyllithium (6.70 ml, 11 mmol), IPTMDOB (2.00 g, 11 mmol) to give 5.62 g (93%) of the product as a green viscous substance. The product was used in the subsequent synthesis without further purification. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 0.87 (s, 3H), 1.17 (s, 3H), 1.34 (s, 12H), 3.61 (d, 2H, *J* = 11.0 Hz), 3.70 (d, 2H, *J* = 11.0 Hz), 6.65 (d, 1H, *J* = 3.7 Hz), 6.94 (d, 1H, *J* = 3.8 Hz), 7.03 (d, 1H, *J* = 3.8 Hz), 7.10 (d, 1H, *J* = 3.8 Hz), 7.20 (d, 1H, *J* = 3.7 Hz), 7.31–7.43 (overlapping peaks, 3H), 7.51 (d, 1H, *J* = 3.7 Hz), 7.57–7.61 (overlapping peaks, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] 22.17, 22.65, 24.70, 30.01, 72.40, 84.14, 99.49, 123.09, 124.38, 124.76, 124.88, 124.95, 126.72, 126.83, 128.36, 128.51, 136.03, 136.78, 137.48, 137.92, 139.85, 143.71, 146.44. Calcd (%) for $C_{30}H_{33}BO_4S_3$: C, 63.82; H, 5.89; S, 17.04. Found: C, 63.95; H, 5.99; S, 16.87.

2-(5,5-Dimethyl-2-phenyl-1,3-dioxan-2-yl)-5-(4-diphenylaminophenyl)thiophene 8a. In an inert atmosphere, deaerateded solutions of (4-bromophenyl)diphenylamine **7** (2.20 g, 7.00 mmol) and compound **3** (4.08 g, 10.00 mmol) in toluene/ethanol mixture (120 and 12 ml correspondingly) and 2 *M* aqueous solution of Na_2CO_3 (6.6 ml) were added to $Pd(PPh_3)_4$ (294 mg, 0.25 mmol). The reaction mixture was stirred under reflux for 11 h, and then it was cooled to room temperature and poured into water (100 ml) and toluene (50 ml). The organic phase was separated, washed with water, dried over sodium sulfate and filtered. The solvent was evaporated and the residue was dried at 1 Torr. The product was purified by column chromatography on silica gel (eluent toluene : hexane = 1 : 2) to give pure compound **8a** (2.46 g, 70%) as yellow solid. M.p.: 239-241ºC. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] 0.88 (s, 3H), 1.16 (s, 3H), 3.60 (d, 2H, *J* = 11.0 Hz), 3.71 (d, 2H, *J* = 11.0 Hz), 6.67 (d, 1H, *J* = 3.70 Hz), 6.94-6.14 (overlapping peaks, 9H), 7.19-7.25 (overlapping peaks, 3H), 7.26-7.46 (overlapping peaks, 6H), 7.54-7.63 (overlapping peaks, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] 22.17, 22.70, 30.06, 72.45, 99.70, 121.50, 123.02, 123.60, 124.45, 126.57, 126.94, 127.02, 128.31, 128.49, 129.28, 140.17, 144.81, 145.53, 147.22, 147.47. Calcd (%) for $C_{34}H_{31}NO_2S$: C, 78.88; H, 6.04; N, 2.71; S, 6.19. Found: C, 79.09; H, 6.14; N, 2.59; S, 5.98. MALDI-MS: found m/z 517.14; calculated for $[M]^+$ 517.70.

2-(5,5-Dimethyl-2-phenyl-1,3-dioxan-2-yl)-5'-(4-diphenylaminophenyl)-2,2'-bithiophene 8b was obtained analogously to the procedure described above for compound **8a** using **4** (2.3 g, 4.77 mmol), **7** (1.29 g, 3.98 mmol), 2 *M* aqueous solution of Na_2CO_3 (3.1 ml), $Pd(PPh_3)_4$ (138 mg, 0.12 mmol) to give a crude product. It was purified by column chromatography on silica gel (eluent toluene : hexane = 1:1) to give pure product **8b** (1.62 g, 68%) as a yellow solid. M.p.: 285-286ºC. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] 0.89 (s, 3H), 1.17 (s, 3H), 3.62 (d, 2H, *J* = 11.0 Hz), 3.72

(d, 2H, *J* = 11.0 Hz), 6.66 (d, 1H, *J* = 3.70 Hz), 6.94 (d, 1H, *J* = 3.70 Hz), 7.00-7.15 (overlapping peaks, 10H), 7.21-7.48 (overlapping peaks, 10H), 7.57-7.64 (overlapping peaks, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] 22.28, 22.73, 30.09, 72.48, 99.61, 122.69, 122.82, 123.15, 123.63, 124.55, 124.63, 126.37, 126.79, 126.90, 128.07, 128.40, 128.56, 129.34, 135.80, 138.17, 140.08, 143.14, 145.87, 147.33, 147.44. Calcd (%) for $C_{38}H_{33}NO_2S_2$: C, 76.09; H, 5.55; N, 2.34; S, 10.69. Found: C, 76.31; H, 5.73; N, 2.19; S, 10.52. MALDI-MS: found m/z 599.02; calculated for $[M]^+$ 599.80.

2-(5,5-Dimethyl-2-phenyl-1,3-dioxan-2-yl)-5''-(4-diphenylaminophenyl)-2,2':5',2''-terthiophene 8c was obtained analogously to the procedure described above for compound **8a** using **6** (2,3 g, 4.07 mmol), **7** (1.1 g, 3.39 mmol), 2 *M* aqueous solution of Na_2CO_3 (2.6 ml), $Pd(PPh_3)_4$ (118 mg, 0.10 mmol) to give a crude product. It was purified by column chromatography on silica gel (eluent toluene : hexane = 1:1) to give pure compound **8c** (1.49 g, 65%) as a yellow solid. M.p.: 132-133ºC. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 0.91 (s, 3H), 1.16 (s, 3H), 3.62 (d, 2H, *J* = 11.0 Hz), 3.72 (d, 2H, *J* = 11.0 Hz), 6.71 (d, 1H, *J* = 3.7 Hz), 6.92–7.24 (overlapping peaks, 14H), 7.26–7.49 (overlapping peaks, 8H), 7.60 (d, 2H, *J* = 7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] 22.24, 22.65, 30.02, 72.45, 99.63, 122.84, 122.95, 123.19, 123.56, 123.92, 124.28, 124.51, 124.59, 124.64, 125.22, 126.45, 126.55, 126.82, 128.13, 128.19, 128.35, 128.93, 129.24, 135.66, 136.21, 136.59, 137.68, 140.54, 143.43, 146.60, 147.57, 147.59. Calcd (%) for $C_{42}H_{35}NO_2S_3$: C, 73.97; H, 5.17; N, 2.05; S, 14.11. Found: C, 74.15; H, 5.22; N, 1.98; S, 13.89. MALDI-MS: found m/z 681.94; calculated for $[M]^+$ 681.93.

[5-(4-Diphenylaminophenyl)-2-thienyl](phenyl)methanone 9a. Hydrochloric acid (1 *M*, 9.0 ml) was added to a solution of ketal **8a** (2.35 g, 4.54 mmol) in THF (60 ml) and the mixture was stirred for 4 hours at reflux, cooled to room temperature and poured into water (150 ml) and toluene (100 ml). The organic phase was separated, washed with water. The solvent was evaporated and the residue was dried at 1 Torr. The product was purified by column chromatography on silica gel (eluent dichloromethane) to give pure ketone **9a** (1.86 g, 95%) as a yellow solid. M.p.: 99-100 ºC. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 7.01-7.17 (overlapping peaks, 8H), 7.22-7.25 (overlapping peaks, 1H), 7.25-7.34 (overlapping peaks, 4H), 7.43-7.62 (overlapping peaks, 6H), 7.83-7.89 (overlapping peaks, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 122.55, 122.72, 123.70, 125.03, 126.51, 127.10, 128.37, 129.03, 129.43, 132.02, 136.31, 138.20, 141.11, 147.01, 148.77, 153.50, 187.95. Calcd. (%) for $C_{29}H_{21}NOS$: C, 80.71; H, 4.90; N, 3.25; S, 7.43. Found: C, 80.89; H, 5.08; N, 3.17; S, 7.52. MALDI-MS: found m/z 431.21; calculated for [M+] 431.54.

[5'-(4-diphenylaminophenyl)-2,2'-bithien-5-yl](phenyl)methanone 9b was obtained by similarly to compound **9a** using 1 *M* HCl (7.5 ml), ketal **8b** (1.50 g, 2.5 mmol) to give pure ketone **9b** (0.96 g, 75%) as orange powder. M.p.: 272-273ºC. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] 7.00–7.21 (overlapping peaks, 10H), 7.24–7.32 (overlapping peaks, 5H), 7.44–7.62 (overlapping peaks, 6H), 7.82–7.88 (overlapping peaks, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] 123.23, 123.43, 123.67, 124.78, 126.58, 126.86, 127.32, 128.47, 129.04, 129.40, 132.16, 135.98, 138.13, 141.21, 145.70, 146.51, 147.29, 147.90, 187.73. Calcd (%) for $C_{33}H_{23}NOS_2$: C, 77.16; H, 4.51; N, 2.73; S, 12.48. Found: C, 77.31; H, 4.65; N, 2.58; S, 12.27. MALDI-MS: found m/z 513.03; calculated for $[M]^+$ 513.66.

[5''-(4-Diphenylaminophenyl)-2,2':5',2''-terthien-5-yl](phenyl)methanone was obtained similarly to compound **9a** using 1 *M* HCl (6.1 ml), ketal **8c** (1.39 g, 2.04 mmol) to give pure ketone **9c** (1.01 g, 83%) as orange solid. M.p.: 295-297ºC. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] 7.00–7.22 (overlapped peaks, 12H), 7.23–7.25 (overlapped peaks, 1H), 7.25–7.33 (overlapped peaks, 4H), 7.42–7.63 (overlapped peaks, 6H), 7.81–7.90 (overlapped peaks, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] 122.94, 123.30, 123.42, 123.77, 124.20, 124.73, 125.22, 126.39, 126.52, 127.85, 128.31, 128.89, 129.27, 131.93, 135.34, 138.36, 138.92, 141.73, 144.34, 145.78, 147.51, 147.83, 187.25. Calcd (%) for $C_{37}H_{25}NOS_3$: C, 74.59; H, 4.23; N, 2.35; S, 16.15. Found: C, 74.88; H, 4.41; N, 2.30; S, 16.02. MALDI-MS: found m/z 595.96; calculated for [M] + 595.80.

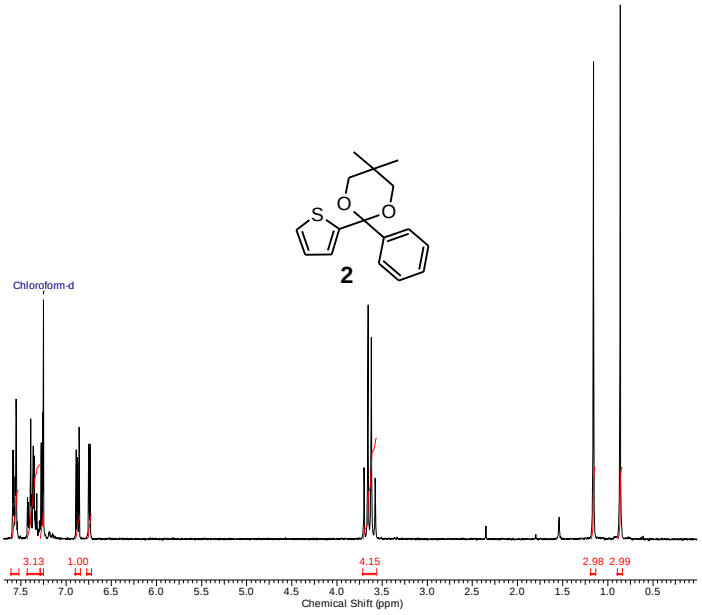
2-(4-Diphenylaminophenyl)-5-(1-phenyl-2,2-dicyanoethenyl)thiophene 10a. Ketone **9a** (0.87 g, 2.0 mmol), malononitrile (0.27 g, 4.0 mmol) and dry pyridine (10.0 ml) were placed in a reaction vessel and stirred under argon for 22 hours at reflux using the microwave heating. After completeness of the reaction, pyridine was evaporated and the residue was dried at 1 Torr. The crude material was purified by column chromatography on silica gel (eluent dichloromethane). Further purification included precipitation of the product from its THF solution with toluene and hexane to give pure product as a red solid (0.71 g, 76%). M.p.: 224 ºC. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] 6.99 (d, 2H, J = 8.9 Hz), 7.04 - 7.16 (overlapping peaks, 6H), 7.25 – 7.34 (overlapping peaks, 5H), 7.42 – 7.62 (overlapping peaks, 7H), 7.63 (d, 1H, J = 4.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] 75.24, 114.35, 114.97, 121.88, 123.56, 124.12, 125.11, 125.31, 127.32, 128.69, 129.34, 129.50, 131.41, 135.92, 136.11, 138.77, 146.67, 149.54, 156.26, 164.03. Calcd. (%) for $C_{32}H_{21}N_3S$: C, 80.14; H, 4.41; N, 8.76; S, 6.69. Found: C, 80.23; H, 4.42; N, 8.75; S, 6.64. MALDI-MS: found m/z 479.11; calculated for [M+] 479.56.

2-(4-Diphenylaminophenyl)-5'-(1-phenyl-2,2-dicyanoethenyl)-2,2'-bithiophene 10b was obtained similarly to compound **10a** from ketone **9b** (0.87 g, 0.8 mmol), malononitrile (0.33 g, 5.1 mmol) and pyridine (13 ml). The crude product was purified by column chromatography on silica gel (eluent dichloromethane). Further purification included precipitation of the product from its

THF solution with toluene and hexane to give pure product as black solid (0.72 g, 76%). M.p. = 183 °C. ^{1}H NMR (250 MHz, DMSO-d_6): δ [ppm] 6.92 (d, 2H, *J* = 8.9 Hz), 7.02–7.14 (overlapping peaks, 6H), 7.28–7.37 (overlapping peaks, 4H), 7.46 (d, 1H, *J* = 3.7 Hz), 7.55–7.70 (overlapping peaks, 10H). ^{13}C NMR (75 MHz, DMSO-d_6): δ [ppm] 75.36, 113.90, 114.52, 122.06, 123.43, 124.05, 124.33, 125.14, 125.99, 126.38, 128.38, 128.46, 128.90, 129.25, 131.12, 132.23, 135.32, 135.54, 138.29, 145.88, 146.36, 147.32, 147.47, 162.97. Calcd (%) for $C_{36}H_{23}N_3S_2$: C, 76.98; H, 4.13; N, 7.48; S, 11.42. Found: C, 76.79; H, 4.30; N, 7.38; S, 11.37. MALDI-MS: found m/z 561.62; calculated for $[M]^+$ 561.72.

2-(4-Diphenylaminophenyl)-5''-(1-phenyl-2,2-dicyanoethenyl)-2,2':5',2''-terthiophene 10c was obtained similarly to compound **10a** from ketone **9c** (0.9 g, 1.5 mmol) and malononitrile (0.299 g, 4.5 mmol). The crude product was purified by column chromatography on silica gel (eluent dichloromethane). Further purification included precipitation of the product from its THF solution with toluene and hexane to give pure product as a black solid (0.71 g, 73%). ^{1}H NMR (250 MHz, DMSO-d_6): δ [ppm] 6.93 (d, 2H, *J* = 8.7 Hz), 7.00–7.13 (overlapped peaks, 6H), 7.28–7.42 (overlapped peaks, 7H), 7.50–7.68 (overlapped peaks, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] 113.82, 114.86, 122.94, 123.20, 123.32, 124.30, 124.52, 124.71, 125.59, 126.45, 127.42, 127.45, 128.70, 129.18, 129.25, 131.36, 133.35, 134.40, 136.08, 136.42, 137.94, 140.29, 144.81, 147.34, 147.87, 148.24, 163.42. Calcd (%) for $C_{40}H_{25}N_3S_3$: C, 74.62; H, 3.91; N, 6.53; S, 14.94. Found: C, 74.58; H, 4.06; N, 6.36; S, 15.01. MALDI-MS: found m/z 643.91; calculated for [M]+ 643.84.

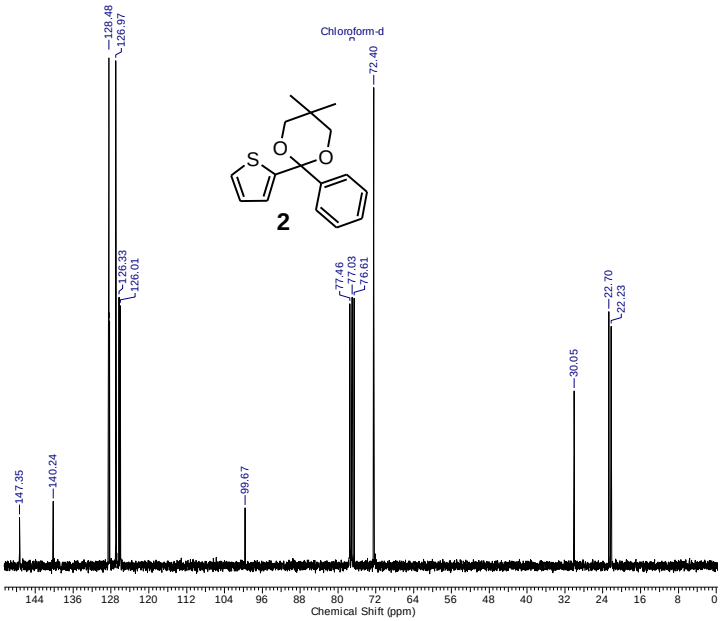
2. ^{1}H, ^{13}C NMR Spectra



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.84 .. 0.89]	2.987	1.69859e+7
2	[1.13 .. 1.19]	2.984	1.69676e+7
3	[3.56 .. 3.71]	4.150	2.35978e+7
4	[6.72 .. 6.77]	0.986	5.60915e+6
5	[6.84 .. 6.90]	1.000	5.68653e+6
6	[7.25 .. 7.29]	1.195	6.79401e+6
7	[7.29 .. 7.43]	3.135	1.78269e+7
8	[7.52 .. 7.61]	2.021	1.14918e+7

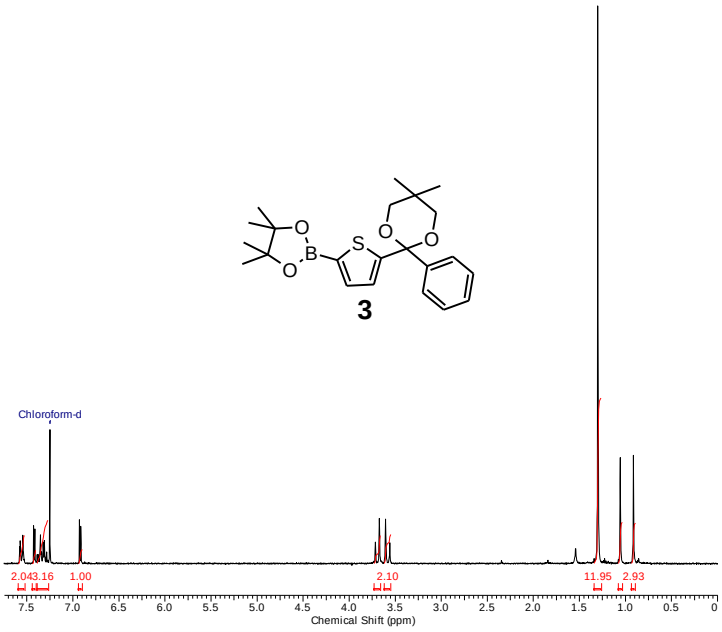
Figure S1. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.



No.	(ppm)	(Hz)	Height
1	22.23	1678.0	0.4694
2	22.70	1713.4	0.4978
3	30.05	2268.2	0.3442
4	72.40	5464.9	0.9318
5	76.61	5782.2	0.5237
6	77.03	5814.3	0.5257
7	77.46	5846.3	0.5129
8	99.67	7523.2	0.1178
9	126.01	9511.0	0.5090
10	126.09	9516.8	0.4894
11	126.33	9535.1	0.5255
12	126.97	9583.2	0.9837
13	128.28	9682.1	0.4796
14	128.48	9697.0	1.0000
15	140.24	10584.7	0.1301
16	147.35	11121.5	0.0993

No.	Annotation	(ppm)
1	Chloroform-d	[76.61 .. 77.46]

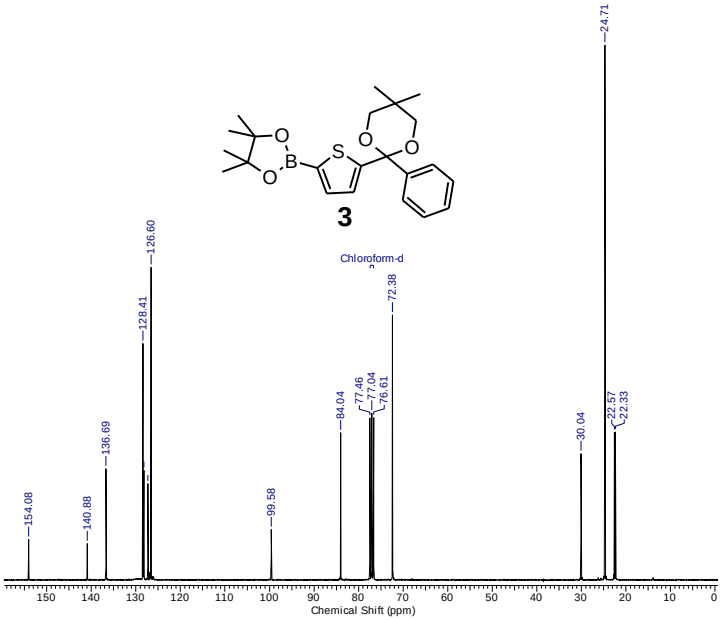
Figure S2. ^{13}C NMR spectrum of compound **2** in $CDCl_3$.



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.89 .. 0.94]	2.933	2.56524e+6
2	[1.03 .. 1.08]	3.010	2.63297e+6
3	[1.26 .. 1.34]	11.954	1.04562e+7
4	[3.55 .. 3.62]	2.098	1.83516e+6
5	[3.66 .. 3.73]	2.040	1.78452e+6
6	[6.90 .. 6.94]	1.000	8.74666e+5
7	[7.26 .. 7.39]	3.158	2.76198e+6
8	[7.40 .. 7.44]	1.007	8.80687e+5
9	[7.52 .. 7.59]	2.044	1.78767e+6

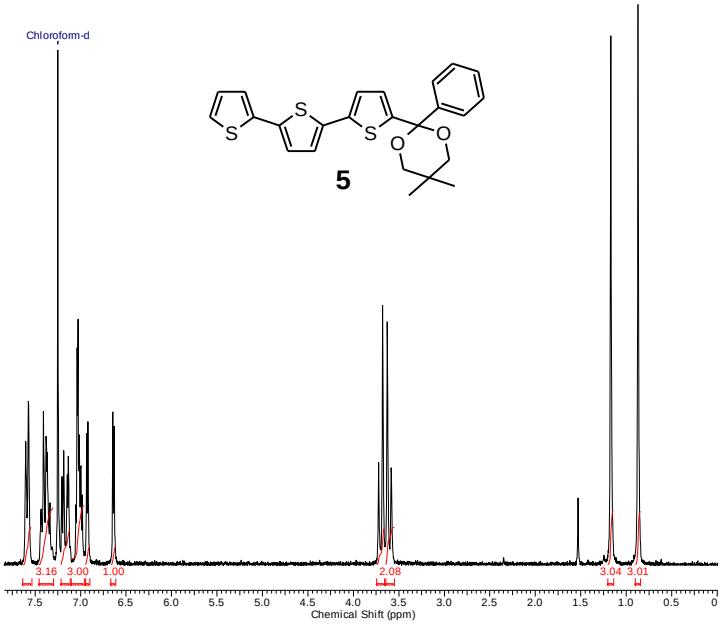
Figure S3. ^{1}H NMR spectrum of compound **3** in $CDCl_3$



No.	(ppm)	(Hz)	Height
1	22.33	1685.2	0.2767
2	22.57	1703.5	0.2756
3	24.71	1865.2	1.0000
4	30.04	2267.1	0.2358
5	72.38	5463.2	0.4953
6	76.61	5782.5	0.3034
7	77.04	5814.6	0.3116
8	77.46	5846.6	0.3029
9	84.04	6343.1	0.2753
10	99.58	7516.3	0.0940
11	126.60	9555.8	0.5848
12	127.29	9607.2	0.1799
13	128.20	9676.0	0.2050
14	128.41	9692.1	0.4419
15	136.69	10316.8	0.2076
16	140.88	10633.6	0.0680
17	154.08	11629.3	0.0755

No.	Annotation	(ppm)
1	Chloroform-d	[76.64 .. 77.43]

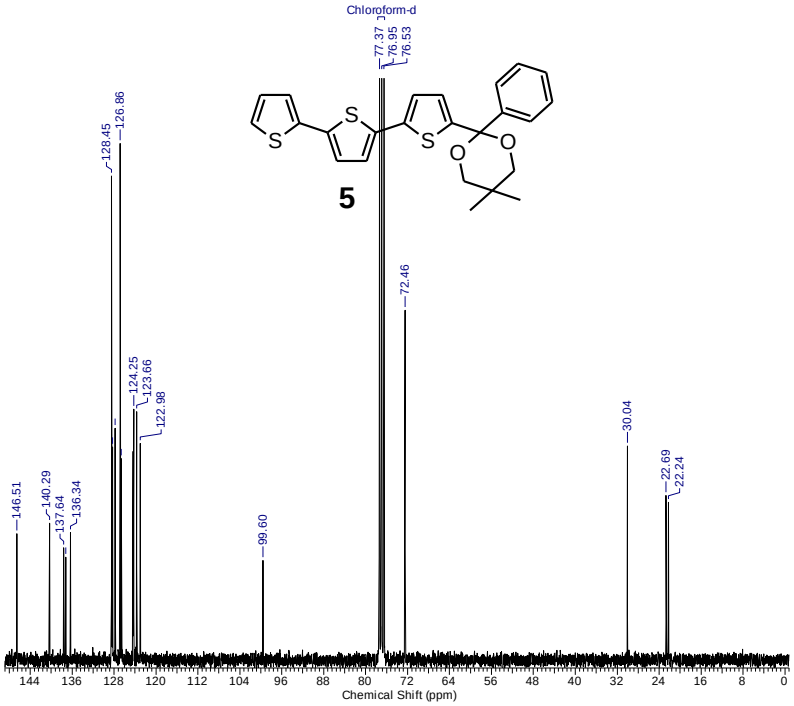
Figure S4. ^{13}C NMR spectrum of compound **3** in $CDCl_3$.



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.84 .. 0.90]	3.008	2.98965e+7
2	[1.14 .. 1.20]	3.039	3.02033e+7
3	[3.55 .. 3.64]	2.084	2.07096e+7
4	[3.66 .. 3.74]	2.063	2.05005e+7
5	[6.61 .. 6.67]	1.003	9.96666e+6
6	[6.90 .. 6.94]	1.003	9.97024e+6
7	[6.96 .. 7.10]	3.000	2.98169e+7
8	[7.11 .. 7.21]	2.013	2.00087e+7
9	[7.30 .. 7.45]	3.158	3.13887e+7
10	[7.53 .. 7.63]	2.069	2.05612e+7

Figure S5. ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

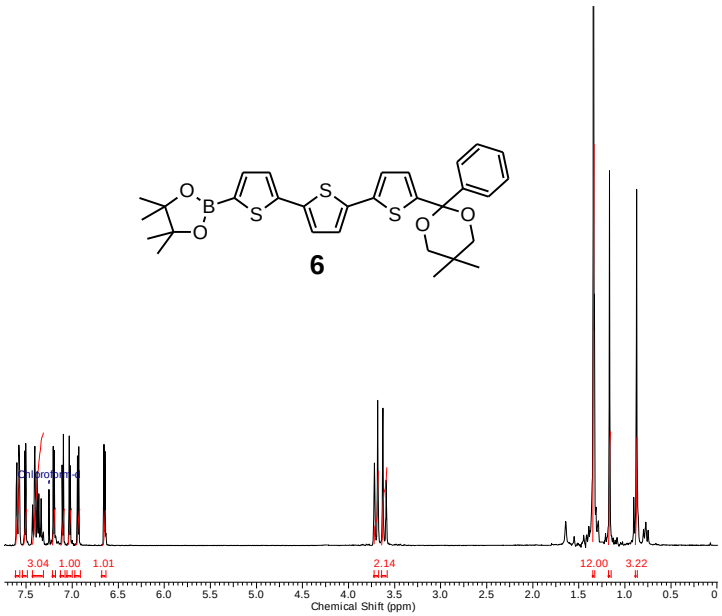


No.	(ppm)	(Hz)	Height
1	22.24	1678.6	0.1733
2	22.69	1712.3	0.1806
3	30.04	2267.1	0.2351
4	72.46	5469.3	0.3840
5	76.53	5776.2	0.9970
6	76.95	5808.2	1.0000
7	77.37	5840.0	0.9865
8	99.60	7517.7	0.1094
9	122.98	9282.4	0.2377
10	123.66	9333.6	0.2728
11	124.25	9378.3	0.2756
12	124.29	9381.1	0.2660

No.	(ppm)	(Hz)	Height
13	124.39	9388.6	0.2290
14	126.63	9558.0	0.2213
15	126.86	9574.9	0.5674
16	127.77	9643.4	0.2546
17	128.30	9683.5	0.2339
18	128.45	9695.4	0.5316
19	136.34	10290.3	0.1397
20	136.35	10291.7	0.1391
21	137.19	10355.0	0.1130
22	137.64	10389.0	0.1233
23	140.29	10588.8	0.1503
24	146.51	11058.2	0.1389

No.	Annotation	(ppm)
1	Chloroform-d	[76.40 .. 77.70]

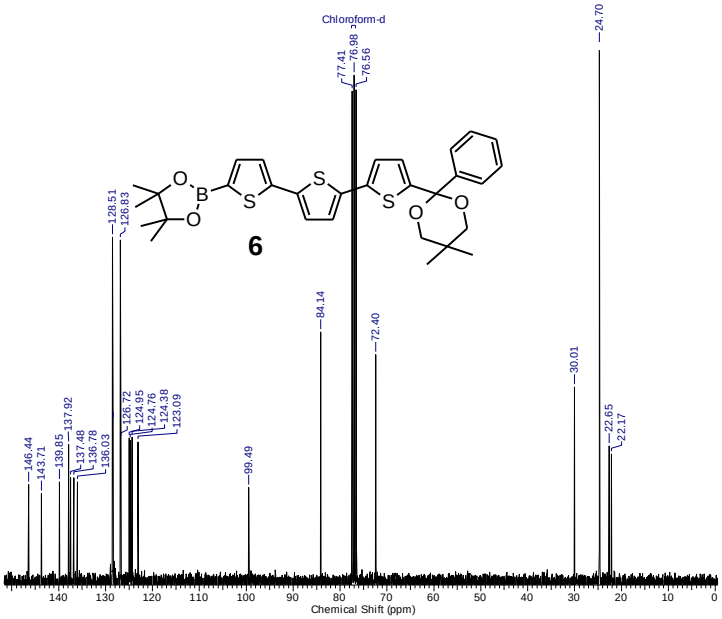
Figure S6. ^{13}C NMR spectrum of compound **5** in $CDCl_3$.



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.87 .. 0.88]	3.225	2.04898e+9
2	[1.15 .. 1.18]	3.149	2.00059e+9
3	[1.33 .. 1.35]	12.000	7.62455e+9
4	[3.58 .. 3.64]	2.139	1.35915e+9
5	[3.67 .. 3.72]	2.051	1.30338e+9
6	[6.64 .. 6.68]	1.010	6.41702e+8
7	[6.91 .. 6.97]	0.983	6.24731e+8
8	[7.00 .. 7.06]	1.003	6.37246e+8
9	[7.08 .. 7.13]	0.989	6.28579e+8
10	[7.18 .. 7.21]	1.031	6.55293e+8
11	[7.31 .. 7.43]	3.037	1.92937e+9
12	[7.49 .. 7.54]	1.000	6.35359e+8
13	[7.57 .. 7.61]	2.024	1.28589e+9

Figure S7. ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

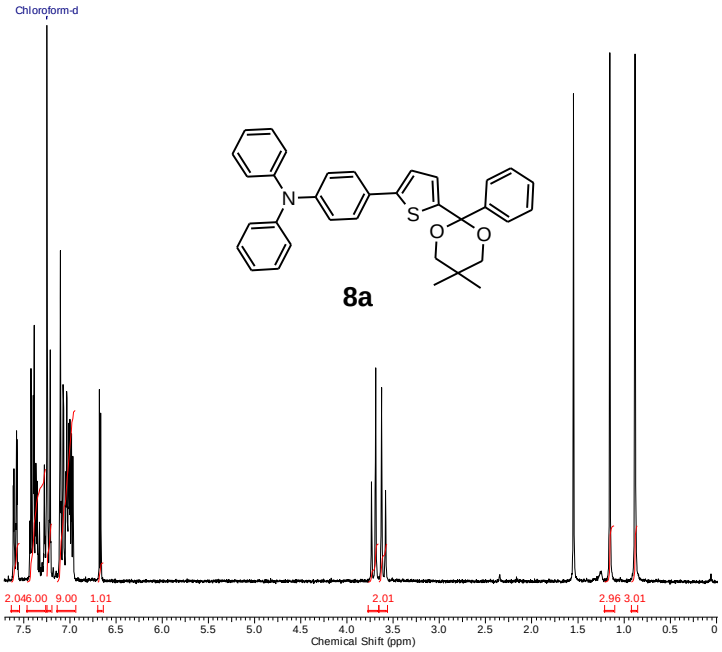


No.	(ppm)	(Hz)	Height
1	22.17	1673.0	0.2452
2	22.65	1709.5	0.2601
3	24.70	1864.0	1.0000
4	30.01	2264.8	0.3652
5	72.40	5464.3	0.4231
6	76.56	5778.6	0.8964
7	76.98	5810.3	0.9229
8	77.41	5842.4	0.8943
9	84.14	6351.0	0.4635
10	99.49	7509.3	0.1855
11	123.09	9290.3	0.2668
12	124.38	9387.6	0.2761
13	124.76	9416.7	0.2700

No.	(ppm)	(Hz)	Height
14	124.88	9425.5	0.0541
15	124.95	9431.0	0.2738
16	126.72	9564.6	0.2729
17	126.83	9572.9	0.6278
18	128.36	9688.1	0.3049
19	128.51	9699.5	0.6334
20	136.03	10267.5	0.1957
21	136.78	10323.6	0.2032
22	137.48	10376.4	0.2039
23	137.92	10409.6	0.2628
24	139.85	10555.6	0.1957
25	143.71	10847.2	0.1753
26	146.44	11052.6	0.1911

No.	Annotation	(ppm)
1	Chloroform-d	[76.75 .. 77.56]

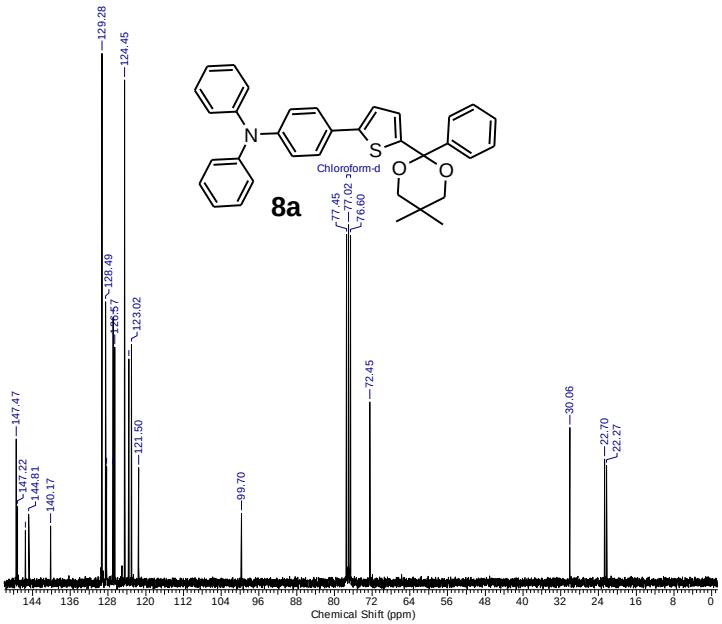
Figure S8. ^{13}C NMR spectrum of compound **6** in $CDCl_3$.



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.85 .. 0.92]	3.006	1.26890e+7
2	[1.10 .. 1.21]	2.965	1.25152e+7
3	[3.56 .. 3.65]	2.013	8.49801e+6
4	[3.66 .. 3.77]	2.009	8.48069e+6
5	[6.64 .. 6.70]	1.014	4.27910e+6
6	[6.94 .. 7.14]	9.004	3.80124e+7
7	[7.19 .. 7.25]	3.073	1.29711e+7
8	[7.26 .. 7.46]	6.003	2.53406e+7
9	[7.54 .. 7.63]	2.037	8.59891e+6

Figure S9. ^{1}H NMR spectrum of compound **8a** in $CDCl_3$.

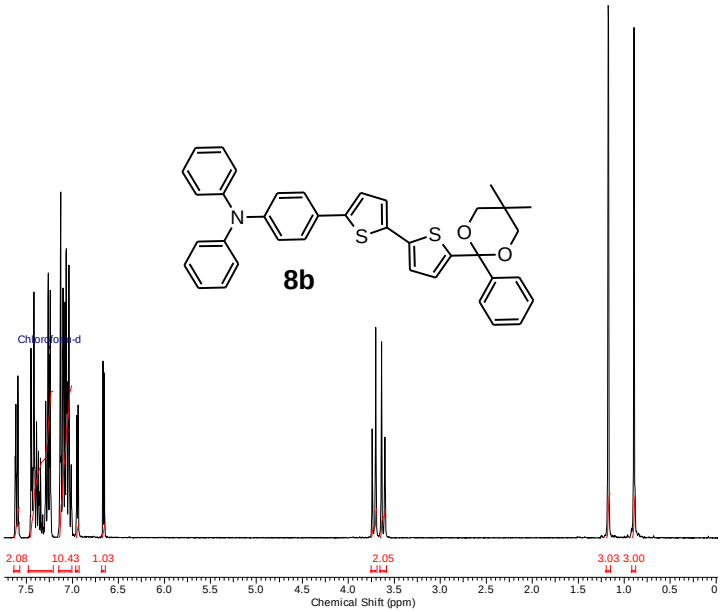


No.	(ppm)	(Hz)	Height
1	22.27	1680.5	0.2260
2	22.70	1713.1	0.2384
3	30.06	2268.8	0.2970
4	72.45	5468.7	0.3450
5	76.60	5781.7	0.6584
6	77.02	5813.5	0.6781
7	77.45	5845.5	0.6596
8	99.70	7525.4	0.1361
9	121.50	9170.7	0.2222
10	123.02	9285.4	0.4532
11	123.60	9329.4	0.4262
12	124.45	9393.5	0.9498

No.	(ppm)	(Hz)	Height
13	126.57	9553.3	0.4480
14	126.94	9581.2	0.5044
15	127.02	9587.0	0.2233
16	128.31	9684.9	0.2240
17	128.49	9697.9	0.5335
18	129.28	9757.6	1.0000
19	140.17	10579.4	0.1123
20	144.81	10930.2	0.1345
21	145.53	10984.1	0.1035
22	147.22	11112.1	0.1487
23	147.47	11130.6	0.2758

No.	Annotation	(ppm)
1	Chloroform-d	[76.59 .. 77.45]

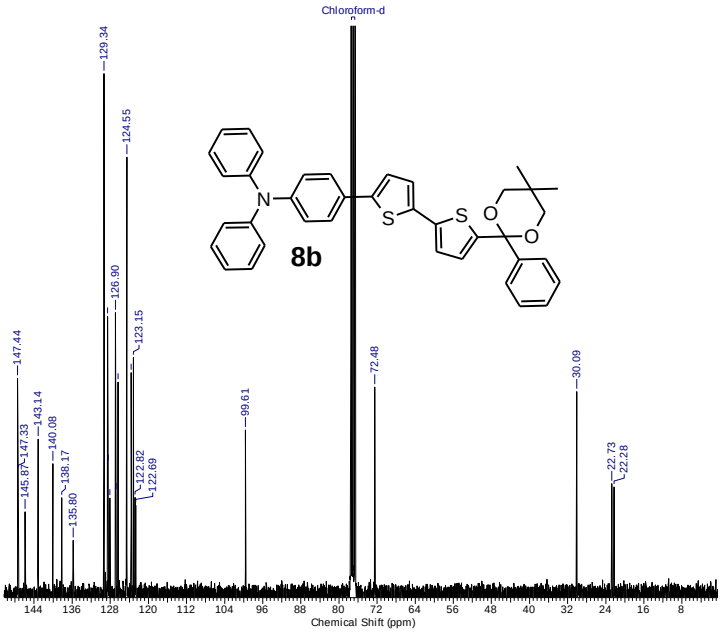
Figure S10. ^{13}C NMR spectrum of compound **8a** in $CDCl_3$.



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.87 .. 0.92]	2.998	1.15588e+10
2	[1.15 .. 1.20]	3.026	1.16640e+10
3	[3.58 .. 3.66]	2.049	7.89963e+9
4	[3.69 .. 3.75]	2.019	7.78269e+9
5	[6.64 .. 6.68]	1.029	3.96759e+9
6	[6.93 .. 6.96]	1.030	3.97186e+9
7	[7.00 .. 7.15]	10.433	4.02190e+10
8	[7.21 .. 7.48]	10.000	3.85503e+10
9	[7.57 .. 7.64]	2.077	8.00721e+9

Figure S11. ^{1}H NMR spectrum of compound **8b** in $CDCl_3$.

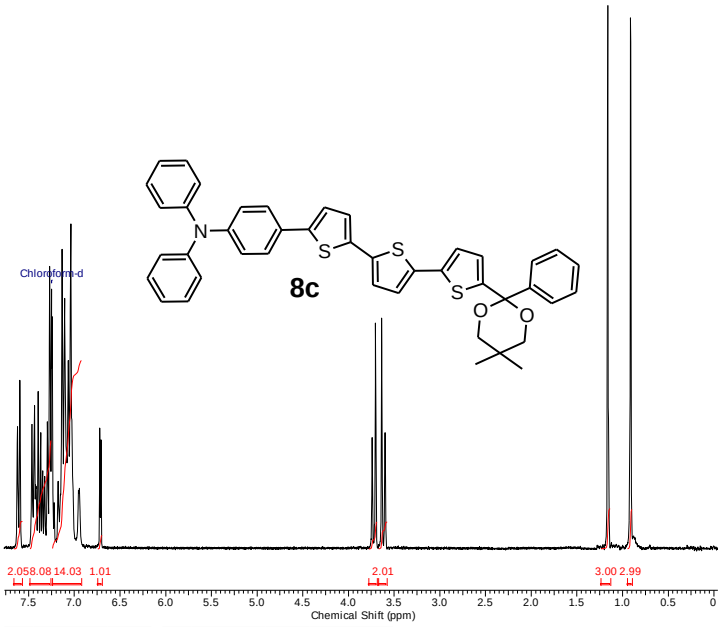


No.	(ppm)	(Hz)	Height
1	22.28	1681.4	0.0565
2	22.73	1715.4	0.0579
3	30.09	2271.0	0.0996
4	72.48	5470.7	0.1018
5	99.61	7518.2	0.0822
6	122.69	9260.6	0.0481
7	122.82	9270.2	0.0517
8	123.15	9295.4	0.1151
9	123.63	9331.1	0.1082
10	124.55	9400.7	0.2059
11	124.63	9406.8	0.0553
12	126.37	9538.1	0.1040
13	126.79	9569.6	0.0543

No.	(ppm)	(Hz)	Height
14	126.90	9578.2	0.1354
15	128.07	9666.7	0.0514
16	128.40	9691.5	0.0671
17	128.56	9703.7	0.1338
18	129.34	9762.3	0.2436
19	135.80	10249.6	0.0324
20	138.17	10429.0	0.0516
21	140.08	10572.8	0.0669
22	143.14	10803.9	0.0781
23	145.87	11010.1	0.0452
24	147.33	11120.4	0.0637
25	147.44	11128.7	0.1057

No.	Annotation	(ppm)
1	Chloroform-d	[76.72 .. 77.37]

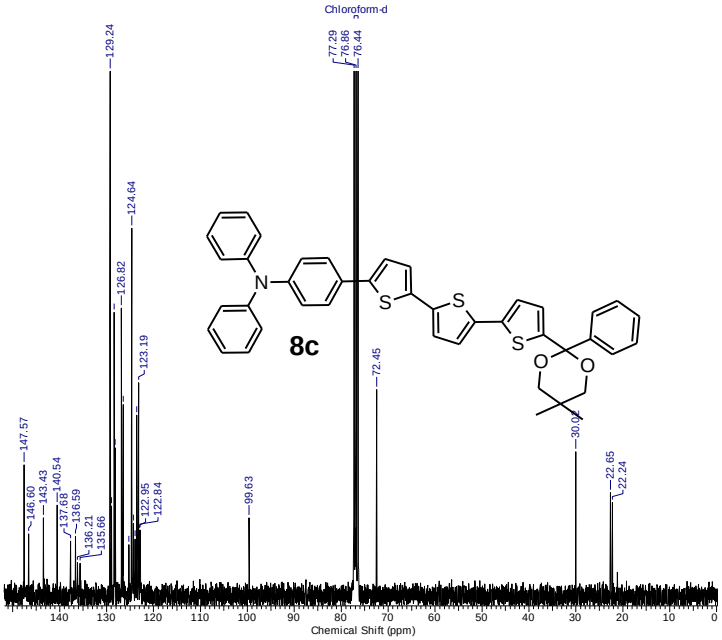
Figure S12. ^{13}C NMR spectrum of compound **8b** in $CDCl_3$.



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.89 .. 0.94]	2.992	9.42237e+9
2	[1.13 .. 1.24]	3.000	9.44950e+9
3	[3.58 .. 3.67]	2.005	6.31595e+9
4	[3.68 .. 3.78]	1.988	6.26256e+9
5	[6.69 .. 6.74]	1.006	3.16926e+9
6	[6.92 .. 7.24]	14.029	4.41856e+10
7	[7.26 .. 7.49]	8.077	2.54412e+10
8	[7.57 .. 7.66]	2.046	6.44290e+9

Figure S13. ^{1}H NMR spectrum of compound **8c** in $CDCl_3$.

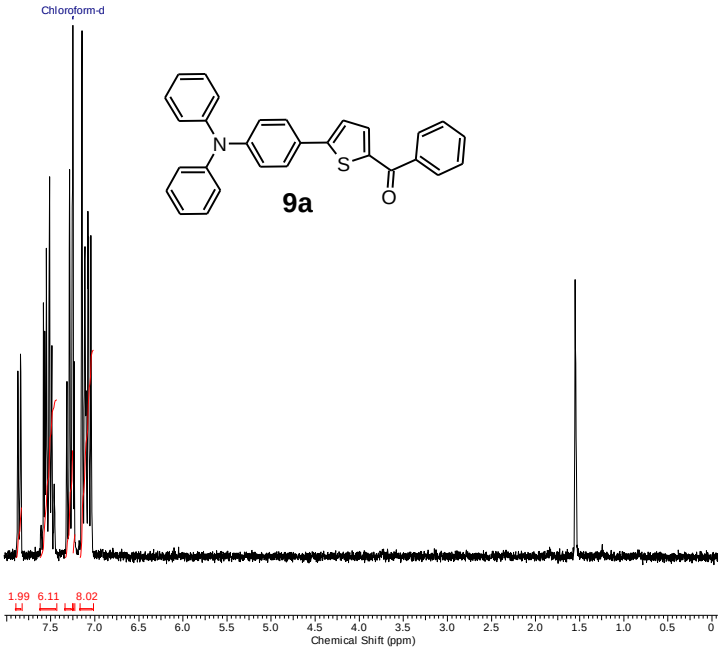


No.	(ppm)	(Hz)	Height
1	22.24	1678.3	0.0747
2	22.65	1709.6	0.0820
3	30.02	2266.0	0.1125
4	72.45	5468.5	0.1588
5	76.44	5769.5	0.9883
6	76.86	5801.3	1.0000
7	77.29	5833.4	0.9850
8	99.63	7519.6	0.0633
9	122.84	9271.9	0.0542
10	122.95	9279.6	0.0535
11	123.19	9297.9	0.1640
12	123.56	9326.4	0.1398
13	123.92	9352.9	0.0473
14	124.28	9380.5	0.0591
15	124.51	9397.4	0.0772
16	124.59	9404.0	0.0634
17	124.64	9407.6	0.2791
18	125.22	9451.3	0.0432

No.	(ppm)	(Hz)	Height
19	126.45	9544.5	0.1477
20	126.55	9551.9	0.0672
21	126.82	9571.8	0.2196
22	128.13	9670.8	0.0882
23	128.19	9675.8	0.1154
24	128.35	9687.9	0.2164
25	128.93	9731.6	0.0719
26	129.24	9755.1	0.3962
27	135.66	10239.7	0.0293
28	136.21	10281.2	0.0298
29	136.59	10309.4	0.0494
30	137.68	10391.7	0.0460
31	140.54	10607.3	0.0728
32	143.43	10825.5	0.0633
33	146.60	11064.8	0.0512
34	147.57	11138.4	0.1028
35	147.59	11139.8	0.1016

No.	Annotation	(ppm)
1	Chloroform-d	[76.42 .. 77.23]

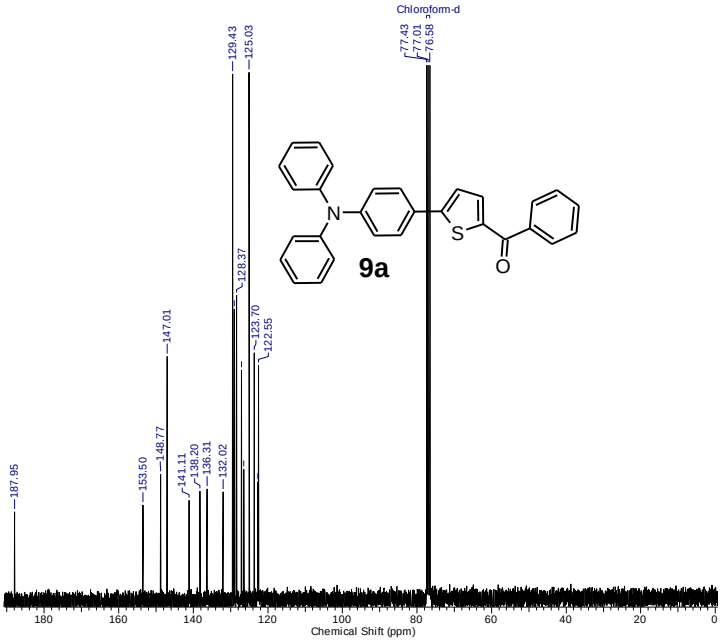
Figure S14. ^{13}C NMR spectrum of compound **8c** in $CDCl_3$.



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[7.01 .. 7.17]	8.022	6.08861e+7
2	[7.22 .. 7.25]	0.928	7.04272e+6
3	[7.25 .. 7.34]	4.146	3.14672e+7
4	[7.43 .. 7.62]	6.109	4.63632e+7
5	[7.83 .. 7.89]	1.991	1.51147e+7

Figure S15. ^{1}H NMR spectrum of compound **9a** in $CDCl_3$.

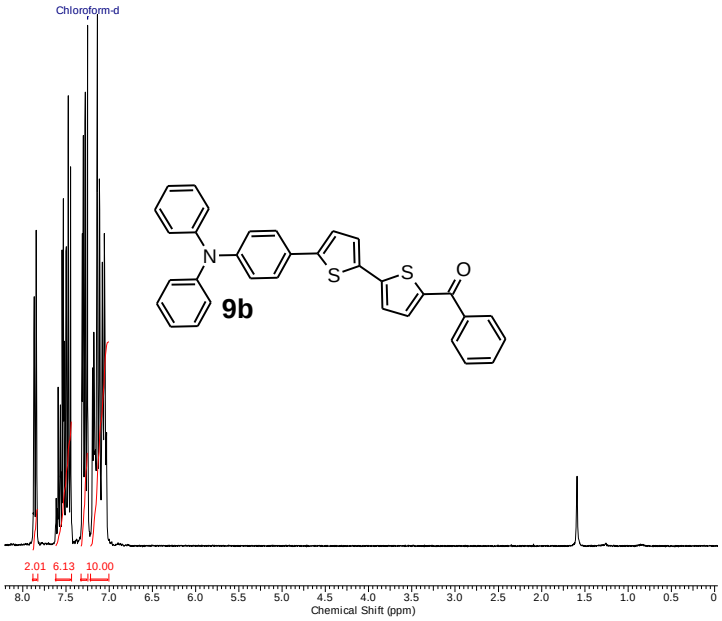


No.	(ppm)	(Hz)	Height
1	76.58	5780.3	0.9933
2	77.01	5812.4	1.0000
3	77.43	5844.2	0.9807
4	122.55	9249.5	0.3099
5	122.72	9262.5	0.1581
6	123.70	9336.3	0.3263
7	125.03	9436.7	0.6915
8	126.51	9548.4	0.1745
9	127.10	9593.4	0.3034
10	128.37	9689.3	0.4008

No.	(ppm)	(Hz)	Height
11	129.03	9738.8	0.3830
12	129.43	9769.2	0.6890
13	132.02	9964.7	0.1449
14	136.31	10288.4	0.1487
15	138.20	10430.7	0.1460
16	141.11	10650.8	0.1341
17	147.01	11096.4	0.3216
18	148.77	11229.1	0.1682
19	153.50	11586.2	0.1279
20	187.95	14185.8	0.1191

No.	Annotation	(ppm)
1	Chloroform-d	[76.58 .. 77.43]

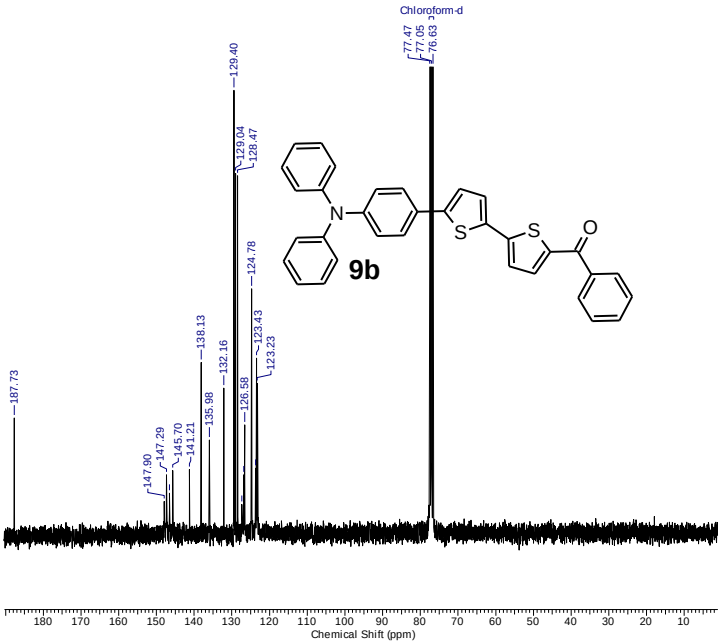
Figure S16. ^{13}C NMR spectrum of compound **9a** in $CDCl_3$.



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[7.00 .. 7.21]	10.000	4.20098e+10
2	[7.24 .. 7.32]	5.259	2.20921e+10
3	[7.44 .. 7.62]	6.133	2.57629e+10
4	[7.82 .. 7.88]	2.006	8.42507e+9

Figure S17. ^{1}H NMR spectrum of compound **9b** in $CDCl_3$.

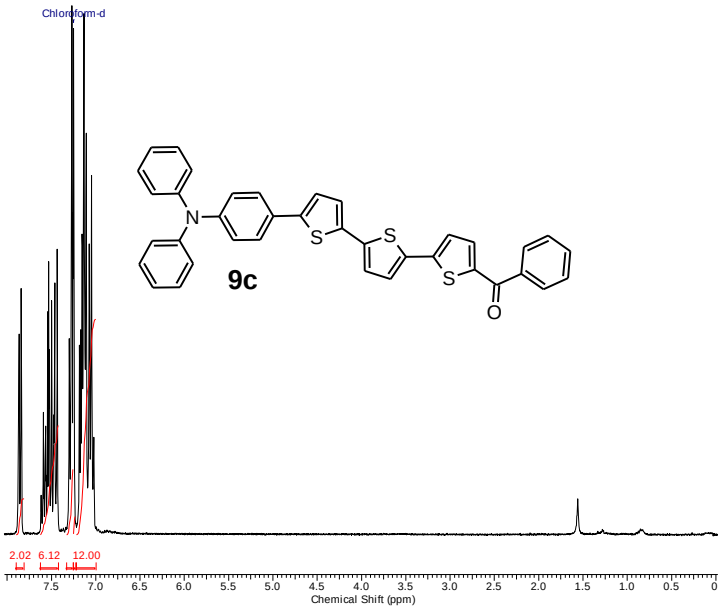


No.	(ppm)	(Hz)	Height
1	76.63	5783.6	0.9802
2	77.05	5815.7	1.0000
3	77.47	5847.5	0.9747
4	123.23	9301.2	0.0726
5	123.43	9315.9	0.0835
6	123.67	9334.4	0.0362
7	124.78	9418.1	0.1133
8	126.58	9553.9	0.0549
9	126.86	9575.4	0.0334
10	127.32	9609.7	0.0207
11	128.47	9696.5	0.1619

No.	(ppm)	(Hz)	Height
12	129.04	9739.6	0.1630
13	129.40	9767.0	0.1986
14	132.16	9975.4	0.0706
15	135.98	10263.5	0.0483
16	138.13	10426.0	0.0817
17	141.21	10658.2	0.0356
18	145.70	10997.4	0.0352
19	146.51	11057.9	0.0254
20	147.29	11117.1	0.0333
21	147.90	11163.5	0.0220
22	187.73	14169.2	0.0578

No.	Annotation	(ppm)
1	Chloroform-d	[76.48 .. 77.71]

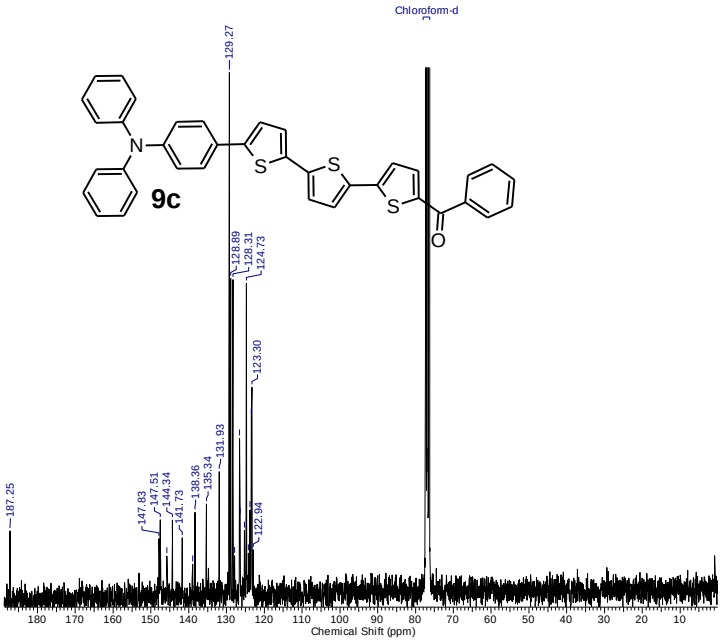
Figure S18. ^{13}C NMR spectrum of compound **9b** in $CDCl_3$.



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[7.00 .. 7.22]	12.000	6.54995e+10
2	[7.23 .. 7.25]	1.058	5.77225e+9
3	[7.25 .. 7.33]	4.111	2.24406e+10
4	[7.42 .. 7.63]	6.124	3.34267e+10
5	[7.81 .. 7.90]	2.015	1.09996e+10

Figure S19. ^{1}H NMR spectrum of compound **9c** in $CDCl_3$.

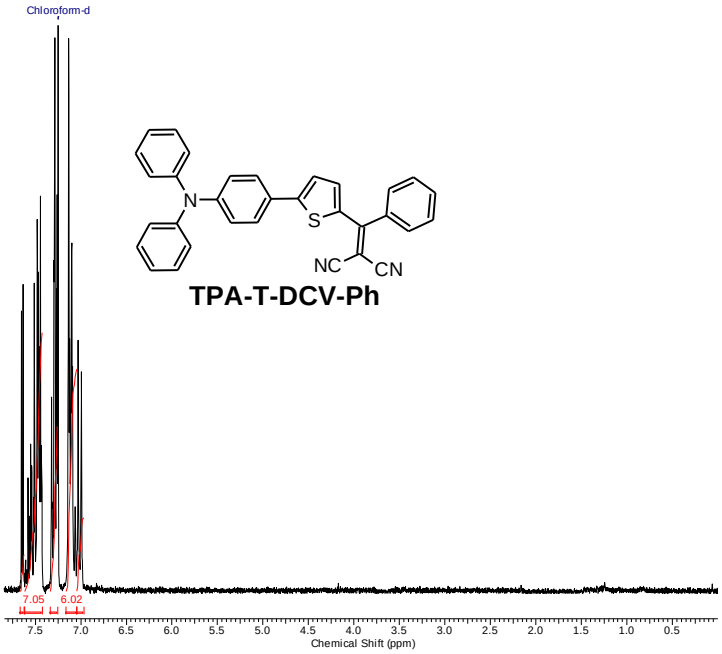


No.	(ppm)	(Hz)	Height
1	122.94	9279.1	0.0282
2	123.30	9306.2	0.0988
3	123.42	9315.3	0.0859
4	123.77	9342.1	0.0454
5	124.20	9374.2	0.0267
6	124.73	9414.3	0.1440
7	125.22	9451.3	0.0365
8	126.39	9539.5	0.0426
9	126.52	9549.2	0.0766
10	127.85	9649.8	0.0256
11	128.31	9684.9	0.1456
12	128.89	9728.0	0.1462

No.	(ppm)	(Hz)	Height
13	129.27	9757.0	0.2356
14	131.93	9958.0	0.0621
15	135.34	10215.4	0.0480
16	138.36	10442.9	0.0445
17	138.92	10485.7	0.0218
18	141.73	10697.5	0.0333
19	144.34	10894.6	0.0411
20	145.78	11003.2	0.0255
21	147.51	11133.4	0.0413
22	147.83	11157.7	0.0330
23	187.25	14133.5	0.0364

No.	Annotation	(ppm)
1	Chloroform-d	[76.24 .. 77.97]

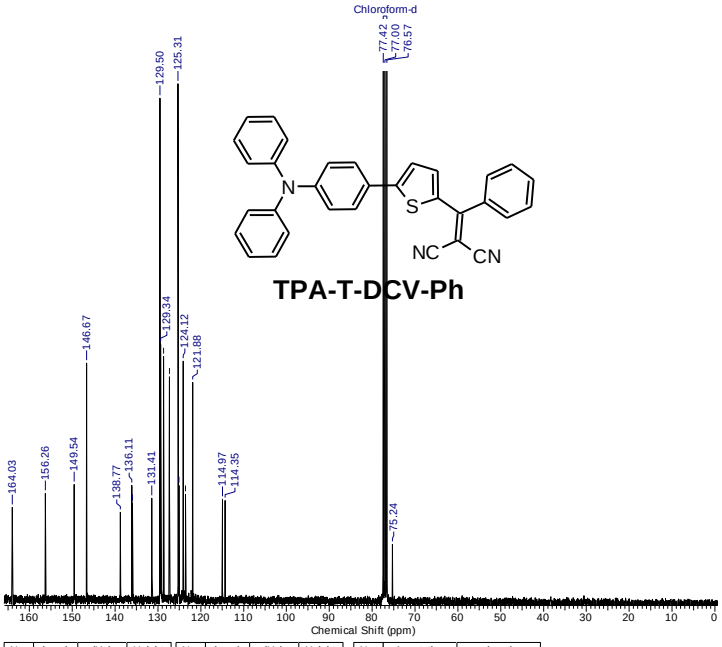
Figure S20. ^{13}C NMR spectrum of compound **9c** in $CDCl_3$.



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[6.97 .. 7.04]	1.992	1.54874e+7
2	[7.04 .. 7.16]	6.022	4.68141e+7
3	[7.25 .. 7.34]	5.038	3.91684e+7
4	[7.42 .. 7.62]	7.053	5.48285e+7
5	[7.62 .. 7.67]	1.000	7.77381e+6

Figure S21. ^{1}H NMR spectrum of compound **TPA-T-DCV-Ph (10a)** in $CDCl_3$.

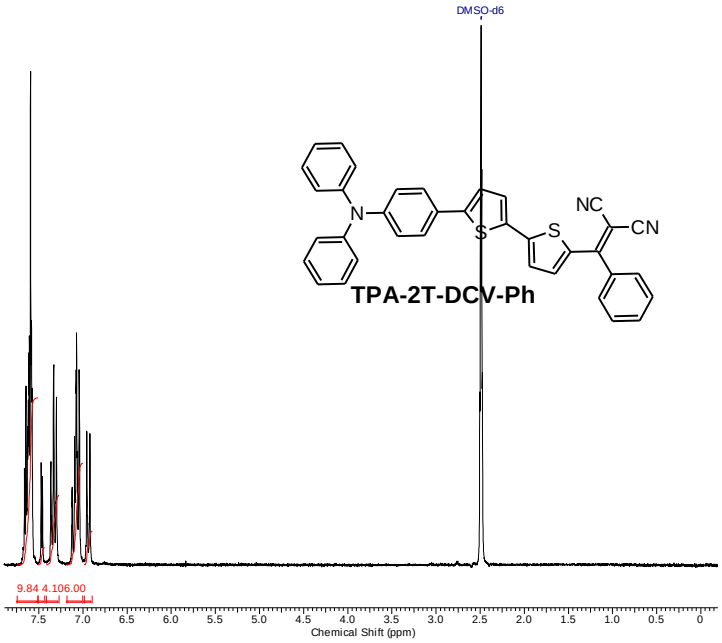


No.	(ppm)	(Hz)	Height
1	75.24	5679.0	0.1103
2	76.57	5779.6	0.9749
3	77.00	5811.7	1.0000
4	77.42	5843.5	0.9676
5	114.35	8631.0	0.1880
6	114.97	8677.5	0.1905
7	121.88	9199.4	0.3972
8	123.56	9326.0	0.1991
9	124.12	9368.3	0.4354
10	125.11	9442.9	0.2148
11	125.31	9457.8	0.9273
12	127.32	9609.9	0.4070

No.	(ppm)	(Hz)	Height
13	128.69	9713.5	0.4432
14	129.34	9762.4	0.4655
15	129.50	9774.1	0.9015
16	131.41	9918.6	0.1923
17	135.92	10258.6	0.1831
18	136.11	10273.0	0.2149
19	138.77	10474.3	0.1672
20	146.67	11070.2	0.4317
21	149.54	11287.0	0.2163
22	156.26	11794.2	0.2005
23	164.03	12380.8	0.1761

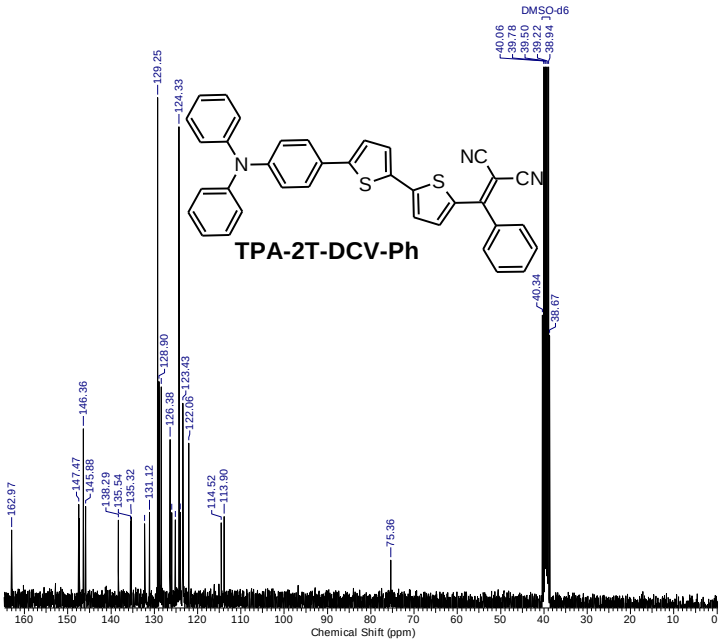
No.	Annotation	(ppm)
1	Chloroform-d	[76.57 .. 77.39]

Figure S22. ^{13}C NMR spectrum of compound **TPA-T-DCV-Ph (10a)** in $CDCl_3$.



No.	(ppm)	Value	Absolute Value
1	[6.89 .. 6.98]	1.997	5.43698e+6
2	[7.00 .. 7.18]	6.000	1.63346e+7
3	[7.27 .. 7.41]	4.098	1.11567e+7
4	[7.43 .. 7.51]	1.021	2.77871e+6
5	[7.51 .. 7.74]	9.841	2.67916e+7

Figure S23. ^{1}H NMR spectrum of compound **TPA-2T-DCV-Ph (10b)** in DMSO-d$_6$.

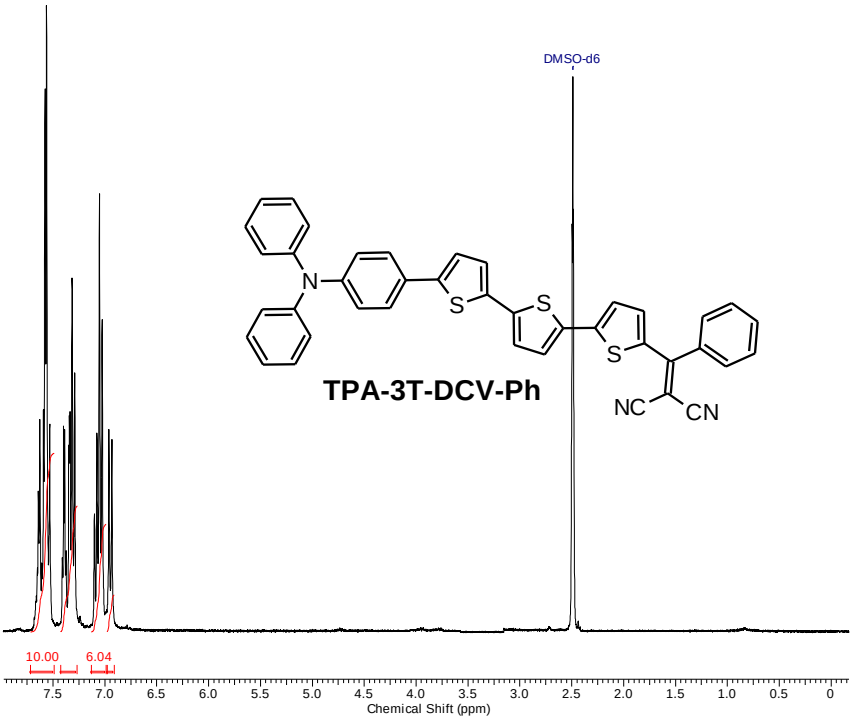


No.	(ppm)	(Hz)	Height
1	38.67	2918.4	0.1370
2	38.94	2939.5	0.4193
3	39.22	2960.5	0.8440
4	39.50	2981.5	1.0000
5	39.78	3002.5	0.8642
6	40.06	3023.5	0.4427
7	40.34	3044.5	0.1472
8	75.36	5688.3	0.0256
9	113.90	8597.2	0.0473
10	114.52	8643.9	0.0442
11	122.06	9212.8	0.0836
12	123.43	9315.9	0.1036
13	124.05	9362.9	0.0494
14	124.33	9384.5	0.2407
15	125.14	9445.5	0.0457
16	125.99	9509.4	0.0492

No.	(ppm)	(Hz)	Height
17	126.38	9538.7	0.0855
18	128.38	9689.9	0.1116
19	128.46	9696.0	0.0517
20	128.90	9728.9	0.1142
21	129.25	9755.7	0.2551
22	131.12	9897.0	0.0493
23	132.23	9980.2	0.0437
24	135.32	10213.7	0.0471
25	135.54	10230.1	0.0446
26	138.29	10438.2	0.0455
27	145.88	11011.0	0.0523
28	146.36	11047.2	0.0909
29	147.32	11119.3	0.0463
30	147.47	11130.4	0.0533
31	162.97	12300.5	0.0405

No.	Annotation	(ppm)
1	DMSO-d6	[38.63 .. 40.41]

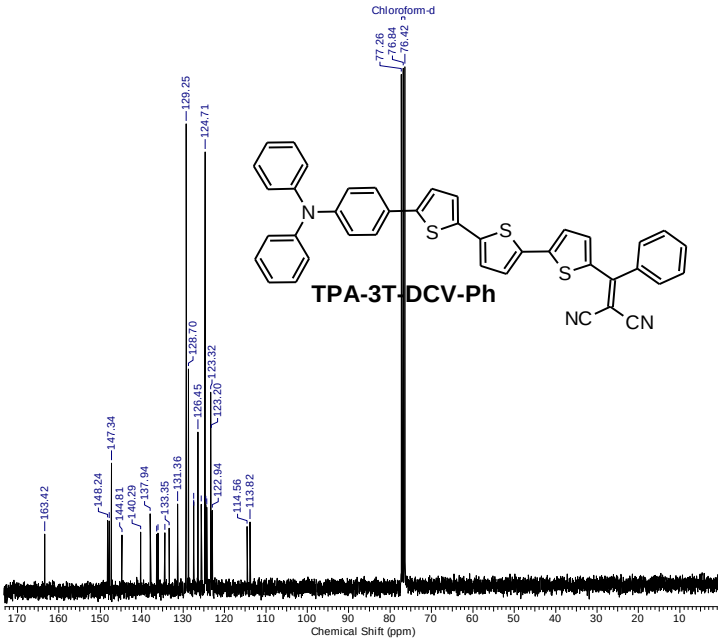
Figure S24. ^{13}C NMR spectrum of compound **TPA-2T-DCV-Ph (10b)** in DMSO-d$_6$.



No.	Annotation	(ppm)
1	DMSO-d6	2.49

No.	(ppm)	Value	Absolute Value
1	[6.91 .. 6.98]	2.076	1.22477e+9
2	[6.99 .. 7.13]	6.043	3.56532e+9
3	[7.27 .. 7.43]	7.065	4.16871e+9
4	[7.49 .. 7.72]	10.000	5.90030e+9

Figure S25. ^{1}H NMR spectrum of compound **TPA-3T-DCV-Ph (10c)** in DMSO-d_6.



No.	(ppm)	(Hz)	Height
1	76.42	5767.8	1.0000
2	76.84	5799.6	0.9951
3	77.26	5831.6	0.9835
4	113.82	8590.7	0.1378
5	114.56	8647.1	0.1296
6	122.94	9279.6	0.1594
7	123.20	9299.2	0.3102
8	123.32	9308.0	0.3832
9	124.30	9381.6	0.1657
10	124.52	9398.7	0.1708
11	124.71	9413.1	0.8371
12	125.59	9479.4	0.1712
13	126.45	9544.1	0.3080
14	127.42	9617.6	0.1765
15	127.45	9619.9	0.1635

No.	(ppm)	(Hz)	Height
16	128.70	9713.8	0.4271
17	129.18	9750.1	0.4789
18	129.25	9755.6	0.8900
19	131.36	9914.8	0.1720
20	133.35	10064.6	0.1260
21	134.40	10144.0	0.1178
22	136.08	10271.1	0.1171
23	136.42	10296.8	0.1144
24	137.94	10411.3	0.1536
25	140.29	10589.0	0.1188
26	144.81	10929.9	0.1133
27	147.34	11120.9	0.2493
28	147.87	11161.0	0.1396
29	148.24	11188.6	0.1412
30	163.42	12334.7	0.1150

No.	Annotation	(ppm)
1	Chloroform-d	[76.41 .. 77.25]

Figure S26. ^{13}C NMR spectrum of compound **TPA-3T-DCV-Ph (10c)** in $CDCl_3$

3. Thermal and optical properties

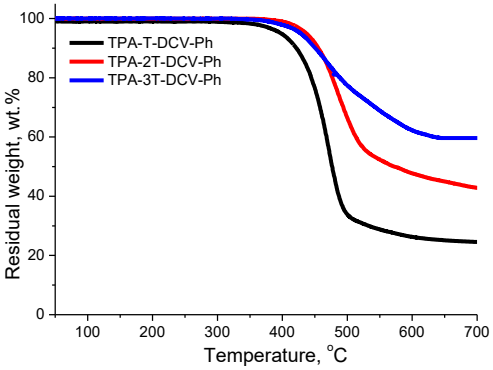


Figure S27. TGA curves of **TPA-T-DCV-Ph** (black), **TPA-2T-DCV-Ph** (red) and **TPA-3T-DCV-Ph** (blue) under argon

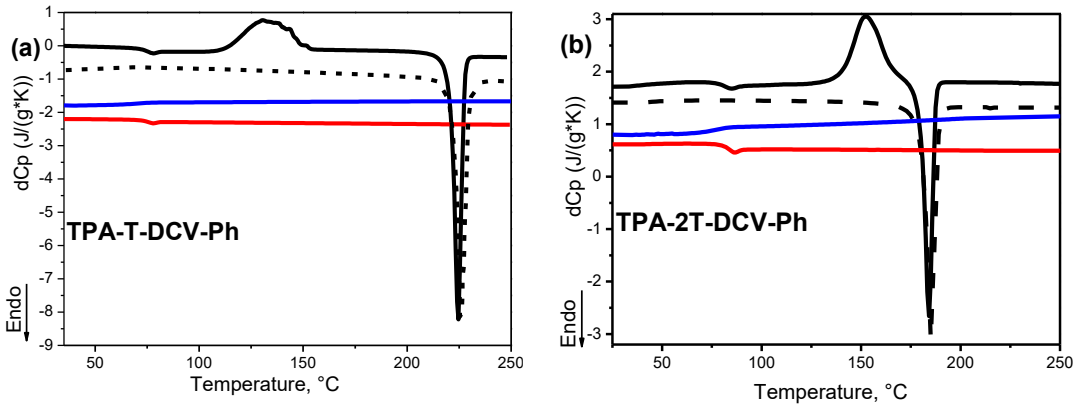


Figure S28. DSC scans of **TPA-T-DCV-Ph 10a** (a), **TPA-2T-DCV-Ph 10b** (b) at the first heating (black), cooling (blue), second heating (red), and heating of the preliminary annealed sample at 115ºC (a) and 170°C (b) (black dashed)

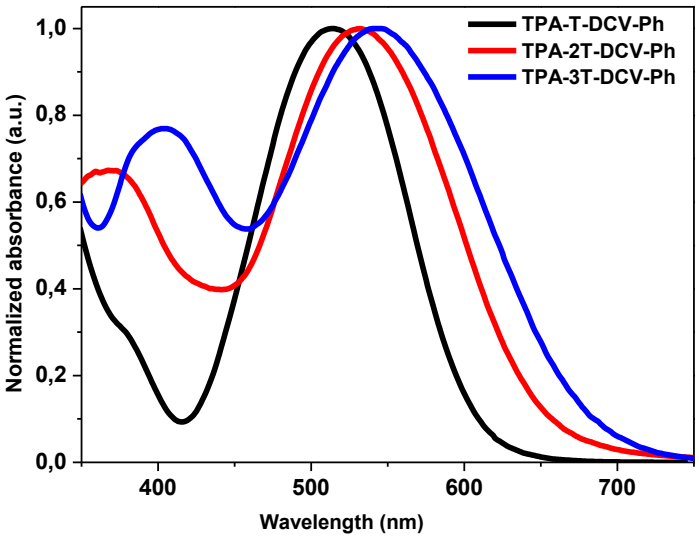


Figure S29. UV-vis absorption spectra of **TPA-T-DCV-Ph 10a** (black), **TPA-2T-DCV-Ph 10b** (red) and **TPA-3T-DCV-Ph 10c** (blue) in film cast from THF

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