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General Considerations:

Unless otherwise indicated all reagents were purchased from commercial sources and were used without further purification. Tri^{n}butyl(9,9'-dioctyl-9*H*-fluoren-2-yl)-stannane, tri^{n}butyl(5-octylthiophen-2-yl)stannane and trimethyl(5-methylthiophen-2-yl)stannane were synthesised by modified literature procedures[1]. All appropriate manipulations were performed using standard Schlenk techniques or in an argon-filled MBraun glovebox (O_2 levels below 0.5 ppm). Glassware was dried in a hot oven overnight and heated under vacuum before use. Solvents and amines were distilled from NaK, CaH_2, or K and degassed prior to use.

^{1}H NMR and ^{13}C NMR spectra were recorded using 400 and 500 MHz spectrometers with chemical shift values being reported in ppm relative to residual protio solvent (e.g. in $CHCl_3$ in $CDCl_3$ δH = 7.27 or δC = 77.2) as internal standards. All coupling constants (J) are reported in Hertz (Hz). Other NMR spectra were recorded with a 400 MHz Bruker AV-400 spectrometer (^{11}B; 162 MHz, ^{27}Al 104.3 MHz). The ^{19}F NMR spectra were referenced to C_6F_6, ^{11}B NMR spectra were referenced to external BF_3:Et_2O, and ^{27}Al to $Al(NO_3)_2$ in D_2O ($Al(D_2O)_6^{3+}$). Unless otherwise stated all NMR are recorded at 293 K. Broad features in the ^{11}B NMR spectra are due to boron materials present in borosilicate glass whilst broad features in ^{27}Al NMR spectra are due to aluminium materials used in the spectrometer probe. Carbon atoms directly bonded to boron are not always observed in the ^{13}C{^{1}H} NMR spectra due to quadrupolar relaxation leading to signal broadening.

MALDI-TOF was performed by the Mass Spectrometry Service, School of Chemistry, University of Manchester. MALDI-TOF analyses were performed using a Shimadzu Axima Confidence spectrometer using a 4k PPG as a calibration reference. 1 μL of a solution of dopant NaI in THF (10 mg mL^{-1}) was spotted onto a well of the MALDI plate and the solvent left to evaporate. Solutions were made up to 10 mg mL^{-1} in DCM. A solution of matrix dithranol was made up to 10 mg mL^{-1} in THF. 2 μL of sample solution and 20 μL of matrix solution were thoroughly mixed and 1 μL of this solution was spotted onto a well with no dopant, and 1 μL spotted by a layered method with the NaI. The solvent was allowed to evaporate before being placed in the spectrometer. Samples were run in positive polarity mode in either linear or reflectron mode.

Data for compound **2-BBr$_2$** **2-BMe$_2$** and **2-BPh$_2$** was recorded on a Bruker APEX-II diffractometer, with Cu Kα radiation (graphite monochromator, monochromator, λ= 1.5418 Å). The Bruker APEX2 software package was used for data collection, and the CrysAlisPro software package was used for cell refinement and data reduction.

Data for compounds **5**, **5-(BPh$_2$)$_2$** and **5-B((C$_6$F$_5$)$_2$)$_2$** were recorded on an Agilent Supernova diffractometer, with Mo Kα radiation (mirror monochromator, λ=0.7107 Å). The CrysAlisPro[2] software package was used for data collection, cell refinement and data reduction. For all data sets the CrysAlisPro[2] software package was used for empirical absorption corrections, which were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. All structures were solved using direct methods[3] and refined against F^2 using the Crystals[4] software package. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all located in a difference map and repositioned geometrically. Experimental details are in Table S8.

All UV-Vis absorption spectra were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer and the solution emission spectra were recorded on a Varian Cary Eclipse fluorometer at room temperature in spectroscopic grade solvents exciting at the relative absorbance maxima. Solid state fluorescence and absolute quantum yields were measured on spin coated films of polymer host / 5 wt % emitter using a Hamamatsu C9920-02 Absolute quantum yield measurement system. The thin film lifetime measurements were performed in host polymer at 5% using a Hamamatsu Picosecond Lifetime system C11200 using a Fianium UV power 343nm fibre laser as excitation source. The OLED efficiency was measured using a Labsphere integrating sphere system (25 cm) equipped with CDS610 spectrometer. The J/V curves were measured on a Botest LIV system.

Cyclic voltammetry was performed using a CH-Instrument 1110C Electrochemical/Analyzer potentiostat under a nitrogen flow. Measurements were made using a 0.001 M analyte solution with 0.1 M tetrabutylammonium hexafluorophosphate (Fluka ≥99.0%) as the supporting electrolyte in dichloromethane that had been degassed prior to use and obtained from a dry solvent system. A glassy carbon electrode served as the working electrode and a platinum wire as the counter electrode. An $Ag/AgNO_3$ non-aqueous reference electrode was used. All scans were calibrated against the ferrocene/ferrocenium (Fc/Fc^+) redox couple, which in this work is taken to be 5.39 eV below vacuum.[5] The half-wave potential of the ferrocene/ferrocenium (Fc/Fc^+) redox

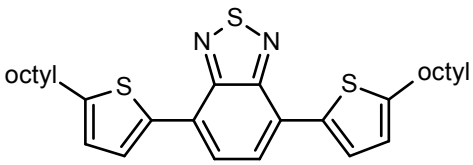
couple ($E_{1/2,\ Fc,Fc+}$) was estimated from $E_{1/2,\ Fc,Fc+} = (E_{ap} + E_{cp})/2$, where E_{ap} and E_{cp} are the anodic and cathodic peak potentials, respectively.

Calculations were performed using the Gaussian09 suite of programmes.[6] Structures were pre-optimised at the HF/3-21G level followed by optimisation at the M06-2X/ 6-311G+(d,p) level with inclusion of a PCM model for solvent correction (DCM).[7] Structures were confirmed as minima by frequency analysis and the absence of imaginary frequencies. Full Cartesian coordinates for all M06-2X/6-311G+(d,p) /PCM(benzene) structures can be found in the computation analysis section (pages S49 – S52).

Attempts to record accurate elemental analyses on the boron containing compounds were consistently low in carbon, even when run in the presence of V_2O_5. To demonstrate the purity of these materials all ^{1}H and ^{13}C NMR spectra are included at the end of this document.

Experimental

Synthesis of **2**



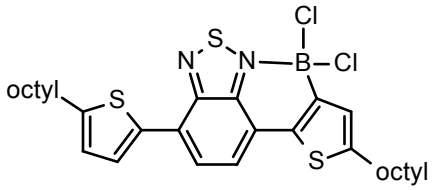
4,7-dibromobenzo[c][1,2,5]thiadiazole (2.00 g, 6.80 mmol), tri^{n}butyl(5-octylthiophen-2-yl)stannane (7.26 g, 14.96 mmol) and $PdCl_2(PPh_3)_2$ (0.48 g, 0.68mmol) were mixed in dry THF (60 ml) under an nitrogen atmosphere and stirred for 22 h at 80 °C under reflux. The mixture was cooled to room temperature and then diluted with DCM (200mL). The reaction mixture was then washed with saturated $NaHCO_3$ solution (1 x 100mL), brine (1 x 200mL), water (1 x 200mL), and then dried over $MgSO_4$. After evaporating the solvent, the residue was purified by column chromatography on silica gel [eluent: hexane/chloroform (4/1)] to afford **2** as an orange powder. Yield: 1.08 g, 30 %.

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.94 (d, J=3.6 Hz, 2H), 7.79 (s, 2H), 6.88 (d, J=3.6 Hz, 2H), 2.90 (t, J= 7.6, 4H), 1.76 (m, 4H), 1.47-1.22 (m, 20H), 0.89 (t, J=7.2, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ =152.62, 147.80, 136.84, 127.32, 125.75, 125.22, 125.12, 31.90, 31.70, 30.33, 29.39, 29.28, 29.20, 22.70, 14.16;

MALDI-TOF: calc. for $C_{36}H_{44}BN_2S_3^+$ 524.2, found 523.9

Synthesis of **2-BCl_2**



BCl_3 (1M solution in heptanes) (0.60 mL, 0.6 mmol) was added to a bright orange solution of **1a** (0.312 g, 0.060 mmol) in DCM (10 mL) in a Schlenk flask resulting in a colour change to dark blue and the reaction mixture was stirred for 16 hours (addition of a base was unnecessary as in the open system of a Schlenk flask gaseous HCl is lost from solution under the flow of nitrogen). The solvent was removed under reduced pressure and **2-BCl_2** was isolated as a dark blue powder (322mg, 89%).

^{1}H NMR (400 MHz, C_6D_6): δ = 7.65 (d, *J* = 3.8 Hz, 1 H), 7.54 (s, 1 H), 7.11 (d, *J* = 7.6 Hz, 1 H), 6.97 (d, *J* = 7.6 Hz, 1 H), 6.73 (d, *J* = 3.8 Hz, 1 H), 2.68 (q, *J*= 8.0 Hz, 4 H), 1.72 - 1.52 (m, 4 H), 1.38 - 1.14 (m, 20 H), 0.92 (t, *J* = 6.9 Hz, 6 H);

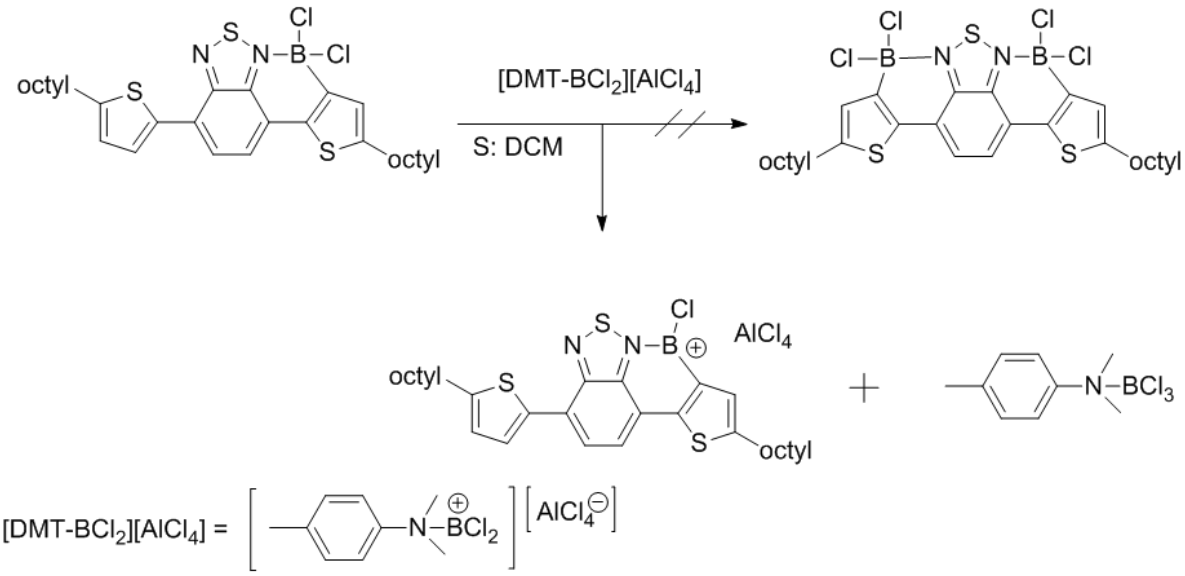
^{13}C NMR (101 MHz, C_6D_6) δ = 151.3, 150.8, 150.0, 145.0, 134.7, 131.7, 129.2, 128.8, 127.9, 126.2, 126.0, 125.7, 122.2, 32.0, 31.7, 31.7, 30.6, 30.4, 29.4, 29.4, 29.2, 22.8, 14.0;

All $\underline{C}H_2$ resonances were not distinctly observed due to similar magnetic environments,

^{11}B NMR (128.4 MHz, C_6D_6) δ =~3 (broad);

Due to the sensitivity of **2-$(BCl_2)_2$** mass spec were not obtainable

Synthesis of **[2-BCl]$^+$**

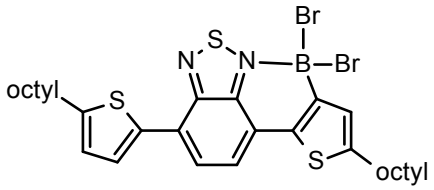


Attempts to form fully fused systems from **2** using highly electrophilic three coordinate borocations resulted instead in halide abstraction from **2-BCl_2** to form **[2-BCl]$^+$**.

[DMT-BCl_2][$AlCl_4$] (0.033 mmols) was added to a dark blue solution of **2-BCl_2** (20mg, 0.33 mmol) in DCM. The solution turned a dark green colour and NMR spectroscopy showed a significant downfield shift in the NMR resonances relative to that of 2-**BCl_2**. The formation of DMT-BCl_3 adduct was also confirmed by multinuclear NMR spectroscopy.[8] These observations are consistent with the chloride abstraction from **2-BCl_2** to form **[2-BCl]$^+$**.

^{1}H NMR (400MHz ,$CDCl_3$) δ = 8.65 (br. d, *J* = 8.1 Hz, 1 H), 8.37 (br. s., 1 H), 8.14 (br. d, *J* = 8.1 Hz, 1 H), 7.54 (br. s., 1 H), 7.14 (br. s., 1 H), 3.13 - 2.87 (m, 4 H), 1.91 - 1.61 (m, 4 H), 1.48 - 1.19 (m, 20 H), 0.88 (t, *J* = 6.4 Hz, 6 H);

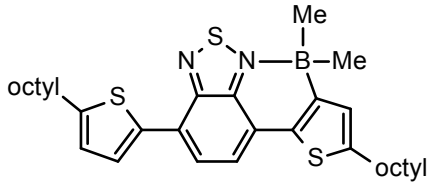
Synthesis of **2-BBr_2**



BBr_3 (1M solution in Heptanes) (0.20 mL, 0.20 mmol) was added to a bright orange solution of **2** (0.026 g, 0.005 mmol) in DCM (0.7mL) in a J. Young's NMR tube resulting in a colour change to dark blue and a blue precipitate was formed. 2,6-Lutidine (0.011mL, 0.1mmol) was added and the reaction mixture was heated at 60°C to dissolve the precipitate. Upon cooling material suitable for x-ray diffraction crystallised from the reaction mixture.

Due to the sensitivity of **2-BBr_2** mass spec were not obtainable

Synthesis of **2-BMe_2**



A solution of $AlMe_3$ (2M solution in heptanes) (0.4 mL, 0.080 mmol) in dry toluene (3mL) was slowly added a stirred solution of **2-BCl_2** (0.20g, 0.33 mmol) in dry toluene (3mL). After stirring for 20 minutes the excess $AlMe_3$ and solvent were removed under reduced pressure. Compound **2-BMe_2** was isolated as a dark blue/purple powder without further purification (178 mg, 96%).

^{1}H NMR (400 MHz, C_6D_6) δ =7.84 (d, *J*=3.8 Hz, 1 H), 7.35 (d, *J*=7.6 Hz, 1 H), 7.11 (s, 1 H), 7.05 (d, *J*=7.3 Hz, 1 H), 6.78 (d, *J*=3.5 Hz, 1 H), 2.81 (t, *J*=7.7 Hz, 2 H), 2.72 (t, *J*=7.6 Hz, 2 H), 1.76 – 1.61 (m, 4 H), 1.38 – 1.17 (m, 20 H), 0.92 (t, J=7.2, 3 H), 0.91 (t, J=7.2, 3 H), 0.72 (s, 6 H);

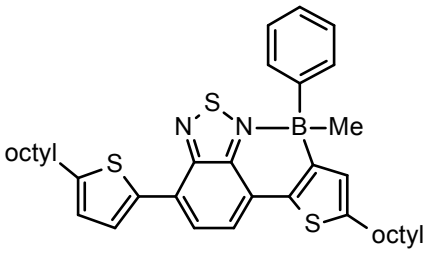
^{13}C NMR (101 MHz, C_6D_6) δ = 152.5, 149.5, 148.1, 147.6, 137.0, 130.8, 130.7, 130.2, 127.8, 127.7, 126.5, 126.0, 123.8, 120.6, 32.6, 32.5, 32.4, 31.3, 30.9, 30.1, 30.0, 29.8, 23.4, 17.8, 14.7, 14.7;

All $\underline{C}H_2$ resonances were not distinctly observed due to similar magnetic environments.

^{11}B NMR (128.4 MHz, C_6D_6) δ = Not observed

MALDI-TOF: calc. for $C_{31}H_{42}BN_2S_3^+$ [M – CH_3]$^+$ 549.7, found 549.6

Synthesis of **2-B(Ph)Me**



$PhBCl_2$ (0.013 mL, 0.1 mmol) was added to a bright orange solution of **2** (0.52 g, 0.010 mmol) in DCM (0.7 mL) in a J. Young's NMR tube resulting in a colour change to dark green and the reaction mixture was rotated for 16 hours. 2,6-Lutidine (0.011 mL, 0.1 mmol) was added to the reaction mixture and after rotating for 16 hours the solvent was removed under reduced pressure to leave a dark blue/green residue. The residue was dissolved in benzene (0.7mL) and $AlMe_3$ (2M solution in heptanes) (0.05 mL, 0.01 mmol) was added. After the reaction mixture had been rotated for 16 hour the excess $AlMe_3$ and solvent were removed under reduced pressure. The crude product was purified by chromatography on base treated (5% NEt_3 in hexane) silica gel by using hexane as eluent and **2-B(Ph)Me** was isolated as a dark blue residue (22.1mg, 35%).

^{1}H NMR (400 MHz, C_6D_6) δ = 7.83 (d, *J* = 3.5 Hz, 1 H), 7.77 (d, *J* = 7.6 Hz, 1 H), 7.46 (d, *J* = 7.6 Hz, 1 H), 7.35 - 7.29 (m, 2 H), 7.23 (t, *J* = 7.3 Hz, 2 H), 7.20 - 7.12 (m, 1 H), 6.85 (d, *J* = 3.5 Hz, 1 H), 6.75 (s, 1 H), 2.88 (t, *J* = 7.6 Hz, 2 H), 2.83 (t, *J* = 7.7 Hz, 2 H), 1.82 - 1.65 (m, 4 H), 1.50 - 1.22 (m, 20 H), 0.90 (dt, *J* = 2.0, 6.8 Hz, 6 H), 0.70 (s, 3 H)

^{13}C NMR (101 MHz, $CDCl_3$) δ =151.9, 149.0, 147.7, 147.3, 135.5, 131.7, 130.2, 129.9, 128.2, 127.7, 127.1, 126.0, 125.4, 125.3, 123.5, 121.0, 31.8, 31.6, 31.5, 30.9, 30.5, 30.2, 29.3, 29.3, 29.2, 29.1, 22.6, 14.1;

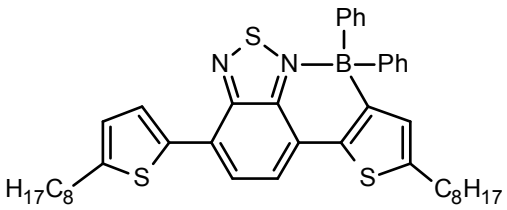
All $\underline{C}H_2$ resonances were not distinctly observed due to similar magnetic environments. No peak was observable in the ^{11}B NMR.

MALDI-TOF: calc. for $C_{36}H_{44}BN_2S_3^+$ [M - C_6H_5]$^+$ 611.8, found 612

^{11}B NMR (128.4 MHz, $CDCl_3$) δ = Not observed

MALDI-TOF: calc. for $C_{36}H_{44}BN_2S_3^+$ $[M - CH_3]^+$ 611.8, found 611.8

Synthesis of compound **2-BPh$_2$**



BCl_3 (1M solution in DCM) (0.12 mL, 0.12 mmol) was added to a bright orange solution of **2** (0.50 g, 0.1 mmol) in DCM (3 mL) in a Schlenk flask. The reaction mixture was stirred for 16 hours under a dynamic flow of nitrogen, where upon a colour change to dark blue was observed. The solvent and excess BCl_3 was removed under reduced pressure to yield a dark blue residue. The residue was redissolved in toluene and $Zn(Ph)_2$ (50 mg, 0.23 mmol) was then added to the reaction mixture and stirred for 3 hours the solution was then filtered through silica gel and the solvent was removed under reduced pressure to afford **2-BPh$_2$** as a dark blue residue. (Yield 46mg, 69%).

^{1}H NMR (400MHz ,$CDCl_3$) δ = 7.76 (d, *J* = 3.7 Hz, 1 H), 7.65 (d, *J* = 7.6 Hz, 1 H), 7.38 (d, *J* = 7.7 Hz, 1 H), 7.31 - 7.14 (m, 10 H), 6.84 - 6.76 (m, 2 H), 2.87 (t, *J* = 7.6 Hz, 2 H), 2.81 (t, *J* = 7.6 Hz, 2 H), 1.73 (quind, *J* = 7.6, 15.1 Hz, 4 H), 1.49 - 1.20 (m, 20 H), 0.98 - 0.83 (m, 6 H);

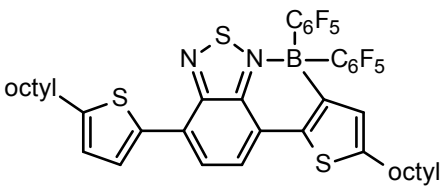
^{13}C NMR (101MHz , $CDCl_3$) δ = 160.7 (broad), 154.0 (broad), 151.5, 148.9, 147.8, 147.4, 135.4, 133.2, 130.9, 130.3, 127.9, 127.6, 127.3, 126.0, 125.4, 124.9, 123.6, 121.6, 31.9, 31.8, 31.6, 31.5, 30.5, 30.2, 29.3, 29.3, 29.2, 29.2, 29.1, 22.7, 14.1;

A number of the $\underline{C}H_2$ resonances were not distinctly observed due to similar magnetic environments.

^{11}B NMR (128.4 MHz, $CDCl_3$) δ = Not observed

MALDI-TOF: calc. for $C_{36}H_{44}BN_2S_3^+$ $[M - C_6H_5]^+$ 611.8, found 612

Synthesis of **2-B(C_6F_5)$_2$**



$Zn(C_6F_5)_2$ (152mg, 0.4mmols) was added to a toluene (5mL) solution of **2-BCl$_2$** (115 mg, 0.19 mmol), the reaction mixture was stirred for 3 hours and then after the addition of wet toluene the solution was passed through a plug of silica. Solvent was removed under reduced pressure to afford a dark blue residue (Yield 151mg, 92%).

^{1}H NMR (400MHz ,$CDCl_3$) δ = 7.88 (d, *J* = 3.8 Hz, 1 H), 7.83 (d, *J* = 7.6 Hz, 1 H), 7.61 (d, *J* = 7.6 Hz, 1 H), 6.89 (d, *J* = 3.5 Hz, 1 H), 6.78 (s, 1 H), 2.89 (t, J=7.6, 2 H), 2.82 (t, J=7.6, 2H), 1.81 - 1.64 (m, 4 H), 1.49 - 1.20 (m, 20 H), 0.89 (t, J= 6.8, 3H), 0.88 (t, J=6.8, 3 H);

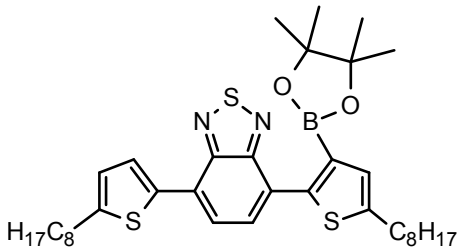
^{13}C NMR (126MHz , $CDCl_3$) δ = 150.4, 148.9, 147.8, 146.0, 133.8, 128.8, 127.0, 127.0, 124.6, 123.4, 122.7, 122.6, 30.8, 30.8, 30.5, 30.5, 29.4, 29.3, 28.3, 28.3, 28.2, 28.1, 28.1, 21.6, 21.6, 13.0, 13.0;

^{19}F NMR (376MHz, $CDCl_3$) δ = -132.43 (dd, J=22.56, 7.90, 4F), -156.58 (t, 20.30, 2F), -162.40 (m, 4F);

^{11}B NMR (128.4 MHz, $CDCl_3$) δ = Not observed

MALDI-TOF: calc. for $C_{42}H_{39}BN_2SF_{10}^+$ 1000.4913.4, found 913.4

Synthesis of compound **2-BPin**



2-BCl$_2$ (83mg, 0.14 mmols) was dissolved in 'wet' THF (5mL) and the dark blue solution was stirred overnight at room temperature were upon the solution had changed colour to dark orange/red. Pinacol (77mg, 0.65 mmols) was then added to the orange/red solution and the reaction mixture stirred overnight. The reaction mixture was then filtered through base treated [hexane/NEt_3 (95:5)] silica gel using hexane as eluent. The solvent was removed under reduced pressure to give **2-BPin** as a dark orange residue (Yield 76mg, 85%).

^{1}H NMR (500MHz ,$CDCl_3$) δ = 7.98 (d, *J* = 3.8 Hz, 1 H), 7.79 (d, *J* = 7.6 Hz, 1 H), 7.73 (d, *J* = 7.3 Hz, 1 H), 7.17 (s, 1 H), 6.90 (d, *J* = 3.8 Hz, 1 H), 2.89 (td, *J* = 7.4, 14.2 Hz, 4 H), 1.85 - 1.67 (m, 4 H), 1.47 - 1.23 (m, 20 H), 1.19 (s, 12 H), 0.99 - 0.80 (m, 6 H);

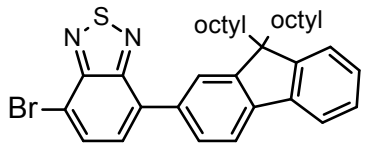
^{13}C NMR (126MHz , $CDCl_3$) δ = 154.4, 152.2, 147.8, 147.0, 145.4, 136.9, 130.9, 129.7, 127.5, 126.9, 126.7, 125.2, 124.6, 83.3, 31.8, 31.6, 30.3, 29.9, 29.3, 29.2, 29.2, 29.2, 29.1, 24.8, 22.6, 14.1;

A number of the $\underline{C}H_2$ resonances were not distinctly observed due to similar magnetic environments.

^{11}B NMR (128.4 MHz, $CDCl_3$) δ = ~29;

MALDI-TOF: calc. for $C_{36}H_{51}O_2BN_2S_3^+$ 650.8, found 650.9

Synthesis of **4-bromo-7-(9,9-dioctyl-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazole**



4,7-dibromobenzo[c][1,2,5]thiadiazole (2.7 g, 9.3 mmol), tri^{n}butyl(9,9'-dioctyl-9*H*-fluoren-2-yl)-stannane, (75 g, 11 mmol) and $PdCl_2(PPh_3)_2$ (0.64 g, 0.092 mmol) were mixed in dry THF (80 ml) under an nitrogen atmosphere and stirred for 36 h under reflux. The mixture was cooled to room temperature and then diluted with ethyl acetate (100mL). The reaction mixture was then washed with brine (2 x 100mL), water (2 x 200mL), and then dried over $MgSO_4$. After evaporating the solvent, the residue was purified by column chromatography on silica gel [eluent: hexane/DCM (9/1)] to afford bromo-7-(9,9-dioctyl-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazole as a yellow viscous oil. Yield: 2.27g, 54%.

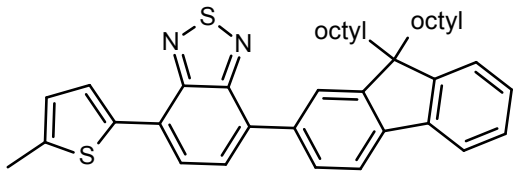
^{1}H NMR (400MHz ,$CDCl_3$) δ = 7.96 (d, *J* = 7.6 Hz, 1 H), 7.94 - 7.90 (m, 1 H), 7.89 - 7.81 (m, 2 H), 7.80 - 7.73 (m, 1 H), 7.66 (d, *J* = 7.6 Hz, 1 H), 7.42 - 7.31 (m, 3 H), 2.02 (td, *J* = 7.0, 9.7 Hz, 4 H), 1.26 - 1.00 (m, 20 H), 0.85 - 0.63 (m, 10 H);

^{13}C NMR (126MHz , $CDCl_3$) δ = 154.0, 153.3, 151.3, 151.2, 141.7, 140.4, 135.2, 134.6, 132.3, 128.1, 127.9, 127.4, 126.9, 123.8, 123.0, 120.0, 119.8, 112.6, 55.2, 40.2, 31.8, 30.0, 29.2, 23.8, 22.6, 14.0;

MALDI-TOF: calc. for $C_{35}H_{43}N_2SBr^+$ $[M + H]^+$ 604.7, found 604.7

This material contained an unidentified minor impurity which could not be removed, but the material was used in the next step with no issues.

Synthesis of **3**



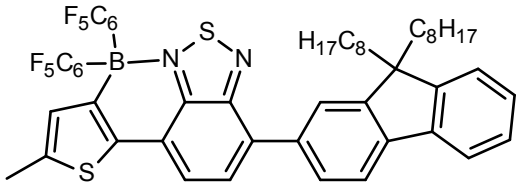
4-bromo-7-(9,9-dioctyl-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazole (250 mg, 0.41 mmols), trimethyl(5-methylthiophen-2-yl)stannane (180 mg, 0.689 mmols) and $Pd(PPh_3)_4$ (23 mg, 0.04 mmols) were dissolved in THF (4 mL) and the reaction mixture was stirred at 90°C in sealed ampule for 20 hours. The reaction mixture was allowed to cool and purified by column chromatography on silica gel [eluent: hexane/DCM (4/1)] to afford **3** as a dark orange residue. Yield: 225 mg, 88%.

^{1}H NMR (400MHz ,$CDCl_3$) δ = 8.07 - 7.93 (m, 3 H), 7.88 (d, *J* = 7.7 Hz, 2 H), 7.80 (t, *J* = 6.8 Hz, 2 H), 7.47 - 7.34 (m, 3 H), 6.90 (d, *J* = 2.7 Hz, 1 H), 2.61 (s, 3 H), 2.19 - 1.95 (m, 4 H), 1.28 - 1.04 (m, 20 H), 0.90 - 0.72 (m, 10 H);

^{13}C NMR (101MHz , $CDCl_3$) δ = 154.0, 152.7, 151.2, 151.0, 141.5, 141.2, 140.6, 137.1, 135.9, 132.7, 128.0, 127.8, 127.5, 127.2, 126.8, 126.3, 126.2, 125.1, 123.7, 122.9, 119.9, 119.6, 55.1, 40.2, 31.8, 30.0, 29.2, 29.2, 23.8, 22.6, 15.5, 14.1;

MALDI-TOF: calc. for $C_{35}H_{43}N_2SBr^+$ 621.0, found 620.9

Synthesis of **3-B(C_6F_5)$_2$**



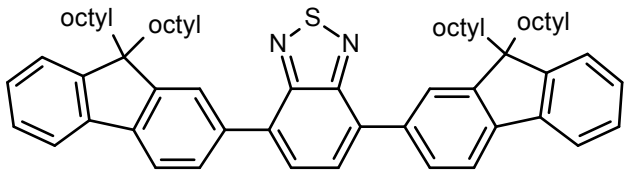
BCl_3 (1M solution in Heptanes) (0.12 mL, 0.12 mmols) was added to an orange solution of **3** dissolved in DCM (3 mL). The reaction mixture instantly changed colour from orange to blue. The reaction mixture was stirred for 16 hours. The solvent and excess BCl_3 was removed under reduced pressure and the residue was dissolved in Toluene. $Zn(C_6F_5)_2$ (70 mg, 0.18 mmols) was added to the reaction mixture and after 2 hours the reaction

mixture was filtered through silica. The solvent was removed under reduced pressure and NMR analysis of the reaction mixture indicated that **3-B(C_6F_5)$_2$** was the major product with a minor impurity of another regioisomer (borylated onto fluorene) present.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 - 7.89 (m, 2 H), 7.87 (d, *J* = 1.0 Hz, 2 H), 7.81 - 7.71 (m, 2 H), 7.42 - 7.34 (m, 3 H), 6.81 (s, 1 H), 2.55 (s, 3 H), 2.03 (dd, *J* = 5.2, 10.7 Hz, 4 H), 1.24 - 1.04 (m, 20 H), 0.80 (t, *J* = 7.1 Hz, 6 H), 0.71 (m, 4 H);

^{19}F NMR (376 MHz , $CDCl_3$) δ = -131.43 (dd, J=24.28, 8.66, 4F), -156.54 (t, 21.08, 2F), -162.39 (m, 4F) ppm;

Synthesis of **4**



4,7-dibromobenzo[c][1,2,5]thiadiazole (1.36 g, 4.6 mmol), tri^{n}butyl(9,9'-dioctyl-9*H*-fluoren-2-yl)-stannane, (6.70 g, 10.2 mmol) and $PdCl_2(PPh_3)_2$ (0.33 g, 0.047 mmol) were mixed in dry THF (80 ml) under an nitrogen atmosphere and stirred for 36 h at 80 °C under reflux. The mixture was cooled to room temperature and then diluted with ethyl acetate (100mL). The reaction mixture was then washed with brine (2 x 100mL), water (2 x 200mL), and then dried over $MgSO_4$. After evaporating the solvent, the residue was purified by column chromatography on silica gel [eluent: hexane/DCM (9/1)] to afford **4** as a yellow viscous oil. Yield: 1.73g, 41%.

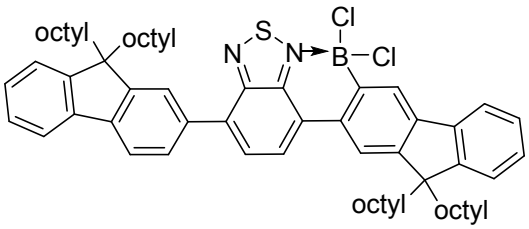
^{1}H NMR (500 MHz, $CDCl_3$) δ =8.04 (dd, J=1.5, 8 Hz, 2H), 7.96 (d, J=1.0 Hz, 2H), 7.90 (s, 2H), 7.88 (d, J=8 Hz, 2H), 7.79 (dd, J=1.0, 6.5, 2H), 7.41-7.33 (m, 6H), 2.05 (m, 8H), 1.25 - 1.07 (m, 40H), 0.81 (t, J=7.0, 6H), 0.79 (m, 8H);

^{13}C NMR (126 MHz, $CDCl_3$) δ = 154.4, 151.3, 151.1, 141.3, 140.7, 136.2, 133.6, 128.1, 127.9, 127.2, 126.8, 123.9, 123.0, 119.9, 119.7, 55.2, 40.3, 31.8, 30.1, 29.2, 29.2, 23.9, 22.6, 14.0;

MALDI-TOF: calc. for $C_{64}H_{84}N_2S^+$ 913.4, found 913.4

The spectra for **4** are consistent with that reported previously: Hung-Min Shih, Ren-Chi Wu, Ping-I Shih, Chien-Lung Wang, Chain-Shu Hsu, Journal of Polymer Science, Part A: Polymer Chemistry, 50(4), 696-710; 2012.

Synthesis of **4-BCl_2**



A 1M BCl_3 solution in DCM (0.15 mL, 0.12 mmol) was added to a bright yellow solution of **4** (0.078 g, 0.085 mmol) in DCM (3 mL) in a Schlenk flask. The reaction mixture was stirred for 16 hours under a dynamic flow of nitrogen (in a closed system some HCl remains in solution, thus borylation is reversible due to protodeboronation of **4-BCl_2** and an equivalent of Brønsted base is then required to drive borylation to completion by sequestering the protic by-product), where upon a colour change to dark blue was observed. The solvent and excess BCl_3 was removed under reduced pressure to yield a dark blue residue.

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 8.61 (d, *J* = 7.6 Hz, 1 H), 8.40 (s, 1 H), 8.16 (d, *J* = 7.3 Hz, 1 H), 8.08 (s, 1 H), 8.06 - 7.99 (m, 2 H), 7.90 (d, *J* = 6.9 Hz, 1 H), 7.96-7.88 (m, 2 H), 7.48 - 7.32 (m, 6 H), 2.21 - 1.99 (m, 8 H), 1.25 - 1.02 (m, 40 H), 0.81 (t, *J* = 6.6 Hz, 6 H), 0.80 (t, *J* = 6.6 Hz, 6 H), 0.74 (m., 8 H);

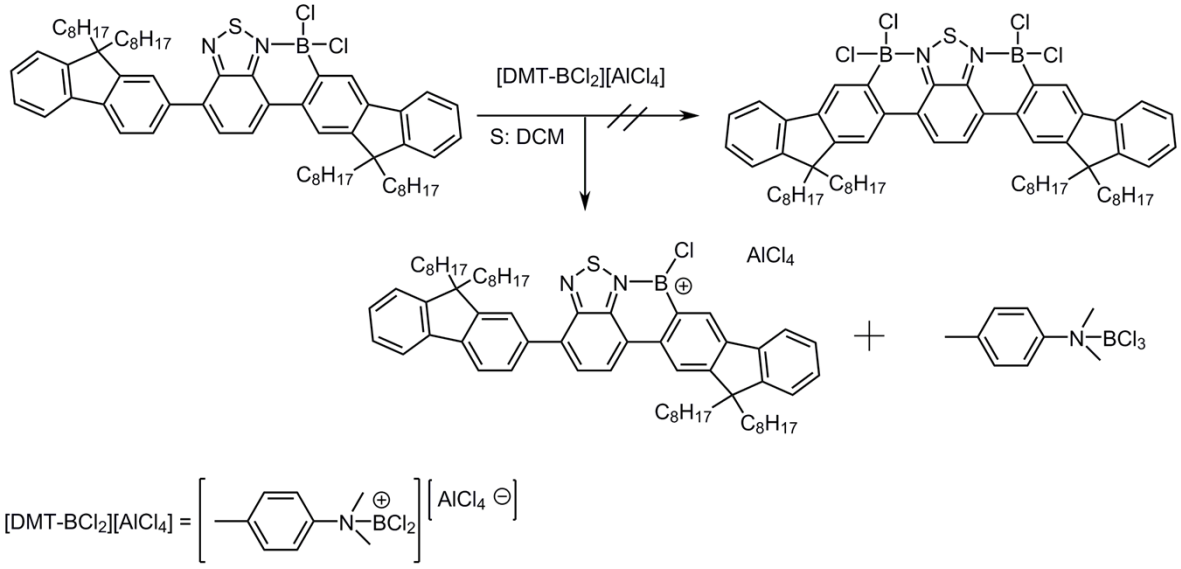
^{13}C NMR (126 MHz, CD_2Cl_2) δ = 155.4, 153.5, 153.4, 153.3, 153.3, 147.5, 145.2, 144.6, 142.3, 142.1, 135.7, 135.4, 132.9, 130.1, 129.9, 129.8, 129.6, 128.9, 128.9, 128.4, 126.9, 125.8, 125.1, 124.9, 122.5, 122.1, 122.0, 118.3, 57.3, 57.1, 42.4, 42.1, 33.7, 32.0, 31.9, 31.1, 31.1, 25.9, 25.8, 24.5, 24.5, 15.7;

A number of $\underline{C}H_2$ or $\underline{C}H$ resonances were not distinctly observed due to similar magnetic environments.

^{11}B NMR (128.4 MHz, CD_2Cl_2): δ = 10.0 (s);

Due to its sensitivity **4-BCl_2** was not amenable to characterisation by mass spec., instead it is functionalised in-situ to generate more stable species (see below).

Synthesis of **[4-BCl]$^+$**

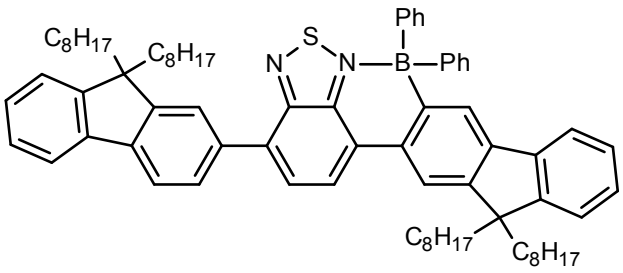


Attempts to form fully fused systems from **4** using highly electrophilic three coordinate borocations resulted instead in halide abstraction from **4-BCl$_2$** to form **[4-BCl]$^+$**.

A preformed tricoordinate borenium [DMT-BCl$_2$][AlCl$_4$] (0.06 mmols) was added to a dark blue solution of **4-BCl$_2$** (60mg, 0.06 mmol) in DCM. The solution turned a dark green colour and NMR spectroscopy showed a significant downfield shift in the NMR resonances relative to that of **4-BCl$_2$**. The formation of DMT-BCl$_3$ adduct was also confirmed in solution by multinuclear NMR spectroscopy.[8] These observations are consistent with the chloride abstraction from **4-BCl$_2$** to form **[4-BCl]$^+$**.

^{1}H NMR (400MHz ,$CDCl_3$) δ = 9.27 (d, *J* = 7.8 Hz, 1 H), 8.81 (s, 1 H), 8.57 - 8.42 (m, 2 H), 8.20 - 8.12 (m, 2 H), 8.00 (d, *J* = 7.8 Hz, 2 H), 7.85 (m, 1 H), 7.51 (m., 6 H), 2.31 - 2.02 (m, 8 H), 1.24 - 0.94 (m, 40 H), 0.79 (m, *J* = 6.9 Hz, 20 H);

Synthesis of **2-BPh$_2$**



$Zn(Ph)_2$ (110 mg, 0.5 mmol) was added to a DCM (5mL) solution of **4-BCl$_2$** (212 mg, 0.213 mmol, made in-situ as described above), the reaction was stirred for 3 hours and then the solution was filtered through silica gel and the solvent removed under reduced pressure to afford **4-BPh$_2$** as a dark purple residue. (Yield 231 mg, 0.213 mmol 99%).

^{1}H NMR (400MHz ,$CDCl_3$) δ = 8.52 (d, *J* = 7.8 Hz, 1 H), 8.18 (s, 1 H), 8.12 (d, *J* = 7.6 Hz, 1 H), 8.06 (s, 1 H), 8.01 (d, *J* = 7.9 Hz, 1 H), 7.95 (d, *J* = 8.0 Hz, 1 H), 7.95 (s, 1 H), 7.87 (dd, *J* = 2.4, 5.4 Hz, 1 H), 7.76 - 7.68 (m, 1 H), 7.53 - 7.24 (m, 16 H), 2.27 – 2.03 (m, 8 H), 1.36 - 1.20 (m, 40 H), 1.00 - 0.76 (m, 20 H) ;

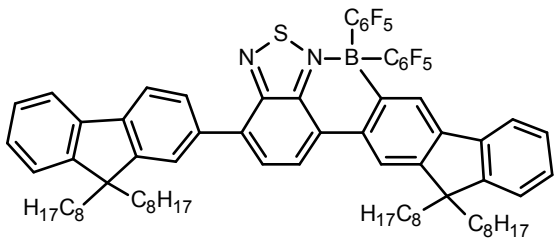
^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.3, 153.0, 152.2, 151.3, 149.1, 147.8, 142.4, 140.7, 135.3, 133.6, 130.1, 128.9, 127.6, 127.4, 126.7, 126.1, 125.8, 123.5, 122.7, 120.6, 116.4, 110.5, 54.8, 40.6, 31.7, 30.0, 29.2, 29.1, 23.9, 22.5, 14.0

^{11}B NMR (128.4 MHz, CD_2Cl_2): δ = ~2.0 (Broad singlet);

A number of the $\underline{C}H_2$ or $\underline{C}H$ resonances were not distinctly observed due to similar magnetic environments.

MALDI-TOF: calc. for $C_{70}H_{88}BN_2S^+$ $[M - C_6H_5]^+$ 1000.4, found 1000.5

Synthesis of **4-B(C_6F_5)$_2$**



$Zn(C_6F_5)_2$ (97 mg, 0.242 mmol) was added to a toluene (5mL) solution of **4-BCl_2** made in-situ (110 mg, 0.11 mmol), the reaction mixture was stirred for 3 hours and then after the addition of 'wet' toluene (unpurified toluene used as received) to quench unreacted diaryl zinc reagent the solution was purified via silica gel chromatography (eluent hexane) to afford a dark purple residue. (Yield 131 mg, 94%).

^{1}H NMR (400MHz ,$CDCl_3$) δ = 8.58 (d, *J* = 8.1 Hz, 1 H), 8.21 - 8.07 (m, 2 H), 8.03 (s, 1 H), 7.94 (m., 2 H), 7.89 - 7.78 (m, 2 H), 7.74 (br. s., 1 H), 7.49 - 7.30 (m, 6 H), 2.11 (m., 8 H), 1.13 (m 40 H), 0.89 - 0.66 (m, 20 H);

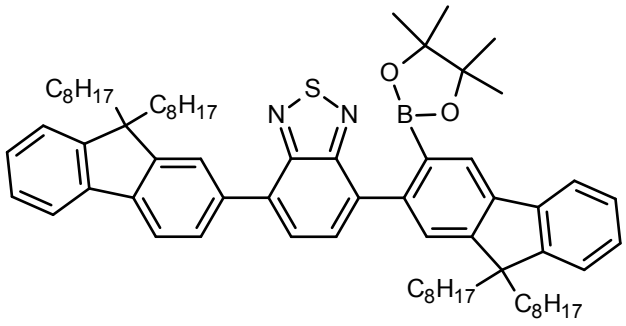
^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.7, 151.5, 151.3, 151.3, 150.2, 147.8, 143.0, 142.4, 140.4, 140.2, 133.6, 133.0, 131.0, 128.1, 128.1, 127.9, 127.8, 127.7, 127.0, 126.9, 125.8, 124.3, 123.8, 123.0, 122.9, 120.4, 120.2, 120.1, 116.3, 55.3, 55.0, 40.7, 40.3, 31.8, 30.1, 30.0, 29.2, 29.2, 29.2, 23.9, 23.8, 22.6, 22.6, 14.0, 14.0;

^{19}F NMR (376MHz , $CDCl_3$) δ = -131.55 (dd, J=23.31, 8.65, 4F), -156.65 (t, 20.68, 2F), -162.62 (m, 4F) ppm;

^{11}B NMR (128.4 MHz, CD_2Cl_2): δ =~ -4.0 (Broad).

MALDI-TOF: calc. for $C_{70}H_{83}BF_5N_2S^+$ $[M - C_6F_5]^+$ 1090.3, found 1090.4

Synthesis of **4-BPin**



A 1M BCl_3 solution in DCM (0.1 mL, 0.1 mmol) was added to a bright yellow solution of **4** (0.071 g, 0.078 mmol) in DCM (3 mL). The reaction mixture was stirred for 16 hours under a dynamic flow of nitrogen, where upon a colour change to dark blue was observed. The solvent and excess BCl_3 was removed under reduced pressure to yield a dark blue residue of **4-BCl_2**. This residue was dissolved in 'wet' THF (5 mL) and stirred at room temperature for 16 hous where upon the solution had turned dark yellow. Pinacol (47 mg, 0.4 mmols) was then added and the reaction mixture was stirred for a further 16 hours. The solvent was removed under reduced pressure and the resulting residue was purifed via base treated [hexane/NEt_3 (95:5)] preparative TLC plate using hexane as eluent. Yield (35 mg, 43%).

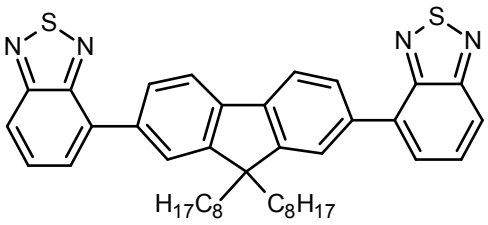
^{1}H NMR (400MHz ,$CDCl_3$) δ = 8.31 (s, 1 H), 8.12 - 8.06 (m, 1 H), 7.96 (s, 1 H), 7.94 - 7.83 (m, 3 H), 7.80 (d, *J* = 6.6 Hz, 1 H), 7.75 (d, *J* = 7.2 Hz, 1 H), 7.51 (s, 1 H), 7.45 - 7.30 (m, 6 H), 2.17 - 1.89 (m, 8 H), 1.25 - 1.05 (m, 40 H), 1.04 (s, 12 H), 0.82 (t, *J* = 7.0 Hz, 20 H);

^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.2, 153.7, 153.6, 151.3, 151.2, 150.9, 142.3, 141.2, 140.8, 140.7, 140.6, 136.6, 136.4, 133.3, 128.4, 128.1, 127.9, 127.3, 127.1, 126.9, 126.6, 124.7, 123.8, 123.0, 122.8, 120.2, 120.0, 119.7, 83.3, 55.4, 55.2, 40.3, 31.9, 31.8, 30.1, 30.1, 29.3, 29.3, 29.2, 24.7, 23.9, 23.9, 22.7, 14.2;

^{11}B NMR (128.4 MHz, CD_2Cl_2): δ =~ 30.0 (Broad).

MALDI-TOF: calc. for $C_{70}H_{83}BO_2N_2S^+$ $[M + H]^+$ 1038.7, found 1039.4

Synthesis of **5**



2-bromobenzothiadiazole (3.90 g, 1.84 mmol), 9,9-dioctylfluorene-2,7-diboronic acid (4.00 g, 8.36 mmol) , K_3PO_4 (10.65g, 5.016 mmol), $Pd_2(dba)_3$ (0.38g, 0.042 mmol) and S-Phos (0.168mmol) were dissolved in THF (120 mL) and heated at 70º C for 24 hours. The reaction mixture was then allowed to cool, filtered (to remove excess K_3PO_4), dissolved in EtOAc (200mL) and washed with water (3 x 100mL) and then with brine (1 x 100mL), dried ($MgSO_4$).and evaporated to dryness. After evaporating the solvent, the residue was purified by column chromatography on silica gel [eluent: hexane/ EtOAc 0-3%], and subsequent recrystallisation by slow evaporation of the eluent to afford **5** as yellow needles. Yield (3.40 g, 62%).

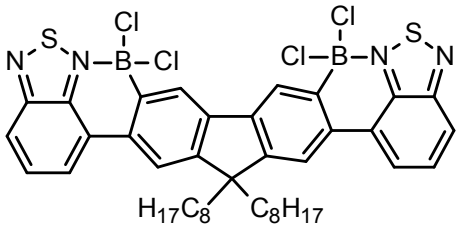
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.08 - 7.98 (m, 4 H), 7.98 - 7.87 (m, 4 H), 7.85 - 7.66 (m, 4 H), 2.17 - 2.06 (m, 4 H), 1.24 - 1.06 (m, 20 H), 0.88 (td, *J* = 4.4, 7.1 Hz, 4 H), 0.78 (t, *J* = 6.9 Hz, 6 H);

^{13}C NMR (101MHz , CD_2Cl_2) δ = 155.7, 153.7, 151.7, 140.9, 136.3, 135.0, 129.7, 128.3, 127.5, 124.0, 120.3, 120.0, 55.4, 40.2, 31.8, 30.1, 29.2, 24.0, 22.6, 14.0;

MALDI-TOF: calc. for $C_{41}H_{46}BN_4S_2^+$ 659.0, found 658.7

The spectra of **5** are consistent with that previously reported: Piyush Anant, Nigel T. Lucas and Josemon Jacob, Org. Lett., 2008, 10 (24), pp 5533–5536.

Synthesis of **5-(BCl_2)$_2$**



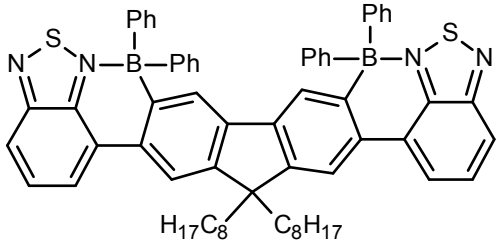
BCl_3 (1M solution in DCM) (0.40 mL, 0.40 mmol) was added to a bright yellow solution of **3** (66 mg, 0.1 mmol) in DCM (0.7mL) in a J. Young's NMR tube. The solution instantly changed colour to a dark red. 2,4,6-Tri^{t}butylpyridine (50 mg) and $AlCl_3$ (40mg, 0.3 mmol) were added as solids to the reaction mixture. After rotating for 16 hours, an additional portion of $AlCl_3$ (14 mg, 0.1 mmol) was added as a solid and the solution was rotated for a further 16 hours whereupon the solution had turned dark green. N^nBu_4Cl (48 mg, 0.2 mmol) was then added to the reaction mixture and the solution turned dark purple. NMR spectroscopy indicated full conversion to the desired product **5-(BCl_2)$_2$** and this reaction mixture was used directly in subsequent steps.

^{1}H NMR (400 MHz, DCM) δ=8.64 (d, *J* = 7.1 Hz, 2 H), 8.47 (s, 2 H), 8.33 - 8.20 (m, 4 H), 8.12 (s, 2 H), 2.19 (m., 4 H), 1.04 (m, 20 H), 0.72 (s, 10 H);

^{11}B NMR (128.4 MHz, CD_2Cl_2): δ = 10.0;

Due to the sensitivity of **5-(BCl_2)$_2$** mass spec were not obtainable.

Synthesis of **5-(BPh_2)$_2$**



A reaction mixture containing **5-(BCl_2)$_2$** (0.45 mmol) and the ionic by-products from borylation (e.g., ammonium[$AlCl_4$]) was dissolved in DCM (15mL) and $ZnPh_2$ (400 mg, 1.82 mmol) was added. The reaction mixture was then stirred for 16 hours after which it was passed through a plug of silica. The solvent was then removed under reduced pressure and the product was isolated by column chromatography on base treated [hexane/NEt_3 (95:5)] silica gel [eluent: hexane/ DCM (8:2)] Yield (236 mg, 53%).

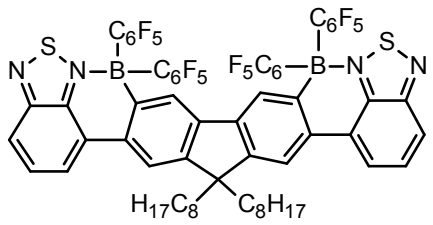
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.39 (d, *J* = 7.1 Hz, 2 H), 8.18 (s, 2 H), 7.90 - 7.77 (m, 6 H), 7.31 - 7.15 (m, 20 H), 2.32 - 2.13 (m, 4 H), 1.18 (m, 20 H), 0.97 (m., 4 H), 0.82 (t, *J* = 6.7 Hz, 6 H);

^{13}C NMR (101MHz, CD_2Cl_2) δ = 155.8, 155.3, 152.7, 150.4, 148.2, 142.4, 134.0, 133.7, 131.0, 130.4, 128.1, 126.5, 126.4, 123.9, 119.5, 117.3, 55.1, 41.3, 32.4, 30.7, 29.8, 24.7, 23.2, 14.4;

^{11}B NMR (128.4 MHz, CD_2Cl_2): δ = 2.0 (Broad);

MALDI-TOF: calc. for $C_{59}H_{59}B_2N_4S_2^+$ [M - C_6H_5]$^+$ 909.9, found 910.0

Synthesis of **5-($B(C_6F_5)_2)_2$**



A reaction mixture of **5-($BCl_2)_2$** (0.45 mmol) also containing the ionic by-products from borylation (e.g., ammonium[$AlCl_4$]) was dissolved in DCM (15mL) and $Zn(C_6F_5)_2$ (728 mg, 1.82 mmol) was added. The reaction mixture was then stirred for 16 hours after which it was passed through a plug of silica. The solvent was then removed under reduced pressure and the product was isolated by column chromatography on base treated [hexane/NEt_3 (95:5)] silica gel [eluent: hexane/ DCM (8:2)] Yield (435 mg, 71%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ =8.48 (d, *J* = 6.8 Hz, 2 H), 8.10 (s, 2 H), 8.02 - 7.85 (m, 4 H), 7.67 (s, 2 H), 2.25 - 2.05 (m, 4 H), 1.20-1.00 (m, 20 H), 0.78-0.68 (m, 10 H);

^{13}C NMR (101MHz, $CDCl_3$) δ = 154.9, 150.7, 147.0, 142.2, 133.5, 129.7, 128.7, 125.0, 125.0, 119.4, 116.5, 55.0, 40.9, 31.8, 30.0, 29.2, 29.1, 22.5, 14.0;

^{19}F NMR (376MHz , $CDCl_3$) δ = -132.23 (dd, J=22.56, 8.27, 8F), -157.83 (t, 20.68, 4F), -163.77 (m, 8F);

^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 3.0 (Broad);

MALDI-TOF: calc. for $C_{59}H_{44}B_2F_{15}N_4S_2^+$ $[M - C_6F_5]^+$ 1179.8, found 1179.7

Absorption & Emission Data

Solution state absorbance and emission data

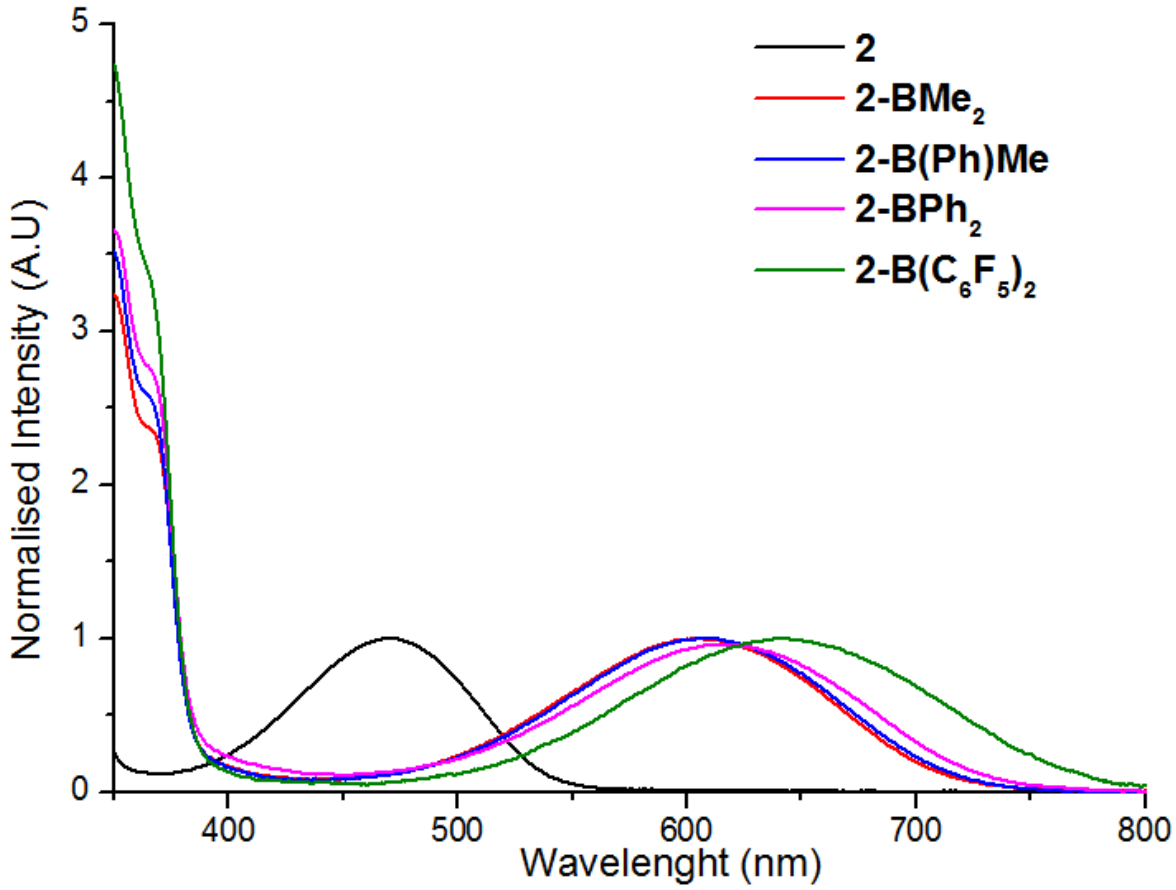


Figure S1. Absorption and fluorescence spectra of **2**, **2-BMe$_2$**, **2-B(Ph)Me**, **2-BPh$_2$** and **2-B(C$_6$F$_5$)$_2$** in toluene (1 x 10^{-5} M).

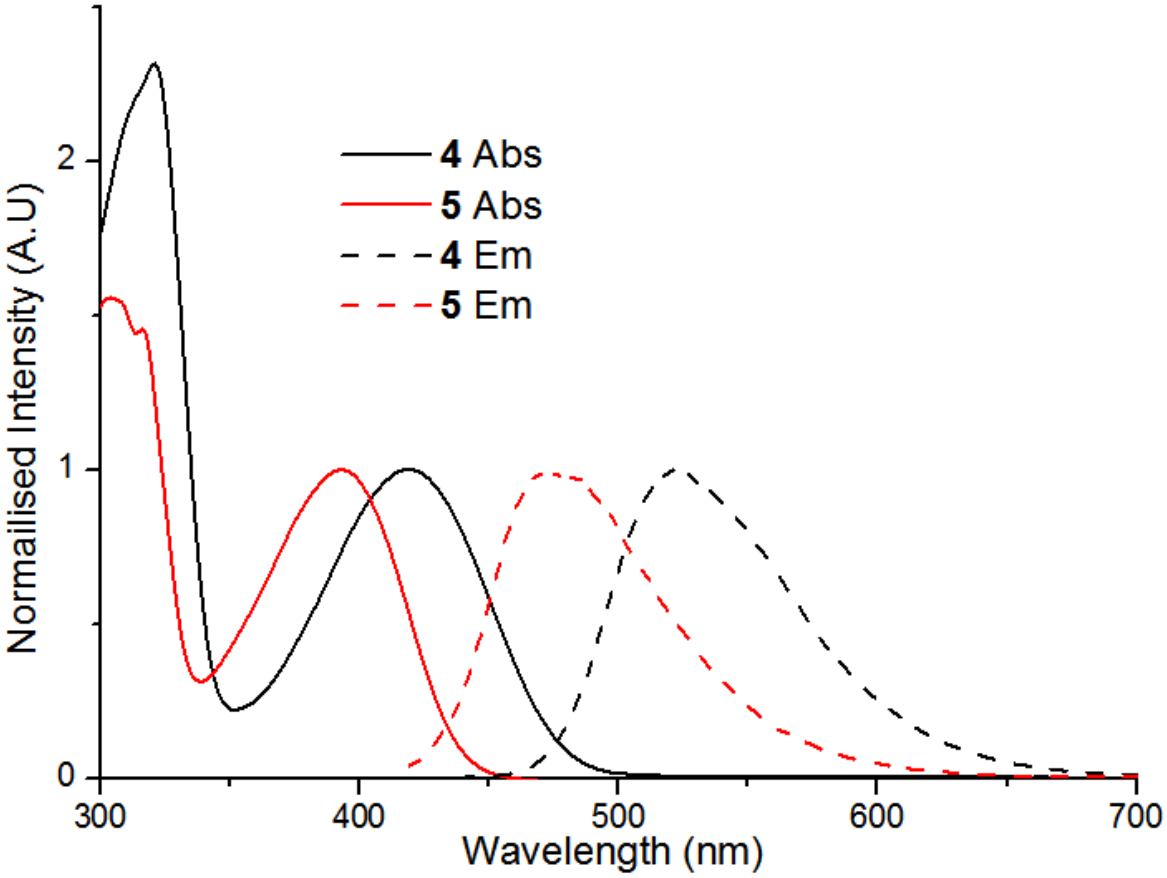


Figure S2. Absorption and fluorescence spectra of **4** and **5** in toluene (1 x 10^{-5} M).

4-BPh$_2$

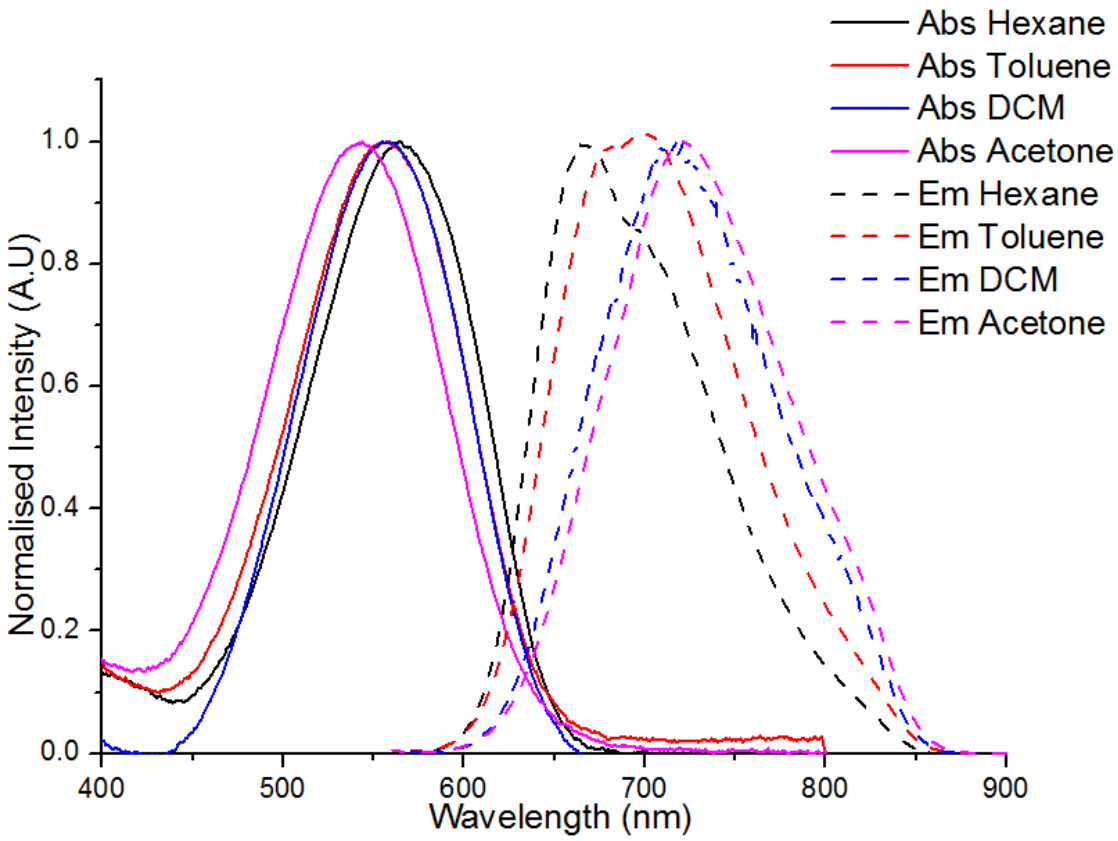


Figure S3. Absorption and fluorescence spectra of **4-BPh$_2$** in different solvents (1 x 10^{-5} M). Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

Solvent	$\lambda_{max\ abs}$	$\lambda_{max\ em}$	**Stokes shift**	ε
Hexane	565 nm	666 nm	101 nm	13800 M^{-1} cm^{-1}
Toluene	559 nm	702 nm	143 nm	12400 M^{-1} cm^{-1}
DCM	555 nm	717 nm	162 nm	12500 M^{-1} cm^{-1}
Acetone	544 nm	721 nm	177 nm	13400 M^{-1} cm^{-1}

Table S1. Absorption and fluorescence photophysical data of **4-BPh$_2$** in different solvents (1 x 10^{-5} M).

4-B(C_6F_5)$_2$

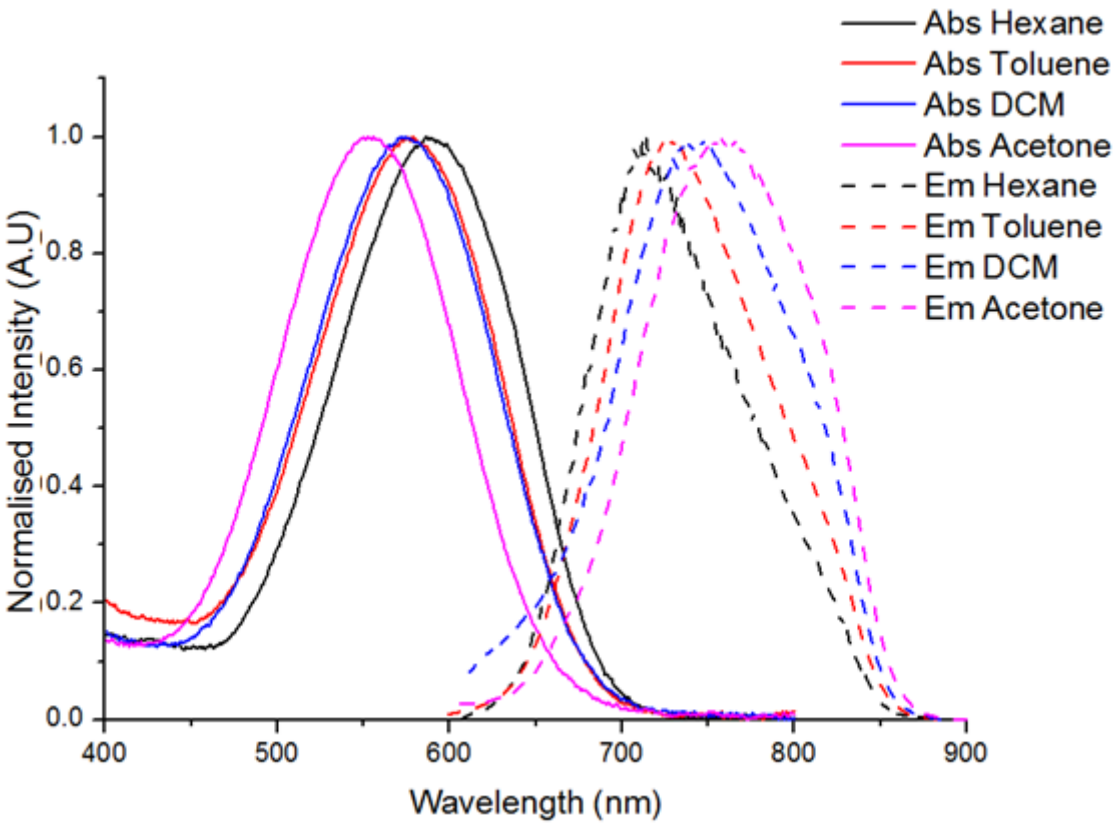


Figure S4. Absorption and fluorescence spectra of **4-B(C_6F_5)$_2$** in different solvents (1 x 10^{-5} M). Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

Solvent	$\lambda_{max\ abs}$	$\lambda_{max\ em}$	**Stokes shift**	ε
Hexane	586 nm	716 nm	130 nm	10300 M^{-1} cm^{-1}
Toluene	579 nm	730 nm	151 nm	9600 M^{-1} cm^{-1}
DCM	576 nm	748 nm	172 nm	10100 M^{-1} cm^{-1}
Acetone	556 nm	761 nm	205 nm	8700 M^{-1} cm^{-1}

Table S2. Absorption and fluorescence photophysical data of **4-B(C_6F_5)$_2$** in different solvents (1 x 10^{-5} M).

5-(BPh_2)$_2$

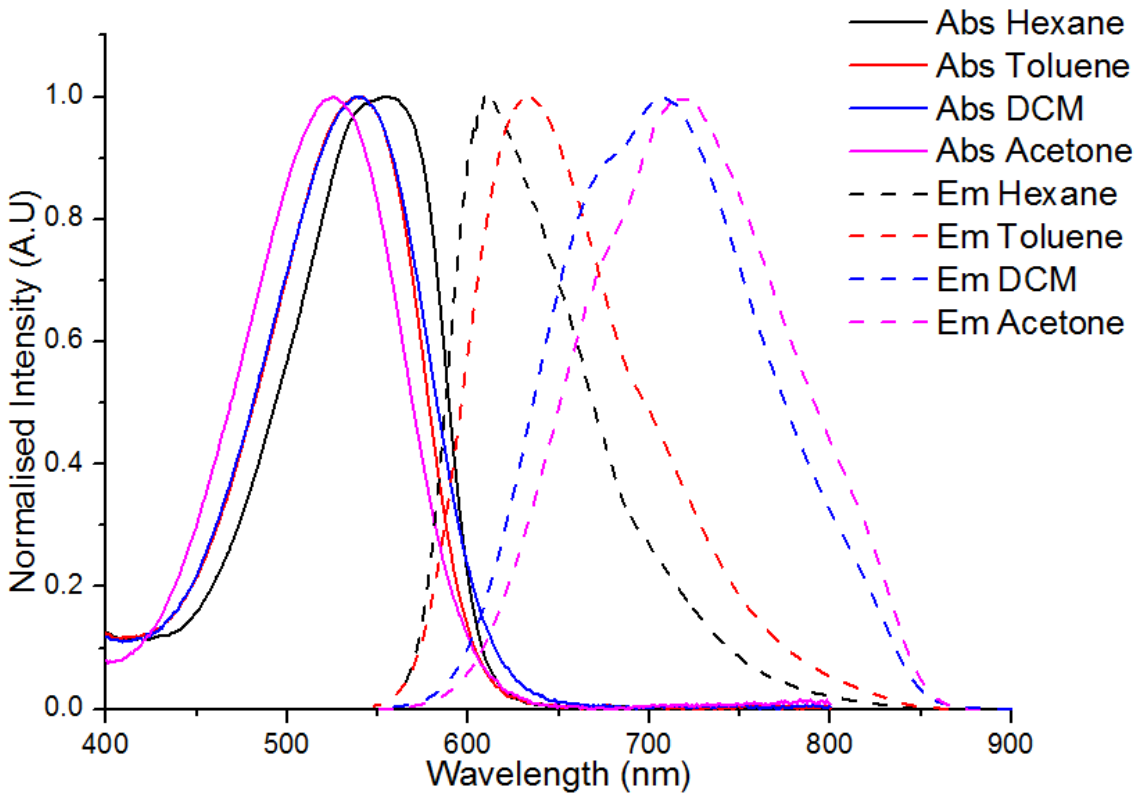


Figure S5. Normalised absorption and fluorescence spectra of **5-(BPh_2)$_2$** in different solvents (1 x 10^{-5} M). Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

Solvent	$\lambda_{max\ abs}$	$\lambda_{max\ em}$	**Stokes shift**	ε
Hexane	553 nm	609 nm	56 nm	19800 M^{-1} cm^{-1}
Toluene	538 nm	636 nm	98 nm	19500 M^{-1} cm^{-1}
DCM	541 nm	708 nm	167 nm	17600 M^{-1} cm^{-1}
Acetone	525 nm	717 nm	192 nm	16500 M^{-1} cm^{-1}

Table S6. Absorption and fluorescence photophysical data of **5-(BPh_2)$_2$** in different solvents (1 x 10^{-5} M).

5-($B(C_6F_5)_2)_2$

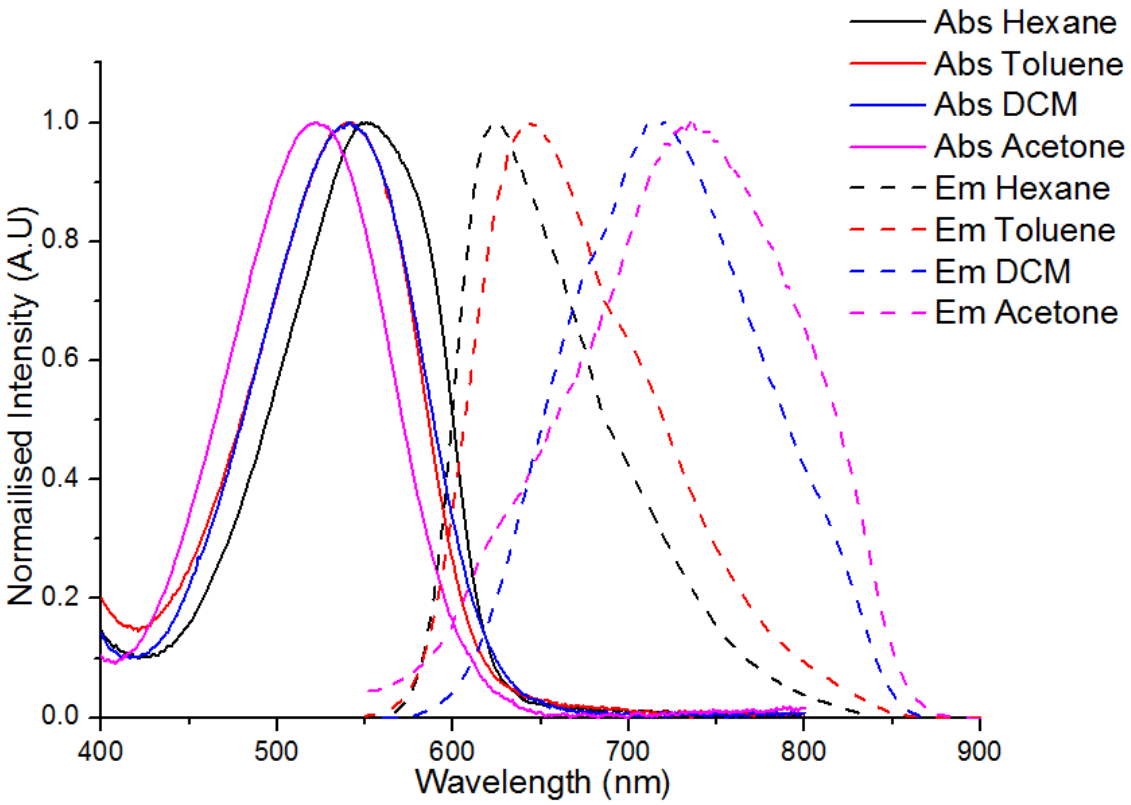


Figure S6. Absorption and fluorescence spectra of **5-($B(C_6F_5)_2)_2$** in different solvents (1 x 10^{-5} M). Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

Solent	$\lambda_{max\ abs}$	$\lambda_{max\ em}$	**Stokes shift**	**ε**
Hexane	551 nm	623 nm	72 nm	14900 M^{-1} cm^{-1}
Toluene	540 nm	645 nm	105 nm	14700 M^{-1} cm^{-1}
DCM	541 nm	721 nm	180 nm	13500 M^{-1} cm^{-1}
Acetone	522 nm	732 nm	210 nm	12100 M^{-1} cm^{-1}

Table S4. Absorption and fluorescence photophysical data of **5-($B(C_6F_5)_2)_2$** in different solvents (1 x 10^{-5} M).

Lippert Mataga Plots

.

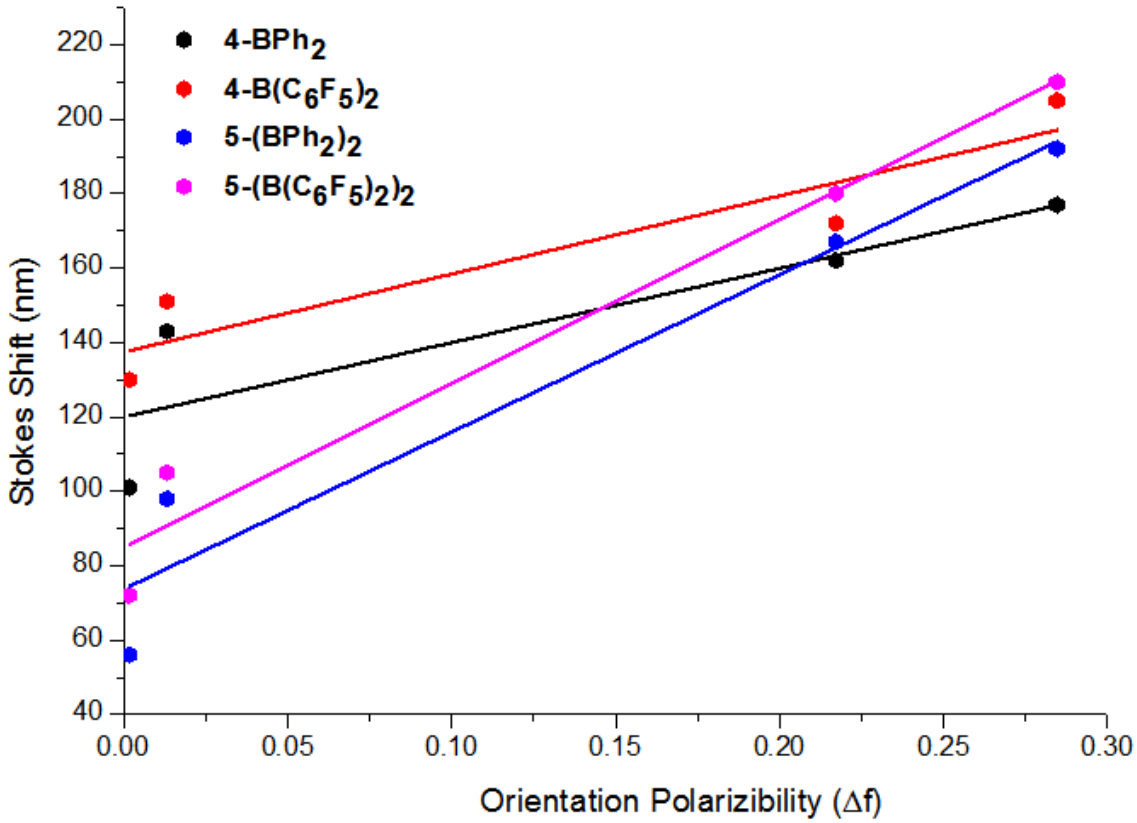


Figure S7. Lippert–Mataga plots of compounds **4-BPh$_2$**, **4-B(C$_6$F$_5$)$_2$**, **5-(BPh$_2$)$_2$** and **5-(B(C$_6$F$_5$)$_2$)$_2$**.

Solid state emission

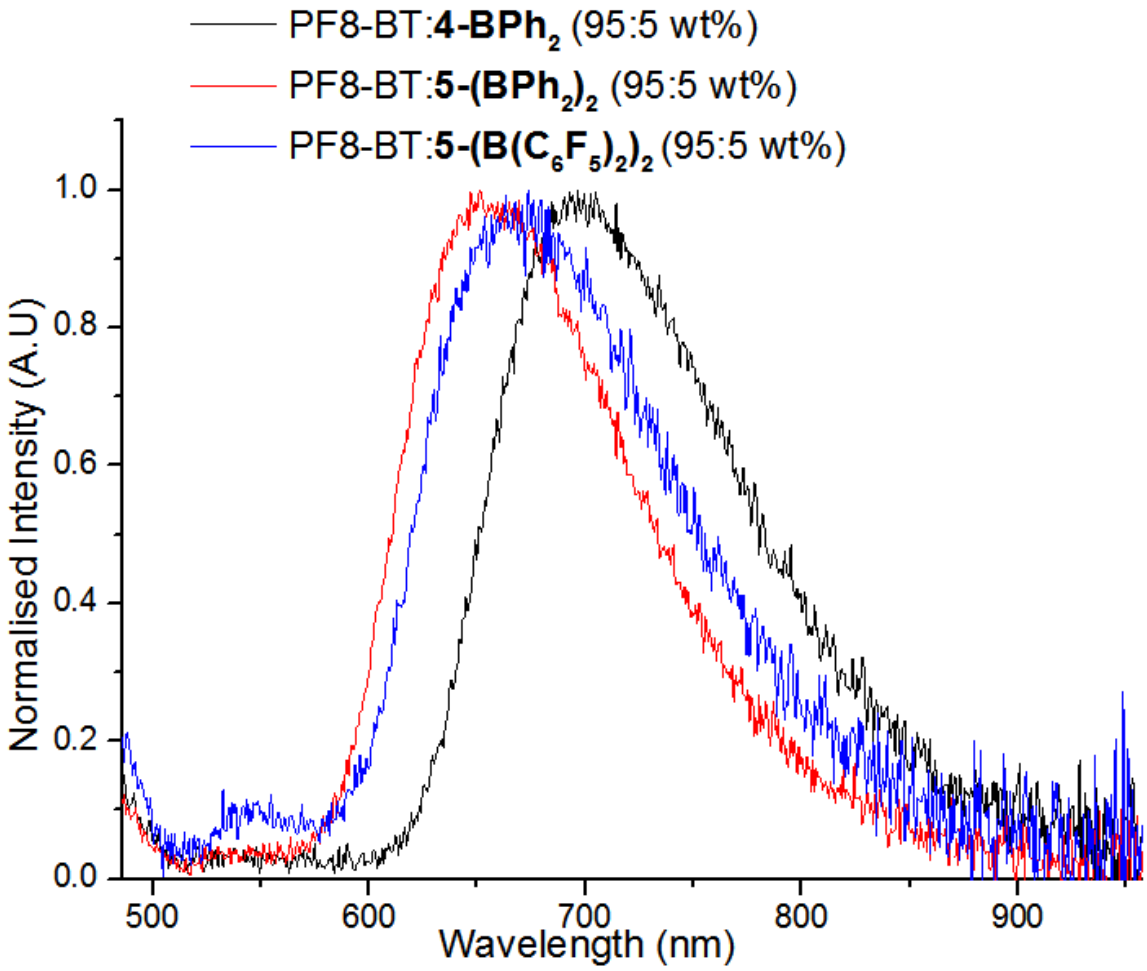


Figure S8. PL spectra of thin films from a 5 wt % mixture of compounds **4-BPh_2**, **5-$(BPh_2)_2$** and **5-$(B(C_6F_5)_2)_2$** dispersed in PF8-BT polymer spin coated from toluene, excited at 468 nm.

Film	Transmittance	PLQY %	CIE X	CIE Y
PF8-BT: **4-BPh_2** (95:5 wt%)	0.36	33.5	0.660	0.338
PF8-BT: **5-$(BPh_2)_2$** (95:5 wt%)	0.36	32.9	0.633	0.360
PF8-BT: **5-$(B(C_6F_5)_2)_2$** (95:5 wt%)	0.36	19.9	0.628	0.368

Table S5. Summary of thin films PL data of compounds **4-BPh_2**, **5-$(BPh_2)_2$** and **5-$(B(C_6F_5)_2)_2$**.

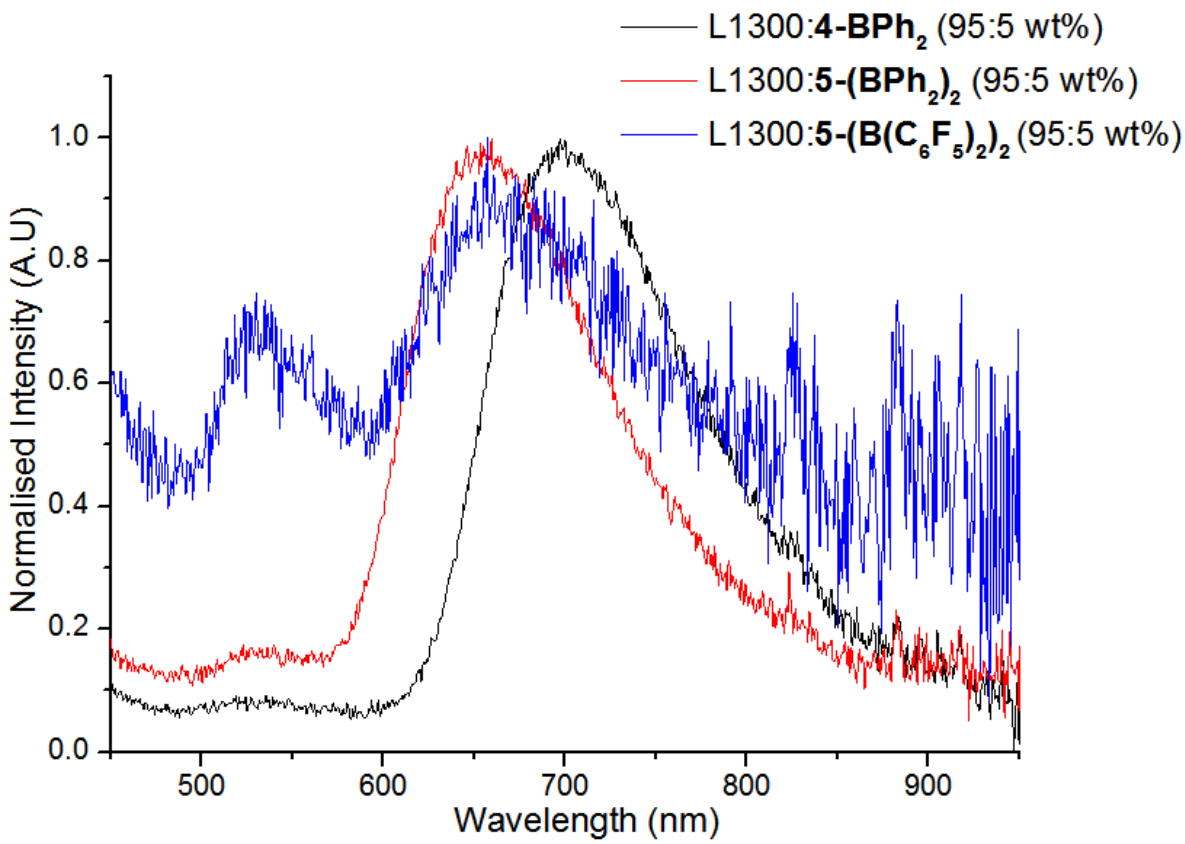


Figure S9. PL spectra of thin films from a 5 wt % mixture of compounds **4-BPh_2**, **5-$(BPh_2)_2$** and **5-$(B(C_6F_5)_2)_2$** dispersed in L1300 polymer spin coated from toluene, excited at 400 nm.

Film	Transmittance	PLQY %	CIE X	CIE Y
L1300: **4-BPh_2** (95:5 wt%)	0.32	24	0.592	0.339
L1300: **5-$(BPh_2)_2$** (95:5 wt%)	0.32	16	0.627	0.342
L1300: **5-$(B(C_6F_5)_2)_2$** (95:5 wt%)	0.32	3	0.455	0.452

Table S6. Summary of thin films PL data of compounds **4-BPh_2**, **5-$(BPh_2)_2$** and **5-$(B(C_6F_5)_2)_2$**.

Lifetime Data

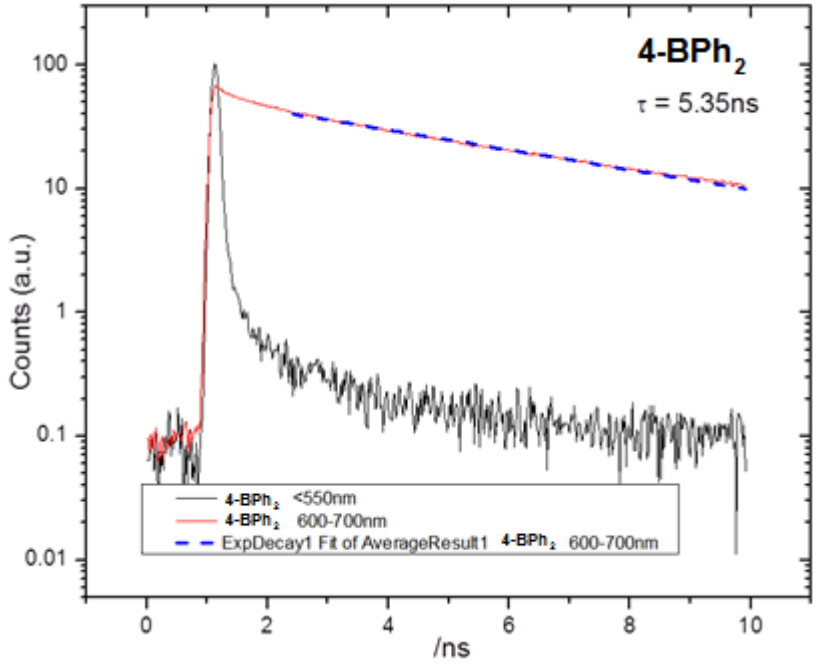


Figure S10. PL lifetime data of a thin film of a 5 wt % mixture of **4-BPh$_2$** dispersed in L1300 polymer spin coated from toluene, excited at 400 nm.

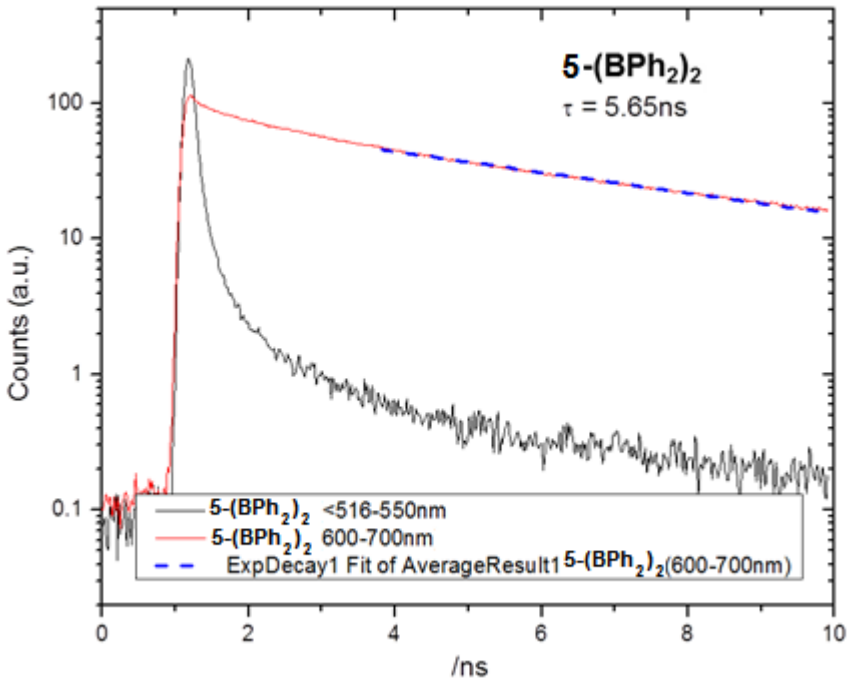


Figure S11. PL lifetime data of a thin film of a 5 wt % mixture of **5-(BPh$_2$)$_2$** dispersed in L1300 polymer spin coated from toluene, excited at 400 nm.

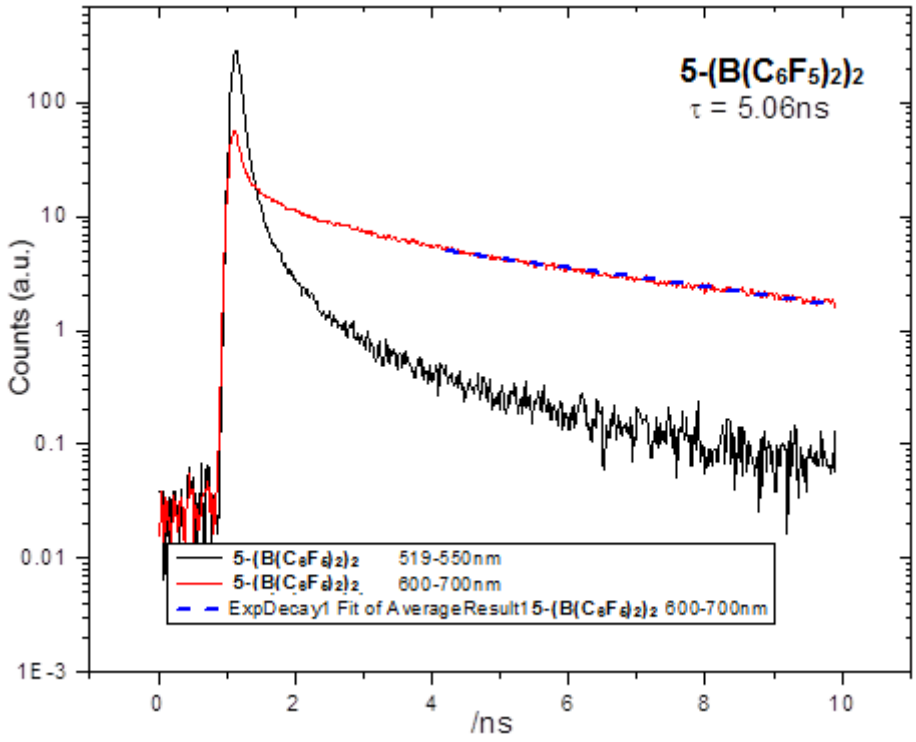


Figure S12. PL lifetime data of a thin film of a 5 wt % mixture of **5-(B(C$_6$F$_5$)$_2$)$_2$** dispersed in L1300 polymer spin coated from toluene, excited at 400 nm.

Cyclic voltammetry Data

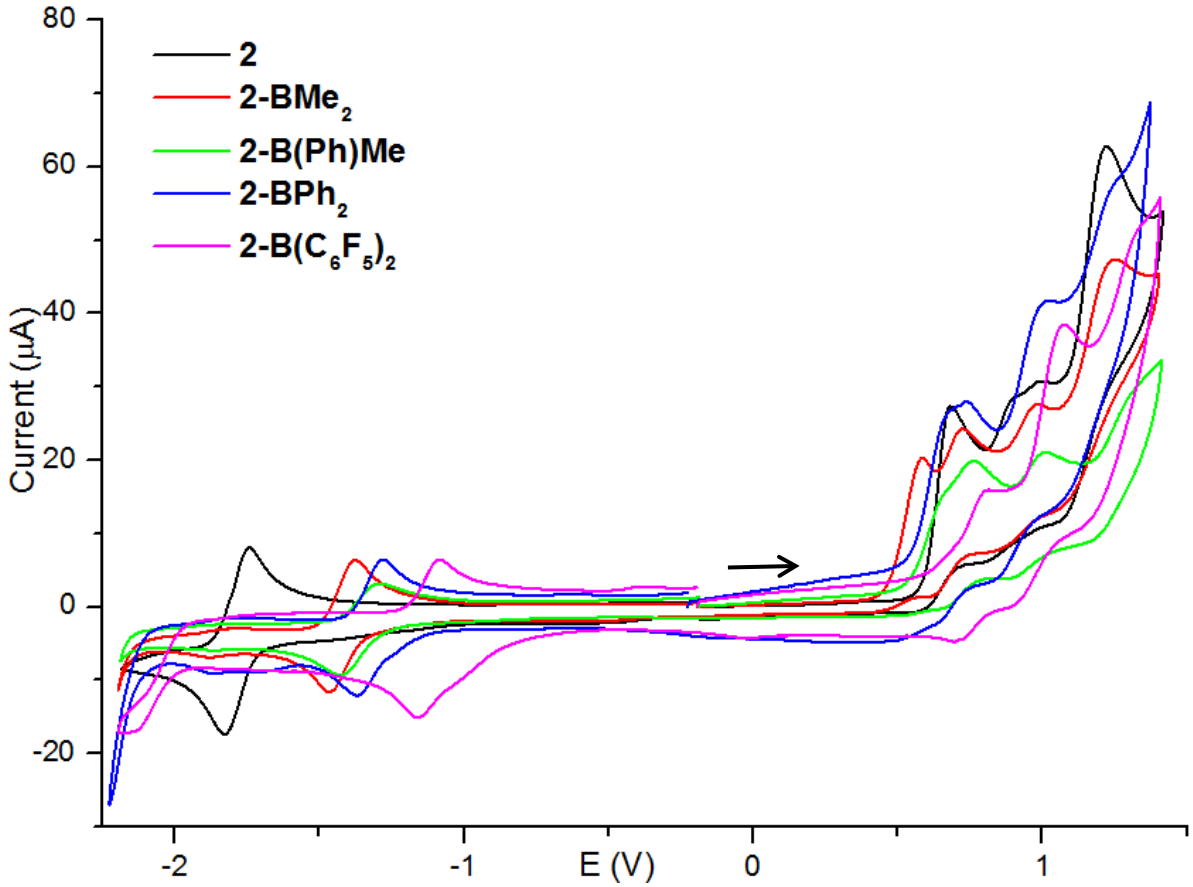


Figure S13. Cyclic voltammagrams of **2, 2-BMe$_2$, 2-BPh$_2$**, **2-B(Ph)Me** and **2-B(C$_6$F$_5$)$_2$**. Measured in DCM (1 mM) with [^{n}Bu$_4$N][PF$_6$] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV/s, relative to Fc/Fc$^+$ redox couple standard.

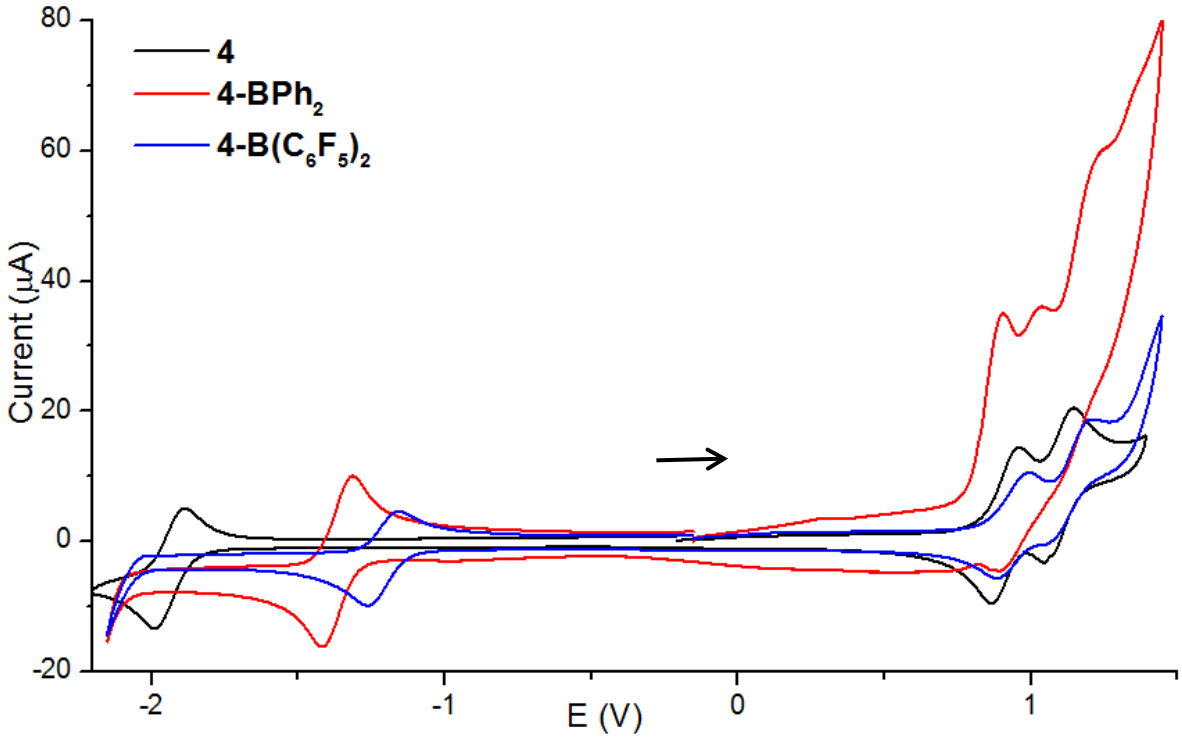


Figure S14. Cyclic voltammagrams of **4, 4-BPh$_2$** and **4-B(C$_6$F$_5$)$_2$**. Measured in DCM (1 mM) with [^{n}Bu$_4$N][PF$_6$] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV/s, relative to Fc/Fc$^+$ redox couple standard.

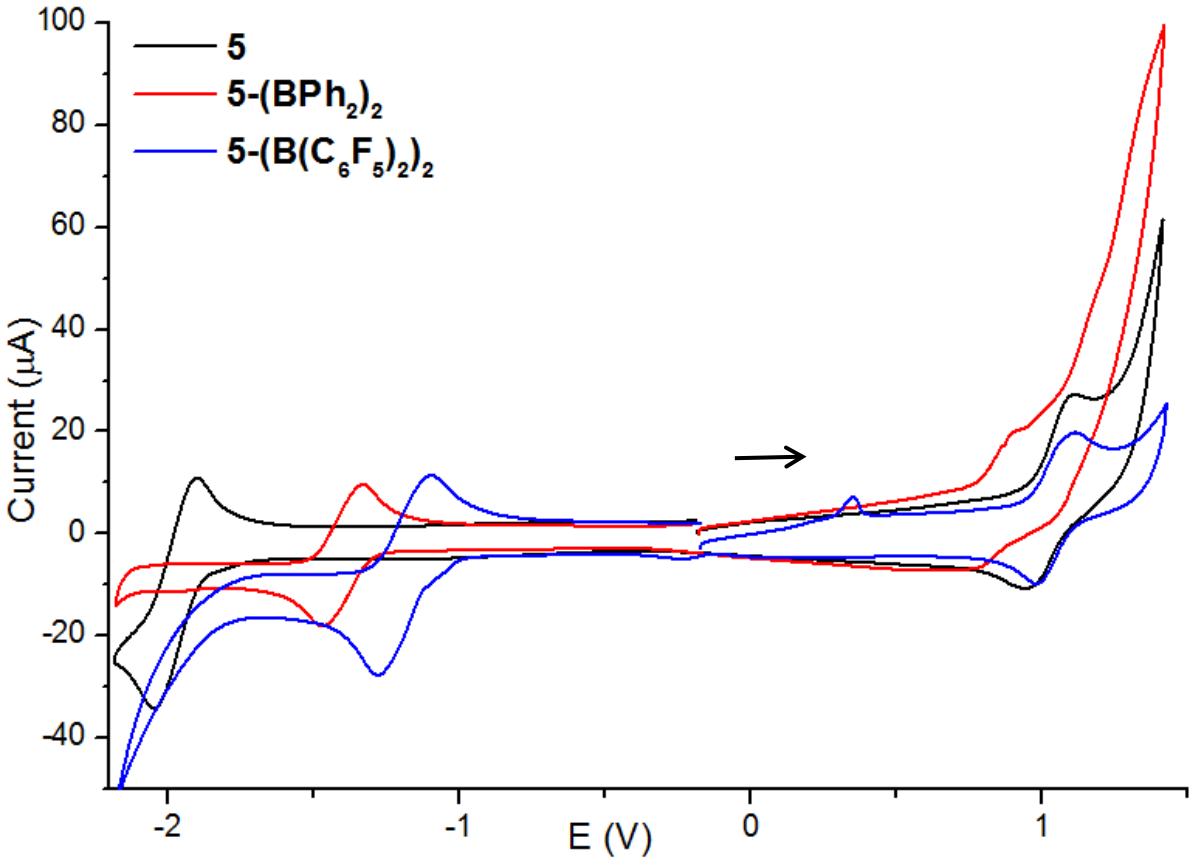


Figure S15. Cyclic voltammagrams of **5, 5-$(BPh_2)_2$** and **5-$(B(C_6F_5)_2)_2$**. Measured in DCM, (1 mM), with [^{n}Bu$_4$N][PF$_6$] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV/s, relative to Fc/Fc$^+$ redox couple standard.

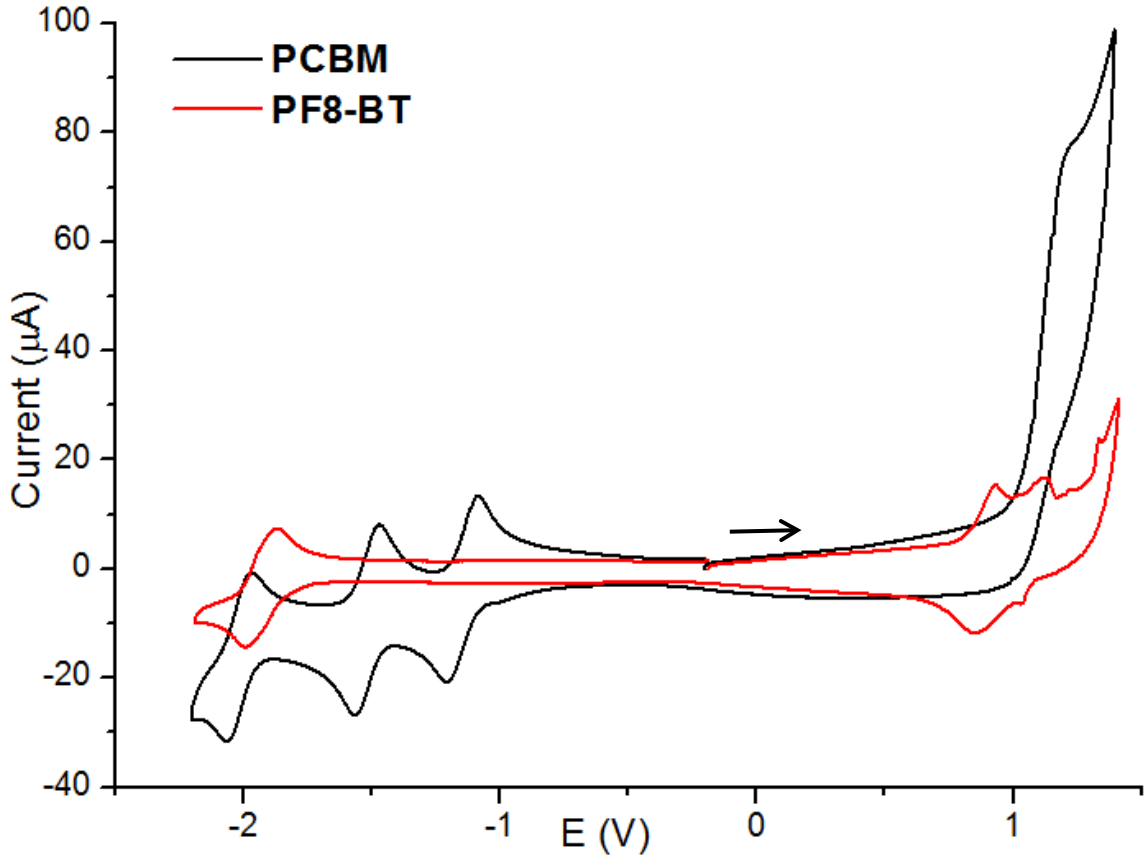


Figure S16. Cyclic voltammagrams of **PCBM** and **PF8-BT**. Measured in DCM, (1 mM), with [$^{n}Bu_4N$][PF_6] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV/s, relative to Fc/Fc^{+} redox couple standard.

Compound	E_{ox}^{onset} (V)[d]	E_{red}^{onset} (V)[d]	HOMO (eV)[d]	LUMO (eV)[de]
PCBM	1.06	-1.06	-6.45	-4.33
PF8-BT	0.75	-1.82	-6.14	-3.57

Table S7. Summary of cyclic voltammetry data for **PCBM** and **PF8-BT**.

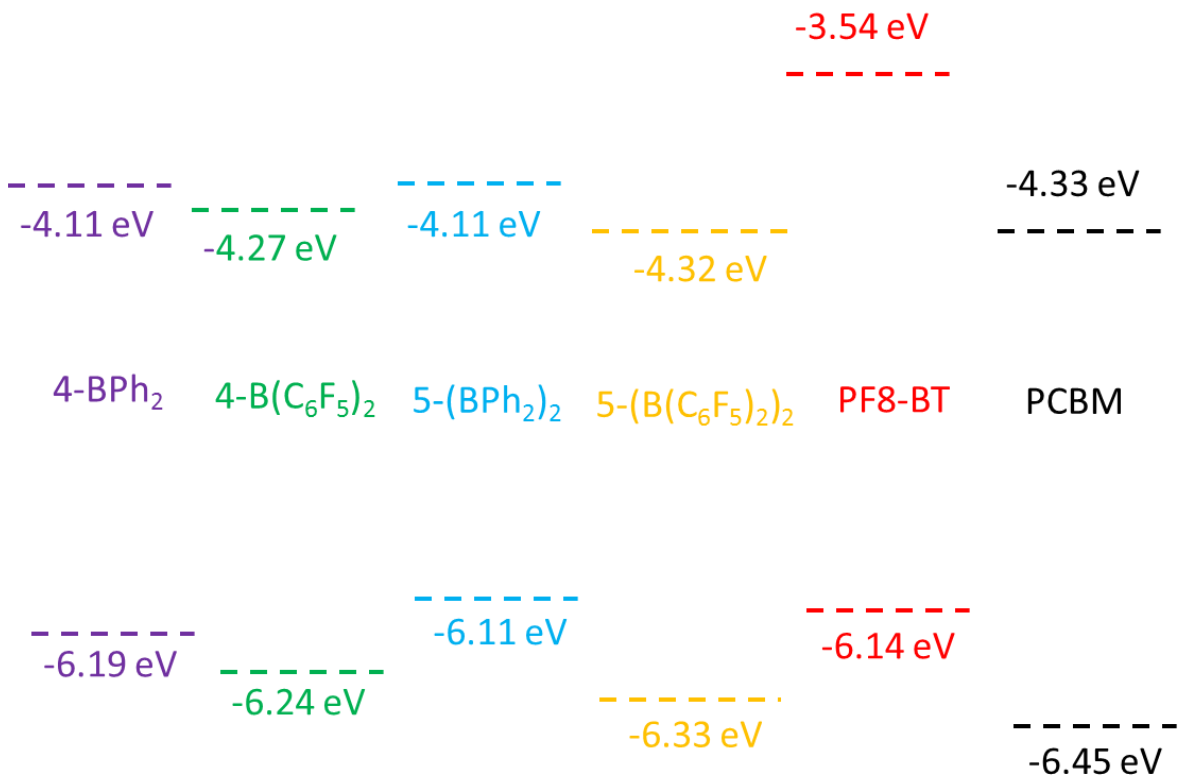


Figure S17. Relative energy level diagrams for **4-BPh_2, 4-$B(C_6F_5)_2$, 5-$(BPh_2)_2$, 5-$(B(C_6F_5)_2)_2$, PF8-BT** and **PCBM** as measured by cyclic voltammetry in DCM, (1 mM), with [^{n}Bu_4N][PF_6] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV/s, relative to Fc/Fc^+ redox couple standard.

OLED Device Data

Light-emitting diodes were prepared on glass/ITO substrates, which were cleaned using polar solvents. They were treated with oxygen plasma prior to the deposition of the organic layers. All organic layers were spin coated from toluene. The Plexcore OC layer was annealed at 170° C for 15 mins, the F8-TFB layer was annealed at 180 ° C for 60 mins and the emissive layer was annealed at 150 ° C for 10 mins. All annealing was conducted under an inert atmosphere. The top barium cathode was deposited via vacuum deposition.

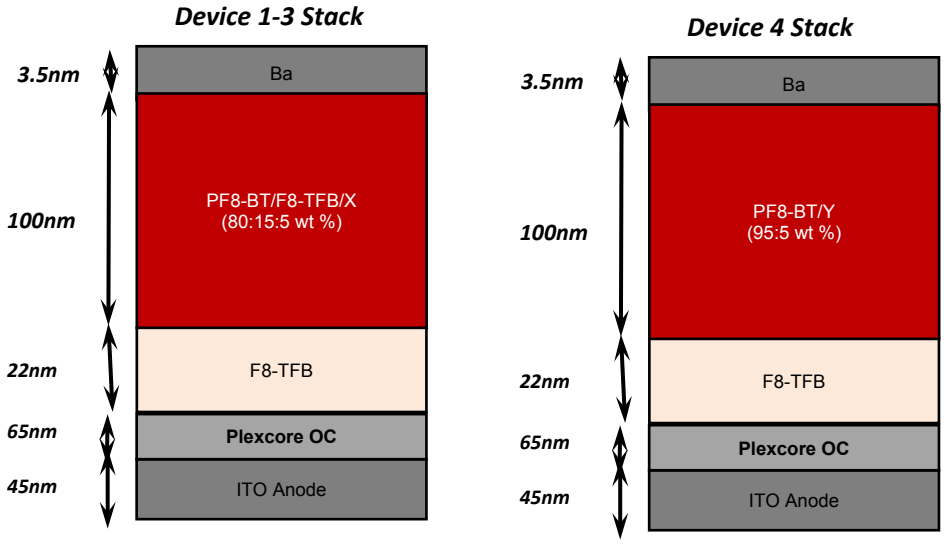


Figure S18. Device architectures for Devices 1-4. X = **4-BPh_2**, **5-$(BPh_2)_2$** or **5-$(B(C_6F_5)_2)_2$**. Y = **4-BPh_2**.

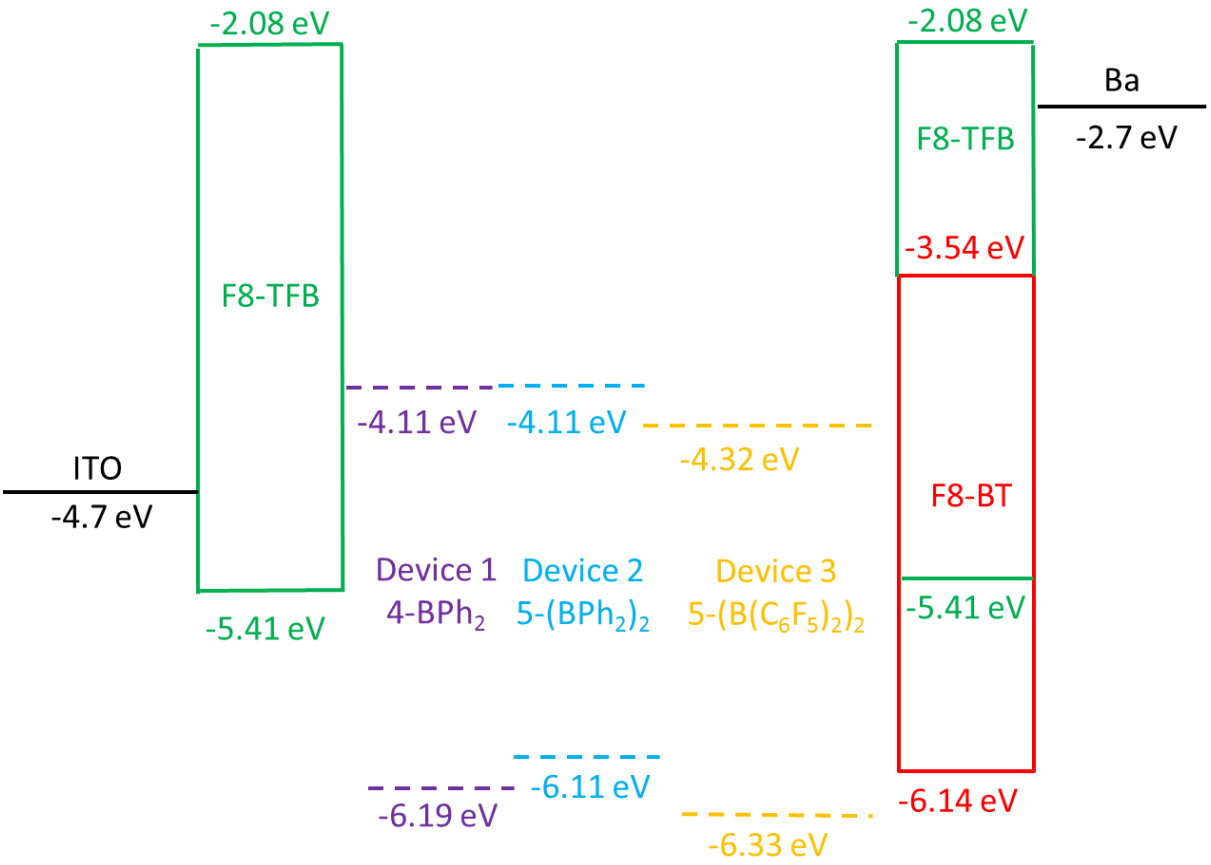


Figure S19. Relative FMO energy levels of device 1-3 layers.

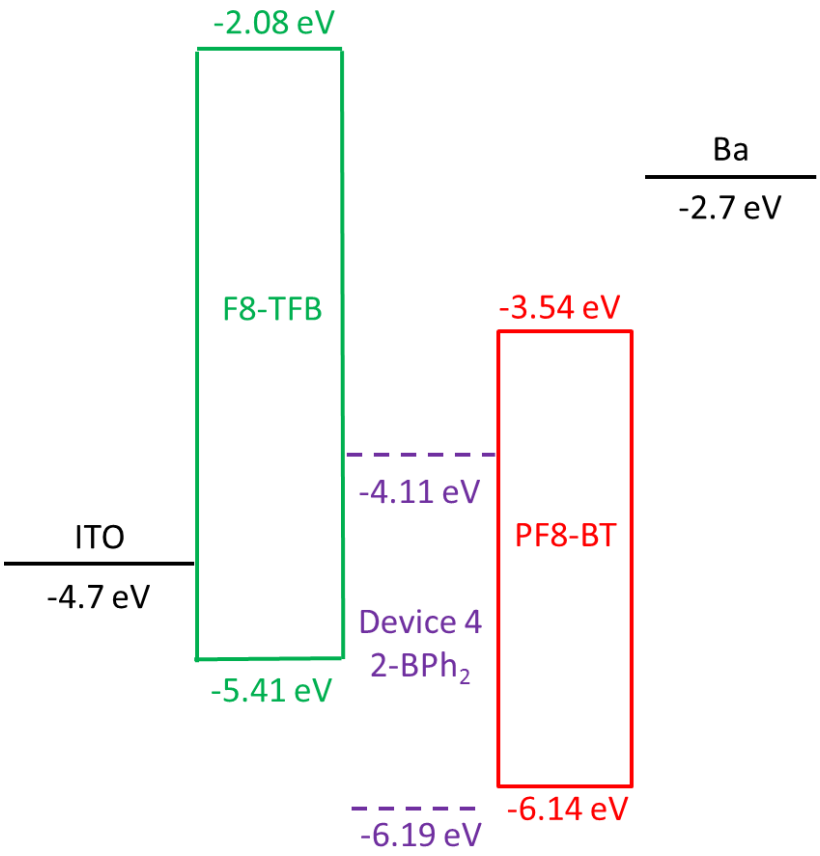


Figure S20. Relative FMO energy levels of device 4 layers.

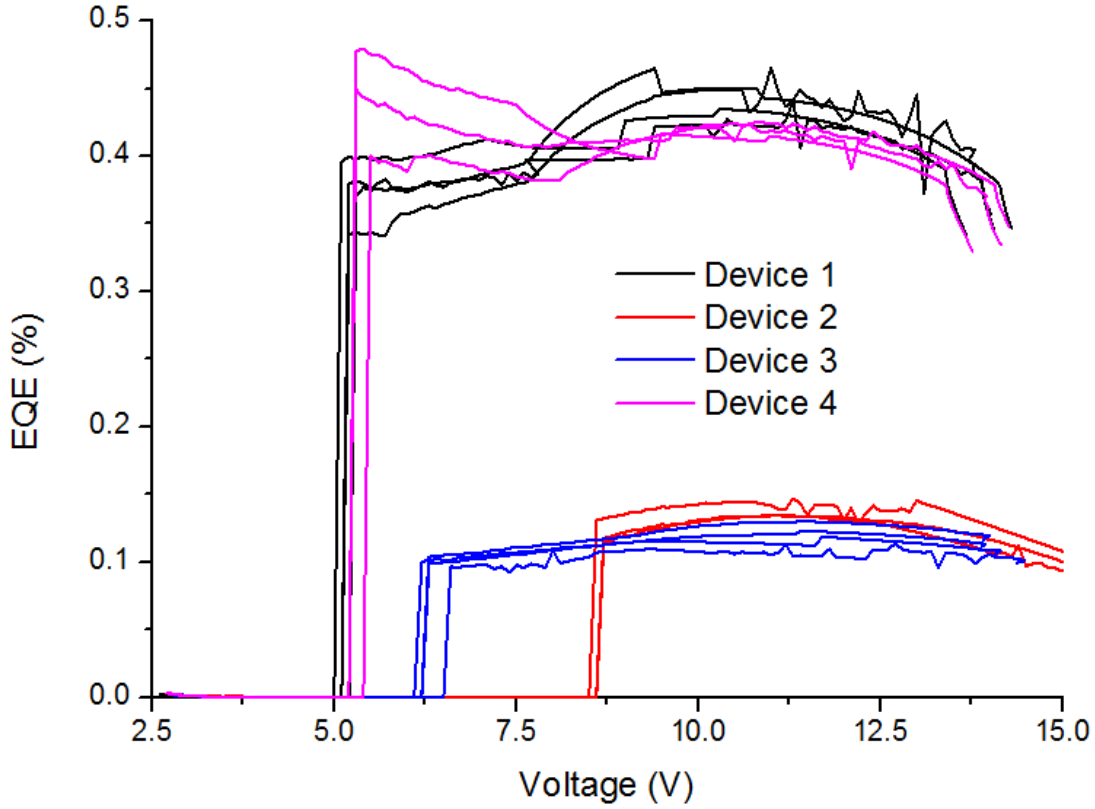


Figure S21. EQE vs Voltage plot for Devices 1-4.

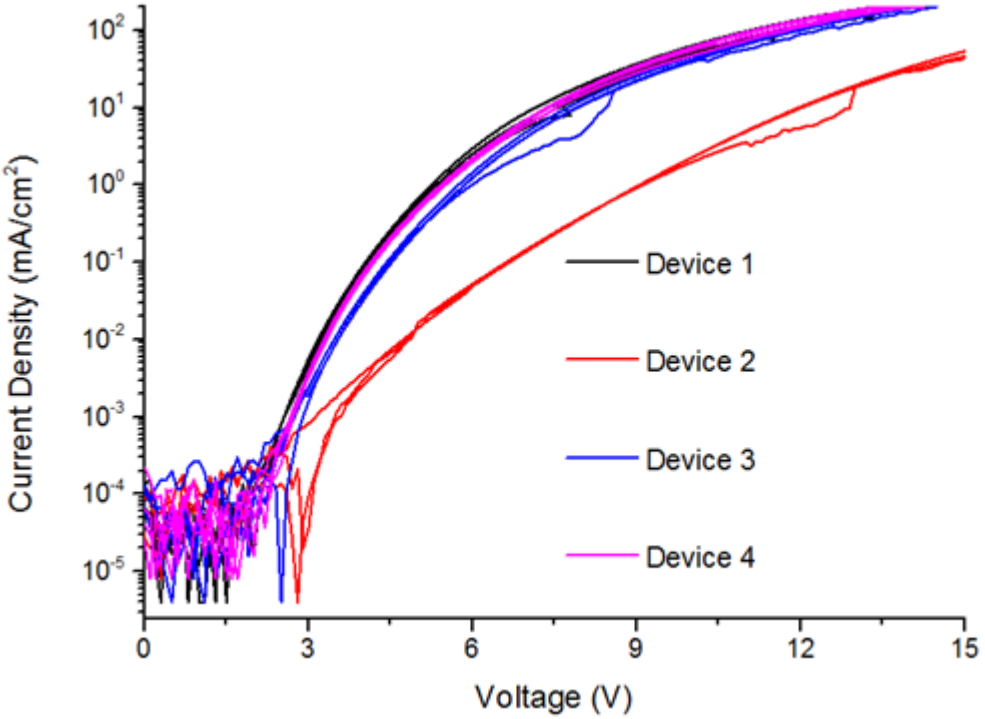


Figure S22. Current Density vs Voltage plot for Devices 1-4.

Crystallography Analysis

	2-BBr_2	**2-BMe_2**	**2-BPh_2**
CCDC reference	1062560	1062559	1050963
Empirical Formula	$C_{30}H_{39}BBr_2N_2S_3$	$C_{32}H_{45}BN_2S_3$	$C_{42}H_{49}B_{1\ N2}S_3$
Fw / g mol^{-1}	694.47	564.69	688.87
Crystal system, space group	Triclinic *P* -1	Triclinic *P* -1	Triclinic *P* -1
***T* / K**	250	100	220
a / Å	10.2773(4)	6.5240(6)	6.3487(6)
b / Å	12.1331(4)	13.6675(11)	16.1168(15)
c / Å	14.8059(4)	18.0034(17)	19.3671(17)
α / deg	65.908(2)	98.640(7)	74.649(8)
β / deg	79.793(2)	95.792(8)	85.857(8)
γ / deg	68.090(2)	101.670(8)	83.373(8)
Vol / Å^3	1563.0(1)	1539.9(2)	1896.4(3)
Z	2	2	2
calc. density (Mg m^{-3})	1.476	1.218	1.206
radiation	Cu *K*\α *λ* = 1.5418 Å	Cu *K*\α *λ* = 1.5418 Å	Cu *K*\α *λ* = 1.5418 Å
abs. coeff. (mm^{-1})	5.326	2.364	2.015
F(000)	712	608.0	736
θ range (deg)	3.3 - 60.7	2.5 – 74.1	2.368 – 57.604
no. of reflns collected / unique	4499 / 4499	17172 / 5846	4765 / 4765
R_{int}	0.054	0.077	0.060
no. of data / restraints / parameters	4455 / 0 / 343	5846 / 0 / 347	4733 / 0 / 434
R (data with [$I^2 > 2\sigma(I^2)$])	0.066 (3886)	0.0868 (3846)	0.1185 (3194)
wR (all data)	0.1734	0.2689	0.3498
S	0.9579	1.048	0.9336
Δρmax, min / e·Å^{-3}	3.22, -0.70	0.66, -6.62	0.67, -0.58

Table S8. Summary of crystallography data for compound **2-BBr_2**, **2-BMe_2** and **2-BPh_2.**

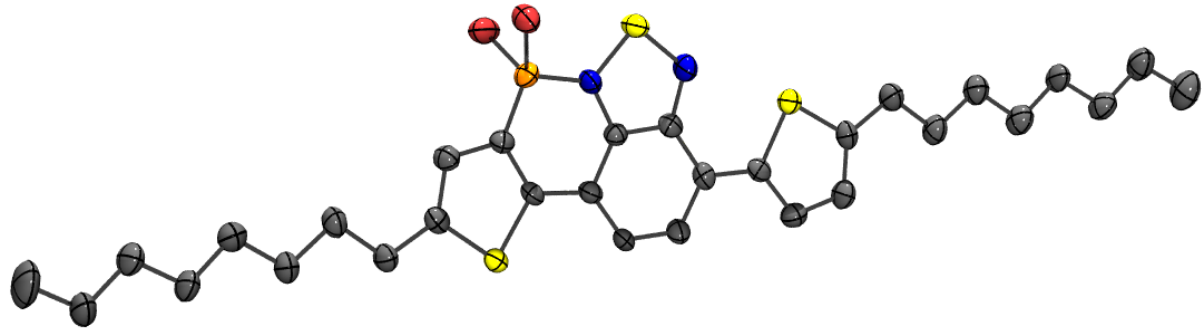


Figure S23.Crystal structure of compound **2-BBr$_2$**.

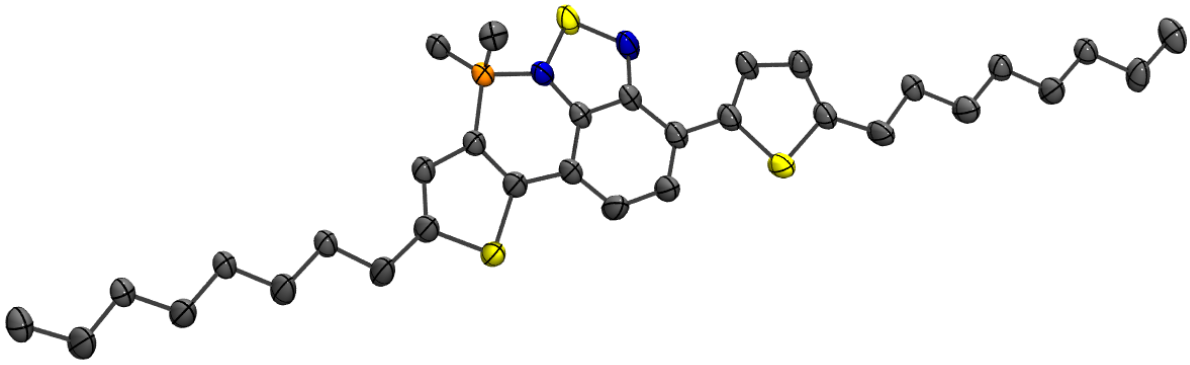


Figure S24.Crystal structure of compound **2-BMe$_2$**.

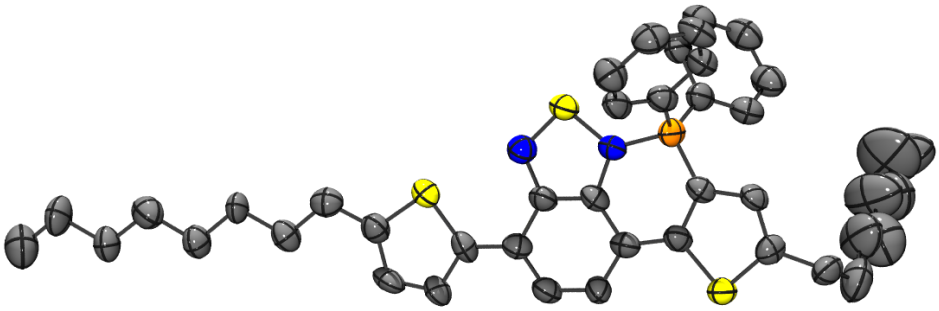


Figure S25.Crystal structure of compound **2-BPh$_2$**.

	5	**5-$(B(C_6F_5)_2)_2$**	**5-$(BPh_2)_2$**
CCDC reference	1050921	1050923	1050922
Empirical Formula	C41 H46 N4 S2	C65 H44 B2 F20 N4 S2, 2(C H Cl3)	C65 H64 B2 N4 S2, 0.5(C6 H14)
Fw / g mol^{-1}	658.97	1585.56	1030.09
Crystal system, space group	Monoclinic *C* 2/c	Monoclinic *P* 2_1/c	Tetragonal *I* 4_1/a
***T* / K**	150	150	150
a / Å	24.1082(9)	14.6207(4)	41.5940(9)
b / Å	18.1370(7)	22.7422(8)	41.5940(9)
c / Å	16.7624(7)	20.0278(7)	13.1413(6)
α / deg	90	90	90
β / deg	106.002(4)	96.749(3)	90
γ / deg	90	90	90
Vol / Å^3	7045.4(5)	6613.2(4)	22735.2(12)
Z	8	4	16
calc. density (Mg m^{-3})	1.242	1.592	1.204
radiation	Mo *K*\α *λ* = 0.71073 Å	Mo *K*\α *λ* = 0.71073 Å	Mo *K*\α *λ* = 0.71073 Å
abs. coeff. (mm^{-1})	0.187	0.427	0.139
F(000)	2816	3200	8784
θ range (deg)	3.107 – 28.552	2.945 – 23.256	3.059 – 21.965
no. of reflns collected / unique	14311 / 7830	16576 / 9431	31516 / 6933
R_{int}	0.031	0.055	0.038
no. of data / restraints / parameters	7816 / 40 / 470	9402 / 0 / 910	6906 / 83 / 768
R (data with [$I^2 > 2\sigma(I^2)$])	0.0613 (5781)	0.0644 (6044)	0.0595 (5402)
wR (all data)	0.1513	0.1752	0.1516
S	0.9999	0.9618	1.0014
Δρmax, min / e·Å^{-3}	0.54, -0.58	1.02, -0.79	0.68, -0.47

Table S9. Summary of crystallography data for **5, 5-$(BPh_2)_2$** and **5-$(B(C_6F_5)_2)_2$**.

* ^{n}octyl chains have been omitted for clarity.

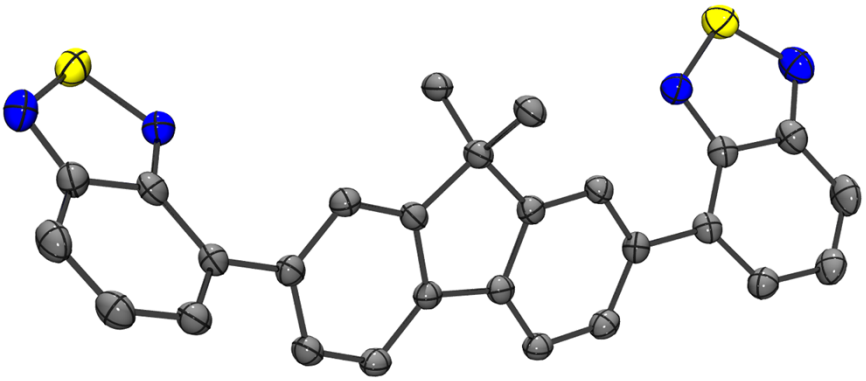


Figure S26. X-ray crystal structure of **5***.

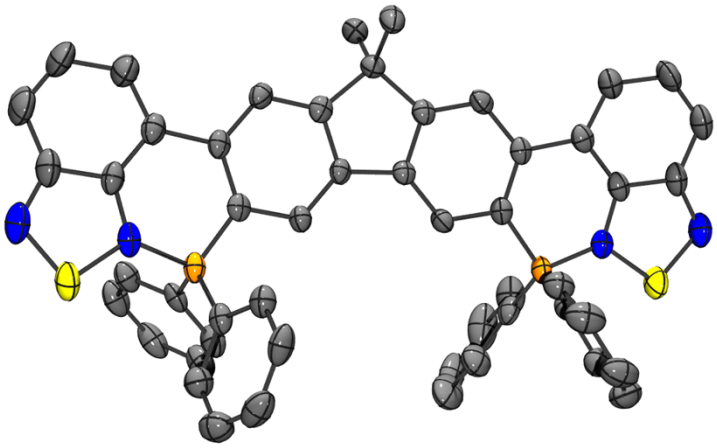


Figure S27. X-ray crystal structure of **5-(BPh$_2$)$_2$***.

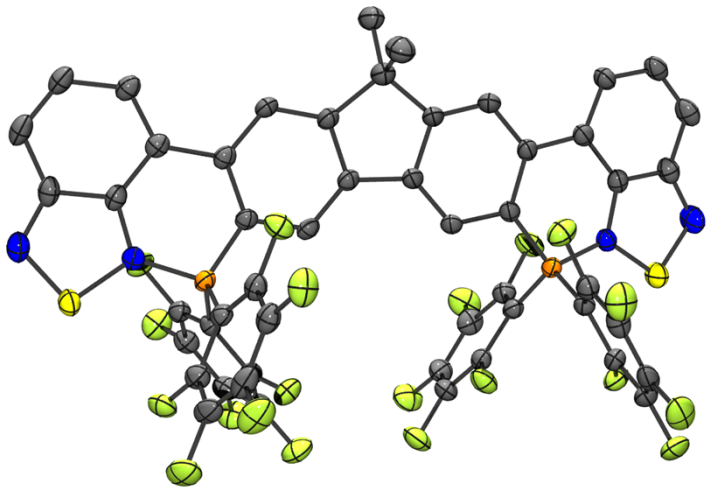
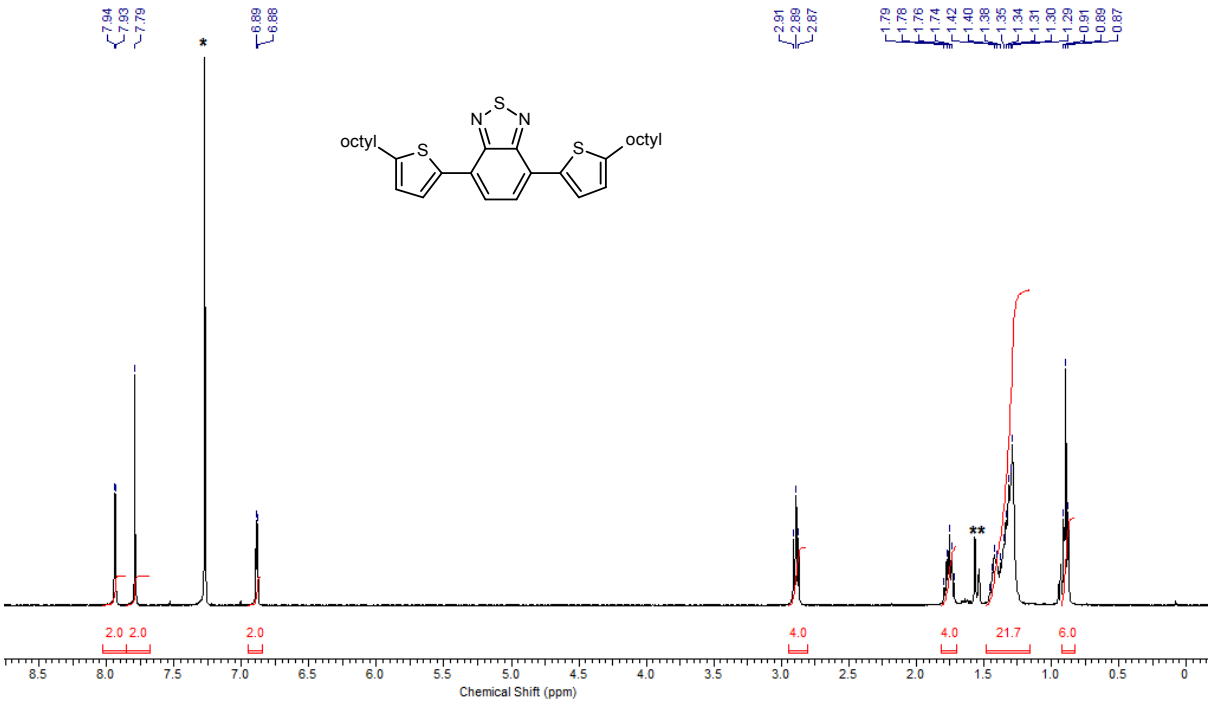


Figure S28. X-ray crystal structure of **5-($B(C_6F_5)_2)_2$***.

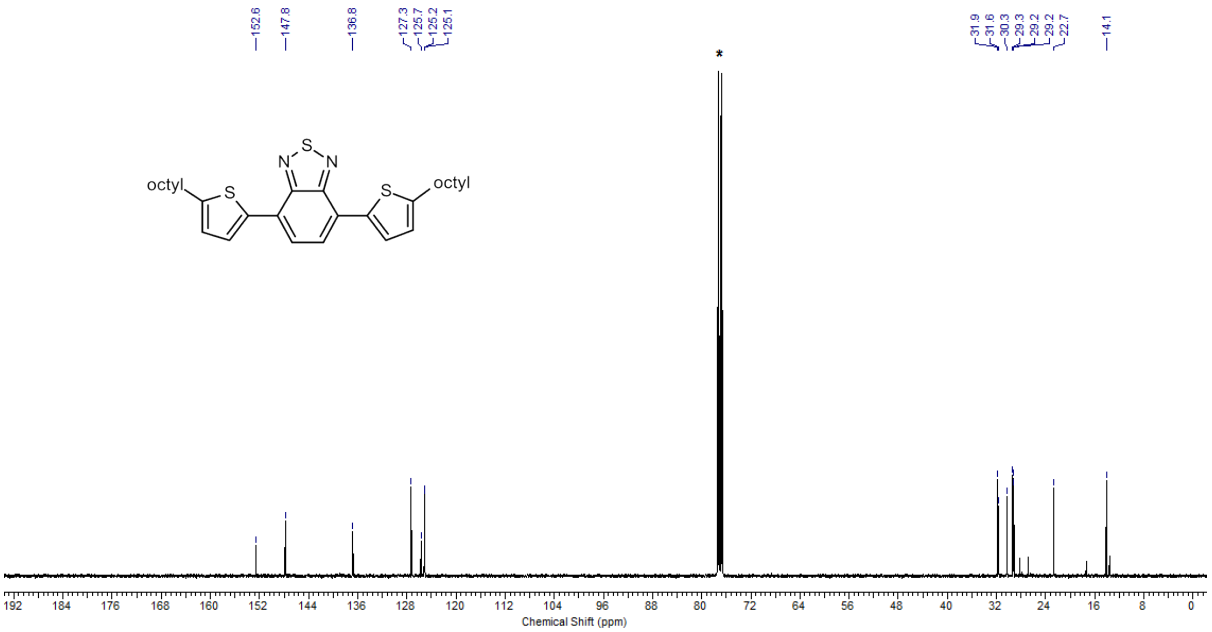
NMR Spectra

2 (^{1}H NMR, $CDCl_3$, 400MHz, 298K):



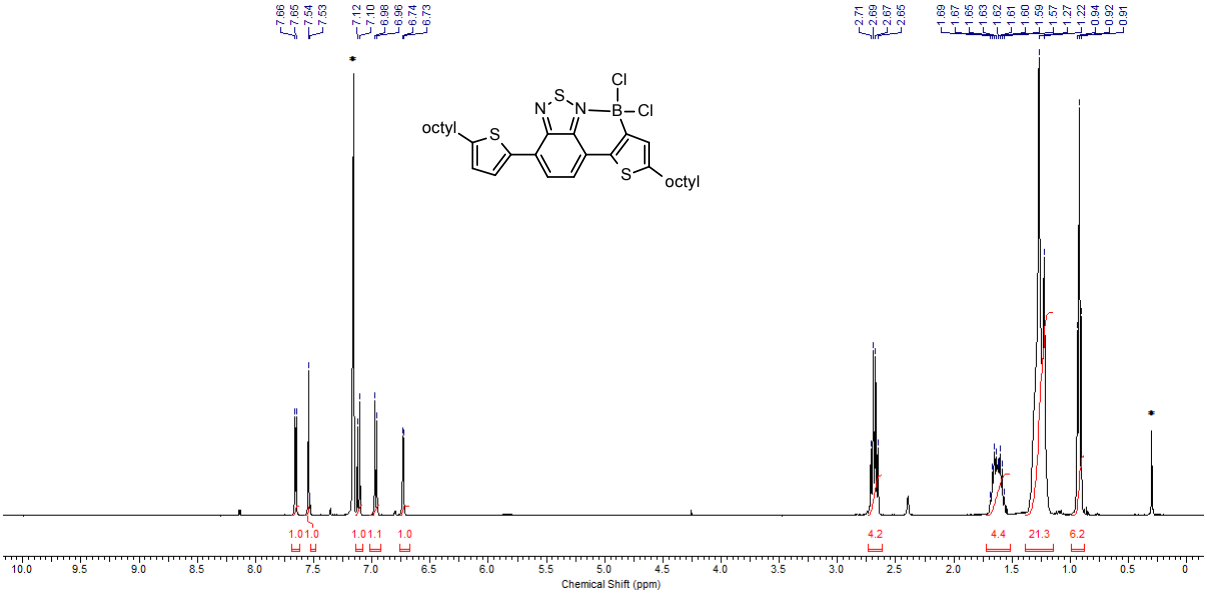
* = $CHCl_3$, ** = H_2O/D_2O

2 ($^{13}C\{^1H\}$ NMR, $CDCl_3$, 100MHz, 298K):



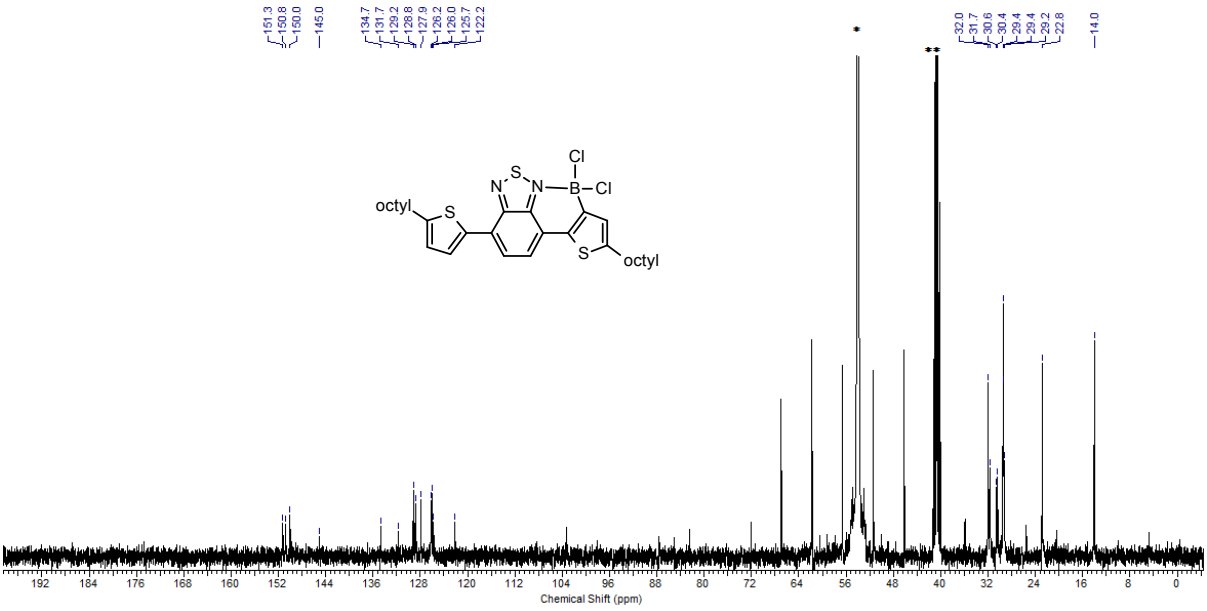
* = $CHCl_3$

2-BCl$_2$ (^{1}H NMR, C_6H_6 with d_6-DMSO capillary insert, 400MHz, 298K):



* = C_6H_6, ** = Silicone grease (resonance at 2.4 is residual protio DMSO in the capillary)

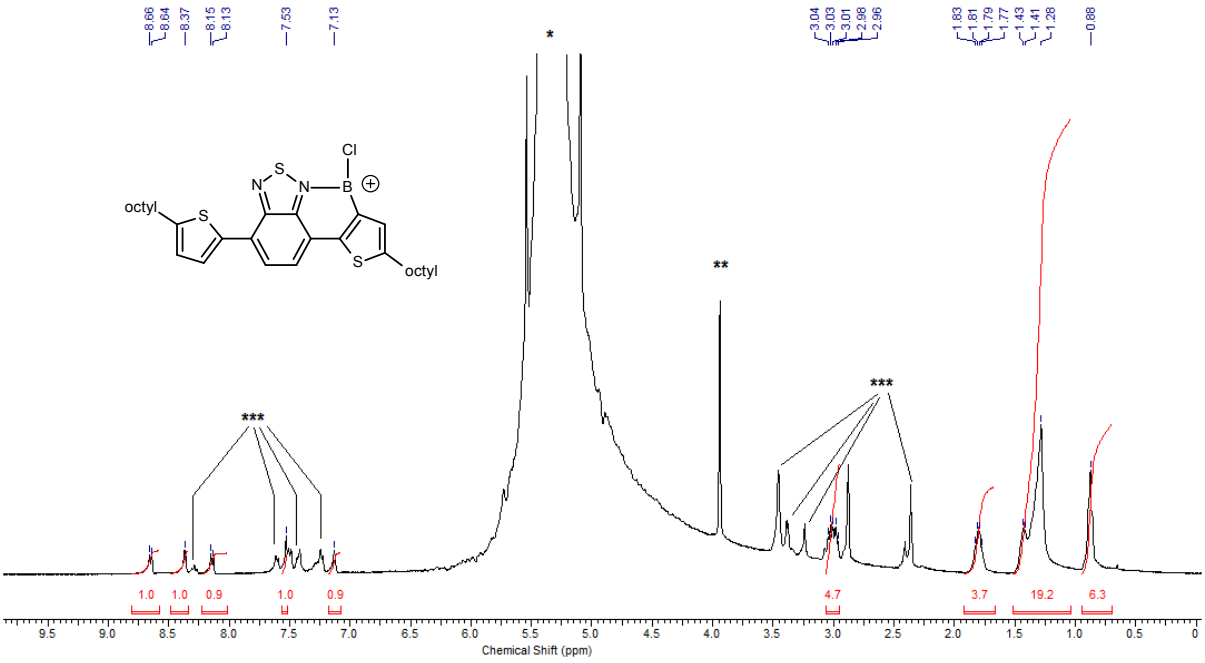
2-BCl$_2$ (^{13}C{^{1}H} NMR, CH2Cl2 with d_6-DMSO capillary insert, 101MHz, 298K):



* = DCM, ** = DMSO

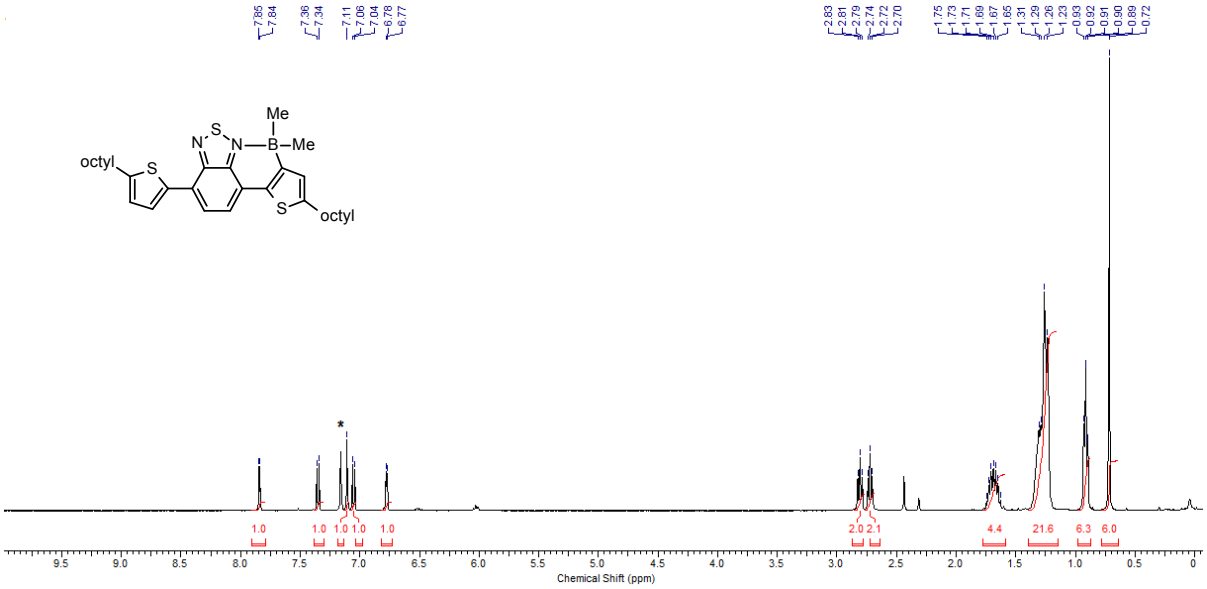
2-BCl2 was poorly soluble in a range of organic solvents in which it is stable, therefore poor signal to noise was observed even after using a large number of scans.

[2-BCl]$^+$ (^{1}H NMR, $CH2Cl_2$, with d_6-DMSO capillary insert 400MHz, 298K):



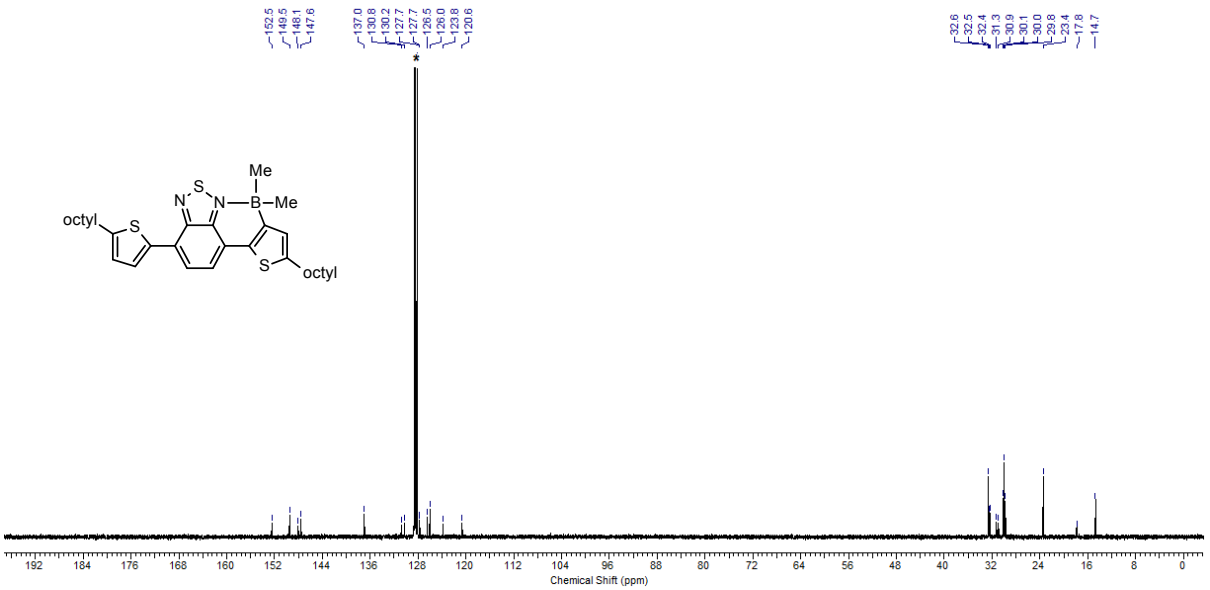
* = DCM, ** = H_2O in d_6-DMSO capillary, *** = DMT-BCl_3/ [DMT-BCl_2][$AlCl_4$]

2-BMe$_2$ (^{1}H NMR, C_6D_6, 400MHz, 298K):



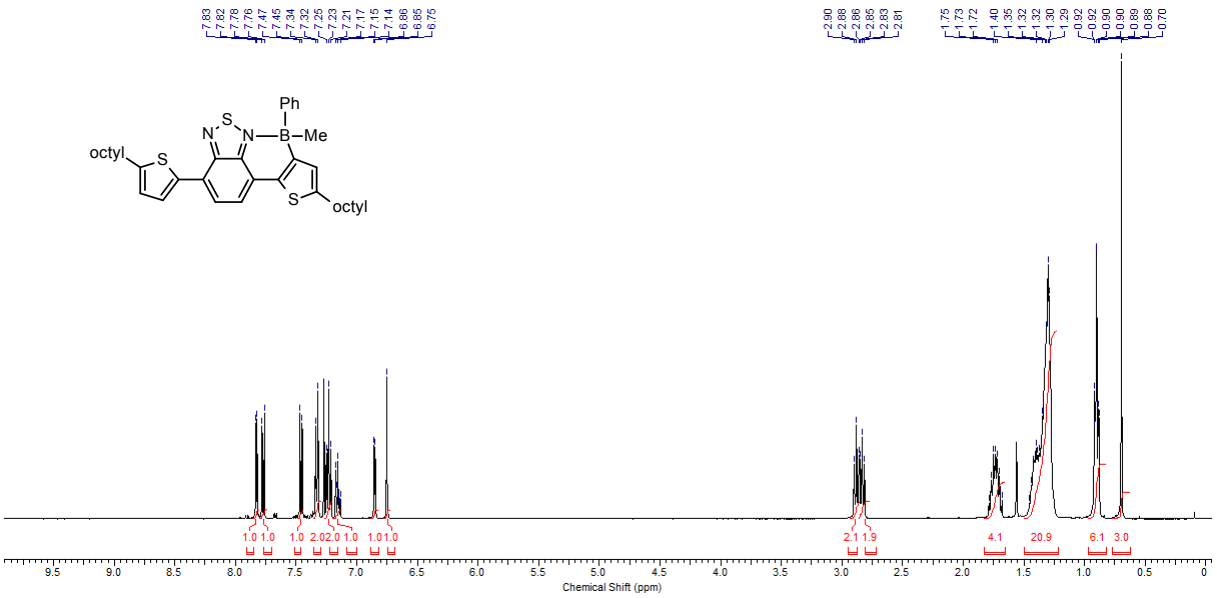
* = residual protio solvent

2-BMe$_2$ (^{13}C{^{1}H} NMR, C_6H_6, 101MHz, 298K):

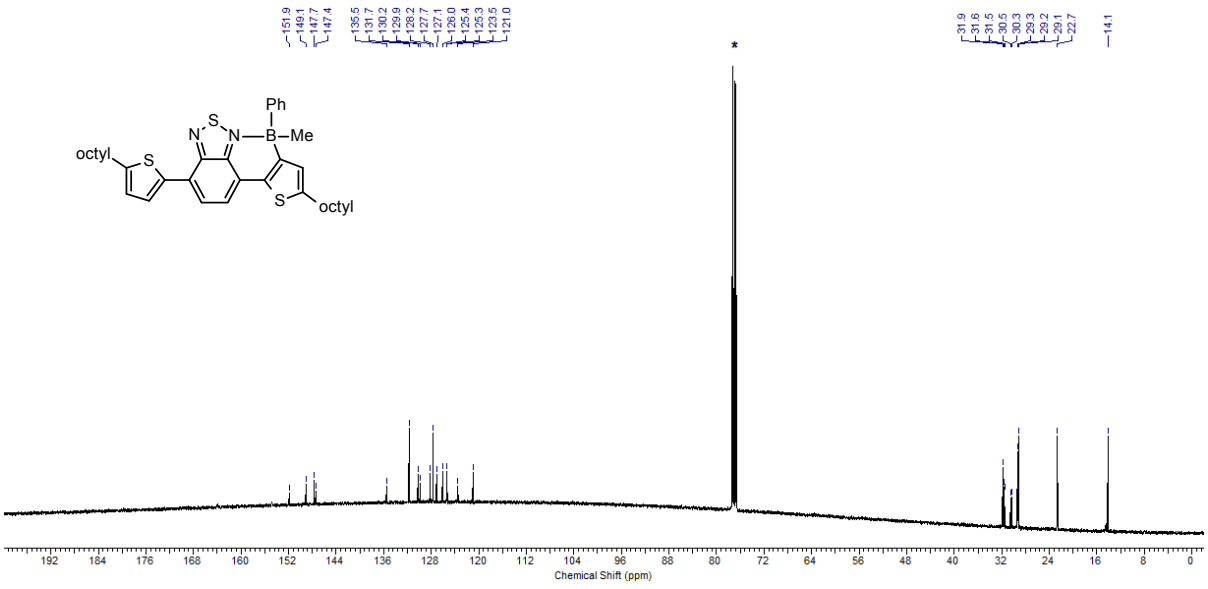


* = C_6D_6

2-B(Ph)Me (^{1}H NMR, $CDCl_3$, 400MHz, 298K):

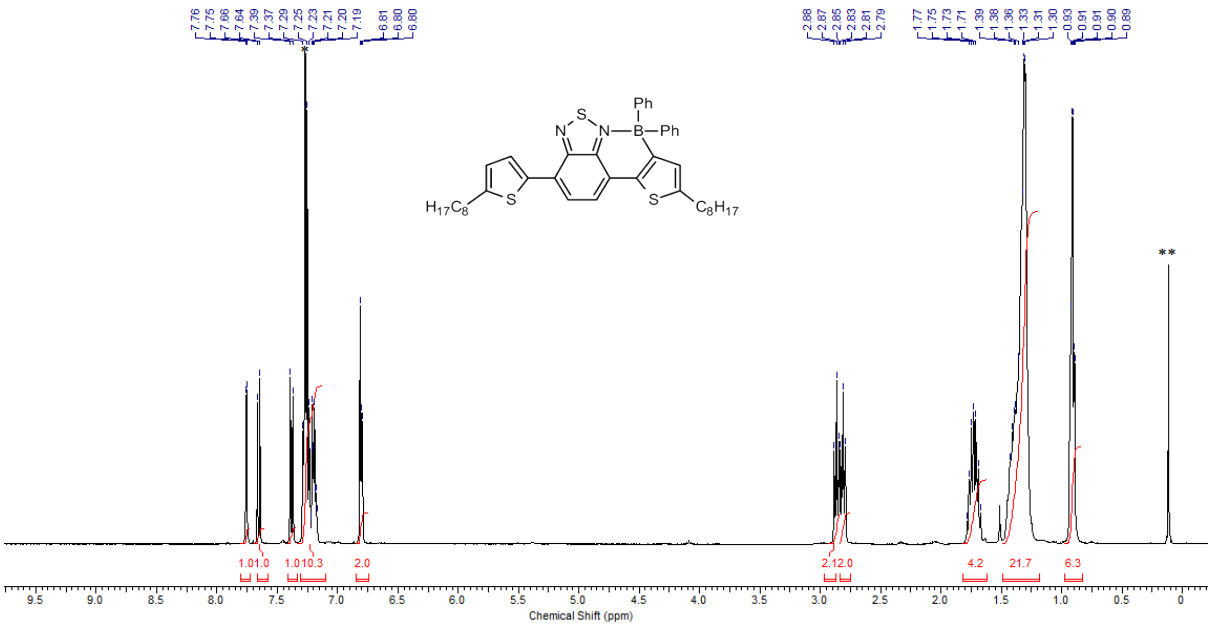


2-B(Ph)Me (^{13}C{^{1}H} NMR, $CDCl_3$, 101MHz, 298K):



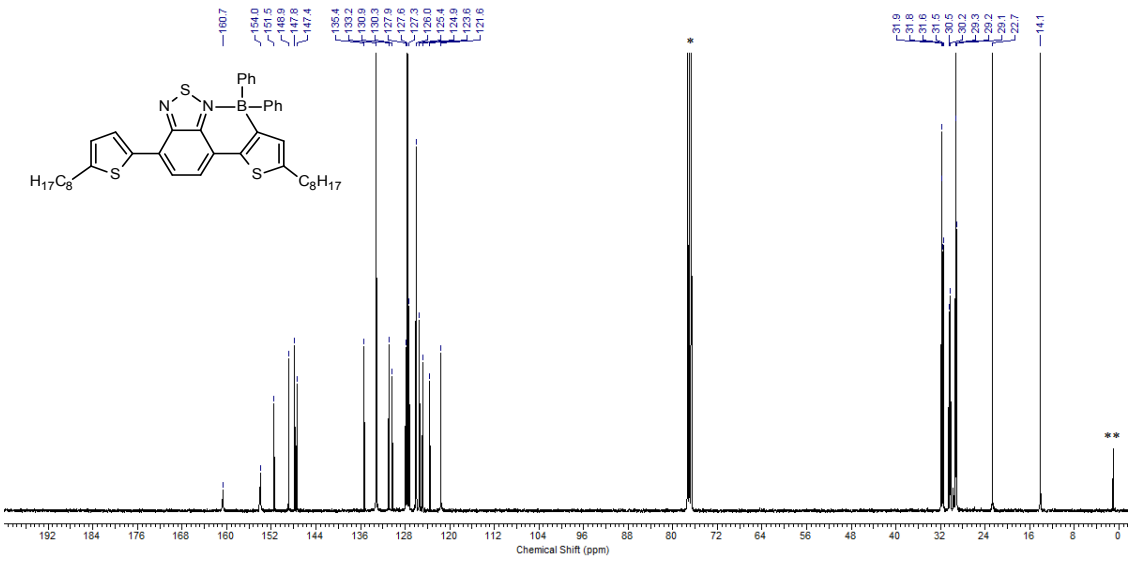
* = $CDCl_3$

2-BPh$_2$ (^{1}H NMR, $CDCl_3$, 400MHz, 298K):



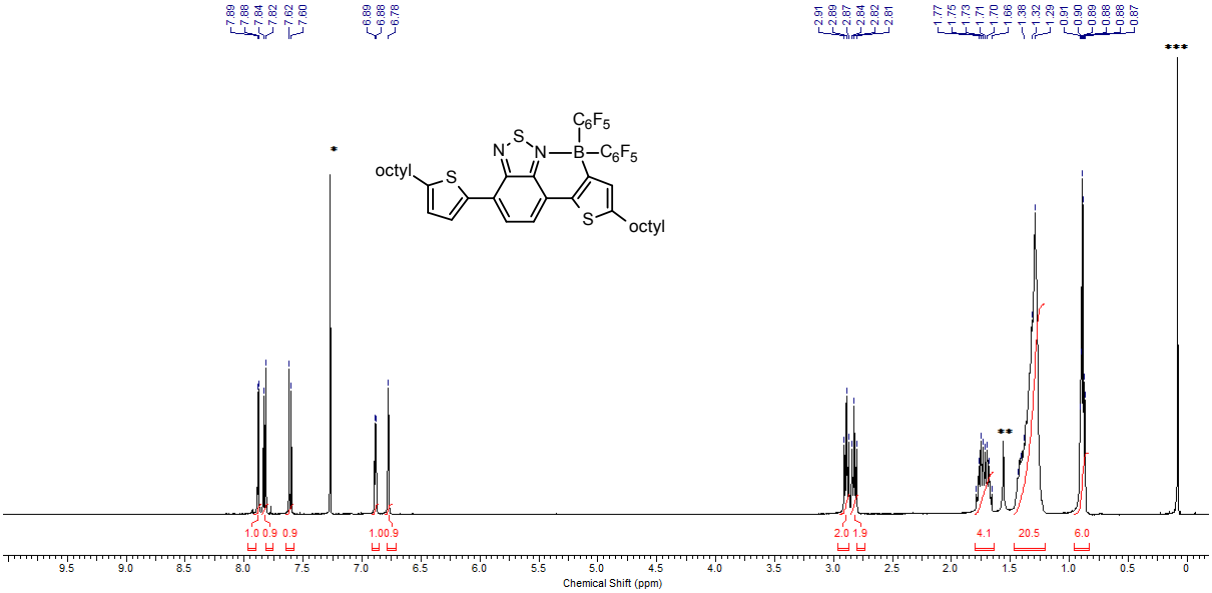
* = $CHCl_3$, ** = Silicone grease

2-BPh$_2$ (^{13}C{^{1}H} NMR, $CDCl_3$, 101MHz, 298K):



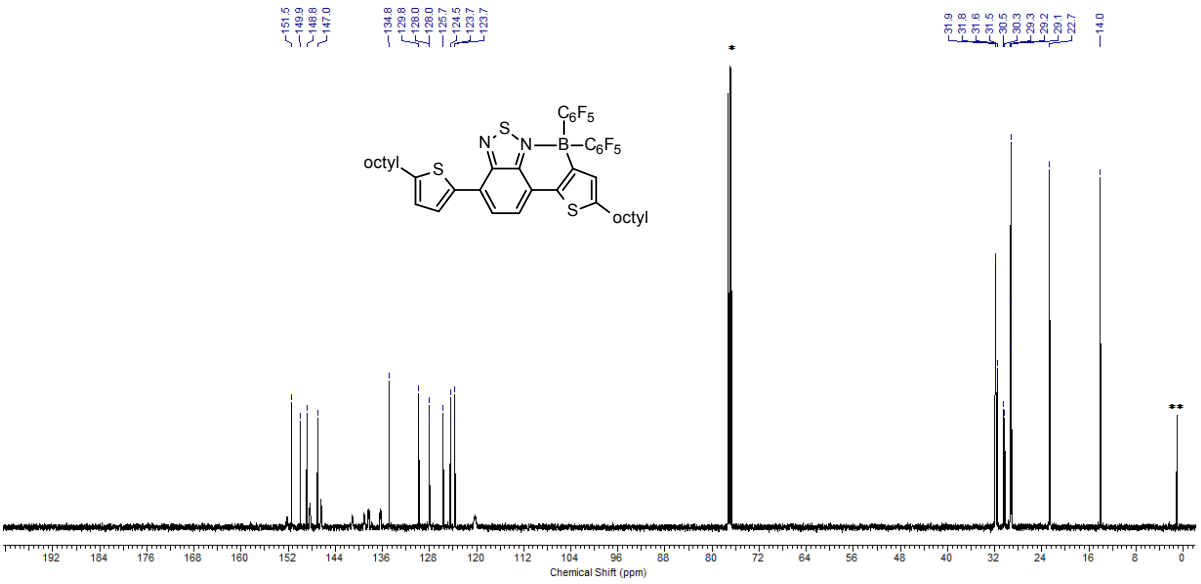
* = $CDCl_3$, ** = Silicone grease

2-B(C_6F_5)$_2$ (^{1}H NMR, $CDCl_3$, 400MHz, 298K):



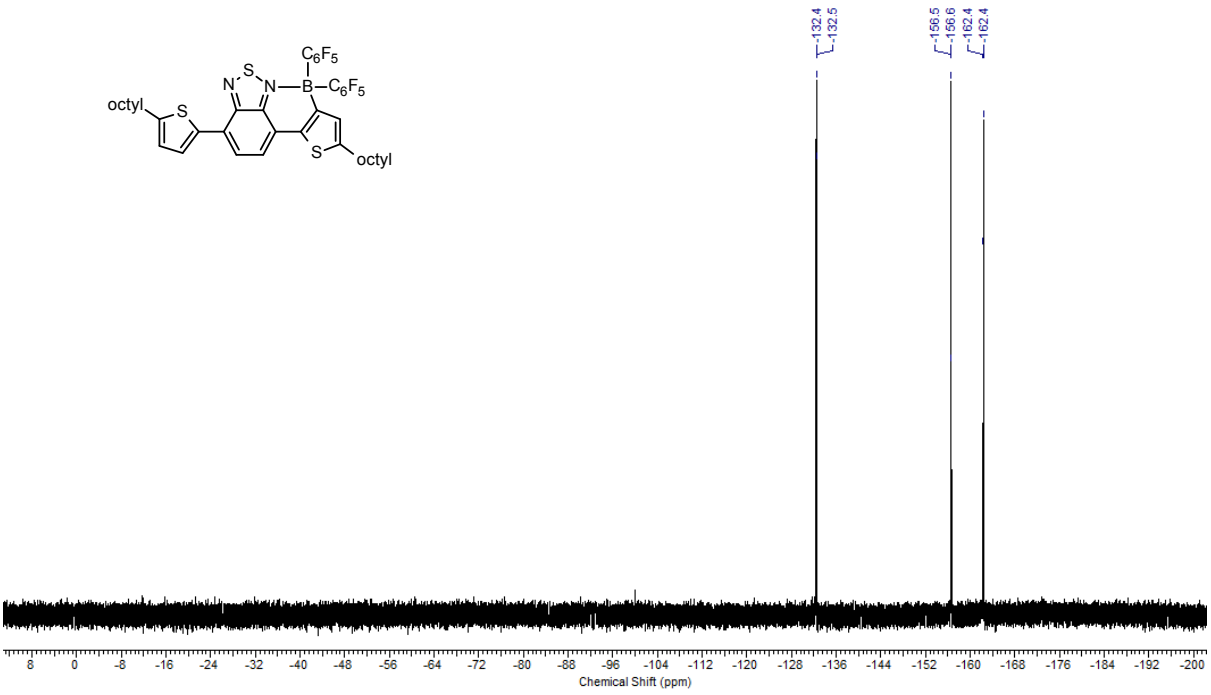
* = $CDCl_3$, ** = H_2O, *** = Silicone grease

2-B(C_6F_5)$_2$ (^{13}C{^{1}H} NMR, $CDCl_3$, 101MHz, 298K):

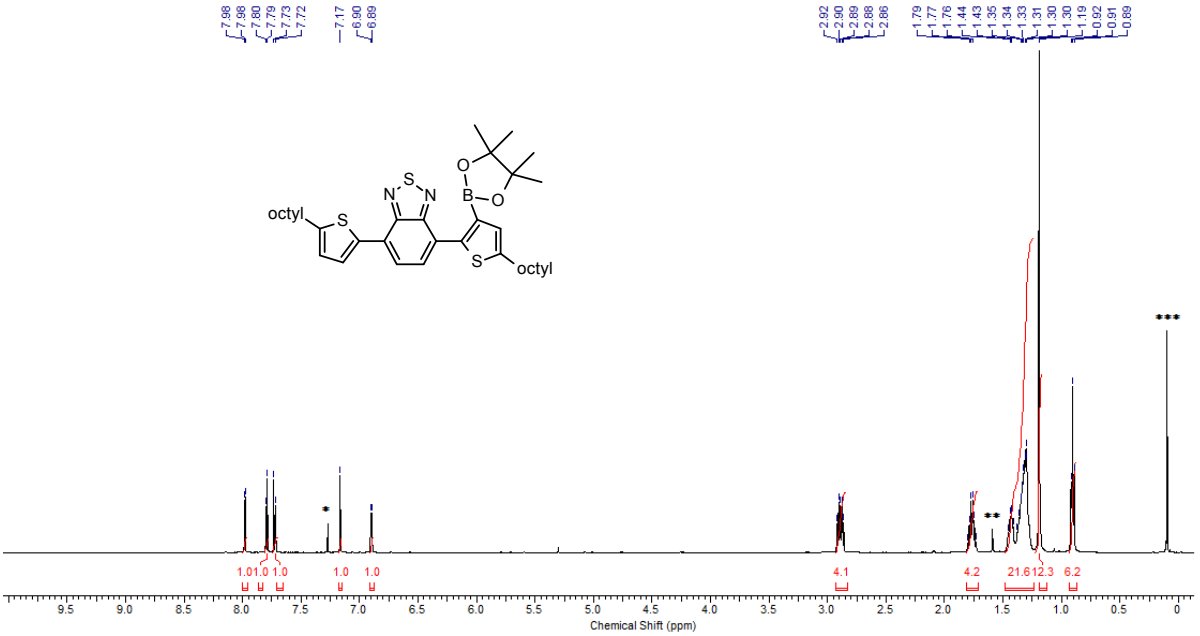


* = $CDCl_3$, ** = Silicone grease

2-B(C_6F_5)$_2$ ($^{19}F\{^1H\}$, $CDCl_3$, 376MHz , $CDCl_3$, 298K):

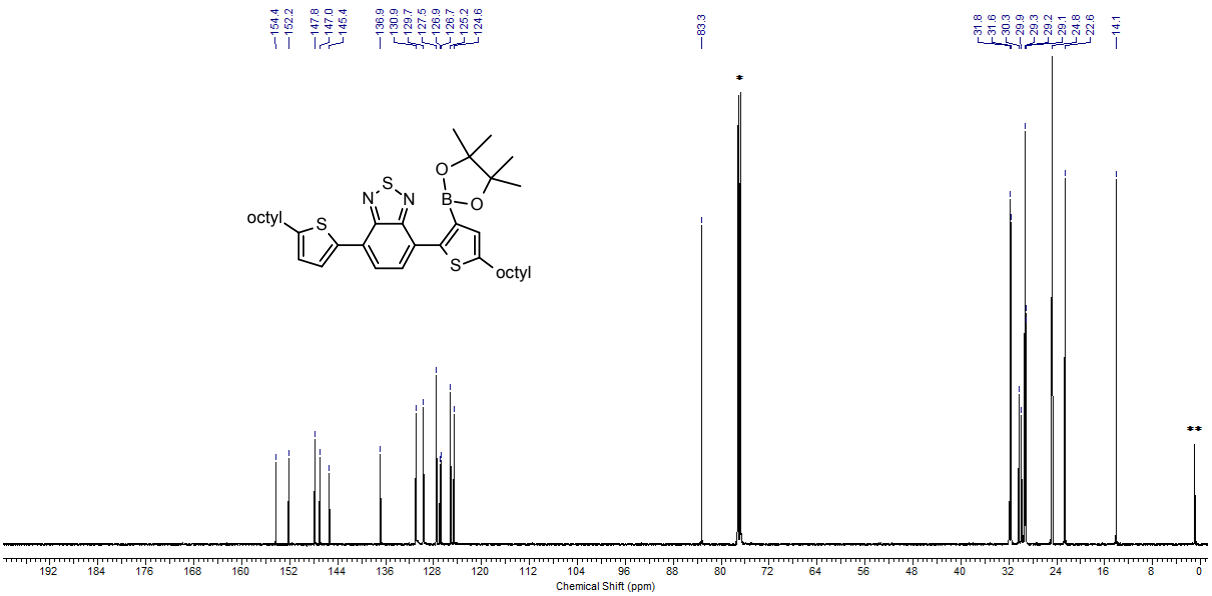


2-BPin (^{1}H NMR, $CDCl_3$, 400MHz, 298K):



* = $CHCl_3$, ** = H_2O, *** = Silicone grease

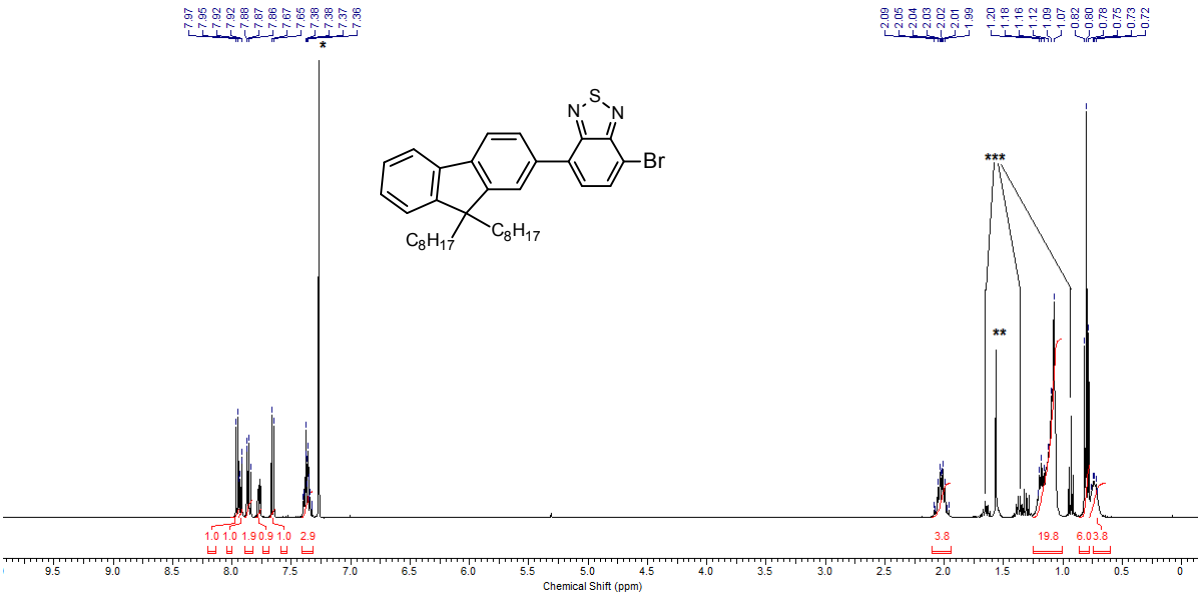
2-BPin (^{13}C{^{1}H} NMR, $CDCl_3$, 101MHz, 298K):



* = $CDCl_3$, ** = Silicone grease

4-bromo-7-(9,9-dioctyl-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazole

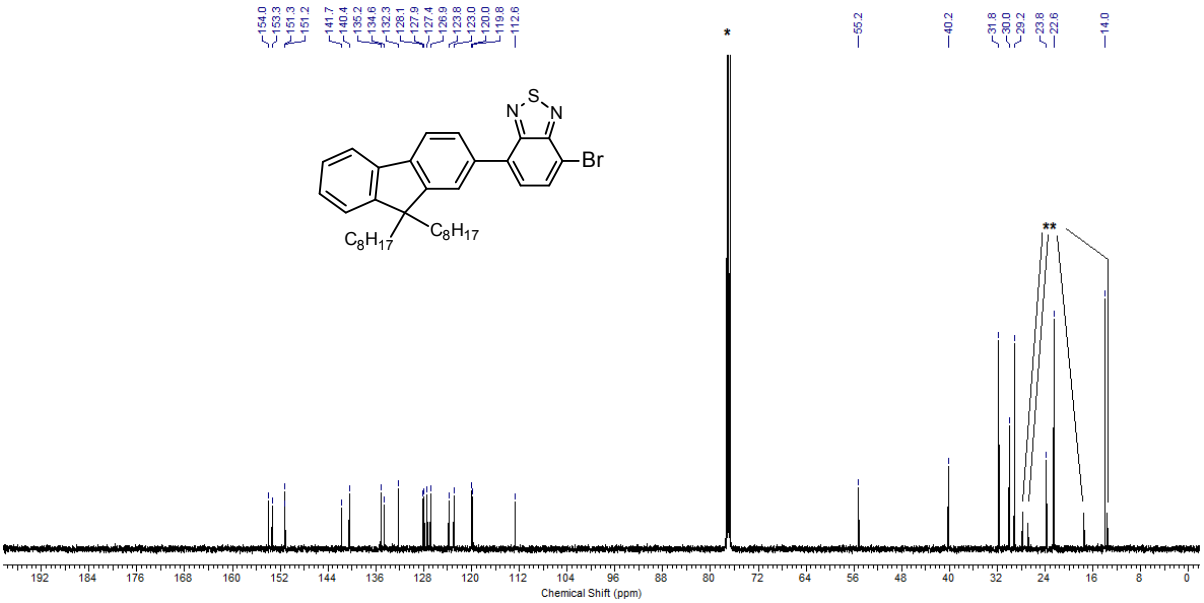
(^{1}H NMR, $CDCl_3$, 400MHz, 298K):



* = $CHCl_3$, ** = H_2O, *** = slight impurity which could not be removed

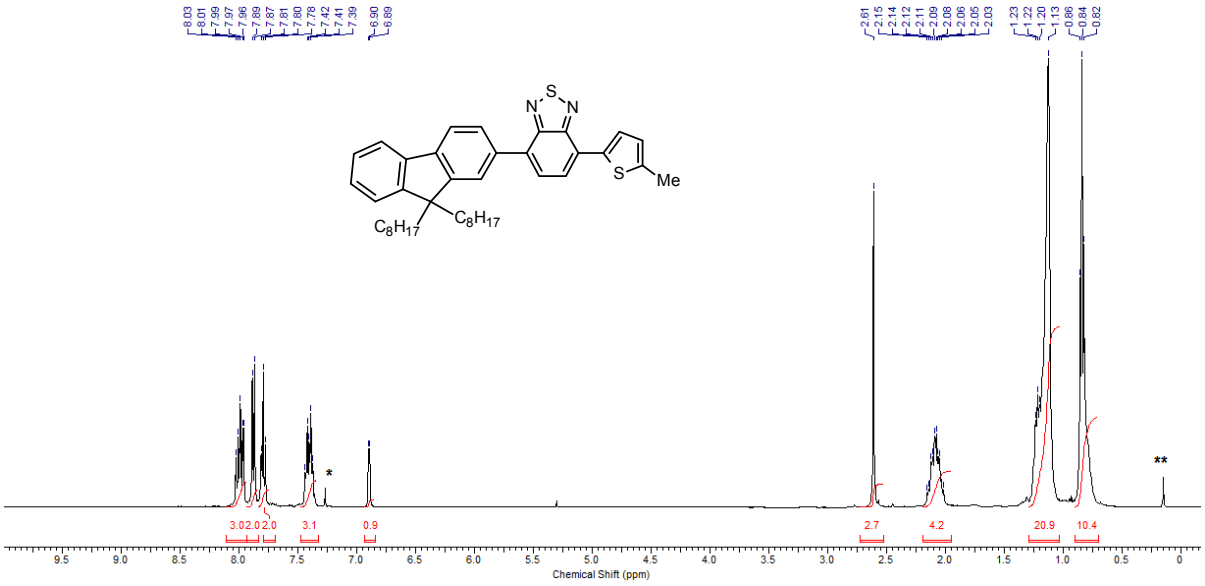
4-bromo-7-(9,9-dioctyl-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazole

($^{13}C\{^1H\}$ NMR, $CDCl_3$, 101MHz, 298K):



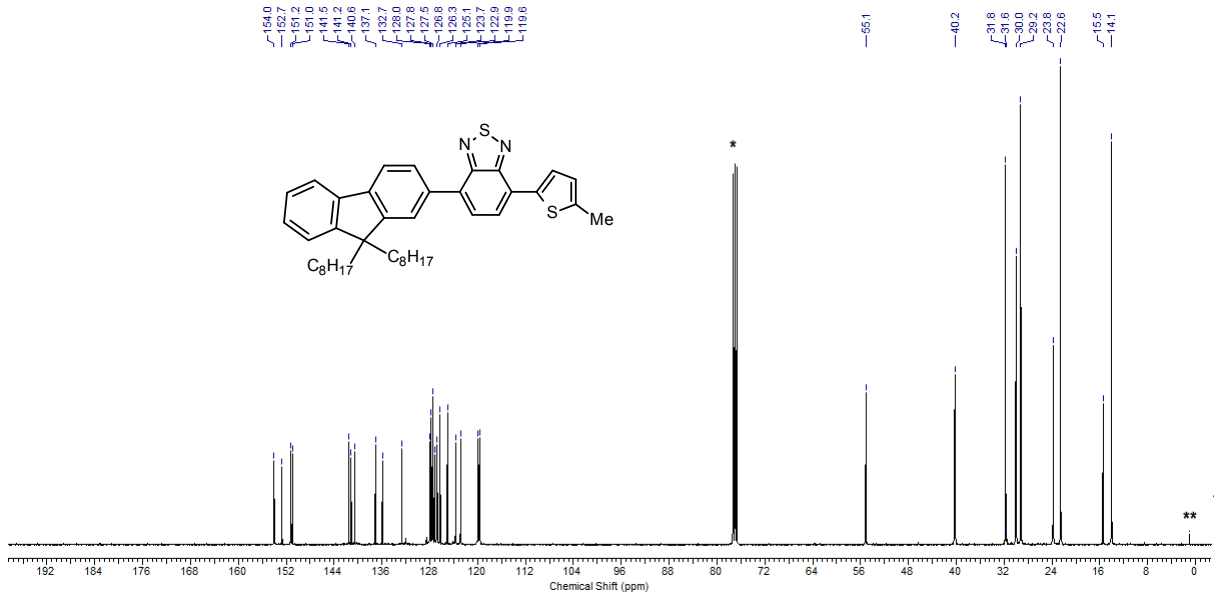
* = $CHCl_3$, ** = slight impurity which could not be removed

3 (^{1}H NMR, $CDCl_3$, 400MHz, 298K):



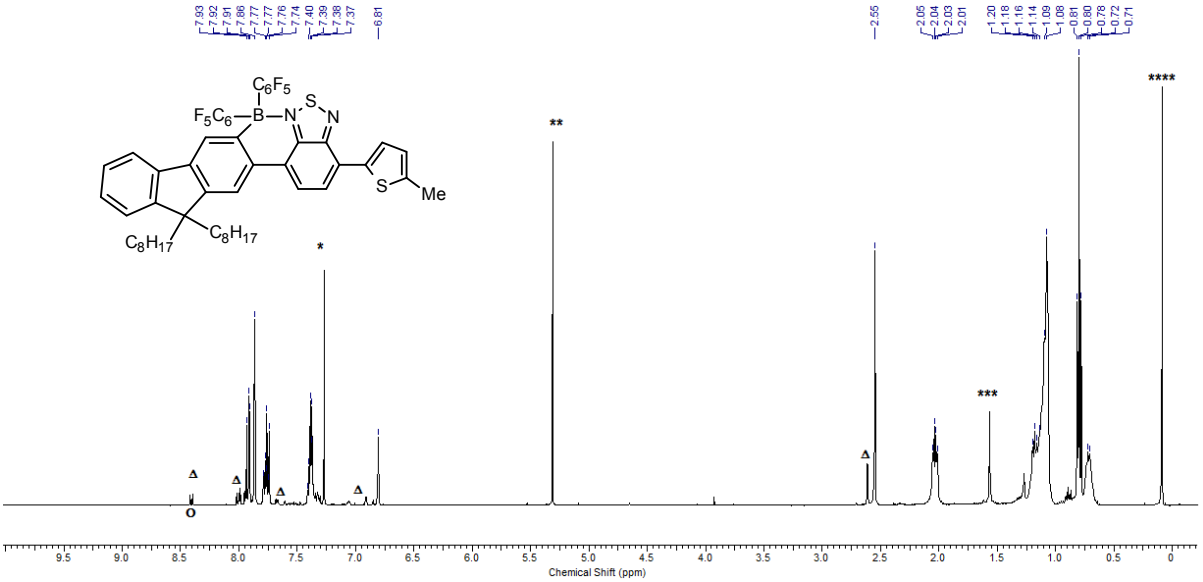
* = $CHCl_3$, ** = Silicone grease

3 (^{13}C{^{1}H} NMR, $CDCl_3$, 101MHz, 298K):



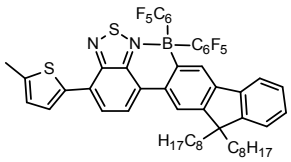
* = $CDCl_3$, ** = Silicone grease

3-B(C_6F_5)$_2$ (^{1}H NMR, $CDCl_3$, 400MHz, 298K):



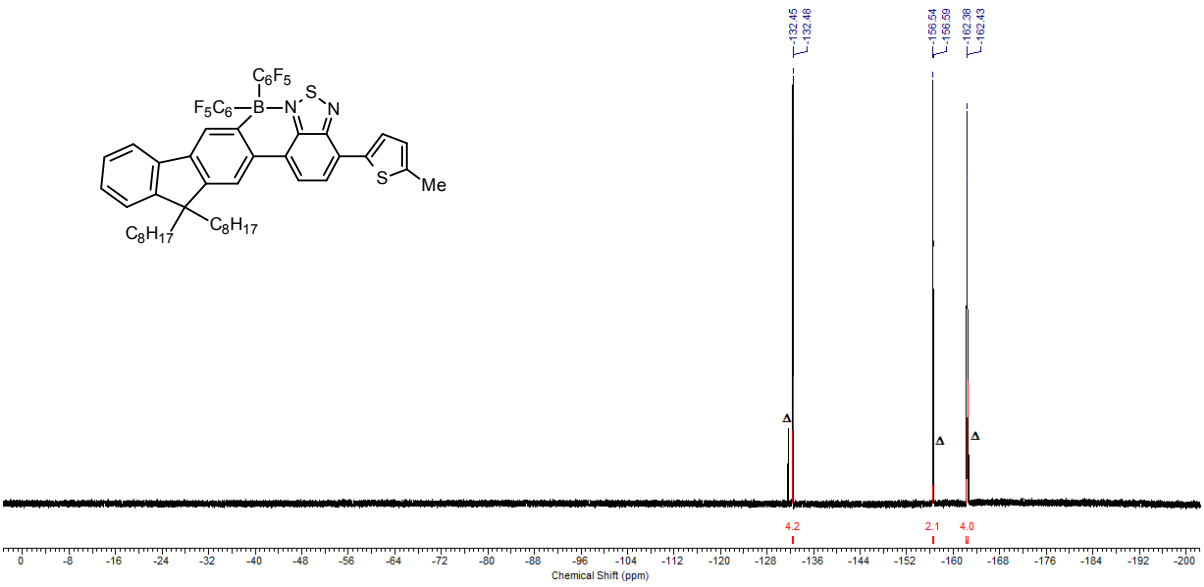
* = $CHCl_3$, ** = DCM, *** = H_2O, **** = Silicone grease.

Δ =

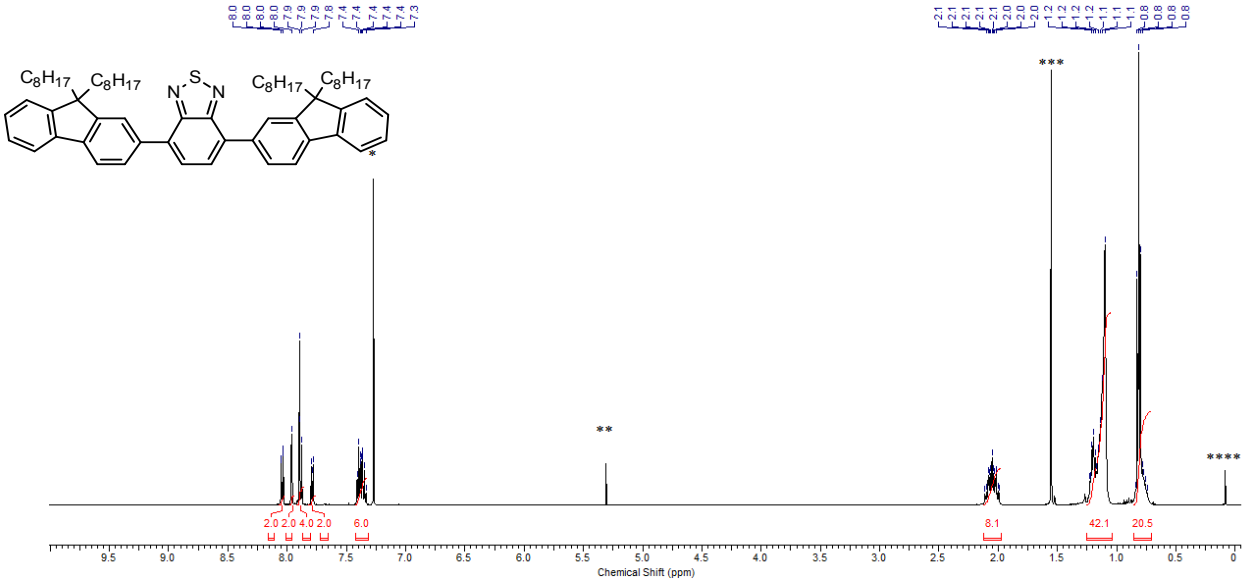


O = Diagnostic resonance at 8.41 ppm is consistent with that of borylated fluorene unit (see **4-B(C_6F_5)$_2$**)

3-B(C_6F_5)$_2$ (^{19}F{^{1}H}, $CDCl_3$, 376MHz , $CDCl_3$, 298K):

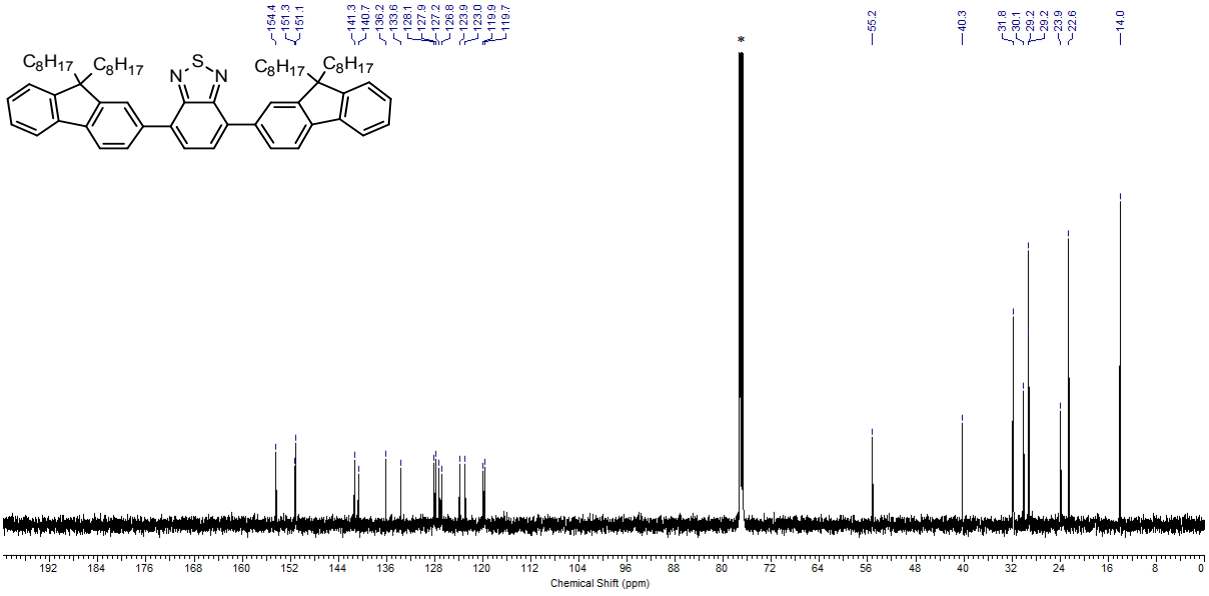


4 (^{1}H NMR, $CDCl_3$, 400MHz, 298K):



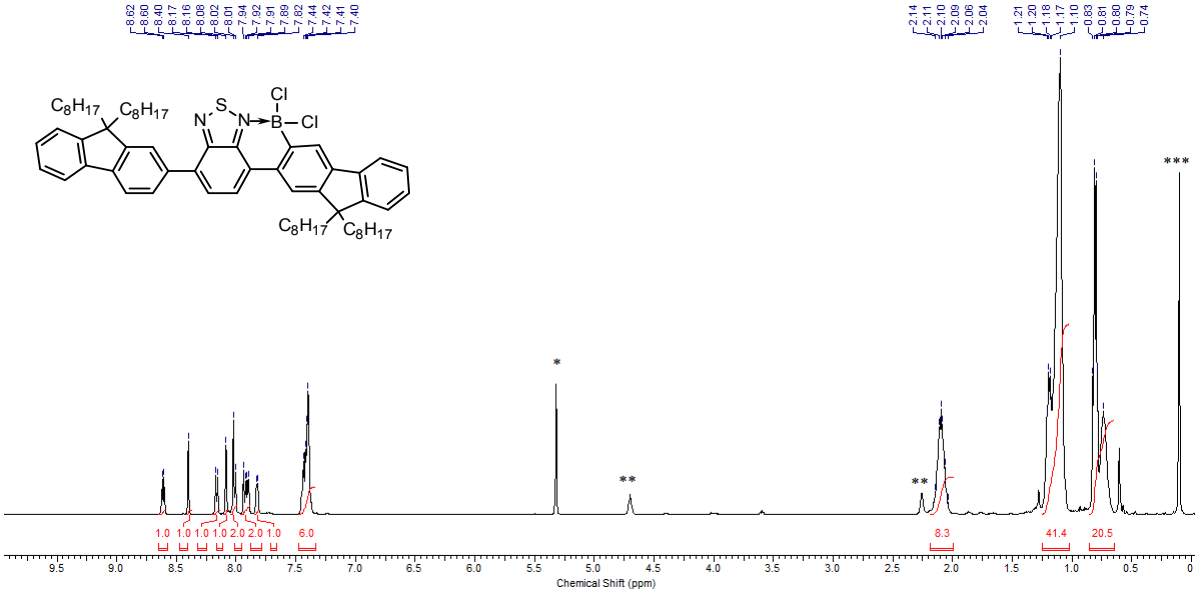
* = $CHCl_3$, ** = DCM, *** = H_2O, **** = Silicone grease

4 ($^{13}C\{^1H\}$ NMR, $CDCl_3$, 101MHz, 298K):



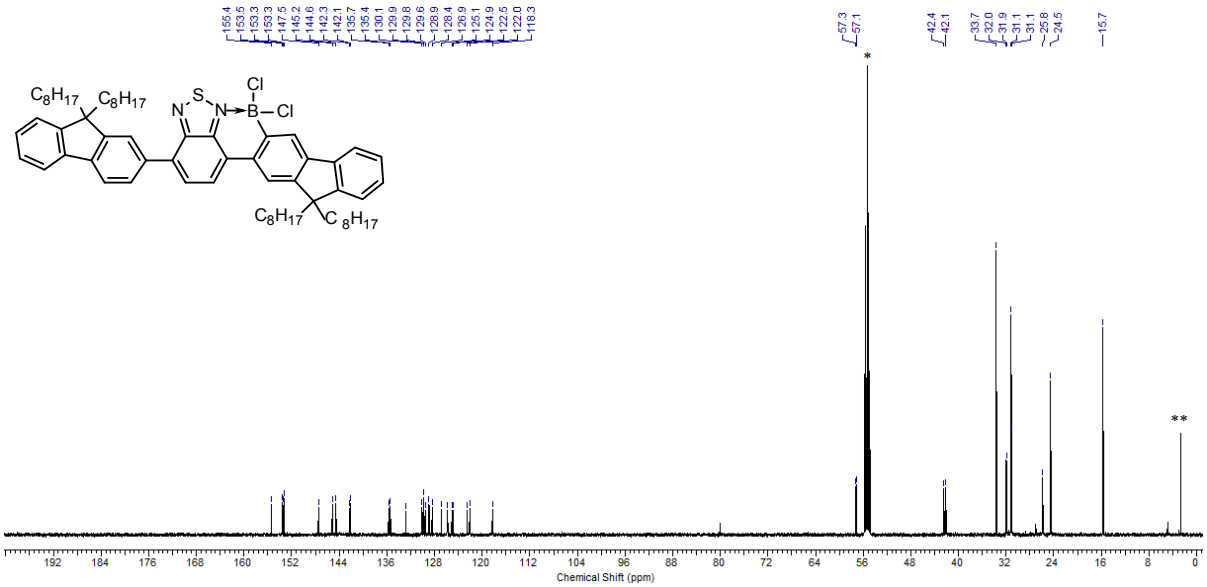
* = $CDCl_3$

4-BCl$_2$ (^{1}H NMR, CD_2Cl_2, 500MHz, 298K):



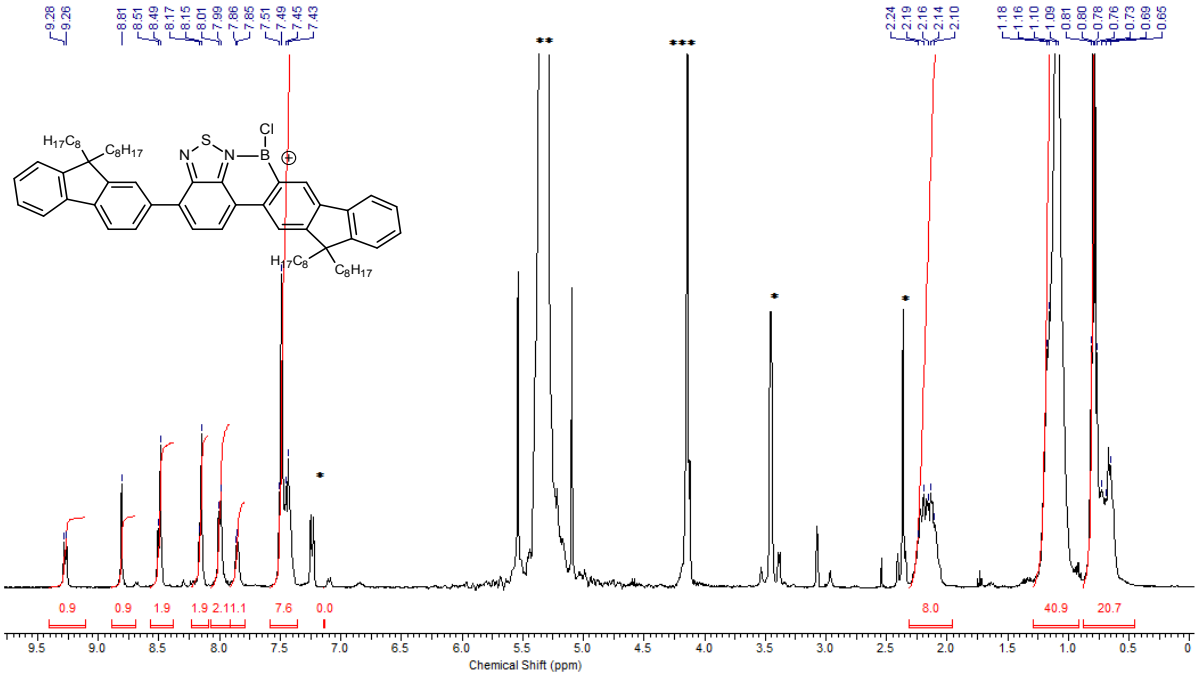
* = CH_2Cl_2, ** = THF, *** = Silicone grease

4-BCl$_2$ (^{13}C{^{1}H} NMR, CD_2Cl_2, 500MHz, 298K):



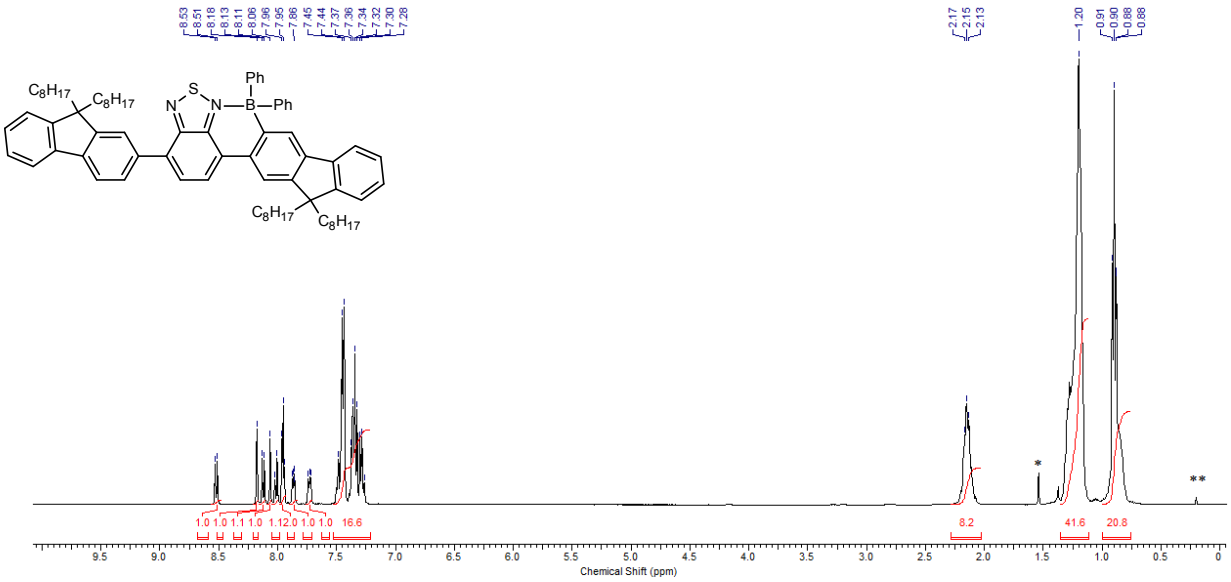
* = CD_2Cl_2,** = Silicone grease

[4-BCl]$^+$ (^{1}H NMR, CD_2Cl_2, 500MHz, 298K):



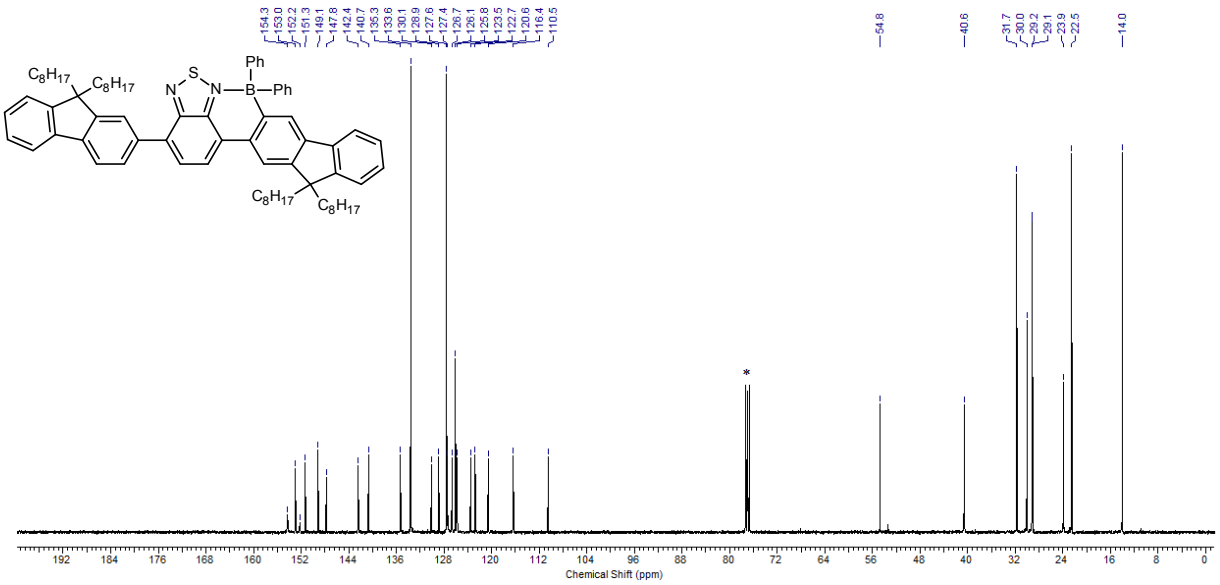
* = DMT-BCl_3, ** = DCM, *** = H_2O in d_6-DMSO capillary

4-BPh$_2$ (^{1}H NMR, $CDCl_3$, 400MHz, 298K):



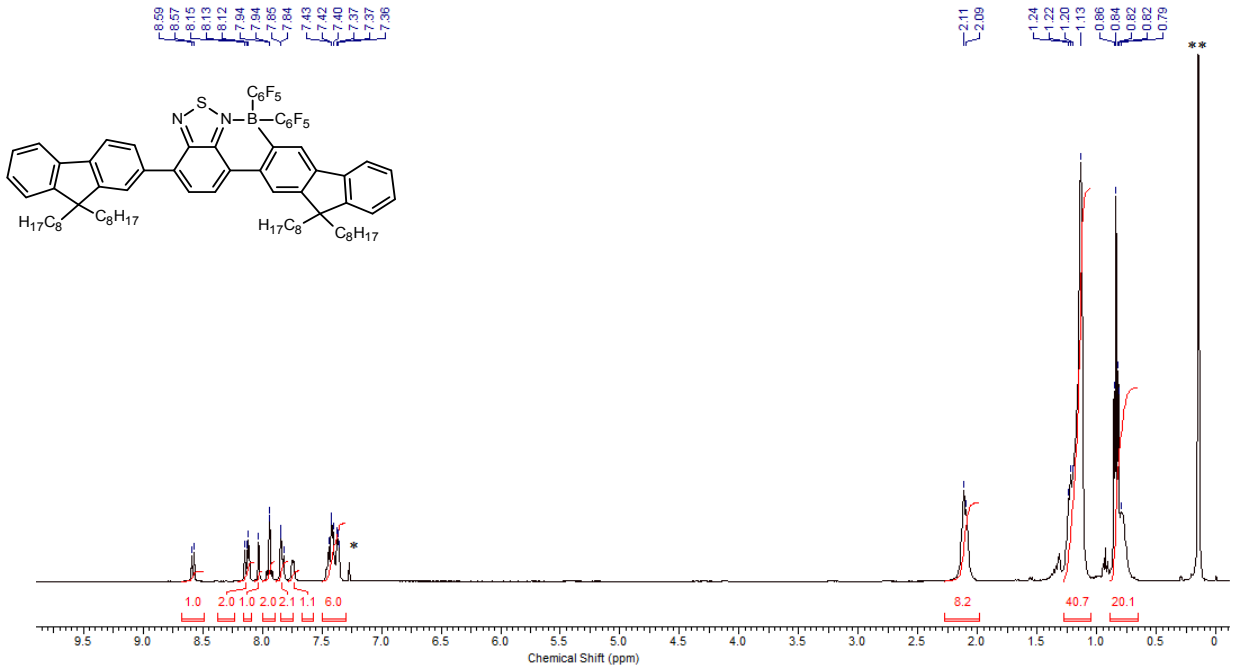
* = H_2O, ** = Silicone grease

4-BPh$_2$ (^{13}C{^{1}H} NMR, $CDCl_3$, 100MHz, 298K):



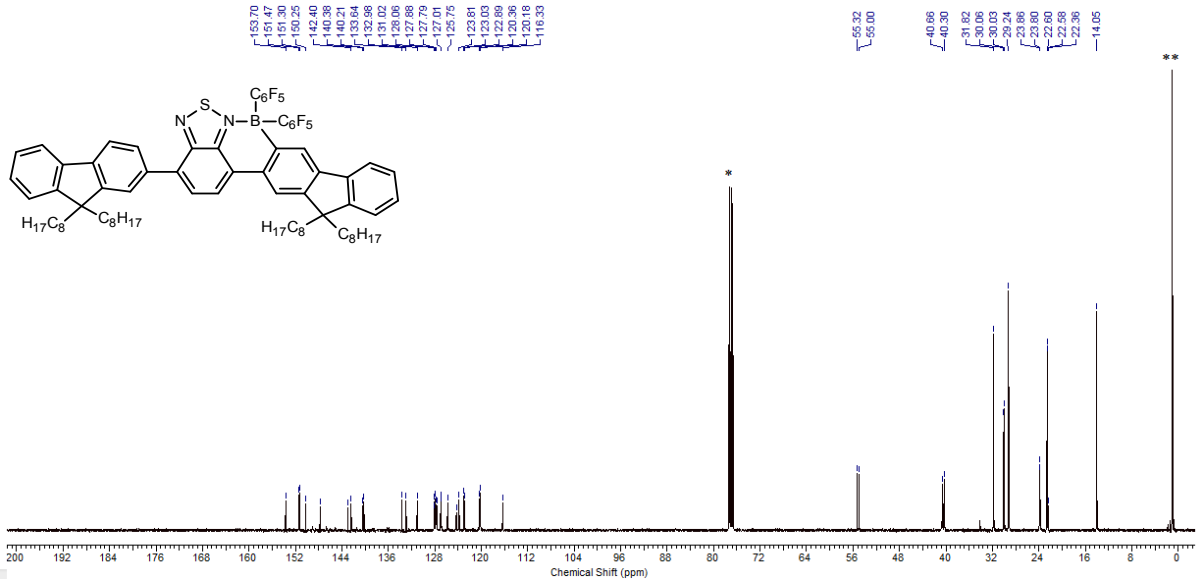
* = $CDCl_3$,

4-B(C_6F_5)$_2$ (^{1}H NMR, $CDCl_3$, 400MHz, 298K):



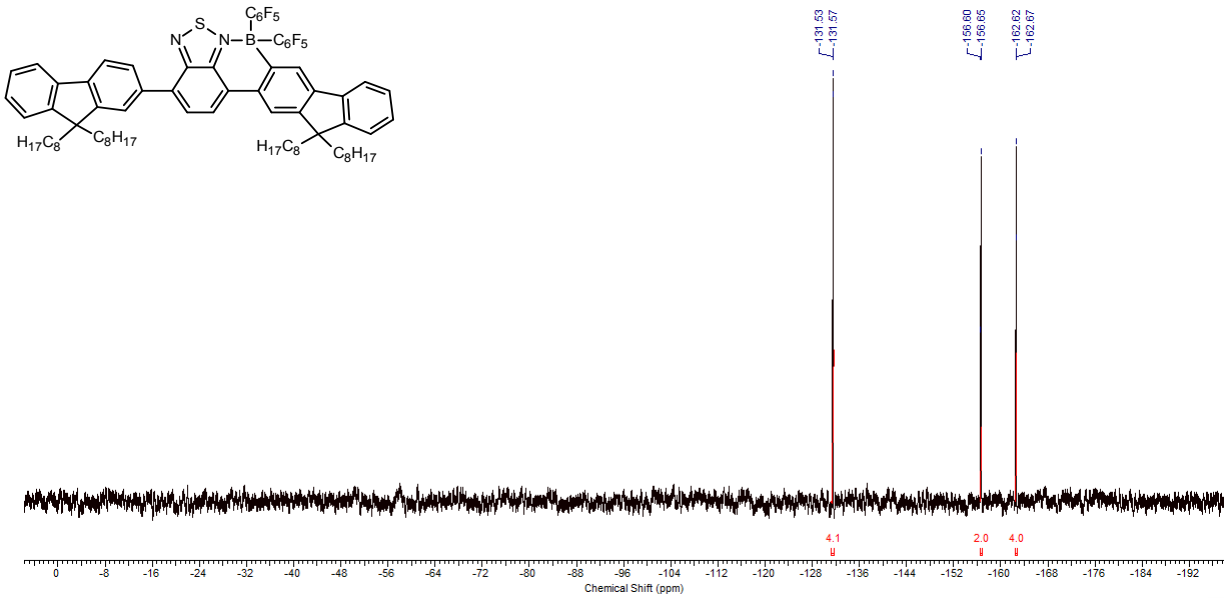
* = $CHCl_3$, ** = Silicone grease

4-B(C_6F_5)$_2$ (^{13}C{^{1}H} NMR, $CDCl_3$, 100MHz, 298K):

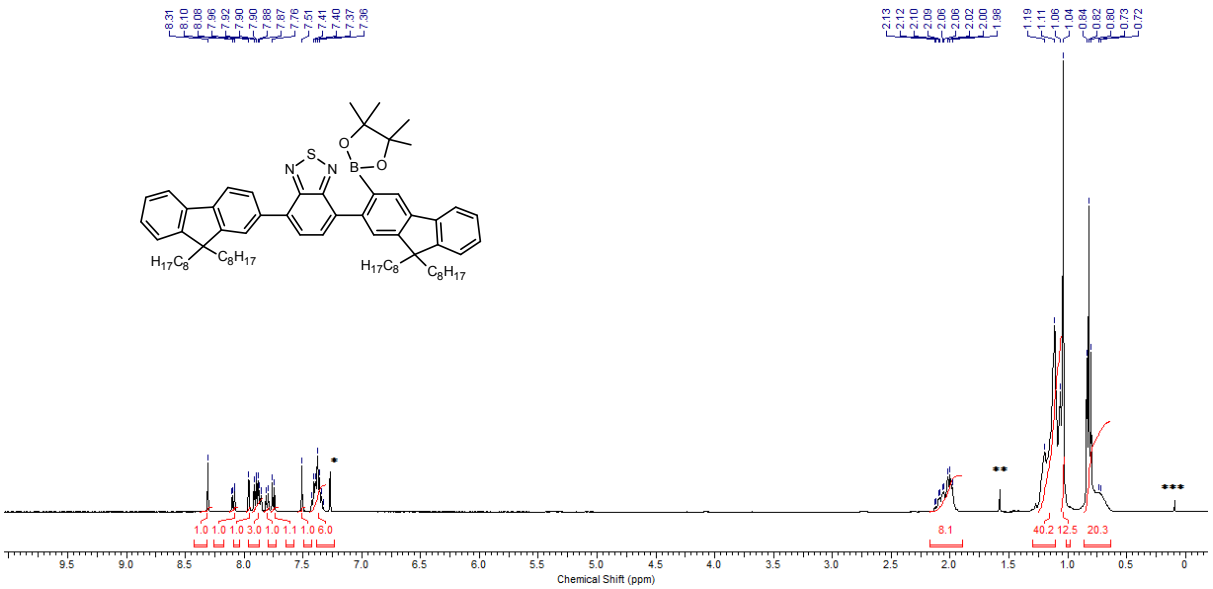


* = $CDCl_3$, ** = Silicone grease

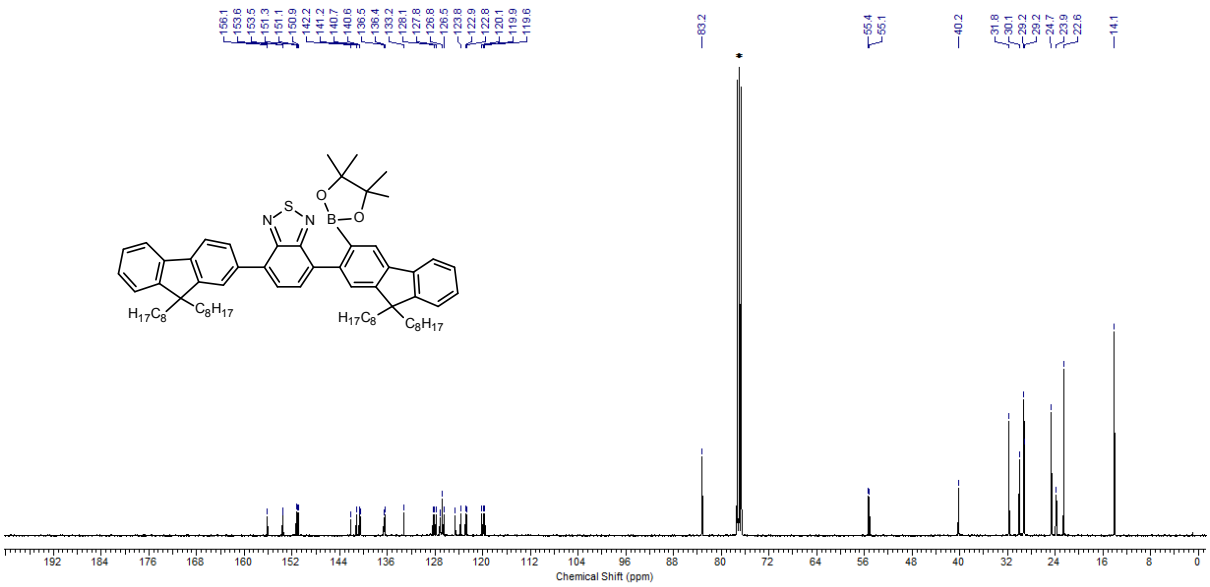
4-B(C_6F_5)$_2$ ($^{19}F\{^1H\}$, $CDCl_3$, 376MHz , $CDCl_3$, 298K):



4-BPin (^1H NMR, $CDCl_3$, 400MHz, 298K):

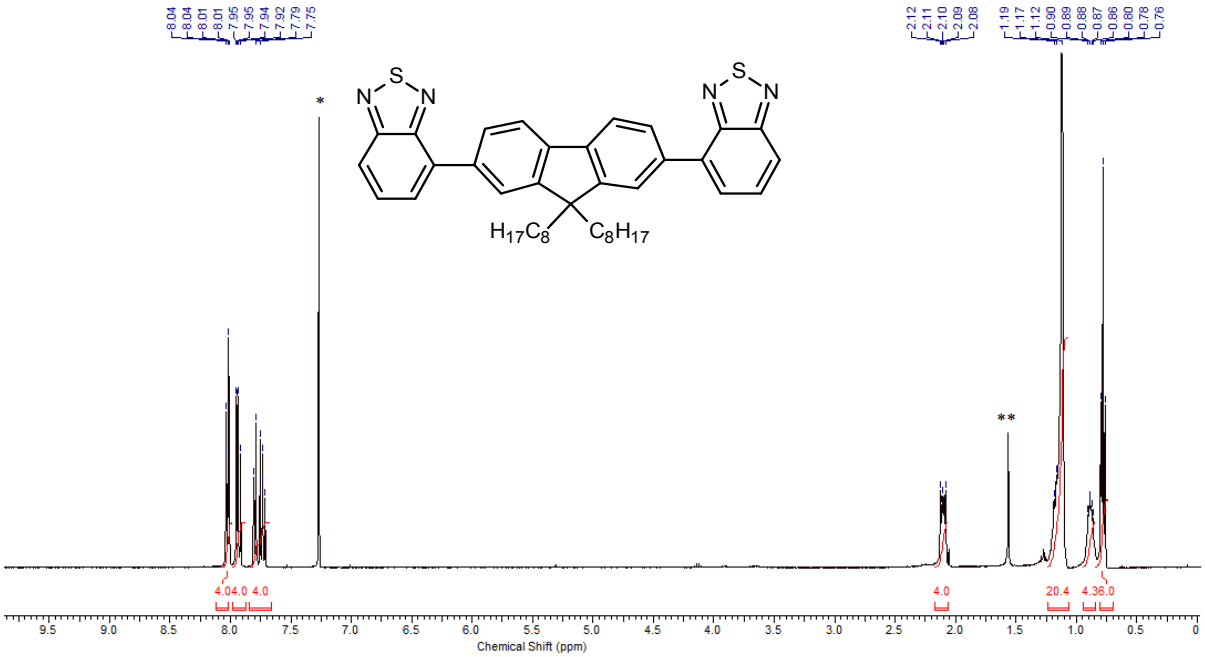


* = $CHCl_3$, ** = H_2O, *** = Silicone grease


156.1
153.6
153.5
151.3
151.1
150.9
142.2
141.2
140.7
140.6
136.5
136.4
133.2
128.1
127.8
126.8
126.5
123.8
122.9
122.8
120.1
119.9
119.6
83.2
55.4
55.1
40.2
31.8
30.1
29.2
29.2
24.7
23.9
22.6
14.1
*
O
S
N
N
B
O
O
H17C8
C8H17
H17C8
C8H17
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

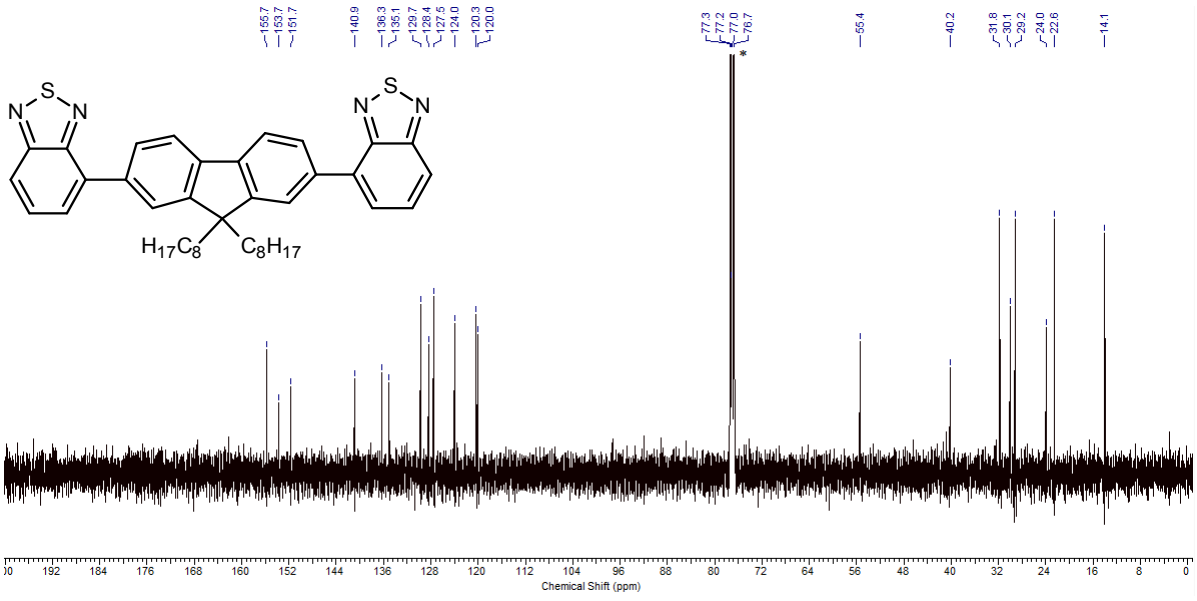
* = $CDCl_3$

5 (^{1}H NMR, $CDCl_3$, 400MHz, 298K):



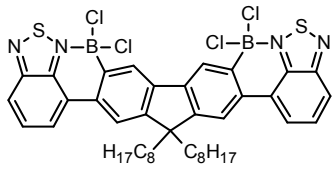
* = $CHCl_3$, ** = H_2O

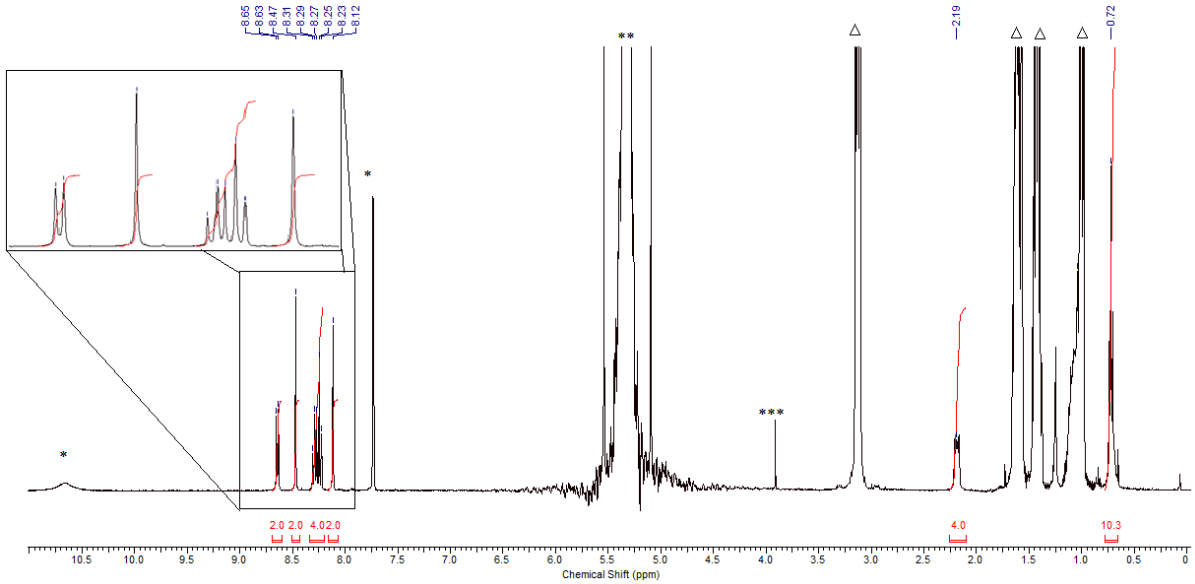
5 ($^{13}C\{^1H\}$ NMR, $CDCl_3$, 100MHz, 298K):



* = $CDCl_3$

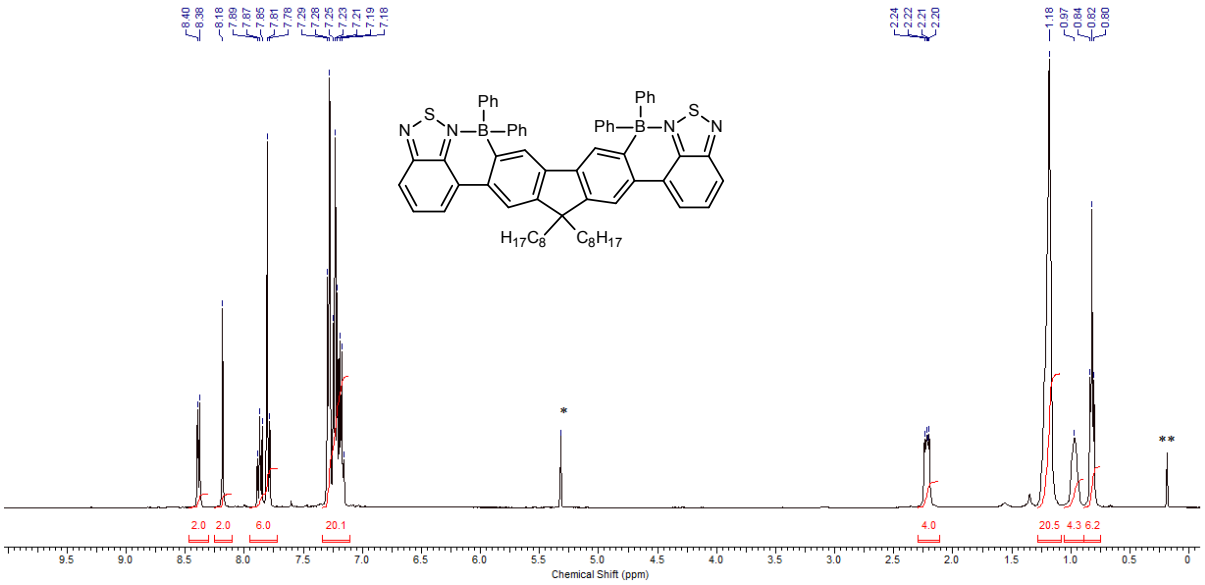
5-(BCl_2)$_2$ reaction mixture (^{1}H NMR, CH_2Cl_2 with d_6-DMSO capillary insert, 400MHz, 298K):





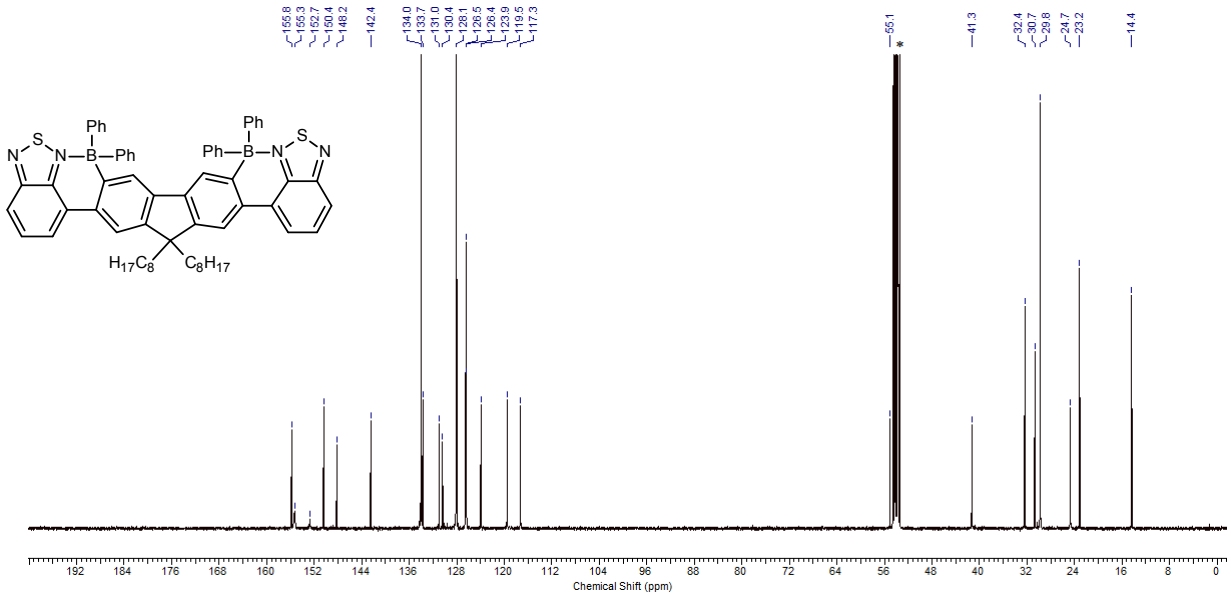
* = [TBP-H][$AlCl_4$], ** = DCM, *** = H_2O in *d*-DMSO capillary, △ = [N^nBu_4][$AlCl_4$]

5-(BPh_2)$_2$ (^{1}H NMR, CD_2Cl_2, 400MHz, 298K):



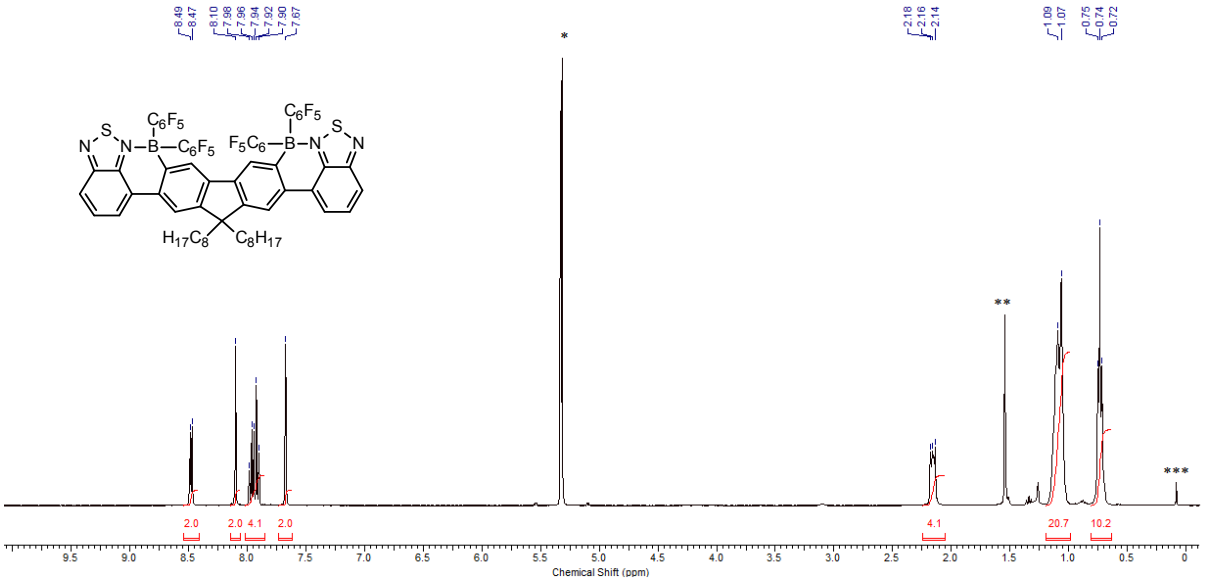
* = DCM, ** = Silicone grease

5-(BPh_2)$_2$ (^{13}C{^{1}H} NMR, CD_2Cl_2, 100MHz, 298K):



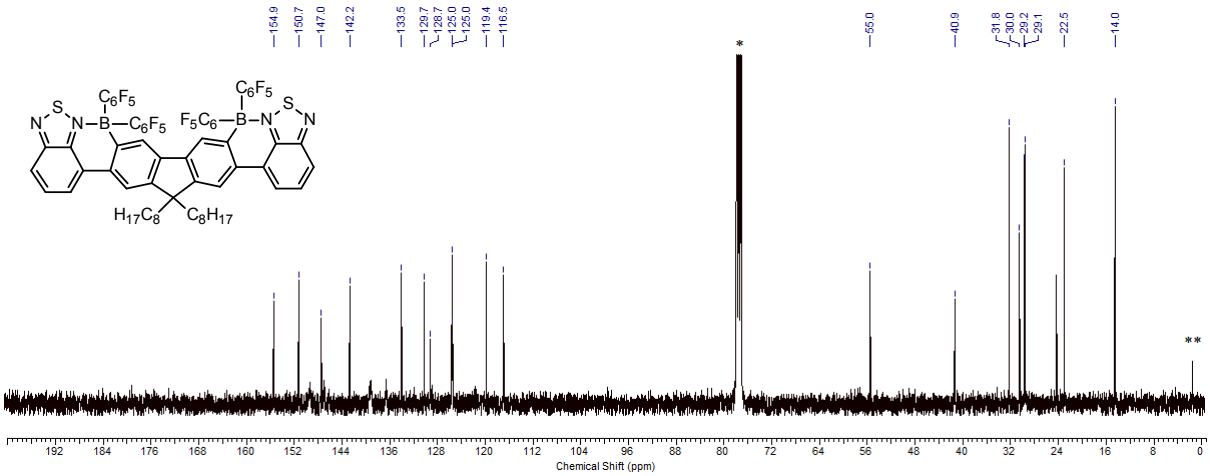
* = CD_2Cl_2

5-($B(C_6F_5)_2$)$_2$ (^{1}H NMR, CD_2Cl_2, 400MHz, 298K):



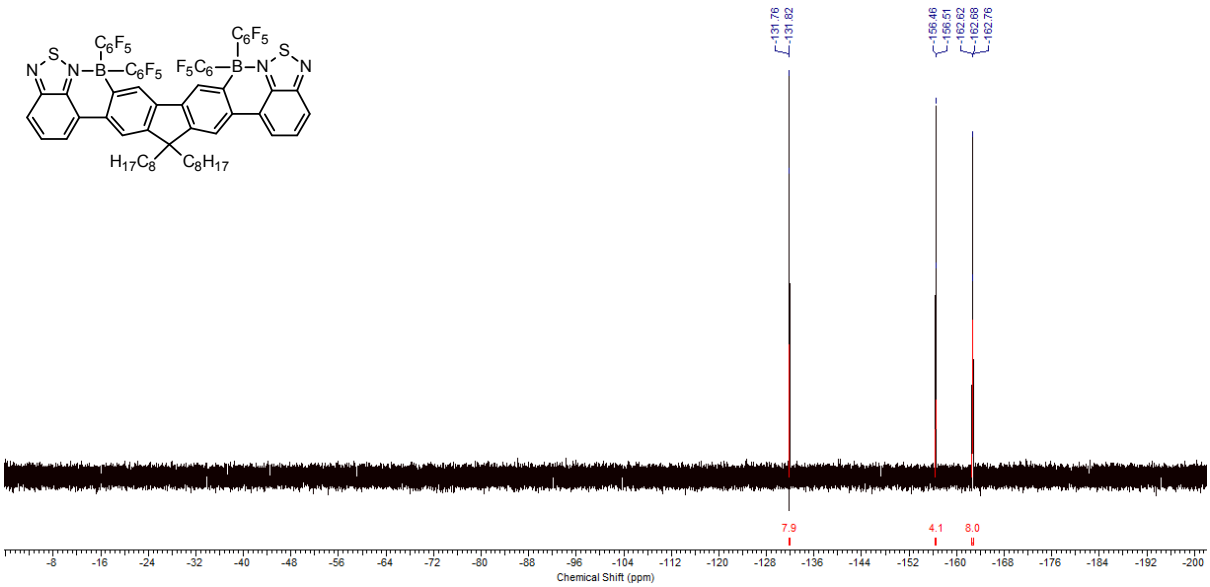
* = DCM, ** = H_2O, *** = Silicone grease

5-($B(C_6F_5)_2$)$_2$ ($^{13}C\{^1H\}$ NMR, $CDCl_3$, 100MHz, 298K):



* = $CDCl_3$, ** = Silicone grease

5-($B(C_6F_5)_2$)$_2$ ($^{19}F\{^1H\}$, $CDCl_3$, 376MHz , $CDCl_3$, 298K):



Computational Analysis

Computational analysis (at the M06-2x/6-311g (d,p) level with PCM solvation (DCM)) of a simplified model of **2-BMe_2** where an octyl and an octylthiophene is replaced for Hydrogen and (termed **2'-BMe_2**).

Cartesian Coordinates and Total Energy of Ground State Structure of **2'-BMe_2**

Symbol	X	Y	Z
C	1.4048750	0.6418530	-0.0001200
C	1.5777230	-0.7243380	0.0000190
C	2.9729190	-1.0470330	-0.0000640
C	3.7921610	0.0412690	-0.0002450
S	2.9070360	1.5199610	-0.0003430
H	3.3521090	-2.0615980	0.0000140
H	4.8715120	0.0689440	-0.0003340
C	0.1069030	1.2883810	-0.0000860
C	-0.1817670	2.6288270	-0.0002100
C	-1.0270870	0.4162550	0.0000910
C	-1.5268200	3.1212490	-0.0001630
H	0.6279710	3.3496550	-0.0003550
C	-2.3757800	0.8993180	0.0001330
C	-2.6177360	2.3040650	0.0000030
H	-1.6700660	4.1948330	-0.0002700
H	-3.6313590	2.6799330	0.0000340
N	-0.9736810	-0.9098050	0.0002150
N	-3.2751100	-0.0811760	0.0002840
S	-2.5150120	-1.5043040	0.0003990
B	0.3899300	-1.8174390	0.0002750
C	0.3603060	-2.7073050	-1.3548980
H	0.2982820	-2.0945150	-2.2602650
H	-0.4805930	-3.4117920	-1.3664530
H	1.2755510	-3.3044310	-1.4265970
C	0.3604780	-2.7067950	1.3557910
H	-0.4804210	-3.4112750	1.3677120
H	1.2757370	-3.3038870	1.4276060
H	0.2985640	-2.0936570	2.2609300

Total energy of **2'-BMe_2**: E(RM062X) = -1394.54072434 a.u.

Computational analysis (at the M06-2x/6-311g (d,p) level with PCM solvation (DCM)) of a simplified model of **4-BMe$_2$** where octyl and an 9, 9'-dioctylFluorene is replaced for Hydrogen and (termed **4'-BMe$_2$**).

Cartesian Coordinates and Total Energy of Ground State Structure of **4'-BMe$_2$**

Symbol	X	Y	Z
C	-3.5302260	3.1030000	0.0001010
C	-2.1936380	2.5882060	0.0002350
C	-1.9065310	1.2459150	0.0001640
C	-3.0578240	0.3981830	0.0000150
C	-4.4034500	0.8981420	-0.0001440
C	-4.6320630	2.3029780	-0.0001160
H	-3.6548590	4.1788850	0.0001380
H	-1.3898560	3.3124300	0.0003630
H	-5.6415640	2.6898610	-0.0002610
C	-0.5677340	0.6234580	0.0001630
C	-0.4596480	-0.7864160	0.0001590
C	0.5785530	1.4424750	0.0001200
C	0.8302540	-1.3384310	0.0001280
C	1.8296830	0.8677500	0.0000850
H	0.4858890	2.5232440	0.0000970
C	1.9567610	-0.5303630	0.0000890
H	0.9431740	-2.4194550	0.0001370
C	3.3886780	-0.8606660	0.0000240
C	4.1179930	0.3371360	-0.0000200
C	4.0389310	-2.0910060	-0.0000030
C	5.5044760	0.3138560	-0.0000900
C	5.4309930	-2.1097150	-0.0000750
H	3.4756440	-3.0175550	0.0000290
C	6.1579710	-0.9187800	-0.0001180
H	6.0773590	1.2357650	-0.0001250
H	5.9565970	-3.0571960	-0.0000980
H	7.2409850	-0.9529550	-0.0001750
N	-5.3179150	-0.0675610	-0.0003930
N	-3.0322980	-0.9279140	-0.0000690
S	-4.5805330	-1.5013210	-0.0001170
C	3.1916280	1.5436470	0.0000230
C	3.3931050	2.3984600	-1.2594380
H	3.2489590	1.8000560	-2.1613990

H	2.6800960	3.2267370	-1.2746450
H	4.4027340	2.8167510	-1.2774240
C	3.3932240	2.3984420	1.2594800
H	3.2491730	1.8000210	2.1614440
H	4.4028530	2.8167360	1.2773700
H	2.6802120	3.2267150	1.2747720
B	-1.6945360	-1.8395890	0.0002960
C	-1.7449330	-2.7345520	1.3550260
H	-1.7905300	-2.1217450	2.2617610
H	-0.8482610	-3.3586820	1.4278750
H	-2.6056210	-3.4150830	1.3666950
C	-1.7446900	-2.7354210	-1.3538580
H	-1.7900560	-2.1232010	-2.2610020
H	-0.8480680	-3.3596870	-1.4261290
H	-2.6054150	-3.4159100	-1.3652920

Total energy of **4'-BMe_2**: E(RM062X) = -1421.50867336 a.u.

Computational analysis (at the M06-2x/6-311g (d,p) level with PCM solvation (DCM)) of a simplified model of **5-$(BPh_2)_2$** where octyl is replaced for methyl (termed **5'-$(BPh_2)_2$**) indicates no contribution to the frontier molecular orbitals from the phenyl substituents on boron. It is these groups that are involved in the extended π-stacking interactions observed in the solid state structure of **5-$(BPh_2)_2$**. The molecular orbital contour plots show that for both **5'** and **5'-$(BPh_2)_2$** the HOMO orbital is delocalised across the fluorene and benzothiadiazole units, whilst the electron density of the LUMO is localised on the benzothiadiazole units.

Samples were optimised at the M06-2x/6311G(dp) level using Gaussian 09 and confirmed to have zero imaginary frequencies.

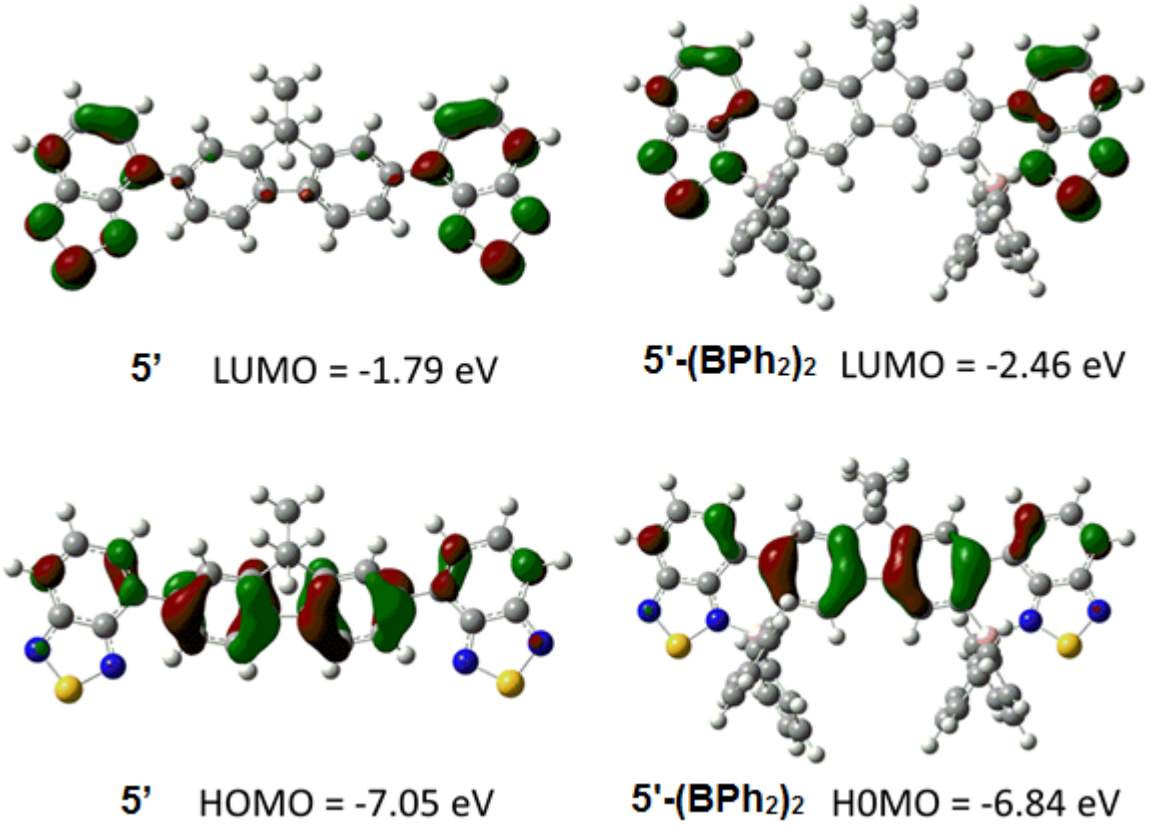


Figure S29. Molecular orbital diagrams (isovalue = 0.04) for the HOMO and LUMO of **5'** and **5'-$(BPh_2)_2$**.

Cartesian Coordinates and Total Energy of Ground State Structure of **5'**

Symbol	X	Y	Z
C	-2.525507	1.116217	0.21749
C	-3.461623	0.237589	-0.347715
C	-3.01026	-0.888529	-1.05135
C	-1.652704	-1.140159	-1.209633
C	-0.73421	-0.257447	-0.649529
C	-1.17387	0.865956	0.063997
H	-2.867238	1.974468	0.788078
H	-3.734806	-1.56583	-1.484181
H	-1.324067	-2.010959	-1.765709
C	0.734205	-0.257452	-0.649545
C	1.173888	0.865948	0.063972
C	1.652682	-1.140168	-1.20967
C	2.52553	1.116201	0.217436
C	3.010243	-0.888546	-1.051416
H	1.324028	-2.010966	-1.765741
C	3.461628	0.237568	-0.34779
H	2.867279	1.974449	0.788017
H	3.734776	-1.565852	-1.484264
C	0.000017	1.675162	0.590802
C	0.000034	1.723715	2.125801
H	0.8854	2.252784	2.48723
H	-0.885322	2.252789	2.487249
H	0.000035	0.716032	2.546063

C	0.000016	3.098255	0.013697
H	0.885297	3.643693	0.350162
H	0.000005	3.074222	-1.077941
H	-0.885255	3.643699	0.35018
C	4.907169	0.532551	-0.228848
C	5.880356	-0.500187	0.006853
C	5.393143	1.809233	-0.331916
C	7.281718	-0.174627	0.120703
C	6.783247	2.128531	-0.217604
H	4.699925	2.61819	-0.531932
C	7.727081	1.172938	0.000275
H	7.079939	3.165399	-0.318433
H	8.781447	1.400611	0.084096
C	-4.907159	0.532581	-0.228742
C	-5.880347	-0.500152	0.006978
C	-5.393129	1.809265	-0.331803
C	-7.281705	-0.174586	0.120851
C	-6.78323	2.12857	-0.217468
H	-4.699911	2.618219	-0.531834
C	-7.727065	1.172981	0.000427
H	-7.079919	3.165438	-0.318295
H	-8.781428	1.400659	0.084262
N	-8.047493	-1.238969	0.351463
N	-5.638635	-1.799977	0.165272
N	8.047503	-1.239012	0.351315
S	-7.065018	-2.526146	0.421086
S	7.065027	-2.526189	0.42092
N	5.638639	-1.800008	0.165163

Total energy of **5'**: E(RM062X) = -2054.88812523 a.u.

Cartesian Coordinates and Total Energy of Ground State Structure of **5'-(BPh_2)$_2$**

Symbol	X	Y	Z
C	2.519082	2.963709	0.084103
C	3.45187	1.909417	0.11604
C	3.027048	0.561855	0.119999
C	1.649703	0.30679	0.075933
C	0.733733	1.347144	0.025925
C	1.17231	2.681748	0.035307
H	2.851059	3.99617	0.107802
H	1.301616	-0.722742	0.080531
C	-0.733763	1.347152	-0.025979
C	-1.17232	2.681762	-0.035523
C	-1.649749	0.306807	-0.075856
C	-2.519088	2.963737	-0.084352
C	-3.02709	0.561886	-0.119949
H	-1.301678	-0.722732	-0.080329
C	-3.451892	1.909455	-0.11616
H	-2.851048	3.9962	-0.108173
C	0.000002	3.649886	-0.000167
C	0.037153	4.527653	-1.259538
H	-0.844331	5.172863	-1.298216
H	0.925749	5.164151	-1.252843
H	0.057033	3.911296	-2.160632
C	-0.037135	4.527803	1.2591

H	-0.925725	5.164309	1.252337
H	-0.057017	3.91155	2.160266
H	0.844355	5.173009	1.297699
C	-4.894771	2.213001	-0.181681
C	-5.81048	1.136114	-0.382832
C	-5.483645	3.451625	-0.118485
C	-7.219606	1.327031	-0.567157
C	-6.892689	3.65714	-0.271708
H	-4.873939	4.33066	0.045264
C	-7.766869	2.639104	-0.505364
H	-7.26359	4.672641	-0.208301
H	-8.828877	2.793105	-0.637562
C	4.894754	2.212949	0.181527
C	5.810441	1.136076	0.382857
C	5.483651	3.451551	0.118147
C	7.219564	1.326996	0.567194
C	6.892696	3.657064	0.271371
H	4.873965	4.330572	-0.045756
C	7.766852	2.63905	0.505213
H	7.263618	4.672548	0.207812
H	8.828858	2.793054	0.637417
N	7.87465	0.187799	0.778454
N	5.481998	-0.148884	0.446377
N	-7.874718	0.187814	-0.778222
S	6.837905	-1.043292	0.747467
S	-6.837992	-1.043288	-0.7471
N	-5.482062	-0.148862	-0.446175
B	4.011323	-0.728439	0.09396
B	-4.011375	-0.728398	-0.093781
C	4.15263	-1.366939	-1.398093
C	4.834995	-2.57653	-1.598449
C	3.653336	-0.726555	-2.5377
C	5.017333	-3.11867	-2.866385
H	5.217775	-3.123095	-0.739554
C	3.824616	-1.261448	-3.814145
H	3.113682	0.209267	-2.430099
C	4.50948	-2.459069	-3.983201
H	5.546243	-4.057936	-2.984383
H	3.421656	-0.741483	-4.676248
H	4.643523	-2.878922	-4.973655
C	3.630196	-1.801574	1.247942
C	2.895957	-2.962871	0.975072
C	3.946607	-1.552709	2.591697
C	2.500824	-3.835051	1.987381
H	2.629141	-3.192704	-0.05221
C	3.565674	-2.41987	3.610748
H	4.496498	-0.651818	2.85359
C	2.839179	-3.568951	3.310058
H	1.930631	-4.724261	1.741906
H	3.828941	-2.197833	4.639127
H	2.537253	-4.247261	4.099665
C	-4.152621	-1.36681	1.398315
C	-4.834943	-2.576409	1.598768
C	-3.653327	-0.72633	2.537868
C	-5.017238	-3.118467	2.866745

H	-5.217725	-3.123044	0.739918
C	-3.824564	-1.26114	3.814353
H	-3.11371	0.209503	2.430192
C	-4.509385	-2.458772	3.983506
H	-5.546115	-4.057742	2.984819
H	-3.421606	-0.741101	4.676413
H	-4.643395	-2.878562	4.97399
C	-3.630292	-1.801597	-1.24772
C	-2.896021	-2.962867	-0.974823
C	-3.946763	-1.552804	-2.591475
C	-2.500918	-3.835093	-1.987105
H	-2.629156	-3.192643	0.052459
C	-3.56586	-2.42001	-3.610499
H	-4.49668	-0.651936	-2.85339
C	-2.839334	-3.569066	-3.30978
H	-1.930701	-4.724281	-1.741609
H	-3.829174	-2.19803	-4.638877
H	-2.53743	-4.24741	-4.099367

Total energy of **5'-(BPh_2)$_2$**: E(RM062X) = -3029.91535869 a.u.

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