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**Bifuran-bridged bisboranes: highly luminescent B-doped oligoheteroarenes**

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## 1 Experimental Section

**General procedures.** All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques or in an MBraun glove box. Solvents (dichloromethane, *n*-pentane, diethylether, toluene, and tetrahydrofuran) were dried and degassed by means of an MBraun SPS-800 solvent purification system. Methanol was dried over magnesium turnings and freshly distilled prior to use. Deuterated solvents for NMR spectroscopy were dried and degassed at reflux over Na ( $C_6D_6$ ) or  $CaH_2$  ( $CDCl_3$  and  $CD_2Cl_2$ ) and freshly distilled prior to use. Solvents for aqueous work up (*n*-hexane, *n*-pentane, dichloromethane, ethanol, diethylether), tribromoborane, bromobenzene, thiophene, 2-bromothiophene, bromine, 1,3,5-tri-*tert*-butylbenzene, 2-bromo-1,3,5-triisopropylbenzene and lithium bis(trifluoromethylsulfonyl)imide were purchased from commercial sources and used as received. Solutions of *n*-butyllithium (1.6 M and 2.5 M in hexane, respectively) were purchased from Sigma Aldrich and used as received as well. Trimethylsilylchloride, methoxytrimethylsilane and furan were commercially purchased and freshly distilled prior to use. Copper (II) chloride was commercially purchased and dried at 180 °C for 5 hours prior to use. 2,4,6-triisopropylphenyllithium,<sup>[1]</sup> trimethylsilylbis(trifluoromethylsulfonyl)imide,<sup>[2]</sup> 2-bromo-1,3,5-tri-*tert*-butylbenzene,<sup>[3]</sup> 2,4,6-tri-*tert*-butylphenyllithium,<sup>[4]</sup> 2,2'-bifuran,<sup>[5]</sup> and 5,5'-bis(trimethylsilyl)-2,2'-bifuran<sup>[6]</sup> were prepared according to methods described in the literature. Compounds **9a**, **9b** and **9c** were prepared according to procedures previously described by us.<sup>[7]</sup> NMR spectra were recorded at 25 °C on a Bruker Avance III HD spectrometer operating at 300 MHz or on a Bruker Avance 500 spectrometer operating at 500 MHz. Chemical shifts were referenced to residual protic impurities in the solvent ( $^1H$ ) or the deuterated solvent itself ( $^{13}C$ ) and reported relative to external  $SiMe_4$  ( $^1H$ ,  $^{13}C$ ) or  $BF_3 \cdot OEt_2$  ( $^{11}B$ ) standards. Mass spectra were obtained with the use of a Thermo Scientific Exactive Plus Orbitrap MS system employing either atmospheric sample analysis probe (ASAP), electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI). Elemental analyses were performed on an Elementar vario MICRO cube elemental analyzer. Cyclic voltammetry experiments were performed using a Gamry Instruments Reference 600 potentiostat. A standard three-electrode cell configuration was employed using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire, separated by a Vycor tip, serving as the reference electrode. Tetra-*n*-butylammonium hexafluorophosphate ( $[n-Bu_4N][PF_6]$ ) was employed as the supporting electrolyte. Compensation for resistive losses (*iR* drop) was employed for all measurements. Cyclic voltammetry scans were conducted with a scan rate of 250 mV/s. The scans were referenced after the addition of a small amount of ferrocene as internal standard. The potentials are reported relative to the ferrocene/ferrocenium couple.

Crystals suitable for single-crystal X-ray diffraction were selected, coated in perfluoropolyether oil, and mounted on MiTeGen sample holders. Diffraction data were collected on Bruker X8 Apex II 4-circle diffractometers with CCD area detectors using Mo-K $\alpha$  radiation. The crystals were cooled using an Oxford Cryostreams low-temperature device. Data were collected at 100 K. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the Bruker software packages. The structures were solved using the intrinsic phasing method (SHELXT)<sup>[8]</sup> and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' in idealized positions, by full-matrix least squares against  $F^2$  of all data, using SHELXL<sup>[9]</sup> software and the SHELXLE graphical user interface.<sup>[10]</sup> Other structural information was extracted using OLEX2 software.<sup>[11]</sup> UV-vis spectra were obtained using a Jasco V-630 spectrophotometer. Emission spectra were recorded using an Edinburgh Instruments FLSP920 spectrometer equipped with a double monochromator for both excitation and emission, operating in right-angle geometry mode, and all spectra were fully corrected for the spectral response of the instrument. Fluorescence quantum yields were measured using a calibrated integrating sphere from Edinburgh Instruments combined with the FLSP920 spectrometer described above.

## Syntheses

**Synthesis of 5.** To a solution of **4** (0.88 g, 3.1 mmol) in dichloromethane (10 mL) was added tribromoborane (1.94 g, 7.75 mmol) at 0 °C. The reaction mixture was stirred for 2 h. Then, the solvent was removed in vacuo, and a green solid was obtained. Yield: 1.476 g (3.1 mmol, 100%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.75 (d, <sup>3</sup>J<sub>HH</sub> = 3.7 Hz, 2H, Fur-CH), 7.11 (d, <sup>3</sup>J<sub>HH</sub> = 3.7 Hz, 2H, Fur-CH) ppm; <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, CDCl<sub>3</sub>):  $\delta$  = 45.3 (s) ppm. In the following, compound **5** was used without prior isolation.

**Synthesis of 7.** To a solution of **4** (2.81 g, 10.0 mmol) in dichloromethane (100 ml) was added tribromoborane (10.02 g, 40.0 mmol) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C, then all volatiles were removed in vacuo. The crude residue was re-dissolved in toluene (50 mL) followed by addition of a solution of TipLi (3 equiv.) in toluene at 0 °C. The reaction mixture was allowed to warm up to ambient temperatures and was stirred overnight. The solvent was removed in vacuo, and the resulting solid was extracted with dichloromethane. The obtained compound **6** was used without prior isolation and was then treated with TMS-OMe (3.02 g, 29.0 mmol) at 0 °C. The mixture was stirred overnight at room temperature. After all volatiles were removed in vacuo, an orange solid was obtained as crude product. Precipitation from DCM/MeOH afforded compound **7** as an orange powder. Overall yield (3 steps): 5.90 g (9.48 mmol, 95%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.99 (s, 4H, Tip-*m*-CH), 6.80 (d, <sup>3</sup>J<sub>HH</sub> = 3.5 Hz, 2H, Fur-*H*), 6.75 (d, <sup>3</sup>J<sub>HH</sub> = 3.5 Hz, 2H, Fur-*H*), 3.80 (s, 6H, O-CH<sub>3</sub>), 2.91 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, Tip-*p*-CH(CH<sub>3</sub>)<sub>2</sub>), 2.65 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, Tip-*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.29 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz,

12H, Tip-*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.24 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 12H, Tip-*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.10 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 12H, Tip-*p*-CH(CH<sub>3</sub>)<sub>2</sub>) ppm; <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>): δ = 42.5 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ = 159.8 (BiFur-C-B), 151.0 (BiFur-C), 150.7 (*o*-Tip-C), 149.6 (*p*-Tip-C), 132.1 (Ph-C-B), 128.8 (BiFur-CH), 120.3 (Ph-CH), 108.1 (BiFur-CH), 56.1 (B-OCH<sub>3</sub>), 35.2 (*o*-Tip-*i*Pr-CH), 34.5 (*p*-Tip-*i*Pr-CH), 24.8 (Tip-*i*Pr-CH<sub>3</sub>), 24.6 (Tip-*i*Pr-CH<sub>3</sub>), 24.2 (Tip-*i*Pr-CH<sub>3</sub>) ppm; HR-MS (APCI): *m/z* = 622.4358; calcd. for C<sub>40</sub>H<sub>56</sub>B<sub>2</sub>O<sub>4</sub>: 622.4365; elem. anal. calcd. % for C<sub>40</sub>H<sub>56</sub>B<sub>2</sub>O<sub>4</sub>: C 77.18, H 9.07; found: C 77.03, H 9.33; UV-Vis (THF): λ<sub>abs,max</sub> = 331 (ε = 40884 L mol<sup>-1</sup> cm<sup>-1</sup>), 339 (ε = 32258 L mol<sup>-1</sup> cm<sup>-1</sup>), 349 nm (ε = 36431 L mol<sup>-1</sup> cm<sup>-1</sup>); fluorescence (THF): λ<sub>em,max</sub> (λ<sub>ex</sub> = 331 nm) = 354 nm, 372 nm (Φ<sub>F</sub> = 27%).

**Synthesis of 2a<sup>Tip</sup>.** To a solution of 2-bromothiophene (489 mg, 3.0 mmol) in *n*-hexane (8 mL) was added *n*-butyllithium (2.5 M, 1.16 mL, 2.9 mmol) at room temperature and the reaction mixture was stirred for 3 h. Subsequently, thus generated **8a** was used *in situ* as a colorless suspension and was added to a solution of **7** (621 mg, 1.0 mmol) in THF (5 mL) at 0 °C and the reaction mixture was allowed to warm up to room temperature overnight. After all volatiles were removed in vacuo, the formed solid was extracted with dichloromethane. After all volatiles were removed in vacuo, a brown solid was obtained as crude product. Precipitation from dichloromethane/MeOH afforded **2a<sup>Tip</sup>** as a yellow solid. Yield: 400 mg (0.55 mmol, 55%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.14 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 3.3 Hz, Thi-*H*), 7.99 (dd, 2H, <sup>3</sup>J<sub>HH</sub> = 4.6 Hz, <sup>4</sup>J<sub>HH</sub> = 0.9 Hz, Thi-*H*), 7.34 (dd, 2H, <sup>3</sup>J<sub>HH</sub> = 4.6 Hz, <sup>3</sup>J<sub>HH</sub> = 3.6 Hz, Thi-*H*), 7.17 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 3.5 Hz, BiFur-*H*), 7.03 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 3.5 Hz, BiFur-*H*), 7.02 (s, 4H, *m*-Tip-*H*), 2.96 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *p*-Tip-*i*Pr-*CH*), 2.57 (sept, 4H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, *o*-Tip-*i*Pr-*CH*), 1.34 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *p*-Tip-*i*Pr-*CH*<sub>3</sub>), 1.09 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, *o*-Tip-*i*Pr-*CH*<sub>3</sub>), 1.09 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, *o*-Tip-*i*Pr-*CH*<sub>3</sub>) ppm; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>): δ = 50.0 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ = 165.0 (BiFur-C-B), 152.5 (*p*-Tip-C-*i*Pr), 150.2 (*o*-Tip-C-*i*Pr), 148.6 (BiFur-C-C), 144.1 (Thi-C-B), 143.2 (Thi-CH), 138.2 (Thi-CH), 136.9 (Tip-C-B), 133.1 (BiFur-CH), 128.9 (Thi-CH), 120.0 (*m*-Tip-CH), 110.0 (BiFur-CH), 35.2 (*o*-Tip-*i*Pr-CH), 34.3 (*p*-Tip-*i*Pr-CH), 24.4 (*o*-Tip-*i*Pr-CH<sub>3</sub>), 24.2 (*o*-Tip-*i*Pr-CH<sub>3</sub>), 24.1 (*p*-Tip-*i*Pr-CH<sub>3</sub>) ppm; HR-MS (APCI): *m/z* = 727.3963 [M+H]<sup>+</sup>; calcd. for C<sub>46</sub>H<sub>56</sub>B<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: 726.3908; elem. anal. calcd. % for C<sub>46</sub>H<sub>56</sub>B<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C 76.03, H 7.77, S 8.82; found: C 75.16, H 7.85, S 8.53; UV-Vis (THF): λ<sub>abs,max</sub> = 375 (ε = 145270 L mol<sup>-1</sup> cm<sup>-1</sup>), 394 (ε = 304626 L mol<sup>-1</sup> cm<sup>-1</sup>), 417 nm (ε = 390019 L mol<sup>-1</sup> cm<sup>-1</sup>); fluorescence (THF): λ<sub>em,max</sub> (λ<sub>ex</sub> = 417 nm) = 429 nm, 453 nm (Φ<sub>F</sub> = 52.8%).

**Synthesis of 2b<sup>Tip</sup>.** To a solution of furan (77.1 mg, 1.1 mmol) in THF (1 mL) was added *n*-butyllithium (2.5 M, 0.41 mL, 1.1 mmol) at -78 °C. The mixture was stirred for 0.5 h at room temperature and then for an additional 3 h at 50 °C. After cooling down to ambient temperature, thus generated **8b** was used *in situ* and added to a solution of **7** (200 mg, 0.28 mmol) in THF (1 mL) at -78 °C and the reaction mixture was allowed to warm up to room temperature

overnight. After all volatiles were removed in vacuo, a brown solid was obtained as crude product. Precipitation from dichloromethane/MeOH afforded **2b**<sup>Tip</sup> as a yellow solid. Yield: 118 mg (0.17 mmol, 53%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.89 (dd, 2H, <sup>3</sup>J<sub>HH</sub> = 1.6 Hz, <sup>4</sup>J<sub>HH</sub> = 0.6 Hz, Fur-*H*), 7.68 (s, 2H, Fur-*H*), 7.31 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 3.0 Hz, BiFur-*H*), 7.01 (s, 4H, *m*-Tip-*H*), 6.94 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 3.6 Hz, BiFur-*H*), 6.62 (dd, 2H, <sup>3</sup>J<sub>HH</sub> = 3.5 Hz, <sup>3</sup>J<sub>HH</sub> = 1.6 Hz, Fur-*H*), 2.95 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *p*-Tip-*i*-Pr-CH), 2.56 (sept, 4H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *o*-Tip-*i*-Pr-CH), 1.32 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, *p*-Tip-*i*-Pr-CH<sub>3</sub>), 1.09 (d, 24H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *o*-Tip-*i*-Pr-CH<sub>3</sub>) ppm; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>): δ = 49.7 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ = 164.5 (BiFur-C-B), 163.6 (Fur-C-B), 152.6 (BiFur-C-C), 150.4 (*o*-Tip-C-<sup>i</sup>Pr), 150.3 (Fur-CH), 148.5 (*p*-Tip-C-<sup>i</sup>Pr), 135.6 (Tip-C-B), 132.9 (BiFur-CH), 131.2 (Fur-CH), 120.1 (*m*-Tip-CH), 112.0 (Fur-CH), 109.9 (BiFur-CH), 35.5 (*o*-Tip-*i*-Pr-CH), 34.4 (*p*-Tip-*i*-Pr-CH), 24.4 (*o*-Tip-*i*-Pr-CH), 24.3 (*p*-Tip-*i*-Pr-CH<sub>3</sub>) ppm; HR-MS (APCI): *m/z* = 695.4425 [M+H]<sup>+</sup>; calcd. for C<sub>46</sub>H<sub>56</sub>B<sub>2</sub>O<sub>4</sub>: 694.4365; elem. anal. calcd. % for C<sub>46</sub>H<sub>56</sub>B<sub>2</sub>O<sub>4</sub>: C 79.55, H 8.13; found: C 78.69, H 8.85; UV-Vis (THF): λ<sub>abs,max</sub> = 374 (ε = 138111 L mol<sup>-1</sup> cm<sup>-1</sup>), 394 (ε = 286233 L mol<sup>-1</sup> cm<sup>-1</sup>), 417 nm (ε = 365475 L mol<sup>-1</sup> cm<sup>-1</sup>); fluorescence (THF): λ<sub>em,max</sub> (λ<sub>ex</sub> = 417 nm) = 428 nm, 453 nm (Φ<sub>f</sub> = 69.9%).

**Synthesis of 2c**<sup>Tip</sup>. To a solution of 1-bromobenzene (235.5 mg, 1.5 mmol) in THF (2 mL) was added *n*-butyllithium (2.5 M, 0.59 mL, 1.48 mmol) at -78 °C and the reaction mixture was stirred for 2 h at -78 °C. After the reaction mixture had been warmed up to ambient temperatures, thus generated **8c** was used *in situ* and added to a solution of **7** (311.3 mg, 0.5 mmol) in THF (2.5 mL) at -78 °C and the reaction mixture was allowed to warm up to room temperature overnight. After all volatiles were removed in vacuo, the formed solid was extracted with dichloromethane. The solvent was again removed in vacuo and a brown solid was obtained as crude product. Precipitation from dichloromethane/MeOH afforded **2c**<sup>Tip</sup> as a yellow solid. Yield: 195 mg (0.27 mmol, 54%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.29 (dd, 4H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, Ph-CH), 7.56 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, Ph-CH), 7.49 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, Ph-CH), 7.19 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 3.6 Hz, BiFur-CH), 7.02 (s, 4H, *m*-Tip-CH), 6.98 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 3.6 Hz, BiFur-C), 2.96 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *p*-Tip-*i*-Pr-CH), 2.49 (sept, 4H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, *o*-Tip-*i*-Pr-CH), 1.34 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *p*-Tip-*i*-Pr-CH<sub>3</sub>), 1.08 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 3.7 Hz, *o*-Tip-*i*-Pr-CH<sub>3</sub>), 1.04 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 3.7 Hz, *o*-Tip-*i*-Pr-CH<sub>3</sub>) ppm; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>): δ = 58.2 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ = 166.2 (BiFur-C-B), 153.0 (*p*-Tip-C), 149.9 (*o*-Tip-C), 148.6 (BiFur-C), 140.6 (Ph-C-B), 139.0 (Ph-CH), 138.2 (Tip-C-B), 134.7 (BiFur-CH), 132.6 (Ph-CH), 128.0 (Ph-CH), 120.1 (*m*-Tip-CH), 109.9 (BiFur-CH), 35.4 (*o*-Tip-<sup>i</sup>Pr-CH), 34.4 (*p*-Tip-<sup>i</sup>Pr-CH), 24.4 (Tip-<sup>i</sup>Pr-CH<sub>3</sub>), 24.3 (Tip-<sup>i</sup>Pr-CH<sub>3</sub>), 24.2 (Tip-<sup>i</sup>Pr-CH<sub>3</sub>) ppm; HR-MS (APCI): *m/z* = 715.4845 [M+H]<sup>+</sup>; calcd. for C<sub>50</sub>H<sub>60</sub>B<sub>2</sub>O<sub>2</sub>: 714.4779; UV-vis (THF): λ<sub>abs,max</sub> = 367 (ε = 179408 L mol<sup>-1</sup> cm<sup>-1</sup>), 386 (ε = 349131 L mol<sup>-1</sup> cm<sup>-1</sup>), 407 nm (ε = 398403 L mol<sup>-1</sup> cm<sup>-1</sup>); fluorescence (THF): λ<sub>em,max</sub> (λ<sub>ex</sub> = 407 nm) = 423 nm, 443 nm (Φ<sub>f</sub> = 85.2%).

**Synthesis of 2a<sup>Mes\*</sup>.** To a solution of **4** (0.281 g, 1.0 mmol) in dichloromethane (3 mL) was added BBr<sub>3</sub> (0.489 g, 1.95 mmol) at 0 °C and the mixture was stirred for 2.5 h at 0 °C. Then, **9a** (0.329 g, 2.1 mmol) and TMS-NTf<sub>2</sub> (0.035 g, 0.1 mmol) as catalyst were added and the reaction mixture was stirred at room temperature for 3 d. Subsequently, the solvent was removed in vacuo to afford **10a**. The obtained solid was suspended in toluene (3 mL) and Mes\*Li (0.631 g, 2.5 mmol) in Et<sub>2</sub>O (2 mL) was added at -78 °C. The reaction mixture was stirred for 2 d at room temperature, then all volatiles were removed in vacuo and the crude product was filtrated with dichloromethane, affording the yellow brown crude product after the solvent was removed again in vacuo. Purification by column chromatography (Al<sub>2</sub>O<sub>3</sub>, *n*-hexane/DCM, 100:4) yielded compound **2a<sup>Mes\*</sup>** as a pale yellow solid. Yield: 0.132 g (0.16 mmol, 16%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.86 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 4.5 Hz, Thi-CH), 7.82 (br, 2H, Thi-CH), 7.45 (s, 4H, Mes\*-CH), 7.21 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 3.9 Hz, Thi-CH), 7.09 (br, 2H, BiFur-CH), 6.99 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 3.3 Hz, BiFur-CH), 1.40 (s, 18H, Mes\*-*o*-<sup>t</sup>Bu-CH<sub>3</sub>), 1.21 (s, 36H, Mes\*-*p*-<sup>t</sup>Bu-CH<sub>3</sub>) ppm; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>): δ = 49.2 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ = 166.2 (BiFur-C-B), 152.3 (Mes\*-C-*o*-<sup>t</sup>Bu) 151.4 (BiFur-C-C), 148.7 (Mes\*-C-*p*-<sup>t</sup>Bu), 147.1 (Thi-C), 141.9 (Thi-C-H), 136.4 (Thi-CH), 133.4 (Mes\*-C-B), 130.5 (BiFur-CH), 128.4 (Thi-*m*-CH), 122.6 (Mes\*-CH), 109.5 (BiFur-CH), 38.8 (Mes\*-*o*-<sup>t</sup>Bu-C), 35.1 (Mes\*-*o*-<sup>t</sup>Bu-CH<sub>3</sub>), 34.9 (Mes\*-*p*-<sup>t</sup>Bu-C), 31.6 (Mes\*-*p*-<sup>t</sup>Bu-CH<sub>3</sub>) ppm; HR-MS (APCI): m/z = 811.4912 [M+H]<sup>+</sup>; calcd. for C<sub>52</sub>H<sub>68</sub>B<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: 810.4847; elem. anal. calcd. % for C<sub>52</sub>H<sub>68</sub>B<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C 77.03, H 8.45, S 7.91; found: C 76.91, H 8.79, S 7.66; UV-Vis (THF): λ<sub>abs,max</sub> = 368 (ε = 195554 L mol<sup>-1</sup> cm<sup>-1</sup>), 385 (ε = 362094 L mol<sup>-1</sup> cm<sup>-1</sup>), 406 nm (ε = 428943 L mol<sup>-1</sup> cm<sup>-1</sup>); fluorescence (THF): λ<sub>em,max</sub> (λ<sub>ex</sub> = 406 nm) = 423 nm, 442 nm (φ<sub>f</sub> = 53.0%).

**Attempted synthesis of 2b<sup>Mes\*</sup>.** To a solution of **4** (0.281 g, 1.0 mmol) in dichloromethane (3 mL) was added BBr<sub>3</sub> (0.489 g, 1.95 mmol) at 0 °C and the mixture was stirred for 2.5 h at 0 °C. Then, **9b** (0.283 g, 2.0 mmol) and TMS-NTf<sub>2</sub> (0.035 g, 0.1 mmol) as catalyst were added and the reaction mixture was stirred at room temperature for 3 d. Subsequently, the solvent was removed in vacuo, re-dispersed in toluene (3 mL) and Mes\*Li (0.631 g, 2.5 mmol) in Et<sub>2</sub>O (2 mL) was added at -78 °C. The reaction mixture was stirred for 2 d at room temperature, then all volatiles were removed in vacuo. Analysis via <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy showed no sign of product formation. However, high-resolution mass spectrometry evidenced the formation of traces of **2b<sup>Mes\*</sup>** (Figure S36).

**Synthesis of 2c<sup>Mes\*</sup>.** To a solution of **4** (0.281 g, 1.0 mmol) in dichloromethane (3 mL) was added BBr<sub>3</sub> (0.491 g, 1.96 mmol) at 0 °C and the mixture was stirred for 2.5 h at 0 °C. Then, **9c** (0.300 g, 2.0 mmol) and TMS-NTf<sub>2</sub> (0.035 g, 0.1 mmol) as catalyst were added and the reaction mixture was stirred at room temperature for 3 d. After the reaction mixture had been stirred for 3 d, the solvent was removed in vacuo to afford crude **10c** and subsequently, Mes\*Li

(0.631 g, 2.5 mmol) was suspended in toluene and added to the reaction mixture. The mixture was again stirred for 3 d and then treated with water (5 mL), followed by an extraction with dichloromethane. After the solution was dried over MgSO<sub>4</sub>, the solvent was removed in vacuo and the resulting red solid was subjected to column chromatography (Al<sub>2</sub>O<sub>3</sub>, *n*-hexane/DCM, 100:0 → 1:99) with increasing gradient. Yield: 56 mg (0.07 mmol, 7%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.25 (br s, 4H, Ph-CH), 7.47 – 7.38 (m, 10 H, Ph-CH/Mes\*-CH), 7.01 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 3.5 Hz, Fur-H), 6.91 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 3.5 Hz, Fur-H) ppm; <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>): δ = 54.6 (s) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ = 166.8 (BiFur-C-B), 152.1 (Mes\*-*o*-C-<sup>t</sup>Bu), 151.5 (BiFur-C-C), 148.6 (Mes\*-*p*-C-<sup>t</sup>Bu), 143.3 (Ph-C-B), 138.5 (Ph-*o*-CH), 134.7 (Mes\*-C-B), 131.7 (BiFur-CH), 131.1 (Ph-*p*-CH), 127.8 (Ph-*m*-CH), 122.4 (Mes\*-CH), 109.1 (BiFur-CH), 38.7 (Mes\*-*o*-C-CH<sub>3</sub>), 35.1 (Mes\*-*o*-CH<sub>3</sub>), 34.9 (Mes\*-*p*-C-CH<sub>3</sub>), 31.6 (Mes\*-*p*-CH<sub>3</sub>) ppm; HR-MS (APCI): *m/z* = 799.5777 [M+H]<sup>+</sup>; calcd. for C<sub>56</sub>H<sub>72</sub>B<sub>2</sub>O<sub>2</sub>: 798.5718; UV-Vis (THF): λ<sub>abs,max</sub> = 356 (ε = 150591 L mol<sup>-1</sup> cm<sup>-1</sup>), 377 (ε = 281330 L mol<sup>-1</sup> cm<sup>-1</sup>), 398 nm (ε = 312512 L mol<sup>-1</sup> cm<sup>-1</sup>); fluorescence (THF): λ<sub>em,max</sub> (λ<sub>ex</sub> = 398 nm) = 415 nm, 431 nm (Φ<sub>f</sub> = 81.4%).

## NMR spectra

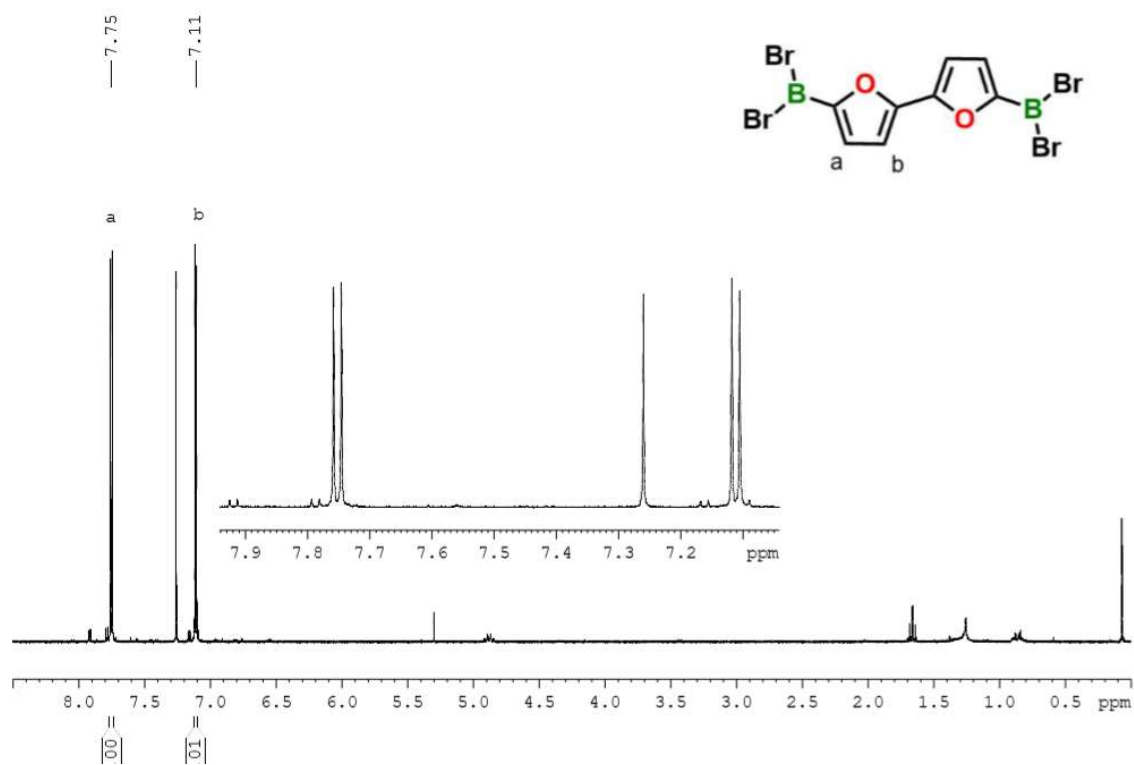


Figure S1.  $^1\text{H}$  NMR spectrum of **5** (300 MHz, in  $\text{CDCl}_3$ ).

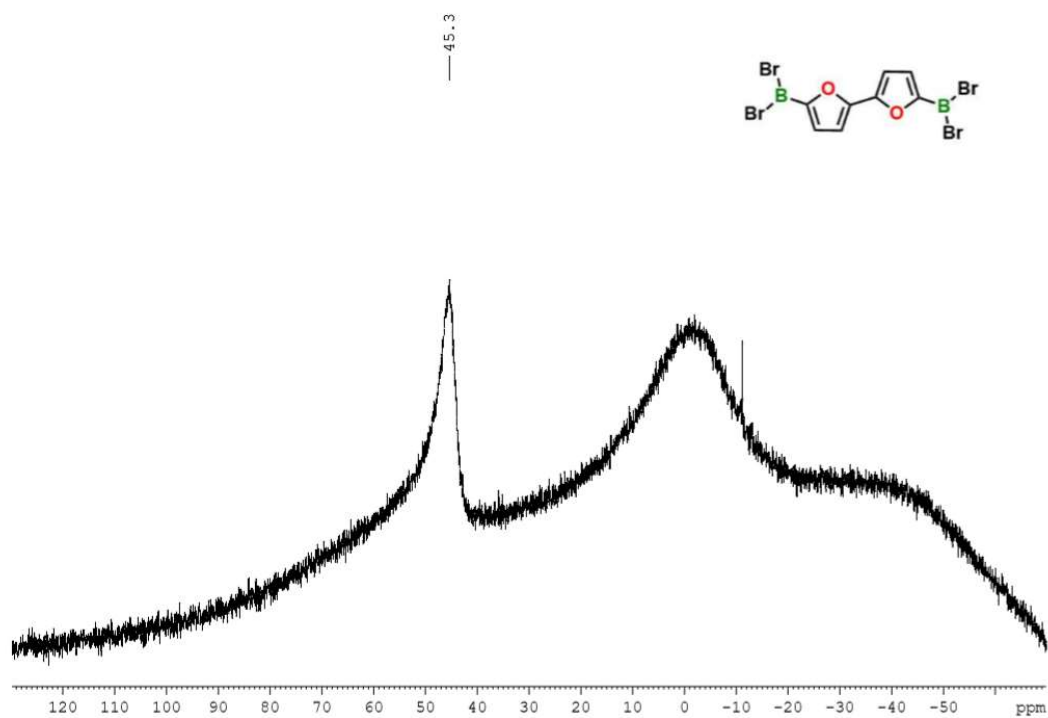


Figure S2.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **5** (96 MHz, in  $\text{CDCl}_3$ ).



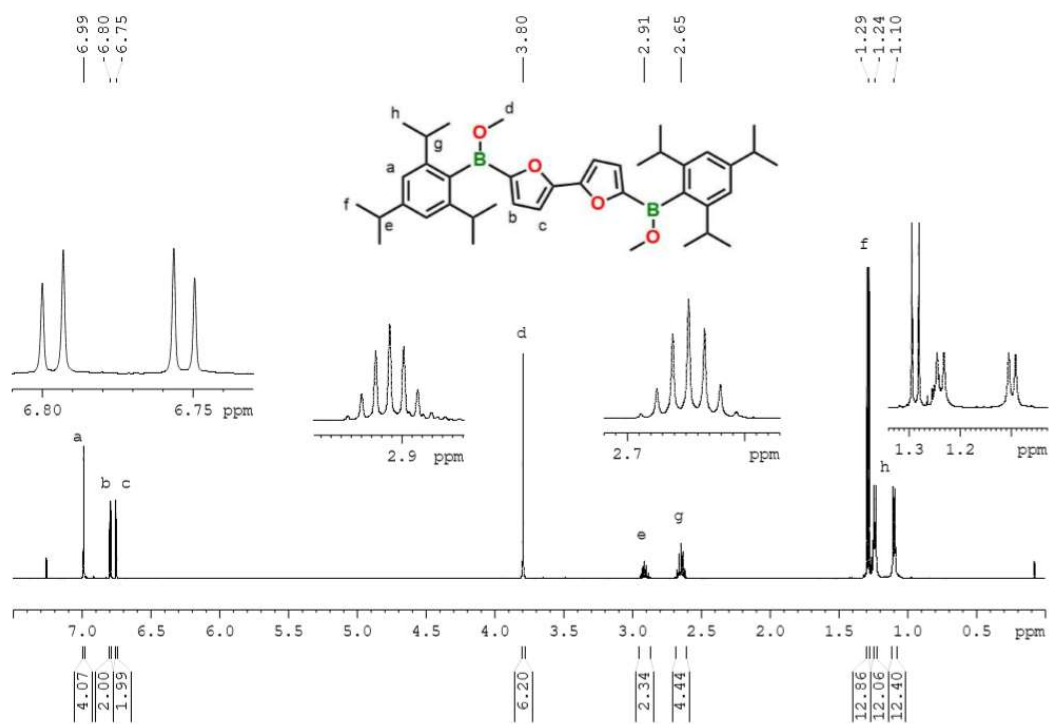


Figure S3.  $^1\text{H}$  NMR spectrum of **7** (500 MHz, in  $\text{CDCl}_3$ ).

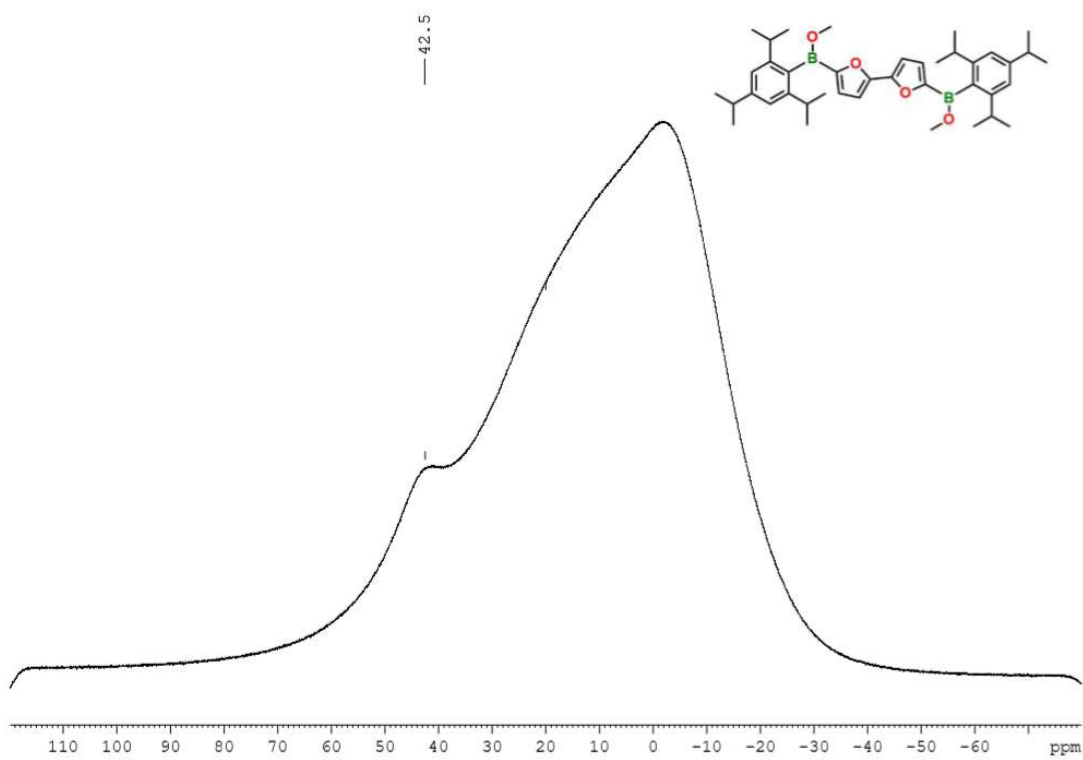


Figure S4.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **7** (160 MHz, in  $\text{CDCl}_3$ ).

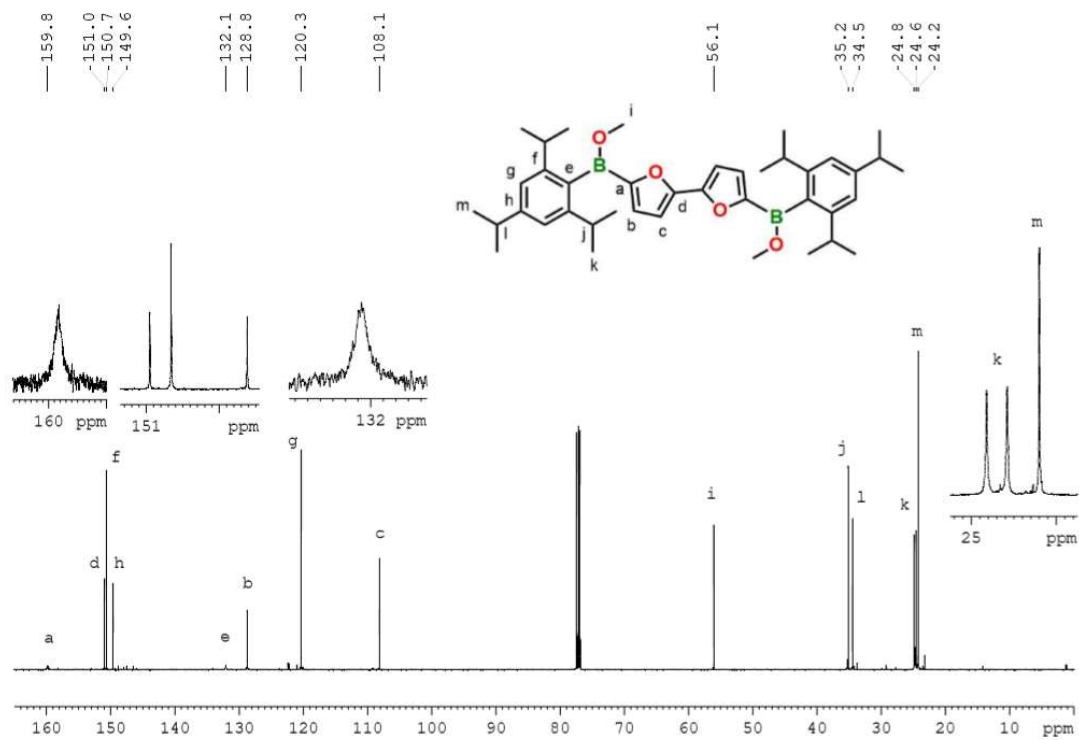


Figure S5.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **7** (126 MHz, in  $\text{CDCl}_3$ ).

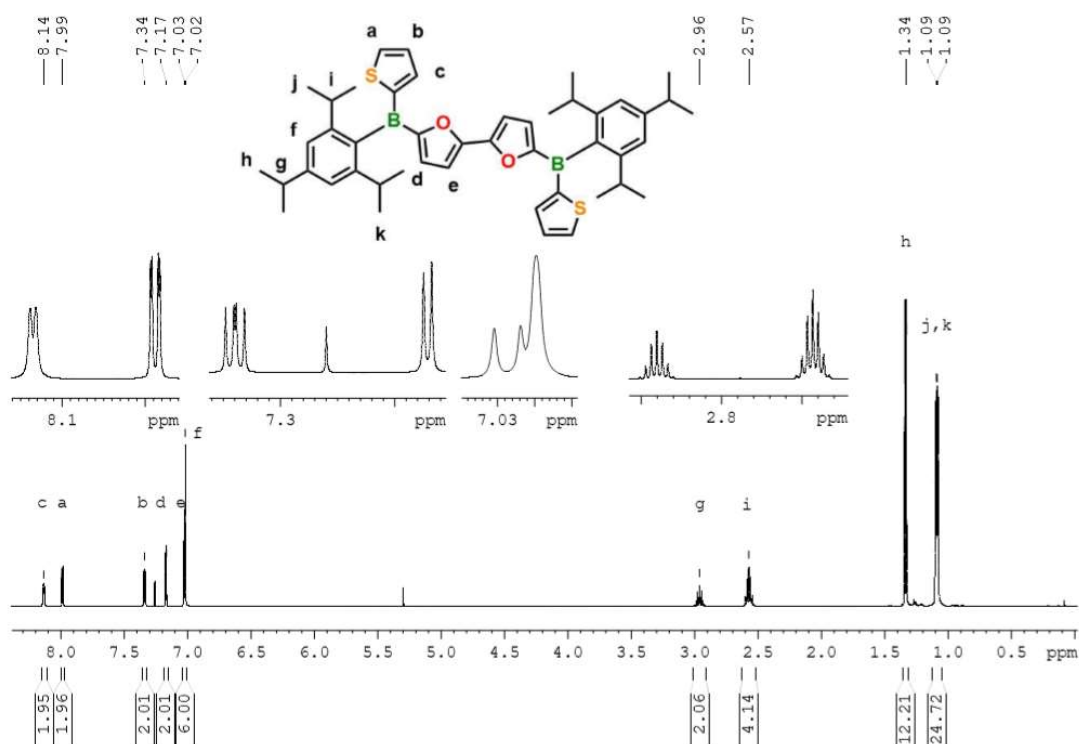


Figure S6.  $^1\text{H}$  NMR spectrum of **2a<sup>TIP</sup>** (500 MHz, in  $\text{CDCl}_3$ ).

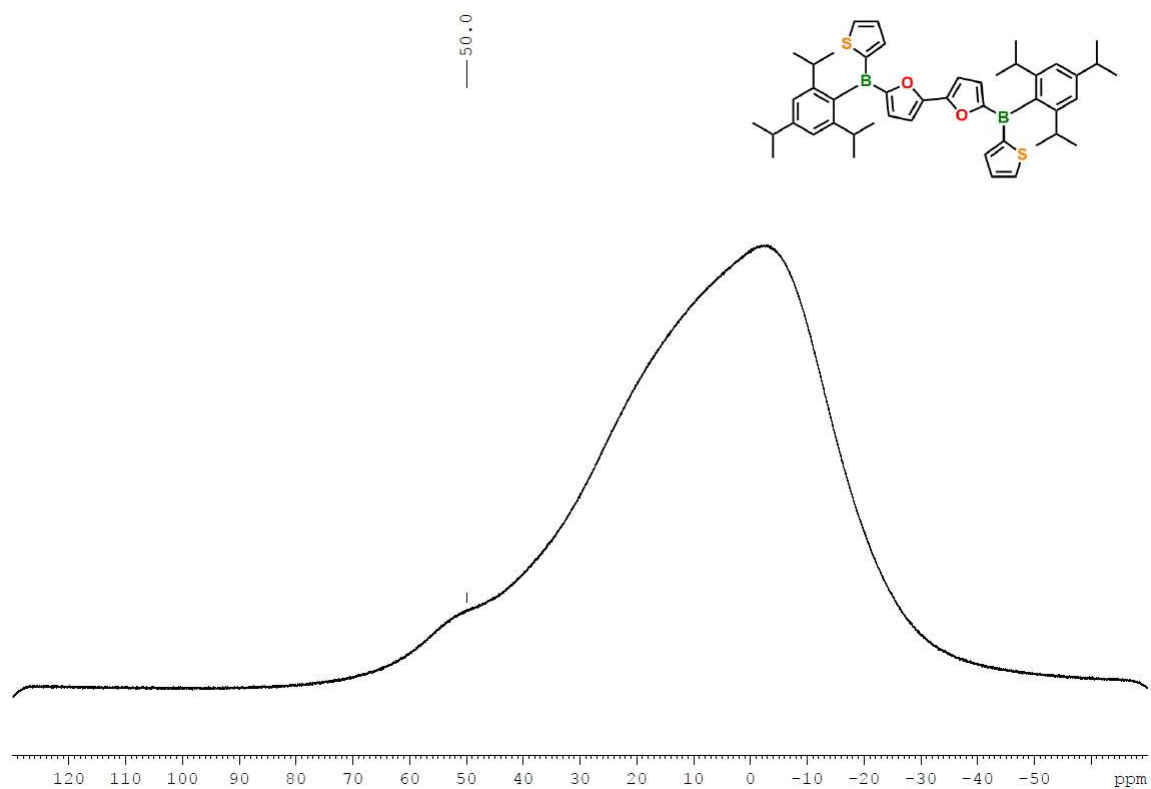


Figure S7.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **2a<sup>Tip</sup>** (160 MHz, in  $\text{CDCl}_3$ ).

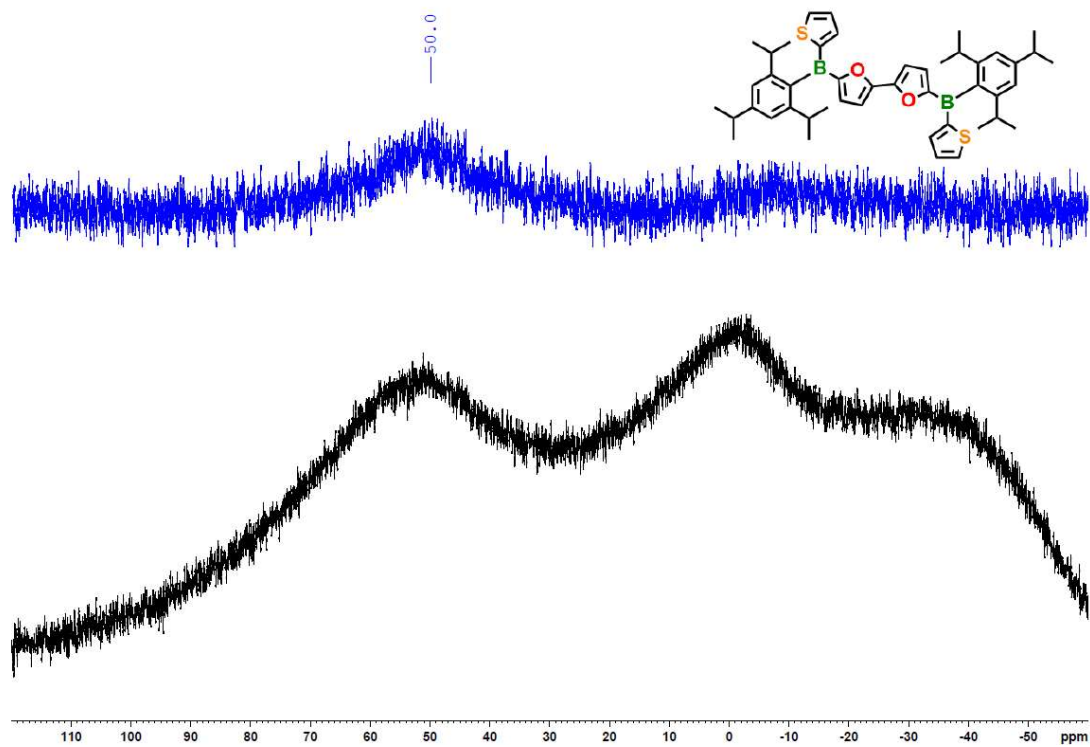


Figure S8.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **2a<sup>Tip</sup>** (96 MHz, in  $\text{CDCl}_3$ ) before (black) and after (blue) background subtraction.

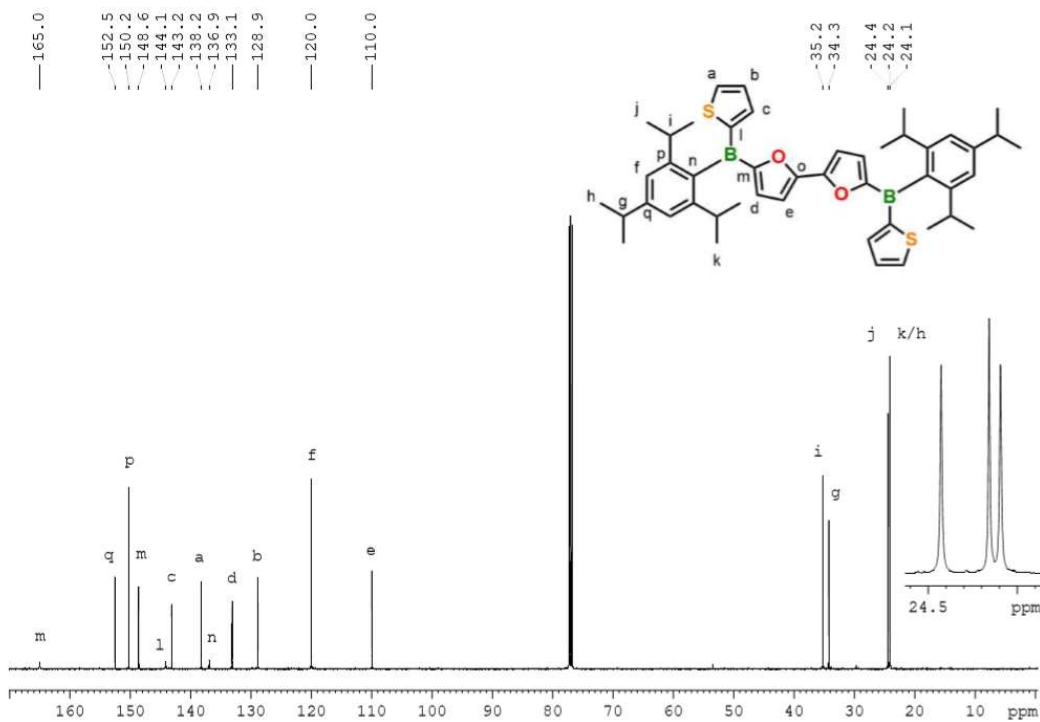


Figure S9. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **2a**<sup>Tip</sup> (126 MHz, in CDCl<sub>3</sub>).

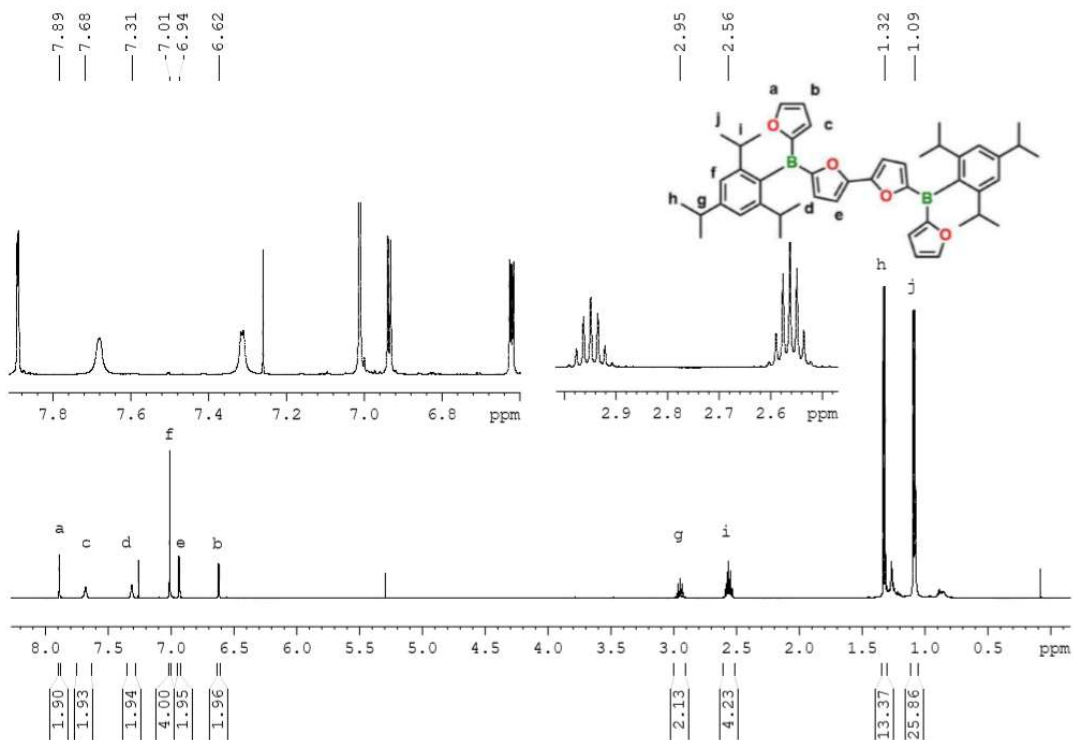


Figure S10. <sup>1</sup>H NMR spectrum of **2b**<sup>Tip</sup> (500 MHz, in CDCl<sub>3</sub>).

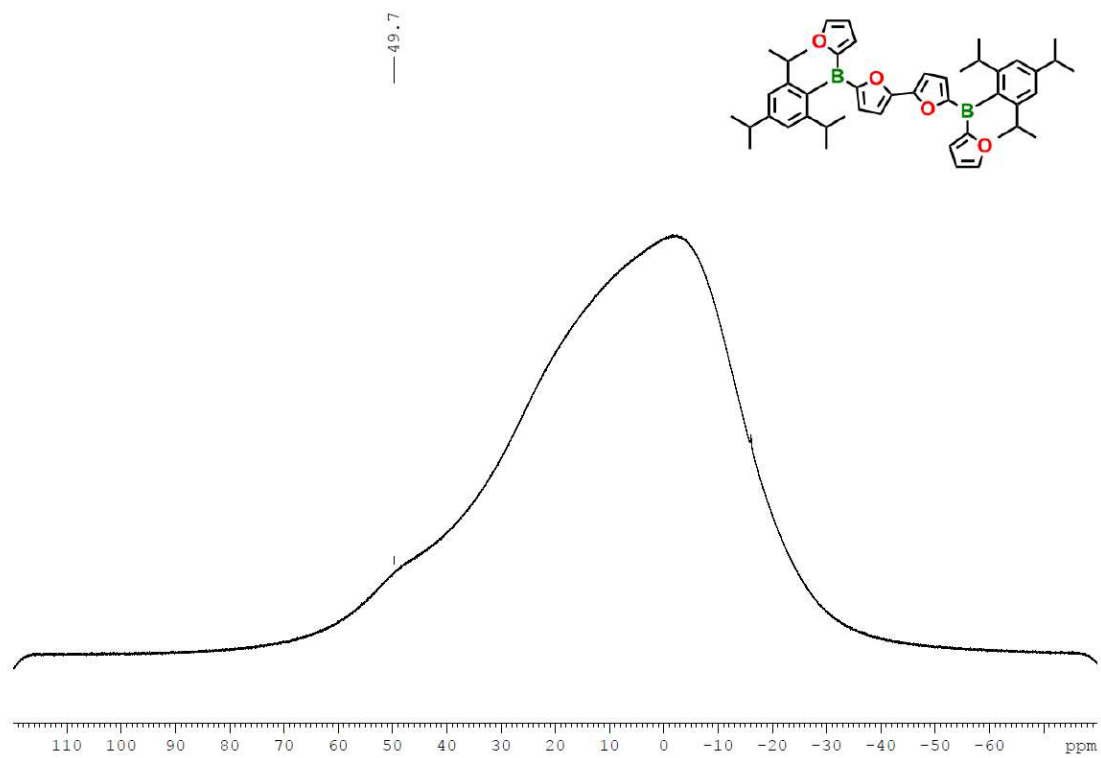


Figure S11.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **2b**<sup>TIP</sup> (160 MHz, in  $\text{CDCl}_3$ ).

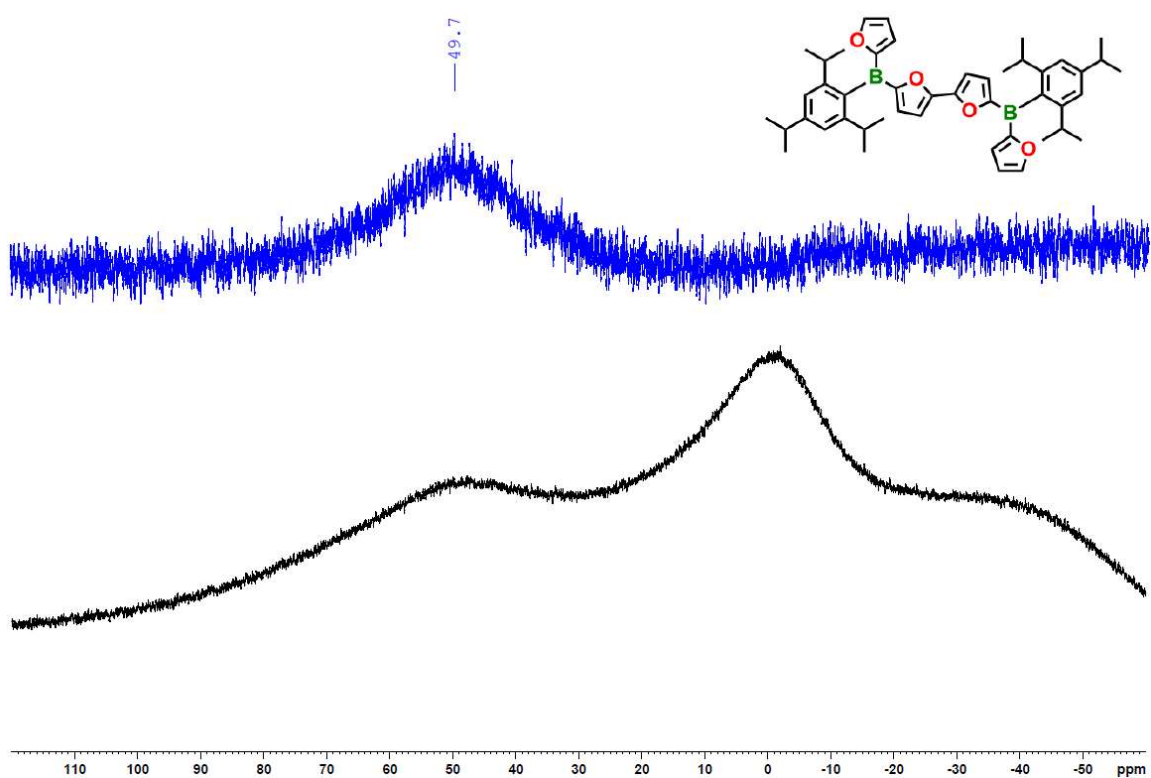


Figure S12.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **2b**<sup>TIP</sup> (96 MHz, in  $\text{CDCl}_3$ ) before (black) and after (blue) background subtraction.

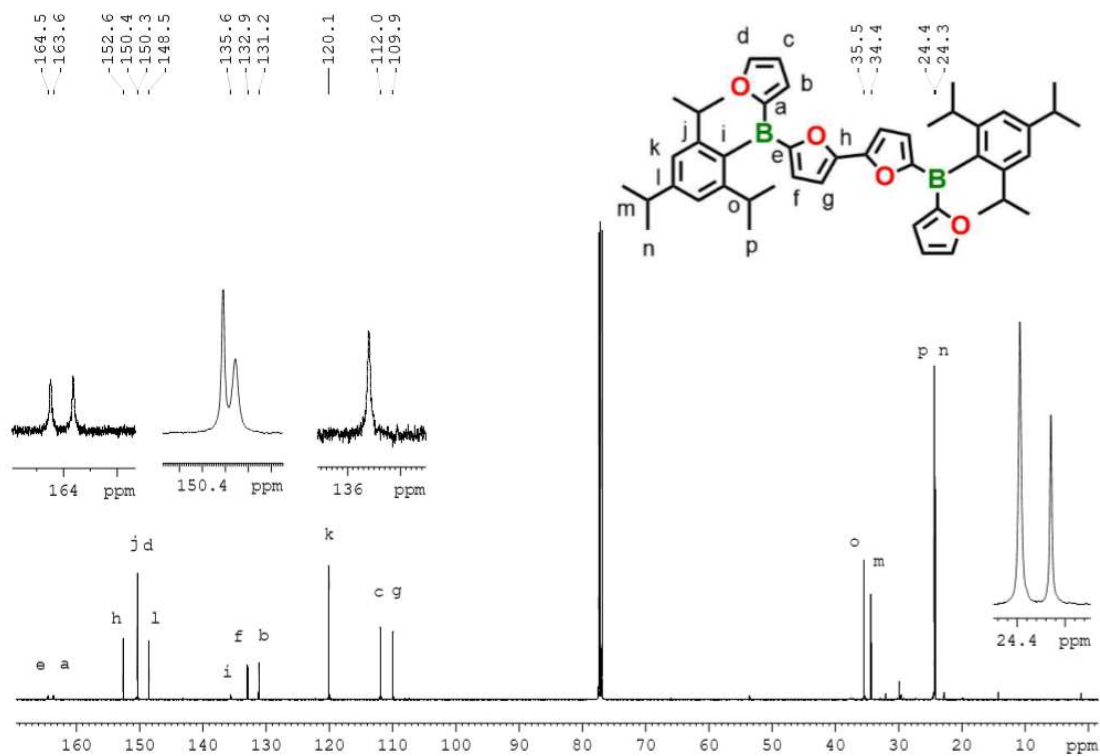


Figure S13. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **2b**<sup>TIP</sup> (126 MHz, in CDCl<sub>3</sub>).

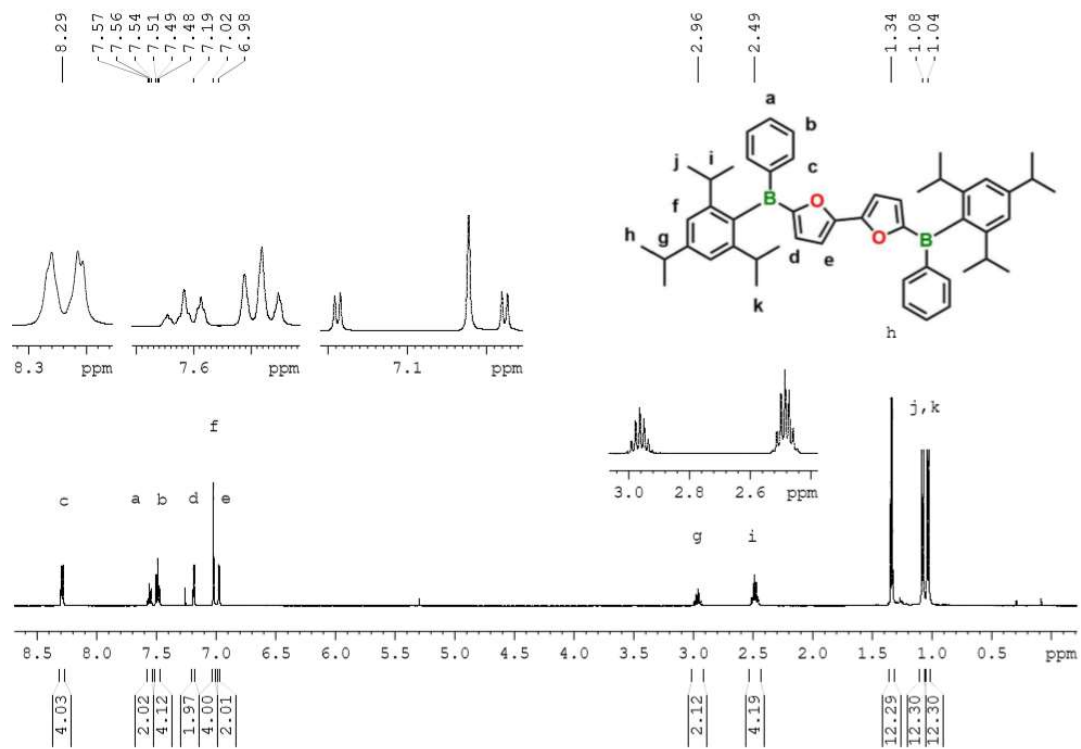


Figure S14. <sup>1</sup>H NMR spectrum of **2c**<sup>TIP</sup> (500 MHz, in CDCl<sub>3</sub>).

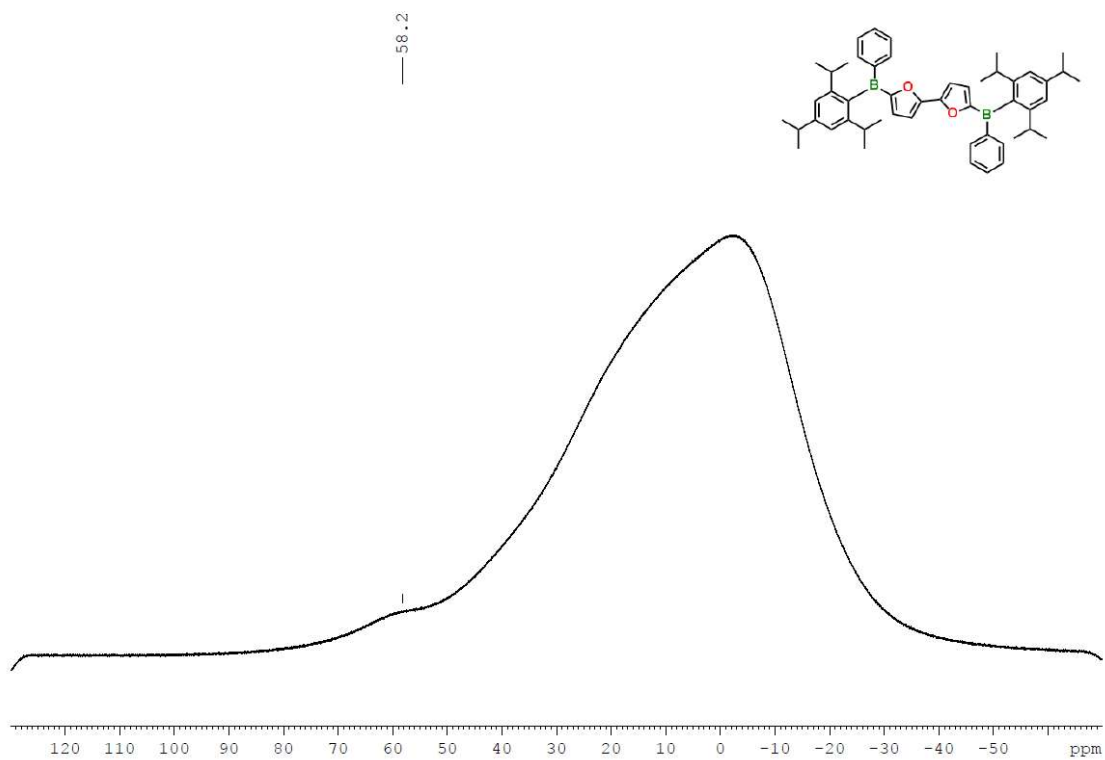


Figure S15.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **2c<sup>TIP</sup>** (160 MHz, in  $\text{CDCl}_3$ ).

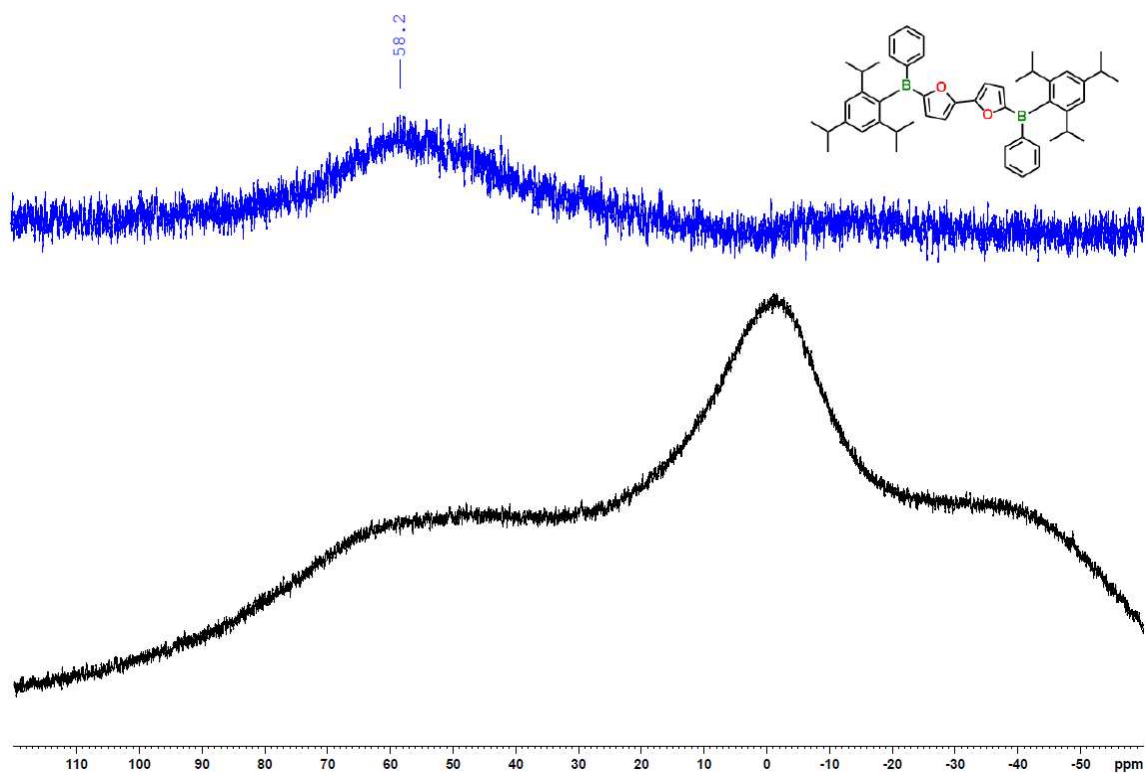


Figure S16.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **2c<sup>TIP</sup>** (96 MHz, in  $\text{CDCl}_3$ ) before (black) and after (blue) background subtraction.

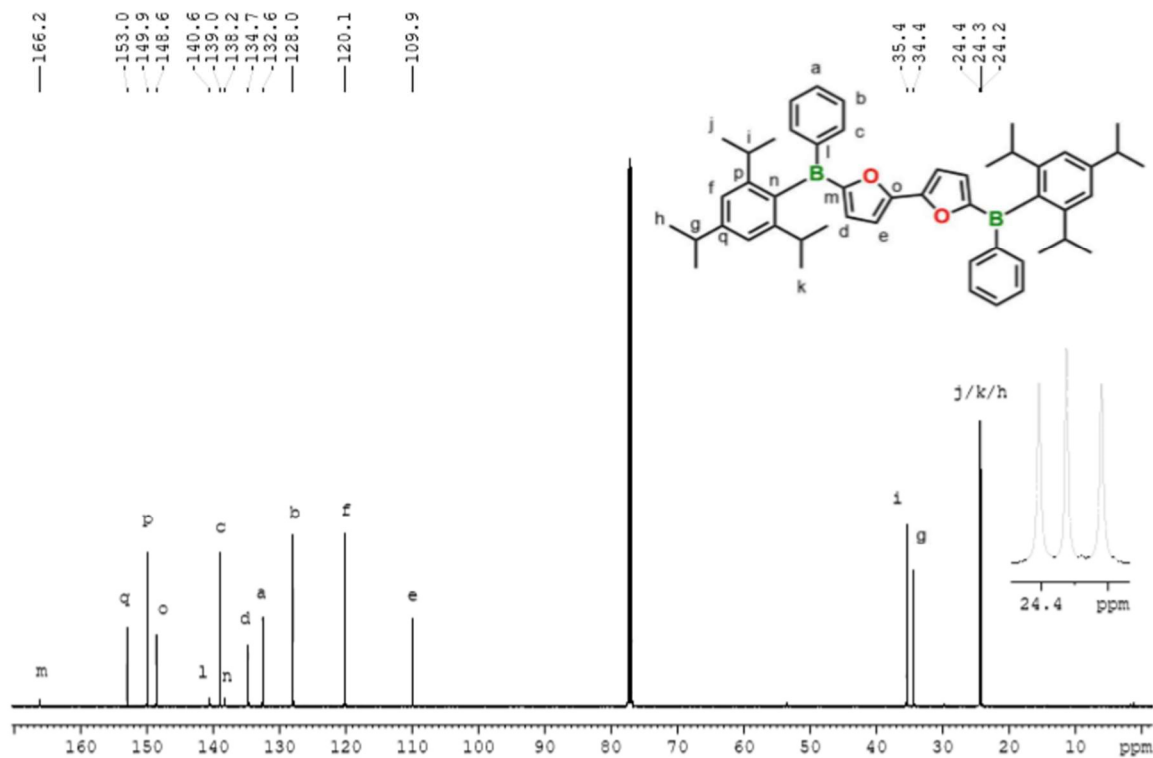


Figure S17. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **2c<sup>TIP</sup>** (126 MHz, in CDCl<sub>3</sub>).

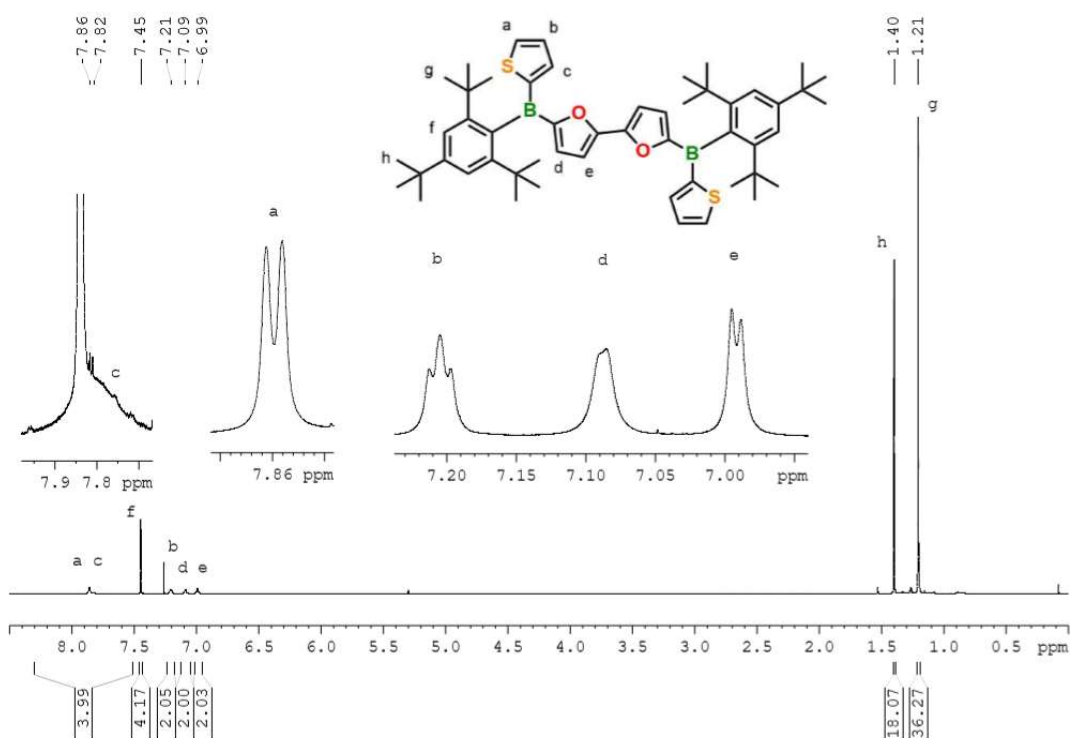


Figure S18. <sup>1</sup>H NMR spectrum of **2a<sup>Mes\*</sup>** (500 MHz, in CDCl<sub>3</sub>).



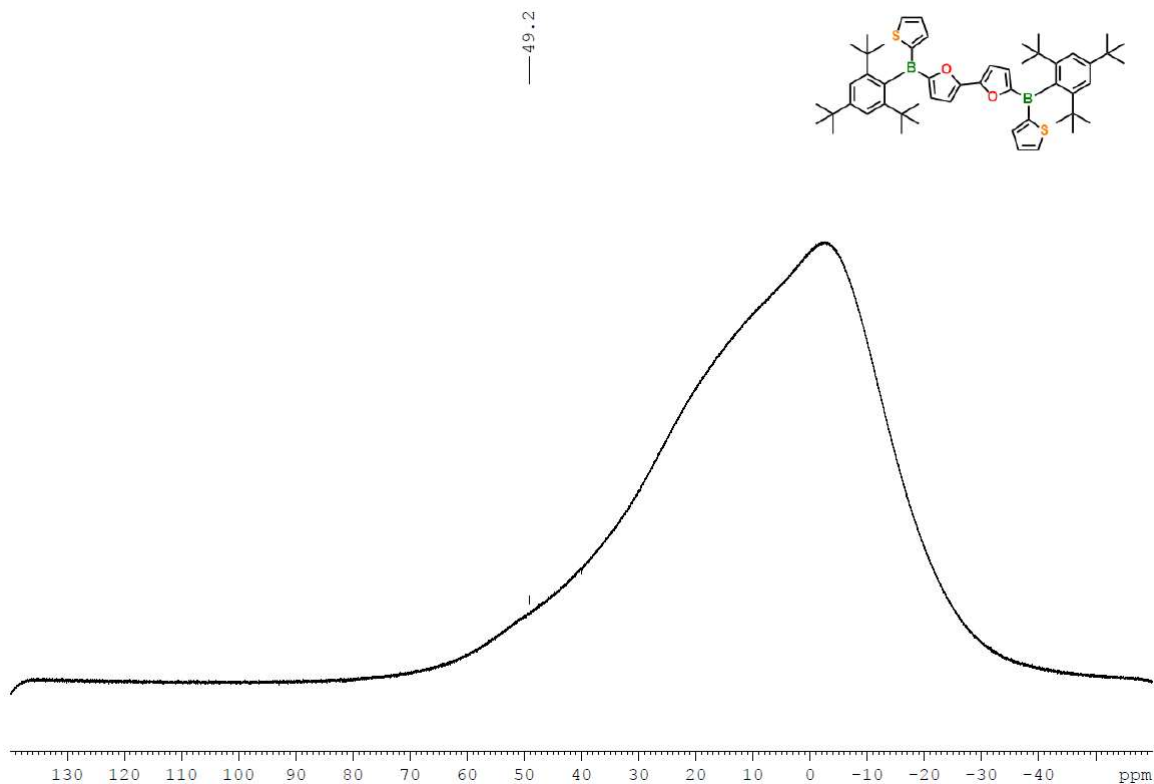


Figure S19.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $2\mathbf{a}^{\text{Mes}^*}$  (160 MHz, in  $\text{CDCl}_3$ ).

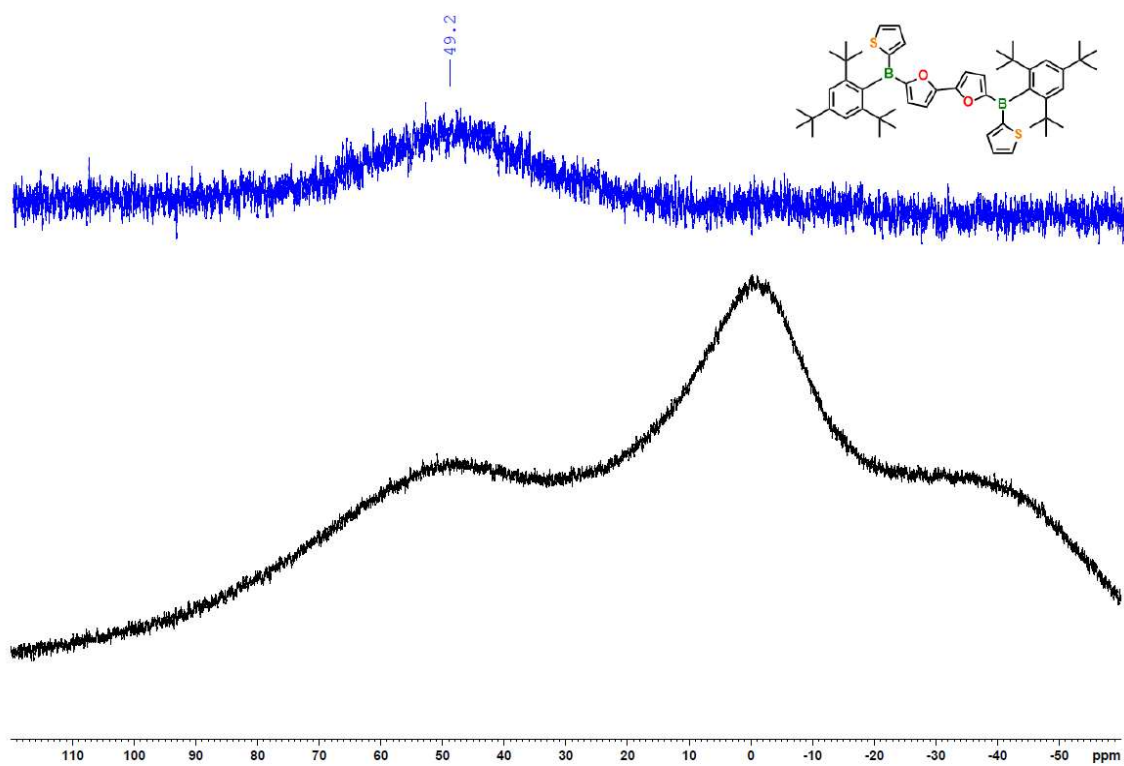


Figure S20.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $2\mathbf{a}^{\text{Mes}^*}$  (96 MHz, in  $\text{CDCl}_3$ ) before (black) and after (blue) background subtraction.

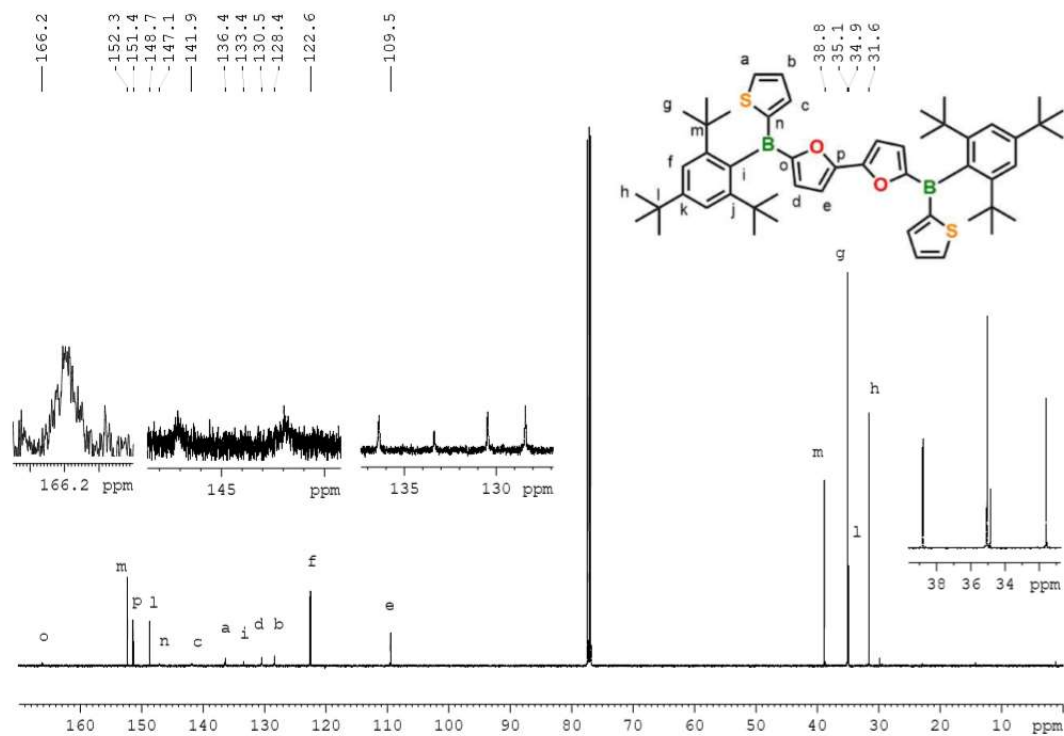


Figure S21.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $2\mathbf{a}^{\text{Mes}^*}$  (126 MHz, in  $\text{CDCl}_3$ ).

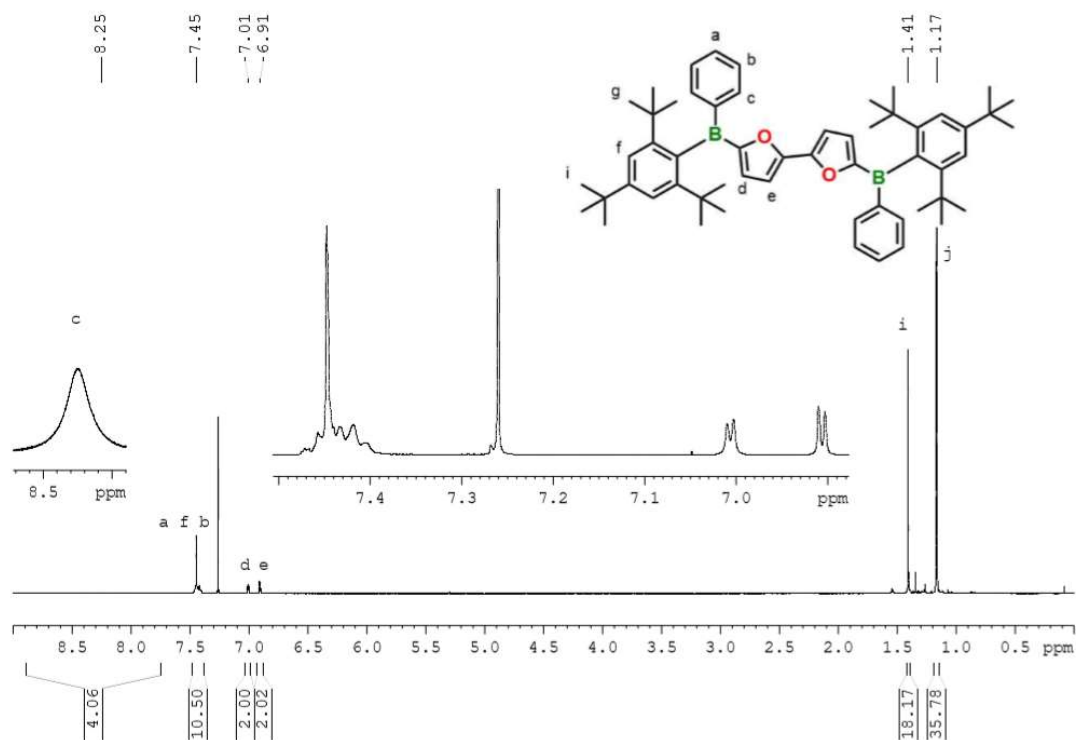


Figure S22.  $^1\text{H}$  NMR spectrum of  $2\mathbf{c}^{\text{Mes}^*}$  (500 MHz, in  $\text{CDCl}_3$ ).

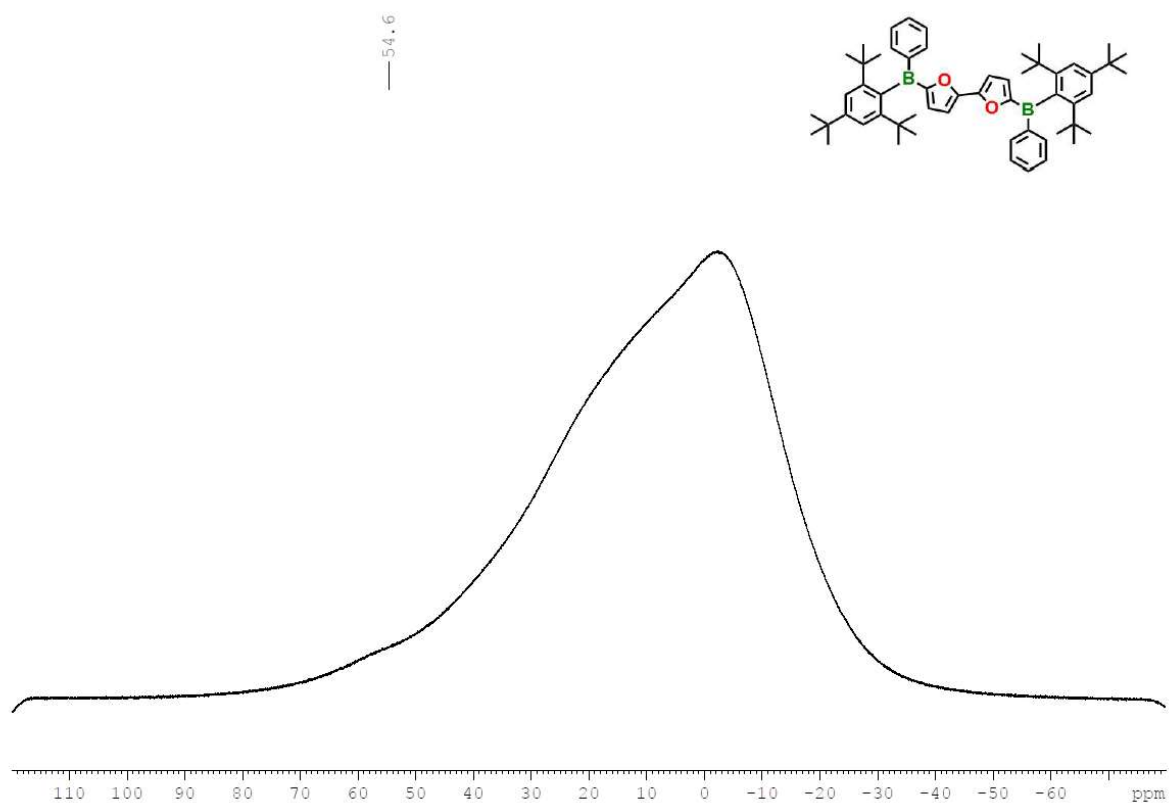


Figure S23.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **2c<sup>Mes\*</sup>** (160 MHz, in  $\text{CDCl}_3$ ).

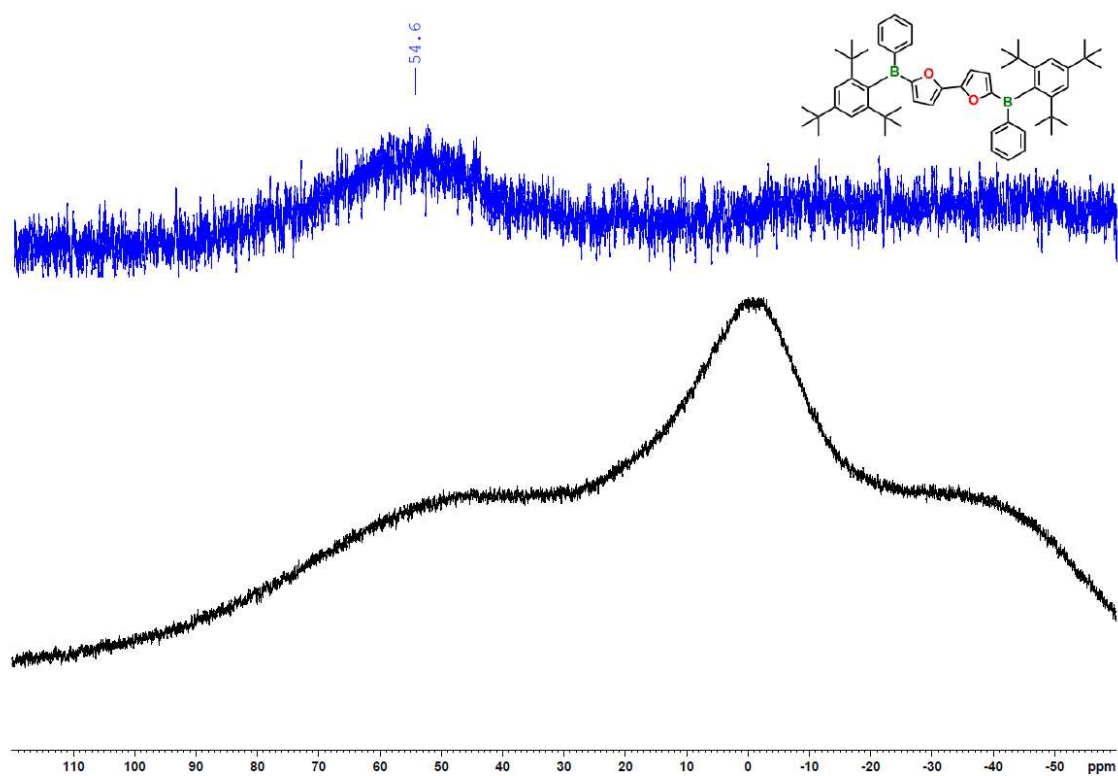


Figure S24.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **2c<sup>Mes\*</sup>** (96 MHz, in  $\text{CDCl}_3$ ) before (black) and after (blue) background subtraction.

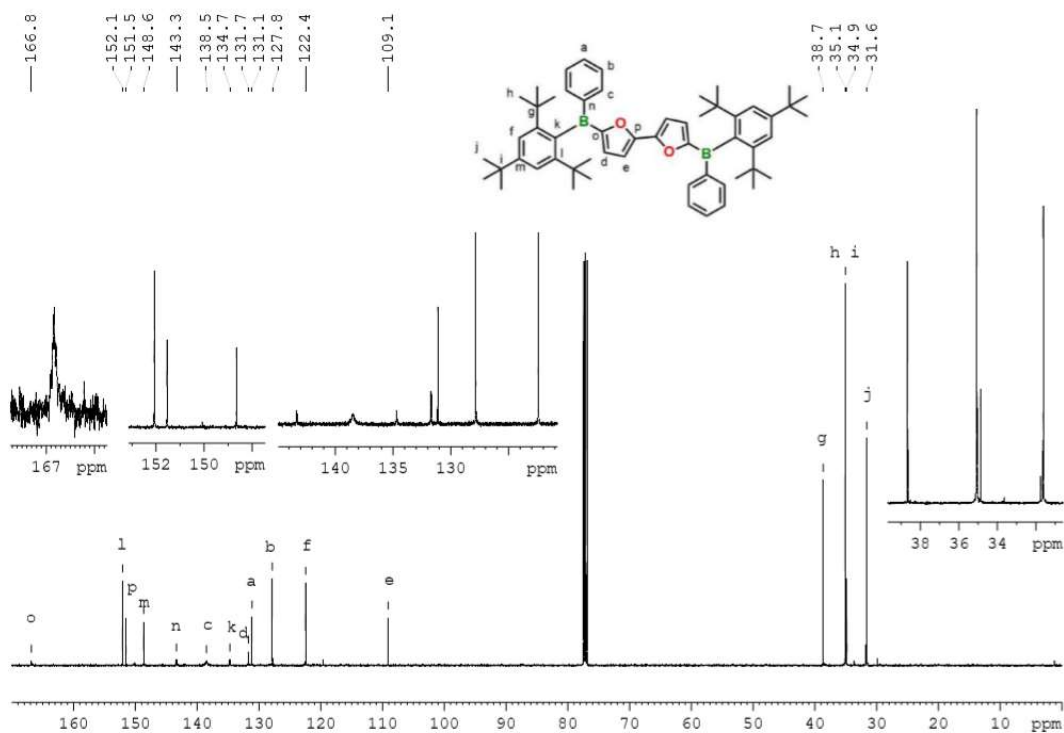


Figure S25.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $2\text{c}^{\text{Mes}^*}$  (126 MHz, in  $\text{CDCl}_3$ ).

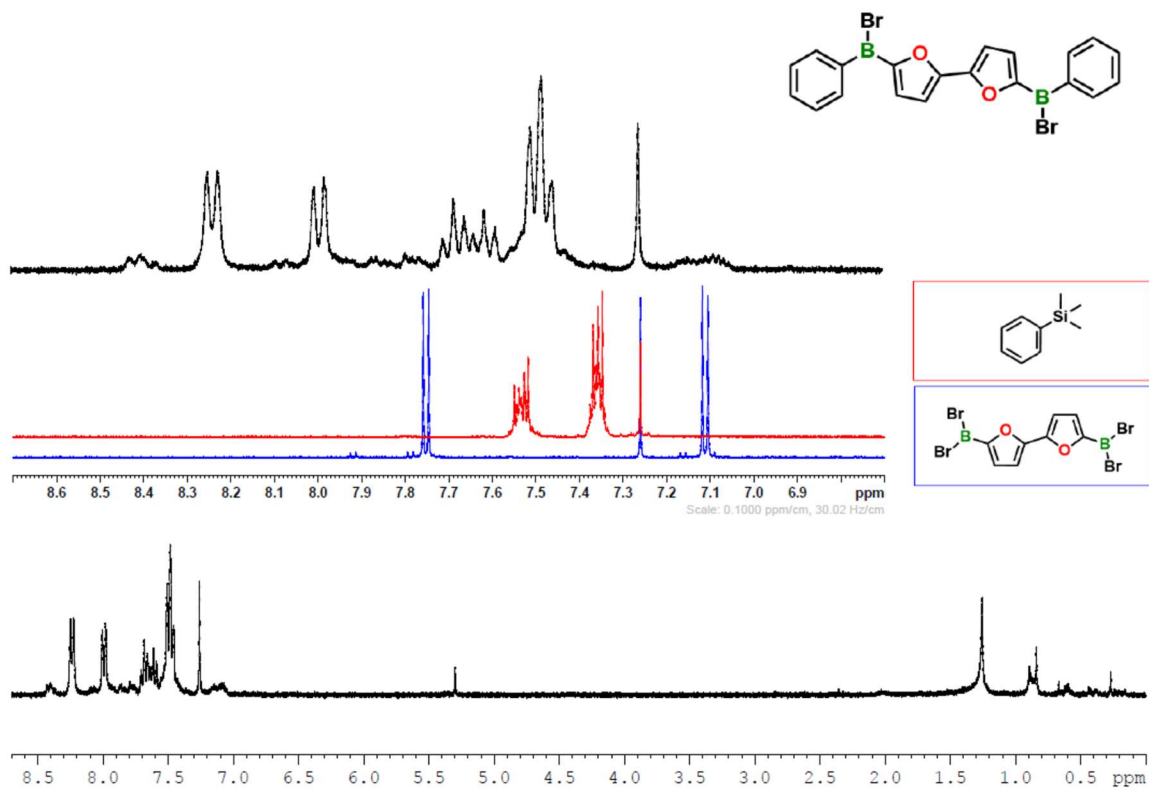


Figure S26.  $^1\text{H}$  NMR spectrum of crude  $10\text{c}$  (300 MHz, in  $\text{CDCl}_3$ ). Inset: expansion of the aromatic region (black), and  $^1\text{H}$  NMR spectra of reactants  $9\text{c}$  (red) and  $5$  (blue) for comparison (300 MHz, in  $\text{CDCl}_3$ ).

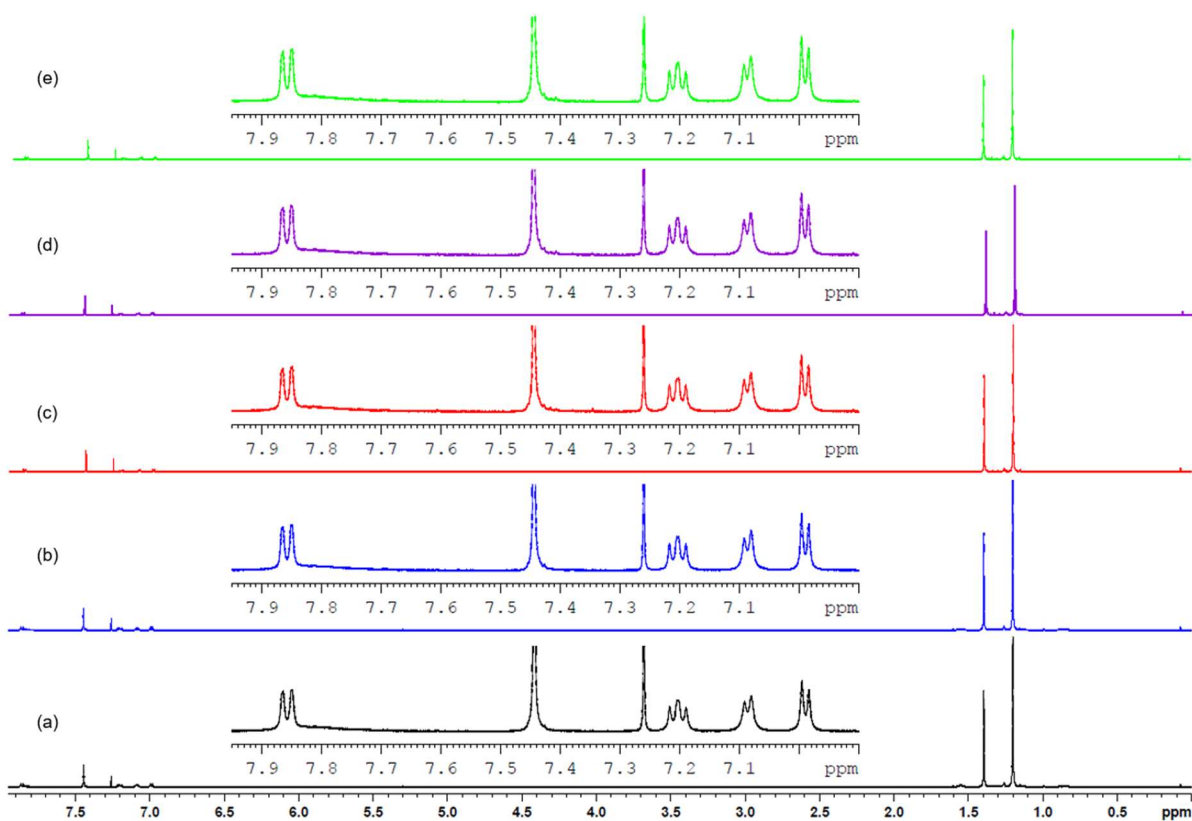


Figure S27. Stability tests of **2a<sup>Mes+</sup>** determined by <sup>1</sup>H NMR spectroscopy (300 MHz) after storage in moist solution (CDCl<sub>3</sub>) in air, a) after 1 h, b) after 1 d, c) after 3 d, d) after 5 d, e) after 7 d.

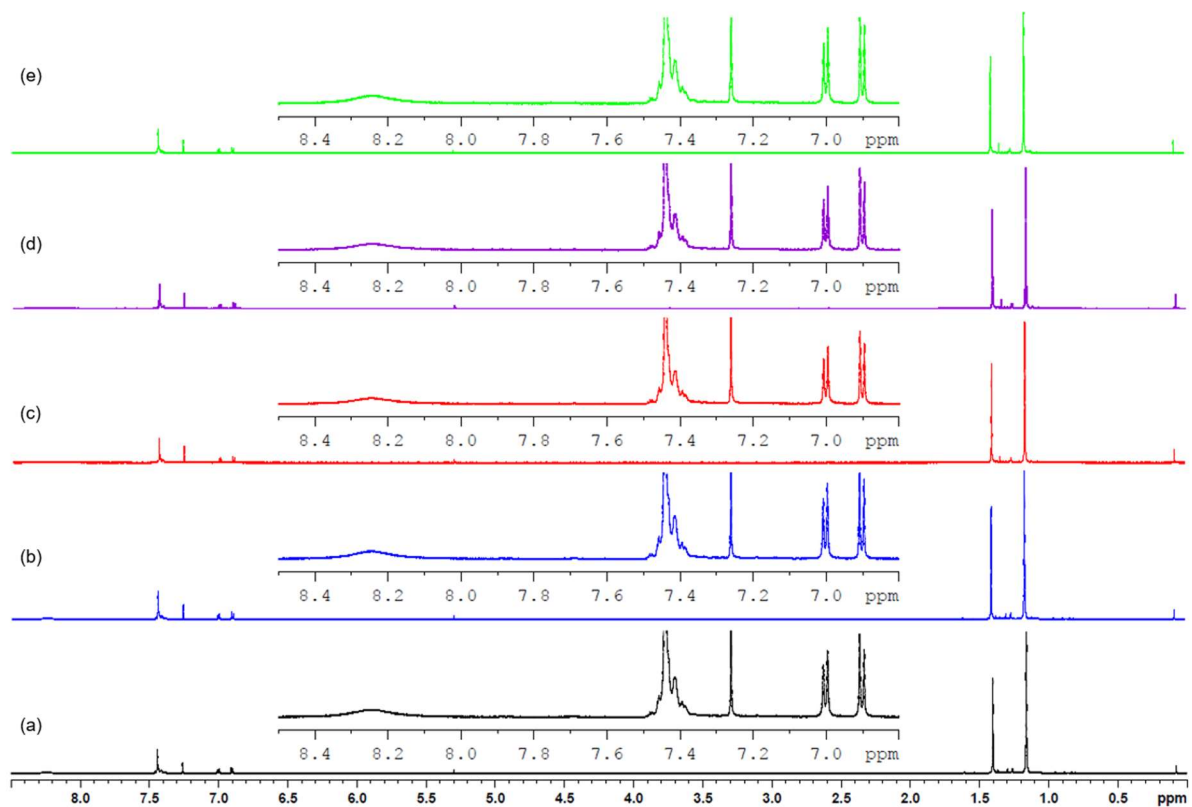


Figure S28. Stability tests of **2c<sup>Mes+</sup>** determined by <sup>1</sup>H NMR spectroscopy (300 MHz) after storage in moist solution (CDCl<sub>3</sub>) in air, a) after 1 h, b) after 1 d, c) after 3 d, d) after 5 d, e) after 7 d.

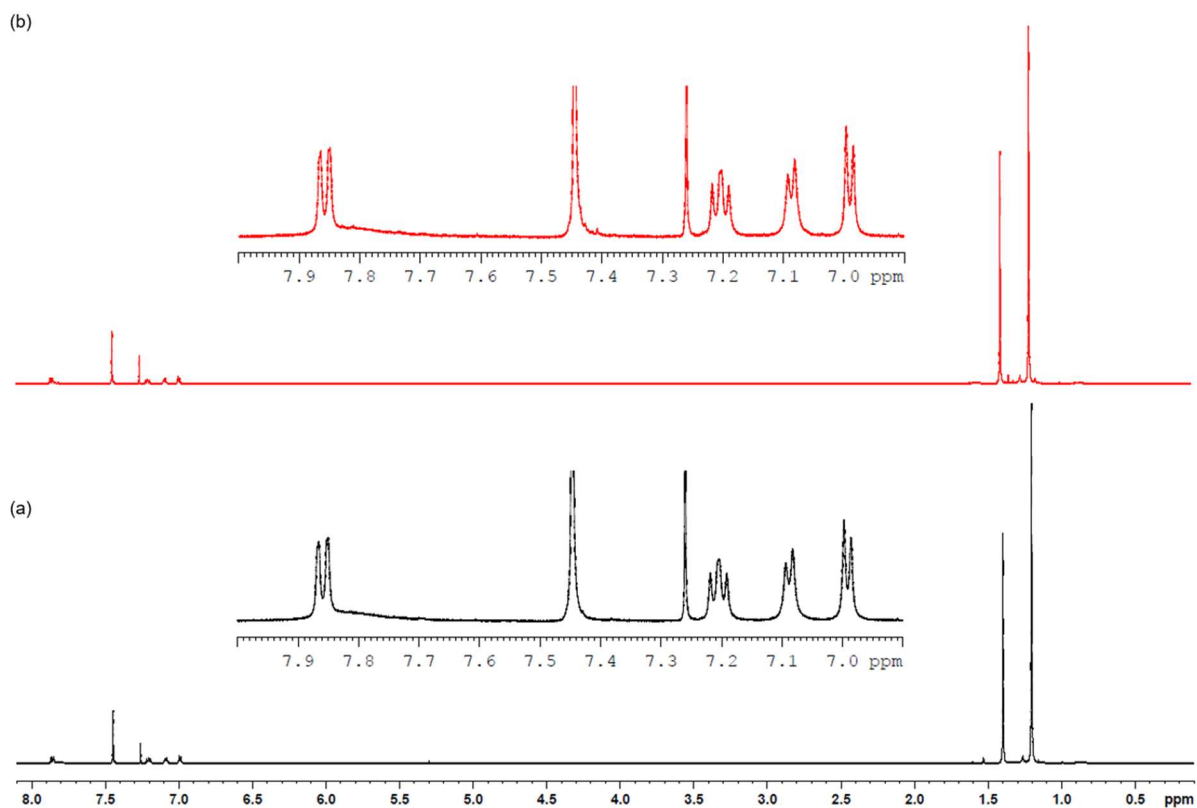


Figure S29. Stability tests of **2a<sup>Mes\*</sup>** determined by <sup>1</sup>H NMR spectroscopy (300 MHz), a) after aqueous work-up, b) after storage as a solid in air for 2 months.

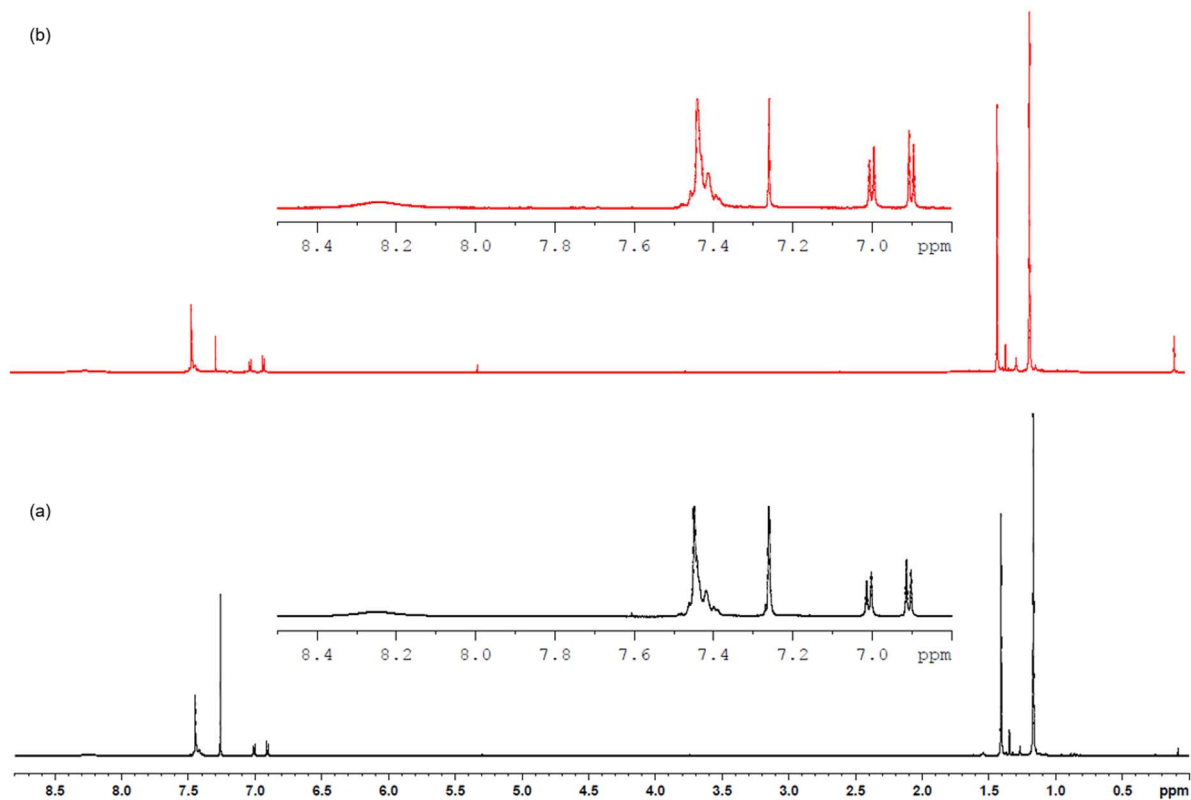


Figure S30. Stability tests of **2c<sup>Mes\*</sup>** determined by <sup>1</sup>H NMR spectroscopy (300 MHz), a) after aqueous work-up, b) after storage as a solid under air for 9 months.

## Mass spectra

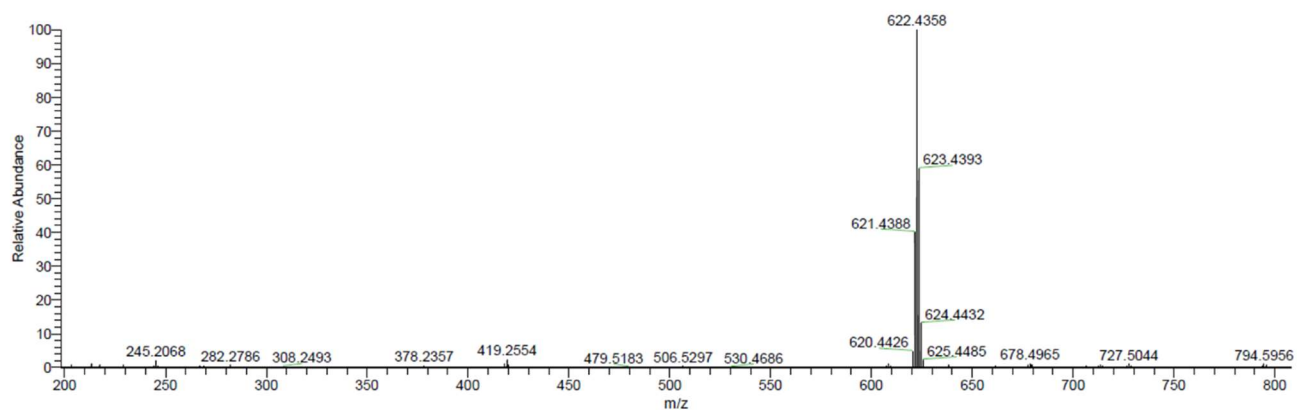


Figure S31. APCI mass spectrum of **7**.

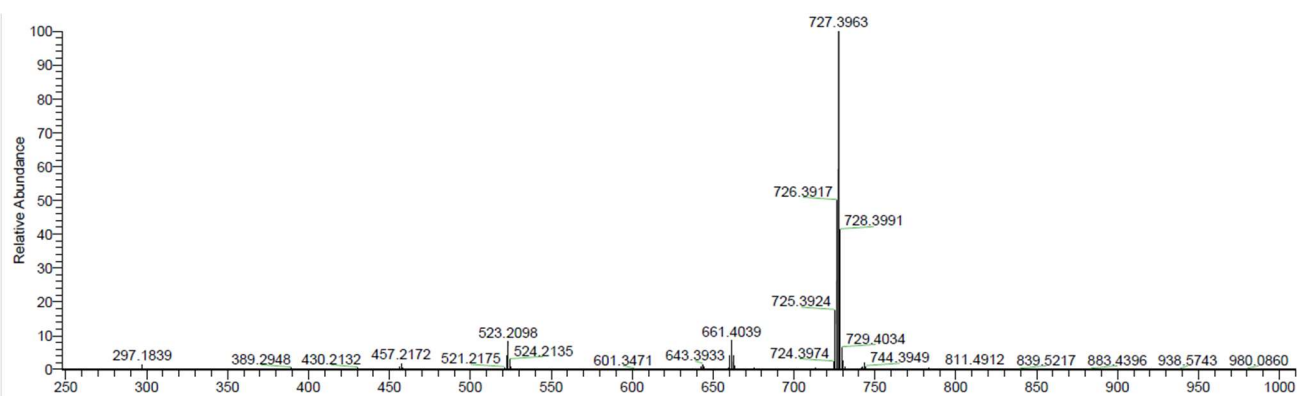


Figure S32. APCI mass spectrum of **2a**<sup>TIP</sup>.

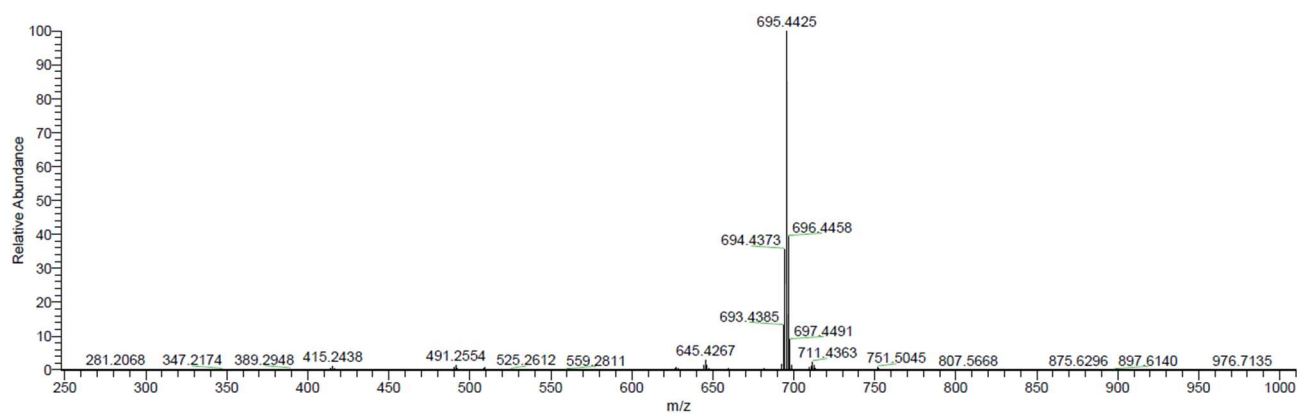


Figure S33. APCI mass spectrum of **2b**<sup>TIP</sup>.

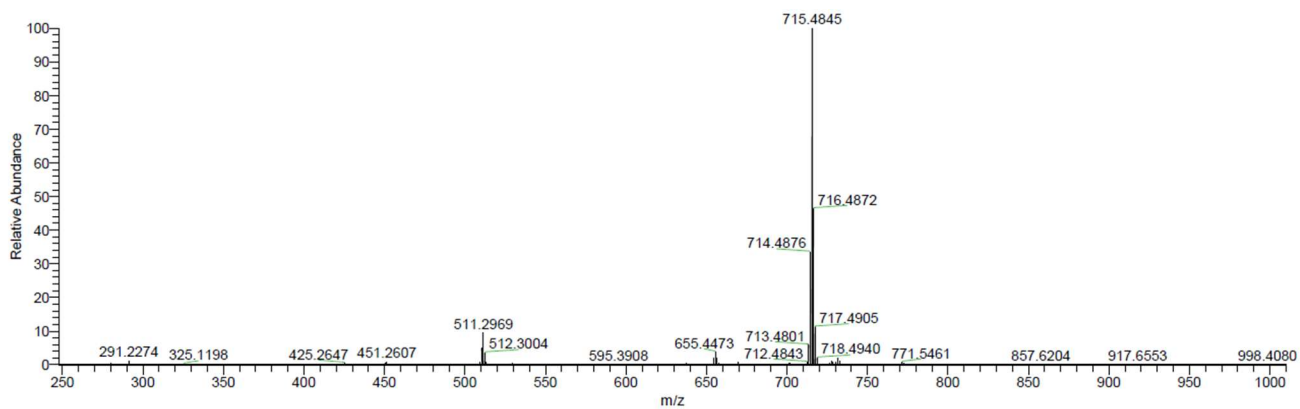


Figure S34. APCI mass spectrum of **2c**<sup>TIP</sup>.

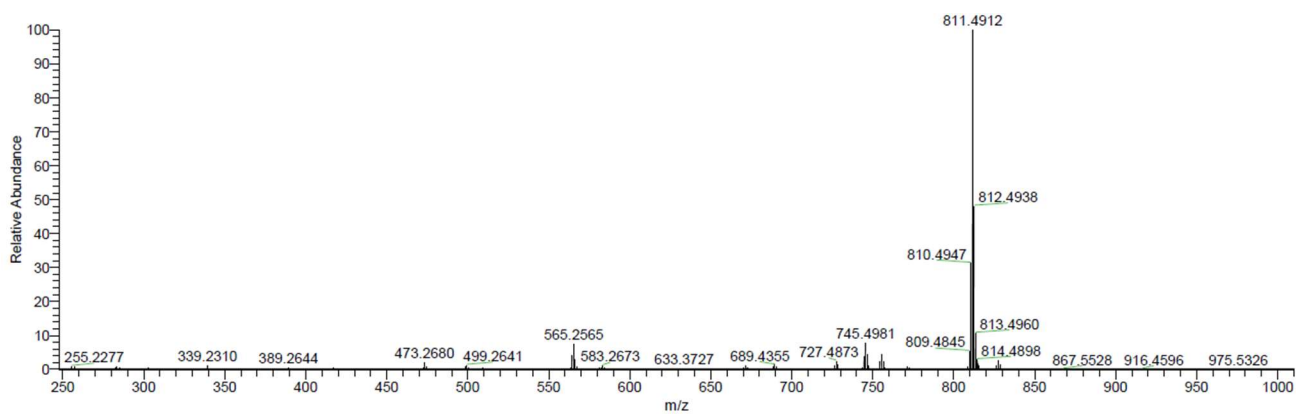


Figure S35. APCI mass spectrum of **2a**<sup>Mes+</sup>.

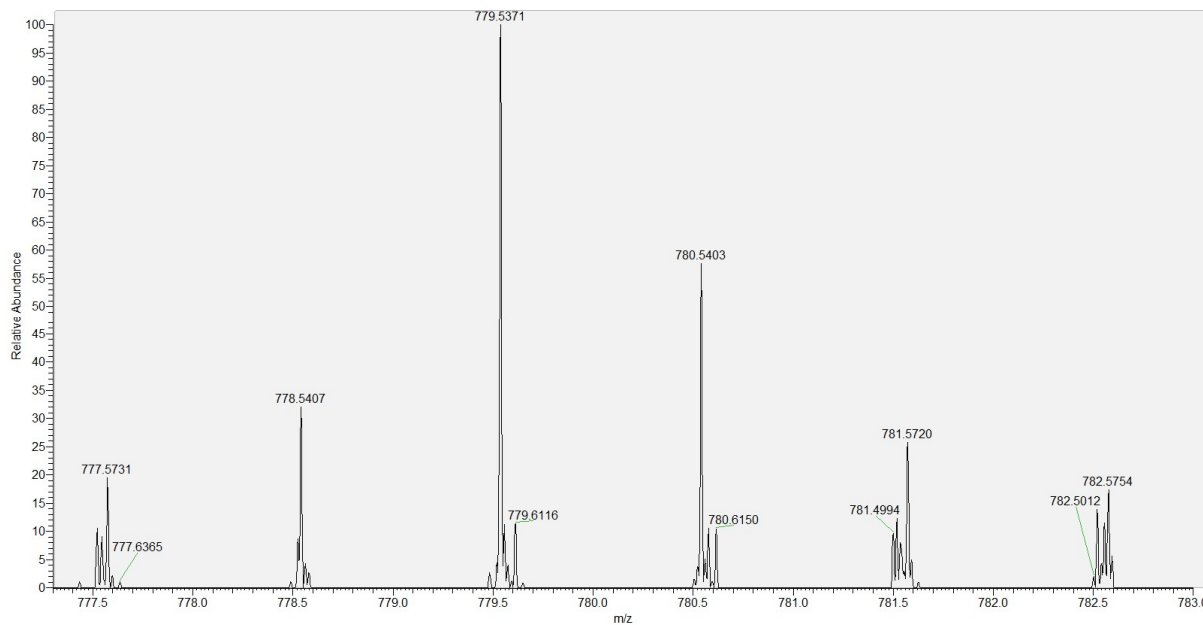


Figure S36. APCI mass spectrum of **2b**<sup>Mes+</sup> traces.



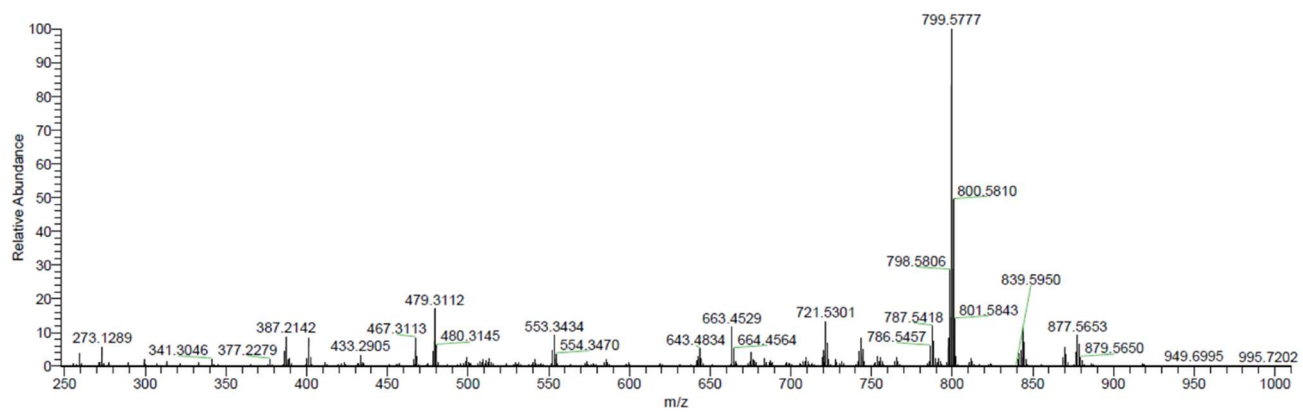


Figure S37. APCI mass spectrum of **2c<sup>Mes\*</sup>**.

## UV/Vis spectra

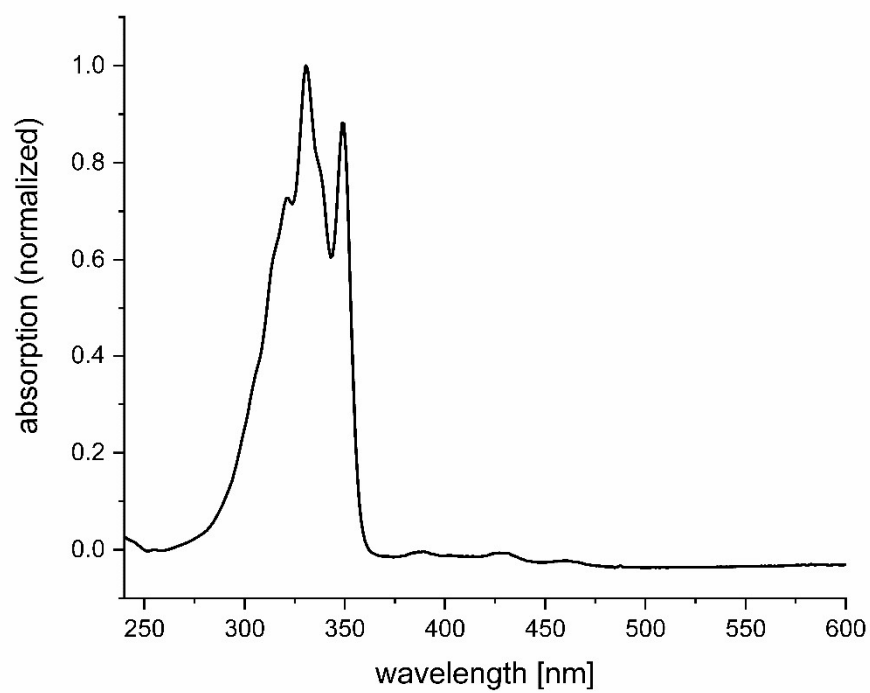


Figure S38. UV-Vis spectrum of **7** (in THF).

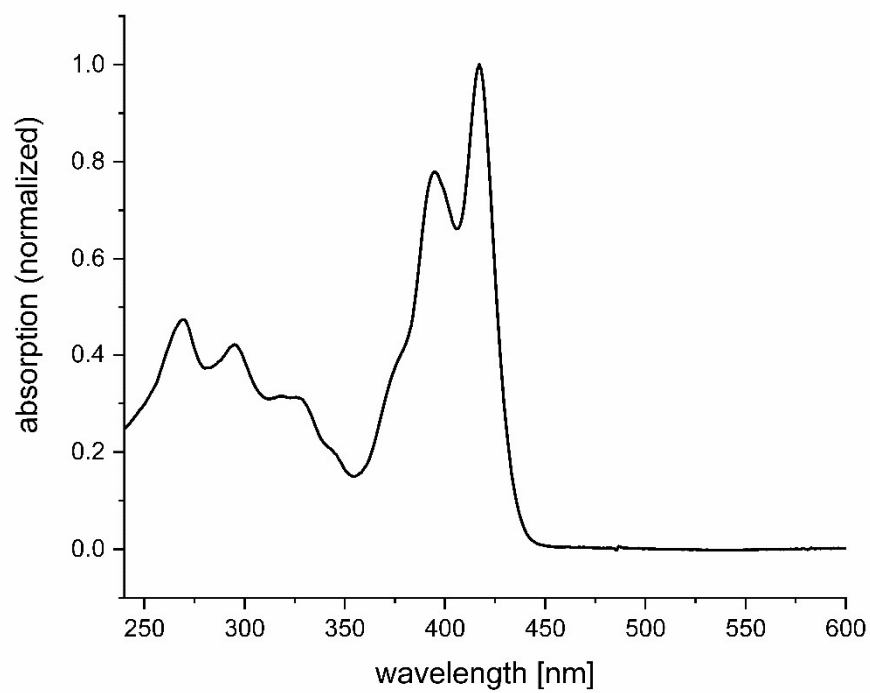


Figure S39. UV-Vis spectrum of **2a<sup>TIP</sup>** (in THF).

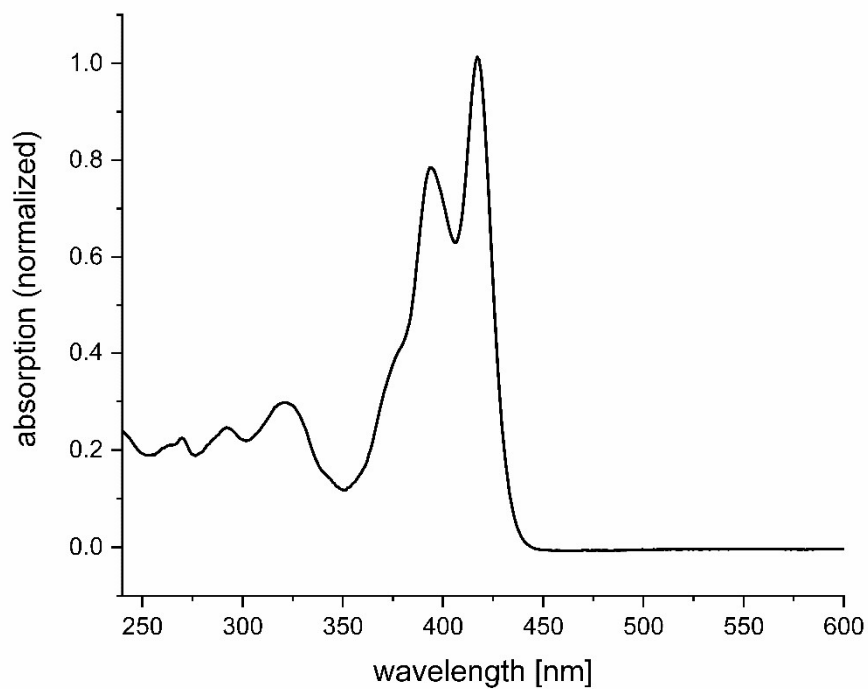


Figure S40. UV-Vis spectrum of **2b**<sup>TIP</sup> (in THF).

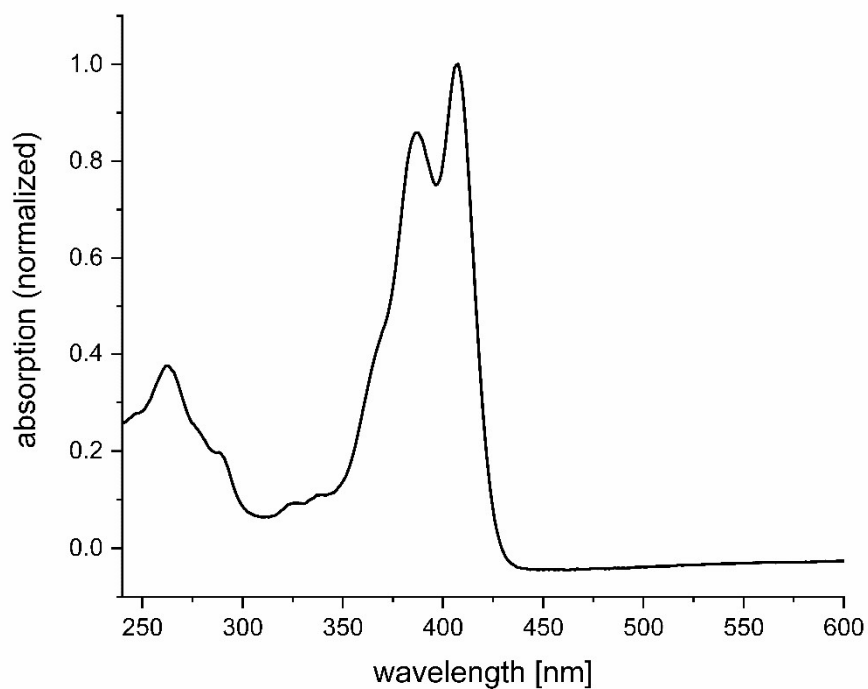


Figure S41. UV-Vis spectrum of **2c**<sup>TIP</sup> (in THF).

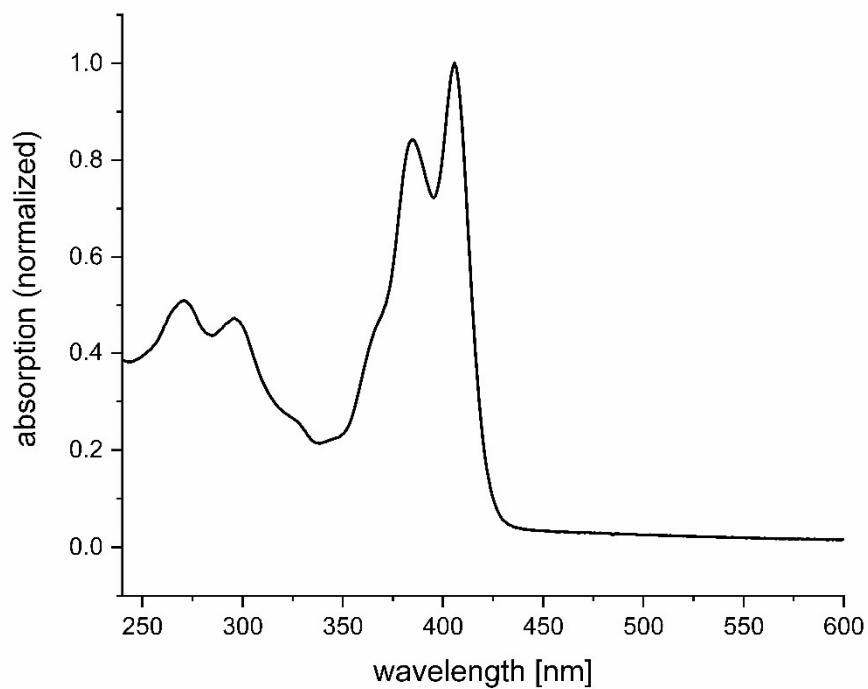


Figure S42. UV-Vis spectrum of **2a<sup>Mes\*</sup>** (in THF).

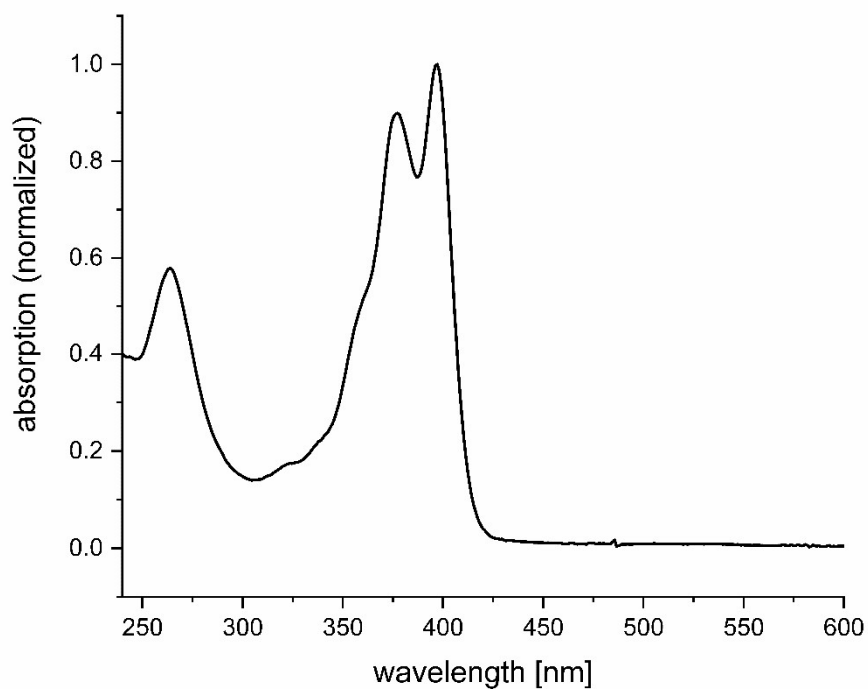


Figure S43. UV-Vis spectrum of **2a<sup>Mes\*</sup>** (in THF).

## Fluorescence spectra

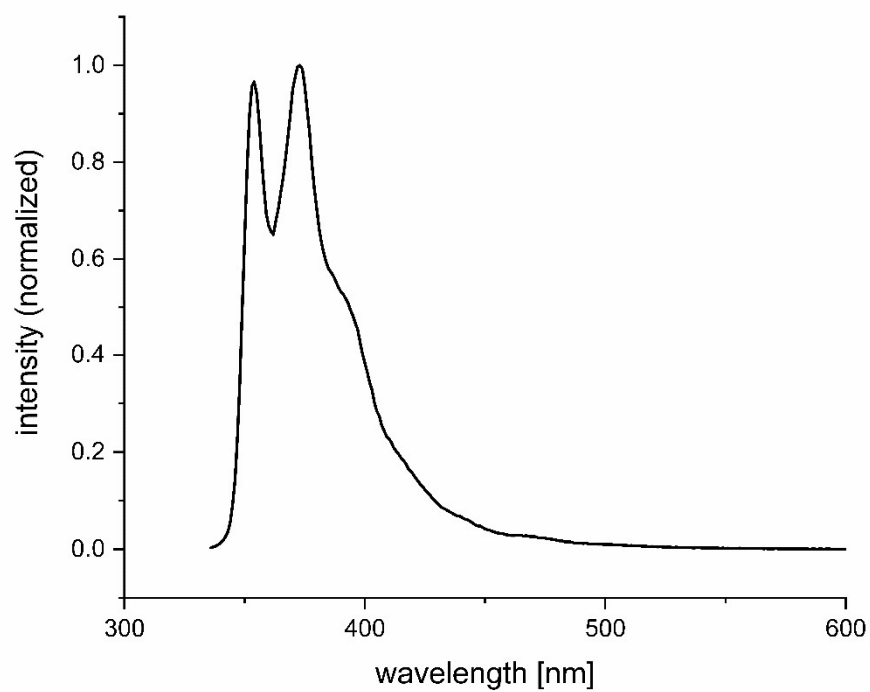


Figure S44. Fluorescence spectrum of **7** (in THF,  $\lambda_{\text{ex}} = 331$  nm).

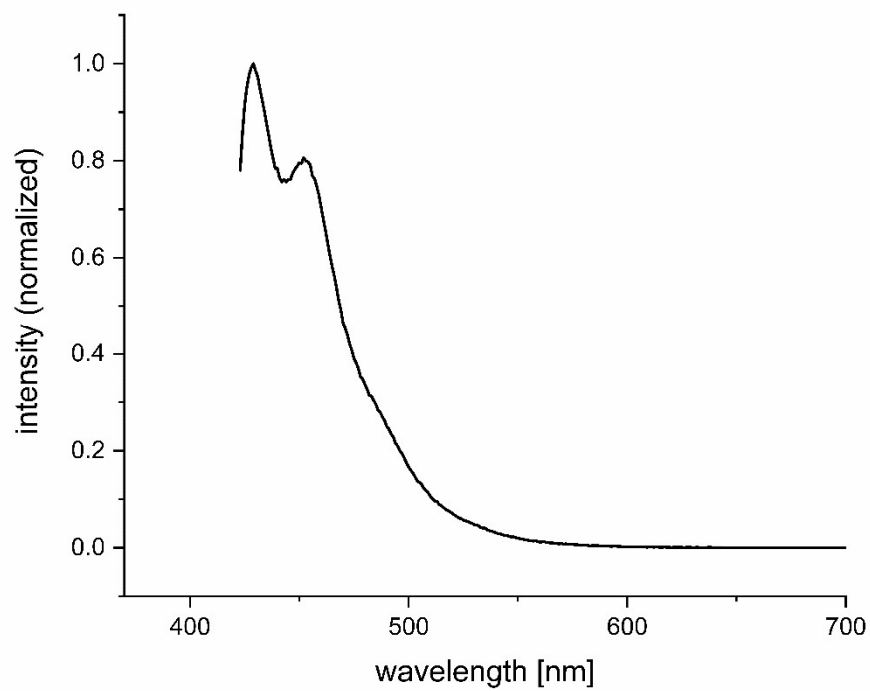


Figure S45. Fluorescence spectrum of **2a<sup>Tip</sup>** (in THF,  $\lambda_{\text{ex}} = 417$  nm).

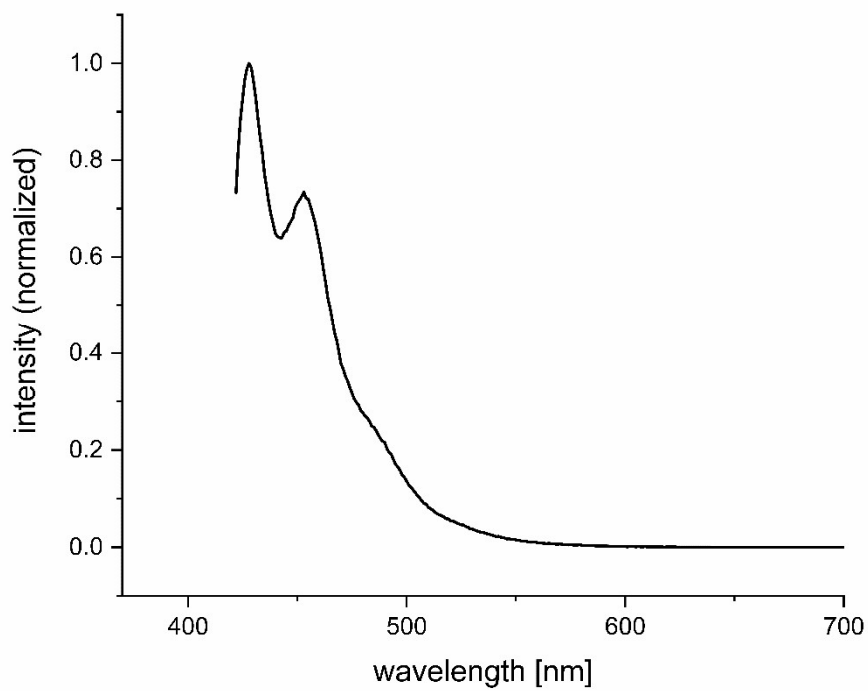


Figure S46. Fluorescence spectrum of **2b**<sup>Tip</sup> (in THF,  $\lambda_{\text{ex}} = 417$  nm).

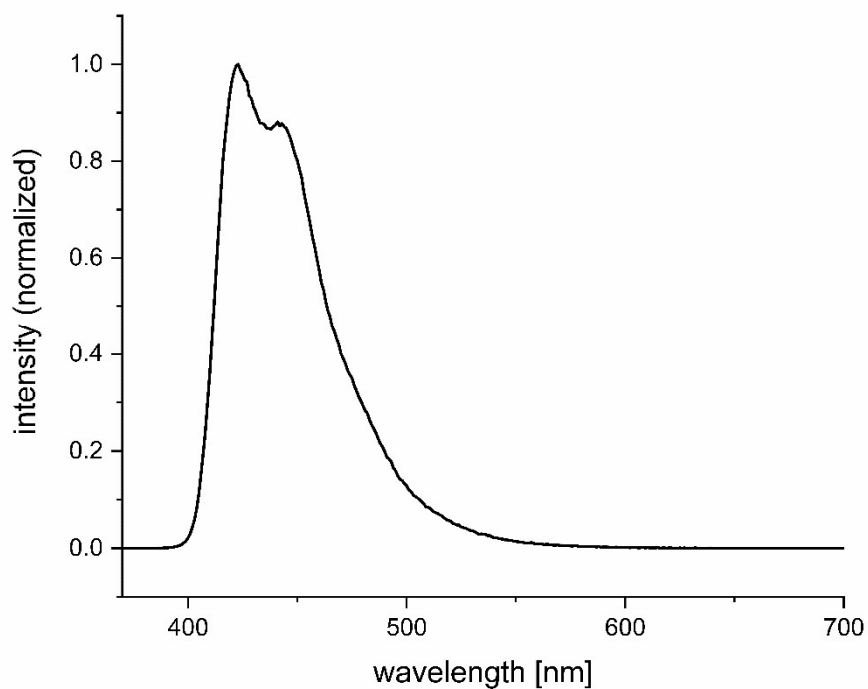


Figure S47. Fluorescence spectrum of **2c**<sup>Tip</sup> (in THF,  $\lambda_{\text{ex}} = 407$  nm).

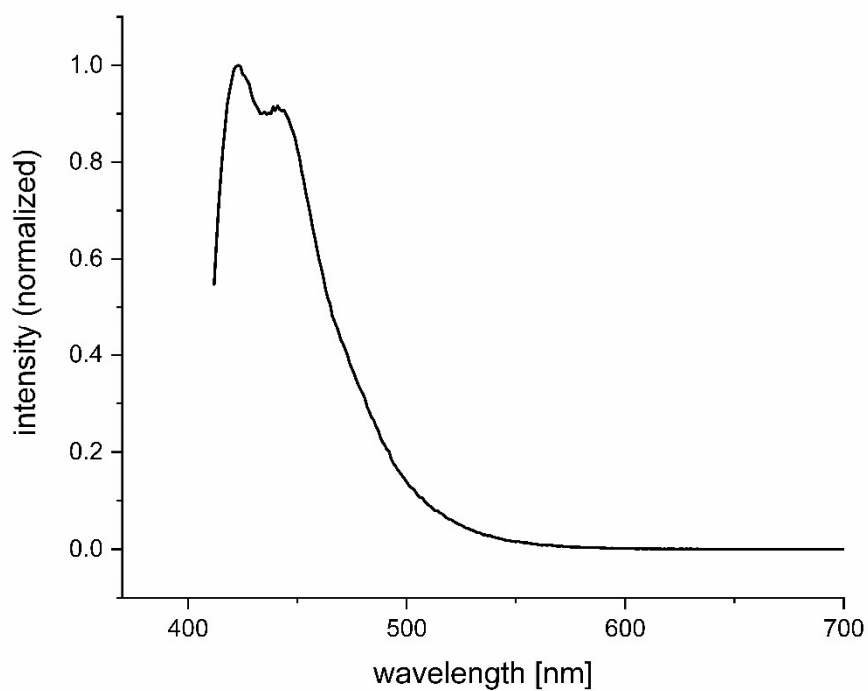


Figure S48. Fluorescence spectrum of **2a<sup>Mes\*</sup>** (in THF,  $\lambda_{\text{ex}} = 406$  nm).

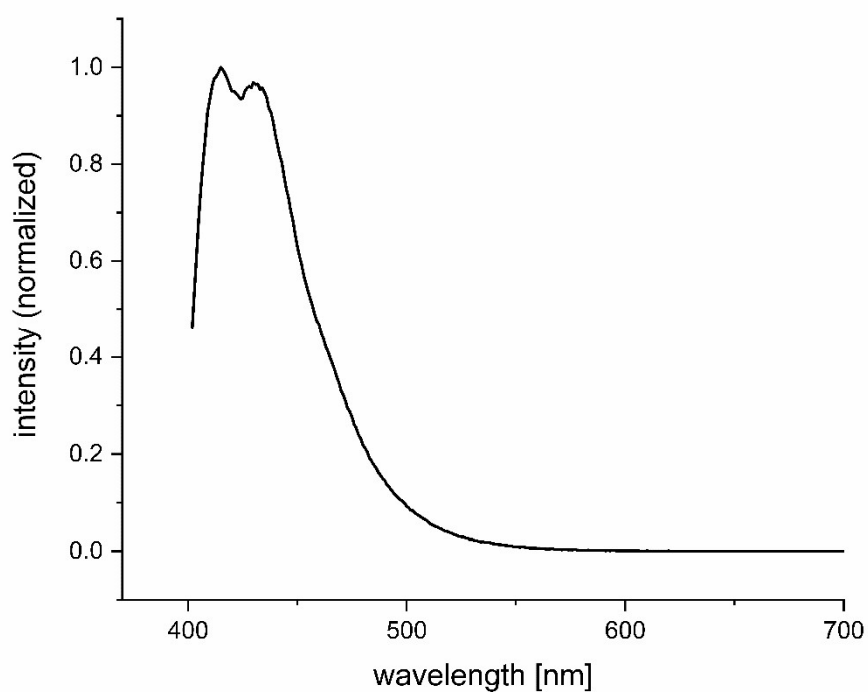


Figure S49. Fluorescence spectrum of **2c<sup>Mes\*</sup>** (in THF,  $\lambda_{\text{ex}} = 398$  nm).

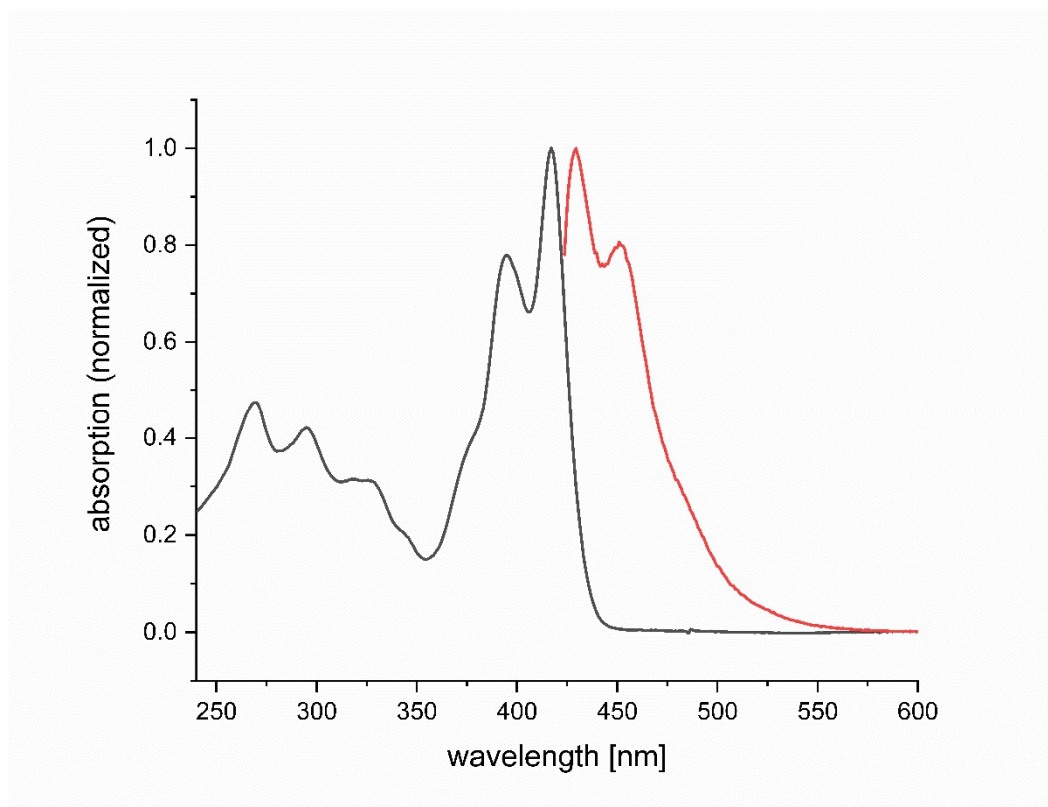


Figure S50. UV-Vis (black) and fluorescence spectrum (red) of **2a**<sup>Tip</sup>.

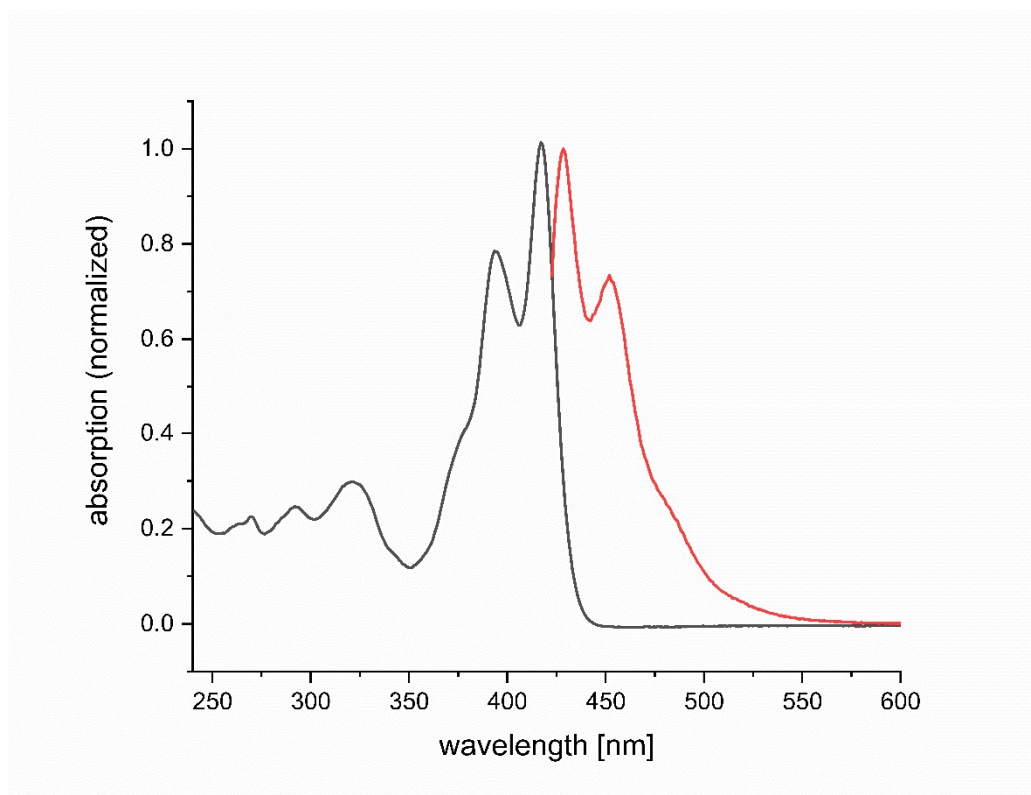


Figure S51. UV-Vis (black) and fluorescence spectrum (red) of **2b**<sup>Tip</sup>.



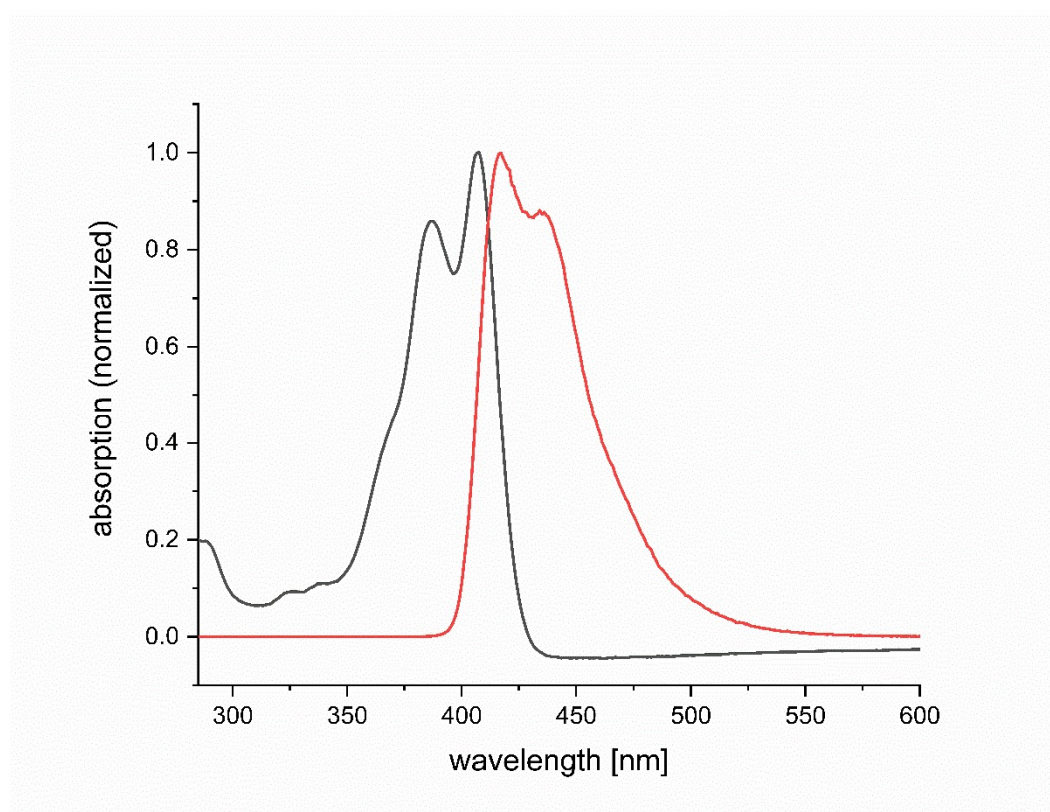


Figure S52. UV-Vis (black) and fluorescence spectrum (red) of **2c<sup>Tip</sup>**.

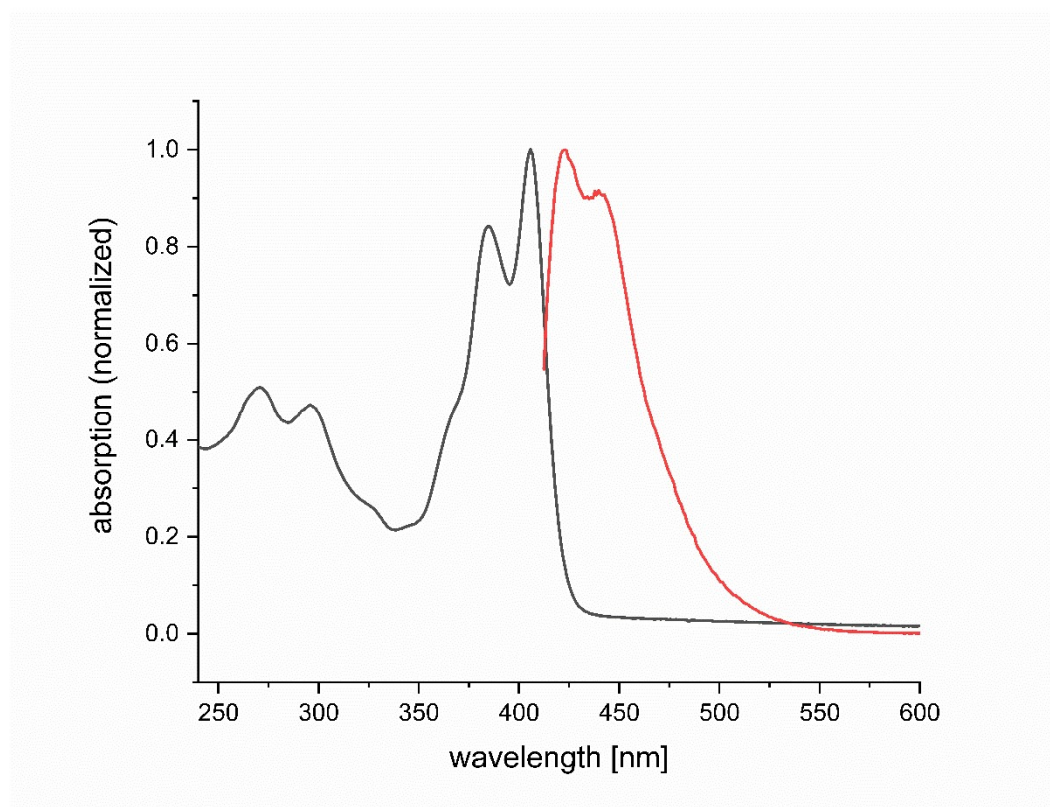


Figure S53. UV-Vis (black) and fluorescence spectrum (red) of **2a<sup>Mes\*</sup>**.

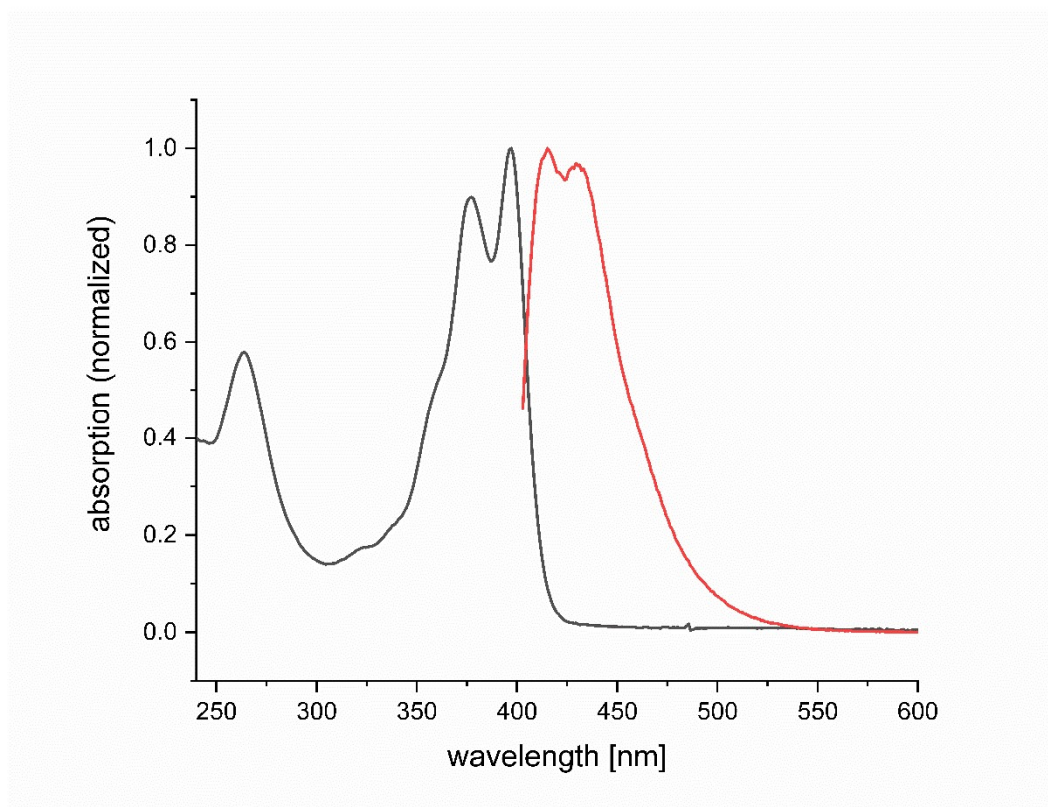


Figure S54. UV-Vis (black) and fluorescence spectrum (red) of **2c<sup>Mes\*</sup>**.

## Cyclic Voltammetry

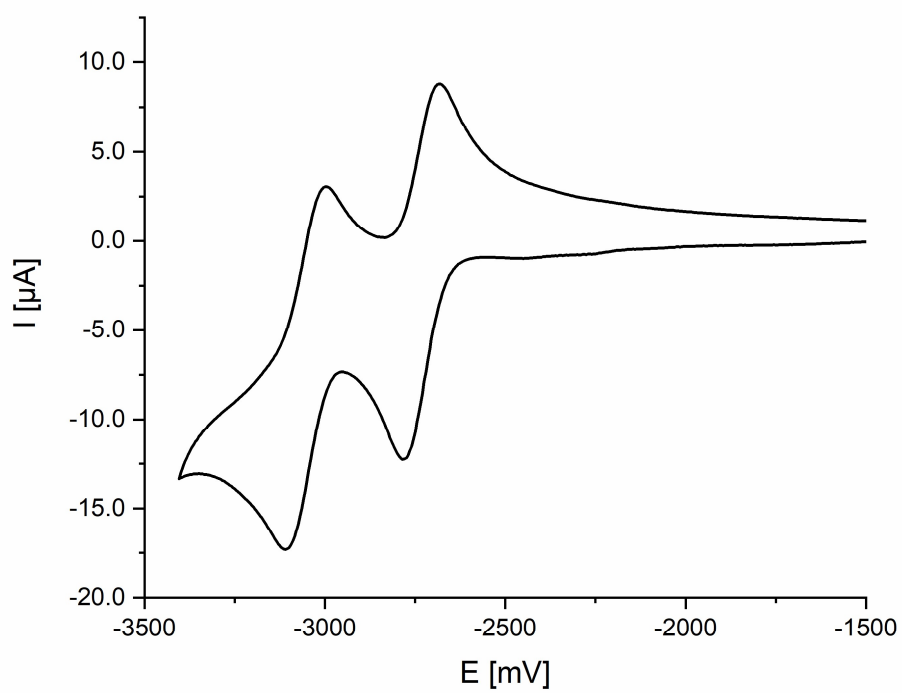


Figure S55. Cyclic voltammogram of 7 (in THF).

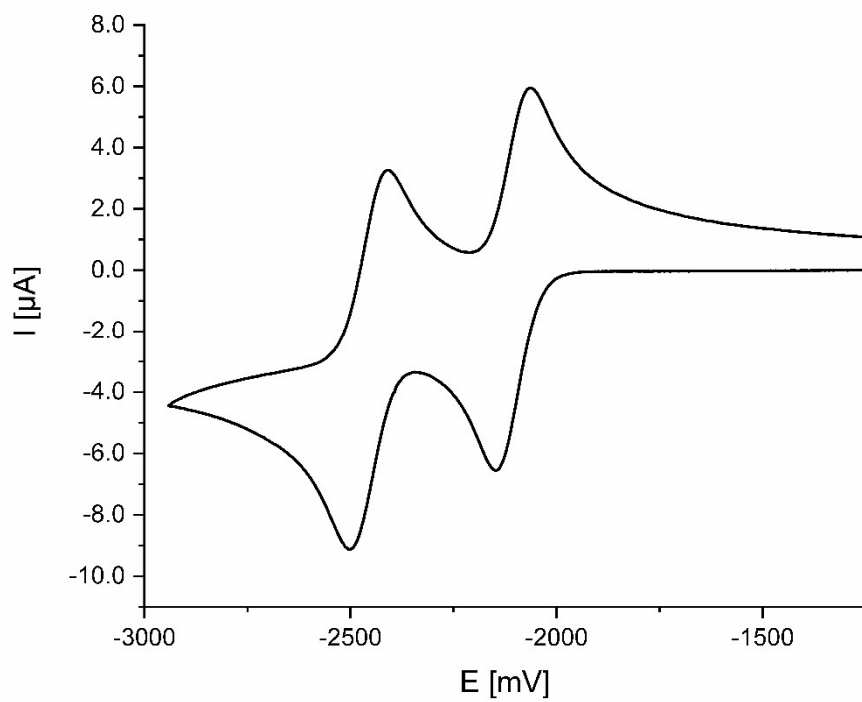


Figure S56. Cyclic voltammogram of 2a<sup>TP</sup> (in THF).

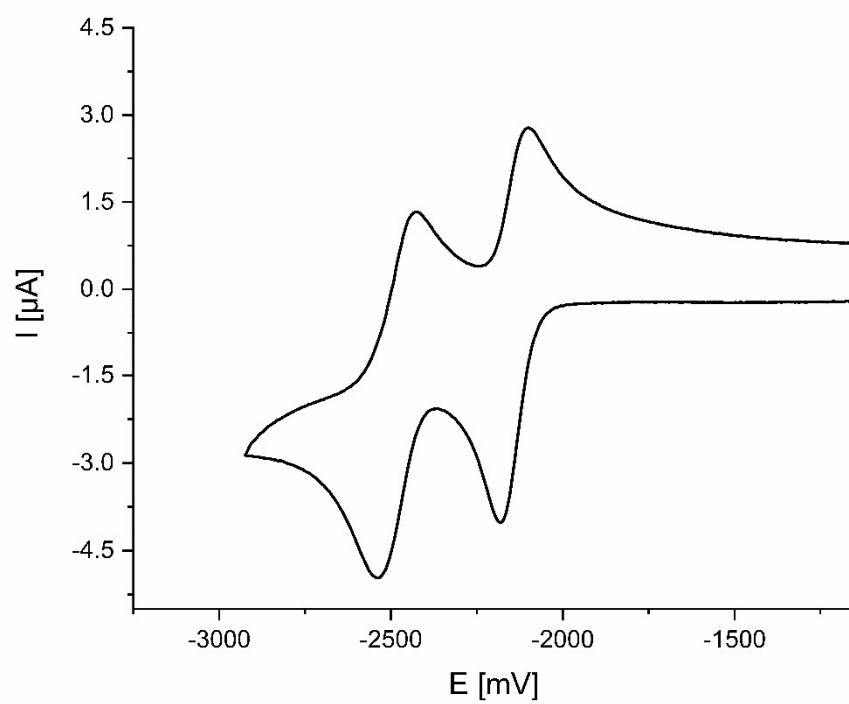


Figure S57. Cyclic voltammogram of **2b**<sup>TIP</sup> (in THF).

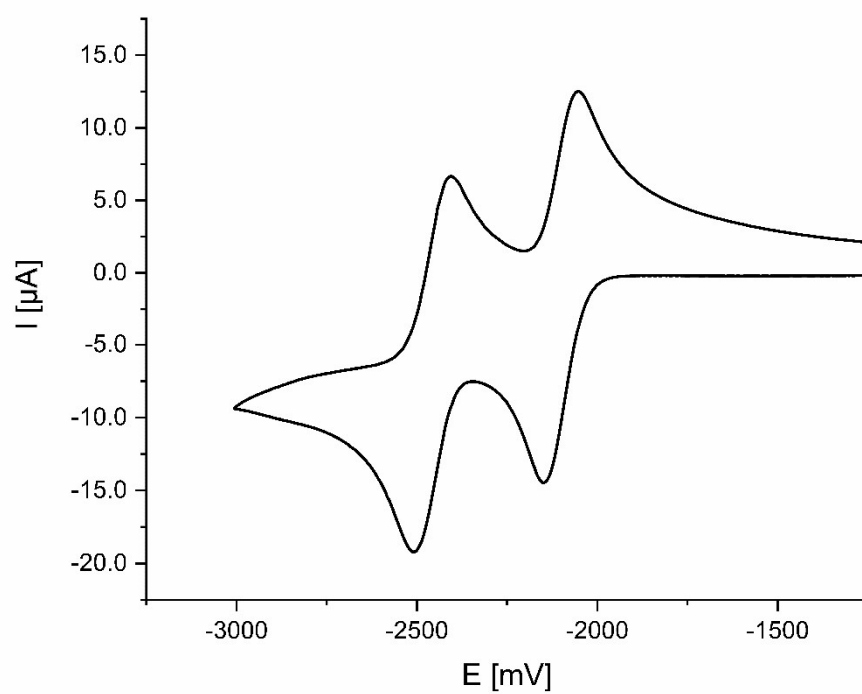


Figure S58. Cyclic voltammogram of **2c**<sup>TIP</sup> (in THF).

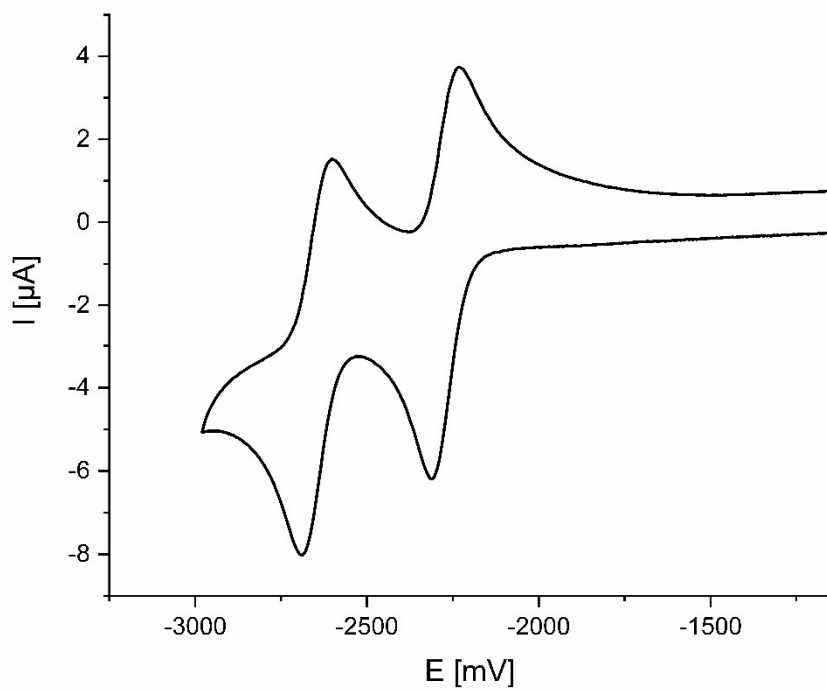


Figure S59. Cyclic voltammogram of **2a**<sup>Mes\*</sup> (in THF).

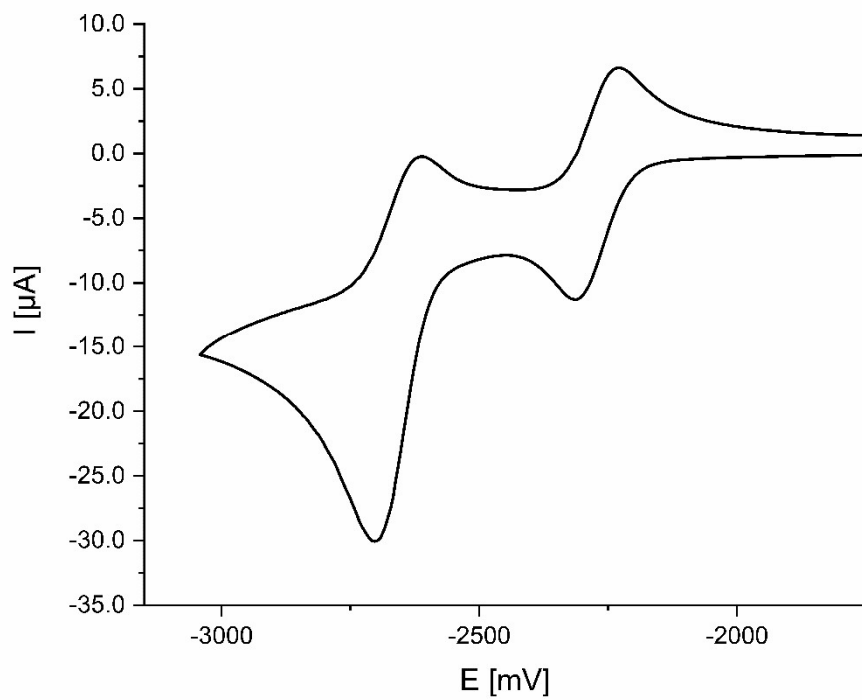


Figure S60. Cyclic voltammogram of **2c**<sup>Mes\*</sup> (in THF).

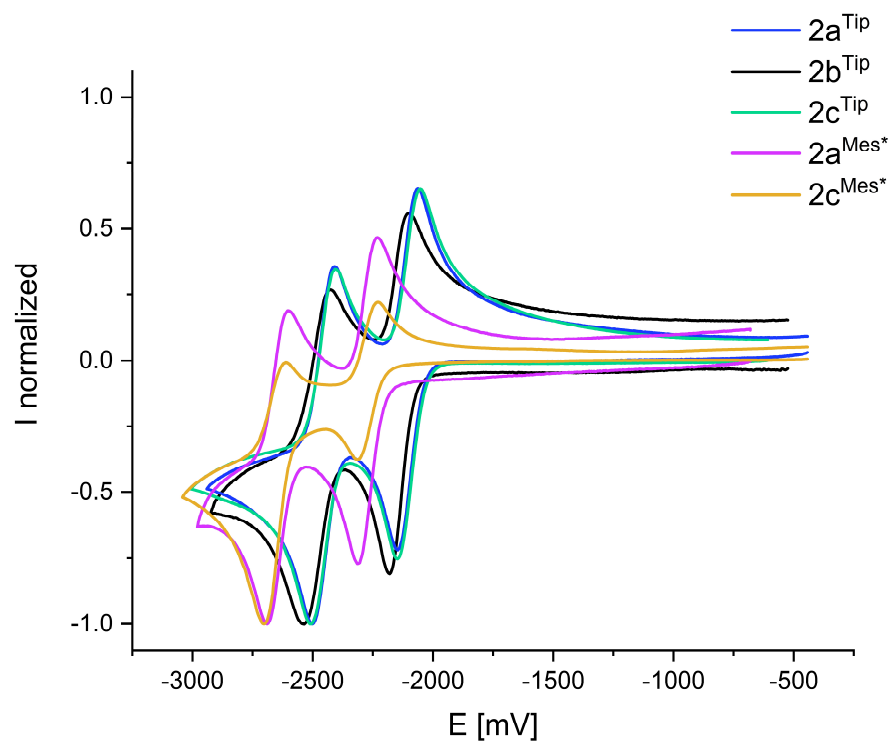


Figure S61. Overlay of cyclic voltammograms of  $2a^{\text{Tip}}$ ,  $2b^{\text{Tip}}$ ,  $2c^{\text{Tip}}$ ,  $2a^{\text{Mes}^*}$  and  $2c^{\text{Mes}^*}$  (in THF).

## X-Ray crystallographic analysis

Table S1. Crystal structure and refinement data for **2a**<sup>Tip</sup>

No.	<b>2a</b> <sup>Tip</sup>
CCDC number	2020145
Size / mm	0.437 x 0.318 x 0.159
Empiric Formula	C <sub>46</sub> H <sub>56</sub> B <sub>2</sub> O <sub>2</sub> S <sub>2</sub>
<i>M</i> / g mol <sup>-1</sup>	795.58
Crystal system	monoclinic
Space group	P 21/c
<i>a</i> / Å	16.0812(14)
<i>b</i> / Å	9.6707(8)
<i>c</i> / Å	17.1517(15)
<i>α</i> / deg	90
<i>β</i> / deg	117.418(2)
<i>γ</i> / deg	90
<i>V</i> / Å <sup>3</sup>	2367.7(4)
<i>Z</i>	2
<i>μ</i> / mm <sup>-1</sup>	0.151
<i>T</i> / K	100
<i>θ</i> <sub>min,max</sub>	2.38, 26.49
Completeness	99.9
Reflections: total / independent	4662, 3672
<i>R</i> <sub>int</sub>	0.1182
Final <i>R</i> 1 and <i>wR</i> 2	0.0590, 0.1596
Largest peak and hole / e Å <sup>-3</sup>	0.31, -0.29
<i>ρ</i> <sub>calc</sub> / g cm <sup>-3</sup>	1.116

## 2 Supporting Computational Information

**Computational methods.** DFT calculations were carried out with the TURBOMOLE V7.3 program package.<sup>[12]</sup> Optimizations were performed with Becke's three parameter exchange-correlation hybrid functional B3LYP<sup>[13]</sup> in combination with the valence-double- $\zeta$  basis set def2-SV(P).<sup>[14]</sup> The empirical dispersion correction DFT-D3 by Grimme was used including the three-body term and with Becke-Johnson (BJ) damping.<sup>[15]</sup> The stationary points were characterized as minima by analytical vibrational frequency calculations.<sup>[16]</sup> Vertical singlet excitations were calculated by means of time-dependent DFT<sup>[17]</sup> using the same density functional–basis set combination as specified above.

Table 2. Results from TD-DFT calculations ( $\pi$ – $\pi^*$  excitation marked in bold).

Compound	No.	$\lambda$ / nm	Oscillator strength $f$	Orbital contributions	$ c ^2$ / %
<b>2a<sup>Mes</sup></b>	<b>1</b>	<b>422.9</b>	<b>0.9345</b>	<b>HOMO</b> $\rightarrow$ <b>LUMO</b>	<b>82.8</b>
				HOMO-2 $\rightarrow$ LUMO	10.2
	3	402.9	0.3170	HOMO-2 $\rightarrow$ LUMO	69.3
				HOMO $\rightarrow$ LUMO	14.9
				HOMO-1 $\rightarrow$ LUMO	9.4
	<b>15</b>	<b>276.0</b>	<b>0.1488</b>	<b>HOMO-5</b> $\rightarrow$ <b>LUMO+1</b>	<b>76.7</b>
HOMO $\rightarrow$ LUMO+3				17.8	
<b>2b<sup>Mes</sup></b>	<b>1</b>	<b>417.8</b>	<b>1.1764</b>	<b>HOMO</b> $\rightarrow$ <b>LUMO</b>	<b>90.1</b>
				HOMO-2 $\rightarrow$ LUMO	82.5
	3	399.6	0.1826	HOMO-3 $\rightarrow$ LUMO+1	8.4
				<b>HOMO-5</b> $\rightarrow$ <b>LUMO+1</b>	<b>85.7</b>
	13	270.7	0.1795	HOMO $\rightarrow$ LUMO+2	12.5
<b>2c<sup>Mes</sup></b>	1	407.0	0.0689	HOMO-1 $\rightarrow$ LUMO	85.7
				HOMO-2 $\rightarrow$ LUMO+1	7.1
	<b>3</b>	<b>403.4</b>	<b>1.0880</b>	<b>HOMO</b> $\rightarrow$ <b>LUMO</b>	<b>91.3</b>



14      285.5      0.1278      HOMO-9 → LUMO      90.9

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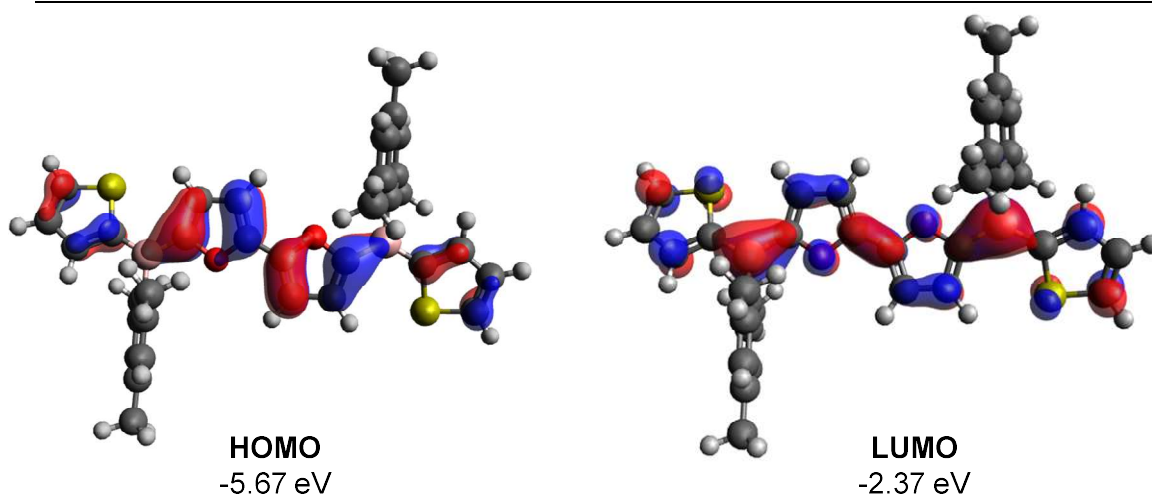


Figure S62. Calculated frontier orbitals of **2a<sup>Mes</sup>** (isovalue 0.03 a.u.).

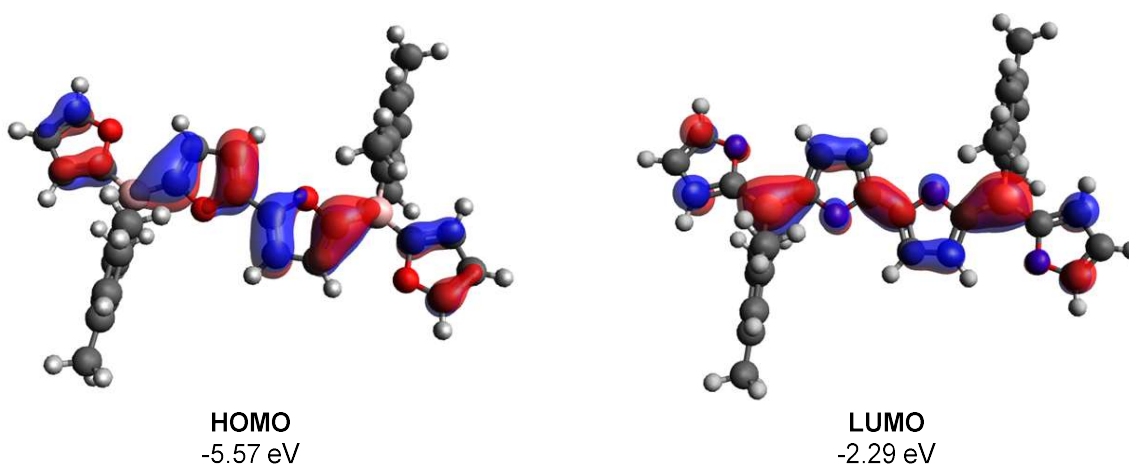


Figure S63. Calculated frontier orbitals of **2b<sup>Mes</sup>** (isovalue 0.03 a.u.).

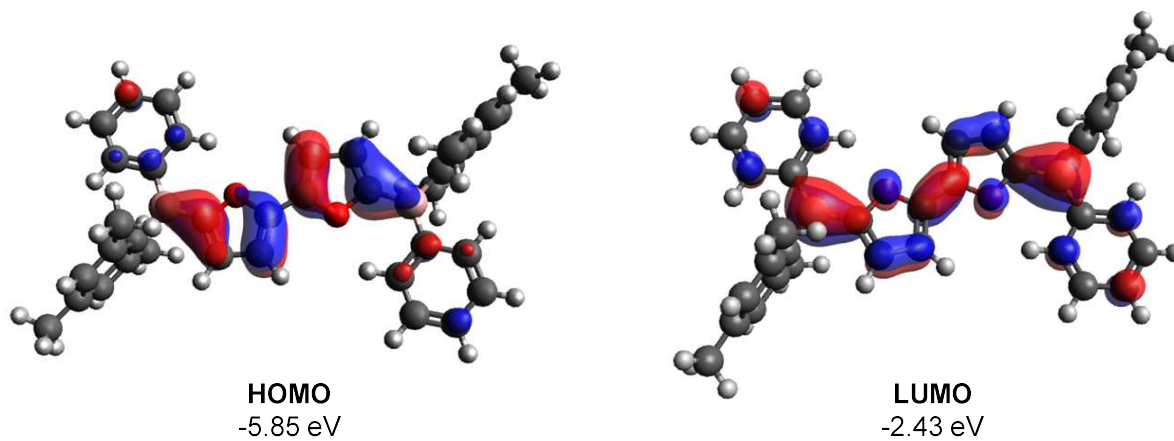


Figure S64. Calculated frontier orbitals of **2c<sup>Mes</sup>** (isovalue of 0.03 a.u.).

## Cartesian coordinates [Å] and total energies [a.u.] of optimized stationary points

2a<sup>Mes</sup>:

Total energy (B3LYP-D3(BJ)/def2-SV(P)): -2309.169520

C	1.245483	2.539436	3.975807
C	0.515235	1.415241	4.420270
C	1.140092	0.487495	5.282134
C	2.465749	0.696368	5.684378
C	3.194592	1.815573	5.264532
C	2.564615	2.726470	4.407227
B	-0.973834	1.195171	3.951561
C	-2.108693	1.507376	4.948324
C	-1.957501	2.147041	6.174572
C	-3.166419	2.315118	6.900292
C	-4.251723	1.790480	6.229831
S	-3.797873	1.101903	4.720174
C	0.391179	-0.736950	5.760255
C	4.607648	2.048763	5.742740
C	0.613366	3.533429	3.027136
C	-1.231747	0.702199	2.518665
O	-0.121596	0.349314	1.769879
C	-0.525552	-0.016640	0.540711
C	-1.903167	0.085975	0.436060
C	-2.345382	0.544105	1.701158
C	0.481563	-0.426162	-0.396451
C	1.859318	-0.528031	-0.293634
C	2.299838	-0.989387	-1.558312
C	1.185195	-1.148277	-2.374135
O	0.076546	-0.790148	-1.626024
B	0.936011	-1.550036	-3.836874
C	2.049103	-2.093487	-4.756083
S	3.634969	-2.615563	-4.224611
C	4.126590	-3.021980	-5.822240
C	3.129234	-2.776587	-6.742869
C	1.955757	-2.257968	-6.134379

C	-0.511633	-1.374275	-4.435233
C	-1.007269	-0.086502	-4.737290
C	-2.292506	0.055506	-5.276158
C	-3.116884	-1.050765	-5.513880
C	-2.620574	-2.320964	-5.194436
C	-1.334933	-2.498652	-4.668029
C	-0.164236	1.140759	-4.469995
C	-0.843340	-3.891215	-4.337615
C	-4.488867	-0.883776	-6.121715
H	-4.911767	0.111993	-5.900630
H	-4.453804	-0.986813	-7.224074
H	-5.193730	-1.646851	-5.746759
H	-3.255017	-3.199745	-5.357893
H	-2.662994	1.059545	-5.512704
H	-1.655578	-4.633745	-4.417074
H	-0.029719	-4.203988	-5.017180
H	-0.436574	-3.944721	-3.310795
H	0.860003	1.029448	-4.870504
H	-0.608442	2.042440	-4.924891
H	-0.067103	1.325162	-3.383965
H	5.120837	-3.431733	-6.009003
H	3.236818	-2.968626	-7.813155
H	3.330846	-1.174426	-1.856742
H	2.452278	-0.289879	0.587474
H	-3.374502	0.754323	1.989451
H	-2.493938	-0.140557	-0.449573
H	-3.237879	2.796277	7.878730
H	-5.292337	1.769099	6.558410
H	2.944373	-0.037742	6.342733
H	1.251703	4.422556	2.889058
H	-0.371681	3.877043	3.392506
H	0.447235	3.080636	2.031894
H	3.118593	3.606374	4.060169
H	5.119163	1.097806	5.973531

H	4.622289	2.660344	6.666015
H	5.207426	2.586392	4.987262
H	-0.430287	-0.464325	6.447536
H	1.059551	-1.436068	6.291133
H	-0.069583	-1.284316	4.917217
H	-0.978622	2.483787	6.525440
H	1.044091	-2.000047	-6.679360

**2b<sup>Mes</sup>:**

Total energy (B3LYP-D3(BJ)/def2-SV(P)): -1663.367040

C	-1.438237	-2.892049	-4.781548
C	-0.755434	-1.682495	-4.530488
C	-1.420360	-0.457206	-4.760687
C	-2.732652	-0.459512	-5.248344
C	-3.418931	-1.652980	-5.509185
C	-2.754995	-2.859977	-5.261672
B	0.725741	-1.692580	-3.992465
C	1.862629	-1.937006	-4.994186
O	3.187729	-1.990434	-4.595332
C	3.949143	-2.202532	-5.680373
C	3.175784	-2.293237	-6.811864
C	1.833441	-2.122024	-6.366396
C	-0.722453	0.851573	-4.466030
C	-4.823866	-1.632044	-6.062496
C	-0.762005	-4.220058	-4.520291
C	1.016625	-1.446237	-2.508897
C	2.169738	-1.390479	-1.734020
C	1.787363	-1.115373	-0.398882
C	0.405141	-1.013975	-0.421756
O	-0.058858	-1.210864	-1.668929
C	-0.554447	-0.745959	0.610957
O	-0.089007	-0.541853	1.856432
C	-1.163105	-0.297434	2.695577
C	-2.317334	-0.359893	1.922874

C	-1.936855	-0.646654	0.589605
B	-0.867640	-0.026776	4.174027
C	-1.997920	0.274757	5.167635
C	-1.956030	0.589853	6.515566
C	-3.295387	0.787568	6.959012
C	-4.079954	0.580751	5.850702
O	-3.327797	0.277049	4.781123
C	0.615622	-0.036305	4.706308
C	1.454143	1.080564	4.495811
C	2.768956	1.063584	4.978035
C	3.287428	-0.043093	5.661993
C	2.451021	-1.150295	5.850342
C	1.128591	-1.161680	5.387702
C	0.940262	2.283666	3.737281
C	0.262369	-2.383087	5.604598
C	4.696917	-0.031928	6.203781
H	-5.427593	-0.828391	-5.604076
H	-4.821626	-1.452250	-7.155402
H	-5.342029	-2.591065	-5.888713
H	-3.278096	-3.805625	-5.443966
H	-3.236379	0.497679	-5.426283
H	-1.463926	-5.061973	-4.645461
H	0.088715	-4.383515	-5.207146
H	-0.355066	-4.269438	-3.493092
H	0.265781	0.905426	-4.959134
H	-1.318265	1.715061	-4.807562
H	-0.547759	0.969795	-3.380377
H	5.023316	-2.268522	-5.509734
H	3.528822	-2.460472	-7.828828
H	3.177399	-1.537222	-2.117962
H	2.418477	-1.000752	0.480488
H	-3.324457	-0.209623	2.306907
H	-2.569248	-0.768515	-0.287863
H	-3.639251	1.047486	7.959524

H	-5.156774	0.616481	5.687918
H	2.840775	-2.032982	6.370129
H	1.662852	3.117185	3.760762
H	-0.014678	2.651040	4.155949
H	0.751012	2.030656	2.677544
H	3.408608	1.937875	4.811742
H	4.727308	0.378810	7.232047
H	5.364184	0.592745	5.584217
H	5.122385	-1.049954	6.247110
H	-0.588466	-2.162387	6.275013
H	0.837620	-3.212362	6.050381
H	-0.168800	-2.744936	4.652589
H	-1.042194	0.665751	7.104397
H	0.926150	-2.128273	-6.969880

**2c<sup>Mes</sup>:**

Total energy (B3LYP-D3(BJ)/def2-SV(P)): -1667.767930

C	-2.955018	1.460027	-11.076149
C	-3.774925	0.532985	-10.396535
C	-4.963396	0.085772	-11.014001
C	-5.313255	0.569086	-12.281425
C	-4.512222	1.494247	-12.962835
C	-3.332548	1.924720	-12.342899
B	-3.359807	-0.004121	-8.969711
C	-2.455118	-1.268586	-8.846589
C	-1.992019	-1.787637	-7.614973
C	-1.179696	-2.921053	-7.563574
C	-0.808013	-3.572014	-8.745929
C	-1.251280	-3.082021	-9.979398
C	-2.060797	-1.946295	-10.023579
C	-5.847037	-0.920706	-10.311588
C	-4.923197	2.031816	-14.312847
C	-1.671143	1.942151	-10.438563
C	-3.910077	0.808721	-7.784666

O	-3.669551	0.481226	-6.460984
C	-4.288095	1.382586	-5.672382
C	-4.948033	2.323316	-6.445029
C	-4.702802	1.949641	-7.789273
C	-4.164179	1.219100	-4.251013
C	-3.506424	0.276403	-3.478902
C	-3.752408	0.648755	-2.134463
C	-4.542992	1.791181	-2.138401
O	-4.781640	2.120791	-3.461930
B	-5.093707	2.602282	-0.952314
C	-4.688678	2.055708	0.473859
C	-5.510331	1.120015	1.138880
C	-5.137486	0.640507	2.401727
C	-3.963000	1.067402	3.033181
C	-3.156035	1.995806	2.362798
C	-3.501287	2.494070	1.100187
C	-6.786415	0.636788	0.486658
C	-3.592086	0.568394	4.409397
C	-2.609331	3.500069	0.407722
C	-5.990126	3.872784	-1.073649
C	-6.432811	4.408431	-2.305691
C	-7.237917	5.547042	-2.355627
C	-7.623247	6.186322	-1.171257
C	-7.200297	5.679822	0.062678
C	-6.397197	4.539489	0.105283
H	-6.214102	-0.529209	-9.344844
H	-5.294613	-1.852484	-10.087655
H	-6.725126	-1.187914	-10.923791
H	-0.993002	1.098111	-10.212792
H	-1.866773	2.457806	-9.479771
H	-1.130044	2.644322	-11.095130
H	-2.685609	2.640818	-12.862388
H	-4.046471	2.326603	-14.915920
H	-5.564284	2.929002	-14.208406

H	-5.499345	1.285404	-14.887548
H	-2.275149	-1.289726	-6.686054
H	-0.832320	-3.302248	-6.597884
H	-0.171292	-4.461940	-8.705386
H	-0.962421	-3.587356	-10.906439
H	-2.402412	-1.565377	-10.990917
H	-5.058601	2.447663	-8.690593
H	-5.527973	3.164458	-6.069982
H	-2.928133	-0.565647	-3.854454
H	-3.398682	0.148676	-1.233453
H	-2.236045	3.110833	-0.557591
H	-3.157537	4.434068	0.182803
H	-1.735182	3.762783	1.027450
H	-7.461112	1.480575	0.250051
H	-6.579332	0.118087	-0.468094
H	-7.336064	-0.063022	1.138622
H	-5.782461	-0.087442	2.906989
H	-4.038091	-0.420230	4.616064
H	-2.497403	0.482186	4.527386
H	-3.950415	1.260656	5.196189
H	-2.230486	2.342348	2.836669
H	-6.070923	4.146057	1.072895
H	-7.499710	6.176097	0.991271
H	-8.254530	7.080163	-1.210629
H	-7.569004	5.941416	-3.321744
H	-6.138994	3.919674	-3.236161
H	-6.235996	0.210203	-12.751466



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