Supporting Information

A Series of Potent BODIPY Photosensitisers Featuring Tellurophene Motifs at Boron

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Experimental Procedures

General Remarks

Reagents were commercially available and used without further purification unless otherwise discussed. Anhydrous solvents were purchased, and used without further drying. The following compounds were synthesised according to literature procedures: tellurophene[1], 4-(3-azidopropyl)-3,5-dimethyl-1H-pyrrole-2-carboxaldehyde,[2] 2,4-dimethyl-3-ethylpyrrole,[3] **2**,[4] **3a**,[5] **3b**,[6] **3c**,[7] **3e**,[8] **3g**,[9] **3h**,[10] **3j**,[5] **3k**,[11] **3m**,[12] **3n**,[13]and **3o**.[14] Manipulations requiring inert atmospheres were conducted under nitrogen and using Schlenk line or glovebox techniques. Nuclear magnetic resonance (NMR) spectra were recorded using 500 MHz and 300 MHz spectrometers. ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane using the solvent residual as an internal standard (δ = 7.26 for chloroform, 5.32 for dichloromethane).[15] ^{13}C chemical shifts are proton decoupled and reported in ppm relative to tetramethylsilane, referenced to the resonances of $CDCl_3$ (δ = 77.20 ppm) or CD_2Cl_2 (δ = 53.84 ppm).[1] Trace impurities and residual solvent peaks were determined using published tables.[15] Coupling constants are reported in hertz (Hz) and spin multiplicities are reported using the following symbols: s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), m (multiplet), p (pentet), sept (septet) and app (apparent). ^{11}B chemical shifts are reported in ppm, externally referenced to boron trifluoride diethyl etherate (δ = 0.00). ^{19}F Chemical shifts are reported in ppm, externally referenced to $CFCl_3$ (δ = 0.00). Thin layer chromatography was performed using commercially prepared silica gel plates and visualised using long- or short-wave UV lamps. Column chromatography was performed using 230-400 mesh silica. The relative proportions of solvents mentioned in reference to TLC and column chromatography procedures correspond to volume-to-volume ratios. Mass spectral data were acquired using a QTOF mass spectrometer operating in positive electrospray ionisation mode.

Absorption and fluorescence spectra were recorded using a quartz cuvette. Using a modified version of a literature procedure,[16] photophysical properties of all compounds were determined in dichloromethane solution at room temperature. Molar absorptivity values were recorded at the peak maximum in dichloromethane for all cases. Fluorescence spectra were determined by exciting at 490 nm in all cases. Fluorescence quantum yield (Φ_f) was determined according to the equation: $\Phi_{unk} = (\Phi_{std})(n/n_{std})^2(I_{unk}/I_{std})(A_{std}/A_{unk})$,[17] where Φ is the quantum yield, I is the area under the peaks in the fluorescence spectra, A is the absorbance at the excitation wavelength, and n is the refractive index (dichloromethane = 1.425,[18] ethanol = 1.357).[19] Rhodamine B (Φ_f = 0.70 in ethanol)[20] was chosen as the standard. Quantum yield measurements were determined in dilute solutions ($\lambda_{abs}^{max} \leq 0.1$) to avoid inner filter effects and are the composites of ten scans in all cases.

The absorbance spectra used for determining singlet oxygen quantum yield (Φ_Δ) and photostability were obtained using a Shimadzu UV-1800 UV Spectrophotometer, with a 1.0 cm path length, and an 800 µL quartz cuvette from Starna Scientific Ltd. For both experiments, measurements were conducted in MeOH containing 1% DMSO and the absorbances of compounds **4a-4f** were matched within 10% of 0.09 AU at 530 nm, while compounds **4g-4i** were matched within 10% of 0.09 AU at 490 nm. Two LEDs, a 490nm (M490L4) and a 530 nm (M530L3), were used for irradiation and were purchased from Thorlabs. The power of each LED was determined to be 17 mW/cm^2 and 2.15 mW/cm^2 for the 490 nm LED and 530 nm LED respectively by using a Newport

Optical Power Meter Model 1916-R at a 1 cm distance from the LED. 1,3-Diphenylisobenzofuran (DPBF) was chosen as the $^1O_2$ sensor and 110 μM was spiked into the samples and Eosin Y (EY, $\Phi_\Delta = 0.42$)[21] was chosen as the standard. Irradiation times varied depending on the compounds to generate a linear correlation between the degradation of DPBF and irradiation. The calculated Φ_Δ were obtained using the following equation:[22]

$$\Phi_{\Delta\text{unk}} = \Phi_{\Delta\text{std}} \left(\frac{1 - 10^{-A_{std}}}{1 - 10^{-A_{unk}}} \right) \left(\frac{m_{unk}}{m_{std}} \right)$$

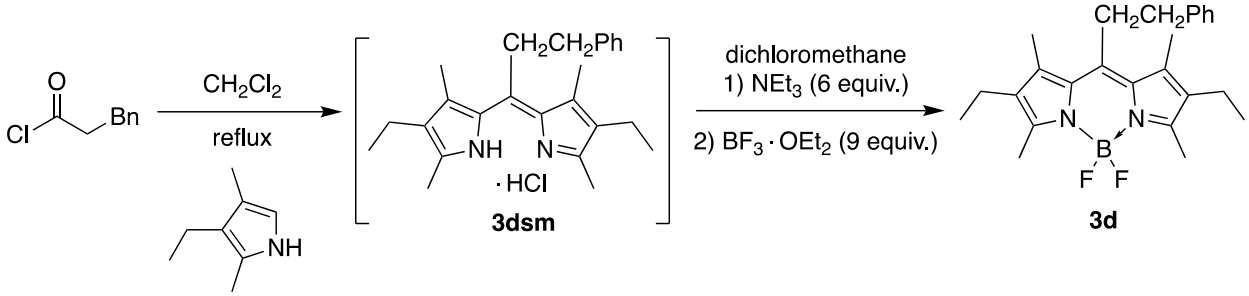
Where: unk = unknown, std = standard, A = absorbance, m = slope of DPBF degradation

The equation does not consider differences in refractive indexes or irradiation powers as the experiments were all conducted in the same composition of solutions with the same LED. Finally, the photostabilities of the compounds were measured by monitoring the λ_{abs}^{max} over the irradiation period. All measurements were conducted in triplicate.

HeLa cells were used for fluorescent imaging and cell viability assays. HeLa cells were maintained in a 75 cm^2 culture flask (Nunc™ 75 cm^2 Nunclon™ Delta Surface) at 37 °C and 5% CO_2 atmosphere in a Thermo Scientific Forma Steri-Cycle CO_2 Incubator. The cells were grown in Dulbecco's Modified Eagle Medium (DMEM) with sodium pyruvate, 4.5 g/L glucose and L-glutamine (Winsent Inc.) supplemented with 10% fetal bovine serum and 1% antibiotics/antimycotics (complete growth medium). Unless otherwise stated, all incubations were conducted in the incubator using DMEM. The 525 nm lamp, Philips LED 90 W equivalent PAR38 Green Lamp (Model #473736) was used, and the power was determined to be 15.60 mW/cm^2 using the Newport Optical Power Meter Model 1916-R at a 1 cm distance.

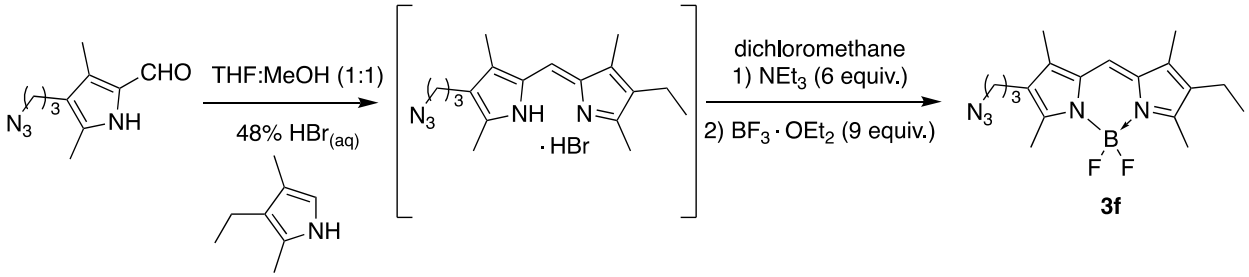
Procedures

Synthesis of 3d



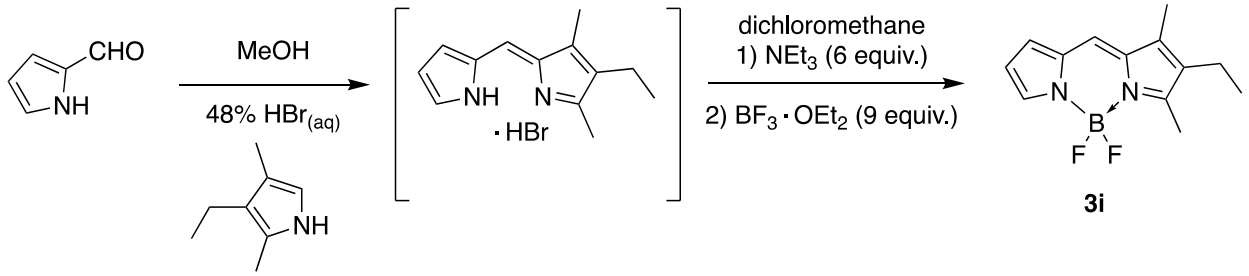
Following a literature procedure for a similar substrate,[7] the requisite HCl dipyrrin salt **3dsm** was synthesised by first dissolving 2,4-dimethyl-3-ethylpyrrole[3] (1.00 g, 8.12 mmol) in dry dichloromethane (8 mL) in a two-necked round-bottom flask equipped with a water condensor and a septum under a nitrogen atmosphere. 3-Phenylpropionyl chloride (1.81 mL, 12.2 mmol) was then added and the resulting mixture was heated at reflux temperature for one hour. The reaction mixture was then allowed to cool before dilution with water (30 mL), and the organic fraction was separated and then dried over sodium sulfate and concentrated under reduced pressure. The resulting solid hydrochloride dipyrrin salt was then triturated with ether and then used without further purification. Next, the dipyrrin salt **3dsm** was dissolved in dichloromethane (30 mL). Following a literature procedure,[23] triethylamine (3.4 mL, 24.4 mmol) was then added to the reaction mixture, *via* syringe, followed by boron trifluoride diethyl etherate (4.5 mL, 36.5 mmol). After stirring the reaction mixture for 1.5 h, second aliquots of triethylamine (3.4 mL, 24.4 mmol) and trifluoride diethyl etherate (4.5 mL, 36.5 mmol) were added, followed by stirring for a further 1.5 h. The crude reaction mixture was filtered through a silica gel plug, eluting with dichloromethane, and the resulting solution was evaporated under reduced pressure. The residue was taken up in ether (50 mL) and washed with 1 M HCl (5x 50 mL), and then 6 M HCl (1x 50 mL). The organic layer was dried over sodium sulfate and concentrated under reduced pressure. The resulting crude solid was purified *via* column chromatography over silica with dry loading and then eluting with 0 ⇒ 5% ethyl acetate in hexanes to afford the desired compound as a dark red crystalline material (0.24 g, 15% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.39 (m, 5H), 3.30-3.41 (m, 2H), 2.91-3.01 (m, 2H), 2.52 (s, 6H), 2.38-2.46 (m, 10H), 1.06 (t, J = 7.6 Hz, 6H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.66 (t, J = 31 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -146.2-(-145.7) (m); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 152.6, 143.6, 140.5, 135.8, 132.9, 131.1, 128.9, 128.0, 126.7, 37.4, 29.6, 17.3, 15.0, 13.8, 12.6; HRMS-ESI$^+$ *m/z* [M^+ + Na] calc. for $C_{25}H_{31}BF_2N_2Na$ = 431.2441, found 431.2459.

Synthesis of 3f



4-(3-Azidopropyl)-3,5-dimethyl-1H-pyrrole-2-carboxaldehyde[2] (800 mg, 3.88 mmol) and 2,4-dimethyl-3-ethylpyrrole[3] (478 mg, 3.88 mmol) were dissolved in tetrahydrofuran (5 mL) and methanol (5 mL). The resulting solution was stirred for 10 minutes. Aqueous hydrobromic acid (48%, 0.68 mL, 7.77 mmol) was added and the reaction mixture was stirred for an additional 16 h. After concentration to half volume under reduced pressure, the mixture was diluted with a diethyl ether:hexanes (1:1, 10 mL) solution. The resulting orange precipitate was isolated *via* filtration and then washed with diethyl ether:hexanes (1:1, 10 mL). The hydrogen bromide dipyrrin salt was allowed to dry in air and then used without further purification. Next, the dipyrrin salt (1.08 g, 2.75 mmol) was dissolved in dichloromethane (30 mL). Following a literature procedure,[23] triethylamine (2.3 mL, 16.5 mmol) was then added to the reaction mixture, *via* syringe, followed by boron trifluoride diethyl etherate (3.0 mL, 24.8 mmol). After stirring for 1.5 h, second aliquots of triethylamine (2.3 mL, 16.5 mmol) and trifluoride diethyl etherate (3.0 mL, 24.8 mmol) were added, followed by stirring for a further 1.5 h. The crude reaction mixture was filtered through a silica gel plug, eluting with dichloromethane, and the resulting solution was evaporated under reduced pressure. The residue was taken up in ether (50 mL) and washed with 1 M HCl (5x 50 mL), and then 6 M HCl (1x 50 mL). The organic layer was dried over sodium sulfate and concentrated under reduced pressure. The resulting crude solid was purified *via* column chromatography over silica, loading as a solution and then eluting with 0 ⇒ 70% dichloromethane in hexanes to afford the desired compound as a dark purple crystalline material (0.80 g, 58% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (s, 1H), 3.29 (t, *J* = 6.6 Hz, 2H), 2.43-2.54 (m, 8H), 2.39 (q, *J* = 7.6 Hz, 2H), 2.14-2.20 (m, 6H), 1.73 (p, *J* = 6.6 Hz, 2H), 1.07 (t, *J* = 7.6 Hz, 3H); ^{11}B NMR (160 MHz, $CDCl_3$) δ 0.88 (t, *J* = 32 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -146.3 (q, *J* = 32 Hz); ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 156.1, 154.0, 137.4, 137.0, 133.0, 132.3, 128.1, 118.9, 50.8, 29.2, 21.2, 17.4, 14.6, 12.8, 12.7, 9.7, 9.5 (one signal missing); HRMS-ESI$^+$ *m/z* [M^+ + Na] calc. for $C_{18}H_{24}BF_2N_5Na$ = 382.1985, found 382.1987.

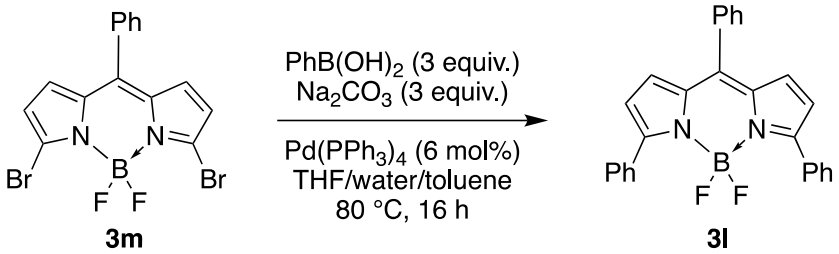
Synthesis of 3i



The title compound **3i** was synthesised by first condensing formyl pyrrole (0.77 g, 8.10 mmol) and 2,4-dimethyl-3-ethylpyrrole[3] (1.00 g, 8.10 mmol) were dissolved in (20 mL), the resulting solution was stirred for 10 minutes. Concentrated aqueous hydrobromic acid (2 mL, excess) was added and reaction mixture was stirred for an additional 2 h. The stirring was stopped and the reaction mixture was left to crystalise overnight. The resulting orange precipitate was isolated *via* filtration and was washed with methanol (4 mL) and then diethyl ether (20 mL). The hydrogen bromide dipyrrin salt was allowed to dry in air and then used without further purification. Next, the dipyrrin salt (1.46 g, 5.19 mmol) was dissolved in dichloromethane (30 mL). Following a literature procedure,[23] triethylamine (4.3 mL, 31.1 mmol) was then added to the reaction mixture, *via* syringe, followed by boron trifluoride diethyl etherate (5.8 mL, 46.7 mmol). After stirring the reaction mixture for 1.5 h, second aliquots of triethylamine (4.3 mL, 31.1 mmol) and trifluoride diethyl etherate (5.8 mL, 46.7 mmol) were added, followed by stirring for a further 1.5 h. The crude reaction mixture was filtered through a silica gel plug, eluting with dichloromethane, and the resulting solution was

evaporated under reduced pressure. The residue was taken up in ether (50 mL) and washed with 1 M HCl (5x 50 mL), and 6 M HCl (1x 50 mL). The organic layer was dried over sodium sulfate and concentrated under reduced pressure to afford the desired compound as a dark purple crystalline material (0.87 g, 43% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.12 (s, 1H), 6.86 (s, 1H), 6.39 (s, 1H), 2.57 (s, 3H), 2.41 (q, *J* = 7.7 Hz, 2H), 2.19 (s, 3H), 1.08 (t, *J* = 7.7 Hz, 3H). This data is in accordance with reported data.[24]

Synthesis of 3l



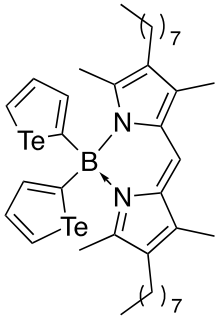
3m **3l**

The title compound was synthesised by first dissolving **3m**[12] (700 mg, 1.64 mmol) in tetrahydrofuran/water/toluene (1:1:1, 50 mL) in a two-necked round-bottomed flask equipped with a water condenser and a stopper. Then, phenylboronic acid (600 mg, 5.01 mmol), sodium carbonate (531 mg, 5.01 mmol) and tetrakis(triphenylphosphine)palladium(0) (113 mg, 0.098 mmol) were added as solids. The reaction mixture was heated to 80 °C for 16 hours. The completion of the reaction was confirmed by analysis using TLC. The resulting mixture was allowed to cool before being extracted with dichloromethane (2x 75 mL). The combined organic fractions were then washed with brine (150 mL) and then dried over sodium sulfate. After concentrating under reduced pressure, the resulting crude solid was purified *via* column chromatography over silica with dry loading and then eluting with 0 ⇒ 30% dichloromethane in hexanes to afford the desired compound as an orange solid (0.38 g, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85-7.90 (m, 4H), 7.51-7.63 (m, 5H), 7.38-7.46 (m, 6H), 6.90 (d, *J* = 4.4 Hz, 2H), 6.63 (d, *J* = 4.4 Hz, 2H). This data is in accordance with reported data.[25]

General procedure for the synthesis of *[Te]*-BODIPYs (GP)

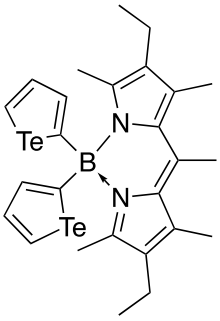
Inside a nitrogen-filled glovebox, a solution of tellurophene[1] (2.2 equiv.) and dry tetrahydrofuran (2 mL) was stirred in a 4-dram vial at room temperature until complete dissolution was achieved (5 min). *n*-Butyllithium (2.0 M in hexanes, 2.4 equiv.) was added dropwise *via* syringe. The vial was then capped and the reaction mixture was stirred for 5 min. In a separate 4-dram vial the corresponding BODIPY (1 equiv.) was stirred in dry tetrahydrofuran (2 mL) until complete dissolution was achieved (5 min). The cap on the reaction vial was removed and the BODIPY solution was then added dropwise *via* syringe to the solution containing the lithiated heterocycle. The capped reaction mixture was stirred for 1 h, and was then removed from the glovebox. The crude reaction mixture dissolved in dichloromethane (20 mL), and the resulting solution was washed with saturated ammonium chloride (1x 20 mL), water (1x 20 mL) and brine (1x 20 mL). The organic layer was dried over sodium sulfate and concentrated under reduced pressure. The resulting crude solid was purified *via* column chromatography over silica with wet-loading and then elution with a gradient solution of dichloromethane/hexanes, ethyl acetate/hexanes or dichloromethane/ethyl acetate. The fractions containing the desired compounds were concentrated under reduced pressure to afford the desired *[Te]*-BODIPYs.

Synthesis of 4a



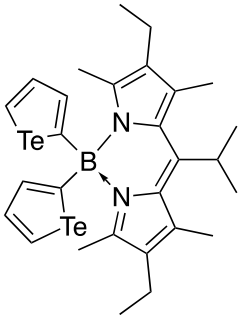
Following **GP**, a solution of tellurophene (84 mg, 0.47 mmol) in tetrahydrofuran was lithiated using *n*-butyllithium (0.51 mmol) and then added to a solution of **3a**[5] (100 mg, 0.21 mmol) in tetrahydrofuran. After workup and column chromatography (0 ⇒ 15% dichloromethane/hexanes), the desired product was afforded as a scarlet red solid (45 mg, 27% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 6.5, 0.5 Hz, 2H), 8.08 (dd, *J* = 3.5, 0.5 Hz, 2H), 7.81 (dd, *J* = 6.5, 3.5 Hz, 2H), 7.10 (s, 1H), 2.28 (t, *J* = 7.6, 4H), 2.21 (s, 6H), 2.10 (s, 6H), 1.15-1.31 (m, 24H), 0.87 (t, *J* = 6.9, 6H); ^{11}B NMR (160 MHz, $CDCl_3$) δ 0.53 (bs); ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 155.1, 140.2, 139.2, 134.9, 131.3, 131.0, 125.6, 118.9, 32.0, 30.3, 29.6, 29.5, 29.4, 24.4, 22.8, 15.1, 14.2, 9.7 (one signal missing); HRMS-ESI$^+$ *m/z* [M^+ + Na] calc. for $C_{37}H_{53}BN_2{}^{130}Te_2Na$ = 819.2318, found 819.2335; $\lambda_{abs}{}^{max}$ = 528 nm (498 nm shoulder); ε = 70000; $\lambda_{em}{}^{max}$ = 559 nm; Φ_f = 0.02; Stokes shift = 31 nm; Φ_Δ = 0.48 ± 0.05.

Synthesis of 4b



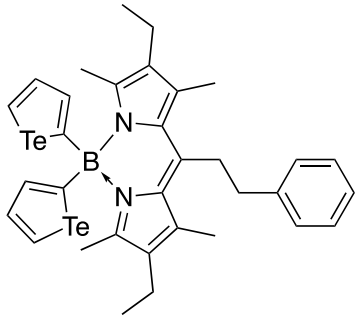
Following **GP**, a solution of tellurophene (124 mg, 0.69 mmol) in tetrahydrofuran was lithiated using *n*-butyllithium (0.75 mmol) and then added to a solution of **3b**[6] (100 mg, 0.31 mmol) in tetrahydrofuran. After workup and column chromatography (0 ⇒ 30% dichloromethane/hexanes), the desired product was afforded as a scarlet red solid (98 mg, 49% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 6.6, 0.9 Hz, 2H), 8.08 (dd, *J* = 3.8, 0.9 Hz, 2H), 7.80 (dd, *J* = 6.6, 3.8 Hz, 2H), 2.70 (s, 3H), 2.39 (s, 6H), 2.31 (q, *J* = 7.5 Hz, 4H), 2.10 (s, 6H), 0.96 (t, *J* = 7.5 Hz, 6H); ^{11}B NMR (160 MHz, $CDCl_3$) δ -0.10 (bs); ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 152.2, 140.1, 139.6, 139.1, 134.3, 133.3, 131.1, 125.4, 17.9, 17.5, 15.1, 15.0, 14.9 (one signal missing); HRMS-ESI$^+$ *m/z* [M^+ + Na] calc. for $C_{26}H_{31}BN_2{}^{130}Te_2Na$ = 665.0597, found 665.0613; $\lambda_{abs}{}^{max}$ = 518 nm (488 nm shoulder); ε = 75600; $\lambda_{em}{}^{max}$ = 554 nm; Φ_f = 0.03; Stokes shift = 36 nm; Φ_Δ = 0.54 ± 0.03.

Synthesis of 4c



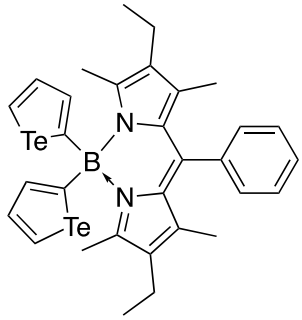
Following **GP**, a solution of tellurophene (81 mg, 0.45 mmol) in tetrahydrofuran was lithiated using *n*-butyllithium (0.49 mmol) and then added to a solution of **3c**[7] (71 mg, 0.20 mmol) in tetrahydrofuran. After workup and column chromatography (0 ⇒ 30% dichloromethane/hexanes), the desired product was afforded as a scarlet red solid (42 mg, 27% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 6.6, 0.8 Hz, 2H), 8.15 (dd, *J* = 3.8, 0.8 Hz, 2H), 7.80 (dd, *J* = 6.6, 3.8 Hz, 2H), 4.04 (sept, *J* = 7.5 Hz, 1H), 2.44 (s, 6H), 2.31 (q, *J* = 7.6 Hz, 4H), 2.08 (s, 6H), 1.58 (d, *J* = 7.5 Hz, 6H), 0.96 (t, *J* = 7.6 Hz, 6H); ^{11}B NMR (160 MHz, $CDCl_3$) δ -0.56 (bs); ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 152.6, 151.8, 140.3, 140.0, 139.1, 134.2, 133.1, 131.4, 125.2, 28.2, 22.1, 17.8, 15.4, 15.3, 14.7; HRMS-ESI$^+$ *m/z* [M^+ + H] calc. for $C_{28}H_{36}BN_2{}^{130}Te_2$ = 671.1091, found 671.1097; $\lambda_{abs}{}^{max}$ = 530 nm (496 nm shoulder); ε = 56000, trace emission; Φ_Δ = 0.17 ± 0.01.

Synthesis of 4d



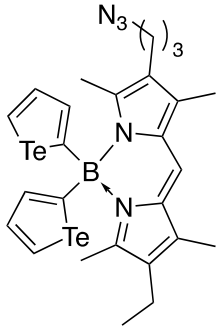
Following **GP**, a solution of tellurophene (97 mg, 0.54 mmol) in tetrahydrofuran was lithiated using *n*-butyllithium (0.59 mmol) and then added to a solution of **3d** (100 mg, 0.24 mmol) in tetrahydrofuran. After workup and column chromatography (0 ⇒ 30% dichloromethane/hexanes), the desired product was afforded as a scarlet red solid (62 mg, 34% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (bs, 2H), 8.21 (app d, 2H), 7.84 (bs, 2H), 7.31-7.41 (m, 4H), 7.26-7.31 (m, 1H), 3.47-3.57 (m, 2H), 3.01-3.12 (m, 2H), 2.48 (s, 6H), 2.34 (q, *J* = 7.7 Hz, 4H), 2.14 (s, 6H), 0.98 (t, *J* = 7.7 Hz, 6H); ^{11}B NMR (160 MHz, $CDCl_3$) δ -0.13 (bs); ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 152.9, 143.5, 140.8, 139.3, 139.0, 133.8, 133.5, 130.0, 128.8, 128.2, 126.6, 125.6, 125.1, 37.9, 29.7, 17.5, 15.1, 15.0, 14.3; HRMS-ESI$^+$ *m/z* [M^+ + H] calc. for $C_{33}H_{38}BN_2{}^{130}Te_2$ = 733.1247, found 733.1259; $\lambda_{abs}{}^{max}$ = 522 nm (498 nm shoulder); ε = 75900; $\lambda_{em}{}^{max}$ = 546 nm; Φ_f = 0.03; Stokes shift = 24 nm; Φ_Δ = 0.85 ± 0.11.

Synthesis of 4e



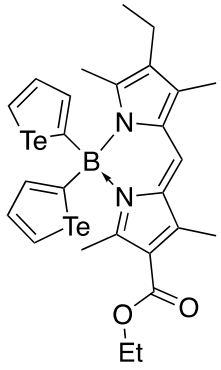
Following **GP**, a solution of tellurophene (104 mg, 0.58 mmol) in tetrahydrofuran was lithiated using *n*-butyllithium (0.63 mmol) and then added to a solution of **3e**[8] (100 mg, 0.26 mmol) in tetrahydrofuran. After workup and column chromatography (0 ⇒ 30% dichloromethane/ethyl acetate), the desired product was afforded as a scarlet red solid (42 mg, 23% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 6.6, 0.8 Hz, 2H), 8.24 (dd, *J* = 3.7, 0.8 Hz, 2H), 7.85 (dd, *J* = 6.6, 3.7 Hz, 2H), 7.45-7.54 (m, 3H), 7.36-7.42 (m, 2H), 2.21 (q, *J* = 7.4 Hz, 4H), 2.13 (s, 6H), 1.32 (s, 6H), 0.89 (t, *J* = 7.4 Hz, 6H); ^{11}B NMR (160 MHz, $CDCl_3$) δ 0.05 (bs); ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 154.2, 140.2, 139.3, 138.0, 136.9, 136.4, 133.8, 129.8, 129.0, 128.9, 128.7, 126.4, 125.5, 17.5, 15.1, 14.9, 12.1; HRMS-ESI$^+$ *m/z* [M^+ + H] calc. for $C_{31}H_{34}BN_2{}^{130}Te_2$ = 705.0934, found 705.0950; $\lambda_{abs}{}^{max}$ = 524 nm (492 nm shoulder); ε = 50100; $\lambda_{em}{}^{max}$ = 541 nm; Φ_f = 0.005; Stokes shift = 17 nm; Φ_Δ = 0.82 ± 0.09.

Synthesis of 4f



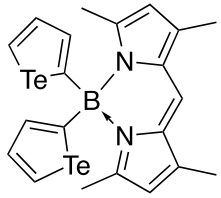
Following **GP**, a solution of tellurophene (110 mg, 0.61 mmol) in tetrahydrofuran was lithiated using *n*-butyllithium (0.69 mmol) and then added to a solution of **3f** (100 mg, 0.28 mmol) in tetrahydrofuran. After workup and column chromatography (0 ⇒ 45% dichloromethane/hexanes), the desired product was afforded as a scarlet red solid (86 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 6.6 Hz, 2H), 8.11 (d, *J* = 3.7 Hz, 2H), 7.82 (dd, *J* = 6.6, 3.7 Hz, 2H), 7.12 (s, 1H), 3.24 (t, *J* = 6.7 Hz, 2H), 2.40 (t, *J* = 7.5 Hz, 2H), 2.31 (q, *J* = 7.5 Hz, 2H), 2.18-2.26 (m, 6H), 2.05-2.17 (m, 6H), 1.66 (dt, *J* = 7.5, 6.7 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{11}B NMR (160 MHz, $CDCl_3$) δ 0.79 (bs); ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 156.2, 154.1, 140.4, 139.3, 135.3, 134.9, 134.0, 133.0, 131.7, 131.0, 128.6, 125.8, 119.2, 50.8, 29.3, 21.3, 17.7, 15.0, 14.9, 14.8, 9.8, 9.6; HRMS-ESI$^+$ *m/z* [M^+ + Na] calc. for $C_{26}H_{30}BN_5{}^{130}Te_2Na$ = 706.0611, found 706.0640; $\lambda_{abs}{}^{max}$ = 526 nm (496 nm shoulder); ε = 60200; $\lambda_{em}{}^{max}$ = 543 nm; Φ_f = 0.01; Stokes shift = 17 nm; Φ_Δ = 0.45 ± 0.02.

Synthesis of 4g



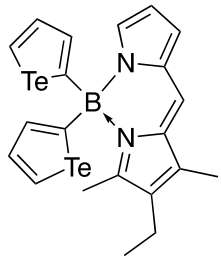
Following **GP**, a solution of tellurophene (170 mg, 0.95 mmol) in tetrahydrofuran was lithiated using *n*-butyllithium (1.03 mmol) and then added to a solution of **3g**[9] (150 mg, 0.43 mmol) in tetrahydrofuran. After workup and column chromatography (0 ⇒ 75% dichloromethane/hexanes), the desired product was afforded as a scarlet red solid (54 mg, 19% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (dd, *J* = 6.6, 0.9 Hz, 2H), 8.13 (dd, *J* = 3.8, 0.9 Hz, 2H), 7.82 (dd, *J* = 6.6, 3.8 Hz, 2H), 7.30 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.52 (s, 3H), 2.44 (s, 3H), 2.32 (q, *J* = 7.6 Hz, 2H), 2.26 (s, 3H), 2.17 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.6 Hz, 3H); ^{11}B NMR (160 MHz, $CDCl_3$) δ 0.97 (bs); ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 165.2, 161.5, 156.5, 140.6, 139.3, 137.8, 135.4, 133.9, 129.6, 126.2, 120.5, 119.0, 59.8, 17.6, 16.9, 15.4, 14.5, 14.4, 12.0, 9.6 (two signals missing); HRMS-ESI$^+$ *m/z* [M^+ + Na] calc. for $C_{26}H_{29}BN_2O_2{}^{130}Te_2Na$ = 695.0339, found 695.0357; $\lambda_{abs}{}^{max}$ = 508 nm (482 nm shoulder); ε = 70600; trace emission; Φ_Δ = 0.55 ± 0.07.

Synthesis of 4h



Following **GP**, a solution of tellurophene (159 mg, 0.89 mmol) in tetrahydrofuran was lithiated using *n*-butyllithium (0.97 mmol) and then added to a solution of **3h**[10] (100 mg, 0.40 mmol) in tetrahydrofuran. After workup and column chromatography (0 ⇒ 20% ethyl acetate/hexanes), the desired product was afforded as a scarlet red solid (22 mg, 10% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (d, *J* = 6.5 Hz, 2H), 8.09 (d, *J* = 3.5 Hz, 2H), 7.82 (dd, *J* = 6.5, 3.5 Hz, 2H), 7.19 (s, 1H), 6.00 (s, 2H), 2.30 (s, 6H), 2.15 (s, 6H); ^{11}B NMR (160 MHz, $CDCl_3$) δ 0.73 (bs); ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 156.7, 140.3, 139.1, 139.0, 132.1, 125.7, 120.5, 120.1, 17.1, 11.3 (one signal missing); HRMS-ESI$^+$ *m/z* [M^+ + Na] calc. for $C_{21}H_{21}BN_2{}^{130}Te_2Na$ = 594.9820, found 594.9815; $\lambda_{abs}{}^{max}$ = 506 nm (480 nm shoulder); ε = 72000; $\lambda_{em}{}^{max}$ = 524 nm; Φ_f = 0.006; Stokes shift = 18 nm; Φ_Δ = 0.57 ± 0.08.

Synthesis of 4i



Following **GP**, a solution of tellurophene (159 mg, 0.89 mmol) in tetrahydrofuran was lithiated using *n*-butyllithium (0.97 mmol) and then added to a solution of **3i** (100 mg, 0.40 mmol) in tetrahydrofuran. After workup and column chromatography (0 ⇒ 20% dichloromethane/hexanes), the desired product was afforded as a scarlet red solid (40 mg, 17% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 6.5, 1.0 Hz, 2H), 7.80 (dd, *J* = 6.5, 3.8 Hz, 2H), 7.72 (dd, *J* = 3.8, 1.0 Hz, 2H), 7.33 (bs, 1H), 7.27 (s, 1H), 6.92 (dd, *J* = 3.9, 1.2 Hz, 1H), 6.38 (dd, *J* = 3.9, 2.0 Hz, 1H), 2.41 (q, *J* = 7.7 Hz, 2H), 2.26 (s, 3H), 2.23 (s, 3H), 1.07 (t, *J* = 7.7 Hz, 3H); ^{11}B NMR (160 MHz, $CDCl_3$) δ 0.82 (bs); ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 161.9, 140.0, 139.9, 139.6, 139.5, 139.0, 135.8, 135.1, 131.4, 126.5, 124.3, 123.9, 115.7, 17.7, 15.8, 14.5, 9.7; HRMS-ESI$^+$ *m/z* [M^+ + Na] calc. for $C_{21}H_{21}BN_2{}^{130}Te_2Na$ = 594.9814, found 594.9816; $\lambda_{abs}{}^{max}$ = 506 nm (476 nm shoulder); ε = 38700; trace emission; Φ_Δ = 0.47 ± 0.04.

Photophysical Spectra

Table S1. Photophysical characteristics of *[Te]*-BODIPYs in CH_2Cl_2 and PBS

	λ_{max}abs (CH_2Cl_2, nm)	Φ_f (CH_2Cl_2)	ε (CH_2Cl_2, $M^{-1}cm^{-1}$)	λ_{max} (PBS, nm)
2	528	0.01	65700	543
4a	528	0.02	70000	538
4b	518	0.03	75600	526
4c	530	N/A	56000	541
4d	522	0.03	75900	533
4e	524	0.005	50100	532
4f	526	0.01	60200	530
4g	508	N/A	70600	515
4h	506	0.006	72000	524
4i	506	N/A	38700	518

Figure S1. Normalised absorption and emission spectra of compound **4a** in CH_2Cl_2

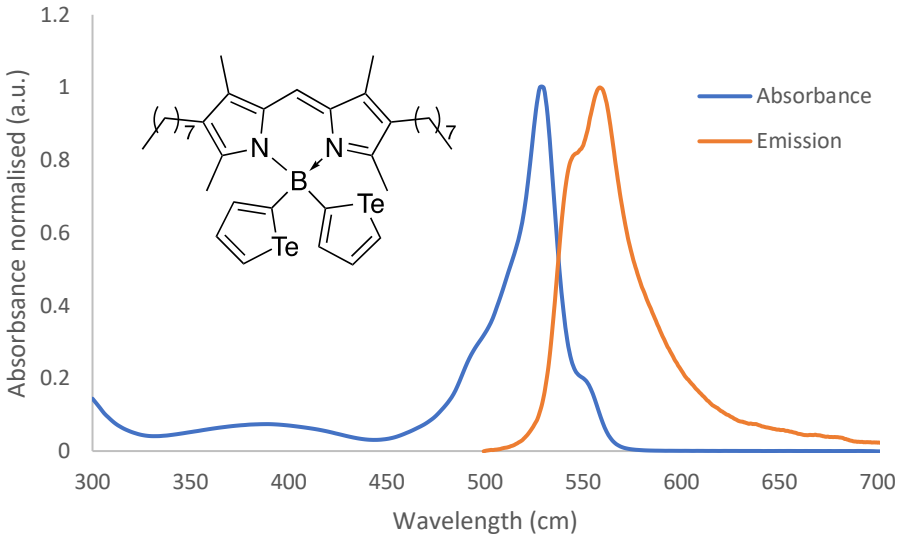


Figure S2. Normalised absorption and emission spectra of compound **4b** in CH_2Cl_2

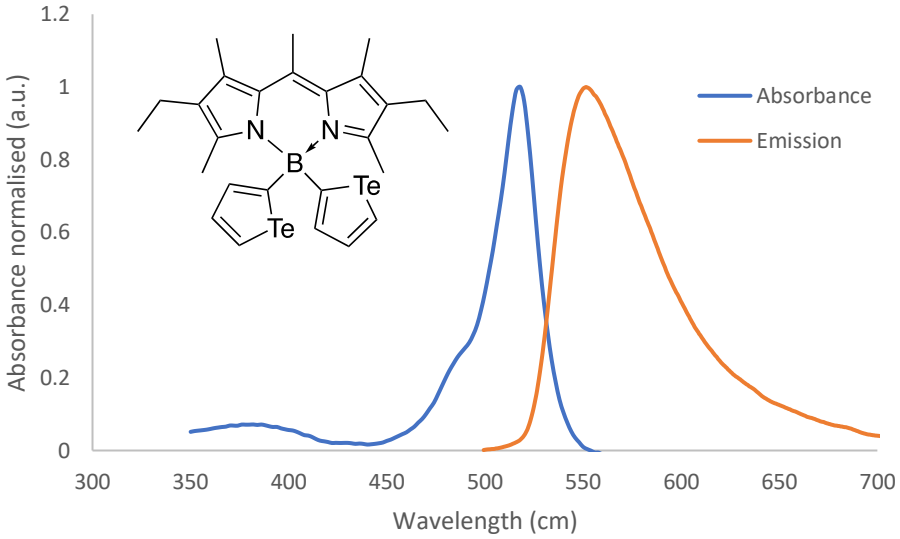


Figure S3. Normalised absorption spectrum of compound **4c** in CH_2Cl_2

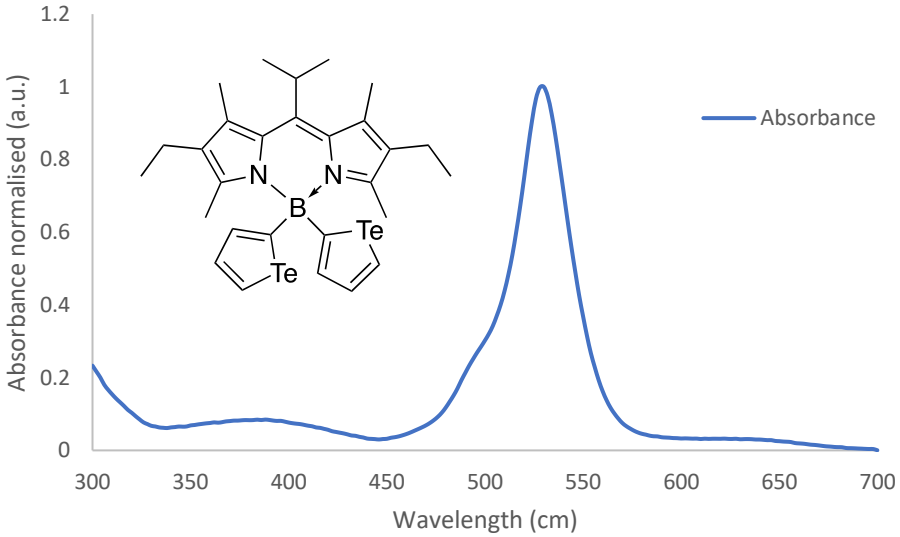


Figure S4. Normalised absorption and emission spectra of compound **4d** in CH_2Cl_2

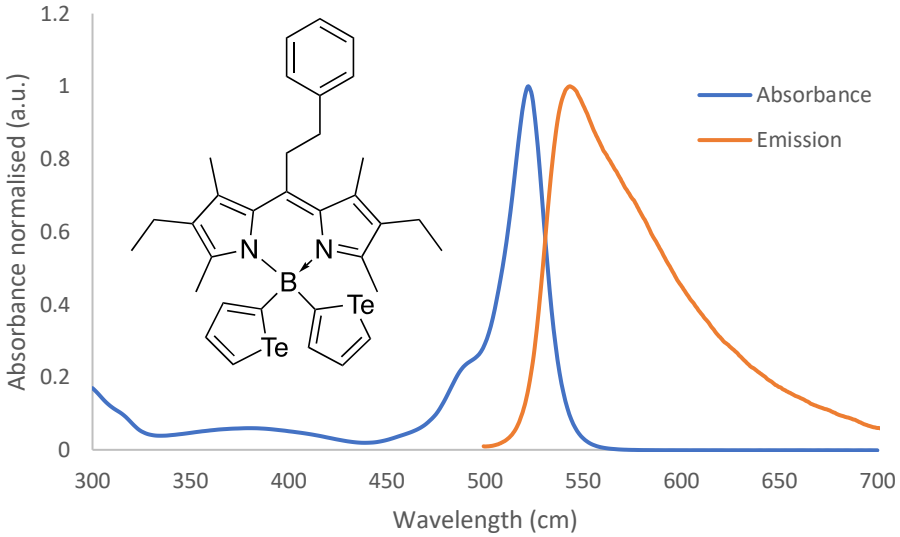


Figure S5. Normalised absorption and emission spectra of compound **4e** in CH_2Cl_2

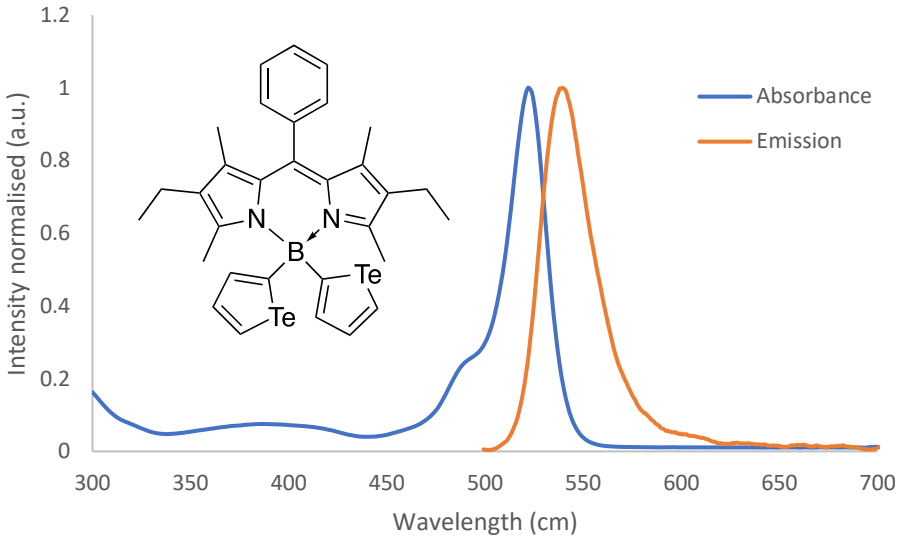


Figure S6. Normalised absorption and emission spectra of compound **4f** in CH_2Cl_2

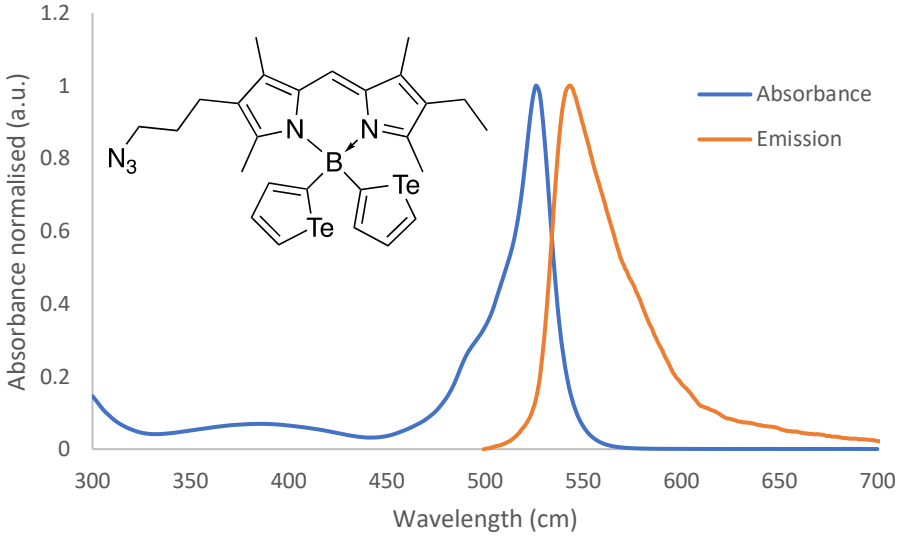


Figure S7. Normalised absorption spectrum of compound **4g** in CH_2Cl_2

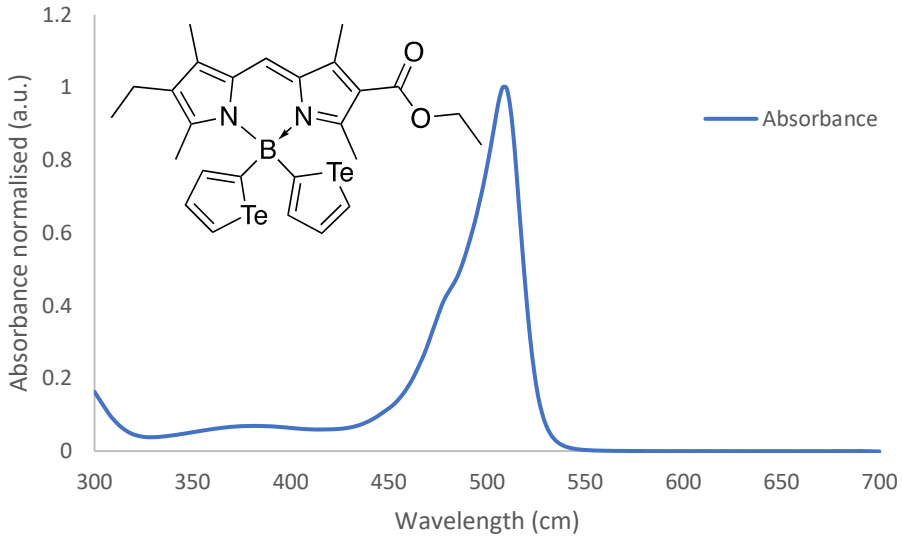


Figure S8. Normalised absorption and emission spectra of compound **4h** in CH_2Cl_2

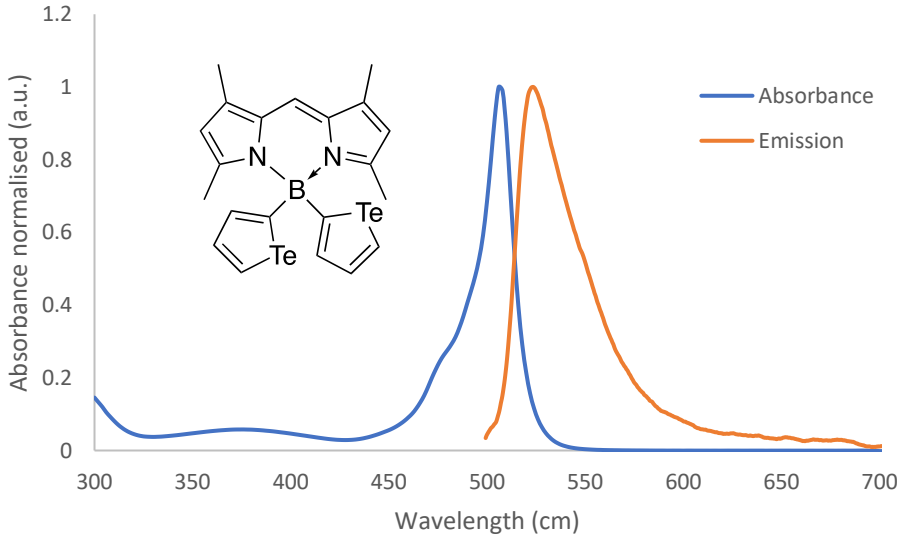


Figure S9. Normalised absorption spectrum of compound **4i** in CH_2Cl_2

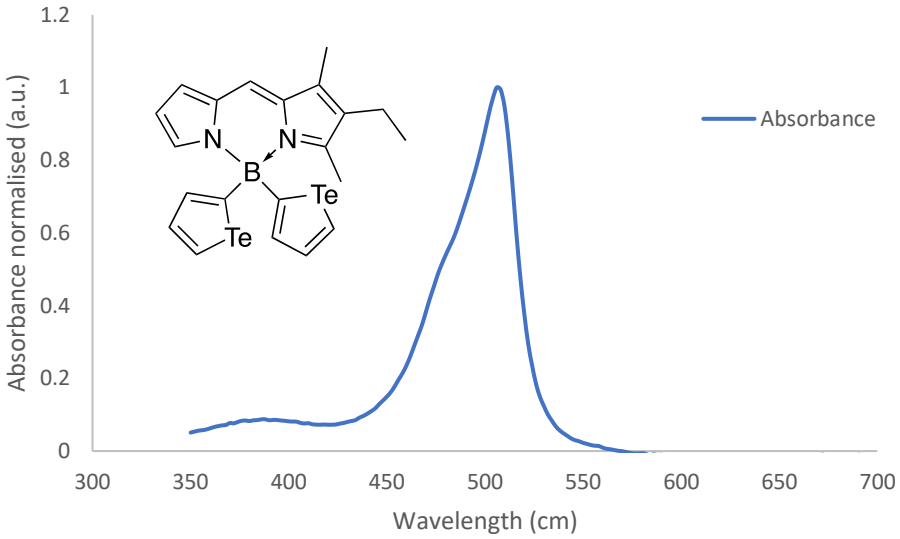


Figure S10. Normalised absorbance spectra of *[Te]*-BODIPYs in MeOH and PBS (containing 1% DMSO)

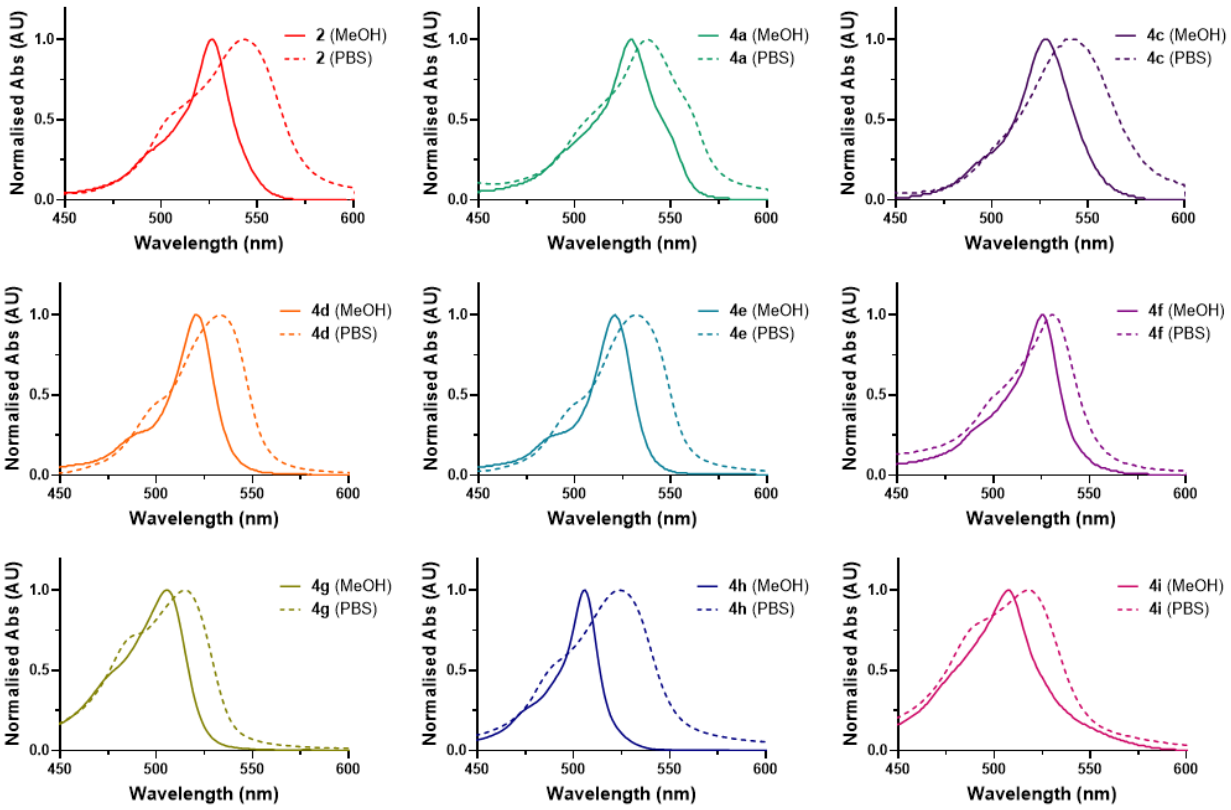


Figure S11. Singlet oxygen generation of *[Te]*-BODIPYs detected by DPBF in 1% DMSO in MeOH

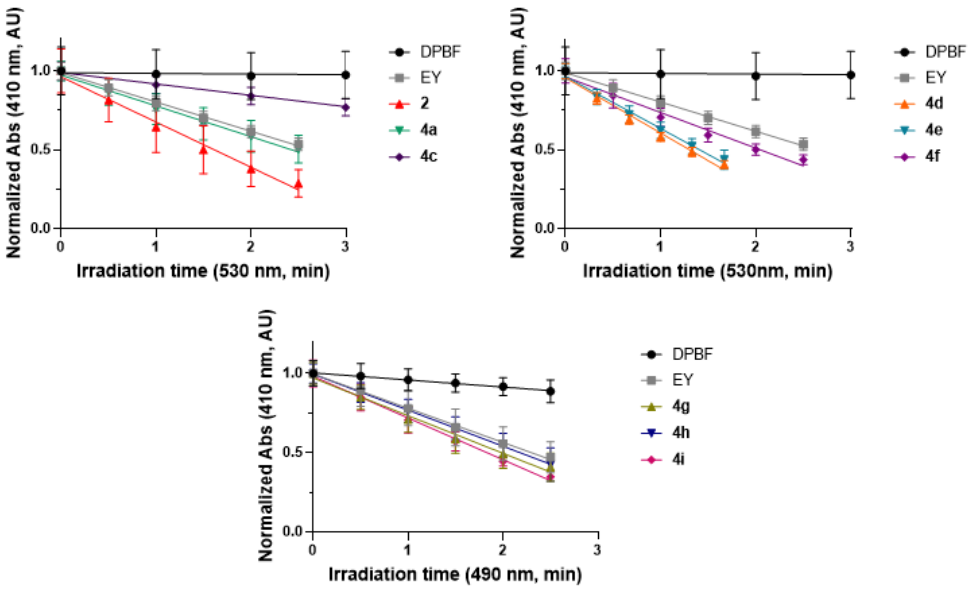
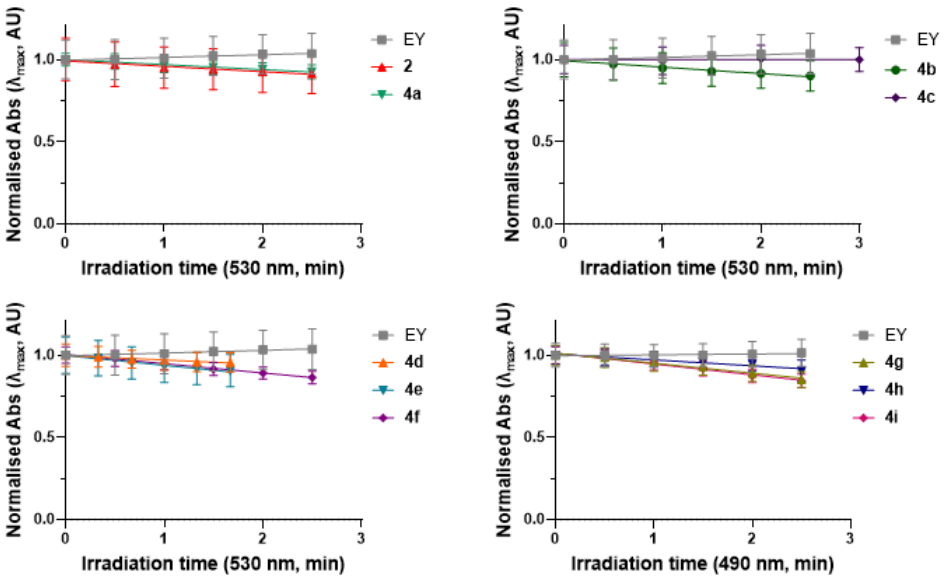


Figure S12. Photostability of *[Te]*-BODIPYs under irradiation

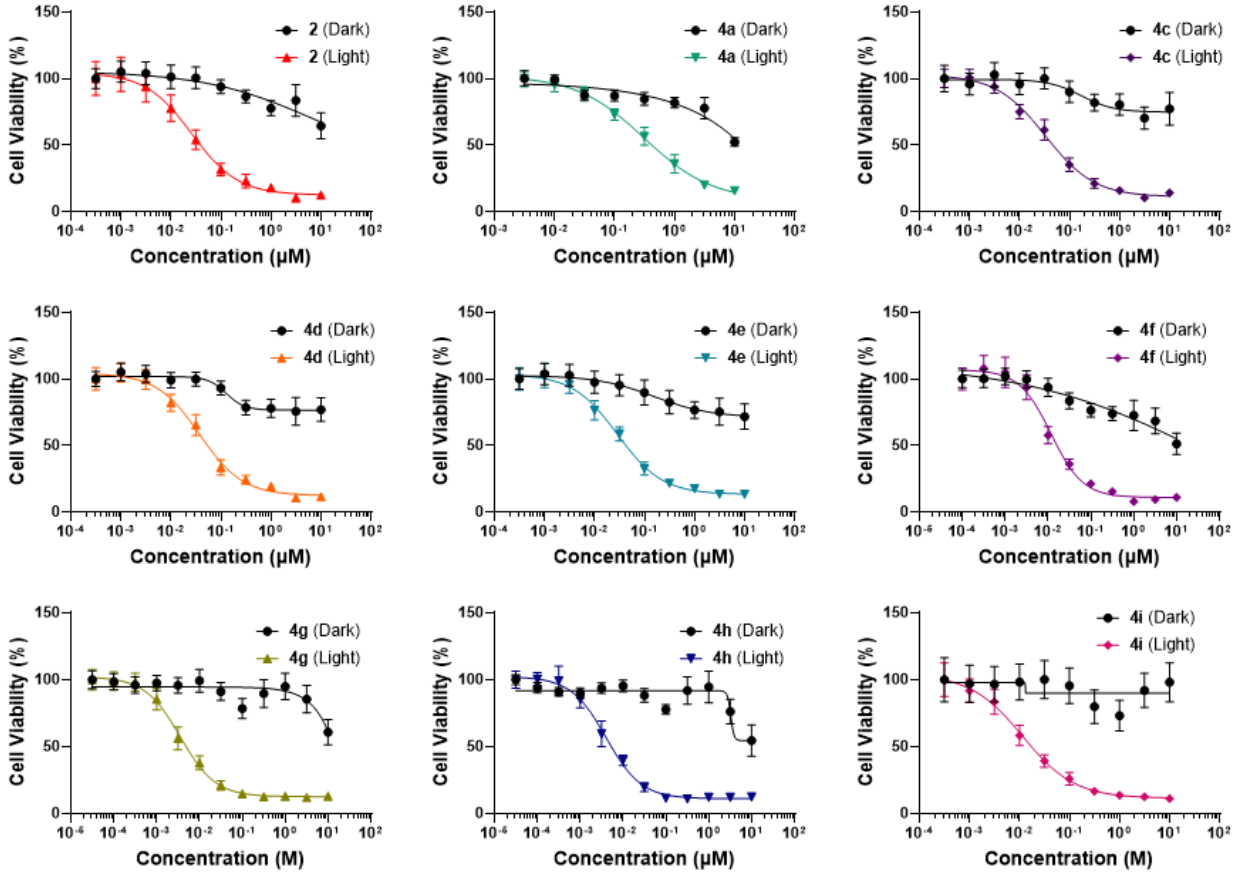


Cell Assays and Viability

HeLa cells were seeded at a density of 10,000 cells per well in 96-well plates (Thermo Scientific Nunclon™ Delta Surface) and incubated in 200 µL DMEM overnight. The cells were then washed with D-PBS and replaced with 200 µL minimal essential media (Opti-MEM). DMSO stocks of the *[Te]*-BODIPY compounds were added at a variety of concentrations to a final DMSO concentration of 1% and incubated for 3 hours. After incubation, cells were washed with D-PBS and the media was replaced with 200 µL DMEM. Plates were either kept in the dark or irradiated with a 525 nm lamp for 5 minutes (15.60 mW/cm^2 or 4.68 J/cm^2) and incubated overnight. On the

following day, 20 µL of a 5 mg/mL solution of thiazolyl blue tetrazolium bromide (MTT) in D-PBS was added to each well and incubated for 3 hours. The media was then removed and 150 µL of DMSO was added to dissolve the formazan products. Plates were read at 560 nm and 800 nm using BioTek Synergy™ HTX Multi-Mode Microplate Reader to determine the concentration of formazan products and the background respectively. Corrected absorbance values were then used to calculate the cell viability. Cell viability experiments were all conducted with n = 9.

Figure S13. Cell viability of HeLa cells incubated with varying concentrations of *[Te]*-BODIPYs in dark or light conditions



NMR Spectra

Figure S14. ^{1}H NMR (400 MHz) spectrum of compound **3d** in $CDCl_3$

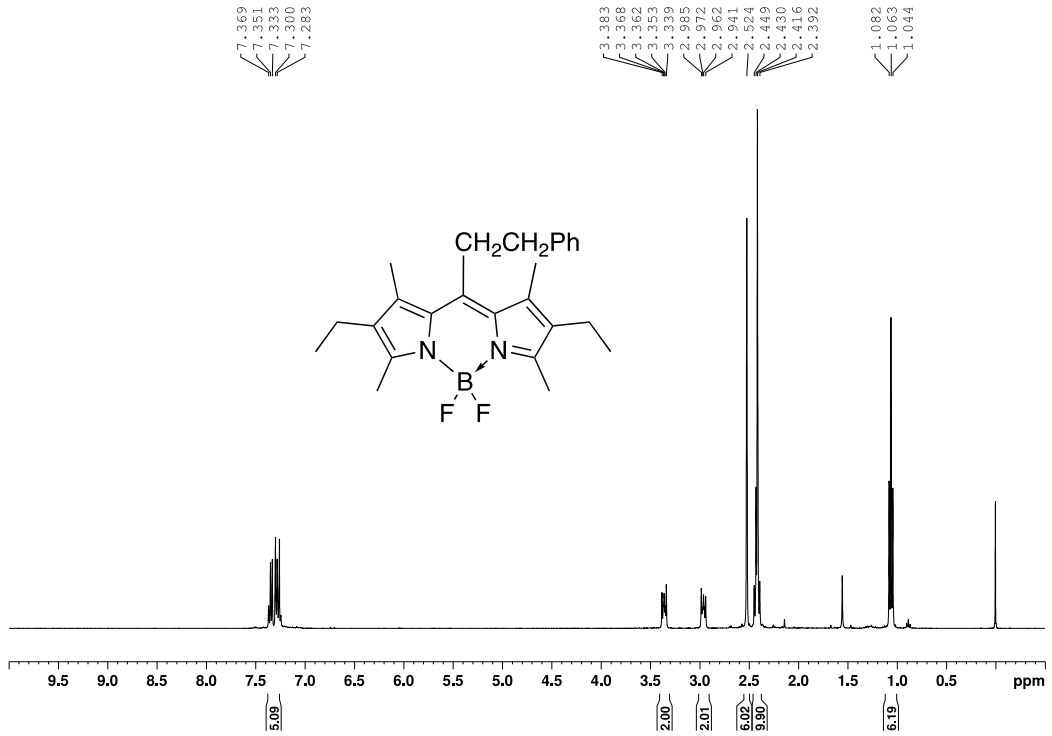


Figure S15. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of compound **3d** in $CDCl_3$

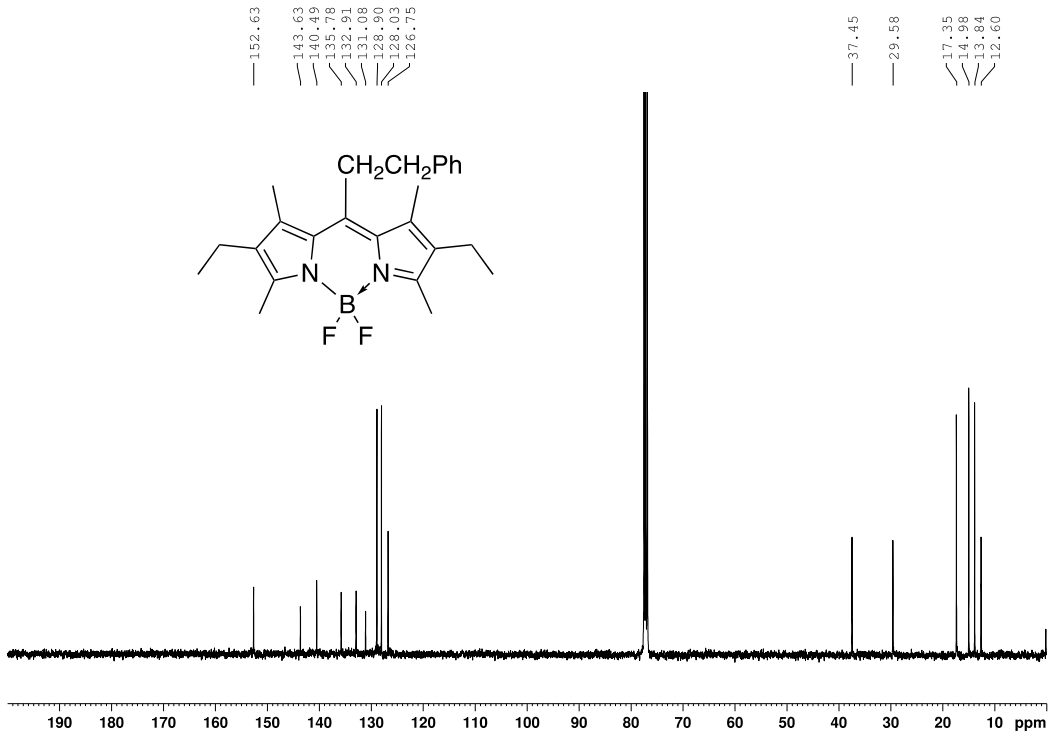


Figure S16. ^{11}B NMR (128 MHz) spectrum of compound **3d** in $CDCl_3$

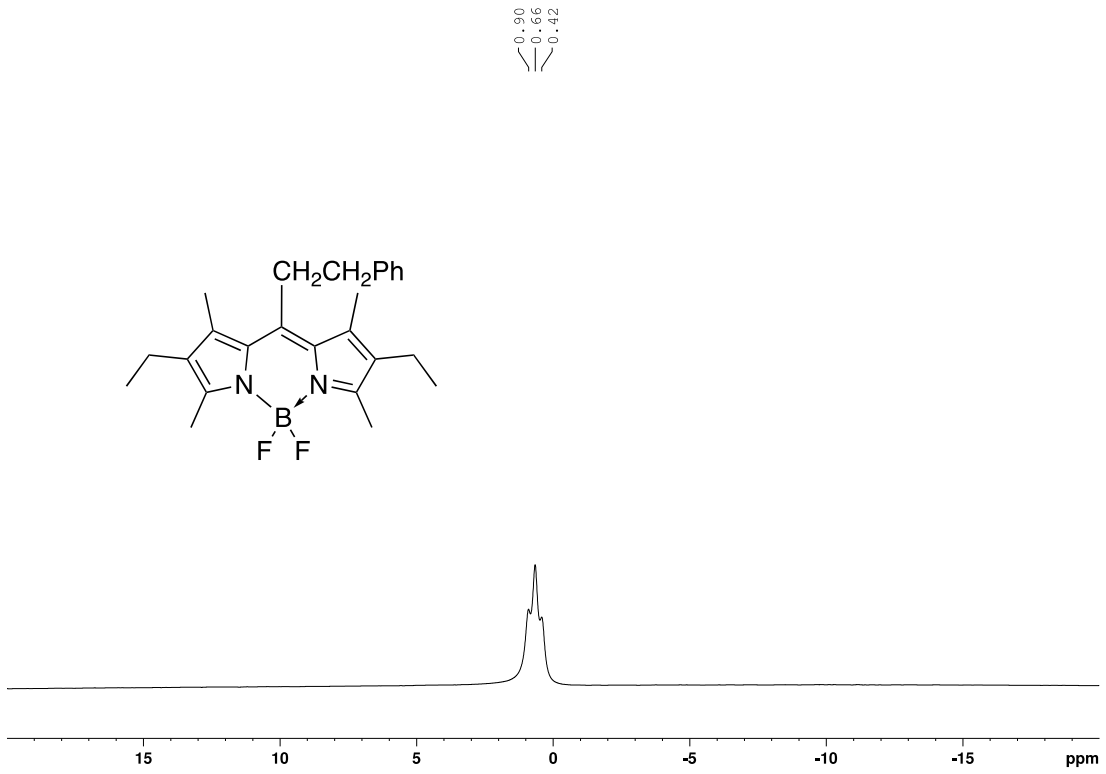


Figure S17. ^{19}F NMR (377 MHz) spectrum of compound **3d** in $CDCl_3$

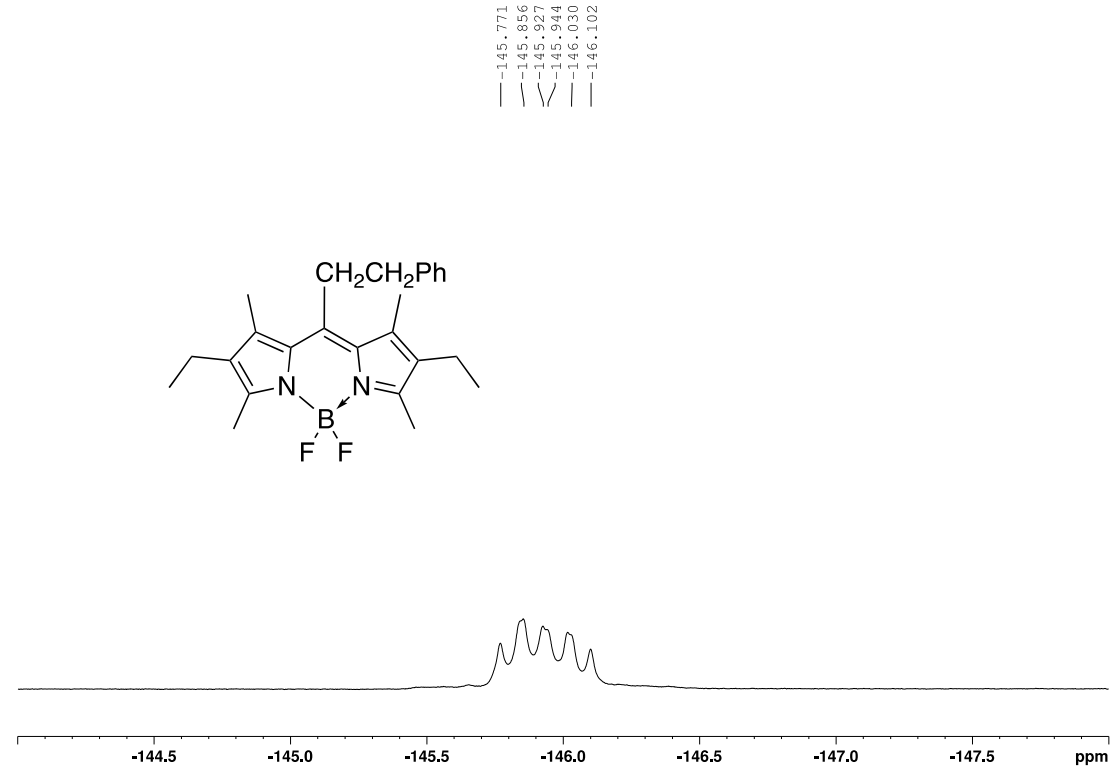


Figure S18. ^{1}H NMR (500 MHz) spectrum of compound **3f** in $CDCl_3$

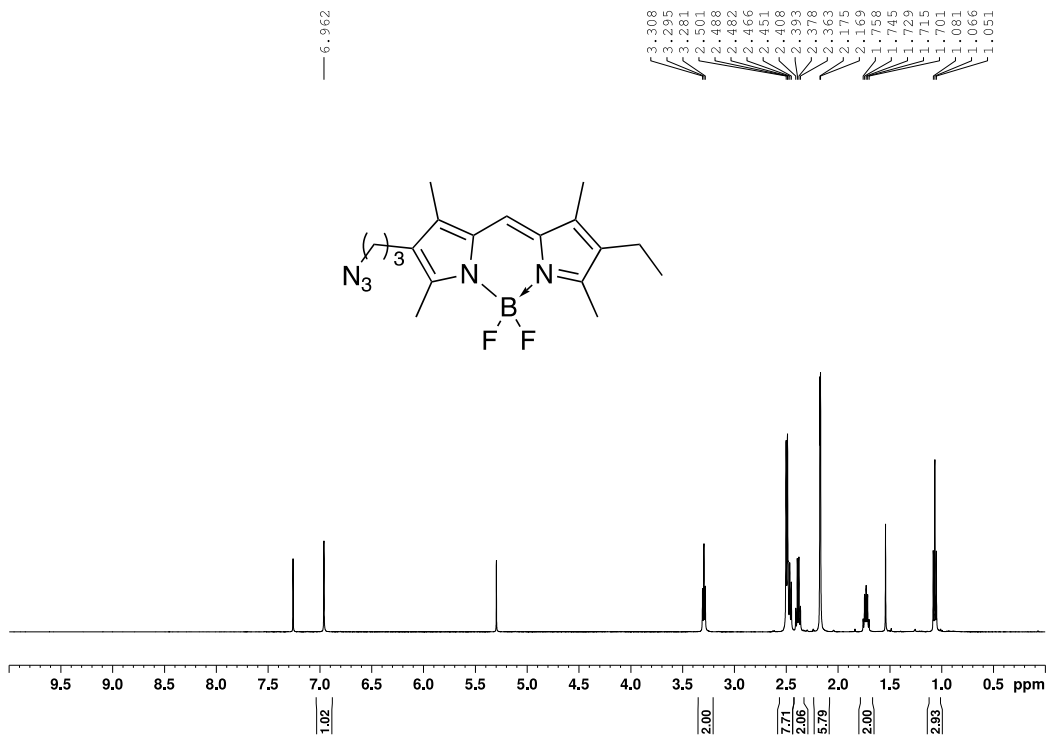


Figure S19. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **3f** in $CDCl_3$

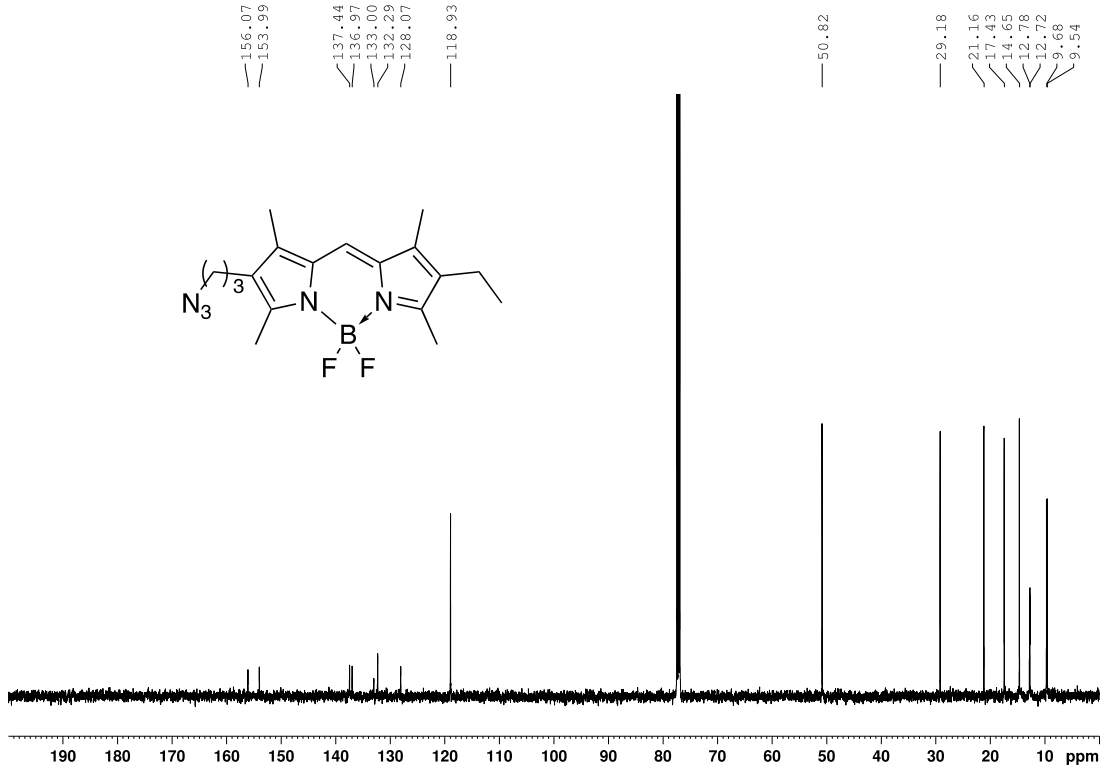


Figure S20. ^{11}B NMR (160 MHz) spectrum of compound **3f** in $CDCl_3$

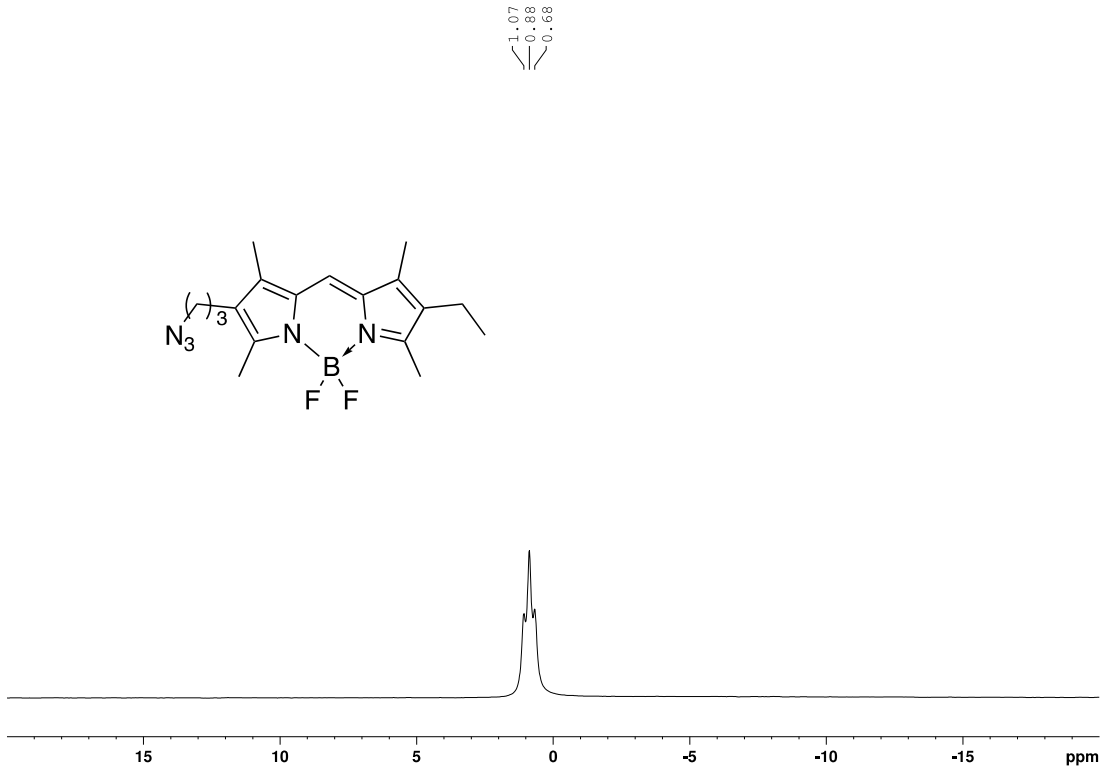


Figure S21. ^{19}F NMR (470 MHz) spectrum of compound **3f** in $CDCl_3$

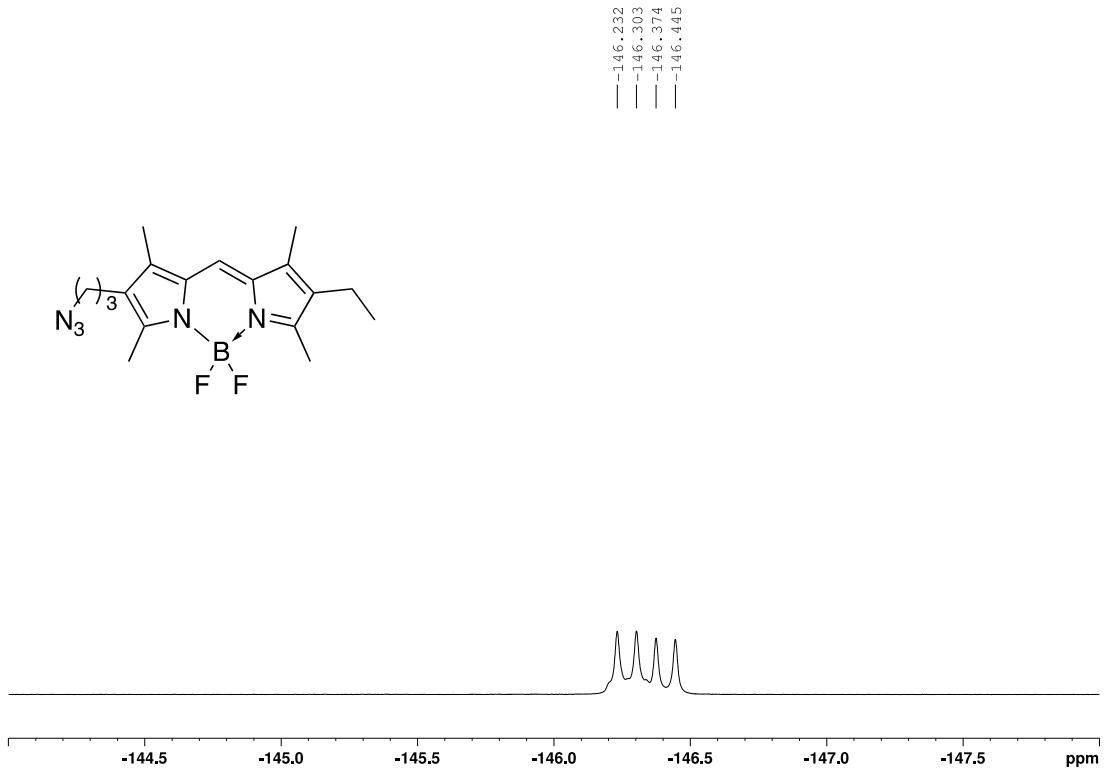


Figure S22. ^{1}H NMR (500 MHz) spectrum of compound **3i** in $CDCl_3$

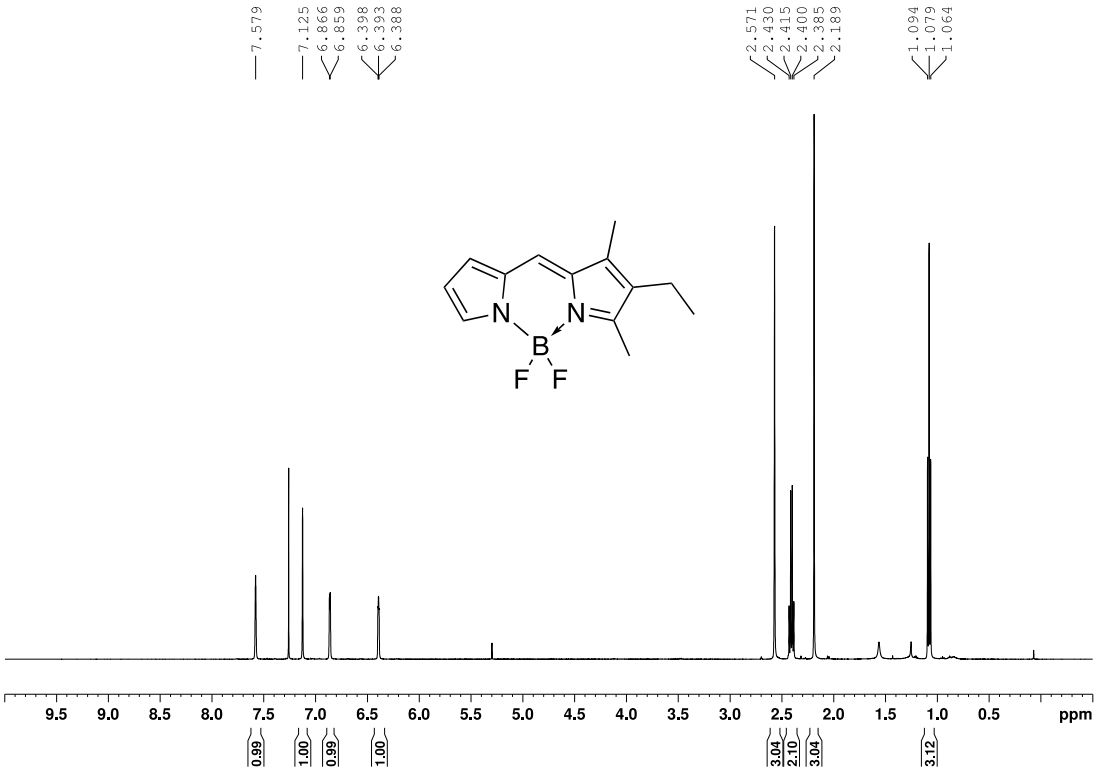


Figure S23. ^{1}H NMR (500 MHz) spectrum of compound **3l** in $CDCl_3$

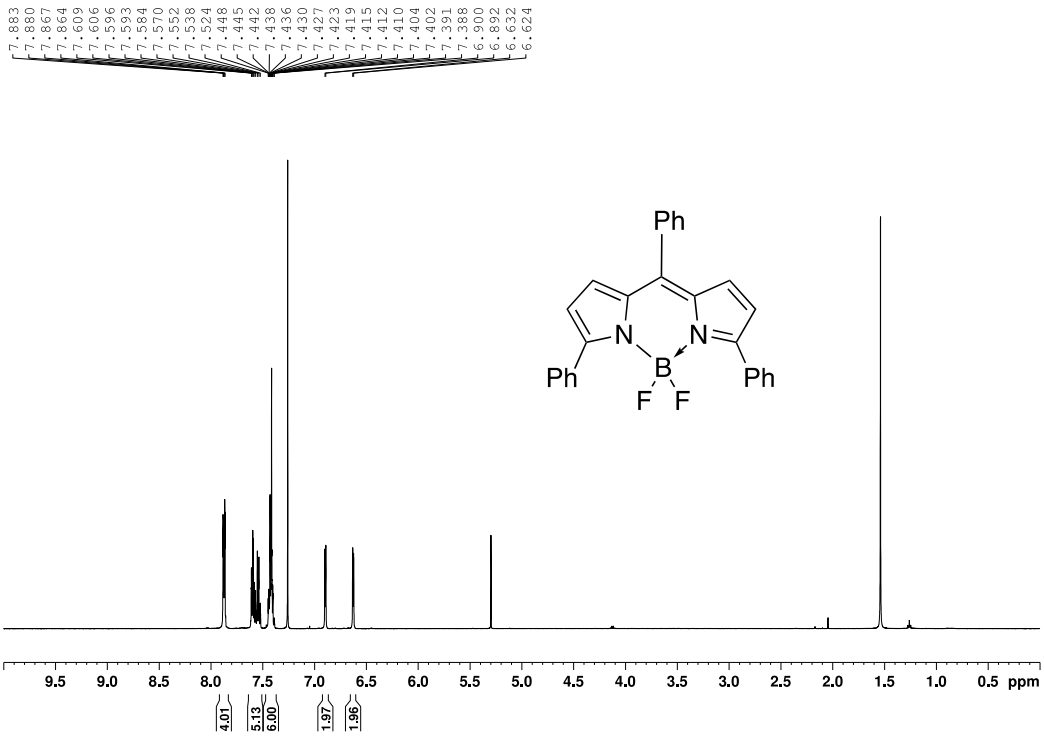


Figure S24. ^{1}H NMR (500 MHz) spectrum of compound **4a** in $CDCl_3$

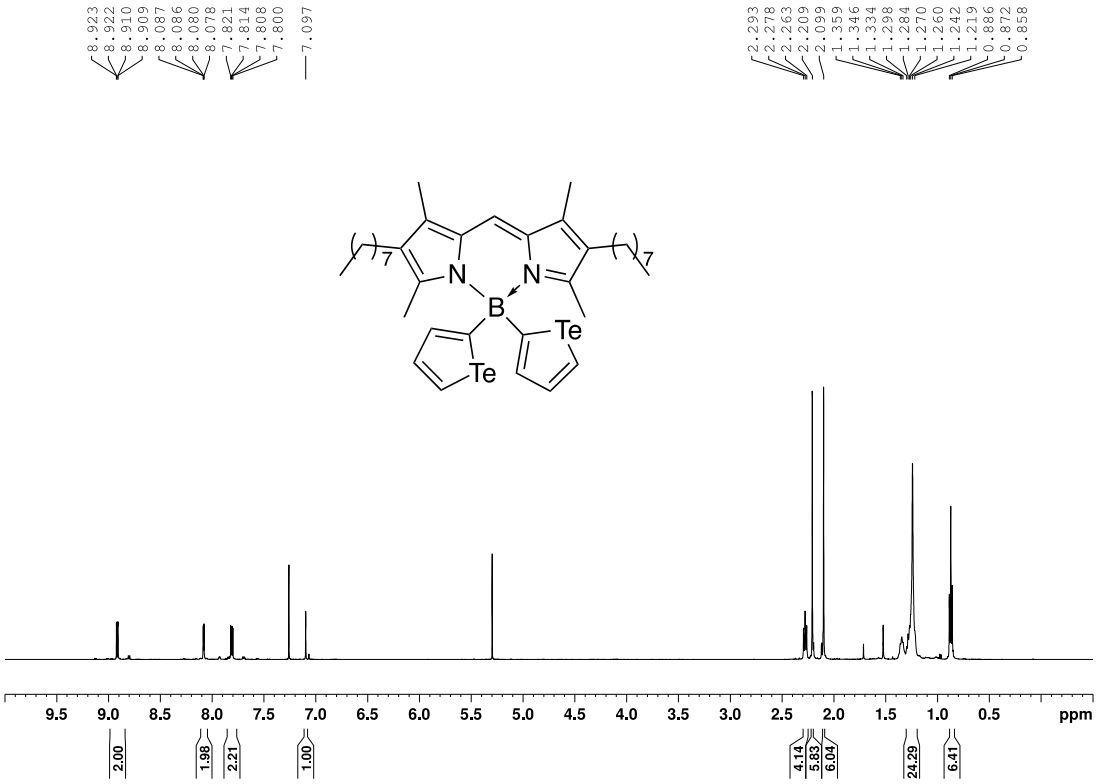


Figure S25. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4a** in $CDCl_3$

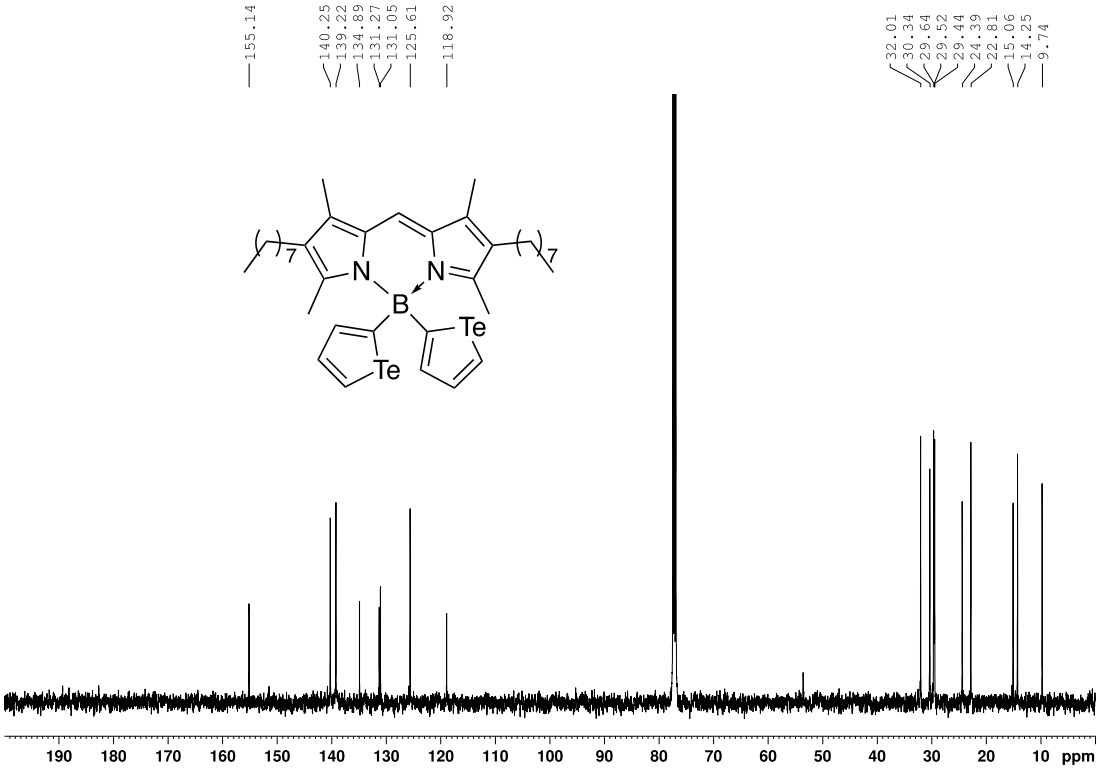


Figure S26. ^{11}B NMR (160 MHz) spectrum of compound **4a** in $CDCl_3$

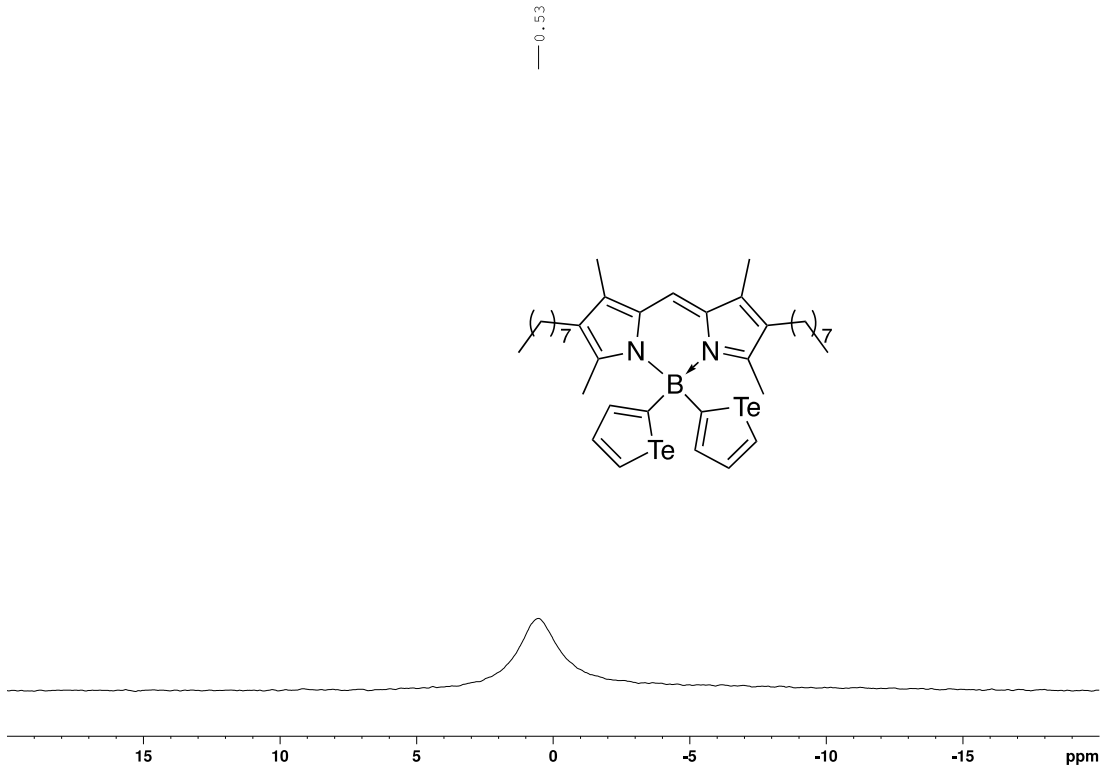


Figure S27. ^{1}H NMR (500 MHz) spectrum of compound **4b** in $CDCl_3$

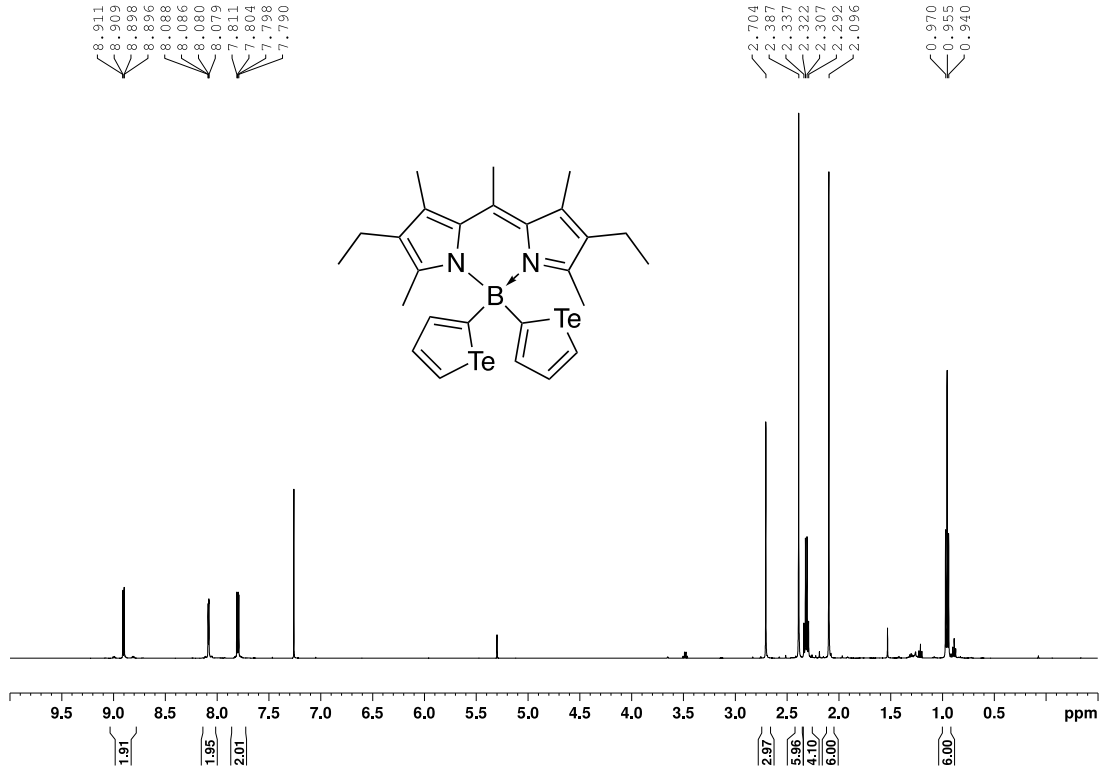


Figure S28. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4b** in $CDCl_3$

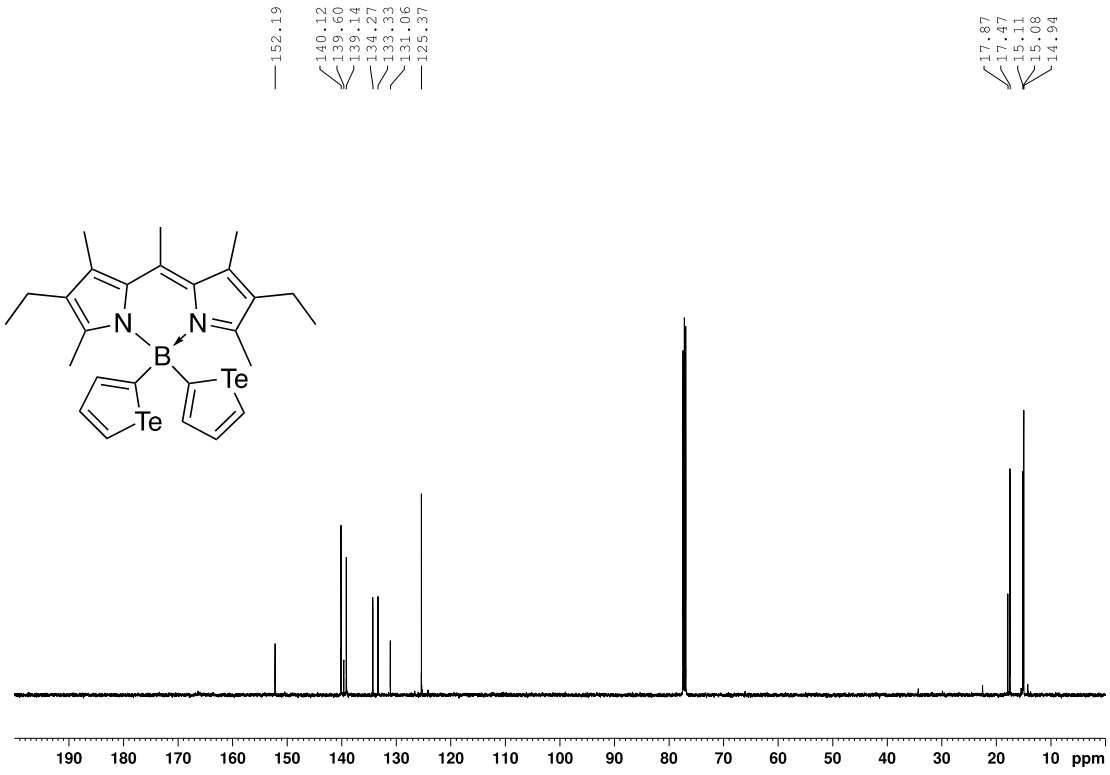


Figure S29. ^{11}B NMR (160 MHz) spectrum of compound **4b** in $CDCl_3$

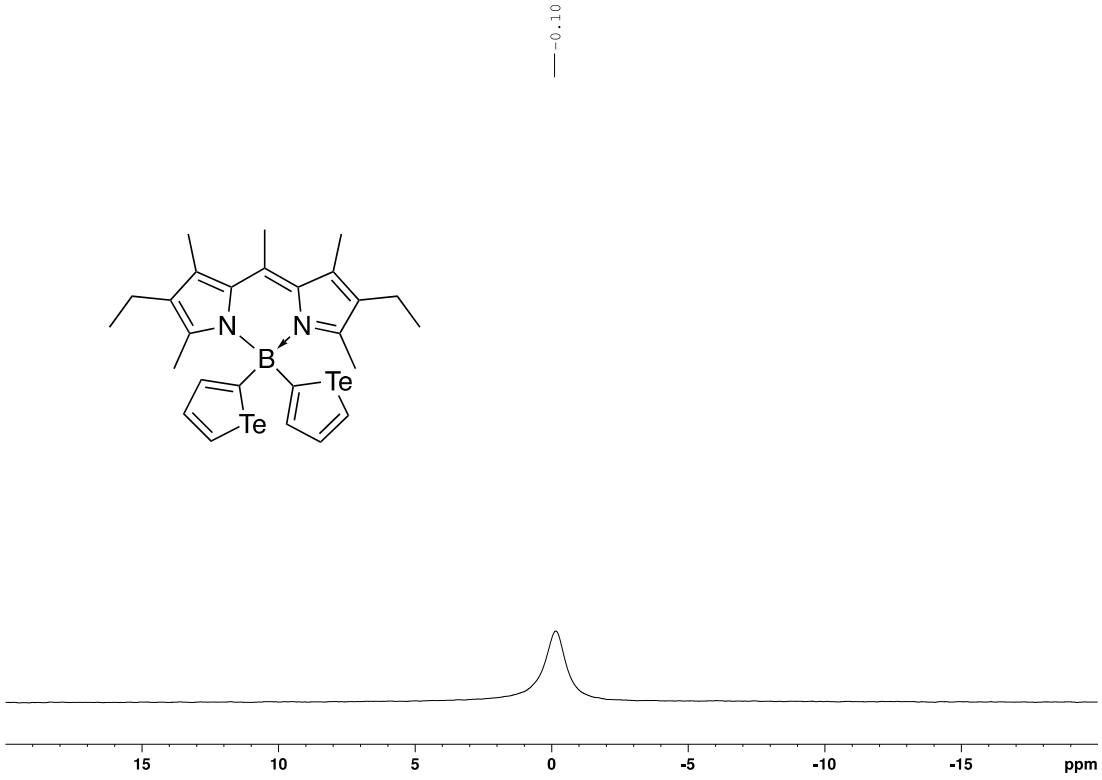


Figure S30. ^{1}H NMR (500 MHz) spectrum of compound **4c** in $CDCl_3$

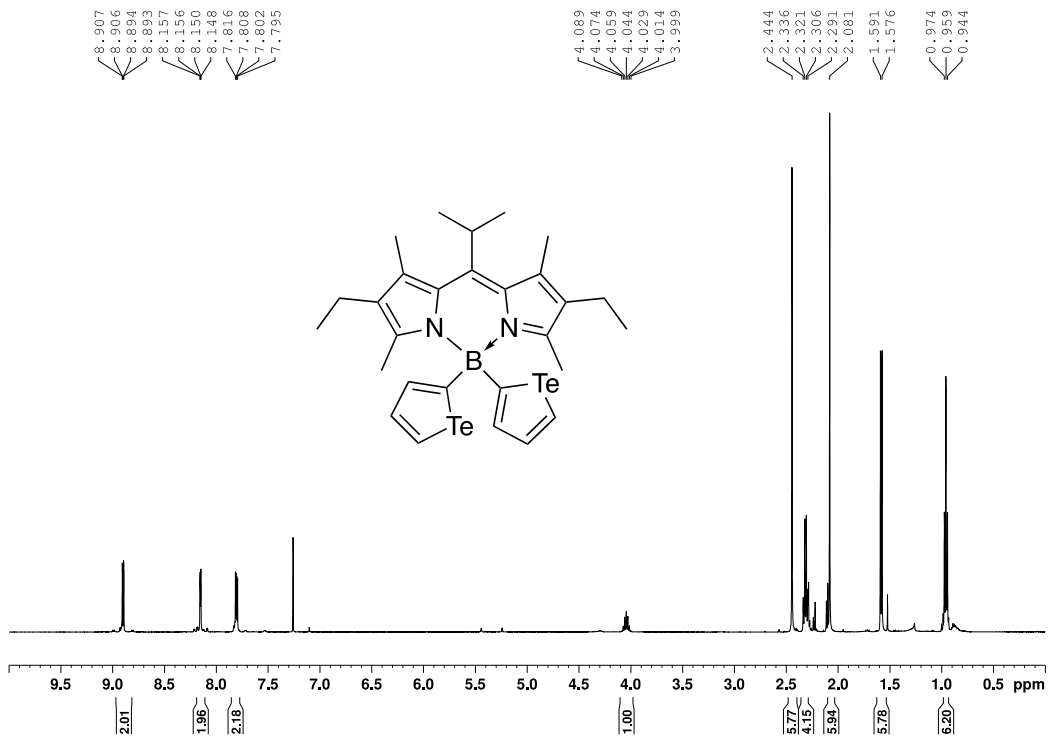


Figure S31. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4c** in $CDCl_3$

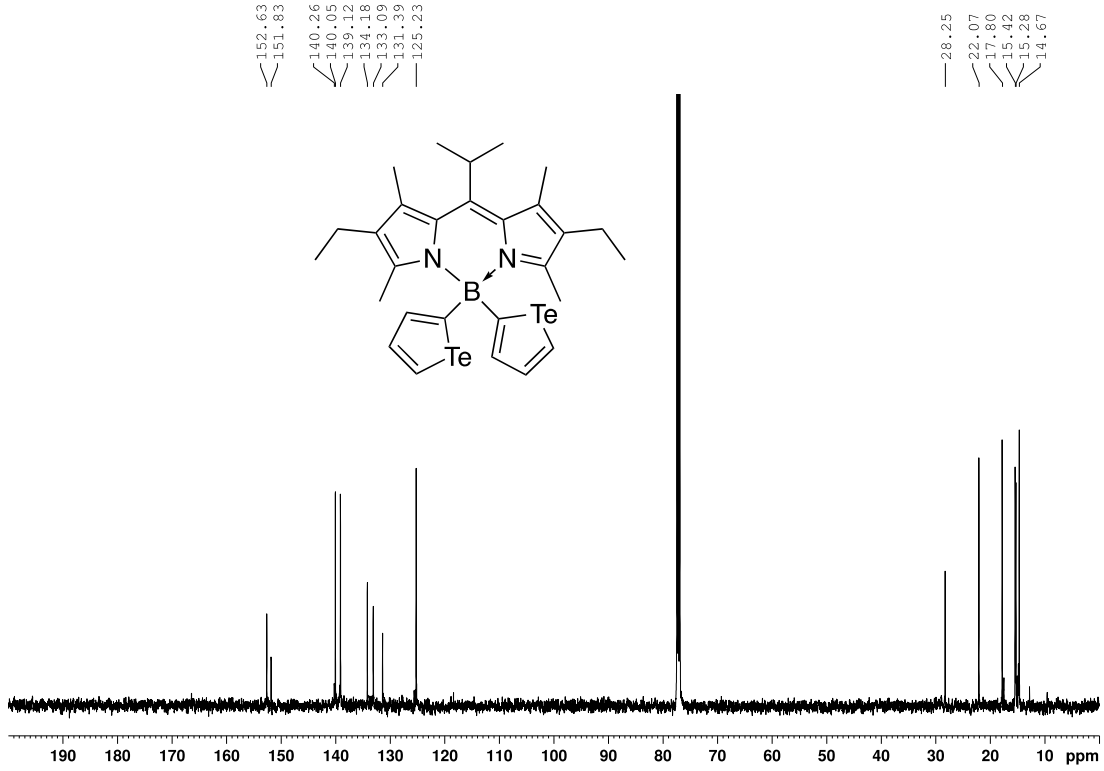


Figure S32. ^{11}B NMR (160 MHz) spectrum of compound **4c** in $CDCl_3$

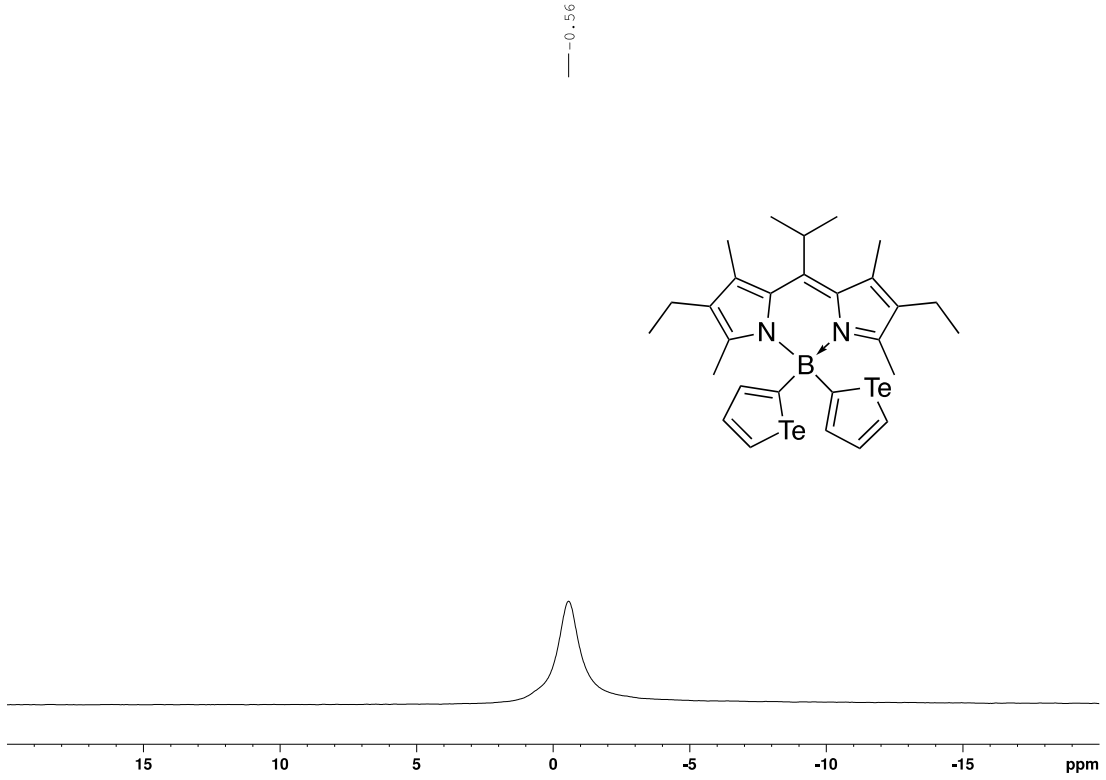


Figure S33. ^{1}H NMR (500 MHz) spectrum of compound **4d** in $CDCl_3$

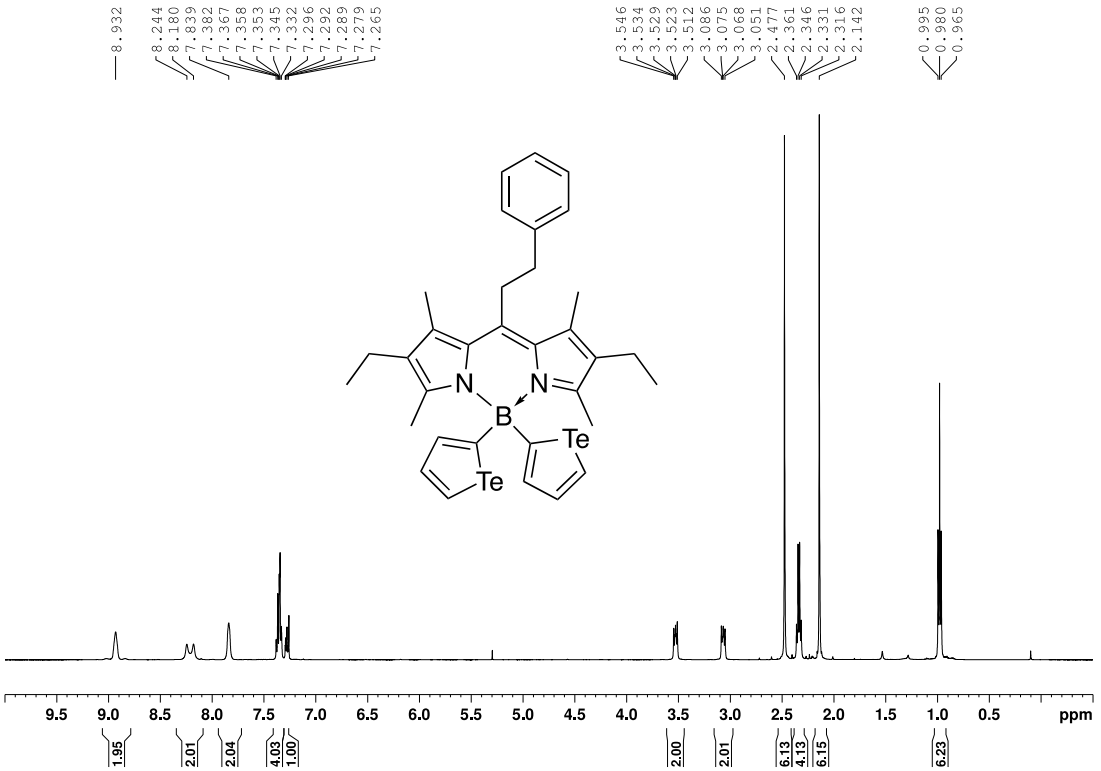


Figure S34. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4d** in $CDCl_3$

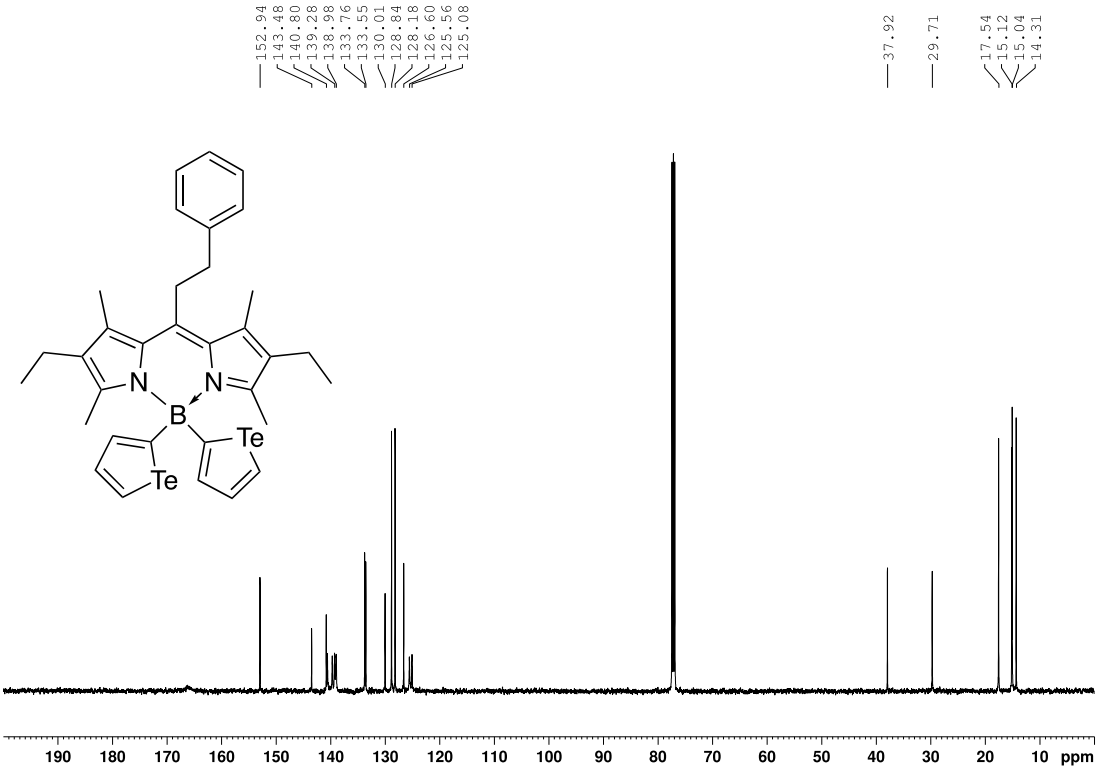


Figure S35. ^{11}B NMR (160 MHz) spectrum of compound **4d** in $CDCl_3$

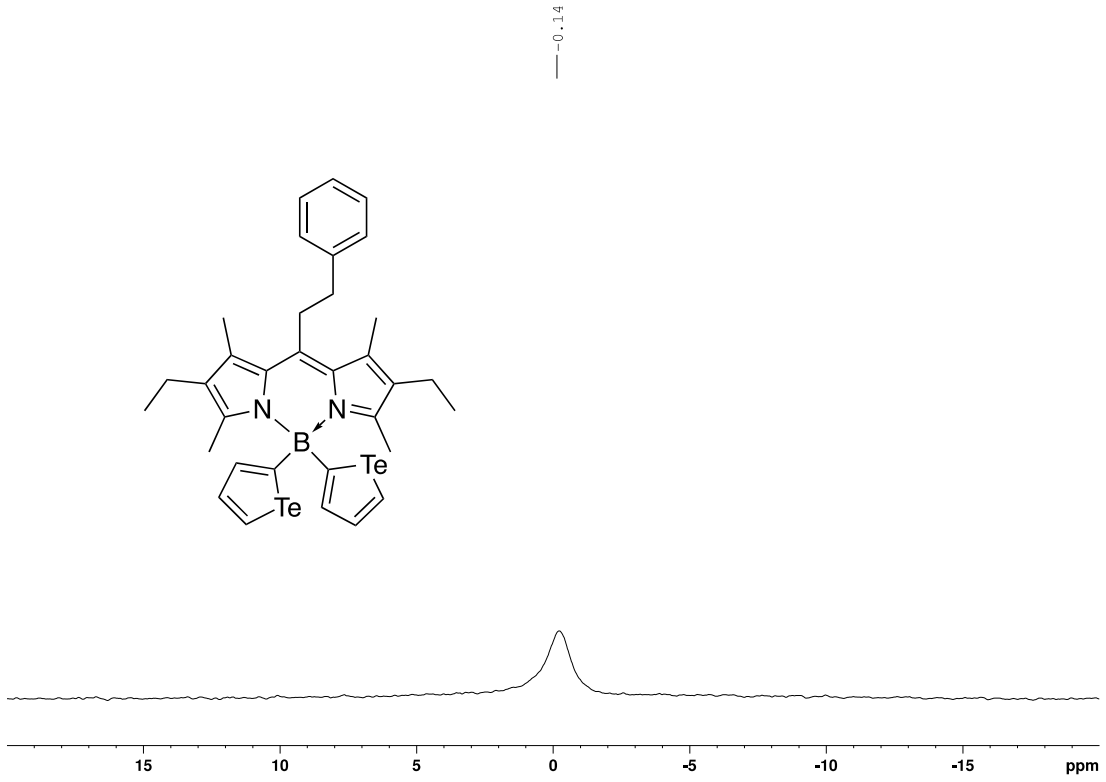


Figure S36. ^{1}H NMR (500 MHz) spectrum of compound **4e** in $CDCl_3$

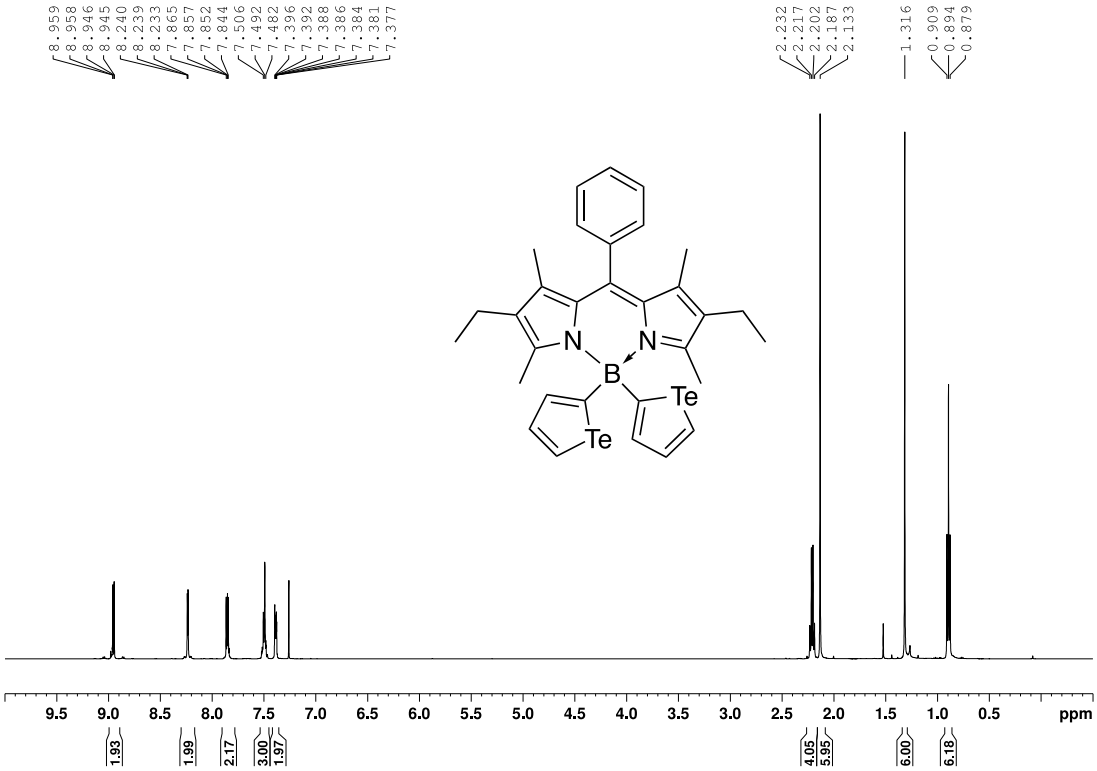


Figure S37. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4e** in $CDCl_3$

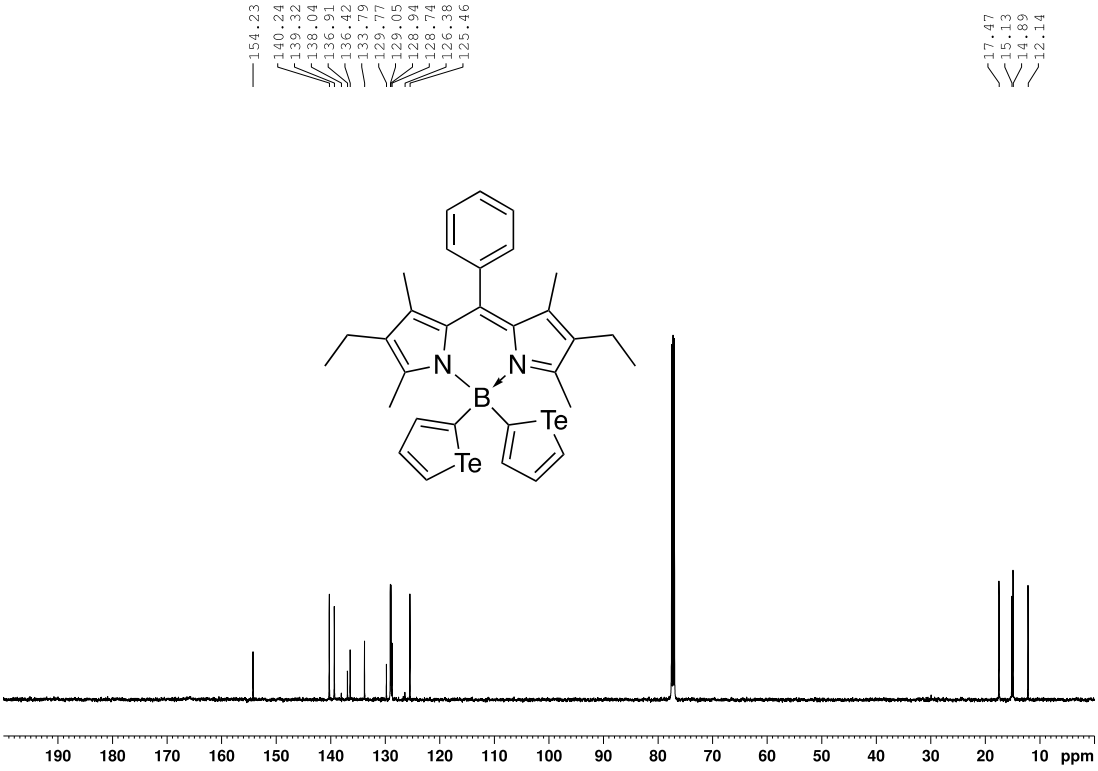


Figure S38. ^{11}B NMR (160 MHz) spectrum of compound **4e** in $CDCl_3$

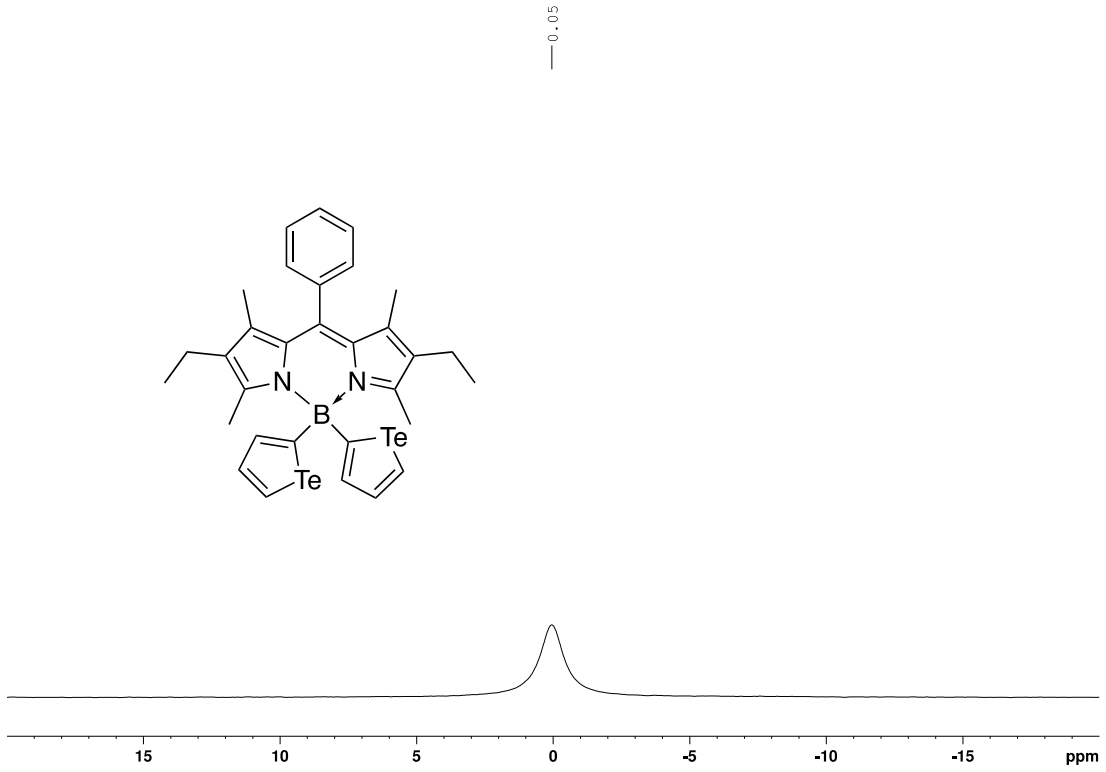


Figure S39. ^{1}H NMR (400 MHz) spectrum of compound **4f** in $CDCl_3$

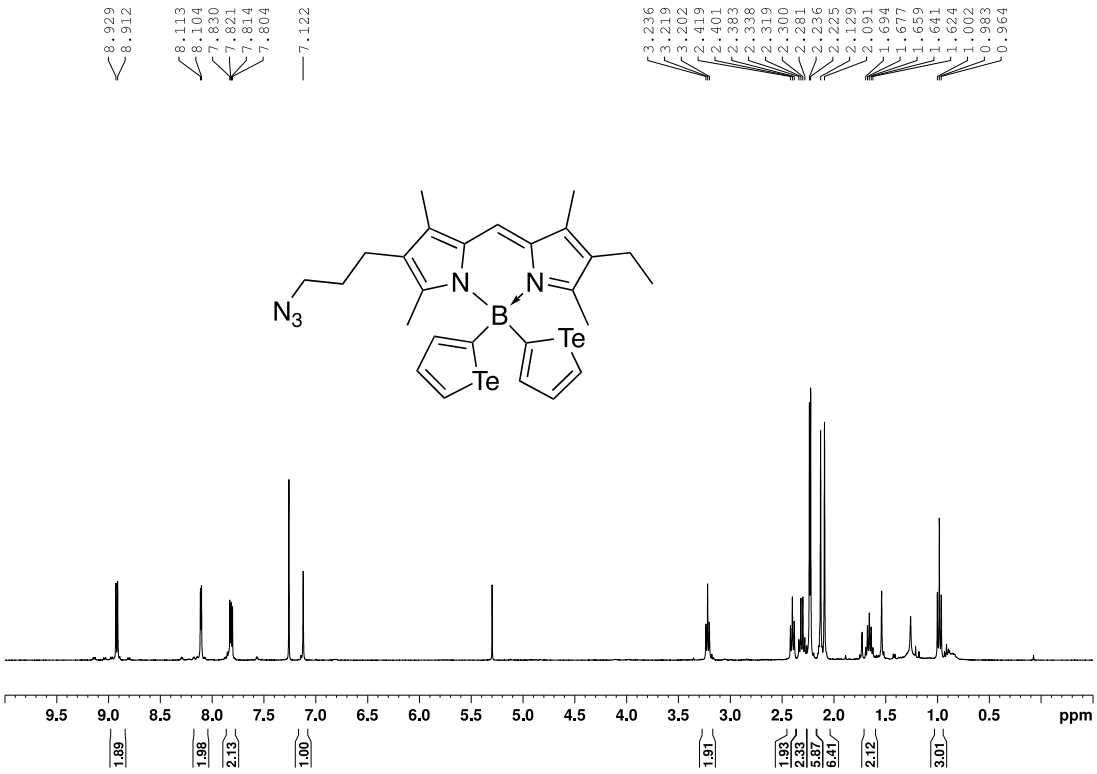


Figure S40. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4f** in $CDCl_3$

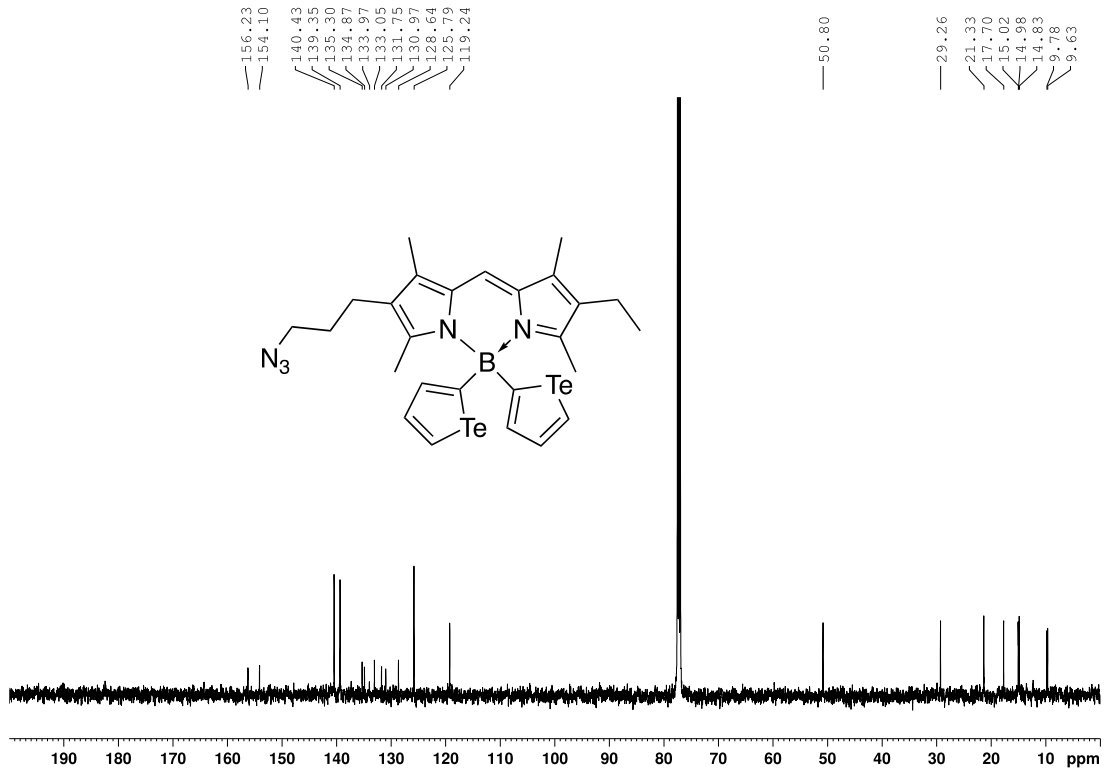


Figure S41. ^{11}B NMR (160 MHz) spectrum of compound **4f** in $CDCl_3$

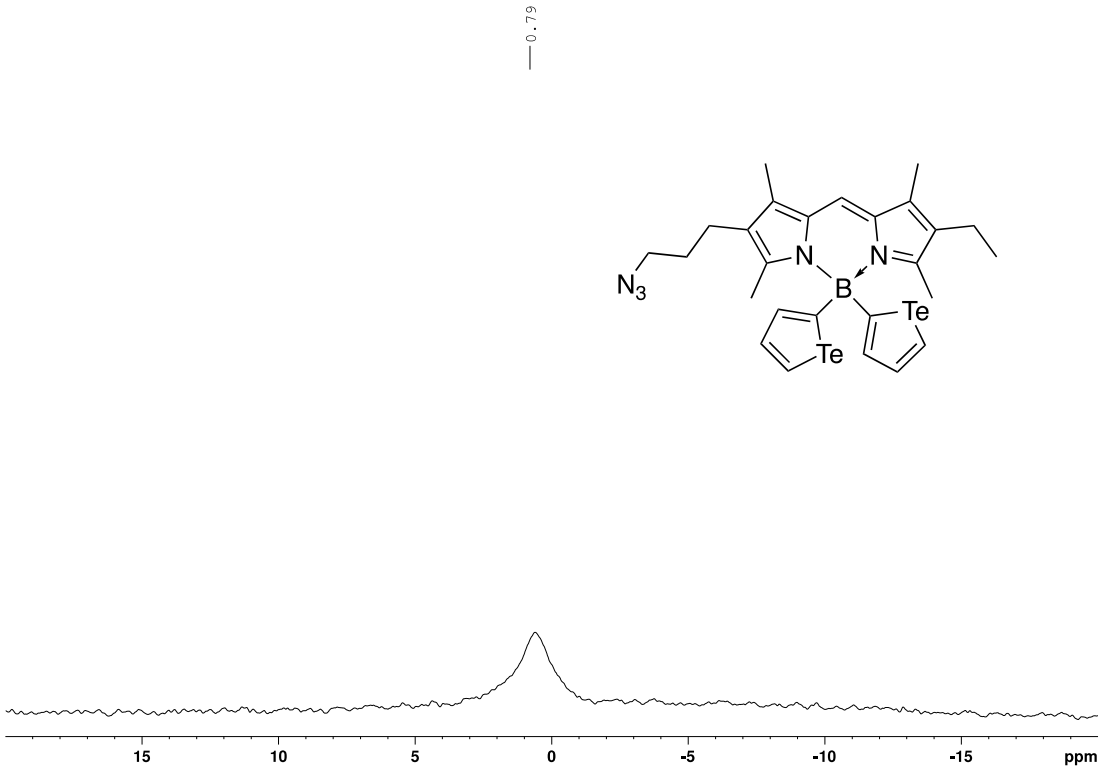


Figure S42. ^{1}H NMR (500 MHz) spectrum of compound **4g** in $CDCl_3$

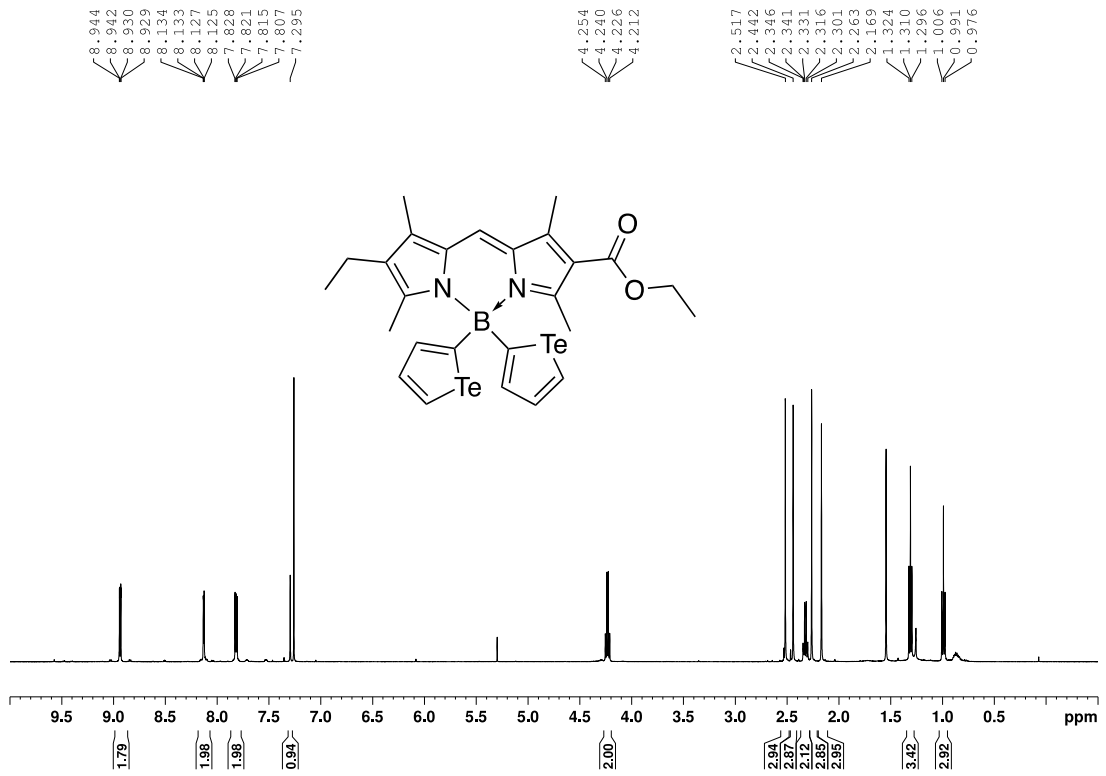


Figure S43. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4g** in $CDCl_3$

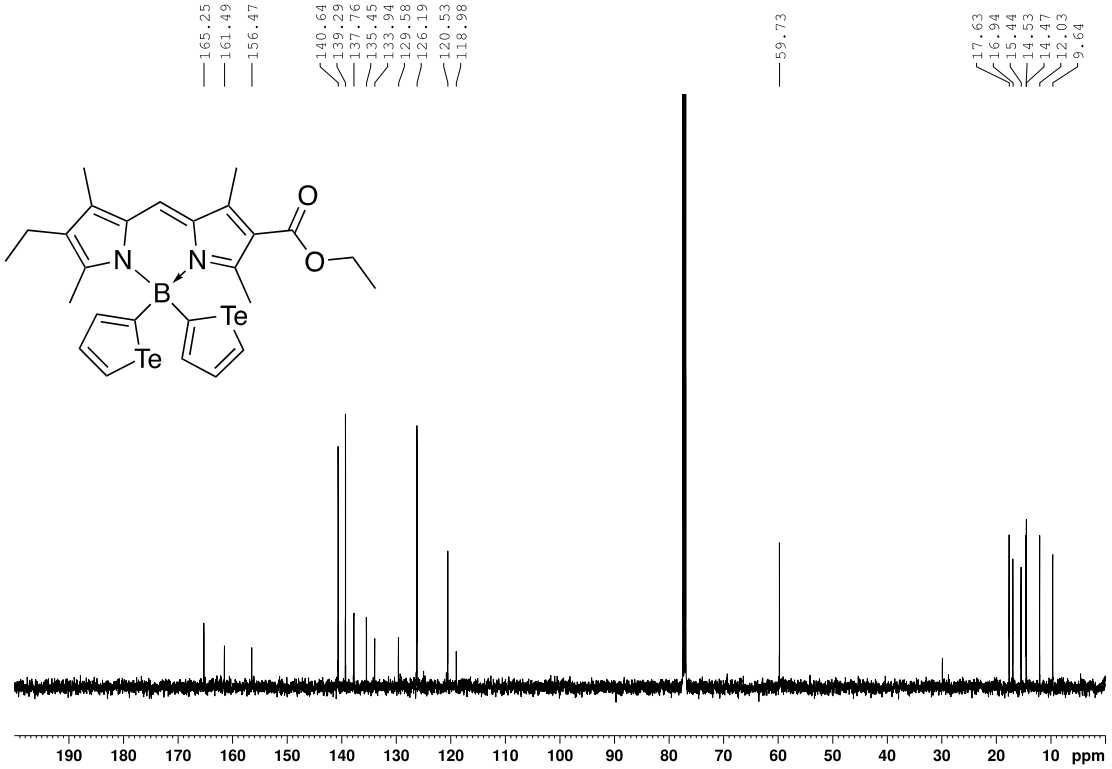


Figure S44. ^{11}B NMR (160 MHz) spectrum of compound **4g** in $CDCl_3$

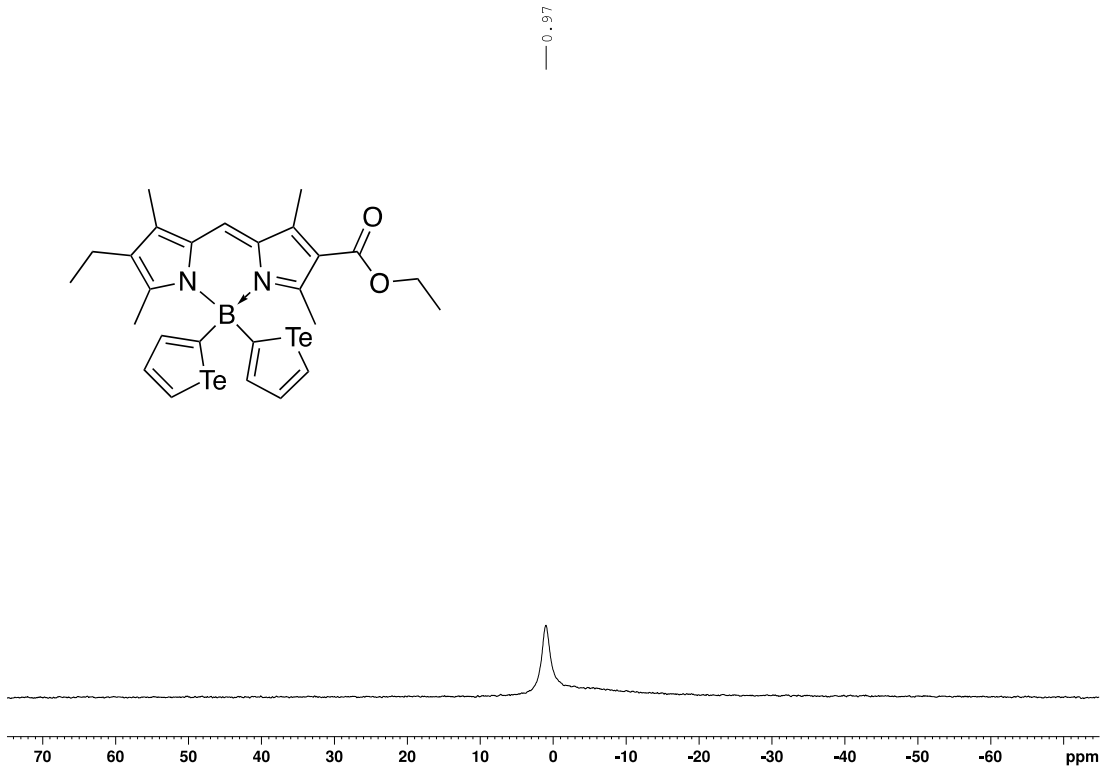


Figure S45. ^{1}H NMR (500 MHz) spectrum of compound **4h** in $CDCl_3$

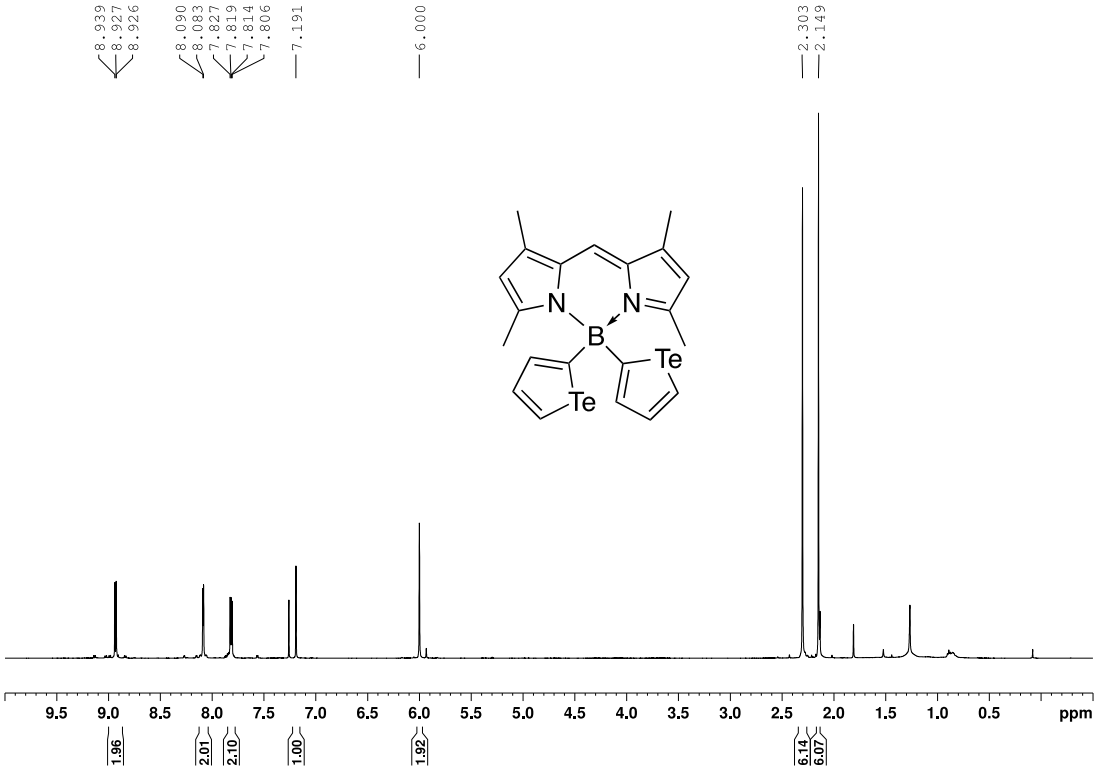


Figure S46. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4h** in $CDCl_3$

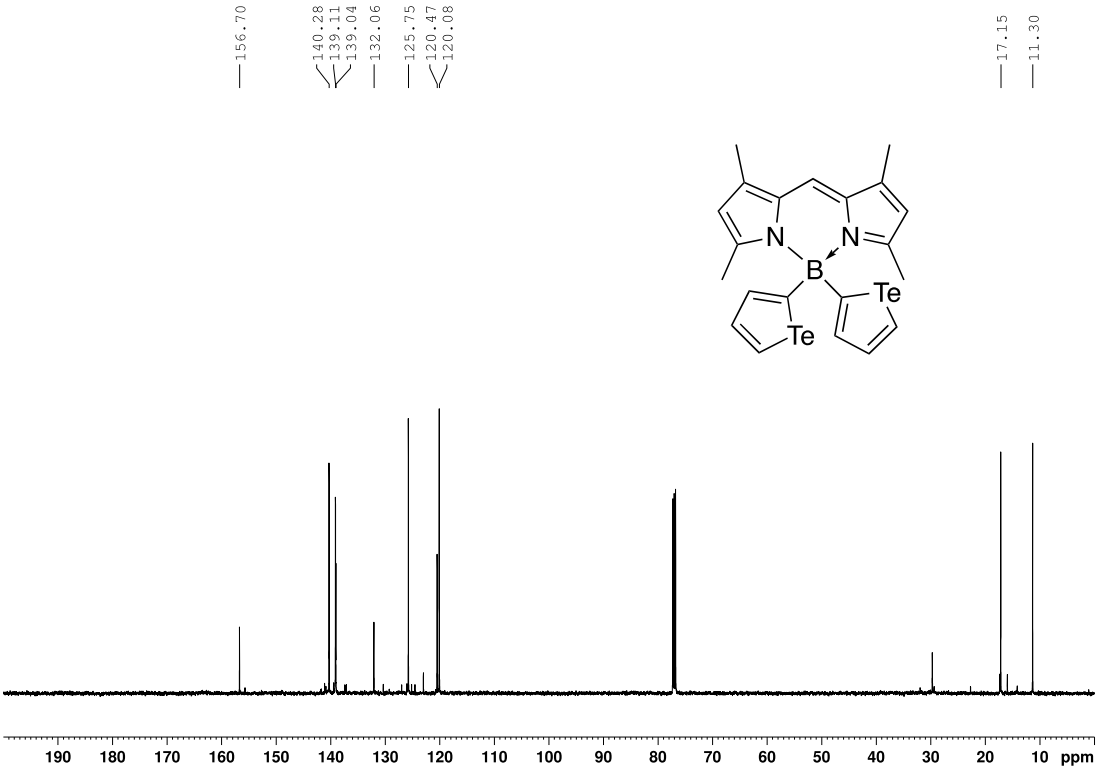


Figure S47. ^{11}B NMR (160 MHz) spectrum of compound **4h** in $CDCl_3$

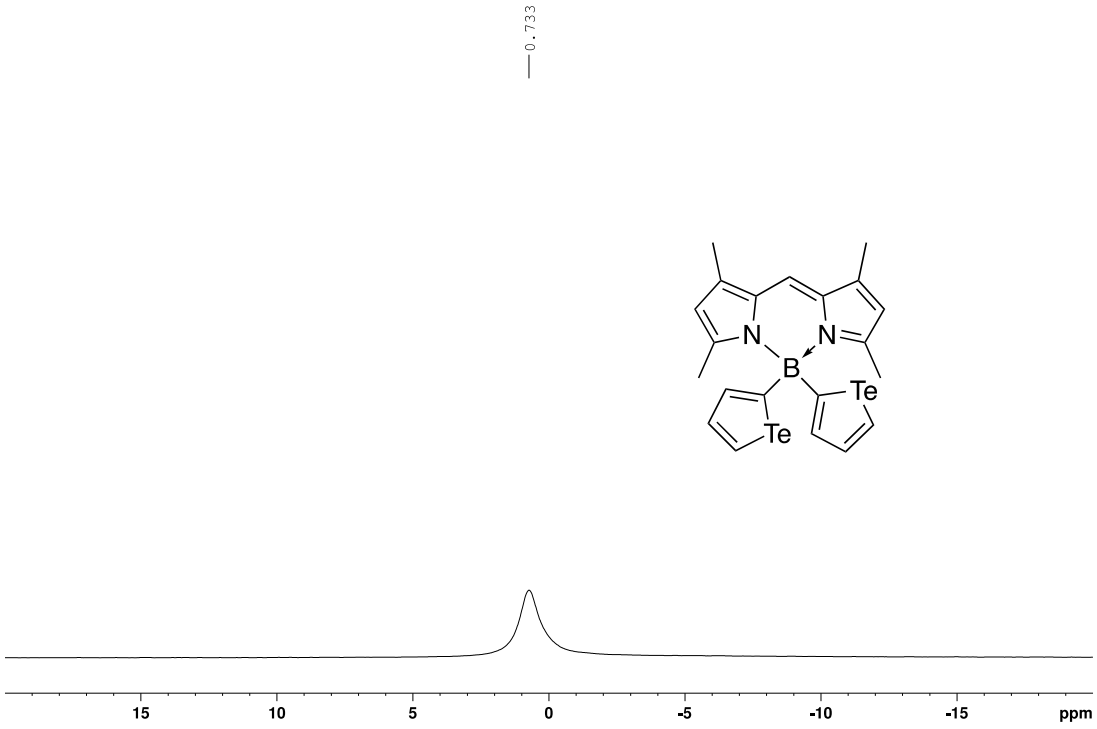


Figure S48. ^{1}H NMR (500 MHz) spectrum of compound **4i** in $CDCl_3$

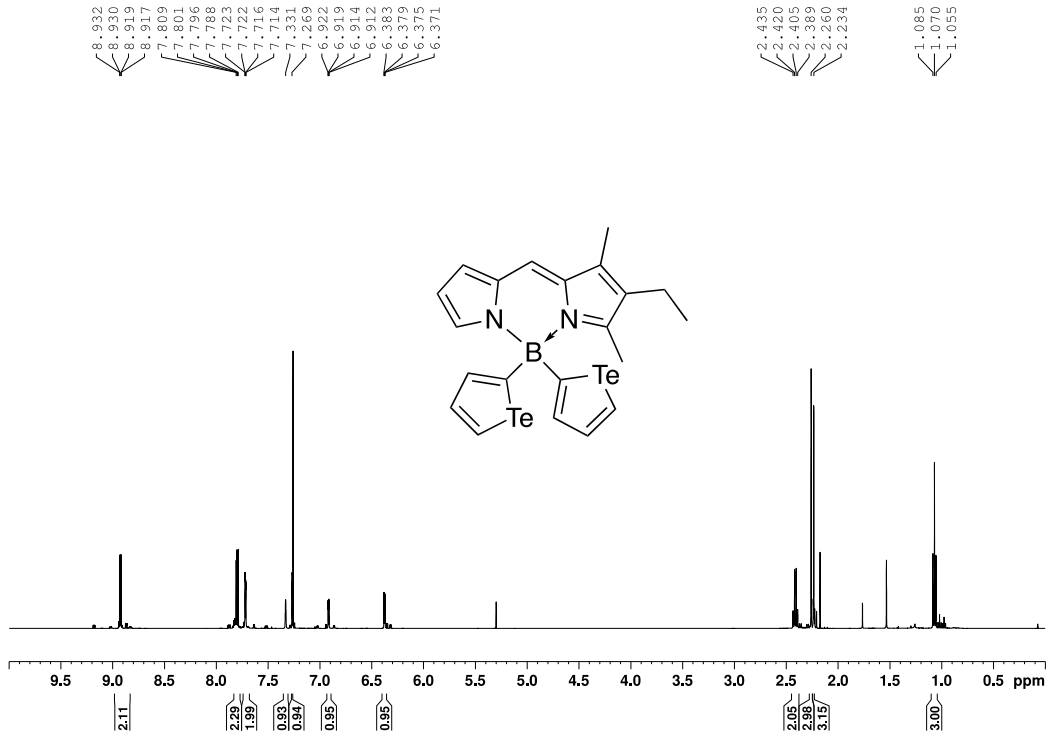


Figure S49. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4i** in $CDCl_3$

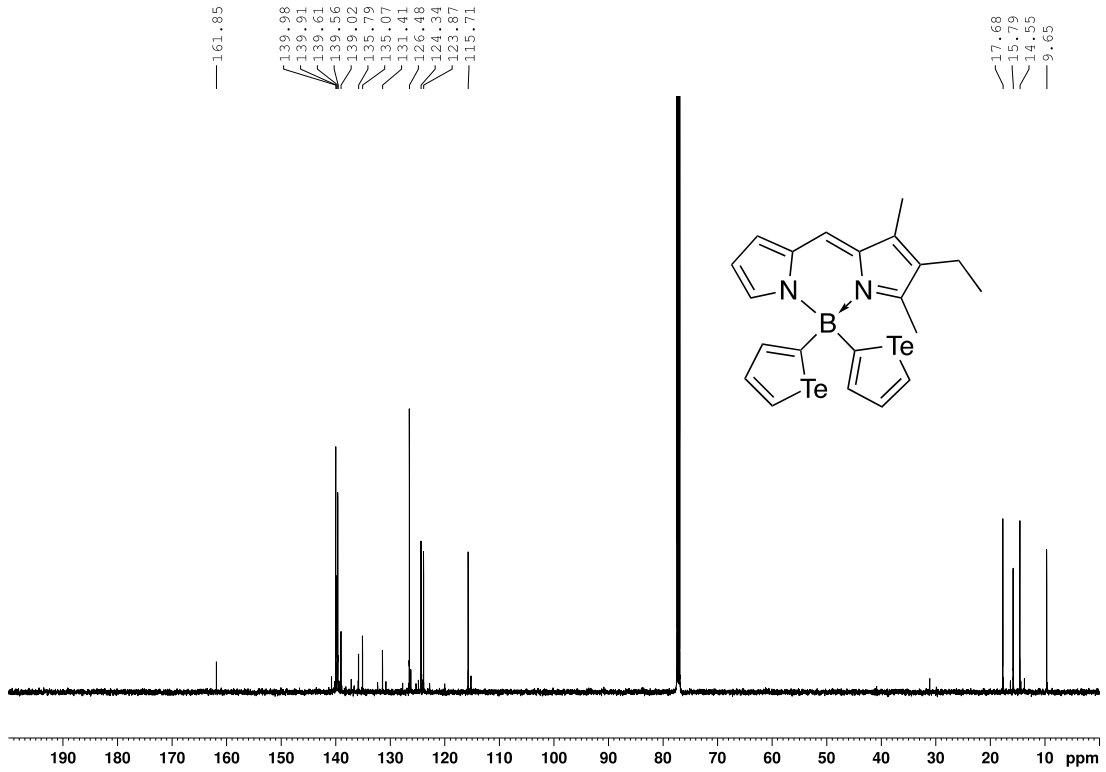
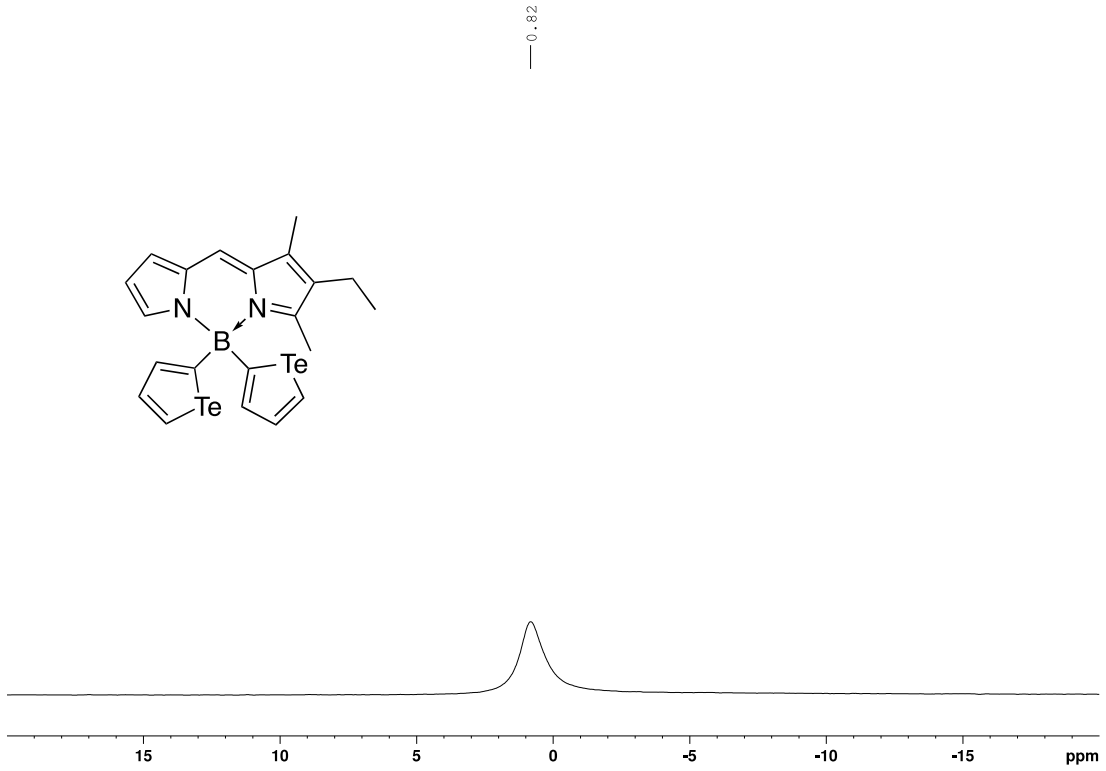


Figure S50. ^{11}B NMR (160 MHz) spectrum of compound **4i** in $CDCl_3$



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