

## **Positive Electrofluorochromism of Bodipy-Ferrocene Monolayers on ITO.**

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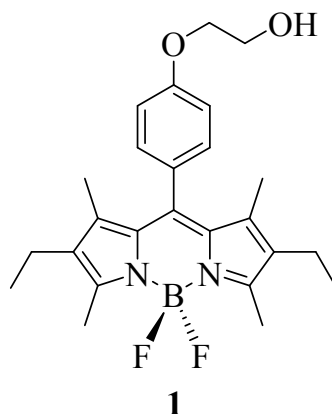
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## Compound 1



*According to this procedure: Grazon, Chloe; Rieger, Jutta; Meallet-Renault, Rachel; Charleux, Bernadette; Clavier, Gilles, Macromolecules, 2013, 46, 13, 5167 – 5176.*

To a 250 mL tricol flask was added hydroxyethoxybenzaldehyde (0.650 g, 3.91 mmol) in anhydrous DCM (50 mL). Argon was bubbled through the solution for 20 min, then kryptopyrrole (1.2 mL, 9 mmol) and TFA (8 drops) were added. The mixture was stirred for 2 hours. Chloranil (0.96 g, 3.9 mmol) was added and the reaction was stirred for 5 minutes. After the addition of DIPEA (4.8 mL, 27.6 mmol), the solution was kept stirring for 15 minutes, then boron trifluoride etherate (5.3 mL, 43 mmol) was introduced to the flask. The mixture was then stirred for 2 hours at room temperature. The DCM was evaporated. After purification by column chromatography on silica gel (DCM), a red solid was obtained (m = 1.26 g; R= 73%). **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)** δ 0.98 (t, *J* = 7.5 Hz, 6H; -CH<sub>2</sub>-CH<sub>3</sub>), 1.32 (s, 6H; -CH<sub>3</sub>), 2.07 (bs, 1H; -OH), 2.30 (q, *J* = 7.6 Hz, 4H; -CH<sub>2</sub>-CH<sub>3</sub>), 2.52 (s, 6H; -CH<sub>3</sub>), 4.03 (t, *J* = 4.5 Hz, 2H; -CH<sub>2</sub>-OH), 4.16 (t, *J* = 4.4 Hz, 2H; -CH<sub>2</sub>-O-), 7.03 (d, *J* = 8.6 Hz, 2H; H<sub>arom</sub>), 7.18 (d, *J* = 8.6 Hz, 2H; H<sub>arom</sub>); **<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)** δ -145.76 (q, *J* = 34.4 Hz); **<sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>)** δ 2.25 (t, *J* = 34.5 Hz).

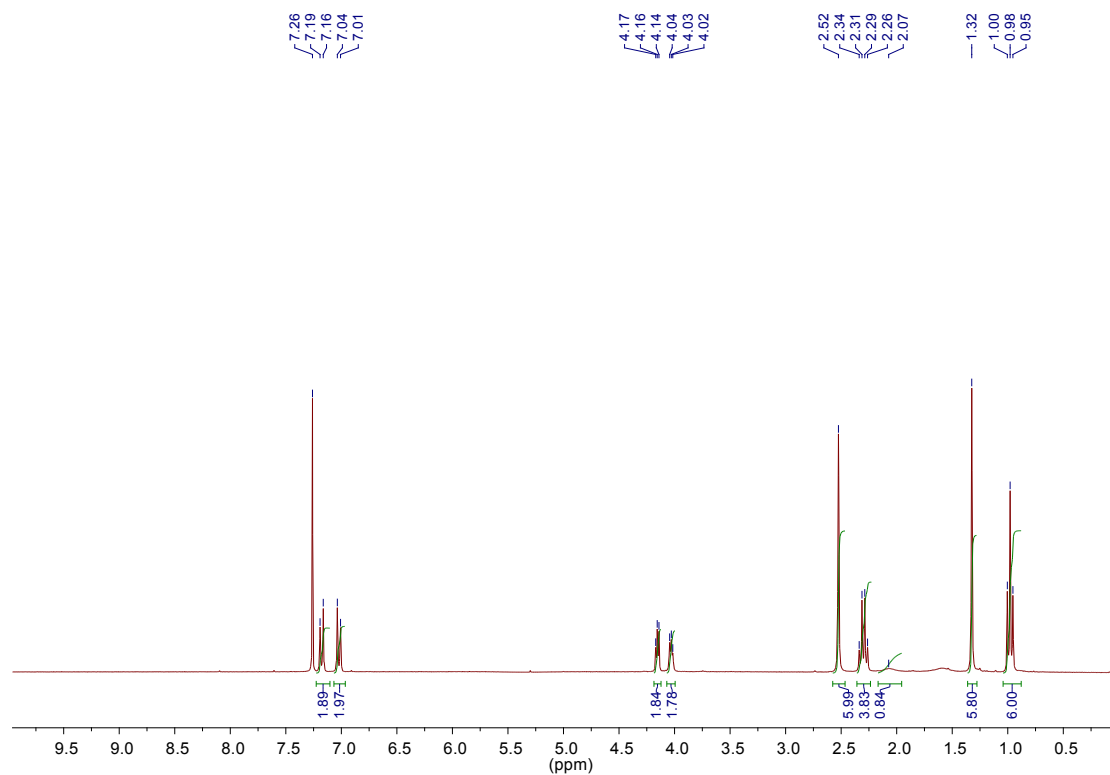


Figure S1.  $^1\text{H}$  NMR of compound **1**

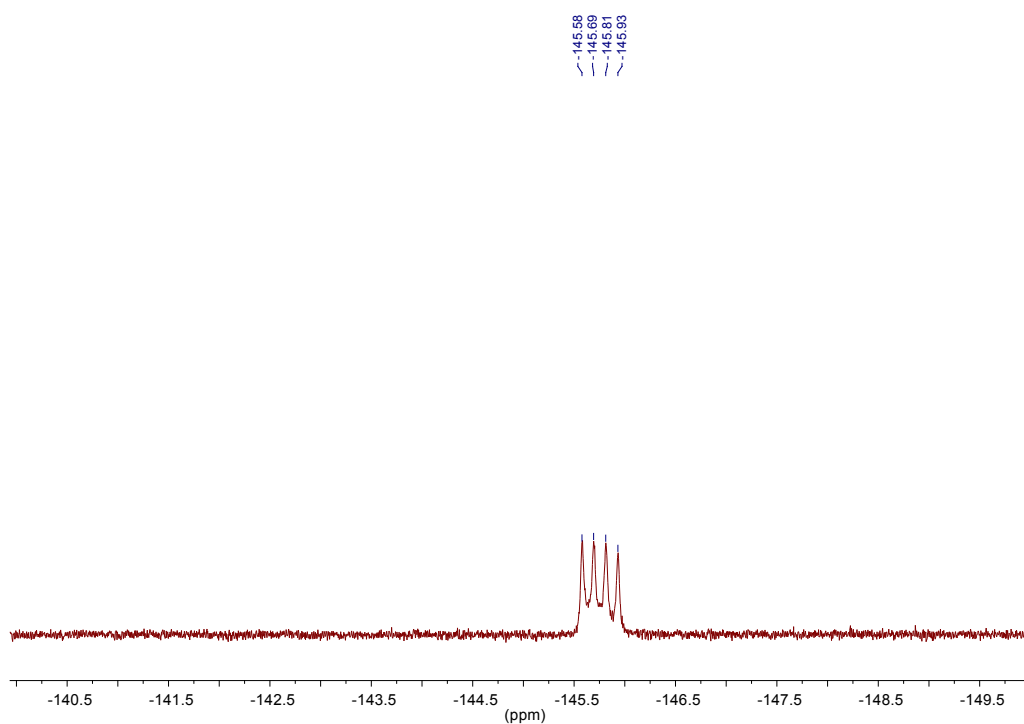
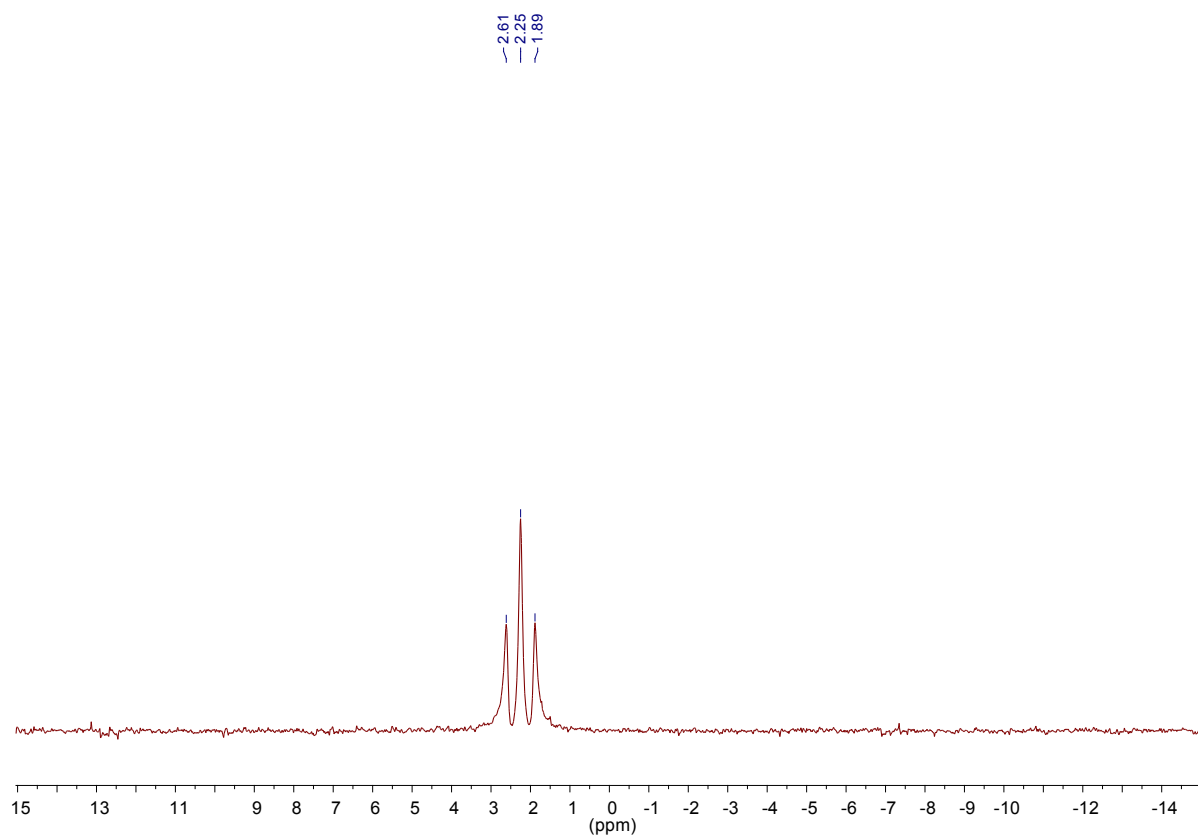
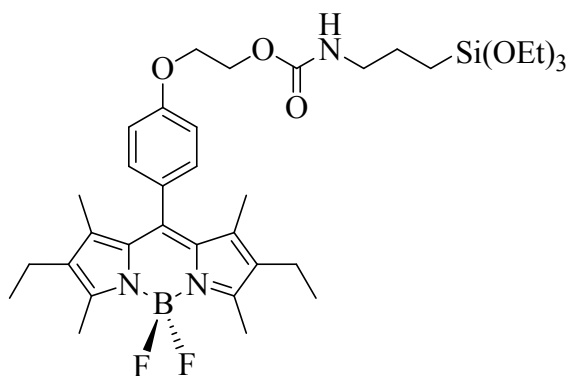


Figure S2.  $^{19}\text{F}$  NMR of compound **1**

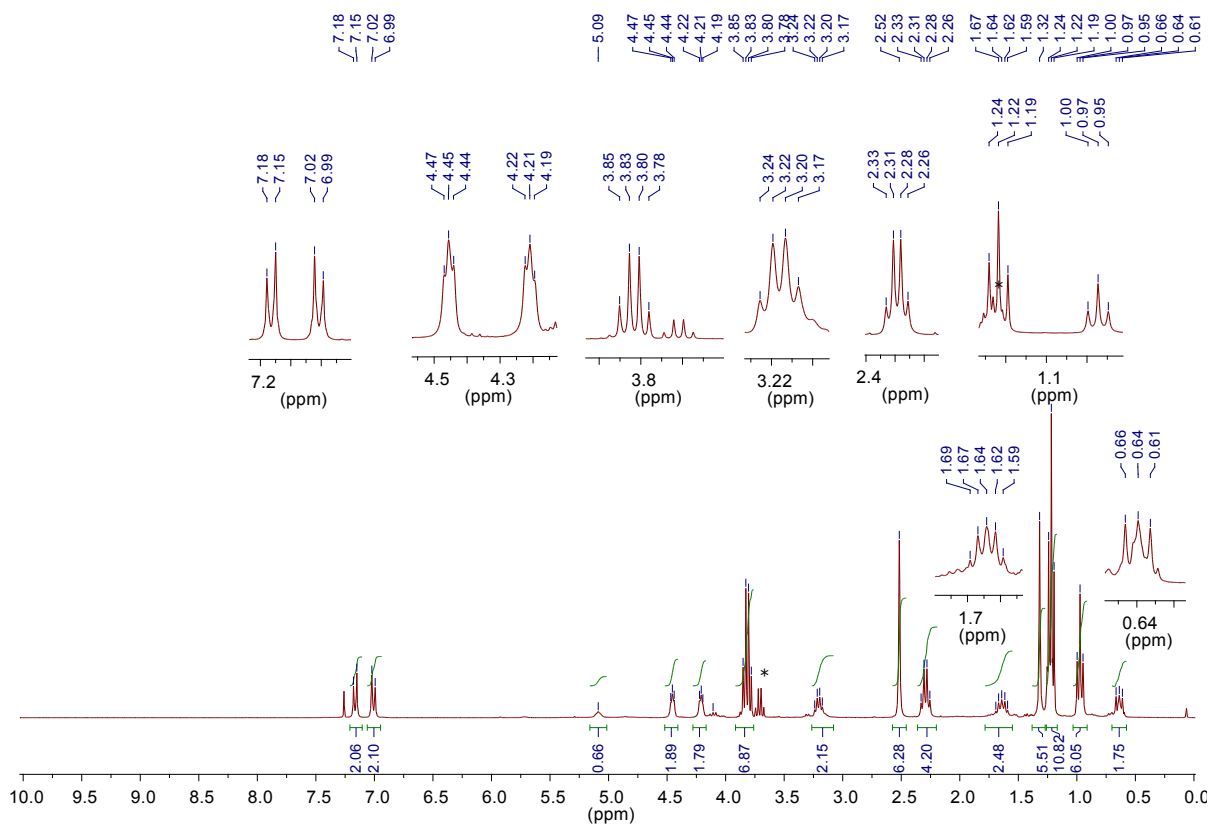


**Figure S3.**  $^{11}\text{B}$  NMR of compound **1**

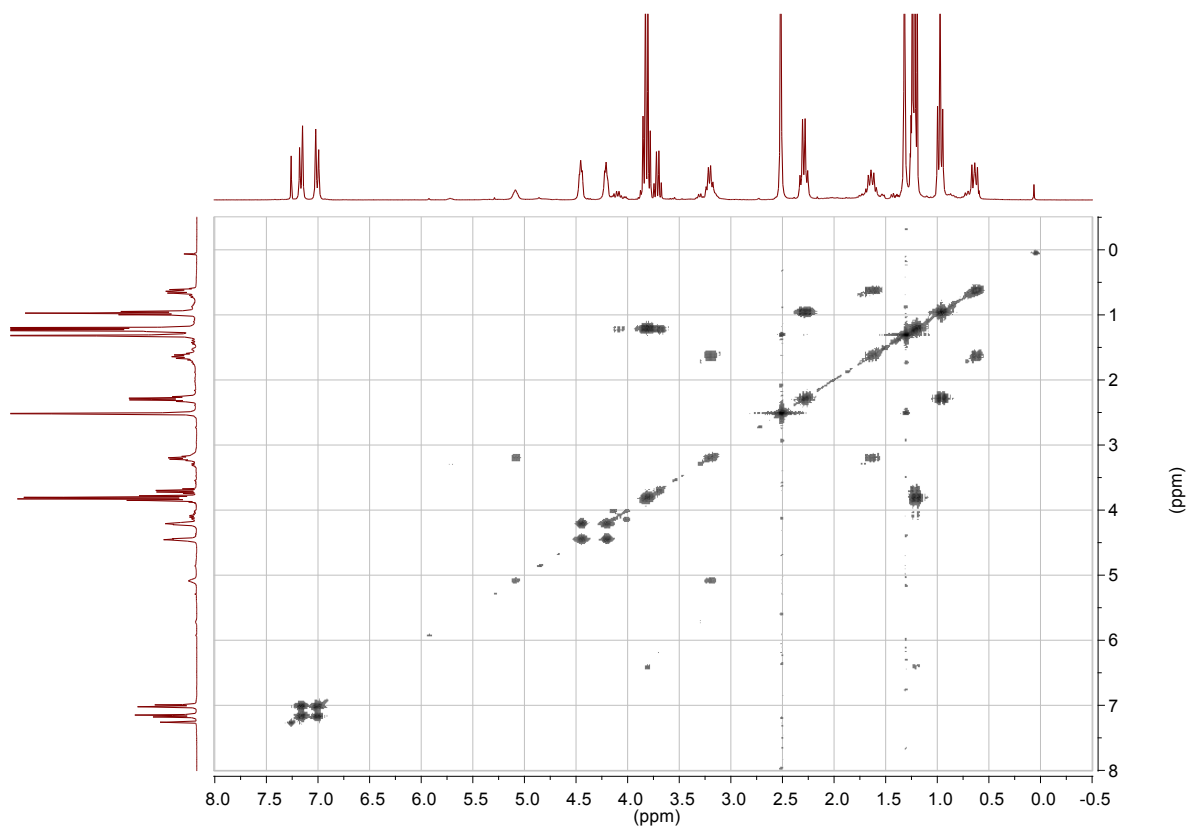
## Compound 2



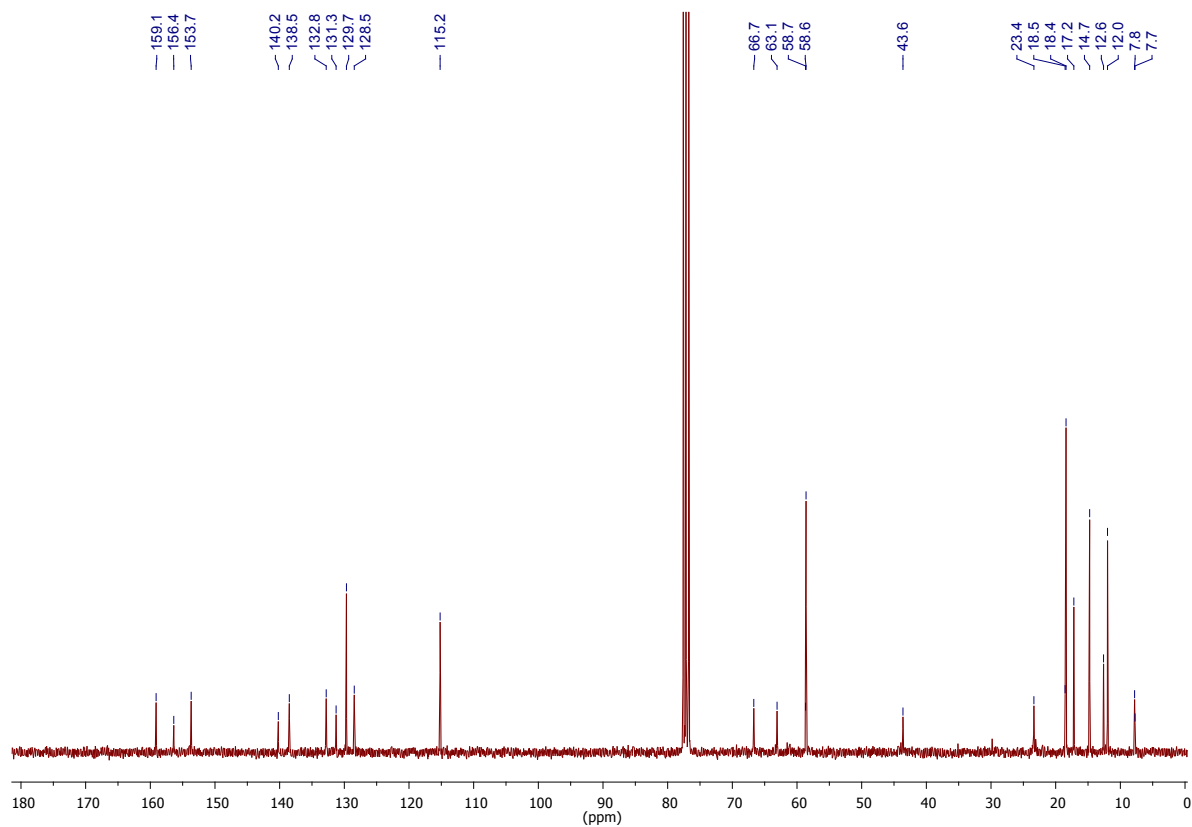
To a solution of Bodipy derivative **1** (100 mg, 227  $\mu\text{mol}$ ) in dry DCM under Ar were added a solution of 3-(triethoxysilyl)propyl isocyanate (225  $\mu\text{L}$ , 909  $\mu\text{mol}$ ) in dry DCM and a solution of DIPEA (160  $\mu\text{L}$ , 909  $\mu\text{mol}$ ) in dry DCM. The reaction was stirred at 40°C under Ar for 4 days. The reaction was concentrated *in vacuo* and purified by column chromatography (DCM/MeOH : 99/1) to yield **2** as a pink-red gum ( $m = 106$  mg ; R= 68%).  **$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )**  $\delta$  0.61-0.66 (m, 2H;  $-\text{CH}_2\text{Si}$ ), 0.97 (t,  $J = 7.5$  Hz, 6H; BDP- $\text{CH}_2\text{-CH}_3$ ), 1.22 (t,  $J = 7$ Hz, 9H;  $\text{SiO-CH}_2\text{-CH}_3$ ), 1.32 (s, 6H; BDP- $\text{CH}_3$ ), 1.59-1.69 (m, 2H;  $\text{CONH-CH}_2\text{-CH}_2$ ), 2.29 (q,  $J = 7.5$  Hz, 4H; BDP- $\text{CH}_2\text{-CH}_3$ ), 2.52 (s, 6H; BDP- $\text{CH}_3$ ), 3.17-3.24 (m, 2H;  $\text{CONH-CH}_2\text{-CH}_2$ ), 3.82 (q,  $J = 7$  Hz, 6H;  $\text{SiO-CH}_2$ ), 4.21 (t,  $J = 4.3$  Hz, 2H;  $\text{PhO-CH}_2$ ), 4.45 (t,  $J = 4.3$  Hz, 2H;  $-\text{CH}_2\text{-OCONH}$ ), 5.09 (s, 1H; NH), 7.01 (d,  $J = 8.6$  Hz, 2H;  $\text{H}_{\text{arom}}$ ), 7.17 (d,  $J = 8.6$  Hz, 2H;  $\text{H}_{\text{arom}}$ );  **$^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.7, 7.8, 12.0, 12.6, 14.8, 17.2, 18.4, 18.5, 23.4, 43.6, 58.6, 58.7, 63.1, 66.7, 115.2, 128.5, 129.7, 131.3, 132.8, 138.5, 140.2, 153.7, 156.4, 159.1;  **$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )**  $\delta$  -145.74 (q,  $J = 33.0$  Hz);  **$^{11}\text{B}$  NMR (96 MHz,  $\text{CDCl}_3$ )**  $\delta$  0.83 (t,  $J = 33.7$  Hz); **HRMS (ESI+)**  $m/z$  calcd for  $\text{C}_{35}\text{H}_{52}\text{BF}_2\text{N}_3\text{O}_6\text{Si-Na}$ : 710.3584  $[\text{M}+\text{Na}]^+$ , found: 710.3616.



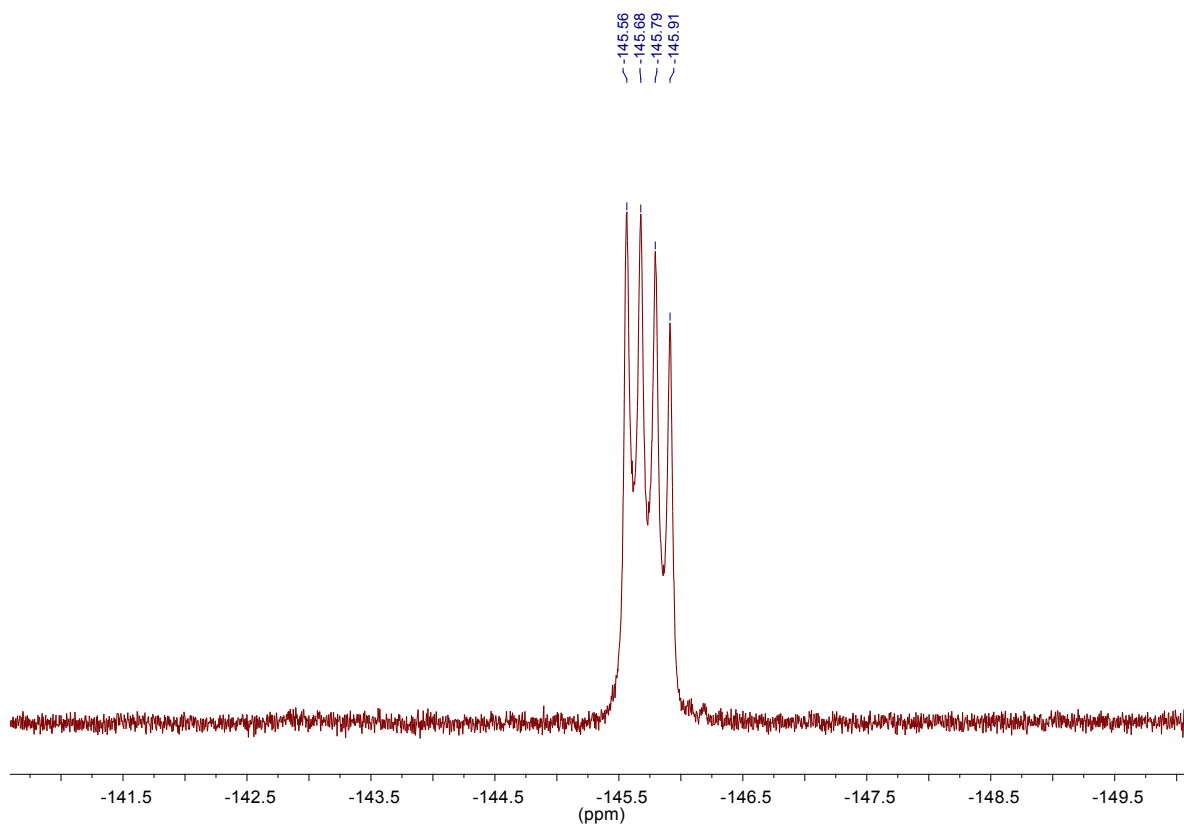
**Figure S4.**  $^1\text{H}$  NMR of compound 2. (\*NMR impurities)



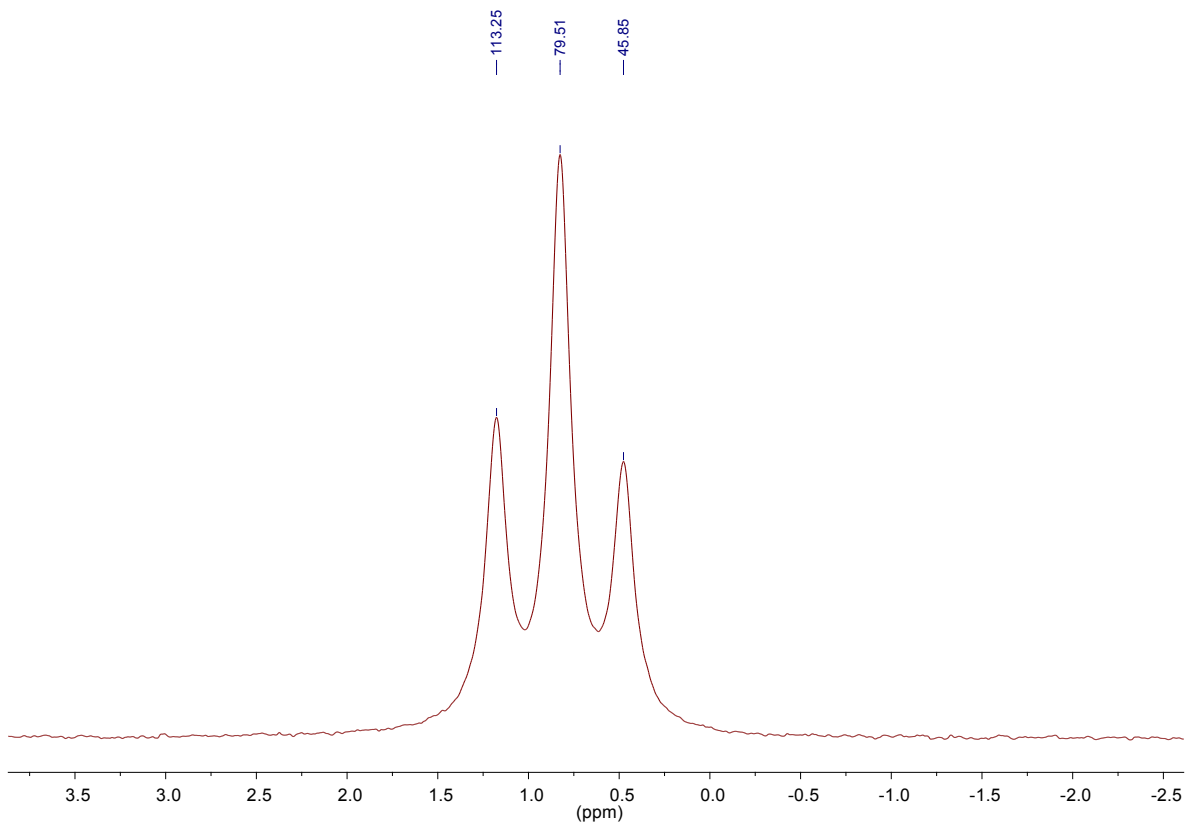
**Figure S5.** COSY of compound 2.



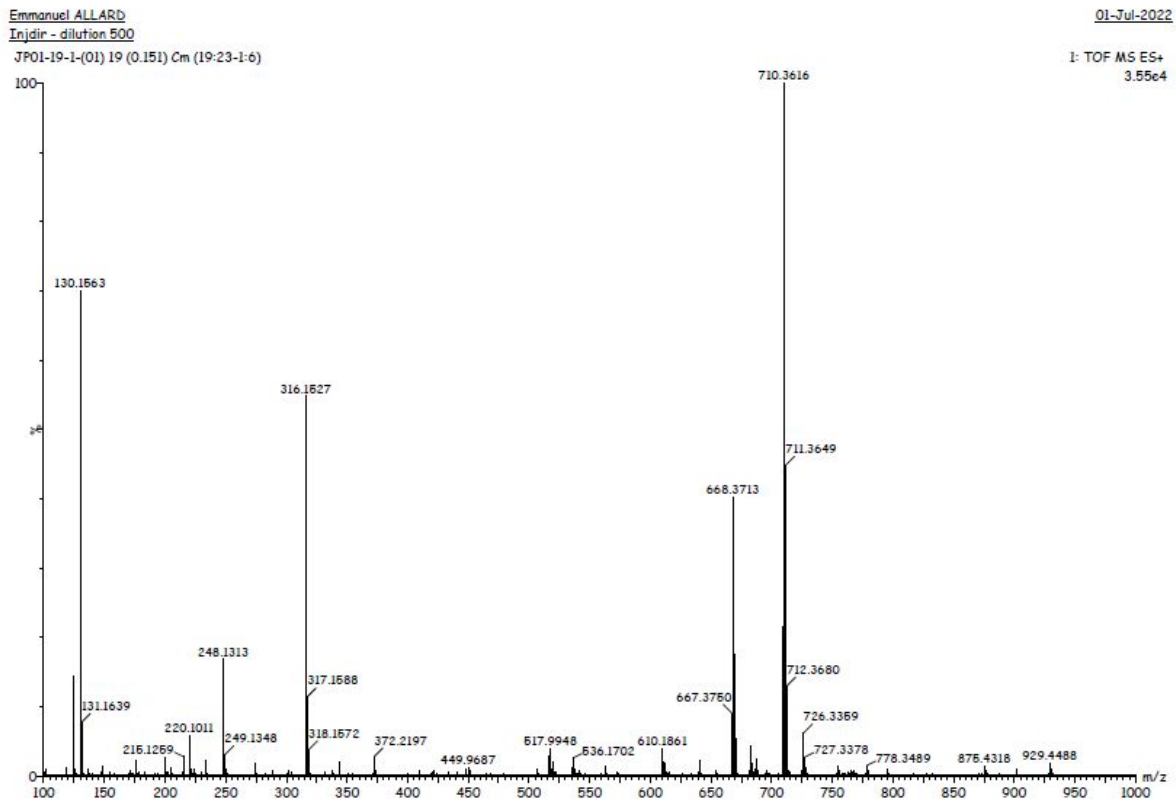
**Figure S6.**  $^{13}\text{C}$  NMR of compound 2



**Figure S7.**  $^{19}\text{F}$  NMR of compound 2



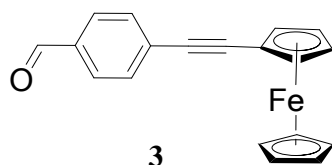
**Figure S8.**  $^{11}\text{B}$  NMR of compound 2



**Figure S9.** Mass spectrum of compound 2

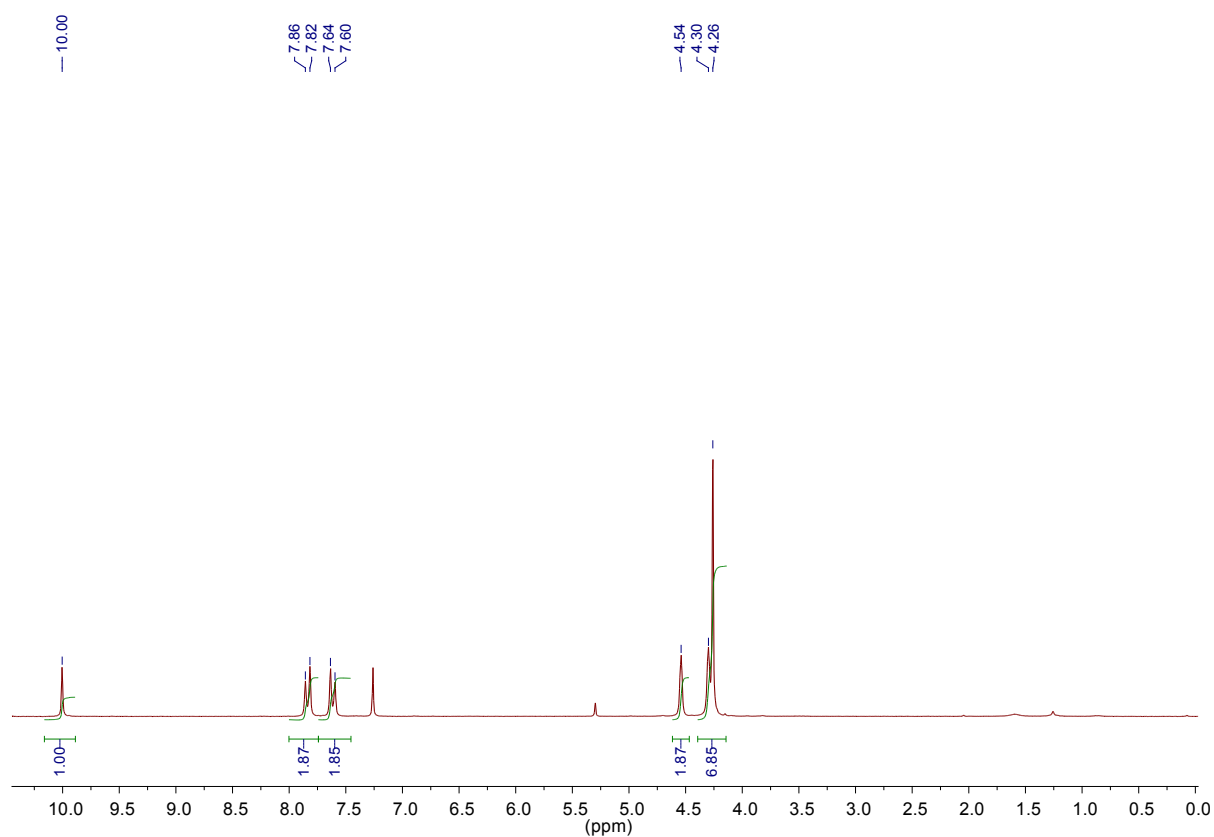


### Compound 3



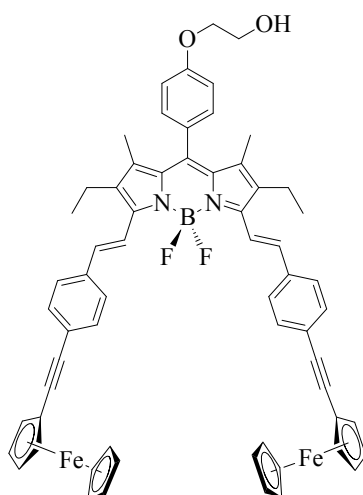
According to this procedure: T. Shoji, N. Kamata, A. Maruyama, S. Ito, T. Okujima, *Bull. Chem. Soc. Jpn.*, **2015**, 88, 1338-1346.

To a 25 mL flask under argon was added CuI (36 mg, 0.19 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (110 mg, 0.095 mmol), and 4-bromobenzaldehyde (200 mg, 1.09 mmol) in a mixture of THF/Et<sub>3</sub>N (1:1, 12 mL). Argon was bubbled through the solution for 30 min. Ethynylferrocene (400 mg, 1.90 mmol) was added. The mixture was heated overnight at 55°C under argon. The mixture was cooled to room temperature and concentrated under reduced pressure. After purification by column chromatography on silica gel (petroleum ether/AcOEt : 4/1), an orange solid was obtained (m = 330 mg ; R = 97%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.20-4.34 (m, 7H; H<sub>FC</sub>), 4.54 (bs, 2H; H<sub>FC</sub>), 7.62 (d, *J* = 8.1 Hz, 2H; H<sub>arom</sub>), 7.84 (d, *J* = 8.1 Hz, 2H; H<sub>arom</sub>), 10.0 (s, 1H; -CHO).



**Figure S10.** <sup>1</sup>H NMR of compound **3**

## Compound 4



4

To a 10 mL flask under argon was added compound **1** (50 mg, 0.13 mmol), compound **3** (143 mg, 0.45 mmol), and piperidine (0.1 mL, 1.0 mmol) in dry acetonitrile (4 mL). Argon was bubbled through the solution for 30 min. The mixture was refluxed overnight at 100°C under argon and in the presence of molecular sieves. The mixture was cooled to room temperature and concentrated under reduced pressure. After purification by column chromatography on silica gel (DCM/Et<sub>2</sub>O: 100/5), a green solid was obtained (m = 90 mg; R= 77%). **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)** δ 1.18 (t, *J* = 7.3 Hz, 6H; -CH<sub>2</sub>-CH<sub>3</sub>), 1.39 (s, 6H; -CH<sub>3</sub>), 2.07 (bs, 1H; -OH), 2.63 (q, *J* = 7.3 Hz, 4H; -CH<sub>2</sub>-CH<sub>3</sub>), 4.05 (bs, 2H; -CH<sub>2</sub>-OH), 4.14-4.21 (m, 2H; -CH<sub>2</sub>-O-), 4.27 (bs, 14H; H<sub>FC</sub>), 4.53 (bs, 4H; H<sub>FC</sub>), 7.06 (d, *J* = 8.4 Hz, 2H; H<sub>arom</sub>), 7.20-7.26 (m, 4H; H<sub>styryl</sub>, H<sub>arom</sub>), 7.51 (d, *J* = 8.2 Hz, 4H; H<sub>arom</sub>), 7.59 (d, *J* = 8.3 Hz, 4H; H<sub>arom</sub>), 7.82 (d, *J* = 16.7 Hz, 2H; H<sub>styryl</sub>); **<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)** δ -138.64 (q, *J* = 34.4 Hz); **<sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>)** δ 2.67 (t, *J* = 34.5 Hz); **<sup>13</sup>C NMR is missing due to insolubility**; **HRMS (ESI+)** m/z calcd for C<sub>63</sub>H<sub>55</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Fe<sub>2</sub>: 1032,3023 [M<sup>+</sup>], found: 1032.3066.

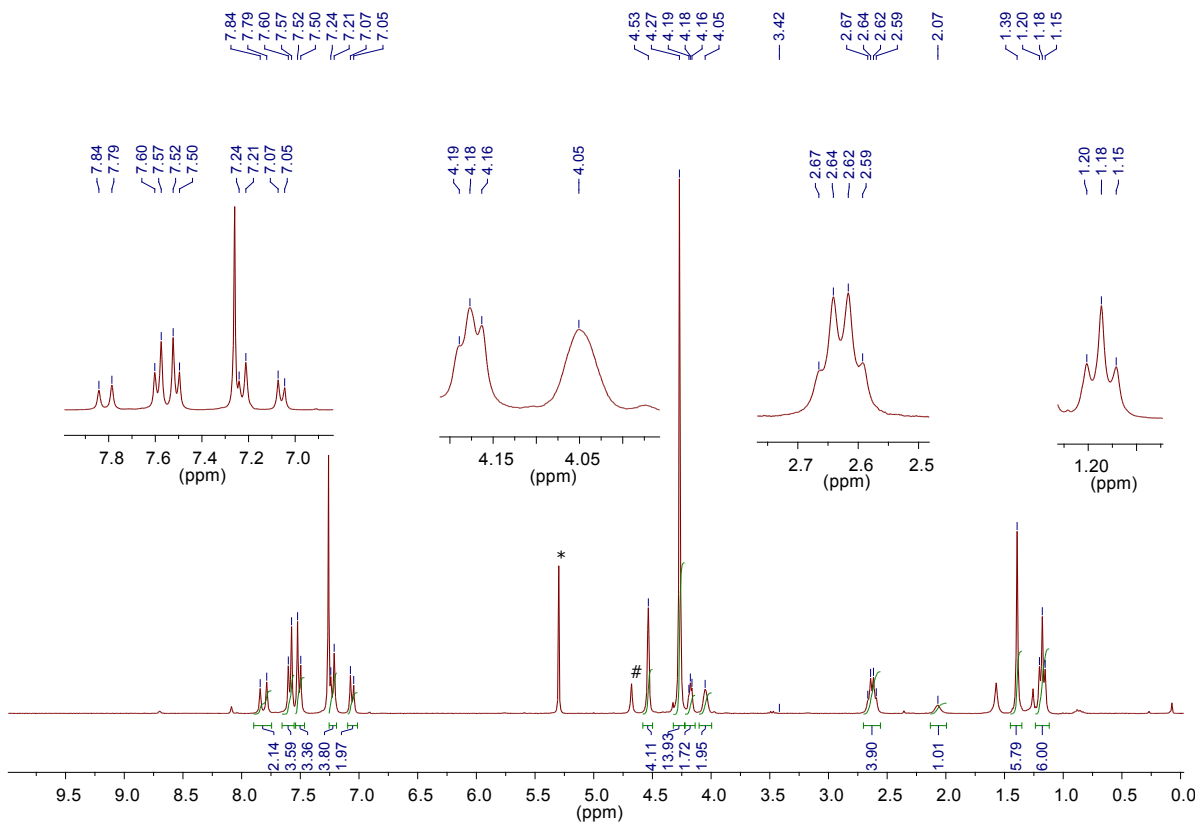


Figure S11.  $^1\text{H}$  NMR of compound 4. (\* solvent impurities; # NMR impurities)

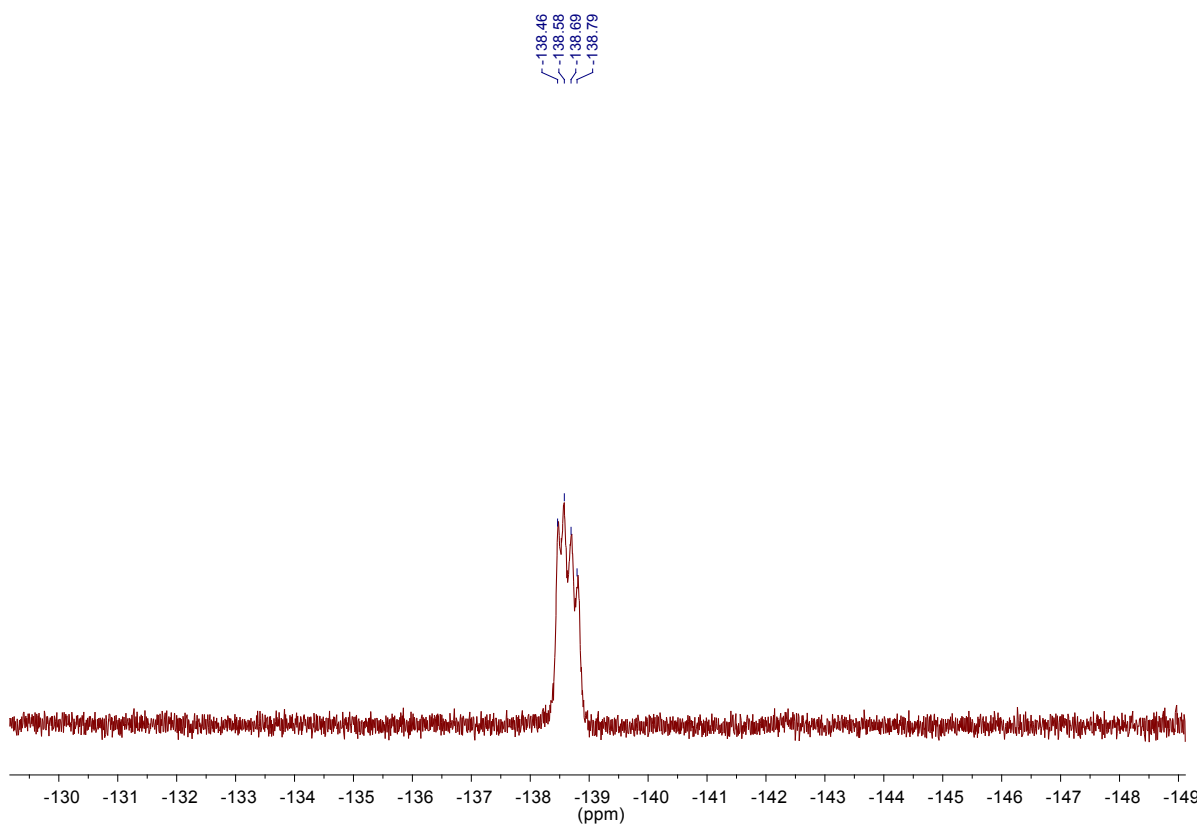


Figure S12.  $^{19}\text{F}$  NMR of compound 4

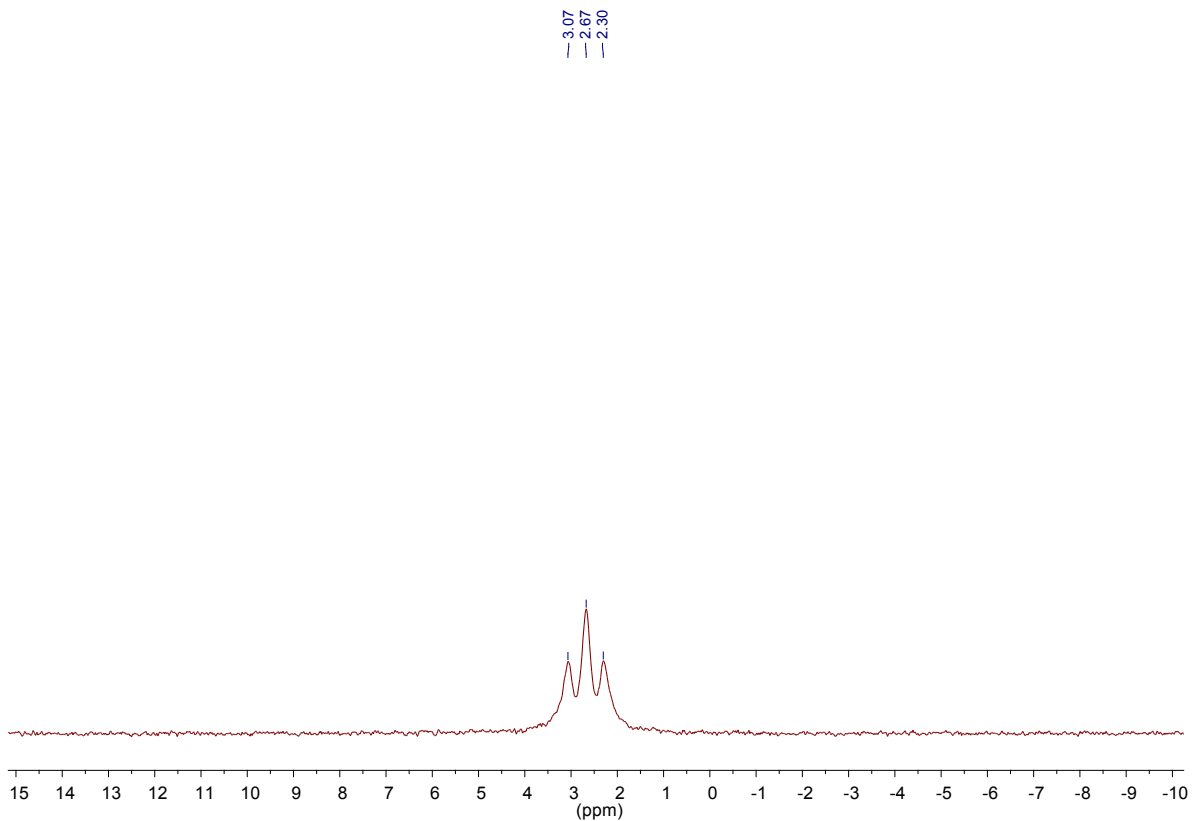


Figure S13.  $^{11}\text{B}$  NMR of compound 4

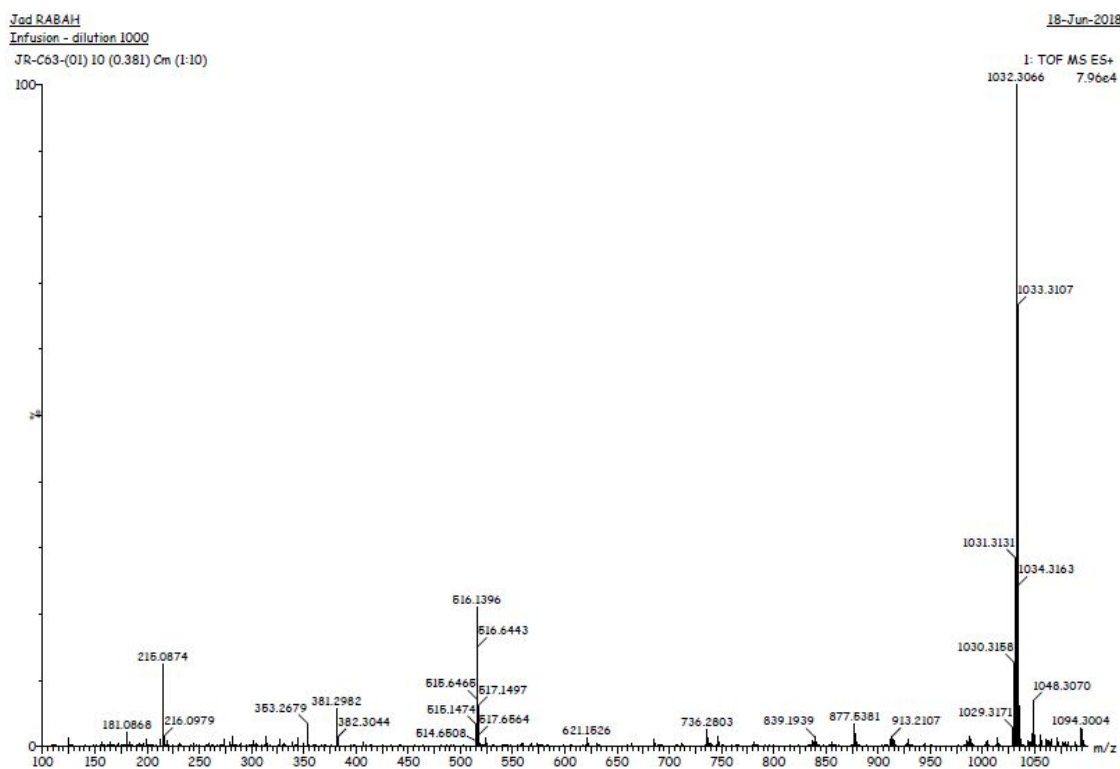
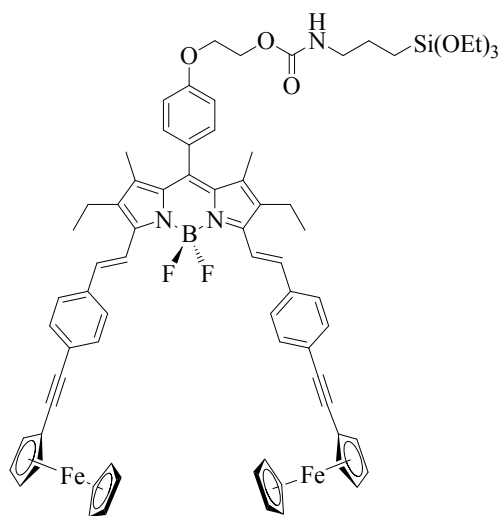


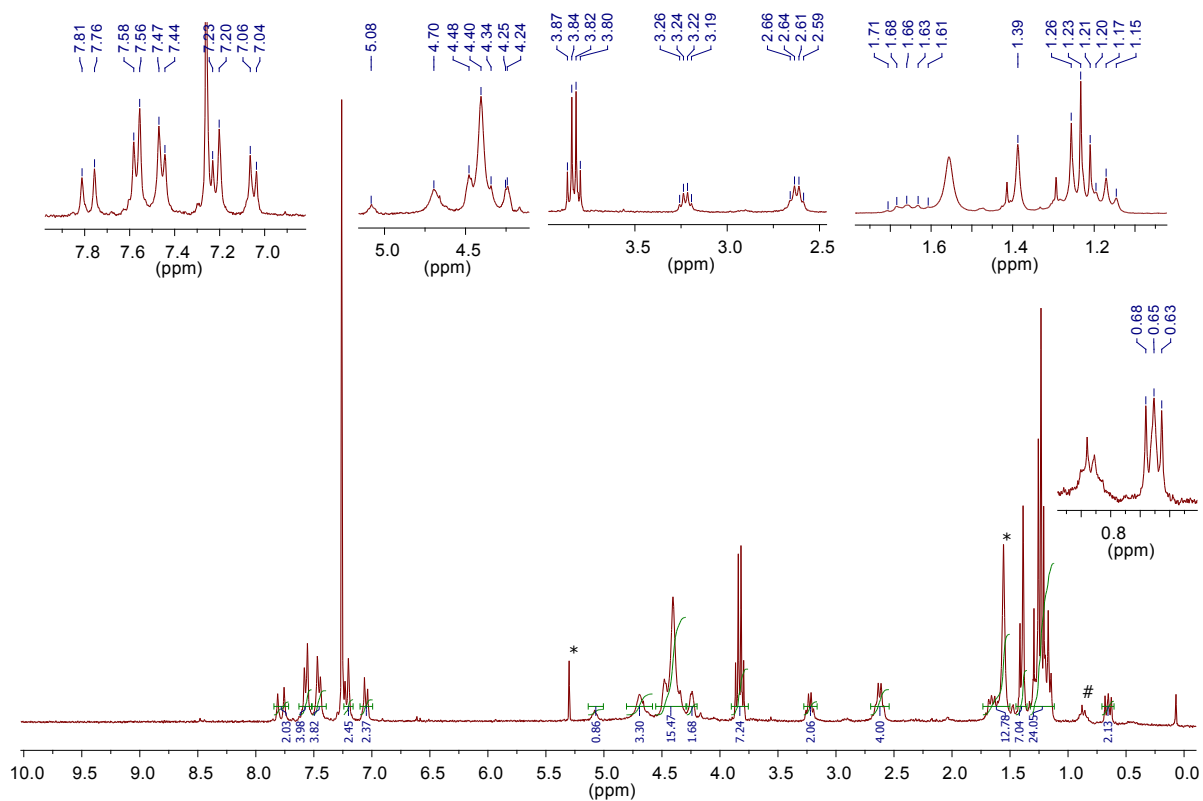
Figure S14. Mass spectrum of compound 4

## Compound 5

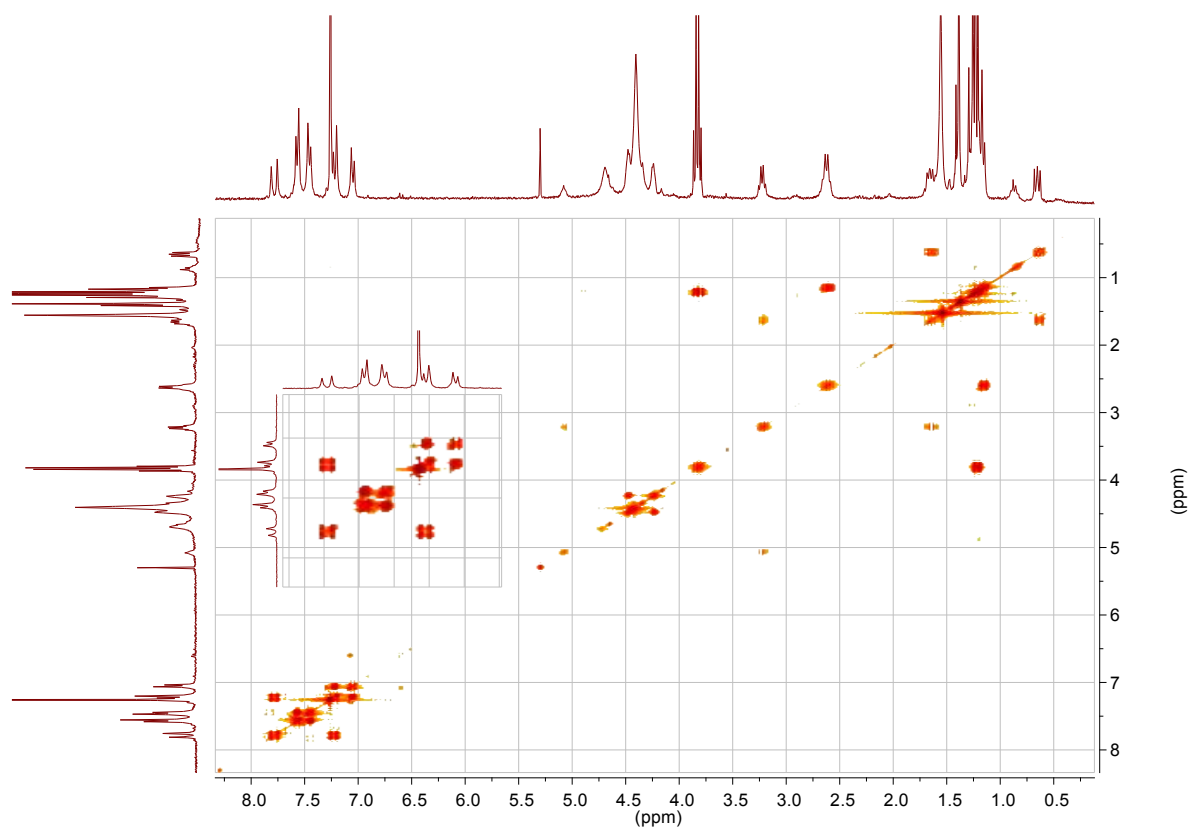


5

To a solution of Bodipy derivative **4** (26 mg, 25  $\mu\text{mol}$ ) in dry DCM (3 mL) under Ar were added 3-(triethoxysilyl)propyl isocyanate (25  $\mu\text{L}$ , 100  $\mu\text{mol}$ ) and DIPEA (17  $\mu\text{L}$ , 100  $\mu\text{mol}$ ). The reaction was stirred in a sealed tube at 40°C under Ar for 3 days. Further isocyanate (25  $\mu\text{L}$ , 100  $\mu\text{mol}$ ) and DIPEA (17  $\mu\text{L}$ , 100  $\mu\text{mol}$ ) were added and stirring at 40°C continued for 4 days. The reaction was concentrated *in vacuo* and purified by column chromatography (DCM/MeOH : 98/2 then 97/3) to yield **5** as a dark green solid ( $m = 27$  mg ;  $R = 84\%$ ).  **$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )**  $\delta$  0.63-0.68 (m, 2H;  $\text{CH}_2\text{-Si}$ ), 1.17 (t,  $J = 7.5$  Hz, 6H;  $\text{BDP-CH}_2\text{-CH}_3$ ), 1.23 (t, 9H,  $J = 7.0$  Hz;  $\text{SiO-CH}_2\text{-CH}_3$ ), 1.39 (s, 6H;  $-\text{CH}_3$ ), 1.61-1.71 (m, 2H;  $\text{CONH-CH}_2\text{-CH}_2$ ), 2.63 (q,  $J = 7.1$  Hz, 4H;  $\text{BDP-CH}_2\text{-CH}_3$ ), 3.19-3.26 (m, 2H;  $\text{CONH-CH}_2\text{-CH}_2$ ), 3.83 (q,  $J = 7.0$  Hz, 6H;  $\text{SiO-CH}_2$ ) 4.19-4.28 (m, 2H;  $\text{PhO-CH}_2$ ), 4.29-4.54 (m, 16H;  $\text{H}_{\text{Fc}}$ ,  $-\text{CH}_2\text{-OCONH}$ ), 4.70 (bs, 4H;  $\text{H}_{\text{Fc}}$ ), 5.09 (s, 1H; NH), 7.05 (d,  $J = 8.3$  Hz, 2H;  $\text{H}_{\text{arom}}$ ), 7.16-7.23 (m, 4H;  $\text{H}_{\text{styryl}}$ ,  $\text{H}_{\text{arom}}$ ), 7.46 (d,  $J = 7.9$  Hz, 4H;  $\text{H}_{\text{arom}}$ ), 7.57 (d,  $J = 7.9$  Hz, 4H;  $\text{H}_{\text{arom}}$ ), 7.79 (d,  $J = 16.7$  Hz, 2H;  $\text{H}_{\text{styryl}}$ );  **$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )**  $\delta$  -138.69 (bq);  **$^{11}\text{B}$  NMR (96 MHz,  $\text{CDCl}_3$ )**  $\delta$  1.48 (t,  $J = 33.6$  Hz).



**Figure S15.**  $^1\text{H}$  NMR of compound **5**. (\* solvent impurities; # NMR impurities)



**Figure S16.** COSY of compound **5**

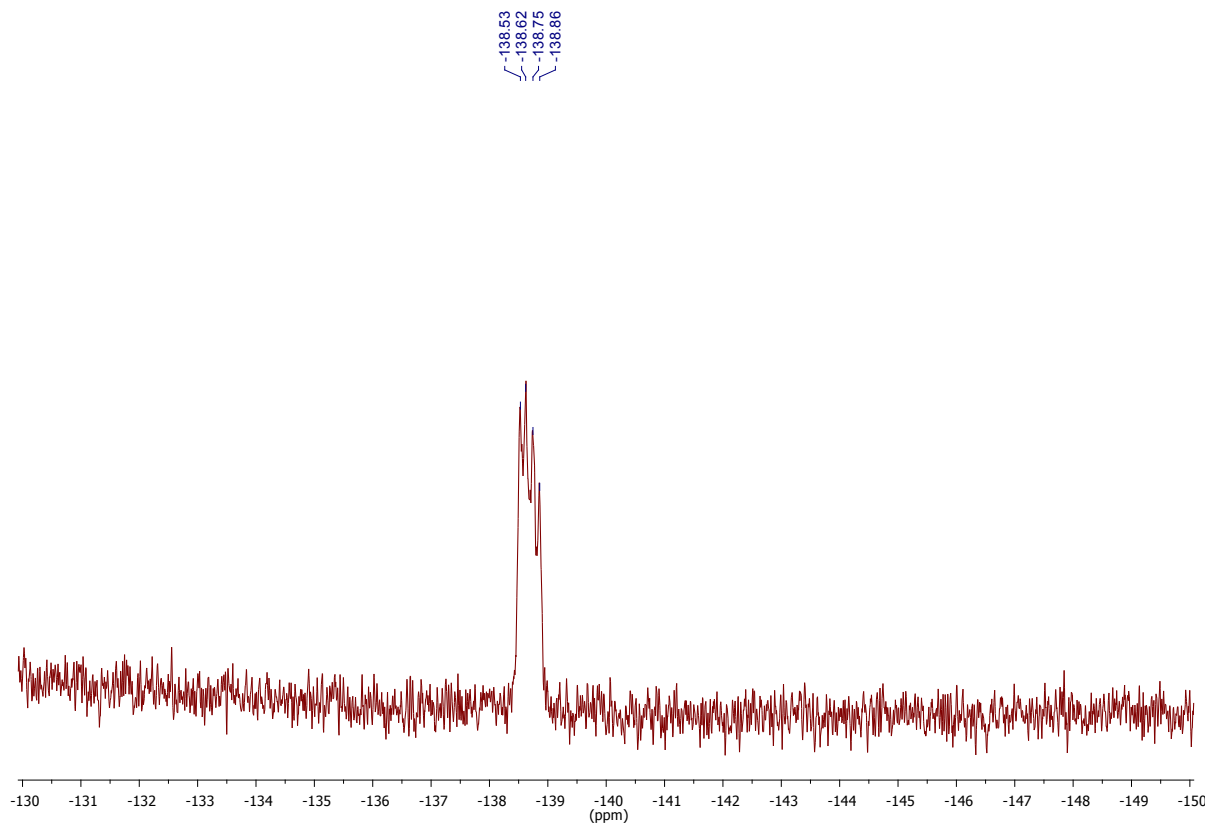


Figure S17.  $^{19}\text{F}$  NMR of compound 5

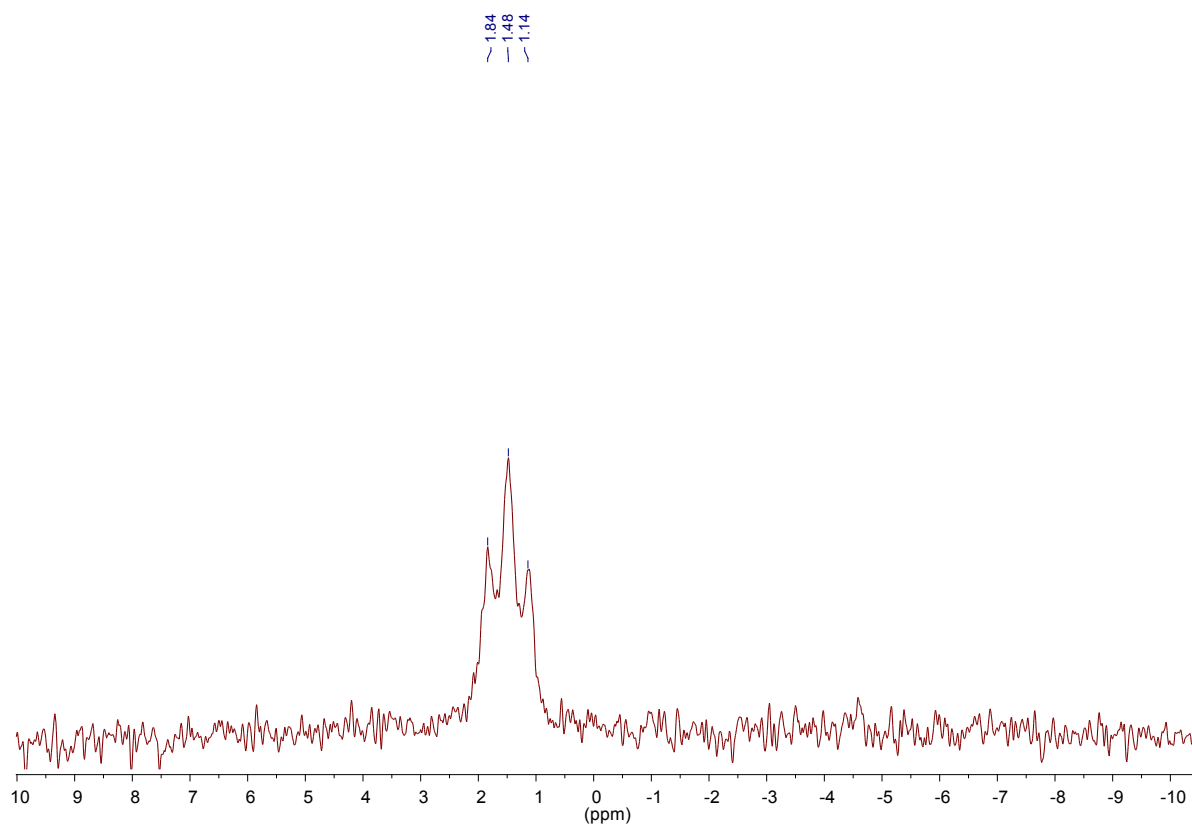
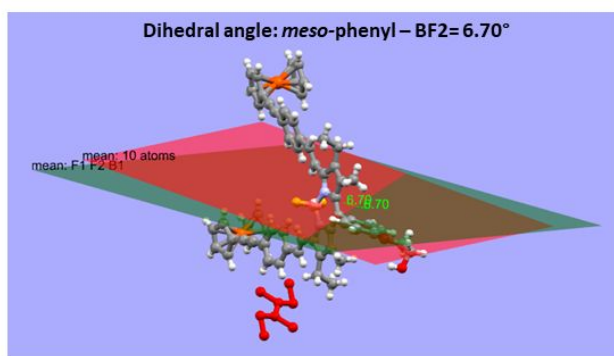
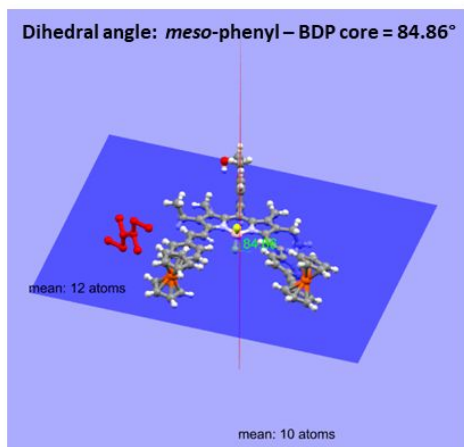
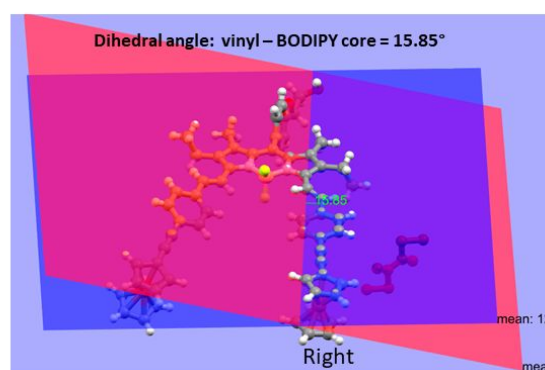
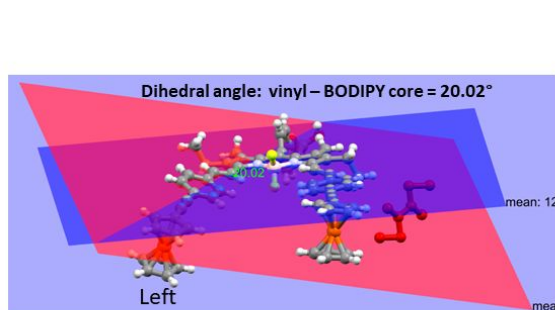


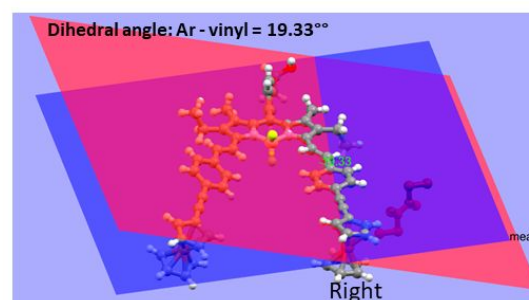
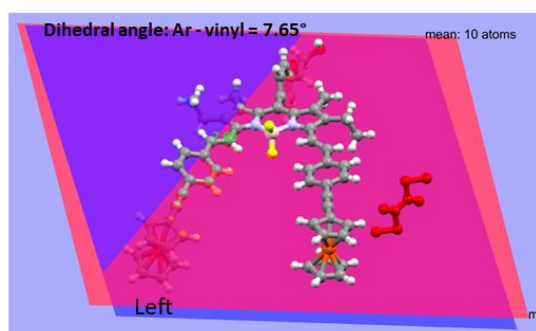
Figure S18.  $^{11}\text{B}$  NMR of compound 5



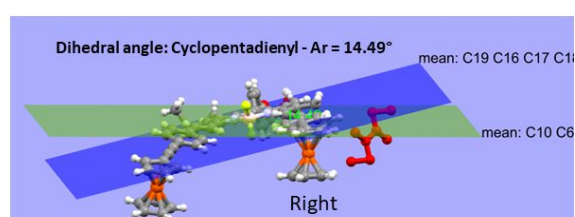
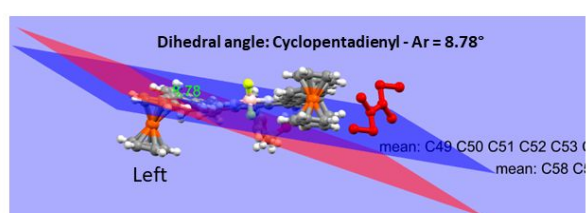
**Figure S19.** Left) Dihedral angle between the *meso*-phenyl group and BODIPY platform; Right) Dihedral angle between the *meso*-phenyl group and BF<sub>2</sub> unit.



**Figure S20.** Dihedral angles between the vinyl group and the BODIPY core.



**Figure S21.** Dihedral angles between the aromatic and the vinyl groups in the styryl unit.



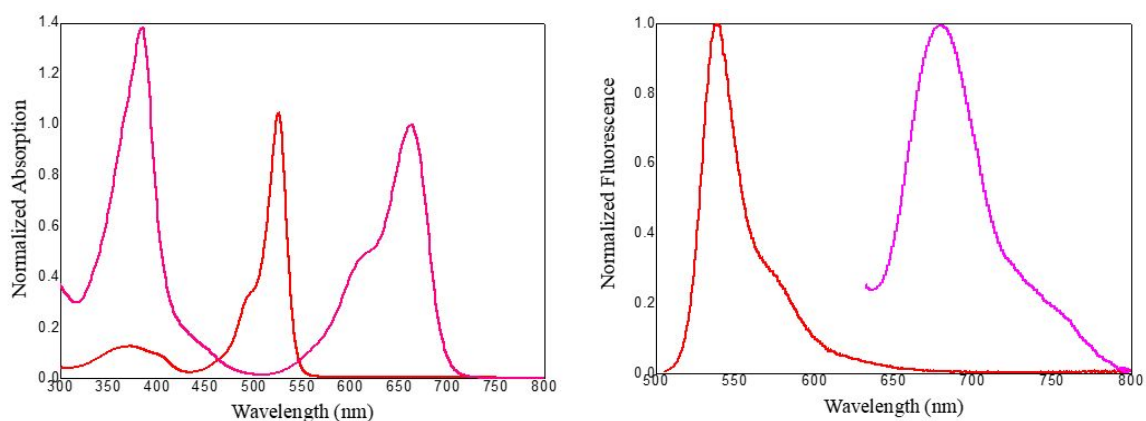
**Figure S22.** Dihedral angles between the cyclopentadienyl unit and the aromatic group.



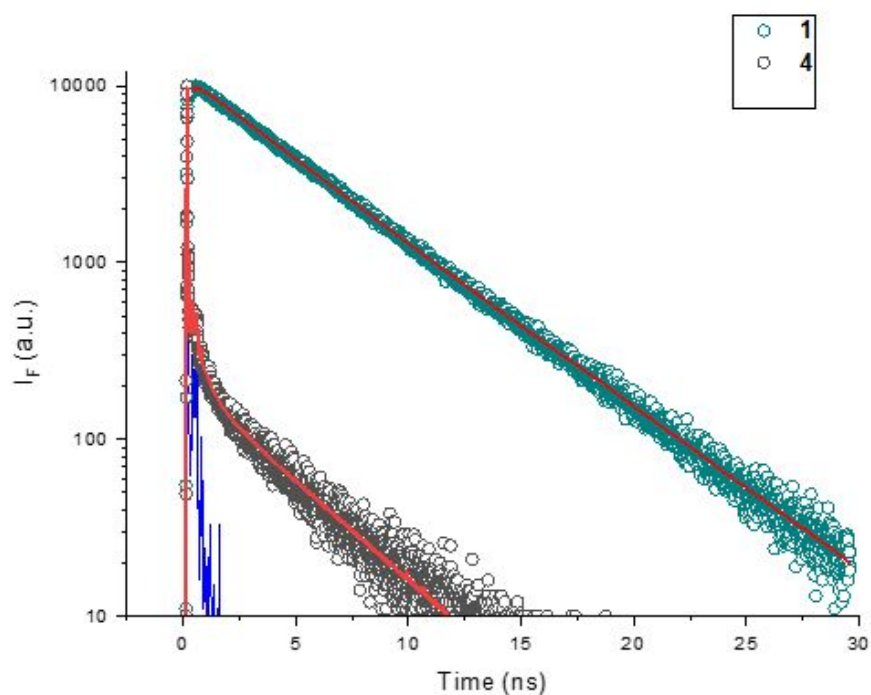
**Table S1.** Selected Dihedral Angles of compound **4**.

	<b>Vinyl - BDP</b>	<b>Ar - Vinyl</b>	<b>Ar - BDP</b>	<b>Cyclopentadieny I- Ar</b>	<b>CyclopentadienyI- BDP</b>
Dihedral angles	20.02 (left) <sup>a</sup> 15.85°(right) <sup>a</sup>	7.65°(left) <sup>a</sup> 19.33°(right) <sup>a</sup>	27.78° (left) <sup>a</sup> 3.46° (right) <sup>a</sup>	8.78° (left) <sup>a</sup> 14.49°(right) <sup>a</sup>	22.49° (left) <sup>a</sup> 11.18° (right) <sup>a</sup>

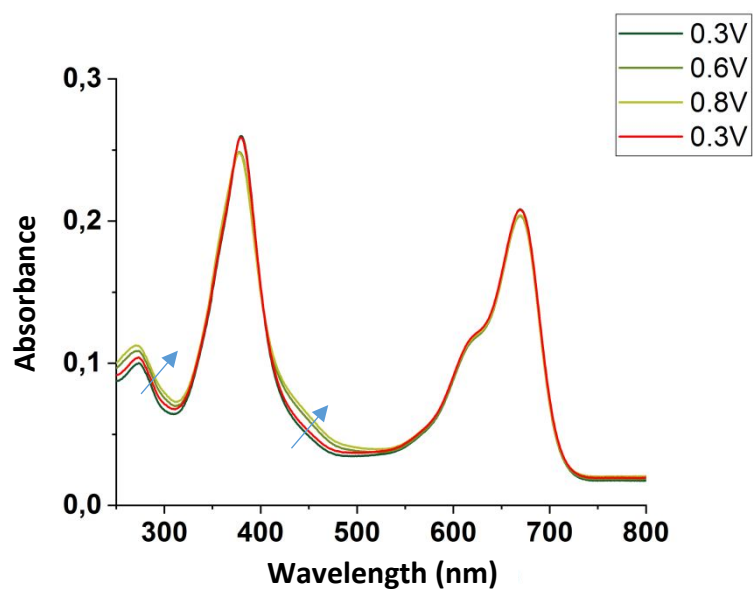
<sup>a</sup> See Figures S20-S22



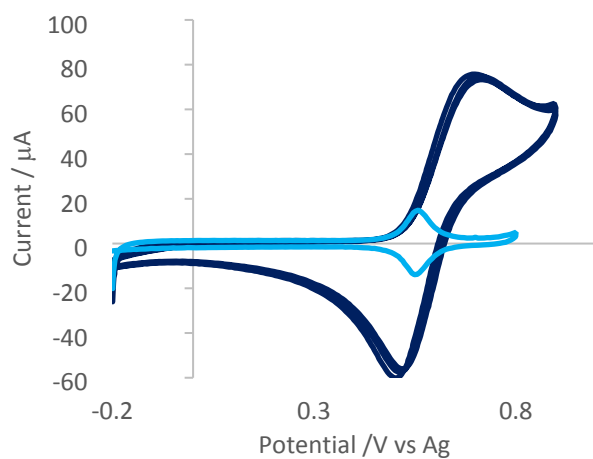
**Figure S23. Left)** Normalized absorption spectra of Bodipy starting material **1** (red) and target assembly **4** (pink). **Right)** Normalized fluorescence spectra of Bodipy starting material **1** (red,  $\lambda_{exc} = 495$  nm) and target assembly **4** (pink,  $\lambda_{exc} = 590$  nm)



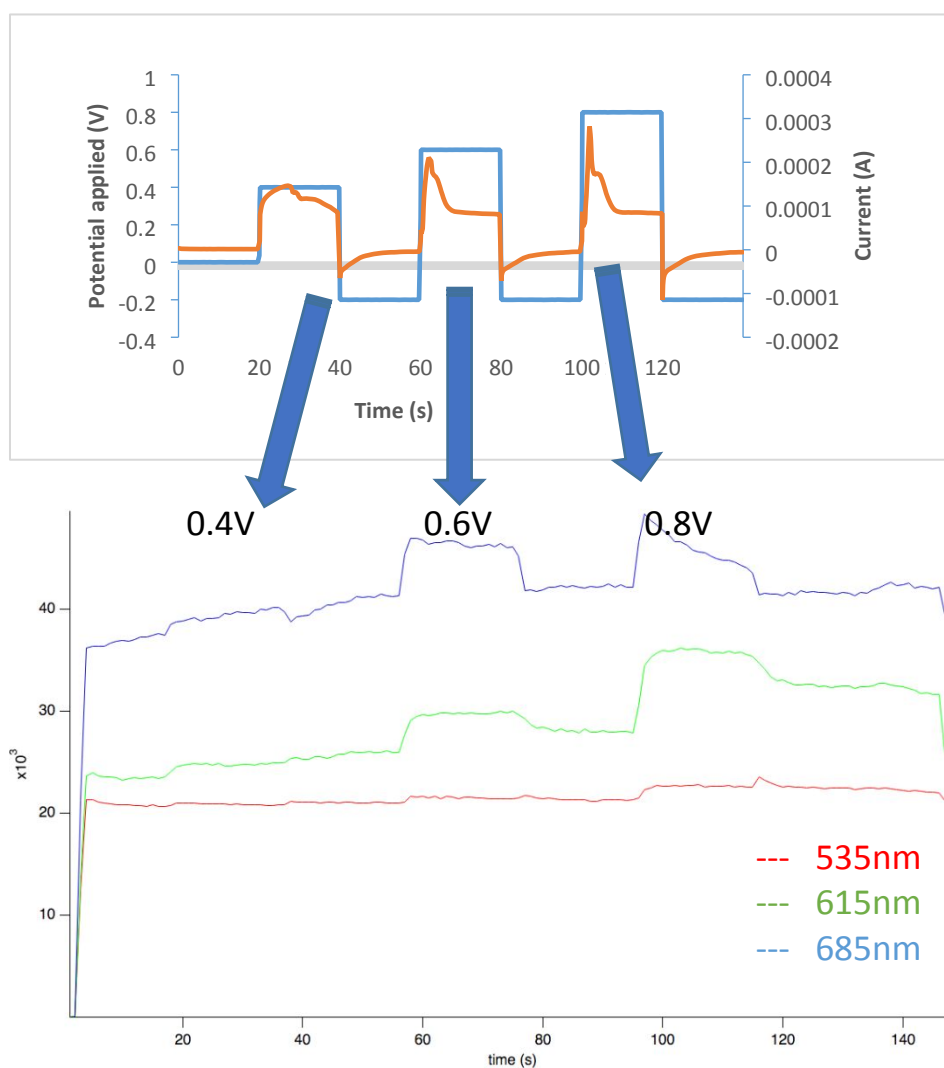
**Figure S24.** Fluorescence decays obtained by TCSPC of BODIPY **1** ( $\lambda_{exc} = 510$  nm,  $\lambda_{em} = 540$  nm) and  $\alpha$ -bis-Fc-ethynylstyryl-BODIPY **4** ( $\lambda_{exc} = 350$  nm,  $\lambda_{em} = 680$  nm) in dichloromethane. Lifetimes: **1**: 5.2 ns, **4**: mean lifetime  $\sim$ IRF



**Figure S25:** UV-vis spectroelectrochemistry of compound **4** 0.2 mM in DCM + TBAPF<sub>6</sub> 0.1M. Potentials vary from 0.3 V to 0.8 V (blue to yellow) and then back to 0.3 V (red).



**Figure S26:** CV of ITO-5 (sky blue) and 5 in acetonitrile + TBAPF<sub>6</sub> 0.1M at 100 mV/s. Potentials refer to Ag wire (-0.35 V vs. Fc<sup>+</sup>/Fc).



**Figure S27:** Electrochemical signal (top) and Fluorescence intensity modulation at various emission wavelengths (bottom) vs. time for **5-ITO** in acetonitrile (+TBAPF<sub>6</sub> 0.1M).