Supporting information for

Modulation of ICT probability in bi(polyarene)-based *O*-BODIPYs: Towards the development of low-cost bright arene-BODIPY dyads

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S1. General

S1.1. Synthesis

Common solvents were dried and distilled by standard procedures. All starting materials and reagents were obtained commercially and used without further purifications. Elution flash chromatography was conducted on silica gel (230-400 mesh ASTM). Thin layer chromatography (TLC) was performed on silica gel plates (silica gel 60 F254, supported on aluminum). NMR spectra were recorded at 20 ºC, and the residual solvent peaks were used as internal standards. NMR signals are given in ppm. DEPT-135 NMR experiments were used for the assignation of the type of carbon nucleus (C, CH, CH_2, CH_3). FTIR spectra were recorded from neat samples using ATR technique. IR bands are given in cm^{-1}. High-resolution mass spectrometry (HRMS) was performed using the ESI technique for the ionization and ion tramp (positive mode) for the detection.

S1.2. Spectroscopic measurements

The photophysical properties were registered using quartz cuvettes with optical pathway of 1 cm in diluted solutions (around 2×10^{-6} M), prepared by adding the corresponding solvent to the residue from the adequate amount of a concentrated stock solution in acetone, after vacuum evaporation of this solvent. UV-Vis absorption and fluorescence spectra were recorded on a Varian model CARY 4E spectrophotometer and an Edinburgh Instruments spectrofluorimeter (model FLSP920), respectively. Fluorescence quantum yield (ϕ) was obtained by using the corresponding commercial dyes (PM567, PM605 and PM650) in ethanol as reference (ϕ^r = 0.84, 0.66 and 0.10, respectively). Radiative decay curves were registered with the time correlated single-photon counting technique (Edinburgh Instruments, model FL920), equipped with a microchannel plate detector (Hamamatsu C4878) of picosecond time-resolution (20 ps). Fluorescence emission was monitored at the maximum emission wavelength after excitation at 470 and 530 nm by means of a diode laser (PicoQuant, model LDH470 and LDH530) with 150 ps FWHM pulses. The fluorescence lifetime (τ) was obtained after the deconvolution of the instrumental response signal from the recorded decay curves by means of an iterative method. The goodness of the exponential fit was controlled by statistical parameters (chi-square) and the analysis of the residuals. Radiative (k_{fl}) and non-radiative (k_{nr}) rate constants were calculated as follows; $k_{fl} = \phi/\tau$ and $k_{nr} = (1-\phi)/\tau$.

S1.3. Computational simulations

Ground state energy minimizations were performed using the Becke´s Three Paramaters (B3LYP) Density Functional (DFT) method and the double valence 6-31+g* (with a diffuse and polarization function). The optimized geometry was taken as a true energy minimum using frequency calculations (no negative frequencies). The absorption profile was simulated with the Time Dependent (TD-DFT) method. The solvent effect (chloroform) was considered in all the calculations by the Polarizable Continuum Model (PCM). All the calculations were performed in Gaussian 09, using the “arina” computational resources provided by the UPV-EHU.

S1.4. Electrochemistry

Voltammograms (Metrohm Autolab) were recorded using a three-electrode set up with a platinum disk (diameter 3 mm), for the commercial dyes, or layer (surface 8 mm x 7.5 mm), for the novel *O*-BODIPYs, as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. 0.1 M solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dry acetonitrile was used as the electrolyte solvent. The studied compounds were dissolved in the solution to achieve a concentration of 0.5-1.0 mM. All redox potentials were reported *vs.* ferrocene, as the internal standard. The solutions were purged with argon and all the measurements were performed under argon.

S2. Photophysical and computational results (Table S1-S2 and Figs. S1-S6)

Table S1. Photophysical properties of BINOL-based *O*-BODIPYs **1a**, **2a** and **3a** (derived from PM567, PM605 and PM650, respectively) in different solvents (2 μM).

BODIPY *solvent*	λ_{ab} [a] (nm)	$\varepsilon_{max}\cdot10^{-4}$ [b] (M^{-1} cm^{-1})	λ_{fl} [c] (nm)	$\Delta\nu_{St}$ [d] (cm^{-1})	Φ [e]	τ [f] (ns)	$k_{fl}\cdot10^{-8}$ [g] (s^{-1})	$k_{nr}10^{-8}$ [h] (s^{-1})
1a								
hexane	523.0	6.7	546.0	805	0.89	5.99	1.48	0.18
acetone	517.0	7.3	537.5	740	0.67	5.86	1.14	0.39
acetonitrile	516.0	7.3	534.0	655	0.65	6.05	1.08	0.58
chloroform	525.0	6.0	550.0	865	0.47	5.84	0.80	0.90
2a								
hexane	549.5	5.6	579.5	940	0.13	1.72	0.75	5.06
acetone	545.5	5.3	563.5	585	0.011	-	-	-
acetonitrile	544.5	5.1	560.5	525	0.008	-	-	-
chloroform	552.0	5.7	563.5	650	0.031	-	-	-
3a								
hexane	587.0	3.6	-	-	0	-	-	-
acetone	587.5	3.1	-	-	0	-	-	-
acetonitrile	586.0	3.2	-	-	0	-	-	-
chloroform	593.5	3.1	-	-	0	-	-	-

[a]Absorption wavelength. [b]Molar absorption. [c]Fluorescence wavelength. [d]Stokes shift. [e]Fluorescence quantum yield. [f]Fluorescence lifetime. [g]Radiative rate constant; [h]Non-radiative rate constants

Table S2. Photophysical properties of BINOL-based *O*-BODIPYs **4a**, **5a**, **6a** and **7a** in hexane (2μM).

	λ_{ab} (nm)	$\varepsilon_{max}\cdot10^{-4}$ (M^{-1} cm^{-1})	λ_{fl} (nm)	$\Delta\nu_{St}$ (cm^{-1})	Φ	τ [a] (ns)
4a	504.0	4.4	536.0	1185	0.017	0.97(22%) - 5.60(78%)
5a	515.0	7.2	532.0	620	0.001	-
6a	503.0	4.5	525.0	835	0.006	-
7a	500.0	6.0	513.0	505	0.021	0.21(73%) - 4.69(27%)

[a]Weight of each lifetime from the biexponential fit.

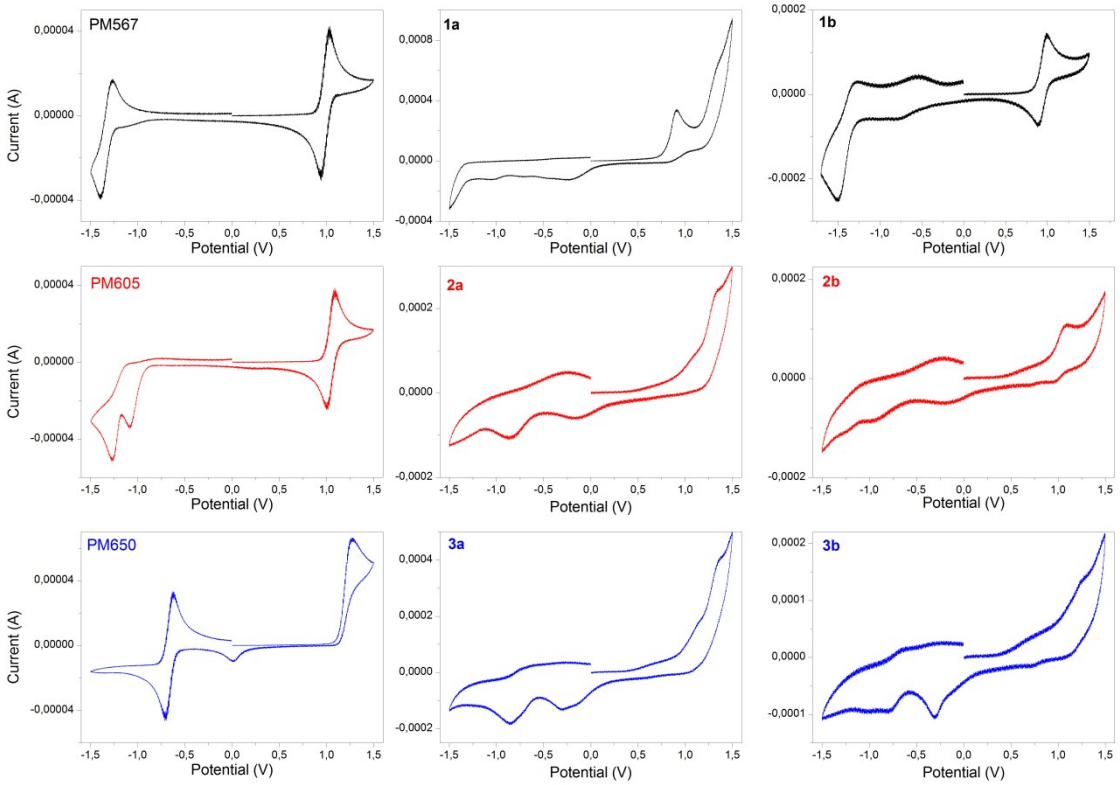


Figure S1. Cyclic voltammograms of PM567, PM605 and PM605 (left column) and their derivatives bearing BINOL (central column) and brominated BINOL (right column) at the boron bridge in milimolar solutions of acetonitrile (0.1 M $TBAPF_6$).

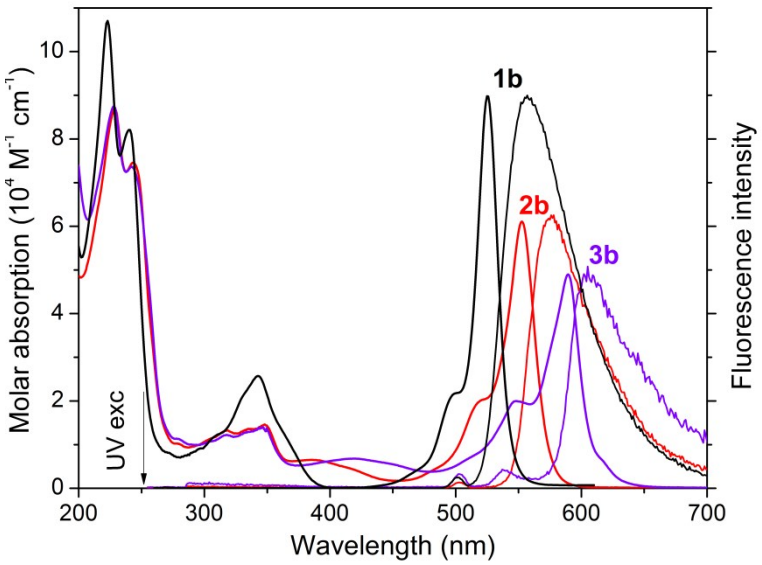


Figure S2. UV-Vis absorption and normalized fluorescence (under excitation at 250 nm) spectra of 3,3´-dibromoBINOLated *O*-BODIPYs **1b**, **2b** and **3b** in hexane.

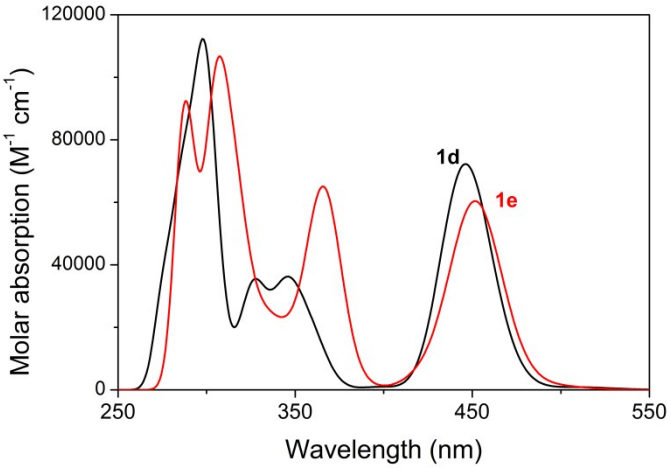


Figure S3. Simulated absorption spectra (TD-B3LYP/6-31+g*) of **1d** and **1e** in chloroform. The spectra were obtained after gaussian convolution of the vertical electronic transitions with a full width at half maximum of 800 cm^{-1}.

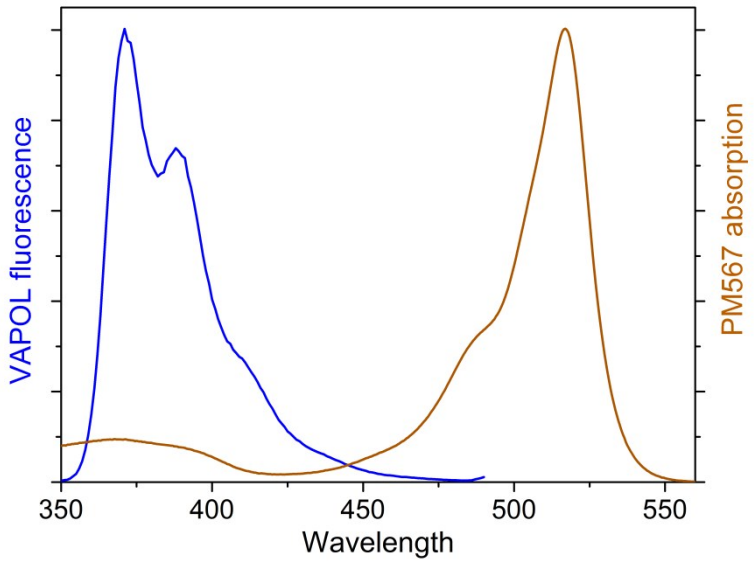


Figure S4. Spectral overlap between the VAPOL fluorescence band and the PM567 absorption band, enabling FRET mechanism in the EET of **1e**.

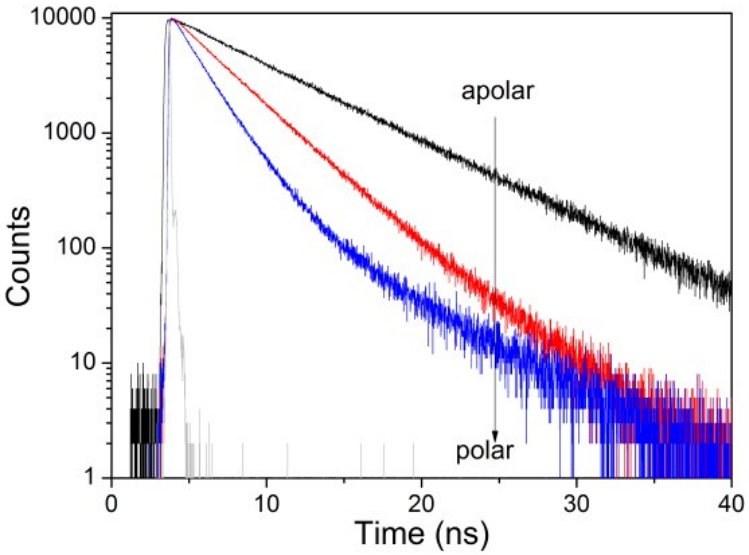


Figure S5. Fluorescence decay curves of **1e** as a function of the solvent polarity. Hexane (black), acetone (red), acetonitrile (blue).

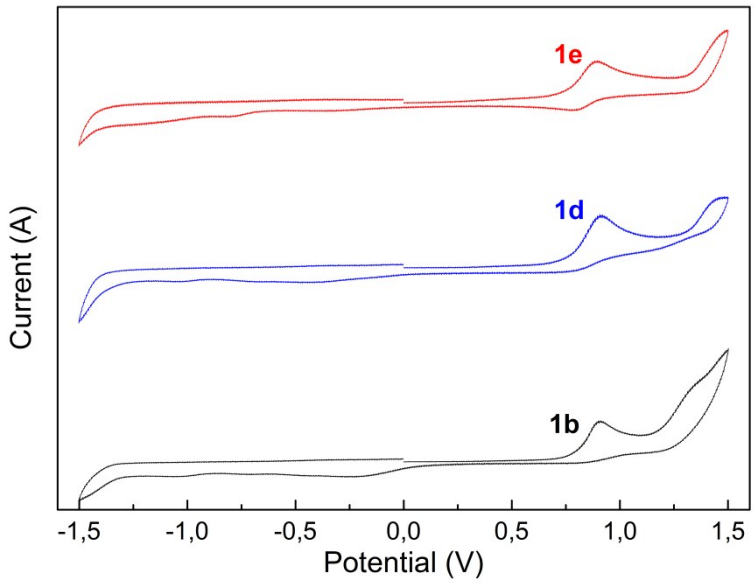


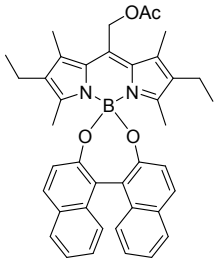
Figure S6. Cyclic voltammograms of PM567 derivatives bearing BINOL (**1b**), VANOl (**1d**) and VAPOL (**1e**) in milimolar solutions of acetonitrile (0.1 M $TBAPF_6$).

S3. Synthetic procedures and characterization data

S3.1. General procedure for the synthesis of the bi(polyarene)-based *O*-BODIPYs

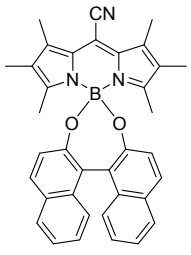
A mixture of *F*-BODIPY (1.00 mmol), aluminum trichloride (2.50 mmol) and dry CH_2Cl_2 (40 mL) was refluxed under argon atmosphere for 2 h (the disappearance of the starting *F*-BODIPY was monitored by TLC). After cooling down to room temperature, a solution of the corresponding dihydroxylated bi(polyarene) (2.00 mmol) in anhydrous acetonitrile (10 mL) was added dropwise, and the resulting mixture was stirred at r.t. for additional 6 h. The reaction mixture was washed with brine (1 × 10 mL) and dried over anhydrous Na_2SO_4. After filtration and solvent evaporation under reduced pressure, the reaction crude was purified by flash chromatography.

S3.2. Synthesis of 2a



According to the general procedure described in section S3.1, commercial PM605 (8-acetoxymethyl-2,6-diethyl-1,3,5,7-tetramethyl-*F*-BODIPY, 30 mg, 0.09 mmol) was reacted with BINOL (1,1'-bi(naphth-2-ol), 46 mg, 0.16 mmol). The reaction crude was purified by flash chromatography (hexane/CH_2Cl_2 8:2) to obtain **2a** (27 mg, 54 %)as a dark red solid. R_f = 0.45 (CH_2Cl_2). ^{1}H NMR (acetone-d_6, 300 MHz) δ 7.89 (d, J = 8.1 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.32 (m, 2H), 7.16-7.13 (m, 4H), 7.09 (d, J = 8.8 Hz, 2H), 5.48 and 5.41 (AB system, J_{AB} = 12.4 Hz, 2H), 2.33 (s, 6H), 2.26 and 2.21 (ABX_3 system, AB part. J_{AB} = 14.5 Hz, J_{AX} = J_{BX} = 7.5 Hz, 4H), 2.18 (s, 3H), 1.72 (s, 6H), 0.85 (ABX_3 system, X part, J_{AX} = J_{BX} = 7.5 Hz, 6H) ppm. ^{13}C NMR (acetone-d_6, 75 MHz) δ 170.9 (C), 156.2 (C), 155.5 (C), 137.4 (C), 134.7 (C), 134.3 (two C), 130.9 (C), 130.0 (CH), 128.9 (CH), 127.4 (CH), 126.1 (CH), 124.7 (CH), 124.1 (CH), 121.9 (C), 59.4 (CH_2), 20.6 (CH_3), 17.6 (CH_2), 14.9 (CH_3), 14.0 (CH_3), 12.8 (CH_3) ppm. FTIR ν 1743, 1562, 1470, 1226, 1182, 1027, 978 cm^{-1}. HRMS *m/z* 623.3076 [(M+H)$^+$] (calcd for: $C_{40}H_{40}BN_2O_4$ 623.3081).

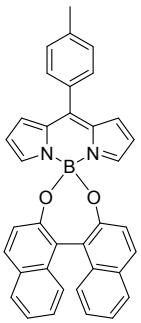
S3.3. Synthesis of 3a



According to the general procedure described in section S3.1, commercial PM650 (8-cyano-1,2,3,5,6,7-hexamethyl-*F*-BODIPY, 20 mg, 0.07 mmol) was reacted with BINOL (38 mg, 0.13 mmol). The reaction crude was purified by flash chromatography (CH_2Cl_2) to obtain **3a** (9 mg, 24 %) as a dark blue solid. R_f = 0.60 (CH_2Cl_2). ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 7.85 (d, J = 8.1 Hz, 2H), 7.78 (d, J = 8.7 Hz, 2H), 7.33 (ddd, J = 8.1, 5.8, 2.2 Hz, 2H), 7.20-7.10 (m, 4H), 7.08 (d, J = 8.8 Hz, 2H), 2.44 (s, 6H), 1.76 (s, 6H), 1.60 (s,

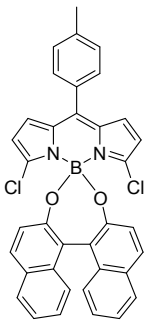
6H) ppm. ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 159.5 (C), 154.7 (C), 138.5 (C), 134.2 (C), 133.4 (C), 130.6 (C), 129.9 (CH), 129.4 (C), 128.5 (CH), 127.4 (CH), 125.8 (CH), 124.1 (CH), 124.0 (CH), 121.8 (C), 116.0 (C), 103.8 (C), 14.4 (CH_3), 12.2 (CH_3), 9.5 (CH_3) ppm. FTIR ν 1567, 1469, 1185, 997, 957 cm^{-1}. HRMS *m/z* 548.2511 [(M+H)$^+$] (calcd for: $C_{36}H_{26}BN_2O_2$ 548.2509).

S3.4. Synthesis of 4a



According to the general procedure described in section S3.1, 8-(*p*-tolyl)-*F*-BODIPY,[1] (20 mg, 0.07 mmol) was reacted with BINOL (40 mg, 0.14 mmol). The reaction crude was purified by flash chromatography (hexane/Et_2O 8:2) to obtain **3a** (26 mg, 71%)as an orange solid. R_f = 0.23 (hexane/Et_2O 8:2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.89 (d,*J* = 9.0 Hz, 4H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.39 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.25 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 2H), 7.18 (br s, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.98 (dd, *J* = 4.3, 1.2 Hz, 2H), 6.35 (dd, *J* = 4.3, 1.9 Hz, 2H), 2.49 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.2 (C), 147.2 (C), 144.2 (CH), 141.2 (C), 135.0 (C), 133.4 (C), 131.5 (C), 131.2 (CH), 130.9 (CH), 130.4 (C), 129.3 (CH), 129.3 (CH), 128.2 (CH), 127.3 (CH), 125.6 (CH), 123.7 (CH), 123.4 (CH), 123.0 (C), 118.0 (CH), 21.6 (CH_3) ppm. FTIR ν 1544, 1409, 1385, 1255, 1218, 1185, 1112, 1076, 984 cm^{-1}. HRMS *m/z* 529.2097 [(M+H)$^+$] (calcd for: $C_{36}H_{26}BN_2O_2$ 529.2087).

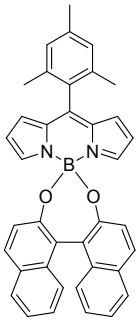
S3.5. Synthesis of 5a



According to the general procedure described in section S3.1, 3,5-dichloro-8-(*p*-tolyl)-*F*-BODIPY,[2] (30 mg, 0.08 mmol) was reacted with BINOL (48 mg, 0.17 mmol). The reaction crude was purified by flash chromatography (hexane/CH_2Cl_2 1:1) to obtain **5a** (31 mg, 61 %)as a red solid. R_f = 0.21 (hexane/CH_2Cl_2 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.36-7.29 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 7.16 (ddd, *J* = 8.5, 6.8,1.4 Hz, 2H), 6.86 (d, *J* = 4.4 Hz, 2H), 6.23 (d, *J* = 4.4 Hz, 2H), 2.48 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4 (C), 145.4 (C), 143.8 (C), 141.1 (C), 134.6

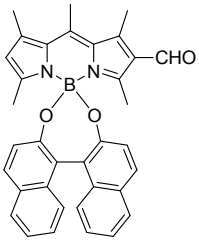
(C), 134.0 (C), 131.4 (CH), 130.7 (CH), 130.3 (CH), 130.3 (CH), 129.3 (CH), 129.1 (CH), 128.0 (CH), 127.5 (CH), 125.2 (CH), 123.7 (CH), 123.4 (CH), 121.9 (CH), 119.3 (CH_2), 21.6 (CH_3) ppm. FTIR ν 1550, 1388, 1251, 1087, 994 cm^{-1}. HRMS *m/z* 597.1299 [$(M+H)^+$] (calcd for: $C_{36}H_{24}BCl_2N_2O_2$ 597.1308).

S3.6. Synthesis of 6a



According to the general procedure described in section S3.1, 8-mesityl-*F*-BODIPY[3] (25 mg, 0.08 mmol) was reacted with BINOL (46 mg, 0.16 mmol). The reaction crude was purified by flash chromatography (hexane/CH_2Cl_2 8:2) to obtain **6a** (31 mg, 69 %)as a reddish orange solid. R_f = 0.32 (hexane:Et_2O 8:2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 9.1 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.39 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 2H), 7.25 (ddd, 8.4, 6.9, 1.5 Hz, 2H), 7.21 (s, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.00 (s, 2H), 6.71 (dd, *J* = 4.2, 1.2 Hz, 2H), 6.28 (dd, *J* = 4.2, 1.9 Hz, 2H), 2.39 (s, 3H), 2.20 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.2 (C), 147.1 (CH), 144.6 (CH), 138.8 (C), 136.6 (C), 135.4 (C), 133.4 (C), 130.4 (C), 130.3 (C), 129.8 (CH), 129.3 (CH), 128.3 (CH), 128.2 (CH), 127.3 (CH), 125.5 (CH), 123.7 (CH), 123.2 (CH), 123.0 (C), 118.1 (CH), 21.3 (CH_3), 20.3 (CH_3) ppm. FTIR ν 1579, 1378, 1275, 1068 cm^{-1}. HRMS *m/z* 557.2403 [$(M+H)^+$] (calcd for: $C_{38}H_{30}BN_2O_2$ 557.2400).

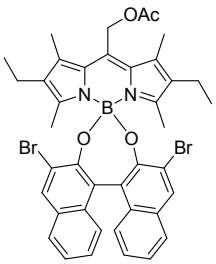
S3.7. Synthesis of 7a



According to the general procedure described in section S3.1, 2-formyl-1,3,5,7,8-pentamethyl-*F*-BODIPY[4] (35 mg, 0.12 mmol) was reacted with BINOL (69 mg, 0.24 mmol). The reaction crude was purified by flash chromatography (hexane/Et_2O 2:8) to obtain **7a** (13 mg, 19 %) as an orange solid. R_f = 0.20 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.90 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.24-7.13 (m, 4H), 7.13 (d, *J* = 8.7 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 5.99 (s, 1H), 2.77 (s, 3H), 2.76 (s, 3H), 2.48 (s, 3H), 2.06 (s, 3H), 1.71 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 186.6 (CHO), 161.4 (C), 156.2 (C), 153.9 (C), 153.9 (C), 145.1 (C), 143.5 (C), 140.0 (C), 136.2 (C), 133.8 (C), 132.1 (C), 130.1 (C), 130.0 (C), 129.6 (CH), 129.5 (CH), 128.1 (CH), 128.0 (CH), 127.3 (CH), 127.2 (CH), 125.7 (br s, CH), 125.5 (CH), 125.3 (br s, C), 123.7 (CH), 123.6 (CH), 123.4 (br s, CH), 121.7 (C), 120.9 (C), 18.3

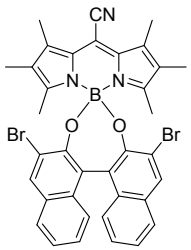
(CH_3), 18.1 (CH_3), 16.4 (CH_3), 14.4 (CH_3), 13.8 (CH_3) ppm. FTIR ν 1668, 1562, 1334, 1176, 984 cm^{-1}. HRMS *m/z* 537.2349 [$(M+H)^+$] (calcd for: $C_{35}H_{30}BN_2O_3$ 537.2349).

S3.8. Synthesis of 2b



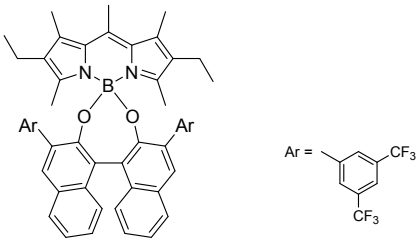
According to the general procedure described in section S3.1, commercial PM605 (30 mg, 0.08 mmol) was reacted with 3,3'-dibromoBINOL (71 mg, 0.16 mmol). The reaction crude was purified by flash chromatography (hexane/CH_2Cl_2 1:1) to obtain **2b** (43 mg, 70 %) as a red solid. R_f = 0.17 (hexane/CH_2Cl_2 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.10 (br s, 2H), 7.74 (br d, *J* = 8.1 Hz, 2H), 7.32 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 2H), 7.14 (ddd, *J* = 8.3, 6.9, 1.1 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 5.43, 5,36 (AB system, J_{AB} = 12.2 Hz, 2H), 2.28 (s, 6H), 2.26, 2,15 (ABX_3 system, AB part, J_{AB} = 14.5 Hz, J_{AX} = J_{BX} = 7.5 Hz, 4H), 2.17 (s, 3H), 1.62 (s, 6H), 0.89 (ABX_3 system, X part, J_{AX} = J_{BX} = 7.5 Hz, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.9 (C), 155.8 (C), 150.9 (C), 136.5 (C), 134.3 (C), 134.0 (C), 133.2 (C), 132.0 (CH), 131.1 (C), 130.2 (C), 127.1 (two CH), 125.8 (CH), 124.5 (CH), 122.8 (C), 119.4 (C), 59.1 (CH_2), 20.9 (CH_3), 17.4 (CH_2), 14.5 (CH_3), 13.4 (CH_3), 12.8 (CH_3) ppm. FTIR ν 1743, 1564, 1216, 1184, 1025, 977 cm^{-1}. HRMS *m/z* 779.1301 [$(M+H)^+$] (calcd for: $C_{40}H_{38}BBr_2N_2O_4$ 779.1291).

S3.9. Synthesis of 3b



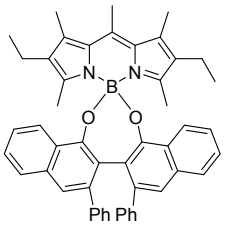
According to the general procedure described in section S3.1, commercial PM650 (30 mg, 0.10 mmol) was reacted with 3,3'-dibromoBINOL (88 mg, 0.20 mmol). The reaction crude was purified by flash chromatography (hexane/CH_2Cl_2 1:1), to obtain **3b** (60 mg, 85 %) as a dark blue solid. R_f = 0.37 (hexane/CH_2Cl_2 1:1). ^{1}H NMR (acetone-d_6, 300 MHz) δ 8.30 (s, 2H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.42 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 2H), 7.23 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 2.46 (s, 6H), 1.84 (s, 6H), 1.60 (s, 6H) ppm. ^{13}C NMR (acetone-d_6, 75 MHz) δ 159.6 (C), 151.4 (C), 139.2 (C), 134.0 (C), 133.8 (C), 133.2 (CH), 131.4 (C), 130.25 (C), 130.20 (C), 128.3 (CH), 127.3 (CH), 127.0 (CH), 125.7 (CH), 123.4 (C), 119.5 (C), 116.0 (C), 13.8 (CH_3), 12.0 (CH_3), 9.2 (CH_3) ppm. FTIR ν 2229, 1566, 1187 cm^{-1}. HRMS *m/z* 704.0727 [$(M+H)^+$] (calcd for: $C_{36}H_{29}BBr_2N_3O_2$ 704.0720).

S3.10. Synthesis of 1c



According to the general procedure described in section S3.1, commercial PM567 (2,6-diethyl-1,3,5,7,8-pentamethyl-*F*-BODIPY, 22 mg, 0.07 mmol) was reacted with 3,3'-bis[3,5-bis(trifluoromethyl)phenyl]BINOL (98 mg, 0.14 mmol). The reaction crude was purified by flash chromatography (silica gel, pentane/acetone 98:2) to obtain **1c** (48 mg, 70 %) as a red solid. R_f = 0.25 (pentane). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.01 (br s, 4H), 7.92 (d, J = 8.4 Hz, 2H), 7.90 (s, 2H), 7.72 (br s, 2H), 7.38 (ddd, J = 8.1, 5.8, 2.2 Hz, 2H), 7.28-7.18 (m, 4H), 2,18, 2,14 (ABX_3 system, AB part, J_{AB} = 14.5 Hz, J_{AX} = J_{BX} = 7.5 Hz, 4H), 2.14 (s, 3H), 2.10 (s, 6H), 1.64 (s, 6H), 0.83 (ABX_3 system, AB part, J_{AX} = J_{BX} = 7.5 Hz, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.8 (C), 151.7 (C), 141.1 (C), 139.2 (C), 136.4 (C), 134.4 (C), 132.8 (C), 132.7 (C), 132.5 (C), 130.8 (q, J = 32.9 Hz, C), 130.0 (br q, J = 2.7 Hz, CH), 129.8 (CH), 129.7 (C), 128.4 (CH), 126.9 (CH), 126.4 (CH), 124.2 (CH), 122.8 (C), 123.7 (q, J = 272.8 Hz, CF_3), 120.3 (hept, J = 3.5 Hz), 17.13 (CH_2), 17.09 (CH_3), 14.7 (CH_3), 14.3 (CH_3), 13.1 (CH_3) ppm. FTIR ν 1558, 1469, 1373, 1278, 1185, 1135 cm^{-1}. HRMS *m/z* 989.3210 [(M+H)$^+$] (calcd for: $C_{54}H_{42}BN_2O_2F_{12}$ 989.3148).

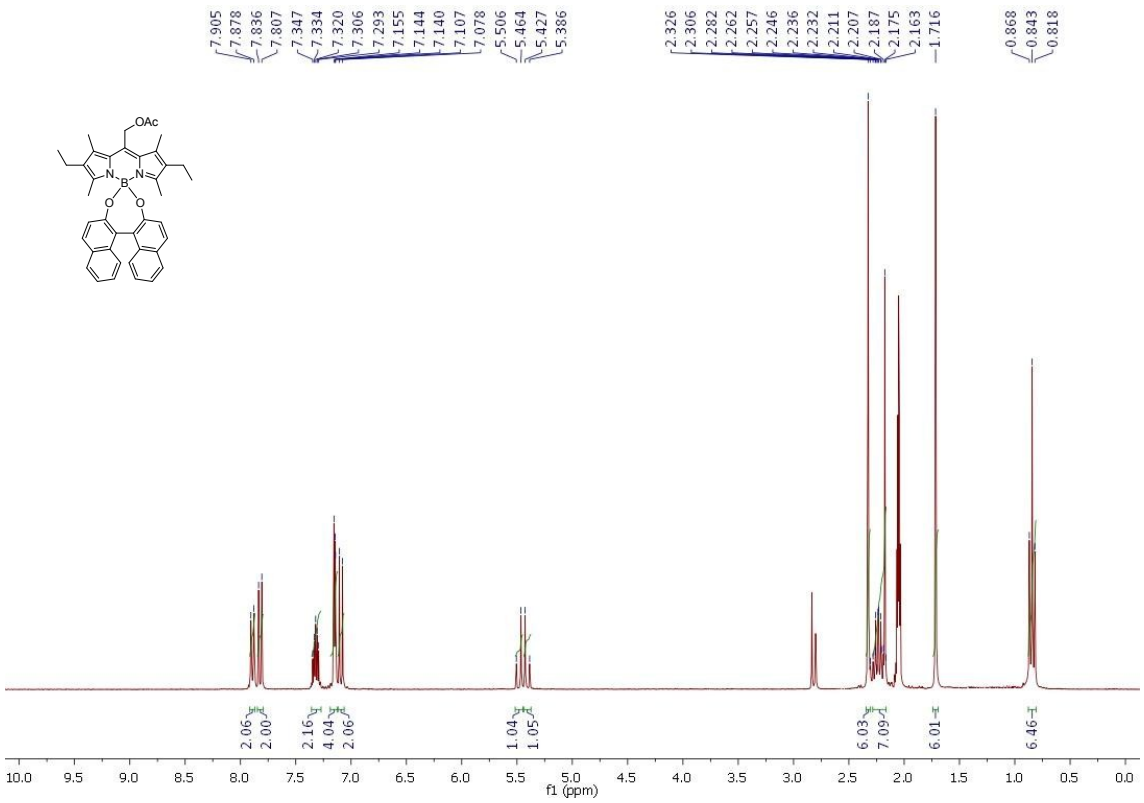
S3.11. Synthesis of 1d



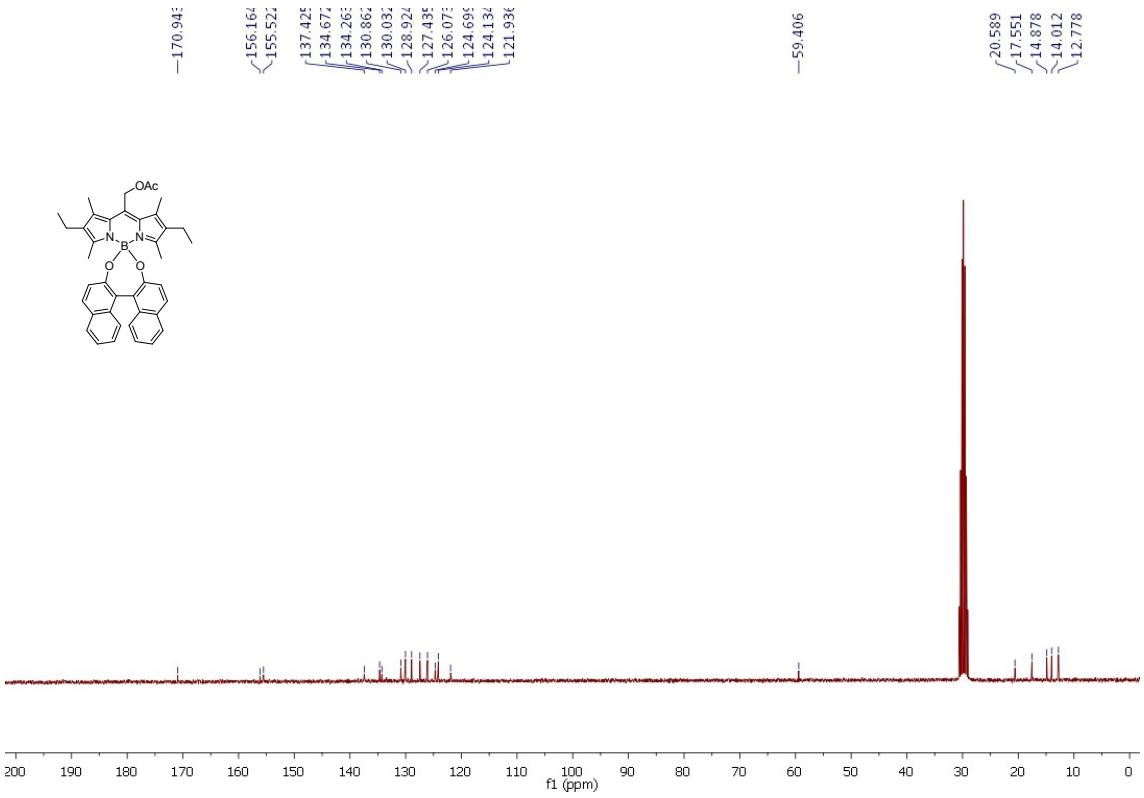
According to the general procedure described in section S3.1, commercial PM567 (22 mg, 0.07 mmol) was reacted with 3,3'-diphenyl-2,2′-bi(naphth-1-ol) (VANOL, 136 mg, 0.14 mmol). The reaction crude was purified by flash chromatography (hexane/CH_2Cl_2 7:3) to obtain **1d** (30 mg, 65 %) as a red solid. R_f = 0.21 (hexane/CH_2Cl_2 8:2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.11 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.38 (dd, J = 8.0, 6.8 Hz, 2H), 7.29 (dd, J = 7.1, 6.9 Hz, 3H include $CDCl_3$), 7.24 (s, 2H), 7.08 (dd, J = 7.7, 6.9 Hz, 2H), 6.93 (dd, J = 7.7, 7.4 Hz, 4H), 6.62 (d, J = 8.3 Hz, 4H), 2.80 (s, 3H), 2.35 (s, 6H), 2.13, 2.04 (ABX_3, AB part, J_{AB} = 14.6 Hz, J_{AX} = J_{AB} = 7.5 Hz, 4H, Me-C$\underline{H_2}$), 1.69 (s, 6H), 0.58 (ABX_3, part X, J_{AX} = J_{AB} = 7.5 Hz, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.1 (C), 152.6 (C), 141.9 (C), 141.6 (C), 138.9 (C), 136.0 (C), 134.0 (C), 133.3 (C), 133.0 (C), 129.5 (CH), 128.6 (CH), 127.38 (CH), 127.35 (CH), 126.1 (CH), 125.9 (CH), 124.7 (CH), 123.3 (CH), 122.9 (CH), 122.8 (C), 17.7 (CH_3), 17.2 (CH_2), 14.7 (CH_3), 14.4 (CH_3), 13.4 (CH_3) ppm. FTIR ν 1557, 1479, 1382, 976 cm^{-1}. HRMS *m/z* 717.3624 [(M+H)$^+$] (calcd for: $C_{50}H_{46}BN_2O_2$ 717.3652).

S4. NMR spectra

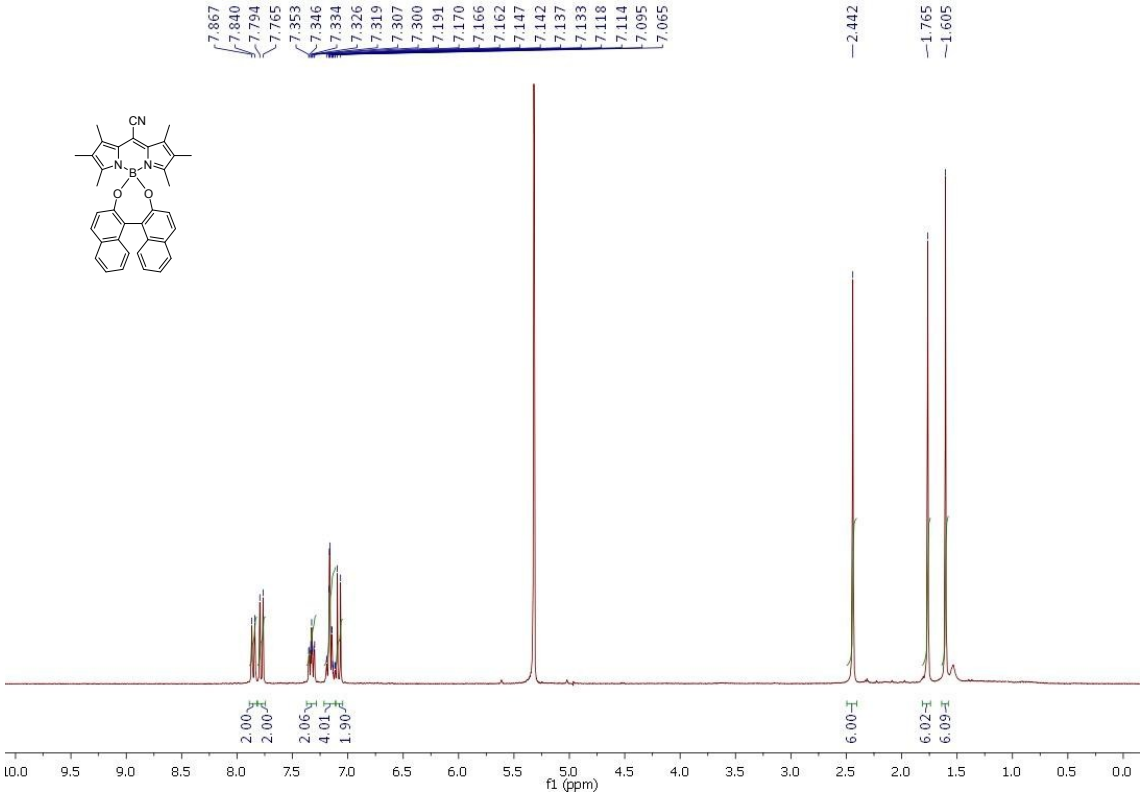
^{1}H-NMR (acetone-d_6, 300 MHz) spectrum of 2a



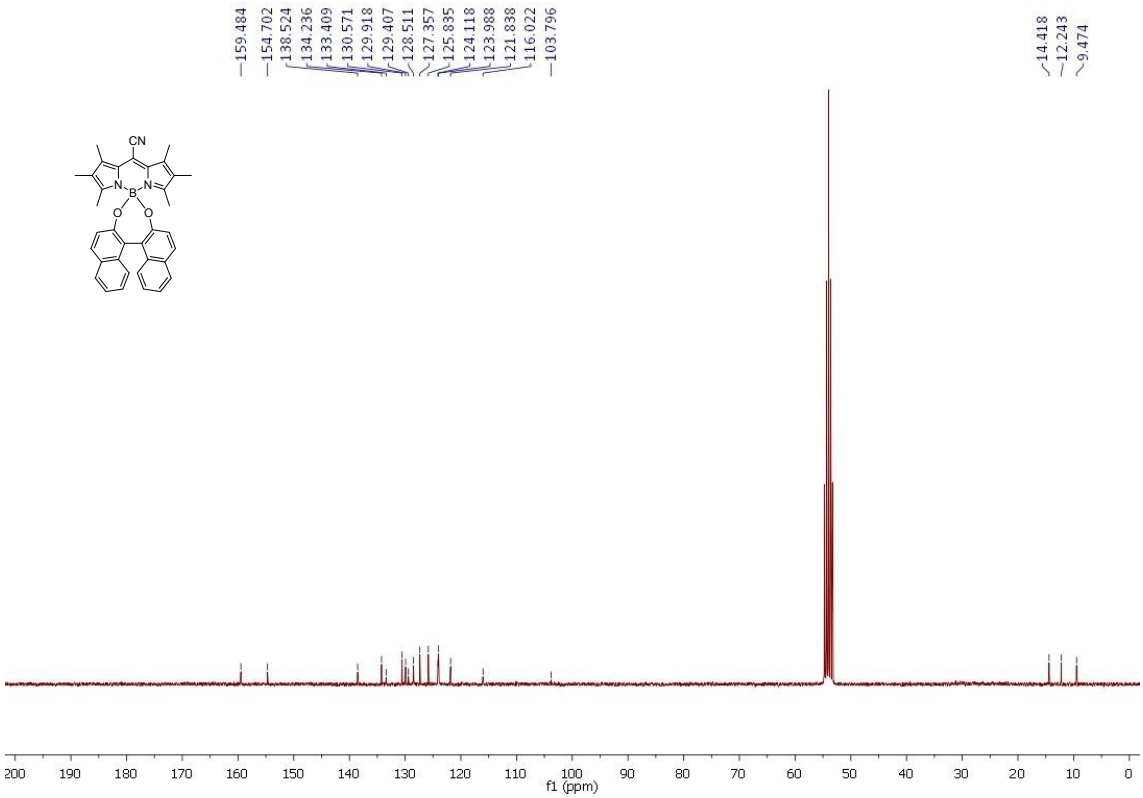
^{13}C-NMR (acetone-d_6, 75 MHz) spectrum of 2a



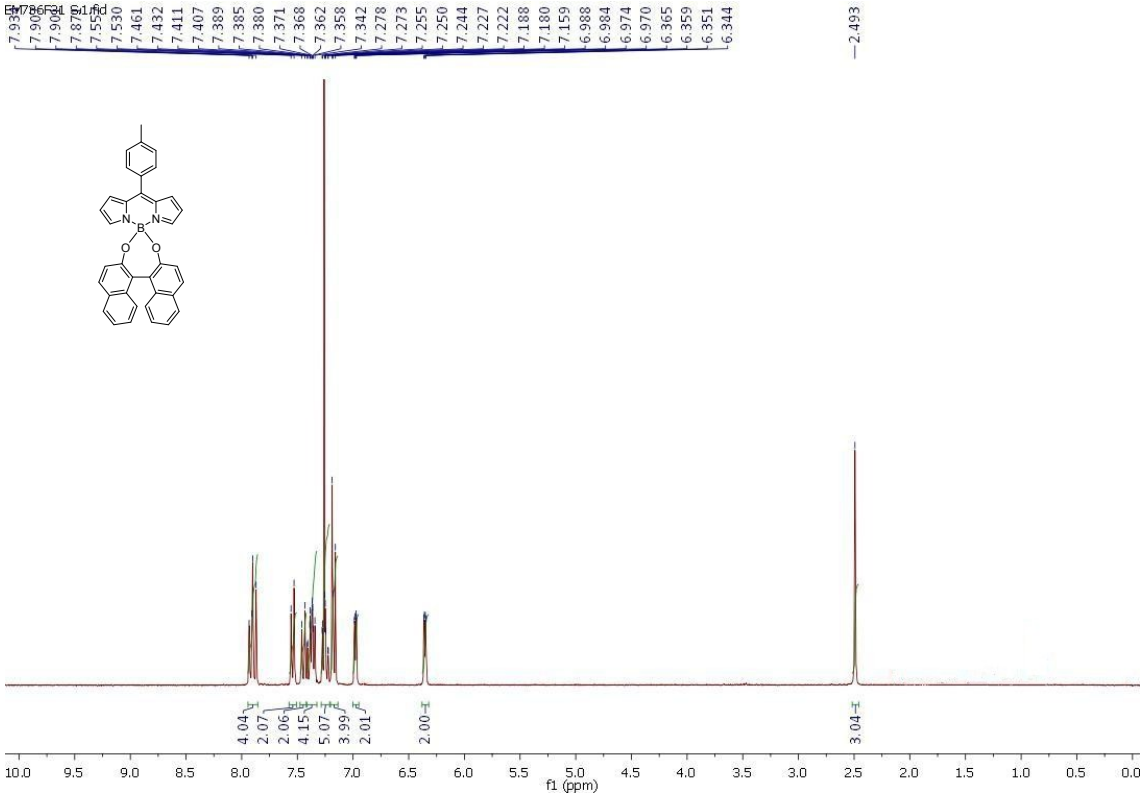
^{1}H-NMR (CD_2Cl_2, 300 MHz) spectrum of 3a



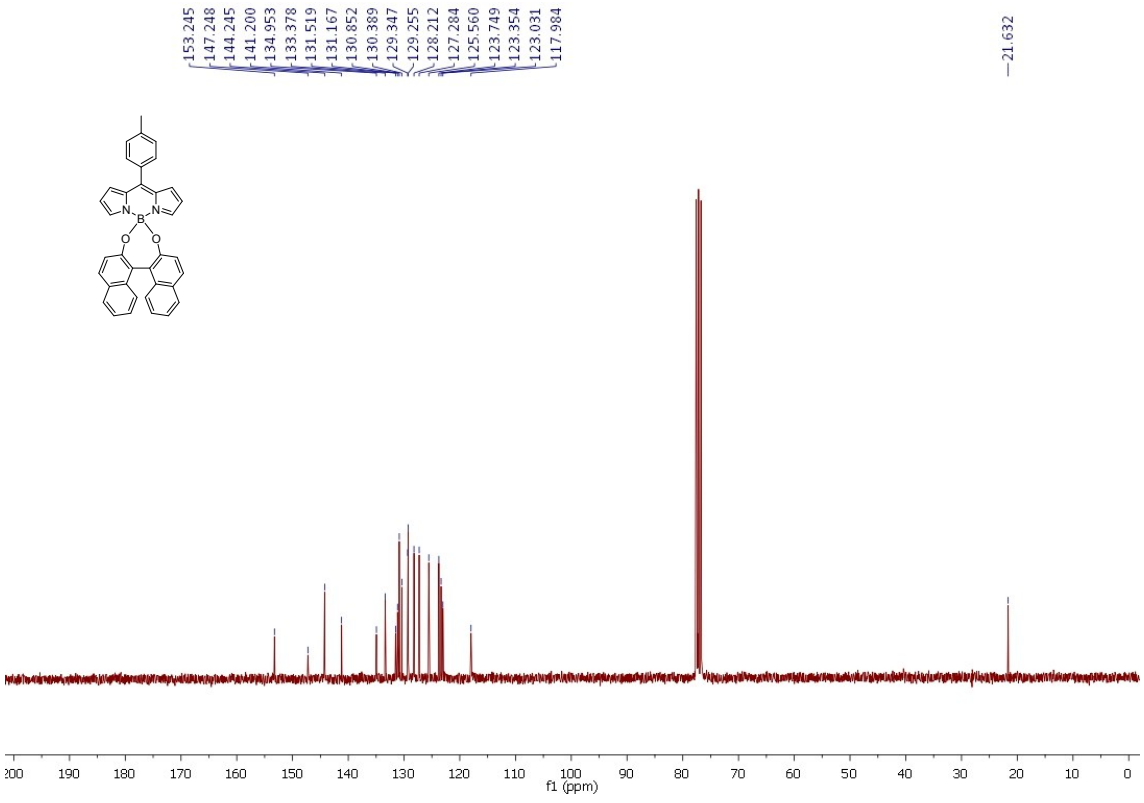
^{13}C-NMR (CD_2Cl_2, 75 MHz) spectrum of 3a



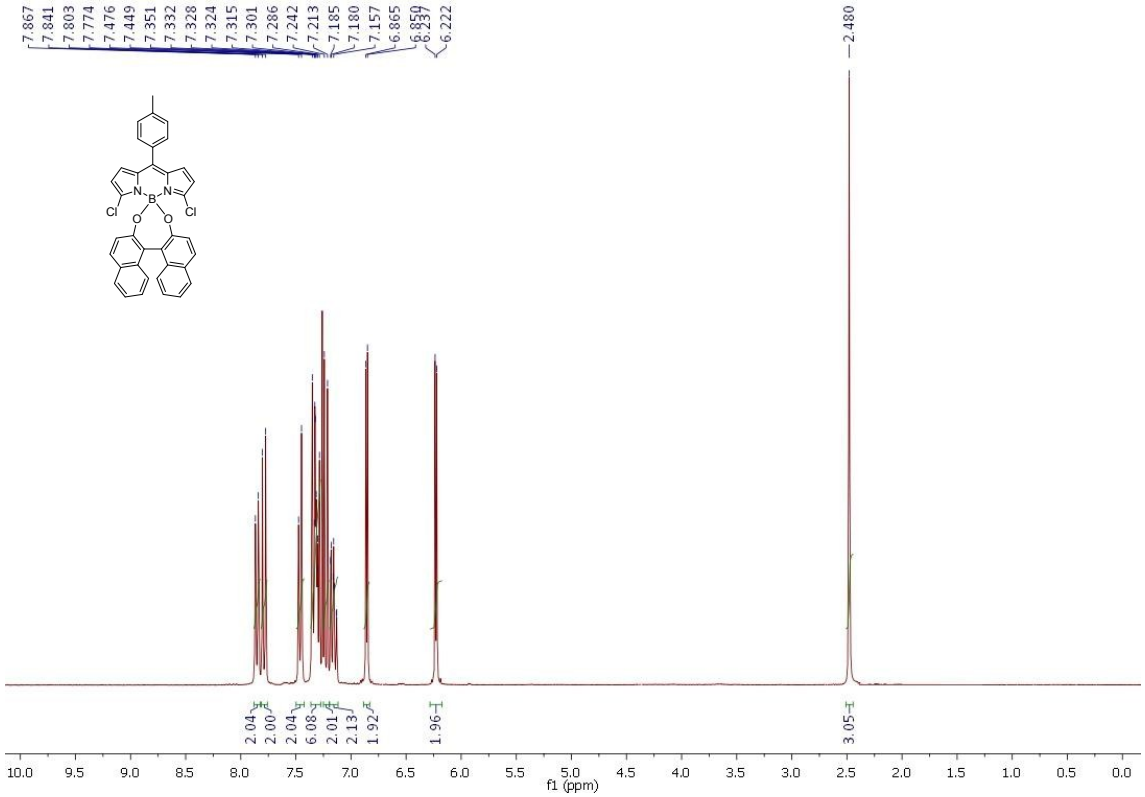
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 4a



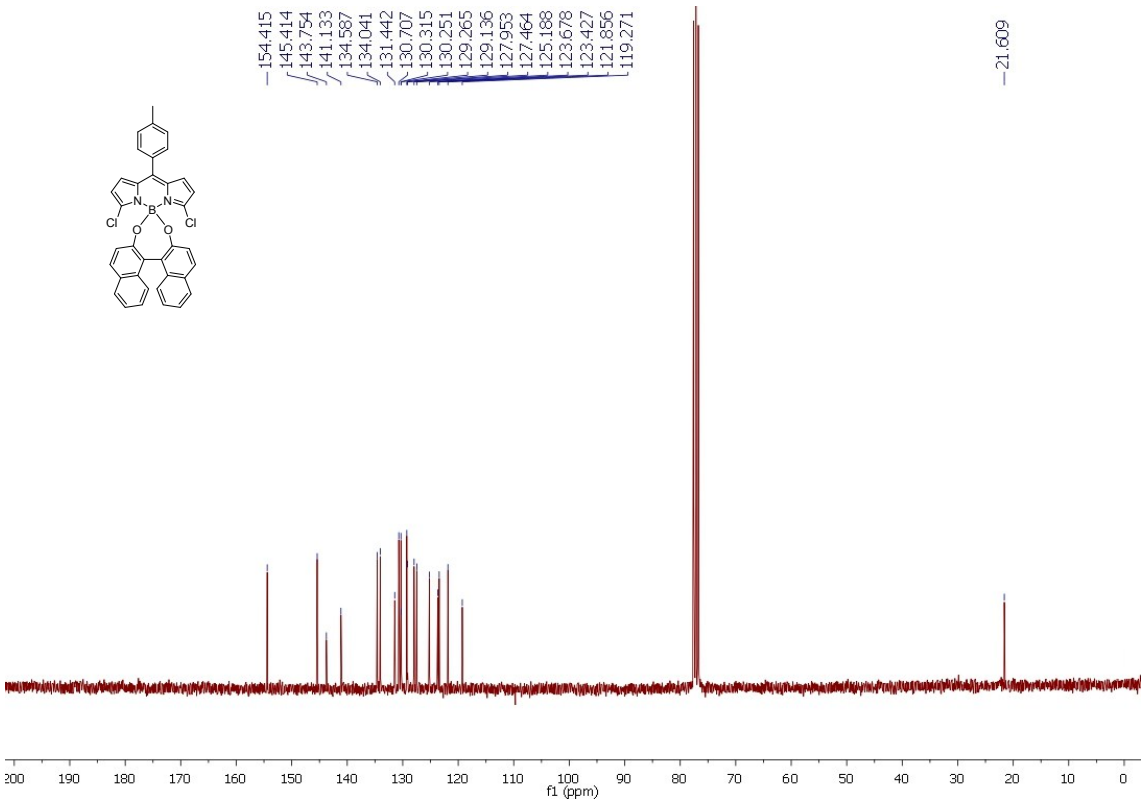
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 4a



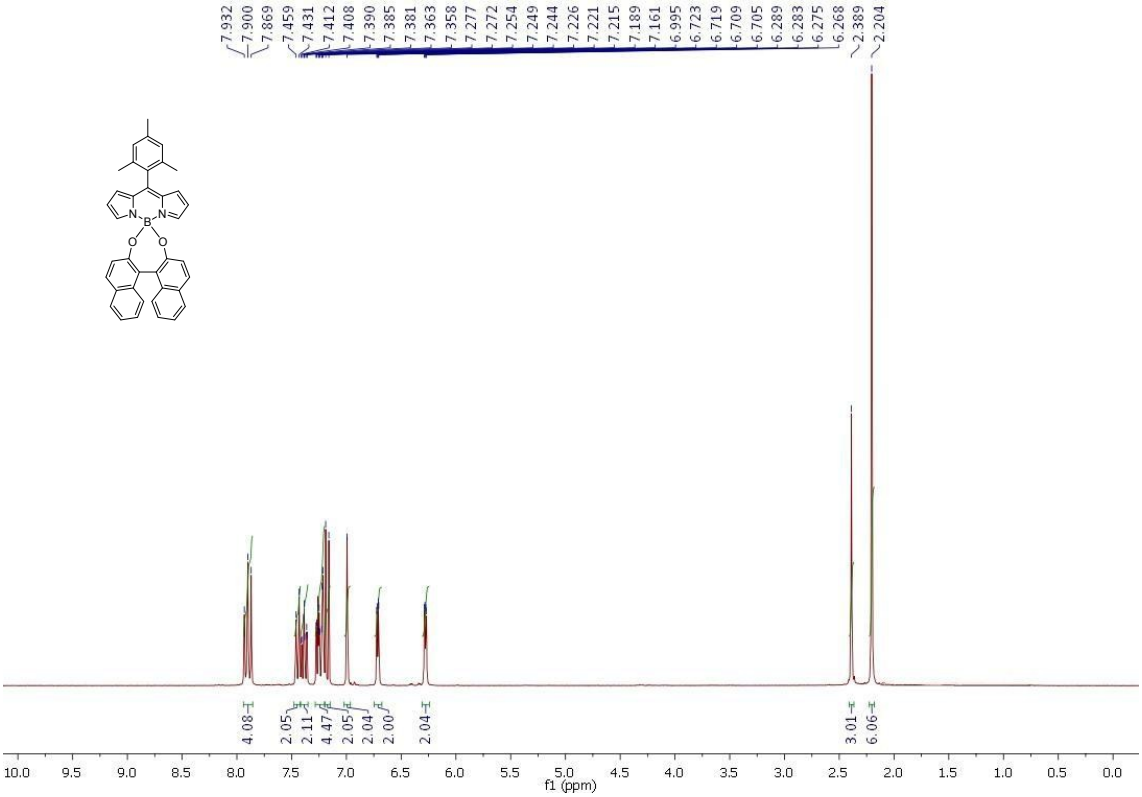
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 5a



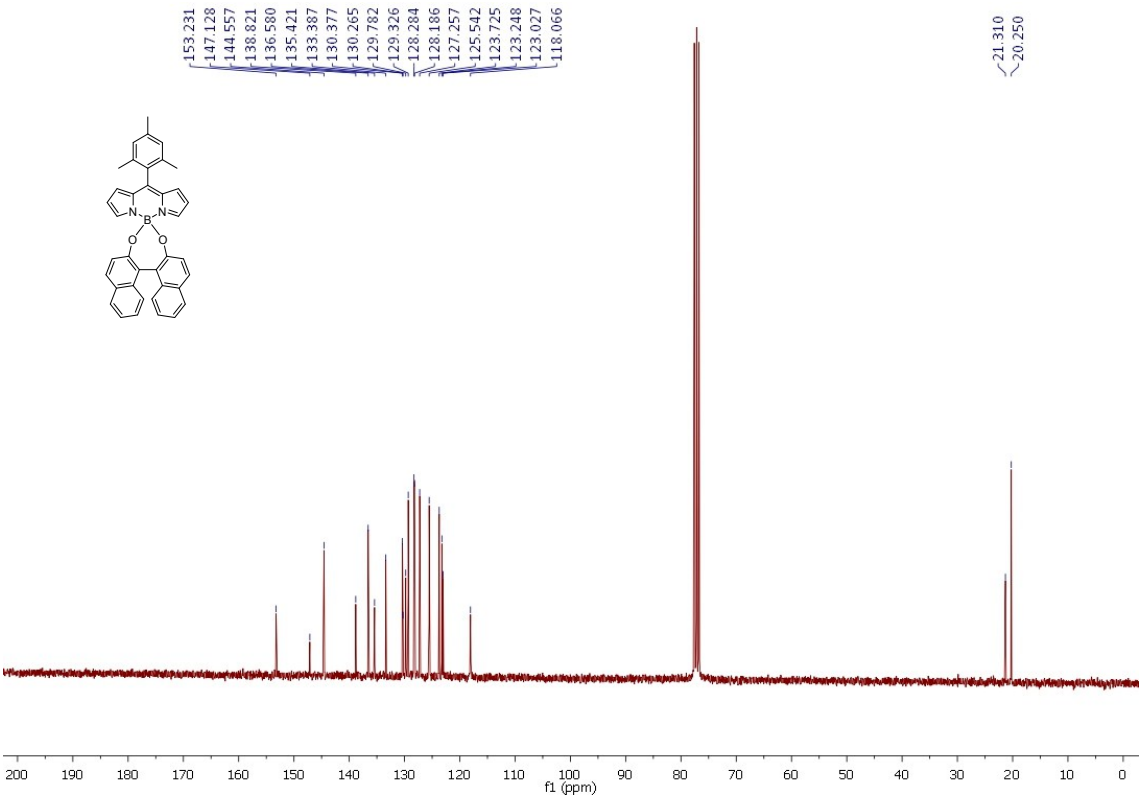
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 5a



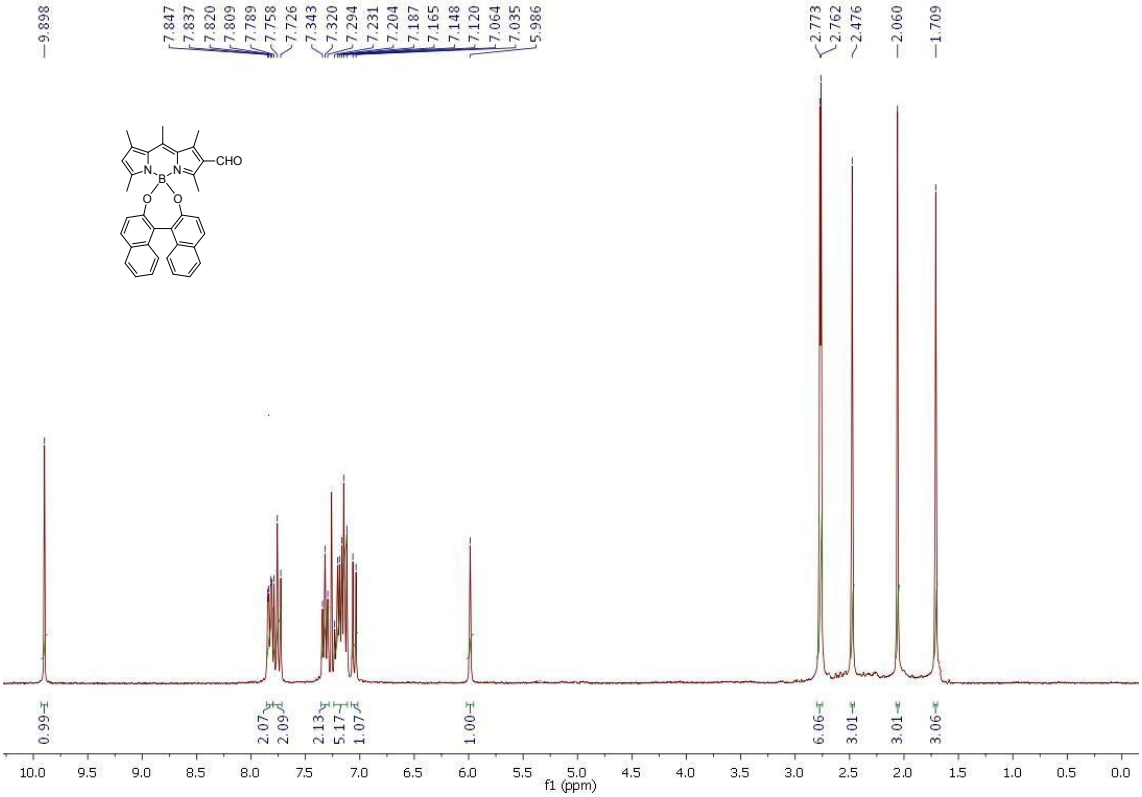
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 6a



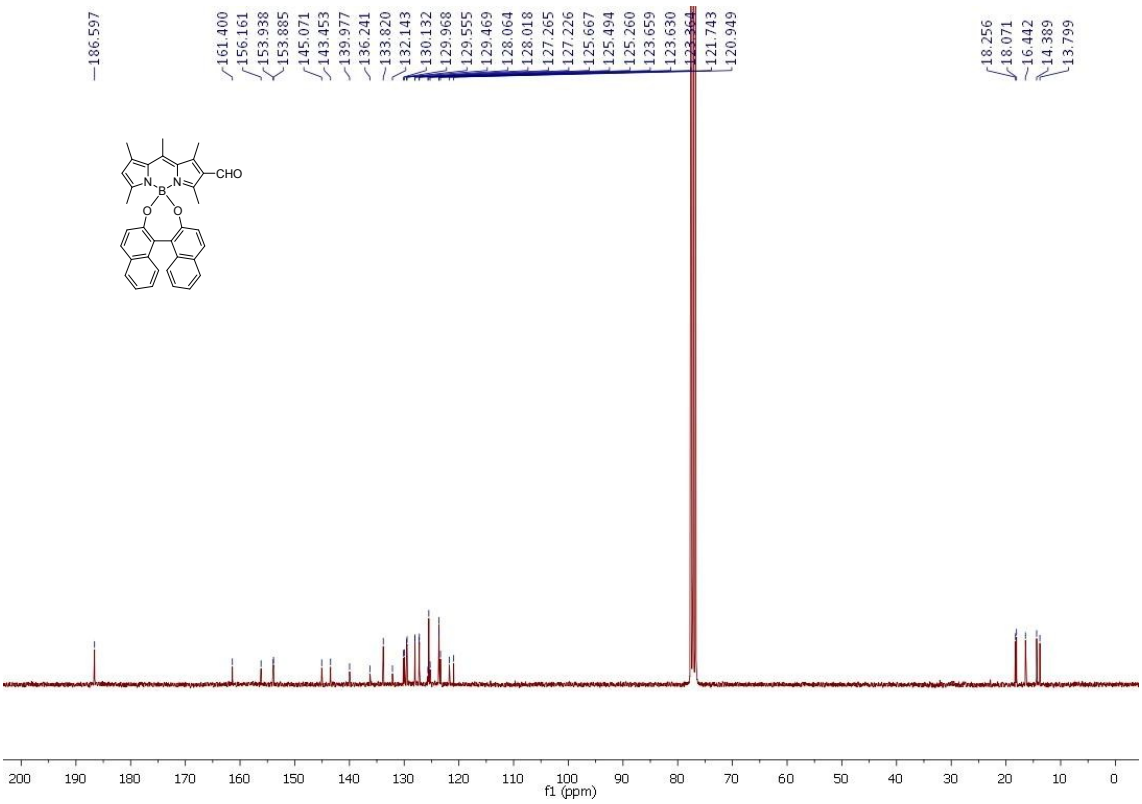
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 6a



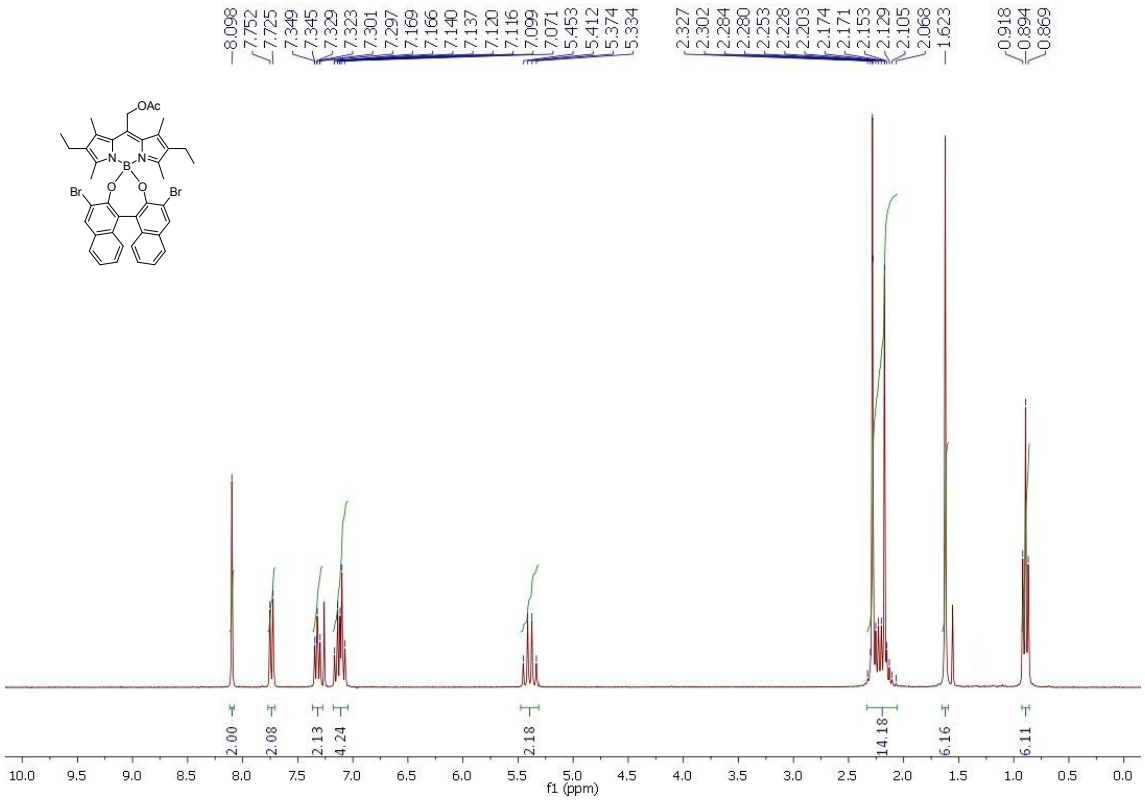
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 7a



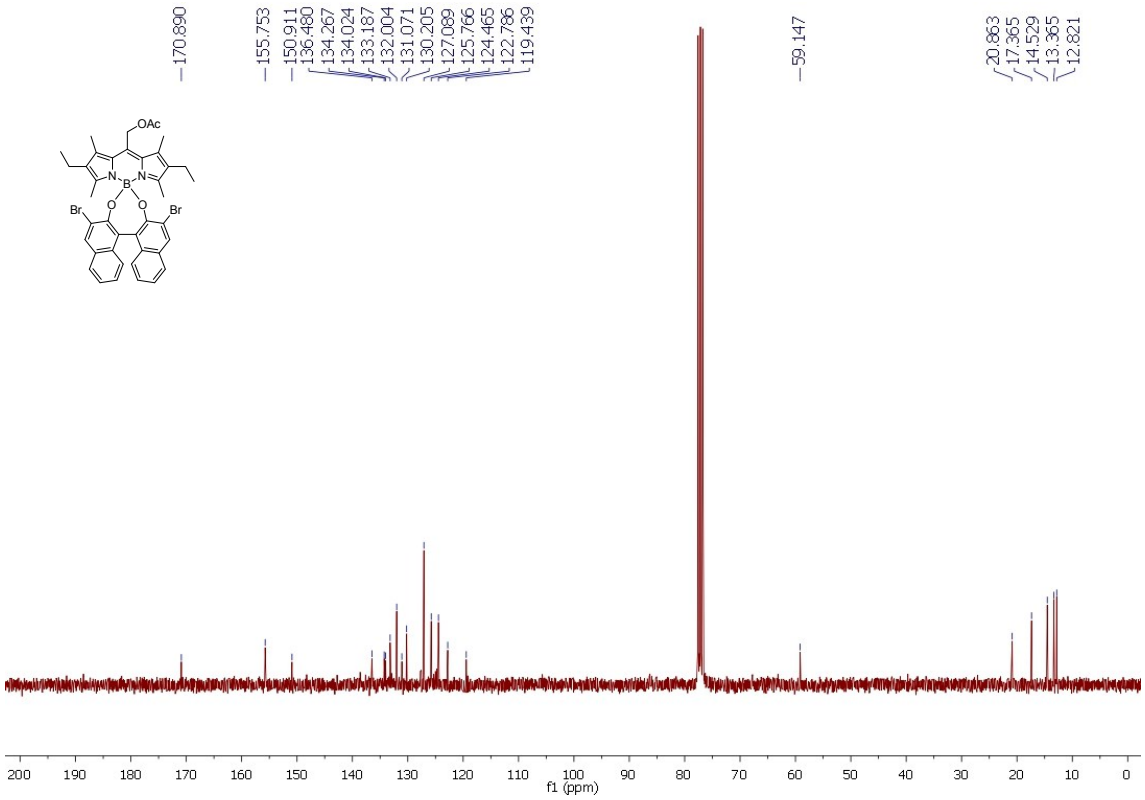
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 7a



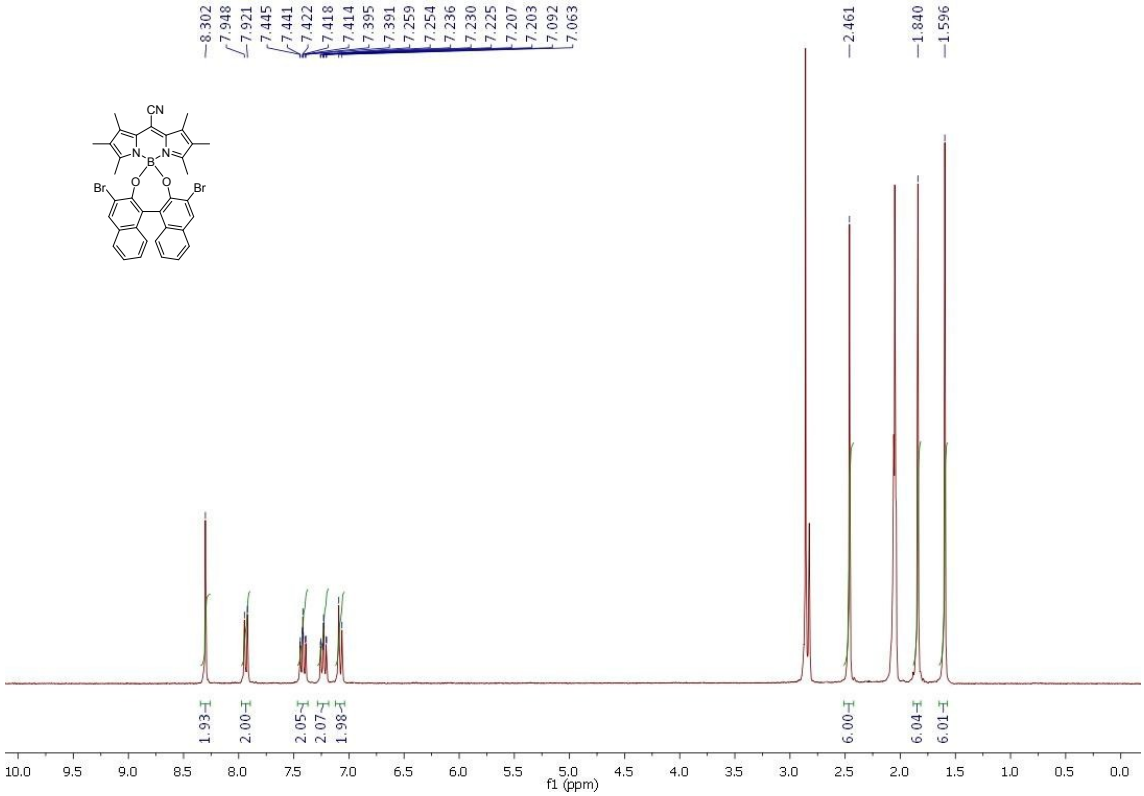
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 2b



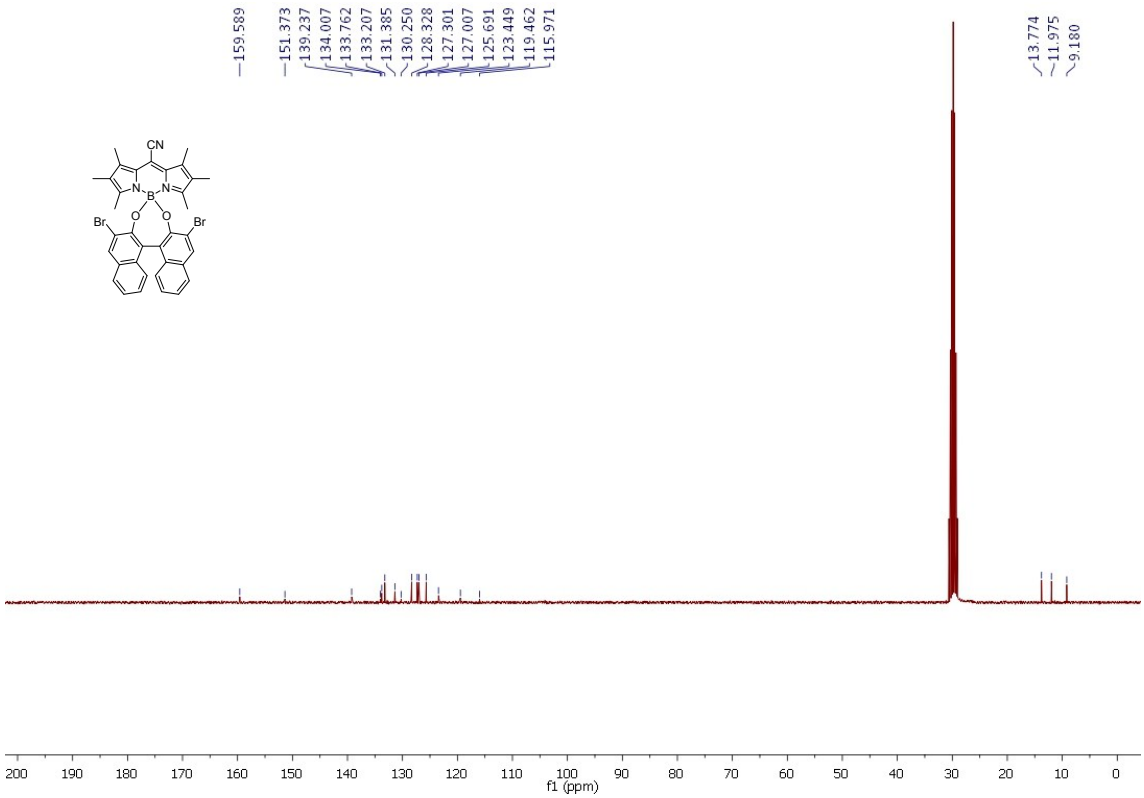
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 2b



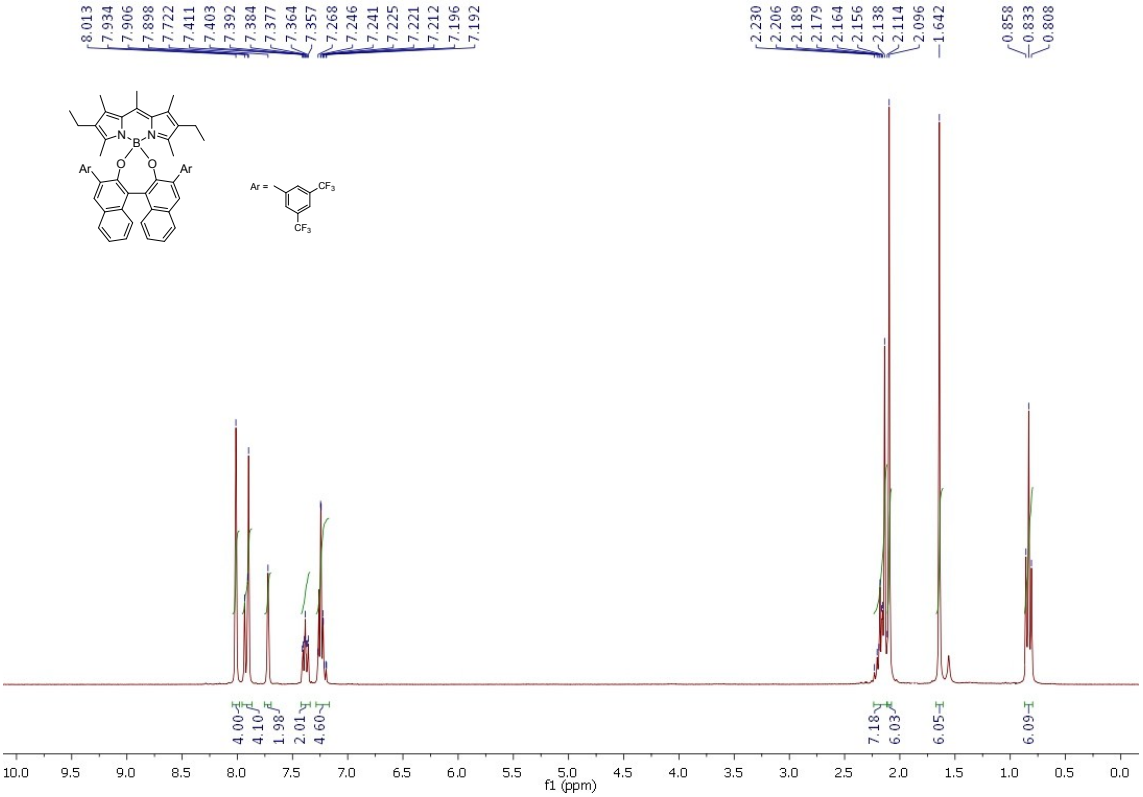
^{1}H-NMR (acetone-d_6, 300 MHz) spectrum of 3b



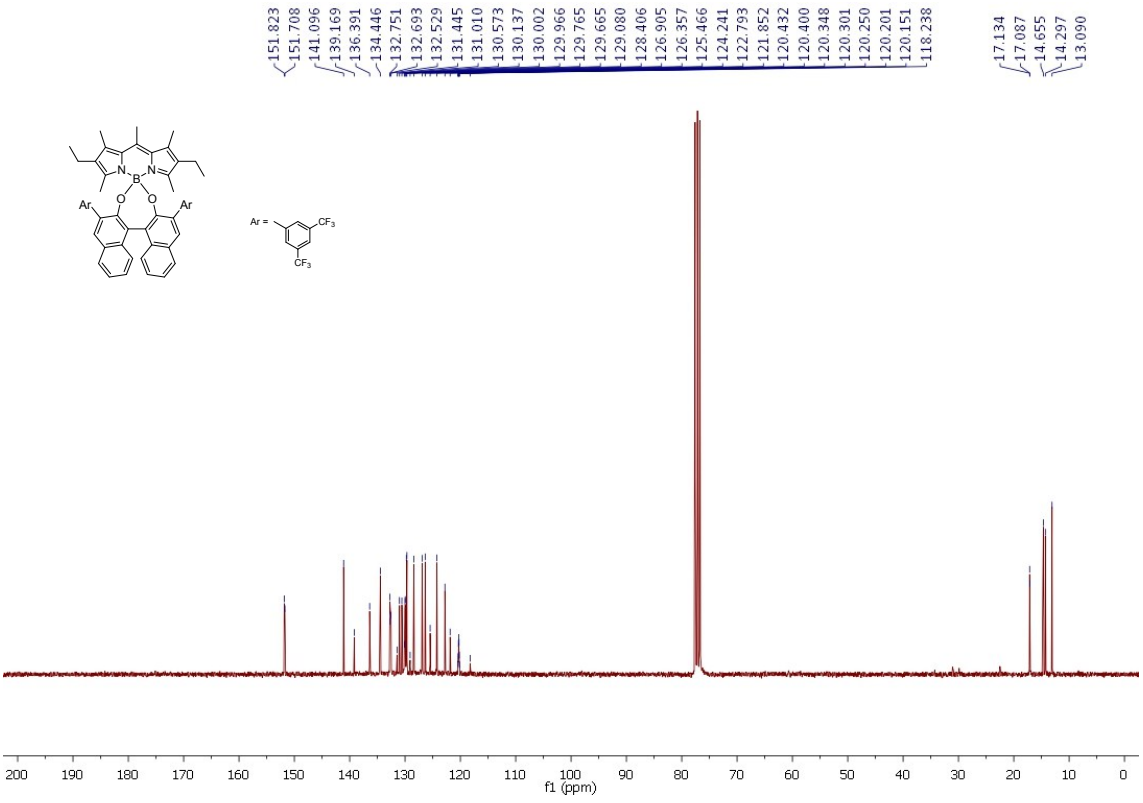
^{13}C-NMR (acetone-d_6, 75 MHz) spectrum of 3b



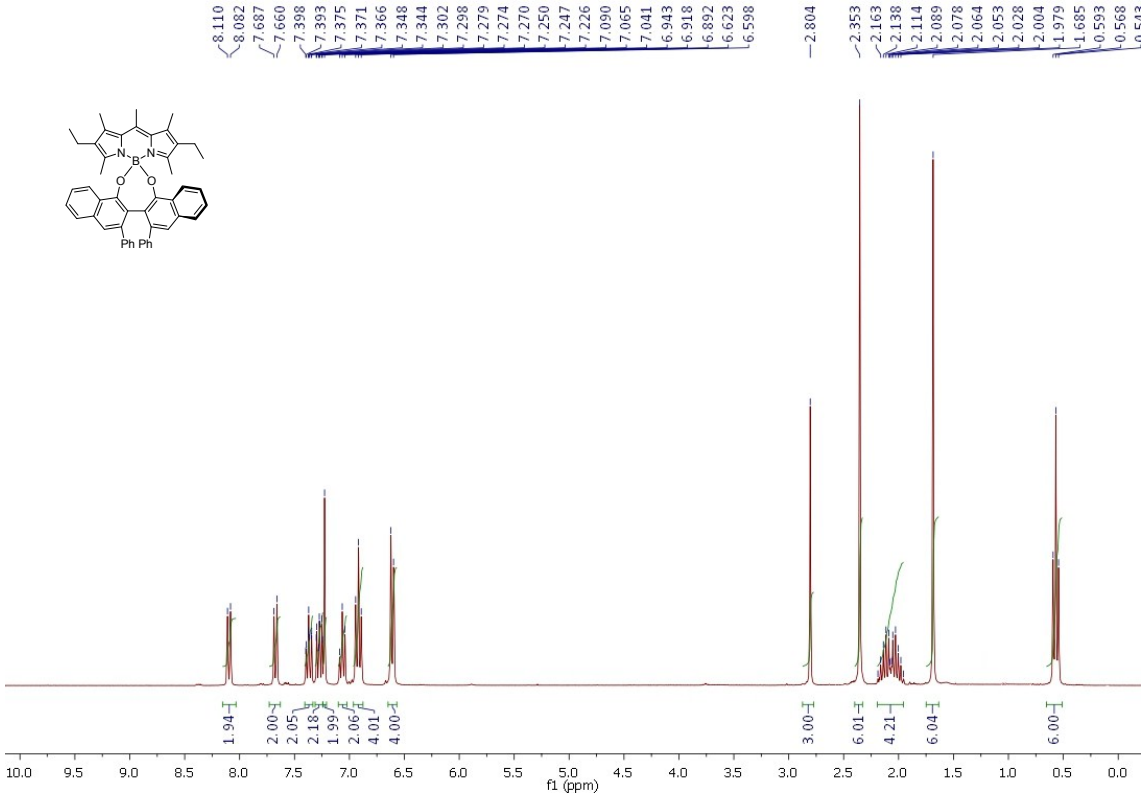
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 1c



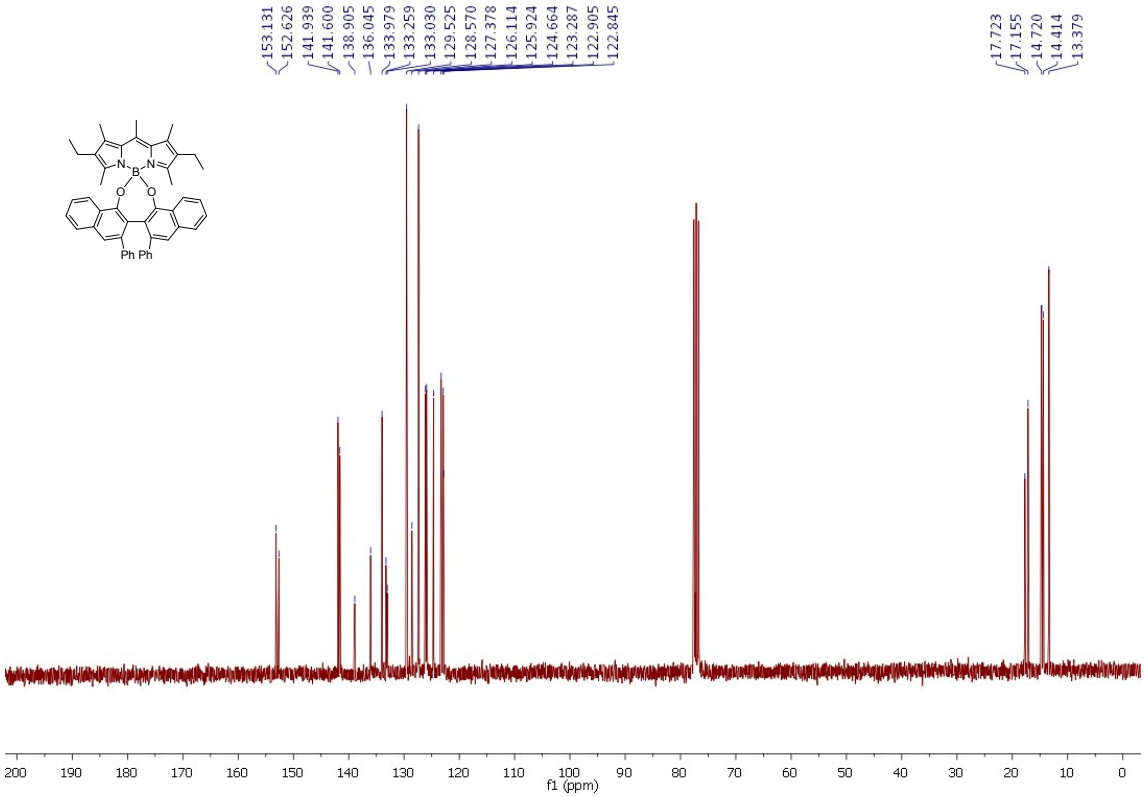
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 1c



^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 1d



^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 1d



S5. References

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