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Electronic Supplementary Information (ESI)

From photosensitizers to light harvesters adapting the molecular structure in all-BODIPY assemblies

Edurne Avellanal-Zaballa,[a] Alejandro Prieto-Castañeda,[b] Carolina Díaz-Norambuena,[a] Jorge Bañuelos,*[a] Antonia R. Agarrabeitia,[b] Inmaculada García-Moreno,[c] Santiago de la Moya,[b] and María J. Ortiz*[b]

[a] Departamento de Química-Física, Universidad del País-Vasco (UPV/EHU), Apartado 644, 48080, Bilbao, Spain.
[b] Departamento de Química Orgánica, Facultad de CC. Químicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain.
[c] Departamento de Sistemas de Baja Dimensionalidad, Superficies y Materia Condensada, Instituto de Química-Física Rocasolano, Centro Superior de Investigaciones Científicas (CSIC), Serrano 119, 28006, Madrid, Spain.

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1. General methods

1.1. Synthesis

Anhydrous solvents were prepared by distillation over standard drying agents according to common methods. All other solvents were of HPLC grade and were used as provided. Starting chemical substrates and reagents were used as commercially provided unless otherwise indicated. Flash chromatography was performed using silica gel (230-400 mesh). NMR spectra were recorded using $CDCl_3$ or CD_2Cl_2 at 20 ºC. ^1H NMR and ^{13}C NMR chemical shifts (δ) were referenced to internal solvent $CDCl_3$ (δ = 7.260 and 77.03 ppm, respectively) or CD_2Cl_2 (5.320 ppm). Multiplicity is indicated as follows: s = singlet; d = doublet; m = multiplet. Coupling constants (*J*) are dated in hertz (Hz). DEPT 135 experiments were used to determine the type of carbon nucleus (C *vs.* CH *vs.* CH_2 *vs.* CH_3). FTIR spectra were obtained from neat samples using the attenuated total reflection (ATR) technique. High-resolution mass spectrometry (HRMS) was performed using electronic impact (EI) or MALDI-TOF and ion tramp (positive mode) for the detection.

1.2. Spectroscopic measurements

The photophysical properties were registered 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 spectrofluorometer (model FLSP 920), respectively. Fluorescence quantum yields (ϕ) were obtained from corrected spectra (detector sensibility to the wavelength) using PM546 (ϕ = 0.85 in ethanol) for dyes **1**-**3** and zinc phthalocyanine (ϕ = 0.30 in toluene with 1% of pyridine) for dye **4**, as reference. The values were corrected by the refractive index of the solvent. Radiative decay curves were registered with the time correlated single-photon counting technique as implemented in the aforementioned spectrofluorometer. Fluorescence emission was monitored at the maximum emission wavelength after excitation by means of a Fianium pulsed laser (time resolution of picoseconds) with tuneable wavelength. 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).

The photoinduced production of singlet oxygen ($^1O_2$) was determined by direct measurement of the luminescence at 1276 nm with a NIR detector integrated in the aforementioned spectrofluorometer (InGaAs detector, Hamamatsu G8605-23). The $^1O_2$ signal was registered in front configuration (front face), 40° and 50° to the excitation and emission beams,

respectively and leaned 30° to the plane formed by the direction of incidence and registration in cells of 1 cm. The signal was filtered by a low cut-off of 850 nm. $^1O_2$-generation quantum yield (ϕ^{Δ}) was determined using the following equation:

$$\phi^{\Delta} = \phi^{\Delta,r} \cdot (\alpha^r/\alpha^{Ps}) \cdot (Se^{Ps}/Se^r)$$

where $\phi^{\Delta,r}$ is the quantum yield of $^1O_2$ generation for the used reference (in our case, phenalenone). Factor $\alpha = 1\text{-}10^{-Abs}$, corrects the different amount of photons absorbed by the sample (α^{Ps}) and reference (α^R). Factor Se is the intensity of the $^1O_2$ phosphorescence signal of the sample (Se^{Ps}) and the reference (Se^r) at 1276 nm. Phenalenone in chloroform was used as reference for visible irradiation (420 nm), its singlet-oxygen quantum yield being ϕ^{Δ} = 0.98. $^1O_2$ quantum yields were averaged from 5 concentrations between 10^{-6} M and 10^{-5} M in chloroform (spectroscopic grade).

1.3. Quantum mechanical calculations

Ground state geometries were optimized with the long-range wb97xd hybrid functional, within the Density Functional Theory (DFT), using the triple valence basis set with a polarization function (6-311g*). The geometries were considered as energy minimum when the corresponding frequency analysis did not give any negative value. The simulation of the absorption spectra was carried out using the Time Dependent (TD) method with the same functional and basis set used for the energy minimization. All the calculation were performed in the Gaussian 16 implemented in the “arina” computational cluster of the UPV/EHU.

1.4. Laser measurements

Laser efficiency was evaluated from concentrated solutions (milimolar) of dyes in chloroform contained in 1-cm optical-path rectangular quartz cells carefully sealed to avoid solvent evaporation during experiments. The liquid solutions were transversely pumped with 5 mJ, 8 ns FWHM pulses from the second (532 nm) and third (355 nm) harmonic of a Q-switched Nd:YAG laser (Lotis TII 2134) at a repetition rate of 1 Hz. The exciting pulses were line-focused onto the cell using a combination of positive and negative cylindrical lenses (f = 15 cm and f = -15 cm, respectively) perpendicularly arranged. The plane parallel oscillation cavity (2 cm length) consisted of a 90% reflectivity aluminium mirror acting as back reflector, and the lateral face of the cell acting as output coupler (4% reflectivity). The pump and output energies were detected by a GenTec powermeter. The photostability of the dyes in chloroform solution was evaluated by using a pumping energy and geometry exactly equal to that of the laser experiments. We used spectroscopic quartz cuvettes with 0.1 cm optical to allow for the minimum solution volume (40 μL) to be excited. The lateral faces were grounded, whereupon no laser oscillation was obtained. Information about photostability was

obtained by monitoring the decrease in laser-induced fluorescence (LIF) intensity after 70 000 pump pulses and 10 Hz repetition rate to speed up the experimental running.

The photostability of the dyes in ethyl acetate solution was evaluated by using a pumping energy and geometry exactly equal to that of the laser experiments. We used spectroscopic quartz cuvettes with 0.1 cm optical to allow for the minimum solution volume (V_S = 40 μL) to be excited. The lateral faces were grounded, whereupon no laser oscillation was obtained. Information about photostabilitiy was obtained by monitoring the decrease in laser-induced fluorescence (LIF) intensity. In order to facilitate comparisons independently of the experimental conditions and sample, the photostability figure of merit was defined as the accumulated pump energy absorbed by the system (E_{dose}), per mole of dye, before the output energy falls to a 50% its initial value. In terms of experimental parameters, this energy dose, in units of GJ mol^{-1}, can be expressed as:

$$E_{dose}^{50\%}(GJ \cdot mol^{-1}) = \frac{E_{\text{pump}}(GJ) \cdot \left(1 - 10^{-\varepsilon CL}\right) \sum_{\#\text{pulses}} f}{CV_S}$$

where E_{pump} is the energy per pulse, C is the molar concentration, ε is the molar absorption coefficient in units of M^{-1} cm^{-1}, L is the depth of the cuvette expressed in cm, V_S is the solution volume, in litres, within the cuvette, and f is the ratio between the LIF intensity after #pulses and the LIF intensity in the first pulse. To speed up the experiment the pump repetition rate was increased up to 15 Hz. The fluorescence emission and laser spectra were monitored perpendicular to the exciting beam, collected by an optical fiber, and imaged onto a spectrometer (Acton Research corporation) and detected with a charge-coupled device (CCD) (SpectruMM:GS128B). The fluorescence emission was recorded by feeding the signal to the boxcar (Stanford Research, model 250) to be integrated before being digitized and processed by a computer. The estimated error in the energy and photostability measurements was 10%.

2. Supplementary table

Table S1. Photophysical properties of BODIPY-based dyads and triads in diluted solutions (micromolar) of different solvents. Solvents were chosen depending on the solubility of the corresponding dye.

	λ_{ab} (nm)	ε_{max} (10^4 $M^{-1}cm^{-1}$)	λ_{fl} (nm)	ϕ	τ (ns)
A*					
c-Hexane	509.0	19.0	524.0	0.92	5.04
Chloroform	505.0	18.0	527.0	0.22	0.47(27%) - 4.20(73%)
Acetone	503.0	17.7	532.0 (660.0)	0.01	0.01(80%)-0.96(19%)-4.50(1%)
Acetonitrile	501.0	16.5	530.0 (715.0)	<0.01	-
1					
c-Hexane	505.0	16.0	535.0	0.85	4.10
Chloroform	505.5	15.2	534.5	0.78	0.83(9%) - 4.57(91%)
Ethyl acetate	501.0	14.2	530.5	0.88	4.56
Methanol	500.0	13.8	526.5	0.16	0.64(95%) – 3.25 (5%)
2[#]					
Chloroform	504.0	20.0	561.0	0.71	4.07
Ethyl acetate	500.0	19.0	557.5	0.83	3.97
Methanol	499.5	18.6	553.5	0.20	0.64(50%) – 1.53 (50%)
3					
c-Hexane	506.5	20.6	547.0	0.77	3.84
Chloroform	507.5	22.6	550.5	0.42	0.49(14%) - 4.21(86%)
Ethyl acetate	503.0	22.0	546.5	0.19	1.89(34%) – 3.18(66%)
Methanol	502.0	21.4	545.5	0.02	0.06(83%)-1.15(13%)-4.56(3%)
4[#]					
Chloroform	670.0	13.5	690.0	0.78	3.88[&]
	504.0	18.1			
	376.5	6.7			
Ethyl acetate	659.5	12.4	678.0	0.66	3.79[&]
	499.5	17.0			
	371.5	7.3			

Absorption (λ_{ab}) and fluorescence (λ_{fl}) wavelength, molar absorption coefficient (ε_{max}), fluorescence (ϕ) quantum yield and lifetime (τ).

*Data collected from *Chem. Eur. J.*, **2017**, *23*, 1837-4848.

[#]Dyes **2** and **4** are not soluble in cyclohexane. **4** is not soluble in methanol.

[&]Same values upon excitation at the central BODIPY (610 nm) and lateral BODIPYs (480 nm) chromophores.

3. Supplementary figures

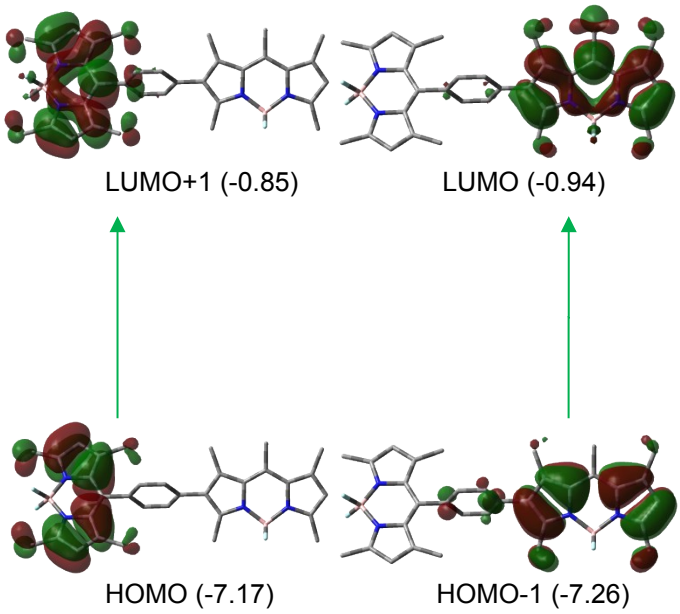


Figure S1. Theoretically predicted (td wb97xd/6-311g*) molecular orbitals and energies (in eV) involved in the main absorption transition of dyad **1**. Both electronic transitions are isoenergetic, with the same enegy gap.

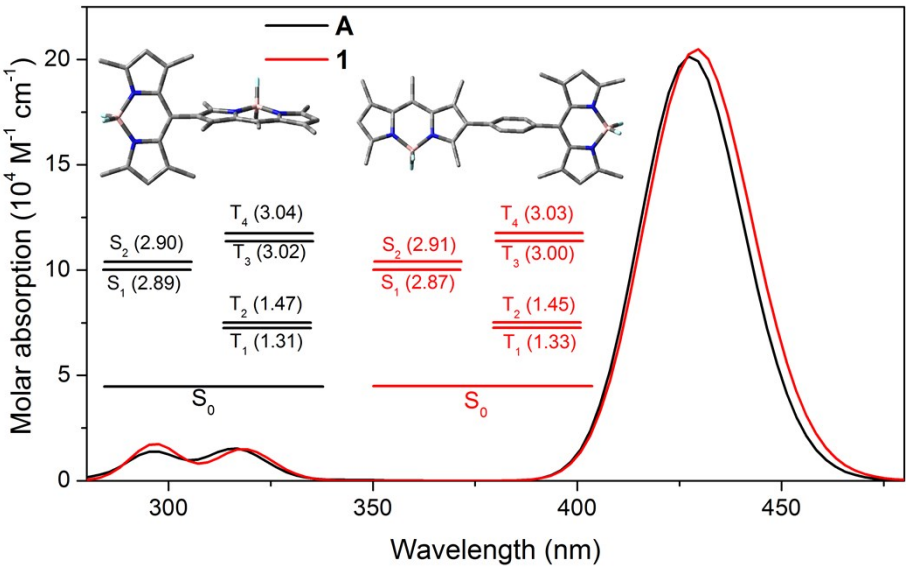


Figure S2. Theoretically predicted (td wb97xd/6-311g*) absorption spectra and singlet and triplet manifold (in eV) for the respresentative dyads **A** (directly connected axial BODIPYs) and **1** (*p*-phenylene bridged BODIPYs) with their corresponding ground state optimized geometries. Note that the td method falls in the reproduction of the absolute energies but accurately describes the relative energies owing to structural factors.[1] Due to the molecular size the energies of the electronic states were calculated as Franck-Condon transitions from the ground state.

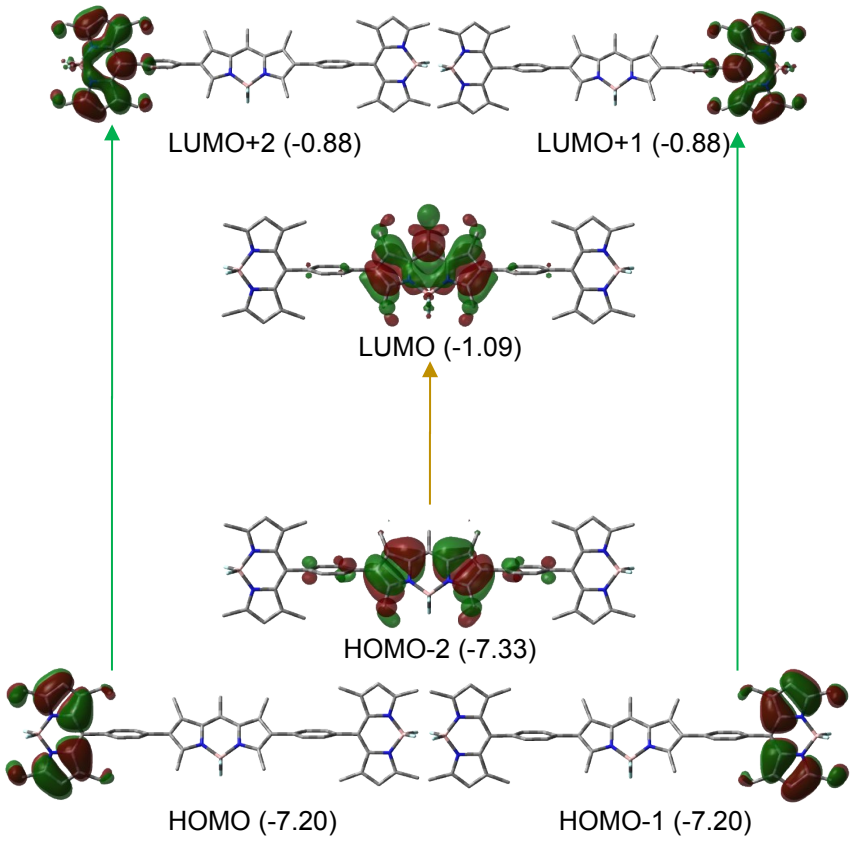


Figure S3. Theoretically predicted (td wb97xd/6-311g*) molecular orbitals and energies (in eV) involved in the main absorption transition of triad **2**. The transitions corresponding to the lateral BODIPY chromophores are isoenergetic, whereas that for the central BODIPY chromophore has a slightly lower energy gap.

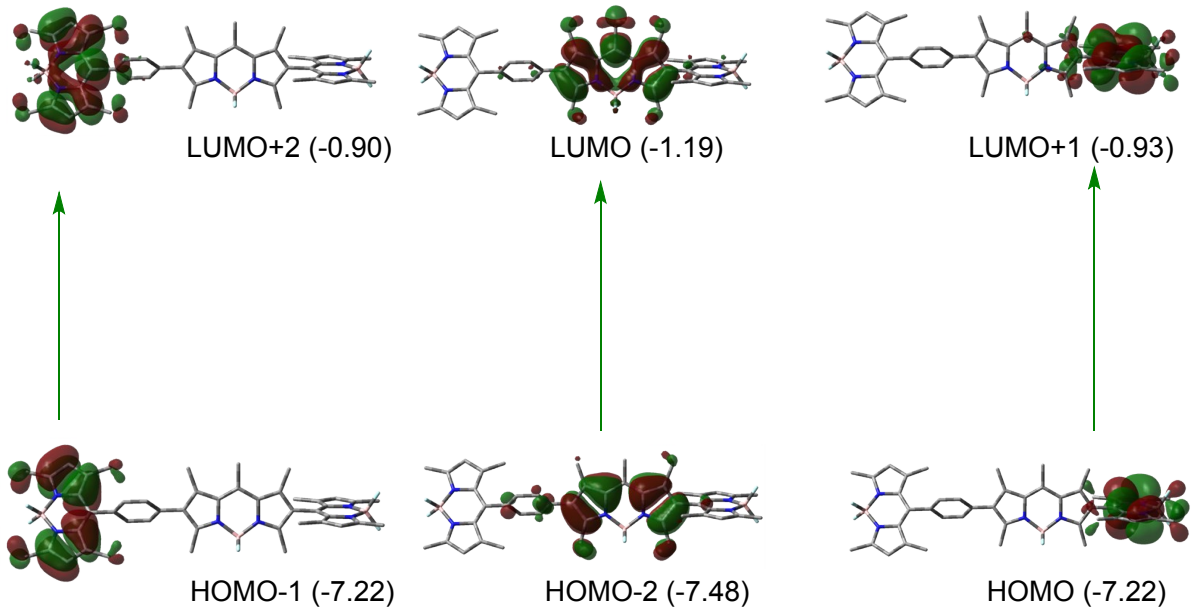


Figure S4. Theoretically predicted (td wb97xd/6-311g*) molecular orbitals and enegies (in eV) involved in the main absorption transition of triad **3**. The three electronic transitions are isoenergetics, with the same energy gaps.

4. Synthetic procedures and characterization data

4.1. General Procedures for Suzuki reaction

The corresponding halogenated derivative (1 mol. equiv.), boronic acid derivative (3-6 mol. equiv.) and K_2CO_3 (3-6 mol. equiv.) were dissolved in toluene/ethanol/water (2:2:1, v/v/v). Then, $Pd(PPh_3)_4$ (5-15% mol. equiv.) was added and the mixture refluxed under argon for 2-24 h. After removal of the solvent under reduced pressure, the obtained crude product was dissolved with CH_2Cl_2 and the obtained solution washed with water, dried over anhydrous Na_2SO_4, filtered, and the solvent evaporated to dryness. The obtained residue was submitted to purification by flash chromatography on silica gel.

4.2. General procedure for the synthesis of BODIPY cores

To a degassed solution of formylBODIPY (1 mol. equiv.) in dry CH_2Cl_2 (18 mL) were added a solution of 2,4-dimethylpyrrole (2-8 mol. equiv.) in dry CH_2Cl_2 (2 mL) and two drops of trifluoroacetic acid (TFA), and the resulting mixture stirred for 1 h at rt. After disappearance of the starting material, a solution of DDQ (1.1-2.2 equiv) in CH_2Cl_2 (10 mL) was added, and the resulting new mixture stirred for 30 min. Then, Et_3N (5-10 mol. equiv.) and $BF_3{\cdot}Et_2O$ (10-20 mol. equiv.) were added to the mixture, and the resulting final mixture stirred for 3 h at rt, washed with HCl 10%, and water. The obtained organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent evaporated to dryness. The obtained residue was submitted to purification by flash chromatography on silica gel.

4.3. Synthesis of 6

According to the general procedure described in section 4.1., 2-iodo-1,3,5,7-tetramethylBODIPY[2] (**5**) (100 mg, 0.26 mmol), 4-formylphenylboronic acid (116 mg, 0.77 mmol), K_2CO_3 (107 mg, 0.77 mmol) and $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) in toluene/ethanol/water (5 mL) were refluxed for 2 h. Flash chromatography (hexane/CH_2Cl_2, 30:70) afforded **6** (82 mg, 87%) as an orange solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.06 (s, 1H, CHO), 7.95 (d, *J* = 8.4 Hz, 2H, 2CH), 7.39 (d, *J* = 8.4 Hz, 2H, 2CH), 6.13 (s, 1H, CH), 2.66 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 2.35 (s, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 191.9 (CHO), 155.4 (C), 150.7 (C), 142.3 (C), 142.0 (C), 140.8 (C), 136.4 (C), 135.0 (C), 132.9 (C), 131.7 (C), 131.1 (CH), 129.8 (CH), 122.1 (CH), 17.6 (CH_3), 16.9 (CH_3), 15.4 (CH_3), 14.6 (CH_3), 13.2 (CH_3) ppm. FTIR ν 2922, 2853, 2722, 1706, 1603, 1550, 1464, 1397, 1314, 1202, 1067, 998, 831 cm^{-1}. HRMS-EI *m/z* 366.1718 (calcd. for $C_{21}H_{21}BF_2N_2O$: 366.1715).

4.4. Synthesis of 1

According to the general procedure described in section 4.2., BODIPY **6** (75 mg, 0.20 mmol), 2,4-dimethylpyrrole (0.05 mL, 0.43 mmol) and TFA (two drops) in CH_2Cl_2 (20 mL) were reacted for 1 h. Then, a solution of DDQ (51 mg, 0.22 mmol) in CH_2Cl_2 (10 mL) was added and the mixture stirred for 30 min. Then, Et_3N (0.14 mL, 1.00 mmol) and $BF_3{\cdot}Et_2O$ (0.25 mL, 2.00 mmol) were added and the mixture stirred for 3 h. Flash chromatography (hexane/CH_2Cl_2, 60:40) afforded **1** (38 mg, 32%) as an orange solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.7 Hz, 2H, 2CH), 7.33 (d, *J* = 7.7 Hz, 2H, 2CH), 6.12 (s, 1H, CH), 6.01 (s, 2H, 2CH), 2.67 (s, 3H, CH_3), 2.57 (s, 6H, $2CH_3$), 2.56 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 1.47 (s, 6H, $2CH_3$) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 155.6 (C), 154.8 (C), 151.1 (C), 143.0 (C), 141.83 (C), 141.80 (C), 141.5 (C) 136.5 (C), 134.9 (C), 133.8 (C), 132.7 (C), 132.5 (C), 131.8 (C) 131.5 (C), 131.2 (CH), 128.1 (CH), 121.9 (CH), 121.4 (CH), 17.6 (CH_3), 16.9 (CH_3), 15.4 (CH_3), 14.64 (CH_3), 14.58 (CH_3), 14.3 (CH_3), 13.2 (CH_3) ppm. FTIR ν 2921, 2852, 1546, 1513, 1510, 1464, 1403, 1371, 1307, 1197, 1068, 978 cm^{-1}. HRMS-EI *m/z* 584.2902 (calcd. for $C_{33}H_{34}B_2F_4N_4$: 584.2906).

4.5. Synthesis of 8

According to the general procedure described in section 4.1., 2,6-diiodo-1,3,5,7-tetramethylBODIPY[2] (**7**) (186 mg, 0.36 mmol), 4-formylphenylboronic acid (326 mg, 2.17 mmol), K_2CO_3 (300 mg, 2.17 mmol) and $Pd(PPh_3)_4$ (63 mg, 0.054 mmol) in toluene/ethanol/water (7 mL) were refluxed for 5 h. Flash chromatography (hexane/EtOAc, 60:40) afforded **8**[3] (86 mg, 50%) as a red solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.08 (s, 2H, 2CHO), 7.98 (d, *J* = 8.4 Hz, 4H, 4CH), 7.42 (d, *J* = 8.4 Hz, 4H, 4CH), 2.75 (s, 3H, CH_3), 2.53 (s, 6H, $2CH_3$), 2.39 (s, 6H, $2CH_3$) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 191.9 (CHO), 152.5 (C), 142.7 (C), 140.4 (C), 137.5 (C), 135.1 (C), 132.6 (C), 131.0 (CH), 129.9 (CH), 17.5 (CH_3), 15.6 (CH_3), 13.4 (CH_3) ppm. FTIR ν 2922, 2852, 2783, 1698, 1604, 1535, 1464, 1386, 1317, 1236, 1185, 1125, 1091, 997 cm^{-1}. HRMS-EI *m/z* 470.1971 (calcd. for $C_{28}H_{25}BF_2N_2O_2$: 470.1977).

4.6. Synthesis of 2

According to the general procedure described in section 4.2., BODIPY **8** (117 mg, 0.25 mmol), 2,4-dimethylpyrrole (0.21 mL, 1.99 mmol) and TFA (two drops) in CH_2Cl_2 (20 mL) were reacted for 1 h. Then, a solution of DDQ (124 mg, 0.55 mmol) in CH_2Cl_2 (10 mL) and the mixture stirred for 30 min. Then, Et_3N (0.35 mL, 2.49 mmol) and $BF_3{\cdot}Et_2O$ (0.61 mL, 4.97 mmol) were added and the mixture stirred for 3 h. Flash chromatography (hexane/CH_2Cl_2/EtOAc, 70:20:10) afforded **2** (44 mg, 20%) as an orange solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.7 Hz, 4H, 4CH), 7.36 (d, *J* = 7.7 Hz, 4H, 4CH), 6.02 (s, 4H,

4CH), 2.77 (s, 3H, CH_3), 2.58 (s, 12H, $4CH_3$), 2.52 (s, 6H, $2CH_3$), 2.39 (s, 6H, $2CH_3$), 1.48 (s, 12H, $4CH_3$) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 155.6 (C), 152.3 (C), 143.0 (C), 142.3 (C), 141.4 (C), 137.2 (C), 134.6 (C), 134.0 (C), 133.0 (C), 132.4 (C), 131.5 (C), 131.2 (CH), 128.2 (CH), 121.4 (CH), 17.4 (CH_3), 15.6 (CH_3), 14.7 (CH_3), 14.4 (CH_3), 13.3 (CH_3) ppm. FTIR ν 2923, 2854, 1545, 1511, 1466, 1310, 1192, 1075, 986 cm^{-1}. HRMS-MALDI-TOF *m/z* 906.4353 (calcd. for $C_{52}H_{51}B_3F_6N_6$: 906.4359).

4.7. Synthesis of 10

According to the general procedure described in section 4.1., 2-formyl-6-iodo-1,3,5,7-tetramethylBODIPY[4] (**9**) (180 mg, 0.43 mmol), 4-formylphenylboronic acid (195 mg, 1.30 mmol), K_2CO_3 (179 mg, 1.30 mmol) and $Pd(PPh_3)_4$ (25 mg, 0.022 mmol) in toluene/ethanol/water (5 mL) were refluxed for 2 h. Flash chromatography (hexane/EtOAc, 60:40) afforded **10** (96 mg, 56%) as an orange solid. ^1H NMR (300 MHz, $CDCl_3$) δ 10.13 (s, 1H, CHO), 10.08 (s, 1H, CHO), 7.99 (d, *J* = 8.1 Hz, 2H, 2CH), 7.40 (d, *J* = 8.1 Hz, 2H, 2CH), 2.81 (s, 3H, CH_3), 2.77 (s, 6H, $2CH_3$), 2.53 (s, 3H, CH_3), 2.39 (s, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7 (CHO), 186.1 (CHO), 157.3 (C), 156.2 (C), 144.7 (C), 141.6 (C), 140.6 (C), 139.2 (C), 135.6 (CH), 134.5 (C), 131.5 (C), 130.9 (CH), 130.0 (CH), 126.3 (C), 17.8 (CH_3), 16.0 (CH_3), 14.2 (CH_3), 13.8 (CH_3), 12.8 (CH_3) ppm. FTIR ν 2921, 2851, 2741, 1699, 1659, 1546, 1456, 1379, 1321, 1227, 1194, 1125, 1071, 999 cm^{-1}. HRMS-EI *m/z* 394.1656 (calcd. for $C_{22}H_{21}BF_2N_2O_2$: 394.1664).

4.8. Synthesis of 3

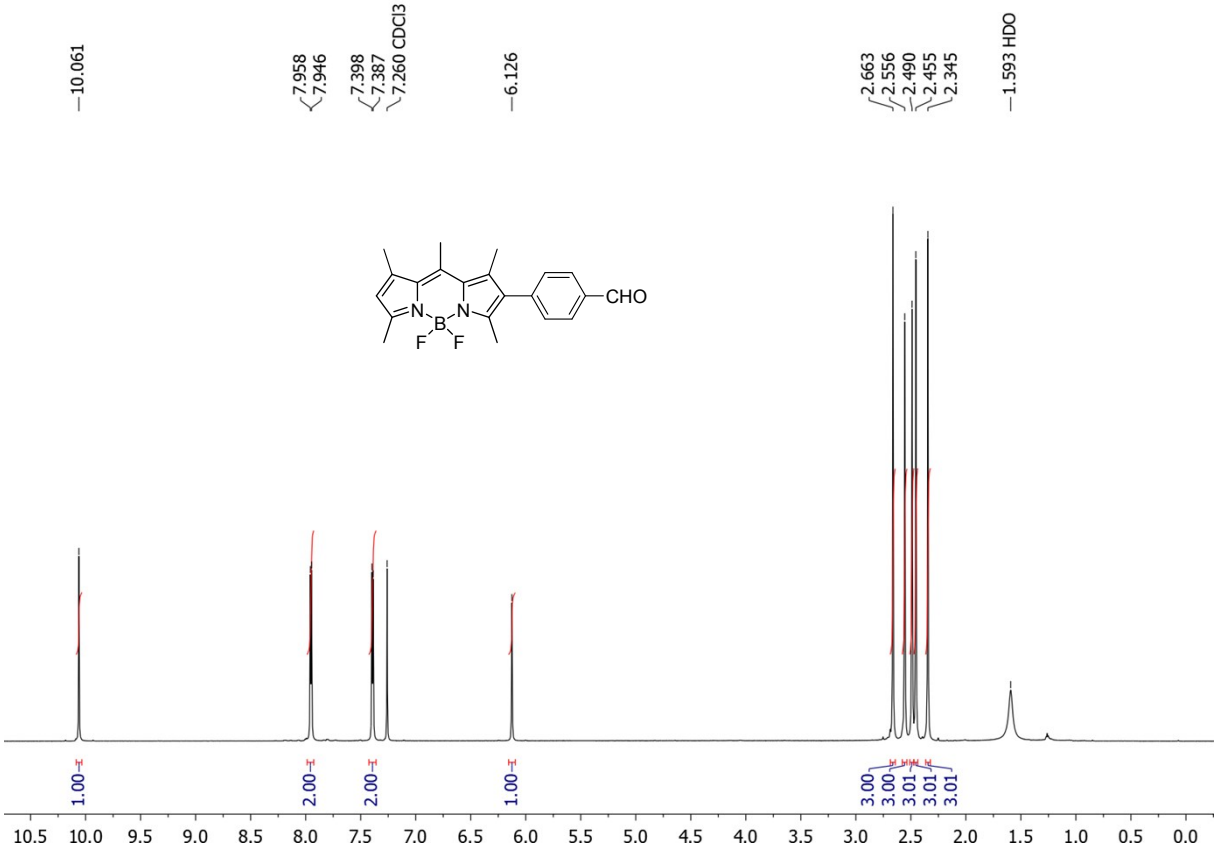
According to the general procedure described in section 4.2., BODIPY **10** (118 mg, 0.30 mmol), 2,4-dimethylpyrrole (0.25 mL, 2.39 mmol) and TFA (two drops) in CH_2Cl_2 (20 mL) were reacted for 1 h. Then, a solution of DDQ (150 mg, 0.66 mmol) in CH_2Cl_2 (10 mL) was added and the mixture stirred for 30 min. Then, Et_3N (0.42 mL, 3.00 mmol) and $BF_3{\cdot}Et_2O$ (0.74 mL, 6.00 mmol) were added to the mixture and stirred for 3 h. Flash chromatography (hexano/CH_2Cl_2/AcOEt, 70:20:10) afforded **3** (30 mg, 12%) as an orange solid. ^1H NMR (700 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.7 Hz, 2H, 2CH), 7.31 (d, *J* = 7.7 Hz, 2H, 2CH), 6.03 (s, 2H, 2CH), 6.02 (s, 2H, 2CH), 2.76 (s, 3H, CH_3), 2.58 (s, 12H, $4CH_3$), 2.51 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 1.72 (s, 6H, $2CH_3$), 1.47 (s, 6H, $2CH_3$) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 156.0 (C), 155.7 (C), 154.5 (C), 149.9 (C), 142.9 (C), 142.7 (C), 142.6 (C), 141.2 (C), 138.8 (C), 136.8 (C), 134.4 (C), 134.2 (C), 134.0 (C), 133.5 (C), 132.8 (C), 132.2 (C), 132.0 (C), 131.4 (C), 131.1 (CH), 128.4 (CH), 125.9 (C), 121.43 (CH), 121.39 (CH), 17.3 (CH_3), 15.7 (CH_3), 15.1 (CH_3), 14.71 (CH_3), 14.66 (CH_3), 14.4 (CH_3), 14.0 (CH_3), 13.4 (CH_3), 12.8 (CH_3) ppm. FTIR ν 2924, 2854, 1547, 1512, 1468, 1311, 1193, 1084, 1003, 980 cm^{-1}. HRMS-MALDI-TOF *m/z* 830.4044 (calcd. for $C_{46}H_{47}B_3F_6N_6$: 830.4046).

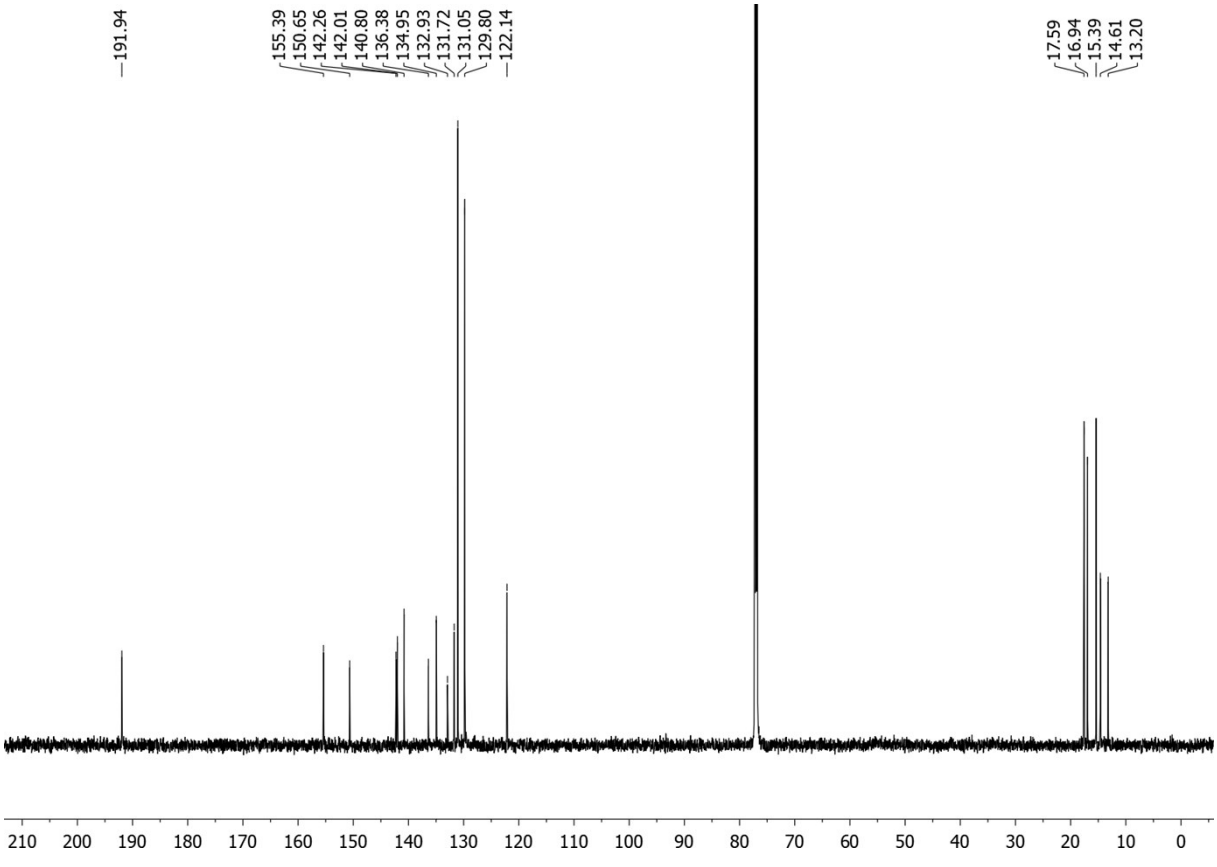
4.9. Synthesis of 4

According to the general procedure described in section 4.1., 2,6-dibromo-1,7-dimethyl-3,5-bis(4-methoxystyryl)BODIPY[5] (**11**) (59 mg, 0.09 mmol), pinacol BODIPYboronate **12**[6] (104 mg, 0.23 mmol), K_2CO_3 (51 mg, 0.37 mmol) and $Pd(PPh_3)_4$ (11 mg, 0.009 mmol) in toluene/ethanol/water (5 mL) were refluxed for 24 h. Flash chromatography (hexane/CH_2Cl_2, 10:90) afforded **4** (46 mg, 44%) as a highly insoluble green solid. ^{1}H NMR (700 MHz, CD_2Cl_2) δ 7.58-7.55 (m, 6H, 6CH), 7.45 (d, *J* = 7.0 Hz, 4H, 4CH), 7.23-7.24 (m, 5H, 5CH), 6.96 (d, *J* = 15.4 Hz, 2H, 2CH), 6.88 (d, *J* = 8.4 Hz , 4H, 4CH), 3.82 (s, 6H, $2CH_3O$), 2.54 (s, 12H, $4CH_3$), 2.15 (s, 6H, $2CH_3$), 1.60 (s, 12H, $4CH_3$) ppm. FTIR ν 2921, 2852, 1583, 1543, 1511, 1223, 1196, 1153, 1061 cm^{-1}. HRMS-MALDI-TOF *m/z* 1128.5006 (calcd. for $C_{67}H_{61}B_3F_6N_6O_2$: 1128.5039).

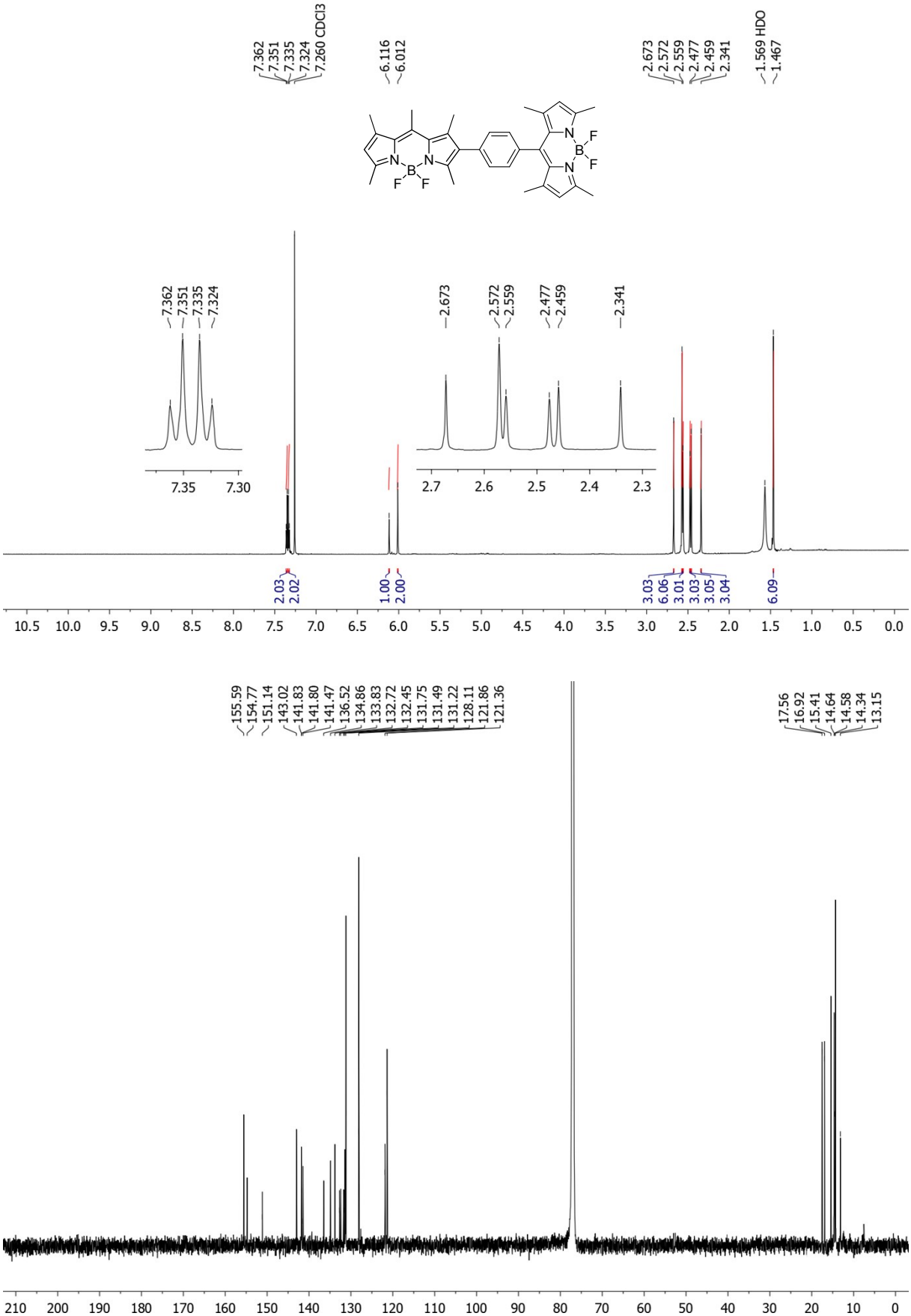
5. ^{1}H NMR and ^{13}C NMR spectra

^{1}H NMR (700 MHz, $CDCl_3$) and ^{13}C NMR (176 MHz, $CDCl_3$) spectra of **6**

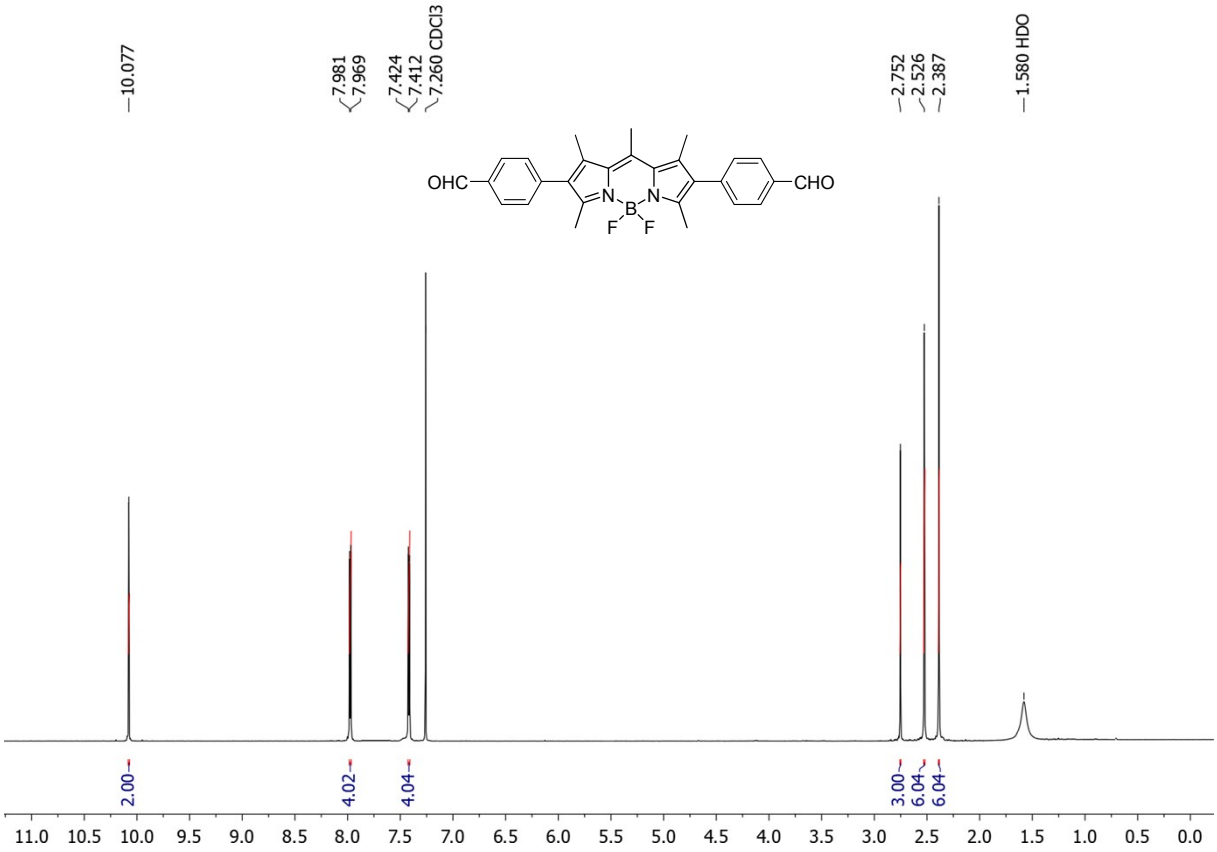


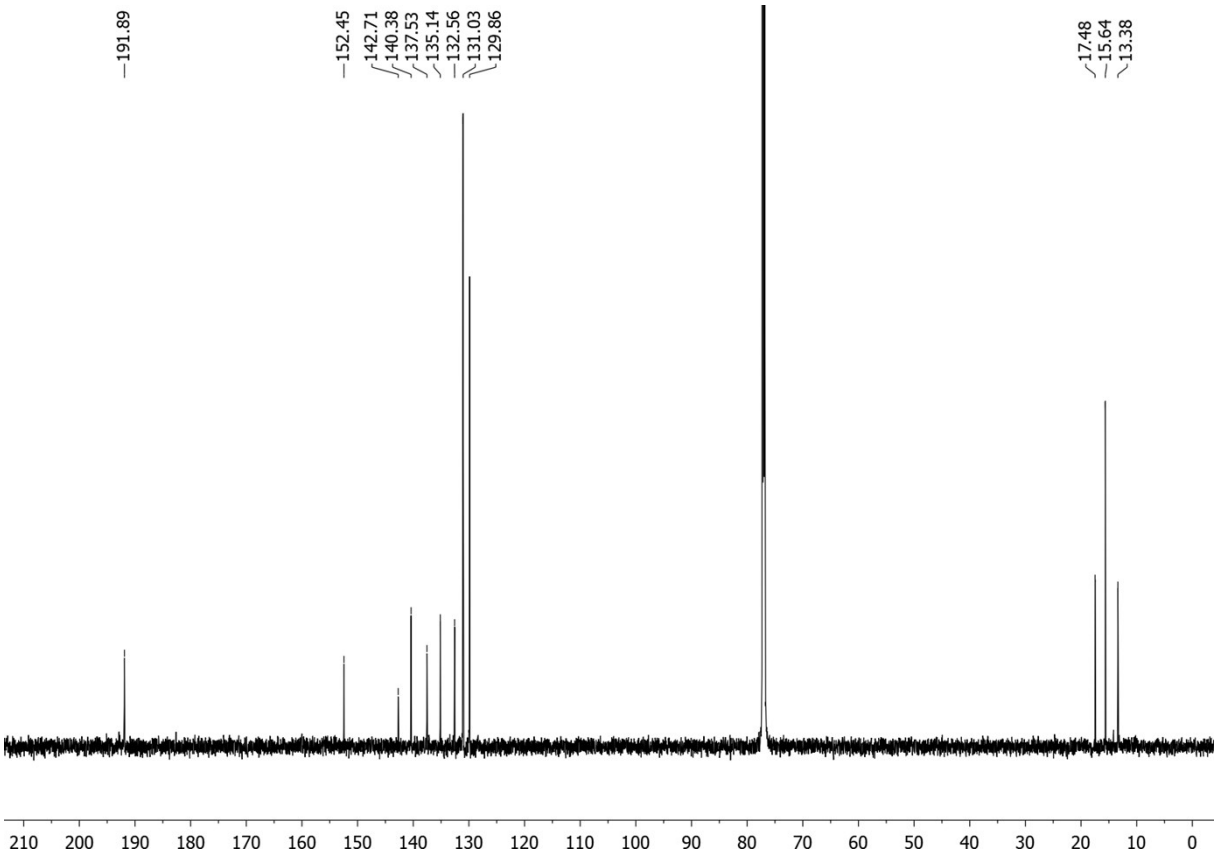


^{1}H NMR (700 MHz, $CDCl_3$) and ^{13}C NMR (176 MHz, $CDCl_3$) spectra of **1**

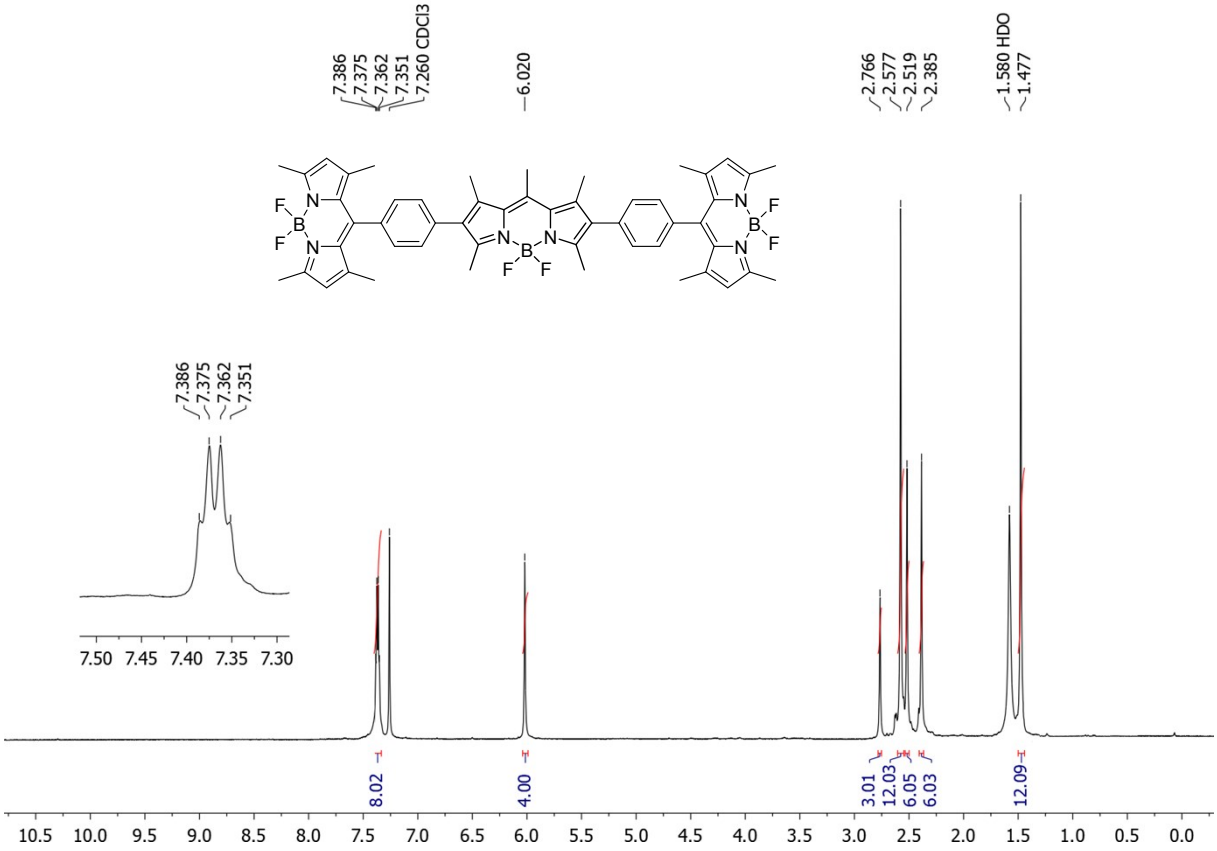


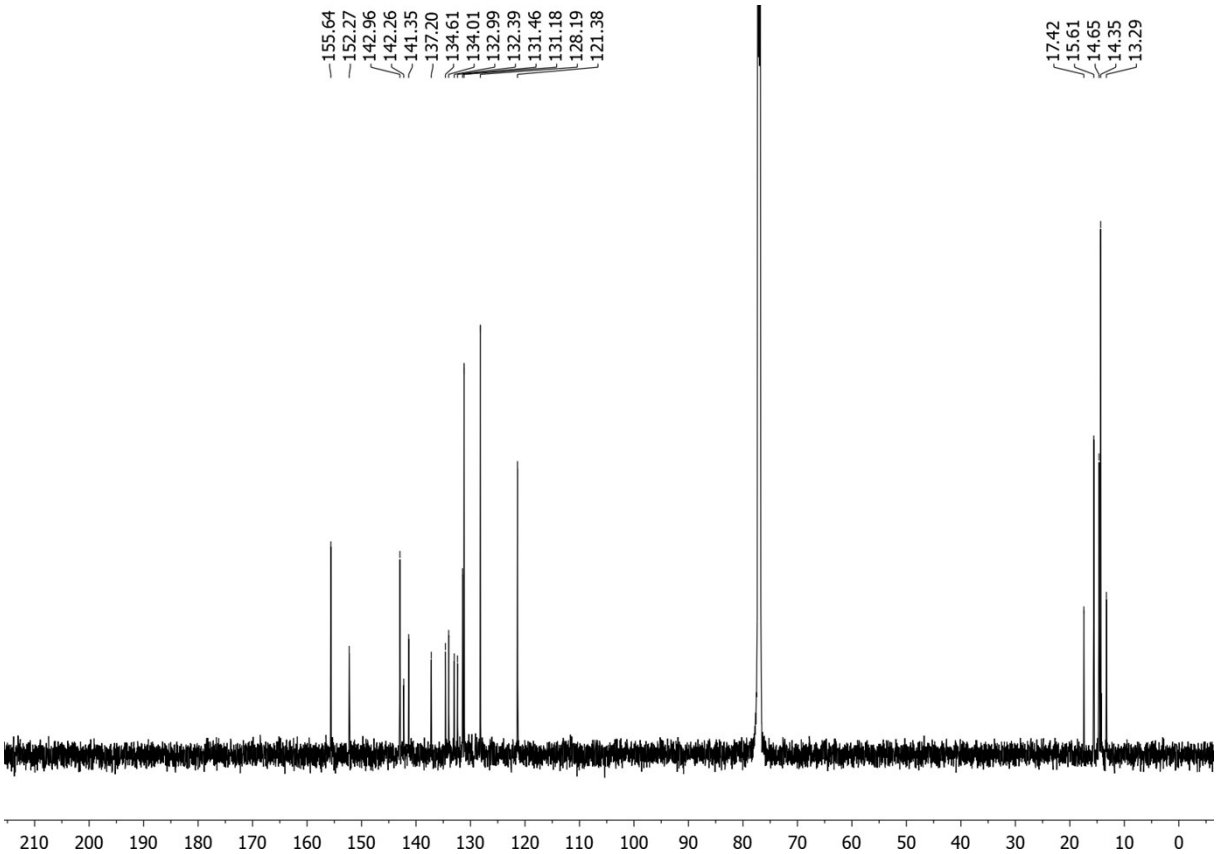
^{1}H NMR (700 MHz, $CDCl_3$) and ^{13}C NMR (176 MHz, $CDCl_3$) spectra of **8**



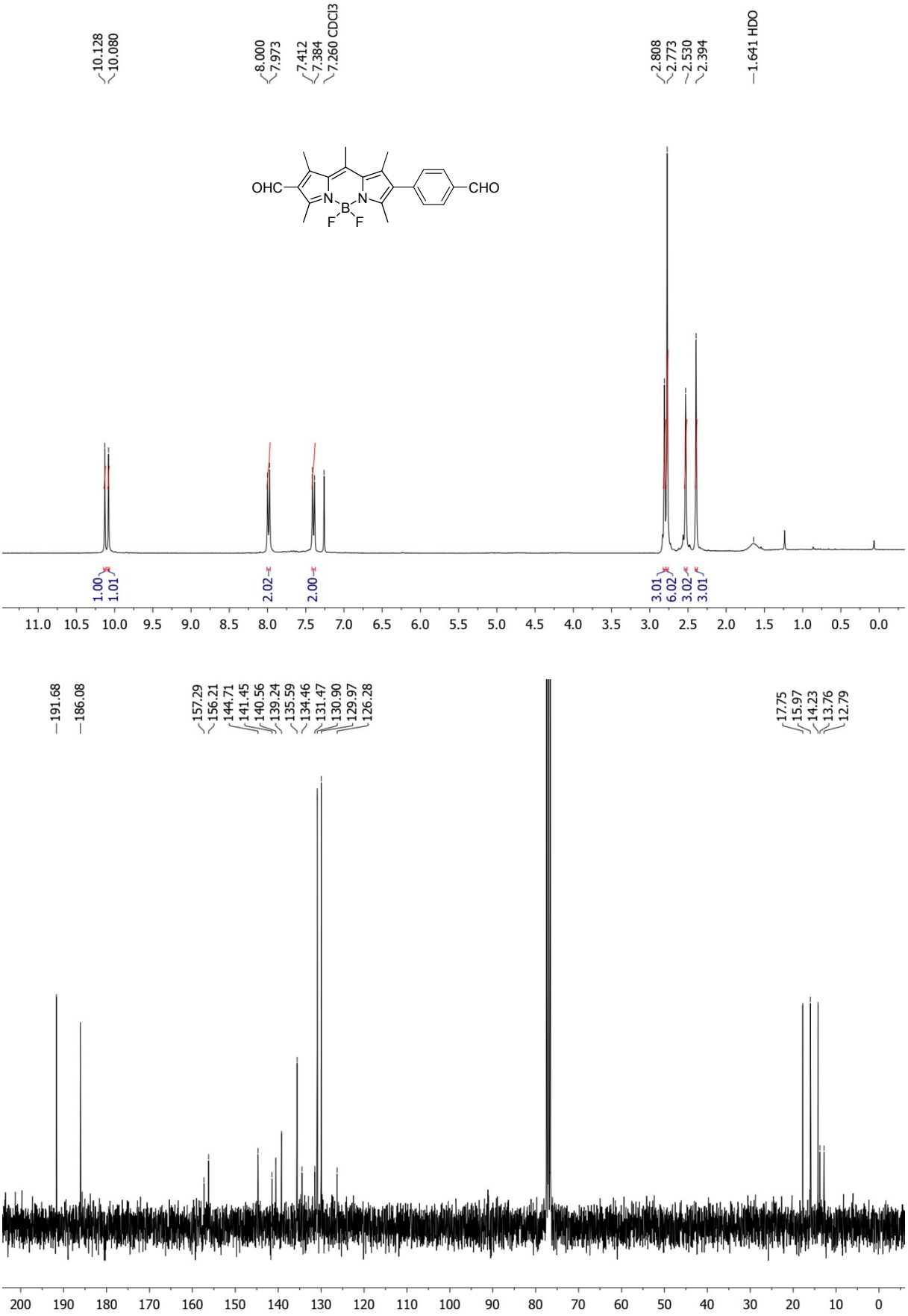


^{1}H NMR (700 MHz, $CDCl_3$) and ^{13}C NMR (176 MHz, $CDCl_3$) spectra of **2**

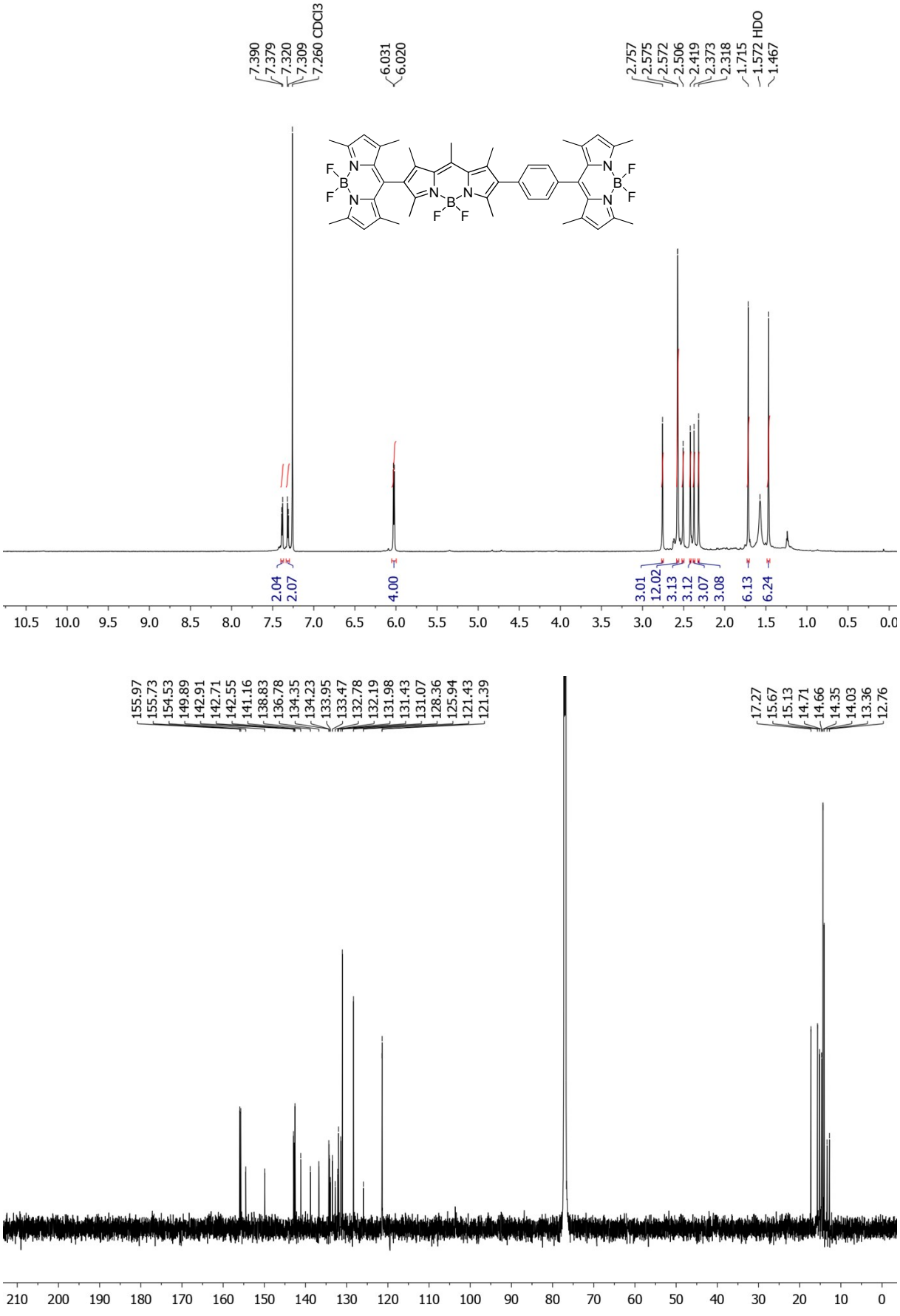




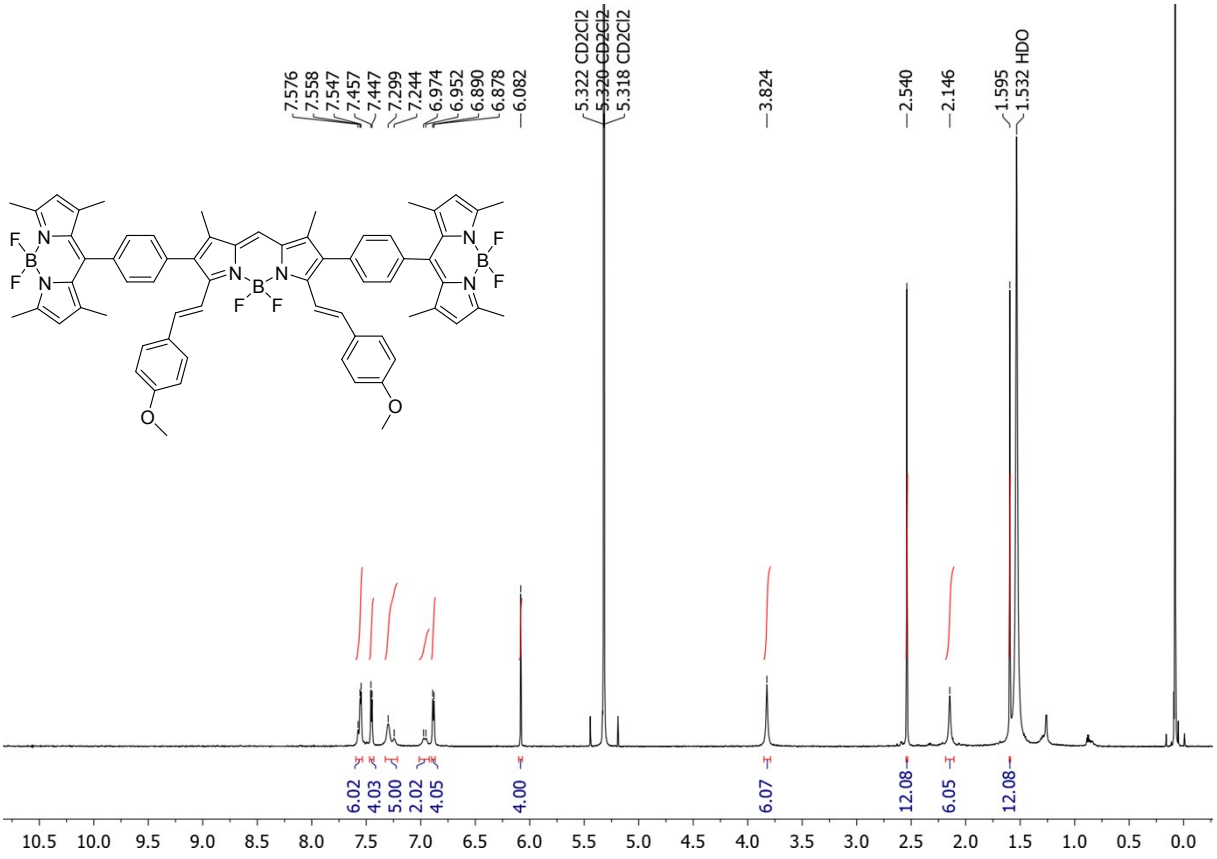
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **10**



^{1}H NMR (700 MHz, $CDCl_3$) and ^{13}C NMR (176 MHz, $CDCl_3$) spectra of **3**



^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **4**



6. References

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