Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for

Coumarin/BODIPY hybrids by heteroatom linkage: versatile, tunable and photostable dye lasers for UV irradiation

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1. General

Synthesis

Common solvents were dried and distilled by standard procedures. All starting materials and reagents were obtained commercially and used without further purifications. Flash chromatography purifications were performed on silica gel 60 (60, 230-400 mesh ASTM). Thin-layer chromatography (TLC) was performed on silica gel plates (silica gel 60, F254, supported on aluminium). NMR spectra were recorded at 20 ºC and the residual solvent peaks were used as internal standards. Complex spin-system signals were additionally simulated by using MestRe-C.[1] FTIR spectra were obtained from neat samples using the ATR technique. High resolution mass spectrometry (HRMS) was performed using the EI technique.

Photophysics

Standard abbreviations: Absorption maximum (λ_{ab}); fluorescence maximum (λ_{fl}); molar extinction coefficient at λ_{ab} (ε_{max}); fluorescence quantum yield (ϕ); mean fluorescence lifetime (τ); Stokes, or pseudo-Stokes when indicated, shift ($\Delta\nu_{St}$). Absorption and fluorescence spectra, as well as fluorescence-decay curves, were recorded in diluted solutions (~$2\cdot10^{-6}$ M) of ethyl acetate (cut-off ~190 nm). UV-Vis absorption and fluorescence spectra were recorded on a Varian CARY 4E spectrophotometer and on an Edinburgh Instruments spectrofluorimeter (model FLSP 920), respectively. ϕ values were obtained using quinine sulfate (ϕ = 0.55, in 0.1N H_2SO_4) as reference for the UV coumarin-chromophore emission, and **1** (ϕ = 0.84 in ethanol), PM597 (ϕ = 0.43 in ethanol), PM605 (ϕ = 0.66 in ethanol) and Nile Blue (ϕ = 0.27 in methanol) for the Vis BODIPY-chromophore emission. These values were calculated from corrected fluorescence spectra (detector sensibility to the wavelength), and corrected by the refractive index of the solvent. Temperature-dependence measurements were performed using a liquid-hydrogen-cooled cryostat (Oxford), and an external electronic temperature-controller device for heating. Radiative-decay curves were registered with the time-correlated single-photon counting technique (Edinburgh Instruments FL920, with picosecond time-resolution). Fluorescence emission was monitored at λ_{fl} upon direct

[1] MestRe-C: C. Cobas, J. Cruces and J. Sardina, MestRe-C, program version 2.3.

excitation at 470 nm and 530 nm by means of a diode laser (PicoQuant LDH470 and LDH530, respectively) with 150 ps full width at half maximum (FWHM) pulses. τ values were 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, Durbin-Watson and analysis of the residuals). The radiative (k_{fl}) and non-radiative (k_{nr}) rate constants were calculated from the fluorescence quantum yield and lifetime: $k_{fl} = \phi/\tau$; $k_{nr} = (1-\phi)/\tau$.

Electrochemistry

Voltammograms (Metrohm Autolab) were recorded using a three-electrode set up with a platinum disk (diameter 3 mm) or layer (surface 8 mm x 7.5 mm) 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.

Quantum mechanical calculations

Ground state geometries were optimized at the Density Functional Theory (DFT) using the hybrid B3LYP method, and the double valence basis set (6-31g). The geometries were considered as energy minimum when the corresponding frequency analysis did not give any negative value. The absorption spectra were simulated by the Time-Dependent (TD) method. The solvent effect (ethyl acetate) was considered in the conducted theoretical simulations by means of the Polarizable Continuum Model (PCM). All the calculations were performed using the Gaussian 09[2] software as implemented in the computational cluster “arina” of the UPV/EHU.

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[2] Gaussian 09: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Laser behavior

Liquid solutions of dyes were contained in 1 cm optical-path rectangular quartz cells carefully sealed to avoid solvent evaporation during the experiments. These solutions were transversely pumped either at 355 nm, with 5 mJ, 8 ns FWHM pulses from the third-harmonic of a Q-switched Nd:YAG laser (Spectron SL282G) or at 532 nm, with 5 mJ, 6 ns full width at half maximum (FWHM) pulses from a frequency-doubled Q-switched Nd:YAG laser (Monocrom OPL-10), at a repetition rate of up to 10 Hz. The exciting pulses were line-focused onto the cell, providing pump fluencies on the active medium in the range 110-180 mJ/cm^2. The oscillation cavity (2 cm length) consisted of a 90% reflectivity aluminium mirror, with the lateral face of the cell or the solid sample as output coupler. The photostability of the dyes in liquid solution was evaluated by irradiating under lasing conditions 10 µL of ethyl acetate solution, contained in a cylindrical Pyrex capillary (1 cm height, 1 mm internal diameter) carefully sealed to avoid solvent evaporation during the experiments. Although the low optical quality of the capillary tube prevents from laser emission from the dye, information about dye photostability can be obtained by monitoring the decrease in the laser-induced fluorescence intensity, by exciting transversally the capillary, as a function of the number of pump pulses at a given repetition rate. The fluorescence emission was monitored perpendicular to the exciting beam, collected by an optical fiber, and imaged onto the input slit of a monochromator (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. Each experience was repeated at least three times. The estimated error in the energy and photostability measurements was 10%.

2. Synthetic procedures and characterization data

General procedure A. To a solution of the corresponding starting BODIPY (1 equiv) and coumarin (1-6 equiv) in dry CH_3CN (15 mL) was added K_2CO_3 (3-6 equiv), or NaH (4 equiv), and the resulting mixture refluxed until consumption of the starting BODIPY (TLC monitoring). The reaction was quenched by addition of water, and the organic layer extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, and concentrated to dryness. The obtained hybrids were purified by flash chromatography on silica gel.

General procedure B. A solution of the corresponding starting BODIPY (1 equiv) and coumarin (3-6 equiv) in dry CH_3CN (3 mL) was placed in a sealed vessel, and reacted in a Biotage® Initiator Classic microwave synthesizer at 150 ºC for 3 h. EtOAc was then added, and the solution was washed with 10% aq HCl, or 10% aq NaOH, and water, dried over $MgSO_4$, filtered, and concentrated to dryness. The obtained hybrids were purified by flash chromatography on silica gel.

General procedure C. To a solution of the corresponding BODIPY (1 equiv) in dry CH_3CN (15 mL) was added coumarin (4-6 equiv), and the resulting mixture refluxed until consumption of the starting BODIPY (TLC monitoring). EtOAc was then added, and the solution washed with 10% aq HCl, or 10% aq NaOH, and water, dried over $MgSO_4$, filtered, and concentrated to dryness. The obtained hybrid were purified by flash chromatography on silica gel.

Hybrid 1dA: To a solution of BODIPY **1**[3] (50 mg, 0.16 mmol) in dry CH_2Cl_2 was added aluminium chloride (41.8 mg, 0.32 mmol) under an argon atmosphere, and the mixture resulting was refluxed for 10 min. Then, coumarin **AH** (111 mg, 0.63 mmol) was added and the mixture was refluxed for 30 min. Water was added, and the solution was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and concentrated to dryness. Flash chromatography using hexane/EtOAc (7:3) afforded **1dA** (60 mg, 55%) as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.7 Hz, 2H), 6.61 (dd, *J* = 8.7 and 2.4 Hz, 2H), 6.17 (d, *J* = 2.4 Hz, 2H), 5.94 (d, *J* = 0.9 Hz, 2H), 2.72 (s, 3H), 2.34 (s, 12H), 2.24 (d, *J* = 0.9 Hz, 6H), 2.20 (q, *J* = 7.5 Hz, 4H), 0.83 (t, *J* = 7.5 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2 (C), 160.1 (C), 155.1 (C), 153.1 (C), 152.5 (C), 140.3 (C), 137.9 (C), 133.6 (C), 132.2 (C), 125.2 (CH), 116.6 (CH), 112.8 (C), 111.0 (CH), 105.1 (CH), 18.6 (CH_3), 17.3 (CH_3), 17.1 (CH_2), 14.8 (CH_3), 12.6 (CH_3) ppm; FTIR υ 2925, 1718, 1606, 1548, 1388,

[3] Laser grade, Exciton. It was used as received with a purity > 99%.

1190, 1138, 1068, 1002, 978 cm^{-1}; HRMS-EI *m/z* calcd for ($C_{38}H_{39}BN_2O_6$) 630.2900, found 630.2895.

Hybrid 2mA: According to the general procedure A, BODIPY **2**[4] (100 mg, 0.286 mmol), coumarin **AH** (49.5 mg, 0.286 mmol) and K_2CO_3 (118.5 mg, 0.858 mmol) were reacted for 24 h. Flash chromatography using hexane/EtOAc (95:5) afforded **2mA** (101 mg, 72%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 9.3 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.17-7.15 (m, 2H), 6.84 (d, *J* = 4.5 Hz, 1H), 6.67 (d, *J* = 4.2 Hz, 1H), 6.28 (d, *J* = 4.2 Hz, 1H), 6.20 (d, *J* = 1.2 Hz, 1H), 5.83 (d, *J* = 4.8 Hz, 1H), 2.38 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5 (C), 160.2 (C), 156.4 (C), 154.5 (C), 151.9 (C), 143.1 (C), 141.1 (C), 139.9 (C), 133.9 (CH), 132.8 (C), 130.5 (CH), 129.8 (CH), 129.6 (C), 129.3 (CH), 128.6 (C), 126.5 (CH), 118.1 (CH), 116.7 (C), 116.4 (CH), 114.6 (CH), 108.6 (CH), 105.9 (CH), 21.5 (CH_3), 18.8 (CH_3) ppm; FTIR υ 2918, 2850, 1727, 1710, 1582, 1509, 1418, 1255, 1097, 1017, 974 cm^{-1}; HRMS-EI *m/z* calcd for ($C_{26}H_{18}BClF_2N_2O_3$) 490.1065, found 490.1060.

Hybrid 2dA: According to the general procedure A, BODIPY **2**[4] (50 mg, 0.142 mmol), coumarin **AH** (150.5 mg, 0.85 mmol) and K_2CO_3 (117 mg, 0.85 mmol) in dry CH_3CN (10 mL) were reacted for 24 h. Flash chromatography using hexane/EtOAc (7:3) afforded **2dA** (48 mg, 54%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 9.3 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.17-7.14 (m, 4H), 6.77 (d, *J* = 4.2 Hz, 2H), 6.19 (d, *J* = 1.2 Hz, 2H), 5.81 (d, *J* = 4.2 Hz, 2H), 2.40 (s, 3H), 2.37 (d, *J* = 1.2 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7 (C), 160.4 (C), 157.4 (C), 154.6 (C), 151.9 (C), 143.0 (C), 140.8 (C), 130.9 (CH), 130.5 (CH), 130.0 (C), 129.2 (CH), 128.5 (C), 126.2 (CH), 117.5 (C), 116.0 (CH), 114.3 (CH), 107.9 (CH), 104.0 (CH), 21.5 (CH_3), 18.8 (CH_3) ppm; FTIR υ 2926, 1732, 1582, 1440, 1249, 1106, 978 cm^{-1}; HRMS-EI *m/z* calcd for ($C_{36}H_{25}BF_2N_2O_6$) 630.1772, found 630.1168.

Hybrid 2mB: According to the general procedure B, BODIPY **2**[4] (40 mg, 0.114 mmol) and coumarin **BH** (120 mg, 0.684 mmol) in dry CH_3CN (15 mL) were reacted at 150 ºC for 3 h. Flash chromatography using hexane/EtOAc (8:2) afforded **2mB** (48 mg, 86%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (broad s, 1H, NH), 7.55 (d, *J* = 8.7 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 2.1 Hz, 1H), 7.04 (dd, *J* = 8.7 and

[4] T. Rohand, M. Baruah, W. Qin, N. Boens and W. Dehaen, *Chem. Commun.*, 2006, 266.

2.1 Hz, 1H), 6.94 (d, *J* = 4.8 Hz, 1H), 6.51 (d, *J* = 4.8 Hz, 1H), 6.48 (d, *J* = 3.9 Hz, 1H), 6.20 (d, *J* = 3.9 Hz, 1H), 6.18 (d, *J* = 1.2 Hz, 1H), 2.38 (s, 3H), 2.37 (d, *J* = 1.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5 (C), 156.3 (C), 154.7 (C), 151.9 (C), 140.9 (C), 140.3 (C), 136.6 (C), 135.6 (CH), 133.6 (C), 132.4 (C), 132.3 (C), 130.4 (C), 130.3 (CH), 129.2 (CH), 126.2 (CH), 124.0 (CH), 116.9 (CH), 114.4 (CH), 114.0 (CH), 110.6 (CH), 107.9 (CH), 21.4 (CH_3), 18.7 (CH_3) ppm; FTIR υ 3353, 2922, 1728, 1709, 1579, 1470, 1383, 1100, 979 cm^{-1}; HRMS-EI *m/z* calcd for ($C_{26}H_{19}BClF_2N_3O_2$) 489.1225, found 489.1220.

Hybrids 3mA and 3dA: According to the general procedure A, BODIPY **3**[5] (50 mg, 0.132 mmol), coumarin **AH** (70 mg, 0.396 mmol) and K_2CO_3 (55 mg, 0.396 mmol) in dry CH_3CN (10 mL) were reacted for 2 h. Flash chromatography using hexane/EtOAc (8:2) afforded, by order of elution, **3mA** (18 mg, 26%) as a red solid, and **3dA** (50 mg, 57%) as a red solid. **3mA**: ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.60 (d, *J* = 9.1 Hz, 1H), 7.23-7.20 (m, 2H), 6.88 (s, 2H), 6.59 (d, *J* = 4.2 Hz, 1H), 6.40 (d, *J* = 4.2 Hz, 1H), 6.23 (s, 2H), 6.22 (d, *J* = 4.2 Hz, 1H), 5.76 (d, *J* = 4.9 Hz, 1H), 2.39 (d, *J* = 1.4 Hz, 3H), 2.28 (s, 3H), 2.05 (s, 6H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ 164.7 (C), 160.2 (C), 156.3 (C), 154.6 (C), 151.7 (C), 142.5 (C), 140.1 (C), 139.0 (C), 136.8 (C), 132.9 (C), 132.4 (CH), 130.0 (C), 128.4 (C), 128.2 (CH), 127.2 (CH), 126.3 (CH), 118.2 (C), 116.9 (CH), 116.6 (CH), 114.8 (CH), 108.9 (CH), 105.9 (CH), 21.1 (CH_3), 20.0 (CH_3), 18.8 (CH_3) ppm; FTIR υ 2924, 1734, 1573, 1436, 1354, 1261, 1104, 1025, 981, cm^{-1}; HRMS-EI *m/z* calcd for ($C_{28}H_{22}BClF_2N_2O_3$) 518.1378, found 518.1371. **3dA**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 9.6 Hz, 2H), 7.19-7.15 (m, 4H), 6.89 (s, 2H), 6.50 (d, *J* = 4.2 Hz, 2H), 6.19 (d, *J* = 1.2 Hz, 2H), 5.73 (d, *J* = 4.2 Hz, 2H), 2.37 (d, *J* = 1.2 Hz, 6H), 2.28 (s, 3H), 2.10 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2 (C), 160.8 (C), 157.6 (C), 155.0 (C), 152.3 (C), 142.7 (C), 139.2 (C), 137.4 (C), 130.0 (CH), 129.1 (C), 128.9 (C), 128.6 (CH), 126.6 (CH), 118.0 (C), 116.5 (CH), 114.7 (CH), 108.5 (CH), 104.3 (CH), 21.5 (CH_3), 20.4 (CH_3), 19.2 (CH_3) ppm; FTIR υ 2921, 1732, 1573, 1429, 1258, 1106, 1011, 978 cm^{-1}; HRMS-EI *m/z* calcd for ($C_{38}H_{29}BF_2N_2O_6$) 658.2085, found 658.2075.

Hybrid 3mB: According to the general procedure B, BODIPY **3**[5] (50 mg, 0.132 mmol) and coumarin **BH** (70 mg, 0.396 mmol) in dry CH_3CN (2.5 mL) were reacted at 150 ºC for 3 h. Flash chromatography using hexane/EtOAc (8:2) afforded **3mB** (62 mg, 90%) as a red

[5] T. Sakida, S. Yamaguchi and H. Shinokubo, *Angew. Chem. Int. Ed.*, 2011, **50**, 2280.

solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (broad s, 1H, NH), 7.55 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 2.1 Hz, 1H), 7.05 (dd, *J* = 8.4 and 2.1 Hz, 1H), 6.87 (s, 2H), 6.67 (d, *J* = 4.8 Hz, 1H), 6.45 (d, *J* = 4.8 Hz, 1H), 6.18 (d, *J* = 1.2 Hz, 1H), 6.17 (d, *J* = 3.9 Hz, 1H), 6.12 (d, *J* = 3.9 Hz, 1H), 2.36 (d, *J* = 1.2 Hz, 3H), 2.27 (s, 3H), 2.04 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8 (C), 157.0 (C), 155.1 (C), 152.2 (C), 141.2 (C), 139.0 (C), 137.4 (C), 137.3 (C), 135.9 (C), 134.8 (CH), 133.7 (C), 133.2 (C), 132.6 (C), 129.3 (C), 128.6 (CH), 126.5 (CH), 123.0 (CH), 117.4 (CH), 114.8 (CH), 114.5 (CH), 111.3 (CH), 108.5 (CH), 21.5 (CH_3), 20.3 (CH_3), 19.0 (CH_3) ppm; FTIR υ 3350, 2932, 1712, 1569, 1455, 1375, 1110, 989 cm^{-1}; HRMS-EI *m/z* calcd for ($C_{28}H_{23}BClF_2N_3O_2$) 517.1538, found 517.1530.

Hybrid 3dB: According to the general procedure B, BODIPY **3**[5] (50 mg, 0.132 mmol) and coumarin **BH** (92.5 mg, 0.528 mmol) in dry CH_3CN (3 mL) were reacted at 150 ºC for 3 h. Flash chromatography using hexane/EtOAc (8:2) afforded, by order of elution, **3mB** (48 mg, 70%) as a red solid (see characterization data above), and **3dB** (10 mg, 11%) as a blue solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.69 (broad s, 2H, 2NH), 7.47 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 2.1 Hz, 2H), 6.99 (dd, *J* = 8.4 and 2.1 Hz, 2H), 6.88 (s, 2H), 6.46 (d, *J* = 4.2 Hz, 2H), 6.29 (d, *J* = 4.2 Hz, 2H), 6.11 (s, 2H), 2.35 (s, 6H), 2.29 (s, 3H), 2.09 (s, 6H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ 160.9 (C), 155.0 (C), 152.1 (C), 150.4 (C), 142.6 (C), 138.3 (C), 137.2 (C), 134.5 (C), 129.8 (C), 129.5 (C), 128.9 (CH), 128.1 (CH), 125.9 (CH), 115.3 (C), 115.2 (CH), 112.8 (CH), 105.5 (CH), 105.4 (CH), 21.2 (CH_3), 19.9 (CH_3), 18.6 (CH_3) ppm; FTIR υ 3351, 2922, 1724, 1544, 1461, 1357, 1010, 977 cm^{-1}; HRMS-EI *m/z* calcd for ($C_{38}H_{31}BF_2N_4O_4$) 656.2404, found 656.2397.

Hybrid 3mC: According to the general procedure A, BODIPY **3**[5] (50 mg, 0.13 mmol), 4-hydroxycoumarin **CH** (85.5 mg, 0.53 mmol) and NaH (72.9 mg, 0.53 mmol) in dry CH_3CN (15 mL) were reacted for 24 h. Flash chromatography using hexane/EtOAc (93:7) afforded **3mC** (14 mg, 21%) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.67-7.63 (m, 1H), 7.41-7.38 (m, 2H), 6.98 (d, *J* = 0.4 Hz, 2H), 6.74 (d, *J* = 4.5 Hz, 1H), 6.63 (d, *J* = 4.3 Hz, 1H), 6.37 (d, *J* = 4.3 Hz, 1H), 6.24 (d, *J* = 4.5 Hz, 1H), 6.11 (s, 1H), 2.37 (s, 3H), 2.14 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9 (C), 161.6 (C), 158.6 (C), 153.7 (C), 145.1 (C), 144.0 (C), 139.3 (C), 136.7 (C), 134.0 (C), 133.4 (CH), 130.9 (CH), 130.0 (CH), 129.5 (C), 128.4 (CH), 128.0 (C), 124.7 (CH), 123.6 (CH), 118.6 (CH), 116.8 (CH), 114.5 (C), 106.7 (CH), 97.5 (CH), 21.1 (CH_3), 20.0 (CH_3) ppm; FTIR υ 1725, 1629, 1594, 1570, 1541, 1520, 1437, 1419, 1381, 1355, 1330, 1286, 1231, 1183,

1110, 1086, 994 cm^{-1}; HRMS (FAB) *m/z* calcd. for $C_{27}H_{21}BClF_2N_2O_3$ $[M+H]^+$ 505.1302, found 505.1309.

Hybrid 4mA: According to the general procedure C, BODIPY **4**[6] (40 mg, 0.137 mmol) and coumarin **AH** (97 mg, 0.55 mmol) in dry CH_3CN (15 mL) were reacted for 12 h. Flash chromatography using hexane/EtOAc (5:5) afforded, by order of elution, starting BODIPY **4** (10 mg, 25%), and **4mA** (37 mg, 59%) as a red solid. ^1H NMR (300 MHz, C_3D_6O) δ 7.86 (d, *J* = 8.7 Hz, 1H), 7.63-7.61 (m, 1H), 7.36 (d, *J* = 2.1 Hz, 1H), 7.31 (dd, *J* = 8.7 and 2.1 Hz, 1H), 7.16-7.14 (m, 1H), 6.47 (d, *J* = 4.2 Hz, 1H), 6.37 (d, *J* = 5.1 Hz, 1H), 6.25 (d, *J* = 1.2 Hz, 1H), 2.41 (d, *J* = 1.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, C_3D_6O) δ 171.0 (C), 160.3 (C), 156.5 (C), 156.0 (C), 153.5 (C), 140.3 (C), 137.0 (CH), 135.2 (C), 130.7 (C), 128.8 (CH), 127.5 (CH), 127.4 (C), 127.3 (q, *J* = 273.4 Hz, CF_3), 120.4 (C), 118.4 (CH), 117.7 (CH), 116.1 (CH), 113.1 (CH), 110.2 (CH), 19.0 (CH_3) ppm; FTIR υ 2923, 1691, 1567, 1444, 1247, 1108, 978 cm^{-1}; HRMS-EI *m/z* calcd for ($C_{20}H_{11}BClF_5N_2O_3$) 468.0471, found 468.0461.

Hybrids 4mB and 4dB: According to the general procedure C, BODIPY **4**[6] (32 mg, 0.11 mmol) and coumarin **BH** (192 mg, 0.66 mmol) in dry CH_3CN (15 mL) were reacted for 16 h. Flash chromatography using hexane/EtOAc (8:2) afforded, by order of elution, **4mB** (32 mg, 62%) as a red solid, and **4dB** (4 mg, 11%) as a blue solid. **4mB**: ^1H NMR (700 MHz, $CDCl_3$) δ 8.50 (broad s, 1H, NH), 7.62 (d, *J* = 8.4 Hz, 1H), 7.47 (m, 1H), 7.19 (d, *J* = 2.1 Hz, 1H), 7.11 (dd, *J* = 8.4 and 2.1 Hz, 1H), 6.89 (m, 1H), 6.61 (d, *J* = 4.9 Hz, 1H), 6.27 (d, *J* = 4.2 Hz, 1H), 6.26 (s, 1H), 2.40 (s, 3H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ 160.0 (C), 159.2 (C), 154.5 (C), 151.5 (C), 139.2 (C), 135.6 (CH), 134.0 (C), 132.0 (C), 127.5 (C), 126.4 (CH), 122.6 (q, $^1J_{CF}$ = 274,6 Hz, CF_3), 122.5 (CH), 119.0 (q, $^2J_{CF}$ = 33.4 Hz, C), 118.5 (C), 118.2 (CH), 115.2 (CH), 115.1 (CH), 114.3 (CH), 110.0 (CH), 18.7 (CH_3) ppm; FTIR υ 3350, 2925, 1732, 1715, 1599, 1525, 1487, 1369, 1100, 983 cm^{-1}; HRMS-EI *m/z* calcd for ($C_{20}H_{12}BClF_5N_3O_2$) 467.0631, found 467.0623. **4dB**: ^1H NMR (700 MHz, $CDCl_3$) δ 7.80 (broad s, 2H, 2NH), 7.53 (d, *J* = 8.4 Hz, 2H), 7.22 (m, 2H), 7.12 (d, *J* = 2.1 Hz, 2H), 7.03 (dd, *J* = 8.4 and 2.1 Hz, 2H), 6.44 (d, *J* = 4.9 Hz, 2H), 6.16 (d, *J* = 1.4 Hz, 2H), 2.37 (d, *J* = 1.4 Hz, 6H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ 160.6 (C), 154.9 (C), 151.9 (C), 141.6 (C), 129.6 (CH), 127.0 (C), 126.1 (CH), 116.2 (C), 115.9 (CH), 113.6 (CH), 107.2 (CH), 106.7 (CH), 18.7 (CH_3), CF_3 not observed; FTIR υ 3354, 2930, 1730, 1710, 1589,

[6] L. Li, B. Nguyen and K. Burgess, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 3112.

1536, 1477, 1355, 1108, 987 cm^{-1}; HRMS-EI *m/z* calcd for ($C_{30}H_{20}BF_5N_4O_4$) 606.1496, found 606.1489.

3. Photophysical, electrochemical and computational results (Figs. S1-S5 and Table S1-S2)

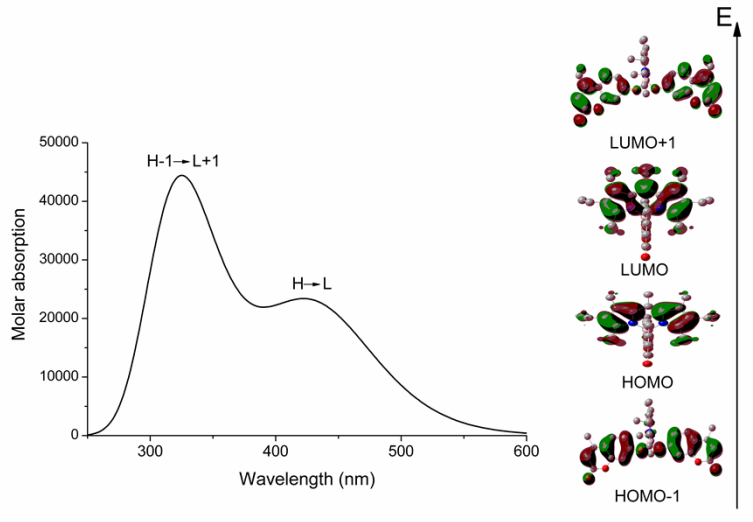


Fig S1. TD simulation of the of the absorption spectrum of **1dA** in acetone (B3LYP/6-31g//PCM) and corresponding contour maps of the molecular orbital involved in the electronic transitions (the TD method predicts accurately the UV transition of the coumarin, but, as it is known, overestimates the energy gap of the Vis transition and, in the case of the BODIPYs, underestimates also their transition probability).

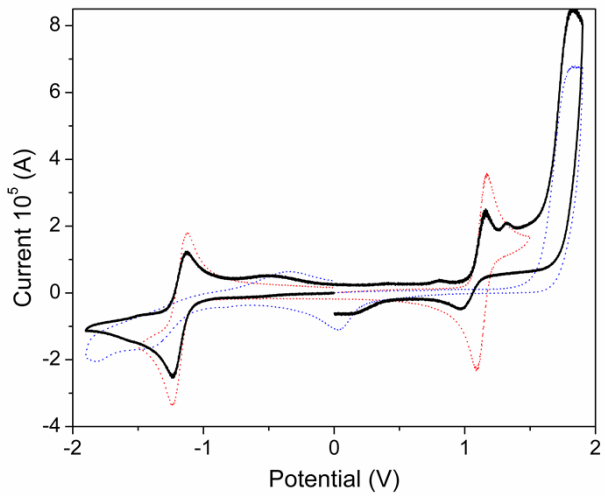


Fig S2. Cyclic voltammograms of **1dA** (solid black), **1** (dotted red) and **AH** (doted blue).

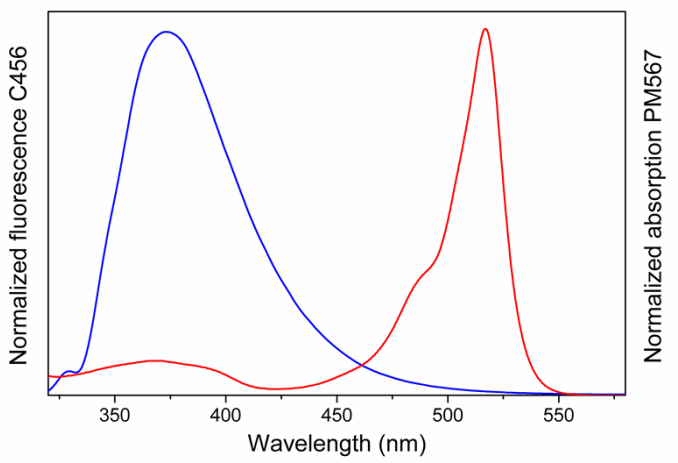


Fig S3. Spectral overlap between **AH** fluorescence (blue) and **1** absorption (red).

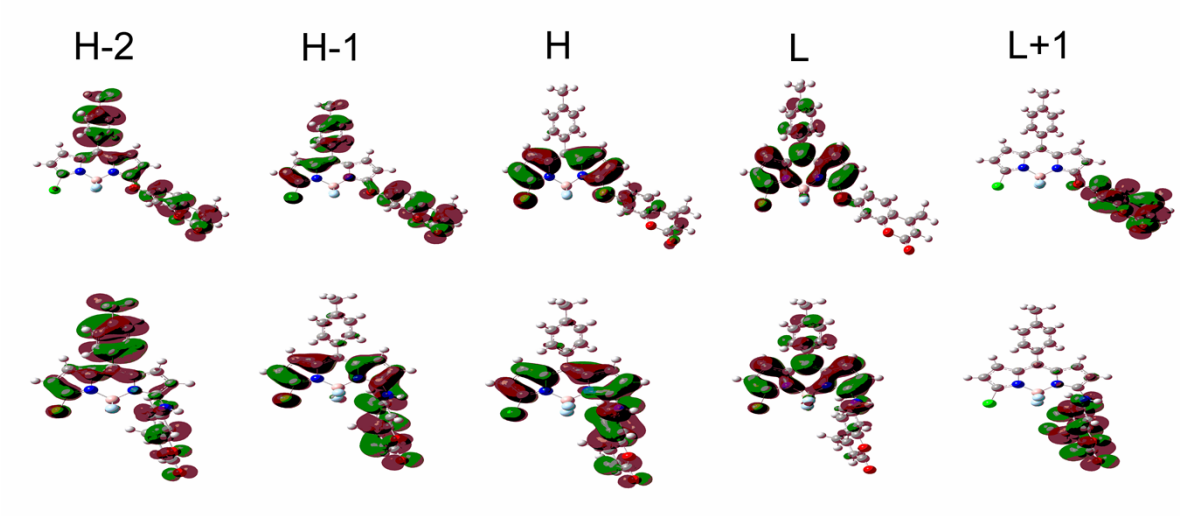


Figure S4. Computed frontier molecular orbitals (contour maps) of **2mA** (up) and **2mB** (down). H and L denotes HOMO and LUMO respectively.

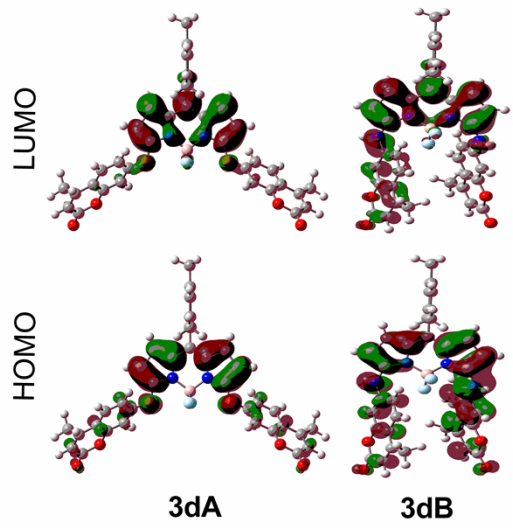


Fig S5. Computed HOMO and LUMO (contour maps) of **3dA** and **3dB**.

Table S1. Photophysical properties of coumarin/BODIPY hybrids **1dA**, **2mA**, **2mB**, **2dA**, **3mA**, **3mB**, **3mC**, **3dA**, **3dB**, **4mA**, **4mB** and **4dB**, and corresponding parent coumarins (**AH** and **BH**) and BODIPYs (**1**-**4**) in ethyl acetate. The fluorescence data were recorded upon excitation of the Vis absorption band.

compound	λ_{ab} (nm)	ε_{max} ($10^4 M^{-1}cm^{-1}$)	λ_{fl} (nm)	ϕ	τ (ns)	k_{fl} (10^8 s^{-1})	k_{nr} (10^8 s^{-1})	$\Delta\nu_{St}$ (cm^{-1})
AH*	323.0	1.4	380.0	0.28	1.2	2.3	6.0	4645
BH	340.0	2.0	400.0	0.82	2.89	2.8	0.62	4410
1	516.5	8.0	531.5	0.84	5.78	1.45	0.28	545
1dA	519.0 323.5	6.7 3.9	537.0	0.82	6.78	1.2	0.26	645
2	509.5	10.3	522.0	0.25	1.93	1.3	3.9	470
2mA	510.0	4.6	525.0	0.16	0.84	1.9	10.0	560
2mB	524.0	4.5	577.0	0.04	0.28	1.4	34.3	1750
2dA	517.5	4.2	532.0	0.36	1.56	2.3	4.1	525
3	511.5	10.7	521.5	0.94	5.90	1.6	0.10	375
3mA	510.5	8.0	522.5	0.95	4.48	2.1	0.11	450
3mB	519.5	5.5	569.0	0.07	0.28 (60%) 0.60 (40%)	2.5	33.2	1675
3mC	510.5	7.5	521.5	0.93	5.02	1.8	0.14	415
3dA	519.5	13.0	530.0	0.90	3.78	2.4	0.26	380
3dB	607.0	9.6	623.5	0.70	3.83	1.8	0.78	435
4	545.0	6.8	552.0	0.82	6.77	1.2	0.26	230
4mA	537.0	6.4	555.0	0.41	2.81	1.5	2.1	605
4mB	520.5	3.7	-	0	-	-	-	-
4dB	642.5	5.3	665.0	0.73	2.50	2.9	1.1	525

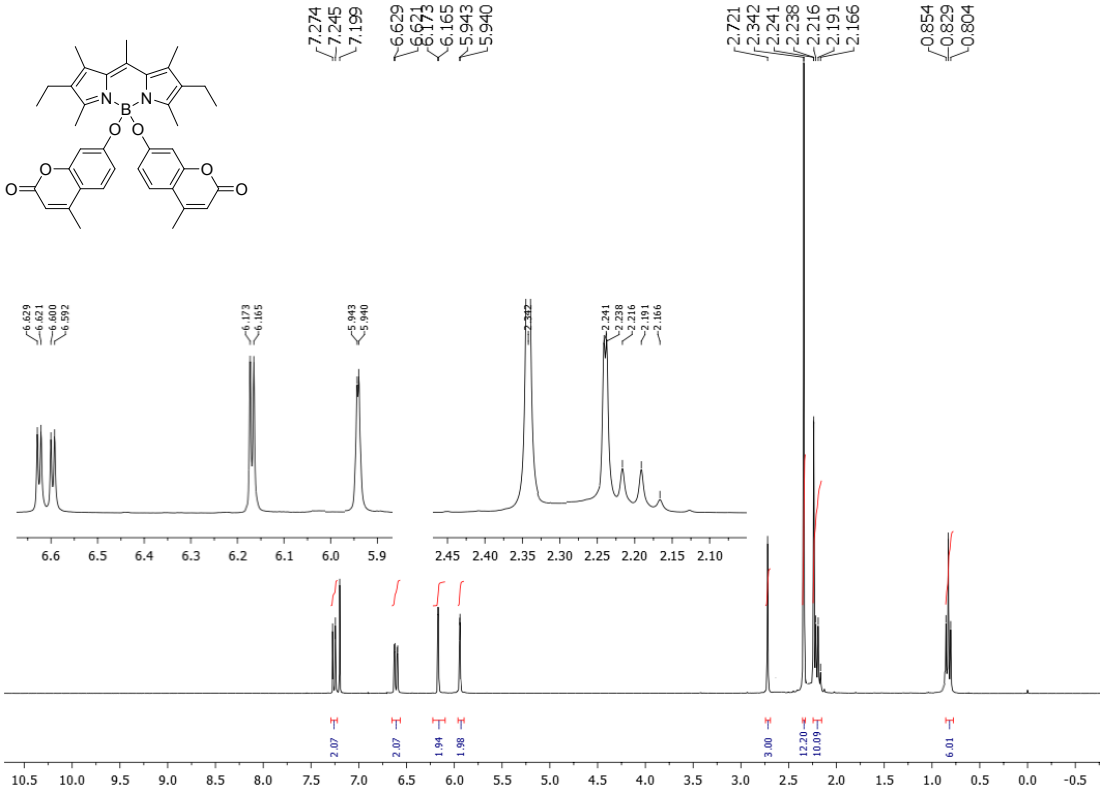
*Data in ethanol.

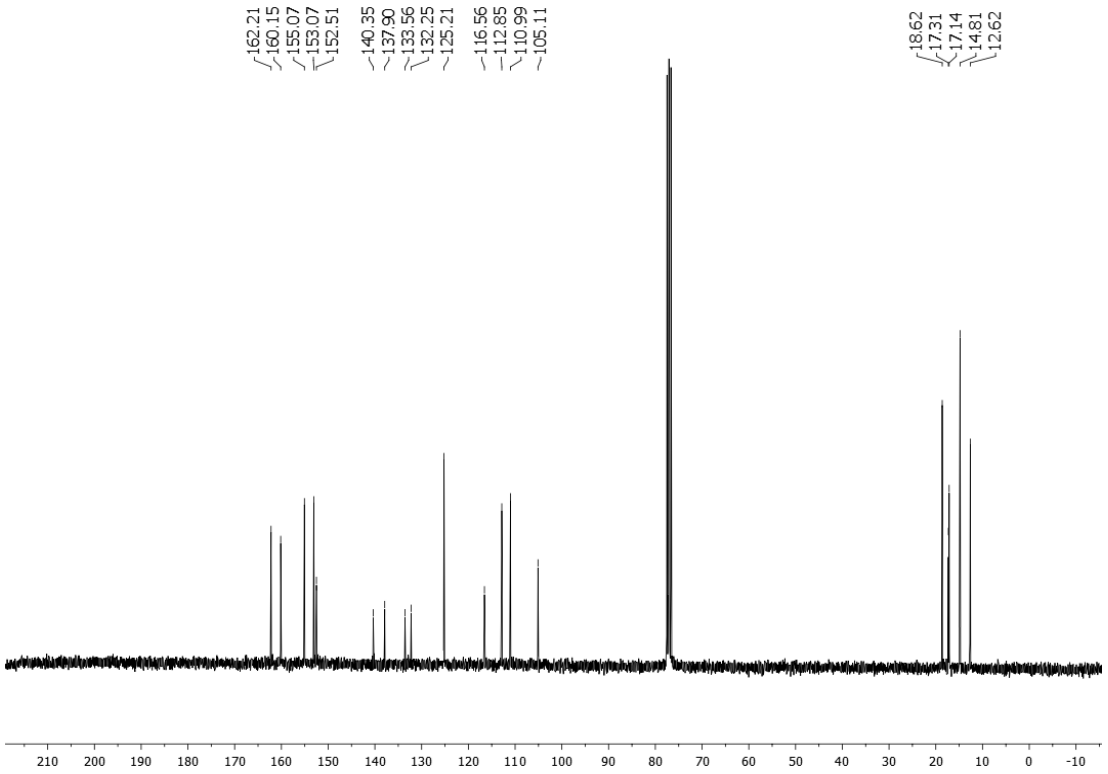
Table S2. TD simulation (B3LYP/6-31g//PCM) of the electronic absorption transition (energy gap, ΔE_{ab}, and oscillator strength, *f*) for the coumarin/BODIPY hybrids **2mA**, **2mB**, **2dA**, **3mA**, **3mB**, **3dA**, **3dB**, **4mA**, **4mB** and **4dB**, and the corresponding parent BODIPYs **2**-**4** in ethyl acetate.

compound	ΔE_{ab} (eV)	*f*	compound	ΔE_{ab} (eV)	*f*	compound	ΔE_{ab} (eV)	*f*
2	2.92	0.512	**3**	2.93	0.529	**4**	2.74	0.543
2mA	2.79	0.835	**3mA**	2.82	0.812	**4mA**	2.62	0.703
2mB	2.43	0.777	**3mB**	2.62	0.657	**4mB**	2.57	0.573
2dA	2.69	1.043	**3dA**	2.71	1.092	**4dB**	2.04	0.350
			3dB	2.28	0.321			

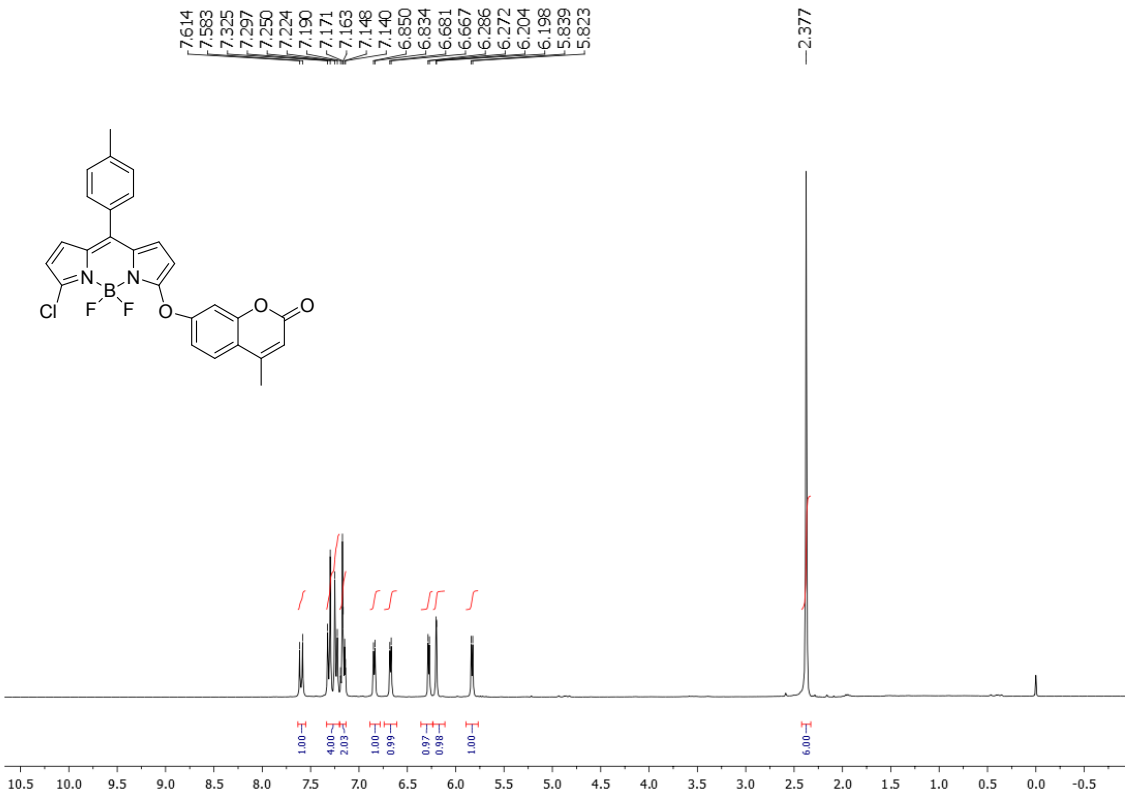
4. ^{1}H NMR and ^{13}C NMR spectra

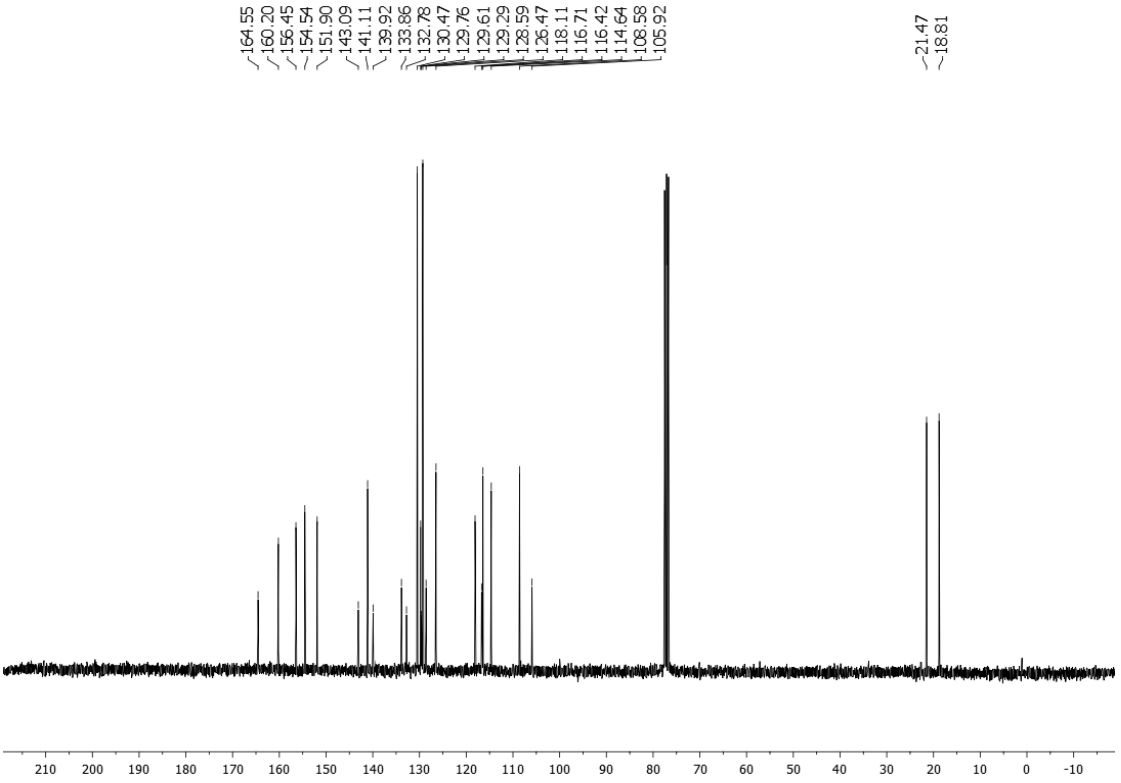
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **1dA**



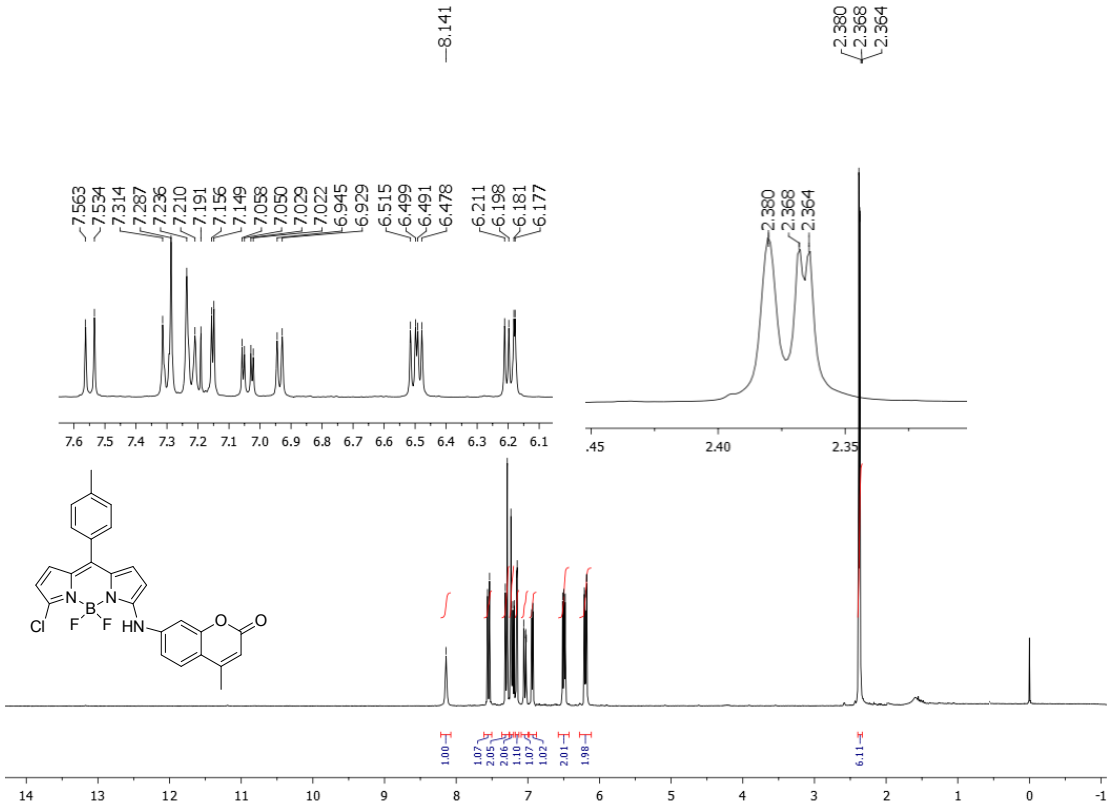


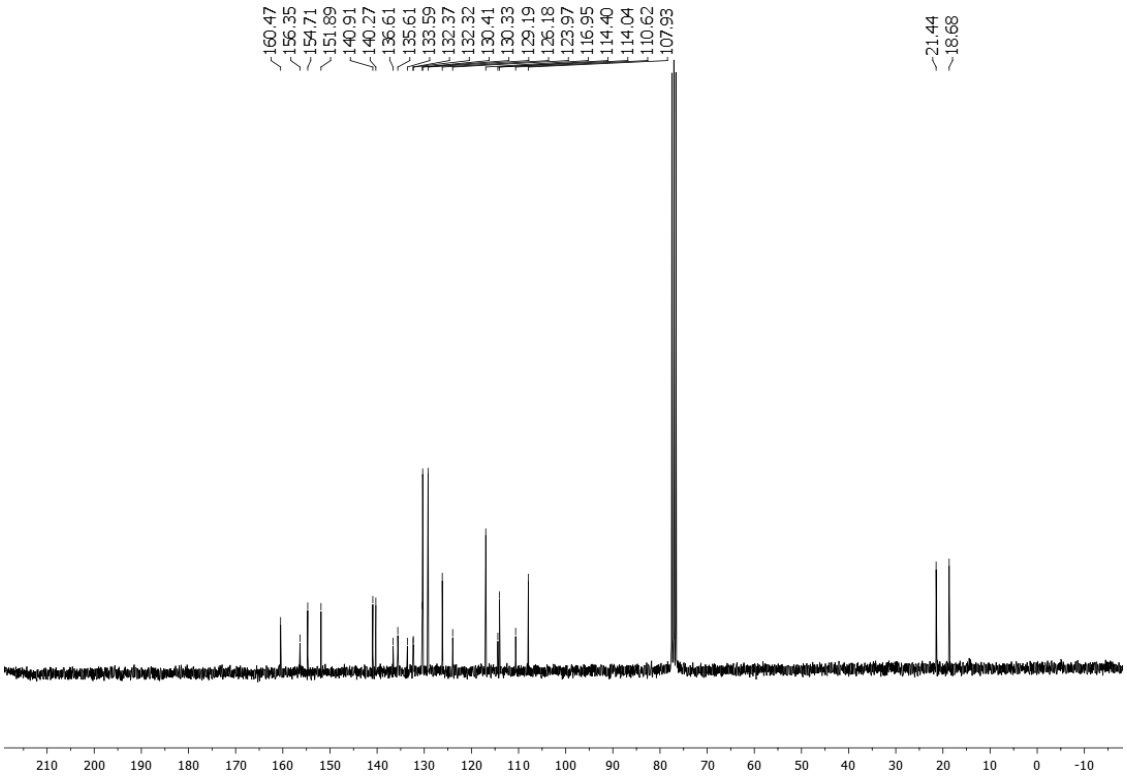
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **2mA**



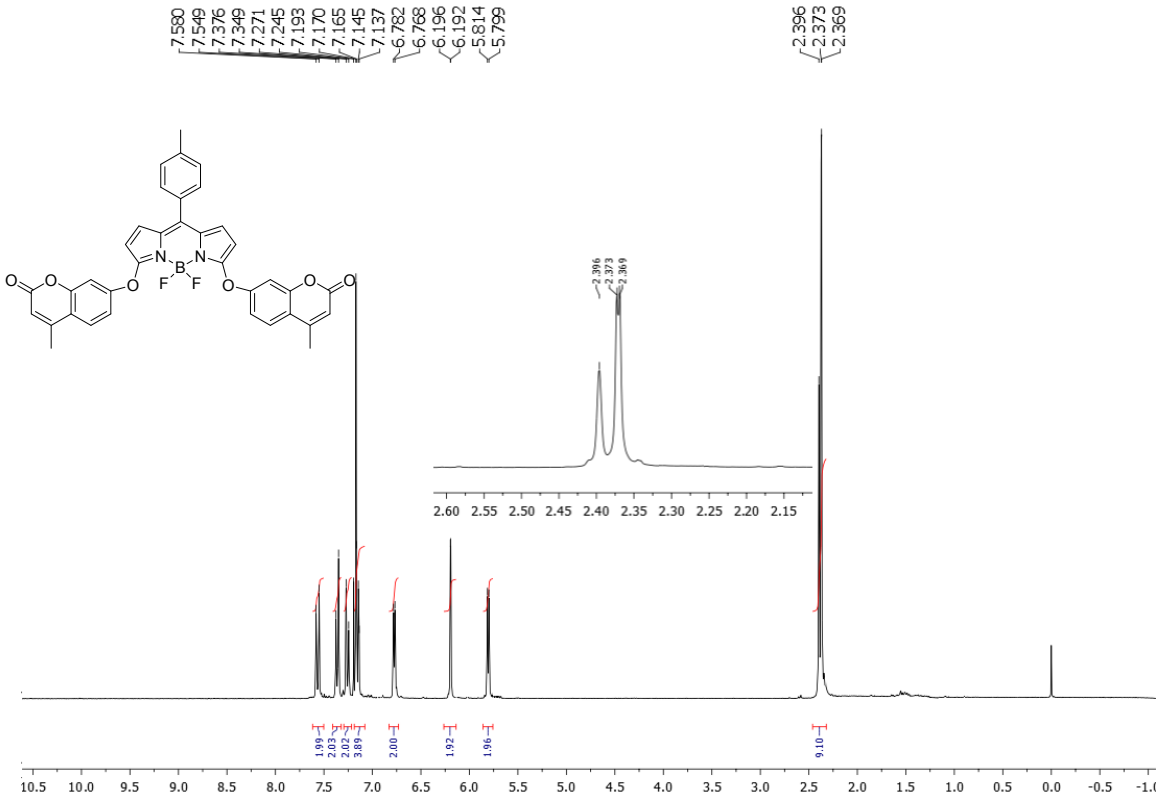


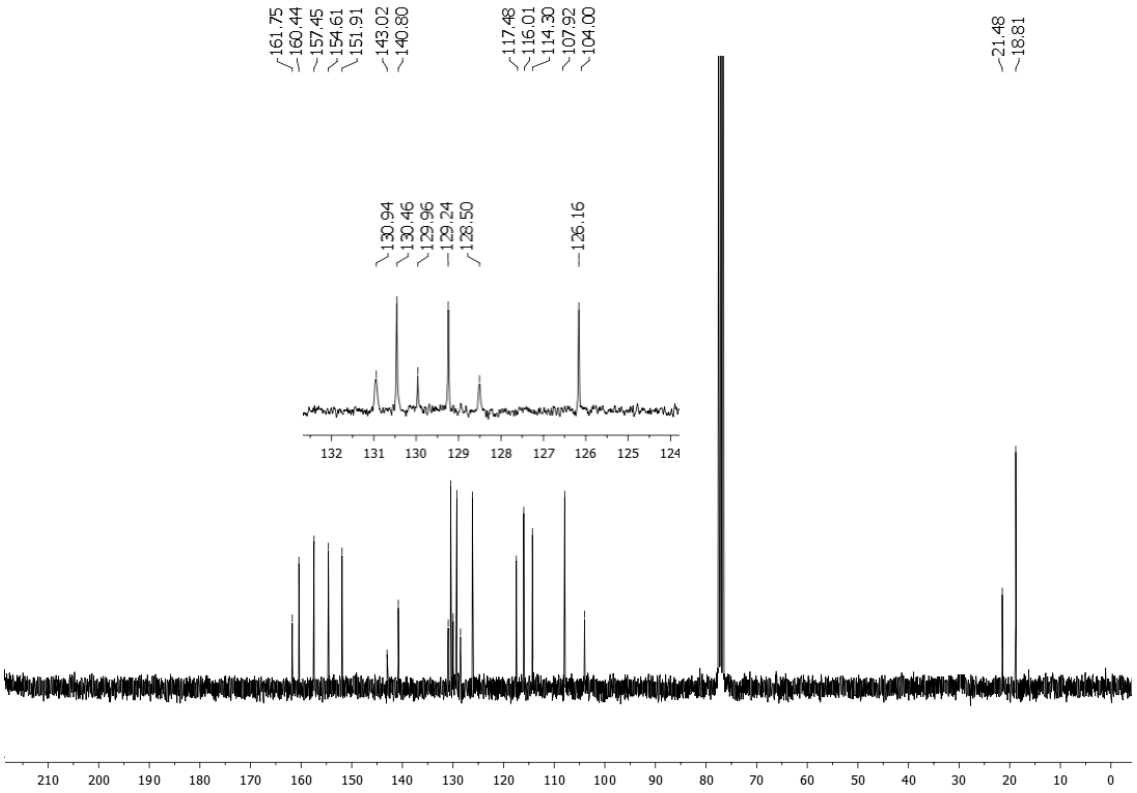
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **2mB**



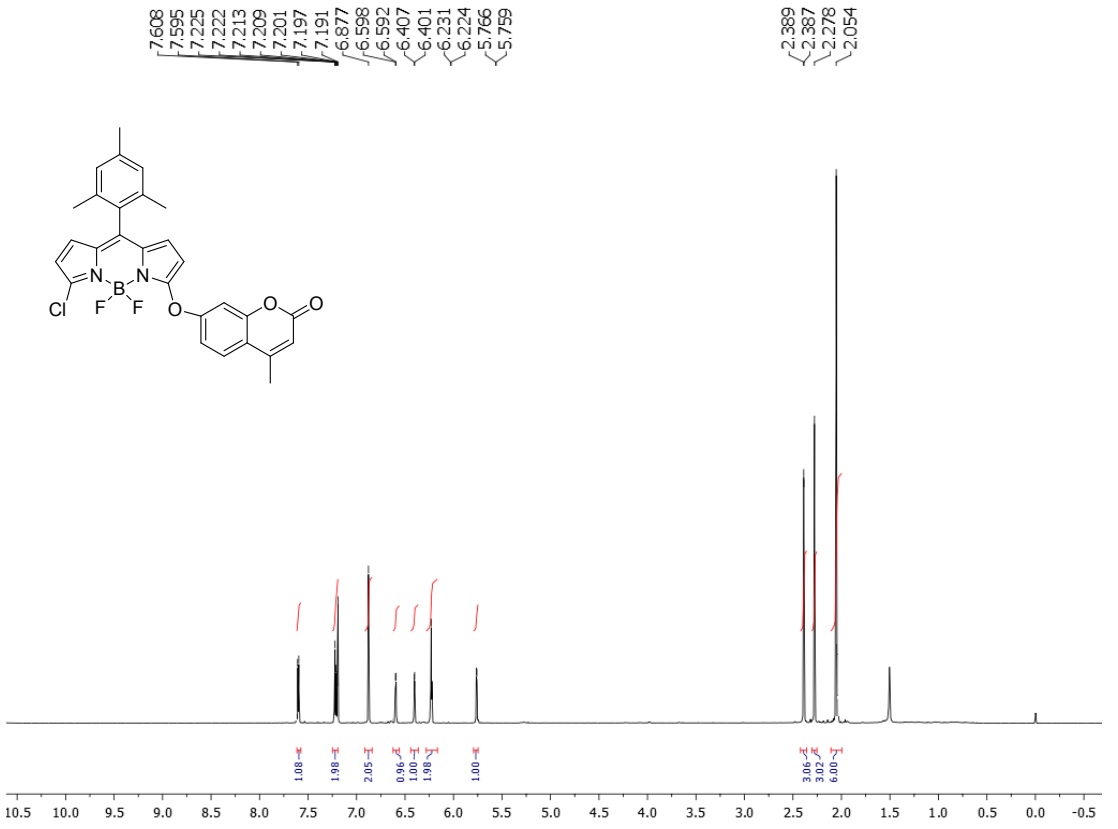


^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **2dA**





^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) spectra of **3mA**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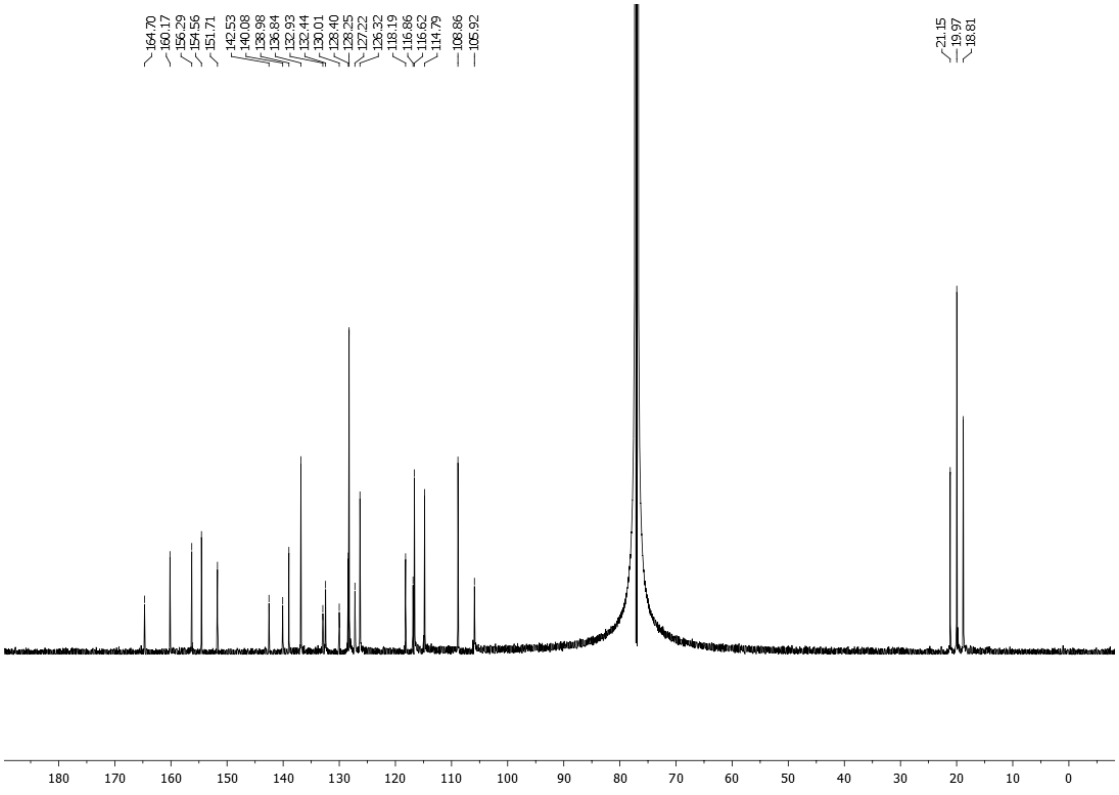
6.592
6.407
6.401
6.231
6.224
5.766
5.759
2.389
2.387
2.278
2.054
Cl
F
B
F
N
N
O
O
O
1.08
1.98
2.05
0.96
1.00
1.98
1.00
3.06
3.02
6.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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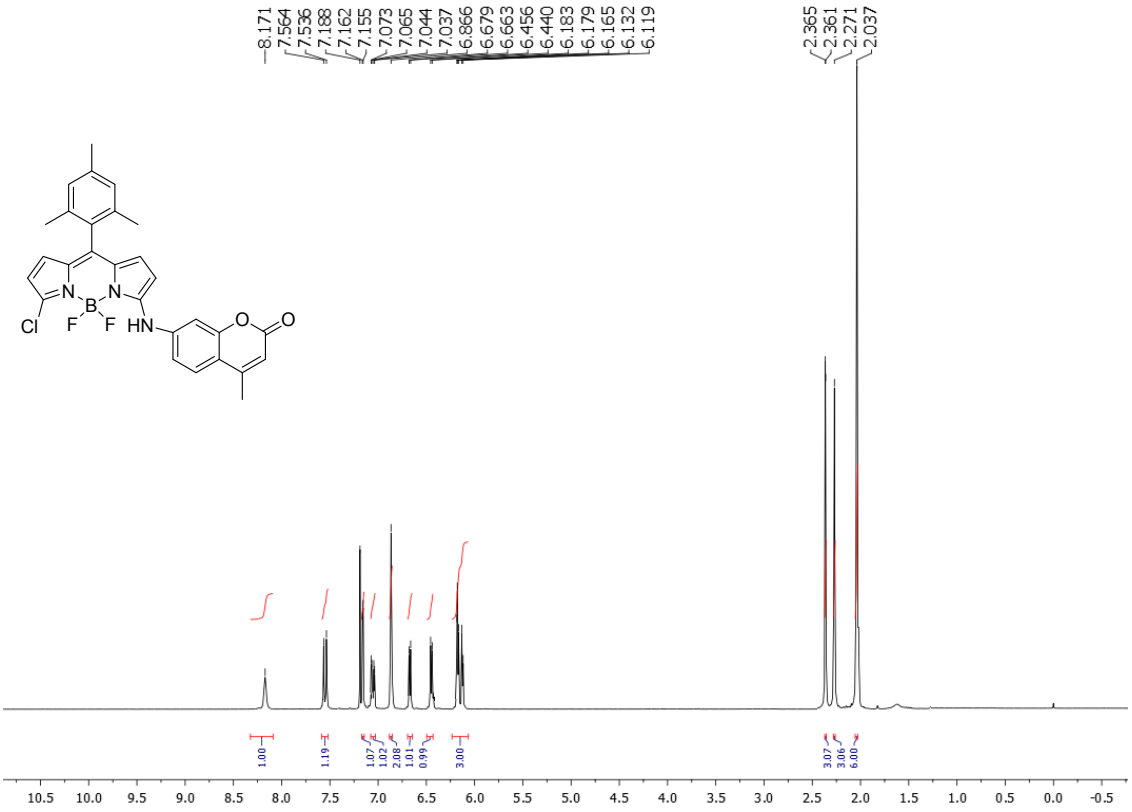
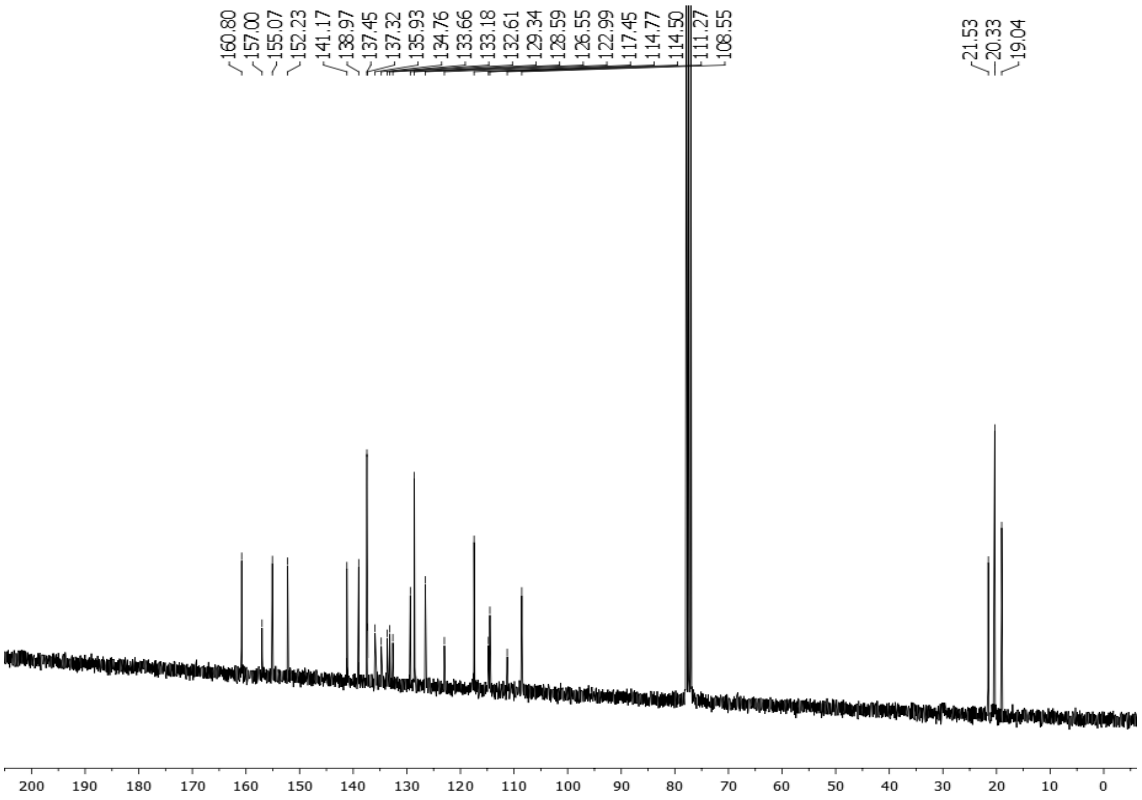
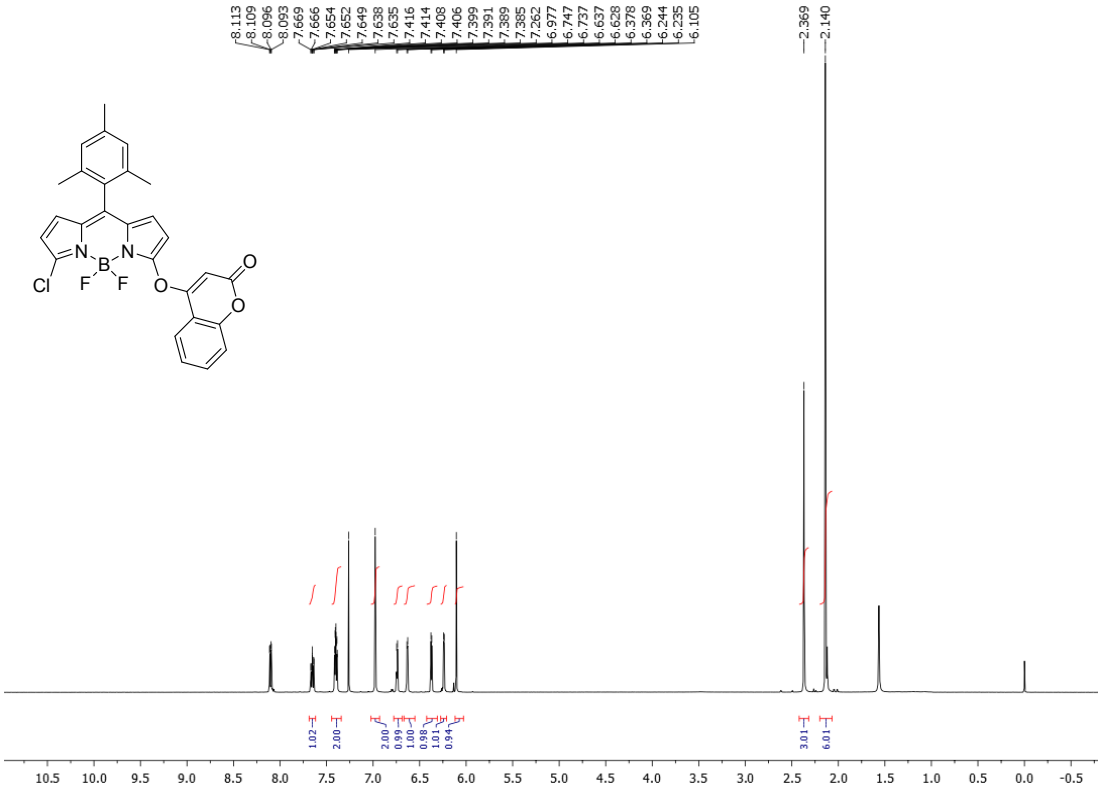
126.32
118.19
116.86
116.62
114.79
108.86
105.92
21.15
19.97
18.81
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

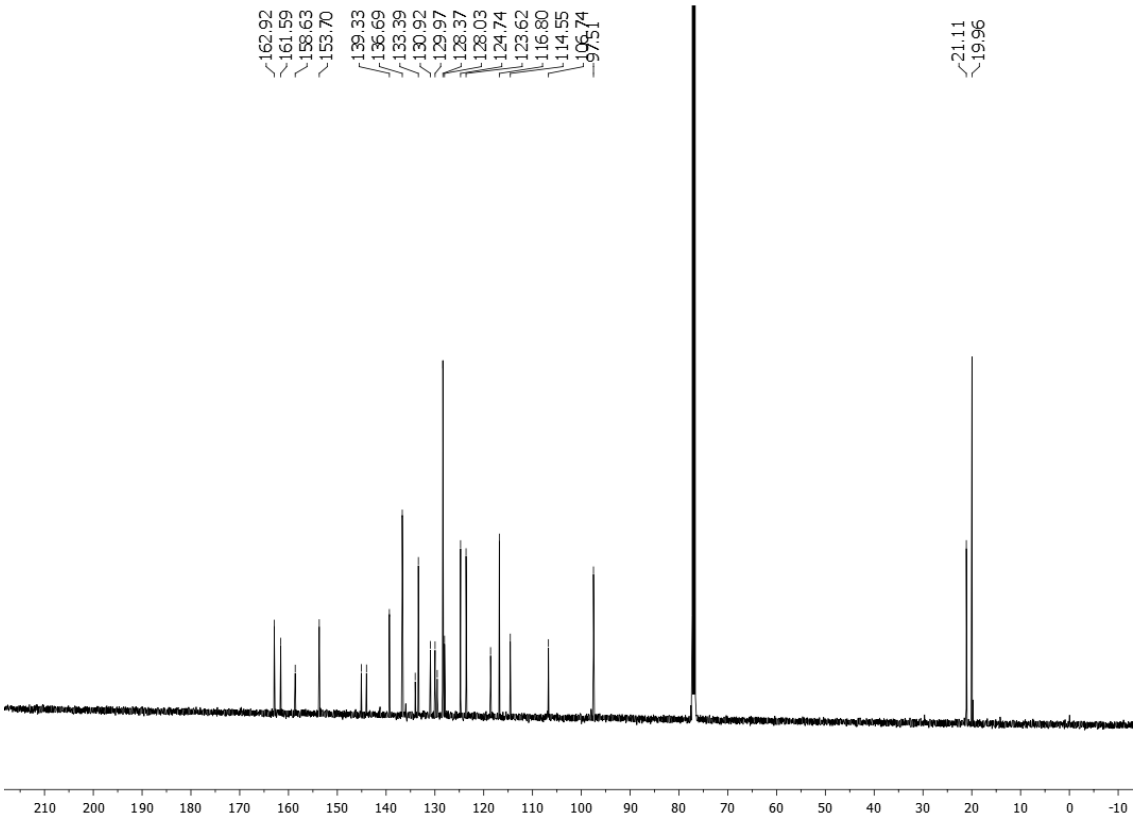
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **3mB**



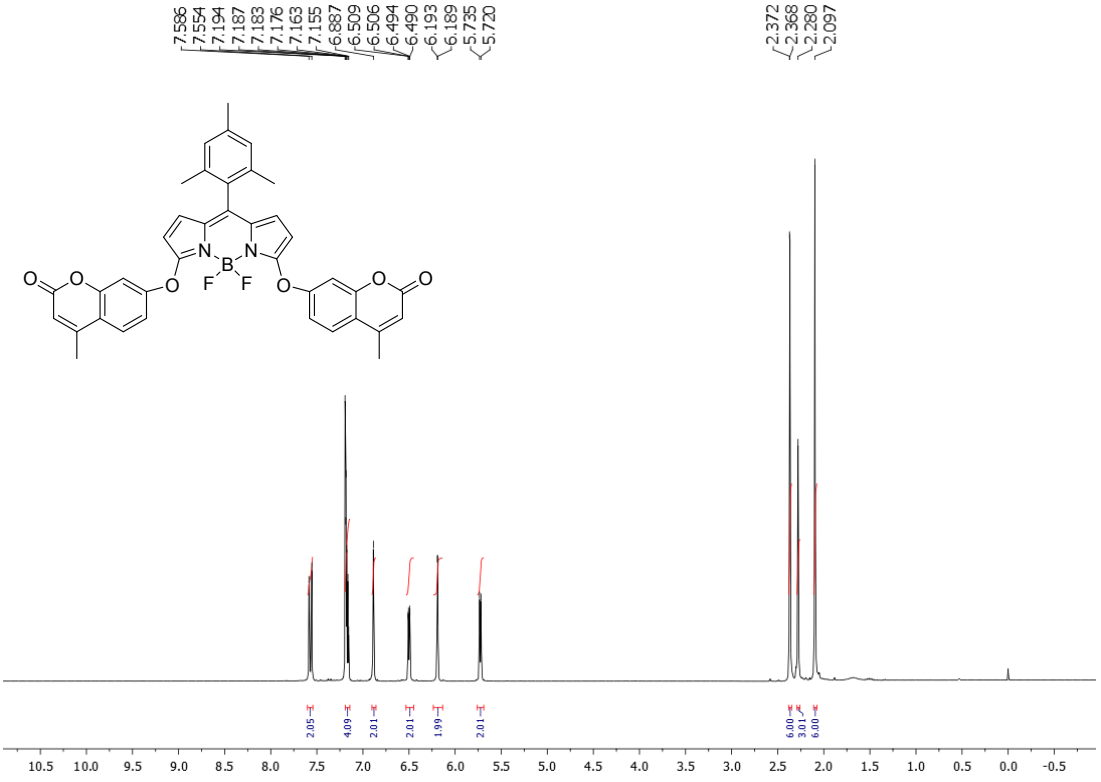


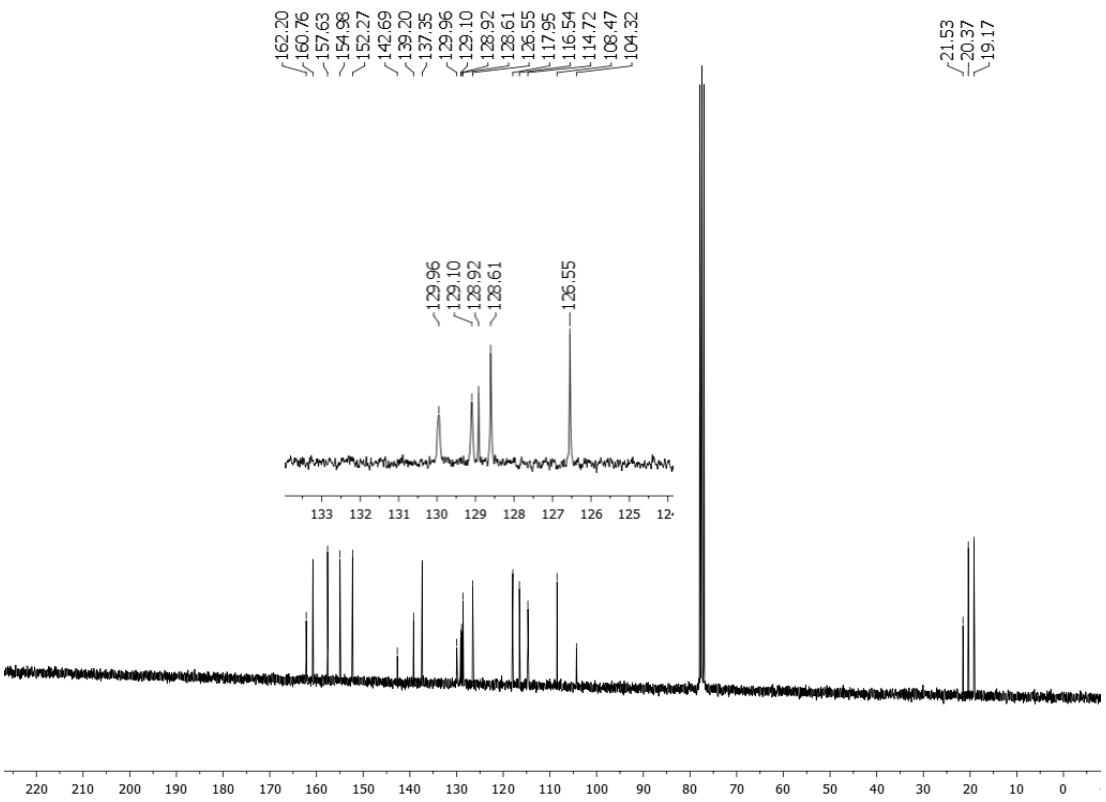
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) spectra of **3mC**



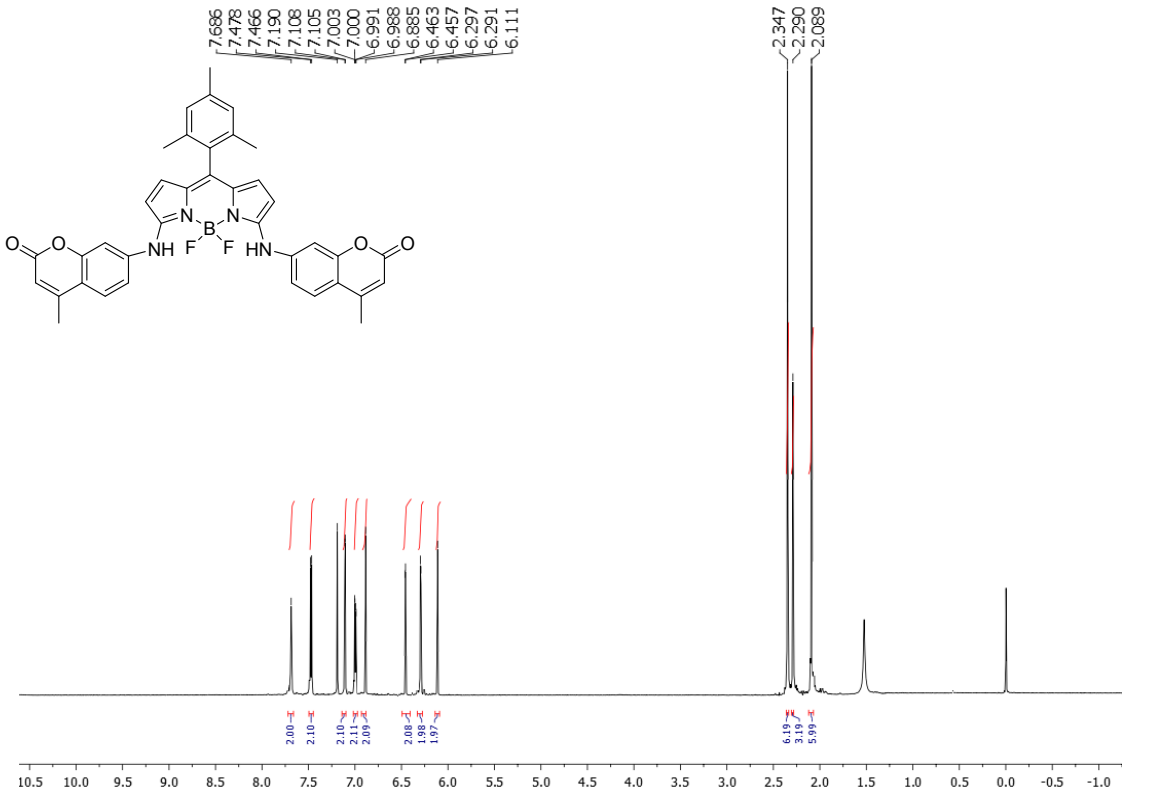


^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **3dA**





^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) spectra of **3dB**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2.290
2.089
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O
NH
F
B
F
N
N
HN
O
O
2.00
2.10
2.10
2.11
2.09
2.08
1.98
1.97
6.19
3.19
5.99
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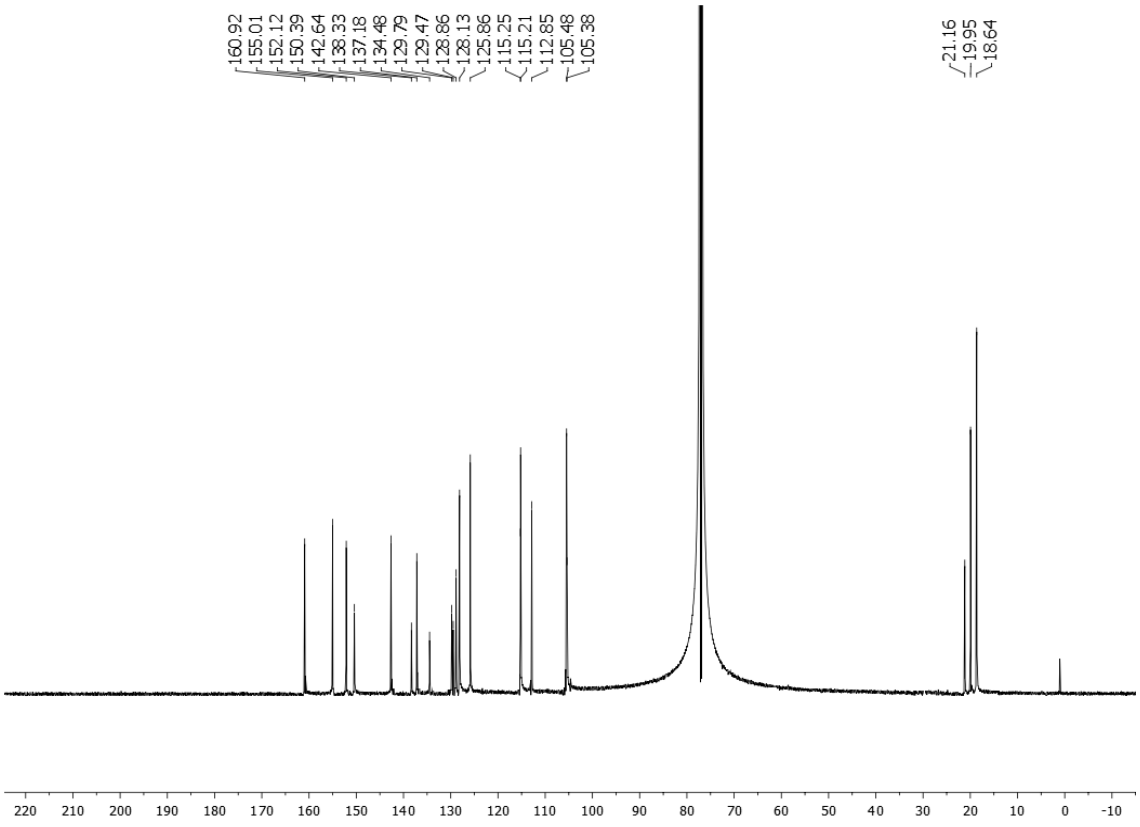
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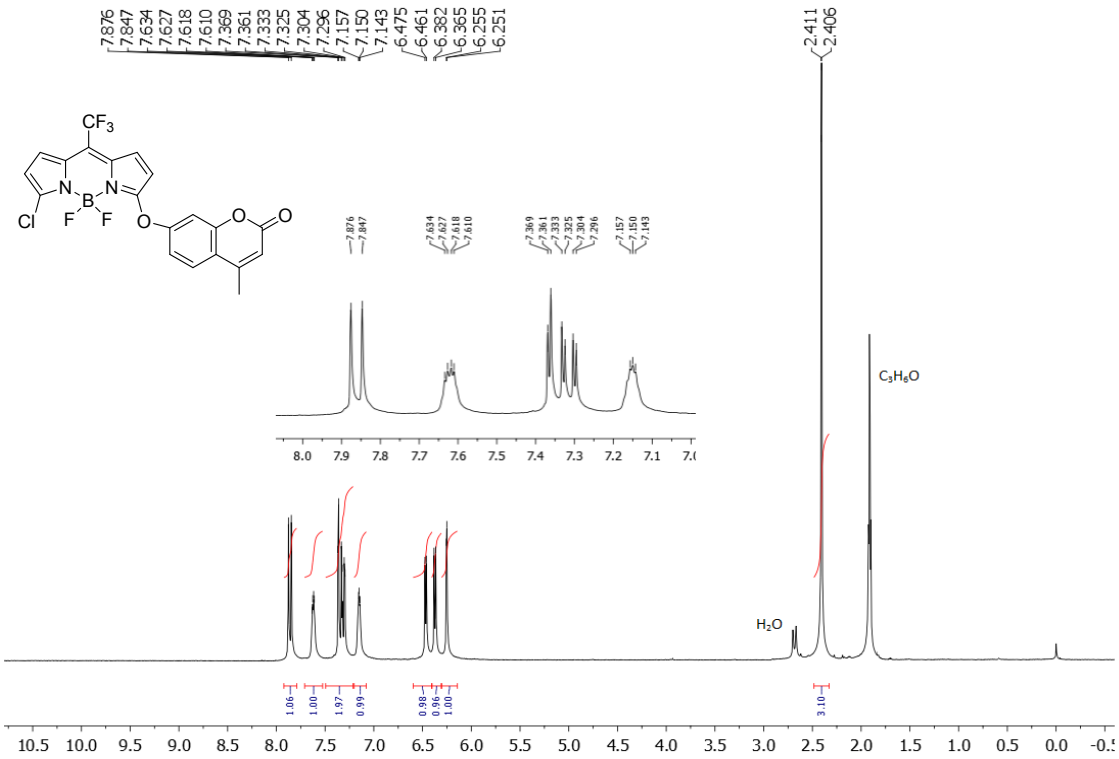
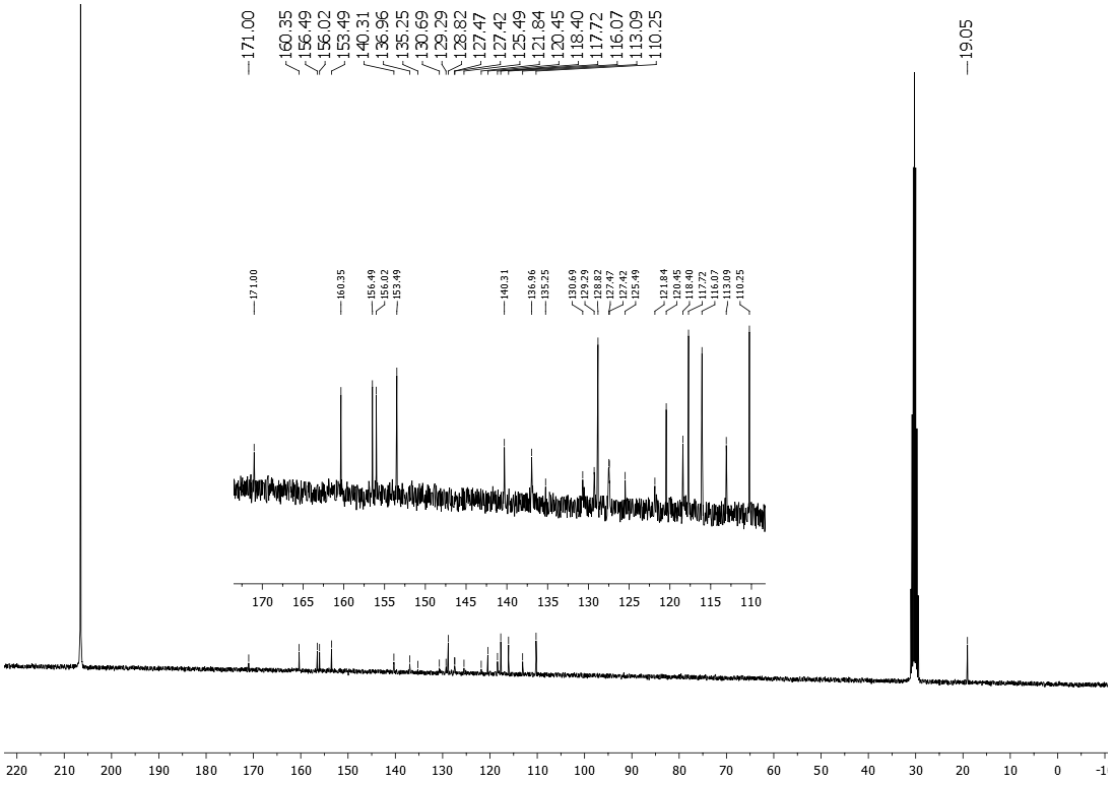
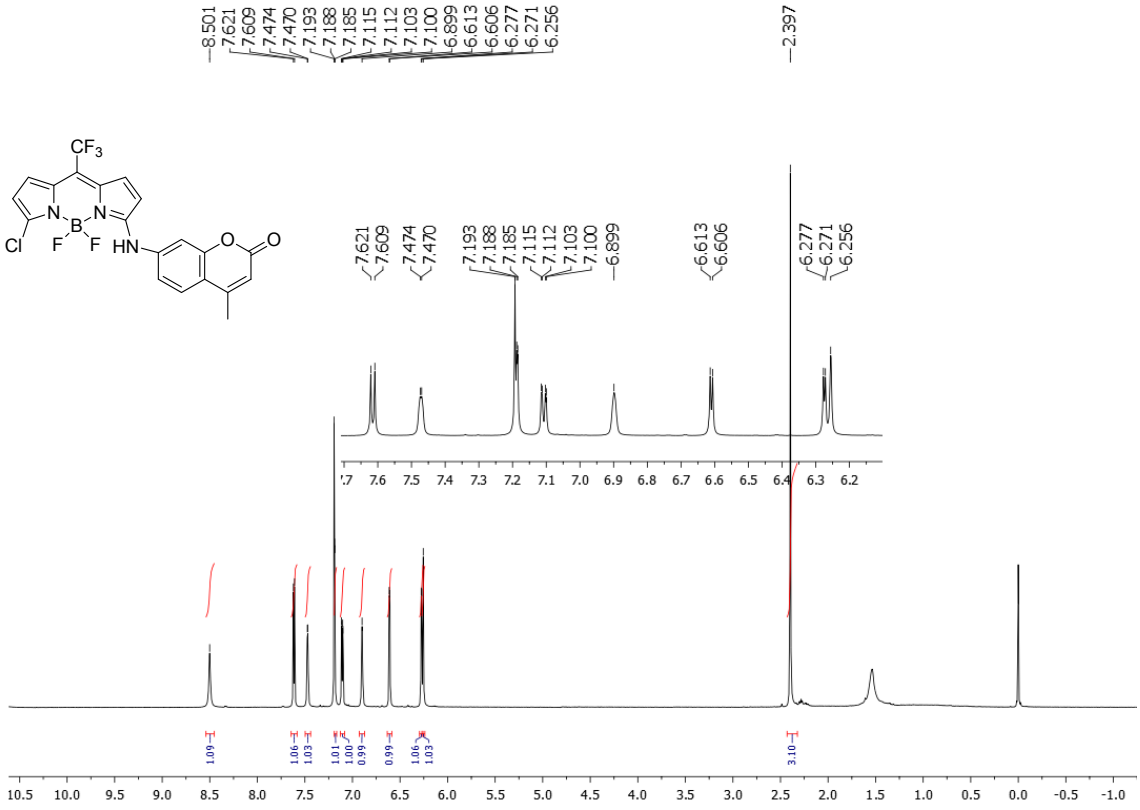
112.85
105.48
105.38
21.16
19.95
18.64
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

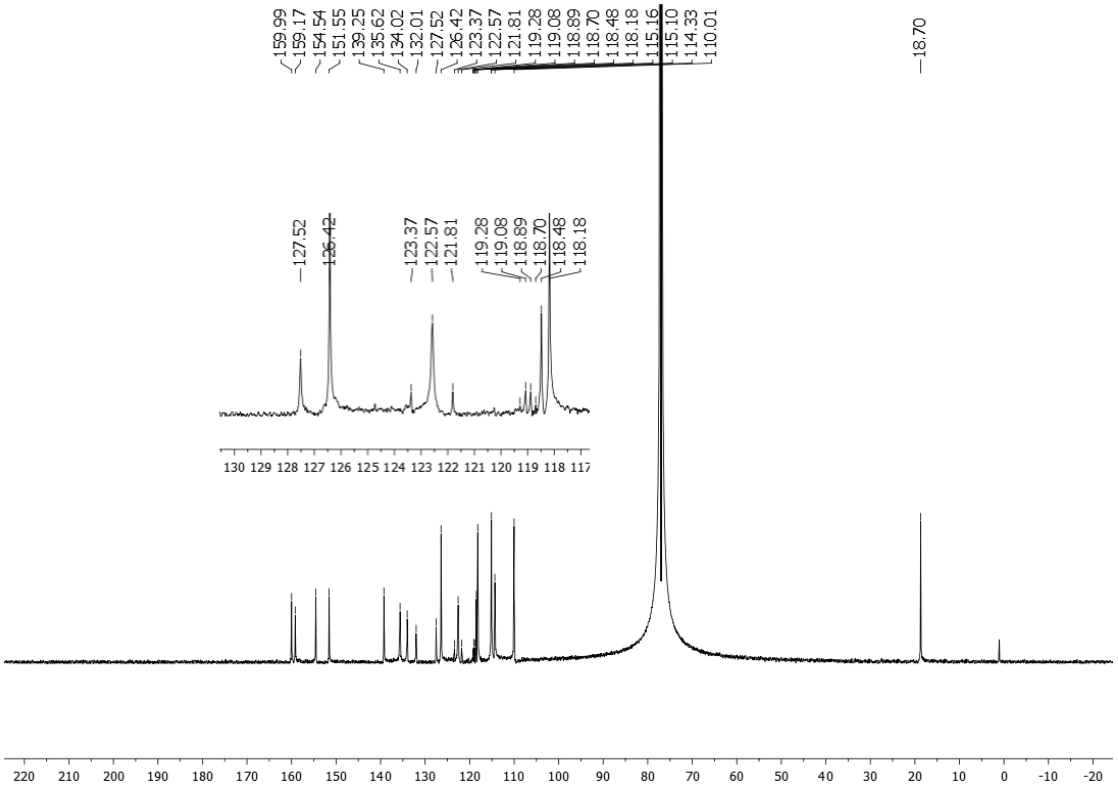
^{1}H (300 MHz, C_3D_6O) and ^{13}C (75 MHz, C_3D_6O) spectra of **4mA**



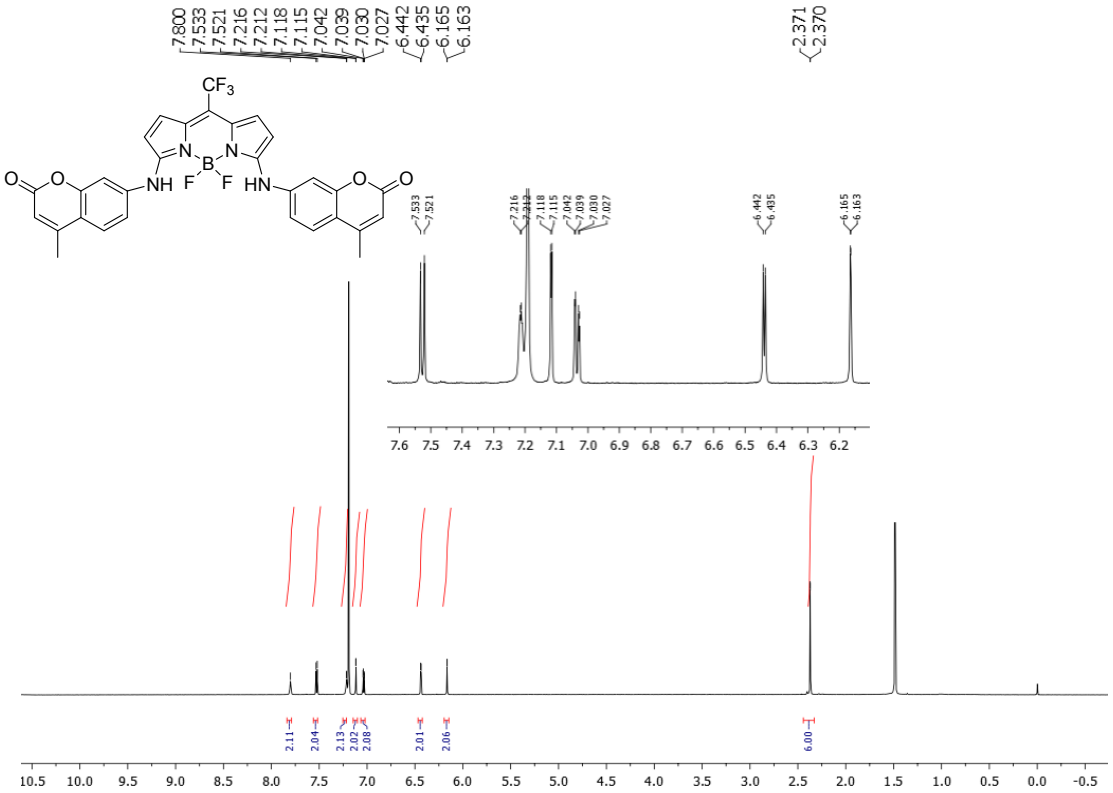


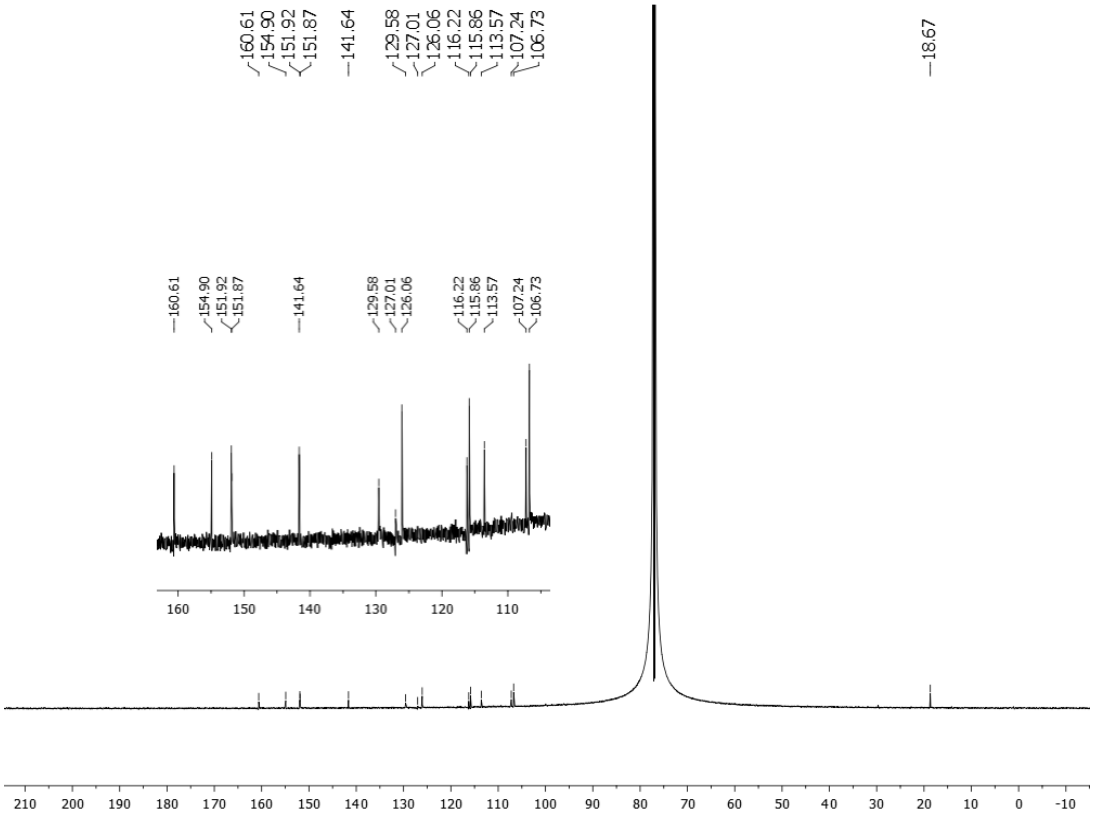
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) spectra of **4mB**





^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) spectra of **4dB**

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18.67
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160 150 140 130 120 110