Supporting Information for

Pyridyl-BODIPY dyes: synthesis, optical properties and adsorption on CdSe quantum dots

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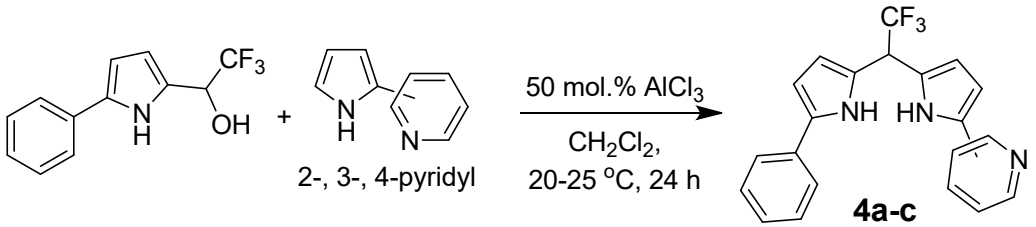
I General Information

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ or acetone-d_6 using a Bruker Avance 400 NMR spectrometer (400.13, 100.6 and 376.5 MHz, respectively). The signals in the ^{1}H NMR spectra were assigned using COSY and NOESY experiments. The resonance signals of the carbon atoms were assigned based on ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC experiments. The ^{1}H chemical shifts (δ) were referenced to the residual deuterated solvent (7.26 ppm for $CDCl_3$ and 2.05 for acetone-d_6), and the ^{13}C chemical shifts were expressed with respect to the deuterated solvent (77.1 ppm for $CDCl_3$ and 29.8 for acetone-d_6). The ^{19}F chemical shifts were referenced to $CFCl_3$. Coupling constants in hertz (Hz) were measured from one-dimensional spectra and multiplicities were abbreviated as follows: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). The chemical shifts were recorded in ppm, and the coupling constants (*J*) were recorded in Hz. IR spectra were obtained on a Varian 3100 IF-IR spectrometer (400–4000 cm^{-1}, KBr pellets or films). The (C, H, N) microanalyses were performed on a Flash EA 1112 CHNS-O/MAS (CHN Analyzer) instrument. The fluorine content was determined on a SPECOL 11 (Carl Zeiss Jena, Germany) spectrophotometer. Melting points (uncorrected) were determined with a Stuart SMP50 apparatus. All solvents (Merck, spectroscopic grade) were used without further purification. The synthesized dyes are stable during storage in the solid-state at room temperature in the light. 2,2,2-Trifluoro-1-(5-phenyl-1*H*-pyrrol-2-yl)ethan-1-ol was obtained according to method.[1] 2-, 3-, and 4-Pyridylpyrroles were obtained from oximes of 2-, 3-, and 4-acetylpyridines and acetylene by Trofimov reaction.[2]

Synthesis of dipyrromethanes (General Procedure)



2-pyridyl (**a**), 3-pyridyl (**b**), 4-pyridyl (**c**)

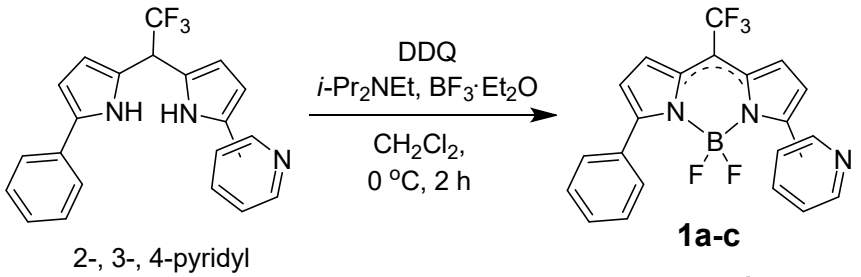
The mixture of 2,2,2-trifluoro-1-(5-phenyl-1*H*-pyrrol-2-yl)ethan-1-ol (0.482 g, 2.0 mmol) and (pyrrol-2-yl)pyridine (0.288 g, 2.0 mmol) in CH_2Cl_2 (10 mL) was added to $AlCl_3$ (0.133 g, 1.0 mmol) and stirred at room temperature overnight. Then, the reaction mixture was washed with $NaHCO_3$ solution, the organic layer was separated, and the water layer was extracted with dichloromethane (2 × 30 mL). The combined organic layers were washed with water (3 × 30 mL) and dried over $CaCl_2$. After removing the solvent, the obtained residue was purified by TLC (SiO_2, *n*-hexane/diethyl ether, 1:1) to yield dipyrromethanes.

2-(5-(2,2,2-Trifluoro-1-(5-phenyl-1*H*-pyrrol-2-yl)ethyl)-1*H*-pyrrol-2-yl)pyridine (4a), yield 0.448 g (61%), pink very viscous oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 9.55 (br s, 1H, NH), 8.44 (m, 1H, H-6 pyridine), 8.33 (br s, 1H, NH), 7.63 (m, 1H, H-*p* Ph), 7.53 (m, 1H, H-3 pyridine), 7.43 (m, 2H, H-*o* Ph), 7.35 (m, 2H, H-*p* Ph), 7.21 (m, 1H, H-4 pyridine), 7.05 (m, 1H, H-5 pyridine), 6.69 (m, 1H, H-pyrrole), 6.49 (m, 1H, H-pyrrole), 6.34 (m, 2H, H-pyrrole), 4.90 (q, *J* = 8.9 Hz, 1H, $CHCF_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 150.1, 148.9, 136.8, 133.1, 132.4, 129.1, 129.0 (2C), 126.7 (q, *J* = 280.0 Hz), 126.6, 125.3, 124.0 (2C), 123.8, 121.0, 118.4, 111.1, 110.9, 108.0, 106.7, 43.6 (q, *J* = 30.4 Hz). IR (KBr): 3434, 3072, 2921, 1597, 1567, 1504, 1445, 1404, 1336, 1255, 1157, 1108, 1050, 994, 909, 865, 756, 517. Anal. Calcd for $C_{21}H_{16}F_3N_3$: C 68.66; H 4.39; F 15.51; N 11.44%. Found: C 68.42; H 4.50; F 15.33; N 11.52%.

3-(5-(2,2,2-Trifluoro-1-(5-phenyl-1*H*-pyrrol-2-yl)ethyl)-1*H*-pyrrol-2-yl)pyridine (4b), yield 0.499 g (68%), white crystals, mp 215–216 °C. ^{1}HNMR (400.13 MHz, acetone-d_6): δ = 10.72 (br s, 1H, NH), 10.53 (br s, 1H, NH), 8.86 (m, 1H, H-2 pyridine), 8.36 (m, 1H, H-6 pyridine), 7.94 (m, 1H, H-4 pyridine), 7.60 (m, 2H, H-*o* Ph), 7.33 (m, 3H, H-*m,p* Ph), 7.16 (m, 1H, H-5 pyridine), 6.63 (m, 1H, H-pyrrole), 6.52 (m, 1H, H-pyrrole), 6.36 (m, 1H, H-pyrrole), 6.31 (m, 1H, H-pyrrole), 5.16 (q, *J* = 8.9 Hz, 1H, $CHCF_3$). ^{13}CNMR (100.6 MHz, acetone-d_6): δ = 147.7, 146.1, 133.8, 133.3, 131.5, 130.1, 129.6, 129.5 (2C), 127.5, 126.8, 126.4 (d, *J* = 279.4 Hz), 126.0, 124.6 (2C), 124.4, 111.1, 110.8, 108.2, 107.0, 44.0 (q, *J* = 30.2 Hz). IR (KBr): 3344, 3110, 3005, 1696, 1604, 1506, 1336, 1256, 1160, 1108, 1043, 760, 708. Anal. Calcd for $C_{21}H_{16}F_3N_3$: C 68.66; H 4.39; F 15.51; N 11.44%. Found: C 68.38; H 4.56; F 15.41; N 11.69%.

4-(5-(2,2,2-Trifluoro-1-(5-phenyl-1*H*-pyrrol-2-yl)ethyl)-1*H*-pyrrol-2-yl)pyridine (4c), yield 0.455 g (62%), white crystals, mp 167-168 °C. ^{1}H NMR (400.13 MHz, acetone-d_6): δ = 10.96 (br s, 1H, NH), 10.60 (br s, 1H, NH), 8.46 (d, *J* = 6.4 Hz, 2H, H-2,6 pyridine), 7.61 (m, 2H, H-*o* Ph), 7.55 (d, *J* = 6.4 Hz, 2H, H-3,5 pyridine), 7.33 (m, 2H, H-*m* Ph), 7.17 (m, 1H, H-*p* Ph), 6.82 (m, 1H, H-pyrrole), 6.52 (m, 1H, H-pyrrole), 6.39 (m, 1H, H-pyrrole), 6.30 (m, 1H, H-pyrrole), 5.18 (q, *J* = 9.3 Hz, 1H, $CHCF_3$). ^{13}C NMR (100.6 MHz, acetone-d_6): δ = 150.8 (2C), 140.3, 133.8, 133.4, 130.4, 129.6 (2C), 128.8, 126.8, 126.4 (d, *J* = 279.1 Hz), 125.8, 124.6 (2C), 118.5 (2C), 111.4, 110.8, 110.1, 107.0, 44.0 (q, *J* = 30.2 Hz). IR (KBr): 3337, 3005, 1705, 1606, 1512, 1433, 1362, 1256, 1219, 1158, 1109, 1050, 999, 826, 761, 693, 640. Anal. Calcd for $C_{21}H_{16}F_3N_3$: C 68.66; H 4.39; F 15.51; N 11.44%. Found: C 68.74; H 4.52; F 15.27; N 11.61%.

Synthesis of BODIPY dyes (General Procedure).



2-, 3-, 4-pyridyl

1a-c

2-pyridyl (**a**), 3-pyridyl (**b**), 4-pyridyl (**c**)

The mixture of dipyrromethanes (0.367 g, 1 mmol) and DDQ (0.227 g, 1 mmol) in dry dichloromethane (30 mL) was stirred at 0 °C for 1 h. The (*i*-Pr)$_2$NEt (1.293 g, 10 mmol) was added, and the solution was stirred for 10 min. Then, boron trifluoride etherate (1.561 g, 11 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h and then diluted with a saturated solution of $NaHCO_3$ (15 mL). The organic layer was separated, and the water layer was extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed with water (3 × 30 mL) and dried over $CaCl_2$. After removing the solvent, the obtained residue was purified by column chromatography (SiO_2, *n*-hexane/diethyl ether, 3:1) to give BODIPY**.**

4,4-Difluoro-3-phenyl-5-(pyridin-2-yl)-8-trifluoromethyl-4-bora-3a,4a-diaza-*s*-indacene (1a), yield 0.182 g (22%), green crystals with metal luster, mp 138–139 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 8.69 (m, 1H, H-6 pyridine), 8.39–8.37 (m, 1H, H-3 pyridine), 7.91 (m, 2H, H-*o* Ph), 7.78 (m, 1H, H-4 pyridine), 7.48 (m, 3H, H-*p,m* Ph), 7.52 (m, 1H, H-1 indacene), 7.48 (m, 1H, H-7 indacene), 7.30 (m, 1H, H-5 pyridine), 7.25 (d, *J* = 4.5 Hz, 1H, H-2 indacene), 6.78 (d, *J* = 4.7 Hz, 1H, H-6 indacene). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 163.1 (C-3), 159.5 (C-5), 149.7 (C-6 pyridine), 149.5 (t, C-2 pyridine), 136.6 (C-4 pyridine), 134.1 (C-1a), 133.8 (C-7a), 131.8 (C-*i* Ph), 131.2 (C-1), 130.8 (C-*p* Ph), 129.9 (C-7), 129.8 (t, *J* = 3.7 Hz, 2C, C-*o* Ph), 128.5 (2C, C-*m* Ph), 127.4 (q, *J* = 33.6 Hz, C-CF_3), 125.5 (t, *J* = 9.1 Hz, C-3 pyridine), 124.4 (C-5 pyridine), 123.8 (C-2), 123.7 (C-6), 122.6 (q, *J* = 276.2 Hz, CF_3). ^{19}F NMR (376.5 MHz, $CDCl_3$) δ –55.0, –133.5. IR (KBr): 1565, 1479, 1452, 1396, 1302, 1225, 1137, 1079, 991, 885, 744, 695.

Anal. Calcd for $C_{21}H_{13}BF_5N_3$: C 61.05; H 3.17; F 22.99; N 10.17%. Found: C 61.29; H 3.26; F 23.16; N 10.40%.

4,4-Difluoro-3-phenyl-5-(pyridin-3-yl)-8-trifluoromethyl-4-bora-3a,4a-diaza-*s*-indacene (1b), yield 0.256 g (31%), green crystals with metal luster, mp 134–135 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 8.95 (m, 1H, H-2 pyridine), 8.64 (m, 1H, H-6 pyridine), 8.27 (m, 1H, H-4 pyridine), 7.87 (m, 2H, H-*o* Ph), 7.53 (m, 1H, H-1 indacene), 7.47 (m, 4H, H-*m,p* Ph, H-7 indacene), 7.38 (m, 1H, H-5 pyridine), 6.80 (m, 1H, H-2 indacene), 6.74 (m, 1H, H-6 indacene). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 163.9 (C-3), 156.8 (C-5), 150.7 (C-6 pyridine), 149.8 (t, *J* = 2.7 Hz, C-2 pyridine), 136.9 (t, *J* = 5.6 Hz, C-4 pyridine), 134.4 (C-1a), 133.1 (C-7a), 131.7 (C-1), 131.4 (C-*i* Ph), 131.1 (C-*p* Ph), 130.0 (C-

7), 129.7 (2C, t, J = 4.1 Hz, C-*o* Ph), 128.6 (2C, C-*m* Ph), 128.4 (C-3 pyridine), 127.2 (q, J = 33.2 Hz, $\underline{C}$-CF_3), 124.1 (C-2), 123.3 (C-5 pyridine), 122.6 (q, J = 275.7 Hz, $\underline{C}F_3$), 122.0 (C-6). ^{19}F NMR (376.5 MHz, $CDCl_3$) δ –55.0, –132.7. IR (KBr): 1634, 1561, 1477, 1420, 1298, 1227, 1138, 1086, 792, 753, 697. Anal. Calcd for $C_{21}H_{13}BF_5N_3$: C 61.05; H 3.17; F 22.99; N 10.17%. Found: C 61.30; H 2.98; F 23.22; N 10.04%.

4,4-Difluoro-3-phenyl-5-(pyridin-4-yl)-8-trifluoromethyl-4-bora-3a,4a-diaza-*s*-indacene (1c), yield 0.231 g (28%), green crystals with metal luster, mp 138–139 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 8.68 (m, 2H, H-2,6 pyridine), 7.89 (m, 2H, H-*o* Ph), 7.70 (m, 2H, H-3,5 pyridine), 7.56 (m, 1H, H-1 indacene), 7.48 (m, 3H, H-*m,p* Ph), 7.43 (m, 1H, H-7 indacene), 6.83 (m, 1H, H-2 indacene), 6.73 (m, 1H, H-6 indacene). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 165.1 (C-3), 156.3 (C-5), 150.0 (2C, C-2,6 pyridine), 139.4 (C-4 pyridine), 135.0, 132.9, 132.3 (2C, C-1, C-7a), 131.4 (C-*p* Ph), 131.2 (C-*i* Ph), 129.9 (2C, t, J = 4.1 Hz, C-*o* Ph), 129.5 (C-7), 128.7 (2C, C-*m* Ph), 127.7 (q, J = 33.2 Hz, $\underline{C}$-CF_3), 124.7 (C-2), 123.3 (2C, t, J = 3.9 Hz, C-3,5 pyridine), 122.5 (q, J = 276.2 Hz, $\underline{C}F_3$), 121.7 (C-6). ^{19}F NMR (376.5 MHz, $CDCl_3$) δ –55.0, –132.4. IR (KBr): 1567, 1511, 1477, 1412, 1290, 1226, 1141, 1090, 977, 757, 692. Anal. Calcd for $C_{21}H_{13}BF_5N_3$: C 61.05; H 3.17; F 22.99; N 10.17%. Found: C 60.89; H 3.47; F 23.26; N 10.36%.

X-ray crystallographic data

X-ray diffraction measurements were carried out on an Xcalibur diffractometer at 100 K using an EOS CCD detector and monochromatized MoK_α radiation (λ = 0.71073 Å). The determination and refinement of the unit cell parameters were performed using *CrysAlisPro* software.[3] All structures were solved by direct methods and refined against all F^2 data. Non-hydrogen atoms were refined with anisotropic thermal parameters; positions of hydrogen atoms were obtained from difference Fourier syntheses and refined using the riding model. Calculations were performed using the SHELXTL software suite.[4, 5] Selected crystallographic parameters and refinement statistics are given in Table S18 (ESI). The X-ray crystal structure data have been deposited at the Cambridge Crystallographic Data Center under numbers CCDC 2235281 for **1a**, 2235282 for **1b,** 2235283 for **1c** and 2241772 for Ph_2BODIPY.

Spectral data

Electronic absorption spectra were recorded on a Shimadzu UV 3101PC and an Ocean Optics HR 2000 spectrophotometers. Luminescence spectra were obtained on a Shimadzu RF-6000 instrument. All measurements were carried out at room temperature (20–25 °C). The fluorescence quantum yield (φ_f) was determined using rhodamine 6G at 25°C in water (φ_{f_r} = 0.92 [6]) as the reference. The measurements were carried out with freshly prepared aerated solutions. The value of φ_f was calculated

by the formula: $\varphi_f = (\varphi_{f\_r} D_{ex\_r} n^2 S)/(D_{ex} n_r^2 S_r)$, where the subscript r refers to the reference parameters, D_{ex} is the optical density at the excitation wavelength, n is the refractive index of the solvent, and S is the integrated intensity of the corrected fluorescence spectrum at the energy scale.

The fluorometric titration data were corrected for reabsorption using the following equation: $I = 10^{(-D/2)}$, where I is the luminescence intensity at a certain wavelength, and D is the optical density of the solution at the same wavelength. The emission spectra were recorded from the center of the cuvette at an angle of 90 degrees. The optical density of the solution at the excitation wavelength did not exceed 0.1. Details of the calculation of stability constants are given in Chapter IX.

Fluorescence lifetime data measurements were performed on a PicoQuant Fluotime 200 fluorescence lifetime spectrometer. A sub-nanosecond pulsed LED with a wavelength of 500 nm, ~800 ps pulse duration (FWHM) and 250 kHz repetition frequency was used as an excitation source, emission was recorded at the corresponding fluorescence maxima. The fluorescence decays were fitted by the PicoQuant's FluoFit Pro 4.6.6 software package using common multiexponential model.

Density functional theory (DFT) calculations

DFT calculations were performed using the Gaussian 09 D.01 program package.[7] Geometry optimizations were carried out with the M06-2X functional[8] and the 6-31+G(d,p) basis set. The two-electron integral accuracy was set to 10^{-10}. The default optimization criteria were tightened three times using the internal option IOp(1/7=100). The SMD polarizable continuum model[9] was employed to simulate the effects of *n*-hexane, toluene and acetonitrile as the experimental solvents. All geometry optimizations were followed by frequency calculations to verify the nature of the stationary points and to compute the thermochemical quantities. Thermochemical analysis was carried out using a scale factor of 0.967 for the harmonic frequencies.[10] The Gibbs free energy in solution $G(s)$ was calculated by the following formula:

$$G(s) = E^{H-L}(s) + G_T^{L-L}(s),$$

where $E^{H-L}(s)$ is the electronic energy derived from the single point M06-2X/6-311++G(2df,2p)/SMD calculation on the M06-2X/6-31+G(d,p)/SMD geometry and $G_T^{L-L}(s)$ is the thermal correction to the free energy, including the zero-point vibrational energy, calculated for the M06-2X/6-31+G(d,p)/SMD geometry.

The energies of the vertical electronic transitions and the molecular orbitals involved were calculated using time-dependent DFT (TDDFT) with the B3LYP functional[11, 12], the 6-311+G(2d,p) basis set, and the SMD solvation model.

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II Figures S1–S3: Absorption and fluorescence spectra

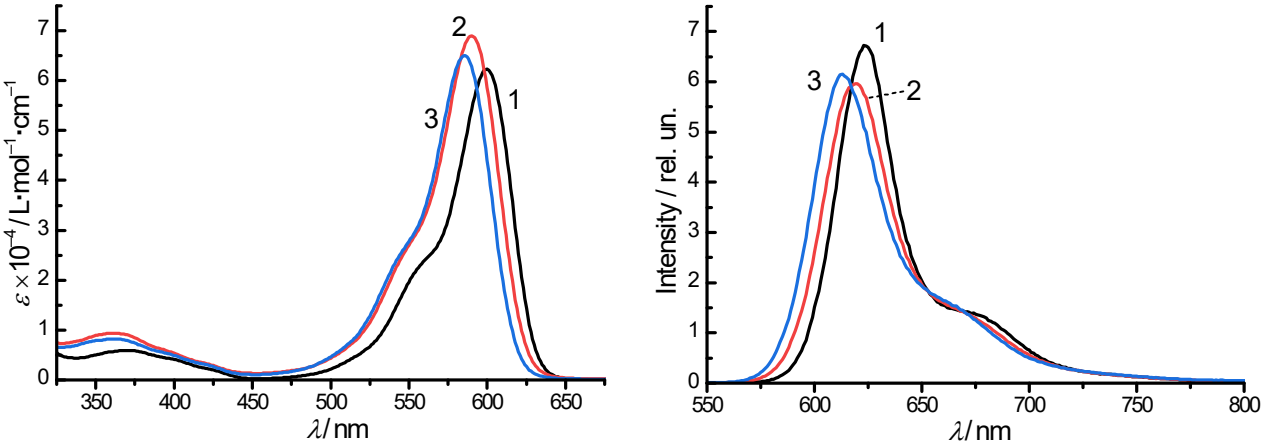


Figure S1. Absorption (left) and fluorescence (right) spectra (excitation at the absorption maximum) of dyes **1a** (1), **1b** (2) and **1c** (3) in *n*-hexane.

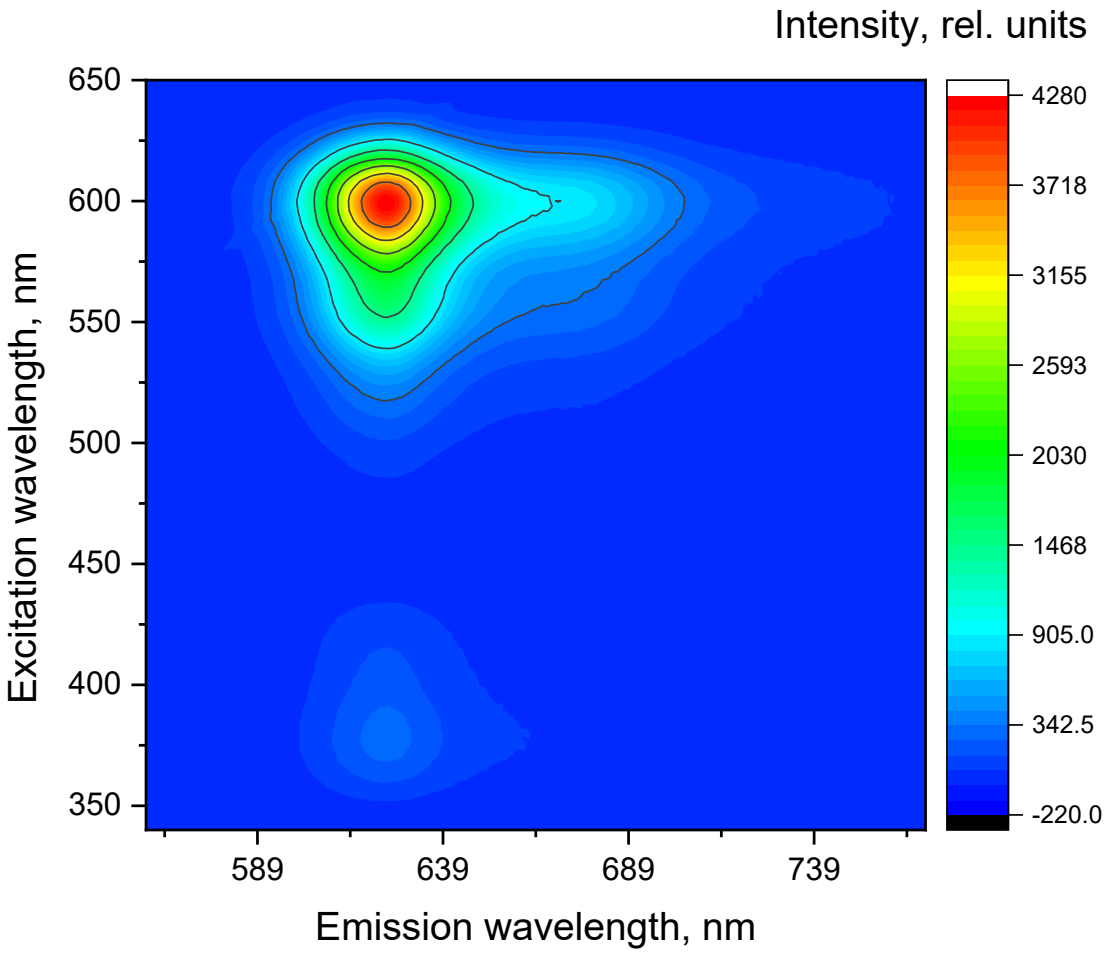


Figure S2. Excitation-emission matrix of 2-PyBODIPY in *n*-hexane.

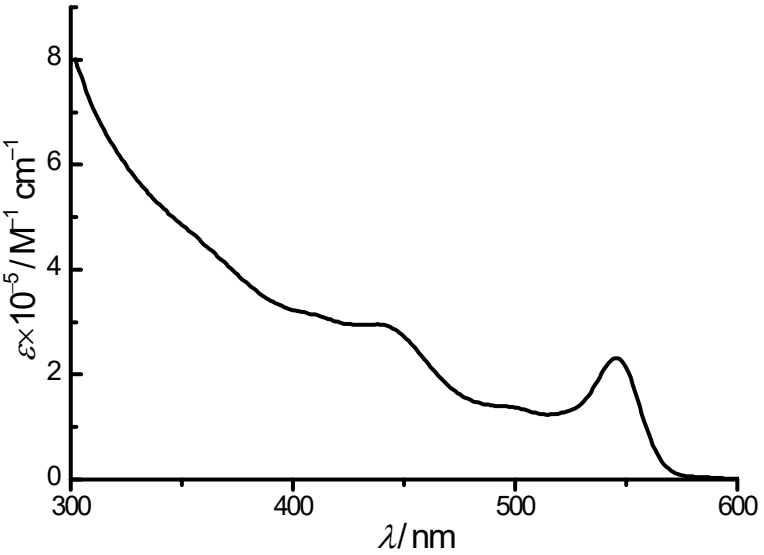


Figure S3. Absorption spectrum of CdSe quantum dots in toluene (4.7×10^{-7} M).

III Tables S1–S8, Figure S4: Gibbs free energies in solution for different conformers of Ph_2BODIPY and Py-BODIPY as derived from DFT/SMD calculations

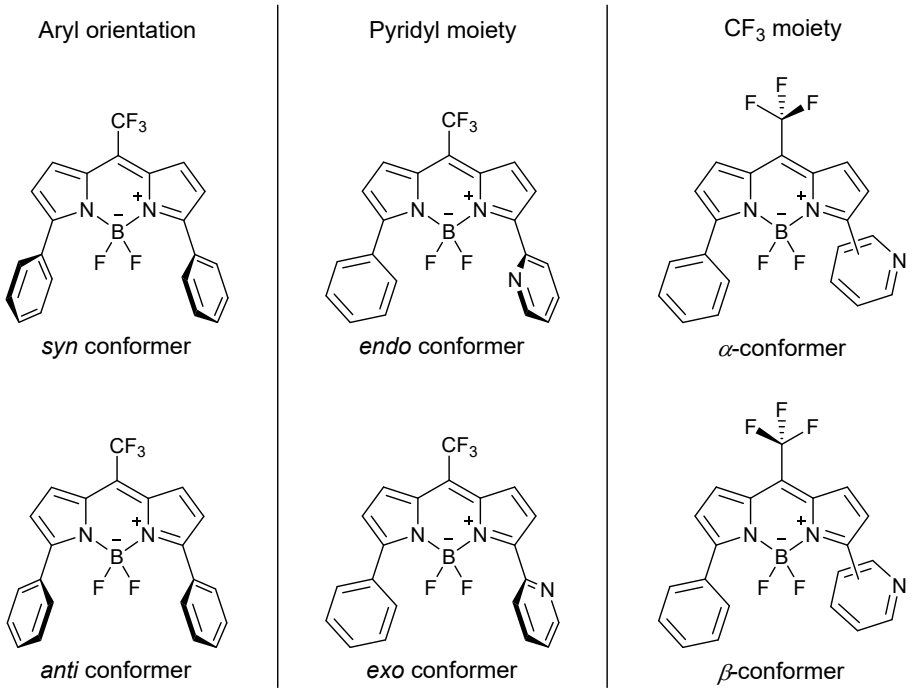


Figure S4. Notation for conformers of the studied BODIPY.

Geometry optimizations were carried out with the M06-2X functional, the 6-31G(d) basis set and Solvation Model based on Density (SMD). The Gibbs free energy in solution $G(s)$ was calculated as follows:

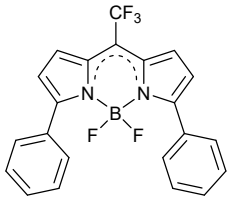
$$G(s) = E^{H-L}(s) + G_T^{L-L}(s),$$

where $E^{H-L}(s)$ is the electronic energy derived from the single point M06-2X/6-311++G(2df,2p)/SMD calculation on the M06-2X/6-31+G(d,p)/SMD geometry and $G_T^{L-L}(s)$ is the thermal correction to the free energy, including the zero-point vibrational energy, calculated for the M06-2X/6-31+G(d,p)/SMD geometry.

For an equilibrium mixture of n conformers, the partial contribution ω of the i-th conformer was calculated according to the Boltzmann distribution:

$$\omega_i = \frac{e^{-G_i(s)/kT}}{e^{-G_1(s)/kT} + e^{-G_2(s)/kT} + \ldots + e^{-G_i(s)/kT} + \ldots + e^{-G_n(s)/kT}} \times 100,$$

where G is the relative free energy of the i-th conformer, kcal mol^{-1}, $k \approx 1.987$ kcal mol^{-1}K^{-1}, and T is the absolute temperature, K.



Ph_2BODIPY

Table S1. Total and relative Gibbs free energies in *n*-hexane for different conformers of the dye Ph_2BODIPY, as derived from DFT/SMD calculations.[a]

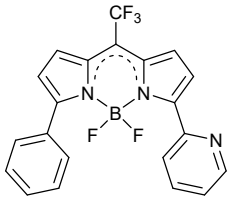
Conformer	G(s) / Hartree	ΔG(s) / kcal mol^{-1}	ω_i / %
anti	–1480.249487	0.15	43.5
syn	–1480.249732	0	56.5

[a] ΔG(s) is the difference between G(s) of the i-th conformer and G(s) of the lowest energy conformer; ω_i is the relative content of conformer in solution.

Table S2. Total and relative Gibbs free energies in MeCN for different conformers of the dye Ph_2BODIPY, as derived from DFT/SMD calculations.[a]

Conformer	G(s) / Hartree	ΔG(s) / kcal mol^{-1}	ω_i / %
anti	–1480.257069	0	69.1
syn	–1480.256308	0.48	30.9

[a] ΔG(s) is the difference between G(s) of the i-th conformer and G(s) of the lowest energy conformer; ω_i is the relative content of conformer in solution.



2-Py-BODIPY

Table S3. Total and relative Gibbs free energies in *n*-hexane for different conformers of the dye 2-Py-BODIPY, as derived from DFT/SMD calculations.[a]

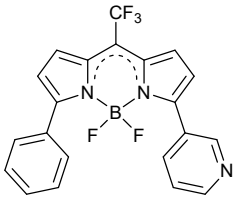
Conformer	G(s) / Hartree	ΔG(s) / kcal mol^{-1}	ω_i / %
anti-endo-α	–1496.298418	2.10	1.2
anti-endo-β	–1496.298417	2.10	1.2
anti-exo-α	–1496.301770	0	43
anti-exo-β	–1496.301653	0.07	38
syn-endo-α	–1496.296222	3.48	0.1
syn-endo-β	not optimized	–	–
syn-exo-α	–1496.299830	1.22	5.5
syn-exo-β	–1496.300474	0.81	11

[a] ΔG(s) is the difference between G(s) of the i-th conformer and G(s) of the lowest energy conformer; ω_i is the relative content of conformer in solution.

Table S4. Total and relative Gibbs free energies in MeCN for different conformers of the dye 2-Py-BODIPY, as derived from DFT/SMD calculations.[a]

Conformer	G(s) / Hartree	ΔG(s) / kcal mol^{-1}	ω_i / %
anti-endo-α	not optimized	–	–
anti-endo-β	not optimized	–	–
anti-exo-α	–1496.310889	0	52.1
anti-exo-β	–1496.309953	0.59	19.3
syn-endo-α	–1496.307342	2.23	1.2
syn-endo-β	–1496.309968	0.58	19.6
syn-exo-α	–1496.308592	1.44	4.6
syn-exo-β	–1496.308264	1.65	3.2

[a] ΔG(s) is the difference between G(s) of the i-th conformer and G(s) of the lowest energy conformer; ω_i is the relative content of conformer in solution.



3-Py-BODIPY

Table S5. Total and relative Gibbs free energies in *n*-hexane for different conformers of the dye 3-Py-BODIPY, as derived from DFT/SMD calculations.[a]

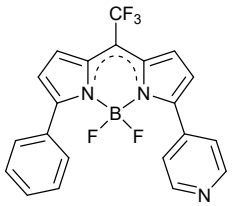
Conformer	G(s) / Hartree	ΔG(s) / kcal mol^{-1}	ω_i / %
anti-endo-α	–1496.299437	0.63	13.7
anti-endo-β	–1496.299348	0.69	12.5
anti-exo-α	–1496.300448	0	40.1
anti-exo-β	not optimized	–	–
syn-endo-α	–1496.298516	1.21	5.2
syn-endo-β	–1496.297759	1.69	2.3
syn-exo-α	–1496.298979	0.92	8.5
syn-exo-β	–1496.299676	0.48	17.7

[a] ΔG(s) is the difference between G(s) of the i-th conformer and G(s) of the lowest energy conformer; ω_i is the relative content of conformer in solution.

Table S6. Total and relative Gibbs free energies in MeCN for different conformers of the dye 3-Py-BODIPY, as derived from DFT/SMD calculations.[a]

Conformer	G(s) / Hartree	ΔG(s) / kcal mol^{-1}	ω_i / %
anti-endo-α	–1496.309490	0.02	24.3
anti-endo-β	–1496.309525	0	25.3
anti-exo-α	–1496.308880	0.40	12.8
anti-exo-β	–1496.308932	0.37	13.5
syn-endo-α	–1496.308382	0.72	7.5
syn-endo-β	–1496.307362	1.36	2.6
syn-exo-α	–1496.308430	0.69	7.9
syn-exo-β	–1496.308181	0.84	6.1

[a] ΔG(s) is the difference between G(s) of the i-th conformer and G(s) of the lowest energy conformer; ω_i is the relative content of conformer in solution.



4-Py-BODIPY

Table S7. Total and relative Gibbs free energies in *n*-hexane for different conformers of the dye 4-Py-BODIPY, as derived from DFT/SMD calculations.[a]

Conformer	G(s) / Hartree	ΔG(s) / kcal mol^{-1}	ω_i / %
anti-α	–1496.298961	0.36	25.8
anti-β	–1496.299536	0	47.4
syn-α	–1496.298089	0.91	10.3
syn-β	–1496.298540	0.63	16.5

[a] ΔG(s) is the difference between G(s) of the i-th conformer and G(s) of the lowest energy conformer; ω_i is the relative content of conformer in solution.

Table S8. Total and relative Gibbs free energies in MeCN for different conformers of the dye 4-Py-BODIPY, as derived from DFT/SMD calculations.[a]

Conformer	G(s) / Hartree	ΔG(s) / kcal mol^{-1}	ω_i / %
anti-α	–1496.308416	0.41	20.8
anti-β	–1496.309071	0	41.6
syn-α	–1496.308777	0.18	30.5
syn-β	–1496.307399	1.05	7.1

[a] ΔG(s) is the difference between G(s) of the i-th conformer and G(s) of the lowest energy conformer; ω_i is the relative content of conformer in solution.

IV Tables S9–S16: TDDFT calculations

TDDFT calculations were performed for M06-2X/6-31+G(d,p)/SMD(*n*-hexane) geometry.

Table S9. Energies and oscillator strengths of the electronic transitions of the Ph_2BODIPY dye calculated by TDDFT/B3LYP/6-311+G(2d,p)/SMD(*n*-hexane).[a]

Conformer	*anti*	*syn*
ω_i / %	44	56
E (S_0–S_1) / eV	2.0946	2.1659
λ (S_0–S_1) / nm	592	572.5
f	0.6156	0.6404
E (S_0–S_2) / eV	3.06329	3.0389
λ (S_0–S_2) / nm	404.8	408.0
f	0.0131	0.0062

[a] The electronic transition energies are given with a correction of –0.1786 eV.

Table S10. Energies and oscillator strengths of the electronic transitions of the 2-Py-BODIPY dye calculated by TDDFT/B3LYP/6-311+G(2d,p)/SMD(*n*-hexane).[a]

Conformer	*anti-exo-a*	*anti-exo-b*	*syn-exo-a*	*syn-exo-b*
ω_i / %	43	38	5.5	11
E (S_0–S_1) / eV	2.1042	2.0967	2.1449	2.1447
λ (S_0–S_1) / nm	589.3	591.4	578.1	578.2
f	0.6818	0.6812	0.7143	0.7105
E (S_0–S_2) / eV	3.0506	3.0480	3.0320	3.0294
λ (S_0–S_2) / nm	406.5	406.8	409.0	409.3
f	0.0346	0.0085	0.0258	0.0168

[a] The electronic transition energies are given with a correction of –0.1786 eV.

Table S11. Energies and oscillator strengths of the electronic transitions of the 3-Py-BODIPY dye calculated by TDDFT/B3LYP/6-311+G(2d,p)/SMD(*n*-hexane).[a]

Conformer	*anti-endo-α*	*anti-endo-β*	*anti-exo-α*	*syn-exo-β*
ω_i / %	14	12	40	18
E (S_0–S_1) / eV	2.1181	2.1129	2.1141	2.1826
λ (S_0–S_1) / nm	585.4	586.9	586.5	568.1
f	0.6844	0.6857	0.6882	0.7169
E (S_0–S_2) / eV	3.0064	2.9998	3.0342	3.0320
λ (S_0–S_2) / nm	412.5	413.4	408.7	409.0
f	0.0104	0.0093	0.0108	0.0118

[a] The electronic transition energies are given with a correction of –0.1786 eV.

Table S12. Energies and oscillator strengths of the electronic transitions of the 4-Py-BODIPY dye calculated by TDDFT/B3LYP/6-311+G(2d,p)/SMD(*n*-hexane).[a]

Conformer	*anti*-α	*anti*-β	*syn*-α	*syn*-β
ω_i / %	26	47	10	17
E (S_0–S_1) / eV	2.1460	2.1532	2.1994	2.2045
λ (S_0–S_1) / nm	577.8	575.9	563.8	562.5
f	0.6828	0.6813	0.7230	0.7150
E (S_0–S_2) / eV	2.9922	2.9951	3.0127	2.9987
λ (S_0–S_2) / nm	414.4	414.0	411.6	413.5
f	0.0100	0.0098	0.0093	0.0081

[a] The electronic transition energies are given with a correction of –0.1786 eV.

TDDFT calculations were performed for M06-2X/6-31+G(d,p)/SMD(MeCN) geometry.

Table S13. Energies and oscillator strengths of the electronic transitions of the Ph_2BODIPY dye calculated by TDDFT/B3LYP/6-311+G(2d,p)/SMD(MeCN).[a]

Conformer	*anti*	*syn*
ω_i / %	69.1	30.9
E (S_0–S_1) / eV	2.108	2.1917
λ (S_0–S_1) / nm	588.2	565.7
f	0.6712	0.6918
E (S_0–S_2) / eV	3.1122	3.0934
λ (S_0–S_2) / nm	398.4	400.8
f	0.0060	0.0704

[a] The electronic transition energies are given with a correction of –0.1786 eV.

Table S14. Energies and oscillator strengths of the electronic transitions of the 2-Py-BODIPY dye calculated by TDDFT/B3LYP/6-311+G(2d,p)/SMD(MeCN).[a]

Conformer	*anti-exo-a*	*anti-exo-b*
ω_i / %	52.1	19.3
E (S_0–S_1) / eV	2.1166	2.1194
λ (S_0–S_1) / nm	585.8	585.0
f	0.6695	0.6624
E (S_0–S_2) / eV	3.0773	3.0711
λ (S_0–S_2) / nm	402.9	403.7
f	0.0076	0.0065

[a] The electronic transition energies are given with a correction of –0.1786 eV.

Table S15. Energies and oscillator strengths of the electronic transitions of the 3-Py-BODIPY dye calculated by TDDFT/B3LYP/6-311+G(2d,p)/SMD(MeCN).[a]

Conformer	*anti-endo-α*	*anti-endo-β*
ω_i / %	24.3	25.3
E (S_0–S_1) / eV	2.1415	2.1336
λ (S_0–S_1) / nm	579.0	581.1
f	0.6622	0.6694
E (S_0–S_2) / eV	3.0845	3.1028
λ (S_0–S_2) / nm	402.0	399.6
f	0.0067	0.0054

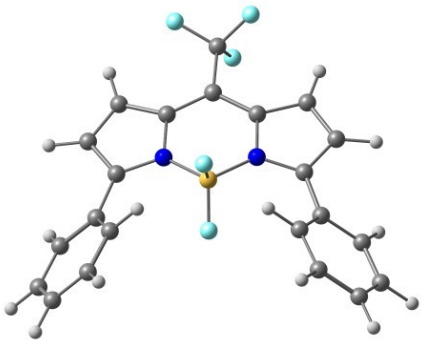
[a] The electronic transition energies are given with a correction of –0.1786 eV.

Table S16. Energies and oscillator strengths of the electronic transitions of the 4-Py-BODIPY dye calculated by TDDFT/B3LYP/6-311+G(2d,p)/SMD(MeCN).[a]

Conformer	*anti-β*	*syn-α*
ω_i / %	41.6	30.5
E (S_0–S_1) / eV	2.1699	2.2329
λ (S_0–S_1) / nm	571.4	555.3
f	0.6611	0.6894
E (S_0–S_2) / eV	3.0494	3.0720
λ (S_0–S_2) / nm	406.6	403.6
f	0.0070	0.0063

[a] The electronic transition energies are given with a correction of –0.1786 eV.

V **Tables S17:** Cartesian coordinates from DFT calculations in solution



anti-(Ph_2BODIPY)

Cartesian coordinates (Å):

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C	-0.265108000	-3.453109000	-0.126738000
C	-2.999694000	1.896130000	-0.258619000
C	-3.374737000	0.577625000	-0.141027000
N	-1.110243000	0.712184000	0.091080000
C	-1.589042000	1.959253000	-0.094449000
C	-1.977447000	-1.548632000	0.103195000
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C	3.397967000	-0.623282000	0.773344000
C	-1.199433000	4.223809000	-0.983503000
C	-0.522798000	5.438468000	-1.003601000
C	0.549708000	5.653112000	-0.138633000
C	0.941661000	4.645713000	0.742041000
C	0.273971000	3.425288000	0.760896000
F	-2.974108000	-3.693725000	0.406549000
F	-4.172005000	-1.971885000	0.871246000
F	-3.732997000	-2.452510000	-1.188779000
B	0.359258000	0.255144000	0.369056000
F	1.236593000	0.920208000	-0.460619000
F	0.648090000	0.479554000	1.721096000
H	1.776164000	-4.243749000	-0.391163000
H	-0.896926000	-4.324762000	-0.192137000
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H	-4.373417000	0.171229000	-0.207795000
H	3.416384000	-2.980189000	-1.681293000
H	5.804538000	-2.348682000	-1.731756000
H	5.114300000	0.482221000	1.427512000
H	2.731702000	-0.147961000	1.483449000
H	1.770818000	4.810082000	1.422857000
H	0.576589000	2.653958000	1.459188000
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H	1.076699000	6.602143000	-0.149802000
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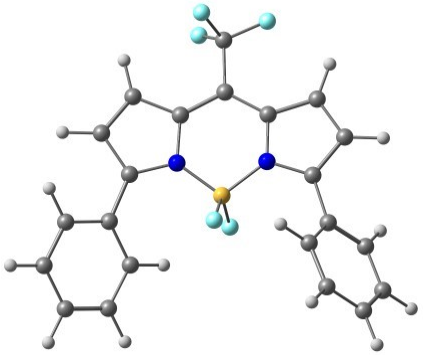

syn-(Ph_2BODIPY)

Cartesian coordinates (Å):

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C	-0.105644000	-2.235709000	-0.058475000
C	0.690467000	-3.416666000	-0.076024000
C	-3.413395000	1.019233000	-0.057678000
C	-3.407009000	-0.355268000	-0.033253000
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C	-1.482934000	-2.030023000	0.012593000
C	-2.046633000	-0.756426000	0.058905000
C	-2.463754000	-3.185920000	-0.021326000
C	3.236431000	-0.768032000	-0.164471000
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C	3.440368000	0.227926000	-1.127593000
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F	0.729701000	0.634596000	1.498574000
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H	4.792522000	1.698042000	-1.909441000
H	2.664093000	0.442815000	-1.851854000
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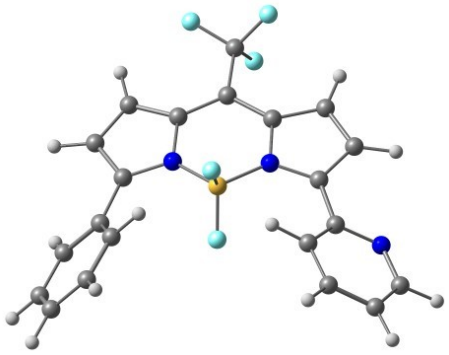
H	-3.207514000	3.435422000	-1.310621000



anti-exo-α-(2-Py-BODIPY)

Cartesian coordinates (Å):

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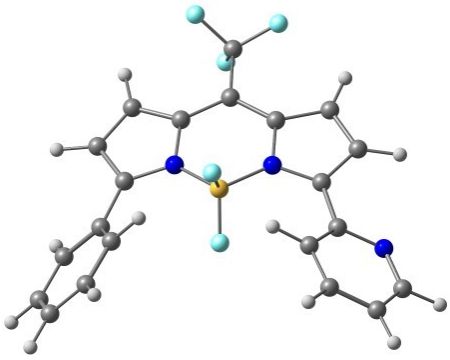
C	0.372111000	-2.196344000	0.100359000
C	1.385293000	-3.181938000	-0.081737000
C	-3.520632000	0.295056000	-0.275707000
C	-3.238166000	-1.046113000	-0.159549000
N	-1.296807000	0.124884000	0.096864000
C	-2.304316000	1.001593000	-0.092163000
C	-1.018079000	-2.282478000	0.104768000
C	-1.837825000	-1.153967000	0.060914000
C	-1.715380000	-3.627111000	0.039677000
C	3.333551000	-0.067654000	-0.081359000
C	-2.211360000	2.474154000	-0.095012000
C	4.385298000	-0.207989000	-0.999452000
C	5.404568000	0.736494000	-1.055233000
C	5.394373000	1.824086000	-0.182753000
C	4.358961000	1.961943000	0.741102000
C	3.330117000	1.026931000	0.793753000
N	-3.169258000	3.070785000	-0.824722000
C	-3.188147000	4.399552000	-0.872695000
C	-2.275226000	5.205938000	-0.191651000
C	-1.304271000	4.584560000	0.584855000
C	-1.265461000	3.195297000	0.640672000
F	-0.916063000	-4.654007000	0.351339000
F	-2.197808000	-3.859323000	-1.192778000
F	-2.754756000	-3.678935000	0.886909000
B	0.219412000	0.400010000	0.360443000
F	0.378613000	0.777827000	1.699959000
F	0.688137000	1.371765000	-0.500687000
H	3.563940000	-2.936624000	-0.320645000
H	1.231352000	-4.247656000	-0.140245000
H	-4.472868000	0.767725000	-0.462885000
H	-3.929276000	-1.872450000	-0.242411000
H	4.387048000	-1.047343000	-1.688787000
H	6.203287000	0.624521000	-1.781528000
H	4.352456000	2.801928000	1.428575000
H	2.534829000	1.135565000	1.521823000
H	-0.583265000	5.170039000	1.146440000
H	-0.531276000	2.686427000	1.251013000
H	6.191253000	2.560366000	-0.221570000
H	-2.337592000	6.286139000	-0.265454000
H	-3.971830000	4.844162000	-1.481026000



anti-exo-β-(2-Py-BODIPY)

Cartesian coordinates (Å):

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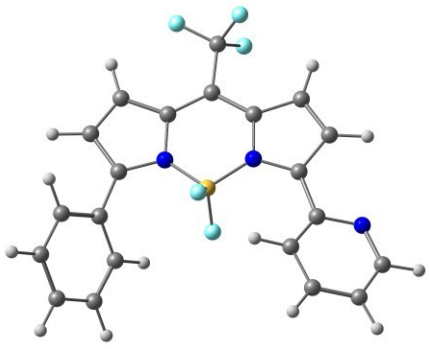
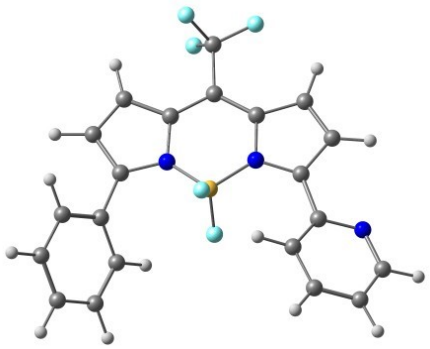
N	1.314055000	-0.199150000	0.115901000
C	1.521430000	-1.572331000	0.100873000
C	2.909033000	-1.816090000	-0.085160000
C	-3.086829000	-1.779648000	-0.303002000
C	-2.097797000	-2.724683000	-0.181224000
N	-1.164161000	-0.658507000	0.093725000
C	-2.487537000	-0.508060000	-0.106009000
C	0.443400000	-2.456887000	0.107256000
C	-0.879867000	-2.023070000	0.056630000
C	0.782707000	-3.933295000	0.050879000
C	2.750132000	1.854530000	-0.090291000
C	-3.255582000	0.752635000	-0.101645000
C	3.711749000	2.341221000	-0.988656000
C	4.010419000	3.698660000	-1.035893000
C	3.362588000	4.584775000	-0.175945000
C	2.415130000	4.105637000	0.728062000
C	2.105273000	2.750051000	0.773458000
N	-4.375122000	0.698906000	-0.843099000
C	-5.156813000	1.773952000	-0.881095000
C	-4.883782000	2.947436000	-0.176647000
C	-3.739890000	2.987429000	0.611735000
C	-2.905690000	1.875213000	0.655362000
F	1.754389000	-4.243064000	0.923971000
F	1.225892000	-4.277488000	-1.170366000
F	-0.254470000	-4.728370000	0.334794000
B	-0.085814000	0.447412000	0.361248000
F	-0.176153000	0.837520000	1.703655000
F	-0.277959000	1.515159000	-0.492127000
H	4.566381000	-0.379402000	-0.341491000
H	3.377733000	-2.788097000	-0.139715000
H	-4.137228000	-1.930075000	-0.500782000
H	-2.206702000	-3.793762000	-0.271225000
H	4.206041000	1.653420000	-1.668487000
H	4.745500000	4.064100000	-1.745886000
H	1.915193000	4.790642000	1.405563000
H	1.377061000	2.383550000	1.487561000
H	-3.495317000	3.871602000	1.191707000
H	-2.018037000	1.873270000	1.273791000
H	3.596979000	5.644236000	-0.208967000
H	-5.558717000	3.793948000	-0.241018000
H	-6.047474000	1.695035000	-1.499404000



syn-exo-α-(2-Py-BODIPY)



syn-exo-b-(2-Py-BODIPY)

Cartesian coordinates (Å):

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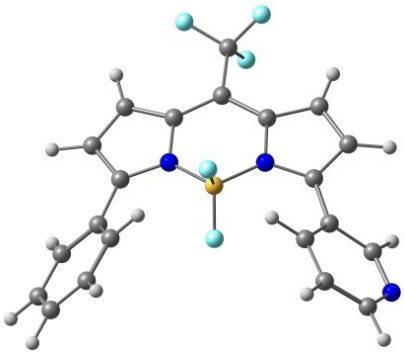
C	2.467558000	-0.796406000	-0.131685000
N	1.120680000	-0.799554000	-0.134352000
C	0.692137000	-2.126976000	-0.105486000
C	1.844921000	-2.963963000	-0.112949000
C	-3.541534000	-0.217821000	0.078929000
C	-3.052117000	-1.501343000	0.078019000
N	-1.284331000	-0.056460000	0.121104000
C	-2.427358000	0.662487000	0.108017000
C	-0.670237000	-2.403376000	-0.008925000
C	-1.634139000	-1.400998000	0.087256000
C	-1.201851000	-3.823775000	-0.025637000
C	3.335532000	0.393620000	-0.122446000
C	-2.569509000	2.132583000	0.102604000
C	4.404106000	0.418333000	0.786167000
C	5.286291000	1.493564000	0.806467000
C	5.124311000	2.545702000	-0.094673000
C	4.076060000	2.516674000	-1.012754000
C	3.183806000	1.448048000	-1.031656000
N	-3.767516000	2.542968000	-0.352215000
C	-4.016138000	3.847280000	-0.396038000
C	-3.101797000	4.818198000	0.016492000
C	-1.873675000	4.391174000	0.505430000
C	-1.594864000	3.028695000	0.553666000
F	-0.246022000	-4.758096000	-0.053146000
F	-1.979099000	-4.029690000	-1.102269000
F	-1.956654000	-4.069063000	1.057521000
B	0.197098000	0.449277000	0.080119000
F	0.557021000	1.028663000	1.294315000
F	0.314920000	1.352127000	-0.965419000
H	3.984494000	-2.416333000	-0.143119000
H	1.849649000	-4.041846000	-0.115254000
H	-4.569828000	0.108685000	0.062183000
H	-3.617571000	-2.421936000	0.058918000
H	4.524377000	-0.397398000	1.493248000
H	6.099192000	1.510179000	1.525601000
H	3.953030000	3.325923000	-1.725552000
H	2.379030000	1.423955000	-1.755548000
H	-1.133661000	5.105691000	0.851579000
H	-0.651015000	2.677711000	0.946092000
H	5.815385000	3.382955000	-0.083611000
H	-3.356917000	5.870786000	-0.040414000
H	-4.993352000	4.134700000	-0.776206000

Cartesian coordinates (Å):

C	3.472041000	-0.876930000	-0.123238000
C	2.543248000	0.194735000	-0.139233000
N	1.288193000	-0.302252000	-0.136191000
C	1.379235000	-1.686959000	-0.098887000
C	2.750625000	-2.050913000	-0.108559000
C	-3.256783000	-1.533530000	0.001690000
C	-2.338121000	-2.551396000	0.008251000
N	-1.216997000	-0.560198000	0.095923000
C	-2.539922000	-0.308040000	0.063677000
C	0.235561000	-2.482865000	-0.017303000
C	-1.046603000	-1.946266000	0.051574000
C	0.481138000	-3.979677000	-0.010653000
C	2.910632000	1.620413000	-0.139432000
C	-3.216613000	1.005647000	0.084874000
C	3.909980000	2.041243000	0.750846000
C	4.330142000	3.367065000	0.762395000
C	3.768887000	4.284312000	-0.125861000
C	2.788457000	3.867848000	-1.024918000
C	2.357779000	2.543907000	-1.035784000
N	-4.459509000	0.961638000	-0.428306000
C	-5.176702000	2.079945000	-0.448049000
C	-4.712763000	3.298526000	0.050636000
C	-3.438989000	3.335042000	0.603547000
C	-2.671312000	2.174535000	0.625448000
F	1.259326000	-4.331075000	1.026934000
F	1.119040000	-4.365555000	-1.128330000
F	-0.632669000	-4.712703000	0.076485000
B	-0.039704000	0.481218000	0.113622000
F	0.054181000	1.085331000	1.365508000
F	-0.280186000	1.413378000	-0.882757000
H	4.545821000	-0.759205000	-0.157092000
H	3.136209000	-3.060380000	-0.110115000
H	-4.332892000	-1.602643000	-0.037980000
H	-2.543957000	-3.608627000	-0.030638000
H	4.337924000	1.327807000	1.449244000
H	5.093222000	3.684452000	1.466021000
H	2.357368000	4.574786000	-1.726760000
H	1.604229000	2.222192000	-1.743659000
H	-3.038999000	4.254490000	1.018917000
H	-1.684340000	2.179840000	1.065940000
H	4.097790000	5.318892000	-0.119822000
H	-5.340956000	4.181699000	0.010939000
H	-6.171438000	2.002049000	-0.879761000



anti-exo-α-(3-Py-BODIPY)

Cartesian coordinates (Å):

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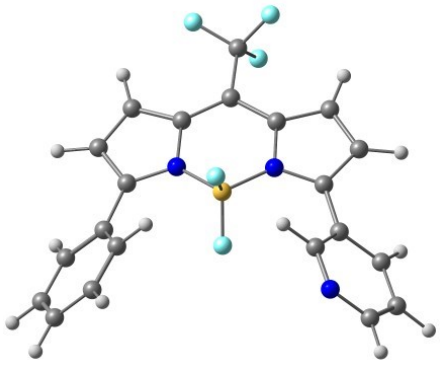
N	0.425959000	-1.281823000	0.105069000
C	-0.695686000	-2.111441000	0.077063000
C	-0.249574000	-3.450818000	-0.129537000
C	-3.003202000	1.893643000	-0.244596000
C	-3.374199000	0.570735000	-0.136400000
N	-1.111815000	0.709236000	0.091626000
C	-1.595012000	1.956988000	-0.084576000
C	-1.969881000	-1.554223000	0.099341000
C	-2.182520000	-0.172950000	0.066098000
C	-3.203161000	-2.434135000	0.044968000
C	2.913538000	-1.586182000	-0.093580000
C	-0.803595000	3.193145000	-0.094207000
C	3.800139000	-2.204619000	-0.988808000
C	5.140694000	-1.836556000	-1.021259000
C	5.615602000	-0.858198000	-0.148558000
C	4.742885000	-0.250245000	0.753223000



anti-endo-α-(3-Py-BODIPY)

Cartesian coordinates (Å):

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N	0.220510000	-1.325597000	0.094065000
C	-1.015410000	-1.975500000	0.066699000
C	-0.776633000	-3.369098000	-0.132915000
C	-2.687921000	2.333779000	-0.243765000
C	-3.256128000	1.081878000	-0.132240000
N	-0.999219000	0.875459000	0.087315000
C	-1.286740000	2.181684000	-0.089847000
C	-2.189230000	-1.232102000	0.092637000
C	-2.190476000	0.166848000	0.064518000
C	-3.545893000	-1.905518000	0.043114000
C	2.633440000	-2.007639000	-0.093807000
C	-0.314628000	3.282473000	-0.112898000
C	3.419383000	-2.775923000	-0.967297000
C	4.800788000	-2.621002000	-0.994666000
C	5.416248000	-1.708280000	-0.138537000
C	4.642849000	-0.951555000	0.740826000

C	3.398536000	-0.606299000	0.783091000
C	-1.196581000	4.229579000	-0.955435000
N	-0.588496000	5.411378000	-1.023539000
C	0.456910000	5.615667000	-0.216869000
C	0.930991000	4.657772000	0.677153000
C	0.292566000	3.426692000	0.743708000
F	-2.959643000	-3.705703000	0.382861000
F	-3.732887000	-2.444725000	-1.189928000
F	-4.155519000	-1.991052000	0.879785000
B	0.357601000	0.260413000	0.372134000
F	0.644212000	0.492990000	1.723673000
F	1.233049000	0.931853000	-0.455726000
H	1.794288000	-4.231374000	-0.393538000
H	-0.877624000	-4.324954000	-0.197893000
H	-3.649538000	2.747691000	-0.387738000
H	-4.372150000	0.162792000	-0.204981000
H	3.428697000	-2.957009000	-1.678276000
H	5.813062000	-2.311041000	-1.728899000
H	5.109923000	0.505116000	1.440659000
H	2.729972000	-0.137526000	1.495406000
H	-2.033809000	4.081239000	-1.634104000
H	1.781756000	4.877816000	1.312613000
H	0.625139000	2.667348000	1.442142000
H	6.662619000	-0.572308000	-0.169646000
H	0.933984000	6.589726000	-0.287634000

C	3.259378000	-1.094197000	0.765719000
C	0.772572000	3.361266000	0.771122000
N	1.635054000	4.376257000	0.783422000
C	1.452763000	5.366331000	-0.094665000
C	0.400260000	5.396157000	-1.007068000
C	-0.498026000	4.337533000	-1.013289000
F	-3.502167000	-3.212215000	0.325961000
F	-4.100175000	-1.780859000	-1.174958000
F	-4.394877000	-1.349806000	0.921363000
B	0.385998000	0.210773000	0.367623000
F	0.700121000	0.387245000	1.719039000
F	1.348485000	0.749450000	-0.459687000
H	1.124007000	-4.451915000	-0.387473000
H	-1.528513000	-4.139443000	-0.198138000
H	-3.195764000	3.276942000	-0.387098000
H	-4.304453000	0.828187000	-0.196939000
H	2.941279000	-3.477613000	-1.644355000
H	5.395340000	-3.210133000	-1.685573000
H	5.117373000	-0.244678000	1.413805000
H	2.669304000	-0.510107000	1.461660000
H	0.937855000	2.578940000	1.505125000
H	0.296435000	6.223948000	-1.699887000
H	-1.321853000	4.313335000	-1.721231000
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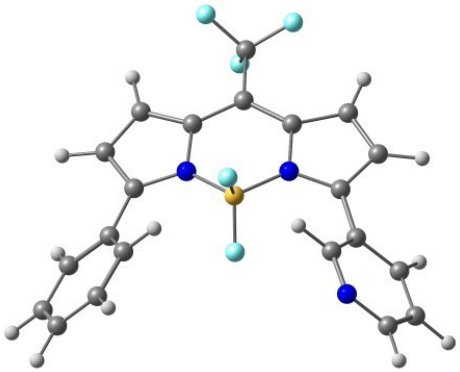

anti-endo-β-(3-Py-BODIPY)

Cartesian coordinates (Å):

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N	-0.662654000	-1.128759000	0.102484000
C	-2.020813000	-0.827912000	0.080104000
C	-2.744326000	-2.037265000	-0.125985000
C	-0.554378000	3.547528000	-0.256643000
C	-1.797550000	2.965644000	-0.141060000
N	-0.211388000	1.346812000	0.098537000
C	0.414443000	2.525127000	-0.089297000
C	-2.463407000	0.490498000	0.104072000
C	-1.583395000	1.576133000	0.071053000
C	-3.961853000	0.710475000	0.040490000
C	0.737189000	-3.207120000	-0.094125000
C	1.867625000	2.738408000	-0.114082000
C	0.835497000	-4.313204000	-0.953152000
C	1.993587000	-5.081897000	-0.983969000
C	3.063657000	-4.763117000	-0.148362000
C	2.967882000	-3.673850000	0.716631000
C	1.814976000	-2.895821000	0.746534000
C	2.748205000	2.120591000	0.787685000
N	4.060705000	2.346606000	0.800527000
C	4.559744000	3.202713000	-0.095403000
C	3.775748000	3.879844000	-1.026861000
C	2.407002000	3.647209000	-1.030709000
F	-4.428939000	0.481551000	-1.198988000
F	-4.325925000	1.952942000	0.378099000
F	-4.615602000	-0.118969000	0.868051000
B	0.437093000	-0.050847000	0.379338000
F	0.790922000	-0.112098000	1.730851000
F	1.524307000	-0.241609000	-0.447183000
H	-1.998439000	-4.094503000	-0.392221000
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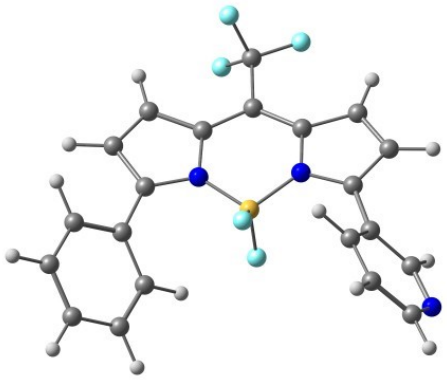
H	-0.329093000	4.593320000	-0.410725000
H	-2.754374000	3.458067000	-0.212944000
H	0.010165000	-4.553840000	-1.616659000
H	2.062217000	-5.925378000	-1.663475000
H	3.794800000	-3.425976000	1.374239000



syn-exo-β-(3-Py-BODIPY)

Cartesian coordinates (Å):

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C	-2.006843000	-0.845083000	0.060026000
C	-3.385262000	-0.502211000	-0.031957000
C	2.141295000	-2.915142000	-0.142458000
C	0.844207000	-3.378671000	-0.095945000
N	0.801616000	-1.098503000	-0.113869000
C	2.086976000	-1.500055000	-0.153594000
C	-1.389722000	-2.090704000	0.015060000
C	-0.002006000	-2.236105000	-0.063581000
C	-2.316760000	-3.290937000	-0.008384000
C	-1.767161000	2.792926000	0.063469000
C	3.262112000	-0.614368000	-0.185811000
C	-2.545187000	3.677989000	-0.699891000
C	-2.283121000	5.043258000	-0.682841000
C	-1.249496000	5.544645000	0.108056000
C	-0.479812000	4.672711000	0.876850000
C	-0.730719000	3.304455000	0.856726000
C	4.301829000	-0.856712000	0.723693000
N	5.433978000	-0.157222000	0.760128000
C	5.579832000	0.827377000	-0.131204000
C	4.616078000	1.146303000	-1.085429000
C	3.436428000	0.413114000	-1.117940000
F	-3.003845000	-3.340003000	-1.162956000
F	-3.219244000	-3.227736000	0.983277000
F	-1.682977000	-4.460760000	0.119896000
B	0.300463000	0.355547000	0.197004000
F	0.787690000	1.262676000	-0.725609000
F	0.709863000	0.670044000	1.490254000
H	-4.337319000	1.484845000	-0.110011000
H	-4.207884000	-1.201528000	-0.076435000
H	3.049881000	-3.497739000	-0.199966000
H	0.525857000	-4.408527000	-0.095288000
H	-3.341477000	3.288469000	-1.327130000
H	-2.883686000	5.714816000	-1.288069000
H	0.320758000	5.057582000	1.500458000

H	1.746233000	-2.060503000	1.433155000
H	2.370256000	1.429367000	1.534327000
H	4.230431000	4.566135000	-1.732723000
H	1.761602000	4.143866000	-1.749661000
H	3.968230000	-5.362855000	-0.169772000
H	5.635358000	3.356550000	-0.063669000
H	-0.134758000	2.637893000	1.468234000
H	4.197036000	-1.647663000	1.463563000
H	4.790459000	1.950227000	-1.791964000
H	2.668678000	0.623317000	-1.852807000
H	-1.046151000	6.610851000	0.126414000
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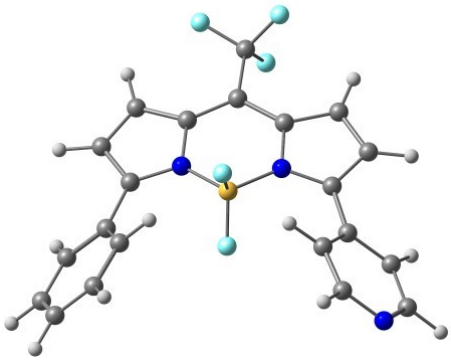

anti-α-(4-Py-BODIPY)

Cartesian coordinates (Å):

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C	-0.208850000	-3.461361000	-0.111161000
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C	-3.379521000	0.525323000	-0.146180000
N	-1.121010000	0.695301000	0.084085000
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C	-1.950401000	-1.581085000	0.096076000
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C	-3.180114000	-2.466182000	0.045616000
C	2.929775000	-1.557974000	-0.090793000
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C	3.403805000	-0.555496000	0.766312000
C	0.224125000	3.437547000	0.754347000
C	0.847986000	4.680740000	0.697839000
N	0.487879000	5.660767000	-0.135232000
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F	-4.108000000	-2.055646000	0.923419000
B	0.354229000	0.266321000	0.363859000
F	0.640675000	0.503546000	1.713183000
F	1.219472000	0.940402000	-0.470860000
H	1.843227000	-4.218266000	-0.363707000
H	-0.825578000	-4.344017000	-0.170007000
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H	3.460420000	-2.955827000	-1.647348000
H	5.837234000	-2.285390000	-1.710848000
H	5.103118000	0.586439000	1.401534000
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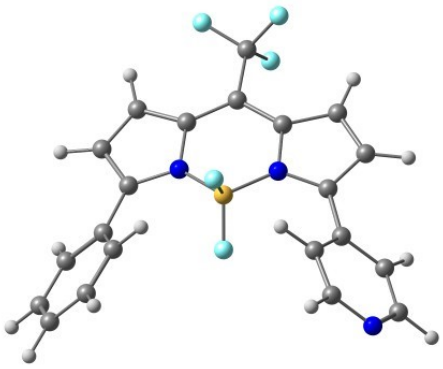

anti-β-(4-Py-BODIPY)

Cartesian coordinates (Å):

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N	-1.013302000	0.852131000	0.080746000
C	-1.326971000	2.151640000	-0.106399000
C	-2.162662000	-1.279293000	0.094060000
C	-2.189563000	0.121205000	0.051005000
C	-3.507369000	-1.977110000	0.047950000
C	2.670855000	-1.963284000	-0.091286000
C	-0.375070000	3.274505000	-0.106785000
C	3.464064000	-2.718552000	-0.969375000
C	4.841660000	-2.535334000	-1.009752000
C	5.445935000	-1.608649000	-0.160817000
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C	3.285316000	-1.035684000	0.761176000
C	0.687779000	3.377555000	0.794595000
C	1.498956000	4.507539000	0.740836000
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C	0.310791000	5.404405000	-0.984945000
C	-0.564006000	4.322836000	-1.014245000
F	-3.440309000	-3.281339000	0.337405000
F	-4.062899000	-1.867973000	-1.170624000
F	-4.364996000	-1.431598000	0.923730000
B	0.385056000	0.217134000	0.362042000
F	0.702924000	0.409876000	1.711295000
F	1.335524000	0.763670000	-0.472959000
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H	-3.251200000	3.207930000	-0.429124000
H	-4.313569000	0.736996000	-0.230791000
H	2.994263000	-3.431438000	-1.640537000
H	5.441865000	-3.113455000	-1.704967000
H	5.132672000	-0.150033000	1.392724000
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H	0.876021000	2.605472000	1.530783000
H	2.328329000	4.610724000	1.435615000
H	0.187828000	6.223792000	-1.688560000
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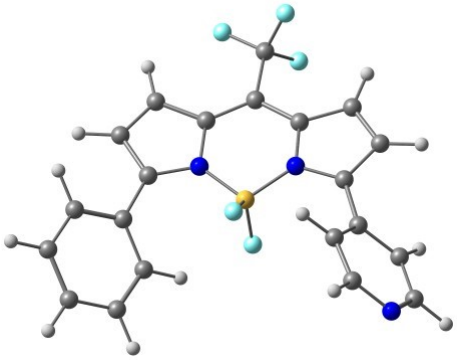

syn-α-(4-Py-BODIPY)

Cartesian coordinates (Å):

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C	3.566629000	0.145493000	-0.191752000
C	3.212456000	-1.189765000	-0.156892000
N	1.310992000	0.063093000	-0.132565000
C	2.371105000	0.899294000	-0.173121000
C	0.929335000	-2.328981000	-0.005263000
C	1.798871000	-1.233728000	-0.101914000
C	1.592801000	-3.692579000	-0.007331000
C	-3.343960000	0.047881000	0.077275000
C	2.308420000	2.372569000	-0.168828000
C	-4.531948000	-0.160065000	-0.643532000
C	-5.531972000	0.805056000	-0.654387000
C	-5.366198000	1.987183000	0.066510000
C	-4.195231000	2.196456000	0.793422000
C	-3.186383000	1.238639000	0.800804000
C	1.501767000	3.113686000	-1.036104000
C	1.567251000	4.503957000	-0.980895000
N	2.360810000	5.181605000	-0.147905000
C	3.135572000	4.467038000	0.672342000
C	3.152165000	3.076154000	0.698161000
F	0.736894000	-4.711930000	0.117475000
F	2.469904000	-3.795659000	1.004393000
F	2.278079000	-3.890737000	-1.145199000
B	-0.176480000	0.432045000	0.177850000
F	-0.688147000	1.310410000	-0.758875000
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H	-1.408430000	-4.204377000	-0.017615000
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H	-4.659993000	-1.071139000	-1.219802000
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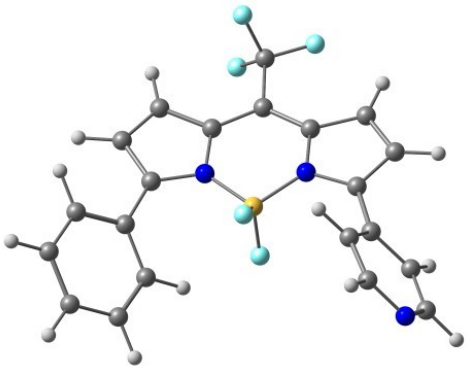

syn-β-(4-Py-BODIPY)

Cartesian coordinates (Å):

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C	0.696219000	-3.414223000	-0.110860000
N	0.753184000	-1.135468000	-0.111258000
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C	-2.458747000	-3.189538000	-0.016717000
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C	3.237370000	-0.759513000	-0.165430000
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C	4.676818000	0.931807000	-1.067049000
N	5.649206000	0.676544000	-0.188214000
C	5.429608000	-0.295107000	0.700936000
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F	-3.354647000	-3.101423000	0.979223000
F	-1.877032000	-4.387810000	0.092219000
B	0.317809000	0.342430000	0.185105000
F	0.821529000	1.213482000	-0.761717000
F	0.765699000	0.657475000	1.465353000
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H	2.714876000	0.504568000	-1.843951000
H	4.875256000	1.721484000	-1.786916000
H	6.229750000	-0.488237000	1.410823000
H	4.129682000	-1.815594000	1.500517000
H	-0.768543000	6.647325000	0.083066000

VI **Table S18 and Figures S5–S11:** X-ray diffraction analysis

Table S18. Crystal data and refinement statistics for **1a-c** and Ph_2BODIPY.

Param. / Comp.	**1a**	**1b**	**1c**	Ph_2BODIPY
Temperature / K	100	100	100	100
CCDC Number	2235281	2235282	2235283	2241772
Empirical formula	$C_{21}H_{13}BF_5N_3$	$C_{21}H_{13}BF_5N_3$	$C_{21}H_{13}BF_5N_3$	$C_{22}H_{14}BF_5N_2$
Formula weight	413.15	413.15	413.15	412.16
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	7.3698(5)	22.481(1)	22.1534(7)	22.4303(8)
b/Å	20.726(2)	7.5423(3)	7.4412(2)	7.4381(2)
c/Å	11.6141(8)	23.184(1)	23.4217(7)	23.5781(8)
β/°	99.476(6)	115.965(6)	113.902(4)	114.362(4)
V/Å3	1749.8(2)	3534.4(3)	3529.9(2)	3583.5(2)
Z, ρ_{calc} /g·cm-3	4, 1.568	8, 1.553	8, 1.555	8, 1.528
μ/mm^{-1}	0.131	0.130	0.130	0.126
F(000)	840	1680	1680	1680
Crystal size/mm^3	0.4 x 0.2 x 0.15	0.45 x 0.25 x 0.2	0.35 x 0.2 x 0.2	0.3 x 0.2 x 0.15
2Θ range /°	2.97 - 26.32	2.87 - 29.07	2.90 - 26.32	2.90 - 29.4
Reflections collected	7487	21235	15015	20120
Independent reflections, [R(int)]	3554 [0.0313]	9450 [0.0349]	7170 [0.0241]	9908 [0.0373]
Data/restraints/ parameters	3554 / 0 / 271	9450 / 0 / 541	7170 / 0 / 541	9908 / 0 / 541
Goodness-of-fit on F2	1.024	1.033	1.042	0.978
Final R indexes [I>=2σ (I)]	0.0428, 0.0949	0.0558, 0.0990	0.0420, 0.0964	0.0517, 0.1046
Final R indexes [all data]	0.0614, 0.1035	0.0941, 0.1152	0.0620, 0.1055	0.0906, 0.1185
Largest diff. peak / hole / e $Å^{-3}$	0.250 / -0.233	0.352 / -0.349	0.331 / -0.341	0.385/ -0.329

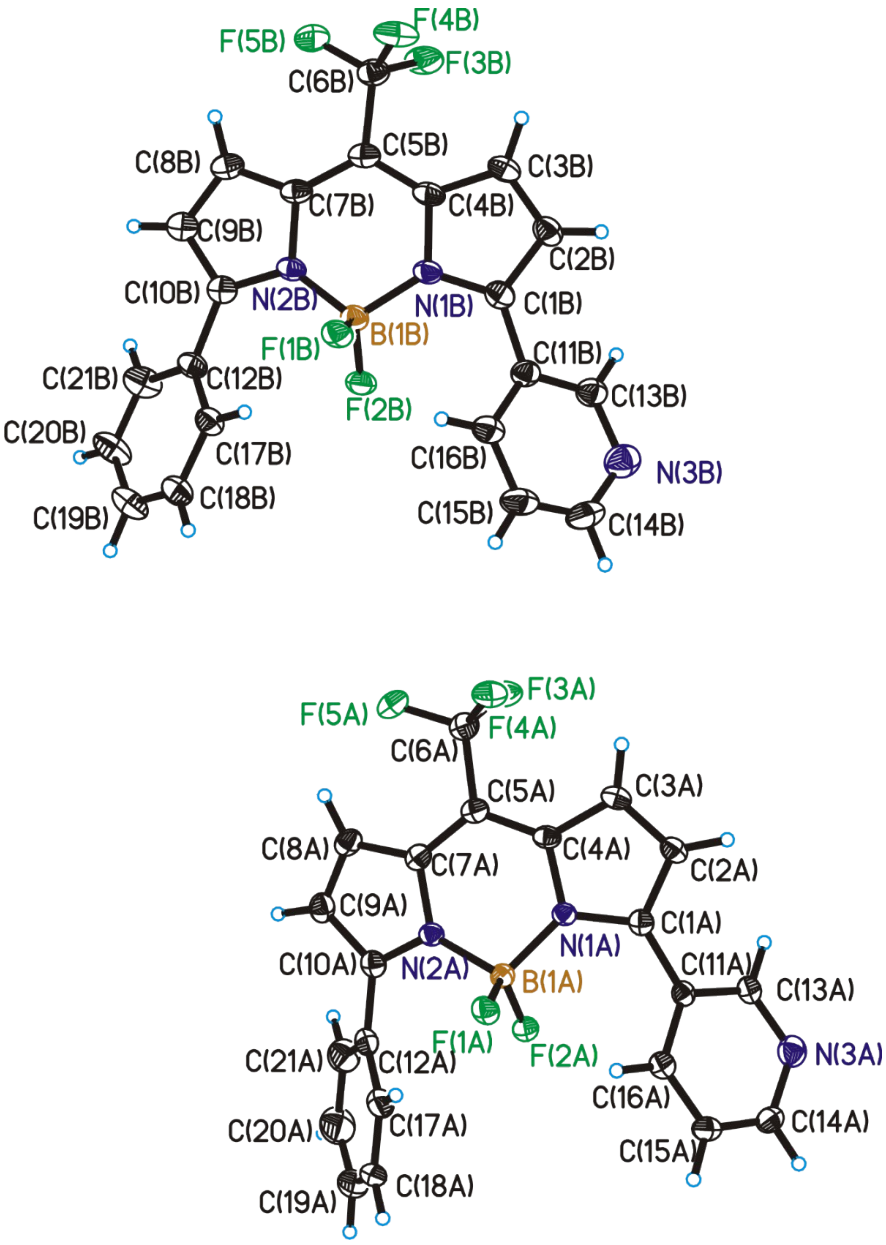

Figure S5. Molecular structures and atom numbering scheme for dye **1b**.

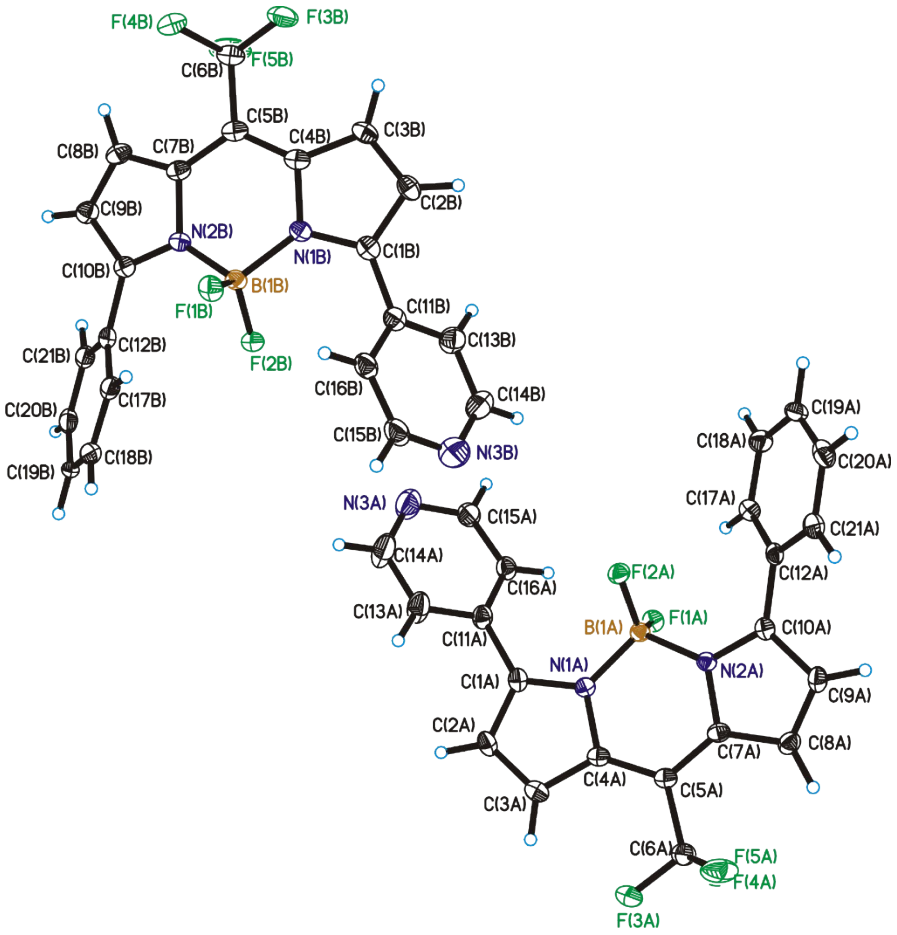

Figure S6. Molecular structures and atom numbering scheme for dye **1c**.

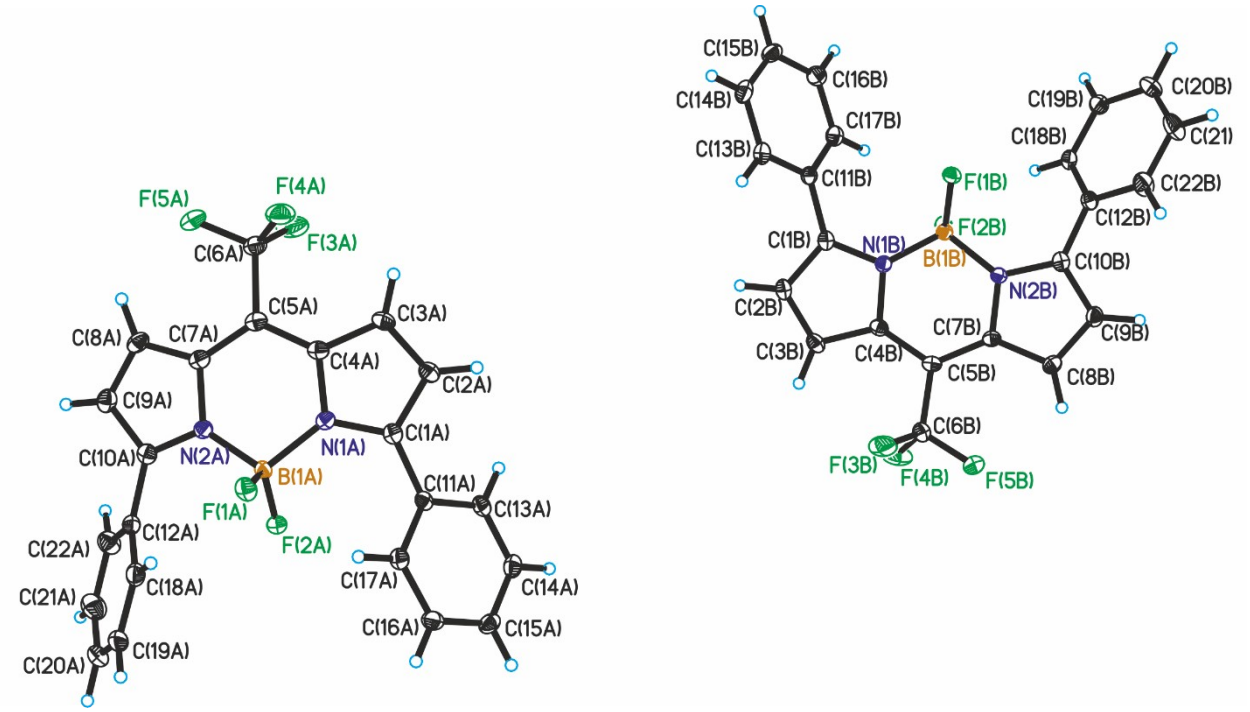

Figure S7. Molecular structures and atom numbering scheme for dye Ph_2BODIPY.

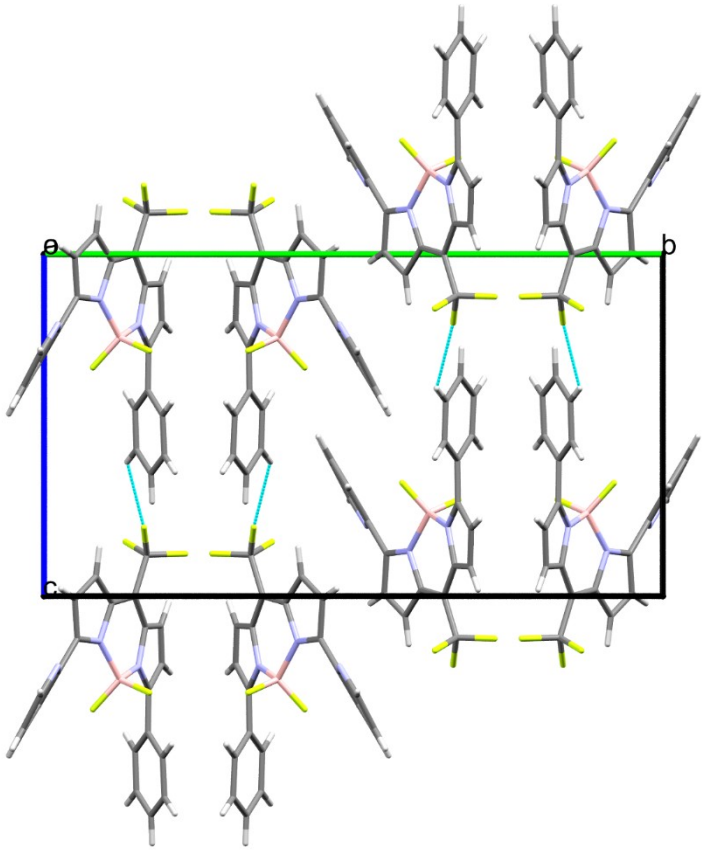

Figure S8. Crystal packing of **1a**: the projection onto the *bc* plane (cyan dashed lines show the intermolecular contacts).

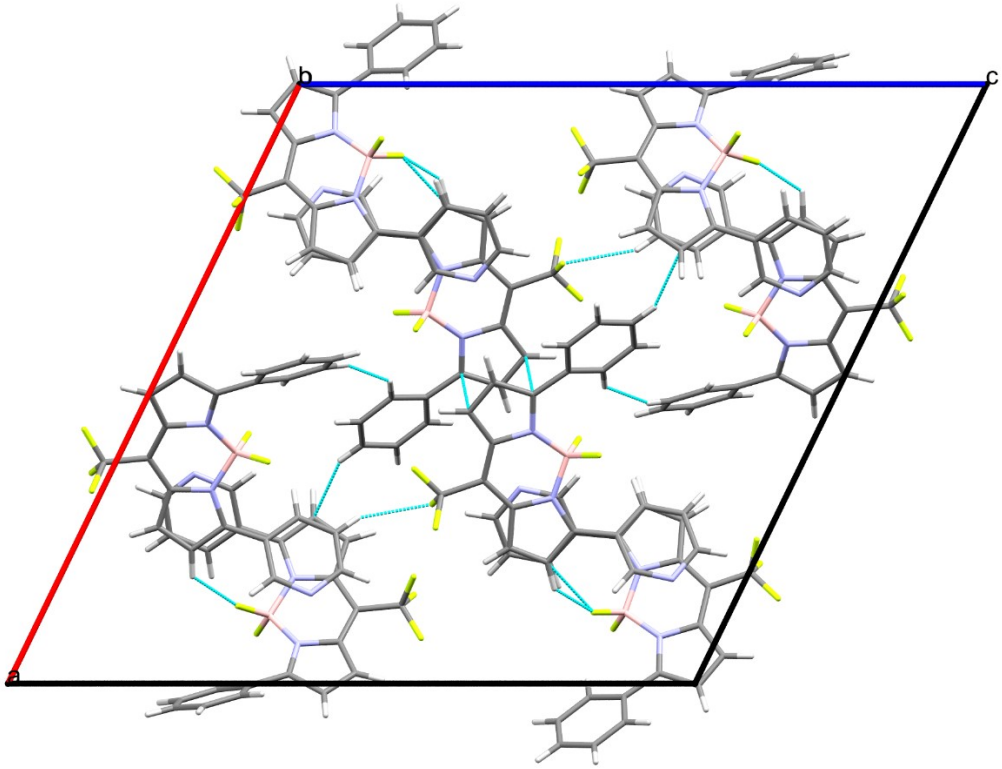

Figure S9. Crystal packing of **1b**: the projection onto the *ac* plane (cyan dashed lines show the intermolecular contacts).

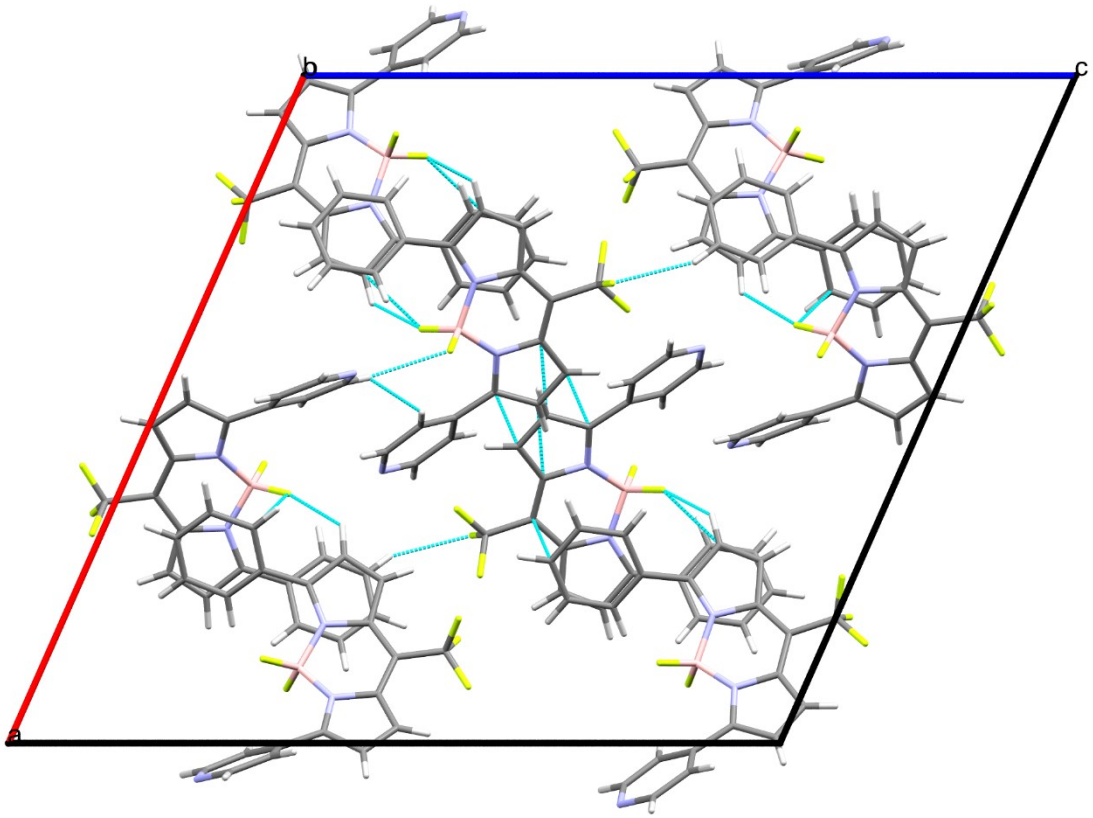

Figure S10. Crystal packing of **1c**: the projection onto the *ac* plane (cyan dashed lines show the intermolecular contacts).

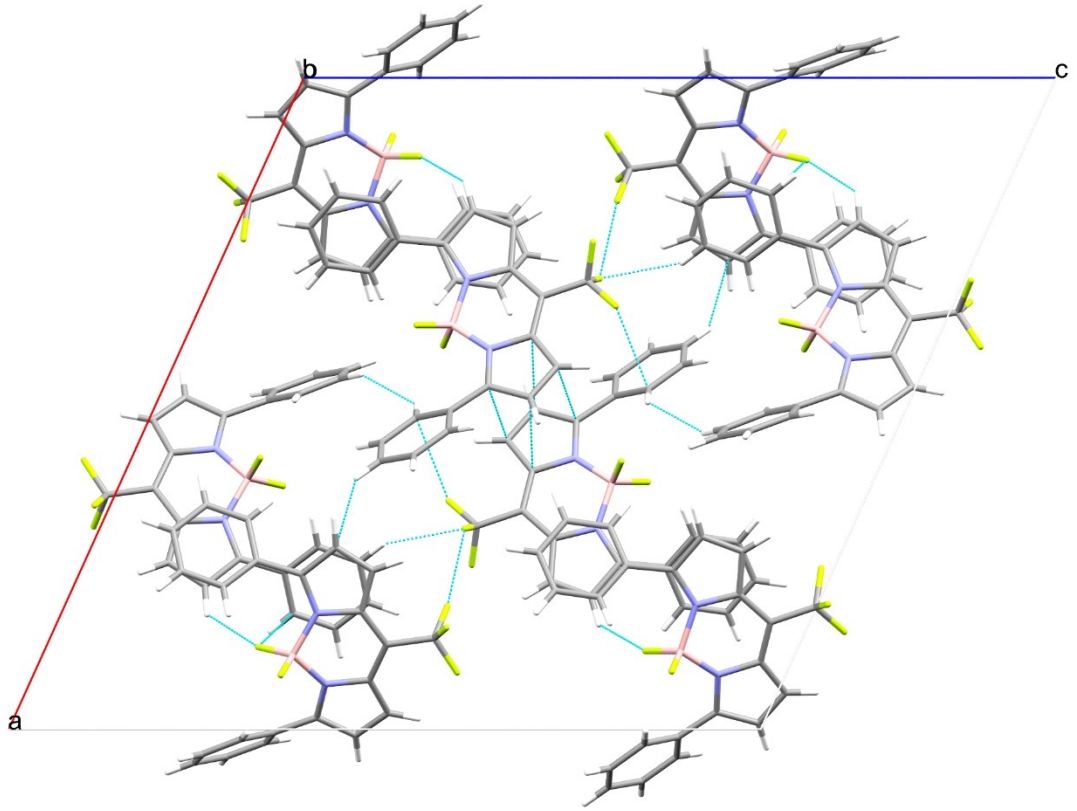

Figure S11. Crystal packing of Ph_2BODIPY: the projection onto the *ac* plane (cyan dashed lines show the intermolecular contacts).

VII **Figures S12–S16:** Fluorometric titration data

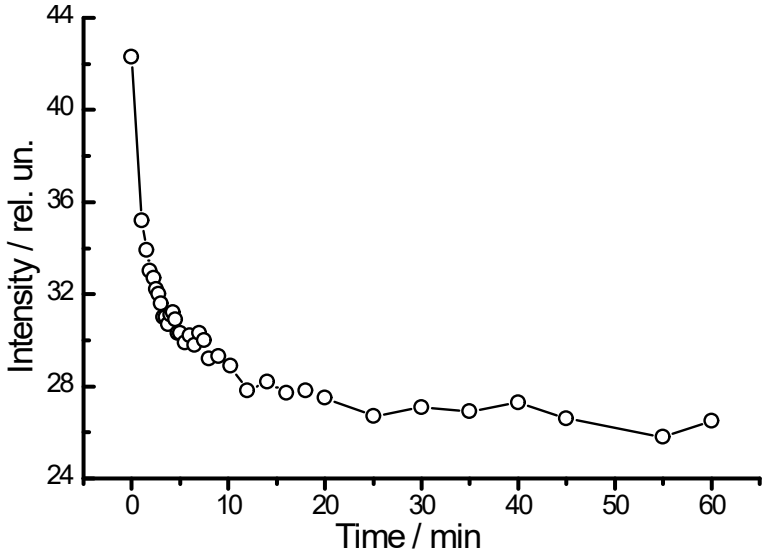

Figure S12. Kinetics of the luminescence intensity at λ = 553 nm of CdSe QDs (5×10^{-7} M) after the addition of 3 equivalent of 4-Py-BODIPY (**1c**) in toluene.

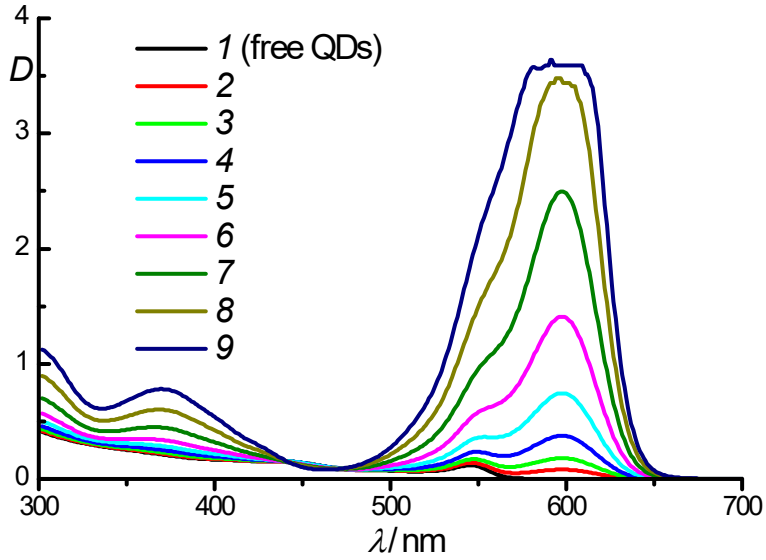

Figure S13. Absorption spectra of the **1b**–QDs (CdSe) system in toluene at various concentrations of the QDs and dye, respectively: 1) 5.21×10^{-7} and 0 M, 2) 5.18×10^{-7} and 7.96×10^{-7} M, 3) 5.13×10^{-7} and 2.36×10^{-6} M, 4) 5.03×10^{-7} and 5.41×10^{-6} M, 5) 4.84×10^{-7} and 1.12×10^{-5} M, 6) 4.51×10^{-7} and 2.15×10^{-5} M, 7) 3.96×10^{-7} and 3.83×10^{-5} M, 8) 3.19×10^{-7} and 6.21×10^{-5} M, 9) 2.29×10^{-7} and 8.97×10^{-5} M.

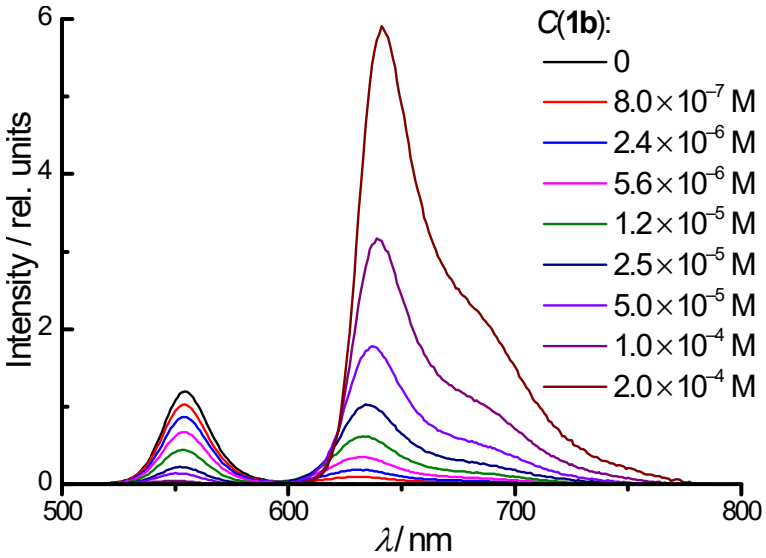

Figure S14. Fluorescence spectra of the **1b**–QDs (CdSe) system in toluene at various dye concentrations, the concentration of QDs is constant (5.21×10^{-7} M). All spectra and concentrations were corrected for dilution.

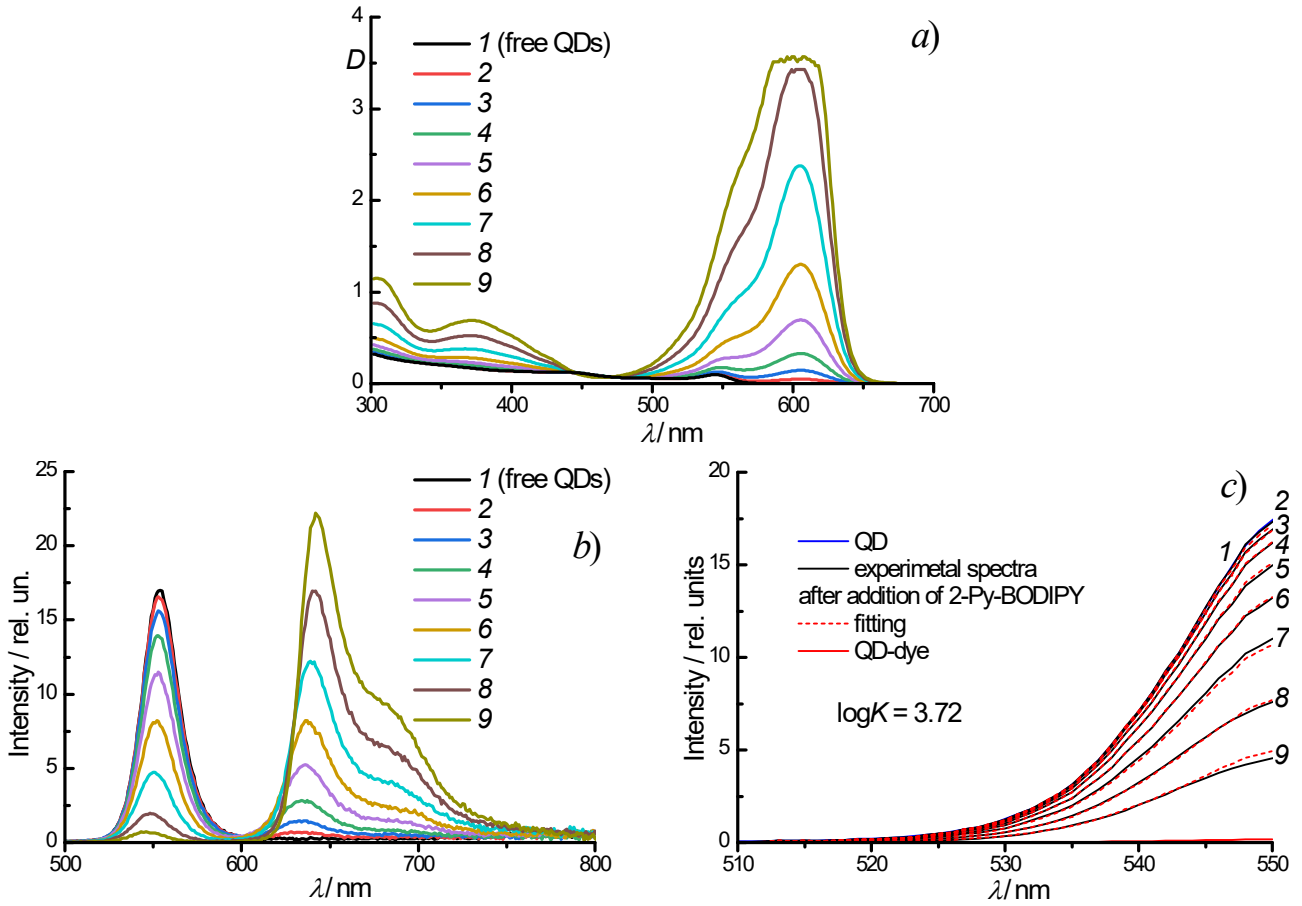

Figure S15. Absorption (*a*) and fluorescence spectra (*b*,*c*) of the **1a**–QDs (CdSe) system in toluene at various concentration of the QDs and dye, respectively: 1) 5.95×10^{-7} and 0 M, 2) 5.92×10^{-7} and 9.45×10^{-7} M, 3) 5.86×10^{-7} and 2.81×10^{-6} M, 4) 5.75×10^{-7} and 6.43×10^{-6} M, 5) 5.53×10^{-7} and 1.33×10^{-5} M, 6) 5.15×10^{-7} and 2.55×10^{-5} M, 7) 4.52×10^{-7} and 4.55×10^{-5} M, 8) 3.64×10^{-7} and 7.38×10^{-5} M, 9) 2.62×10^{-7} and 1.06×10^{-4} M. In the *c* figure the spectra are corrected for reabsorption, the fitting is made using equilibrium (*1*).

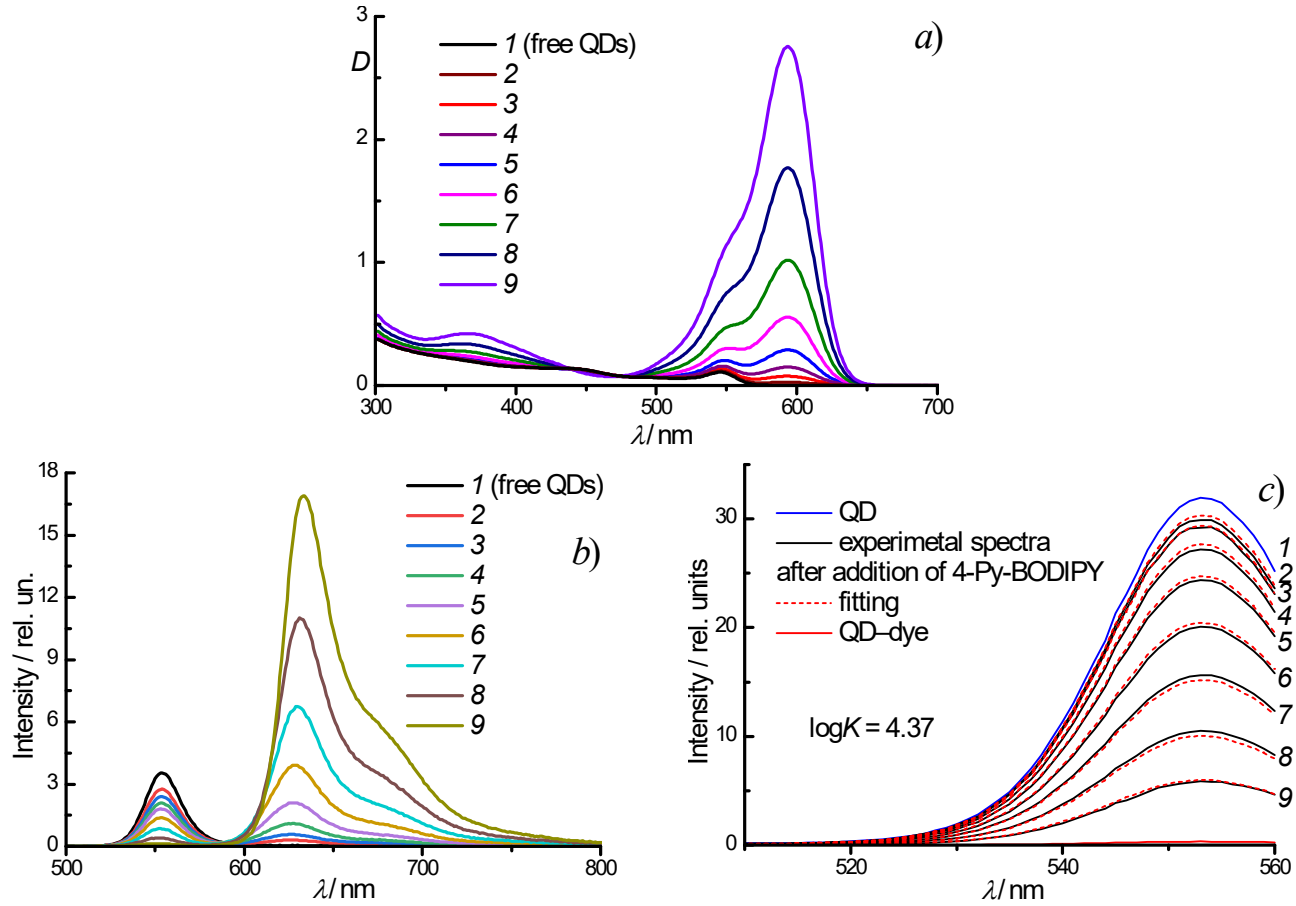

Figure S16. Absorption (*a*) and fluorescence spectra (*b*,*c*) of the **1c**–QDs (CdSe) system in toluene at various concentration of the QDs and dye, respectively: 1) 4.68×10^{-7} and 0 M, 2) 4.65×10^{-7} and 4.98×10^{-7} M, 3) 4.61×10^{-7} and 1.48×10^{-6} M, 4) 4.52×10^{-7} and 3.38×10^{-6} M, 5) 4.35×10^{-7} and 6.98×10^{-6} M, 6) 4.05×10^{-7} and 1.34×10^{-5} M, 7) 3.56×10^{-7} and 2.40×10^{-5} M, 8) 2.86×10^{-7} and 3.88×10^{-5} M, 9) 2.06×10^{-7} and 5.60×10^{-5} M. In the *c* figure the spectra are corrected for reabsorption, the fitting is made using equilibrium (*1*).

VIII Figures S17–S28: NMR spectra of synthesized compounds

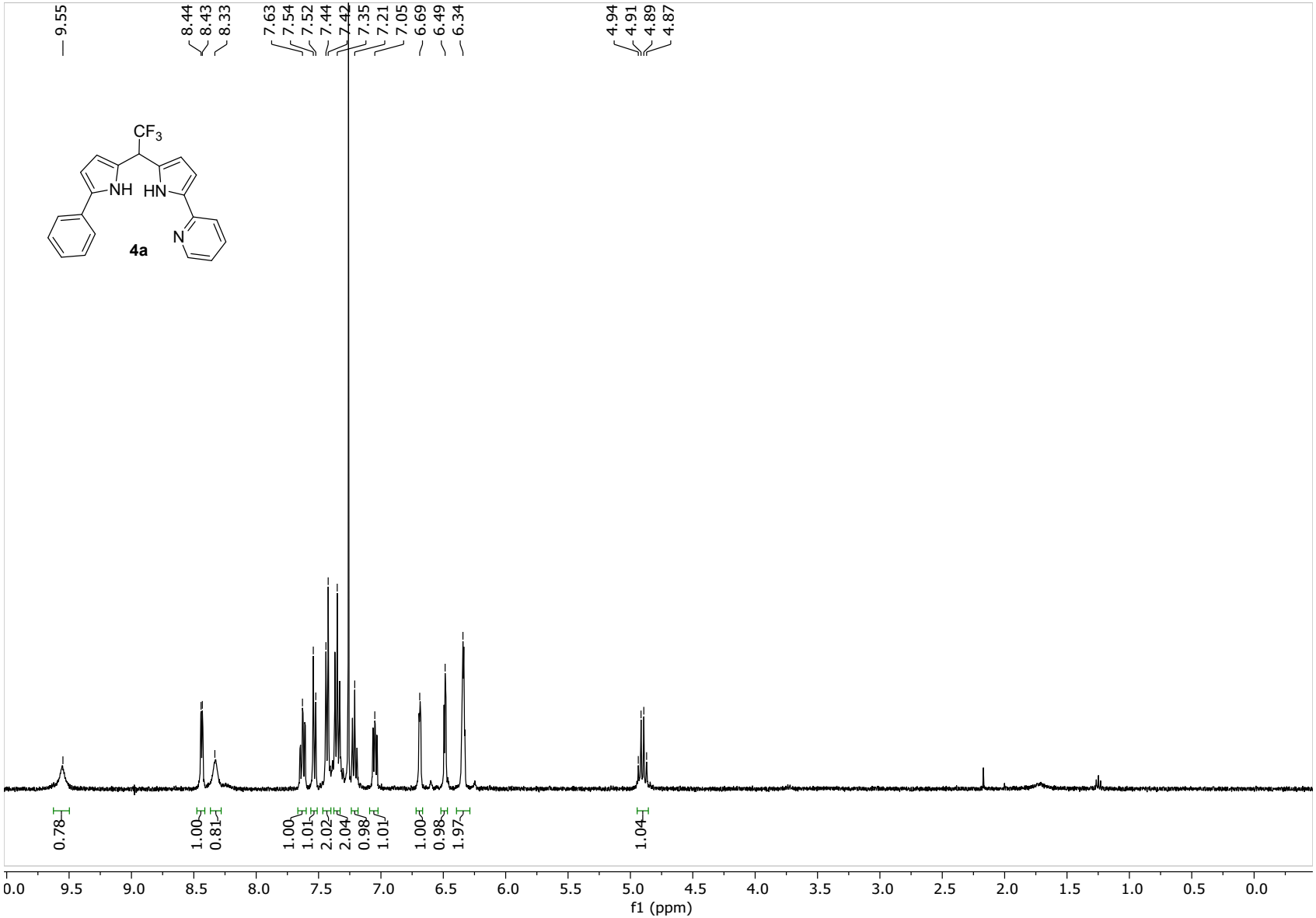

Figure S17. ^{1}H NMR spectrum of 2-(5-(2,2,2-trifluoro-1-(5-phenyl-1*H*-pyrrol-2-yl)ethyl)-1*H*-pyrrol-2-yl)pyridine (**4a**) in $CDCl_3$.

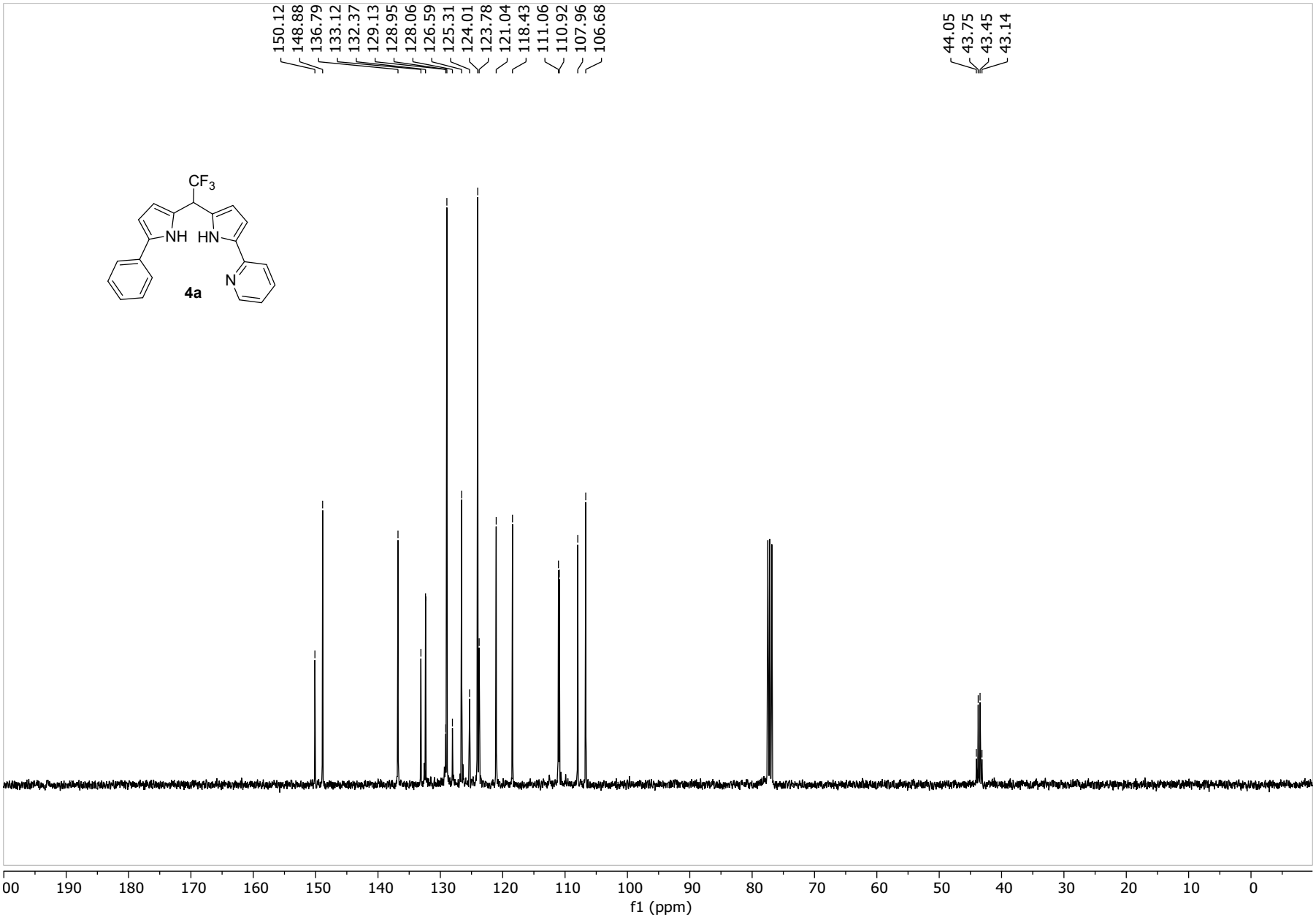

Figure S18. ^{13}C NMR spectrum of 2-(5-(2,2,2-trifluoro-1-(5-phenyl-1*H*-pyrrol-2-yl)ethyl)-1*H*-pyrrol-2-yl)pyridine (**4a**) in $CDCl_3$.

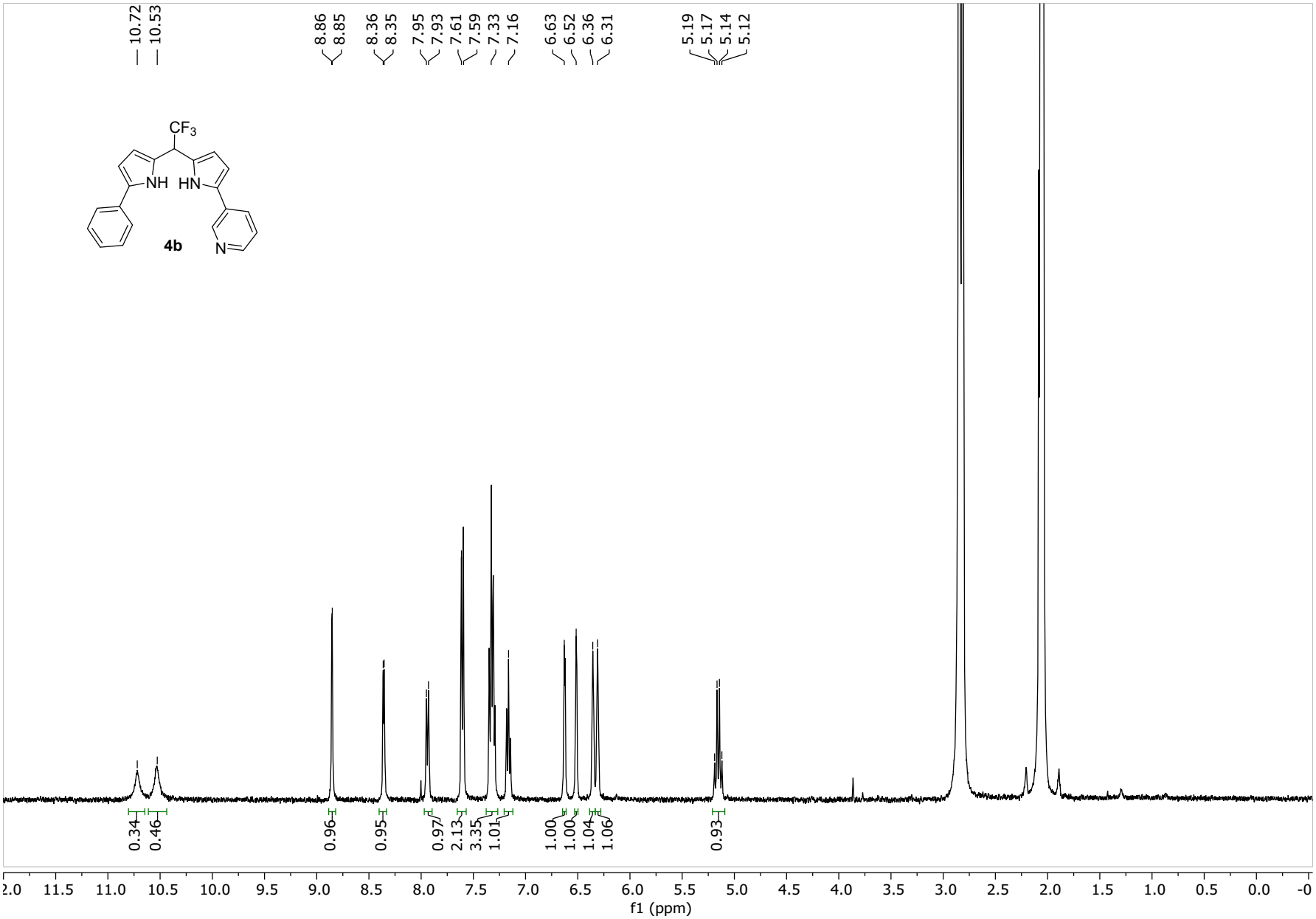

Figure S19. ^{1}H NMR spectrum of 3-(5-(2,2,2-trifluoro-1-(5-phenyl-1H-pyrrol-2-yl)ethyl)-1H-pyrrol-2-yl)pyridine (**4b**) in acetone-d6.

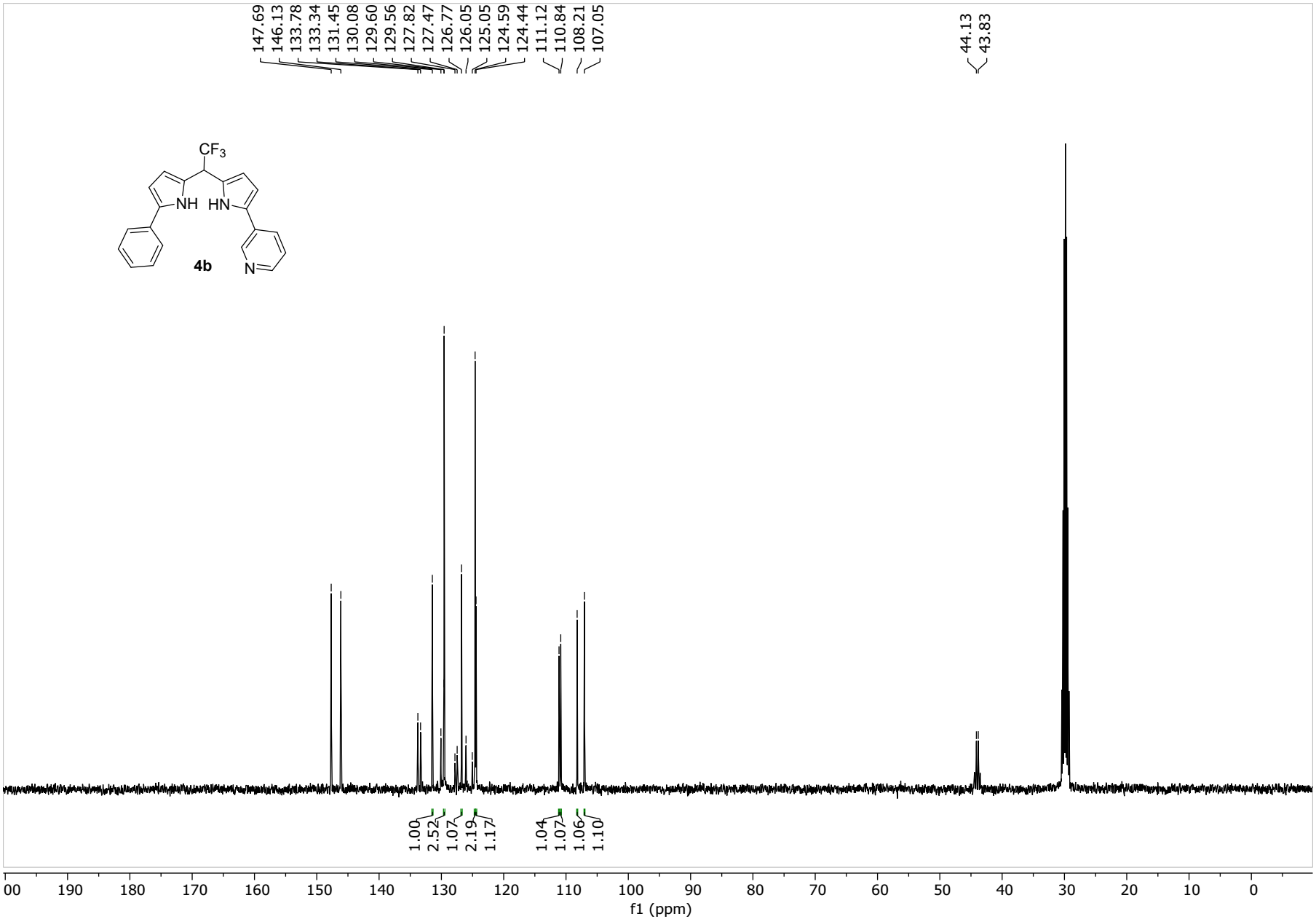

Figure S20. ^{13}C NMR spectrum of 3-(5-(2,2,2-trifluoro-1-(5-phenyl-1H-pyrrol-2-yl)ethyl)-1H-pyrrol-2-yl)pyridine (**4b**) in acetone-d6.

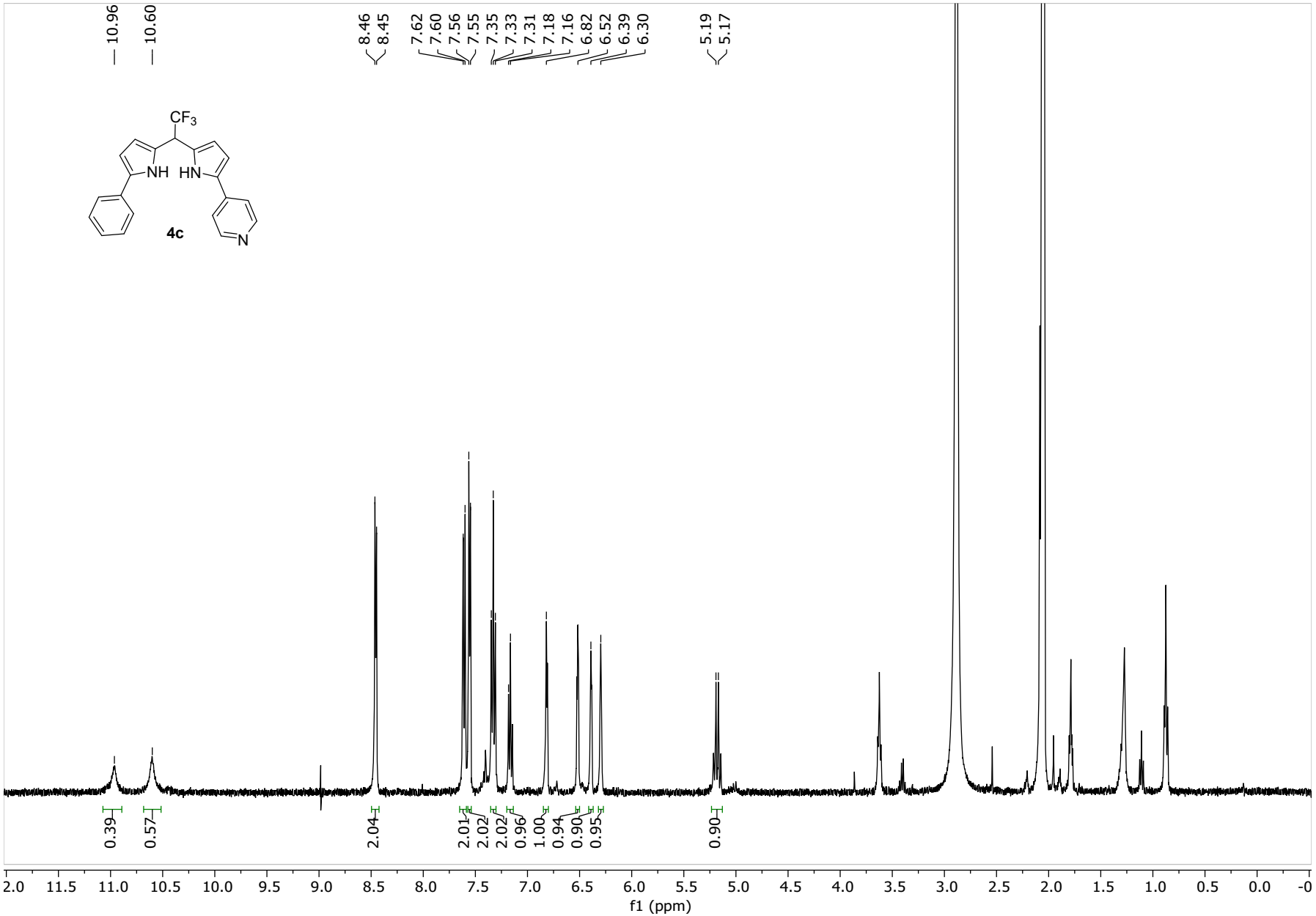

Figure S21. ^{1}H NMR spectrum of 4-(5-(2,2,2-trifluoro-1-(5-phenyl-1H-pyrrol-2-yl)ethyl)-1H-pyrrol-2-yl)pyridine (**4c**) in acetone-d6.

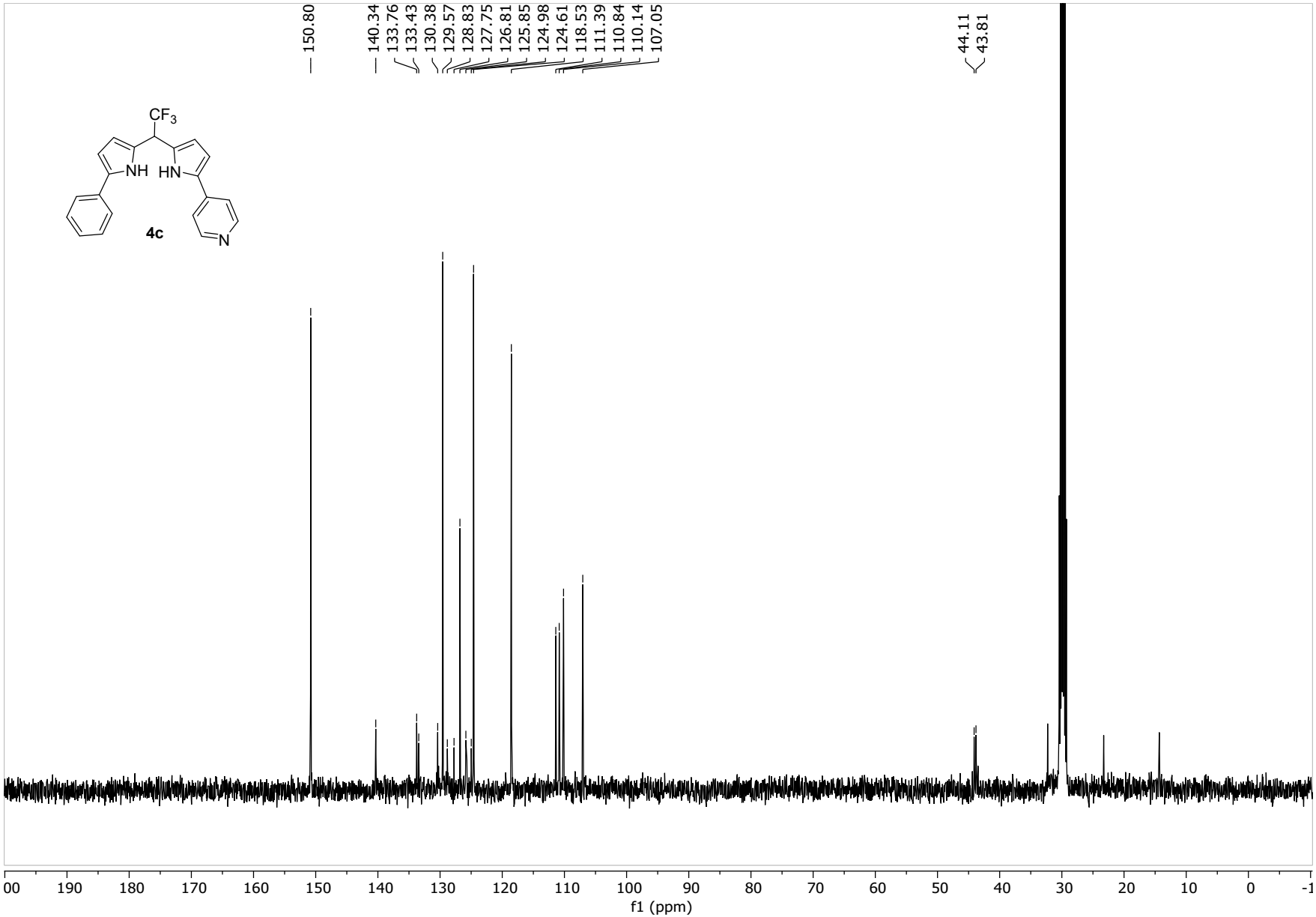

Figure S22. ^{13}C NMR spectrum of 4-(5-(2,2,2-trifluoro-1-(5-phenyl-1H-pyrrol-2-yl)ethyl)-1H-pyrrol-2-yl)pyridine (**4c**) in acetone-d6.

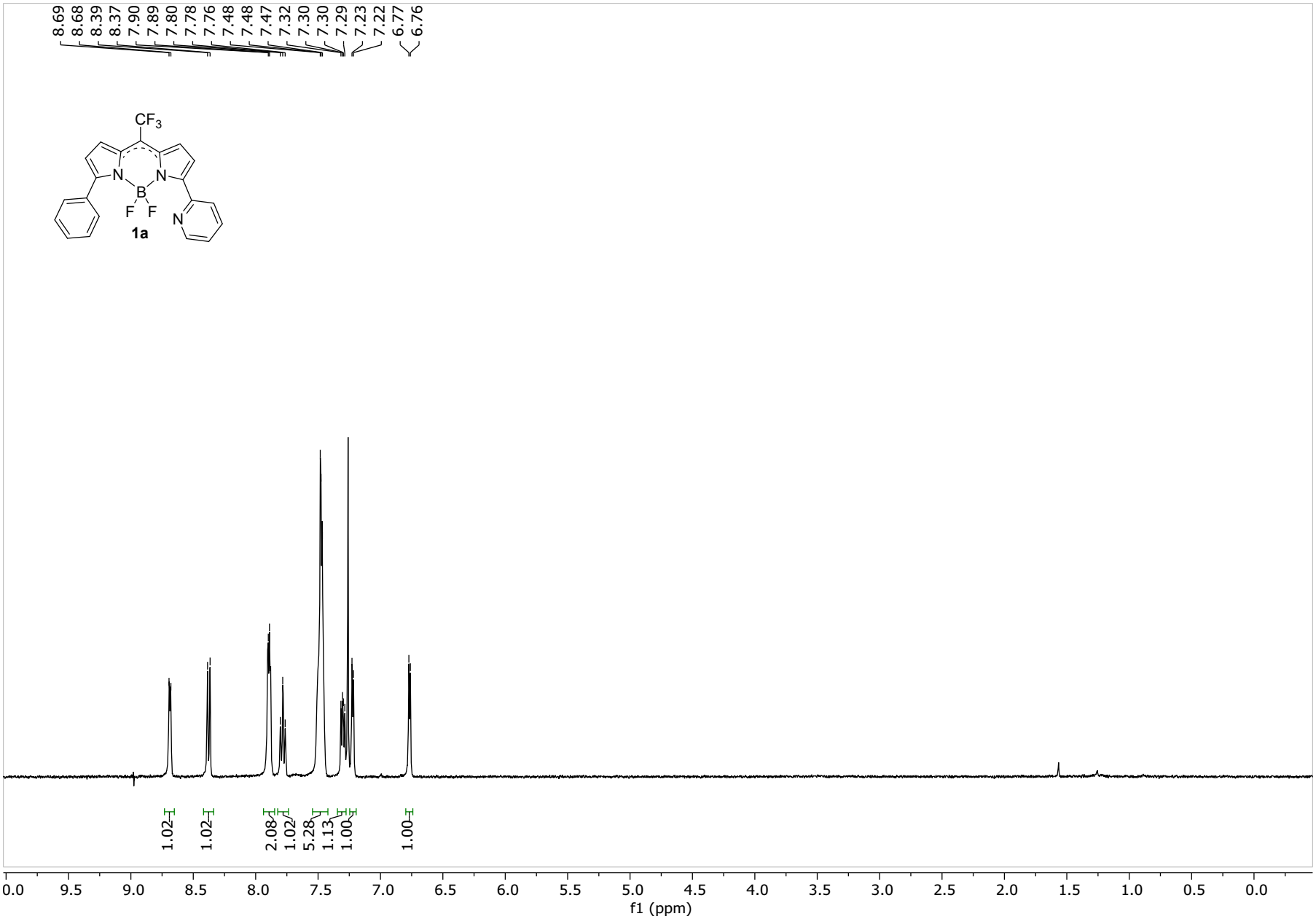

Figure S23. ^{1}H NMR spectrum of 4,4-difluoro-3-phenyl-5-(pyridin-2-yl)-8-trifluoromethyl-4-bora-3a,4a-diaza-s-indacene (**1a**) in $CDCl_3$.

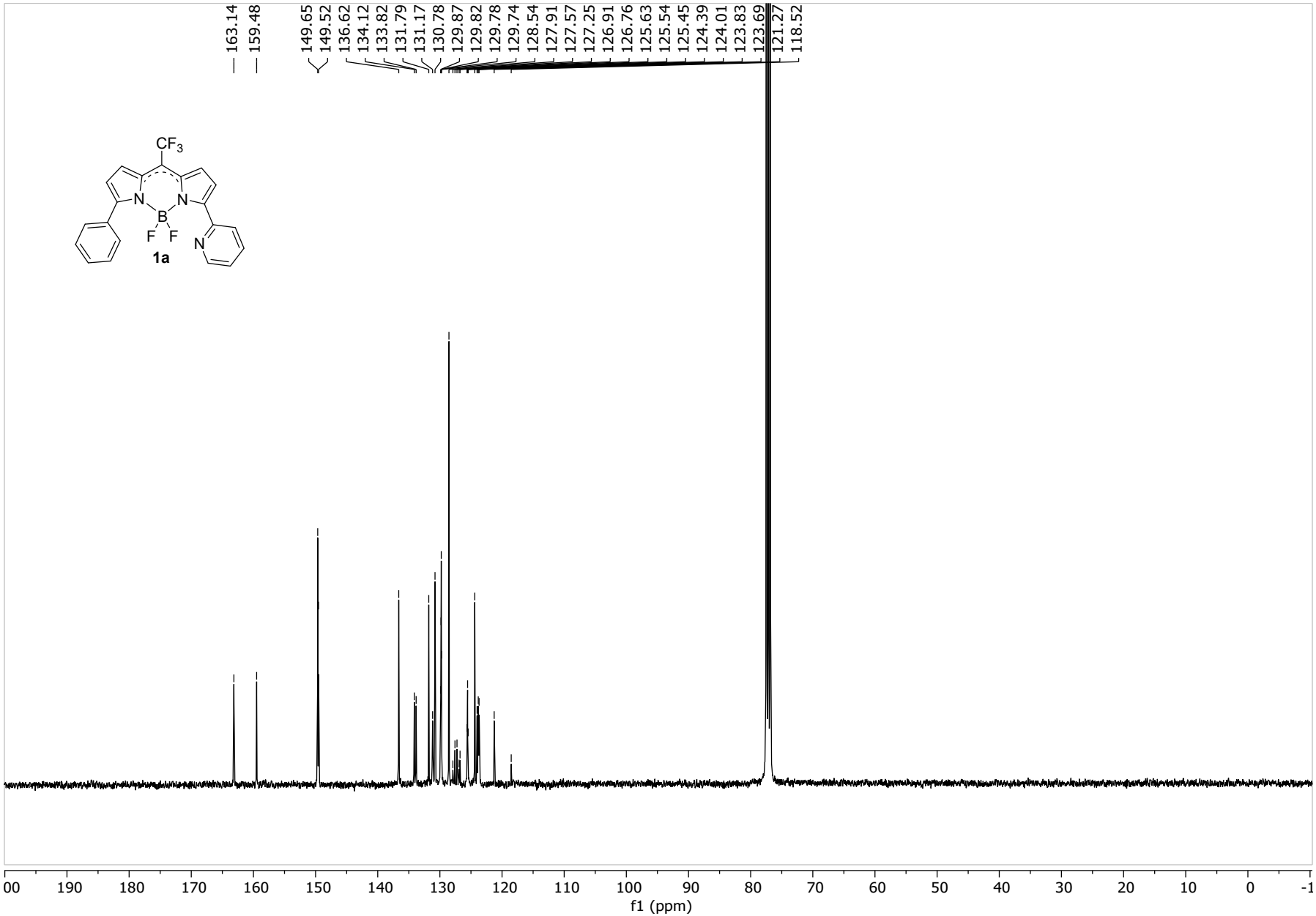

Figure S24. ^{13}C NMR spectrum of 4,4-difluoro-3-phenyl-5-(pyridin-2-yl)-8-trifluoromethyl-4-bora-3a,4a-diaza-s-indacene (**1a**) in $CDCl_3$.

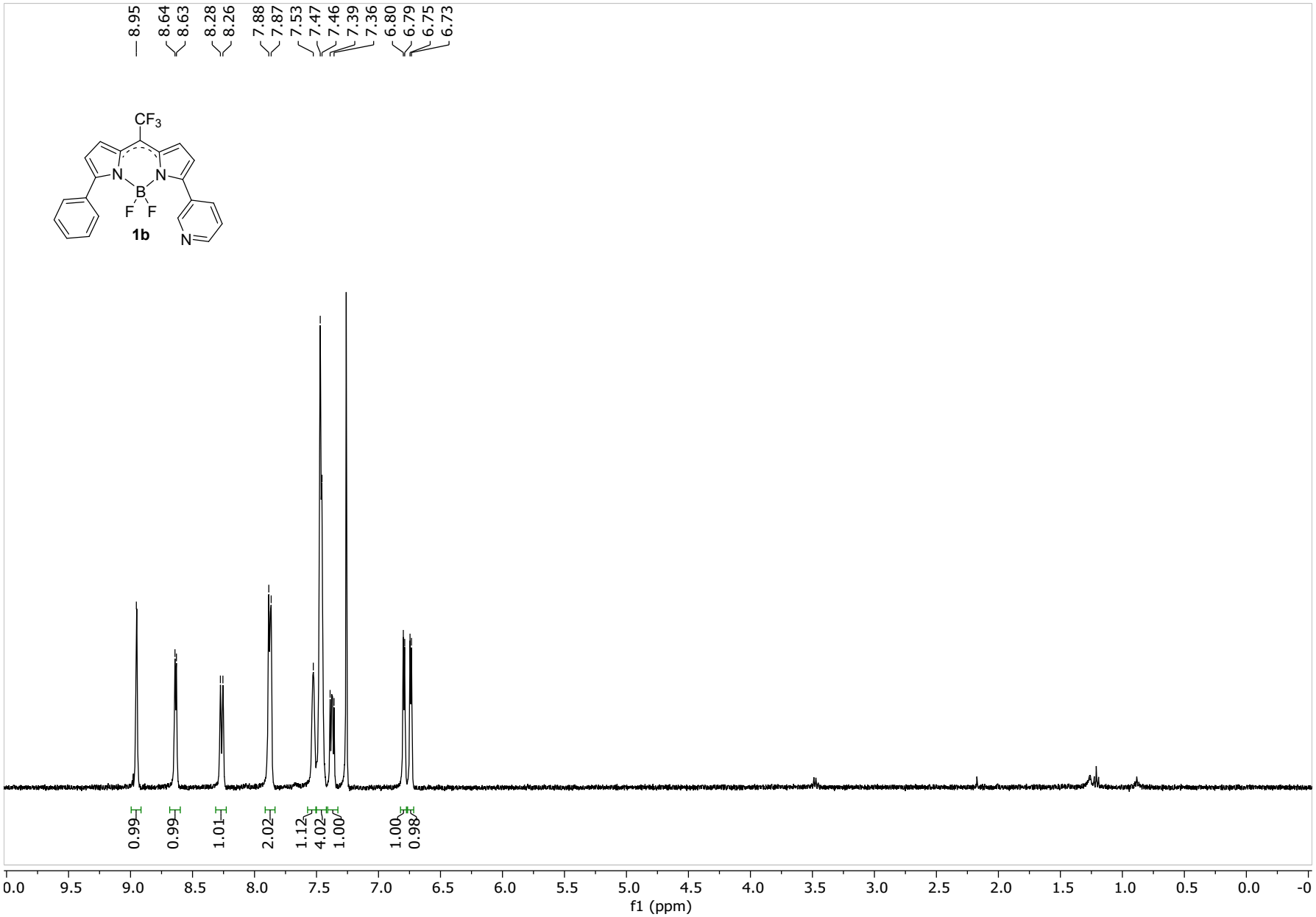

Figure S25. ^{1}H NMR spectrum of 4,4-difluoro-3-phenyl-5-(pyridin-3-yl)-8-trifluoromethyl-4-bora-3a,4a-diaza-s-indacene (**1b**) in $CDCl_3$.

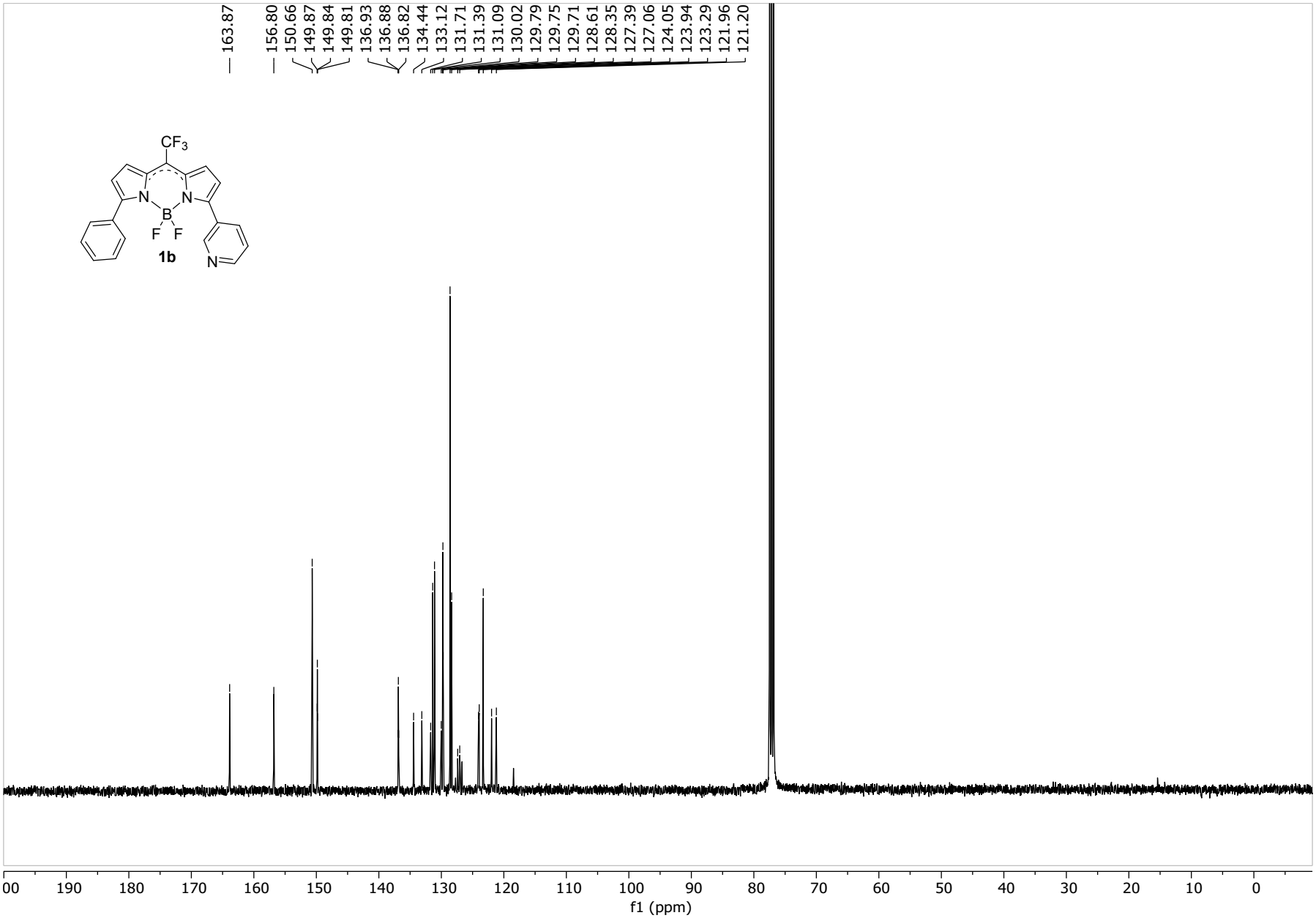

Figure S26. ^{13}C NMR spectrum of 4,4-difluoro-3-phenyl-5-(pyridin-3-yl)-8-trifluoromethyl-4-bora-3a,4a-diaza-s-indacene (**1b**) in $CDCl_3$.

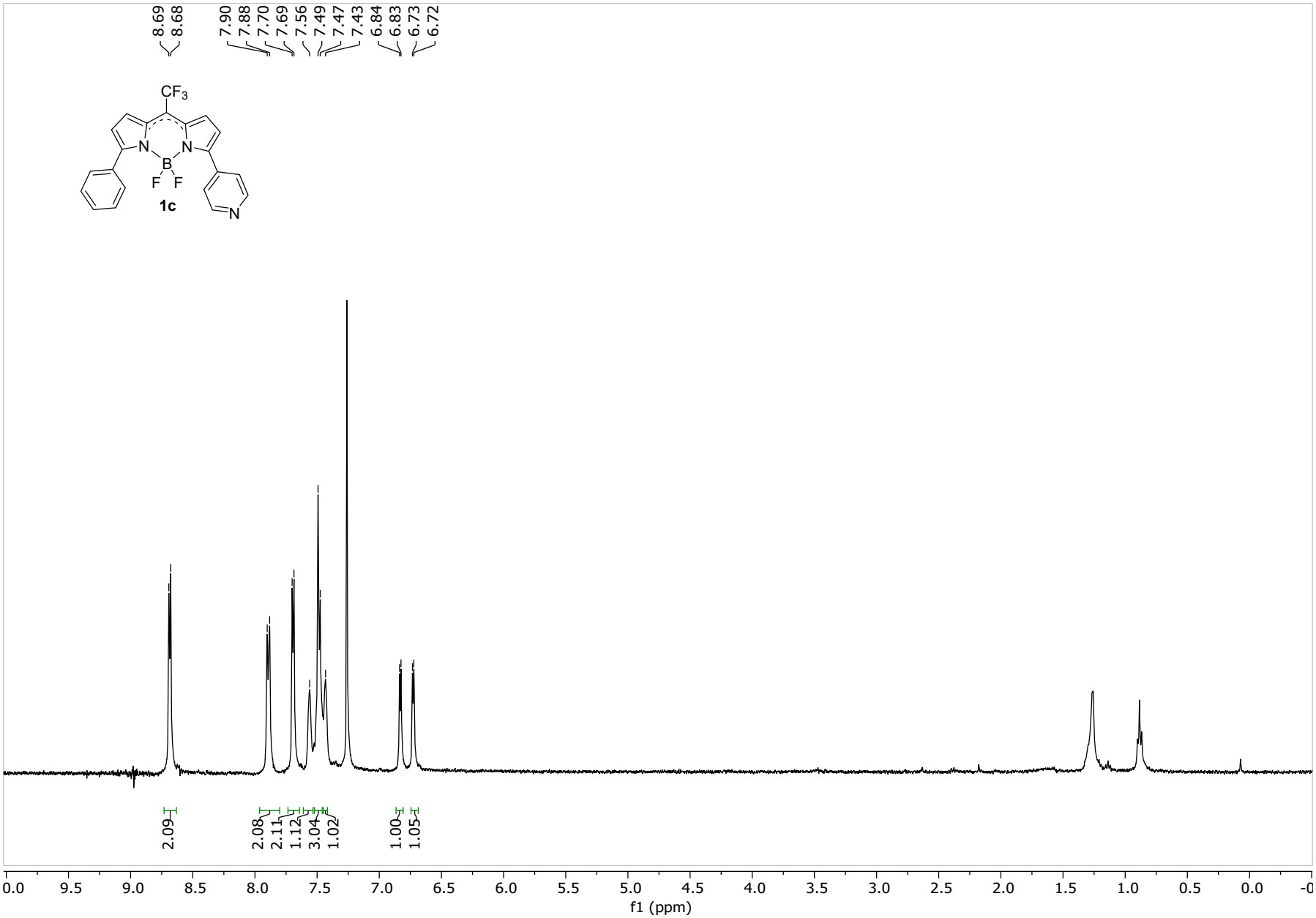

Figure S27. ^{1}H NMR spectrum of 4,4-difluoro-3-phenyl-5-(pyridin-4-yl)-8-trifluoromethyl-4-bora-3a,4a-diaza-s-indacene (**1c**) in $CDCl_3$.

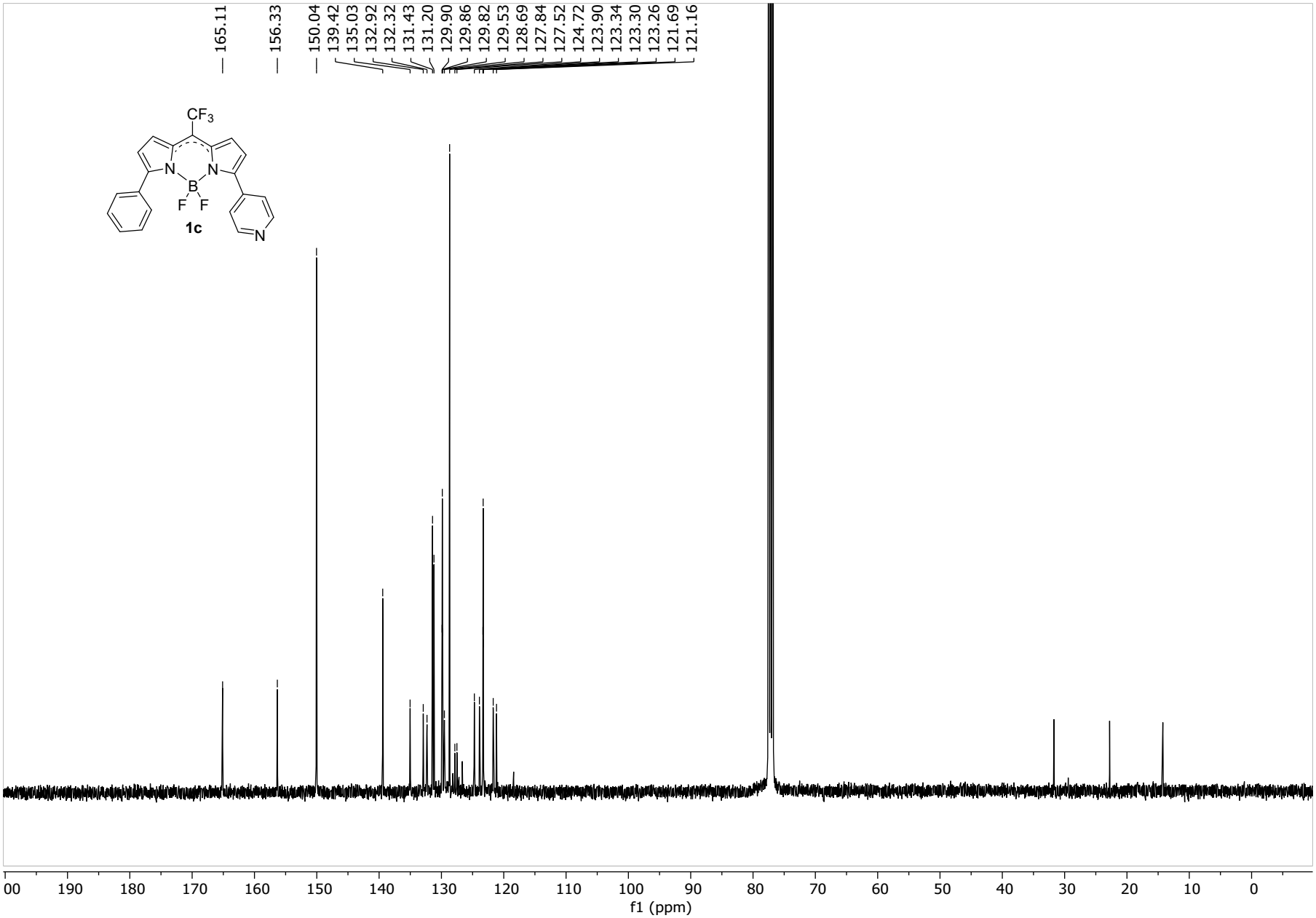

Figure S28. ^{13}C NMR spectrum of 4,4-difluoro-3-phenyl-5-(pyridin-4-yl)-8-trifluoromethyl-4-bora-3a,4a-diaza-s-indacene (**1c**) in $CDCl_3$.

IX Parameterized matrix modeling of spectral titration data

The fluorescence spectra obtained in titration experiments were corrected for reabsorption and used to compose the data matrix $\mathbf{I}_{exp}$ with dimensions $n \times m$ (n is the number of intensity values in the spectrum, m is the number of spectra). We considered the range of 500–560 nm, where only QDs and QD–dye associate fluoresce. The concentration dependences of the fluorescence spectra of **1a**–QDs, **1b**–QDs and **1c**–QDs systems can be described by the simple complexation model:

$$Q + B \overset{K_{obs}}{\rightleftarrows} QB, \quad (1)$$

where Q is the CdSe quantum dot, B is the BODIPY dye molecule, K_{obs} is the observed stability constant of the QB associate (QD–dye in the article).

The mass balance equations for this model are as follows:

$$[Q] + [QB] = C_Q, \quad (2)$$

$$[B] + [QB] = C_B, \quad (3)$$

where C_B is the total dye concentration, C_Q is the total quantum dots concentration.

Law of mass action:

$$[QB] = K_{obs}[Q][B]. \quad (4)$$

We will use the following designation: $x = [Q]/C_Q$. The set of equations (2)–(4) can be reduced to the quadratic equation for the concentration of one of the components (5)

$$K_{obs}C_Q x^2 + (K_{obs}C_B - K_{obs}C_Q + 1)x - 1 = 0. \quad (5)$$

The equilibrium constant K_{obs} was found by parameterized matrix modeling (PMM). The total concentration C_Q was determined from the optical density of the QDs solution at 350 nm before adding BODIPY dye. The PMM procedure was started from the postulation of K_{obs} and analytical solution of equation (5) for x using the function "fminbnd" in Matlab7 resulting in the equilibrium concentration of quantum dots [Q]. The associate concentration [QB] was calculated from the mass balance equation (2). From m values of [Q] and [QB] a concentration matrix $\mathbf{C}$ of dimension $2 \times m$ is compiled. Then a theoretical matrix of some coefficients of components $\mathbf{E}_{cal}$ of dimension $n \times 2$ is generated (n is the number of intensity values in the fluorescence spectrum):

$$\mathbf{E}_{cal} = \mathbf{I}_{exp}\mathbf{C}^T(\mathbf{C}\mathbf{C}^T)^{-1}. \quad (6)$$

Equation (6) is the matrix representation of the analog of light absorption law $\mathbf{I} = \mathbf{E}\mathbf{C}$ for fluorescence. The light intensity I measured during fluorometry can be written as

$$I = kI_0\varepsilon C\varphi, \quad (7)$$

where I_0 is the intensity of exciting light, k is the instrumental factor, which did not change during all experiments, including the thickness of the absorbing layer, ε is the molar absorption coefficient at excitation wavelength, C is the concentration of fluorophore. Thus, in our case, the $\mathbf{E}_{cal}$ matrix contains

some coefficients that are equal to the $kI_0\varepsilon\varphi$. The emission spectrum of the QB associate was fixed as $I(\mathrm{Q})/(99C_\mathrm{Q})$.

The theoretical matrix $\mathbf{I}_{cal}$, reproducing $\mathbf{I}_{exp}$, was calculated as $\mathbf{I}_{cal} = \mathbf{E}_{cal}\mathbf{C}$. The K_{obs} was found by minimizing the standard deviation $\sigma_\mathrm{I}(K_{obs})$ between the theoretical matrix $\mathbf{I}_{cal}$ and the matrix of experimental spectra $\mathbf{I}_{exp}$:

$$\sigma_\mathrm{I}(K_{obs}) = \sqrt{\frac{\sum_{i=1}^{n}\sum_{j=1}^{m}(\mathbf{I}_{exp}^{ij} - \mathbf{I}_{cal}^{ij})^2}{(n-q)m}}, \tag{8}$$

where q is the number of fluorescent components. Minimization was performed using the function "fminsearch" in Matlab7. The σ_I value is the criterion for the validity of the reaction model. Apart from the instrumental errors, it contains errors of the measurement of concentrations, cell length, *etc.* Previously, it was established by experiments that $\sigma_\mathrm{I} < 0.02\%$ of maximum intensity value is adequate for the instruments and techniques that we use.