

SUPPORTING INFORMATION

Energy Transfer Cassettes with Extremely Well Resolved Fluorescent Outputs

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General Experimental Methods.

All reactions were carried out under an atmosphere of dry nitrogen. Glasswares were oven-dried prior to use. Unless otherwise indicated, common reagents or materials were obtained from commercial sources and used without further purification. All solvents were dried prior to use with appropriate drying agents. Dry distilled DMF was obtained from Acros and used as such. Flash column chromatography was performed using silica gel 60 (230-400 mesh). Analytical thin layer chromatography (TLC) was carried out on Merck silica gel plates with QF-254 indicator and visualized by UV. Fluorescence spectra were obtained on a Varian Cary Eclipse fluorescence spectrophotometer at room temperature. Absorbance spectra were obtained on a Varian 100 Bio UV-Vis spectrophotometer at room temperature. Atomic force microscopy (AFM) images were taken on a Digital Instruments Nanoscope AFM using tapping mode.

Water was deionized using a Millipore Milli-Q system (Billerica MA) and pH adjusted to 7 using 0.1M KOH solution. The deionized water was degassed using a vacuum aspirator (Brinkmann Model B-169) for 2 h to remove CO₂ and used immediately for synthesis and purification of nanoparticles. The pH measurements were carried out using a pH meter (Mettler Toledo delta 320) which was calibrated with pH 4 and pH 7 buffer before use.

¹H and ¹³C spectra were recorded on a Varian 300 (300 MHz ¹H; 75 MHz ¹³C) or Varian 500 (500 MHz ¹H; 125 MHz ¹³C) spectrometer at room temperature. Chemical shifts were reported in ppm relative to the residual CDCl₃ (δ 7.26 ppm ¹H; δ 77.0 ppm ¹³C), CD₃OD (δ 3.34 ppm ¹H; δ 49.0 ppm ¹³C), acetone-*d*₆ (δ 2.54 ppm ¹H; δ 40.45 ppm ¹³C) or DMSO-*d*₆ (δ 2.54 ppm ¹H; δ 40.45 ppm ¹³C). Coupling constants (*J*) were reported in Hertz.

Photophysical Properties and Determination of Quantum Yields

Steady-state fluorescence spectroscopic studies were performed on a Cary Eclipse fluorometer. The slit width was 5 nm for both excitation and emission. The relative quantum yields of the samples were obtained by comparing the area under the corrected emission spectrum of the test sample with that of a standard.¹ The quantum yield of fluorescence were measured three times for each dye and averaged. The following equation was used for calculating quantum yields:

$$\Phi_x = \Phi_{st} (I_x/I_{st}) (A_{st}/A_x) (\eta_x^2/\eta_{st}^2)$$

where Φ_{st} is the reported quantum yield of the standard, I is the area under the emission spectra, A is the absorbance at the excitation wavelength and η is the refractive index of the solvent used, measured on a pocket refractometer from ATAGO. The X subscript denotes unknown, and st denotes standard.^{2,3} Molar extinction coefficients were obtained from the slope of a graph of absorbance vs concentration for each dye with five different concentrations (10^{-6} M). For cassette **1c** the ETE was calculated by the ratio of relative fluorescence area when excited at donor and at the acceptor.

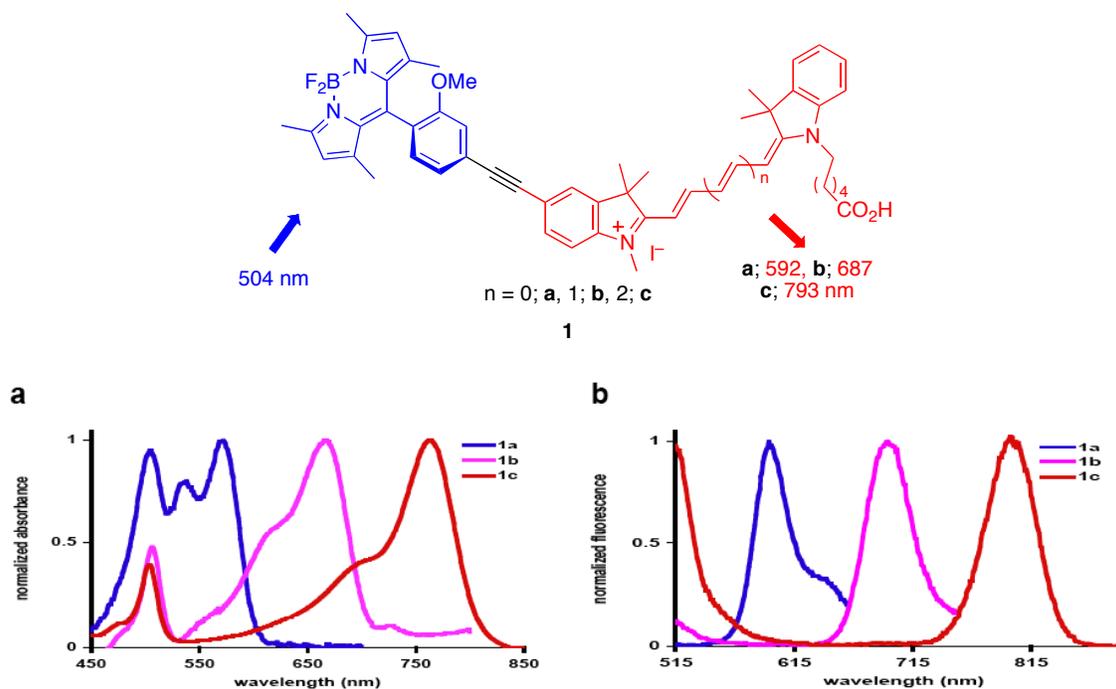


Figure S1. Normalized **a** absorbance and **b** fluorescence of cassettes encapsulated in calcium phosphate nanoparticles in pH 7.4 (0.1 M phosphate buffer).

Measurements of Energy Transfer Rates

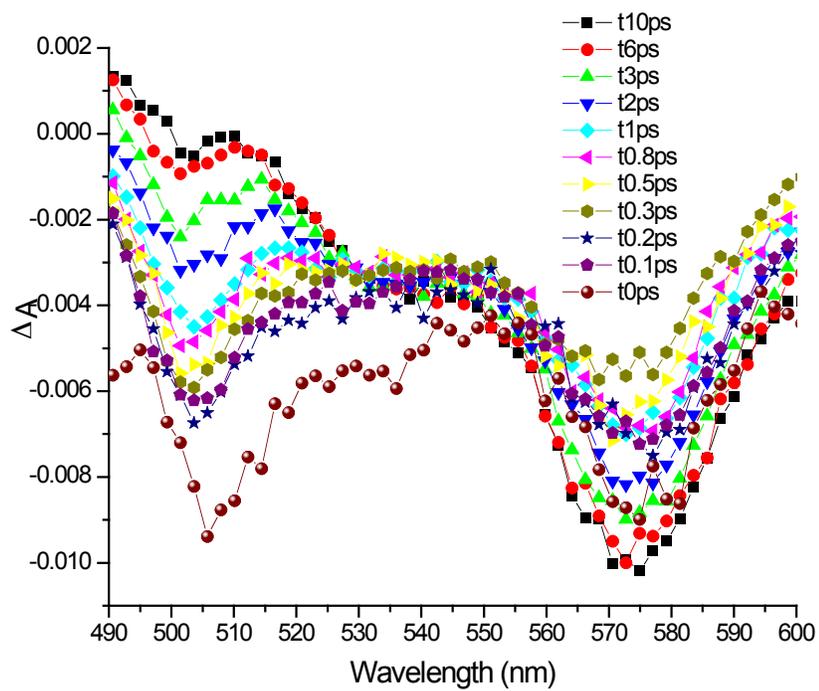
Absorption spectra were recorded using a HP single beam spectrophotometer with a diode array. The light source consisted of Deuterium (D2) and Tungsten Iodide (50W) lamps for the ultraviolet and visible regions respectively. The concentration of the solutions was adjusted so that the measured absorbances would range between 0.1 and 0.3 for the optical measurements.

Emission spectra were recorded using a spectrofluorometer from Edinburgh Analytical Instruments (FL/FS 900). The focal length for both excitation and emission monochromators is 300mm. Both monochromators have a Czerny-Turner design triple grating turret. The resolution for the monochromators is 0.05nm. The detector is a single photon counting photomultiplier. The lifetimes were measured in the same spectrofluorometer using a hydrogen lamp, with repetition rate of 40 KHz.

The concentration chosen for the spectroscopic measurements was 3.1×10^{-6} M in an ethanol solution. This concentration was the same for cassettes **1a**, **1b**, **1c** and the mixtures of donor-acceptors of cassettes.

The ultrafast transient measurements were carried out in a femtosecond transient absorption spectrometer. The spectrometer is based on a Ti: Sapphire regenerative amplifier – TOPAS-C combination. The amplified 800-nm output, ~ 0.9 mJ pulse⁻¹, ~ 90 fs pulse width, 1 kHz repetition rate, is split into two parts. The major part pumps the TOPAS-C to generate 350-nm excitation pulses. The pump energy at the sample position is varied between 3 and 11 μ J. The minor part of the amplified output is sent to the optical delay line and then focused onto a 3-mm CaF₂ window to generate white-light continuum. The white-light continuum beam is split into reference and probe beams. The probe and pump beam are focused onto the sample at an angle of 8 degree with the beam diameters of 115 and 290 μ m, respectively. As described by El-Khoury and Tarnovsky.⁴

a



b

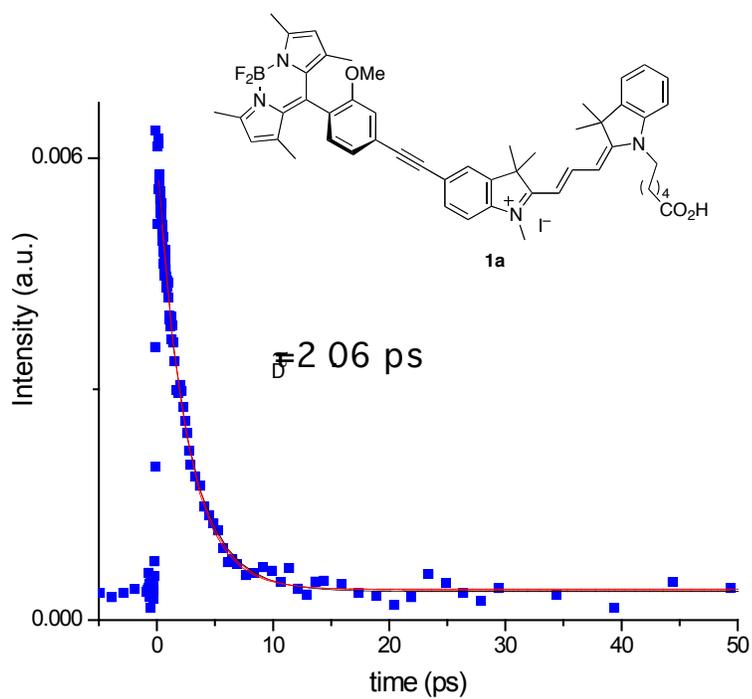
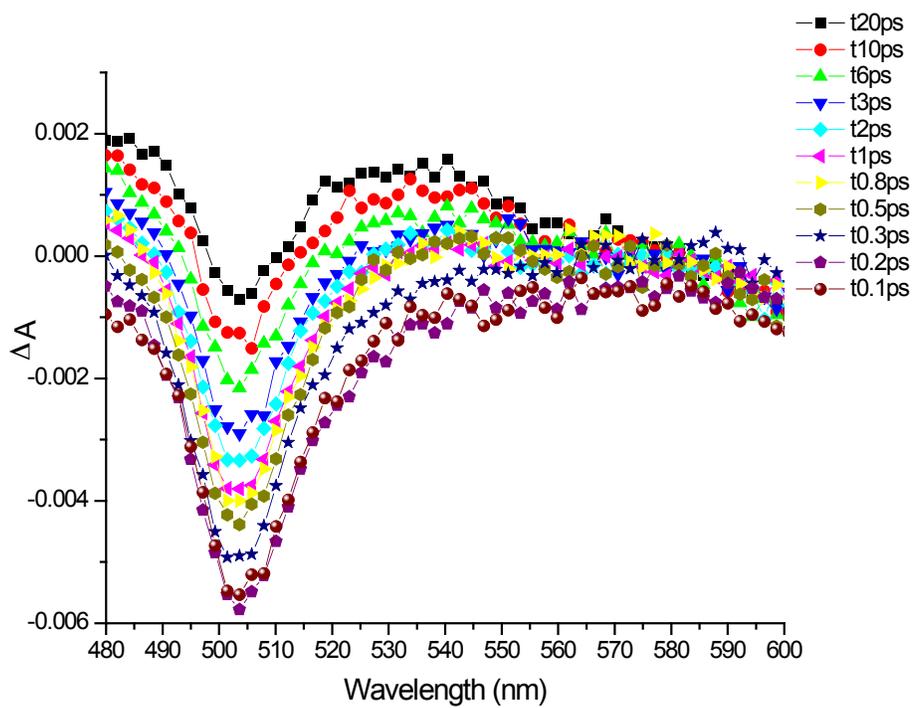


Figure S2. (a) Ultrafast transient absorption for cassette **1a**, excited at 420 nm.

(b) Intensity decay profile at 505 nm.

a



b

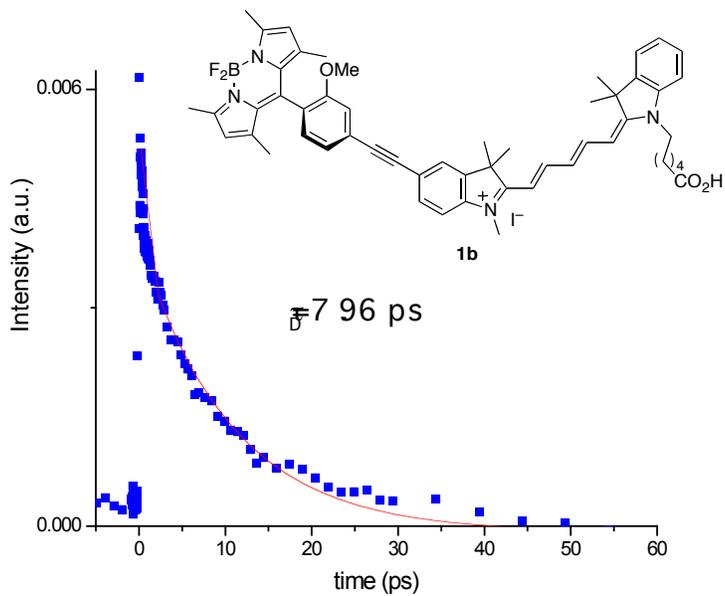
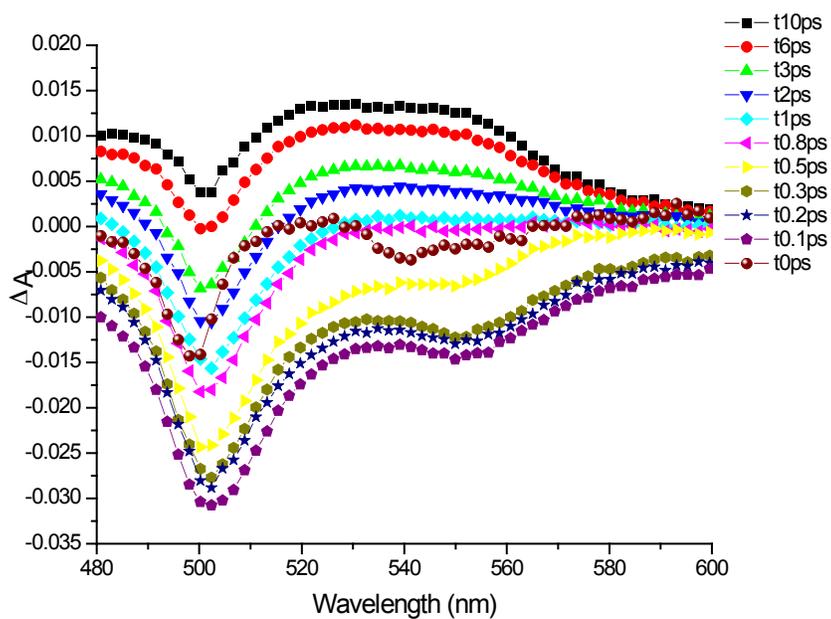


Figure S3. (a) Ultrafast transient absorption for cassette **1b**, excited at 420 nm. (b) Intensity decay profile at 505 nm.

a



b

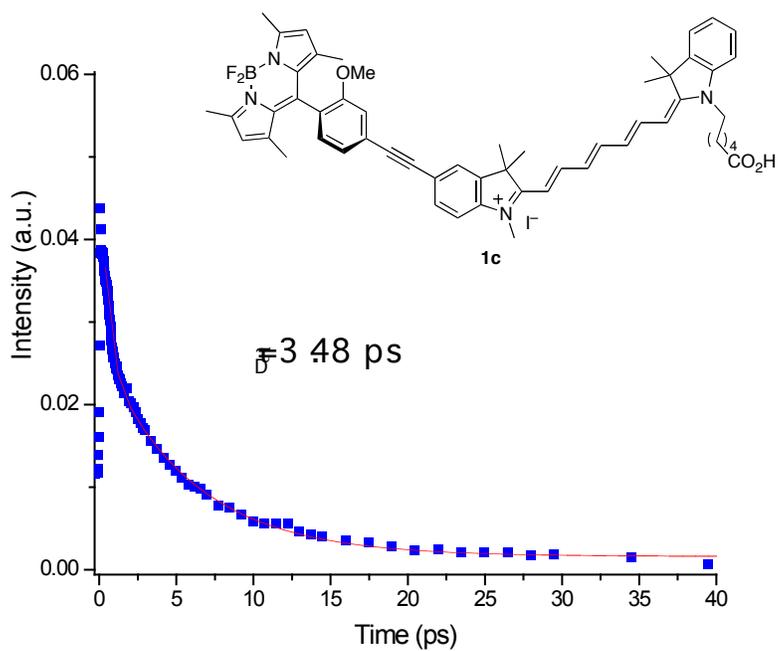
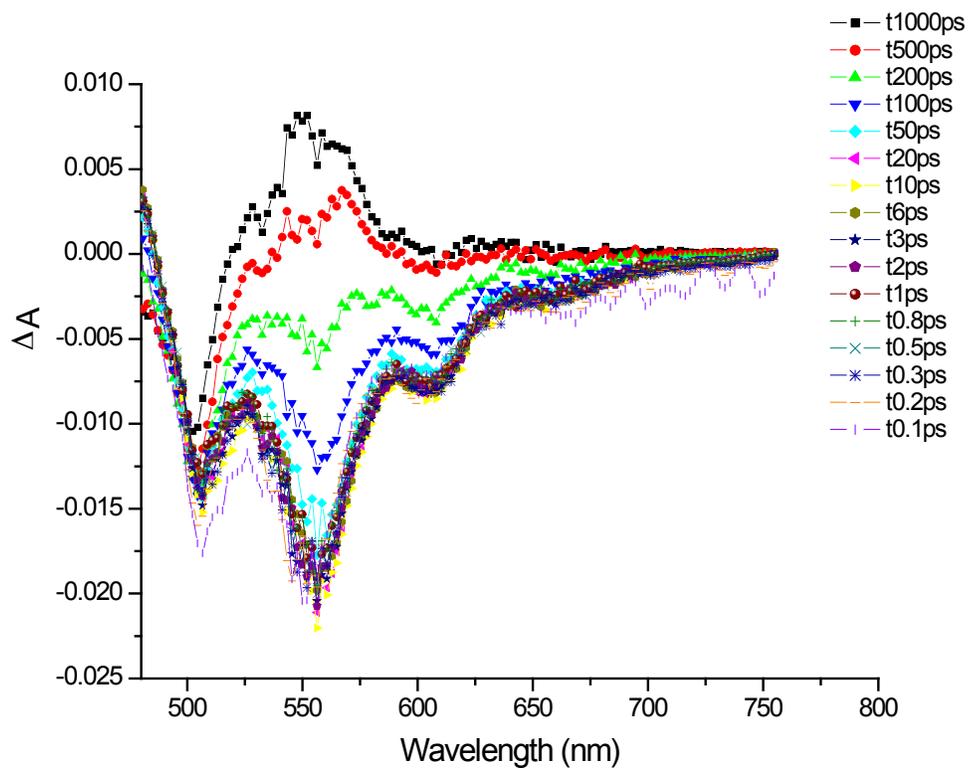


Figure S4. (a) Ultrafast transient absorption for cassette **1c**, excited at 450 nm.

(b) Rise of acceptor's excited state at 760 nm.

a



b

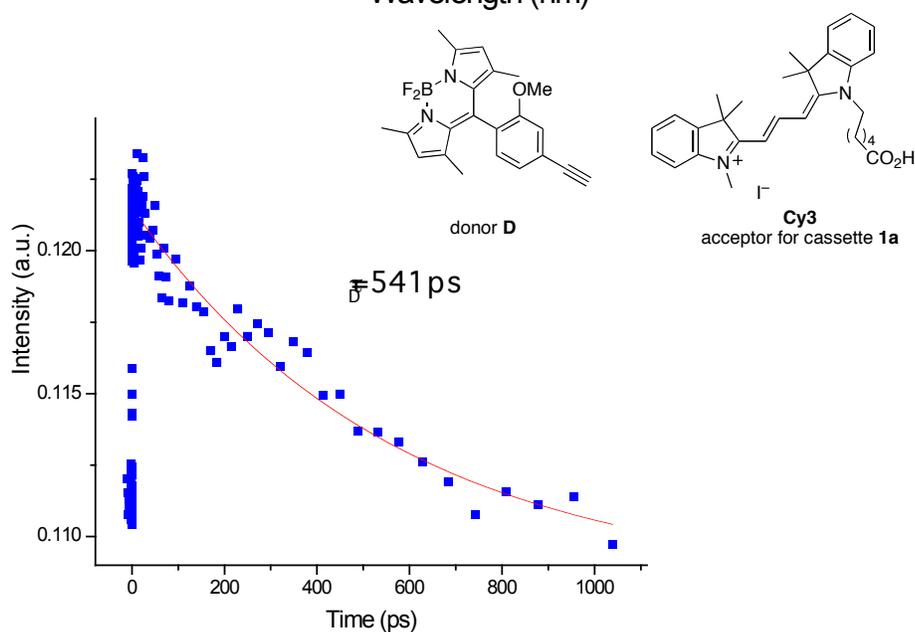


Figure S5. (a) Ultrafast transient absorption for donor acceptor mixture of cassette 1a **D** : **Cy3**, excited at 450 nm. **(b)** Intensity decay profile at 505 nm.

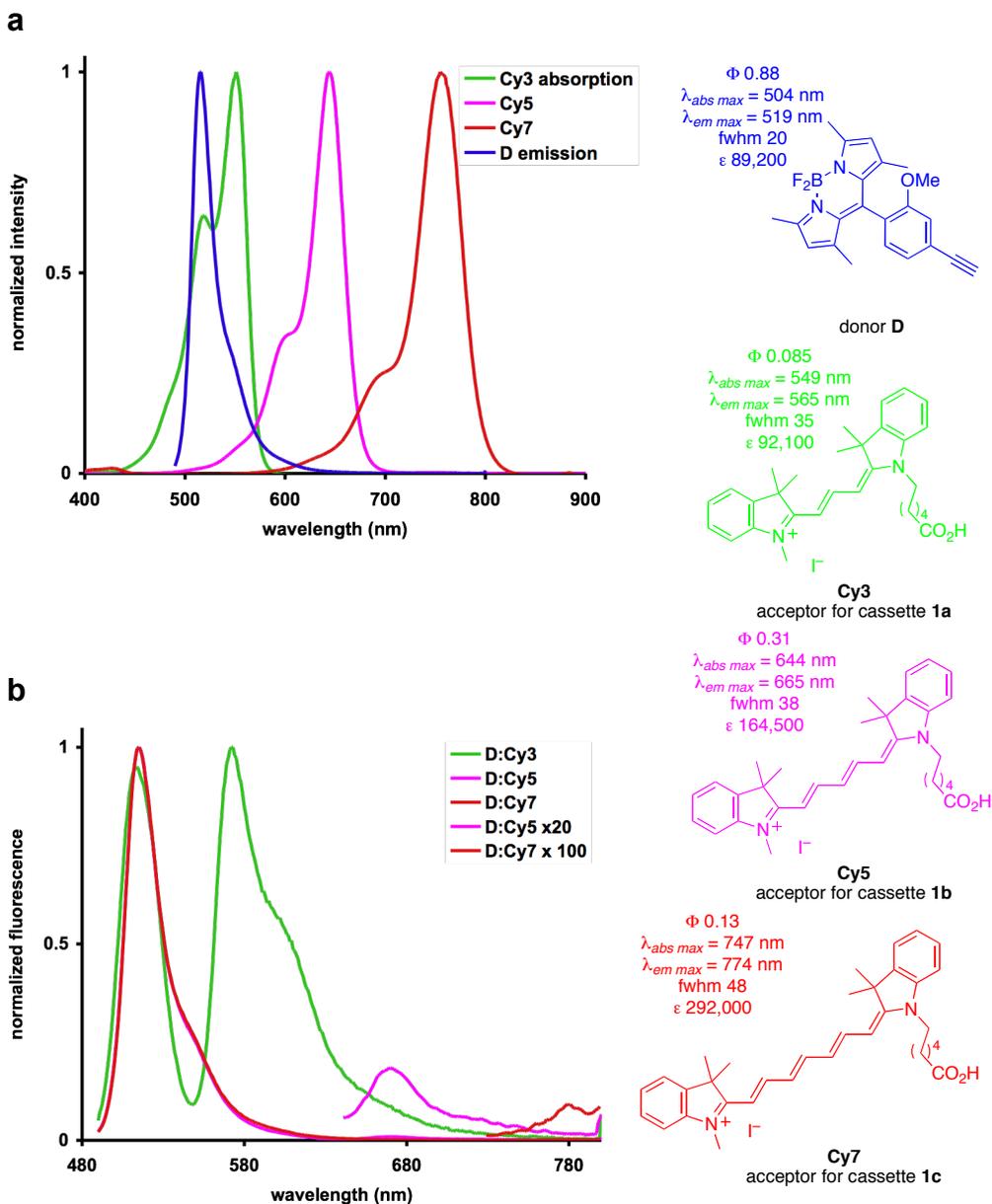


Figure S6. (a) Spectral overlap between the donor D emission and the acceptors Cy3, Cy5, Cy7 absorbance. (b) Normalized fluorescence of the Donor D – Acceptor Cy3, Cy5, Cy7 (1:1) mixtures. The Donor was excited at 480 nm. All measurements carried out in EtOH (concentration: 3.1×10^{-6} M).

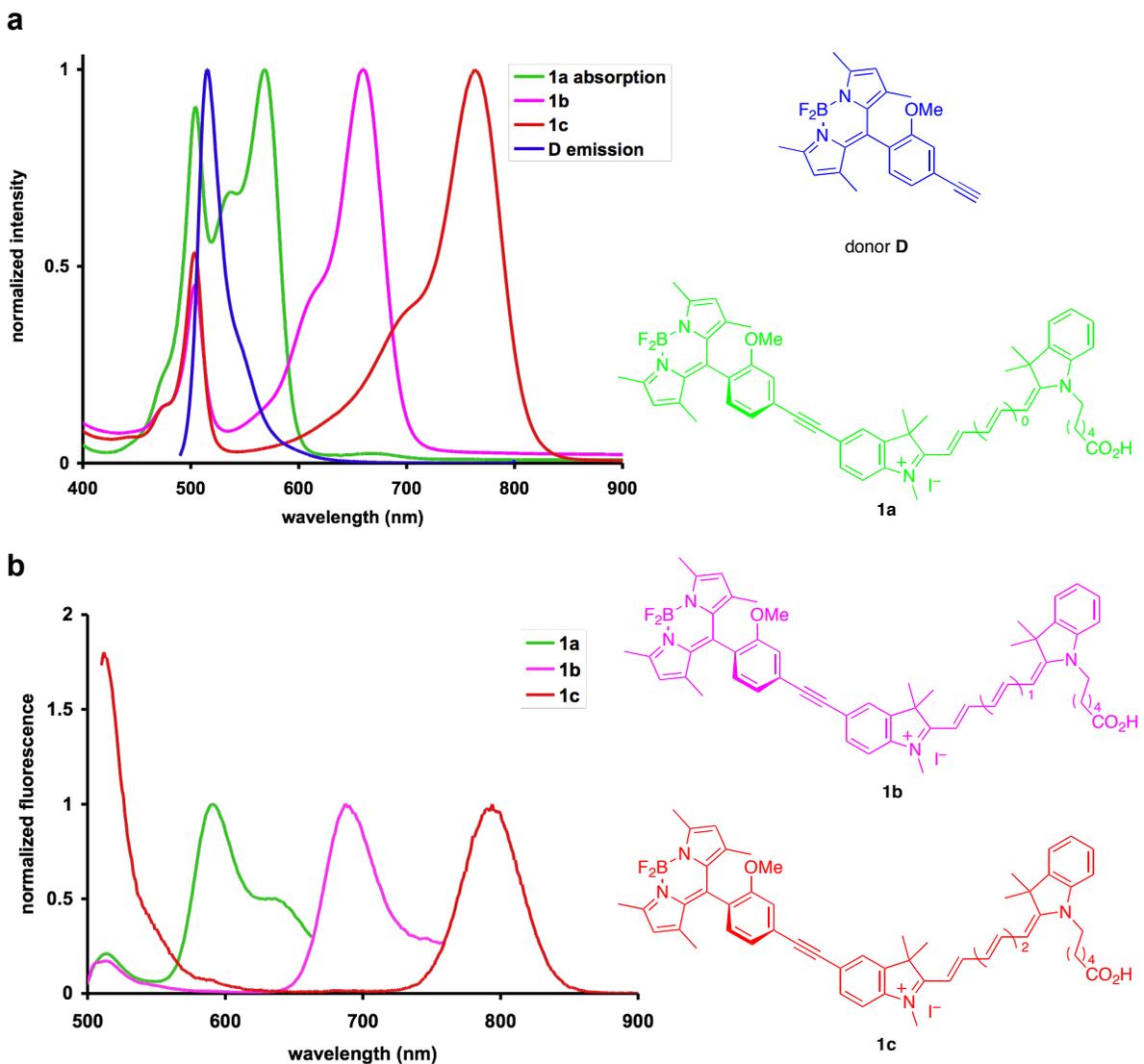


Figure S7. (a) The spectral overlap between the donor **D** emission and the cassettes **1a**, **1b**, **1c** absorbance. (b) Normalized fluorescence of the cassettes upon donor **D** excitation at 480 nm. All measurements carried out in EtOH (concentration: 3.1×10^{-6} M). This illustrates the efficiency of the through-bond energy transfer.

Table S1. Cassettes energy transfer rate measurements

Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8
	Measured transfer rate (s ⁻¹)	Cassettes R ₀ (Å)	Mixtures R ₀ (Å)	Cassettes J (M ⁻¹ cm ³ nm ⁴)	Mixtures J (M ⁻¹ cm ³ nm ⁴)	Transfer rate calcd from Förster theory for cassettes (s ⁻¹)	Transfer rate calcd from Förster theory for Mixture of Acceptor: Donor 1:1 (s ⁻¹)
Mix D+Cy3	1.85×10 ⁹	-	107	-	1.16×10 ¹⁷	-	1.90×10 ⁹
1a	4.85 × 10 ¹¹	129	-	3.47 × 10 ¹⁷	-	8.59 × 10 ⁹	-
1b	1.26 × 10 ¹¹	100	89	7.61 × 10 ¹⁶	3.85×10 ¹⁶	1.88 × 10 ⁹	1.37×10 ⁸
1c	1.26 × 10 ⁰⁹	94	69	5.14 × 10 ¹⁶	8.07×10 ¹⁵	1.39 × 10 ⁹	2.02×10 ⁸

Physical mixture of Donor and Acceptor 1 (D:Cy3) and Cassette (1a⁵) Compared
(see yellow highlight in the table)

- R_0 was calculated as a center-to-center distance measured upon excitation at 480 nm in a concentration of 3×10^{-6} in ethanol. The r was calculated using formula $r = \left(\frac{R_0^6}{E} - R_0^6 \right)^{1/6}$ and $E = 1 - \frac{F_{DA}}{F_D}$ using the 66.41 Å as an average of 64.52, 66.59 and 68.12 Å for the respective cassettes. The absolute value of the calculated energy transfer rate change is less than 5%.
- First, the spectral overlap integral **J** for both D:Cy3 (donor:acceptor mixture) and cassette **1a** (col 5 and 6) are virtually the same (as they should be). The high value of the D:Cy3 and **1a** overlap integral **J** leads to a large Förster distance $R_0 \sim 107$ and 129 Å (col 3 and 4). This leads to high efficiency in dipole-dipole coupling and high FRET efficiency (Figure **5a** and **5b**).
- Both the D:Cy3 mixture and **1a** display >90% FRET efficiency.
- Using the Förster theory of through-the-space energy transfer, the calculated rates are shown in col 7 and 8. One can see that for the D:Cy3 mixture, the measured rate is essentially the same as the rate predicted from the theory (col 2 vs. col 8). However, the rate measured for the cassette is 2 orders of magnitude larger than predicted using the Förster theory. This strongly suggests that a different-than-through-the-space FRET is involved in the cassette 1. Because the FRET rate is 2 orders of magnitudes more efficient, the best explanation appears to be FRET through the conjugated bridge.

Other cassettes (1b and 1c)

- The predicted FRET rates for cassettes **1b** and **1c** are in the same magnitude as the rate predicted for **1a** (col 7). At the same time, the measured rates for cassettes **1b** and **1c** are of the same magnitude as cassette **1a**. The measured vs. calculated rates for **1b** and **1c** show also 2 orders of magnitude difference.
- Indirectly, this suggests that also in cassettes **1b** and **1c** the FRET rates are due to mechanism more efficient than the through the space Förster model.

Atomic Force Microscopy (AFM).

Particle size of the calcium phosphate nanoparticles was measured using atomic force microscopy (AFM). A freshly cut mica surface was pressed with adhesive tape and then peeled off to clean the mica surface. A drop of nanoparticle dispersion in water was placed on the mica surface and dried with compressed nitrogen for 5 min. The surface was scanned with Digital Instruments Nanoscope AFM in tapping mode. An SPM ULTRASHARP silicon cantilever of the NSC15 series with a resonance frequency of 325 KHz was used for scanning. The typical tip curvature radius of the uncoated probe was < 10.0 nm. Particle size of the calcium nanoparticles was in the range of 14-29 nm and they were spherical in shape and well dispersed.

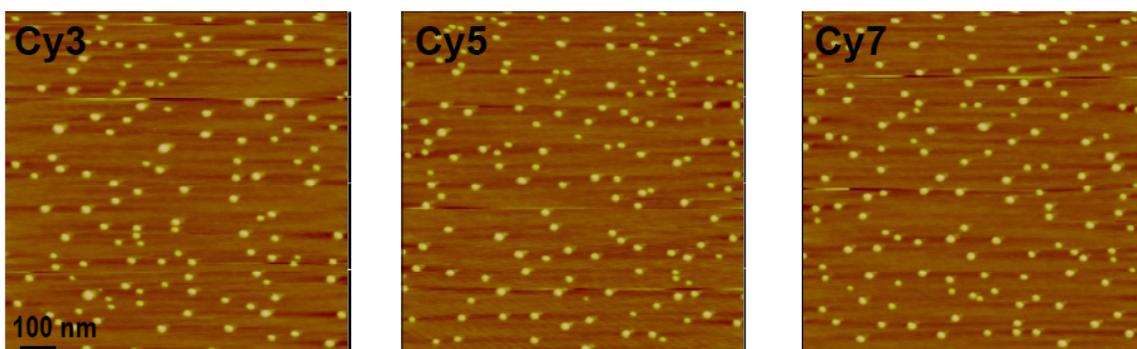
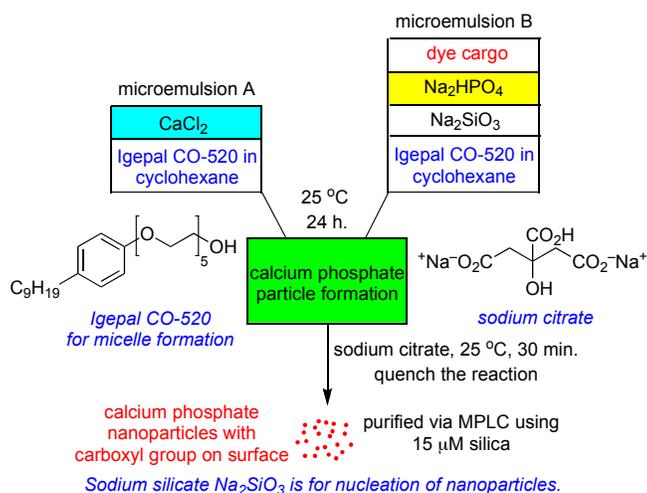
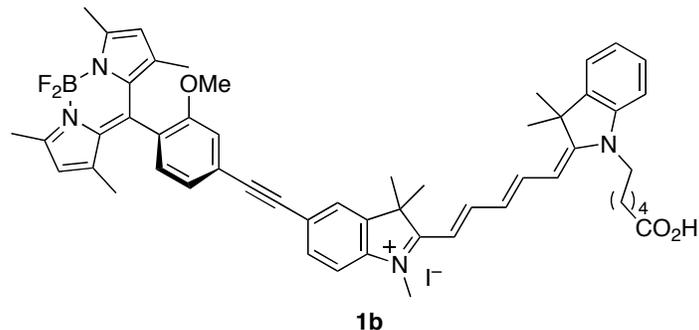


Figure S8. AFM images of acceptors encapsulated in calcium phosphate nanoparticles. Particle size: 14-29 nm.

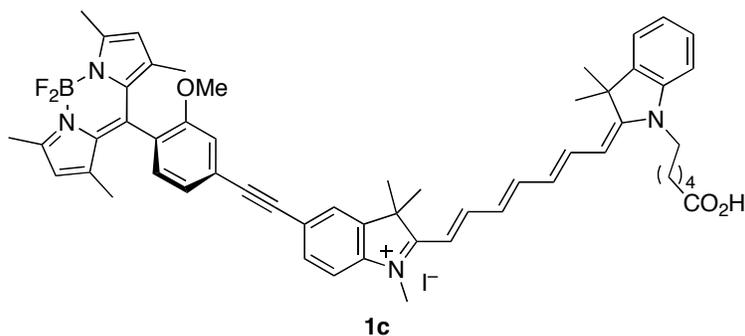
General Synthesis of Calcium Phosphate Nanoparticles.



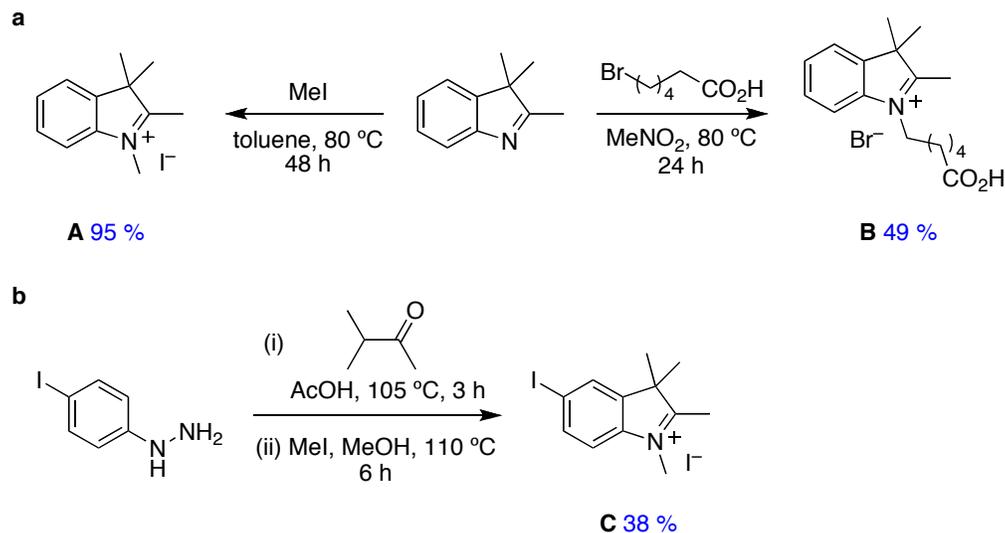
Synthesis of calcium phosphate nanoparticles was based on a previously reported procedure from Adair *et al.*⁶ Briefly two reverse microemulsions were formed from Igepal CO-520 in cyclohexane and water. 650 μL of freshly prepared 10⁻² M CaCl₂ was added to 14 mL of 29 vol % of Igepal CO-520 in cyclohexane under constant stirring to form microemulsion A. 650 μL of freshly prepared 6 × 10⁻³ M disodium phosphate and 65 μL 8.3 × 10⁻⁴ M of disodium silicate were added sequentially under constant stirring to 14 mL of 29 vol % of Igepal CO-520 in cyclohexane to form microemulsion B. The dye solution, 1 mL of 10⁻³ M was added to microemulsion B. Both microemulsions were stirred at 25 °C for 1 h. Microemulsion A was added drop wise to microemulsion B in 10 min and the combined microemulsion C stirred at 25 °C for 24 h. The reaction was quenched by addition of 225 μL of 10⁻³ M sodium citrate at 25 °C and stirring for 30 min. The micelles were broken by addition of 50 mL EtOH and purified via medium pressure liquid chromatography (MPLC) using silica microbeads (Stellar phases Inc., Langhorne, PA, dimension 15 μm average diameter and 59 Angstrom pore size). EtOH was used as an eluent to remove any free dye and all reaction precursors. The polarity of the solvent was increased to 7/3 EtOH/H₂O to elute the calcium phosphate nanoparticles. A portion of the collected calcium phosphate nanoparticles were dialyzed against water in a Spectra/por molecular membrane tubing MWCO: 6000-8000, flat width: 50 mm and diameter: 32 mm (Spectrum LABS, Houston, TX) for 8 h and then for further 8 h against pH 7.4 (0.1 M sodium phosphate buffer).



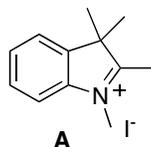
A solution of 5-iodo-Cy5 **2b** (62 mg, 0.084 mmol), 4-ethynyl BODIPY **D** (54 mg, 0.14 mmol), Pd(PPh₃)₄ (20 mg, 0.020 mmol), CuI (3.0 mg, 0.020 mmol) in DMF (2.0 mL) was freeze-pump-thawed at -78 °C. Et₃N (58 μL, 0.42 mmol) was added to a solution and the reaction mixture was stirred at 40 °C for 1 h under nitrogen. Ether (60 mL) was added to the reaction mixture and the precipitate was filtered off to afford product **1b** as a dark purple solid. The residue was purified by flash chromatography eluting with 100 % EtOAc and 10 to 50 % MeOH/CH₂Cl₂ to afford product as a dark purple solid (21 mg, 26 %). *R_f* = 0.5 (10 % MeOH/CH₂Cl₂). ¹H NMR (500 MHz, CD₃OD) δ 8.35-8.21 (m, 2H), 7.67 (s, 1H), 7.60 (d, 1H, *J* = 10.0 Hz), 7.55 (d, 1H, *J* = 5.0 Hz), 7.45 (t, 1H, *J* = 10.0 Hz), 7.39 (d, 1H, 5.0 Hz), 7.35-7.31 (m, 3H), 7.28 (d, 1H, *J* = 10.0 Hz), 7.20 (d, 1H, *J* = 5.0 Hz), 6.68 (t, 1H, *J* = 10.0 Hz), 6.42 (d, 1H, *J* = 15.0 Hz), 6.24 (d, 1H, *J* = 15.0 Hz), 6.07 (s, 2H), 4.22-4.17 (m, 2H), 3.87 (s, 3H), 3.60 (s, 3H), 2.49 (s, 6H), 2.37-2.33 (m, 2H), 1.88-1.83 (m, 2H), 1.75 (s, 6H), 1.73 (s, 6H), 1.66-1.63 (m, 2H), 1.54 (s, 6H), 1.39-1.34 (br, 2H); ¹³CNMR (125 MHz, CD₃OD) δ 176.1, 173.8, 172.3, 157.1, 156.2 (2C), 153.9, 142.3, 142.1, 138.9, 133.1, 133.0, 131.7, 131.5, 130.2, 128.9, 126.1, 125.8, 124.9, 124.7, 124.3, 124.1 (2C), 123.0, 121.9, 119.3, 114.2, 111.9, 110.8, 105.6, 104.3, 80.2, 79.7, 68.2, 65.7, 55.8, 49.7, 44.1, 39.2, 26.6, 26.4, 25.1, 24.9, 14.1; (1 carbon missing). MS (MALDI) *m/z* 859.29 (M)⁺.



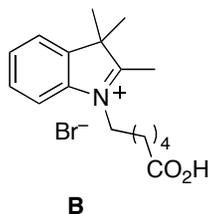
A solution of 5-iodo-Cy7 **2c** (80 mg, 0.10 mmol), 4-ethynyl BODIPY **D** (67 mg, 0.18 mmol), Pd(PPh₃)₄ (24 mg, 0.021 mmol), CuI (4 mg, 0.021 mmol) in DMF (4.0 mL) was freeze-pump-thawed at -78 °C. Et₃N (70 μL, 0.49 mmol) was added to a solution and the reaction mixture was stirred at 40 °C for 45 min under nitrogen. Ether (100 mL) was added to the reaction mixture and the precipitate was filtered off to afford dark red solids. The residue was purified by flash chromatography eluting with 100 % EtOAc and 10 to 50 % MeOH/CH₂Cl₂ to afford product **1c** as a dark green solid (35 mg, 33 %). *R_f* = 0.5 (10 % MeOH/CH₂Cl₂). ¹H NMR (500 MHz, CD₃OD) δ 8.07 (t, 1H, *J* = 12.0 Hz), 7.88 (t, 1H, *J* = 12.0 Hz), 7.66-7.61 (m, 2H), 7.58 (t, 2H, *J* = 7.5 Hz), 7.48 (t, 1H, *J* = 7.5 Hz), 7.42 (d, 1H, *J* = 8.0 Hz), 7.37-7.33 (m, 3H), 7.22-7.19 (m, 2H), 6.66 (t, 1H, *J* = 13.0 Hz), 6.59 (t, 1H, *J* = 13.0 Hz), 6.50 (d, 1H, *J* = 14.5 Hz), 6.17 (d, 1H, *J* = 13.0 Hz), 6.09 (s, 2H), 4.21 (t, 2H, *J* = 7.5 Hz), 3.88 (s, 3H), 3.55 (s, 3H), 2.52 (s, 6H), 2.36 (t, 2H, *J* = 7.5 Hz), 1.91-1.85 (m, 2H), 1.75 (s, 6H), 1.74-1.69 (m, 2H), 1.73 (s, 6H), 1.55 (s, 6H), 1.54-1.50 (m, 2H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 175.3, 174.7, 169.8, 157.0, 155.7, 154.0, 149.8, 144.8, 143.1, 142.7, 142.6, 141.9, 139.2, 133.1, 131.6, 130.6, 129.6, 127.3, 126.7, 126.6, 126.4, 126.1, 125.5, 124.1, 123.6, 122.2 (2C), 117.4, 115.3, 112.9, 111.3, 106.9, 104.0, 92.1, 89.9, 57.0, 50.4, 48.7, 44.9, 34.5, 31.7, 28.2, 28.0, 27.9, 26.6, 25.2, 15.2, 14.6; MS (MALDI) *m/z* 885.35 (M)⁺.



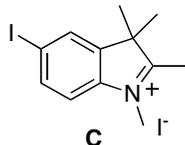
Scheme S1. Synthesis of indolium Salts **A**, **B**, **C**.



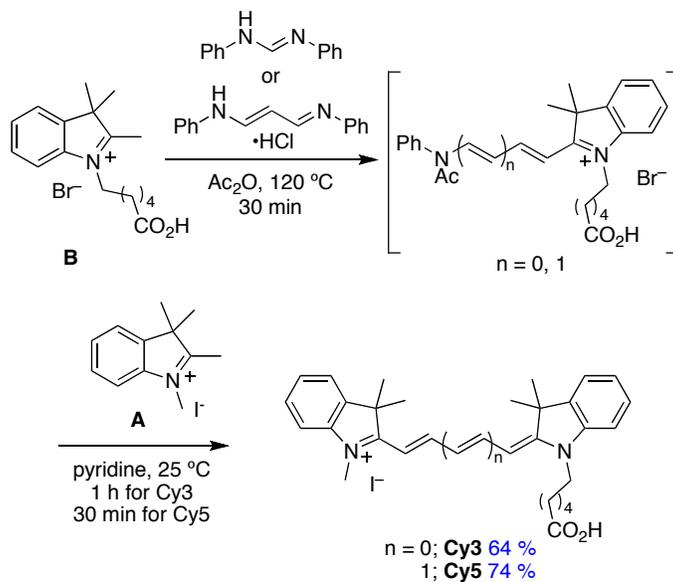
This compound was synthesized following a previously published procedure (Scheme S1a).⁷ A solution of 2,3,3-trimethylindolenine (3.0 g, 18.8 mmol) and iodomethane (3.2 g, 22.6 mmol) in toluene (60 mL) was heated at 80 °C for 48 h. The reaction mixture was cooled to room temperature and the solvent was concentrated under reduced pressure. The residue was suspended in hexanes (100 mL), sonicated for 10 min and filtered off to afford product **A** as a brown solid (5.4 g, 95 %). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.96-7.95 (m, 1H), 7.88-7.86 (m, 1H), 7.68-7.64 (m, 2H), 4.01 (s, 3H), 2.81 (s, 3H), 1.57 (s, 6H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 196.9, 143.1, 142.5, 130.3, 129.8, 124.3, 116.1, 54.9, 35.7, 22.6, 15.1.



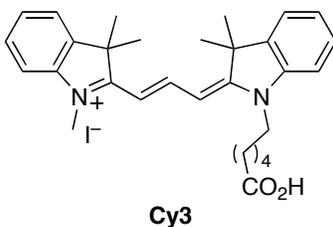
This compound was synthesized following a previously published procedure (Scheme S1b).⁸ 6-Bromohexanoic acid (3.7 g, 18.8 mmol) was added to a solution of 2,3,3-trimethylindolenine (3.0 g, 18.8 mmol) in nitromethane (10 mL). The reaction mixture was heated at 80 °C for 24 h. The reaction mixture was cooled to room temperature and triturated with ether (60 mL). The precipitate was filtered off and washed with ether to afford product **B** as a purple solid (3.3 g, 49 %). ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.03-8.00 (m, 1H), 7.90-7.87 (m, 1H), 7.68-7.65 (m, 2H), 4.49 (t, 2H, *J* = 7.9 Hz), 2.88 (s, 3H), 2.27 (t, 2H, *J* = 7.1 Hz), 1.93-1.83 (m, 2H), 1.65-1.53 (m, 2H), 1.57 (s, 6H), 1.51-1.43 (m, 2H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 198.1, 176.5, 143.4, 142.4, 131.2, 130.7, 125.1, 116.9, 55.8, 49.0, 34.9, 28.4, 26.9, 25.5, 23.6, 15.4.



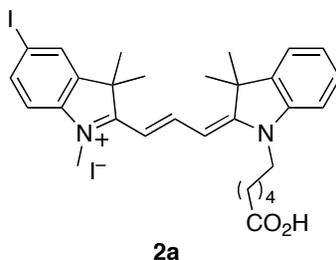
This compound was synthesized following a previously published procedure (Scheme S1b).⁹ *para*-Iodo-phenylhydrazine (2.0 g, 8.46 mmol) and *iso*-propylmethyl ketone (0.92 ml, 8.46 mmol) were dissolved in acetic acid (5.0 ml) and heated to 105 °C for 3 h. The reaction mixture was cooled to 25 °C and diluted with water (10 mL) and pH adjusted to 7 by adding solid NaHCO₃. The indole formed was then extracted with diethyl ether (10 mL) three times and the organic layer was dried with Na₂SO₄ followed by solvent evaporation to obtain a brown oil (2.37 g, 8.30 mmol). This oil was dissolved in methanol (10 mL) along with iodomethane (1.12 ml, 17.95 mmol) and heated at 110 °C in a sealed tube for 6 h. The reaction mixture was cooled to 25 °C and filtered and washed with methanol and dried to obtain the product **C** as a brown colored solid (1.37 g, 38 %). ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.27 (s, 1H), 7.98 (d, 1H, *J* = 5.0 Hz), 7.70 (d, 1H, *J* = 5.0 Hz), 3.92 (s, 3H), 2.72 (s, 3H), 1.50 (s, 6H); ¹³CNMR (125 MHz, DMSO-*d*₆) δ 196.8, 144.9, 142.6, 138.7, 132.9, 117.8, 96.8, 55.0, 35.5, 22.5, 15.3.



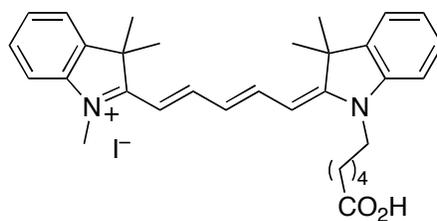
Scheme S2. Synthesis of non-iodinated acceptor fragments **Cy3** and **Cy5**.



This compound was synthesized following a previously published procedure.⁸ A solution of indolium bromide **B** (100 mg, 0.28 mmol) and *N,N'*-diphenylformamidine (66 mg, 0.34 mmol) in Ac₂O (1.5 mL) was heated at 120 °C for 30 min. The reaction mixture was cooled to room temperature and a solution of indolium iodide **A** (102 mg, 0.34 mmol) in pyridine (1.5 mL) was added. The reaction mixture was stirred at 25 °C for 1 h. Ether (100 mL) was added and dark red oil was obtained after the removal of ether. The residue was purified by flash chromatography eluting with 100 % EtOAc and 2 % to 10 % MeOH/CH₂Cl₂ to afford product **Cy3** as a dark red foam (106 mg, 64 %). *R_f* 0.3 (10 % MeOH/CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃) δ 8.42 (t, 1H, *J* = 13.4 Hz), 7.40-7.35 (m, 4H), 7.27-7.22 (m, 4H), 7.18 (d, 1H, *J* = 13.5 Hz), 7.14 (dd, 1H, *J* = 8.3, 3.5 Hz), 4.21 (t, 2H, *J* = 7.5 Hz), 3.80 (s, 3H), 2.45 (t, 2H, *J* = 7.0 Hz), 1.91-1.85 (m, 2H), 1.78-1.63 (m, 4H), 1.71 (s, 6H), 1.70 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 178.1, 174.2, 173.5, 150.7, 142.6, 141.9, 140.5, 140.4, 128.9, 128.8, 125.3 (2C), 122.1, 122.0, 110.9, 110.8, 105.0, 104.4, 48.9, 48.8, 44.7, 33.9, 32.8, 28.14, 28.07, 27.1, 26.1, 24.4.

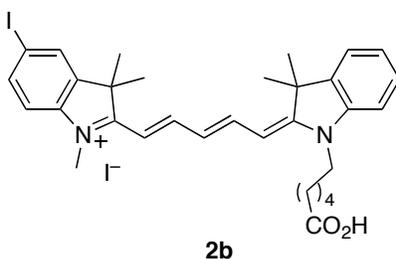


A solution of indolium bromide **B** (170 mg, 0.48 mmol) and *N,N'*-diphenylformamidinium (113 mg, 0.58 mmol) in Ac₂O (2 mL) was heated at 120 °C for 30 min. The reaction mixture was cooled to room temperature and a solution of indolium iodide **C** (287 mg, 0.67 mmol) in pyridine (7 mL) was added. The reaction mixture was stirred at 25 °C for 24 h. Ether (100 mL) was added and the reaction mixture was filtered off to afford dark red solids. The residue was purified by flash chromatography eluting with 100 % EtOAc and 4 % to 10 % MeOH/CH₂Cl₂ to afford product **2a** as a dark red solid (213 mg, 62 %). *R_f* 0.4 (10 % MeOH/CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃) δ 8.40 (t, 1H, *J* = 13.0 Hz), 7.70 (dd, 1H, *J* = 8.3, 1.5 Hz), 7.61 (d, 1H, *J* = 1.5 Hz), 7.43-7.38 (m, 2H), 7.28 (t, 1H, *J* = 7.5 Hz), 7.21 (d, 2H, *J* = 13.5 Hz), 7.16 (d, 1H, *J* = 8.0 Hz), 6.91 (d, 1H, *J* = 8.0 Hz), 4.24 (t, 2H, *J* = 8.0 Hz), 3.76 (s, 3H), 2.47 (t, 2H, *J* = 6.5 Hz), 1.93-1.87 (m, 2H), 1.80-1.65 (m, 4H), 1.72 (s, 6H), 1.70 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 178.1, 174.3, 172.7, 150.7, 142.6, 142.5, 141.8, 140.7, 137.7, 131.0, 129.0, 125.7, 122.2, 112.5, 111.3, 105.3, 104.8, 88.2, 49.1, 48.5, 44.9, 33.9, 32.9, 29.6, 28.1, 27.2, 26.1, 24.4; MS (ESI) *m/z* 583.18 (M)⁺.

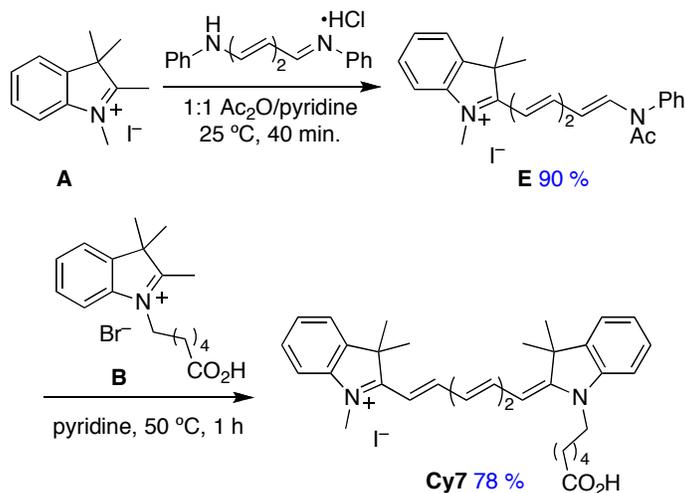


Cy5

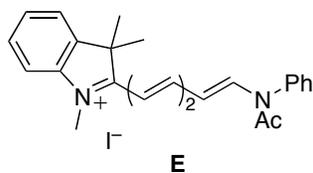
This compound was synthesized following a previously published procedure.⁸ A solution of indolium bromide **B** (100 mg, 0.28 mmol) and malondialdehyde bis(phenylimine) monohydrochloride (88 mg, 0.34 mmol) in Ac₂O (1 mL) was heated at 120 °C for 30 min. The reaction mixture was cooled to room temperature and a solution of indolium iodide **A** (119 mg, 0.34 mmol) in pyridine (1.5 mL) was added. The reaction mixture was stirred at 25 °C for 30 min. Ether (100 mL) was added and a dark blue oil was obtained after the removal of ether. The residue was purified by flash chromatography eluting with 100 % EtOAc and 10 % to 15 % MeOH/CH₂Cl₂ to afford product **Cy5** as a dark purple solid (128 mg, 74 %). *R_f* 0.3 (10 % MeOH/CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃) δ 8.05 (t, 2H, *J* = 10.0 Hz) 7.39-7.34 (br, 4H), 7.24-7.21 (br, 2H), 7.15-7.12 (br, 2H), 6.94 (t, 1H, *J* = 10.0 Hz), 6.43 (d, 1H, *J* = 5.0 Hz), 6.36 (d, 1H, *J* = 5.0 Hz), 4.08 (m, 2H), 3.71 (s, 3H), 2.44 (t, 4H, *J* = 7.0 Hz), 1.84 (m, 2H), 1.74 (s, 6H), 1.72 (s, 6H), 1.57 (m, 2H); ¹³CNMR (125 MHz, CDCl₃) δ 173.8, 172.9, 172.2, 153.6, 153.5, 143.2, 142.2, 141.5 (2C), 141.2, 129.0, 126.9, 125.4, 122.5, 122.4, 110.7, 110.6, 104.6, 104.0, 49.5, 49.4, 44.5, 34.3, 32.7, 28.4, 28.3, 27.2, 26.5, 24.6. (1 carbon overlapping)



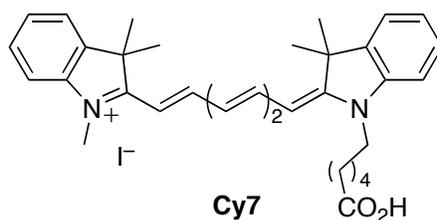
A solution of indolium bromide **B** (150 mg, 0.43 mmol) and malondialdehyde bis(phenylimine) monohydrochloride (132 mg, 0.51 mmol) in Ac₂O (1.2 mL) was heated at 120 °C for 30 min. The reaction mixture was cooled to 25 °C and a solution of indolium iodide **C** (254 mg, 0.59 mmol) in pyridine (1.2 mL) was added. The reaction mixture was stirred at 25 °C for 30 min. Ether (25 mL) was added and the reaction mixture was filtered off to afford **2b** as dark blue solid. The residue was purified by flash chromatography eluting with 100 % EtOAc and 5 % to 15 % MeOH/CH₂Cl₂ to afford product as a dark purple solid (203 mg, 65 %). *R_f* = 0.4 (10 % MeOH/CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃) δ 8.09 (t, 1H, *J* = 10.0 Hz), 8.02 (t, 1H, *J* = 10.0 Hz), 7.63 (dd, 1H, *J* = 5.0 Hz, *J* = 1.0 Hz), 7.57 (d, 1H, *J* = 1.0 Hz), 7.40-7.35 (m, 2H), 7.24-7.19 (m, 2H), 6.95 (t, 1H, *J* = 5.0 Hz), 6.88 (d, 1H, *J* = 5.0 Hz), 6.48 (d, 1H, *J* = 7.5 Hz), 6.29 (d, 1H, *J* = 7.5 Hz), 4.14 (m, 2H), 3.62 (s, 3H), 2.40 (m, 2H), 1.79-1.74 (m, 4H), 1.74 (s, 6H), 1.72 (s, 6H), 1.57 (m, 2H); ¹³CNMR (125MHz, CDCl₃) δ 174.2, 171.4, 154.5, 153.0, 152.9, 143.2, 143.0, 142.0, 141.7, 137.9, 131.4, 129.1, 127.3, 125.7, 122.6, 112.4, 111.6, 105.3, 103.8, 87.9, 50.0, 49.1, 45.0, 34.8 (2C), 30.1, 28.3, 27.5, 26.7, 24.8; MS (ESI) *m/z* 609.15 (M)⁺.



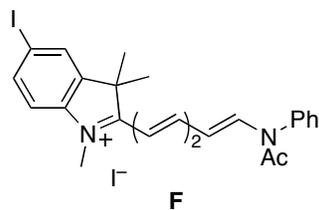
Scheme S3. Synthesis of non-iodinated acceptor fragment **Cy7**.



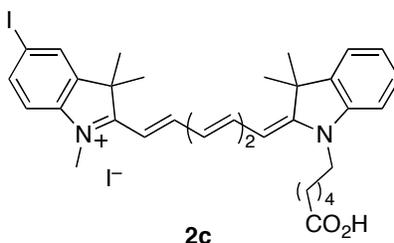
Indolium iodide **A** (1.0 g, 3.3 mmol) and glutacanaldehydedianil hydrochloride (1.4 g, 5.0 mmol) were added to a solution of Ac₂O (5.0 mL) and pyridine (5.0 mL). The reaction mixture was stirred at 25 °C for 40 min. Ether (200 mL) was added and the reaction mixture was filtered off to afford dark red oil. The residue was purified by flash chromatography eluting with 100 % EtOAc and 4 % to 10 % MeOH/CH₂Cl₂ to afford product as **E** a dark brown solid (1.48 g, 90 %). *R_f* 0.5 (10 % MeOH/CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃) δ 8.17 (d, 1H, *J* = 13.8 Hz), 7.90-7.81 (m, 1H), 7.64-7.46 (m, 8H), 7.20-7.17 (m, 3H), 6.94 (m, 1H), 5.45-5.37 (m, 1H), 4.21 (s, 3H), 1.97 (s, 3H), 1.72 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 180.5, 169.4, 155.9, 151.6, 142.5, 141.5, 141.0, 137.8, 130.7, 130.1, 129.9, 129.4, 128.8, 128.1, 122.4, 113.9, 113.7, 113.5, 51.4, 35.9, 27.1, 23.4; MS (ESI) *m/z* 371.21 (M)⁺.



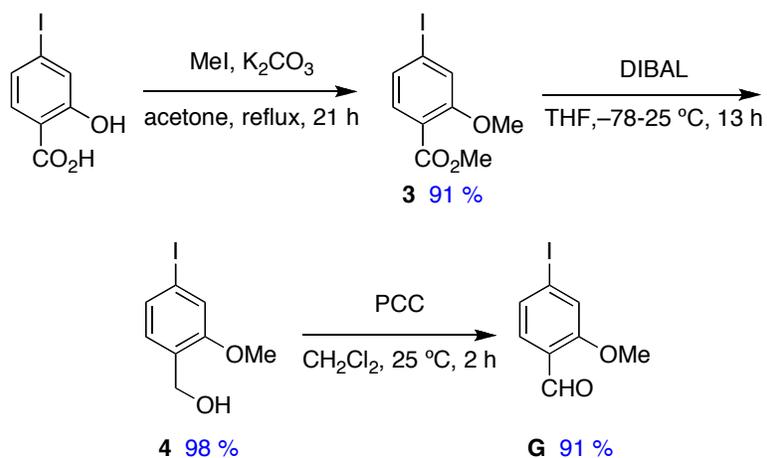
Indolium bromide **B** (200 mg, 0.56 mmol) was added to a solution of hemicyanine **E** (281 mg, 0.56 mmol) in pyridine (6.0 mL). The reaction mixture was stirred at 50 °C for 1 h. After cooling to room temperature, ether (100 mL) was added and the reaction mixture was filtered off to afford a dark green solid. The residue was purified by flash chromatography eluting with 100 % EtOAc and 2 % to 10 % MeOH/CH₂Cl₂ to afford product **Cy7** as a purple solid (280 mg, 78 %). *R_f* 0.5 (10 % MeOH/CH₂Cl₂). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.95-7.88 (m, 2H), 7.83-7.78 (m, 1H), 7.63-7.61 (m, 2H), 7.46-7.39 (m, 4H), 7.29-7.24 (m, 2H), 6.57 (q, 2H, *J* = 12.5 Hz), 6.38 (dd, 2H, *J* = 13.5, 4.0 Hz), 4.09 (t, 2H, *J* = 7.0 Hz), 3.63 (s, 3H), 2.24 (t, 2H, *J* = 7.0 Hz), 1.75-1.68 (m, 2H), 1.67 (s, 6H), 1.66 (s, 6H), 1.62-1.56 (m, 2H), 1.45-1.39 (m, 2H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 175.4, 172.9, 171.8, 157.0, 152.1, 151.8, 150.6, 143.8, 143.2, 141.9, 129.42, 129.36, 126.2, 125.6, 125.4, 124.9, 123.4, 123.3, 112.0, 111.9, 105.1, 104.5, 49.6, 49.5, 44.3, 34.5, 32.1, 28.2, 28.0, 27.7, 26.7, 25.2; MS (ESI) *m/z* 509.32 (M)⁺.



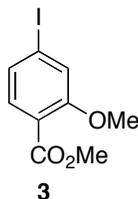
Indolium iodide **C** (300 mg, 0.70 mmol) and glutacanaldehydedianil hydrochloride (300 mg, 1.05 mmol) were added to a solution of Ac_2O (3 mL) and pyridine (3 mL). The reaction mixture was stirred at 25 °C for 1 h. Ether (100 mL) was added and the reaction mixture was filtered off to afford dark brown solids. The residue was purified by flash chromatography eluting with 100 % EtOAc and 1 % to 5 % MeOH/ CH_2Cl_2 to afford product **F** as a dark brown solid (327 mg, 74 %). R_f 0.4 (10 % MeOH/ CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3) δ 8.20 (d, 1H, $J = 14.0$ Hz), 7.88-7.82 (m, 2H), 7.77 (d, 1H, $J = 1.5$ Hz), 7.60-7.54 (m, 4H), 7.24 (d, 2H, $J = 8.5$ Hz), 7.20-7.18 (m, 2H), 6.92-6.87 (m, 1H), 5.46-5.41 (m, 1H), 4.18 (s, 3H), 1.98 (s, 3H), 1.72 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 179.7, 169.5, 156.6, 152.6, 144.2, 141.8, 141.4, 138.5, 137.8, 131.6, 130.8, 130.7, 130.1, 128.1, 115.3, 113.8, 113.7, 93.7, 51.2, 35.5, 27.2, 23.4; MS (ESI) m/z 497.11 (M) $^+$.



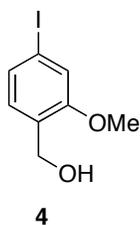
Indolium bromide **B** (150 mg, 0.42 mmol) was added to a solution of 5-iodo hemicyanine **F** (264 mg, 0.42 mmol) in pyridine (5 mL). The reaction mixture was stirred at 50 °C for 1.5 h. After cooling to room temperature, ether (100 mL) was added and the reaction mixture was filtered off to afford dark green solids. The residue was purified by flash chromatography eluting with 100 % EtOAc and 5 % to 10 % MeOH/CH₂Cl₂ to afford product **2c** as a purple solid (234 mg, 72 %). *R_f* 0.5 (10 % MeOH/CH₂Cl₂). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.97 (t, 1H, *J* = 13.0 Hz), 7.95 (d, 1H, *J* = 1.5 Hz), 7.86-7.77 (m, 2H), 7.73 (dd, 1H, *J* = 10.0, 1.5 Hz), 7.66 (d, 1H, *J* = 7.5 Hz), 7.50-7.44 (m, 2H), 7.32 (t, 1H, *J* = 7.5 Hz), 7.17 (d, 1H, *J* = 8.5 Hz), 6.62 (t, 1H, *J* = 13.0 Hz), 6.57-6.51 (m, 2H), 6.23 (d, 1H, *J* = 13.0 Hz), 4.16 (t, 2H, *J* = 7.0 Hz), 3.52 (s, 3H), 2.23 (t, 2H, *J* = 7.5 Hz), 1.76-1.70 (m, 2H), 1.68 (s, 6H), 1.65 (s, 6H), 1.61-1.55 (m, 2H), 1.46-1.40 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 177.9, 173.2, 168.8, 156.7, 153.0, 149.4, 143.0, 142.6, 141.8, 141.3, 137.2, 131.0, 128.8, 127.3, 126.8, 125.7, 122.3, 111.5, 111.2, 105.7, 103.1, 86.8, 49.6, 48.2, 44.8, 33.9, 31.8, 28.0, 27.9, 27.3, 26.2, 24.4; MS (ESI) *m/z* 635.21 (M)⁺.



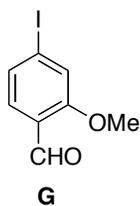
Scheme S4. Synthesis of 4-Iodo-2-methoxybenzaldehyde **G**.



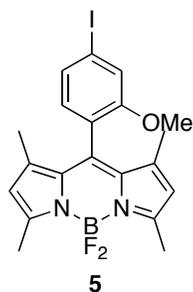
A solution of 2-hydroxy-4-iodobenzoic acid (4.0 g, 15.2 mmol), iodomethane (9.7 g, 68.2 mmol) and K_2CO_3 (9.4 g, 68.2 mmol) in acetone (90 mL) was refluxed at 60 °C for 20 h. The reaction mixture was cooled to room temperature, filtered and the solvents were concentrated under reduced pressure. Water (50 mL) was added and the aqueous layer was extracted with EtOAc (1 x 40 mL). The organic layer was washed with sat. NaHCO_3 (1 x 40 mL) and brine (1 x 40 mL) and dried over Na_2SO_4 . The solvents were evaporated and the residue was purified by flash chromatography eluting with 10 % EtOAc/hexanes to afford product **3** as a yellow oil (4.0 g, 91 %). R_f 0.5 (20 % EtOAc/hexanes). ^1H NMR (500 MHz, CDCl_3) δ 7.48 (d, 1H, $J = 8.1$ Hz), 7.33 (d, 1H, $J = 8.1$ Hz), 7.30 (s, 1H), 3.88 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.0, 159.1, 132.7, 129.4, 121.5, 119.4, 100.0, 56.2, 52.1; MS (ESI) m/z 292.97 ($\text{M}+\text{H}$) $^+$.



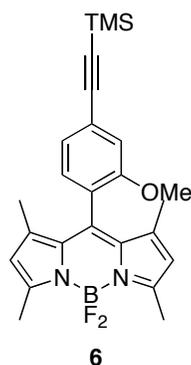
To a solution of methyl ester **3** (3.3 g, 11.2 mmol) in THF (70 mL) was added DIBAL (33.7 mL, 33.7 mmol) dropwise at -78 °C. The reaction mixture was stirred at 25 °C for 13 h. The reaction was quenched by the slow addition of sat. NH_4Cl at 0 °C. The reaction mixture was filtered and aqueous layer was extracted with EtOAc (5 x 250 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to afford pure product **4** as a colorless oil (2.9 g, 98 %). R_f 0.5 (30 % EtOAc/hexanes). ^1H NMR (300 MHz, CDCl_3) δ 7.29 (dd, 1H, $J = 8.0, 1.5$ Hz), 7.17 (d, 1H, $J = 1.5$ Hz), 7.00 (d, 1H, $J = 8.0$ Hz), 4.61 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.7, 129.9, 129.8, 128.8, 119.5, 93.2, 61.3, 55.5; MS (ESI) m/z 270.98 ($\text{M}+\text{Li}$) $^+$.



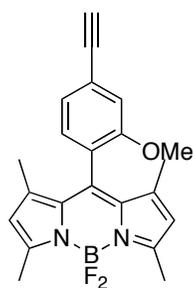
To a slurry of pyridinium chlorochromate (2.7 g, 12.5 mmol) in CH_2Cl_2 (70 mL) was added a solution of alcohol **4** (2.2 g, 8.3 mmol) in CH_2Cl_2 (20 mL) dropwise at 25 °C. The reaction mixture was stirred at 25 °C for 2 h. The reaction mixture was filtered through celite and washed with ether. The solvents were concentrated under reduced pressure and the residue was purified by flash chromatography eluting with 10 % EtOAc/hexanes to afford product **G** as an off-white solid (2.0 g, 91 %). R_f 0.8 (20 % EtOAc/hexanes). ^1H NMR (500 MHz, CDCl_3) δ 10.40 (s, 1H), 7.51 (d, 1H, $J = 8.0$ Hz), 7.41 (dd, 1H, $J = 8.0, 1.5$ Hz), 7.36 (d, 1H, $J = 1.5$ Hz), 3.92 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 189.1, 161.4, 130.3, 129.5, 124.2, 121.3, 103.4, 56.0; MS (ESI) m/z 262.95 ($\text{M}+\text{H}$) $^+$.



A solution of aldehyde **G** (1.3 g, 5.0 mmol), 2,4-dimethylpyrrole (1.1 g, 11.0 mmol) and one drop of TFA in CH₂Cl₂ (30 mL) was stirred at 25 °C under nitrogen for 1.5 h. Then chloranil (1.5 g, 6.0 mmol) was added to a reaction mixture and the reaction was stirred at 25 °C for 40 min under air. The reaction mixture was filtered through celite and washed with CH₂Cl₂ and the solvents were evaporated. The residue was purified by flash chromatography (aluminum oxide, activated, basic) eluting with CH₂Cl₂ and 10 % EtOAc/CH₂Cl₂. The obtained orange solids were dissolved in toluene (20 mL) and Et₃N (2.1 mL, 15.0 mmol) was added and stirred at 25 °C for 10 min. BF₃•Et₂O (3.2 mL, 25.0 mmol) was added and stirred at 25 °C for 20 h. The reaction mixture was diluted with CH₂Cl₂ (30 mL) and washed with water (3 x 30 mL). The organic layer was dried over Na₂SO₄ and evaporated. The residue was purified by flash chromatography eluting with 5 % EtOAc/hexanes to afford product **5** as an orange solid (813 mg, 34 %). *R_f* 0.5 (10 % EtOAc/hexanes). ¹H NMR (500 MHz, CDCl₃) δ 7.44 (dd, 1H, *J* = 8.0, 1.5 Hz), 7.31 (d, 1H, *J* = 1.5 Hz), 6.87 (d, 1H, *J* = 8.0 Hz), 5.97 (s, 2H), 3.76 (s, 3H), 2.54 (s, 6H), 1.46 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 156.8, 155.2, 142.3, 137.3, 131.2, 130.8, 130.7, 123.6, 121.0, 120.6, 95.2, 55.9, 14.5, 14.0; MS (MALDI) *m/z* 479.76 (M)⁺.

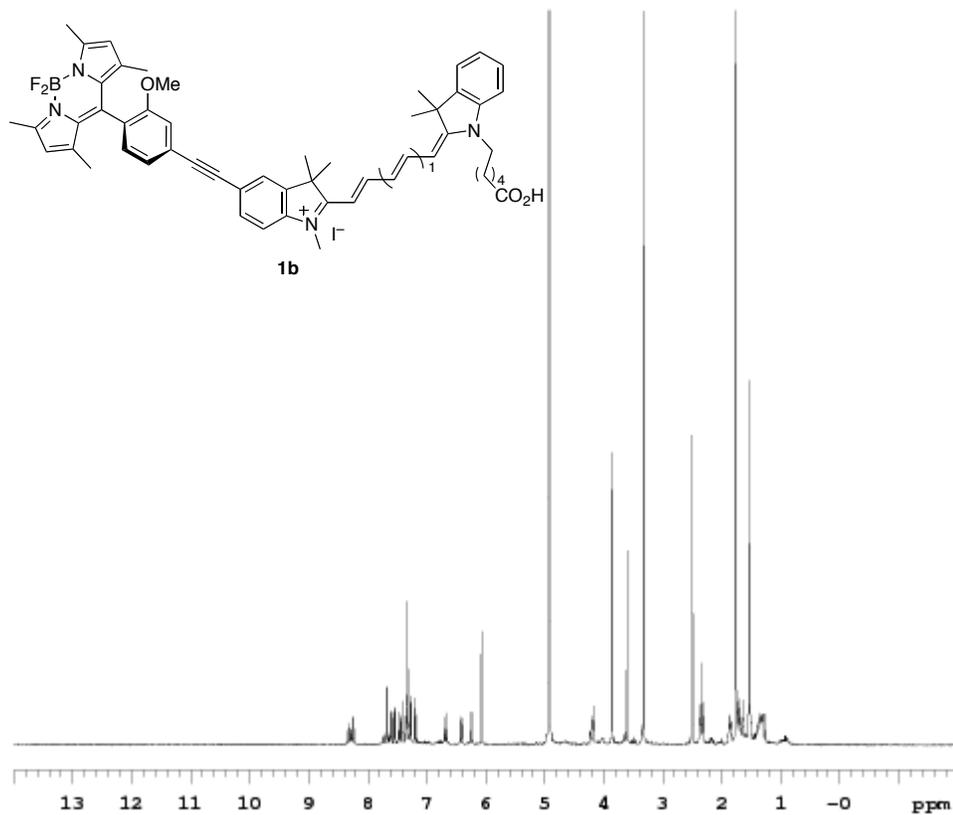


A solution of 4-iodo BODIPY **5** (0.6 g, 1.2 mmol), trimethylsilyl acetylene (1.2 g, 12.4 mmol), PdCl₂(PPh₃)₂ (88 mg, 0.12 mmol), CuI (24 mg, 0.12 mmol) and Et₃N (1.7 mL, 12.5 mmol) in THF (15 mL) was stirred at 25 °C for 12 h. The solvents were concentrated under reduced pressure. The residue was purified by flash chromatography eluting with 3 % EtOAc/hexanes to afford product **6** as an orange solid (548 mg, 97 %). *R_f* 0.4 (10 % EtOAc/hexanes). ¹H NMR (500 MHz, CDCl₃) δ 7.22 (dd, 1H, *J* = 7.7, 1.5 Hz), 7.084 (d, 1H, *J* = 1.5 Hz), 7.081 (d, 1H, *J* = 7.7 Hz), 5.96 (s, 2H), 3.78 (s, 3H), 2.54 (s, 6H), 1.44 (s, 6H), 0.28 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 156.2, 155.2, 142.4, 137.9, 131.3, 129.5, 125.3, 125.2, 124.6, 120.9, 114.4, 104.3, 95.4, 55.7, 14.6, 14.0, -0.12; MS (MALDI) *m/z* 450.28 (M)⁺.

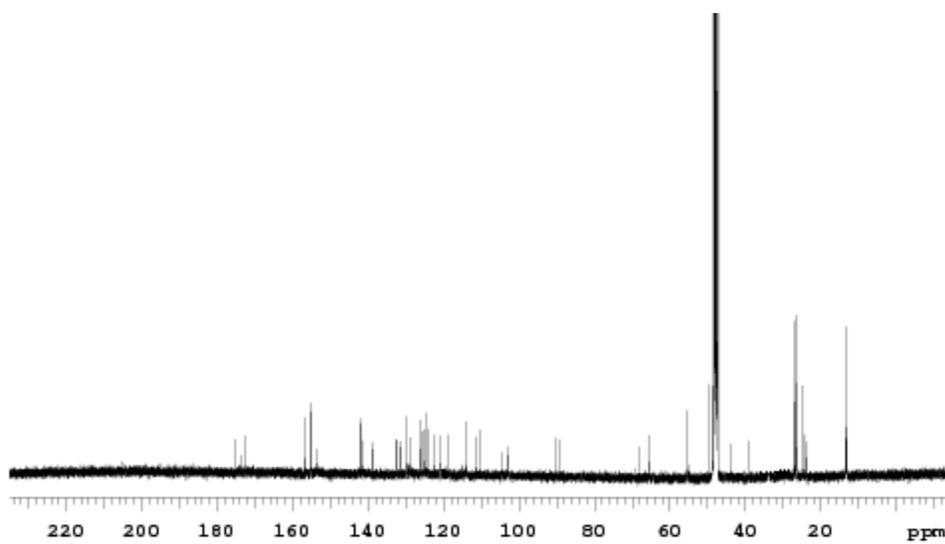


D

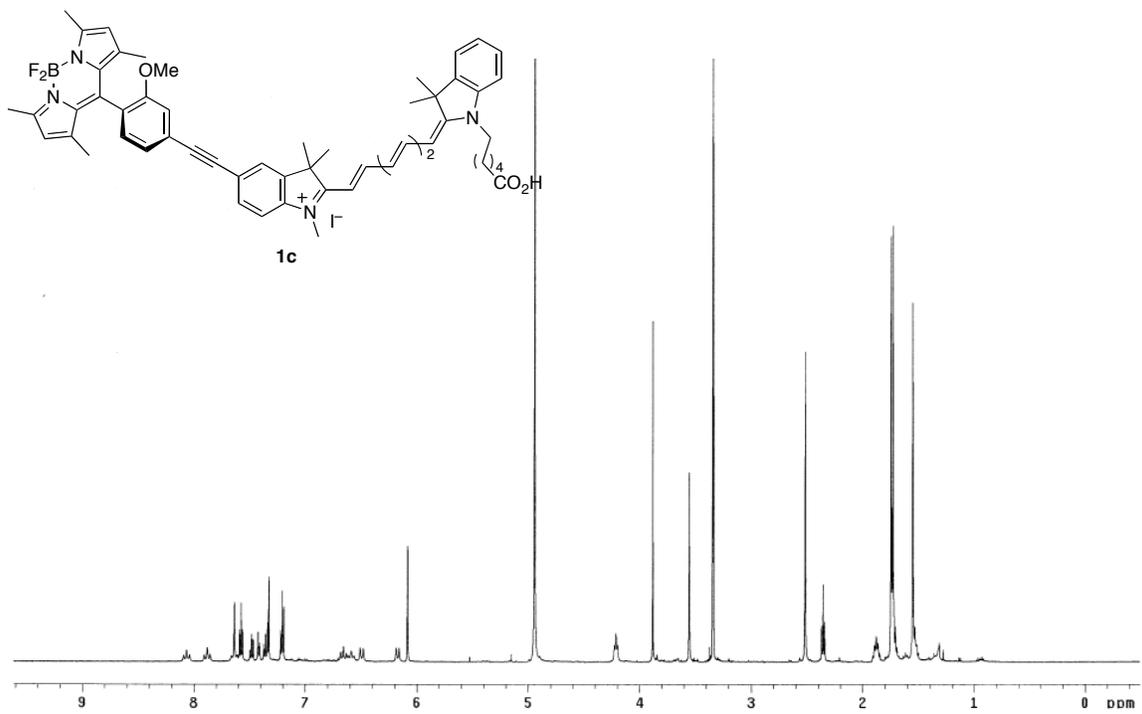
To a solution of TMS-protected BODIPY **6** (500 mg, 1.1 mmol) in THF (20 mL) was added TBAF (1.3 mL, 1.3 mmol, 1 M in THF) dropwise at -78 °C. After stirring at -78 °C for 5 min, the reaction was quenched with water (20 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with water (1 x 15 mL) and dried over Na_2SO_4 . The solvents was concentrated under the reduced pressure and the residue purified by short flash chromatography eluting with 3 % EtOAc/hexanes to afford product **D** as an orange solid (388 mg, 92 %). R_f 0.4 (20 % EtOAc/hexanes). ^1H NMR (500 MHz, CDCl_3) δ 7.24 (dd, 1H, $J = 7.7, 1.0$ Hz), 7.107 (d, 1H, $J = 7.7$ Hz), 7.105 (d, 1H, $J = 1.0$ Hz), 5.97 (s, 2H), 3.78 (s, 3H), 3.18 (s, 1H), 2.55 (s, 6H), 1.45 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.2, 155.2, 142.4, 137.7, 131.2, 129.6, 125.4, 124.9, 124.3, 121.0, 114.6, 83.0, 78.2, 55.7, 14.6, 14.0; MS (MALDI) m/z 378.28 (M) $^+$.



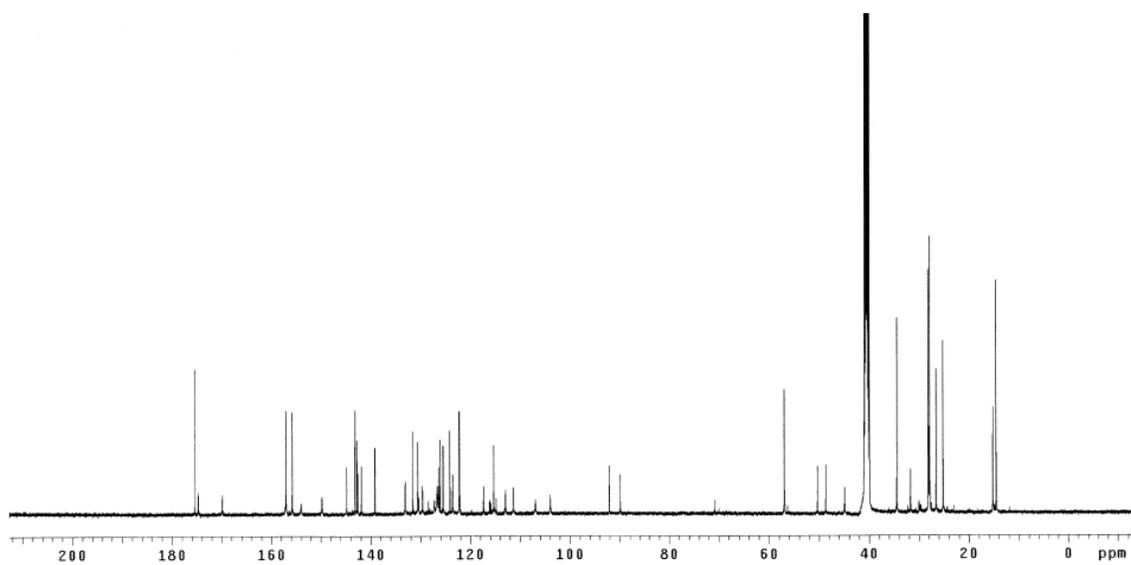
¹H NMR (CD₃OD)



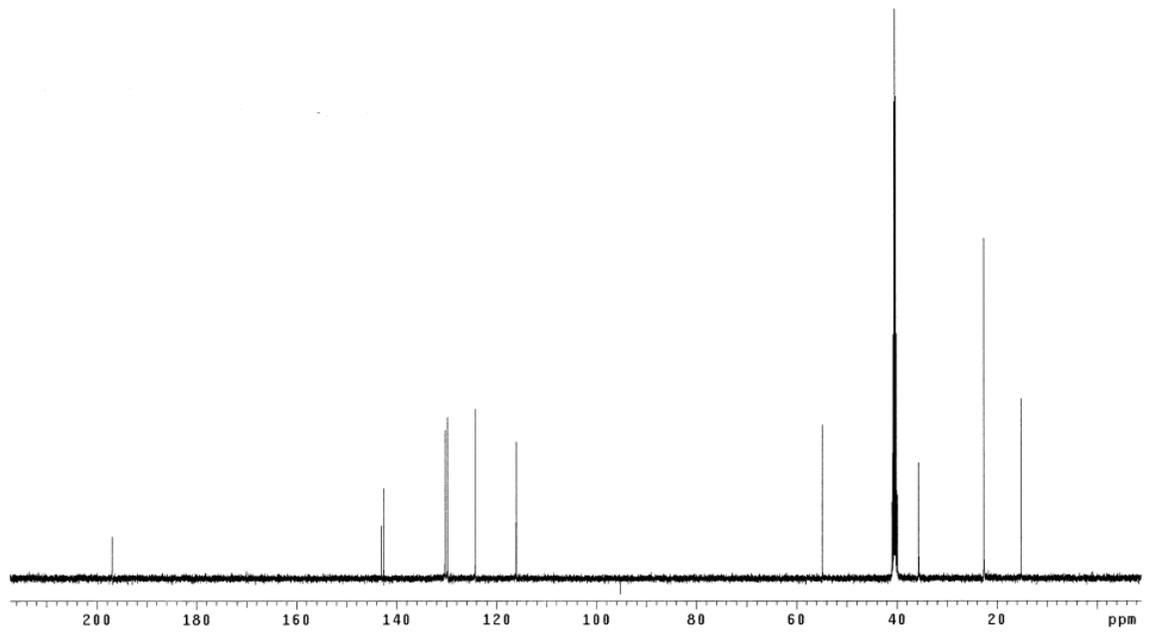
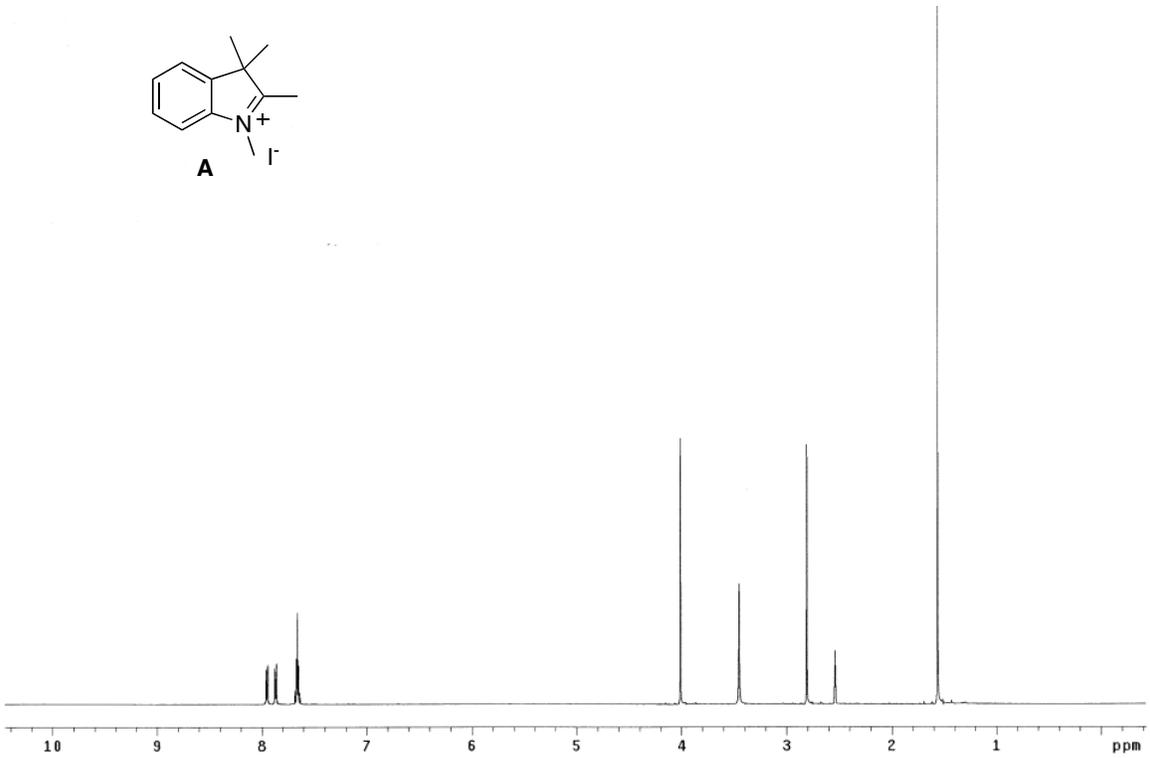
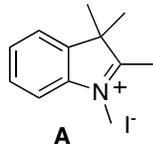
¹³C NMR (CD₃OD)

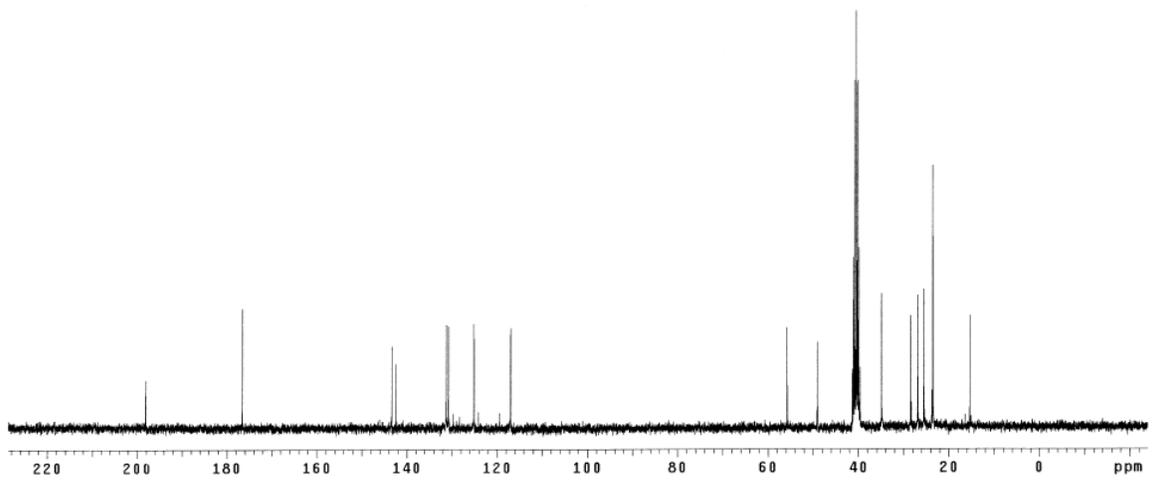
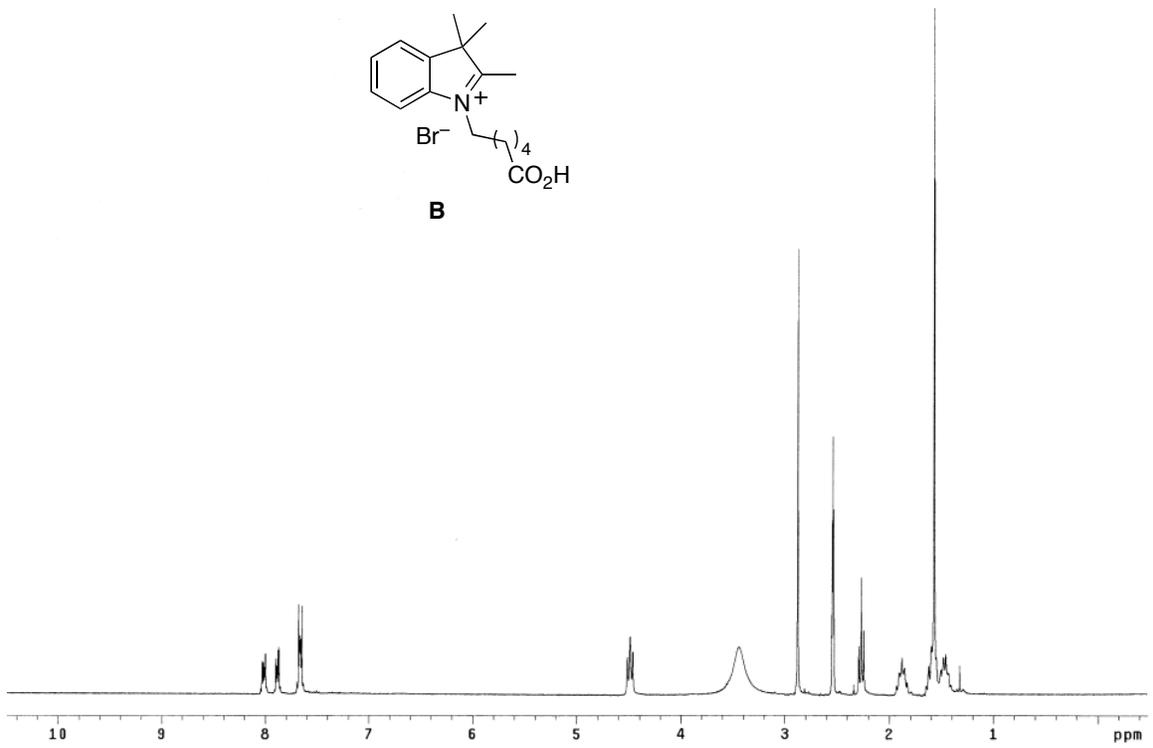
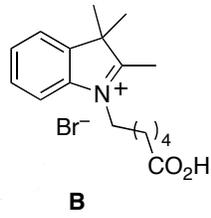


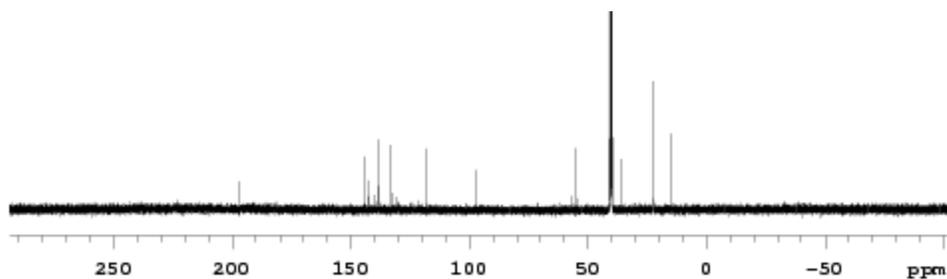
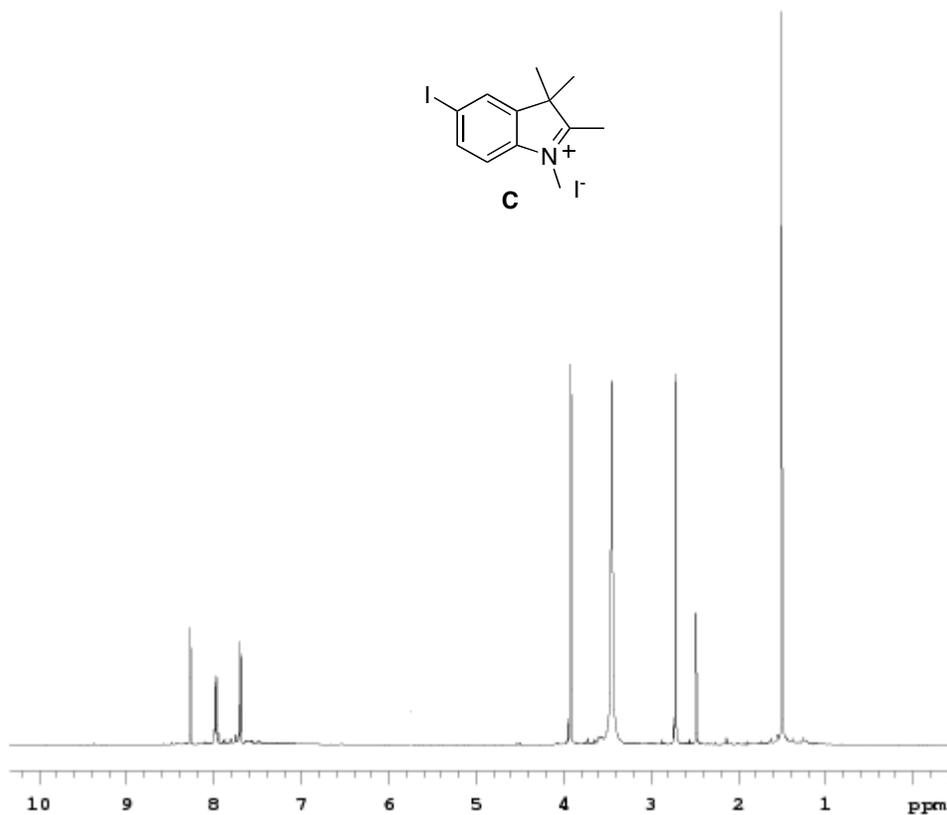
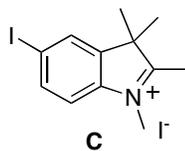
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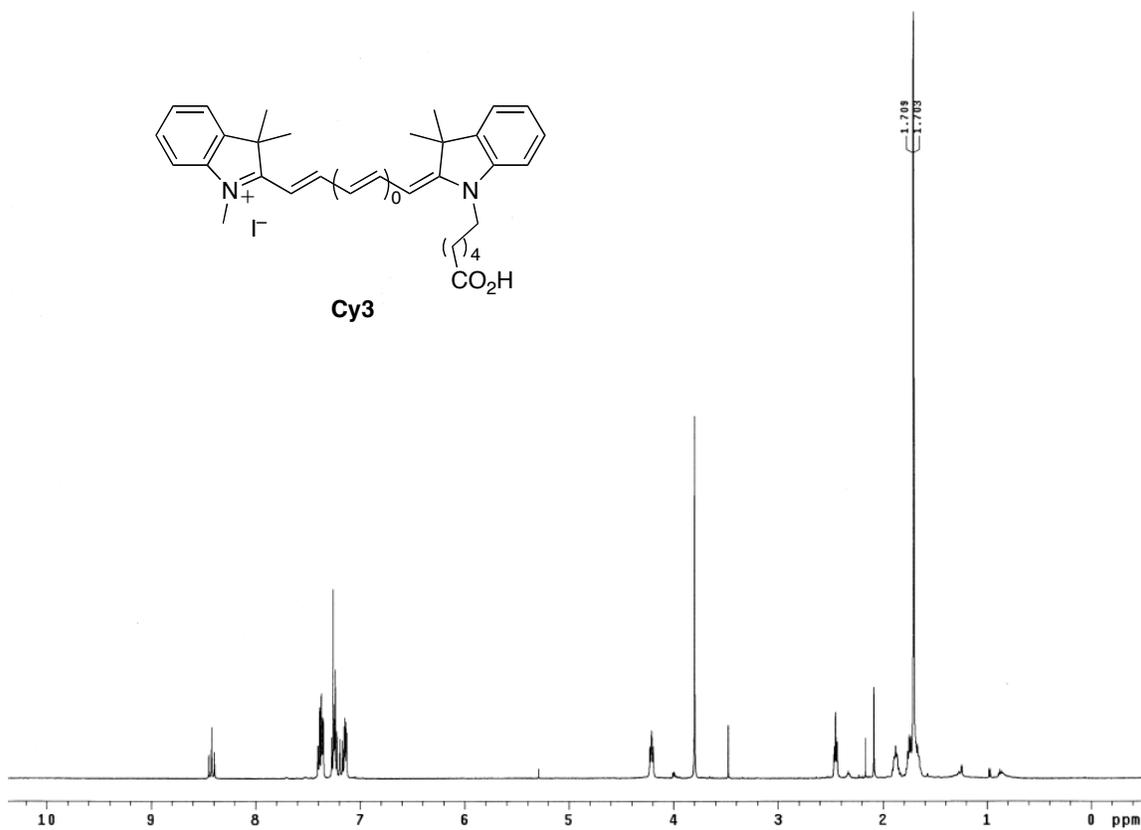
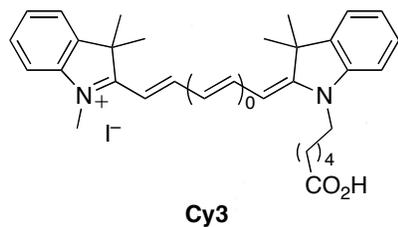


¹³C NMR (DMSO-*d*₆)

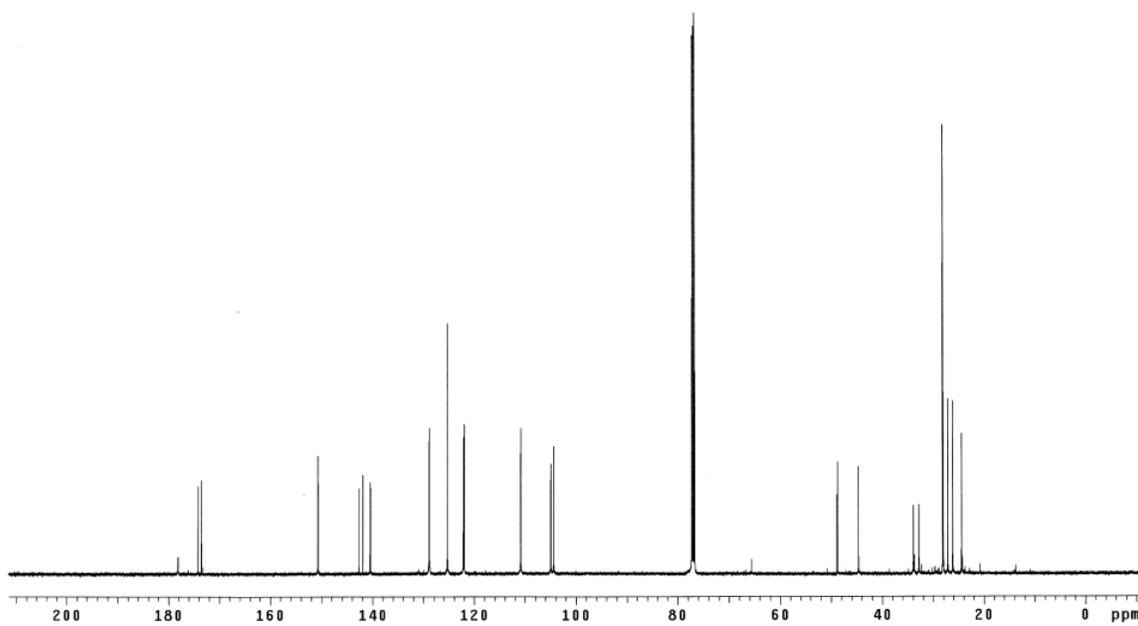




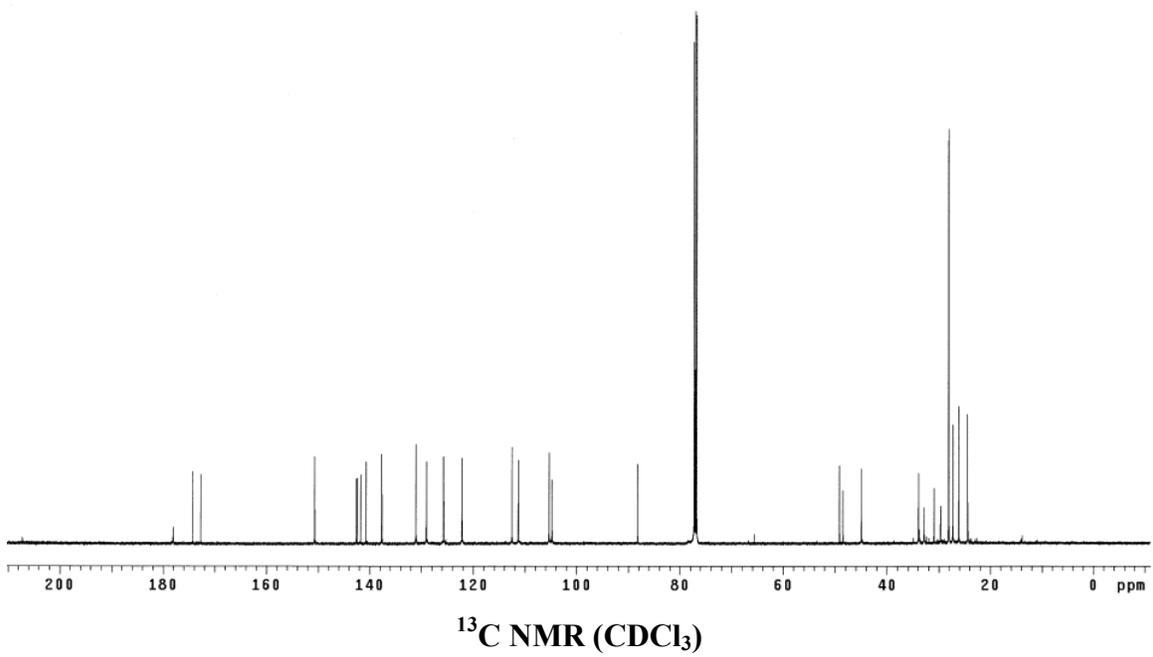
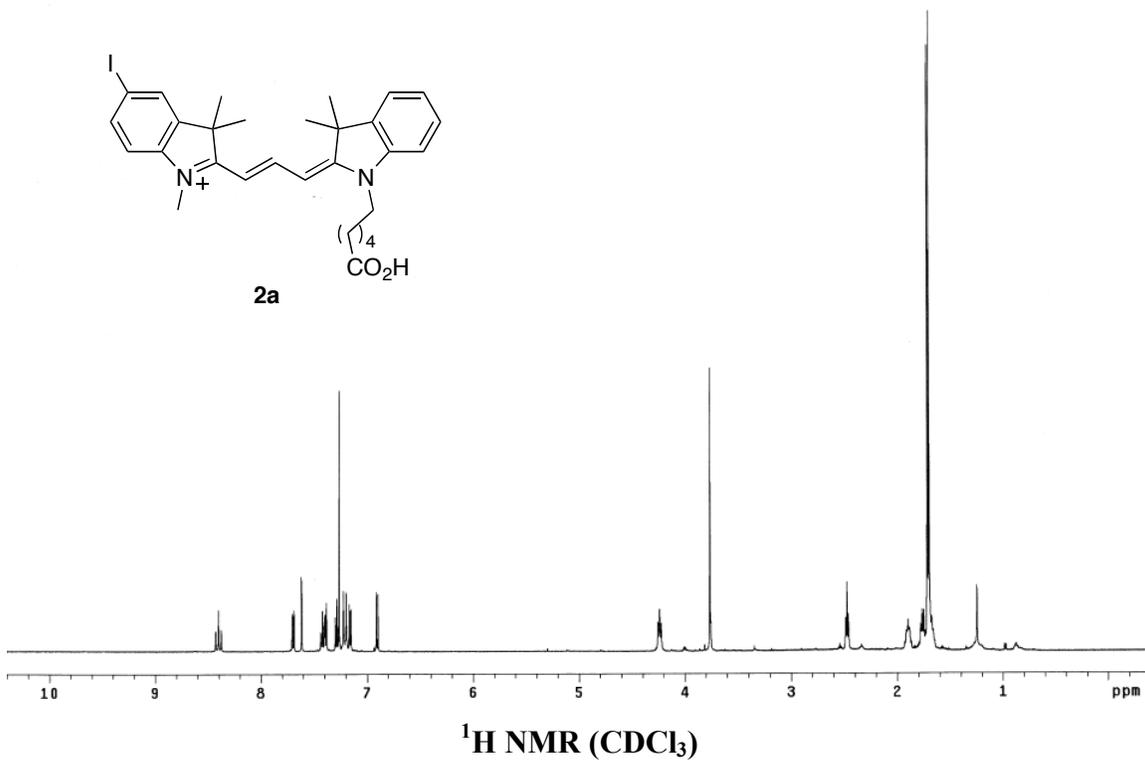
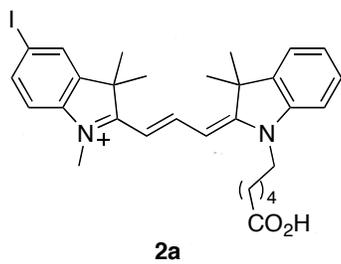


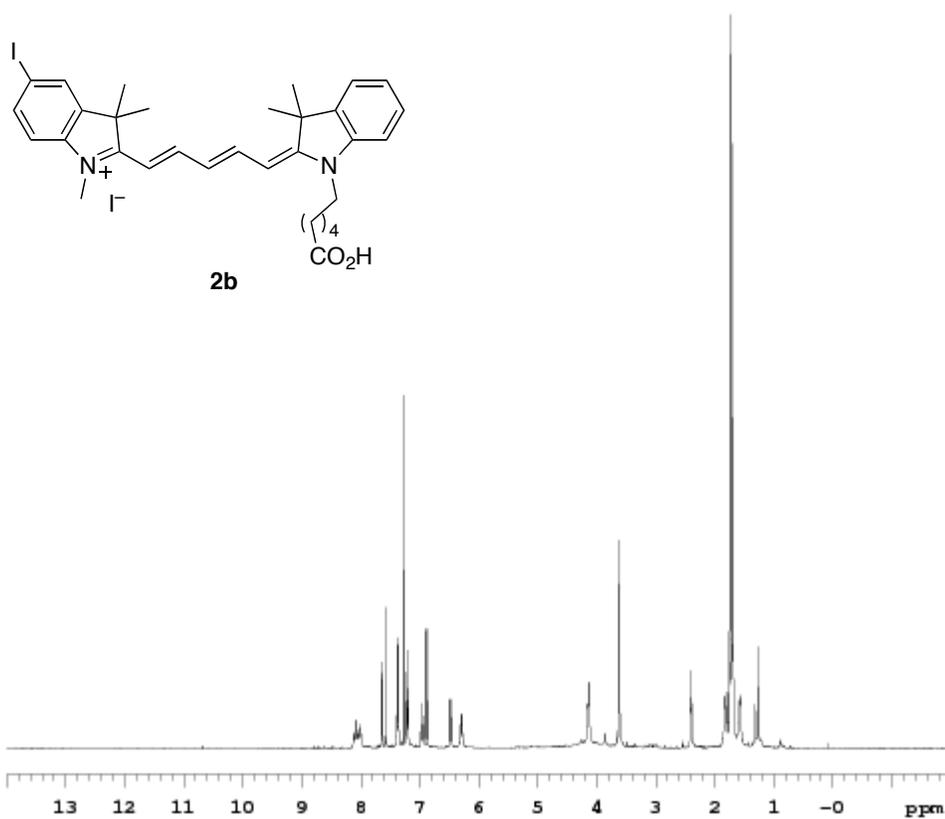


¹H NMR (CDCl₃)

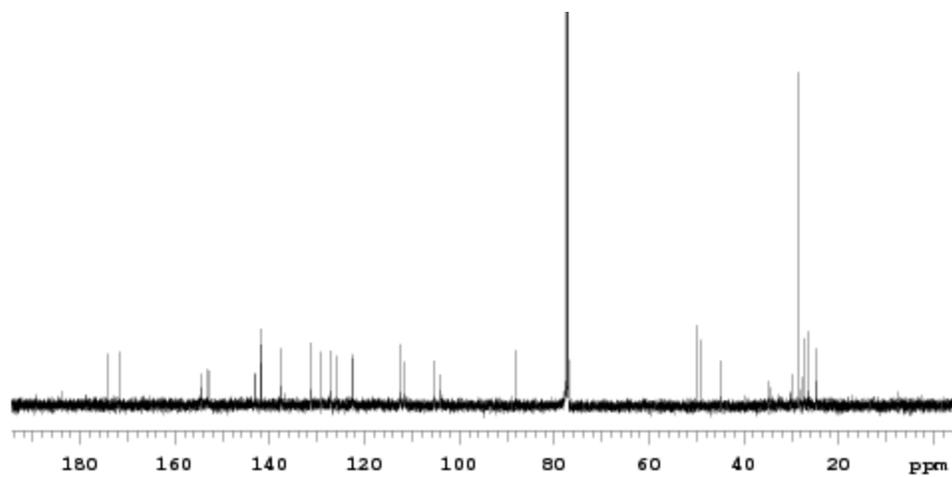


¹³C NMR (CDCl₃)

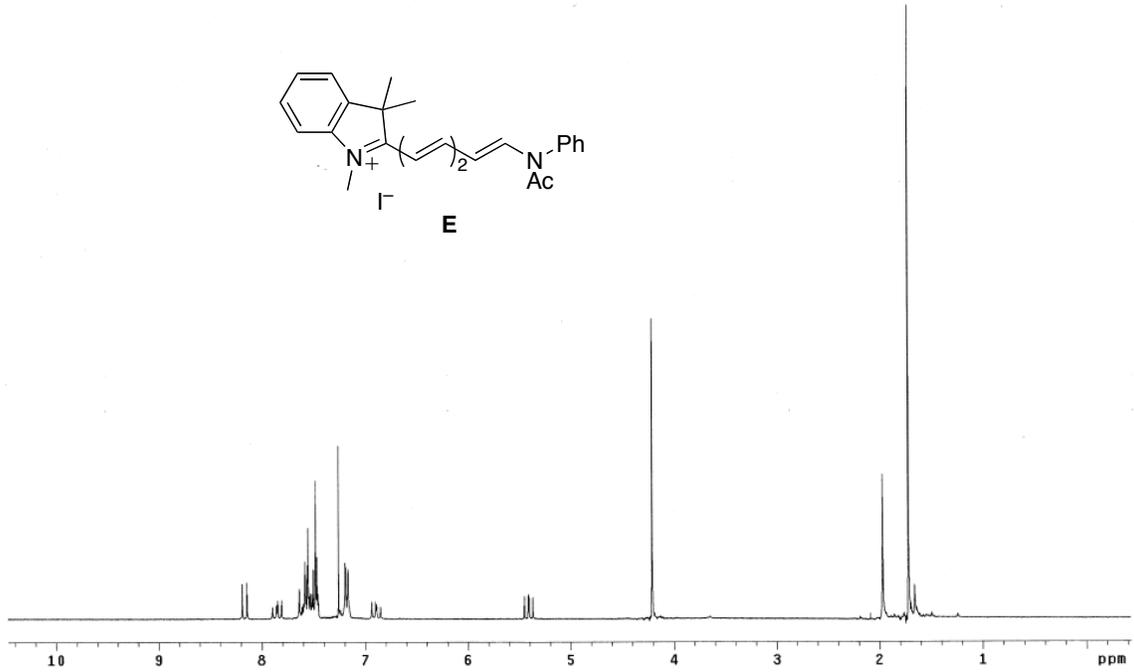
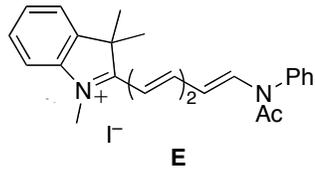




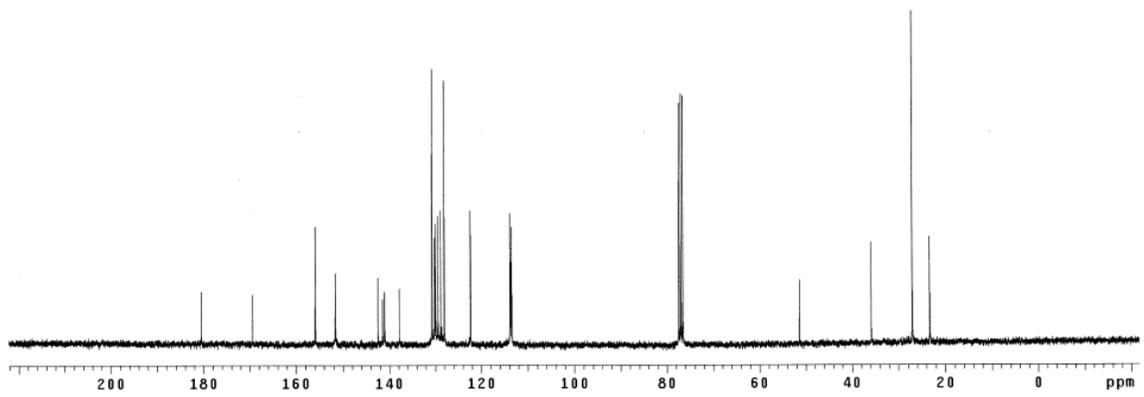
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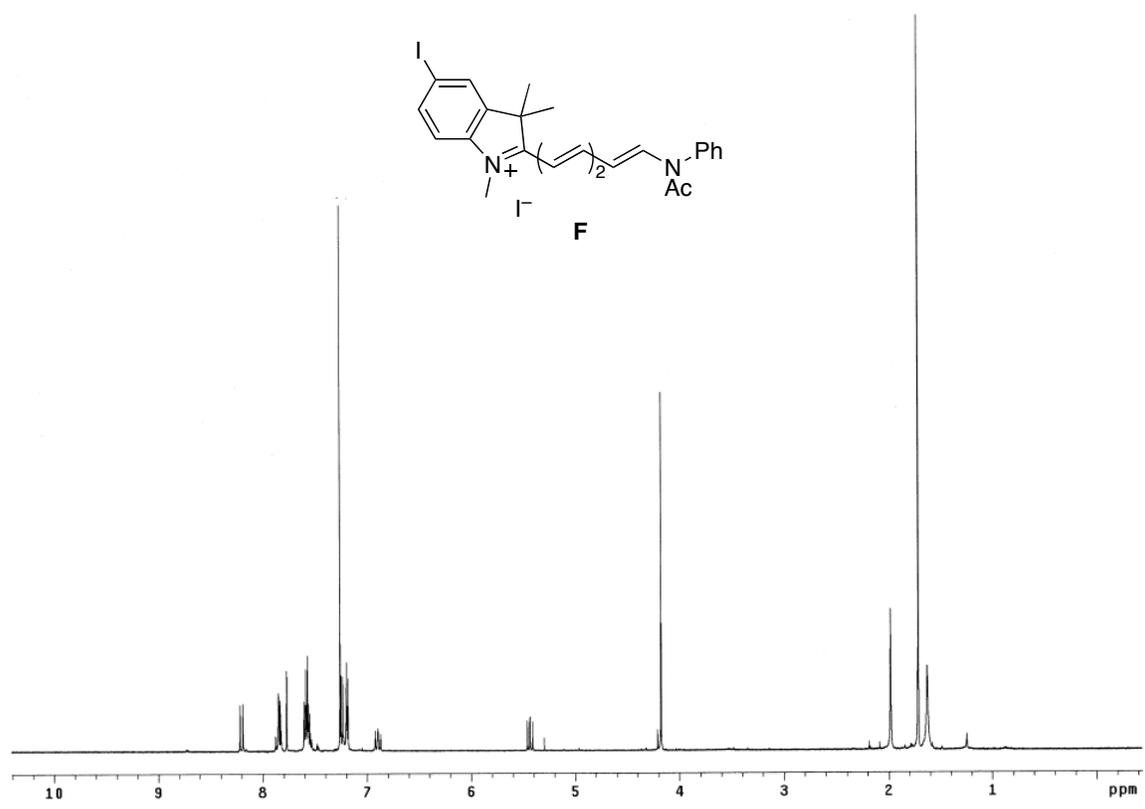
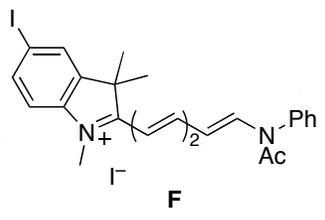
^{13}C NMR (CDCl_3)



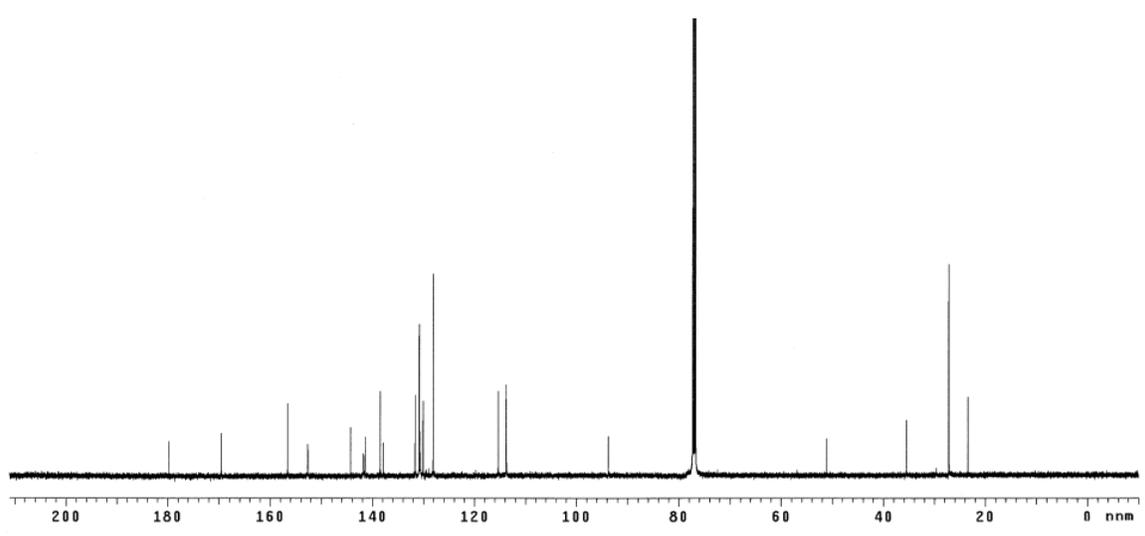
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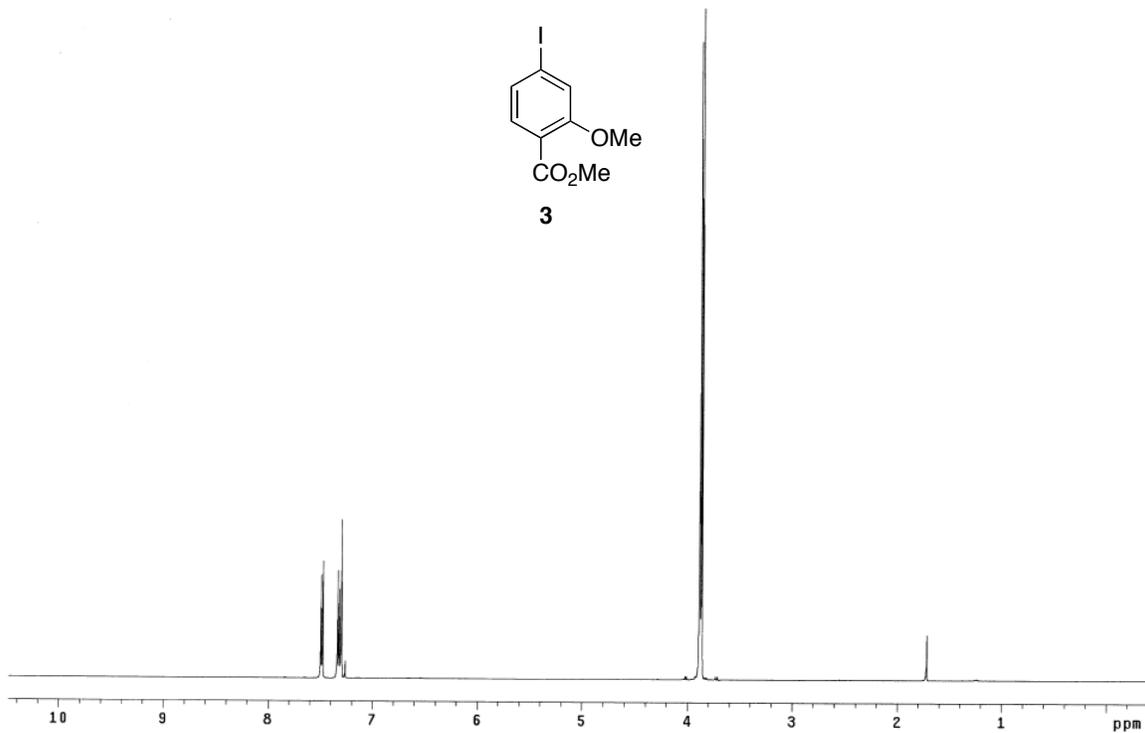
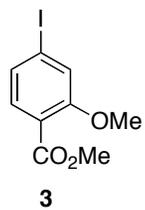
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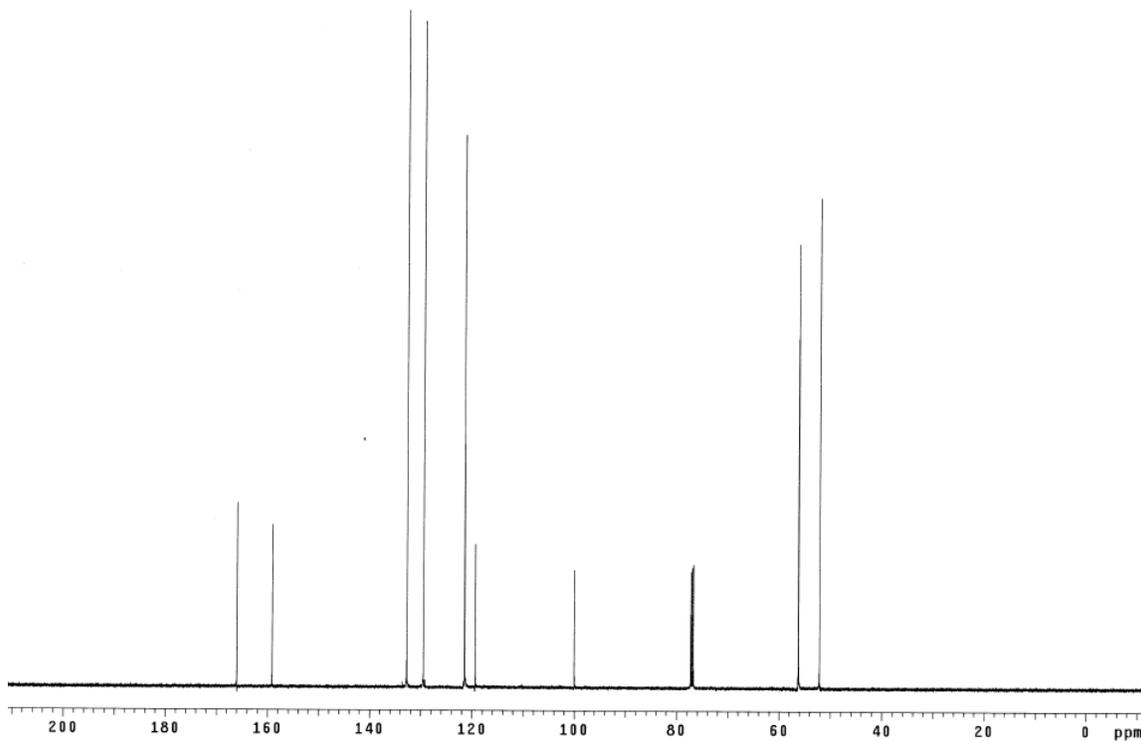
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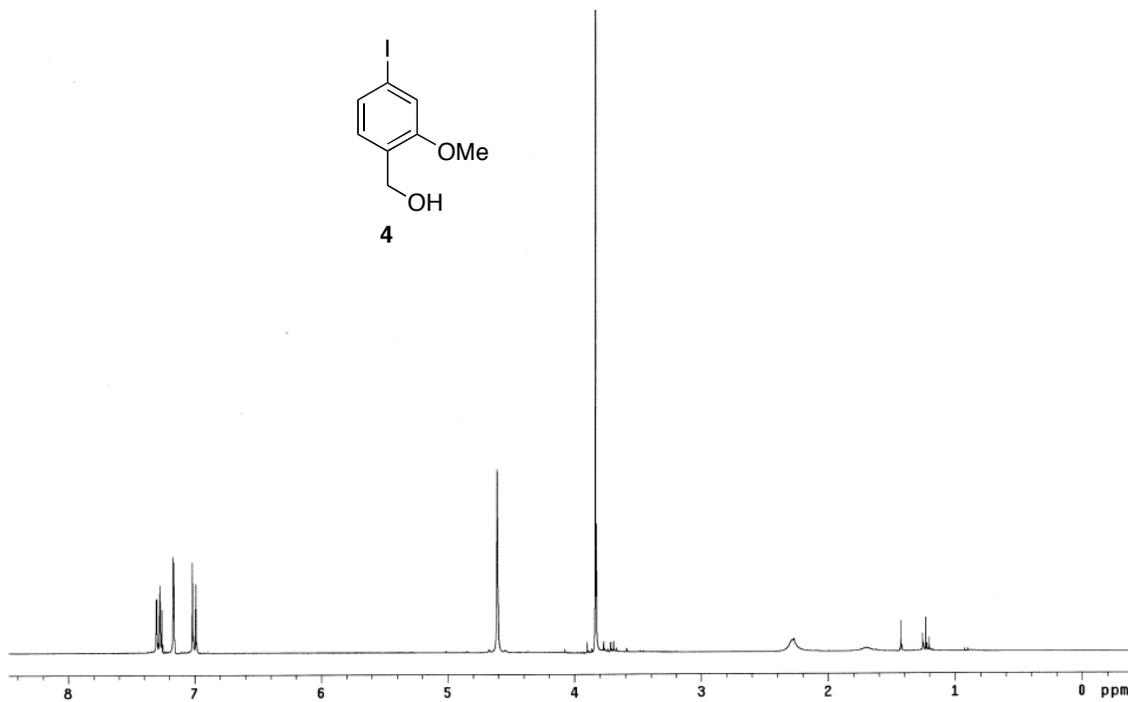
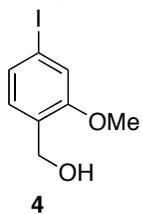
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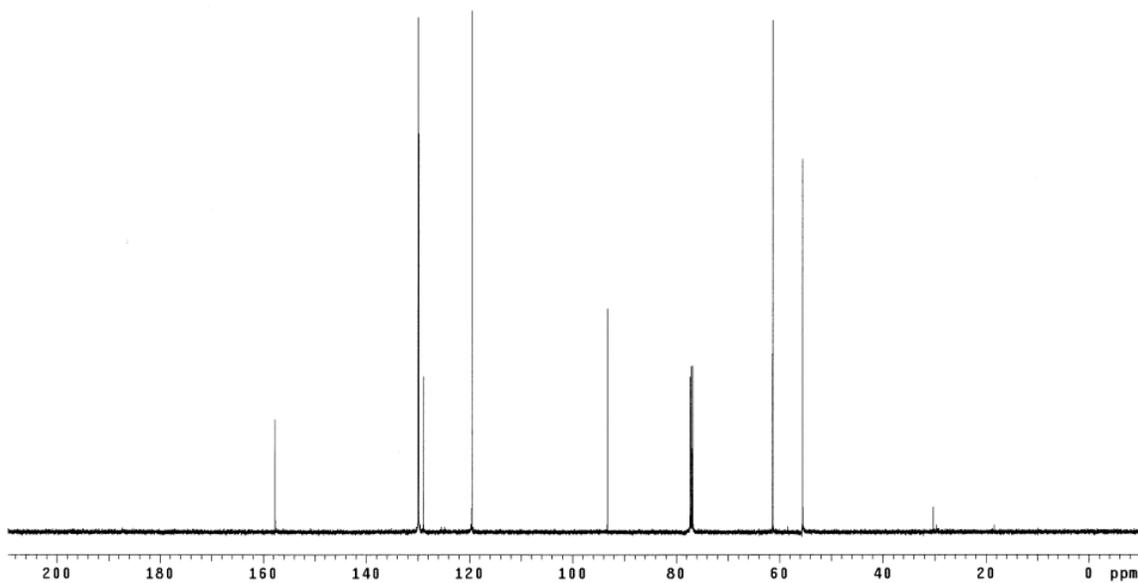
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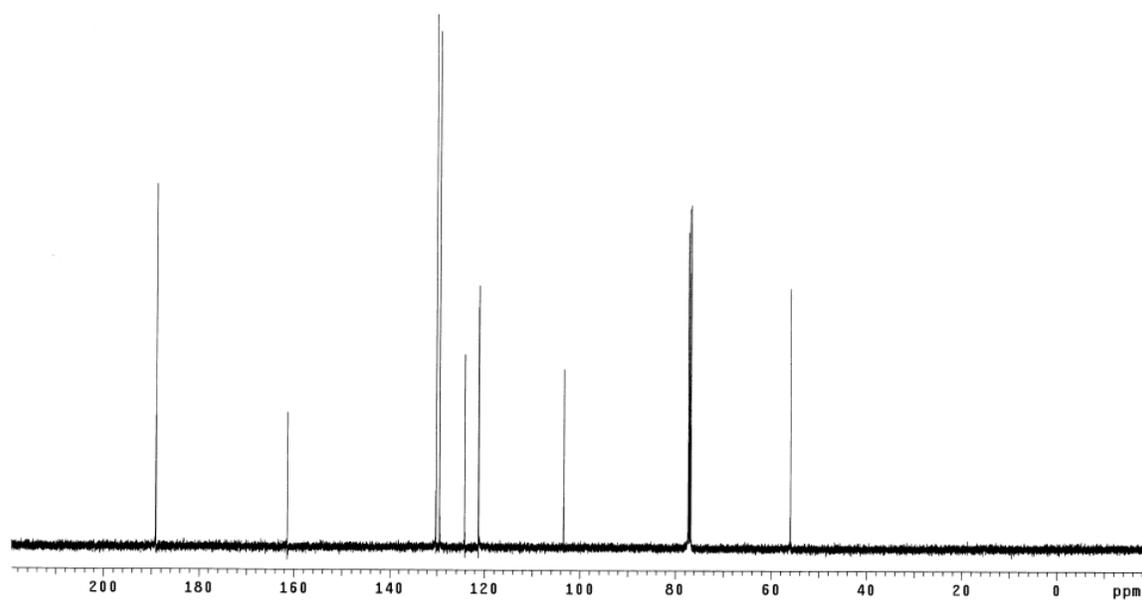
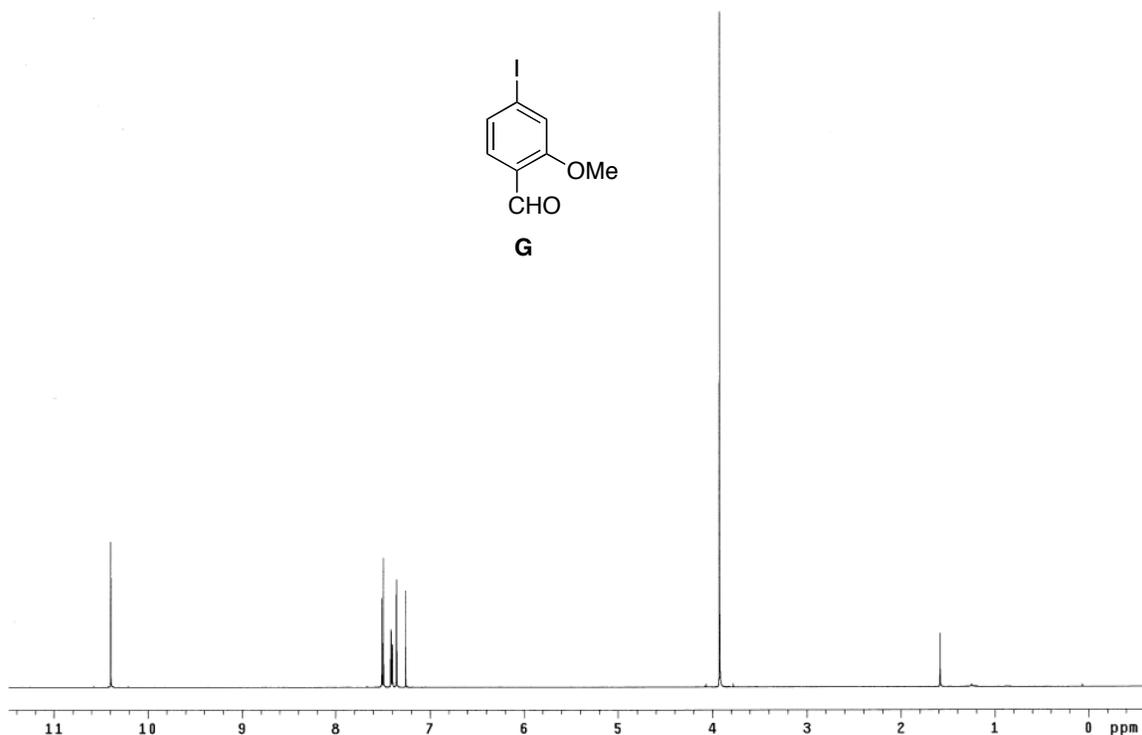
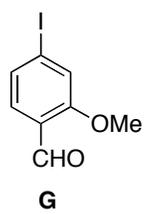
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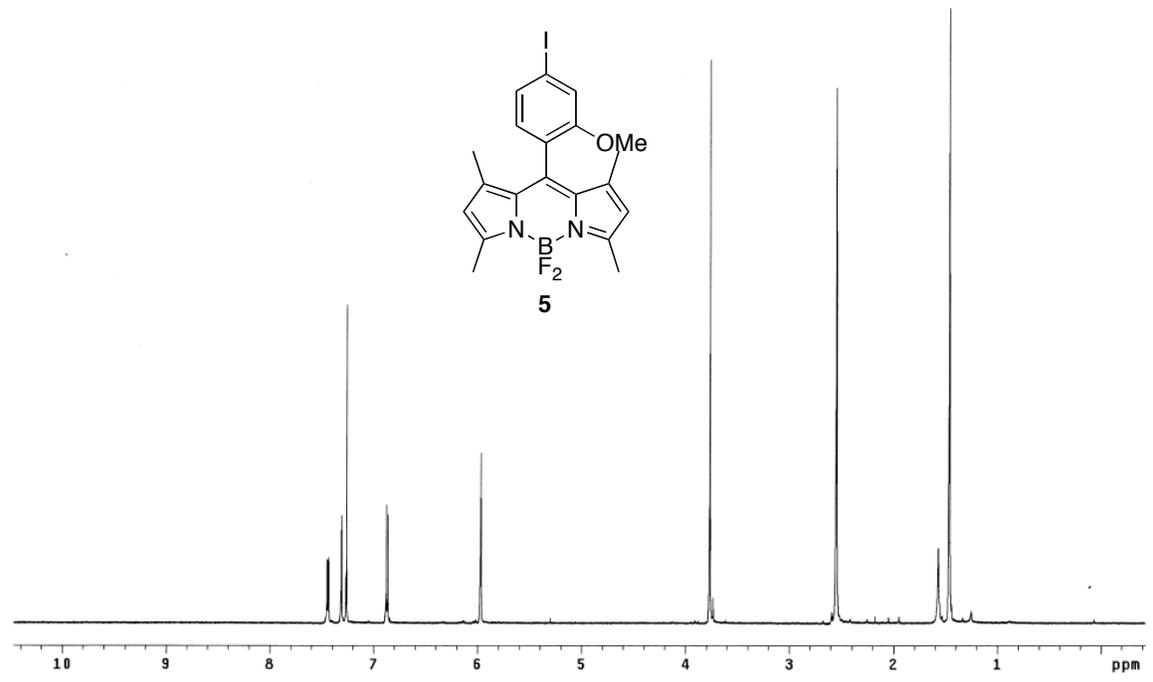
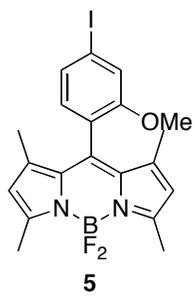


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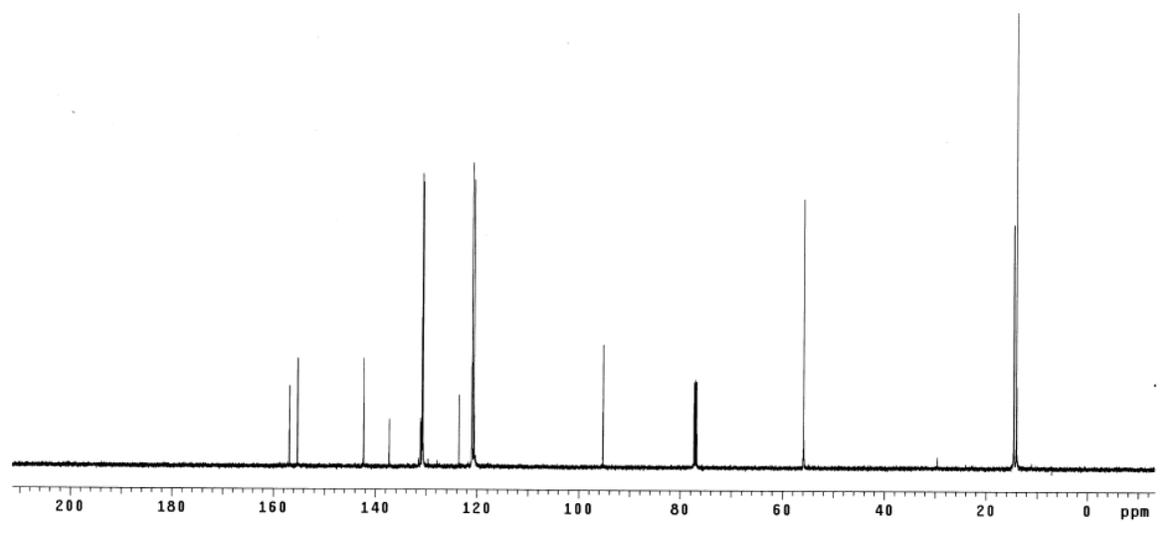


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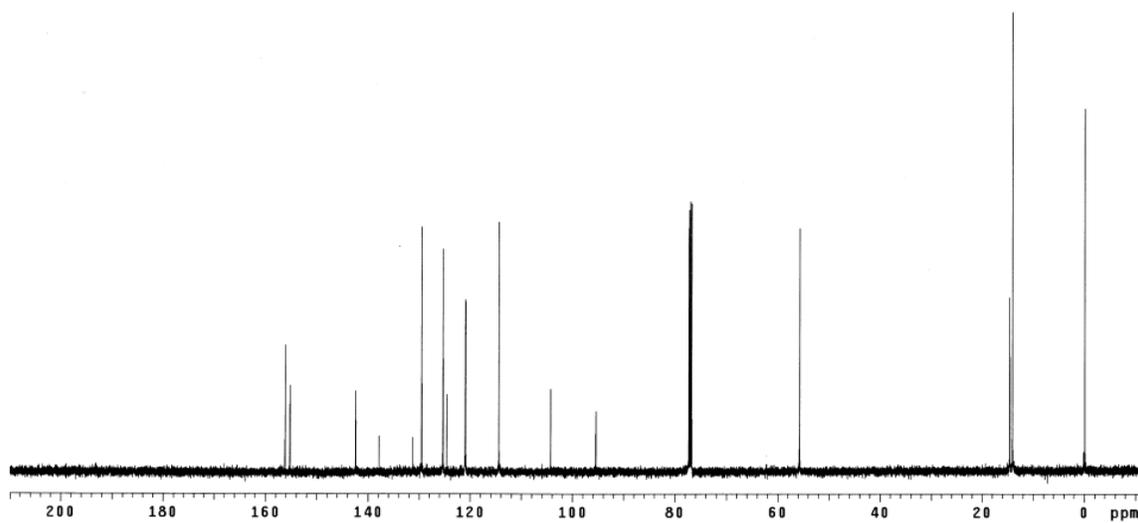
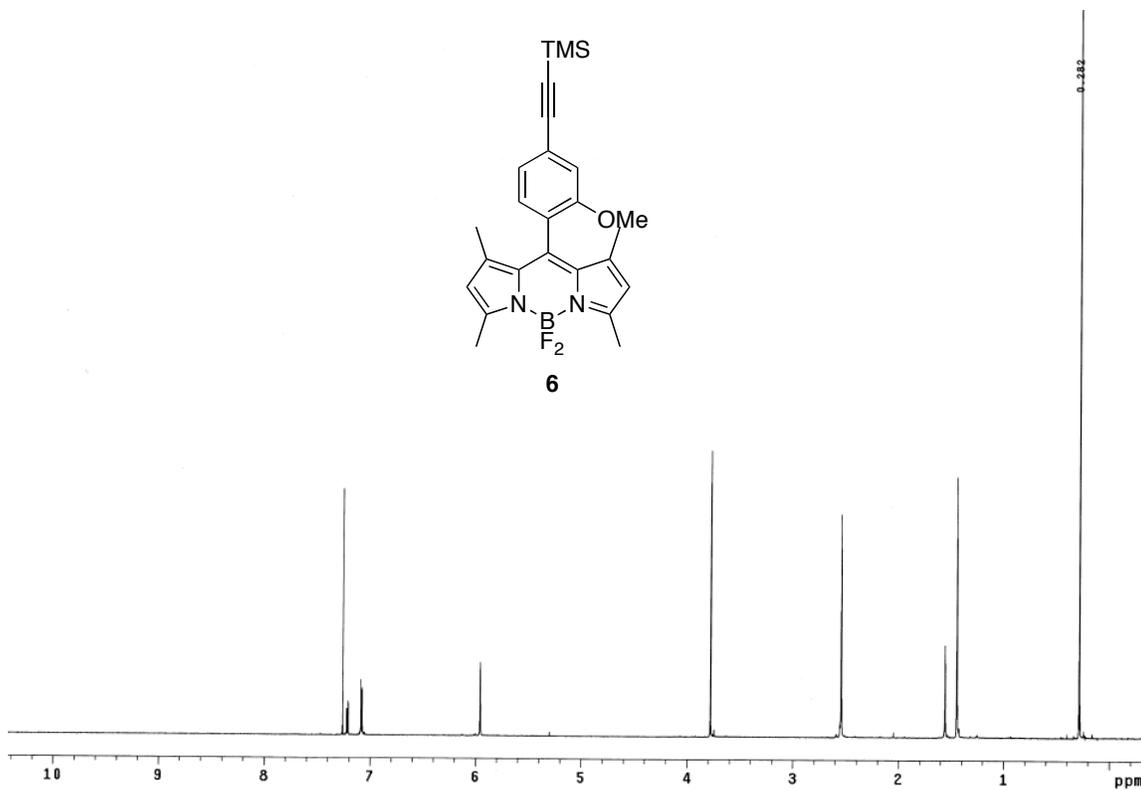
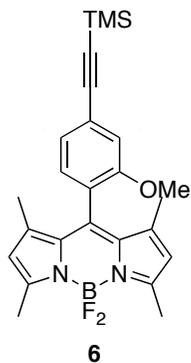


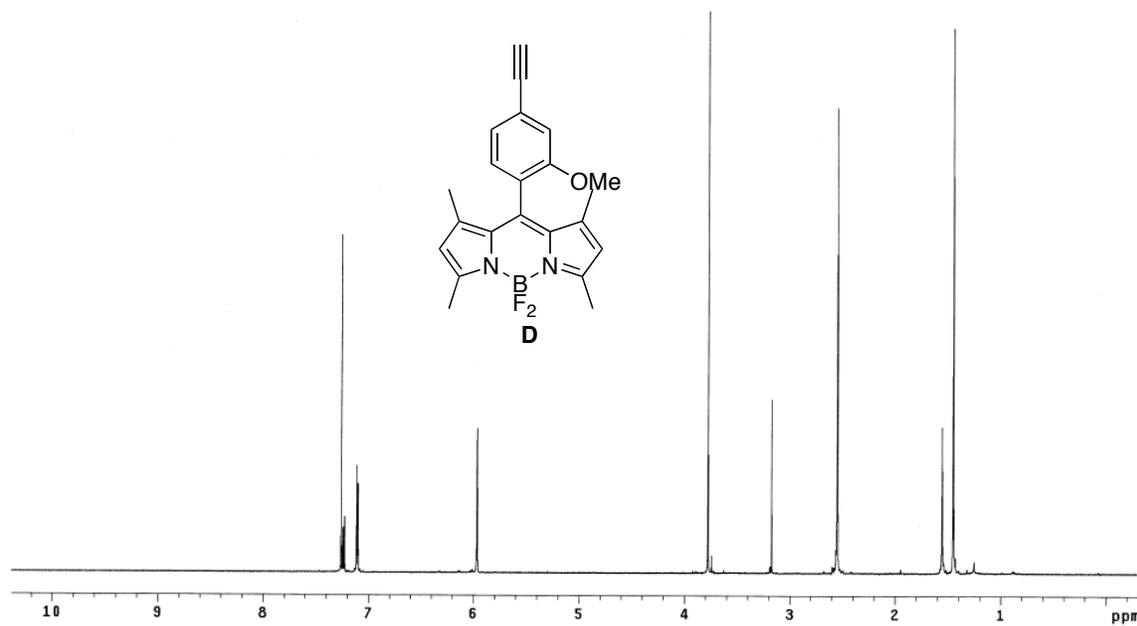


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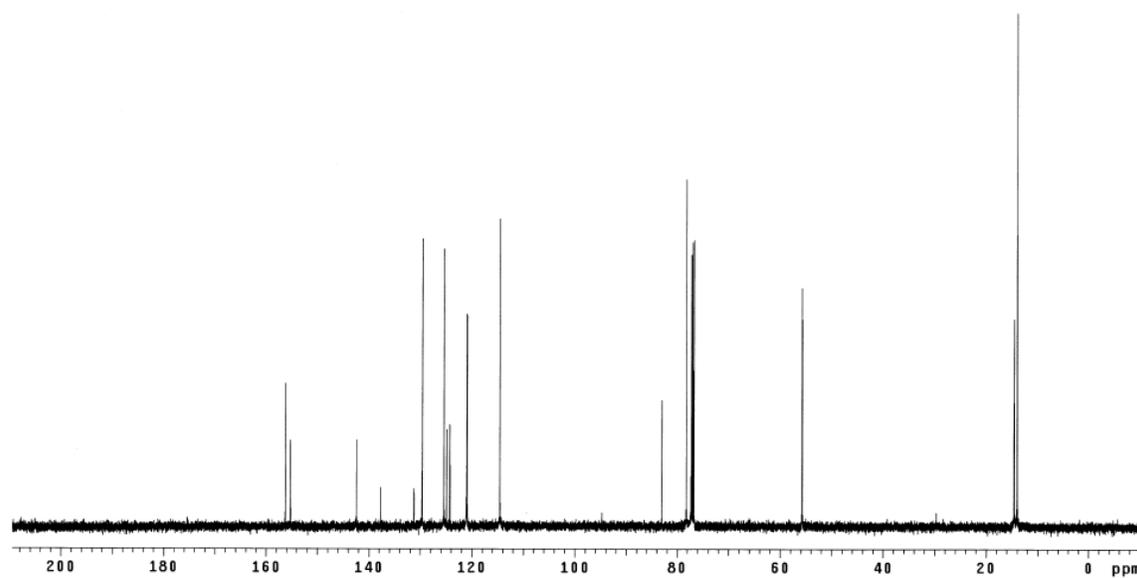


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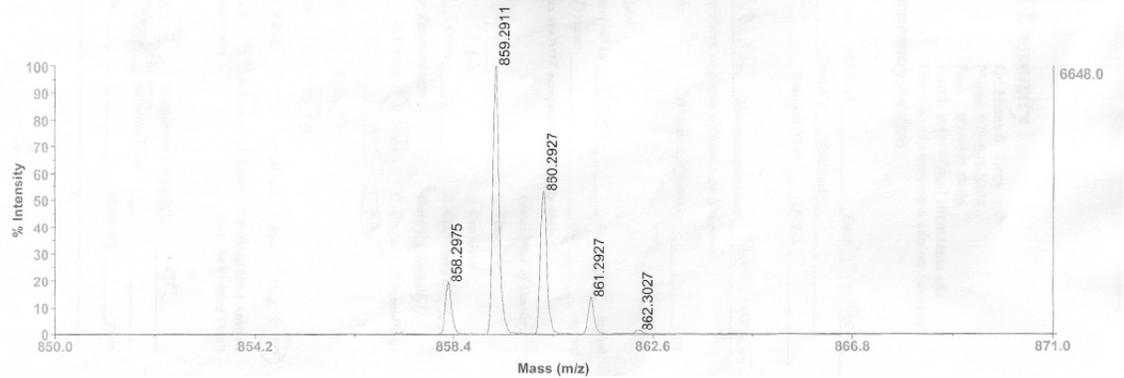
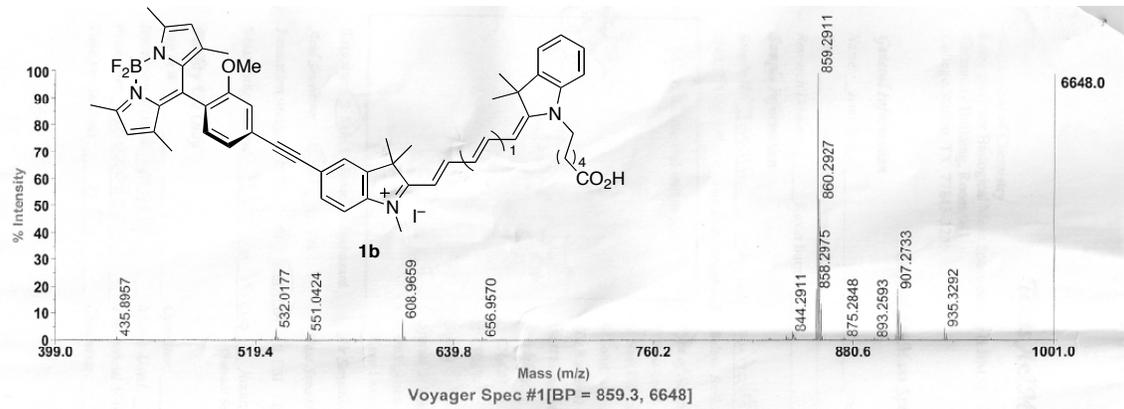
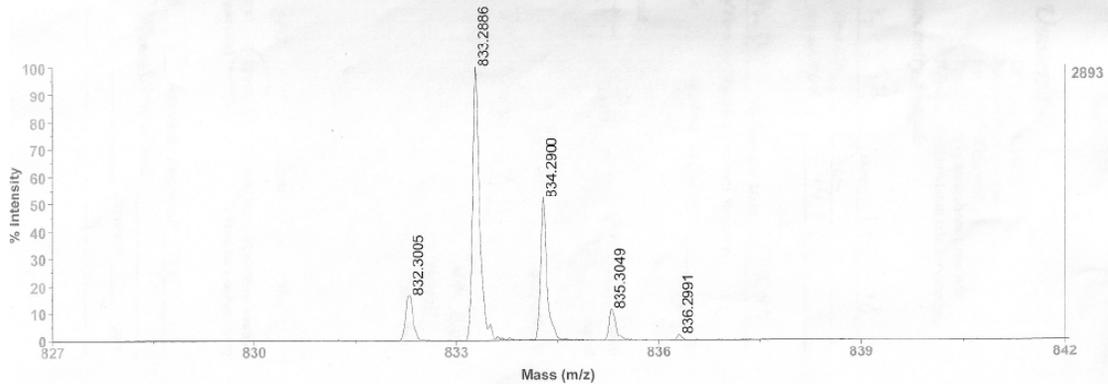
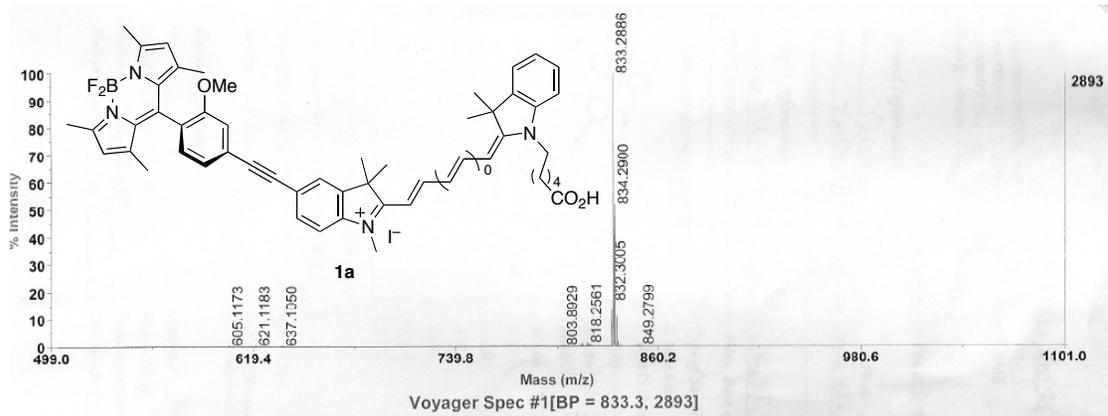


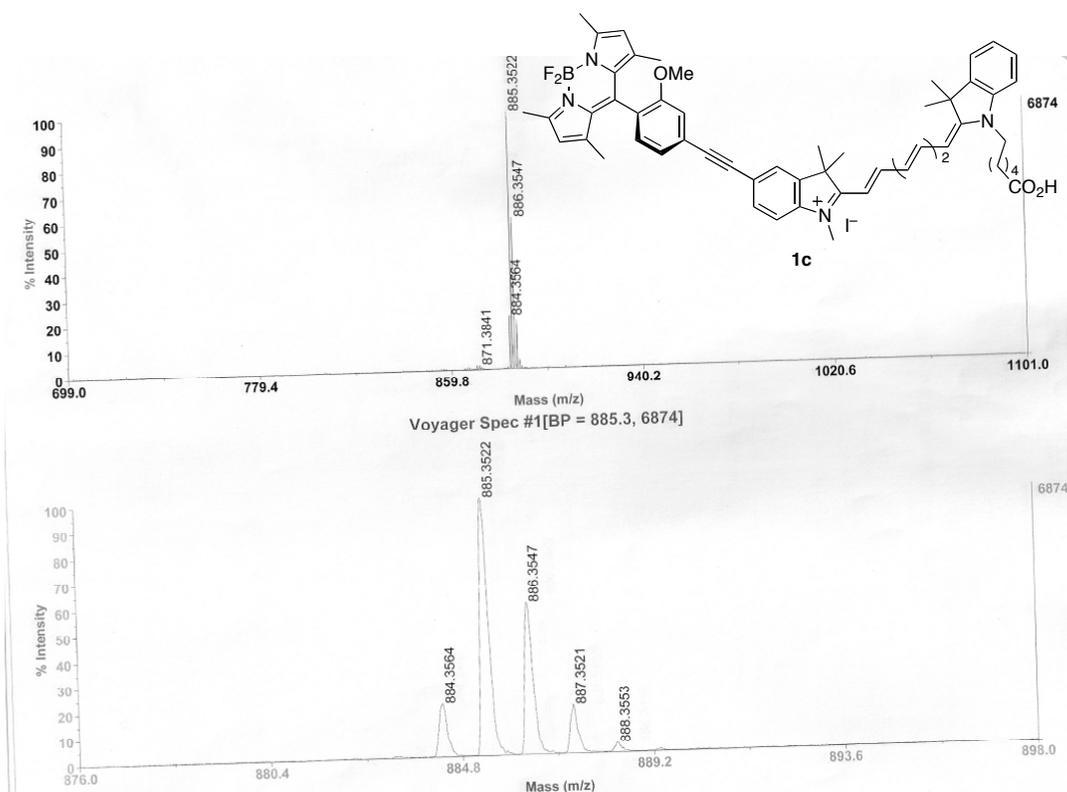
^1H NMR (CDCl_3)



^{13}C NMR (CDCl_3)

Mass Spectra for Cassettes 1,2,3





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