

# SUPPORTING INFORMATION

## Energy transfer dyads based on Nile Red

Jiney Jose, Yuichiro Ueno, Juan C. Castro, Lingling Li, and Kevin Burgess\*

*Department of Chemistry, Texas A & M University, Box 30012, College Station, TX 77842, USA.*

Tel: +1 979 845-4345; Fax: +1 979 845-8839; E-mail: burgess@tamu.edu

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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. IR spectra were recorded on a Bruker Tensor 27 spectrometer.

$^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded on a Varian 300 (300 MHz  $^1\text{H}$ ; 75 MHz  $^{13}\text{C}$ ) or Varian 500 (500 MHz  $^1\text{H}$ ; 125 MHz  $^{13}\text{C}$ ) spectrometer at room temperature. Chemical shifts were reported in ppm relative to the residual  $\text{CDCl}_3$  ( $\delta$  7.26 ppm  $^1\text{H}$ ;  $\delta$  77.16 ppm  $^{13}\text{C}$ ),  $\text{CD}_3\text{OD}$  ( $\delta$  3.31 ppm  $^1\text{H}$ ;  $\delta$  49.0 ppm  $^{13}\text{C}$ ),  $\text{DMSO}-d_6$  ( $\delta$  2.54 ppm  $^1\text{H}$ ;  $\delta$  39.52 ppm  $^{13}\text{C}$ ) or acetone- $d_6$  ( $\delta$  2.05 ppm  $^1\text{H}$ ;  $\delta$  29.84 and 206.26 ppm  $^{13}\text{C}$ ). Coupling constants ( $J$ ) were reported in Hertz. Trichloro-fluoro-methane ( $\text{CFCl}_3$ ,  $\delta$  0.00 ppm  $^{19}\text{F}$ ) was used a standard for fluorine NMR.

## Photophysical Properties and Determination of Quantum Yields

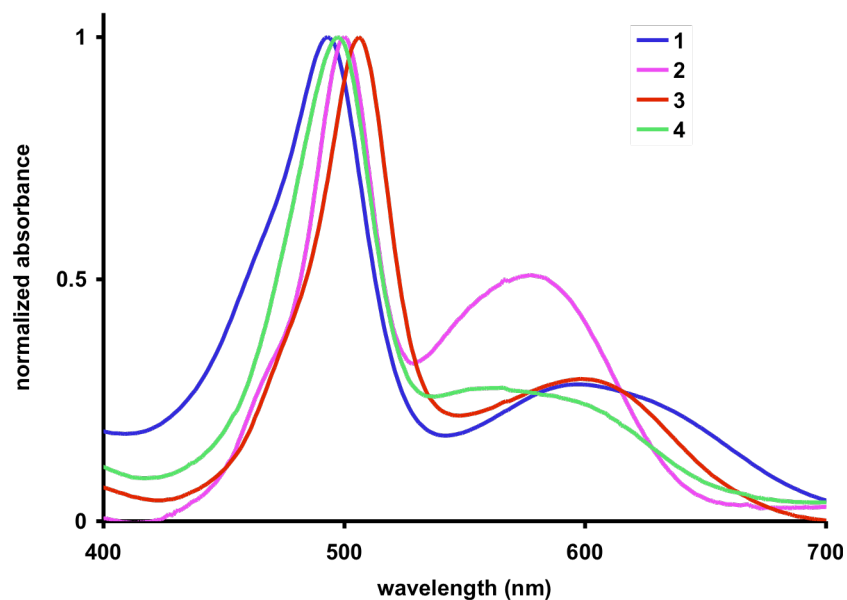
Steady-state fluorescence spectroscopic studies were performed on a Cary Eclipse fluorometer. The slit width was 5 nm for both excitation and emission. The relative quantum yields of the samples were obtained by comparing the area under the corrected emission spectrum of the test sample with that of a standard dye.<sup>1</sup> The quantum efficiencies of fluorescence were obtained from three measurements with the following equation:

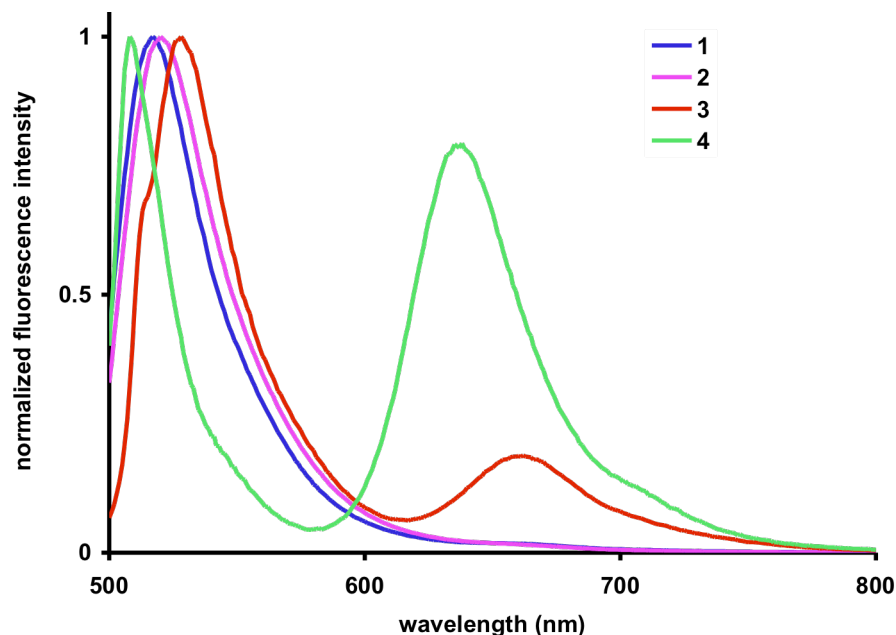
$$\Phi_x = \Phi_{st} (I_x/I_{st}) (A_{st}/A_x) (\eta_x^2/\eta_{st}^2)$$

Where  $\Phi_{st}$  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  $\eta$  is the refractive index of the solvent used, measured on a pocket refractometer from ATAGO<sup>®</sup>.  $X$  subscript denotes unknown, and  $st$  denotes standard.<sup>2</sup>

### Photophysical Properties of dyads 1-4 in pH 7.4 phosphate buffer.

**a**



**b**

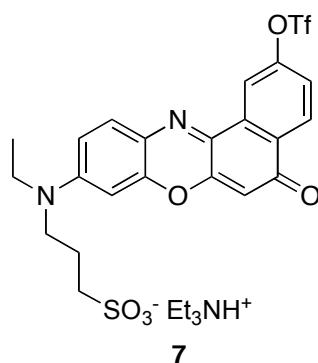
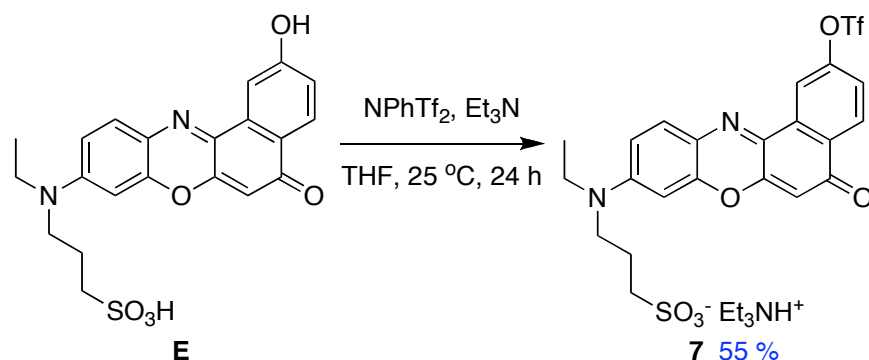
**Figure S1.** Normalized absorbance (a) and fluorescence (b) spectra of dyads **1 - 4** in pH 7.4, 0.1 M phosphate buffer (at  $10^{-6}$  and  $10^{-7}$  M for absorbance and fluorescence measurements, respectively). All dyads excited at their respective donor absorption maxima. Dyad **5** was not soluble enough in water to measure absorbance and fluorescence accurately.

**Table S2.** Photophysical properties of dyads **1-4** in pH 7.4 (0.1 M sodium phosphate buffer).

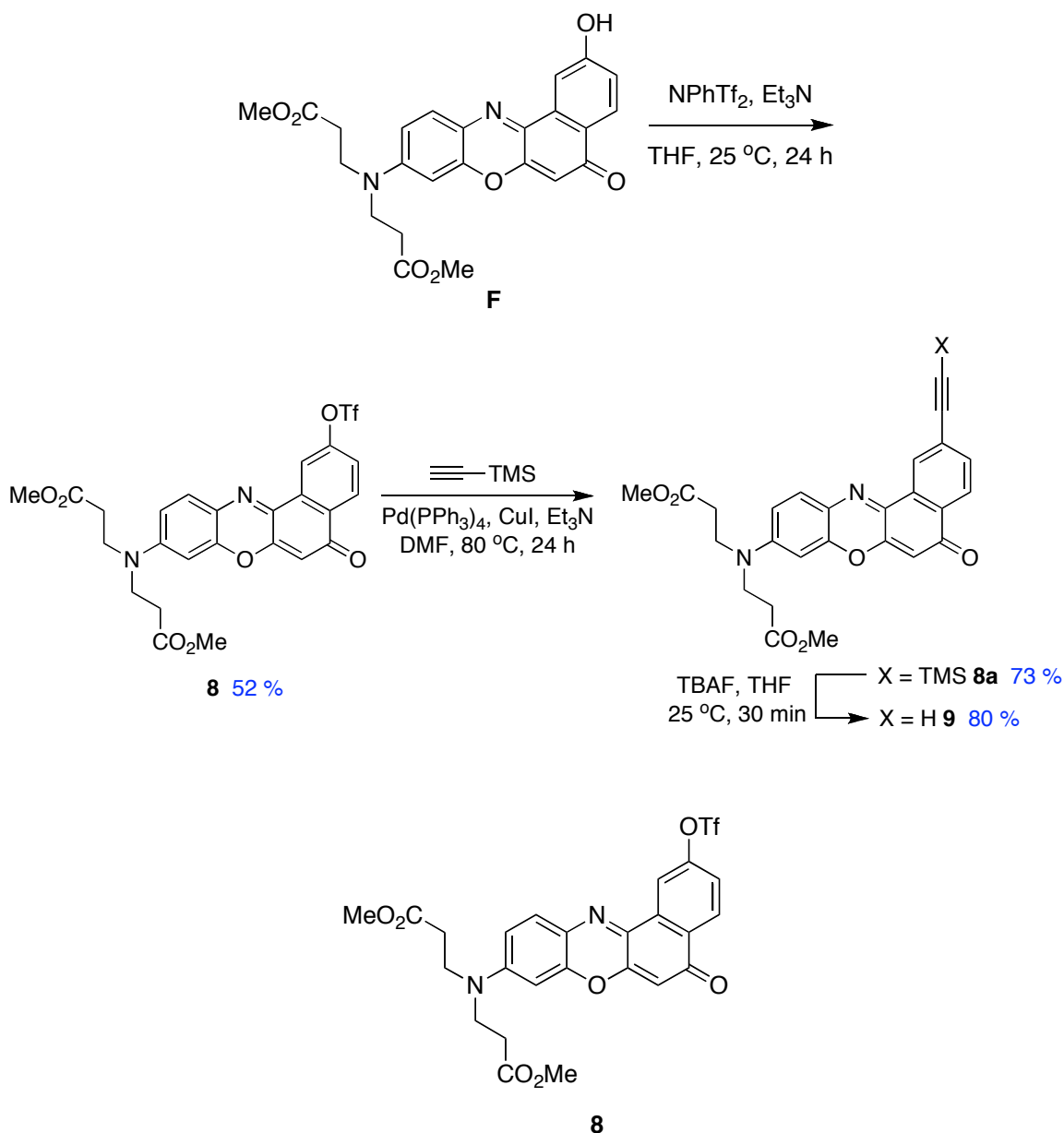
dye	$\lambda_{\text{abs}}(\text{nm})$	$\lambda_{\text{em.}}(\text{nm})$	$\Phi_{\text{D}}$	$\Phi_{\text{A}}^{\text{c}}$	E. T. E % ( $\Phi_{\text{D}}/\Phi_{\text{A}}$ )
<b>1</b>	493, 591	517	0.010 <sup>a</sup>	0.14+/-0.02	7
<b>2</b>	500, 577	520	0.008 <sup>b</sup>	0.12+/-0.01	6
<b>3</b>	506, 593	528, 662	0.016 <sup>b</sup>	0.11+/-0.03	14
<b>4</b>	497, 575	509, 637	0.10 <sup>a</sup>	0.24+/-0.01	42

$\Phi_{\text{D}}$  values correspond to excitation of dyads at the donor absorption maxima;  $\Phi_{\text{A}}$  relates to excitation of dyads at the acceptor absorption maxima. Standards used for quantum yield measurement: <sup>a</sup>fluorescein in 0.1 M NaOH ( $\Phi$ : 0.92), <sup>b</sup>rhodamine 6G in EtOH ( $\Phi$ : 0.94), <sup>c</sup>sulforhodamine in EtOH ( $\Phi$ : 1.0); quantum yields were repeated three times and averaged.

## Experimental Section

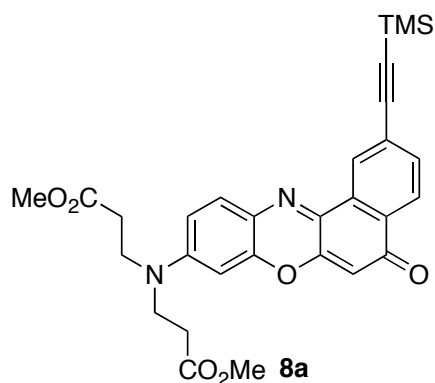


Phenyl triflamide (0.21 g, 0.60 mmol) was added gradually over a period of 10 min to a solution of **E** (0.10 g, 0.24 mmol) and triethylamine (0.13 mL, 0.96 mmol) in 5 mL dry distilled THF. The mixture was stirred at 25 °C for 24 h. Reaction mixture was diluted with EtOAc and washed with 0.1 M HCl (2 x 10 mL). The organic layer was dried over sodium sulfate and evaporated under reduced pressure and purified by flash chromatography eluting with 1/1 EtOAc/hexanes to afford **7** as a red solid (0.07 g, 55 %).  $R_f = 0.2$  (1/1 EtOAc/hexanes).  $^1\text{H NMR}$  (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  8.49 (s, 1H), 8.24 (d, 1H,  $J = 6.3$  Hz), 7.69-7.61 (br, 2H), 6.94 (dd, 1H,  $J = 6.3$  Hz,  $J = 3.2$  Hz), 6.70 (s, 1H), 6.23 (s, 1H), 3.71-3.54 (m, 4H), 3.21 (br, 6H), 2.96 (t, 2H,  $J = 7.2$  Hz), 2.19-2.10 (br, 2H), 1.32-1.29 (br, 12H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  182.0, 153.6, 152.2, 151.9, 146.7, 136.3, 134.1, 132.0, 131.2, 128.9, 125.7, 122.5, 118.2, 115.3, 111.6, 103.9, 96.8, 49.3, 49.1, 45.3(2C), 22.3, 10.9, 10.1.  $^{19}\text{F NMR}$  (282 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  104.1. **IR** (neat,  $\text{cm}^{-1}$ ) 3402, 2917, 1644; **MS** (ESI)  $m/z$  calculated for  $(\text{M})^-$  559.04 found 558.95  $(\text{M})^-$

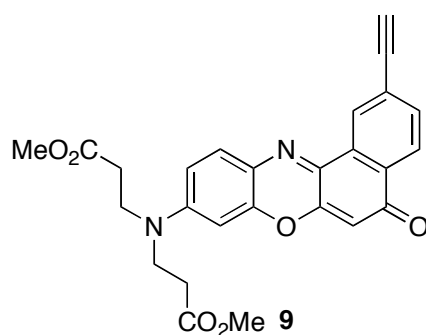


Phenyl triflamide (1.9 g, 5.5 mmol) was added gradually over a period of 10 minutes to a solution of **F** (1.0 g, 2.2 mmol) and triethylamine (1.2 mL, 8.8 mmol) in 20 mL dry distilled THF. The mixture was stirred at 25 °C for 24 h. Reaction mixture was diluted with EtOAc and washed with 0.1 M HCl (2 x 10 mL). The organic layer was dried over sodium sulfate and evaporated under reduced pressure and purified by flash chromatography eluting with 1/1 EtOAc/hexanes to afford **8** as a red solid (0.67g, 52 %).  $R_f = 0.4$  (1/1 EtOAc/hexanes)  $^1\text{H NMR}$  (300 MHz, acetone- $d_6$ )  $\delta$  8.57 (s, 1H), 8.38 (d, 1H,  $J = 8.4$  Hz), 7.79 (d, 1H,  $J = 8.4$  Hz), 7.70 (d, 1H,  $J = 9.3$  Hz), 6.98 (d, 1H,  $J = 9.3$

Hz), 6.79 (s, 1H), 6.30 (s, 1H), 3.93 (t, 4H,  $J = 7.3$  Hz), 3.67 (s, 6H), 2.78 (t, 4H,  $J = 7.3$  Hz)  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )  $\delta$  181.9, 173.1, 153.3, 152.0, 151.8, 146.3, 139.8, 135.7 (2C), 133.7, 129.1, 124.3, 123.43, 118.1(2C), 111.1, 106.8, 98.2, 60.4, 49.3, 33.43.  $^{19}\text{F}$  NMR (282 MHz, acetone- $d_6$ )  $\delta$  104.4. IR (neat,  $\text{cm}^{-1}$ ) 3421, 2938, 1638; MS (ESI)  $m/z$  calculated for ( $\text{M}^+$ ) 582.09 found 582.09 ( $\text{M}^+$ ).

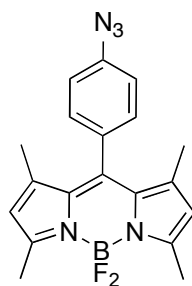


$\text{Pd}(\text{PPh}_3)_4$  (50.0 mg, 0.04 mmol),  $\text{CuI}$  (8.2 mg, 0.04 mmol) was added to a solution of **8** (200 mg, 0.4 mmol) in 5 mL of dry DMF. To the above mixture was added an excess of TMS alkyne (0.6 mL, 4.3 mmol) and triethyl amine (0.6 mL, 4.3 mmol). Reaction mixture was freeze-pump-thawed three times with nitrogen after cooling to  $-78$  °C in an acetone/dry ice bath. The acetone/dry ice bath was removed and the temperature was allowed to rise to  $25$  °C and then heated to  $80$  °C for 24 h. The reaction mixture was filtered through a sintered glass funnel and filtrate was evaporated under reduced pressure. Purified by flash chromatography using 30 % EtOAc/hexanes to obtain **8a** (125 mg, 73 %) as a red solid.  $R_f = 0.6$  (30 % EtOAc/hexanes)  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ )  $\delta$  8.62 (s, 1H), 8.14 (d, 1H,  $J = 8.1$  Hz), 7.72 (d, 1H,  $J = 6.6$  Hz), 7.66 (d, 1H,  $J = 8.1$  Hz), 6.90 (d, 1H,  $J = 6.6$  Hz), 6.70 (s, 1H), 6.22 (s, 1H), 3.89 (t, 4 H,  $J = 7.2$  Hz), 3.62 (s, 6H), 2.77 (t, 4H,  $J = 7.2$  Hz), 0.31 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )  $\delta$  181.7, 171.9, 152.4, 151.2, 146.9, 139.7, 132.9, 131.4, 127.1, 126.2, 125.9, 125.3, 110.7, 105.6, 104.3, 100.1, 97.39, 51.3, 47.0, 31.8, 0.7. (2C are missing). MS (ESI)  $m/z$  calculated for ( $\text{M}^+$ ) 530.19 found 530.14 ( $\text{M}^+$ ).



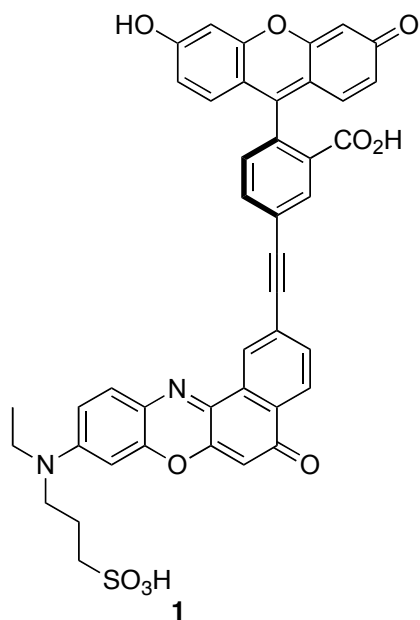
TBAF (1.0 M solution in THF, 0.6 mL, 0.6 mmol) was added to a solution of **8a** (100 mg, 0.17 mmol) in 10 mL of dry distilled THF at  $-78\text{ }^{\circ}\text{C}$ . The reaction mixture was allowed to warm to  $25\text{ }^{\circ}\text{C}$  for 30 min. Reaction mixture was diluted with EtOAc and excess TBAF was removed by washing with water (2 x 10 mL). The organic layer was dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by flash chromatography using 50 % EtOAc/ hexanes to yield **9** (63 mg, 80 %) as a red solid.  $R_f = 0.4$  (1/1 EtOAc/hexanes)  $^1\text{H NMR}$  (300 MHz,  $\text{CD}_3\text{OD}/\text{CDCl}_3$ )  $\delta$  8.80 (s, 1H), 8.22 (d, 1H,  $J = 8.0$  Hz), 7.72 (d, 1H,  $J = 8.0$  Hz), 7.68 (br, 1H), 6.83 (d, 1H,  $J = 6.5$  Hz), 6.60 (s, 1H), 6.49 (s, 1H), 3.71 (s, 6H), 3.60 (t, 4H,  $J = 6.5$  Hz), 3.53 (s, 1H), 2.72 (t, 4H,  $J = 6.5$  Hz).  $^{13}\text{C NMR}$  (75 MHz,  $\text{DMSO}-d_6$ )  $\delta$  181.8, 172.4, 153.8, 152.8, 147.5, 137.9, 133.2, 132.4, 131.8, 131.4, 127.2, 126.3(2C), 125.6, 125.4(2C), 105.4, 84.2, 83.4, 52.2, 39.1, 34.8; **MS (ESI)**  $m/z$  calculated for  $(\text{M}+\text{H})^+$  459.15 found 459.15  $(\text{M}+\text{H})^+$ .



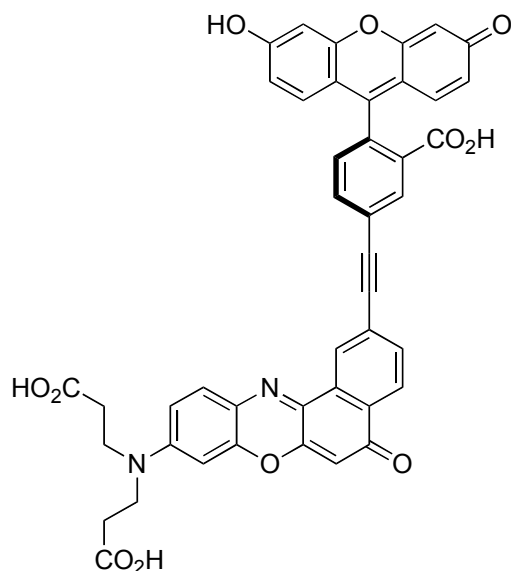


**6**

Nitro BODIPY **D** (100.0 mg, 0.27 mmol) and hydrazine (0.2 mL) along with 10 % Pd/C (38.0 mg, 0.36 mmol) were dissolved in EtOH (4 mL) and refluxed for 30 min. The reaction mixture was cooled to 25 °C and filtered through celite to remove Pd/C and any solid impurities. The filtrate obtained was then evaporated under reduced pressure and purified by flash column chromatography using 1/1 EtOAc/hexanes as eluent. The yellowish orange solid (54.0 mg) obtained was dissolved in 1/1 HCl (1.0 M)/MeOH (3 mL) and cooled to 0 °C for 10 min. Sodium nitrite (31.0 mg, 0.44 mmol) in H<sub>2</sub>O (0.5 mL) was added dropwise over 5 min and stirred at 0 °C for 1 h. Sodium azide (57.0 mg, 0.88 mmol) in water (1 mL) was added and the reaction mixture stirred for further 1 h at 25 °C. The solvent was evaporated and crude product purified using flash chromatography eluting with 30 % EtOAc/hexanes to yield **6** as a yellowish orange solid (47.0 mg, 38 %)  $R_f = 0.6$  (30 % EtOAc/hexanes). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.25 (br, 2H), 7.15 (br, 2H), 5.98 (s, 2H), 2.56 (s, 6H), 1.41 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 155.7, 142.9, 141.0, 140.6, 131.5, 129.6, 121.4, 119.7, 119.6, 14.6 (2C); MS (ESI) m/z calculated for (M+ Li)<sup>+</sup> 372.17 found 372.18.



Compound **7** (40.0 mg, 0.08 mmol), **A** (38.0 mg, 0.12 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (8.0 mg, 0.008 mmol), copper(I)iodide (1.4 mg, 0.08 mmol) and triethylamine (0.10 mL, 0.8 mmol) were dissolved in 4 mL dry distilled DMF. The solution was freeze-pump-thawed three times with nitrogen after cooling to -78 °C in an acetone/dry ice bath. The acetone/dry ice bath was removed and the temperature was allowed to rise to 25 °C and then heated to 130 °C for 12 h. The solution was concentrated *in vacuo* and purified by flash chromatography eluting with 30% MeOH/EtOAc to afford **1** (27.0 mg, 49%) as a red solid.  $R_f = 0.2$  (1/1 EtOAc/hexanes). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) δ 8.91(s, 1H), 8.53(d, 1H,  $J = 3.1$  Hz), 8.22(br, 2H), 7.89(s, 1H), 7.79-7.71(br, 2H), 7.32(d, 3H,  $J = 6.1$  Hz), 7.09-7.01(br, 2H), 6.71(s, 1H), 6.63(br, 3H), 3.77-3.63(br, 4H), 2.92(q, 2H,  $J = 6.7$  Hz), 2.19-2.10(br, 2H), 1.32-1.29(br, 3H); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD) δ 179.8, 168.3, 161.7, 153.5, 153.3, 152.4, 152.2, 147.1, 137.8, 134.2, 133.9, 131.8, 131.7, 128.9, 128.1, 125.6, 125.5, 123.7, 122.6, 118.6, 118.4, 113.1, 111.8, 109.6, 108.4, 102.9, 98.7, 96.5, 96.4, 82.1, 80.2, 75.3, 49.4, 49.3, 45.4, 23.7, 10.8. IR (neat, cm<sup>-1</sup>) 3451, 2887, 2911, 1657; MS (ESI): m/z calculated for (M-H)<sup>-</sup> 765.15 found 764.99 (M-H)<sup>-</sup>

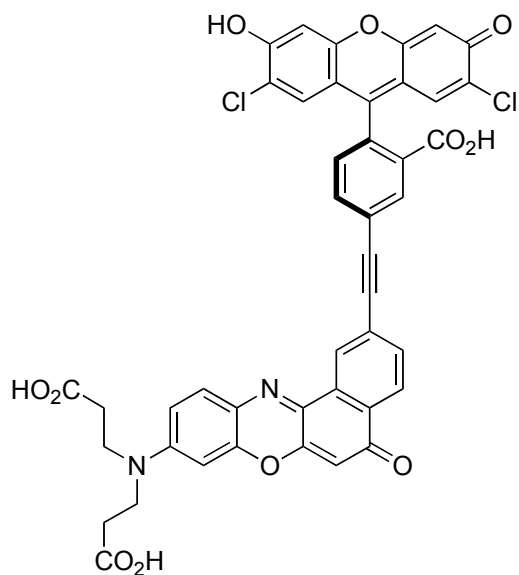


**2**

Compound **8** (110.0 mg, 0.2 mmol), **A** (101.0 mg, 0.3 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (22.0 mg, 0.02 mmol), copper(I)iodide (3.6 mg, 0.02 mmol) and triethylamine (0.37 mL, 1.9 mmol) were dissolved in 10 mL of dry distilled DMF. The solution was freeze-pump-thawed three times with nitrogen after cooling to -78 °C in an acetone/dry ice bath. The acetone/dry ice bath was removed and the temperature was allowed to rise to 25 °C and then heated to 130 °C for 12 h. The solution was concentrated in *vacuo* and purified by flash chromatography eluting with 30 % MeOH/EtOAc to afford 111.0 mg of red solid.  $R_f = 0.3$  (1/1 EtOAc/hexanes).

The above Red solid (30 mg, 0.04 mmol) and potassium carbonate (66.7 mg, 0.48 mmol) was dissolved in MeOH/water (5 mL, 1:1) and heated to 40 °C for 12 h. The solution was filtered to remove solid impurities and concentrated *in vacuo*. The crude residue was dissolved in 5 mL water and washed with ethyl acetate (5 mL, three times) to remove any organic impurities. The pH of the aqueous layer was adjusted to 6 by careful drop wise addition of HCl (5 to 6 drops, 1.0 M). The aqueous layer was then extracted with 2:1 CHCl<sub>3</sub>: *iso*-propanol (5 mL, three times). The organic extract was dried with magnesium sulfate and the solvent evaporated. The residue obtained was further purified by reverse phase preparative HPLC (20-95% CH<sub>3</sub>CN/1 % TFA in H<sub>2</sub>O to afford the desired product **2** as dark blue solid (22.0 mg, 59 %). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.72 (s, 1H), 8.24 (s, 1H), 8.17 (d, 1H,  $J = 7.8$  Hz), 8.01 (d, 1H,  $J = 7.8$  Hz), 7.90 (d, 1H,  $J = 8.9$  Hz), 7.68 (d, 1H,  $J = 8.9$  Hz), 7.35 (d, 1H,  $J = 8.7$  Hz), 6.88 (d, 1H,  $J = 8.8$  Hz), 6.75 (s, 1H),

6.68 (m, 2H), 6.63 (m, 2H), 6.56 (m, 2H), 6.33 (s, 1H), 3.73 (m, 4H), 2.65 (t, 4H,  $J = 7.3$  Hz).  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  182.0, 172.4, 168.6, 160.3, 153.3, 152.8, 152.5, 151.4, 147.0, 139.1, 133.3, 132.8, 132.4, 132.1, 131.7, 131.4, 129.9, 129.4, 128.4, 127.6, 127.3, 126.5, 125.6, 125.4, 124.9, 124.4, 113.6, 111.5, 109.9, 105.7, 103.0, 97.9, 90.7, 47.0, 32.1. IR (neat,  $\text{cm}^{-1}$ ) 3424, 3061, 2931, 1641, 2887; MS (ESI)  $m/z$  calculated for  $(\text{M}-2\text{H})^{2-}$  379.07 found 379.02  $(\text{M}-2\text{H})^{2-}$  MS (MALDI)  $m/z$  calculated for  $(\text{M}+3\text{H})^+$  763.19 found 763.21  $(\text{M}+3\text{H})^+$ .

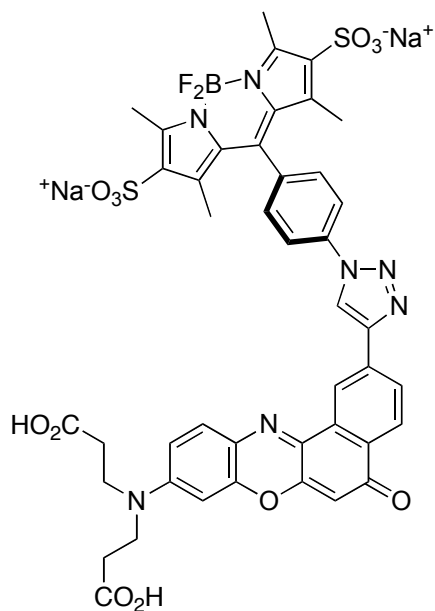


**3**

Compound **8** (50.0 mg, 0.09 mmol), **B** (50.0 mg, 0.11 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (10.0 mg, 0.009 mmol), copper(I)iodide (2.0 mg, 0.009 mmol) and triethylamine (0.12 mL, 1.9 mmol) were dissolved in 5 mL of dry distilled DMF. The solution was freeze-pump-thawed three times with nitrogen after cooling to -78 °C in an acetone/dry ice bath. The acetone/dry ice bath was removed and the temperature was allowed to rise to 25 °C and then heated to 130 °C for 12 h. The solution was concentrated in *vacuo* and purified by flash chromatography eluting with 30% MeOH/EtOAc to afford 21.0 mg of red solid.  $R_f = 0.3$  (1/1 EtOAc/hexanes).

The above red solid (20.0 mg, 0.02 mmol) and potassium carbonate (19.0 mg, 0.14 mmol) was dissolved in MeOH/water (5 mL, 1:1) and heated to 40 °C for 12 h. The solution was filtered to remove solid impurities and concentrated *in vacuo*. The crude residue was dissolved in 5 mL water and washed with ethyl acetate (5 mL, three times) to remove any organic impurities. The pH of the aqueous layer was adjusted to 6 by careful

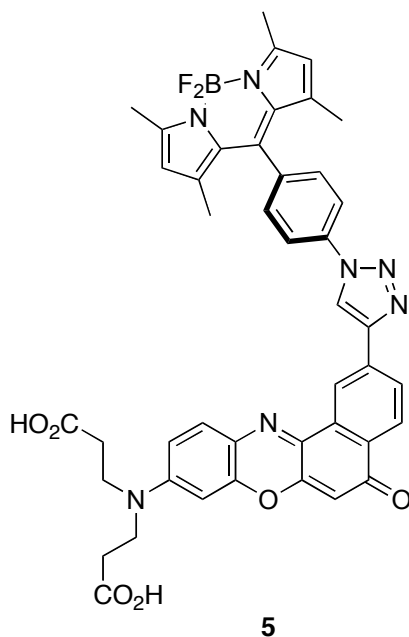
drop wise addition of HCl (5 to 6 drops, 1.0 M). The aqueous layer was then extracted with 2/1 CHCl<sub>3</sub>/*iso*-propanol (5 mL, three times). The organic extract was dried with magnesium sulfate and solvent evaporated. The residue obtained was further purified by reverse phase preparative HPLC (20-95 % CH<sub>3</sub>CN/1 % TFA in H<sub>2</sub>O to afford **3** (9.0 mg, 12 %) as a dark blue solid. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 11.17 (br, 2H), 8.74 (s, 1H), 8.24 (s, 1H), 8.18 (d, 1H, *J* = 8.6 Hz), 8.05 (d, 1H, *J* = 8.1 Hz), 7.91 (d, 1H, *J* = 8.1 Hz), 7.70 (br, 1H), 7.43 (br, 2H), 6.91 (br, 2H), 6.81 (br, 2H), 6.75 (s, 1H), 6.35 (s, 1H), 3.73 (br, 4H), 2.57 (t, 4H, *J* = 7.1 Hz). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 181.7, 173.3, 167.9, 155.7, 152.6, 152.0, 151.3, 150.5, 146.8, 139.1, 138.7, 132.9, 132.3, 132.1, 131.6, 131.5, 131.2, 128.9, 127.3, 127.0, 126.2, 125.2, 125.1, 124.5, 116.8, 111.3, 110.4, 105.9, 104.1, 97.3, 90.9, 90.8, 82.3, 47.1, 32.3; IR(neat, cm<sup>-1</sup>) 3416, 3023, 2897, 1703; MS (ESI) *m/z* calculated for (M+2H)<sup>2+</sup> 415.05 found 415.06 (M+2H)<sup>2+</sup> MS (MALDI) *m/z* calculated for (M+2H)<sup>+</sup> 830.10 found 830.17 (M+2H)<sup>+</sup>



**4**

Compound **C** (42.0 mg, 0.07 mmol) and alkyne **9** (68.0 mg, 0.14 mmol) along with copper metal (5.0 mg, 0.07 mmol), CuSO<sub>4</sub> (0.1 mL, 0.1 M) and tris[(1 - benzyl - 1H - 1,2,3 - triazol - 4 - yl)methyl] amine (TBTA) (1.0 mg, 0.02 mmol) were taken in THF/H<sub>2</sub>O mixture (5 mL, 4/1) and stirred at 25 °C for 24 h. The reaction mixture was filtered through celite to remove metallic copper. The filtrate obtained was evaporated

under reduced pressure and columned on flash chromatography using CH<sub>2</sub>Cl<sub>2</sub>/MeOH (4/1) as eluent. The red colored material obtained (60.0 mg) was dissolved in MeOH/H<sub>2</sub>O (4 mL, 1/1) along with K<sub>2</sub>CO<sub>3</sub> (33.0 mg, 0.24 mmol) and heated at 40 °C for 12 h. The solvent was evaporated and the residue dissolved in water (2 mL) and washed with EtOAc (1 mL) three times to remove any organic impurities. The aqueous layer was purified on a reverse phase medium pressure liquid chromatography (MPLC) C-18 column using CH<sub>3</sub>CN/H<sub>2</sub>O (1/1) as eluent. The solvent was evaporated and dried under vacuum overnight to obtain product **4** as a dark purple colored material (27 mg, 39 %); **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>) δ 9.83 (s, 1H), 9.18 (s, 1H), 8.26 (br, 4H), 7.75 (d, 1H, *J* = 8.2 Hz), 7.68 (d, 2H, *J* = 9.7 Hz), 6.91 (d, 1H, *J* = 7.3 Hz), 6.78 (br, 1H), 6.34 (s, 1H), 3.74 (br, 4H), 2.65 (s, 6H), 2.53 (br, 4H), 1.61 (s, 6H); **<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>) δ 182.8, 172.4, 166.9, 155.1, 152.5, 151.0, 147.1, 146.7, 142.6, 140.0, 138.3, 137.5, 135.2, 133.6, 132.7, 131.4, 131.1, 130.3, 130.0, 126.6, 125.2, 121.7, 121.2, 120.4, 111.1, 105.4, 97.4, 47.2, 31.9, 14.2, 13.2 (1 carbon is missing); **MS (ESI)** *m/z* calculated for (M-2H)<sup>2-</sup> 475.58 found 475.24 (M-2H)<sup>2-</sup>

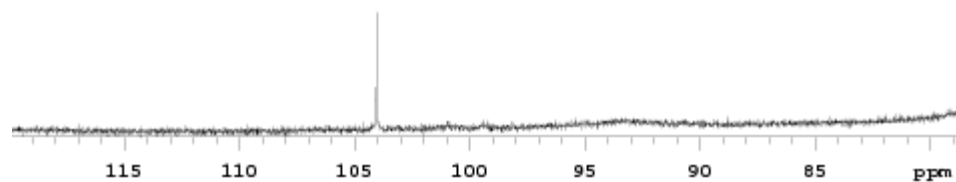


BODIPY azide **6** (35.0 mg, 0.1 mmol) and alkyne **9** (65.0 mg, 0.14 mmol) along with copper metal (6.0 mg, 0.1 mmol), CuSO<sub>4</sub> (0.1 mL, 0.1 M) and tris[(1 - benzyl - 1H - 1,2,3 - triazol - 4 - yl)methyl] amine (TBTA) (1.0 mg, 0.02 mmol) were taken in THF/H<sub>2</sub>O mixture (5 mL, 4/1) and stirred at 25 °C for 24 h. The reaction mixture was filtered

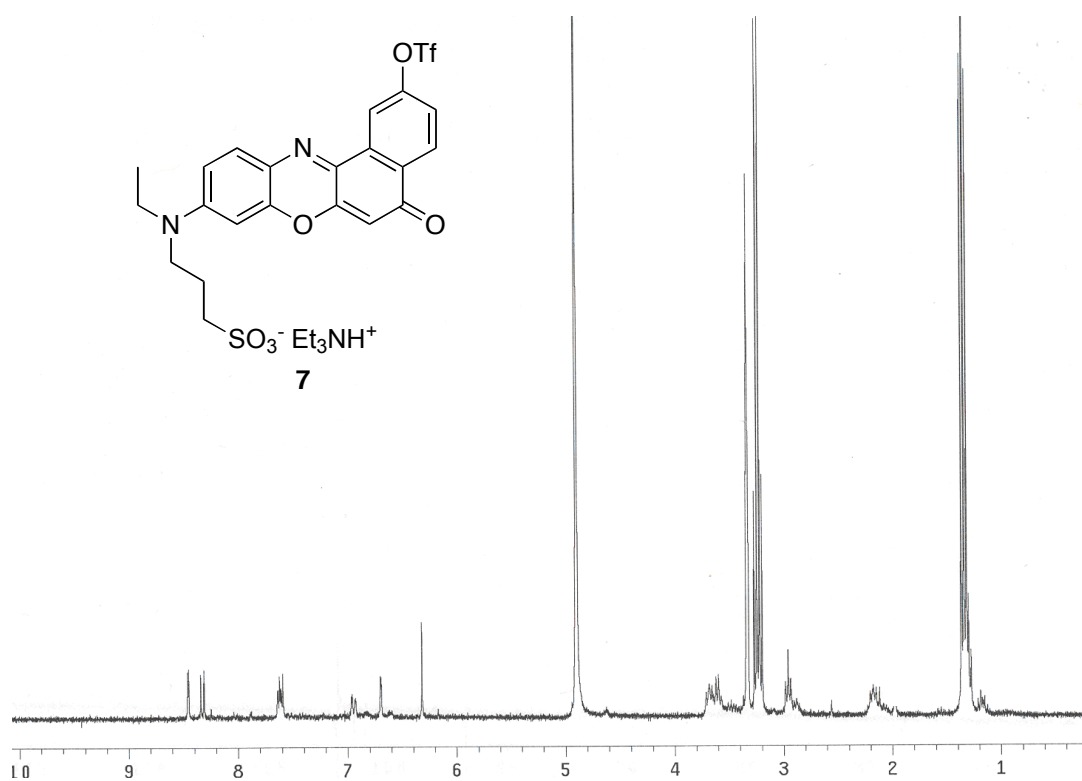
through celite to remove metallic copper. The filtrate obtained was evaporated under reduced pressure and residue obtained was dissolved in  $\text{CH}_2\text{Cl}_2$  (5 mL) and washed with water (2 mL) three times and the organic layer was dried over sodium sulfate. The solvent was evaporated and flash chromatography performed on silica gel with EtOAc/hexanes (1/1) to obtain a red colored material after solvent evaporation under reduced pressure and drying. The red material (42.0 mg), and  $\text{K}_2\text{CO}_3$  (28.0 mg, 0.2 mmol) were dissolved in MeOH/ $\text{H}_2\text{O}$  (4 mL, 1/1) and heated at 40 °C for 12 h. The blue solution obtained was evaporated under reduced pressure and the residue purified by flash chromatography eluting with EtOAc/hexanes (1/1) and then with EtOAc/MeOH (4/1) to obtain a dark purple colored material which was further purified on a reverse phase medium pressure liquid chromatography (MPLC) C-18 column using  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (7/3) as eluent. The solvent was evaporated and dried under vacuum overnight to obtain product **5** as a dark purple colored material (23 mg, 30 %)  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.15 (s, 1H), 8.59 (br, 1H), 8.38 (br, 1H), 8.25 (s, 1H), 8.08 (br, 2H), 7.69 (br, 1H), 7.56 (br, 2H), 6.72 (s, 1H), 6.51 (d, 1H,  $J = 4.7$  Hz), 6.42 (d, 1H,  $J = 4.7$  Hz), 6.02 (s, 2H), 3.81 (t, 4 H,  $J = 8.8$  Hz), 2.71 (t, 4 H,  $J = 8.8$  Hz), 2.58 (s, 6H), 1.48 (s, 6H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  183.1, 171.8, 156.2, 152.0, 150.0, 147.9, 146.6, 142.8, 141.0, 139.5, 137.4, 135.8, 133.0, 132.5, 131.5, 131.3, 131.2, 130.0, 127.5, 126.7, 125.6, 124.8, 121.6, 121.0, 118.7, 110.1, 106.3, 97.3, 47.1, 32.1, 14.8 (2C); **MS (ESI)**  $m/z$  calculated for  $(\text{M}-\text{H})^-$  794.27 found 794.21 (M-H).

## Copies of $^1\text{H}$ and $^{13}\text{C}$ Spectra

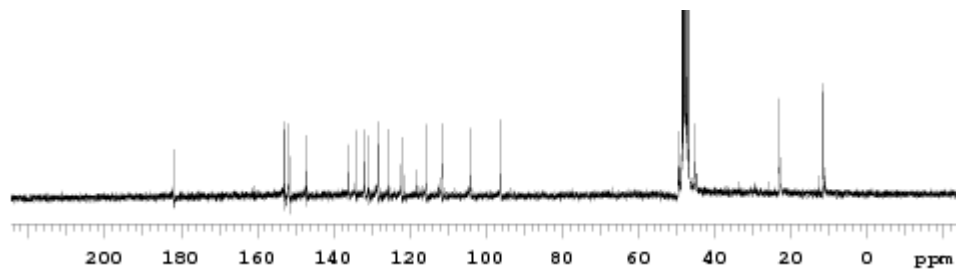
### $^{19}\text{F}$ NMR ( $\text{CD}_3\text{OD}$ )



### $^1\text{H}$ NMR ( $\text{CD}_3\text{OD}$ )

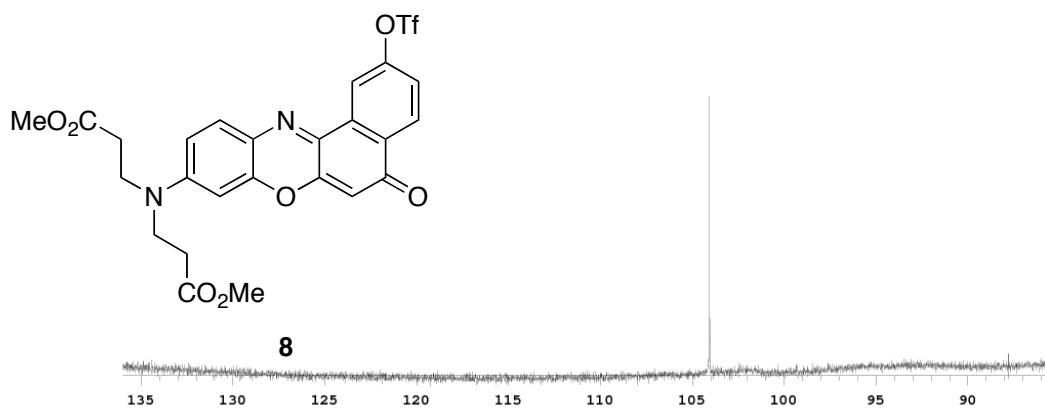


### $^{13}\text{C}$ NMR ( $\text{CD}_3\text{OD}$ )

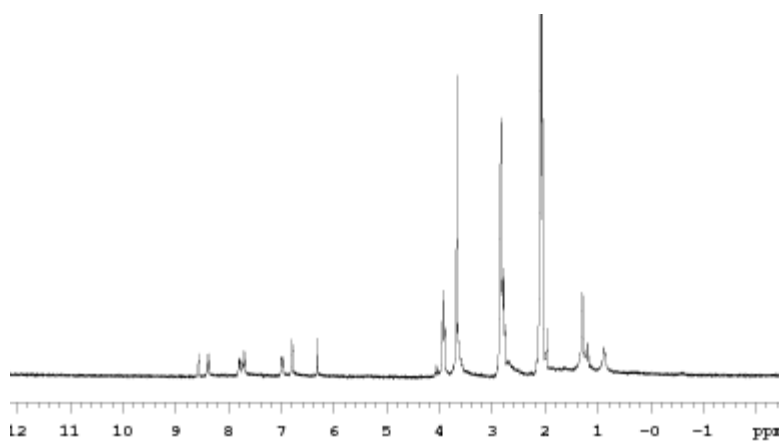




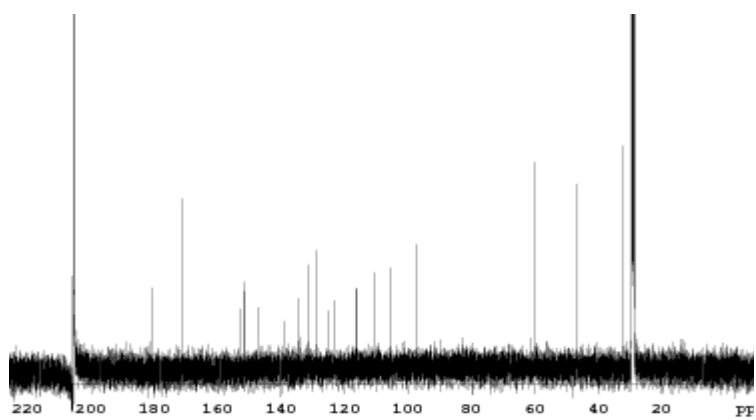
**$^{19}\text{F}$  NMR (acetone- $d_6$ )**



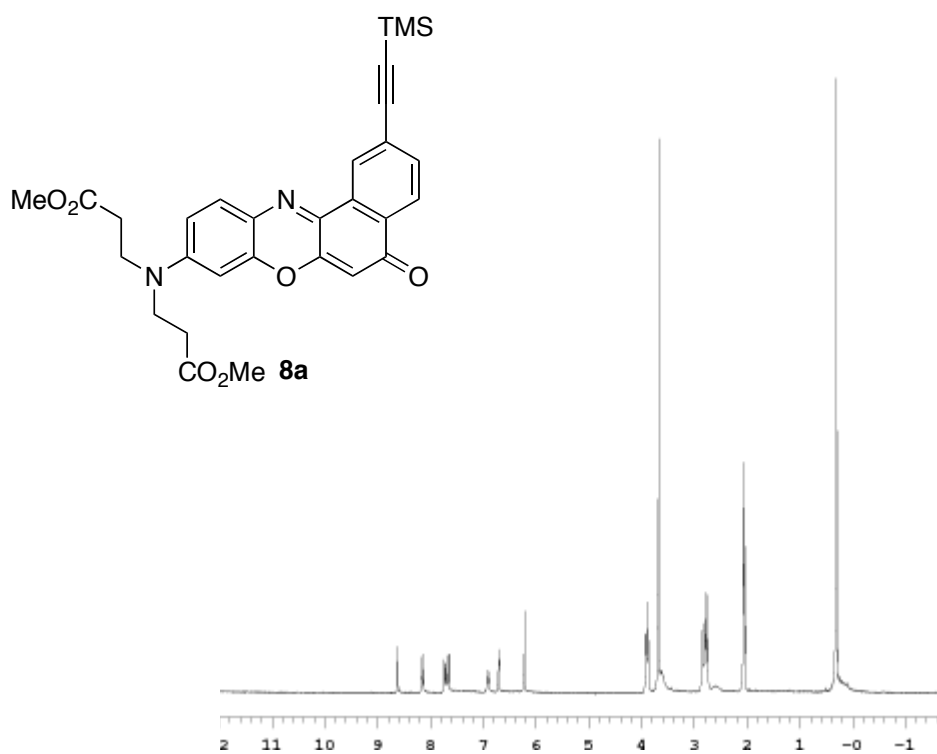
**$^1\text{H}$  NMR (acetone- $d_6$ )**



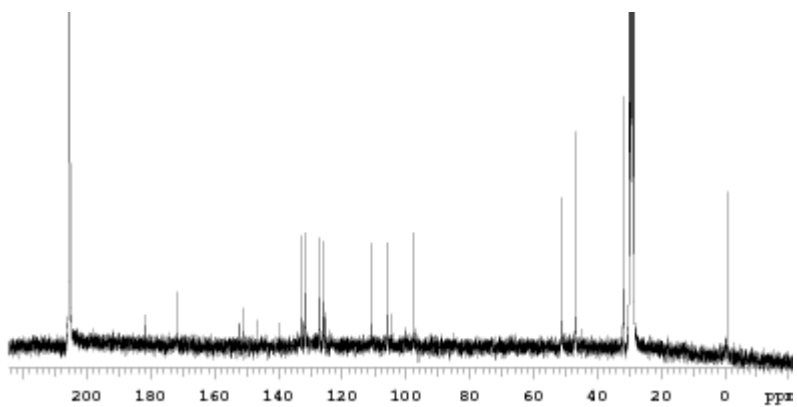
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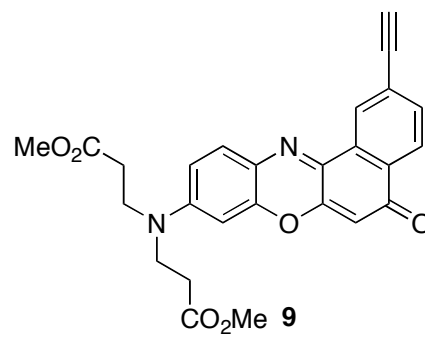
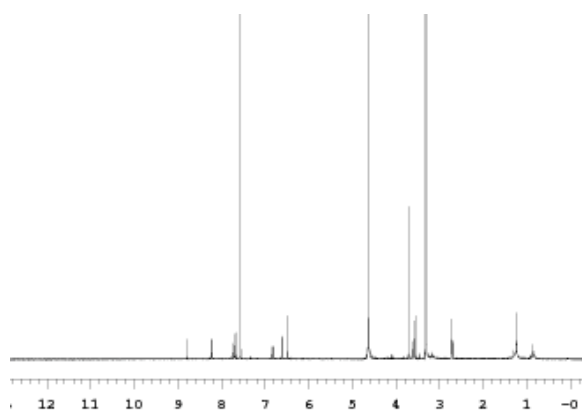
**$^1\text{H}$  NMR (acetone- $d_6$ )**



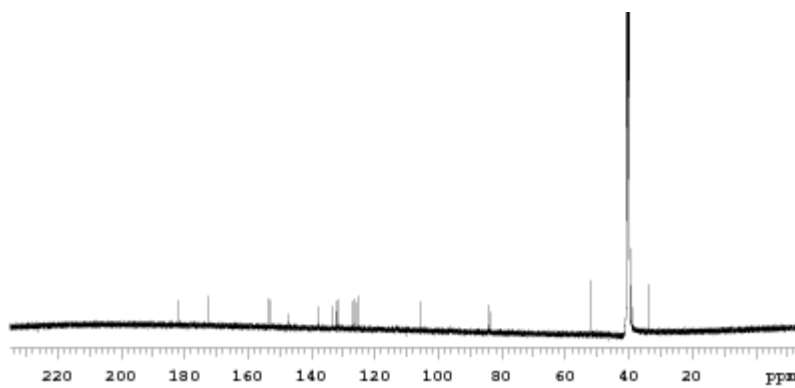
**$^{13}\text{C}$  NMR (acetone- $d_6$ )**



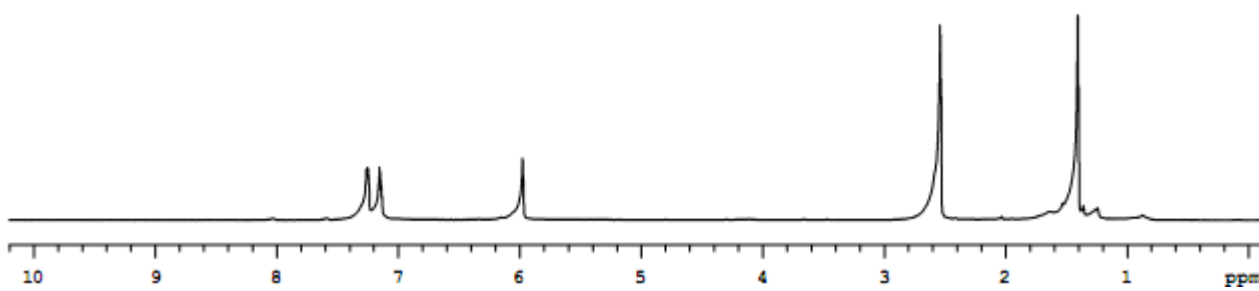
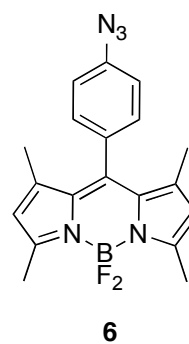
**$^1\text{H}$  NMR ( $\text{CD}_3\text{OD}/\text{CDCl}_3$ )**



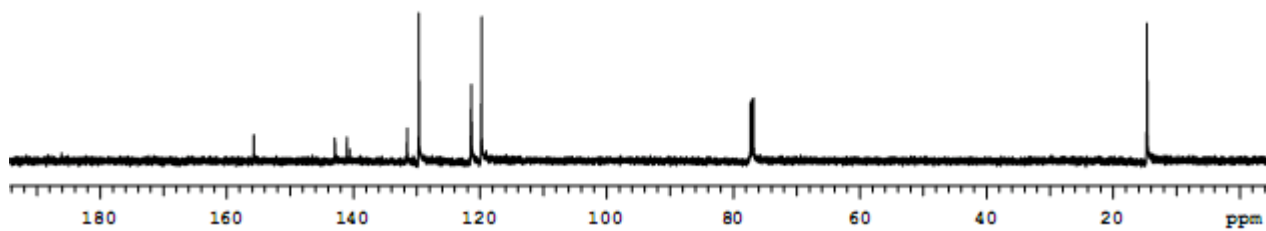
**$^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ )**

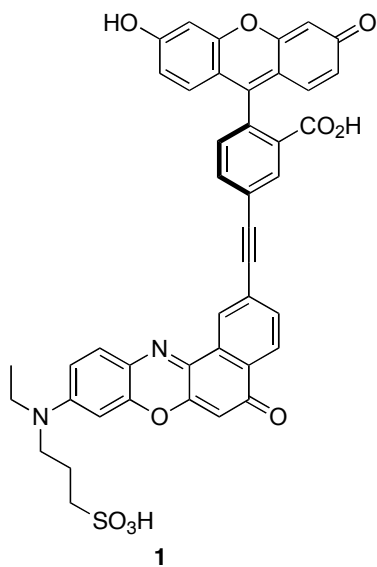


**<sup>1</sup>H NMR (CDCl<sub>3</sub>)**

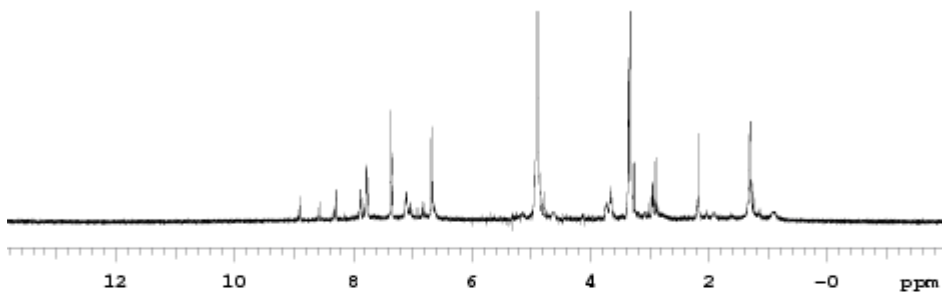


**<sup>13</sup>C NMR (CDCl<sub>3</sub>)**

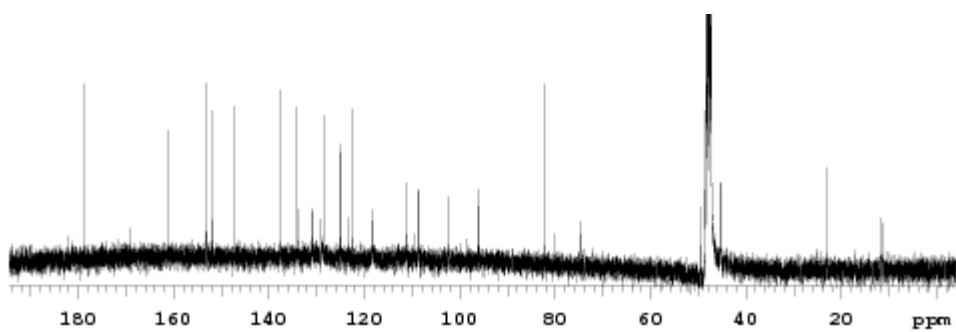


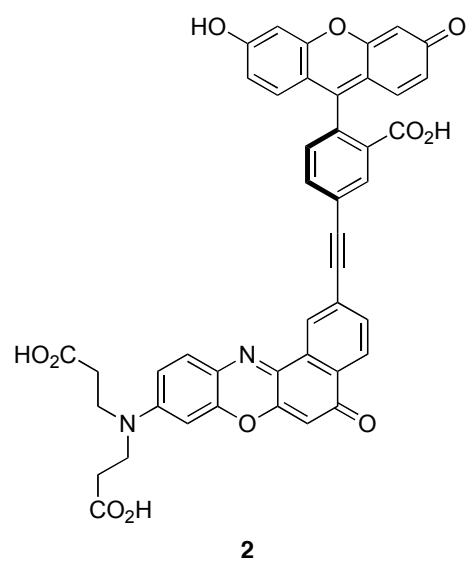


**<sup>1</sup>H NMR (CD<sub>3</sub>OD)**

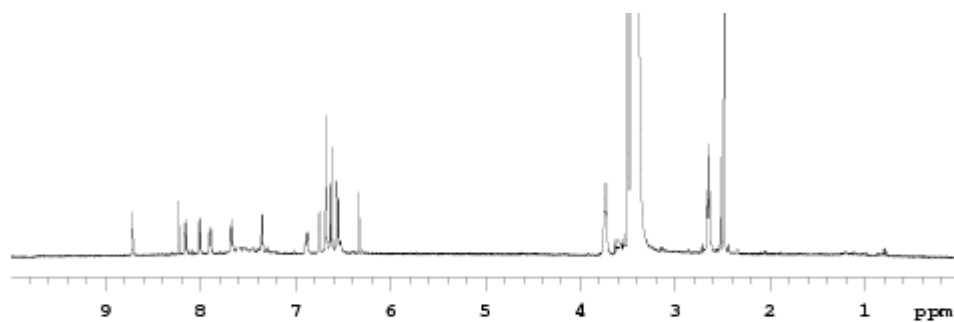


**<sup>13</sup>C NMR (CD<sub>3</sub>OD)**

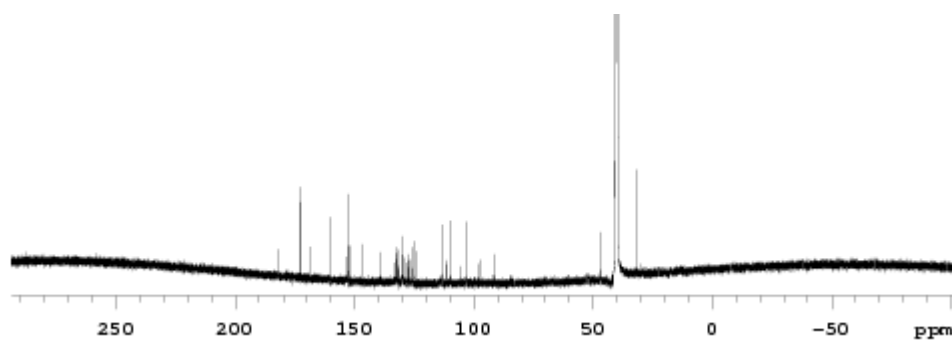


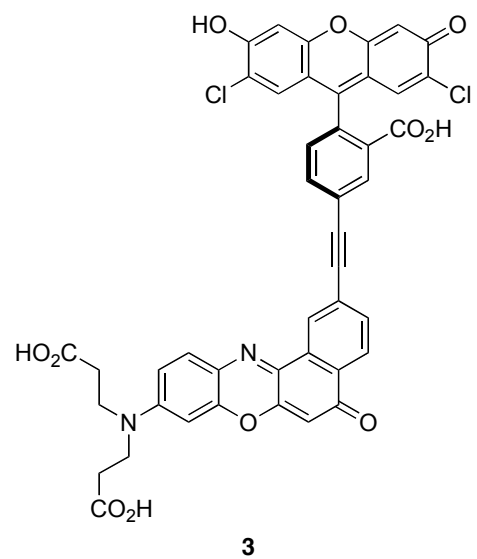


**<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>)**

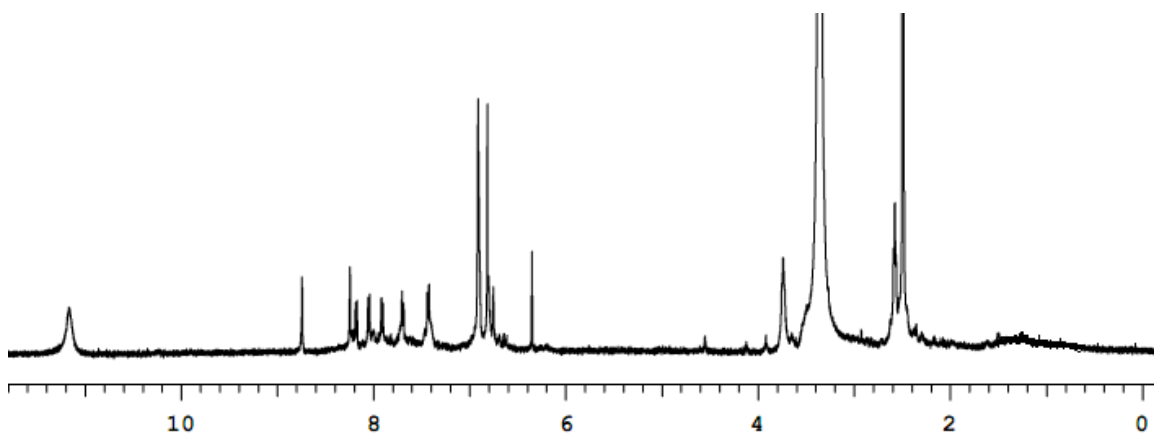


**<sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>)**

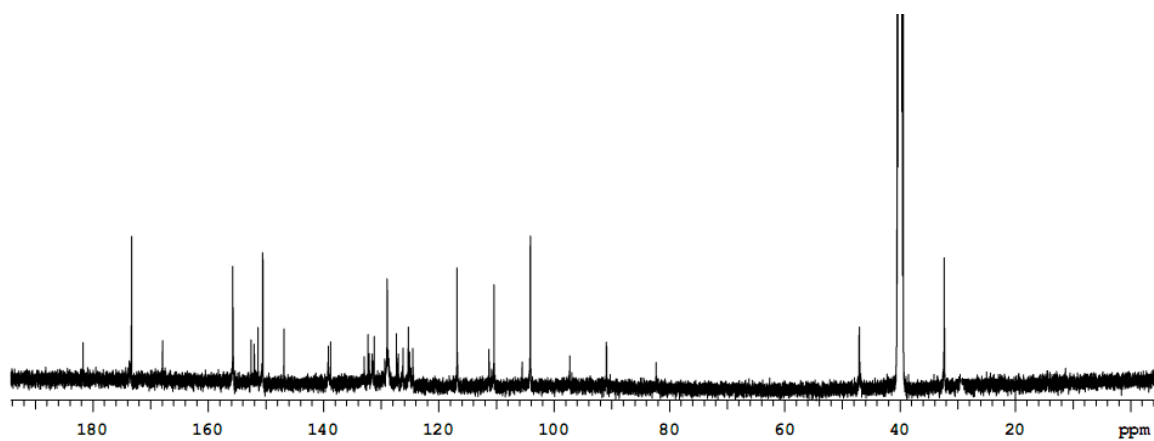




**<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>)**



**<sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>)**









## References

- (1) Rurack, K. *Springer Ser. Fluoresc.* **2008**, *5*, 101-145.
- (2) Parker, C. A.; Rees, W. T. *Analyst* **1962**, *87*, 83-111.