

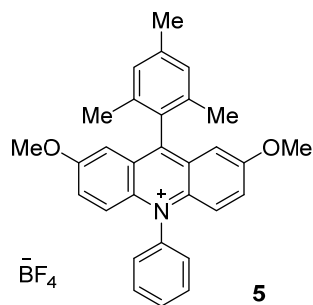
Acridinium Based Photocatalysts: A Sustainable Option in Photoredox Catalysis

Amruta Joshi-Pangu, François Lévesque, Hudson G. Roth, Steven F. Oliver, Louis-Charles Campeau, David Nicewicz*, and Daniel A. DiRocco*

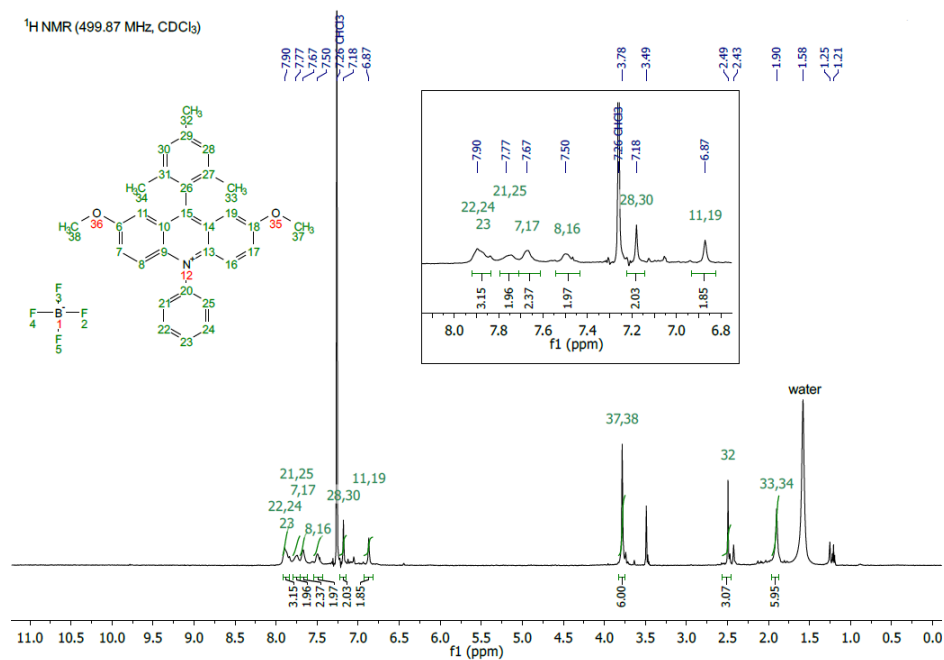
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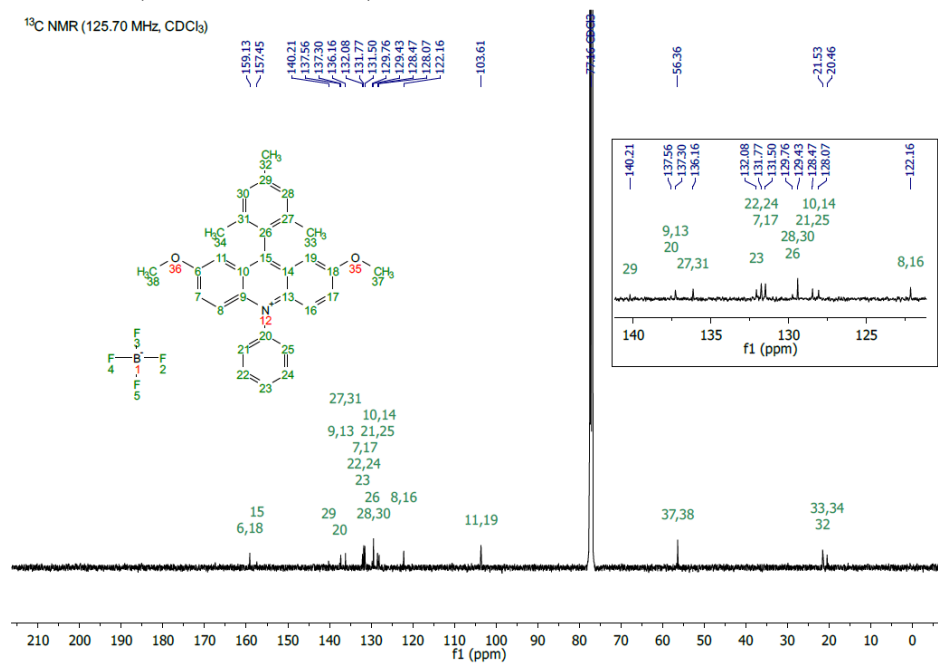
NMR and HRMS Spectra of Catalysts 5-8



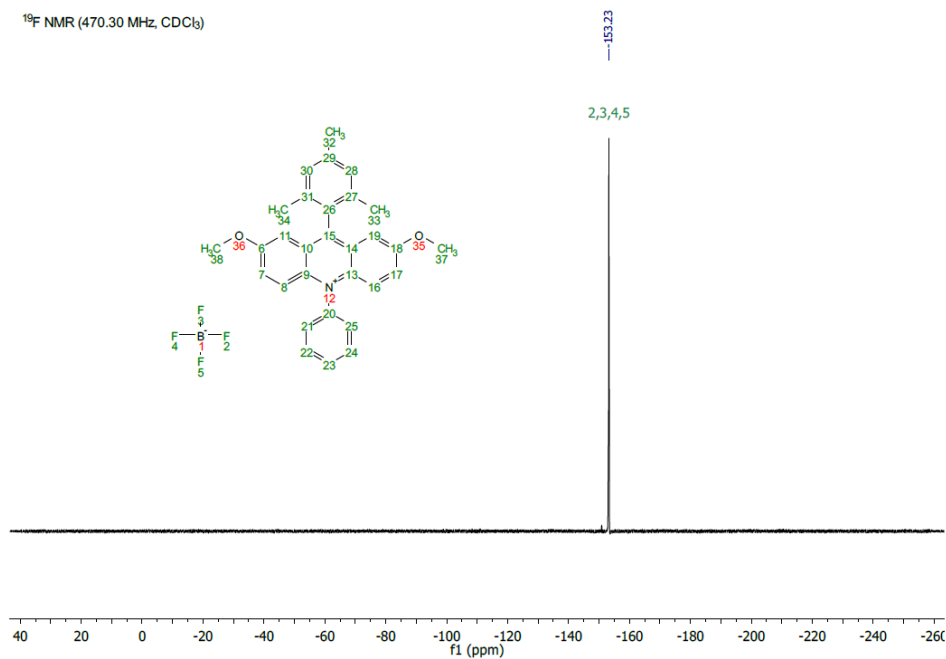
^1H NMR (500 MHz, CDCl_3) of **5**:



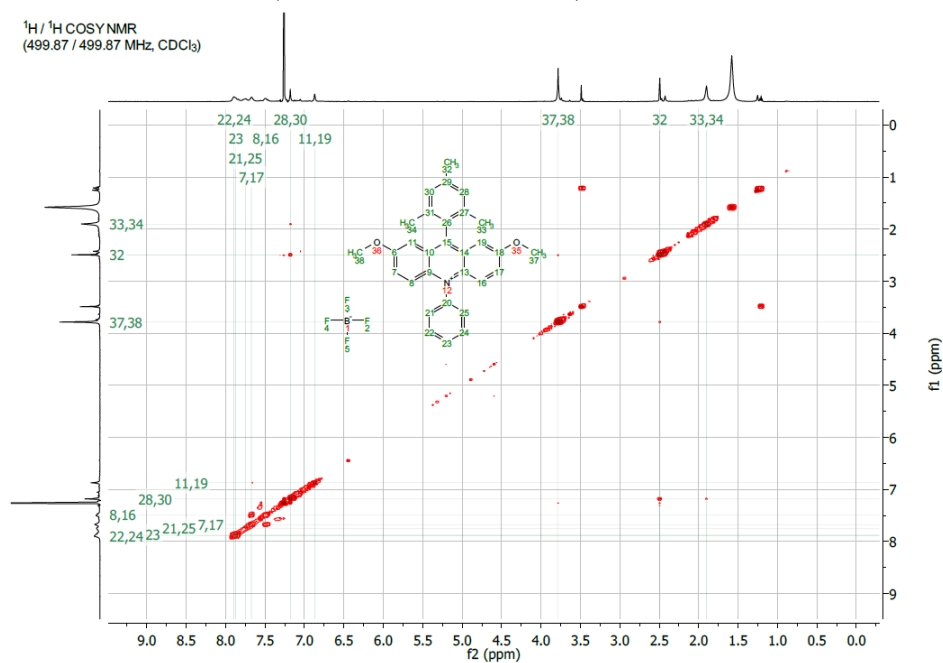
^{13}C NMR (125 MHz, CDCl_3) of **5**:



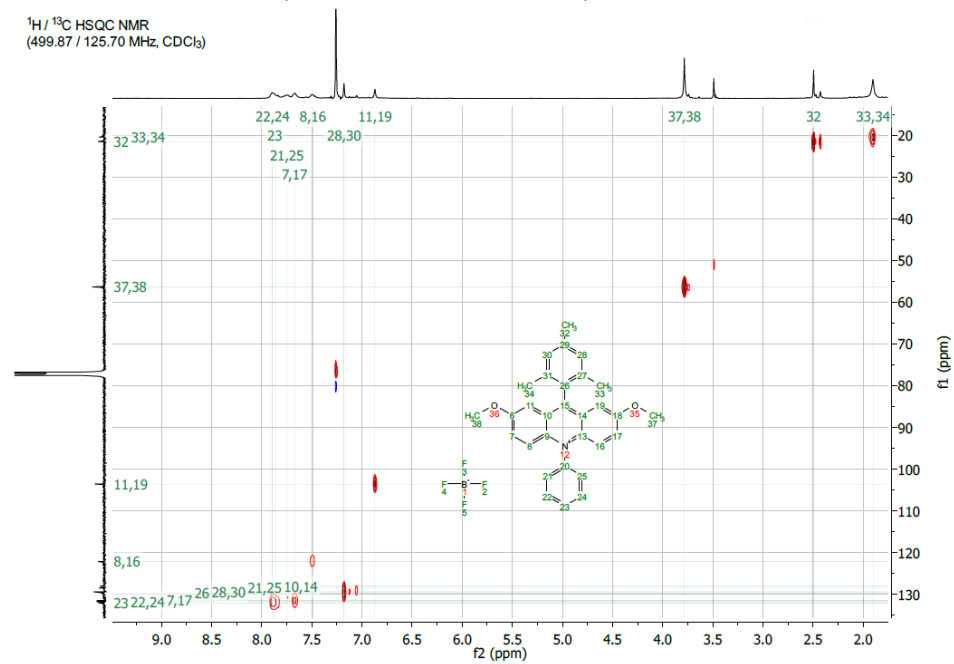
^{19}F NMR (470 MHz, CDCl_3) of **5**:



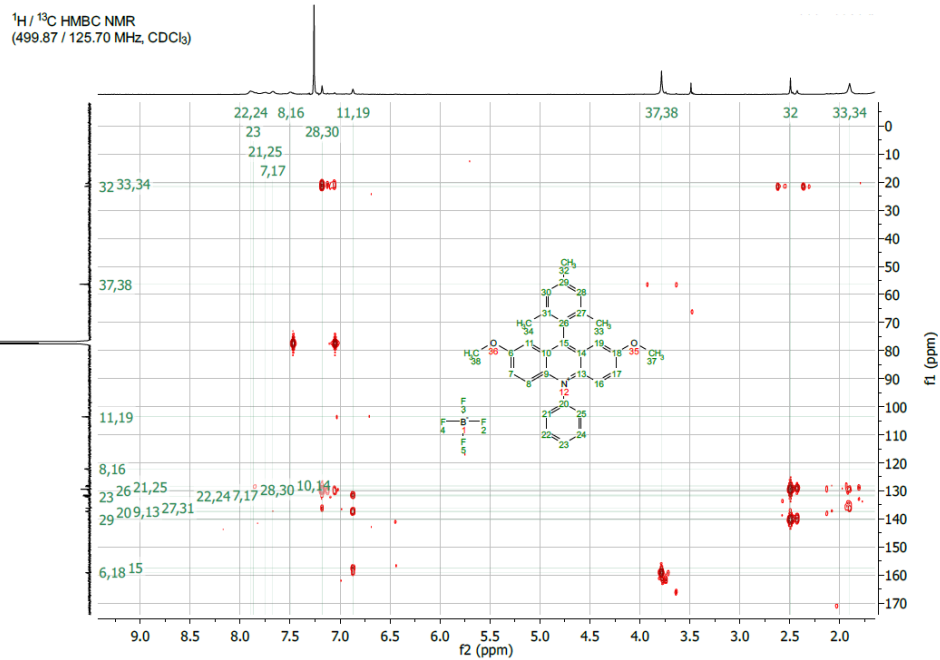
$^1\text{H}/^1\text{H}$ COSY NMR (500 / 500 MHz, CDCl_3) of **5**:



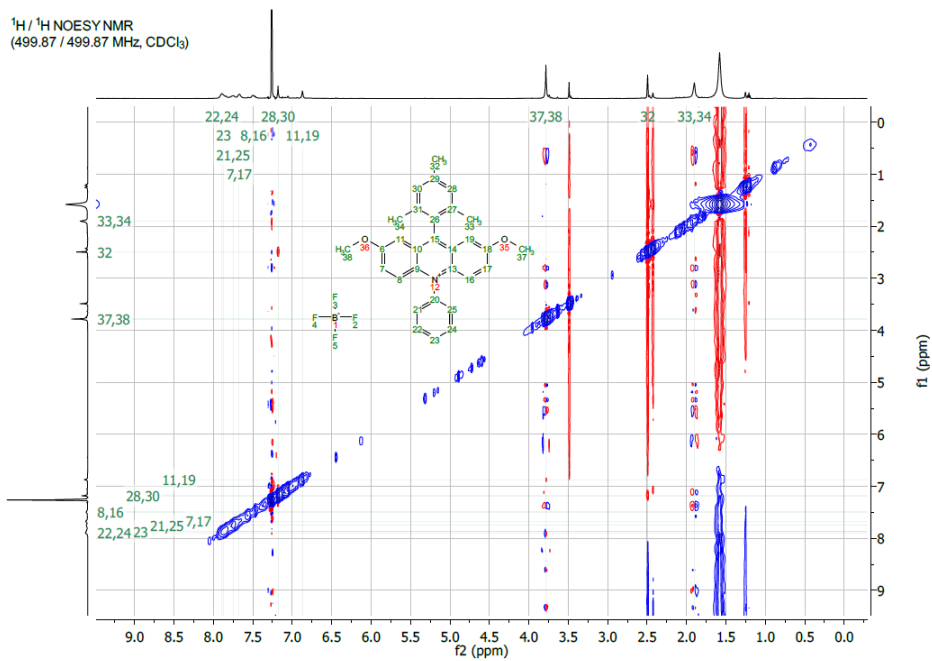
$^1\text{H}/^{13}\text{C}$ HSQC NMR (500 / 125 MHz, CDCl_3) of **5**:



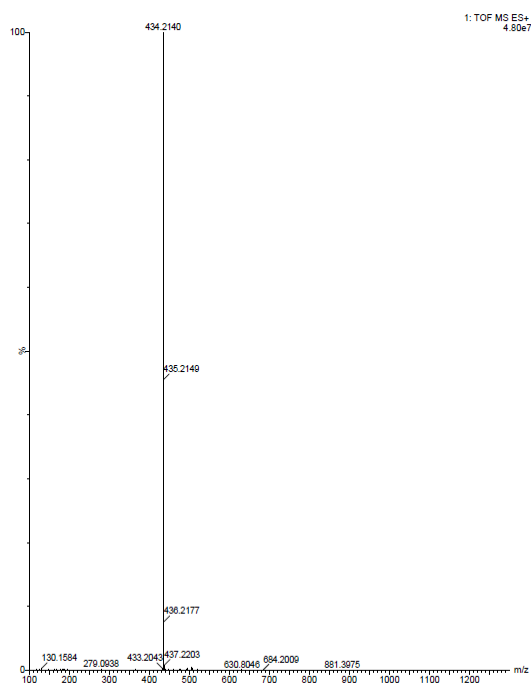
$^1\text{H}/^{13}\text{C}$ HMBC NMR (500 / 125 MHz, CDCl_3) of **5**:

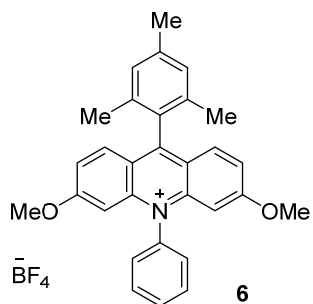


$^1\text{H}/^1\text{H}$ NOESY NMR (500 / 500 MHz, CDCl_3) of **5**:

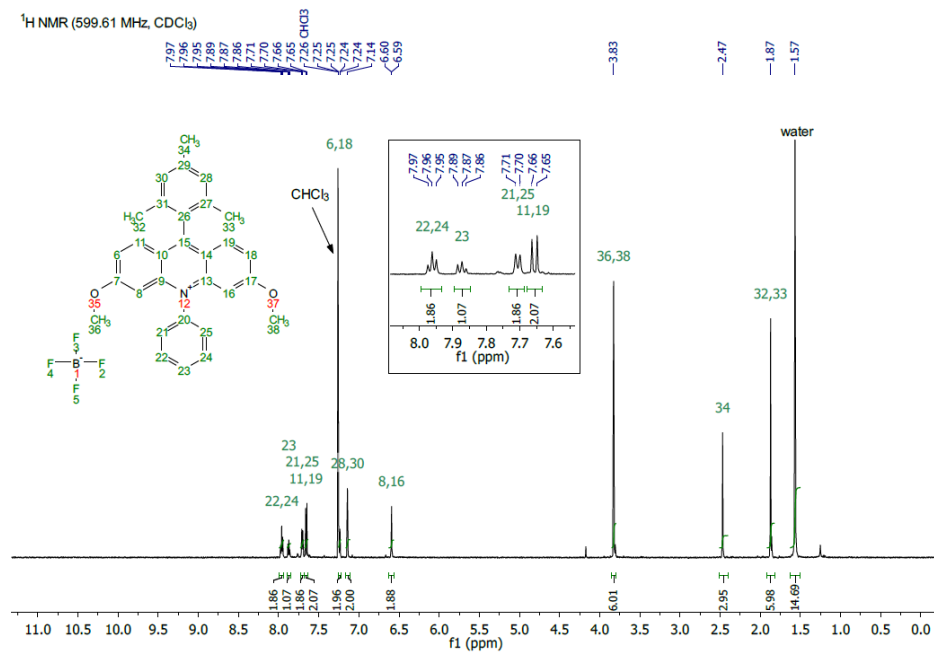


HRMS of catalyst **5**:

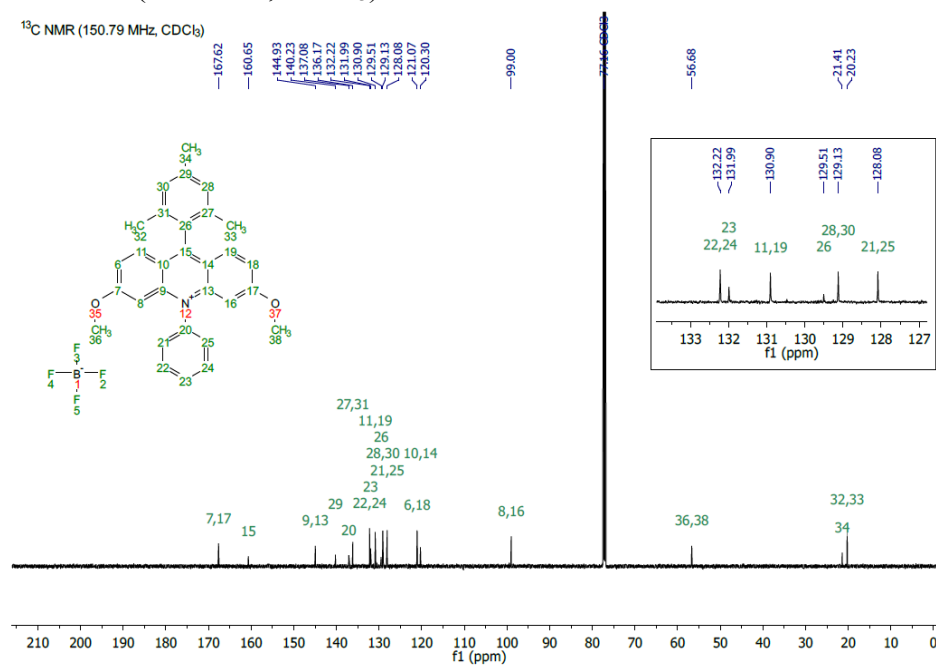




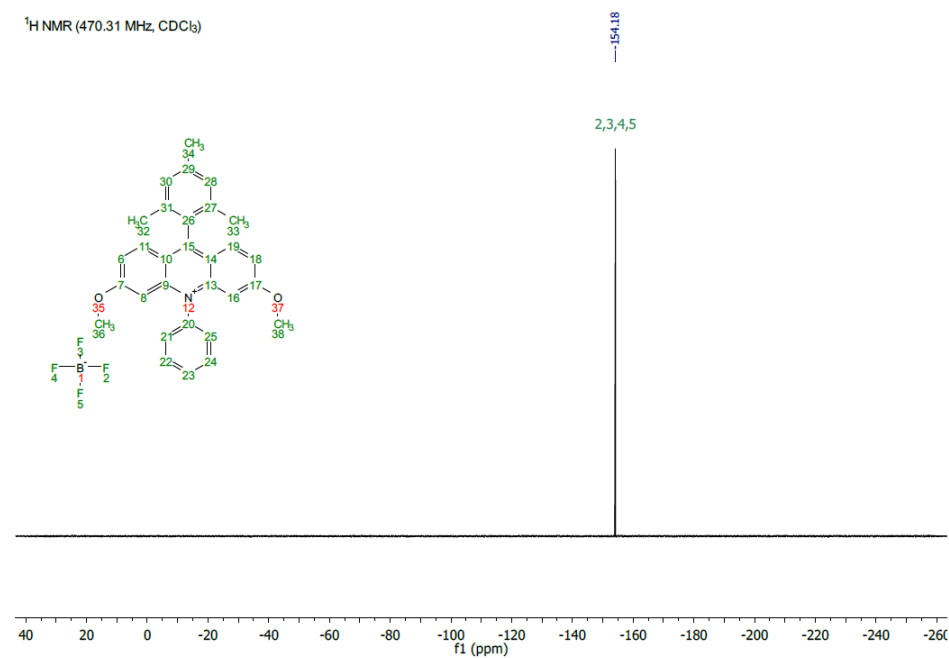
^1H NMR (600 MHz, CDCl_3) of **6**:

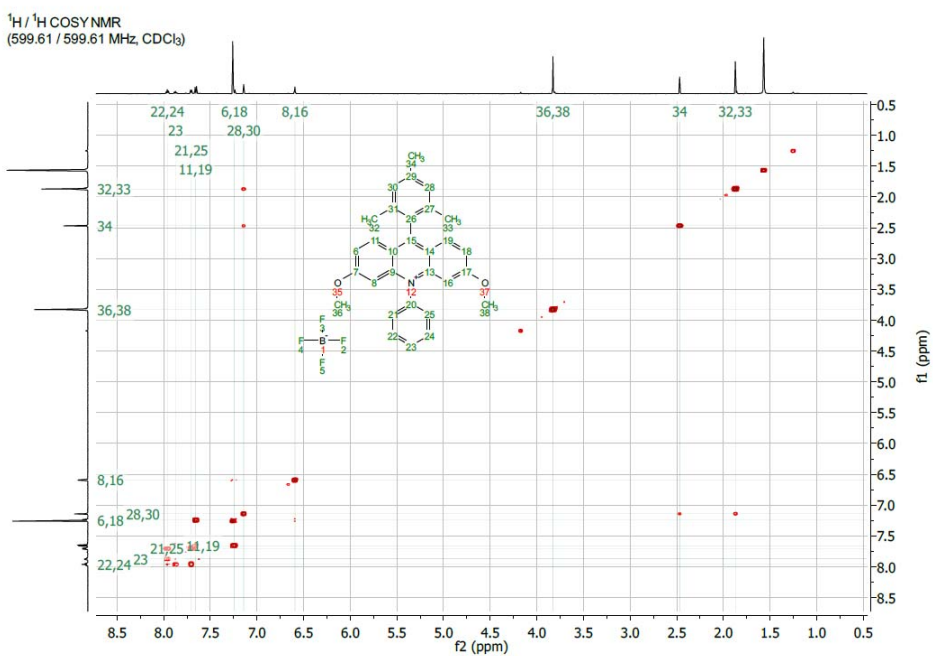
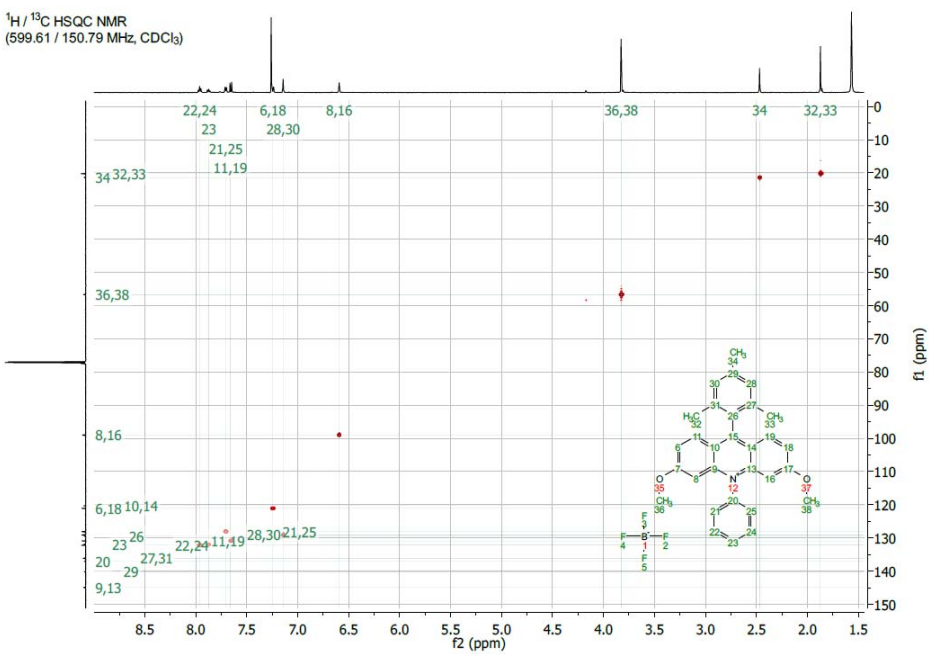


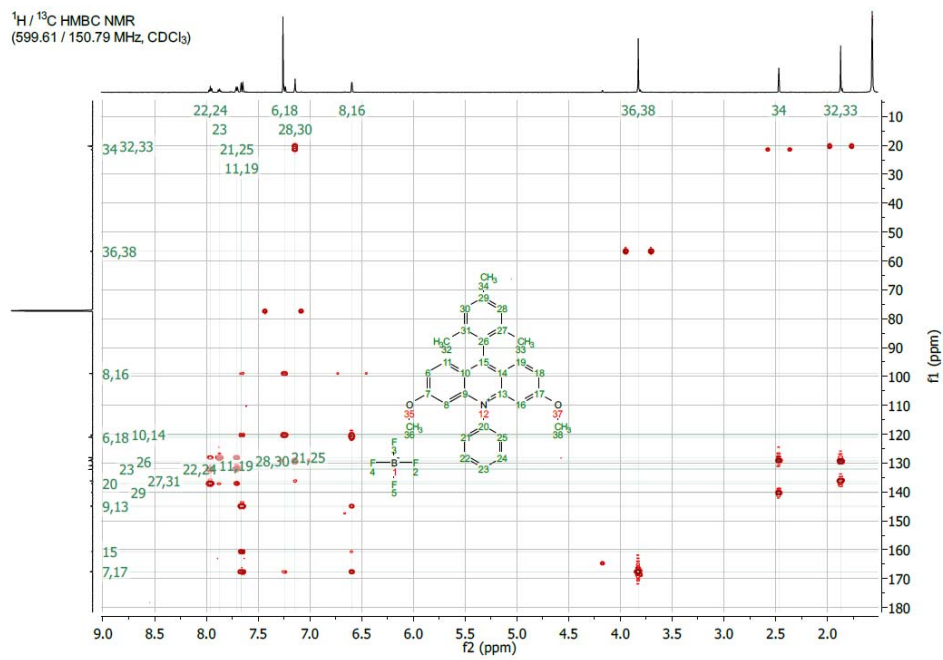
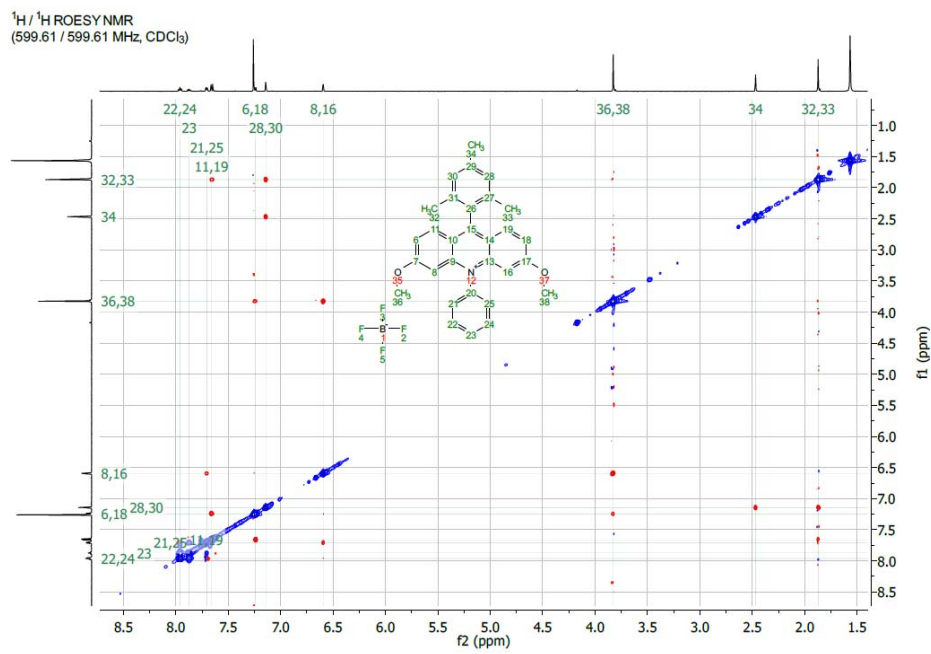
^{13}C NMR (151 MHz, CDCl_3) of **6**:



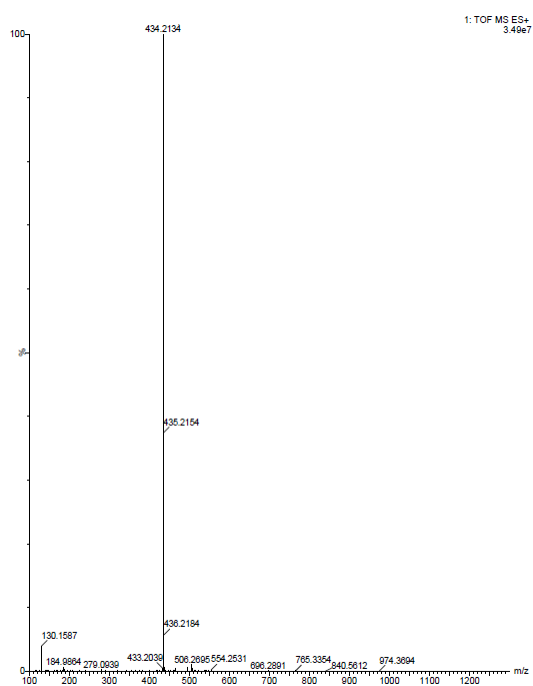
^{19}F NMR (470 MHz, CDCl_3) of **6**:

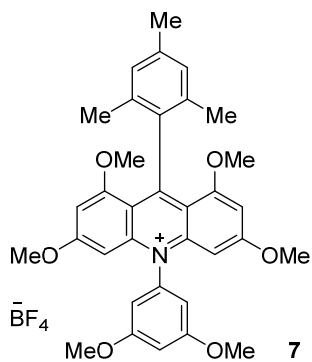


¹H/ ¹H COSY NMR (600 / 600 MHz, CDCl₃) of **6**:¹H/ ¹³C HSQC NMR (600 / 151 MHz, CDCl₃) of **6**:

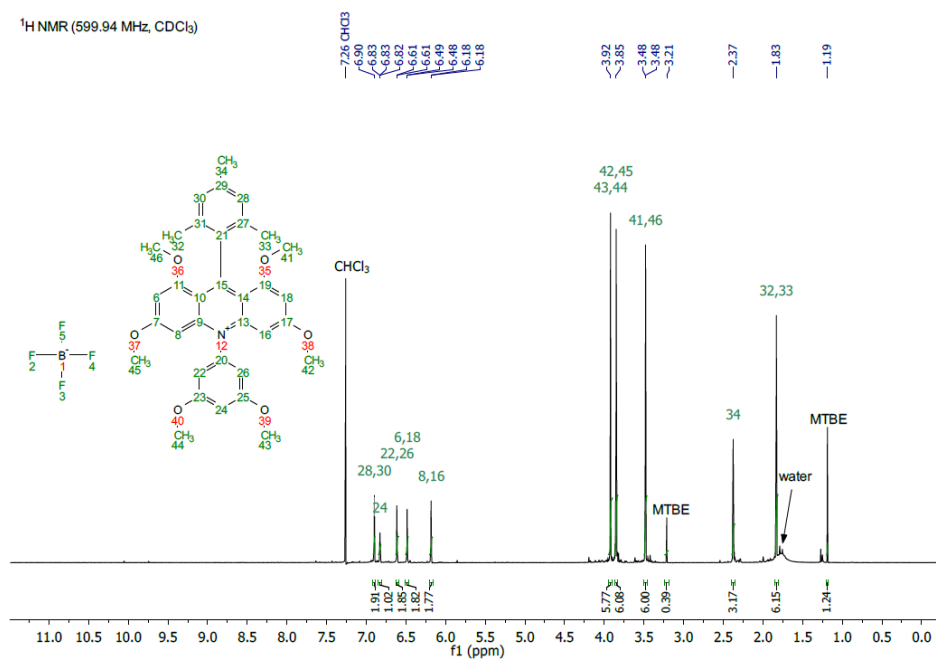
¹H/ ¹³C HMBC NMR (600 / 151 MHz, CDCl₃) of **6**:¹H / ¹H ROESY NMR (600 / 600 MHz, CDCl₃) of **6**:

HRMS of catalyst **6**:

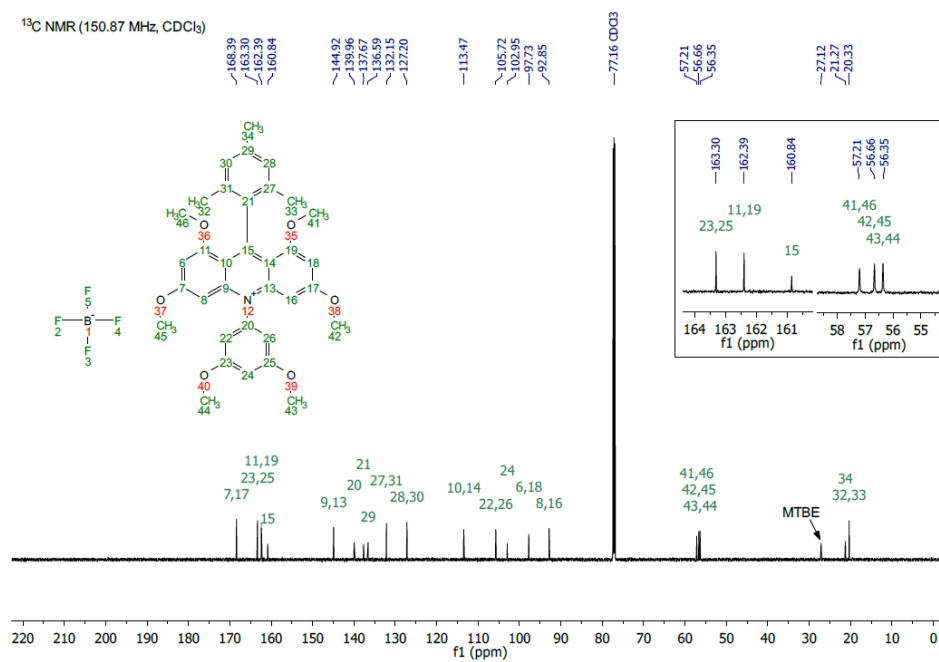




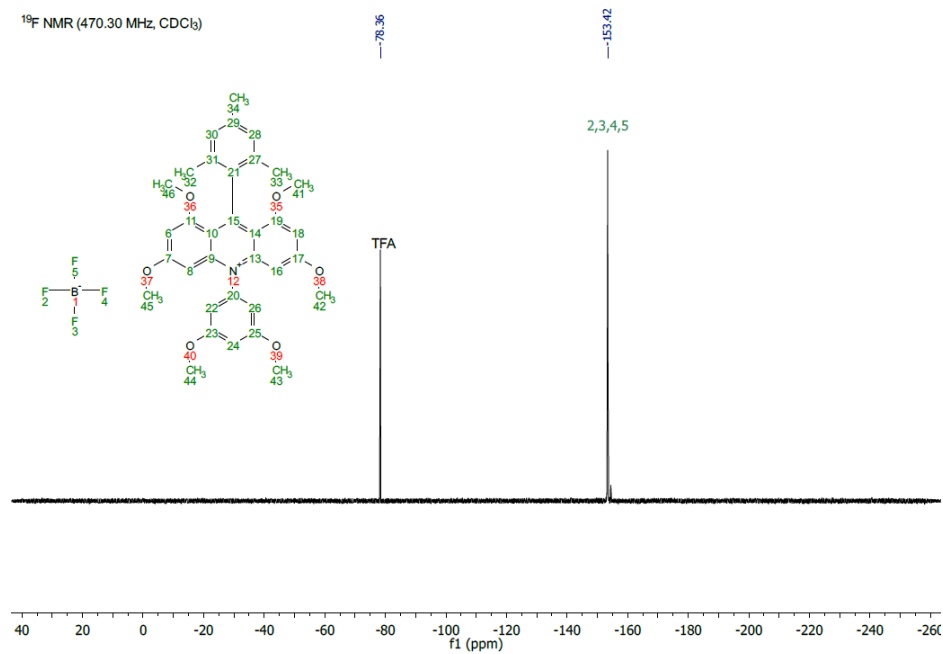
^1H NMR (600 MHz, CDCl_3) of **7**:



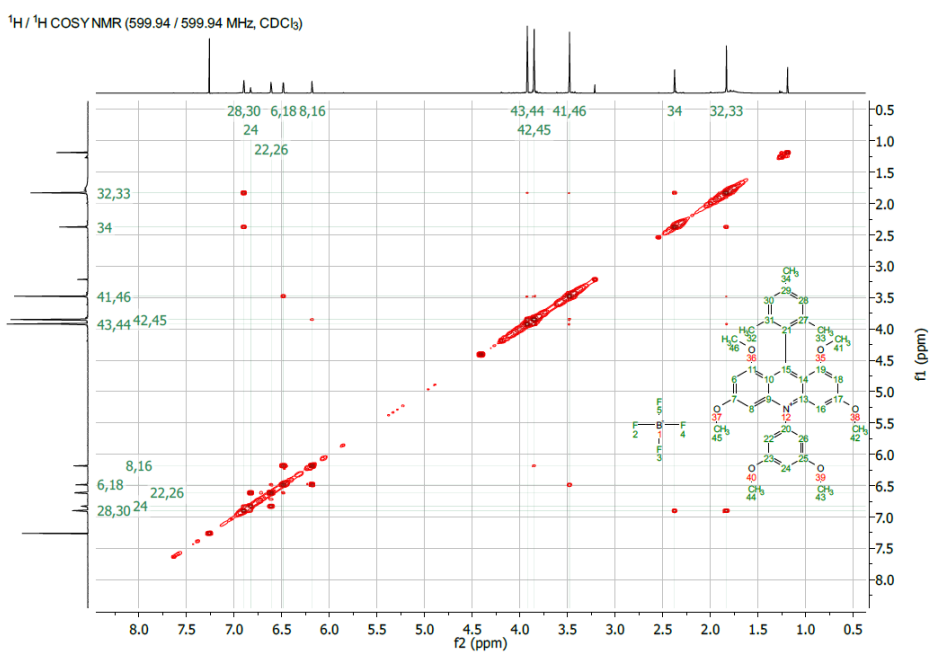
^{13}C NMR (151 MHz, CDCl_3) of **7**:



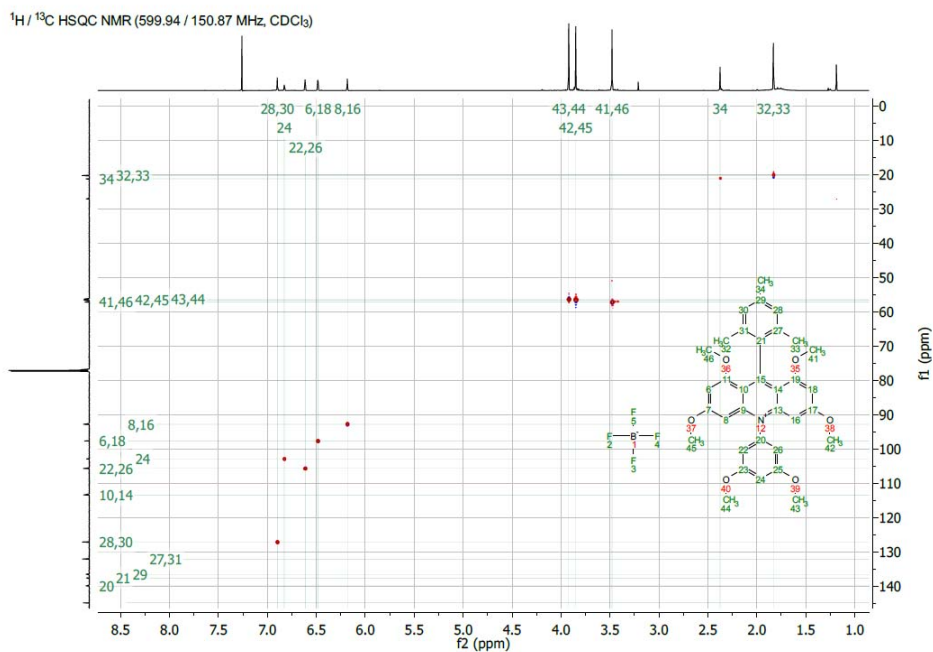
^{19}F NMR (470 MHz, CDCl_3) of **7**:



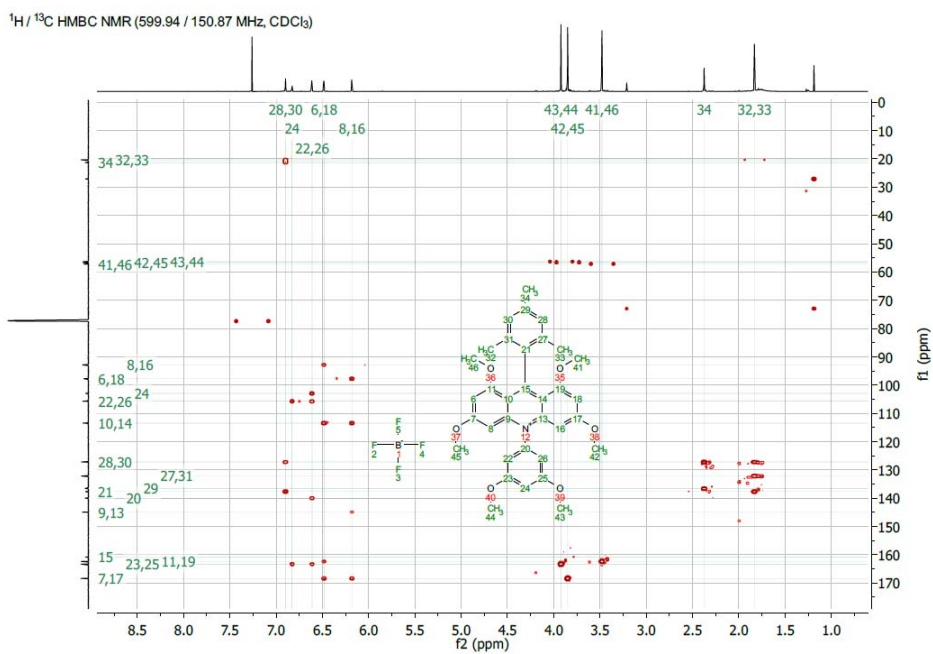
$^1\text{H}/^1\text{H}$ COSY NMR (600 / 600 MHz, CDCl_3) of **7**:



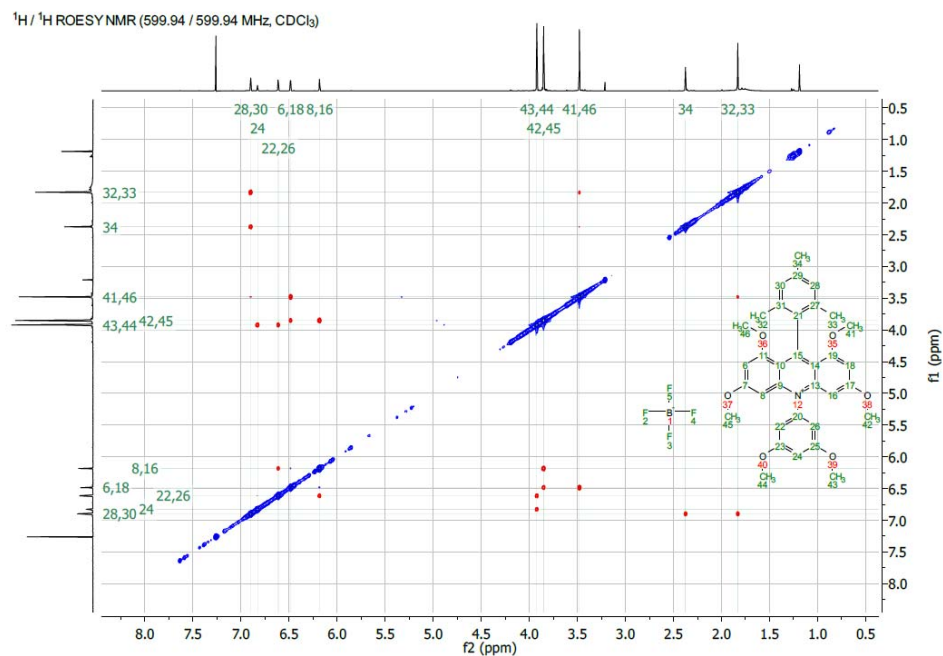
$^1\text{H}/^{13}\text{C}$ HSQC NMR (600/ 151 MHz, CDCl_3) of **7**:



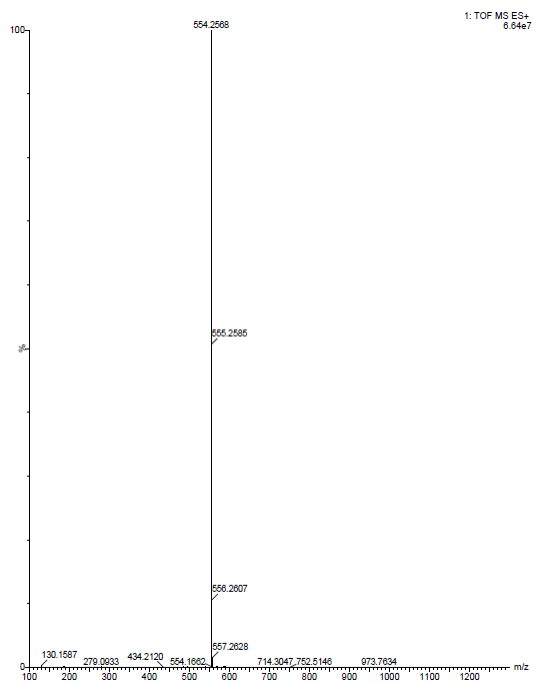
$^1\text{H}/^{13}\text{C}$ HMBC NMR (600/ 151 MHz, CDCl_3) of **7**:

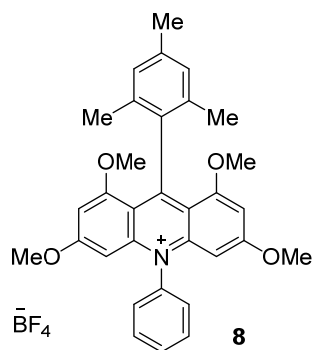


$^1\text{H}/^1\text{H}$ ROESY NMR (600 / 600 MHz, CDCl_3) of **7**:

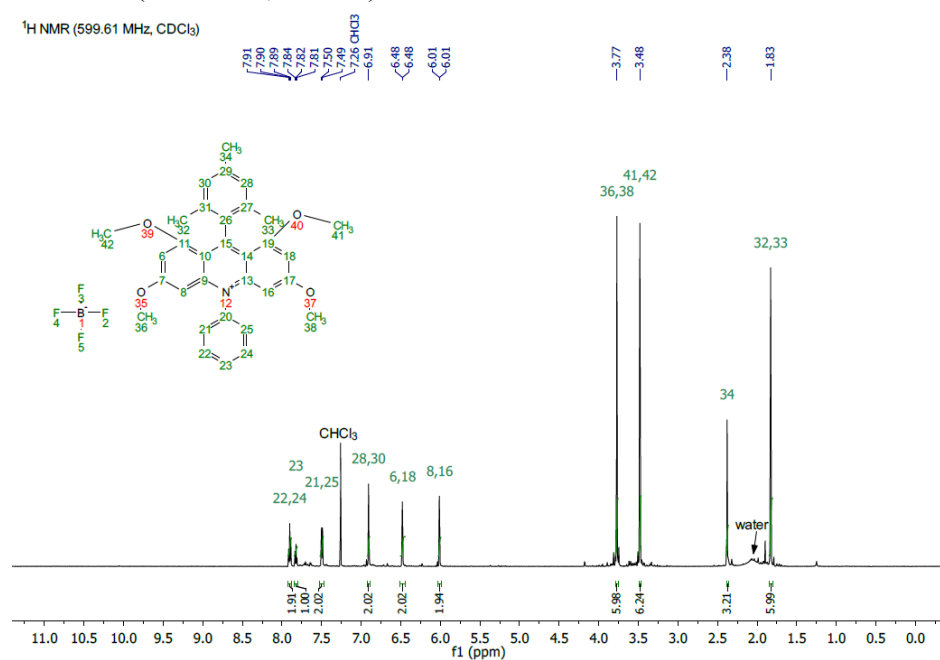


HRMS of catalyst 7:

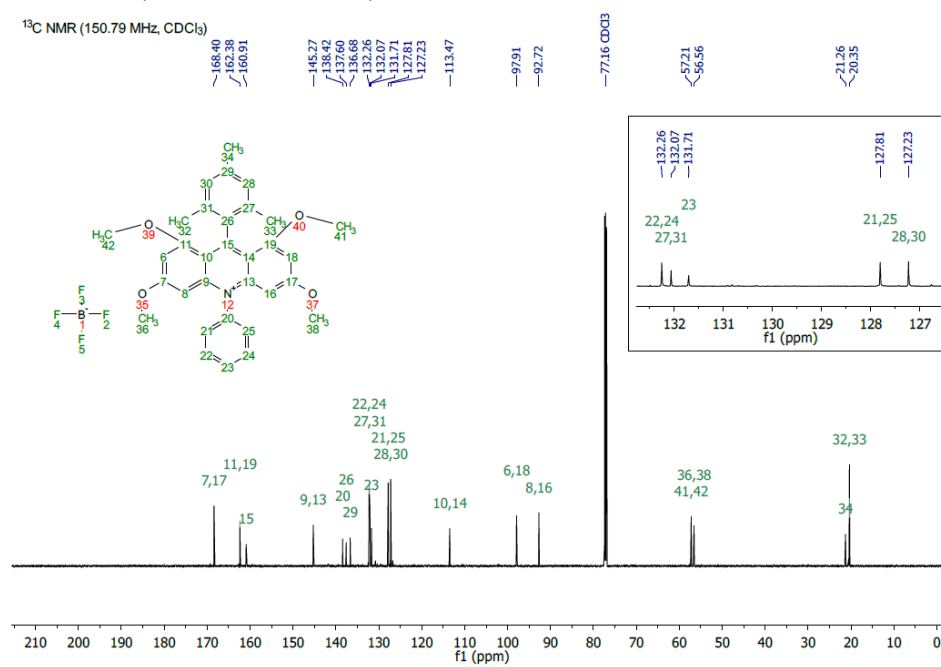




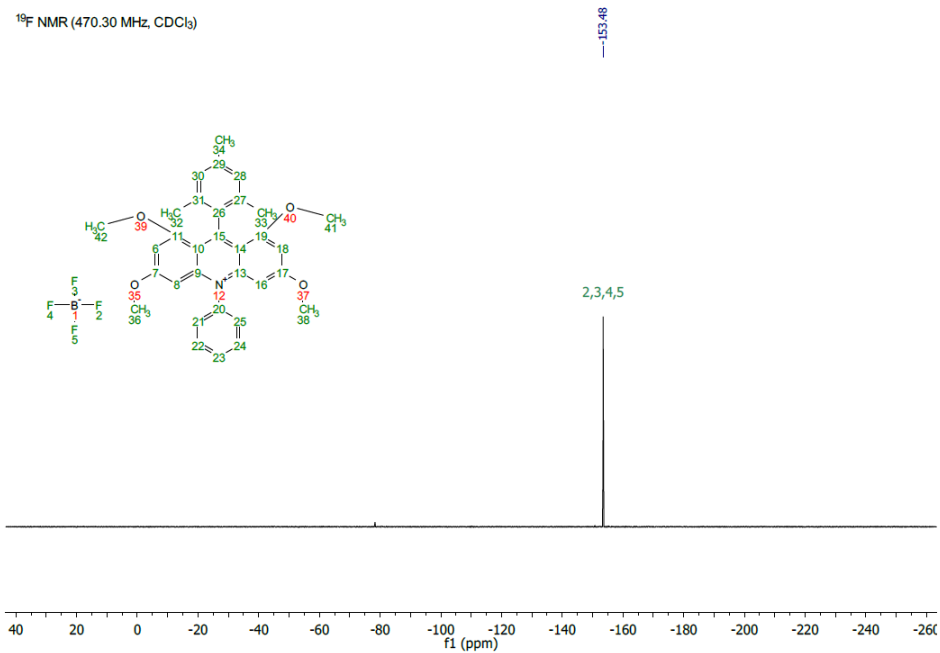
^1H NMR (600 MHz, CDCl_3) of **8**:



^{13}C NMR (151 MHz, CDCl_3) of **8**:

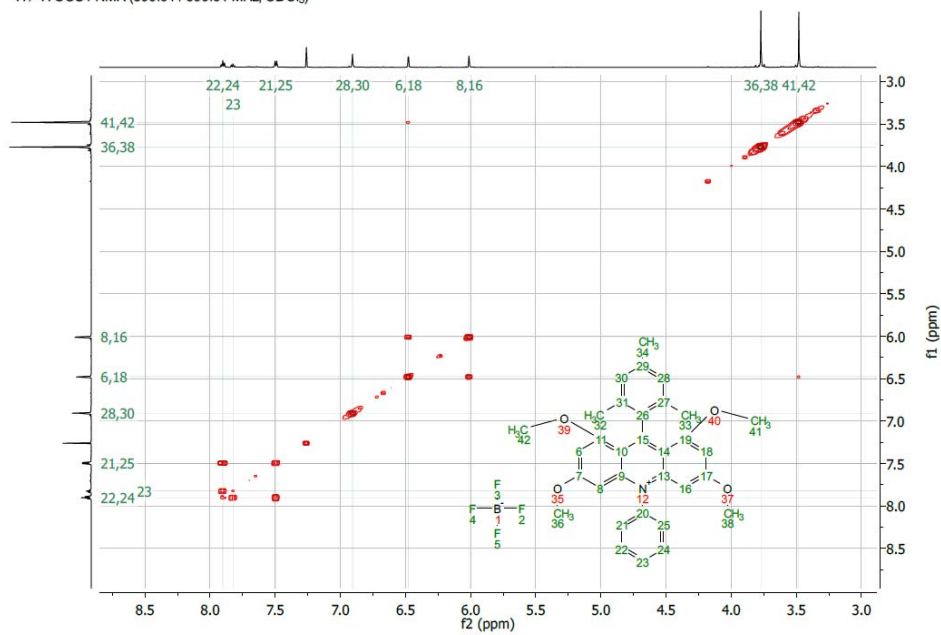


^{19}F NMR (470 MHz, CDCl_3) of **8**:



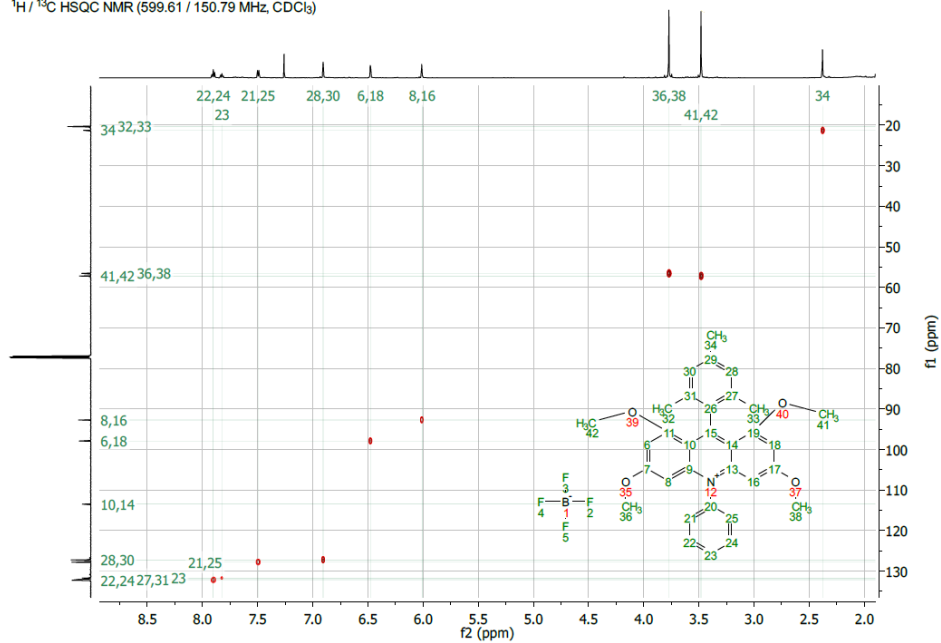
$^1\text{H}/^1\text{H}$ COSY NMR (600 / 600 MHz, CDCl_3) of **8**:

$^1\text{H}/^1\text{H}$ COSY NMR (599.61 / 599.61 MHz, CDCl_3)



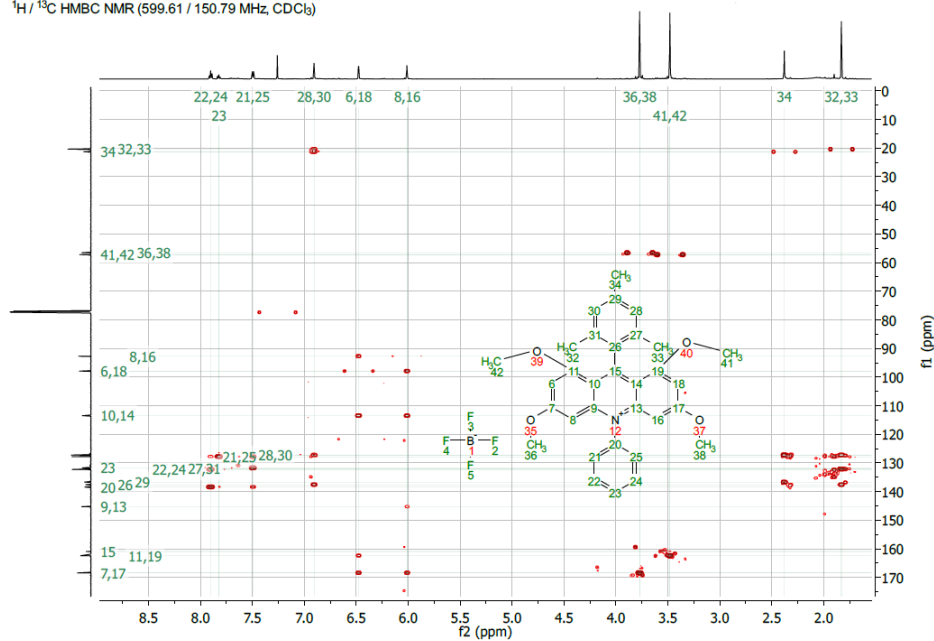
$^1\text{H}/^{13}\text{C}$ HSQC NMR (600 / 151 MHz, CDCl_3) of **8**:

$^1\text{H}/^{13}\text{C}$ HSQC NMR (599.61 / 150.79 MHz, CDCl_3)



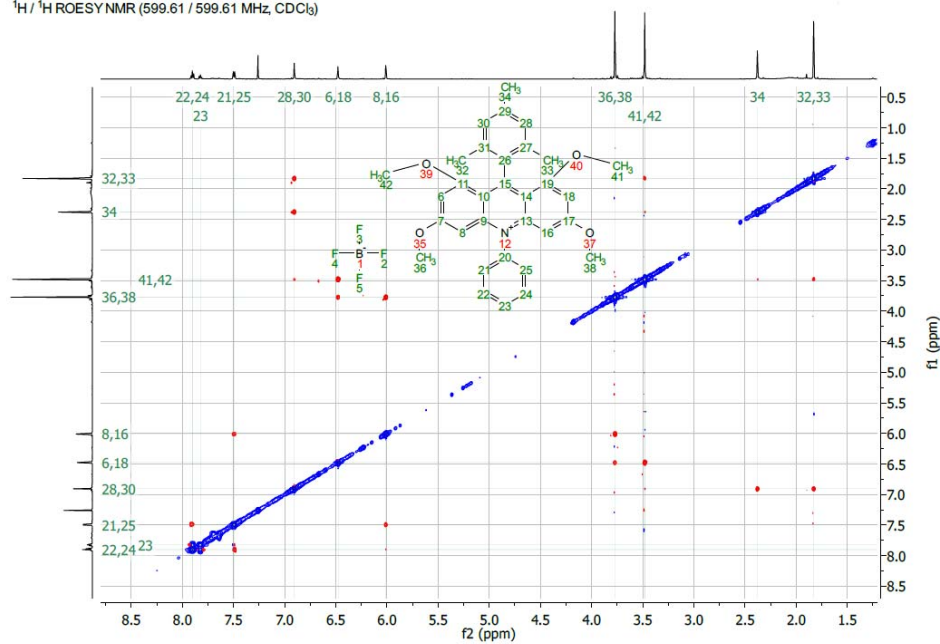
$^1\text{H}/^{13}\text{C}$ HMBC NMR (600 / 151 MHz, CDCl_3) of **8**:

$^1\text{H}/^{13}\text{C}$ HMBC NMR (599.61 / 150.79 MHz, CDCl_3)

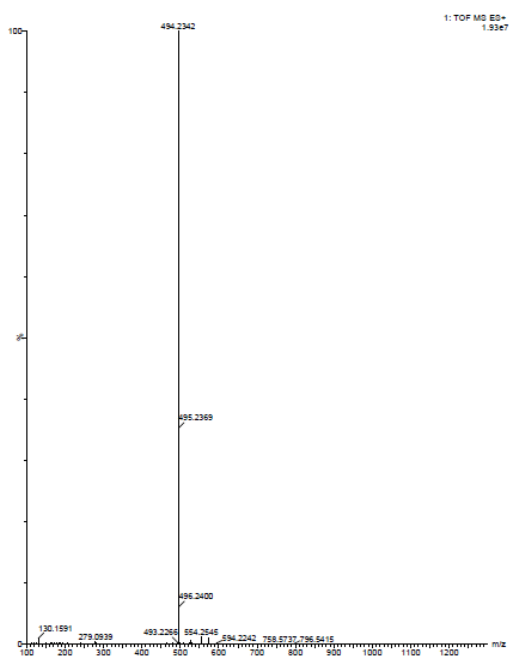


$^1\text{H}/^1\text{H}$ ROESY NMR (600 / 600 MHz, CDCl_3) of **8**:

$^1\text{H}/^1\text{H}$ ROESY NMR (599.61 / 599.61 MHz, CDCl_3)



HRMS of catalyst **8**:

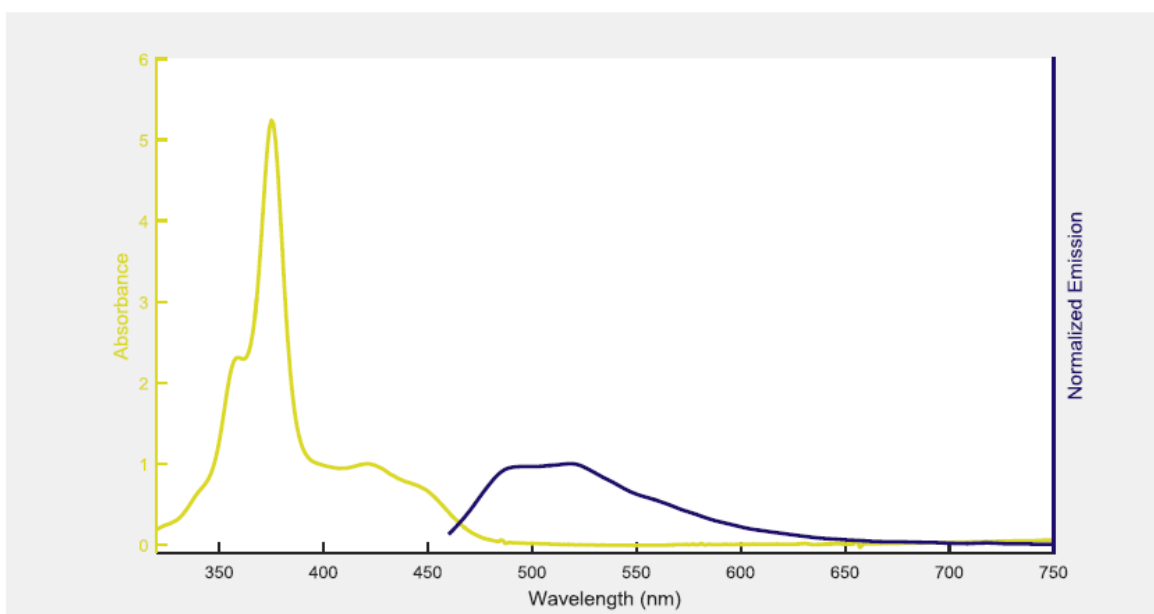
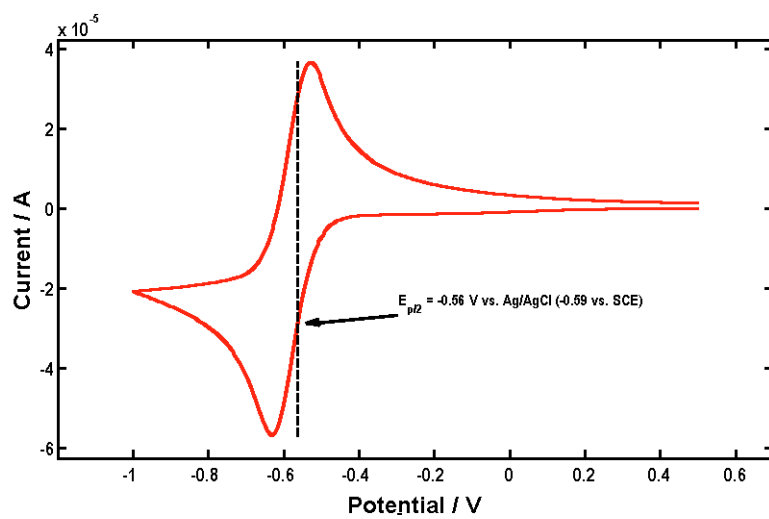
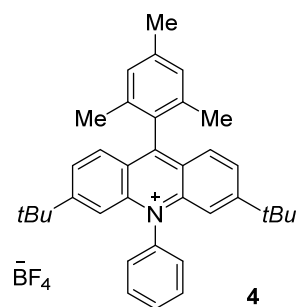


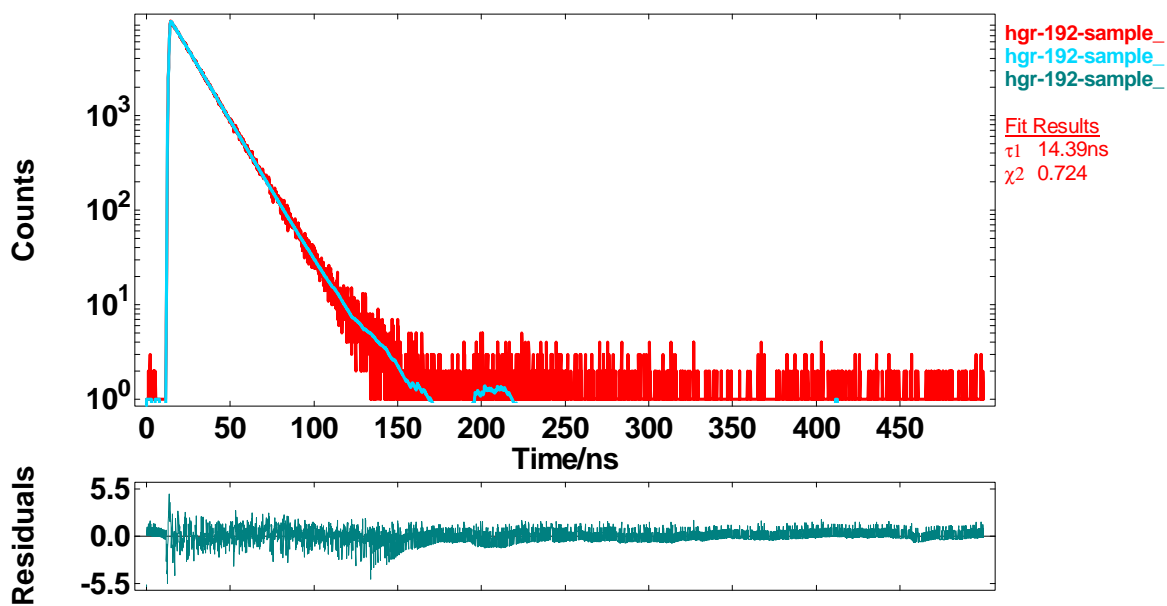
Photophysical and Redox Properties of Acridinium Salts:

Samples for electrochemical measurements were prepared with 5 mL of a 0.1 M tetra-*n*-butylammonium hexafluorophosphate solution in dry, degassed acetonitrile and 0.05 mmol of substrate. The corresponding cyclic voltammograms were collected with a Pine WaveNow Potentiostat employing a glassy carbon working electrode, platinum wire counter electrode, 3.5 M NaCl silver-silver chloride reference electrode, and a scan rate of 100 mV/s; the glassy carbon electrode was polished between scans. Data was analyzed with MATLAB by subtracting the electrolyte solution background current prior to identifying the maximum current (C_p) and determining the potential ($E_{p/2}$) at half this value ($C_{p/2}$). The obtained value was referenced to Ag|AgCl and converted to SCE by subtracting 0.03 V.

Samples for photophysical measurements were prepared in a nitrogen-filled glovebox using spectrophotometric grade 1,2-dichloroethane, which was freshly distilled from P_2O_5 . Stock solutions of the substrates were diluted to a concentration of 15 μ M and a total volume of 4 mL before being transferred to a 4 mL quartz cell and sealed with a PTFE-lined screw cap. The solvent absorbance background was subtracted from the reported spectra. Emission spectra (1 nm step size, 5 nm bandwidth) are fully corrected for the spectral response of the instrument. Time resolved emission measurements were made by the timecorrelate single photon counting (TCSPC) capability of the same instrument (FLS920) with pulsed excitation light (444.2 nm, typical pulse width = 95 ps) generated by a Edinburgh EPL- 445 ps pulsed laser diode operating at a repetition rate of 5 MHz. The lifetime of fluorescence was determined by reconvolution fit with the instrument response function using the Edinburgh FS900 software. Fluorescence decay fit satisfactorily according to the function $I_t = A_0e^{-t/\tau}$ or $I_t = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}$ where two τ -values are reported.

Excited state reduction potentials ($E_{p/2}^*$) were calculated by subtracting the ground-state reduction potential ($E_{p/2}$), obtained by cyclic voltammetry, from the excitation energy ($E_{0,0}$); $E_{0,0}$ is determined by calculating the energy of the wavelength at which the substrate's UV-Vis absorption and emission spectra overlap.





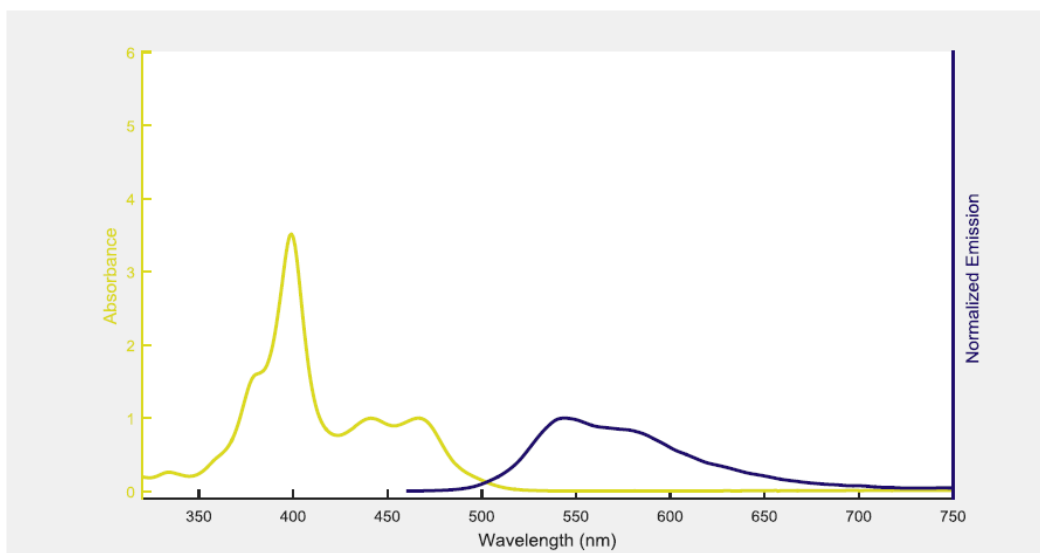
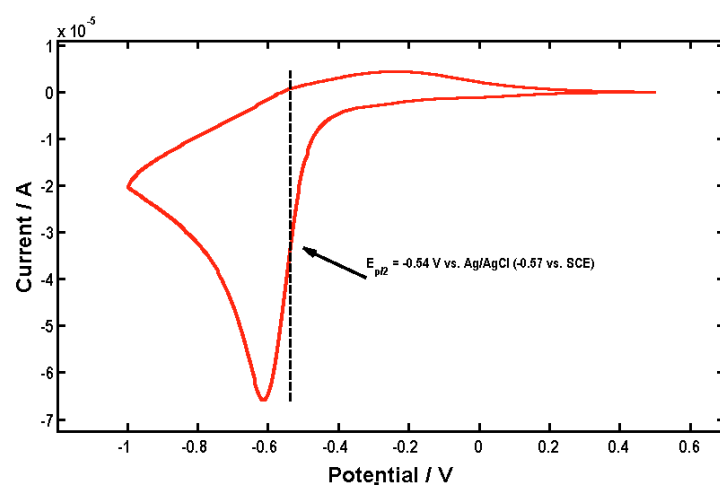
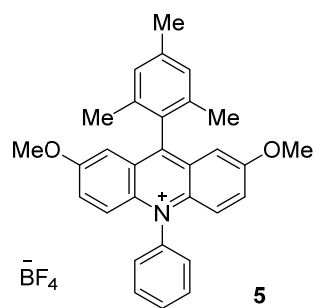
Emission $\lambda_{\text{max}} = 517 \text{ nm}$

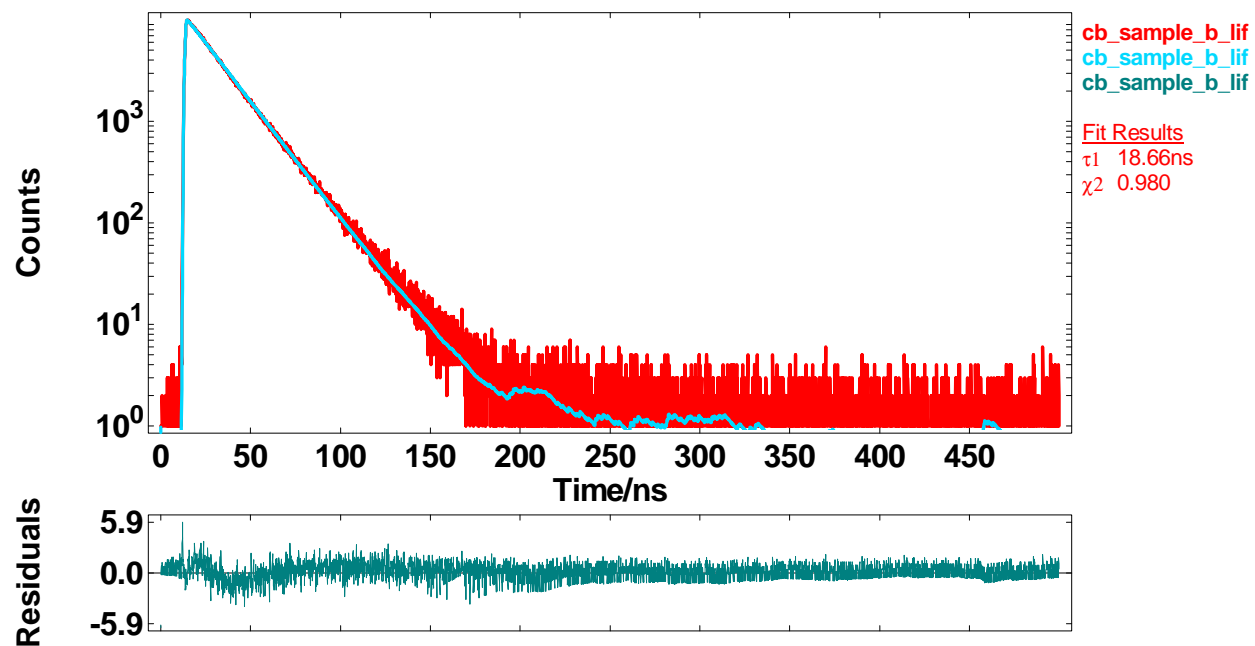
Absorbance $\lambda_{\text{max}} = 420 \text{ nm}$

$E_{0,0} = 2.67 \text{ eV}$

$E^*_{p/2} = 2.67 \text{ V} - 0.59 \text{ V} = 2.08 \text{ V}$

Lifetime: $\tau_F = 14.4 \text{ ns}$





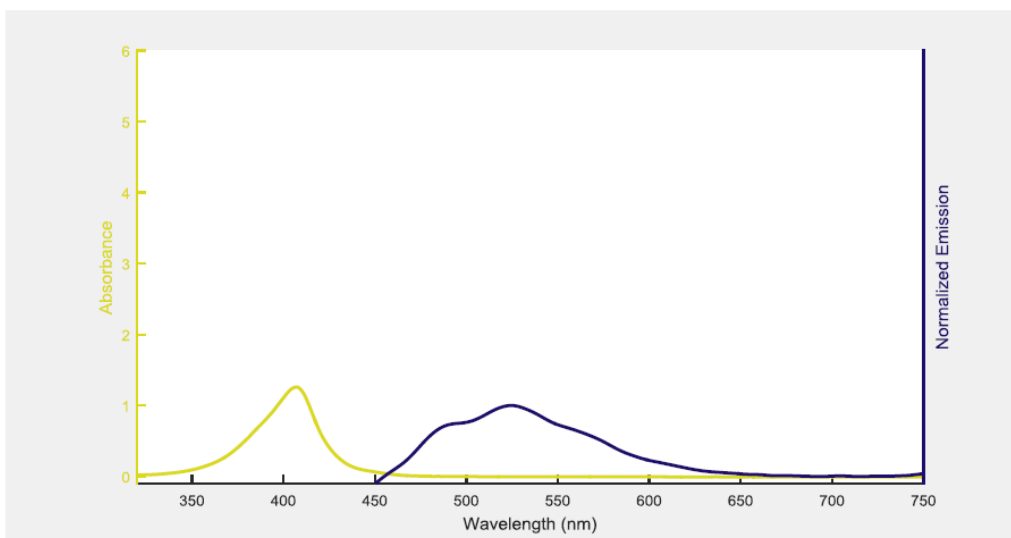
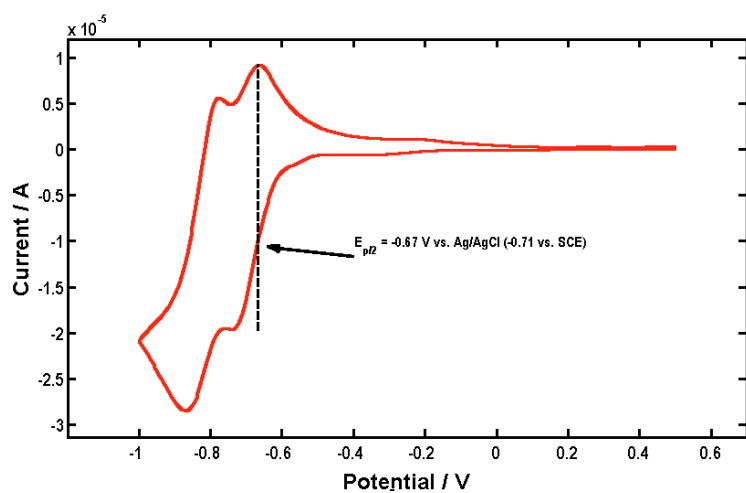
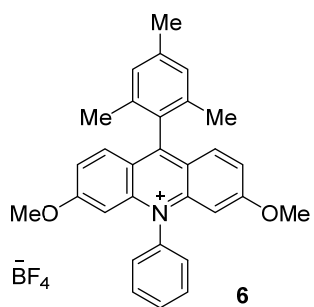
Emission $\lambda_{\text{max}} = 545 \text{ nm}$

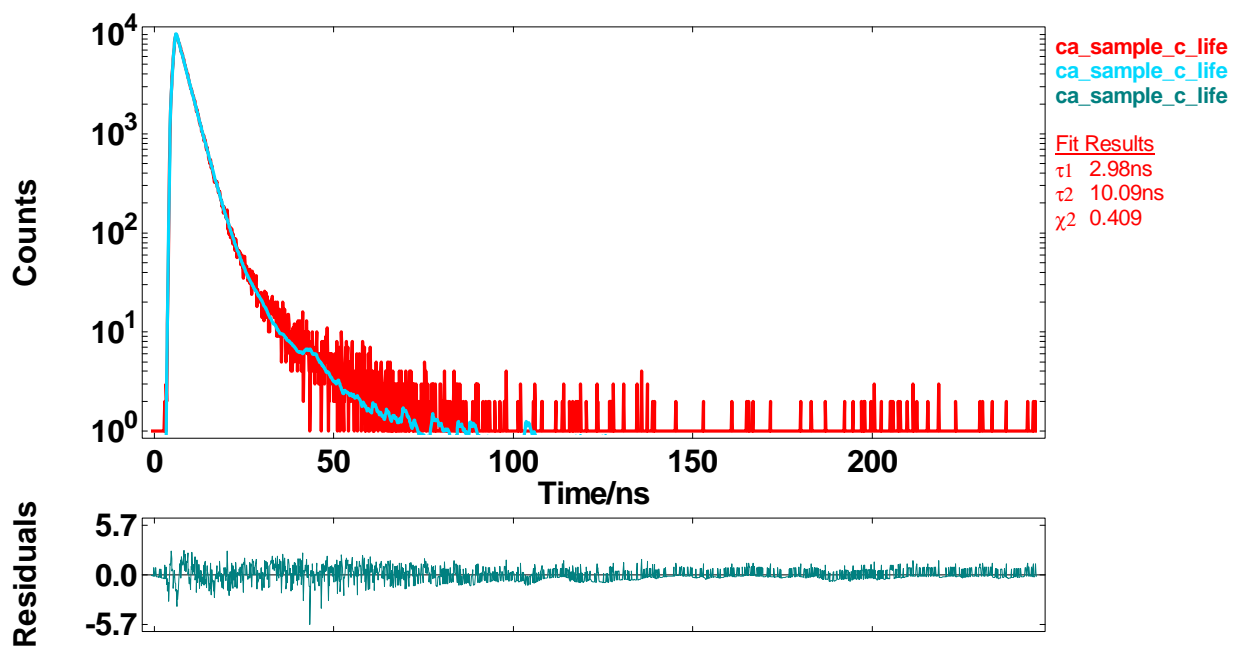
Absorbance $\lambda_{\text{max}} = 466 \text{ nm}$

$E_{0,0} = 2.47 \text{ eV}$

$E^*_{p/2} = 2.47 \text{ V} - 0.57 = 1.90 \text{ V}$

Lifetime: $\tau_f = 18.7 \text{ ns}$





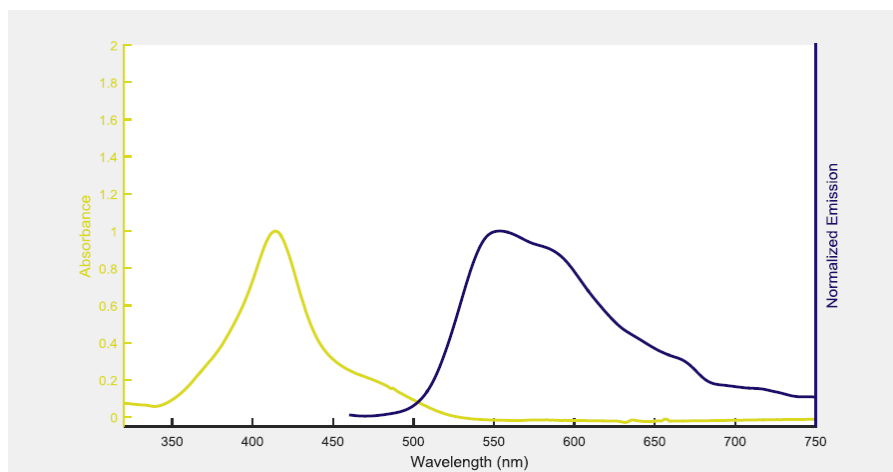
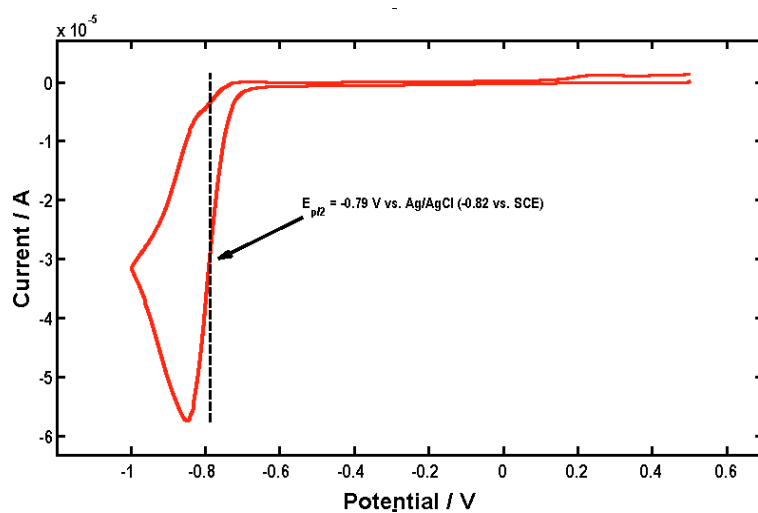
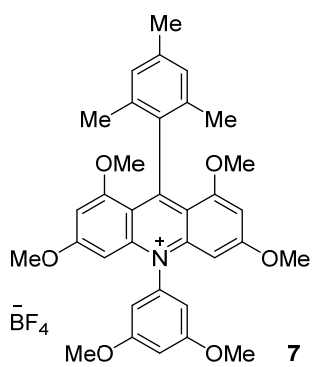
Emission $\lambda_{\max} = 525 \text{ nm}$

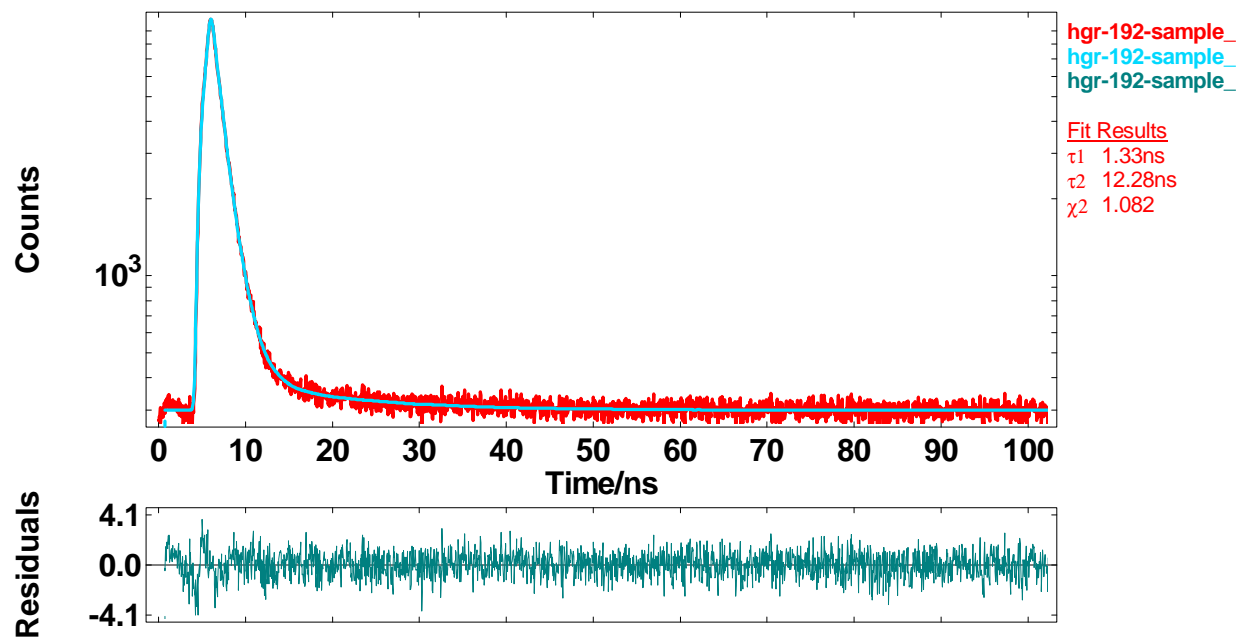
Absorbance $\lambda_{\max} = 407 \text{ nm}$

$E_{0,0} = 2.72 \text{ eV}$

$E^*_{p/2} = 2.72 \text{ V} - 0.71 \text{ V} = 2.01 \text{ V}$

Lifetime: $\tau_{F1} = 3.0 \text{ ns}$, $\tau_{F2} = 10.1 \text{ ns}$





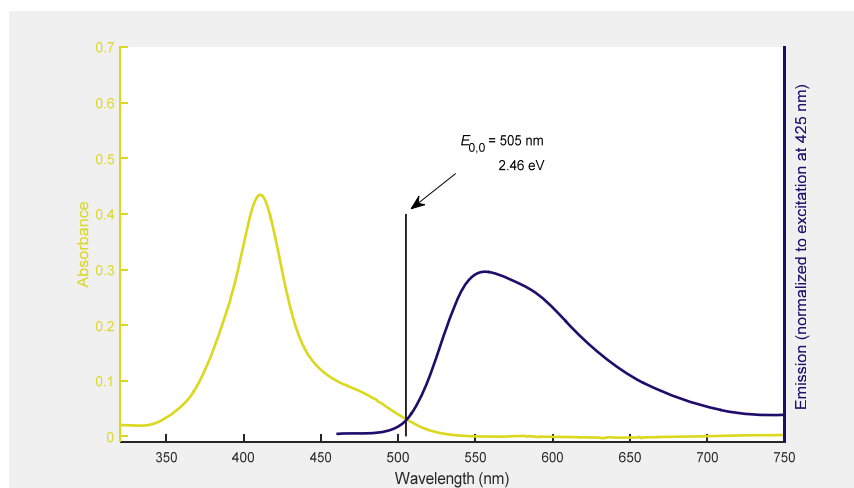
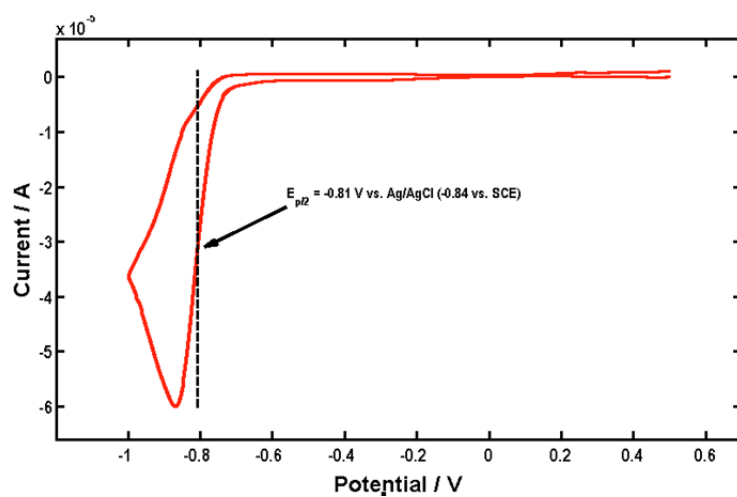
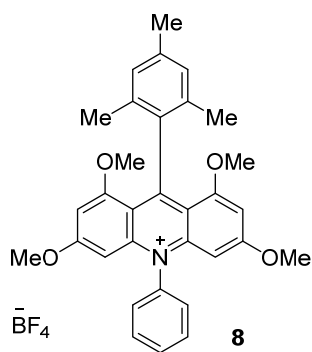
Emission $\lambda_{\max} = 550 \text{ nm}$

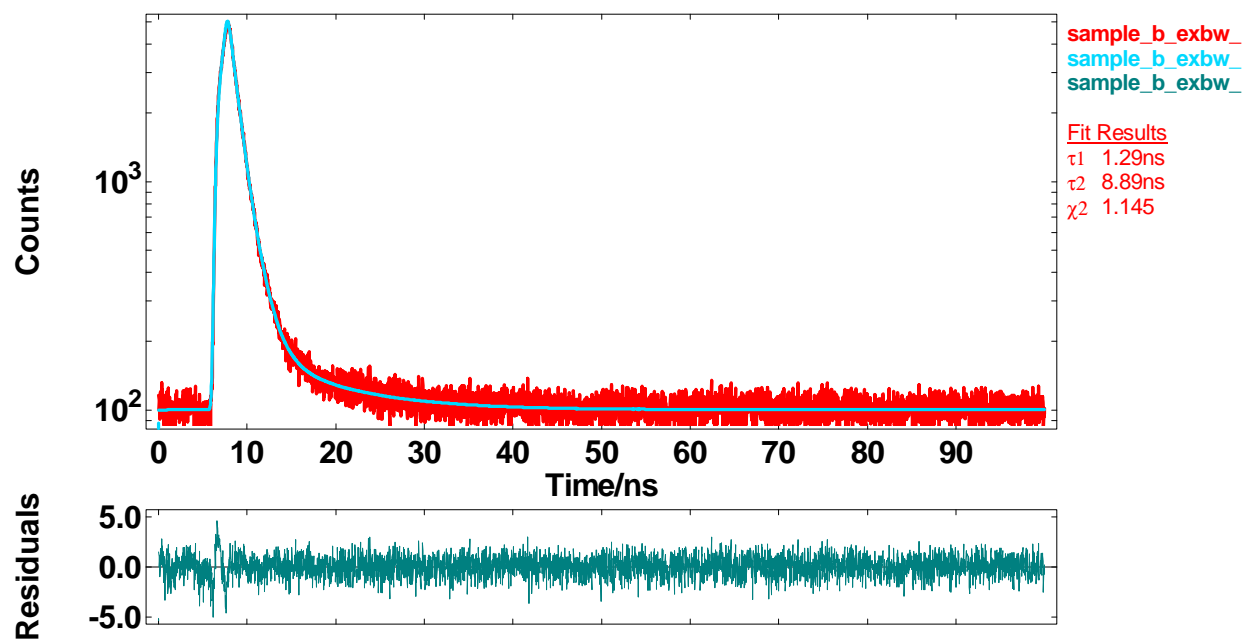
Absorbance $\lambda_{\max} = 414 \text{ nm}$

$E_{0,0} = 2.47 \text{ eV}$

$E^*_{p/2} = 2.47 \text{ V} - 0.82 \text{ V} = 1.65 \text{ V}$

Lifetime: $\tau_{F1} = 1.3 \text{ ns}$, $\tau_{F2} = 12.3 \text{ ns}$





Emission $\lambda_{\text{max}} = 550 \text{ nm}$

Absorbance $\lambda_{\text{max}} = 412 \text{ nm}$

$E_{0,0} = 2.46 \text{ eV}$

$E^*_{p/2} = 1.62 \text{ V}$

Lifetime: $\tau_{F1} = 1.3 \text{ ns}$ (92%), $\tau_{F2} = 8.9 \text{ ns}$ (8%)