

Supplementary Information as noted in the text

1,5-diaminonaphtalene is a highly-performing electron-transfer secondary reaction matrix for laser desorption-ionization mass spectrometry of indolenine-based croconaines

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Number of Figures: 13 (S1-S13)

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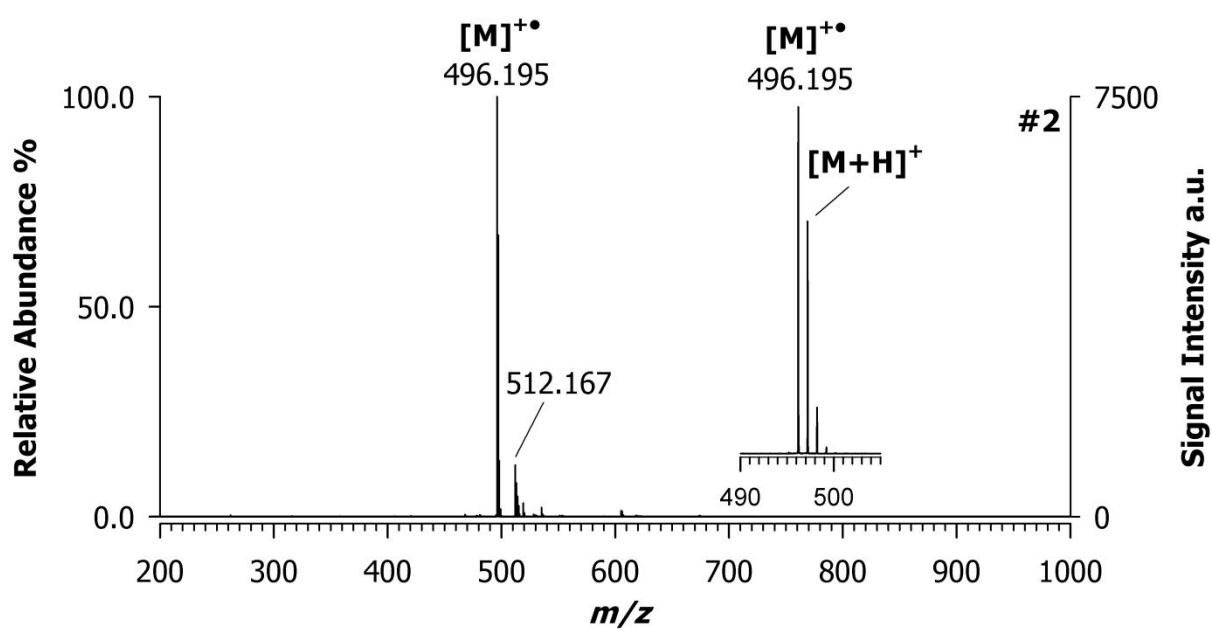


Figure S1. Positive ion LDI-ToF mass spectrum of croconaine dye #5. Enlarged isotopic pattern of the main peak detected is shown in inset.

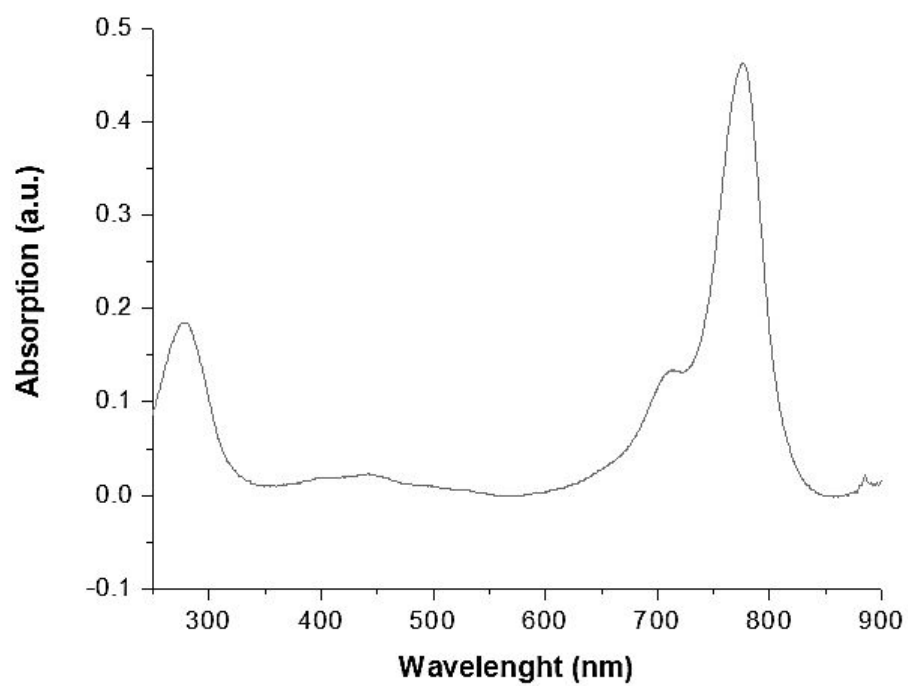


Figure S2. Absorption UV-visible-NIR spectrum of compound **#5** (see Table 1).

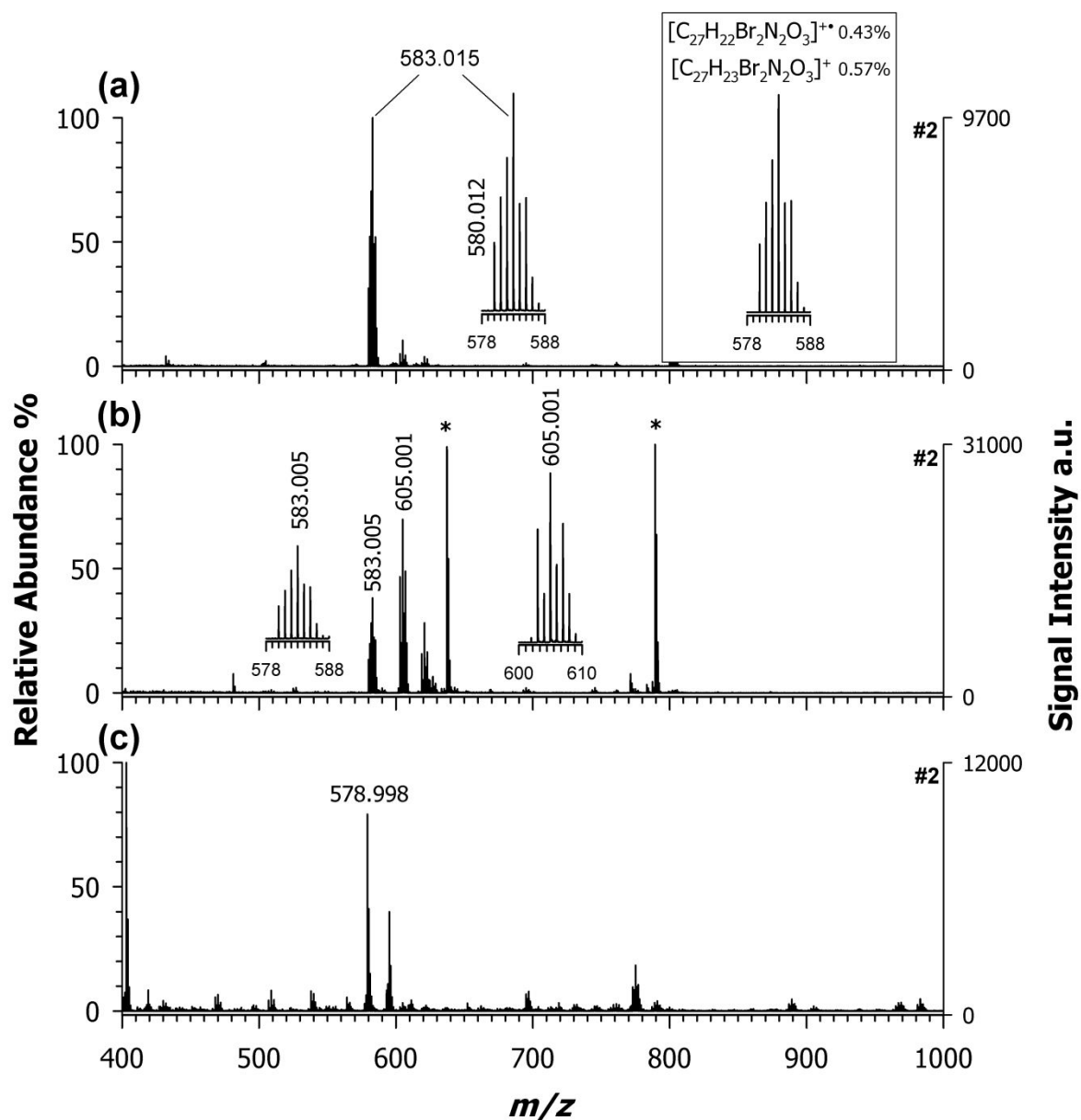


Figure S3. Positive ion mass spectra by MALDI-ToF MS of croconaine dye #2 obtained by using (a) CHCA, (b) DHB and (c) 9AA as matrices. Enlarged isotopic patterns of the main peaks detected in each spectrum are shown in insets. Peaks labelled with asterisk (plot b) are due to the matrix used. Note that peak signals of plot (c) are not related to croconaine dye #2.

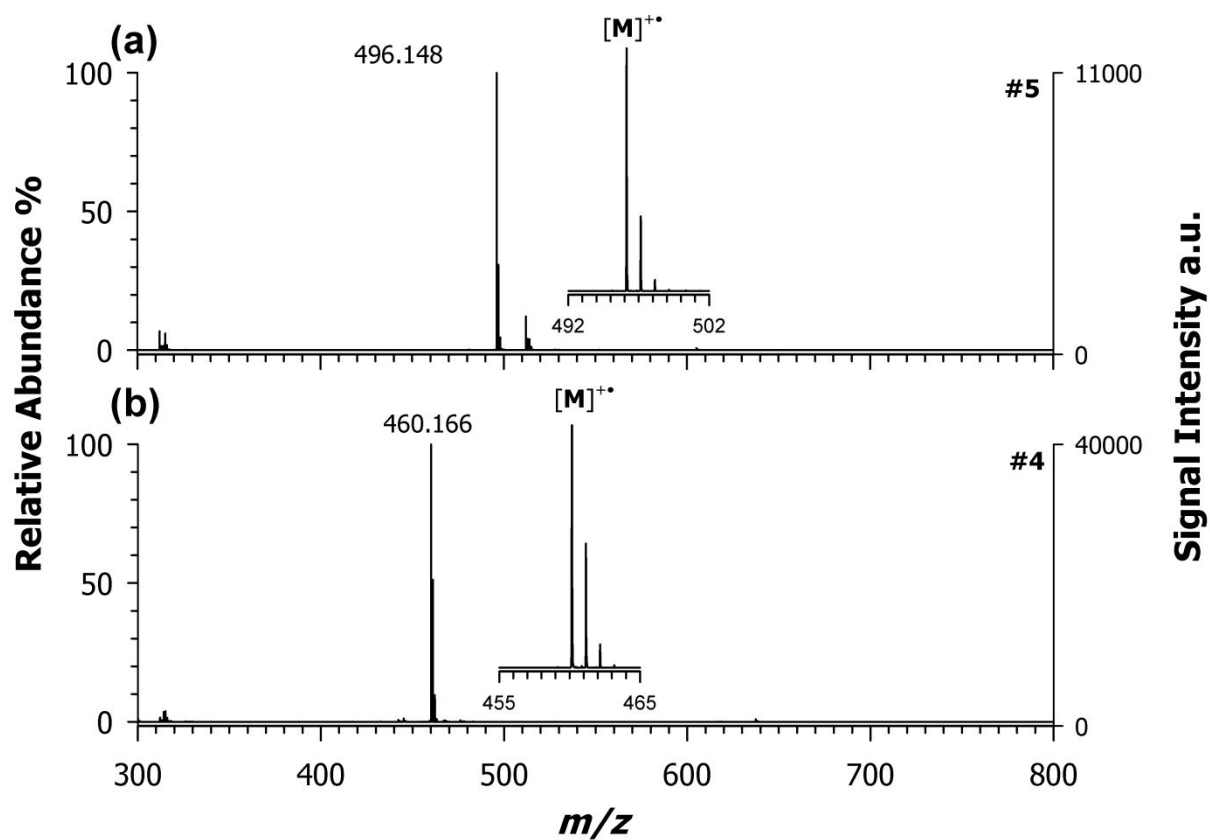


Figure S4. Positive ion mass spectra by MALDI-ToF MS of (a) croconaine dyes #5 ($C_{27}H_{20}F_4N_2O_3$) and (b) #4 ($C_{27}H_{22}F_2N_2O_3$) obtained by using DAN as matrix. Enlarged ion clusters are shown in insets.

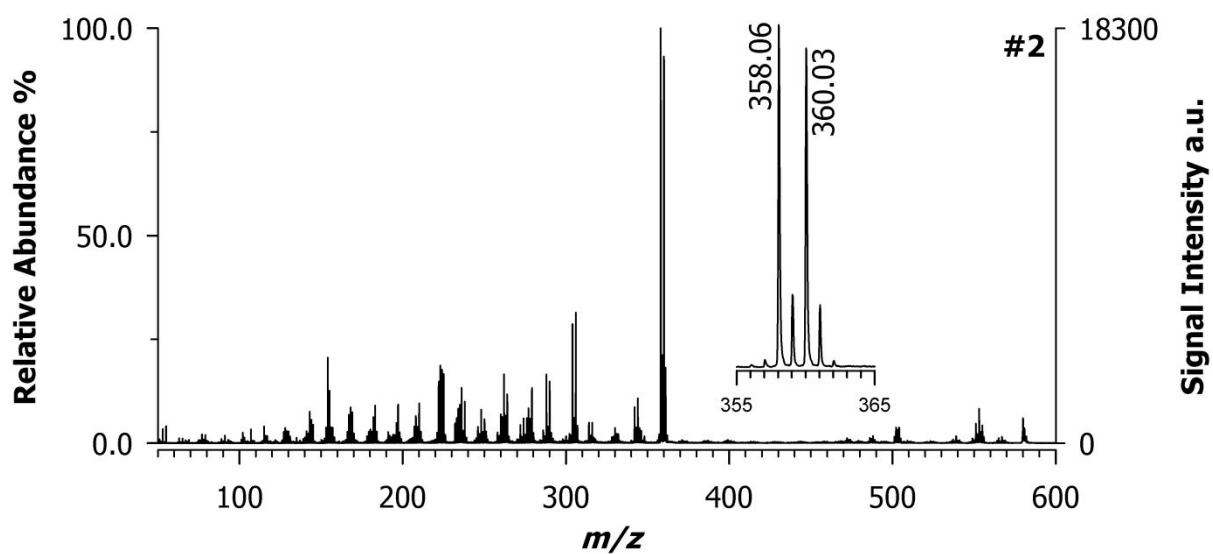


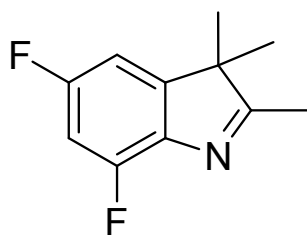
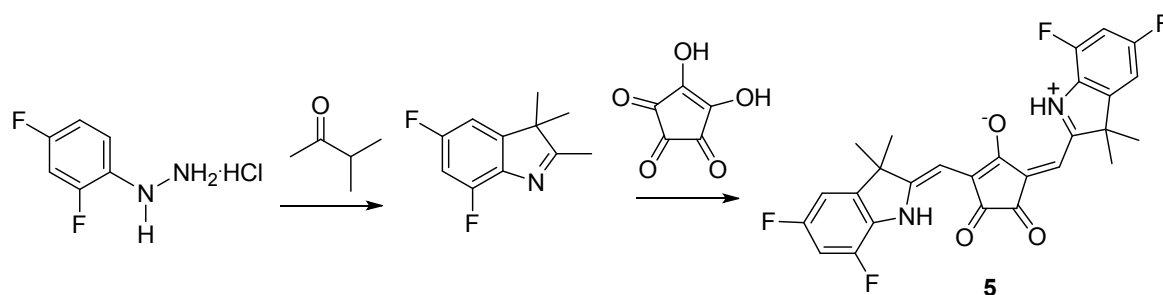
Figure S5. Positive mass spectrum by MALDI-ToF/ToF MS of croconaine dye #2 using CHCA as a matrix.

Synthesis of croconaine #5

Reagents were purchased at the highest commercial quality from Sigma-Aldrich, Apollo Scientific and TCI Europe and used without further purification. Preparative column chromatography was carried out using Macherey-Nagel silica gel (60, particle size 0.063-0.2 mm). Macherey-Nagel aluminum sheets with silica gel 60 F₂₅₄ were used for TLC analyses. All new compounds were characterized by ¹H NMR, ¹³C NMR, FT-IR spectroscopy and LC-MS analysis. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Inova at 500 and at 125 MHz and on a Bruker Avance 2 at 600 and at 151 MHz respectively, by using the residual proton peak of CDCl₃ at $\delta = 7.26$ ppm as internal standard for ¹H spectra and the signal of CDCl₃ at $\delta = 77$ ppm as internal standard for ¹³C spectra. IR spectra were recorded on a Perkin-Elmer IR Spectrum Bx.

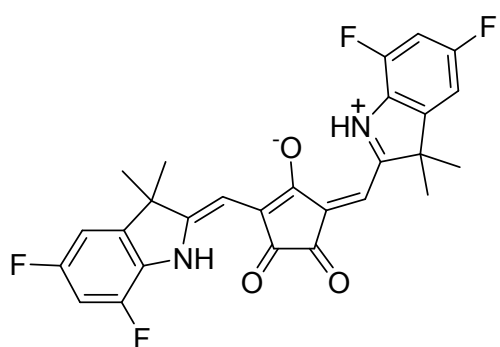
High-resolution mass spectra were acquired on a Shimadzu ion trap-time of flight mass spectrometer (IT-TOF) *via* direct infusion of the samples using methanol as the elution solvent.

Melting points were determined on a Stuart Scientific Melting point apparatus SMP3.



Synthesis of 5,7-difluoro-2,3,3-trimethyl-3H-indole. Title compound was synthesized from 2,4-difluorophenylhydrazine hydrochloride (1.98 g, 11 mmol) and 3-methylbutan-2-one (2 mL, 21 mmol) in acetic acid (15 mL) in accordance with the general

procedure. The crude mixture was purified by column chromatography (silica gel, diethyl ether/chloroform, 1:1) yielding the desired product. Brown oil, yield 47%; LCMS-IT-TOF calculated for $C_{11}H_{12}NF_2$ $[M+H]^+$: 196.0932, found: m/z 196.0918; 1H NMR ($CDCl_3$, 400 MHz) δ : 6.81 - 6.72 (m, 2H), 2.27 (s, 3H), 1.28 (s, 6H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ : 187.9 (d, $J = 3.0$ Hz), 161.0 (dd, $J = 246.8, 9.4$ Hz), 152.9 (dd, $J = 256.1, 12.6$ Hz), 149.9 (dd, $J = 9.5, 4.5$ Hz), 136.5 (dd, $J = 11.1, 2.2$ Hz), 104.9 (dd, $J = 24.0, 3.9$ Hz), 102.9 (dd, $J = 27.2, 22.7$ Hz), 54.8 (dd, $J = 2.2, 1.8$ Hz), 22.9, 15.4; IR (KBr, cm^{-1}) ν : 2967, 1601, 1511, 1458, 1267, 1107, 848.



Synthesis of 3-(5,7-difluoro-3,3-dimethyl-1,3-dihydro-indol-2-ylidenemethyl)-5-(5,7-difluoro-3,3-dimethyl-3H-indol-2-ylmethylene)-4-hydroxy-cyclopent-3-ene-1,2-dione (5).

Compound **5** was synthesized from **1** (780 mg, 4 mmol) and croconic acid (284 mg, 2 mmol) in a refluxing mixture (110°C) of 1-butanol (10 mL) and dry toluene (10 mL) using Dean-Stark apparatus to remove water. After 3h, the reaction mixture was cooled to -20 °C for 24 h. The reaction mixture was warmed to room temperature and the precipitate was filtered off and washed with diethyl ether and hexane. Finally, compound **5** was purified by column chromatography (silica gel, diethyl ether/chloroform, 9:1). Dark green solid, yield 35%; m.p. 282-285°C; LCMS-IT-TOF calculated for $C_{27}H_{19}F_4N_2O_3$ $[M-H]^-$: 495.1337, found: m/z 495.1367; 1H -NMR ($CDCl_3$, 500 MHz) δ : 16.61-14.56 (m, 2H), 6.96-6.80 (m, 4H), 6.20-5.96 (m, 2H), 1.54-1.53 (m, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 185.6, 185.5, 184.7, 177.6, 176.4, 174.1, 160.5 (dm, $J = 244$ Hz), 148.4 (dm, $J = 245$ Hz), 146.2, 145.8, 145.2, 144.8, 144.6, 144.0, 126.0, 125.6, 125.5, 106.6, 104.3, 104.2, 96.1, 94.8, 91.9, 51.9, 51.6, 51.1, 26.4, 25.9, 25.8; IR (KBr, cm^{-1}) ν : 2920, 1479, 1337, 1300, 1178, 900.

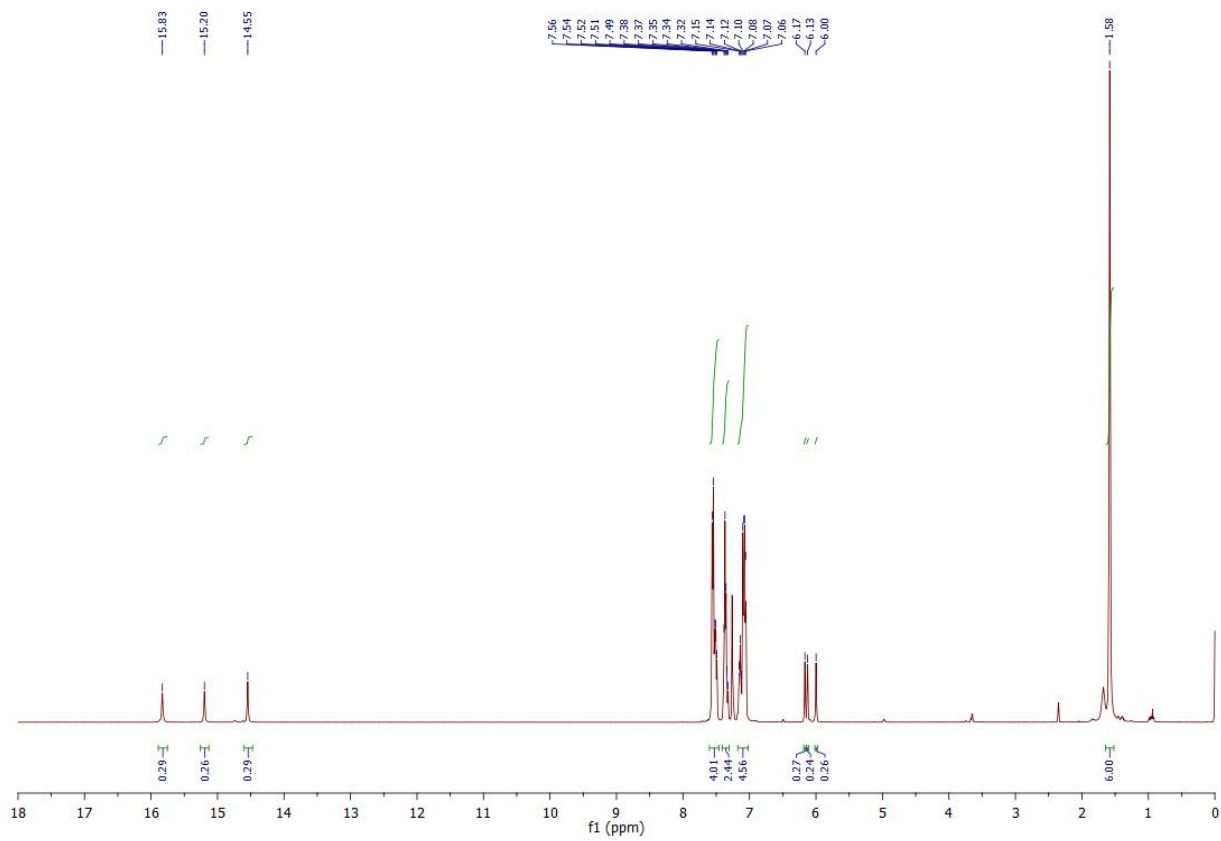


Figure S6. ^1H NMR spectrum of croconaine **#1** (500 MHz, CDCl_3).

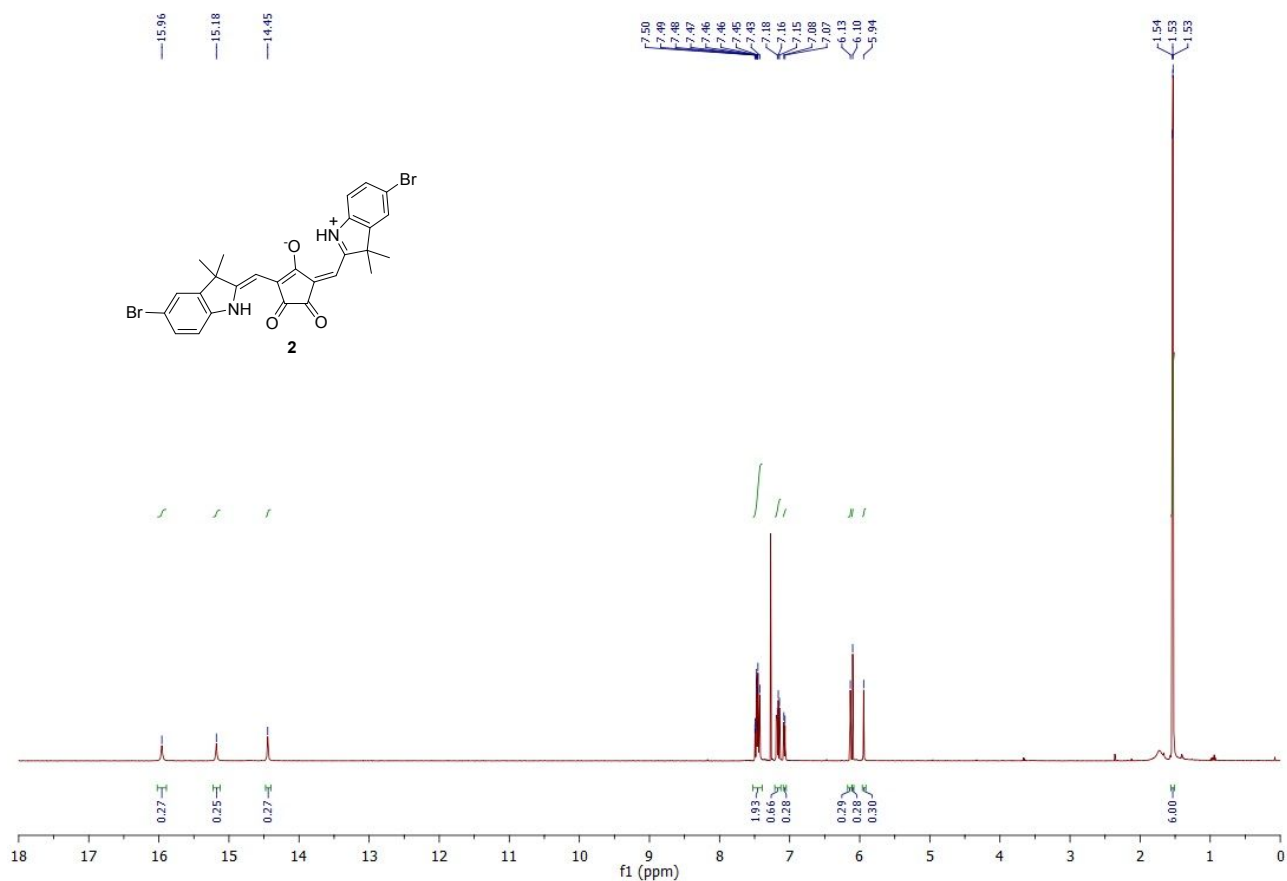


Figure S7. ¹H NMR spectrum of croconaine #2 (600 MHz, CDCl₃).

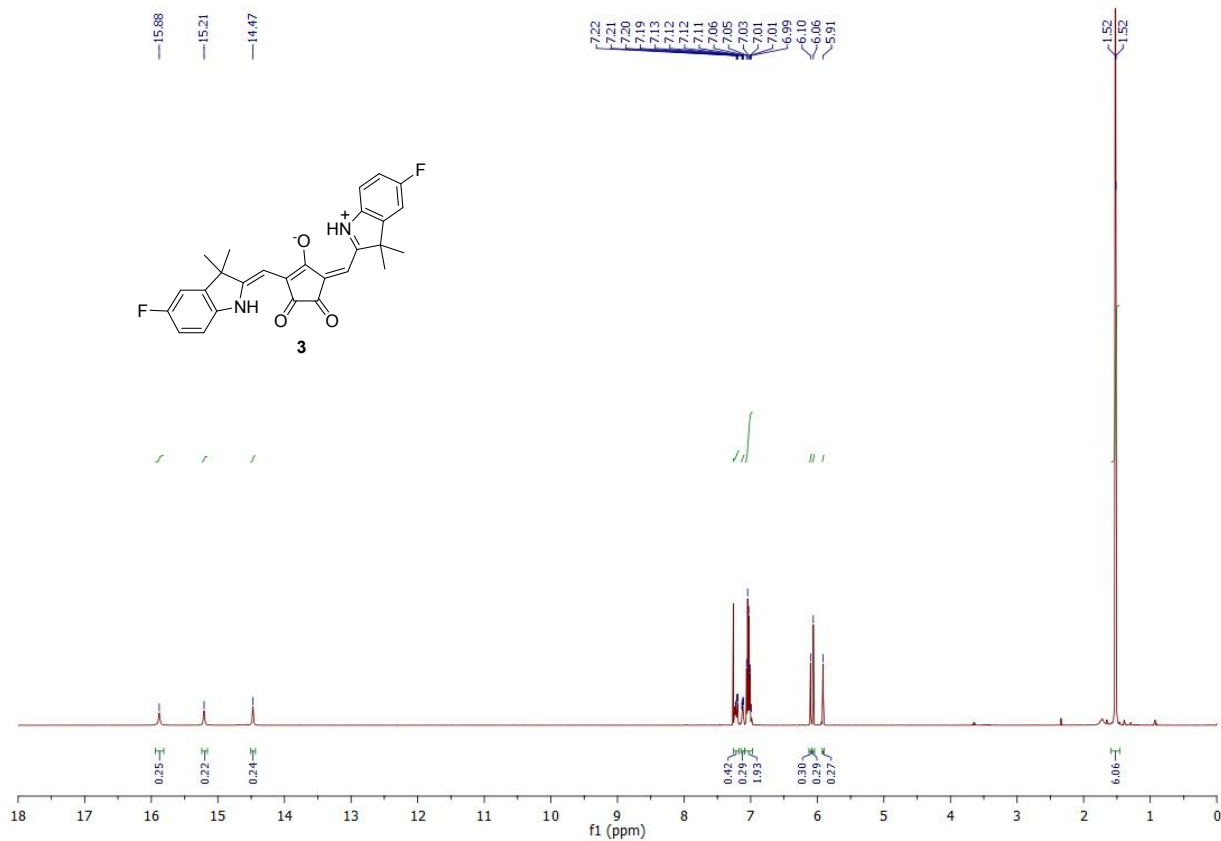


Figure S8. ¹H NMR spectrum of croconaine #3 (500 MHz, CDCl₃).

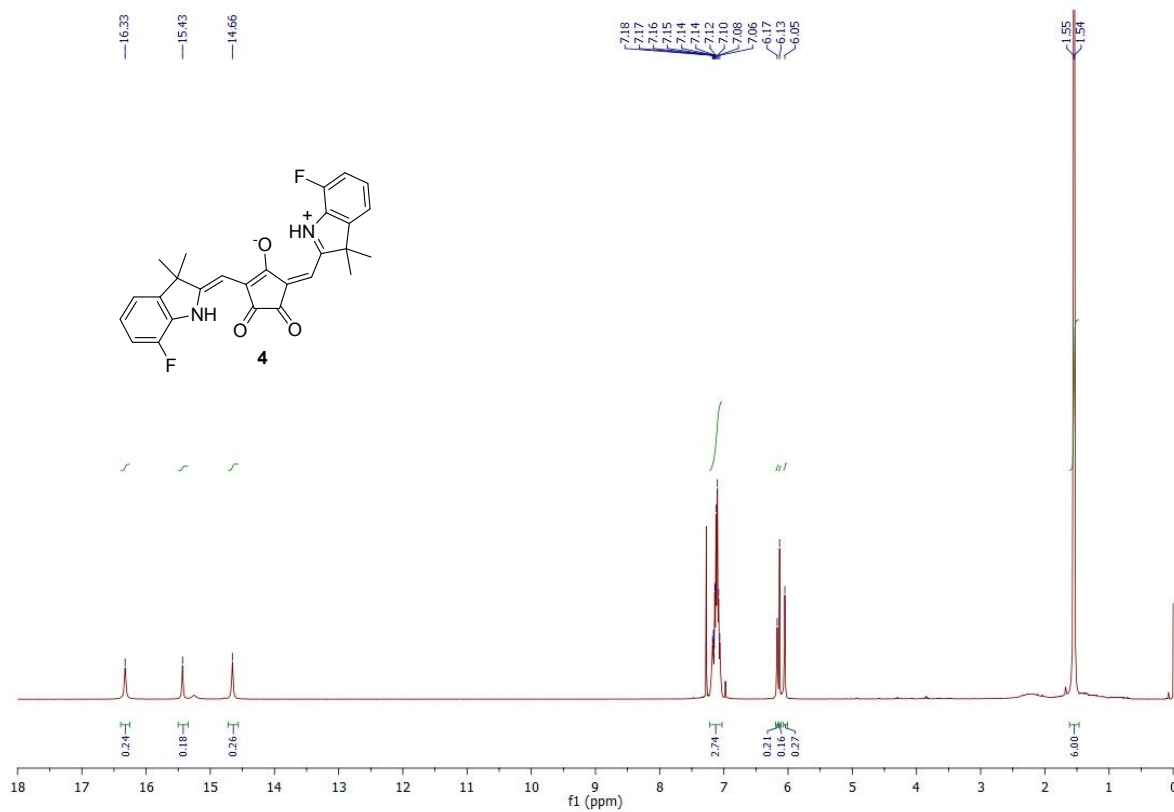


Figure S9. ¹H NMR spectrum of croconaine #4 (500 MHz, CDCl₃).

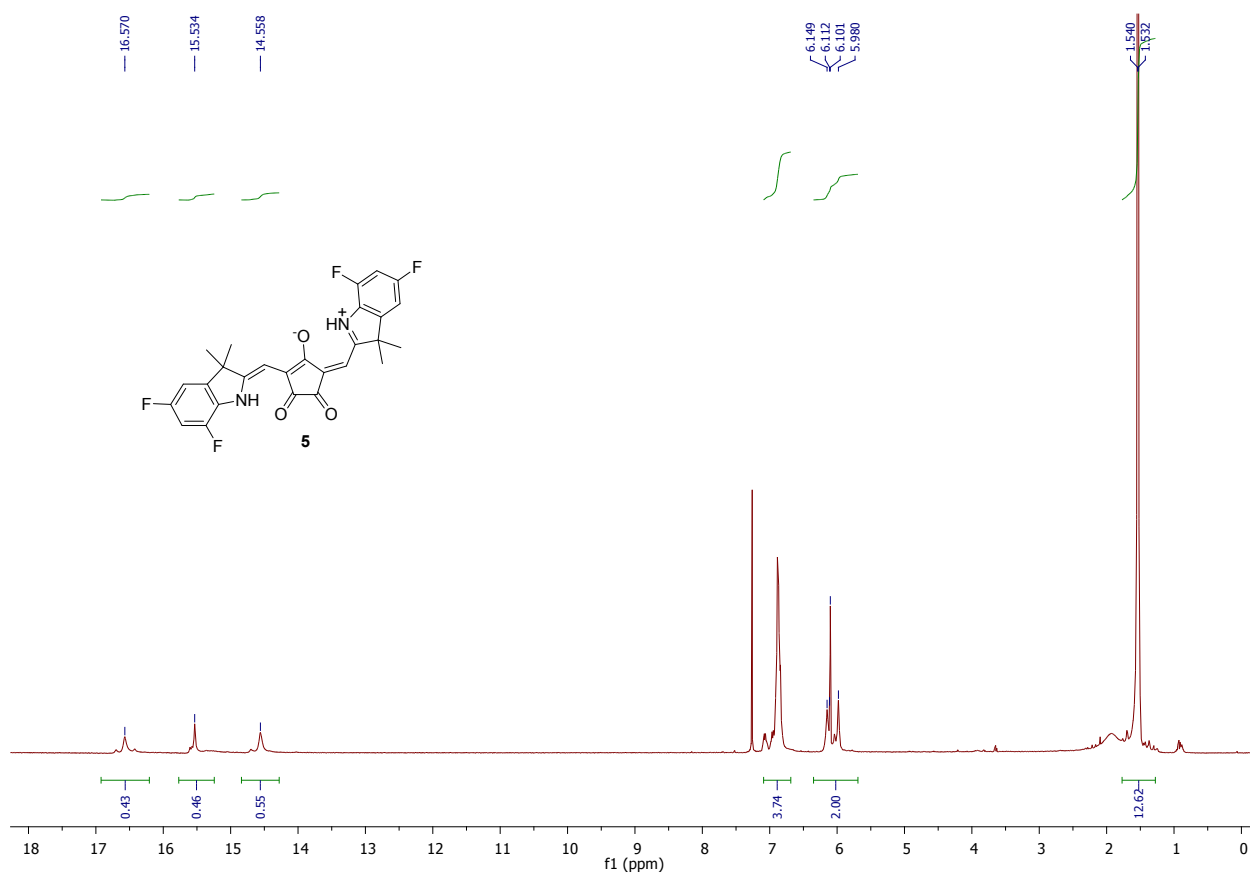


Figure S10. ¹H NMR spectrum of croconaine #5 (500 MHz, CDCl₃).

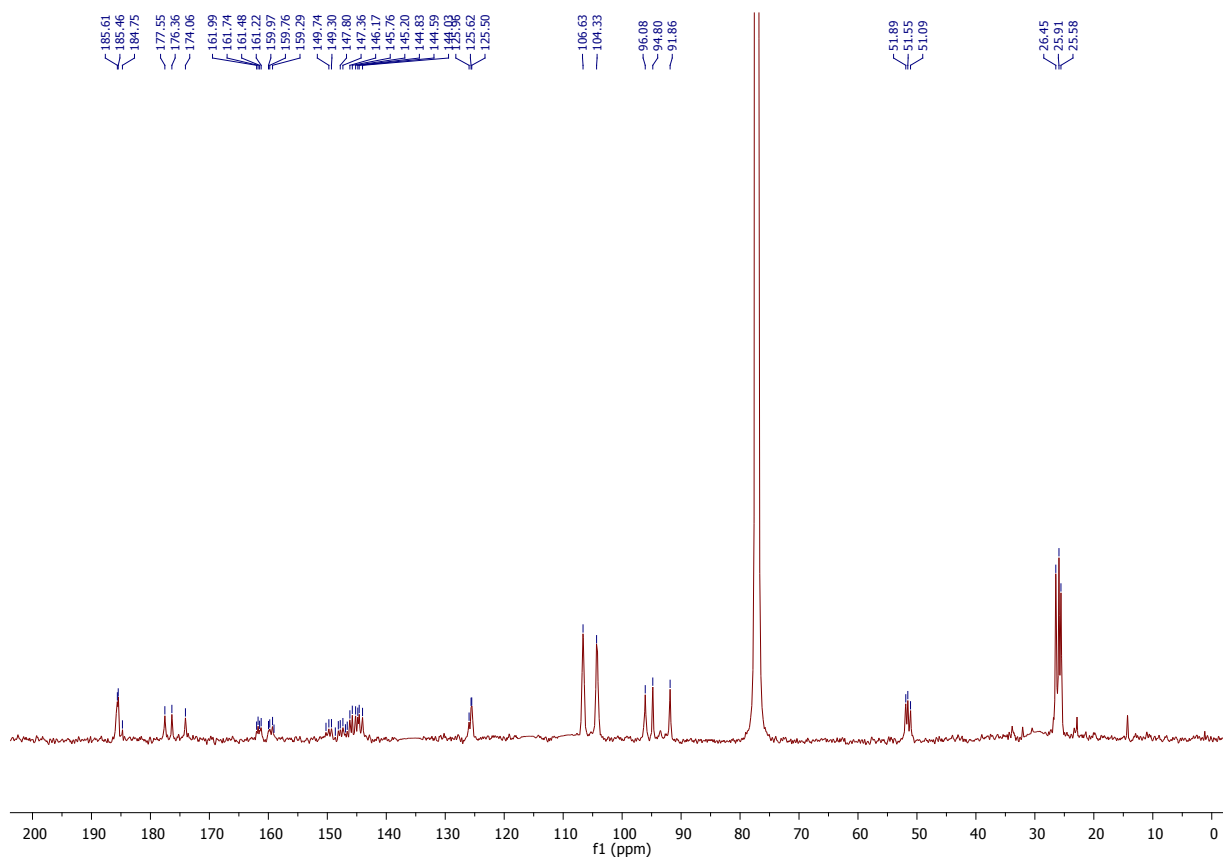


Figure S11. ^{13}C NMR spectrum of croconaine #5 (125 MHz, CDCl_3).

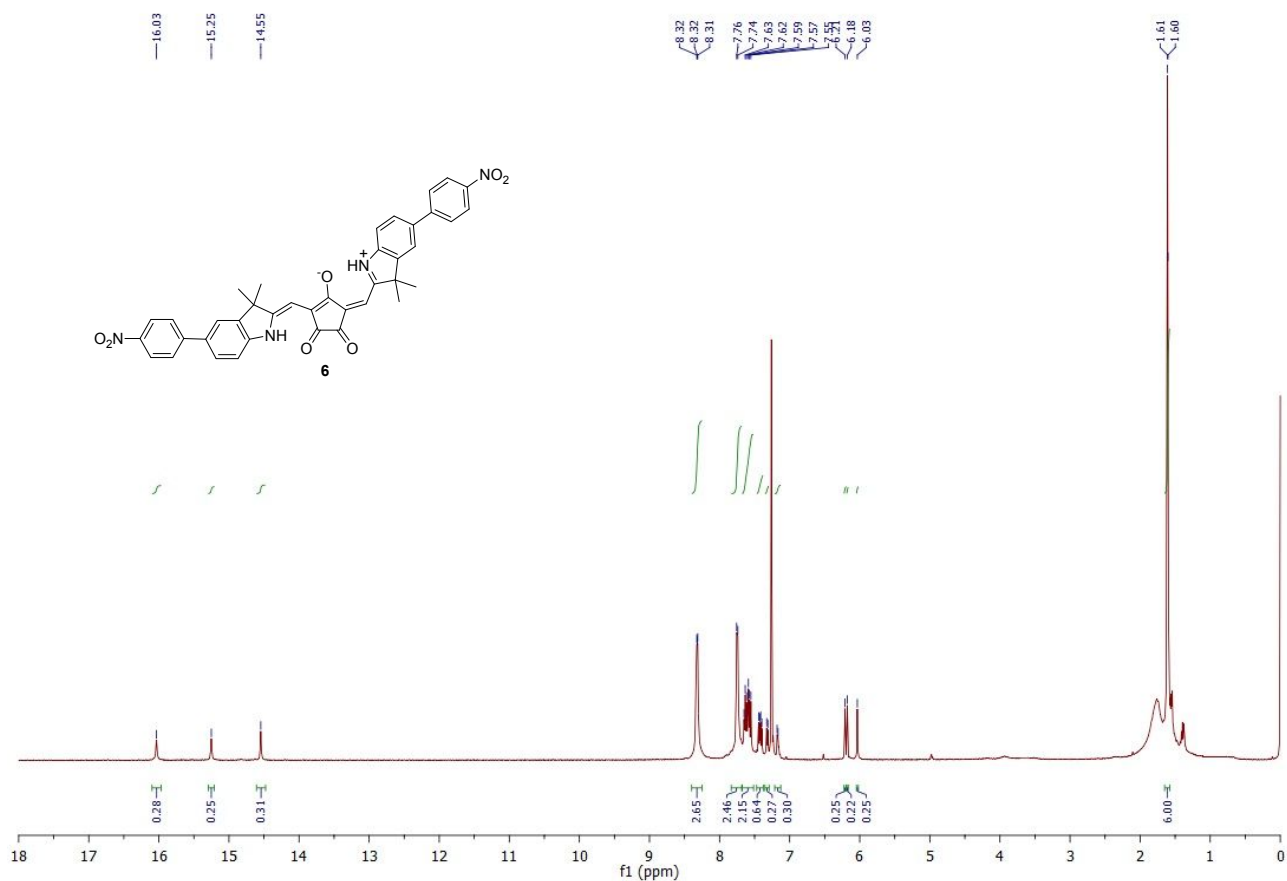


Figure S12. ^1H NMR spectrum of croconaine #6 (500 MHz, CDCl_3).

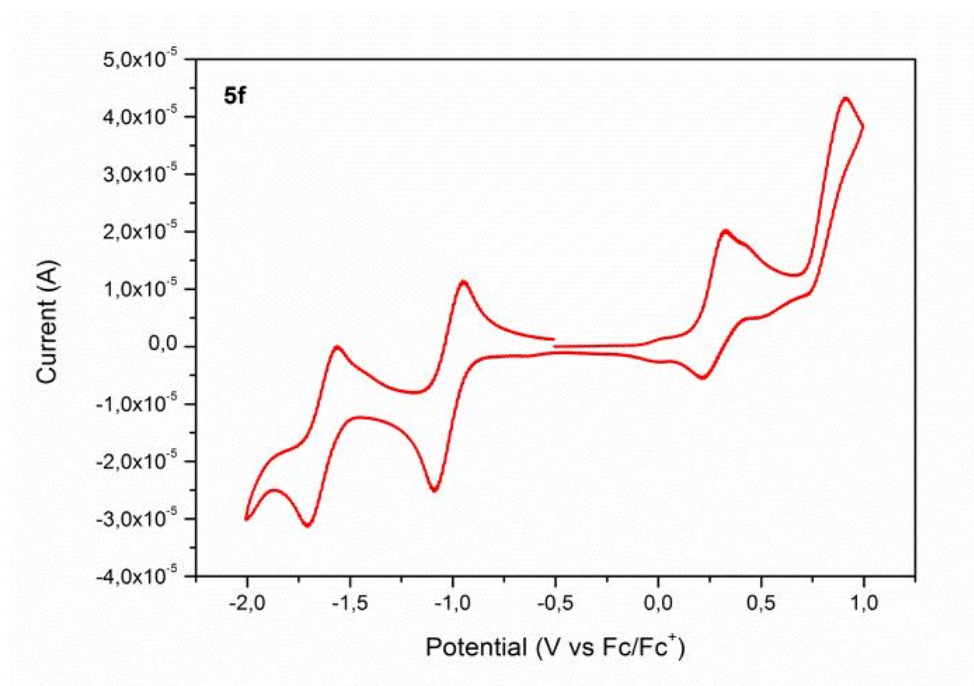


Figure S13. Cyclic voltammogram of croconaine #5.