RSC Advances

Supporting Information

Highly Emissive, Naked-Eye Solvatochromic probe Based on Styryl Tetrahydrodibenzo[a,i]phenanthridine for Acidochromic Applications

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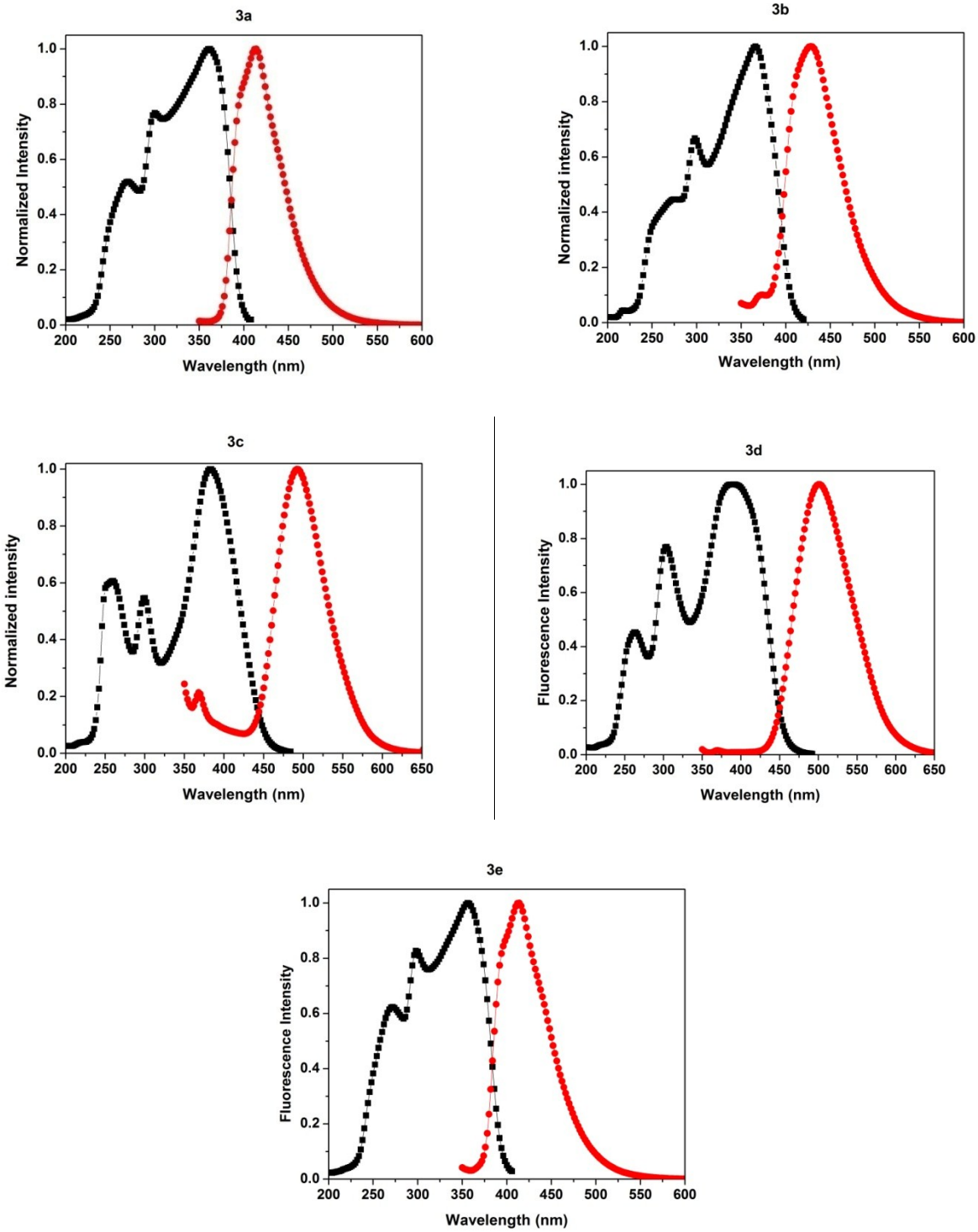
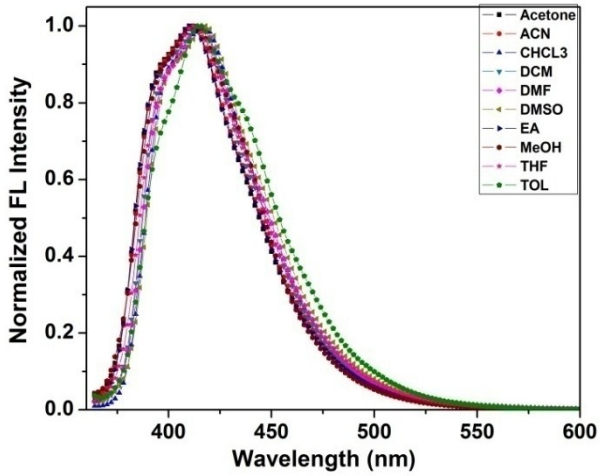
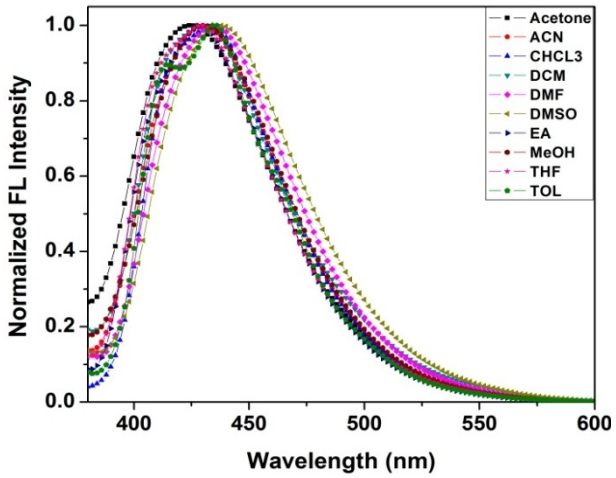


SI Figure 2. Solvatochromism spectra of dyes 3a, 3b and 3e measured in different solvents

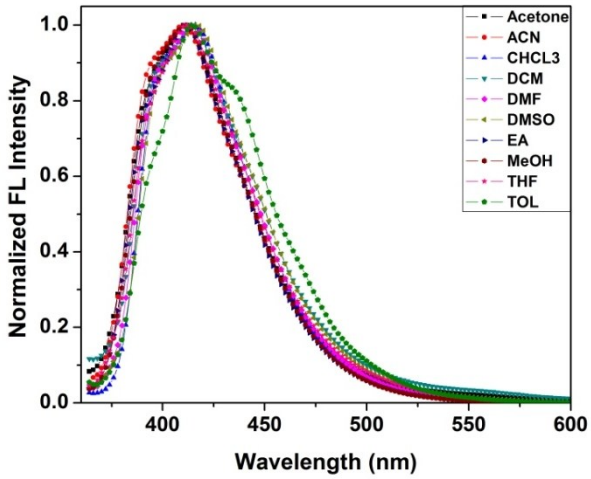
3a



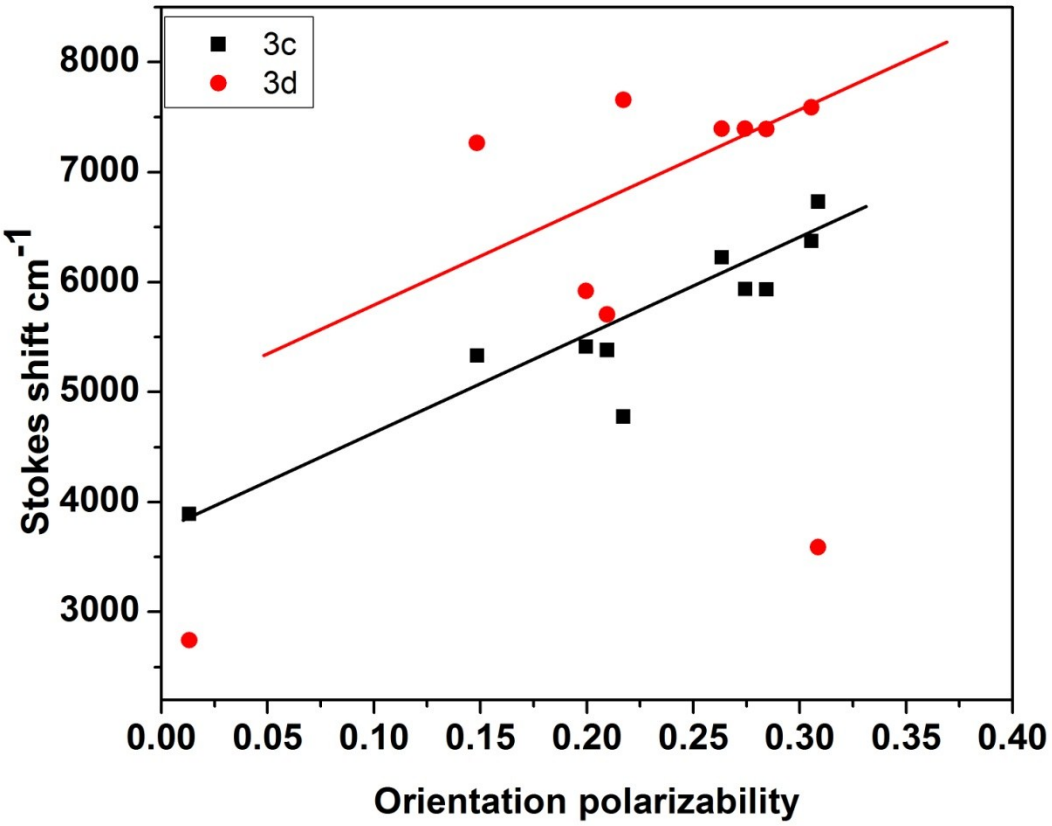
3b



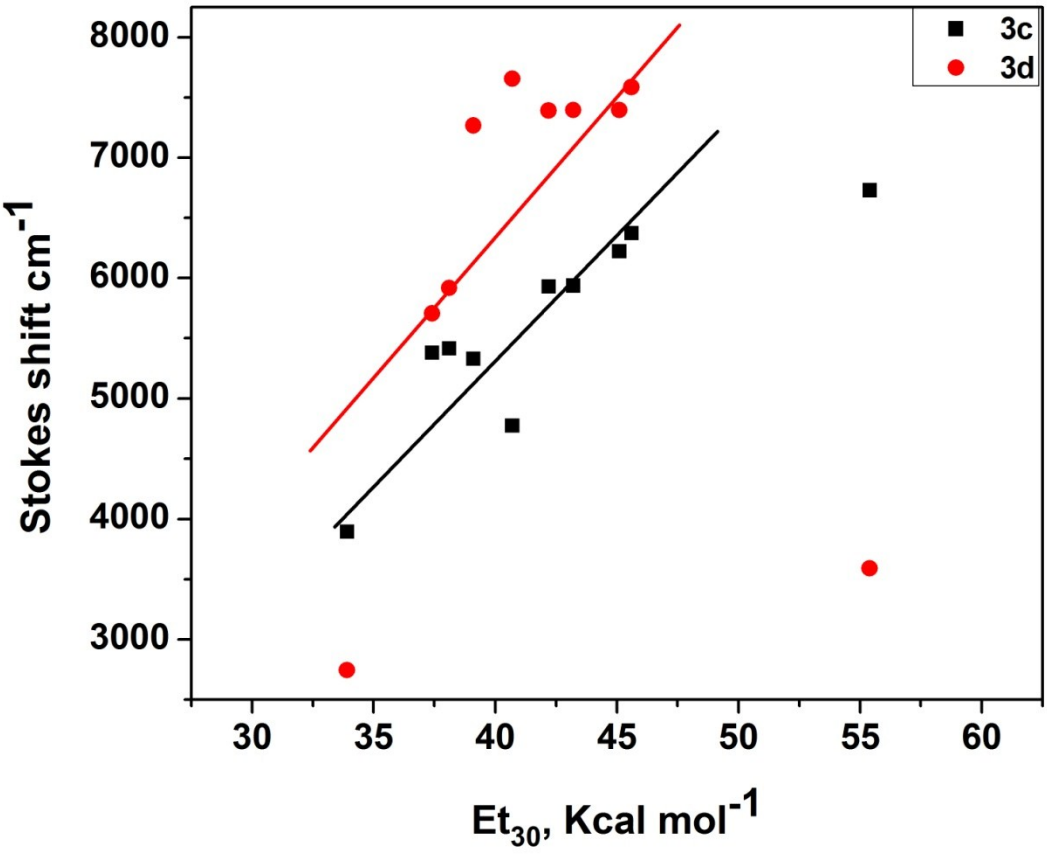
3c



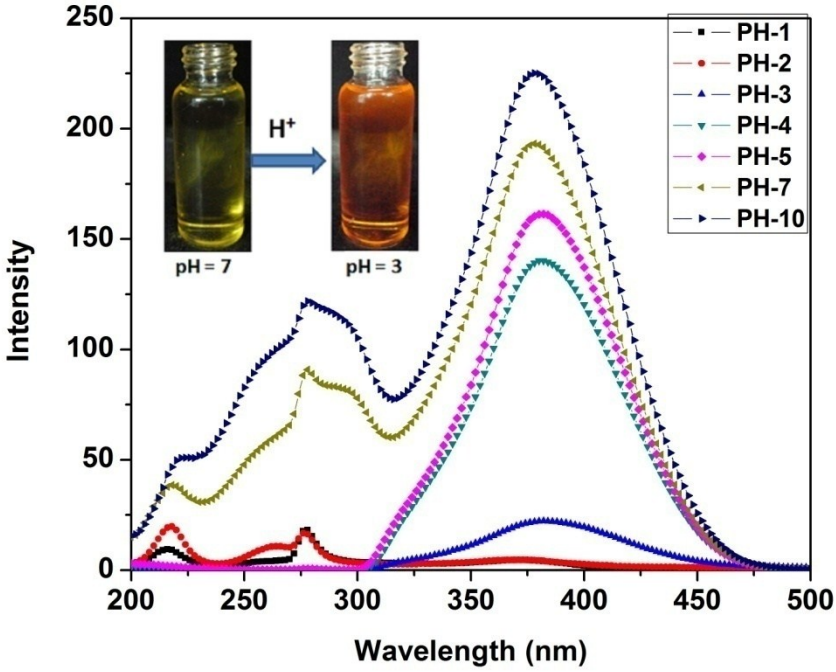
SI Figure 3. Lippert-Mataga plot



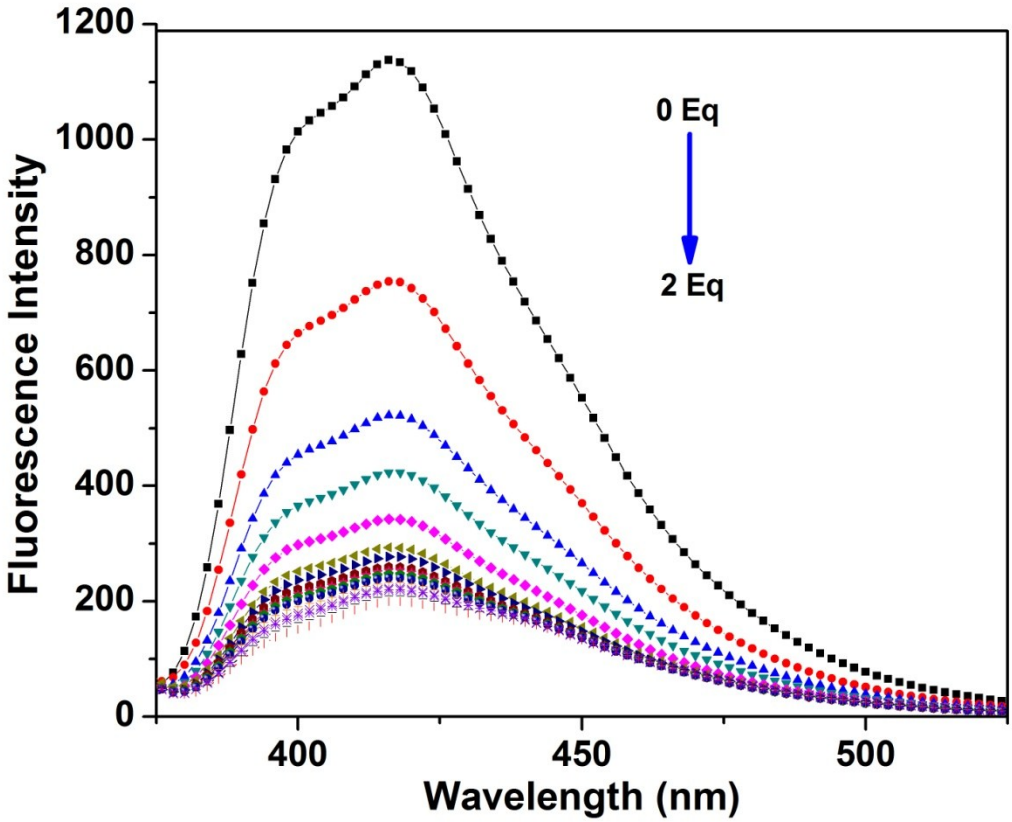
SI Figure 4. Plot of Et_{30} and Stokes shift



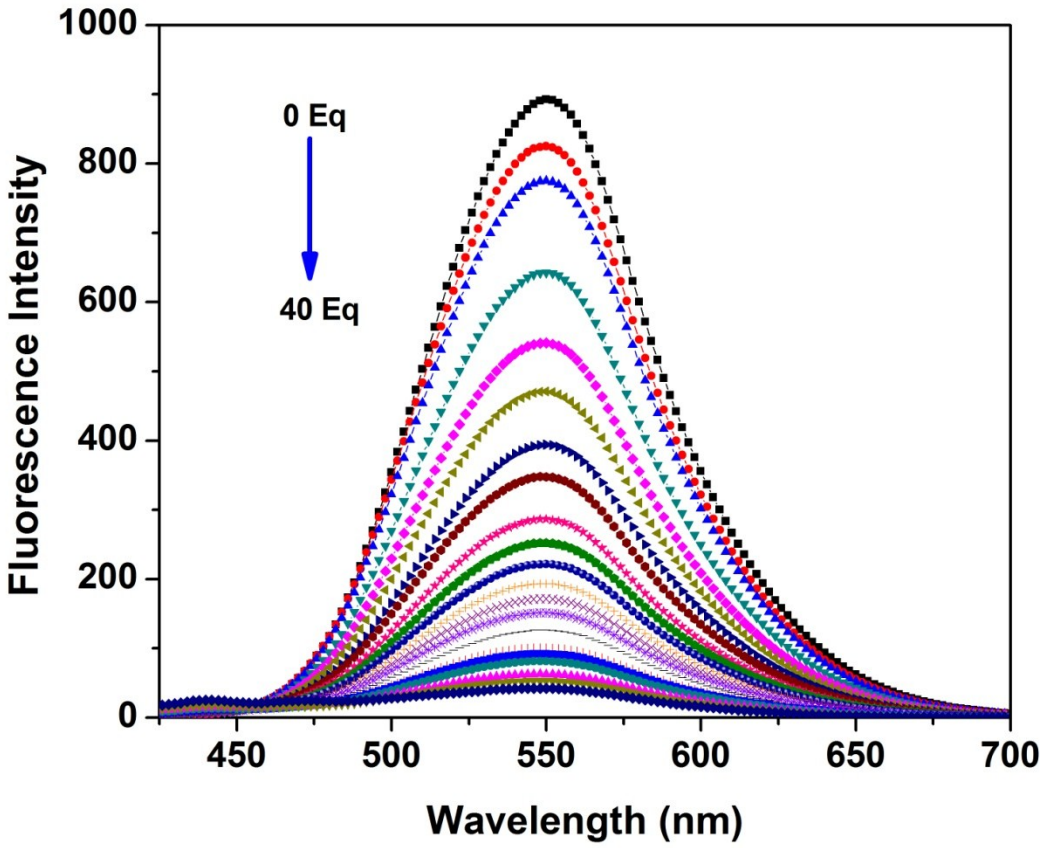
SI Figure 5. Excitation spectral changes with various pH levels



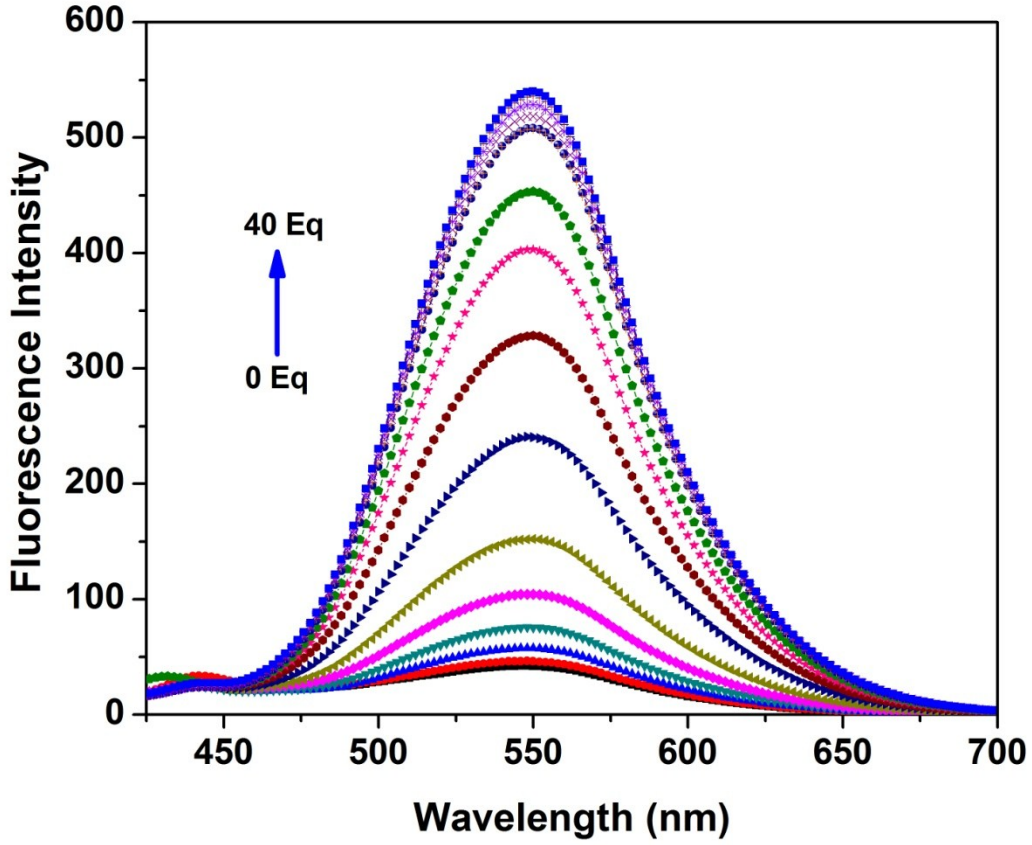
SI Figure 6. Emission spectra of dye 3a recorded with different concentrations of TFA



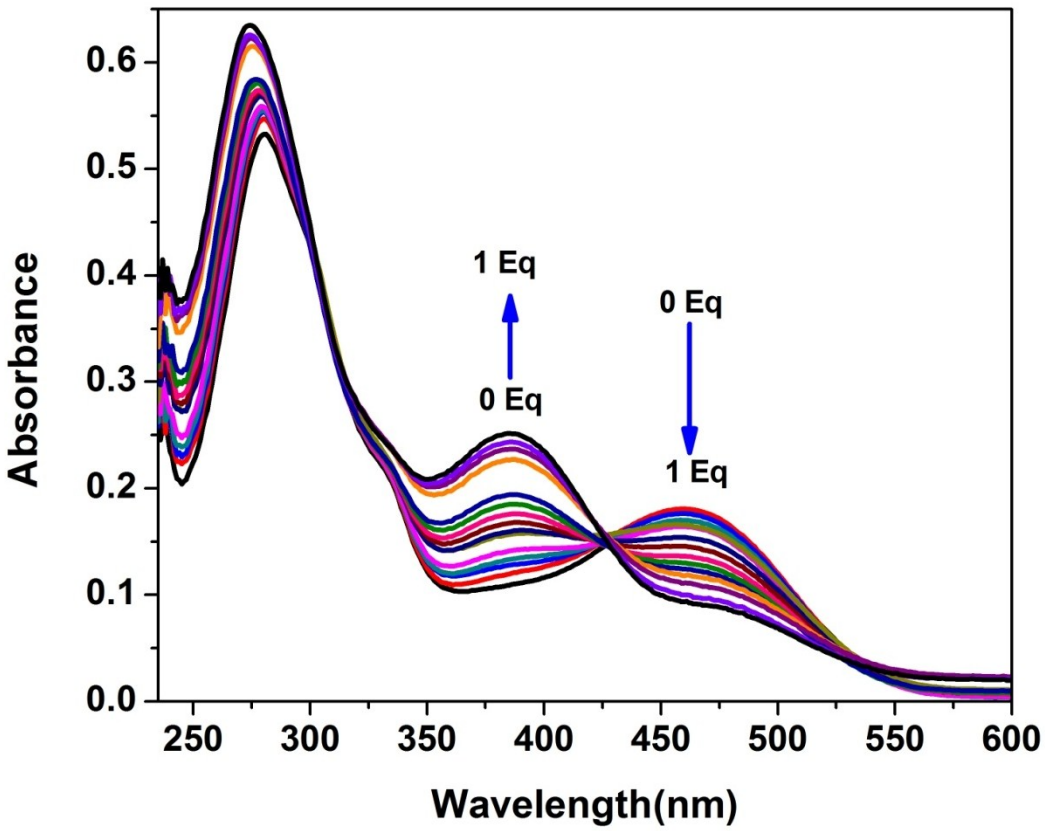
SI Figure 7. Emission spectra of dye 3d recorded with different concentrations of TFA



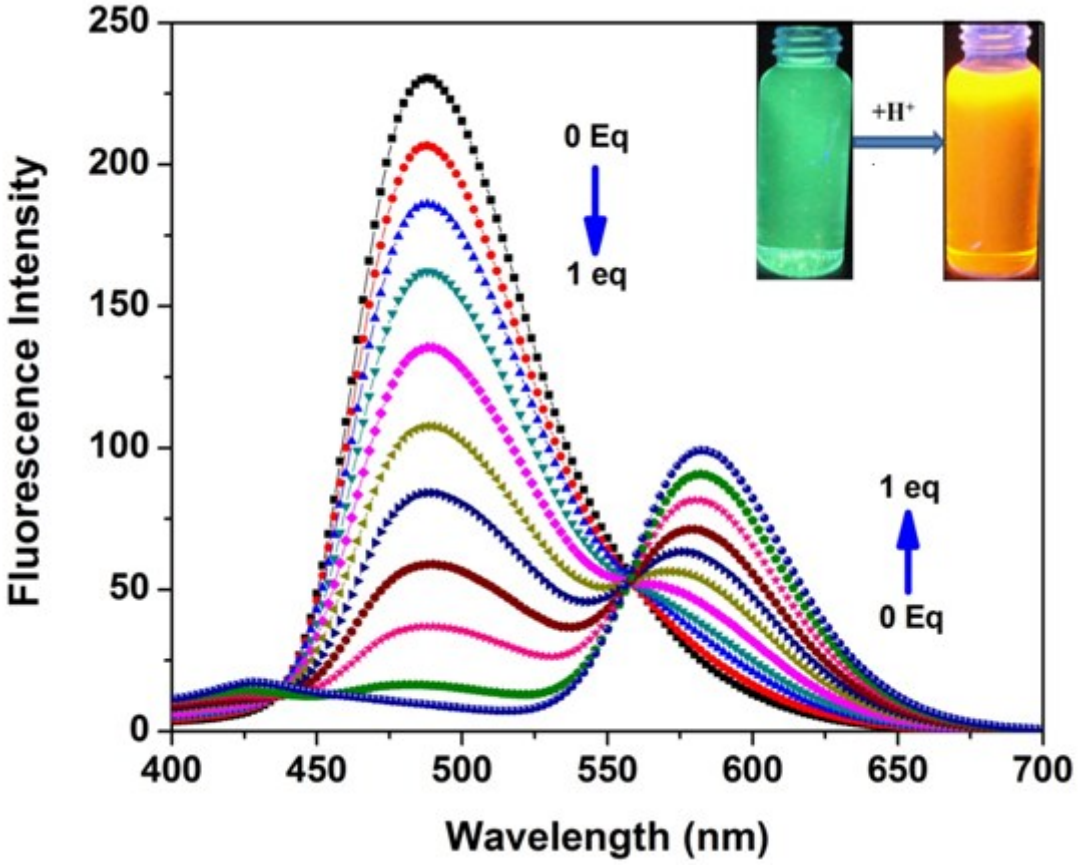
SI Figure 8. Reversible Emission spectra of dye 3d (containing TFA) recorded with different concentrations of TEA



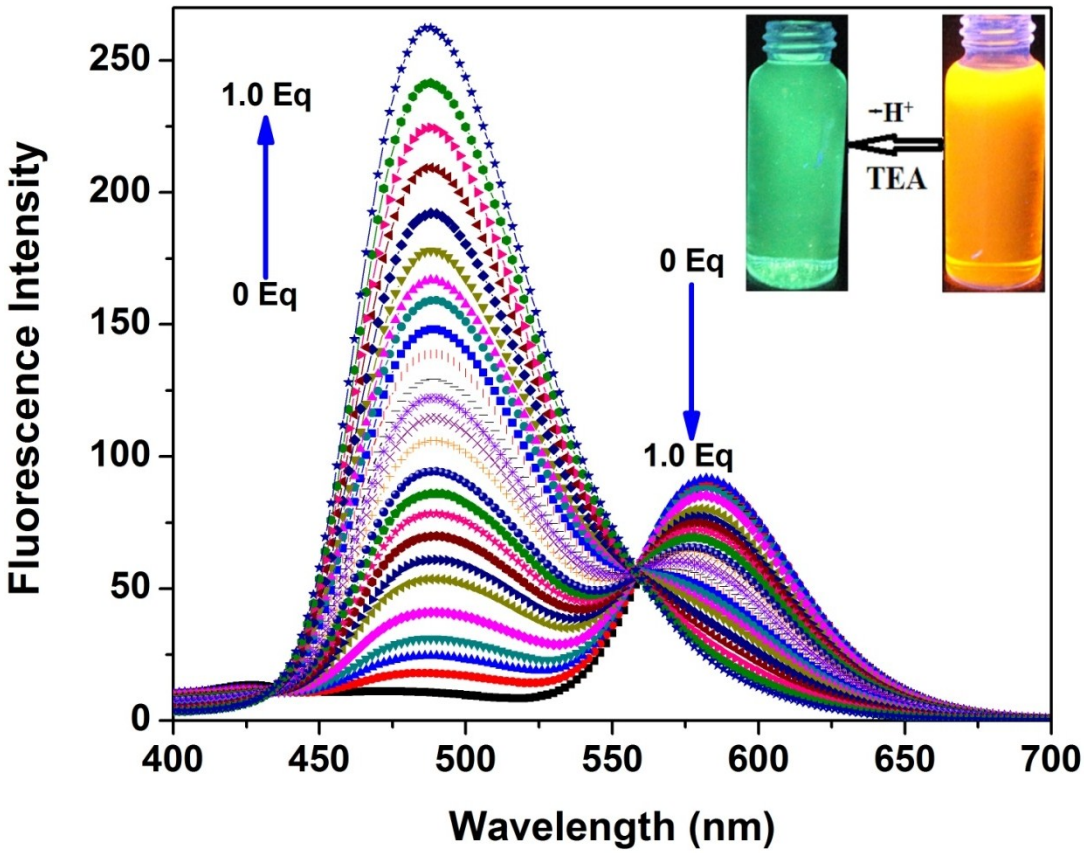
SI Figure 9. Reversible absorbance spectra of dye 3c (containing 1 eq of MSA) recorded with 1 Eq of TEA



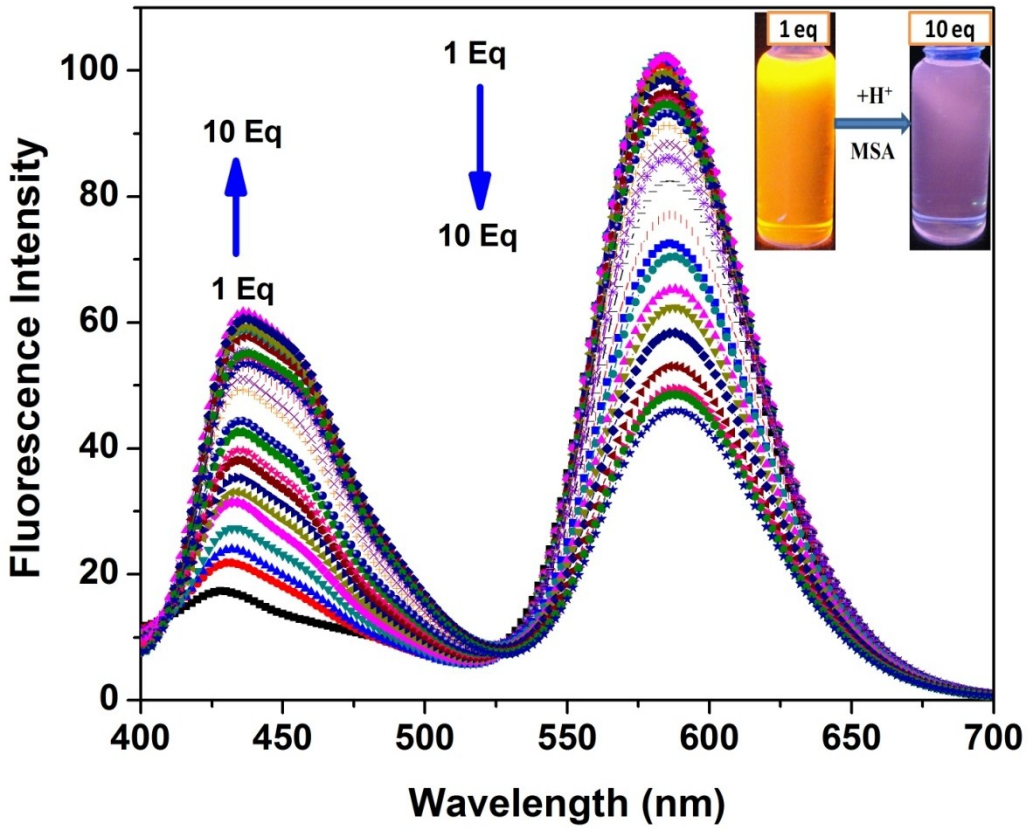
SI Figure 10.Emission spectra of dye 3c recorded with different concentrations of MSA



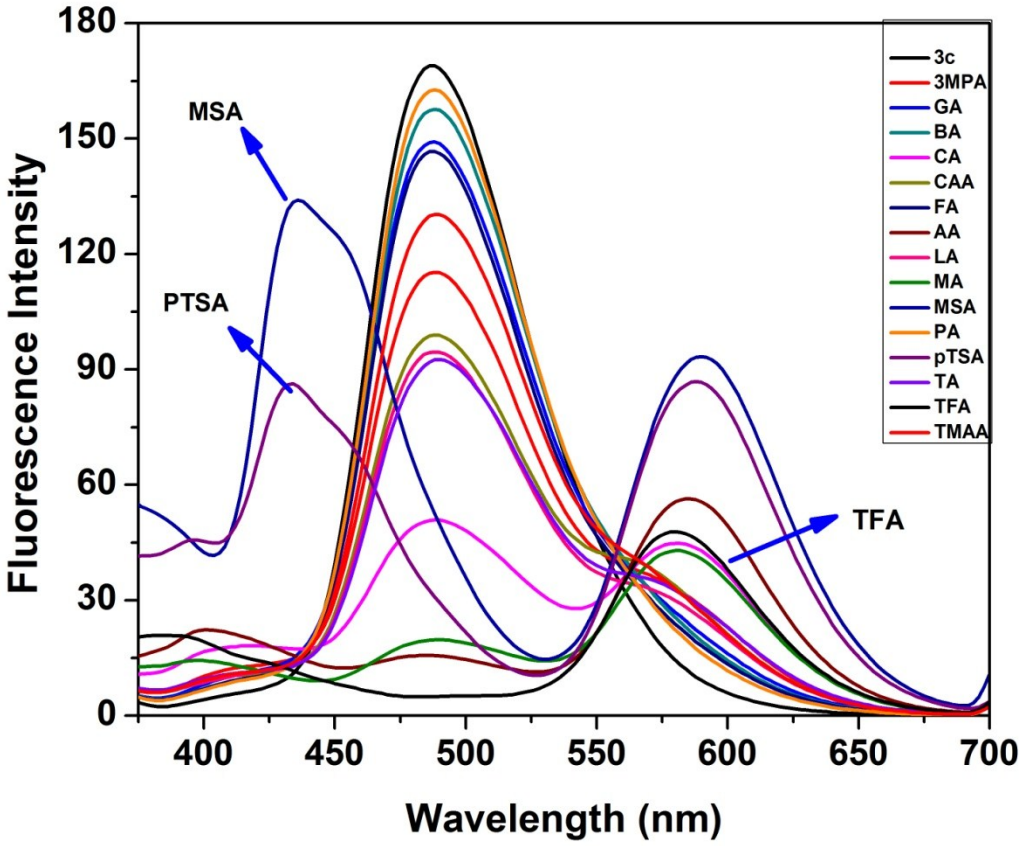
SI Figure 11. Reversible Emission spectra of dye 3c recorded with different concentrations of TEA containing 1 Eq of MSA



SI Figure 12. Emission spectra of dye 3c recorded with higher concentrations of MSA

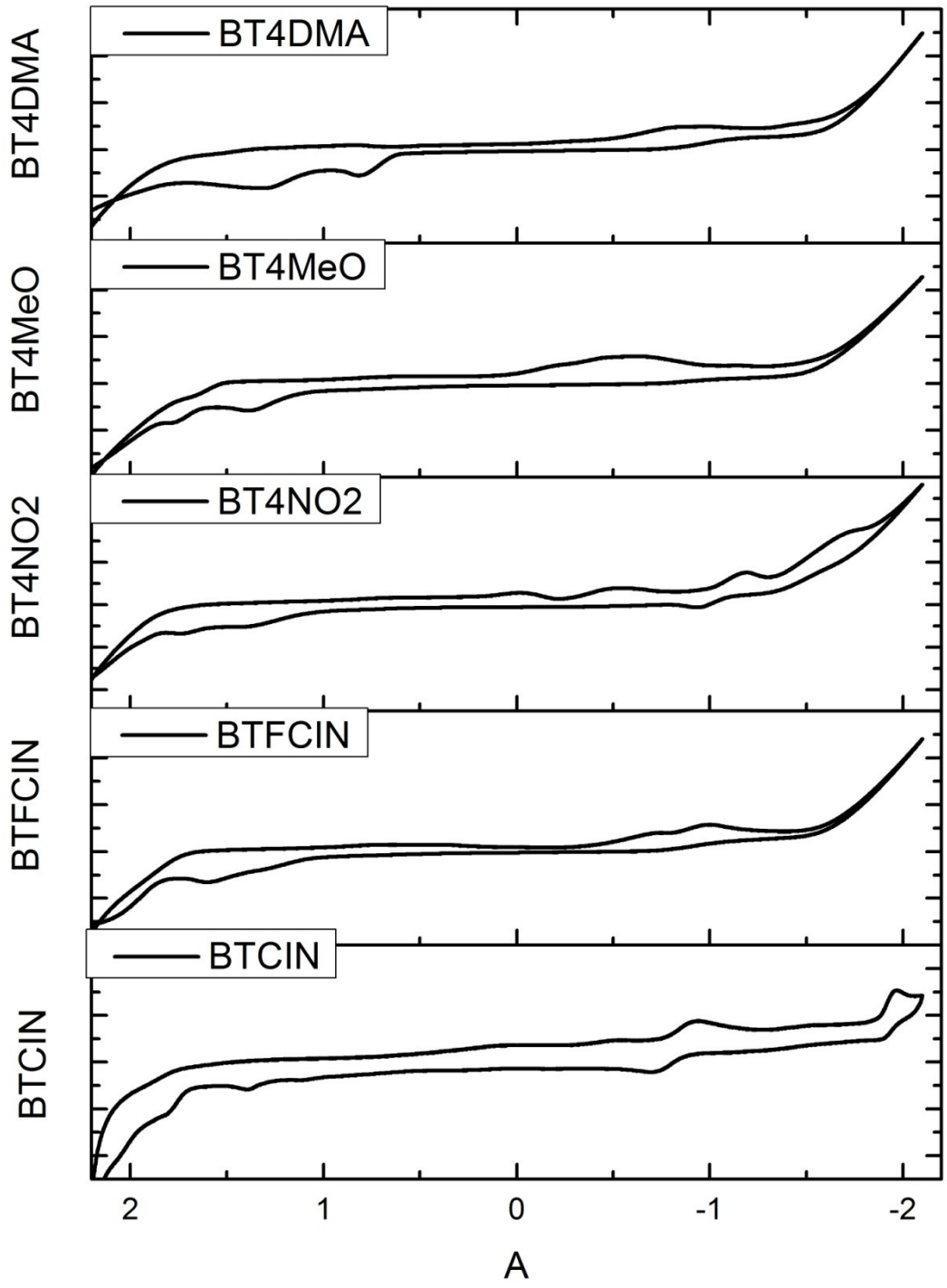


SI Figure 13. Selectivity of dye 3c towards various organic acids.



3MPA- 3-Mercaptopropanoic acid GA-Glutaric acid BA-Benzoic acid CA-Citric acid CAA-Chloroacetic acid FA-Formic Acid, AA-Acetic acid LA-Lactic acid MA-Mandelic acid MSA-Methane sulphonic acid PA-Propanoic acid PTSA-p-Toluene sulphonic acid TA-Tartaric acid TFA-Trifluoroacetic acid TMAA-Trimethylacetic acid.

SI Figure 14. Cyclic voltammograms of dyes recorded in acetonitrile solvent using glassy carbon as working electrode and 0.1 M $TBAPF_6$ as supporting electrolyte.



Tables

SI Table 1. Determination of pH in biological fluids

Determination of pH in biological fluids: The biological fluids, newborn-calf serum sample or human urine sample (the sample was taken from a healthy volunteer), were respectively adjusted to fixed pH value by addition of aliquot hydrochloric acid or aqueous sodium hydroxide. Then 2 mL of the biological fluid was added directly to 2 mL of sensor **1a** (2.0 μM) in ethanol. The resulting solution was shaken well and incubated for 20 min at room temperature. After centrifugation, the emission ratio (I_{526}:I_{442}) (λ_{ex} = 375 nm) was recorded.

Sample	pH known [a]	pH found [b]
Serum sample 1	4.47	4.43
Serum sample 2	4.82	4.80
Urine sample 1	4.36	4.35
Urine sample 2	4.71	4.74

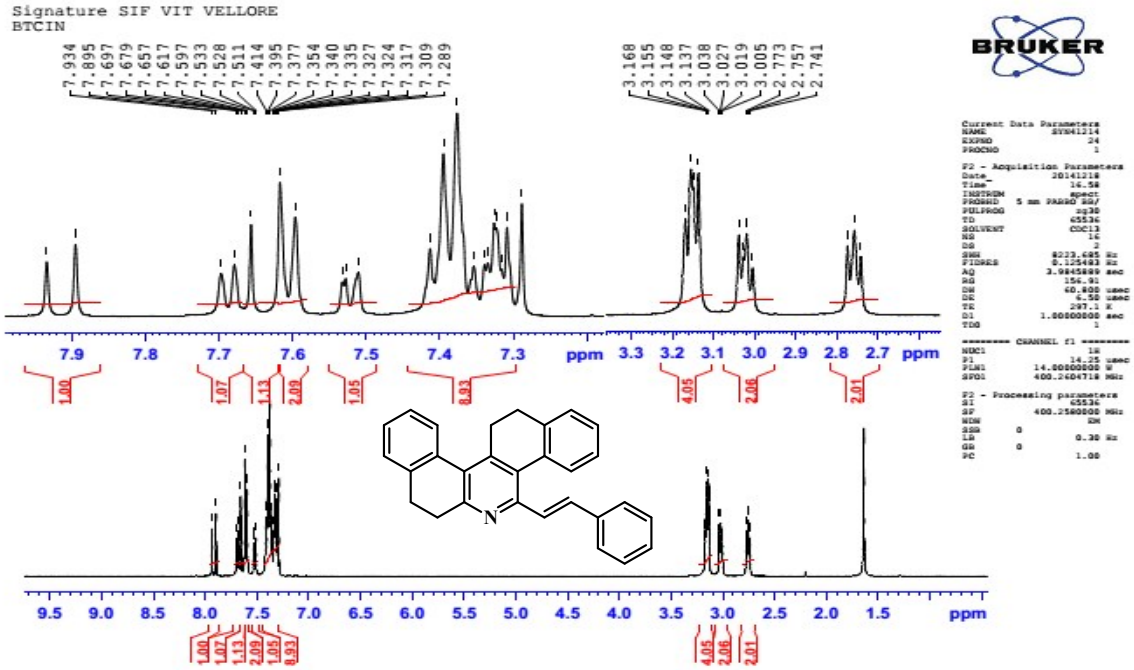
a. Measured by a pH-3c digital pH-meter.
b. Obtained from the linear relationship between the ratiometric response (I_{526}:I_{442}) of **1a** and the pH value (4.0-6.0).

SI Table 2. Electrochemical data measured in acetonitrile solvent.

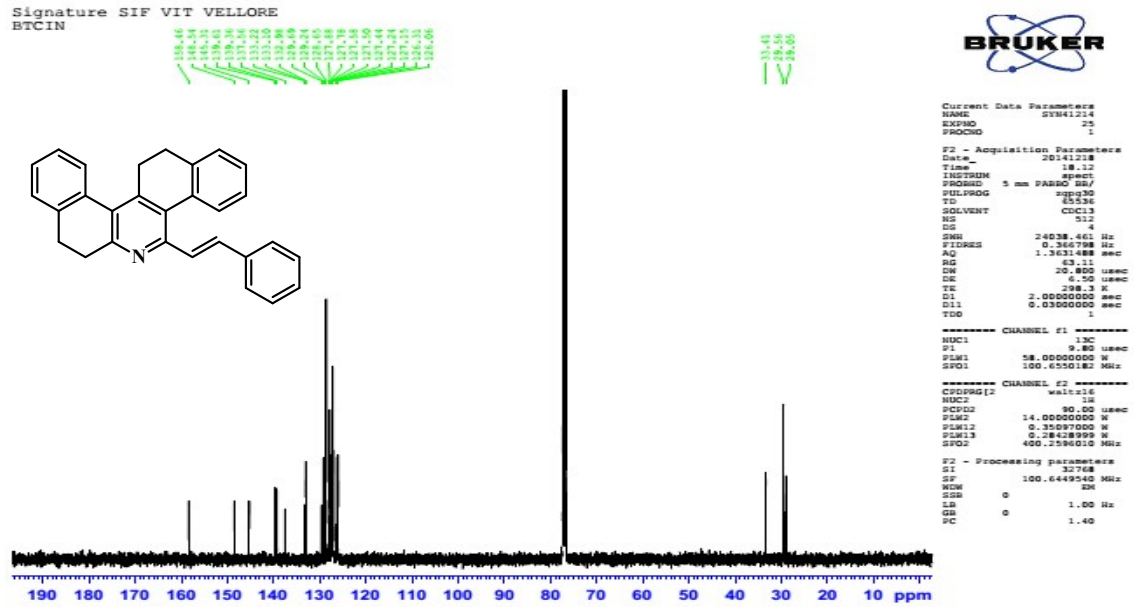
	$E_{1/2}$ ox	E ½ red	HOMO[b] [eV]	LUMO[b] [eV]
3a	1.39	-1.87	-5.79	2.53
3b	1.37	-1.45	-5.77	2.95
3c	1.32	-1.42	-5.72	2.98
3d	1.39	-0.94	-5.79	3.46
3e	1.35	-1.44	-5.75	2.96

NMR copies

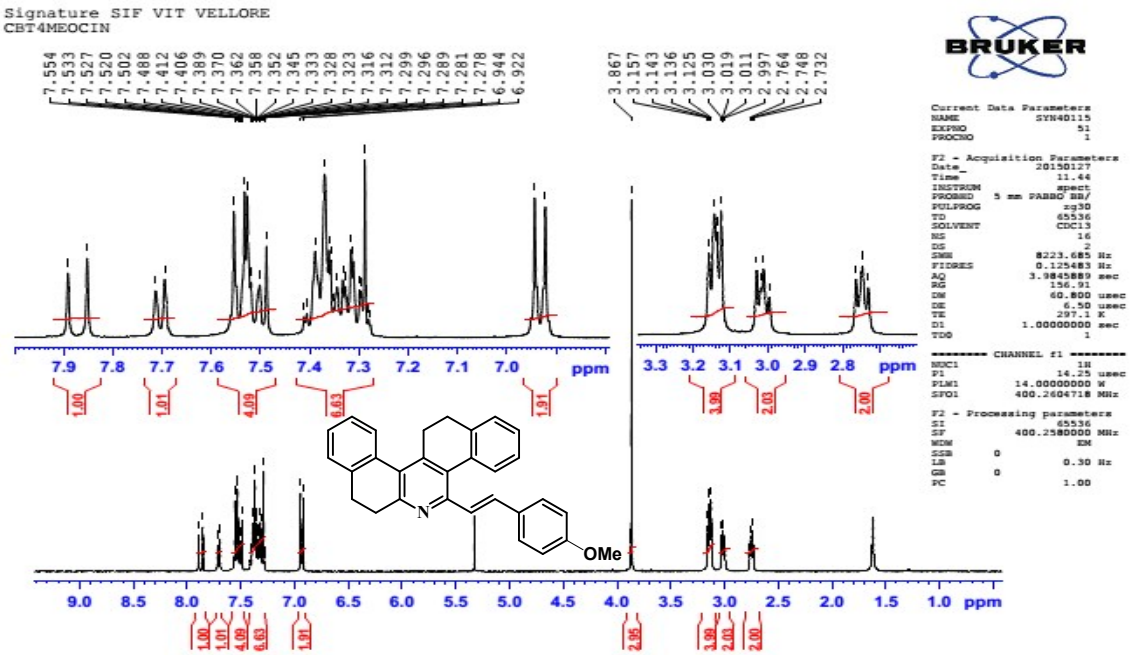
^{1}H-NMR spectrum of 3a



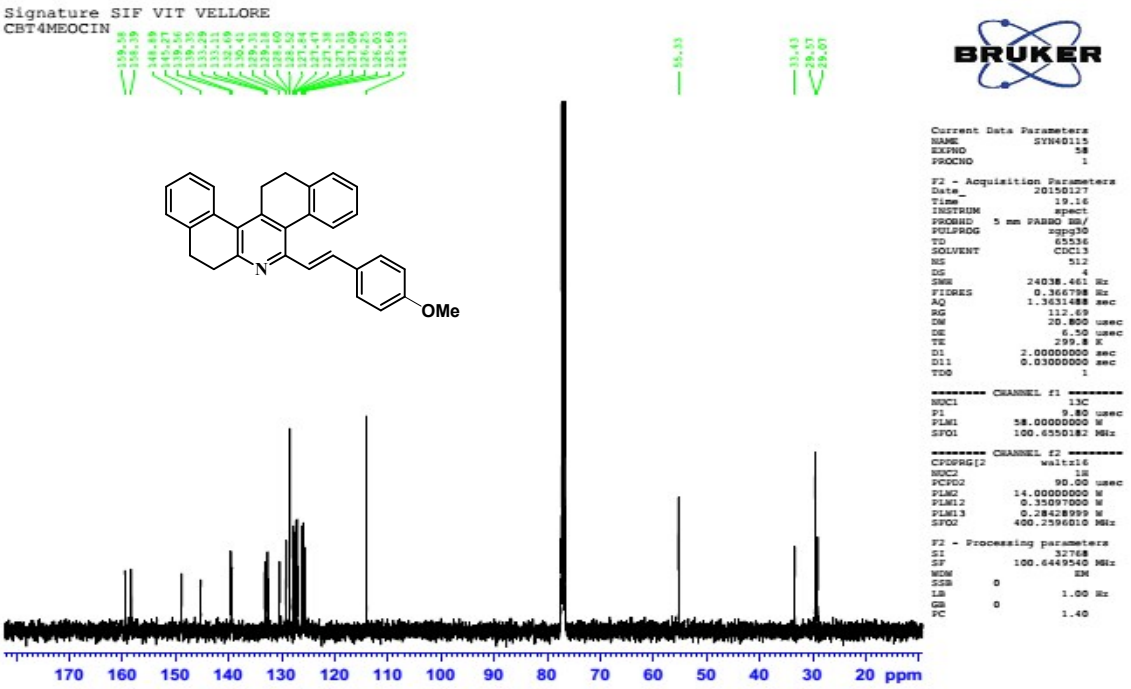
^{13}C-NMR spectrum of 3a



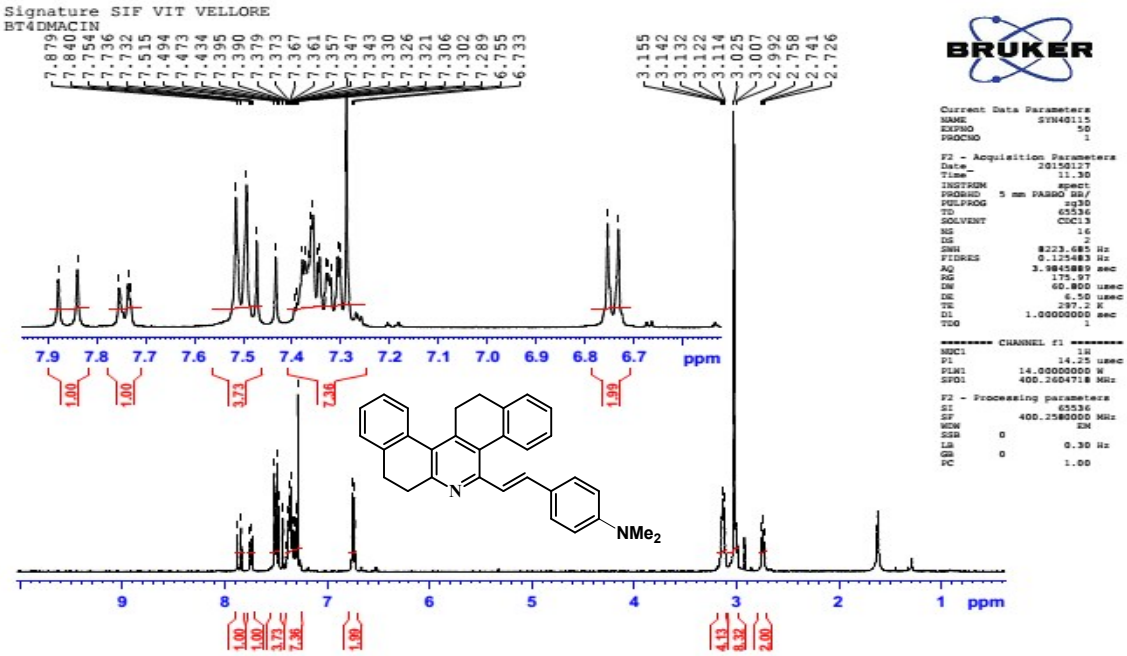
^{1}H-NMR spectrum of 3b



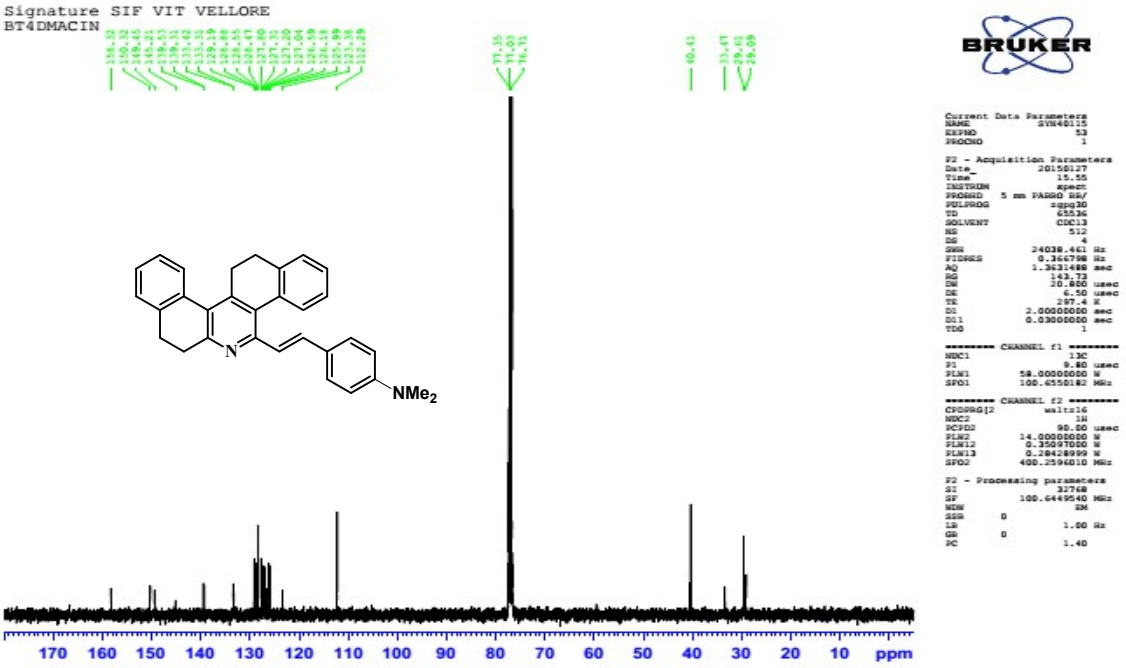
^{13}C-NMR spectrum of 3b



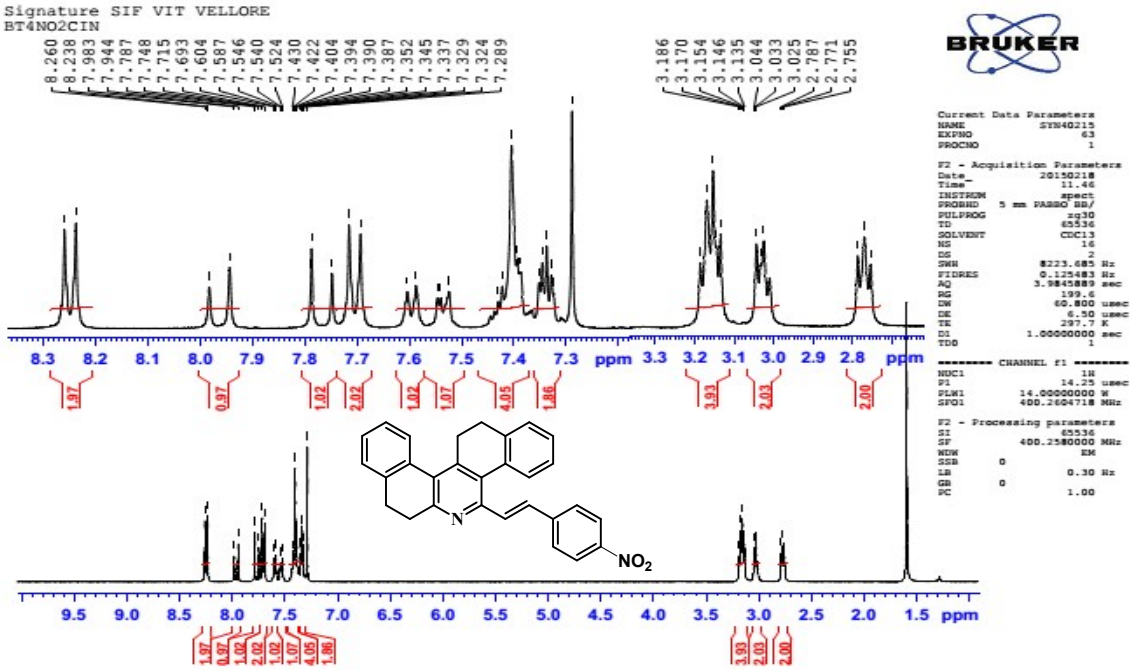
^{1}H-NMR spectrum of 3c



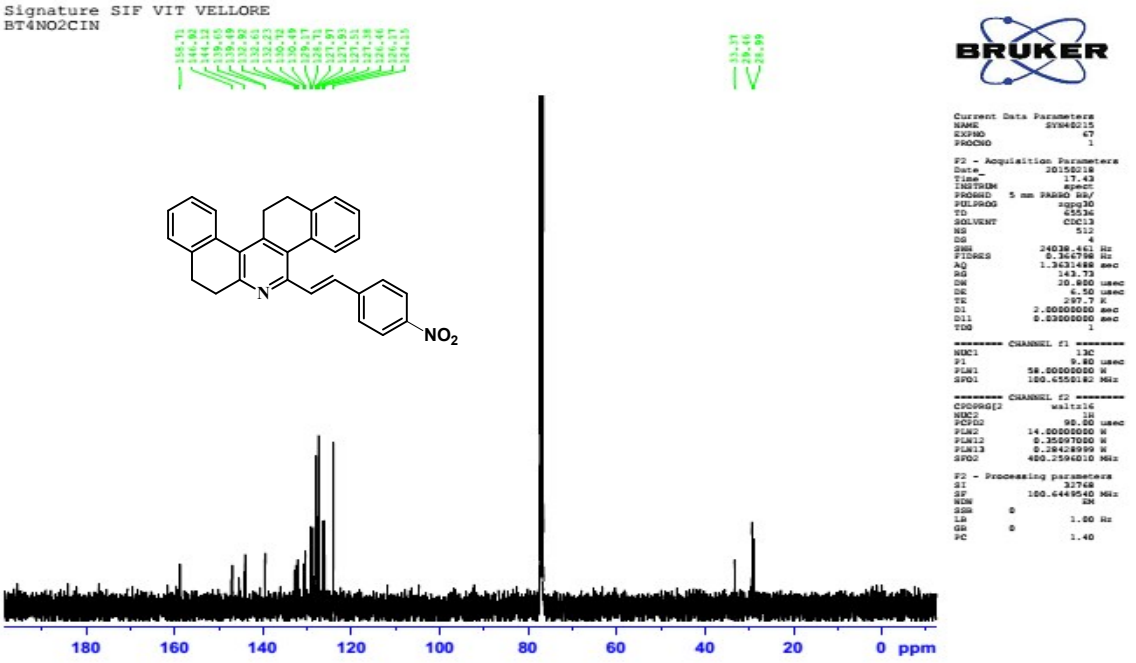
^{13}C-NMR spectrum of 3c



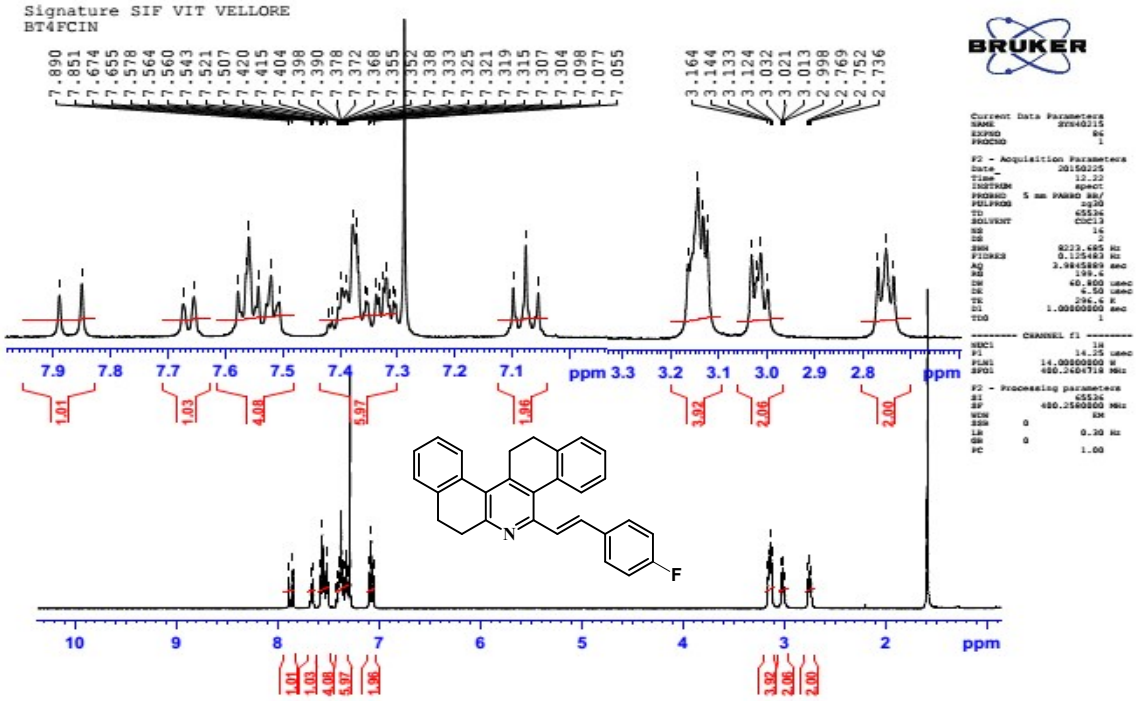
^{1}H-NMR spectrum of 3d



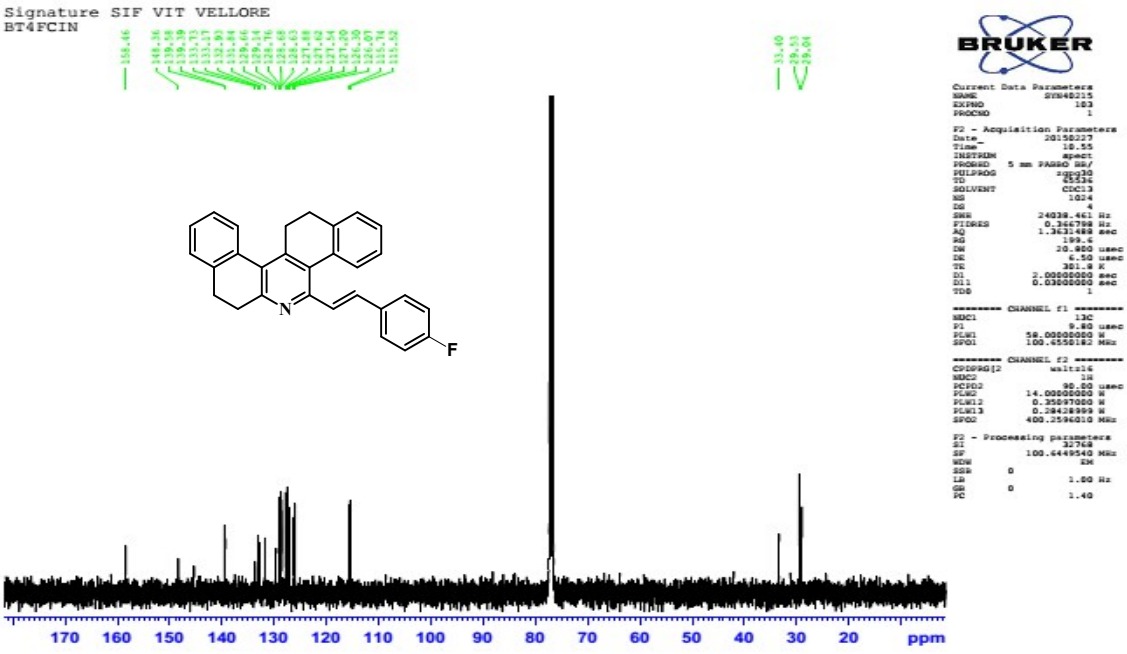
^{13}C-NMR spectrum of 3d



^{1}H-NMR spectrum of 3e



^{13}C-NMR spectrum of 3e



Crystal data;

Table 1. Crystal data and structure refinement for 3d_cif.

Identification code	shelx	
Empirical formula	C29 H22 N2 O2	
Formula weight	430.48	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 7.6171(9) Å	α= 90°.
	b = 21.660(3) Å	β= 101.311(4)°.
	c = 13.2670(17) Å	γ = 90°.
Volume	2146.4(5) Å^3	
Z	4	
Density (calculated)	1.332 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	904	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.826 to 24.009°.	
Index ranges	-6<=h<=8, -24<=k<=24, -15<=l<=15	
Reflections collected	27079	
Independent reflections	3365 [R(int) = 0.0443]	
Completeness to theta = 25.242°	86.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3365 / 0 / 298	
Goodness-of-fit on F^2	1.241	
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.1313	
R indices (all data)	R1 = 0.0840, wR2 = 0.1688	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.265 and -0.344 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for no2cin_cif. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	2833(3)	4720(1)	5699(2)	34(1)
C(24)	3513(3)	3895(1)	2871(2)	32(1)
C(1)	2566(3)	5078(1)	4852(2)	30(1)
C(21)	2571(3)	4959(1)	6577(2)	34(1)
C(23)	3398(3)	4209(1)	3826(2)	35(1)
C(22)	2726(3)	4769(1)	3901(2)	33(1)
C(12)	1920(3)	5558(1)	6679(2)	32(1)
C(2)	2023(3)	5694(1)	4886(2)	31(1)
C(25)	3261(4)	4197(1)	1931(2)	47(1)
C(8)	583(4)	6572(1)	3850(2)	40(1)
C(11)	1569(3)	5922(1)	5792(2)	33(1)
C(13)	1718(3)	5758(1)	7718(2)	38(1)
C(27)	3835(4)	3277(1)	1097(2)	47(1)
C(29)	3935(4)	3272(1)	2882(2)	45(1)
C(4)	3138(4)	6105(1)	3351(2)	42(1)
C(10)	635(4)	6540(1)	5712(2)	41(1)
C(28)	4084(4)	2959(1)	1999(2)	51(1)
C(20)	2921(4)	4536(1)	7489(2)	45(1)
C(3)	1910(3)	6119(1)	4004(2)	35(1)
C(26)	3425(4)	3894(2)	1049(2)	55(1)
N(2)	4068(4)	2960(2)	165(2)	70(1)
C(14)	1801(4)	6370(1)	8040(2)	49(1)
C(5)	2949(4)	6490(1)	2509(2)	50(1)
C(18)	1564(4)	5301(1)	8452(2)	44(1)
C(9)	-531(4)	6633(1)	4655(2)	45(1)
C(17)	1488(4)	5477(2)	9446(2)	57(1)
O(1)	4630(4)	2432(1)	244(2)	97(1)
O(2)	3747(5)	3236(2)	-650(2)	117(1)
C(7)	388(4)	6948(1)	2990(2)	53(1)
C(19)	1550(4)	4633(1)	8151(2)	49(1)
C(6)	1541(5)	6897(1)	2317(2)	60(1)

C(15)	1662(4)	6534(2)	9019(2)	60(1)
C(16)	1504(5)	6089(2)	9726(2)	67(1)

Table 3. Bond lengths [Å] and angles [°] for no2cin_cif.

N(1)-C(21)	1.325(3)
N(1)-C(1)	1.348(3)
C(24)-C(29)	1.387(4)
C(24)-C(25)	1.387(4)
C(24)-C(23)	1.455(3)
C(1)-C(2)	1.401(3)
C(1)-C(22)	1.455(3)
C(21)-C(12)	1.407(3)
C(21)-C(20)	1.499(4)
C(23)-C(22)	1.329(3)
C(12)-C(11)	1.398(3)
C(12)-C(13)	1.481(3)
C(2)-C(11)	1.403(3)
C(2)-C(3)	1.479(3)
C(25)-C(26)	1.369(4)
C(8)-C(7)	1.386(4)
C(8)-C(3)	1.395(4)
C(8)-C(9)	1.494(4)
C(11)-C(10)	1.510(3)
C(13)-C(14)	1.391(4)
C(13)-C(18)	1.408(4)
C(27)-C(28)	1.362(4)
C(27)-C(26)	1.371(4)
C(27)-N(2)	1.455(4)
C(29)-C(28)	1.377(4)
C(4)-C(5)	1.380(4)
C(4)-C(3)	1.394(4)
C(10)-C(9)	1.520(4)
C(20)-C(19)	1.505(4)
N(2)-O(2)	1.218(4)
N(2)-O(1)	1.219(4)
C(14)-C(15)	1.371(4)
C(5)-C(6)	1.373(4)
C(18)-C(17)	1.384(4)

C(18)-C(19)	1.500(4)
C(17)-C(16)	1.375(5)
C(7)-C(6)	1.374(4)
C(15)-C(16)	1.367(5)

C(21)-N(1)-C(1)	118.9(2)
C(29)-C(24)-C(25)	117.4(2)
C(29)-C(24)-C(23)	119.9(2)
C(25)-C(24)-C(23)	122.7(2)
N(1)-C(1)-C(2)	121.3(2)
N(1)-C(1)-C(22)	115.7(2)
C(2)-C(1)-C(22)	122.9(2)
N(1)-C(21)-C(12)	124.2(2)
N(1)-C(21)-C(20)	116.0(2)
C(12)-C(21)-C(20)	119.8(2)
C(22)-C(23)-C(24)	125.5(2)
C(23)-C(22)-C(1)	125.7(2)
C(11)-C(12)-C(21)	116.8(2)
C(11)-C(12)-C(13)	125.6(2)
C(21)-C(12)-C(13)	117.5(2)
C(1)-C(2)-C(11)	119.1(2)
C(1)-C(2)-C(3)	122.6(2)
C(11)-C(2)-C(3)	118.3(2)
C(26)-C(25)-C(24)	121.5(3)
C(7)-C(8)-C(3)	119.4(3)
C(7)-C(8)-C(9)	123.5(2)
C(3)-C(8)-C(9)	117.1(2)
C(12)-C(11)-C(2)	119.0(2)
C(12)-C(11)-C(10)	124.6(2)
C(2)-C(11)-C(10)	116.4(2)
C(14)-C(13)-C(18)	117.5(2)
C(14)-C(13)-C(12)	123.8(2)
C(18)-C(13)-C(12)	118.5(2)
C(28)-C(27)-C(26)	121.7(3)
C(28)-C(27)-N(2)	119.2(3)
C(26)-C(27)-N(2)	119.0(3)

C(28)-C(29)-C(24)	121.8(3)
C(5)-C(4)-C(3)	120.9(3)
C(11)-C(10)-C(9)	111.3(2)
C(27)-C(28)-C(29)	118.6(3)
C(21)-C(20)-C(19)	110.6(2)
C(4)-C(3)-C(8)	118.7(2)
C(4)-C(3)-C(2)	122.4(2)
C(8)-C(3)-C(2)	118.8(2)
C(25)-C(26)-C(27)	119.1(3)
O(2)-N(2)-O(1)	122.9(3)
O(2)-N(2)-C(27)	119.0(3)
O(1)-N(2)-C(27)	118.0(3)
C(15)-C(14)-C(13)	122.0(3)
C(6)-C(5)-C(4)	119.4(3)
C(17)-C(18)-C(13)	119.3(3)
C(17)-C(18)-C(19)	121.3(3)
C(13)-C(18)-C(19)	119.3(2)
C(8)-C(9)-C(10)	109.7(2)
C(16)-C(17)-C(18)	121.5(3)
C(6)-C(7)-C(8)	120.6(3)
C(18)-C(19)-C(20)	108.8(2)
C(7)-C(6)-C(5)	120.4(3)
C(16)-C(15)-C(14)	120.0(3)
C(15)-C(16)-C(17)	119.5(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for no2cin_cif. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	36(1)	36(1)	31(1)	0(1)	5(1)	3(1)
C(24)	31(1)	33(1)	32(1)	-2(1)	6(1)	0(1)
C(1)	28(1)	32(1)	29(1)	-1(1)	4(1)	1(1)
C(21)	32(1)	39(1)	31(1)	2(1)	4(1)	-1(1)
C(23)	37(1)	36(2)	31(1)	2(1)	7(1)	2(1)
C(22)	36(1)	35(1)	29(1)	1(1)	5(1)	2(1)
C(12)	31(1)	37(1)	29(1)	-4(1)	6(1)	-2(1)
C(2)	31(1)	31(1)	30(1)	0(1)	5(1)	0(1)
C(25)	60(2)	40(2)	39(2)	0(1)	7(1)	14(1)
C(8)	47(2)	30(1)	40(2)	-3(1)	5(1)	1(1)
C(11)	31(1)	31(1)	37(2)	-5(1)	5(1)	-2(1)
C(13)	32(1)	48(2)	34(2)	-4(1)	6(1)	-2(1)
C(27)	47(2)	54(2)	37(2)	-16(1)	6(1)	1(1)
C(29)	58(2)	35(2)	43(2)	4(1)	14(1)	4(1)
C(4)	49(2)	38(2)	39(2)	-2(1)	9(1)	0(1)
C(10)	48(2)	34(1)	43(2)	-2(1)	14(1)	-1(1)
C(28)	63(2)	37(2)	54(2)	-11(1)	16(2)	3(1)
C(20)	49(2)	48(2)	36(2)	4(1)	4(1)	4(1)
C(3)	40(1)	31(1)	33(1)	-5(1)	6(1)	-2(1)
C(26)	67(2)	63(2)	33(2)	2(1)	4(1)	16(2)
N(2)	77(2)	80(2)	51(2)	-29(2)	10(2)	4(2)
C(14)	51(2)	54(2)	42(2)	-12(1)	10(1)	-5(1)
C(5)	69(2)	44(2)	41(2)	2(1)	19(2)	-4(2)
C(18)	39(2)	60(2)	34(2)	0(1)	7(1)	2(1)
C(9)	47(2)	37(2)	50(2)	1(1)	9(1)	11(1)
C(17)	60(2)	76(2)	38(2)	6(2)	14(1)	3(2)
O(1)	137(3)	76(2)	81(2)	-37(2)	32(2)	13(2)
O(2)	172(3)	136(3)	40(2)	-19(2)	13(2)	41(2)
C(7)	74(2)	36(2)	48(2)	6(1)	9(2)	11(1)
C(19)	54(2)	54(2)	38(2)	8(1)	8(1)	-3(1)
C(6)	95(3)	40(2)	47(2)	10(1)	16(2)	4(2)

C(15)	65(2)	67(2)	48(2)	-19(2)	11(2)	0(2)
C(16)	77(2)	87(3)	39(2)	-15(2)	17(2)	5(2)

SI Scheme 1 Mechanism for the formation of Phenanthridine.