Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Fluorescent imidazole-based chemosensors for the reversible detection of cyanide and mercury ions

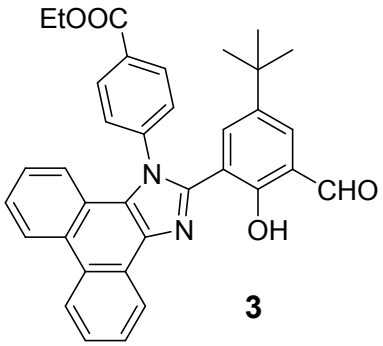
Ganapathi Emandi[a], Keith J. Flanagan[a] and Mathias O. Senge[a,b,*]

[a] School of Chemistry, SFI Tetrapyrrole Laboratory, Trinity Biomedical Sciences Institute, 152-160 Pearse Street, Trinity College Dublin, the University of Dublin, Dublin 2, Ireland

[b] Medicinal Chemistry, Trinity Translational Medicine Institute, Trinity Centre for Health Sciences, Trinity College Dublin, the University of Dublin, St. James's Hospital, Dublin 8, Ireland

E-mail: sengem@tcd.ie

Entry	Contents	Page no



3

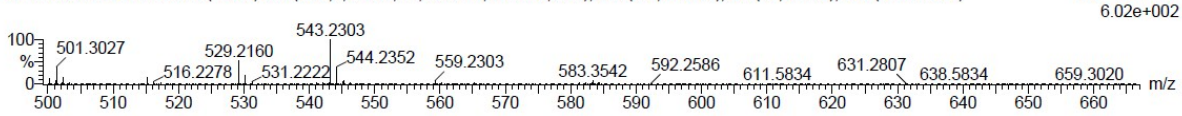
Elemental Composition Report Page 1

Calcd mol. Wt. = 543.2284

Observed mol. Wt. = 543.2303

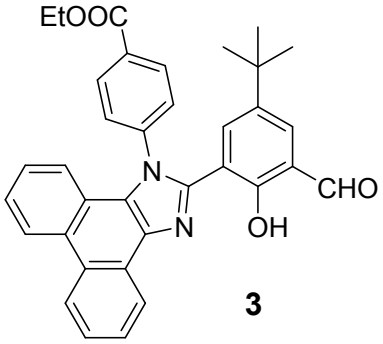
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 5

Monoisotopic Mass, Odd and Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 10 closest results for each mass)
Elements Used:
C: 0-35 H: 0-31 N: 0-2 O: 0-4
Ganapathi (MSe), Gana-125
Q-TOF20170825MF003 59 (1.089) AM (Cen,4, 80.00, Ht,10000.0,1570.68,0.70); Sm (SG, 2x3.00); Sb (15,10.00); Cm (7:81-58:67) TOF MS LD+ 6.02e+002



Minimum:				-1.5			
Maximum:		5.0	10.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
543.2303	543.2284	1.9	3.5	21.5	47.8	0.0	C35 H31 N2 O4

Figure S1. The HR-MS of compound **3**.



3

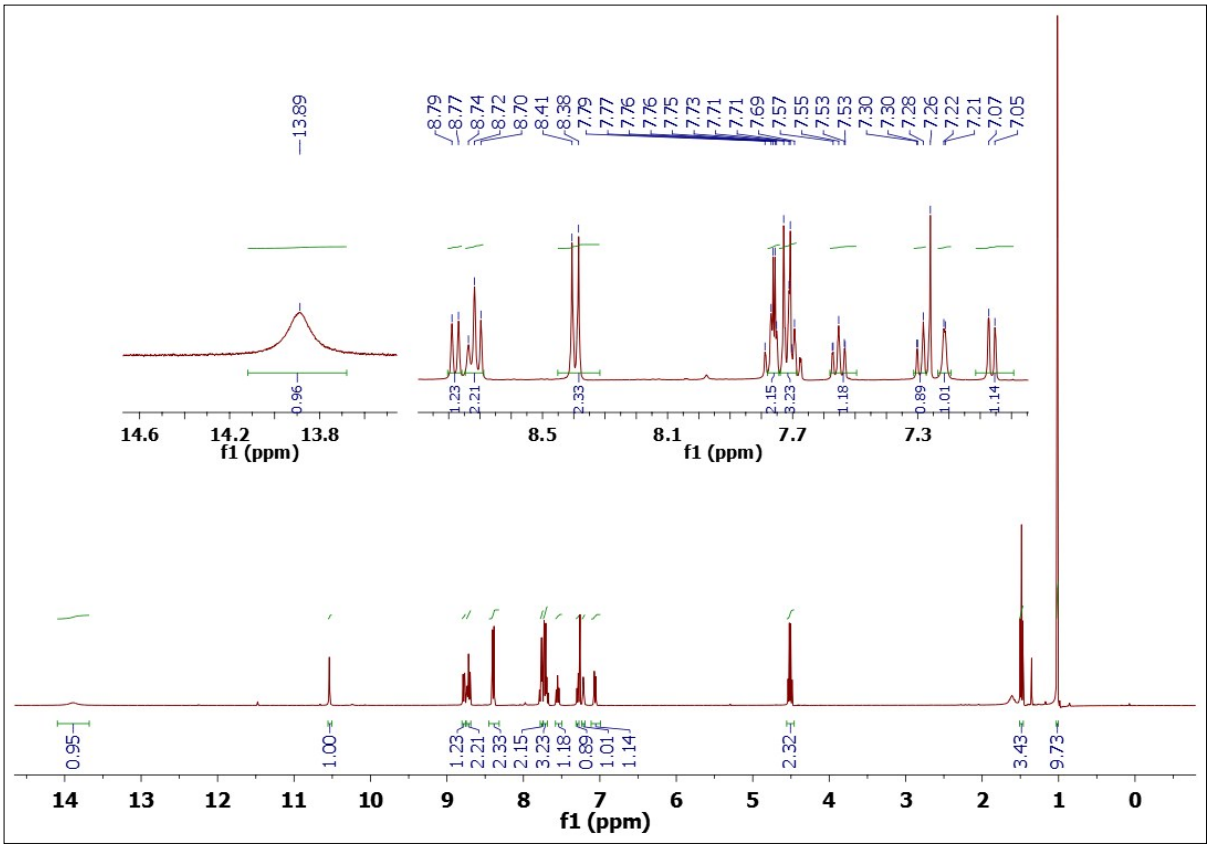


Figure S2. The ^{1}H NMR spectrum of compound **3** that was recorded in $CDCl_3$**.** The inset displays an expansion of the high-field region of the spectrum.

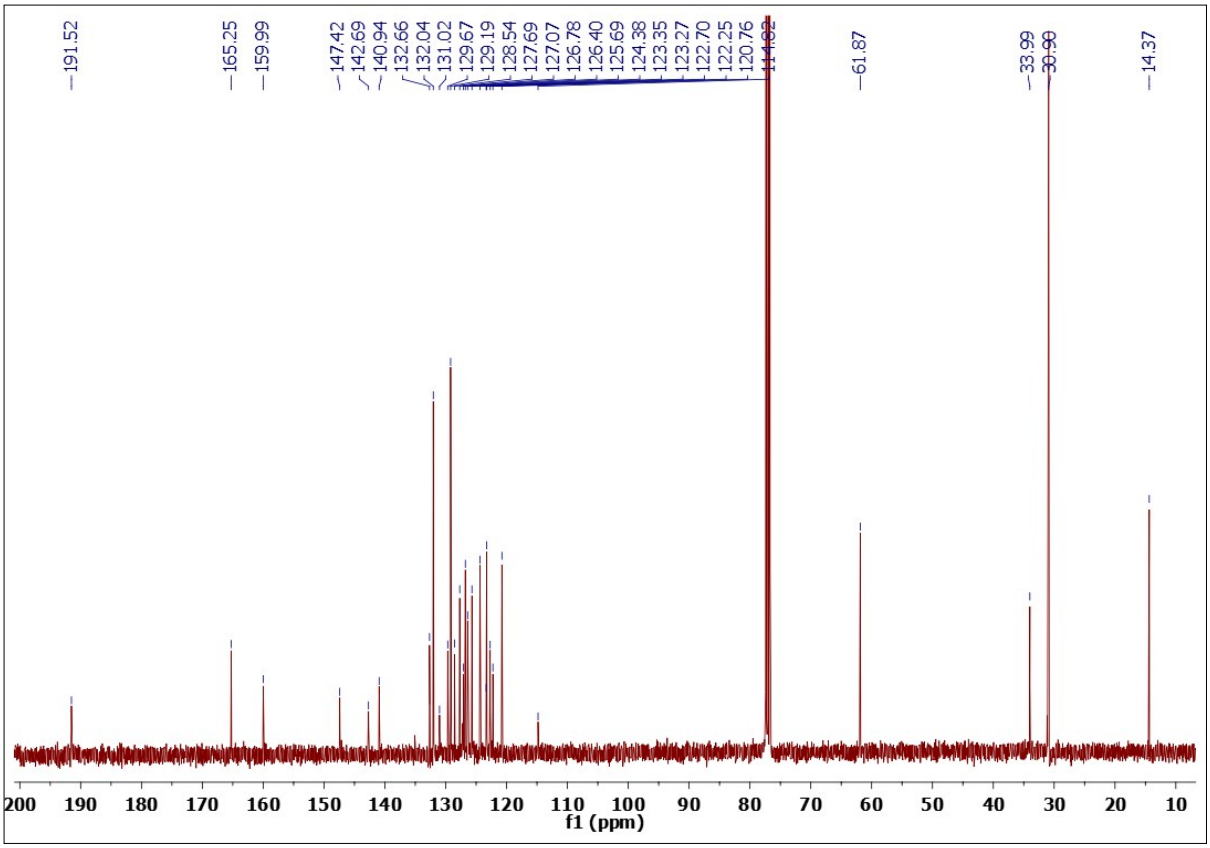
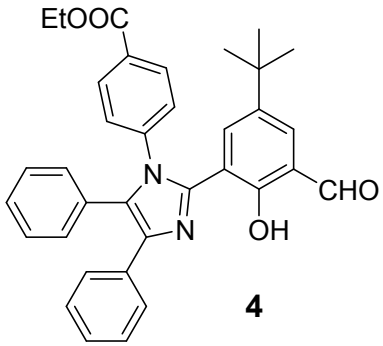


Figure S3. The ^{13}C NMR spectrum of compound **3** that was recorded in $CDCl_3$**.**

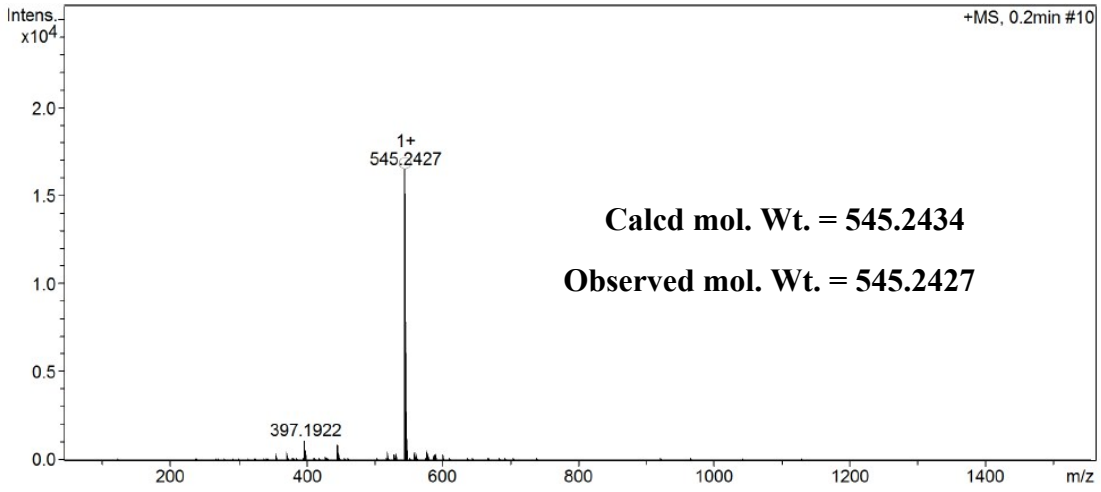


4

Trinity College Dublin

Bruker Open Access LC-MS - Formula Identification Report

Sample-ID		Station	
Submitter		Supervisor	
Analysis Name	Gana-120-1_RB5_01_8407.d	Acquisition Date	04/05/2017 08:15:22
Sample Description			

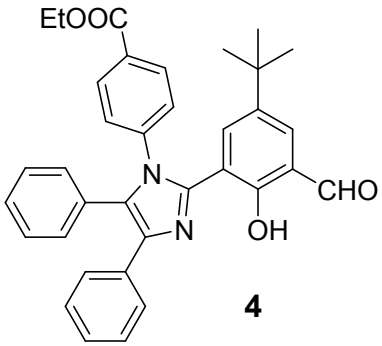


Calcd mol. Wt. = 545.2434

Observed mol. Wt. = 545.2427

Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
545.242738	1	C35H33N2O4	545.243484	0.7	1.4	20.5	ok	even	9.6

Figure S4. The HR-MS of compound **4**.



4

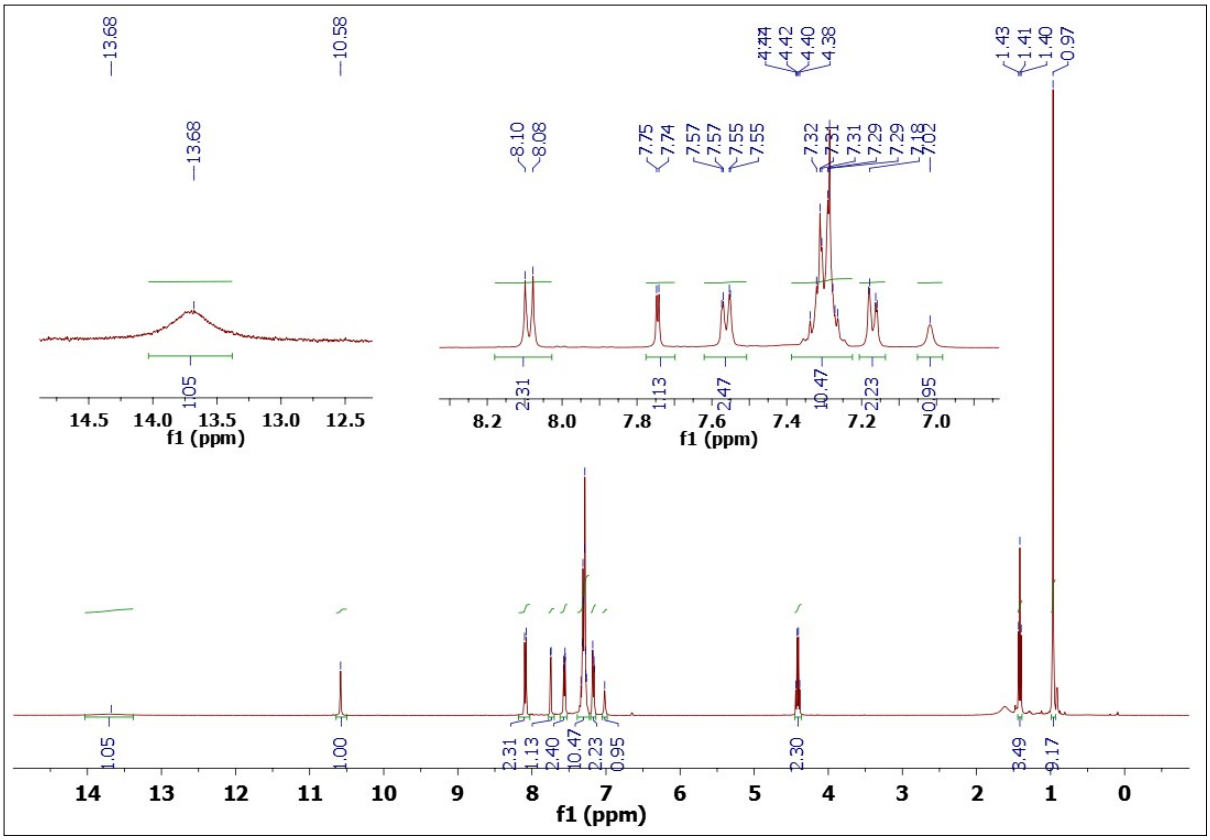


Figure S5. The ^{1}H NMR spectrum of compound **4** that was recorded in $CDCl_3$**.** The inset displays an expansion of the high-field region of the spectrum.

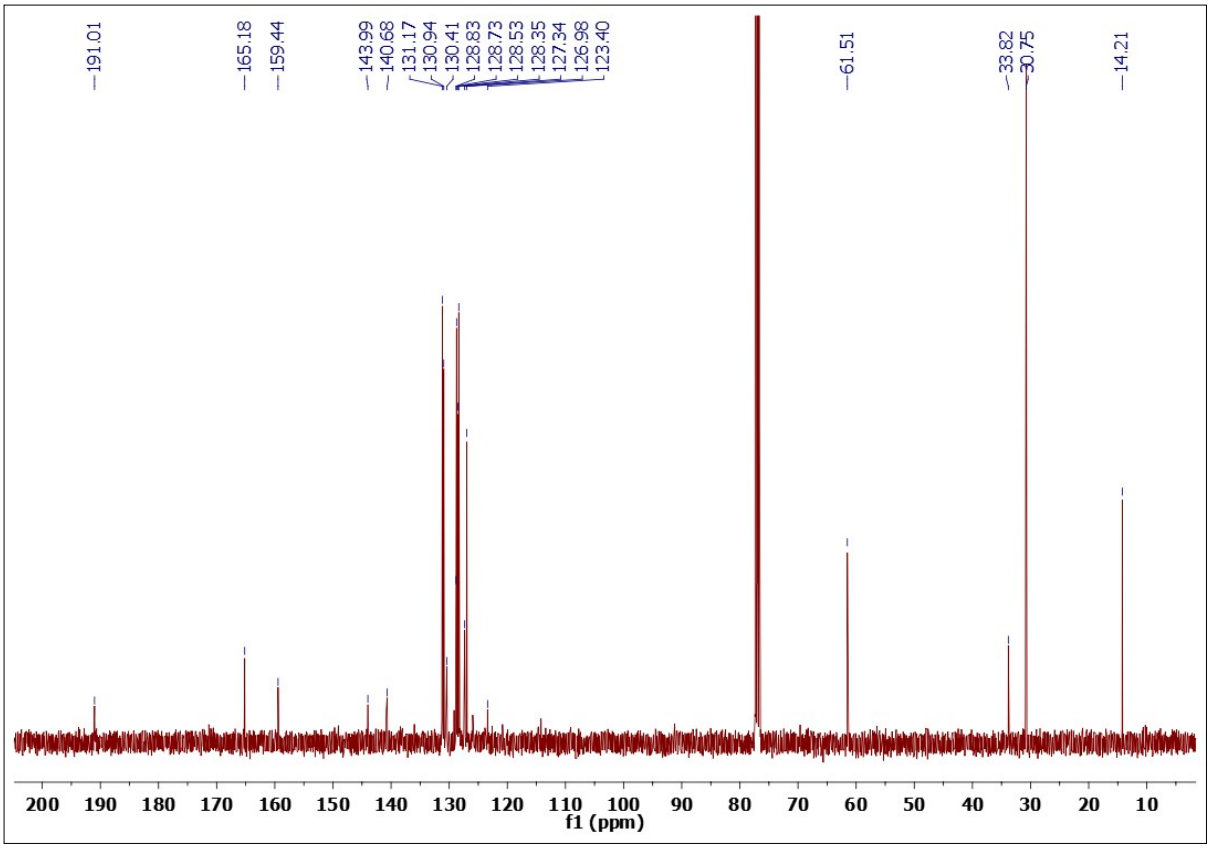
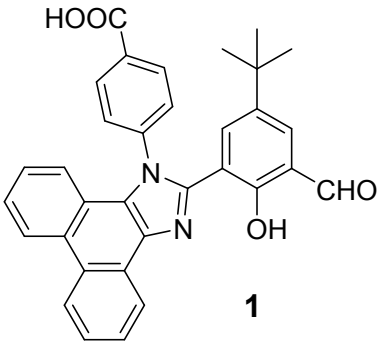


Figure S6. The ^{13}C NMR spectrum of compound **4** that was recorded in $CDCl_3$**.**

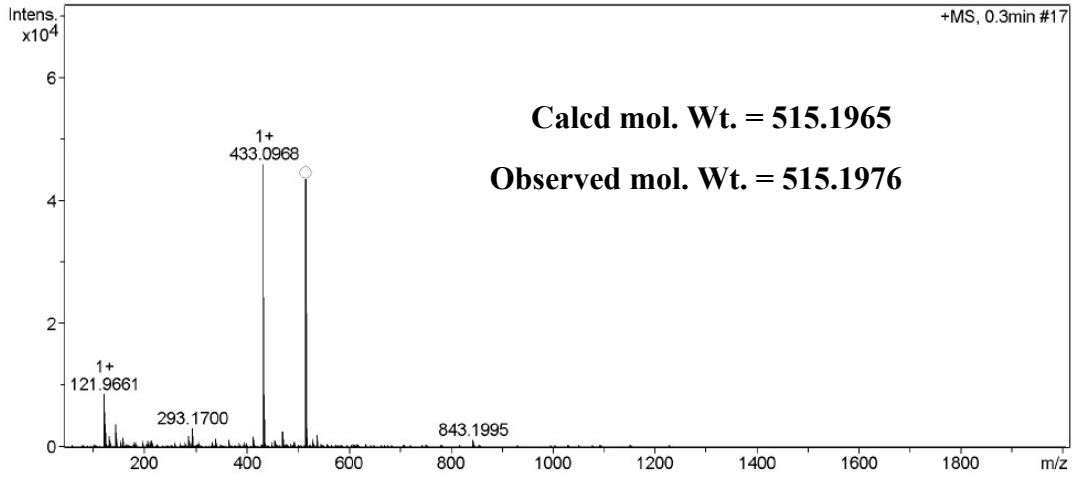


1

Trinity College Dublin

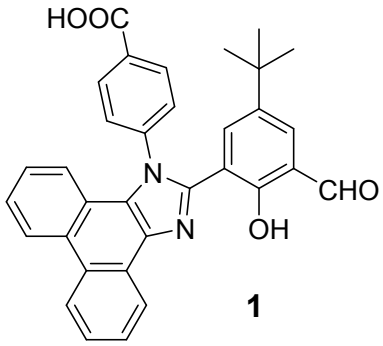
Bruker Open Access LC-MS - Formula Identification Report

Sample-ID		Station	
Submitter		Supervisor	
Analysis Name	Gana-128_RB4_01_12936.d	Acquisition Date	07/12/2017 12:22:15
Sample Description			



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
515.197687	1	C33H27N2O4	515.196534	1.2	2.2	21.5	ok	even	22.7

Figure S7. The HR-MS of compound **1**.



1

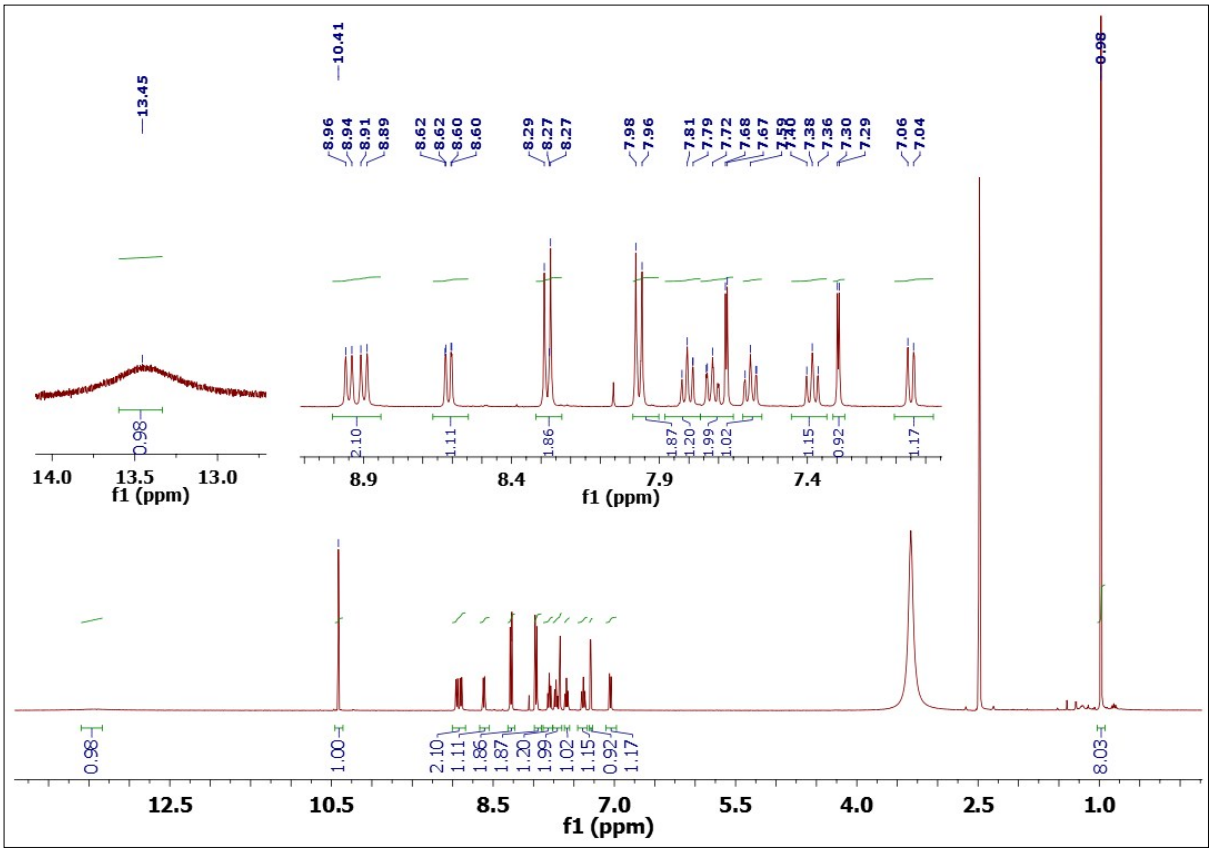


Figure S8. The ^{1}H NMR spectrum of compound **1** that was recorded in DMSO-d_6**.** The inset displays an expansion of the high-field region of the spectrum.

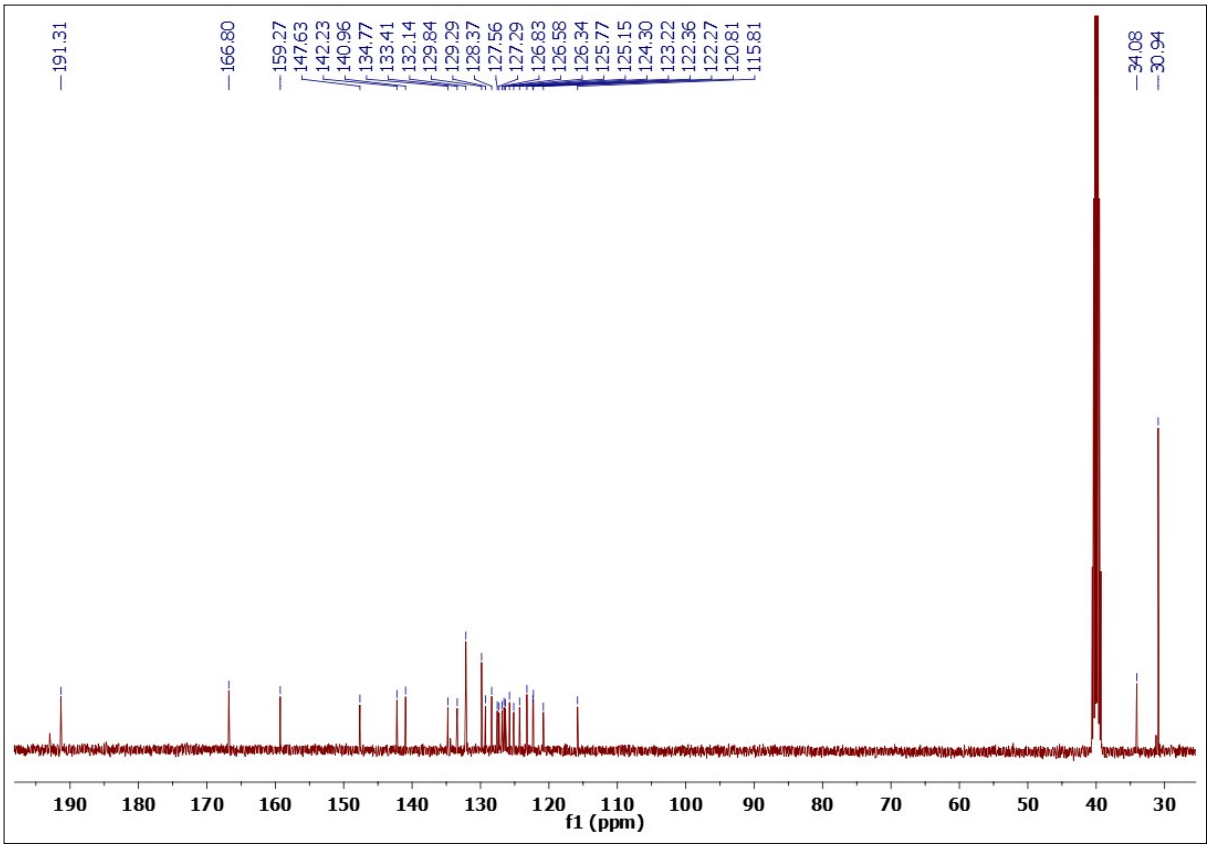
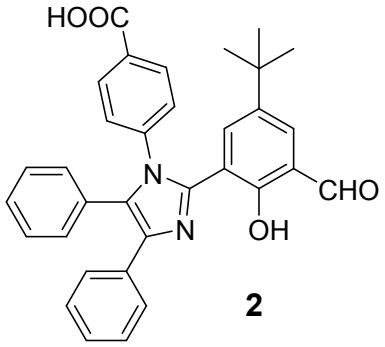


Figure S9. The ^{13}C NMR spectrum of compound **1** that was recorded in DMSO-d_6**.**

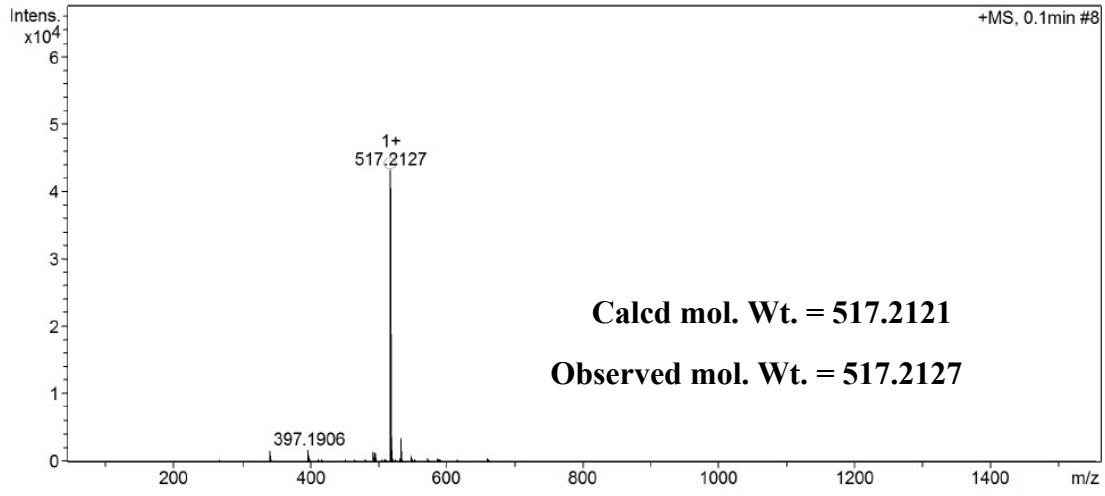


2

Trinity College Dublin

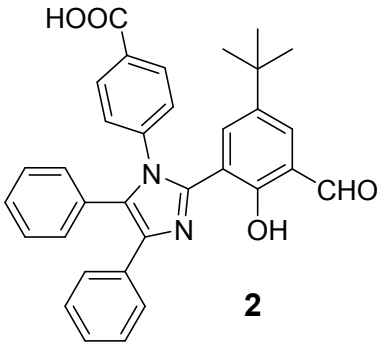
Bruker Open Access LC-MS - Formula Identification Report

Sample-ID		Station	
Submitter		Supervisor	
Analysis Name	Gana-120-4_RA4_01_9994.d	Acquisition Date	02/08/2017 08:12:45
Sample Description			



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
517.212700	1	C33H29N2O4	517.212184	-0.5	-1.0	20.5	ok	even	9.5

Figure S10. The HR-MS of compound **2**.



2

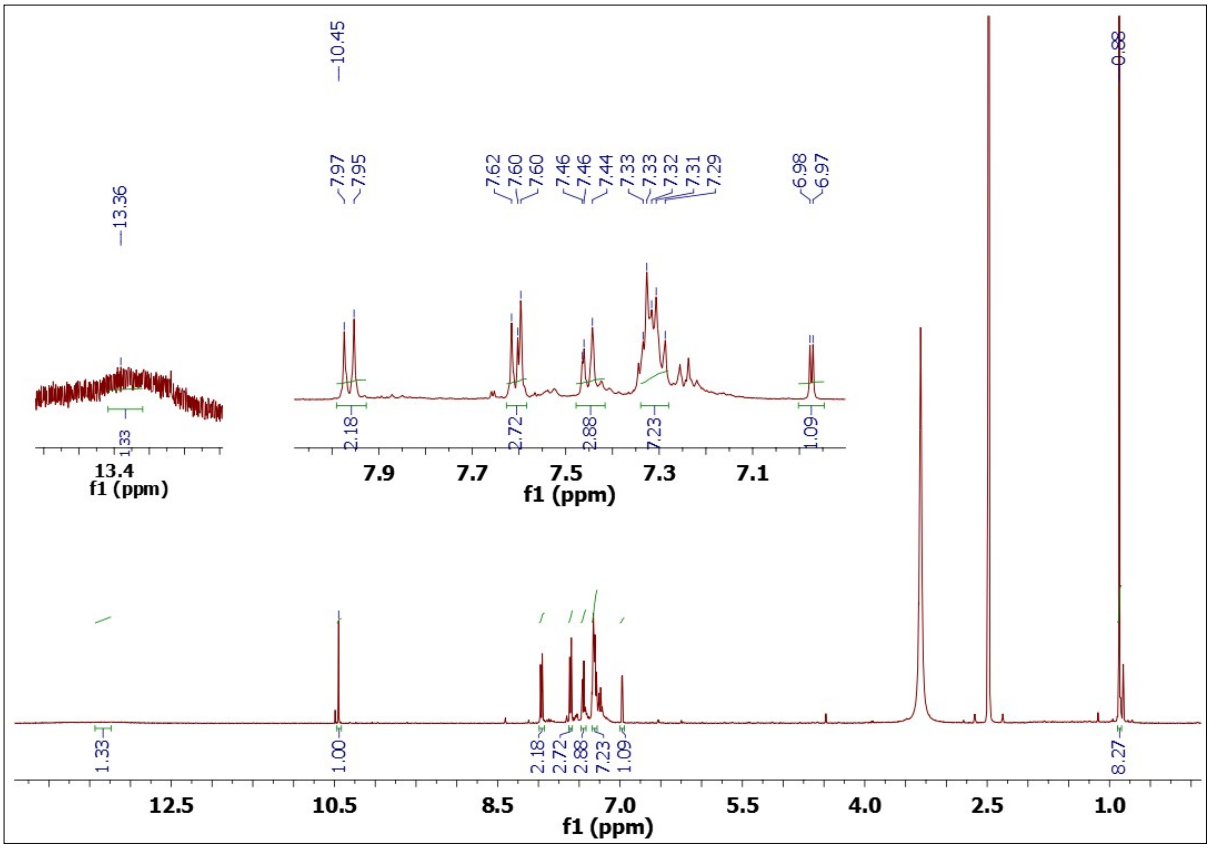


Figure S11. The ^{1}H NMR spectrum of compound **2** that was recorded in DMSO-d_6**.** The inset displays an expansion of the high-field region of the spectrum.

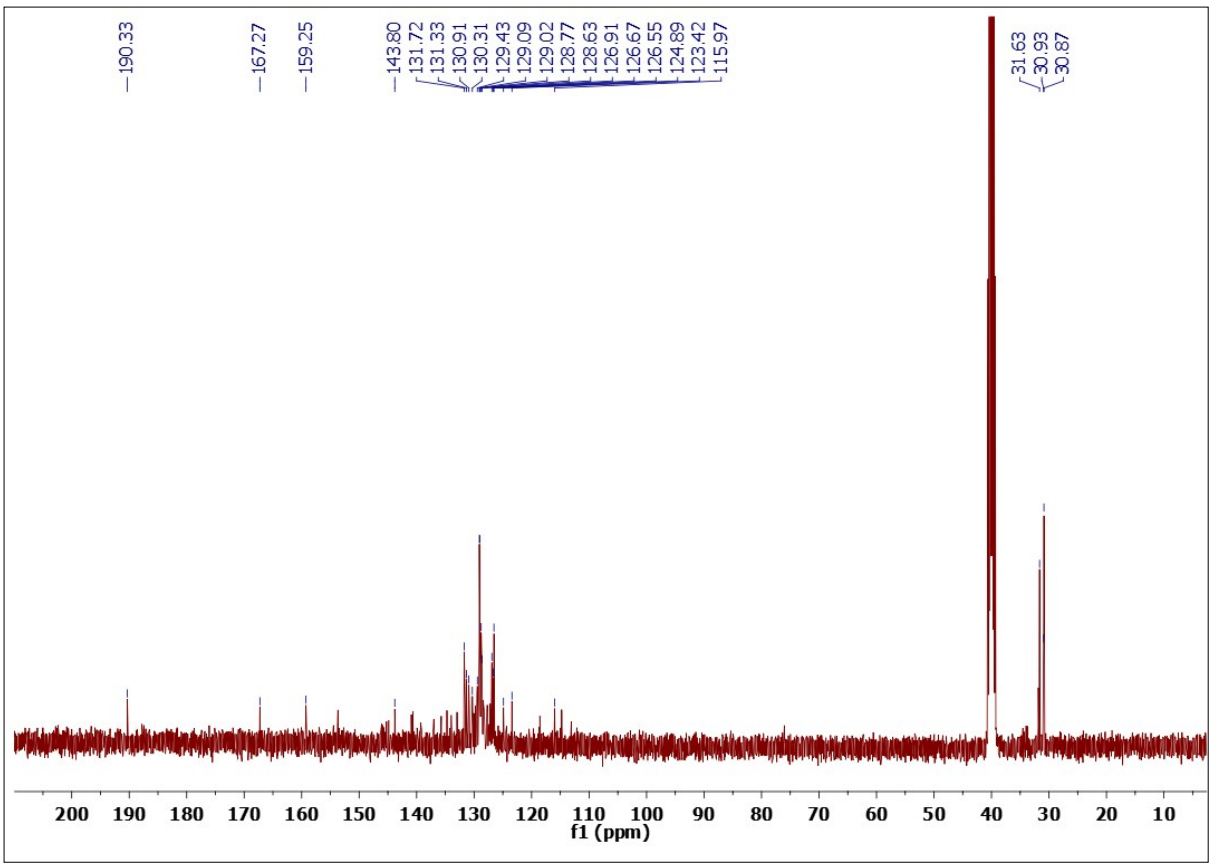


Figure S12. The ^{13}C NMR spectrum of compound **2** that was recorded in DMSO-d_6**.**

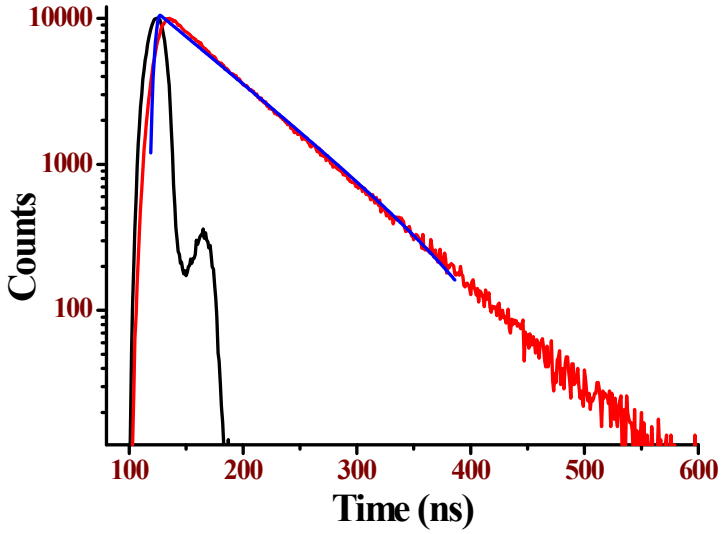


Figure S13. The fluorescence-decay profile of compound **1** in acetonitrile. The excitation wavelength used was 370 nm and emission were detected at the emission-peak maxima (490 nm).

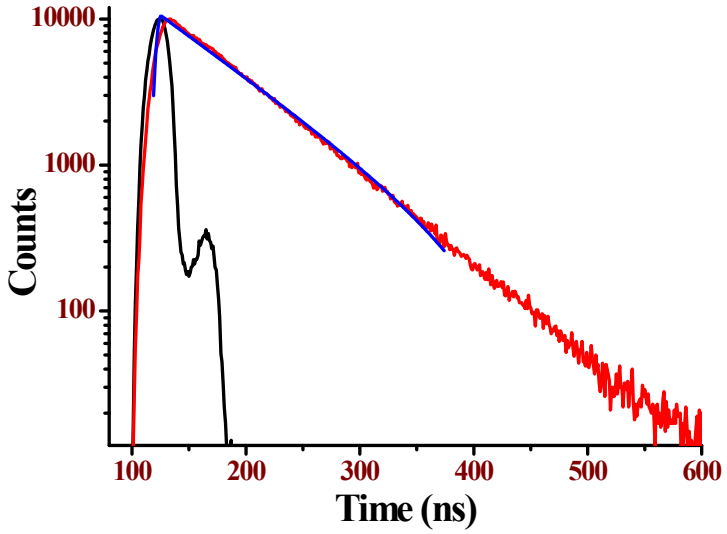


Figure S14. The fluorescence-decay profile of compound **2** in acetonitrile. The excitation wavelength used was 370 nm and emission was detected at the emission-peak maxima (490 nm).

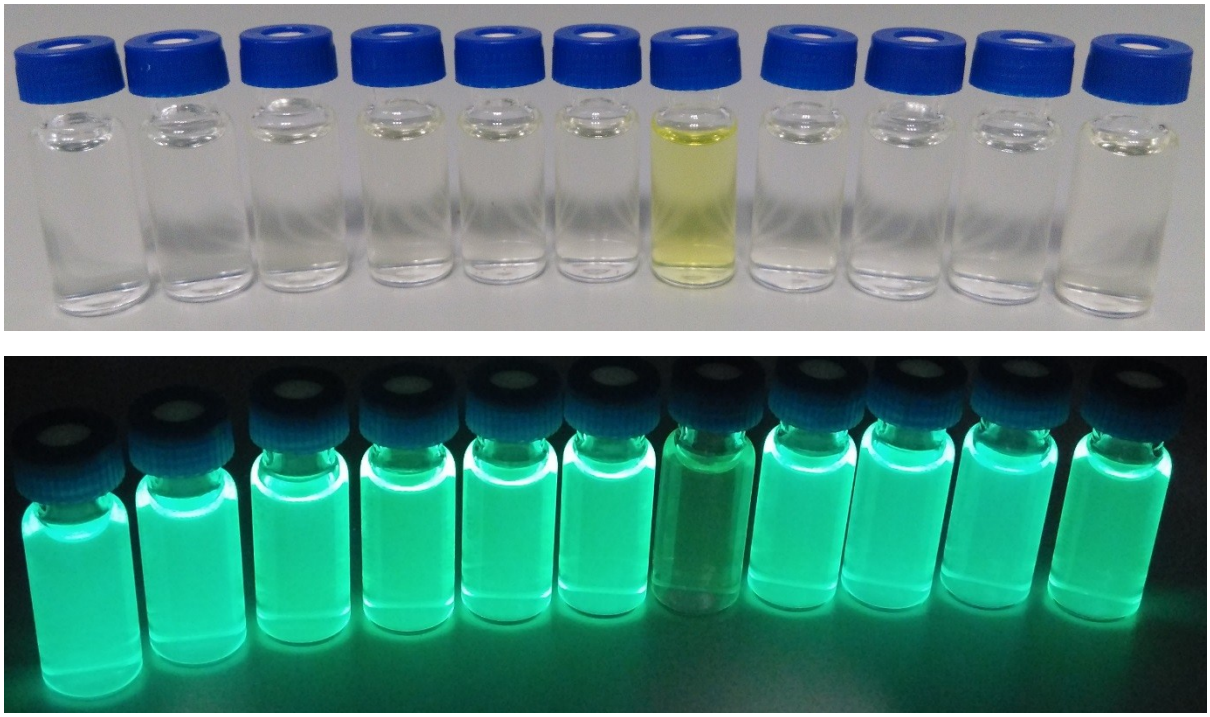


Figure S15. Changes in the colour of **1** upon addition of 10 equiv. of different anions in CH_3CN/H_2O (1:1). Top: naked-eye at day light; bottom: excitation at 360 nm. From left to right: (1) no anion, (2) F^-, (3) Cl^-, (4) Br^-, (5) I^-, (6) N_3^-, (7) CN^-, (8) AcO^-, (9) ClO_4^-, (10) $H_2PO_4^-$, (11) HSO_4^-

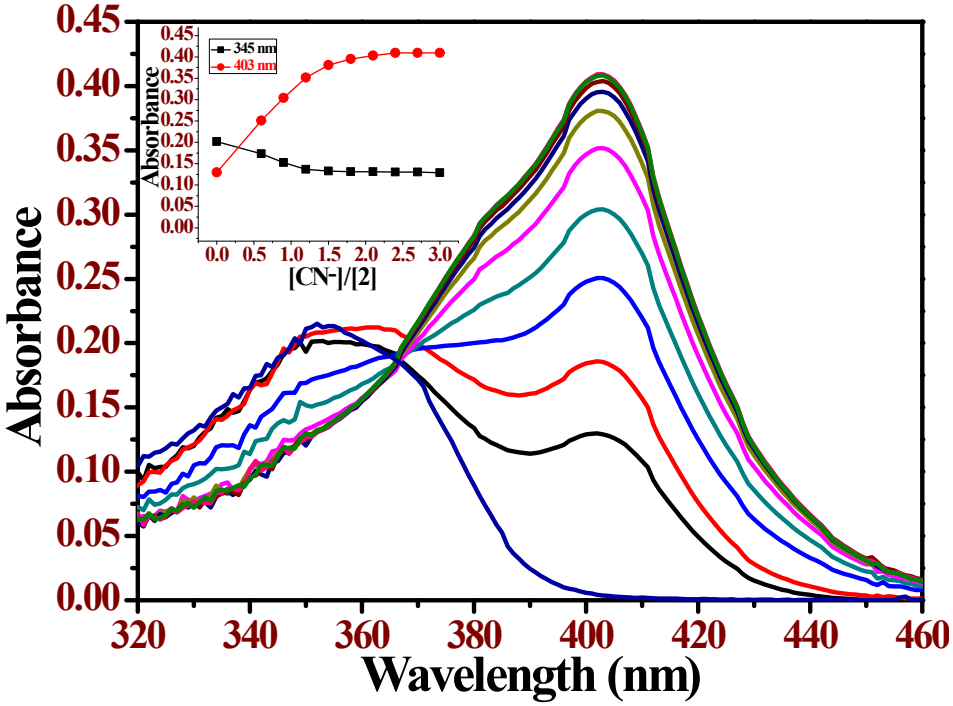


Figure S16. Changes in absorption spectra of compound **2** (10 μM) upon titration with CN^- (0-3.0 equiv.) in CH_3CN/H_2O (1:1) (λ_{ex} = 350 nm). Insets show: plot of absorbance *v*s. [CN^-]/[**2**] molar ratio for absorbance at 375 and 425 nm, respectively.

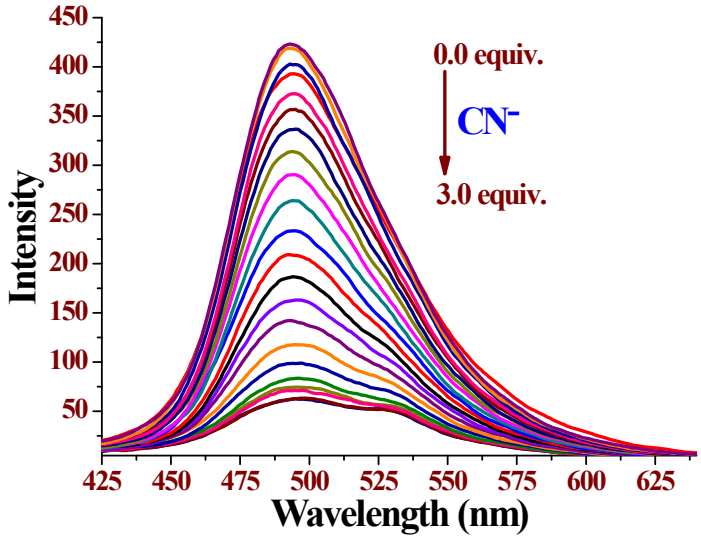


Figure S17. Changes in fluorescence spectra of compound **2** (10 μM) upon titration with CN^- (0.0-3.0 equiv.) in CH_3CN/H_2O (1:1) (λ_{ex}=350 nm).

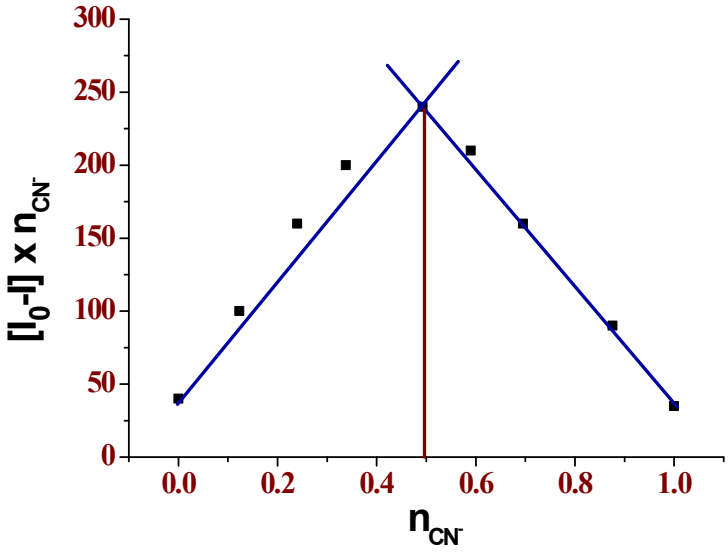


Figure S18. Job's plot for the evolution of binding stoichiometry between compound **1** and CN^- ion in CH_3CN-H_2O (1:1). Where n_{CN^-} is the mole fraction of the host and I is the intensity of compound **1** in the presence of CN^- ion and I_0 is the intensity of compound **1** in the absence of CN^- ion which forms 1:1 complex.

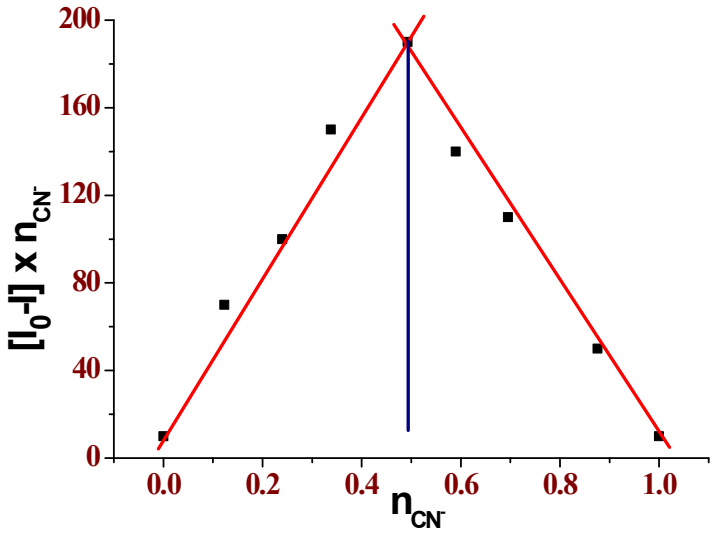


Figure S19. Job's plot for the evolution of binding stoichiometry between compound **2** and CN^- ion in CH_3CN-H_2O (1:1). Where n_{CN^-} is the mole fraction of the host and I is the intensity of compound **2** in the presence of CN^- ion and I_0 is the intensity of compound **2** in the absence of CN^- ion which forms 1:1 complex.

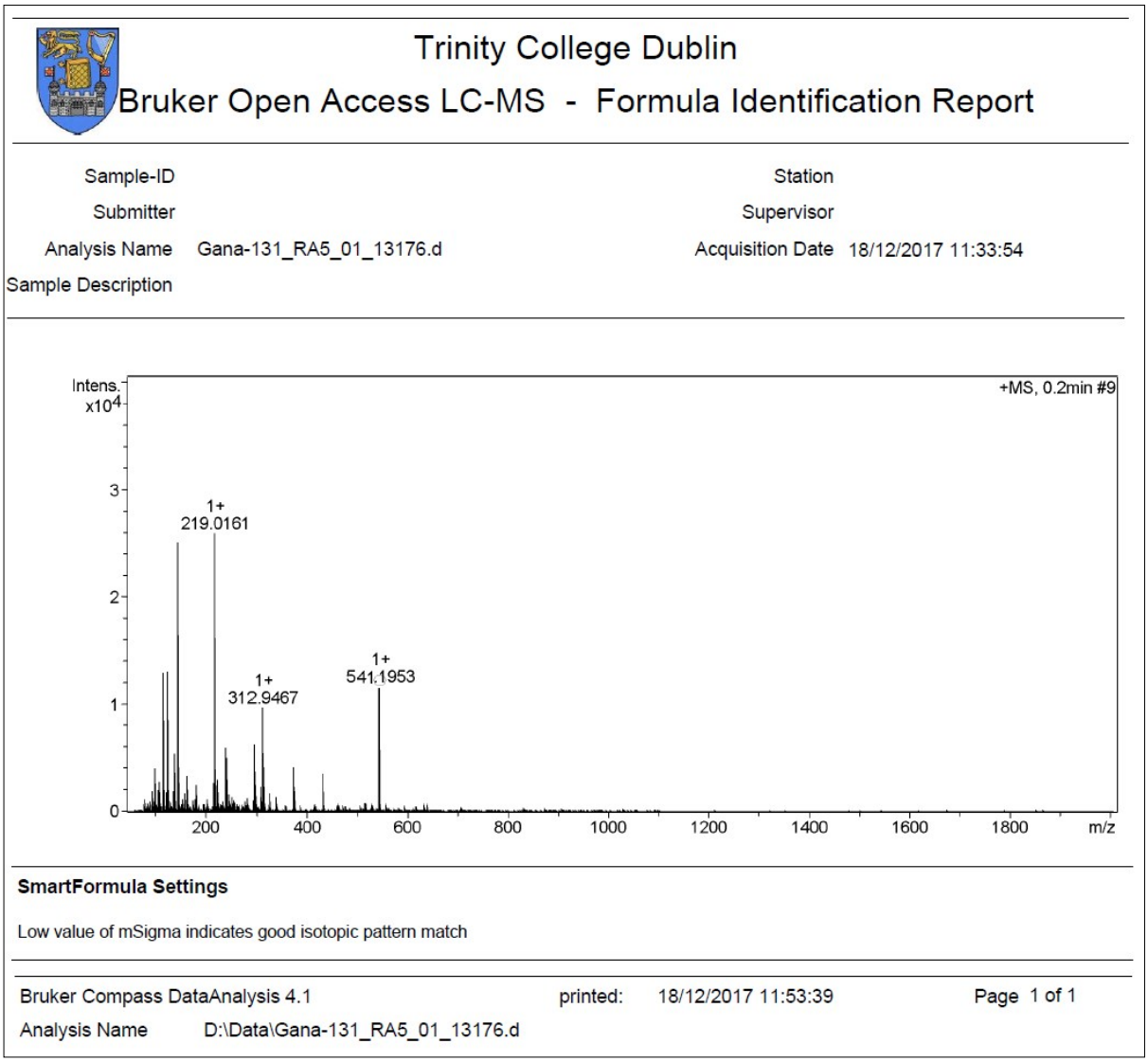


Figure S20. LC-MS of cyanohydrin formation of compound **1** with CN^-

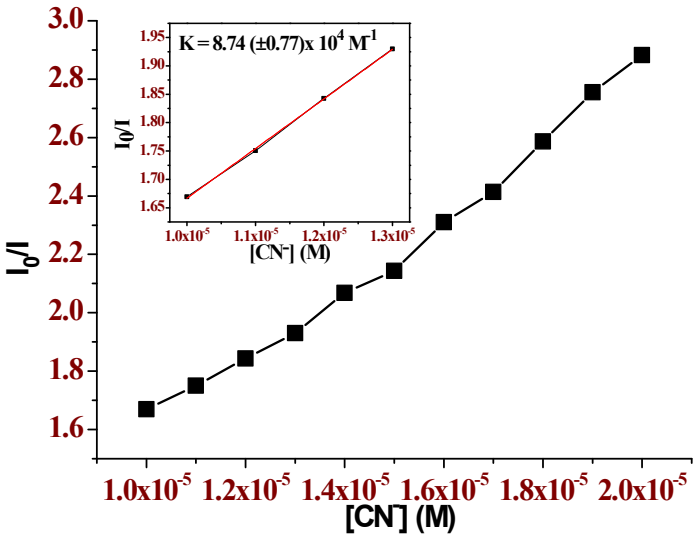


Figure S21. Determination of Stern-Volmer quenching constant for compound **1** (10 μM) with CN^- ion.

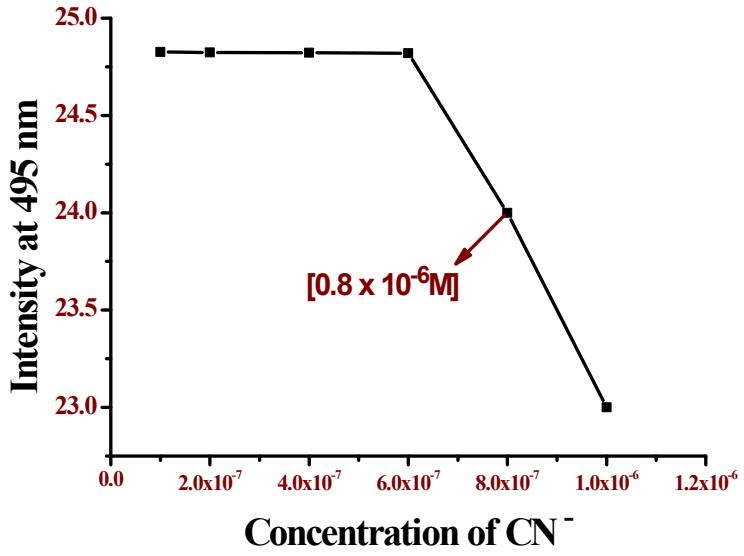


Figure S22. Changes in initial fluorescence intensity of the compound **1** upon gradual addition of CN^-. (The excitation wavelength λ_{ex} = 370 nm, excitation and emission slit width = 5 nm).

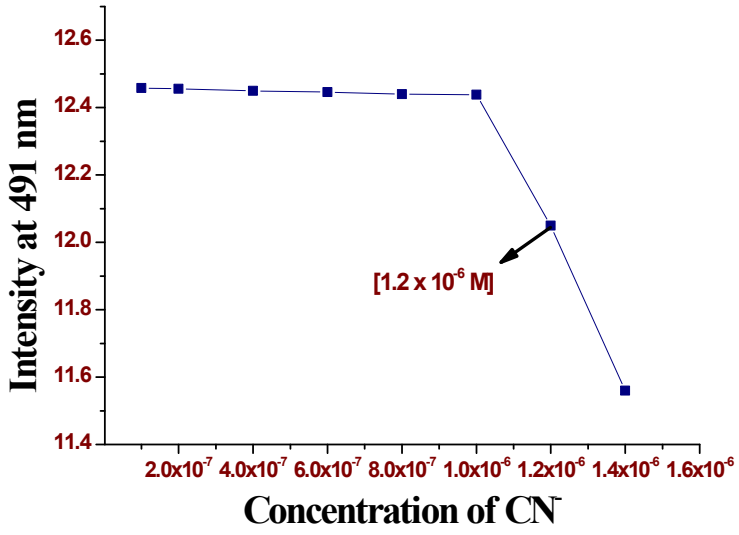


Figure S23. Changes in initial fluorescence intensity of the compound **2** upon gradual addition of CN^-. (The excitation wavelength λ_{ex} = 370 nm, excitation and emission slit width = 5 nm).

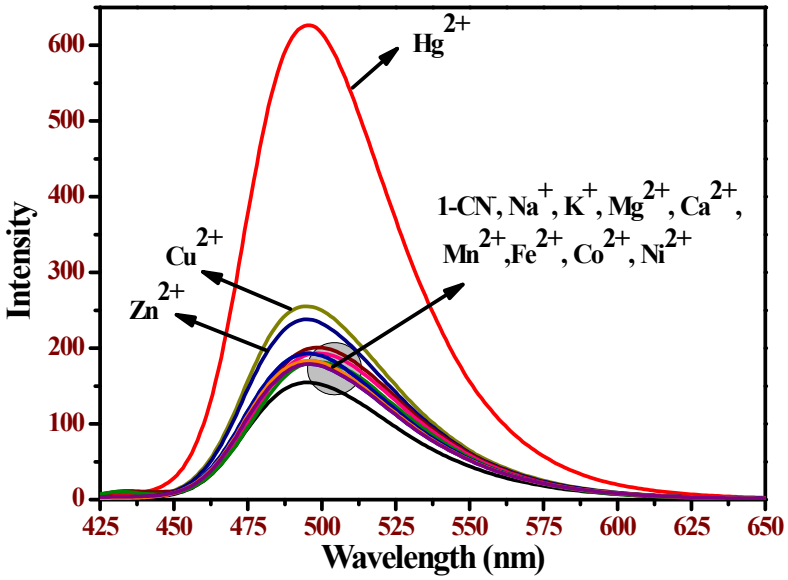


Figure S24: The emission response of **1**-CN^- (10 μM) upon addition of various cations (4.0 equiv.) in CH_3CN/H_2O (1:1). (λ_{ex}=370 nm).

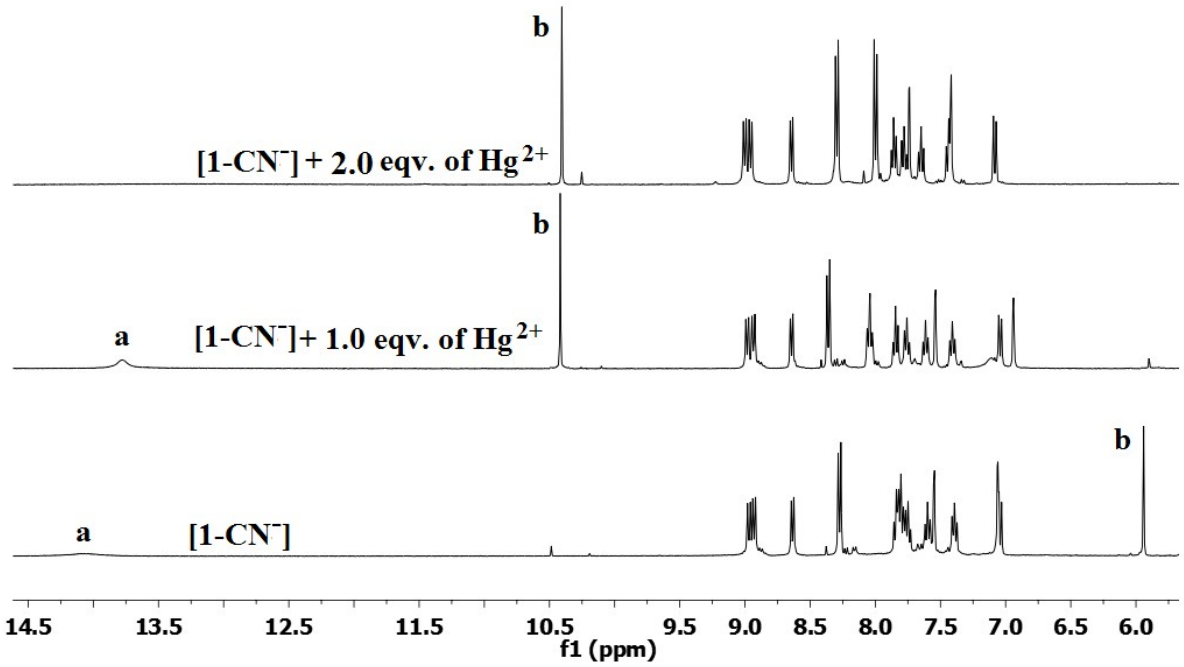
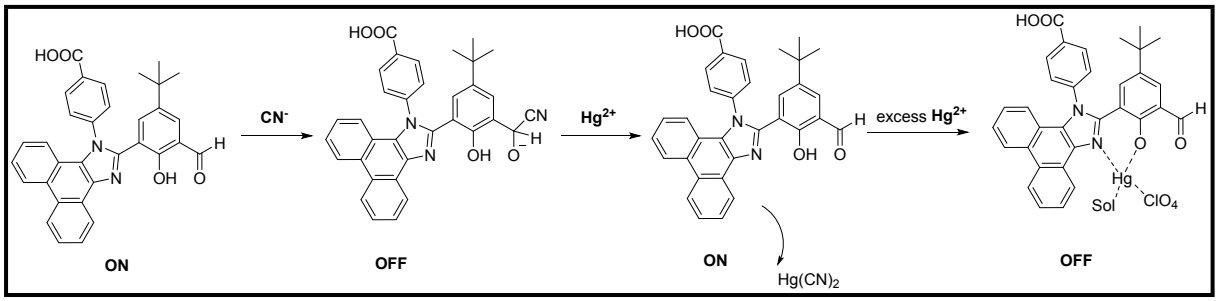


Figure 25. Partial ^{1}H NMR spectra of compound **1-CN^{-}** (0.3 mM) in 0.3 mL of DMSO in the presence of increasing concentration of Hg^{2+}. (a) 0.0 equiv. of Hg^{2+} (b) 1.0 equiv. of Hg^{2+} (c) 2.0 equiv. of Hg^{2+}.

Possible mechanism



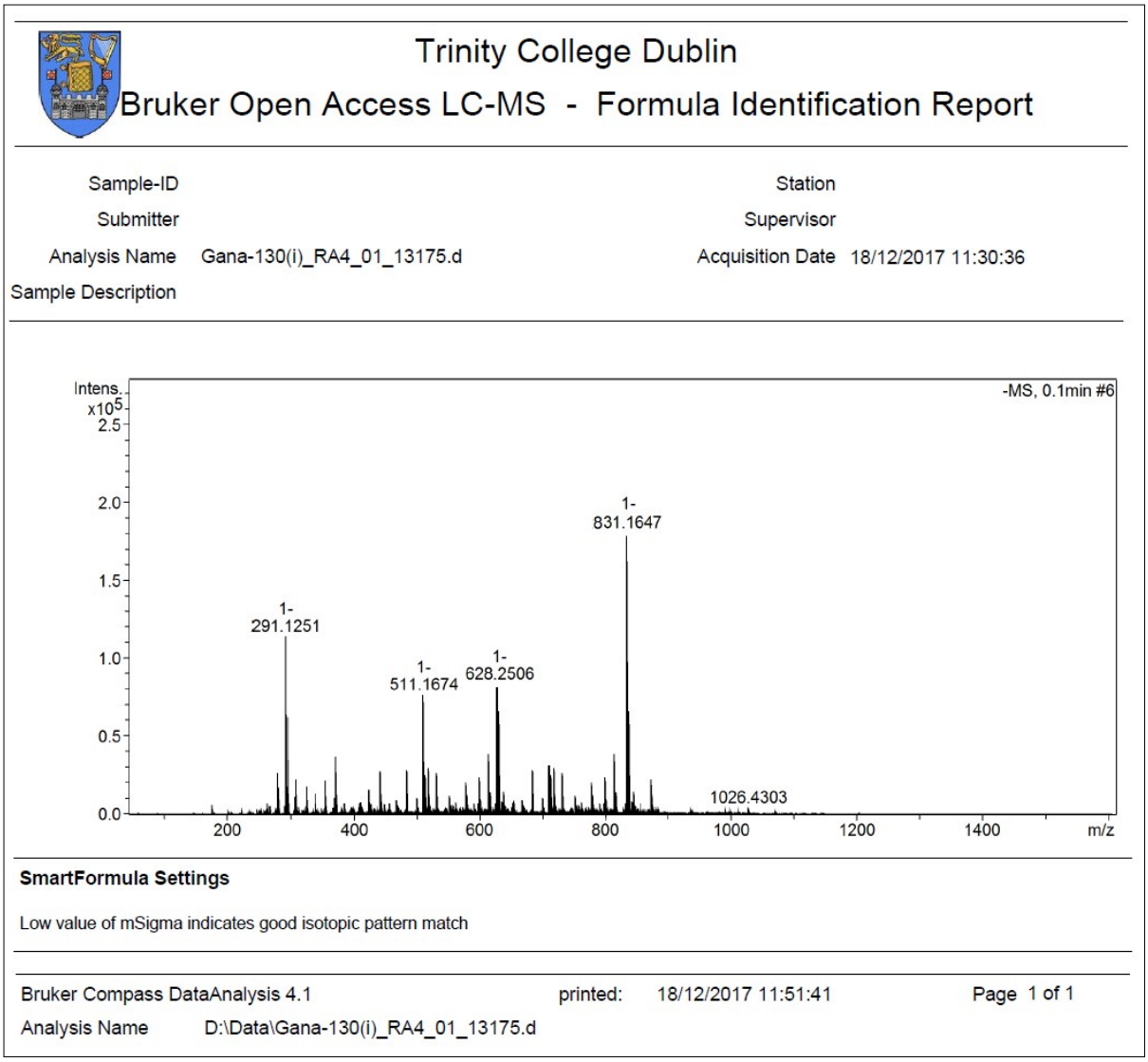


Figure S26. LC-MS of complex between compound **1-Hg^{2+}**

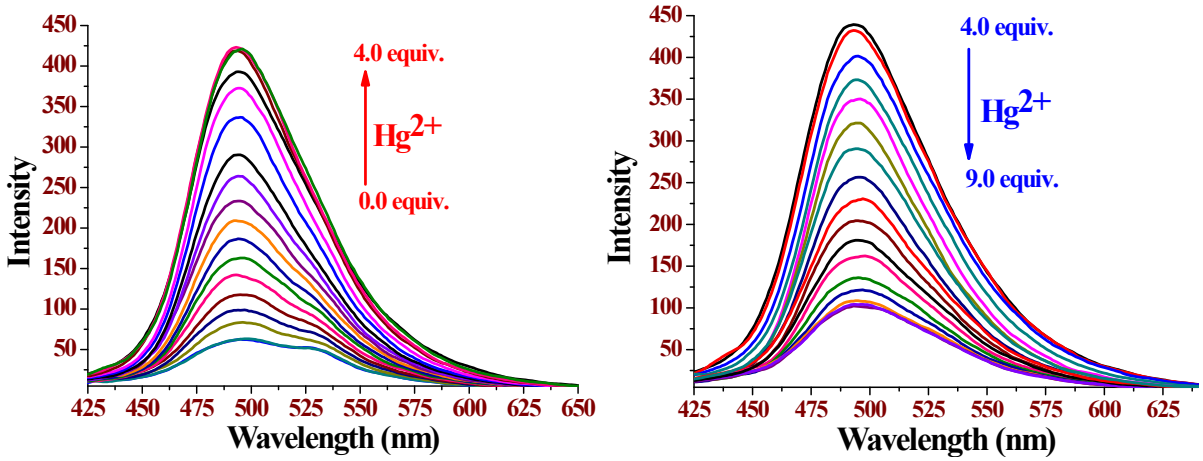


Figure S27. Changes in emission spectra of compound {**2-CN**$^-$} (10 μM) upon titration with Hg^{2+} (10 equiv.) in CH_3CN/H_2O (1:1). (λ_{ex}=350 nm). (a) addition of 0.0 to 4.0 equiv. (b) 4.0 to 9.0 equiv. of Hg^{2+} ions.

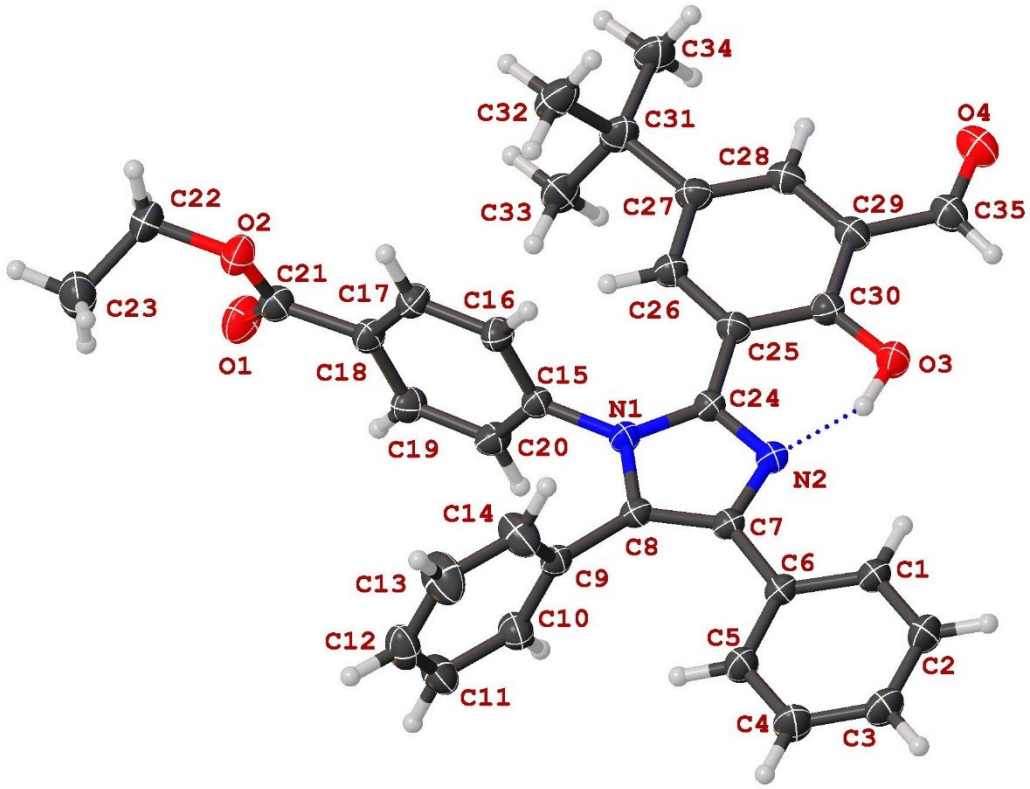


Figure S28: Molecular structure of compound **4** (thermal displacement 50%). Hydrogen atom labels have been omitted for clarity.

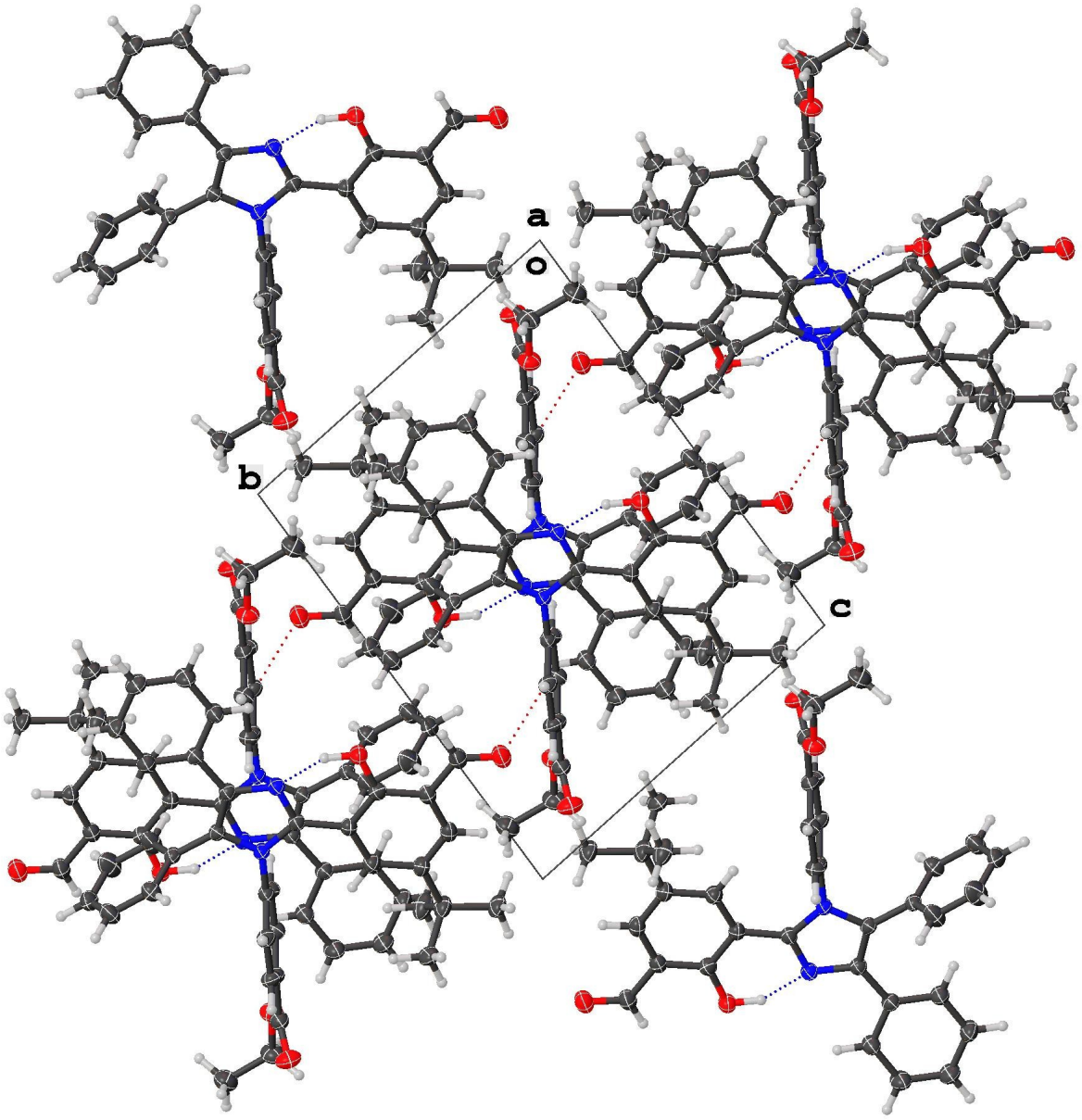


Figure S29: Moiety packing of compound **4** looking down the a-axis showing the stacking between the imidazole and hydrogen-bonding network between the aldehyde moiety and phenyl ring. Atom labels have been omitted for clarity.

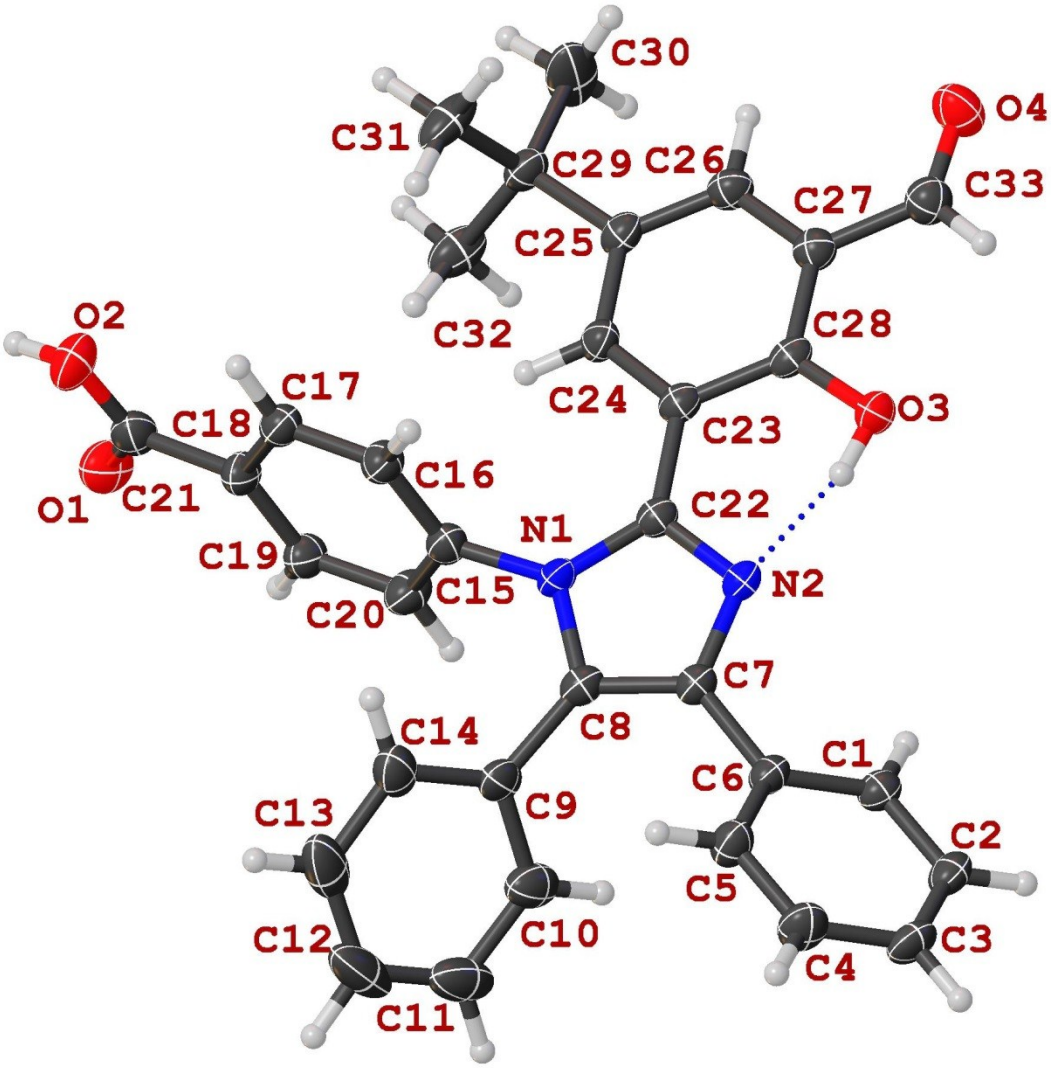


Figure S30: Molecular structure of compound **2** (thermal displacement 50%). Hydrogen atom labels and solvent DMSO molecule have been omitted for clarity.

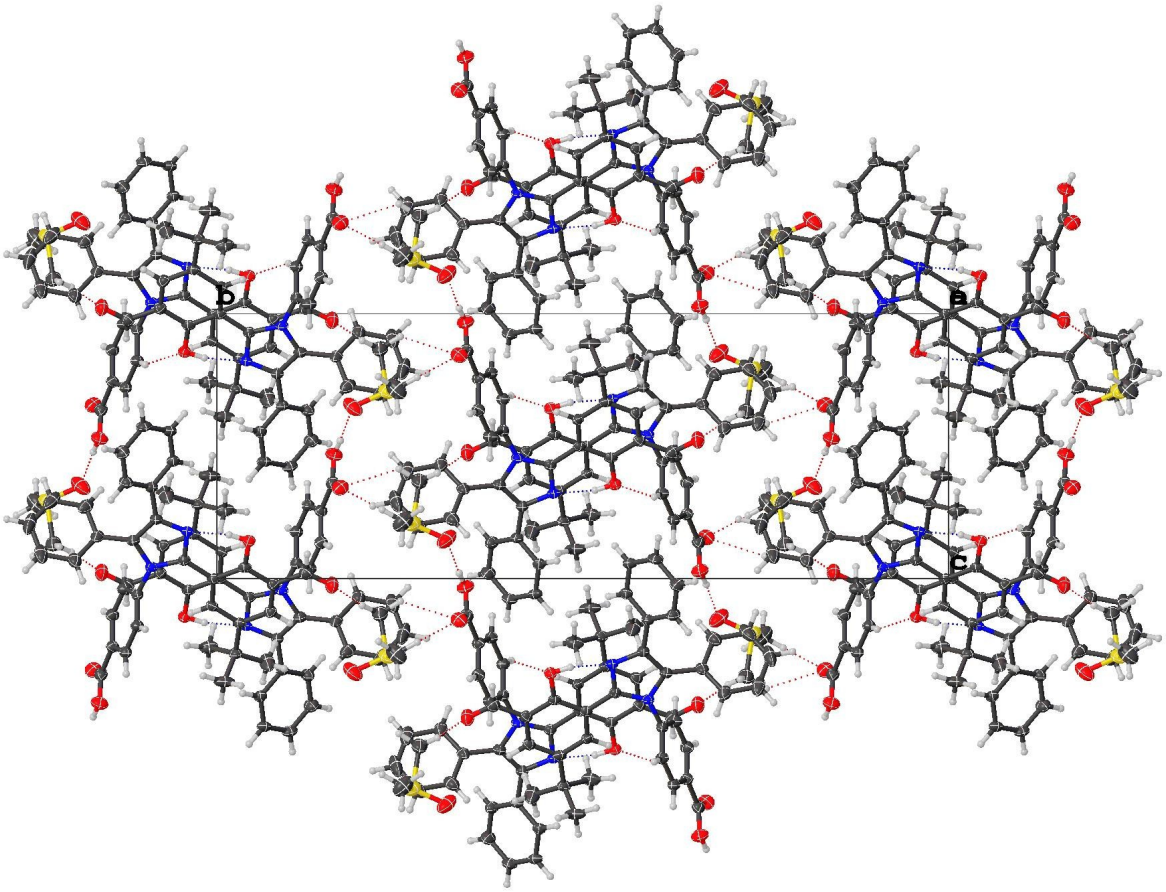


Figure S31: Moiety packing of compound **2** looking down the a-axis showing the hydrogen-bonding interactions between the benzoic acid moiety and solvent DMSO molecules within the unit cell. Atom labels have been omitted for clarity.

Table S1: Photophysical data of imidazoles **1** and **2** recorded in CH_3CN/H_2O.

C.No.	λ_{max} (nm)	λ_{em} (nm)	$\Delta\nu_{st}$ (cm^{-1})	φ_f	τ(ns)	K_r (10^9 s^{-1})	K_{nr} (10^9 s^{-1})
1	370	495	7045	0.19	4.6	0.041	0.176
2	345	491	8618	0.12	3.9	0.030	0.225

Table S2: Details of X-ray Crystallography data refinement

Compound	**4**	**2**
Empirical formula	$C_{35}H_{32}N_2O_4$	$C_{35}H_{34}N_2O_5S$
Formula weight	544.62	594.70
Temperature/K	100.0	100(2)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	10.1174(6)	9.5779(3)
b/Å	10.6043(6)	29.6464(9)
c/Å	14.0472(8)	10.7257(3)
α/°	83.9560(10)	90
β/°	72.1820(10)	92.205(2)
γ/°	87.3180(10)	90
Volume/Å³	1426.66(14)	3043.31(16)
Z	2	4
D_{calc} *g/cm³*	1.268	1.298
μ/mm⁻¹	0.083	1.315
F(000)	576.0	1256.0
Crystal size/mm³	0.433 × 0.419 × 0.188	0.521 × 0.458 × 0.144
Radiation	MoKα	CuKα
Wavelength/Å	λ = 0.71073	λ = 1.54178
2θ/°	3.06 to 59.318	5.962 to 133.996
Reflections collected	69783	38472
Independent reflections	8057	5433
R_{int}	0.0437	0.0765
R_{sigma}	0.0264	0.0444
Restraints	54	6
Parameters	408	400
GooF	1.052	1.150
R_1 *[I> 2σ (I)]*	0.0506	0.0697
wR_2 *[I> 2σ (I)]*	0.1299	0.1626
R_1 *[all data]*	0.0779	0.0781
wR_2 *[all data]*	0.1464	0.1669
Largest peak/e Å⁻³	0.42	0.7
Deepest hole/e Å⁻³	-0.25	-0.54

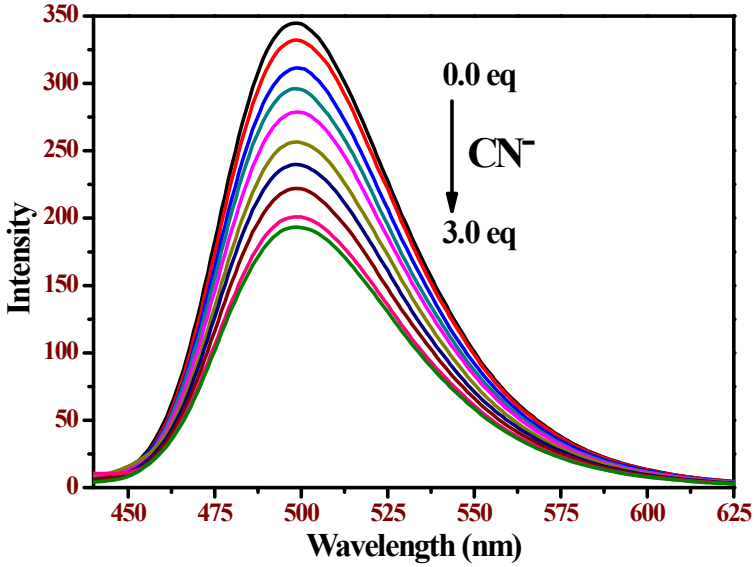


Figure S32. Changes in fluorescence spectra of compound **1** (10 μM) upon titration with CN^- (0.0-3.0 equiv.) in CH_3CN/H_2O (1:1) (λ_{ex}=392 nm).