Electronic Supplementary Information

A highly sensitive and selective fluorescent turn-on chemosensor bearing 7-Diethylaminocoumarin moiety for detection of cyanide in organic and aqueous solutions

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1. Materials and Methods

All reactants, reagents, and catalysts were purchased from Sigma-Aldrich. All solvents and materials purchased were used without further purification. Thin-layer chromatography (TLC) was used for monitoring the reactions using precoated silica gel 60 F254 plates. Column chromatography was performed on silica gel (60-120 mesh, Merck Chemicals). NMR spectra were measured on Bruker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) spectrometers at 20 ºC (293 K). Chemical shifts (δ) are given in parts per million (ppm) using the residue solvent peaks as a reference relative to TMS. Coupling constants (J) are given in hertz (Hz). Signals are abbreviated as follows: singlet. s; doublet. d; doublet-doublet. dd; triplet. t; multiplet. m. Mass spectra were recorded using a Waters LCT Premier XE (LC–MS) (Ankara University, Laboratories, Department of Pharmacological Sciences, Turkey) mass spectrometer. The melting points were measured using Electrothermal IA9200 apparatus. Absorption spectra were recorded on a Shimadzu 1800 spectrophotometer; fluorescence spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer.

Anion Titration Study:The UV-vis absorption and fluorescence spectra were recorded in order to study the selectivity of various anions (F^-, I^-, Cl^-, Br^-, AcO^-, CN^-, $H_2PO_4^-$, NO_3^-, ClO_4^- and HSO_4^-) towards the chemosensors. To a DMSO solution of the componds **1**, **2** and **3** (20 μM), 10 equivalents of each anion (10 mM in DMSO), were added. Both UV-vis and fluorescence spectra were taken at room temperature.

pH Study : The UV-vis absorption and fluorescence spectra were recorded in a mixture of DMSO and Britton–Robinson buffer (10 μM) as the pH range from 6 to 11, 9:1(v/v). Both UV-vis and fluorescence spectra were taken at room temperature.

Cation Titration Study: The UV-vis absorption was recorded in order to study the selectivity of various cations (K^+, Mg^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Hg_2^{2+}, Al^{3+}, Sn^{2+}) towards the chemosensors. To a DMSO solution of the compounds **4- 9** (20 μM), 50 equivalents of each cation (10 mM in DMSO), were added. UV-vis spectra was taken at room temperature.

^{1}H NMR titration study: Spectra were recorded first on **5** (10 mM), followed by the addition of aliquots of a solution of anions, F^- and CN^-, (1 M) in DMSO-d_6.

Theoretical Methods: The optimizations were done using Density Functinal Theory (DFT) calculations at B3LYP/631+g(d,p)[1,2] in gas phase and various solvents. The absorption spectra were calculated using TD-DFT calculations at the same level. The integral equation formalism of the Polarizable Continuum Model (PCM)[3,4] was used to consider the solvent effects. All calculations were carried out using Gaussian 09 package program[5].

2. Synthesis of Compounds

*3-acetyl-7-(diethylamino)-2H-chromen-2-one (**1**):*

The compound **1** was synthesized by mixing of 4-(diethylamino)-2-hydroxybenzaldehyde (1 mmol, 193 mg) and of ethyl 3-oxobutanoate (1.2 mmol, 153 µL) in 20 mL ethanol. The mixture was refluxed for 24 h and then cooled, filtered. The pure product was obtained by recrystallization from ethanol. Yield: 164 mg (87 %) m.p.: 152 - 154 °C; (lit. mp: 152 - 154 °C).[6]

^{1}H-NMR (300 MHz, DMSO-d_6): δ = 8.50 (s,1 H), 7.65 (d, *J* = 9.0 Hz, 1 H), 6.78 (dd, *J* = 2.4, 9.0 Hz, 1 H), 6.56 (d, *J* = 2.3 Hz, 1 H), 3.48 (q, *J* = 7.0 Hz, 4 H), 3.22 (s, 3 H), 1.13 (t, *J* = 7.0 Hz, 1 H).

*3-(2-bromoacetyl)-7-(diethylamino)-2H-chromen-2-one (**2**):*

The compound **2** was synthesis by mixing of 3-acetyl-7-(diethylamino)-2*H*-chromen-2-one (**1**) (1 mmol, 259 mg) and of copper(ii) bromide (1.2 mmol, 268 mg) in 20 mL ethanol. The mixture was irradiated with microwaves to 100 ^{o}C for 2 min with 300 W. The mixture was cooled to room temperature and added 2 mL water. The precipitated yellow solid filtered and washed with ammonia solutioni 5% (v/v). The pure product was obtained by recrystallization from acetonitrile. Yield: 305 mg (90 %) m.p.: 211 - 212 °C; (lit. mp: 211 - 212 °C).[6]

^{1}H NMR (300 MHz, $CDCl_3$-d_1): *δ* = 8.55 (s, 1 H); 7.45 (d, *J* = 9.1 Hz, 1 H); 6.65 (dd, *J* = 9.1, *J* = 2.4 Hz, 1 H); 6.48 (d, *J* = 2.2 Hz, 1 H); 4.80 (s, 2 H); 3.50 (q, *J* = 7.1 Hz, 4 H); 1.27 (t, *J* = 7.2 Hz, 6 H).

*3-(2-aminothiazol-4-yl)-7-(diethylamino)-2H-chromen-2-one (**3**):*

The compound **3** was synthesized by mixing of 3-(2-bromoacetyl)-7-(diethylamino)coumarin (**2**) (1 mmol, 340 mg) and of thiourea (1 mmol, 76 mg) in 20 mL ethanol. The mixture was refluxed for 2 h and then cooled, filtered and the dark orange solid was washed with ammonia solution, 5% (v/v). The pure product was obtained by recrystallization from ethanol. Yield: 248 mg (78 %) m.p.: 198 - 200 °C; (lit. mp: 199 - 201 °C).[7]

^{1}H NMR (300 MHz, $CDCl_3$-d_1): *δ* = 8.39 (s, 1 H); 7.61 (d, *J* = 8.8 Hz, 1 H); 6.61 (dd, *J* = 8.8, *J* = 2.5 Hz, 1 H); 6.53 (d, *J* = 2.4 Hz, 1 H); 5.01 (s, 2 H); 3.44 (q, *J* = 7.2 Hz, 4 H); 1.24 (t, *J* = 7.1 Hz, 6 H).

3. FT-IR, ^{1}H-NMR, ^{13}C-NMR , LC-MS and X-Ray Spectra of Compounds

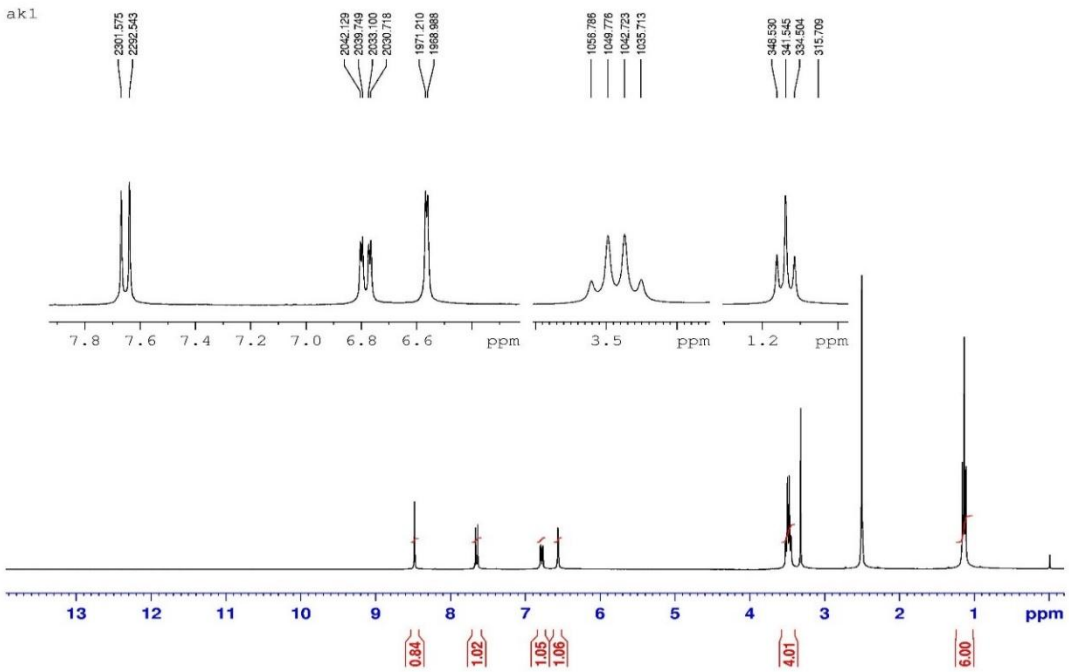

Fig. S1. ^{1}H-NMR (DMSO-d_6) Spectrum of **1**.

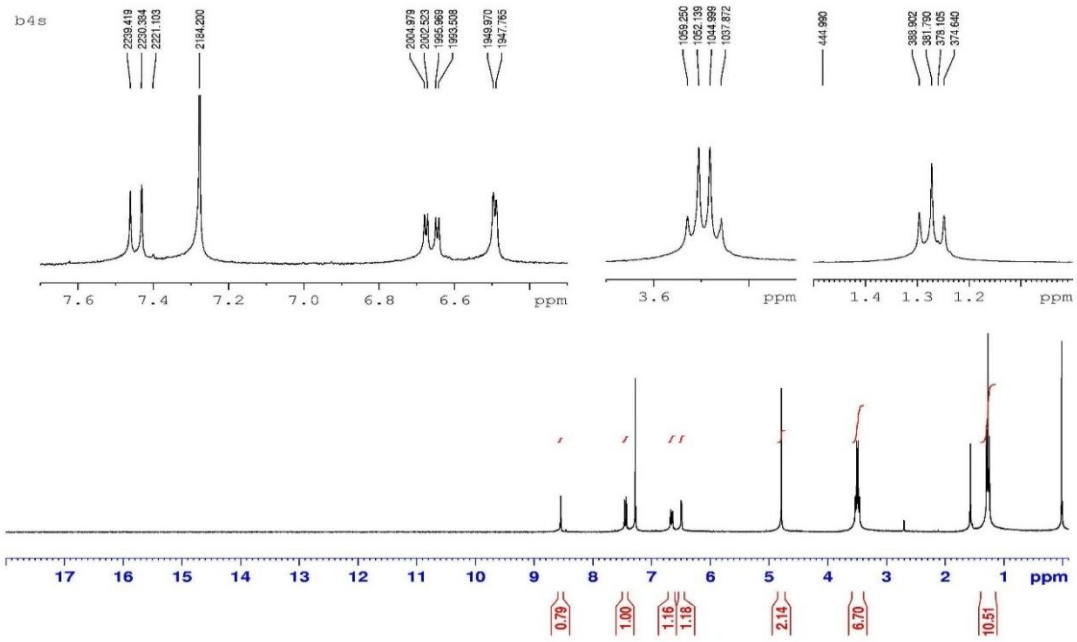

Fig. S2. ^{1}H-NMR (DMSO-d_6) Spectrum of **2**.

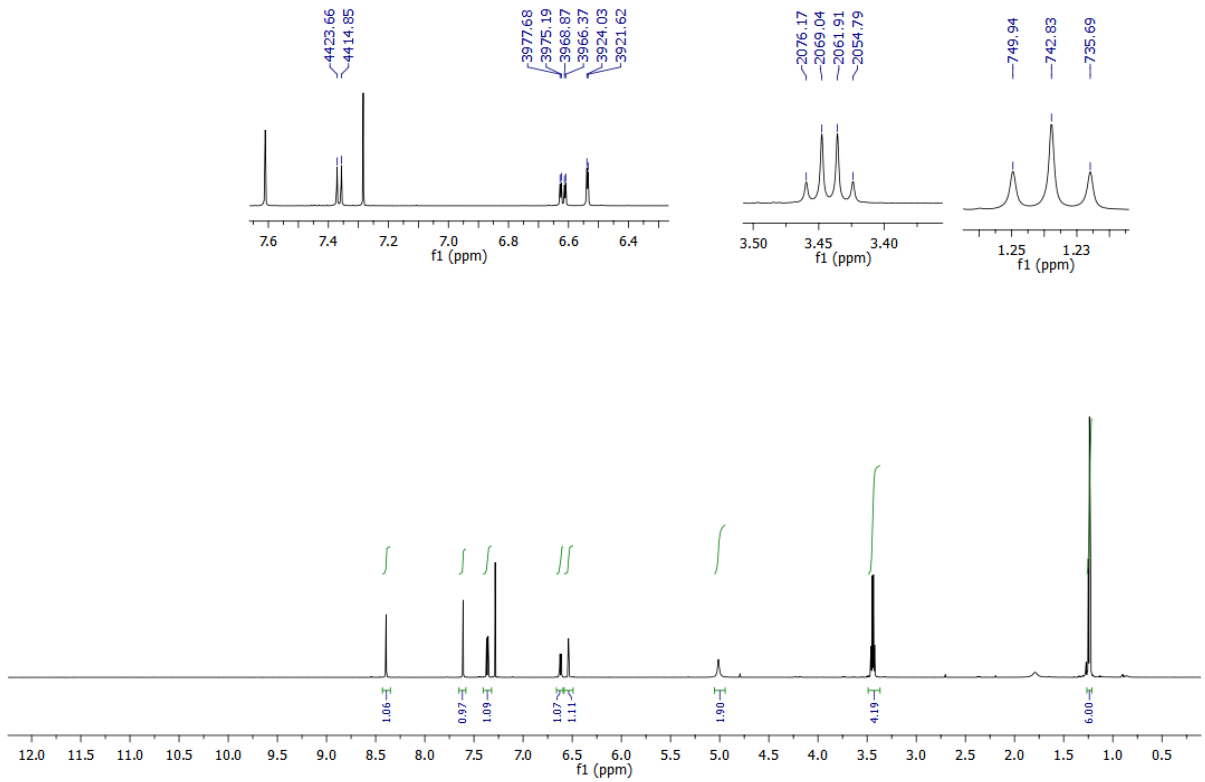

Fig. S3. ^{1}H-NMR ($CDCl_3$-d_1) Spectrum of **3**.

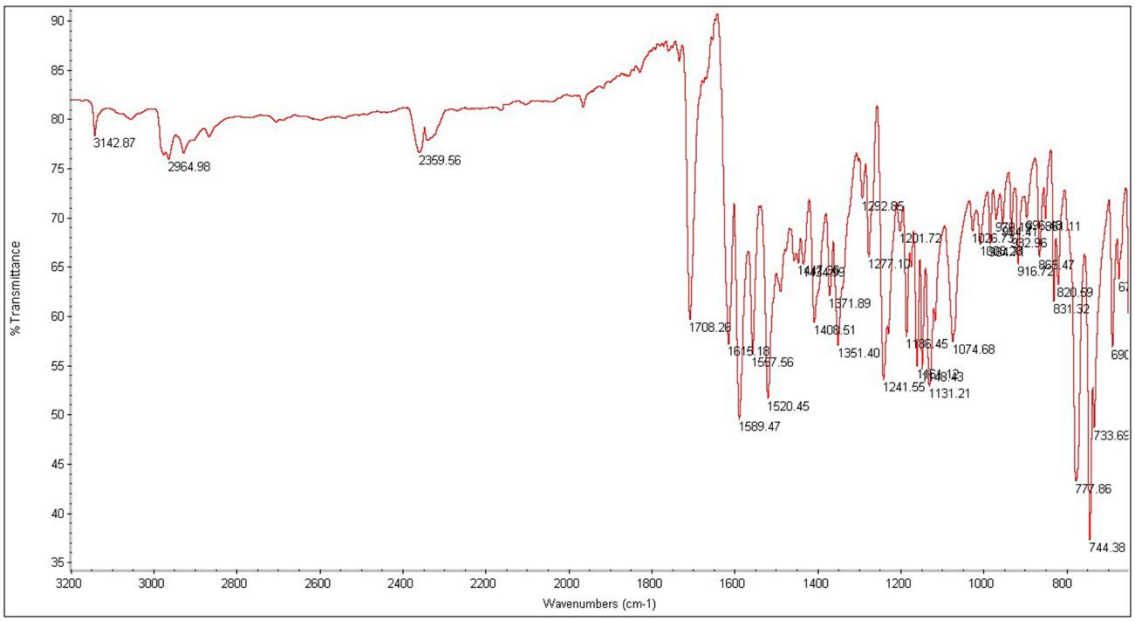

Fig. S4. FT-IR spectrum of **4**.

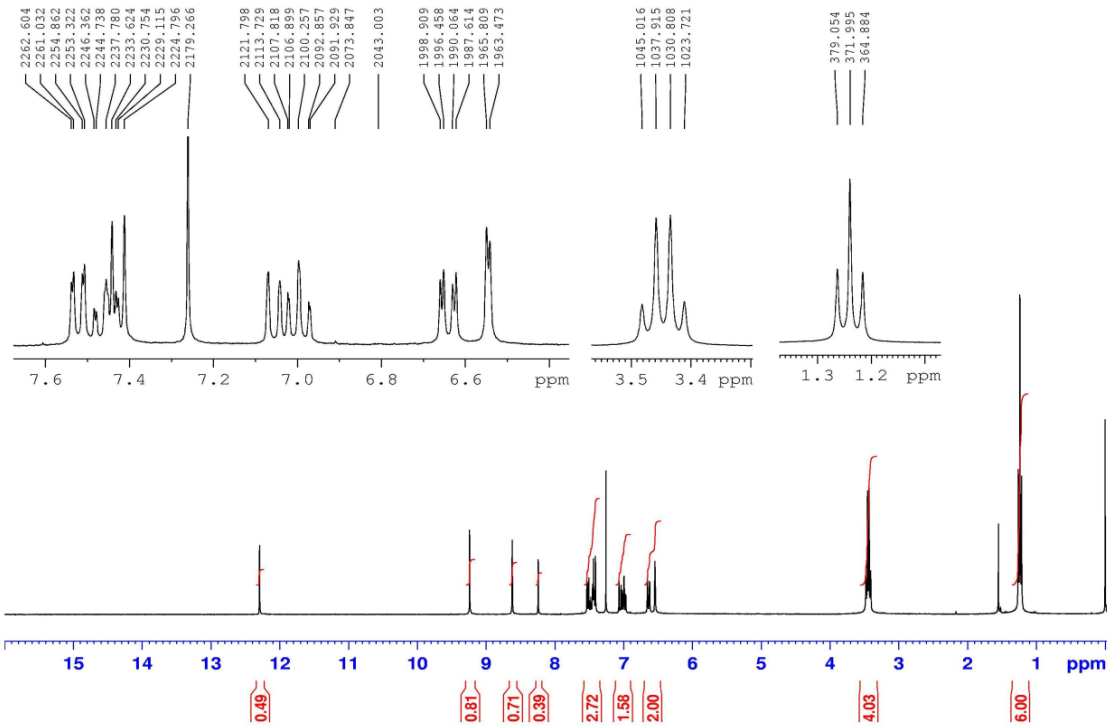

Fig. S5. ^{1}H-NMR ($CDCl_3$-d_1) Spectrum of **4**.

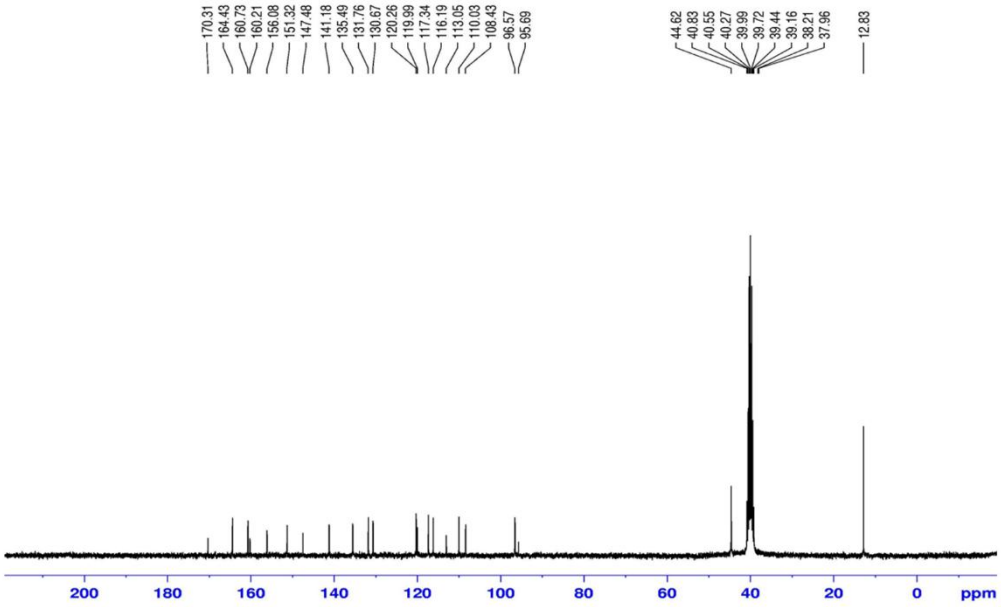

Fig. S6. ^{13}C-NMR (DMSO-d_6) Spectrum of **4**.

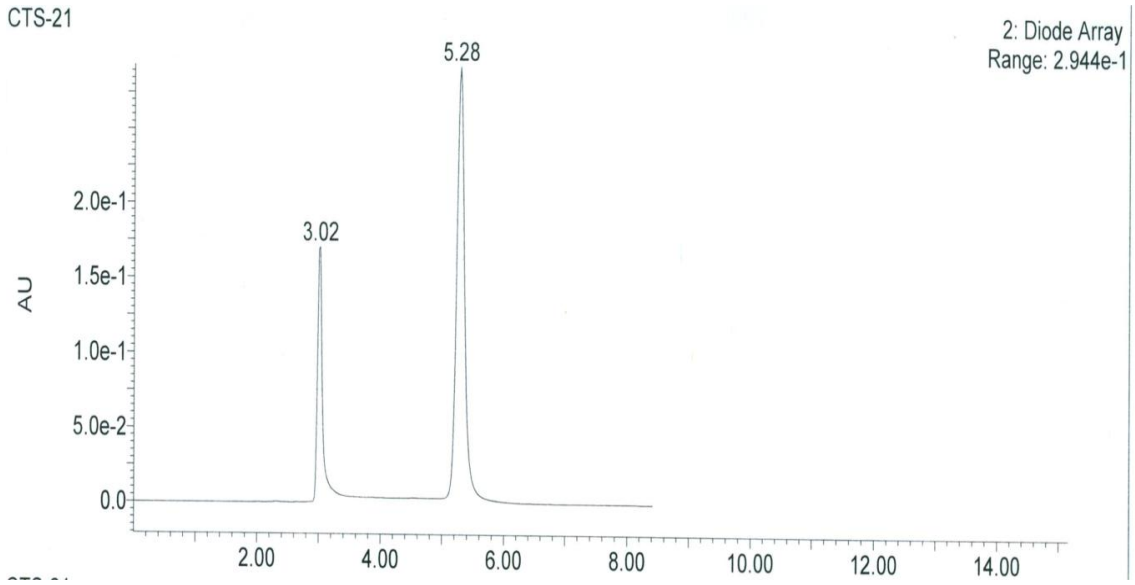

Fig. S7. LC Spectrum of **4**.

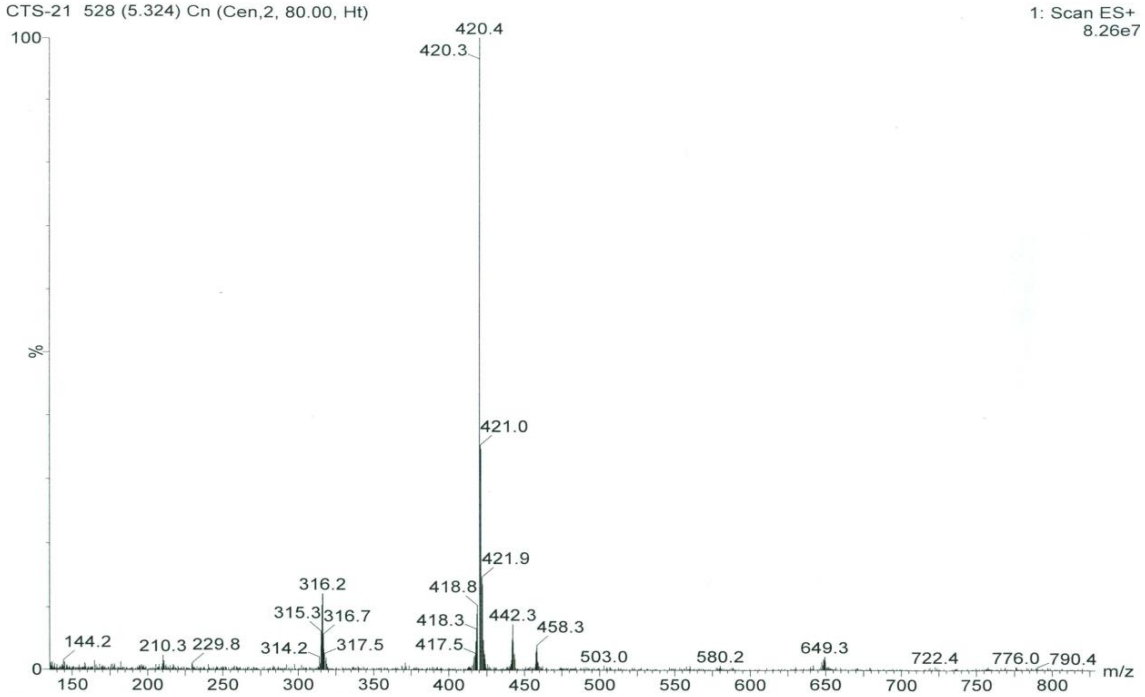

Fig. S8. MS Spectrum of **4**.

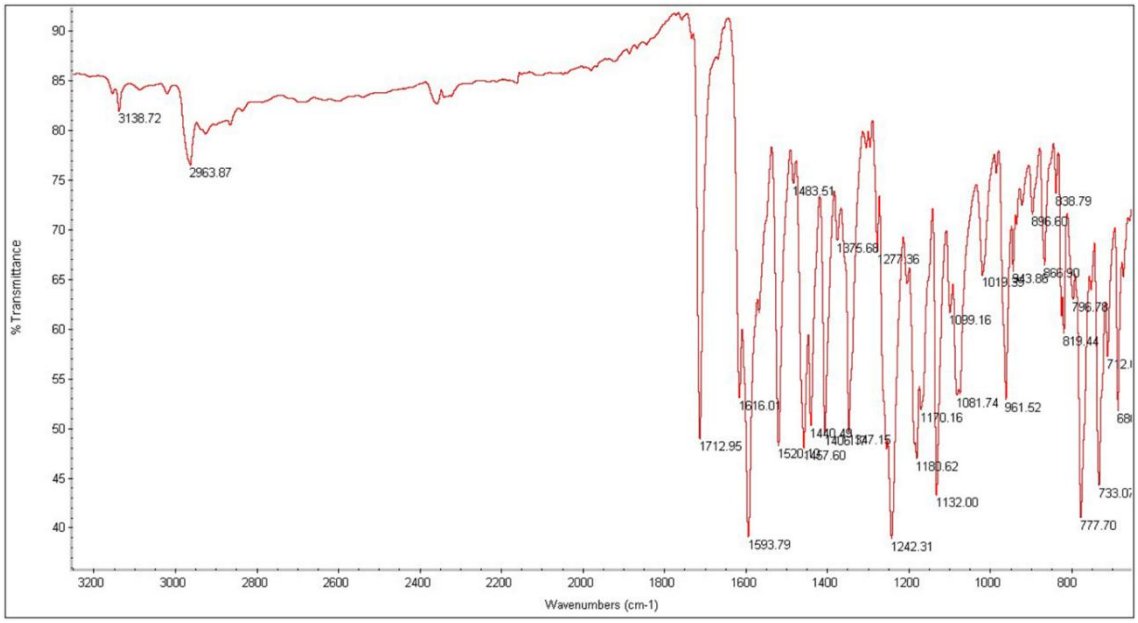

Fig. S9. FT-IR spectrum of **5**.

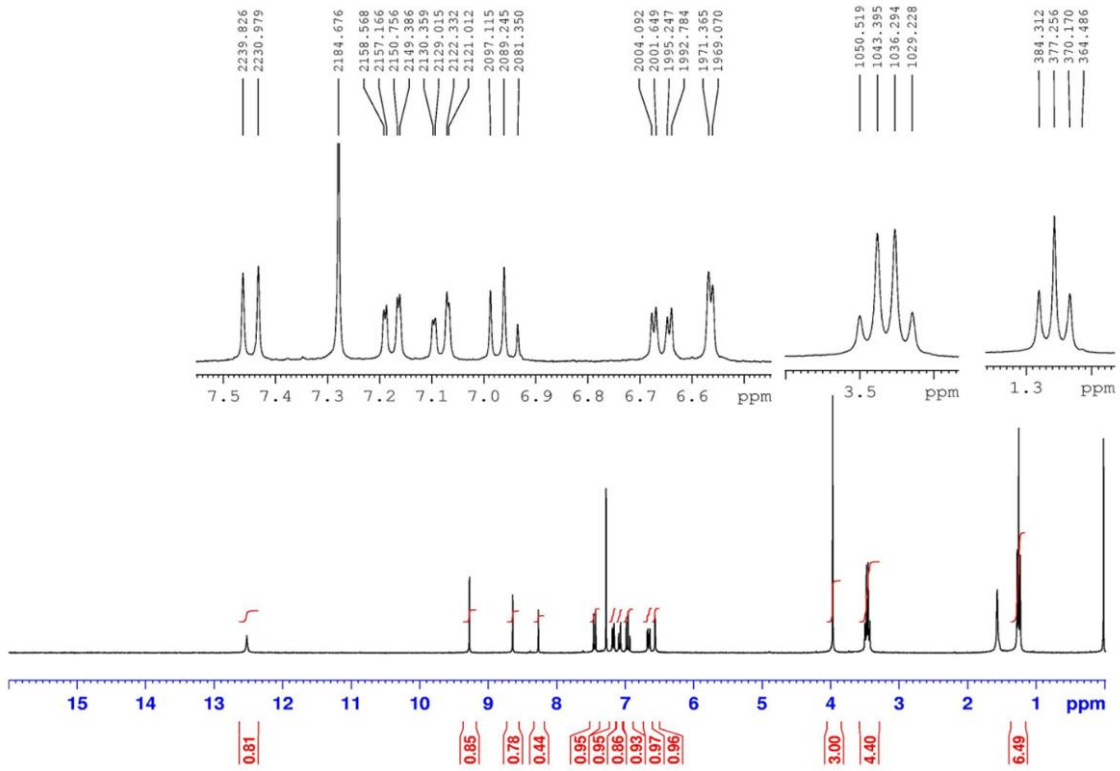

Fig. S10. ^{1}H-NMR ($CDCl_3$-d_1) Spectrum of **5**.

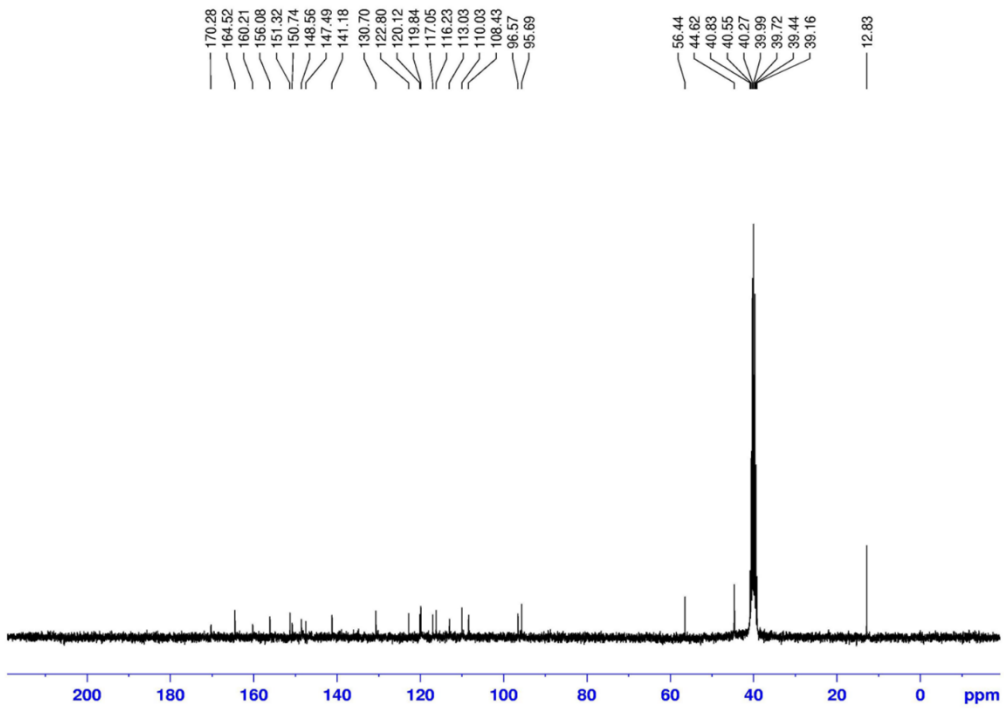

Fig. S11. ^{13}C-NMR (DMSO-d_6) Spectrum of **5**.

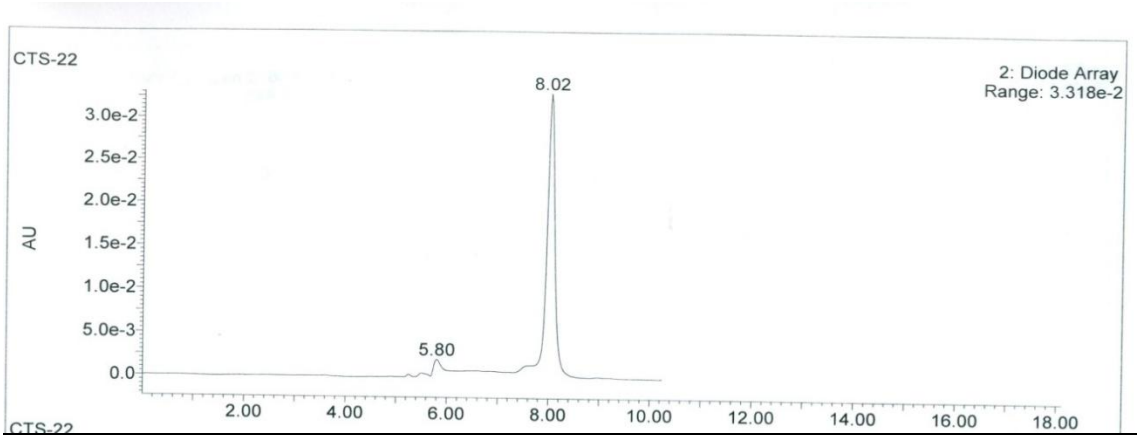

Fig. S12. LC Spectrum of **5**.

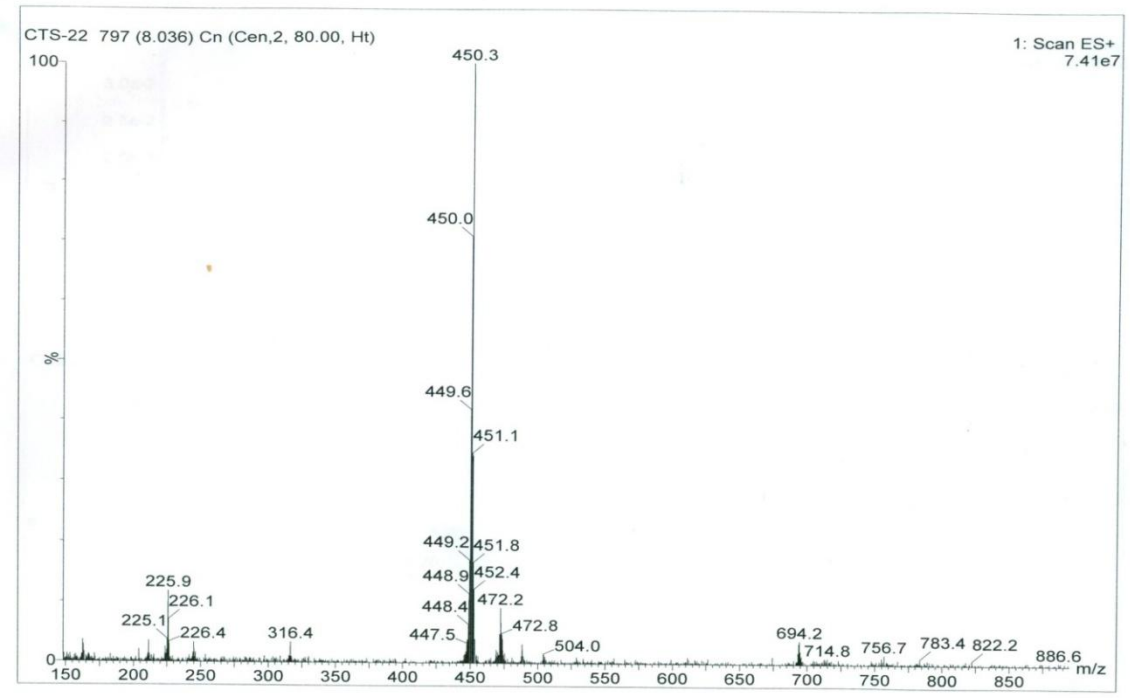

Fig. S13. MS Spectrum of **5**.

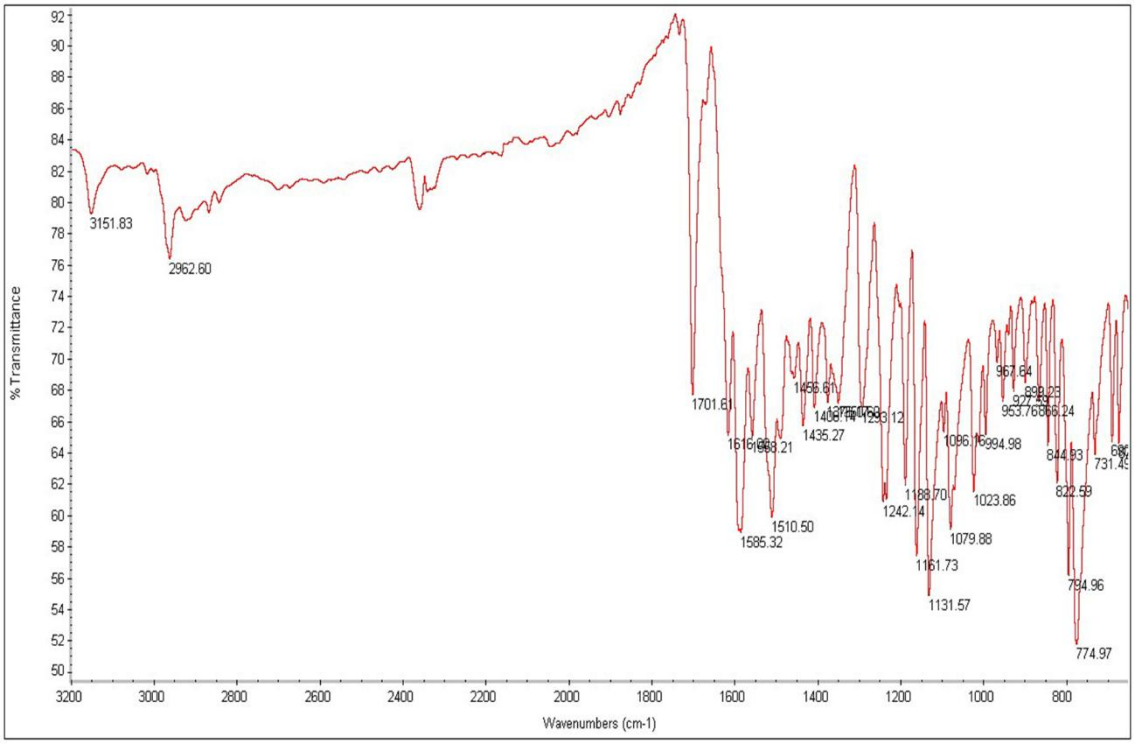

Fig. S14. FT-IR spectrum of **6**.

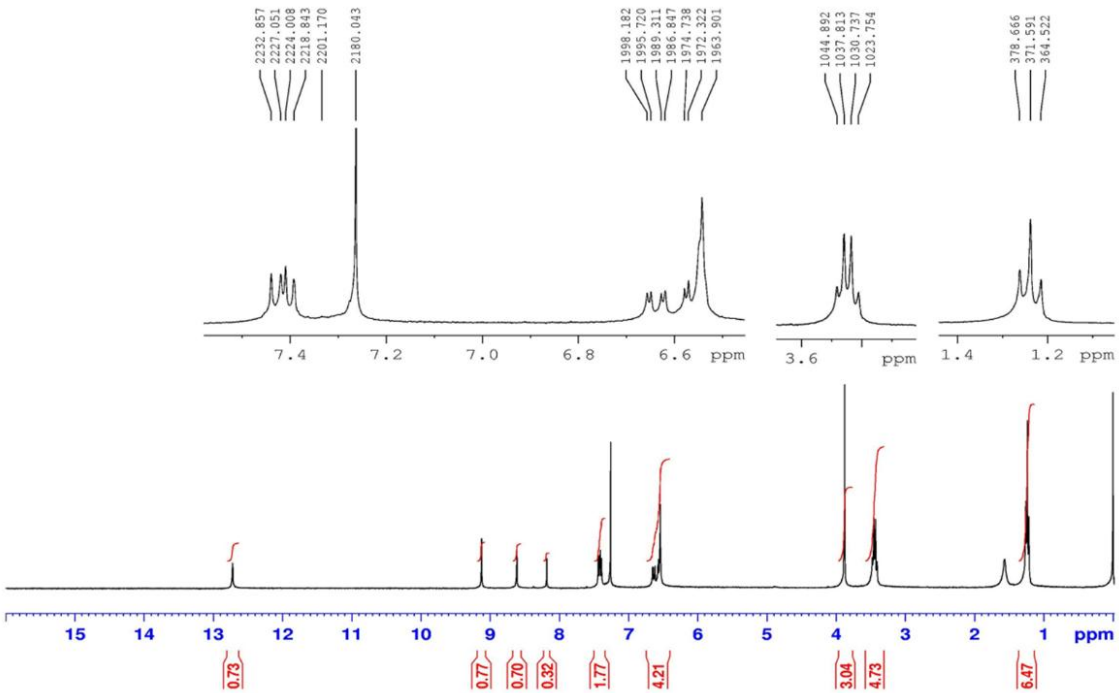

Fig. S15. ^{1}H-NMR ($CDCl_3$-d_1) Spectrum of **6**.

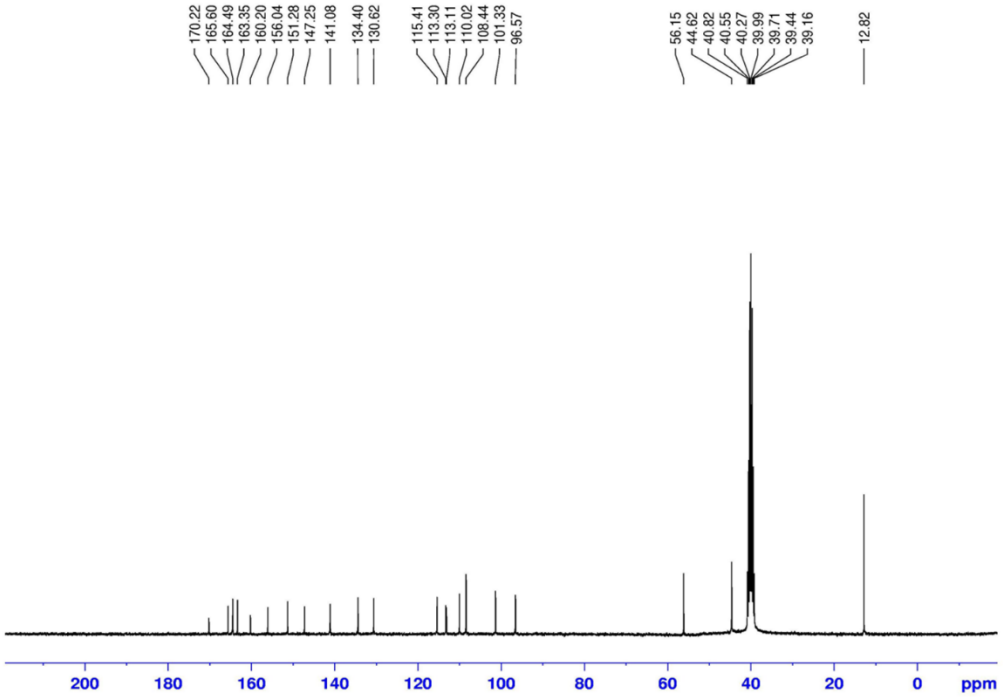

Fig. S16. ^{13}C-NMR (DMSO-d_6) Spectrum of **6**.

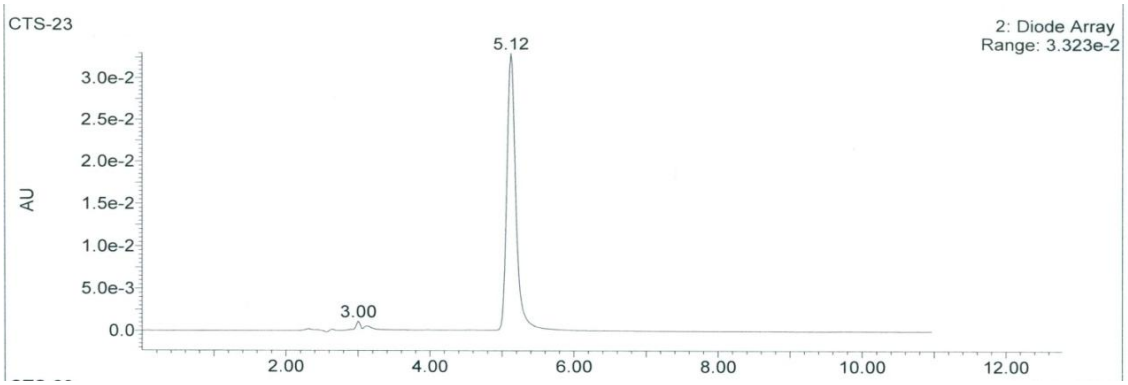

Fig. S17. LC Spectrum of **6**.

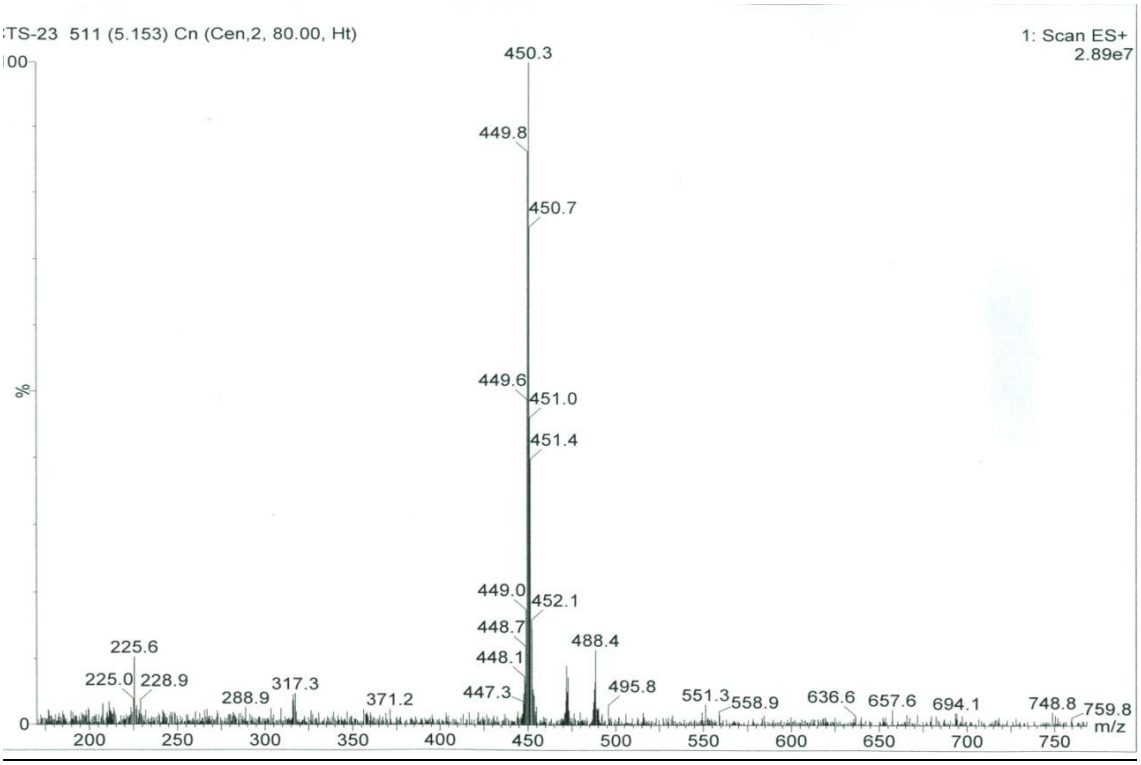

Fig. S18. MS Spectrum of **6**.

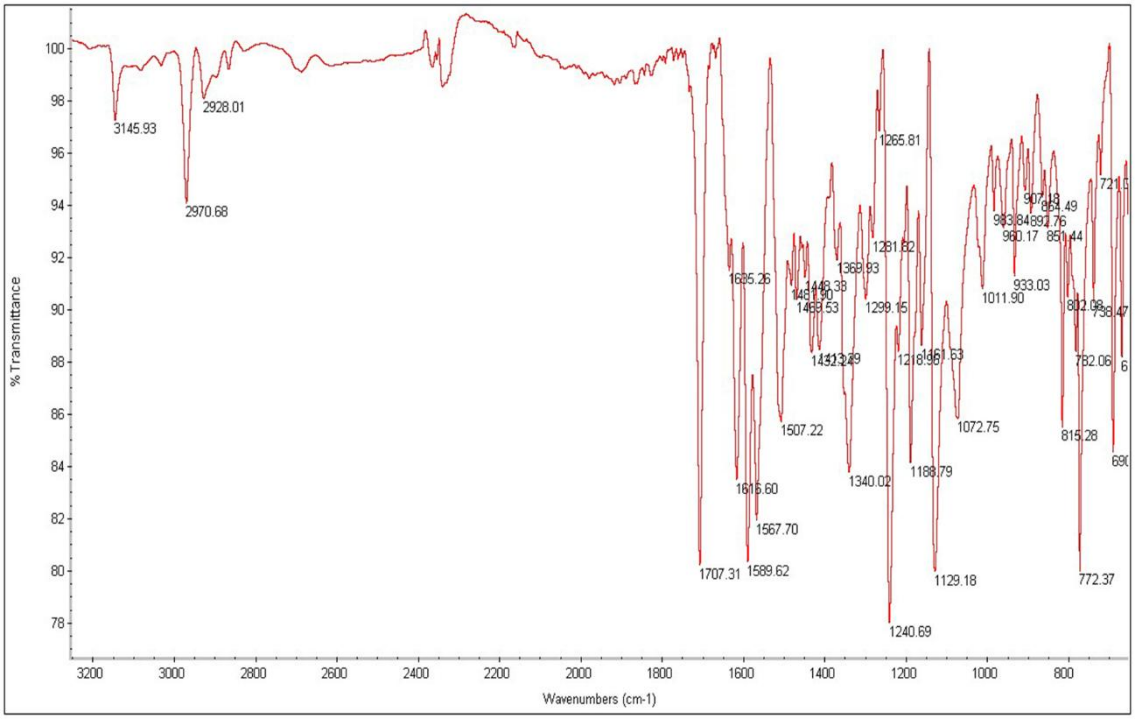

Fig. S19. FT-IR spectrum of **7**.

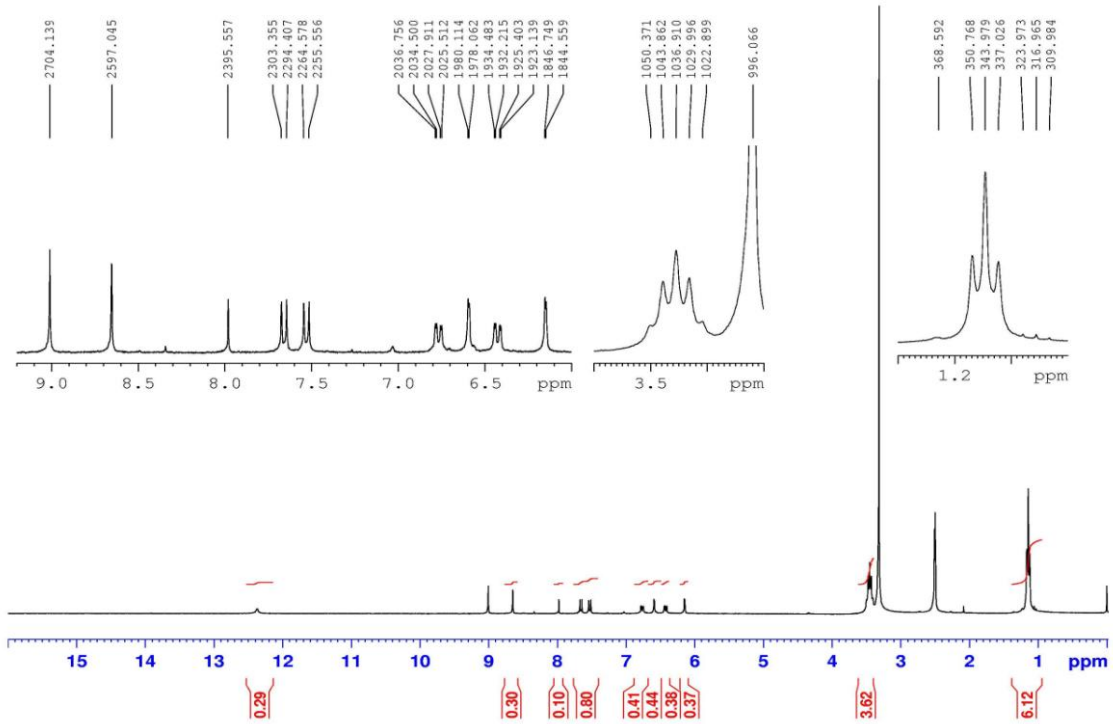

Fig. S20. ^{1}H-NMR (DMSO-d_6) Spectrum of **7**.

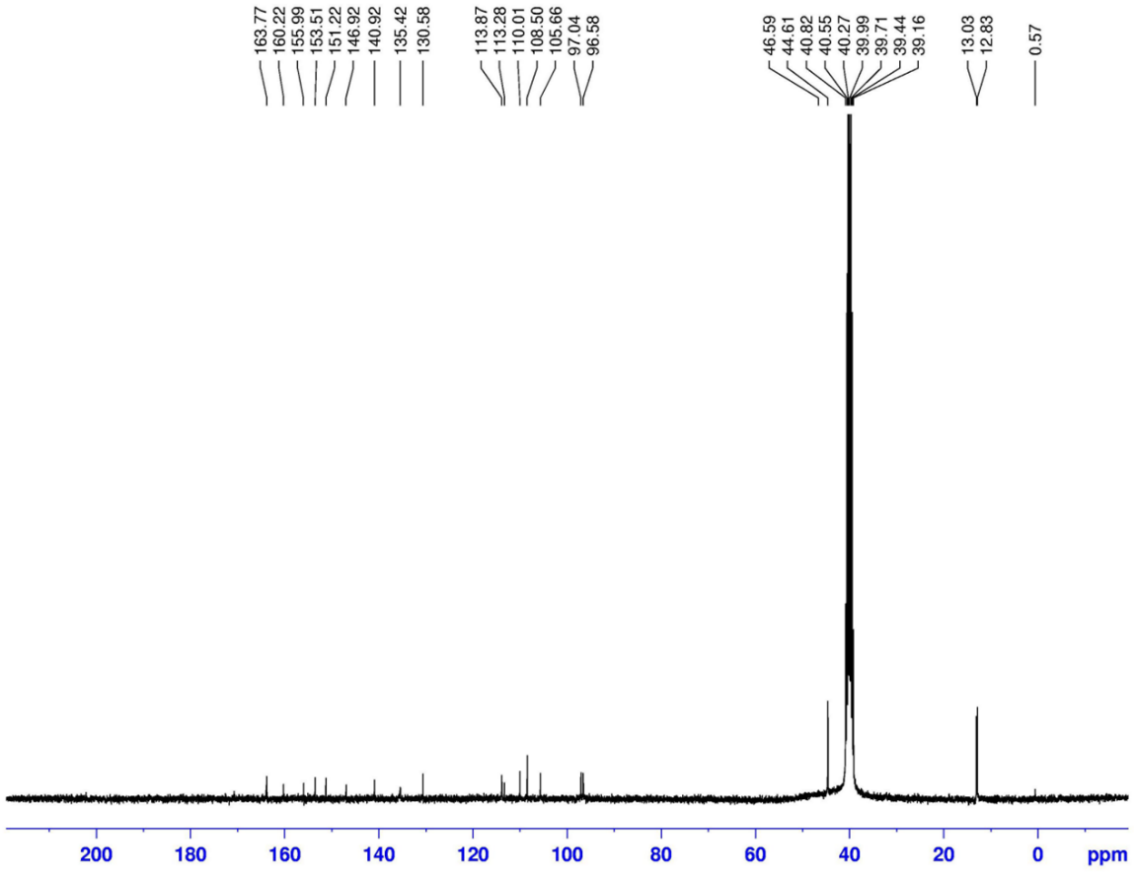

Fig. S21. ^{13}C-NMR (DMSO-d_6) Spectrum of **7**.

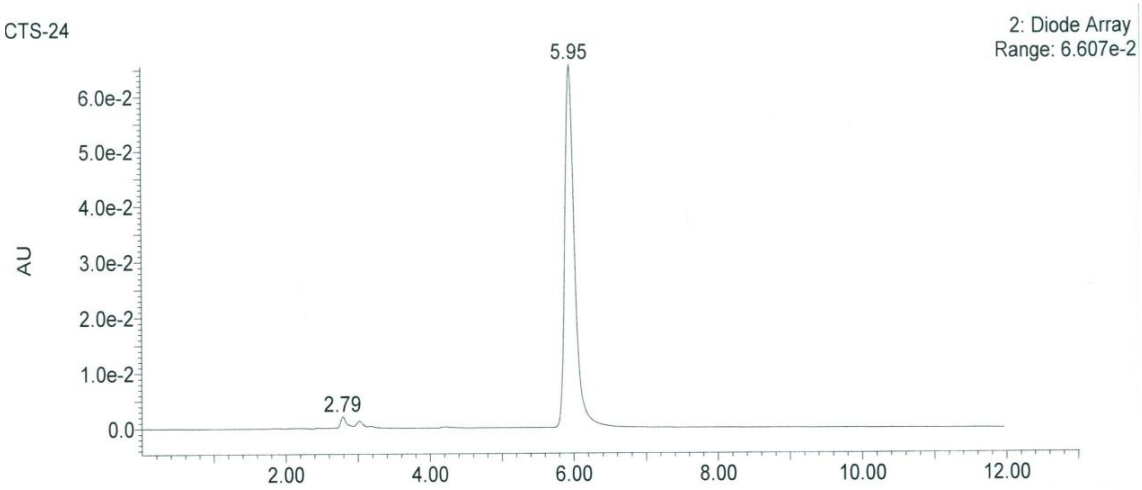

Fig. S22. LC Spectrum of **7**.

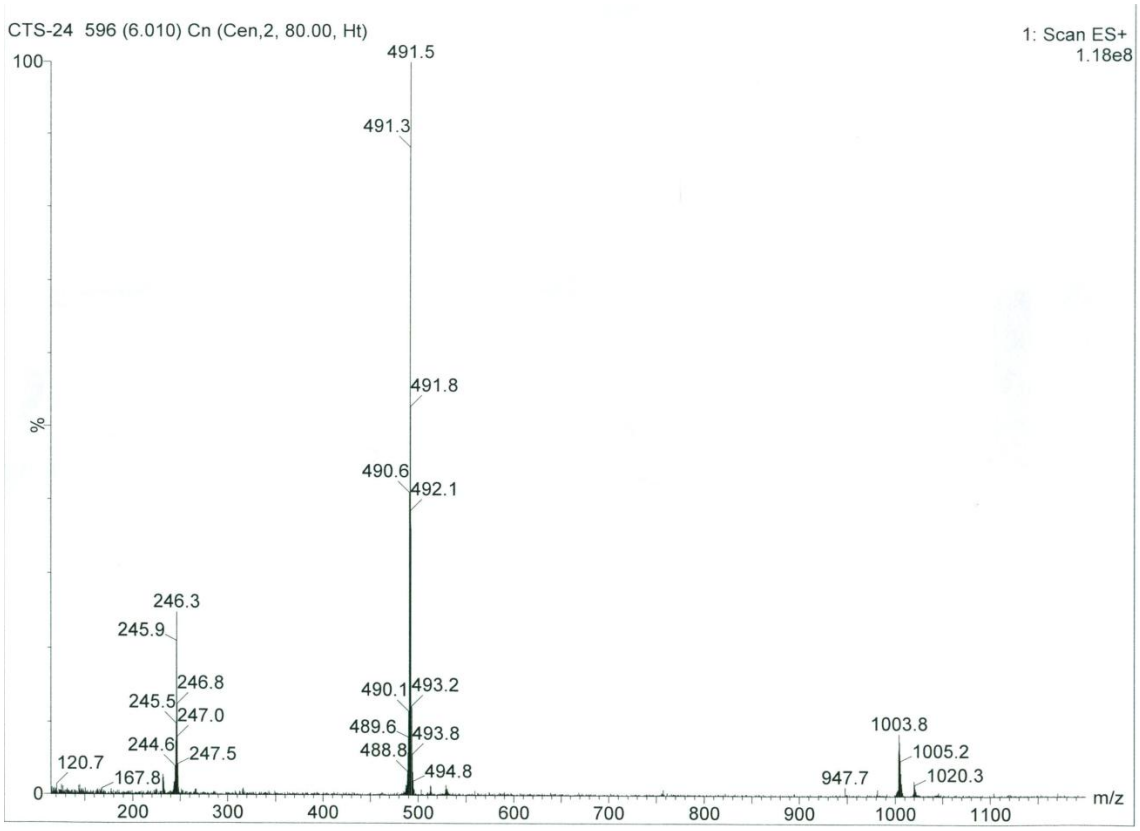

Fig. S23. MS Spectrum of **7**.

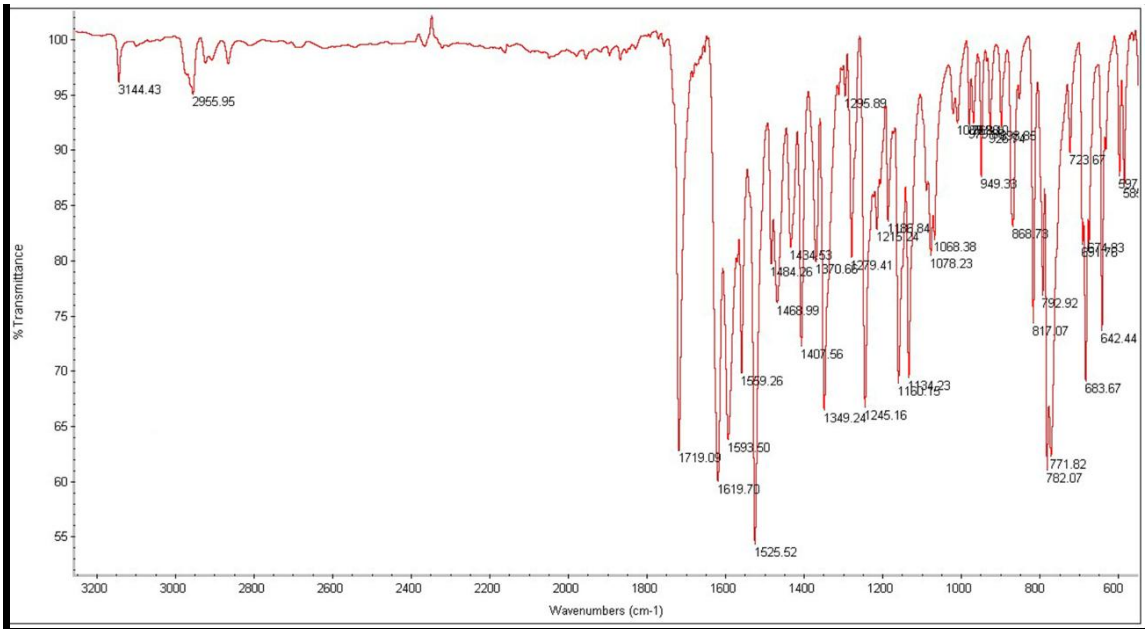

Fig. S24. FT-IR spectrum of **8**.

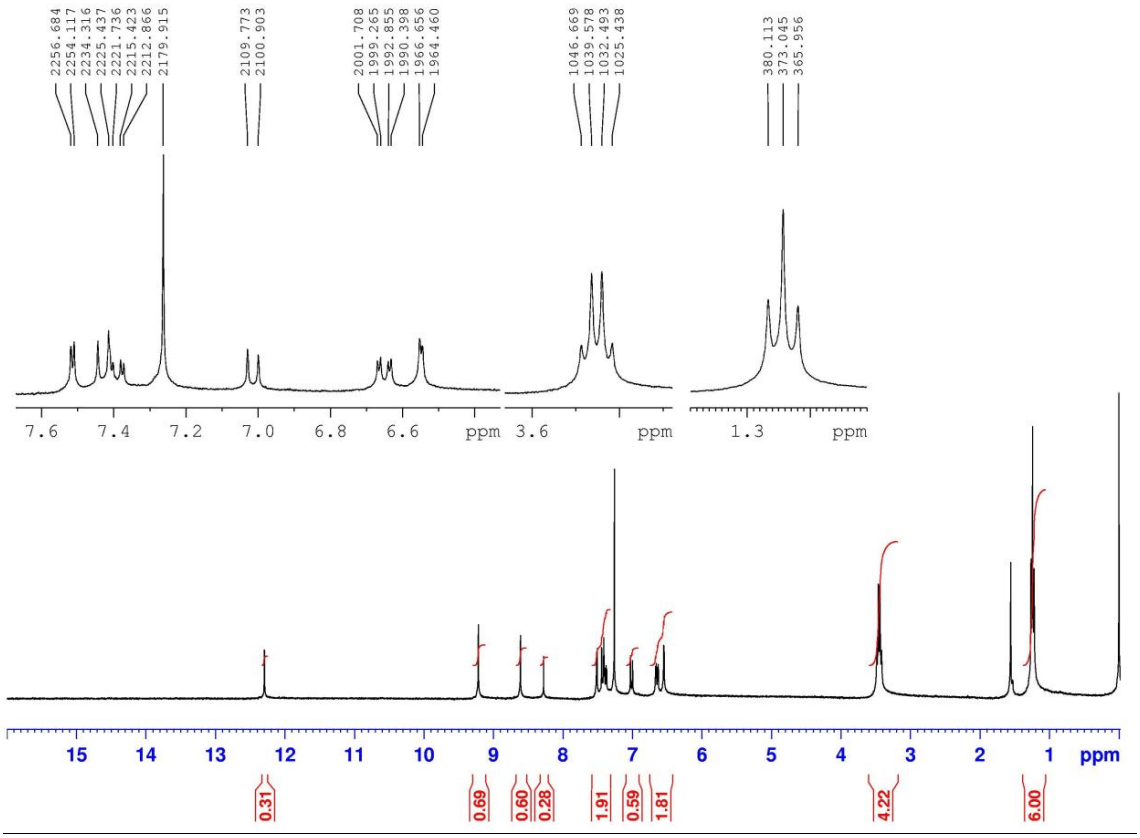

Fig. S25. ^{1}H-NMR ($CDCl_3$-d_1) Spectrum of **8**.

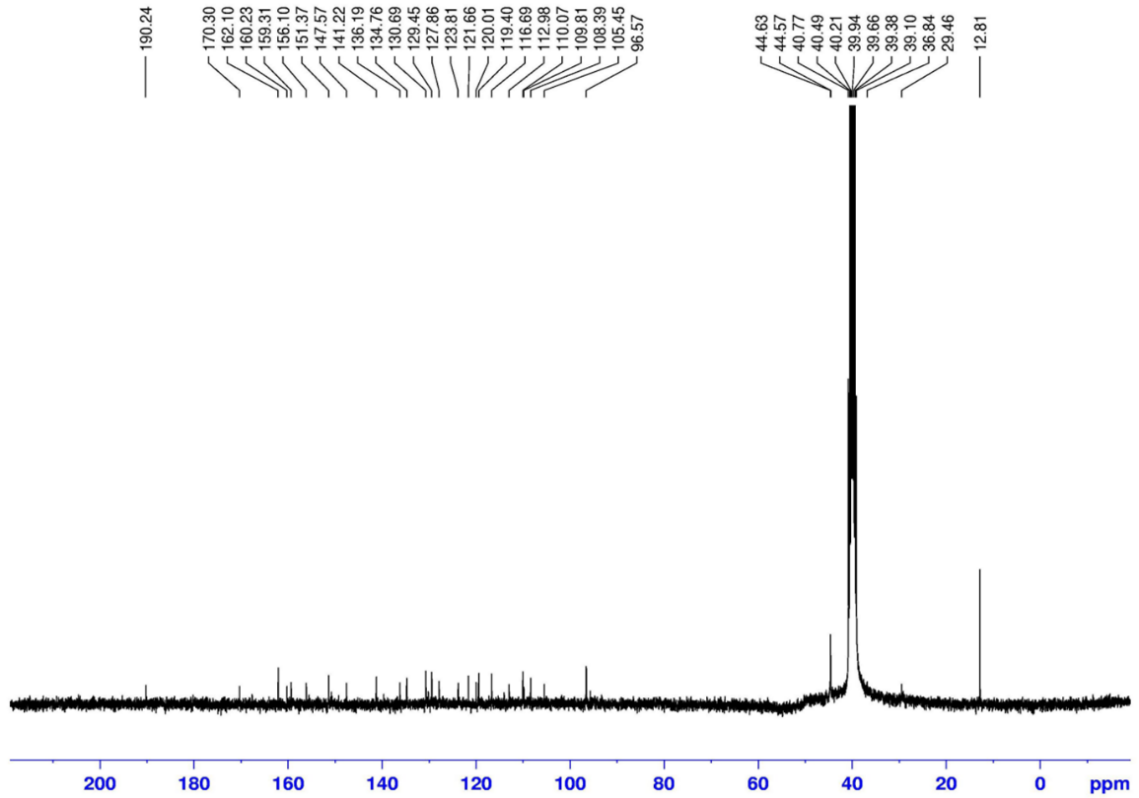

Fig. S26. ^{13}C-NMR (DMSO-d_6) Spectrum of **8**.

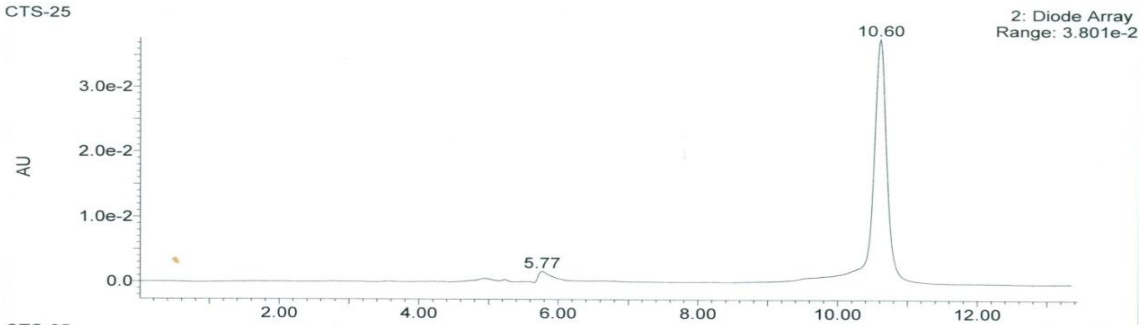

Fig. S27. LC Spectrum of **8**.

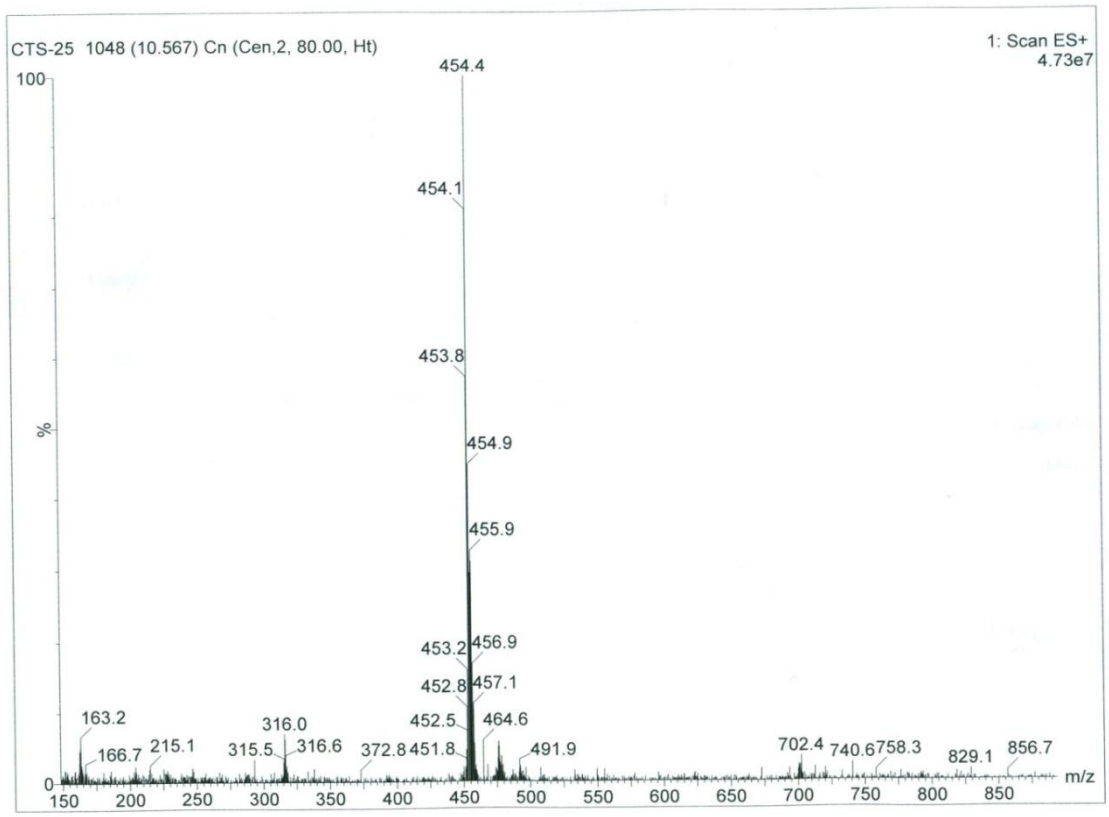

Fig. S28. MS Spectrum of **8**.

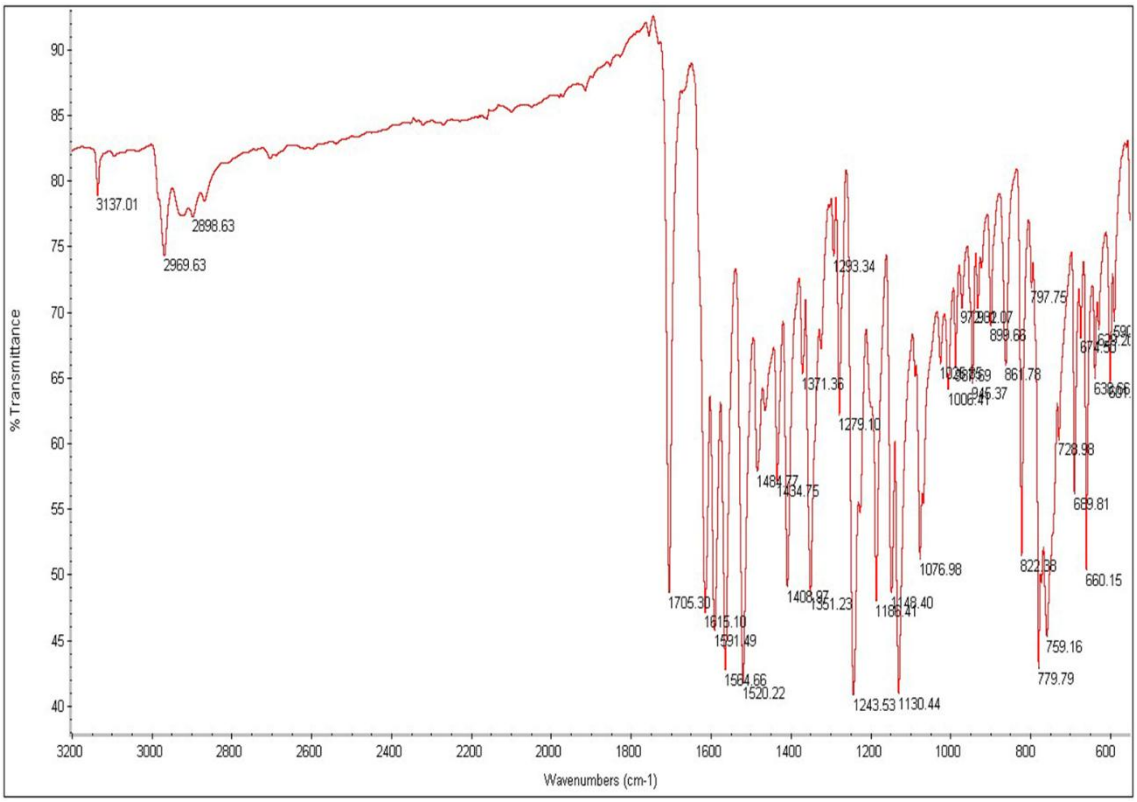

Fig. S29. FT-IR spectrum of **9.**

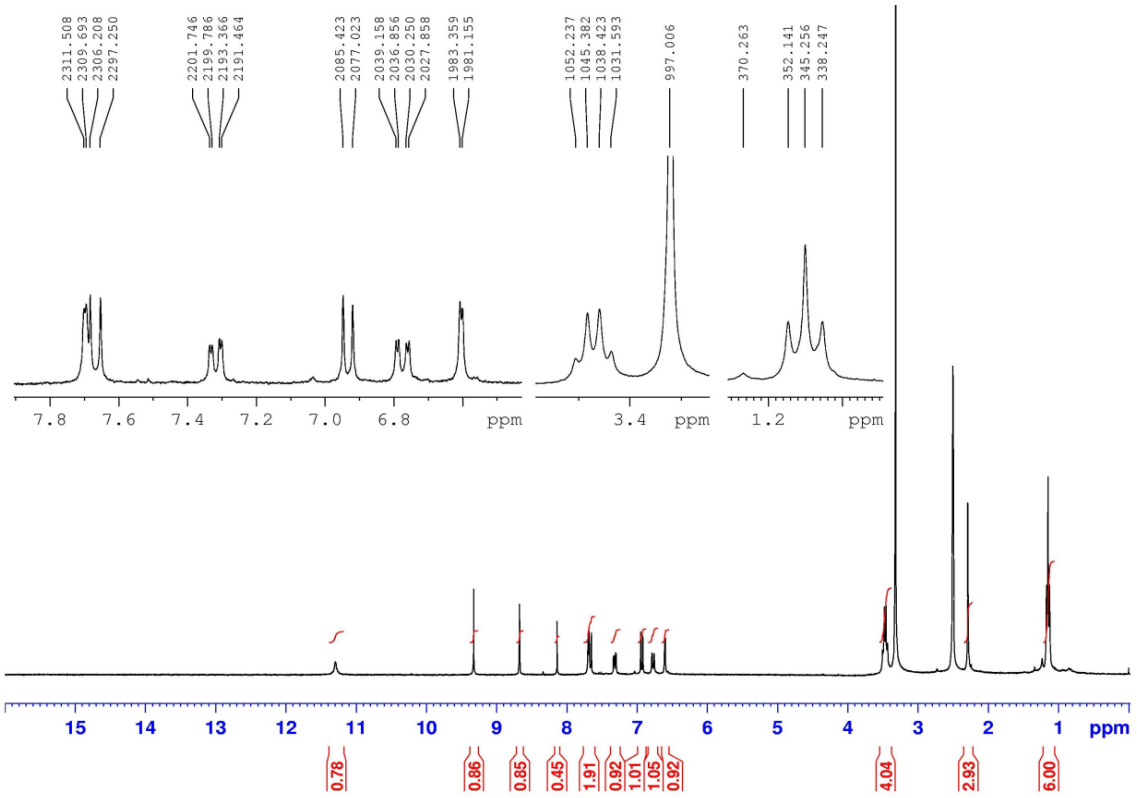

Fig. S30. ^{1}H-NMR (DMSO-d_6) Spectrum of **9**.

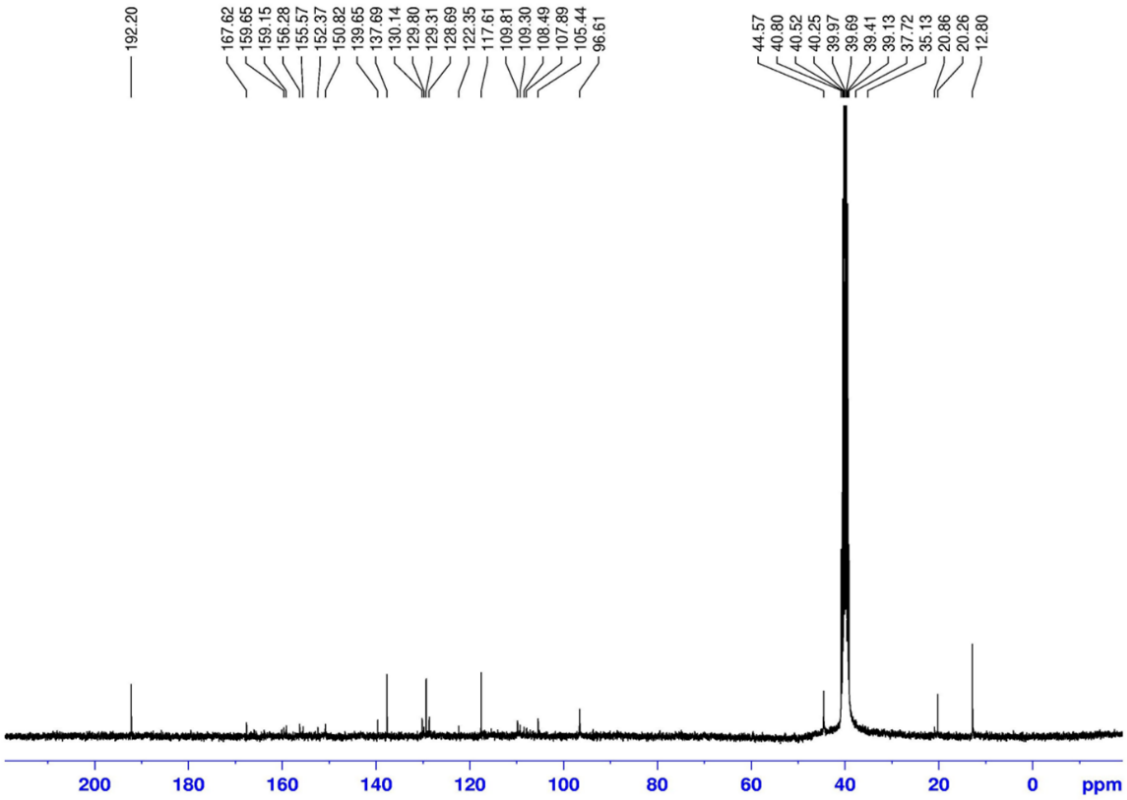

Fig. S31. ^{13}C-NMR (DMSO-d_6) Spectrum of **9**.

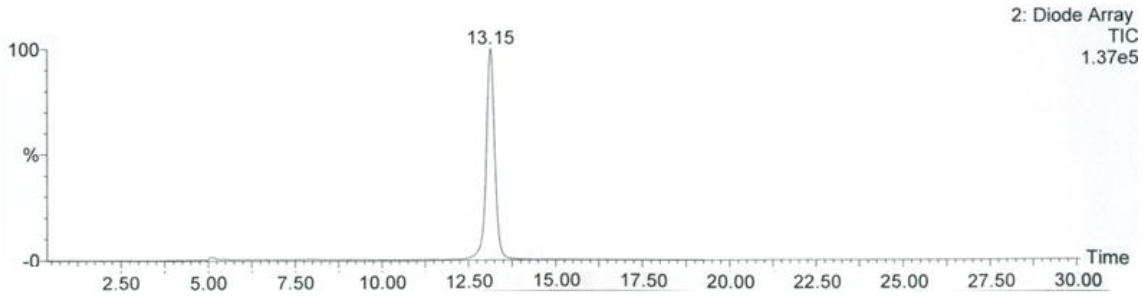

Fig. S32. LC Spectrum of **9**.

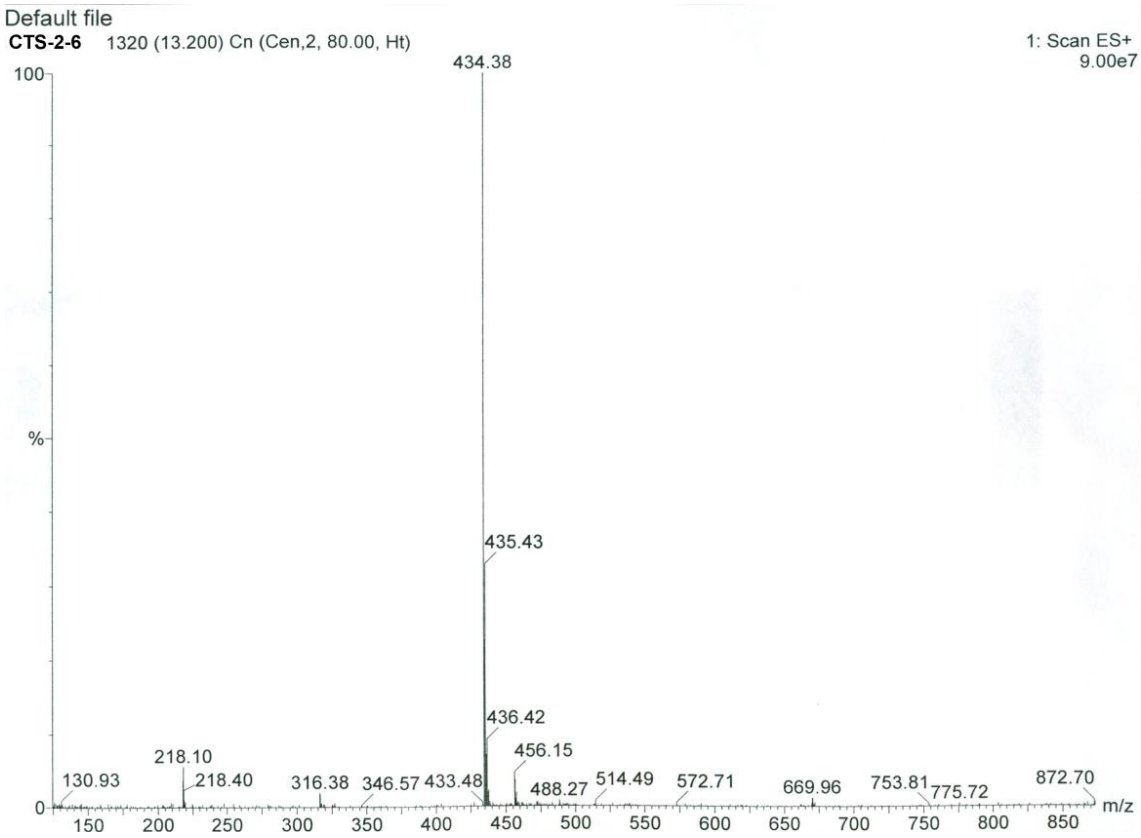

Fig. S33. MS Spectrum of **9**.

4. UV-Vis and Fluoroscence Spectral Studies

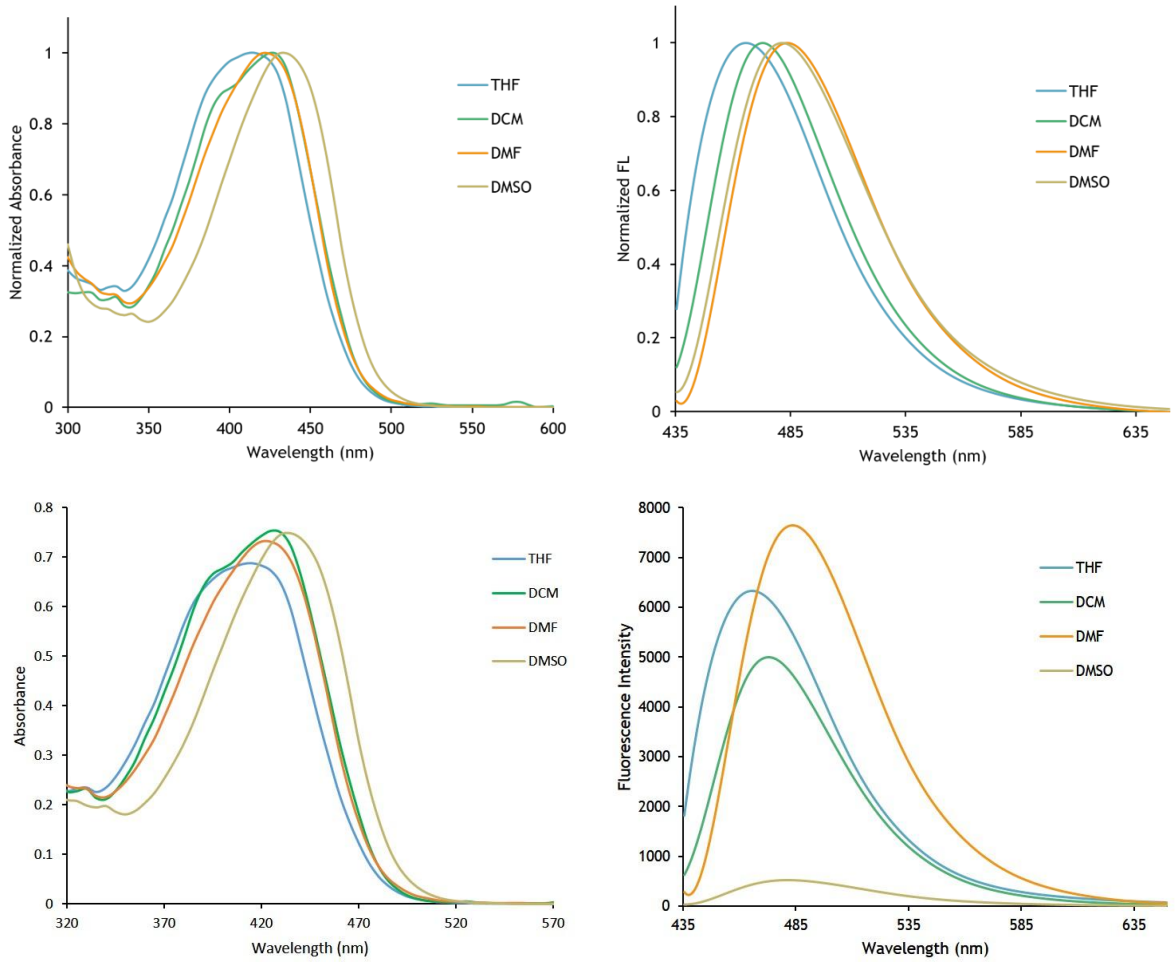

Fig. S34. Absorption (20 µM in DMSO) (left) and emission (2 µM in DMSO) (left) spectra of **4** in various solvents with different polarity (Normalized absorption and emission spectra are in above).

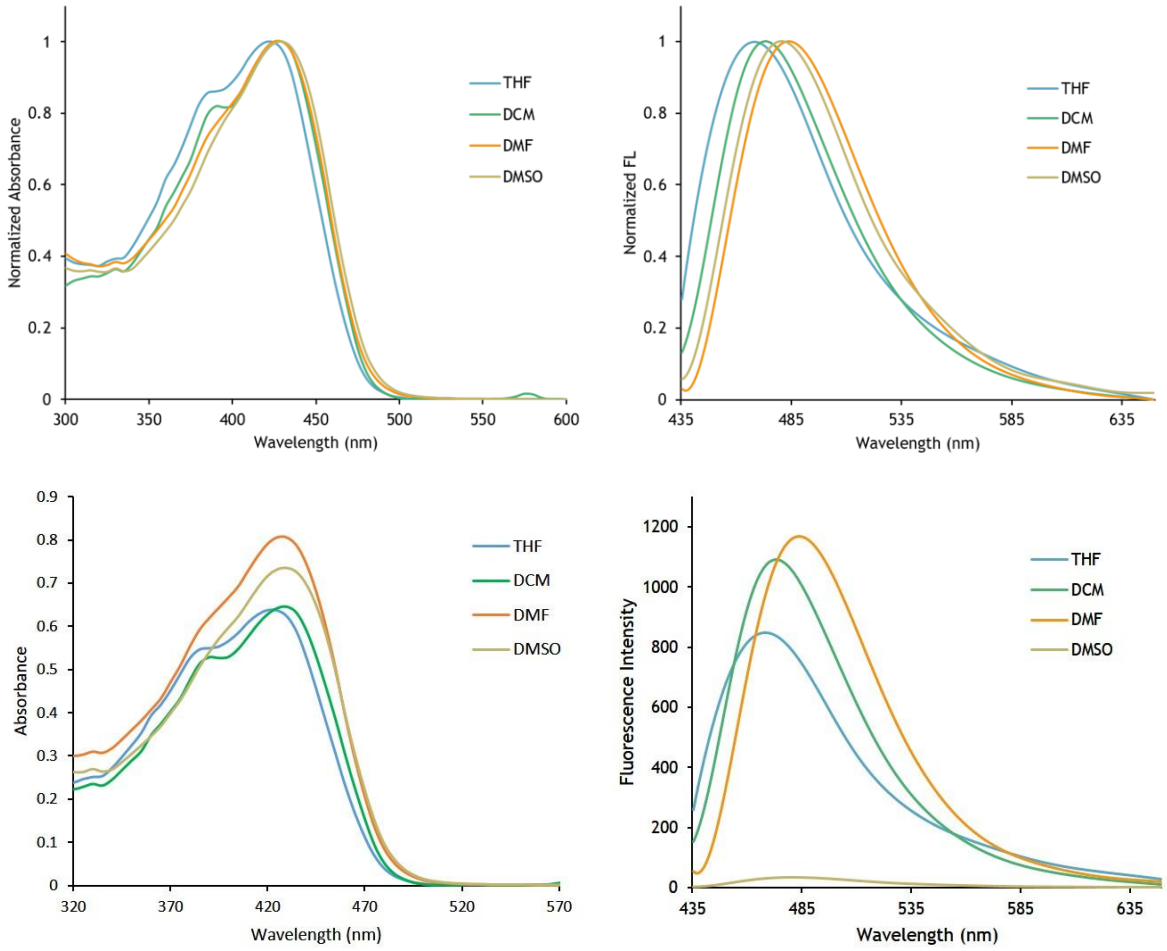

Fig. S35. Absorption (20 µM in DMSO) (left) and emission (2 µM in DMSO) (left) spectra of **6** in various solvents with different polarity (Normalized absorption and emission spectra are in above).

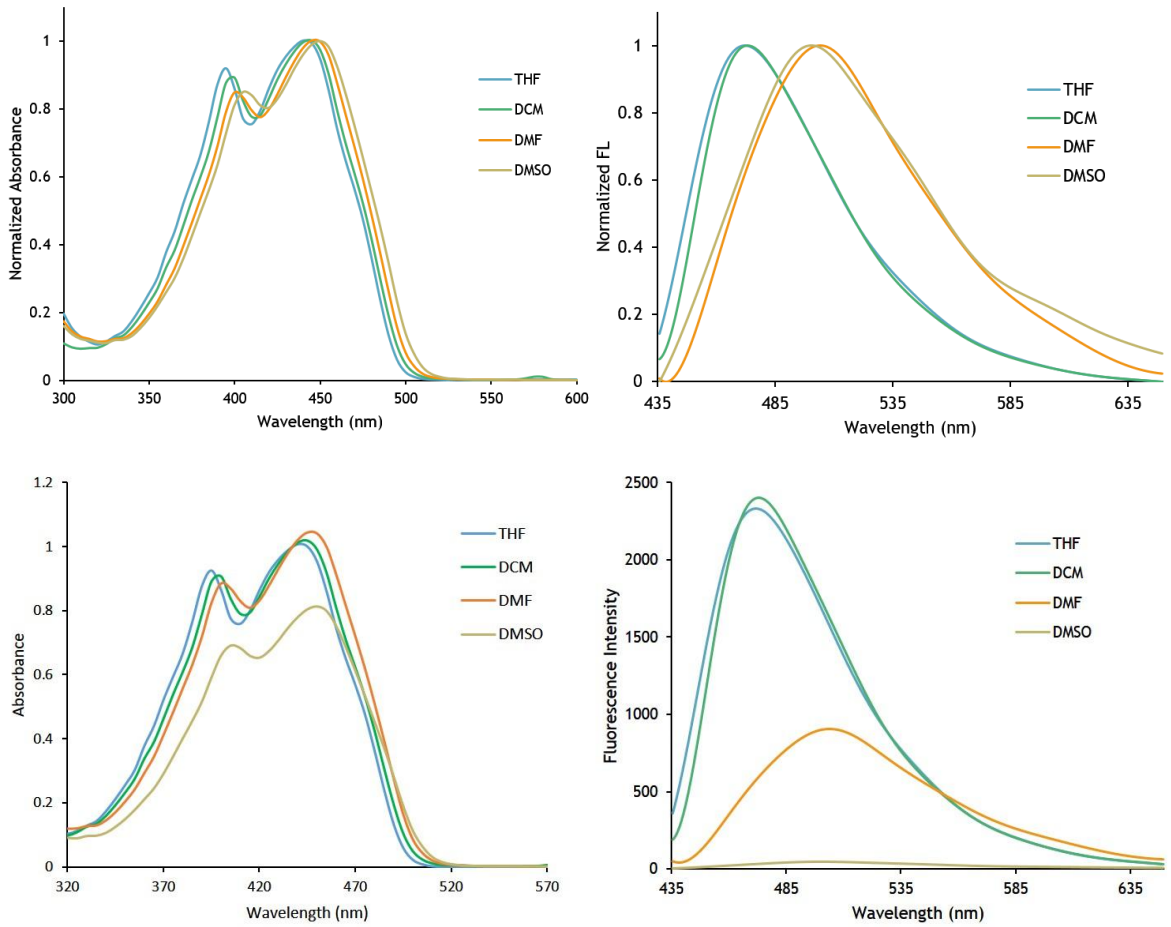

Fig. S36. Absorption (20 µM in DMSO) (left) and emission (2 µM in DMSO) (left) spectra of **7** in various solvents with different polarity (Normalized absorption and emission spectra are in above).

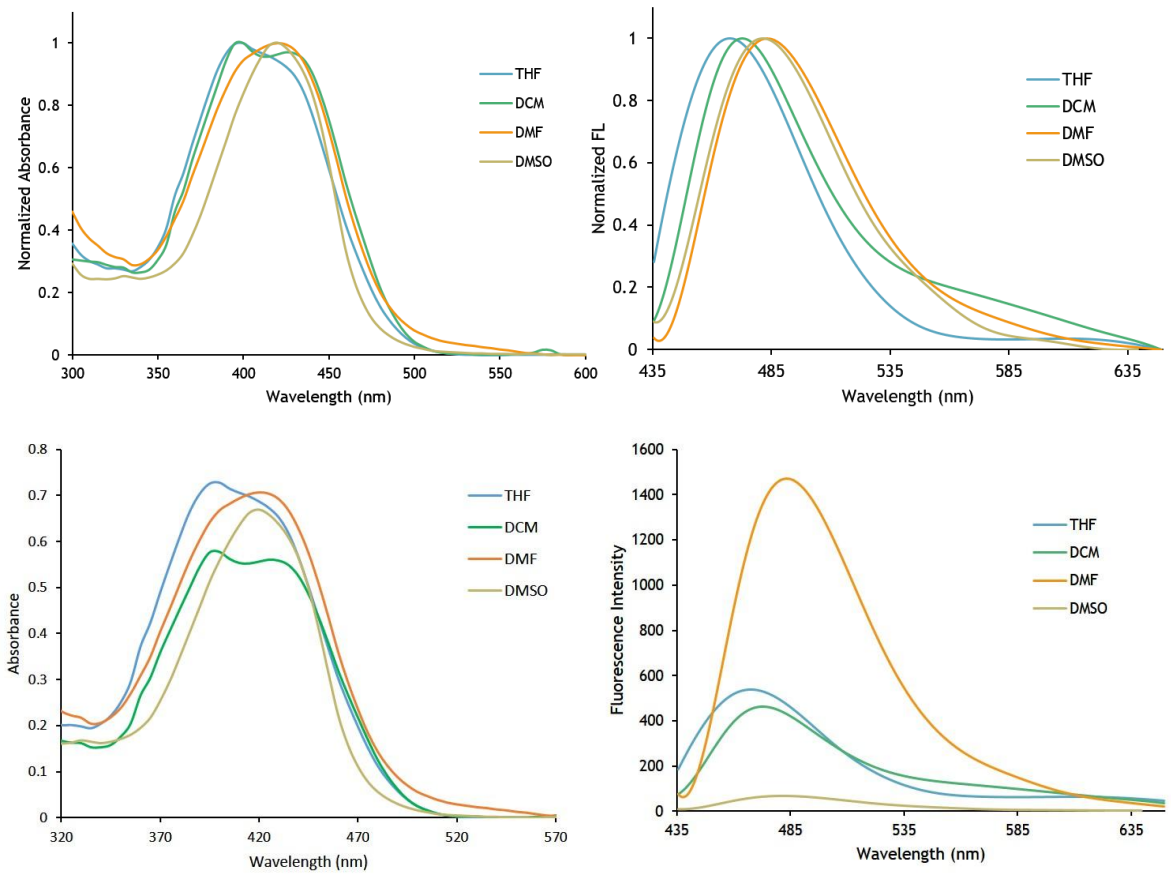

Fig. S37. Absorption (20 μM in DMSO) (left) and emission (2 μM in DMSO) (left) spectra of **8** in various solvents with different polarity (Normalized absorption and emission spectra are in above).

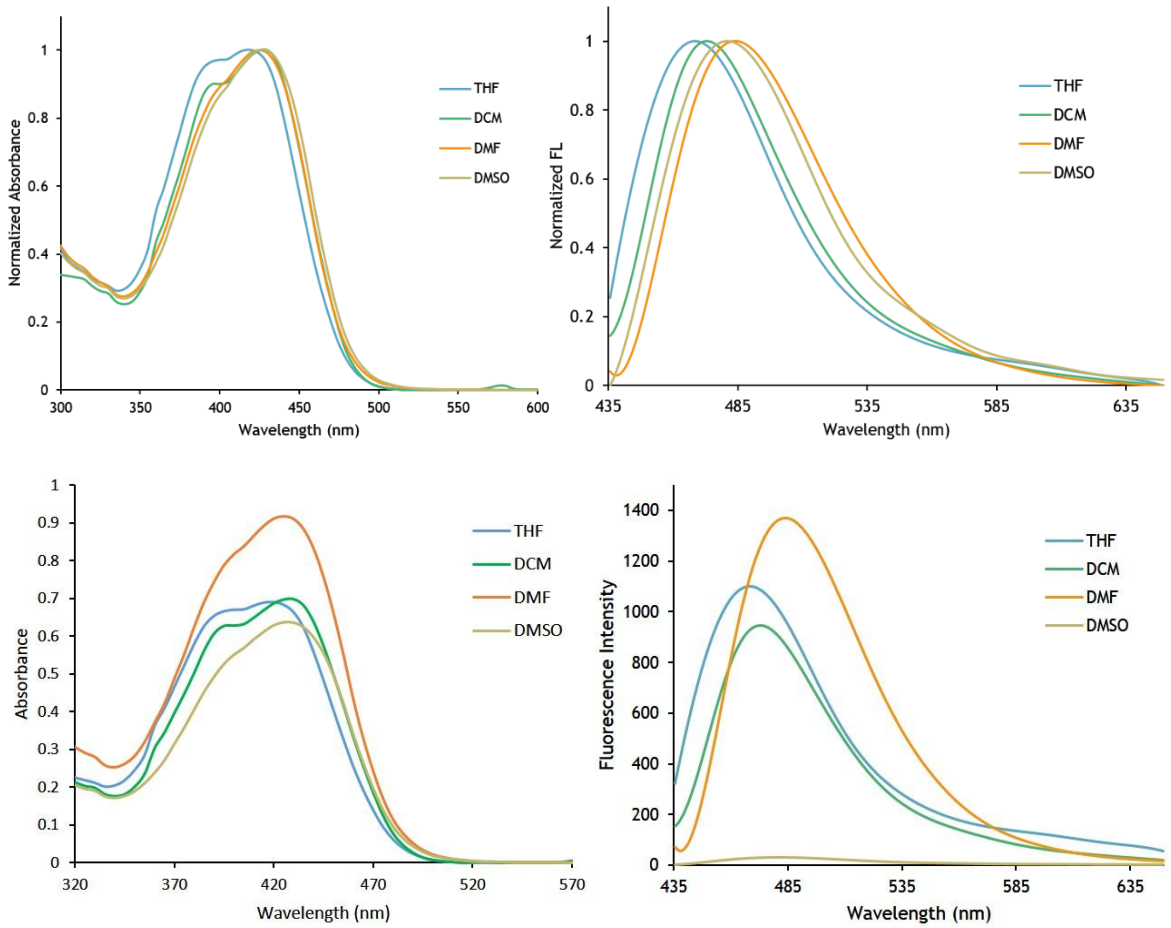

Fig. S38. Absorption (20 µM in DMSO) (left) and emission (2 µM in DMSO) (left) spectra of **9** in various solvents with different polarity (Normalized absorption and emission spectra are in above).

5. Spectrophotometric and Spectrofluorimetric Determination of Ions In Organic and Partial Aqueous Media

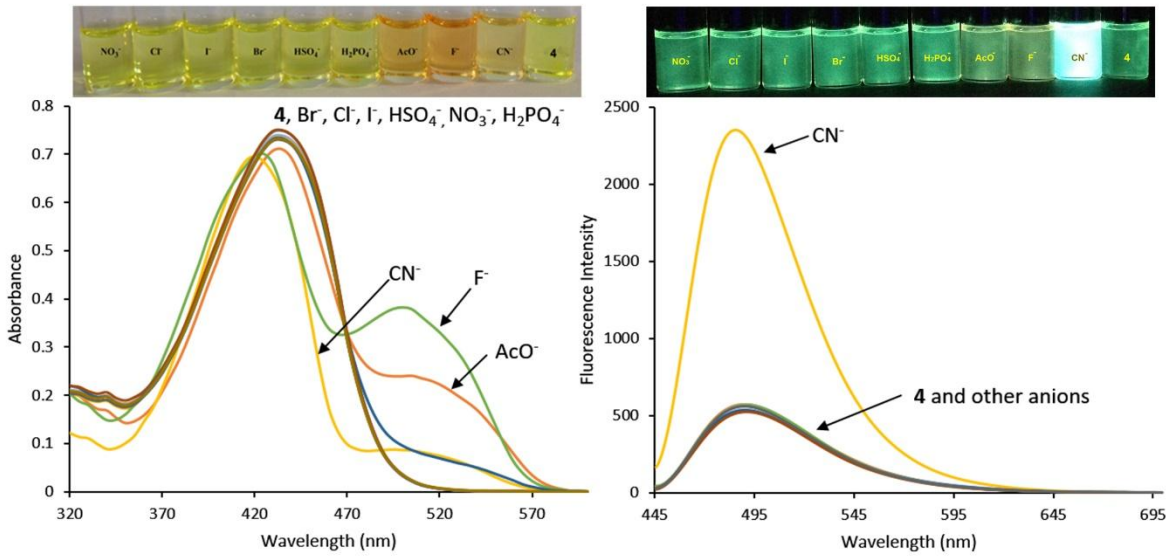

Fig. S39. Absorption spectra (20 µM in DMSO) (left) and emission spectra (2 µM in DMSO) (right) of **4** after addition of 20 equiv. of all the anions. Insets: Color and fluorescence changes after addition of 20 equiv. of anions.

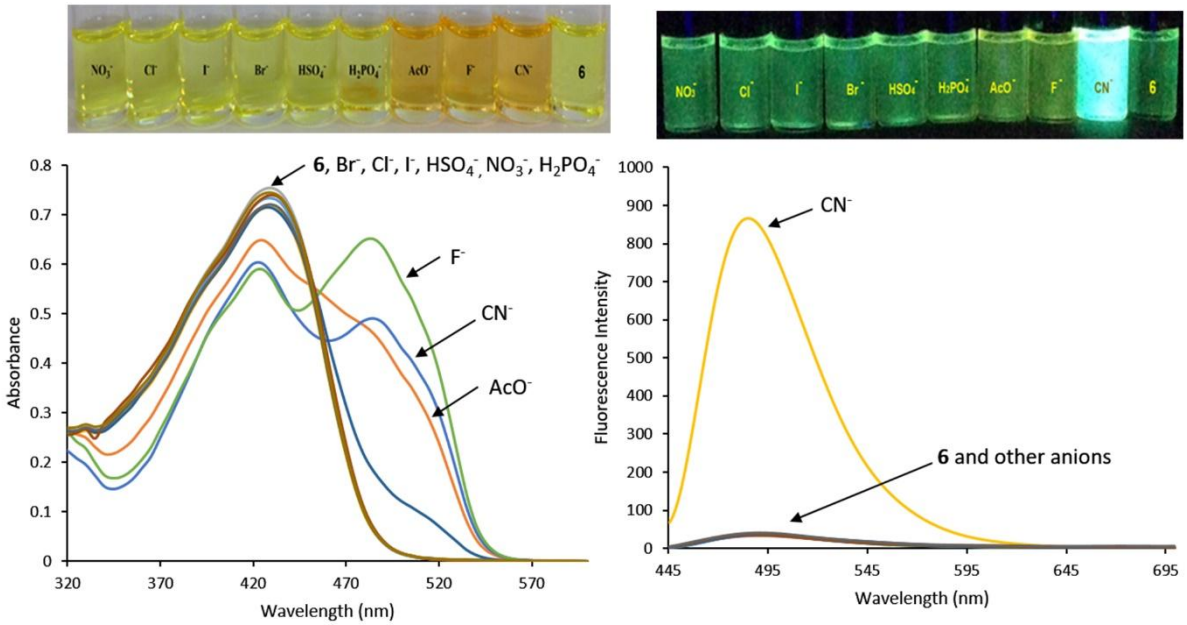

Fig. S40. Absorption spectra (20 µM in DMSO) (left) and emission spectra (2 µM in DMSO) (right) of **6** after addition of 20 equiv. of all the anions. Insets: Color and fluorescence changes after addition of 20 equiv. of anions.

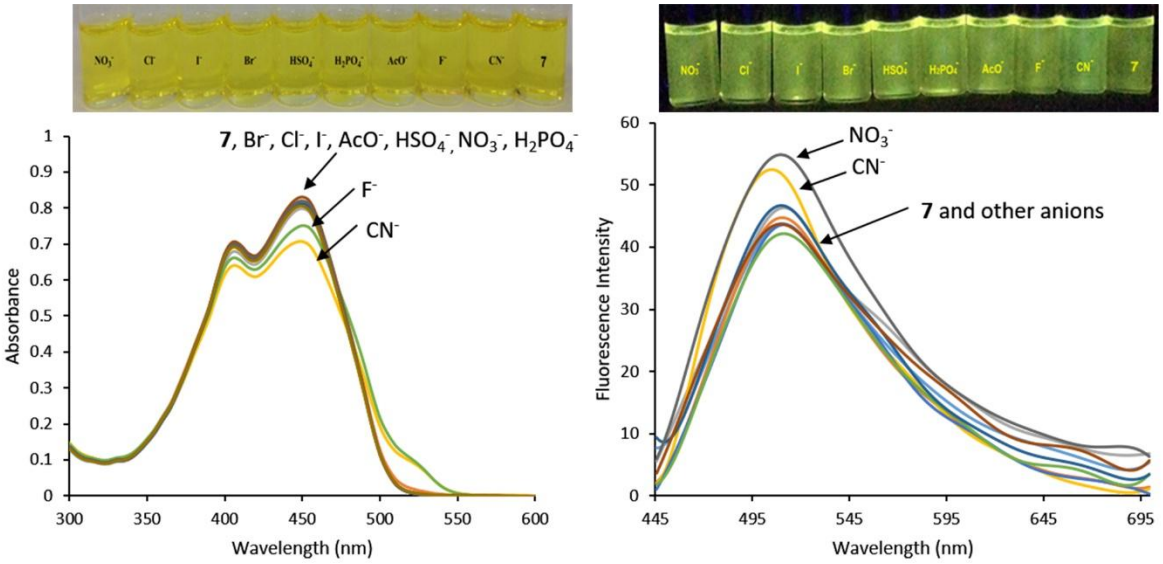

Fig. S41. Absorption spectra (20 µM in DMSO) (left) and emission spectra (2 µM in DMSO) (right) of **7** after addition of 20 equiv. of all the anions. Insets: Color and fluorescence changes after addition of 20 equiv. of anions.

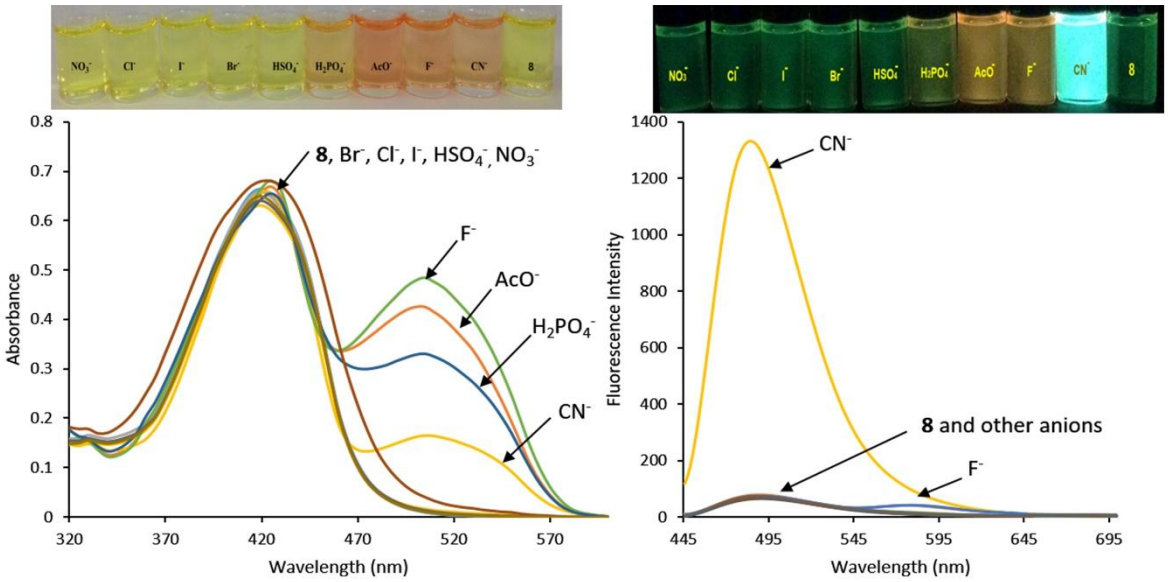

Fig. S42. Absorption spectra (20 µM in DMSO) (left) and emission spectra (2 µM in DMSO) (right) of **8** after addition of 20 equiv. of all the anions. Insets: Color and fluorescence changes after addition of 20 equiv. of anions.

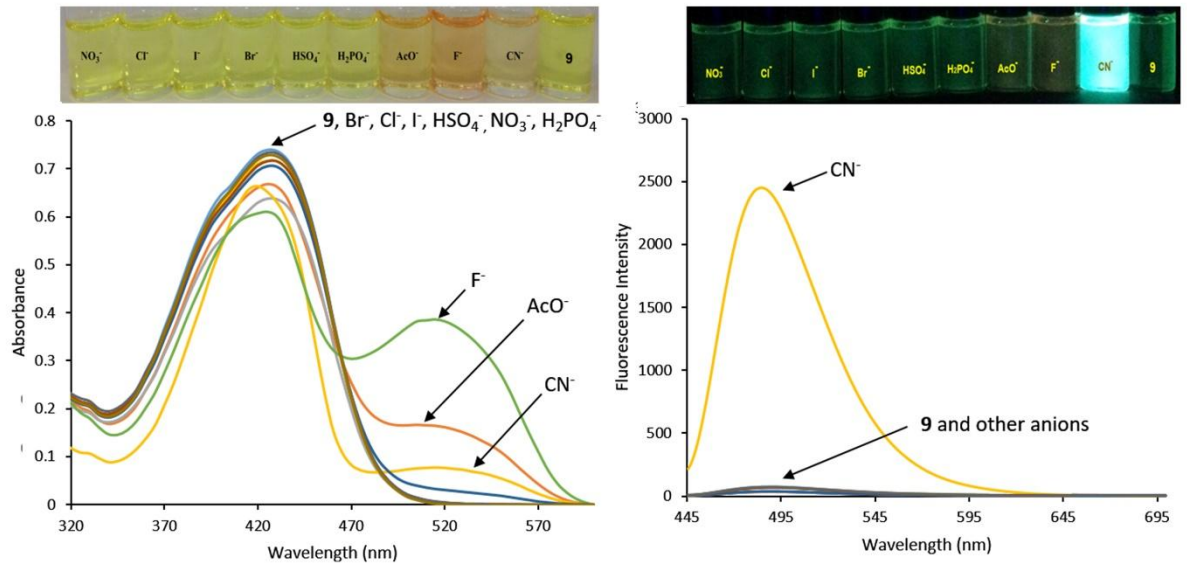

Fig. S43. Absorption spectra (20 µM in DMSO) (left) and emission spectra (2 µM in DMSO) (right) of **9** after addition of 20 equiv. of all the anions. Insets: Color and fluorescence changes after addition of 20 equiv. of anions.

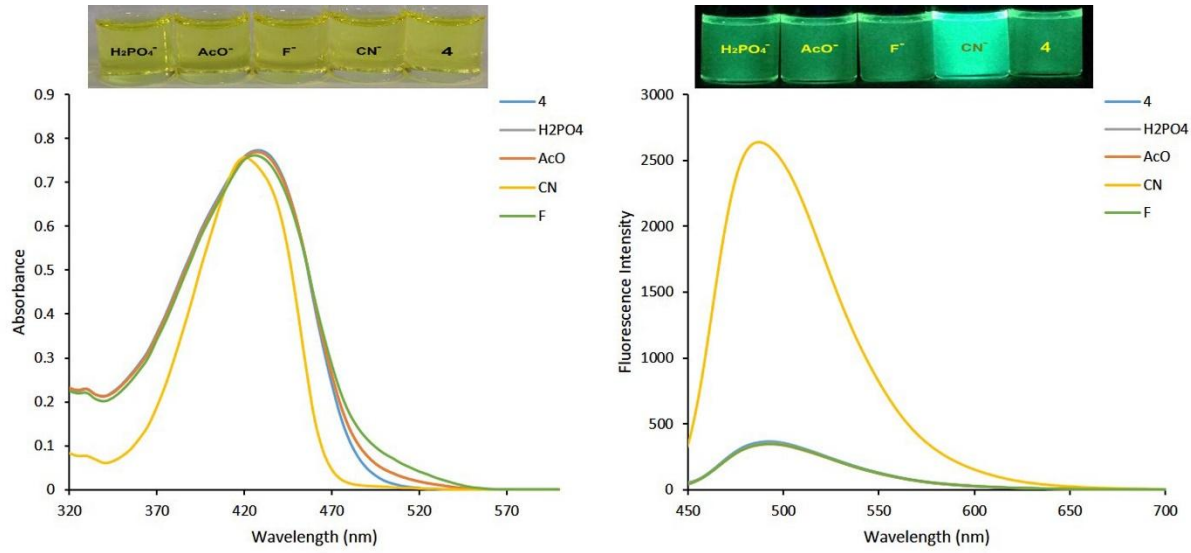

Fig. S44. Absorption spectra (20 µM) (left) and emission spectra (0.2 µM) (right) of **4** after addition of 50 equiv. of the anions in 9:1, DMSO:water (v/v). Insets: Color fluorescence changes after addition of 50 equiv. of anions.

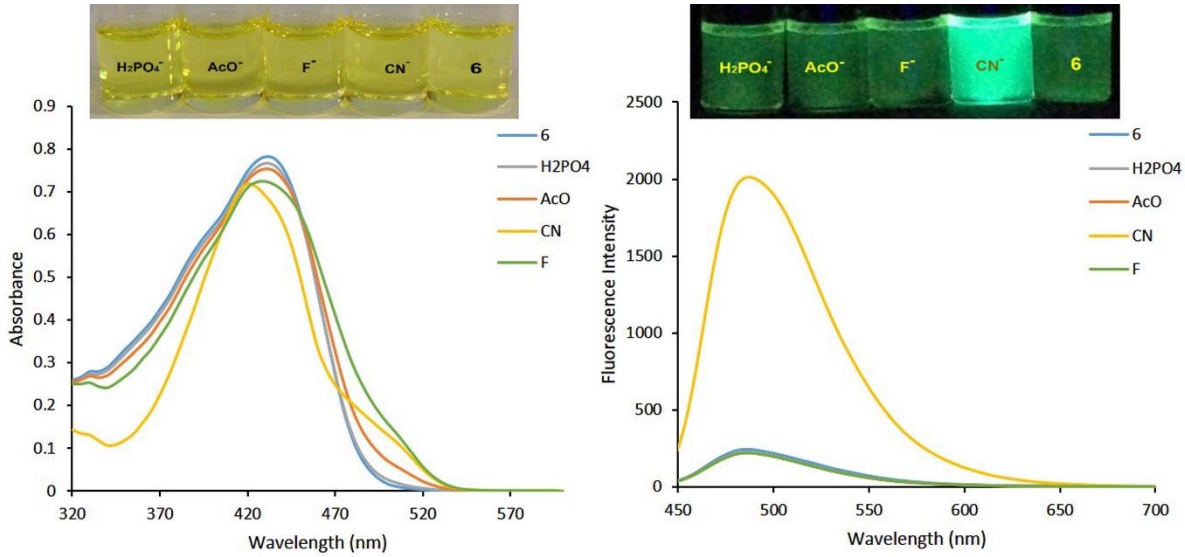

Fig. S45. Absorption spectra (20 µM) (left) and emission spectra (0.2 µM) (right) of **6** after addition of 50 equiv. of the anions in 9:1, DMSO:water (v/v). Insets: Color fluorescence changes after addition of 50 equiv. of anions.

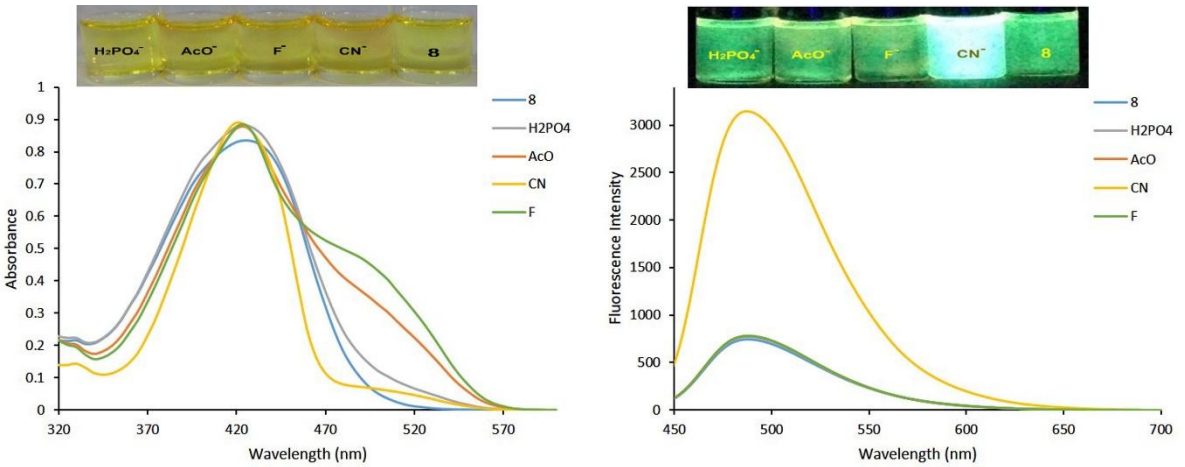

Fig. S46. Absorption spectra (20 µM) (left) and emission spectra (0.2 µM) (right) of **8** after addition of 50 equiv. of the anions in 9:1, DMSO:water (v/v). Insets: Color fluorescence changes after addition of 50 equiv. of anions.

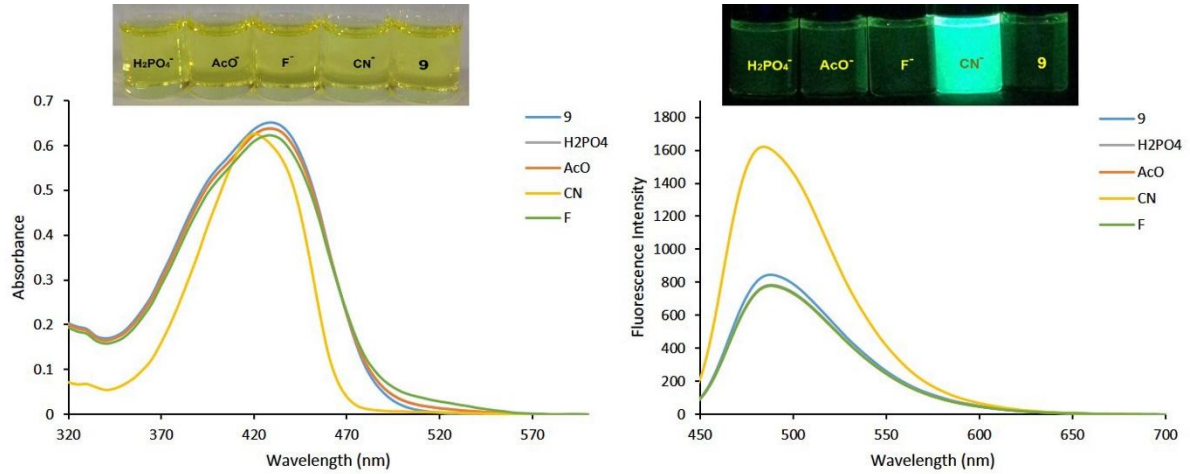

Fig. S47. Absorption spectra (20 µM) (left) and emission spectra (0.2 µM) (right) of **9** after addition of 50 equiv. of the anions in 9:1, DMSO:water (v/v). Insets: Color fluorescence changes after addition of 50 equiv. of anions.

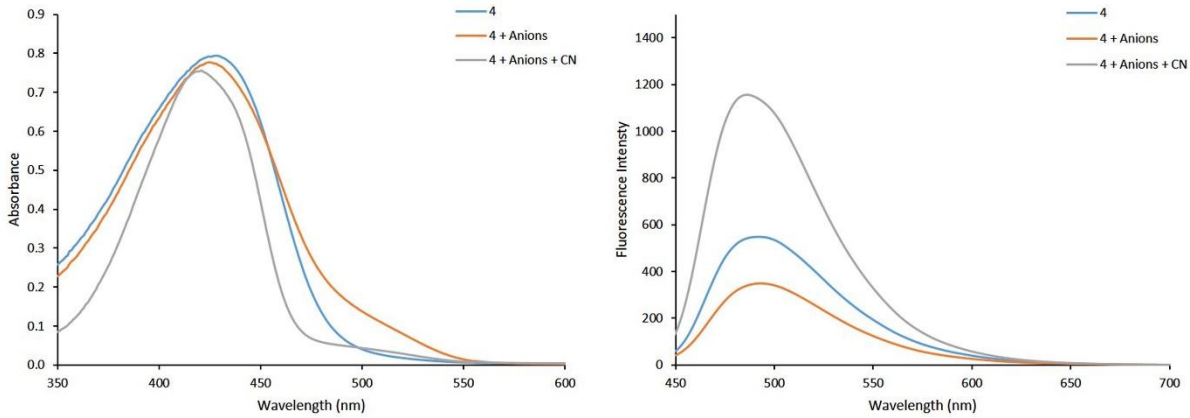

Fig. S48. Absorption spectra (20 µM) (left) and emission spectra (0.2 µM) (right) of **4** and after addition of 50 equiv. of the anions (F^-, AcO^-, and $H_2PO_4^-$) and CN^- in 9:1, DMSO:water (v/v).

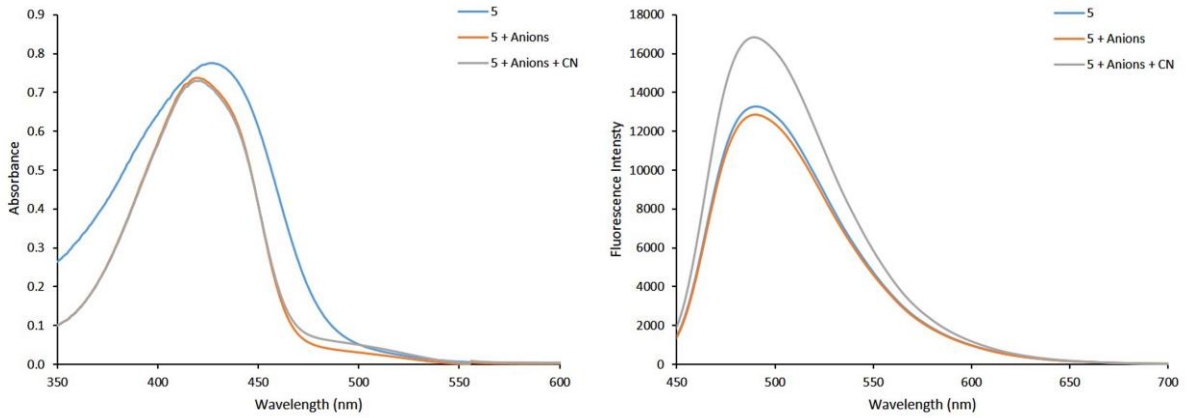

Fig. S49. Absorption spectra (20 µM) (left) and emission spectra (0.2 µM) (right) of **5** and after addition of 50 equiv. of the anions (F^-, AcO^-, and $H_2PO_4^-$) and CN^- in 9:1, DMSO:water (v/v).

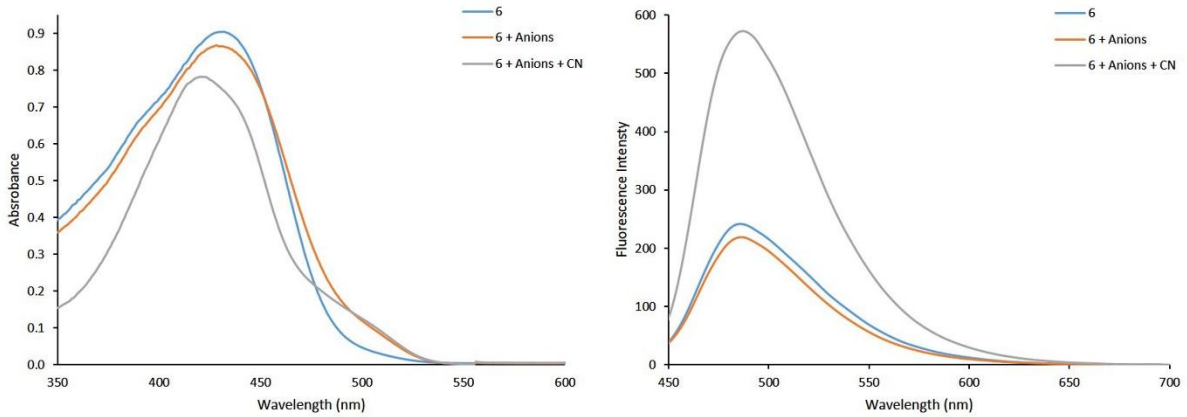

Fig. S50. Absorption spectra (20 µM) (left) and emission spectra (0.2 µM) (right) of **6** and after addition of 50 equiv. of the anions (F^-, AcO^-, and $H_2PO_4^-$) and CN^- in 9:1, DMSO:water (v/v).

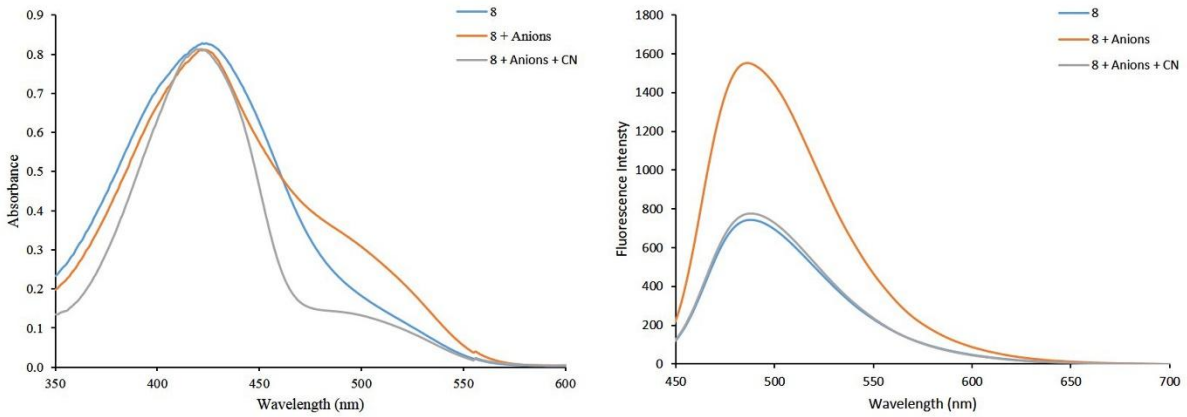

Fig. S50. Absorption spectra (20 µM) (left) and emission spectra (0.2 µM) (right) of **8** and after addition of 50 equiv. of the anions (F^-, AcO^-, and $H_2PO_4^-$) and CN^- in 9:1, DMSO:water (v/v).

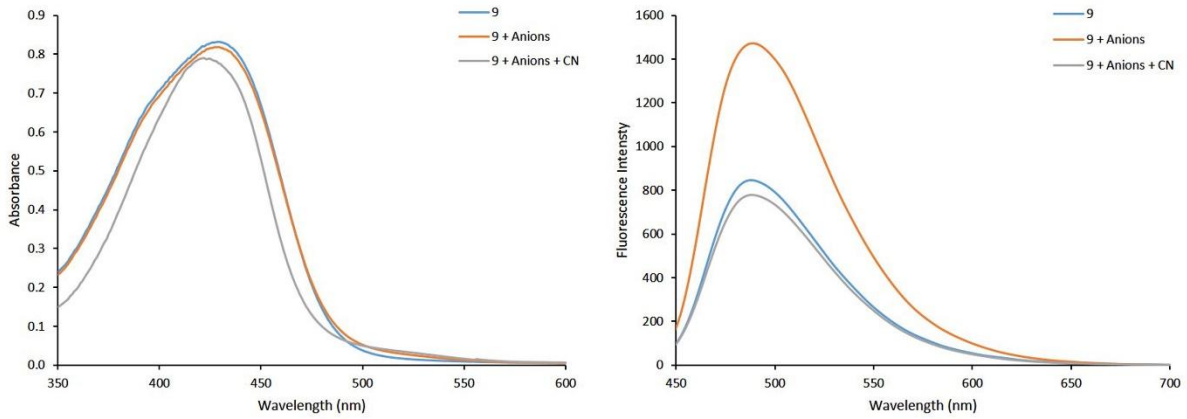

Fig. S52. Absorption spectra (20 µM) (left) and emission spectra (0.2 µM) (right) of **9** and after addition of 50 equiv. of the anions (F^-, AcO^-, and $H_2PO_4^-$) and CN^- in 9:1, DMSO:water (v/v).

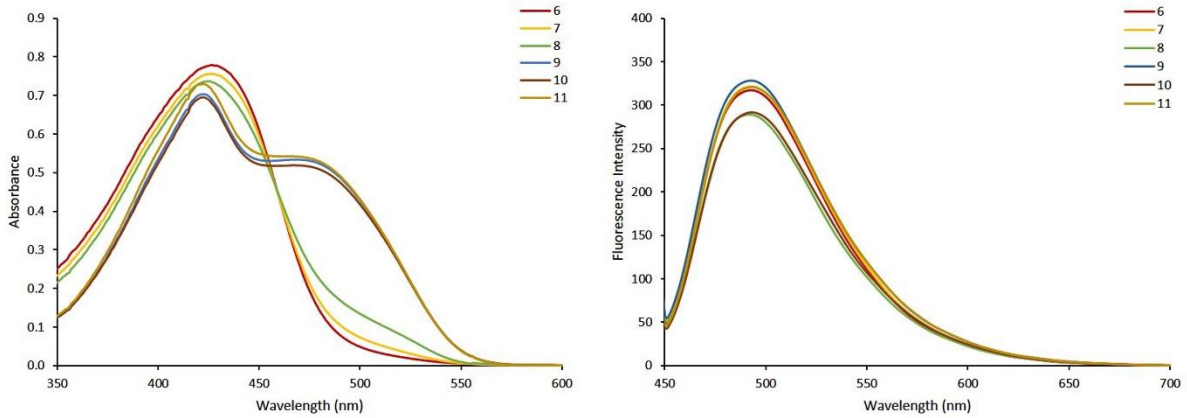

Fig. S53. Absorption and emission spectra of **4** (10 µM) at different pH Britton–Robinson buffer (9:1, DMSO:buffer (v/v)).

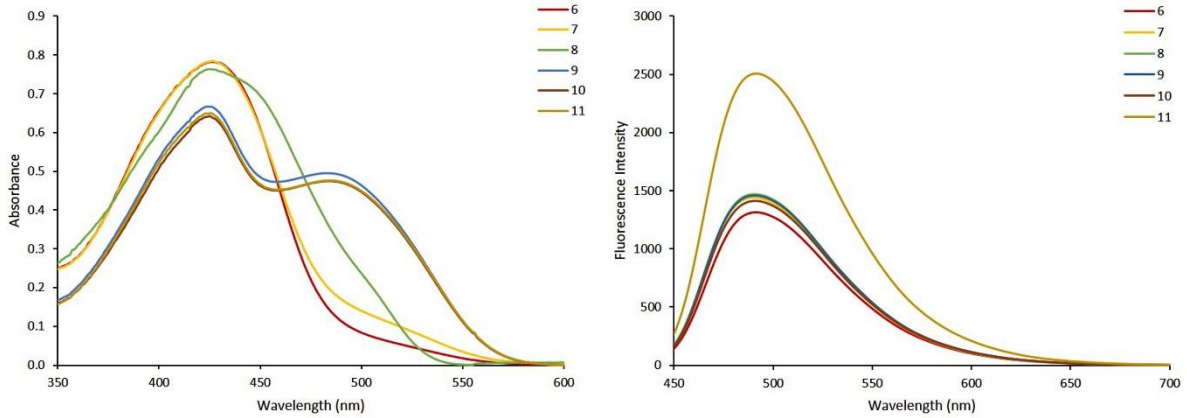

Fig. S54. Absorption and emission spectra of **5** (10 µM) at different pH Britton–Robinson buffer (9:1, DMSO:buffer (v/v)).

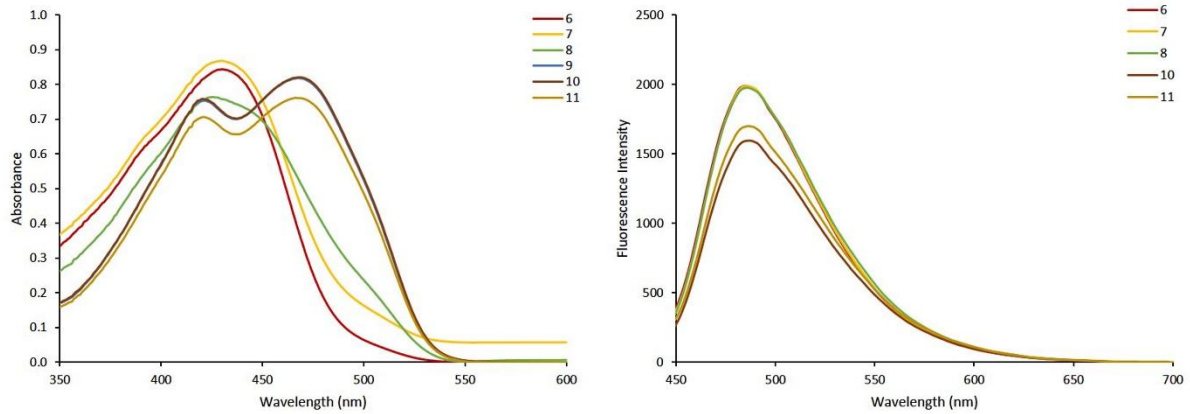

Fig. S55. Absorption and emission spectra of **6** (10 μM) at different pH Britton–Robinson buffer (9:1, DMSO:buffer (v/v)).

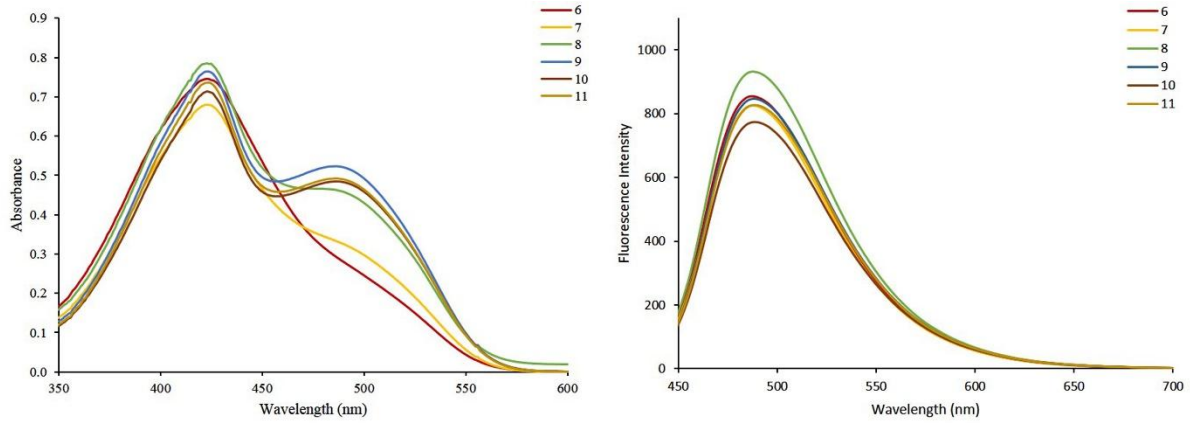

Fig. S56. Absorption and emission spectra of **8** (10 μM) at different pH Britton–Robinson buffer (9:1, DMSO:buffer (v/v)).

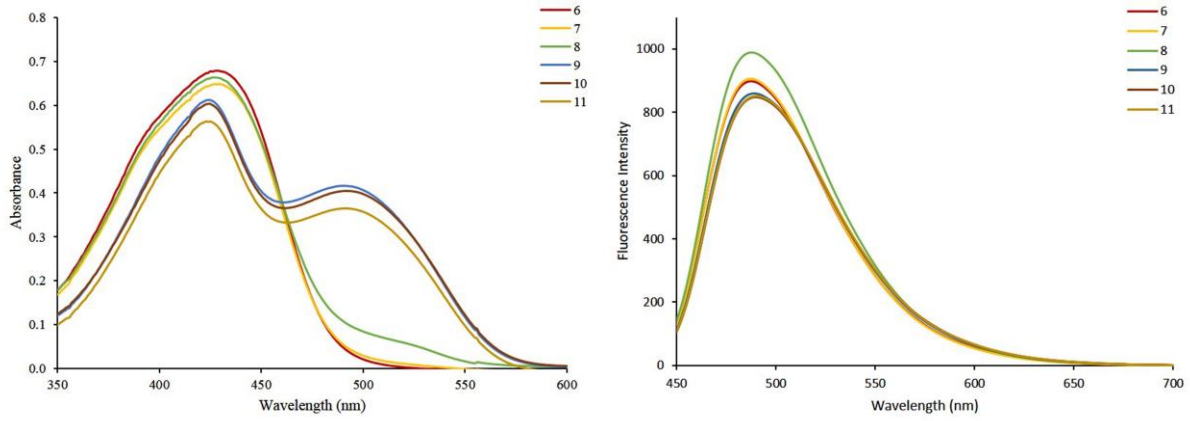

Fig. S57. Absorption and emission spectra of **9** (10 μM) at different pH Britton–Robinson buffer (9:1, DMSO:buffer (v/v)).

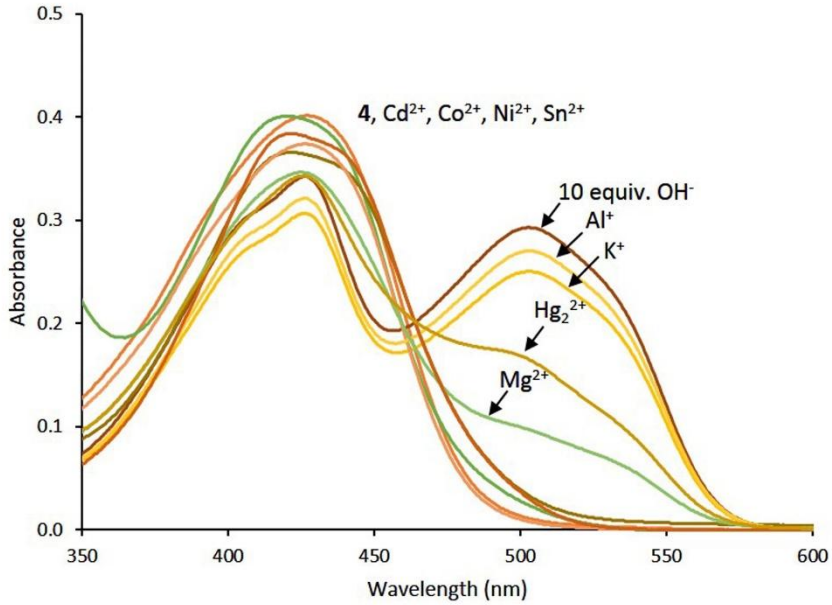

Fig. S51. Absorption spectra (20 µM in DMSO) of **4** after addition of 50 equiv. of all the cations.

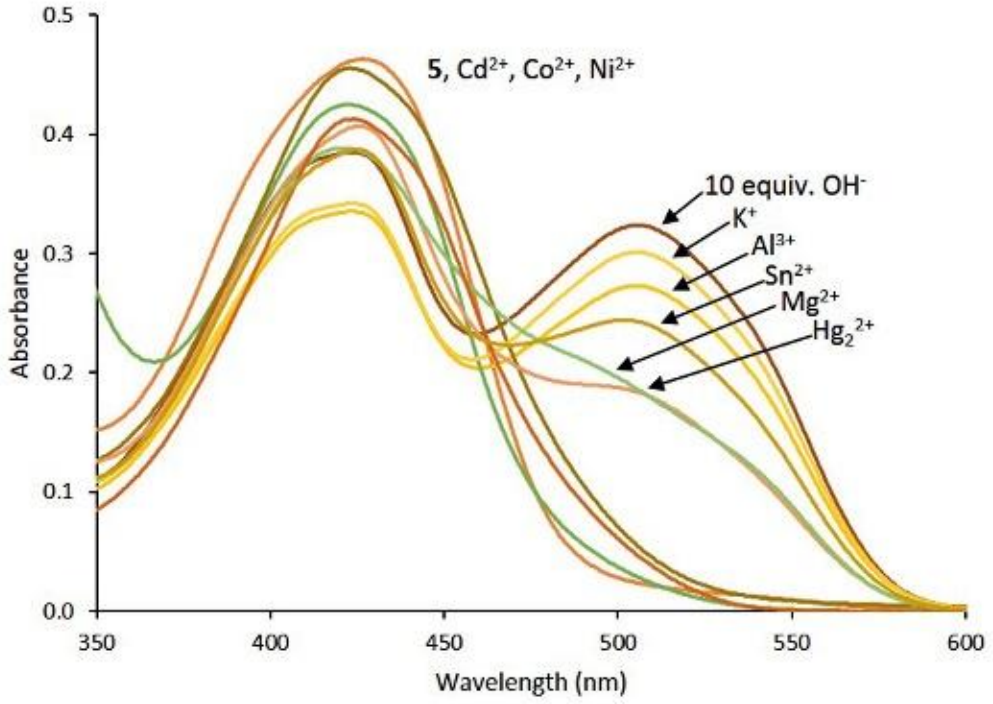

Fig. S52. Absorption spectra (20 µM in DMSO) of **5** after addition of 50 equiv. of all the cations.

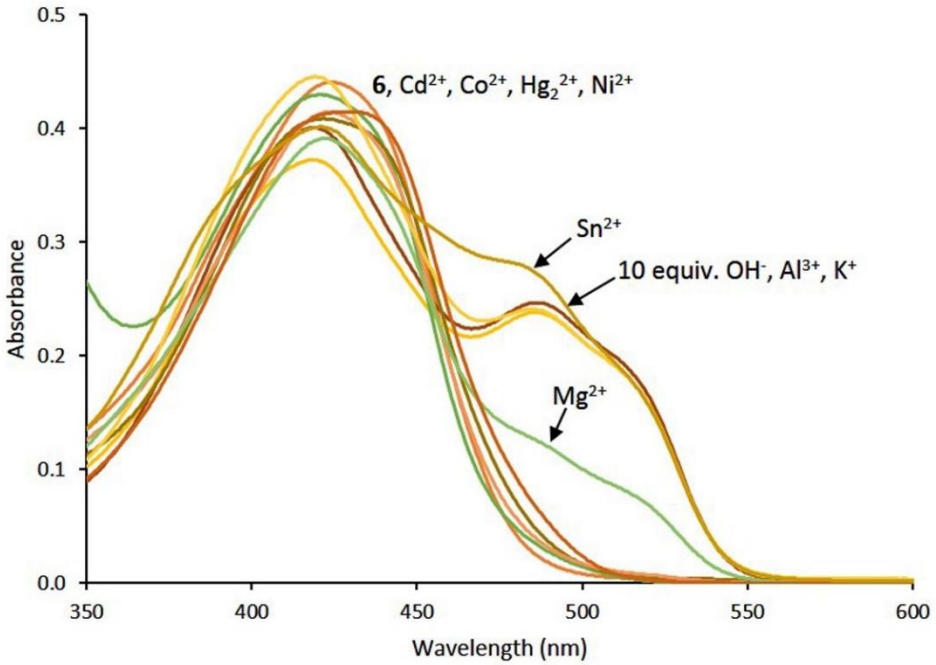

Fig. S60. Absorption spectra (20 µM in DMSO) of **6** after addition of 50 equiv. of all the cations.

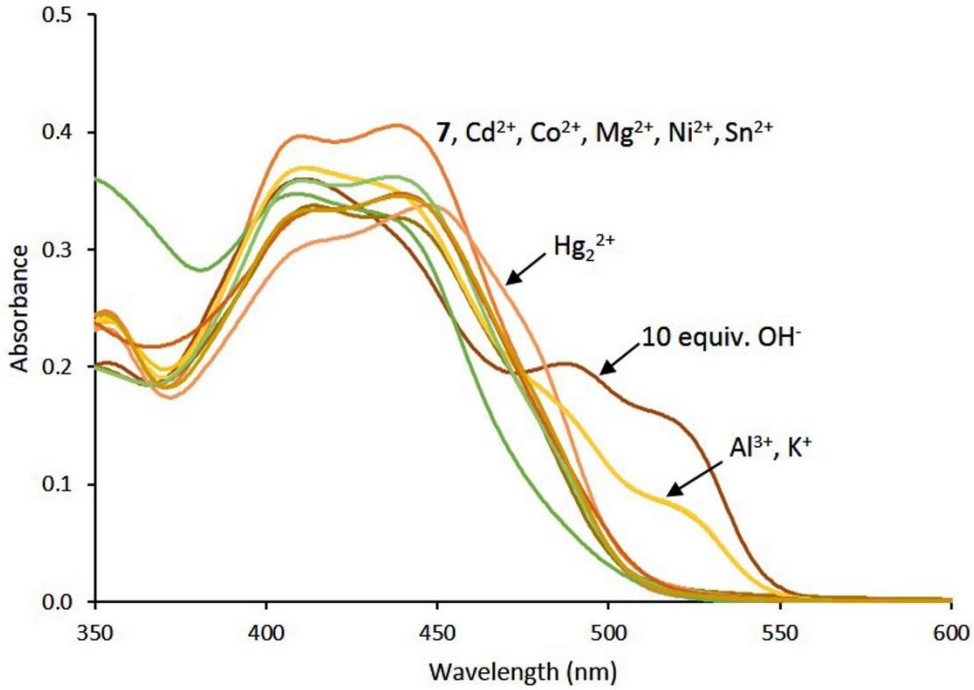

Fig. S53. Absorption spectra (20 µM in DMSO) of **7** after addition of 50 equiv. of all the cations.

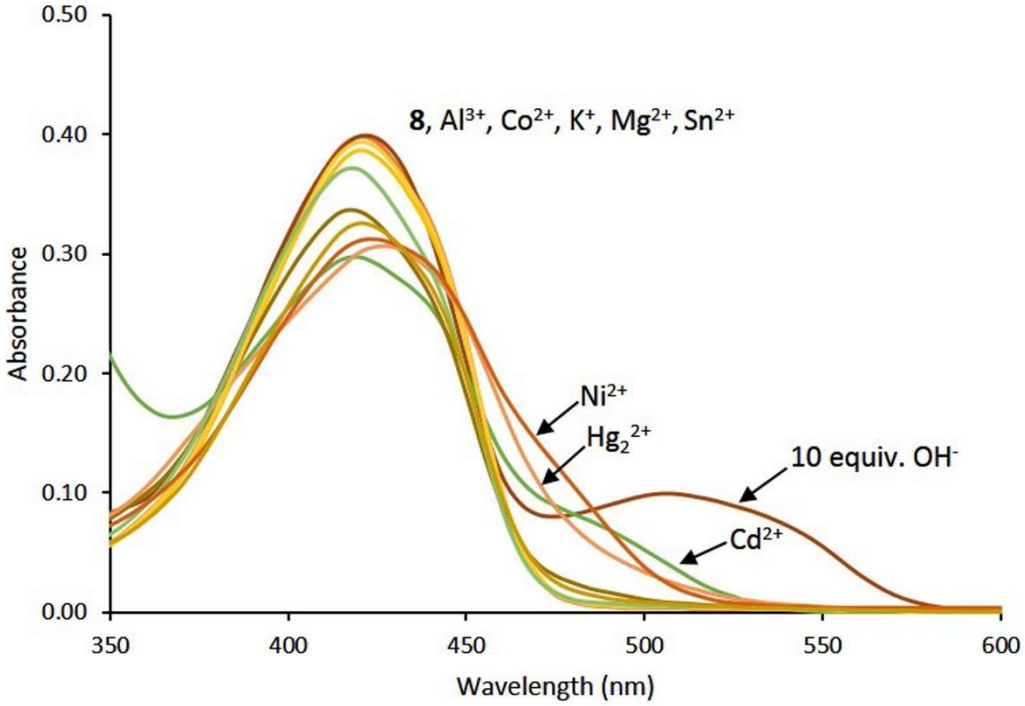

Fig. S54. Absorption spectra (20 µM in DMSO) of **8** after addition of 50 equiv. of all the cations.

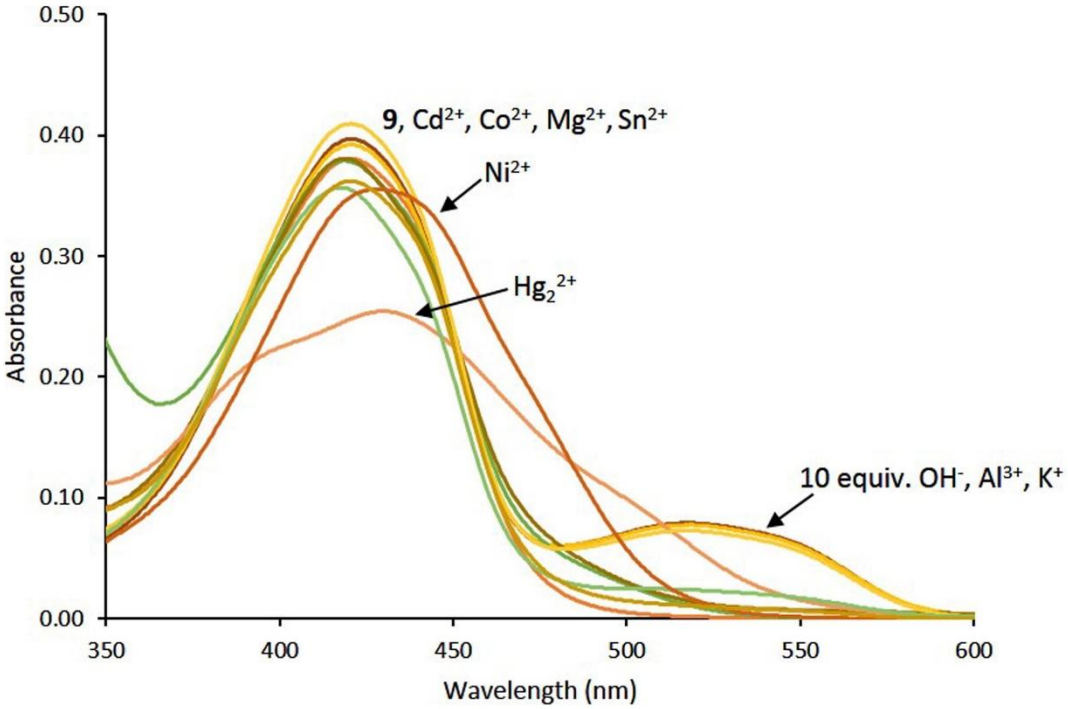

Fig. S55. Absorption spectra (20 µM in DMSO) of **9** after addition of 50 equiv. of all the cations.

6. X-Ray Analysis

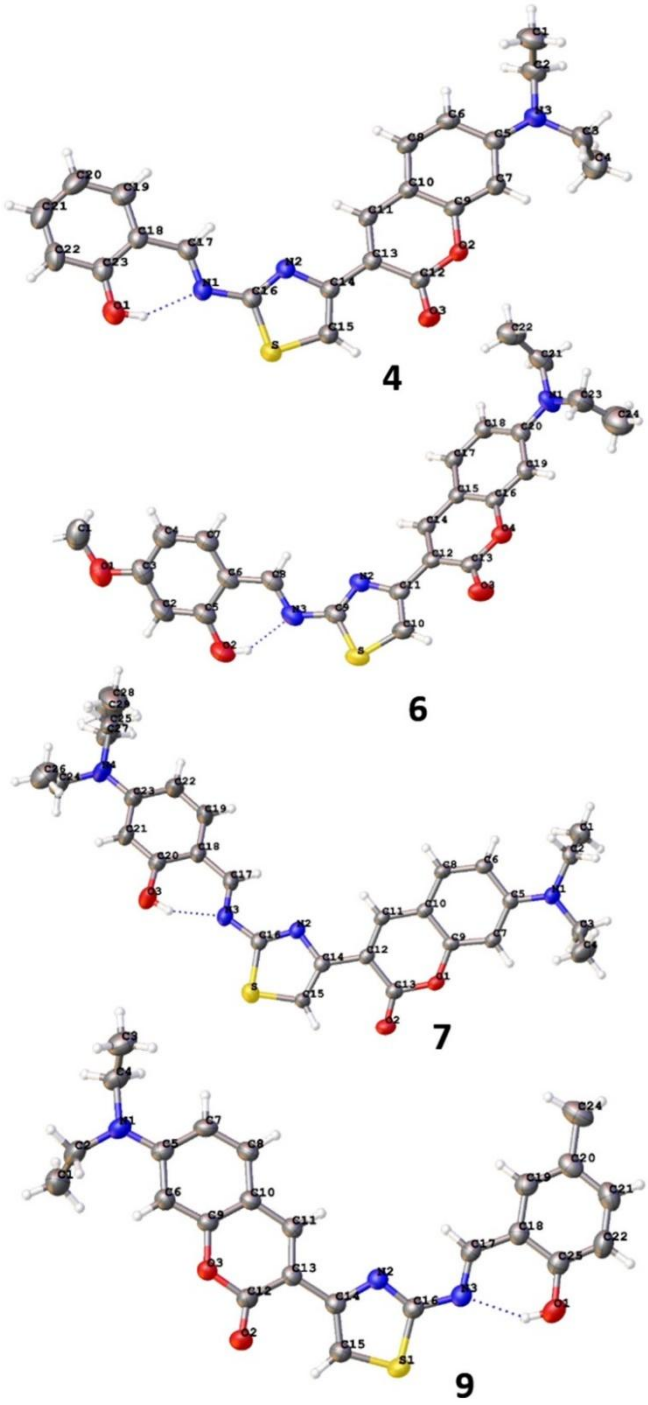

Fig. S64. Thermal ellipsoids for compounds 4, 6, 7, and 9

X-Ray Analyis

Crystal Structure Report for 4

A **dark orange rod-like** specimen of **$C_{23}H_{21}N_3O_3S$**, approximate dimensions **0.020** mm x **0.050** mm x **0.400** mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 VENTURE system equipped with a multilayer monochromator and a Mo Kα Sealed tube (λ = 0.71073 Å).

Table S1. Data collection details for **4.**

Axis	dx/mm	2θ/°	ω/°	ϕ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	49.998	12.68	-169.32	144.00	54.70	1.00	184	5.00	0.71076	50	30.0	304
Omega	49.998	12.68	-169.32	0.00	54.70	1.00	184	5.00	0.71076	50	30.0	304
Omega	49.998	13.79	-169.21	-131.24	54.70	1.00	186	5.00	0.71076	50	30.0	304
Omega	49.998	-55.75	-238.75	-255.16	54.70	1.00	186	5.00	0.71076	50	30.0	304
Omega	49.998	12.68	-169.32	72.00	54.70	1.00	184	5.00	0.71076	50	30.0	304
Phi	49.998	12.68	15.68	0.00	54.70	1.00	360	5.00	0.71076	50	30.0	304
Phi	49.998	12.68	-170.32	0.00	54.70	1.00	360	5.00	0.71076	50	30.0	304

A total of 1644 frames were collected. The total exposure time was 2.28 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a **triclinic** unit cell yielded a total of **47651** reflections to a maximum θ angle of **28.38°** (**0.75** Å resolution), of which **5146** were independent (average redundancy **9.260**, completeness = **99.8**%, R_{int} = **9.32**%, R_{sig} = **4.48**%) and **3331** (**64.73**%) were greater than $2\sigma(F^2)$. The final cell constants of a = **8.4790(7)** Å, b = **10.8451(8)** Å, c = **12.1470(10)** Å, α = **75.707(4)°**, β = **89.516(4)°**, γ = **72.029(3)°**, volume = **1026.82(14)** $Å^3$, are based upon the refinement of the XYZ-centroids of **9934** reflections above 20 σ(I) with **4.631°** < 2θ < **51.35°**. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was **0.966**. The calculated minimum and maximum transmission coefficients (based on crystal size) are **0.9290** and **0.9960**.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group **P -1**, with Z = **2** for the formula unit, **$C_{23}H_{21}N_3O_3S$**. The final anisotropic full-matrix least-squares refinement on F^2 with **274** variables converged at R1 = **4.57**%, for the observed data and wR2 = **11.79**% for all data. The goodness-of-fit was **1.008**. The largest peak in the final difference electron density synthesis was **0.275** $e^-/Å^3$ and the largest hole was **-0.201** $e^-/Å^3$ with an RMS deviation of **0.045** $e^-/Å^3$. On the basis of the final model, the calculated density was **1.357** g/cm^3 and F(000), **440** e^-.

Table S2. Sample and crystal data for **4**.

Identification code	**4**	
Chemical formula	$C_{23}H_{21}N_3O_3S$	
Formula weight	419.49 g/mol	
Temperature	304(0) K	
Wavelength	0.71073 Å	
Crystal size	0.020 x 0.050 x 0.400 mm	
Crystal habit	dark orange rod	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.4790(7) Å	α = 75.707(4)°
	b = 10.8451(8) Å	β = 89.516(4)°
	c = 12.1470(10) Å	γ = 72.029(3)°
Volume	1026.82(14) $Å^3$	
Z	2	
Density (calculated)	1.357 g/cm^3	
Absorption coefficient	0.188 mm^{-1}	
F(000)	440	

Table S3. Data collection and structure refinement for **4.**

Diffractometer	Bruker D8 VENTURE
Radiation source	Sealed tube, Mo Kα
Theta range for data collection	2.32 to 28.38°
Index ranges	-11<=h<=11, -14<=k<=14, -16<=l<=16
Reflections collected	47651
Independent reflections	5146 [R(int) = 0.0932]
Coverage of independent reflections	99.8%
Absorption correction	multi-scan
Max. and min. transmission	0.9960 and 0.9290
Structure solution technique	direct methods
Structure solution program	SHELXS-1997 (Sheldrick, 1997)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5146 / 0 / 274
Goodness-of-fit on F^2	1.008
Final R indices	3331 data; I>2σ(I) R1 = 0.0457, wR2 = 0.1043
	all data R1 = 0.0851, wR2 = 0.1179
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0570P)^2+0.1070P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.275 and -0.201 eÅ^{-3}
R.M.S. deviation from mean	0.045 eÅ^{-3}

Table S4. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **4**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
S	0.84392(5)	0.12823(4)	0.54689(4)	0.05109(15)
O2	0.41683(12)	0.54729(9)	0.76802(9)	0.0414(3)
O1	0.12685(15)	0.13933(12)	0.22432(11)	0.0591(3)
O3	0.47781(16)	0.33651(11)	0.76852(11)	0.0606(3)
N1	0.96406(15)	0.26483(12)	0.37030(11)	0.0414(3)
N2	0.79107(14)	0.38174(12)	0.49450(10)	0.0380(3)
N3	0.28370(17)	0.99112(13)	0.80856(12)	0.0497(3)
C10	0.53925(17)	0.69606(14)	0.64460(12)	0.0354(3)
C13	0.61354(17)	0.46378(14)	0.63695(12)	0.0352(3)
C9	0.43505(17)	0.67234(13)	0.73119(12)	0.0351(3)
C14	0.70660(17)	0.35237(14)	0.59003(12)	0.0363(3)
C11	0.62625(17)	0.58843(14)	0.59861(12)	0.0375(3)
C12	0.50345(19)	0.44031(15)	0.72633(13)	0.0393(3)
C8	0.55169(18)	0.82581(15)	0.61375(13)	0.0412(4)
C5	0.36349(18)	0.89601(14)	0.75392(13)	0.0399(4)
C18	0.08047(18)	0.37325(16)	0.21016(13)	0.0422(4)
C6	0.46765(19)	0.92196(15)	0.66544(13)	0.0430(4)
C16	0.86746(17)	0.27353(15)	0.46332(13)	0.0390(3)
C7	0.34773(18)	0.76709(15)	0.78447(13)	0.0402(4)
C17	0.98592(18)	0.37214(16)	0.30879(13)	0.0442(4)
C23	0.14890(19)	0.25734(18)	0.17179(14)	0.0469(4)
C15	0.7223(2)	0.21990(15)	0.62929(14)	0.0456(4)
C2	0.3041(2)	0.12300(15)	0.78063(15)	0.0529(4)
C3	0.1809(2)	0.96284(17)	0.90174(16)	0.0550(5)
C19	0.1092(2)	0.49089(18)	0.15144(15)	0.0586(5)
C22	0.2427(2)	0.2626(2)	0.07789(16)	0.0628(5)
C20	0.2020(2)	0.4948(2)	0.05855(17)	0.0695(6)
C21	0.2686(2)	0.3801(2)	0.02193(17)	0.0726(6)
C1	0.1844(3)	0.22188(18)	0.68393(19)	0.0734(6)
C4	0.2803(3)	0.8901(2)	0.01433(17)	0.0772(6)

Table S5. Bond lengths (Å) for **4.**

S-C15	1.7015(16)	S-C16	1.7188(15)
O2-C12	1.3784(17)	O2-C9	1.3755(16)
O1-C23	1.350(2)	O1-H21	0.82
O3-C12	1.2006(17)	N1-C17	1.2840(19)
N1-C16	1.3949(19)	N2-C16	1.2987(18)
N2-C14	1.3803(19)	N3-C5	1.3645(19)
N3-C2	1.4502(19)	N3-C3	1.453(2)
C10-C9	1.394(2)	C10-C8	1.401(2)
C10-C11	1.415(2)	C13-C11	1.3543(19)
C13-C12	1.452(2)	C13-C14	1.467(2)
C9-C7	1.369(2)	C14-C15	1.362(2)
C11-H14	0.93	C8-C6	1.359(2)
C8-H13	0.93	C5-C7	1.403(2)
C5-C6	1.415(2)	C18-C19	1.391(2)
C18-C23	1.403(2)	C18-C17	1.436(2)
C6-H11	0.93	C7-H12	0.93
C17-H16	0.93	C23-C22	1.385(2)
C15-H15	0.93	C2-C1	1.512(3)
C2-H4	0.97	C2-H5	0.97
C3-C4	1.510(3)	C3-H9	0.97
C3-H10	0.97	C19-C20	1.370(3)
C19-H17	0.93	C22-C21	1.369(3)
C22-H20	0.93	C20-C21	1.378(3)
C20-H18	0.93	C21-H19	0.93
C1-H3	0.96	C1-H1	0.96
C1-H2	0.96	C4-H7	0.96
C4-H6	0.96	C4-H8	0.96

Table S6. Bond angles (°) for **4**.

C15-S-C16	88.92(7)	C12-O2-C9	122.77(11)
C23-O1-H21	109.5	C17-N1-C16	118.72(13)
C16-N2-C14	110.63(12)	C5-N3-C2	121.72(13)
C5-N3-C3	121.56(13)	C2-N3-C3	116.65(13)
C9-C10-C8	115.74(13)	C9-C10-C11	118.33(13)
C8-C10-C11	125.89(13)	C11-C13-C12	118.95(13)
C11-C13-C14	121.87(13)	C12-C13-C14	119.18(12)
C7-C9-O2	116.35(12)	C7-C9-C10	123.87(13)
O2-C9-C10	119.78(12)	C15-C14-N2	114.17(13)
C15-C14-C13	128.09(14)	N2-C14-C13	117.74(12)
C13-C11-C10	122.34(13)	C13-C11-H14	118.8
C10-C11-H14	118.8	O3-C12-O2	115.32(13)
O3-C12-C13	126.92(13)	O2-C12-C13	117.76(12)
C6-C8-C10	121.91(14)	C6-C8-H13	119.0
C10-C8-H13	119.0	N3-C5-C7	121.26(14)
N3-C5-C6	121.70(13)	C7-C5-C6	117.03(13)
C19-C18-C23	118.32(15)	C19-C18-C17	119.88(15)
C23-C18-C17	121.79(15)	C8-C6-C5	121.69(14)
C8-C6-H11	119.2	C5-C6-H11	119.2
N2-C16-N1	126.64(14)	N2-C16-S	115.26(11)
N1-C16-S	118.10(11)	C9-C7-C5	119.74(14)
C9-C7-H12	120.1	C5-C7-H12	120.1
N1-C17-C18	122.59(14)	N1-C17-H16	118.7
C18-C17-H16	118.7	O1-C23-C22	118.50(16)
O1-C23-C18	121.84(14)	C22-C23-C18	119.66(17)
C14-C15-S	111.02(12)	C14-C15-H15	124.5
S-C15-H15	124.5	N3-C2-C1	113.15(15)
N3-C2-H4	108.9	C1-C2-H4	108.9
N3-C2-H5	108.9	C1-C2-H5	108.9
H4-C2-H5	107.8	N3-C3-C4	113.10(15)
N3-C3-H9	109.0	C4-C3-H9	109.0
N3-C3-H10	109.0	C4-C3-H10	109.0
H9-C3-H10	107.8	C20-C19-C18	121.42(18)
C20-C19-H17	119.3	C18-C19-H17	119.3
C21-C22-C23	120.58(18)	C21-C22-H20	119.7
C23-C22-H20	119.7	C19-C20-C21	119.61(19)
C19-C20-H18	120.2	C21-C20-H18	120.2
C22-C21-C20	120.41(18)	C22-C21-H19	119.8
C20-C21-H19	119.8	C2-C1-H3	109.5
C2-C1-H1	109.5	H3-C1-H1	109.5
C2-C1-H2	109.5	H3-C1-H2	109.5
H1-C1-H2	109.5	C3-C4-H7	109.5
C3-C4-H6	109.5	H7-C4-H6	109.5
C3-C4-H8	109.5	H7-C4-H8	109.5
H6-C4-H8	109.5		

Table S7. Anisotropic atomic displacement parameters (Å^2) for **4**.

The anisotropic atomic 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}
S	0.0622(3)	0.0340(2)	0.0549(3)	-0.01326(19)	0.0202(2)	-0.01111(18)
O2	0.0538(6)	0.0336(5)	0.0417(6)	-0.0126(5)	0.0206(5)	-0.0191(5)
O1	0.0691(8)	0.0549(7)	0.0632(8)	-0.0301(6)	0.0236(6)	-0.0223(6)
O3	0.0857(9)	0.0384(6)	0.0674(8)	-0.0175(6)	0.0400(7)	-0.0312(6)
N1	0.0418(7)	0.0425(7)	0.0384(7)	-0.0130(6)	0.0096(6)	-0.0094(6)
N2	0.0408(7)	0.0360(7)	0.0342(7)	-0.0089(5)	0.0072(5)	-0.0082(5)
N3	0.0645(9)	0.0367(7)	0.0529(8)	-0.0188(6)	0.0157(7)	-0.0175(6)
C10	0.0396(8)	0.0338(8)	0.0321(8)	-0.0057(6)	0.0057(6)	-0.0127(6)
C13	0.0377(7)	0.0355(8)	0.0319(8)	-0.0083(6)	0.0042(6)	-0.0112(6)
C9	0.0417(8)	0.0306(7)	0.0334(8)	-0.0061(6)	0.0039(6)	-0.0138(6)
C14	0.0391(8)	0.0357(8)	0.0328(8)	-0.0080(6)	0.0051(6)	-0.0105(6)
C11	0.0405(8)	0.0386(8)	0.0323(8)	-0.0064(6)	0.0092(6)	-0.0133(6)
C12	0.0492(9)	0.0346(8)	0.0370(8)	-0.0109(7)	0.0121(7)	-0.0160(7)
C8	0.0473(8)	0.0381(8)	0.0369(8)	-0.0037(7)	0.0099(7)	-0.0162(7)
C5	0.0453(8)	0.0358(8)	0.0381(8)	-0.0102(7)	0.0028(7)	-0.0116(7)
C18	0.0396(8)	0.0466(9)	0.0362(8)	-0.0091(7)	0.0052(7)	-0.0093(7)
C6	0.0530(9)	0.0308(8)	0.0447(9)	-0.0051(7)	0.0054(7)	-0.0161(7)
C16	0.0382(8)	0.0381(8)	0.0377(8)	-0.0100(7)	0.0050(7)	-0.0080(6)
C7	0.0467(8)	0.0396(8)	0.0388(8)	-0.0128(7)	0.0125(7)	-0.0180(7)
C17	0.0455(9)	0.0407(9)	0.0426(9)	-0.0134(7)	0.0069(7)	-0.0064(7)
C23	0.0428(8)	0.0567(10)	0.0398(9)	-0.0154(8)	0.0049(7)	-0.0113(7)
C15	0.0530(9)	0.0377(8)	0.0440(9)	-0.0107(7)	0.0151(7)	-0.0114(7)
C2	0.0683(11)	0.0401(9)	0.0577(11)	-0.0222(8)	0.0074(9)	-0.0202(8)
C3	0.0572(10)	0.0479(10)	0.0650(12)	-0.0280(9)	0.0199(9)	-0.0138(8)
C19	0.0627(11)	0.0531(11)	0.0512(11)	-0.0040(9)	0.0089(9)	-0.0131(9)
C22	0.0599(11)	0.0788(14)	0.0468(11)	-0.0245(10)	0.0162(9)	-0.0115(10)
C20	0.0658(12)	0.0742(14)	0.0546(12)	0.0083(10)	0.0114(10)	-0.0222(10)
C21	0.0589(11)	0.0991(17)	0.0454(11)	-0.0048(11)	0.0165(9)	-0.0160(11)
C1	0.0836(14)	0.0442(11)	0.0805(15)	-0.0097(10)	0.0006(12)	-0.0082(10)
C4	0.0909(15)	0.0828(15)	0.0536(12)	-0.0212(11)	0.0166(11)	-0.0190(12)

Table S8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **4**.

	x/a	y/b	z/c	U(eq)
H21	1.0725	0.1481	0.2797	0.089
H14	0.6946	0.6038	0.5400	0.045
H13	0.6194	0.8468	0.5562	0.049
H11	0.4789	1.0070	0.6421	0.052
H12	0.2782	0.7461	0.8407	0.048
H16	0.9386	0.4523	0.3289	0.053
H15	0.6730	0.1842	0.6927	0.055
H4	0.4170	1.1148	0.7600	0.063
H5	0.2881	1.1577	0.8476	0.063
H9	0.1175	0.9088	0.8837	0.066
H10	0.1026	1.0467	0.9090	0.066
H17	1.0644	0.5686	0.1758	0.07
H20	1.2885	0.1858	0.0526	0.075
H18	1.2200	0.5743	0.0204	0.083
H19	1.3316	0.3824	-0.0412	0.087
H3	0.2007	1.1889	0.6169	0.11
H1	0.2041	1.3068	0.6689	0.11
H2	0.0723	1.2327	0.7046	0.11
H7	0.3537	0.8047	1.0092	0.116
H6	0.2061	0.8769	1.0730	0.116
H8	0.3444	0.9426	1.0324	0.116

Crystal Structure Report for 6

A **dark yellow square-like** specimen of **$C_{24}H_{23}N_3O_4S$**, approximate dimensions **0.020** mm x **0.030** mm x **0.200** mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 VENTURE system equipped with a multilayer monochromator and a Mo Kα Sealed tube (λ = 0.71073 Å).

Table S9. Data collection details for **6**.

Axis	dx/mm	2θ/°	ω/°	ϕ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	49.966	8.67	-173.33	0.00	54.70	1.00	184	8.00	0.71076	50	30.0	305
Omega	49.966	-52.44	-235.44	5.77	54.70	1.00	186	8.00	0.71076	50	30.0	305
Omega	49.966	9.78	-173.22	64.01	54.70	1.00	186	8.00	0.71076	50	30.0	305
Omega	49.966	-9.78	-192.78	135.01	54.70	1.00	186	8.00	0.71076	50	30.0	305
Phi	49.966	8.67	11.67	0.00	54.70	1.00	360	8.00	0.71076	50	30.0	305
Phi	49.966	8.67	-174.33	0.00	54.70	1.00	360	8.00	0.71076	50	30.0	305

A total of 1462 frames were collected. The total exposure time was 3.25 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a **triclinic** unit cell yielded a total of **40160** reflections to a maximum θ angle of **25.00°** (**0.84** Å resolution), of which **3857** were independent (average redundancy **10.412**, completeness = **100.0**%, R_{int} = **3.36**%, R_{sig} = **1.40**%) and **3256** (**84.42**%) were greater than $2\sigma(F^2)$. The final cell constants of a = **8.0871(5)** Å, b = **8.3785(5)** Å, c = **16.9875(10)** Å, α = **98.318(3)°**, β = **91.468(3)°**, γ = **105.343(3)°**, volume = **1095.87(12)** $Å^3$, are based upon the refinement of the XYZ-centroids of **9116** reflections above 20 σ(I) with **4.857°** < 2θ < **56.12°**. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was **0.954**.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group **P -1**, with Z = **2** for the formula unit, **$C_{24}H_{23}N_3O_4S$**. The final anisotropic full-matrix least-squares refinement on F^2 with **293** variables converged at R1 = **5.37**%, for the observed data and wR2 = **14.63**% for all data. The goodness-of-fit was **1.064**. The largest peak in the final difference electron density synthesis was **0.940** $e^-/Å^3$ and the largest hole was **-0.474** $e^-/Å^3$ with an RMS deviation of **0.058** $e^-/Å^3$. On the basis of the final model, the calculated density was **1.362** g/cm^3 and F(000), **472** e^-.

Table S10. Sample and crystal data for **6**.

Identification code	**6**	
Chemical formula	$C_{24}H_{23}N_3O_4S$	
Formula weight	449.52 g/mol	
Temperature	305(0) K	
Wavelength	0.71073 Å	
Crystal size	0.020 x 0.030 x 0.200 mm	
Crystal habit	dark yellow square	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.0871(5) Å	α = 98.318(3)°
	b = 8.3785(5) Å	β = 91.468(3)°
	c = 16.9875(10) Å	γ = 105.343(3)°
Volume	1095.87(12) $Å^3$	
Z	2	
Density (calculated)	1.362 g/cm^3	
Absorption coefficient	0.185 mm^{-1}	
F(000)	472	

Table S11. Data collection and structure refinement for **6**.

Diffractometer	Bruker D8 VENTURE
Radiation source	Sealed tube, Mo Kα
Theta range for data collection	2.43 to 25.00°
Index ranges	-9<=h<=9, -9<=k<=9, -20<=l<=20
Reflections collected	40160
Independent reflections	3857 [R(int) = 0.0336]
Coverage of independent reflections	100.0%
Absorption correction	multi-scan
Structure solution technique	direct methods
Structure solution program	SHELXS-1997 (Sheldrick, 1997)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3857 / 0 / 293
Goodness-of-fit on F^2	1.064
Final R indices	3256 data; I>2σ(I) R1 = 0.0537, wR2 = 0.1359
	all data R1 = 0.0635, wR2 = 0.1463
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0705P)^2+0.6691P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.940 and -0.474 eÅ^{-3}
R.M.S. deviation from mean	0.058 eÅ^{-3}

Table S12. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **6**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
S	0.62363(8)	0.79474(8)	0.32025(4)	0.0574(2)
O4	0.2291(2)	0.63054(17)	0.60956(9)	0.0437(4)
O3	0.4332(2)	0.8257(2)	0.57031(11)	0.0606(5)
N3	0.5808(2)	0.4981(3)	0.22587(12)	0.0515(5)
N2	0.4415(2)	0.5110(2)	0.34909(11)	0.0447(4)
O2	0.6538(3)	0.4667(3)	0.07539(12)	0.0797(6)
C15	0.1074(3)	0.3628(2)	0.52939(12)	0.0360(5)
N1	0.8534(3)	0.2090(3)	0.72935(12)	0.0601(6)
C12	0.3253(3)	0.5738(2)	0.47723(13)	0.0387(5)
C16	0.1216(3)	0.4708(2)	0.60115(12)	0.0373(5)
O1	0.7746(3)	0.9753(3)	0.95894(12)	0.0849(7)
C14	0.2125(3)	0.4196(3)	0.46818(13)	0.0383(5)
C13	0.3382(3)	0.6868(3)	0.55226(13)	0.0423(5)
C19	0.0343(3)	0.4262(3)	0.66610(13)	0.0425(5)
C17	0.9891(3)	0.2050(3)	0.52490(13)	0.0399(5)
C11	0.4337(3)	0.6303(3)	0.41349(13)	0.0415(5)
C20	0.9275(3)	0.2625(3)	0.66318(13)	0.0428(5)
C6	0.6337(3)	0.2501(3)	0.15613(14)	0.0485(6)
C18	0.9014(3)	0.1558(3)	0.58877(13)	0.0411(5)
C9	0.5380(3)	0.5809(3)	0.29675(14)	0.0474(5)
C8	0.5853(3)	0.3453(3)	0.22408(14)	0.0483(6)
C10	0.5259(3)	0.7891(3)	0.40774(16)	0.0504(6)
C7	0.6530(3)	0.0910(3)	0.15978(15)	0.0575(6)
C4	0.6998(4)	0.9943(4)	0.09687(17)	0.0625(7)
C5	0.6672(3)	0.3128(3)	0.08378(15)	0.0565(6)
C21	0.7632(3)	0.0338(3)	0.72958(16)	0.0618(7)
C3	0.7291(3)	0.0583(4)	0.02594(16)	0.0619(7)
C2	0.7120(4)	0.2161(4)	0.02024(16)	0.0685(8)
C22	0.8819(4)	0.9231(4)	0.7355(2)	0.0791(9)
C23	0.9223(5)	0.3070(4)	0.8109(2)	0.0865(10)
C1	0.7939(5)	0.8118(5)	0.9598(2)	0.0929(11)
C24	0.8233(6)	0.4221(6)	0.8329(3)	0.1145(14)

Table S13. Bond lengths (Å) for **6**.

S-C10	1.702(3)	S-C9	1.724(3)
O4-C16	1.375(2)	O4-C13	1.380(3)
O3-C13	1.205(3)	N3-C8	1.287(3)
N3-C9	1.399(3)	N2-C9	1.299(3)
N2-C11	1.386(3)	O2-C5	1.350(3)
O2-H7	0.82	C15-C16	1.392(3)
C15-C17	1.402(3)	C15-C14	1.416(3)
N1-C20	1.365(3)	N1-C21	1.457(3)
N1-C23	1.515(4)	C12-C14	1.356(3)
C12-C13	1.457(3)	C12-C11	1.463(3)
C16-C19	1.369(3)	O1-C3	1.357(3)
O1-C1	1.421(4)	C14-H10	0.93
C19-C20	1.407(3)	C19-H13	0.93
C17-C18	1.366(3)	C17-H11	0.93
C11-C10	1.361(3)	C20-C18	1.415(3)
C6-C7	1.393(4)	C6-C5	1.410(3)
C6-C8	1.429(3)	C18-H12	0.93
C8-H8	0.93	C10-H9	0.93
C7-C4	1.369(4)	C7-H6	0.93
C4-C3	1.389(4)	C4-H5	0.93
C5-C2	1.369(4)	C21-C22	1.512(4)
C21-H14	0.97	C21-H15	0.97
C3-C2	1.382(4)	C2-H4	0.93
C22-H17	0.96	C22-H18	0.96
C22-H16	0.96	C23-C24	1.425(5)
C23-H20	0.97	C23-H19	0.97
C1-H3	0.96	C1-H1	0.96
C1-H2	0.96	C24-H22	0.96
C24-H23	0.96	C24-H21	0.96

Table S14. Bond angles (°) for **6**.

C10-S-C9	88.91(11)	C16-O4-C13	123.06(17)
C8-N3-C9	117.68(19)	C9-N2-C11	110.19(19)
C5-O2-H7	109.5	C16-C15-C17	116.03(19)
C16-C15-C14	118.12(19)	C17-C15-C14	125.85(19)
C20-N1-C21	121.6(2)	C20-N1-C23	119.4(2)
C21-N1-C23	114.4(2)	C14-C12-C13	119.07(19)
C14-C12-C11	121.8(2)	C13-C12-C11	119.16(19)
C19-C16-O4	116.80(18)	C19-C16-C15	123.30(19)
O4-C16-C15	119.90(18)	C3-O1-C1	119.0(3)
C12-C14-C15	122.5(2)	C12-C14-H10	118.8
C15-C14-H10	118.8	O3-C13-O4	115.5(2)
O3-C13-C12	127.4(2)	O4-C13-C12	117.13(18)
C16-C19-C20	120.1(2)	C16-C19-H13	120.0
C20-C19-H13	120.0	C18-C17-C15	122.1(2)
C18-C17-H11	119.0	C15-C17-H11	119.0
C10-C11-N2	114.5(2)	C10-C11-C12	127.9(2)
N2-C11-C12	117.49(19)	N1-C20-C19	121.4(2)
N1-C20-C18	121.5(2)	C19-C20-C18	117.05(19)
C7-C6-C5	117.2(2)	C7-C6-C8	120.6(2)
C5-C6-C8	122.3(2)	C17-C18-C20	121.0(2)
C17-C18-H12	119.5	C20-C18-H12	119.5
N2-C9-N3	126.1(2)	N2-C9-S	115.43(19)
N3-C9-S	118.49(16)	N3-C8-C6	122.7(2)
N3-C8-H8	118.6	C6-C8-H8	118.6
C11-C10-S	110.91(19)	C11-C10-H9	124.5
S-C10-H9	124.5	C4-C7-C6	123.2(2)
C4-C7-H6	118.4	C6-C7-H6	118.4
C7-C4-C3	118.2(3)	C7-C4-H5	120.9
C3-C4-H5	120.9	O2-C5-C2	118.9(2)
O2-C5-C6	121.1(2)	C2-C5-C6	120.0(3)
N1-C21-C22	113.5(2)	N1-C21-H14	108.9
C22-C21-H14	108.9	N1-C21-H15	108.9
C22-C21-H15	108.9	H14-C21-H15	107.7
O1-C3-C2	115.6(2)	O1-C3-C4	124.3(3)
C2-C3-C4	120.1(3)	C5-C2-C3	121.2(2)
C5-C2-H4	119.4	C3-C2-H4	119.4
C21-C22-H17	109.5	C21-C22-H18	109.5
H17-C22-H18	109.5	C21-C22-H16	109.5
H17-C22-H16	109.5	H18-C22-H16	109.5
C24-C23-N1	108.3(3)	C24-C23-H20	110.0
N1-C23-H20	110.0	C24-C23-H19	110.0
N1-C23-H19	110.0	H20-C23-H19	108.4
O1-C1-H3	109.5	O1-C1-H1	109.5
H3-C1-H1	109.5	O1-C1-H2	109.5
H3-C1-H2	109.5	H1-C1-H2	109.5
C23-C24-H22	109.5	C23-C24-H23	109.5
H22-C24-H23	109.5	C23-C24-H21	109.5
H22-C24-H21	109.5	H23-C24-H21	109.5

Table S15. Anisotropic atomic displacement parameters (Å^2) for **6**.

The anisotropic atomic 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}
S	0.0548(4)	0.0507(4)	0.0726(5)	0.0309(3)	0.0181(3)	0.0121(3)
O4	0.0519(9)	0.0334(8)	0.0417(8)	0.0048(6)	0.0010(7)	0.0055(7)
O3	0.0745(12)	0.0357(9)	0.0598(11)	0.0080(7)	-0.0014(9)	-0.0053(8)
N3	0.0456(11)	0.0617(13)	0.0499(12)	0.0213(10)	0.0098(9)	0.0118(9)
N2	0.0412(10)	0.0472(10)	0.0480(11)	0.0169(9)	0.0069(8)	0.0105(8)
O2	0.1150(18)	0.0776(14)	0.0598(12)	0.0344(11)	0.0261(12)	0.0346(13)
C15	0.0387(11)	0.0328(10)	0.0400(11)	0.0086(8)	0.0041(9)	0.0142(9)
N1	0.0715(14)	0.0571(13)	0.0419(11)	0.0076(9)	0.0152(10)	-0.0006(11)
C12	0.0382(11)	0.0346(11)	0.0472(12)	0.0132(9)	0.0024(9)	0.0130(9)
C16	0.0391(11)	0.0321(10)	0.0423(11)	0.0069(8)	-0.0011(9)	0.0119(8)
O1	0.1033(17)	0.0904(16)	0.0610(13)	0.0047(11)	0.0232(12)	0.0288(13)
C14	0.0422(11)	0.0344(10)	0.0413(11)	0.0069(9)	0.0037(9)	0.0147(9)
C13	0.0474(12)	0.0352(11)	0.0453(12)	0.0114(9)	-0.0013(10)	0.0106(10)
C19	0.0462(12)	0.0430(12)	0.0372(11)	0.0036(9)	0.0021(9)	0.0118(10)
C17	0.0454(12)	0.0330(11)	0.0418(12)	0.0025(9)	0.0039(9)	0.0129(9)
C11	0.0377(11)	0.0406(11)	0.0505(13)	0.0157(10)	0.0028(9)	0.0137(9)
C20	0.0414(12)	0.0461(12)	0.0422(12)	0.0104(10)	0.0062(9)	0.0118(10)
C6	0.0413(12)	0.0605(15)	0.0417(12)	0.0166(11)	0.0031(9)	0.0056(10)
C18	0.0419(11)	0.0352(11)	0.0453(12)	0.0081(9)	0.0051(9)	0.0076(9)
C9	0.0412(12)	0.0548(14)	0.0512(13)	0.0223(11)	0.0073(10)	0.0141(10)
C8	0.0410(12)	0.0625(15)	0.0404(12)	0.0181(11)	0.0036(9)	0.0069(11)
C10	0.0498(13)	0.0419(12)	0.0642(15)	0.0192(11)	0.0107(11)	0.0140(10)
C7	0.0595(15)	0.0662(16)	0.0484(14)	0.0217(12)	0.0072(11)	0.0129(13)
C4	0.0635(16)	0.0644(17)	0.0604(16)	0.0144(13)	0.0080(13)	0.0161(13)
C5	0.0580(15)	0.0649(16)	0.0483(14)	0.0221(12)	0.0101(11)	0.0121(12)
C21	0.0592(16)	0.0643(16)	0.0512(15)	0.0173(12)	0.0113(12)	-0.0072(13)
C3	0.0563(15)	0.0748(18)	0.0493(15)	0.0059(13)	0.0090(12)	0.0104(13)
C2	0.080(2)	0.082(2)	0.0450(15)	0.0226(14)	0.0172(13)	0.0182(16)
C22	0.091(2)	0.0687(19)	0.073(2)	0.0230(15)	-0.0010(17)	0.0092(17)
C23	0.106(3)	0.075(2)	0.084(2)	0.0316(18)	0.037(2)	0.0218(19)
C1	0.098(3)	0.090(2)	0.087(2)	-0.0063(19)	0.020(2)	0.028(2)
C24	0.121(3)	0.130(4)	0.114(3)	0.052(3)	0.024(3)	0.053(3)

Table S16. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **6**.

	x/a	y/b	z/c	U(eq)
H7	0.6316	0.5135	0.1180	0.12
H10	0.2037	0.3485	0.4200	0.046
H13	0.0457	0.5041	0.7122	0.051
H11	-0.0302	0.1316	0.4769	0.048
H12	-0.1768	0.0505	0.5833	0.049
H8	0.5559	0.2946	0.2689	0.058
H9	0.5343	0.8821	0.4464	0.061
H6	0.6332	0.0483	0.2073	0.069
H5	0.7117	-0.1114	0.1015	0.075
H14	-0.3108	-0.0081	0.6810	0.074
H15	-0.3095	0.0264	0.7742	0.074
H4	0.7313	0.2574	-0.0276	0.082
H17	-0.0446	-0.0693	0.6919	0.119
H18	-0.1849	-0.1909	0.7333	0.119
H16	-0.0493	-0.0407	0.7850	0.119
H20	-0.0861	0.2312	0.8497	0.104
H19	0.0422	0.3671	0.8095	0.104
H3	0.8819	-0.1835	-0.0003	0.139
H1	0.8256	-0.2307	-0.0915	0.139
H2	0.6873	-0.2608	-0.0283	0.139
H22	-0.1678	0.4964	0.7942	0.172
H23	-0.1341	0.4861	0.8843	0.172
H21	-0.2948	0.3615	0.8348	0.172

Crystal Structure Report for 7

A **dark orange rod-like** specimen of **$C_{27}H_{30}N_4O_3S$**, approximate dimensions **0.070** mm x **0.400** mm x **0.700** mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 VENTURE system equipped with a multilayer monochromator and a Mo Kα Sealed tube (λ = 0.71073 Å).

Table S17. Data collection details for **7**.

Axis	dx/mm	2θ/°	ω/°	ϕ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	48.557	12.88	-168.62	-11.97	54.70	1.00	183	4.00	0.71076	50	30.0	311
Omega	48.557	55.71	-125.79	149.07	54.70	1.00	183	4.00	0.71076	50	30.0	311
Omega	48.557	11.77	-168.73	-144.00	54.70	1.00	181	4.00	0.71076	50	30.0	311
Omega	48.557	12.88	-168.62	-98.68	54.70	1.00	183	4.00	0.71076	50	30.0	311
Omega	48.557	11.77	-168.73	72.00	54.70	1.00	181	4.00	0.71076	50	30.0	311
Omega	48.557	11.77	-168.73	-72.00	54.70	1.00	181	4.00	0.71076	50	30.0	311
Phi	48.557	11.77	-169.85	0.00	54.70	1.00	360	4.00	0.71076	50	30.0	311

A total of 1452 frames were collected. The total exposure time was 1.61 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a **triclinic** unit cell yielded a total of **39732** reflections to a maximum θ angle of **28.34°** (**0.75** Å resolution), of which **6282** were independent (average redundancy **6.325**, completeness = **99.8**%, R_{int} = **3.74**%, R_{sig} = **3.10**%) and **4283** (**68.18**%) were greater than $2\sigma(F^2)$. The final cell constants of a = **7.6487(14)** Å, b = **8.7524(14)** Å, c = **20.607(3)** Å, α = **94.791(7)°**, β = **100.141(7)°**, γ = **109.862(7)°**, volume = **1261.8(4)** $Å^3$, are based upon the refinement of the XYZ-centroids of 9902 reflections above 20 σ(I) with **5.009°** < 2θ < **56.51°**. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was **0.922**. The calculated minimum and maximum transmission coefficients (based on crystal size) are **0.8940** and **0.9890**.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group **P -1**, with Z = **2** for the formula unit, **$C_{27}H_{30}N_4O_3S$**. The final anisotropic full-matrix least-squares refinement on F^2 with **342** variables converged at R1 = **5.60**%, for the observed data and wR2 = **16.64**% for all data. The goodness-of-fit was **1.020**. The largest peak in the final difference electron density synthesis was **0.416** $e^-/Å^3$ and the largest hole was **-0.312** $e^-/Å^3$ with an RMS deviation of 0.052 $e^-/Å^3$. On the basis of the final model, the calculated density was **1.291** g/cm^3 and F(000), **520** e^-.

Table S18. Sample and crystal data for **7**.

Identification code	Compound 7	
Chemical formula	$C_{27}H_{30}N_4O_3S$	
Formula weight	490.61 g/mol	
Temperature	311(0) K	
Wavelength	0.71073 Å	
Crystal size	0.070 x 0.400 x 0.700 mm	
Crystal habit	dark orange rod	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.6487(14) Å	α = 94.791(7)°
	b = 8.7524(14) Å	β = 100.141(7)°
	c = 20.607(3) Å	γ = 109.862(7)°
Volume	1261.8(4) $Å^3$	
Z	2	
Density (calculated)	1.291 g/cm^3	
Absorption coefficient	0.164 mm^{-1}	
F(000)	520	

Table S19. Data collection and structure refinement for **7.**

Diffractometer	Bruker D8 VENTURE
Radiation source	Sealed tube, Mo Kα
Theta range for data collection	2.50 to 28.34°
Index ranges	-10<=h<=10, -11<=k<=11, -27<=l<=27
Reflections collected	39732
Independent reflections	6282 [R(int) = 0.0374]
Coverage of independent reflections	99.8%
Absorption correction	multi-scan
Max. and min. transmission	0.9890 and 0.8940
Structure solution technique	direct methods
Structure solution program	SHELXS-1997 (Sheldrick, 1997)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6282 / 380 / 342
Goodness-of-fit on F^2	1.020
Final R indices	4283 data; I>2σ(I) R1 = 0.0560, wR2 = 0.1475
	all data R1 = 0.0902, wR2 = 0.1664
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0829P)^2+0.5104P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.416 and -0.312 eÅ^{-3}
R.M.S. deviation from mean	0.052 eÅ^{-3}

Table S20. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **7.** U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
S	0.94363(8)	0.18159(7)	0.30569(3)	0.05352(19)
O1	0.35052(18)	0.64462(15)	0.56584(6)	0.0348(3)
O2	0.1247(2)	0.40439(17)	0.52530(7)	0.0477(4)
N2	0.2697(2)	0.41767(18)	0.33398(7)	0.0336(3)
N1	0.8359(2)	0.1565(2)	0.66991(8)	0.0391(4)
N3	0.1823(3)	0.2693(2)	0.22225(8)	0.0426(4)
O3	0.0732(2)	0.1411(3)	0.09681(8)	0.0746(6)
C12	0.3058(2)	0.5365(2)	0.44905(8)	0.0286(4)
C10	0.5608(2)	0.7946(2)	0.50023(9)	0.0294(4)
C5	0.7460(2)	0.0378(2)	0.61515(9)	0.0314(4)
C9	0.5031(2)	0.7799(2)	0.56056(9)	0.0293(4)
C15	0.0220(2)	0.2891(2)	0.38517(9)	0.0323(4)
C7	0.5894(3)	0.8962(2)	0.61680(9)	0.0327(4)
C11	0.4569(2)	0.6696(2)	0.44500(9)	0.0307(4)
C6	0.8082(3)	0.0533(2)	0.55394(9)	0.0340(4)
C14	0.1963(3)	0.4108(2)	0.39075(9)	0.0325(4)
C16	0.1527(3)	0.3038(2)	0.28605(9)	0.0363(4)
C8	0.7178(3)	0.9359(2)	0.49931(9)	0.0338(4)
C2	0.9914(3)	0.3080(2)	0.66735(10)	0.0400(5)
C13	0.2494(3)	0.5184(2)	0.51280(9)	0.0339(4)
C17	0.3536(3)	0.3261(3)	0.21276(10)	0.0451(5)
C18	0.3987(3)	0.2983(3)	0.14959(10)	0.0452(5)
C3	0.7822(3)	0.1366(3)	0.73388(10)	0.0475(5)
C20	0.2567(3)	0.2059(3)	0.09290(10)	0.0471(5)
C1	0.1836(3)	0.2908(3)	0.67973(12)	0.0566(6)
C21	0.3017(3)	0.1783(3)	0.03239(11)	0.0536(6)
C23	0.4887(4)	0.2421(3)	0.02408(12)	0.0612(7)
N4	0.5329(3)	0.2110(4)	0.96439(11)	0.0898(9)
C19	0.5850(4)	0.3603(3)	0.14020(12)	0.0659(7)
C22	0.6316(4)	0.3371(4)	0.08064(13)	0.0750(9)
C24	0.3893(4)	0.0974(4)	0.90818(13)	0.0702(8)
C4	0.6161(4)	0.1880(4)	0.73966(14)	0.0696(8)
C26	0.2774(6)	0.1760(5)	0.86740(17)	0.0960(11)
C27	0.7394(13)	0.2419(9)	0.9572(3)	0.068(3)
C28	0.794(2)	0.4064(11)	0.9321(5)	0.116(4)
C25	0.6962(11)	0.3442(10)	0.9445(3)	0.057(2)
C29	0.8528(12)	0.2740(10)	0.9473(4)	0.085(3)

Table S21. Bond lengths (Å) for **7**.

S-C15	1.7148(18)	S-C16	1.733(2)
O1-C9	1.379(2)	O1-C13	1.391(2)
O2-C13	1.206(2)	N2-C16	1.299(2)
N2-C14	1.381(2)	N1-C5	1.368(2)
N1-C3	1.455(3)	N1-C2	1.462(2)
N3-C17	1.291(3)	N3-C16	1.398(2)
O3-C20	1.343(3)	O3-H17	0.82
C12-C11	1.355(2)	C12-C13	1.457(2)
C12-C14	1.468(2)	C10-C9	1.392(2)
C10-C8	1.405(2)	C10-C11	1.416(2)
C5-C7	1.408(3)	C5-C6	1.425(2)
C9-C7	1.376(2)	C15-C14	1.374(3)
C15-H15	0.93	C7-H11	0.93
C11-H14	0.93	C6-C8	1.361(3)
C6-H12	0.93	C8-H13	0.93
C2-C1	1.507(3)	C2-H5	0.97
C2-H4	0.97	C17-C18	1.426(3)
C17-H16	0.93	C18-C19	1.397(3)
C18-C20	1.414(3)	C3-C4	1.505(4)
C3-H6	0.97	C3-H7	0.97
C20-C21	1.374(3)	C1-H3	0.96
C1-H2	0.96	C1-H1	0.96
C21-C23	1.395(3)	C21-H20	0.93
C23-N4	1.362(3)	C23-C22	1.420(3)
N4-C24	1.468(3)	N4-C25	1.536(9)
N4-C27	1.546(10)	C19-C22	1.355(3)
C19-H18	0.93	C22-H19	0.93
C24-C26	1.468(5)	C24-H25	0.97
C24-H24	0.97	C4-H8	0.96
C4-H9	0.96	C4-H10	0.96
C26-H21	0.96	C26-H22	0.96
C26-H23	0.96	C27-C25	1.090(9)
C27-H28	0.97	C27-H26	0.97
C28-C29	1.418(11)	C28-H34	0.96
C28-H1B	0.96	C28-H30	0.96
C25-H29	0.97	C25-H32	0.97
C29-H31	0.96	C29-H33	0.96
C29-H27	0.96		

Table S22. Bond angles (°) for **7**.

C15-S-C16	89.23(9)	C9-O1-C13	122.65(13)
C16-N2-C14	110.29(16)	C5-N1-C3	121.28(16)
C5-N1-C2	121.88(15)	C3-N1-C2	116.83(16)
C17-N3-C16	118.48(17)	C20-O3-H17	109.5
C11-C12-C13	119.18(16)	C11-C12-C14	121.67(16)
C13-C12-C14	119.15(16)	C9-C10-C8	116.32(16)
C9-C10-C11	118.33(16)	C8-C10-C11	125.34(16)
N1-C5-C7	121.72(16)	N1-C5-C6	120.83(16)
C7-C5-C6	117.45(16)	C7-C9-O1	116.61(15)
C7-C9-C10	123.34(16)	O1-C9-C10	120.05(15)
C14-C15-S	109.72(13)	C14-C15-H15	125.1
S-C15-H15	125.1	C9-C7-C5	119.80(16)
C9-C7-H11	120.1	C5-C7-H11	120.1
C12-C11-C10	122.47(16)	C12-C11-H14	118.8
C10-C11-H14	118.8	C8-C6-C5	120.85(17)
C8-C6-H12	119.6	C5-C6-H12	119.6
C15-C14-N2	115.44(16)	C15-C14-C12	126.83(16)
N2-C14-C12	117.67(16)	N2-C16-N3	126.45(18)
N2-C16-S	115.29(14)	N3-C16-S	118.24(14)
C6-C8-C10	122.23(16)	C6-C8-H13	118.9
C10-C8-H13	118.9	N1-C2-C1	113.13(18)
N1-C2-H5	109.0	C1-C2-H5	109.0
N1-C2-H4	109.0	C1-C2-H4	109.0
H5-C2-H4	107.8	O2-C13-O1	115.52(16)
O2-C13-C12	127.23(18)	O1-C13-C12	117.25(15)
N3-C17-C18	122.83(19)	N3-C17-H16	118.6
C18-C17-H16	118.6	C19-C18-C20	116.23(19)
C19-C18-C17	122.11(19)	C20-C18-C17	121.7(2)
N1-C3-C4	112.66(19)	N1-C3-H6	109.1
C4-C3-H6	109.1	N1-C3-H7	109.1
C4-C3-H7	109.1	H6-C3-H7	107.8
O3-C20-C21	118.0(2)	O3-C20-C18	120.76(19)
C21-C20-C18	121.3(2)	C2-C1-H3	109.5
C2-C1-H2	109.5	H3-C1-H2	109.5
C2-C1-H1	109.5	H3-C1-H1	109.5
H2-C1-H1	109.5	C20-C21-C23	121.5(2)
C20-C21-H20	119.2	C23-C21-H20	119.2
N4-C23-C21	121.2(2)	N4-C23-C22	121.3(2)
C21-C23-C22	117.5(2)	C23-N4-C24	121.3(2)
C23-N4-C25	118.4(3)	C24-N4-C25	114.8(3)
C23-N4-C27	122.6(3)	C24-N4-C27	113.1(3)

C25-N4-C27	41.4(3)	C22-C19-C18	123.3(2)
C22-C19-H18	118.3	C18-C19-H18	118.3
C19-C22-C23	120.2(2)	C19-C22-H19	119.9
C23-C22-H19	119.9	N4-C24-C26	113.4(3)
N4-C24-H25	108.9	C26-C24-H25	108.9
N4-C24-H24	108.9	C26-C24-H24	108.9
H25-C24-H24	107.7	C3-C4-H8	109.5
C3-C4-H9	109.5	H8-C4-H9	109.5
C3-C4-H10	109.5	H8-C4-H10	109.5
H9-C4-H10	109.5	C24-C26-H21	109.5
C24-C26-H22	109.5	H21-C26-H22	109.5
C24-C26-H23	109.5	H21-C26-H23	109.5
H22-C26-H23	109.5	C25-C27-N4	68.8(7)
C25-C27-H28	116.8	N4-C27-H28	116.8
C25-C27-H26	116.8	N4-C27-H26	116.8
H28-C27-H26	113.8	C29-C28-H34	109.5
C29-C28-H1B	109.5	H34-C28-H1B	109.5
C29-C28-H30	109.5	H34-C28-H30	109.5
H1B-C28-H30	109.5	C27-C25-N4	69.8(7)
C27-C25-H29	116.7	N4-C25-H29	116.7
C27-C25-H32	116.7	N4-C25-H32	116.7
H29-C25-H32	113.7	C28-C29-H31	109.5
C28-C29-H33	109.5	H31-C29-H33	109.5
C28-C29-H27	109.5	H31-C29-H27	109.5
H33-C29-H27	109.5		

Table S23. Anisotropic atomic displacement parameters (Å^2) for **7**.

The anisotropic atomic 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}
S	0.0453(3)	0.0527(3)	0.0478(3)	-0.0065(2)	0.0114(2)	0.0019(2)
O1	0.0349(7)	0.0387(7)	0.0304(6)	0.0060(5)	0.0148(5)	0.0089(6)
O2	0.0499(9)	0.0437(8)	0.0450(8)	0.0093(6)	0.0216(7)	0.0052(7)
N2	0.0393(8)	0.0330(8)	0.0294(8)	0.0039(6)	0.0091(6)	0.0135(7)
N1	0.0398(9)	0.0407(9)	0.0331(8)	-0.0009(7)	0.0127(7)	0.0091(7)
N3	0.0496(10)	0.0421(9)	0.0312(8)	-0.0004(7)	0.0084(7)	0.0120(8)
O3	0.0466(10)	0.1141(16)	0.0399(9)	-0.0152(9)	0.0133(7)	0.0042(10)
C12	0.0298(8)	0.0328(9)	0.0272(8)	0.0062(7)	0.0084(7)	0.0150(7)
C10	0.0298(8)	0.0336(9)	0.0289(9)	0.0069(7)	0.0101(7)	0.0143(7)
C5	0.0309(9)	0.0354(9)	0.0309(9)	0.0035(7)	0.0077(7)	0.0158(7)
C9	0.0266(8)	0.0323(9)	0.0325(9)	0.0081(7)	0.0106(7)	0.0125(7)
C15	0.0291(9)	0.0319(9)	0.0328(9)	-0.0002(7)	0.0107(7)	0.0065(7)
C7	0.0353(9)	0.0387(10)	0.0284(9)	0.0054(7)	0.0129(7)	0.0156(8)
C11	0.0319(9)	0.0374(9)	0.0262(8)	0.0063(7)	0.0113(7)	0.0142(7)
C6	0.0326(9)	0.0336(9)	0.0367(10)	0.0073(8)	0.0133(8)	0.0099(7)
C14	0.0382(10)	0.0318(9)	0.0322(9)	0.0060(7)	0.0101(8)	0.0174(8)
C16	0.0403(10)	0.0350(10)	0.0327(9)	0.0033(8)	0.0074(8)	0.0131(8)
C8	0.0342(9)	0.0389(10)	0.0307(9)	0.0073(7)	0.0146(7)	0.0122(8)
C2	0.0451(11)	0.0327(10)	0.0375(10)	-0.0016(8)	0.0071(9)	0.0108(8)
C13	0.0334(9)	0.0364(10)	0.0348(9)	0.0064(8)	0.0119(8)	0.0140(8)
C17	0.0523(13)	0.0399(11)	0.0328(10)	-0.0030(8)	0.0058(9)	0.0075(9)
C18	0.0515(12)	0.0400(11)	0.0347(10)	-0.0019(8)	0.0101(9)	0.0061(9)
C3	0.0588(13)	0.0481(12)	0.0296(10)	0.0015(9)	0.0093(9)	0.0129(10)
C20	0.0475(12)	0.0506(12)	0.0358(10)	0.0023(9)	0.0105(9)	0.0088(10)
C1	0.0400(12)	0.0678(15)	0.0526(14)	0.0054(11)	0.0054(10)	0.0107(11)
C21	0.0517(13)	0.0640(14)	0.0319(10)	-0.0040(10)	0.0098(9)	0.0067(11)
C23	0.0563(14)	0.0690(16)	0.0402(12)	-0.0035(11)	0.0173(11)	-0.0007(12)
N4	0.0594(14)	0.132(2)	0.0426(12)	-0.0175(13)	0.0243(10)	-0.0100(14)
C19	0.0536(14)	0.0702(16)	0.0446(13)	-0.0153(12)	0.0092(11)	-0.0079(12)
C22	0.0514(14)	0.090(2)	0.0510(14)	-0.0131(13)	0.0195(12)	-0.0134(13)
C24	0.0663(17)	0.092(2)	0.0440(13)	-0.0017(13)	0.0219(12)	0.0162(15)
C4	0.086(2)	0.0759(18)	0.0633(16)	0.0110(14)	0.0435(15)	0.0364(15)
C26	0.112(3)	0.112(3)	0.068(2)	0.0243(19)	0.032(2)	0.037(2)
C27	0.070(6)	0.078(4)	0.051(3)	0.005(3)	0.023(3)	0.020(4)
C28	0.129(9)	0.078(5)	0.099(6)	0.031(4)	0.016(5)	-0.016(5)
C25	0.069(4)	0.048(4)	0.045(3)	0.004(2)	0.026(3)	0.006(3)
C29	0.050(4)	0.101(5)	0.096(5)	0.002(4)	0.033(3)	0.012(3)

Table S24. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **7**.

	x/a	y/b	z/c	U(eq)
H17	0.0621	0.1710	0.1341	0.112
H15	-0.0437	0.2681	0.4193	0.039
H11	0.5445	0.8814	0.6558	0.039
H14	0.4939	0.6792	0.4044	0.037
H12	0.9119	1.1449	0.5513	0.041
H13	0.7614	0.9496	0.4600	0.041
H5	0.9938	1.3945	0.7005	0.048
H4	0.9671	1.3407	0.6238	0.048
H16	0.4518	0.3878	0.2486	0.054
H6	0.8905	1.2017	0.7693	0.057
H7	0.7497	1.0222	0.7398	0.057
H3	1.2135	1.2676	0.7242	0.085
H2	1.2787	1.3915	0.6748	0.085
H1	1.1809	1.2026	0.6481	0.085
H20	0.2053	0.1157	-0.0039	0.064
H18	0.6819	0.4205	0.1767	0.079
H19	0.7575	0.3835	0.0768	0.09
H25	0.3034	0.0086	-0.0746	0.084
H24	0.4526	0.0496	-0.1199	0.084
H8	0.6502	1.3030	0.7367	0.104
H9	0.5829	1.1683	0.7818	0.104
H10	0.5091	1.1256	0.7041	0.104
H21	0.2042	0.2139	-0.1063	0.144
H22	0.1931	0.0979	-0.1703	0.144
H23	0.3617	0.2676	-0.1479	0.144
H28	0.8344	0.2624	-0.0019	0.081
H26	0.7556	0.1739	-0.0793	0.081
H34	0.7613	0.4507	-0.0294	0.175
H1B	0.6842	0.3675	-0.1043	0.175
H30	0.8951	0.4905	-0.0801	0.175
H29	0.6784	0.3584	-0.1021	0.068
H32	0.7572	0.4468	-0.0248	0.068
H31	0.9809	0.2982	-0.0584	0.127
H33	0.7698	0.1753	-0.0822	0.127
H27	0.8478	0.2590	-0.0074	0.127

Crystal Structure Report for 9

A **dark orange rod-like** specimen of **$C_{24}H_{23}N_3O_3S$**, approximate dimensions **0.200** mm x **0.400** mm x **0.800** mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 VENTURE system equipped with a multilayer monochromator and a Mo Kα Sealed tube (λ = 0.71073 Å).

Table S25. Data collection details for **9**.

Axis	dx/mm	2θ/°	ω/°	ϕ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	52.054	13.85	-169.65	-144.00	54.70	1.00	187	10.00	0.71076	50	30.0	303
Omega	52.054	14.95	-169.55	10.12	54.70	1.00	189	10.00	0.71076	50	30.0	303
Omega	52.054	13.85	-169.65	72.00	54.70	1.00	187	10.00	0.71076	50	30.0	303
Omega	52.054	56.31	-128.19	-161.80	54.70	1.00	189	10.00	0.71076	50	30.0	303
Omega	52.054	13.85	-169.65	-72.00	54.70	1.00	187	10.00	0.71076	50	30.0	303
Omega	52.054	13.85	-169.65	144.00	54.70	1.00	187	10.00	0.71076	50	30.0	303
Omega	52.054	14.95	-169.55	-40.44	54.70	1.00	189	10.00	0.71076	50	30.0	303
Phi	52.054	13.85	18.60	0.00	54.70	1.00	360	10.00	0.71076	50	30.0	303

A total of 1675 frames were collected. The total exposure time was 4.65 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a **triclinic** unit cell yielded a total of **42764** reflections to a maximum θ angle of **26.58°** (**0.79** Å resolution), of which **4415** were independent (average redundancy **9.686**, completeness = **99.0**%, R_{int} = **6.28**%, R_{sig} = **3.29**%) and 3188 (**72.21**%) were greater than 2σ(F^2). The final cell constants of a = **8.569(2)** Å, b = **11.153(3)** Å, c = **12.206(3)** Å, α = **101.257(9)°**, β = **91.058(9)°**, γ = **110.621(9)°**, volume = **1065.9(4)** $Å^3$, are based upon the refinement of the XYZ-centroids of **9954** reflections above 20 σ(I) with **4.665°** < 2θ < **52.08°**. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was **0.950**. The calculated minimum and maximum transmission coefficients (based on crystal size) are **0.8670** and **0.9640**.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group **P -1**, with Z = **2** for the formula unit, **$C_{24}H_{23}N_3O_3S$**. The final anisotropic full-matrix least-squares refinement on F^2 with **284** variables converged at R1 = **4.55**%, for the observed data and wR2 = **12.79**% for all data. The goodness-of-fit was **1.012**. The largest peak in the final difference electron density synthesis was **0.247** $e^-/Å^3$ and the largest hole was **-0.161** $e^-/Å^3$ with an RMS deviation of **0.044** $e^-/Å^3$. On the basis of the final model, the calculated density was **1.351** g/cm^3 and F(000), **456** e^-.

Table S26. Sample and crystal data for **9**.

Identification code	Compound 9	
Chemical formula	$C_{24}H_{23}N_3O_3S$	
Formula weight	433.51 g/mol	
Temperature	303(2) K	
Wavelength	0.71073 Å	
Crystal size	0.200 x 0.400 x 0.800 mm	
Crystal habit	dark orange rod	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.569(2) Å	α = 101.257(9)°
	b = 11.153(3) Å	β = 91.058(9)°
	c = 12.206(3) Å	γ = 110.621(9)°
Volume	1065.9(4) $Å^3$	
Z	2	
Density (calculated)	1.351 g/cm^3	
Absorption coefficient	0.184 mm^{-1}	
F(000)	456	

Table S27. Data collection and structure refinement for **9**.

Diffractometer	Bruker D8 VENTURE
Radiation source	Sealed tube, Mo Kα
Theta range for data collection	2.33 to 26.58°
Index ranges	-10<=h<=10, -13<=k<=14, -15<=l<=15
Reflections collected	42764
Independent reflections	4415 [R(int) = 0.0628]
Coverage of independent reflections	99.0%
Absorption correction	multi-scan
Max. and min. transmission	0.9640 and 0.8670
Structure solution technique	direct methods
Structure solution program	SHELXS-1997 (Sheldrick, 1997)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4415 / 0 / 284
Goodness-of-fit on F^2	1.012
Δ/σ_{max}	0.006
Final R indices	3188 data; I>2σ(I) R1 = 0.0455, wR2 = 0.1129
	all data R1 = 0.0722, wR2 = 0.1279
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0594P)^2+0.3735P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.247 and -0.161 eÅ^{-3}
R.M.S. deviation from mean	0.044 eÅ^{-3}

Table S28. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **9**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
S1	0.85032(7)	0.87220(5)	0.55833(5)	0.05333(18)
O3	0.40824(16)	0.43031(12)	0.76403(11)	0.0430(3)
O1	0.1342(2)	0.87819(14)	0.23665(14)	0.0622(4)
O2	0.4723(2)	0.63991(14)	0.77028(13)	0.0607(4)
N2	0.78738(19)	0.62489(15)	0.50344(12)	0.0393(4)
N3	0.96554(19)	0.75026(15)	0.38400(13)	0.0427(4)
N1	0.2823(2)	0.98941(16)	0.79828(15)	0.0532(5)
C10	0.5302(2)	0.29867(17)	0.64112(15)	0.0378(4)
C9	0.4262(2)	0.31128(17)	0.72547(15)	0.0371(4)
C13	0.6072(2)	0.53029(17)	0.63950(14)	0.0368(4)
C14	0.7039(2)	0.64582(17)	0.59663(15)	0.0382(4)
C18	0.0758(2)	0.64874(18)	0.22873(16)	0.0412(4)
C16	0.8685(2)	0.73483(18)	0.47462(16)	0.0400(4)
C12	0.4967(2)	0.54202(18)	0.72656(16)	0.0413(4)
C7	0.4611(2)	0.07348(18)	0.65730(16)	0.0456(5)
C8	0.5436(2)	0.17509(18)	0.60863(16)	0.0437(5)
C5	0.3579(2)	0.08853(18)	0.74438(16)	0.0423(4)
C17	0.9819(2)	0.64664(19)	0.32536(16)	0.0434(4)
C19	0.0982(2)	0.53353(19)	0.17419(16)	0.0466(5)
C6	0.3391(2)	0.21060(18)	0.77525(16)	0.0429(4)
C11	0.6186(2)	0.41111(17)	0.59932(15)	0.0391(4)
C25	0.1501(2)	0.76301(19)	0.18843(17)	0.0460(5)
C15	0.7244(3)	0.77398(18)	0.63705(17)	0.0466(5)
C20	0.1911(3)	0.5293(2)	0.08393(17)	0.0502(5)
C22	0.2420(3)	0.7587(2)	0.09664(19)	0.0597(6)
C4	0.3119(3)	0.86575(19)	0.77386(19)	0.0529(5)
C2	0.1806(3)	0.0064(2)	0.8904(2)	0.0609(6)
C21	0.2622(3)	0.6446(2)	0.04640(18)	0.0585(6)
C1	0.2829(4)	0.0799(2)	0.0012(2)	0.0742(7)
C3	0.1933(3)	0.7656(2)	0.6787(2)	0.0698(7)
C24	0.2172(3)	0.4056(3)	0.0291(2)	0.0712(7)

Table S29. Bond lengths (Å) for **9**.

S1-C15	1.704(2)	S1-C16	1.7257(19)
O3-C12	1.381(2)	O3-C9	1.382(2)
O1-C25	1.359(2)	O1-H17	0.82
O2-C12	1.207(2)	N2-C16	1.299(2)
N2-C14	1.380(2)	N3-C17	1.289(2)
N3-C16	1.397(2)	N1-C5	1.367(2)
N1-C2	1.459(3)	N1-C4	1.464(2)
C10-C9	1.393(3)	C10-C8	1.403(2)
C10-C11	1.415(3)	C9-C6	1.371(3)
C13-C11	1.362(2)	C13-C12	1.454(3)
C13-C14	1.466(3)	C14-C15	1.364(3)
C18-C25	1.399(3)	C18-C19	1.406(3)
C18-C17	1.439(3)	C7-C8	1.361(3)
C7-C5	1.418(3)	C7-H11	0.93
C8-H13	0.93	C5-C6	1.406(3)
C17-H16	0.93	C19-C20	1.375(3)
C19-H18	0.93	C6-H12	0.93
C11-H14	0.93	C25-C22	1.384(3)
C15-H15	0.93	C20-C21	1.387(3)
C20-C24	1.504(3)	C22-C21	1.371(3)
C22-H23	0.93	C4-C3	1.510(3)
C4-H6	0.97	C4-H7	0.97
C2-C1	1.513(4)	C2-H5	0.97
C2-H4	0.97	C21-H22	0.93
C1-H3	0.96	C1-H2	0.96
C1-H1	0.96	C3-H8	0.96
C3-H9	0.96	C3-H10	0.96
C24-H20	0.96	C24-H21	0.96
C24-H19	0.96		

Table S30. Bond angles (°) for **9**.

C15-S1-C16	88.98(9)	C12-O3-C9	122.72(14)
C25-O1-H17	109.5	C16-N2-C14	110.74(16)
C17-N3-C16	117.36(16)	C5-N1-C2	121.44(16)
C5-N1-C4	121.78(17)	C2-N1-C4	116.54(16)
C9-C10-C8	116.21(17)	C9-C10-C11	118.10(16)
C8-C10-C11	125.62(17)	C6-C9-O3	116.57(15)
C6-C9-C10	123.38(16)	O3-C9-C10	120.05(16)
C11-C13-C12	118.92(16)	C11-C13-C14	121.26(16)
C12-C13-C14	119.83(16)	C15-C14-N2	114.38(17)
C15-C14-C13	128.65(17)	N2-C14-C13	116.97(16)
C25-C18-C19	118.37(18)	C25-C18-C17	122.20(18)
C19-C18-C17	119.40(17)	N2-C16-N3	126.23(17)
N2-C16-S1	115.07(14)	N3-C16-S1	118.69(13)
O2-C12-O3	115.46(16)	O2-C12-C13	126.94(17)
O3-C12-C13	117.59(15)	C8-C7-C5	121.05(17)
C8-C7-H11	119.5	C5-C7-H11	119.5
C7-C8-C10	122.06(17)	C7-C8-H13	119.0
C10-C8-H13	119.0	N1-C5-C6	121.06(17)
N1-C5-C7	121.46(17)	C6-C5-C7	117.46(17)
N3-C17-C18	122.87(17)	N3-C17-H16	118.6
C18-C17-H16	118.6	C20-C19-C18	122.65(19)
C20-C19-H18	118.7	C18-C19-H18	118.7
C9-C6-C5	119.77(17)	C9-C6-H12	120.1
C5-C6-H12	120.1	C13-C11-C10	122.53(16)
C13-C11-H14	118.7	C10-C11-H14	118.7
O1-C25-C22	119.01(18)	O1-C25-C18	121.84(18)
C22-C25-C18	119.14(19)	C14-C15-S1	110.83(15)
C14-C15-H15	124.6	S1-C15-H15	124.6
C19-C20-C21	117.1(2)	C19-C20-C24	121.6(2)
C21-C20-C24	121.3(2)	C21-C22-C25	120.7(2)
C21-C22-H23	119.6	C25-C22-H23	119.6
N1-C4-C3	112.82(18)	N1-C4-H6	109.0
C3-C4-H6	109.0	N1-C4-H7	109.0
C3-C4-H7	109.0	H6-C4-H7	107.8
N1-C2-C1	113.5(2)	N1-C2-H5	108.9
C1-C2-H5	108.9	N1-C2-H4	108.9
C1-C2-H4	108.9	H5-C2-H4	107.7
C22-C21-C20	122.0(2)	C22-C21-H22	119.0
C20-C21-H22	119.0	C2-C1-H3	109.5
C2-C1-H2	109.5	H3-C1-H2	109.5
C2-C1-H1	109.5	H3-C1-H1	109.5
H2-C1-H1	109.5	C4-C3-H8	109.5
C4-C3-H9	109.5	H8-C3-H9	109.5
C4-C3-H10	109.5	H8-C3-H10	109.5
H9-C3-H10	109.5	C20-C24-H20	109.5
C20-C24-H21	109.5	H20-C24-H21	109.5
C20-C24-H19	109.5	H20-C24-H19	109.5
H21-C24-H19	109.5		

Table S31. Anisotropic atomic displacement parameters (Å^2) for **9**.

The anisotropic atomic 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}
S1	0.0633(4)	0.0342(3)	0.0611(4)	0.0100(2)	0.0199(3)	0.0155(2)
O3	0.0531(8)	0.0379(7)	0.0459(7)	0.0124(6)	0.0184(6)	0.0236(6)
O1	0.0744(11)	0.0468(9)	0.0773(11)	0.0281(8)	0.0285(9)	0.0277(8)
O2	0.0838(11)	0.0425(8)	0.0693(10)	0.0171(7)	0.0362(8)	0.0350(8)
N2	0.0407(9)	0.0365(8)	0.0385(8)	0.0068(7)	0.0052(7)	0.0120(7)
N3	0.0424(9)	0.0401(9)	0.0455(9)	0.0117(7)	0.0083(7)	0.0134(7)
N1	0.0662(12)	0.0377(9)	0.0625(11)	0.0178(8)	0.0188(9)	0.0226(8)
C10	0.0405(10)	0.0354(9)	0.0353(9)	0.0027(7)	0.0035(8)	0.0137(8)
C9	0.0422(10)	0.0341(9)	0.0374(10)	0.0058(8)	0.0040(8)	0.0177(8)
C13	0.0390(10)	0.0378(10)	0.0326(9)	0.0057(7)	0.0029(8)	0.0138(8)
C14	0.0394(10)	0.0372(10)	0.0363(10)	0.0058(8)	0.0030(8)	0.0131(8)
C18	0.0381(10)	0.0439(11)	0.0407(10)	0.0109(8)	0.0043(8)	0.0129(8)
C16	0.0396(10)	0.0352(10)	0.0430(10)	0.0080(8)	0.0046(8)	0.0110(8)
C12	0.0489(11)	0.0374(10)	0.0426(10)	0.0112(8)	0.0089(9)	0.0201(9)
C7	0.0519(12)	0.0322(9)	0.0505(12)	0.0011(8)	0.0056(9)	0.0169(9)
C8	0.0475(11)	0.0385(10)	0.0421(10)	0.0015(8)	0.0104(9)	0.0154(9)
C5	0.0455(11)	0.0353(10)	0.0459(11)	0.0078(8)	0.0039(9)	0.0149(8)
C17	0.0452(11)	0.0368(10)	0.0466(11)	0.0131(8)	0.0081(9)	0.0106(8)
C19	0.0484(12)	0.0428(11)	0.0457(11)	0.0081(9)	0.0033(9)	0.0138(9)
C6	0.0465(11)	0.0417(10)	0.0451(11)	0.0117(9)	0.0137(9)	0.0197(9)
C11	0.0413(10)	0.0390(10)	0.0361(10)	0.0056(8)	0.0074(8)	0.0147(8)
C25	0.0439(11)	0.0471(11)	0.0500(11)	0.0169(9)	0.0070(9)	0.0167(9)
C15	0.0522(12)	0.0393(11)	0.0483(11)	0.0079(9)	0.0132(9)	0.0171(9)
C20	0.0463(12)	0.0589(13)	0.0429(11)	0.0019(10)	0.0004(9)	0.0209(10)
C22	0.0619(14)	0.0631(14)	0.0597(14)	0.0299(12)	0.0214(11)	0.0201(12)
C4	0.0638(14)	0.0408(11)	0.0620(13)	0.0183(10)	0.0078(11)	0.0243(10)
C2	0.0651(14)	0.0467(12)	0.0828(17)	0.0313(12)	0.0330(13)	0.0242(11)
C21	0.0533(13)	0.0764(16)	0.0475(12)	0.0157(11)	0.0156(10)	0.0239(12)
C1	0.104(2)	0.0671(16)	0.0634(16)	0.0252(13)	0.0284(15)	0.0378(15)
C3	0.0778(17)	0.0449(13)	0.0802(17)	0.0108(12)	0.0033(14)	0.0161(12)
C24	0.0743(17)	0.0762(17)	0.0614(15)	-0.0076(13)	0.0050(13)	0.0371(14)

Table S32. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **9**.

	x/a	y/b	z/c	U(eq)
H17	1.0810	0.8686	0.2915	0.093
H11	0.4725	-0.0071	0.6330	0.055
H13	0.6110	0.1623	0.5521	0.052
H16	0.9309	0.5671	0.3464	0.052
H18	1.0481	0.4571	0.2002	0.056
H12	0.2679	0.2230	0.8292	0.052
H14	0.6870	0.4034	0.5422	0.047
H15	0.6763	0.8037	0.6992	0.056
H23	1.2906	0.8340	0.0688	0.072
H6	0.2997	-0.1704	0.8407	0.064
H7	0.4261	-0.1169	0.7549	0.064
H5	0.1063	-0.0793	0.8987	0.073
H4	0.1117	0.0536	0.8715	0.073
H22	1.3254	0.6446	-0.0147	0.07
H3	0.3578	0.0376	1.0179	0.111
H2	0.2094	0.0802	1.0596	0.111
H1	0.3466	0.1686	0.9966	0.111
H8	0.0802	-0.2545	0.6982	0.105
H9	0.2191	-0.3128	0.6654	0.105
H10	0.2053	-0.1995	0.6121	0.105
H20	1.3316	0.4155	0.0453	0.107
H21	1.1919	0.3891	-0.0506	0.107
H19	1.1447	0.3334	0.0576	0.107

Table S33. Hydrogen bonding parameters**.**

D-H---A	D-H	H---A	D---A	D-H---A^o
O2-H7---N3	0.82 Å	1.90 Å	2.63 Å	147.2^o
O3-H17---N3	0.82 Å	1.87 Å	2.60 Å	147.6^o
O1-H21---N1	0.82 Å	1.90 Å	2.65 Å	146.7^o
O1-H17---N3	0.82 Å	1.92 Å	2.65 Å	146.6^o

7. Computational Analysis

Table S34. The total energies (E) for the enol-imine and keto-amine forms of **4-9**.

		E (a.u)				
		Gas phase	THF	DCM	DMF	DMSO
4	Enol-imine	-1677.308861	-1677.322425	-1677.323019	-1677.325457	-1677.325627
	Keto-amine	-1677.29893	-1677.315122	-1677.315834	-1677.318761	-1677.318967
5	Enol-imine	-1791.831684	-1791.848059	-1791.848791	-1791.851807	-1791.852018
	Keto-amine	-1791.823333	-1791.84221	-1791.843064	-1791.846591	-1791.846839
6	Enol-imine	-1791.840001	-1791.855714	-1791.856402	-1791.859224	-1791.859421
	Keto-amine	-1791.829785	-1791.848796	-1791.849636	-1791.853088	-1791.85333
7	Enol-imine	-1889.929071	-1889.945677	-1889.946408	-1889.949415	-1889.949625
	Keto-amine	-1889.920557	-1889.940115	-1889.940986	-1889.944572	-1889.944824
8	Enol-imine	-2136.901418	-2136.914958	-2136.91554	-2136.91792	-2136.918086
	Keto-amine	-2136.892023	-2136.908207	-2136.908906	-2136.911765	-2136.911965
9	Enol-imine	-1716.629164	-1716.642857	-1716.643457	-1716.645917	-1716.646089
	Keto-amine	-1716.619647	-1716.635827	-1716.636538	-1716.639456	-1716.639661

Table S35. The maxima wavelength (λ), oscillator strength (f) and relevance transitions and their contributions obtained from TD-DFT calculations for **4-6** before and after deprotonation with F^-, CN^-, AcO^- and $H_2PO_4^-$.

			F^-		**CN^-**		**AcO^-**		**$H_2PO_4^-$**	
	λ (nm), f	Transition, w(%)	λ (nm), f	Transition, w(%)	λ (nm), f	Transition, w(%)	λ (nm), f	Transition, w(%)	λ (nm), f	Transition, w(%)
4	407 (0.9289)	H-1→L 12.5 H→L+1 85.3	407 (0.2556)	H-1→L 3.14 H-1→L 94.6	421 (0.2105)	H-1→L 10.1 H→L 11.8 H→L+1 74.6	416 (0.1503)	H-1→L 3.9 H→L 7.3 H→L+1 83.3	-	-
			456 (0.7494)	H→L 97.2	458 (0.6463)	H→L 87.2 H→L+1 11.3	457 (0.7413)	H→L 91.3 H→L+1 6.8	-	-
5	411 (0.5640)	H-1→L 66.0 H→L+1 31.6	416 (0.0677)	H-1→L 78.6 H→L+1 18.3	411 (0.3894)	H-1→L 82.4 H→L+1 5.7	410 (0.3356)	H-1→L 81.4 H→L+1 4.2	406 (0.7675)	H-1→L 3.8 H→L+1 91.4
			463 (0.6630)	H→L 93.9 H→L+1 3.6	476 (0.3717)	H→L 91.6 H→L+1 6.8	466 (0.4873)	H→L 84.3 H→L+1 13.2	458 (0.3857)	H→L 96.6
6	407 (0.8428)	H-1→L 11.2 H→L 2.1 H→L+1 85.8	402 (0.2519)	H-1→L 2.4 H→L 3.4 H→L+1 91.2	412 (0.2951)	H-1→L 16.7 H→L 9.8 H→L+1 68.3	404 (0.2212)	H-1→L 8.5 H→L 10.5 H→L+1 74.6	-	-
			448 (0.8232)	H→L 93.7 H→L+1 3.8	452 (0.6364)	H→L 87.8 H→L+1 10.8	447 (0.7865)	H→L 86.58 H→L+1 11.2	-	-

Table S36. The maxima wavelength (λ), oscillator strength (f) and relevance transitions and their contributions obtained from TD-DFT calculations for **7-9** before and after deprotonation with F^-, CN^-, AcO^- and $H_2PO_4^-$.

			F^-		**CN^-**		**AcO^-**		**$H_2PO_4^-$**	
	λ (nm), f	Transition, w(%)	λ (nm), f	Transition, w(%)	λ (nm), f	Transition, w(%)	λ (nm), f	Transition, w(%)	λ (nm), f	Transition, w(%)
7	462 (0.8972)	H→L 94.6 H→L+1 4.4	462 (0.6358)	H→L 92.2 H→L+1 6.5	480 (0.4088)	H→L 96.1 H→L+1 3.1	-	-	-	-
	412 (0.3418)	H-1→L 21.7 H→L 3.4 H→L+1 73.7	413 (0.5912)	H-1→L 23.9 H→L 5.9 H→L+1 67.5	419 (0.7731)	H-2→L 24.8 H→L 2.5 H→L +1 67.2	-	-	-	-
8	410 (0.9615)	H-1→L 22.1 H→L+1 76.1	410 (0.5357)	H-1→L 28.2 H→L+1 66.5	412 (0.1374)	H-1→L 4.5 H→L+1 82.5	414 (0.1917)	H-1→L 2.6 H→L+1 93.8	412 (0.5074)	H-1→L 42.1 H→L 4.8 H→L+1 51.7
			462 (0.5486)	H→L 95.6 H→L+1 2.5	458 (0.6943)	H→L 90.1 H→L+1 7.7	460 (0.7299)	H→L 97.6	460 (0.4528)	H→L 94.5 H→L+1 2.5
9	409 (0.9079)	H-1→L 19.9 H→L+1 77.3	412 (0.1861)	H→L 6.3 H→L+1 86.7	407 (0.1075)	H-1→L 87.7 H-1→L+1 9.7	401 (0.2788)	H-1→L 84.3 H→L+1 4.6		
			453 (0.7152)	H→L 91.5 H→L+1 5.7	466 (0.7041)	H→L 91.1 H→L+1 6.8	462 (0.6060)	H→L 86.3 H→L+1 11.9	-	-

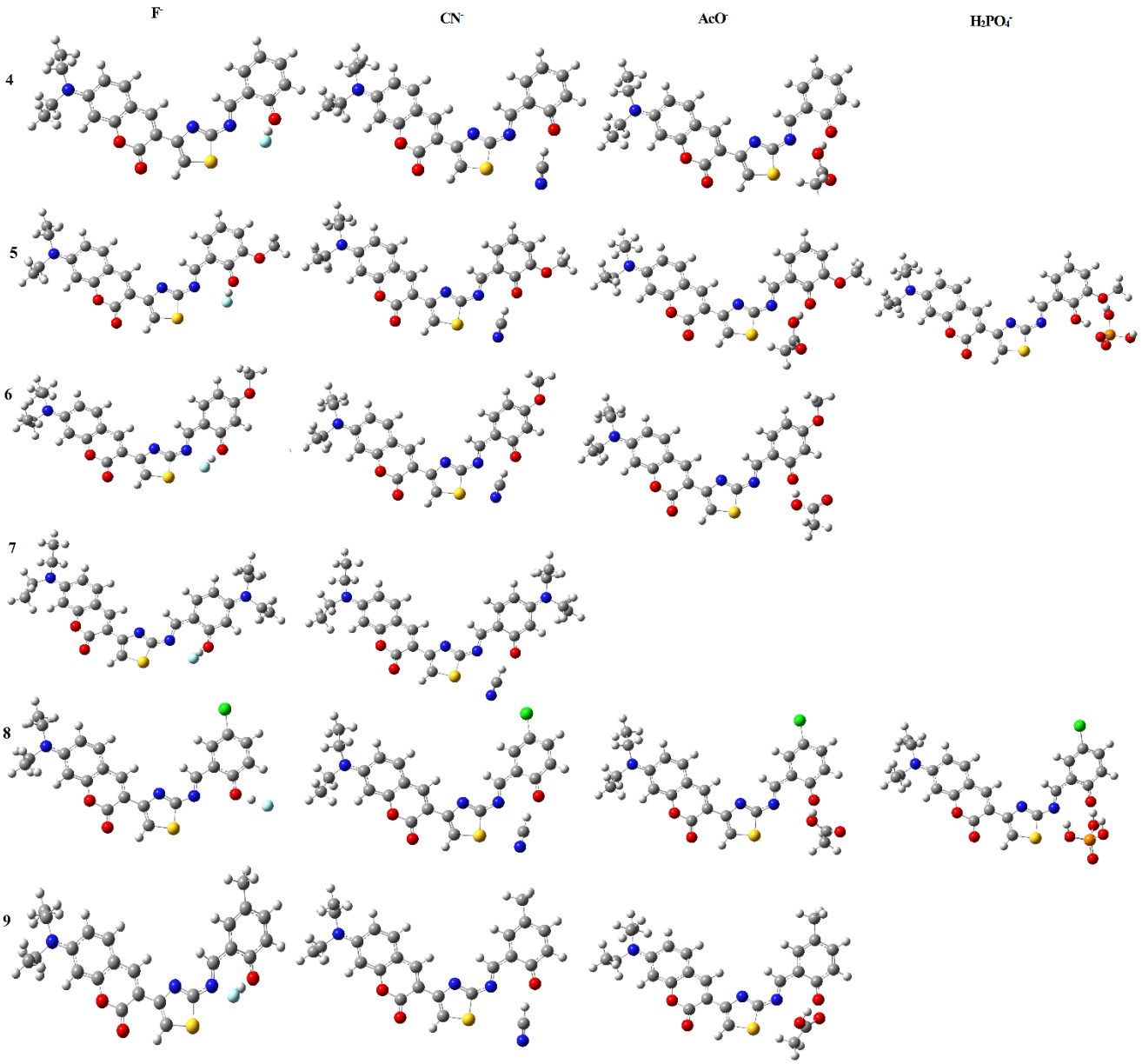

Figure S65. The optimized structures of each compound of adduct formed via deprotonation with F^-, AcO^-, CN^- and $H_2PO_4^-$ anions.

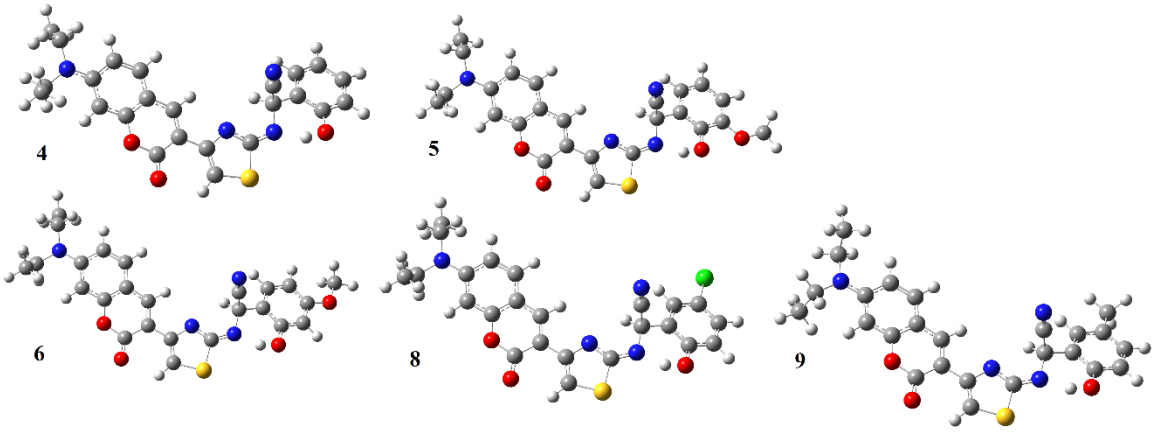

Figure S66. The optimized structures of the adducts formed via addition of CN^- for **4-6** and **8-9**.

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