Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Synthesis and characterization of polymethine dyes carrying thiobarbituric and a carboxylic acid moieties

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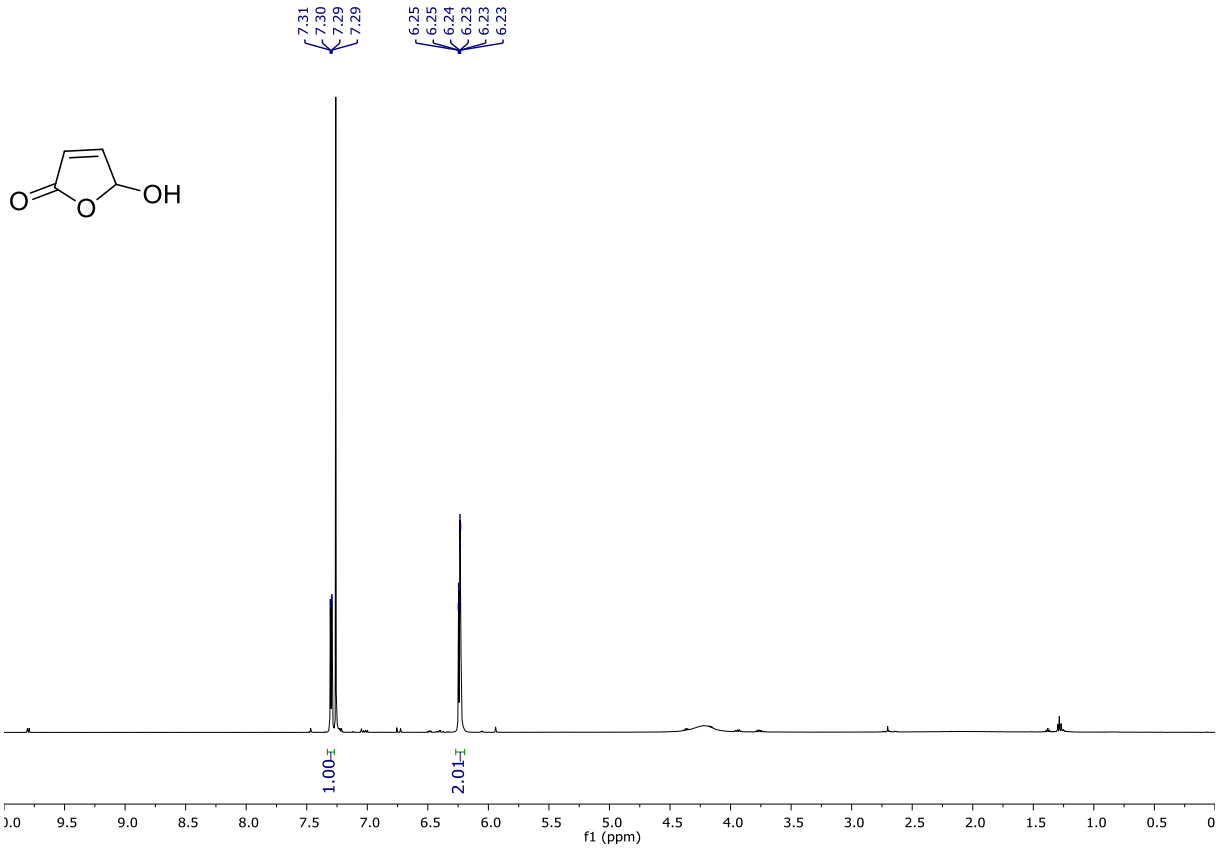
1. Preparation of 5-ethoxy-2(5H)-furanone

5-Hydroxyfuran-2(5H)-one.

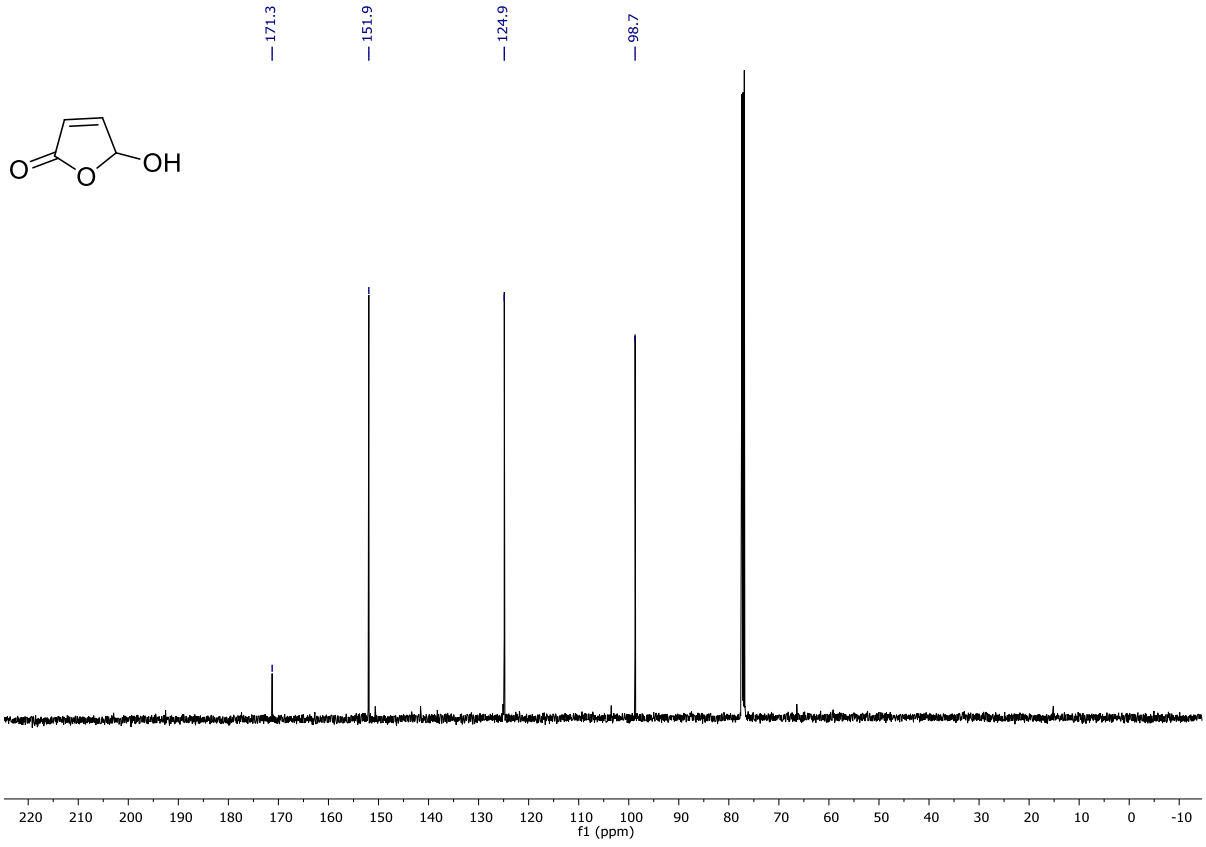
In a 2 L photochemical immersion well reactor were introduced freshly distilled furfural (100 g, 1 mol, 1 eq.), EtOH (1.5 L) and Rose Bengale (1.0 g, 1 mmol, 0.001 eq.). Air injection was performed at the bottom of the reactor with a pump as it is used for aquaria or hydroponic systems. The irradiation was carried out with a medium pressure mercury vapor lamp set to 400 W that was placed inside the reactor. Rose Bengale (0.5 g, 0.5 mmol, 0.0005 eq.) was added twice inside the photoreactor when the solution started decoloring. Consumption of furfural was followed by ^{1}H NMR. After 10 h, furfural was totally converted into 5-Hydroxyfuran-2(5H)-one. EtOH was removed under reduced pressure (the temperature was kept below 30 °C) to obtain an orange oil that solidified. The photosensitizer was removed partially by filtration in diethyl ether over silica and charcoal. After evaporation, 5 g of liquid side products were separated from the solid by filtration on a frit glass (φ = 3). 5-Hydroxyfuran-2(5H)-one was obtained as an off-white powder (94 g, 90 %).^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.30 (dd, *J* = 5.6 Hz, 1.2 Hz, 1H; CH), 6.24 (m, 1H; CH), 6.23 (m, 1H; CH), 4.22 (s, broad, 1H; OH*).*^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ 171.3 (Cq), 151.9 (CH), 124.9 (CH), 98.7 (CH). Spectroscopic data are in agreement with those previously reported (M. I. Burguete, R. Gavara, F. Galindo and S. V. Luis, *Tetrahedron Lett.* 2010, **51**, 3360-3363).

Photochemical immersion well reactor equipped with a medium pressure mercury vapor lamp that have been used for the photooxygenation of furfural.

^{1}H NMR (500 MHz) spectrum of 5-Hydroxyfuran-2(5H)-one in $CDCl_3$



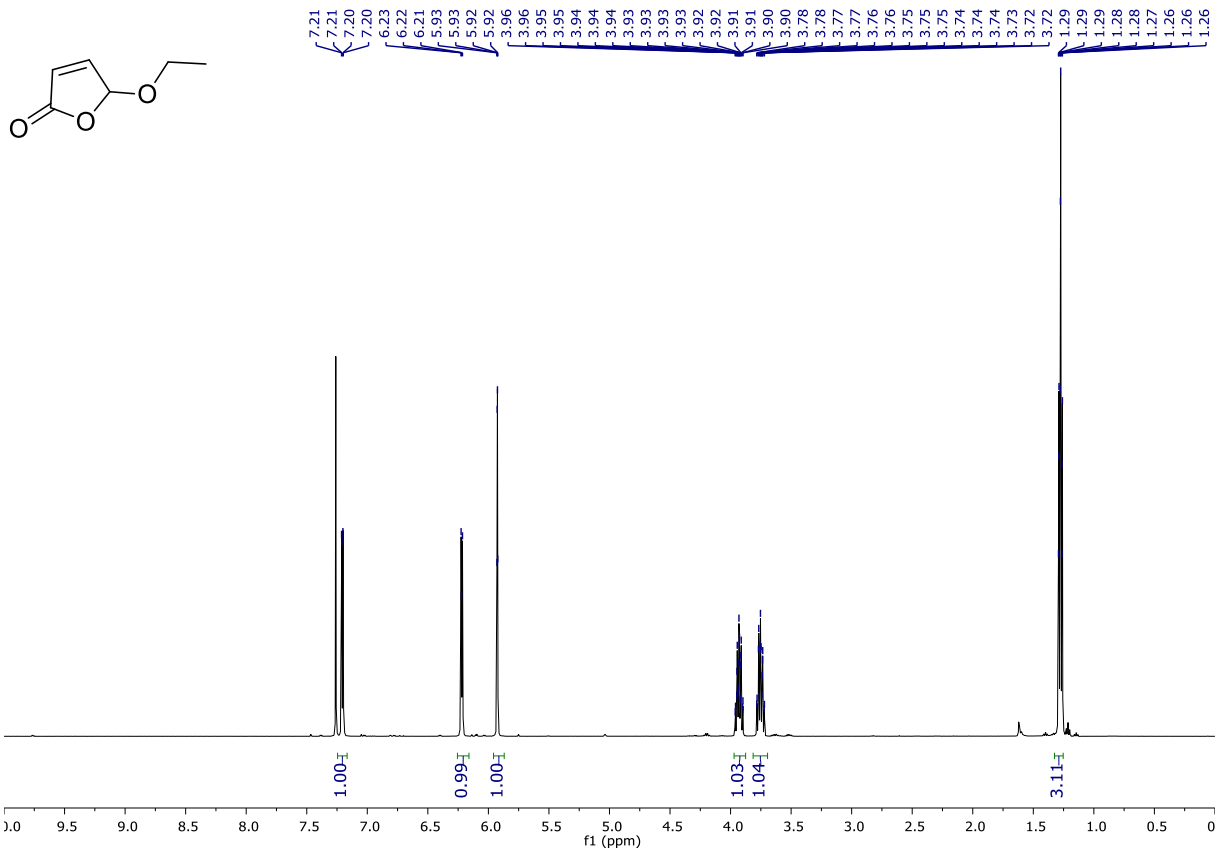
$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum 5-Hydroxyfuran-2(5H)-one in $CDCl_3$



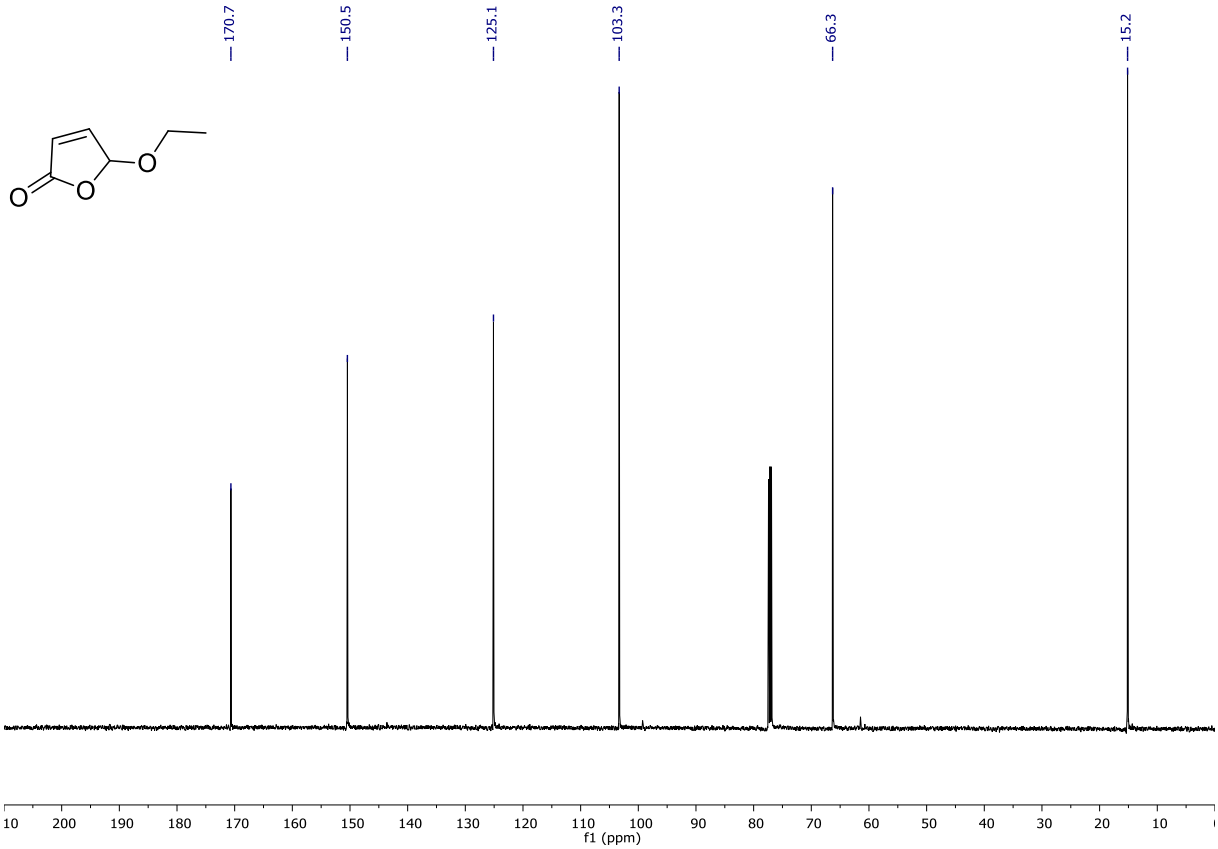
5-Ethoxy-2(5H)-furanone.

In a two-neck round bottom flask equipped with a stirring bar and an inverse Dean-Stark apparatus were introduced 5-Hydroxyfuran-2(5H)-one (30 g, 0.3 mol, 1 eq.), $CHCl_3$ (100 mL) and a solution of PTSA (0.26 g, 1.5 mmol, 0.005 eq) in dry ethanol (23 mL, 0.39 mol, 1.3 eq.). The reaction mixture was stirred at reflux. After 14 h, the mixture was cooled and poured in a separatory funnel. The organic layer was washed with a saturated aqueous $NaHCO_3$ solution (100 mL). An impurity of unsaturated aldehyde was removed by washing the organic layer with a saturated aqueous $NaHSO_3$ solution (2 x 100 mL). The organic fraction was washed with H_2O, dried over $MgSO_4$ and concentrated under reduced pressure. The yellow oil was further purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 8:2, $KMnO_4$) to yield 5-ethoxy-2(5H)-furanone as a yellowish liquid (17.1 g, 45 %). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.21 (m, 1H; CH), 6.22 (m, 1H; CH), 5.92 (m, 1H; CH), 3.92 (m, 1H; CH_2), 3.74 (m, 1H; CH_2), 1.27 (td, *J* = 7 Hz, J=1.1 Hz, 3H; CH_3).^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ 170.7 (Cq), 150.5 (CH), 125.1 (CH), 103.3 (CH), 66.3 (CH_2), 15.2 (CH_3). Spectroscopic data are in agreement with those previously reported (T. Schmidt, N. Heise, K. Merzweiler, H.-P. Deigner, A. Al-Harrasi and R. Csuk, *Molecules* 2021, **26**, 3676).

^{1}H NMR (500 MHz) spectrum of Ethoxyfuranone in $CDCl_3$

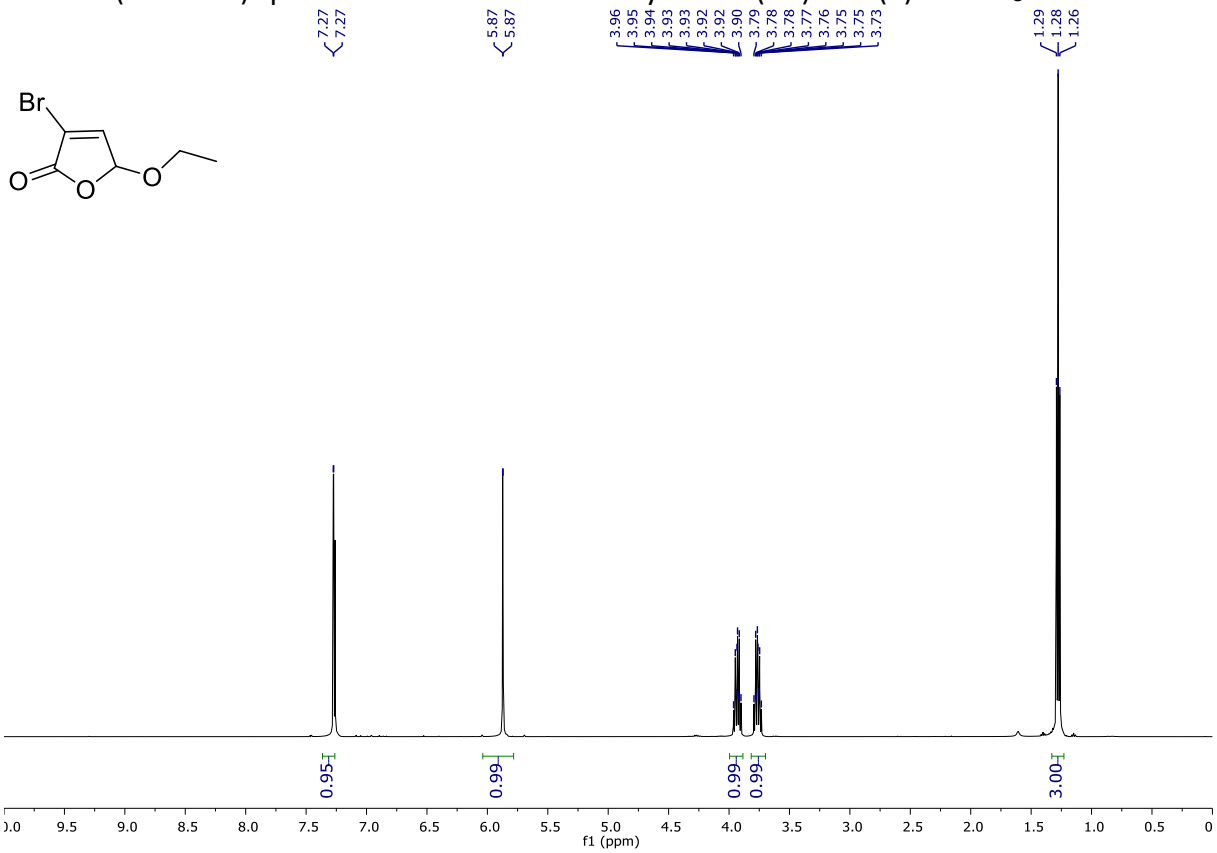


$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum Ethoxyfuranone in $CDCl_3$

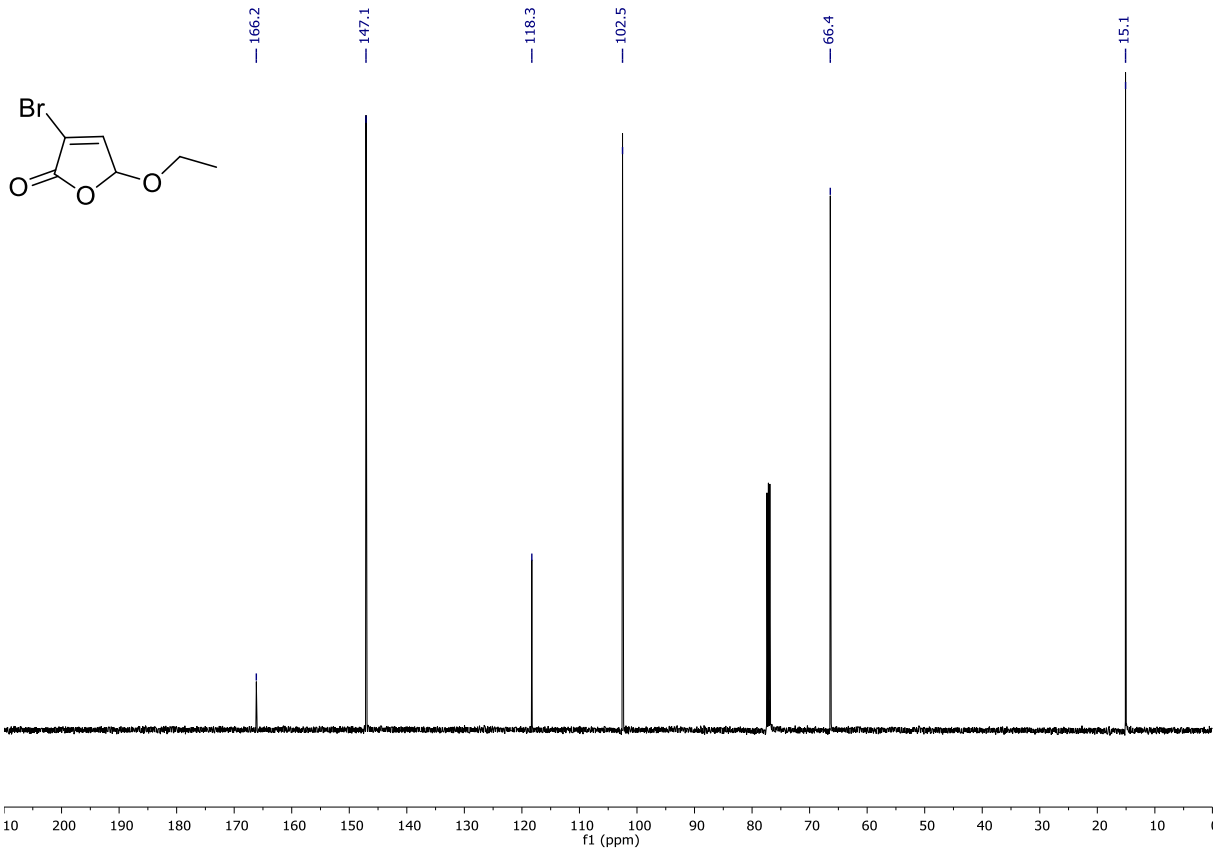


2. NMR Spectra

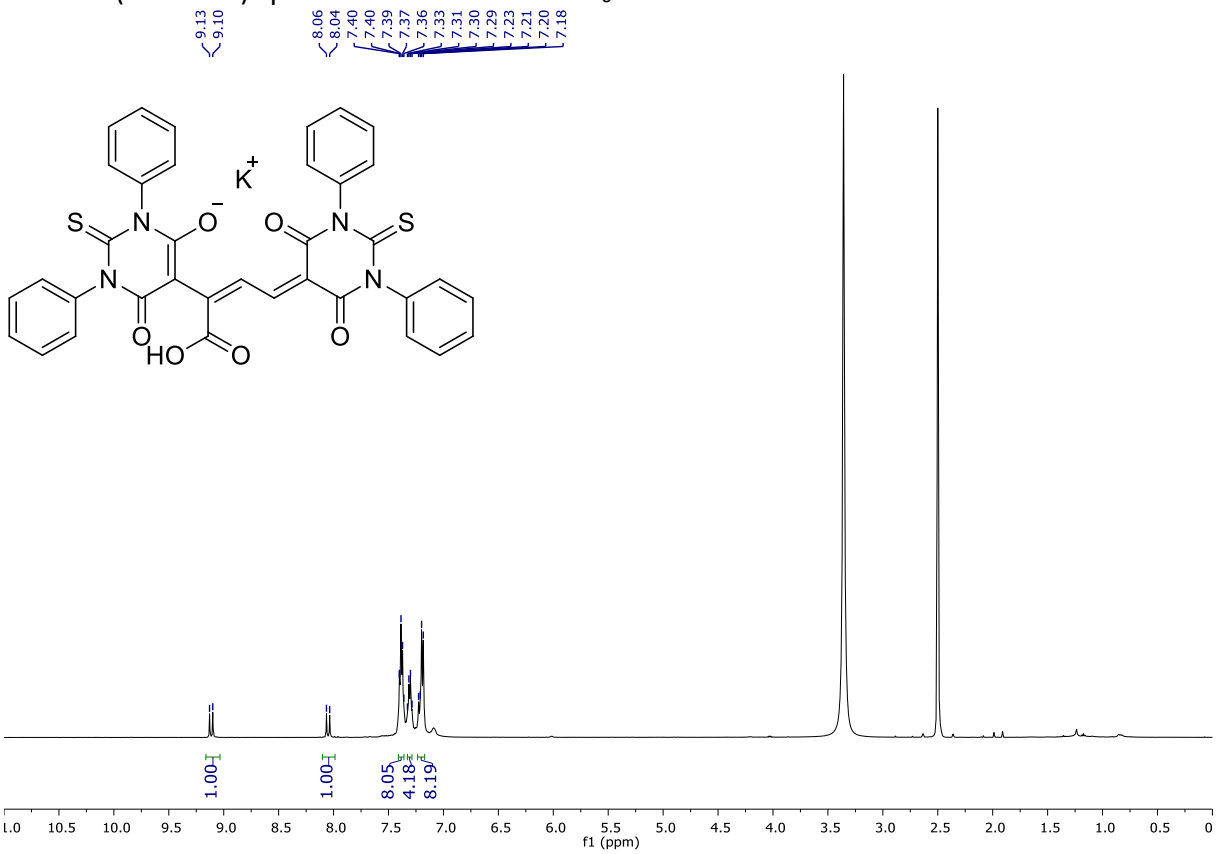
^{1}H NMR (500 MHz) spectrum of 3-bromo-5-ethoxyfuran-2(5H)-one (**2**) in $CDCl_3$



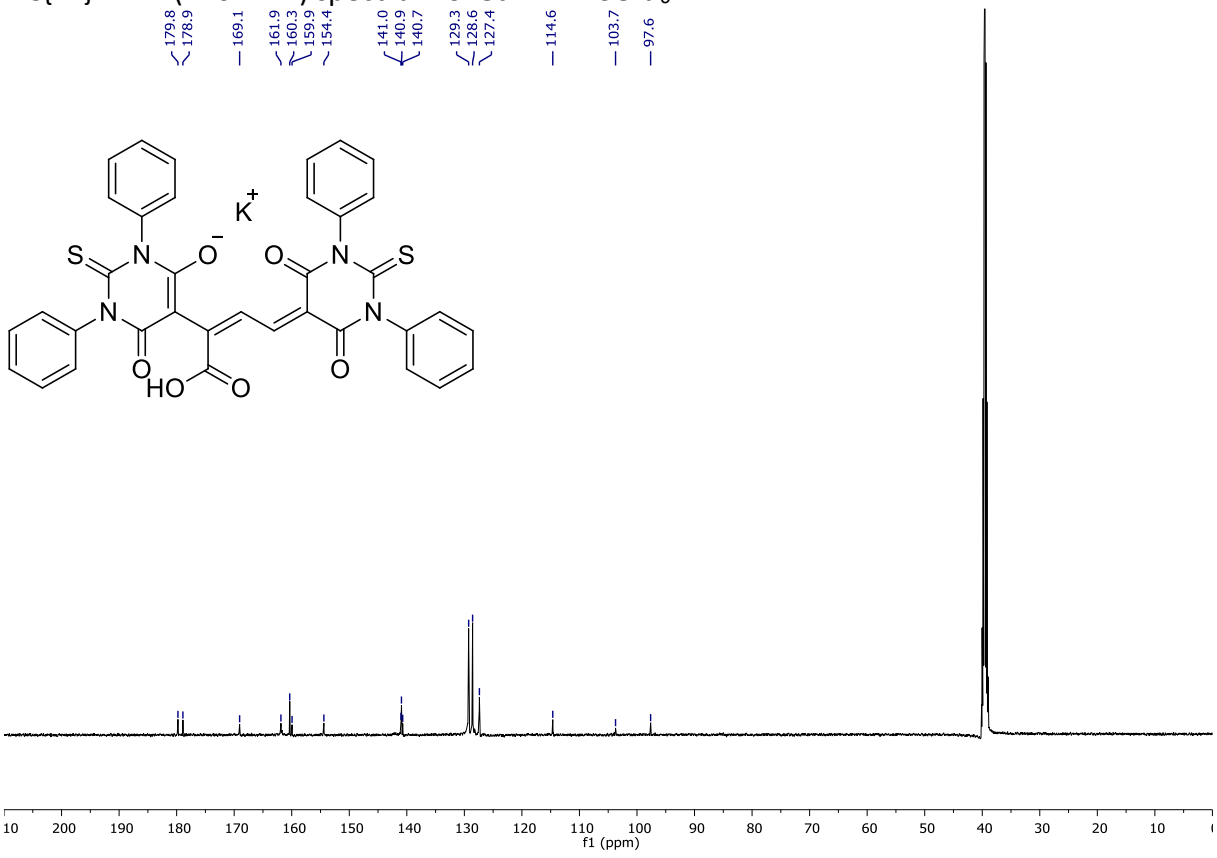
^{13}C{^{1}H} NMR (126 MHz) spectrum of 3-bromo-5-ethoxyfuran-2(5H)-one (**2**) in $CDCl_3$



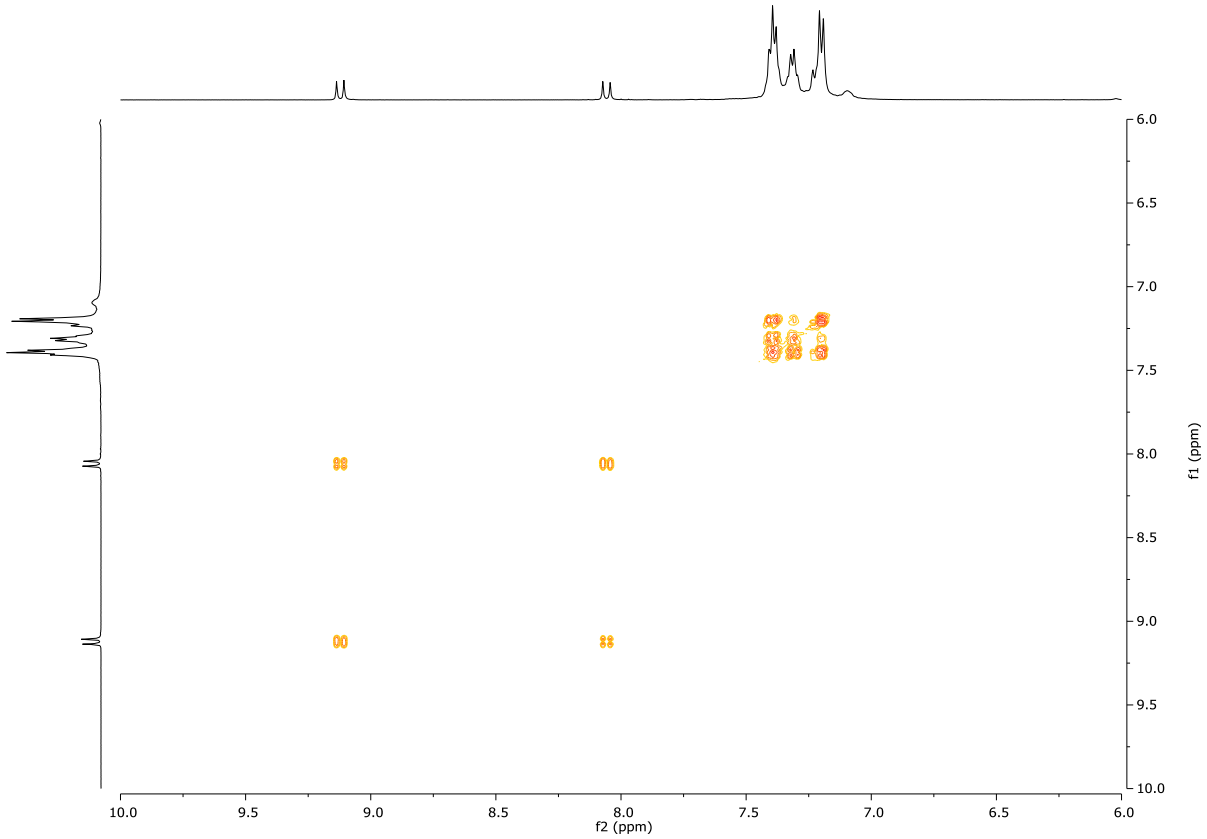
^{1}H NMR (500 MHz) spectrum of **5a** in DMSO-d_6



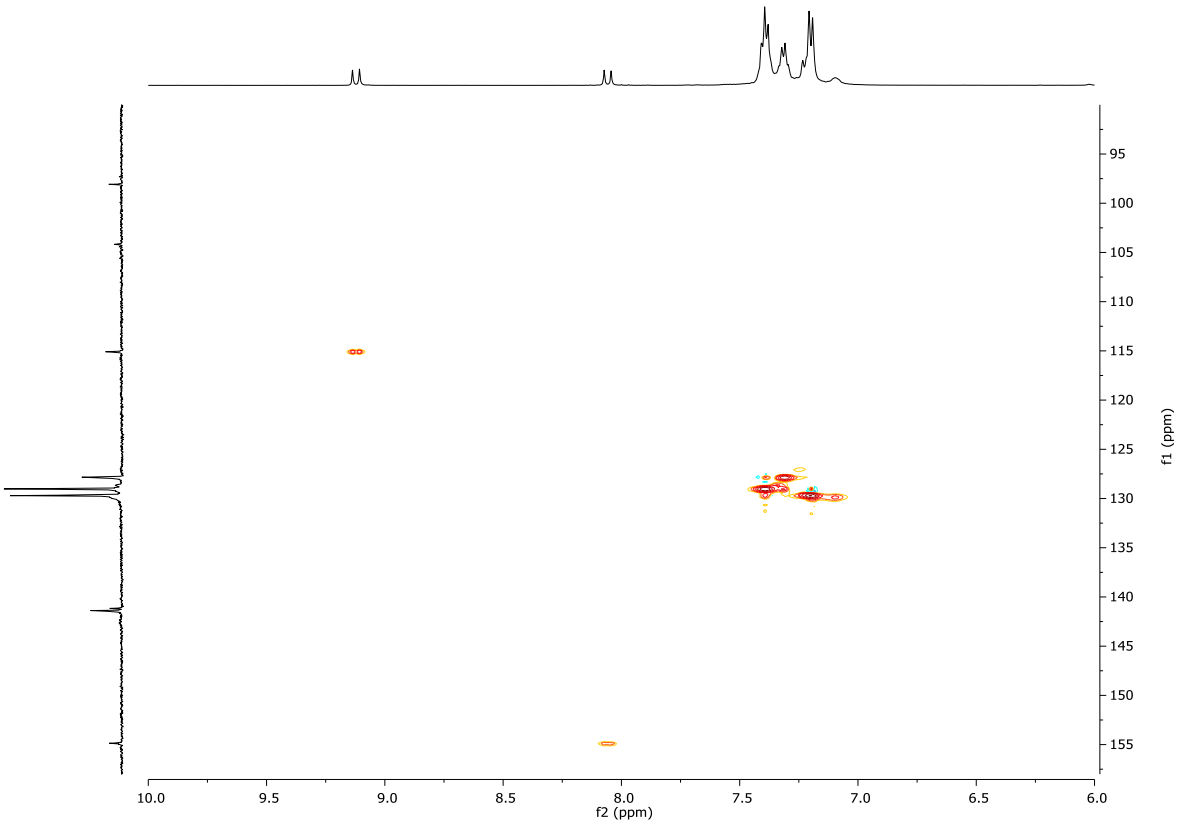
^{13}C{^{1}H} NMR (126 MHz) spectrum of **5a** in DMSO-d_6



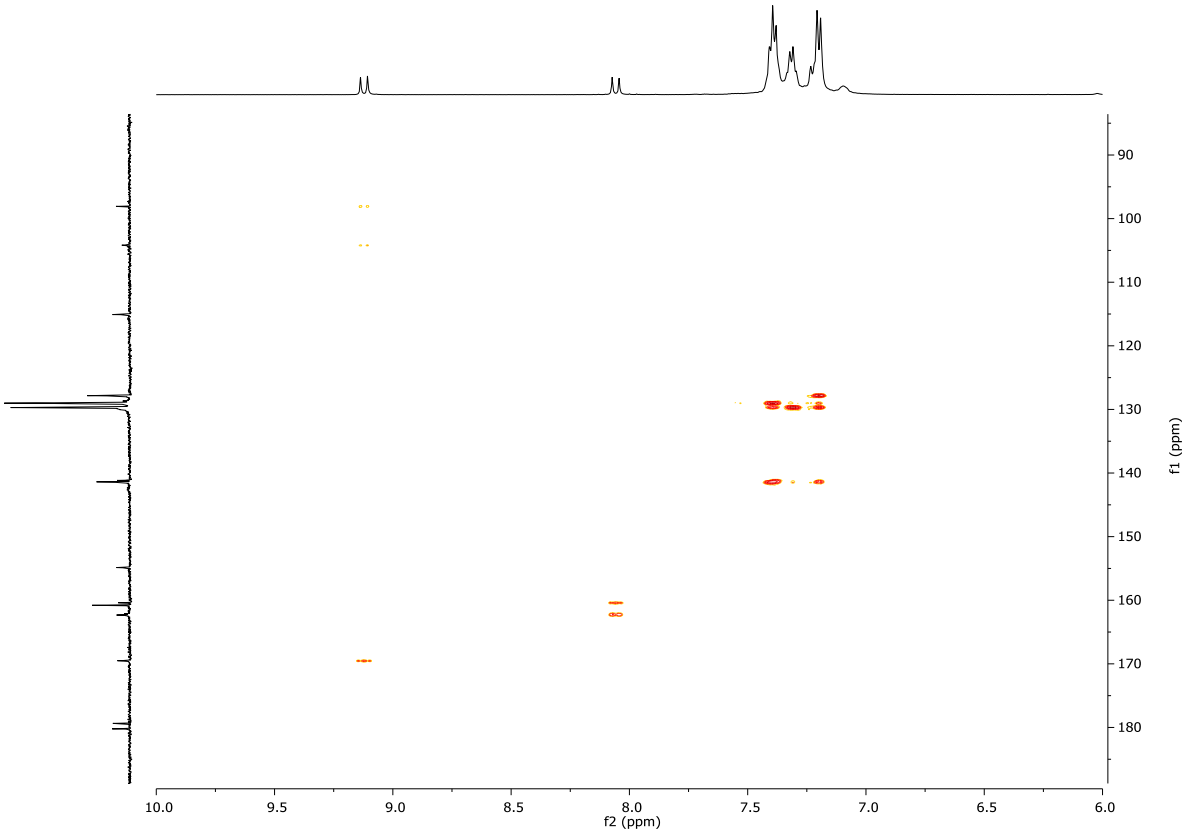
^{1}H-^{1}H cosy NMR spectrum of **5a** in DMSO-d_6



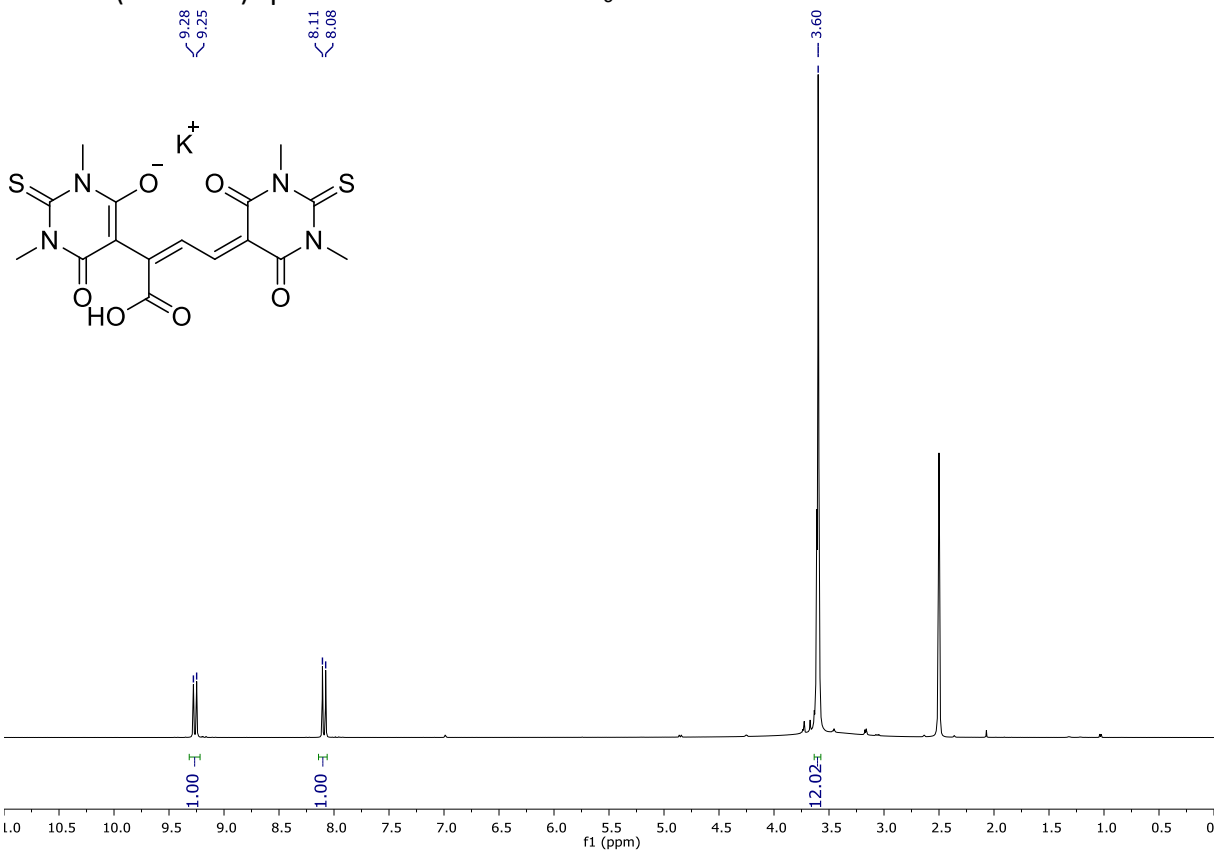
^{1}H-^{13}C HSQC NMR spectrum of **5a** in DMSO-d_6



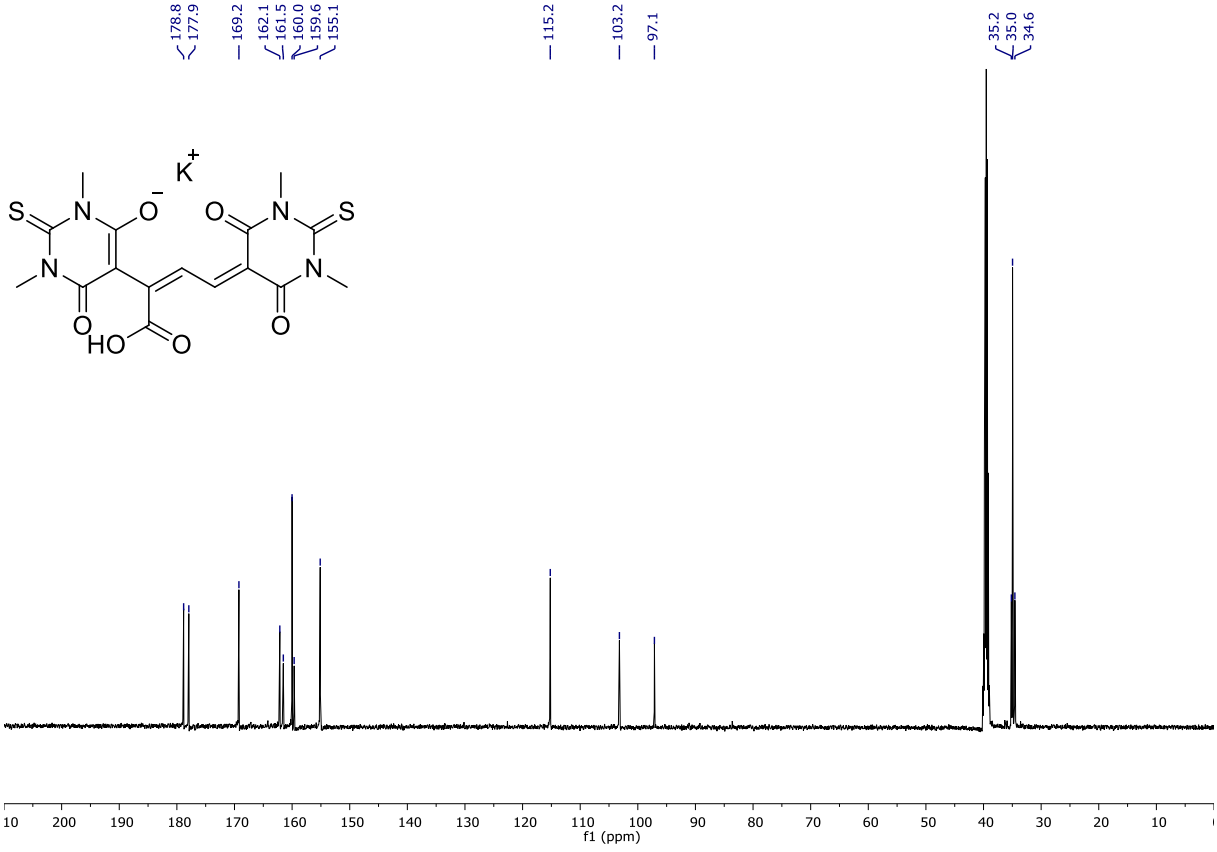
^{1}H-^{13}C HMBC NMR spectrum of **5a** in DMSO-d_6



^{1}H NMR (500 MHz) spectrum of **5b** in DMSO-d_6

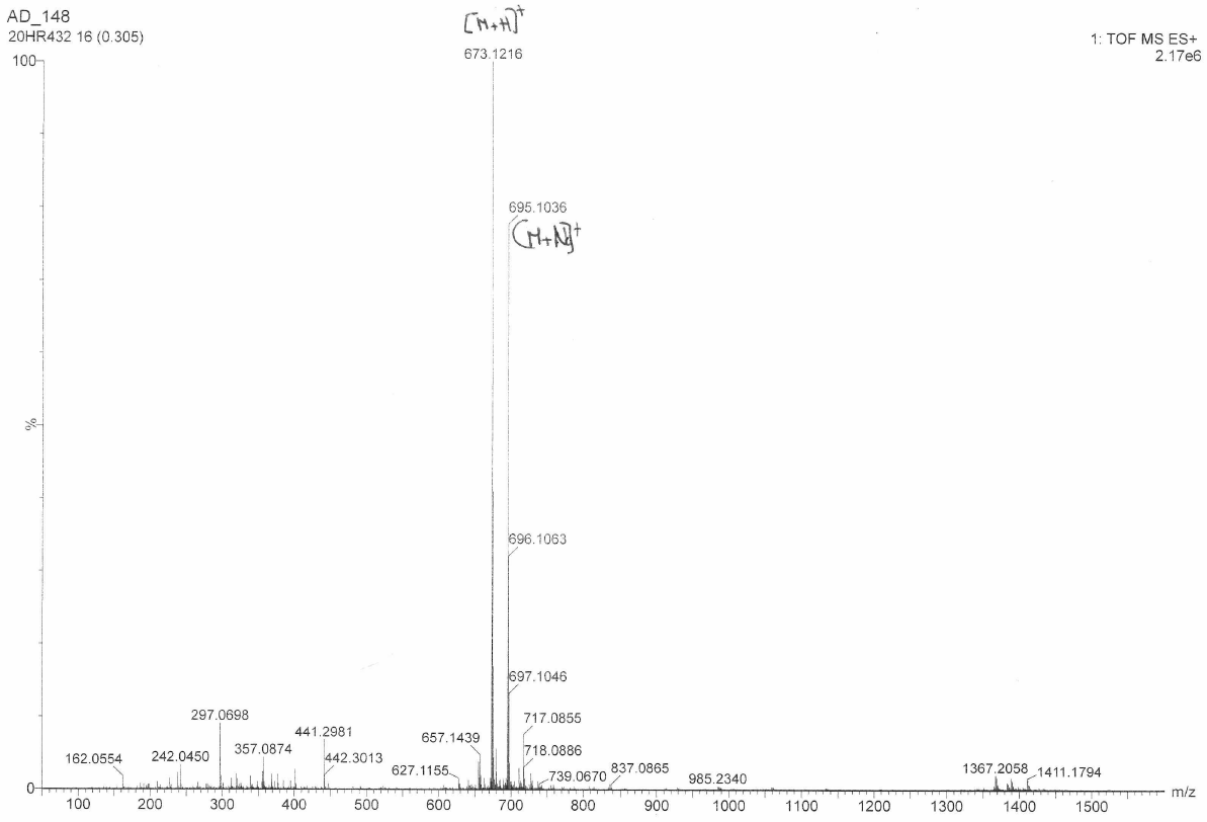


^{13}C{^{1}H} NMR (126 MHz) spectrum of **5b** in DMSO-d_6



3. HRMS spectra and data of compounds 5a, 5b

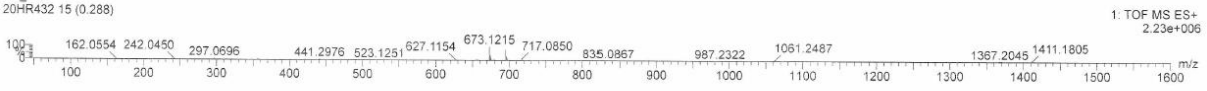
HRMS spectrum and data of compounds **5a**



Elemental Composition Report Page 1

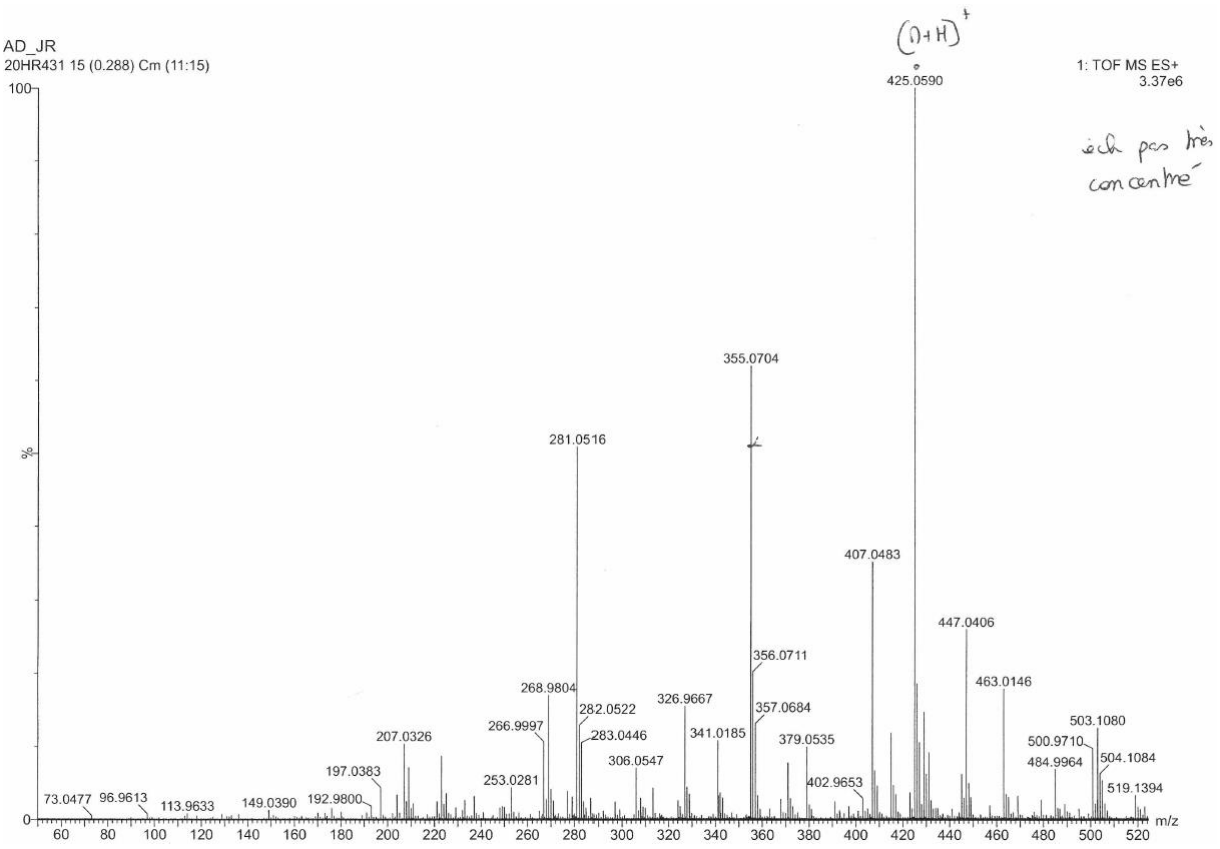
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2337 formula(e) evaluated with 15 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-80 H: 0-100 N: 0-6 O: 0-15 S: 0-2
AD_148
20HR432 15 (0.288)



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
673.1215	673.1216	-0.1	-0.1	26.5	1513.1	0.610	54.36	C36 H25 N4 O6 S2
	673.1222	-0.7	-1.0	35.5	1521.1	8.582	0.02	C44 H21 N2 O4 S
	673.1207	0.8	1.2	27.5	1524.7	12.209	0.00	C35 H21 N4 O11
	673.1227	-1.2	-1.8	17.5	1519.0	6.471	0.15	C31 H29 O15 S
	673.1202	1.3	1.9	45.5	1525.6	13.105	0.00	C48 H13 N6
	673.1202	1.3	1.9	21.5	1513.3	0.802	44.84	C35 H29 O10 S2
	673.1229	-1.4	-2.1	44.5	1526.2	13.741	0.00	C52 H17 O2
	673.1200	1.5	2.2	18.5	1519.3	6.790	0.11	C27 H25 N6 O13 S
	673.1234	-1.9	-2.8	13.5	1518.6	6.073	0.23	C24 H29 N6 O13 S2
	673.1235	-2.0	-3.0	40.5	1522.3	9.800	0.01	C45 H17 N6 S
	673.1193	2.2	3.3	22.5	1524.8	12.306	0.00	C34 H25 O15
	673.1241	-2.6	-3.9	22.5	1519.1	6.584	0.14	C32 H25 N4 O11 S
	673.1188	2.7	4.0	40.5	1525.2	12.732	0.00	C47 H17 N2 O4
	673.1247	-3.2	-4.8	31.5	1524.9	12.465	0.00	C40 H21 N2 O9
	673.1182	3.3	4.9	31.5	1519.1	6.568	0.14	C39 H21 N4 O6 S

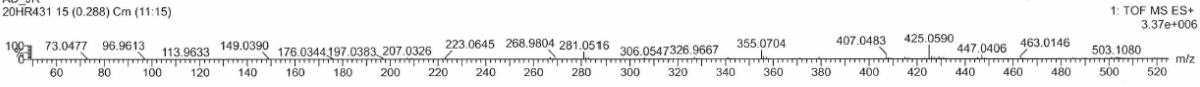
HRMS spectrum and data of compounds **5a**



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1347 formula(e) evaluated with 9 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-80 H: 0-100 N: 0-6 O: 0-15 S: 0-2
AD_JR
20HR431 15 (0.288) Cm (11:15)



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
425.0590	425.0590	0.0	0.0	10.5	1077.2	0.232	79.30	C16 H17 N4 O6 S2
	425.0596	-0.6	-1.4	19.5	1088.1	11.129	0.00	C24 H13 N2 O4 S
	425.0581	0.9	2.1	11.5	1091.7	14.806	0.00	C15 H13 N4 O11
	425.0601	-1.1	-2.6	1.5	1085.2	8.308	0.02	C11 H21 O15 S
	425.0603	-1.3	-3.1	28.5	1094.7	17.744	0.00	C32 H9 O2
	425.0576	1.4	3.3	5.5	1078.5	1.577	20.66	C15 H21 O10 S2
	425.0576	1.4	3.3	29.5	1094.0	17.108	0.00	C28 H5 N6
	425.0574	1.6	3.8	2.5	1086.2	9.285	0.01	C7 H17 N6 O13 S
	425.0609	-1.9	-4.5	24.5	1089.2	12.246	0.00	C25 H9 N6 S

4. Photophysical Studies

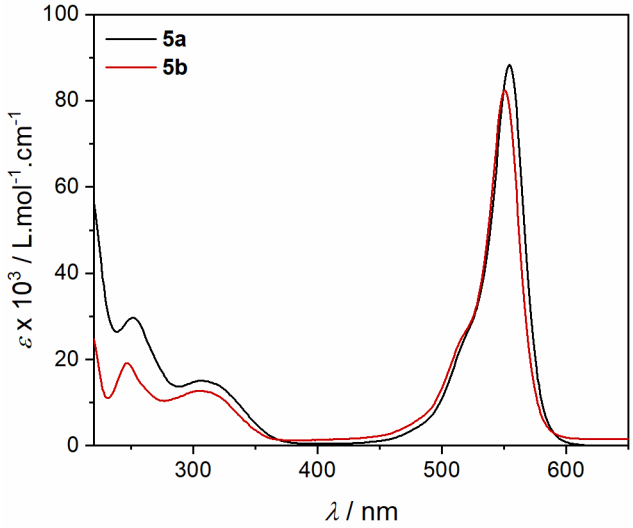


Figure S1: Absorption spectra of compounds **5a** (tetraPh, black), and **5b** (tetraMe, red) as acetonitrile solutions (6.1×10^{-6} mol.L^{-1} and 7.2×10^{-6} mol.L^{-1} for compound **5a** and **5b**, respectively).

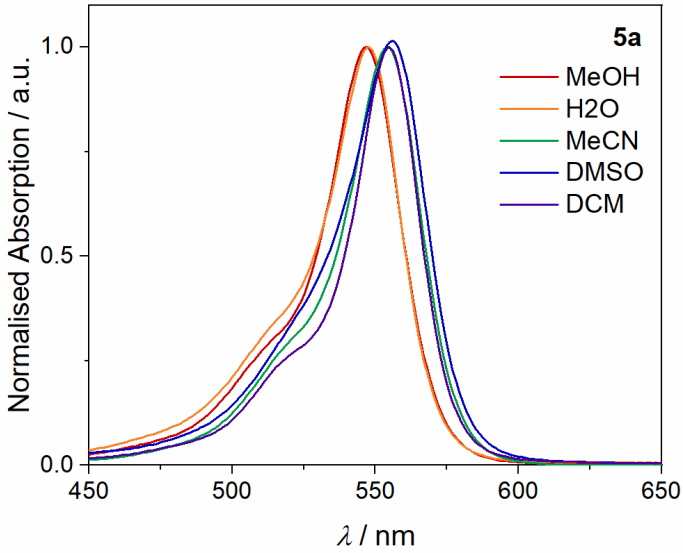


Figure S2: Normalized absorption spectra of compound **5a** (tetraPh) (conc. 6.1×10^{-6} mol.L^{-1})

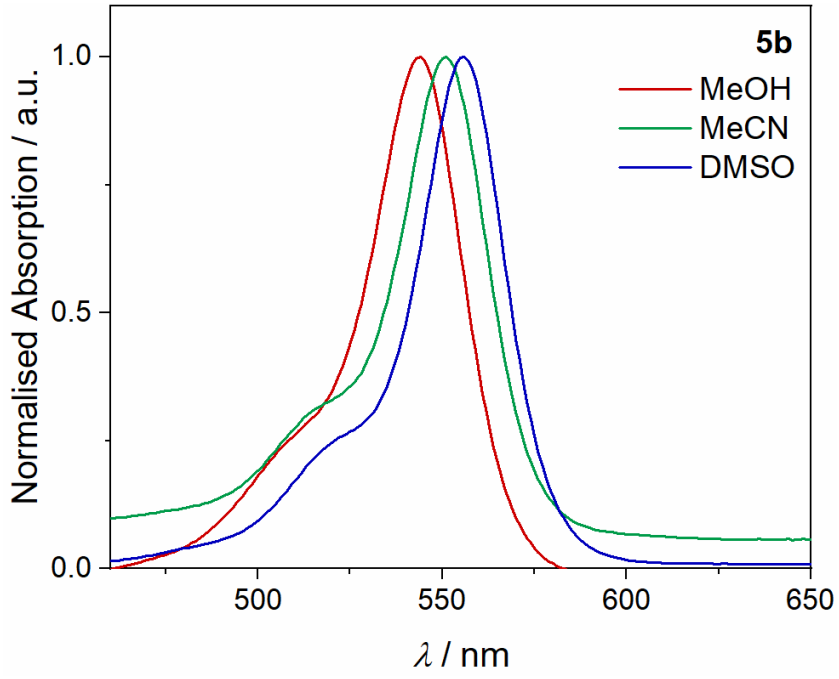


Figure S3: Normalized absorption spectra of compound **5b** (tetraMe) (conc. 6.1×10^{-6} mol.L^{-1}).

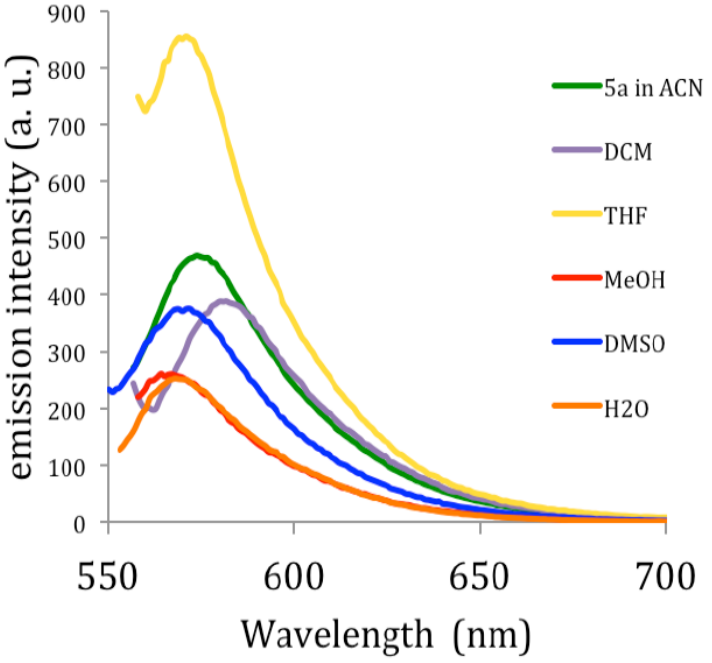


Figure S4: Non-normalized (emission spectra of compound **5a** (tetraPh); conc. around 10^{-6} mol.L^{-1}

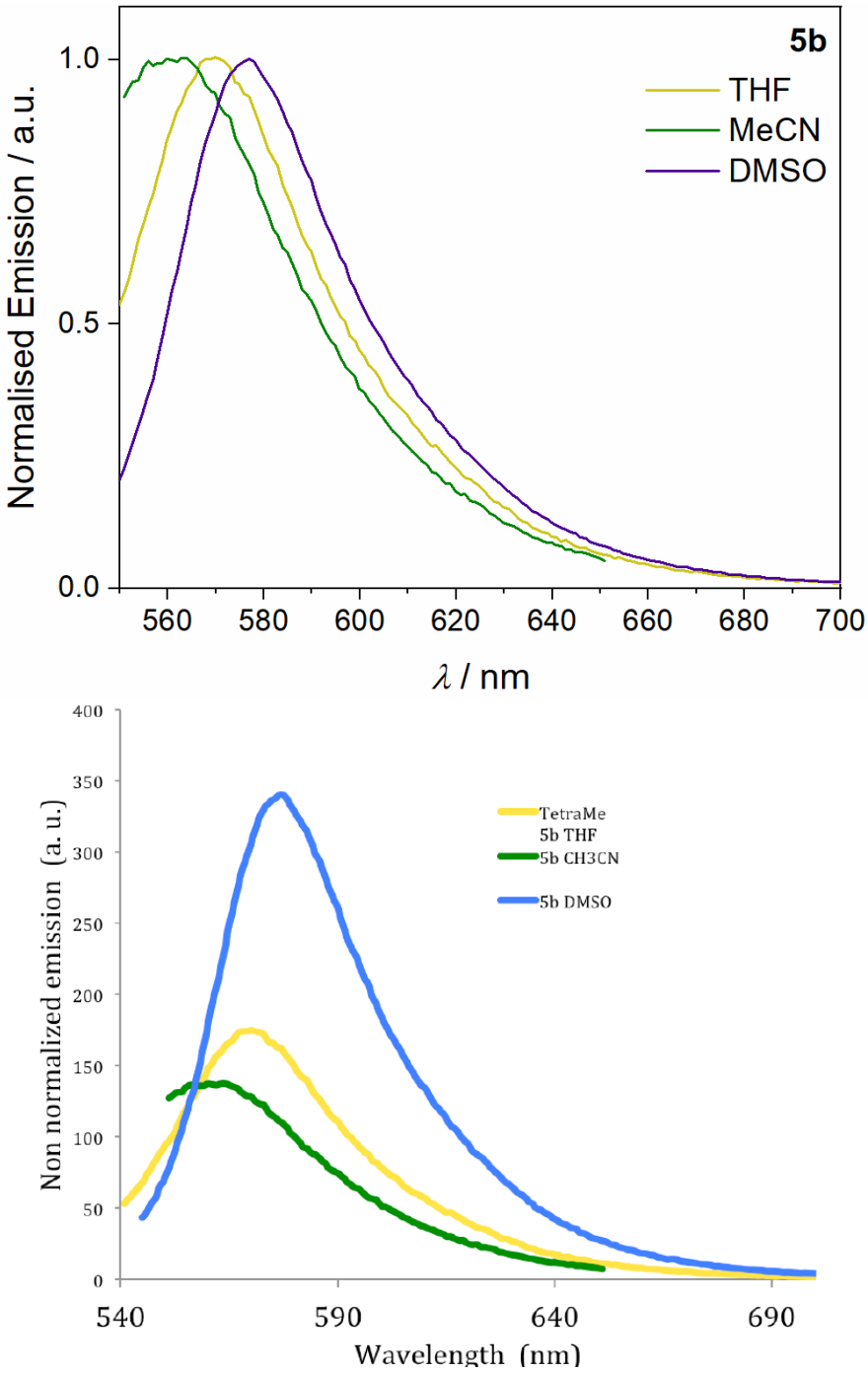


Figure S5: Normalized (up) and non-normalized (bottom) emission spectra of compound **5b** (tetraMe); conc. around 10^{-6} mol.L^{-1}

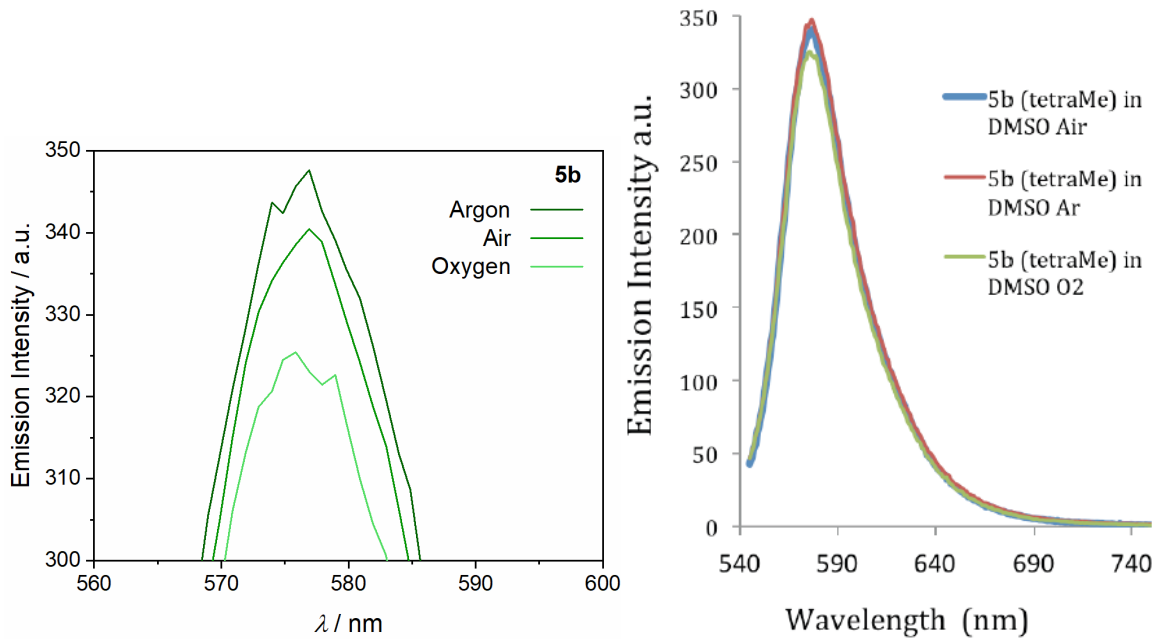


Figure S6: Emission spectra of compound **5b** (tetraMe) in deoxygenated (dark green), air-equilibrated (green) and O_2 saturated (light green) DMSO solutions (excitation 530 nm; same other experimental conditions for all measurements)

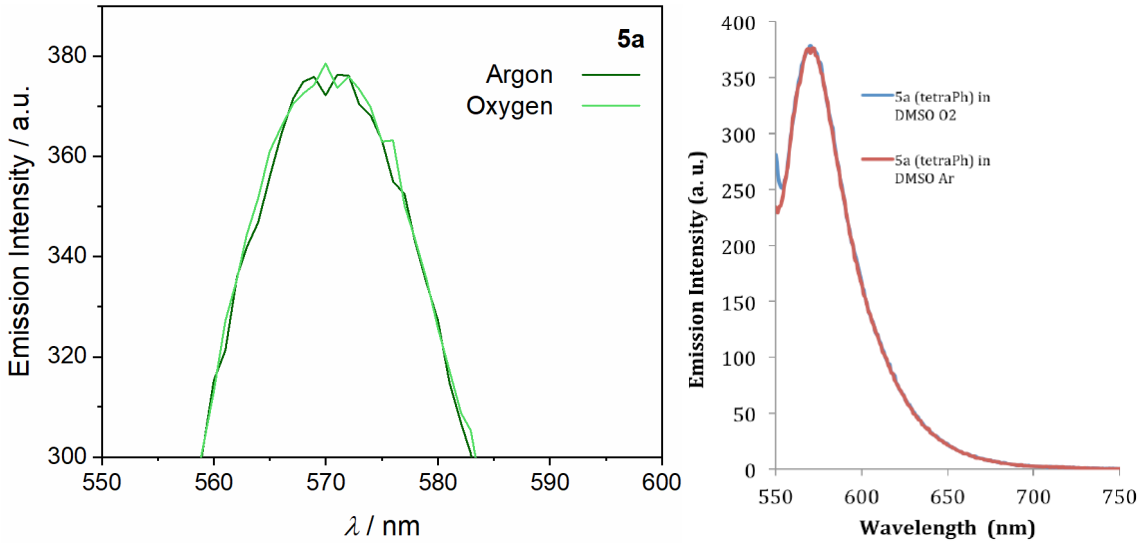


Figure S7: Emission spectra of compound **5a** (tetraPh) in deoxygenated (dark green) and O_2 saturated (light green) DMSO solutions (same other experimental conditions for both measurements)

5. Computational Studies

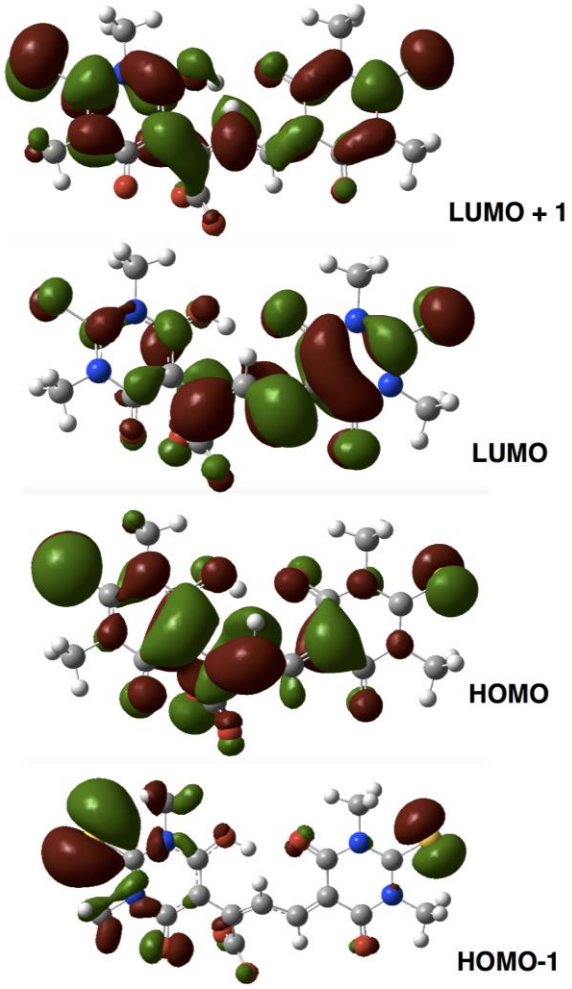


Figure S8: HOMOs and LUMOs for tautomer **A**

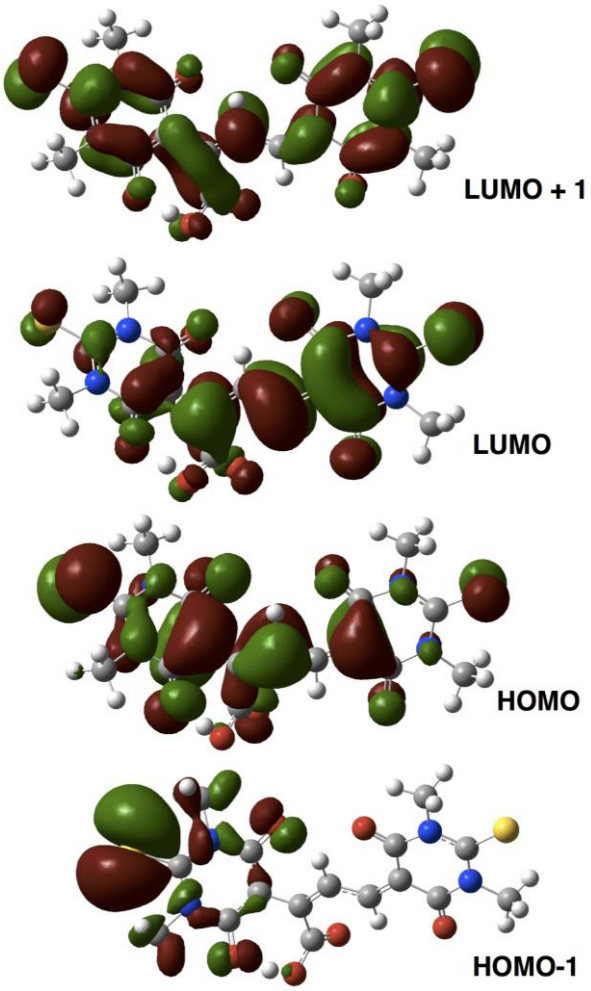


Figure S9: HOMOs and LUMOs for tautomer **C**

Optimized Cartesian coordinates

Structure A

C	-4.757312	-0.965085	-0.075544
C	-3.556208	1.149838	-0.494421
C	-2.310525	0.477031	-0.203005
C	-2.342909	-0.872686	0.118936
C	-1.087603	1.276195	-0.144936
C	0.097452	0.727548	-0.557722
H	0.082082	-0.227799	-1.068370
C	1.379976	1.295181	-0.308938
H	1.441736	2.373308	-0.189333
C	-1.131694	2.637572	0.577228
O	-1.615868	2.587355	1.738288
O	-1.301908	-1.615902	0.483466
N	-4.738402	0.372909	-0.384351
N	-3.529132	-1.578730	0.139852
S	-6.197893	-1.833581	0.038536
O	-3.622901	2.333925	-0.831447
O	-0.640446	3.624658	-0.025155
C	2.572776	-0.866094	-0.057045
C	2.557303	0.585115	-0.206817
C	3.807512	1.344416	-0.129849
C	5.039115	-0.794296	-0.058097
O	1.551549	-1.554471	0.075814
O	3.849494	2.574420	-0.136997
S	6.505439	-1.616589	-0.057762
N	3.835224	-1.482720	-0.027503
N	4.996040	0.588661	-0.070511
C	-3.511755	-3.030544	0.433218
H	-3.971141	-3.212524	1.405995
H	-4.081773	-3.549847	-0.335536
H	-2.485132	-3.377076	0.434896
C	3.862547	-2.955144	0.067598
H	4.386201	-3.368373	-0.794788
H	4.379172	-3.256953	0.979614
H	2.834349	-3.302414	0.087049
C	6.264886	1.339886	-0.045418
H	6.830035	1.078135	0.849804
H	6.857840	1.095051	-0.927687
H	6.018565	2.397273	-0.039107
C	-6.015463	1.062550	-0.634838
H	-6.525024	0.599674	-1.481492
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H	-5.788458	2.101858	-0.852195
H	-0.431722	-1.170231	0.413063

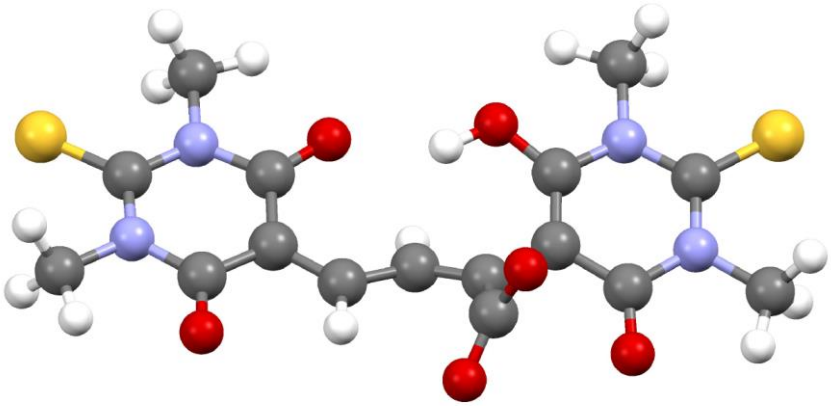
Structure B

C	-5.093703	-0.833635	-0.067760
C	-3.596136	1.123930	-0.066797
C	-2.443589	0.246090	-0.066644
C	-2.639072	-1.189810	-0.071406
C	-1.154096	0.834864	-0.063047
C	0.075596	0.159700	-0.022332
H	0.065915	-0.915200	0.011677
C	1.301046	0.837798	-0.020747
H	1.290085	1.923530	-0.062129
C	-1.049410	2.347264	-0.144745
O	-0.946266	2.914499	1.071499
H	-0.843282	3.876111	0.954960
O	-1.730404	-2.027348	-0.078830
N	-4.877064	0.527598	-0.072285
N	-3.987805	-1.651053	-0.067778
S	-6.661786	-1.469485	-0.062562
O	-3.504820	2.359187	-0.060722
O	-0.888885	2.952882	-1.187903
C	2.887164	-1.101776	0.078206
C	2.600699	0.315378	0.024584
C	3.685943	1.284044	0.012932
C	5.307937	-0.576787	0.098263
O	2.025199	-1.987295	0.093049
O	3.512547	2.508339	-0.028178
S	6.914476	-1.106142	0.135176
N	4.261141	-1.472016	0.114939
N	5.004359	0.768600	0.050926
C	-4.188028	-3.110996	-0.065563
H	-4.748501	-3.406255	0.822688
H	-4.746726	-3.409594	-0.953894
H	-3.207827	-3.577021	-0.064048
C	4.559773	-2.913397	0.170612
H	5.145018	-3.205937	-0.702558
H	5.130317	-3.139604	1.072565
H	3.612180	-3.443144	0.182327
C	6.105534	1.747369	0.036282
H	6.713599	1.635360	0.935064
H	6.734455	1.585839	-0.840436
H	5.661604	2.737586	0.003260
C	-6.037643	1.435725	-0.075316
H	-6.649332	1.250433	-0.959194
H	-6.641876	1.267713	0.817342
H	-5.658679	2.452890	-0.086421

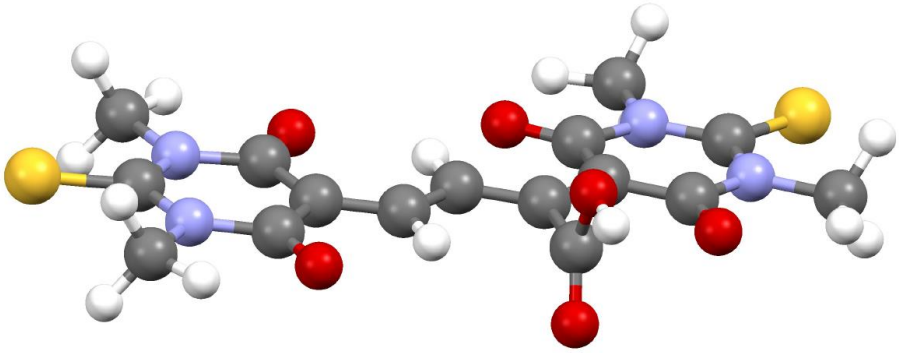
Structure C

C	-4.908329	-0.918394	-0.090955
C	-3.468697	0.989102	-0.648427
C	-2.424444	0.453871	0.150524
C	-2.602808	-0.817799	0.807764
C	-1.125732	1.120565	0.255939
C	0.048745	0.406012	0.142659
H	-0.025603	-0.648669	-0.071850
C	1.344801	0.980021	0.218260
H	1.412511	2.042447	0.424699
C	-1.061280	2.604054	0.604659
O	-1.713916	3.460698	-0.160894
H	-2.357004	2.944477	-0.782534
O	-1.744833	-1.389753	1.492473
N	-4.676847	0.275539	-0.741650
N	-3.889784	-1.421815	0.678259
S	-6.389784	-1.726827	-0.242941
O	-3.369625	2.051571	-1.332208
O	-0.414831	2.978341	1.575758
C	2.740692	-1.061429	-0.204675
C	2.574226	0.365485	0.047838
C	3.751595	1.234664	0.143648
C	5.194924	-0.730746	-0.241928
O	1.804485	-1.856161	-0.306629
O	3.679862	2.448478	0.347104
S	6.740695	-1.380325	-0.411423
N	4.071168	-1.529563	-0.331758
N	5.011648	0.620024	-0.009296
C	-4.106809	-2.683614	1.405607
H	-4.971748	-2.584544	2.062693
H	-4.290127	-3.495068	0.698721
H	-3.211046	-2.885879	1.984508
C	4.246383	-2.973297	-0.575980
H	4.761779	-3.128408	-1.524721
H	4.836929	-3.414701	0.227823
H	3.258910	-3.422862	-0.607233
C	6.196834	1.492129	0.086637
H	6.834112	1.161213	0.907685
H	6.763274	1.449912	-0.844519
H	5.845386	2.503143	0.267470
C	-5.739222	0.836779	-1.597395
H	-5.975676	0.135447	-2.398996
H	-6.635784	1.010377	-1.001184
H	-5.374416	1.771147	-2.010563

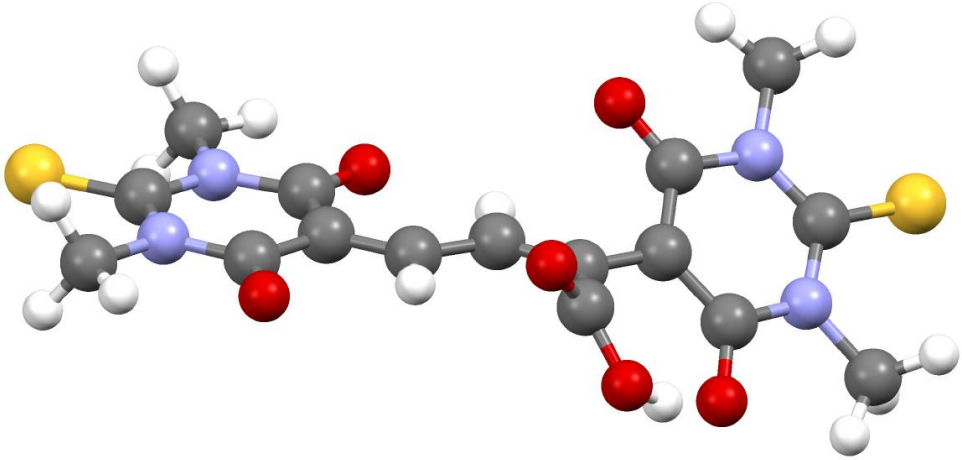
Structure A



Structure B



Structure C



Computed oscillator strength values.

Electonic states	Oscillator strength
S_1	1.5010
S_2	0.0002
S_3	0.0009