Electronic Supplementary Information for

Visualization of the photodegradation of a therapeutic drug by chemometric-assisted fluorescence spectroscopy

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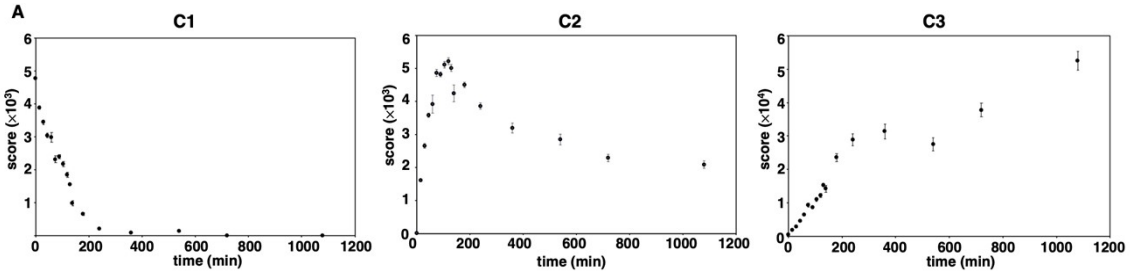


Fig. S1. Fluorescence intensity scores of each components for **1** in CH_3OH by the PARAFAC model.

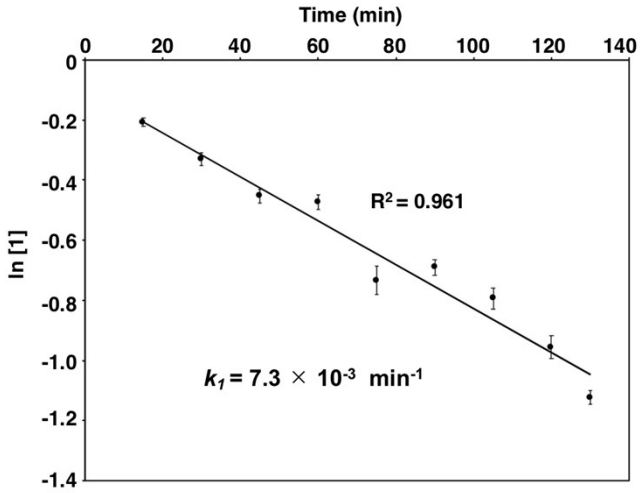


Fig. S2. The ln [**1**] vs. time plots for the photodegradation process of **1**. The curves were fitted with first-order kinetics to calculate the thermal bleaching rate constant: $k_{293\,K} = 7.3 \times 10^{-3}$ min^{-1}.

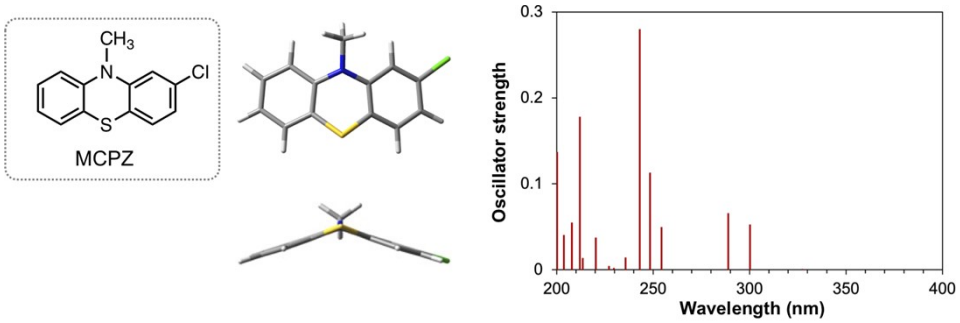
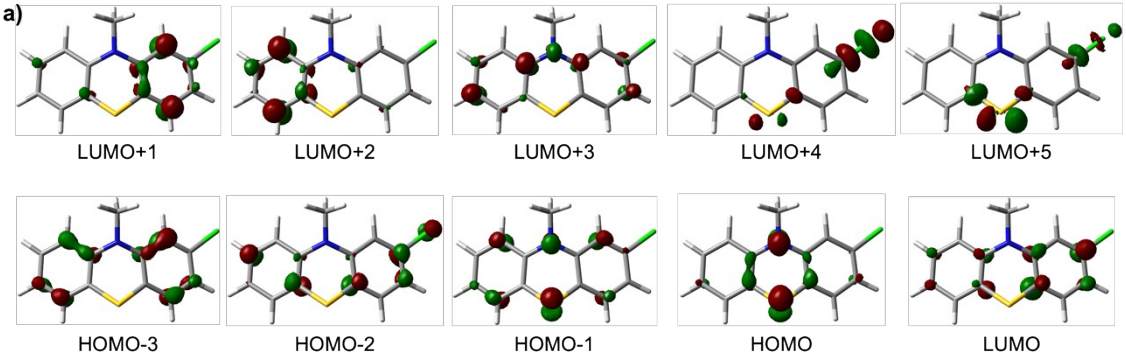


Fig. S3. Optimized structures and calculated absorption spectra of MCPZ. We carried out the density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) level. The excitation energies and oscillator strengths for the optimized structures of MCPZ were obtained using the time-dependent DFT method.

a)



b)

Excited state	Wavelength [nm]	*f*	Contribution
1	327.36	0.0010	HOMO → LUMO (95%) HOMO → LUMO+1 (2%)
2	300.17	0.0527	HOMO → LUMO+1 (88%) HOMO–1 → LUMO (3%) HOMO → LUMO+2 (2%)
3	288.90	0.0659	HOMO → LUMO+2 (87%) HOMO–1 → LUMO (5%) HOMO → LUMO+1 (3%)
4	254.40	0.0496	HOMO → LUMO+3 (88%) HOMO–2 → LUMO (3%) HOMO–3 → LUMO (2%)
5	248.42	0.1131	HOMO → LUMO+4 (60%) HOMO–1 → LUMO (20%) HOMO → LUMO+5 (12%)
6	243.07	0.2800	HOMO–1 → LUMO (59%) HOMO → LUMO+4 (24%) HOMO–2 → LUMO+1 (6%) HOMO → LUMO+2 (4%)
7	235.68	0.0142	HOMO–1 → LUMO+1 (89%) HOMO–2 → LUMO+2 (3%)

Fig. S4. (a) Frontier molecular orbitals of MCPZ (isovalue = 0.08). (b) Calculated absorption wavelength (nm), oscillator strength (*f*), and major contribution (%) for MCPZ.

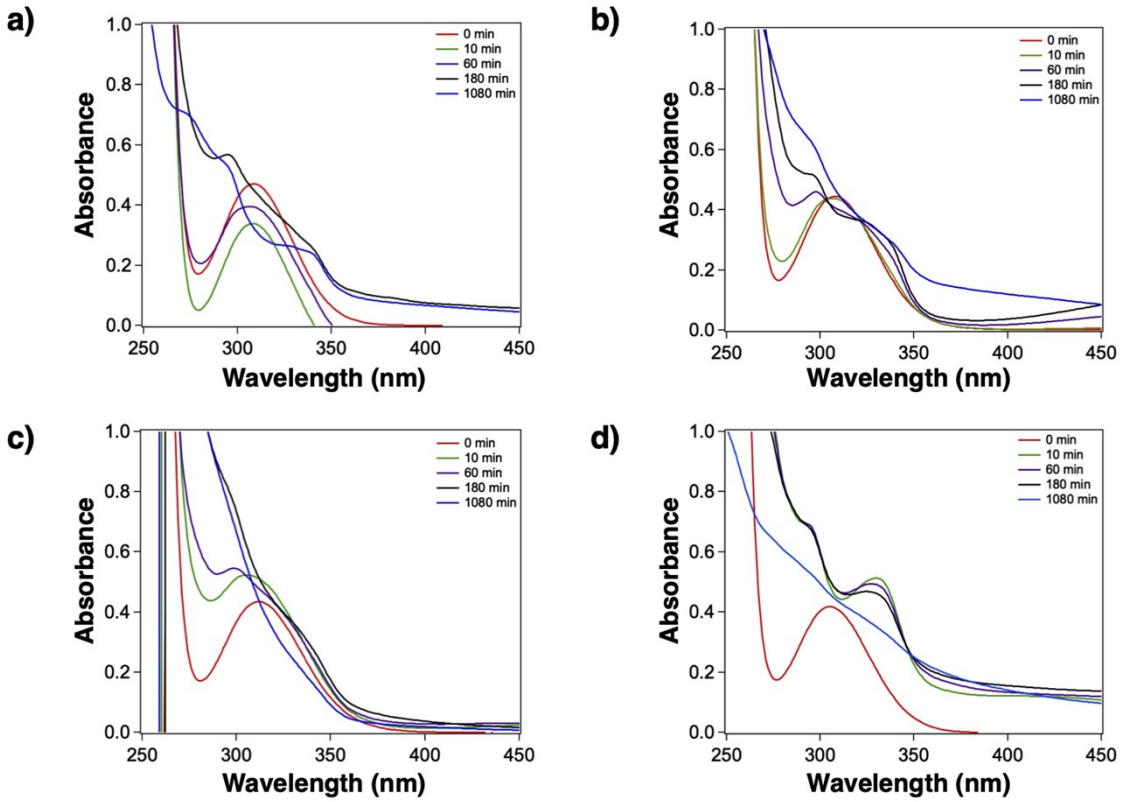


Fig. S5. Absorption spectra of 10 μM of **1** in (a) CH_2Cl_2, (b) CH_3CN, (c) DMF, and (d) H_2O before and after UV irradiation.

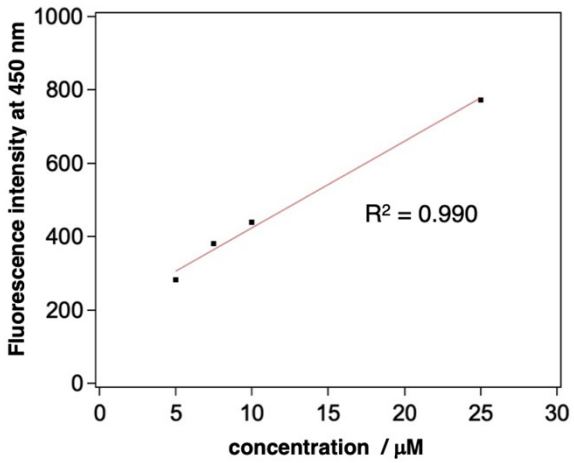
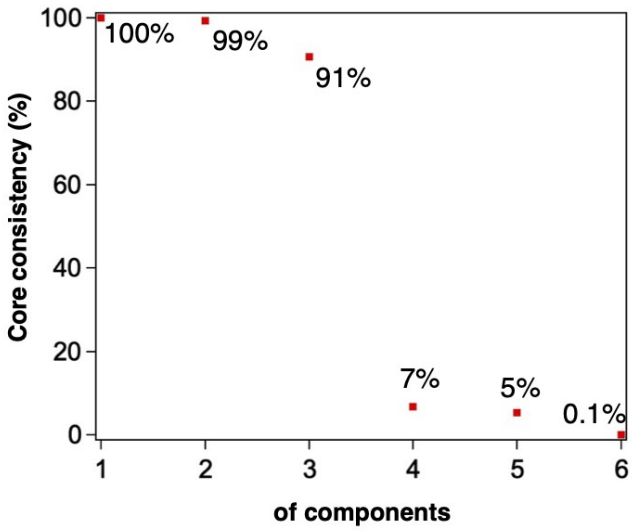


Fig. S6. Calibration curve of the changes in fluorescence emission intensity at 450 nm of **1**. All measurements were performed at 260 nm of excitation wavelength.



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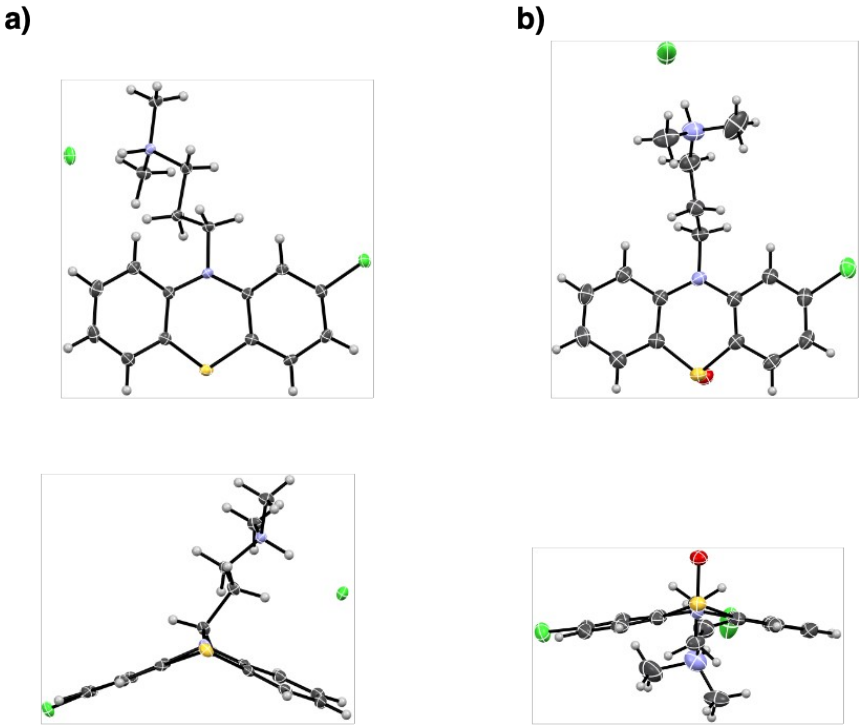


Fig. S8. Crystal structures of (a) **1** and (b) **2**.

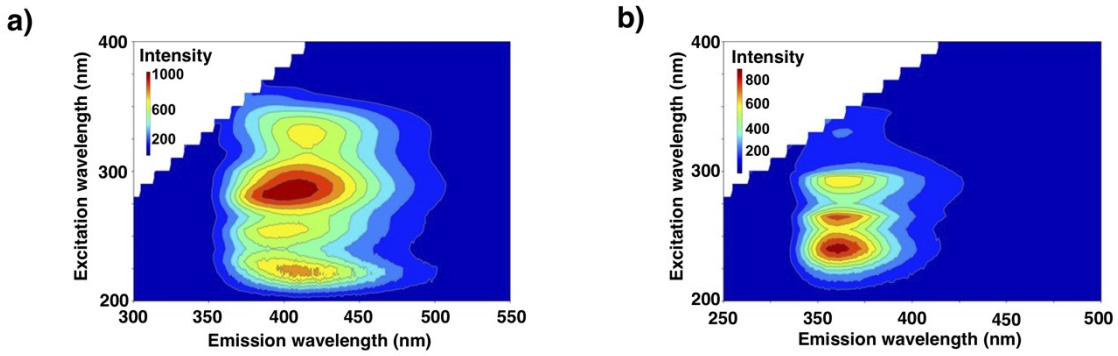


Fig. S9. EEMs of isolated photodegradation products of (a) **4** and (b) **5** in CH_3OH.

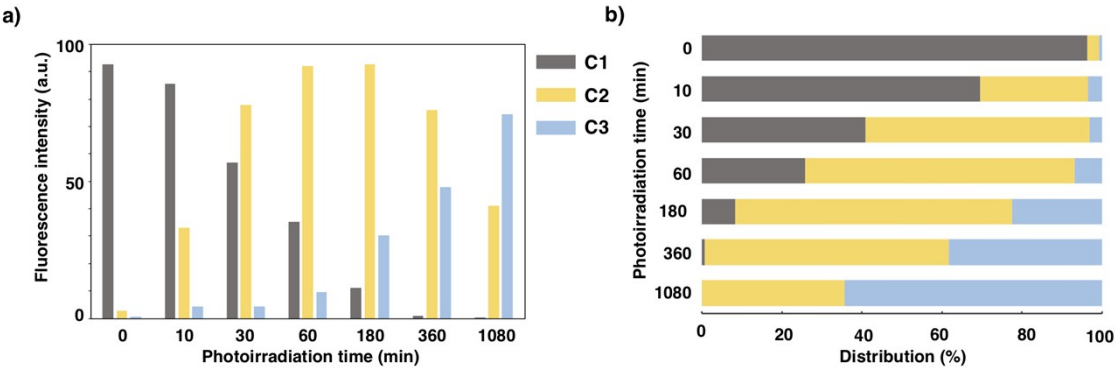


Fig. S10. (a) Normalized fluorescence emission intensity, and (b) relative distribution calculated from EEM-PARAFAC of **1** in CH_3OH.

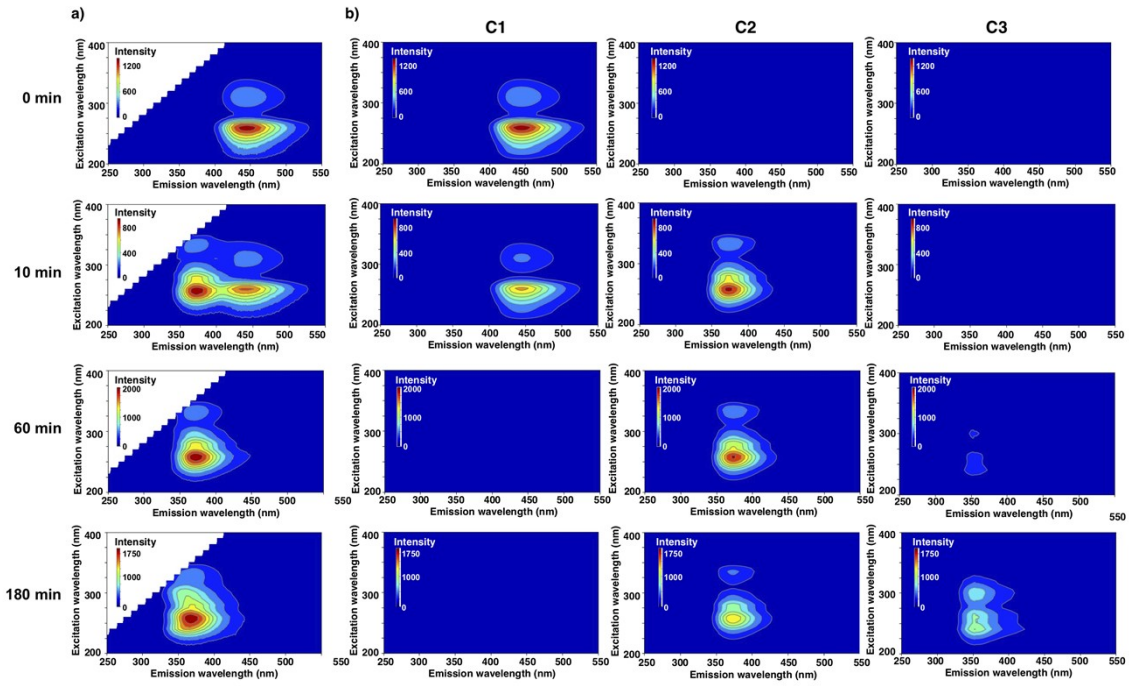


Fig. S11. (a) EEMs of 10 μM of **6** in CH_3OH before and after UV irradiation. (b) Three-component fingerprints from EEM-PARAFAC.

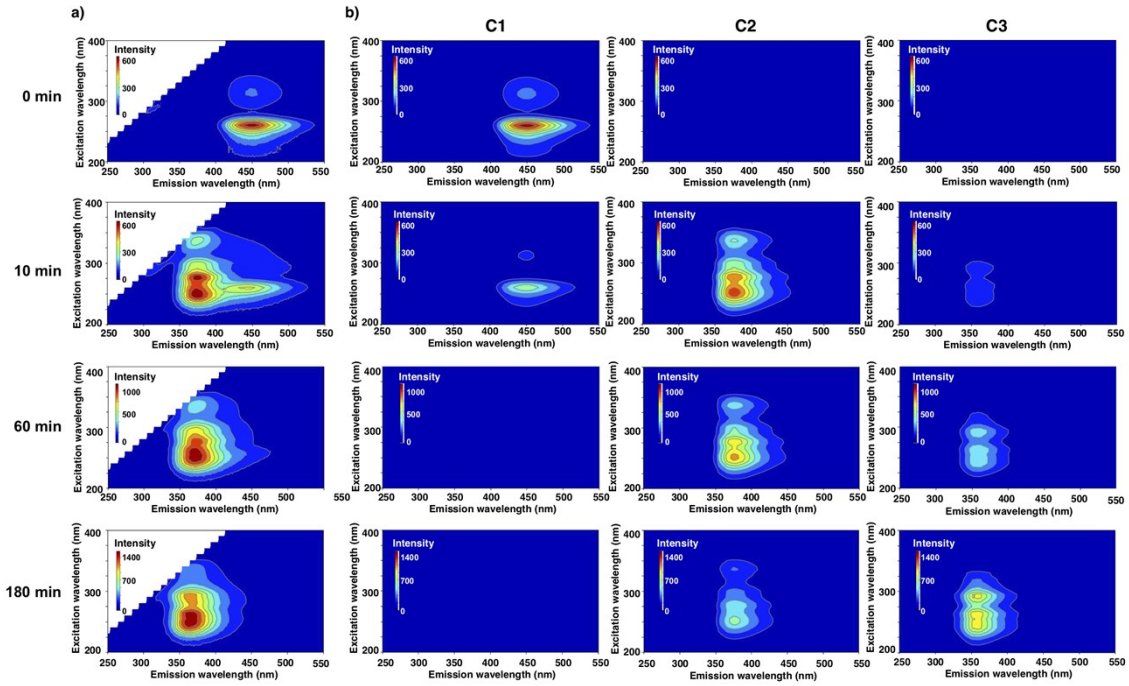


Fig. S12. (a) EEMs of 10 μM of **7** in CH_3OH before and after UV irradiation. (b) Three-component fingerprints from EEM-PARAFAC.

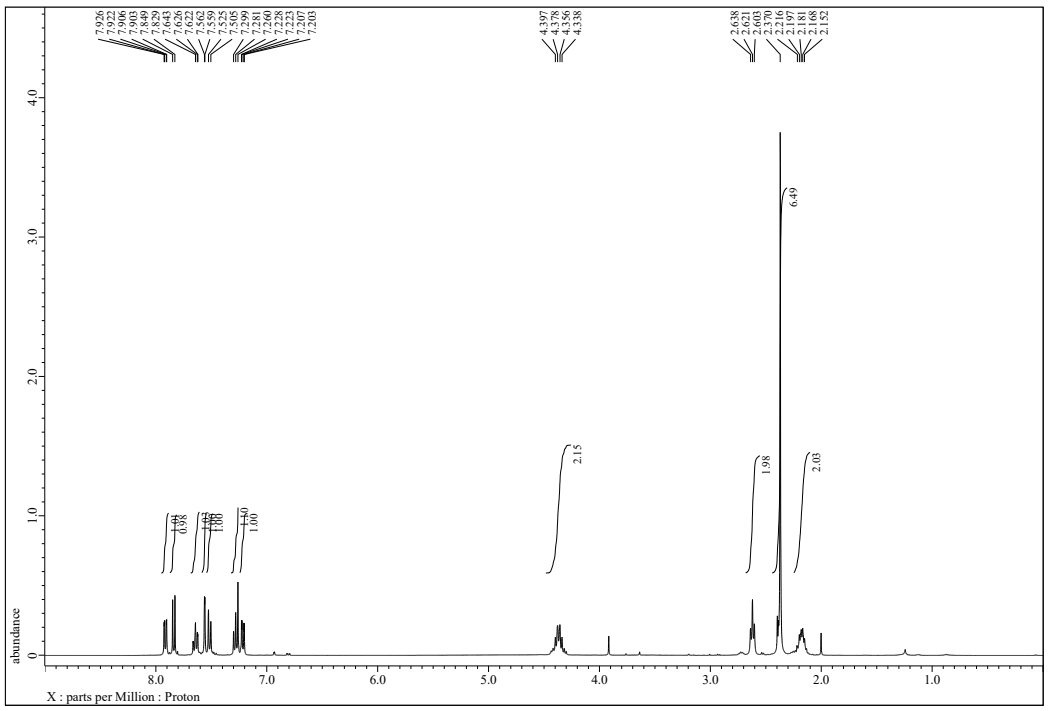
2. Crystallographic data collection and structure refinement

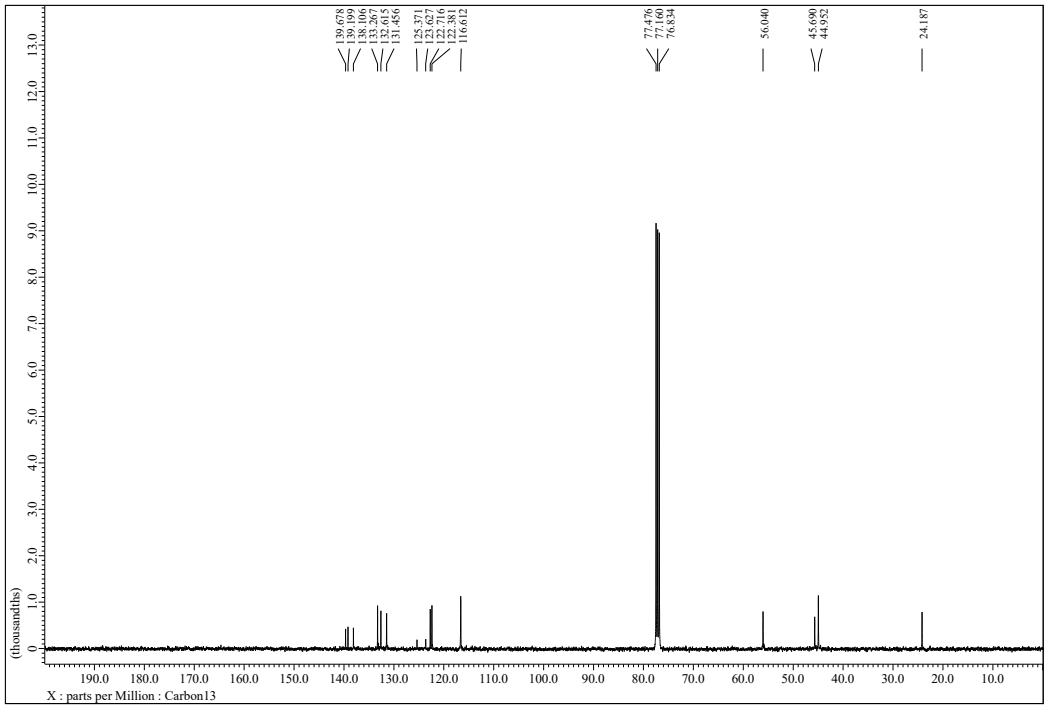
Table S1 Crystal data and structure refinement for compounds **1** and **2**.

	1	**2**
Chemical formula	$2(C_{17}H_{20}Cl_2N_2S) \bullet H_2O$	$C_{17}H_{20}Cl_2N_2OS$
Formula Weight	728.63	371.31
Crystal Color, Habit	colorless, block	colorless, block
Crystal Dimensions	0.391×0.263×0.119 mm	0.118×0.074×0.032 mm
crystal system	monoclinic	triclinic
space group [No.]	P 2_1/c	P 1
a, Å	11.88268(13)	7.5231(2)
b, Å	31.7078(4)	8.4336(3)
c, Å	9.56006(10)	15.3632(5)
α, °	90	75.928(3)
β, °	99.2494(11)	89.441(3)
γ, °	90	84.786(2)
volume, Å^3	3555.15(7)	941.51(5)
Z	4	2
D_{calcd}, g/cm^3	1.361	1.310
T, K	103.15	103.15
radiation[a]	CuKα	CuKα
μ, mm^{-1}	4.386	4.172
$2\theta_{max}$, °	68.428	68.186
F(000)	1528	388
unique reflns	6466	3393
No. of parameters	417	210
R1 factor (I > 2.00σ(I))	0.0356	0.0695
R factor (all reflection)	0.0381	0.0751
wR factor	0.0931	0.1845
GOF	0.946	1.055
CCDC No.	2101545	2101549

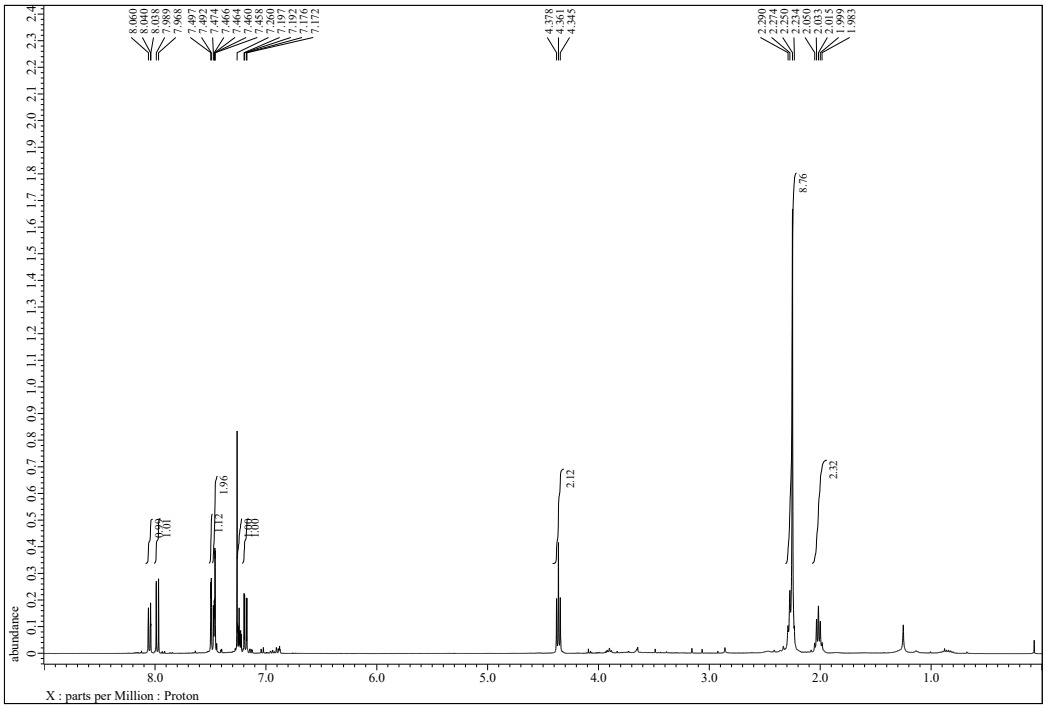
3. NMR spectra data.

Compound **2**





Compound **3**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8.040
8.038
7.989
7.968
7.497
7.492
7.474
7.466
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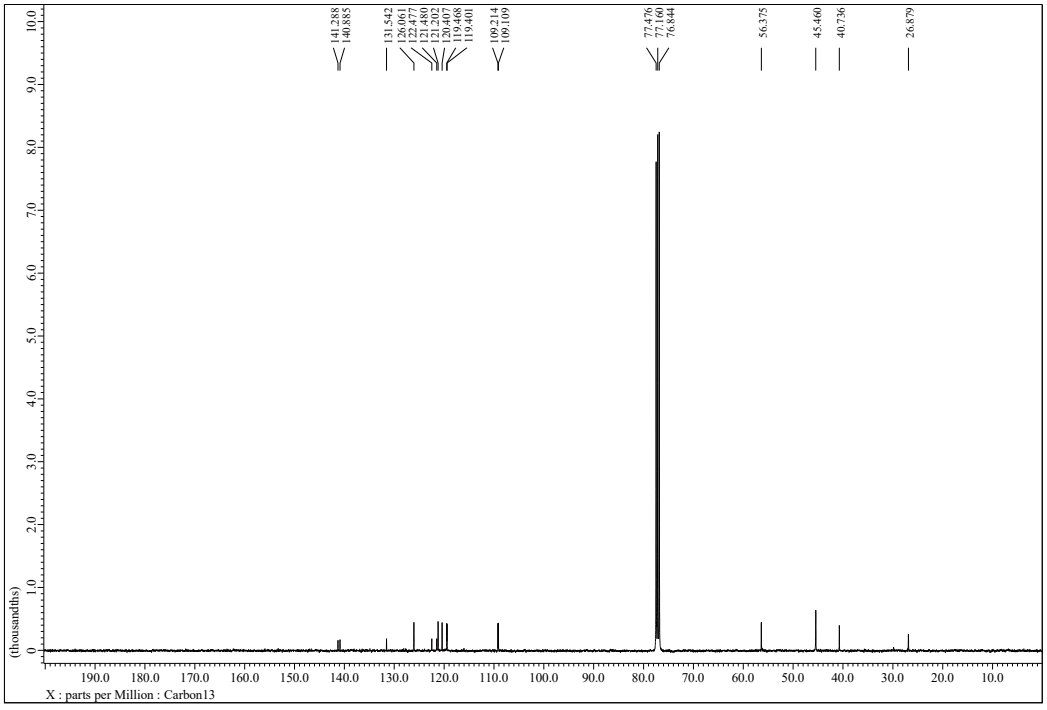
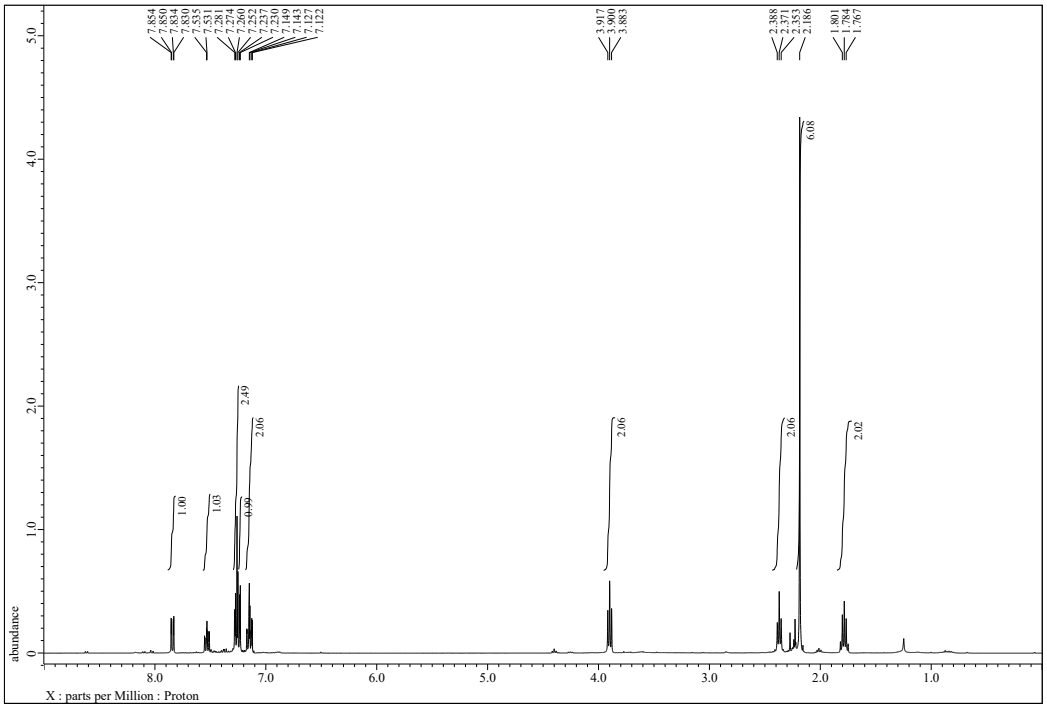
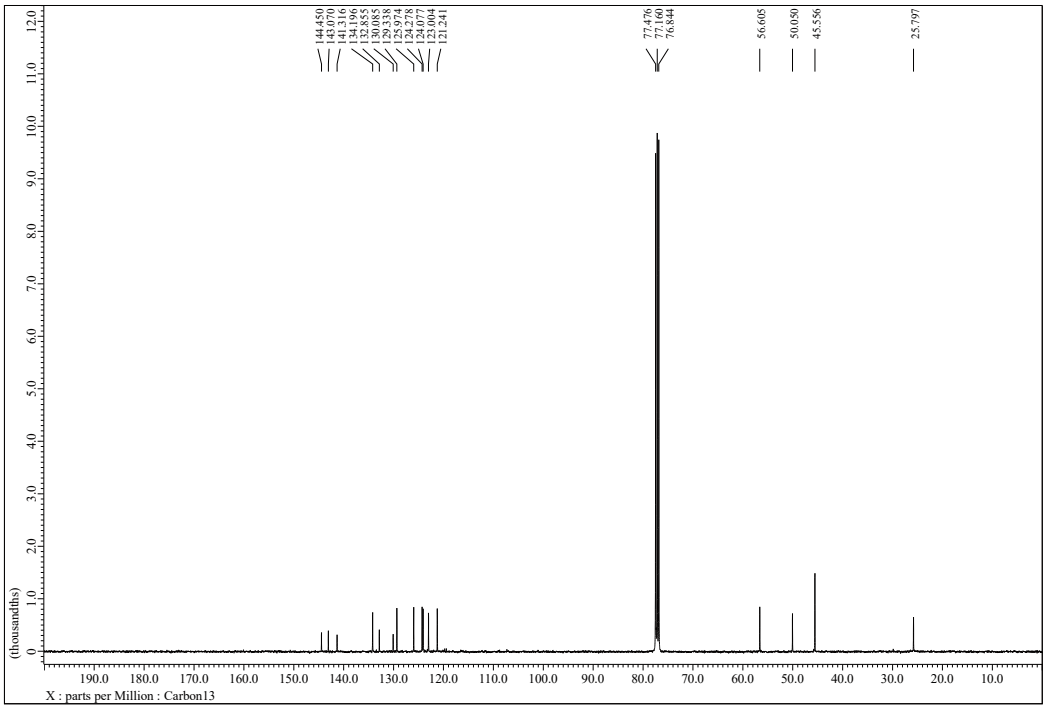
7.460
7.456
7.260
7.197
7.192
7.176
7.172
4.378
4.361
4.345
2.290
2.274
2.250
2.234
2.065
2.035
2.015
1.999
1.983
8.76
2.12
2.32
1.96
1.72
1.01
abundance
X : parts per Million : Proton


141.288
140.885
131.542
126.661
125.477
122.480
121.202
120.407
119.468
119.401
109.214
109.109
77.476
77.160
76.844
56.375
45.460
40.736
26.879
(thousandths)
X : parts per Million : Carbon13

Compound **5**


7.854
7.850
7.834
7.830
7.535
7.531
7.294
7.274
7.260
7.252
7.237
7.210
7.149
7.143
7.127
7.122
3.917
3.900
3.883
2.388
2.371
2.353
2.186
1.801
1.784
1.767
6.08
2.49
2.06
2.06
2.06
2.02
1.00
1.03
0.99
abundance
X : parts per Million : Proton


144.450
143.070
141.316
134.196
132.855
130.085
129.238
125.974
124.278
124.077
123.004
121.241
77.476
77.160
76.844
56.605
50.050
45.556
25.797
(thousandths)
X : parts per Million : Carbon13

4. Cartesian Coordinates (in Å) and Energies

MCPZ

B3LYP/6-31G(d,p)

E(RB3LYP) = –1414.559385

C	2.865802	-1.383439	-0.315847
C	1.614642	-1.960341	-0.09104
C	0.512866	-1.17796	0.247533
C	0.631185	0.224932	0.328067
C	1.879859	0.808758	0.066893
C	-1.760754	0.660476	0.1442
C	-2.133526	-0.69452	0.049026
C	-3.376651	-1.055814	-0.468183
H	-3.631221	-2.108511	-0.544512
C	-4.28912	-0.07621	-0.863511
C	-3.931986	1.266309	-0.76898
C	-2.673983	1.63357	-0.287746
H	3.727945	-1.994125	-0.554975
H	1.497931	-3.037255	-0.161242
H	2.008237	1.882591	0.086763
H	-5.263108	-0.364069	-1.245805
H	-4.625103	2.040486	-1.083815
H	-2.406698	2.683063	-0.25391
N	-0.492035	1.006268	0.670921
C	-0.272648	2.382456	1.089935
H	-0.078807	3.073575	0.255655
H	-1.153932	2.732162	1.630756
H	0.579401	2.415004	1.771806
S	-1.03319	-1.94624	0.682341
C	2.975809	-0.000573	-0.229832
Cl	4.533627	0.765129	-0.524572