

Supplementary Information

6-Aminocoumarin-Naphthoquinone Conjugates: Design, Synthesis, Photophysical and Electrochemical Properties and DFT Calculations

Fabio S. Miranda,* Célia M. Ronconi, Mikaelly O. B. Sousa,
Gleiciani Q. Silveira and Maria D. Vargas*

Instituto de Química, Universidade Federal Fluminense,
Campus do Valongo, Centro, 24020-141 Niterói-RJ, Brazil

1. FTIR and ^1H , ^{13}C and NMR spectra

1.1. 2-chloro-3-(2-oxo-2H-chromen-6-ylamino)naphthalene-1,4-dione **1**

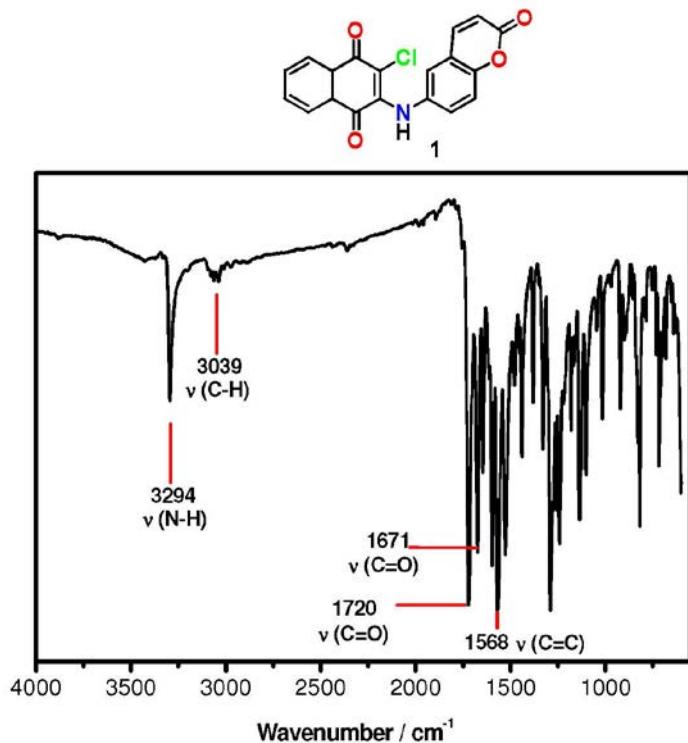


Figure S1. FTIR spectrum of compound **1** (KBr).

*e-mail: miranda@vm.uff.br, mdvargascp@gmail.com

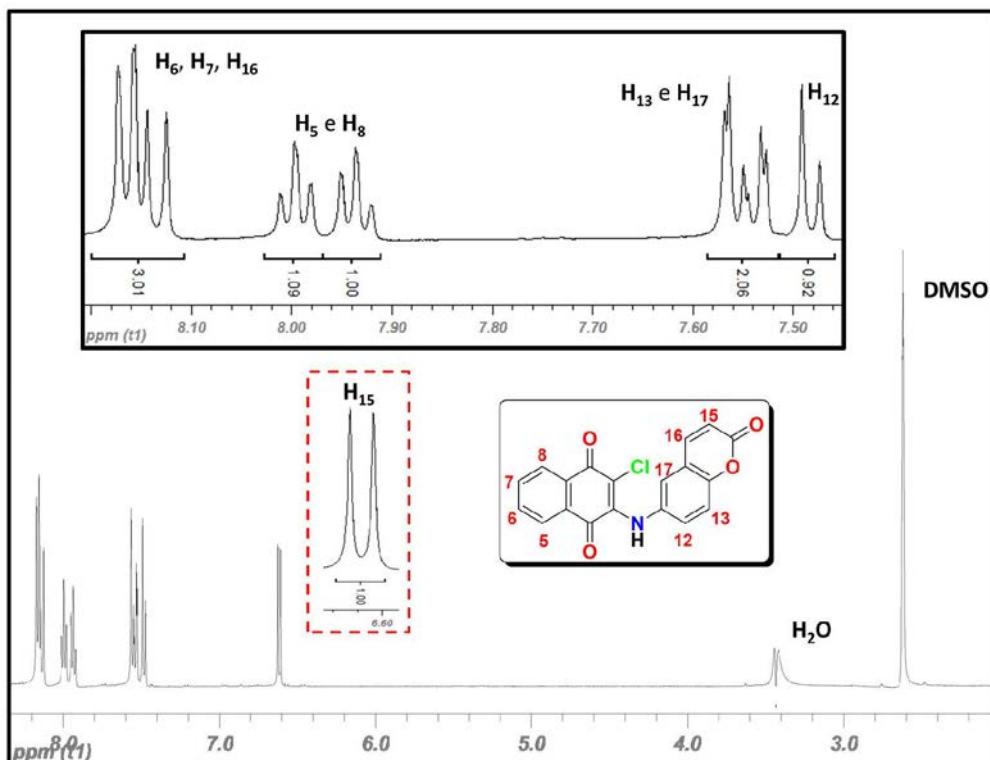


Figure S2. ^1H NMR spectrum of **1** in DMSO-d_6 (500 MHz).

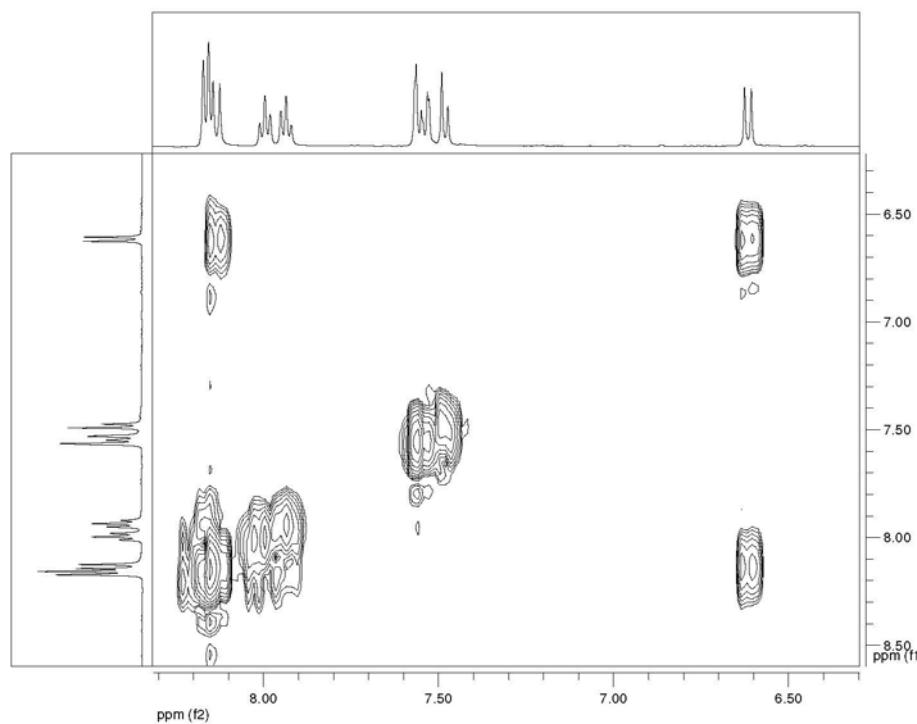


Figure S3. $^1\text{H} \times ^1\text{H}$ – COSY of **1** in DMSO-d_6 (500 MHz).

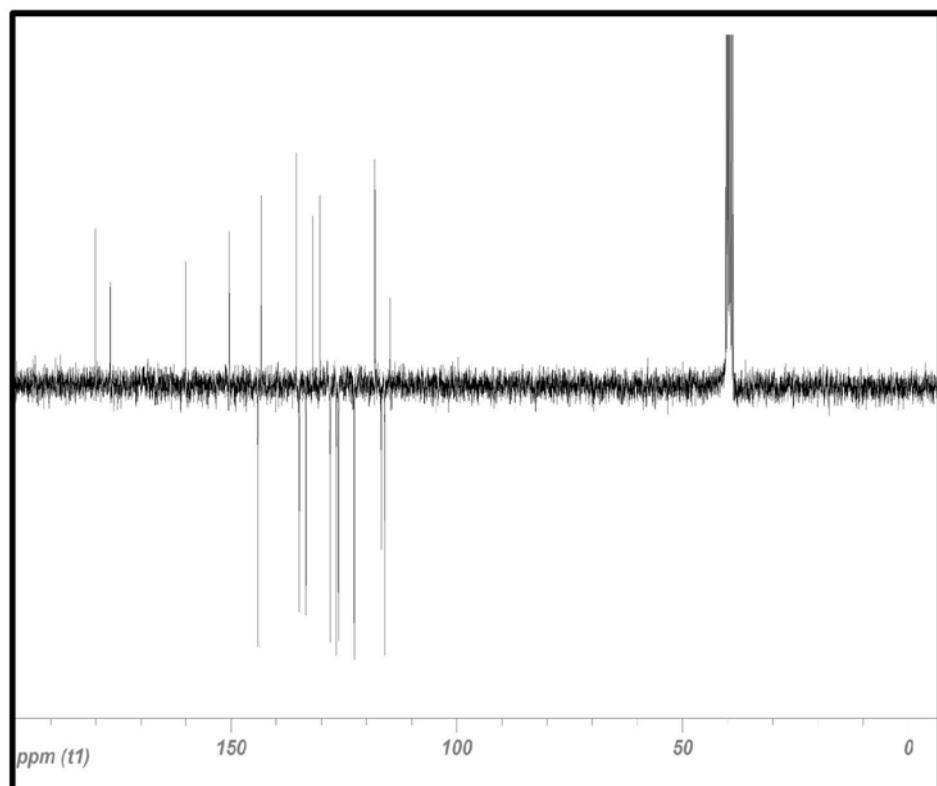


Figure S4. ¹³C NMR-APT spectrum of **1** in DMSO-d₆ (75 MHz).

1.2. 2-chloro-3-(methyl(2-oxo-2H-chromen-6-yl)amino)naphthalene-1,4-dione **2**

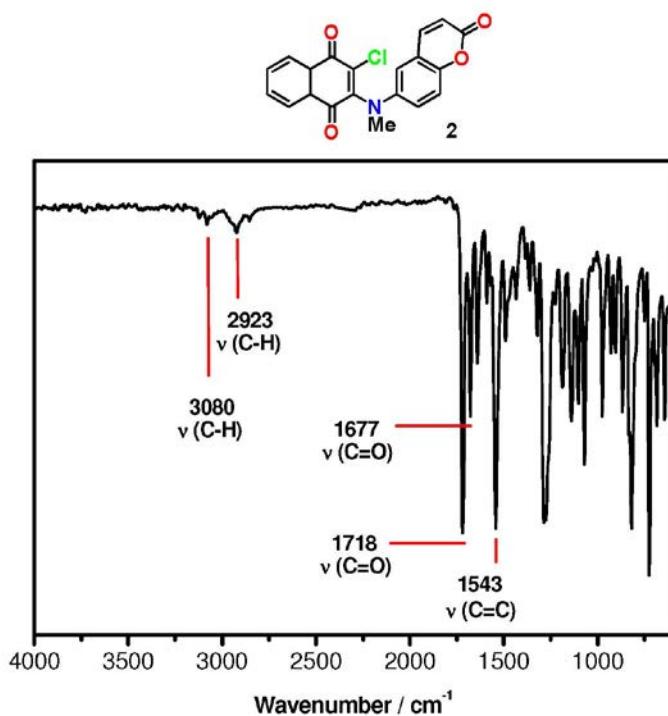


Figure S5. FTIR spectrum of compound **2** (KBr).

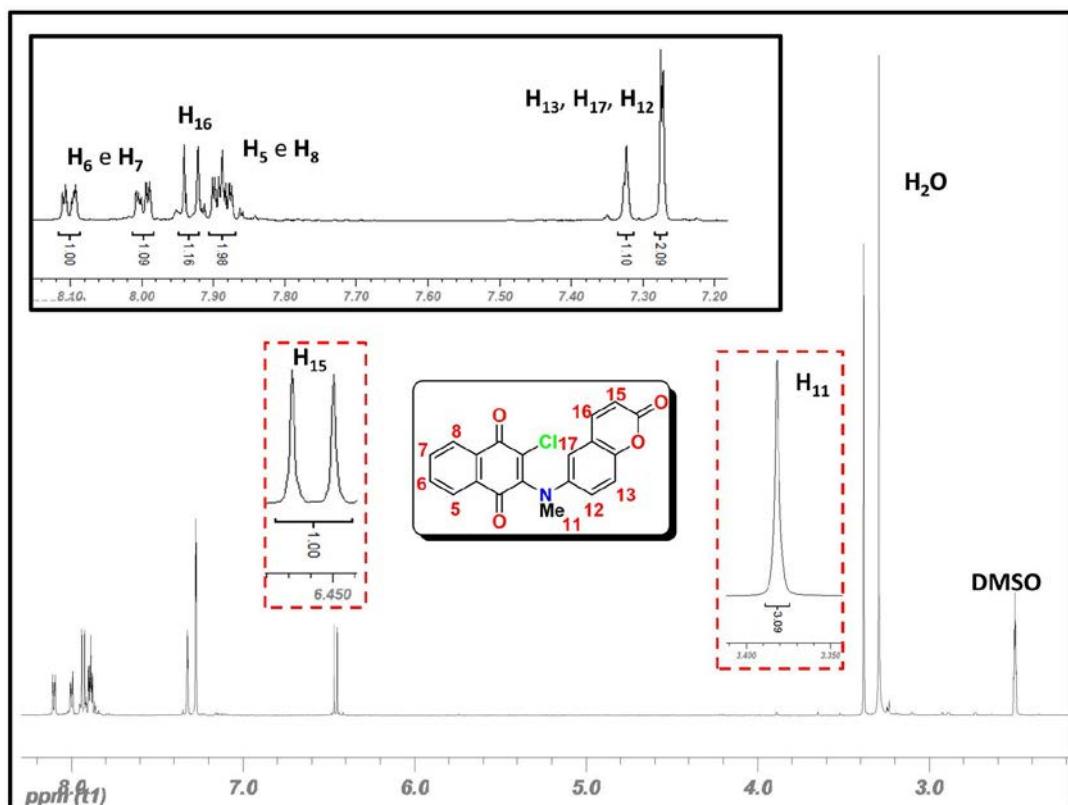


Figure S6. ^1H NMR spectrum of **2** in DMSO-d_6 (500 MHz).

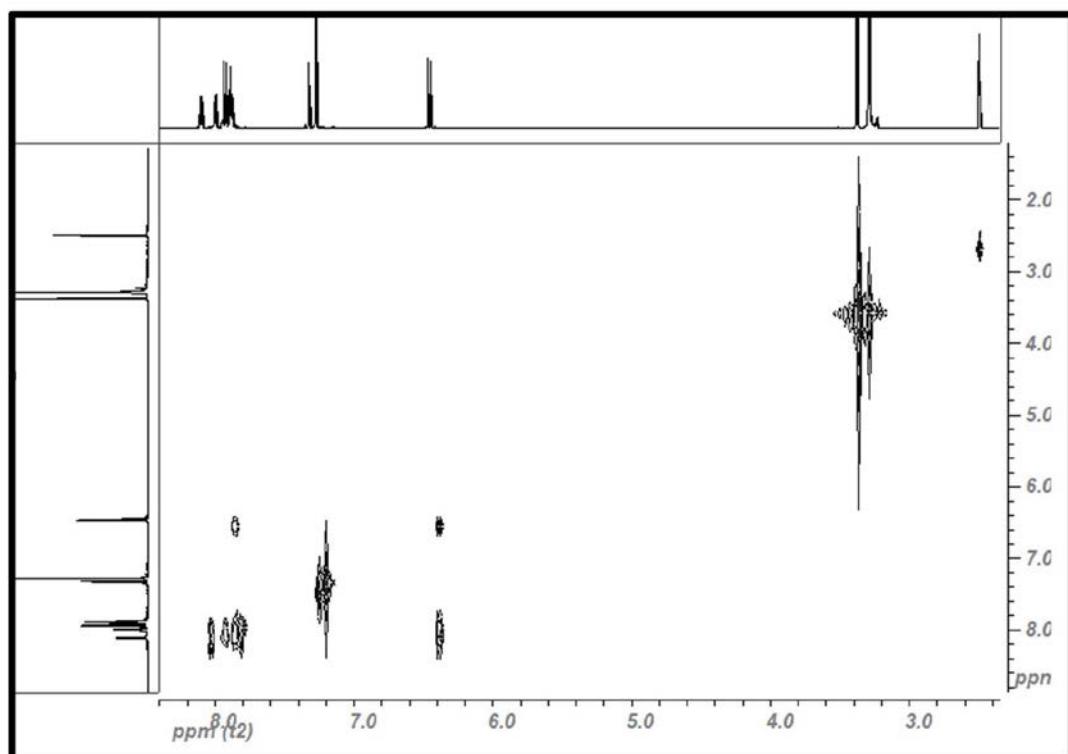


Figure S7. $^1\text{H} \times ^1\text{H}$ – COSY of **2** in DMSO-d_6 (500MHz).

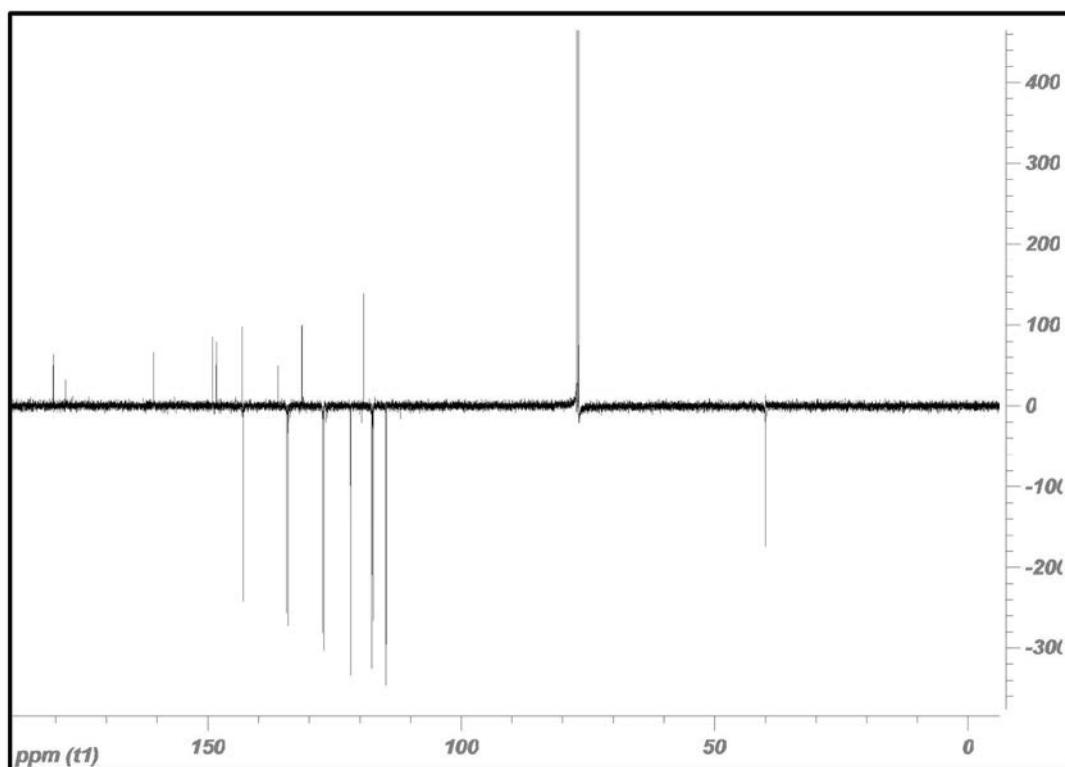


Figure S8. ¹³C NMR-APT spectrum of **2** in CDCl₃ (75 MHz).

1.3. 2-(2-oxo-2H-chromen-6-ylamino)-3-(propylthio)naphthalene-1,4-dione **3**

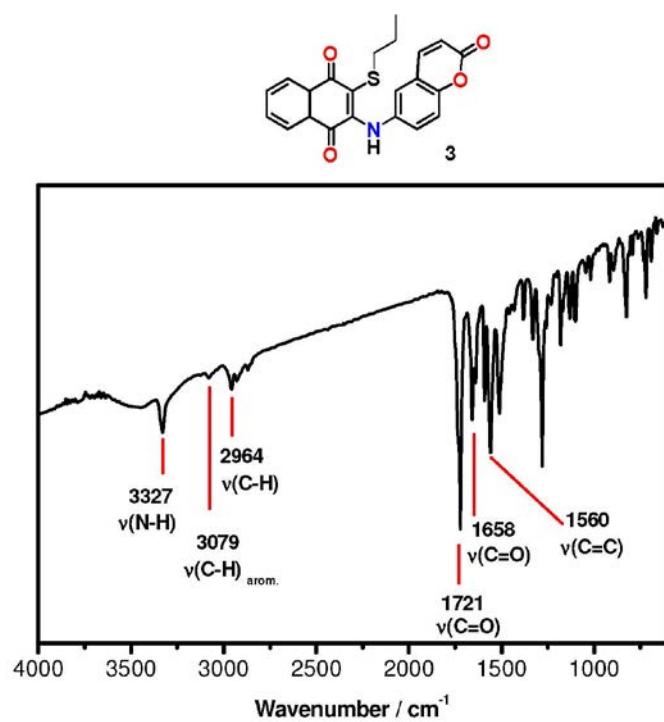


Figure S9. FTIR spectrum of compound **3** (KBr).

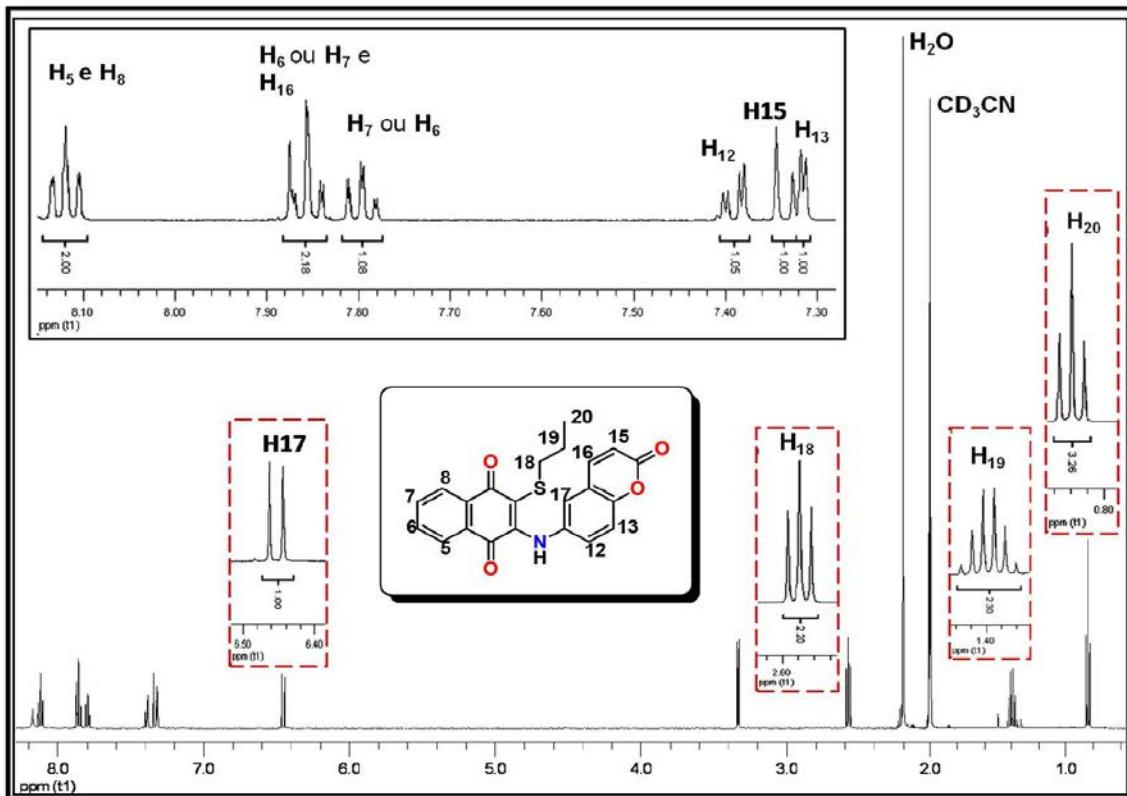


Figure S10. ^1H NMR spectrum of **3** in CD_3CN (500 MHz).

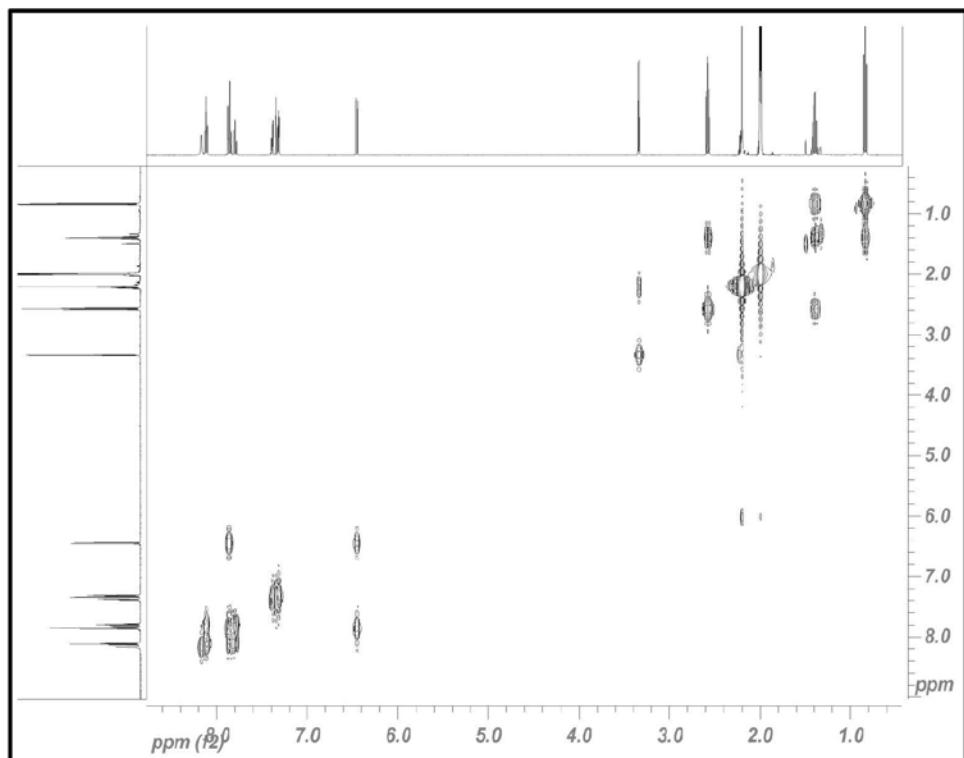


Figure S11. $^1\text{H} \times ^1\text{H}$ – COSY of **3** in CD_3CN (500 MHz).

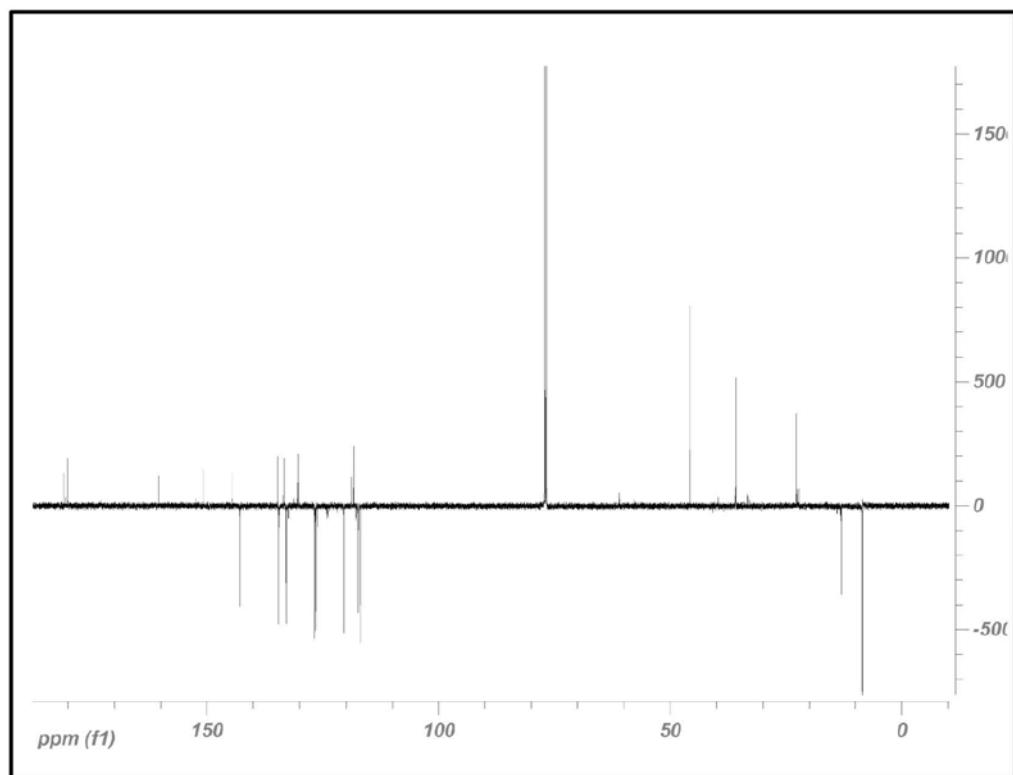


Figure S12. ¹³C NMR-APT spectrum of **3** in CDCl₃ (75 MHz).

1.4. 2-(2-oxo-2H-chromen-6-ylamino)-3-(phenylthiol)naphthalene-1,4(4aH,8aH)-dione **4**

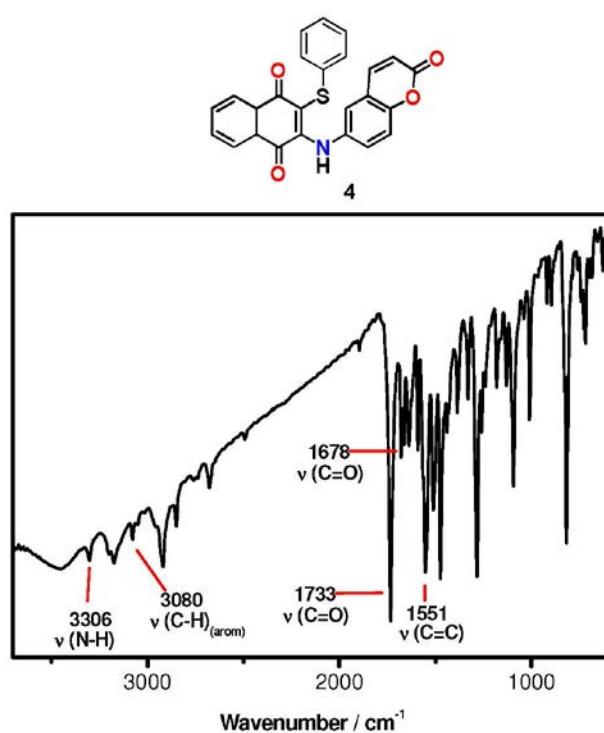


Figure S13. FTIR spectrum of compound **4** (KBr).

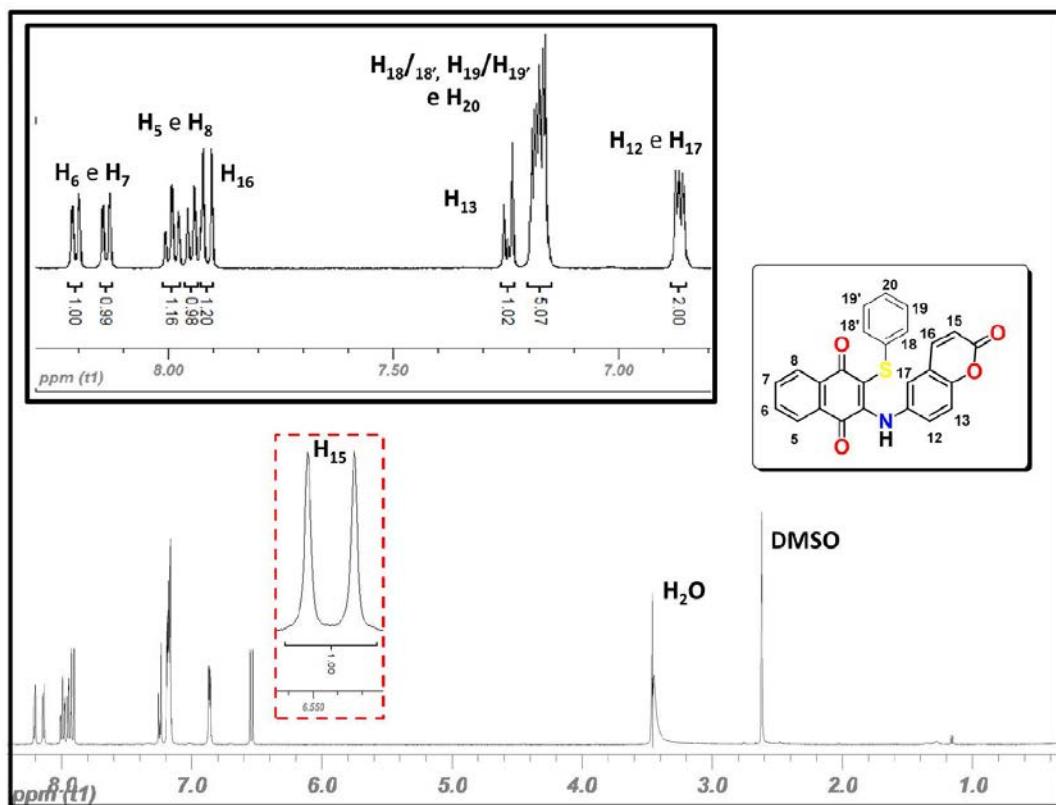


Figure S14 ^1H NMR spectrum of **4** in DMSO-d_6 . (500 MHz).

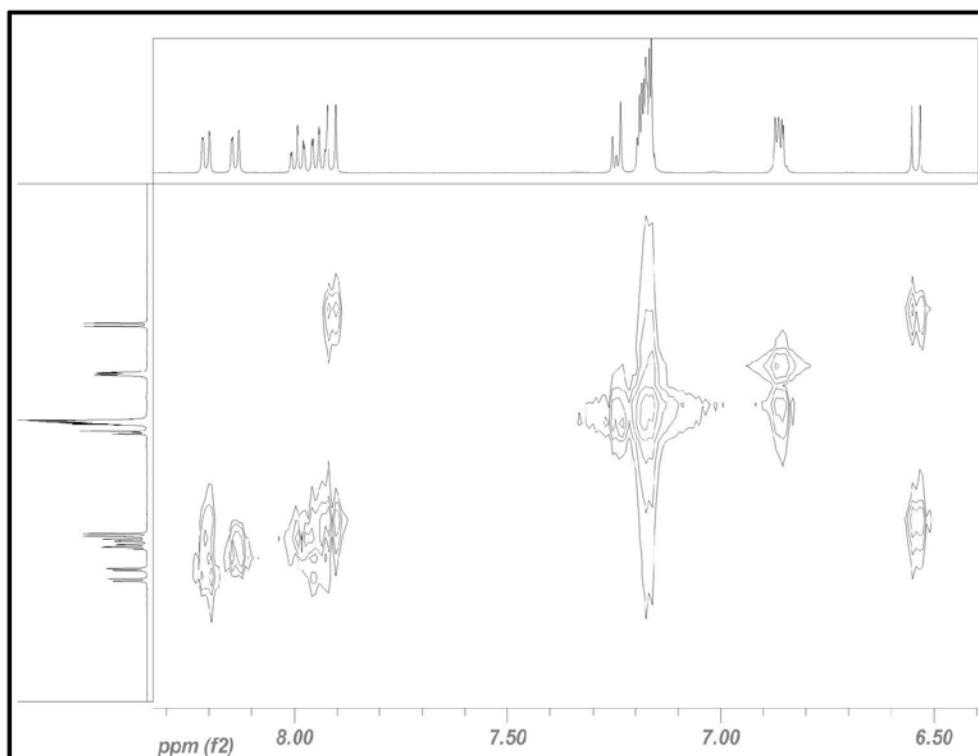


Figure S15. $^1\text{H} \times ^1\text{H}$ – COSY of **4** in DMSO-d_6 (500 MHz).

1.5. 2-(4-chlorophenylthiol)-3-(2-oxo-2H-chromen-6-ylamino)naphthalene-1,4(4aH, 8aH)-dione **5**

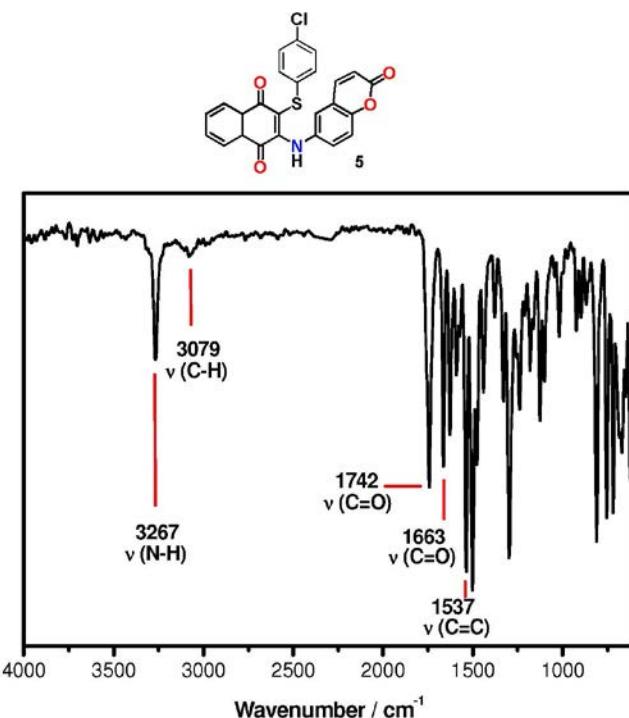


Figure S16. FTIR spectrum of compound **5** (KBr).

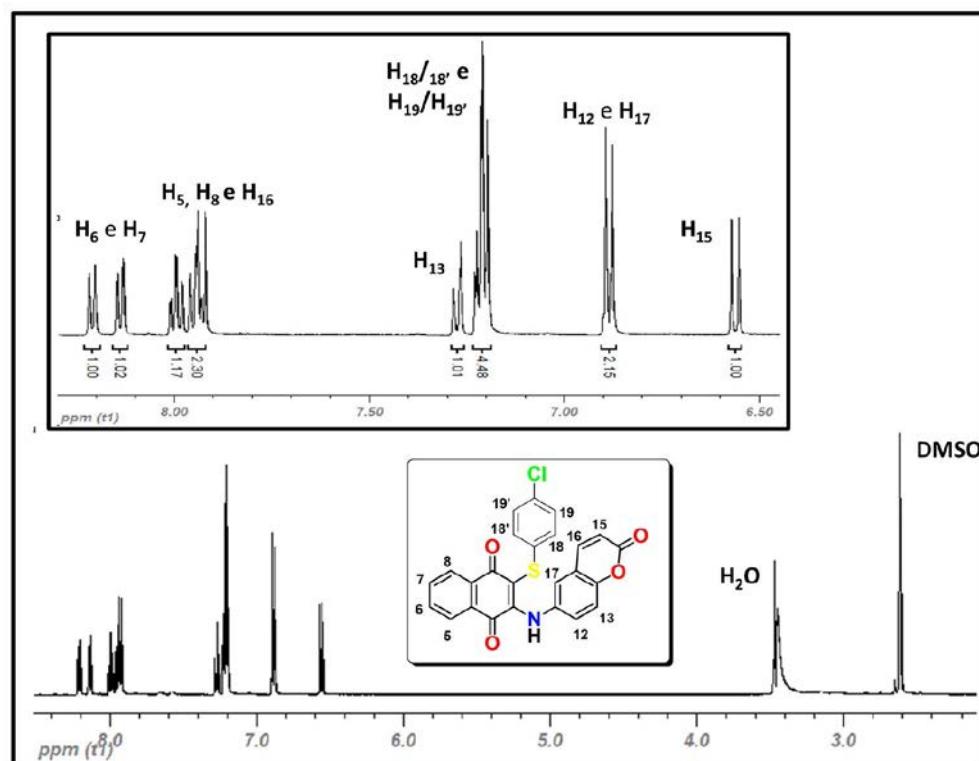


Figure S17. ^1H NMR spectrum of **5** in DMSO-d_6 (500 MHz).

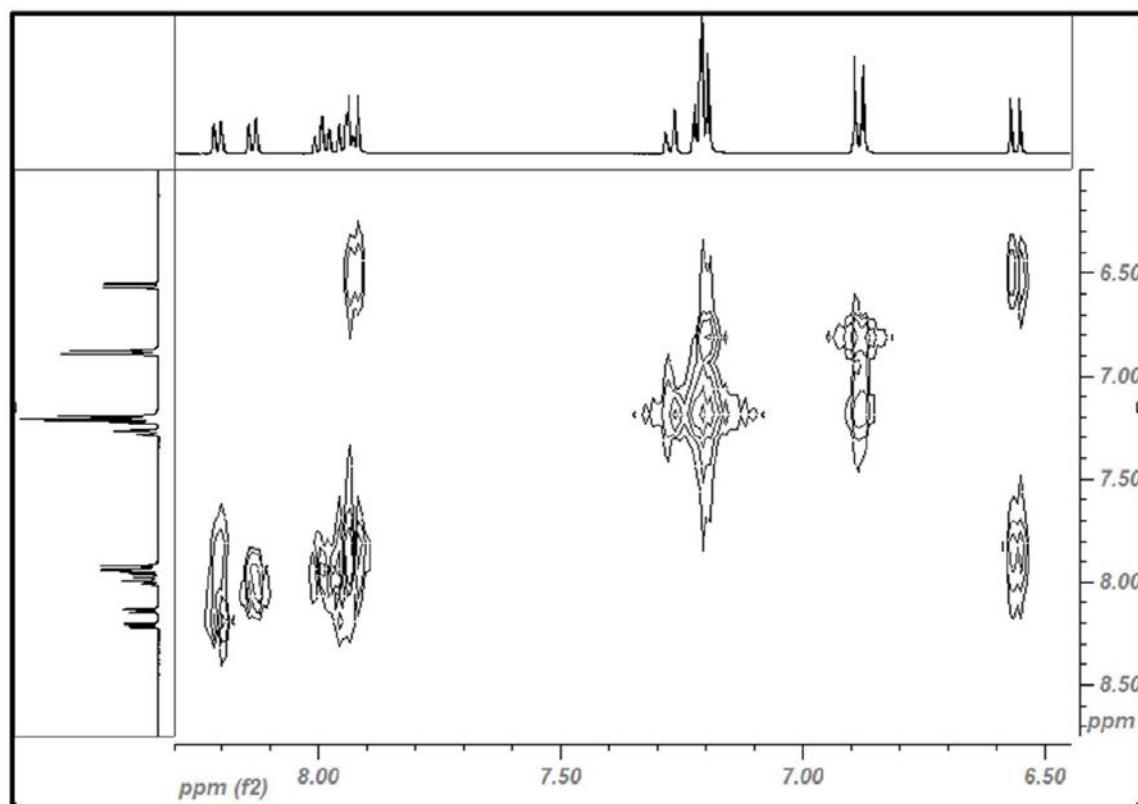
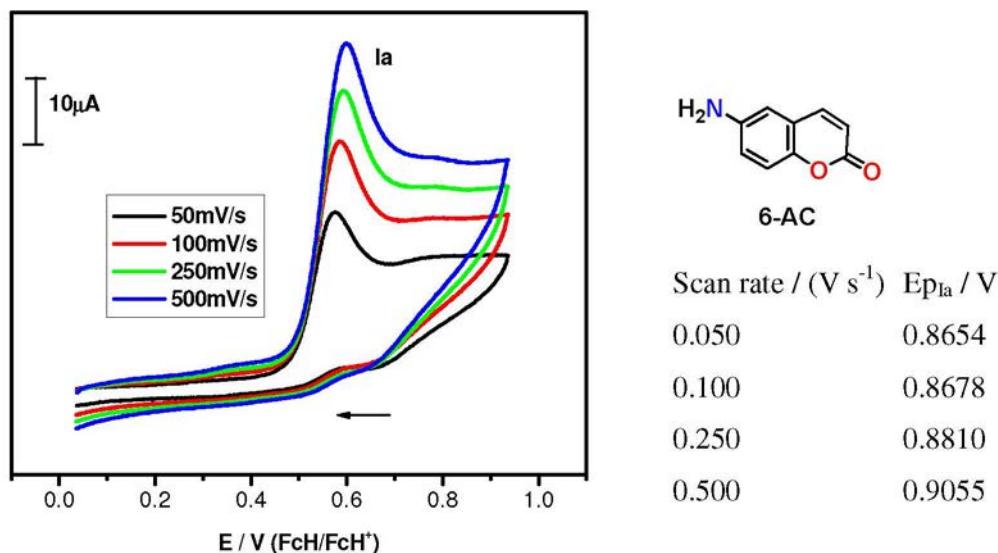
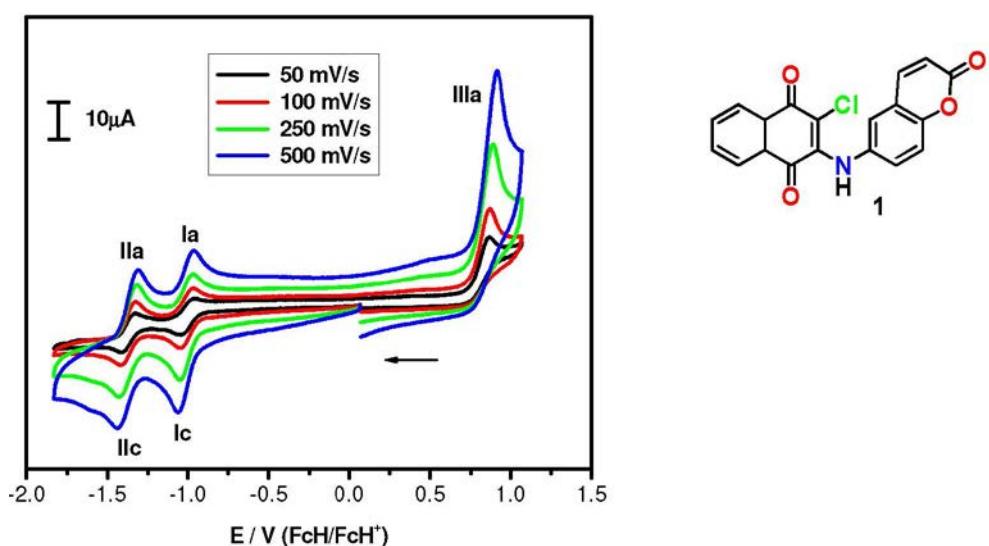


Figure S18. $^1\text{H} \times ^1\text{H}$ – COSY of **5** in DMSO-d_6 (500 MHz).

2. Cyclic voltammograms

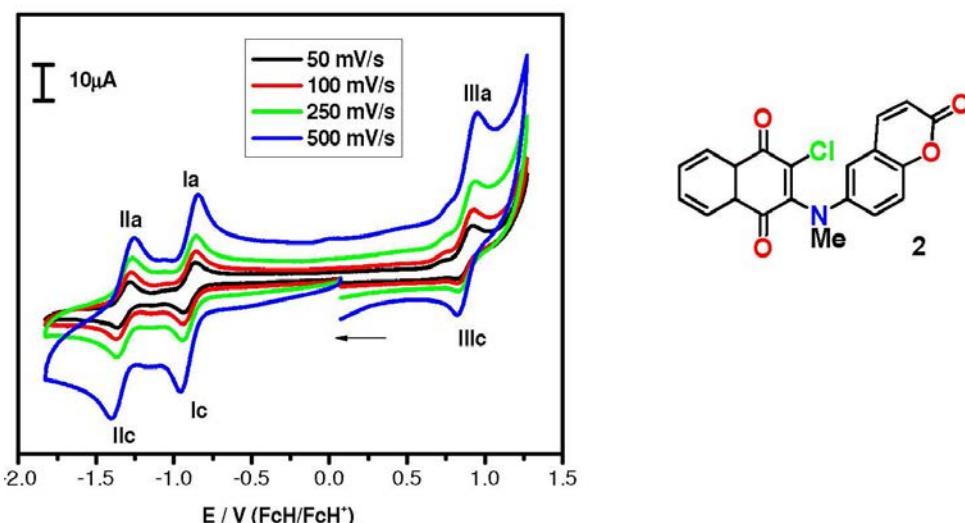
Obtained with a BAS Epsilon potentiostat–galvanostat system at room temperature, using $n\text{-Bu}_4\text{NClO}_4$ (0.1 mol L $^{-1}$) as the supporting electrolyte in CH_3CN (spectroscopic grade) solutions of the compounds (at 1.0×10^{-3} mol L $^{-1}$). The electrochemical cell was a conventional one with three electrodes: Ag/Ag^+ was used as the reference electrode, a

platinum wire as the auxiliary electrode and glassy carbon as the working electrode. The ferrocene/ferrocenium (FcH/FcH^+) couple was used as the internal standard. Pure argon was bubbled through the electrolytic solution to remove oxygen in all experiments. The potential scan was initiated in the anodic direction. Both anodic and cathodic peaks are indicated in the voltammograms.

**Figure S19.** Cyclic voltammograms of 6-aminocoumarin 6-AC; values vs. FcH/FcH⁺.

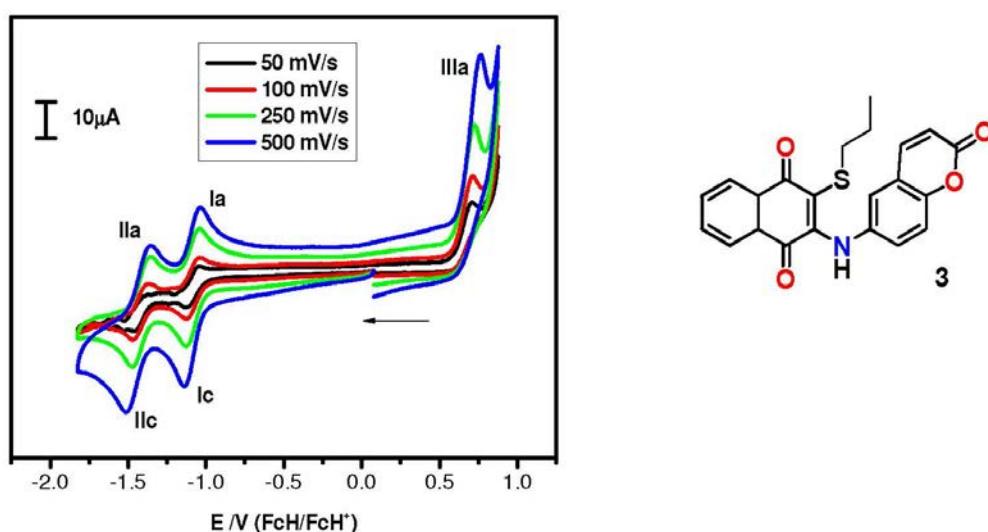
Scan rate / (V s ⁻¹)	E_{pIc} / V	E_{pIa} / V	E_{pIIc} / V	E_{pIIa} / V	E_{pIIIa} / V	E_{pI} / V	E_{pII} / V	$E_{1/2pI} / V$	$E_{1/2pII} / V$
0.050	-1.038	-0.961	-1.420	-1.328	0.865	0.077	0.093	0.999	1.374
0.100	-1.038	-0.961	-1.420	-1.328	0.868	0.077	0.093	0.999	1.374
0.250	-1.049	-0.972	-1.431	-1.328	0.881	0.077	0.103	1.010	1.379
0.500	-1.059	-0.961	-1.447	-1.317	0.906	0.097	0.125	1.001	1.379

Figure S20. Cyclic voltammograms of 2-chloro-3-(2-oxo-2H-chromen-6-ylamino)naphthalene-1,4-dione **1**; values vs. FcH/FcH⁺.



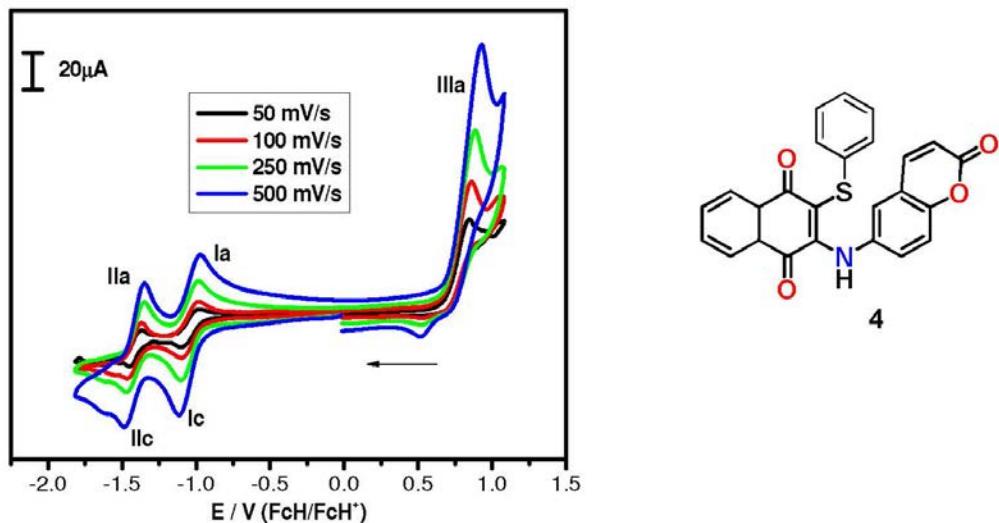
Scan rate / (V s^{-1})	$E_{\text{pIc}} / \text{V}$	$E_{\text{pIa}} / \text{V}$	$E_{\text{pIIc}} / \text{V}$	$E_{\text{pIIa}} / \text{V}$	$E_{\text{pIIIc}} / \text{V}$	$E_{\text{pIIa}} / \text{V}$	$\Delta E_{\text{pI}} / \text{V}$	$\Delta E_{\text{pII}} / \text{V}$	$\Delta E_{\text{pIII}} / \text{V}$	$E_{\frac{1}{2}\text{pI}} / \text{V}$	$E_{\frac{1}{2}\text{pII}} / \text{V}$	$E_{\frac{1}{2}\text{pIII}} / \text{V}$
0.050	-0.943	-0.868	-1.409	-1.276	0.835	0.920	0.075	0.133	0.085	-0.905	-1.342	0.877
0.100	-0.953	-0.857	-1.367	-1.273	0.835	0.921	0.096	0.094	0.086	-0.905	-1.320	0.878
0.250	-0.952	-0.857	-1.372	-1.274	0.825	0.931	0.095	0.098	0.106	-0.904	-1.323	0.878
0.500	-0.964	-0.855	-1.374	-1.268	0.814	0.947	0.109	0.106	0.133	-0.909	-1.321	0.880

Figure S21. Cyclic voltammogram of 2-chloro-3-(methyl(2-oxo-2H-chromen-6-yl)amino)-naphthalene-1,4-dione **2**; values vs. FcH/FcH^+ .



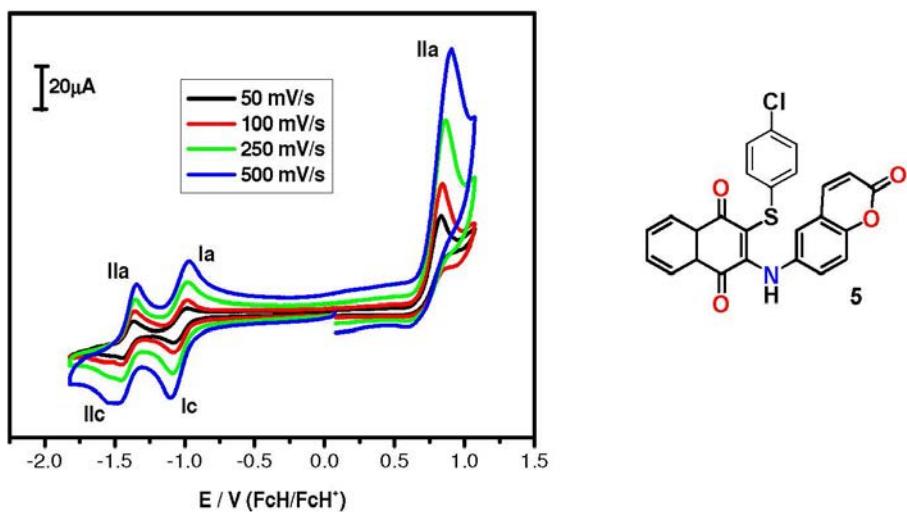
Scan rate / (V s^{-1})	$E_{\text{pIc}} / \text{V}$	$E_{\text{pIa}} / \text{V}$	$E_{\text{pIIc}} / \text{V}$	$E_{\text{pIIa}} / \text{V}$	$E_{\text{pIIIa}} / \text{V}$	$\Delta E_{\text{pI}} / \text{V}$	$\Delta E_{\text{pII}} / \text{V}$	$E_{\frac{1}{2}\text{pI}} / \text{V}$	$E_{\frac{1}{2}\text{pII}} / \text{V}$
0.050	-1.121	-1.046	-1.462	-1.374	0.705	0.075	0.088	1.083	1.418
0.100	-1.121	-1.047	-1.472	-1.372	0.710	0.074	0.100	1.084	1.422
0.250	-1.121	-1.046	-1.479	-1.362	0.721	0.075	0.117	1.083	1.420
0.500	-1.142	-1.035	-1.521	-1.359	0.763	0.107	0.162	1.088	1.440

Figure S22. Cyclic voltammogram of 2-(2-oxo-2H-chromen-6-ylamino)-3-(propylthio)-naphthalene-1,4-dione **3**; values vs. FcH/FcH^+ .



Scan rate / ($V s^{-1}$)	E_{pIc} / V	E_{pIa} / V	E_{pIIc} / V	E_{pIIa} / V	E_{pIIIa} / V	$\Delta E_{pI} / V$	$\Delta E_{pII} / V$	$E_{1/2pI} / V$	$E_{1/2pII} / V$
0.050	-1.106	-0.984	-1.449	-1.369	0.840	0.122	0.080	-1.045	-1.409
0.100	-1.107	-0.984	-1.472	-1.368	0.863	0.123	0.104	-1.045	-1.420
0.250	-1.106	-0.984	-1.472	-1.358	0.885	0.122	0.114	-1.045	-1.415
0.500	-1.117	-0.972	-1.495	-1.346	0.920	0.145	0.149	-1.044	-1.420

Figure S23. Cyclic voltammogram of 2-(2-oxo-2H-chromen-6-ylamino)-3-(phenylthiol)-naphthalene-1,4(4aH,8aH)-dione **4**; values vs. FcH/FcH^+ .

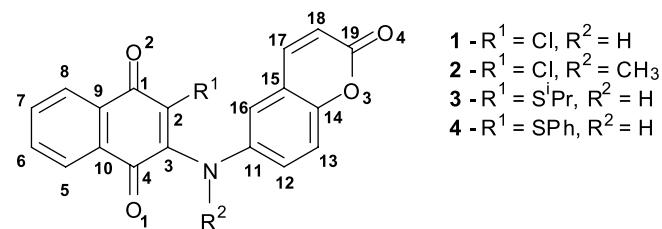


Scan rate / ($V s^{-1}$)	E_{pIc} / V	E_{pIa} / V	E_{pIIc} / V	E_{pIIa} / V	E_{pIIIa} / V	E_{pI} / V	E_{pII} / V	$E_{1/2pI} / V$	$E_{1/2pII} / V$
0.050	-1.079	-0.988	-1.443	-1.363	0.831	0.091	0.080	-1.033	-1.403
0.100	-1.087	-0.985	-1.455	-1.360	0.842	0.102	0.095	-1.036	-1.407
0.250	-1.091	-0.977	-1.455	-1.360	0.854	0.114	0.095	-1.034	-1.407
0.500	-1.102	-0.977	-1.458	-1.352	0.900	0.125	0.106	-1.039	-1.405

Figure S24. Cyclic voltammogram of 2-(4-chlorophenylthiol)-3-(2-oxo-2H-chromen-6-ylamino)-naphthalene-1,4(4aH, 8aH)-dione **5**; values vs. FcH/FcH^+ .

3. Computational details

Table S1. Selected bond lengths (\AA) for the ground (S_0) and excited (S_1) states of compounds **1–4**

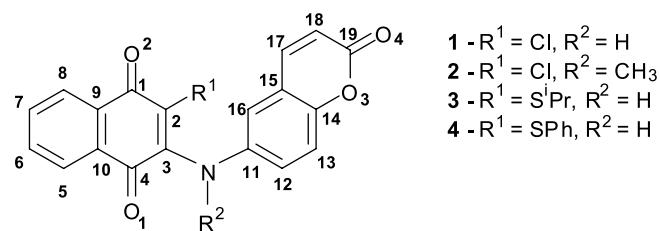


Bond	X-ray	1		2		3		4	
		S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C1–C2	1.461	1.466	1.445	1.484	1.445	1.475	1.453	1.474	1.453
C2–C3	1.356	1.375	1.390	1.369	1.389	1.381	1.392	1.381	1.392
C2–R ¹	1.727	1.747	1.751	1.739	1.751	1.782	1.783	1.786	1.783
C3–N1	1.361	1.359	1.432	1.391	1.441	1.365	1.438	1.360	1.438
N1–R ²	0.880	1.019	1.017	1.471	1.472	1.018	1.017	1.018	1.017
C3–C4	1.511	1.518	1.441	1.514	1.440	1.511	1.439	1.516	1.441
C4–O1	1.214	1.229	1.262	1.227	1.262	1.232	1.264	1.231	1.263
C4–C10	1.474	1.474	1.474	1.483	1.474	1.475	1.473	1.473	1.474
C10–C5	1.389	1.401	1.409	1.400	1.409	1.400	1.410	1.401	1.409
C5–C6	1.383	1.395	1.388	1.396	1.388	1.395	1.388	1.395	1.388
C6–C7	1.379	1.399	1.408	1.400	1.408	1.399	1.408	1.399	1.408
C7–C8	1.392	1.398	1.388	1.396	1.388	1.398	1.388	1.398	1.388
C8–C9	1.384	1.397	1.410	1.399	1.410	1.397	1.410	1.397	1.410
C9–C10	1.406	1.407	1.418	1.407	1.418	1.406	1.418	1.407	1.418
C9–C1	1.492	1.496	1.479	1.488	1.479	1.499	1.479	1.499	1.481
C1–O2	1.220	1.234	1.258	1.230	1.258	1.236	1.260	1.234	1.256
C11–N1	1.411	1.416	1.343	1.410	1.355	1.417	1.346	1.420	1.348
C11–C12	1.398	1.410	1.437	1.414	1.436	1.410	1.435	1.408	1.435
C12–C13	1.370	1.389	1.368	1.391	1.372	1.389	1.370	1.390	1.371
C13–C14	1.376	1.396	1.414	1.393	1.411	1.395	1.412	1.395	1.412
C14–O3	1.387	1.372	1.343	1.374	1.346	1.373	1.346	1.372	1.346
O3–C19	1.386	1.384	1.410	1.381	1.408	1.383	1.407	1.384	1.407
C19–O4	1.198	1.221	1.210	1.223	1.211	1.222	1.211	1.221	1.211
C19–C18	1.447	1.453	1.454	1.453	1.454	1.453	1.454	1.453	1.454
C18–C17	1.332	1.356	1.351	1.356	1.352	1.356	1.352	1.356	1.352
C17–C15	1.447	1.441	1.446	1.442	1.446	1.441	1.445	1.441	1.445
C15–C14	1.385	1.406	1.420	1.406	1.416	1.406	1.418	1.407	1.418
C15–C16	1.396	1.407	1.387	1.404	1.388	1.407	1.389	1.407	1.389
C16–C11	1.380	1.393	1.423	1.400	1.425	1.394	1.421	1.393	1.420

Table S2. Selected bond lengths (\AA) for the ground state (S_0) of compounds **3–5**

3 - $R^1 = S^i\text{Pr}$, $R^2 = H$
4 - $R^1 = \text{SPh}$, $R^2 = H$
5 - $R^1 = S(\text{C}_6\text{H}_4\text{Cl})$, $R^2 = H$

Bond	3	4	5
C1–C2	1.475	1.474	1.474
C2–C3	1.381	1.381	1.381
C2–R ¹	1.782	1.786	1.786
C3–N1	1.365	1.360	1.359
N1–R ²	1.018	1.018	1.019
C3–C4	1.511	1.516	1.517
C4–O1	1.232	1.231	1.230
C4–C10	1.475	1.473	1.473
C10–C5	1.400	1.401	1.401
C5–C6	1.395	1.395	1.395
C6–C7	1.399	1.399	1.399
C7–C8	1.398	1.398	1.398
C8–C9	1.397	1.397	1.397
C9–C10	1.406	1.407	1.407
C9–C1	1.499	1.499	1.499
C1–O2	1.236	1.234	1.234
C11–N1	1.417	1.420	1.421
C11–C12	1.410	1.408	1.408
C12–C13	1.389	1.390	1.390
C13–C14	1.395	1.395	1.395
C14–O3	1.373	1.372	1.372
O3–C19	1.383	1.384	1.384
C19–O4	1.222	1.221	1.221
C19–C18	1.453	1.453	1.453
C18–C17	1.356	1.356	1.356
C17–C15	1.441	1.441	1.441
C15–C14	1.406	1.407	1.407
C15–C16	1.407	1.407	1.406
C16–C11	1.394	1.393	1.393

Table S3. Mulliken charges for the ground (S_0) and excited (S_1) states of compounds 1-4

Atom	1		2		3		4	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C1	-0.457	0.110	0.133	0.157	0.228	0.001	0.224	-0.012
O2	-0.504	-0.655	-0.516	-0.656	-0.516	-0.613	-0.437	-0.574
C2	0.741	-0.006	-0.049	-0.246	-0.020	0.127	-0.299	0.297
R ¹	0.214	0.191	0.247	0.221	0.159	0.342	-0.138	0.256
C3	0.196	-0.120	-0.925	-0.737	-0.152	0.072	-0.334	-0.508
N1	-0.258	-0.181	0.224	0.442	-0.181	-0.196	-0.223	-0.219
R ²	0.357	0.375	-0.101	-0.035	0.357	0.368	0.361	0.363
C4	-0.556	0.005	0.020	0.278	0.199	0.066	0.293	0.331
O1	-0.540	-0.637	-0.458	-0.590	-0.524	-0.667	-0.515	-0.679
C5	-0.045	0.099	0.017	-0.201	0.135	0.011	-0.010	-0.222
C6	-0.200	-0.145	-0.095	-0.146	-0.191	-0.189	-0.195	-0.169
C7	-0.173	-0.197	-0.168	-0.193	-0.165	-0.117	-0.140	-0.163
C8	-0.058	-0.089	-0.037	-0.152	0.167	0.074	0.257	-0.026
C9	0.296	0.062	0.305	0.161	-0.168	-0.014	0.015	-0.165
C10	0.326	0.450	0.292	0.188	-0.107	-0.197	-0.067	0.091
C11	-0.189	-0.377	0.217	0.194	-0.214	-0.042	-0.115	-0.248
C12	0.297	-0.239	-0.287	-0.198	0.156	0.172	0.236	0.168
C13	-0.351	0.113	-0.205	-0.355	-0.265	-0.324	-0.495	-0.335
C14	-1.395	-1.705	-1.551	-1.755	-1.224	-1.208	-1.070	-1.213
C15	1.744	1.889	1.688	1.726	1.690	1.769	1.834	1.866
C16	-0.224	0.010	0.068	0.166	-0.202	-0.248	-0.298	-0.179
O3	-0.423	-0.368	-0.428	-0.375	-0.431	-0.415	-0.431	-0.422
C17	-0.399	-0.249	-0.419	-0.048	-0.431	-0.534	-0.510	-0.451
C18	0.065	0.010	0.017	-0.095	0.136	0.178	0.145	0.160
C19	0.588	0.594	0.594	0.607	0.577	0.564	0.588	0.581
O4	-0.555	-0.489	-0.560	-0.498	-0.557	-0.533	-0.554	-0.548

Table S4. Selected bond lengths (\AA) for the ground (S_0) and excited (S_1) states of the individual molecules

Bond	6-AC		6	
	S_0	S_1	S_0	S_1
C1–C2	—	—	1.453	1.481
C2–C3	—	—	1.374	1.422
C2–R ¹	—	—	1.753	1.708
C3–N1	—	—	1.339	1.321
N1–R ²	1.012	1.011	1.011	1.018
C3–C4	—	—	1.513	1.488
C4–O1	—	—	1.228	1.267
C4–C10	—	—	1.476	1.432
C10–C5	—	—	1.400	1.421
C5–C6	—	—	1.396	1.378
C6–C7	—	—	1.398	1.423
C7–C8	—	—	1.398	1.378
C8–C9	—	—	1.396	1.419
C9–C10	—	—	1.409	1.446
C9–C1	—	—	1.501	1.449
C1–O2	—	—	1.237	1.249
C11–N	1.396	1.351	—	—
C11–C12	1.416	1.422	—	—
C12–C13	1.390	1.385	—	—
C13–C14	1.394	1.411	—	—
C14–O3	1.378	1.359	—	—
O3–C19	1.377	1.459	—	—
C19–O4	1.225	1.235	—	—
C19–C18	1.453	1.406	—	—
C18–C17	1.357	1.406	—	—
C17–C15	1.441	1.432	—	—
C15–C14	1.406	1.426	—	—
C15–C16	1.408	1.399	—	—
C16–C11	1.398	1.428	—	—

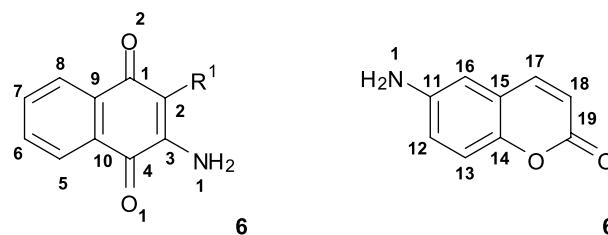
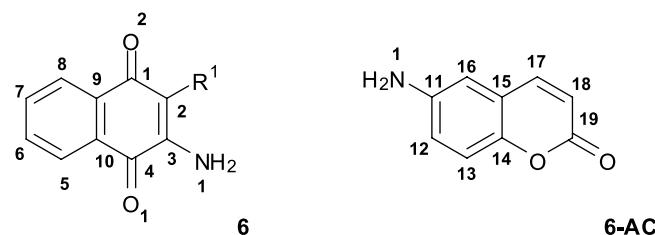
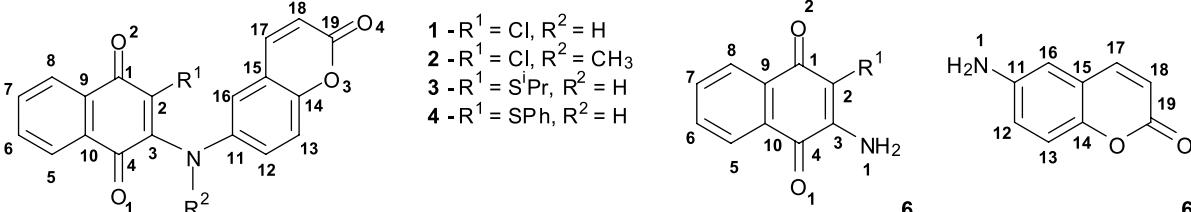


Table S5. Mulliken charges for the ground (S_0) and excited (S_1) states of individual molecules

Atom	6-AC		6	
	S_0	S_1	S_0	S_1
C1	–	–	-0.244	-0.362
O2	–	–	-0.568	-0.619
C2	–	–	0.145	0.360
R ¹	–	–	0.178	0.332
C3	–	–	0.884	0.786
N1	-0.617	-0.493	-0.633	-0.519
R ²	0.317	0.363	0.350	0.368
C4	–	–	-0.830	-0.923
O1	–	–	-0.505	-0.663
C5	–	–	0.197	0.100
C6	–	–	-0.201	-0.164
C7	–	–	-0.216	-0.214
C8	–	–	0.105	0.032
C9	–	–	0.044	0.106
C10	–	–	0.281	0.374
C11	-0.101	0.002	–	–
C12	0.275	0.227	–	–
C13	-0.246	-0.238	–	–
C14	-1.686	-1.634	–	–
C15	1.218	1.150	–	–
C16	-0.030	-0.007	–	–
O3	-0.426	-0.451	–	–
C17	0.197	0.143	–	–
C18	-0.024	-0.113	–	–
C19	0.592	0.551	–	–
O4	-0.580	-0.631	–	–

Table S6. Percent $S_0 - S_1$ bond distance differences


1 - $R^1 = Cl, R^2 = H$
2 - $R^1 = Cl, R^2 = CH_3$
3 - $R^1 = S^iPr, R^2 = H$
4 - $R^1 = SPh, R^2 = H$

Bond	1	2	3	4	6-AC	6
C1–C2	-1.4	-2.6	-1.5	-1.4		1.9
C2–C3	1.1	1.5	0.8	0.8		3.5
C2–R1	0.2	0.7	0.1	-0.2		-2.6
C3–N1	5.4	3.6	5.3	5.7		-1.3
N1–R2	-0.2	0.1	-0.1	-0.1	-0.1	0.7
C3–C4	-5.1	-4.9	-4.8	-4.9		-1.7
C4–O1	2.7	2.9	2.6	2.6		3.2
C4–C10	0.0	-0.6	-0.1	0.1		-3.0
C10–C5	0.6	0.6	0.7	0.6		1.5
C5–C6	-0.5	-0.6	-0.5	-0.5		-1.3
C6–C7	0.6	0.6	0.6	0.6		1.8
C7–C8	-0.7	-0.6	-0.7	-0.7		-1.4
C8–C9	0.9	0.8	0.9	0.9		1.6
C9–C10	0.8	0.8	0.9	0.8		2.6
C9–C1	-1.1	-0.6	-1.3	-1.2		-3.5
C1–O2	1.9	2.3	1.9	1.8		1.0
C11–N1	-5.2	-3.9	-5.0	-5.1	-3.2	
C11–C12	1.9	1.6	1.8	1.9	0.4	
C12–C13	-1.5	-1.4	-1.4	-1.4	-0.4	
C13–C14	1.3	1.3	1.2	1.2	1.2	
C14–O3	-2.1	-2.0	-2.0	-1.9	-1.4	
O3–C19	1.9	2.0	1.7	1.7	6.0	
C19–O4	-0.9	-1.0	-0.9	-0.8	0.8	
C19–C18	0.1	0.1	0.1	0.1	-3.2	
C18–C17	-0.4	-0.3	-0.3	-0.3	3.6	
C17–C15	0.3	0.3	0.3	0.3	-0.6	
C15–C14	1.0	0.7	0.9	0.8	1.4	
C15–C16	-1.4	-1.1	-1.3	-1.3	-0.6	
C16–C11	2.2	1.8	1.9	1.9	2.1	

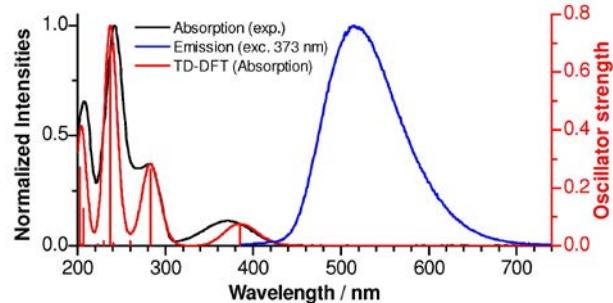


Figure S25. Simulated electronic spectrum (TD-DFT – B3LYP/6-31+G(d,p)/PCM(CH₃CN)) of compound 6-AC (red) and experimental absorption (black) and emission (blue) spectra.

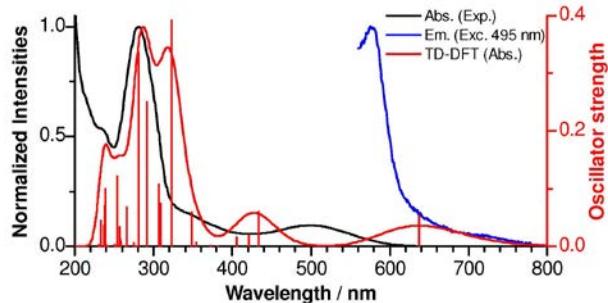


Figure S29. Simulated electronic spectrum (TD-DFT – B3LYP/6-31+G(d,p)/PCM(CH₃CN)) of compound 3 (red) and experimental absorption (black) and emission (blue) spectra.

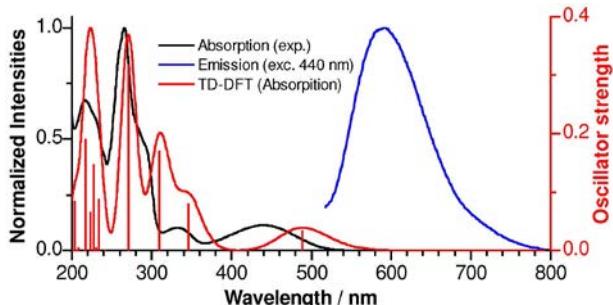


Figure S26. Simulated electronic spectrum (TD-DFT – B3LYP/6-31+G(d,p)/PCM(CH₃CN)) of compound 6 (red) and experimental absorption (black) and emission (blue) spectra.

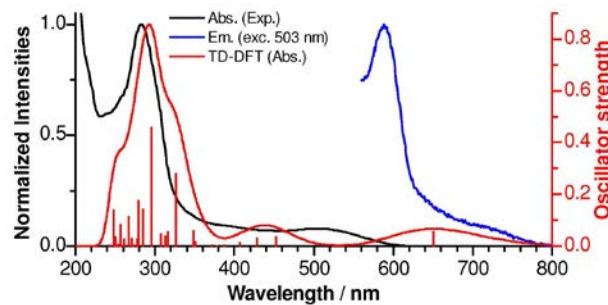


Figure S30. Simulated electronic spectrum (TD-DFT – B3LYP/6-31+G(d,p)/PCM(CH₃CN)) of compound 4 (red) and experimental absorption (black) and emission (blue) spectra.

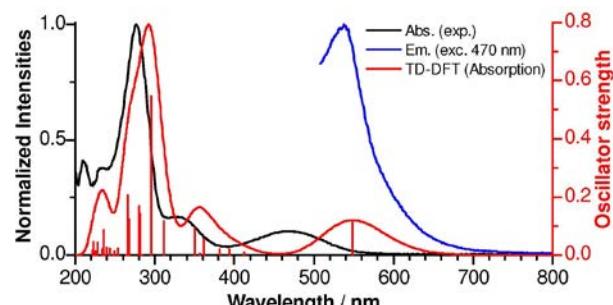


Figure S27. Simulated electronic spectrum (TD-DFT – B3LYP/6-31+G(d,p)/PCM(CH₃CN)) of compound 1 (red) and experimental absorption (black) and emission (blue) spectra.

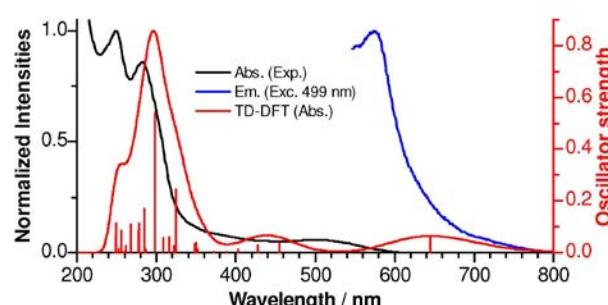


Figure S31. Simulated electronic spectrum (TD-DFT – B3LYP/6-31+G(d,p)/PCM(CH₃CN)) of compound 5 (red) and experimental absorption (black) and emission (blue) spectra.

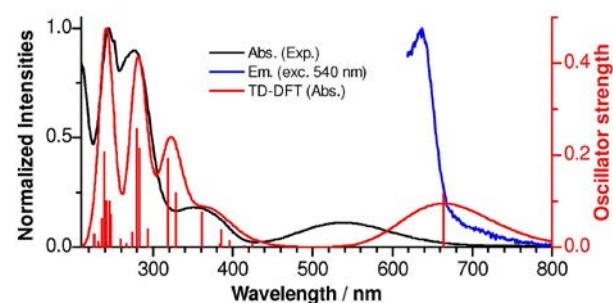


Figure S28. Simulated electronic spectrum (TD-DFT – B3LYP/6-31+G(d,p)/PCM(CH₃CN)) of compound 2 (red) and experimental absorption (black) and emission (blue) spectra.

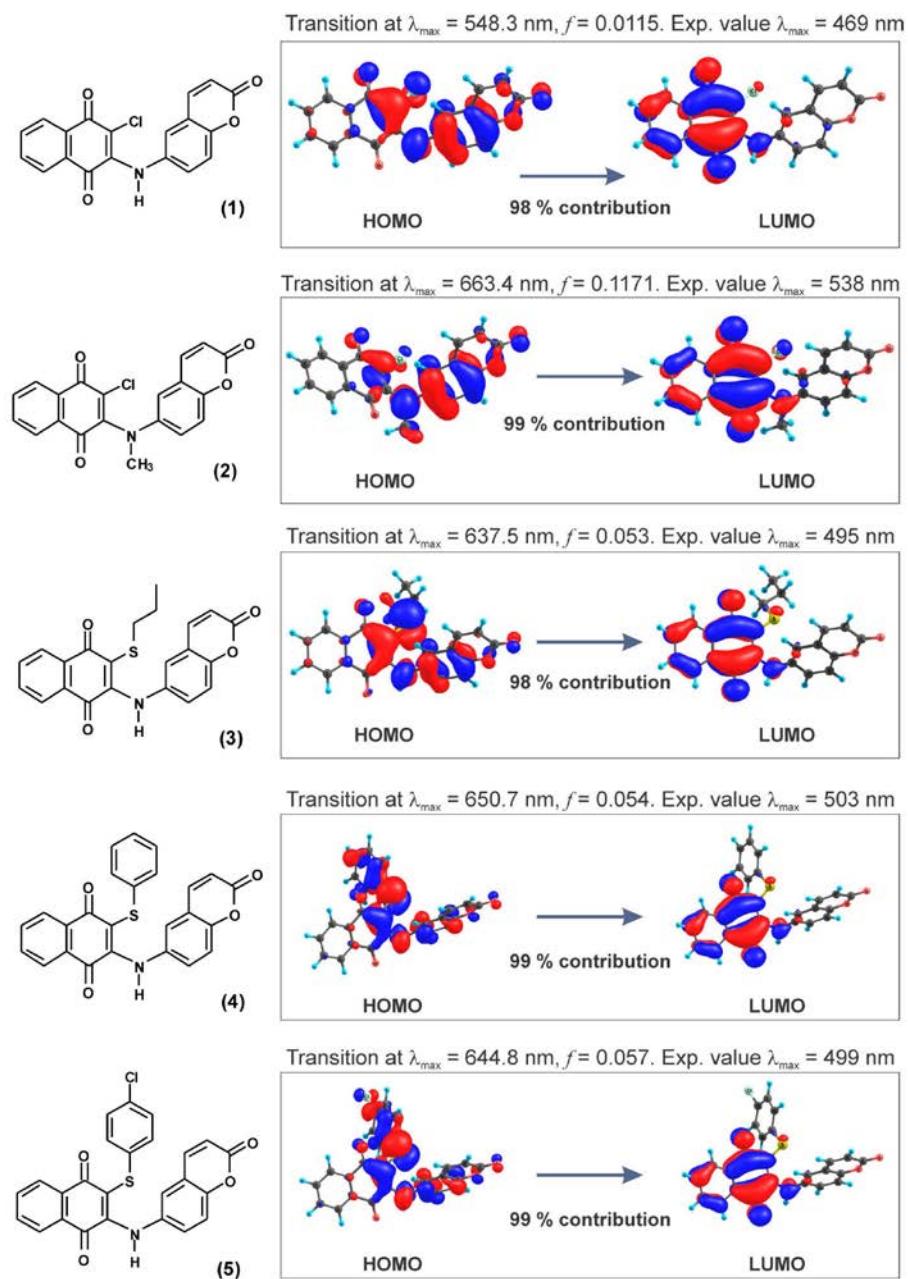
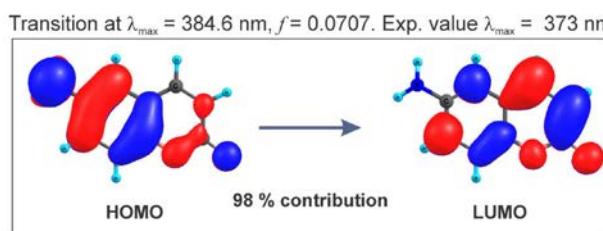
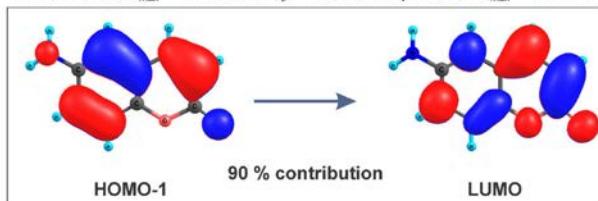


Figure S32. Molecular orbitals of **1–5** involved in the lowest energy transition (contour values plotted at 0.03 (e/Bohr^3) $^{1/2}$).



Transition at $\lambda_{\max} = 283.0$ nm, $f = 0.263$. Exp. value $\lambda_{\max} = 282$ nm



Transition at $\lambda_{\max} = 237.2$ nm, $f = 0.691$. Exp. value $\lambda_{\max} = 272$ nm

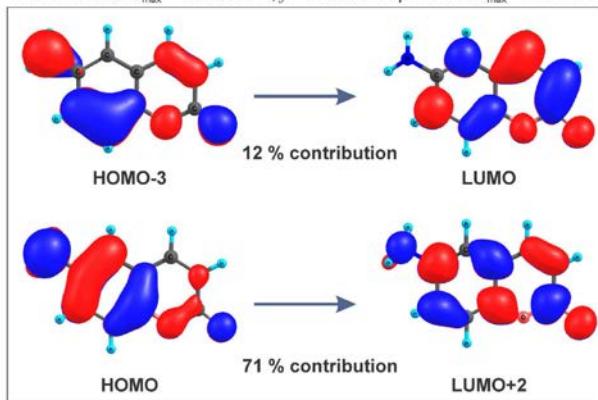
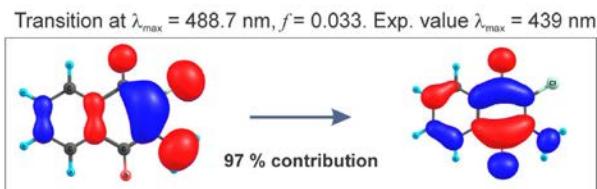
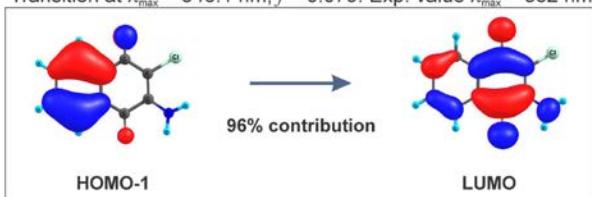


Figure S33. Molecular orbitals of 6-AC involved in the three lowest energy electronic transitions (contour values plotted at $0.03 \text{ (e/Bohr}^3)^{1/2}$).



Transition at $\lambda_{max} = 346.1$ nm, $f = 0.079$, Exp. value $\lambda_{max} = 332$ nm



Transition at $\lambda_{\max} = 310.1$ nm, $f = 0.169$. Exp. value $\lambda_{\max} = 287$ nm



Transition at $\lambda_{\max} = 270.6$ nm, $f = 0.316$. Exp. value $\lambda_{\max} = 265$ nm

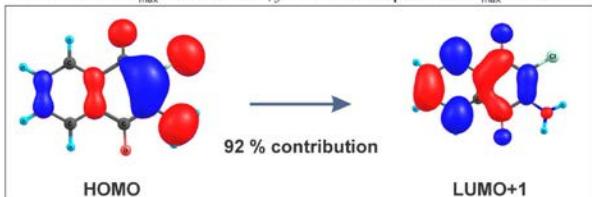


Figure S34. Molecular orbitals of **6** involved in the four lowest energy electronic transitions (contour values plotted at 0.03 (e/Bohr³)^{1/2}).

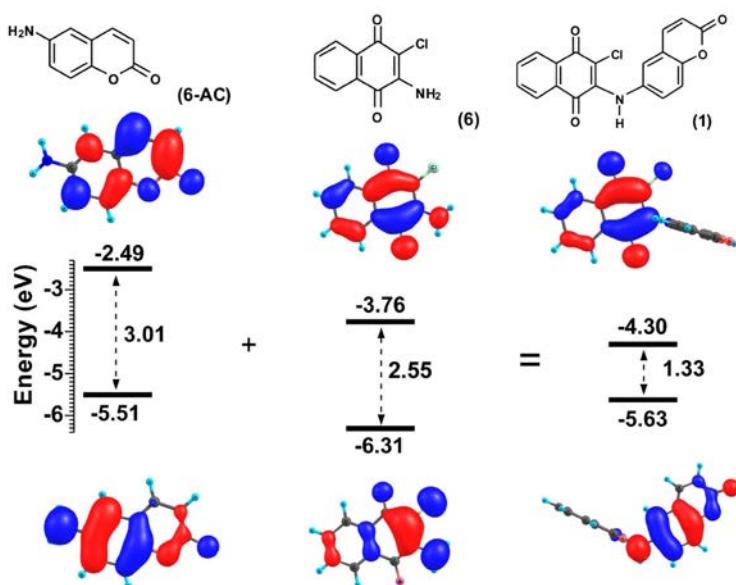


Figure S35. Molecular orbital diagrams for 6-AC, **6** and conjugate **1** in the excited state (contour values plotted at 0.03 ($e/Bohr^3$) $^{1/2}$).