Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic supplementary information

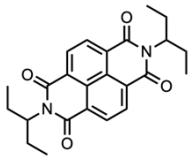
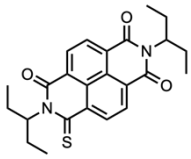
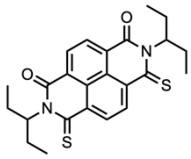
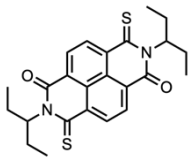
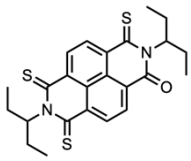
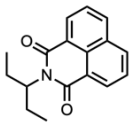
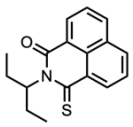
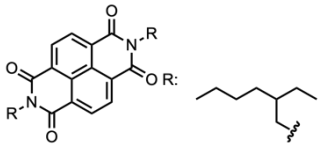
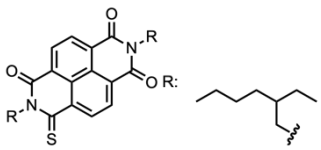
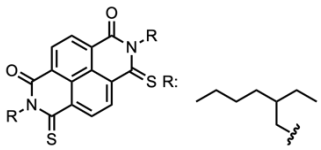
Why does thionating a carbonyl molecule make it a better electron acceptor?

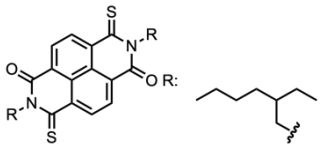
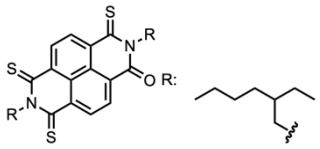
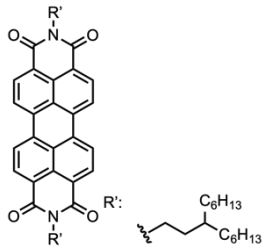
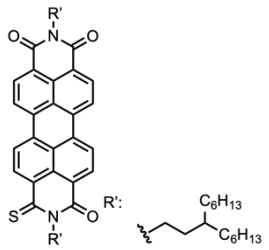
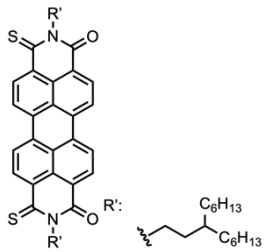
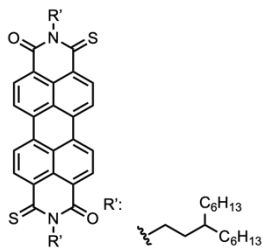
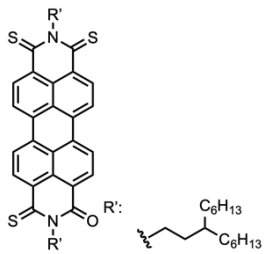
Yi-Lin Wu* and Anna I. Wright
School of Chemistry, Cardiff University, Park Place, Cardiff CF10 3AT, United Kingdom
E-mail: wuyl@cardiff.ac.uk

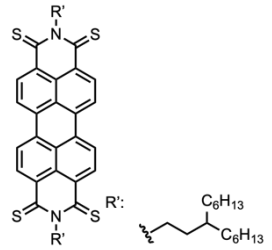
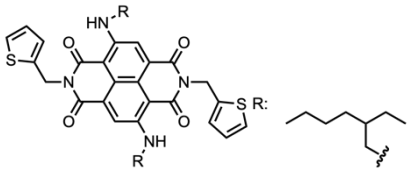
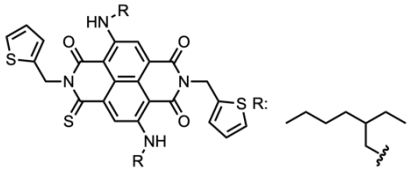
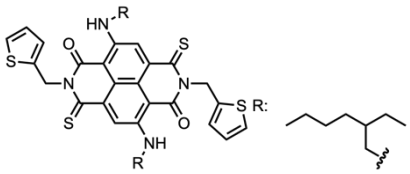
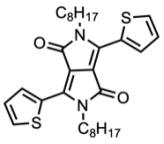
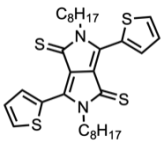
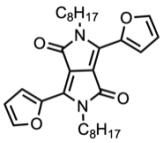
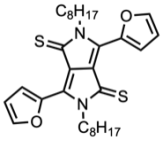
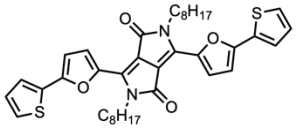
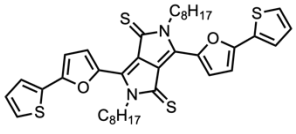
Table of Contents

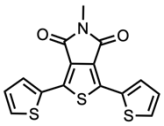
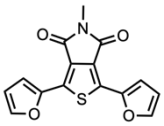
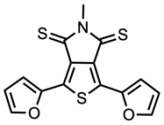
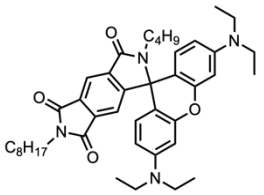
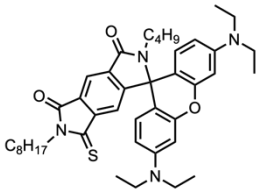
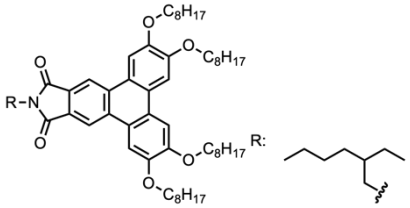
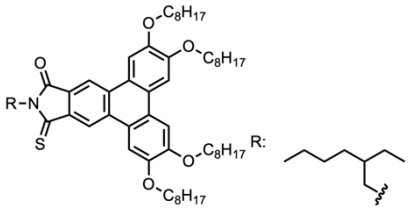
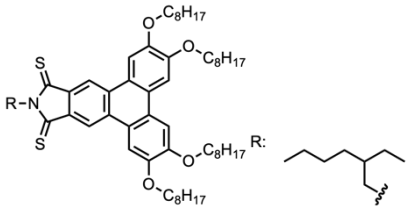
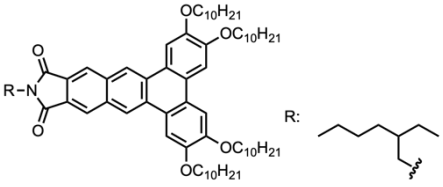
1. Electrochemical reduction potential of (thio)carbonyls from literature

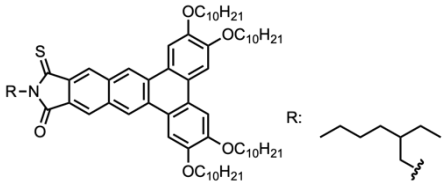
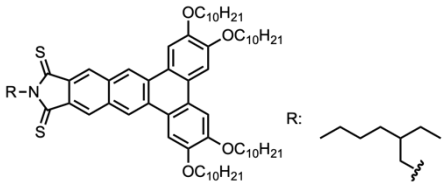
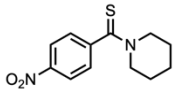
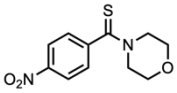
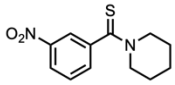
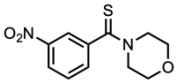
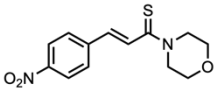
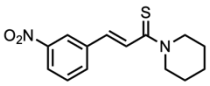
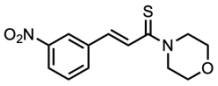
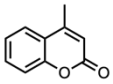
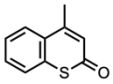
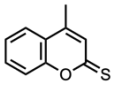
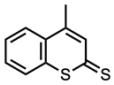
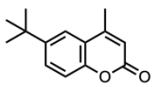
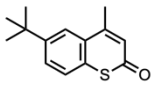
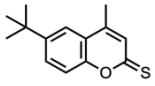
Table S1. Reported Reduction Potential of (Thio)carbonyls.

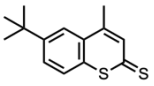
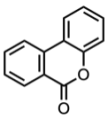
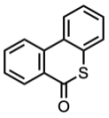
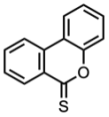
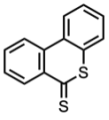
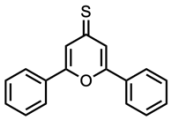
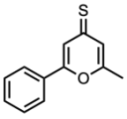
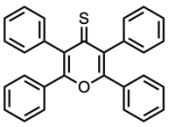
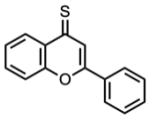
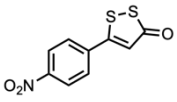
Entry	Compound	Reported E_{RED}[a] (V)	E_{RED} vs. SCE (V)	Reference
1.1[b]		–1.07[c], –1.53[c]	–0.61, –1.07	1
1.2[b]		–0.88, –1.29	–0.42, –0.83	1
1.3[b]		–0.73, –1.05	–0.27, –0.59	1
1.4[b]		–0.75, –1.08	–0.29, –0.62	1
1.5[b]		–0.61, –0.91	–0.15, –0.45	1
2.1[b]		–1.82	–1.36	1
2.2[b]		–1.44	–0.98	1
3.1[c]		–0.91	–0.68	2
3.2[c]		–0.62	–0.39	2
3.3[c]		–0.55	–0.32	2

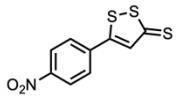
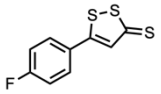
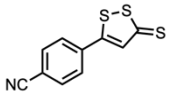
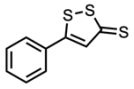
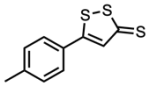
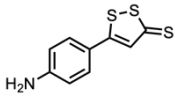
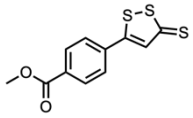
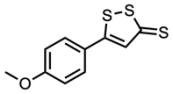
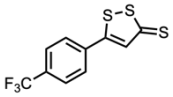
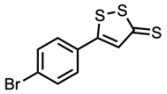
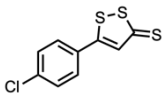
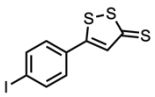
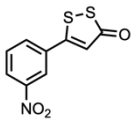
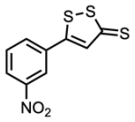
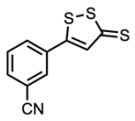
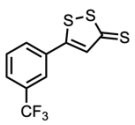
3.4[c]		–0.59	–0.36	2
3.5[c]		–0.42	–0.19	2
4.1[d]		–0.68[e], –0.91[e]	–0.22, –0.45	3
4.2[d]		–0.55, –0.72	–0.09, –0.26	3
4.3[d]		–0.48, –0.57	–0.02, –0.11	3
4.4[d]		–0.51, –0.61	–0.05, –0.15	3
4.5[d]		–0.36, –0.45	0.10, 0.01	3

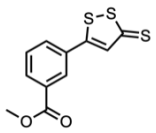
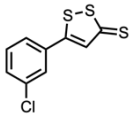
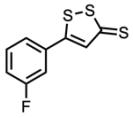
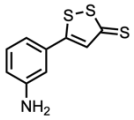
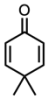
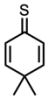
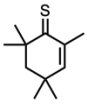
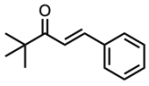
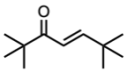
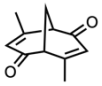
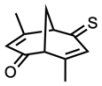
4.6[d]		–0.23, –0.33	0.23, 0.13	3
5.1[f]		–1.39, –1.76	–0.93, –1.30	4
5.2[f]		–1.17, –1.52	–0.71, –1.06	4
5.3[f]		–1.03, –1.34	–0.57, –0.88	4
6.1[g]		3.92[e]	–1.25	5
6.2[g]		4.06[e]	–1.11	5
6.3[g]		3.89[e]	–1.28	5
6.4[g]		4.14[e]	–1.03	5
6.5[g]		4.01[e]	–1.16	5
6.6[g]		4.08[e]	–1.09	5

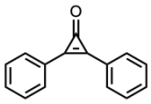
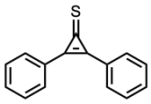
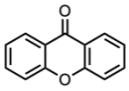
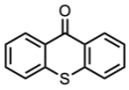
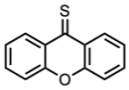
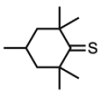
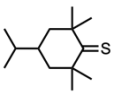
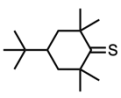
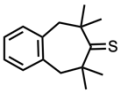
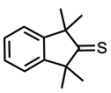
6.7[g]		3.12[e]	–2.05	5
6.8[g]		3.22[e]	–1.95	5
6.9[g]		4.01[e]	–1.16	5
7.1[h]		–1.86	–1.40	6
7.2[h]		–1.42	–0.96	6
8.1[i]		3.09	–1.71	7
8.2[i]		3.14	–1.66	7
8.3[i]		3.50	–1.30	7
8.4[i]		2.89	–1.91	8

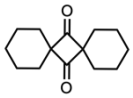
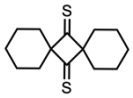
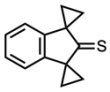
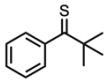
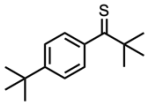
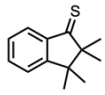
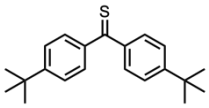
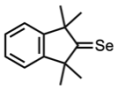
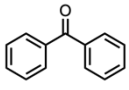
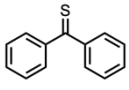
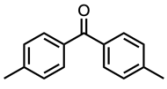
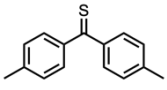
8.5[i]		2.91	–1.89	8
8.6[j]		3.30	–1.50	8
9.1[j]		–0.80	-	9
9.2[j]		–0.79	-	9
9.3[j]		–0.82	-	9
9.4[j]		–0.81	-	9
9.5[j]		–0.73	-	9
9.6[j]		–0.87	-	9
9.7[j]		–0.84	-	9
10.1[k]		–1.81	–1.81	10
10.2[l]		-1.13	–1.13	11
10.3[l]		–0.75[e]	–0.75	11
10.4[l]		–0.66	–0.66	11
10.5[l]		–1.34[e]	–1.34	11
10.6[l]		–1.17	–1.17	11
10.7[l]		–0.84[e]	–0.84	11

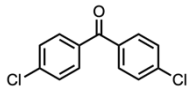
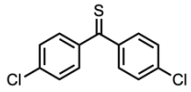
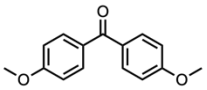
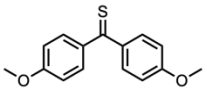
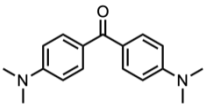
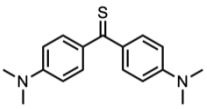
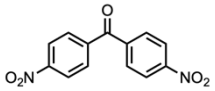
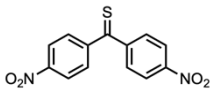
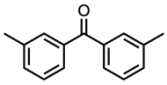
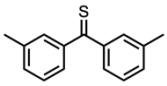
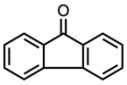
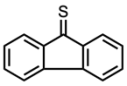
10.8[l]		–0.71	–0.71	11
11.1[l]		–1.41	–1.41	12
11.2[l]		–1.27	–1.27	12
11.3[l]		–1.07	–1.07	12
11.4[l]		–0.72	–0.72	12
11.5[l]		–1.32	–1.32	12
11.6[l]		–1.16	–1.16	12
11.7[l]		–0.68	–0.68	12
11.8[l]		–0.58[e]	–0.58	12
12.1[m]		–1.35	–0.39	13
12.2[m]		–0.88	0.08	13
12.3[m]		–1.35	–0.39	13
12.4[m]		–1.00	–0.04	13
12.5[m]		–0.73	0.23	13
13.1[n]		–0.83	–0.83	14

13.2[o]		–1.22	–0.75	15
13.3[o]		–1.53	–1.06	15
13.4[o]		–1.40	–0.93	15
13.5[o]		–1.57	–1.10	15
13.6[o]		–1.58	–1.11	15
13.7[o]		–1.66	–1.19	15
13.8[o]		–1.42	–0.95	15
13.9[o]		–1.60	–1.13	15
13.10[o]		–1.43	–0.96	15
13.11[o]		–1.50	–1.03	15
13.12[o]		–1.51	–1.04	15
13.13[o]		–1.45	–0.98	15
14.1[n]		–0.97	–0.97	14
14.2[o]		–1.40	–0.93	15
14.3[o]		–1.46	–0.99	15
14.4[o]		–1.42	–0.95	15

14.5[o]		–1.48	–1.01	15
14.6[o]		–1.48	–1.01	15
14.7[o]		–1.45	–0.98	15
14.8[o]		–1.58	–1.11	15
15.1[p]		–2.31	–2.31	16
15.2[p]		–1.56	–1.56	16
15.3[p]		–1.48, –2.41	–1.48, –2.41	17
15.4[p]		–1.42	–1.42	16
15.5[p]		–2.21	–2.21	16
15.6[p]		–1.55	–1.55	16
15.7[p]		–1.49	–1.49	16
15.8[p]		–1.71, –2.22	–1.71, –2.22	16
15.9[p]		–2.24	–2.24	16
15.10[q]		–1.91	–1.91	18
15.11[p]		–1.56, –1.93	–1.56, –1.93	16
15.12[p]		–1.13, –1.84	–1.13, –1.84	16

16.1[r]		–1.70	–1.70	19
16.2[p]		–1.40	–1.40	16
17.1[p]		–1.65	–1.65	20
17.2[p]		–1.62	–1.62	20
17.3[q]		–1.12	–1.12	21
18.1[q]		–1.99	–1.99	18
18.2[q]		–1.88	–1.88	18
18.3[q]		–1.93	–1.93	18
18.4[q]		–1.86	–1.86	18
18.5[q]		–1.92	–1.92	18
18.6[q]		–1.93	–1.93	18
18.7[q]		–1.85	–1.85	18
18.8[q]		–1.86	–1.86	18
18.9[q]		–1.84	–1.84	18
18.10[q]		–1.77	–1.77	18
18.11[q]		–1.61	–1.61	18
18.12[q]		–1.77	–1.77	18

18.13[q]		–1.55	–1.55	18
18.14[q]		–1.36	–1.36	18
18.15[q]		–1.63	–1.63	18
18.16[q]		–1.44	–1.44	18
19.1[q]		–1.94	–1.94	18
19.2[q]		–1.77	–1.77	18
19.3[q]		–1.76	–1.76	18
19.4[q]		–1.43	–1.43	18
19.5[q]		–1.51	–1.51	18
19.6[q]		–1.41	–1.41	18
19.7[q]		–1.20	–1.20	18
20.1[q]		–1.66	–1.66	18
20.2[q]		–1.56	–1.56	18
21.1[s]		–1.57	–1.57	22
21.2[s]		–1.04	–1.04	22
21.3[s]		–1.75	–1.75	22
21.4[s]		–0.96	–0.96	22

21.5		(de-chlorination)	(de-chlorination)	22
21.6[s]		–0.90	–0.90	22
21.7[s]		–1.86	–1.86	22
21.8[s]		–1.19	–1.19	22
21.9[t]		–2.16	–2.12	23
21.10[t]		–1.51	–1.47	23
21.11[s]		–0.67	–0.67	22
21.12[s]		–0.39	–0.39	22
21.13[s]		–1.65	–1.65	22
21.14[s]		–0.95	–0.95	22
21.15[s]		–1.14	–1.14	22
21.16[s]		–0.82	–0.82	22

[a] The electrochemical conditions and their conversion factors (for *vs.* SCE) for each entry are given individually.

[b] 0.1 M nBu$_4$NBF$_4$ supporting electrolyte in CH_2Cl_2, V *vs.* Fc/Fc$^+$, Pt wire counter electrode, SCE reference electrode and glassy carbon working electrode; conversion factor: (E_{red} *vs.* SCE) = (E_{red} *vs.* Fc/Fc$^+$) + 0.46.[24]

[c] 0.1 M nBu$_4$NPF$_6$ supporting electrolyte in CH_2Cl_2, V *vs.* Pt/Pt$_x$O; conversion factor: (E_{red} *vs.* SCE) = (E_{red} *vs.* Pt/Pt$_x$O$^+$) + 0.23.[2]

[d] 0.1 M nBu$_4$NPF$_6$ supporting electrolyte in CH_2Cl_2, V *vs.* Fc/Fc$^+$, Pt wire counter electrode, Ag reference electrode, Pt button working electrode; conversion factor: (E_{red} *vs.* SCE) = (E_{red} *vs.* Fc/Fc$^+$) + 0.46.[24]

[e] Irreversible peak potential.

[f] 0.1 M nBu$_4$NPF$_6$ supporting electrolyte in CH_2Cl_2, V *vs.* Fc/Fc$^+$, Pt wire counter electrode, Pt reference electrode, glassy carbon working electrode; conversion factor: (E_{red} *vs.* SCE) = (E_{red} *vs.* Fc/Fc$^+$) + 0.46.[24]

[g] 0.1 M nBu$_4$NClO$_4$ supporting electrolyte in CH_2Cl_2, electron affinity (EA) reported, Pt wire counter electrode, Ag reference electrode, Pt button working electrode; conversion factor: (E_{red} *vs.* SCE) = EA – 5.17.[25]

[h] 0.1 M nBu$_4$NPF$_6$ supporting electrolyte in CH_2Cl_2, V *vs.* Fc/Fc$^+$, Pt wire counter electrode, Ag/AgNO$_3$ reference electrode, glassy carbon working electrode; conversion factor: (E_{red} *vs.* SCE) = ($E_{red\ d}$ *vs.* Fc/Fc$^+$) + 0.46.[24]

[i] 0.1 M nBu$_4$NPF$_6$ supporting electrolyte in CH_2Cl_2, LUMO (reported) *vs.* Fc/Fc$^+$; conversion factor: (E_{red} *vs.* SCE) = LUMO – 4.8.[7,8]

[j] 0.1 M nBu$_4$NClO$_4$ supporting electrolyte in DMSO, V *vs.* Ag/Ag$^+$, Pt wire counter electrode, Ag/Ag$^+$ reference electrode, Pt button working electrode; cannot convert the given E_{red}.

[k] DMF, V *vs.* SCE, glassy carbon counter electrode, Ag/AgCl in EtOH/LiCl (salt) reference electrode, hanging Hg working electrode.

[l] Tetrapropylammonium bromide supporting electrolyte in DMF, V *vs.* SCE, Ag/Ag$^+$/AgBr/Br$^-$ reference electrode, mercury working electrode.

[m] 0.2 M Et$_4$NClO$_4$ supporting electrolyte in DMF, V *vs.* Ag/AgI, Ag/AgI reference electrode, mercury working electrode; conversion factor: (E_{red} *vs.* SCE) = (E_{red} *vs.* Fc/Fc$^+$) + 0.96.[24]

[n] 0.1 M nBu$_4$NBF$_4$ supporting electrolyte in DMF, V *vs.* SCE, graphite rod counter electrode, SCE reference electrode, glassy carbon working electrode.

[o] 0.1 M nBu$_4$NBF$_4$ supporting electrolyte in DMF, V *vs.* Fc/Fc$^+$, graphite rod counter electrode, Ag/AgCl reference electrode, Pt disk working electrode; conversion factor: (E_{red} *vs.* SCE) = (E_{red} *vs.* Fc/Fc$^+$) + 0.47.[26]

[p] MeCN, V *vs.* SCE, no additional details given.

[q] 0.1 M nBu$_4$NPF$_6$ supporting electrolyte in MeCN, V *vs.* SCE.

[r] 0.1 M Triethylamine phosphate supporting electrolyte in DMF, V *vs.* SCE, glassy carbon working electrode.

[s] 0.1 M Triammonium phosphate acid supporting electrolyte in MeCN, V *vs.* SCE.

[t] 0.05 M Triethylamine phosphate supporting electrolyte in MeCN, V *vs.* SCE, cylinder Pt counter electrode, Ag/AgCl (in 0.1 M TEAP in MeCN) reference electrode, dropping Hg working electrode; conversion factor (E_{red} *vs.* SCE) = (E_{red} *vs.* Ag/AgCl) + 0.044.[27,28]

2. LUMO plots

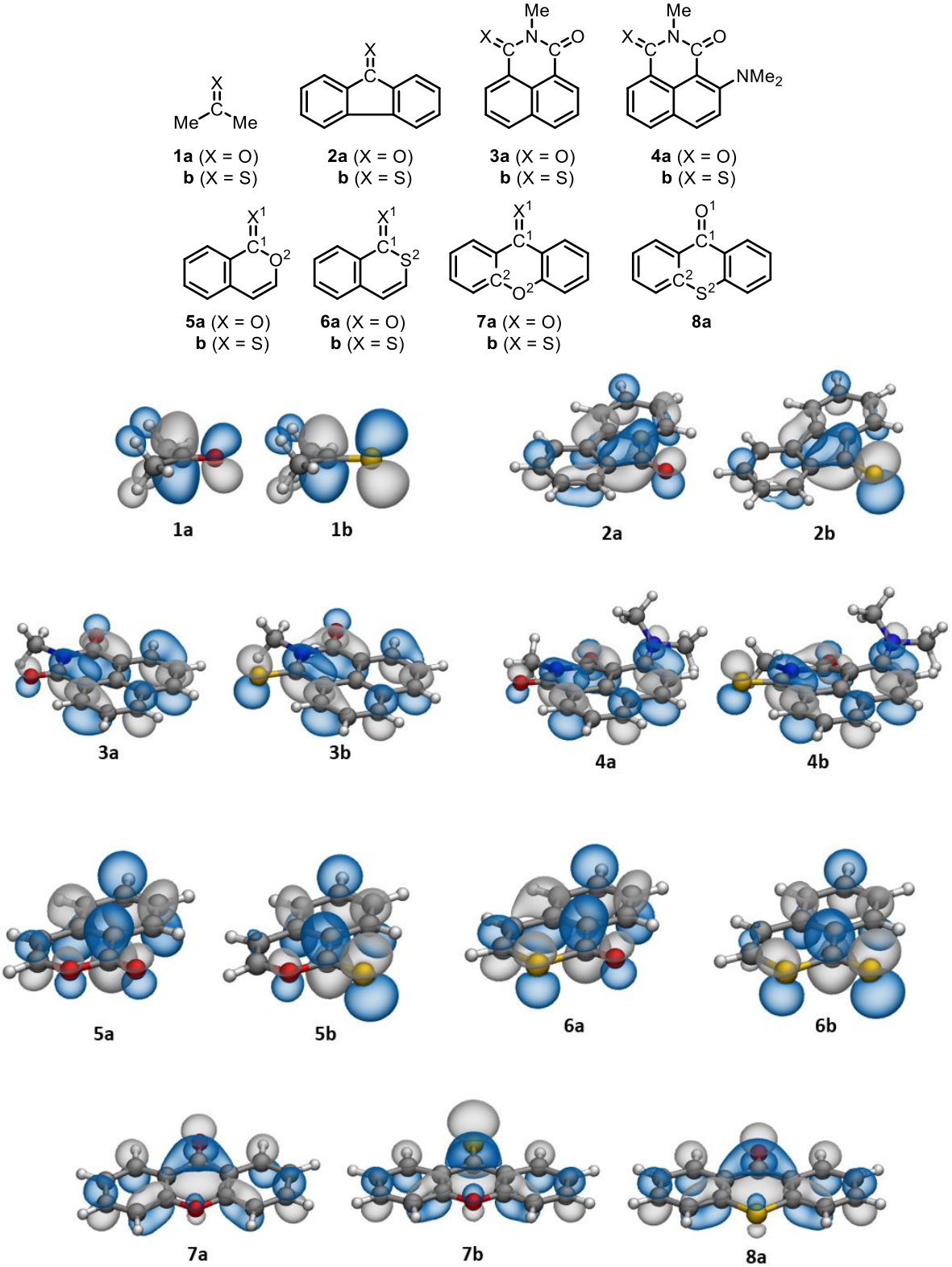
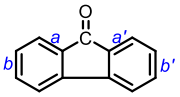
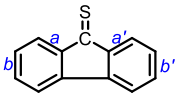
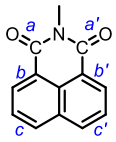
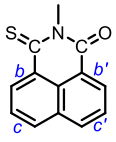


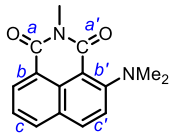
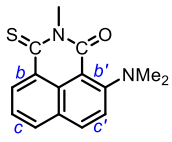
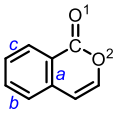
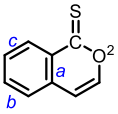
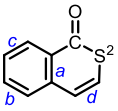
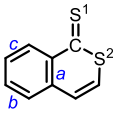
Fig. S1. LUMO of **1**–**8**. Colour code for molecular structure: C = grey, H = white, O = red, S = yellow. Orbitals are plotted at isosurface = 0.04 a.u. Besides the larger lobe on sulfur than that on the analogous oxygen, a high similarity in LUMO can be seen for each C=O/C=S pair.

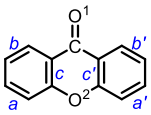
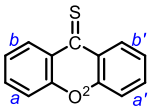
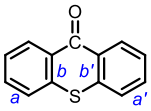
3. Leading (> 5%) NBO contributions to LUMO

The LUMO of **1**–**8** can be expressed in terms of a complete orthonormal set of localised NBOs: LUMO $= \Sigma\, c_i \times \mathrm{NBO}_i$, and the coefficient c represents the percentage contribution ($100 \times c^2$) of each NBO to LUMO.

Table S2. NBO Contributions to LUMO of **1**–**8**.

Compound	Contributing NBO	Coefficient
 **1a**	π*(C=O)	0.892
 **1b**	π*(C=S)	0.912
 **2a**	π*(C=O) π*(C=C, *a*) π*(C=C, *a*') π*(C=C, *b*) π*(C=C, *b*')	0.588 0.343 0.343 0.330 0.330
 **2b**	π*(C=O) π*(C=C, *a*) π*(C=C, *a*') π*(C=C, *b*) π*(C=C, *b*')	0.723 0.286 0.286 0.261 0.261
 **3a**	π*(C=O, *a*) π*(C=O, *a*') π*(C=C, *b*) π*(C=C, *b*') π*(C=C, *c*) π*(C=C, *c*')	–0.348 0.351 0.442 -0.443 -0.383 0.384
 **3b**	π*(C=S) π*(C=O) π*(C=C, *b*) π*(C=C, *b*') π*(C=C, *c*) π*(C=C, *c*')	–0.502 0.358 0.409 –0.378 –0.347 0.308

 **4a**	π*(C=O, *a*) π*(C=O, *a*') π*(C=C, *b*) π*(C=C, *b*') π*(C=C, *c*) π*(C=C, *c*')	–0.326 –0.321 –0.436 0.374 0.352 0.448
 **4b**	π*(C=S) π*(C=O) π*(C=C, *b*) π*(C=C, *b*') π*(C=C, *c*) π*(C=C, *c*')	–0.474 –0.330 –0.402 0.316 0.325 0.371
 **5a**	π*(C=O^1) out-of-plane lone pair (O^2) π*(C=C, *a*) π*(C=C, *b*) π(C=C, *c*)	0.425 –0.234 –0.532 0.437 –0.348
 **5b**	π*(C=S) out-of-plane lone pair (O^2) π*(C=C, *a*) π*(C=C, *b*) π(C=C, *c*)	–0.660 0.254 0.355 –0.414 0.264
 **6a**	π*(C=O) out-of-plane lone pair (S^2) π*(C=C, *a*) π*(C=C, *b*) π(C=C, *c*) π*(C=C, *d*) π(C=C, *b*)	0.454 –0.304 –0.518 0.342 –0.327 –0.287 0.241
 **6b**	π*(C=S^1) out-of-plane lone pair (S^2) π*(C=C, *a*) π*(C=C, *b*) π(C=C, *c*)	–0.685 0.336 0.329 –0.346 0.240

 **7a**	π*(C=O[1]) π*(C=C, *a*) π*(C=C, *a*') π*(C=C, *b*) π*(C=C, *b*') π*(C=C, *c*) π*(C=C, *c*')	–0.560 –0.386 –0.386 0.263 0.263 0.231 0.231
 **7b**	π*(C=S) π*(C=C, *a*) π*(C=C, *a*') π*(C=C, *b*) π*(C=C, *b*')	–0.687 –0.313 –0.313 0.241 0.241
 **8a**	π*(C=O) π*(C=C, *a*) π*(C=C, *a*') π*(C=C, *b*) π*(C=C, *b*')	–0.585 –0.354 –0.354 0.259 0.259

4. Electrostatic potential map and Mulliken charges

Fig. S2–S4 show the molecular electrostatic potential map of **1**–**8**. In each C=O/C=S pair, the lighter (paler) blue colour around the sulfur atom in C=S indicates the less negative electrostatic potential around this region, which is corroborated by the smaller negative atomic Mulliken charge, reflecting the lower electronegativity of sulfur than oxygen (cf. Pauling's original definition of electronegativity based on bond ionicity/polarisation). When the sulfur atom is substituted at a position π-conjugated with C=O/C=S, its atomic charge is close to zero.

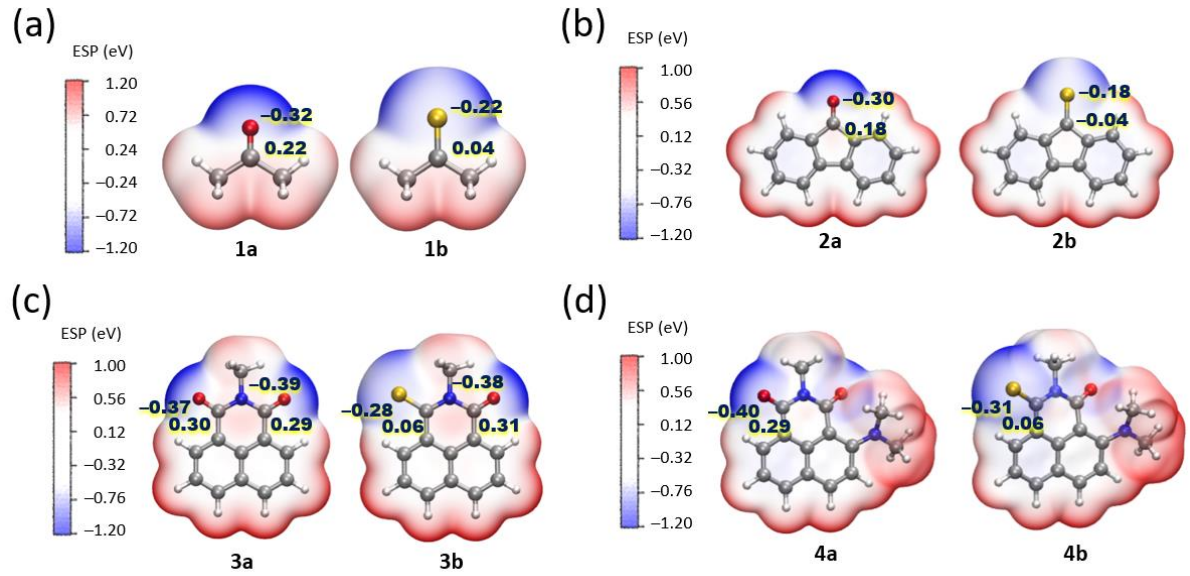


Fig. S2. Molecular electrostatic potential map of (a) **1**, (b) **2**, (c) **3,** and (d) **4**. Mulliken charges of the C, O, and S atoms in C=O/C=S functionalities are indicated next to the respective atoms.

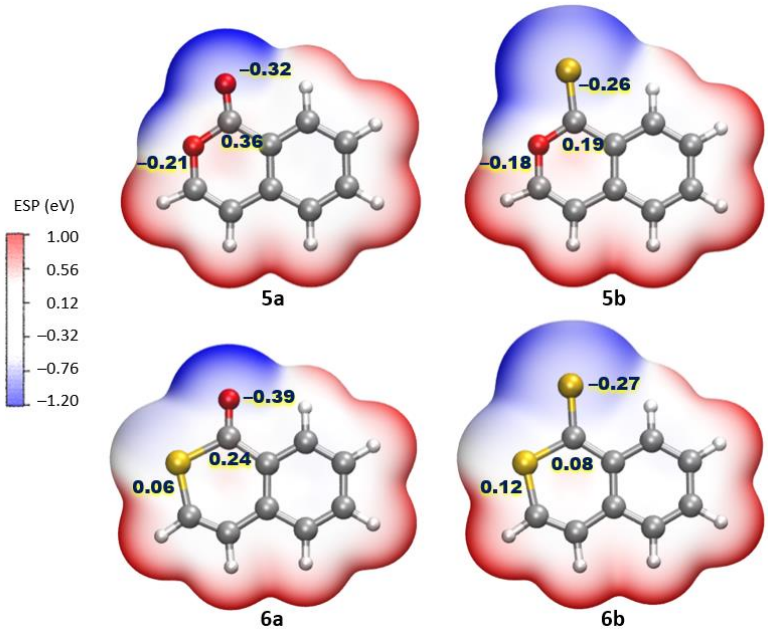


Fig. S3. Molecular electrostatic potential map of isochromenone derivatives **5**–**6**. Mulliken charges of the C, O, and S atoms in C=O/C=S and conjugated O/S functionalities are indicated next to the respective atoms.

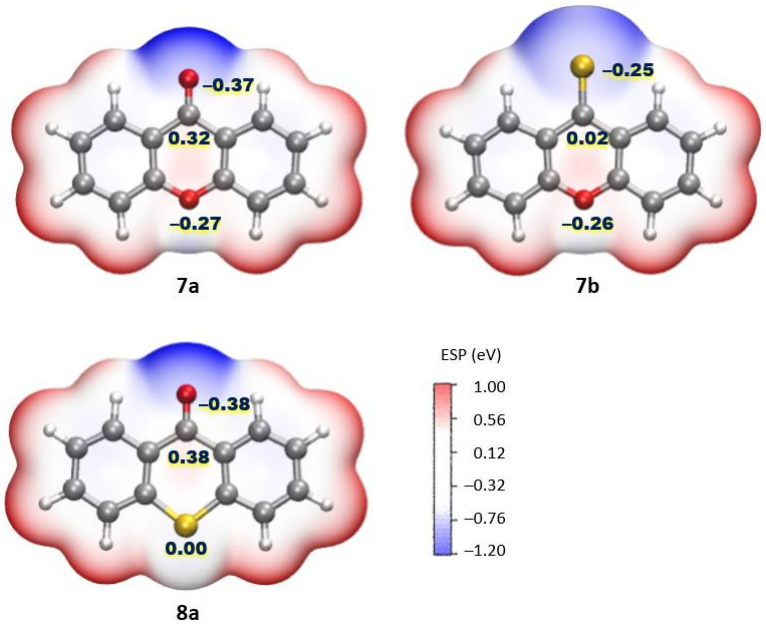


Fig. S4. Molecular electrostatic potential map of xanthenone derivatives **7**–**8**. Mulliken charges of the C, O, and S atoms in C=O/C=S and conjugated O/S functionalities are indicated next to the respective atoms.

5. Orbital interactions in (thio)ester

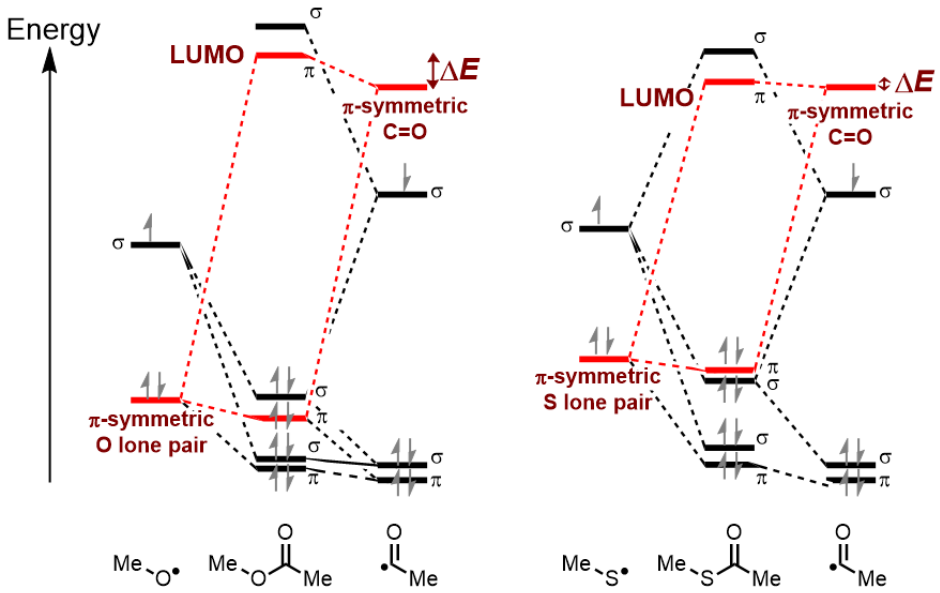


Fig. S5. Orbital interaction diagrams for the formation of frontier molecular orbitals (MOs) of methyl acetate (MeOAc, left) and methyl thioacetate (MeSAc, right) considering the fragment orbitals (FOs) of Ac• radical and MeO• or MeS• radical, respectively. The symmetry (σ or π) with respect to the molecular plane is indicated next to each MO/FO.

Due to the weaker coupling between the S lone pair FO in MeS• and the π* C=O FO in Ac•, the overall antibonding character (signified by Δ*E*) is smaller in MeSAc, resulting in lower LUMO energy. The orbital interactions highlighted in red are analogous to those shown in Fig. 3a in the main text.

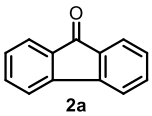
6. Cartesian coordinates for optimized geometries

1a

O	0.000000	-1.391087	0.000000
C	0.000000	-0.186643	0.000000
C	-1.282913	0.610731	0.001499
H	-2.138248	-0.055366	0.085428
H	-1.284774	1.328158	0.825060
H	-1.357356	1.187095	-0.924020
C	1.282913	0.610731	-0.001500
H	1.284773	1.328159	-0.825060
H	1.357357	1.187094	0.924020
H	2.138248	-0.055366	-0.085429

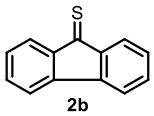
1b

S	1.367990	0.000000	0.000000
C	-0.249486	0.000000	0.000000
C	-1.057754	1.262263	0.000000
H	-0.425025	2.145505	0.000003
H	-1.711952	1.282264	-0.876810
H	-1.711955	1.282261	0.876808
C	-1.057754	-1.262263	0.000000
H	-1.711946	-1.282266	0.876814
H	-1.711961	-1.282259	-0.876803
H	-0.425025	-2.145505	-0.000009



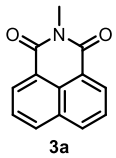
2a

O	0.000000	2.779277	0.000001
C	0.000000	1.576200	0.000004
C	3.007575	-1.388336	-0.000001
C	1.649122	-1.698446	0.000001
C	0.740374	-0.659948	0.000002
C	1.186723	0.663291	0.000000
C	2.528387	0.975484	-0.000002
C	3.445908	-0.071053	-0.000002
C	-1.186723	0.663291	0.000000
C	-0.740374	-0.659948	0.000002
C	-1.649122	-1.698446	0.000001
H	-1.323940	-2.731322	0.000001
C	-3.007575	-1.388336	-0.000001
C	-3.445908	-0.071053	-0.000002
C	-2.528387	0.975484	-0.000002
H	3.735262	-2.190250	-0.000001
H	1.323940	-2.731322	0.000001
H	2.849078	2.009731	-0.000002
H	4.507361	0.140187	-0.000003
H	-3.735262	-2.190250	-0.000001
H	-4.507361	0.140187	-0.000003
H	-2.849078	2.009731	-0.000002



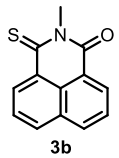
2b

S	0.000000	-2.900782	-0.000002
C	0.000000	-1.282351	0.000000
C	3.007474	1.666688	0.000000
C	1.650459	1.981290	0.000000
C	0.737147	0.947543	0.000000
C	1.173442	-0.383990	0.000000
C	2.518149	-0.695725	0.000001
C	3.438237	0.346644	0.000001
C	-1.173442	-0.383990	0.000000
C	-0.737147	0.947543	0.000000
C	-1.650459	1.981290	0.000000
H	-1.328024	3.015025	-0.000001
C	-3.007474	1.666688	0.000000
C	-3.438237	0.346644	0.000001
C	-2.518149	-0.695725	0.000001
H	3.738842	2.465177	0.000000
H	1.328024	3.015025	-0.000001
H	2.836278	-1.730939	0.000001
H	4.498418	0.129338	0.000001
H	-3.738842	2.465177	0.000000
H	-4.498418	0.129338	0.000001
H	-2.836278	-1.730939	0.000001



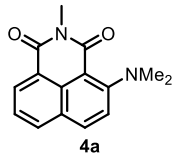
3a

O	-2.073340	2.287451	-0.000002
C	-1.448059	1.252107	0.000000
O	-2.115900	-2.239990	-0.000004
C	-1.461066	-1.222521	-0.000001
N	-2.095467	0.016632	0.000002
C	-3.552875	-0.007814	0.000003
C	0.034751	1.225327	0.000000
C	0.019941	-1.223399	0.000000
H	-3.913766	-0.533611	0.882511
H	-3.904919	1.017710	0.000042
H	-3.913772	-0.533543	-0.882543
C	0.726170	-0.003462	0.000001
C	0.729335	2.406889	-0.000001
C	0.697619	-2.414441	0.000000
C	2.139250	-0.012832	0.000001
C	2.134301	2.404468	-0.000001
H	0.175324	3.336257	-0.000001
C	2.102553	-2.430358	0.000001
C	2.823768	1.223451	0.000000
C	2.807216	-1.258262	0.000001
H	2.668339	3.345516	-0.000001
H	2.624537	-3.378148	0.000001
H	3.907375	1.221498	0.000000
H	3.890755	-1.270505	0.000001
H	0.130899	-3.336210	-0.000001



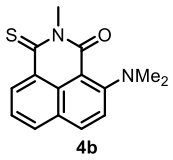
3b

S	2.857424	-1.557071	0.000029
C	1.564528	-0.535441	0.000002
O	0.957372	2.965081	-0.000005
C	0.710064	1.782283	-0.000005
N	1.745973	0.829718	-0.000015
C	3.106634	1.356496	-0.000025
C	0.171815	-1.033259	-0.000005
C	-0.670911	1.268018	0.000003
H	3.045133	2.438132	-0.000073
H	3.638367	1.001757	0.881440
H	3.638382	1.001676	-0.881447
C	-0.907507	-0.118927	-0.000001
C	-0.101554	-2.381489	-0.000015
C	-1.715968	2.157599	0.000011
C	-2.241849	-0.589756	0.000000
C	-1.421508	-2.855129	-0.000018
H	0.726161	-3.077273	-0.000021
C	-3.039672	1.694168	0.000015
C	-2.472671	-1.981997	-0.000009
C	-3.295726	0.350595	0.000009
H	-1.599280	-3.922410	-0.000027
H	-3.855413	2.404857	0.000022
H	-3.493180	-2.345996	-0.000009
H	-4.316789	-0.012236	0.000011
H	-1.497015	3.216993	0.000013



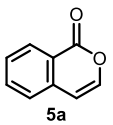
4a

O	3.112426	-1.933036	0.293733
C	2.062171	-1.351732	0.122672
O	-1.286430	-2.160294	-0.686223
C	-0.376624	-1.454927	-0.296805
N	0.879662	-2.041503	-0.106273
C	1.959345	0.120129	0.095418
C	0.701933	0.751705	-0.003497
C	-0.497061	-0.010527	-0.050588
C	3.117244	0.861460	0.158151
C	3.077825	2.256762	0.104782
C	1.868669	2.893409	-0.014895
C	0.670521	2.162292	-0.069017
C	-0.592333	2.789259	-0.203097
C	-1.740653	2.071769	-0.190159
C	-1.738265	0.648562	-0.036600
H	4.057278	0.332684	0.245313
H	1.821187	3.975023	-0.069172
H	-2.684213	2.595047	-0.233423
H	3.996352	2.826224	0.151255
N	-2.929207	0.018477	0.156544
H	-0.635065	3.869326	-0.283507
C	-3.076841	-1.112164	1.048696
H	-3.283074	-2.036328	0.509208
H	-2.168705	-1.253798	1.630838
H	-3.895244	-0.898356	1.742720
C	-4.176388	0.640485	-0.228727
H	-4.915933	-0.144595	-0.385836
H	-4.564347	1.325080	0.536400
H	-4.068991	1.180218	-1.168097
C	0.942183	-3.487938	-0.265290
H	0.736480	-3.764301	-1.298975
H	1.938791	-3.809587	0.016774
H	0.193965	-3.960091	0.368279



4b

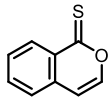
S	3.624407	-1.223226	0.365832
C	2.066292	-0.762788	0.057650
O	-1.010232	-2.255805	-0.840953
C	-0.277409	-1.394487	-0.400064
N	1.095583	-1.688303	-0.218319
C	1.646281	0.646275	0.026565
C	0.272150	0.975880	-0.034078
C	-0.718078	-0.040249	-0.073707
C	2.586957	1.657858	0.059293
C	2.215287	3.000873	0.022909
C	0.887115	3.336581	-0.044069
C	-0.098331	2.339356	-0.071041
C	-1.477618	2.651396	-0.151687
C	-2.426758	1.686655	-0.118280
C	-2.081840	0.303582	-0.002379
H	3.630753	1.380573	0.113857
H	0.581377	4.375869	-0.079184
H	-3.467244	1.974847	-0.117991
H	2.976683	3.768929	0.044267
N	-3.076977	-0.595165	0.214322
H	-1.773689	3.692629	-0.206138
C	-2.901981	-1.775153	1.033998
H	-2.884049	-2.689084	0.440171
H	-1.969393	-1.711608	1.591442
H	-3.724407	-1.818246	1.753259
C	-4.454429	-0.279024	-0.095971
H	-4.993448	-1.213397	-0.249826
H	-4.953011	0.274286	0.709409
H	-4.524635	0.293853	-1.018982
C	1.481372	-3.087375	-0.358802
H	2.229417	-3.187483	-1.144238
H	1.924573	-3.438402	0.571975
H	0.594109	-3.656714	-0.607752



5a

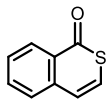
C	2.408948	0.981787	-0.000019
C	1.095413	1.398530	-0.000177
C	0.067435	0.456899	-0.000077
C	0.357444	-0.912798	0.000183

C	1.694494	-1.319327	0.000341
C	2.704840	-0.381354	0.000240
H	3.209538	1.709597	-0.000097
H	0.836261	2.448817	-0.000378
C	-1.326982	0.925859	-0.000250
C	-0.747842	-1.839722	0.000277
H	1.928432	-2.376780	0.000542
H	3.737710	-0.706408	0.000363
C	-1.992080	-1.366139	0.000111
H	-0.579156	-2.906762	0.000478
H	-2.883757	-1.976260	0.000162
O	-1.681926	2.067635	-0.000462
O	-2.295456	-0.049462	-0.000143



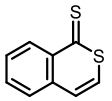
5b

C	-2.138354	-1.643828	0.000048
C	-0.767003	-1.536691	-0.000113
C	-0.153729	-0.279165	-0.000020
C	-0.952948	0.876593	0.000239
C	-2.345489	0.750539	0.000401
C	-2.930871	-0.494966	0.000307
H	-2.602452	-2.621238	-0.000026
H	-0.137727	-2.416071	-0.000313
C	1.304800	-0.160702	-0.000187
C	-0.300568	2.159536	0.000327
H	-2.956432	1.644806	0.000600
H	-4.009917	-0.583550	0.000434
C	1.028815	2.203100	0.000159
H	-0.872443	3.076104	0.000523
H	1.627278	3.101849	0.000201
S	2.377227	-1.390021	-0.000480
O	1.806017	1.098991	-0.000087



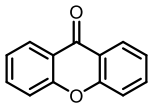
6a

C	2.726091	0.902805	0.000015
C	1.430378	1.366349	-0.000148
C	0.350927	0.477213	-0.000057
C	0.585460	-0.908625	0.000195
C	1.913731	-1.356236	0.000359
C	2.966642	-0.469901	0.000270
H	3.552802	1.600994	-0.000054
H	1.215803	2.426392	-0.000343
C	-0.994736	1.087990	-0.000235
C	-0.482649	-1.882607	0.000296
H	2.103962	-2.422638	0.000556
H	3.983390	-0.841973	0.000399
C	-1.781087	-1.574445	0.000155
H	-0.199864	-2.928415	0.000492
H	-2.543207	-2.343220	0.000231
O	-1.197465	2.276032	-0.000478
S	-2.426357	0.027834	-0.000160



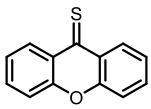
6b

C	-2.564898	-1.400297	0.000060
C	-1.194097	-1.490202	-0.000102
C	-0.384534	-0.344276	-0.000009
C	-1.007360	0.922920	0.000252
C	-2.408515	0.988664	0.000418
C	-3.179240	-0.148629	0.000325
H	-3.164126	-2.301374	-0.000019
H	-0.706037	-2.454946	-0.000305
C	1.072936	-0.525908	-0.000187
C	-0.268448	2.161533	0.000352
H	-2.880843	1.963459	0.000621
H	-4.259050	-0.071298	0.000456
C	1.064623	2.229943	0.000201
H	-0.838865	3.082493	0.000555
H	1.590802	3.175962	0.000274
S	1.857311	-1.971762	-0.000473
S	2.109896	0.861964	-0.000117



7a

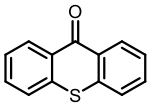
C	-3.556765	-0.966475	0.000012
C	-2.332229	-1.597228	-0.000004
C	-1.173039	-0.826595	-0.000010
C	-1.236970	0.563797	-0.000003
C	-2.491435	1.179177	0.000013
C	-3.643070	0.427125	0.000022
C	0.000000	1.365280	-0.000013
C	1.236970	0.563797	-0.000003
C	1.173039	-0.826595	-0.000008
C	2.332229	-1.597228	-0.000003
H	2.247189	-2.675474	-0.000009
C	3.556765	-0.966475	0.000012
C	3.643070	0.427125	0.000021
C	2.491435	1.179177	0.000013
H	-4.460433	-1.562728	0.000018
H	-2.247189	-2.675474	-0.000011
H	-2.519327	2.261154	0.000018
H	-4.611033	0.910017	0.000037
H	4.460433	-1.562728	0.000018
H	4.611033	0.910017	0.000035
H	2.519327	2.261154	0.000018
O	0.000000	2.579040	-0.000029
O	0.000000	-1.505943	-0.000023



7b

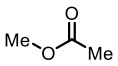
C	3.550775	1.236578	0.000001
C	2.319223	1.847409	0.000000
C	1.168868	1.062433	-0.000001
C	1.230721	-0.332032	-0.000001

C	2.504840	-0.920455	0.000000
C	3.645866	-0.156938	0.000001
C	0.000001	-1.125503	-0.000002
C	-1.230720	-0.332032	-0.000001
C	-1.168869	1.062433	-0.000001
C	-2.319224	1.847409	0.000000
H	-2.214994	2.923902	0.000000
C	-3.550776	1.236576	0.000001
C	-3.645865	-0.156940	0.000000
C	-2.504839	-0.920456	-0.000001
H	4.448012	1.842236	0.000002
H	2.214992	2.923902	0.000000
H	2.557402	-2.000815	0.000000
H	4.616590	-0.634222	0.000001
H	-4.448013	1.842233	0.000001
H	-4.616589	-0.634224	0.000001
H	-2.557400	-2.000816	-0.000001
S	0.000001	-2.767303	0.000002
O	-0.000003	1.740471	-0.000001

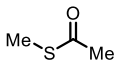


8a

C	-3.773516	-0.625382	0.000001
C	-2.625313	-1.384311	0.000000
C	-1.371188	-0.764804	0.000000
C	-1.281544	0.627762	0.000000
C	-2.464224	1.376174	0.000002
C	-3.696632	0.766258	0.000002
C	0.000000	1.376813	-0.000002
C	1.281544	0.627761	0.000000
C	1.371188	-0.764804	0.000000
C	2.625312	-1.384311	0.000001
H	2.686850	-2.465768	0.000000
C	3.773516	-0.625382	0.000001
C	3.696632	0.766258	0.000001
C	2.464224	1.376174	0.000001
H	-4.737850	-1.117496	0.000000
H	-2.686850	-2.465768	-0.000002
H	-2.370398	2.453764	0.000002
H	-4.599778	1.361932	0.000003
H	4.737850	-1.117496	0.000002
H	4.599778	1.361933	0.000001
H	2.370398	2.453763	0.000000
O	0.000001	2.591943	-0.000003
S	0.000000	-1.838103	-0.000001



C	1.861270	-0.162064	0.000004
H	2.021037	0.451586	-0.886601
H	2.021028	0.451573	0.88662
H	2.538565	-1.011976	0.000002
O	0.547292	-0.712543	-0.000007
C	-0.457514	0.175451	-0.000005
O	-0.287818	1.363748	-0.000001
C	-1.790607	-0.516145	0.000002
H	-1.875670	-1.155053	-0.879398
H	-2.583908	0.225631	-0.000106
H	-1.875744	-1.154860	0.879536



C	1.987047	0.389079	0.000007
H	1.928544	1.014035	-0.888132
H	1.928579	1.013974	0.888192
H	2.920403	-0.171006	-0.000028
S	0.655665	-0.818517	-0.000005
C	-0.742295	0.270821	-0.000002
O	-0.636498	1.467270	-0.000005
C	-2.070082	-0.444279	0.000006
H	-2.630591	-0.132366	-0.881916
H	-2.630594	-0.132333	0.881916
H	-1.963014	-1.527924	0.000025

7. References

1 N. Pearce, E. S. Davies, R. Horvath, C. R. Pfeiffer, X.-Z. Sun, W. Lewis, J. McMaster, M. W. George and N. R. Champness, *Phys. Chem. Chem. Phys*, 2018, **20**, 752–764.

2 W. Chen, J. Zhang, G. Long, Y. Liu and Q. Zhang, *J. Mater. Chem. C*, 2015, **3**, 8219.

3 A. J. Tilley, R. D. Pensack, T. S. Lee, B. Djukic, G. D. Scholes and D. S. Seferos, *J. Phys. Chem. C*, 2014, **118**, 9996–10004.

4 F. S. Etheridge, R. Fernando, J. A. Golen, A. L. Rheingold and G. Sauve, *RSC Adv.*, 2015, **5**, 46534–46539.

5 S. Le, D. Gendron, N. Be, Ois. Grenier, M. Leclerc and M. Co, *J. Phys. Chem. C*, 2014, **118**, 3953–3959.

6 X. Chen, A. A. Sukhanov, Y. Yan, D. Bese, C. Bese, J. Zhao, V. K. Voronkova, A. Barbon and H. G. Yaglioglu, *Angew. Chem. Int. Ed.*, 2022, **61**, e202203758.

7 K. M. Psutka, J. Ledrew, H. Taing, S. H. Eichhorn and K. E. Maly, *J. Org. Chem.*, 2019, **84**, 10796–10804.

8 K. M. Psutka and K. E. Maly, *RSC Adv.*, 2016, **6**, 78784–78790.

9 M. Ciureanu, M. Hillebrand, A. Meghea and E. Volanschi, *J. Electroanal. Chem.*, 1988, **239**, 227–237.

10 M. F. Nielsen, B. Batanero, T. Löhl, H. J. Schäfer, E. U. Würthwein and R. Fröhlich, *Chem. Eur. J.*, 1997, **3**, 2011–2024.

11 J. Voss and R. Edler, *J. Chem. Res.*, 2007, 226–228.

12 J. Voss, G. Kupczik and H. Stahncke, *J. Chem. Res.*, 2009, 283–286.

13 G. Mabon and J. Simonet, *Tetrahedron Lett.*, 1984, **25**, 193–196.

14 J. L. Burgot, A. Darchen and M. Sädi, *Electrochim. Acta*, 2002, **48**, 107–112.

15 M. L. Abasq, J. L. Burgot, A. Darchen and S. E. Dervout, *J. Electroanal. Chem.*, 2002, **537**, 145–150.

16 W. Schumuser and J. Voss, *J. Chem. Res. (M)*, 1980, 3361–3386.

17 M. A. Fox, K. Campbell, G. Maier and L. H. Franz, *J. Org. Chem.*, 1983, **48**, 1762–1765.

18 C.-P. Klages and J. Voss, *Chem. Ber.*, 1980, **113**, 2255–2277.

19 L. Mattiello and L. Rampazzo, in *Papers presented at the International Symposium on Electroorganic Synthesis*, 1997, pp. 209–210.

20 H. J. Timpe and K. P. Kronfeld, *J Photochem. Photobiol. A Chem.*, 1989, **46**, 253–267.

21 P.-A. Muller and E. Vauthey, *J. Phys. Chem. A*, 2001, **105**, 5994–6000.

22 L. Lunazzi, G. Maccagnani, G. Mazzanti and G. Placucci, *J. Chem. Soc. (B).*, 1971, 162–166.

23 R. O. Loutfy and R. O. Loutfy, *J. Phys. Chem.*, 1972, **76**, 1650–1655.

24 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910.

25 C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale and G. C. Bazan, *Adv. Mater.*, 2011, **23**, 2367–2371.

26 D. Bao, B. Millare, W. Xia, B. G. Steyer, A. A. Gerasimenko, A. Ferreira, A. Contreras and V. I. Vullev, *J. Phys. Chem. A*, 2009, **113**, 1259–1267.

27 J. R. Aranzaes, M.-C. Daniel and D. Astruc, *Can. J. Chem.*, 2006, **84**, 288–299.

28 R. G. Bates and J. B. Macaskill, *Pure Appl. Chem.*, 1978, **50**, 1701–1706.