Electronic supplementary information for

The emergent intramolecular hydrogen bonding effect on the electronic structures of organic electron acceptors

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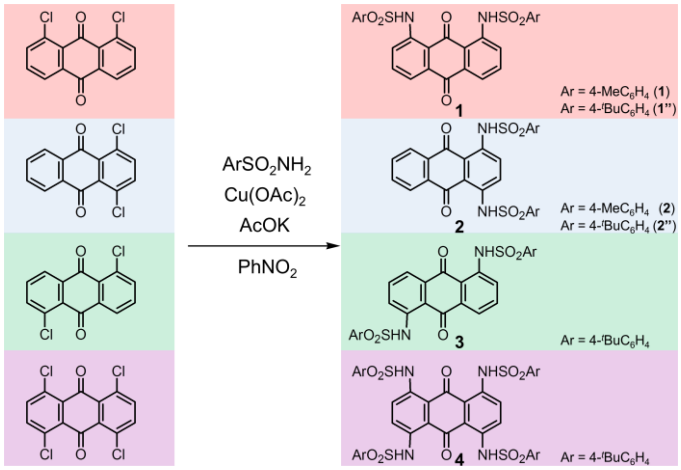
CONTENTS

1. Preparation of 1-4

The preparation of arylsulfonamide-substituted AQ **1-4** is summarized in Scheme 1. The corresponding chloroAQs were treated with arylsulfonamide in the presence of $Cu(OAc)_2$ at high temperature to give compounds **1-4**. For 1,5-disubstituted derivative **3** and tetrasubstituted derivative **4**, the introduction of a *tert*-butyl group on terminal aryl units was necessary to improve the solubility enough for purification. The negligible electronic contribution of the terminal alkyl group was confirmed by the comparison of **1,2** and **1'',2''** by UV-Vis spectroscopy and cyclic voltammetry, respectively. Although some of these compounds (**1**,**2**) were synthesized in a similar to that for intermediates of the corresponding aminoAQs,[S1,2] electronic, photophysical and crystal studies have not been performed before.



Scheme S1 Preparation of **1-4**.

2. Cyclic voltammogram of 1', 1,4-bis(methylamino)anthraquinone and 1-(methylamino)anthraquinone

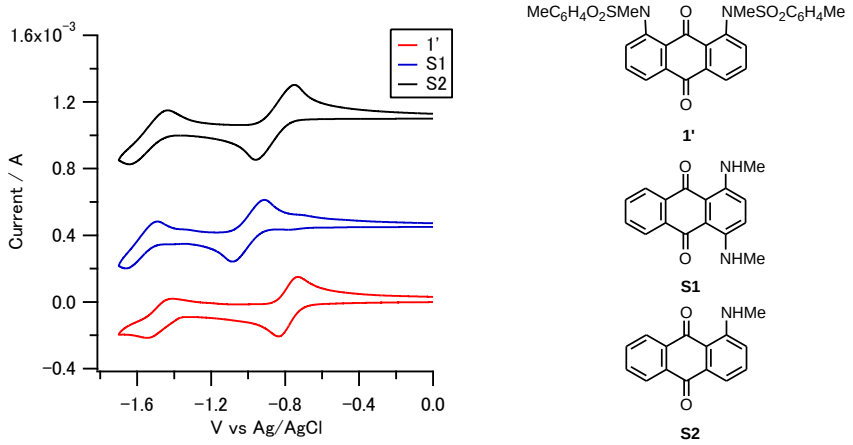


Figure S1 Cyclic voltammogram of **1'**, 1,4-Bis(methylamino)anthraquinone (**S1**) and 1-(methylamino)anthraquinone (**S2**) in DMF (0.1 M Bu_4NBF_4 vs Ag/AgCl).

3. IR spectra of 1-4 in $CHCl_3$

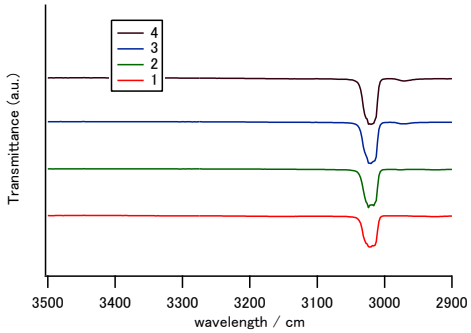


Figure S2 IR spectra of **1-4** in $CHCl_3$ (~1.0×10^{-3} M, light path: 0.5 mm).

4. ORTEP drawings of 2

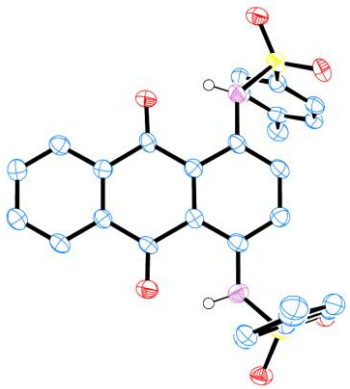


Figure S3 ORTEP drawing of **2** determined by single-crystal X-ray analysis. Displacement ellipsoids are drawn at the 50% probability level. Protons, except for those on amino groups, were omitted for clarity.

5. Calculated frontier orbitals and Mulliken charge distribution of 1-4.

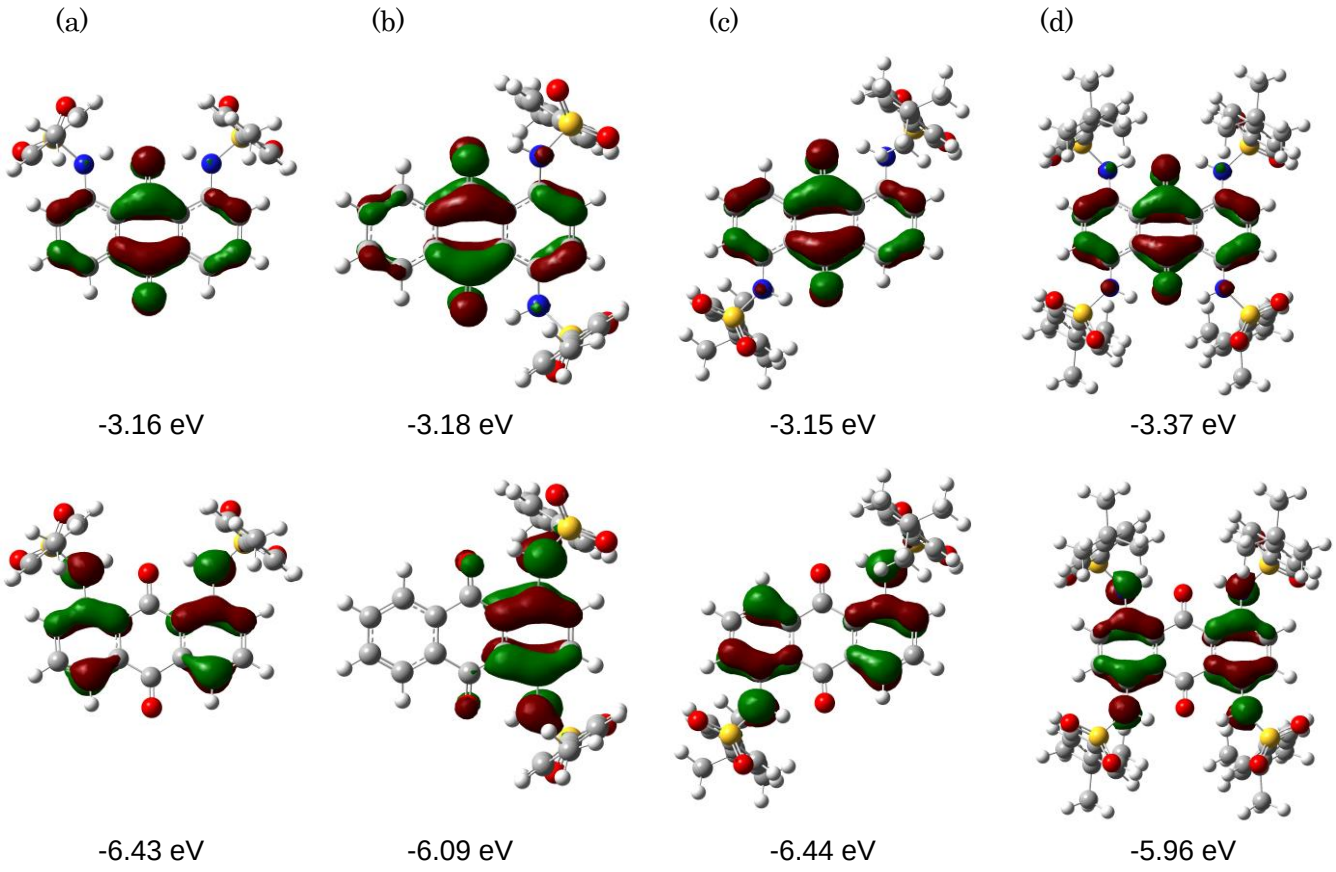
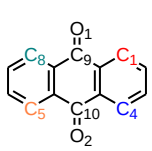
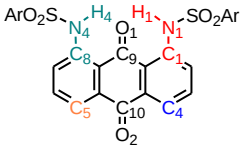


Figure S4 LUMO (top), HOMO (bottom) and their energies of (a) **1**, (b) **2**, (c) **3**, and (d) **4**.

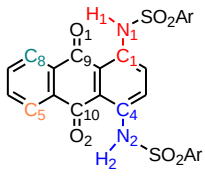
Table S1 Mulliken charge distribution of **1**-**4** and AQ



AQ



1



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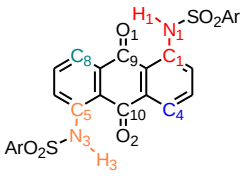

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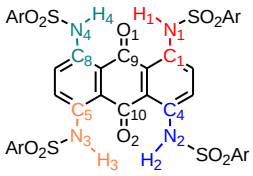


4

Atom	AQ	1	2	3	4
C_1	-0.172	0.289	0.289	0.293	0.297
C_4	-0.172	-0.168	0.289	-0.171	0.297
C_5	-0.172	-0.167	-0.172	0.293	0.296
C_8	-0.172	0.289	-0.172	-0.171	0.297
C_9	0.347	0.400	0.361	0.367	0.386
C_{10}	0.347	0.343	0.361	0.367	0.386
O_1	-0.478	-0.598	-0.537	-0.532	-0.613
O_2	-0.478	-0.477	-0.537	-0.532	-0.613
N_1	———	-0.819	-0.816	-0.817	-0.823
H_1	———	0.416	0.413	0.413	0.417
N_2	———	———	-0.817	———	-0.823
H_2	———	———	0.413	———	0.417
N_3	———	———	———	-0.817	-0.823
H_3	———	———	———	0.413	0.417
N_4	———	-0.819	———	———	-0.823
H_4	———	-0.416	———	———	0.417

6. E_{LUMO} - ϕ and E_{total} – ϕ plots of 1-3

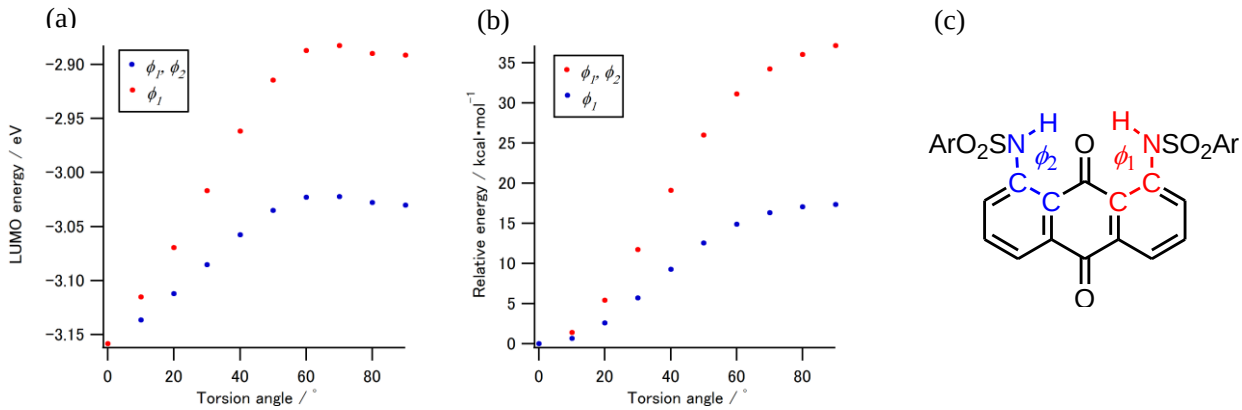


Figure S5 (a) E_{LUMO} - ϕ plots and (b) ΔE_{total} - ϕ plots of **1**. The inset legends show rotated torsion angles: the other torsion angles were fixed at 0 °. (c) Definitions of torsion angles ϕ_1-ϕ_2 of **1**.

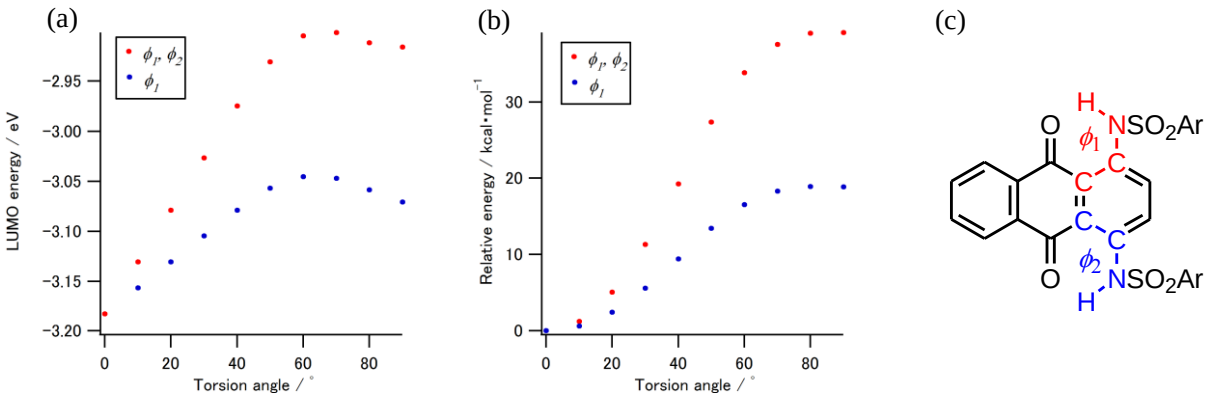


Figure S6 (a) E_{LUMO} - ϕ plots and (b) ΔE_{total} - ϕ plots of **2**. The inset legends show rotated torsion angles: the other torsion angles were fixed at 0 °. (c) Definitions of torsion angles ϕ_1-ϕ_2 of **2**.

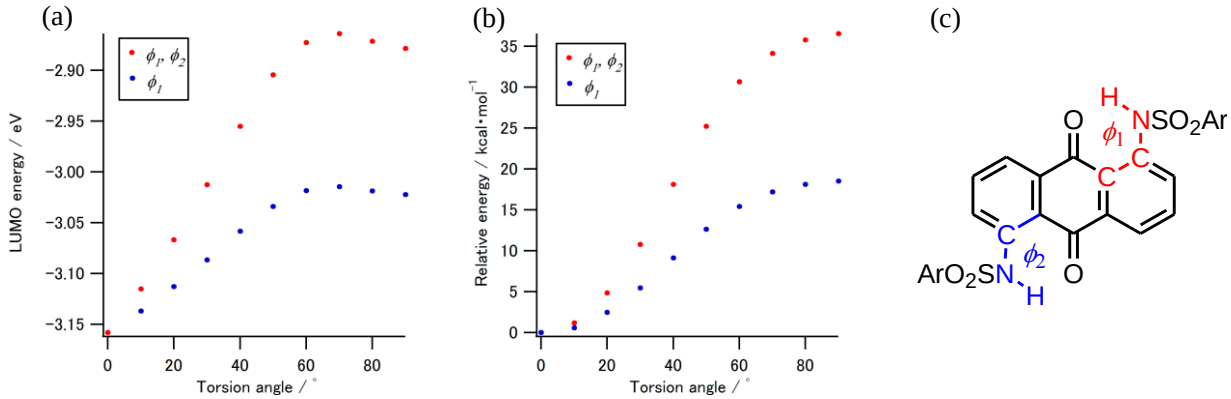


Figure S7 (a) E_{LUMO} - ϕ plots of and (b) ΔE_{total} - ϕ plots of **3**. The inset legends indicates rotated torsion angles and the other torsion angles were fixed at 0 °. (c) Definitions of torsion angles ϕ_1-ϕ_2 of **3**.

7. Halochromic behavior of 1-4.

The photophysical properties of **1-4** could be modulated by the addition of triethylamine. Figures S8-11 show changes in the UV-Vis spectra of **1-4** with an increase in the concentration of triethylamine in CH_2Cl_2. Upon the addition of triethylamine, a distinct bathochromic shift was initially observed with an isosbestic point. Further addition of the base induced a hypsochromic shift. This result could be accounted for by stepwise deprotonation. Initial deprotonation of the amine unit of **1-4** enhanced the electron-donating properties of the aniline/phenylenediamine subunit to induce stronger intramolecular charge transfer, whereas subsequent deprotonation increased on-site Coulombic repulsion to reduce intramolecular charge transfer. Tetrasubstituted **4** showed a more sensitive and multistep response toward triethylamine (Figure S11).

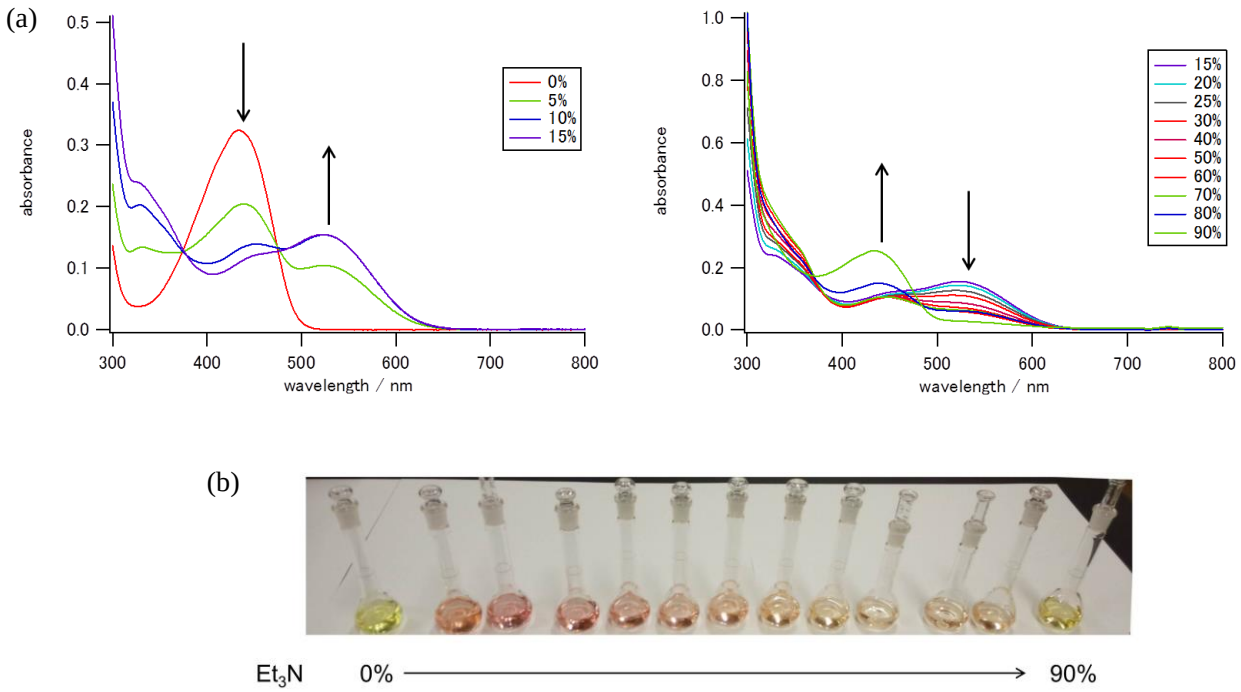


Figure S8 Halochromic behavior of **1** in CH_2Cl_2 with an increase in Et_3N. (a) UV-Vis spectra of **1** in CH_2Cl_2/Et_3N. (b) Picture of a solution of **1** in CH_2Cl_2/Et_3N.

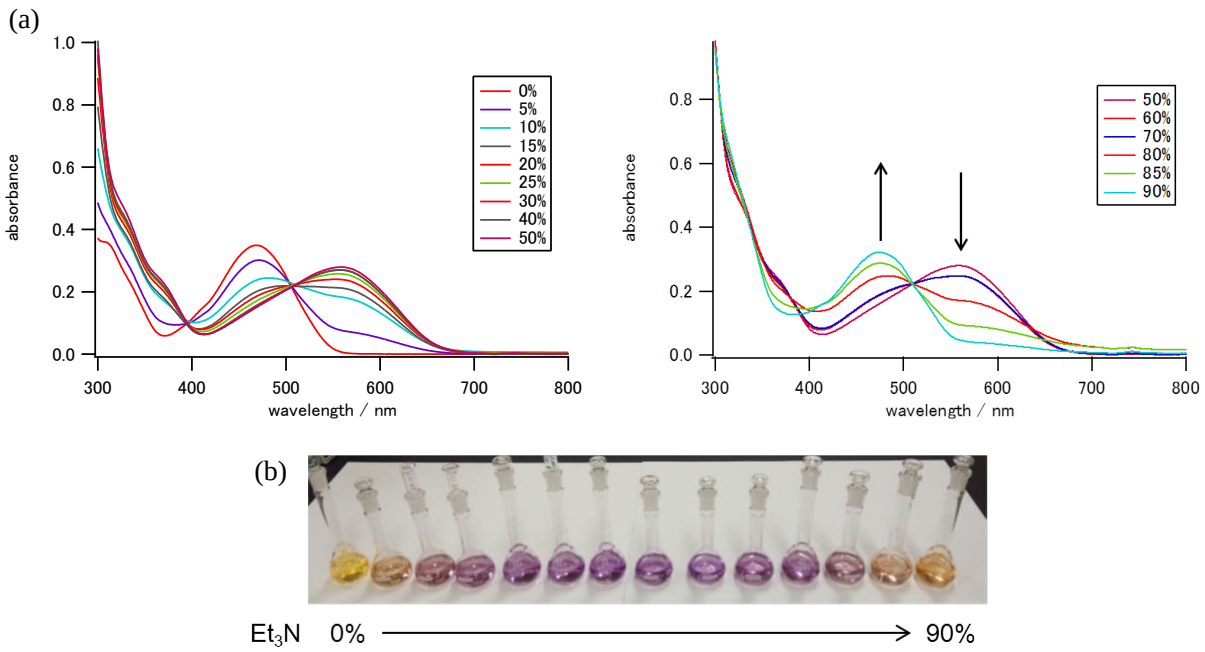


Figure S9 Halochromic behavior of **2** in CH_2Cl_2 with an increase in Et_3N. (a) UV-Vis spectra of **2** in CH_2Cl_2/Et_3N. (b) Picture of a solution of **2** in CH_2Cl_2/Et_3N.

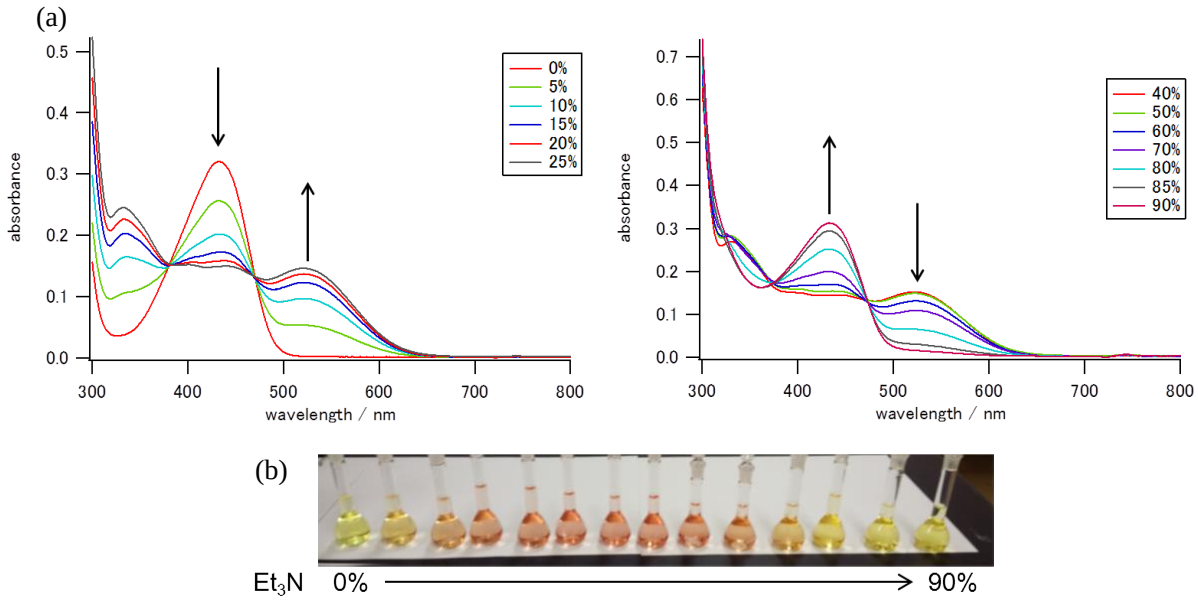


Figure S10 Halochromic behavior of **3** in CH_2Cl_2 with an increase in Et_3N. (a) UV-Vis spectra of **3** in CH_2Cl_2/Et_3N. (b) Picture of a solution of **3** in CH_2Cl_2/Et_3N.

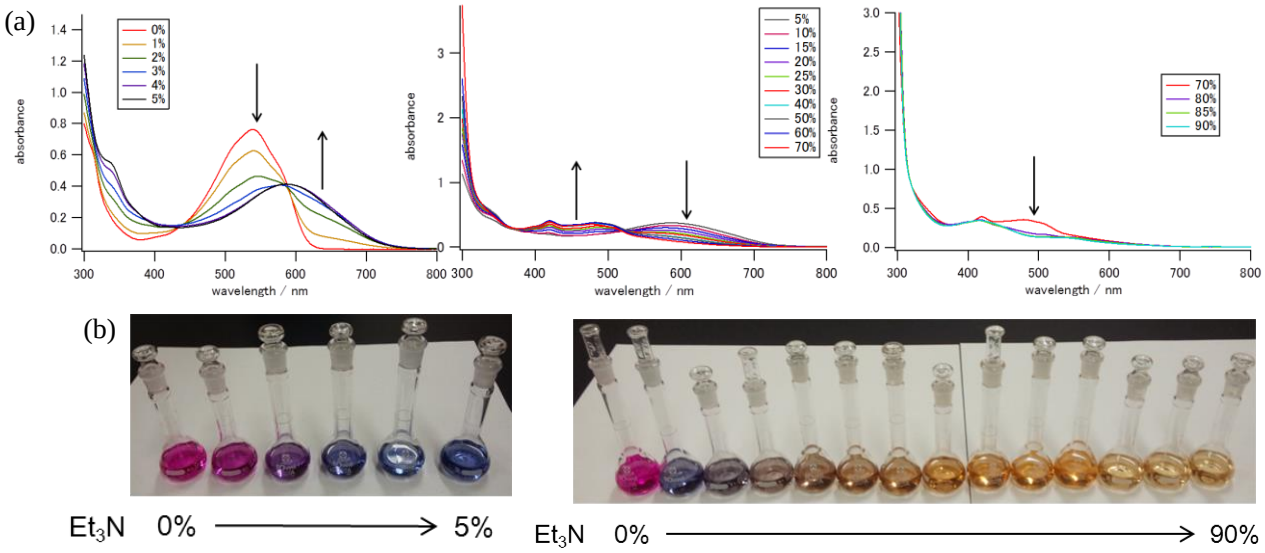


Figure S11 Halochromic behavior of **4** in CH_2Cl_2 with an increase in Et_3N. (a) UV-Vis spectra of **4** in CH_2Cl_2/Et_3N. (b) Picture of a solution of **4** in CH_2Cl_2/Et_3N

8. Experimental Section

General methods. Commercially available reagents and solvents were used as received. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance III 400 NMR and Bruker Avance III 500 NMR spectrometers. Chemical shifts (δ) are expressed in ppm referred to tetramethylsilane (^{1}H 0.00 ppm) or residual nondeuterated solvent ($CDCl_3$; ^{13}C 77.0 ppm) as an internal standard. Mass spectra were recorded on a JMS-700 spectrometer at the NMR and MS Laboratory, Graduate School of Agriculture, Tohoku University. Elemental analyses were performed on a Microcoder JM10 at the Elementary Analysis Laboratory, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. IR spectra were measured on a Thermo Scientific NICOLET 6700 FT-IR spectrometer. Thermogravimetric analysis was performed on a Rigaku Thermoplus EVO2 at a scan rate of 10 $Kmin^{-1}$.

Preparation of 1.

A mixture of 1,8-dichloroanthraquinone (5.01 g, 18.1 mmol), *p*-toluenesulfonamide (9.20 g, 53.7 mmol), Copper(II) acetate monohydrate (250 mg, 1.25 mmol) and potassium carbonate (4.00 g, 40.8 mmol) in nitrobenzene (50 mL) was stirred at 200 °C under air for 14.5 h. After cooling to rt, the resulting mixture was diluted with water and $CHCl_3$. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layers were washed with brine and dried over $MgSO_4$. Recrystallization from benzene gave compound **1** (6.16 g, 62%) as a yellow solid.

Mp: 274−275 °C. ^{1}H NMR (400 MHz): δ 11.8 (s, 2H), 8.02 (dd, J = 8.5, 1.2 Hz, 2H), 7.92 (dd, J = 7.5, 1.2 Hz, 2H), 7.86 (d, J = 8.5 Hz, 4H), 7.65 (br t, J = 8.1Hz, 2H), 7.30 (d, J = 8.1 Hz, 4H), 2.38 (s, 6H). ^{13}C NMR (100 MHz): δ 190.6, 181.5, 144.6, 141.5, 136.2, 135.9, 133.6, 130.0, 127.3, 123.9, 122.3, 118.0, 21.6 IR: 3129, 1668, 1619, 1596, 1575, 1483, 1459, 1386, 1343, 1299, 1263, 1236, 1160, 1090, 993, 886, 863, 844, 812, 743, 718, 664, 563, 544, 513, 464 cm^{-1}. HRMS (FAB) calcd for $C_{28}H_{23}N_2O_6S_2$: 547.0998 [$(M+1)^+$]; found: 547.0992. Anal. Calcd for $C_{28}H_{22}N_2O_6S_2$: C, 61.52 H, 4.06; N, 5.12. Found: C, 61.49 H, 4.21; N,5.07.

Preparation of 2.

A mixture of 1,4-dichloroanthraquinone (5.00 g, 18.1 mmol), *p*-toluenesulfonamide (9.20 g, 53.7 mmol), Copper(II) acetate monohydrate (250 mg, 1.25 mmol), and potassium carbonate (4.00 g, 40.8 mmol) in nitrobenzene (50 mL) was stirred at 200 °C under air for 10 h. After cooling to rt, the resulting mixture was diluted with water and $CHCl_3$. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layers were washed with brine and dried over $MgSO_4$. The obtained crude solid was washed with a small amount of $CHCl_3$ and then recrystallized from $CHCl_3$ to give compound **2** (2.04 g) as a red solid. Combined filtrate was subjected to silica gel column

chromatography ($CHCl_3$) to give an additional amount of compound **2** (5.18 g). Total yield: 7.22 g (73%).

Mp: 245−246 °C. ^{1}H NMR (400 MHz): δ 12.3 (s, 2H), 8.22 (dd, J = 9.2, 5.9 Hz, 2H), 7.97 (s, 2H), 7.80 (dd, J = 9.2, 5.9 Hz, 2H), 7.76(d, J = 8.2 Hz, 4H), 7.24 (d, J = 8.2 Hz, 4H), 2.36 (s, 6H). ^{13}C NMR (100 MHz): δ 186.2, 144.5, 137.4, 136.3, 134.8, 132.9, 129.9, 127.3, 127.2, 126.3, 117.1, 21.5. IR: 3019, 1639, 1590, 1475, 1379, 1352, 1287, 1254, 1186, 1164, 1090, 1072, 971, 920, 896, 859, 839, 818, 726, 714, 656, 579, 558, 544 cm^{-1}. HRMS (FAB) calcd for $C_{28}H_{22}N_2O_6S_2Na$: 569.0817 [$(M+Na)^+$]; found: 569.0817. Anal. Calcd for $C_{28}H_{22}N_2O_6S_2$: C, 61.52 H, 4.06; N, 5.12. Found: C, 61.60 H, 4.31; N,5.05.

Preparation of 3.

A mixture of 1,5-dichloroanthraquinone (4.71 g, 17.0 mmol), 4-*tert*-butylbenzenesulfonamide (10.0 g, 46.9 mmol), Copper(II) acetate monohydrate (218 mg, 1.09 mmol), and potassium carbonate (3.49 g, 35.6 mmol) in nitrobenzene (50 mL) was stirred at 200 °C under air for 11.5 h. After cooling to rt, the resulting mixture was diluted with water and $CHCl_3$. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layers were washed with brine and dried over $MgSO_4$. The obtained crude solid was subjected to silica gel column chromatography ($CHCl_3$) followed by recrystallization from toluene to give compound **3** as a yellow solid (6.82 g, 63%).

Mp: >300 °C. ^{1}H NMR (400 MHz): δ 12.1 (s, 2H), 7.99 (dd, J = 8.5, 1.1 Hz, 2H), 7.96 (dd, J = 7.7, 1.1 Hz, 2H), 7.87-7.83 (m, 4H), 7.68 (t, J = 8.2 Hz), 7.49-7.44 (m, 4H), 1.26 (s, 18H). ^{13}C NMR (100 MHz): δ 185.8, 157.4, 141.3, 136.2, 135.8, 134.5, 127.1, 126.3, 123.4, 122.5, 116.9, 35.2, 30.9. IR: 3080, 2965, 1637, 1593, 1475, 1385, 1348, 1264, 1199, 1163, 1113, 1086. 1055, 889, 835, 770, 753, 711, 654, 624, 570, 548 cm^{-1}. HRMS (FAB) calcd for $C_{34}H_{35}N_2O_6S_2$: 631.1937 [$(M+H)^+$]; found: 631.1937. Anal. Calcd for $C_{34}H_{34}N_2O_6S_2$: C, 64.74 H, 5.43; N, 4.44. Found: C, 64.90 H, 5.49; N,4.37.

Preparation of 4.

A mixture of 1,4,5,8-tetrachloroanthraquinone (3.00 g, 8.67 mmol), 4-*tert*-butylbenzenesulfonamide (10.0 g, 46.9 mmol), Copper(II) acetate monohydrate (277 mg, 1.39 mmol), and potassium carbonate (3.57 g, 36.4 mmol) in nitrobenzene (50 mL) was stirred at 200 °C under air for 18.5 h. After cooling to rt, the resulting mixture was diluted with water and $CHCl_3$. The aqueous layer was separated and extracted with $CHCl_3$. Theombined organic layers were washed with brine and dried over $MgSO_4$. Obtained crude solid was subjected to silica gel column chromatography ($CHCl_3$) followed by recrystallization from toluene to give compound **4** as a dark purple solid (5.11 g, 56%).

Mp: decomposed above 270 °C. ^{1}H NMR (400 MHz): δ 11.8 (s, 4H), 7.97 (s, 4H), 7.75 (d, J =8.7 Hz, 8H), 7.50 (d, J = 8.7 Hz, 8H), 1.28 (s, 36H). ^{13}C NMR (100 MHz): δ 188.6, 157.8, 137.4, 136.0, 127.1, 126.6, 126.5, 116.9, 35.3, 30.9. IR: 2964, 1595, 1479, 1377, 1221, 1198, 1167, 1112, 1084, 981, 862,

837, 791, 755, 647, 622, 571, 546 cm^{-1}. HRMS (FAB) calcd for $C_{54}H_{60}N_4O_{10}S_4Na$: 1075.3090 [$(M+Na)^+$]; found: 1075.3085. Anal. Calcd for $C_{54}H_{60}N_4O_{10}S_4$: C, 61.57 H, 5.74; N, 5.32. Found: C, 61.81 H, 5.88; N, 5.24.

Preparation of 1'.

To a suspension of NaH (60% in oil, 333 mg, 8.33 mmol) in dry DMF (20 mL) was added **1** (303 mg, 554 μmol) under N_2. The mixture was stirred at rt for 45 min. To the resulting solution was added MeI (700 μL, 11.0 mmol) at this temperature. The mixture was stirred at rt for 12 h. The mixture was diluted with an excess amount of water. The resulting precipitate was collected by filtration, washed with water, and then dried under vacuum. Recrystallization from EtOH gave **1'** (171 mg, 54%) as an orange crystalline solid.

Mp: 236-237 °C. ^{1}H NMR (400 MHz): δ 8.24 (dd, J = 7.8, 1.3 Hz, 2H), 7.70 (d, J = 7.8 Hz, 4H), 7.63 (t, J = 7.6 Hz, 2H), 7.47 (dd, J = 7.8, 1.3 Hz, 2H), 7.31 (d, J = 7.8 Hz, 4H), 3.24 (s, 6H), 2.43 (s, 6H). ^{13}C NMR (100 MHz): δ 182.6, 182.3, 143.5, 140.3, 136.0, 134.6, 133.6, 133.0, 129.6, 127.9, 126.9, 38.8, 21.6. IR: 3072, 2948, 2919, 1680, 1585, 1495, 1461, 1436, 1400, 1345, 1318, 1249, 1216, 1188, 1150, 1089, 1020, 1011, 957, 871, 850, 802, 752, 730, 688, 675, 651, 581, 563, 545, 517 cm^{-1}. HRMS (FAB) calcd for $C_{30}H_{27}N_2O_6S_2$: 575.1311 [$(M+H)^+$]; found: 575.1309. Anal. Calcd for $C_{30}H_{26}N_2O_6S_2$: C, 62.70 H, 4.56; N, 4.87. Found: C, 62.55 H, 4.73; N, 4.78.

X-ray structural analysis. Crystallographic data for single crystal of **2** was collected using a diffractometer equipped with a rotating anode fitted with a multilayer confocal optic using Cu-Kα (λ = 1.54187 Å) radiation. Structure refinements were carried out using the full-matrix least-squares method on F^2. Calculations were performed using the Crystal Structure and SHELEX software packages.[S3] Parameters were refined using anisotropic temperature factors, except for the hydrogen atom.

Crystal data of 2: Single-crystalline sample was obtained by recrystallization from toluene. $C_{28}H_{22}N_2O_6S_2$, M = 546.61, P-1 (#2), a = 8.13783(15) Å, b = 11.6634(2) Å, c = 13.4980(3) Å, α = 93.4739(9) °, β = 96.7310(10) °, γ = 103.8825(11) °, V = 1229.92(4) $Å^3$, Z= 2, Dc= 1.476 g cm^{-3}. Independent reflection 4398 (all), T = 100K, μ= 23.81 cm^{-1}, R = 7.0%. CCDC 1550105.

9. ^{1}H and ^{13}C NMR spectra of 1-4 and 1’

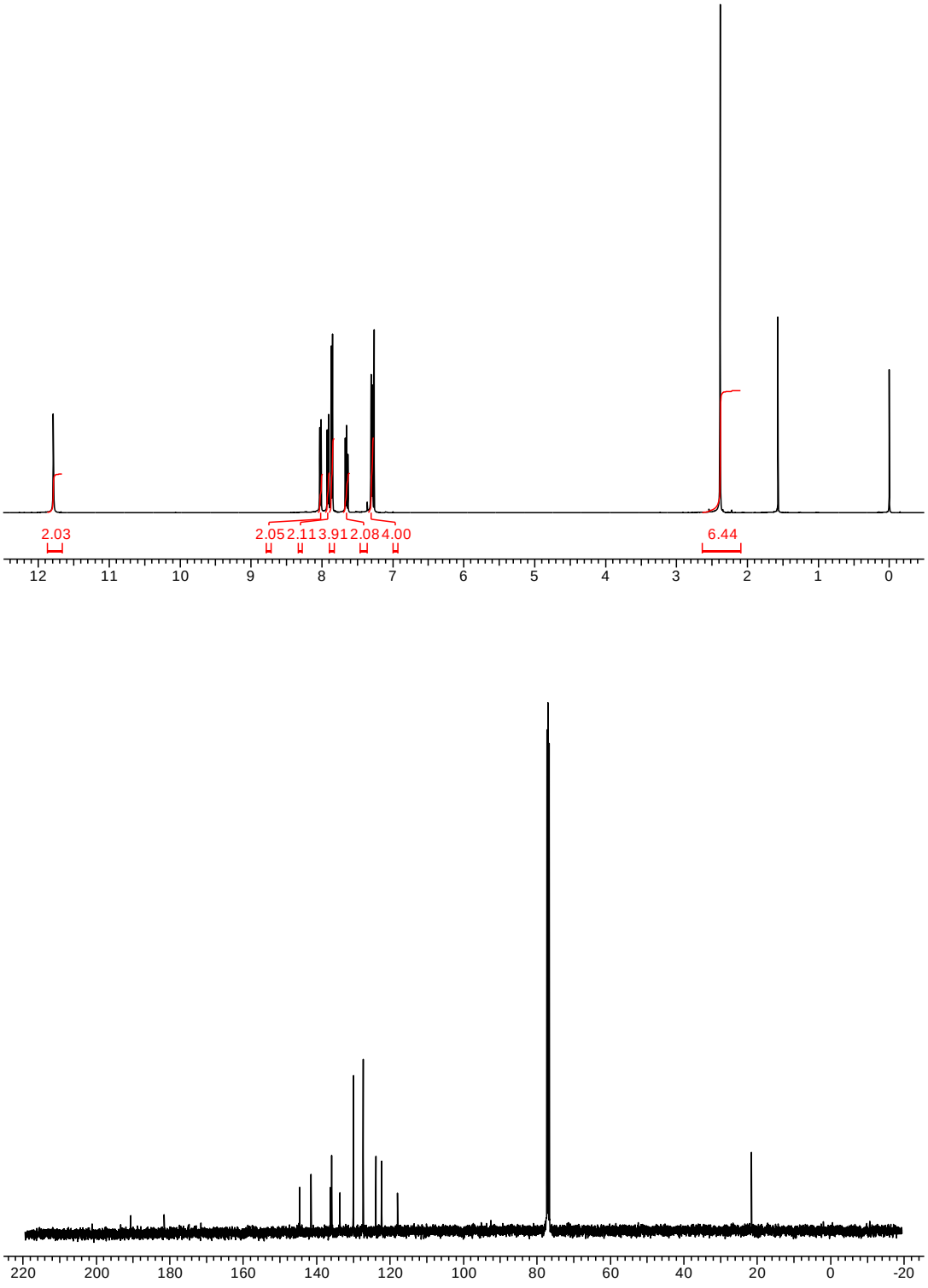


Figure S12 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **1**.

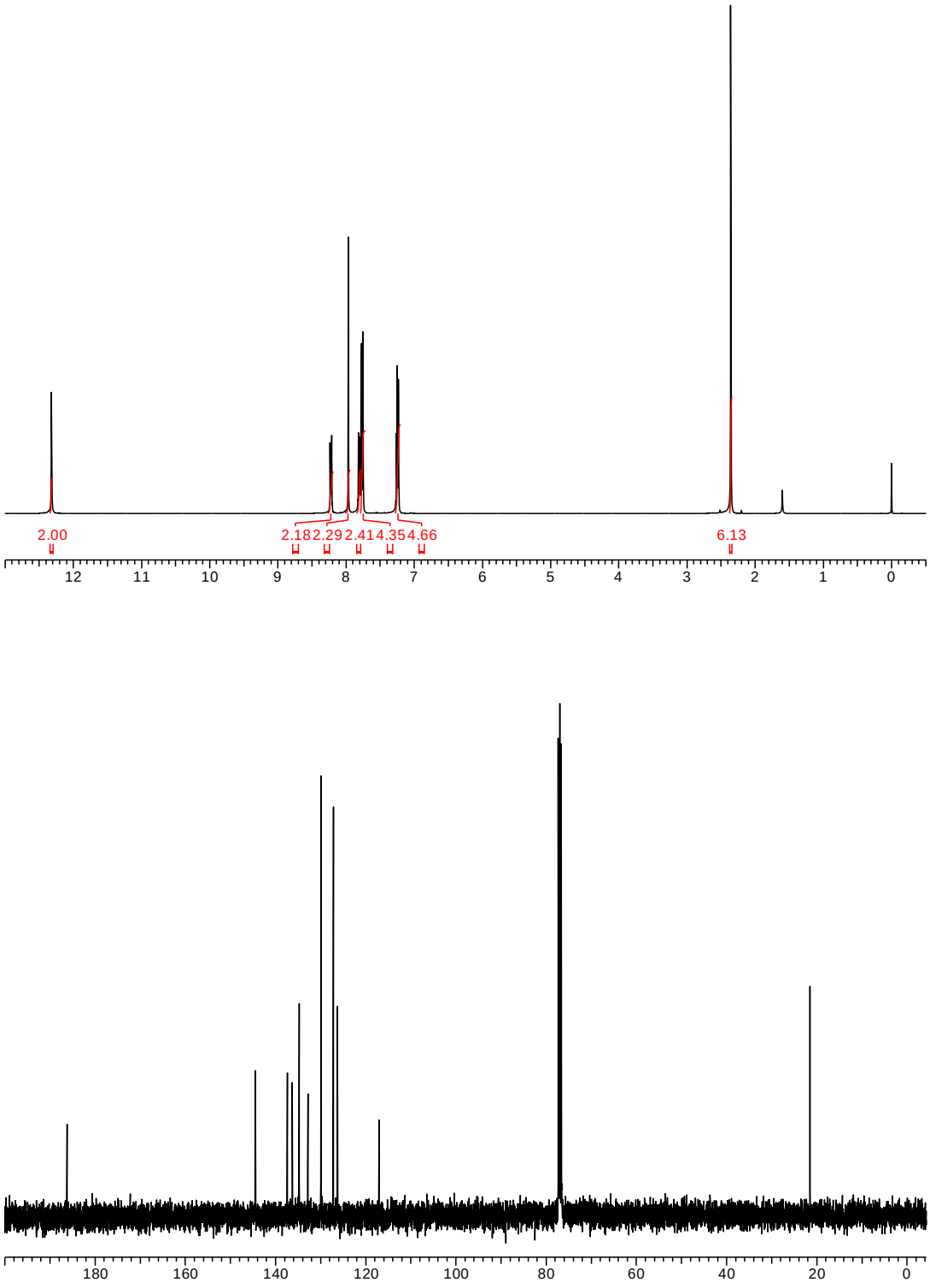


Figure S13 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2**.

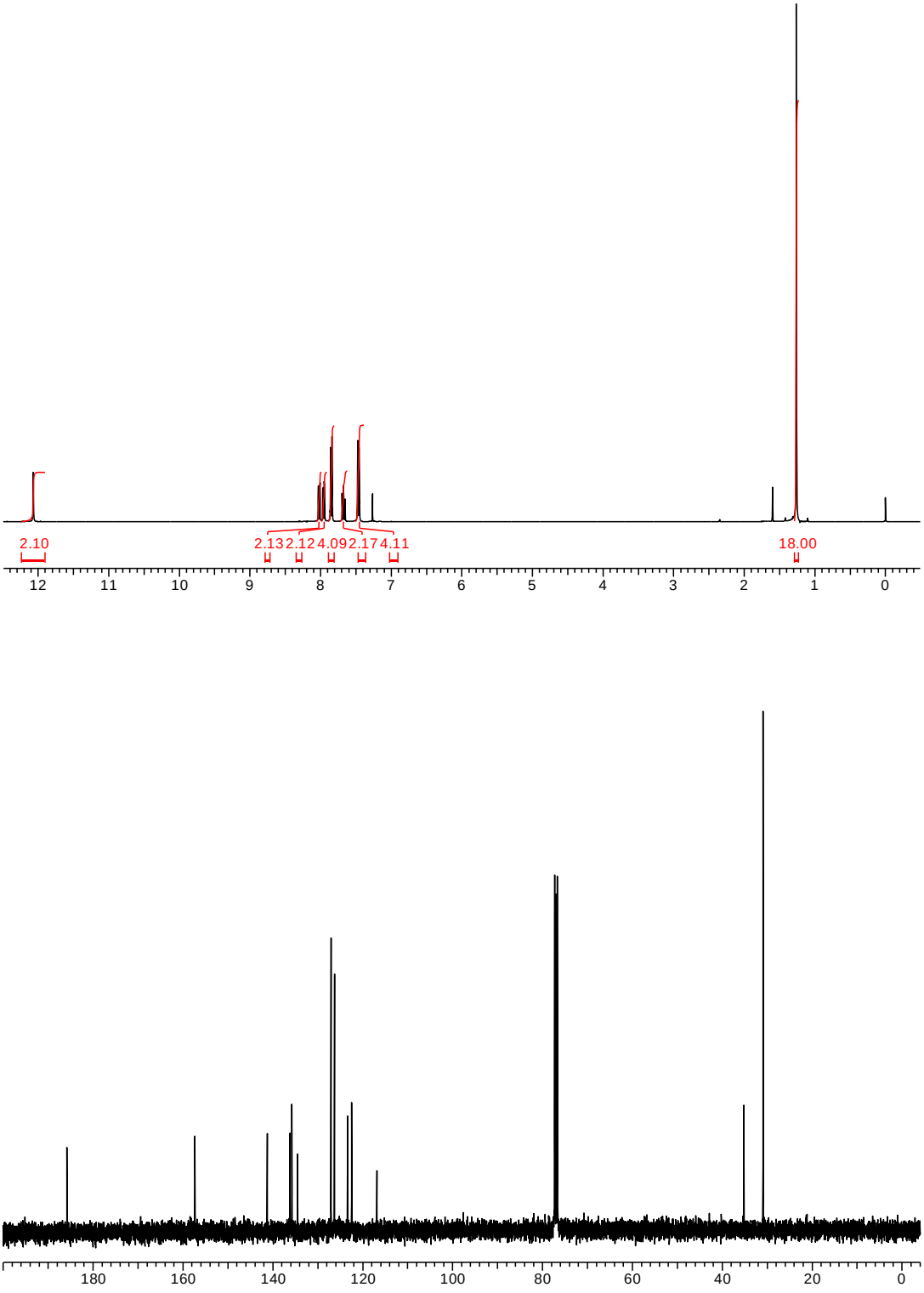


Figure S14 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3**.

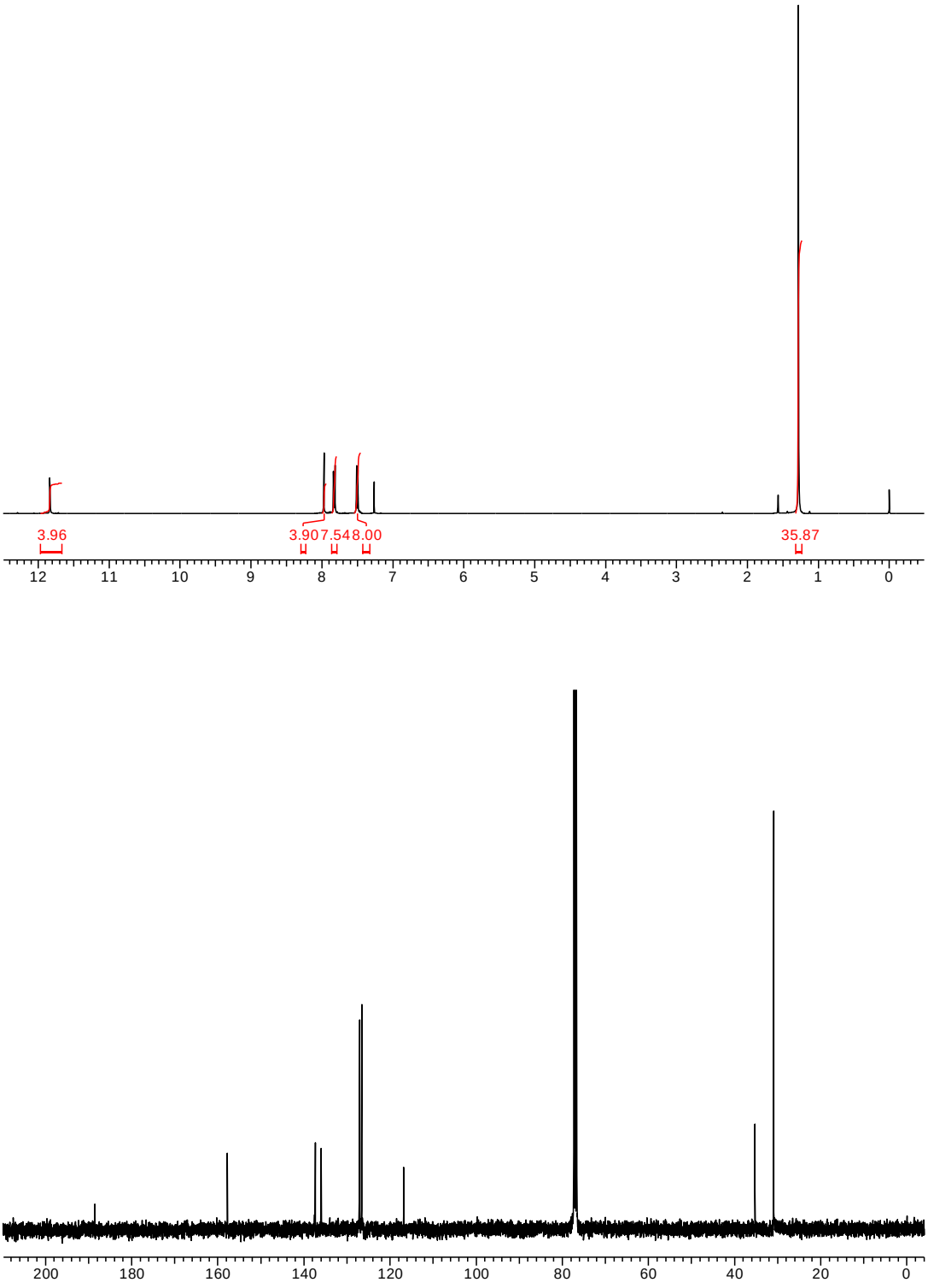


Figure S15 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4**.

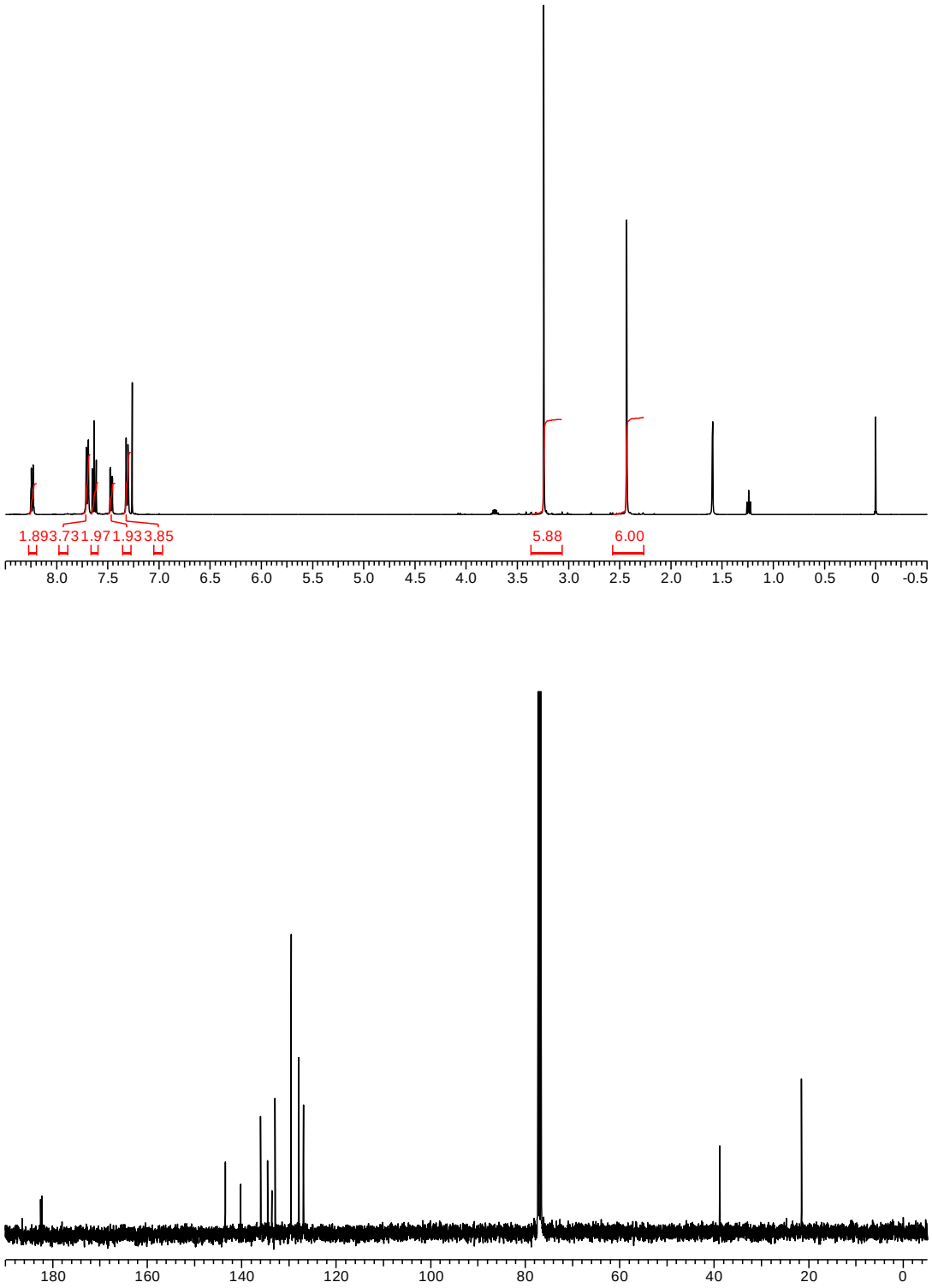


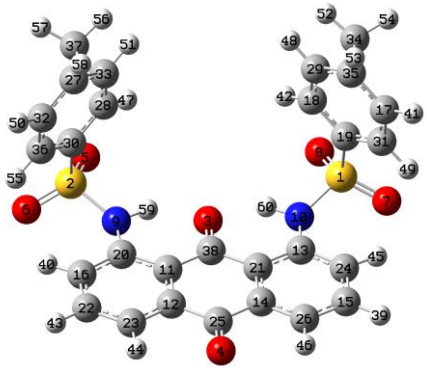
Figure S16 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **1'**.

10. Cartesian Coordinates for optimized structures 1-4

a. Optimized structure of **1**

E(RB3LYP) = -2437.36434183 a.u.

Number of imaginary frequency: 0



Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
1	S	−3.839801	0.310018	1.870099
2	S	3.837615	0.307612	1.871983
3	O	−0.001526	−0.833445	1.429284
4	O	−0.001592	−4.337014	−2.682050
5	O	3.321446	0.976680	3.063222
6	O	5.117131	−0.402755	1.869337
7	O	−5.120281	−0.398592	1.864859
8	O	−3.324647	0.977597	3.062605
9	N	2.601858	−0.791265	1.485923
10	N	−2.604994	−0.790422	1.485313
11	C	1.280381	−2.123234	−0.090179
12	C	1.275728	−3.052989	−1.159899
13	C	−2.546403	−1.685918	0.418660
14	C	−1.278871	−3.052555	−1.160228
15	C	−3.683323	−3.105313	−1.197599
16	C	3.727395	−2.206701	−0.142874
17	C	−4.809566	2.300417	−1.534825
18	C	−2.928545	2.531609	0.515469
19	C	−3.867160	1.495719	0.525866
20	C	2.543284	−1.686825	0.419380
21	C	−1.283509	−2.122770	−0.090534
22	C	3.680170	−3.106533	−1.196619

Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
31	C	−4.814415	1.375439	−0.491127
32	C	4.817893	2.296301	−1.53095
33	C	2.945095	3.440484	−0.537095
34	C	−3.899271	4.362921	−2.689883
35	C	−3.878128	3.34567	−1.574403
36	C	4.819648	1.371946	−0.48658
37	C	3.909391	4.357023	−2.69093
38	C	−0.001545	−1.641925	0.473249
39	H	−4.61242	−3.4901	−1.608775
40	H	4.677699	−1.912551	0.283604
41	H	−5.54773	2.210942	−2.327792
42	H	−2.214455	2.625783	1.327177
43	H	4.609251	−3.491595	−1.607572
44	H	2.395107	−4.241303	−2.531828
45	H	−4.680834	−1.910934	0.282353
46	H	−2.398269	−4.240525	−2.532438
47	H	2.212472	2.62188	1.321634
48	H	−2.2162	4.255648	−0.542643
49	H	−5.553628	0.5833	−0.452933
50	H	5.558986	2.206859	−2.321169
51	H	2.219675	4.250366	−0.549231
52	H	−2.885766	4.658403	−2.981878

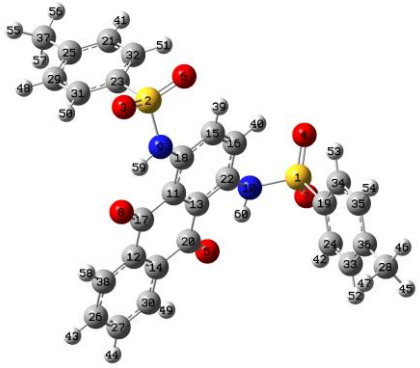
23	C	2.457569	−3.533148	−1.713741
24	C	−3.730532	−2.205447	−0.143877
25	C	−0.001578	−3.547881	−1.742934
26	C	−2.460724	−3.532330	−1.714385
27	C	3.885880	3.340762	−1.574594
28	C	2.929453	2.527567	0.512489
29	C	−2.941120	3.445290	−0.533601
30	C	3.868752	1.492246	0.526894

53	H	−4.410317	3.975746	−3.57671
54	H	−4.425571	5.274873	−2.378853
55	H	5.559266	0.580345	−0.445189
56	H	2.896182	4.637342	−2.998733
57	H	4.417297	5.276987	−2.373086
58	H	4.439303	3.976304	−3.569388
59	H	1.687569	−0.498554	1.841461
60	H	−1.690623	−0.498206	1.841068

b. Optimized structure of **2**

E(RB3LYP) = -2437.36582586 a.u.

Number of imaginary frequency: 0



Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
1	S	−3.342205	−1.526368	−2.005691
2	S	3.339433	−1.533019	2.002978
3	O	4.161644	−1.018258	3.095132
4	O	−2.744575	−2.862143	−2.051508
5	O	−2.009446	2.220223	−1.804454
6	O	2.740697	−2.868420	2.044922
7	O	−4.164896	−1.008211	−3.095879
8	O	2.010788	2.215081	1.807501
9	N	2.090244	−0.382587	1.888108
10	N	−2.092073	−0.377172	−1.888926
11	C	0.540943	0.881965	0.472760
12	C	0.529356	3.436159	0.463831
13	C	−0.540910	0.883350	−0.472053
14	C	−0.525587	3.437500	−0.460001
15	C	0.507563	−1.555106	0.459718

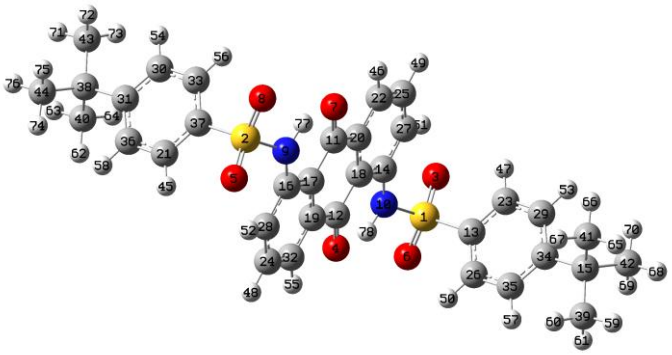
Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
31	C	5.160719	−0.332746	0.316041
32	C	4.078972	−2.335121	−0.538418
33	C	−5.863494	−0.213791	0.880979
34	C	−4.081997	−2.335894	0.533213
35	C	−4.797655	−2.203935	1.723315
36	C	−5.691096	−1.143625	1.919401
37	C	6.447071	−0.986115	−3.217156
38	C	1.054015	4.650589	0.925468
39	H	0.89339	−2.494264	0.83611
40	H	−0.897563	−2.491896	−0.840432
41	H	4.659053	−2.93596	−2.516191
42	H	−5.311343	0.384831	−1.117486
43	H	0.939032	6.794697	0.824338
44	H	−0.929746	6.797074	−0.817062
45	H	−7.487052	−0.701098	3.04427

16	C	−0.510592	−1.553780	−0.462614	46	H	−6.442197	−1.920591	3.795648
17	C	1.094992	2.162555	0.971616	47	H	−5.992911	−0.211648	3.845579
18	C	1.066741	−0.349523	0.939358	48	H	6.57021	0.602896	−1.00097
19	C	−4.265490	−1.390661	−0.475687	49	H	−1.861694	4.628968	−1.637046
20	C	−1.093339	2.165345	−0.969057	50	H	5.314007	0.376298	1.123288
21	C	4.795663	−2.200442	−1.727590	51	H	3.403478	−3.16958	−0.38654
22	C	−1.068314	−0.346790	−0.940397	52	H	−6.565586	0.60658	1.008361
23	C	4.264167	−1.394121	0.474138	53	H	−3.408555	−3.171353	0.377781
24	C	−5.159299	−0.327661	−0.313034	54	H	−4.662375	−2.942755	2.509052
25	C	5.691872	−1.141631	−1.919118	55	H	7.489315	−0.698133	−3.041214
26	C	0.530113	5.854452	0.465232	56	H	6.443316	−1.913755	−3.797245
27	C	−0.522379	5.855791	−0.458914	57	H	5.996477	−0.20405	−3.842143
28	C	−6.445084	−0.991121	3.218498	58	H	1.867363	4.624226	1.642156
29	C	5.865961	−0.216160	−0.877095	59	H	2.399428	0.549578	2.186331
30	C	−1.048274	4.653263	−0.920366	60	H	−2.400409	0.555776	−2.185555

c. Optimized structure of **3**

E(RB3LYP) = -2673.24185913 a.u.

Number of imaginary frequency: 0



Atom No.	Element	Cartesian Coordinates			Atom No.	Element	Cartesian Coordinates		
		X	Y	Z			X	Y	Z
1	S	4.526451	−2.923566	0.429243	40	C	−7.061617	−3.189488	1.105251
2	S	−4.527321	2.923812	−0.428959	41	C	7.063333	3.188408	−1.105907
3	O	4.750985	−3.729265	−0.772115	42	C	9.196436	1.91066	−0.657466
4	O	1.347899	−1.073002	2.080642	43	C	−7.961706	−3.008975	−1.222219
5	O	−4.752324	3.729261	0.772479	44	C	−9.195219	−1.912615	0.656705
6	O	4.716193	−3.462751	1.773222	45	H	−5.839923	1.667477	1.836561
7	O	−1.348252	1.074259	−2.080303	46	H	0.110668	−0.168649	−3.459071
8	O	−4.717193	3.463077	−1.772887	47	H	5.839292	−1.668023	−1.83658

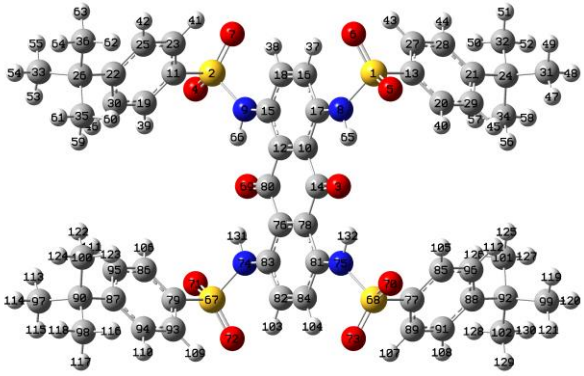
9	N	−2.904824	2.417282	−0.441662
10	N	2.904203	−2.416304	0.442028
11	C	−0.753207	0.594814	−1.104196
12	C	0.752767	−0.593662	1.104533
13	C	5.495880	−1.424885	0.276412
14	C	2.190157	−1.813608	−0.592378
15	C	7.789990	2.252706	−0.109998
16	C	−2.190753	1.814561	0.592723
17	C	−1.115960	0.928776	0.284669
18	C	1.115447	−0.927715	−0.284326
19	C	−0.378250	0.352139	1.347757
20	C	0.377749	−0.351062	−1.347416
21	C	−5.999870	1.039209	0.967413
22	C	0.694634	−0.632854	−2.673390
23	C	5.999658	−1.039758	−0.967507
24	C	−1.744352	1.508401	2.959582
25	C	1.743695	−1.507511	−2.959235
26	C	5.728261	−0.645673	1.409270
27	C	2.478322	−2.099060	−1.942247
28	C	−2.479001	2.099922	1.942592
29	C	6.730230	0.140836	−1.065792
30	C	−6.462358	−0.533667	−1.288991
31	C	−6.97624	−0.957215	−0.053346
32	C	−0.695196	0.633859	2.673733
33	C	−5.727901	0.645435	−1.409351
34	C	6.977114	0.956296	0.052936
35	C	6.463245	0.533077	1.288699
36	C	−6.729917	−0.141728	1.065485
37	C	−5.49607	1.424666	−0.276393
38	C	−7.788564	−2.253997	0.109354
39	C	7.963606	3.007744	1.22148

48	H	−1.984406	1.744868	3.992485
49	H	1.983694	−1.744042	−3.992135
50	H	5.353147	−0.96445	2.376504
51	H	3.265733	−2.805921	−2.170353
52	H	−3.266507	2.80668	2.170693
53	H	7.120463	0.425245	−2.038342
54	H	−6.635138	−1.121641	−2.182799
55	H	−0.111208	0.169681	3.459413
56	H	−5.352775	0.964456	−2.376499
57	H	6.636444	1.121041	2.182432
58	H	−7.120187	−0.426387	2.037947
59	H	8.546405	3.919673	1.0522
60	H	7.001209	3.307641	1.651406
61	H	8.500613	2.407817	1.964961
62	H	−6.951582	−2.729917	2.092981
63	H	−7.628194	−4.119562	1.23222
64	H	−6.06048	−3.448641	0.742715
65	H	7.630282	4.118237	−1.233012
66	H	6.953014	2.728795	−2.093587
67	H	6.062338	3.448006	−0.743301
68	H	9.78602	2.826802	−0.781396
69	H	9.736262	1.250146	0.030388
70	H	9.148145	1.412656	−1.631409
71	H	−8.544127	−3.921174	−1.053097
72	H	−8.498888	−2.409205	−1.965699
73	H	−6.999131	−3.308413	−1.652069
74	H	−9.14725	−1.414697	1.630708
75	H	−9.735252	−1.252256	−0.031135
76	H	−9.784426	−2.82902	0.780478
77	H	−2.585211	2.144947	−1.378019
78	H	2.584704	−2.143812	1.378388

d. Optimized structure of **4**

E(RB3LYP) = -2673.24185913 a.u.

Number of imaginary frequency: 0



Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
1	S	2.706436	3.774376	2.786221
2	S	−2.703416	3.774135	−2.788940
3	O	1.526499	0.003866	2.227805
4	O	−3.259145	3.239571	−4.029371
5	O	3.260575	3.240511	4.027659
6	O	2.031948	5.072554	2.731493
7	O	−2.027897	5.071855	−2.736033
8	N	1.605498	2.566055	2.313956
9	N	−1.602896	2.565413	−2.316649
10	C	0.418172	1.285603	0.580736
11	C	−3.987595	3.773413	−1.540689
12	C	−0.416818	1.285427	−0.582142
13	C	3.991874	3.771531	1.539261
14	C	0.829352	0.003759	1.183475
15	C	−0.822612	2.518688	−1.163335
16	C	0.390703	3.722247	0.563459
17	C	0.825391	2.519065	1.160556
18	C	−0.386262	3.722038	−0.567799
19	C	−4.970618	2.779670	−1.574270
20	C	4.974364	2.777346	1.575064
21	C	6.011679	3.741217	−0.418319
22	C	−6.005384	3.746469	0.419026
23	C	−4.004184	4.754935	−0.552904
24	C	7.132807	3.691417	−1.471191
25	C	−5.009220	4.732386	0.416523
26	C	−7.125453	3.698396	1.473116
27	C	4.009973	4.751856	0.550315
28	C	5.015999	4.727626	−0.418039

Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
67	S	−2.707041	−3.768188	−2.785029
68	S	2.703961	−3.76788	2.787625
69	O	−1.526814	0.003188	−2.227691
70	O	3.263102	−3.231889	4.025917
71	O	−3.264703	−3.232857	−4.024269
72	O	−2.030239	−5.065331	−2.734273
73	O	2.026298	−5.064641	2.738568
74	N	−1.607234	−2.558884	−2.312798
75	N	1.604453	−2.558271	2.315411
76	C	−0.418492	−1.278431	−0.5806
77	C	3.985391	−3.771661	1.536576
78	C	0.416921	−1.278258	0.58196
79	C	−3.98968	−3.770078	−1.53521
80	C	−0.829532	0.003384	−1.183446
81	C	0.823195	−2.511509	1.162819
82	C	−0.391032	−3.71506	−0.563342
83	C	−0.826091	−2.511879	−1.160171
84	C	0.386654	−3.714855	0.567412
85	C	4.968898	−2.778213	1.564682
86	C	−4.972808	−2.776323	−1.565472
87	C	−6.005296	−3.747632	0.426817
88	C	5.999103	−3.752285	−0.427444
89	C	3.999569	−4.756587	0.552152
90	C	−7.124195	−3.701882	1.482252
91	C	5.002582	−4.737801	−0.419458
92	C	7.11701	−3.708119	−1.484007
93	C	−4.00516	−4.753818	−0.549623
94	C	−5.009111	−4.733503	0.420983

29	C	5.966761	2.771963	0.602505
30	C	−5.962000	2.775958	−0.600673
31	C	8.504985	3.808253	−0.764802
32	C	7.022869	4.832326	−2.499854
33	C	−8.498318	3.814905	0.768009
34	C	7.05859	2.34591	−2.232574
35	C	−7.050968	2.353797	2.236076
36	C	−7.014028	4.84051	2.500273
37	H	0.673927	4.662354	1.019337
38	H	−0.66826	4.661925	−1.024899
39	H	−4.966884	2.035622	−2.364442
40	H	4.969461	2.034271	2.366147
41	H	−3.255608	5.539338	−0.554066
42	H	−5.006502	5.507684	1.173537
43	H	3.261797	5.536639	0.549795
44	H	5.014469	5.502016	−1.175986
45	H	6.728392	1.999337	0.646057
46	H	−6.724042	2.003644	−0.642458
47	H	8.671447	2.99407	−0.051854
48	H	9.31365	3.773091	−1.504428
49	H	8.586258	4.754109	−0.21767
50	H	6.080879	4.790691	−3.058179
51	H	7.100265	5.81797	−2.027286
52	H	7.839036	4.751492	−3.225971
53	H	−8.665842	2.999928	0.056218
54	H	−9.306226	3.78094	1.508519
55	H	−8.579802	4.760133	0.219825
56	H	7.175582	1.488299	−1.561362
57	H	6.098436	2.238441	−2.749588
58	H	7.856276	2.292277	−2.982817
59	H	−7.168978	1.495393	1.566064
60	H	−6.090326	2.246605	2.752243
61	H	−7.847908	2.301406	2.9872
62	H	−6.071504	4.799168	3.057714
63	H	−7.091503	5.825606	2.026576

95	C	−5.963087	−2.774833	−0.590759
96	C	5.958221	−2.778246	0.589003
97	C	−8.49784	−3.816805	0.77841
98	C	−7.011674	−4.846277	2.506747
99	C	8.491296	−3.822596	−0.781344
100	C	−7.04882	−2.35899	2.248122
101	C	7.041283	−2.366129	−2.251423
102	C	7.0032	−4.8537	−2.507027
103	H	−0.674368	−4.655186	−1.019111
104	H	0.668893	−4.654771	1.024304
105	H	4.967095	−2.031404	2.352252
106	H	−4.969996	−2.030482	−2.353956
107	H	3.25069	−5.540684	0.557549
108	H	4.997937	−5.515694	−1.173791
109	H	−3.256571	−5.5382	−0.553382
110	H	−5.005492	−5.510497	1.17625
111	H	−6.725188	−2.002446	−0.629913
112	H	6.720616	−2.006069	0.626446
113	H	−8.666176	−3.00023	0.068644
114	H	−9.304919	−3.784507	1.5199
115	H	−8.579934	−4.760803	0.228198
116	H	−6.068553	−4.806178	3.063266
117	H	−7.089686	−5.830317	2.03095
118	H	−7.826377	−4.768207	3.234797
119	H	8.660551	−3.005224	−0.072713
120	H	9.297673	−3.79141	−1.523644
121	H	8.573648	−4.765961	−0.230087
122	H	−7.16757	−1.499067	1.580195
123	H	−6.087601	−2.252982	2.763456
124	H	−7.844919	−2.308272	3.00025
125	H	7.160891	−1.50542	−1.584666
126	H	6.079613	−2.260487	−2.76599
127	H	7.836696	−2.316545	−3.004351
128	H	6.059565	−4.814004	−3.0627
129	H	7.081407	−5.837191	−2.030132

64	H	−7.829511	4.760868	3.227285	130	H	7.817237	−4.776694	−3.235933
65	H	1.848331	1.645056	2.68943	131	H	−1.850428	−1.638039	−2.688375
66	H	−1.846793	1.644314	−2.691156	132	H	1.848555	−1.637339	2.690144

11. References

S1. M. Yamashita, Y. Yamamoto, K. Akiba, D. Hashizume, F. Iwasaki, N. Takagi, S. Nagase *J. Am. Chem. Soc.* 2005, **127**, 4354-4371.

S2. A. T. Peters, D. Walker *J. Chem. Soc.* 1957, 1525.

S3. G. M. Sheldrick *Acta Crystallogr.* 2008, **64A**, 112-122.