Synthesis, Spectroscopic, SC-XRD/DFT and Non-Linear Optical (NLO) Properties of Chromene Derivatives

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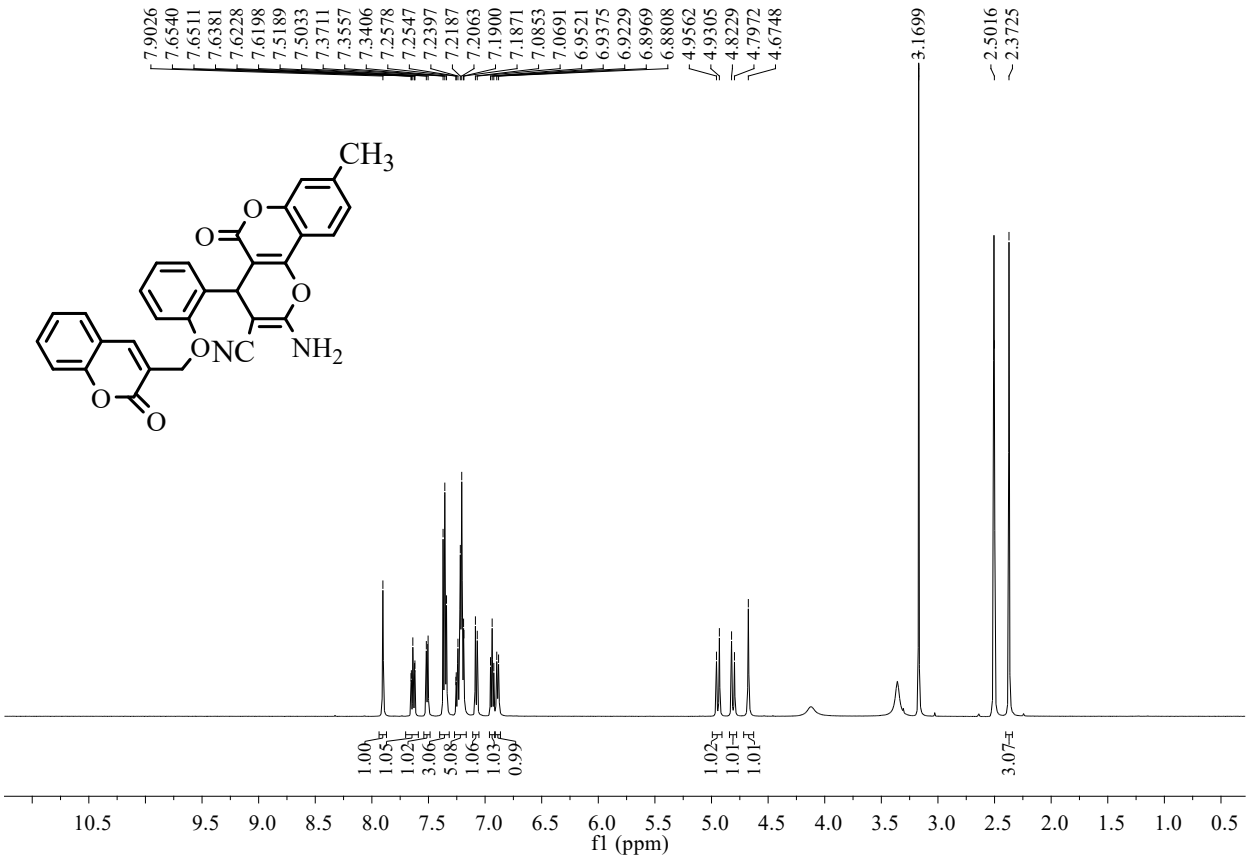


Figure S1: ^{1}H NMR spectrum of compound **4a**

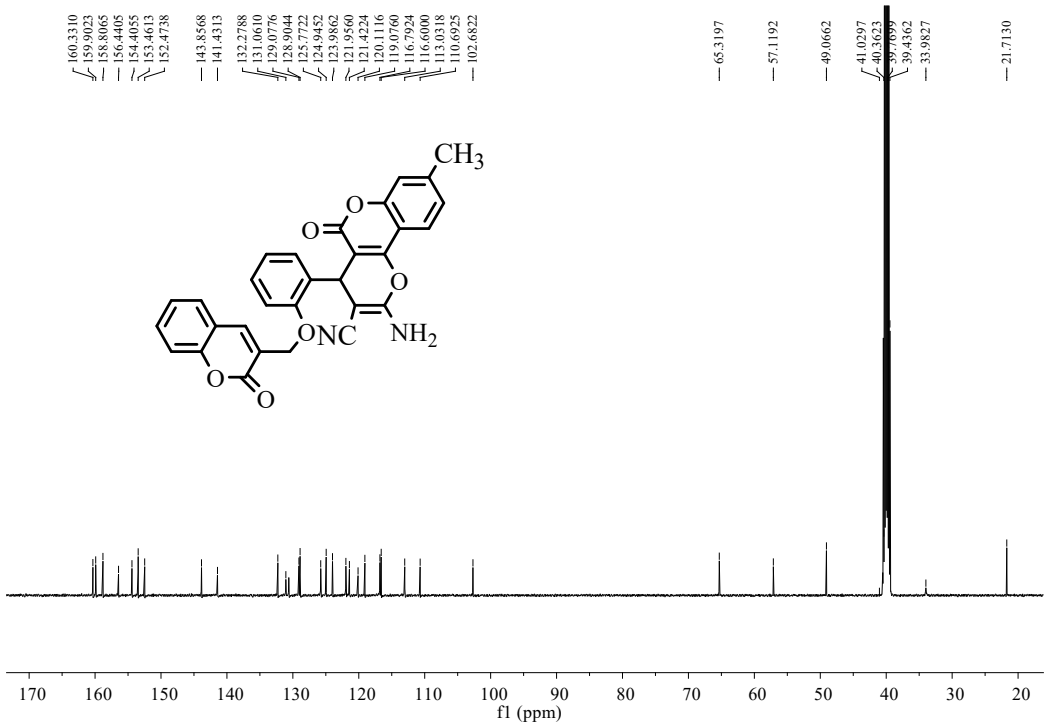


Figure S2: ^{13}C NMR spectrum of compound **4a**

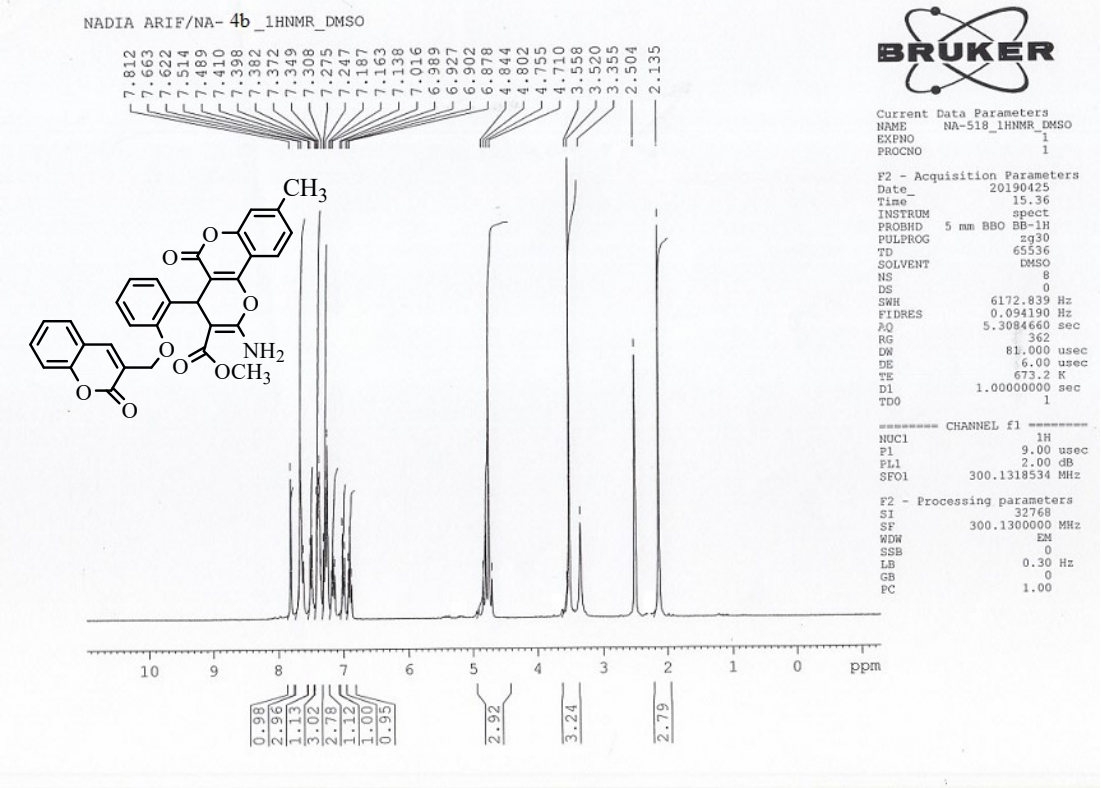


Figure S3: [1]H NMR spectrum of compound **4b**

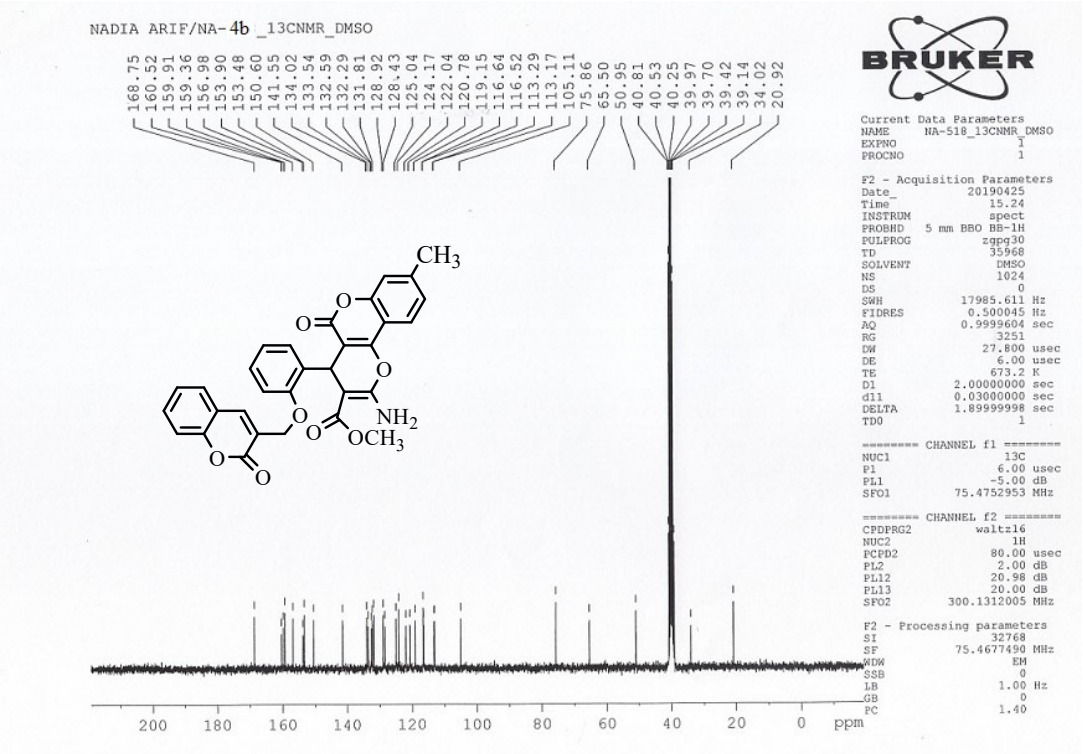


Figure S4: [13]C NMR spectrum of compound **4b**

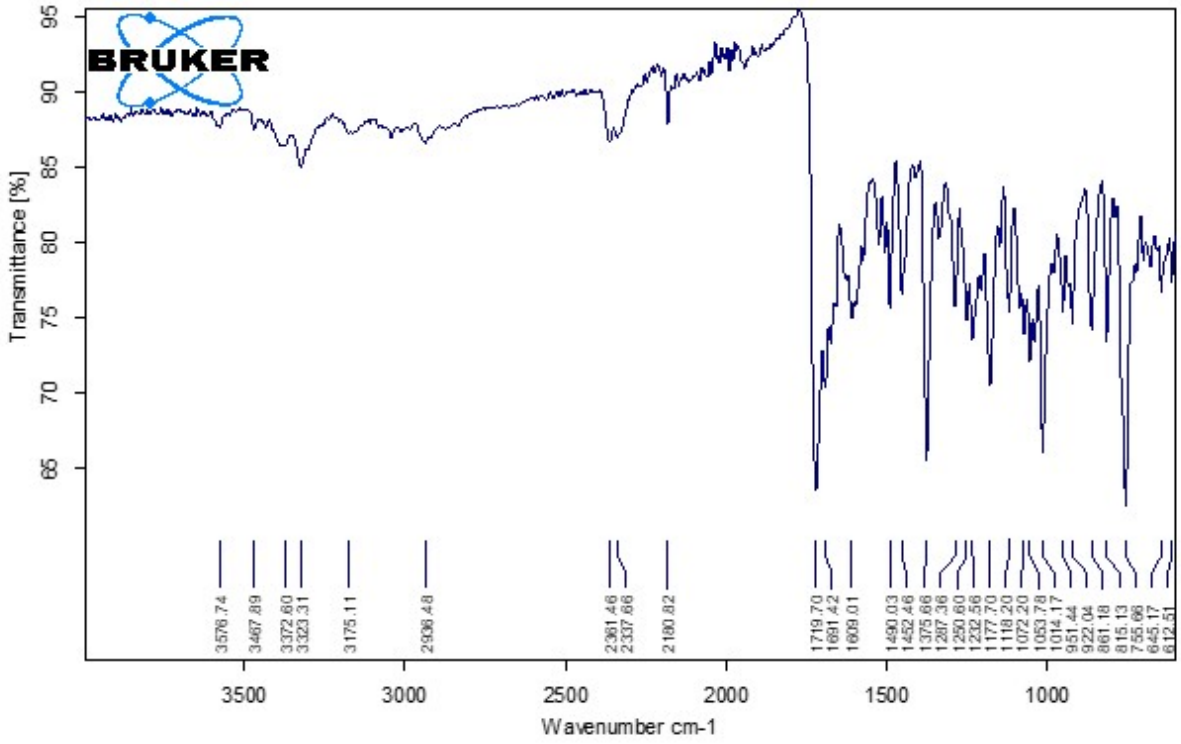


Figure S5: IR spectrum of **4a** compound

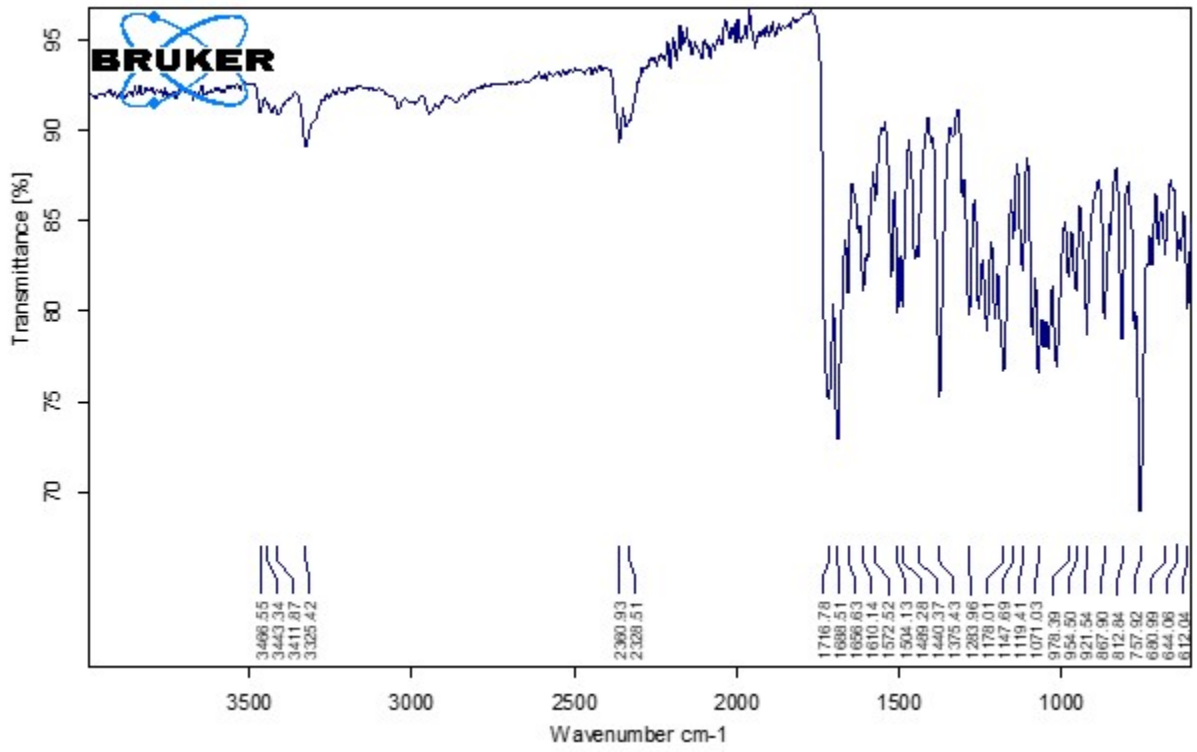


Figure S6: IR spectrum of **4b** compound

Table S1: Comparison of selected bond lengths (Å) and angles (°) of **4a**

Bond Lengths			Bond Angles		
	DFT	**XRD**		**DFT**	**XRD**
O1-C10	1.355	1.366(3)	C10-O1-C15	118.3	118.5
O1-C15	1.366	1.368(3)	O1-C10-C11	123.7	123.2
N2-C15	1.342	1.344(3)	O1-C10-C12	114.1	113.4
O3-C20	1.368	1.373(3)	O1-C15-N2	110.4	109.8
O3-C22	1.364	1.375(3)	O1-C15-C14	121.9	122.1
O4-C9	1.369	1.372(3)	N2-C15-C14	127.6	128
O4-C31	1.415	1.431(3)	C20-O3-C22	122.8	122.6
O5-C17	1.36	1.381(3)	O3-C20-O7	117.6	116.4
O5-C18	1.385	1.387(3)	O3-C20-C26	117.6	117.8
O6-C18	1.202	1.202(3)	O3-C22-C29	120.9	120.1
O7-C20	1.211	1.204(3)	O3-C22-C35	117.3	117.5
C8-C9	1.403	1.395(3)	C9-O4-C31	117.2	118.3
C8-C16	1.521	1.527(3)	O4-C9-C8	116	115
C8-C24	1.389	1.385(3)	O4-C9-C21	123.2	124
C9-C21	1.393	1.387(3)	O4-C31-C26	108.8	106.2
C10-C11	1.347	1.34(3)	C17-O5-C18	122.6	121.9
C10-C12	1.444	1.436(3)	O5-C17-C12	121.7	120.9
C11-C16	1.507	1.5(3)	O5-C17-C27	117.6	117.7
C11-C18	1.459	1.45(3)	O5-C18-O6	117.9	116.6
C12-C13	1.4	1.392(3)	O5-C18-C11	117.2	118.1
C12-C17	1.398	1.39(3)	O6-C18-C11	124.9	125.3
C13-C28	1.386	1.375(3)	O7-C20-C26	124.8	125.9
C14-C15	1.361	1.347(3)	C9-C8-C16	121	121.8
C14-C16	1.516	1.523(3)	C9-C8-C24	118.4	117.7
C14-C25	1.418	1.41(3)	C8-C9-C21	120.7	120.9
C17-C27	1.392	1.376(3)	C16-C8-C24	120.5	120.4
C19-C25	1.162	1.149(3)	C8-C16-C11	113.6	114
C20-C26	1.464	1.444(3)	C8-C16-C14	111.8	111.7
C21-C23	1.394	1.375(3)	C8-C24-C32	121.5	121.6
C22-C29	1.399	1.395(3)	C9-C21-C23	119.6	119.2
C22-C35	1.391	1.371(3)	C11-C10-C12	122.3	123.4
C23-C32	1.388	1.36(3)	C10-C11-C16	122.4	123.2
C24-C32	1.394	1.391(3)	C10-C11-C18	119.6	118.6
C26-C30	1.349	1.338(3)	C10-C12-C13	124	125.1
C26-C31	1.501	1.496(3)	C10-C12-C17	116.5	116.8
C27-C33	1.392	1.379(3)	C16-C11-C18	118	118.2
C28-C33	1.403	1.396(3)	C11-C16-C14	108.2	108.2
C29-C30	1.442	1.43(3)	C13-C12-C17	119.5	118.1
C29-C34	1.402	1.398(3)	C12-C13-C28	119.5	120.3
C33-C36	1.506	1.505(3)	C12-C17-C27	120.8	121.5

C34-C38	1.384	1.374(3)	C13-C28-C33	121.1	121.1
C35-C37	1.387	1.359(3)	C15-C14-C16)	122.6	123.2
C37-C38	1.401	1.378(3)	C15-C14-C25	117.2	117.9
O39-C40	1.412	1.328(3)	C16-C14-C25	120	118.9

Table S1 Continue: Comparison of selected bond lengths (Å) and angles (°) of **4a**

Bond Angles		
	DFT	**XRD**
C14-C25-N19	177.9	178.7
C17-C27-C33	119.9	120.4
C20-C26-C30	119.6	119.9
C20-C26-C31	116.9	115.9
C21-C23-C32	120.4	121.5
C29-C22-C35	121.8	122.4
C22-C29-C30	117.5	117.7
C22-C29-C34	118.5	117.5
C22-C35-C37	118.6	118.9
C23-C32-C24	119.4	118.9
C30-C26-C31	123.5	124.2
C26-C30-C29	121.3	121.9
C27-C33-C28	119.2	118.5
C27-C33-C36	120.3	121.2
C28-C33-C36	120.5	120.3
C30-C29-C34	124	124.8
C29-C34-C38	120.4	119.7
C34-C38-C37	119.9	120.9
C35-C37-C38	120.8	120.6

Table S2: Comparison of selected bond lengths (Å) and angles (°) of **4b**

Bond Lengths			**Bond Angles**		
	DFT	**XRD**		**DFT**	**XRD**
O1-C10	1.381	1.381(3)	C10-O1-C32	114.7	118.6(2)
O1-C32	1.418	1.421(3)	O1-C10-C30	120	123.3(2)
O2-C15	1.361	1.364(3)	O1-C10-C35	118.9	115.6(2)
O2-C16	1.364	1.377(3)	O1-C32-C18	107.9	107.1(2)
O3-C19	1.374	1.376(3)	C15-O2-C16	118.8	118.7(2)
O3-C27	1.362	1.378(3)	O2-C15-C11	123.2	123.6(2)
O4-C22	1.361	1.376(3)	O2-C15-C14	114.5	113.5(2)
O4-C24	1.38	1.387(3)	O2-C16-N9	109.6	109.4(2)
O5-C26	1.345	1.338(3)	O2-C16-C13	123	122.1(2)
O5-C40	1.425	1.436(3)	C19-O3-C27	122.3	122.1(2)
O6-C24	1.202	1.215(3)	O3-C19-O7	118.4	116.5(2)
O7-C19	1.205	1.202(3)	O3-C19-C18	117	117.7(2)

O8-C26	1.224	1.222(3)	O3-C27-C21	121.3	120.6(2)
N9-C16	1.355	1.336(3)	O3-C27-C37	117.3	116.8(2)
C10-C30	1.393	1.385(3)	C22-O4-C24	122.6	121.3(2)
C10-C35	1.399	1.393(3)	O4-C22-C14	121.6	121.2(2)
C11-C12	1.505	1.512(3)	O4-C22-C25	117.4	117.4(2)
C11-C15	1.346	1.339(3)	O4-C24-O6	118.3	115.8(2)
C11-C24	1.462	1.439(3)	O4-C24-C11	117.1	118.5(2)
C12-C13	1.515	1.513(3)	C26-O5-C40	115.1	117.6(2)
C12-C35	1.526	1.534(3)	O5-C26-O8	121.6	121.7(2)
C13-C16	1.361	1.356(3)	O5-C26-C13	111.9	112.1(2)
C13-C26	1.455	1.449(3)	O6-C24-C11	124.6	125.7(2)
C14-C15	1.443	1.436(3)	O7-C19-C18	124.6	125.8(2)
C14-C20	1.402	1.391(3)	O8-C26-C13	126.5	126.2(2)
C14-C22	1.398	1.38(3)	N9-C16-C13	127.5	128.5(2)
C17-C28	1.39	1.38(3)	C30-C10-C35	121.1	121.1(2)
C17-C35	1.395	1.387(3)	C10-C30-C33	119.8	119.5(2)
C18-C19	1.47	1.452(3)	C10-C35-C12	121.6	122.8(2)
C18-C23	1.345	1.336(3)	C10-C35-C17	118	117.7(2)
C18-C32	1.499	1.493(3)	C12-C11-C15	122.8	121.9(2)
C20-C31	1.381	1.374(3)	C12-C11-C24	117.6	119.2(2)
C21-C23	1.444	1.43(3)	C11-C12-C13	109.3	109.5(2)
C21-C27	1.4	1.383(3)	C11-C12-C35	110.7	111.9(2)
C21-C34	1.402	1.398(3)	C15-C11-C24	119.5	118.7(2)
C22-C25	1.392	1.391(3)	C11-C15-C14	122.2	122.9(2)
C25-C29	1.389	1.381(3)	C13-C12-C35	112.5	112.9(2)
C27-C37	1.393	1.383(3)	C12-C13-C16	121.8	122.3(2)
C28-C33	1.393	1.372(3)	C12-C13-C26	120.1	120.2(2)
C29-C31	1.406	1.393(3)	C12-C35-C17	120.4	119.5(2)
C29-C36	1.504	1.501(3)	C16-C13-C26	118.1	117.5(2)
C30-C33	1.39	1.383(3)	C15-C14-C20	124.4	124.3(2)
C34-C38	1.385	1.363(3)	C15-C14-C22	116.4	116.9(2)
C37-C39	1.387	1.374(3)	C20-C14-C22	119	118.7(2)
C38-C39	1.4	1.377(3)	C14-C20-C31	119.9	120.3(2)

Table S2 Continue: Comparison of selected bond lengths (Å) and angles (°) of **4b**

Bond Angles		
	DFT	**XRD**
C28-C17-C35	121.4	121.7(2)
C17-C28-C33	119.8	119.4(3)
C19-C18-C23	120.8	119.5(3)
C19-C18-C32	115.4	117.9(3)
C23-C18-C32	123.7	122.5(3)
C18-C23-C21	120.3	122.3(3)

C20-C31-C29	120.9	120.8(3)
C23-C21-C27	117.9	117.6(3)
C23-C21-C34	123.5	124.4(3)
C27-C21-C34	118.6	118(3)
C21-C27-C37	121.4	122.6(3)
C21-C34-C38	120.5	120.4(3)
C22-C25-C29	119.9	119.4(3)
C25-C29-C31	119.2	119.3(3)
C25-C29-C36	120.5	120.8(3)
C27-C37-C39	118.9	117.2(3)
C28-C33-C30	119.8	120.5(3)
C31-C29-C36	120.2	119.9(3)
C34-C38-C39	119.8	119.8(3)
C37-C39-C38	120.7	122(3)

Table S3: Selected Torsion angles (°) of entitled compounds

4a	EXP	**4b**	EXP
O6-C19-C18-C17	1.4(3)	O6-C21-C20-C19	179.7(3)
O6-C19-C18-C23	-179.5(3)	O6-C21-C16-C11	-3.1(3)
O6-C19-C25-C29	4.0(3)	O6-C21-C16-C17	179.4(3)
O6-C19-C25-C24	-175.2(2)	O6-C22-C23-C27	-107.0(3)
O6-C20-C21-C17	-5.2(3)	O6-C22-C23-C24	69.2(3)
O6-C20-C21-C22	177.4(3)	O3-C8-C9-C11	-5.4(3)
N1-C20-C21-C17	178.0(3)	O3-C8-C9-C10	177.9(3)
N1-C20-C21-C22	0.6(4)	O3-C8-C5-C4	4.9(3)
O1-C9-C8-C7	-1.4(3)	O3-C8-C5-C6	-176.8(2)
O1-C9-C8-C10	178.8(2)	O3-C13-C12-C11	4.1(3)
O1-C1-C6-C7	-2.1(3)	O3-C13-C12-C14	-177.9(3)
O1-C1-C6-C5	179.8(3)	O8-C27-C23-C24	4.7(3)
O1-C1-C2-C3	179.9(3)	O8-C27-C23-C22	-179.0(3)
O3-C11-C16-C17	5.0(3)	O8-C26-C25-C24	0.2(3)
O3-C11-C16-C15	-177.7(2)	O8-C26-C25-C31	-179.3(3)
O3-C11-C12-C13	178.4(3)	O8-C26-C28-C29	179.5(3)
O3-C10-C8-C9	-76.1(3)	O1-C6-C5-C8	0.4(3)
O3-C10-C8-C7	104.2(3)	O1-C6-C5-C4	178.7(3)
O4-C24-C25-C19	-4.9(3)	O1-C6-C7-C2	-178.5(3)
O4-C24-C25-C29	175.9(3)	O1-C10-C9-C11	-178.7(2)
O4-C24-C26-C27	-176.6(3)	O1-C10-C9-C8	-1.9(3)
O4-C23-C18-C19	-6.0(3)	O5-C14-C12-C11	-5.3(3)
O4-C23-C18-C17	173.2(2)	O5-C14-C12-C13	176.7(2)
O5-C23-C18-C19	174.7(3)	O2-C10-C9-C11	2.8(4)
O5-C23-C18-C17	-6.1(4)	O2-C10-C9-C8	179.6(3)

O2-C9-C8-C7	177.5(3)	O7-C27-C23-C24	-176.8(3)
O2-C9-C8-C10	-2.3(3)	O7-C27-C23-C22	-0.5(4)
C16-C11-C12-C13	-1.2(3)	O4-C14-C12-C11	173.8(3)
C16-C17-C18-C19	114.0(2)	O4-C14-C12-C13	-4.2(4)
C16-C17-C18-C23	-65.2(3)	N1-C13-C12-C11	-175.3(3)
C16-C17-C21-C20	-113.4(2)	N1-C13-C12-C14	2.7(4)
C16-C17-C21-C22	63.9(3)	C21-C20-C19-C18	0.6(4)
C16-C15-C14-C13	-0.5(4)	C21-C16-C11-C9	57.5(3)
C11-C12-C13-C14	-0.4(4)	C21-C16-C11-C12	-66.5(3)
C19-C18-C17-C21	-11.0(3)	C21-C16-C17-C18	1.0(3)
C19-C25-C29-C28	-177.4(3)	C9-C11-C12-C13	-13.5(3)
C19-C25-C24-C26	75.7(2)	C9-C11-C12-C14	168.5(2)
C18-C17-C21-C20	12.9(3)	C9-C11-C16-C17	-125.0(2)
C18-C17-C21-C22	-169.8(2)	C9-C8-C5-C4	-173.0(3)
C25-C29-C28-C27	0.7(3)	C9-C8-C5-C6	5.3(3)
C25-C24-C26-C27	2.8(3)	C11-C16-C17-C18	-176.6(3)
C29-C28-C27-C26	-1.5(3)	C5-C4-C3-C2	1.4(3)
C29-C28-C27-C30	177.8(3)	C5-C6-C7-C2	0.9(4)
C24-C26-C27-C28	-0.2(3)	C17-C18-C19-C20	-0.9(4)
C24-C26-C27-C30	-179.5(3)	C23-C24-C25-C26	-1.6(3)
C9-C8-C7-C6	1.1(3)	C23-C24-C25-C31	177.9(3)
C12-C13-C14-C15	1.3(4)	C4-C3-C2-C7	-1.1(4)
C1-C6-C7-C8	0.6(3)	C4-C3-C2-C1	178.1(3)
C1-C6-C5-C4	0.1(3)	C25-C26-C28-C29	0.1(4)
C1-C2-C3-C4	0.5(4)	C25-C31-C30-C29	1.1(4)
C8-C7-C6-C5	178.5(3)	C6-C7-C2-C3	-0.0(4)
C6-C5-C4-C3	0.1(4)	C6-C7-C2-C1	-179.2(3)
C5-C4-C3-C2	-0.4(4)	C26-C28-C29-C30	0.3(4)
		C31-C30-C29-C28	-0.9(5)

Table S4: The results of these parameters, including electron affinity (*EA*), ionization potential (*I*), global hardness (η), global electrophilicity (ω), electronegativity (*X*), chemical potential (μ) and global softness (σ), are estimated with the help of Equations and their outcomes are tabulated

$$IP = -E_{HOMO} \quad (5)$$

$$EA = -E_{LUMO} \quad (6)$$

$$X = -\frac{[E_{LUMO} + E_{HOMO}]}{2} \quad (7)$$

$$\eta = -\frac{[E_{LUMO} - E_{HOMO}]}{2} \quad (8)$$

$$\mu = \frac{E_{HOMO} + E_{LUMO}}{2} \quad (9)$$

$$\sigma = \frac{1}{2\eta} \quad (10)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (11)$$

Table S5: Natural bond orbital (NBO) analysis of investigated compound **4a**

Comp.	Donor(*i*)	Type	Acceptor(*j*)	Type	$E^{(2)a}$ [*kcal/mol*]	$E(j) - E(i)^b$ (*a.u.*)
C27-C33	π	C12-C17	π*	34.85	0.34	0.1
C35-C37	π	C22-C29	π*	32.24	0.35	0.097
C9-C21	π	C23-C32	π*	30.54	0.37	0.095
C8-C24	π	C9-C21	π*	29.64	0.35	0.092
C12-C17	π	C13-C28	π*	27.03	0.38	0.092
C22-C29	π	C34-C38	π*	25.91	0.38	0.09
C34-C38	π	C22-C29	π*	24.89	0.34	0.085
C35-C37	π	C34-C38	π*	23.43	0.37	0.084
C27-C33	π	C13-C28	π*	22.89	0.36	0.082
C12-C17	π	C10-C11	π*	21.52	0.38	0.084
C22-C29	π	C26-C30	π*	19.31	0.38	0.082
C26-C30	π	C22-C29	π*	12.31	0.38	0.065
C10-C11	π	C12-C17	π*	11.28	0.39	0.063
C14-C15	π	C14-C15	π*	7.52	0.39	0.051
O6-C18	π	C10-C11	π*	5.04	0.53	0.049
O7-C20	π	C26-C30	π*	4.8	0.54	0.047
C10-C11	π	C10-C11	π*	2.1	0.41	0.027
C12-C17	π	C12-C17	π*	1.21	0.35	0.019
C14-C15	π	C8-C24	π*	0.72	0.41	0.016
C8-C24	π	C14-C15	π*	0.56	0.34	0.013
C11-C18	σ	O1-C10	σ*	6.8	1.2	0.081
C14-C25	σ	O1-C15	σ*	6.51	1.21	0.079
C21-C23	σ	O4-C9	σ*	5.63	1.21	0.074
C27-H39	σ	C12-C17	σ*	5.11	1.21	0.07
C21-H45	σ	C8-C9	σ*	4.92	1.22	0.069

C8-C24	σ	C8-C9	σ*	4.08	1.4	0.068
C36-H58	σ	C27-C33	σ*	3.98	1.21	0.062
C12-C17	σ	O1-C10	σ*	3.87	1.22	0.061
C26-C31	σ	O3-C20	σ*	3.74	1.13	0.059
C21-C23	σ	C9-C21	σ*	3.51	1.4	0.063
C26-C30	σ	C26-C31	σ*	3.38	1.32	0.06
C9-C21	σ	C8-C16	σ*	3.3	1.26	0.058
C10-C12	σ	O1-C15	σ*	3.28	1.19	0.056
C29-C30	σ	C22-C29	σ*	2.94	1.37	0.057
N2-C15	σ	C14-C16	σ*	2.38	1.41	0.052
O1-C15	σ	N2-H51	σ*	2.07	1.59	0.051
O1-C10	σ	C11-C18	σ*	1.92	1.55	0.049
O5-C17	σ	C12-C13	σ*	1.69	1.66	0.047
C27-H39	σ	C17-C27	σ*	1.06	1.22	0.032
O7-C20	σ	C26-C30	σ*	0.98	1.9	0.039
C31-H55	σ	C26-C31	σ*	0.65	1.07	0.024
C26-C31	σ	C31-H54	σ*	0.51	1.23	0.022
N2	LP(1)	C14-C15	π*	77.62	0.36	0.153
O3	LP(2)	O7-C20	π*	52.97	0.45	0.139
O5	LP(2)	O6-C18	π*	46.77	0.45	0.132
O6	LP(2)	O5-C18	σ*	45.47	0.72	0.164
O7	LP(2)	O3-C20	σ*	38.74	0.76	0.155
O3	LP(2)	C22-C29	π*	34.3	0.46	0.117
O4	LP(2)	C9-C21	π*	30.42	0.45	0.112
O7	LP(2)	C20-C26	σ*	20.85	0.85	0.122
N19	LP(1)	C14-C25	σ*	12.49	1.2	0.109
O5	LP(1)	C12-C17	σ*	8.17	1.24	0.09
O3	LP(1)	C22-C29	σ*	7.63	1.25	0.087
O1	LP(1)	C14-C15	σ*	6.94	1.31	0.085
O4	LP(2)	C31-H54	σ*	4.04	0.9	0.055
O6	LP(1)	C11-C18	σ*	3.36	1.3	0.06
O3	LP(1)	O7-C20	σ*	2.99	1.31	0.056
O7	LP(1)	C20-C26	σ*	1.89	1.29	0.044
O5	LP(1)	C17-C27	σ*	0.98	1.26	0.032
O4	LP(2)	C8-C9	σ*	0.71	1.02	0.025
O4	LP(2)	C26-C31	σ*	0.7	0.87	0.023
O4	LP(1)	C31-H55	σ*	0.66	1.15	0.025

LP= lone pair, (i) donor; (j) acceptor; E(2) means energy of hyper conjugative interaction (stabilization energy); E(j) – E(i) is the energy difference between donor and acceptor i and j NBO orbitals; F(i, j) is the Fock matrix element between i and j NBO orbitals.

Table S6: Natural bond orbital (NBO) analysis of investigated compound **4b**

Comp.	**Donor(*i*)**	**Type**	**Acceptor(*j*)**	**Type**	***E*$^{(2)a}$ [*kcal/mol*]**	***E*(*j*) - *E*(*i*)^{b} (*a.u.*)**

C16-C19	π	O8-C33	π*	34.95	0.37	0.106
C31-C37	π	C17-C27	π*	34.78	0.34	0.099
C54-C58	π	C26-C34	π*	31.26	0.35	0.096
C47-C56	π	C54-C58	π*	29.85	0.36	0.093
C13-C18	π	O6-C30	π*	28.79	0.39	0.098
C12-C49	π	C38-C45	π*	27.77	0.36	0.09
C38-C45	π	C20-C35	π*	26.34	0.37	0.088
C47-C56	π	C26-C34	π*	25.09	0.35	0.086
C54-C58	π	C47-C56	π*	24.25	0.37	0.085
C31-C37	π	C24-C40	π*	22.98	0.36	0.082
C17-C27	π	C31-C37	π*	20.63	0.38	0.081
C26-C34	π	C22-C28	π*	17.68	0.39	0.079
C22-C28	π	C26-C34	π*	13.09	0.38	0.067
C13-C18	π	C17-C27	π*	11.26	0.39	0.063
C16-C19	π	C16-C19	π*	7.13	0.39	0.049
O7-C23	π	C22-C28	π*	5.21	0.54	0.049
O6-C30	π	C13-C18	π*	4.95	0.53	0.048
C17-C27	π	C17-C27	π*	1.09	0.36	0.018
O6-C30	π	O6-C30	π*	0.87	0.51	0.02
O7-C23	π	O7-C23	π*	0.78	0.51	0.019
C13-C30	σ	O2-C18	σ*	6.82	1.19	0.08
N9-H11	σ	C16-C19	σ*	5.51	1.39	0.078
C20-H21	σ	C12-C49	σ*	4.87	1.22	0.069
C40-H41	σ	C31-C37	σ*	4.43	1.24	0.066
C35-H36	σ	C38-C45	σ*	4.01	1.23	0.063
C47-C56	σ	C26-C28	σ*	3.99	1.35	0.066
C20-C35	σ	C14-C49	σ*	3.92	1.23	0.062
C22-C23	σ	C22-C28	σ*	3.64	1.48	0.065
C13-C14	σ	C16-C33	σ*	3.27	1.24	0.057
C14-C49	σ	C12-C38	σ*	2.98	1.32	0.056
C34-C54	σ	C54-C58	σ*	2.65	1.44	0.055
C12-C49	σ	C20-H21	σ*	2.24	1.34	0.049
C26-C34	σ	C54-H55	σ*	1.98	1.35	0.046
C13-C14	σ	C13-C30	σ*	1.82	1.21	0.042
C24-C40	σ	C24-H25	σ*	1.74	1.34	0.043
C13-C30	σ	C14-C16	σ*	1.39	1.25	0.037
C14-H15	σ	C14-C16	σ*	1.09	1.04	0.03
O3-C34	σ	C26-C34	σ*	0.84	1.65	0.033
C13-C18	σ	O2-C18	σ*	0.67	1.27	0.026
C22-C28	σ	C42-H43	σ*	0.51	1.34	0.023
O5	LP(2)	O8-C33	π*	59.26	0.43	0.148
O3	LP(2)	O7-C23	π*	49.71	0.45	0.135
O6	LP(2)	O4-C30	σ*	45.22	0.73	0.164

O8	LP(2)	O5-C33	σ*	37.65	0.79	0.156
O4	LP(2)	C17-C27	π*	35.94	0.45	0.119
O3	LP(2)	C26-C34	π*	34.52	0.45	0.117
O6	LP(2)	C13-C30	σ*	20.83	0.84	0.121
O7	LP(2)	C22-C23	σ*	20.79	0.84	0.121
O5	LP(1)	O8-C33	σ*	8.77	1.3	0.096
O4	LP(1)	C17-C27	σ*	8.1	1.24	0.09
O1	LP(2)	C42-H43	σ*	7.96	0.95	0.079
O3	LP(1)	C22-C23	σ*	6.82	1.13	0.079
O5	LP(2)	C60-H61	σ*	5.53	0.92	0.067
O1	LP(1)	C42-H44	σ*	4.42	1.11	0.063
O8	LP(1)	N9-H10	σ*	3.88	1.35	0.065
O3	LP(1)	O7-C23	σ*	2.83	1.32	0.055
O1	LP(2)	C12-C38	σ*	1.95	1.08	0.042
O4	LP(1)	C27-C31	σ*	0.99	1.26	0.032
O5	LP(1)	C13-C14	σ*	0.61	1.13	0.023
O8	LP(1)	O5-C60	σ*	0.5	1.14	0.021

LP= lone pair, (i) donor; (j) acceptor; E(2) means energy of hyper conjugative interaction (stabilization energy); E(j) – E(i) is the energy difference between donor and acceptor i and j NBO orbitals; F(i, j) is the Fock matrix element between i and j NBO orbitals.

Table S7: Computed transition energy (*eV*), absorption wavelengths (*nm*), oscillator strengths (f_{os}) and transition natures of compounds **4a** and **4b**

Comp.	[a]λ_{max} (*nm*)	*E* (*eV*)	f_{os}	MO contributions
4a	328.923	3.769	0.0021	H→L (89%), H-1→L+1 (8%)
	306.634	4.043	0.0044	H→L+1 (83%), H-1→L+2 (8%)
	293.336	4.226	0.018	H→L+1 (89%), H-1→L+2 (6%)
	290.558	4.267	0.036	H→L+1 (81%), H-1→L+2 (5%)
	278.504	4.452	0.027	H→L+1 (18%), H-1→L+2 (47%)
	268.579	4.616	0.337	H-1→L (68%), H→L (2%)
4b	292.498	4.239	0.012	H→L (39%), H-1→L+1 (50%)
	271.300	4.570	0.124	H→L+1 (23%), H-1→L+2 (10%)
	269.513	4.600	0.374	H→L+1 (36%), H-1→L+2 (30%)
	256.951	4.825	0.015	H→L+1 (43%), H-1→L+2 (10%)
	251.494	4.929	0.039	H→L+1 (18%), H-1→L+2 (12%)
	249.134	4.976	0.007	H-1→L (31%), H→L (16%)

[a]**DFT**

Table S8: The dipole moment (*D*) and linear polarizability (*esu*) values for compounds (**4a** and **4b**)

	4a	**4b**		**4a** ×10^{-23}	**4b** ×10^{-23}
μ_{xx}	-5.874	-1.621	α_{xx}	9.678	8.990
μ_{yy}	-0.328	-2.752	α_{yy}	6.448	6.962
μ_{zz}	2.067	-0.632	α_{zz}	4.185	4.146
μ_{tot}	6.236	3.256	$\langle\alpha\rangle$	6.770	6.699

Table S9: The second hyperpolarizability (γ_{tot}) major contributing tensors for compounds (**4a** and **4b**)

γ	**4a** × 10^4	**4b** × 10^4
γ_{xx}	0.102	8.907
γ_{yy}	2.054	3.515
γ_{zz}	2.324	2.031
γ_{tot}	0.145	0.145

γ = Second hyperpolarizability (*esu*)

Table S10: Calculated vibrational frequencies of compound **4a**

[a]*Freq*	[a]I_{IR}	*Exp*	**Vibrational assignments**
3742	120		υ(as)(N-H)
3700	501		υ(N-H) + υ(C-H)
3509	495	5376	υ(s)(N-H)
3232	7	3372	υ(s) C-H_{Ben}
3222	20	3323	υ(s) + υ(as) C-H_{Ben}
3209	7		υ(s) + υ(as) C-H_{Ben}
3207	5		υ(s)C-H_{Ben}
3188	12	3175	υ(as) C-H_{Ben}
3161	10		υ(as) C-H_{CH3}
3106	62		υ(as) C-H_{CH3}
3072	21		υ(s) C-H_{CH3}
3056	22		υ(s) C-H_{CH2}
3043	77	2908	υ(s) C-H_{CH3}
2377	113	2381	υ(C-N)
1887	559		υ(C-O)
1845	588		υ(C-O)
1775	528	1719	υ(C-N) + υ (C-C) + υ (C=C-C=O_{pyr})
1724	72		υ (C=C-C=O_{pyr}) + υ(δ)(N-H)
1711	110		υ (C=C-C=C_{Ben}) + υ(δ) C-H_{Ben}
1701	28		υ (C=C-C=C_{Ben})
1665	27	1691	υ(ρ) C-H_{Ben} + υ (C=C-C=C_{Ben})
1644	182	1609	υ(δ)(N-H) + υ (C=C-C=O_{pyr})
1550	10		υ(ρ) C-H_{Ben} + υ (C=C-C=C_{Ben})
1519	22		υ(ρ) C-H_{CH2} + υ(ρ) C-H_{Ben} + υ (C=C-C=C_{Ben})
1509	55		υ(ρ) C-H_{Ben}+ υ(δ) C-H
1479	10		υ(ρ) C-H_{Ben} + υ (C=C-C=C_{Ben}) + υ(*w*) C-H_{CH3}
1444	321	1490	υ(ρ) C-H_{Ben} + υ (C=C-C=O_{pyr})
1435	49	1452	υ(*w*) C-H_{CH2} + υ(ρ) C-H_{Ben}
1422	77		υ(ρ) C-O + υ(*w*) C-H_{CH3}
1389	21		υ(ρ) C-H_{Ben} + υ (C=C-C=C_{Ben})
1385	39	1375	υ(ρ) C-H_{Ben} + υ (C=C-C=C_{Ben})
1358	25		υ(ρ) C-H_{Ben} + υ (C=C-C=O_{pyr})
1315	187		υ(ρ) C-H_{Ben}
1289	41	1260	υ(ρ) C-H_{Ben} + υ (C-C=C-O_{pyr})

1253	38		υ(ρ)N-H + υ (C-C=C-O_{pyr})
1228	81	1232	υ (ρ) C-H_{Ben} + υ(ρ) C-H_{CH2}
1192	11		υ(ρ)C-H_{Ben} + υ (C-C=C-C_{Ben}) + υ (ρ) +(δ) C-H_{CH3}
1138	89	1177	υ(ρ) C-H + υ (ρ)C-H_{CH3}
1120	118	1118	υ(ρ) C-H + υ(ρ)C-H_{CH3}+ υ (C-C=C-O_{pyr})
1089	58		υ(ρ) + (δ) C-H_{Ben} + υ (C-C=C-C_{Ben})
1059	13	1072	υ(ρ)C-H_{CH2} + γ (C-H)
994	16	951	υ (τ) C-H_{CH2} + υ(ρ) C-H_{Ben}
978	14	922	υ (τ)+ (*w*)C-H_{Ben}
892	20		υ (C=C-C=C_{Ben}) + υ (τ)C-H_{Ben}
845	10	861	υ(γ)C-H_{Ben} + υ (*w*)C-H_{Ben}
838	32	815	υ (C=C-C=C_{Ben}) υ(*w*) + (τ)C-H_{Ben}
775	71		υ(γ)N-H + υ (*w*)C-H_{Ben}
765	44	766	υ (C=C-C=C_{Ben}) + υ(γ)N-H + υ(γ)O-H
606	11	645	υ (C=C-C=C_{Ben}) + υ(γ)N-H
573	19	612	υ (C=C-C=C_{Ben}) + υ(γ)N-H + υ(γ)O-H

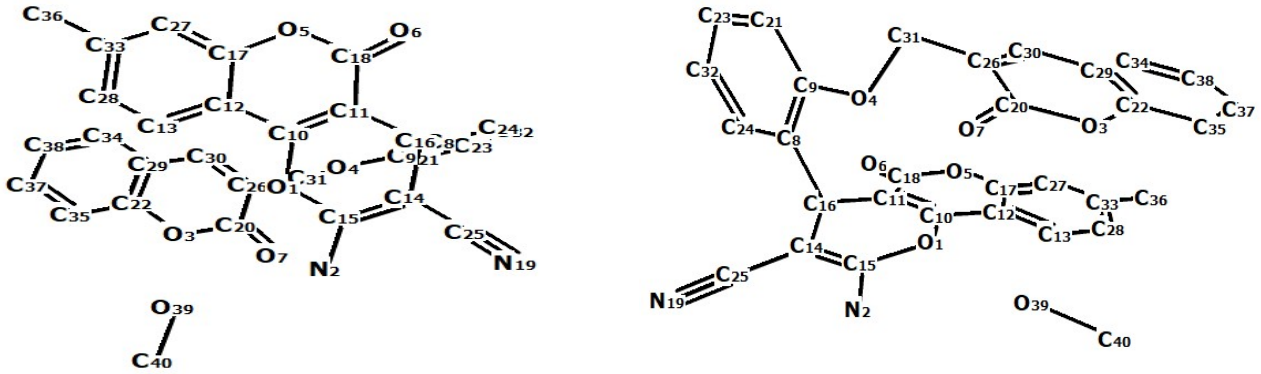
Frequencies are given in cm^{-1}, υ =stretching, β=in-plane bending, γ=out-plane bending δ=scissoring, ρ=rocking, *w*= wagging, s =symmetric, as=asymmetric,τ=twisting, Ben=benzene ring, pyr = pyran structure Exp=Experimental values

Table S11: Calculated vibrational frequencies of compound **4b**

[a]*Freq*	[a]I_{IR}	*Exp*	**Vibrational assignments**
3710	91.8		υ(N-H)
3538	135	3466	υ(N-H)
3250	4	3325	υ(s) C-H_{Ben}
3242	9		υ(s) + υ(as) C-H_{Ben}
3241	18		υ(s) C-H_{Ben}
3231	14		υ(s) + υ(as) C-H_{Ben}
3221	5		υ(as) C-H_{Ben}
3206	12		υ(s) + υ(as) C-H_{CH3}
3173	18		υ(as) C-H_{CH3}
3148	14		υ(s) + υ(as) C-H_{CH3}
3092	38		υ(s) C-H_{CH3}
3081	18		υ(as) C-H_{CH2}
3075	15		υ(s) C-H_{CH3}
3045	11		υ(s) C-H_{CH2}
1889	553		υ(C-O)
1879	474		υ(C-O)
1815	346		υ(C-O) + υ (C-C)
1769	289	1716	υ (C=C-C=O_{pyr}) + υ(C-O)
1710	241		υ (C=C-C=O_{pyr}) + υ(C-O)
1700	40		υ (C=C-C=C_{Ben})

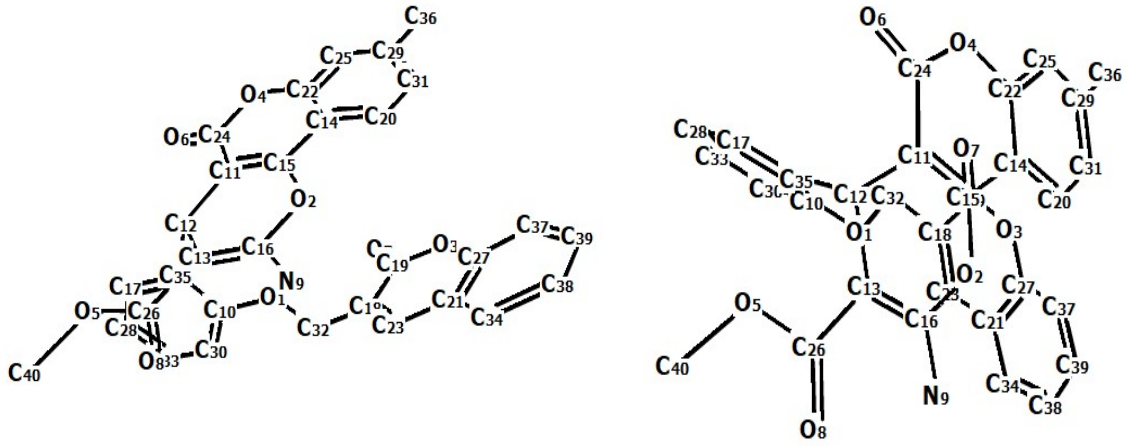
1693	10	1688	υ(ρ) + υ(δ) C-H_{Ben} + υ (C=C-C=C_{Ben})
1662	13		υ (ρ) C-H_{Ben} + υ (C=C-C=C_{Ben})
1655	12	1656	υ(ρ) C-H_{Ben} + υ (C=C-C=C_{Ben})
1592	189		υ(δ) N-H + υ (ρ) C-H_{Ben}
1568	108	1572	υ(ρ) C-H_{Ben} + υ (C=C-C=C_{Ben}) + υ(δ) N-H
1506	43		υ(ρ) C-H_{Ben} + υ (C=C-C=C_{Ben}) + υ(δ) C-H
1497	63	1489	υ(*w*) C-H_{CH3}
1450	67		υ(*w*) C-H_{CH2}
1433	303	1440	υ(δ) N-H + υ (C-C=C-O_{pyr})
1380	267	1375	υ(ρ) N-H + υ(*w*) C-H_{CH3}+ υ (C=C-C=C_{Ben})
1345	140		υ(*w*) C-H_{CH3}+ υ (C=C-C=C_{Ben}) + υ(ρ) N-H + υ(C-O)
1303	134		υ(ρ) C-H_{Ben} + υ (C=C-C=C_{Ben})
1278	34	1283	υ(ρ) N-H + υ(ρ)C-H + υ (C-C=C-O_{pyr})
1246	171		υ(ρ)N-H + υ(ρ)C-H_{Ben} + υ (C-C=C-O_{pyr})
1221	160		υ(δ)C-H_{Ben} + υ (ρ) C-H_{Ben} + υ(ρ) N-H
1197	51		υ(ρ)C-H_{Ben} + υ (C-C=C-C_{Ben}) + υ (ρ) C-H_{CH3}
1170	63	1178	υ(ρ) C-H + υ(ρ)C-H_{CH3}
1104	213	1147	υ(ρ) N-H + υ(ρ) C-H + υ (C-C=C-O_{pyr})
1075	75	1071	υ(ρ)C-H_{Ben} + υ (C-C=C-C_{Ben}) + υ (C-C=C-O_{pyr})
1042	5		υ(ρ)C-H_{CH2} + γ (C-H)
980	19	976	Y (τ) C-H_{CH2} + υ (τ)+ (*w*)C-H_{Ben}
955	21	954	υ (τ) C-H_{CH2} + υ (τ)+ (*w*)C-H_{Ben}
884	8	867	υ (C=C-C=C_{Ben}) + υ (τ)C-H_{Ben}
837	37		υ(γ)C-H_{Ben} + υ (*w*)C-H_{Ben}
832	13	812	υ (C=C-C=C_{Ben}) υ (ρ) C-H_{Ben}
791	44	757	υ (C=C-C=C_{Ben}) + υ(γ)N-H
735	13		υ(*w*) C-H_{CH3} + υ (C=C-C=C_{Ben}) + υ(γ)N-H
659	38	644	υ (C=C-C=C_{Ben}) + υ(γ)N-H
543	18		υ (C=C-C=C_{Ben}) + υ(γ)N-H

Frequencies are given in cm^{-1}, υ =stretching, β=in-plane bending, γ=out-plane bending δ=scissoring, ρ=rocking, *w*= wagging, s =symmetric, as=asymmetric,τ=twisting, Ben=benzene ring, pyr = pyran structure



XRD **DFT**

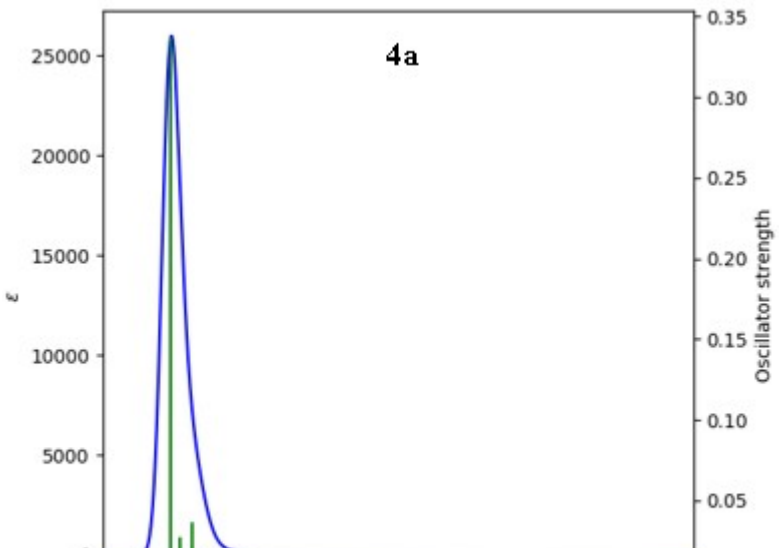
4a



XRD **DFT**

4b

Figure S7: Geometrical structures of studied compounds (**4a** and **4b**)



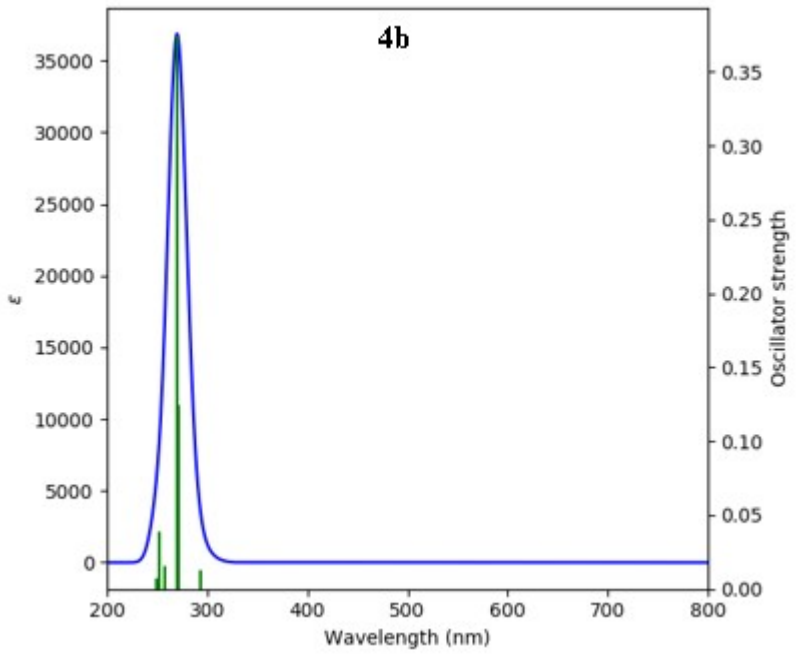
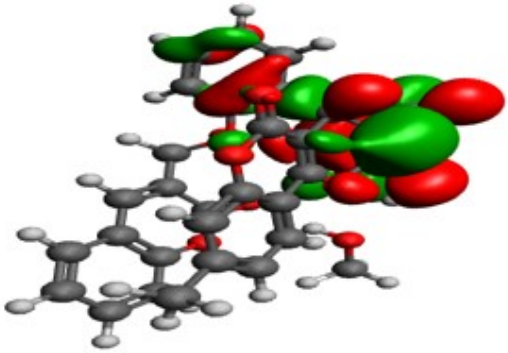
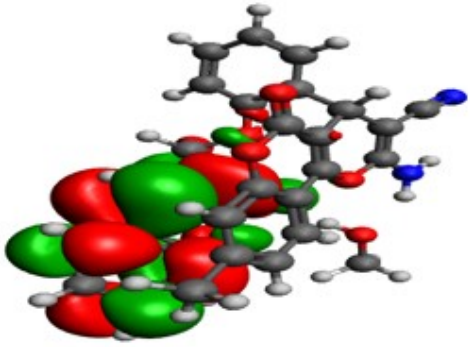


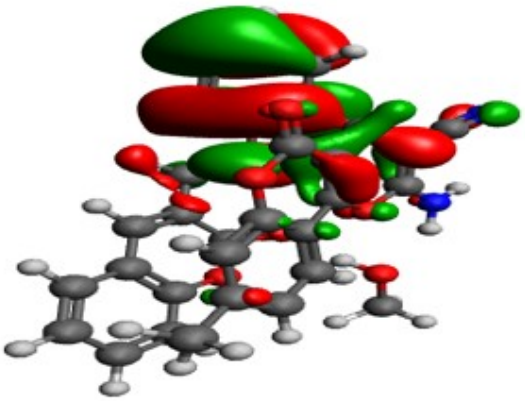
Figure S8: UV-vis graphs of **4a** and **4b**



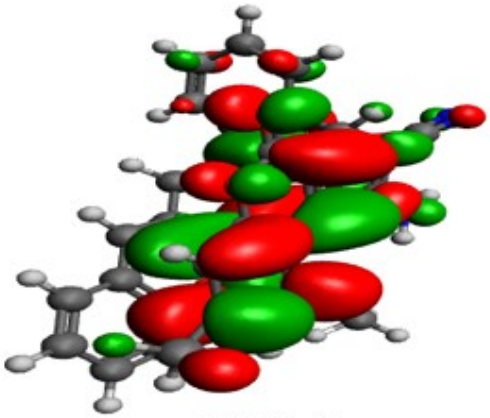
HOMO



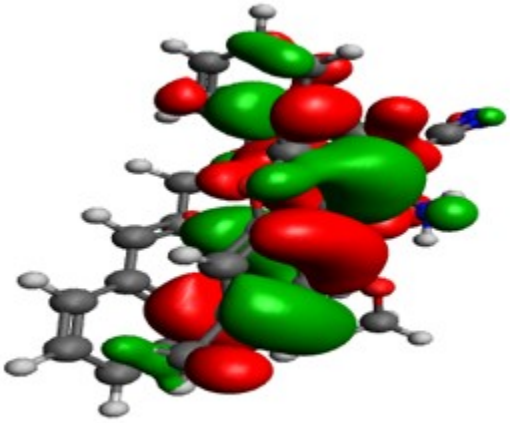
LUMO



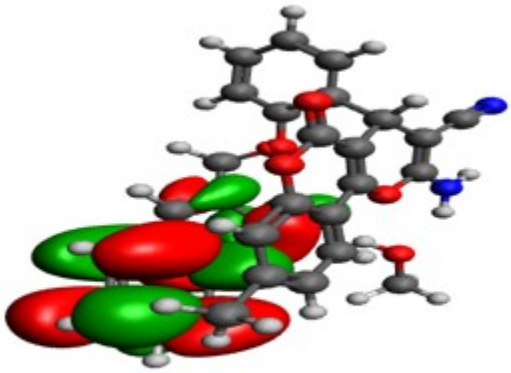
HOMO-1



LUMO+1

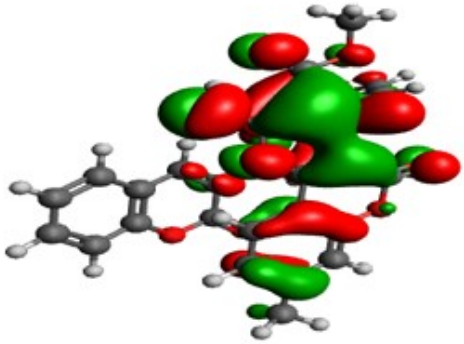


HOMO-2

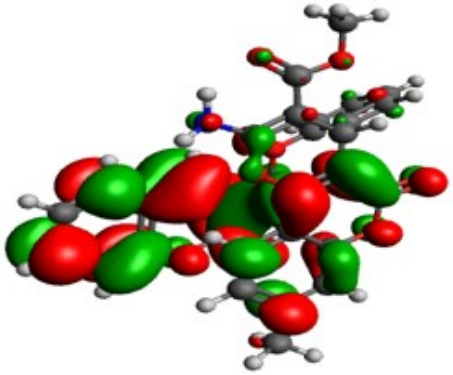


LUMO+2

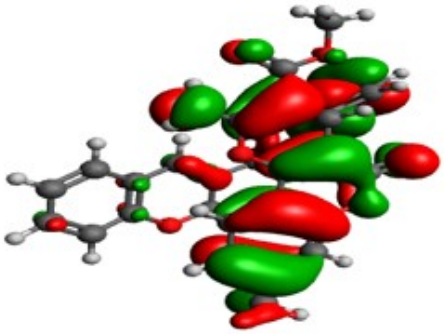
4a



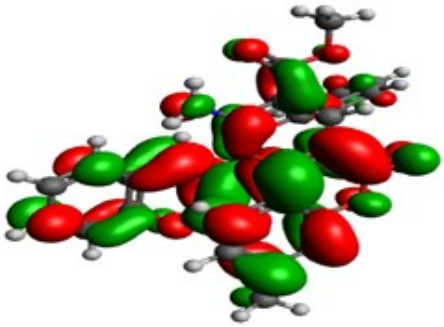
HOMO



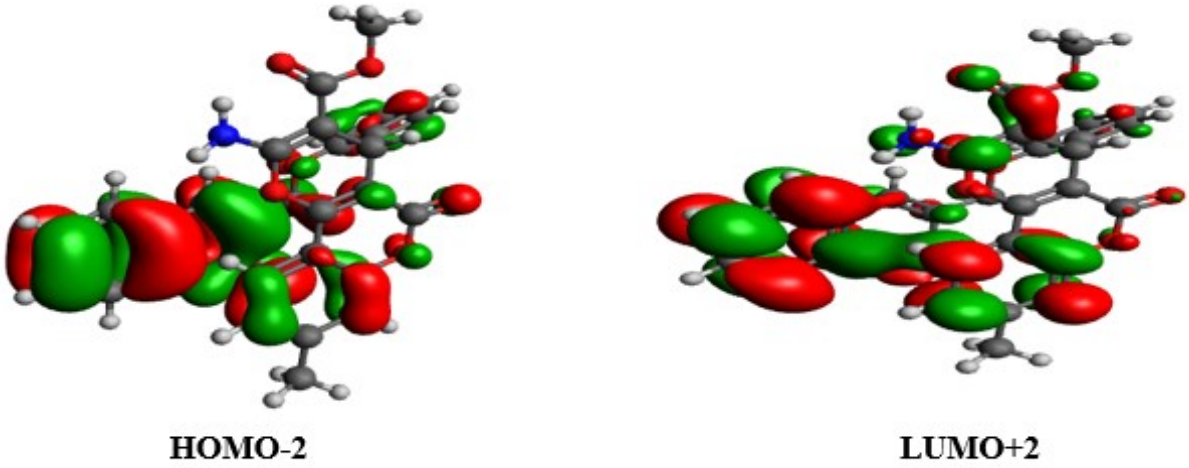
LUMO



HOMO-1

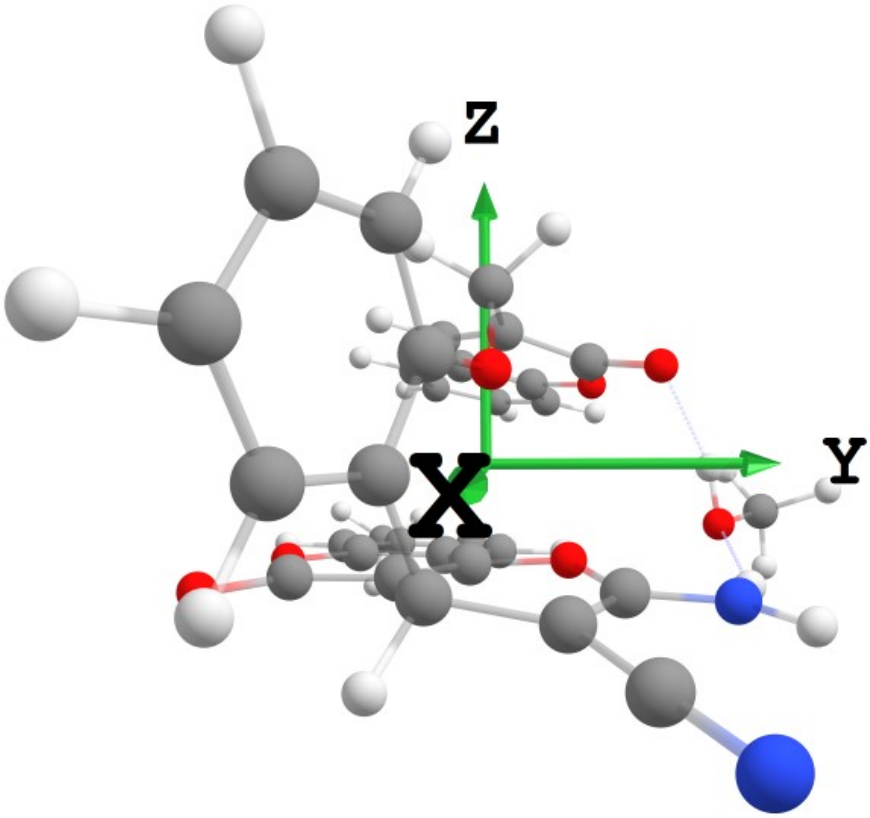


LUMO+1



4b

Figure S9: The HOMO-LUMO structures of **4a** and **4b**



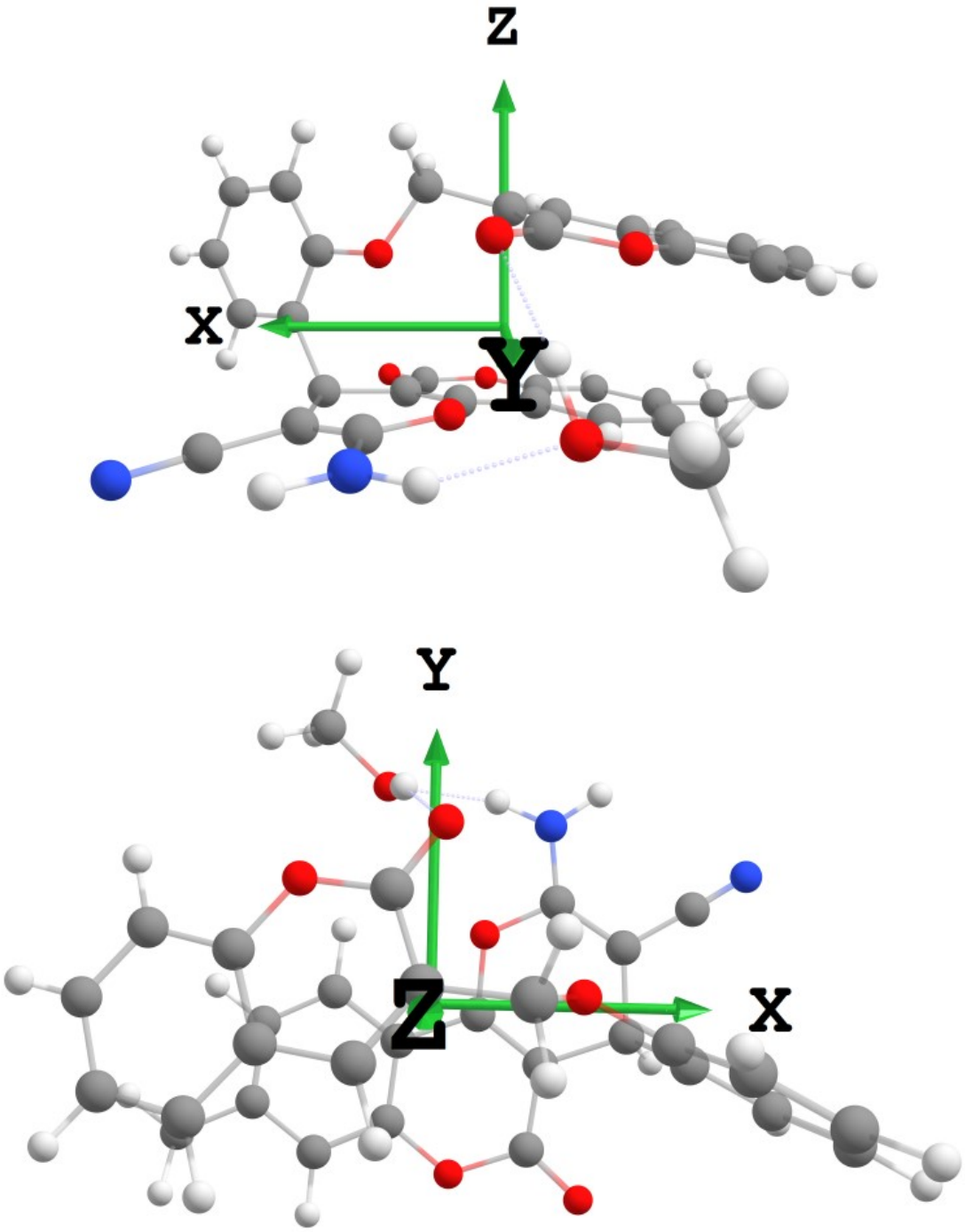
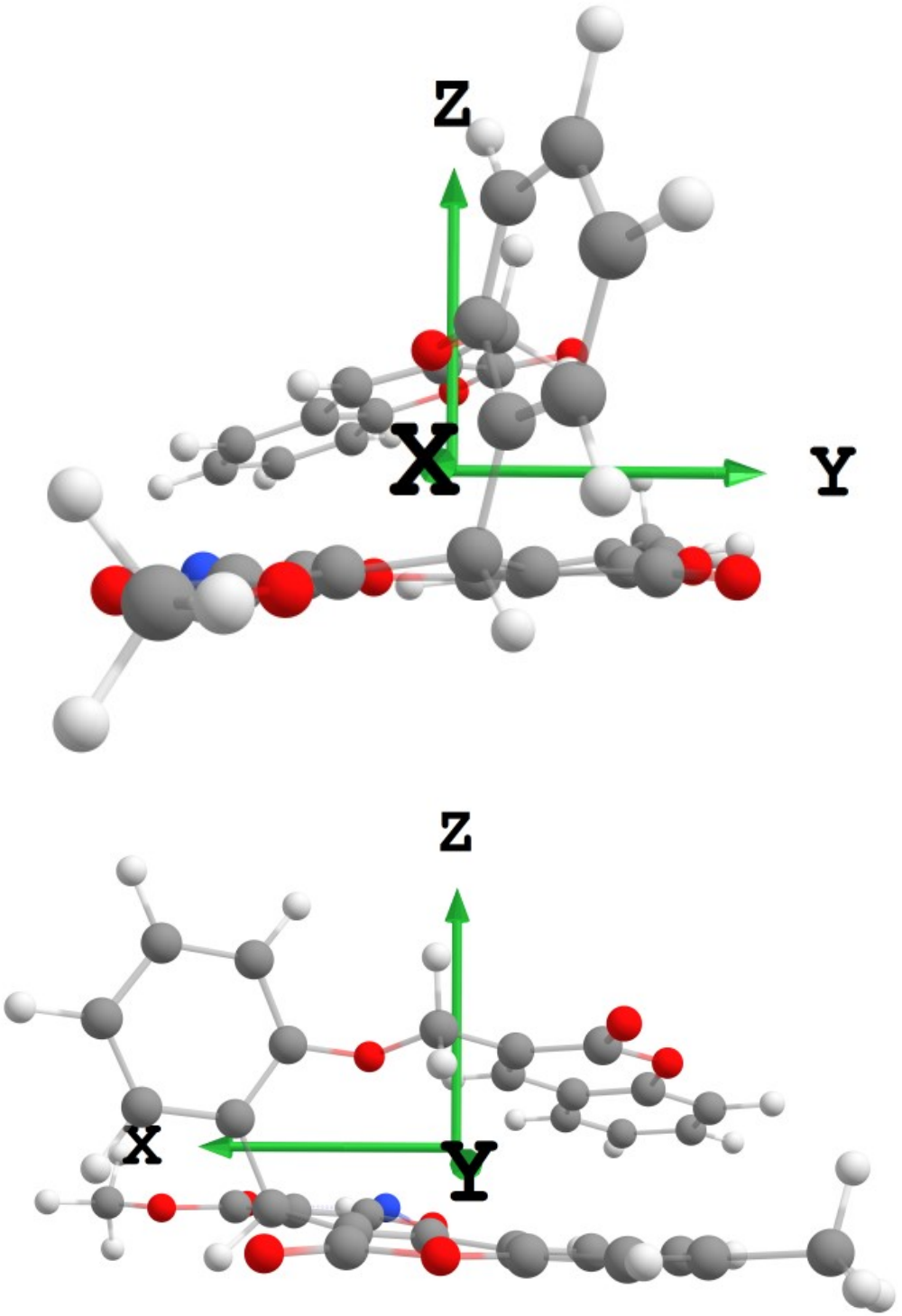


Figure S10: Orientation of the **4a** molecule along x,y and z axis.


Z
X
Y
Z
X
Y

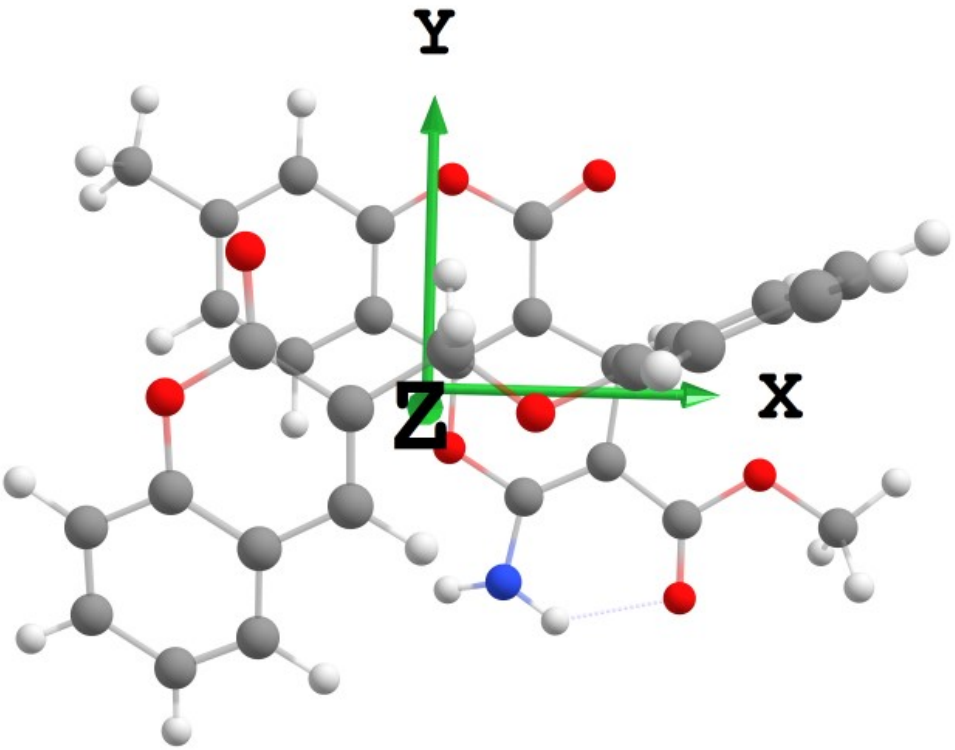


Figure S11: Orientation of the **4b** molecule along x,y and z axis.