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

Influence of Charge Transfer on the Isomerisation of Stilbene Derivatives for Application in Cancer Therapy

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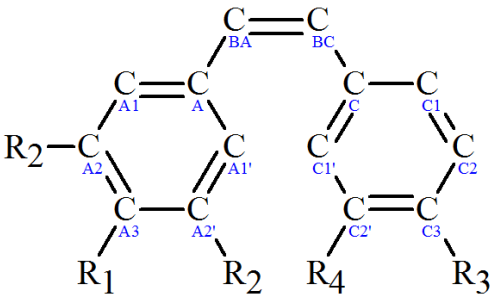
Supporting Information

Scheme S1: Structure of the stilbene derivatives **1c**-**4c**.



1: $R_1 = O_{A3}C_{OA3}H_3$, $R_2 = O_{A2}C_{OA2}H_3$, $R_3 = O_{C3}C_{OC3}H_3$, $R_4 = O_{C2}H$
2: $R_1 = O_{A3}C_{OA3}H_3$, $R_2 = O_{A2}C_{OA2}H_3$, $R_3 = O_{C3}C_{OC3}H_3$, $R_4 = F$
3: $R_1 = O_{A3}C_{OA3}H_3$, $R_2 = O_{A2}C_{OA2}H_3$, $R_3 = CN$, $R_4 = H$
4: $R_1 = NH_2$, $R_2 = H$, $R_3 = CN$, $R_4 = H$

Table S1: Absorption and fluorescence spectrum of **1c**, calculated with B3LYP/def2-TZVPP//CAM-B3LYP/def2-TZVPP.

Absorption

Exc.	E [eV]	E [nm]	Osc. Str.	Composition
1	4.2049	294.85	0.53501	HOMO → LUMO
11	6.4335	192.71	0.29102	HOMO-2 → LUMO+1, HOMO → LUMO+2, HOMO-1 → LUMO+1
5	5.5787	222.24	0.23506	HOMO → LUMO+1, HOMO-3 → LUMO, HOMO-2 → LUMO, HOMO → LUMO+2
21	7.0163	176.70	0.22918	HOMO-1 → LUMO+2, HOMO-3 → LUMO+1
8	6.0587	204.63	0.22556	HOMO-3 → LUMO+1, HOMO-2 → LUMO+2, HOMO-1 → LUMO+3
7	5.8657	211.37	0.20708	HOMO → LUMO+3, HOMO-2 → LUMO
20	6.9702	177.87	0.14085	HOMO-3 → LUMO+1, HOMO-3 → LUMO+2, HOMO-1 → LUMO+2
4	5.2572	235.83	0.11260	HOMO-1 → LUMO, HOMO → LUMO+1, HOMO-3 → LUMO
18	6.8221	181.73	0.11218	HOMO-3 → LUMO+1, HOMO-1 → LUMO+3, HOMO-2 → LUMO+3, HOMO-2 → LUMO+2
6	5.8030	213.65	0.10320	HOMO-3 → LUMO, HOMO → LUMO+2, HOMO-1 → LUMO+1
14	6.5734	188.61	0.10002	HOMO → LUMO+7, HOMO-1 → LUMO+7, HOMO-1 → LUMO+2
15	6.6637	186.05	0.08368	HOMO → LUMO+4, HOMO-5 → LUMO, HOMO → LUMO+8
17	6.7780	182.92	0.06706	HOMO-5 → LUMO, HOMO → LUMO+5, HOMO-1 → LUMO+3
12	6.4673	191.70	0.06503	HOMO-1 → LUMO+2, HOMO → LUMO+7, HOMO-1 → LUMO+1
16	6.7082	184.82	0.06377	HOMO-2 → LUMO+3

Fluorescence

Exc.	E (eV)	E (nm)	Osc. Str.	Composition
1	2.4882	498.28	0.34496	HOMO → LUMO
5	4.7543	260.78	0.27543	HOMO-3 → LUMO, HOMO → LUMO+1
18	6.4417	192.47	0.24719	HOMO-1 → LUMO+2, HOMO-2 → LUMO+2
4	4.5126	274.74	0.18018	HOMO → LUMO+1, HOMO-3 → LUMO, HOMO-1 → LUMO
13	6.0069	206.40	0.17942	HOMO-1 → LUMO+1, HOMO → LUMO+9
7	5.2093	238.00	0.15711	HOMO → LUMO+3, HOMO → LUMO+2
22	6.7545	183.55	0.14389	HOMO-1 → LUMO+3, HOMO-3 → LUMO+2, HOMO-2 → LUMO+3, HOMO-4 → LUMO+1
29	7.1313	173.86	0.13693	HOMO-3 → LUMO+1, HOMO-4 → LUMO+1, HOMO-1 → LUMO+7, HOMO-2 → LUMO+2
30	7.1393	173.66	0.13648	HOMO-1 → LUMO+2, HOMO-2 → LUMO+3, HOMO-2 → LUMO+7
26	6.9427	178.58	0.12751	HOMO → LUMO+14, HOMO-3 → LUMO+1
19	6.5112	190.41	0.10438	HOMO-3 → LUMO+1, HOMO-1 → LUMO+3, HOMO-2 → LUMO+3
16	6.2343	198.87	0.07789	HOMO → LUMO+9, HOMO-1 → LUMO+1, HOMO-2 → LUMO+1
36	7.3136	169.52	0.07589	HOMO-2 → LUMO+2
41	7.5320	164.61	0.07238	HOMO-3 → LUMO+2, HOMO-2 → LUMO+3, HOMO-5 → LUMO+1
2	3.8680	320.53	0.06917	HOMO-1 → LUMO, HOMO → LUMO+1
25	6.9110	179.40	0.06105	HOMO → LUMO+14, HOMO → LUMO+10, HOMO-2 → LUMO+3
38	7.4287	166.90	0.06095	HOMO-3 → LUMO+3
40	7.5090	165.11	0.05650	HOMO-11 → LUMO, HOMO-14 → LUMO

Table S2: Absorption and fluorescence spectrum of **2c**, calculated at B3LYP/def2-TZVPP//CAM-B3LYP/def2-TZVPP.

Absorption

Exc.	E (eV)	E (nm)	Osc. Str.	Composition
1	4.1619	297.90	0.47592	HOMO → LUMO
5	5.5899	221.80	0.32759	HOMO → LUMO+1, HOMO → LUMO+2, HOMO-1 → LUMO, HOMO-3 → LUMO
8	6.1257	202.40	0.25723	HOMO-1 → LUMO+3, HOMO-2 → LUMO+2, HOMO-3 → LUMO+1, HOMO-4 → LUMO, HOMO-1 → LUMO+1
19	6.9391	178.67	0.20964	HOMO-2 → LUMO+2, HOMO-3 → LUMO+2, HOMO-1 → LUMO+4
17	6.8326	181.46	0.19399	HOMO-3 → LUMO+1, HOMO → LUMO+4
4	5.2882	234.45	0.17490	HOMO-2 → LUMO, HOMO-1 → LUMO
6	5.8347	212.49	0.13800	HOMO → LUMO+3, HOMO → LUMO+2, HOMO-2 → LUMO
21	7.0543	175.75	0.11493	HOMO-1 → LUMO+4, HOMO-2 → LUMO+2
27	7.3745	168.12	0.10497	HOMO → LUMO+8, HOMO-3 → LUMO+2, HOMO-7 → LUMO
23	7.1515	173.36	0.10230	HOMO-2 → LUMO+3, HOMO-1 → LUMO+2, HOMO-4 → LUMO+3
18	6.8625	180.66	0.09424	HOMO-1 → LUMO+3, HOMO-6 → LUMO, HOMO-3 → LUMO+1
10	6.4654	191.76	0.09316	HOMO-5 → LUMO, HOMO-1 → LUMO+1, HOMO → LUMO+3
14	6.6519	186.38	0.06934	HOMO → LUMO+7, HOMO → LUMO+5, HOMO → LUMO+4
13	6.6085	187.61	0.06741	HOMO → LUMO+6, HOMO-5 → LUMO, HOMO-1 → LUMO+2
16	6.7981	182.38	0.06202	HOMO-6 → LUMO, HOMO-2 → LUMO+3
12	6.5581	189.05	0.05936	HOMO-2 → LUMO+1, HOMO → LUMO+4
24	7.2422	171.19	0.05757	HOMO-2 → LUMO+2, HOMO-7 → LUMO, HOMO → LUMO+8
3	4.9236	251.81	0.05133	HOMO-3 → LUMO, HOMO → LUMO+1, HOMO-2 → LUMO

Fluorescence

Exc.	E (eV)	E (nm)	Osc. Str.	Composition
1	2.4888	498.16	0.34132	HOMO → LUMO
5	4.8413	256.09	0.32972	HOMO→ LUMO+1, HOMO-2 → LUMO
25	6.9695	177.89	0.22041	HOMO-3→ LUMO+1, HOMO-1 → LUMO+3
18	6.4543	192.09	0.21430	HOMO-2 → LUMO+1, HOMO → LUMO+9, HOMO-1 → LUMO+3
4	4.5066	275.11	0.14414	HOMO-2 → LUMO, HOMO-1 → LUMO, HOMO → LUMO+1
22	6.8259	181.63	0.16600	HOMO-1 → LUMO+3, HOMO → LUMO+11, HOMO-4 → LUMO+1
37	7.5221	164.82	0.16219	HOMO-3→ LUMO+2, HOMO-3 → LUMO+3
6	5.1919	238.80	0.16098	HOMO → LUMO+3, HOMO → LUMO+2
30				HOMO-1 → LUMO+2, HOMO-2 → LUMO+3, HOMO-2 → LUMO+7
23	6.8698	180.47	0.11446	HOMO → LUMO+11, HOMO-4 → LUMO+1
33	7.3147	169.50	0.10480	HOMO-2 → LUMO+2, HOMO-5 → LUMO+1, HOMO-5 → LUMO+3
31	7.2233	171.64	0.09855	HOMO-2 → LUMO+2
3	4.3339	286.07	0.09482	HOMO → LUMO+1, HOMO-3 → LUMO, HOMO-2 → LUMO
19	6.5520	189.23	0.09181	HOMO-1 → LUMO+2, HOMO-2 → LUMO+3, HOMO-3 → LUMO+1
34	7.3267	169.22	0.08030	HOMO → LUMO+14, HOMO → LUMO+10
13	6.0902	203.58	0.07754	HOMO → LUMO+9, HOMO-6 → LUMO, HOMO-1 → LUMO+1

Table S3: Absorption and fluorescence spectrum of **3c**, calculated at B3LYP/def2-TZVPP//CAM-B3LYP/def2-TZVPP.

Absorption

Exc.	E (eV)	E (nm)	Osc. Str.	Composition
1	4.0060	309.49	0.48169	HOMO → LUMO
19	6.8714	180.43	0.33644	HOMO-3 → LUMO+1, HOMO-2 → LUMO+2
5	5.4445	227.72	0.26131	HOMO → LUMO+3, HOMO-1 → LUMO, HOMO → LUMO+2, HOMO → LUMO+1
4	5.2277	237.16	0.25950	HOMO-2 → LUMO
10	6.3365	195.66	0.24813	HOMO-1 → LUMO+2, HOMO → LUMO+3
17	6.7802	182.86	0.20413	HOMO-3 → LUMO+1, HOMO → LUMO+4, HOMO → LUMO+7
28	7.3472	168.75	0.16578	HOMO-3 → LUMO+2, HOMO-2 → LUMO+3
9	6.1614	201.22	0.15478	HOMO-4 → LUMO, HOMO-1 → LUMO+1, HOMO-1 → LUMO+2, HOMO-4 → LUMO+2
8	6.0533	204.82	0.15163	HOMO-4 → LUMO, HOMO-2 → LUMO+2, HOMO-1 → LUMO+3
15	6.5930	188.05	0.15023	HOMO-2 → LUMO+1, HOMO-1 → LUMO+1, HOMO-3 → LUMO
18	6.8215	181.75	0.12263	HOMO-2 → LUMO+2, HOMO-1 → LUMO+3
11	6.4121	193.36	0.10923	HOMO-6 → LUMO, HOMO-1 → LUMO+2, HOMO-5 → LUMO
2	4.5893	270.15	0.07034	HOMO-1 → LUMO, HOMO-1 → LUMO+2, HOMO → LUMO+3
7	5.8372	212.40	0.07008	HOMO-3 → LUMO, HOMO → LUMO+2, HOMO → LUMO+3, HOMO-1 → LUMO+2
34	7.6859	161.31	0.06217	HOMO-6 → LUMO+1

Fluorescence

Exc.	E (eV)	E (nm)	Osc. Str.	Composition
5	4.8725	254.45	0.44343	HOMO-3 → LUMO, HOMO → LUMO+1, HOMO → LUMO+3
1	2.5202	491.95	0.31743	HOMO → LUMO
6	4.9604	249.94	0.25157	HOMO → LUMO+2
35	7.3739	168.14	0.24519	HOMO-2 → LUMO+3, HOMO-4 → LUMO+3, HOMO-3 → LUMO+2
25	6.8996	179.69	0.19905	HOMO-1 → LUMO+3, HOMO-3 → LUMO+1
14	6.2275	199.09	0.14553	HOMO → LUMO+5, HOMO → LUMO+7, HOMO-1 → LUMO+1
15	6.3084	196.53	0.13124	HOMO-1 → LUMO+2, HOMO-1 → LUMO+1, HOMO → LUMO+3
24	6.8833	180.12	0.11563	HOMO-15 → LUMO, HOMO-2 → LUMO+2, HOMO-10 → LUMO, HOMO-3 → LUMO+1
21	6.7152	184.63	0.09569	HOMO-2 → LUMO+2, HOMO-2 → LUMO+3
2	3.8641	320.85	0.08696	HOMO-1 → LUMO
28	7.0710	175.34	0.07709	HOMO-3 → LUMO+1, HOMO-1 → LUMO+3, HOMO-2 → LUMO+2
16	6.4189	193.15	0.07315	HOMO→ LUMO+6, HOMO → LUMO+7, HOMO-1→ LUMO+1, HOMO-1 → LUMO+2
3	4.3618	284.24	0.06855	HOMO → LUMO+1, HOMO-3 → LUMO
26	6.9629	178.06	0.06827	HOMO → LUMO+11, HOMO → LUMO+13, HOMO → LUMO+9
32	7.1781	172.72	0.05988	HOMO-9 → LUMO
7	5.3564	231.46	0.05071	HOMO-4 → LUMO, HOMO → LUMO+3, HOMO-3 → LUMO

Table S4: Absorption and fluorescence spectrum of **4c**, calculated at B3LYP/def2-TZVPP//CAM-B3LYP/def2-TZVPP.

Absorption

Exc.	E (eV)	E (nm)	Osc. Str.	Composition
1	3.8052	325.82	0.53336	HOMO → LUMO
15	6.7811	182.83	0.32040	HOMO-1 → LUMO+2, HOMO-1 → LUMO+2, HOMO-3 → LUMO+1
6	5.5210	224.56	0.29310	HOMO-2 → LUMO, HOMO → LUMO+1, HOMO → LUMO+2, HOMO-3 → LUMO
10	6.4255	192.95	0.24236	HOMO-1 → LUMO+1, HOMO-3 → LUMO
4	5.2151	237.74	0.24208	HOMO-1 → LUMO
18	6.9233	179.08	0.23946	HOMO → LUMO+6, HOMO-3 → LUMO+1, HOMO-2 → LUMO+3, HOMO → LUMO+7
17	6.8627	180.66	0.21157	HOMO-3 → LUMO+1, HOMO-1 → LUMO+2, HOMO-4 → LUMO
11	6.4771	191.41	0.13392	HOMO → LUMO+6, HOMO-4 → LUMO
19	6.9604	178.12	0.10772	HOMO → LUMO+8, HOMO-1 → LUMO+8
27	7.4574	166.25	0.08039	HOMO-3 → LUMO+2, HOMO-2 → LUMO+3, HOMO-2 → LUMO+1
7	5.7754	214.67	0.07528	HOMO-2 → LUMO, HOMO → LUMO+3, HOMO-3 → LUMO
14	6.7107	184.75	0.06027	HOMO-1 → LUMO+3
2	4.5680	271.41	0.05856	HOMO → LUMO+1, HOMO → LUMO+3
16	6.8157	181.91	0.05741	HOMO → LUMO+9, HOMO → LUMO+10, HOMO → LUMO+8, HOMO → LUMO+7
5	5.3578	231.40	0.05004	HOMO → LUMO+2, HOMO → LUMO+1

Fluorescence

Exc.	E (eV)	E (nm)	Osc. Str.	Composition
24	7.0205	176.60	0.50524	HOMO-3 → LUMO+1, HOMO-2 → LUMO+2, HOMO-2 → LUMO+3
1	2.5472	486.74	0.39942	HOMO → LUMO
5	4.8886	253.61	0.38944	HOMO-2 → LUMO, HOMO-1 → LUMO, HOMO → LUMO+2, HOMO → LUMO+1
6	4.9632	249.80	0.36185	HOMO → LUMO+2, HOMO-2 → LUMO
19	6.6072	187.65	0.17546	HOMO-1 → LUMO+3, HOMO-2 → LUMO+1, HOMO-4 → LUMO+1
31	7.4317	166.83	0.14408	HOMO-3 → LUMO+2, HOMO-12 → LUMO, HOMO-9 → LUMO
23	6.9063	179.52	0.12860	HOMO-1 → LUMO+3, HOMO-2 → LUMO+1, HOMO-1 → LUMO+2
2	4.0504	306.10	0.09652	HOMO → LUMO+1, HOMO-2 → LUMO
30	7.3309	169.12	0.07333	HOMO-9 → LUMO, HOMO-10 → LUMO
26	7.1797	172.68	0.06676	HOMO-3 → LUMO+1, HOMO-1 → LUMO+3, HOMO-2 → LUMO+2
20	6.6831	185.51	0.06637	HOMO-2 → LUMO+1, HOMO-1 → LUMO+2, HOMO-6 → LUMO
25	7.1435	173.56	0.06334	HOMO-2 → LUMO+2, HOMO → LUMO+12, HOMO-2 → LUMO+3
34	7.5763	163.64	0.06177	HOMO → LUMO+14, HOMO-12 → LUMO
4	4.5930	269.94	0.06046	HOMO-1 → LUMO, HOMO → LUMO+2, HOMO → LUMO+3

Table S5: Energy differences between scan value at θ_B = -90˚ and values at 2˚ left (θ_B = -92˚) and right (θ_B = -88˚) calculated as single point and vertical excitation energy calculations with CAM-B3LYP/def2-TZVPP. The *trans* and *cis* excited state structures were chosen as reference points.

[kcal/mol]	*trans* reference				*cis* reference			
	$\Delta E_{(90^\circ\text{-}92^\circ)}$ S_0	**$\Delta E_{(90^\circ\text{-}92^\circ)}$ S_1**	$\Delta E_{(90^\circ\text{-}88^\circ)}$ S_0	$\Delta E_{(90^\circ\text{-}88^\circ)}$ S_1	$\Delta E_{(90^\circ\text{-}92^\circ)}$ S_0	$\Delta E_{(90^\circ\text{-}92^\circ)}$ S_1	**$\Delta E_{(90^\circ\text{-}88^\circ)}$ S_0**	**$\Delta E_{(90^\circ\text{-}88^\circ)}$ S_1**
1	**3.0**	**-5.4**	0.8	-2.1	0.4	-1.6	**3.6**	**-5.6**
2	**3.0**	**-4.9**	0.4	-0.9	0.1	-0.6	**3.6**	**-5.3**
3	**2.9**	**-4.4**	-0.1	0.3	0.1	-0.9	**3.5**	**-5.4**
4	**2.8**	**-5.9**	1.0	-3.0	-0.4	0.8	**3.4**	**-4.4**

Table S6: WBOs of **1-4** for S_0 and S_1 calculated with CAM-B3LYP/def2-TZVPP.

	1t		**2t**		**3t**		**4t**		**1c**		**2c**		**3c**		**4c**	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C_{OA3}-O_{A3}/N	0.88	0.88	0.88	0.88	0.88	0.87			0.88	0.88	0.88	0.88	0.88	0.87		
O_{A3}-C_{A3}	0.95	0.96	0.95	0.96	0.95	0.98	1.13	1.16	0.95	0.96	0.95	0.96	0.95	0.98	1.12	1.18
C_{A3}-C_{A2}	1.31	1.23	1.31	1.22	1.31	1.21	1.34	1.25	1.30	1.22	1.30	1.21	1.30	1.19	1.34	1.24
C_{A3}-$C_{A2'}$	1.35	1.31	1.35	1.30	1.35	1.30	1.32	1.27	1.36	1.32	1.36	1.32	1.36	1.32	1.33	1.27
C_{A2}-C_{A1}	1.39	1.45	1.39	1.45	1.39	1.44	1.46	1.54	1.39	1.44	1.39	1.44	1.37	1.43	1.46	1.55
$C_{A2'}$-$C_{A1'}$	1.39	1.43	1.39	1.43	1.39	1.44	1.49	1.52	1.37	1.41	1.37	1.41	1.36	1.41	1.47	1.52
C_{A1}-C_{A}	1.34	1.23	1.34	1.23	1.34	1.24	1.36	1.24	1.35	1.24	1.35	1.25	1.35	1.26	1.36	1.24
$C_{A1'}$-C_{A}	1.36	1.21	1.36	1.20	1.36	1.20	1.33	1.20	1.39	1.22	1.39	1.21	1.37	1.20	1.35	1.21
A	1.08	1.23	1.08	1.23	1.08	1.22	1.09	1.21	1.04	1.18	1.04	1.19	1.04	1.18	1.06	1.18
B	1.79	1.36	1.79	1.35	1.78	1.37	1.76	1.39	1.85	1.43	1.85	1.42	1.85	1.45	1.84	1.47
C	1.08	1.23	1.08	1.23	1.08	1.23	1.09	1.22	1.05	1.19	1.05	1.20	1.05	1.20	1.05	1.18
C_{C}-C_{C1}	1.32	1.21	1.34	1.20	1.34	1.20	1.34	1.20	1.34	1.22	1.36	1.20	1.36	1.21	1.36	1.21
C_{C}-$C_{C1'}$	1.39	1.23	1.36	1.24	1.36	1.24	1.36	1.24	1.40	1.23	1.37	1.24	1.37	1.24	1.37	1.24
C_{C1}-C_{C2}	1.43	1.44	1.43	1.46	1.47	1.53	1.48	1.53	1.42	1.43	1.42	1.44	1.46	1.50	1.46	1.51
$C_{C1'}$-$C_{C2'}$	1.39	1.47	1.44	1.52	1.45	1.52	1.45	1.52	1.39	1.48	1.45	1.53	1.45	1.54	1.45	1.54
C_{C2}-C_{C3}	1.26	1.22	1.31	1.28	1.35	1.28	1.34	1.28	1.27	1.23	1.32	1.30	1.35	1.30	1.35	1.29
$C_{C2'}$-C_{C3}	1.41	1.32	1.37	1.28	1.36	1.26	1.36	1.26	1.41	1.30	1.37	1.26	1.36	1.24	1.36	1.24
C_{C3}-O_{C2}/F	1.02	1.03	0.87	0.87					1.02	1.03	0.87	0.87				
C_{C3}-O_{C3}/C	0.97	0.98	0.98	1.00	1.07	1.10	1.07	1.10	0.96	0.98	0.98	0.99	1.07	1.10	1.07	1.10
O_{C3}/C-C_{OC3}/N	0.89	0.89	0.89	0.88	2.86	2.81	2.86	2.81	0.89	0.89	0.89	0.88	2.86	2.81	2.86	2.81

Table S7: Natural Charges of **1-4** of S_0 and S_1 calculated with CAM-B3LYP/def2-TZVPP.

[e]	**1t**		**2t**		**3t**		**4t**		**1c**		**2c**		**3c**		**4c**	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C_{OA3}	-0.232	-0.233	-0.232	-0.233	-0.232	-0.235			-0.232	-0.233	-0.232	-0.233	-0.232	-0.236		
O_{A3}/N	-0.586	-0.576	-0.586	-0.573	-0.585	-0.566	-0.809	-0.757	-0.587	-0.578	-0.586	-0.575	-0.585	-0.566	-0.812	-0.745
C_{OA2}	-0.245	-0.245	-0.245	-0.246	-0.246	-0.248			-0.245	-0.245	-0.245	-0.246	-0.246	-0.249		
O_{A2}	-0.553	-0.548	-0.553	-0.545	-0.552	-0.537			-0.553	-0.542	-0.552	-0.537	-0.552	-0.527		
$C_{A2'}$	-0.236	-0.236	-0.236	-0.237	-0.237	-0.238			-0.236	-0.236	-0.236	-0.237	-0.237	-0.238		
$O_{A2'}$	-0.585	-0.584	-0.585	-0.583	-0.584	-0.579			-0.583	-0.583	-0.583	-0.581	-0.583	-0.576		
C_{A3}	0.237	0.243	0.240	0.255	0.246	0.284	0.207	0.212	0.237	0.239	0.239	0.250	0.243	0.289	0.205	0.224
C_{A2}	0.317	0.317	0.317	0.321	0.317	0.330	-0.278	-0.257	0.316	0.329	0.317	0.335	0.317	0.346	-0.277	-0.247
$C_{A2'}$	0.311	0.305	0.312	0.305	0.313	0.304	-0.270	-0.249	0.310	0.296	0.311	0.295	0.312	0.294	-0.273	-0.252
C_{A1}	-0.305	-0.263	-0.304	-0.313	-0.300	-0.314	-0.170	-0.165	-0.308	-0.337	-0.309	-0.338	-0.306	-0.334	-0.174	-0.170
$C_{A1'}$	-0.263	-0.313	-0.261	-0.255	-0.257	-0.235	-0.169	-0.196	-0.263	-0.242	-0.265	-0.233	-0.264	-0.199	-0.178	-0.179
C_{A}	-0.049	-0.049	-0.052	-0.039	-0.059	-0.012	-0.122	-0.031	-0.062	-0.060	-0.066	-0.050	-0.071	-0.007	-0.135	-0.009
C_{BA}	-0.196	-0.211	-0.189	-0.218	-0.167	-0.226	-0.158	-0.249	-0.203	-0.228	-0.197	-0.236	-0.179	-0.255	-0.171	-0.281
C_{BC}	-0.185	-0.226	-0.191	-0.212	-0.205	-0.162	-0.226	-0.157	-0.193	-0.245	-0.199	-0.232	-0.211	-0.167	-0.229	-0.140
C_{C}	-0.076	-0.054	-0.077	-0.067	-0.045	-0.094	-0.040	-0.106	-0.089	-0.054	-0.090	-0.070	-0.057	-0.118	-0.052	-0.147
C_{C1}	-0.253	-0.308	-0.261	-0.307	-0.201	-0.221	-0.204	-0.225	-0.251	-0.300	-0.257	-0.301	-0.198	-0.223	-0.203	-0.239
$C_{C1'}$	-0.214	-0.165	-0.205	-0.178	-0.202	-0.183	-0.206	-0.187	-0.217	-0.177	-0.206	-0.193	-0.202	-0.208	-0.204	-0.208
C_{C2}	0.325	0.339	0.380	0.392	-0.167	-0.171	-0.167	-0.172	0.324	0.335	0.377	0.385	-0.168	-0.177	-0.170	-0.179
$C_{C2'}$	-0.295	-0.315	-0.243	-0.262	-0.167	-0.120	-0.167	-0.200	-0.296	-0.310	-0.245	-0.254	-0.170	-0.188	-0.182	-0.198
C_{C3}	0.269	0.269	0.271	0.263	-0.181	-0.198	-0.186	-0.208	0.268	0.271	0.273	0.264	-0.178	-0.211	-0.170	-0.229
O_{C2}/F	-0.694	-0.683	-0.358	-0.356					-0.693	-0.681	-0.358	-0.357				
O_{C3}/C	-0.579	-0.559	-0.564	-0.544	0.312	0.304	0.313	0.305	-0.579	-0.557	-0.564	-0.543	0.313	0.305	0.313	0.306
C_{OC3}/N	-0.241	-0.243	-0.239	-0.240	-0.330	-0.354	-0.334	-0.364	-0.241	-0.243	-0.239	-0.240	-0.330	-0.365	-0.333	-0.381

Table S8: WBOs of **1** in the S_0 and S_1 states for a scan between 180 and -100˚ along the double-bond rotation coordinate calculated with CAM-B3LYP/def2-TZVPP.

1	180˚		-170˚		-160˚		-150˚		-140˚		-130˚		-120˚		-110˚		-100˚	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C_{OA3}-O_{A3}	0.88	0.87	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88
O_{A3}-C_{A3}	0.96	0.97	0.96	0.97	0.96	0.97	0.96	0.97	0.96	0.97	0.96	0.97	0.96	0.97	0.96	0.96	0.96	0.96
C_{A3}-C_{A2}	1.28	1.21	1.28	1.21	1.28	1.21	1.28	1.22	1.28	1.22	1.27	1.23	1.27	1.24	1.26	1.24	1.26	1.25
C_{A3}-$C_{A2'}$	1.34	1.31	1.34	1.31	1.34	1.31	1.34	1.32	1.34	1.32	1.34	1.32	1.34	1.33	1.34	1.33	1.34	1.33
C_{A2}-C_{A1}	1.42	1.48	1.42	1.48	1.42	1.48	1.42	1.48	1.43	1.48	1.43	1.47	1.44	1.47	1.44	1.46	1.45	1.46
$C_{A2'}$-$C_{A1'}$	1.41	1.44	1.41	1.44	1.41	1.44	1.41	1.44	1.41	1.43	1.41	1.43	1.41	1.43	1.41	1.42	1.41	1.42
C_{A1}-C_{A}	1.31	1.20	1.30	1.20	1.30	1.20	1.30	1.20	1.29	1.21	1.28	1.21	1.27	1.21	1.26	1.22	1.25	1.22
$C_{A1'}$-C_{A}	1.33	1.18	1.33	1.18	1.33	1.19	1.32	1.19	1.32	1.20	1.31	1.22	1.30	1.23	1.29	1.24	1.28	1.25
A	1.15	1.31	1.15	1.31	1.15	1.31	1.16	1.31	1.18	1.32	1.19	1.32	1.21	1.32	1.24	1.32	1.28	1.32
B	1.68	1.26	1.68	1.26	1.67	1.24	1.65	1.22	1.64	1.19	1.61	1.16	1.58	1.14	1.53	1.12	1.48	1.13
C	1.15	1.30	1.15	1.30	1.15	1.30	1.16	1.30	1.17	1.31	1.19	1.31	1.21	1.31	1.24	1.31	1.27	1.31
C_{C}-C_{C1}	1.30	1.19	1.30	1.19	1.30	1.20	1.30	1.20	1.29	1.21	1.29	1.21	1.28	1.22	1.27	1.23	1.26	1.23
C_{C}-$C_{C1'}$	1.34	1.21	1.34	1.21	1.34	1.22	1.33	1.22	1.33	1.22	1.32	1.23	1.31	1.24	1.29	1.24	1.28	1.25
C_{C1}-C_{C2}	1.44	1.45	1.44	1.45	1.44	1.45	1.44	1.45	1.44	1.45	1.44	1.45	1.44	1.45	1.44	1.45	1.44	1.45
$C_{C1'}$-$C_{C2'}$	1.43	1.50	1.43	1.50	1.43	1.50	1.43	1.50	1.44	1.50	1.44	1.49	1.45	1.49	1.46	1.48	1.47	1.48
C_{C2}-C_{C3}	1.27	1.24	1.27	1.24	1.27	1.24	1.27	1.25	1.27	1.25	1.27	1.25	1.27	1.26	1.27	1.26	1.27	1.26
$C_{C2'}$-C_{C3}	1.38	1.30	1.38	1.31	1.38	1.31	1.38	1.31	1.38	1.32	1.37	1.33	1.37	1.33	1.36	1.34	1.35	1.35
C_{C3}-O_{C2}	1.01	1.02	1.01	1.02	1.01	1.02	1.01	1.02	1.01	1.02	1.01	1.02	1.01	1.02	1.01	1.02	1.02	1.02
C_{C3}-O_{C3}	0.97	0.98	0.97	0.98	0.97	0.98	0.97	0.98	0.97	0.98	0.97	0.98	0.97	0.98	0.97	0.98	0.97	0.98
O_{C3}-C_{OC3}	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89

Table S9: WBOs Indices of **3** in the S_0 and S_1 states for a scan between 180 and -100˚ calculated with CAM-B3LYP/def2-TZVPP.

3	180˚		-170˚		-160˚		-150˚		-140˚		-130˚		-120˚		-110˚		-100˚	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C_{OA3}-O_{A3}	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87
O_{A3}-C_{A3}	0.99	1.02	0.99	1.02	1.00	1.02	1.02	1.02	1.00	1.01	1.00	1.01	1.00	1.01	1.00	1.01	1.01	1.01
C_{A3}-C_{A2}	1.28	1.20	1.28	1.20	1.28	1.20	1.28	1.21	1.27	1.21	1.27	1.22	1.26	1.23	1.26	1.24	1.25	1.24
C_{A3}-$C_{A2'}$	1.31	1.27	1.31	1.27	1.31	1.27	1.31	1.28	1.31	1.28	1.31	1.29	1.31	1.29	1.31	1.30	1.31	1.30
C_{A2}-C_{A1}	1.42	1.47	1.42	1.47	1.42	1.47	1.42	1.47	1.42	1.47	1.43	1.47	1.43	1.47	1.44	1.47	1.45	1.46
$C_{A2'}$-$C_{A1'}$	1.43	1.47	1.43	1.47	1.43	1.46	1.43	1.46	1.43	1.46	1.43	1.45	1.43	1.45	1.43	1.45	1.43	1.45
C_{A1}-C_{A}	1.31	1.22	1.31	1.22	1.31	1.22	1.30	1.22	1.29	1.23	1.29	1.22	1.28	1.22	1.26	1.22	1.25	1.22
$C_{A1'}$-C_{A}	1.32	1.18	1.32	1.18	1.31	1.19	1.31	1.19	1.31	1.20	1.30	1.21	1.30	1.22	1.28	1.23	1.26	1.23
A	1.15	1.28	1.15	1.28	1.16	1.29	1.17	1.29	1.18	1.30	1.20	1.31	1.22	1.31	1.25	1.32	1.28	1.33
B	1.67	1.30	1.67	1.30	1.66	1.28	1.65	1.25	1.63	1.22	1.60	1.18	1.56	1.15	1.52	1.13	1.46	1.14
C	1.15	1.29	1.16	1.29	1.16	1.30	1.17	1.30	1.18	1.31	1.20	1.31	1.22	1.32	1.25	1.32	1.29	1.33
C_{C}-C_{C1}	1.31	1.19	1.31	1.19	1.30	1.19	1.30	1.19	1.30	1.20	1.29	1.21	1.28	1.22	1.27	1.22	1.26	1.23
C_{C}-$C_{C1'}$	1.32	1.22	1.32	1.22	1.32	1.22	1.31	1.22	1.31	1.22	1.30	1.22	1.29	1.23	1.27	1.23	1.26	1.23
C_{C1}-C_{C2}	1.49	1.54	1.49	1.53	1.49	1.53	1.49	1.53	1.49	1.52	1.50	1.52	1.50	1.52	1.50	1.51	1.50	1.51
$C_{C1'}$-$C_{C2'}$	1.48	1.55	1.49	1.55	1.49	1.55	1.49	1.55	1.49	1.55	1.50	1.54	1.50	1.54	1.51	1.54	1.53	1.54
C_{C2}-C_{C3}	1.33	1.29	1.33	1.29	1.33	1.29	1.33	1.30	1.33	1.30	1.33	1.31	1.33	1.31	1.33	1.31	1.32	1.31
$C_{C2'}$-C_{C3}	1.33	1.25	1.33	1.25	1.33	1.25	1.33	1.26	1.32	1.27	1.32	1.27	1.31	1.28	1.31	1.28	1.30	1.29
C_{C3}-C	1.09	1.11	1.09	1.11	1.09	1.11	1.09	1.10	1.09	1.10	1.09	1.10	1.09	1.10	1.09	1.10	1.09	1.10
C-N	2.85	2.81	2.85	2.81	2.85	2.81	2.85	2.82	2.85	2.85	2.85	2.83	2.84	2.83	2.84	2.83	2.84	2.83

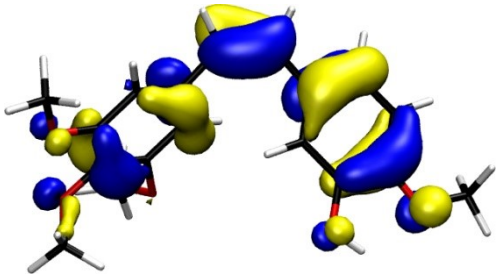
Table S10: Natural charges of **1** in the S_0 and S_1 states for a scan between 180 and -90˚ calculated with CAM-B3LYP/def2-TZVPP.

1 [e]	180˚		-170˚		-160˚		-150˚		-140˚		-130˚		-120˚		-110˚		-100˚		-90˚	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C_{OA3}	-0.232	-0.233	-0.231	-0.233	-0.231	-0.233	-0.231	-0.233	-0.231	-0.233	-0.231	-0.233	-0.231	-0.232	-0.231	-0.232	-0.231	-0.232	-0.231	-0.234
O_{A3}	-0.585	-0.573	-0.585	-0.573	-0.585	-0.573	-0.585	-0.574	-0.585	-0.575	-0.584	-0.577	-0.584	-0.578	-0.584	-0.579	-0.583	-0.580	-0.583	-0.578
C_{OA2}	-0.556	-0.245	-0.245	-0.245	-0.245	-0.245	-0.245	-0.245	-0.245	-0.245	-0.245	-0.245	-0.245	-0.245	-0.245	0.245	-0.245	-0.245	-0.245	-0.245
O_{A2}	-0.245	-0.552	-0.556	-0.552	-0.556	-0.553	-0.556	-0.553	-0.556	-0.554	-0.557	-0.555	-0.557	-0.556	-0.557	-0.556	-0.557	-0.557	-0.557	-0.557
$C_{A2'}$	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236
$O_{A2'}$	-0.585	-0.583	-0.585	-0.583	-0.585	-0.583	-0.585	-0.584	-0.585	-0.584	-0.585	-0.584	-0.585	-0.584	-0.585	-0.584	-0.585	-0.584	-0.584	-0.585
C_{A3}	0.251	0.257	0.251	0.257	0.251	0.258	0.251	0.258	0.252	0.258	0.253	0.257	0.253	0.256	0.254	0.254	0.255	0.253	0.256	0.233
C_{A2}	0.308	0.310	0.308	0.310	0.308	0.309	0.308	0.309	0.307	0.308	0.307	0.307	0.306	0.306	0.306	0.306	0.305	0.306	0.305	0.313
$C_{A2'}$	0.301	0.296	0.301	0.296	0.300	0.296	0.300	0.296	0.299	0.296	0.299	0.296	0.298	0.296	0.298	0.296	0.297	0.297	0.297	0.300
C_{A1}	-0.304	-0.311	-0.304	-0.310	-0.304	-0.309	-0.303	-0.307	-0.303	-0.305	-0.302	-0.304	-0.302	-0.303	-0.302	-0.303	-0.302	-0.304	-0.302	-0.322
$C_{A1'}$	-0.252	-0.257	-0.253	-0.258	-0.253	-0.258	-0.254	-0.258	-0.254	-0.257	-0.253	-0.256	-0.253	-0.254	-0.253	-0.253	-0.254	-0.254	-0.257	-0.249
C_{A}	-0.059	-0.050	-0.059	-0.051	-0.061	-0.052	-0.063	-0.054	-0.065	-0.058	-0.068	-0.063	-0.071	-0.069	-0.073	-0.073	-0.075	-0.075	-0.077	-0.074
C_{BA}	-0.199	-0.212	-0.199	-0.212	-0.201	-0.213	-0.202	-0.214	-0.204	-0.213	-0.205	-0.212	-0.207	-0.211	-0.208	-0.210	-0.209	-0.210	-0.211	-0.188
C_{BC}	-0.185	-0.213	-0.185	-0.213	-0.186	-0.213	-0.187	-0.212	-0.188	-0.209	-0.188	-0.205	-0.187	-0.199	-0.185	-0.192	-0.182	-0.184	-0.177	-0.160
C_{C}	-0.085	-0.067	-0.085	-0.068	-0.087	-0.069	-0.089	-0.073	-0.091	-0.078	-0.093	-0.084	-0.096	-0.090	-0.098	-0.095	-0.101	-0.099	-0.103	-0.097
C_{C1}	-0.245	-0.284	-0.245	-0.283	-0.246	-0.282	-0.246	-0.278	-0.245	-0.273	-0.247	-0.266	-0.247	-0.260	-0.247	-0.255	-0.249	-0.252	-0.252	-0.244
$C_{C1'}$	-0.209	-0.182	-0.208	-0.182	-0.208	-0.183	-0.207	-0.184	-0.205	-0.186	-0.204	-0.189	-0.201	-0.191	-0.199	-0.194	-0.196	-0.196	-0.192	-0.223
C_{C2}	0.317	0.323	0.316	0.322	0.316	0.321	0.316	0.320	0.315	0.318	0.315	0.317	0.314	0.315	0.314	0.314	0.313	0.314	0.313	0.317
$C_{C2'}$	-0.298	-0.306	-0.298	-0.306	-0.299	-0.306	-0.299	-0.305	-0.299	-0.303	-0.300	-0.302	-0.300	-0.301	-0.300	-0.301	-0.301	-0.300	-0.301	-0.296
C_{C3}	0.275	0.273	0.275	0.273	0.278	0.274	0.276	0.274	0.276	0.275	0.277	0.275	0.277	0.276	0.278	0.276	0.278	0.276	0.279	0.268
O_{C2}	-0.695	-0.691	-0.695	-0.691	-0.695	-0.691	-0.695	-0.691	-0.695	-0.692	-0.695	-0.693	-0.695	-0.693	-0.694	-0.693	-0.694	-0.693	-0.694	-0.694
O_{C3}	-0.577	-0.563	-0.577	-0.563	-0.577	-0.563	-0.577	-0.564	-0.576	-0.566	-0.576	-0.568	-0.575	-0.569	-0.575	-0.571	-0.574	-0.571	-0.572	-0.575
C_{OC3}	-0.240	-0.242	-0.240	0.242	-0.240	-0.242	-0.241	-0.242	-0.241	-0.242	-0.241	-0.242	-0.241	-0.241	0.241	-0.241	-0.241	-0.241	-0.241	-0.240
sep.	-0.017	-0.008	-0.018	-0.008	-0.018	-0.009	-0.019	-0.010	-0.020	-0.012	-0.021	-0.015	-0.023	-0.019	-0.026	-0.024	-0.030	-0.031	-0.036	-0.033

Table S11: Natural charges of **3** in the S_0 and S_1 states for a scan between 180 and -90˚ calculated with CAM-B3LYP/def2-TZVPP.

3 [e]	180˚		-170˚		-160˚		-150˚		-140˚		-130˚		-120˚		-110˚		-100˚		-90˚	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C_{OA3}	-0.231	-0.234	-0.231	-0.234	-0.231	-0.234	-0.231	-0.233	-0.231	-0.233	-0.231	-0.233	-0.231	-0.232	-0.231	-0.232	-0.231	-0.232	-0.232	-0.234
O_{A3}	-0.569	-0.541	-0.569	-0.541	-0.568	-0.542	-0.568	-0.545	-0.567	-0.548	-0.567	-0.551	-0.565	-0.554	-0.564	-0.556	-0.561	-0.557	-0.558	-0.556
C_{OA2}	-0.246	-0.247	-0.246	-0.247	-0.246	-0.247	-0.246	-0.247	-0.246	-0.247	-0.246	-0.246	-0.246	-0.246	-0.246	-0.246	-0.246	-0.246	-0.246	-0.247
O_{A2}	-0.562	-0.551	-0.562	-0.552	-0.562	-0.553	-0.562	-0.554	-0.562	-0.556	-0.562	-0.558	-0.562	-0.560	-0.562	-0.561	-0.562	-0.561	-0.561	-0.561
$C_{A2'}$	-0.236	-0.237	-0.236	-0.237	-0.236	-0.237	-0.236	-0.237	-0.236	-0.237	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.236	-0.237	-0.237	-0.236
$O_{A2'}$	-0.581	-0.577	-0.581	-0.577	-0.581	-0.577	-0.581	-0.578	-0.581	-0.578	-0.580	-0.579	-0.580	-0.579	-0.580	-0.579	-0.579	-0.579	-0.579	-0.579
C_{A3}	0.282	0.300	0.283	0.299	0.283	0.299	0.285	0.298	0.286	0.297	0.289	0.296	0.292	0.296	0.296	0.298	0.302	0.302	0.310	0.285
C_{A2}	0.288	0.306	0.288	0.305	0.288	0.304	0.287	0.301	0.287	0.297	0.287	0.294	0.286	0.290	0.285	0.288	0.285	0.286	0.284	0.291
$C_{A2'}$	0.299	0.300	0.299	0.300	0.299	0.299	0.298	0.299	0.297	0.298	0.296	0.297	0.295	0.296	0.294	0.294	0.293	0.293	0.291	0.298
C_{A1}	-0.290	-0.308	-0.290	-0.307	-0.290	-0.305	-0.289	-0.302	-0.288	-0.298	-0.286	-0.293	-0.284	-0.289	-0.282	-0.284	-0.279	-0.280	-0.275	-0.292
$C_{A1'}$	-0.239	-0.243	-0.239	-0.244	-0.239	-0.245	-0.239	-0.245	-0.238	-0.244	-0.235	-0.242	-0.233	-0.238	-0.229	-0.232	-0.225	0.293	-0.220	-0.218
C_{A}	-0.080	-0.020	-0.081	-0.022	-0.082	-0.026	-0.084	-0.034	-0.087	-0.045	-0.089	-0.058	-0.092	-0.073	-0.095	-0.085	-0.098	-0.095	-0.102	-0.098
C_{BA}	-0.158	-0.231	-0.158	-0.231	-0.158	-0.229	-0.157	-0.225	-0.156	-0.216	-0.153	-0.202	-0.147	-0.183	-0.137	-0.158	-0.123	-0.126	-0.099	-0.094
C_{BC}	-0.216	-0.166	-0.216	-0.167	-0.218	-0.171	-0.221	-0.175	-0.224	-0.181	-0.229	-0.190	-0.234	-0.203	-0.242	-0.223	-0.253	-0.250	-0.272	-0.237
C_{C}	-0.046	-0.092	-0.046	-0.092	-0.048	-0.090	-0.050	-0.088	-0.053	-0.086	-0.056	-0.083	-0.059	-0.080	-0.063	-0.076	-0.066	-0.071	-0.068	-0.061
C_{C1}	-0.200	-0.212	-0.201	-0.213	-0.202	-0.213	-0.203	-0.212	-0.204	-0.211	-0.206	-0.210	-0.208	-0.210	-0.212	-0.213	-0.218	-0.219	-0.227	-0.212
$C_{C1'}$	-0.206	-0.188	-0.206	-0.188	-0.206	-0.187	-0.206	-0.188	-0.205	-0.189	-0.205	-0.191	-0.205	-0.195	-0.205	-0.200	-0.205	-0.207	-0.207	-0.245
C_{C2}	-0.170	-0.175	-0.170	-0.175	-0.170	-0.175	-0.171	-0.175	-0.171	-0.174	-0.171	-0.174	-0.171	-0.173	-0.171	-0.172	-0.171	-0.171	-0.170	-0.172
$C_{C2'}$	-0.167	-0.192	-0.168	-0.191	-0.168	-0.190	-0.169	-0.189	-0.169	-0.186	-0.170	-0.184	-0.172	-0.180	-0.173	-0.177	-0.175	-0.175	-0.176	-0.156
C_{C3}	-0.185	-0.196	-0.185	-0.195	-0.185	-0.194	-0.186	-0.193	-0.186	-0.191	-0.187	-0.191	-0.189	-0.192	-0.192	-0.195	-0.195	-0.201	-0.201	-0.223
C	0.308	0.302	0.308	0.302	0.309	0.303	0.309	0.303	0.309	0.304	0.309	0.305	0.309	0.306	0.309	0.307	0.309	0.308	0.309	0.310
N	-0.334	-0.352	-0.334	-0.352	-0.334	-0.350	-0.335	-0.348	-0.336	-0.346	-0.337	-0.344	-0.339	-0.343	-0.341	-0.345	-0.344	-0.348	-0.349	-0.359
sep.	0.079	0.155	0.080	0.153	0.083	0.147	0.087	0.139	0.094	0.130	0.105	0.124	0.120	0.128	0.141	0.147	0.171	0.185	0.217	0.203

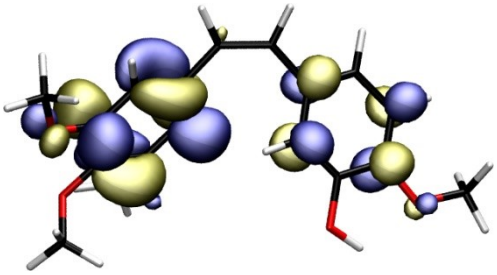
Figure S1: HOMO-3 - LUMO+3 of **1c** calculated with B3LYP/def2-TZVPP.



HOMO

CAM-B3LYP/def2-TZVPP: E = -6.83 eV

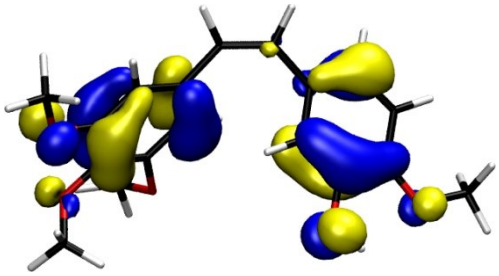
B3LYP//CAM-B3LYP/def2-TZVPP: E = -6.76 eV



LUMO+3

CAM-B3LYP/def2-TZVPP: E = 1.59 eV

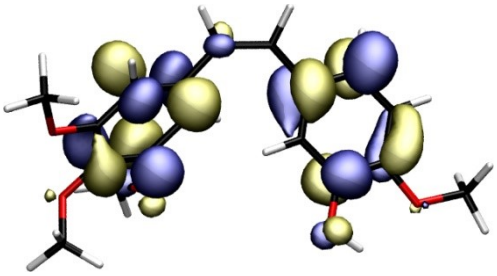
B3LYP//CAM-B3LYP/def2-TZVPP: E = 1.57 eV



HOMO-1

CAM-B3LYP/def2-TZVPP: E = -7.38 eV

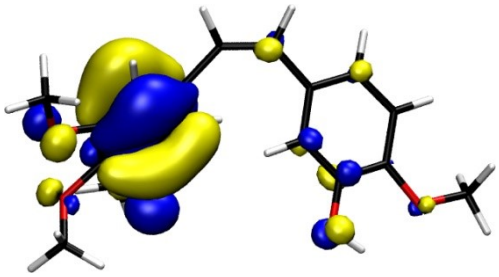
B3LYP//CAM-B3LYP/def2-TZVPP: E = -7.40 eV



LUMO+2

CAM-B3LYP/def2-TZVPP: E = 1.52 eV

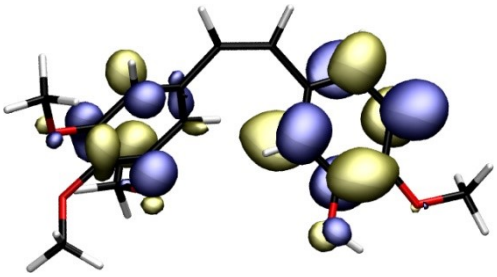
B3LYP//CAM-B3LYP/def2-TZVPP: E = 1.46 eV



HOMO-2

CAM-B3LYP/def2-TZVPP: E = -7.74 eV

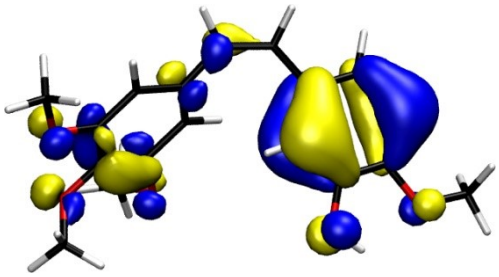
B3LYP//CAM-B3LYP/def2-TZVPP: E = -7.73 eV



LUMO+1

CAM-B3LYP/def2-TZVPP: E = 1.09 eV

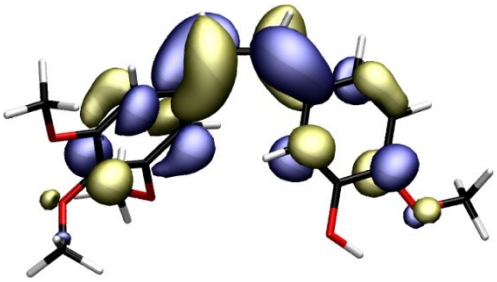
B3LYP//CAM-B3LYP/def2-TZVPP: E = 1.06 eV



HOMO-3

CAM-B3LYP/def2-TZVPP: E = -8.12 eV

B3LYP//CAM-B3LYP/def2-TZVPP: E = -8.10 eV

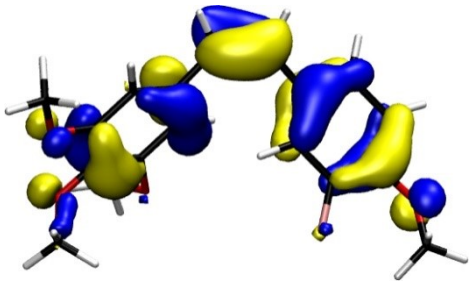


LUMO

CAM-B3LYP/def2-TZVPP: E = -0.08 eV

B3LYP//CAM-B3LYP/def2-TZVPP: E = -0.07 eV

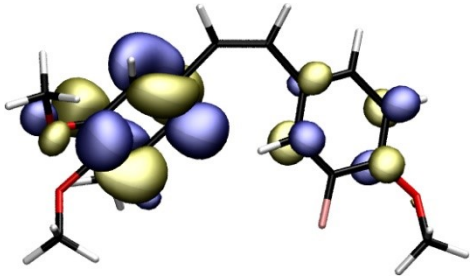
Figure S2: HOMO-3 - LUMO+3 of **2c** calculated with B3LYP/def2-TZVPP.



HOMO

CAM-B3LYP/def2-TZVPP: E = -7.04 eV

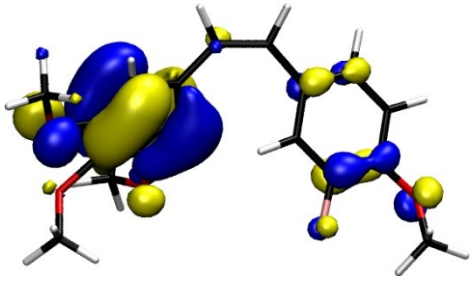
B3LYP//CAM-B3LYP/def2-TZVPP: E = -6.97 eV



LUMO+3

CAM-B3LYP/def2-TZVPP: E = 1.41 eV

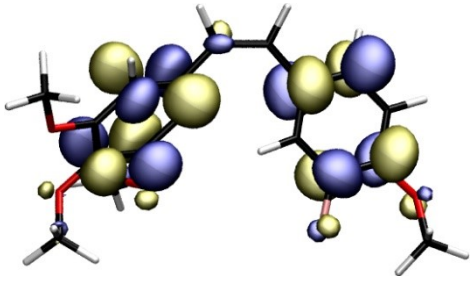
B3LYP//CAM-B3LYP/def2-TZVPP: E = 1.38 eV



HOMO-1

CAM-B3LYP/def2-TZVPP: E = -7.75 eV

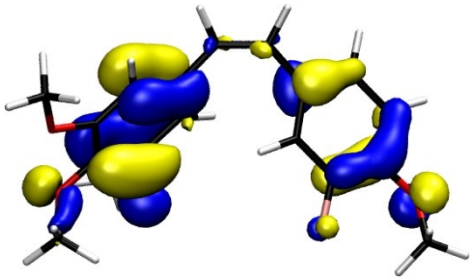
B3LYP//CAM-B3LYP/def2-TZVPP: E = -7.74 eV



LUMO+2

CAM-B3LYP/def2-TZVPP: E = 1.29 eV

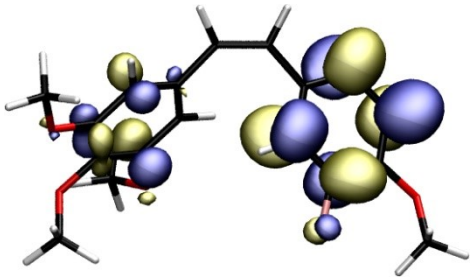
B3LYP//CAM-B3LYP/def2-TZVPP: E = 1.25 eV



HOMO-2

CAM-B3LYP/def2-TZVPP: E = -7.95 eV

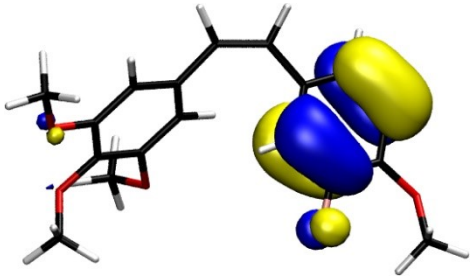
B3LYP//CAM-B3LYP/def2-TZVPP: E = -7.96 eV



LUMO+1

CAM-B3LYP/def2-TZVPP: E = 0.83 eV

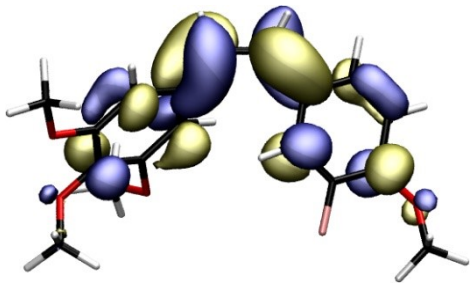
B3LYP//CAM-B3LYP/def2-TZVPP: E = 0.82 eV



HOMO-3

CAM-B3LYP/def2-TZVPP: E = -8.52 eV

B3LYP//CAM-B3LYP/def2-TZVPP: E = -8.51 eV

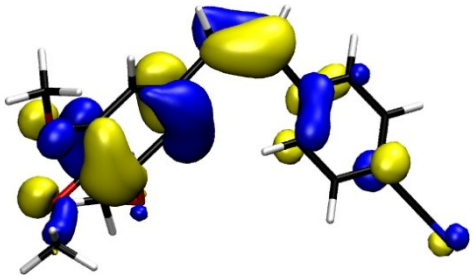


LUMO

CAM-B3LYP/def2-TZVPP: E = -0.15 eV

B3LYP//CAM-B3LYP/def2-TZVPP: E = -0.29 eV

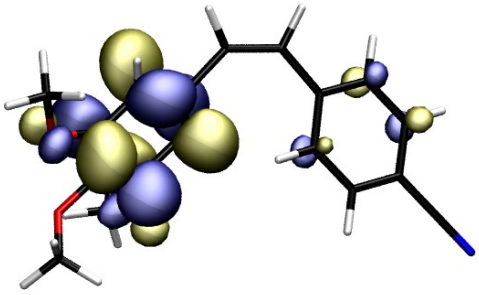
Figure S3: HOMO-3 - LUMO+3 of **3c** calculated with B3LYP/def2-TZVPP.



HOMO

CAM-B3LYP/def2-TZVPP: E = -7.44 eV

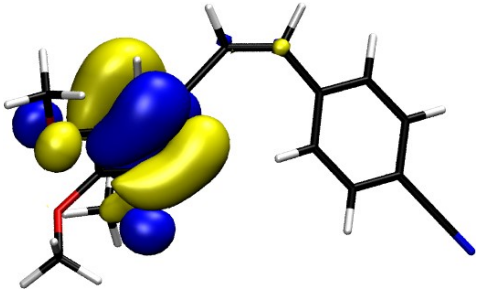
B3LYP//CAM-B3LYP/def2-TZVPP: E = -7.39 eV



LUMO+3

CAM-B3LYP/def2-TZVPP: E = 1.13 eV

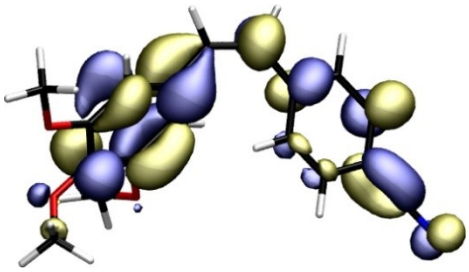
B3LYP//CAM-B3LYP/def2-TZVPP: E = 1.08 eV



HOMO-1

CAM-B3LYP/def2-TZVPP: E = -8.04 eV

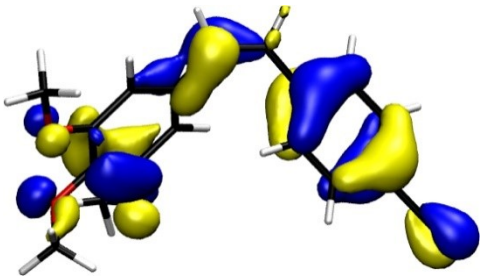
B3LYP//CAM-B3LYP/def2-TZVPP: E = -8.03 eV



LUMO+2

CAM-B3LYP/def2-TZVPP: E = 0.52 eV

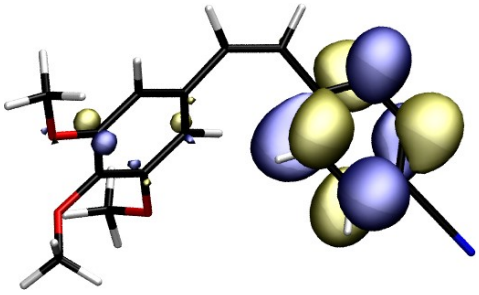
B3LYP//CAM-B3LYP/def2-TZVPP: E = 0.48 eV



HOMO-2

CAM-B3LYP/def2-TZVPP: E = -8.56 eV

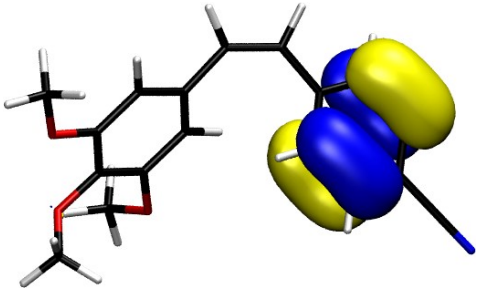
B3LYP//CAM-B3LYP/def2-TZVPP: E = -8.54 eV



LUMO+1

CAM-B3LYP/def2-TZVPP: E = 0.31 eV

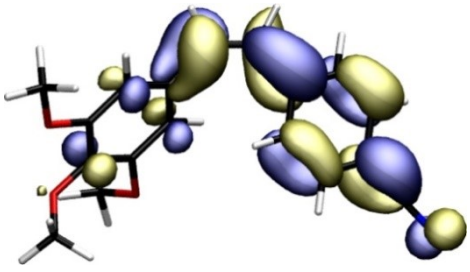
B3LYP//CAM-B3LYP/def2-TZVPP: E = 0.28 eV



HOMO-3

CAM-B3LYP/def2-TZVPP: E = -9.16 eV

B3LYP//CAM-B3LYP/def2-TZVPP: E = -9.14 eV

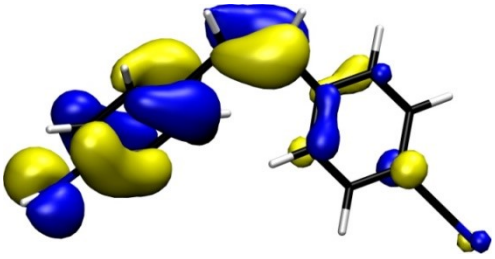


LUMO

CAM-B3LYP/def2-TZVPP: E = -0.90 eV

B3LYP//CAM-B3LYP/def2-TZVPP: E = -1.03 eV

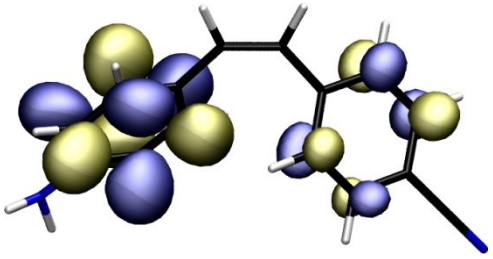
Figure S4: HOMO-3 - LUMO+3 of **4c** calculated with B3LYP/def2-TZVPP.



HOMO

CAM-B3LYP/def2-TZVPP: E = -7.03 eV

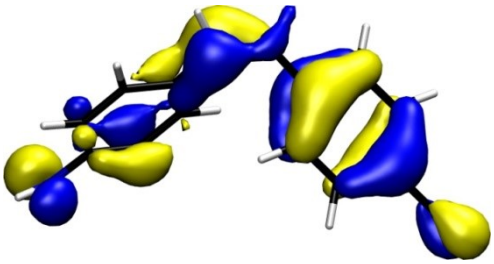
B3LYP//CAM-B3LYP/def2-TZVPP: E = -6.99 eV



LUMO+3

CAM-B3LYP/def2-TZVPP: E = 0.81 eV

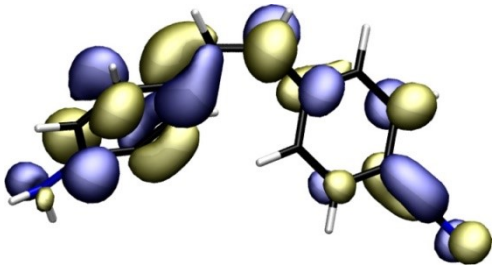
B3LYP//CAM-B3LYP/def2-TZVPP: E = 0.75 eV



HOMO-1

CAM-B3LYP/def2-TZVPP: E = -8.43 eV

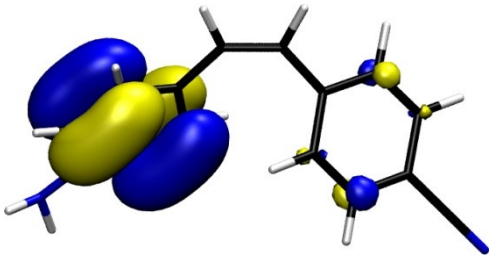
B3LYP//CAM-B3LYP/def2-TZVPP: E = -8.41 eV



LUMO+2

CAM-B3LYP/def2-TZVPP: E = 0.71 eV

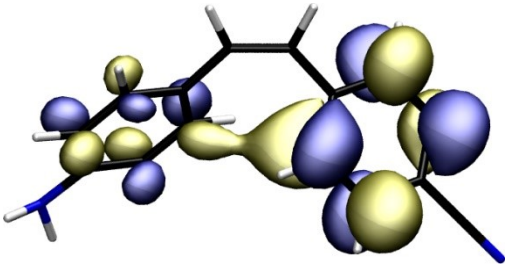
B3LYP//CAM-B3LYP/def2-TZVPP: E = 0.67 eV



HOMO-2

CAM-B3LYP/def2-TZVPP: E = -8.74 eV

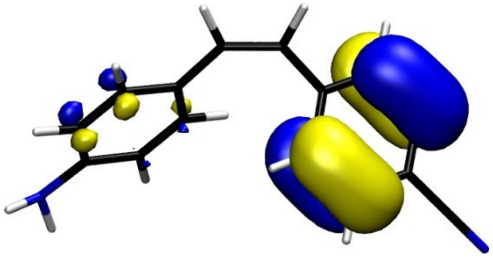
B3LYP//CAM-B3LYP/def2-TZVPP: E = -8.75 eV



LUMO+1

CAM-B3LYP/def2-TZVPP: E = 0.28 eV

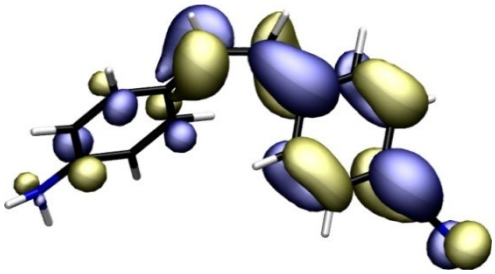
B3LYP//CAM-B3LYP/def2-TZVPP: E = 0.27 eV



HOMO-3

CAM-B3LYP/def2-TZVPP: E = -9.15 eV

B3LYP//CAM-B3LYP/def2-TZVPP: E = -9.13 eV



LUMO

CAM-B3LYP/def2-TZVPP: E = -0.79 eV

B3LYP//CAM-B3LYP/def2-TZVPP: E = -0.92 eV

Figure S5: PES along the rotational coordinate of bond B with the excited state of the *trans* structures (left) and the *cis* structures (right) as reference points. See text for details.

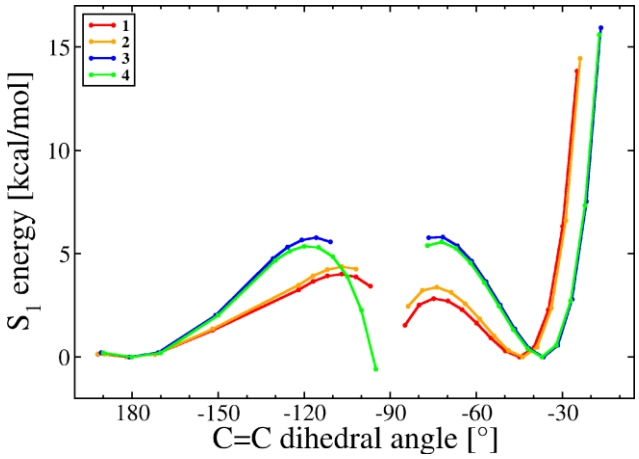


Figure S6: S_0 and S_1 PES along the rotational coordinate of the *para* methoxy group in **3t** with the ground state of the *trans* structure as reference point. The scan was carried out as a series of single-point and vertical excitation energy calculations with CAM-B3LYP/def2-TZVPP by rotating the C_{A3}–O_{CA3} bond in 20˚ steps.

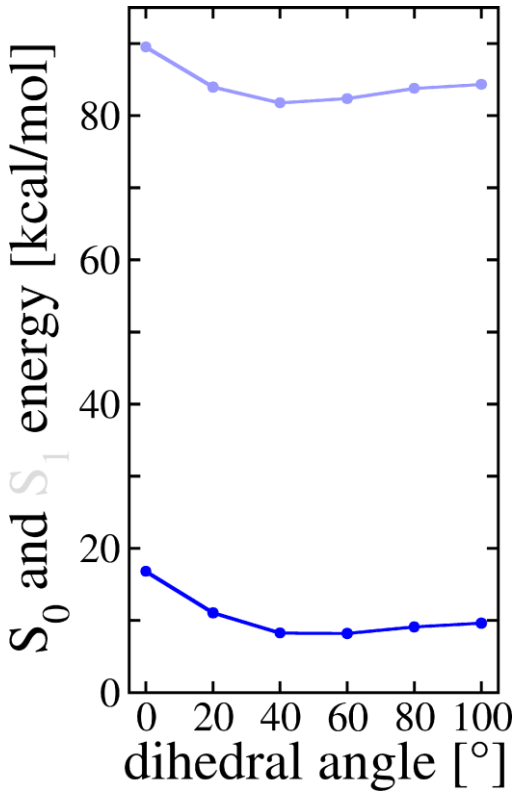


Figure S7: S_0 and S_1 PES along the coordinate of the simultaneous rotation of the two phenyl rings in **3t** with the ground state of the *trans* structure as reference point. The scan was carried out as a series of single-point and vertical excitation energy calculations with CAM-B3LYP/def2-TZVPP by rotating bonds A and C.