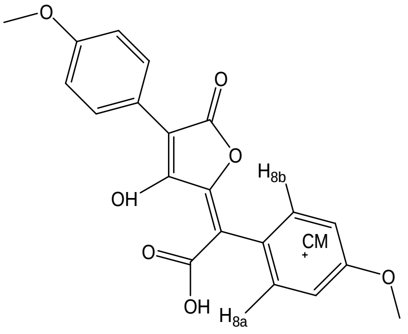
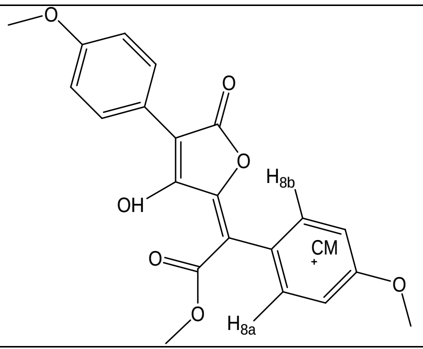
	Pulv2^{0}	Pulv2$^{-1}_{COOH}$	Pulv2$^{-1}_{enol}$	Pulv2^{-2}	Pulv3^{0}	Pulv3^{-1}
HF/6-31G(d)//HF/6-31G(d)						
E_{tot}(Z)	-1290.7009	-1290.1836	-1290.1454	-1289.5147	-1329.7255	-1329.2061
E_{tot}(E)	-1290.7123	-1290.1937	-1290.1797	-1289.5125	-1329.7397	-1329.2119
ΔE_{tot}(Z-E)	7.2	6.3	21.5	-1.4	8.9	3.6
HF/6-31G(d,p)//HF/6-31G(d)						
E_{tot}(Z)	-1290.7382	-1290.2155	-1290.1773	-1289.5400	-1329.7609	-1329.2350
E_{tot}(E)	-1290.7499	-1290.2262	-1290.2162	-1289.5379	-1329.7754	-1329.2407
ΔE_{tot}(Z-E)	7.3	6.7	24.4	-1.3	9.1	3.6
δ (H_{8a} / H_{8b}) Z	7.9 / 7.7	7.6 / 7.5	9.3 / 7.7	9.1 / 8.3	7.8 / 7.6	8.3 / 8.2
δ (H_{8a} / H_{8b}) E	7.6 / 7.7	7.6 / 7.6	8.6 / 7.6	9.2 / 8.3	7.4 / 7.5	8.2 / 8.4
$< \delta >$ Z $^{a)}$	7.8	7.6	8.5	8.7	7.7	8.2
$< \delta >$ E $^{a)}$	7.7	7.6	8.1	8.7	7.4	8.3
B3LYP/6-311G^{++}(d,p)//HF/6-31G(d)						
E_{tot}(Z)	-1298.6649	-1298.1656	-1298.1354	-1297.5192	-1337.9683	-1337.4638
E_{tot}(E)	-1298.6798	-1298.1768	-1298.1635	-1297.5160	-1337.9861	-1337.4692
ΔE_{tot}(Z-E)	9.3	7.0	17.6	-2.0	11.2	3.4

Table S1 : Total energies (E_{tot}, in Hartree) and relative (ΔE_{tot}, in kcal/mol) QM energies, and δ (^{1}H) NMR chemical shift (in ppm) of the H_8 protons of the different Pulv2 and Pulv3 species. Comparison of HF/6-31G(d)//HF/6-31G(d), HF/6-31G(d,p)//HF/6-31G(d) and DFT-B3LYP/6-311G^{++}(d,p) // HF/6-31G(d) results.

a) Mean value of the chemical shifts of the two ortho protons.



Pulv2



Pulv3

	E_{tot}(E/E)		E_{tot}(Z/Z)		ΔE_{tot}(E/E-Z/Z)			
	HF 6-31G(d)	B3LYP 6-31G(d)	HF 6-31G(d)	B3LYP 6-31G(d)	HF 6-31G(d)	B3LYP 6-31G(d)	AMBER gas phase	AMBER methanol
NBA^{2-}_{COOH}	-2457.7744	-2471.8703	-2457.7598	-2471.8546	-9.2	-9.8	-11	-5
NBA^{2-}_{enol}	-2457.7552	-2471.8703 a)	-2457.7001	-2471.7981	-34.6 a)	-45.3	-20	-31
NBA^{4-}	-2456.2664	-2470.3620	-2456.2626	-2470.3547	-2.6	-4.6	-16	-8

Table S2 : Total (E_{tot}, in hartree) and relative (ΔE_{tot}, in kcal/mol) QM and MM energies of the NBA^{2-} and NBA^{4-}.

a) Upon B3LYP/6-31G(d) optimisation of the NBA^{2-}_{enol}, the OH proton spontaneously transferred to the CO_2^- group forming NBA^{2-}_{COOH}. Therefore the ΔE (E/E – Z/Z) DFT energy corresponds to different protonic state.

		$Cs_1 \cdots O_{NBA}$	$Cs_1 \cdots O_{MeOH}$	$Cs_2 \cdots O_{NBA}$	$Cs_2 \cdots O_{MeOH}$
$NBA^{2-}{}_{COOH}$	Z/Z	0.0	6.3	2.1	4.5
	E/E	2.0	4.9	0.0	6.3
$NBA^{2-}{}_{enol}$	Z/Z	0.9	6.0	0.0	6.2
	E/E	0.0	5.9	1.3	5.0
NBA^{4-}	Z/Z	2.7	5.6	2.8	5.8
	Z/E	3.2	5.3	3.2	5.6
	E/Z	3.0	6.0	3.4	5.5
	E/E	1.9	6.2	4.4	4.8

Table S3 : NBA^{2-} $2Cs^+$ and NBA^{4-} $2Cs^+$ complexes simulated in methanol. Average coordination number of the Cs^+ cations obtained by integration of the Radial Distribution Functions (RDF's) of O_{NBA} and O_{MeOH} oxygens up to 4 Å. Averages during the last 200 ps of dynamics.

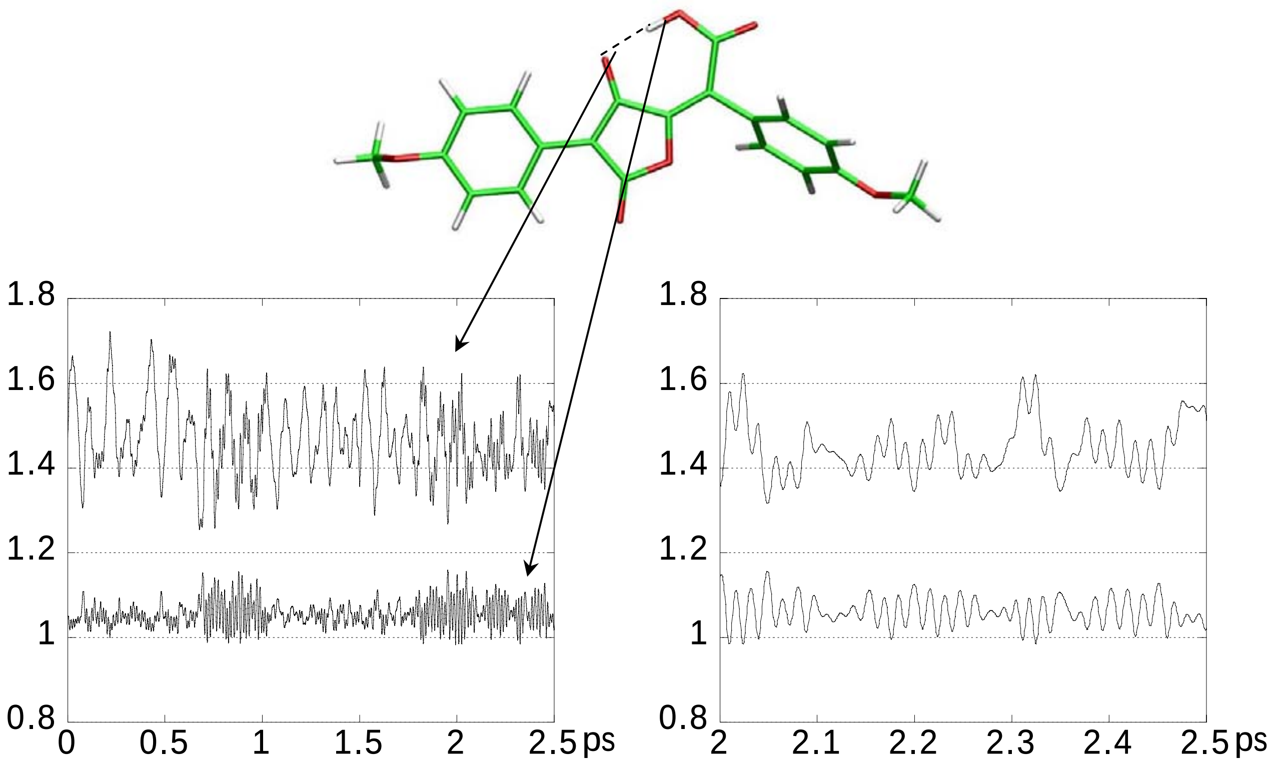


Figure S1 : CP-MD simulation on the Pulv^{-1} E_{COOH} species. H_{COOH}…$O_{enolate}$ and (CO)O-H distances (in Å) as a function of time (after 1 ps of equilibration; not shown).

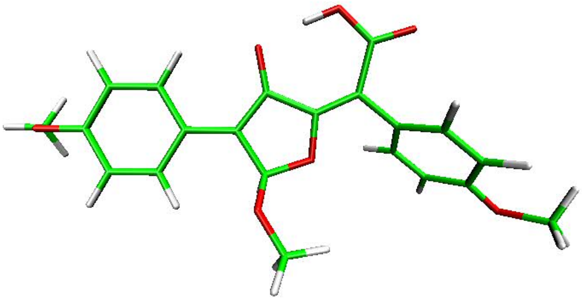
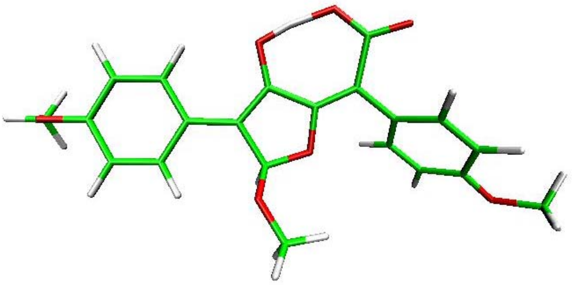
PulvMe$_{COOH}$	PulvMe$_{OH}$
	
E_{tot} = -1330.3391 Hartree ΔE_{tot} = 0.0 kcal/mol d(H-bond) = 1.535 Å d(COO-H)=0.986 Å	E_{tot}= -1330.3321 Hartree ΔE_{tot} = 4.4 kcal/mol d(H-bond) = 1.412 Å d(CO-H) = 1.023 Å

Figure S2 : Optimized structures and energies of the COOH and enol(OH) forms of the methylated PulvMe analogue of the Pulv2 pulvinic acid.

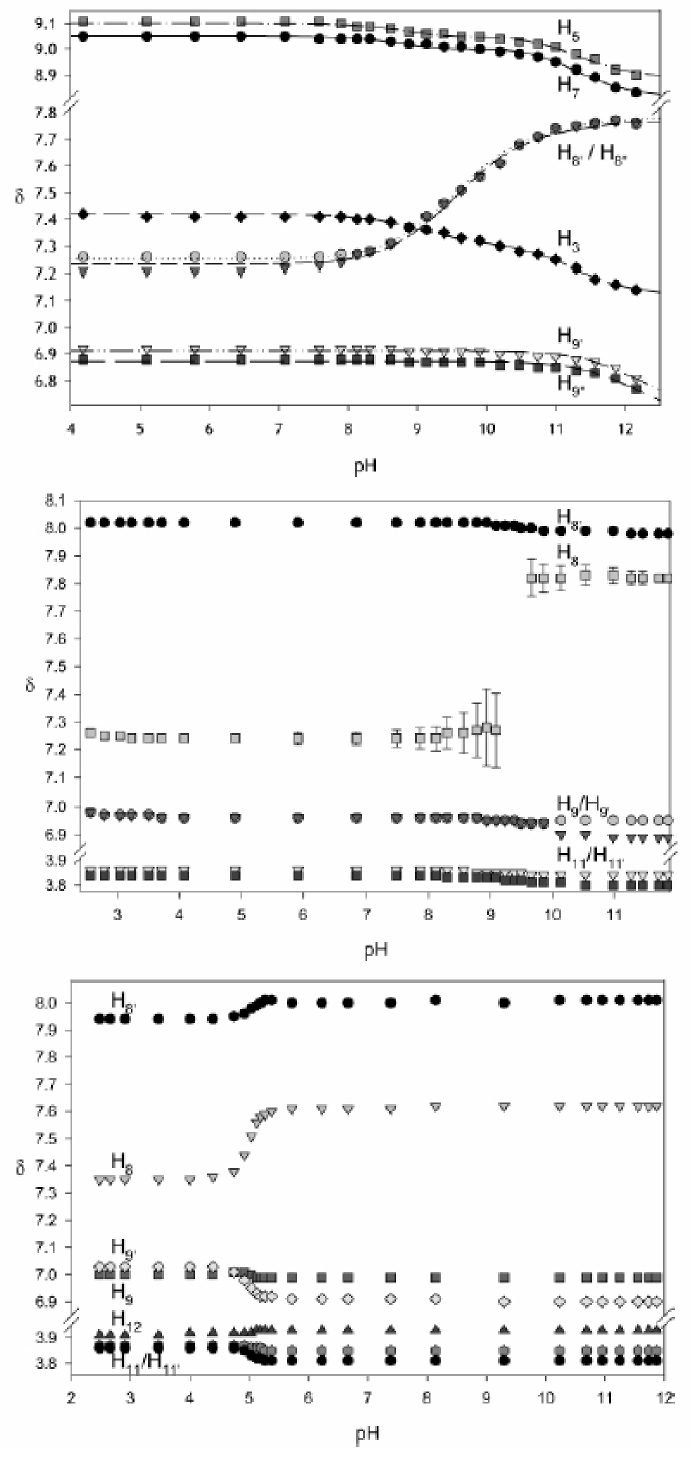


Figure S3 : Experimental chemical shifts d from 1H NMR titrations as a function of pH at 25°C (CD_3OD:D_2O-80:20) for the NBA (top), Pulv2 (middle) and Pulv3 (bottom) species (from Kuad et al, *J. Am. Chem. Soc.*, **2005**, *127*, 1323-1333). See Figure 2 for the proton labels.

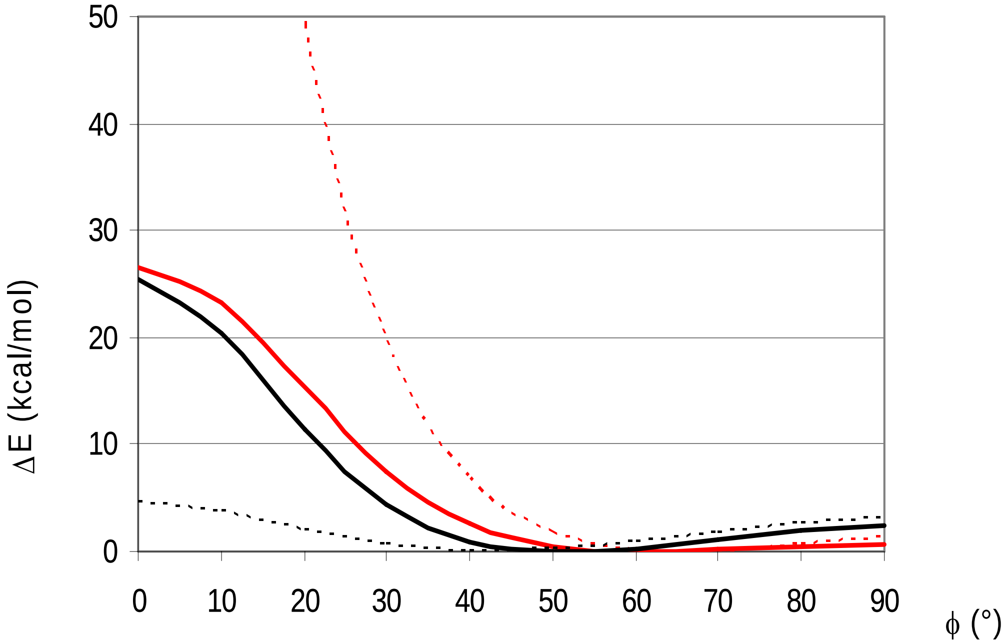
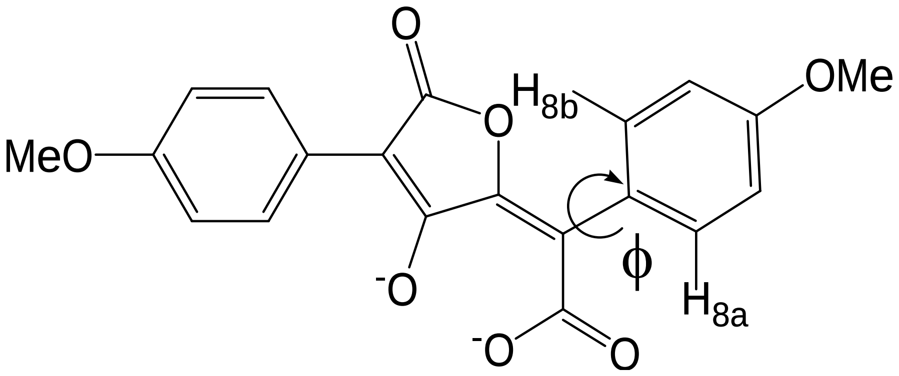


Figure S4 : Relative energies of the Pulv2^{-1} et Pulv2^{-2} (HF/6-31G(d) calculations) as a function of the ϕ angle. Calculated by stepwise rotating the ϕ angle (from 0 to 180° by increments of 30°), and optimizing all other degrees of freedom.

Plain red curve : Pulv2$^{-1}_{COOH}$(E), dotted red : Pulv2$^{-1}_{COOH}$(Z), plain black : Pulv2^{-2}(Z), dotted black : Pulv2^{-2}(E).



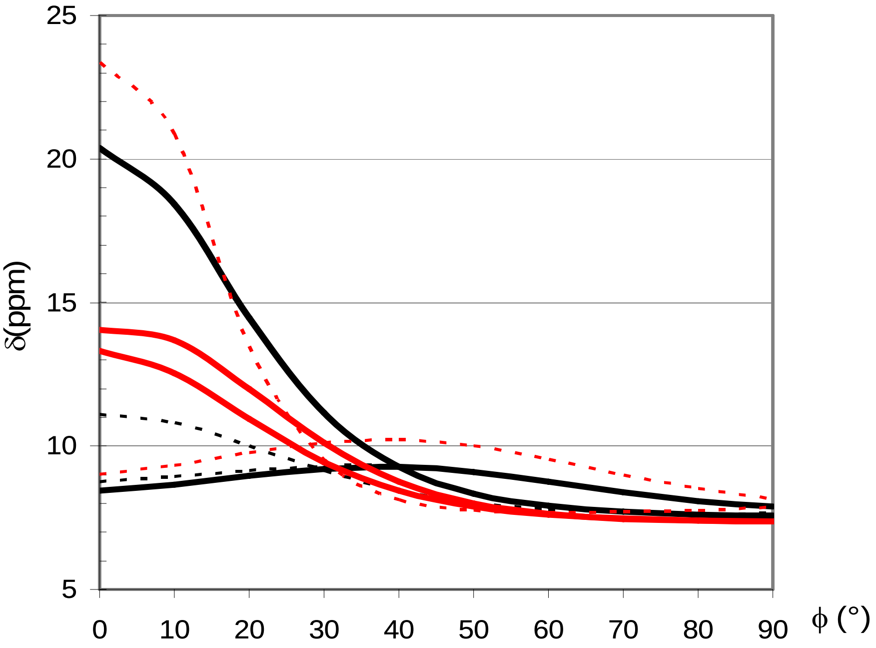
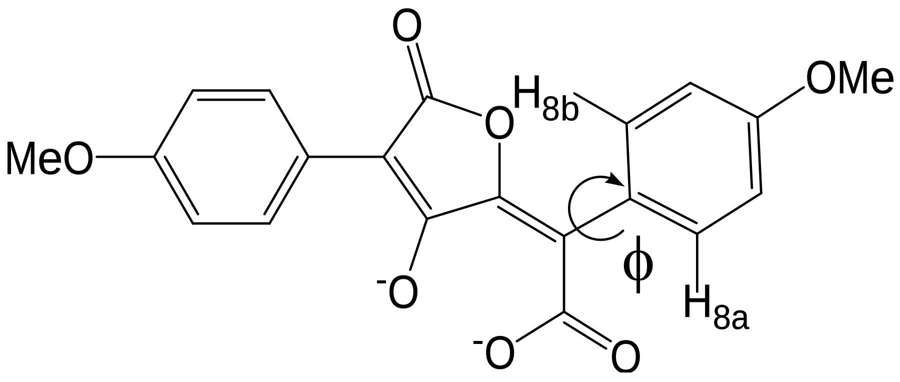


Figure S5 : NMR shifts of the H_8 protons of the Pulv2 species (HF/6-31G(d,p)// HF/6-31G(d) calculations) calculated as a function of the ϕ angle.

Plain red curves : Pulv2^{-1}_{COOH}(E), dotted red : Pulv2^{-1}_{COOH}(Z), plain black : Pulv2^{-2}(Z), dotted black : Pulv2^{-2}(E).



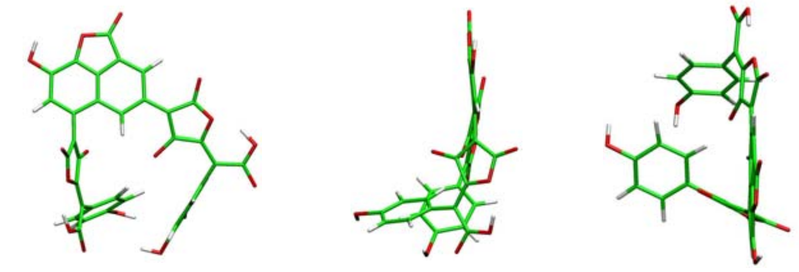
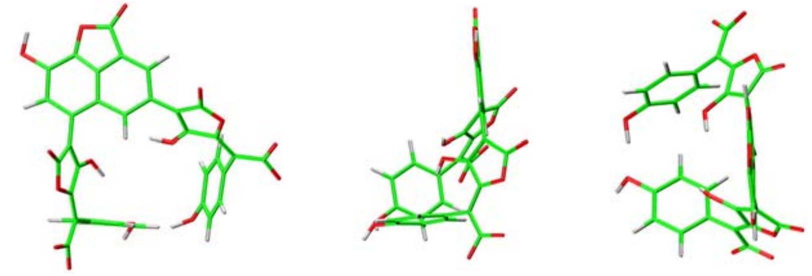
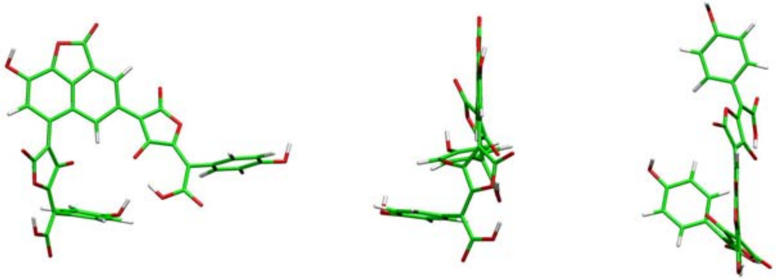
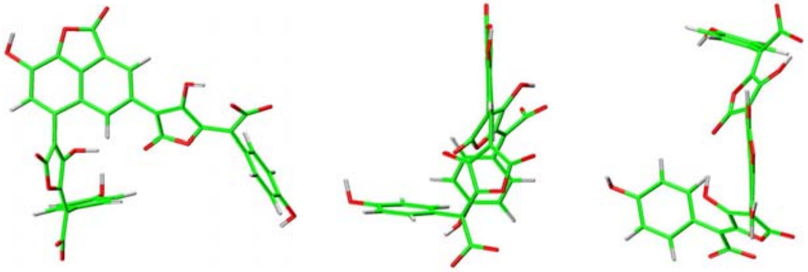
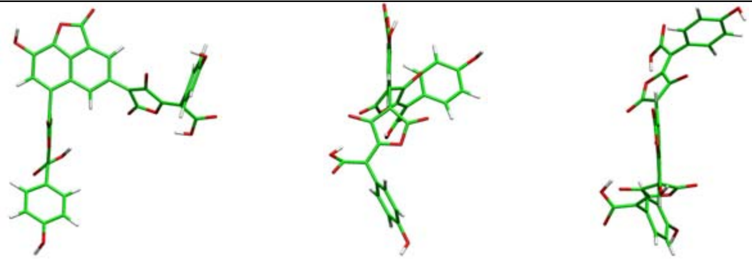
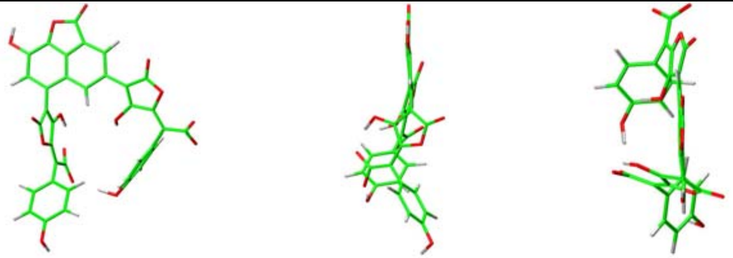
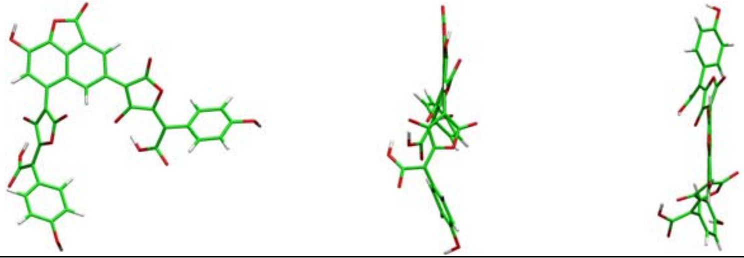
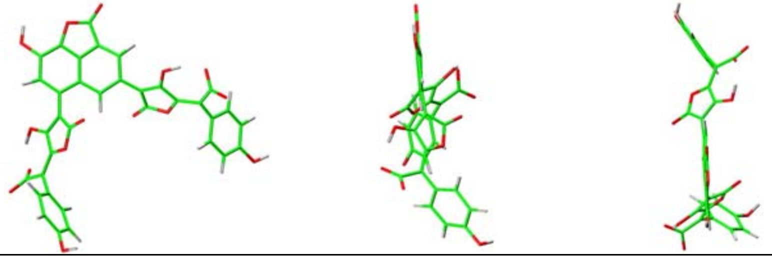
	NBA^{2-}_{COOH}	NBA^{2-}_{enol}
Z/Z		
Z/E		
E/Z		
E/E		

Figure S6 : Final snapshots of the Z/Z, Z/E, E/Z and E/E isomers of NBA^{2-}_{COOH} and NBA^{2-}_{enol} simulated by MD in the gas phase. Orthogonal views (left and middle) and top views (right).

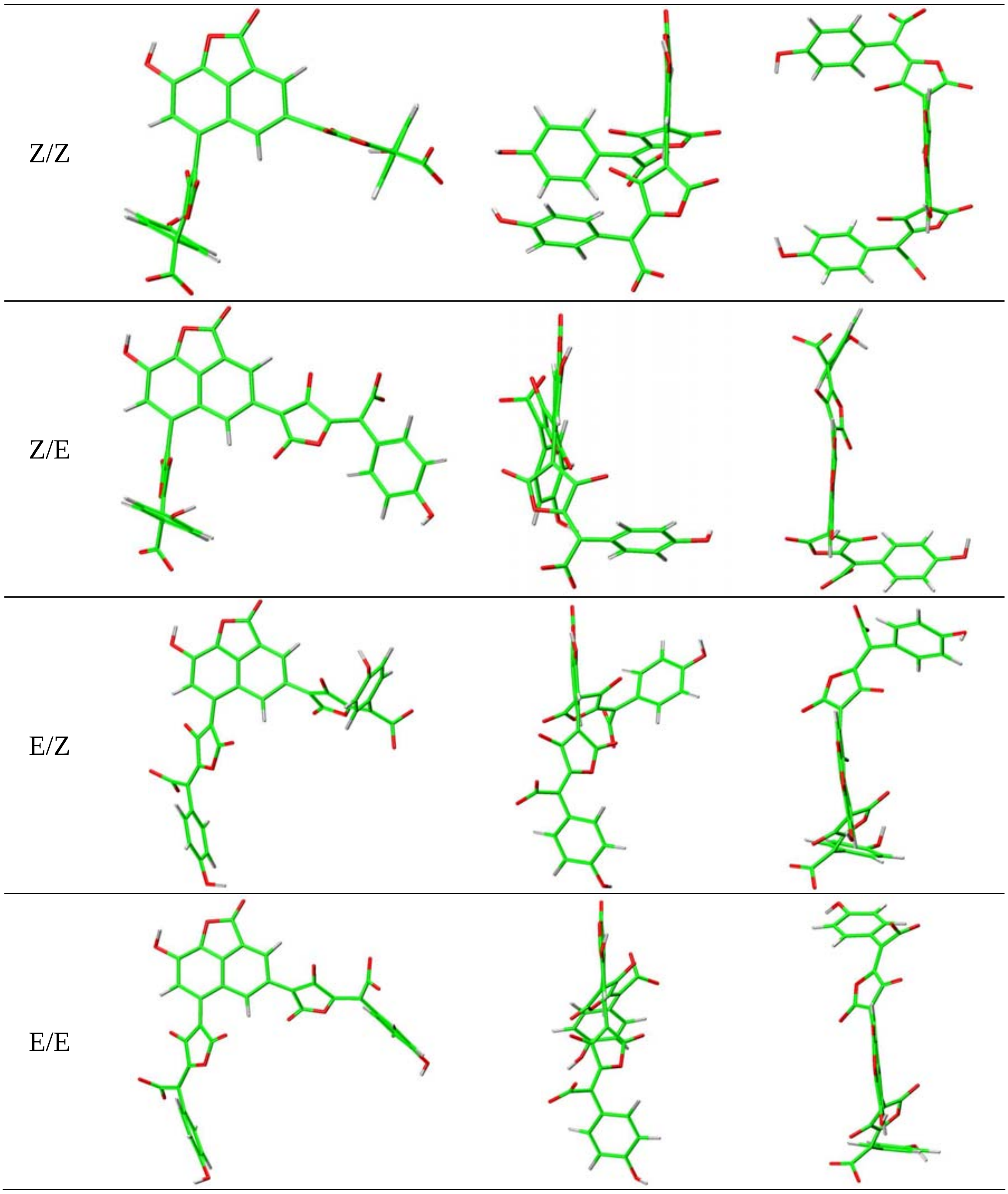


Figure S7 : Final snapshots of the Z/Z, Z/E, E/Z and E/E isomers of the NBA^{4-} molecule simulated by MD in the gas phase. Orthogonal (left and middle) and top views (right).

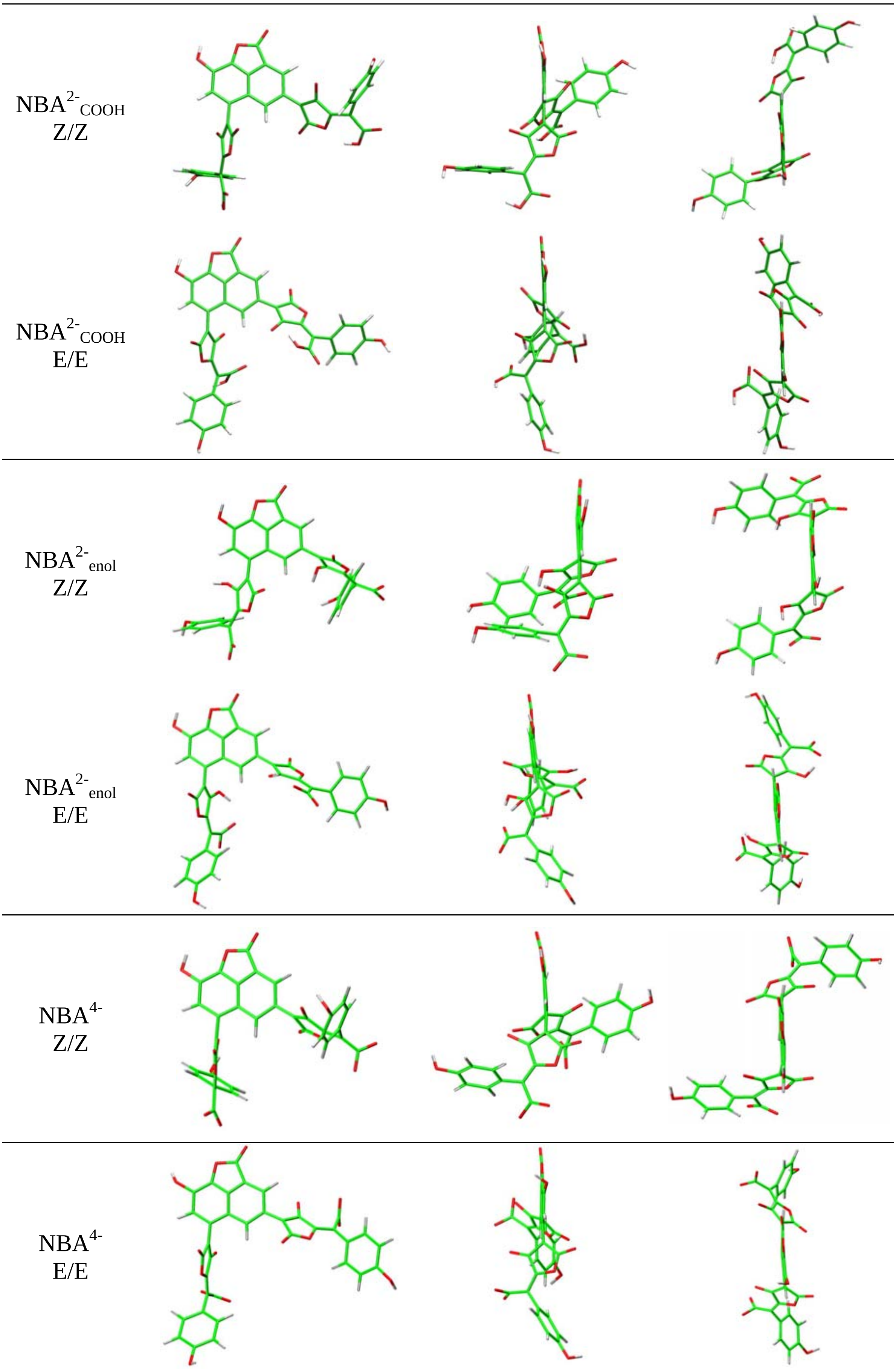


Figure S8 : Final snapshots of NBA$^{2-}_{enol}$, NBA$^{2-}_{COOH}$ and NBA^{4-} with the Z/Z and E/E isomers of the norbadione in methanol. Orthogonal (left and middle) and top views (right).

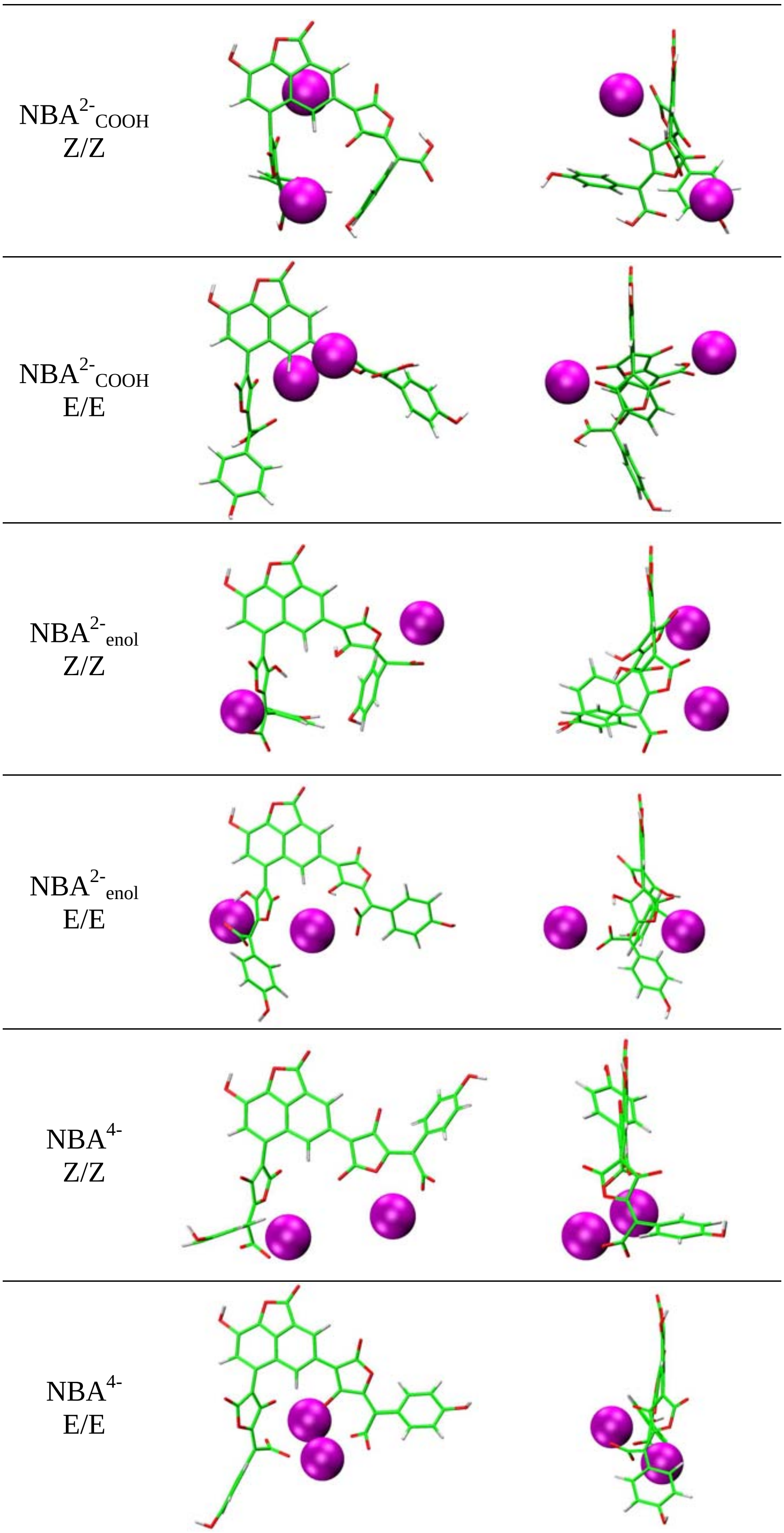


Figure S9 : Final snapshots of the NBA^{2-}_{COOH} $2Cs^+$ and $NBA^{2-}_{enol}2Cs^+$ and $NBA^{4-}2Cs^+$ complexes with the Z/Z and E/E isomers of the norbadione simulated by MD in the gas phase. Orthogonal views.