Electronic Supporting Information:

The effect of electrophilic group on the hierarchy of nucleofuge in the aminolysis reactions of thiol- and dithiocarbonates with Secondary Alicyclic Amines. Kinetic and theoretical study.

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Table S1. Experimental conditions and pseudo-first order rate constants (k_{obs}) for the reaction of S-phenyl O-(4-nitrophenyl) dithiocarbonate (**1**) with SA-amines in aqueous ethanol 44 wt %, at 25 °C and ionic strength 0.2M (KCl).

a) Piperidine							
pH=9.5, F_N=0.0457		pH=10.52, F_N=0.33		pH=10.82, F_N=0.5		pH=11.12, F_N=0.67	
10^2 $[N]_{Tot}$ / M	10^2 k_{obs}/s^{-1}	10^2 $[N]_{Tot}$/ M	10^2 k_{obs}/s^{-1}	10^2 $[N]_{Tot}$/ M	10^2 k_{obs}/s^{-1}	10^2 $[N]_{Tot}$/ M	10^2 k_{obs}/s^{-1}
0.453	0.0448	0.392	0.297	0.418	0.528	0.363	0.776
1.13	0.106	0.981	0.792	1.05	1.32	0.907	1.57
1.81	0.166	1.57	1.26	1.67	2.07	1.45	2.48
2.49	0.235	2.75	2.39	2.30	3.72	2.00	3.47
3.17	0.303	3.33	3.01	2.95	3.75	2.54	4.74
3.85	0.394	3.92	3.41	3.55	5.22	3.08	5.63
4.53	0.500			4.18	6.04	3.63	6.36

b) Piperazine					
pH=9.41, F_N=0.33		pH=9.71,F_N=0.5		pH=10.01,F_N=0.67	
10^2 $[N]_{Tot}$/M	10^2 k_{obs}/s^{-1}	10^2 $[N]_{Tot}$/M	10^2 k_{obs}/s^{-1}	10^2 $[N]_{Tot}$/M	10^2 k_{obs}/s^{-1}
0.363	0.209	0.471	0.337	0.352	0.438
0.908	0.545	1.18	1.04	0.879	1.17
1.45	0.956	1.88	1.77	1.41	2.05
2.00	1.40	2.59	2.76	1.93	2.83
2.54	1.86	3.30	3.51	2.46	3.70
3.09	2.20	4.01	3.78	2.99	4.45

3.63	2.98	4.71	4.79	3.52	5.08

c) 1-(2-Hydroxyethyl)piperazine					
pH=8.79, F_N=0.33		pH=9.09, F_N=0.5		pH=9.39, F_N=0.67	
10^2 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}	10^2 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}	10^2 $[N]_{Tot}$/M	10^2 k_{obs}/s^{-1}
0.489	0.348	0.471	0.770	0.471	0.116
1.22	1.38	1.18	2.45	1.18	0.426
1.96	3.08	1.88	5.12	1.88	0.791
2.69	5.21	2.59	7.72	2.59	1.17
3.42	6.37	3.30	10.8	3.30	1.64
4.16	8.23	4.00	12.9	4.00	1.83
4.89	10.9	4.71	17.1	4.71	2.28

d) Morpholine			
pH=8.48, F_N=0.5		pH=9.08, F_N=0.81	
10^2 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}	10^2 $[N]_{Tot}$/M	10^2 k_{obs}/s^{-1}
0.595	0.900	0.550	0.179
1.48	3.21	1.38	0.635
2.38	6.50	2.20	1.36
3.27	8.18	3.03	1.41
4.16	11.8	3.85	2.06
5.06	16.9	4.68	2.70
5.95	21.1	5.50	3.27

e) Formylpiperazine					
pH=7.33, F_N=0.33		pH=7.63, F_N=0.5		pH=7.93, F_N=0.67	
10^2 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}	10^2 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}	10^2 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}
0.811	0.415	0.728	0.347	0.797	0.608
2.03	0.568	1.82	0.604	1.99	1.22
4.46	1.61	2.91	1.45	3.19	2.82
5.67	2.26	4.00	2.14	4.38	4.18
6.89	3.22	5.10	3.50	6.78	9.10
8.11	4.04	6.19	4.46	7.97	10.7
		7.28	5.31		

Table S2. Experimental conditions and pseudo-first order rate constants (k_{obs}) for the reaction of S-(4-chlorophenyl) O-(4-nitrophenyl) dithiocarbonate (**3**) with SA-amines in aqueous ethanol 44 wt %, at 25 °C and ionic strength 0.2M (KCl).

a) Piperidine					
pH=10.52, F_N=0.33		pH=10.82, F_N=0.5		pH=11.12, F_N=0.67	
10^3 $[N]_{Tot}$/M	10^2 k_{obs}/s^{-1}	10^3 $[N]_{Tot}$/M	10^2 k_{obs}/s^{-1}	10^3 $[N]_{Tot}$/M	10^2 k_{obs}/s^{-1}
0.968	0.311	0.930	0.327	0.916	0.505
2.42	0.563	2.33	0.600	2.29	1.03
3.87	0.933	3.72	1.41	3.66	1.84
5.32	1.16	5.12	1.89	5.04	2.32
6.77	1.69	6.51	2.58	6.41	3.42
8.23	1.91	7.91	3.15	7.79	3.61
9.68	2.21	9.30	3.55	9.16	4.38

b) Piperazine					
pH=9.41, F_N=0.33		pH=9.71, F_N=0.5		pH=10.01, F_N=0.67	
10^3 $[N]_{Tot}$/M	10^2 k_{obs}/s^{-1}	10^3 $[N]_{Tot}$/M	10^2 k_{obs}/s^{-1}	10^3 $[N]_{Tot}$/M	10^2 k_{obs}/s^{-1}
0.820	0.218	0.743	0.299	1.76	1.16
2.05	0.545	1.86	0.774	2.81	1.94
3.28	1.11	2.97	1.32	3.87	2.92
4.51	1.53	4.09	1.90	4.92	4.00
5.74	1.93	5.20	2.51	5.98	4.64
6.97	2.49	6.32	3.25	7.04	5.63
8.20	2.94	7.43	4.08		

c) 1-(2-Hydroxyethyl)piperazine					
pH=8.79, F_N=0.33		pH=9.09, F_N=0.5		pH=9.39, F_N=0.67	
10^3 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}	10^3 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}	10^3 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}
0.972	0.774	0.793	0.888	0.897	1.35
2.43	1.92	1.98	2.23	2.24	3.57
3.89	2.94	3.17	3.91	3.59	5.85
5.35	4.59	4.36	4.73	4.93	8.33
6.81	5.22	5.55	6.48	6.28	10.8
8.27	8.26	6.74	7.63	7.63	13.2
9.72	8.59	7.93	9.73		

d) Morpholine					
pH=8.18, F_N=0.33		pH=8.48, F_N=0.50		pH=8.78, F_N=0.67	
10^3 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}	10^3 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}	10^3 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}
1.60	1.45	1.42	1.98	1.38	2.76
4.00	3.77	3.56	5.62	3.44	7.63
6.40	6.18	5.69	9.83	5.51	13.5
8.80	8.74	7.83	13.7	7.58	18.9
11.2	11.9	9.93	17.8	9.64	25.5
13.6	15.4	12.1	22.6	11.7	30.3
16.0	19.1	14.2	28.1		

e) Formylpiperazine					
pH=7.33, F_N=0.33		pH=7.63, F_N=0.5		pH=7.93, F_N=0.67	
10^3 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}	10^3 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}	10^3 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}
1.37	0.374	1.24	0.476	1.25	0.722
3.43	0.986	3.11	1.28	3.14	1.62
5.48	1.53	4.98	2.05	5.02	2.54
7.54	2.12	6.84	2.92	6.90	3.89
9.59	2.83	8.71	3.79	8.78	5.00
11.6	3.46	10.6	4.68	10.7	6.28
13.7	4.27	12.4	5.44	12.5	7.71

f) Piperazine + piperazinium Ion									
pH=7.75 F_N=0.00634277 (piperazine) F_N=0.98237803 (piperazinium ion)		pH=8.00 F_N=0.01127966 (piperazine) F_N=0.98242011 (piperazinium ion)		pH=8.25 F_N=0.01993791 (piperazine) F_N=0.97651657 (piperazinium ion)		pH=8.5 F_N=0.0349682 (piperazine) F_N=0.96310733 (piperazinium ion)		pH=9.00 F_N=0.10293459 (piperazine) F_N=0.89652561 (piperazinium ion)	
10^3 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}	10^3 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}	10^3 $[N]_{Tot}$/M	10^3 k_{obs}/s^{-1}	10^3 $[N]_{Tot}$/M	10^2 k_{obs}/s^{-1}	10^3 $[N]_{Tot}$/M	10^2 k_{obs}/s^{-1}
5.05	2.92	4.93	3.14	4.87	3.90	4.89	5.43	4.86	1.14
6.95	3.98	6.78	4.32	6.69	5.26	6.72	7.16	6.68	1.36

8.84	5.00	8.63	4.93	8.52	6.99	8.55	8.93	8.50	1.82
10.7	5.68	10.5	6.41	10.3	8.29	10.4	11.0	10.3	2.15
12.6	7.08	12.3	7.33	12.2	10.1	12.2	13.5	12.1	2.56

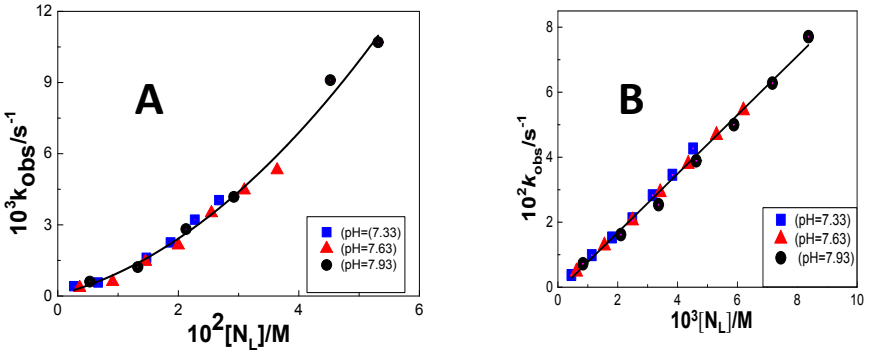
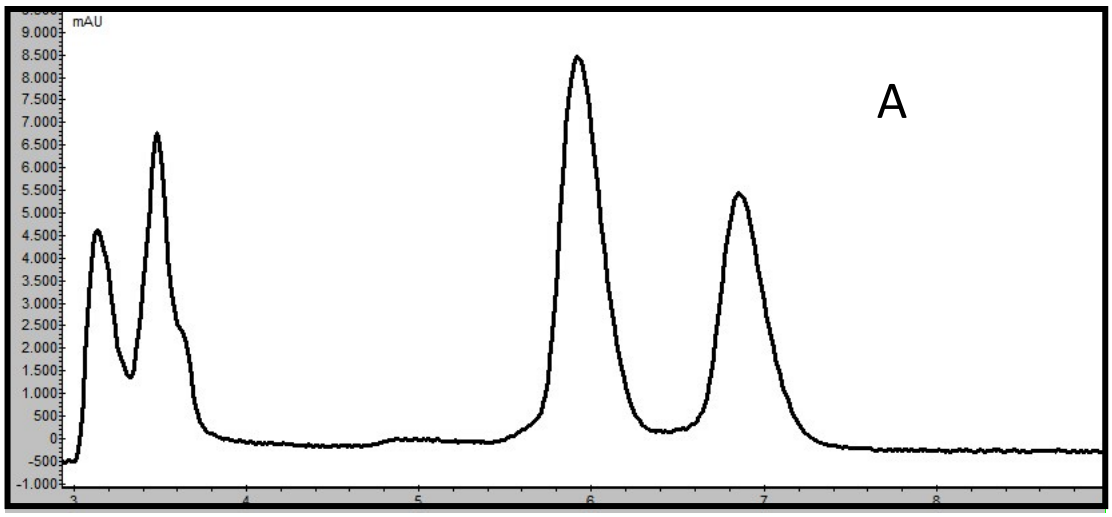


Figure S1: Plot of k_{obs} vs. free Formylpiperazine concentration, for the reactions of **1** (A) and **2** (B)



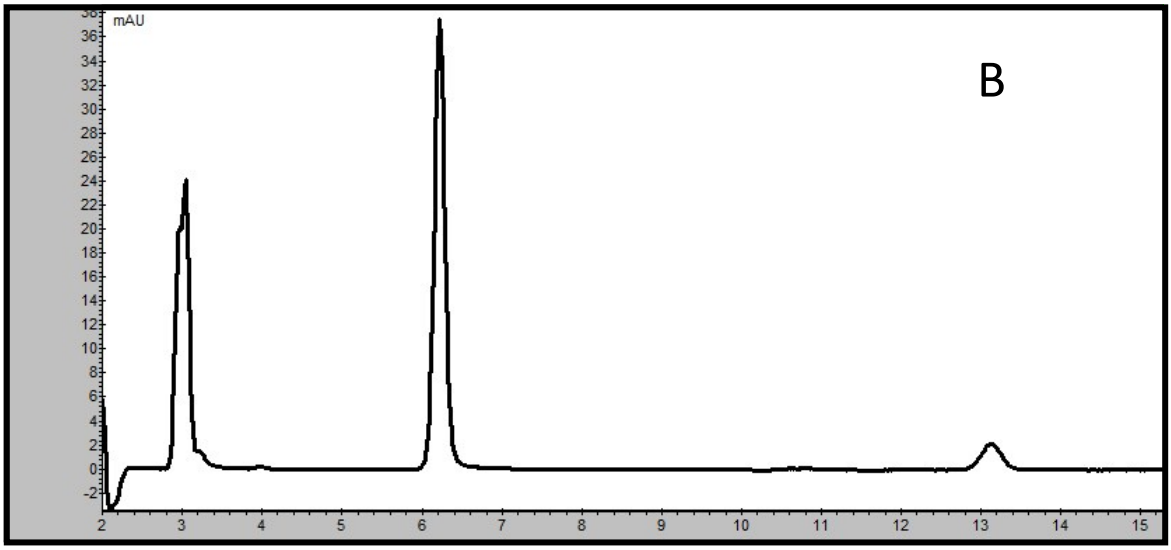


Figure S2. HPLC analysis of the reaction of **1**(A) and **3(**B) with excess of morpholine at wavelength 290 nm. The number are defined in Scheme 1 in the manuscript.

Table S3. Energy gap (kcal mol^{-1}) of intermediate T- and the corresponding TS for the reaction of compounds **1, 2, 3** and **4** with morpholine, assisted by zero, one and two explicit water molecules with ethanol as implicit solvent.

		Nucleofuge			Theoretical prediction	Experimetal results
Explicit Water	Intermediate	O-Ph-NO_2	S-Ph-H	S-Ph-Cl	O-Ph-NO_2	
0	8a	9.27	7.11	----	10%	56%
	8b	9.54	----	6.97	7.6%	47%
	9a	11.05	9.24	----	16%	100%
	9b	11.82	----	10.38	24%	100%
1	8a	5.12	5.18	----	52%	56%
	8b	5.61	----	5.60	51%	47%
	9a	4.65	19.29	----	100%	100%
	9b	4.78	----	18.71	100%	100%
2	8a	4.18	5.39	----	77%	56%
	8b	3.87	----	5,49	83%	47%
	9a	3.23	9.45	----	100%	100%
	9b	3.12	----	9.60	100%	100%

Table S4. Energy gap (kcal mol^{-1}) of intermediate T± and the corresponding TS for the reaction of compounds **1, 2, 3** and **4** with morpholine, assisted by zero, one and two explicit water molecules with ethanol as implicit solvent.

		Nucleofuge			Theoretical prediction%	Experimetal results%
Explicit Water	Intermediate	O-Ph-NO_2	S-Ph-H	S-Ph-Cl	O-Ph-NO_2	
0	6a	15.58	15.26	----	15%	56%
	6b	14.21	----	13.69	35%	47%
	7a	19.65	17.29	----	8%	100%
	7b	20.48	----	18.42	8%	100%
1	6a	5.12	5.18	----	64%	56%
	6b	5.61	----	5.60	5%	47%
	7a	4.65	19.29	----	98%	100%
	7b	4.78	----	18.71	98%	100%
2	6a	5.12	5.18	----	64%	56%
	6b	5.61	----	5.60	5%	47%
	7a	4.65	19.29	----	98%	100%
	7b	4.78	----	18.71	98%	100%

Table S5. Natural atomic charges over reactive center for the T- and TS, for the intermediate 8a.

	S[1]	C[1]	S	O	N
Intermediate	-0,511	0,159	0,193	-0,582	-0,588
Expelling S-Ph-H	-0,418	0,331	-0,148	-0,556	-0,568
Expelling O-Ph-NO2	0,099	-0,111	0,311	-0,732	-0,51

[1]Corresponds to sulfur and carbon atoms in thiocarbonyl group

Table S6. Natural atomic charges over reactive center for the T- and TS, for the intermediate 8b

	S[1]	C[1]	S	O	N
Intermediate	-0,509	0,159	0,196	-0,582	-0,588
Expelling S-Ph-Cl	-0,401	0,346	-0,168	-0,552	-0,557
Expelling O-Ph-NO2	0,101	-0,113	0,316	-0,733	-0,509

[1]Corresponds to sulfur and carbon atoms in thiocarbonyl group

Table S7. Natural atomic charges over reactive center for the T- and TS, for the intermediate 9a

	O[1]	C[1]	S	O	N
Intermediate	-0.827	0.600	0.113	-0.581	0.594
Expelling S-Ph-Cl	-0.813	0.783	-0.187	-0,555	-0,574
Expelling O-Ph-NO2	-0.651	0.584	0.269	-0.599	-0.527

[1]Corresponds to oxygen and carbon atoms in carbonyl group

Table S8. Natural atomic charges over reactive center for the T- and TS, for the intermediate 9b

	O[1]	C[1]	S	O	N
Intermediate	-0.827	0.600	0.166	-0.582	-0.595
Expelling S-Ph-H	-0.802	0.784	-0,184	-0,555	-0,574
Expelling O-Ph-NO2	-0.649	0.582	0.274	-0.734	-0.526

[1]Corresponds to oxygen and carbon atoms in carbonyl group

Table S9. 1B Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of $4BZS^-$ anion from **8a** with one explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.344656	0.526302	0.599708
2	8	0	0.751213	1.100684	-0.028732
3	6	0	-2.199650	1.883185	1.529096
4	6	0	-1.424429	2.260316	-0.744511
5	6	0	-3.586503	2.279652	1.057093
6	1	0	-1.702254	2.751094	1.967633
7	1	0	-2.276491	1.124601	2.288802
8	6	0	-2.847684	2.652282	-1.106248
9	1	0	-0.843773	3.160125	-0.534197
10	1	0	-0.972387	1.753784	-1.584255
11	1	0	-4.123441	2.769072	1.861518
12	1	0	-4.140956	1.393652	0.753207
13	1	0	-2.834935	3.415731	-1.876077
14	1	0	-3.385007	1.784877	-1.482391
15	7	0	-1.425417	1.372503	0.406889
16	8	0	-3.532738	3.192718	-0.008628
17	6	0	-2.469843	-1.416285	-0.779770
18	6	0	-3.331866	-1.255859	-1.866364
19	6	0	-3.011918	-1.867849	0.425682
20	6	0	-4.686227	-1.537245	-1.756561
21	1	0	-2.929987	-0.911650	-2.802548
22	6	0	-4.368400	-2.135329	0.537926
23	1	0	-2.367227	-2.001420	1.273395
24	6	0	-5.214819	-1.975222	-0.550913
25	1	0	-5.327202	-1.409685	-2.612853
26	1	0	-4.761882	-2.479376	1.479535
27	6	0	2.021091	0.667936	-0.052240
28	6	0	2.957259	1.677516	-0.287768
29	6	0	2.437596	-0.654176	0.066476
30	6	0	4.295903	1.380511	-0.402569
31	1	0	2.609331	2.689610	-0.372239
32	6	0	3.781948	-0.952266	-0.048242
33	1	0	1.736546	-1.436313	0.254082
34	6	0	4.700292	0.058970	-0.281095
35	1	0	5.018202	2.151997	-0.579973
36	1	0	4.112363	-1.967668	0.043311
37	7	0	6.106933	-0.264301	-0.401382
38	8	0	6.877389	0.633391	-0.604881
39	8	0	6.437313	-1.410170	-0.294167
40	16	0	-0.737720	-1.088177	-0.964905
41	8	0	0.466260	-3.640066	1.291566
42	1	0	0.094866	-3.392141	0.456717
43	1	0	0.391094	-2.849443	1.810662
44	1	0	-6.265750	-2.191014	-0.461888

45	16	0	-0.077641	-0.204344	2.164878

Total Energy (a.u.) = -2077.995253 ; **NIMAG = i148.47**

Table S10. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of $4NPO^-$ anion from **8a** with one explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.137740	0.897150	0.145499
2	8	0	1.862016	1.348160	-0.897366
3	6	0	-0.600676	3.015411	1.234757
4	6	0	-0.879815	2.901189	-1.165788
5	6	0	-1.728864	4.039560	1.285857
6	1	0	0.372274	3.529286	1.165560
7	1	0	-0.601077	2.405588	2.140752
8	6	0	-2.008670	3.922160	-1.046009
9	1	0	0.071777	3.415856	-1.365687
10	1	0	-1.081713	2.218731	-1.994261
11	1	0	-1.551125	4.767400	2.083687
12	1	0	-2.685620	3.526525	1.477546
13	1	0	-2.036436	4.567991	-1.929423
14	1	0	-2.975899	3.400371	-0.956641
15	7	0	-0.805458	2.137900	0.077609
16	8	0	-1.826459	4.790686	0.074414
17	6	0	-2.258181	-0.997929	-0.737576
18	6	0	-2.992140	-1.773471	-1.658216
19	6	0	-2.777768	-0.851730	0.562370
20	6	0	-4.202287	-2.371276	-1.307074
21	1	0	-2.607790	-1.910954	-2.665193
22	6	0	-3.991828	-1.444590	0.919220
23	1	0	-2.218681	-0.299911	1.307815
24	6	0	-4.699892	-2.196834	-0.015871
25	1	0	-4.753858	-2.964241	-2.029354
26	1	0	-4.376433	-1.327082	1.927874
27	6	0	2.925371	0.593764	-0.710119
28	6	0	4.201677	1.155838	-1.009867
29	6	0	2.891250	-0.757584	-0.253265
30	6	0	5.365706	0.420366	-0.884937
31	1	0	4.231504	2.185909	-1.351063
32	6	0	4.060022	-1.489787	-0.125157
33	1	0	1.938399	-1.212939	-0.024600

34	6	0	5.299925	-0.911213	-0.439210
35	1	0	6.330465	0.852800	-1.122078
36	1	0	4.029926	-2.520280	0.209642
37	7	0	6.507512	-1.684264	-0.307281
38	8	0	7.592102	-1.156462	-0.615060
39	8	0	6.427089	-2.855561	0.103702
40	16	0	-0.730709	-0.298369	-1.318285
41	8	0	3.238649	0.989802	2.476086
42	1	0	3.327285	1.063668	1.517053
43	1	0	2.266613	1.015426	2.625633
44	1	0	-5.632376	-2.644013	0.258727
45	16	0	0.069307	0.218138	1.541810

Total Energy (a.u.) = -2077.995348 ; **NIMAG = i149.19**

Table S11. 1B Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4-Cl-BZS$^-$ anion from **8b** with one explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.229940	0.689815	0.610059
2	8	0	1.366358	1.142935	-0.044934
3	6	0	-1.474302	2.237767	1.529461
4	6	0	-0.699236	2.488378	-0.761598
5	6	0	-2.823795	2.753974	1.064990
6	1	0	-0.890492	3.063897	1.941359
7	1	0	-1.612038	1.507132	2.307733
8	6	0	-2.083819	3.006039	-1.115297
9	1	0	-0.032773	3.333217	-0.579600
10	1	0	-0.309381	1.922423	-1.594541
11	1	0	-3.300282	3.310202	1.864054
12	1	0	-3.464198	1.918288	0.788811
13	1	0	-2.009560	3.747399	-1.903030
14	1	0	-2.706434	2.185611	-1.464353
15	7	0	-0.768167	1.630658	0.410366
16	8	0	-2.698711	3.633709	-0.022558
17	6	0	-2.089651	-1.071700	-0.697451
18	6	0	-2.947929	-0.854164	-1.777055
19	6	0	-2.654945	-1.442483	0.524774
20	6	0	-4.321195	-1.002648	-1.644315
21	1	0	-2.528546	-0.570839	-2.725881
22	6	0	-4.028967	-1.576871	0.659650

23	1	0	-2.013847	-1.617917	1.367567
24	6	0	-4.871775	-1.361189	-0.422378
25	1	0	-4.959288	-0.833742	-2.495588
26	1	0	-4.439899	-1.860714	1.613795
27	6	0	2.588909	0.590697	-0.073532
28	6	0	3.613315	1.500929	-0.344098
29	6	0	2.879557	-0.762111	0.071328
30	6	0	4.915910	1.075187	-0.467991
31	1	0	3.361958	2.539436	-0.448234
32	6	0	4.187732	-1.189475	-0.052525
33	1	0	2.110109	-1.469474	0.285785
34	6	0	5.194592	-0.275837	-0.320241
35	1	0	5.705643	1.770153	-0.672254
36	1	0	4.421444	-2.229447	0.058980
37	7	0	6.562296	-0.734322	-0.449818
38	8	0	7.411582	0.081070	-0.683727
39	8	0	6.783799	-1.903782	-0.319576
40	16	0	-0.337005	-0.914411	-0.911154
41	8	0	0.651093	-3.518370	1.390243
42	1	0	0.293077	-3.254894	0.554314
43	1	0	0.658795	-2.712778	1.891400
44	16	0	0.448602	-0.027791	2.188706
45	17	0	-6.613399	-1.545262	-0.247839

Total Energy (a.u.) = -2073.994583 ; **NIMAG = i148.30**

Table S12. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4-NPO^- anion from **8b** with one explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.95396	0.41616	0.1752
2	8	0	0.95361	1.06773	-0.95174
3	6	0	-1.79085	2.54801	0.97687
4	6	0	-2.02278	2.06473	-1.38242
5	6	0	-3.0813	3.35673	0.90616
6	1	0	-0.92223	3.20989	0.82548
7	1	0	-1.69315	2.07507	1.95641
8	6	0	-3.31399	2.87948	-1.38464
9	1	0	-1.17409	2.70605	-1.66311

10	1	0	-2.09421	1.25229	-2.10886
11	1	0	-3.0413	4.20509	1.5965
12	1	0	-3.93528	2.71499	1.17857
13	1	0	-3.44593	3.38565	-2.34623
14	1	0	-4.17578	2.21369	-1.21229
15	7	0	-1.82785	1.50058	-0.04903
16	8	0	-3.29729	3.90926	-0.3936
17	6	0	-2.70135	-1.91665	-0.42062
18	6	0	-3.24462	-2.96176	-1.19543
19	6	0	-3.28558	-1.65333	0.83259
20	6	0	-4.33436	-3.7096	-0.75009
21	1	0	-2.80536	-3.19261	-2.16207
22	6	0	-4.38029	-2.39616	1.28268
23	1	0	-2.8661	-0.8874	1.47303
24	6	0	-4.90195	-3.41628	0.48969
25	1	0	-4.73965	-4.50997	-1.36056
26	1	0	-4.81615	-2.18439	2.25443
27	6	0	2.13075	0.54284	-0.68014
28	6	0	3.29179	1.27369	-1.07075
29	6	0	2.32931	-0.71971	-0.04565
30	6	0	4.56532	0.77649	-0.86487
31	1	0	3.14413	2.23769	-1.54747
32	6	0	3.60691	-1.21246	0.16287
33	1	0	1.46872	-1.29953	0.25561
34	6	0	4.72936	-0.4738	-0.24362
35	1	0	5.44173	1.33491	-1.17162
36	1	0	3.75444	-2.17778	0.63331
37	7	0	6.05229	-0.9991	-0.02638
38	8	0	7.03065	-0.33625	-0.41762
39	8	0	6.17419	-2.10029	0.53916
40	16	0	-1.31068	-1.04921	-1.10862
41	8	0	2.33568	1.411384	2.42162
42	1	0	2.36653	1.39631	1.45628
43	1	0	1.43336	1.08146	2.63372
44	1	0	-0.70543	0.06414	1.35752
45	17	0	-6.2875	-4.3416	1.05682

Total Energy (a.u.) = -2073.994567 ; **NIMAG = i149.54**

Table S13. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4-BZS$^-$ anion from **9a** with one explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.345667	0.522692	0.690858
2	8	0	0.749917	1.088090	0.053834
3	6	0	-2.200482	1.892608	1.601292
4	6	0	-1.426104	2.237081	-0.677779
5	6	0	-3.587545	2.282101	1.124127
6	1	0	-1.703026	2.766787	2.027124
7	1	0	-2.276972	1.145021	2.371857
8	6	0	-2.849530	2.623655	-1.044611
9	1	0	-0.845472	3.139882	-0.480634
10	1	0	-0.974303	1.718570	-1.510311
11	1	0	-4.124252	2.782984	1.921620
12	1	0	-4.142008	1.391764	0.833212
13	1	0	-2.837136	3.375954	-1.825346
14	1	0	-3.386890	1.750873	-1.408049
15	7	0	-1.426589	1.365919	0.486272
16	8	0	-3.534255	3.179750	0.045365
17	6	0	-2.471128	-1.439756	-0.659784
18	6	0	-3.333552	-1.295065	-1.748268
19	6	0	-3.012728	-1.873993	0.552230
20	6	0	-4.687843	-1.574984	-1.633949
21	1	0	-2.932041	-0.964315	-2.689448
22	6	0	-4.369141	-2.139972	0.668790
23	1	0	-2.367724	-1.995290	1.401548
24	6	0	-5.215962	-1.995630	-0.421939
25	1	0	-5.329134	-1.459820	-2.491760
26	1	0	-4.762254	-2.470482	1.615389
27	6	0	2.019834	0.655181	0.036102
28	6	0	2.955808	1.661367	-0.214253
29	6	0	2.436526	-0.665043	0.173674
30	6	0	4.294444	1.362882	-0.325245
31	1	0	2.607740	2.672105	-0.313149
32	6	0	3.780870	-0.964612	0.062779
33	1	0	1.735627	-1.444474	0.372758
34	6	0	4.699021	0.043267	-0.184920
35	1	0	5.016596	2.131812	-0.513983
36	1	0	4.111428	-1.978557	0.168809
37	7	0	6.105655	-0.281554	-0.301043
38	8	0	6.875941	0.613198	-0.517705
39	8	0	6.436198	-1.425728	-0.177476
40	16	0	-0.739106	-1.114164	-0.850233
41	8	0	0.465949	-3.633210	1.442281
42	1	0	0.094233	-3.397356	0.604084
43	1	0	0.390879	-2.835210	1.949978
44	8	0	-0.126689	-0.056590	1.979804

45	1	0	-6.260450	-2.208925	-0.330010

Total Energy (a.u.) = -2154.411390; **NIMAG = i147.11**

Table S14. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4-NPO^- anion from **9a** with one explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.972328	0.413165	0.254558
2	8	0	0.922552	1.060261	-0.877121
3	6	0	-1.806657	2.546472	1.055006
4	6	0	-2.048235	2.057909	-1.302222
5	6	0	-3.097692	3.354573	0.987895
6	1	0	-0.938928	3.208329	0.898548
7	1	0	-1.704710	2.075733	2.035171
8	6	0	-3.339742	2.872187	-1.300857
9	1	0	-1.200956	2.698922	-1.587860
10	1	0	-2.122390	1.243847	-2.026573
11	1	0	-3.055136	4.204463	1.676191
12	1	0	-3.950296	2.713123	1.265276
13	1	0	-3.475874	3.376194	-2.263008
14	1	0	-4.200557	2.206375	-1.123451
15	7	0	-1.847540	1.496771	0.031577
16	8	0	-3.319296	3.904155	-0.312166
17	6	0	-2.721433	-1.926471	-0.323499
18	6	0	-3.302462	-2.937018	-1.116557
19	6	0	-3.265727	-1.697058	0.954123
20	6	0	-4.390458	-3.683658	-0.664982
21	1	0	-2.894426	-3.141530	-2.102616
22	6	0	-4.358476	-2.438781	1.410755
23	1	0	-2.816523	-0.959214	1.607248
24	6	0	-4.918034	-3.424056	0.599738
25	1	0	-4.825151	-4.457136	-1.289722
26	1	0	-4.763257	-2.253560	2.401188
27	6	0	2.101005	0.536428	-0.609270
28	6	0	3.260133	1.266838	-1.006330
29	6	0	2.302670	-0.724645	0.027163
30	6	0	4.534700	0.770553	-0.804662
31	1	0	3.110134	2.229728	-1.484548
32	6	0	3.581313	-1.216478	0.231447

33	1	0	1.443560	-1.304114	0.333277
34	6	0	4.701782	-0.478309	-0.181339
35	1	0	5.409612	1.328598	-1.116287
36	1	0	3.731158	-2.180702	0.703391
37	7	0	6.025800	-1.002653	0.031542
38	8	0	7.002279	-0.340311	-0.365233
39	8	0	6.150459	-2.102551	0.598989
40	16	0	-1.337715	-1.056481	-1.022225
41	8	0	-0.722809	0.069437	1.417655
42	8	0	2.322319	1.413202	2.487370
43	1	0	2.401812	1.369561	1.525687
44	1	0	1.360135	1.288517	2.650250
45	1	0	-5.758785	-3.985706	0.949862

Total Energy (a.u.) =-2154.434721 ; **NIMAG = i147.75**

Table S15. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4-Cl-BZS$^-$ anion from **9b** with one explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.245991	0.687639	0.699294
2	8	0	1.384615	1.137009	0.045550
3	6	0	-1.460877	2.240845	1.604861
4	6	0	-0.678366	2.478991	-0.684997
5	6	0	-2.808753	2.754815	1.133269
6	1	0	-0.878222	3.069060	2.014198
7	1	0	-1.601281	1.514428	2.386598
8	6	0	-2.061689	2.995018	-1.045940
9	1	0	-0.012312	3.324664	-0.505389
10	1	0	-0.285947	1.908492	-1.513625
11	1	0	-3.287697	3.315422	1.927791
12	1	0	-3.448440	1.917784	0.859517
13	1	0	-1.984729	3.732121	-1.837400
14	1	0	-2.683350	2.172850	-1.392592
15	7	0	-0.751264	1.627593	0.491329
16	8	0	-2.679970	3.628671	0.041421
17	6	0	-2.069747	-1.080417	-0.606217
18	6	0	-2.924488	-0.868513	-1.689739
19	6	0	-2.639062	-1.444517	0.616150
20	6	0	-4.298208	-1.016011	-1.560639

21	1	0	-2.501984	-0.590373	-2.638715
22	6	0	-4.013541	-1.577906	0.747309
23	1	0	-2.000725	-1.615547	1.461939
24	6	0	-4.852806	-1.367874	-0.338578
25	1	0	-4.933514	-0.851554	-2.414863
26	1	0	-4.427612	-1.856538	1.701633
27	6	0	2.607132	0.584384	0.023865
28	6	0	3.632603	1.492946	-0.248277
29	6	0	2.897021	-0.767684	0.176928
30	6	0	4.935499	1.066287	-0.365675
31	1	0	3.381806	2.530929	-0.358801
32	6	0	4.205497	-1.195965	0.059596
33	1	0	2.126732	-1.473732	0.392695
34	6	0	5.213412	-0.283978	-0.209771
35	1	0	5.726036	1.759990	-0.571117
36	1	0	4.438624	-2.235370	0.177440
37	7	0	6.581428	-0.743423	-0.332467
38	8	0	7.431640	0.070533	-0.568009
39	8	0	6.802259	-1.912210	-0.195231
40	16	0	-0.316386	-0.924624	-0.815102
41	8	0	0.663719	-3.516377	1.503427
42	1	0	0.308459	-3.257325	0.664943
43	1	0	0.669976	-2.708106	2.000272
44	8	0	0.420596	0.107435	1.994585
45	17	0	-6.595023	-1.550662	-0.168676

Total Energy (a.u.) = -2153.102226 ; **NIMAG = i143.07**

Table S16. 1A Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of $4NPO^-$ anion from 9**b** with one explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.245991	0.687639	0.699294
2	8	0	1.384615	1.137009	0.045550
3	6	0	-1.460877	2.240845	1.604861
4	6	0	-0.678366	2.478991	-0.684997
5	6	0	-2.808753	2.754815	1.133269
6	1	0	-0.878222	3.069060	2.014198
7	1	0	-1.601281	1.514428	2.386598
8	6	0	-2.061689	2.995018	-1.045940
9	1	0	-0.012312	3.324664	-0.505389

10	1	0	-0.285947	1.908492	-1.513625
11	1	0	-3.287697	3.315422	1.927791
12	1	0	-3.448440	1.917784	0.859517
13	1	0	-1.984729	3.732121	-1.837400
14	1	0	-2.683350	2.172850	-1.392592
15	7	0	-0.751264	1.627593	0.491329
16	8	0	-2.679970	3.628671	0.041421
17	6	0	-2.069747	-1.080417	-0.606217
18	6	0	-2.924488	-0.868513	-1.689739
19	6	0	-2.639062	-1.444517	0.616150
20	6	0	-4.298208	-1.016011	-1.560639
21	1	0	-2.501984	-0.590373	-2.638715
22	6	0	-4.013541	-1.577906	0.747309
23	1	0	-2.000725	-1.615547	1.461939
24	6	0	-4.852806	-1.367874	-0.338578
25	1	0	-4.933514	-0.851554	-2.414863
26	1	0	-4.427612	-1.856538	1.701633
27	6	0	2.607132	0.584384	0.023865
28	6	0	3.632603	1.492946	-0.248277
29	6	0	2.897021	-0.767684	0.176928
30	6	0	4.935499	1.066287	-0.365675
31	1	0	3.381806	2.530929	-0.358801
32	6	0	4.205497	-1.195965	0.059596
33	1	0	2.126732	-1.473732	0.392695
34	6	0	5.213412	-0.283978	-0.209771
35	1	0	5.726036	1.759990	-0.571117
36	1	0	4.438624	-2.235370	0.177440
37	7	0	6.581428	-0.743423	-0.332467
38	8	0	7.431640	0.070533	-0.568009
39	8	0	6.802259	-1.912210	-0.195231
40	16	0	-0.316386	-0.924624	-0.815102
41	8	0	0.663719	-3.516377	1.503427
42	1	0	0.308459	-3.257325	0.664943
43	1	0	0.669976	-2.708106	2.000272
44	8	0	0.420596	0.107435	1.994585
45	17	0	-6.595023	-1.550662	-0.168676

Total Energy (a.u.) = -2153.124425 ; NIMAG = i146.12

Table S17. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of BZS^- anion from **8a** without explicit water molecules, calculated using B3LYP/6-31G++(d,p) level theory

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.24115	-1.32283	0.81679
2	16	0	0.96622	-2.0069	2.21864
3	8	0	1.01318	-0.64838	-0.07361
4	6	0	2.10957	0.06987	0.28517
5	6	0	3.22467	-0.08705	-0.50832
6	6	0	2.10716	0.9867	1.32677
7	6	0	4.33793	0.69155	-0.24563
8	1	0	3.22569	-0.7984	-1.3077
9	6	0	3.23919	1.74309	1.56608
10	1	0	1.22841	1.08142	1.93066
11	6	0	4.37246	1.60809	0.78344
12	1	0	3.23684	2.44893	2.37636
13	6	0	-2.01304	1.10615	0.70628
14	6	0	-3.14478	1.54271	1.43756
15	6	0	-1.97857	1.43374	-0.66946
16	6	0	-4.15306	2.25719	0.84488
17	1	0	-3.18144	1.30162	2.48438
18	6	0	-2.99761	2.14619	-1.2535
19	1	0	-1.13708	1.12356	-1.25583
20	6	0	-4.10166	2.57189	-0.51509
21	1	0	-4.99715	2.57933	1.4298
22	1	0	-2.94296	2.38687	-2.30117
23	6	0	-1.58699	-3.06107	-1.91099
24	6	0	-0.34673	-2.70362	-1.1089
25	6	0	-1.70689	-2.75322	0.87714
26	6	0	-2.90195	-3.08535	0.00263
27	1	0	0.29631	-2.08317	-1.71317
28	1	0	0.19738	-3.61352	-0.84644
29	1	0	-1.3156	-3.68475	-2.75506
30	1	0	-2.04879	-2.1481	-2.28646
31	1	0	-1.25536	-3.67002	1.2506
32	1	0	-2.0159	-2.16212	1.72641
33	1	0	-3.42487	-2.17222	-0.27716
34	1	0	-3.58931	-3.72932	0.53783
35	7	0	-0.75364	-1.98488	0.09215
36	8	0	-2.51067	-3.78403	-1.15081
37	7	0	5.58209	2.40743	1.02581
38	8	0	5.62282	3.16488	1.95157
39	8	0	6.54357	2.26393	0.32767
40	1	0	5.20377	0.57805	-0.86396
41	1	0	-4.89039	3.12627	-0.97927
42	16	0	-0.75842	0.24896	1.53336

Total Energy (a.u.) = -1864.892386 ; **NIMAG = i159.59**

Table S18. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of $4NPO^-$ anion from **8a** without explicit water molecules, calculated using B3LYP/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.23289	1.28716	-0.29143
2	16	0	0.01655	0.59866	-1.84026
3	8	0	0.46334	0.02586	0.82468
4	6	0	1.31465	-0.94123	0.81829
5	6	0	2.33393	-1.09772	1.78032
6	6	0	1.23038	-1.94336	-0.17054
7	6	0	3.16526	-2.1947	1.72158
8	1	0	2.46653	-0.36767	2.5485
9	6	0	2.08122	-3.03024	-0.19217
10	1	0	0.45529	-1.84183	-0.90944
11	6	0	3.07899	-3.18003	0.75506
12	1	0	1.96802	-3.77528	-0.96132
13	6	0	-3.0572	0.13884	0.2863
14	6	0	-4.35994	0.60517	0.19385
15	6	0	-2.79876	-1.2239	0.26579
16	6	0	-5.41009	-0.28094	0.08201
17	1	0	-4.53336	1.66448	0.21114
18	6	0	-3.851	-2.1062	0.15008
19	1	0	-1.79583	-1.58318	0.33048
20	6	0	-5.16078	-1.64611	0.05861
21	1	0	-6.41861	0.08271	0.00898
22	1	0	-3.65474	-3.16233	0.13115
23	6	0	2.29172	3.86893	0.51579
24	6	0	1.74416	2.68945	-0.2665
25	6	0	-0.43039	3.69782	-0.14574
26	6	0	0.19186	4.85463	0.61737
27	1	0	1.85146	2.8705	-1.33471
28	1	0	2.2985	1.80105	-0.00971
29	1	0	2.29607	3.63219	1.57937
30	1	0	3.30537	4.08888	0.2037
31	1	0	-0.45645	3.93169	-1.21246
32	1	0	-1.44253	3.55585	0.1998
33	1	0	-0.31694	5.78007	0.37189
34	1	0	0.08949	4.67386	1.68783
35	7	0	0.35454	2.49543	0.10221
36	8	0	1.53896	5.03259	0.29086

37	7	0	4.02065	-4.30871	0.73859
38	8	0	3.94287	-5.14046	-0.11842
39	8	0	4.86507	-4.39588	1.58221
40	1	0	3.92428	-2.29019	2.46969
41	16	0	-1.96272	1.24007	0.51935
42	1	0	-5.97049	-2.34005	-0.02919

Total Energy (a.u.) = -1864.888943 ; **NIMAG = i158.25**

Table S19. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of 4-ClBZS$^-$ anion from **8b**, without explicit water molecules, calculated using B3LYP/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.25562	-1.27319	0.52408
2	16	0	0.9807	-1.95726	1.92593
3	8	0	1.02766	-0.59873	-0.36632
4	6	0	2.12404	0.11951	-0.00754
5	6	0	2.15942	1.42834	-0.43582
6	6	0	3.11947	-0.37999	0.8202
7	6	0	3.2058	2.2322	-0.01935
8	1	0	1.3933	1.80962	-1.07823
9	6	0	4.15449	0.44868	1.21122
10	1	0	3.06888	-1.40307	1.13104
11	6	0	4.21398	1.76813	0.79823
12	1	0	4.92694	0.05837	1.8482
13	6	0	-0.39822	1.86062	1.89082
14	6	0	-0.38043	3.13071	1.26411
15	6	0	-0.29476	1.84506	3.30157
16	6	0	-0.27887	4.2896	1.98869
17	1	0	-0.46047	3.15559	0.19254
18	6	0	-0.18848	3.01313	4.01675
19	1	0	-0.3077	0.90329	3.81249
20	6	0	-0.17802	4.25478	3.38146
21	1	0	-0.27391	5.23946	1.48257
22	1	0	-0.11706	2.97251	5.08995
23	6	0	-1.57251	-3.01142	-2.2037
24	6	0	-0.33226	-2.65398	-1.40161
25	6	0	-1.69241	-2.70358	0.58444
26	6	0	-2.88748	-3.03571	-0.29007
27	1	0	0.31078	-2.03353	-2.00587
28	1	0	0.21186	-3.56388	-1.13914
29	1	0	-1.30112	-3.63511	-3.04777

30	1	0	-2.03432	-2.09846	-2.57917
31	1	0	-1.24088	-3.62038	0.95789
32	1	0	-2.00142	-2.11248	1.43371
33	1	0	-3.4104	-2.12258	-0.56987
34	1	0	-3.57483	-3.67968	0.24513
35	7	0	-0.73917	-1.93523	-0.20056
36	8	0	-2.4962	-3.73439	-1.44352
37	7	0	5.30782	2.66053	1.20818
38	8	0	6.20596	2.23765	1.87671
39	8	0	5.32585	3.79648	0.83173
40	1	0	3.23342	3.25145	-0.3438
41	16	0	-0.57568	0.44435	0.91327
42	17	0	-0.04104	5.74211	4.31242

Total Energy (a.u.) = -1863.723169 ; **NIMAG = i160.33**

Table S20. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of $4NPO^-$ anion from **8b** without explicit water molecules, calculated using B3LYP/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.23289	1.28716	-0.29143
2	16	0	0.01655	0.59866	-1.84026
3	8	0	0.46095	0.03019	0.82086
4	6	0	1.37619	-0.87639	0.84297
5	6	0	2.32775	-1.00785	1.87553
6	6	0	1.43816	-1.83587	-0.18887
7	6	0	3.23624	-2.04284	1.83871
8	1	0	2.3498	-0.30628	2.6805
9	6	0	2.36252	-2.86118	-0.18679
10	1	0	0.71635	-1.75299	-0.98209
11	6	0	3.29334	-2.98673	0.8296
12	1	0	2.3609	-3.57635	-0.99178
13	6	0	-3.0572	0.13884	0.2863
14	6	0	-4.36574	0.59721	0.25869
15	6	0	-2.79002	-1.22003	0.20645
16	6	0	-5.41299	-0.29308	0.15294
17	1	0	-4.54592	1.65369	0.32111
18	6	0	-3.83952	-2.10638	0.09706
19	1	0	-1.78286	-1.57294	0.22122
20	6	0	-5.15502	-1.65434	0.07046
21	1	0	-6.42606	0.06446	0.13021
22	1	0	-3.6366	-3.15944	0.0323

23	6	0	2.27207	3.9373	0.33526
24	6	0	1.66614	2.78571	-0.44556
25	6	0	-0.50784	3.66917	0.05778
26	6	0	0.17006	4.80333	0.80736
27	1	0	1.60879	3.04296	-1.50193
28	1	0	2.28874	1.91224	-0.33645
29	1	0	2.44144	3.63069	1.36703
30	1	0	3.21924	4.23007	-0.10113
31	1	0	-0.699	3.972	-0.97421
32	1	0	-1.4519	3.45195	0.5327
33	1	0	-0.40743	5.71533	0.70564
34	1	0	0.23261	4.54648	1.86526
35	7	0	0.35454	2.49543	0.10221
36	8	0	1.44647	5.07258	0.30611
37	7	0	4.31057	-4.04785	0.84234
38	8	0	4.35697	-4.84307	-0.05086
39	8	0	5.09234	-4.11655	1.74591
40	1	0	3.94093	-2.12121	2.64007
41	16	0	-1.96272	1.24007	0.51935
42	17	0	-6.48317	-2.80098	-0.06687

Total Energy (a.u.) = -1863.719073 ; **NIMAG = i159.81**

Table S21. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of BZS^- anion from **9a** without explicit water molecules, calculated using B3LYP/6-31G++(d,p) level theory

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.1121	1.14965	0.74829
2	8	0	-0.88414	0.47519	-0.14211
3	6	0	-1.98052	-0.24305	0.21667
4	6	0	-3.09563	-0.08613	-0.57682
5	6	0	-1.97811	-1.15989	1.25827
6	6	0	-4.20888	-0.86473	-0.31413
7	1	0	-3.09665	0.62521	-1.37619
8	6	0	-3.11014	-1.91628	1.49758
9	1	0	-1.09936	-1.2546	1.86217
10	6	0	-4.24341	-1.78127	0.71495
11	1	0	-3.10779	-2.62211	2.30786
12	6	0	1.92091	-1.04459	0.91178
13	6	0	3.05266	-1.48115	1.64306
14	6	0	1.88644	-1.37218	-0.46396

15	6	0	4.06093	-2.19564	1.05038
16	1	0	3.08932	-1.24006	2.68988
17	6	0	2.90549	-2.08463	-1.04801
18	1	0	1.04496	-1.062	-1.05034
19	6	0	4.00953	-2.51033	-0.3096
20	1	0	4.90503	-2.51777	1.6353
21	1	0	2.85084	-2.32531	-2.09567
22	6	0	1.71604	2.88788	-1.97949
23	6	0	0.47578	2.53044	-1.1774
24	6	0	1.83593	2.58004	0.80865
25	6	0	3.031	2.91217	-0.06587
26	1	0	-0.16726	1.90998	-1.78167
27	1	0	-0.06833	3.44034	-0.91493
28	1	0	1.44465	3.51156	-2.82356
29	1	0	2.17784	1.97491	-2.35496
30	1	0	1.38441	3.49683	1.1821
31	1	0	2.14495	1.98893	1.65791
32	1	0	3.55392	1.99904	-0.34566
33	1	0	3.71836	3.55614	0.46934
34	7	0	0.88269	1.81169	0.02365
35	8	0	2.63972	3.61084	-1.21931
36	8	0	-0.71677	1.72012	1.91736
37	7	0	-5.45304	-2.58061	0.95731
38	8	0	-6.40477	-2.45698	0.24223
39	8	0	-5.46805	-3.39058	1.83832
40	1	0	-5.07472	-0.75123	-0.93245
41	1	0	4.79827	-3.06471	-0.77377
42	16	0	0.78494	-0.26846	1.66064

Total Energy (a.u.) = -1866.713347508 ; **NIMAG = i161.89**

Table S22. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of $4NPO^-$ anion from **9a** without explicit water molecules, calculated using B3LYP/6-31G++(d,p) level theory

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.23289	1.28716	-0.29143
2	8	0	0.6464	0.243	1.02598
3	6	0	1.28162	-0.87696	0.97871
4	6	0	2.31849	-1.15468	0.06401
5	6	0	0.97719	-1.89567	1.90536
6	6	0	2.97613	-2.36373	0.1243

7	1	0	2.59073	-0.43502	-0.67669
8	6	0	1.6633	-3.0932	1.9354
9	1	0	0.19188	-1.69835	2.61347
10	6	0	2.68108	-3.36037	1.03652
11	1	0	1.40111	-3.83464	2.67092
12	6	0	-2.99627	0.16779	0.27675
13	6	0	-4.29901	0.63413	0.1843
14	6	0	-2.73783	-1.19495	0.25624
15	6	0	-5.34917	-0.25198	0.07246
16	1	0	-4.47243	1.69344	0.2016
17	6	0	-3.79007	-2.07724	0.14053
18	1	0	-1.7349	-1.55422	0.32093
19	6	0	-5.09986	-1.61715	0.04906
20	1	0	-6.35768	0.11167	-5.7273
21	1	0	-3.59381	-3.13338	0.1216
22	6	0	2.29172	3.86893	0.51579
23	6	0	1.74416	2.68945	-0.2665
24	6	0	-0.43039	3.69782	-0.14574
25	6	0	0.19186	4.85463	0.61737
26	1	0	1.85146	2.8705	-1.33471
27	1	0	2.2985	1.80105	-0.00971
28	1	0	2.29607	3.63219	1.57937
29	1	0	3.30537	4.08888	0.2037
30	1	0	-0.45645	3.93169	-1.21246
31	1	0	-1.44253	3.55585	0.1998
32	1	0	-0.31694	5.78007	0.37189
33	1	0	0.08949	4.67386	1.68783
34	7	0	0.35454	2.49543	0.10221
35	8	0	1.53896	5.03259	0.29086
36	7	0	3.42307	-4.62937	1.03785
37	8	0	3.13612	-5.48951	1.81897
38	8	0	4.3141	-4.80238	0.25782
39	1	0	3.76352	-2.54265	-0.57777
40	8	0	-0.02584	0.71565	-1.57707
41	16	0	-1.92968	1.24097	0.50387
42	1	0	-5.90957	-2.31109	-0.03874

Total Energy (a.u.) = -1866.710463 ; **NIMAG = i160.93**

Table S23. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4-ClBZS$^-$ anion from **9b** without explicit water molecules, calculated using B3LYP/6-31G++(d,p) level theory

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-0.1121	1.14965	0.74829
2	8	0	-0.88414	0.47519	-0.14211
3	6	0	-1.98052	-0.24305	0.21667
4	6	0	-3.18731	0.20532	-0.27356
5	6	0	-1.90955	-1.41692	0.95324
6	6	0	-4.3234	-0.54217	-0.01836
7	1	0	-3.24007	1.11353	-0.83692
8	6	0	-3.06537	-2.13528	1.19598
9	1	0	-0.95878	-1.73647	1.32712
10	6	0	-4.29067	-1.70978	0.71364
11	1	0	-3.00884	-3.04141	1.77086
12	6	0	0.70871	-0.85722	3.10979
13	6	0	0.86377	-2.26314	3.18441
14	6	0	0.21147	-0.20915	4.26475
15	6	0	0.5576	-2.9617	4.32312
16	1	0	1.24281	-2.76669	2.31375
17	6	0	-0.0966	-0.92071	5.39874
18	1	0	0.08322	0.85453	4.24828
19	6	0	0.06801	-2.30461	5.45438
20	1	0	0.69212	-4.02922	4.34948
21	1	0	-0.46777	-0.40145	6.26541
22	6	0	1.78489	2.73329	-2.02621
23	6	0	0.51686	2.36059	-1.27618
24	6	0	1.71064	2.73743	0.78045
25	6	0	2.94132	3.07347	-0.04161
26	1	0	-0.02807	1.6269	-1.84921
27	1	0	-0.11378	3.24424	-1.15648
28	1	0	1.53325	3.23773	-2.95211
29	1	0	2.34274	1.82754	-2.26324
30	1	0	1.16288	3.64763	1.01576
31	1	0	1.9968	2.269	1.71041
32	1	0	3.55249	2.18298	-0.17958
33	1	0	3.53388	3.82679	0.46335
34	7	0	0.88269	1.81169	0.02365
35	8	0	2.58885	3.60891	-1.29091
36	8	0	-0.71972	1.7229	1.92306
37	7	0	-5.52693	-2.46508	0.96281
38	8	0	-6.56449	-2.08145	0.50593
39	8	0	-5.4876	-3.48983	1.57988
40	1	0	-5.26179	-0.20137	-0.40332
41	16	0	1.11735	-0.11619	1.79166
42	17	0	-0.33159	-3.20154	6.915

Total Energy (a.u.) = -1866.497530892 ; **NIMAG = i162.17**

Table S24. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4-NPO^- anion from **9b** without explicit water molecules, calculated using B3LYP/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.23289	1.28716	-0.29143
2	8	0	0.627	0.22569	1.00018
3	6	0	1.28157	-0.8829	0.94917
4	6	0	2.34809	-1.12591	0.059
5	6	0	0.96802	-1.92455	1.84683
6	6	0	3.02351	-2.32535	0.11439
7	1	0	2.62915	-0.38743	-0.65954
8	6	0	1.67256	-3.11142	1.87301
9	1	0	0.16004	-1.75383	2.53609
10	6	0	2.71938	-3.3445	0.99833
11	1	0	1.40204	-3.87142	2.58625
12	6	0	-2.99627	0.16779	0.27675
13	6	0	-4.304	0.62769	0.23815
14	6	0	-2.73042	-1.19188	0.20698
15	6	0	-5.35176	-0.26188	0.13138
16	1	0	-4.48315	1.68477	0.29289
17	6	0	-3.78041	-2.07754	0.09654
18	1	0	-1.72385	-1.54601	0.23022
19	6	0	-5.09511	-1.62396	0.05894
20	1	0	-6.3642	0.09683	0.10012
21	1	0	-3.5785	-3.13124	0.03956
22	6	0	2.2792	3.92052	0.37614
23	6	0	1.68681	2.76276	-0.40595
24	6	0	-0.49275	3.67736	0.01011
25	6	0	0.17242	4.81642	0.76366
26	1	0	1.66752	3.00323	-1.46764
27	1	0	2.29565	1.88464	-0.26206
28	1	0	2.4107	3.6291	1.41779
29	1	0	3.24358	4.19603	-0.03295
30	1	0	-0.64606	3.96523	-1.03243
31	1	0	-1.45445	3.47799	0.45659
32	1	0	-0.39116	5.7327	0.62806
33	1	0	0.19685	4.57631	1.82705
34	7	0	0.35454	2.49543	0.10221
35	8	0	1.46773	5.06386	0.30116
36	7	0	3.48174	-4.60136	0.99601
37	8	0	3.18715	-5.48131	1.75181
38	8	0	4.39701	-4.74467	0.23834
39	1	0	3.8331	-2.47776	-0.56842

40	8	0	-0.02584	0.71565	-1.57707
41	16	0	-1.92968	1.24097	0.50387
42	17	0	-6.42391	-2.7697	-0.07957

Total Energy (a.u.) = -1866.495236 ; **NIMAG = i163.23**

Table S25. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of BZS- anion from **8a** with two explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.76511	0.63599	0.18884
2	8	0	0.13725	1.34861	-0.51027
3	6	0	-2.74697	1.96541	0.87423
4	6	0	-2.27257	1.74532	-1.5733
5	6	0	-4.16669	2.36039	0.48151
6	1	0	-2.1008	2.84125	0.97329
7	1	0	-2.74319	1.36893	1.78856
8	6	0	-3.72994	2.12976	-1.81098
9	1	0	-1.63487	2.62901	-1.56734
10	1	0	-1.90962	1.02967	-2.31256
11	1	0	-4.55098	3.07766	1.21043
12	1	0	-4.81804	1.47479	0.48853
13	1	0	-3.80524	2.67603	-2.75388
14	1	0	-4.3604	1.23142	-1.87326
15	7	0	-2.15206	1.08819	-0.21897
16	8	0	-4.20532	2.9996	-0.78918
17	6	0	-0.48739	-2.45918	-0.47124
18	6	0	-0.33091	-2.5684	0.92499
19	6	0	-0.30783	-3.62555	-1.24401
20	6	0	-0.00797	-3.79305	1.51958
21	1	0	-0.46241	-1.69268	1.55095
22	6	0	0.01051	-4.84514	-0.64543
23	1	0	-0.41928	-3.56522	-2.32215
24	6	0	0.16426	-4.94032	0.74222
25	1	0	0.10947	-3.84475	2.59952
26	1	0	0.14235	-5.72603	-1.26877
27	6	0	1.50647	1.11609	-0.34463
28	6	0	2.31805	2.24404	-0.46862
29	6	0	2.02956	-0.16258	-0.15303
30	6	0	3.69927	2.09812	-0.38622
31	1	0	1.8679	3.21755	-0.62834
32	6	0	3.41291	-0.30547	-0.06915
33	1	0	1.37631	-1.02129	-0.08249
34	6	0	4.22637	0.82203	-0.18415

35	1	0	4.36329	2.94863	-0.47402
36	1	0	3.86096	-1.28038	0.07671
37	7	0	5.68694	0.66396	-0.0913
38	8	0	6.38152	1.67581	-0.20995
39	8	0	6.13108	-0.46843	0.10124
40	16	0	-0.89632	-0.91762	-1.28328
41	8	0	-3.55902	-0.60454	2.64917
42	1	0	-2.64151	-0.37822	2.84148
43	1	0	-3.61229	-0.80774	1.70236
44	8	0	-3.68139	-0.94999	-0.21659
45	1	0	-4.21894	-1.74809	-0.28983
46	1	0	-2.90776	-0.9924	-0.84499
47	1	0	0.415	-5.88969	1.20624
48	16	0	-0.57409	-0.10937	1.55323

Total Energy (a.u.) = -2400.926847 ; **NIMAG = i144.07**

Table S26. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4NPO- anion from **8a** with two explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.91589	-0.71756	0.92134
2	8	0	-0.20405	-0.48251	-0.81222
3	6	0	2.64482	-0.54817	-1.03732
4	6	0	3.12668	-1.92773	0.94278
5	6	0	3.61262	-1.43427	-1.81634
6	1	0	3.17981	0.28293	-0.58147
7	1	0	1.83697	-0.1719	-1.66138
8	6	0	4.09917	-2.72268	0.07425
9	1	0	3.61812	-1.08207	1.42871
10	1	0	2.65791	-2.56235	1.6954
11	1	0	4.09955	-0.83336	-2.58776
12	1	0	3.07726	-2.26334	-2.30122
13	1	0	4.93512	-3.05756	0.6934
14	1	0	3.59747	-3.61141	-0.34031
15	7	0	2.01936	-1.36038	0.07774
16	8	0	4.64527	-1.93518	-0.97239

17	6	0	1.72996	2.11834	0.3702
18	6	0	2.93435	2.79352	0.61646
19	6	0	0.91347	2.50286	-0.70148
20	6	0	3.32864	3.84208	-0.21922
21	1	0	3.55585	2.50372	1.45858
22	6	0	1.32546	3.53997	-1.54112
23	1	0	-0.02279	1.99055	-0.88283
24	6	0	2.52913	4.21145	-1.3036
25	1	0	4.26011	4.36438	-0.02211
26	1	0	0.69377	3.83213	-2.37486
27	6	0	-1.52004	-0.33148	-0.6975
28	6	0	-2.37251	-0.95527	-1.64973
29	6	0	-2.12471	0.45078	0.32006
30	6	0	-3.74814	-0.79365	-1.60248
31	1	0	-1.92706	-1.54099	-2.44877
32	6	0	-3.50406	0.60117	0.37653
33	1	0	-1.51065	0.93752	1.06667
34	6	0	-4.31128	-0.01842	-0.58214
35	1	0	-4.39408	-1.25813	-2.33779
36	1	0	-3.96267	1.20007	1.15422
37	7	0	-5.75663	0.14438	-0.52125
38	8	0	-6.44246	-0.40758	-1.39093
39	8	0	-6.22926	0.82486	0.39705
40	16	0	1.20266	0.91004	1.60835
41	8	0	0.53288	-2.97114	-1.58669
42	1	0	-0.05725	-3.66628	-1.26758
43	1	0	0.03591	-2.1199	-1.49371
44	8	0	-1.79755	0.34432	4.04522
45	1	0	-1.26933	-0.24517	3.4825
46	1	0	-2.6838	-0.03796	4.05128
47	16	0	0.08232	-1.76358	1.91991
48	1	0	2.83689	5.02368	-1.95524

Total Energy (a.u.) = -2400.928776 ; **NIMAG = i144.61**

Table S27. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4-Cl-BZS- anion from

8b with two explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.76389	0.63498	0.1302
2	8	0	0.13847	1.34759	-0.56891
3	6	0	-2.74575	1.9644	0.8156
4	6	0	-2.27135	1.7443	-1.63194
5	6	0	-4.16547	2.35937	0.42287
6	1	0	-2.09958	2.84023	0.91465
7	1	0	-2.74196	1.36791	1.72992
8	6	0	-3.72871	2.12874	-1.86961
9	1	0	-1.63364	2.62799	-1.62598
10	1	0	-1.90839	1.02865	-2.3712
11	1	0	-4.54975	3.07664	1.15179
12	1	0	-4.81682	1.47377	0.42989
13	1	0	-3.80401	2.67501	-2.81252
14	1	0	-4.35918	1.23041	-1.9319
15	7	0	-2.15084	1.08717	-0.27761
16	8	0	-4.20409	2.99859	-0.84781
17	6	0	-0.42922	-2.61015	-1.66222
18	6	0	0.45454	-2.88085	-2.72596
19	6	0	-0.92157	-3.70675	-0.92406
20	6	0	0.82731	-4.19331	-3.03594
21	1	0	0.8539	-2.06245	-3.3148
22	6	0	-0.54355	-5.0134	-1.23519
23	1	0	-1.60698	-3.52332	-0.10246
24	6	0	0.33402	-5.2692	-2.29477
25	1	0	1.5085	-4.37042	-3.86501
26	1	0	-0.94055	-5.83706	-0.64708
27	6	0	1.5077	1.11508	-0.40327
28	6	0	2.31928	2.24302	-0.52726
29	6	0	2.03079	-0.1636	-0.21167
30	6	0	3.7005	2.09711	-0.44486
31	1	0	1.86913	3.21653	-0.68697
32	6	0	3.41414	-0.30648	-0.12779
33	1	0	1.37754	-1.02231	-0.14113
34	6	0	4.2276	0.82101	-0.24279
35	1	0	4.36452	2.94762	-0.53265
36	1	0	3.86219	-1.28139	0.01807
37	7	0	5.68817	0.66294	-0.14994
38	8	0	6.38275	1.67479	-0.26859
39	8	0	6.13231	-0.46944	0.0426
40	16	0	-0.94126	-0.95183	-1.22535

41	8	0	-3.5671	-0.60275	2.65739
42	1	0	-2.63493	-0.80414	2.51414
43	1	0	-3.98875	-0.55881	1.78512
44	8	0	-3.77001	-0.94623	-0.20058
45	1	0	-3.95641	-1.89082	-0.26614
46	1	0	-2.95602	-0.7145	-0.7287
47	17	0	0.80539	-6.91864	-2.68815
48	8	0	-0.57413	-0.10543	1.48553

Total Energy (a.u.) = -2400.117797 ; **NIMAG = i147.56**

Table S28. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4NPO- anion from **8b** with two explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.92336	-0.71912	0.9277
2	8	0	-0.20698	-0.48191	-0.81674
3	6	0	2.65227	-0.54973	-1.03095
4	6	0	3.13415	-1.92929	0.94914
5	6	0	3.62009	-1.43583	-1.80998
6	1	0	3.18728	0.28136	-0.57511
7	1	0	1.84444	-0.17346	-1.65501
8	6	0	4.10664	-2.72425	0.08061
9	1	0	3.62560	-1.08363	1.43507
10	1	0	2.66538	-2.56392	1.70176
11	1	0	4.10703	-0.83492	-2.58139
12	1	0	3.08473	-2.26491	-2.29486
13	1	0	4.94259	-3.05913	0.69977
14	1	0	3.60495	-3.61297	-0.33395
15	7	0	2.02683	-1.36194	0.0841
16	8	0	4.65275	-1.93674	-0.96603
17	6	0	1.82007	2.09502	0.3936
18	6	0	3.02483	2.74828	0.69165
19	6	0	1.06338	2.48627	-0.7188
20	6	0	3.47958	3.78134	-0.13255
21	1	0	3.59963	2.45365	1.56471
22	6	0	1.53575	3.50743	-1.54602
23	1	0	0.12668	1.99102	-0.94053

24	6	0	2.74016	4.15691	-1.25669
25	1	0	4.41105	4.28673	0.10462
26	1	0	0.95045	3.80469	-2.41121
27	6	0	-1.52296	-0.33087	-0.70202
28	6	0	-2.37544	-0.95466	-1.65425
29	6	0	-2.12763	0.45139	0.31555
30	6	0	-3.75107	-0.79304	-1.60699
31	1	0	-1.92998	-1.54037	-2.45328
32	6	0	-3.50698	0.60178	0.37201
33	1	0	-1.51357	0.93813	1.06215
34	6	0	-4.3142	-0.01781	-0.58665
35	1	0	-4.3970	-1.25751	-2.3423
36	1	0	-3.96564	1.20068	1.14971
37	7	0	-5.75952	0.14499	-0.52576
38	8	0	-6.44538	-0.40697	-1.39545
39	8	0	-6.23218	0.82547	0.39254
40	16	0	1.21013	0.90847	1.61471
41	8	0	0.52833	-2.97019	-1.58854
42	1	0	-0.05215	-3.66965	-1.26128
43	1	0	0.03543	-2.12014	-1.46731
44	8	0	-1.79755	0.34432	4.04522
45	1	0	-1.32796	-0.32984	3.52736
46	1	0	-2.73364	0.20053	3.85899
47	16	0	0.08980	-1.76514	1.92627
48	1	0	3.31521	5.45381	-2.29831

Total Energy (a.u.) = -2400.120378 ; **NIMAG = i145.85**

Table S29. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of BZS- anion from **9a** with two explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.92861	-0.66381	0.46717
2	8	0	0.27587	-1.66834	-0.44535
3	6	0	3.23198	-1.91543	0.85901
4	6	0	2.62058	-1.28662	-1.48816
5	6	0	4.68875	-1.84964	0.41142
6	1	0	2.82715	-2.92466	0.74622
7	1	0	3.12651	-1.55976	1.88593
8	6	0	4.11685	-1.24323	-1.78161
9	1	0	2.21664	-2.27864	-1.69246
10	1	0	2.06341	-0.53516	-2.05236
11	1	0	5.26584	-2.58835	0.97209
12	1	0	5.10364	-0.85452	0.62607
13	1	0	4.28463	-1.53664	-2.82024
14	1	0	4.51222	-0.22605	-1.642
15	7	0	2.39969	-0.9928	-0.02166
16	8	0	4.82988	-2.16767	-0.96779
17	6	0	-0.51582	2.27038	0.34516
18	6	0	-0.80439	2.17317	1.72211
19	6	0	-1.17574	3.27667	-0.39091
20	6	0	-1.71274	3.04236	2.3333
21	1	0	-0.30871	1.41174	2.31753
22	6	0	-2.08399	4.14111	0.22248
23	1	0	-0.96005	3.37983	-1.44733
24	6	0	-2.36107	4.03128	1.58914
25	1	0	-1.9124	2.94299	3.39764
26	1	0	-2.57521	4.90823	-0.37106
27	6	0	-1.12233	-1.67719	-0.24021
28	6	0	-1.72532	-2.92013	-0.07269
29	6	0	-1.83588	-0.48419	-0.29554
30	6	0	-3.11114	-2.97592	0.05983
31	1	0	-1.12314	-3.82164	-0.04815
32	6	0	-3.22169	-0.54247	-0.15859
33	1	0	-1.31699	0.45508	-0.4597
34	6	0	-3.8349	-1.78365	0.01764
35	1	0	-3.62901	-3.91704	0.19498
36	1	0	-3.82113	0.35853	-0.19228
37	7	0	-5.30221	-1.8415	0.16187
38	8	0	-5.81782	-2.94948	0.32156
39	8	0	-5.92387	-0.78061	0.11584
40	16	0	0.63114	1.16027	-0.45575
41	8	0	3.90393	0.54316	3.03318
42	1	0	3.48443	0.6993	3.88792
43	1	0	3.34472	0.97747	2.36378

44	8	0	3.14558	1.53747	0.51744
45	1	0	3.77274	2.17617	0.15124
46	1	0	2.23388	1.73544	0.10838
47	1	0	-3.06698	4.70568	2.06489
48	8	0	0.80878	-0.54426	1.65014

Total Energy (a.u.) = -2409.438161027; **NIMAG = i142.25**

Table S30. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4NPO- anion from **9b** with two explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.89983	-0.69693	0.95697
2	8	0	-0.19942	-0.48348	-0.80505
3	6	0	2.62874	-0.52753	-1.00168
4	6	0	3.11062	-1.90709	0.97841
5	6	0	3.59657	-1.41364	-1.78071
6	1	0	3.16376	0.30356	-0.54584
7	1	0	1.82091	-0.15127	-1.62574
8	6	0	4.08311	-2.70205	0.10988
9	1	0	3.60207	-1.06144	1.46434
10	1	0	2.64186	-2.54172	1.73103
11	1	0	4.0835	-0.81273	-2.55212
12	1	0	3.06121	-2.24271	-2.26559
13	1	0	4.91907	-3.03693	0.72904
14	1	0	3.58142	-3.59078	-0.30468
15	7	0	2.0033	-1.33975	0.11337
16	8	0	4.62922	-1.91454	-0.93676
17	6	0	1.64357	2.15605	0.39472
18	6	0	2.84534	2.84998	0.59766
19	6	0	0.77847	2.5338	-0.64063
20	6	0	3.18826	3.91068	-0.24534
21	1	0	3.50489	2.56516	1.41211
22	6	0	1.13907	3.58339	-1.48837
23	1	0	-0.1555	2.00685	-0.78822
24	6	0	2.33988	4.27366	-1.29416
25	1	0	4.11801	4.44743	-0.08174
26	1	0	0.46969	3.87034	-2.29403
27	6	0	-1.5154	-0.33246	-0.69032
28	6	0	-2.36788	-0.95625	-1.64256
29	6	0	-2.12007	0.44981	0.32724

30	6	0	-3.7435	-0.79462	-1.5953
31	1	0	-1.92242	-1.54196	-2.44159
32	6	0	-3.49942	0.6002	0.3837
33	1	0	-1.50601	0.93654	1.07385
34	6	0	-4.30664	-0.01939	-0.57496
35	1	0	-4.38944	-1.2591	-2.33061
36	1	0	-3.95804	1.19909	1.1614
37	7	0	-5.75196	0.14341	-0.51407
38	8	0	-6.43782	-0.40855	-1.38375
39	8	0	-6.22462	0.82389	0.40423
40	16	0	1.18661	0.93067	1.64398
41	8	0	0.53288	-2.97114	-1.58669
42	1	0	-0.03921	-3.71158	-1.34635
43	1	0	0.06416	-2.15034	-1.29202
44	8	0	-1.7756	0.32261	4.0193
45	1	0	-1.17598	-0.11097	3.3903
46	1	0	-2.60907	-0.15892	3.9481
47	1	0	2.60764	5.09536	-1.95156
48	17	0	0.24998	-1.51241	1.73547

Total Energy (a.u.) = -2409.448073 ; **NIMAG = i144.32**

Table S31. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4-Cl-BZS- anion from **9b** with two explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.81025	0.62211	0.14503
2	8	0	0.09211	1.33473	-0.55407
3	6	0	-2.79211	1.95153	0.83043
4	6	0	-2.31771	1.73144	-1.61711
5	6	0	-4.21183	2.34651	0.43771
6	1	0	-2.14594	2.82737	0.92948
7	1	0	-2.78833	1.35505	1.74475

8	6	0	-3.77508	2.11588	-1.85478
9	1	0	-1.6801	2.61513	-1.61115
10	1	0	-1.95475	1.01579	-2.35637
11	1	0	-4.59612	3.06378	1.16663
12	1	0	-4.86318	1.4609	0.44472
13	1	0	-3.85038	2.66215	-2.79769
14	1	0	-4.40554	1.21754	-1.91707
15	7	0	-2.1972	1.0743	-0.26278
16	8	0	-4.25046	2.98572	-0.83298
17	6	0	0.06389	-2.07278	-2.22179
18	6	0	0.32121	-1.90835	-3.59751
19	6	0	0.57853	-3.22532	-1.59201
20	6	0	1.0613	-2.85819	-4.31001
21	1	0	-0.05795	-1.03387	-4.11473
22	6	0	1.31918	-4.16756	-2.30662
23	1	0	0.38978	-3.37574	-0.53362
24	6	0	1.56698	-3.9933	-3.67282
25	1	0	1.24033	-2.70492	-5.3717
26	1	0	1.7022	-5.04537	-1.79219
27	6	0	1.46134	1.10221	-0.38844
28	6	0	2.27292	2.23015	-0.51242
29	6	0	1.98443	-0.17646	-0.19684
30	6	0	3.65413	2.08424	-0.43003
31	1	0	1.82276	3.20367	-0.67214
32	6	0	3.36777	-0.31935	-0.11296
33	1	0	1.33117	-1.03517	-0.12629
34	6	0	4.18124	0.80815	-0.22796
35	1	0	4.31815	2.93475	-0.51782
36	1	0	3.81582	-1.29426	0.03291
37	7	0	5.6418	0.65008	-0.1351
38	8	0	6.33638	1.66193	-0.25376
39	8	0	6.08594	-0.48231	0.05743
40	16	0	-0.87931	-0.89126	-1.26395
41	8	0	-3.51862	-0.59643	2.60293
42	1	0	-2.56904	-0.63243	2.43857
43	1	0	-3.96045	-0.61682	1.73983
44	8	0	-3.69964	-0.94723	-0.1886
45	1	0	-4.22481	-1.75456	-0.24944
46	1	0	-2.83664	-1.05562	-0.67716
47	17	0	2.49735	-5.18575	-4.57286
48	8	0	-0.64483	-0.02337	1.32659

Total Energy (a.u.) = 2409.141067 ; **NIMAG = 144.95**

Table S32. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4NPO- anion from **9b** with two explicit water molecule, calculated using B3LYP/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.331210	-0.044060	0.073407
2	8	0	-0.797816	1.897521	-0.072502
3	6	0	-3.222096	1.082411	-1.383394
4	6	0	-3.742989	-0.783248	0.152574
5	6	0	-4.698635	1.466172	-1.311330
6	1	0	-3.052037	0.377109	-2.199206
7	1	0	-2.571909	1.949334	-1.493822
8	6	0	-5.193959	-0.311341	0.133001
9	1	0	-3.549877	-1.513082	-0.637369
10	1	0	-3.484691	-1.189753	1.130476
11	1	0	-5.004917	1.902343	-2.264972
12	1	0	-4.860921	2.212479	-0.518120
13	1	0	-5.856725	-1.174722	0.227424
14	1	0	-5.378821	0.363427	0.982089
15	7	0	-2.831357	0.393766	-0.103361
16	8	0	-5.523385	0.327974	-1.095036
17	6	0	0.406831	-2.003271	-0.875228
18	6	0	-0.096109	-3.309539	-0.833375
19	6	0	1.733854	-1.755183	-0.504765
20	6	0	0.715485	-4.363539	-0.412843
21	1	0	-1.120138	-3.507252	-1.132728
22	6	0	2.552303	-2.803037	-0.081541
23	1	0	2.125432	-0.744391	-0.538422
24	6	0	2.033861	-4.098143	-0.038342
25	1	0	0.331738	-5.377134	-0.377967
26	1	0	3.579796	-2.615417	0.209733
27	6	0	0.504804	2.151870	-0.029983
28	6	0	1.109475	2.907192	-1.067348
29	6	0	1.325804	1.703634	1.037590
30	6	0	2.460856	3.216162	-1.036981
31	1	0	0.485192	3.245613	-1.888144
32	6	0	2.681946	2.000548	1.064807
33	1	0	0.876890	1.122865	1.835201
34	6	0	3.243820	2.756877	0.029797

35	1	0	2.924241	3.798717	-1.824288
36	1	0	3.313565	1.665107	1.878999
37	7	0	4.664032	3.071765	0.062758
38	8	0	5.130174	3.756178	-0.856644
39	8	0	5.336395	2.637771	1.007115
40	16	0	-0.613782	-0.664294	-1.492444
41	8	0	-3.433825	-0.047607	3.275948
42	1	0	-3.268666	-0.517776	4.101941
43	1	0	-2.578429	0.306153	2.986409
44	8	0	-2.601734	2.471357	1.746108
45	1	0	-1.758217	2.572924	1.241953
46	1	0	-2.581896	3.040513	2.523407
47	8	0	-1.051057	-0.461970	1.172441
48	17	0	3.059239	-5.420545	0.490017

Total Energy (a.u.) = 2409.130741 ; **NIMAG = i145.86**