Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supporting Information:

Experimental and theoretical study on the nucleofugality ratio in the aminolysis reactions of *O*-(4-cyanophenyl) *O*-(3-nitrophenyl) thionocarbonate with amines in aqueous ethanol.

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Figure S1. HPLC analysis of the reaction of **1** with excess of morpholine at wavelength 250 and 300 nm in red and blue, respectively (see experimental). The number are defined in Scheme 2 in the manuscript.

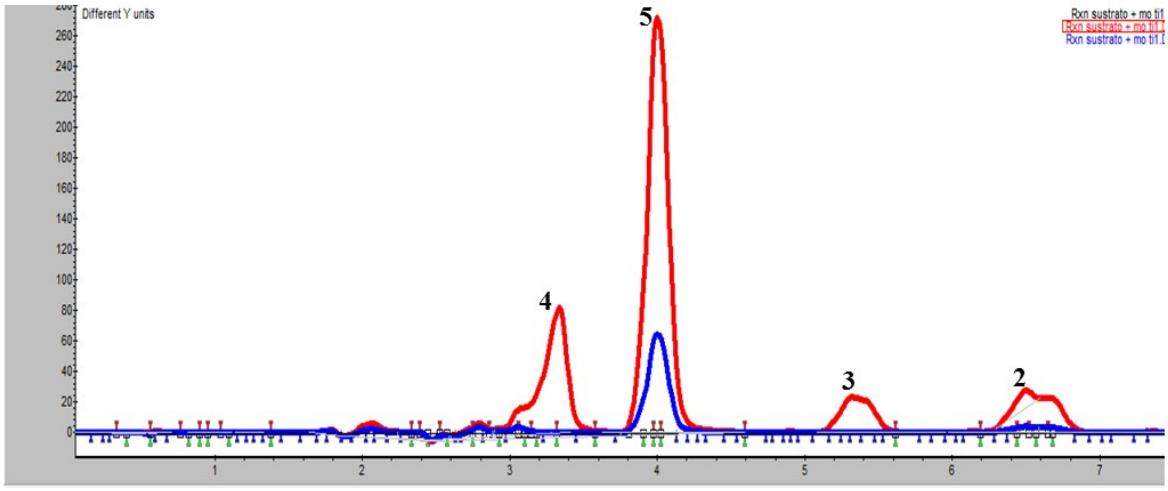


Table S-1. Experimental conditions and k_{obs} values for the reactions *O*-(3-nitrophenyl) *O*-(4-cyanophenyl) thiocarbonate (**1**) with piperidine, in aqueous ethanol 44wt. %, 25.0 ºC, μ = 0.2 M in KCl.

pH=10.52 F_N= 0.333		pH=10.82 F_N= 0.5	
10^3 $[Amine]_{tot}$/mol l^{-1}	10^3 k_{obs}/s^{-1}	10^3 $[Amine]_{tot}$/mol l^{-1}	10^3 k_{obs}/s^{-1}
1.15	5.69	1.15	7.74
2.31	9.71	2.31	15.4
3.46	14.0	3.46	25.9
4.61	18.6	4.61	37.3
5.77	22.8	5.77	43.0
6.92	25.5	6.92	50.9
		8.07	57.9

Table S-2. Experimental conditions and k_{obs} values for the reactions *O*-(3-nitrophenyl) *O*-(4-cyanophenyl) thiocarbonate (**1**) with piperazine, in aqueous ethanol 44wt. %, 25.0 ºC, μ = 0.2 M in KCl.

pH=9.71 F_N= 0.5		pH=10.01 F_N= 0.666	
10^3 $[Amine]_{tot}$/mol l^{-1}	10^3 k_{obs}/s^{-1}	10^3 $[Amine]_{tot}$/mol l^{-1}	10^3 k_{obs}/s^{-1}
1.06	3.38	1.06	5.29
2.11	9.25	2.11	8.27
3.17	12.6	3.17	13.3
4.23	15.0	4.23	24.3
5.28	21.0	5.28	26.8
6.34	30.2	6.34	32.6

Table S-3. Experimental conditions and k_{obs} values for the reactions *O*-(3-nitrophenyl) *O*-(4-cyanophenyl) thiocarbonate (**1**) with 2-(hydroxyethyl)piperazine, in aqueous ethanol 44wt. %, 25.0 ºC, μ = 0.2 M in KCl.

pH=9.09 F_N= 0.5		pH=9.39 F_N= 0.666	
10^3 [Amine]$_{tot}$/mol l^{-1}	10^3 k_{obs}/s^{-1}	10^3 [Amine]$_{tot}$/mol l^{-1}	10^3 k_{obs}/s^{-1}
1.39	1.30	1.20	2.00
2.77	3.20	2.41	4.34
4.16	5.90	3.61	8.58
5.54	8.80	4.82	11.6
6.93	12.2	6.02	14.5
8.31	14.6	7.23	16.2
9.07	17.0	8.43	25.4

Table S-4. Experimental conditions and k_{obs} values for the reactions *O*-(3-nitrophenyl) *O*-(4-cyanophenyl) thiocarbonate (**1**) with morpholine, in aqueous ethanol 44wt. %, 25.0 ºC, μ = 0.2 M in KCl.

pH=8.48 F_N=0.5		pH=8.78 F_N=0.666	
10^3 [Amine]$_{tot}$/mol l^{-1}	10^3 k_{obs}/s^{-1}	10^3 [Amine]$_{tot}$/mol l^{-1}	10^3 k_{obs}/s^{-1}
0.596	0.488	0.596	0.645
1.19	0.988	1.19	1.30
2.38	2.28	2.38	3.30
3.57	3.74	3.57	4.98
4.77	5.38	4.77	7.71
5.36	7.83	5.36	7.50
5.96	9.04	5.96	8.98
8.34	11.5	8.34	12.6
10.7	14.9	10.7	18.5

Table S-5. Experimental conditions and k_{obs} values for the reactions *O*-(3-nitrophenyl) *O*-(4-cyanophenyl) thiocarbonate (**1**) with N-formylpiperazine, in aqueous ethanol 44wt. %, 25.0 ºC, μ = 0.2 M in KCl.

pH= 7.33 F_N=0.333		pH=7.63 F_N=0.5	
10^2 [Amine]$_{tot}$/mol l^{-1}	10^3 k_{obs}/s^{-1}	10^2 [Amine]$_{tot}$/mol l^{-1}	10^3 k_{obs}/s^{-1}
0.0792	0.0520	0.080	0.0387
0.198	0.100	0.200	0.140
0.317	0.169	0.292	0.692
0.429	0.707	0.320	0.325
0.554	0.326	0.440	0.539
0.673	0.510	0.560	0.827
0.792	0.884	0.584	1.83
0.861	1.51	0.876	3.10
1.29	2.69	1.17	4.16
1.72	3.97	1.46	6.83
2.15	5.82	1.75	8.97
2.58	8.00	3.04	16.2
6.09	22.0	4.06	22.7
7.62	32.5	5.08	30.6

Table S-6. Experimental conditions and k_{obs} values for the reactions *O*-(3-nitrophenyl) *O*-(4-cyanophenyl) thiocarbonate (**1**) with phenylendiamine, in aqueous ethanol 44wt. %, 25.0 ºC, μ = 0.2 M in KCl, borate buffer 0.07M.

pH= 8.4		pH=9.8	
10^3 [Amine]$_{tot}$/mol l^{-1}	$10^3 k_{obs}$/s^{-1}	10^3 [Amine]$_{tot}$/mol l^{-1}	$10^3 k_{obs}$/s^{-1}
1.60	2.11	1.60	2.85
3.00	3.87	3.00	4.70
6.00	8.04	6.00	9.76
9.50	14.4	9.50	15.2
16.0	13.5	11.0	20.4
		13.5	23.9
		16.0	27.5

Table S-7. Experimental conditions and k_{obs} values for the reactions *O*-(3-nitrophenyl) *O*-(4-cyanophenyl) thiocarbonate (**1**) with 4-methoxyaniline, in aqueous ethanol 44wt. %, 25.0 ºC, μ = 0.2 M in KCl, borate buffer 0.07M.

pH= 8.4		pH=9.8	
10^3 [Amine]$_{tot}$/mol l^{-1}	$10^3 k_{obs}$/s^{-1}	10^3 [Amine]$_{tot}$/mol l^{-1}	$10^3 k_{obs}$/s^{-1}
1.60	0.583	1.60	0.599
3.00	1.06	3.00	1.08
6.00	2.14	6.00	2.16
9.50	3.41	9.50	3.94
11.0	3.94	11.0	4.17
13.5	4.80	13.5	5.09
16.0	6.13	16.0	6.83

Table S-8. Experimental conditions and k_{obs} values for the reactions *O*-(3-nitrophenyl) *O*-(4-cyanophenyl) thiocarbonate (**1**) with 4-methylaniline, in aqueous ethanol 44wt. %, 25.0 ºC, μ = 0.2 M in KCl, borate buffer 0.07M.

pH= 8.4		pH=9.8	
10^3 [Amine]$_{tot}$/mol l^{-1}	$10^3 k_{obs}$/s^{-1}	10^3 [Amine]$_{tot}$/mol l^{-1}	$10^3 k_{obs}$/s^{-1}
1.60	0.496	1.60	0.508
3.00	0.728	3.00	0.725
6.00	1.35	6.00	1.33
9.50	2.20	9.50	2.11
		11.0	2.72
		13.5	3.12
		16.0	3.60

Table S-9. Experimental conditions and k_{obs} values for the reactions *O*-(3-nitrophenyl) *O*-(4-cyanophenyl) thiocarbonate (**1**) with aniline, in aqueous ethanol 44wt. %, 25.0 ºC, μ = 0.2 M in KCl, borate buffer 0.07M.

pH= 8.4		pH=9.8	
10^3 [Amine]$_{tot}$/mol l^{-1}	$10^3 k_{obs}$/s^{-1}	10^3 [Amine]$_{tot}$/mol l^{-1}	$10^3 k_{obs}$/s^{-1}
3.00	0.318	1.60	0.134
6.00	0.573	3.00	0.271
9.50	0.824	6.00	0.506
11.0	0.881	9.50	0.787
13.5	1.15	11.0	0.932
16.0	1.19	13.5	1.15
35.0	2.63	16.0	1.35

Table S-10. Experimental conditions and k_{obs} values for the reactions *O*-(3-nitrophenyl) *O*-(4-cyanophenyl) thiocarbonate (**1**) with 3-amino acetophenone, in aqueous ethanol 44wt. %, 25.0 ºC, μ = 0.2 M in KCl, borate buffer 0.07M.

pH= 8.4		pH=9.8	
10^2 [Amine]$_{tot}$/mol l^{-1}	$10^4 k_{obs}$/s^{-1}	10^2 [Amine]$_{tot}$/mol l^{-1}	$10^4 k_{obs}$/s^{-1}
0.95	2.67	0.95	2.42
1.10	2.76	1.10	2.73
1.35	2.70	1.35	3.02
1.60	3.06	1.60	3.18
2.00	4.20	2.00	3.84
		2.50	4.69

Estimation of pK_a of $T^{\pm}$

The pK_a of intermediate $\mathbf{T}^{\pm}$ can be estimated by Jencks' method (eqn. 1),[1] where σ_I and σ_I(ref) are the Hammett inductive substituent constants of the varying group and of the reference, respectively. The Hammett inductive equilibrium constant (ρ_I) for the pK_a of the tetrahedral intermediates has been estimated as $\rho_I = -9.2$.[2]

$$pK_a - pK_a(\text{ref}) = \rho_I (\sigma_I - \sigma_I(\text{ref})) \qquad (1)$$

We consider as reference the reaction of 4-methylphenyl 3-nitrophenyl thionocarbonate with SAA, in which the pK_a of the tetrahedral intermediate formed was estimated as 7.1 units lower than that of the respective amine.[3] Substitution of 4-methylphenyl in this intermediate by 4-cyanophenyl yields the intermediate $\mathbf{T}^{\pm}$ in Scheme S1.

To our knowledge, the σ_I value for 4-cyanophenoxy has not been reported. In view of the greater electron-withdrawing effect of the 4-cyano group compared to that of 4-methyl, we can assume ($\sigma_I - \sigma_I(\text{ref}) > 0$ in eqn 1, and considering pK_a(ref) = 7.1 and $\rho_I = -9.2$, a pK_a value of intermediate $\mathbf{T}^{\pm}$ can be estimated as more than 7.1 units lower than that of the corresponding conjugate acid of the amine.

1. Sayer, J. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1973**, *95*, 5637-5649. Fox, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 1436-1449.
2. Taylor, P. J. *J. Chem. Soc., Perkin Trans. 2* 1993, 1423-1427.
3. E. A. Castro, P. Garcia, L. Leandro, N. Quesieh, A. Rebolledo, J. G. Santos. *J. Org. Chem.* **2000**, 65, 9047-9053.

Figure S2. Corrected Bronsted plot for the reactions of **1** with SA amines. The k_1 values, as well as those of the pK_a of the conjugate acids of these amines, were statistically corrected with $q = 2$ for piperazine ($q = 1$ for all the other SA amines) and $p = 2$ for all the conjugate acids of the amines.

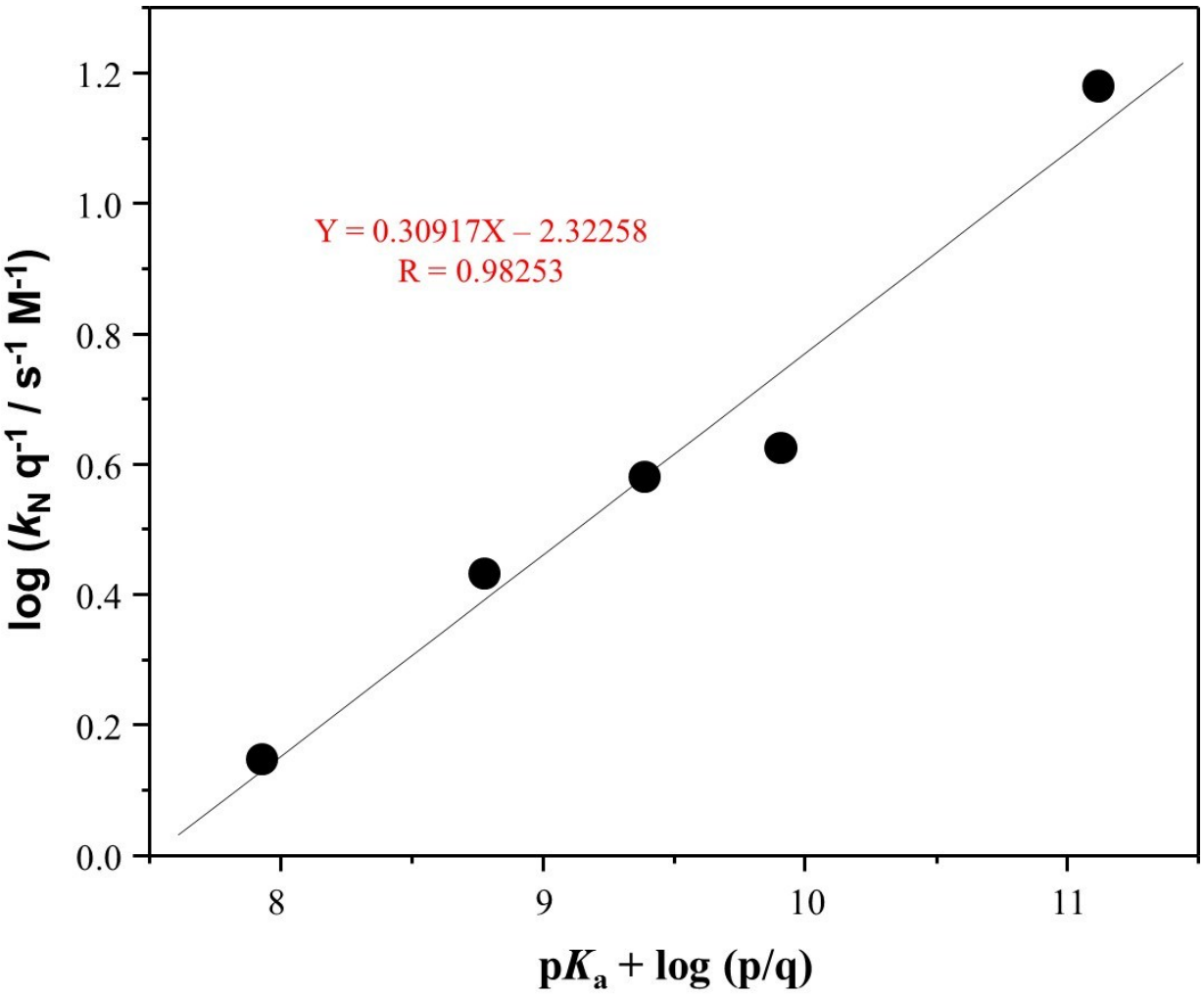


Figure S3. Corrected Bronsted plot for the reactions of **1** with anilines. The k_N values, as well as those of the pK_a of the conjugate acids of these anilines, were statistically corrected with q = 2 for 4-phenylendiamine (q = 1 for all the other anilines) and p = 3 for all the conjugate acids of the anilines.

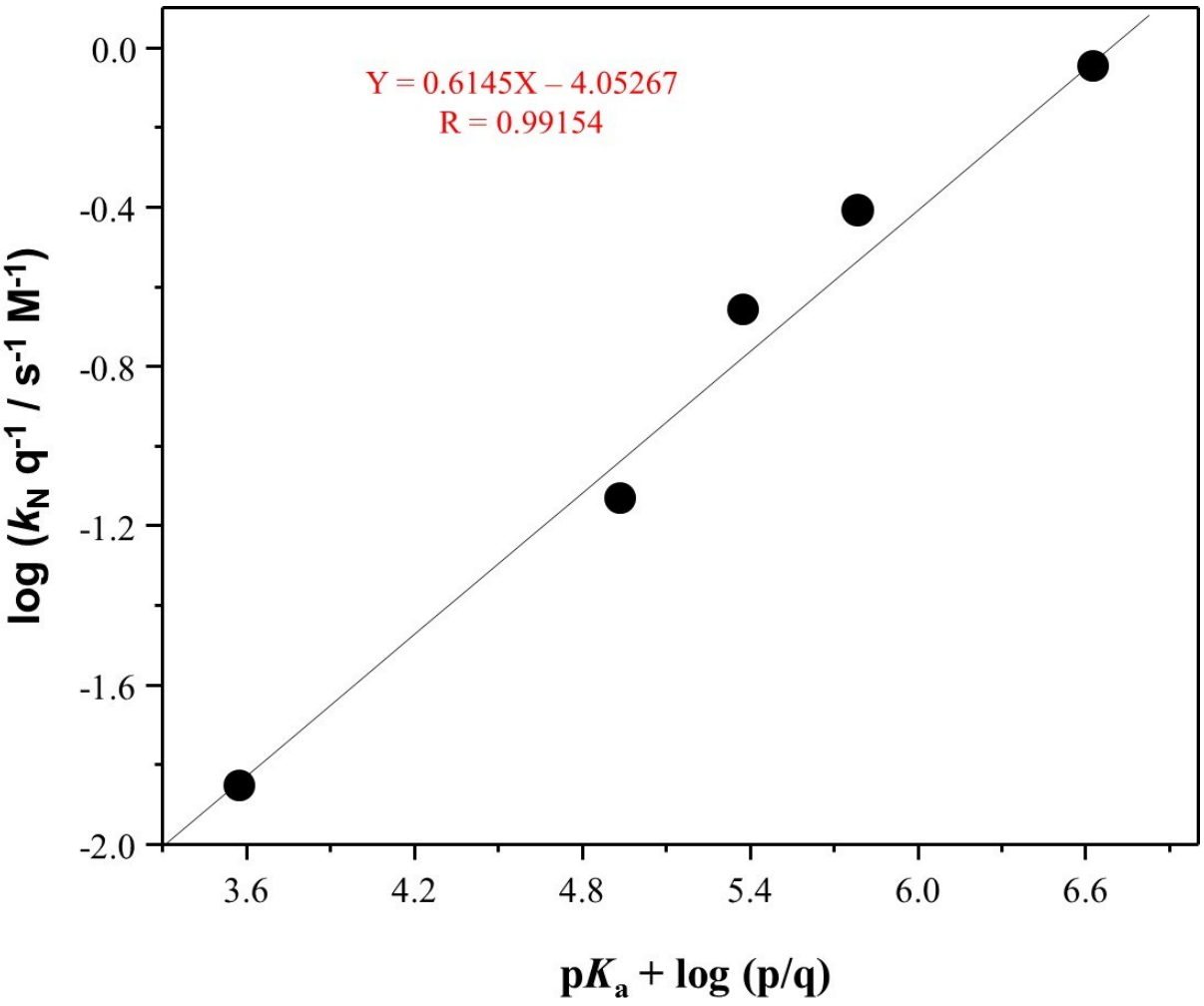
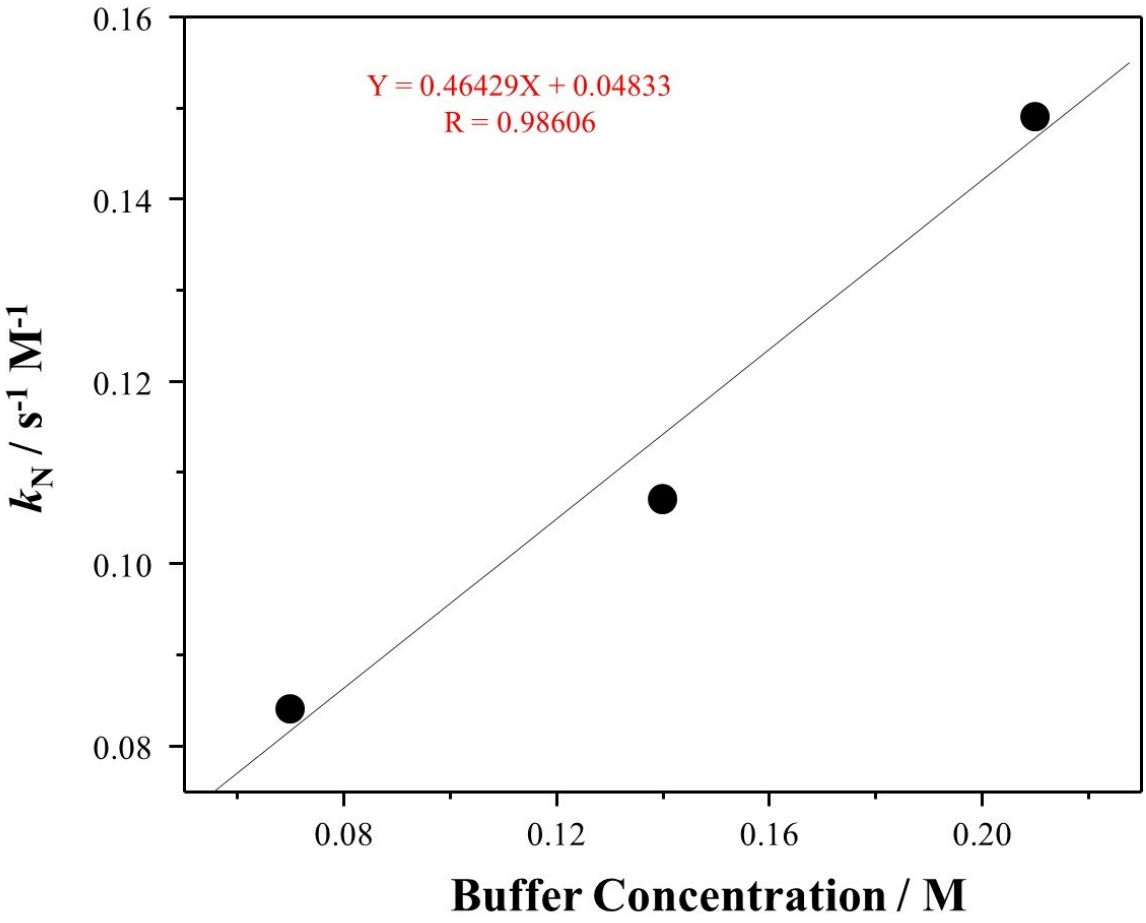


Table S-11. Experimental conditions and k_{obs} values for the reactions *O*-(3-nitrophenyl) *O*-(4-cyanophenyl) thiocarbonate (**1**) with aniline, in aqueous ethanol 44wt. %, 25.0 ºC, μ = 0.2 M in KCl, borate buffer 0.14 and 0.21M.

10^2[aniline]/mol l^{-1}	k_{obs}/s^{-1}	
	[Buffer]=0.14mol l^{-1}	[Buffer]=0.21mol l^{-1}
0.950	1.27	2.05
1.10	1.55	1.96
1.35	1.84	2.50
1.60	2.14	2.64
2.50	3.38	4.08
3.50	4.28	5.70
4.50	5.05	7.15

Figure S4. Dependence of k_N values with buffer concentration.



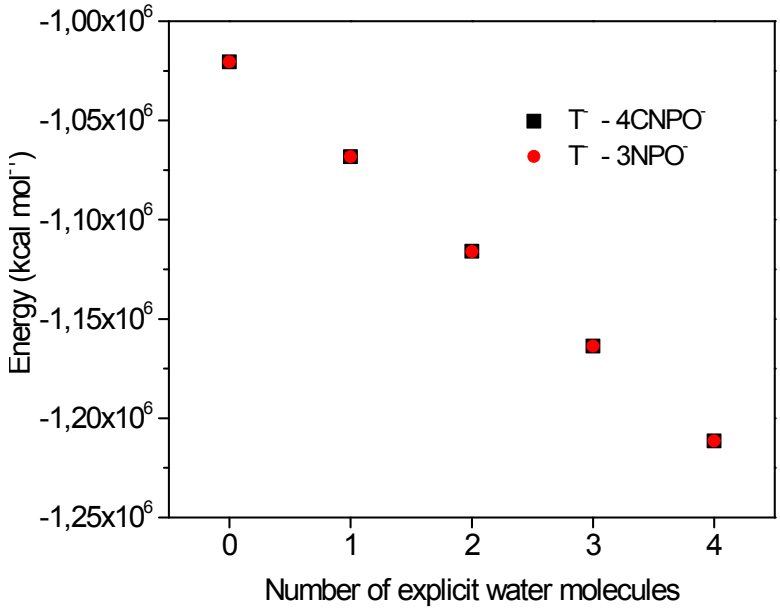


Figure S5. Energy profile, of systems containing T^-, as a function of the explicit water molecules included.

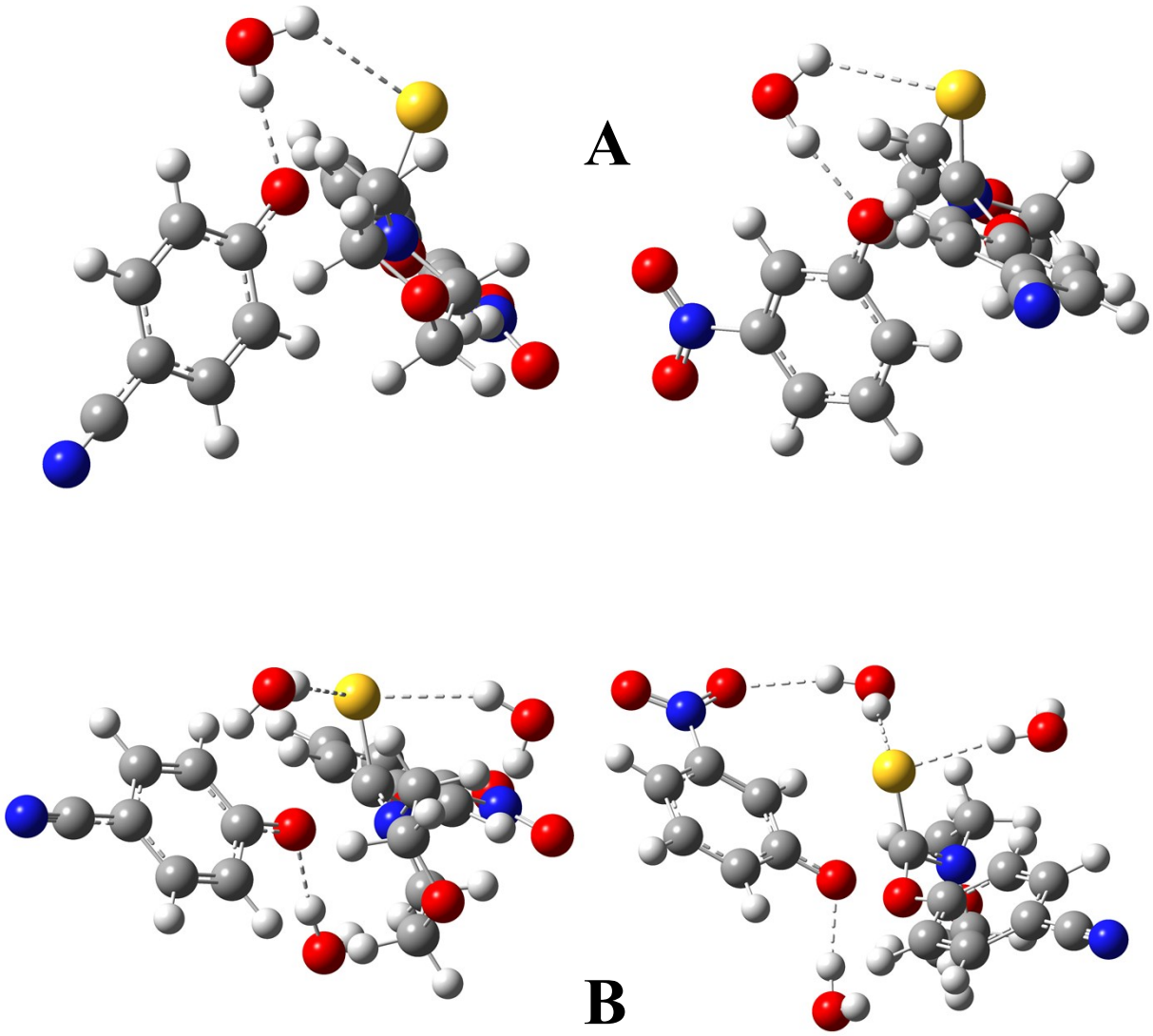


Figure S6. Structure of the TS2 for the departure of 4-$CNPO^-$ and 3-NPO^- with a) assistance of one explicit water molecule, b) assistance of three explicit water assistance water molecules.

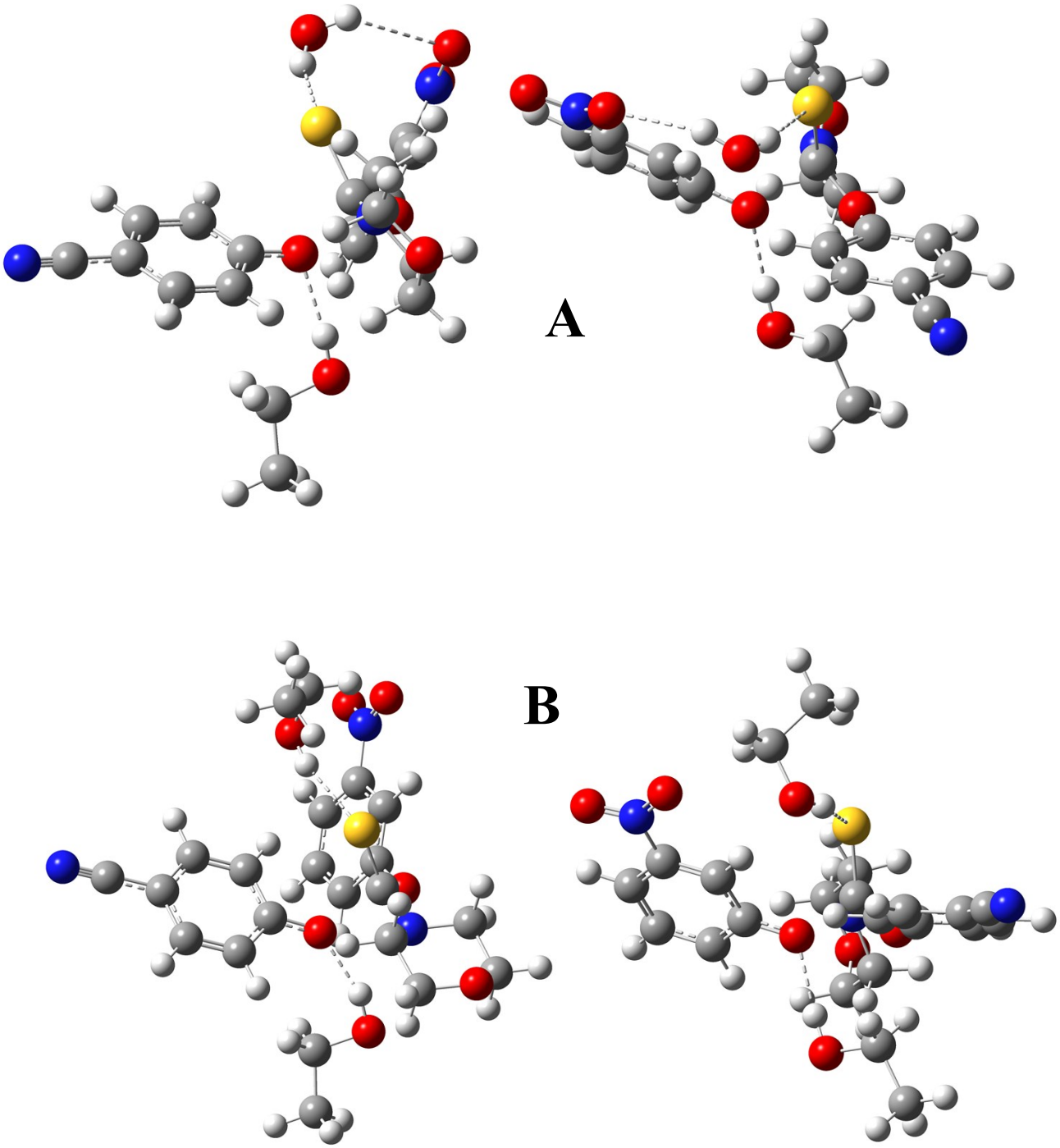


Figure S7. Structure of the TS2 for the departure of 4-$CNPO^-$ (left) and 3-NPO^- (right) with a) the assistance of one explicit water molecule and one explicit ethanol molecule, b) the assistance of two explicit ethanol molecules

Table S12. Energy gap (kcal mol^{-1}) of TS2 as a function of the number of assisting water and ethanol molecules.

	Departure	0	1	2	3		1W+1Eth*
Implicit water	$4CNPO^-$	1.98	4.58	12.64	4.79	Implicit Water	7.87
	$3NPO^-$	1.27	4.12	12.94	5.58		7.75
Explicit Ethanol	$4CNPO^-$	---	16.24	13.34	---	Implicit ethanol	7.93
	$3NPO^-$	---	10.09	7.64	---		13.24

*1W+1Eth= one explicit water molecule and one explicit ethanol molecule

Table S-13. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4-$CNPO^-$ anion for compound **1** without explicit water molecules, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.002430	1.203353	0.551256
2	16	-0.300169	0.420769	2.052532
3	8	-0.154769	0.081758	-0.848898
4	8	1.322155	1.572052	0.235506
5	6	-0.764395	-1.077473	-0.801306
6	6	-2.022533	-1.275255	-0.200520
7	6	-0.154013	-2.193116	-1.409619
8	6	-2.604330	-2.530589	-0.242903
9	1	-2.529517	-0.462497	0.294351
10	6	-0.770559	-3.435516	-1.439687
11	1	0.820338	-2.044034	-1.862030
12	6	-2.011475	-3.631525	-0.848020
13	1	-0.274197	-4.268902	-1.925913
14	1	-2.508792	-4.590639	-0.847485
15	6	2.378172	0.741475	0.238647
16	6	3.595384	1.372163	-0.045620
17	6	2.354219	-0.635971	0.477586
18	6	4.769160	0.648623	-0.106339
19	1	3.591057	2.441542	-0.218788

20	6	3.533475	-1.356065	0.414050
21	1	1.428294	-1.127385	0.728827
22	6	4.749514	-0.731056	0.121382
23	1	5.706156	1.145813	-0.328788
24	1	3.511596	-2.424225	0.597192
25	7	-3.929986	-2.704642	0.374797
26	8	-4.383439	-3.835777	0.449091
27	8	-4.515911	-1.716928	0.776453
28	6	5.960591	-1.488048	0.057454
29	7	6.941685	-2.093389	0.002767
30	6	-2.687542	3.746537	0.438212
31	6	-2.185552	2.315074	0.518145
32	6	-0.589587	2.832985	-1.187020
33	6	-1.133049	4.252368	-1.223830
34	1	-2.292900	1.928154	1.531251
35	1	-2.780017	1.685497	-0.164036
36	1	-2.164547	4.356377	1.190451
37	1	-3.760979	3.784502	0.633259
38	1	0.471086	2.838015	-1.431102
39	1	-1.109605	2.208799	-1.927011
40	1	-1.074032	4.656332	-2.237062
41	1	-0.535547	4.888778	-0.552362
42	7	-0.782888	2.285925	0.150195
43	8	-2.495142	4.309962	-0.848000

Total Energy (a.u.) =-1633.954009; **NIMAG = i252.36**

Table S-14. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of 3-NPO^- anion for compound **1**, without explicit water molecules, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.002430	1.203353	0.551256
2	16	-0.300169	0.420769	2.052532
3	8	-0.154769	0.081758	-0.848898
4	8	1.322155	1.572052	0.235506
5	6	-0.764395	-1.077473	-0.801306
6	6	-2.022533	-1.275255	-0.200520
7	6	-0.154013	-2.193116	-1.409619
8	6	-2.604330	-2.530589	-0.242903
9	1	-2.529517	-0.462497	0.294351
10	6	-0.770559	-3.435516	-1.439687
11	1	0.820338	-2.044034	-1.862030
12	6	-2.011475	-3.631525	-0.848020
13	1	-0.274197	-4.268902	-1.925913
14	1	-2.508792	-4.590639	-0.847485
15	6	2.378172	0.741475	0.238647
16	6	3.595384	1.372163	-0.045620
17	6	2.354219	-0.635971	0.477586
18	6	4.769160	0.648623	-0.106339
19	1	3.591057	2.441542	-0.218788
20	6	3.533475	-1.356065	0.414050
21	1	1.428294	-1.127385	0.728827
22	6	4.749514	-0.731056	0.121382
23	1	5.706156	1.145813	-0.328788
24	1	3.511596	-2.424225	0.597192
25	7	-3.929986	-2.704642	0.374797
26	8	-4.383439	-3.835777	0.449091
27	8	-4.515911	-1.716928	0.776453
28	6	5.960591	-1.488048	0.057454
29	7	6.941685	-2.093389	0.002767
30	6	-2.687542	3.746537	0.438212
31	6	-2.185552	2.315074	0.518145
32	6	-0.589587	2.832985	-1.187020
33	6	-1.133049	4.252368	-1.223830
34	1	-2.292900	1.928154	1.531251
35	1	-2.780017	1.685497	-0.164036
36	1	-2.164547	4.356377	1.190451
37	1	-3.760979	3.784502	0.633259
38	1	0.471086	2.838015	-1.431102
39	1	-1.109605	2.208799	-1.927011

40	1	-1.074032	4.656332	-2.237062
41	1	-0.535547	4.888778	-0.552362
42	7	-0.782888	2.285925	0.150195
43	8	-2.495142	4.309962	-0.848000

Total Energy (a.u.) =-1633.954455; **NIMAG = i232.51**

Table S-15. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4-$CNPO^-$ anion for compound **1**, with one water molecule, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.078839	-1.284984	0.145490
2	16	0.709345	-2.654602	0.988579
3	8	0.985792	-0.397467	-0.439608
4	8	-0.679335	-0.264645	1.381745
5	6	2.131190	-0.015428	0.180652
6	6	3.183110	0.308346	-0.665247
7	6	2.265419	0.135419	1.561519
8	6	4.360100	0.786777	-0.109975
9	1	3.083433	0.184742	-1.734239
10	6	3.463324	0.608587	2.080649
11	1	1.434687	-0.114162	2.204468
12	6	4.529365	0.942430	1.256986
13	1	3.563502	0.722380	3.153619
14	1	5.464324	1.315972	1.650045
15	6	-1.587631	0.616052	0.993205
16	6	-1.379670	1.510200	-0.075494
17	6	-2.822952	0.663172	1.668708
18	6	-2.362731	2.405365	-0.447867
19	1	-0.437278	1.479999	-0.604708
20	6	-3.801286	1.564715	1.299108
21	1	-2.995715	-0.037525	2.477956
22	6	-3.586165	2.445192	0.231924
23	1	-2.188974	3.089043	-1.271665
24	1	-4.747644	1.587193	1.828074
25	7	5.468255	1.136627	-1.009135
26	8	5.287243	1.036629	-2.208893
27	8	6.513663	1.512695	-0.508373
28	6	-4.599056	3.374492	-0.156423
29	7	-5.417175	4.126610	-0.469634
30	6	-1.973975	-1.198954	-2.959668
31	6	-0.701323	-1.516103	-2.187741
32	6	-2.073779	-2.281048	-0.365632
33	6	-3.301628	-1.923327	-1.186464
34	1	-0.352652	-2.532862	-2.434709
35	1	0.074783	-0.805887	-2.467291
36	1	-2.241485	-0.145123	-2.788099
37	1	-1.819897	-1.359439	-4.029134
38	1	-1.803772	-3.336555	-0.516456

39	1	-2.279784	-2.137635	0.696210
40	1	-4.120676	-2.610493	-0.966587
41	1	-3.618134	-0.897732	-0.944800
42	7	-0.985072	-1.405230	-0.766295
43	8	-3.048761	-2.032616	-2.578066
44	8	-1.608312	-2.054206	3.377991
45	1	-1.227459	-1.361611	2.812773
46	1	-1.128070	-2.821236	3.051979

Total Energy (a.u.) =-1702.439389; **NIMAG = i269.25**

Table S-16. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of 3-NPO^- anion for compound **1**, with one explicit water molecule, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.566790	1.195312	0.538019
2	16	1.210444	1.739397	2.040718
3	8	-0.071394	-0.459244	0.840782
4	8	1.458394	0.957804	-0.512442
5	6	-0.978500	-0.917026	-0.008934
6	6	-2.202517	-1.401684	0.482582
7	6	-0.778363	-0.924611	-1.401510
8	6	-3.152243	-1.873912	-0.408346
9	1	-2.399684	-1.390597	1.547369
10	6	-1.758703	-1.392323	-2.264524
11	1	0.158040	-0.547865	-1.790874
12	6	-2.966995	-1.878473	-1.784453
13	1	-1.576780	-1.382390	-3.334015
14	1	-3.740560	-2.251743	-2.439778
15	6	2.630113	0.298329	-0.353889
16	6	3.609402	0.603059	-1.299515
17	6	2.866022	-0.678150	0.615135
18	6	4.823070	-0.058958	-1.286659
19	1	3.400544	1.370125	-2.035175
20	6	4.083859	-1.334218	0.626425
21	1	2.099901	-0.912644	1.337586
22	6	5.070592	-1.034897	-0.318113
23	1	5.583937	0.180565	-2.019992
24	1	4.274067	-2.092784	1.376415
25	7	-4.429242	-2.382193	0.125649
26	8	-4.589551	-2.385163	1.330290
27	8	-5.265647	-2.774693	-0.671774
28	6	6.324852	-1.723573	-0.299882
29	7	7.337200	-2.276615	-0.292963
30	6	-2.925162	2.292600	0.087983
31	6	-1.635558	2.148523	0.878298
32	6	-0.417816	2.757775	-1.109957
33	6	-1.751337	2.896174	-1.830328
34	1	-1.398765	3.085992	1.402404
35	1	-1.745513	1.365479	1.630294
36	1	-3.206031	1.318872	-0.339728
37	1	-3.730984	2.642204	0.735424
38	1	-0.105767	3.734913	-0.704232

39	1	0.337493	2.418460	-1.816387
40	1	-1.695967	3.685629	-2.583606
41	1	-1.989107	1.942018	-2.325601
42	7	-0.567510	1.786823	-0.039107
43	8	-2.797140	3.251085	-0.950520
44	8	-0.914330	-0.411755	3.535978
45	1	-0.560455	-0.568784	2.644509
46	1	-0.462306	0.408148	3.756355

Total Energy (a.u.) = -1702.443851; **NIMAG = i273.41**

Table S-17. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of 4-$CNPO^-$ anion for compound **1**, with two water molecules, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.974163	-0.966398	-0.326893
2	16	0.314928	-0.428335	-1.804894
3	8	0.272418	-1.802185	0.520366
4	8	1.086131	0.509242	0.884607
5	6	-1.023750	-1.504176	0.847024
6	6	-2.070065	-1.880139	0.016175
7	6	-1.261527	-0.877068	2.068123
8	6	-3.363188	-1.599314	0.442313
9	1	-1.879676	-2.358660	-0.934452
10	6	-2.570106	-0.616122	2.465319
11	1	-0.408094	-0.585040	2.668511
12	6	-3.639522	-0.974603	1.652464
13	1	-2.755259	-0.115539	3.409460
14	1	-4.665446	-0.770398	1.930656
15	6	0.733815	1.733229	0.560251
16	6	1.687138	2.776652	0.626893
17	6	-0.582450	2.063560	0.166786
18	6	1.343174	4.082145	0.329639
19	1	2.698533	2.526333	0.934249
20	6	-0.923650	3.368934	-0.146486
21	1	-1.334231	1.285327	0.122113
22	6	0.031379	4.393405	-0.066626
23	1	2.084954	4.872427	0.395329
24	1	-1.938755	3.598682	-0.454606
25	7	-4.479322	-1.960094	-0.431458
26	8	-4.224560	-2.297840	-1.583006
27	8	-5.612465	-1.908014	0.027235
28	6	-0.321641	5.746622	-0.374159
29	7	-0.599284	6.849463	-0.616146
30	6	4.027849	-3.093700	-0.142060
31	6	2.585675	-2.766870	-0.504793
32	6	3.272965	-0.505073	-0.942636
33	6	4.686598	-0.893241	-0.540886
34	1	2.409711	-2.979599	-1.573374
35	1	1.911937	-3.383724	0.092380
36	1	4.166570	-2.993746	0.947514
37	1	4.263588	-4.121911	-0.429785
38	1	3.144496	-0.611854	-2.030288
39	1	3.078310	0.534888	-0.673863

40	1	5.414175	-0.318702	-1.119022
41	1	4.839327	-0.692695	0.530645
42	7	2.331337	-1.352402	-0.220117
43	8	4.948904	-2.262288	-0.817304
44	8	-2.905790	0.541591	-2.084897
45	1	-1.959511	0.374596	-1.935940
46	1	-3.251823	-0.309689	-2.371780
47	8	2.887733	-0.484882	2.701048
48	1	2.965818	-1.222073	2.084524
49	1	2.267273	0.073913	2.193007

Total Energy (a.u.) =-1778.506327; **NIMAG = i247.82***

Table S-18. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of 3-NPO^- anion for compound **1**, with two explicit water molecules, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.974163	-0.966398	-0.326893
2	16	0.314928	-0.428335	-1.804894
3	8	0.272418	-1.802185	0.520366
4	8	1.086131	0.509242	0.884607
5	6	-1.023750	-1.504176	0.847024
6	6	-2.070065	-1.880139	0.016175
7	6	-1.261527	-0.877068	2.068123
8	6	-3.363188	-1.599313	0.442313
9	1	-1.879676	-2.358660	-0.934452
10	6	-2.570106	-0.616122	2.465319
11	1	-0.408094	-0.585040	2.668511
12	6	-3.639522	-0.974602	1.652464
13	1	-2.755259	-0.115539	3.409460
14	1	-4.665446	-0.770397	1.930656
15	6	0.733815	1.733229	0.560251
16	6	1.687138	2.776652	0.626893
17	6	-0.582450	2.063560	0.166786
18	6	1.343175	4.082145	0.329639
19	1	2.698533	2.526333	0.934249
20	6	-0.923649	3.368934	-0.146486
21	1	-1.334231	1.285327	0.122113
22	6	0.031380	4.393405	-0.066626
23	1	2.084955	4.872427	0.395329
24	1	-1.938754	3.598682	-0.454606
25	7	-4.479322	-1.960093	-0.431458
26	8	-4.224560	-2.297839	-1.583006
27	8	-5.612465	-1.908013	0.027235
28	6	-0.321640	5.746622	-0.374159
29	7	-0.599283	6.849463	-0.616146
30	6	4.027848	-3.093701	-0.142060
31	6	2.585674	-2.766870	-0.504793
32	6	3.272965	-0.505074	-0.942636
33	6	4.686598	-0.893242	-0.540886
34	1	2.409710	-2.979599	-1.573374
35	1	1.911936	-3.383724	0.092380
36	1	4.166569	-2.993747	0.947514
37	1	4.263587	-4.121912	-0.429785
38	1	3.144496	-0.611855	-2.030288
39	1	3.078310	0.534887	-0.673863

40	1	5.414175	-0.318703	-1.119022
41	1	4.839327	-0.692696	0.530645
42	7	2.331337	-1.352402	-0.220117
43	8	4.948904	-2.262289	-0.817304
44	8	-2.905790	0.541591	-2.084897
45	1	-1.959511	0.374596	-1.935940
46	1	-3.251823	-0.309689	-2.371780
47	8	2.887733	-0.484883	2.701048
48	1	2.965818	-1.222074	2.084524
49	1	2.267273	0.073913	2.193007

Total Energy (a.u.)= -1778.50518; **NIMAG = i273.41**

Table S-19. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of 4-$CNPO^-$ anion for compound **1**, with three water molecules, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.024027	0.542097	0.512373
2	16	0.161593	0.054819	2.171676
3	8	-1.333407	0.585238	-0.004462
4	8	0.499604	-0.791432	-0.558094
5	6	-2.262932	-0.397471	0.139172
6	6	-3.567078	0.009486	-0.138050
7	6	-2.001691	-1.728702	0.477396
8	6	-4.588297	-0.928850	-0.070572
9	1	-3.776972	1.039008	-0.398579
10	6	-3.054559	-2.637016	0.541811
11	1	-0.985837	-2.034985	0.671957
12	6	-4.363876	-2.256666	0.270894
13	1	-2.842071	-3.668229	0.803479
14	1	-5.188464	-2.956050	0.313482
15	6	1.778039	-1.133497	-0.490088
16	6	2.709016	-0.591342	-1.395777
17	6	2.233481	-2.060461	0.468703
18	6	4.044603	-0.956234	-1.350678
19	1	2.348611	0.101563	-2.146703
20	6	3.568478	-2.429114	0.516817
21	1	1.520674	-2.468528	1.175139
22	6	4.487864	-1.877740	-0.389921
23	1	4.752788	-0.536902	-2.058280
24	1	3.911347	-3.141067	1.260621
25	7	-5.956579	-0.496652	-0.374970
26	8	-6.131770	0.661882	-0.727100
27	8	-6.856064	-1.321337	-0.264285
28	6	5.866477	-2.270739	-0.350602
29	7	6.982387	-2.592197	-0.324441
30	6	1.383641	2.959969	-1.911563
31	6	0.219224	2.246739	-1.233871
32	6	1.372938	2.566952	0.883823
33	6	2.501228	3.219712	0.107407
34	1	-0.580950	2.977148	-1.034127
35	1	-0.171662	1.481877	-1.907573
36	1	2.115485	2.220537	-2.271114
37	1	1.015243	3.528017	-2.769603
38	1	0.674507	3.333488	1.252811
39	1	1.786807	2.034970	1.736395

40	1	2.987603	3.979151	0.723247
41	1	3.244891	2.457199	-0.172632
42	7	0.657521	1.634393	0.017477
43	8	2.027873	3.880762	-1.056364
44	8	3.480971	0.378411	2.541311
45	1	2.524912	0.191636	2.516304
46	1	3.831084	-0.110320	1.790227
47	8	-1.896554	2.765783	2.107582
48	1	-2.020886	2.467905	1.200778
49	1	-1.334393	2.066843	2.479720
50	8	-0.788353	-0.640246	-3.005998
51	1	-0.302227	-0.748171	-2.163691
52	1	-1.712865	-0.726204	-2.759510

Total Energy (a.u.) =-1854.561346; **NIMAG = i268.12**

Table S-20. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of 3-NPO^- anion for compound **1**, with three explicit water molecules, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.354408	0.358247	0.019168
2	16	0.169942	-0.133545	-1.557195
3	8	0.973260	-0.005349	1.228232
4	8	-1.251402	-0.530466	0.654856
5	6	1.882851	-0.900453	0.876672
6	6	3.052540	-0.490245	0.225231
7	6	1.706838	-2.270199	1.125296
8	6	3.987767	-1.438512	-0.151481
9	1	3.204283	0.560482	0.023336
10	6	2.666207	-3.196830	0.741157
11	1	0.797809	-2.584971	1.624167
12	6	3.827319	-2.796029	0.094288
13	1	2.504588	-4.250732	0.939031
14	1	4.584161	-3.500537	-0.220162
15	6	-2.514528	-0.687943	0.194120
16	6	-3.165559	0.177696	-0.685740
17	6	-3.185478	-1.799301	0.712365
18	6	-4.481007	-0.078916	-1.034414
19	1	-2.660185	1.038036	-1.101657
20	6	-4.499525	-2.043701	0.368582
21	1	-2.648167	-2.467099	1.375204
22	6	-5.161540	-1.180972	-0.511355
23	1	-4.983936	0.587876	-1.724600
24	1	-5.016946	-2.906316	0.771372
25	7	5.194945	-0.993074	-0.857465
26	8	5.228826	0.151542	-1.283187
27	8	6.110374	-1.784230	-0.989217
28	6	-6.524405	-1.430216	-0.868636
29	7	-7.624491	-1.635032	-1.148529
30	6	1.129606	3.326309	0.624858
31	6	0.074863	2.761043	-0.314882
32	6	-1.173362	2.049021	1.623544
33	6	-0.091154	2.674474	2.500726
34	1	-0.656617	3.541490	-0.556949
35	1	0.538521	2.413823	-1.233268
36	1	1.891581	2.561596	0.819850
37	1	1.606186	4.198742	0.175706
38	1	-1.970999	2.782119	1.452356
39	1	-1.597413	1.185994	2.130302

40	1	-0.540602	3.079287	3.409857
41	1	0.645315	1.910615	2.771257
42	7	-0.647504	1.662672	0.314618
43	8	0.545302	3.755954	1.844040
44	8	-1.757564	2.018978	-3.101830
45	1	-1.201835	1.297721	-2.753417
46	1	-1.135470	2.735339	-3.233381
47	8	2.787547	1.822194	-2.259296
48	1	3.605849	1.350133	-2.079093
49	1	2.088394	1.167357	-2.100540
50	8	-0.415640	-0.742264	3.547478
51	1	0.148861	-0.465347	2.800565
52	1	-1.210888	-1.032551	3.099224

Total Energy (a.u.) = -1854.560868; **NIMAG = i293.71**

Table S-21. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of 4-$CNPO^-$ anion for compound **1**, with four water molecules, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.222074	0.604905	0.350735
2	16	0.388401	0.433912	-1.380777
3	8	1.335706	0.436446	1.122076
4	8	-0.591033	-0.880601	0.957847
5	6	2.312573	-0.466991	0.824569
6	6	3.387436	-0.052546	0.061764
7	6	2.283513	-1.735137	1.370619
8	6	4.409776	-0.949519	-0.165069
9	1	3.410371	0.936921	-0.342329
10	6	3.332742	-2.611181	1.131623
11	1	1.451198	-2.025499	1.978247
12	6	4.407925	-2.231000	0.356025
13	1	3.304980	-3.597818	1.556484
14	1	5.224317	-2.894896	0.157615
15	6	-1.674268	-1.353052	0.403814
16	6	-2.945308	-0.961926	0.852658
17	6	-1.605284	-2.306040	-0.626645
18	6	-4.089826	-1.508007	0.312679
19	1	-3.009053	-0.235614	1.639918
20	6	-2.748165	-2.847818	-1.164432
21	1	-0.636845	-2.594461	-0.985891
22	6	-4.005919	-2.457238	-0.701952
23	1	-5.055103	-1.203839	0.676727
24	1	-2.677896	-3.577862	-1.950737
25	7	5.536550	-0.532203	-0.998202
26	8	5.448669	0.498708	-1.583811
27	8	6.483686	-1.248895	-1.049906
28	6	-5.198788	-3.043607	-1.249639
29	7	-6.139497	-3.509092	-1.676221
30	6	-1.640504	2.610965	2.833403
31	6	-0.400046	1.908435	2.308128
32	6	-0.970100	2.756997	0.101859
33	6	-2.186345	3.408663	0.731122
34	1	0.468620	2.548657	2.460221
35	1	-0.247775	0.998574	2.867027
36	1	-2.481796	1.917325	2.843478
37	1	-1.466403	2.946183	3.848956
38	1	-0.154613	3.479905	0.048001
39	1	-1.218749	2.453793	-0.896783

40	1	-2.423441	4.323215	0.206638
41	1	-3.041088	2.737616	0.650947
42	7	-0.564560	1.598728	0.892063
43	8	-1.965015	3.738117	2.076592
44	8	3.027238	2.764814	-2.061717
45	1	2.228675	2.262542	-1.984660
46	1	3.686449	2.142202	-2.317878
47	8	-2.947625	3.618747	-2.796868
48	1	-2.094800	3.742155	-3.175176
49	1	-3.056161	2.676595	-2.764287
50	8	-2.787258	0.711939	-2.651058
51	1	-1.894961	0.542865	-2.371410
52	1	-3.317580	0.122954	-2.142289
53	8	-0.575082	-1.695968	3.696556
54	1	-1.266029	-2.334328	3.691665
55	1	-0.557383	-1.353680	2.809213

Total Energy (a.u.) = -1930.621708; **NIMAG = i262.62**

Table S-22. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of 3-NPO^- anion for compound **1**, with four explicit water molecules, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.231382	-0.171849	-0.201546
2	16	0.495487	-0.051034	-1.784207
3	8	0.724270	-1.728069	0.508031
4	8	0.783039	0.665149	0.816510
5	6	-0.559600	-1.795798	0.874936
6	6	-1.554313	-2.180113	-0.034188
7	6	-0.940282	-1.469336	2.185680
8	6	-2.871828	-2.219158	0.394551
9	1	-1.292615	-2.457916	-1.044787
10	6	-2.270224	-1.518756	2.580421
11	1	-0.165094	-1.188145	2.887323
12	6	-3.261951	-1.895317	1.686136
13	1	-2.537555	-1.257911	3.598228
14	1	-4.304781	-1.944841	1.966295
15	6	-0.054466	1.727356	0.584686
16	6	0.504494	3.000865	0.614146
17	6	-1.421852	1.552859	0.421533
18	6	-0.309559	4.112312	0.477343
19	1	1.576214	3.105538	0.724597
20	6	-2.236003	2.661970	0.263547
21	1	-1.845676	0.559762	0.384462
22	6	-1.685698	3.945081	0.298622
23	1	0.115609	5.108713	0.502087
24	1	-3.296440	2.525139	0.094527
25	7	-3.910678	-2.627308	-0.560943
26	8	-3.630401	-2.634860	-1.748260
27	8	-5.001729	-2.938613	-0.121870
28	6	-2.526414	5.097461	0.158395
29	7	-3.193010	6.032371	0.056191
30	6	4.656604	-1.508613	-0.621228
31	6	3.339028	-0.976676	-1.159227
32	6	3.417536	0.721071	0.558876
33	6	4.740513	0.125954	1.020114
34	1	3.525543	-0.275823	-1.985848
35	1	2.753507	-1.809890	-1.541947
36	1	4.458089	-2.291492	0.125302
37	1	5.246107	-1.934123	-1.435055
38	1	3.597617	1.548067	-0.144858

39	1	2.890424	1.115747	1.425892
40	1	5.386232	0.916658	1.408895
41	1	4.550301	-0.612245	1.812094
42	7	2.611631	-0.311816	-0.087423
43	8	5.444092	-0.485004	-0.041239
44	8	-2.851709	0.268333	-2.100453
45	1	-1.891011	0.258566	-1.971256
46	1	-3.064773	-0.647690	-2.299803
47	8	2.319410	2.657958	-2.143268
48	1	1.864636	1.797656	-2.176957
49	1	1.593018	3.275645	-2.044335
50	8	1.026630	-3.437187	-1.792597
51	1	1.017146	-3.080143	-0.891485
52	1	0.808238	-2.650168	-2.304840
53	8	2.325588	-1.587010	2.880409
54	1	1.922035	-1.769082	2.012850
55	1	2.312111	-0.629633	2.916274

Total Energy (a.u.) = -1930.621596; **NIMAG = i282.34**

Table S-23. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of $4CNPO^-$ anion for compound **1**, with one explicit ethanol molecule, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.100308	0.852124	0.552239
2	16	0.610298	2.499820	0.456341
3	8	1.083434	-0.137392	0.635371
4	8	-0.648730	0.487167	-1.013007
5	6	2.221450	-0.094515	-0.103339
6	6	3.326804	-0.702355	0.476001
7	6	2.304018	0.437527	-1.390848
8	6	4.504932	-0.772543	-0.251747
9	1	3.266701	-1.107932	1.475927
10	6	3.504267	0.356361	-2.084514
11	1	1.432549	0.900303	-1.829221
12	6	4.623334	-0.248737	-1.529663
13	1	3.564109	0.772469	-3.083275
14	1	5.560906	-0.321549	-2.062424
15	6	-1.484859	-0.536456	-1.081400
16	6	-1.177282	-1.812338	-0.569163
17	6	-2.743473	-0.348292	-1.685575
18	6	-2.087811	-2.846481	-0.657914
19	1	-0.216170	-1.967510	-0.098772
20	6	-3.649027	-1.386370	-1.779847
21	1	-2.993039	0.637447	-2.062059
22	6	-3.335194	-2.649013	-1.262508
23	1	-1.837636	-3.824111	-0.260544
24	1	-4.614545	-1.224831	-2.246305
25	7	5.670254	-1.424381	0.361462
26	8	5.536163	-1.918627	1.465964
27	8	6.713417	-1.440248	-0.268319
28	6	-4.272730	-3.722870	-1.353159
29	7	-5.029914	-4.591344	-1.427504
30	6	-1.806077	-0.845952	3.262532
31	6	-0.589619	-0.108337	2.721929
32	6	-2.083670	1.325814	1.497232
33	6	-3.250884	0.532706	2.061089
34	1	-0.291959	0.692351	3.419539
35	1	0.239063	-0.807052	2.622036
36	1	-2.017287	-1.708951	2.612778
37	1	-1.615309	-1.200764	4.277899
38	1	-1.870976	2.200300	2.129515

39	1	-2.326911	1.688180	0.497213
40	1	-4.118404	1.179758	2.202918
41	1	-3.515707	-0.275888	1.363617
42	7	-0.928046	0.447331	1.421922
43	8	-2.944463	-0.012472	3.334403
44	8	-1.769438	2.935469	-1.907632
45	1	-1.428173	2.062830	-1.650246
46	6	-1.104514	3.758703	-0.945829
47	1	-0.055738	3.777889	-1.157015
48	1	-1.263673	3.361170	0.034750
49	6	-1.668828	5.189796	-1.017396
50	1	-2.717284	5.170815	-0.804608
51	1	-1.170160	5.806174	-0.298850
52	1	-1.511127	5.586730	-1.998453

Total Energy (a.u.) = - 1748.664578; **NIMAG = i273,55**

Table S-24. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of $3NPO^-$ anion for compound **1**, with one explicit ethanol molecule, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.584059	0.922015	0.671819
2	16	-1.189008	2.408739	0.045632
3	8	0.049058	0.008132	-0.742564
4	8	-1.501305	0.008838	1.200594
5	6	0.933045	-0.946218	-0.493150
6	6	2.164556	-0.940659	-1.169943
7	6	0.700830	-1.969756	0.443774
8	6	3.090097	-1.936004	-0.902747
9	1	2.386275	-0.155420	-1.881989
10	6	1.657652	-2.942203	0.695671
11	1	-0.241570	-1.979758	0.974974
12	6	2.873168	-2.945719	0.025382
13	1	1.451215	-3.716971	1.426510
14	1	3.628736	-3.697065	0.203651
15	6	-2.673756	-0.296531	0.596375
16	6	-3.672361	-0.762986	1.451527
17	6	-2.894270	-0.242086	-0.780789
18	6	-4.890123	-1.176170	0.943830
19	1	-3.475015	-0.787503	2.516262
20	6	-4.116193	-0.652294	-1.283095
21	1	-2.113409	0.112750	-1.435168
22	6	-5.122254	-1.121456	-0.432733
23	1	-5.665946	-1.535701	1.609340
24	1	-4.294504	-0.611892	-2.351112
25	7	4.375384	-1.916425	-1.625161
26	8	4.563377	-1.037205	-2.442778
27	8	5.190362	-2.786546	-1.363985
28	6	-6.380664	-1.547892	-0.964083
29	7	-7.396520	-1.895901	-1.385599
30	6	2.904372	1.259742	1.819466
31	6	1.632318	1.770539	1.164180
32	6	0.373492	0.750106	2.947804
33	6	1.691021	0.285870	3.551931
34	1	1.414386	2.796534	1.495008
35	1	1.753954	1.789270	0.079929
36	1	3.168329	0.278987	1.397071
37	1	3.727380	1.954836	1.645525
38	1	0.077883	1.717706	3.387294

39	1	-0.400303	0.017568	3.169839
40	1	1.623971	0.269357	4.642327
41	1	1.910475	-0.730290	3.189296
42	7	0.540854	0.874683	1.509630
43	8	2.759331	1.149992	3.226764
44	8	0.954179	2.001420	-2.527063
45	1	0.476890	1.247734	-2.141375
46	6	0.298617	3.083566	-1.860656
47	1	-0.760558	2.983589	-1.974901
48	1	0.548419	3.065589	-0.820379
49	6	0.757520	4.418717	-2.475780
50	1	0.268145	5.228506	-1.976126
51	1	1.816906	4.517997	-2.362887
52	1	0.506357	4.437318	-3.515718

,Total Energy (a.u.) = -1748.674384; **NIMAG = i270,72**

Table S-25. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of $4CNPO^-$ anion for compound **1**, with one explicit water molecule and one ethanol molecule, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.215527	1.005682	-0.478540
2	16	0.712228	0.319712	-1.997851
3	8	1.139203	1.123928	0.525842
4	8	-0.774177	-0.209876	0.392778
5	6	2.100362	0.186830	0.756441
6	6	3.325706	0.318897	0.133167
7	6	1.891618	-0.812468	1.688483
8	6	4.321419	-0.581430	0.448704
9	1	3.485331	1.094579	-0.584616
10	6	2.914197	-1.699874	1.987196
11	1	0.939518	-0.885210	2.172687
12	6	4.143033	-1.597522	1.367496
13	1	2.745232	-2.477960	2.708936
14	1	4.941530	-2.278587	1.579072
15	6	-1.771886	-0.824898	-0.186867
16	6	-3.081834	-0.337171	-0.068614
17	6	-1.576779	-2.020101	-0.897907
18	6	-4.145866	-1.012067	-0.626115
19	1	-3.242430	0.571241	0.480143
20	6	-2.639472	-2.689972	-1.453812
21	1	-0.576568	-2.391336	-1.002277
22	6	-3.938212	-2.195980	-1.325051
23	1	-5.144194	-0.625668	-0.520404
24	1	-2.472922	-3.603862	-1.995697
25	7	5.613571	-0.458253	-0.222225
26	8	5.705998	0.318233	-1.118850
27	8	6.509431	-1.133198	0.169565
28	6	-5.049622	-2.904875	-1.897480
29	7	-5.928880	-3.463804	-2.343736
30	6	-1.993198	3.684967	0.800767
31	6	-0.695393	2.895786	0.771641
32	6	-0.855336	2.897849	-1.654377
33	6	-2.151388	3.672585	-1.507106
34	1	0.147088	3.584816	0.843559
35	1	-0.666094	2.242230	1.628714
36	1	-2.836976	3.004469	0.911809
37	1	-1.990874	4.363600	1.645303
38	1	-0.033282	3.596125	-1.824425

39	1	-0.918626	2.243121	-2.505930
40	1	-2.277023	4.344122	-2.347951
41	1	-2.992022	2.979078	-1.488586
42	7	-0.614177	2.112619	-0.453619
43	8	-2.161737	4.462257	-0.349789
44	8	3.608702	-1.639293	-2.723419
45	1	2.754875	-1.379655	-2.410111
46	1	4.068858	-0.825863	-2.838934
47	8	-1.394201	0.015517	3.164964
48	1	-1.247522	0.107980	2.228787
49	6	-2.446325	-0.947402	3.268504
50	1	-2.084055	-1.906004	2.960700
51	1	-3.260694	-0.654945	2.639081
52	6	-2.928698	-1.025643	4.728913
53	1	-3.714802	-1.747370	4.806701
54	1	-2.113916	-1.316460	5.358559
55	1	-3.292533	-0.067461	5.036177

Total Energy (a.u.) = -1865.127290; **NIMAG = i283.59**

Table S-26. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of $3NPO^-$ anion for compound **1**, with one explicit water molecule and one ethanol molecule, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.009779	0.904413	-0.919979
2	16	0.232736	-0.279440	-2.169099
3	8	0.536314	0.177073	0.676351
4	8	-1.258920	1.168599	-0.486375
5	6	1.749942	-0.296614	0.802914
6	6	2.042896	-1.622174	0.455584
7	6	2.793089	0.480431	1.311544
8	6	3.324797	-2.098130	0.605855
9	1	1.263894	-2.248094	0.081632
10	6	4.073771	-0.030249	1.456943
11	1	2.576874	1.489484	1.607133
12	6	4.366694	-1.331087	1.101801
13	1	4.852317	0.596735	1.855171
14	1	5.348919	-1.743367	1.204827
15	6	-2.275980	0.273380	-0.461648
16	6	-3.480763	0.726183	-0.978500
17	6	-2.185197	-0.983789	0.113916
18	6	-4.600534	-0.074985	-0.924137
19	1	-3.518477	1.702626	-1.422882
20	6	-3.304396	-1.789986	0.151354
21	1	-1.251818	-1.317939	0.510771
22	6	-4.516834	-1.341799	-0.359732
23	1	-5.534697	0.273392	-1.324931
24	1	-3.229203	-2.774882	0.572473
25	7	3.603371	-3.485194	0.221428
26	8	2.735240	-4.116478	-0.292271
27	8	4.689959	-3.916777	0.440616
28	6	-5.687849	-2.179296	-0.303716
29	7	-6.616357	-2.825248	-0.257815
30	6	2.567029	3.474982	-1.707996
31	6	1.492514	2.480112	-2.104120
32	6	0.242315	3.206758	-0.145427
33	6	1.372684	4.180020	0.141759
34	1	0.832656	2.935267	-2.845170
35	1	1.947388	1.613775	-2.551791
36	1	3.313862	2.980312	-1.087326
37	1	3.056030	3.859741	-2.594958
38	1	-0.549735	3.729041	-0.684385

39	1	-0.162056	2.852945	0.788920
40	1	0.974135	5.076501	0.601249
41	1	2.084104	3.730187	0.832968
42	7	0.733272	2.080108	-0.928684
43	8	2.035427	4.576313	-1.024813
44	8	-0.438654	-3.712547	-1.150985
45	1	-0.427032	-2.852935	-1.546311
46	1	0.461694	-3.992212	-1.141344
47	8	-0.851663	1.438046	2.860847
48	1	-0.317530	1.090967	2.153768
49	6	-2.192252	1.292493	2.384889
50	1	-2.273654	1.725961	1.410015
51	1	-2.442222	0.253291	2.335160
52	6	-3.159036	2.007550	3.346982
53	1	-2.910073	3.047052	3.395478
54	1	-4.162290	1.897275	2.991704
55	1	-3.076473	1.575147	4.322231

Total Energy (a.u.) = -1865.118828; **NIMAG = i290.65**

Table S-27. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of $4CNPO^-$ anion for compound **1**, with two explicit ethanol molecules, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.755915	-1.100525	-0.587590
2	16	-0.289077	-0.533826	-1.810469
3	8	0.307073	-1.921466	0.428988
4	8	1.259300	0.363121	0.535854
5	6	-0.828390	-1.588525	1.118509
6	6	-2.081933	-1.928673	0.629262
7	6	-0.681622	-0.963053	2.354685
8	6	-3.186016	-1.613664	1.413095
9	1	-2.190859	-2.406076	-0.334659
10	6	-1.809499	-0.667276	3.115372
11	1	0.317893	-0.699712	2.679825
12	6	-3.079375	-0.989407	2.650035
13	1	-1.696806	-0.167928	4.071520
14	1	-3.973313	-0.757671	3.214645
15	6	0.863995	1.598879	0.325820
16	6	1.825693	2.613999	0.109800
17	6	-0.499477	1.969539	0.332249
18	6	1.448667	3.930805	-0.076900
19	1	2.874927	2.332656	0.109659
20	6	-0.878529	3.286255	0.129421
21	1	-1.254254	1.213553	0.510052
22	6	0.088092	4.282293	-0.074414
23	1	2.200358	4.698981	-0.231707
24	1	-1.932139	3.547147	0.129952
25	7	-4.518374	-1.936341	0.903099
26	8	-4.620122	-2.273532	-0.272056
27	8	-5.466740	-1.854794	1.671913
28	6	-0.299181	5.647132	-0.268402
29	7	-0.602662	6.759097	-0.421159
30	6	3.667003	-3.315910	-1.296259
31	6	2.191986	-2.945336	-1.223743
32	6	2.788251	-0.701340	-1.847238
33	6	4.245535	-1.132666	-1.873995
34	1	1.706229	-3.145742	-2.194289
35	1	1.703531	-3.546566	-0.454989
36	1	4.119941	-3.227301	-0.294560
37	1	3.778329	-4.348517	-1.638174
38	1	2.345474	-0.797080	-2.850072
39	1	2.711035	0.341959	-1.535446

40	1	4.789769	-0.575409	-2.640140
41	1	4.709575	-0.943791	-0.893834
42	7	2.073363	-1.526085	-0.880081
43	8	4.375519	-2.506801	-2.212168
44	8	-3.421684	0.530127	-1.141919
45	1	-2.470478	0.352901	-1.238444
46	8	3.481756	-0.694546	1.750574
47	1	2.748388	-0.497188	1.135310
48	6	-3.952568	0.304626	-2.450434
49	1	-3.905749	-0.739571	-2.679259
50	1	-4.970822	0.631688	-2.483458
51	6	-3.126150	1.093917	-3.482738
52	1	-2.131269	0.701680	-3.518258
53	1	-3.579958	1.003196	-4.447481
54	1	-3.093023	2.125279	-3.199726
55	6	3.529269	0.552543	2.448722
56	1	3.597104	1.353991	1.743045
57	1	2.641305	0.667374	3.034584
58	6	4.760808	0.576805	3.373017
59	1	4.795585	1.509384	3.896455
60	1	4.693665	-0.225492	4.077794
61	1	5.648855	0.463382	2.787007

Total Energy (a.u.) = -1843.715480610; **NIMAG = i255.49**

Table S-28. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG)for Transition State (TS2) associated to the departure of $3NPO^-$ anion for compound **1**, with two explicit ethanol molecule, calculated using WB97XD/6-311++G(d,p) level theory

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.041962	-1.026009	-0.929421
2	16	-0.236279	0.351334	-1.947796
3	8	-0.497042	-0.614172	0.771700
4	8	1.323498	-1.314047	-0.552424
5	6	-1.726385	-0.217364	0.982939
6	6	-2.071542	1.136664	0.877868
7	6	-2.735353	-1.111812	1.347032
8	6	-3.368957	1.528969	1.112807
9	1	-1.319606	1.848384	0.620014
10	6	-4.032877	-0.684461	1.583450
11	1	-2.479114	-2.148331	1.457843
12	6	-4.377197	0.646623	1.466072
13	1	-4.784013	-1.401576	1.865170
14	1	-5.373207	0.996105	1.642621
15	6	2.306680	-0.398978	-0.372286
16	6	3.522105	-0.705701	-0.965827
17	6	2.174916	0.731268	0.418392
18	6	4.611638	0.115668	-0.773521
19	1	3.591673	-1.585268	-1.577266
20	6	3.263552	1.560506	0.595067
21	1	1.233831	0.953300	0.871642
22	6	4.486524	1.257583	0.007998
23	1	5.553967	-0.119474	-1.233288
24	1	3.155975	2.451103	1.185223
25	7	-3.702354	2.950635	0.982110
26	8	-2.862193	3.696292	0.589428
27	8	-4.802955	3.294177	1.274752
28	6	5.625956	2.116295	0.208322
29	7	6.530119	2.779088	0.365418
30	6	-2.424685	-3.511988	-2.155758
31	6	-1.391946	-2.421902	-2.371223
32	6	-0.097004	-3.436573	-0.576425
33	6	-1.187394	-4.488171	-0.464138
34	1	-0.722523	-2.712252	-3.183196
35	1	-1.883157	-1.507955	-2.656322
36	1	-3.183722	-3.164666	-1.455099
37	1	-2.907170	-3.751503	-3.095814
38	1	0.708886	-3.823827	-1.201862
39	1	0.302703	-3.239222	0.404899

40	1	-0.751268	-5.436040	-0.172597
41	1	-1.908606	-4.196109	0.297958
42	7	-0.637116	-2.208384	-1.145366
43	8	-1.845811	-4.695929	-1.680909
44	8	0.316458	3.571814	-0.336782
45	1	0.484941	2.778958	-0.824979
46	8	0.955564	-2.188957	2.693983
47	1	0.402891	-1.742927	2.060442
48	6	2.285801	-1.906285	2.251868
49	1	2.377957	-2.156413	1.215604
50	1	2.493029	-0.865318	2.387311
51	6	3.287473	-2.740085	3.072252
52	1	3.081239	-3.781086	2.935558
53	1	4.282930	-2.527395	2.742512
54	1	3.194217	-2.491103	4.108694
55	6	-0.637276	4.296894	-1.117520
56	1	-0.769355	5.274021	-0.701976
57	1	-1.572535	3.777136	-1.111002
58	6	-0.128205	4.419478	-2.565767
59	1	-0.082492	3.447683	-3.011217
60	1	-0.796373	5.038254	-3.127521
61	1	0.847955	4.857668	-2.564812

Total Energy (a.u.) = -1843.726553; **NIMAG = i283.48**