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

Supporting Information

NUCLEOFUGALITY HIERARCHY, IN THE AMINOLYSIS REACTION OF 4-CYANOPHENYL 4-NITROPHENYL CARBONATE AND THIONOCARBONATE. EXPERIMENTAL AND THEORETICAL STUDY

Rodrigo Montecinos,* Margarita E. Aliaga, Paulina Pavez, Patricio Cornejo and José G. Santos*.

Departamento de Quimica Fisica, Facultad de Quimica y de Farmacia, Pontificia Universidad Católica de Chile, Casilla 306, Santiago, Chile.

* Corresponding Authors, E-mail: jgsantos@uc.cl (J.G. Santos) and rmontecinoe@uc.cl> (R. Montecinos)

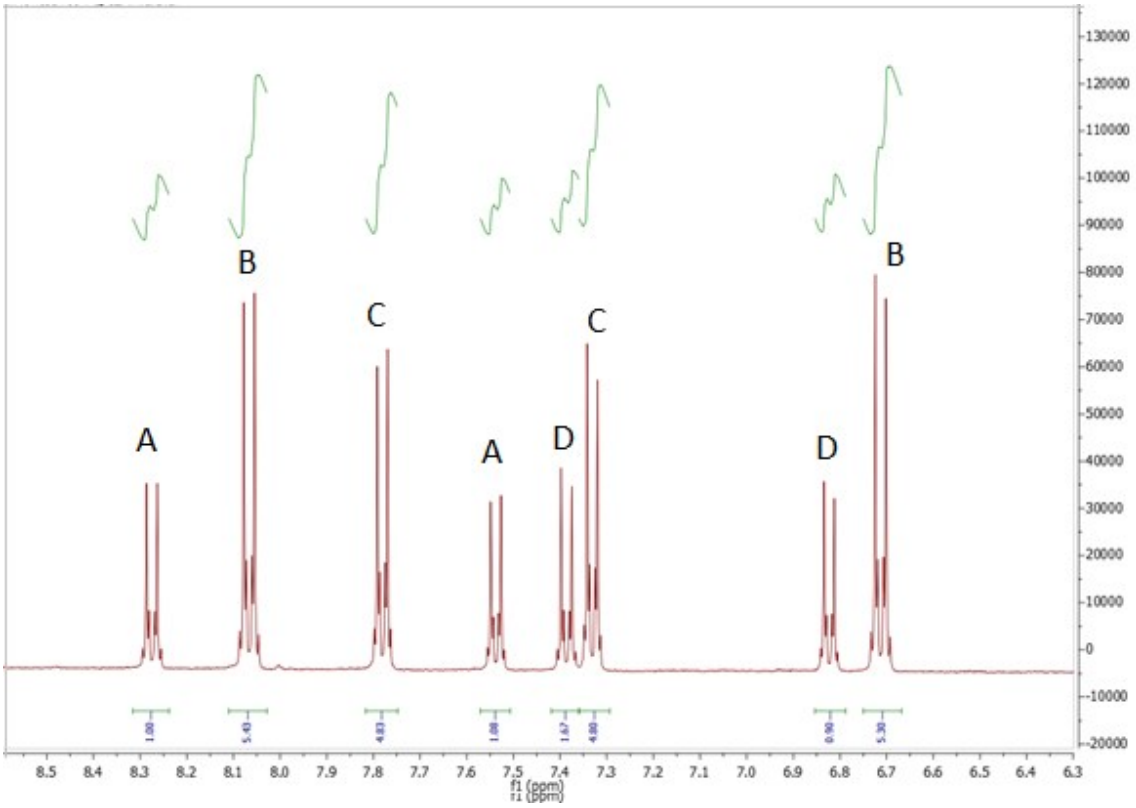

Figure S1.- ^{1}H-NMR spectrum for the reaction of **9** with excess of morpholine in acetonitrile-d_3

A: Morpholine 4-nitrophenyl carbamate, B: 4-nitrophenol, C: Morpholine 4-cyanophenyl carbamate, D: 4-cyanophenol

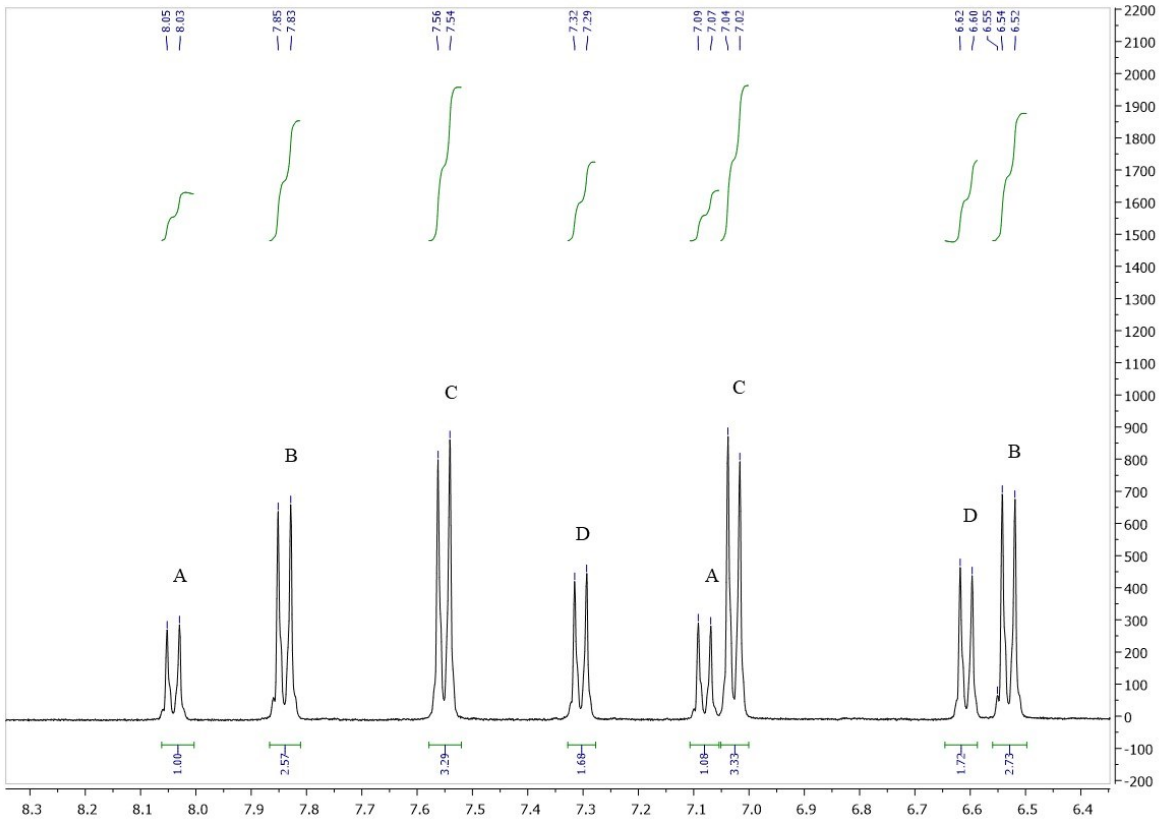

Figure S2.- ^{1}H-NMR spectrum for the reaction of **7** with excess of morpholine in deuterated acetonitrile-d_3. A: Morpholine 4-nitrophenyl thiocarbamate, B: 4-nitrophenol, C: Morpholine 4-cyanophenyl thiocarbamate, D: 4-cyanophenol

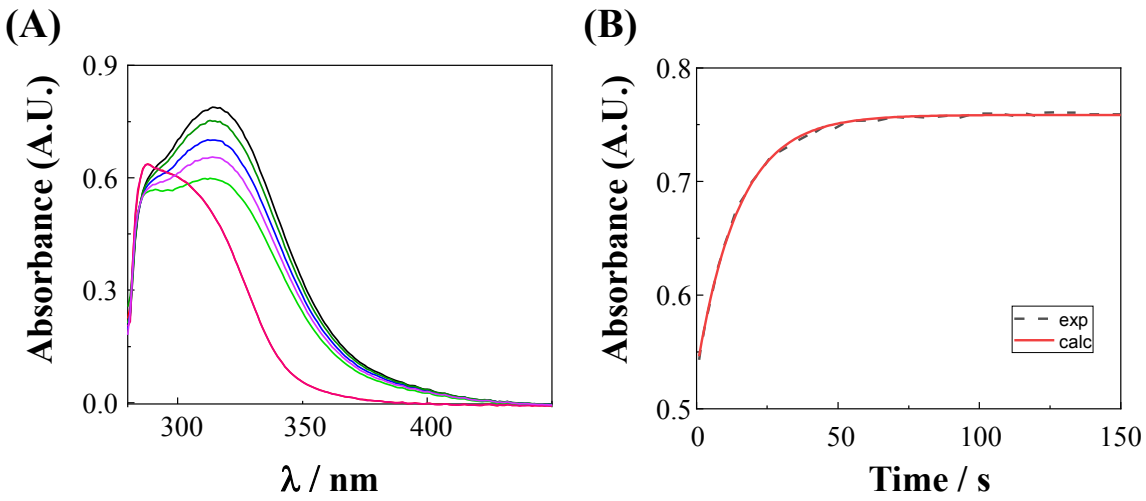

Figure S3.- Primary kinetic data for the reaction of **7** ($2.7x10^{-5}$ M) with piperidine ($4.35 x10^{-3}$ M) in toluene solution. **(A)** Absorption spectra for such reaction at different times (0-100 s). **(B)** Representative kinetic profile (experimental and calculated by fittting) obtained at λ=320 nm.

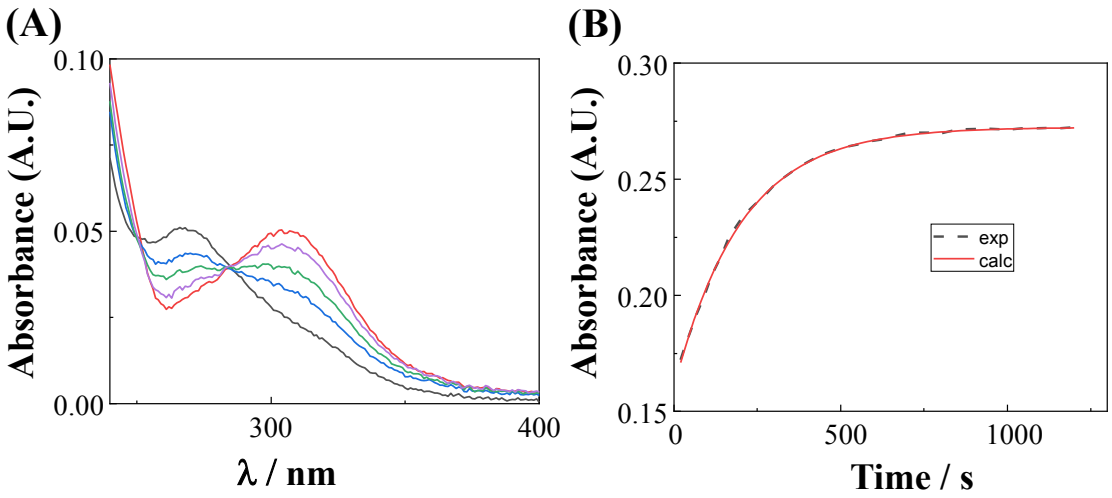

Figure S4.- Primary kinetic data for the reaction of **7** ($2.7x10^{-5}$ M) with 1-(2-hydroxyethyl)piperazine ($9.0x10^{-4}$ M) in acetonitrile solution. **(A)** Absorption spectra for

such reaction at different times (0-1000 s). **(B)** Representative kinetic profile (experimental and calculated by fittting) obtained at λ=300 nm.

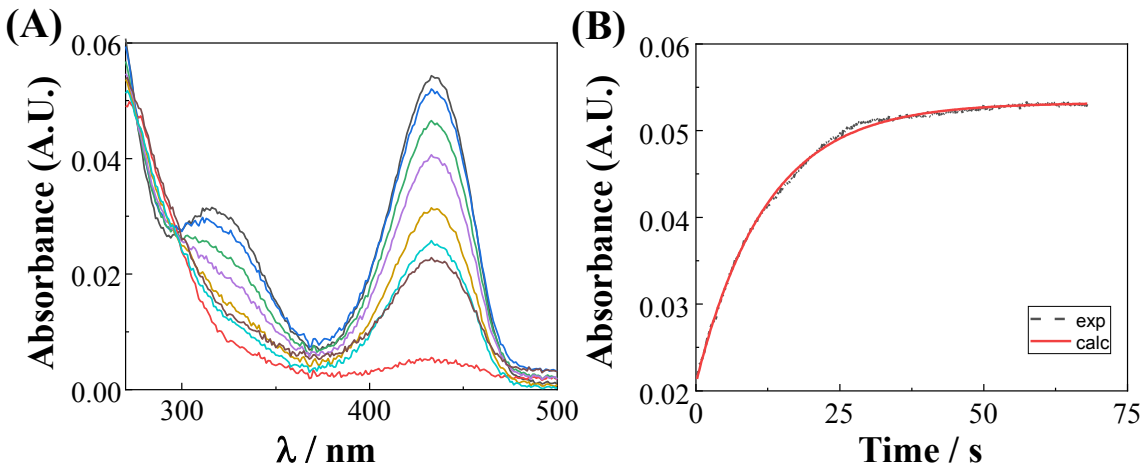

Figure S5.- Primary kinetic data for the reaction of **9** ($3.0x10^{-5}$ M) with morpholine ($6.09x10^{-4}$ M) in dimethyl sulfoxide solution. **(A)** Absorption spectra for such reaction at different times (0-50 s). **(B)** Representative kinetic profile (experimental and calculated by fittting) obtained at λ=430 nm.

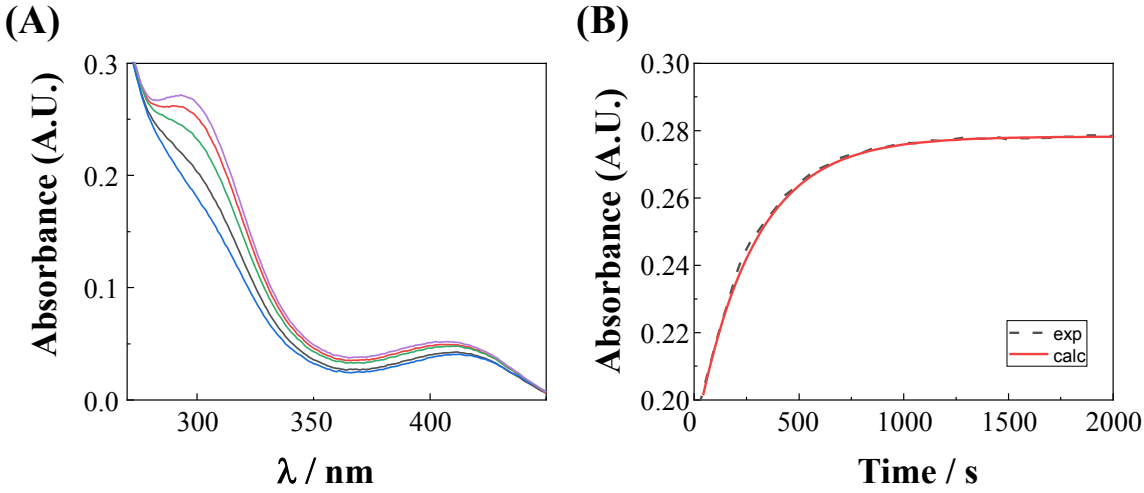

Figure S6.- Primary kinetic data for the reaction of **9** ($3.0x10^{-5}$ M) with morpholine ($9.0x10^{-4}$ M) in acetonitrile solution. **(A)** Absorption spectra for such reaction at different times (0-1000 s). **(B)** Representative kinetic profile (experimental and calculated by fittting) obtained at λ=292 nm.

Table S1.- Total amine concentration $[N]_T$ and pseudo first order rate constants (k_{obs}) for the reaction of **7** with Secondary Alicyclic Amines in Acetonitrile solution, at 25 ± 0.1 ° C.

	$10^3\ k_{obs}/s^{-1}$				
$10^4[N]_T/M$	Morpholine	1-(formyl)piperazine	1-(2-hydroxyethyl)piperazine	Piperazine	Piperidine
4.00	0.156	1.97	1.96	13.1	14.0
5.00	0.439	2.71	2.85	16.4	21.2
6.00	0.674		4.15		27.6
7.00	0.951	5.48		38.0	
8.00		6.50	6.51		44.9
9.00	1.42	7.71		54.2	
10.0		8.90	9.03	59.6	59.8

Table S2.- Total amine concentration $[N]_T$ and pseudo first order rate constants (k_{obs}) for the reaction of **9** with Secondary Alicyclic Amines in Acetonitrile solution, at 25 ± 0.1 ° C.

	$10^3\ k_{obs}/s^{-1}$				
$10^4[N]_T/M$	Morpholine	1-(formyl)piperazine	1-(2-hydroxyethyl)piperazine	Piperazine	Piperidine
4.00	0.861		2.31	10.8	54.1
5.00	1.02		2.84	13.4	64.8
6.00	1.20		3.08	15.8	73.8
7.00	1.45		3.60	18.0	85.6
8.00	1.60		3.90	21.5	100
9.00			4.48	23.1	110
43.5		8.02			
52.2		9.70			
60.9		12.2			
69.6		13.7			
78.3		16.3			
87.0		19.3			

Table S3.- Experimental conditions and pseudo first order rate constants for the reactions of **7** with piperidine at 25°C, in different solvents.[a)]

	$10^3 k_{obs}/s^{-1}$								
10^4[Piperidine/M]	Tol	DX	EA	MP	IP	E	M	AC	DMSO
4.00									187
5.00									238
6.00									291
7.00									331
8.00	0.88	2.34	11.1	4.12	5.26	4.01	4.62	30.2	375
9.00	1.25	2.97	13.5	4.80	6.40	4.67	5.02	35.0	446
10.0	1.68	3.48	16.4	5.44	7.40	5.30	5.48	43.4	
11.0	1.97	4.12	18.6	6.13	8.05	6.42	5.90	51.5	
12.0	2.41	4.71	20.8	7.00	9.00	7.64	6.52	57.1	
13.0	2.85		23.0	7.34	9.90	8.33	6.91	64.4	
14.0	3.25		25.0	8.09	11.0	9.07	7.30		

[a)] Toluene (Tol), Dioxane (DX), Ethyl acetate (EA), 2-Methyl propanol (MP), Isopropanol (IP), Ethanol (E), Methanol (M), Acetone (AC), Dimethyl sulfoxide (DMSO).

Table S4.- Total piperidine concentration and pseudo first order rate constants (k_{obs}) for the reaction of **9** with piperidine in different solvents[a)], at 25 ± 0.1 ° C.

	$10^2 k_{obs}/s^{-1}$								
10^4Piperidine/M	Tol	DX	EA	AC	E	MP	IP	M	DMSO
1.17									87.7
1.48									105
1.78									116
2.04									125
2.34									134
4.00		1.41	2.03	6.08	1.82	1.45	1.98	2.54	
5.00		1.73	2.78	8.09	2.45	1.76	2.90	3.08	
6.00		1.92	2.96	9.56	2.53	2.07	3.50	3.93	
7.00		2.13	3.64	10.9	3.09	2.49	4.04	4.53	
8.00		2.55	3.94	13.5	4.01	2.62	4.57	5.20	
9.00		2.83	4.72	15.7	4.45	2.92	5.54	5.69	
43.6	6.68								
52.2	8.28								
60.9	10.1								
69.6	11.4								
78.3	13.5								
87.0	14.8								

b) Toluene (Tol), Dioxane (DX), Ethyl acetate (EA), 2-Methyl propanol (MP), Isopropanol (IP), Ethanol (E), Methanol (M), Acetone (AC) , Dimethyl sulfoxide (DMSO).

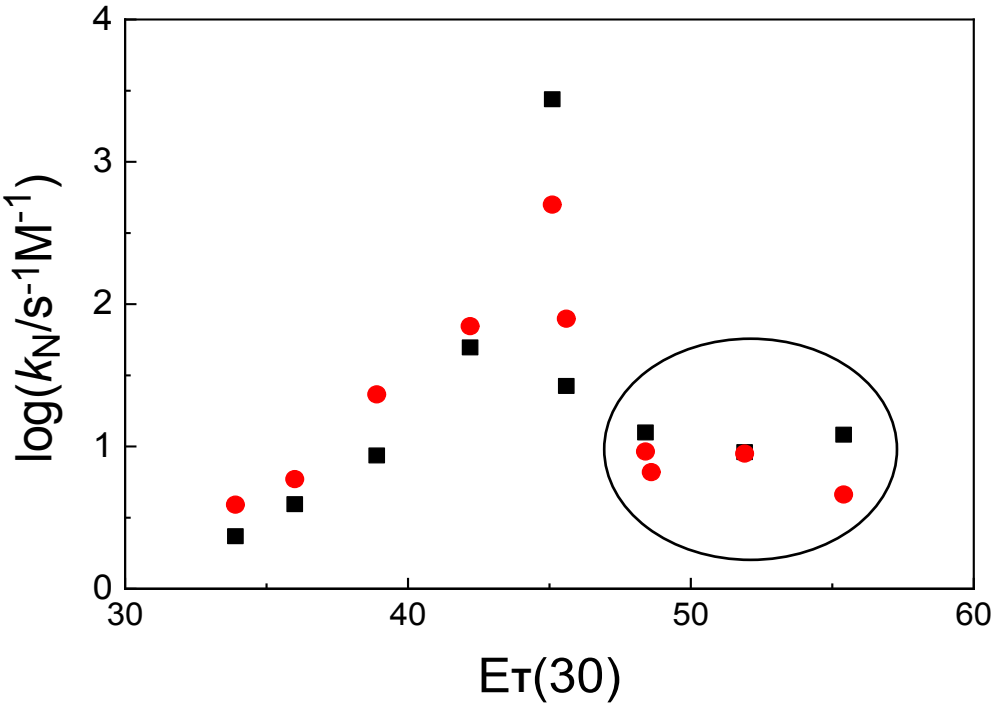

Figure S7.- log k_N against $E_T(30)$ for the reactions of **7** (●) and **9** (■) with piperidine in different solvents

Table S5. Statistical data from the stepwise regression procedure including Catalan's parameters for the reacion of **7** with piperidine.

Eqn. N°	A_0	b[a]	c[a]	d[a]	R^b	F^c	Prob>F
S1	-3.2±1.4	5.4±1.6			0.54	11	0.01
S2	1.5±0.3		-1.4±1.0		0.08	1.8	0.21
S3	1.2±0.6			0.06±1.1	-1.25	0.003	0.96
S4	1.0±0.6		-1.9±1.2	1.0±1.2	0.05	1.2	0.35
S5	-3.7±1.2	6.9±1.5		-1.4±0.7	0.66	9.9	0.009
S6	-3.7±0.4	6.4±0.5	-2.0±0.2		0.96	125	$3.3x10^{-6}$
S7	-3.8±0.4	6.8±0.4	-1.9±0.2	-0.4±0.2	0.98	123	$8.9x10^{-6}$

[a)]Eqn 2 coeficients, [b)]correlation coefficient, [c)]Statistical F.

Table S6. Statistical data from the stepwise regression procedure including Catalan's parameters for the reacion of **9** with piperidine

Eqn. N°	A0	b[a]	c[a]	d[a]	R^b	F^c	. Prob>F
S8	0.8±0.6	3.2±0.7			0.74	18.5	0.008
S9	1.7±0.3		0.2±0.6		-0.16	0.16	0.71
S10	1.3±0.3			0.7±0.6	0.1	1.7	0.25
S11	1.3±0.3		-0.1±0.6	0.8±0.7	0.11	0.7	0.55
S12	-1.3±0.7	4.2±1.0		-0.5±0.4	0.77	11	0.024
S13	-1.4±0.4	4.1±0.6	-0.6±0.2		0.88	24	0.006
S14	-1.8±0.4	4.7±0.7	-0.5±0.2	-0.5±0.2	0.91	21	0.015

Table S7. Bond length of the reactive center in reactant, concerted TS (CTS), first transition state (TS1), intermediate (T±), second transition state and products for the reaction of compound **7** with morpholine in acetonitrile. All bond length are in Å.

7+morph	reactant	CTS…NO2
C=S	1.64	1.63
S=C...O-f-NO2	1.35	2.14
S=C...O-f-CN	1.35	1.34
C-N	----	1.51
H...O-NO2	----	1.78
H...O-CN	----	----

Table S8. Bond length of the reactive center in reactant, concerted TS (CTS), first transition state (TS1), intermediate (T±), second transition state and products for the reaction of compound **7** with piperidine in acetonitrile. All bond length are in Å.

7+pip	reactant	CTS…NO2	C
C=S	1.64	1.63	
S=C...O-f-NO2	1.35	2.14	
S=C...O-f-CN	1.35	1.34	
C-N	----	1.50	
H...O-NO2	----	2.04	
H...O-CN	----	----	

Table S9. Bond length of the reactive center in reactant, concerted TS (CTS), first transition state (TS1), intermediate (T±), second transition state and products for the reaction of compound **9** with morpholine in acetonitrile. All bond length are in Å.

9+morph	reactant	C
C=O	1.20	
O=C...O-f-NO2	1.36	
O=C...O-f-CN	1.35	
C-N	---	
H...O-NO2	----	
H...O-CN	----	

Table S10. Bond length of the reactive center in reactant, concerted TS (CTS), first transition state (TS1), intermediate (T±), second transition state and products for the reaction of compound **9** with piperidine in acetonitrile. All bond length are in Å.

9+pip	reactant	CTS…NO2	CTS...CN	TS1	T+-
C=O	1.20	1.20	1.20	1.210	1.23
O=C...O-f-NO2	1.36	2.02	1.35	1.36	1.46
O=C...O-f-CN	1.35	1.37	2.06	1.38	1.45
C-N	---	1.75	1.51	2.28	1.61
H...O-NO2	----	1.84	----	----	----
H...O-CN	----	----	2.07	----	----

Table S11. Total and relative ΔG energies for the structures along the concerted and stepwise mechanism of the aminolysis reaction of compounds 7 with morpholine and piperidine, in acetonitrile (PCM).

	Compound 7 + morpholine				Compound 7 + piperidine			
Leaving group	4-nitrophenol		4-cyanophenol		4-nitrophenol		4-cyanophenol	
Structure	G [Hartree]	ΔGrel [kcal/mol]	G [Hartree]	ΔGrel [kcal/mol]	G [Hartree]	ΔGrel [kcal/mol]	G [Hartree]	ΔGrel [kcal/mol]
Reactants	-1633.797592	0	-1633.79759	0	-1597.88793	0	-1597.88793	0
CTS	-1633.769662	17.52	-1633.76329	21.52	-1597.86576	13.92	-1597.85867	18.36
TS1	-1633.780107	10.97	-1633.78011	10.97	-1597.87310	9.3	-1597.87310	9.3
T+-	-1633.793062	2.84	-1633.79306	2.84	-1597.88784	0.1	-1597.88784	0.1
TS2	-1633.769501	17.63	-1633.76724	19.05	-1597.86573	13.93	-1597.86354	15.31

Table S12. Total and relative ΔG energies for the structures along the concerted and stepwise mechanism of the aminolysis reaction of compounds 9 with morpholine and piperidine, in acetonitrile.

	Compound 9 + morpholine				Compound 9 + piperidine			
Leaving group	4-nitrophenol		4-cyanophenol		4-nitrophenol		4-cyanophenol	
Structure	G [Hartree]	ΔGrel [kcal/mol]	G [Hartree]	ΔGrel [kcal/mol]	G [Hartree]	ΔGrel [kcal/mol]	G [Hartree]	ΔGrel [kcal/mol]
Reactants	-1310.862799	0	-1310.862799	0	-1274.953833	0	-1274.953833	0
CTS	-1310.835744	14.51	-1310.833261	16.07	-1274.929878	15.03	-1274.923457	19.06
TS1	-1310.849015	8.64	-1310.849015	8.64	-1274.939976	8.70	-1274.939976	8.70
T+-	-1310.852858	6.24	-1310.852858	6.24	-1274.947616	3.90	-1274.947616	3.90
TS2	-1310.831436	17.21	-1310.827924	19.41	-1274.932141	13.61	-1274.928649	15.80

Table S13. Cartesian coordinates, energy (u.a.) for the reactants associated to the nucleophilic attack of morpholine to compound **7** in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.974832	0.172947	-0.150424
2	6	0	-2.652832	0.367078	-0.533475
3	6	0	-1.844868	-0.747445	-0.714070
4	6	0	-2.305386	-2.049596	-0.552332
5	6	0	-3.625197	-2.243389	-0.172102
6	6	0	-4.430010	-1.126702	0.024827
7	1	0	-4.643548	1.009230	0.008164
8	1	0	-2.251741	1.365186	-0.691710
9	1	0	-1.641895	-2.889228	-0.722609
10	1	0	-4.031989	-3.236545	-0.032893
11	7	0	-5.825580	-1.332398	0.427897
12	8	0	-6.215403	-2.478331	0.569179
13	8	0	-6.520546	-0.346332	0.600138
14	8	0	-0.551008	-0.519630	-1.171715
15	6	0	0.512077	-0.817360	-0.420465
16	8	0	1.565663	-0.544096	-1.184633
17	6	0	2.856088	-0.678924	-0.670812
18	6	0	3.357267	0.316936	0.156725
19	6	0	3.601790	-1.772804	-1.082998
20	6	0	4.669434	0.202128	0.594776
21	1	0	2.713960	1.148556	0.446214
22	6	0	4.914858	-1.882331	-0.642757
23	1	0	3.159369	-2.515995	-1.736003
24	6	0	5.443355	-0.895034	0.195434
25	1	0	5.097701	0.957639	1.243634
26	1	0	5.526049	-2.724702	-0.944910
27	6	0	6.803937	-1.005622	0.651633
28	7	0	7.898024	-1.092363	1.019436
29	6	0	-0.226509	2.419066	1.309898
30	6	0	-1.308244	3.438702	0.972463
31	6	0	-0.348485	3.831932	-1.132415
32	6	0	0.748945	2.811025	-0.859837
33	1	0	-2.262110	3.170824	1.436190
34	1	0	-0.589770	1.415925	1.054079
35	1	0	-0.017200	2.426952	2.383398
36	1	0	-0.608016	3.865422	-2.193477
37	1	0	-0.015455	4.834228	-0.818400
38	1	0	0.435188	1.838332	-1.259184
39	1	0	1.674047	3.096261	-1.369879
40	1	0	-1.011198	4.437713	1.329834
41	7	0	1.018726	2.649054	0.572447
42	1	0	1.451582	3.503444	0.920806
43	16	0	0.517786	-1.381266	1.119066
44	8	0	-1.535716	3.486305	-0.430618

Total Energy (a.u.) = -1634.07816627

Table S14. Cartesian coordinates, energy (u.a.) for the reactants associated to the nucleophilic attack of piperidine to compound **7** in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.214235	-1.900993	-0.734450
2	6	0	-2.887107	-1.870668	-1.144919
3	6	0	-2.074583	-0.838791	-0.696676
4	6	0	-2.530229	0.172881	0.141898
5	6	0	-3.854450	0.143141	0.553127
6	6	0	-4.667600	-0.893946	0.107087
7	1	0	-4.886807	-2.685246	-1.056663
8	1	0	-2.482046	-2.628859	-1.804356
9	1	0	-1.838061	0.951704	0.443831
10	1	0	-4.259172	0.906022	1.205642
11	7	0	-6.067844	-0.923017	0.542453
12	8	0	-6.457325	-0.027274	1.271632
13	8	0	-6.768417	-1.841116	0.152726
14	8	0	-0.777752	-0.795489	-1.192167
15	6	0	0.263265	-0.930900	-0.376910
16	8	0	1.337886	-0.682079	-1.130530
17	6	0	2.617238	-0.937701	-0.648060
18	6	0	3.032077	-2.249939	-0.452601
19	6	0	3.466263	0.145312	-0.474991
20	6	0	4.337474	-2.481260	-0.046808
21	1	0	2.341102	-3.068817	-0.615910
22	6	0	4.774771	-0.086721	-0.069613
23	1	0	3.109564	1.151520	-0.664604
24	6	0	5.204853	-1.398820	0.147667
25	1	0	4.688792	-3.493629	0.115261
26	1	0	5.458316	0.741657	0.074900
27	6	0	6.559474	-1.641974	0.568498
28	7	0	7.648621	-1.838609	0.907241
29	6	0	0.901183	2.386385	0.889860
30	6	0	1.721324	3.670490	0.743930
31	6	0	0.060559	4.443733	-0.980036
32	6	0	-0.703087	3.134448	-0.768009
33	1	0	2.218187	3.908624	1.690414
34	1	0	0.171958	2.510513	1.703230
35	1	0	1.536199	1.536926	1.165550
36	1	0	-0.632740	5.239613	-1.272359
37	1	0	0.770473	4.311756	-1.807712
38	1	0	-1.478230	3.288955	-0.003451
39	1	0	-1.213680	2.821222	-1.684340
40	1	0	2.511283	3.511220	-0.003887
41	7	0	0.146004	2.028891	-0.313403
42	1	0	0.795951	1.796163	-1.063696
43	6	0	0.823999	4.825658	0.290859
44	1	0	1.414267	5.733004	0.128766
45	1	0	0.102283	5.050867	1.088003
46	16	0	0.245163	-1.364275	1.205934

Total Energy (a. u.) = -1598.18993873

Table S15. Cartesian coordinates, energy (u.a.) for the reactants associated to the nucleophilic attack of morpholine to compound **9** in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.020723	-0.125729	0.908663
2	6	0	2.712006	-0.224017	1.358955
3	6	0	1.847130	-1.130485	0.750896
4	6	0	2.263712	-1.970391	-0.279961
5	6	0	3.572074	-1.872138	-0.732537
6	6	0	4.421943	-0.949215	-0.135560
7	1	0	4.718946	0.573226	1.350588
8	1	0	2.355840	0.389180	2.179228
9	1	0	1.577483	-2.678780	-0.723465
10	1	0	3.934250	-2.502453	-1.534421
11	7	0	5.799992	-0.844007	-0.622700
12	8	0	6.135185	-1.563952	-1.547272
13	8	0	6.537671	-0.040730	-0.078264
14	8	0	0.568761	-1.181610	1.277317
15	6	0	-0.482960	-1.195036	0.432056
16	8	0	-1.576475	-1.178678	1.207830
17	6	0	-2.814183	-1.034673	0.601183
18	6	0	-3.033957	-0.078937	-0.387344
19	6	0	-3.833793	-1.840731	1.092107
20	6	0	-4.314337	0.061228	-0.902086
21	1	0	-2.210659	0.535600	-0.729875
22	6	0	-5.114655	-1.695957	0.577303
23	1	0	-3.615823	-2.566967	1.866401
24	6	0	-5.352417	-0.746761	-0.422596
25	1	0	-4.512331	0.798128	-1.672122
26	1	0	-5.925180	-2.315538	0.943259
27	6	0	-6.676814	-0.598028	-0.963834
28	7	0	-7.741540	-0.477789	-1.402169
29	6	0	-1.093247	2.721801	0.773345
30	6	0	-0.298013	4.022427	0.757072
31	6	0	1.239625	3.120153	-0.761916
32	6	0	0.487257	1.795855	-0.786230
33	1	0	-0.949686	4.888940	0.897711
34	1	0	-1.887832	2.781466	0.018714
35	1	0	-1.565599	2.571068	1.748371
36	1	0	1.708604	3.329981	-1.726840
37	1	0	2.027504	3.079576	0.009521
38	1	0	-0.238165	1.807846	-1.609989
39	1	0	1.175877	0.963305	-0.964457
40	1	0	0.448054	4.009040	1.569155
41	8	0	0.355373	4.196121	-0.490394
42	7	0	-0.254960	1.559686	0.457287
43	1	0	0.415165	1.439672	1.217345
44	8	0	-0.443197	-1.271739	-0.762110

Total Energy (a. u.) = -1311.14581172

Table S16. Cartesian coordinates, energy (u.a.) for the reactants associated to the nucleophilic attack of piperidine to compound **9** in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.426925	-1.532400	0.812007
2	6	0	3.120918	-1.721955	1.237032
3	6	0	2.087596	-1.044053	0.594905
4	6	0	2.323943	-0.169935	-0.465589
5	6	0	3.630875	0.018284	-0.892191
6	6	0	4.656223	-0.665303	-0.249292
7	1	0	5.254515	-2.042735	1.287348
8	1	0	2.887788	-2.384980	2.061699
9	1	0	1.500086	0.351216	-0.934026
10	1	0	3.859345	0.689385	-1.710277
11	7	0	6.032006	-0.459181	-0.704052
12	8	0	6.218882	0.308157	-1.633322
13	8	0	6.921147	-1.064676	-0.129397
14	8	0	0.833877	-1.240549	1.136379
15	6	0	-0.246260	-1.230841	0.337590
16	8	0	-1.310154	-1.226310	1.164126
17	6	0	-2.581711	-1.192583	0.614368
18	6	0	-2.980487	-2.073542	-0.386767
19	6	0	-3.458092	-0.267892	1.173684
20	6	0	-4.286102	-2.005296	-0.852377
21	1	0	-2.282859	-2.792302	-0.795847
22	6	0	-4.763228	-0.202154	0.707508
23	1	0	-3.114508	0.383192	1.969796
24	6	0	-5.174283	-1.069274	-0.310232
25	1	0	-4.620361	-2.679006	-1.632960
26	1	0	-5.459536	0.514632	1.126946
27	6	0	-6.525598	-1.003444	-0.799125
28	7	0	-7.613171	-0.949852	-1.191912
29	6	0	-1.070493	1.843873	-0.748581
30	6	0	-1.781984	3.194796	-0.653400
31	6	0	-0.032334	3.911976	1.008470
32	6	0	0.617223	2.535141	0.849314
33	1	0	-2.273523	3.429262	-1.603650
34	1	0	-0.342409	1.869114	-1.572551
35	1	0	-1.778243	1.039302	-0.976042
36	1	0	0.729460	4.661590	1.248156
37	1	0	-0.731801	3.878581	1.854716
38	1	0	1.385074	2.584067	0.064233
39	1	0	1.120109	2.225495	1.771069
40	1	0	-2.569639	3.123294	0.109655
41	7	0	-0.334717	1.486039	0.468443
42	1	0	-1.004522	1.381956	1.230706
43	6	0	-0.790092	4.294724	-0.265605
44	1	0	-1.305885	5.251153	-0.134632
45	1	0	-0.068791	4.430453	-1.083164
46	8	0	-0.265172	-1.298303	-0.857640

Total Energy (a. u.) = -1275.26125082

Table S17. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS1) associated to the nucleophilic attack of morpholine to compound **7** in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.219244	-1.910648	-0.211782
2	6	0	-1.886594	-1.604909	0.016240
3	6	0	-1.502849	-0.275040	0.181051
4	6	0	-2.423590	0.767947	0.106026
5	6	0	-3.760224	0.463026	-0.116580
6	6	0	-4.133268	-0.865743	-0.268557
7	1	0	-3.549964	-2.932892	-0.342111
8	1	0	-1.132698	-2.382377	0.063928
9	1	0	-2.107980	1.794056	0.224460
10	1	0	-4.506130	1.244688	-0.182111
11	7	0	-5.544436	-1.176803	-0.508204
12	8	0	-6.337326	-0.251118	-0.533602
13	8	0	-5.851580	-2.345440	-0.669951
14	8	0	-0.140705	-0.093451	0.322016
15	6	0	0.461407	0.702324	1.236338
16	8	0	1.684422	0.207870	1.559766
17	6	0	2.216807	-0.888587	0.893341
18	6	0	1.691591	-2.158197	1.122499
19	6	0	3.331313	-0.691030	0.088409
20	6	0	2.277931	-3.251962	0.505539
21	1	0	0.839356	-2.276829	1.782478
22	6	0	3.922662	-1.787441	-0.528597
23	1	0	3.741544	0.304831	-0.040273
24	6	0	3.390845	-3.063653	-0.324706
25	1	0	1.882258	-4.248274	0.665960
26	1	0	4.791876	-1.655292	-1.162615
27	6	0	4.000033	-4.198189	-0.966576
28	7	0	4.490642	-5.109794	-1.484287
29	6	0	2.182770	2.969303	0.345334
30	6	0	2.702234	3.985083	-0.665680
31	6	0	0.805757	3.706751	-2.005215
32	6	0	0.225074	2.683626	-1.034606
33	1	0	3.288146	4.759714	-0.166012
34	1	0	1.605389	3.481893	1.123776
35	1	0	3.005294	2.433749	0.827393
36	1	0	0.007471	4.276242	-2.486276
37	1	0	1.389637	3.191695	-2.784509
38	1	0	-0.408381	3.199805	-0.301775
39	1	0	-0.373694	1.939482	-1.567483
40	1	0	3.342917	3.481796	-1.407256
41	7	0	1.278542	2.002779	-0.280528
42	1	0	1.792466	1.373748	-0.899393
43	16	0	-0.294752	1.704979	2.340745
44	8	0	1.625108	4.635273	-1.318709

Total Energy (a.u.) = -1634.06436923; **NIMAG =i168.79**

Table S18.- Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for concerted Transition State (CTS) associated to the departure of 4-nitrophenol for the reaction of compound **7** with morpholine in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.784798	-0.949489	-0.770951
2	6	0	-2.767942	-0.093759	-1.133665
3	6	0	-1.404445	-0.380007	-0.822525
4	6	0	-1.136002	-1.584895	-0.108765
5	6	0	-2.154939	-2.439813	0.261123
6	8	0	-0.457718	0.430408	-1.166528
7	6	0	-3.473904	-2.119708	-0.069324
8	1	0	-4.817790	-0.732786	-1.015612
9	1	0	-2.982832	0.817528	-1.684142
10	1	0	-0.105675	-1.826782	0.128526
11	1	0	-1.949480	-3.357787	0.798751
12	7	0	-4.535019	-3.015164	0.314276
13	8	0	-5.687312	-2.723539	0.011029
14	8	0	-4.248243	-4.035769	0.931194
15	6	0	0.760294	1.304475	0.374180
16	6	0	2.636332	0.047989	-0.267902
17	6	0	3.093082	-2.172178	-1.010920
18	6	0	2.289673	-1.040695	-1.057820
19	6	0	3.751688	0.058863	0.557198
20	1	0	1.403617	-0.977504	-1.678961
21	6	0	4.554936	-1.073365	0.599624
22	1	0	3.981161	0.938352	1.147502
23	6	0	4.221651	-2.185305	-0.182447
24	1	0	5.434644	-1.097710	1.232023
25	1	0	2.852198	-3.039928	-1.614123
26	6	0	5.055214	-3.357958	-0.140554
27	7	0	5.724576	-4.301687	-0.108703
28	6	0	-1.241152	2.824645	0.499024
29	6	0	-1.808592	4.089295	-0.125537
30	6	0	0.303914	5.003368	-0.458137
31	6	0	0.999583	3.779610	0.120720
32	1	0	0.216364	4.903467	-1.550116
33	1	0	0.906217	5.885547	-0.237316
34	1	0	1.141775	3.871813	1.199527
35	1	0	1.951744	3.588299	-0.371547
36	1	0	-2.776354	4.302058	0.330266
37	1	0	-1.955796	3.950858	-1.207675
38	1	0	-1.107173	2.942063	1.574451
39	1	0	-1.856140	1.949379	0.290908
40	8	0	1.867499	1.205253	-0.367661
41	7	0	0.115579	2.575494	-0.089334
42	1	0	-0.023953	2.389714	-1.095500
43	8	0	-0.967101	5.196329	0.123301
44	16	0	0.445435	0.614689	1.819297

Total Energy (a.u.) = -1634.05525116-; **NIMAG =i207.16**

Table S19. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for concerted Transition State (CTS) associated to the departure of 4-cyanophenol for the reaction of compound **7** with morpholine in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.882506	-2.969930	-0.623751
2	6	0	0.607478	-2.423385	-0.677997
3	6	0	0.403733	-1.138558	-0.190044
4	6	0	1.428782	-0.368491	0.349750
5	6	0	2.703298	-0.916060	0.405873
6	8	0	-0.890456	-0.647583	-0.352727
7	6	0	2.903653	-2.202780	-0.079368
8	1	0	2.084759	-3.967129	-0.992112
9	1	0	-0.226251	-2.977122	-1.093553
10	1	0	1.238849	0.634952	0.710323
11	1	0	3.533528	-0.353573	0.814033
12	7	0	4.252817	-2.774796	-0.017132
13	8	0	5.136613	-2.098322	0.479048
14	8	0	4.417130	-3.896628	-0.464209
15	6	0	-1.617776	-0.194280	0.659938
16	6	0	-0.589889	2.355645	-0.156755
17	6	0	1.407869	3.312593	0.888832
18	6	0	0.075308	2.949163	0.957204
19	6	0	0.171436	2.190901	-1.352871
20	1	0	-0.495862	3.105231	1.866638
21	6	0	1.499470	2.556125	-1.419108
22	1	0	-0.322056	1.747715	-2.212786
23	6	0	2.139268	3.109495	-0.293933
24	1	0	2.064564	2.407132	-2.334278
25	1	0	1.900360	3.751338	1.751449
26	6	0	3.521108	3.472992	-0.355735
27	7	0	4.643237	3.765949	-0.402782
28	6	0	-3.272969	-0.221855	-1.271278
29	6	0	-4.762629	-0.093544	-1.540153
30	6	0	-5.331118	-1.087591	0.477816
31	6	0	-3.874798	-1.245367	0.890848
32	1	0	-5.731450	-0.142165	0.873095
33	1	0	-5.904331	-1.911573	0.905356
34	1	0	-3.464413	-2.201423	0.558673
35	1	0	-3.750667	-1.136789	1.967287
36	1	0	-4.930718	-0.166994	-2.615595
37	1	0	-5.132322	0.883880	-1.195201
38	1	0	-2.897839	-1.183878	-1.619653
39	1	0	-2.699439	0.600548	-1.693543
40	8	0	-1.802748	1.932413	-0.071347
41	7	0	-3.053350	-0.171043	0.221797
42	1	0	-3.353403	0.763311	0.536526
43	8	0	-5.482012	-1.140729	-0.923206
44	16	0	-1.225552	-0.081118	2.237755

Total Energy (a.u.) =-1634.04844247; **NIMAG =i187.82**

Table S20. Cartesian coordinates, energy (u.a.) for the intermediate structure (T±) associated to the reaction of compound **7** with morpholine in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.340555	0.669421	-0.926210
2	6	0	1.966633	0.545400	-1.063039
3	6	0	4.012556	-0.271423	-0.155805
4	1	0	3.884977	1.475883	-1.400263
5	6	0	1.294531	-0.507457	-0.438577
6	1	0	1.394688	1.255070	-1.650156
7	6	0	3.360573	-1.328681	0.467542
8	7	0	5.461822	-0.148557	0.000171
9	6	0	1.986020	-1.452901	0.321809
10	1	0	3.926765	-2.043146	1.051199
11	8	0	6.038069	-0.983220	0.677650
12	8	0	6.020577	0.782341	-0.555681
13	1	0	1.458370	-2.262393	0.806339
14	1	0	-2.016887	-1.765646	-1.289404
15	7	0	-1.813649	-2.017755	-0.313416
16	6	0	-0.945713	-3.233792	-0.307676
17	6	0	-3.109514	-2.306386	0.381674
18	6	0	-3.760785	-3.529252	-0.246901
19	1	0	-3.738549	-1.421240	0.298287
20	1	0	0.148338	1.563992	0.713588
21	6	0	-1.712660	-4.411992	-0.892602
22	1	0	-3.864534	1.812091	-0.802529
23	1	0	-4.666645	-3.771355	0.310511
24	1	0	-4.038790	-3.325759	-1.291873
25	1	0	-2.855117	-2.486582	1.426843
26	8	0	-0.046337	-0.590563	-0.720670
27	1	0	-1.094331	-5.307402	-0.814417
28	1	0	-0.682343	-3.413513	0.736869
29	1	0	-0.053687	-3.015207	-0.895458
30	6	0	-0.617698	3.539566	0.396685
31	6	0	-1.870563	1.544041	-0.064897
32	6	0	-2.886197	3.696999	-0.443865
33	8	0	-2.070983	0.199659	-0.162747
34	6	0	-2.964713	2.316382	-0.469056
35	6	0	-1.706033	4.316103	-0.010854
36	1	0	-1.933447	-4.233531	-1.955914
37	6	0	-1.085500	-0.735154	0.237599
38	6	0	-0.692655	2.152833	0.374325
39	1	0	0.293238	4.021164	0.734687
40	6	0	-1.614315	5.749277	0.016496
41	1	0	-3.732592	4.297756	-0.756910
42	7	0	-1.539867	6.904936	0.038577
43	16	0	-0.715669	-0.820664	1.945871
44	8	0	-2.904327	-4.650445	-0.175120

Total Energy (a.u.) = -1634.08136877

Table S21. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4-nitrophenol from the reaction of compound **7** with morpholine, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.784564	-0.949775	-0.771331
2	6	0	-2.767699	-0.094025	-1.133971
3	6	0	-1.404267	-0.380023	-0.822296
4	6	0	-1.135875	-1.584712	-0.108192
5	6	0	-2.154821	-2.439639	0.261624
6	6	0	-3.473712	-2.119762	-0.069298
7	1	0	-4.817512	-0.733272	-1.016366
8	1	0	-2.982526	0.817097	-1.684746
9	1	0	-0.105572	-1.826467	0.129353
10	1	0	-1.949413	-3.357475	0.799519
11	7	0	-4.534760	-3.015261	0.314248
12	8	0	-4.247892	-4.035372	0.931944
13	8	0	-5.686965	-2.724130	0.010177
14	8	0	-0.457498	0.430350	-1.166206
15	6	0	0.760529	1.304791	0.374271
16	8	0	1.867587	1.205391	-0.367745
17	6	0	2.636206	0.047962	-0.268060
18	6	0	3.751270	0.058365	0.557449
19	6	0	2.289600	-1.040439	-1.058408
20	6	0	4.554249	-1.074060	0.599886
21	1	0	3.980758	0.937621	1.148093
22	6	0	3.092738	-2.172118	-1.011484
23	1	0	1.403761	-0.976982	-1.679835
24	6	0	4.220991	-2.185730	-0.182584
25	1	0	5.433699	-1.098767	1.232627
26	1	0	2.851834	-3.039686	-1.614937
27	6	0	5.054210	-3.358625	-0.140595
28	7	0	5.723284	-4.302558	-0.108706
29	16	0	0.445930	0.615383	1.819629
30	6	0	0.999786	3.779810	0.119761
31	6	0	0.303736	5.003619	-0.458568
32	6	0	-1.808556	4.089476	-0.125075
33	6	0	-1.240860	2.824913	0.499409
34	1	0	0.906131	5.885785	-0.237945
35	1	0	1.143009	3.872018	1.198430
36	1	0	1.951466	3.588405	-0.373402
37	1	0	-2.776234	4.302232	0.330902
38	1	0	-1.955935	3.950910	-1.207172
39	1	0	-1.106432	2.942436	1.574767
40	1	0	-1.855940	1.949630	0.291615
41	1	0	0.215646	4.903845	-1.550516
42	7	0	0.115630	2.575667	-0.089476
43	1	0	-0.024295	2.389471	-1.095495
44	8	0	-0.967002	5.196508	0.123500

Total Energy (a.u.) = -1634.05525114; **NIMAG = i207.13**

Table S22. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4-cyanophenol from the reaction of compound **7** with morpholine, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.181785	-0.943685	0.560466
2	6	0	2.949155	-1.580273	0.497828
3	6	0	1.945068	-1.005562	-0.268641
4	6	0	2.114150	0.175035	-0.982241
5	6	0	3.344994	0.814303	-0.916808
6	6	0	4.349897	0.240916	-0.145972
7	1	0	4.998781	-1.349419	1.142899
8	1	0	2.761764	-2.505822	1.029280
9	1	0	1.281079	0.558409	-1.560859
10	1	0	3.532586	1.736152	-1.452344
11	7	0	5.651739	0.915005	-0.079392
12	8	0	5.784609	1.960675	-0.690911
13	8	0	6.530420	0.393213	0.584562
14	8	0	0.734208	-1.680643	-0.383519
15	6	0	-0.293074	-1.285146	0.374379
16	8	0	-1.004528	0.075463	-1.179349
17	6	0	-1.555748	1.186571	-0.802976
18	6	0	-2.924561	1.467074	-1.082824
19	6	0	-0.826578	2.171520	-0.078929
20	6	0	-3.516297	2.646748	-0.680389
21	1	0	-3.490976	0.726598	-1.640972
22	6	0	-1.423076	3.350682	0.327805
23	1	0	0.218570	1.980462	0.141520
24	6	0	-2.772473	3.602817	0.033889
25	1	0	-4.558609	2.843877	-0.911480
26	1	0	-0.849460	4.092319	0.875309
27	6	0	-3.385240	4.825166	0.454105
28	7	0	-3.881964	5.816743	0.795908
29	6	0	-2.753116	-1.763376	0.554354
30	6	0	-3.849445	-2.602620	-0.082282
31	6	0	-2.382504	-4.336722	-0.578374
32	6	0	-1.191405	-3.591647	0.005580
33	1	0	-4.792179	-2.391316	0.423981
34	1	0	-2.648679	-1.991039	1.615257
35	1	0	-2.917789	-0.694483	0.416610
36	1	0	-2.231269	-5.407233	-0.432634
37	1	0	-2.456260	-4.138069	-1.657963
38	1	0	-1.064463	-3.807335	1.068696
39	1	0	-0.274950	-3.814914	-0.537931
40	1	0	-3.960699	-2.347255	-1.147395
41	7	0	-1.449134	-2.109268	-0.100624
42	1	0	-1.521387	-1.806147	-1.087434
43	16	0	-0.252296	-0.525781	1.815427
44	8	0	-3.582585	-3.981265	0.072163

Total Energy (a.u.) = -1634.05230170; **NIMAG = i189.87**

Table S23. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS1) associated to the nucleophilic attack of piperidine to compound **7** in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.250610	-1.931469	-0.216978
2	6	0	-1.918785	-1.637359	0.030299
3	6	0	-1.527088	-0.311390	0.207694
4	6	0	-2.438521	0.739317	0.126429
5	6	0	-3.774265	0.445868	-0.116021
6	6	0	-4.155618	-0.879112	-0.280099
7	1	0	-3.587609	-2.950359	-0.357040
8	1	0	-1.171703	-2.420886	0.084054
9	1	0	-2.115700	1.762134	0.253142
10	1	0	-4.513175	1.233627	-0.187213
11	7	0	-5.565987	-1.177809	-0.539217
12	8	0	-6.351363	-0.245849	-0.568869
13	8	0	-5.880158	-2.343051	-0.711699
14	8	0	-0.165746	-0.142940	0.370415
15	6	0	0.427502	0.650739	1.287468
16	8	0	1.656991	0.175379	1.599719
17	6	0	2.219823	-0.890402	0.909286
18	6	0	1.719747	-2.177787	1.090093
19	6	0	3.345245	-0.643592	0.133278
20	6	0	2.343999	-3.238857	0.453105
21	1	0	0.858049	-2.337199	1.728727
22	6	0	3.974136	-1.707091	-0.503616
23	1	0	3.733018	0.365305	0.042475
24	6	0	3.468685	-3.000723	-0.347922
25	1	0	1.969095	-4.248306	0.576830
26	1	0	4.852671	-1.535329	-1.114842
27	6	0	4.117272	-4.101305	-1.009874
28	7	0	4.639826	-4.985207	-1.544083
29	6	0	2.147560	2.958268	0.377536
30	6	0	2.754840	3.957776	-0.608010
31	6	0	0.741033	3.634827	-2.072873
32	6	0	0.199740	2.641522	-1.043088
33	1	0	3.368379	4.680960	-0.061695
34	1	0	1.538727	3.486160	1.123648
35	1	0	2.919248	2.405738	0.922399
36	1	0	-0.095721	4.124677	-2.580430
37	1	0	1.306803	3.084343	-2.835585
38	1	0	-0.437287	3.169848	-0.319160
39	1	0	-0.400809	1.863911	-1.525030
40	1	0	3.419992	3.422832	-1.298701
41	7	0	1.258256	1.990065	-0.268624
42	1	0	1.791916	1.372867	-0.881981
43	6	0	1.650394	4.662377	-1.398115
44	1	0	2.081103	5.340417	-2.140770
45	1	0	1.052312	5.275394	-0.710802
46	16	0	-0.327644	1.658536	2.382335

Total Energy (a.u.) = -1598.1806269; **NIMAG = i176.33**

Table S24. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for concerted Transition State (CTS) associated to the departure of 4-nitrophenol for the reaction of compound **7** with piperidine, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.769037	-0.984734	-0.767474
2	6	0	-2.759232	-0.118658	-1.124409
3	6	0	-1.393678	-0.392912	-0.810402
4	6	0	-1.116391	-1.596482	-0.097435
5	6	0	-2.128443	-2.461939	0.266716
6	8	0	-0.454803	0.427256	-1.151471
7	6	0	-3.449388	-2.154123	-0.067995
8	1	0	-4.803290	-0.776742	-1.014386
9	1	0	-2.980681	0.793252	-1.671154
10	1	0	-0.084689	-1.828387	0.143781
11	1	0	-1.916345	-3.378894	0.803526
12	7	0	-4.502971	-3.060396	0.309464
13	8	0	-5.657182	-2.778443	0.003781
14	8	0	-4.208933	-4.080607	0.923925
15	6	0	0.754297	1.314307	0.378713
16	6	0	2.632774	0.063944	-0.272162
17	6	0	3.101196	-2.153129	-1.019110
18	6	0	2.292206	-1.025517	-1.063916
19	6	0	3.748917	0.078266	0.552304
20	1	0	1.405530	-0.965975	-1.684409
21	6	0	4.557867	-1.049840	0.592810
22	1	0	3.974075	0.957717	1.144356
23	6	0	4.229888	-2.162342	-0.190795
24	1	0	5.437750	-1.070946	1.225110
25	1	0	2.864335	-3.021120	-1.623601
26	6	0	5.068509	-3.331350	-0.150024
27	7	0	5.741782	-4.272342	-0.118607
28	6	0	-1.269731	2.796868	0.507953
29	6	0	-1.915382	4.000870	-0.161020
30	6	0	0.353735	5.016384	-0.483818
31	6	0	0.984962	3.790124	0.160487
32	1	0	0.346949	4.884348	-1.572181
33	1	0	1.001362	5.870085	-0.268780
34	1	0	1.072648	3.890857	1.245689
35	1	0	1.960492	3.559802	-0.264292
36	1	0	-2.908225	4.128317	0.277168
37	1	0	-2.060915	3.793071	-1.228366
38	1	0	-1.132680	2.951668	1.579783
39	1	0	-1.826625	1.875032	0.346286
40	8	0	1.859029	1.216983	-0.369687
41	7	0	0.102241	2.582657	-0.070111
42	1	0	-0.025220	2.419320	-1.080308
43	16	0	0.461800	0.621687	1.830385
44	6	0	-1.065910	5.257286	0.027118
45	1	0	-1.516087	6.102112	-0.499278
46	1	0	-1.032383	5.516407	1.092035

Total Energy (a.u.) = -1598.17528934; **NIMAG = i209.48**

Table S25. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for concerted Transition State (CTS) associated to the departure of 4-cyanophenol for the reaction of compound **7** with piperidine, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.876209	-2.976200	-0.622677
2	6	0	0.603233	-2.425033	-0.675038
3	6	0	0.403692	-1.138701	-0.188360
4	6	0	1.433127	-0.372040	0.348626
5	6	0	2.705737	-0.924117	0.403116
6	8	0	-0.888167	-0.645698	-0.351910
7	6	0	2.901117	-2.212134	-0.080947
8	1	0	2.074228	-3.974441	-0.990538
9	1	0	-0.233215	-2.976223	-1.088592
10	1	0	1.247615	0.632479	0.708195
11	1	0	3.538699	-0.363971	0.808949
12	7	0	4.248184	-2.788614	-0.020805
13	8	0	5.135331	-2.115292	0.473889
14	8	0	4.408221	-3.911094	-0.468049
15	6	0	-1.616521	-0.179641	0.656434
16	6	0	-0.575927	2.357753	-0.160710
17	6	0	1.423297	3.310558	0.886891
18	6	0	0.089413	2.951770	0.953201
19	6	0	0.187209	2.189623	-1.355460
20	1	0	-0.482910	3.111554	1.861198
21	6	0	1.516441	2.550724	-1.419886
22	1	0	-0.306020	1.747589	-2.216128
23	6	0	2.156265	3.103166	-0.294181
24	1	0	2.082663	2.398972	-2.333921
25	1	0	1.915675	3.748924	1.749797
26	6	0	3.539512	3.461448	-0.353618
27	7	0	4.662858	3.750170	-0.398492
28	6	0	-3.263583	-0.220452	-1.276518
29	6	0	-4.738544	-0.017871	-1.585641
30	6	0	-5.335268	-1.086199	0.594359
31	6	0	-3.856842	-1.251186	0.912782
32	1	0	-5.694794	-0.151493	1.041129
33	1	0	-5.867386	-1.902326	1.089699
34	1	0	-3.457208	-2.201952	0.548610
35	1	0	-3.657108	-1.159580	1.978876
36	1	0	-4.851033	-0.050156	-2.672383
37	1	0	-5.046244	0.983963	-1.261800
38	1	0	-2.915609	-1.200956	-1.606490
39	1	0	-2.632007	0.563444	-1.686940
40	8	0	-1.789595	1.937309	-0.075635
41	7	0	-3.051286	-0.171263	0.222621
42	1	0	-3.365226	0.757722	0.536262
43	16	0	-1.211707	-0.054458	2.232820
44	6	0	-5.598254	-1.084155	-0.910125
45	1	0	-6.657198	-0.901836	-1.107231
46	1	0	-5.352113	-2.068117	-1.326928

Total Energy (a.u.) = -1598.16794899; **NIMAG = i193.21**

Table S26. Cartesian coordinates, energy (u.a.) for the intermediate structure (T±) associated to the reaction of compound **7** with piperidine in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.387429	0.094364	-0.912545
2	6	0	2.012318	0.219877	-1.032712
3	6	0	3.889450	-0.961684	-0.161779
4	1	0	4.062924	0.798326	-1.381313
5	6	0	1.168600	-0.705311	-0.413946
6	1	0	1.569997	1.029625	-1.602071
7	6	0	3.065452	-1.893601	0.457246
8	7	0	5.338662	-1.100400	-0.022678
9	6	0	1.689456	-1.769773	0.325577
10	1	0	3.500719	-2.706386	1.024604
11	8	0	5.763576	-2.003509	0.678660
12	8	0	6.049234	-0.305444	-0.615372
13	1	0	1.031216	-2.481879	0.803127
14	1	0	-2.327345	-1.364845	-1.242716
15	7	0	-2.149567	-1.662583	-0.274934
16	6	0	-1.491257	-3.007843	-0.319035
17	6	0	-3.472547	-1.732603	0.436374
18	6	0	-4.395404	-2.723011	-0.260637
19	1	0	-3.879663	-0.722864	0.449649
20	1	0	0.389116	1.501864	0.835207
21	6	0	-2.394518	-4.020125	-1.012597
22	1	0	-3.439246	2.475317	-0.853197
23	1	0	-5.334520	-2.748302	0.298004
24	1	0	-4.631971	-2.359972	-1.268430
25	1	0	-3.239727	-2.038338	1.458247
26	8	0	-0.166503	-0.543505	-0.683212
27	1	0	-1.880680	-4.984656	-0.998127
28	1	0	-1.295139	-3.277698	0.722165
29	1	0	-0.547708	-2.888594	-0.851076
30	6	0	0.035170	3.578407	0.439654
31	6	0	-1.563486	1.848796	-0.028775
32	6	0	-2.128974	4.146176	-0.493549
33	8	0	-2.020834	0.567624	-0.098150
34	6	0	-2.472038	2.806489	-0.492936
35	6	0	-0.866995	4.538492	-0.027359
36	1	0	-2.514252	-3.737093	-2.065557
37	6	0	-1.212488	-0.535471	0.279891
38	6	0	-0.306205	2.232029	0.444721
39	1	0	1.009279	3.885734	0.803830
40	6	0	-0.500490	5.927268	-0.028014
41	1	0	-2.830573	4.889094	-0.855813
42	7	0	-0.205078	7.047309	-0.029211
43	6	0	-3.760178	-4.110219	-0.335270
44	1	0	-4.409085	-4.796877	-0.884312
45	1	0	-3.640670	-4.512334	0.677876
46	16	0	-0.849021	-0.704079	1.986026

Total Energy (a.u.) = -1598.20030489;

Table S27. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS2) associated to the departure of 4-nitrophenol from the reaction of compound **7** with piperidine in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.770347	-0.983325	-0.767574
2	6	0	-2.760239	-0.117616	-1.124519
3	6	0	-1.394752	-0.392289	-0.810507
4	6	0	-1.117897	-1.595983	-0.097565
5	6	0	-2.130257	-2.461064	0.266614
6	6	0	-3.451104	-2.152814	-0.068053
7	1	0	-4.804521	-0.774947	-1.014466
8	1	0	-2.981366	0.794443	-1.671131
9	1	0	-0.086312	-1.828343	0.143695
10	1	0	-1.918461	-3.378091	0.803431
11	7	0	-4.504924	-3.058743	0.309550
12	8	0	-4.211110	-4.078747	0.924454
13	8	0	-5.659080	-2.776754	0.003674
14	8	0	-0.455642	0.427617	-1.151514
15	6	0	0.754970	1.313618	0.378168
16	8	0	1.859191	1.215890	-0.370897
17	6	0	2.633124	0.062990	-0.272907
18	6	0	3.750903	0.078796	0.549324
19	6	0	2.291073	-1.027941	-1.062030
20	6	0	4.559917	-1.049253	0.590395
21	1	0	3.977220	0.959351	1.139260
22	6	0	3.100144	-2.155447	-1.016707
23	1	0	1.403300	-0.969780	-1.681059
24	6	0	4.230433	-2.163188	-0.190527
25	1	0	5.440999	-1.069191	1.221057
26	1	0	2.862126	-3.024498	-1.619209
27	6	0	5.069127	-3.332127	-0.149310
28	7	0	5.742382	-4.273124	-0.117656
29	16	0	0.463028	0.620872	1.829868
30	6	0	0.986064	3.789549	0.160773
31	6	0	0.355095	5.016142	-0.483234
32	6	0	-1.914079	4.001117	-0.160340
33	6	0	-1.268705	2.796672	0.508127
34	1	0	1.003051	5.869574	-0.268122
35	1	0	1.073493	3.890250	1.246006
36	1	0	1.961599	3.559169	-0.263972
37	1	0	-2.906979	4.128553	0.277716
38	1	0	-2.059477	3.793631	-1.227759
39	1	0	-1.131571	2.950890	1.580022
40	1	0	-1.825994	1.875200	0.345857
41	1	0	0.348036	4.884348	-1.571624
42	7	0	0.103161	2.582321	-0.070164
43	1	0	-0.024530	2.419362	-1.080439
44	6	0	-1.064357	5.257258	0.028136
45	1	0	-1.514487	6.102424	-0.497756
46	1	0	-1.030446	5.515902	1.093162

Total Energy (a.u.) = -1598.17528906;**NIMAG=i209.27**

Table S28. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for concerted Transition State (TS2) associated to the departure of 4-cyanophenol for the reaction of compound **7** with piperidine in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.161248	-1.002047	0.552041
2	6	0	2.921209	-1.623896	0.489809
3	6	0	1.922848	-1.037545	-0.275776
4	6	0	2.106369	0.140783	-0.989704
5	6	0	3.344685	0.765569	-0.924850
6	6	0	4.343090	0.180727	-0.154207
7	1	0	4.973557	-1.417502	1.134195
8	1	0	2.723266	-2.546831	1.021992
9	1	0	1.277379	0.534345	-1.567239
10	1	0	3.542723	1.685102	-1.460584
11	7	0	5.652325	0.839907	-0.087357
12	8	0	5.796747	1.885146	-0.697076
13	8	0	6.525607	0.307319	0.575257
14	8	0	0.704156	-1.697032	-0.389644
15	6	0	-0.315122	-1.297852	0.378723
16	8	0	-1.007746	0.084987	-1.166555
17	6	0	-1.526223	1.211175	-0.792154
18	6	0	-2.885549	1.532485	-1.078059
19	6	0	-0.772896	2.174917	-0.063221
20	6	0	-3.443836	2.729621	-0.680373
21	1	0	-3.471442	0.807347	-1.636196
22	6	0	-1.336247	3.371556	0.339086
23	1	0	0.264592	1.953205	0.164519
24	6	0	-2.675862	3.664389	0.037002
25	1	0	-4.478959	2.956727	-0.916562
26	1	0	-0.743863	4.095588	0.890286
27	6	0	-3.254419	4.904014	0.454304
28	7	0	-3.723991	5.909423	0.794454
29	6	0	-2.786311	-1.693359	0.542951
30	6	0	-3.928423	-2.435675	-0.133649
31	6	0	-2.389516	-4.360300	-0.585969
32	6	0	-1.247279	-3.591684	0.063065
33	1	0	-4.858449	-2.112479	0.340433
34	1	0	-2.711237	-1.941805	1.603349
35	1	0	-2.861673	-0.612250	0.431910
36	1	0	-2.200035	-5.424879	-0.426969
37	1	0	-2.366536	-4.187913	-1.668481
38	1	0	-1.183132	-3.775943	1.139042
39	1	0	-0.288550	-3.812399	-0.402605
40	1	0	-3.985766	-2.138664	-1.188365
41	7	0	-1.482965	-2.104135	-0.085078
42	1	0	-1.542269	-1.836404	-1.080868
43	6	0	-3.746064	-3.948394	-0.016283
44	1	0	-4.548347	-4.470357	-0.542729
45	1	0	-3.803685	-4.240009	1.039253
46	16	0	-0.247218	-0.548845	1.826201

Total Energy (a.u.) = -1598.17227063;**NIMAG=i186.54**

Table S29. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (**TS1**) associated to the nucleophilic attack of morpholine to compound **9** in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.269613	-2.667624	-0.938076
2	6	0	-1.188207	-1.805617	-1.005131
3	6	0	-1.178184	-0.642761	-0.232284
4	6	0	-2.242385	-0.317732	0.609829
5	6	0	-3.325578	-1.185223	0.679653
6	6	0	-3.322058	-2.340383	-0.090229
7	1	0	-2.301919	-3.577493	-1.523206
8	1	0	-0.339137	-2.017798	-1.644383
9	1	0	-2.224677	0.582933	1.205045
10	1	0	-4.168826	-0.967068	1.322510
11	7	0	-4.467443	-3.246482	-0.006109
12	8	0	-5.385561	-2.942543	0.736739
13	8	0	-4.444959	-4.260392	-0.683428
14	8	0	-0.061722	0.141160	-0.425051
15	6	0	0.456114	0.918648	0.567077
16	8	0	1.777750	1.167805	0.267204
17	6	0	2.616837	0.082366	0.192333
18	6	0	2.316719	-1.145094	0.784102
19	6	0	3.820028	0.287957	-0.480986
20	6	0	3.232557	-2.182723	0.686520
21	1	0	1.388825	-1.288932	1.327593
22	6	0	4.736124	-0.747207	-0.569438
23	1	0	4.016669	1.256492	-0.925847
24	6	0	4.441665	-1.987513	0.010792
25	1	0	3.014228	-3.142832	1.140183
26	1	0	5.676021	-0.601401	-1.089601
27	6	0	5.388058	-3.064479	-0.087259
28	7	0	6.151773	-3.931162	-0.168122
29	6	0	0.618880	3.917708	0.278609
30	6	0	0.111970	5.298913	-0.117922
31	6	0	-1.964074	4.424638	-0.745374
32	6	0	-1.523547	3.015111	-0.364858
33	1	0	0.557176	6.074029	0.510768
34	1	0	0.429688	3.749357	1.346190
35	1	0	1.693617	3.829025	0.101920
36	1	0	-3.035015	4.558999	-0.575068
37	1	0	-1.751160	4.605929	-1.811170
38	1	0	-1.805074	2.821970	0.678547
39	1	0	-2.009113	2.269316	-1.001940
40	1	0	0.374944	5.504019	-1.168179
41	7	0	-0.072601	2.852332	-0.450907
42	1	0	0.226751	2.836568	-1.424627
43	8	0	-1.293617	5.386472	0.050998
44	8	0	-0.014008	1.086266	1.658924

Total Energy (a.u.) = -1311.13339693; **NIMAG = i128.08**

Table S30. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for concerted Transition State (CTS) associated to the departure of 4-nitrophenol for the reaction of compound **9** with morpholine in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.681455	-1.091380	0.854543
2	6	0	2.697208	-0.203404	1.228408
3	6	0	1.351580	-0.345269	0.774882
4	6	0	1.067862	-1.437139	-0.098905
5	6	0	2.053939	-2.323070	-0.477149
6	8	0	0.437231	0.489288	1.147535
7	6	0	3.357374	-2.151798	0.000919
8	1	0	4.700383	-0.982949	1.206584
9	1	0	2.922707	0.628099	1.888906
10	1	0	0.052893	-1.555201	-0.462249
11	1	0	1.837365	-3.155418	-1.136472
12	7	0	4.381244	-3.081732	-0.390151
13	8	0	5.518936	-2.920409	0.042054
14	8	0	4.083050	-4.005283	-1.141850
15	6	0	-0.773116	1.358369	-0.342719
16	6	0	-2.638035	0.113760	0.246332
17	6	0	-3.083996	-2.123086	0.949066
18	6	0	-2.311383	-0.973894	1.047078
19	6	0	-3.700236	0.099612	-0.646207
20	1	0	-1.459850	-0.898289	1.713485
21	6	0	-4.474055	-1.049831	-0.739919
22	1	0	-3.915213	0.976361	-1.246042
23	6	0	-4.162947	-2.157020	0.057611
24	1	0	-5.313741	-1.091842	-1.423851
25	1	0	-2.856779	-2.989671	1.559251
26	6	0	-4.967779	-3.346673	-0.035694
27	7	0	-5.615678	-4.303132	-0.107993
28	6	0	1.205635	2.800727	-0.679183
29	6	0	1.866437	4.095002	-0.235206
30	6	0	-0.171705	5.086144	0.291516
31	6	0	-0.961631	3.849642	-0.110438
32	1	0	0.055503	5.053401	1.367256
33	1	0	-0.776983	5.971198	0.091143
34	1	0	-1.240620	3.884784	-1.165649
35	1	0	-1.847520	3.716853	0.509019
36	1	0	2.772297	4.250633	-0.822609
37	1	0	2.145725	4.035185	0.827411
38	1	0	0.955859	2.822465	-1.740218
39	1	0	1.821544	1.928164	-0.459201
40	8	0	-1.896379	1.285924	0.390106
41	7	0	-0.085997	2.637513	0.064176
42	1	0	0.138033	2.475758	1.057476
43	8	0	-0.530384	0.819017	-1.381042
44	8	0	1.016519	5.201185	-0.461314

Total Energy (a.u.) = -1311.12384833; **NIMAG = i128.08**

Table S31. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for concerted Transition State (CTS) associated to the departure of 4-cyanophenol for the reaction of compound **9** with morpholine in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.070118	-1.117301	-0.657129
2	6	0	-2.827070	-1.727461	-0.549723
3	6	0	-1.866229	-1.141077	0.262411
4	6	0	-2.089044	0.033039	0.972843
5	6	0	-3.329671	0.647007	0.862426
6	6	0	-4.291983	0.057539	0.050628
7	1	0	-4.853372	-1.535544	-1.275913
8	1	0	-2.600085	-2.644393	-1.080551
9	1	0	-1.287141	0.436798	1.580891
10	1	0	-3.556195	1.562163	1.394105
11	7	0	-5.604088	0.704683	-0.062598
12	8	0	-5.785295	1.739380	0.555153
13	8	0	-6.442975	0.173351	-0.769163
14	8	0	-0.641569	-1.788156	0.412420
15	6	0	0.365885	-1.310517	-0.334403
16	8	0	1.025113	0.059359	1.181577
17	6	0	1.481914	1.201067	0.767986
18	6	0	2.764210	1.671339	1.170766
19	6	0	0.732065	2.034176	-0.110063
20	6	0	3.253130	2.889494	0.743051
21	1	0	3.349451	1.042141	1.835027
22	6	0	1.225561	3.249844	-0.540313
23	1	0	-0.241873	1.688044	-0.439984
24	6	0	2.490070	3.696081	-0.119032
25	1	0	4.231222	3.230626	1.068378
26	1	0	0.636261	3.871750	-1.207451
27	6	0	2.996809	4.955513	-0.567264
28	7	0	3.408466	5.977157	-0.933579
29	6	0	2.783284	-1.619290	-0.728160
30	6	0	4.005772	-2.396321	-0.269492
31	6	0	2.735380	-4.231788	0.387049
32	6	0	1.428310	-3.564625	-0.016142
33	1	0	4.857385	-2.117807	-0.891169
34	1	0	2.552911	-1.819580	-1.775036
35	1	0	2.895079	-0.545812	-0.570499
36	1	0	2.638763	-5.309053	0.245149
37	1	0	2.945717	-4.035932	1.448778
38	1	0	1.174364	-3.790943	-1.053944
39	1	0	0.608859	-3.849663	0.641978
40	1	0	4.242707	-2.151496	0.776798
41	7	0	1.598655	-2.071627	0.071667
42	1	0	1.737142	-1.755463	1.046178
43	8	0	3.805736	-3.787410	-0.418448
44	8	0	0.303731	-0.709980	-1.364512

Total Energy (a.u.) = -1311.12062533; **NIMAG = i160.40**

Table S32. Cartesian coordinates, energy (u.a.) for the intermediate structure (T±) associated to the reaction of compound **9** with morpholine in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.114667	-1.181447	1.108931
2	6	0	-1.855996	-0.635688	1.291392
3	6	0	-0.790334	-1.024919	0.469724
4	6	0	-0.986613	-1.965331	-0.549746
5	6	0	-2.250193	-2.506671	-0.740238
6	6	0	-3.292638	-2.110975	0.088789
7	1	0	-3.950689	-0.894428	1.733819
8	1	0	-1.672092	0.099096	2.066716
9	1	0	-0.166875	-2.254204	-1.190833
10	1	0	-2.428955	-3.237355	-1.518863
11	7	0	-4.616135	-2.690006	-0.115639
12	8	0	-4.757968	-3.498640	-1.019112
13	8	0	-5.518454	-2.338333	0.627743
14	8	0	0.413606	-0.476349	0.788090
15	6	0	1.369867	-0.114115	-0.240927
16	8	0	1.804441	1.198716	0.169722
17	6	0	0.941965	2.236515	0.028444
18	6	0	-0.314985	2.146170	-0.582077
19	6	0	1.387310	3.456263	0.552756
20	6	0	-1.118144	3.275998	-0.651167
21	1	0	-0.649677	1.213997	-1.018336
22	6	0	0.585809	4.580680	0.476604
23	1	0	2.365364	3.497257	1.018568
24	6	0	-0.677391	4.494361	-0.124406
25	1	0	-2.093597	3.212739	-1.121019
26	1	0	0.930160	5.525126	0.883085
27	6	0	-1.517051	5.656624	-0.198419
28	7	0	-2.193511	6.595466	-0.254785
29	6	0	3.878006	-0.531947	-0.491416
30	6	0	5.070302	-1.387049	-0.090582
31	6	0	3.706474	-3.146950	0.577217
32	6	0	2.442282	-2.385137	0.207993
33	1	0	5.916955	-1.150598	-0.737076
34	1	0	3.607452	-0.694829	-1.537059
35	1	0	4.066172	0.527589	-0.321629
36	1	0	3.540459	-4.214620	0.425487
37	1	0	3.956255	-2.978462	1.635535
38	1	0	2.166944	-2.577486	-0.831915
39	1	0	1.612228	-2.642593	0.867415
40	1	0	5.357031	-1.175870	0.950627
41	8	0	4.785877	-2.762492	-0.249035
42	7	0	2.675403	-0.918608	0.300598
43	1	0	2.799872	-0.645044	1.280512
44	8	0	1.122334	-0.329973	-1.429093

Total Energy (a.u.) = -1311.14246800;

Table S33. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for concerted Transition State (TS2) associated to the departure of 4-nitrophenol for the reaction of compound **9** with morpholine, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.863434	-2.399186	-0.466046
2	6	0	-0.501350	-2.312064	-0.268162
3	6	0	0.043514	-1.476395	0.749173
4	6	0	-0.874585	-0.818464	1.620450
5	6	0	-2.233493	-0.894771	1.418970
6	6	0	-2.724173	-1.673077	0.362653
7	1	0	-2.279853	-3.005488	-1.261889
8	1	0	0.188438	-2.845370	-0.913051
9	1	0	-0.466023	-0.198404	2.412347
10	1	0	-2.928355	-0.351439	2.048556
11	7	0	-4.139213	-1.708172	0.114911
12	8	0	-4.874074	-1.004869	0.803283
13	8	0	-4.564373	-2.432727	-0.780401
14	8	0	1.318210	-1.273882	0.849267
15	6	0	1.885483	-0.041553	-0.757238
16	8	0	1.403106	1.108145	-0.265806
17	6	0	0.061356	1.449618	-0.374749
18	6	0	-0.819510	0.902131	-1.304707
19	6	0	-0.347966	2.399148	0.558685
20	6	0	-2.156501	1.272073	-1.240878
21	1	0	-0.483309	0.177779	-2.031106
22	6	0	-1.680222	2.772165	0.608526
23	1	0	0.377628	2.803828	1.254645
24	6	0	-2.591495	2.193731	-0.283722
25	1	0	-2.866894	0.837621	-1.935761
26	1	0	-2.020223	3.494727	1.341478
27	6	0	-3.982968	2.549014	-0.217457
28	7	0	-5.103486	2.836247	-0.165052
29	6	0	3.623890	0.526761	1.027458
30	6	0	5.023388	0.126422	1.467344
31	6	0	5.679253	-0.407053	-0.702010
32	6	0	4.316695	-0.052494	-1.278740
33	1	0	5.311199	0.731132	2.328085
34	1	0	3.587707	1.583247	0.762064
35	1	0	2.860766	0.289575	1.767413
36	1	0	6.447225	-0.195142	-1.447101
37	1	0	5.715539	-1.479126	-0.456763
38	1	0	4.274235	0.999237	-1.569736
39	1	0	4.047219	-0.687753	-2.121926
40	1	0	5.044649	-0.933053	1.762760
41	7	0	3.278537	-0.249889	-0.210227
42	1	0	3.225417	-1.244477	0.054767
43	8	0	1.574125	-0.620620	-1.758154
44	8	0	5.963814	0.371422	0.440623

Total Energy (a.u.) = -1311.12141587; **NIMAG = i220.28**

Table S34. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for concerted Transition State (TS2) associated to the departure of 4-cyanophenol for the reaction of compound **9** with morpholine, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.574904	0.168419	-0.960536
2	6	0	-2.239612	-0.203557	-0.907426
3	6	0	-1.714254	-0.619612	0.314888
4	6	0	-2.473225	-0.661803	1.479255
5	6	0	-3.807564	-0.284823	1.425486
6	8	0	-0.376835	-0.954540	0.449974
7	6	0	-4.332729	0.118040	0.203957
8	1	0	-4.026888	0.500699	-1.886259
9	1	0	-1.598133	-0.161457	-1.779574
10	1	0	-2.015630	-0.988173	2.405639
11	1	0	-4.435120	-0.303930	2.307030
12	7	0	-5.742225	0.511662	0.141343
13	8	0	-6.391924	0.476820	1.172455
14	8	0	-6.191975	0.854067	-0.938841
15	6	0	0.197282	-1.645536	-0.554229
16	6	0	1.357465	0.977323	-1.202654
17	6	0	1.218990	2.998526	0.161277
18	6	0	0.611755	1.905914	-0.427538
19	6	0	2.746340	1.235928	-1.366969
20	1	0	-0.453567	1.741576	-0.303703
21	6	0	3.353269	2.329786	-0.778179
22	1	0	3.325901	0.553579	-1.983594
23	6	0	2.596800	3.221044	-0.001326
24	1	0	4.416094	2.504381	-0.913644
25	1	0	0.632655	3.692779	0.755202
26	6	0	3.222229	4.351537	0.614404
27	7	0	3.729559	5.266991	1.114844
28	6	0	2.154667	-1.233954	1.064646
29	6	0	3.646760	-1.507413	1.178475
30	6	0	3.481485	-3.508944	-0.000600
31	6	0	1.980495	-3.353068	-0.187631
32	1	0	4.013766	-3.082905	-0.864682
33	1	0	3.724110	-4.570155	0.068149
34	1	0	1.429038	-3.799597	0.642019
35	1	0	1.636096	-3.769991	-1.132590
36	1	0	4.013525	-1.090391	2.117122
37	1	0	4.179614	-1.019586	0.347565
38	1	0	1.604701	-1.681578	1.893205
39	1	0	1.940146	-0.166840	1.010175
40	8	0	0.815700	-0.090101	-1.724278
41	7	0	1.654776	-1.886053	-0.194808
42	1	0	2.115446	-1.440141	-1.005242
43	8	0	-0.335776	-2.378701	-1.334423
44	8	0	3.912308	-2.894208	1.195331

Total Energy (a.u.) = -1311.12141587; **NIMAG = i227.78**

Table S35. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for Transition State (TS1) associated to the nucleophilic attack of piperidine to compound **9**, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.247754	-2.701564	-0.915717
2	6	0	-1.161730	-1.843928	-0.963021
3	6	0	-1.163793	-0.678160	-0.194567
4	6	0	-2.243980	-0.346619	0.624621
5	6	0	-3.331836	-1.209415	0.674315
6	6	0	-3.316819	-2.367116	-0.091765
7	1	0	-2.271684	-3.613095	-1.498655
8	1	0	-0.300535	-2.061547	-1.583987
9	1	0	-2.234733	0.557185	1.215238
10	1	0	-4.187861	-0.985197	1.297880
11	7	0	-4.468100	-3.267446	-0.030590
12	8	0	-5.401935	-2.955839	0.689193
13	8	0	-4.434929	-4.284418	-0.702908
14	8	0	-0.042618	0.102937	-0.368510
15	6	0	0.451125	0.891505	0.625799
16	8	0	1.770112	1.162410	0.343577
17	6	0	2.626720	0.094060	0.231506
18	6	0	2.356907	-1.151712	0.798922
19	6	0	3.818227	0.338693	-0.448884
20	6	0	3.292297	-2.168345	0.669437
21	1	0	1.436924	-1.325418	1.347239
22	6	0	4.754016	-0.675568	-0.569471
23	1	0	3.990753	1.320575	-0.874060
24	6	0	4.490375	-1.933814	-0.013639
25	1	0	3.098230	-3.142217	1.104418
26	1	0	5.685251	-0.499401	-1.095741
27	6	0	5.458023	-2.988372	-0.143625
28	7	0	6.239576	-3.836204	-0.249847
29	6	0	0.597702	3.917335	0.255466
30	6	0	0.151223	5.308858	-0.197258
31	6	0	-2.076529	4.326434	-0.814013
32	6	0	-1.559603	2.967061	-0.339224
33	1	0	0.670896	6.072698	0.390353
34	1	0	0.394477	3.790644	1.328168
35	1	0	1.671017	3.773217	0.106011
36	1	0	-3.160253	4.380852	-0.668758
37	1	0	-1.886555	4.424242	-1.890817
38	1	0	-1.818037	2.826773	0.720527
39	1	0	-2.018473	2.148573	-0.903864
40	1	0	0.442193	5.453123	-1.246151
41	7	0	-0.105788	2.832012	-0.433178
42	1	0	0.179500	2.796764	-1.410521
43	8	0	-0.039140	1.067242	1.706725
44	6	0	-1.366081	5.455103	-0.063834
45	1	0	-1.694083	6.430532	-0.435825
46	1	0	-1.639688	5.407883	0.998934

Total Energy (a.u.) = -1275.24897809; **NIMAG = i128.72**

Table S36. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for concerted Transition State (**CTS**) associated to the departure of 4-nitrophenol for the reaction of compound **9** with piperidine, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.917079	-2.586522	-0.902439
2	6	0	-0.673771	-2.071955	-0.602835
3	6	0	-0.433080	-1.378253	0.620428
4	6	0	-1.529828	-1.261869	1.526699
5	6	0	-2.770178	-1.783154	1.232528
6	6	0	-2.964905	-2.438854	0.011762
7	1	0	-2.095904	-3.112079	-1.832967
8	1	0	0.145853	-2.189652	-1.301689
9	1	0	-1.357378	-0.760351	2.473628
10	1	0	-3.596697	-1.693834	1.927518
11	7	0	-4.258558	-2.980168	-0.302584
12	8	0	-5.166245	-2.848329	0.513575
13	8	0	-4.411707	-3.554112	-1.377051
14	8	0	0.724564	-0.883540	0.922501
15	6	0	1.663240	0.263016	-0.521522
16	8	0	1.655625	1.407442	0.186883
17	6	0	0.496079	2.170291	0.078972
18	6	0	0.354557	3.070542	-0.968035
19	6	0	-0.460816	2.020489	1.074179
20	6	0	-0.790506	3.855528	-1.017233
21	1	0	1.128900	3.154238	-1.721536
22	6	0	-1.606043	2.802356	1.023000
23	1	0	-0.291086	1.292982	1.858131
24	6	0	-1.766552	3.718538	-0.023077
25	1	0	-0.930265	4.571720	-1.818543
26	1	0	-2.371051	2.706147	1.784914
27	6	0	-2.950341	4.535478	-0.075637
28	7	0	-3.901863	5.193374	-0.116087
29	6	0	3.548314	-0.136009	1.143887
30	6	0	4.688857	-1.097331	1.441613
31	6	0	5.054768	-1.418846	-1.019284
32	6	0	3.900353	-0.471298	-1.310765
33	1	0	5.138114	-0.795216	2.390916
34	1	0	3.902917	0.891108	1.039830
35	1	0	2.751031	-0.176342	1.884274
36	1	0	5.765425	-1.341588	-1.845883
37	1	0	4.680464	-2.449571	-1.012688
38	1	0	4.235449	0.566513	-1.393276
39	1	0	3.347401	-0.745069	-2.208543
40	1	0	4.286697	-2.107529	1.584148
41	7	0	2.914522	-0.505104	-0.172134
42	1	0	2.538298	-1.455918	-0.061449
43	8	0	1.114279	0.057683	-1.566971
44	6	0	5.723881	-1.094918	0.316595
45	1	0	6.512363	-1.821552	0.525951
46	1	0	6.196941	-0.107254	0.258371

Total Energy (a.u.) = -1275.24025347; **NIMAG = i205.31**

Table S37. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for concerted Transition State (**CTS**) associated to the departure of 4-cyanophenol for the reaction of compound 9 with piperidine, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.906965	-0.940550	0.871284
2	6	0	1.527247	-0.814106	0.807212
3	6	0	0.850274	-1.445212	-0.234769
4	6	0	1.506113	-2.179485	-1.215988
5	6	0	2.887092	-2.301038	-1.154132
6	8	0	-0.518886	-1.308530	-0.392926
7	6	0	3.559182	-1.681697	-0.107791
8	1	0	3.475782	-0.468581	1.662019
9	1	0	0.974583	-0.242124	1.542991
10	1	0	0.933781	-2.645337	-2.009340
11	1	0	3.437195	-2.865325	-1.895896
12	7	0	5.016194	-1.812143	-0.035574
13	8	0	5.576413	-2.454371	-0.907489
14	8	0	5.592955	-1.271215	0.892342
15	6	0	-1.281190	-1.314888	0.719241
16	6	0	-0.763059	1.758339	0.749734
17	6	0	0.433615	3.012559	-0.975343
18	6	0	-0.133197	1.834766	-0.524901
19	6	0	-0.773165	2.948237	1.534531
20	1	0	-0.103026	0.950369	-1.151994
21	6	0	-0.208454	4.120623	1.081463
22	1	0	-1.247546	2.902510	2.509497
23	6	0	0.406259	4.170802	-0.183110
24	1	0	-0.232128	5.012698	1.699986
25	1	0	0.906067	3.046663	-1.952499
26	6	0	0.990731	5.385990	-0.656579
27	7	0	1.463057	6.374350	-1.040893
28	6	0	-2.954052	-0.487593	-1.020072
29	6	0	-4.442166	-0.230152	-1.210927
30	6	0	-4.968661	-2.170328	0.286368
31	6	0	-3.480957	-2.418005	0.480171
32	1	0	-5.335007	-1.530930	1.098532
33	1	0	-5.480016	-3.131732	0.378378
34	1	0	-3.079485	-3.101091	-0.273666
35	1	0	-3.244069	-2.795723	1.473945
36	1	0	-4.576870	0.210762	-2.201656
37	1	0	-4.780171	0.514684	-0.480388
38	1	0	-2.565730	-1.183499	-1.766157
39	1	0	-2.364353	0.428696	-1.033360
40	8	0	-1.311363	0.679729	1.220264
41	7	0	-2.721860	-1.124340	0.322044
42	1	0	-3.032984	-0.448607	1.034028
43	6	0	-5.253159	-1.518181	-1.065700
44	1	0	-6.320155	-1.305374	-1.164304
45	1	0	-4.982722	-2.212163	-1.870620
46	8	0	-1.031794	-1.843295	1.762474

Total Energy (a.u.) = -1275.23675630; **NIMAG = i154.77**

Table S38. Cartesian coordinates, energy (u.a.) for the intermediate structure (T±) associated to the reaction of compound **9** with piperidine in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.813867	-1.671762	1.093809
2	6	0	-1.666391	-0.919817	1.273157
3	6	0	-2.818164	-2.646114	0.100389
4	1	0	-3.697008	-1.508610	1.698320
5	6	0	-0.537533	-1.151329	0.476825
6	1	0	-1.617858	-0.139595	2.024247
7	6	0	-1.711046	-2.887975	-0.704262
8	7	0	-4.024910	-3.440277	-0.102173
9	6	0	-0.557561	-2.140092	-0.514906
10	1	0	-1.756945	-3.659874	-1.462393
11	8	0	-4.025393	-4.269573	-0.998283
12	8	0	-4.977037	-3.236451	0.634521
13	1	0	0.312012	-2.304867	-1.134664
14	1	0	2.913267	-0.063819	1.248512
15	7	0	2.848250	-0.353966	0.267768
16	6	0	2.930504	-1.841530	0.182293
17	6	0	3.938970	0.299943	-0.519097
18	6	0	5.310546	-0.183054	-0.066408
19	1	0	3.821297	1.375669	-0.395970
20	1	0	-0.830565	1.001871	-1.115973
21	6	0	4.287754	-2.349982	0.649188
22	1	0	1.517734	3.857748	1.068459
23	1	0	6.062851	0.301217	-0.694687
24	1	0	5.490376	0.149002	0.963419
25	1	0	3.736294	0.038760	-1.561461
26	8	0	0.554395	-0.403392	0.785775
27	1	0	4.296689	-3.437525	0.539361
28	1	0	2.754522	-2.080866	-0.870645
29	1	0	2.113836	-2.245245	0.782257
30	6	0	-1.783486	2.878540	-0.694649
31	6	0	0.454115	2.332935	0.001235
32	6	0	-0.458388	4.508295	0.515505
33	8	0	1.537307	1.526960	0.126779
34	6	0	0.586200	3.603902	0.575534
35	6	0	-1.654603	4.146868	-0.118887
36	1	0	4.411069	-2.133224	1.717131
37	6	0	1.409680	0.139318	-0.262855
38	6	0	-0.735677	1.970315	-0.642681
39	1	0	-2.707710	2.603873	-1.191340
40	6	0	-2.745303	5.078093	-0.183521
41	8	0	1.196694	-0.143474	-1.445365
42	1	0	-0.355485	5.491441	0.961251
43	7	0	-3.625608	5.829424	-0.236690
44	6	0	5.418591	-1.704471	-0.149645
45	1	0	6.388625	-2.038844	0.226651
46	1	0	5.349102	-2.018437	-1.198377

Total Energy (a.u.) = -1275.26064431

Table S39. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for concerted Transition State (TS2) associated to the departure of 4-nitrophenol for the reaction of compound **9** with piperidine in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.607436	-1.203443	0.826526
2	6	0	2.669444	-0.264593	1.194108
3	6	0	1.312447	-0.354766	0.760773
4	6	0	0.968584	-1.449861	-0.087410
5	6	0	1.908504	-2.386982	-0.459394
6	8	0	0.442604	0.527171	1.128434
7	6	0	3.224623	-2.265170	-0.001058
8	1	0	4.635279	-1.134749	1.162232
9	1	0	2.940437	0.570234	1.832967
10	1	0	-0.055975	-1.529840	-0.433972
11	1	0	1.645685	-3.222466	-1.097539
12	7	0	4.201159	-3.246847	-0.385901
13	8	0	5.350282	-3.128243	0.029958
14	8	0	3.853424	-4.170046	-1.116635
15	6	0	-0.729033	1.415890	-0.361382
16	6	0	-2.591021	0.166326	0.229526
17	6	0	-3.101226	-2.016513	1.053267
18	6	0	-2.339874	-0.858429	1.133836
19	6	0	-3.564476	0.076202	-0.755786
20	1	0	-1.549378	-0.731088	1.863892
21	6	0	-4.325239	-1.082945	-0.835227
22	1	0	-3.721782	0.902771	-1.438952
23	6	0	-4.092366	-2.124312	0.070409
24	1	0	-5.095236	-1.183711	-1.591246
25	1	0	-2.932825	-2.832907	1.746143
26	6	0	-4.886746	-3.322024	-0.007363
27	7	0	-5.526979	-4.284491	-0.067701
28	6	0	1.276128	2.824983	-0.664193
29	6	0	2.006759	4.063762	-0.170798
30	6	0	-0.194796	5.151719	0.330313
31	6	0	-0.919206	3.903690	-0.153190
32	1	0	-0.058800	5.090006	1.416481
33	1	0	-0.847015	6.007036	0.136903
34	1	0	-1.134852	3.947263	-1.224504
35	1	0	-1.842524	3.722844	0.394683
36	1	0	2.946522	4.136117	-0.723830
37	1	0	2.266876	3.936763	0.887381
38	1	0	1.041486	2.881679	-1.729109
39	1	0	1.827732	1.905271	-0.469092
40	8	0	-1.863597	1.346285	0.361265
41	7	0	-0.041722	2.690851	0.046630
42	1	0	0.156275	2.544817	1.046246
43	6	0	1.157377	5.320080	-0.360508
44	1	0	1.677580	6.192586	0.041609
45	1	0	1.001704	5.497273	-1.431390
46	8	0	-0.489253	0.877563	-1.402372

Total Energy (a.u.) = -1275.24381243; **NIMAG = i161.52**

Table S40. Cartesian coordinates, energy (u.a.) and number of imaginary frequencies (NIMAG) for concerted Transition State (TS2) associated to the departure of 4-cyanophenol for the reaction of compound **9** with piperidine in acetonitrile, calculated using M06-2X/6-31G++(d,p) level theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.049534	-1.160835	-0.664743
2	6	0	-2.797278	-1.752420	-0.561996
3	6	0	-1.844876	-1.159910	0.256359
4	6	0	-2.086900	0.005257	0.975839
5	6	0	-3.337013	0.600623	0.871111
6	6	0	-4.290336	0.003525	0.054197
7	1	0	-4.826009	-1.585704	-1.287568
8	1	0	-2.556269	-2.661221	-1.100617
9	1	0	-1.291593	0.416331	1.587379
10	1	0	-3.577852	1.506912	1.411570
11	7	0	-5.612982	0.629436	-0.051696
12	8	0	-5.814150	1.650462	0.582579
13	8	0	-6.441174	0.095371	-0.768924
14	8	0	-0.614845	-1.792587	0.405898
15	6	0	0.391009	-1.305596	-0.343106
16	8	0	1.017363	0.069282	1.158129
17	6	0	1.451416	1.221394	0.750109
18	6	0	2.719718	1.717718	1.166012
19	6	0	0.691550	2.041232	-0.131885
20	6	0	3.185857	2.947907	0.748115
21	1	0	3.312262	1.097862	1.832500
22	6	0	1.162593	3.269346	-0.552595
23	1	0	-0.271512	1.675024	-0.471808
24	6	0	2.413019	3.741419	-0.117706
25	1	0	4.153297	3.308897	1.083748
26	1	0	0.566059	3.881454	-1.222397
27	6	0	2.895465	5.014025	-0.555086
28	7	0	3.287688	6.046533	-0.912237
29	6	0	2.812841	-1.569157	-0.733168
30	6	0	4.077749	-2.248888	-0.232999
31	6	0	2.725225	-4.249448	0.438965
32	6	0	1.462869	-3.555796	-0.052525
33	1	0	4.912312	-1.882735	-0.836043
34	1	0	2.604057	-1.805850	-1.778695
35	1	0	2.842636	-0.486209	-0.612093
36	1	0	2.578795	-5.325649	0.317351
37	1	0	2.843728	-4.060269	1.512553
38	1	0	1.267524	-3.765424	-1.108033
39	1	0	0.588528	-3.824155	0.537653
40	1	0	4.270550	-1.940611	0.801973
41	7	0	1.628852	-2.059163	0.052889
42	1	0	1.765491	-1.766946	1.032942
43	8	0	0.312859	-0.713410	-1.378441
44	6	0	3.961609	-3.770380	-0.320226
45	1	0	3.883809	-4.070449	-1.372204
46	1	0	4.858944	-4.241946	0.087136

Total Energy (a.u.) = -1275.24056202; **NIMAG = i159.34**

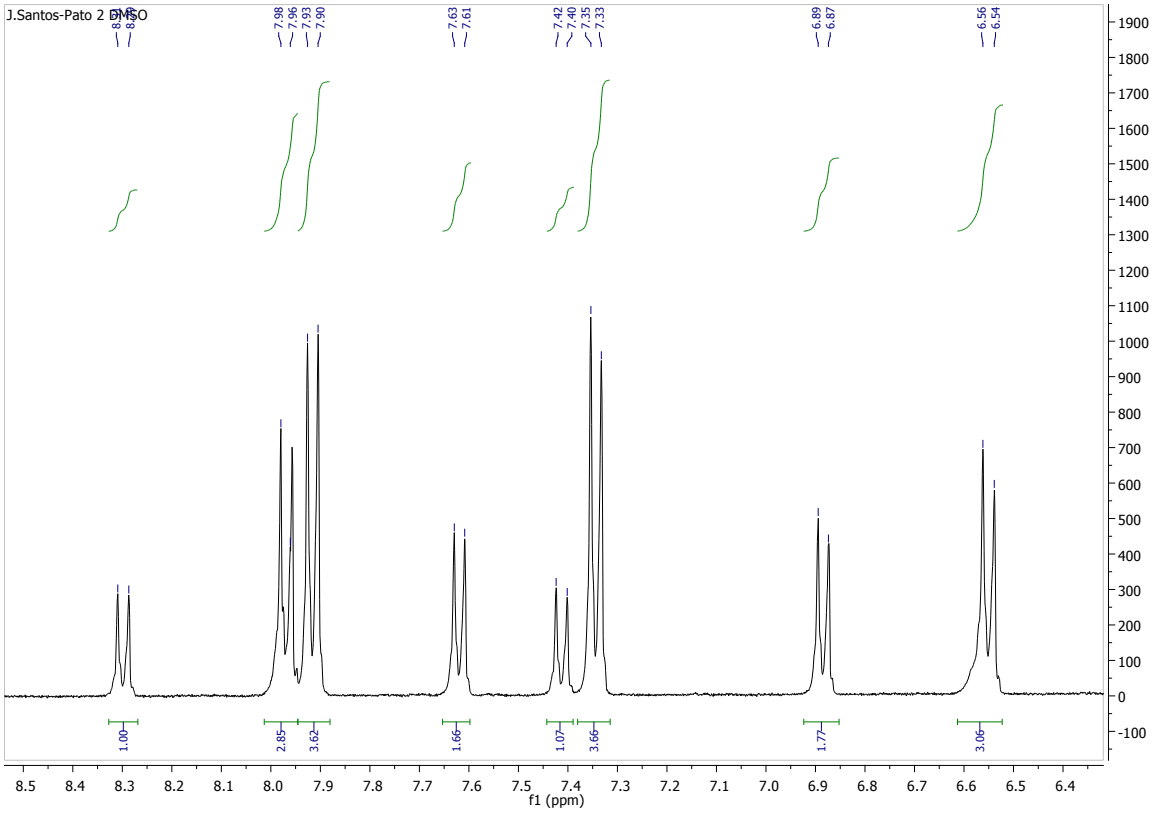

Figure S10.- ^{1}H-NMR spectrum for the reaction of **7** with excess of morpholine in dimethyl sulfoxide-d_6.

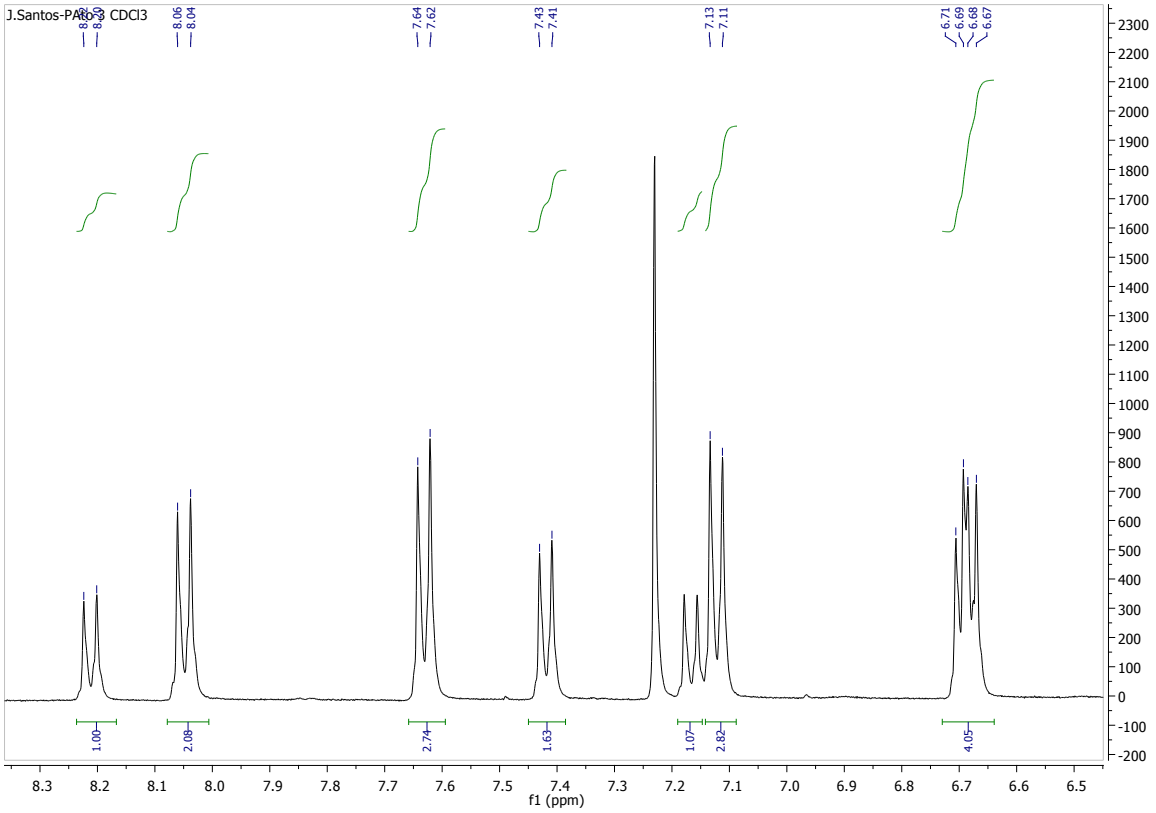

Figure S11.- ^{1}H-NMR spectrum for the reaction of **7** with excess of morpholine in chloroform-d_1

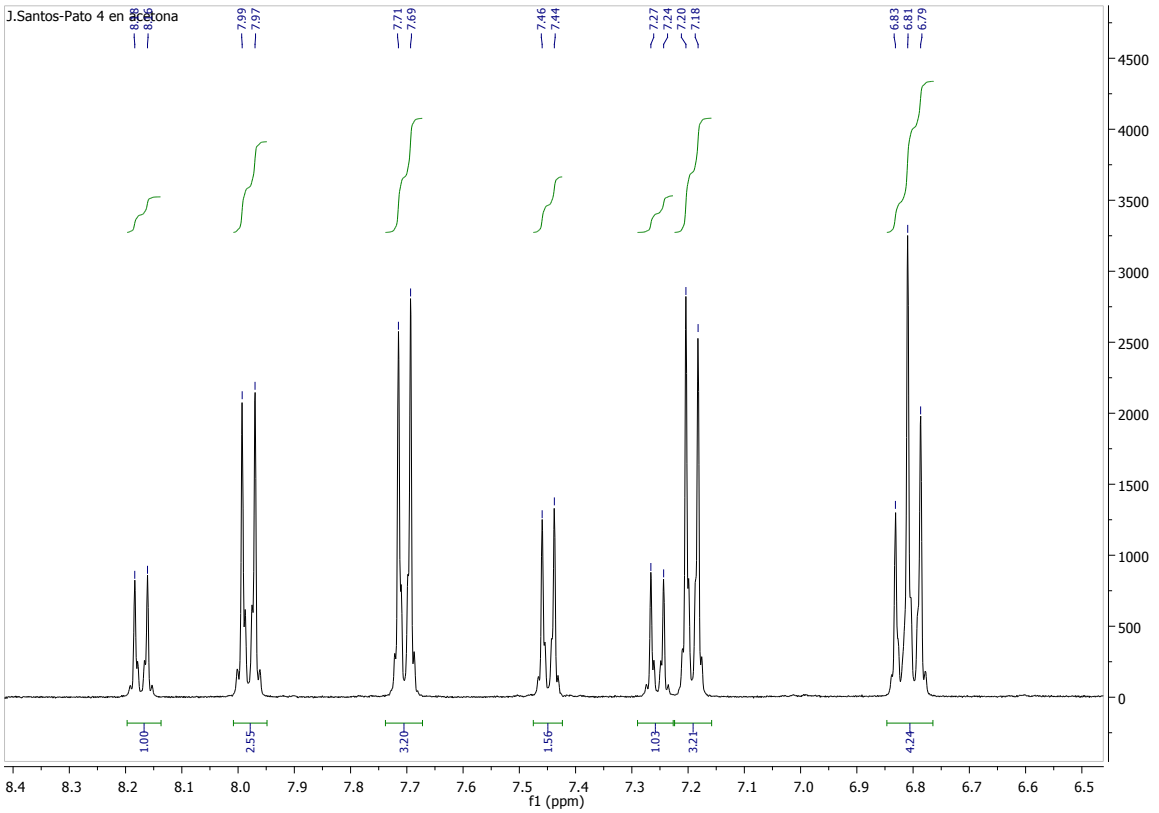

Figure S12.- ^{1}H-NMR spectrum for the reaction of **7** with excess of morpholine in acetone-d_6.

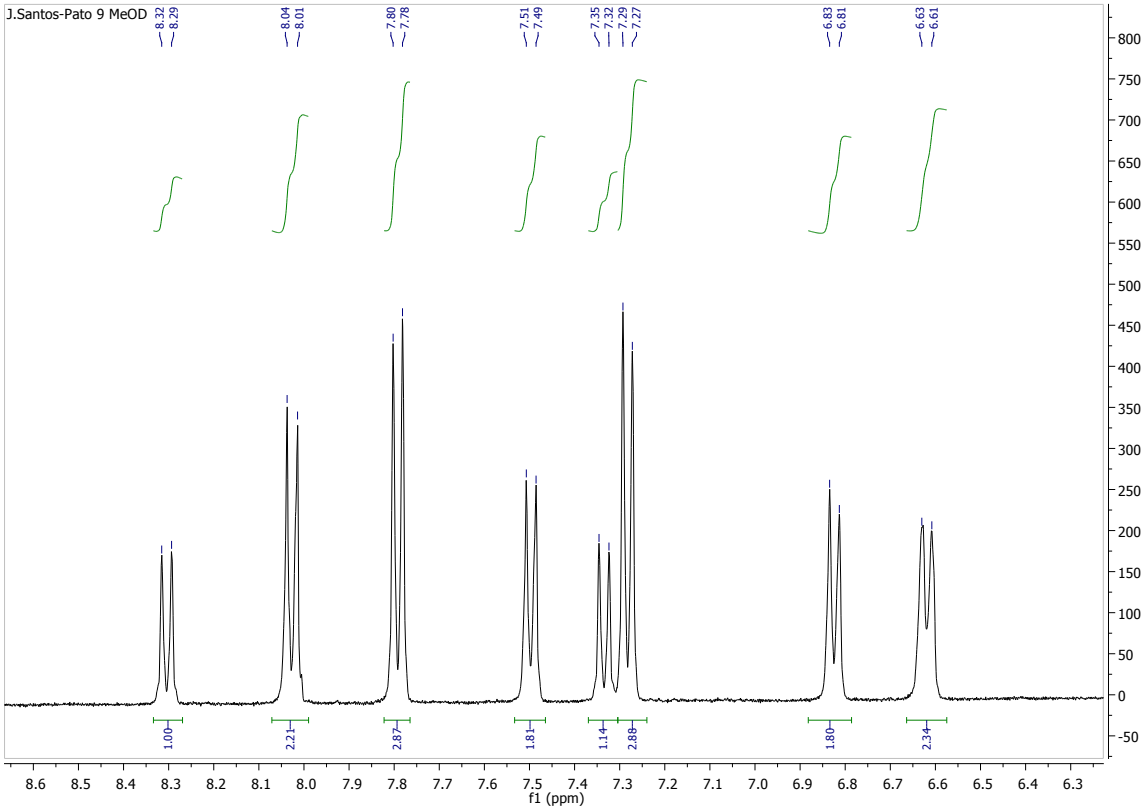

Figure S13.- ^{1}H-NMR spectrum for the reaction of **7** with excess of morpholine in methanol-d_4.

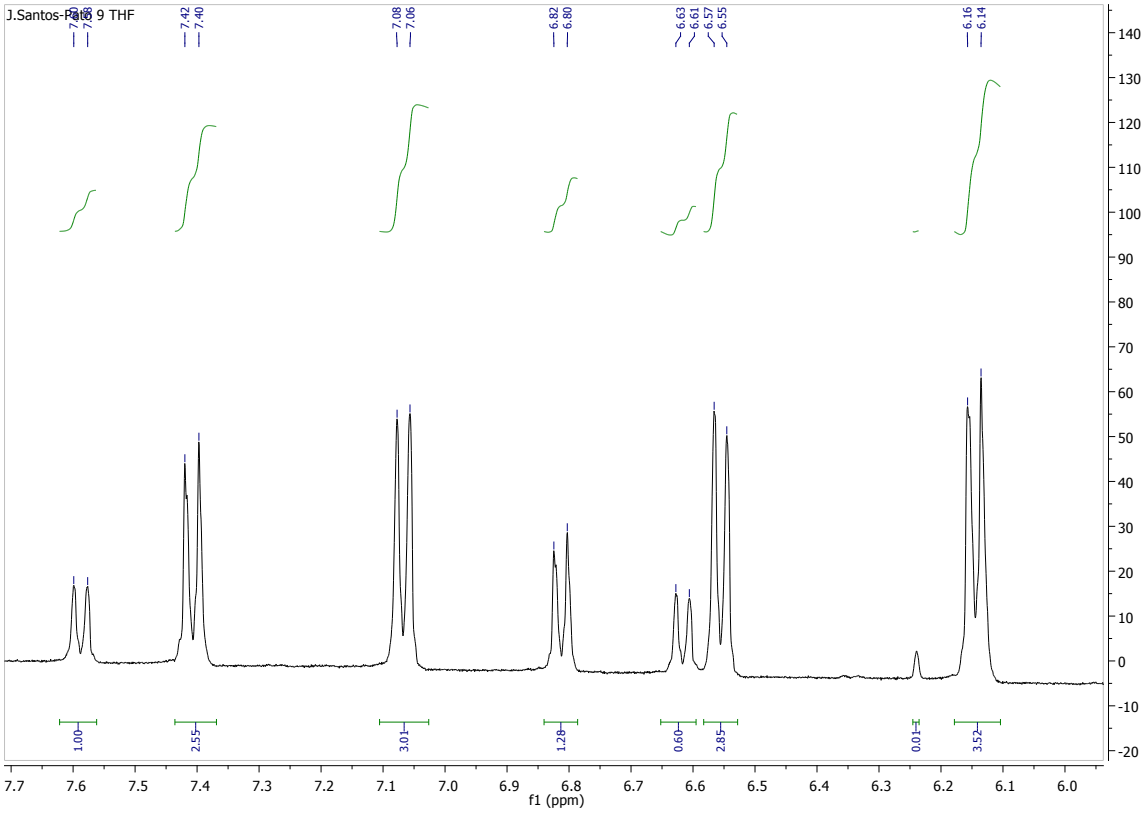

Figure S14.- ^{1}H-NMR spectrum for the reaction of **7** with excess of morpholine in tetrahydrofuran-d_8.

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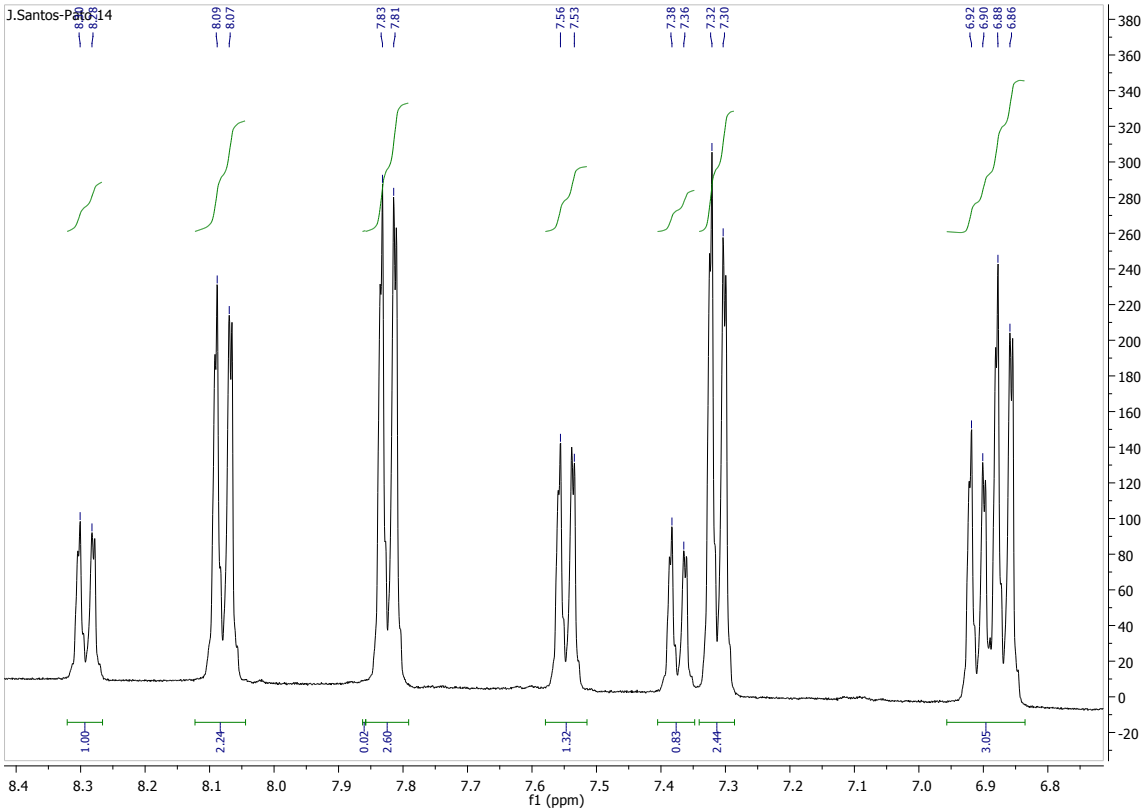

Figure S15.- ^{1}H-NMR spectrum for the reaction of **7** with excess of morpholine in acetone

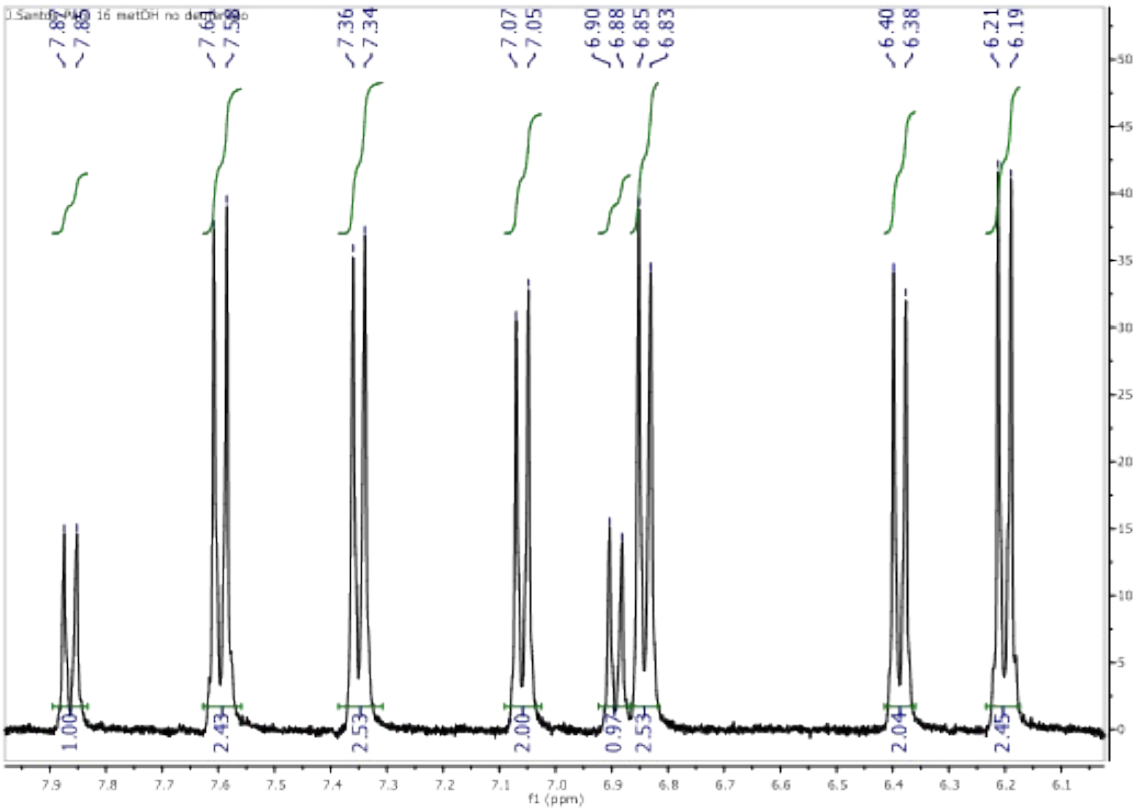

Figure S16.- ^{1}H-NMR spectrum for the reaction of **7** with excess of morpholine in methanol.

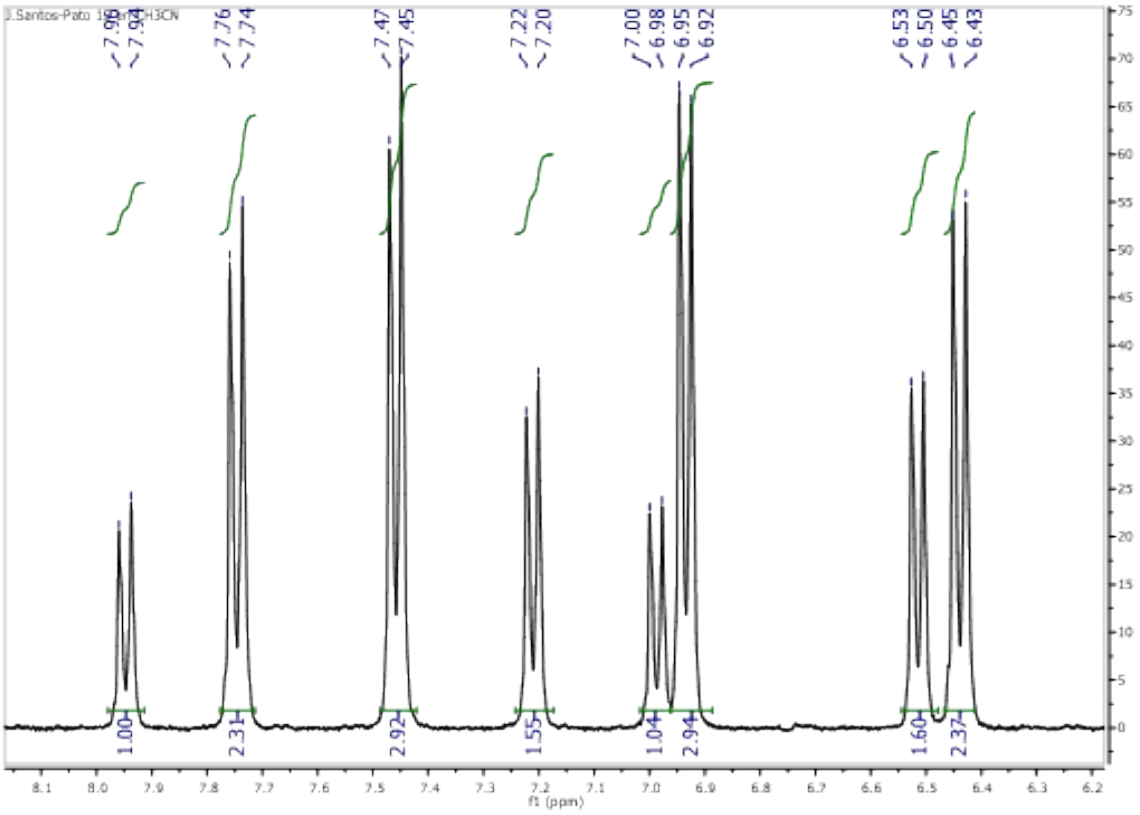

Figure S17.- ^{1}H-NMR spectrum for the reaction of **7** with excess of morpholine in acetonitrile.

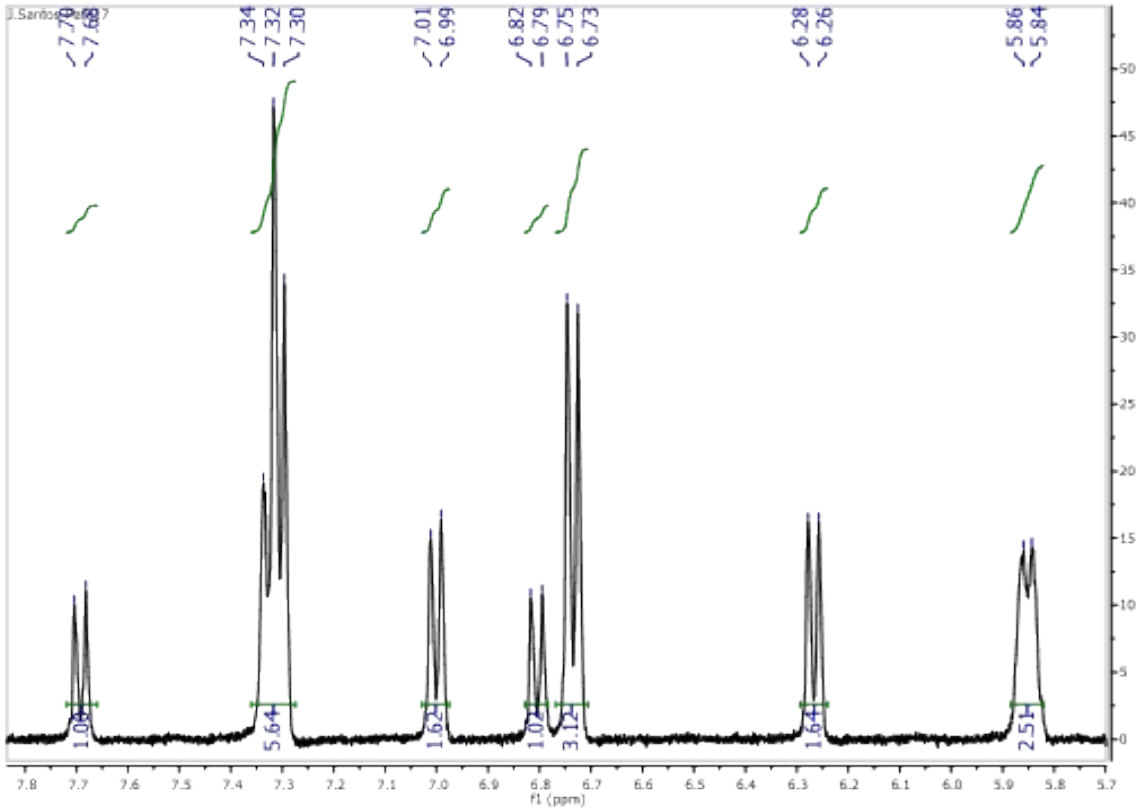

Figure S18.- ^{1}H-NMR spectrum for the reaction of **7** with excess of morpholine in dimethylsulfoxide.

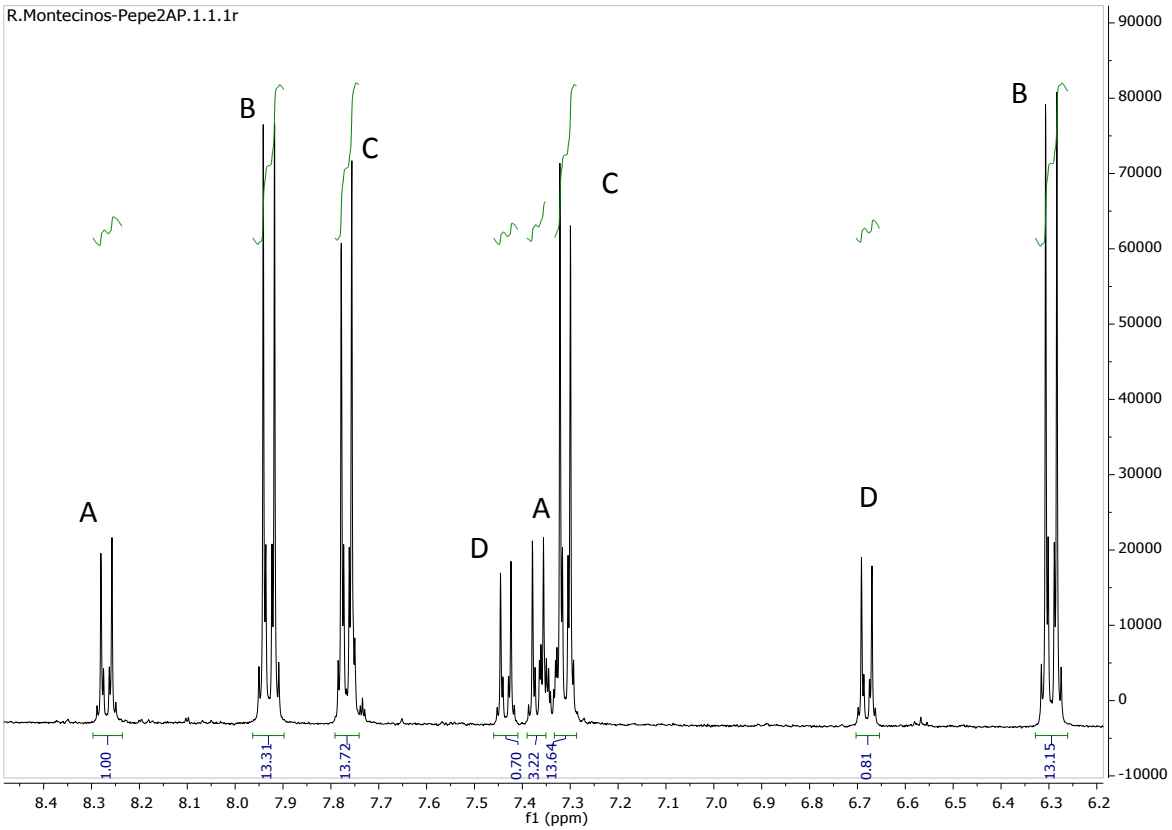

Figure S19.- ^{1}H-NMR spectrum for the reaction of **9** with excess of piperidine in acetonitrile-d_3.
A: Piperidine 4-nitrophenyl carbamate, B: 4-nitrophenol, C: Piperidine 4-cyanophenyl carbamate, D: 4-cyanophenol