Supplementary Material (ESI) for New Journal of Chemistry
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Regioselectivity of the Coupling Between Radicals and Ambident Nucleophiles. A Theoretical Study.

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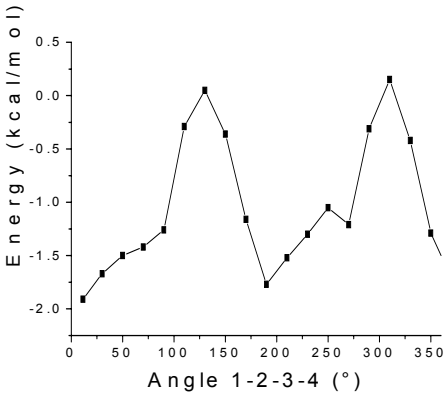
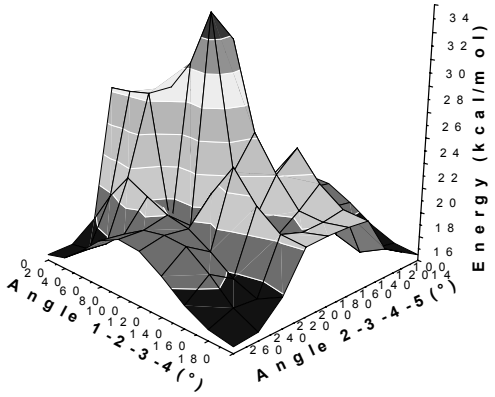
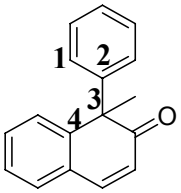
Supplementary information

Figure S1: AM1 conformational search for RAs formed by reaction of phenyl radical (**10**) at the C_1 and O sites of anion **2**.







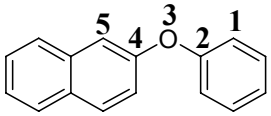


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Table S1: ΔE_{solv} (kcal/mol) in methanol for the coupling of aromatic and aliphatic radicals with the nucleophiles of Chart 1.

Anion	Posit	ΔE^a with **10**			ΔE with **11**[a]			ΔE with **12**[a]		
		React[b]	RA	TS	React[c]	RA	TS	React[d]	RA	TS
1	C_2				-150.28	-119.89	-107.12	-146.15	-120.47	-111.66
	O					-129.06	-106.66		-129.42	-105.74
2	C_1	-130.10	-111.17	-111.50						
	O		-101.95	-103.07						
6	C_5	-139.80	-132.78	-125.81						
	N		-119.40	-112.83						
7	C_2	-142.98	-123.40	-116.87						
	C_3		-122.15	-117.61						
	N		-106.61	-111.98						
8	C_2				-159.72	-133.38	-109.78			
	C_4					-130.97	-112.47			
	N					-133.46	-120.61			

[a] ΔE (kcal/mol) = Energies of RA (TS) in solvent - Energies of RA (TS) in gas phase.

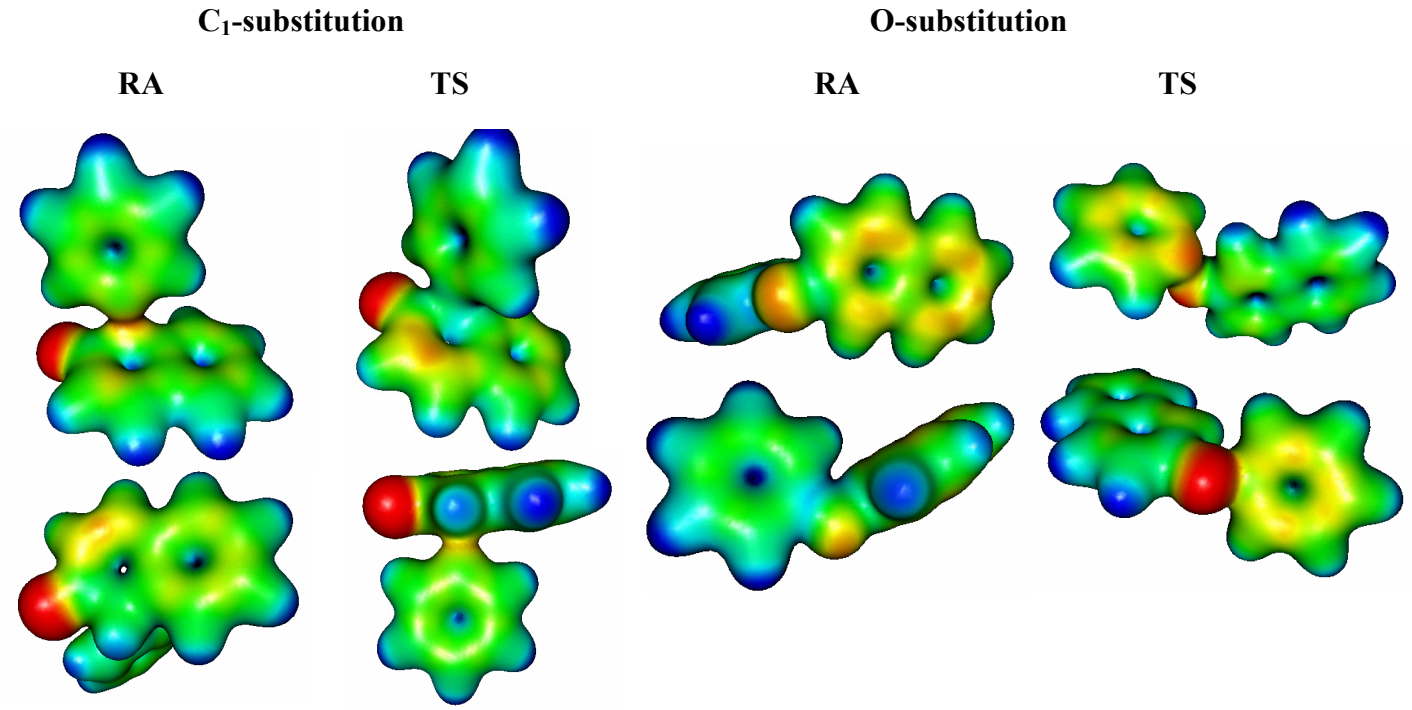
[b] ΔE phenyl radical **10** = - 6.56 kcal/mol.

[c] ΔE 4-nitrobezyl radical **11** = - 19.09 kcal/mol.

[d] ΔE 4-nitrophenyl radical **12** = - 14.95 kcal/mol.

Figure S2: Gas phase B3LYP electrostatic potential (from red (negative) to blue (positive)) and spin distribution for radical anions and transition states formed by reaction of phenyl radical (**10**) at the C_1 and O sites of anion **2**.

Electrostatic potential



Spin distribution

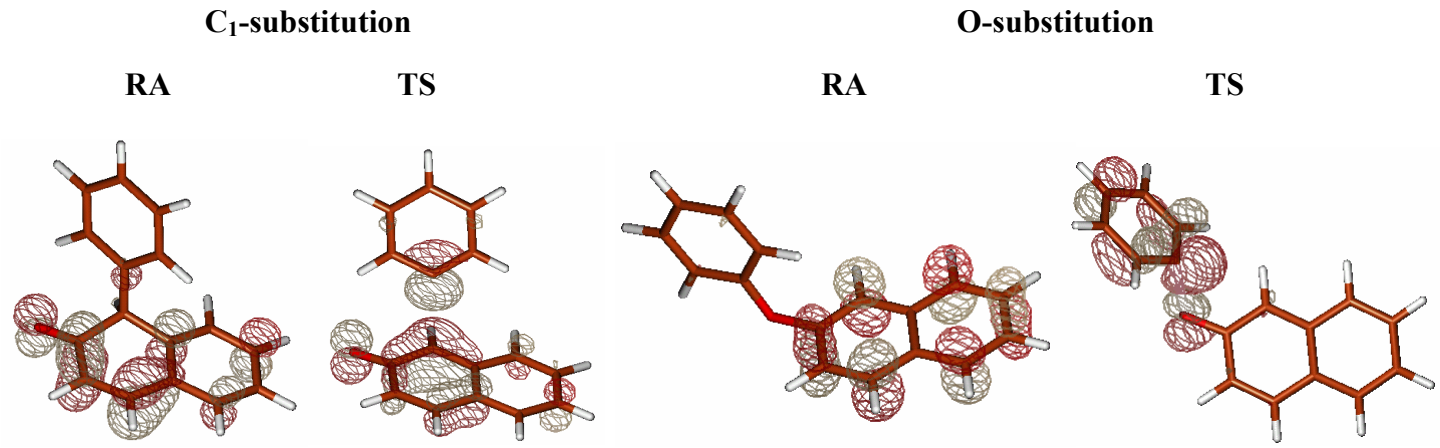
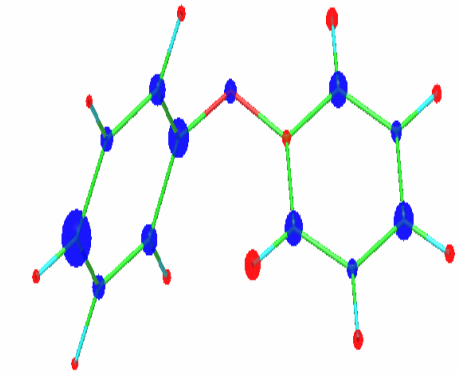


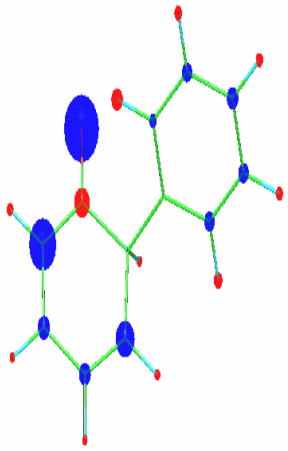
Figure S3: Charge distribution for the radical anions formed by reaction of phenyl radical (**10**) at hetereatom and C positions of anions **1**, **5** and **8**.

Anion **1**

O-substitution

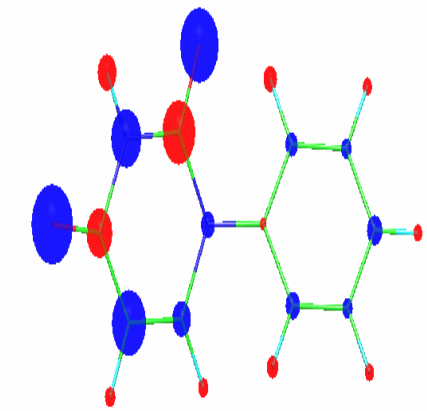


C_1-substitution

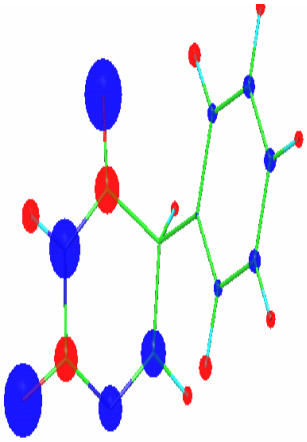


Anion **5**

N-substitution

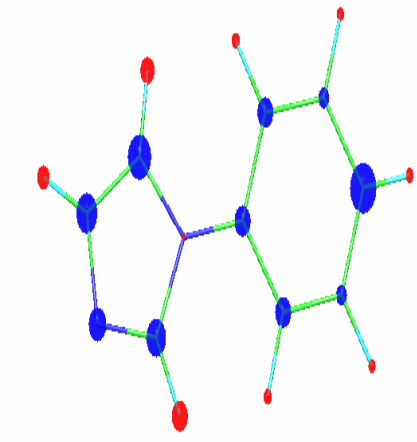


C_5-substitution

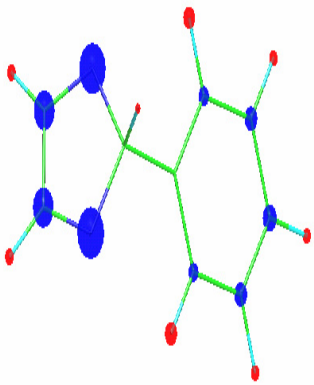


Anion **8**

N-substitution



C_2-substitution



C_4-substitution

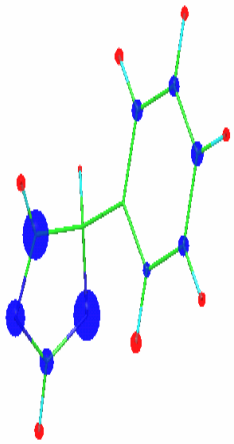


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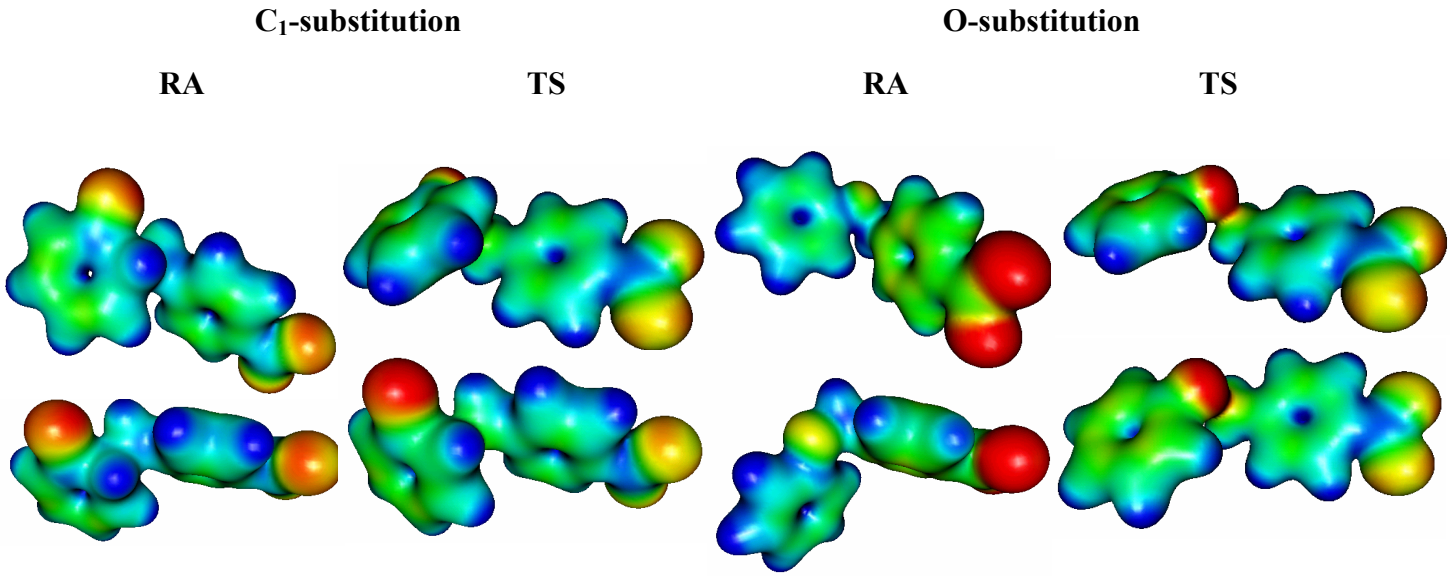
Table S2: AM1 SOMO for RAs

Anion	Position[a]	RAs of **10**	RAs of **11**
1	C_2	-2.175951	-2.674606
	O	-1.384733	-2.694593
3	C_1	-2.449492	-2.659505
	C_3	-2.808059	-3.047611
	O	-1.963007	-2.746072
5	C_5	-2.781553	-3.003690
	N	-2.328421	-3.121256
8	C_2	-1.770456	-2.523271
	C_4	-1.876079	-2.754480
	N	-1.612966	-2.913055
9	C_2	-2.764304	-2.991464
	N	-1.933987	-3.000483

Figure S4: Gas phase B3LYP electrostatic potential (from red (negative) to blue (positive)) and spin distribution for radical anions and transition sates formed by reaction of radical **11** at the C_1 and O sites of anion **1**.

Electrostatic potential



Spin distribution

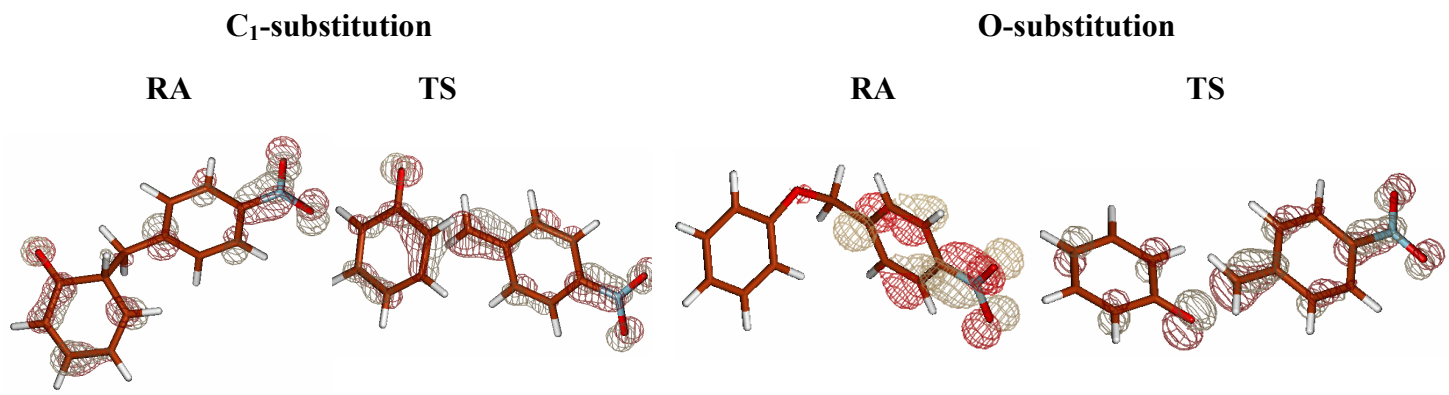
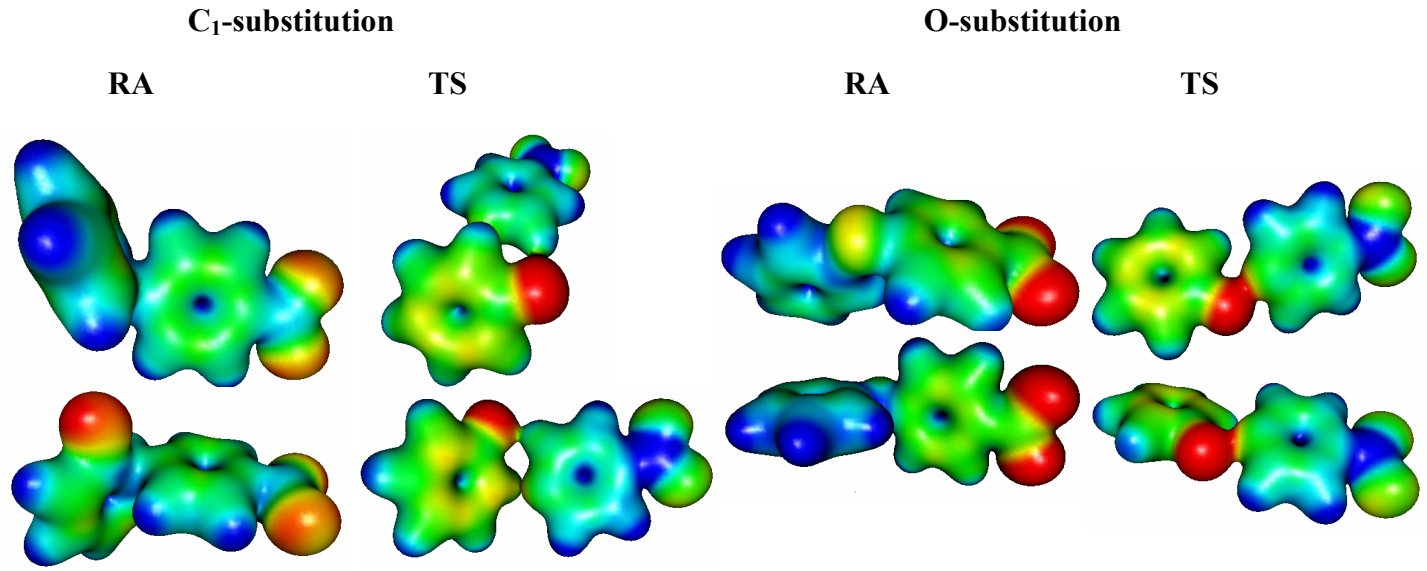


Figure S5: Gas phase B3LYP electrostatic potential (from red (negative) to blue (positive)) and spin distribution for radical anions and transition sates formed by reaction of radical **12** at the C_1 and O sites of anion **1**.

Electrostatic potential



Spin distribution

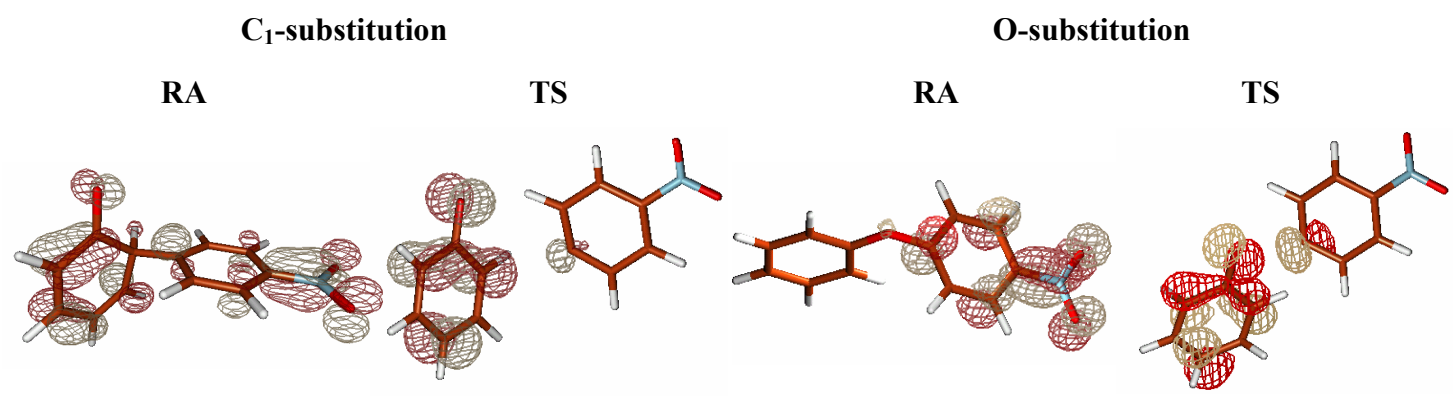


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Table S3: Energy differences between relevant points of the potential energy surface (PES) for the reaction of phenyl radicals (**10**) with anion **2** calculated with different bases set.

Bases set	C_1-substitution		O-substitution			
	E_a [a]	ΔE_r [b]	E_a [a]	ΔE_r [b]	ΔE_a	$\Delta\Delta E_r$
6-31 G*	-8.01	-39.58	-1.66	-24.84	6.35	14.74
6-31+ G*	-4.96	-36.34	2.94	-19.91	7.90	16.99
6-31 G* Continuum solvent[c]	10.57	-20.61	25.36	3.31	14.79	23.91
6-31+ G* Continuum solvent[c]	6.15	-24.74	27.66	17.21	21.51	41.95

[a] E_a (kcal/mol) = energy difference between transition states and reactants (anion + phenyl radical). [b] ΔE_r (kcal/mol) = reaction energy (energy difference between radical anion of product and reactants). [c] Continuum solvent model for methanol, without geometry optimization. Differences in total solution phase energies informed.