Supplementary Materials: Theoretical and Kinetic Tools for Selecting Effective Antioxidants: Application to the Protection of Omega-3 Oils with Natural and Synthetic Phenols

Romain Guitard, Véronique Nardello-Rataj and Jean-Marie Aubry

Table S1. Bond Dissociation Enthalpies BDEs (O-H).

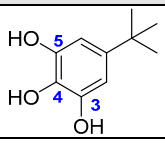
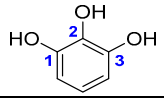
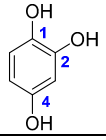
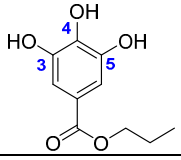
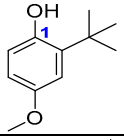
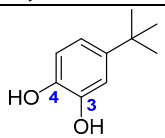
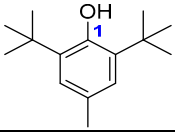
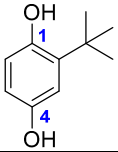
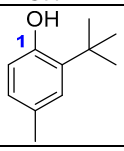
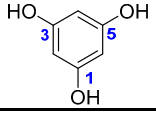
Number	Name	Structure	Site	BDE O-H (kcal·mol^{-1})
Synthetic antioxidants				
1	5-*Tert*-butyl-pyrogallol		**4**	**66.6**
			3,5	74.1
2	Pyrogallol		**2**	**68.0**
			1,3	74.4
3	Hydroxyquinol		**1**	**69.1**
			2	72.1
			4	75.9
4	Propyl gallate		**4**	**69.6**
			3,5	75.7
5	BHA		**1**	**72.3**
6	4-*Tert*-butyl-catechol		**4**	**72.3**
			3	73.2
7	BHT		**1**	**72.4**
8	TBHQ		**1**	**74.3**
			4	76.7
9	*o*-*Tert*-butyl-*p*-cresol		**1**	**77.4**
10	Phloroglucinol		**1,3,5**	**83.0**

Table S1. *Cont.*

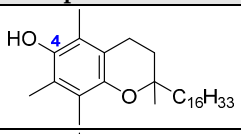
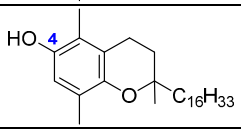
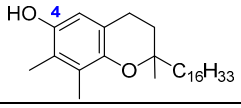
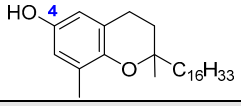
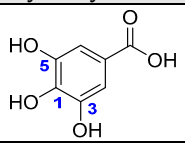
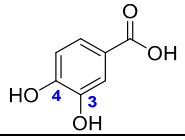
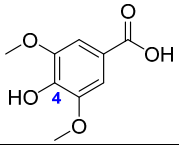
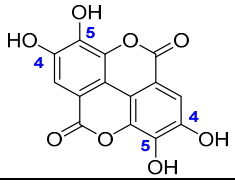
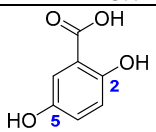
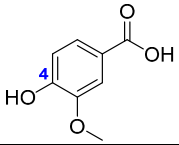
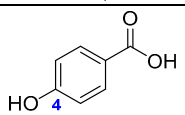
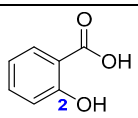
Number	Name	Structure	Site	BDE O-H (kcal·mol^{-1})
Tocopherols				
11	α-Tocopherol		**4**	**69.1**
12	β-Tocopherol		**4**	**73.4**
13	γ-Tocopherol		**4**	**73.5**
14	δ-Tocopherol		**4**	**75.4**
Derivatives of hydroxybenzoic acids				
15	Gallic acid		**4** 3,5	**70.2** 76.3
16	Protocatechuic acid		**4** 3	**75.5** 75.6
17	Syringic acid		**4**	**78.1**
18	Ellagic acid		**4** 5	**78.4** 78.9
19	Gentisic acid		**5** 2	**79.5** 84.6
20	Vanillic acid		**4**	**83.1**
21	PHBA		**4**	**84.7**
22	Salicylic acid		**1**	**95.2**

Table S1. *Cont.*

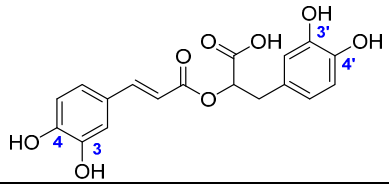
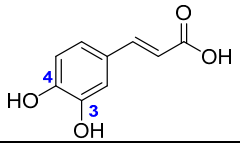
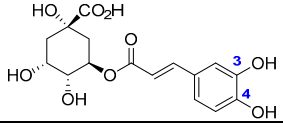
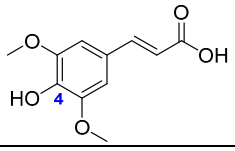
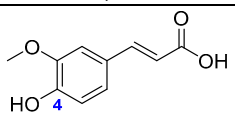
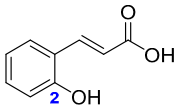
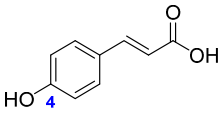
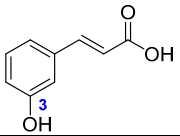
Number	Name	Structure	Site	BDE O-H (kcal·mol^{-1})
Hydroxycinnamic acid derivatives				
23	Rosmarinic acid		**4**	**69.2**
			3	75.2
			4′	72.4
			3′	75.9
24	Caffeic acid		**4**	**72.1**
			3	74.6
25	Chlorogenic acid		**4**	**73.4**
			3	75.9
26	Sinapic acid		**4**	**75.4**
27	Ferulic acid		**4**	**79.7**
28	*o*-Coumaric acid		**2**	**80.1**
29	*p*-Coumaric acid		**4**	**80.5**
30	*m*-Coumaric acid		**3**	**84.4**

Table S1. *Cont.*

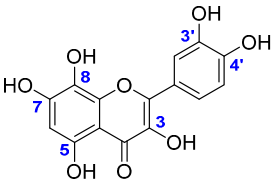
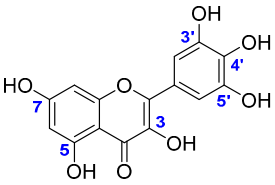
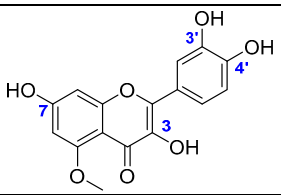
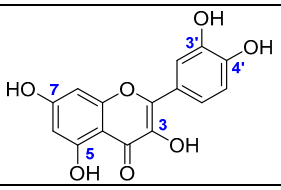
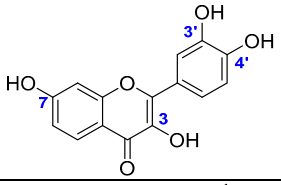
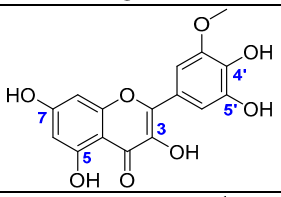
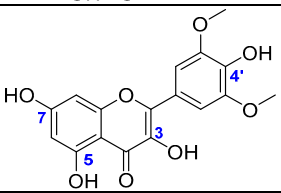
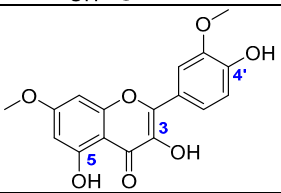
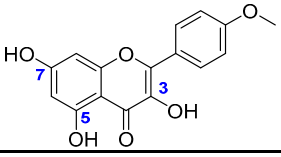
Number	Name	Structure	Site	BDE O-H (kcal·mol^{-1})
		Flavonols		
31	Gossypetin		3′	75.1
			4′	72.4
			3	79.8
			5	88.2
			7	71.7
			8	**66.6**
32	Myricetin		3′	76.1
			4′	**67.4**
			5′	76.3
			3	79.6
			5	93.8
			7	85.8
33	Azaleatin		3′	73.9
			4′	**71.1**
			3	81.9
			7	84.6
34	Quercetin		3′	74.3
			4′	**71.8**
			3	80.4
			5	95.0
			7	84.9
35	Fisetin		3′	75.3
			4′	**72.3**
			3	80.9
			7	83.9
36	Laricitrin		**4′**	**72.5**
			5′	79.4
			3	80.6
			5	94.9
			7	84.7
37	Syringetin		**4′**	**75.7**
			3	79.0
			5	93.7
			7	85.4
38	Rhamnazin		**4′**	**79.6**
			3	80.8
			5	93.3
39	Kaempferide		**3**	**79.8**
			5	93.9
			7	85.4

Table S1. *Cont.*

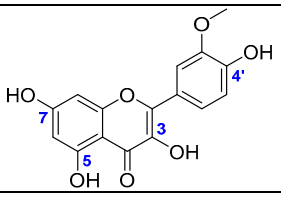
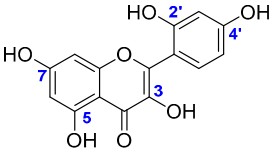
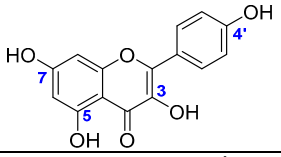
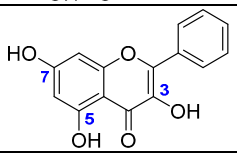
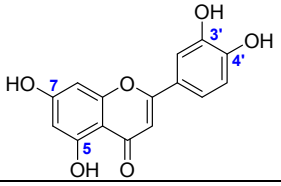
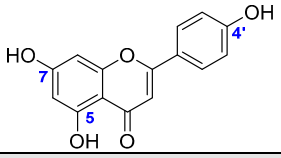
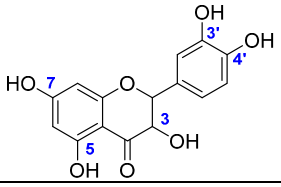
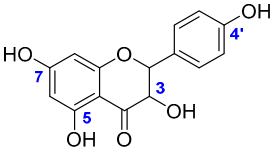
Number	Name	Structure	Site	BDE O-H (kcal·mol^{-1})
40	Isorhamnetin		**4′**	**79.8**
			3	80.2
			5	94.0
			7	85.1
41	Morin		2′	82.9
			4′	82.2
			3	**79.8**
			5	94.6
			7	85.8
42	Kaempferol		**4′**	**80.1**
			3	80.5
			5	94.8
			7	85.2
43	Galangin		**3**	**81.2**
			5	94.0
			7	86.2
		Flavones		
44	Luteolin		3′	74.9
			4′	**73.1**
			5	113.2
			7	86.6
45	Apigenin		**4′**	**82.1**
			5	98.4
			7	86.5
		Flavanonols		
46	Taxifolin		**4′**	**73.2**
			3′	73.5
			3	103.4
			5	94.8
			7	87.3
47	Aromadedrin		4′	**82.3**
			3	97.8
			5	95.7
			7	88.4

Table S1. *Cont.*

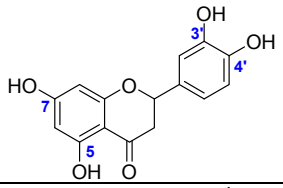
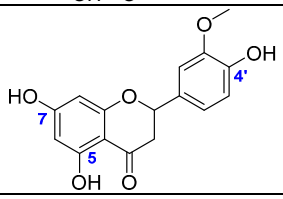
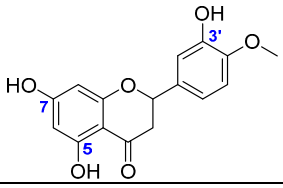
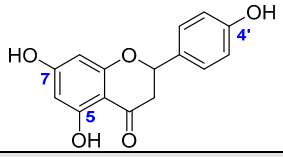
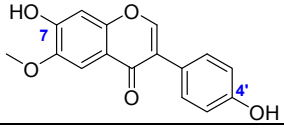
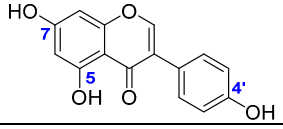
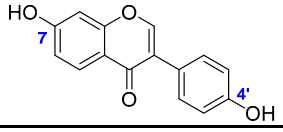
Number	Name	Structure	Site	BDE O-H (kcal·mol^{-1})
		Flavanones		
48	Eriodictyol		3′	73.8
			4′	**73.6**
			5	103.8
			7	87.6
49	Homoeriodictyol		**4′**	**80.8**
			5	96.8
			7	87.8
50	Hesperetin		**3′**	**82.2**
			5	103.6
			7	87.7
51	Naringenin		**4′**	**82.4**
			5	96.7
			7	87.8
		Isoflavones		
52	Glycitein		**4′**	**80.1**
			7	84.1
53	Genistein		**4′**	**81.0**
			5	112.5
			7	87.3
54	Daidzein		**4′**	**81.9**
			7	84.8

Table S1. *Cont.*

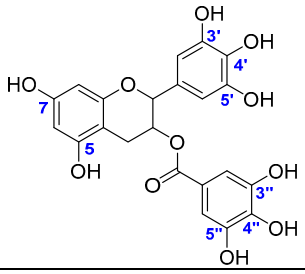
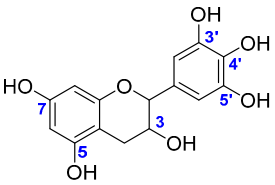
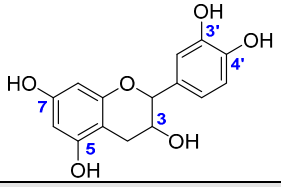
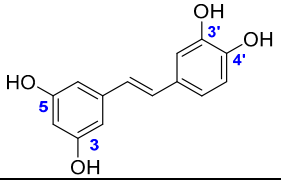
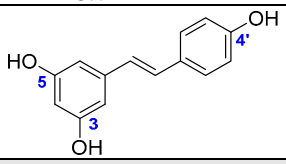
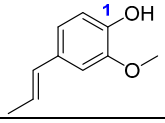
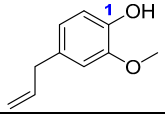
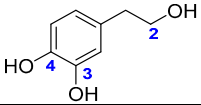
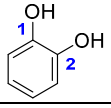
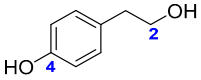
Number	Name	Structure	Site	BDE O-H (kcal·mol^{-1})
		Catechins		
55	Epigallocatechin gallate		3′	73.5
			4′	**66.5**
			5′	73.1
			3′′	75.8
			4′′	68.6
			5′′	75.4
			5	79.6
			7	83.4
56	Gallocatechin		3′	75.8
			4′	**68.6**
			5′	75.2
			3	100.8
			5	79.2
			7	82.0
57	Catechin		3′	82.5
			4′	**74.4**
			3	102.4
			5	79.1
			7	82.9
		Stilbenes		
58	Piceatannol		**4′**	**68.7**
			5′	71.2
			3	82.1
			5	82.9
59	Resveratrol		**4′**	**76.7**
			3	82.7
			5	82.0
		Eugenol derivatives		
60	Isoeugenol		**1**	**76.6**
61	Eugenol		**1**	**80.2**
		Antioxidants found in olive oil		
62	Hydroxytyrosol		**4**	**72.1**
			3	72.8
			2	97.4
63	Catechol		**1,2**	**73.4**
64	Tyrosol		**4**	**81.0**
			2	97.5

Table S1. *Cont.*

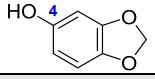
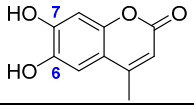
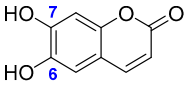
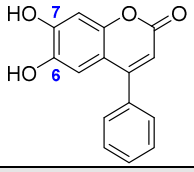
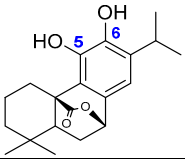
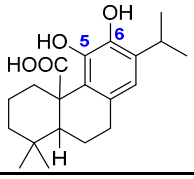
Number	Name	Structure	Site	BDE O-H (kcal·mol^{-1})
		Lignans		
65	Sesamol		**4**	**75.1**
		Coumarins		
66	Methylesculetin		**6**	**72.0**
			7	73.4
67	Aesculetin		**6**	**72.5**
			7	73.0
68	Nordalbergin		**6**	**72.6**
			7	73.2
		Antioxidants found in Rosemary extract		
69	Carnosol		**6**	**70.7**
			5	71.6
70	Carnosic acid		**6**	**70.8**
			5	71.4

Table S2. Kinetic rate constants of hydrogen transfer from phenolic antioxidants to the DPPH$^{\bullet}$ radical in toluene at 20 °C.

Phenols	Methods	10^4 × [DPPH$^{\bullet}$] (M)	10^3 × [ArOH]$_0$ (M)	10^3 × k_{app}	k (M^{-1}·s^{-1})
1	SOK	1.25	0.125	809.2 802.5 805.6	9480
4	SOK	1.25	0.125	107.7 104.9 103.9	1240
5	SOK	1.25	0.125	14.6 15.8 16.8	184
6	SOK	1.25	0.125	67.4 64.5 65.9	776
7	FOK	1.25	2.0 3.0 4.0 5.0	0.63 0.76 0.98 1.16	0.18
8	SOK	1.25	0.125	51.1 51.3 51.4	600

Table S2. *Cont.*

Phenols	Methods	$10^4 \times$ [DPPH·] (M)	$10^3 \times$ [ArOH]$_0$ (M)	$10^3 \times k_{app}$	k ($M^{-1} \cdot s^{-1}$)
9	FOK	1.25	0.9	0.38	0.36
			1.35	0.58	
			1.80	0.70	
			2.25	0.88	
11	SOK	1.25	0.125	231.4	2690
				226.9	
				227.6	
17	SOK	1.25	0.125	0.90	10.6
				0.92	
				0.87	
20	SOK	1.25	0.125	0.12	1.4
				0.12	
				0.12	
20	FOK	1.25	2.0	2.03	1.0
			3.0	3.04	
			4.0	3.92	
			5.0	5.01	
26	SOK	1.25	0.125	12.2	165
				15.9	
				14.1	
27	SOK	1.25	0.125	0.65	8.4
				0.76	
				0.73	
60	SOK	1.25	0.125	3.01	38
				3.29	
				3.33	
61	FOK	1.25	0.9	2.58	2.7
			1.35	3.88	
			1.8	5.23	
			2.25	6.23	
61	SOK	1.25	0.125	0.34	3.9
				0.32	
				0.33	
62	SOK	1.25	0.125	88.6	1070
				90.9	
				92.9	
63	SOK	1.25	0.125	34.2	400
				34.3	
				34.8	
65	SOK	1.25	0.125	21.4	250
				21.4	
				21.6	
69	SOK	1.25	0.125	132.8	1680
				145.6	
				149.8	
70	SOK	1.25	0.125	54.5	640
				54.3	
				54.0	

Table S3. Determination of the stoichiometric numbers (σ_{exp}) of the hydrogen transfer from phenols to the DPPH• radical in toluene at 20 °C at 515 nm, [DPPH•] = 1.5×10^{-4} mol·L^{-1}.

Phenols	$10^5 \times [ArOH]_0$ (M)	A_0	A_f	σ_{exp}
1	2.07	1.60	1.09	2.1
4	2.07	1.60	0.64	3.9
5	2.07	1.60	1.12	2.0
6	2.07	1.60	0.98	2.5
7	2.07	1.60	1.10	2.0
8	2.07	1.60	1.12	2.0
9	2.07	1.60	0.98	2.5
11	2.07	1.60	1.12	2.0
15 *	2.07	1.60	0.46	5.0
16 *	2.07	1.60	1.18	1.8
17	2.07	1.60	1.33	1.1
23 *	2.07	1.60	0.65	4.1
24 *	2.07	1.63	1.17	2.0
25 *	2.07	1.60	1.17	1.9
26	2.07	1.60	1.10	1.4
27	2.07	1.60	1.15	1.8
32 *	2.07	1.61	0.83	3.4
34 *	2.07	1.60	1.17	1.9
55 *	2.07	1.60	0.35	5.4
58 *	2.07	1.60	1.12	2.0
59 *	2.07	1.60	1.40	0.9
60	2.07	1.60	1.38	0.9
61	2.07	1.60	1.08	2.1
62	2.07	1.60	1.12	2.0
63	2.07	1.60	1.13	1.9
65	2.07	1.60	1.10	2.1
67 *	2.07	1.61	1.11	2.1
69	2.07	1.60	1.14	1.9
70	2.07	1.60	1.12	2.0

*: ethyl acetate used as solvent; nd: not determined

Table S4. Induction periods (IP) and oxidation rates (R_{ox}) for the inhibition of FAMEs linseed oil oxidation by phenolic antioxidants during the Rapidoxy® test.

Phenols	Induction Period IP (min)	IP Average (min)	Std. dev. IP (min)	Oxidation rate R_{ox} (mM·min^{-1})	R_{ox} Average (mM·min^{-1})	Std. dev. R_{ox} (mM·min^{-1})
	230			0.10		
1	240	234	5	0.04	0.06	0.03
	232			0.04		
	170			0.25		
4	150	162	11	0.28	0.26	0.02
	167			0.25		
	169			0.35		
5	166	167	2	0.40	0.35	0.05
	165			0.31		
	220			0.40		
6	210	220	10	0.36	0.37	0.02
	230			0.36		
	132			0.45		
7	132	131	1	0.37	0.44	0.07
	130			0.51		

Table S4. *Cont.*

Phenols	Induction Period IP (min)	IP Average (min)	Std. dev. IP (min)	Oxidation rate R_{ox} (mM·min^{-1})	R_{ox} Average (mM·min^{-1})	Std. dev. R_{ox} (mM·min^{-1})
	43			0.47		
8	43	45	2	0.56	0.53	0.06
	45			0.57		
	56			0.76		
9	58	56	2	0.76	0.77	0.02
	54			0.79		
	177			0.17		
11	179	177	2	0.18	0.17	0.01
	176			0.16		
	178			0.29		
15	172	178	6	0.30	0.32	0.04
	184			0.37		
	50			0.59		
16	46	50	4	0.62	0.62	0.03
	53			0.65		
	42			0.79		
17	38	37	6	0.86	0.76	0.11
	31			0.64		
	5			1.00		
20	5	5	1	1.08	1.03	0.04
	6			1.02		
	7			1.16		
21	6	6	1	1.18	1.20	0.05
	5			1.26		
	250			0.26		
23	260	262	14	0.28	0.27	0.01
	277			0.27		
	150			0.34		
24	142	148	5	0.36	0.36	0.02
	152			0.37		
	139			0.47		
25	136	138	2	0.48	0.48	0.02
	138			0.50		
	56			0.62		
26	58	54	6	0.52	0.57	0.05
	47			0.56		
	26			0.80		
26	28	28	2	0.82	0.82	0.02
	30			0.84		
	269			0.13		
32	252	262	9	0.10	0.11	0.02
	264			0.11		
	131			0.33		
34	130	135	8	0.35	0.34	0.01
	144			0.35		
	438			0.04		
55	477	476	37	0.09	0.08	0.03
	512			0.10		
	313			0.28		
58	321	313	8	0.30	0.29	0.04
	306			0.28		
	64			0.72		
59	68	67	2	0.69	0.68	0.04
	68			0.64		
	48			0.72		
60	48	49	1	0.74	0.72	0.02
	50			0.71		
	25			0.90		
61	28	27	2	0.99	0.93	0.05
	27			0.91		

Table S4. *Cont.*

Phenols	Induction Period IP (min)	IP Average (min)	Std. dev. IP (min)	Oxidation rate R_{ox} (mM·min^{-1})	R_{ox} Average (mM·min^{-1})	Std. dev. R_{ox} (mM·min^{-1})
62	169	172	3	0.29	0.30	0.02
	175			0.32		
	173			0.30		
63	145	147	3	0.46	0.46	0.01
	150			0.46		
	146			0.47		
65	164	161	2	0.57	0.55	0.01
	160			0.55		
	160			0.55		
67	120	112	8	0.50	0.50	0.03
	111			0.53		
	104			0.48		
69	162	166	6	0.35	0.35	0.01
	163			0.34		
	173			0.36		
70	229	230	8	0.32	0.29	0.02
	222			0.28		
	238			0.28		

2 mL of FAMEs linseed oil, $[phenols]_0$ = 0.5 mM, T = 90°C, P = 450 kPa, Std. dev. = Standard deviation.

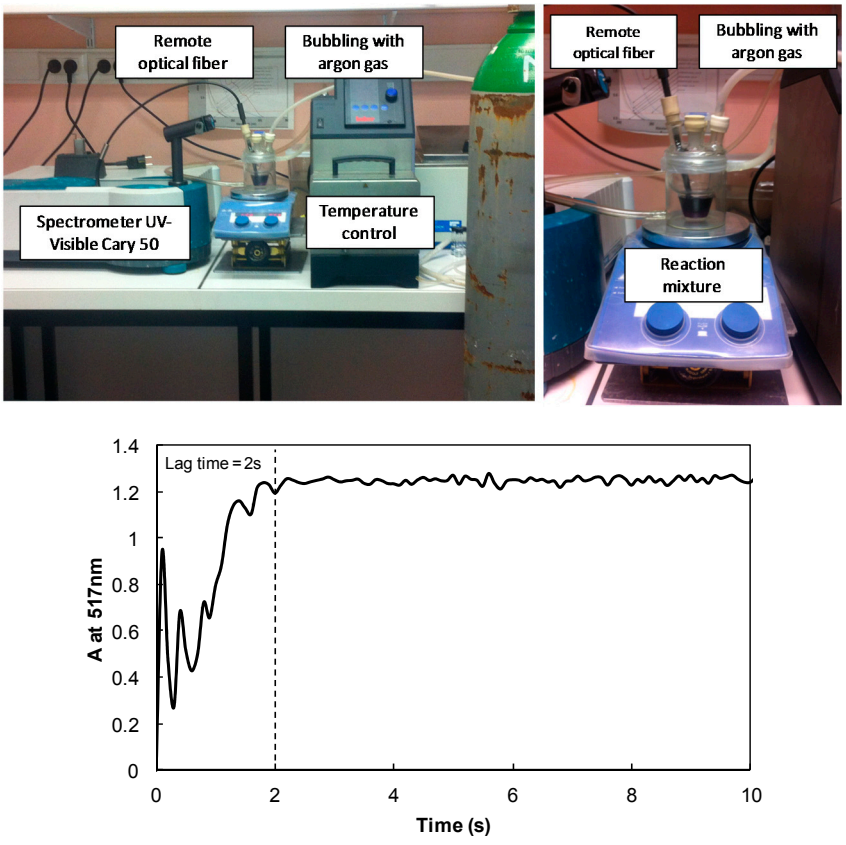


Figure S1. Equipment for UV-visible analysis and evolution of the absorbance of DPPH• radical at 515 nm (0.12 mM) without phenol in toluene at 20 °C (visualization of the lag time).

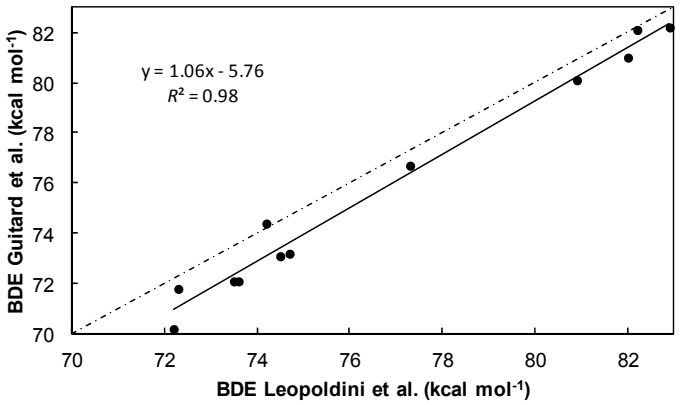


Figure S2. Correlation of BDEs obtained by Guitard et al. and Leopoldini et al. [22].

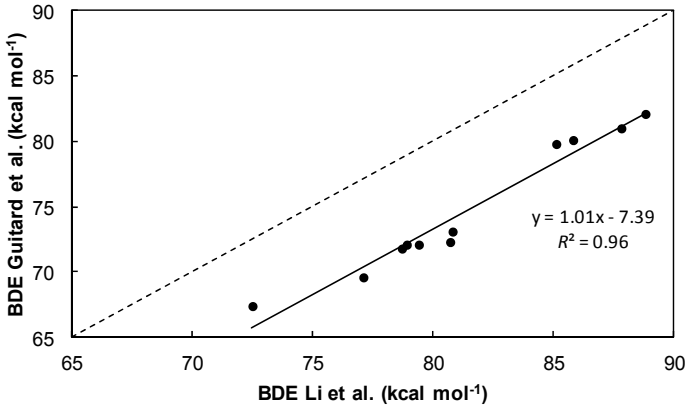


Figure S3. Correlation of BDEs obtained by Guitard et al. and Li et al. [23].

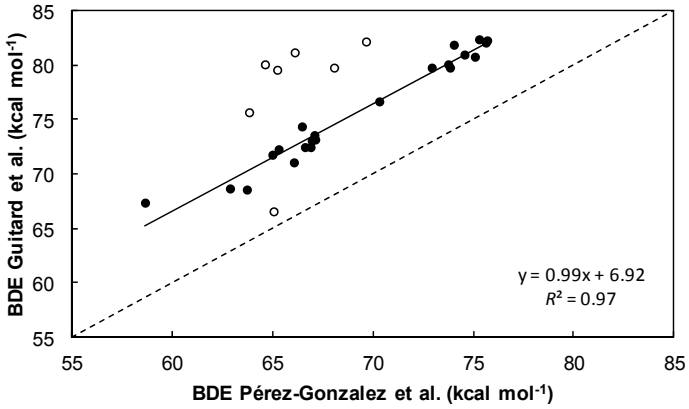


Figure S4. Correlation of BDEs obtained by Guitard et al. and Pérez-Gonzalez et al. [20].