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Supplementary information: A density functional theory benchmark on antioxidant-related properties of polyphenols[†]

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S1 Introduction

In this file, we provide the reader with all the data produced throughout this work, considering each molecular species, theoretical method, and medium, for both properties, namely, BDE and ionization potential (IP).

S2 Results and Discussion

In this work, the statistical analysis was performed by obtaining the values of mean absolute deviation (MAD), mean signed deviation (MSD), and maximum absolute deviation (MAX). They were calculated according to the following equations:

$$\text{MAD} = \frac{1}{N}\sum_{i=1}^{N} |X_i - X_{\text{ref}}|, \tag{1}$$

$$\text{MSD} = \frac{1}{N}\sum_{i=1}^{N} X_i - X_{\text{ref}}, \tag{2}$$

and

$$\text{MAX} = \max|X_i - X_{\text{ref}}|, \tag{3}$$

where X is the property of interest, $i.e.$ BDE or IP. The sums include the i-th up to the total number, N, of exchange-correlation (XC) functionals, from which the reference values, computed at the DLPNO-CCSD(T)/6-311+G(d,p)//M06-2X/6-311+G(d,p) or DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) level of theory, are subtracted.

Another analysis performed was the linear fitting of the BDE data to obtain an equation that behaves as

$$y = ax + b, \tag{4}$$

with a and b being the slope and intercept of the curve, respectively. For that, the values are plotted so that the DFT/6-311+G(d,p) BDEs are placed in the x axis and the DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) BDEs are placed in the y axis. Using a least-square minimum methodology, we can calculate the slope and the intercept:

$$a = \frac{n\sum_{j}^{n}(x_j)_{\text{obs}}(y_j)_{\text{obs}} - \sum_{j}^{n}(x_j)_{\text{obs}}\sum_{j}^{n}(y_j)_{\text{obs}}}{n\sum_{j}^{n}(x_j^2)_{\text{obs}} - \left[\sum_{j}^{n}(x_j)_{\text{obs}}\right]^2} \tag{5}$$

and

$$b = \frac{\sum_{j}^{n}(y_j)_{\text{obs}} - a\sum_{j}^{n}(x_j)_{\text{obs}}}{n}. \tag{6}$$

where the sums go over the j-th up to the total number, n, of observed ("obs") data. The R^2, a parameter used to evaluate the goodness of the fitting model, is given by

$$R^2 = 1 - \frac{\sum[(y_j)_{\text{obs}} - (y_j)_{\text{calc}}]^2}{\sum[(y_j)_{\text{obs}} - \langle(y_j)_{\text{obs}}\rangle]^2}, \tag{7}$$

where the numerator designates the sum of the square of the residuals and the denominator shows the square of the distance the observed data is away from the average. This analysis was performed for the BDEs alone since the quantity of data is larger in comparison to the IPs.

S2.1 Molecular Total Energies

Table S1: Total energies of caffeic and gallic acids computed in the DLPNO-CCSD(T)/CBS[TZ-QZ,def2]//M06-2X/6-311+G(d,p), DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p), and DLPNO-CCSD(T)/6-311+G(d,p)//M06-2X/6-311+G(d,p) approximations for the neutral, radical, and cationic states in gas-phase or considering water or methanol as solvents (C-PCM).

Molecule	Basis Set	Medium	Total Energy (a.u.)				
			ArOH	3-ArO$^{\bullet}$	4-ArO$^{\bullet}$	9-ArO$^{\bullet}$	ArOH$^+$
Caffeic acid							
	CBS[TZ-QZ,def2]	Gas	−647.95068	−647.30848	−647.29967		−647.65393
		H$_2$O	−647.97215	−647.32603	−647.32560	−647.29250	−647.74897
		CH$_3$OH	−647.97169	−647.32565	−647.32501	−647.29079	−647.74712

		Gas	−647.921 15	−647.285 30	−647.276 37	−647.223 49	−647.624 04	
CBS[DZ-TZ,def2]	Gas	−647.921 15	−647.285 30	−647.276 37	−647.223 49	−647.624 04
	H₂O	−647.943 88	−647.303 32	−647.302 84	−647.269 46	−647.720 06
	CH₃OH	−647.943 39	−647.302 94	−647.302 22	−647.267 70	−647.718 19
6-311+G(d,p)	Gas	−647.244 54	−646.611 06	−646.603 05	−646.538 13	−646.957 36
	H₂O	−647.268 65	−646.630 99	−646.631 45	−646.597 68	−647.055 92
	CH₃OH	−647.268 13	−646.630 56	−646.630 80	−646.595 77	−647.054 00

Gallic Acid		ArOH	3-ArO•	4-ArO•	5-ArO•	7-ArO•	ArOH+
CBS[TZ-QZ,def2]	Gas	−645.831 38	−645.187 13	−645.186 95	−645.173 69	−645.113 76	−645.521 71
	H₂O	−645.852 62	−645.204 11	−645.208 80	−645.199 26	−645.168 47	−645.617 83
	CH₃OH	−645.852 15	−645.203 76	−645.208 32	−645.198 68	−645.167 06	−645.615 98
CBS[DZ-TZ,def2]	Gas	−645.804 97	−645.167 16	−645.166 32	−645.153 69	−645.094 44	−645.494 90
	H₂O	−645.827 31	−645.184 75	−645.189 32	−645.180 30	−645.148 54	−645.593 29
	CH₃OH	−645.828 83	−645.184 38	−645.188 83	−645.179 74	−645.147 06	−645.591 43
6-311+G(d,p)	Gas	−645.126 32	−644.490 26	−644.490 63	−644.477 96	−644.364 32	−644.826 76
	H₂O	−645.150 65	−644.510 59	−644.515 77	−644.506 61	−644.475 18	−644.928 32
	CH₃OH	−645.150 14	−644.510 15	−644.515 23	−644.505 95	−644.473 55	−644.926 35

S2.2   Bond Dissociation Energy (BDE) Values

Table S2: O−H BDE values (in kcal/mol) computed via DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) approximation in gas-phase or considering water or methanol as solvents (C-PCM) for all radical structures of all flavonoids studied herein.

Molecule	Radical	Gas	H₂O	CH₃OH
Caffeic acid	3-ArO•	78.234	81.213	81.144
	4-ArO•	84.035	81.879	81.956
	9-ArO•	116.281	102.808	103.597
Cyanicin	3'-ArO•	93.656	86.954	87.117
	4'-ArO•	85.505	83.945	84.004
	3-ArO•	83.672	86.727	86.650
	5-ArO•	86.166	86.763	86.647
	7-ArO•	88.262	91.482	91.598
Ellagic acid	3-ArO•	82.988	83.358	83.342
	4-ArO•	86.520	85.306	85.310
Gallic acid	3-ArO•	79.849	82.859	82.785
	4-ArO•	80.449	80.100	80.106
	5-ArO•	88.037	85.603	85.649
	7-ArO•	124.297	104.655	105.273
Myricetin	3'-ArO•	78.509	82.235	82.097
	4'-ArO•	77.630	77.192	77.182
	5'-ArO•	87.019	84.655	84.625
	3-ArO•	84.957	82.258	82.200
	5-ArO•	104.408	100.165	93.382
	7-ArO•	93.718	117.468	91.628
Phloretin	2'-ArO•	96.742	140.050	141.180
	4'-ArO•	89.823	132.028	133.139
	6'-ArO•	84.665	129.561	130.415
	4-ArO•	83.617	138.796	139.989

Table S3: O−H BDE values (in kcal/mol) computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM) for all radical structures of caffeic acid studied herein.

Radical	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H₂O	CH₃OH	Gas	H₂O	CH₃OH	Gas	H₂O	CH₃OH	Gas	H₂O	CH₃OH
3-ArO•	SVWN5	81.829	84.569	84.508	82.133	84.969	84.906	82.947	85.732	85.668	84.418	86.690	86.640
	BLYP	69.053	70.712	70.676	70.266	72.006	71.963	70.795	72.500	72.462	72.152	73.320	73.295
	PBE	70.212	72.334	72.287	71.479	73.697	73.645	71.805	73.955	73.906	73.096	74.737	74.701
	TPSS	71.976	73.883	73.842	72.693	74.683	74.637	73.023	74.933	74.890	74.144	75.611	75.580
	VSXC	72.155	73.833	73.796	73.671	75.412	75.375	73.554	75.232	75.193	74.110	75.907	75.882
	B1LYP	73.294	74.786	74.755	74.075	75.650	75.616	74.337	75.897	75.863	74.758	76.470	76.446
	B3LYP	74.021	75.562	75.529	74.832	76.462	76.426	75.136	76.745	76.709	76.187	77.343	77.319
	B3LYP-D3	74.504	76.019	75.987	75.376	76.989	76.955	75.663	77.258	77.224	76.107	77.837	77.814
	B97-2	73.878	75.591	75.555	74.679	76.507	76.467	74.499	76.278	76.239	74.794	76.773	76.743
	BHandHLYP	75.281	76.880	76.846	75.976	77.587	77.553	76.103	77.706	77.671	76.308	78.144	78.118
	mPW1PW91	74.279	76.135	76.095	75.073	77.022	76.980	75.117	77.013	76.972	75.404	77.500	77.469
	PBE0	74.523	76.438	76.396	75.338	77.344	77.300	75.388	77.340	77.297	75.717	77.858	77.825
	X3LYP	74.350	75.894	75.861	75.146	76.775	76.739	75.404	77.009	76.974	75.877	77.627	77.603
	BMK	75.955	77.738	77.700	75.919	77.725	77.681	75.525	78.143	78.096	76.351	77.690	77.686

Radical	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	M05-2X	79.964	81.647	81.611	79.969	84.273	81.077	80.618	84.418	82.267	81.311	84.111	81.997
	M06	76.825	78.453	78.418	76.477	78.128	78.092	76.254	77.976	77.937	76.598	78.486	78.459
	M06-2X	79.738	81.358	81.324	80.437	82.137	82.100	80.752	82.399	82.364	80.877	82.174	82.147
	M06-HF	87.974	89.657	89.621	88.442	90.349	90.309	87.705	88.947	88.909	88.115	88.996	88.968
	CAM-B3LYP	76.246	77.795	77.762	76.755	78.361	78.326	76.915	78.520	78.485	77.344	78.492	78.468
	LC-PBE	79.278	81.356	81.312	78.522	80.626	80.582	78.590	80.642	80.598	79.401	81.024	80.991
	LC-ωPBE	75.127	76.360	76.321	74.862	76.741	76.701	74.915	76.741	76.701	75.727	77.136	77.107
	ωB97X	76.199	77.273	77.238	75.901	77.614	77.578	75.680	77.926	77.892	76.566	77.886	77.856
	ωB97X-D	75.732	77.418	77.380	76.395	78.215	78.175	76.162	77.910	77.875	76.997	78.386	78.349
4-ArO•	SVWN5	92.310	89.766	89.831	93.574	91.803	91.847	93.278	91.493	91.537	93.848	91.105	91.177
	BLYP	76.345	73.450	73.522	77.351	75.259	75.307	77.326	75.230	75.284	78.010	74.907	74.991
	PBE	78.153	75.544	75.610	79.359	77.577	77.620	79.111	77.319	77.365	79.709	76.987	77.061
	TPSS	79.550	76.787	76.857	80.174	78.185	78.233	80.018	78.009	78.061	80.594	77.750	77.828
	VSXC	79.431	76.476	76.549	80.153	78.111	78.163	79.541	77.516	77.567	80.139	77.166	77.246
	B1LYP	79.850	76.707	76.787	80.314	77.981	78.040	80.174	77.870	77.930	80.795	77.608	77.694
	B3LYP	80.824	77.674	77.754	81.362	79.057	79.115	81.232	78.938	78.998	81.857	78.670	78.756
	B3LYP-D3	81.274	78.124	78.205	81.805	79.494	79.553	81.677	79.390	79.450	82.307	79.129	79.214
	B97-2	80.638	77.570	77.648	81.108	78.933	78.990	80.545	78.396	78.452	81.084	78.170	78.248
	BHandHLYP	81.145	78.122	78.200	81.398	79.046	79.107	81.177	78.881	78.941	81.768	78.719	78.801
	mPW1PW91	81.104	78.165	78.240	81.653	79.563	79.617	81.312	79.236	79.290	81.845	78.996	79.073
	PBE0	81.463	78.572	78.646	82.054	80.020	80.072	81.700	79.684	79.736	82.250	79.440	79.516
	X3LYP	81.168	78.024	78.104	81.700	79.386	79.444	81.525	79.231	79.291	82.147	78.953	79.039
	BMK	82.480	79.276	79.354	82.310	79.980	80.039	82.148	79.848	79.907	82.757	79.586	79.670
	M05-2X	87.807	83.891	83.976	87.310	81.101	84.342	87.552	82.220	84.518	87.999	81.919	84.245
	M06	83.573	80.372	80.453	82.843	80.489	80.548	82.199	79.972	80.028	82.822	79.763	79.844
	M06-2X	87.358	83.460	84.136	87.071	84.662	84.724	86.898	84.519	84.581	87.378	84.261	84.344
	M06-HF	95.733	92.389	92.476	96.029	93.548	93.614	95.297	92.166	92.234	95.531	91.724	91.813
	CAM-B3LYP	83.223	79.989	80.070	83.497	81.076	81.138	83.247	80.840	80.901	83.879	80.546	80.634
	LC-PBE	86.438	83.385	83.461	86.215	83.997	84.054	85.930	83.672	83.730	86.463	83.361	83.442
	LC-ωPBE	81.813	78.785	78.861	81.815	79.642	79.698	81.557	79.349	79.404	82.084	79.031	79.112
	ωB97X	82.982	79.825	79.906	82.982	80.614	80.676	82.295	79.979	80.039	82.938	79.791	79.875
	ωB97X-D	83.217	79.989	80.069	83.658	81.243	81.304	82.937	80.599	80.659	83.490	80.398	80.481
9'-ArO•	SVWN5	105.278	100.745	100.927	109.417	104.659	104.845	109.546	104.346	104.545	108.904	101.413	101.687
	BLYP	90.807	86.785	86.960	94.614	90.199	90.376	95.055	90.227	90.424	94.510	87.007	87.290
	PBE	92.167	88.397	88.565	96.251	92.124	92.295	96.420	91.914	92.101	95.922	88.913	89.182
	TPSS	93.393	90.685	90.849	97.184	93.794	93.969	97.659	93.730	93.924	98.017	90.989	91.270
	VSXC	94.723	90.970	91.154	99.094	95.007	95.199	98.931	94.542	94.746	99.485	92.002	92.301
	B1LYP	98.538	98.546	98.772	102.419	101.150	101.372	102.886	100.249	100.546	103.225	98.006	98.644
	B3LYP	98.873	98.950	98.959	102.772	100.511	102.984	103.281	100.212	100.480	103.643	98.652	99.279
	B3LYP-D3	99.294	98.029	98.238	103.184	100.914	101.166	103.694	100.626	100.893	104.054	99.006	99.653
	B97-2	98.880	99.060	98.046	102.946	100.633	100.867	102.902	103.088	100.190	103.181	96.142	96.524
	BHandHLYP	101.268	105.236	105.851	106.442	107.461	108.064	106.539	106.495	107.109	115.368	101.830	102.503
	mPW1PW91	99.570	99.809	100.026	103.493	102.355	102.534	103.650	101.858	102.061	103.925	99.855	100.480
	PBE0	99.771	100.067	102.863	103.745	102.712	102.886	103.894	102.229	102.426	104.179	100.290	100.917
	X3LYP	99.416	98.583	98.811	103.316	101.438	101.687	103.786	101.060	101.349	104.144	98.988	99.619
	BMK	105.015	104.191	104.771	107.849	106.167	106.711	108.302	105.429	105.994	108.578	101.102	101.770
	M05-2X	106.964	109.366	109.962	111.848	110.214	111.470	112.663	109.863	110.557	113.720	105.018	106.403
	M06	103.780	101.476	101.786	107.805	103.463	103.792	107.748	102.749	103.091	108.084	100.054	100.688
	M06-2X	107.359	109.978	110.566	112.034	112.289	112.865	112.533	111.430	112.021	112.712	107.144	107.789
	M06-HF	112.926	120.781	121.414	144.043	122.220	122.841	141.249	118.456	119.076	138.749	114.144	114.819
	CAM-B3LYP	103.573	105.771	106.371	107.198	108.002	108.591	107.592	106.787	107.392	107.966	101.669	102.343
	LC-PBE	109.676	110.721	111.379	114.037	113.048	113.691	114.337	111.450	112.105	114.679	106.626	107.341
	LC-ωPBE	104.411	106.906	107.552	107.911	109.362	109.993	108.140	107.802	108.449	108.458	102.806	102.920
	ωB97X	104.676	106.658	107.280	108.025	108.998	109.607	107.882	107.397	108.018	108.322	101.839	102.533
	ωB97X-D	103.245	105.516	106.115	107.040	107.737	108.323	106.902	106.271	106.869	107.239	101.631	102.303

Table S4: O−H BDE values (in kcal/mol) computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM) for all radical structures of cyanidin studied herein.

Radical	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
3'-ArO•	SVWN5	102.589	95.738	95.904	104.168	98.137	98.288	103.800	97.659	97.813	104.292	97.175	97.360
	BLYP	85.682	79.068	79.232	87.052	81.094	81.245	86.974	80.907	81.062	87.567	80.385	80.576
	PBE	87.631	81.142	81.300	89.201	83.510	83.653	88.905	83.098	83.245	89.419	82.521	82.704
	TPSS	88.548	82.140	82.299	89.712	83.889	84.037	89.549	83.641	83.791	90.059	83.249	83.429
	VSXC	89.054	82.308	82.474	90.282	84.419	84.573	89.610	83.679	83.828	90.135	83.069	83.264
	B1LYP	88.312	81.624	81.795	89.583	83.496	83.643	89.454	83.271	83.422	90.046	82.922	83.110
	B3LYP	89.528	82.794	82.956	90.763	84.600	84.753	90.638	84.406	84.565	91.220	84.056	84.246
	B3LYP-D3	90.021	83.254	83.419	91.242	85.113	85.260	91.117	84.899	85.053	91.693	84.476	84.668
	B97-2	89.291	82.546	82.710	90.533	84.440	84.593	89.980	83.834	83.989	90.443	83.521	83.702
	BHandHLYP	79.086	82.477	82.629	90.536	83.205	83.386	90.373	82.913	83.101	90.972	82.479	82.691
	mPW1PW91	89.694	83.149	83.308	91.059	85.103	85.254	90.744	84.726	84.878	91.249	84.421	84.600
	PBE0	90.083	83.574	83.732	91.479	85.595	85.744	91.149	85.211	85.361	91.675	84.880	85.058
	X3LYP	89.820	83.124	83.290	91.083	84.955	85.099	90.913	84.693	84.848	91.509	84.350	84.536

Radical	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	BMK	91.291	84.264	84.514	91.842	85.257	85.413	91.661	85.097	85.259	91.937	85.199	85.373
	M05-2X	95.007	86.045	86.242	95.728	89.352	89.525	96.028	89.604	89.770	96.433	89.268	89.450
	M06	92.596	85.565	85.736	92.568	86.308	86.452	91.837	85.645	85.801	92.531	85.194	85.388
	M06-2X	95.300	86.387	88.519	95.979	89.815	89.970	95.810	89.560	89.719	96.193	89.207	89.377
	M06-HF	101.024	89.906	95.471	101.865	96.456	96.606	102.161	95.822	96.006	101.644	94.550	94.712
	CAM-B3LYP	91.580	82.401	82.602	92.674	86.433	86.583	92.451	86.121	86.276	93.059	85.698	85.894
	LC-PBE	95.247	86.035	86.232	95.902	89.589	89.743	95.670	89.240	89.397	96.209	88.977	89.163
	LC-ωPBE	90.376	81.766	81.953	91.141	85.022	85.165	90.908	84.610	84.766	91.425	84.380	84.561
	ωB97X	91.251	82.576	82.098	92.087	85.726	85.839	91.466	85.150	85.297	92.053	84.888	85.080
	ωB97X-D	91.523	84.734	84.890	92.672	86.268	86.441	92.067	85.644	85.786	92.665	85.479	85.666
4'-ArO•	SVWN5	88.640	86.244	86.319	89.320	86.945	87.020	89.502	87.157	87.231	90.701	87.810	87.903
	BLYP	75.003	72.299	72.376	76.120	73.399	73.480	76.293	73.544	73.626	77.519	74.213	74.315
	PBE	76.519	74.061	74.134	77.749	75.350	75.423	77.732	75.289	75.362	78.859	75.815	75.909
	TPSS	78.335	75.813	75.887	78.963	76.391	76.469	78.982	76.363	76.442	79.975	76.906	77.001
	VSXC	78.220	75.586	75.661	79.440	76.842	76.924	79.051	76.372	76.450	80.051	76.792	76.896
	B1LYP	80.074	77.316	77.393	80.559	77.800	77.878	80.519	77.744	77.824	81.480	78.205	78.301
	B3LYP	80.678	77.937	78.013	81.235	78.509	78.587	81.230	78.488	78.567	82.216	78.960	79.058
	B3LYP-D3	81.106	78.355	78.433	81.704	78.983	79.062	81.683	78.940	79.020	82.652	79.386	79.485
	B97-2	80.646	78.036	78.108	81.187	78.620	78.692	80.743	78.107	78.183	81.567	78.465	78.557
	BHandHLYP	82.625	79.356	79.450	82.854	80.055	80.135	82.707	79.884	79.966	83.446	80.183	80.279
	mPW1PW91	81.326	78.799	78.870	81.869	79.347	79.420	81.644	79.065	79.140	82.459	79.423	79.512
	PBE0	81.567	79.081	79.151	82.129	79.666	79.736	81.914	79.394	79.468	82.760	79.768	79.856
	X3LYP	81.065	78.319	78.395	81.591	78.867	78.946	81.538	78.801	78.881	82.544	79.293	79.388
	BMK	82.637	80.361	80.447	82.148	79.769	79.893	82.500	79.872	79.970	83.036	79.996	80.068
	M05-2X	86.880	84.362	84.427	86.739	84.204	84.268	87.082	84.526	84.589	87.672	84.815	84.910
	M06	83.589	80.836	80.913	82.784	79.983	80.050	82.310	79.452	79.526	83.222	79.932	80.032
	M06-2X	87.017	84.544	84.645	86.770	84.413	84.477	86.797	84.381	84.450	87.504	84.816	84.901
	M06-HF	93.760	86.810	92.290	94.021	92.000	92.055	93.664	91.600	91.668	94.155	90.363	91.617
	CAM-B3LYP	83.261	80.520	80.599	83.482	80.737	80.813	83.358	80.611	80.686	84.364	81.083	81.180
	LC-PBE	86.527	84.076	84.148	85.995	83.554	83.614	85.816	83.285	83.351	86.663	83.754	83.842
	LC-ωPBE	82.137	79.719	79.780	82.127	79.615	79.683	81.971	79.415	79.486	82.833	79.893	79.977
	ωB97X	83.215	80.707	80.772	83.217	80.575	80.606	82.733	79.968	80.034	83.638	80.533	80.653
	ωB97X-D	83.516	81.067	81.136	84.090	81.152	81.242	83.590	80.606	80.673	84.272	81.027	81.134
3-ArO•	SVWN5	84.583	83.725	83.743	88.397	87.192	87.219	88.040	86.791	86.818	88.553	87.198	87.230
	BLYP	70.491	69.839	69.853	73.596	72.580	72.604	73.337	72.270	72.294	73.912	72.742	72.770
	PBE	72.248	71.622	71.635	75.719	74.739	74.762	75.348	74.324	74.346	75.870	74.665	74.693
	TPSS	73.598	73.101	73.111	76.370	75.449	75.470	76.148	75.180	75.202	76.625	75.564	75.587
	VSXC	74.617	73.319	73.335	77.900	76.340	76.367	77.057	75.414	75.436	76.295	75.642	75.675
	B1LYP	75.223	75.047	75.048	77.949	77.270	77.284	77.604	76.850	76.867	78.005	77.141	77.162
	B3LYP	75.786	75.495	75.497	78.574	77.805	77.823	78.251	77.417	77.436	78.676	77.725	77.747
	B3LYP-D3	76.566	76.253	76.258	79.357	78.603	78.620	79.039	78.205	78.224	79.449	78.497	78.520
	B97-2	75.734	75.480	75.482	78.591	77.801	77.816	77.956	77.079	77.097	78.331	77.359	77.381
	BHandHLYP	78.234	80.609	80.570	80.948	80.589	80.597	80.571	80.117	80.128	80.843	80.295	80.307
	mPW1PW91	76.577	76.442	76.443	79.524	78.859	78.873	79.096	78.338	78.354	79.472	78.591	78.610
	PBE0	76.862	76.717	76.719	79.880	79.214	79.228	79.441	78.692	78.708	79.817	78.931	78.951
	X3LYP	76.173	75.919	75.923	78.962	78.218	78.235	78.586	77.773	77.792	79.004	78.077	78.097
	BMK	78.096	77.644	77.683	80.038	79.558	79.566	79.670	78.872	78.887	79.447	78.594	78.607
	M05-2X	82.309	82.455	82.449	84.742	83.476	83.486	84.326	83.587	83.600	84.707	83.805	83.823
	M06	78.579	78.389	78.386	80.342	79.601	79.610	79.741	78.927	78.940	80.226	79.222	79.246
	M06-2X	82.482	82.627	82.617	84.695	83.515	83.529	84.598	83.286	83.303	84.253	83.532	83.550
	M06-HF	99.343	91.636	97.103	98.874	92.216	92.212	97.797	91.685	91.704	97.263	91.692	91.643
	CAM-B3LYP	79.251	79.278	79.278	81.921	81.387	81.398	81.478	80.877	80.889	81.914	81.167	81.183
	LC-PBE	84.056	84.298	84.285	86.556	86.028	86.040	86.168	85.507	85.525	86.672	85.944	85.964
	LC-ωPBE	79.910	80.138	80.127	82.535	82.039	82.051	82.175	81.590	81.606	82.642	82.014	82.031
	ωB97X	79.957	80.161	80.157	82.462	81.887	81.895	81.802	81.050	81.059	82.288	81.533	81.552
	ωB97X-D	79.841	80.140	80.142	82.740	81.938	81.959	82.243	81.261	81.278	82.678	81.739	81.761
5-ArO•	SVWN5	91.983	89.594	89.675	95.505	92.686	92.774	95.157	92.233	92.324	95.507	92.106	92.215
	BLYP	76.773	74.600	74.671	79.729	77.124	77.203	79.540	76.861	76.940	79.979	76.770	76.870
	PBE	78.545	76.552	76.619	81.848	79.407	79.482	81.493	78.956	79.033	81.857	78.823	78.920
	TPSS	79.561	77.813	77.873	82.304	80.020	80.090	82.113	79.719	79.791	82.435	79.616	79.706
	VSXC	79.276	77.247	77.313	82.587	80.107	80.188	81.904	79.347	79.426	82.253	79.210	79.309
	B1LYP	79.938	78.685	78.724	82.825	80.874	80.931	82.631	80.594	80.655	82.921	80.435	80.510
	B3LYP	81.026	79.585	79.630	83.897	81.816	81.877	83.703	81.529	81.594	84.002	81.370	81.451
	B3LYP-D3	81.562	80.115	80.160	84.436	82.351	82.413	84.248	82.070	82.135	84.543	81.924	82.004
	B97-2	80.931	79.635	79.675	83.869	81.895	81.953	83.290	81.185	81.247	83.510	81.044	81.119
	BHandHLYP	80.892	82.446	82.433	84.046	82.615	82.659	83.846	82.325	82.373	84.061	82.140	82.197
	mPW1PW91	81.111	80.082	80.117	84.199	82.443	82.496	83.850	81.966	82.023	84.066	81.799	81.868
	PBE0	81.491	80.471	80.506	84.642	82.902	82.955	84.283	82.426	82.483	84.516	82.267	82.336
	X3LYP	81.307	79.932	79.976	84.213	82.176	82.236	83.973	81.849	81.912	84.279	81.689	81.766
	BMK	83.185	81.907	81.984	85.263	83.454	83.511	85.270	83.300	83.357	85.294	83.144	83.207
	M05-2X	86.433	85.983	86.006	89.137	87.487	87.531	89.225	87.443	87.493	89.402	87.189	87.253
	M06	83.808	82.433	82.475	85.533	83.556	83.609	84.991	82.833	82.891	85.285	82.573	82.651
	M06-2X	87.034	86.453	86.472	89.704	88.136	88.185	89.395	87.773	87.823	89.484	87.575	87.634
	M06-HF	102.420	92.065	97.547	102.575	96.065	96.087	101.728	94.947	94.993	101.509	94.439	94.424
	CAM-B3LYP	83.151	82.198	82.231	85.983	84.258	84.308	85.681	83.871	83.922	85.920	83.648	83.715
	LC-PBE	86.106	85.649	85.660	88.775	87.396	87.436	88.451	86.907	86.955	88.541	86.591	86.651
	LC-ωPBE	81.836	81.231	81.247	84.534	83.104	83.146	84.180	82.633	82.678	84.290	82.327	82.385
	ωB97X	83.040	82.477	82.493	85.615	84.103	84.143	85.042	83.403	83.444	85.211	83.184	83.246

Radical	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	ωB97X-D	83.491	82.853	82.867	86.331	84.742	84.796	85.774	83.946	83.994	85.981	83.797	83.863
7-ArO•	SVWN5	100.476	95.221	95.396	103.650	98.090	98.264	103.123	97.400	97.579	103.221	96.716	96.926
	BLYP	84.966	80.043	80.199	87.644	82.304	82.470	87.326	81.829	82.006	87.561	81.244	81.444
	PBE	86.958	82.179	82.337	89.972	84.724	84.888	89.480	84.098	84.264	89.629	83.478	83.668
	TPSS	88.135	83.557	83.702	90.591	85.425	85.588	90.252	84.931	85.088	90.367	84.398	84.588
	VSXC	87.824	82.872	83.028	90.682	85.347	85.513	89.893	84.484	84.648	90.029	83.842	84.041
	B1LYP	89.110	85.137	85.253	91.545	86.894	87.032	91.191	86.466	86.609	91.362	85.767	86.000
	B3LYP	90.111	85.855	85.984	92.527	87.672	87.817	92.174	87.237	87.387	92.323	86.571	86.737
	B3LYP-D3	90.433	86.151	86.284	92.824	88.004	88.147	92.467	87.570	87.719	92.633	86.974	87.149
	B97-2	90.201	86.129	86.251	92.700	87.906	88.048	91.963	87.051	87.197	92.022	86.362	86.522
	BHandHLYP	78.670	89.218	89.273	86.889	89.004	89.117	86.552	88.605	88.715	86.581	88.166	88.305
	mPW1PW91	90.571	86.774	86.891	93.223	88.658	88.793	92.724	88.039	88.178	92.800	87.325	87.492
	PBE0	90.955	87.133	87.253	93.661	89.092	89.225	93.147	88.461	88.601	93.233	87.895	88.059
	X3LYP	90.436	86.261	86.389	92.882	88.078	88.223	92.478	87.596	87.743	92.636	86.929	87.069
	BMK	85.154	88.771	88.997	94.138	89.783	89.914	94.129	88.839	88.928	94.193	88.681	88.848
	M05-2X	88.656	92.984	93.086	91.832	93.869	94.002	91.823	93.740	93.885	91.769	93.161	93.287
	M06	93.233	88.956	89.086	94.358	89.474	89.626	93.623	88.601	88.749	93.847	87.984	88.161
	M06-2X	89.054	93.186	93.300	92.130	94.212	94.341	91.801	93.755	93.882	91.688	93.346	93.486
	M06-HF	104.399	93.714	99.201	104.823	98.179	101.920	104.016	100.922	101.022	103.638	100.219	100.254
	CAM-B3LYP	85.536	89.165	89.274	88.846	90.738	90.863	94.540	90.175	90.304	88.362	89.458	89.626
	LC-PBE	88.266	93.160	93.246	91.385	94.134	94.246	90.864	93.441	93.563	90.757	92.815	92.970
	LC-ωPBE	84.239	88.693	88.784	87.380	89.875	89.989	86.867	89.240	89.359	86.799	88.617	88.768
	ωB97X	85.468	89.779	89.887	88.647	90.703	90.824	87.810	89.818	89.943	87.700	89.453	89.606
	ωB97X-D	86.046	89.990	90.104	89.578	91.314	91.461	94.906	90.440	90.585	94.900	90.056	90.211

Table S5: O−H BDE values (in kcal/mol) computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM) for all radical structures of ellagic acid studied herein.

Radical	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
3-ArO•	SVWN5	86.840	85.929	85.959	85.695	85.602	85.615	86.587	86.317	86.333	88.125	87.229	87.265
	BLYP	73.711	72.306	72.346	73.403	72.686	72.710	74.140	73.246	73.274	75.561	74.005	74.052
	PBE	74.865	73.793	73.825	74.524	74.214	74.229	75.008	74.511	74.530	76.335	75.228	75.266
	TPSS	76.877	75.641	75.676	76.027	75.508	75.528	76.499	75.799	75.822	77.637	76.431	76.469
	VSXC	77.507	75.943	75.986	77.185	76.335	76.361	77.102	76.126	76.156	78.271	76.677	76.725
	B1LYP	79.114	77.508	77.549	78.024	77.224	77.247	78.370	77.435	77.462	79.485	78.038	78.080
	B3LYP	79.650	78.090	78.131	78.645	77.890	77.912	79.054	78.153	78.179	80.193	78.767	78.809
	B3LYP-D3	80.343	78.753	78.794	79.381	78.604	78.627	79.778	78.854	78.881	80.910	79.457	79.499
	B97-2	79.522	78.087	78.124	78.354	77.804	77.822	78.203	77.508	77.530	79.152	77.993	78.028
	BHandHLYP	82.184	80.500	80.542	80.698	79.828	79.853	80.777	79.802	79.829	81.737	80.355	80.393
	mPW1PW91	80.153	78.820	78.853	78.968	78.495	78.511	79.061	78.434	78.455	79.984	78.928	78.961
	PBE0	80.338	79.059	79.093	79.166	78.757	78.771	79.271	78.709	78.727	80.247	79.239	79.271
	X3LYP	80.059	78.496	78.537	79.024	78.269	78.292	79.381	78.485	78.511	80.535	79.109	79.155
	BMK	81.859	80.035	80.063	80.358	79.511	79.529	80.567	79.890	79.912	81.328	80.502	80.525
	M05-2X	86.461	84.897	84.937	84.332	83.702	83.721	85.162	84.264	84.291	85.928	84.607	84.646
	M06	82.999	81.470	81.507	80.496	79.684	79.706	80.202	79.363	79.387	81.170	79.844	79.883
	M06-2X	86.313	84.691	84.732	84.305	83.628	83.648	84.674	83.807	83.831	85.450	84.202	84.237
	M06-HF	94.704	93.049	93.092	92.572	92.034	92.055	92.544	91.679	91.703	92.970	91.794	91.829
	CAM-B3LYP	82.383	80.767	80.808	80.947	80.181	80.203	81.225	80.304	80.329	82.389	80.953	80.993
	LC-PBE	85.984	84.596	84.631	83.599	83.185	83.199	83.790	83.178	83.196	84.825	83.772	83.803
	LC-ωPBE	81.311	79.881	79.917	79.519	79.003	79.019	79.711	78.997	79.017	80.766	79.584	79.617
	ωB97X	82.384	80.783	80.821	80.642	79.913	79.937	80.450	79.541	79.563	81.480	80.277	80.311
	ωB97X-D	82.603	81.052	81.088	81.207	80.533	80.558	80.966	80.053	80.073	81.900	80.756	80.787
4-ArO•	SVWN5	93.467	90.859	90.930	94.718	92.561	92.622	94.391	92.181	92.243	95.051	91.977	92.066
	BLYP	78.061	75.310	75.383	79.018	76.667	76.730	78.972	76.573	76.639	79.682	76.391	76.483
	PBE	79.748	77.266	77.332	80.917	78.872	78.929	80.646	78.535	78.594	81.332	78.388	78.471
	TPSS	81.158	78.665	78.729	81.842	79.713	79.771	81.671	79.473	79.533	82.303	79.376	79.459
	VSXC	81.495	78.706	78.779	82.270	79.937	79.999	81.621	79.253	79.317	82.285	79.074	79.163
	B1LYP	82.096	79.523	79.588	82.680	80.474	80.531	82.499	80.261	80.320	83.185	80.211	80.291
	B3LYP	82.971	80.334	80.402	83.584	81.337	81.394	83.425	81.135	81.195	84.103	81.064	81.146
	B3LYP-D3	83.474	80.832	80.900	84.065	81.811	81.869	83.905	81.612	81.672	84.597	81.550	81.632
	B97-2	82.797	80.291	80.355	83.318	81.246	81.300	82.717	80.595	80.651	83.275	80.493	80.568
	BHandHLYP	83.882	81.583	81.640	84.430	82.403	82.455	84.150	82.105	82.158	84.757	82.122	82.191
	mPW1PW91	83.387	81.059	81.116	84.061	82.123	82.172	83.682	81.691	81.744	84.247	81.615	81.686
	PBE0	83.679	81.382	81.440	84.399	82.501	82.550	84.015	82.069	82.120	84.602	81.997	82.068
	X3LYP	83.324	80.708	80.774	83.945	81.716	81.773	83.739	81.468	81.527	84.418	81.400	81.482
	BMK	84.717	82.184	82.248	84.940	82.704	82.759	84.874	82.614	82.669	85.396	82.677	82.745
	M05-2X	89.341	86.904	86.966	89.204	87.160	87.211	89.458	87.307	87.363	89.928	87.165	87.239
	M06	86.016	83.476	83.537	85.330	83.053	83.110	84.576	82.348	82.404	85.181	82.258	82.336
	M06-2X	89.284	86.753	86.815	89.184	87.126	87.180	89.015	86.931	86.984	89.515	86.838	86.908
	M06-HF	97.148	94.844	94.902	97.295	95.496	95.543	96.688	94.818	94.866	96.971	94.562	94.626
	CAM-B3LYP	85.679	83.149	83.212	86.139	84.003	84.057	85.867	83.692	83.746	86.572	83.659	83.735
	LC-PBE	89.488	87.177	87.234	89.497	87.649	87.694	89.186	87.249	87.298	89.744	87.170	87.238
	LC-ωPBE	84.805	82.518	82.573	85.033	83.209	83.254	84.758	82.848	82.895	85.338	82.770	82.837

Radical	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	ωB97X	85.617	83.172	83.232	85.863	83.857	83.907	85.174	83.159	83.209	85.866	83.180	83.249
	ωB97X-D	85.797	83.347	83.406	86.309	84.283	84.332	85.608	83.571	83.622	86.216	83.572	83.641

Table S6: O−H BDE values (in kcal/mol) computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM) for all radical structures of gallic acid studied herein.

Radical	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
3-ArO$^\bullet$	SVWN5	83.641	86.384	86.318	83.336	86.298	86.229	84.229	87.005	86.939	85.930	88.313	88.254
	BLYP	70.436	72.219	72.173	71.213	73.059	73.015	71.762	73.518	73.473	73.168	74.489	74.455
	PBE	71.629	73.834	73.781	72.405	74.688	74.635	72.747	74.897	74.845	74.127	75.893	75.849
	TPSS	73.375	75.429	75.381	73.698	75.831	75.781	74.030	76.038	75.989	75.191	76.869	76.828
	VSXC	73.628	75.452	75.408	74.671	76.529	76.484	74.563	76.344	76.301	75.730	77.147	77.112
	B1LYP	74.641	76.346	76.305	75.122	76.909	76.866	75.364	77.071	77.031	76.342	77.688	77.654
	B3LYP	75.411	77.140	77.098	75.892	77.714	77.671	76.183	77.919	77.877	77.215	78.581	78.547
	B3LYP-D3	75.848	77.551	77.510	76.386	78.181	78.139	76.665	78.373	78.333	77.685	79.019	78.987
	B97-2	75.257	77.156	77.111	75.717	77.734	77.687	75.506	77.407	77.362	76.373	77.948	77.909
	BHandHLYP	76.665	78.510	78.466	77.129	79.009	78.956	77.189	78.992	78.950	77.895	79.413	79.370
	mPW1PW91	75.658	77.694	77.646	76.143	78.285	78.234	76.157	78.189	78.141	77.011	78.731	78.690
	PBE0	75.907	77.981	77.932	76.405	78.589	78.538	76.425	78.500	78.451	77.324	79.081	79.039
	X3LYP	75.739	77.476	77.433	76.216	78.049	78.005	76.458	78.204	78.163	77.501	78.873	78.840
	BMK	77.738	79.420	79.379	77.076	79.265	79.206	77.138	79.786	79.737	78.388	79.891	79.869
	M05-2X	81.625	83.500	83.455	82.167	83.538	83.493	82.143	83.960	83.918	83.313	84.254	84.217
	M06	78.347	80.287	80.240	77.613	79.592	79.545	77.433	79.311	79.267	78.351	79.869	79.837
	M06-2X	81.939	83.715	83.672	81.881	83.752	83.708	82.112	83.846	83.805	82.787	84.259	84.222
	M06-HF	89.523	91.469	91.422	90.409	92.435	92.388	89.339	91.268	91.220	90.245	91.427	91.383
	CAM-B3LYP	77.923	79.666	79.624	78.133	79.963	79.920	78.266	80.019	79.977	79.236	80.618	80.584
	LC-PBE	81.367	83.547	83.496	80.932	83.210	83.158	80.945	83.119	83.068	81.698	83.555	83.510
	LC-ωPBE	77.105	79.056	79.009	77.111	79.157	79.110	77.120	79.054	79.009	77.868	79.469	79.430
	ωB97X	78.057	79.877	79.834	77.989	79.956	79.914	77.713	79.509	79.468	78.634	80.102	80.065
	ωB97X-D	78.158	80.021	79.975	78.287	80.387	80.342	78.011	79.927	79.887	78.993	80.509	80.469
4-ArO$^\bullet$	SVWN5	84.188	83.820	83.825	83.561	84.000	83.988	84.162	84.536	84.525	86.002	85.737	85.742
	BLYP	70.720	69.755	69.773	70.483	70.251	70.254	71.095	70.782	70.786	72.889	71.864	71.887
	PBE	71.818	71.170	71.182	71.611	71.745	71.740	71.976	72.032	72.028	73.681	73.092	73.104
	TPSS	73.913	73.032	73.048	73.126	72.998	72.998	73.478	73.284	73.285	74.999	74.248	74.265
	VSXC	74.731	73.577	73.599	74.213	73.855	73.860	74.054	73.661	73.666	75.618	74.573	74.594
	B1LYP	76.111	74.679	74.708	74.933	74.333	74.345	75.213	74.563	74.575	76.672	75.424	75.452
	B3LYP	76.623	75.262	75.289	75.574	75.051	75.060	75.906	75.324	75.335	77.396	76.207	76.234
	B3LYP-D3	77.233	75.855	75.882	76.211	75.671	75.682	76.536	75.938	75.949	78.019	76.812	76.839
	B97-2	76.379	75.104	75.129	75.183	74.828	74.834	74.972	74.575	74.582	76.265	75.340	75.360
	BHandHLYP	79.292	77.711	77.743	77.554	76.790	76.797	77.585	76.796	76.812	78.800	77.519	77.543
	mPW1PW91	77.037	75.830	75.854	75.798	75.483	75.488	75.823	75.451	75.458	77.118	76.228	76.249
	PBE0	77.222	76.068	76.090	76.003	75.751	75.754	76.035	75.730	75.735	77.377	76.534	76.552
	X3LYP	77.041	75.671	75.698	75.949	75.420	75.430	76.235	75.644	75.655	77.741	76.541	76.569
	BMK	78.990	76.834	76.874	76.891	75.752	75.725	77.247	76.765	76.770	78.376	77.536	77.556
	M05-2X	83.584	82.006	82.037	81.941	80.752	80.764	82.125	81.352	81.368	83.799	81.925	81.954
	M06	79.755	78.440	78.466	77.364	76.834	76.844	77.051	76.531	76.540	78.432	77.349	77.378
	M06-2X	83.601	82.065	82.096	81.483	80.920	80.931	81.799	81.134	81.148	82.902	81.743	81.768
	M06-HF	92.248	90.582	90.617	90.843	90.236	90.251	90.127	89.247	89.266	91.453	89.531	89.557
	CAM-B3LYP	79.479	77.956	77.988	77.934	77.279	77.292	78.139	77.418	77.432	79.650	78.298	78.329
	LC-PBE	83.117	81.684	81.712	80.600	80.125	80.135	80.717	80.147	80.159	82.050	80.924	80.951
	LC-ωPBE	78.473	77.024	77.053	76.559	76.033	76.043	76.687	76.061	76.074	78.015	76.816	76.844
	ωB97X	79.470	77.918	77.950	77.605	76.925	76.940	77.305	76.667	76.679	78.774	77.546	77.575
	ωB97X-D	79.514	78.000	78.031	78.001	77.348	77.363	77.702	77.122	77.130	78.972	77.959	77.986
5-ArO$^\bullet$	SVWN5	94.336	91.172	91.255	96.528	93.875	93.947	96.343	93.681	93.754	97.140	93.749	93.843
	BLYP	78.906	75.993	76.072	80.612	78.094	78.160	80.663	78.139	78.205	81.517	78.202	78.294
	PBE	80.551	77.779	77.853	82.497	80.154	80.216	82.337	79.972	80.034	83.102	80.026	80.110
	TPSS	81.763	78.987	79.060	83.232	80.831	80.894	83.173	80.752	80.816	83.873	80.825	80.909
	VSXC	82.506	79.489	79.568	84.096	81.505	81.572	83.491	80.925	80.996	84.216	80.926	81.013
	B1LYP	82.139	79.227	79.302	83.550	80.971	81.037	83.500	80.915	80.984	84.239	80.963	81.049
	B3LYP	83.146	80.172	80.249	84.586	81.977	82.044	84.552	81.930	81.999	85.294	81.977	82.067
	B3LYP-D3	83.692	80.727	80.803	85.098	82.493	82.561	85.069	82.455	82.524	85.820	82.508	82.598
	B97-2	82.952	80.058	80.134	84.360	81.843	81.909	83.884	81.355	81.421	84.510	81.385	81.469
	BHandHLYP	83.541	80.865	80.934	84.959	82.504	82.558	84.823	82.367	82.430	85.469	82.414	82.491
	mPW1PW91	83.323	80.556	80.628	84.860	82.454	82.517	84.611	82.184	82.248	85.233	82.204	82.287
	PBE0	83.641	80.892	80.964	85.233	82.857	82.919	84.973	82.580	82.644	85.621	82.608	82.690
	X3LYP	83.459	80.497	80.573	84.914	82.314	82.380	84.831	82.219	82.288	85.583	82.262	82.352
	BMK	85.296	82.112	82.197	86.348	83.471	83.533	86.269	83.597	83.668	86.882	83.535	83.616
	M05-2X	89.111	86.095	86.174	89.954	87.270	87.339	89.751	87.553	87.625	90.864	87.474	87.564
	M06	85.993	82.977	83.055	86.298	83.642	83.712	85.786	83.195	83.264	86.517	83.255	83.349
	M06-2X	89.283	86.251	86.330	90.051	87.418	87.486	89.999	87.322	87.392	90.552	87.340	87.425
	M06-HF	96.575	93.674	93.752	97.634	95.684	95.750	97.063	94.384	94.454	97.314	94.187	94.272
	CAM-B3LYP	85.448	82.432	82.511	86.714	84.059	84.128	86.556	83.883	83.952	87.302	83.905	83.996
	LC-PBE	88.981	86.004	86.080	89.896	87.349	87.416	89.695	87.076	87.145	90.309	87.032	87.120

Radical	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	LC-ωPBE	84.419	81.576	81.648	85.430	82.998	83.060	85.247	82.743	82.808	85.849	82.680	82.765
	ωB97X	85.466	82.513	82.591	86.377	83.827	83.894	85.804	83.277	83.343	86.555	83.356	83.444
	ωB97X-D	85.738	82.692	82.771	86.788	84.254	84.321	86.281	83.761	83.828	86.970	83.853	83.938
7-ArO$^\bullet$	SVWN5	104.896	101.278	101.425	108.736	104.775	104.930	109.008	104.719	104.890	109.144	103.410	103.637
	BLYP	90.251	87.271	87.402	93.769	90.258	90.404	94.306	90.470	90.630	94.348	88.697	88.930
	PBE	91.591	88.751	88.881	95.386	92.071	92.212	95.652	92.036	92.190	95.737	90.467	90.686
	TPSS	93.383	91.264	91.381	96.745	93.956	94.096	97.146	94.042	94.197	97.363	92.665	92.886
	VSXC	94.974	92.290	92.424	98.966	95.664	95.821	98.784	95.254	95.425	99.089	94.126	94.360
	B1LYP	98.375	99.075	99.063	101.976	102.694	102.680	102.430	103.171	103.157	102.901	103.501	103.490
	B3LYP	98.683	99.361	99.349	102.313	103.019	103.005	102.813	103.542	103.528	103.300	103.295	103.285
	B3LYP-D3	99.114	99.805	99.793	102.732	103.445	103.431	103.234	103.972	103.958	103.730	103.735	103.725
	B97-2	98.627	99.423	99.409	102.418	103.222	103.207	102.352	103.159	103.143	102.742	103.433	103.420
	BHandHLYP	101.643	108.274	108.797	106.412	107.439	107.935	106.506	107.053	107.565	106.905	103.785	104.331
	mPW1PW91	99.390	100.268	100.251	103.046	103.920	103.903	103.188	104.062	104.046	103.581	104.337	104.323
	PBE0	99.603	100.504	100.487	103.307	104.200	104.182	103.436	104.331	104.313	103.846	104.619	104.604
	X3LYP	99.255	99.946	99.934	102.881	103.599	103.585	103.337	104.077	104.063	103.831	103.834	103.823
	BMK	104.897	105.475	105.460	107.341	108.367	108.349	107.772	108.927	108.905	108.365	109.304	109.281
	M05-2X	107.445	110.717	111.246	112.368	110.715	111.217	112.632	109.974	110.486	113.536	107.602	108.145
	M06	103.504	104.478	104.459	107.358	108.222	108.206	107.297	108.199	108.182	107.738	108.531	108.520
	M06-2X	107.604	111.653	112.177	111.669	111.719	112.218	112.176	110.917	110.769	112.457	107.867	108.409
	M06-HF	116.561	121.380	121.930	141.151	120.678	121.249	118.220	117.819	118.337	137.529	115.355	115.902
	CAM-B3LYP	103.387	104.253	104.235	106.757	107.628	107.611	107.151	108.044	108.025	107.650	103.822	104.343
	LC-PBE	109.997	111.262	111.804	113.528	111.231	111.751	113.929	109.877	110.405	114.340	106.775	107.341
	LC-ωPBE	104.444	107.227	107.767	107.390	107.523	108.038	126.510	106.199	106.723	108.045	103.581	103.511
	ωB97X	104.519	107.388	107.909	107.573	107.053	108.133	107.403	106.169	106.676	107.913	103.559	104.116
	ωB97X-D	103.048	105.967	106.478	106.572	106.925	107.395	106.421	106.117	106.001	106.816	103.012	103.762

Table S7: O−H BDE values (in kcal/mol) computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM) for all radical structures of myricetin studied herein.

Radical	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
3'-ArO$^\bullet$	SVWN5	81.469	83.851	83.797	71.869	75.132	75.053	81.474	84.044	83.986	83.355	85.357	85.312
	BLYP	69.014	70.519	70.483	69.694	71.227	71.191	70.310	71.745	71.711	71.691	72.641	72.617
	PBE	70.107	72.051	72.005	70.703	72.677	72.632	71.134	72.983	72.941	72.511	73.909	73.876
	TPSS	72.088	73.925	73.881	72.234	74.096	74.053	72.634	74.374	74.334	73.785	74.547	74.514
	VSXC	72.447	74.024	73.986	72.799	74.930	74.894	72.710	74.758	74.724	74.464	75.535	75.510
	B1LYP	73.820	75.438	75.398	74.381	76.020	75.981	74.634	76.211	76.173	75.577	76.797	76.766
	B3LYP	74.526	76.143	76.104	75.050	76.693	76.654	75.356	76.926	76.889	76.353	77.563	77.534
	B3LYP-D3	74.991	76.579	76.541	75.587	77.207	77.168	75.877	77.428	77.391	76.267	78.042	78.013
	B97-2	74.381	76.229	76.186	74.861	76.723	76.679	74.676	76.429	76.387	74.945	76.955	76.921
	BHandHLYP	75.880	77.715	77.671	76.516	78.336	78.294	76.593	78.359	78.317	76.617	78.691	78.655
	mPW1PW91	74.858	76.849	76.802	75.402	77.407	77.360	75.438	77.335	77.291	76.266	77.851	77.813
	PBE0	75.104	77.135	77.088	75.651	77.692	77.644	75.696	77.627	77.582	76.573	78.186	78.147
	X3LYP	74.876	76.510	76.470	75.406	77.065	77.025	75.661	77.249	77.211	76.670	77.896	77.865
	BMK	75.794	77.794	77.760	76.448	79.051	79.004	75.990	79.595	79.551	77.994	79.480	79.447
	M05-2X	80.673	82.103	82.057	80.111	82.757	82.710	80.698	83.211	83.167	81.918	83.505	83.466
	M06	77.573	79.340	79.299	77.509	78.598	78.559	76.721	78.350	78.311	77.615	78.869	78.839
	M06-2X	81.083	82.297	82.255	80.599	83.016	82.975	80.819	83.158	83.116	81.492	83.579	83.542
	M06-HF	88.717	90.196	90.147	88.435	90.735	90.684	88.547	90.804	90.749	88.913	90.969	90.918
	CAM-B3LYP	77.152	78.862	78.820	77.514	79.246	79.206	77.651	79.325	79.285	77.993	79.911	79.879
	LC-PBE	80.530	82.740	82.688	80.351	82.601	82.550	80.368	82.533	82.483	80.407	82.866	82.821
	LC-ωPBE	76.305	78.301	78.254	75.962	78.581	78.534	76.566	78.500	78.454	77.268	78.828	78.788
	ωB97X	77.401	78.505	78.461	77.573	79.284	79.242	77.265	78.965	78.923	78.057	79.551	79.516
	ωB97X-D	77.532	78.562	78.517	77.955	79.647	79.610	77.720	79.332	79.293	78.421	79.931	79.893
4'-ArO$^\bullet$	SVWN5	80.622	79.517	79.546	79.719	79.500	79.509	80.246	80.000	80.008	81.963	80.880	80.912
	BLYP	67.515	65.870	65.909	67.052	66.218	66.238	67.626	66.737	66.759	69.314	68.098	68.146
	PBE	68.583	67.287	67.318	68.140	67.707	67.719	68.456	67.966	67.979	70.056	69.323	69.360
	TPSS	70.803	69.280	69.316	69.737	69.067	69.084	70.051	69.322	69.340	71.481	70.021	70.060
	VSXC	71.536	69.669	69.711	70.857	70.544	70.566	70.691	70.364	70.385	72.144	70.386	70.431
	B1LYP	73.474	71.492	71.536	72.094	71.633	71.657	72.344	71.860	71.885	73.734	72.510	72.550
	B3LYP	73.892	71.960	72.002	72.634	72.222	72.246	72.931	72.489	72.514	74.343	73.148	73.193
	B3LYP-D3	74.507	72.556	72.599	73.285	72.863	72.887	73.570	73.118	73.142	74.977	73.766	73.812
	B97-2	73.685	71.863	71.903	72.239	72.024	72.042	71.997	71.775	71.794	73.225	72.358	72.395
	BHandHLYP	76.775	74.717	74.762	74.846	74.285	74.312	74.868	74.314	74.340	76.045	74.886	74.927
	mPW1PW91	74.403	72.683	72.720	72.956	72.798	72.815	72.946	72.758	72.776	74.172	73.352	73.388
	PBE0	74.580	72.917	72.953	73.145	73.049	73.064	73.146	73.023	73.040	74.422	73.647	73.682
	X3LYP	74.335	72.400	72.444	73.037	72.623	72.646	73.283	72.846	72.870	74.721	73.515	73.559
	BMK	75.921	73.849	73.896	73.636	73.323	73.347	74.231	73.899	73.928	75.760	74.971	74.957
	M05-2X	81.061	79.076	79.120	78.611	77.732	77.752	78.707	78.326	78.348	80.418	78.827	78.867
	M06	77.014	75.019	75.063	74.879	73.840	73.864	73.921	73.562	73.584	75.812	74.178	74.218
	M06-2X	81.180	79.222	79.265	78.900	78.589	78.609	79.143	78.796	78.817	80.220	78.695	78.732
	M06-HF	90.410	88.462	88.504	88.192	87.441	87.459	88.435	86.909	86.930	88.661	87.147	87.188
	CAM-B3LYP	77.029	75.062	75.105	75.369	74.930	74.954	75.545	75.072	75.095	77.010	75.801	75.845

Radical	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	LC-PBE	80.574	78.798	78.835	78.045	77.870	77.887	78.131	77.892	77.910	79.443	78.576	78.610
	LC-ωPBE	76.058	74.310	74.347	74.110	73.930	73.946	74.818	73.977	73.994	76.202	74.051	74.086
	ωB97X	77.193	75.260	75.304	75.941	75.048	75.069	75.735	74.113	74.138	76.471	74.765	74.803
	ωB97X-D	77.162	75.222	75.268	76.326	75.502	75.522	76.071	75.130	75.158	76.839	74.940	74.976
5'-ArO•	SVWN5	93.695	89.906	90.012	95.663	92.375	92.465	95.448	92.115	92.207	96.213	91.954	92.076
	BLYP	78.247	74.730	74.824	79.817	76.743	76.827	79.879	76.771	76.857	80.694	77.205	77.321
	PBE	79.901	76.547	76.638	81.689	78.809	78.888	81.522	78.599	78.680	82.256	79.032	79.142
	TPSS	81.168	77.864	77.954	82.481	79.585	79.664	82.423	79.483	79.564	83.097	79.372	79.478
	VSXC	81.733	78.182	78.277	82.584	80.142	80.225	82.012	79.537	79.620	83.317	79.354	79.466
	B1LYP	81.609	78.284	78.372	82.958	80.626	80.703	82.909	80.572	80.650	83.619	79.876	79.980
	B3LYP	82.612	79.190	79.280	83.974	81.574	81.653	83.938	81.525	81.606	84.651	80.828	80.935
	B3LYP-D3	83.144	79.726	79.817	84.482	82.088	82.167	84.450	81.450	81.531	85.171	81.337	81.444
	B97-2	82.458	79.137	79.224	83.759	80.885	80.961	83.279	80.385	80.463	83.884	80.284	80.383
	BHandHLYP	82.925	79.951	80.029	84.340	81.643	81.715	84.215	81.528	81.599	84.782	81.407	81.500
	mPW1PW91	82.813	79.660	79.744	84.289	82.145	82.216	84.035	81.867	81.943	84.634	81.165	81.855
	PBE0	83.136	80.007	80.090	84.659	82.540	82.612	84.394	82.255	82.329	85.023	82.157	82.253
	X3LYP	82.930	79.534	79.623	84.312	81.928	82.007	84.229	81.834	81.914	84.953	81.135	81.241
	BMK	84.202	80.796	80.886	85.134	82.735	82.817	85.069	82.181	82.257	85.733	82.149	82.243
	M05-2X	88.708	85.395	85.484	89.470	86.593	86.670	89.231	86.863	86.943	90.364	86.714	86.815
	M06	85.695	82.249	82.341	86.443	82.770	82.851	85.274	82.253	82.333	85.924	82.141	82.245
	M06-2X	88.825	85.479	85.567	89.614	86.719	86.796	89.527	86.644	86.720	90.069	86.539	86.636
	M06-HF	96.184	93.099	93.183	97.269	93.952	94.026	96.726	93.966	94.041	97.082	93.735	93.827
	CAM-B3LYP	84.874	81.528	81.615	86.104	83.758	83.836	85.943	82.988	83.067	86.667	82.884	82.988
	LC-PBE	88.268	85.113	85.195	89.217	87.092	87.163	89.006	86.218	86.292	89.608	86.080	86.175
	LC-ωPBE	83.694	80.629	80.709	84.734	82.130	82.198	84.548	81.877	81.948	85.134	81.650	81.743
	ωB97X	84.723	81.479	81.566	86.331	82.892	82.967	85.140	82.275	82.351	85.837	82.187	82.285
	ωB97X-D	85.009	81.699	81.787	86.812	83.338	83.412	85.555	82.699	82.774	86.138	82.534	82.626
3-ArO•	SVWN5	89.384	84.488	84.630	90.957	86.630	86.756	90.977	86.574	86.704	91.916	86.754	86.911
	BLYP	74.511	69.986	70.114	75.979	71.880	71.997	76.099	71.941	72.061	77.143	72.715	72.864
	PBE	76.139	71.657	71.784	77.774	73.786	73.903	77.715	73.674	73.792	78.668	74.443	74.588
	TPSS	77.797	73.394	73.519	78.907	74.910	75.026	78.921	74.878	74.996	79.799	75.072	75.214
	VSXC	78.210	73.702	73.829	79.866	76.327	76.444	79.263	75.661	75.781	80.849	75.235	75.384
	B1LYP	78.560	74.546	74.655	79.622	76.542	76.643	79.564	76.453	76.556	80.592	76.745	76.873
	B3LYP	79.354	75.183	75.297	80.477	77.282	77.388	80.454	77.218	77.326	81.461	77.482	77.616
	B3LYP-D3	79.799	75.643	75.756	80.909	77.703	77.809	80.885	77.644	77.752	81.906	77.920	78.054
	B97-2	79.000	74.863	74.977	80.061	76.908	77.012	79.638	76.449	76.556	80.513	76.695	76.824
	BHandHLYP	80.850	77.345	77.439	81.712	79.000	79.089	81.539	78.811	78.901	82.550	79.212	79.322
	mPW1PW91	79.803	75.870	75.978	80.932	77.971	78.070	80.716	77.701	77.804	81.602	77.962	78.085
	PBE0	80.122	76.197	76.305	81.306	78.358	78.457	81.086	78.087	78.189	82.004	78.358	78.482
	X3LYP	79.755	75.625	75.738	80.876	77.717	77.821	80.800	77.602	77.710	81.829	77.873	78.005
	BMK	79.957	76.203	76.306	80.504	77.500	77.598	80.636	77.686	77.782	81.789	78.210	78.330
	M05-2X	85.054	81.330	81.431	85.498	82.745	82.837	86.031	83.168	83.264	87.538	82.898	83.014
	M06	82.424	78.299	78.412	83.110	79.308	79.413	81.870	78.703	78.808	83.431	78.398	78.525
	M06-2X	84.558	80.938	81.037	85.096	82.427	82.518	85.173	82.472	82.563	86.082	82.186	82.297
	M06-HF	91.405	88.333	88.416	92.072	89.436	89.510	92.735	89.343	89.422	92.864	89.559	89.668
	CAM-B3LYP	81.789	78.143	78.241	82.813	80.083	80.173	82.685	79.905	79.996	83.773	80.265	80.383
	LC-PBE	85.367	82.219	82.302	86.079	83.819	83.896	85.988	83.612	83.692	87.005	84.031	84.130
	LC-ωPBE	80.448	77.391	77.472	81.392	79.221	79.295	81.891	79.019	79.096	82.882	78.734	78.831
	ωB97X	81.396	78.111	78.200	82.880	79.773	79.856	82.340	79.231	79.315	83.434	79.008	79.114
	ωB97X-D	81.743	78.257	78.355	83.494	80.077	80.168	82.858	79.504	79.596	83.844	79.133	79.247
5-ArO•	SVWN5	106.717	100.909	101.072	104.705	101.076	101.223	106.261	100.861	101.019	106.871	100.502	100.692
	BLYP	88.991	83.588	83.734	89.863	84.674	84.817	89.431	84.150	84.298	89.776	84.038	84.222
	PBE	91.154	85.807	85.953	91.988	86.936	87.079	91.437	86.289	86.435	91.787	86.269	86.449
	TPSS	92.467	87.207	87.350	93.017	87.965	88.104	92.529	87.382	87.526	92.815	86.815	86.988
	VSXC	91.272	85.712	85.861	92.136	87.418	87.563	91.251	85.888	86.035	91.440	85.025	85.209
	B1LYP	93.819	88.670	88.804	94.826	90.481	90.611	94.178	89.791	89.923	94.315	88.399	88.563
	B3LYP	94.806	89.579	89.715	95.728	91.334	91.465	95.105	90.656	90.791	95.267	89.286	90.044
	B3LYP-D3	95.358	90.138	90.274	96.278	91.879	92.010	95.655	91.200	91.335	95.830	89.835	90.002
	B97-2	94.492	89.293	89.428	108.754	90.999	91.131	94.384	89.959	90.093	94.500	88.674	88.836
	BHandHLYP	105.665	90.618	90.747	110.281	92.004	92.134	110.005	91.239	91.370	110.338	90.479	90.636
	mPW1PW91	95.462	102.527	90.514	96.517	108.138	108.184	95.739	91.431	91.562	95.842	90.142	90.893
	PBE0	95.942	102.862	102.907	96.993	108.542	108.581	96.203	91.935	92.065	96.317	91.221	91.379
	X3LYP	95.293	90.087	90.223	96.245	91.870	92.000	95.570	91.142	91.276	95.722	90.334	90.495
	BMK	108.347	91.340	91.479	112.055	92.591	92.724	111.861	92.227	92.357	112.422	91.079	90.828
	M05-2X	110.702	96.363	96.499	114.366	97.156	97.288	114.944	96.787	96.922	115.230	96.097	96.258
	M06	107.515	92.349	92.491	112.248	92.330	92.467	111.642	91.311	91.446	96.619	90.607	90.774
	M06-2X	109.833	96.200	96.331	114.075	97.267	97.392	114.149	96.505	96.631	114.465	95.819	95.971
	M06-HF	108.191	103.973	104.087	110.496	106.156	106.272	109.170	104.457	104.583	108.974	103.595	103.739
	CAM-B3LYP	107.990	93.088	93.221	112.186	94.923	95.051	98.418	93.461	94.183	98.458	92.571	92.731
	LC-PBE	103.069	98.007	98.138	103.910	99.655	99.781	103.034	98.061	98.191	102.869	97.121	97.276
	LC-ωPBE	107.735	92.268	92.396	112.125	93.432	93.553	111.925	92.468	92.593	97.114	91.487	91.638
	ωB97X	97.998	92.980	93.112	99.461	94.003	94.129	111.586	92.765	92.894	97.696	91.904	92.062
	ωB97X-D	108.374	92.960	93.095	99.667	94.139	94.269	98.605	93.032	93.166	98.164	92.057	92.219
7-ArO•	SVWN5	93.031	91.496	91.574	95.986	93.918	94.006	95.628	93.469	93.562	95.938	93.046	93.164
	BLYP	78.293	77.102	77.159	80.864	79.095	79.168	80.729	78.905	78.982	81.102	78.526	78.627
	PBE	80.041	78.995	79.051	82.885	81.243	81.316	82.558	80.816	80.893	82.844	80.404	80.504
	TPSS	81.397	80.680	80.724	83.730	82.347	82.410	83.570	82.071	82.138	83.801	81.064	81.744
	VSXC	81.321	80.533	80.578	83.533	82.636	82.699	82.878	81.948	82.014	83.725	81.544	81.631

Radical	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	B1LYP	83.075	83.365	83.370	85.846	85.443	85.467	85.688	85.238	85.265	85.856	84.759	84.806
	B3LYP	83.905	83.948	83.963	86.571	86.503	86.537	86.415	86.289	86.327	86.594	85.216	85.275
	B3LYP-D3	84.275	84.325	84.340	86.937	86.284	86.317	86.784	86.073	86.111	86.970	85.597	85.655
	B97-2	83.988	101.316	101.265	86.689	86.171	86.203	86.122	85.492	85.528	86.208	84.995	85.049
	BHandHLYP	84.925	85.899	85.887	88.344	88.626	88.629	88.173	88.410	88.413	88.184	87.937	87.956
	mPW1PW91	84.432	84.967	84.969	87.362	87.142	87.164	87.039	86.700	86.726	87.105	86.182	86.226
	PBE0	84.776	85.315	85.317	87.765	87.540	87.562	87.421	87.082	87.109	87.502	86.567	86.613
	X3LYP	84.269	84.391	84.403	86.990	87.002	87.033	86.786	86.744	86.779	86.968	85.668	85.723
	BMK	86.746	87.450	87.448	88.464	89.253	89.272	88.855	88.923	88.941	106.290	88.693	88.731
	M05-2X	90.812	91.759	91.750	93.659	93.818	93.826	93.264	93.895	93.906	108.699	93.254	93.281
	M06	102.540	87.563	87.573	89.572	88.340	88.373	88.390	87.718	87.753	88.472	87.169	87.223
	M06-2X	90.985	91.879	91.870	93.877	94.072	94.077	93.668	93.818	93.824	108.010	93.280	93.301
	M06-HF	97.888	99.547	99.520	102.178	102.424	102.434	101.469	102.276	102.267	101.404	101.901	101.903
	CAM-B3LYP	100.562	87.959	87.957	90.291	90.223	90.235	90.017	89.917	89.930	106.356	89.352	89.383
	LC-PBE	92.248	93.141	93.132	95.170	95.396	95.402	94.825	94.950	94.957	94.595	94.173	94.196
	LC-ωPBE	87.596	88.393	88.385	89.899	90.693	90.697	90.144	90.256	90.262	89.966	89.471	89.577
	ωB97X	88.196	88.921	88.916	105.958	91.014	91.022	105.682	90.281	90.288	106.410	89.709	89.751
	ωB97X-D	87.979	88.673	88.670	106.586	90.855	90.866	106.299	90.174	90.187	106.947	89.598	89.620

Table S8: O−H BDE values (in kcal/mol) computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM) for all radical structures of phloretin studied herein.

Radical	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
2'-ArO$^\bullet$	SVWN5	107.373	105.557	105.604	111.845	110.205	110.249	111.184	109.471	109.516	111.321	109.364	109.424
	BLYP	89.778	87.937	87.985	93.869	92.265	92.307	93.533	91.880	91.924	93.710	91.715	91.772
	PBE	91.580	89.849	89.893	95.959	94.456	94.501	95.457	93.914	93.955	95.593	93.772	93.823
	TPSS	92.242	90.460	90.506	96.331	94.817	94.855	96.036	94.503	94.543	96.208	94.460	94.507
	VSXC	92.507	90.580	90.632	96.605	94.843	94.892	95.876	91.447	91.584	96.021	89.853	90.080
	B1LYP	94.982	91.353	91.463	101.571	93.523	93.629	101.418	91.927	92.025	101.663	89.985	90.152
	B3LYP	97.500	92.943	93.057	101.792	95.134	95.238	101.609	93.493	93.597	101.836	100.134	91.652
	B3LYP-D3	98.209	96.319	93.558	102.475	95.632	95.738	102.295	94.041	94.149	102.524	92.176	92.310
	B97-2	97.062	95.165	95.214	97.591	100.195	94.338	101.140	99.673	99.708	101.300	99.674	99.715
	BHandHLYP	95.763	91.680	91.788	97.298	94.058	94.159	96.067	92.647	92.751	95.206	91.080	91.187
	mPW1PW91	97.108	93.526	93.640	98.972	95.687	96.176	102.621	94.352	94.454	102.801	92.664	92.780
	PBE0	98.497	94.301	94.416	99.710	96.882	96.986	102.872	95.184	95.291	103.056	93.492	93.607
	X3LYP	97.065	93.430	93.547	102.438	95.679	95.787	102.231	93.997	94.104	102.463	92.040	92.158
	BMK	98.090	93.132	93.256	98.875	95.768	95.888	97.661	94.361	94.470	96.888	92.143	92.280
	M05-2X	102.023	98.101	98.292	104.501	100.680	100.798	102.679	99.754	99.231	101.717	97.446	97.616
	M06	99.337	95.841	95.970	106.101	96.136	96.254	105.451	94.324	94.419	105.712	92.617	92.232
	M06-2X	102.133	97.906	98.020	103.452	100.394	100.499	102.089	98.742	98.659	101.246	97.202	97.327
	M06-HF	107.570	103.871	103.971	111.602	109.090	109.196	108.987	106.267	106.373	107.720	104.507	104.614
	CAM-B3LYP	102.500	100.643	100.691	106.827	105.416	105.452	106.683	105.269	105.303	106.942	105.342	105.383
	LC-PBE	104.579	100.164	100.276	105.909	102.751	102.858	104.263	100.777	100.886	103.069	98.848	98.972
	LC-ωPBE	97.301	93.563	93.669	98.973	95.811	95.910	97.310	93.780	93.868	95.981	91.808	91.919
	ωB97X	102.829	100.989	101.037	107.325	105.957	105.992	106.854	105.520	105.552	107.150	105.649	105.686
	ωB97X-D	101.904	100.042	100.091	106.492	105.064	105.101	105.965	104.518	104.555	106.163	104.611	104.651
4'-ArO$^\bullet$	SVWN5	96.667	97.364	97.369	100.571	101.016	101.022	100.408	100.910	100.918	100.520	100.268	100.306
	BLYP	80.943	81.415	81.415	84.230	84.404	84.409	84.164	84.335	84.342	84.371	83.866	83.892
	PBE	82.917	83.729	83.721	86.535	87.027	87.027	86.304	86.766	86.767	86.448	86.283	86.301
	TPSS	83.764	84.627	84.616	86.850	87.369	87.365	86.758	87.222	87.221	86.899	86.847	86.859
	VSXC	83.538	84.263	84.257	87.189	87.517	87.519	86.562	86.943	86.941	86.570	86.386	86.399
	B1LYP	97.049	84.493	84.486	102.117	87.443	87.446	102.425	87.314	87.317	87.192	86.951	86.968
	B3LYP	84.918	85.604	85.597	88.254	88.537	88.538	88.141	88.421	88.424	88.302	88.046	88.065
	B3LYP-D3	85.275	85.978	85.971	103.263	88.865	88.868	88.498	88.754	88.757	88.651	88.390	88.408
	B97-2	85.049	85.934	85.923	88.504	88.985	88.983	88.011	88.434	88.432	88.085	88.018	88.029
	BHandHLYP	84.831	85.847	85.834	88.683	89.123	89.122	88.539	88.937	88.936	88.630	88.636	88.648
	mPW1PW91	97.852	86.251	86.237	102.982	89.406	89.402	103.061	89.091	89.089	103.747	88.690	88.701
	PBE0	98.201	86.672	86.657	103.359	89.897	89.891	89.010	89.571	89.568	89.087	89.172	89.182
	X3LYP	98.872	85.897	85.890	88.564	88.860	88.858	103.669	88.700	88.703	88.574	88.326	88.344
	BMK	87.115	87.807	87.798	90.319	90.789	90.797	90.368	91.004	90.996	90.373	90.482	90.487
	M05-2X	90.885	92.035	92.020	94.864	94.907	94.903	94.484	95.691	94.989	94.394	94.574	94.485
	M06	88.129	88.922	88.914	106.511	90.567	90.571	89.873	90.091	90.095	106.940	89.663	89.697
	M06-2X	90.895	91.355	91.975	94.333	94.891	94.891	94.123	94.645	94.643	94.111	94.220	94.227
	M06-HF	135.925	98.875	98.851	101.108	102.703	102.686	101.140	101.491	101.476	100.770	100.844	100.837
	CAM-B3LYP	87.406	88.145	88.139	90.765	91.051	91.054	90.536	90.796	90.799	90.585	90.315	90.334
	LC-PBE	91.606	92.677	92.665	95.003	95.561	95.559	94.729	95.209	95.210	94.525	94.500	94.514
	LC-ωPBE	86.994	87.908	87.898	90.314	90.769	90.768	90.010	90.395	90.395	89.840	89.755	89.770
	ωB97X	87.704	88.594	88.585	90.898	91.259	91.260	90.240	90.558	90.558	90.265	90.131	90.144
	ωB97X-D	87.654	88.511	88.500	91.150	91.626	91.625	90.660	91.072	91.072	90.694	90.544	90.617
6'-ArO$^\bullet$	SVWN5	89.460	90.401	90.385	92.306	93.196	93.174	92.409	93.277	93.266	92.780	93.296	93.289
	BLYP	74.946	75.517	75.510	77.512	77.885	77.878	77.789	78.149	78.134	78.251	78.257	78.262
	PBE	76.489	77.358	77.341	79.286	79.940	79.929	79.359	79.931	79.923	79.733	80.004	80.002
	TPSS	77.737	78.513	78.499	79.979	80.513	80.504	80.114	80.555	80.551	80.466	80.624	80.625

Radical	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	VSXC	78.453	79.032	79.026	81.337	81.583	81.586	80.892	81.055	81.059	81.293	81.151	81.160
	B1LYP	78.616	79.292	79.279	80.784	81.182	81.178	80.912	81.249	81.246	81.241	81.264	81.268
	B3LYP	79.511	80.152	80.141	81.729	82.123	82.118	81.887	82.224	82.222	82.231	82.251	82.255
	B3LYP-D3	79.974	80.633	80.622	82.190	82.584	82.580	82.347	82.688	82.684	82.693	82.724	82.728
	B97-2	79.435	80.263	80.248	81.708	82.258	82.250	81.409	81.854	81.849	81.670	81.825	81.825
	BHandHLYP	80.587	81.571	81.552	82.683	83.198	83.192	82.678	83.121	83.115	82.888	83.043	83.045
	mPW1PW91	79.721	80.671	80.653	81.986	82.632	82.622	81.908	82.452	82.445	82.155	82.412	82.411
	PBE0	80.115	81.091	81.072	82.445	83.111	83.099	82.352	82.924	82.916	82.619	82.895	82.893
	X3LYP	79.862	80.522	80.510	82.082	82.485	82.492	82.194	82.539	82.536	82.543	82.568	82.571
	BMK	82.346	82.123	82.833	83.843	84.421	84.419	83.852	84.512	84.499	84.072	84.320	84.312
	M05-2X	85.723	86.662	86.643	87.682	87.666	87.655	87.463	88.594	87.888	87.548	87.169	87.907
	M06	82.570	83.269	83.257	83.665	83.958	83.955	83.350	83.609	83.609	83.609	83.528	83.605
	M06-2X	86.427	87.439	87.417	87.647	88.878	88.867	88.311	88.833	88.827	88.503	88.746	88.745
	M06-HF	94.097	95.488	95.381	96.204	97.119	97.100	95.198	96.055	96.039	95.662	95.747	95.736
	CAM-B3LYP	82.202	82.937	82.923	84.138	84.578	84.572	84.133	84.520	84.515	84.374	84.433	84.435
	LC-PBE	85.856	86.935	86.914	87.130	87.876	87.863	86.997	87.652	87.642	87.012	87.362	87.358
	LC-ωPBE	81.462	82.398	82.380	83.143	83.773	83.763	82.957	83.483	83.477	83.010	83.242	83.242
	ωB97X	82.563	83.400	83.386	84.283	84.786	84.779	83.927	84.345	84.340	84.134	84.229	84.231
	ωB97X-D	82.507	83.388	83.373	84.563	84.423	84.417	84.278	84.645	84.641	84.497	84.588	84.591
4-ArO•	SVWN5	89.563	89.598	89.604	93.779	93.634	93.644	93.437	93.343	93.350	93.455	92.525	92.562
	BLYP	74.469	74.187	74.201	77.979	77.552	77.566	77.821	77.403	77.419	77.924	76.633	76.674
	PBE	76.244	76.300	76.306	80.109	80.001	80.009	79.778	79.646	79.656	79.831	78.896	78.928
	TPSS	76.985	77.006	77.014	80.227	80.073	80.083	80.056	79.842	79.855	80.137	79.203	79.235
	VSXC	76.111	76.027	76.036	79.888	79.640	79.654	79.258	78.998	79.010	79.352	78.330	78.362
	B1LYP	76.375	76.426	76.434	79.777	79.538	79.551	79.642	79.404	79.417	79.750	78.791	78.825
	B3LYP	77.594	77.568	77.577	81.034	80.753	80.766	80.895	80.616	80.629	80.989	79.969	80.003
	B3LYP-D3	77.909	77.865	77.875	81.324	81.044	81.057	81.182	80.905	80.919	81.274	80.252	80.287
	B97-2	77.516	77.665	77.671	81.044	80.937	80.947	80.540	80.389	80.400	80.568	79.772	79.799
	BHandHLYP	76.780	77.292	77.290	80.193	80.237	80.243	80.082	80.118	80.124	80.226	79.676	79.699
	mPW1PW91	77.549	77.897	77.898	81.178	81.225	81.231	80.909	80.914	80.922	80.970	80.333	80.359
	PBE0	77.947	78.332	78.333	81.657	81.739	81.744	81.364	81.412	81.418	81.424	80.817	80.842
	X3LYP	77.808	77.813	77.821	81.269	81.006	81.012	81.085	80.828	80.841	81.183	80.185	80.220
	BMK	78.794	78.816	78.823	81.841	81.909	81.920	81.365	81.988	81.993	81.469	81.369	81.394
	M05-2X	82.658	83.075	83.072	86.217	85.535	85.543	85.718	86.270	85.580	85.632	84.927	84.954
	M06	79.815	79.925	79.930	82.286	82.039	82.051	81.945	81.755	81.767	81.323	81.161	81.207
	M06-2X	83.517	83.785	83.788	86.672	86.598	86.605	86.365	86.283	86.293	86.343	85.669	85.696
	M06-HF	90.649	91.226	91.225	93.302	94.029	94.033	92.061	92.243	92.248	92.293	91.448	91.469
	CAM-B3LYP	79.579	79.722	79.728	82.874	82.688	82.699	82.601	82.417	82.428	82.647	81.738	81.770
	LC-PBE	82.508	83.150	83.146	85.596	85.814	85.817	85.272	85.450	85.454	85.208	84.750	84.771
	LC-ωPBE	78.623	79.138	79.136	81.714	81.854	81.859	81.387	81.464	81.470	81.324	80.765	80.789
	ωB97X	79.559	79.968	79.966	82.666	82.624	82.633	81.997	81.970	81.975	82.037	81.333	81.360
	ωB97X-D	79.859	80.030	80.036	83.299	83.162	83.173	82.770	82.624	82.635	82.806	82.037	82.066

S2.3 Statistical Analyses of BDEs

Table S9: Caffeic acid's MAD, MSD, and MAX values (in kcal/mol) calculated regarding the DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) reference for the O−H BDE results computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM).

Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
MAD	SVWN5	7.624	4.435	4.636	6.767	5.177	4.967	6.897	5.224	5.018	7.791	5.366	5.542
	BLYP	14.115	11.651	11.846	12.106	9.479	9.684	11.791	9.314	9.509	11.293	10.222	10.374
	PBE	12.673	9.875	10.078	10.487	7.501	7.712	10.405	7.571	7.775	9.941	8.421	8.584
	TPSS	11.210	8.182	8.383	9.500	6.413	6.619	9.283	6.409	6.607	8.598	7.183	7.340
	VSXC	10.747	8.207	8.399	8.544	5.790	5.987	8.841	6.203	6.397	8.272	6.942	7.089
	B1LYP	8.956	5.287	5.461	7.247	3.706	3.890	7.051	3.961	4.119	6.591	4.605	4.638
	B3LYP	8.277	4.571	4.818	6.528	3.290	2.724	6.300	3.335	3.503	5.621	3.745	3.781
	B3LYP-D3	7.826	4.576	4.756	6.062	2.834	3.008	5.839	2.875	3.043	5.361	3.309	3.345
	B97-2	8.385	4.560	5.149	6.606	3.276	3.458	6.868	2.899	3.939	6.497	4.938	5.061
	BHandHLYP	6.952	3.506	3.436	4.911	3.704	3.636	4.910	3.397	3.333	1.702	2.402	2.425
	mPW1PW91	7.866	3.930	4.112	6.110	2.320	2.522	6.157	2.598	2.791	5.792	3.183	3.225
	PBE0	7.598	3.608	2.931	5.804	1.941	2.146	5.856	2.216	2.413	5.468	2.771	2.813
	X3LYP	7.872	4.466	4.640	6.129	2.767	2.942	5.945	2.867	3.028	5.461	3.444	3.479
	BMK	5.033	2.487	2.407	4.157	2.915	2.831	4.192	2.574	2.498	3.621	2.507	2.524
	M05-2X	4.940	3.001	2.951	3.148	3.748	3.442	3.173	3.534	3.548	3.201	1.716	1.983
	M06	4.791	1.866	2.013	3.808	1.710	1.552	4.116	1.734	1.880	3.682	2.532	2.569
	M06-2X	4.583	2.965	3.110	3.162	4.396	4.331	3.043	4.149	4.090	3.185	2.560	2.528
	M06-HF	8.264	12.309	12.271	16.655	13.406	13.356	15.234	11.223	11.174	14.615	9.655	9.634
	CAM-B3LYP	5.169	2.757	2.681	3.700	2.950	2.877	3.599	2.570	2.503	3.120	1.731	1.751
	LC-PBE	3.351	3.187	3.152	1.571	4.315	4.251	1.398	3.669	3.609	1.732	1.830	1.794
	LC-ωPBE	5.733	4.015	3.958	4.654	4.421	4.366	4.646	3.999	3.949	4.094	2.309	2.519
	ωB97X	4.898	3.281	3.213	3.881	3.685	3.619	4.231	3.259	3.197	3.575	2.128	2.144

Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	ωB97X-D	5.452	2.798	2.723	3.819	2.854	2.782	4.183	2.682	2.613	3.608	1.828	1.855
MSD	SVWN5	0.289	3.060	2.856	2.191	5.177	4.967	2.407	5.224	5.018	2.873	4.436	4.269
	BLYP	−14.115	−11.651	−11.846	−12.106	−9.479	−9.684	−11.791	−9.314	−9.509	−11.293	−10.222	−10.374
	PBE	−12.673	−9.875	−10.078	−10.487	−7.501	−7.712	−10.405	−7.571	−7.775	−9.941	−8.421	−8.584
	TPSS	−11.210	−8.182	−8.383	−9.500	−6.413	−6.619	−9.283	−6.409	−6.607	−8.598	−7.183	−7.340
	VSXC	−10.747	−8.207	−8.399	−8.544	−5.790	−5.987	−8.841	−6.203	−6.397	−8.272	−6.942	−7.089
	B1LYP	−8.956	−5.287	−5.461	−7.247	−3.706	−3.890	−7.051	−3.961	−4.119	−6.591	−4.605	−4.638
	B3LYP	−8.277	−4.571	−4.818	−6.528	−3.290	−2.724	−6.300	−3.335	−3.503	−5.621	−3.745	−3.781
	B3LYP-D3	−7.826	−4.576	−4.756	−6.062	−2.834	−3.008	−5.839	−2.875	−3.043	−5.361	−3.309	−3.345
	B97-2	−8.385	−4.560	−5.149	−6.606	−3.276	−3.458	−6.868	−2.713	−3.939	−6.497	−4.938	−5.061
	BHandHLYP	−6.952	−1.887	−1.933	−4.911	−0.602	−0.658	−4.910	−0.939	−0.992	−1.702	−2.402	−2.425
	mPW1PW91	−7.866	−3.930	−4.112	−6.110	−2.320	−2.522	−6.157	−2.598	−2.791	−5.792	−3.183	−3.225
	PBE0	−7.598	−3.608	−2.931	−5.804	−1.941	−2.146	−5.856	−2.216	−2.413	−5.468	−2.771	−2.813
	X3LYP	−7.872	−4.466	−4.640	−6.129	−2.767	−2.942	−5.945	−2.867	−3.028	−5.461	−3.444	−3.479
	BMK	−5.033	−1.565	−1.624	−4.157	−0.676	−0.755	−4.192	−0.827	−0.900	−3.621	−2.507	−2.524
	M05-2X	−1.272	3.001	2.951	0.192	3.229	3.397	0.761	3.534	3.548	1.493	1.716	1.983
	M06	−4.791	−1.866	−2.013	−3.808	−1.273	−1.422	−4.116	−1.734	−1.880	−3.682	−2.532	−2.569
	M06-2X	−1.365	2.965	3.110	0.331	4.396	4.331	0.544	4.149	4.090	0.806	2.560	2.528
	M06-HF	6.028	12.309	12.271	16.655	13.406	13.356	15.234	11.223	11.174	14.615	9.655	9.634
	CAM-B3LYP	−5.169	−0.782	−0.831	−3.700	0.513	0.453	−3.599	0.082	0.027	−3.120	−1.731	−1.751
	LC-PBE	−1.053	3.187	3.152	0.075	3.924	3.877	0.102	3.288	3.245	0.664	1.704	1.692
	LC-ωPBE	−5.733	−1.283	−1.321	−4.654	−0.052	−0.102	−4.446	−0.669	−0.714	−4.094	−2.309	−2.519
	ωB97X	−4.898	−0.715	−0.758	−3.881	0.442	0.388	−4.231	−0.199	−0.249	−3.575	−2.128	−2.144
	ωB97X-D	−5.452	−0.992	−1.044	−3.819	0.432	0.368	−4.183	−0.373	−0.431	−3.608	−1.828	−1.855
MAX	SVWN5	11.003	7.887	7.875	9.539	9.924	9.891	9.243	9.614	9.581	9.813	9.226	9.221
	BLYP	25.474	16.023	16.637	21.667	12.609	13.221	21.226	12.581	13.173	21.771	15.801	16.307
	PBE	24.114	14.411	15.032	20.030	10.684	11.302	19.861	10.894	11.496	20.359	13.895	14.415
	TPSS	22.888	12.123	12.748	19.097	9.014	9.628	18.622	9.078	9.673	18.264	11.819	12.327
	VSXC	21.558	11.838	12.443	17.187	7.801	8.398	17.350	8.266	8.851	16.796	10.806	11.296
	B1LYP	17.743	6.427	6.389	13.862	5.563	5.528	13.395	5.316	5.281	13.056	4.802	4.953
	B3LYP	17.408	5.651	5.615	13.509	4.751	4.718	13.000	4.468	4.435	12.638	4.156	4.318
	B3LYP-D3	16.987	5.194	5.359	13.097	4.224	4.189	12.587	3.955	3.920	12.227	3.802	3.964
	B97-2	17.401	5.622	5.589	13.335	4.706	4.677	13.379	4.935	4.905	13.100	6.666	7.073
	BHandHLYP	15.013	4.333	4.298	9.839	4.653	4.467	9.742	3.687	3.512	2.267	3.160	3.155
	mPW1PW91	16.711	5.078	5.049	12.788	4.191	4.164	12.631	4.200	4.172	12.356	3.713	3.675
	PBE0	16.510	4.775	4.748	12.356	3.869	3.844	12.387	3.873	3.847	12.102	3.355	3.319
	X3LYP	16.865	5.319	5.283	12.965	4.438	4.405	12.495	4.204	4.170	12.137	3.820	3.978
	BMK	11.266	3.475	3.444	8.432	3.488	3.463	7.979	3.070	3.048	7.703	3.523	3.458
	M05-2X	9.317	6.558	6.365	4.433	7.406	7.873	3.618	7.055	6.960	3.964	2.898	2.806
	M06	12.501	2.760	2.726	8.476	3.085	3.052	8.533	3.237	3.207	8.197	2.754	2.909
	M06-2X	8.922	7.170	6.969	4.247	9.481	9.268	3.748	8.622	8.424	3.569	4.336	4.192
	M06-HF	11.698	17.973	17.817	27.762	19.412	19.244	24.968	15.648	15.479	22.468	11.336	11.222
	CAM-B3LYP	12.708	3.418	3.382	9.083	5.194	4.994	8.689	3.979	3.795	8.315	2.721	2.676
	LC-PBE	6.605	7.913	7.782	2.244	10.240	10.094	1.944	8.642	8.508	2.428	3.818	3.744
	LC-ωPBE	11.870	4.853	4.823	8.370	6.554	6.396	8.141	4.994	4.852	7.823	4.077	4.037
	ωB97X	11.605	3.940	3.906	8.256	6.190	6.010	8.399	4.589	4.421	7.959	3.327	3.288
	ωB97X-D	13.036	3.795	3.764	9.241	4.929	4.726	9.379	3.463	3.272	9.042	2.827	2.795

Table S10: Cyanidin's MAD, MSD, and MAX values (in kcal/mol) calculated regarding the DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) reference for the O−H BDE results computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM).

Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
MAD	SVWN5	6.202	4.131	4.167	8.756	5.436	5.510	8.472	5.074	5.150	9.003	5.027	5.124
	BLYP	8.869	12.004	11.937	6.624	9.874	9.803	6.758	10.092	10.018	6.145	10.103	10.008
	PBE	7.072	10.063	9.998	5.238	7.628	7.562	5.348	8.021	7.953	4.872	8.114	8.024
	TPSS	5.817	8.689	8.629	4.796	6.939	6.872	4.839	7.207	7.140	4.402	7.228	7.141
	VSXC	5.654	8.908	8.841	4.242	6.563	6.490	4.602	7.315	7.246	4.406	7.463	7.366
	B1LYP	5.260	7.612	7.561	4.273	5.907	5.850	4.344	6.189	6.128	3.929	6.280	6.187
	B3LYP	4.766	6.841	6.787	3.759	5.094	5.032	3.818	5.359	5.293	3.389	5.438	5.355
	B3LYP-D3	4.383	6.349	6.292	3.364	4.563	4.503	3.423	4.837	4.773	3.007	4.923	4.838
	B97-2	4.867	6.809	6.758	3.851	5.042	4.983	4.146	5.723	5.661	3.782	5.824	5.747
	BHandHLYP	7.551	4.353	4.332	2.398	4.081	4.024	2.642	4.405	4.347	2.272	4.522	4.447
	mPW1PW91	4.520	6.125	6.077	3.462	4.292	4.236	3.625	4.747	4.689	3.258	4.862	4.787
	PBE0	4.338	5.779	5.731	3.254	3.880	3.826	3.419	4.337	4.279	3.040	4.426	4.351
	X3LYP	4.562	6.463	6.409	3.554	4.715	4.655	3.641	5.032	4.968	3.207	5.107	5.032
	BMK	3.380	4.585	4.478	3.117	3.610	3.544	3.153	3.978	3.923	3.043	4.051	3.983
	M05-2X	0.950	1.576	1.526	2.183	1.804	1.825	2.245	1.862	1.884	2.544	1.642	1.672
	M06	3.080	3.938	3.884	2.774	3.390	3.334	3.096	4.083	4.022	2.664	4.193	4.108
	M06-2X	1.201	1.456	1.591	2.403	2.129	2.146	2.228	1.953	1.971	2.372	1.799	1.826
	M06-HF	12.737	3.652	9.119	12.979	7.809	8.573	12.421	7.821	7.875	12.190	7.078	7.327
	CAM-B3LYP	2.896	4.462	4.406	1.105	2.464	2.410	2.462	2.843	2.788	0.768	2.963	2.884
	LC-PBE	0.612	1.254	1.206	2.268	1.402	1.413	1.942	1.254	1.266	2.316	0.900	0.854

Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	LC-ωPBE	3.753	4.865	4.825	1.909	3.243	3.196	2.232	3.677	3.624	1.854	3.728	3.659
	ωB97X	2.866	4.034	4.122	1.201	2.575	2.542	1.682	3.296	3.248	1.274	3.256	3.176
	ωB97X-D	2.569	3.417	3.375	0.962	2.091	2.023	2.394	2.795	2.740	2.008	2.755	2.676
MSD	SVWN5	6.202	2.930	3.004	8.756	5.436	5.510	8.472	5.074	5.150	9.003	5.027	5.124
	BLYP	−8.869	−12.004	−11.937	−6.624	−9.874	−9.803	−6.758	−10.092	−10.018	−6.145	−10.103	−10.008
	PBE	−7.072	−10.063	−9.998	−4.554	−7.628	−7.562	−4.861	−8.021	−7.953	−4.325	−8.114	−8.024
	TPSS	−5.817	−8.689	−8.629	−3.864	−6.939	−6.872	−4.043	−7.207	−7.140	−3.560	−7.228	−7.141
	VSXC	−5.654	−8.908	−8.841	−3.274	−6.563	−6.490	−3.949	−7.315	−7.246	−3.700	−7.463	−7.366
	B1LYP	−4.921	−7.612	−7.561	−2.960	−5.907	−5.850	−3.172	−6.189	−6.128	−2.689	−6.280	−6.187
	B3LYP	−4.026	−6.841	−6.787	−2.053	−5.094	−5.032	−2.253	−5.359	−5.293	−1.765	−5.438	−5.355
	B3LYP-D3	−3.515	−6.349	−6.292	−1.540	−4.563	−4.503	−1.741	−4.837	−4.773	−1.258	−4.923	−4.838
	B97-2	−4.092	−6.809	−6.758	−2.076	−5.042	−4.983	−2.666	−5.723	−5.661	−2.278	−5.824	−5.747
	BHandHLYP	−7.551	−4.353	−4.332	−2.398	−4.081	−4.024	−2.642	−4.405	−4.347	−2.272	−4.522	−4.447
	mPW1PW91	−3.596	−6.125	−6.077	−1.477	−4.292	−4.236	−1.841	−4.747	−4.689	−1.443	−4.862	−4.787
	PBE0	−3.261	−5.779	−5.731	−1.094	−3.880	−3.826	−1.465	−4.337	−4.279	−1.052	−4.426	−4.351
	X3LYP	−3.692	−6.463	−6.409	−1.706	−4.715	−4.655	−1.955	−5.032	−4.968	−1.458	−5.107	−5.032
	BMK	−3.380	−4.585	−4.478	−0.766	−3.610	−3.544	−0.806	−3.978	−3.923	−0.671	−4.051	−3.983
	M05-2X	0.405	−0.808	−0.761	2.183	0.503	0.559	2.245	0.606	0.664	2.544	0.473	0.541
	M06	−1.091	−3.938	−3.884	−0.335	−3.390	−3.334	−0.952	−4.083	−4.022	−0.430	−4.193	−4.108
	M06-2X	0.725	−0.535	−0.093	2.403	0.844	0.897	2.228	0.577	0.632	2.372	0.521	0.586
	M06-HF	12.737	3.652	9.119	12.979	7.809	8.573	12.421	7.821	7.875	12.190	7.078	7.327
	CAM-B3LYP	−2.896	−4.462	−4.406	−0.871	−2.464	−2.410	0.049	−2.843	−2.788	−0.728	−2.963	−2.884
	LC-PBE	0.588	−0.531	−0.489	2.268	0.966	1.013	1.942	0.502	0.555	2.316	0.442	0.515
	LC-ωPBE	−3.753	−4.865	−4.825	−1.909	−3.243	−3.196	−2.232	−3.677	−3.624	−1.854	−3.728	−3.659
	ωB97X	−2.866	−4.034	−4.122	−1.047	−2.575	−2.542	−1.682	−3.296	−3.248	−1.274	−3.256	−3.176
	ωB97X-D	−2.569	−3.417	−3.375	−0.370	−2.091	−2.023	0.264	−2.795	−2.740	0.647	−2.755	−2.676
MAX	SVWN5	12.214	8.784	8.787	15.388	11.183	11.171	14.861	10.705	10.696	14.959	10.221	10.243
	BLYP	13.181	16.888	16.797	10.076	14.147	14.046	10.335	14.457	14.356	9.760	13.985	13.880
	PBE	11.424	15.105	15.015	7.953	11.988	11.888	8.324	12.403	12.304	7.802	12.062	11.957
	TPSS	10.074	13.626	13.539	7.302	11.278	11.180	7.524	11.547	11.448	7.047	11.163	11.063
	VSXC	9.055	13.408	13.315	6.065	10.387	10.283	6.615	11.313	11.214	7.377	11.085	10.975
	B1LYP	8.449	11.680	11.602	5.723	9.457	9.366	6.068	9.877	9.783	5.667	9.586	9.488
	B3LYP	7.886	11.232	11.153	5.098	8.922	8.827	5.421	9.310	9.214	4.996	9.002	8.903
	B3LYP-D3	7.106	10.474	10.392	4.562	8.124	8.030	4.633	8.522	8.426	4.371	8.230	8.130
	B97-2	7.938	11.247	11.168	5.081	8.926	8.834	5.716	9.648	9.553	5.341	9.368	9.269
	BHandHLYP	14.570	6.118	6.080	3.120	6.138	6.053	3.283	6.610	6.522	2.829	6.432	6.343
	mPW1PW91	7.095	10.285	10.207	4.961	7.868	7.777	4.576	8.389	8.296	4.538	8.136	8.040
	PBE0	6.810	10.010	9.931	5.399	7.513	7.422	4.885	8.035	7.942	4.971	7.796	7.699
	X3LYP	7.499	10.808	10.727	4.710	8.509	8.415	5.086	8.954	8.858	4.668	8.650	8.553
	BMK	5.576	9.083	8.967	5.876	7.169	7.084	5.867	7.855	7.763	5.931	8.133	8.043
	M05-2X	1.375	4.272	4.201	3.570	3.251	3.164	3.561	3.140	3.050	3.507	2.922	2.827
	M06	5.093	8.338	8.264	6.096	7.126	7.040	5.361	7.800	7.710	5.585	7.505	7.404
	M06-2X	1.644	4.100	4.033	3.868	3.212	3.121	3.539	3.441	3.347	3.426	3.195	3.100
	M06-HF	16.254	5.302	10.900	16.561	9.502	10.322	15.754	9.440	9.424	15.376	8.737	8.656
	CAM-B3LYP	4.421	7.449	7.372	2.023	5.340	5.252	6.278	5.850	5.761	1.758	5.560	5.467
	LC-PBE	1.591	2.429	2.365	3.123	2.652	2.648	2.602	2.286	2.280	3.000	2.023	2.046
	LC-ωPBE	4.330	6.589	6.523	3.378	4.688	4.599	3.534	5.137	5.044	2.672	4.713	4.619
	ωB97X	3.715	6.566	6.493	2.288	4.840	4.755	2.772	5.677	5.591	1.867	5.194	5.098
	ωB97X-D	3.831	6.587	6.508	1.415	4.789	4.691	6.644	5.466	5.372	6.638	4.988	4.889

Table S11: Ellagic acid's MAD, MSD, and MAX values (in kcal/mol) calculated regarding the DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) reference for the O−H BDE results computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM).

Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
MAD	SVWN5	5.400	4.062	4.119	5.453	4.750	4.793	5.735	4.917	4.962	6.834	5.271	5.340
	BLYP	8.868	10.524	10.462	8.544	9.656	9.606	8.198	9.423	9.370	7.132	9.134	9.059
	PBE	7.448	8.803	8.748	7.034	7.789	7.747	6.927	7.809	7.764	5.921	7.524	7.458
	TPSS	5.737	7.179	7.124	5.820	6.722	6.677	5.669	6.696	6.649	4.784	6.429	6.362
	VSXC	5.236	7.008	6.944	5.027	6.196	6.146	5.393	6.643	6.590	4.476	6.457	6.382
	B1LYP	4.149	5.817	5.758	4.402	5.483	5.437	4.320	5.484	5.435	3.419	5.208	5.141
	B3LYP	3.443	5.120	5.060	3.640	4.719	4.673	3.515	4.688	4.639	2.606	4.417	4.349
	B3LYP-D3	2.845	4.540	4.479	3.031	4.125	4.078	2.912	4.099	4.050	2.001	3.829	3.761
	B97-2	3.595	5.143	5.087	3.918	4.807	4.765	4.294	5.281	5.236	3.540	5.089	5.028
	BHandHLYP	1.721	3.291	3.235	2.190	3.217	3.172	2.290	3.379	3.333	1.507	3.094	3.034
	mPW1PW91	2.984	4.393	4.342	3.239	4.023	3.985	3.382	4.270	4.227	2.639	4.061	4.003
	PBE0	2.746	4.112	4.060	2.972	3.703	3.666	3.111	3.943	3.903	2.330	3.714	3.657
	X3LYP	3.063	4.730	4.671	3.270	4.340	4.294	3.194	4.356	4.307	2.278	4.078	4.008
	BMK	1.466	3.223	3.171	2.105	3.225	3.182	2.034	3.080	3.036	1.392	2.743	2.691
	M05-2X	3.147	1.569	1.626	2.014	1.099	1.140	2.556	1.454	1.501	3.174	1.554	1.617
	M06	0.257	1.859	1.804	1.841	2.964	2.918	2.365	3.477	3.431	1.579	3.281	3.217
	M06-2X	3.045	1.390	1.448	1.991	1.045	1.088	2.091	1.037	1.082	2.729	1.188	1.247
	M06-HF	11.172	9.615	9.671	10.180	9.433	9.473	9.862	8.917	8.959	10.217	8.846	8.902

Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	CAM-B3LYP	0.723	2.374	2.316	1.211	2.240	2.196	1.208	2.334	2.289	0.326	2.026	1.962
	LC-PBE	2.982	1.555	1.607	1.794	1.258	1.264	1.734	1.062	1.067	2.531	1.139	1.195
	LC-ωPBE	1.696	3.133	3.081	2.478	3.226	3.190	2.520	3.410	3.370	1.702	3.155	3.099
	ωB97X	0.753	2.355	2.300	1.502	2.447	2.404	1.942	2.982	2.940	1.081	2.604	2.546
	ωB97X-D	0.554	2.133	2.079	0.996	1.924	1.881	1.467	2.520	2.479	0.696	2.168	2.112
MSD	SVWN5	5.400	4.062	4.119	5.453	4.750	4.793	5.735	4.917	4.962	6.834	5.271	5.340
	BLYP	−8.868	−10.524	−10.462	−8.544	−9.656	−9.606	−8.198	−9.423	−9.370	−7.132	−9.134	−9.059
	PBE	−7.448	−8.803	−8.748	−7.034	−7.789	−7.747	−6.927	−7.809	−7.764	−5.921	−7.524	−7.458
	TPSS	−5.737	−7.179	−7.124	−5.820	−6.722	−6.677	−5.669	−6.696	−6.649	−4.784	−6.429	−6.362
	VSXC	−5.236	−7.008	−6.944	−5.027	−6.196	−6.146	−5.393	−6.643	−6.590	−4.476	−6.457	−6.382
	B1LYP	−4.149	−5.817	−5.758	−4.402	−5.483	−5.437	−4.320	−5.484	−5.435	−3.419	−5.208	−5.141
	B3LYP	−3.443	−5.120	−5.060	−3.640	−4.719	−4.673	−3.515	−4.688	−4.639	−2.606	−4.417	−4.349
	B3LYP-D3	−2.845	−4.540	−4.479	−3.031	−4.125	−4.078	−2.912	−4.099	−4.050	−2.001	−3.829	−3.761
	B97-2	−3.595	−5.143	−5.087	−3.918	−4.807	−4.765	−4.294	−5.281	−5.236	−3.540	−5.089	−5.028
	BHandHLYP	−1.721	−3.291	−3.235	−2.190	−3.217	−3.172	−2.290	−3.379	−3.333	−1.507	−3.094	−3.034
	mPW1PW91	−2.984	−4.393	−4.342	−3.239	−4.023	−3.985	−3.382	−4.270	−4.227	−2.639	−4.061	−4.003
	PBE0	−2.746	−4.112	−4.060	−2.972	−3.703	−3.666	−3.111	−3.943	−3.903	−2.330	−3.714	−3.657
	X3LYP	−3.063	−4.730	−4.671	−3.270	−4.340	−4.294	−3.194	−4.356	−4.307	−2.278	−4.078	−4.008
	BMK	−1.466	−3.223	−3.171	−2.105	−3.225	−3.182	−2.034	−3.080	−3.036	−1.392	−2.743	−2.691
	M05-2X	3.147	1.569	1.626	2.014	1.099	1.140	2.556	1.454	1.501	3.174	1.554	1.617
	M06	−0.246	−1.859	−1.804	−1.841	−2.964	−2.918	−2.365	−3.477	−3.431	−1.579	−3.281	−3.217
	M06-2X	3.045	1.390	1.448	1.991	1.045	1.088	2.091	1.037	1.082	2.729	1.188	1.247
	M06-HF	11.172	9.615	9.671	10.180	9.433	9.473	9.862	8.917	8.959	10.217	8.846	8.902
	CAM-B3LYP	−0.723	−2.374	−2.316	−1.211	−2.240	−2.196	−1.208	−2.334	−2.289	−0.273	−2.026	−1.962
	LC-PBE	2.982	1.555	1.607	1.794	1.085	1.121	1.734	0.881	0.921	2.531	1.139	1.195
	LC-ωPBE	−1.696	−3.133	−3.081	−2.478	−3.226	−3.190	−2.520	−3.410	−3.370	−1.702	−3.155	−3.099
	ωB97X	−0.753	−2.355	−2.300	−1.502	−2.447	−2.404	−1.942	−2.982	−2.940	−1.081	−2.604	−2.546
	ωB97X-D	−0.554	−2.133	−2.079	−0.996	−1.924	−1.881	−1.467	−2.520	−2.479	−0.696	−2.168	−2.112
MAX	SVWN5	6.947	5.553	5.620	8.198	7.255	7.312	7.871	6.875	6.933	8.531	6.671	6.756
	BLYP	9.277	11.052	10.996	9.585	10.672	10.632	8.848	10.112	10.068	7.427	9.353	9.290
	PBE	8.123	9.565	9.517	8.464	9.144	9.113	7.980	8.847	8.812	6.653	8.130	8.076
	TPSS	6.111	7.717	7.666	6.961	7.850	7.814	6.489	7.559	7.520	5.351	6.927	6.873
	VSXC	5.448	7.415	7.356	5.803	7.023	6.981	5.886	7.232	7.186	4.717	6.681	6.617
	B1LYP	4.424	5.850	5.793	4.964	6.134	6.095	4.618	5.923	5.880	3.503	5.320	5.262
	B3LYP	3.549	5.268	5.211	4.343	5.468	5.430	3.934	5.205	5.163	2.795	4.591	4.533
	B3LYP-D3	3.046	4.605	4.548	3.607	4.754	4.715	3.210	4.504	4.461	2.078	3.901	3.843
	B97-2	3.723	5.271	5.218	4.634	5.554	5.520	4.785	5.850	5.812	3.836	5.365	5.314
	BHandHLYP	2.638	3.723	3.670	2.290	3.530	3.489	2.370	3.556	3.513	1.763	3.184	3.119
	mPW1PW91	3.133	4.538	4.489	4.020	4.863	4.831	3.927	4.924	4.887	3.004	4.430	4.381
	PBE0	2.841	4.299	4.249	3.822	4.601	4.571	3.717	4.649	4.615	2.741	4.119	4.071
	X3LYP	3.196	4.862	4.805	3.964	5.089	5.050	3.607	4.873	4.831	2.453	4.249	4.187
	BMK	1.803	3.323	3.279	2.630	3.847	3.813	2.421	3.468	3.430	1.660	2.856	2.817
	M05-2X	3.473	1.598	1.656	2.684	1.854	1.901	2.938	2.001	2.053	3.408	1.859	1.929
	M06	0.504	1.888	1.835	2.492	3.674	3.636	2.786	3.995	3.955	1.818	3.514	3.459
	M06-2X	3.325	1.447	1.505	2.664	1.820	1.868	2.495	1.625	1.674	2.995	1.532	1.598
	M06-HF	11.716	9.691	9.750	10.775	10.190	10.233	10.168	9.512	9.556	10.451	9.256	9.316
	CAM-B3LYP	0.841	2.591	2.534	2.041	3.177	3.139	1.763	3.054	3.013	0.599	2.405	2.349
	LC-PBE	2.996	1.871	1.924	2.977	2.343	2.384	2.666	1.943	1.988	3.224	1.864	1.928
	LC-ωPBE	1.715	3.477	3.425	3.469	4.355	4.323	3.277	4.361	4.325	2.222	3.774	3.725
	ωB97X	0.903	2.575	2.521	2.346	3.445	3.405	2.538	3.817	3.779	1.508	3.081	3.031
	ωB97X-D	0.723	2.306	2.254	1.781	2.825	2.784	2.022	3.305	3.269	1.088	2.602	2.555

Table S12: Gallic acid's MAD, MSD, and MAX values (in kcal/mol) calculated regarding the DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) reference for the O−H BDE results computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM).

Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
MAD	SVWN5	9.713	5.827	5.946	8.950	5.523	5.573	8.849	5.480	5.555	9.123	5.850	5.949
	BLYP	15.282	11.591	11.696	13.841	9.982	10.090	13.455	9.732	9.837	12.438	9.640	9.713
	PBE	13.824	10.022	10.129	12.360	8.354	8.466	12.159	8.285	8.393	11.230	8.191	8.271
	TPSS	12.486	8.621	8.729	11.215	7.226	7.335	11.068	7.199	7.304	10.167	7.083	7.160
	VSXC	11.445	7.879	7.979	10.059	6.321	6.424	10.235	6.577	6.674	9.342	6.476	6.548
	B1LYP	10.149	5.774	5.911	9.070	4.376	4.520	8.827	4.162	4.305	7.901	3.687	3.819
	B3LYP	9.583	5.218	5.354	8.443	3.747	3.891	8.174	3.512	3.655	7.239	3.180	3.310
	B3LYP-D3	9.334	4.918	5.056	8.219	3.469	3.613	8.072	3.361	3.505	7.173	3.054	3.186
	B97-2	9.502	5.030	5.169	8.386	3.579	3.727	8.559	3.784	3.929	7.805	3.411	3.549
	BHandHLYP	8.125	3.978	3.935	6.891	3.442	3.403	6.890	3.402	3.362	6.112	2.692	2.690
	mPW1PW91	9.244	4.646	4.787	8.131	3.193	3.342	8.146	3.255	3.403	7.344	2.842	2.979
	PBE0	9.107	4.569	4.710	7.968	3.090	3.238	7.933	3.093	3.240	7.072	2.646	2.782
	X3LYP	8.785	4.421	4.557	7.953	3.155	3.303	7.773	2.873	3.018	6.772	2.672	2.800
	BMK	6.344	2.055	1.885	6.130	2.718	2.570	5.947	2.679	2.521	5.656	2.669	2.506
	M05-2X	5.641	2.758	2.744	4.389	2.912	2.883	4.368	3.017	2.992	4.609	2.408	2.396
	M06	6.405	1.330	1.484	5.949	2.422	2.264	6.228	2.627	2.470	5.759	2.594	2.428

Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	M06-2X	7.691	4.555	4.553	6.559	4.819	4.803	6.231	4.356	4.179	6.801	3.790	3.793
	M06-HF	7.500	9.618	9.608	9.640	9.784	9.772	6.591	8.483	8.459	8.532	7.739	7.726
	CAM-B3LYP	6.497	1.601	1.751	5.615	1.922	1.762	5.508	2.013	1.852	5.007	1.257	1.271
	LC-PBE	5.164	3.099	3.086	3.879	3.012	2.987	3.756	2.637	2.614	3.953	1.941	1.935
	LC-ωPBE	6.810	3.164	3.125	6.316	3.111	3.072	2.725	2.948	2.910	5.522	2.509	2.657
	ωB97X	6.255	2.711	2.665	5.698	2.455	2.556	6.027	2.551	2.509	5.099	2.062	2.052
	ωB97X-D	7.056	2.511	2.469	6.134	2.568	2.519	6.523	2.680	2.486	6.395	2.793	2.745
MSD	SVWN5	−4.694	−1.182	−1.284	−3.149	0.623	0.517	−2.839	0.809	0.707	−1.795	1.042	0.966
	BLYP	−15.282	−11.591	−11.696	−13.841	−9.982	−10.090	−13.455	−9.732	−9.837	−12.438	−9.640	−9.713
	PBE	−13.824	−10.022	−10.129	−12.360	−8.354	−8.466	−12.159	−8.285	−8.393	−11.230	−8.191	−8.271
	TPSS	−12.486	−8.621	−8.729	−11.215	−7.226	−7.335	−11.068	−7.199	−7.304	−10.167	−7.083	−7.160
	VSXC	−11.445	−7.879	−7.979	−10.059	−6.321	−6.424	−10.235	−6.577	−6.674	−9.342	−6.476	−6.548
	B1LYP	−10.149	−5.774	−5.911	−9.070	−4.376	−4.520	−8.827	−4.162	−4.305	−7.901	−3.687	−3.819
	B3LYP	−9.583	−5.218	−5.354	−8.443	−3.747	−3.891	−8.174	−3.512	−3.655	−7.239	−3.180	−3.310
	B3LYP-D3	−9.334	−4.918	−5.056	−8.219	−3.469	−3.613	−8.072	−3.361	−3.505	−7.173	−3.054	−3.186
	B97-2	−9.502	−5.030	−5.169	−8.386	−3.579	−3.727	−8.559	−3.784	−3.929	−7.805	−3.411	−3.549
	BHandHLYP	−8.125	−2.168	−2.173	−6.891	−2.050	−2.072	−6.890	−2.203	−2.216	−6.112	−2.692	−2.690
	mPW1PW91	−9.244	−4.646	−4.787	−8.131	−3.193	−3.342	−8.146	−3.255	−3.403	−7.344	−2.842	−2.979
	PBE0	−9.107	−4.569	−4.710	−7.968	−3.090	−3.238	−7.933	−3.093	−3.240	−7.072	−2.646	−2.782
	X3LYP	−8.785	−4.421	−4.557	−7.953	−3.155	−3.303	−7.773	−2.873	−3.018	−6.772	−2.672	−2.800
	BMK	−5.456	−1.324	−1.457	−4.971	−0.522	−0.678	−4.800	0.008	−0.138	−3.924	0.353	0.214
	M05-2X	−3.536	1.472	1.471	−2.685	1.278	1.263	−2.673	1.243	1.233	−1.521	0.913	0.922
	M06	−5.360	−0.902	−1.040	−4.933	−0.192	−0.336	−5.097	−0.361	−0.505	−4.290	0.044	−0.086
	M06-2X	−0.655	4.555	4.553	0.245	4.819	4.803	0.170	4.356	4.179	0.881	3.790	3.793
	M06-HF	2.669	8.021	8.028	8.782	8.336	8.339	2.761	7.063	7.055	8.225	6.619	6.626
	CAM-B3LYP	−5.738	−1.257	−1.396	−5.074	−0.260	−0.406	−4.960	−0.188	−0.334	−4.083	−0.909	−0.909
	LC-PBE	−3.358	1.197	1.198	−2.874	1.161	1.150	−2.793	0.734	0.726	−2.016	0.246	0.257
	LC-ωPBE	−6.810	−1.878	−1.878	−6.316	−1.677	−1.690	−1.619	−2.176	−2.185	−5.522	−2.509	−2.657
	ωB97X	−6.255	−1.344	−1.347	−5.698	−1.256	−1.126	−6.027	−1.794	−1.807	−5.099	−2.062	−2.052
	ωB97X-D	−5.186	0.005	−0.007	−4.578	0.517	0.483	−4.667	0.270	0.088	−3.618	0.026	0.074
MAX	SVWN5	19.401	10.640	10.612	15.561	9.800	9.770	15.289	9.341	9.312	15.153	8.370	8.330
	BLYP	34.046	17.384	17.871	30.528	14.397	14.869	29.991	14.185	14.643	29.949	15.958	16.343
	PBE	32.706	15.904	16.392	28.911	12.584	13.061	28.645	12.619	13.083	28.560	14.188	14.587
	TPSS	30.914	13.391	13.892	27.552	10.699	11.177	27.151	10.613	11.076	26.934	11.990	12.387
	VSXC	29.323	12.365	12.849	25.331	8.991	9.452	25.513	9.401	9.848	25.208	10.529	10.913
	B1LYP	25.922	6.376	6.347	22.321	5.767	5.761	21.867	5.537	5.531	21.396	4.676	4.654
	B3LYP	25.614	5.431	5.924	21.984	5.049	5.046	21.484	4.776	4.771	20.997	3.893	3.872
	B3LYP-D3	25.183	5.703	5.674	21.565	5.125	5.098	21.063	5.452	5.423	20.567	4.911	4.876
	B97-2	25.670	5.545	5.864	21.879	5.272	5.272	21.945	5.525	5.524	21.555	4.760	4.746
	BHandHLYP	22.654	5.165	5.139	17.885	4.574	4.551	17.791	4.670	4.644	17.392	4.128	4.095
	mPW1PW91	24.907	5.047	5.022	21.251	4.617	4.618	21.109	4.649	4.648	20.716	3.872	3.857
	PBE0	24.694	5.383	5.352	20.990	4.810	4.780	20.861	4.655	4.622	20.451	3.986	3.945
	X3LYP	25.042	5.106	5.339	21.416	4.680	4.676	20.960	4.456	4.451	20.466	3.559	3.537
	BMK	19.400	3.491	3.452	16.956	4.348	4.381	16.525	4.272	3.632	15.932	4.649	4.008
	M05-2X	16.852	6.062	5.973	11.929	6.060	5.944	11.665	5.319	5.213	10.761	2.990	2.948
	M06	20.793	2.626	2.594	16.939	3.567	3.262	17.000	3.569	3.566	16.559	3.876	3.247
	M06-2X	16.693	8.610	8.637	12.628	9.576	9.603	12.121	8.409	8.435	11.840	8.568	8.598
	M06-HF	11.799	16.725	16.657	16.854	16.023	15.976	9.678	13.164	13.064	13.232	10.700	10.629
	CAM-B3LYP	20.910	3.171	3.138	17.540	2.973	2.814	17.146	3.389	2.752	16.647	1.802	1.777
	LC-PBE	14.300	6.607	6.531	10.769	6.576	6.478	10.368	5.222	5.132	9.957	3.390	3.355
	LC-ωPBE	19.853	4.027	4.001	16.907	4.067	4.063	3.762	4.039	4.032	16.252	3.284	3.262
	ωB97X	19.778	3.090	3.058	16.724	3.175	3.166	16.894	3.433	3.427	16.384	2.554	2.531
	ωB97X-D	21.249	3.720	3.719	17.725	3.900	3.882	17.876	4.436	4.419	17.481	5.637	5.636

Table S13: Myricetin's MAD, MSD, and MAX values (in kcal/mol) calculated regarding the DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) reference for the O−H BDE results computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM).

Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
MAD	SVWN5	3.342	6.356	3.271	4.323	7.661	5.331	3.966	6.848	4.395	5.003	7.227	4.659
	BLYP	11.612	17.030	11.482	10.495	15.689	10.146	10.361	15.621	10.074	9.420	15.125	9.553
	PBE	10.053	15.272	9.728	8.844	13.803	8.263	8.903	13.941	8.399	8.020	13.432	7.866
	TPSS	8.420	13.604	8.062	7.689	12.667	7.129	7.686	12.744	7.203	6.911	12.847	7.186
	VSXC	8.287	13.692	8.145	7.411	11.996	6.454	7.906	12.636	7.093	6.717	12.816	7.247
	B1LYP	6.981	12.030	6.497	6.086	10.538	5.009	6.154	10.641	5.110	5.425	10.815	5.263
	B3LYP	6.191	11.328	5.792	5.301	9.728	4.195	5.340	9.812	4.277	4.595	10.075	4.420
	B3LYP-D3	5.695	10.834	5.298	4.794	9.325	3.793	4.837	9.510	3.975	4.187	9.579	4.022
	B97-2	6.373	8.545	6.234	4.762	10.044	4.514	6.024	10.581	5.049	5.494	10.669	5.118
	BHandHLYP	3.623	9.621	4.097	3.658	8.347	2.824	3.674	8.552	3.029	3.264	8.560	3.020
	mPW1PW91	5.745	9.357	5.065	4.797	9.053	5.818	5.055	9.364	3.835	4.437	9.553	3.809
	PBE0	5.430	9.156	5.917	4.454	8.834	5.599	4.716	8.994	3.467	4.067	8.973	3.426
	X3LYP	5.797	10.904	5.369	4.896	9.295	3.764	4.985	9.426	3.892	4.230	9.592	4.038
	BMK	3.859	9.424	3.890	4.216	8.253	2.725	4.084	8.244	2.716	4.571	8.232	2.763

Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	M05-2X	2.764	5.533	1.141	2.599	5.024	1.662	2.924	5.363	1.906	6.321	5.648	1.765
	M06	2.890	8.192	2.656	3.027	8.131	2.598	3.815	8.679	3.147	3.061	8.769	3.215
	M06-2X	2.748	5.632	1.256	2.653	5.118	1.876	2.723	5.340	1.760	5.683	5.556	1.561
	M06-HF	7.759	9.247	8.791	8.734	9.377	9.879	8.474	9.028	9.480	8.610	9.011	9.355
	CAM-B3LYP	2.950	8.222	2.693	2.920	6.802	1.833	2.664	7.218	1.860	3.543	7.198	1.651
	LC-PBE	1.572	4.849	1.529	1.255	4.604	2.594	1.310	4.756	2.069	1.794	5.259	2.016
	LC-ωPBE	3.510	8.780	3.259	3.909	7.664	2.206	3.564	7.979	2.461	2.946	8.292	2.742
	ωB97X	3.222	8.120	2.593	3.763	6.993	1.721	4.463	7.724	2.201	3.953	7.808	2.264
	ωB97X-D	2.729	8.100	2.570	3.523	6.736	1.507	4.049	7.350	1.823	3.724	7.630	2.089
MSD	SVWN5	3.113	-2.301	3.253	2.110	-2.557	2.983	3.966	-1.152	4.395	5.003	-0.913	4.659
	BLYP	-11.612	-17.030	-11.482	-10.495	-15.689	-10.146	-10.361	-15.621	-10.074	-9.420	-15.125	-9.553
	PBE	-10.053	-15.272	-9.728	-8.844	-13.803	-8.263	-8.903	-13.941	-8.399	-8.020	-13.432	-7.866
	TPSS	-8.420	-13.604	-8.062	-7.689	-12.667	-7.129	-7.686	-12.744	-7.203	-6.911	-12.847	-7.186
	VSXC	-8.287	-13.692	-8.145	-7.411	-11.996	-6.454	-7.906	-12.636	-7.093	-6.717	-12.816	-7.247
	B1LYP	-6.981	-12.030	-6.497	-6.086	-10.538	-5.009	-6.154	-10.641	-5.110	-5.425	-10.815	-5.263
	B3LYP	-6.191	-11.328	-5.792	-5.301	-9.728	-4.195	-5.340	-9.812	-4.277	-4.595	-10.075	-4.420
	B3LYP-D3	-5.695	-10.834	-5.298	-4.794	-9.325	-3.793	-4.837	-9.510	-3.975	-4.187	-9.579	-4.022
	B97-2	-6.373	-8.545	-3.022	-3.313	-10.044	-4.514	-6.024	-10.581	-5.049	-5.494	-10.669	-5.118
	BHandHLYP	-3.204	-9.621	-4.097	-1.700	-8.347	-2.824	-1.808	-8.552	-3.029	-1.288	-8.560	-3.020
	mPW1PW91	-5.745	-8.570	-5.065	-4.797	-6.395	-0.884	-5.055	-9.364	-3.835	-4.437	-9.553	-3.809
	PBE0	-5.430	-8.257	-2.742	-4.454	-6.042	-0.532	-4.716	-8.994	-3.467	-4.067	-8.973	-3.426
	X3LYP	-5.797	-10.904	-5.369	-4.896	-9.295	-3.764	-4.985	-9.426	-3.892	-4.230	-9.592	-4.038
	BMK	-2.546	-9.424	-3.890	-1.667	-8.253	-2.725	-1.600	-8.244	-2.716	2.291	-8.232	-2.763
	M05-2X	1.795	-4.658	0.871	2.579	-3.862	1.662	2.772	-3.621	1.906	6.321	-3.780	1.765
	M06	1.087	-8.192	-2.656	-0.413	-8.131	-2.598	-1.404	-8.679	-3.147	-3.061	-8.769	-3.215
	M06-2X	1.704	-4.660	0.869	2.653	-3.647	1.876	2.706	-3.763	1.760	5.683	-3.979	1.561
	M06-HF	7.759	3.273	8.791	8.734	4.362	9.879	8.474	3.964	9.480	8.610	3.822	9.355
	CAM-B3LYP	0.526	-8.222	-2.693	-0.327	-6.802	-1.277	-2.664	-7.218	-1.593	0.669	-7.198	-1.651
	LC-PBE	0.636	-3.993	1.529	1.089	-2.923	2.594	0.852	-3.451	2.069	1.281	-3.521	2.016
	LC-ωPBE	-2.401	-8.780	-3.259	-1.337	-7.664	-2.149	-1.058	-7.979	-2.461	-2.946	-8.292	-2.742
	ωB97X	-3.222	-8.120	-2.593	0.317	-6.993	-1.472	1.918	-7.724	-2.201	0.277	-7.808	-2.264
	ωB97X-D	-1.407	-8.100	-2.570	0.766	-6.736	-1.211	0.145	-7.350	-1.823	0.685	-7.630	-2.089
MAX	SVWN5	6.676	25.972	7.690	8.644	23.550	7.841	8.429	23.999	7.637	9.194	24.422	7.451
	BLYP	15.425	40.366	14.469	14.545	38.373	12.460	14.977	38.563	12.646	14.632	38.942	13.001
	PBE	13.677	38.473	12.577	12.420	36.225	10.312	12.971	36.652	10.735	12.621	37.064	11.124
	TPSS	12.321	36.788	10.904	11.391	35.121	9.218	11.879	35.397	9.490	11.593	36.404	9.884
	VSXC	13.136	36.935	11.050	12.272	34.832	8.929	13.157	35.520	9.614	12.968	35.924	9.997
	B1LYP	10.643	34.103	8.258	9.582	32.025	6.161	10.230	32.230	6.363	10.093	32.709	6.822
	B3LYP	9.813	33.520	7.665	8.680	30.965	5.443	9.303	31.179	5.301	9.141	32.252	6.353
	B3LYP-D3	9.443	33.143	7.288	8.130	31.184	5.311	8.753	31.395	5.517	8.578	31.871	5.973
	B97-2	9.916	16.152	9.637	7.029	31.297	5.425	10.024	31.976	6.100	9.908	32.473	6.579
	BHandHLYP	8.793	31.569	5.741	5.873	28.842	3.803	5.597	29.058	3.780	5.930	29.531	3.672
	mPW1PW91	9.286	32.501	6.659	7.891	30.326	14.802	8.669	30.768	4.902	8.566	31.286	5.402
	PBE0	8.942	32.153	9.525	7.415	29.928	15.199	8.205	30.386	4.519	8.091	30.901	5.015
	X3LYP	9.449	33.077	7.225	8.163	30.466	5.072	8.838	30.724	4.886	8.686	31.800	5.905
	BMK	6.972	30.018	5.894	7.647	28.215	4.602	7.453	28.545	4.418	12.572	28.775	3.870
	M05-2X	6.294	25.709	3.117	9.958	23.650	3.906	10.536	23.573	3.540	14.981	24.214	2.876
	M06	8.822	29.905	4.055	7.840	29.128	3.538	7.234	29.750	3.875	7.789	30.299	4.405
	M06-2X	5.425	25.589	2.949	9.667	23.396	4.010	9.741	23.650	3.249	14.292	24.188	2.589
	M06-HF	12.780	17.921	11.322	10.562	15.044	12.890	10.805	15.192	11.201	11.031	15.567	10.357
	CAM-B3LYP	6.844	29.509	3.959	7.778	27.245	2.891	5.990	27.551	2.812	12.638	28.116	2.245
	LC-PBE	2.944	24.327	4.756	2.198	22.072	6.399	1.987	22.518	4.809	2.589	23.295	3.894
	LC-ωPBE	6.122	29.075	4.728	7.717	26.775	3.563	7.517	27.212	3.643	7.294	27.997	3.369
	ωB97X	6.410	28.547	4.000	12.240	26.454	2.855	11.964	27.187	3.174	12.692	27.759	3.086
	ωB97X-D	5.739	28.795	3.845	12.868	26.613	2.487	12.581	27.294	2.804	13.229	27.870	2.953

Table S14: Phloretin's MAD, MSD, and MAX values (in kcal/mol) calculated regarding the DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) reference for the O−H BDE results computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM).

Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
MAD	SVWN5	7.054	39.379	40.440	10.914	35.596	36.659	10.648	35.859	36.918	10.807	36.246	37.286
	BLYP	8.678	55.345	56.403	5.314	52.082	53.141	5.385	52.167	53.226	5.148	52.491	53.531
	PBE	6.904	53.300	54.366	3.240	49.753	50.814	3.487	50.045	51.106	3.311	50.370	51.417
	TPSS	6.030	52.457	53.522	2.865	49.416	50.479	2.971	49.578	50.638	2.784	49.825	50.874
	VSXC	6.060	52.633	53.692	2.457	49.213	50.268	3.065	50.498	51.532	2.903	51.179	52.181
	B1LYP	5.569	52.218	53.265	6.211	49.687	50.730	6.252	50.135	51.180	3.711	50.861	51.878
	B3LYP	4.210	51.042	52.088	3.035	48.472	49.516	3.012	48.920	49.963	2.919	47.509	50.687
	B3LYP-D3	4.104	49.910	51.674	5.985	48.078	49.120	2.908	48.512	49.554	2.817	49.223	50.248
	B97-2	4.106	50.352	51.417	1.925	47.015	49.551	3.136	47.521	48.584	3.085	47.787	48.839
	BHandHLYP	4.222	51.011	52.065	1.776	48.455	49.502	1.870	48.903	49.949	1.974	49.500	50.536
	mPW1PW91	4.852	50.523	51.574	5.127	47.871	48.823	6.146	48.407	49.453	6.285	49.084	50.118
	PBE0	5.088	50.010	51.061	5.171	47.202	48.251	2.877	47.836	48.883	2.822	48.515	49.550

Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	X3LYP	4.996	50.693	51.739	2.972	48.101	49.144	6.085	48.593	49.635	2.882	49.329	50.358
	BMK	2.800	49.639	50.503	1.307	46.887	47.925	1.132	47.143	48.191	0.859	48.030	49.063
	M05-2X	2.090	45.141	46.174	4.604	42.912	43.956	3.874	42.532	44.259	3.611	44.080	44.940
	M06	2.547	48.120	49.163	7.095	46.934	47.973	2.937	47.664	48.708	7.359	48.367	49.496
	M06-2X	2.081	44.988	45.881	4.314	42.419	43.466	4.010	42.983	44.075	3.839	43.650	44.682
	M06-HF	18.349	37.744	38.824	11.842	34.374	35.427	10.635	36.095	37.147	10.400	36.972	38.017
	CAM-B3LYP	3.669	47.247	48.311	3.074	44.176	45.237	3.051	44.358	45.420	3.056	44.652	45.700
	LC-PBE	2.980	44.377	45.431	4.698	42.108	43.157	4.104	42.837	43.883	3.742	43.744	44.777
	LC-ωPBE	2.896	49.357	50.410	1.537	47.057	48.106	1.173	47.828	48.878	1.182	48.716	49.751
	ωB97X	3.592	46.871	47.937	3.248	43.952	45.015	3.222	44.511	45.575	3.240	44.773	45.826
	ωB97X-D	3.312	47.116	48.181	2.874	44.040	45.102	2.824	44.394	45.455	2.818	44.664	45.700
MSD	SVWN5	7.054	−39.379	−40.440	10.914	−35.596	−36.659	10.648	−35.859	−36.918	10.807	−36.246	−37.286
	BLYP	−8.678	−55.345	−56.403	−5.314	−52.082	−53.141	−5.385	−52.167	−53.226	−5.148	−52.491	−53.531
	PBE	−6.904	−53.300	−54.366	−3.240	−49.753	−50.814	−3.487	−50.045	−51.106	−3.311	−50.370	−51.417
	TPSS	−6.030	−52.457	−53.522	−2.865	−49.416	−50.479	−2.971	−49.578	−50.638	−2.784	−49.825	−50.874
	VSXC	−6.060	−52.633	−53.693	−2.457	−49.213	−50.268	−3.065	−50.498	−51.532	−2.903	−51.179	−52.181
	B1LYP	−1.956	−52.218	−53.265	2.351	−49.687	−50.730	2.388	−50.135	−51.180	−1.250	−50.861	−51.878
	B3LYP	−3.831	−51.042	−52.088	−0.509	−48.472	−49.516	−0.579	−48.920	−49.963	−0.372	−47.509	−50.687
	B3LYP-D3	−3.370	−49.910	−51.674	3.601	−48.078	−49.120	−0.131	−48.512	−49.554	0.074	−49.223	−50.248
	B97-2	−3.946	−50.352	−51.417	−1.500	−47.015	−49.551	−0.937	−47.521	−48.584	−0.806	−47.787	−48.839
	BHandHLYP	−4.222	−51.011	−52.065	−1.498	−48.455	−49.502	−1.870	−48.903	−49.949	−1.974	−49.500	−50.536
	mPW1PW91	−0.654	−50.523	−51.574	2.568	−47.871	−48.823	3.413	−48.407	−49.453	3.707	−49.084	−50.118
	PBE0	−0.022	−50.010	−51.061	3.081	−47.202	−48.251	0.188	−47.836	−48.883	0.335	−48.515	−49.550
	X3LYP	−0.310	−50.693	−51.739	−0.124	−48.101	−49.144	3.583	−48.593	−49.635	−0.021	−49.329	−50.358
	BMK	−2.126	−49.639	−50.503	0.008	−46.887	−47.925	−0.400	−47.143	−48.191	−0.511	−48.030	−49.063
	M05-2X	1.611	−45.141	−46.174	4.604	−42.912	−43.956	3.874	−42.532	−44.259	3.611	−44.080	−44.940
	M06	−1.249	−48.120	−49.163	5.929	−46.934	−47.973	1.443	−47.664	−48.708	5.684	−48.367	−49.496
	M06-2X	2.031	−44.988	−45.881	4.314	−42.419	−43.466	4.010	−42.983	−44.075	3.839	−43.650	−44.682
	M06-HF	18.349	−37.744	−38.824	11.842	−34.374	−35.427	10.635	−36.095	−37.147	10.400	−36.972	−38.017
	CAM-B3LYP	−0.790	−47.247	−48.311	2.439	−44.176	−45.237	2.277	−44.358	−45.420	2.425	−44.652	−45.700
	LC-PBE	2.425	−44.377	−45.431	4.698	−42.108	−43.157	4.104	−42.837	−43.883	3.742	−43.744	−44.777
	LC-ωPBE	−2.617	−49.357	−50.410	−0.176	−47.057	−48.106	−0.796	−47.828	−48.878	−1.173	−48.716	−49.751
	ωB97X	−0.548	−46.871	−47.937	2.581	−43.952	−45.015	2.043	−44.511	−45.575	2.185	−44.773	−45.826
	ωB97X-D	−0.731	−47.116	−48.181	2.664	−44.040	−45.102	2.207	−44.394	−45.455	2.328	−44.664	−45.700
MAX	SVWN5	10.631	49.198	50.385	15.103	45.162	46.345	14.442	45.453	46.639	14.579	46.271	47.427
	BLYP	9.719	64.609	65.788	7.153	61.244	62.423	6.876	61.393	62.570	6.414	62.163	63.315
	PBE	8.176	62.496	63.683	5.379	58.795	59.980	5.306	59.150	60.333	4.932	59.900	61.061
	TPSS	6.928	61.790	62.975	4.686	58.723	59.906	4.551	58.954	60.134	4.199	59.593	60.754
	VSXC	7.506	62.769	63.953	3.729	59.156	60.335	4.359	59.798	60.979	4.265	60.466	61.627
	B1LYP	7.242	62.370	63.555	12.294	59.258	60.438	12.602	59.392	60.572	4.921	60.005	61.164
	B3LYP	6.023	61.228	62.412	5.050	58.043	59.223	4.867	58.180	59.360	5.094	58.827	59.986
	B3LYP-D3	5.708	60.931	62.114	13.440	57.752	58.932	5.553	57.891	59.070	5.782	58.544	59.702
	B97-2	6.101	61.131	62.318	2.957	57.859	59.042	4.398	58.407	59.589	4.558	59.024	60.190
	BHandHLYP	6.837	61.504	62.699	3.424	58.559	59.746	3.535	58.678	59.865	3.391	59.120	60.290
	mPW1PW91	8.029	60.899	62.091	13.159	57.571	58.758	13.238	57.882	59.067	13.924	58.463	59.630
	PBE0	8.378	60.464	61.656	13.536	57.057	58.245	6.130	57.384	58.571	6.314	57.979	59.147
	X3LYP	9.049	60.983	62.168	5.696	57.790	58.977	13.846	57.968	59.148	5.721	58.611	59.769
	BMK	4.823	59.980	61.166	2.133	56.887	58.069	2.252	56.808	57.996	2.148	57.427	58.595
	M05-2X	5.281	55.721	56.917	7.759	53.261	54.446	5.937	52.526	54.409	4.975	53.869	55.035
	M06	3.802	58.871	60.059	16.688	56.757	57.938	8.709	57.041	58.222	17.117	57.635	58.782
	M06-2X	5.391	55.011	56.201	6.710	52.198	53.384	5.347	52.513	53.696	4.504	53.127	54.293
	M06-HF	46.102	47.570	48.764	14.860	44.767	45.956	12.245	46.553	47.741	10.997	47.348	48.520
	CAM-B3LYP	5.758	59.074	60.261	10.085	56.108	57.290	9.941	56.379	57.561	10.200	57.058	58.219
	LC-PBE	7.837	55.646	56.843	9.167	52.982	54.172	7.521	53.346	54.535	6.327	54.046	55.218
	LC-ωPBE	4.994	59.658	60.853	2.231	56.942	58.130	2.230	57.332	58.519	2.293	58.031	59.200
	ωB97X	6.087	58.828	60.023	10.583	56.172	57.356	10.112	56.826	58.014	10.408	57.463	58.629
	ωB97X-D	5.162	58.766	59.953	9.750	55.634	56.816	9.223	56.172	57.354	9.421	56.759	57.923

Table S15: Overall MAD, MSD, and MAX values (in kcal/mol) calculated regarding the DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) reference for the O−H BDE results computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM).

Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
MAD	SVWN5	6.091	10.580	10.045	7.301	10.679	10.276	7.191	10.505	10.076	7.966	10.858	10.456
	BLYP	11.297	20.315	19.127	9.471	18.381	17.196	9.336	18.331	17.143	8.612	18.339	17.124
	PBE	9.719	18.502	17.319	7.853	16.359	15.178	7.879	16.522	15.340	7.224	16.529	15.322
	TPSS	8.293	17.013	15.831	6.981	15.444	14.263	6.924	15.522	14.338	6.299	15.647	14.416
	VSXC	7.989	17.011	15.823	6.328	14.878	13.691	6.740	15.555	14.363	6.071	15.796	14.575
	B1LYP	6.958	15.437	14.257	6.263	13.830	12.652	6.232	13.987	12.805	5.255	14.150	12.933
	B3LYP	6.179	14.649	13.477	5.161	13.020	11.748	5.095	13.134	11.952	4.487	12.954	12.073
	B3LYP-D3	5.767	14.103	13.042	5.249	12.552	11.372	4.677	12.692	11.509	4.120	12.821	11.606
	B97-2	6.282	13.840	13.521	4.922	12.857	11.929	5.605	13.257	12.188	5.147	13.516	12.320
	BHandHLYP	5.507	13.155	11.925	3.614	12.287	11.051	3.691	12.446	11.209	2.938	12.310	11.080

| Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	mPW1PW91	5.969	13.679	12.813	5.175	12.306	11.691	5.464	12.634	11.459	5.016	12.806	11.550
	PBE0	5.799	13.362	12.652	4.946	11.928	11.330	4.686	12.234	11.060	4.184	12.339	11.133
	X3LYP	6.019	14.292	13.110	4.860	12.607	11.428	5.352	12.770	11.586	4.244	12.941	11.729
	BMK	3.958	12.623	11.316	3.657	11.837	10.574	3.569	11.854	10.593	3.348	11.959	10.717
	M05-2X	3.068	10.120	9.182	3.169	9.721	9.022	3.177	9.781	9.213	4.227	9.780	8.998
	M06	3.452	11.570	10.385	4.146	11.525	10.250	3.844	12.015	10.779	4.038	12.215	10.966
	M06-2X	3.077	10.132	9.237	3.182	9.871	9.231	3.105	9.928	9.185	4.003	9.791	8.971
	M06-HF	11.188	13.532	14.737	11.766	14.071	14.528	10.633	13.694	13.989	10.933	13.387	13.702
	CAM-B3LYP	3.759	11.773	10.565	2.998	10.558	9.440	3.176	10.748	9.533	2.755	10.518	9.286
	LC-PBE	2.494	9.784	9.120	2.493	9.468	9.133	2.293	9.429	8.925	2.635	9.328	8.681
	LC-ωPBE	4.175	12.759	11.528	3.508	11.808	10.592	2.821	12.026	10.795	2.926	11.965	10.782
	ωB97X	3.723	11.746	10.540	3.304	10.702	9.559	3.711	11.135	9.903	3.196	10.936	9.704
	ωB97X-D	3.588	11.499	10.263	3.078	10.345	9.180	3.636	10.748	9.487	3.198	10.663	9.423
MSD	SVWN5	3.500	−5.414	−4.225	4.879	−3.741	−2.559	5.356	−3.448	−2.262	6.089	−3.479	−2.268
	BLYP	−11.297	−20.315	−19.127	−9.471	−18.381	−17.196	−9.336	−18.331	−17.143	−8.612	−18.339	−17.124
	PBE	−9.719	−18.502	−17.319	−7.711	−16.359	−15.178	−7.777	−16.522	−15.340	−7.110	−16.529	−15.322
	TPSS	−8.293	−17.013	−15.831	−6.787	−15.444	−14.263	−6.759	−15.522	−14.338	−6.124	−15.647	−14.416
	VSXC	−7.989	−17.011	−15.823	−6.126	−14.878	−13.691	−6.604	−15.555	−14.363	−5.923	−15.796	−14.575
	B1LYP	−6.285	−15.437	−14.257	−4.563	−13.830	−12.652	−4.548	−13.987	−12.805	−4.587	−14.150	−12.933
	B3LYP	−5.962	−14.649	−13.477	−4.385	−13.020	−11.748	−4.364	−13.134	−11.952	−3.724	−12.954	−12.073
	B3LYP-D3	−5.464	−14.103	−13.042	−3.271	−12.552	−11.372	−3.863	−12.692	−11.509	−3.274	−12.821	−11.606
	B97-2	−6.093	−13.840	−12.718	−4.119	−12.857	−11.929	−4.930	−13.234	−12.188	−4.454	−13.516	−12.320
	BHandHLYP	−5.402	−12.652	−11.443	−3.078	−11.667	−10.456	−3.224	−11.939	−10.725	−2.444	−12.310	−11.080
	mPW1PW91	−5.077	−13.482	−12.813	−3.479	−11.642	−10.458	−3.499	−12.634	−11.459	−2.973	−12.806	−11.550
	PBE0	−4.730	−13.137	−11.859	−3.121	−11.230	−10.063	−3.768	−12.234	−11.060	−3.244	−12.339	−11.133
	X3LYP	−5.057	−14.292	−13.110	−4.000	−12.607	−11.428	−3.389	−12.770	−11.586	−3.403	−12.941	−11.729
	BMK	−3.517	−12.439	−11.202	−2.311	−11.248	−10.058	−2.337	−11.279	−10.091	−1.080	−11.572	−10.383
	M05-2X	0.452	−7.971	−6.753	1.800	−7.140	−5.899	1.865	−6.904	−5.794	3.117	−7.514	−6.217
	M06	−1.826	−11.570	−10.385	−0.814	−11.173	−9.990	−2.065	−11.720	−10.537	−1.399	−11.892	−10.695
	M06-2X	0.573	−7.852	−6.504	1.776	−6.728	−5.518	1.779	−6.963	−5.785	2.719	−7.409	−6.181
	M06-HF	10.264	−0.543	1.796	11.766	1.359	2.719	10.126	0.396	1.607	10.933	−0.234	1.029
	CAM-B3LYP	−2.410	−11.526	−10.334	−1.382	−9.877	−8.690	−1.765	−10.135	−8.921	−0.776	−10.518	−9.286
	LC-PBE	0.421	−7.590	−6.377	1.367	−6.604	−5.395	1.153	−7.122	−5.908	1.544	−7.560	−6.328
	LC-ωPBE	−3.851	−12.203	−10.991	−2.639	−11.023	−9.814	−1.947	−11.442	−10.270	−2.924	−11.965	−10.782
	ωB97X	−3.216	−11.198	−10.013	−1.281	−9.986	−8.757	−1.238	−10.626	−9.417	−1.234	−10.936	−9.704
	ωB97X-D	−2.827	−11.164	−9.953	−0.959	−9.745	−8.535	−1.195	−10.338	−9.153	−0.685	−10.663	−9.423
MAX	SVWN5	19.401	49.198	50.385	15.561	45.162	46.345	15.289	45.453	46.639	15.153	46.271	47.427
	BLYP	34.046	64.609	65.788	30.528	61.244	62.423	29.991	61.393	62.570	29.949	62.163	63.315
	PBE	32.706	62.496	63.683	28.911	58.795	59.980	28.645	59.150	60.333	28.560	59.900	61.061
	TPSS	30.914	61.790	62.975	27.552	58.723	59.906	27.151	58.954	60.134	26.934	59.593	60.754
	VSXC	29.323	62.769	63.953	25.331	59.156	60.335	25.513	59.798	60.979	25.208	60.466	61.627
	B1LYP	25.922	62.370	63.555	22.321	59.258	60.438	21.867	59.392	60.572	21.396	60.005	61.164
	B3LYP	25.614	61.228	62.412	21.984	58.043	59.223	21.484	58.180	59.360	20.997	58.827	59.986
	B3LYP-D3	25.183	60.931	62.114	21.565	57.752	58.932	21.063	57.891	59.070	20.567	58.544	59.702
	B97-2	25.670	61.131	62.318	21.879	57.859	59.042	21.945	58.407	59.589	21.555	59.024	60.190
	BHandHLYP	22.654	61.504	62.699	17.885	58.559	59.746	17.791	58.678	59.865	17.392	59.120	60.290
	mPW1PW91	24.907	60.899	62.091	21.251	57.571	58.758	21.109	57.882	59.067	20.716	58.463	59.630
	PBE0	24.694	60.464	61.656	20.990	57.057	58.245	20.861	57.384	58.571	20.451	57.979	59.147
	X3LYP	25.042	60.983	62.168	21.416	57.790	58.977	20.960	57.968	59.148	20.466	58.611	59.769
	BMK	19.400	59.980	61.166	16.956	56.887	58.069	16.525	56.808	57.996	15.932	57.427	58.595
	M05-2X	16.852	55.721	56.917	11.929	53.261	54.446	11.665	52.526	54.409	14.981	53.869	55.035
	M06	20.793	58.871	60.059	16.939	56.757	57.938	17.000	57.041	58.222	17.117	57.635	58.782
	M06-2X	16.693	55.011	56.201	12.628	52.198	53.384	12.121	52.513	53.696	14.292	53.127	54.293
	M06-HF	46.102	47.570	48.764	27.762	44.767	45.956	24.968	46.553	47.741	22.468	47.348	48.520
	CAM-B3LYP	20.910	59.074	60.261	17.540	56.108	57.290	17.146	56.379	57.561	16.647	57.058	58.219
	LC-PBE	14.300	55.646	56.843	10.769	52.982	54.172	10.368	53.346	54.535	9.957	54.046	55.218
	LC-ωPBE	19.853	59.658	60.853	16.907	56.942	58.130	8.141	57.332	58.519	16.252	58.031	59.200
	ωB97X	19.778	58.828	60.023	16.724	56.172	57.356	16.894	56.826	58.014	16.384	57.463	58.629
	ωB97X-D	21.249	58.766	59.953	17.725	55.634	56.816	17.876	56.172	57.354	17.481	56.759	57.923
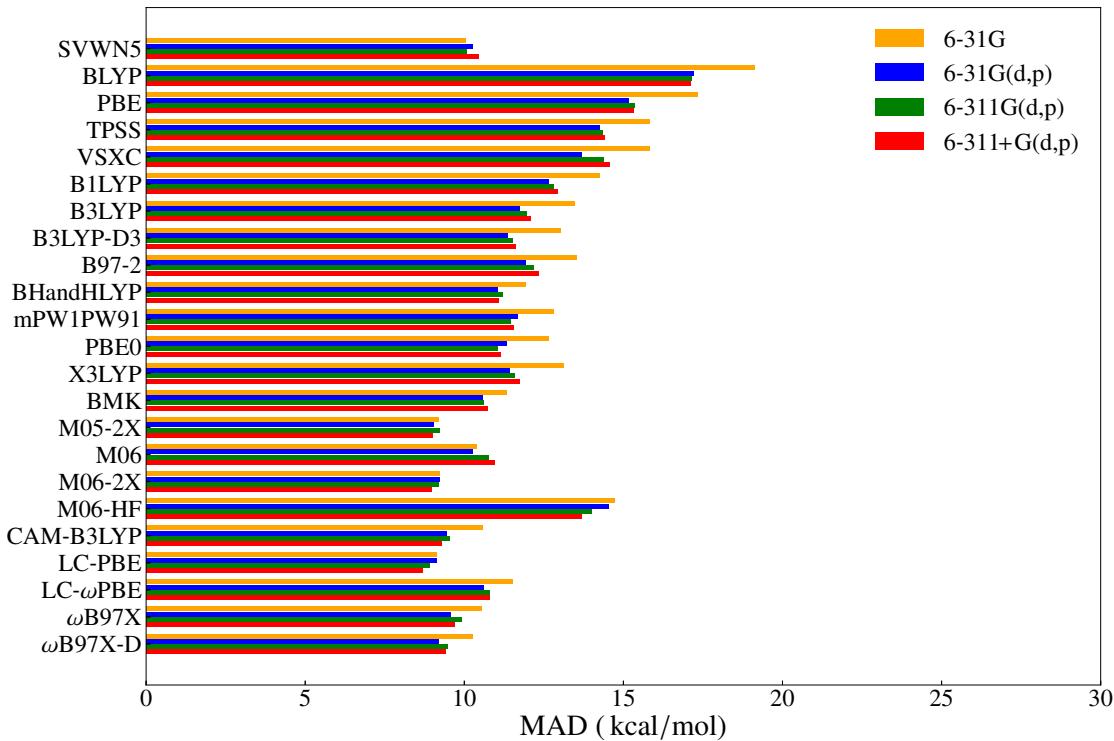
Figure S1: Mean absolute deviations (MADs), considering the O−H BDEs for all the molecules under study and methanol (C-PCM) as solvent. Benchmark results are DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p).

S2.4 Linear Fittings of BDEs

Table S16: Linear fitting parameters calculated for the DFT/6-311+G(d,p) *versus* DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) BDE curves of each flavonoid studied herein in gas-phase.

Molecule	XC Functional	Slope	Intercept	R^2
Caffeic acid	SVWN5	1.60824	−61.09625	0.93892
	BLYP	1.75671	−50.42296	0.98719
	PBE	1.72740	−50.36675	0.97957
	TPSS	1.64743	−45.94858	0.98513
	VSXC	1.54029	−37.42474	0.99238
	B1LYP	1.36407	−24.81355	0.99633
	B3LYP	1.41203	−30.32006	0.99699
	B3LYP-D3	1.39315	−29.03596	0.99499
	B97-2	1.37146	−25.57985	0.99503
	BHandHLYP	0.96901	4.52698	0.99984
	mPW1PW91	1.36652	−26.11621	0.99438
	PBE0	1.37061	−26.91696	0.99379
	X3LYP	1.37737	−27.51729	0.99499
	BMK	1.20018	−14.24062	0.99780
	M05-2X	1.19618	−20.00167	0.99701
	M06	1.22801	−16.64884	0.99791
	M06-2X	1.21697	−21.12621	0.99725
	M06-HF	0.74959	12.29547	0.99996
	CAM-B3LYP	1.26855	−20.97653	0.99616
	LC-PBE	1.09686	−9.72210	0.99767
	LC-ωPBE	1.18001	−11.88318	0.99822
	ωB97X	1.21869	−15.94871	0.99762
	ωB97X-D	1.28495	−21.82165	0.99599
Cyanidin	SVWN5	0.47334	41.79673	0.77492
	BLYP	0.54285	43.31398	0.74625
	PBE	0.52914	43.46667	0.73402
	TPSS	0.53566	42.51416	0.73213
	VSXC	0.54060	42.17588	0.75294
	B1LYP	0.55162	40.69528	0.67855
	B3LYP	0.54169	41.03590	0.69119
	B3LYP-D3	0.55748	39.40101	0.69920
	B97-2	0.53375	41.98985	0.66417
	BHandHLYP	0.99486	2.70555	0.98470

Continuation of Table S16.

Molecule	XC Functional	Slope	Intercept	R^2
	mPW1PW91	0.54362	40.69611	0.66596
	PBE0	0.53958	40.83252	0.66582
	X3LYP	0.54212	40.83301	0.69000
	BMK	0.49436	44.55114	0.62903
	M05-2X	0.85118	10.84883	0.96356
	M06	0.53373	41.00609	0.68011
	M06-2X	0.83199	12.71909	0.94726
	M06-HF	0.55602	32.04975	0.31099
	CAM-B3LYP	0.89292	10.01468	0.97726
	LC-PBE	0.95080	2.10015	0.97032
	LC-ωPBE	1.03500	-1.14188	0.97320
	ωB97X	0.98692	2.40159	0.98182
	ωB97X-D	0.55788	38.30350	0.61117
Ellagic acid	SVWN5	0.50996	38.04756	1.00000
	BLYP	0.85707	18.22667	1.00000
	PBE	0.70682	29.03258	1.00000
	TPSS	0.75697	24.21949	1.00000
	VSXC	0.87992	14.11576	1.00000
	B1LYP	0.95459	7.11205	1.00000
	B3LYP	0.90332	10.54767	1.00000
	B3LYP-D3	0.95796	5.47942	1.00000
	B97-2	0.85666	15.18182	1.00000
	BHandHLYP	1.16954	-12.60640	1.00000
	mPW1PW91	0.82852	16.71930	1.00000
	PBE0	0.81102	17.90593	1.00000
	X3LYP	0.90961	9.73288	1.00000
	BMK	0.86824	12.37578	1.00000
	M05-2X	0.88300	7.11358	1.00000
	M06	0.88058	11.51145	1.00000
	M06-2X	0.86888	8.74215	1.00000
	M06-HF	0.88278	0.91601	1.00000
	CAM-B3LYP	0.84437	13.42119	1.00000
	LC-PBE	0.71803	22.08093	1.00000
	LC-ωPBE	0.77253	20.59397	1.00000
	ωB97X	0.80529	17.37301	1.00000
	ωB97X-D	0.81835	15.96511	1.00000
Gallic acid	SVWN5	1.81041	-78.02353	0.90152
	BLYP	2.03726	-70.80134	0.94697
	PBE	1.97292	-67.95427	0.93526
	TPSS	1.95316	-68.67377	0.94897
	VSXC	1.87292	-63.53663	0.96185
	B1LYP	1.68134	-49.82044	0.98572
	B3LYP	1.70481	-53.11666	0.98185
	B3LYP-D3	1.71232	-54.63814	0.98172
	B97-2	1.67648	-49.29703	0.98089
	BHandHLYP	1.55551	-42.58703	0.99432
	mPW1PW91	1.67110	-50.11463	0.98161
	PBE0	1.67157	-50.66742	0.98040
	X3LYP	1.69145	-52.58375	0.98286
	BMK	1.48106	-37.17918	0.98785
	M05-2X	1.48211	-44.49701	0.99540
	M06	1.51375	-39.68822	0.98939
	M06-2X	1.50084	-45.18101	0.99268
	M06-HF	0.93756	-4.47490	0.99820
	CAM-B3LYP	1.57472	-46.14093	0.98909
	LC-PBE	1.36892	-32.91878	0.99283
	LC-ωPBE	1.47632	-35.93812	0.99226
	ωB97X	1.52134	-40.67308	0.99109
	ωB97X-D	1.59507	-47.10895	0.98703
Myricetin	SVWN5	1.05424	-10.03145	0.93165
	BLYP	1.33328	-16.67118	0.94615
	PBE	1.24941	-11.85478	0.94496
	TPSS	1.27936	-15.66099	0.95042
	VSXC	1.39497	-25.27175	0.92841
	B1LYP	1.33454	-22.10181	0.98008
	B3LYP	1.31441	-21.53536	0.97552
	B3LYP-D3	1.29920	-20.80272	0.97568
	B97-2	1.27414	-17.04332	0.97621
	BHandHLYP	0.77399	20.81936	0.93708
	mPW1PW91	1.27013	-18.05730	0.97963
	PBE0	1.25783	-17.49814	0.97904
	X3LYP	1.30972	-21.62458	0.97694
	BMK	0.62618	31.35162	0.92448
	M05-2X	0.67591	24.15259	0.94395
	M06	1.31374	-23.49533	0.97804
	M06-2X	0.67903	24.29261	0.93924
	M06-HF	1.26974	-34.58993	0.98784
	CAM-B3LYP	0.72931	23.25293	0.71655
	LC-PBE	1.13351	-13.16151	0.99201
	LC-ωPBE	1.27150	-20.06698	0.99294
	ωB97X	0.71608	24.70295	0.69504

Molecule	XC Functional	Slope	Intercept	R^2
	ωB97X-D	0.71148	24.81725	0.69428
Phloretin	SVWN5	0.69244	19.80077	0.98722
	BLYP	0.81040	20.99117	0.99456
	PBE	0.79895	20.48058	0.99319
	TPSS	0.79556	20.35152	0.99571
	VSXC	0.80276	19.82732	0.99571
	B1LYP	0.59417	36.74436	0.97993
	B3LYP	0.62343	33.63868	0.98377
	B3LYP-D3	0.61316	34.27215	0.98227
	B97-2	0.62601	33.68228	0.98708
	BHandHLYP	0.89695	10.91254	0.98666
	mPW1PW91	0.41441	50.41287	0.75103
	PBE0	0.59993	35.28981	0.98491
	X3LYP	0.61157	34.47132	0.98252
	BMK	0.86411	12.49656	0.98508
	M05-2X	0.81914	13.08636	0.99424
	M06	0.37555	53.26119	0.74749
	M06-2X	0.89925	5.48565	0.99507
	M06-HF	0.88481	1.01672	0.97994
	CAM-B3LYP	0.53524	39.93127	0.97549
	LC-PBE	0.73577	20.68764	0.99744
	LC-ωPBE	0.88681	11.08163	0.98765
	ωB97X	0.52038	41.41133	0.97437
	ωB97X-D	0.55824	37.88981	0.97895
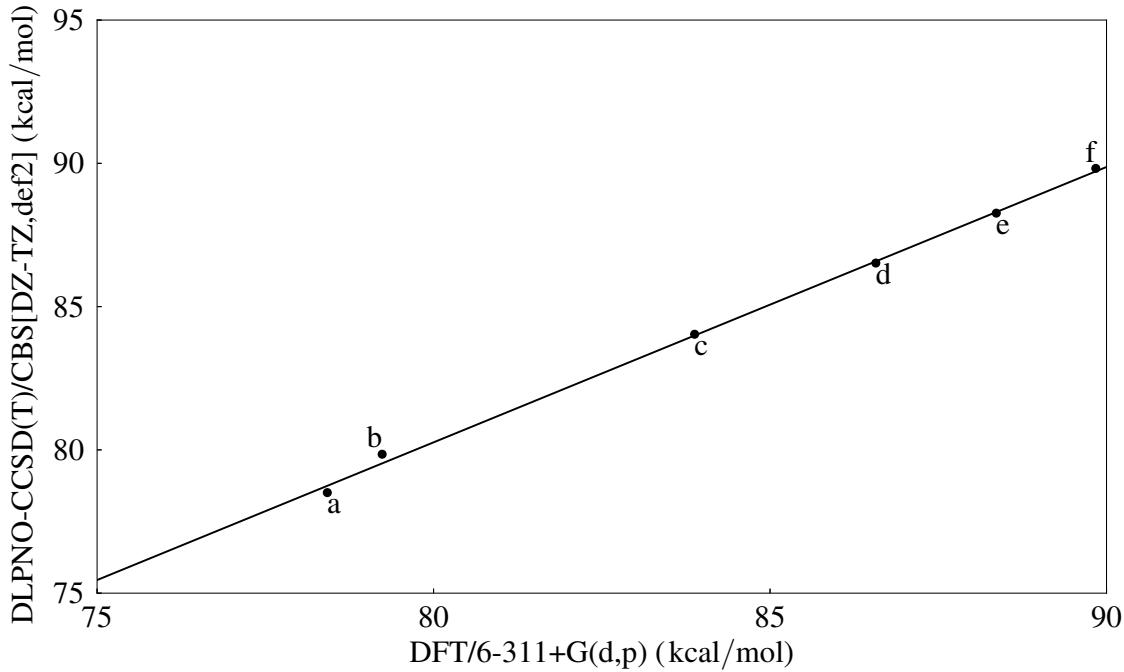
Figure S2: Linear fit of the "best DFT"/6-311+G(d,p) *vs.* DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) BDEs. The letters near the points stand for: (a) 3'-ArO$^\bullet$ radical of myricetin at ωB97X-D; (b) 3-ArO$^\bullet$ radical of gallic acid at CAM-B3LYP; (c) 4-ArO$^\bullet$ radical of caffeic acid at CAM-B3LYP; (d) 4-ArO$^\bullet$ radical of ellagic acid at CAM-B3LYP; (e) 7-ArO$^\bullet$ radical of cyanidin at CAM-B3LYP; and (f) 4'-ArO$^\bullet$ radical of phloretin at LC-ωPBE.

Table S17: Linear fitting parameters calculated for the DFT/6-311+G(d,p) *versus* DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) BDE curves of each flavonoid studied herein considering water as solvent (C-PCM).

Molecule	XC Functional	Slope	Intercept	R^2
Caffeic acid	SVWN5	1.56671	−57.17929	0.92917
	BLYP	1.63524	−39.58770	0.99376
	PBE	1.60008	−39.71261	0.98541
	TPSS	1.46661	−30.82181	0.98971
	VSXC	1.37062	−23.33480	0.99813
	B1LYP	1.01312	3.50252	0.99961

Continuation of Table S17.

Molecule	XC Functional	Slope	Intercept	R^2
	B3LYP	1.02823	1.34857	0.99919
	B3LYP-D3	1.03447	0.36858	0.99925
	B97-2	1.13603	−6.44699	0.99859
	BHandHLYP	0.90880	10.26628	0.99997
	mPW1PW91	0.98210	4.71234	0.99893
	PBE0	0.98025	4.46684	0.99870
	X3LYP	1.02564	1.25992	0.99920
	BMK	0.94333	7.38819	0.99790
	M05-2X	0.95694	2.17460	0.98724
	M06	1.01451	1.28299	0.99934
	M06-2X	0.88541	7.89043	0.99767
	M06-HF	0.88761	1.39161	0.99484
	CAM-B3LYP	0.95584	5.56892	0.99719
	LC-PBE	0.86621	10.38246	0.99692
	LC-ωPBE	0.85780	14.58474	0.99847
	ωB97X	0.92147	8.92105	0.99802
	ωB97X-D	0.95225	5.97288	0.99739
Cyanidin	SVWN5	0.38918	51.29168	0.46076
	BLYP	0.51512	47.47333	0.49993
	PBE	0.50182	47.50021	0.52587
	TPSS	0.51218	46.22746	0.52891
	VSXC	0.53117	44.83398	0.51501
	B1LYP	0.62966	36.23884	0.66592
	B3LYP	0.59266	38.73257	0.62941
	B3LYP-D3	0.62259	35.96570	0.65473
	B97-2	0.59691	38.61560	0.65653
	BHandHLYP	0.77994	22.70987	0.87614
	mPW1PW91	0.62142	36.02376	0.68340
	PBE0	0.60730	36.92102	0.68637
	X3LYP	0.59570	38.28641	0.63494
	BMK	0.54358	41.99010	0.65816
	M05-2X	0.61489	33.28060	0.72040
	M06	0.61209	36.38237	0.68197
	M06-2X	0.58841	35.57360	0.70480
	M06-HF	0.68398	22.70693	0.91342
	CAM-B3LYP	0.69171	28.92509	0.79914
	LC-PBE	0.75010	21.45369	0.91170
	LC-ωPBE	0.79571	20.77510	0.93756
	ωB97X	0.72935	25.96875	0.89125
	ωB97X-D	0.70145	27.95810	0.86976
Ellagic acid	SVWN5	0.41028	47.56986	1.00000
	BLYP	0.81643	22.93816	1.00000
	PBE	0.61646	36.98327	1.00000
	TPSS	0.66146	32.80194	1.00000
	VSXC	0.81268	21.04394	1.00000
	B1LYP	0.89646	13.40033	1.00000
	B3LYP	0.84806	16.55865	1.00000
	B3LYP-D3	0.93072	9.40567	1.00000
	B97-2	0.77920	22.58585	1.00000
	BHandHLYP	1.10243	−5.22804	1.00000
	mPW1PW91	0.72497	26.13740	1.00000
	PBE0	0.70631	27.39079	1.00000
	X3LYP	0.85028	16.09291	1.00000
	BMK	0.89563	11.25782	1.00000
	M05-2X	0.76153	18.92702	1.00000
	M06	0.80696	18.92713	1.00000
	M06-2X	0.73900	21.13285	1.00000
	M06-HF	0.70376	18.75731	1.00000
	CAM-B3LYP	0.71988	25.08141	1.00000
	LC-PBE	0.57328	35.33332	1.00000
	LC-ωPBE	0.61142	34.69835	1.00000
	ωB97X	0.67103	29.48973	1.00000
	ωB97X-D	0.69176	27.49412	1.00000
Gallic acid	SVWN5	1.38043	−39.80267	0.94094
	BLYP	1.48622	−28.08609	0.97514
	PBE	1.43677	−26.45023	0.96703
	TPSS	1.35451	−21.61635	0.98085
	VSXC	1.27370	−15.74813	0.98895
	B1LYP	0.85966	15.75423	0.99889
	B3LYP	0.89625	12.10934	0.99946
	B3LYP-D3	0.89946	11.38387	0.99919
	B97-2	0.86630	15.07916	0.99966
	BHandHLYP	0.91366	9.92791	0.99806
	mPW1PW91	0.86412	14.53036	0.99951
	PBE0	0.86598	14.08046	0.99958
	X3LYP	0.88819	12.47255	0.99935
	BMK	0.75645	22.06475	0.99828
	M05-2X	0.94717	2.76151	0.99958
	M06	0.77279	20.87749	0.99857
	M06-2X	0.93268	4.08079	0.99976
	M06-HF	0.92848	−2.33874	0.99778

Molecule	XC Functional	Slope	Intercept	R^2
	CAM-B3LYP	0.95351	5.67274	0.99957
	LC-PBE	0.94792	3.39769	0.99958
	LC-ωPBE	0.91212	10.19308	0.99984
	ωB97X	0.93887	7.42955	0.99980
	ωB97X-D	0.97798	3.87235	0.99962
Myricetin	SVWN5	1.50650	−44.54466	0.46299
	BLYP	1.92206	−54.52502	0.49237
	PBE	1.80371	−48.63863	0.49117
	TPSS	1.84377	−52.81084	0.50330
	VSXC	2.21879	−82.06309	0.57025
	B1LYP	2.13718	−79.98684	0.66486
	B3LYP	2.08477	−77.34352	0.63734
	B3LYP-D3	2.08101	−78.07171	0.62965
	B97-2	2.07416	−75.25706	0.65880
	BHandHLYP	2.20877	−90.68197	0.73830
	mPW1PW91	2.02040	−73.21010	0.65709
	PBE0	1.89426	−64.07857	0.62335
	X3LYP	1.98697	−70.42215	0.62309
	BMK	2.10216	−82.61926	0.74250
	M05-2X	1.97435	−80.87398	0.72654
	M06	2.06550	−78.48959	0.67467
	M06-2X	1.97610	−80.63173	0.73775
	M06-HF	2.00738	−99.00367	0.79011
	CAM-B3LYP	2.04443	−79.97425	0.71397
	LC-PBE	1.85797	−71.24329	0.74324
	LC-ωPBE	1.98126	−72.53422	0.76971
	ωB97X	2.00878	−75.77310	0.76166
	ωB97X-D	2.01136	−76.34521	0.74505
Phloretin	SVWN5	0.30028	105.42168	0.21127
	BLYP	0.31068	109.44122	0.17158
	PBE	0.31736	108.21613	0.18082
	TPSS	0.30244	109.31526	0.16983
	VSXC	0.20536	117.87278	0.04321
	B1LYP	0.20853	117.54023	0.04383
	B3LYP	0.25435	112.82802	0.20176
	B3LYP-D3	0.22991	115.36274	0.05913
	B97-2	0.25615	112.74090	0.20140
	BHandHLYP	0.12447	124.45286	0.01601
	mPW1PW91	0.24475	114.05377	0.07395
	PBE0	0.25041	113.42498	0.08113
	X3LYP	0.23230	115.18190	0.06018
	BMK	0.11352	125.22396	0.01275
	M05-2X	0.18608	118.17050	0.04683
	M06	0.20447	117.37253	0.04514
	M06-2X	0.16657	119.87462	0.02888
	M06-HF	0.11927	123.40408	0.01787
	CAM-B3LYP	0.22540	114.72001	0.21670
	LC-PBE	0.20010	116.82662	0.06425
	LC-ωPBE	0.15966	121.31542	0.02678
	ωB97X	0.21815	115.40205	0.21453
	ωB97X-D	0.23287	114.04717	0.21175

S2.5 Ionization Potential (IP) Values

Table S18: IP values (in kcal/mol) computed via DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) approximation in gas-phase or considering water or methanol as solvents (C-PCM) for all flavonoids studied herein.

Molecule	Gas	H_2O	CH_3OH
Caffeic acid	186.731	140.929	141.792
Cyanicin	254.448	151.350	153.346
Ellagic acid	188.154	146.359	147.141
Gallic acid	194.936	147.066	147.928
Myricetin	176.987	139.488	140.186
Phloretin	200.866	153.811	154.766

Table S19: IP values (in kcal/mol) computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM) for the HOMO of caffeic acid.

XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
	Gas	H_2O	CH_3OH	Gas	H_2O	CH_3OH	Gas	H_2O	CH_3OH	Gas	H_2O	CH_3OH
SVWN5	175.035	134.409	135.162	171.757	131.281	132.039	177.859	137.240	137.996	181.772	140.636	141.403
BLYP	167.251	125.930	126.702	163.411	122.301	123.065	169.338	128.060	128.829	174.159	132.297	133.081
PBE	171.611	130.830	131.591	167.737	127.136	127.888	172.755	131.946	132.706	176.994	135.632	136.405
TPSS	172.045	130.946	131.712	167.583	126.674	127.433	172.116	131.004	131.770	175.758	134.174	134.950
VSXC	172.182	130.871	131.639	167.727	126.651	127.416	171.409	130.158	130.925	175.553	133.852	134.630
B1LYP	173.140	131.198	131.978	168.197	126.441	127.217	173.049	131.176	131.956	176.956	134.658	135.448
B3LYP	176.220	134.398	135.176	171.534	129.908	130.682	176.520	134.770	135.548	180.421	138.246	139.034
B3LYP-D3	176.187	134.380	135.158	171.499	129.885	130.660	176.482	134.739	135.517	180.396	138.216	139.004
B97-2	176.496	134.992	135.764	171.435	130.133	130.902	175.054	133.558	134.331	178.236	136.355	137.138
BHandHLYP	177.367	135.079	135.866	171.311	129.158	129.943	175.229	132.980	133.767	178.357	135.782	136.575
mPW1PW91	178.295	136.790	137.562	173.295	131.962	132.729	177.275	135.787	136.558	180.392	138.514	139.295
PBE0	177.674	136.213	136.985	172.656	131.363	132.130	176.579	135.142	135.911	179.805	137.976	138.757
X3LYP	175.298	133.442	134.222	170.543	128.874	129.649	175.536	133.748	134.526	179.551	137.323	138.112
BMK	179.088	137.399	138.164	173.930	132.047	132.829	178.491	136.505	137.283	181.334	139.128	139.916
M05-2X	183.969	142.213	142.993	178.424	136.487	137.560	183.575	141.536	142.584	186.207	143.869	144.984
M06	178.157	136.581	137.355	173.183	131.616	132.389	177.680	135.964	136.741	180.734	138.657	139.444
M06-2X	184.064	142.124	142.907	178.801	136.951	137.732	183.130	141.263	142.045	186.079	143.827	144.617
M06-HF	192.330	150.409	151.196	186.659	144.865	145.647	191.773	149.995	150.776	194.163	152.164	152.954
CAM-B3LYP	178.604	136.323	137.111	173.638	131.487	132.272	178.600	136.371	137.159	182.508	139.870	140.667
LC-PBE	185.540	143.448	144.230	180.426	138.296	139.080	184.745	142.541	143.326	187.581	145.067	145.859
LC-ωPBE	182.306	140.044	140.831	176.994	134.838	135.622	181.093	138.841	139.629	184.272	141.664	142.459
ωB97X	180.253	137.933	138.723	174.881	132.662	133.450	178.774	136.483	137.271	182.164	139.618	140.412
ωB97X-D	179.381	137.444	138.223	174.558	132.574	133.355	178.381	136.300	137.077	181.361	138.995	139.783

Table S20: IP values (in kcal/mol) computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM) for the HOMO of cyanidin.

XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
	Gas	H_2O	CH_3OH	Gas	H_2O	CH_3OH	Gas	H_2O	CH_3OH	Gas	H_2O	CH_3OH
SVWN5	244.323	141.988	143.860	241.191	138.472	140.356	246.636	143.904	145.785	249.244	146.293	148.177
BLYP	236.138	134.039	135.899	232.262	129.785	131.675	237.520	134.977	136.868	241.030	138.385	140.280
PBE	240.792	138.865	140.707	236.923	134.692	136.568	241.319	138.967	140.842	244.299	141.668	143.555
TPSS	241.583	139.524	141.356	237.097	134.659	136.543	241.085	138.521	140.408	243.577	140.913	142.803
VSXC	242.505	139.837	141.698	237.680	134.803	136.704	240.728	137.719	139.604	243.643	140.390	142.294
B1LYP	244.822	142.124	144.023	239.642	136.545	138.445	243.939	140.738	142.647	246.780	143.543	145.455
B3LYP	247.429	144.880	146.771	242.546	139.538	141.440	246.966	143.856	145.758	249.791	146.585	148.493
B3LYP-D3	247.433	144.830	146.718	242.490	139.540	141.438	246.929	143.887	145.787	249.748	146.621	148.525
B97-2	247.903	145.423	147.322	242.688	139.805	141.699	245.822	142.738	144.635	248.010	144.786	146.690
BHandHLYP	234.492	145.054	146.840	231.029	137.082	138.989	234.549	140.168	142.084	236.534	142.352	144.274
mPW1PW91	250.328	147.844	149.722	245.135	142.200	144.094	248.636	145.506	147.402	250.802	147.504	149.407
PBE0	249.680	147.216	149.103	244.460	141.532	143.429	247.903	144.805	146.699	250.162	146.885	148.788
X3LYP	246.741	144.113	146.007	241.732	138.651	140.556	246.156	142.976	144.880	249.084	145.829	147.735
BMK	244.554	148.213	149.763	245.278	142.229	144.159	249.404	146.230	148.131	251.252	148.108	149.986
M05-2X	239.807	149.260	150.921	238.015	147.644	149.542	242.964	152.304	154.209	244.956	154.037	155.916
M06	250.092	147.338	149.321	244.747	141.491	143.377	248.575	145.229	147.126	250.651	147.150	149.060
M06-2X	240.023	149.051	151.005	238.146	147.612	149.524	242.464	151.424	153.337	252.722	153.618	155.524
M06-HF	255.965	153.213	159.962	250.814	148.138	149.859	255.777	157.618	159.451	257.291	159.210	160.891
CAM-B3LYP	244.881	143.345	145.193	241.306	142.454	144.356	250.007	146.811	148.712	248.533	149.667	151.583
LC-PBE	240.908	150.974	152.804	248.495	146.152	148.050	252.644	150.087	151.972	254.671	152.246	154.139
LC-ωPBE	248.834	147.791	149.776	244.994	142.803	144.693	248.908	149.068	150.933	251.235	148.931	150.833
ωB97X	246.629	145.609	147.484	242.918	140.389	142.386	246.524	146.679	148.546	248.882	146.577	148.481
ωB97X-D	246.108	145.134	146.952	242.871	143.259	145.178	250.314	146.497	148.413	248.545	148.852	150.788

Table S21: IP values (in kcal/mol) computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM) for the HOMO of ellagic acid.

XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
	Gas	H_2O	CH_3OH	Gas	H_2O	CH_3OH	Gas	H_2O	CH_3OH	Gas	H_2O	CH_3OH
SVWN5	174.867	135.950	136.671	168.841	130.548	131.254	174.901	136.469	137.178	179.213	140.237	140.960
BLYP	167.062	127.773	128.504	160.612	121.968	122.682	166.430	127.613	128.331	171.721	132.269	133.004
PBE	171.600	132.719	133.442	164.992	126.825	127.529	169.846	131.450	132.158	174.561	135.551	136.276
TPSS	172.814	133.636	134.367	165.681	127.190	127.902	170.052	131.341	132.057	174.024	134.811	135.541
VSXC	173.649	134.186	134.919	165.954	127.256	127.971	169.393	130.574	131.292	173.962	134.688	135.421
B1LYP	176.466	136.406	137.155	168.267	129.023	129.752	172.878	133.479	134.210	177.154	137.230	137.977
B3LYP	178.812	138.943	139.688	170.986	131.889	132.613	175.766	136.511	137.240	180.060	140.278	141.021
B3LYP-D3	178.783	138.928	139.671	170.939	131.863	132.587	175.718	136.483	137.211	180.019	140.261	141.003
B97-2	179.388	139.779	140.518	171.036	132.251	132.969	174.319	135.334	136.057	177.729	138.297	139.033

XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
BHandHLYP	184.449	143.613	144.382	174.456	134.588	135.333	177.929	137.946	138.693	181.172	140.796	141.555
mPW1PW91	182.028	142.388	143.126	173.693	134.873	135.593	177.348	138.332	139.055	180.689	141.226	141.961
PBE0	181.221	141.644	142.382	172.864	134.112	134.829	176.480	137.540	138.262	179.956	140.560	141.294
X3LYP	178.130	138.186	138.932	170.174	131.029	131.756	174.946	135.645	136.375	179.355	139.521	140.266
BMK	183.169	143.037	143.783	174.698	135.917	136.636	179.140	140.176	140.898	182.335	142.707	143.426
M05-2X	189.376	149.442	150.190	180.538	141.433	142.161	185.667	146.329	147.062	188.241	148.594	149.337
M06	182.161	142.504	143.241	173.476	134.232	134.958	177.323	138.030	138.756	180.505	140.834	141.570
M06-2X	188.135	148.236	148.982	179.535	140.529	141.246	183.868	144.669	145.398	186.792	147.230	147.970
M06-HF	198.212	158.291	159.046	189.659	150.823	151.549	195.200	156.138	156.876	197.625	158.485	158.767
CAM-B3LYP	183.900	143.584	144.342	175.451	135.993	136.730	180.160	140.557	141.297	184.402	144.277	145.030
LC-PBE	193.894	153.283	154.079	184.855	145.311	146.064	188.878	149.189	149.943	191.851	151.800	152.564
LC-ωPBE	189.752	149.319	150.105	180.813	141.400	142.149	184.628	145.055	145.797	187.975	147.946	148.708
ωB97X	186.762	146.381	147.147	177.937	138.558	139.290	181.448	141.984	142.724	185.057	145.171	145.924
ωB97X-D	185.062	145.107	145.859	176.773	137.699	138.424	180.217	141.017	141.745	183.345	143.769	144.512

Table S22: IP values (in kcal/mol) computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM) for the HOMO of gallic acid.

XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
SVWN5	182.272	139.332	140.123	177.972	134.734	135.530	184.156	140.753	141.551	189.166	145.396	146.204
BLYP	175.731	132.051	132.859	170.634	126.960	127.767	176.593	132.668	133.479	182.628	138.160	138.984
PBE	179.464	136.347	137.146	174.422	131.126	131.924	179.481	135.919	136.722	184.860	140.780	141.595
TPSS	180.728	137.227	138.032	174.709	131.392	132.196	179.569	135.728	136.536	184.172	139.926	140.744
VSXC	181.493	137.695	138.503	175.418	131.522	132.332	179.061	135.027	135.839	184.346	139.928	140.750
B1LYP	182.648	138.525	139.340	176.092	131.894	132.709	180.879	136.510	137.328	194.492	141.033	141.861
B3LYP	185.446	141.417	142.232	179.235	135.133	135.945	184.178	139.898	140.714	189.110	144.430	145.257
B3LYP-D3	185.428	141.396	142.209	179.206	135.118	135.932	184.154	139.889	140.706	189.093	144.430	145.255
B97-2	185.722	141.924	142.732	178.987	135.138	135.946	182.547	138.476	139.289	194.283	142.191	143.013
BHandHLYP	188.241	143.917	144.735	180.139	135.703	136.507	183.909	139.297	140.120	187.855	142.973	143.788
mPW1PW91	187.543	143.797	144.603	180.848	137.010	137.817	184.790	140.728	141.540	188.812	144.403	145.224
PBE0	186.714	143.002	143.807	180.007	136.204	137.010	183.906	139.890	140.700	196.070	143.700	144.519
X3LYP	184.577	140.525	141.339	178.270	134.139	134.952	183.201	138.896	139.713	188.259	143.542	144.369
BMK	187.630	143.444	144.262	181.159	136.843	137.658	185.781	141.496	142.318	196.884	144.292	145.108
M05-2X	193.171	149.385	150.193	186.297	142.094	142.906	191.581	147.232	148.049	195.091	150.405	151.229
M06	187.585	143.913	144.718	181.064	137.065	137.876	185.144	140.960	141.775	189.137	144.631	145.458
M06-2X	192.655	148.916	149.722	185.684	141.637	142.448	190.195	145.955	146.771	201.556	149.368	150.191
M06-HF	199.844	156.601	157.389	193.443	150.011	150.805	198.899	155.215	156.012	201.998	158.070	158.872
CAM-B3LYP	187.386	143.233	144.048	180.822	136.520	137.336	185.758	141.302	142.122	199.712	145.916	146.746
LC-PBE	193.863	150.116	150.924	187.026	142.905	143.718	191.441	147.153	147.969	195.318	150.773	151.596
LC-ωPBE	190.474	146.506	147.319	183.495	139.344	140.158	187.696	143.361	144.180	191.934	147.287	148.113
ωB97X	188.698	144.603	145.418	181.548	137.401	138.215	185.405	141.125	141.943	189.929	145.387	146.213
ωB97X-D	188.115	144.040	144.851	181.290	137.401	138.212	185.087	141.008	141.823	189.149	144.799	145.622

Table S23: IP values (in kcal/mol) computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM) for the HOMO of myricetin.

XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
SVWN5	157.320	124.777	125.371	152.240	119.761	120.351	158.619	126.068	126.657	163.441	130.248	130.851
BLYP	150.678	117.456	118.063	145.035	111.979	112.582	151.259	118.058	118.663	157.112	123.132	123.755
PBE	154.795	122.056	122.652	149.060	116.452	117.046	154.309	121.524	122.120	159.471	125.991	126.604
TPSS	156.208	123.167	123.771	149.880	117.034	117.634	154.677	121.634	122.237	159.089	125.440	126.058
VSXC	156.677	123.476	124.085	150.040	117.060	117.661	154.013	120.905	121.507	159.131	125.446	126.062
B1LYP	160.870	126.648	127.283	153.699	119.779	120.408	158.779	124.719	125.350	163.609	128.922	129.567
B3LYP	163.025	129.081	129.707	156.180	122.498	123.120	161.409	127.590	128.215	166.227	131.793	132.432
B3LYP-D3	162.988	129.044	129.671	156.158	122.483	123.105	161.391	127.577	128.202	166.232	131.778	132.414
B97-2	163.356	129.719	130.342	156.015	122.644	123.262	159.797	126.241	126.840	163.757	129.674	130.272
BHandHLYP	168.843	133.553	134.213	160.305	125.410	126.062	164.345	129.308	129.964	168.174	132.650	133.321
mPW1PW91	165.984	132.231	132.852	158.720	125.230	125.843	162.876	129.192	129.790	166.761	132.529	133.147
PBE0	165.174	131.471	132.093	157.877	124.445	125.062	161.975	128.356	128.977	166.003	131.837	132.470
X3LYP	162.383	128.354	128.983	155.437	121.685	122.309	160.666	126.772	127.399	165.629	131.092	131.732
BMK	167.168	132.876	133.520	159.790	125.861	126.456	164.974	130.859	131.511	168.338	134.403	135.042
M05-2X	173.602	139.328	139.965	166.188	132.190	132.828	171.949	137.685	138.331	175.286	140.622	141.274
M06	166.151	132.307	132.934	158.820	124.993	125.619	163.200	129.290	129.917	167.115	132.672	133.310
M06-2X	172.996	138.648	139.286	165.524	131.533	132.170	170.418	136.226	136.867	174.002	139.324	139.974
M06-HF	183.863	148.913	149.581	176.821	142.539	143.185	182.779	148.066	148.965	185.683	150.961	151.613
CAM-B3LYP	168.479	133.592	134.245	161.257	126.690	127.337	166.472	131.760	132.409	171.398	136.085	136.750
LC-PBE	177.690	142.392	143.060	170.290	135.295	135.960	174.875	139.707	140.376	178.610	143.079	143.753
LC-ωPBE	173.885	138.713	139.376	166.438	131.581	132.241	170.843	135.780	136.443	174.948	139.353	140.024

XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
ωB97X	171.420	136.215	136.879	163.779	128.974	129.620	167.867	133.054	133.713	172.222	136.924	137.599
ωB97X-D	169.699	135.074	135.735	162.365	128.007	128.634	166.354	132.082	132.728	170.228	135.361	136.033

Table S24: IP values (in kcal/mol) computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM) for the HOMO of phloretin.

XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
SVWN5	161.941	130.995	131.557	159.358	134.268	128.691	166.026	140.613	141.307	169.397	143.573	144.277
BLYP	155.257	123.486	124.065	151.934	125.684	126.463	158.083	126.271	126.849	162.387	130.042	130.560
PBE	159.616	128.359	128.928	156.335	124.903	125.472	161.594	130.093	136.075	165.337	133.315	139.286
TPSS	160.662	129.097	129.677	156.861	125.280	125.852	161.582	135.015	135.741	164.768	137.704	138.445
VSXC	160.937	129.211	129.798	157.410	125.784	126.364	161.346	136.650	137.377	165.222	135.248	140.532
B1LYP	168.263	132.447	133.200	164.086	129.007	129.763	169.117	133.503	134.257	172.489	135.884	136.650
B3LYP	169.847	135.672	136.413	165.842	132.465	133.208	171.026	137.079	137.820	174.428	139.463	140.219
B3LYP-D3	169.817	135.538	136.282	165.830	132.322	133.065	171.004	136.936	137.680	174.402	139.316	140.073
B97-2	170.374	136.203	136.940	166.094	132.679	133.416	169.923	135.950	136.687	172.651	137.813	138.562
BHandHLYP	176.558	142.589	143.408	172.389	134.685	135.481	175.982	138.602	139.399	178.165	140.872	141.682
mPW1PW91	173.499	138.154	138.898	169.351	134.662	135.408	173.562	138.293	139.041	176.211	140.074	140.832
PBE0	172.864	137.674	138.415	168.696	134.149	134.892	172.851	137.725	138.470	175.595	139.592	140.348
X3LYP	169.447	134.746	135.490	165.403	131.466	132.210	170.600	136.099	136.848	174.097	138.565	139.324
BMK	177.153	144.225	145.037	172.864	137.695	138.484	177.628	142.868	143.639	180.213	144.858	145.636
M05-2X	182.021	147.990	148.757	178.477	141.134	141.893	182.810	146.799	147.338	184.458	148.385	154.273
M06	173.236	137.364	138.100	169.161	133.814	134.561	174.161	138.344	139.094	176.737	140.045	140.832
M06-2X	182.521	148.928	149.718	179.198	142.188	142.954	182.903	146.795	147.574	184.900	148.863	149.651
M06-HF	197.998	156.443	157.219	189.925	149.878	150.628	195.557	155.443	156.209	197.752	157.014	157.790
CAM-B3LYP	170.782	137.842	138.608	174.909	136.162	136.936	179.400	141.423	142.212	182.121	144.405	145.201
LC-PBE	189.871	149.480	150.245	182.781	142.322	143.082	187.392	146.505	147.233	189.620	148.431	149.169
LC-ωPBE	186.437	146.394	147.190	179.459	139.016	139.810	183.833	143.357	144.139	186.453	145.621	146.412
ωB97X	187.611	139.285	140.050	187.228	138.065	138.849	191.427	142.127	142.916	194.388	144.687	145.484
ωB97X-D	170.436	138.720	139.479	175.603	135.349	136.120	179.098	139.009	139.778	181.184	140.741	141.518

S2.6 Statistical Analyses of IPs

Table S25: Overall MAD, MSD, and MAX values (in kcal/mol) calculated regarding the DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p) reference for the IP results computed via DFT approximation with four distinct Pople basis sets in gas-phase or considering water or methanol as solvents (C-PCM).

Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
MAD	SVWN5	16.865	11.944	13.460	20.906	15.007	16.010	14.790	9.011	9.308	10.871	5.453	5.483
	BLYP	24.254	19.727	21.216	28.924	23.404	23.265	23.063	18.575	18.625	18.191	14.133	12.797
	PBE	19.871	14.988	16.581	24.575	19.663	19.801	19.638	14.868	14.198	15.360	11.026	9.342
	TPSS	18.897	14.251	15.885	24.191	19.480	19.642	19.725	14.310	14.560	16.086	11.020	9.963
	VSXC	18.365	13.970	15.561	23.861	19.338	19.609	20.270	14.678	14.821	16.027	11.589	9.718
	B1LYP	15.342	11.956	13.483	21.349	17.734	17.662	16.592	13.160	13.225	11.190	9.634	8.643
	B3LYP	12.894	9.116	10.626	18.604	14.610	14.542	13.701	9.897	9.988	9.743	6.381	5.991
	B3LYP-D3	12.915	9.162	10.675	18.635	14.647	14.582	13.731	9.929	10.019	9.768	6.409	6.016
	B97-2	12.431	8.509	10.135	18.561	14.408	14.625	15.059	11.133	11.392	10.589	8.328	7.633
	BHandHLYP	11.443	5.879	7.535	18.141	13.743	13.749	14.438	10.130	10.247	11.440	7.275	6.458
	mPW1PW91	10.025	6.315	7.934	16.102	12.194	12.345	12.220	8.543	8.813	9.089	5.806	5.466
	PBE0	10.742	6.979	8.607	16.842	12.882	13.049	13.011	9.273	9.531	8.804	6.423	5.991
	X3LYP	13.600	9.953	11.467	19.405	15.541	15.463	14.501	10.825	10.889	10.429	7.201	6.657
	BMK	9.875	4.985	6.634	15.081	11.415	11.369	10.481	6.826	7.044	7.011	4.264	4.028
	M05-2X	6.857	2.446	3.713	11.720	6.302	6.199	6.838	1.793	1.812	5.131	3.002	1.608
	M06	10.086	6.514	8.100	16.239	12.647	12.671	11.992	8.545	8.783	8.920	5.848	5.523
	M06-2X	6.709	2.144	3.309	11.880	6.439	6.438	7.646	2.234	2.345	5.259	2.230	1.766
	M06-HF	5.951	7.465	6.650	3.613	3.577	11.243	5.417	7.232	15.897	7.070	9.471	16.584
	CAM-B3LYP	10.761	6.860	8.337	15.181	11.629	11.467	9.692	6.809	6.806	6.639	3.142	3.009
	LC-PBE	5.762	3.337	4.029	7.430	4.800	4.746	3.870	2.206	2.132	3.552	3.847	3.175
	LC-ωPBE	5.015	2.705	4.211	11.047	8.350	8.326	6.929	3.936	4.056	3.930	2.203	2.130
	ωB97X	6.211	4.849	6.375	11.708	10.505	10.494	7.861	6.271	6.349	4.371	3.451	3.278
	ωB97X-D	9.909	5.595	7.111	14.141	10.799	10.858	9.825	7.196	7.375	7.479	4.427	4.149
MSD	SVWN5	−17.727	−11.925	−12.069	−21.794	−14.990	−16.156	−15.654	−8.993	−9.114	−11.648	−5.437	−5.548
	BLYP	−25.001	−19.711	−19.845	−29.706	−23.388	−23.488	−23.817	−18.559	−18.690	−18.848	−14.120	−14.249
	PBE	−20.707	−14.971	−15.115	−25.442	−19.645	−19.789	−20.470	−14.851	−14.089	−16.100	−11.011	−10.240
	TPSS	−19.680	−14.234	−14.374	−25.007	−19.462	−19.600	−20.507	−14.293	−14.402	−16.789	−11.006	−11.103
	VSXC	−19.113	−13.955	−14.086	−24.649	−19.321	−19.452	−21.029	−14.662	−14.769	−16.711	−11.575	−10.912

| Statistics	XC Functional	6-31G			6-31G(d,p)			6-311G(d,p)			6-311+G(d,p)		
		Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH	Gas	H$_2$O	CH$_3$OH
	B1LYP	−15.986	−11.943	−12.030	−22.023	−17.719	−17.811	−17.247	−13.146	−13.235	−11.774	−9.622	−9.700
	B3LYP	−13.557	−9.102	−9.195	−19.300	−14.595	−14.692	−14.376	−9.883	−9.977	−10.348	−6.368	−6.451
	B3LYP-D3	−13.581	−9.148	−9.242	−19.333	−14.632	−14.729	−14.407	−9.915	−10.009	−10.372	−6.397	−6.481
	B97-2	−13.147	−8.494	−8.590	−19.311	−14.392	−14.494	−15.777	−11.118	−11.220	−11.243	−8.315	−8.408
	BHandHLYP	−12.029	−5.866	−5.952	−18.749	−13.730	−13.807	−15.030	−10.117	−10.189	−11.978	−7.263	−7.327
	mPW1PW91	−10.741	−6.300	−6.399	−16.847	−12.178	−12.279	−12.939	−8.527	−8.629	−9.743	−5.792	−5.882
	PBE0	−11.466	−6.964	−7.062	−17.594	−12.866	−12.968	−13.738	−9.258	−9.357	−9.089	−6.409	−6.497
	X3LYP	−14.258	−9.939	−10.031	−20.094	−15.526	−15.621	−15.170	−10.811	−10.903	−11.025	−7.189	−7.270
	BMK	−10.560	−4.968	−5.105	−15.734	−11.402	−11.490	−11.117	−6.812	−6.896	−6.961	−4.251	−4.341
	M05-2X	−6.696	−0.231	−0.357	−12.364	−6.337	−6.378	−7.263	−1.186	−1.264	−4.647	1.151	1.976
	M06	−10.790	−6.499	−6.582	−16.945	−12.632	−12.730	−12.673	−8.531	−8.625	−9.541	−5.836	−5.914
	M06-2X	−6.955	−0.517	−0.590	−12.539	−6.426	−6.514	−8.191	−2.112	−2.195	−2.678	0.538	0.461
	M06-HF	4.348	7.478	8.206	−2.467	1.208	9.883	2.977	7.245	16.156	5.398	9.484	18.444
	CAM-B3LYP	−11.348	−6.847	−6.935	−15.790	−11.616	−11.699	−10.288	−6.797	−6.875	−5.575	−3.131	−3.197
	LC-PBE	−3.393	1.782	1.697	−8.042	−4.787	−4.867	−3.691	−0.637	−0.723	−0.745	2.066	1.987
	LC-ωPBE	−5.072	−1.706	−1.760	−11.655	−8.337	−8.414	−7.520	−3.923	−4.006	−4.218	−1.367	−1.435
	ωB97X	−6.792	−4.830	−4.910	−12.305	−10.492	−10.558	−8.446	−6.258	−6.341	−4.913	−3.440	−3.508
	ωB97X-D	−10.553	−5.581	−5.677	−14.777	−10.786	−10.873	−10.445	−7.182	−7.266	−8.052	−4.414	−4.484
MAX	SVWN5	38.925	22.816	23.209	41.508	19.727	26.075	34.840	13.420	13.529	31.469	10.238	10.489
	BLYP	45.609	30.325	30.701	48.932	28.127	28.303	42.783	27.540	27.917	38.479	23.769	24.206
	PBE	41.250	25.452	25.838	44.531	28.908	29.294	39.272	23.718	18.691	35.529	20.496	15.480
	TPSS	40.204	24.714	25.089	44.005	28.531	28.914	39.284	18.796	19.025	36.098	16.107	16.321
	VSXC	39.929	24.600	24.968	43.456	28.027	28.402	39.520	18.583	18.679	35.644	18.563	14.234
	B1LYP	32.603	21.364	21.566	36.780	24.804	25.003	31.749	20.308	20.509	28.377	17.927	18.116
	B3LYP	31.019	18.139	18.353	35.024	21.346	21.558	29.840	16.732	16.946	26.438	14.348	14.547
	B3LYP-D3	31.049	18.273	18.484	35.036	21.489	21.701	29.862	16.875	17.086	26.464	14.495	14.693
	B97-2	30.492	17.608	17.826	34.772	21.132	21.350	30.943	17.861	18.079	28.215	15.998	16.204
	BHandHLYP	24.308	11.222	15.420	28.477	19.126	19.285	24.884	15.209	15.367	22.701	12.939	13.084
	mPW1PW91	27.367	15.657	15.868	31.515	19.149	19.358	27.304	15.518	15.725	24.655	13.737	13.934
	PBE0	28.002	16.137	16.351	32.170	19.662	19.874	28.015	16.086	16.296	25.271	14.219	14.418
	X3LYP	31.419	19.065	19.276	35.463	22.345	22.556	30.266	17.712	17.918	26.769	15.246	15.442
	BMK	23.713	9.586	12.801	28.002	16.116	16.282	23.238	10.943	11.127	20.653	8.953	9.130
	M05-2X	18.845	5.821	8.307	22.389	12.677	12.873	18.056	7.012	7.428	16.408	5.426	3.301
	M06	27.630	16.447	16.666	31.705	19.997	20.205	26.705	15.467	15.672	24.129	13.766	13.934
	M06-2X	18.345	4.883	7.930	21.668	11.623	11.812	17.963	7.016	7.192	15.966	4.948	5.115
	M06-HF	10.058	11.932	11.905	10.941	4.464	48.647	9.066	9.779	55.248	11.235	12.126	57.962
	CAM-B3LYP	30.084	15.969	16.158	25.957	17.649	17.830	21.466	12.388	12.554	18.745	9.406	9.565
	LC-PBE	13.540	6.924	6.938	18.085	11.489	11.684	13.474	7.306	7.533	11.246	5.441	5.597
	LC-ωPBE	14.429	7.417	9.737	21.407	14.795	14.956	17.033	10.454	10.627	14.413	8.190	8.354
	ωB97X	13.255	14.526	14.716	13.638	15.746	15.917	9.531	11.684	11.850	6.478	9.124	9.282
	ωB97X-D	30.430	15.091	15.287	25.263	18.462	18.646	21.768	14.802	14.988	19.682	13.070	13.248
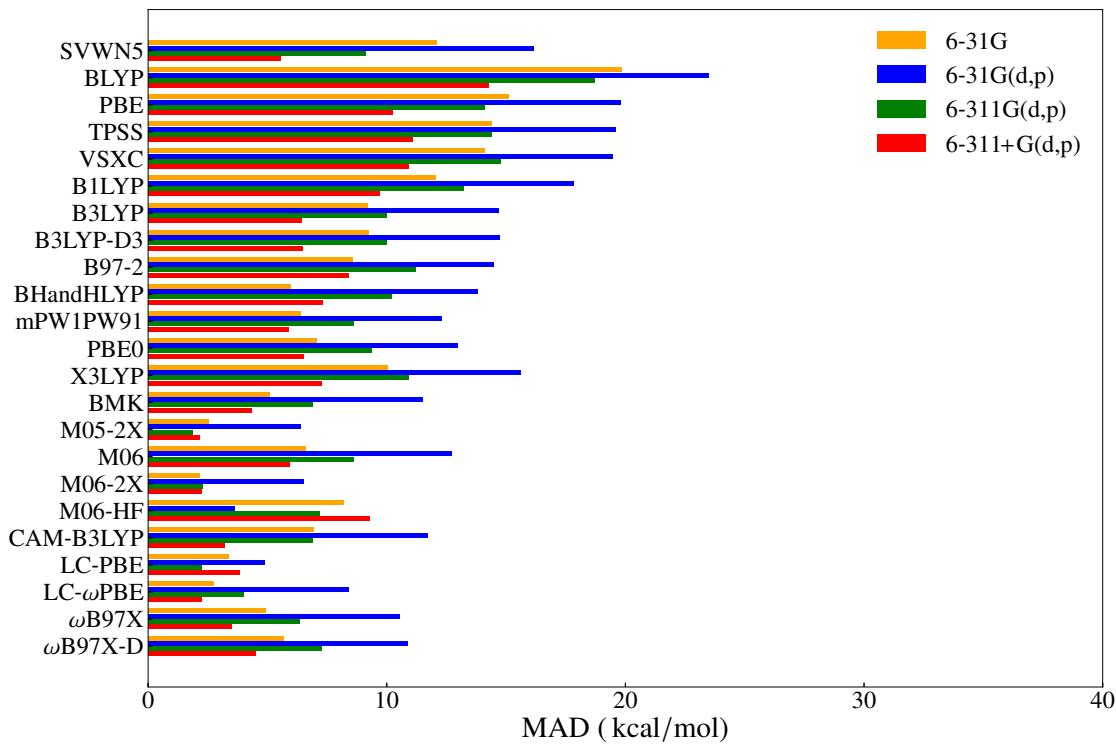
Figure S3: Mean absolute deviation (MAD) values, considering the IPs for all molecules under study as determined in methanol (C-PCM). Benchmark results are DLPNO-CCSD(T)/CBS[DZ-TZ,def2]//M06-2X/6-311+G(d,p).