Supporting Information

We estimated the rate constant of the reaction between coumarin boronate and DEPMPO-superoxide adduct (DEPMPO-$^{\bullet}$OOH) by monitoring the formation of a highly fluorescent product, 7-hydroxycoumarin. The DEPMPO-OOH adduct was generated in incubations containing xanthine (X, 200 µM), xanthine oxidase (XO, generating a flux of $O_2^{\bullet-}$ of 6 µM/min), DEPMPO (20 mM) and DTPA (100 µM) in a phosphate buffer (50 mM, pH 7.4). After a 10 min incubation, the formation of DEPMPO-$^{\bullet}$OOH spin adduct was inhibited by adding SOD (0.05 mg/ml). Following the addition of CBE to the reaction mixture, the formation of COH was measured by monitoring the fluorescence intensity (excitation at 332 nm, emission at 450 nm) and the pseudo-first order rate constant was determined. The second order rate constant of that reaction calculated from the dependence of the pseudo-first order rate constants on CBE concentrations (see Figure S1) was *ca*. 39 $M^{-1}s^{-1}$. The quantitative data on the yield of the products of the reaction of APBA with $ONOO^-$ in the absence and presence of radical scavengers/H-atom donors are presented in Supporting Information, Figure S2. These materials also include the optimized geometries of all stationary points, the calculated spin and charge distribution (Tables S1 and S2) as well as a complete reference (*16*) (G09).

Supporting Information - Tables

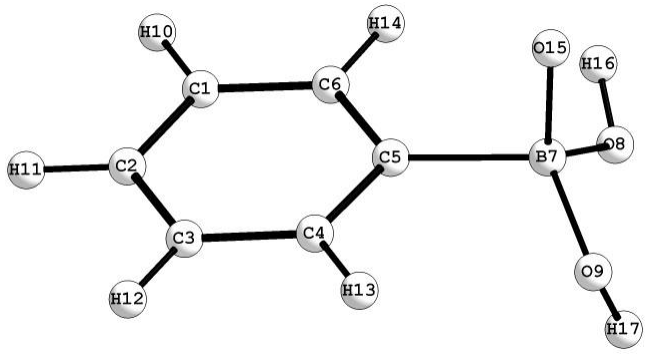


Table S1. PCM/M06-2X/6-31+G(d,p) computed APT atomic charges, and spin densities of $PhB(OH)_2O^{\bullet-}$ radical anion (RA), transition state of its fragmentation (carbon-boron bond cleavage) (TS), and the products of fragmentation process (P).

	RA		TS		P	
	CHARGES	SPIN DENSITIES	CHARGES	SPIN DENSITIES	CHARGES	SPIN DENSITIES
1 C	-0.041	-0.016	0.012	0.022	0.002	0.062
2 C	-0.102	0.046	-0.150	-0.010	-0.107	-0.043
3 C	-0.037	-0.019	0.014	0.024	0.007	0.048
4 C	-0.081	0.033	-0.191	-0.026	-0.092	-0.112
5 C	-0.272	0.106	0.440	0.706	-0.013	1.022
6 C	-0.068	0.039	-0.193	-0.035	-0.095	-0.054
7 B	1.414	-0.036	1.528	-0.030	1.887	-0.008
8 O	-1.056	0.008	-1.035	0.009	-1.091	0.007
9 O	-1.034	0.004	-1.018	0.004	-1.074	0.010
10 H	0.025	0.001	0.018	0.005	0.048	0.007
11 H	0.034	-0.002	0.044	0.001	0.059	0.002
12 H	0.023	0.001	0.017	0.006	0.048	0.007
13 H	0.045	0.000	0.075	0.015	0.095	0.023
14 H	0.013	0.000	0.046	0.015	0.083	0.022
15 O	-0.494	0.834	-1.269	0.295	-1.421	0.007
16 H	0.314	-0.001	0.329	-0.001	0.331	0.000
17 H	0.317	-0.001	0.333	-0.001	0.333	-0.001
Ph	-0.461	0.191	0.132	0.723	0.035	0.984
BA	-0.539	0.809	-1.132	0.277	-1.035	0.016

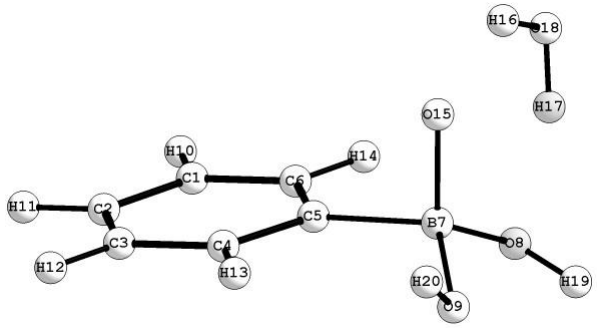


Table S2. PCM/M06-2X/6-31+G(d,p) computed APT atomic charges, and spin densities of $PhB(OH)_2O^{\bullet-}$ radical anion water complex (RA), transition state of $PhB(OH)_2O^{\bullet-}$ water-assisted fragmentation (carbon-boron bond cleavage) (TS), and the products of fragmentation process (P).

	RA		TS		P	
	CHARGES	SPIN DENSITIES	CHARGES	SPIN DENSITIES	CHARGES	SPIN DENSITIES
1 C	-0.046	-0.017	0.016	0.022	0.012	0.039
2 C	-0.089	0.051	-0.136	-0.010	-0.105	-0.042
3 C	-0.050	-0.015	0.000	0.025	-0.010	0.086
4 C	-0.051	0.030	-0.176	-0.063	-0.087	0.141
5 C	-0.274	0.078	0.405	0.704	-0.040	0.979
6 C	-0.069	0.058	-0.210	0.004	-0.129	-0.274
7 B	1.379	-0.035	1.561	-0.023	1.884	-0.003
8 O	-1.089	0.006	-1.052	0.013	-1.081	0.005
9 O	-1.036	0.005	-1.041	0.006	-1.069	0.008
10 H	0.024	0.001	0.021	0.005	0.047	0.007
11 H	0.034	-0.002	0.046	0.001	0.060	0.003
12 H	0.027	0.001	0.022	0.006	0.050	0.007
13 H	0.025	0.000	0.079	0.015	0.084	0.020
14 H	0.049	0.000	0.091	0.015	0.171	0.025
15 O	-0.532	0.840	-1.360	0.284	-1.500	-0.002
16 H	0.461	-0.002	0.721	-0.004	0.785	0.000
17 H	0.514	0.000	0.365	0.000	0.341	0.000
18 O	-0.916	0.002	-1.014	0.002	-1.082	0.000
19 H	0.318	0.001	0.333	-0.001	0.331	0.000
20 H	0.322	0.000	0.330	-0.001	0.338	0.000
Ph	-0.421	0.185	0.156	0.723	0.052	0.992
BA	-0.638	0.815	-1.229	0.279	-1.096	0.008
H2O	0.059	0.000	0.073	-0.002	0.045	0.000

Supporting Information - Figure Legends

Figure S1. Determination of the rate constant of the reaction between DEPMPO-$^{\bullet}$OOH spin adduct and CBE. Xanthine (X, 200 μM), xanthine oxidase (XO, generating a flux of $O_2^{\bullet-}$ of 4 μM/min) and DEPMPO (20 mM) were pre-incubated in a phosphate buffer (50 mM, pH 7.4) containing DTPA (100 μM). Ten minutes after the reaction, the accumulation of the DEPMPO-$^{\bullet}$OOH adduct was stopped by adding SOD (8 μg/ml). After the addition of CBE, the formation of COH was followed by monitoring the fluorescence intensity (excitation at 332 nm, emission at 450 nm) and the pseudo-first order rate constant was determined.

Figure S2. The effect of H-atom donors/radical scavengers on the yield of major/minor products of the reaction between APBA and $ONOO^-$. APBA (250 μM) in phosphate buffer (50 mM, pH 7.4) containing DTPA (100 μM) was reacted with $ONOO^-$ (190 ± 10 μM) in the absence and presence of radical scavengers: GSH (1 mM), NADH (1 mM), $AscH_2$ (1 mM), MeCN (2.5% by vol.), MNP (20 mM, 2.5% MeCN), 2-PrOH (2.5% by vol.), tyrosine (2 mM) and ABTS (2 mM). Error bars represent standard deviation (n = 3).

Figure S1

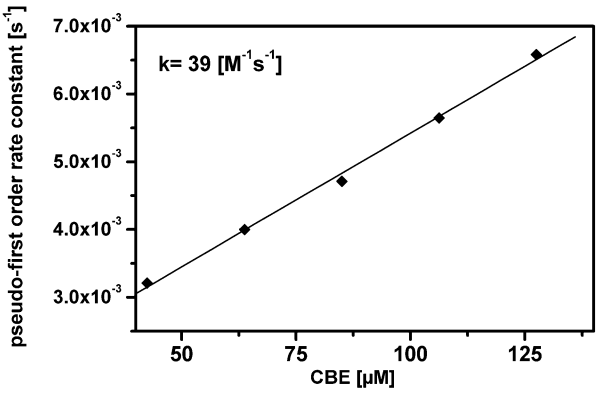
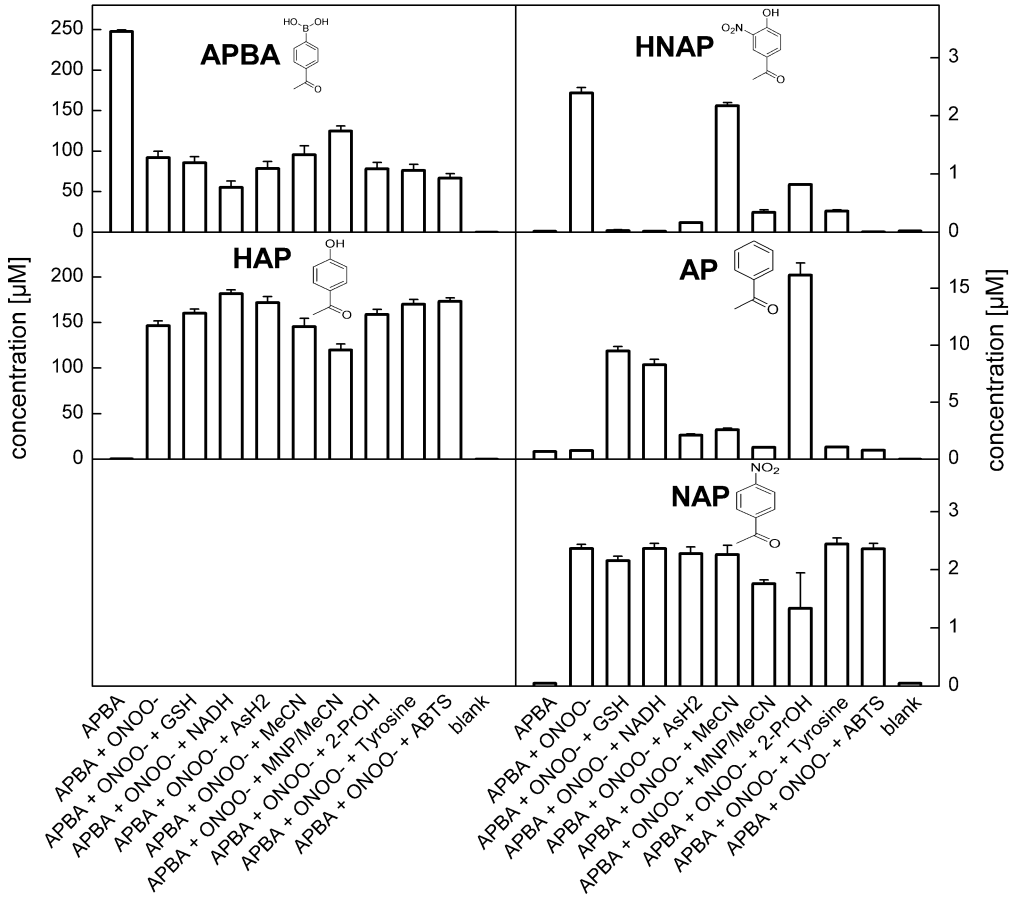

pseudo-first order rate constant [s^{-1}]
7.0x10^{-3}
6.0x10^{-3}
5.0x10^{-3}
4.0x10^{-3}
3.0x10^{-3}
k= 39 [M^{-1}s^{-1}]
50
75
100
125
CBE [µM]

Figure S2


APBA
HNAP
HAP
AP
NAP
concentration [µM]
concentration [µM]
APBA
APBA + ONOO-
APBA + ONOO- + GSH
APBA + ONOO- + NADH
APBA + ONOO- + AsH2
APBA + ONOO- + MeCN
APBA + ONOO- + MNP/MeCN
APBA + ONOO- + 2-PrOH
APBA + ONOO- + Tyrosine
APBA + ONOO- + ABTS
blank

Full reference 16:

(16) Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A. Jr., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B. Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W. Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J., and Fox, D. J. (2009) *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford CT.

Energies and geometries of all stationary points located

and characterized in the course of this study;

Note: All structures are optimized taking into account the influence of the environment, which was modeled using the polarizable continuum solvent model (PCM) with parameters for water as implemented in Gaussian 09; energies are in hartree.

Radical Anion

-1 2

6	2.166819000	-1.196418000	-0.067101000
6	2.861713000	0.014439000	-0.087331000
6	2.150754000	1.215115000	-0.038055000
6	0.755730000	1.198063000	0.028329000
6	0.034435000	-0.004886000	0.031005000
6	0.771888000	-1.197988000	-0.000264000
5	-1.644254000	0.010603000	0.058968000
8	-2.240566000	-1.078198000	-0.738544000
8	-2.195316000	1.276381000	-0.438659000
1	2.712155000	-2.135976000	-0.102036000
1	3.946699000	0.021805000	-0.138897000
1	2.684844000	2.161827000	-0.051407000
1	0.205654000	2.135810000	0.060090000
1	0.251212000	-2.154426000	0.016831000
8	-1.757870000	-0.133995000	1.481164000
1	-2.021449000	-1.931635000	-0.352199000
1	-2.455856000	1.166121000	-1.358411000

Electronic energy= -483.405886
Sum of electronic and zero-point Energies= -483.280659
Sum of electronic and thermal Energies= -483.271006
Sum of electronic and thermal Enthalpies= -483.270062
Sum of electronic and thermal Free Energies= -483.316308

Transition State

-1 2

6	2.275169000	-1.179120000	-0.092241000
6	2.930835000	0.053704000	-0.136535000
6	2.195693000	1.238159000	-0.050976000
6	0.802008000	1.194415000	0.078972000
6	0.170854000	-0.040439000	0.106107000
6	0.882578000	-1.230023000	0.041230000
5	-1.976693000	-0.008053000	0.125912000
8	-2.335684000	-0.995861000	-0.854265000
8	-2.276341000	1.305676000	-0.350383000
1	2.847048000	-2.101480000	-0.154996000
1	4.011694000	0.090676000	-0.233727000
1	2.706357000	2.197406000	-0.084316000
1	0.218819000	2.109557000	0.139256000
1	0.373449000	-2.190299000	0.088490000
8	-1.780332000	-0.271589000	1.418113000
1	-2.184659000	-1.871182000	-0.483012000
1	-2.493206000	1.279608000	-1.288316000

Electronic energy= -483.400330
Sum of electronic and zero-point Energies= -483.275691

Sum of electronic and thermal Energies= -483.266368
Sum of electronic and thermal Enthalpies= -483.265424
Sum of electronic and thermal Free Energies= -483.311314

Phenyl Radical B(OH)2O- Pair

-1 2

6	-2.626195000	1.169858000	0.033986000
6	-3.220151000	-0.091903000	0.110872000
6	-2.439285000	-1.249409000	0.059801000
6	-1.047219000	-1.154885000	-0.069358000
6	-0.513206000	0.113696000	-0.141785000
6	-1.235251000	1.286853000	-0.095532000
5	2.521989000	-0.042927000	0.161599000
8	2.563724000	1.137902000	-0.645187000
8	2.381044000	-1.200263000	-0.653292000
1	-3.240799000	2.064604000	0.073840000
1	-4.297862000	-0.173957000	0.211462000
1	-2.910025000	-2.226485000	0.122130000
1	-0.419491000	-2.039742000	-0.108779000
1	-0.757568000	2.260295000	-0.157165000
8	2.626831000	-0.070781000	1.461665000
1	2.653368000	1.900724000	-0.065009000
1	2.277483000	-0.950931000	-1.577856000

Electronic energy= -483.411137
Sum of electronic and zero-point Energies= -483.285536
Sum of electronic and thermal Energies= -483.275080
Sum of electronic and thermal Enthalpies= -483.274136
Sum of electronic and thermal Free Energies= -483.325197

Radical Anion and Water Complex

-1 2

6	-2.084088000	1.475174000	-0.374514000
6	-3.089752000	0.575272000	-0.015393000
6	-2.750641000	-0.734389000	0.329818000
6	-1.413162000	-1.134955000	0.312560000
6	-0.389167000	-0.253341000	-0.061084000
6	-0.750284000	1.062739000	-0.386233000
5	1.195793000	-0.751901000	-0.118083000
8	1.921662000	0.034932000	-1.138271000
8	1.389668000	-2.171325000	-0.433523000
1	-2.340858000	2.497047000	-0.641282000
1	-4.128504000	0.892695000	-0.002147000
1	-3.527815000	-1.439822000	0.612008000
1	-1.163649000	-2.160328000	0.579795000
1	0.028091000	1.769975000	-0.664791000
8	1.498739000	-0.418097000	1.256271000
1	2.240546000	1.476416000	1.209640000
1	2.496051000	1.579963000	-0.245115000
8	2.613610000	2.105088000	0.570005000
1	2.640434000	-0.505600000	-1.483644000
1	1.249876000	-2.698629000	0.359169000

Electronic energy= -559.824847
Sum of electronic and zero-point Energies= -559.674128
Sum of electronic and thermal Energies= -559.661783
Sum of electronic and thermal Enthalpies= -559.660839
Sum of electronic and thermal Free Energies= -559.713435

Transition State and Water Complex

-1 2

6	2.167981000	1.405557000	0.425825000
6	3.140090000	0.458493000	0.093791000
6	2.759277000	-0.817672000	-0.326417000
6	1.402655000	-1.154415000	-0.415141000
6	0.461517000	-0.201239000	-0.060251000
6	0.809800000	1.080166000	0.337933000
5	-1.550596000	-0.788682000	0.036333000
8	-2.031440000	-0.066490000	1.182350000
8	-1.457245000	-2.208426000	0.164857000
1	2.466410000	2.399752000	0.748185000
1	4.192914000	0.716173000	0.158681000
1	3.516748000	-1.553305000	-0.584865000
1	1.092254000	-2.146202000	-0.732214000
1	0.041136000	1.809277000	0.580743000
8	-1.638429000	-0.224161000	-1.177651000
1	-2.073522000	1.319815000	-0.896111000
1	-2.469675000	2.058716000	0.371846000
8	-2.380783000	2.221454000	-0.575849000
1	-1.954422000	-0.544424000	2.013431000
1	-1.443609000	-2.520731000	1.074556000

Electronic energy= -559.818028
Sum of electronic and zero-point Energies= -559.669328
Sum of electronic and thermal Energies= -559.657105
Sum of electronic and thermal Enthalpies= -559.656161
Sum of electronic and thermal Free Energies= -559.708961

Phenyl Radical, B(OH)2O- and Water Complex

-1 2

6	2.058496000	1.407442000	-0.177933000
6	3.294644000	0.756263000	-0.167254000
6	3.366831000	-0.627256000	0.007233000
6	2.194361000	-1.378418000	0.173160000
6	1.004728000	-0.683045000	0.156203000
6	0.872749000	0.678928000	-0.012930000
5	-2.184361000	-0.717745000	-0.162849000
8	-2.024736000	-0.361164000	1.202965000
8	-2.056114000	-2.084599000	-0.502515000
1	2.012708000	2.484346000	-0.314294000
1	4.207419000	1.329801000	-0.295037000
1	4.331392000	-1.126928000	0.014497000
1	2.234732000	-2.455092000	0.308168000
1	-0.101278000	1.162959000	-0.017763000
8	-2.460008000	0.198362000	-1.063038000
1	-2.364026000	1.552082000	-0.363296000
1	-2.107266000	2.085891000	1.069467000
8	-2.266502000	2.418922000	0.178202000
1	-1.846711000	-2.666952000	0.234044000
1	-1.737144000	-1.073033000	1.782670000

Electronic energy= -559.830786
Sum of electronic and zero-point Energies= -559.680755
Sum of electronic and thermal Energies= -559.667835
Sum of electronic and thermal Enthalpies= -559.666891
Sum of electronic and thermal Free Energies= -559.723360
