

## Supporting Information (SI) for

# Semi-Automated Computational Investigation of the Oxidative Degradation Mechanisms of Bisphenol A in Fenton-Type Processes

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## S1. Zenodo Repository

The most relevant data obtained in this study have been uploaded to the following Zenodo repository:

- <https://doi.org/10.5281/zenodo.15654453>

The contents are briefly explained below.

### 1. AutoMeKin/

This directory contains the possible unimolecular reaction pathways for BPA degradation under Fenton-type conditions, as obtained using AutoMeKin. Each subdirectory—named according to the chemical species described in the article—includes:

- a. A .dat file corresponding to the AutoMeKin input for the species under study.
- b. A .xyz file containing the Cartesian coordinates of the molecular structure.
- c. A FINAL\_LL\*/ subdirectory with the results of the "Low Level" calculations performed using the semi-empirical PM7 method.
- d. A FINAL\_HL\*/ subdirectory with the results of the "High Level" calculations performed using the HF/3-21G method.

Detailed explanations about the installation and use of AutoMeKin can be found at:

- <https://github.com/emartineznunez/AutoMeKin>

### 2. DFT/

This directory contains the results of  $\omega$ B97XD/def2-TZVPP calculations for the chemical species discussed in the article. The content is organized into three subdirectories:

- a. GAS/: Contains Gaussian .log files for the chemical species. Each file is named according to the species name used in the article. For transition states (TS), the accompanying acronyms refer to the minima connected by each TS. TS labels including \_w1 or \_w2 indicate the inclusion of one or two water molecules, respectively.
- b. IRC/: This directory contains .molden files describing the intrinsic reaction path (IRC) associated to each TS in the GAS/ folder.
- c. SMD/: This folder contains the solvent (H<sub>2</sub>O) correction for each of the results contained in GAS/.

### 3. PILGRIM/

This folder contains the input files for the execution with Pilgrim, as well as the corresponding output files.

Detailed explanations about the installation and use of Pilgrim can be found at:

- <https://github.com/cathedralpkg/Pilgrim>

## S2. Gibbs Free Energies and Reaction Rate Constants

The table in the next page summarizes key data for each reaction step. Notice that:

- The `_w1` and `_w2` in the name of the reaction indicate that one or two explicit water molecules were included in the calculation, respectively.
- The RPD column indicates the reaction path degeneracy ( $\sigma$ )
- Third to fifth columns include Gibbs free energies (GFE), given in  $\text{kcal}\cdot\text{mol}^{-1}$  and calculated at the standard reference concentration ( $c^\circ = 1 \text{ M}$ ).

- $\Delta G(\text{rc})$  represents the GFE of reaction:

$$\Delta G(\text{rc}) = G(\text{products}) - G(\text{reactants})$$

- $\Delta G\#$  represents the GFE of activation; forward and backward directions are indicated with (fw) and (bw), respectively:

$$\Delta G\#(\text{fw}) = G(\text{transition state}) - G(\text{reactants})$$

$$\Delta G\#(\text{bw}) = G(\text{transition state}) - G(\text{products})$$

- Notice that the following relationship holds:

$$\Delta G(\text{rc}) = \Delta G\#(\text{fw}) - \Delta G\#(\text{bw})$$

- The last two columns are the thermal rate constants. Their values were computed using eq. (2) for unimolecular reactions ( $\text{s}^{-1}$ ) and eq. (4) for bimolecular reactions ( $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ ).
- The value for the rate constant for the diffusion-controlled step, given by eq. (3), is  $1.232\text{E-}11 \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$  (in water at 298 K).

Reaction	RPD	DG(rc)	DG#(fw)	DG#(bw)	k(fw)	k(bw)
r1C1D	2	-0.3	59.3	59.6	2.090E-31	2.227E-52
r1C1D_w1	2	2.5	56.7	54.2	2.676E-50	1.778E-48
r1C1D_w2	2	6.8	52.6	45.8	2.882E-47	2.791E-42
r2A2B	1	-39.9	50.2	90.1	9.703E-25	8.673E-75
r2A2B_w1	1	-37.2	48.6	85.8	2.390E-44	1.332E-71
r2A2B_w2	1	-32.9	58.4	91.2	1.695E-51	1.377E-75
r2BR09	1	-4.3	10.7	15.0	1.399E-16	1.061E-19
r2BR10	1	-5.2	9.1	14.3	2.309E-15	3.542E-19
r2BR11	1	-9.7	9.9	19.5	6.120E-16	4.949E-23
r3A3B	1	-41.4	46.4	87.7	6.377E-22	5.010E-73
r3A3B_w1	1	-38.6	42.0	80.6	1.621E-39	7.942E-68
r3A3B_w2	1	-34.3	43.5	77.8	1.338E-40	9.553E-66
r3BR12	1	-7.0	8.9	15.9	3.083E-15	2.312E-20
r3BR13	1	-6.1	25.6	31.8	1.668E-27	5.299E-32
r3BR14	1	-8.4	10.1	18.5	3.986E-16	2.634E-22
r4A4B	1	2.8	40.6	37.8	1.102E-17	2.029E-36
r4A4B_w1	1	5.5	39.9	34.4	5.889E-38	6.761E-34
r4A5B	1	-14.1	36.3	50.5	1.421E-14	1.064E-45
r4A5B_w1	1	-11.4	29.4	40.8	2.821E-30	1.317E-38
r4B4C	1	1.5	9.9	8.4	3.696E+05	4.654E+06
r4BR08	1	-60.2	8.2	68.3	1.084E-14	8.673E-59
r4C4D	1	3.0	38.5	35.5	3.937E-16	5.951E-14
r4C4D_w1	1	3.0	24.7	21.8	7.491E-27	1.132E-24
r4E4F	1	-1.7	36.2	37.9	1.723E-14	9.719E-16
r4E4F_w1	1	-1.7	20.5	22.2	9.003E-24	5.079E-25
r4E4F_w2	1	-1.7	14.4	16.1	2.978E-19	1.680E-20
r5A3B	1	-22.3	44.5	66.8	1.403E-20	6.430E-37
r5A3B_w1	1	-22.3	28.4	50.7	1.667E-29	7.640E-46
r5A3B_w2	1	-22.3	18.4	40.7	3.349E-22	1.535E-38
r5BR15	1	-15.1	14.8	29.9	1.419E-19	1.241E-30
rBPAR01	2	-10.3	6.4	16.7	2.195E-13	3.725E+00
rBPAR02	4	-8.8	5.5	14.3	8.524E-13	2.121E+02
rBPAR03	4	-11.9	2.6	14.5	1.130E-11	1.461E+02
rBPAR04	2	-13.1	5.3	18.4	1.214E-12	2.134E-01
rBPAR05	1	-36.7	0.8	37.6	1.226E-11	2.962E-36
rBPAR06	2	-9.7	9.3	19.1	1.493E-15	1.114E-22
rBPAR07	2	-6.8	8.3	15.1	8.979E-15	8.609E-20
rR011B	1	-18.7	11.6	30.4	1.822E+04	5.658E-31
rR022A	1	-58.2			1.232E-11	1.545E-33
rR033A	1	-53.5			1.232E-11	4.469E-30
rR044A	2	-55.4			1.232E-11	1.931E-31
rR055A	4	-47.8			1.232E-11	7.093E-26
rR055B	2	-45.8			1.232E-11	1.982E-24
rR062B	1	-97.2			1.232E-11	4.287E-62
rR073B	1	-100.0			1.232E-11	3.924E-64
rR084E	2	-64.8			1.232E-11	2.439E-38
rR093C	1	-98.4			1.232E-11	5.363E-63
rR103E	1	-99.3			1.232E-11	1.252E-63
rR112C	1	-91.8			1.232E-11	4.005E-58
rR123C	1	-95.8			1.232E-11	4.618E-61
rR133D	1	-100.0			1.232E-11	3.645E-64
rR143E	1	-96.1			1.232E-11	2.471E-61
rR155C	1	-25.1	-1.3	23.8	5.232E+13	3.649E-26
rR1A1C	2	-70.1			1.232E-11	2.940E-42



### S3. Structures of interest along the IRCs

This section presents representative structures along the calculated intrinsic reaction coordinates (IRC) at the  $\omega$ B97XD/def2-TZVPP level of theory. For each IRC, we show the first point, the corresponding transition state, and the final point. The first and last points are close to the respective reactants and products connected by the transition state.

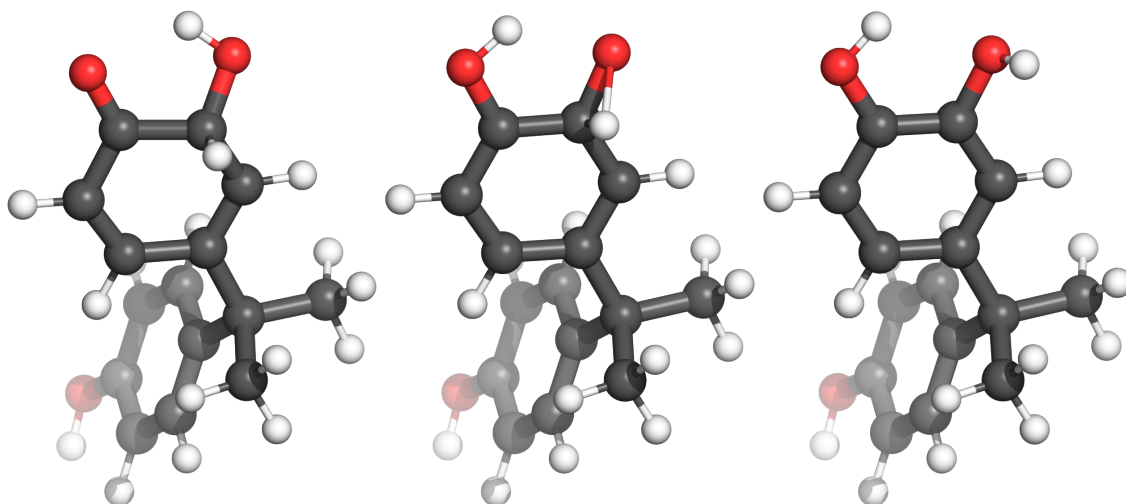


Figure S1: Representative points along the IRC connecting species 5A and 3B. The structure in the center represents the transition state.

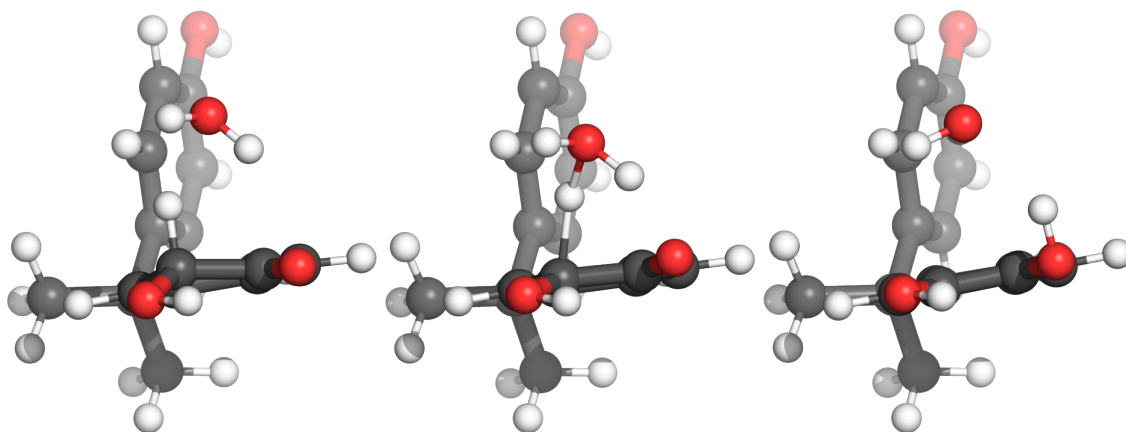


Figure S2: Representative points along the IRC connecting species 5A and 3B. The structure in the center represents the transition state. One explicit water molecule is considered.

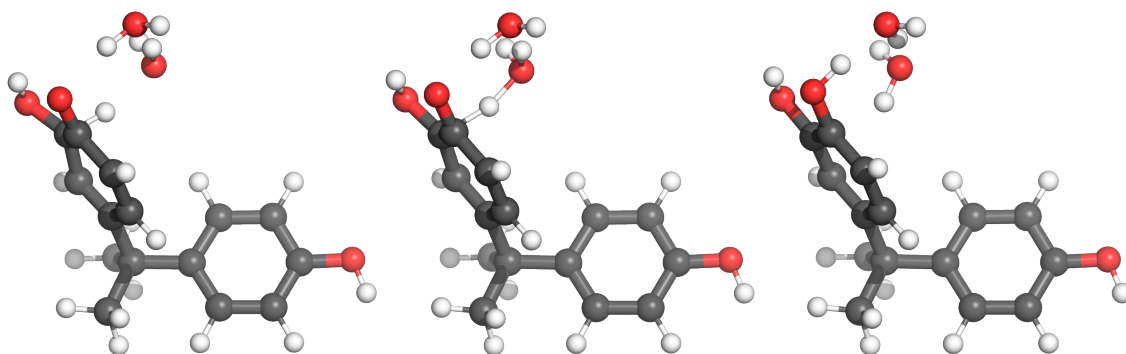


Figure S3: Representative points along the IRC connecting species 5A and 3B. The structure in the center represents the transition state. Two explicit water molecules are considered.

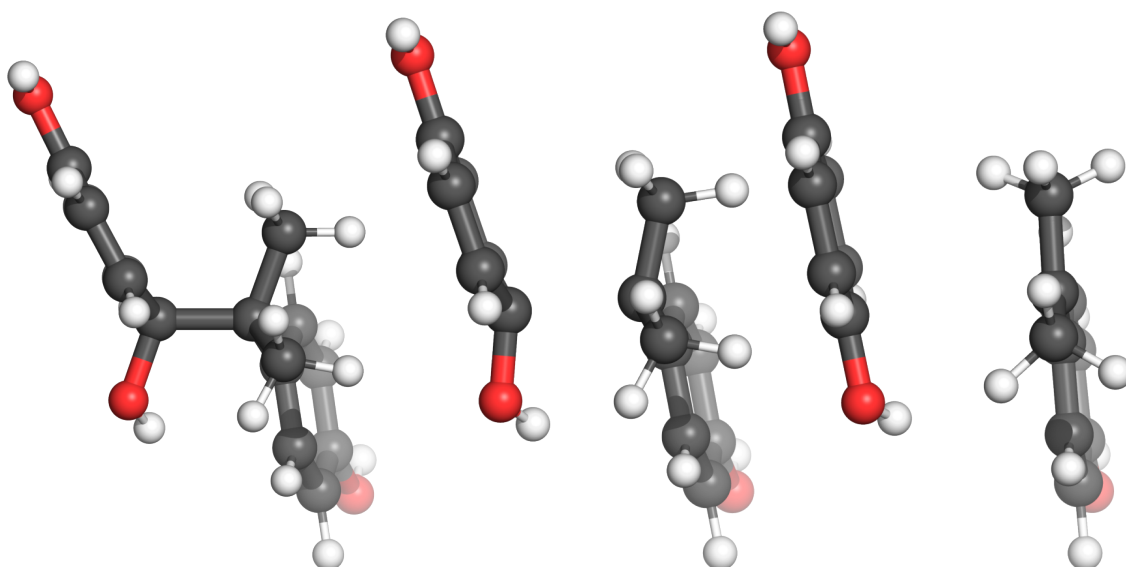


Figure S4: Representative points along the IRC connecting species R01 and 1B. The structure in the center represents the transition state.

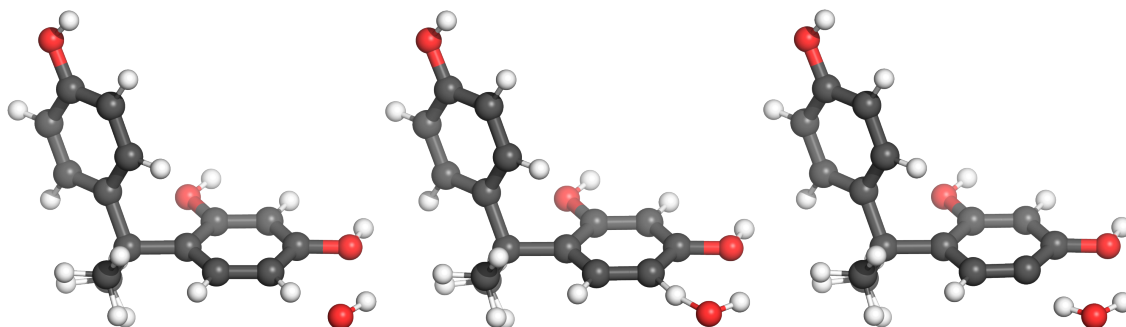


Figure S5: Representative points along the IRC connecting species 2B and R10. The structure in the center represents the transition state.

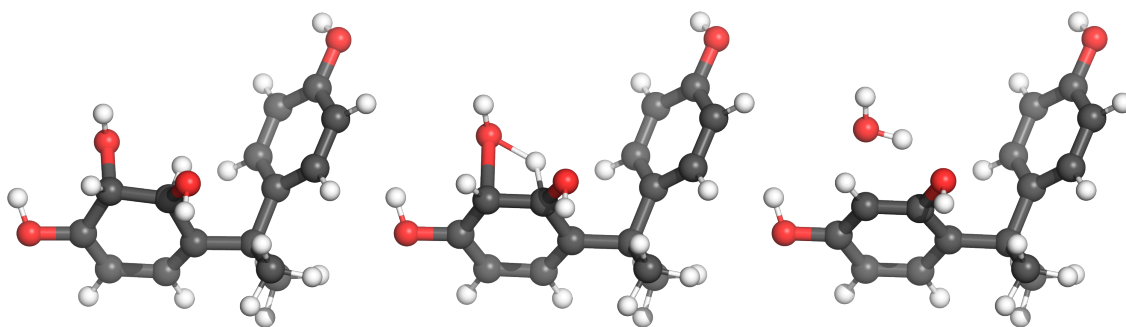


Figure S6: Representative points along the IRC connecting species 2A and 2B. The structure in the center represents the transition state.

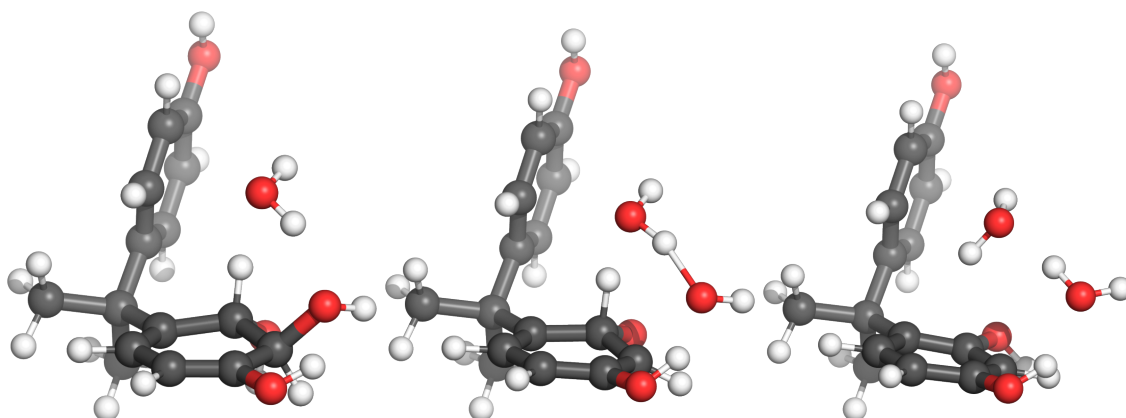


Figure S7: Representative points along the IRC connecting species 2A and 2B. The structure in the center represents the transition state. One explicit water molecule is considered.

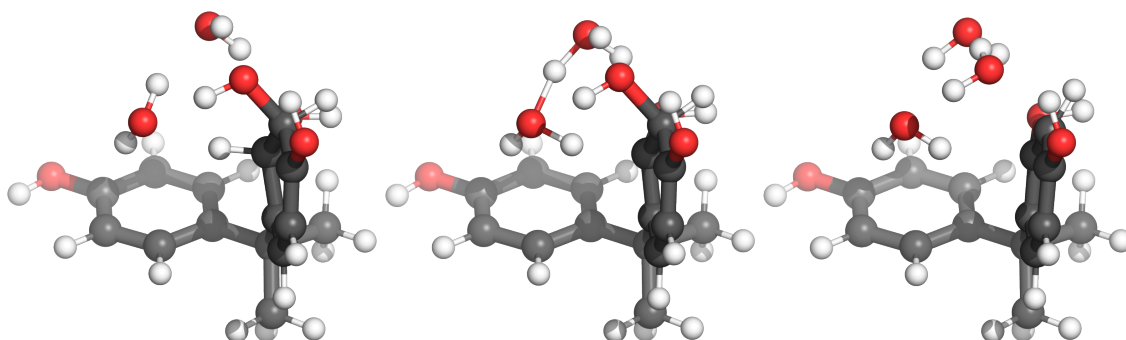


Figure S8: Representative points along the IRC connecting species 2A and 2B. The structure in the center represents the transition state. Two explicit water molecules are considered.

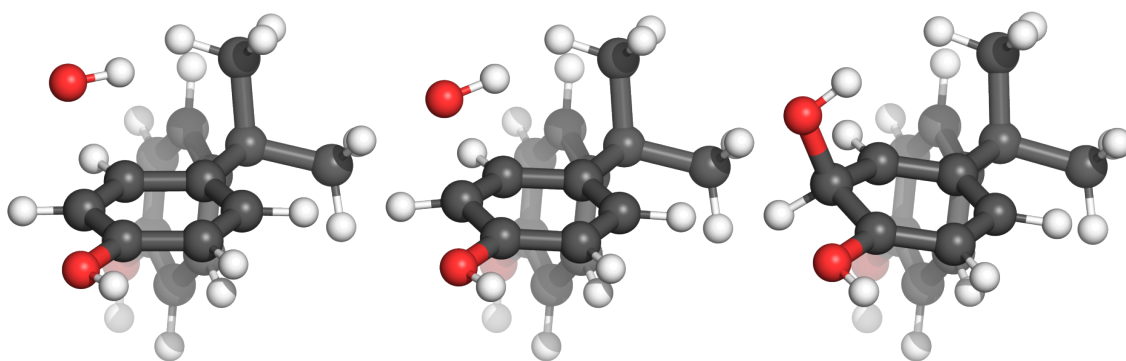


Figure S9: Representative points along the IRC connecting species BPA and R03. The structure in the center represents the transition state.

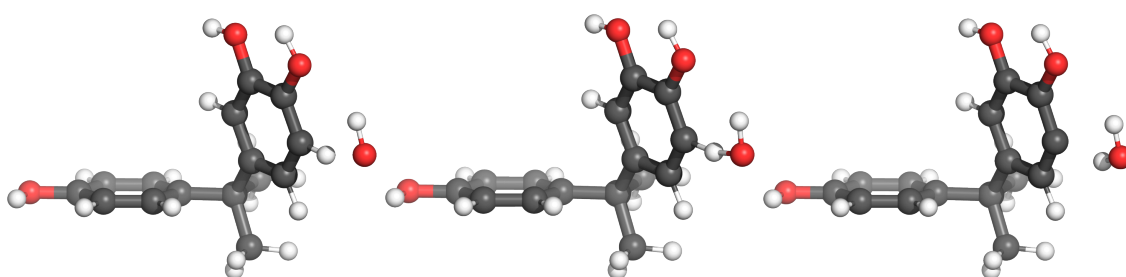


Figure S10: Representative points along the IRC connecting species 3B and R13. The structure in the center represents the transition state.

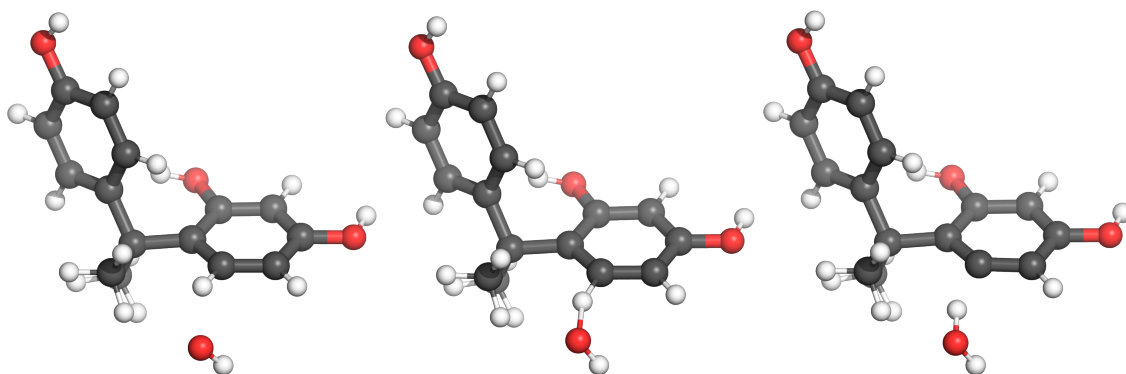


Figure S11: Representative points along the IRC connecting species 2B and R11. The structure in the center represents the transition state.

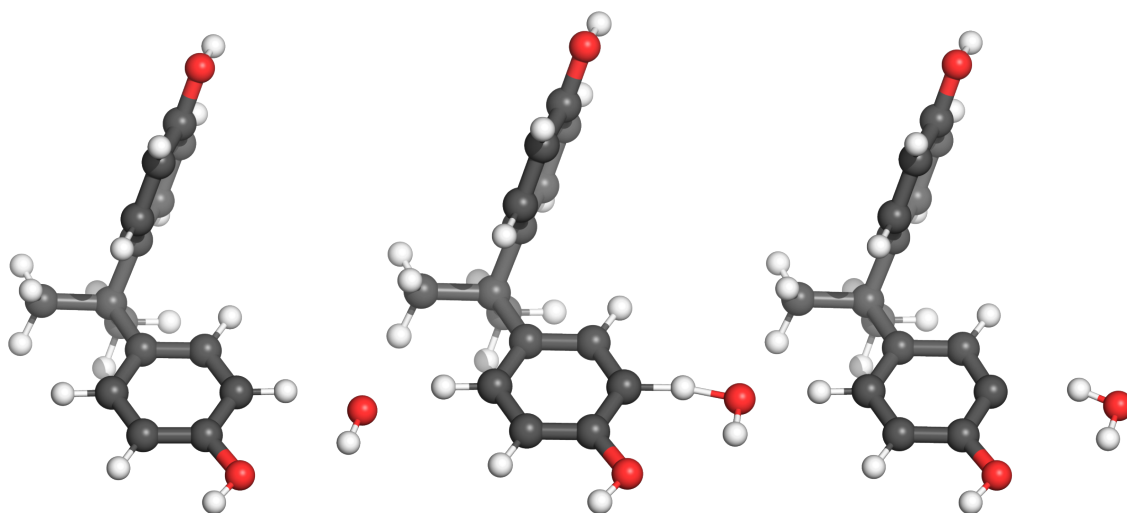


Figure S12: Representative points along the IRC connecting species BPA and R07. The structure in the center represents the transition state.

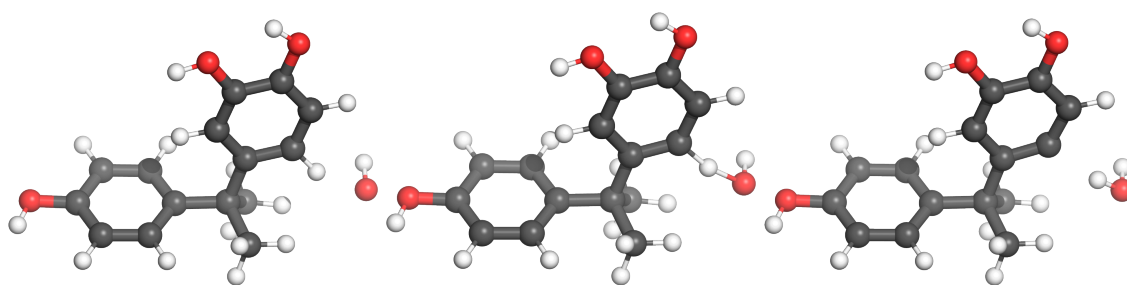


Figure S13: Representative points along the IRC connecting species 3B and R14. The structure in the center represents the transition state.

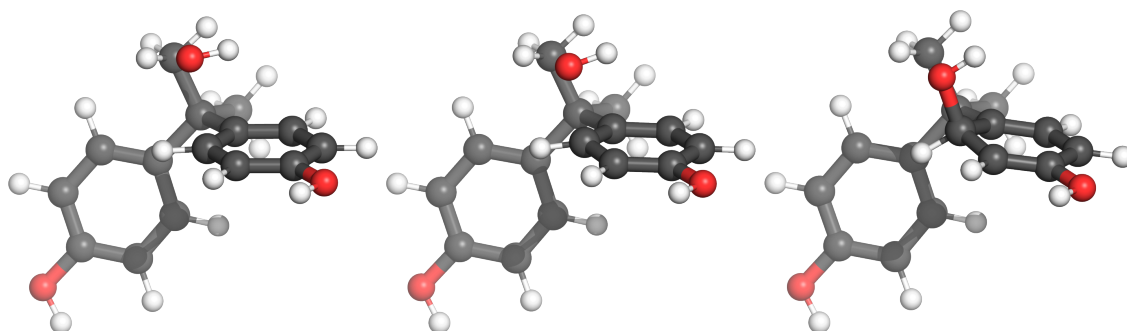


Figure S14: Representative points along the IRC connecting species BPA and R02. The structure in the center represents the transition state.

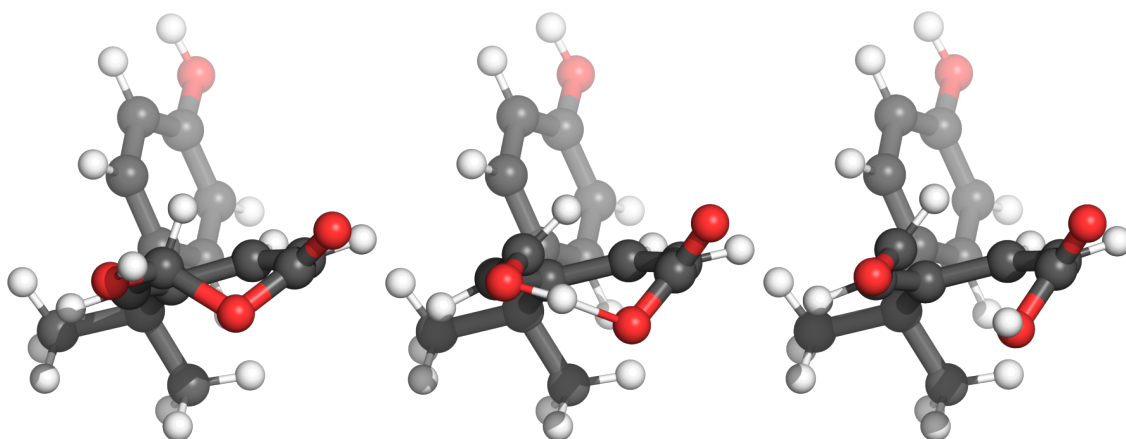


Figure S15: Representative points along the IRC connecting species 4E and 4F. The structure in the center represents the transition state.

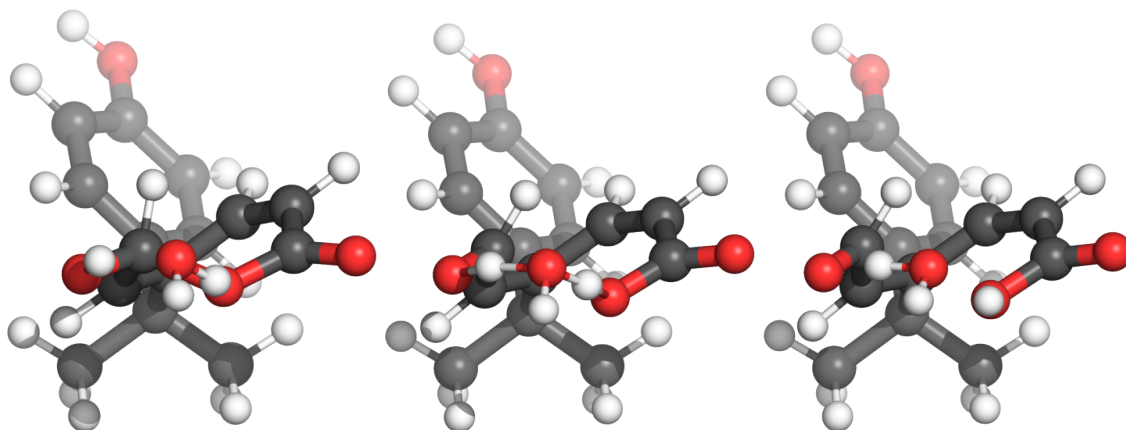


Figure S16: Representative points along the IRC connecting species 4E and 4F. The structure in the center represents the transition state. One explicit water molecule is considered.

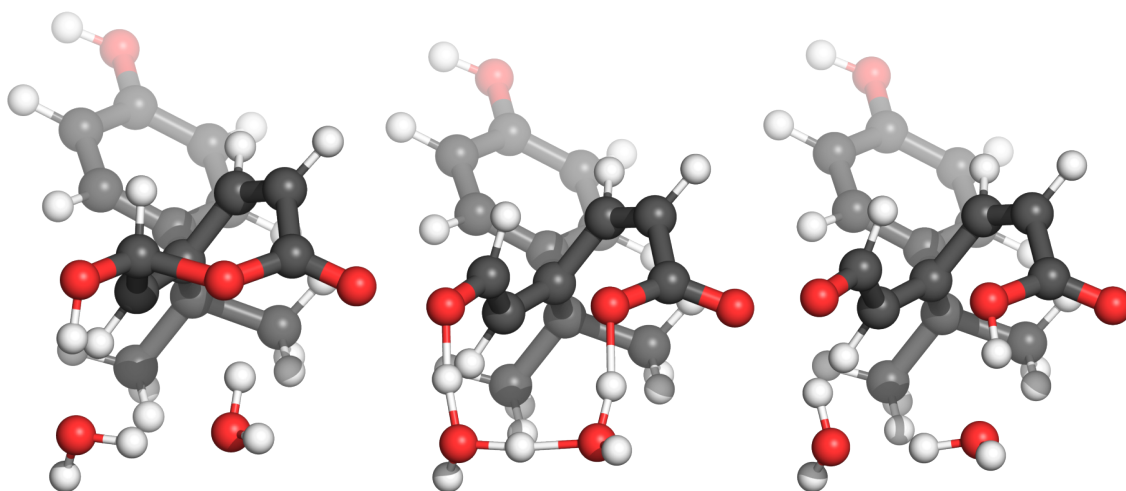


Figure S17: Representative points along the IRC connecting species 4E and 4F. The structure in the center represents the transition state. Two explicit water molecules are considered.

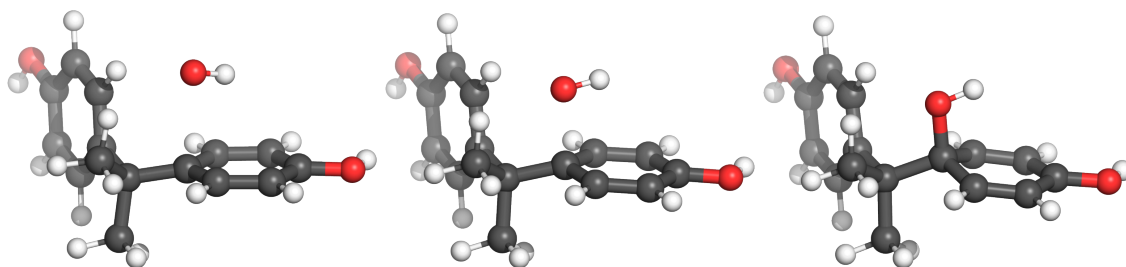


Figure S18: Representative points along the IRC connecting species BPA and R01. The structure in the center represents the transition state.

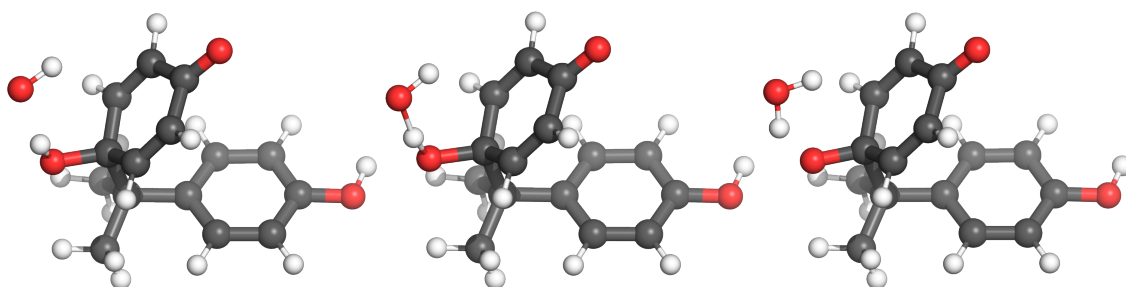


Figure S19: Representative points along the IRC connecting species 5B and R15. The structure in the center represents the transition state.



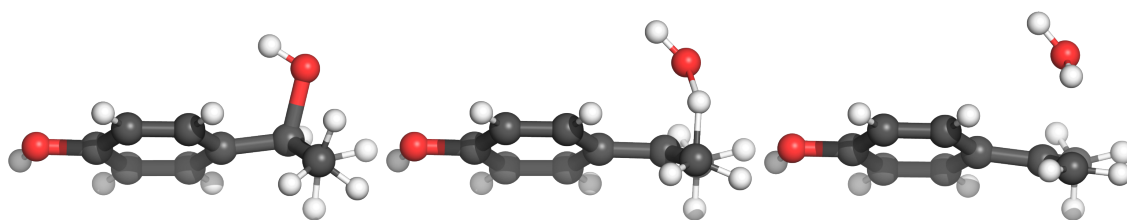


Figure S20: Representative points along the IRC connecting species 1C and 1D. The structure in the center represents the transition state.

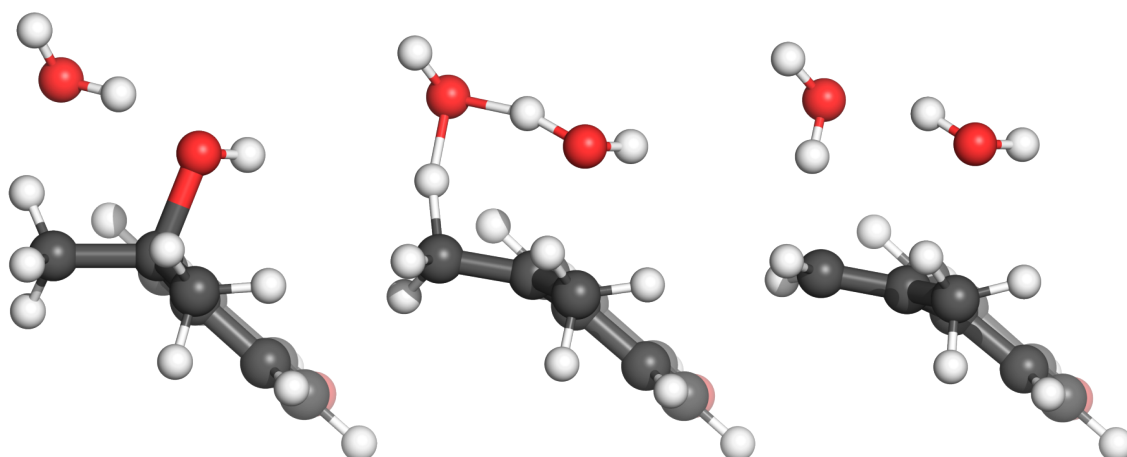


Figure S21: Representative points along the IRC connecting species 1C and 1D. The structure in the center represents the transition state. One explicit water molecule is considered.

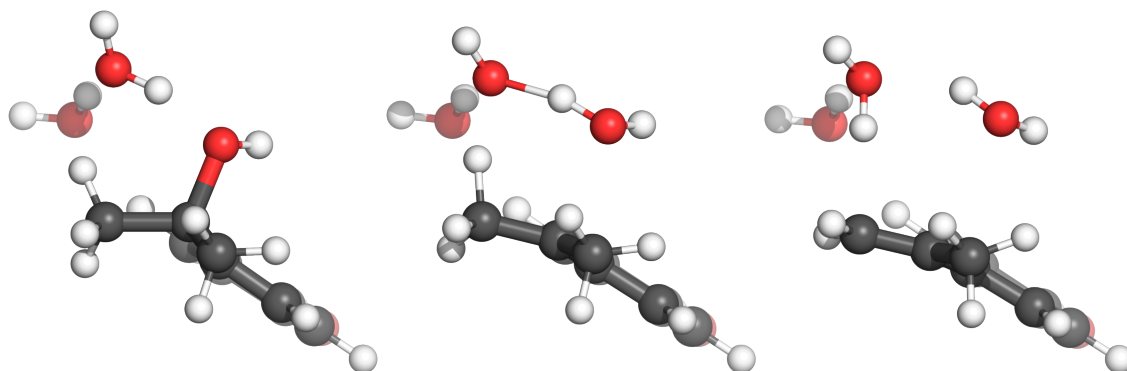


Figure S22: Representative points along the IRC connecting species 1C and 1D. The structure in the center represents the transition state. Two explicit water molecules are considered.



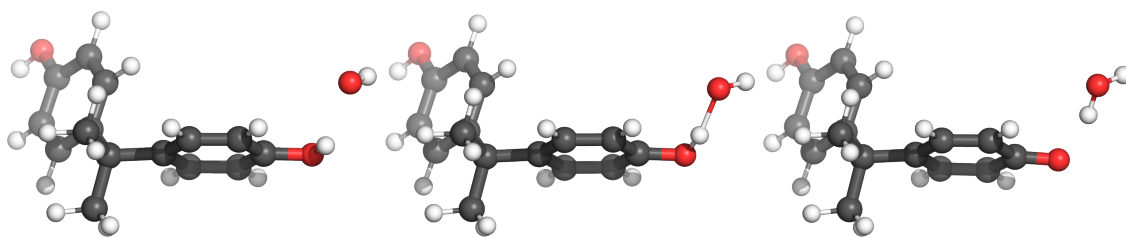


Figure S23: Representative points along the IRC connecting species BPA and R05. The structure in the center represents the transition state.

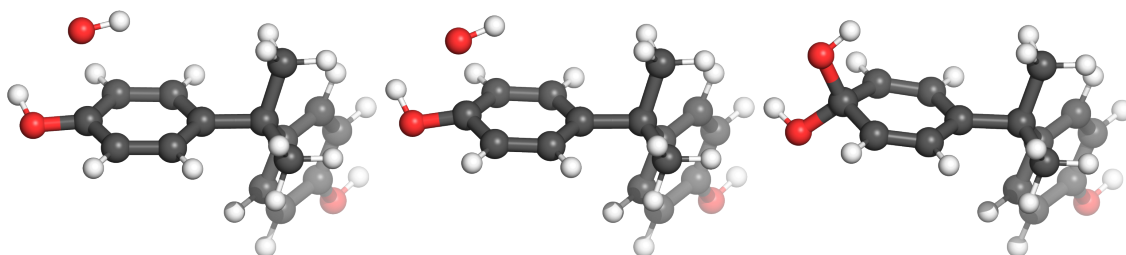


Figure S24: Representative points along the IRC connecting species BPA and R04. The structure in the center represents the transition state.

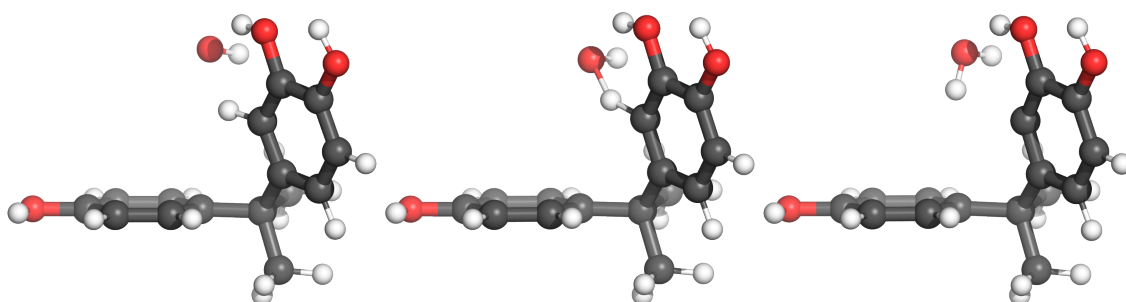


Figure S25: Representative points along the IRC connecting species 3B and R12. The structure in the center represents the transition state.

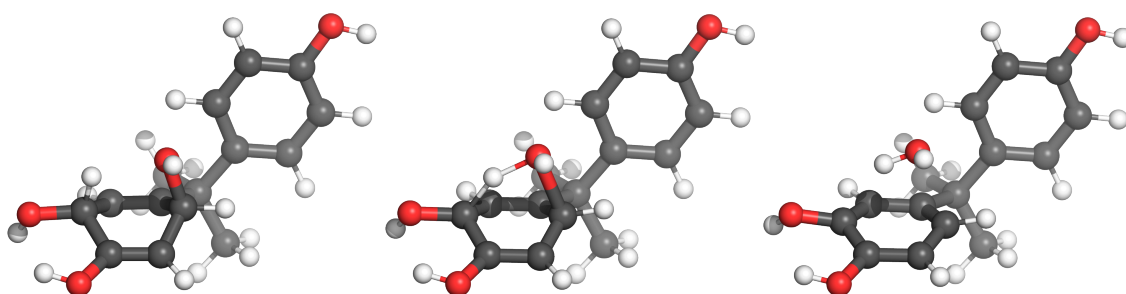


Figure S26: Representative points along the IRC connecting species 3A and 3B. The structure in the center represents the transition state.

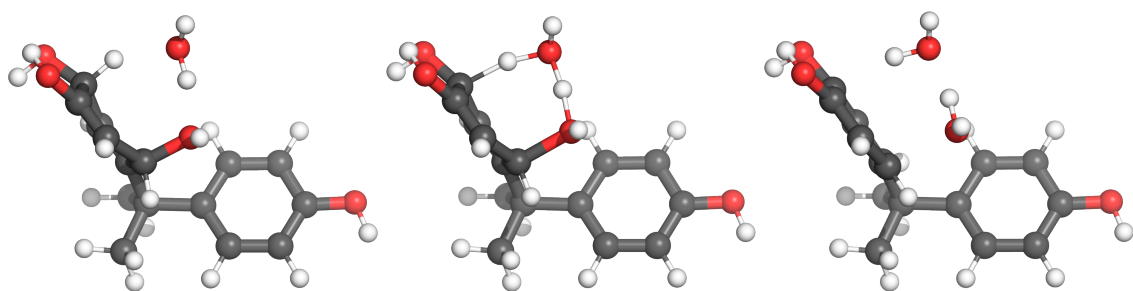


Figure S27: Representative points along the IRC connecting species 3A and 3B. The structure in the center represents the transition state. One explicit water molecule is considered.

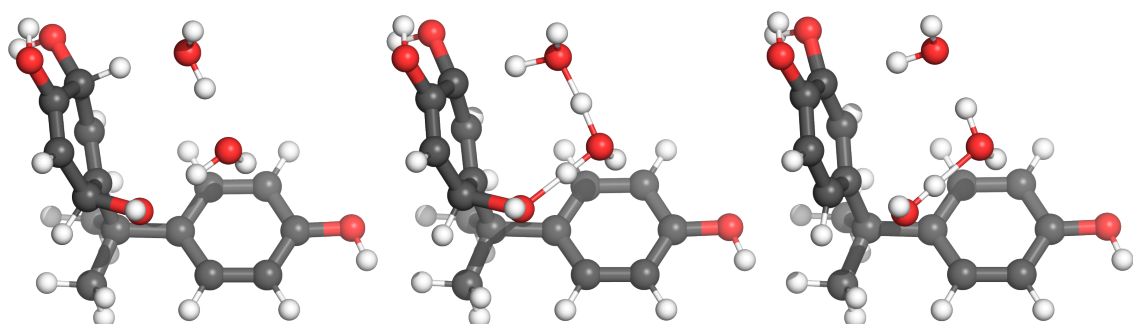


Figure S28: Representative points along the IRC connecting species 3A and 3B. The structure in the center represents the transition state. Two explicit water molecules are considered.

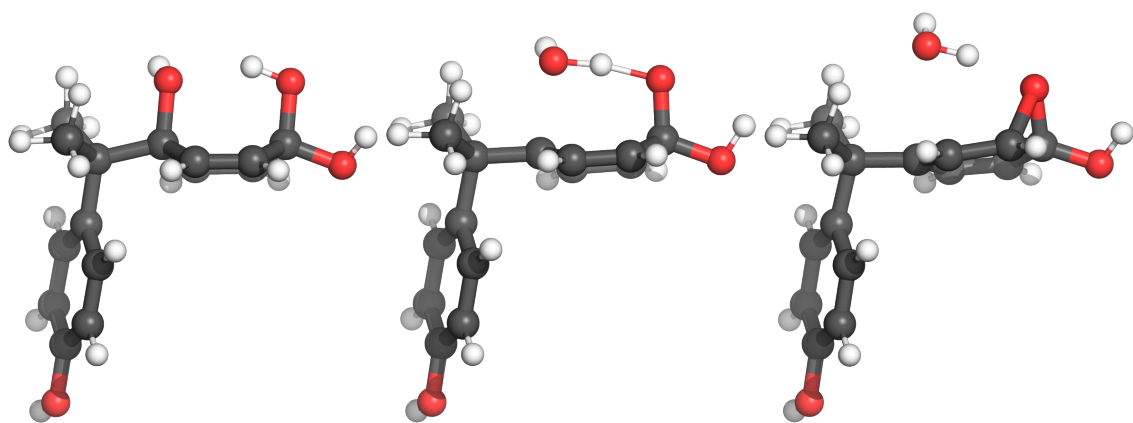


Figure S29: Representative points along the IRC connecting species 4A and 4B. The structure in the center represents the transition state.

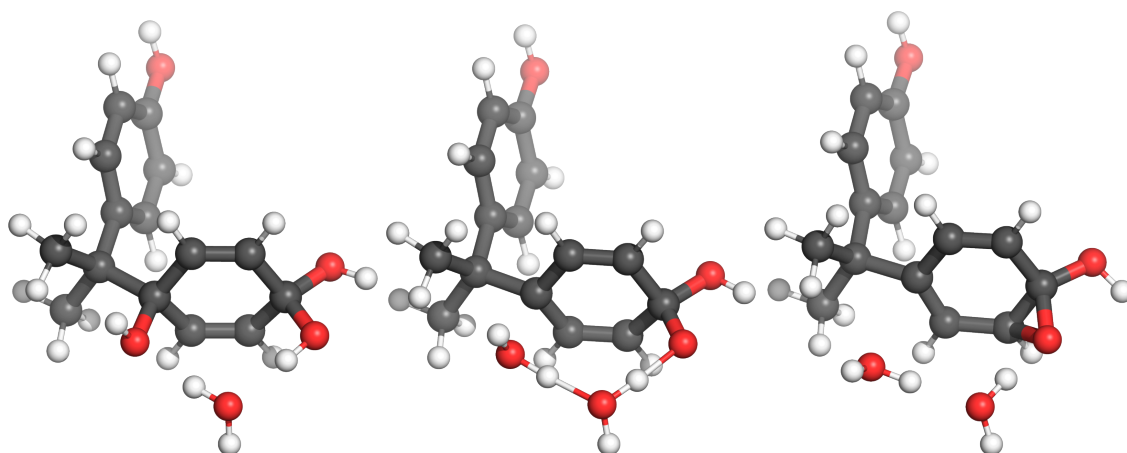


Figure S30: Representative points along the IRC connecting species 4A and 4B. The structure in the center represents the transition state. One explicit water molecule is considered.

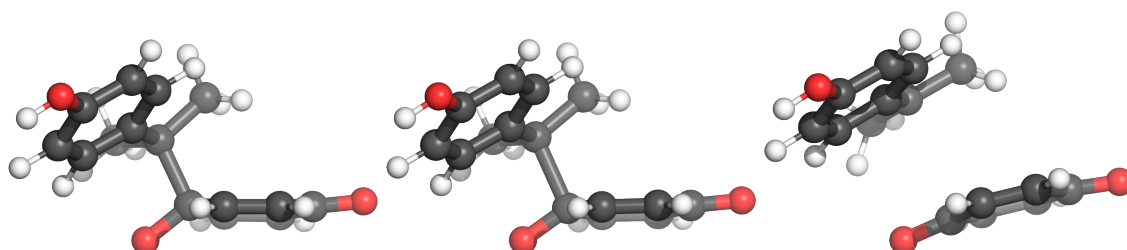


Figure S31: Representative points along the IRC connecting species R15 and 5C. The structure in the center represents the transition state.

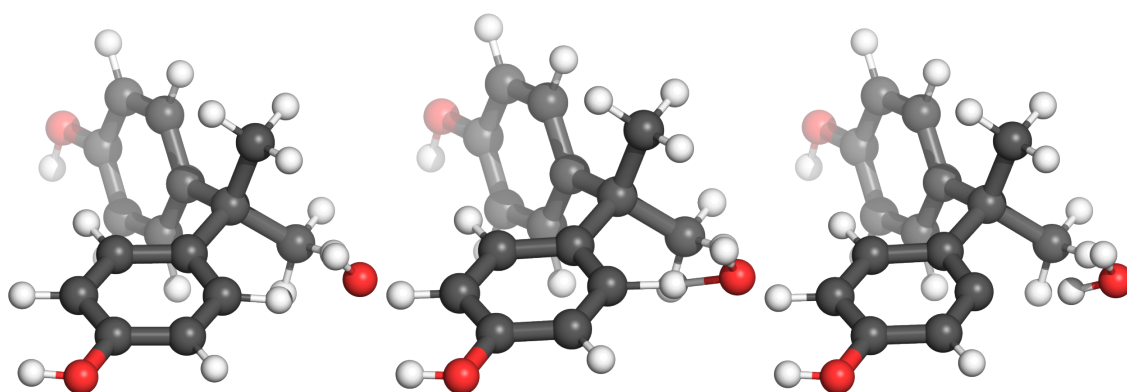


Figure S32: Representative points along the IRC connecting species BPA and R06. The structure in the center represents the transition state.

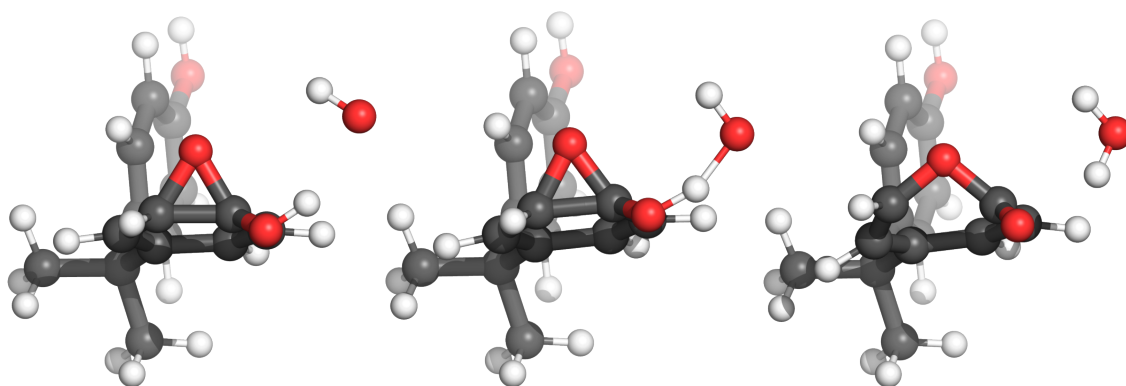


Figure S33: Representative points along the IRC connecting species 4B and R08. The structure in the center represents the transition state.

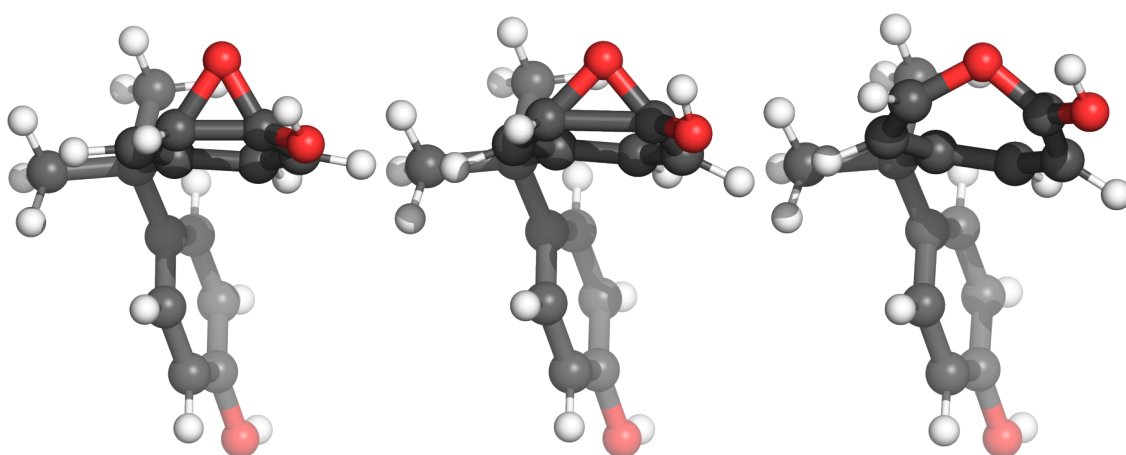


Figure S34: Representative points along the IRC connecting species 4B and 4C. The structure in the center represents the transition state.

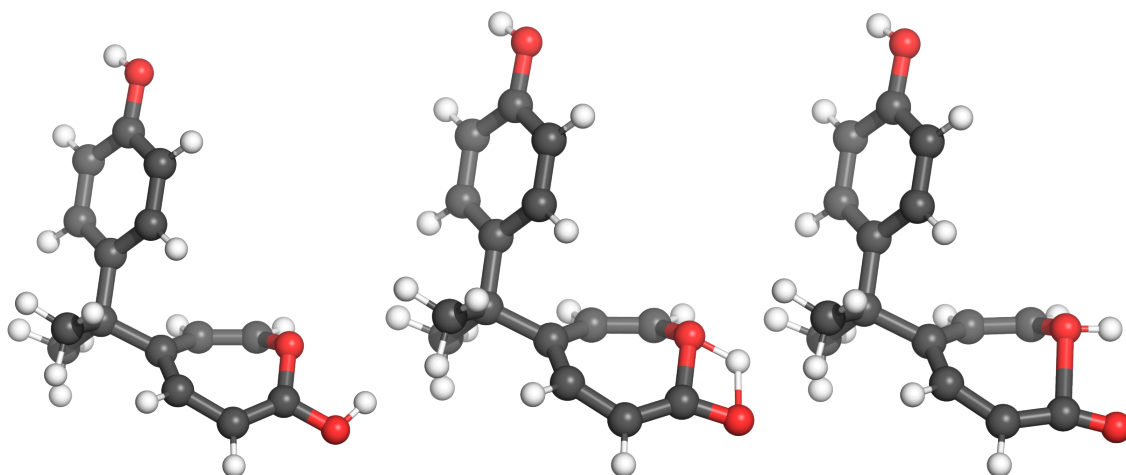


Figure S35: Representative points along the IRC connecting species 4C and 4D. The structure in the center represents the transition state.

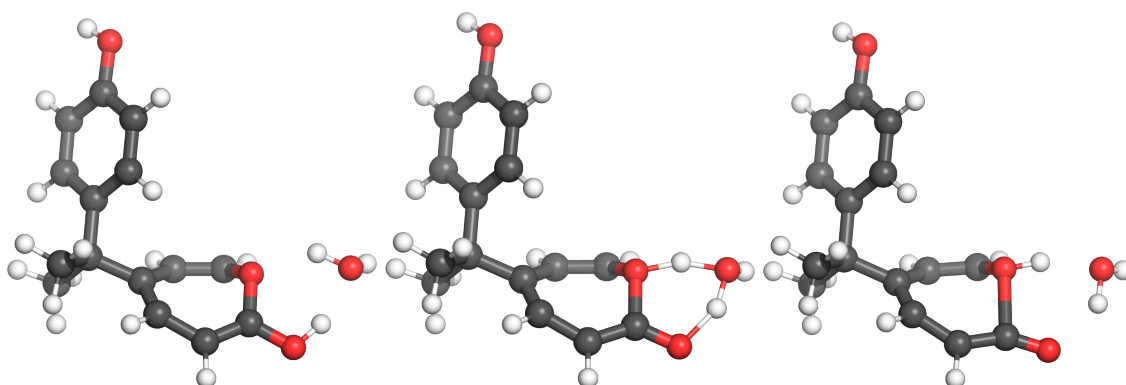


Figure S36: Representative points along the IRC connecting species 4C and 4D. The structure in the center represents the transition state. One explicit water molecule is considered.

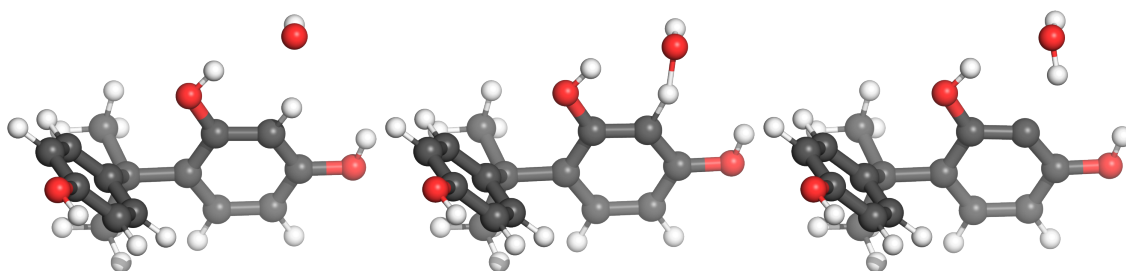


Figure S37: Representative points along the IRC connecting species 2B and R09. The structure in the center represents the transition state.

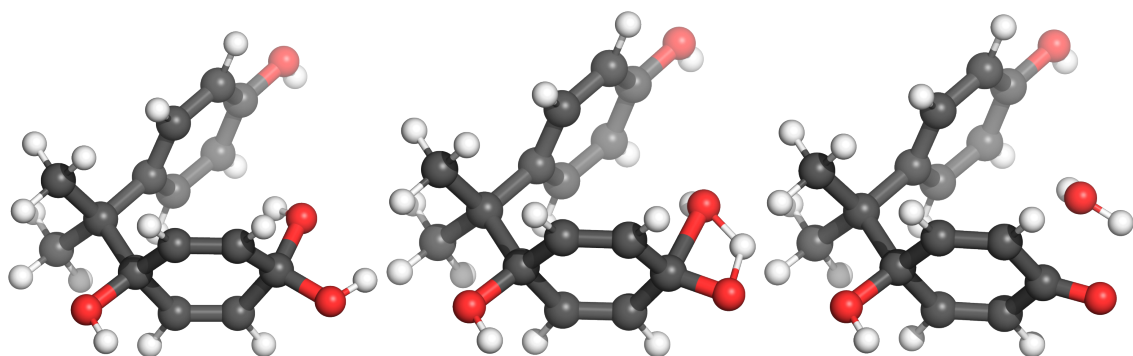


Figure S38: Representative points along the IRC connecting species 4A and 5B. The structure in the center represents the transition state.

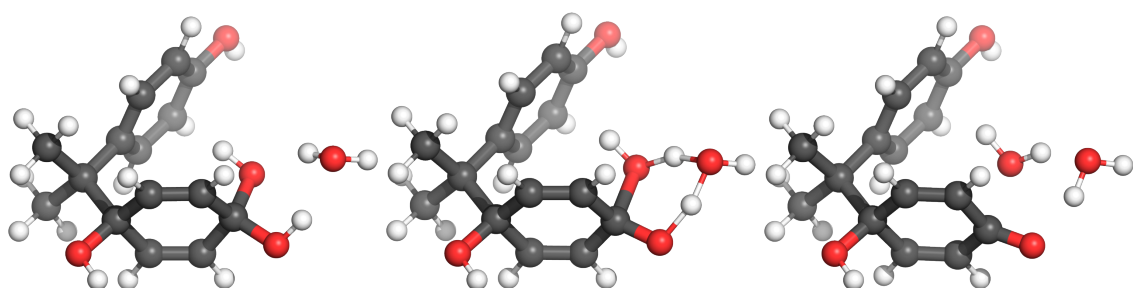


Figure S39: Representative points along the IRC connecting species 4A and 5B. The structure in the center represents the transition state. One explicit water molecule is considered.