

## Shining light on the electronic structure and relaxation dynamics of the isolated oxyluciferin anion

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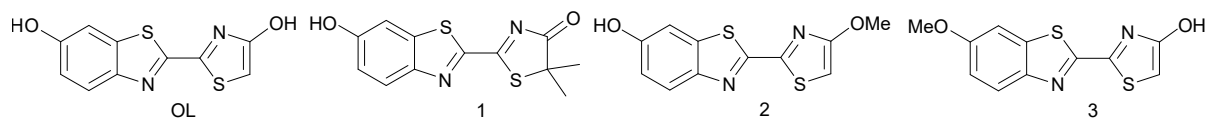
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\*\*For whom correspondence should be addressed

# 1 Synthesis

## 1.1 Method

Unless otherwise stated, all reactions were carried out under an atmosphere of nitrogen. All glassware was flame dried under a stream of nitrogen before use. Cooling to 0 °C was effected using an ice-water bath. Reactions were monitored by thin layer chromatography (TLC) using Polygram Sil G/UV<sub>254</sub> 0.25 mm silica gel precoated plastic plates with fluorescent indicator. Sheets were visualised using ultraviolet light (254 nm), ninhydrin or KMnO<sub>4</sub>, as appropriate. Flash chromatography was performed using Fluorochem silica gel 60, 35-70  $\mu$ . The liquid phase was analytical grade 40-60 petroleum ether and ethyl acetate (EtOAc) unless otherwise stated. Removal of solvents *in vacuo* was achieved using a Vacuubrand diaphragm pump or house vacuum and Büchi rotary evaporators. All NMR data was collected using a Bruker AMX 300 MHz, Bruker AVANCE III 400 MHz, Bruker AVANCE 500 MHz or Bruker AVANCE III 600 MHz. Data was manipulated directly using Bruker XwinNMR (version 2.6), TopSpin (version 2.1) or MestreNova. Reference values for residual solvents were taken as  $\delta = 7.27$  (CDCl<sub>3</sub>) for <sup>1</sup>H NMR;  $\delta = 77.16$  ppm (CDCl<sub>3</sub>) for <sup>13</sup>C NMR. Multiplicities for coupled signals were denoted as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. = broad, apt. = apparent and dd = double doublet *etc.* Coupling constants (*J*) are given in Hz and are uncorrected. Where appropriate, COSY, DEPT, HMBC, HMQC and NOE experiments were carried out to aid assignment. Mass spectroscopy data was collected on a Thermo Finnigan Mat900xp (EI/CI) VG 70se (FAB) and Waters LCT Premier XE (ES) instruments. Infrared data was collected using a Perkin Elmer 1600 FTIR machine as a thin film unless otherwise stated. Elemental analysis was performed on an Exeter Analytical Inc. EA440 horizontal load analyser. Melting points are uncorrected and were recorded on a Stuart Scientific SMP3 system. Commercial solvents and reagents were used as supplied or purified in accordance with standard procedures, as described below. THF, Et<sub>2</sub>O and toluene were obtained from solvent towers, where the degassed solvent was passed through a 7 micron filter under 4 bar pressure.



### Oxyluciferin (OL)<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  11.02 (1H, s), 10.07 (1H, s), 7.87 (1H, d, *J* = 8.8 Hz), 7.42 (1H, d, *J* = 2.4 Hz), 7.02 (1H, dd, *J* = 8.9, 2.4 Hz), 6.50 (1H, s). Data is in agreement with the literature.<sup>1</sup>

### 2-(6-hydroxybenzo[d]thiazol-2-yl)-5,5-dimethylthiazol-4(5H)-one (1)<sup>2</sup>

<sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD)  $\delta$  8.02 (1H, d, *J* = 9.0 Hz), 7.41 (1H, d, *J* = 2.3 Hz), 7.15 (1H, dd, *J* = 9.0, 2.4 Hz), 1.70 (6H, s). Data is in agreement with the literature.<sup>2</sup>

### 2-(4-methoxythiazol-2-yl)benzo[d]thiazol-6-ol (2)<sup>3</sup>

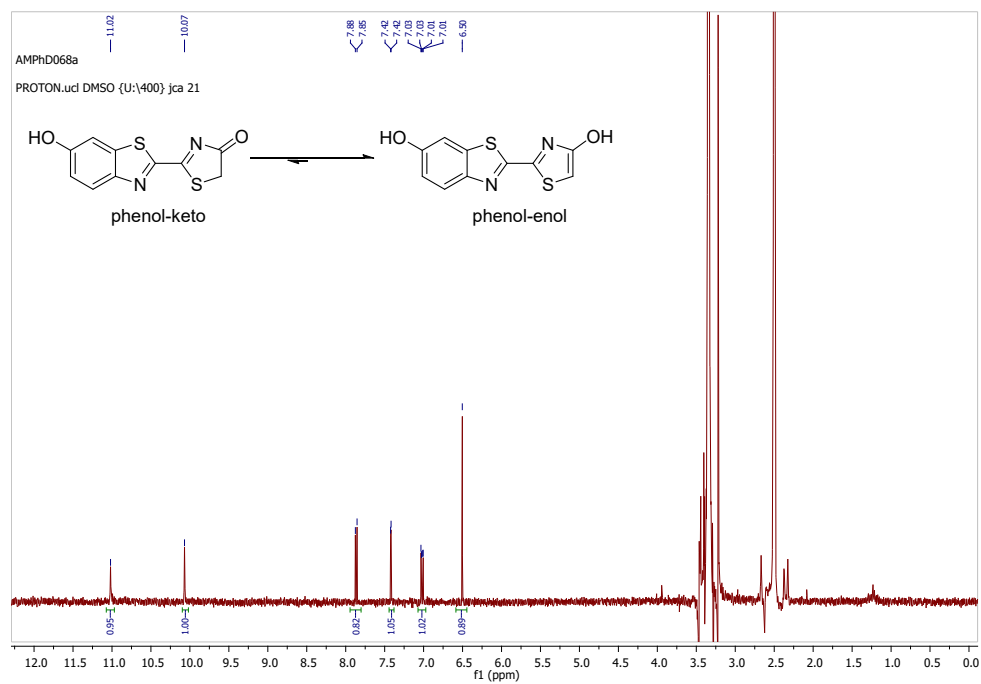
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.11 (s, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.44 (d, *J* = 2.4 Hz, 1H), 7.03 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.88 (s, 1H), 3.90 (s, 3H). Data is in agreement with the literature.<sup>3</sup>

### 2-(6-methoxybenzo[d]thiazol-2-yl)thiazol-4-ol (3)<sup>3</sup>

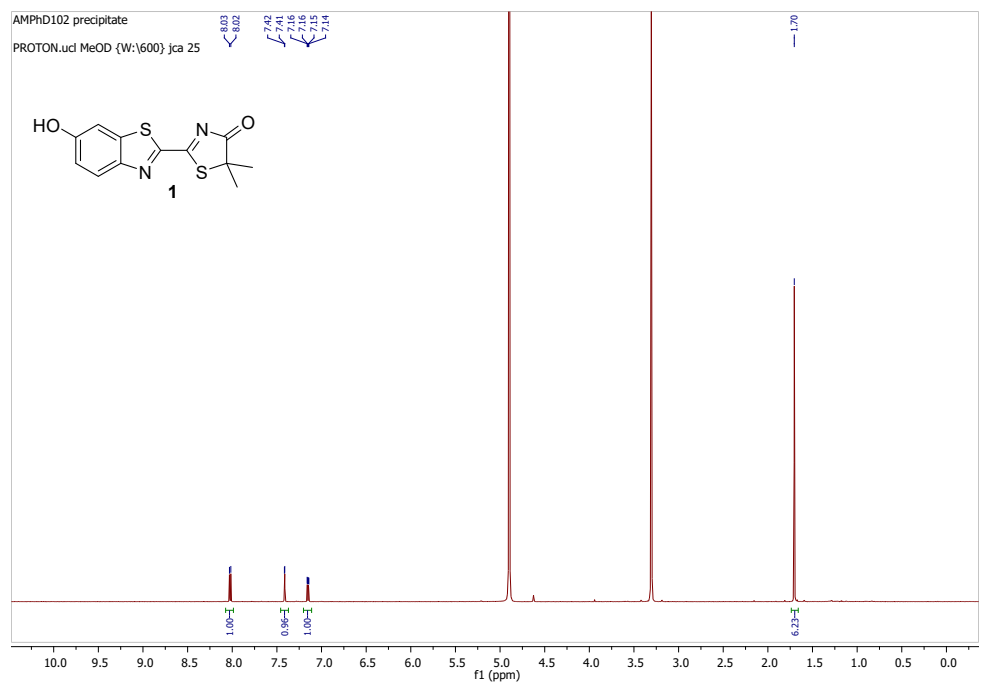
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.11 (s, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.44 (d, *J* = 2.4 Hz, 1H), 7.03 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.88 (s, 1H), 3.90 (s, 3H). Data is in agreement with the literature.<sup>3</sup>

## 1.2 $^1\text{H}$ NMR spectra

### Oxyluciferin (OL)<sup>†</sup>

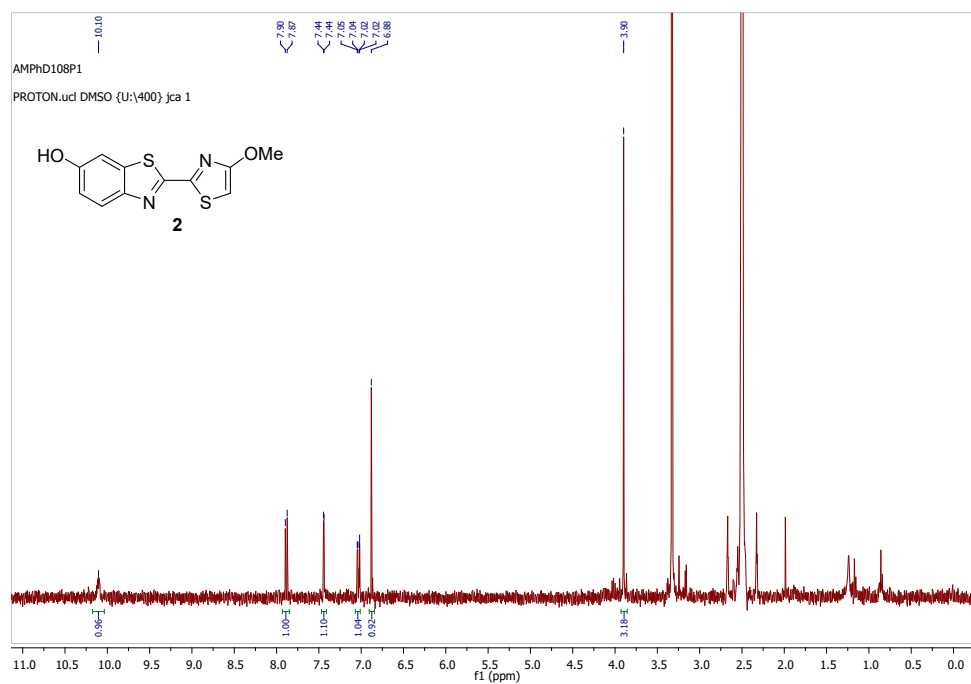


### 2-(6-hydroxybenzo[d]thiazol-2-yl)-5,5-dimethylthiazol-4(5H)-one (1)

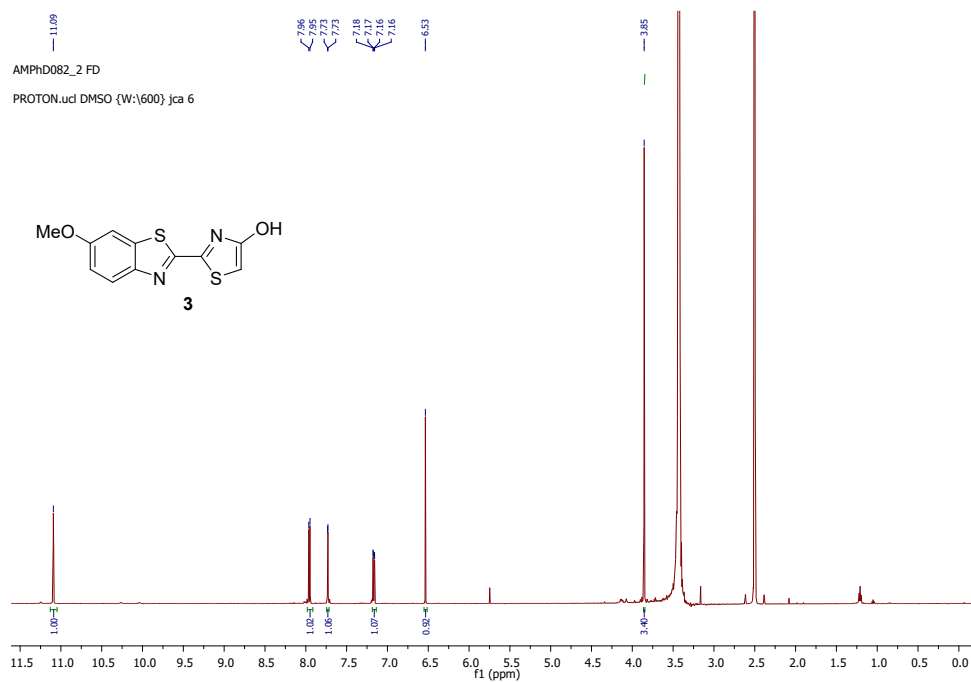


<sup>†</sup>The phenol-enol species was found to be > 99% abundant in deuterated DMSO-d<sub>6</sub> by  $^1\text{H}$  NMR

## 2-(4-methoxythiazol-2-yl)benzo[d]thiazol-6-ol (2)



## 2-(6-methoxybenzo[d]thiazol-2-yl)thiazol-4-ol (3)





## 2 Photoelectron spectroscopy

### 2.1 VMI images

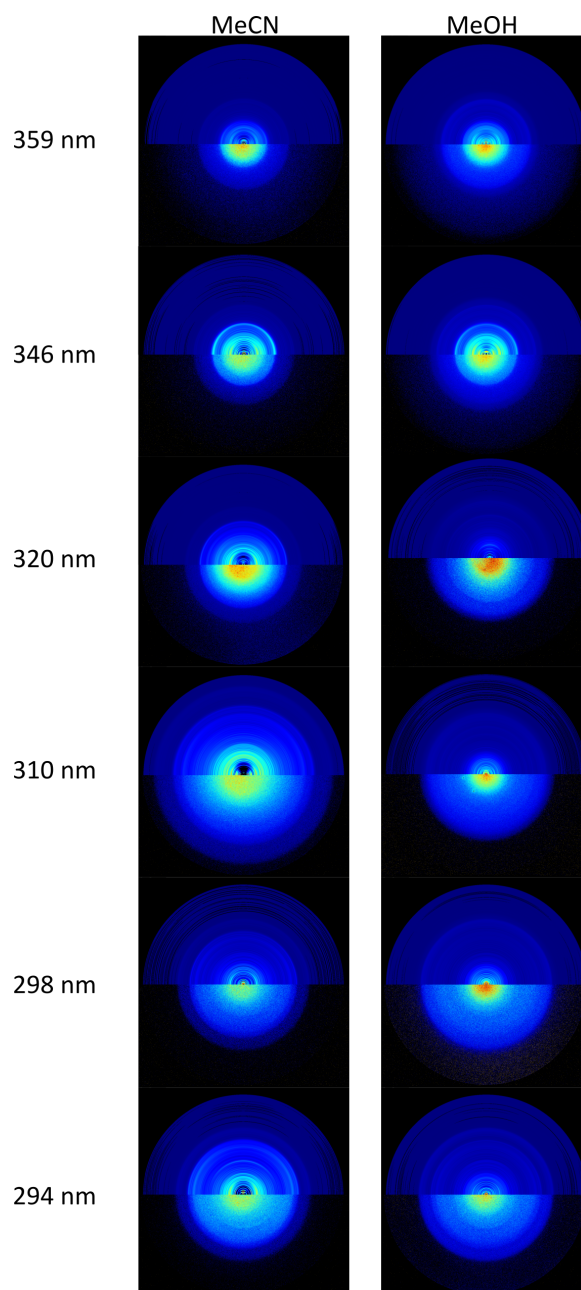


Figure S1: Photoelectron images recorded for  $OL^-$  in MeCN and MeOH (bottom halves are raw VMI images; top halves are pBasex inverted images). The polarisation axis of the laser is vertical with respect to the images. The photoelectron image at 310 nm for  $OL^-$  in MeCN was recorded at lower voltages.

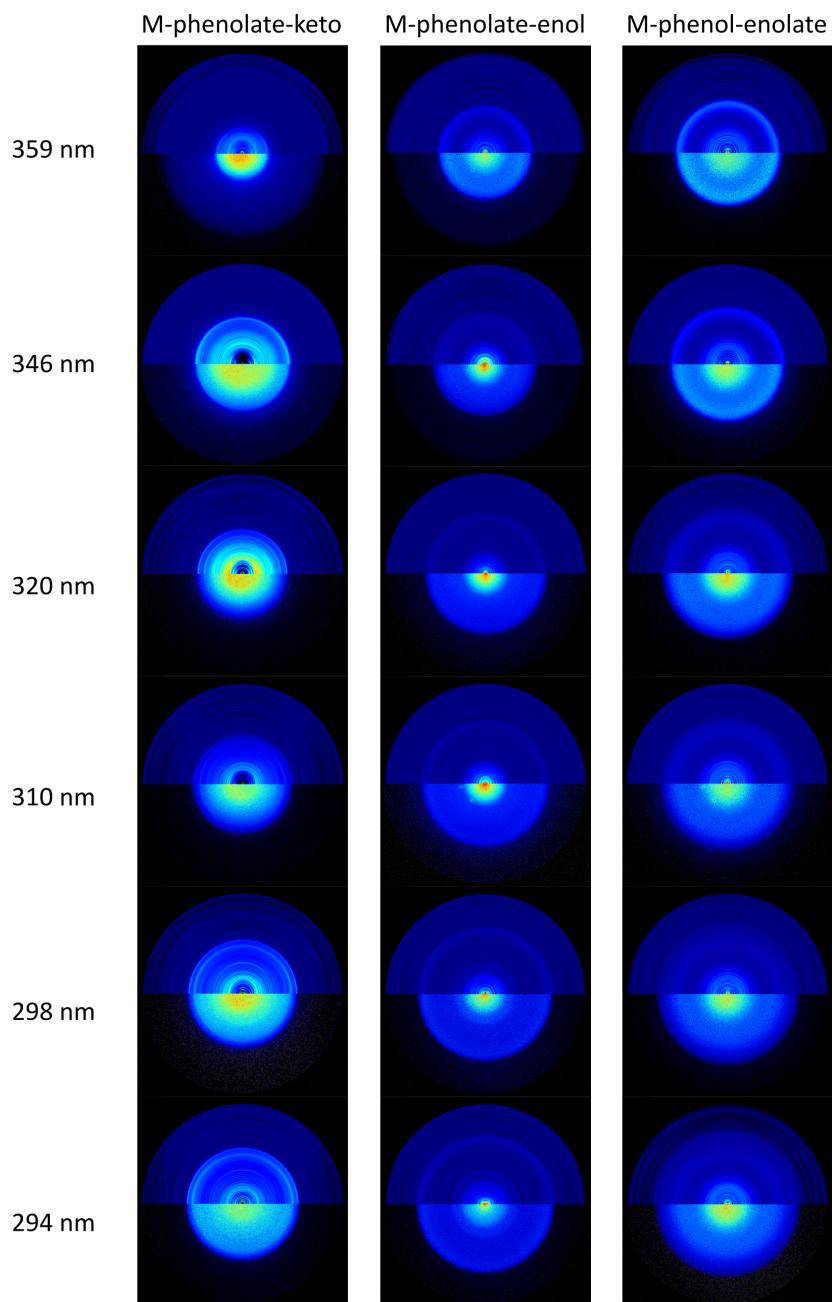


Figure S2: Photoelectron images recorded for M-phenolate-keto, M-phenolate-enol and M-phenol-enolate in MeOH (bottom halves are raw VMI images; top halves are pBasex inverted images). The polarisation axis of the laser is vertical with respect to the images.

## 2.2 Photoelectron angular distributions

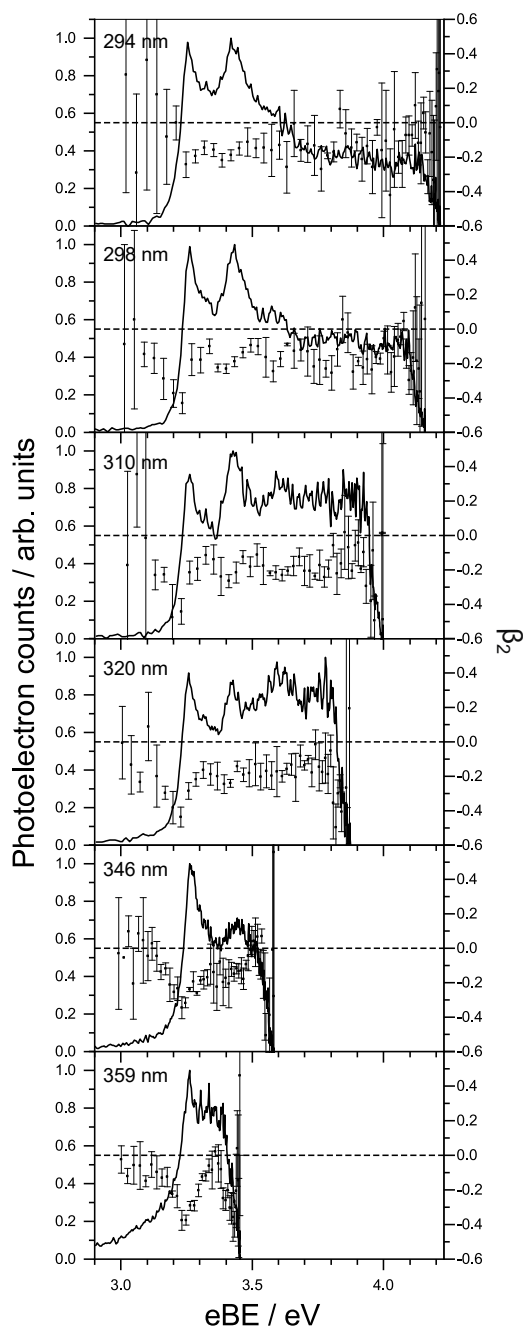


Figure S3: Photoelectron spectra recorded at 294 nm (4.22 eV), 298 nm (4.16 eV), 310 nm (4.00 eV), 320 nm (3.87 eV), 346 nm (3.58 eV) and 359 nm (3.45 eV) for M-phenolate-keto, along with the  $\beta_2$  anisotropy parameters (right axis) and plotted as a function of eBE. The  $\beta_2$  values are averaged over five data points and the error bars give the standard deviation. The horizontal dashed line represents  $\beta_2 = 0$ . In the region of the direct feature at 3.2 eV a negative anisotropy is observed ( $\beta_2 < 0$ ) but it decreases with increasing photon energy. We attribute this to competing detachment from a photofragment (Fig. S4).

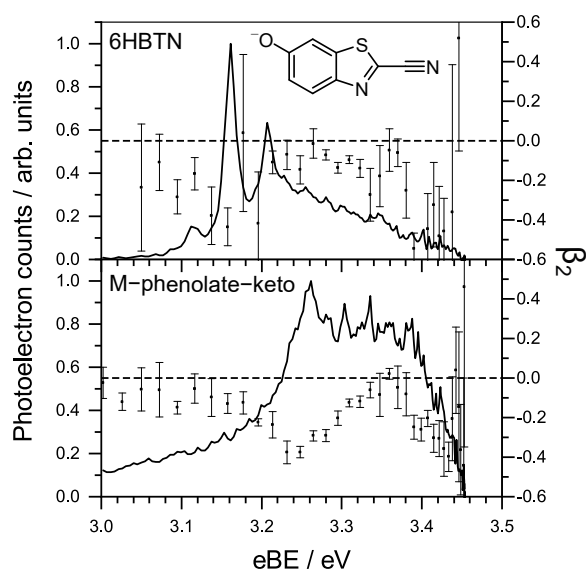


Figure S4: Photoelectron spectra recorded at 359 nm (3.45 eV) for M-phenolate-keto and 2-cyanobenzo[*d*]thiazol-6-olate (6HBTN), along with the  $\beta_2$  anisotropy parameters (right axis) and plotted as a function of eBE. The  $\beta_2$  values are averaged over five data points and the error bars give the standard deviation. The horizontal dashed line represents  $\beta_2 = 0$ . The PADs between 3.0 - 3.2 eV, corresponding to the rising edge of the photoelectron spectrum of M-phenolate-keto, are slightly negative. This region coincides with the sharp direct detachment feature at 3.16 eV in the photoelectron spectrum of 6HBTN which has  $\beta_2 < 0$ . This suggests that the rising edge in the M-phenolate-keto photoelectron spectrum could be attributed to photodetachment of the 6HBTN fragment ion.

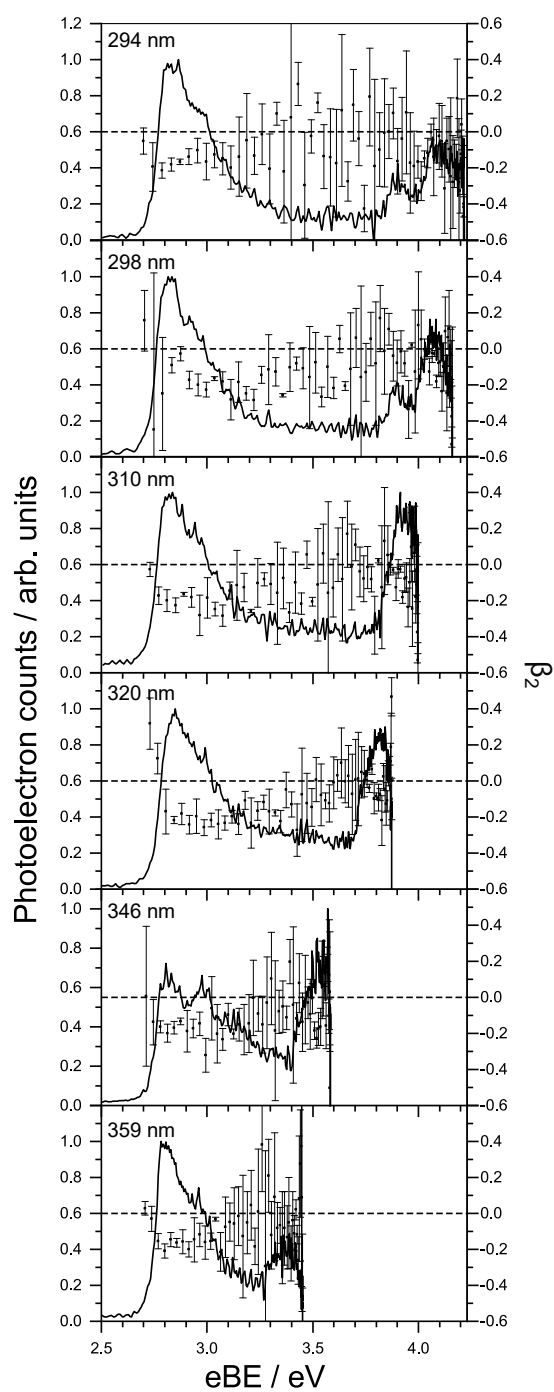


Figure S5: Photoelectron spectra recorded at 294 nm (4.22 eV), 298 nm (4.16 eV), 310 nm (4.00 eV), 320 nm (3.87 eV), 346 nm (3.58 eV) and 359 nm (3.45 eV) for M-phenolate-enol, along with the  $\beta_2$  anisotropy parameters (right axis) and plotted as a function of eBE. The  $\beta_2$  values are averaged over five data points and the error bars give the standard deviation. The horizontal dashed line represents  $\beta_2 = 0$ . The  $\beta_2$  values are slightly negative across all the photoelectron spectra.

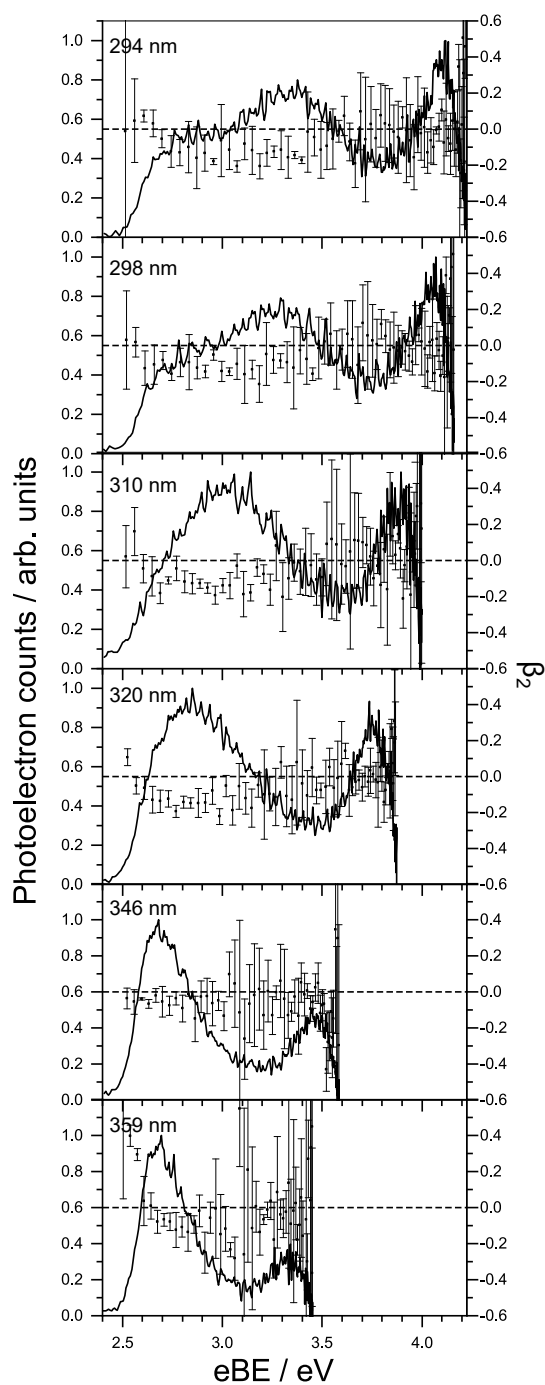


Figure S6: Photoelectron spectra recorded at 294 nm (4.22 eV), 298 nm (4.16 eV), 310 nm (4.00 eV), 320 nm (3.87 eV), 346 nm (3.58 eV) and 359 nm (3.45 eV) for M-phenol-enolate, along with the  $\beta_2$  anisotropy parameters (right axis) and plotted as a function of eBE. The  $\beta_2$  values are averaged over five data points and the error bars give the standard deviation. The horizontal dashed line represents  $\beta_2 = 0$ . The PADs are reasonably isotropic ( $\beta_2 = 0$ ) in the region corresponding to direct detachment  $\sim 2.7$  eV. However, between 320 - 294 nm, the photoelectron spectra are broad due to excitation of a resonant excited state and the resulting  $\beta_2$  values are slightly negative.

## 2.3 $OL^-$ spectra reconstructed from spectra of the model analogues

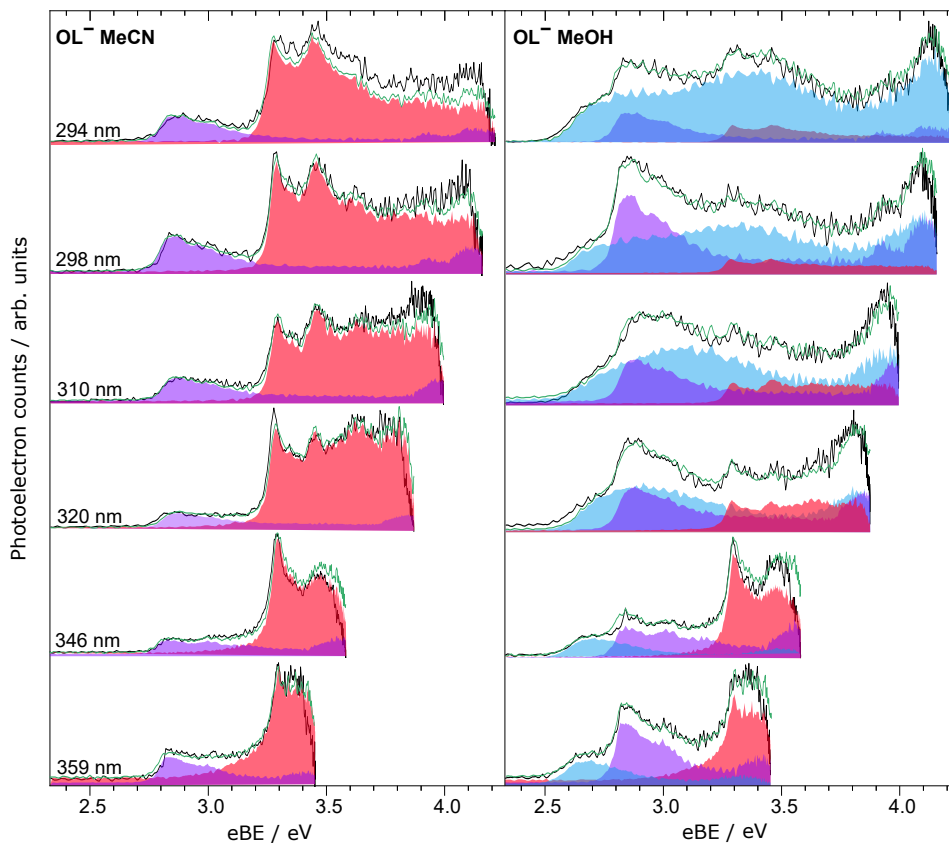


Figure S7: 359 nm (3.45 eV), 346 nm (3.58 eV), 320 nm (3.87 eV), 310 nm (4.00 eV), 298 nm (4.16 eV) and 294 nm (4.22 eV) photoelectron spectra of  $OL^-$  (black) in MeCN (left) and MeOH (right) overlapped with the reconstructed spectra (green line) obtained by summing shifted spectra of the model analogues M-phenolate-keto (red), M-phenolate-enol (purple) and M-phenol-enolate (blue).

## 2.4 Low eKE features

Klots' formula provides a model for the electron kinetic energy ( $\varepsilon$ ) distribution for photoelectrons emitted through thermionic emission (TE).<sup>4,5</sup>

$$P(\varepsilon) \propto \varepsilon^{\frac{1}{2}} \exp(-\varepsilon/k_B T_{M\cdot}) \quad (1)$$

where  $k_B$  is the Boltzmann constant and  $T_{M\cdot}$  is the temperature of the neutral radical,<sup>6-8</sup>

$$T_{M\cdot} = T_{M^-} + (h\nu - ADE)/C_v \quad (2)$$

$T_{M^-}$  is the microcanonical temperature of the anions before photoexcitation and  $C_v$  is the microcanonical heat capacity.

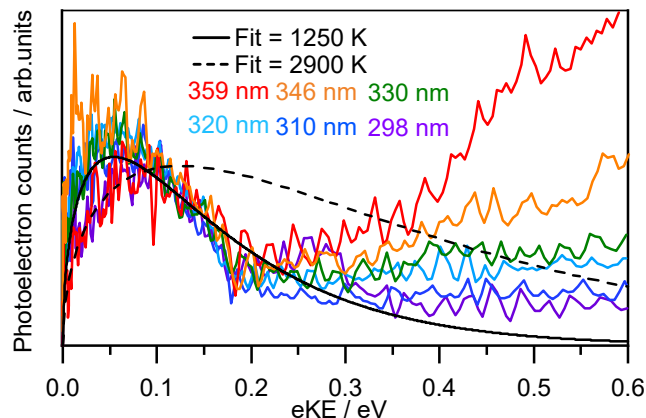


Figure S8: Photoelectron spectra of M-phenolate-enol presented as a function of eKE and normalised on the peak maxima at  $\sim 0.9$  eV. Modelled TE profiles using (1) with  $T_M = 1250$  K (black solid) and 2900 K (black dash), aligning to the tails and rising edges of the low eKE features, respectively.  $C_v \approx C_{\text{canonical}} - k \approx C_{\text{canonical}}$ , since heat capacities are  $\approx 10^{-3}$  eV K $^{-1}$ . Using  $C_{\text{canonical}}$  derived from quantum chemistry calculations and assuming that  $T_{M^-} = 298$  K,  $T_M$  is estimated to be 600 K, which suggests that M-phenol-enolate does not exhibit TE.

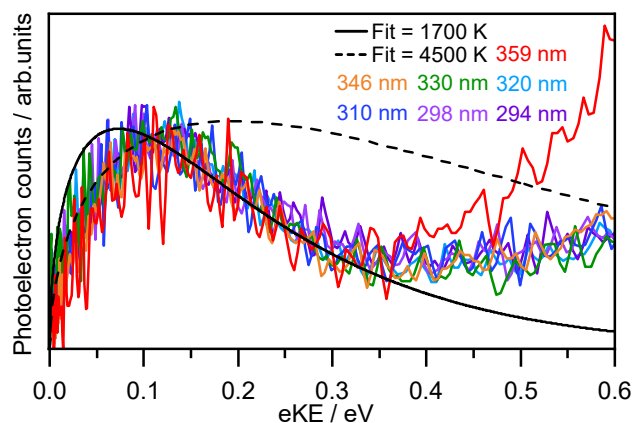


Figure S9: Photoelectron spectra of M-phenol-enolate presented as a function of eKE and normalised on the peak maxima. Modelled TE profiles using (1) with  $T_M = 1700$  K (black solid) and 4500 K (black dash), aligning to the tails and rising edges of the low eKE features, respectively.  $C_v \approx C_{\text{canonical}} - k \approx C_{\text{canonical}}$ , since heat capacities are  $\approx 10^{-3}$  eV K $^{-1}$ . Using  $C_{\text{canonical}}$  derived from quantum chemistry calculations and assuming that  $T_{M^-} = 298$  K,  $T_M$  is estimated to be 648 K, which suggests that M-phenol-enolate does not exhibit TE.



## 2.5 Resonance

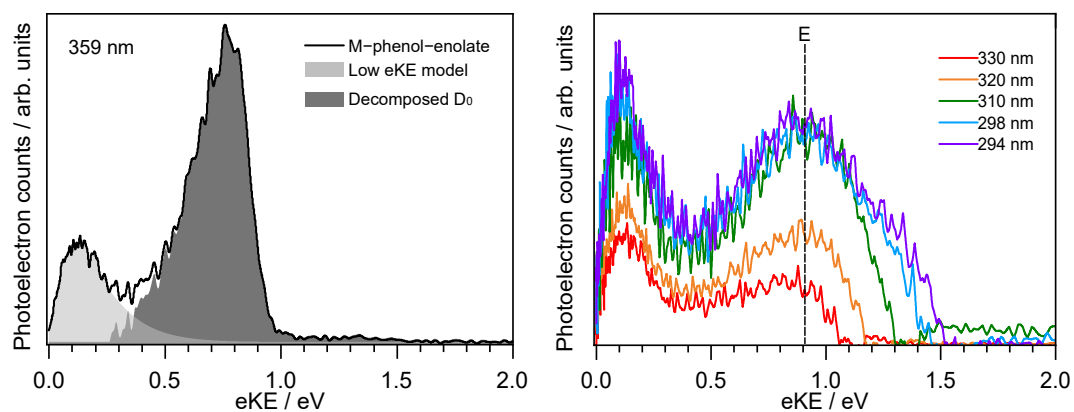


Figure S10: Left: 359 nm (3.45 eV) photoelectron spectrum of M-phenol-enolate recorded as a function of eKE (black line), decomposed into its low eKE (light shade) and high eKE (dark shade) components. Right: 330 nm (3.76 eV) 320 nm (3.87 eV), 310 nm (4.00 eV), 298 nm (4.16 eV) and 294 nm (4.22 eV) difference spectra of M-phenol-enolate plotted as a function of eKE. Photoelectron spectra were normalised to the rising edge ( $\sim 2.63$  eV) in the 359 nm eBE spectrum. The decomposed 359 nm spectrum showing contributions from direct detachment only (dark shade) was subtracted from the normalised photoelectron spectra to give the difference spectra. The dashed line in the eKE panel marks the constant eKE feature, E.

### 3 Computational

#### 3.1 EOM-IP-CCSD vertical detachment energies

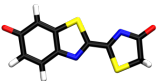
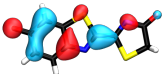
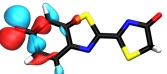
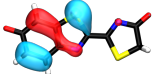
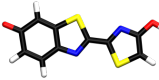
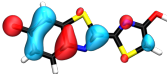
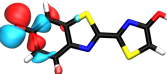
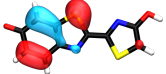
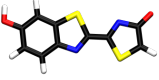
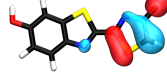
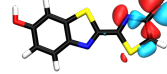
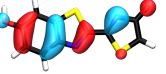
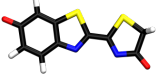
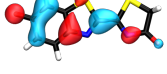
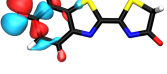
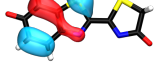
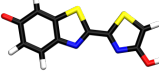
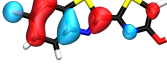
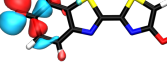
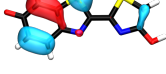
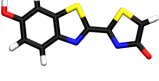
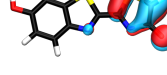
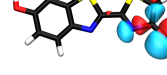
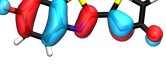
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|------------------------------|---|----------------|--|----------------|---|----------------|---|
|                              |   | VDE            | hole orbital   | VDE            | hole orbital  | VDE            | hole orbital  |
| <i>trans</i> -phenolate-keto |    | 3.30           | $\pi_{\text{H}}$<br>   | 5.07           | $n_{\text{O(ph)}}$<br>   | 5.39           | $\pi_{\text{H-1}}$<br>   |
| <i>trans</i> -phenolate-enol |    | 2.66           | $\pi_{\text{H}}$<br>   | 4.38           | $n_{\text{O(ph)}}$<br>   | 4.81           | $\pi_{\text{H-1}}$<br>   |
| <i>trans</i> -phenol-enolate |    | 2.49           | $\pi_{\text{H}}$<br>   | 4.18           | $n_{\text{O(en)}}$<br>   | 5.07           | $\pi_{\text{H-1}}$<br>   |
| <i>cis</i> -phenolate-keto   |    | 3.31           | $\pi_{\text{H}}$<br>   | 5.12           | $n_{\text{O(ph)}}$<br>   | 5.46           | $\pi_{\text{H-1}}$<br>   |
| <i>cis</i> -phenolate-enol   |    | 2.69           | $\pi_{\text{H}}$<br>   | 4.42           | $n_{\text{O(ph)}}$<br>   | 4.83           | $\pi_{\text{H-1}}$<br>   |
| <i>cis</i> -phenol-enolate   |  | 2.50           | $\pi_{\text{H}}$<br> | 4.17           | $n_{\text{O(en)}}$<br> | 5.11           | $\pi_{\text{H-1}}$<br> |

Table S1: Deprotonated  $\text{OL}^-$  anions optimised with B3LYP/6-311++G(2df,2pd) and EOM-IP-CCSD/aug-cc-pVDZ VDEs (given in eV) together with the leading molecular orbitals ( $> 0.9$ ) from which detachment occurs.

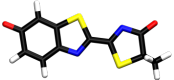
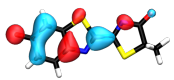
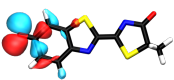
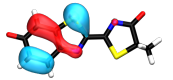
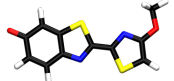
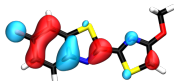
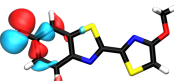
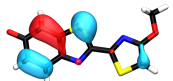
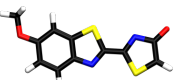
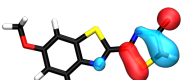
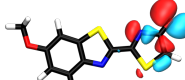
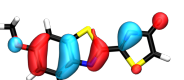
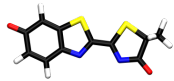
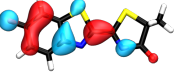
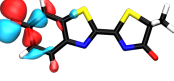
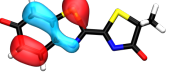
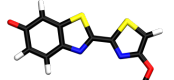
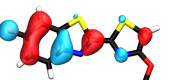
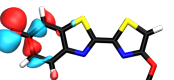
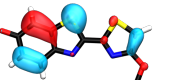
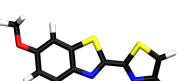
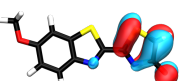
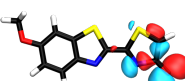
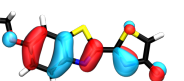
| Anion                          | Geometry  | D <sub>0</sub> |  | D <sub>1</sub> |   | D <sub>2</sub> |  |
|--------------------------------|---|----------------|--|----------------|---|----------------|--|
|                                |   | VDE            | hole orbital   | VDE            | hole orbital  | VDE            | hole orbital   |
| <i>trans</i> -M-phenolate-keto |  | 3.26           | $\pi_{\text{H}}$  | 5.07           | $n_{\text{O}(\text{ph})}$  | 5.35           | $\pi_{\text{H}-1}$  |
| <i>trans</i> -M-phenolate-enol |  | 2.65           | $\pi_{\text{H}}$  | 4.38           | $n_{\text{O}(\text{ph})}$  | 4.80           | $\pi_{\text{H}-1}$  |
| <i>trans</i> -M-phenol-enolate |  | 2.45           | $\pi_{\text{H}}$  | 4.15           | $n_{\text{O}(\text{en})}$  | 4.99           | $\pi_{\text{H}-1}$  |
| <i>cis</i> -M-phenolate-keto   |  | 3.27           | $\pi_{\text{H}}$  | 5.09           | $n_{\text{O}(\text{ph})}$  | 5.41           | $\pi_{\text{H}-1}$  |
| <i>cis</i> -M-phenolate-enol   |  | 2.68           | $\pi_{\text{H}}$  | 4.41           | $n_{\text{O}(\text{ph})}$  | 4.79           | $\pi_{\text{H}-1}$  |
| <i>cis</i> -M-phenol-enolate   |  | 2.46           | $\pi_{\text{H}}$  | 4.14           | $n_{\text{O}(\text{en})}$  | 5.04           | $\pi_{\text{H}-1}$  |

Table S2: Deprotonated methylated analogue anions optimised with B3LYP/6-311++G(2df,2pd) and EOM-IP-CCSD/aug-cc-pVDZ VDEs (given in eV) together with the leading molecular orbitals ( $> 0.9$ ) from which detachment occurs.

### 3.2 Vertical excitation energies

| State           | Sym   | VEE/eV | Excitation    | $c^2$ | $f$    |
|-----------------|-------|--------|---------------|-------|--------|
| S <sub>1</sub>  | 1a'   | 2.20   | 12a'' → 14a'' | 92    | 0.7964 |
| S <sub>2</sub>  | 1a''  | 2.65   | 52a' → 14a''  | 93    | 0.0000 |
| S <sub>3</sub>  | 2a''  | 3.49   | 12a'' → 54a'  | 39    | 0.0001 |
|                 |       |        | 12a'' → 53a'  | 24    |        |
| S <sub>4</sub>  | 2a'   | 3.68   | 11a'' → 14a'' | 89    | 0.1815 |
| S <sub>5</sub>  | 3a''  | 3.71   | 12a'' → 53a'  | 59    | 0.0008 |
| S <sub>6</sub>  | 4a''  | 3.76   | 51a' → 14a''  | 70    | 0.0003 |
| S <sub>7</sub>  | 5a''  | 3.83   | 12a'' → 54a'  | 37    | 0.0000 |
|                 |       |        | 12a'' → 55a'  | 35    |        |
| S <sub>8</sub>  | 3a'   | 3.92   | 12a'' → 15a'' | 24    | 0.0324 |
|                 |       |        | 12a'' → 17a'' | 24    |        |
|                 |       |        | 12a'' → 19a'' | 16    |        |
| S <sub>9</sub>  | 4a'   | 4.05   | 52a' → 54a'   | 59    | 0.0085 |
|                 |       |        | 52a' → 55a'   | 20    |        |
| S <sub>10</sub> | 6a''  | 4.20   | 12a'' → 56a'  | 51    | 0.0014 |
|                 |       |        | 12a'' → 55a'  | 30    |        |
| S <sub>11</sub> | 5a'   | 4.26   | 10a'' → 14a'' | 44    | 0.0287 |
|                 |       |        | 12a'' → 13a'' | 42    |        |
| S <sub>12</sub> | 6a'   | 4.28   | 12a'' → 13a'' | 44    | 0.0404 |
|                 |       |        | 10a'' → 14a'' | 42    |        |
| S <sub>13</sub> | 7a''  | 4.36   | 52a' → 17a''  | 24    | 0.0006 |
|                 |       |        | 52a' → 19a''  | 24    |        |
|                 |       |        | 52a' → 15a''  | 20    |        |
| S <sub>14</sub> | 7a'   | 4.38   | 52a' → 55a'   | 52    | 0.0110 |
|                 |       |        | 52a' → 54a'   | 19    |        |
| S <sub>15</sub> | 8a''  | 4.43   | 50a' → 14a''  | 51    | 0.0000 |
| S <sub>16</sub> | 9a''  | 4.44   | 12a'' → 61a'  | 16    | 0.0011 |
| S <sub>17</sub> | 8a'   | 4.53   | 52a' → 53a'   | 49    | 0.0042 |
|                 |       |        | 52a' → 56a'   | 33    |        |
| S <sub>18</sub> | 10a'' | 4.55   | 12a'' → 57a'  | 46    | 0.0002 |
|                 |       |        | 12a'' → 60a'  | 23    |        |
| S <sub>19</sub> | 11a'' | 4.67   | 49a' → 14a''  | 74    | 0.0003 |
|                 |       |        | 50a' → 14a''  | 18    |        |
| S <sub>20</sub> | 9a'   | 4.72   | 52a' → 53a'   | 24    | 0.0198 |
|                 |       |        | 52a' → 56a'   | 23    |        |
| S <sub>21</sub> | 10a'  | 4.77   | 12a'' → 22a'' | 32    | 0.0183 |
|                 |       |        | 52a' → 56a'   | 15    |        |
| S <sub>22</sub> | 12a'' | 4.80   | 12a'' → 59a'  | 37    | 0.0013 |
| S <sub>23</sub> | 13a'' | 4.97   | 12a'' → 58a'  | 34    | 0.0043 |
|                 |       |        | 12a'' → 57a'  | 21    |        |
| S <sub>24</sub> | 11a'  | 4.98   | 9a'' → 14a''  | 34    | 0.0959 |

Table S3: Excited states calculated with ADC(2)/aug-cc-pVDZ for phenolate-keto. Listed are all excitations with a contribution of more than 15%.

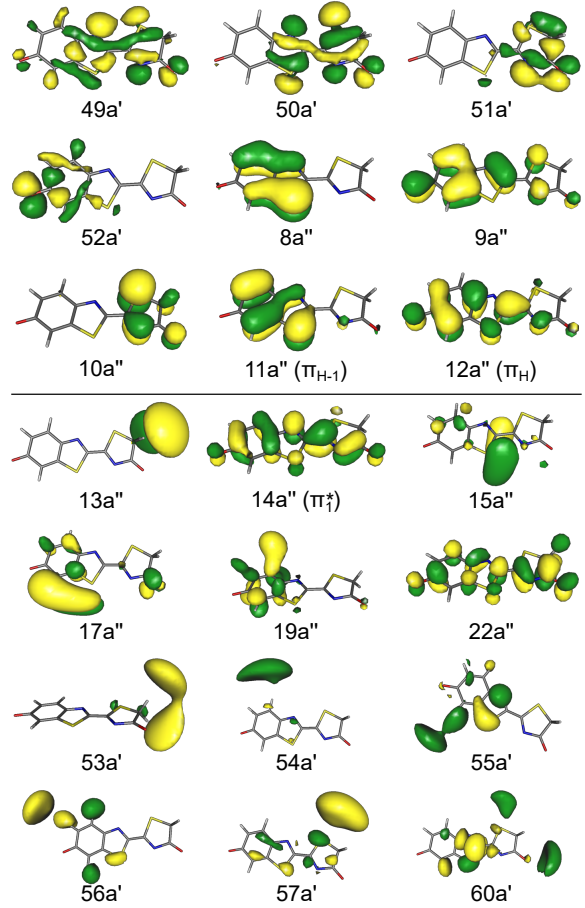


Figure S11: Hartree-Fock orbitals of phenolate-keto used in the ADC(2) calculation.

| State           | Sym   | VEE/eV | Excitation    | $c^2$ | $f$    |
|-----------------|-------|--------|---------------|-------|--------|
| S <sub>1</sub>  | 1a'   | 2.18   | 12a'' → 13a'' | 92    | 0.6476 |
| S <sub>2</sub>  | 1a''  | 2.68   | 12a'' → 53a'  | 88    | 0.0005 |
| S <sub>3</sub>  | 2a''  | 2.82   | 52a' → 13a''  | 90    | 0.0000 |
| S <sub>4</sub>  | 3a''  | 3.06   | 12a'' → 55a'  | 61    | 0.0001 |
|                 |       |        | 12a'' → 56a'  | 18    |        |
| S <sub>5</sub>  | 4a''  | 3.29   | 12a'' → 54a'  | 46    | 0.0004 |
|                 |       |        | 12a'' → 56a'  | 34    |        |
| S <sub>6</sub>  | 5a''  | 3.41   | 12a'' → 54a'  | 28    | 0.0001 |
|                 |       |        | 12a'' → 56a'  | 25    |        |
|                 |       |        | 12a'' → 55a'  | 24    |        |
| S <sub>7</sub>  | 2a'   | 3.59   | 52a' → 53a'   | 39    | 0.0003 |
|                 |       |        | 52a' → 55a'   | 33    |        |
| S <sub>8</sub>  | 3a'   | 3.63   | 52a' → 53a'   | 50    | 0.0002 |
|                 |       |        | 52a' → 55a'   | 21    |        |
| S <sub>9</sub>  | 6a''  | 3.69   | 12a'' → 57a'  | 70    | 0.0030 |
| S <sub>10</sub> | 4a'   | 3.70   | 12a'' → 17a'' | 17    | 0.0348 |
|                 |       |        | 12a'' → 19a'' | 17    |        |
| S <sub>11</sub> | 5a'   | 3.87   | 11a'' → 13a'' | 82    | 0.1185 |
| S <sub>12</sub> | 7a''  | 3.89   | 12a'' → 58a'  | 30    | 0.0011 |
| S <sub>13</sub> | 6a'   | 3.91   | 52a' → 56a'   | 65    | 0.0119 |
|                 |       |        | 52a' → 55a'   | 18    |        |
| S <sub>14</sub> | 8a''  | 4.12   | 52a' → 19a''  | 30    | 0.0007 |
|                 |       |        | 52a' → 17a''  | 18    |        |
| S <sub>15</sub> | 7a'   | 4.13   | 52a' → 57a'   | 63    | 0.0052 |
|                 |       |        | 52a' → 54a'   | 25    |        |
| S <sub>16</sub> | 9a''  | 4.18   | 12a'' → 61a'  | 33    | 0.0000 |
| S <sub>17</sub> | 10a'' | 4.26   | 12a'' → 59a'  | 42    | 0.0001 |
| S <sub>18</sub> | 8a'   | 4.28   | 52a' → 54a'   | 59    | 0.0024 |
|                 |       |        | 52a' → 57a'   | 18    |        |
| S <sub>19</sub> | 11a'' | 4.36   | 10a'' → 53a'  | 43    | 0.0025 |
|                 |       |        | 11a'' → 53a'  | 18    |        |
| S <sub>20</sub> | 9a'   | 4.37   | 12a'' → 14a'' | 72    | 0.0155 |
| S <sub>21</sub> | 12a'' | 4.47   | 12a'' → 60a'  | 24    | 0.0003 |
|                 |       |        | 12a'' → 58a'  | 20    |        |
| S <sub>22</sub> | 10a'  | 4.47   | 10a'' → 13a'' | 68    | 0.0355 |
| S <sub>23</sub> | 11a'  | 4.54   | 12a'' → 16a'' | 26    | 0.0248 |
| S <sub>24</sub> | 13a'' | 4.60   | 12a'' → 64a'  | 34    | 0.0004 |
| S <sub>25</sub> | 14a'' | 4.61   | 12a'' → 60a'  | 43    | 0.0007 |
|                 |       |        | 12a'' → 58a'  | 18    |        |
| S <sub>26</sub> | 12a'  | 4.81   | 52a' → 58a'   | 34    | 0.0044 |
|                 |       |        | 52a' → 61a'   | 19    |        |
| S <sub>27</sub> | 13a'  | 4.86   | 12a'' → 18a'' | 25    | 0.0113 |
| S <sub>28</sub> | 15a'' | 4.88   | 51a' → 13a''  | 80    | 0.0006 |
| S <sub>29</sub> | 14a'  | 4.92   | 52a' → 59a'   | 42    | 0.0046 |
|                 |       |        | 52a' → 62a'   | 27    |        |
| S <sub>30</sub> | 16a'' | 4.92   | 11a'' → 53a'  | 45    | 0.0033 |
| S <sub>31</sub> | 17a'' | 4.94   | 52a' → 16a''  | 14    | 0.0000 |
| S <sub>32</sub> | 15a'  | 4.99   | 12a'' → 15a'' | 41    | 0.0537 |

Table S4: Excited states calculated with ADC(2)/aug-cc-pVDZ for phenolate-enol. Listed are all excitations with a contribution of at least 18%.

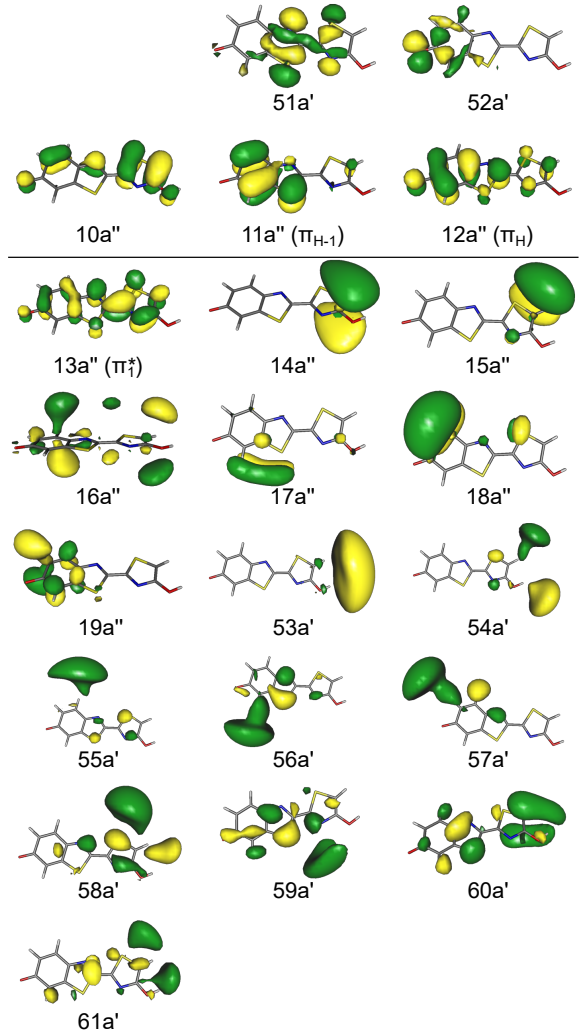


Figure S12: Hartree-Fock orbitals of phenolate-enol used in the ADC(2) calculation.

| State           | Sym   | VEE/eV | Excitation    | $c^2$ | $f$    |
|-----------------|-------|--------|---------------|-------|--------|
| S <sub>1</sub>  | 1a'   | 1.64   | 12a'' → 13a'' | 85    | 0.1475 |
| S <sub>2</sub>  | 1a''  | 2.41   | 12a'' → 53a'  | 76    | 0.0000 |
| S <sub>3</sub>  | 2a''  | 2.56   | 52a' → 13a''  | 86    | 0.0001 |
| S <sub>4</sub>  | 3a''  | 2.61   | 12a'' → 57a'  | 48    | 0.0002 |
| S <sub>5</sub>  | 4a''  | 2.76   | 12a'' → 54a'  | 55    | 0.0017 |
|                 |       |        | 12a'' → 57a'  | 28    |        |
| S <sub>6</sub>  | 2a'   | 2.86   | 12a'' → 14a'' | 62    | 0.0088 |
| S <sub>7</sub>  | 5a''  | 3.01   | 12a'' → 55a'  | 43    | 0.0005 |
| S <sub>8</sub>  | 6a''  | 3.30   | 12a'' → 56a'  | 55    | 0.0016 |
| S <sub>9</sub>  | 3a'   | 3.43   | 52a' → 53a'   | 80    | 0.0001 |
| S <sub>10</sub> | 7a''  | 3.52   | 12a'' → 58a'  | 24    | 0.0009 |
| S <sub>11</sub> | 4a'   | 3.60   | 52a' → 57a'   | 68    | 0.0076 |
| S <sub>12</sub> | 8a''  | 3.72   | 12a'' → 60a'  | 35    | 0.0000 |
| S <sub>13</sub> | 5a'   | 3.73   | 12a'' → 15a'' | 31    | 0.0234 |
| S <sub>14</sub> | 6a'   | 3.75   | 52a' → 54a'   | 59    | 0.0030 |
| S <sub>15</sub> | 9a''  | 3.88   | 12a'' → 58a'  | 37    | 0.0000 |
|                 |       |        | 12a'' → 59a'  | 19    |        |
| S <sub>16</sub> | 10a'' | 3.95   | 12a'' → 59a'  | 26    | 0.0012 |
|                 |       |        | 12a'' → 60a'  | 21    |        |
| S <sub>17</sub> | 7a'   | 4.01   | 12a'' → 17a'' | 55    | 0.0039 |
| S <sub>18</sub> | 8a'   | 4.03   | 52a' → 55a'   | 46    | 0.0008 |
| S <sub>19</sub> | 11a'' | 4.12   | 52a' → 14a''  | 69    | 0.0000 |
| S <sub>20</sub> | 12a'' | 4.20   | 51a' → 13a''  | 82    | 0.0002 |
| S <sub>21</sub> | 9a'   | 4.29   | 52a' → 56a'   | 59    | 0.0016 |
|                 |       |        | 52a' → 60a'   | 18    |        |
| S <sub>22</sub> | 13a'' | 4.33   | 12a'' → 61a'  | 19    | 0.0005 |
| S <sub>23</sub> | 10a'  | 4.34   | 11a'' → 13a'' | 32    | 0.2498 |
| S <sub>24</sub> | 14a'' | 4.37   | 12a'' → 63a'  | 14    | 0.0005 |
| S <sub>25</sub> | 11a'  | 4.39   | 11a'' → 13a'' | 26    | 0.0861 |
|                 |       |        | 12a'' → 16a'' | 24    |        |
| S <sub>26</sub> | 15a'' | 4.41   | 11a'' → 53a'  | 63    | 0.0000 |
| S <sub>27</sub> | 12a'  | 4.60   | 52a' → 59a'   | 28    | 0.0054 |
| S <sub>28</sub> | 16a'' | 4.61   | 12a'' → 63a'  | 27    | 0.0020 |
|                 |       |        | 12a'' → 66a'  | 18    |        |
| S <sub>29</sub> | 13a'  | 4.65   | 11a'' → 14a'' | 30    | 0.1355 |
|                 |       |        | 11a'' → 13a'' | 15    |        |
| S <sub>30</sub> | 14a'  | 4.68   | 52a' → 60a'   | 34    | 0.0361 |
| S <sub>31</sub> | 15a'  | 4.80   | 12a'' → 20a'' | 29    | 0.0146 |
|                 |       |        | 12a'' → 18a'' | 20    |        |
| S <sub>32</sub> | 16a'  | 4.87   | 52a' → 58a'   | 27    | 0.0163 |
| S <sub>33</sub> | 17a'' | 4.90   | 12a'' → 61a'  | 32    | 0.0007 |
|                 |       |        | 11a'' → 54a'  | 18    |        |
| S <sub>34</sub> | 18a'' | 4.92   | 52a' → 15a''  | 40    | 0.0002 |
| S <sub>35</sub> | 17a'  | 4.93   | 12a'' → 16a'' | 16    | 0.0082 |
| S <sub>36</sub> | 19a'' | 4.97   | 11a'' → 54a'  | 45    | 0.0042 |
| S <sub>37</sub> | 18a'  | 4.99   | 10a'' → 13a'' | 34    | 0.0583 |

Table S5: Excited states calculated with ADC(2)/aug-cc-pVDZ for phenol-enolate. Listed are all excitations with a contribution of at least 18%.

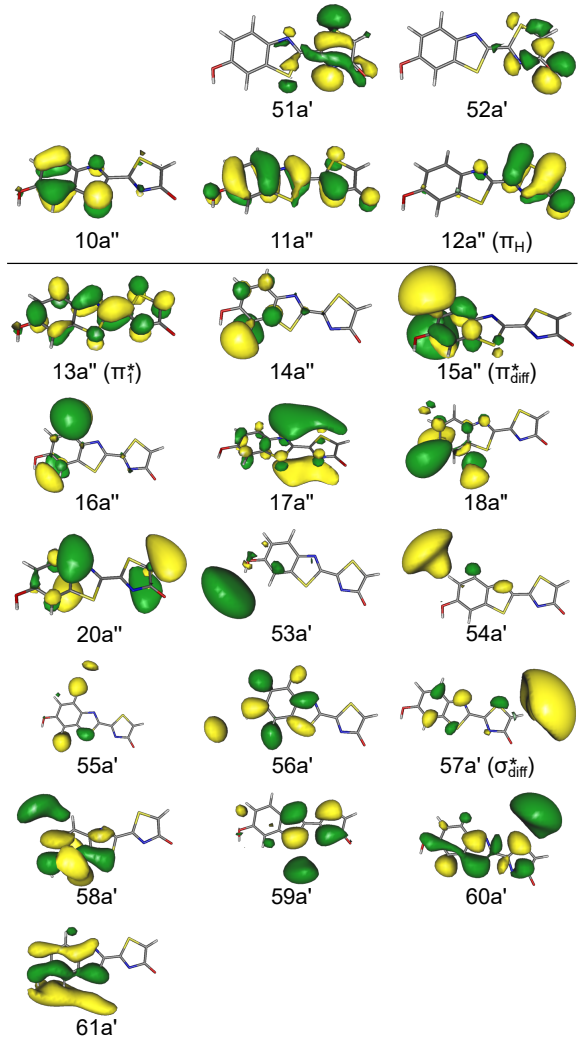


Figure S13: Hartree-Fock orbitals of phenol-enolate used in the ADC(2) calculation.

### 3.3 Vibrational modes and ezSpectrum simulations

| $\nu$ | anion<br>$\omega_e / \text{cm}^{-1}$ | radical<br>$\omega_e / \text{cm}^{-1}$ | $\nu$ | anion<br>$\omega_e / \text{cm}^{-1}$ | radical<br>$\omega_e / \text{cm}^{-1}$ |
|-------|--------------------------------------|--|-------|--------------------------------------|--|
| 1     | 33.86                                | 33.83                                  | 39    | 942.24                               | 935.54                                 |
| 2     | 49.15                                | 42.48                                  | 40    | 954.75                               | 960.20                                 |
| 3     | 66.27                                | 67.16                                  | 41    | 981.78                               | 1005.34                                |
| 4     | 66.84                                | 62.76                                  | 42    | 1023.64                              | 1031.70                                |
| 5     | 134.24                               | 126.58                                 | 43    | 1028.58                              | 1033.99                                |
| 6     | 190.07                               | 187.95                                 | 44    | 1120.62                              | 1110.77                                |
| 7     | 195.73                               | 200.96                                 | 45    | 1156.08                              | 1124.62                                |
| 8     | 206.06                               | 204.31                                 | 46    | 1157.54                              | 1154.90                                |
| 9     | 222.15                               | 222.95                                 | 47    | 1188.08                              | 1165.50                                |
| 10    | 236.53                               | 232.83                                 | 48    | 1228.45                              | 1222.28                                |
| 11    | 245.35                               | 244.08                                 | 49    | 1240.09                              | 1242.60                                |
| 12    | 265.79                               | 266.32                                 | 50    | 1257.08                              | 1266.69                                |
| 13    | 297.25                               | 296.13                                 | 51    | 1282.61                              | 1287.26                                |
| 14    | 318.95                               | 316.24                                 | 52    | 1355.53                              | 1319.11                                |
| 15    | 335.69                               | 333.54                                 | 53    | 1376.04                              | 1366.38                                |
| 16    | 349.70                               | 357.68                                 | 54    | 1393.05                              | 1402.53                                |
| 17    | 371.27                               | 371.64                                 | 55    | 1412.29                              | 1422.13                                |
| 18    | 438.44                               | 416.26                                 | 56    | 1430.17                              | 1406.45                                |
| 19    | 439.70                               | 437.18                                 | 57    | 1473.69                              | 1470.11                                |
| 20    | 462.48                               | 461.08                                 | 58    | 1481.83                              | 1484.55                                |
| 21    | 510.62                               | 509.18                                 | 59    | 1486.62                              | 1485.62                                |
| 22    | 526.31                               | 528.81                                 | 60    | 1498.16                              | 1507.10                                |
| 23    | 533.09                               | 529.64                                 | 61    | 1505.63                              | 1485.71                                |
| 24    | 548.06                               | 550.26                                 | 62    | 1515.99                              | 1501.49                                |
| 25    | 635.92                               | 624.42                                 | 63    | 1542.92                              | 1533.28                                |
| 26    | 645.52                               | 659.25                                 | 64    | 1588.16                              | 1549.50                                |
| 27    | 660.83                               | 682.52                                 | 65    | 1638.62                              | 1606.04                                |
| 28    | 664.29                               | 683.10                                 | 66    | 1723.59                              | 1788.42                                |
| 29    | 687.59                               | 668.03                                 | 67    | 3025.17                              | 3039.59                                |
| 30    | 714.83                               | 721.38                                 | 68    | 3029.32                              | 3042.44                                |
| 31    | 759.34                               | 767.66                                 | 69    | 3087.60                              | 3109.66                                |
| 32    | 770.49                               | 777.39                                 | 70    | 3091.86                              | 3113.42                                |
| 33    | 799.78                               | 803.12                                 | 71    | 3105.43                              | 3115.31                                |
| 34    | 817.75                               | 830.08                                 | 72    | 3107.45                              | 3116.97                                |
| 35    | 822.13                               | 837.60                                 | 73    | 3158.68                              | 3191.83                                |
| 36    | 861.64                               | 851.13                                 | 74    | 3179.10                              | 3208.96                                |
| 37    | 866.14                               | 894.55                                 | 75    | 3181.43                              | 3206.31                                |
| 38    | 898.20                               | 904.37                                 |       |                                      |  |

Table S6: Harmonic vibrational frequencies for the *trans*-M-phenolate-keto anion and neutral radical, calculated using the B3LYP/6-311G++(2df,2pd) method. The mode numbering ( $\nu$ ) employed in this work is the one used in the Gaussian 09 Software Package.

| $\nu$ | anion<br>$\omega_e / \text{cm}^{-1}$ | radical<br>$\omega_e / \text{cm}^{-1}$ | $\nu$ | anion<br>$\omega_e / \text{cm}^{-1}$ | radical<br>$\omega_e / \text{cm}^{-1}$ |
|-------|--------------------------------------|--|-------|--------------------------------------|--|
| 1     | 33.94                                | 38.95                                  | 39    | 940.02                               | 943.99                                 |
| 2     | 43.21                                | 11.24                                  | 40    | 954.50                               | 960.41                                 |
| 3     | 56.73                                | 56.75                                  | 41    | 986.71                               | 1007.49                                |
| 4     | 75.39                                | 74.45                                  | 42    | 1024.79                              | 1032.95                                |
| 5     | 126.27                               | 123.72                                 | 43    | 1027.16                              | 1031.95                                |
| 6     | 186.33                               | 187.30                                 | 44    | 1120.40                              | 1115.54                                |
| 7     | 199.13                               | 195.92                                 | 45    | 1155.03                              | 1160.27                                |
| 8     | 212.74                               | 209.08                                 | 46    | 1157.48                              | 1156.36                                |
| 9     | 222.73                               | 223.78                                 | 47    | 1171.91                              | 1132.41                                |
| 10    | 236.75                               | 236.16                                 | 48    | 1207.03                              | 1187.29                                |
| 11    | 238.78                               | 237.90                                 | 49    | 1239.32                              | 1230.85                                |
| 12    | 263.40                               | 265.40                                 | 50    | 1243.49                              | 1242.96                                |
| 13    | 296.84                               | 295.99                                 | 51    | 1271.02                              | 1284.02                                |
| 14    | 321.44                               | 315.95                                 | 52    | 1360.73                              | 1363.95                                |
| 15    | 345.40                               | 342.25                                 | 53    | 1378.94                              | 1316.13                                |
| 16    | 350.95                               | 355.68                                 | 54    | 1391.96                              | 1423.11                                |
| 17    | 361.94                               | 362.13                                 | 55    | 1411.53                              | 1397.35                                |
| 18    | 440.60                               | 438.72                                 | 56    | 1416.99                              | 1403.66                                |
| 19    | 441.65                               | 414.66                                 | 57    | 1470.79                              | 1506.63                                |
| 20    | 477.42                               | 475.01                                 | 58    | 1482.16                              | 1484.85                                |
| 21    | 494.65                               | 494.52                                 | 59    | 1486.80                              | 1470.28                                |
| 22    | 518.36                               | 524.65                                 | 60    | 1497.76                              | 1484.90                                |
| 23    | 518.92                               | 522.86                                 | 61    | 1506.34                              | 1486.13                                |
| 24    | 545.99                               | 548.13                                 | 62    | 1518.32                              | 1501.85                                |
| 25    | 630.40                               | 621.15                                 | 63    | 1534.57                              | 1545.46                                |
| 26    | 636.14                               | 652.64                                 | 64    | 1589.19                              | 1535.03                                |
| 27    | 655.49                               | 674.57                                 | 65    | 1638.74                              | 1604.72                                |
| 28    | 663.31                               | 663.73                                 | 66    | 1720.59                              | 1788.96                                |
| 29    | 686.80                               | 684.26                                 | 67    | 3026.38                              | 3040.32                                |
| 30    | 695.76                               | 694.44                                 | 68    | 3030.82                              | 3043.14                                |
| 31    | 761.55                               | 766.21                                 | 69    | 3089.09                              | 3109.84                                |
| 32    | 768.78                               | 776.17                                 | 70    | 3093.57                              | 3113.51                                |
| 33    | 783.26                               | 783.45                                 | 71    | 3107.76                              | 3116.84                                |
| 34    | 818.18                               | 825.12                                 | 72    | 3109.77                              | 3118.45                                |
| 35    | 820.22                               | 830.95                                 | 73    | 3162.12                              | 3193.98                                |
| 36    | 866.52                               | 854.48                                 | 74    | 3180.89                              | 3209.54                                |
| 37    | 867.87                               | 894.09                                 | 75    | 3183.63                              | 3207.07                                |
| 38    | 926.49                               | 927.89                                 |       |                                      |  |

Table S7: Harmonic vibrational frequencies for the *cis*-M-phenolate-keto anion and neutral radical, calculated using the B3LYP/6-311G++(2df,2pd) method. The mode numbering ( $\nu$ ) employed in this work is the one used in the Gaussian 09 Software Package.



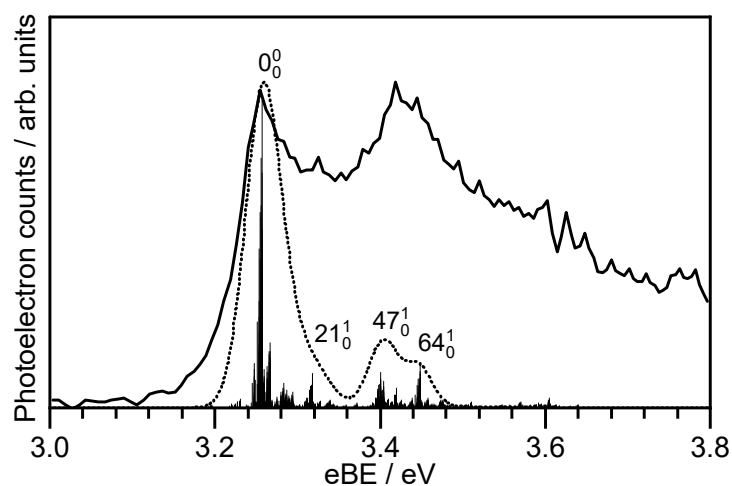


Figure S14: Calculated *M-cis*-phenolate-keto  $S_0$ - $D_0$  stick spectrum at 300 K convoluted with the instrument function (dotted line) and compared with the experimental 294 nm (4.22 eV) photoelectron spectrum (solid line).

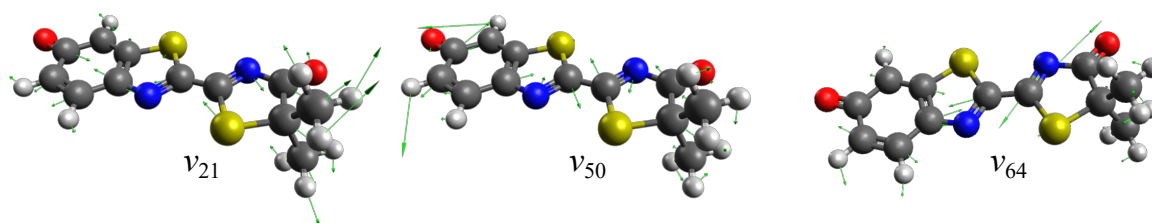


Figure S15: Atomic displacement vectors of the  $\nu_{21}$ ,  $\nu_{50}$  and  $\nu_{64}$  modes of the *trans*-*M*-phenolate-keto radical, which respectively correspond to in-plane distortions, in-plane distortions/stretch and phenolate CN stretch/ in-plane distortions.

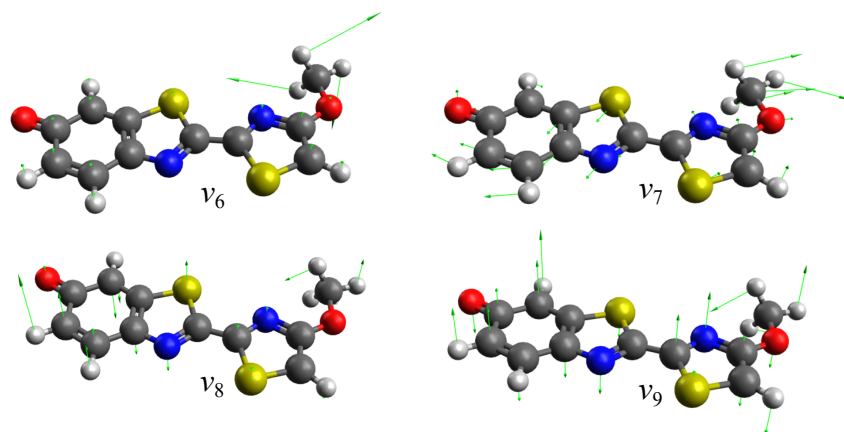


Figure S16: Atomic displacement vectors of the  $\nu_6$  ( $167\text{ cm}^{-1}$ ),  $\nu_7$  ( $184\text{ cm}^{-1}$ ),  $\nu_8$  ( $192\text{ cm}^{-1}$ ) and  $\nu_9$  ( $222\text{ cm}^{-1}$ ) modes of the *trans*-*M*-phenolate-enol radical, which respectively correspond to out-of-plane distortions, in-plane distortions/stretch, out-of-plane distortions on the benzothiazole moiety and out-of-plane distortions.

### 3.4 Coordinates of optimised structures

| atom | <i>trans</i> coordinates /Å |           |           | <i>cis</i> coordinates /Å |           |           |
|------|-----------------------------|-----------|-----------|---------------------------|-----------|-----------|
|      | <i>x</i>                    | <i>y</i>  | <i>z</i>  | <i>x</i>                  | <i>y</i>  | <i>z</i>  |
| C    | 0.129819                    | 1.838185  | 0.000000  | 4.365470                  | -0.044196 | -0.000155 |
| C    | 1.035883                    | 4.193824  | 0.000000  | 3.271359                  | -0.991244 | -0.000067 |
| C    | -0.498590                   | 3.995221  | 0.000000  | 1.978131                  | -0.545231 | -0.000044 |
| C    | 0.000000                    | 0.437220  | 0.000000  | 1.639846                  | 0.854964  | -0.000052 |
| C    | 0.648812                    | -1.675712 | 0.000000  | 2.702034                  | 1.801325  | -0.000051 |
| C    | -0.771249                   | -1.917228 | 0.000000  | 3.991380                  | 1.374402  | -0.000072 |
| C    | -1.299042                   | -3.180235 | 0.000000  | -0.433752                 | 0.084077  | -0.000049 |
| C    | -0.426792                   | -4.334086 | 0.000000  | -1.846677                 | 0.107040  | -0.000056 |
| C    | 1.013634                    | -4.054356 | 0.000000  | -4.294712                 | -0.566805 | 0.000125  |
| C    | 1.524515                    | -2.795590 | 0.000000  | -3.934206                 | 0.940676  | 0.000054  |
| H    | -2.365109                   | -3.362162 | 0.000000  | 3.522846                  | -2.042934 | -0.000033 |
| H    | 1.662022                    | -4.921286 | 0.000000  | 2.448674                  | 2.854032  | -0.000025 |
| H    | 2.592107                    | -2.613354 | 0.000000  | 4.813633                  | 2.078496  | -0.000053 |
| H    | 1.326294                    | 4.758940  | 0.883960  | -4.884246                 | -0.798708 | 0.884999  |
| H    | 1.326294                    | 4.758940  | -0.883960 | -4.884308                 | -0.798783 | -0.884687 |
| N    | -0.877029                   | 2.677797  | 0.000000  | 0.341061                  | 1.155097  | -0.000037 |
| N    | 1.027894                    | -0.395491 | 0.000000  | -2.588415                 | 1.184878  | -0.000027 |
| O    | -0.855003                   | -5.506785 | 0.000000  | 5.562896                  | -0.396090 | -0.000023 |
| O    | -1.247325                   | 4.954624  | 0.000000  | -4.817845                 | 1.777745  | 0.000067  |
| S    | 1.780229                    | 2.542027  | 0.000000  | 0.487181                  | -1.456612 | 0.000021  |
| S    | -1.587790                   | -0.368488 | 0.000000  | -2.729604                 | -1.469339 | 0.000110  |

Table S8: Cartesian coordinates of the *trans* and *cis* isomers of phenolate-keto optimised using B3LYP/6-311++G(2df,2pd).

| atom | <i>trans</i> coordinates /Å |           |          | <i>cis</i> coordinates /Å |           |           |
|------|-----------------------------|-----------|----------|---------------------------|-----------|-----------|
|      | <i>x</i>                    | <i>y</i>  | <i>z</i> | <i>x</i>                  | <i>y</i>  | <i>z</i>  |
| C    | 0.008196                    | 1.842394  | 0.000000 | -4.391878                 | -0.007245 | 0.000592  |
| C    | 0.750348                    | 3.912454  | 0.000000 | -3.308530                 | -0.964217 | 0.000147  |
| C    | -0.579961                   | 4.220386  | 0.000000 | -2.006488                 | -0.531740 | -0.000013 |
| C    | 0.000000                    | 0.418502  | 0.000000 | -1.646481                 | 0.853045  | -0.000138 |
| C    | 0.544911                    | -2.000808 | 0.000000 | -2.691560                 | 1.807276  | -0.000316 |
| C    | -0.837184                   | -1.629963 | 0.000000 | -3.993777                 | 1.398497  | -0.000179 |
| C    | 0.961361                    | -3.309247 | 0.000000 | 0.417969                  | 0.053268  | -0.000113 |
| C    | -0.006079                   | -4.382471 | 0.000000 | 1.848397                  | 0.043012  | 0.000016  |
| C    | -1.408426                   | -3.969379 | 0.000000 | 4.228687                  | -0.583831 | -0.000444 |
| C    | -1.803640                   | -2.662856 | 0.000000 | 3.931591                  | 0.751034  | 0.000236  |
| H    | 2.008509                    | -3.581179 | 0.000000 | -3.569046                 | -2.014047 | 0.000087  |
| H    | -2.138025                   | -4.769731 | 0.000000 | -2.428417                 | 2.858170  | -0.000620 |
| H    | -2.852320                   | -2.389816 | 0.000000 | -4.801487                 | 2.119797  | -0.000461 |
| H    | -1.049436                   | 5.189077  | 0.000000 | 5.189716                  | -1.068081 | -0.000915 |
| H    | 1.430248                    | 5.691324  | 0.000000 | 5.721314                  | 1.403765  | 0.000081  |
| N    | 1.083489                    | 2.603821  | 0.000000 | -0.325463                 | 1.129553  | -0.000270 |
| N    | -1.093255                   | -0.303432 | 0.000000 | 2.631518                  | 1.102411  | 0.000425  |
| O    | 0.320185                    | -5.593394 | 0.000000 | -5.598314                 | -0.348731 | -0.000345 |
| O    | 1.789907                    | 4.800576  | 0.000000 | 4.835785                  | 1.776353  | 0.000313  |
| S    | -1.504497                   | 2.746477  | 0.000000 | -0.524546                 | -1.471148 | -0.000237 |
| S    | 1.505215                    | -0.529847 | 0.000000 | 2.744433                  | -1.482534 | 0.000378  |

Table S9: Cartesian coordinates of the *trans* and *cis* isomers of phenolate-enol optimised using B3LYP/6-311++G(2df,2pd).

| atom | <i>trans</i> coordinates /Å |           |          | <i>cis</i> coordinates /Å |           |           |
|------|-----------------------------|-----------|----------|---------------------------|-----------|-----------|
|      | <i>x</i>                    | <i>y</i>  | <i>z</i> | <i>x</i>                  | <i>y</i>  | <i>z</i>  |
| C    | 2.374887                    | -2.124477 | 0.000000 | -2.628428                 | 1.798535  | 0.162999  |
| C    | 1.230503                    | -1.319693 | 0.000000 | -1.580699                 | 0.877527  | 0.068150  |
| C    | -0.040262                   | -1.943018 | 0.000000 | -1.894478                 | -0.495005 | -0.062931 |
| C    | -0.166102                   | -3.329303 | 0.000000 | -3.212590                 | -0.940376 | -0.096828 |
| C    | 0.989009                    | -4.101222 | 0.000000 | -4.230913                 | 0.000740  | -0.001745 |
| C    | 2.252709                    | -3.504720 | 0.000000 | -3.943296                 | 1.361455  | 0.127351  |
| C    | 0.000000                    | 0.520406  | 0.000000 | 0.508870                  | 0.132276  | 0.001027  |
| C    | -0.413707                   | 1.892959  | 0.000000 | 1.951521                  | 0.096938  | 0.008035  |
| C    | -1.840366                   | 3.664723  | 0.000000 | 4.109199                  | 0.809116  | -0.055288 |
| C    | -0.562770                   | 4.303618  | 0.000000 | 4.275324                  | -0.602807 | 0.084392  |
| H    | -1.141706                   | -3.802036 | 0.000000 | -3.446428                 | -1.994013 | -0.196361 |
| H    | 3.126730                    | -4.141299 | 0.000000 | -4.764696                 | 2.060772  | 0.199063  |
| H    | 3.349015                    | -1.655001 | 0.000000 | -2.395069                 | 2.849262  | 0.264426  |
| H    | 0.023215                    | -5.761592 | 0.000000 | -5.622673                 | -1.317606 | -0.125872 |
| H    | -0.392213                   | 5.366730  | 0.000000 | 5.214606                  | -1.122924 | 0.160953  |
| N    | 1.214880                    | 0.052950  | 0.000000 | -0.242931                 | 1.184724  | 0.097789  |
| N    | -1.665665                   | 2.260224  | 0.000000 | 2.729129                  | 1.131887  | -0.093152 |
| O    | -2.955936                   | 4.216393  | 0.000000 | 5.012157                  | 1.659592  | -0.134934 |
| O    | 0.942385                    | -5.481260 | 0.000000 | -5.561762                 | -0.363265 | -0.031254 |
| S    | -1.284214                   | -0.724609 | 0.000000 | -0.421844                 | -1.409249 | -0.176205 |
| S    | 0.743930                    | 3.197377  | 0.000000 | 2.788356                  | -1.440761 | 0.172452  |

Table S10: Cartesian coordinates of the *trans* and *cis* isomers of phenol-enolate optimised using B3LYP/6-311++G(2df,2pd).

| atom | <i>trans</i> coordinates /Å |           |           | <i>cis</i> coordinates /Å |           |           |
|------|-----------------------------|-----------|-----------|---------------------------|-----------|-----------|
|      | <i>x</i>                    | <i>y</i>  | <i>z</i>  | <i>x</i>                  | <i>y</i>  | <i>z</i>  |
| C    | 0.905216                    | -0.883969 | 0.000000  | 1.162935                  | -0.526712 | 0.000000  |
| C    | 1.944532                    | -3.220593 | 0.000000  | 2.856126                  | -2.462997 | 0.000000  |
| C    | 2.869962                    | -1.963109 | 0.000000  | 3.358426                  | -0.981781 | 0.000000  |
| C    | 0.013722                    | 0.205451  | 0.000000  | -0.026268                 | 0.238571  | 0.000000  |
| C    | -1.927399                   | 1.262471  | 0.000000  | -1.324650                 | 2.029833  | 0.000000  |
| C    | -1.081184                   | 2.427904  | 0.000000  | -2.382394                 | 1.052168  | 0.000000  |
| C    | -1.586550                   | 3.700149  | 0.000000  | -3.706271                 | 1.397460  | 0.000000  |
| C    | -3.016715                   | 3.915802  | 0.000000  | -4.092049                 | 2.791982  | 0.000000  |
| C    | -3.850915                   | 2.708716  | 0.000000  | -2.994293                 | 3.765144  | 0.000000  |
| C    | -3.336342                   | 1.451299  | 0.000000  | -1.684258                 | 3.406236  | 0.000000  |
| C    | 2.212907                    | -4.048088 | 1.261942  | 3.358426                  | -3.171966 | 1.262282  |
| C    | 2.212907                    | -4.048088 | -1.261942 | 3.358426                  | -3.171966 | -1.262282 |
| H    | -0.950989                   | 4.575178  | 0.000000  | -4.498349                 | 0.661320  | 0.000000  |
| H    | -4.920630                   | 2.875153  | 0.000000  | -3.288537                 | 4.806957  | 0.000000  |
| H    | -3.972589                   | 0.574819  | 0.000000  | -0.890076                 | 4.142210  | 0.000000  |
| H    | 1.591280                    | -4.944880 | 1.281197  | 3.039287                  | -4.215374 | 1.279108  |
| H    | 3.262067                    | -4.347255 | 1.274068  | 4.448687                  | -3.137395 | 1.275545  |
| H    | 2.007998                    | -3.470774 | 2.162606  | 2.986829                  | -2.684905 | 2.162753  |
| H    | 1.591280                    | -4.944880 | -1.281197 | 3.039287                  | -4.215374 | -1.279108 |
| H    | 3.262067                    | -4.347255 | -1.274068 | 4.448687                  | -3.137395 | -1.275545 |
| H    | 2.007998                    | -3.470774 | -2.162606 | 2.986829                  | -2.684905 | -2.162753 |
| N    | 2.212907                    | -0.763431 | 0.000000  | 2.377106                  | -0.032620 | 0.000000  |
| N    | -1.303166                   | 0.081920  | 0.000000  | -0.077192                 | 1.559138  | 0.000000  |
| O    | -3.530447                   | 5.053802  | 0.000000  | -5.283870                 | 3.162957  | 0.000000  |
| O    | 4.080295                    | -2.107793 | 0.000000  | 4.558443                  | -0.765835 | 0.000000  |
| S    | 0.239046                    | -2.538623 | 0.000000  | 1.029867                  | -2.316634 | 0.000000  |
| S    | 0.585560                    | 1.892092  | 0.000000  | -1.646965                 | -0.532965 | 0.000000  |

Table S11: Cartesian coordinates of the *trans* and *cis* isomers of M-phenolate-keto optimised using B3LYP/6-311++G(2df,2pd).

| atom | <i>trans</i> coordinates /Å |           |           | <i>cis</i> coordinates /Å |           |           |
|------|-----------------------------|-----------|-----------|---------------------------|-----------|-----------|
|      | <i>x</i>                    | <i>y</i>  | <i>z</i>  | <i>x</i>                  | <i>y</i>  | <i>z</i>  |
| C    | 0.914513                    | -0.908564 | -0.035908 | 0.603874                  | -1.126787 | 0.000000  |
| C    | 1.941468                    | -3.242138 | -0.044975 | 1.021405                  | -3.623920 | 0.000000  |
| C    | 2.864916                    | -1.990786 | -0.025869 | 2.232738                  | -2.650671 | 0.000000  |
| C    | 0.005430                    | 0.235976  | -0.035331 | 0.024543                  | 0.206185  | 0.000000  |
| C    | -0.625343                   | 2.341796  | -0.023919 | -1.531247                 | 1.756009  | 0.000000  |
| C    | -1.924771                   | 1.744244  | -0.041432 | -0.380737                 | 2.605352  | 0.000000  |
| C    | -3.067013                   | 2.500184  | -0.046185 | -0.498051                 | 3.971187  | 0.000000  |
| C    | -2.952030                   | 3.950177  | -0.033006 | -1.824218                 | 4.567343  | 0.000000  |
| C    | -1.608558                   | 4.531255  | -0.015207 | -2.979620                 | 3.668456  | 0.000000  |
| C    | -0.494079                   | 3.759248  | -0.010838 | -2.837716                 | 2.320103  | 0.000000  |
| C    | 2.181117                    | -4.076058 | 1.218195  | 1.059369                  | -4.486305 | 1.266846  |
| C    | 2.205695                    | -4.055459 | -1.316596 | 1.059369                  | -4.486305 | -1.266846 |
| H    | -4.061592                   | 2.078370  | -0.059298 | 0.349832                  | 4.640999  | 0.000000  |
| H    | -1.555069                   | 5.610637  | -0.005721 | -3.951897                 | 4.140416  | 0.000000  |
| H    | 0.500960                    | 4.181700  | 0.002324  | -3.687432                 | 1.651493  | 0.000000  |
| H    | 1.555506                    | -4.968177 | 1.218968  | 0.228552                  | -5.191201 | 1.280353  |
| H    | 3.226986                    | -4.382820 | 1.238680  | 1.994145                  | -5.047053 | 1.278659  |
| H    | 1.972100                    | -3.505800 | 2.121926  | 1.010961                  | -3.878231 | 2.168942  |
| H    | 1.580492                    | -4.947446 | -1.343955 | 0.228552                  | -5.191201 | -1.280353 |
| H    | 3.251858                    | -4.361856 | -1.321820 | 1.994145                  | -5.047053 | -1.278659 |
| H    | 2.014034                    | -3.470640 | -2.214858 | 1.010961                  | -3.878231 | -2.168942 |
| N    | 2.192485                    | -0.760919 | -0.022380 | 1.883874                  | -1.293282 | 0.000000  |
| N    | 0.410965                    | 1.479445  | -0.021035 | -1.265370                 | 0.431654  | 0.000000  |
| O    | -3.965740                   | 4.667181  | -0.036849 | -1.967590                 | 5.801022  | 0.000000  |
| O    | 4.062255                    | -2.105022 | -0.015232 | 3.365419                  | -3.056830 | 0.000000  |
| S    | 0.237433                    | -2.540589 | -0.055738 | -0.458633                 | -2.520894 | 0.000000  |
| S    | -1.743079                   | 0.010546  | -0.054134 | 1.059369                  | 1.618022  | 0.000000  |

Table S12: Cartesian coordinates of the *trans* and *cis* isomers of the deprotonated M-phenolate-keto neutral radical optimised using B3LYP/6-311++G(2df,2pd).

| atom | <i>trans</i> coordinates /Å |           |           | <i>cis</i> coordinates /Å |           |           |
|------|-----------------------------|-----------|-----------|---------------------------|-----------|-----------|
|      | <i>x</i>                    | <i>y</i>  | <i>z</i>  | <i>x</i>                  | <i>y</i>  | <i>z</i>  |
| C    | 4.619769                    | -0.454730 | 0.000175  | -4.648901                 | 0.231380  | 0.000025  |
| C    | 3.417785                    | -1.255956 | 0.000007  | -3.661564                 | -0.824265 | 0.000009  |
| C    | 2.183738                    | -0.653531 | -0.000014 | -2.323876                 | -0.517735 | 0.000003  |
| C    | 2.016108                    | 0.766859  | 0.000012  | -1.833004                 | 0.825461  | -0.000001 |
| C    | 3.178163                    | 1.572717  | -0.000008 | -2.781988                 | 1.874697  | -0.000008 |
| C    | 4.413867                    | 0.991746  | 0.000010  | -4.117745                 | 1.592200  | -0.000003 |
| C    | -0.132911                   | 0.236654  | -0.000012 | 0.145434                  | -0.169769 | -0.000003 |
| C    | -1.544824                   | 0.424963  | 0.000014  | 1.569328                  | -0.313535 | -0.000002 |
| C    | -3.830727                   | 1.315517  | 0.000046  | 3.891326                  | -1.139805 | -0.000013 |
| C    | -3.700663                   | -0.044135 | 0.000018  | 3.712072                  | 0.216336  | -0.000004 |
| C    | -4.502152                   | -2.273434 | -0.000003 | 4.438451                  | 2.469789  | 0.000015  |
| H    | 3.534036                    | -2.331527 | -0.000065 | -4.020807                 | -1.844542 | 0.000006  |
| H    | 3.060603                    | 2.649933  | -0.000050 | -2.420367                 | 2.896048  | -0.000019 |
| H    | 5.311215                    | 1.598078  | -0.000043 | -4.852482                 | 2.387772  | -0.000013 |
| H    | -4.733772                   | 1.898116  | 0.000058  | 4.810576                  | -1.695951 | -0.000020 |
| H    | -3.935788                   | -2.566705 | 0.884520  | 3.861329                  | 2.742324  | 0.883870  |
| H    | -5.475013                   | -2.760613 | -0.000016 | 5.394724                  | 2.988828  | 0.000011  |
| H    | -3.935763                   | -2.566710 | -0.884509 | 3.861309                  | 2.742350  | -0.883819 |
| N    | 0.739511                    | 1.212679  | 0.000004  | -0.490210                 | 0.973427  | -0.000005 |
| N    | -2.441847                   | -0.543589 | -0.000004 | 2.441922                  | 0.676142  | 0.000000  |
| O    | 5.770632                    | -0.954066 | -0.000127 | -5.882697                 | 0.006791  | -0.000010 |
| O    | -4.775432                   | -0.875841 | -0.000011 | 4.759281                  | 1.080984  | -0.000010 |
| S    | 0.589002                    | -1.391029 | -0.000114 | -0.938592                 | -1.595460 | -0.000004 |
| S    | -2.250233                   | 2.033219  | 0.000098  | 2.335708                  | -1.900448 | 0.000008  |

Table S13: Cartesian coordinates of the *trans* and *cis* isomers of M-phenolate-enol optimised using B3LYP/6-311++G(2df,2pd).

| atom | radical coordinates /Å |           |           |
|------|------------------------|-----------|-----------|
|      | <i>x</i>               | <i>y</i>  | <i>z</i>  |
| C    | -4.584014              | -0.457591 | 0.000371  |
| C    | -3.383743              | -1.276751 | 0.000072  |
| C    | -2.159649              | -0.668320 | 0.000016  |
| C    | -2.024658              | 0.757290  | 0.000000  |
| C    | -3.185895              | 1.576314  | -0.000065 |
| C    | -4.412865              | 0.995343  | -0.000015 |
| C    | 0.115015               | 0.237216  | -0.000012 |
| C    | 1.533060               | 0.438089  | 0.000019  |
| C    | 3.786718               | 1.323401  | -0.000053 |
| C    | 3.674218               | -0.052239 | -0.000009 |
| C    | 4.515944               | -2.266385 | -0.000031 |
| H    | -3.513042              | -2.349572 | 0.000001  |
| H    | -3.059253              | 2.650245  | -0.000176 |
| H    | -5.320302              | 1.582759  | -0.000128 |
| H    | 4.688874               | 1.908470  | -0.000111 |
| H    | 3.961660               | -2.568214 | -0.887939 |
| H    | 5.502594               | -2.719272 | -0.000085 |
| H    | 3.961763               | -2.568201 | 0.887946  |
| N    | -0.756378              | 1.218942  | -0.000025 |
| N    | 2.415165               | -0.539183 | 0.000028  |
| O    | -5.714892              | -0.973586 | -0.000087 |
| O    | 4.747713               | -0.853159 | -0.000056 |
| S    | -0.563291              | -1.387431 | -0.000141 |
| S    | 2.229469               | 2.030009  | 0.000134  |

Table S14: Cartesian coordinates of the deprotonated *trans*-M-phenolate-enol neutral radical optimised using B3LYP/6-311++G(2df,2pd).

| atom | <i>trans</i> coordinates /Å |           |           | <i>cis</i> coordinates /Å |           |           |
|------|-----------------------------|-----------|-----------|---------------------------|-----------|-----------|
|      | <i>x</i>                    | <i>y</i>  | <i>z</i>  | <i>x</i>                  | <i>y</i>  | <i>z</i>  |
| C    | 3.862679                    | 0.189630  | -0.000004 | 3.863614                  | 0.337862  | 0.018536  |
| C    | 2.861444                    | -0.775568 | 0.000000  | 2.901291                  | -0.665638 | -0.028360 |
| C    | 1.533265                    | -0.348922 | -0.000021 | 1.558586                  | -0.288064 | -0.026971 |
| C    | 1.191287                    | 1.021233  | -0.000042 | 1.161110                  | 1.064657  | 0.022798  |
| C    | 2.222278                    | 1.969765  | -0.000044 | 2.154098                  | 2.050870  | 0.070716  |
| C    | 3.540531                    | 1.554830  | -0.000026 | 3.487948                  | 1.687875  | 0.067959  |
| C    | -0.866927                   | 0.208523  | -0.000055 | -0.878498                 | 0.193095  | -0.012531 |
| C    | -2.296560                   | 0.096868  | -0.000015 | -2.316957                 | 0.071527  | -0.009363 |
| C    | -4.683943                   | 0.467020  | -0.000159 | -4.595403                 | -0.759368 | 0.112211  |
| C    | -4.333143                   | -0.917103 | 0.000002  | -4.513046                 | 0.644415  | -0.137144 |
| C    | 5.596811                    | -1.455890 | 0.000058  | 5.662008                  | -1.236884 | -0.037659 |
| H    | 3.092786                    | -1.829721 | 0.000014  | 3.173831                  | -1.708977 | -0.066325 |
| H    | 1.971685                    | 3.021775  | -0.000056 | 1.860241                  | 3.090604  | 0.110278  |
| H    | 4.350266                    | 2.271512  | -0.000028 | 4.268657                  | 2.435088  | 0.104000  |
| H    | -5.685898                   | 0.861058  | -0.000293 | -5.502368                 | -1.327256 | 0.228554  |
| H    | 6.684649                    | -1.461234 | 0.000081  | 6.749104                  | -1.198113 | -0.029576 |
| H    | 5.235233                    | -1.980227 | 0.890021  | 5.317469                  | -1.814724 | 0.825584  |
| H    | 5.235271                    | -1.980285 | -0.889887 | 5.327571                  | -1.735096 | -0.952922 |
| N    | -0.152689                   | 1.297701  | -0.000043 | -0.192112                 | 1.293791  | 0.027410  |
| N    | -2.923008                   | -1.047128 | 0.000091  | -3.154170                 | 1.046335  | -0.194816 |
| O    | 5.208373                    | -0.099469 | 0.000007  | 5.218710                  | 0.101283  | 0.019195  |
| O    | -5.109999                   | -1.889338 | -0.000021 | -5.464375                 | 1.430588  | -0.286678 |
| S    | 0.078859                    | -1.307706 | -0.000028 | 0.143389                  | -1.294599 | -0.097404 |
| S    | -3.323075                   | 1.507160  | 0.000137  | -3.061191                 | -1.496263 | 0.273111  |

Table S15: Cartesian coordinates of the *trans* and *cis* isomers of M-phenol-enolate optimised using B3LYP/6-311++G(2df,2pd).



| atom | radical coordinates /Å |           |           |
|------|------------------------|-----------|-----------|
|      | <i>x</i>               | <i>y</i>  | <i>z</i>  |
| C    | 3.844022               | 0.222601  | 0.000031  |
| C    | 2.884980               | -0.783262 | 0.000038  |
| C    | 1.544147               | -0.399279 | 0.000017  |
| C    | 1.155961               | 0.958952  | -0.000010 |
| C    | 2.146900               | 1.954202  | -0.000018 |
| C    | 3.468616               | 1.585140  | 0.000002  |
| C    | -0.850830              | 0.056547  | 0.000008  |
| C    | -2.292191              | -0.020199 | 0.000023  |
| C    | -4.641237              | 0.586272  | -0.000042 |
| C    | -4.376265              | -0.839557 | 0.000067  |
| C    | 5.654964               | -1.339244 | 0.000079  |
| H    | 3.159083               | -1.826163 | 0.000056  |
| H    | 1.855341               | 2.994807  | -0.000039 |
| H    | 4.256151               | 2.324851  | -0.000004 |
| H    | -5.627791              | 1.017711  | -0.000127 |
| H    | 6.738692               | -1.270906 | 0.000089  |
| H    | 5.325348               | -1.875978 | 0.892530  |
| H    | 5.325369               | -1.876015 | -0.892357 |
| N    | -0.194911              | 1.177345  | -0.000024 |
| N    | -2.980822              | -1.097058 | -0.000004 |
| O    | 5.180077               | -0.000357 | 0.000046  |
| O    | -5.229946              | -1.714486 | -0.000061 |
| S    | 0.128677               | -1.407012 | 0.000005  |
| S    | -3.231022              | 1.517974  | -0.000065 |

Table S16: Cartesian coordinates of the deprotonated *trans*-M-phenol-enolate neutral radical optimised using B3LYP/6-311++G(2df,2pd).

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