Title: Reaction paths of keto-enol tautomerization of β-diketones

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Figure S1 to Figure S5 which are auxiliary to Figure 7 and discussions in the text.

Figure S1 Another transition-state geometry of the tautomerization in (malonaldehyde)$_2$.

Figure S2 Transition-state geometries of the tautomerization in (malonaldehyde)$_3$. One keto-form molecule and two enol-form ones are concerned with proton relays.

Figure S3 Another transition-state geometry of the tautomerization in (malonaldehyde)$_3$.

Figure S4 Transition-state geometries of the tautomerization in (malonaldehyde)$_n$ ($n=3$ and 4). One keto-form and n-1 enol-form molecules are concerned with proton relays.

Figure S5 A transition-state geometry of the tautomerization in (malonaldehyde)$_4$. One keto-form and two enol-form
molecules are concerned with proton relays, and another enol-form one works as a catalyst.
(MDA)$_2$

$$\Delta E^\ddagger = 31.00 \text{ kcal/mol}$$
$$\nu^\ddagger = 1232.94 \text{ cm}^{-1}$$

**Figure S1** Another transition-state geometry of the tautomerization in (malonaldehyde)$_2$. 
Figure S2 Transition-state geometries of the tautomerization in (malonaldehyde). One keto-form molecule and two enol-form ones are concerned with proton relays.

\[ \Delta E^+ = 27.37 \text{ kcal/mol} \]
\[ \nu^+ = 743.34 \text{ cm}^{-1} \]

\[ \Delta E^+ = 34.26 \text{ kcal/mol} \]
\[ \nu^+ = 201.59 \text{ cm}^{-1} \]
Figure S3  Another transition-state geometry of the tautomerization in (malonaldehyde)$_3$. 

\[ \Delta E^\ddagger = 46.23 \text{ kcal/mol} \]
\[ v^\ddagger = 1135.08 \text{ cm}^{-1} \]
Figure S4  Transition-state geometries of the tautomerization in \((\text{malonaldehyde})_n\) (n=3 and 4). One keto-form and \(n-1\) enol-form molecules are concerned with proton relays.
Figure S5  A transition-state geometry of the tautomerization in (malonaldehyde)$_4$. One keto-form and two enol-form molecules are concerned with proton relays, and another enol-form one works as a catalyst.