Supporting Information

Active Role of Hydrogen Bonds in Rupe and Meyer-Schuster Rearrangements

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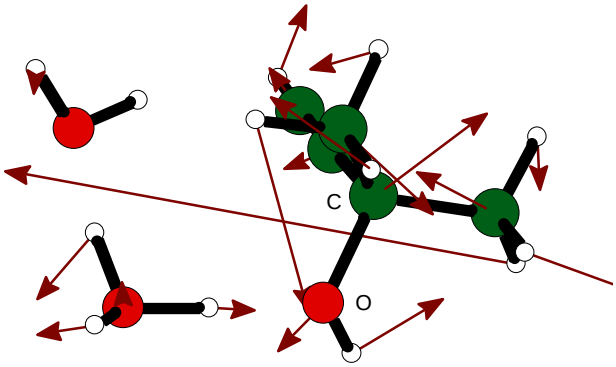
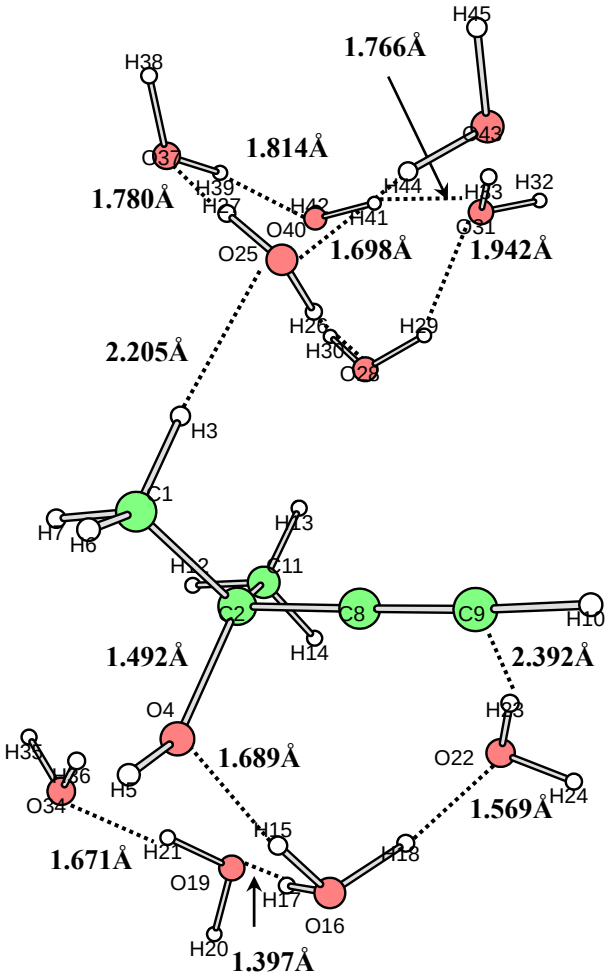
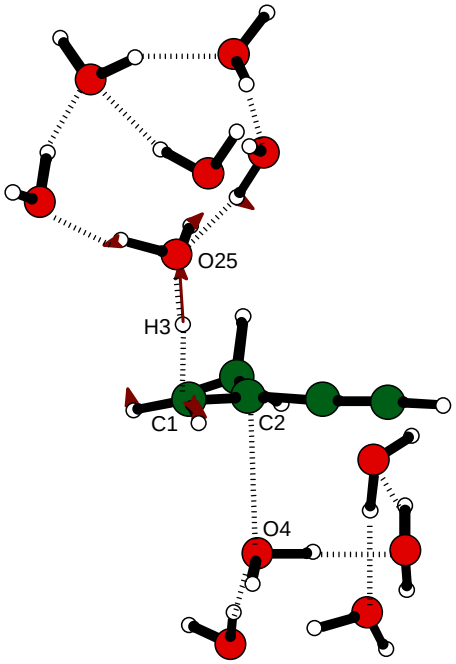


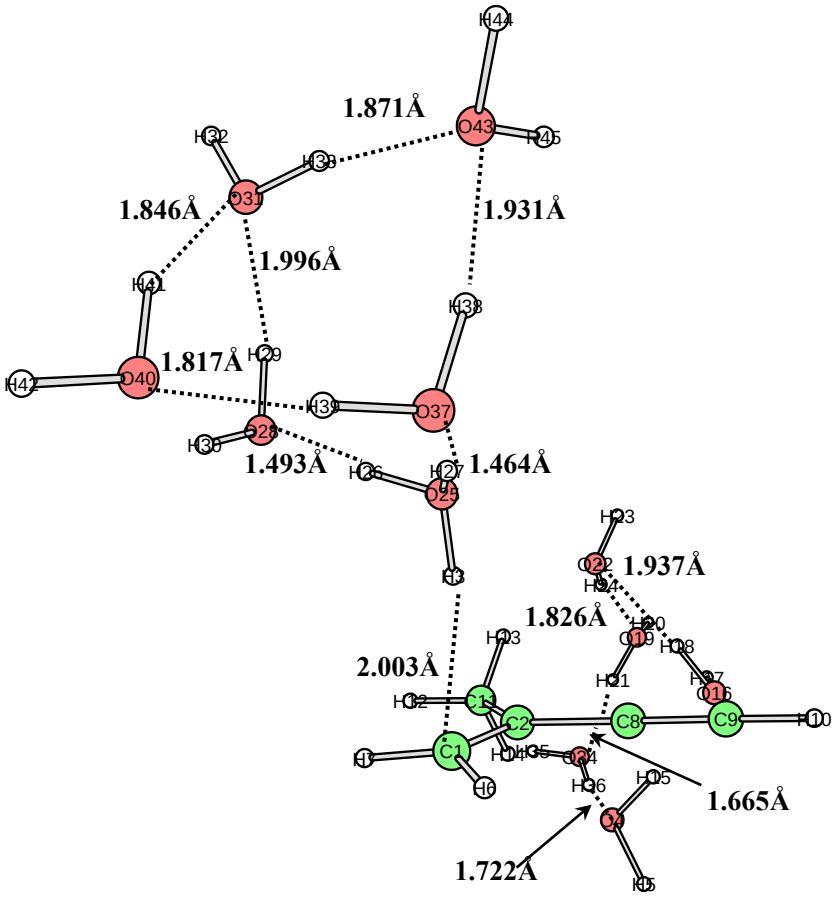
Figure S1. The 28th normal-mode vibration (frequency ν = 967.15 cm^{-1}) of $Me_2C(OH)C{\equiv}CH$ with $H_3O^+(H_2O)$.



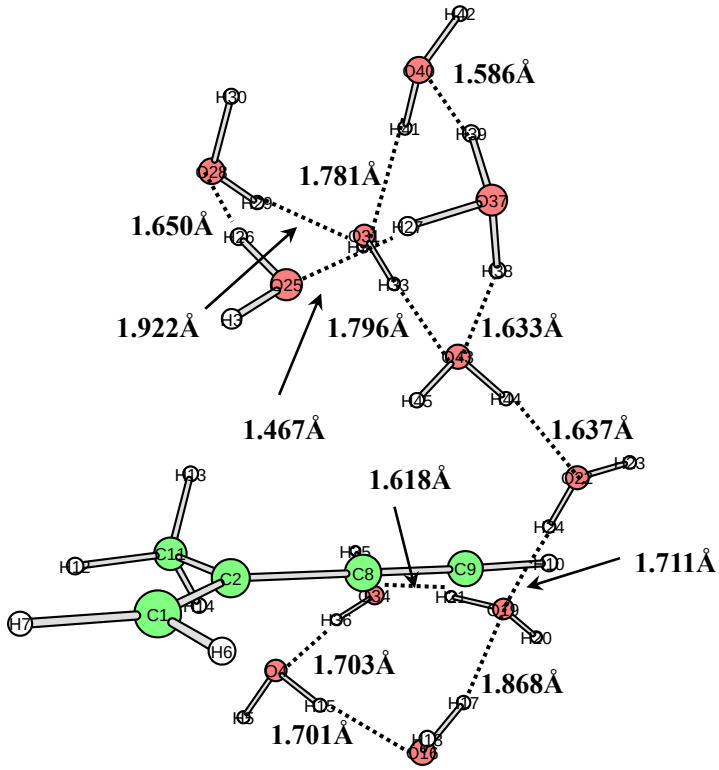
F2-1
ΔE= 0 kcal/mol
(ΔE= 0 kcal/mol)
ΔG°= 0 kcal/mol



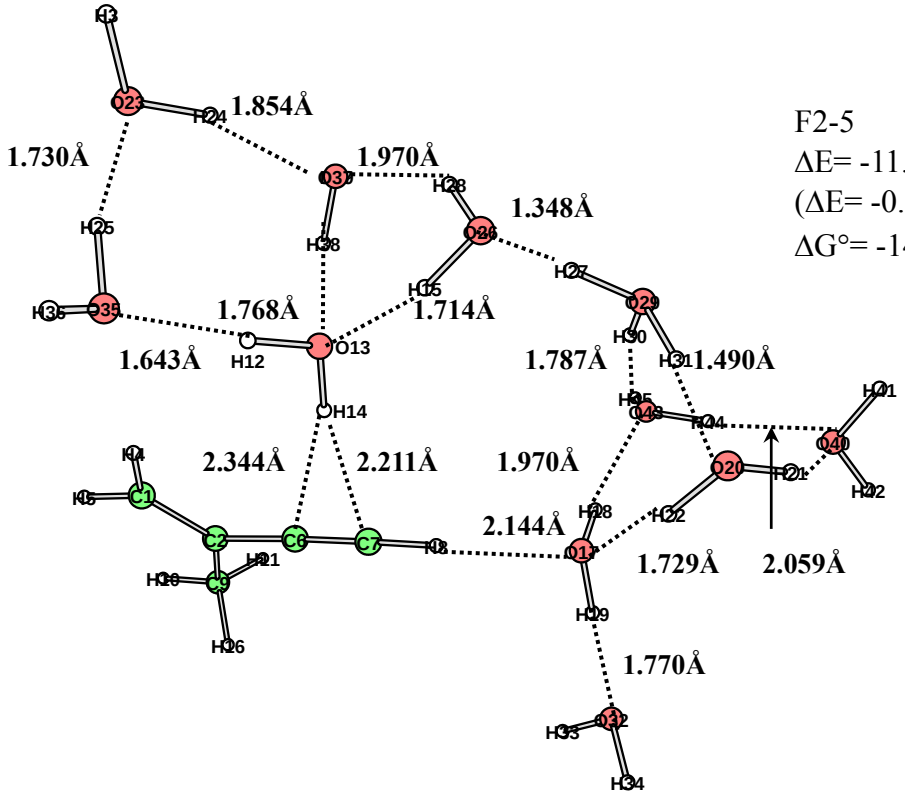
F2-2 **(TS1)**
$\Delta E^{\ddagger}$= +12.29 kcal/mol
($\Delta E^{\ddagger}$= +19.75 kcal/mol)
$\Delta G^{\ddagger}$= +10.89 kcal/mol
$\nu^{\ddagger}$= 922.26í cm^{-1}



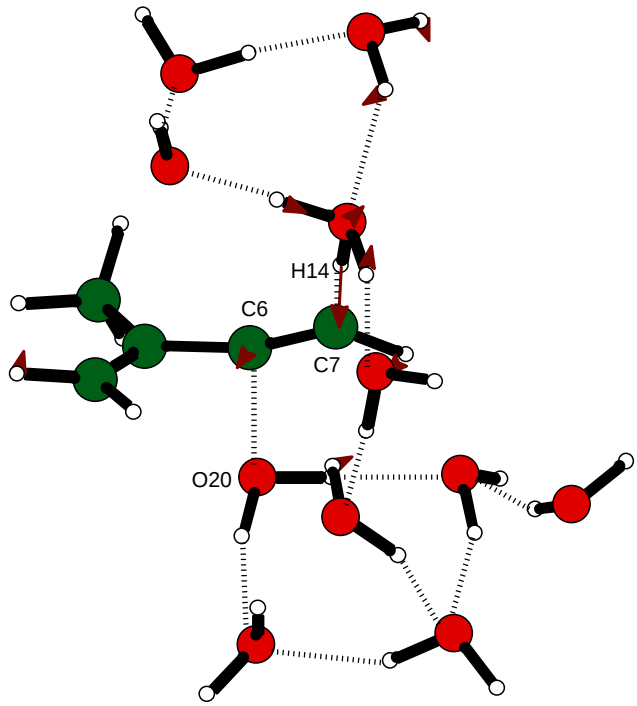
F2-3
ΔE= -7.72 kcal/mol
(ΔE= +12.29 kcal/mol)
ΔG°= -9.60 kcal/mol



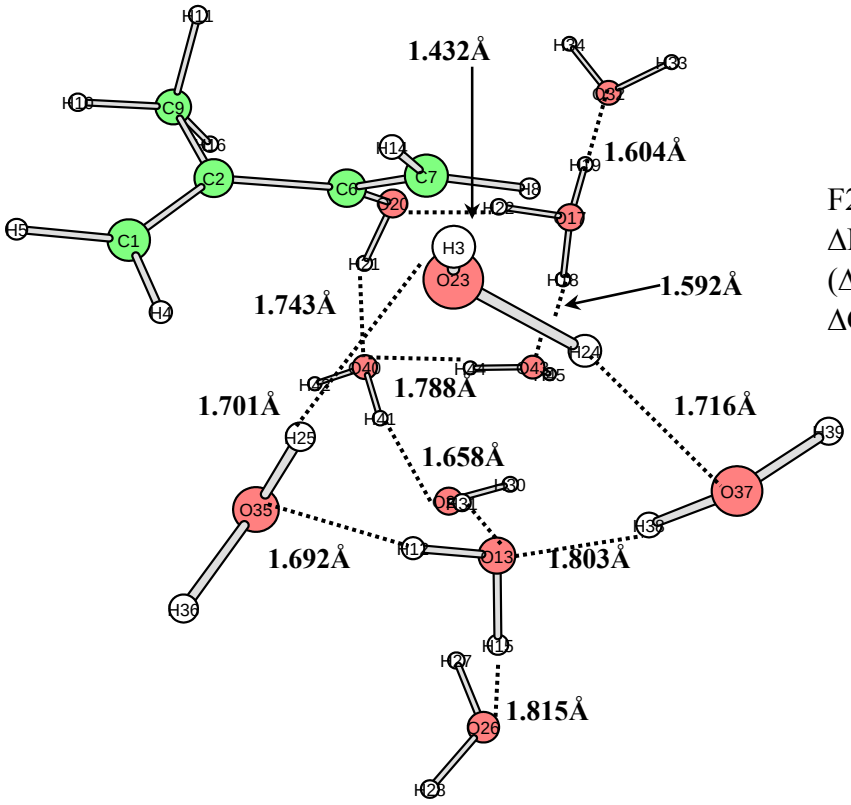
F2-4
ΔE= -6.93 kcal/mol
(ΔE= -2.01 kcal/mol)
ΔG°= -6.87 kcal/mol



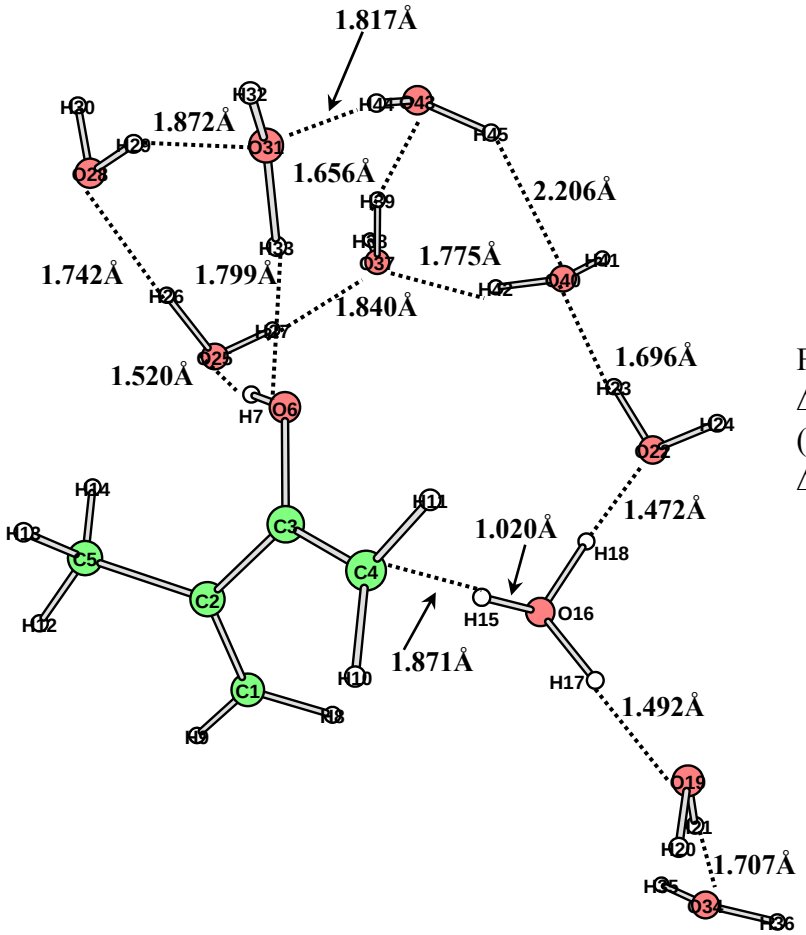
F2-5
ΔE= -11.73 kcal/mol
(ΔE= -0.20 kcal/mol)
ΔG°= -14.88 kcal/mol



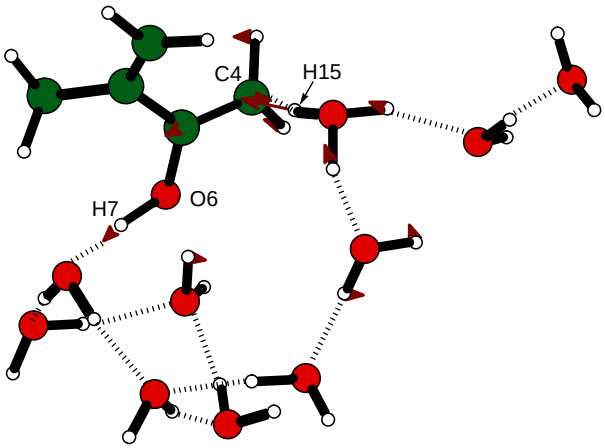
F2-6 **(TS2)**
$\Delta E^{\ddagger}$= +18.05 kcal/mol
($\Delta E^{\ddagger}$= +22.82 kcal/mol)
$\Delta G^{\ddagger}$= +17.16 kcal/mol
$\nu^{\ddagger}$= 791.65í cm^{-1}



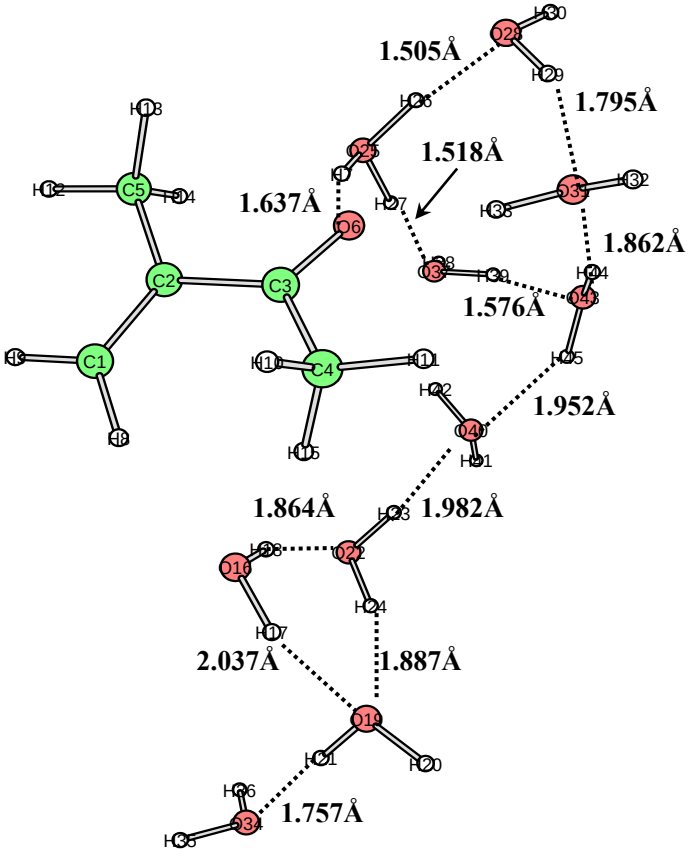
F2-7
ΔE= -22.48 kcal/mol
(ΔE= -21.21 kcal/mol)
ΔG°= -22.87 kcal/mol



F2-8
ΔE= -29.05 kcal/mol
(ΔE= -25.97 kcal/mol)
ΔG°= -30.28 kcal/mol

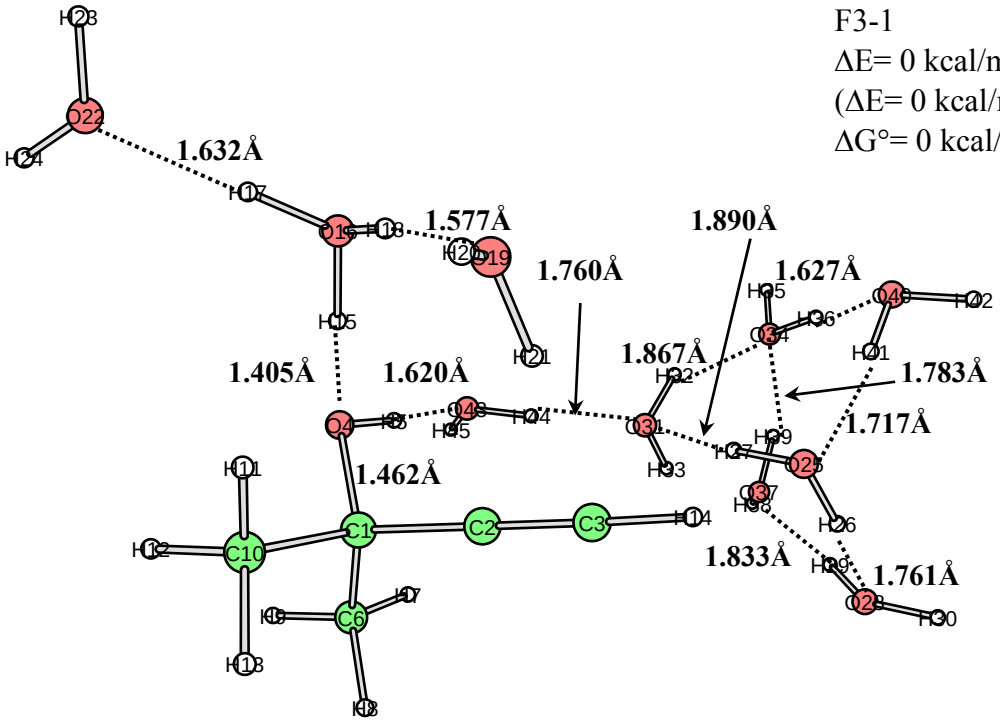


F2-9 **(TS3)**
$\Delta E^{\ddagger}$= -22.85 kcal/mol
($\Delta E^{\ddagger}$= -24.57 kcal/mol)
$\Delta G^{\ddagger}$= -22.37 kcal/mol
$\nu^{\ddagger}$= 846.24i cm^{-1}

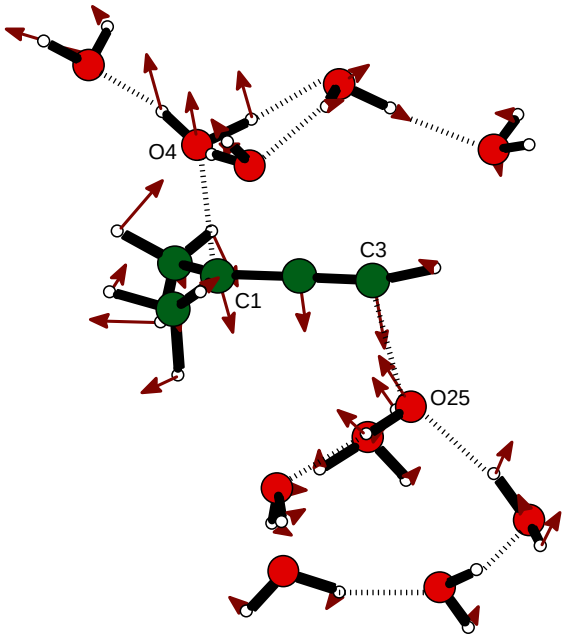


F2-10 **(Product α,β-enone)**
ΔE= -32.04 kcal/mol
(ΔE= -37.65 kcal/mol)
ΔG°= -33.71 kcal/mol

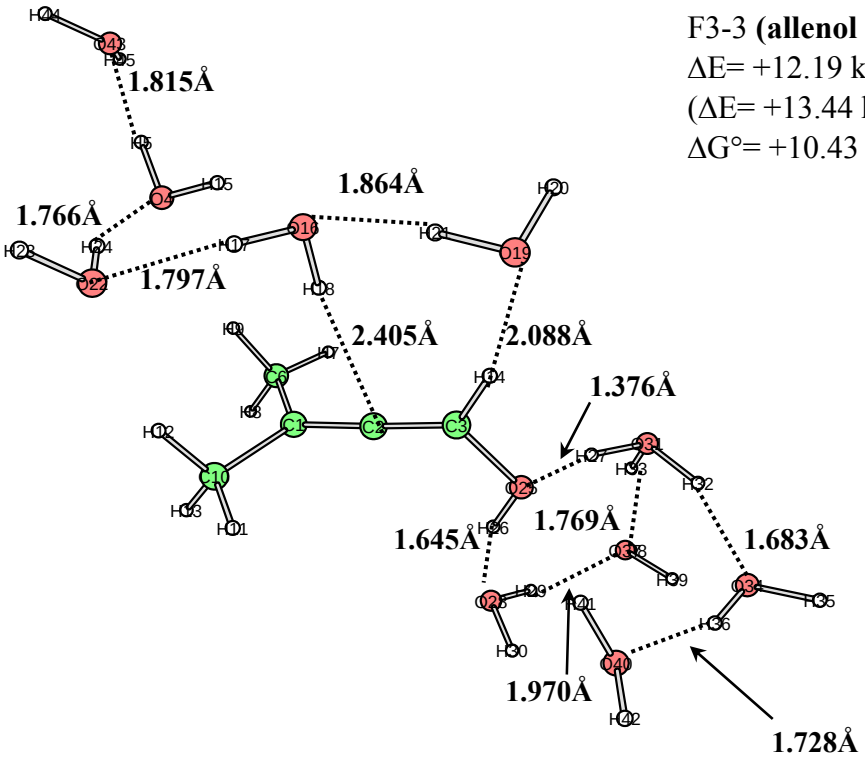
Figure S2. Geometries in the Rupe rearrangement. Reaction-coordinate vectors are shown for TS structures. The geometries of TS structures are shown in Figure 2 in the text.



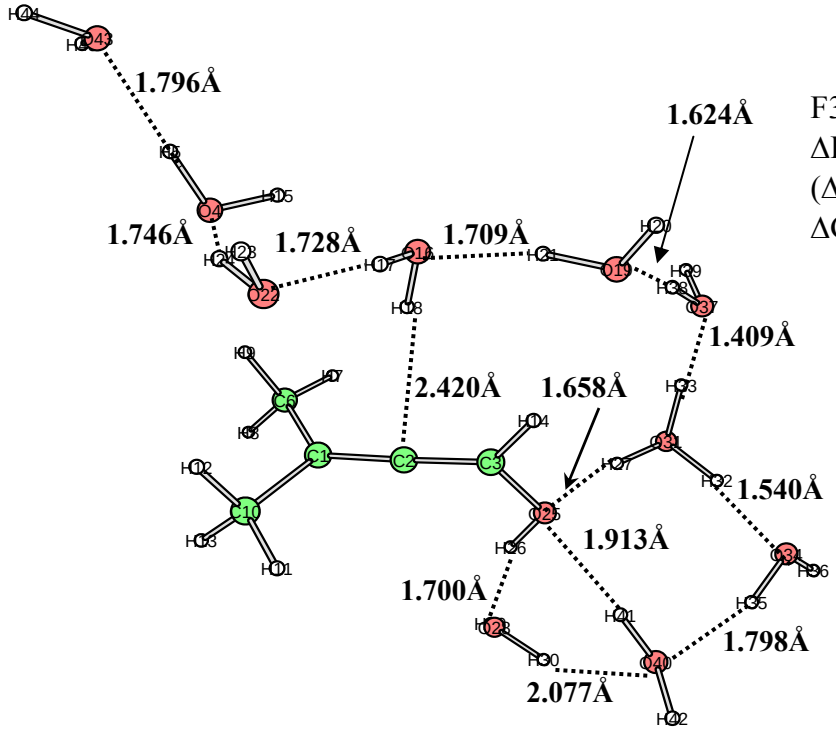
F3-1
ΔE= 0 kcal/mol
(ΔE= 0 kcal/mol)
ΔG°= 0 kcal/mol



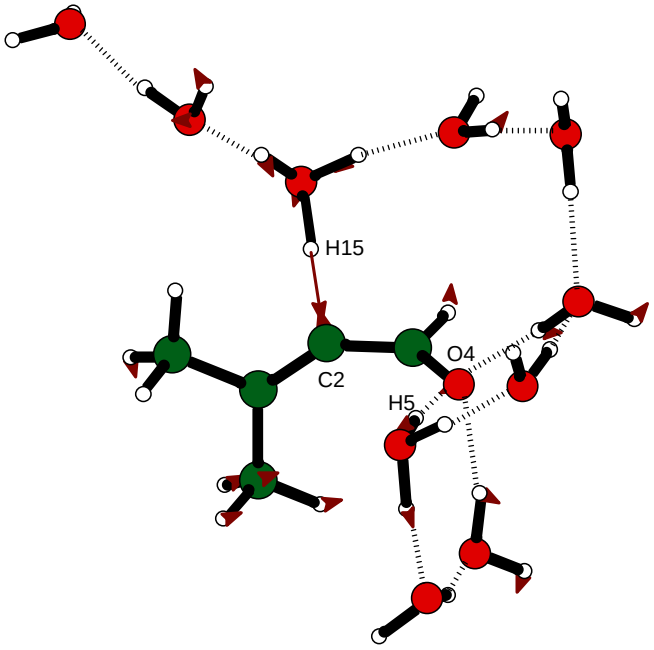
F3-2 **(TS1)**
ΔE= +29.92 kcal/mol
(ΔE= +33.43 kcal/mol)
$\Delta G^{\ddagger}$= +28.58 kcal/mol
$\nu^{\ddagger}$=142.66i cm^{-1}



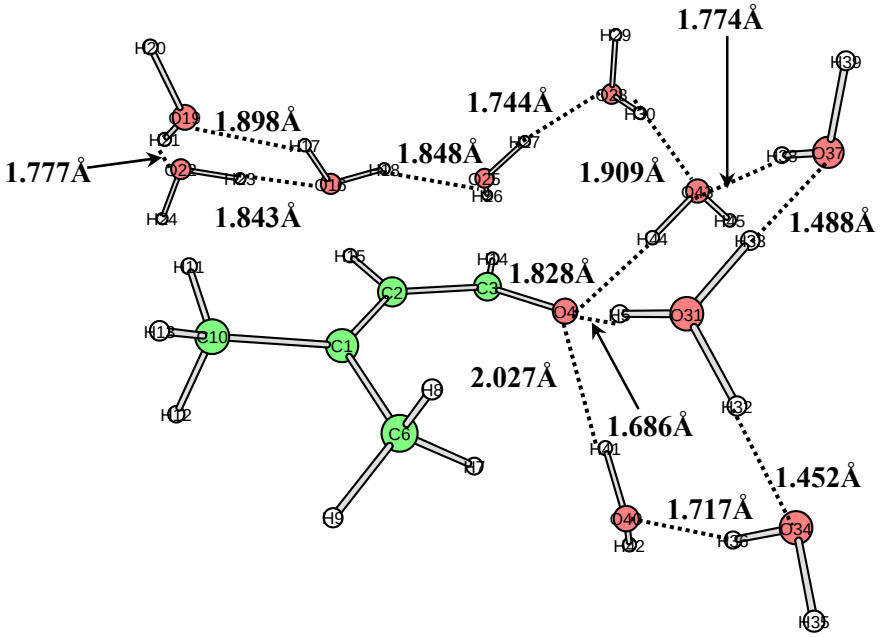
F3-3 **(allenol intermediate)**
ΔE= +12.19 kcal/mol
(ΔE= +13.44 kcal/mol)
ΔG°= +10.43 kcal/mol



F3-4
ΔE= +0.34 kcal/mol
(ΔE= -1.80 kcal/mol)
ΔG°= -1.80 kcal/mol



F3-5 **(TS2)**
ΔE= +2.02 kcal/mol
(ΔE= +0.48 kcal/mol)
$\Delta G^{\ddagger}$= +0.71 kcal/mol
$\nu^{\ddagger}$=348.18í cm^{-1}



F3-6
(Product aldehyde)
ΔE= -18.72 kcal/mol
(ΔE= -21.41 kcal/mol)
ΔG°= -19.46 kcal/mol

Figure S3. Geometries in the Meyer-Schuster rearrangement. Reaction-coordinate vectors are shown for TS structures. The geometries of TS structures are shown in Figure 3 in the text.

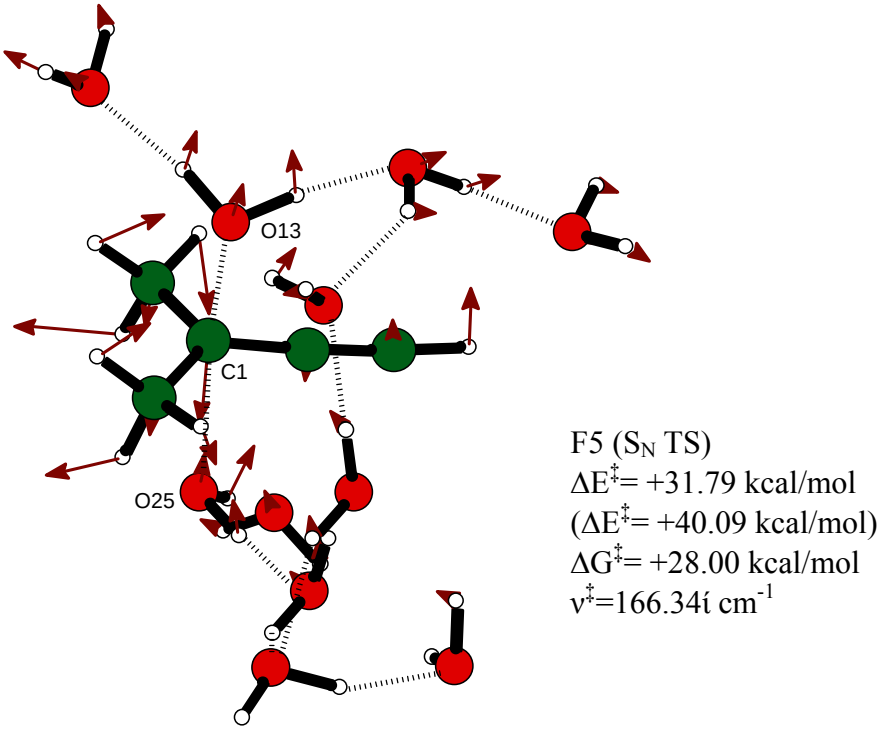
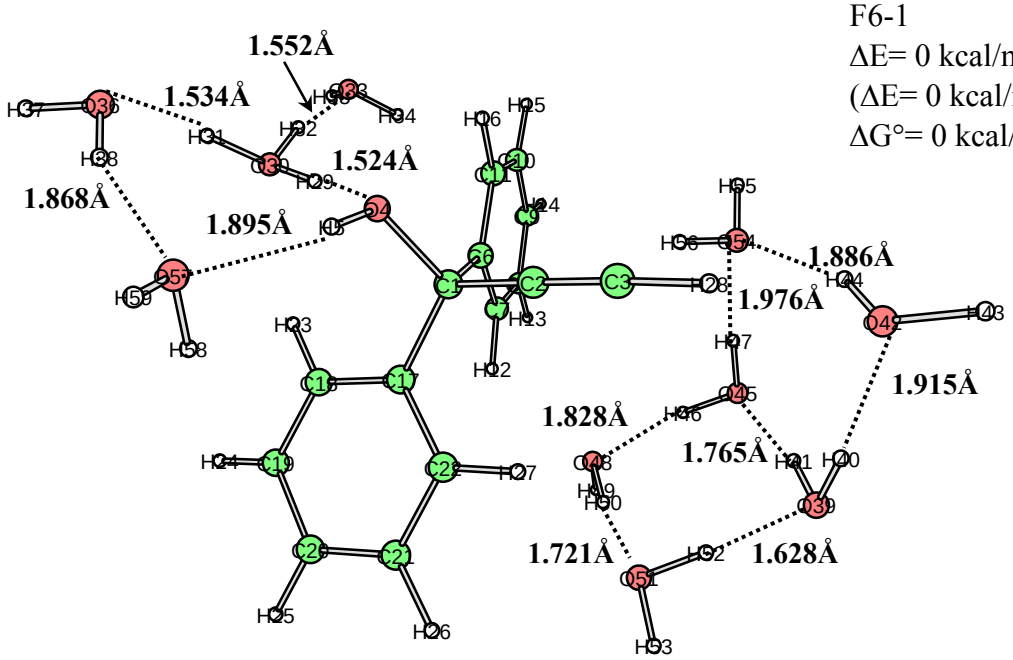
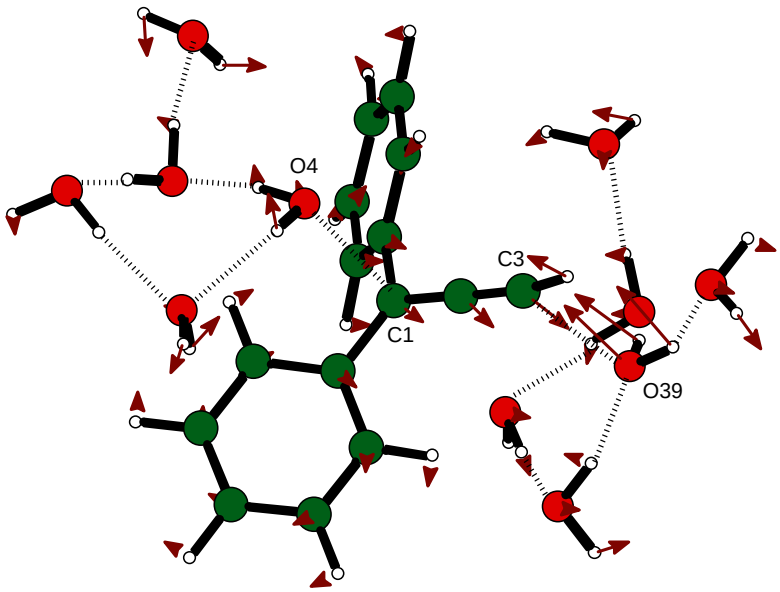


Figure S4. Reaction-coordinate vectors for TS structure F5 (S_N TS).



F6-1
ΔE= 0 kcal/mol
(ΔE= 0 kcal/mol)
ΔG°= 0 kcal/mol



F6-2 **(TS1)**
ΔE= +13.42 kcal/mol
(ΔE= +16.03 kcal/mol)
$\Delta G^{\ddagger}$= +8.09 kcal/mol
$\nu^{\ddagger}$=105.20í cm^{-1}

F6-3 **(allenol intermediate)**
ΔE= -16.80 kcal/mol
(ΔE= -26.84 kcal/mol)
ΔG°= -17.73 kcal/mol

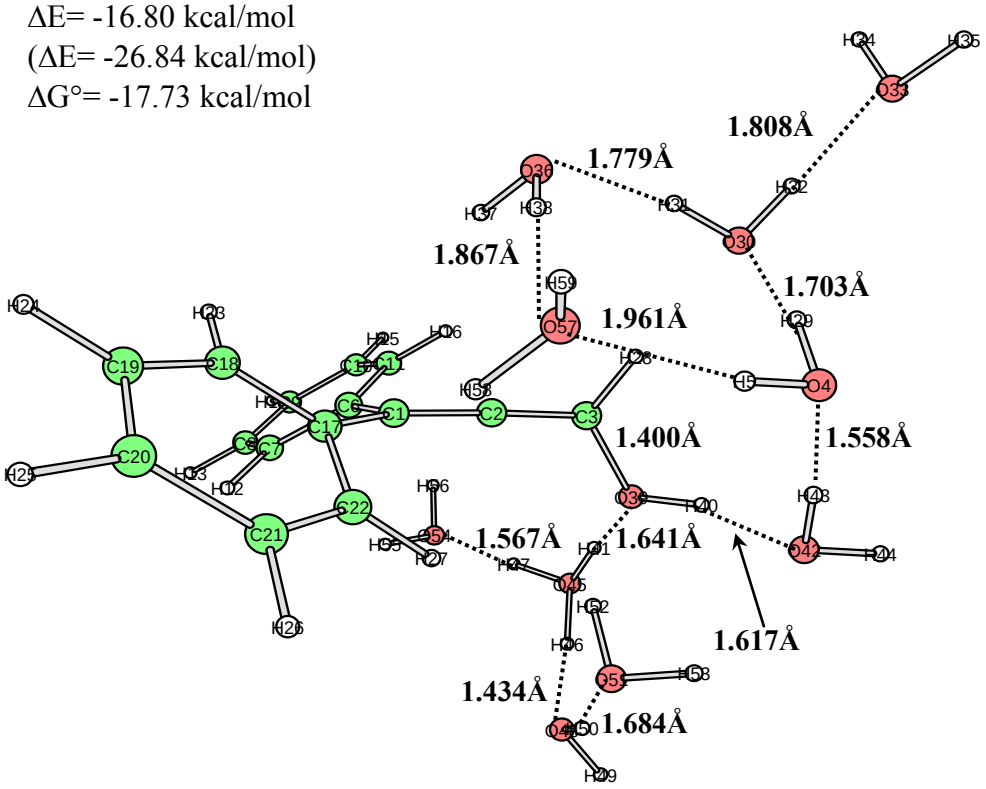


Figure S5. Geometries in the first and the rate-determining step of the Meyer-Schuster rearrangement for the system of $Ph_2C(OH)$-C≡C-H + $H_3O^+(H_2O)_9$. Reaction-coordinate vectors are shown for TS structure of F6-2 (TS1). The geometry of TS structure is shown in Figure 6 in the text.

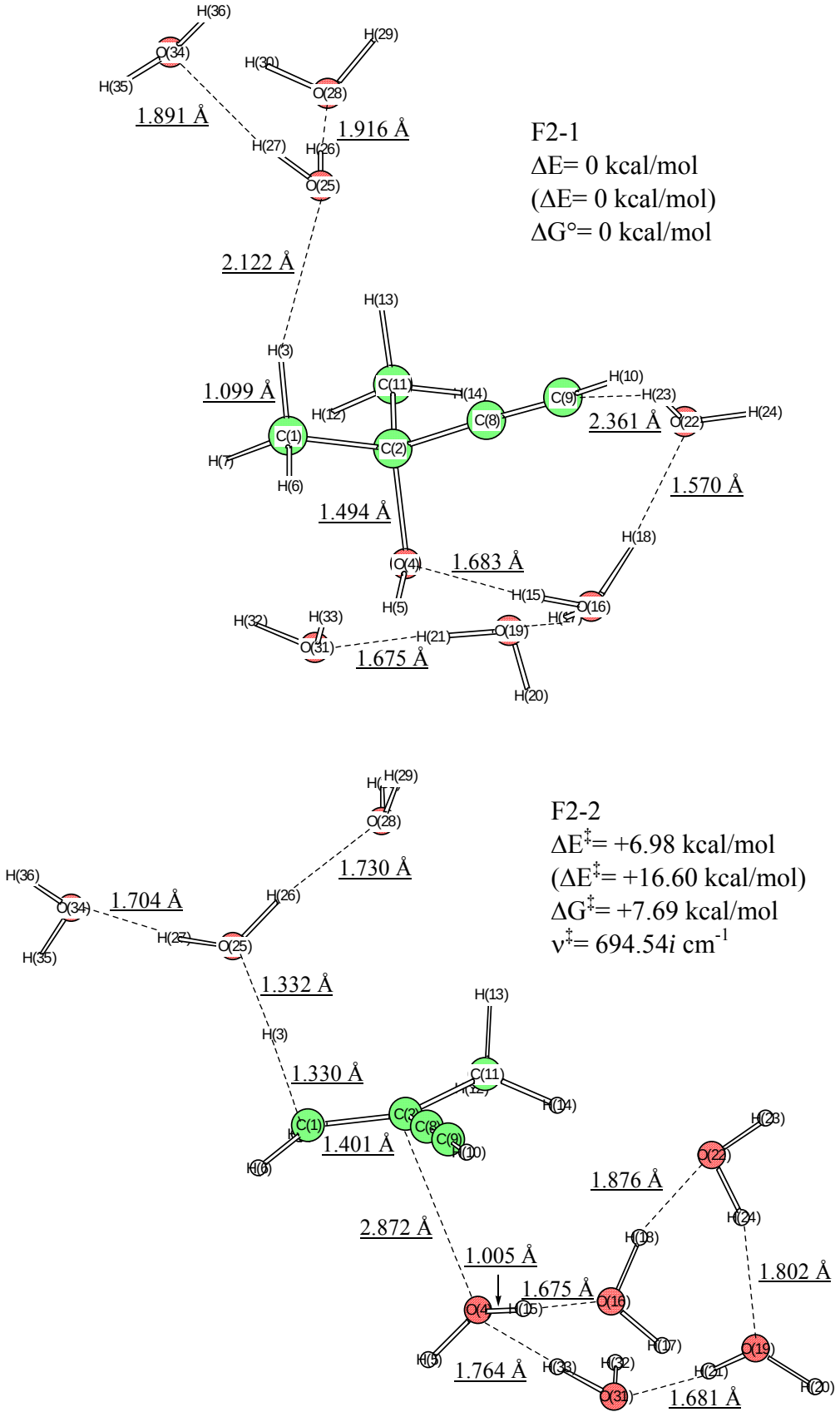


Figure S6. Geometries of the reactant (F2-1) and TS1 (F2-2) of the $Me_2C(OH)C{\equiv}CH$ + $H_3O^+(H_2O)_6$ system. Important data are attached to the geometry of TS1 (F2-2) in Figure 2 by the underlined numbers.