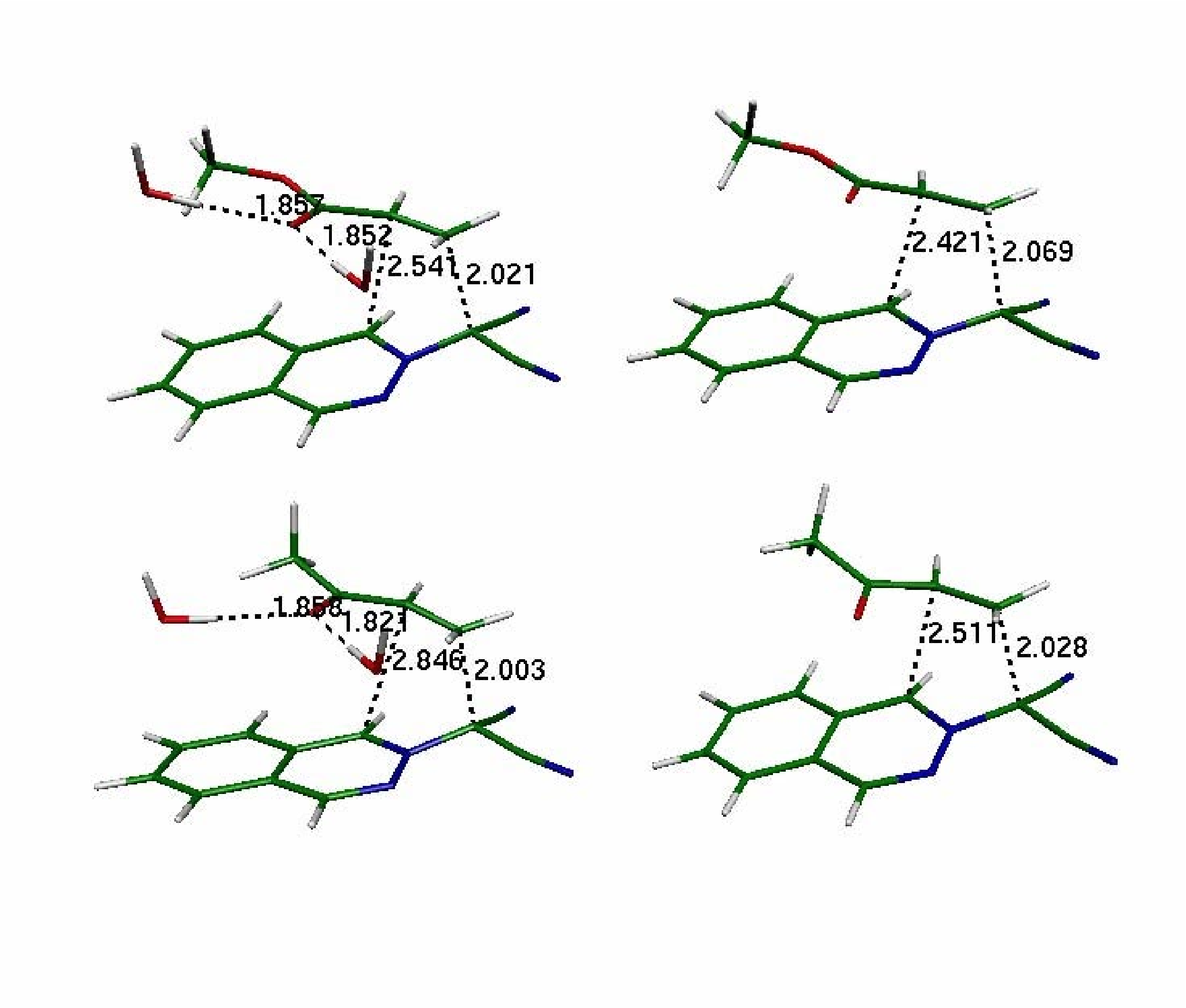
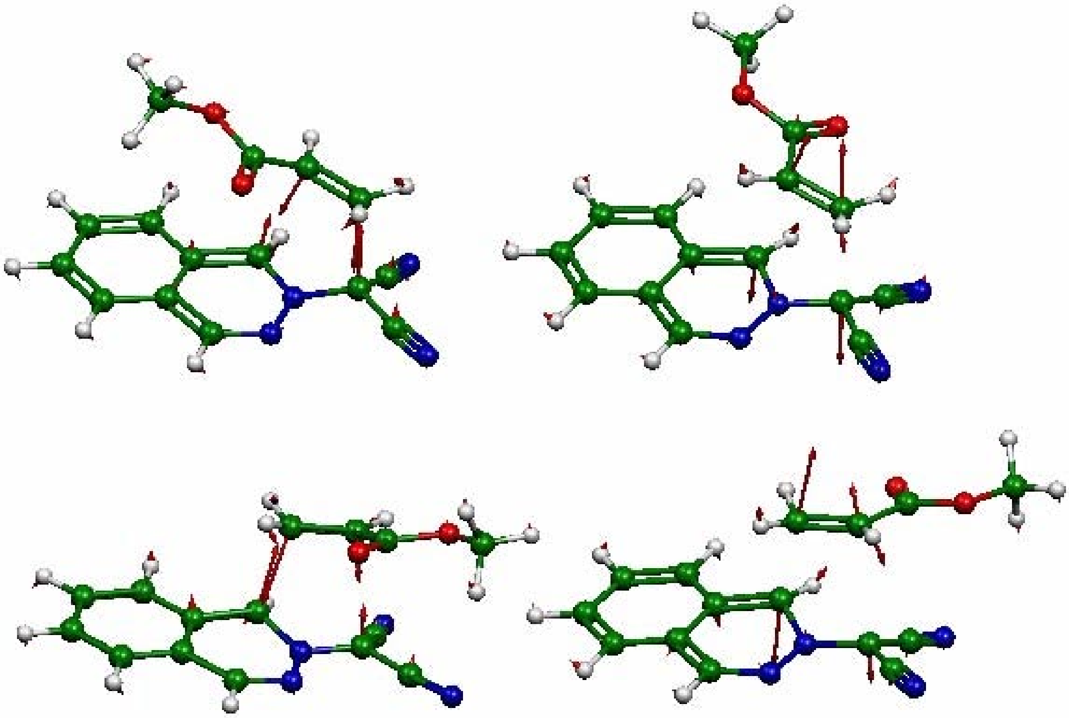
Supplementary data



SupFigure 1. B3LYP/6-31G(d) optimised transition state structure for the cycloaddition in the CH/endo orientation of **1** and **MVK** with none or two H_2O molecules (bottom) and **MAC** (top). Dotted lines show the distances (Å) of the new bonds between the dipole and dipolarophile in the TS. The carbonyl O atom is H-bonded to each of the two waters leaving a free OH directed away from the dipole. (Green C; blue N; red O atoms)



Sup.Figure 2. B3LYP/6-31G(d) optimised transition state structure for the four stereoisomeric cycloadditions of **1** and **MAC**. Arrows show the vectors of the forces between the dipole and dipolarophile for each imaginary vibrational frequency.

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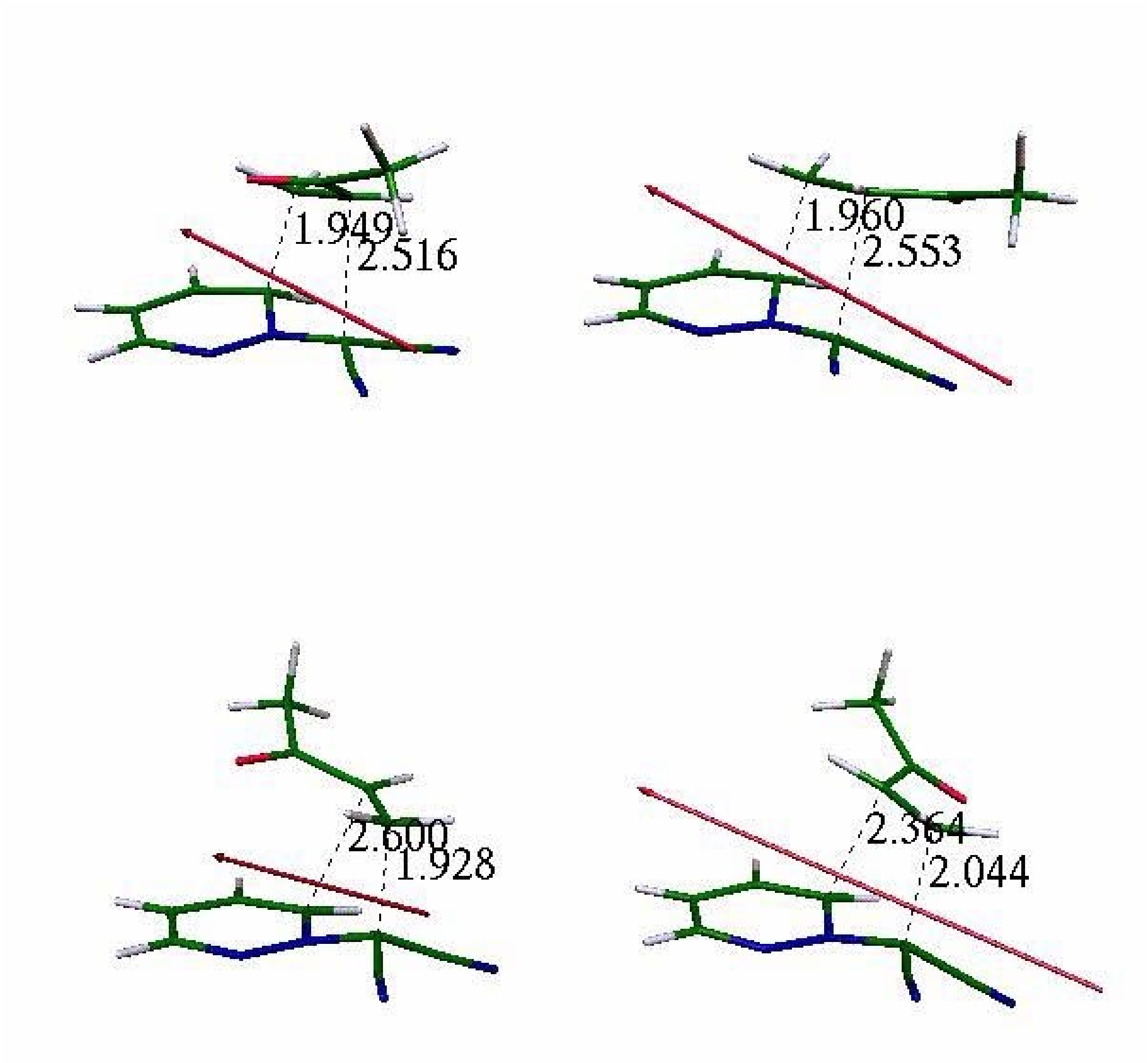
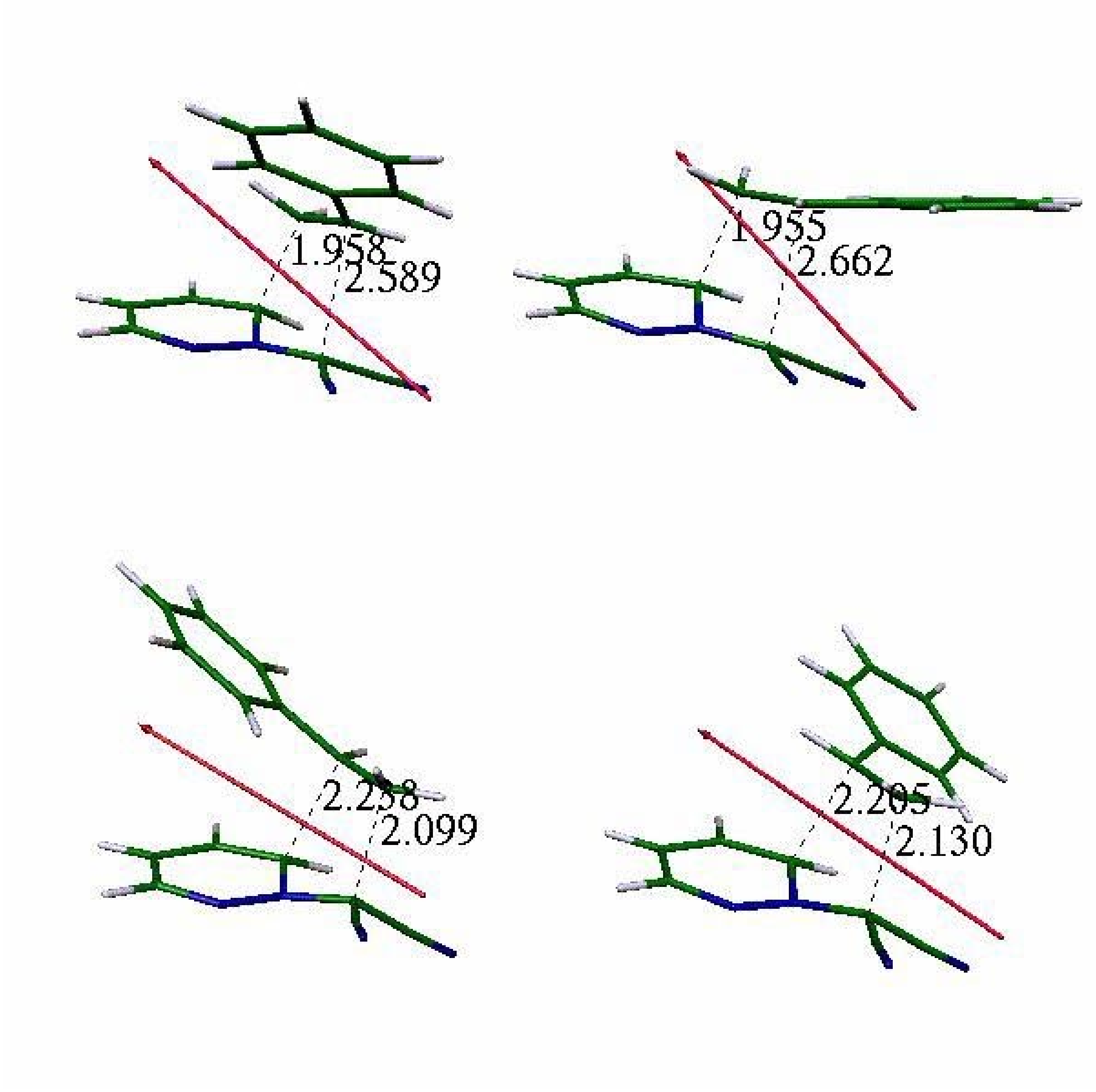


Sup.Figure 3. B3LYP/6-31G(d) optimised transition state structure for the four stereoisomeric cycloaddition of **2** and **MVK**. Dotted lines show the distances (Å) of the new bonds between the dipole and dipolarophile in the TS. The dipole moment vectors are displayed



Sup.Figure 4. B3LYP/6-31G(d) optimised transition state structure for the four stereoisomeric cycloaddition of **2** and **STY**. Dotted lines show the distances (Å) of the new bonds between the dipole and dipolarophile in the TS. The dipole moment vectors are displayed.