Electronic supplementary information (ESI) for:

Exploration of Carvacrol Aggregation by Laser Spectroscopy.

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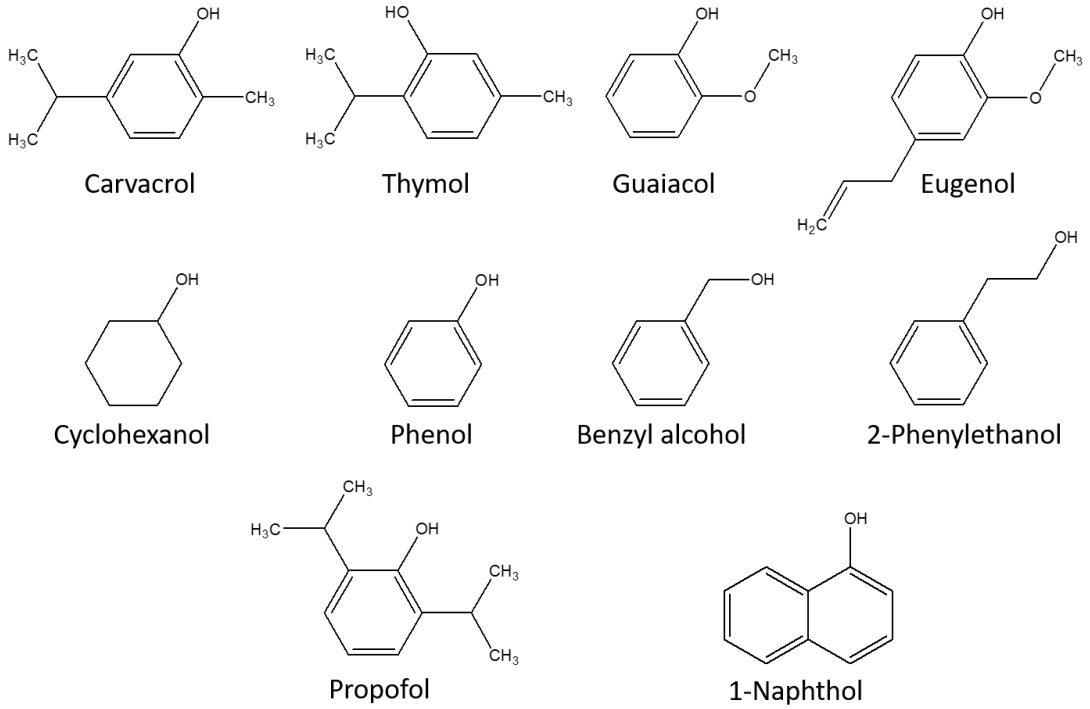

Scheme S1. Carvacrol (carOH) and other related systems mentioned in the main text of the manuscript.

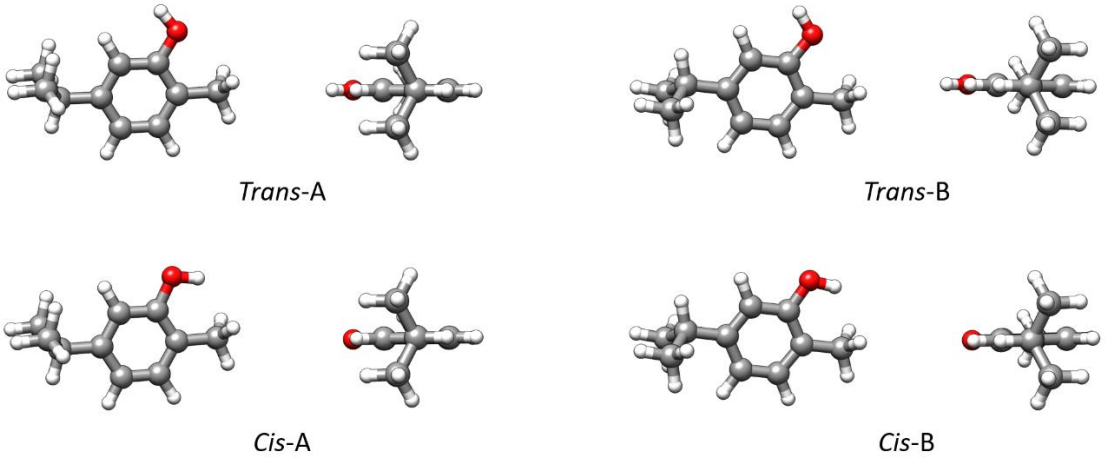

Figure S1. Ball and stick representation of the four carOH isomers.

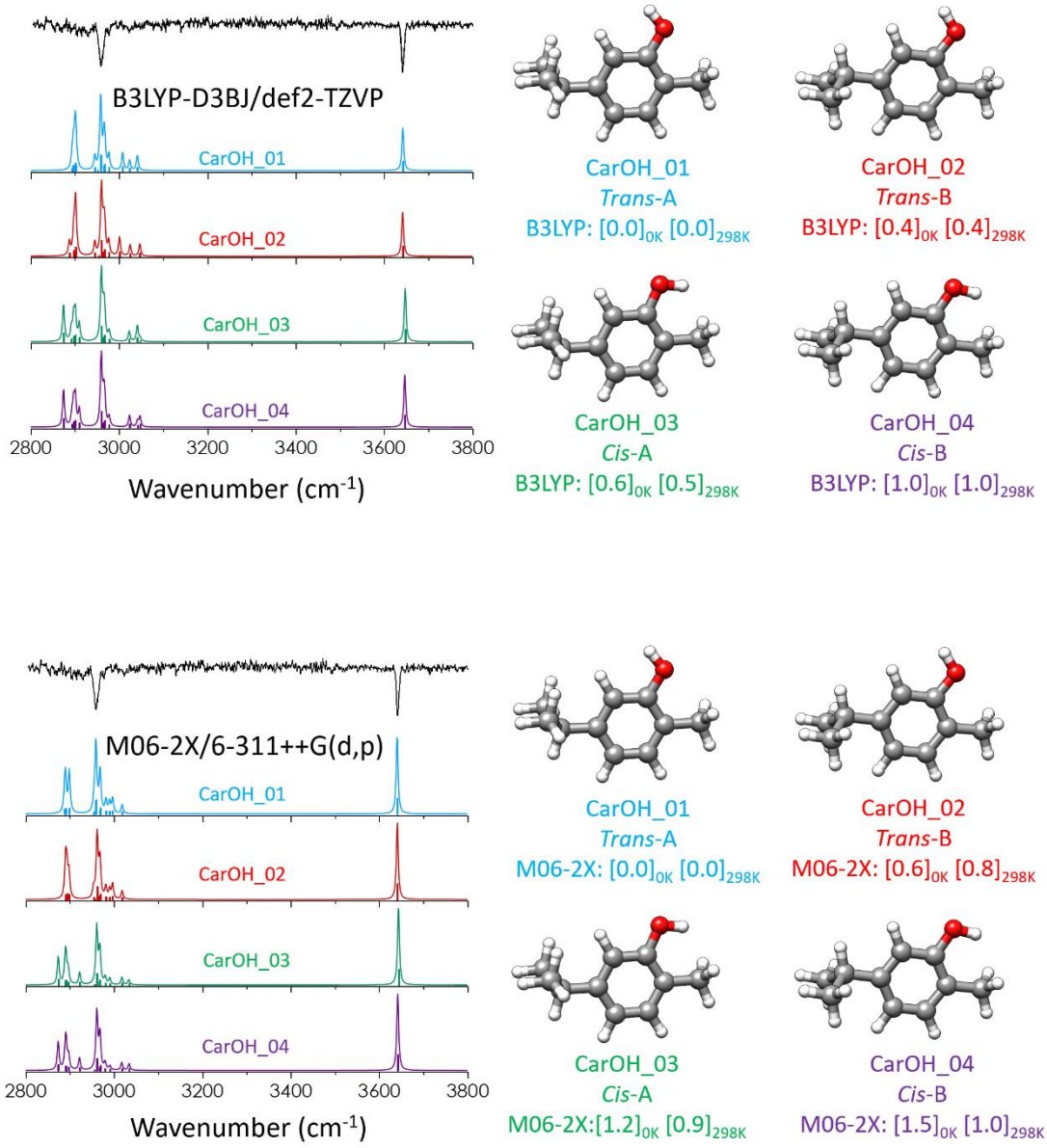

Figure S2. Experimental (black trace) and simulated (coloured traces) IDIR spectra for the four carOH isomers. The simulations were done based on a) B3LYP-D3BJ/def2-TZVP structures using a scaling factor of 0.957; and on b) M06-2X/6-311++G(d,p) structures using scaling factors of 0.946 and 0.932 for CH and OH stretching modes, respectively, to account for anharmonicity. The Gibbs free energies (kJ·mol^{-1}) are given at the B3LYP-D3BJ/def2-TZVP and M06-2X/6-311++G(d,p) levels of theory at 0 and 298 K. Panel b) is reproduced from Figure 2 from the main text for a better comparison of the simulations.

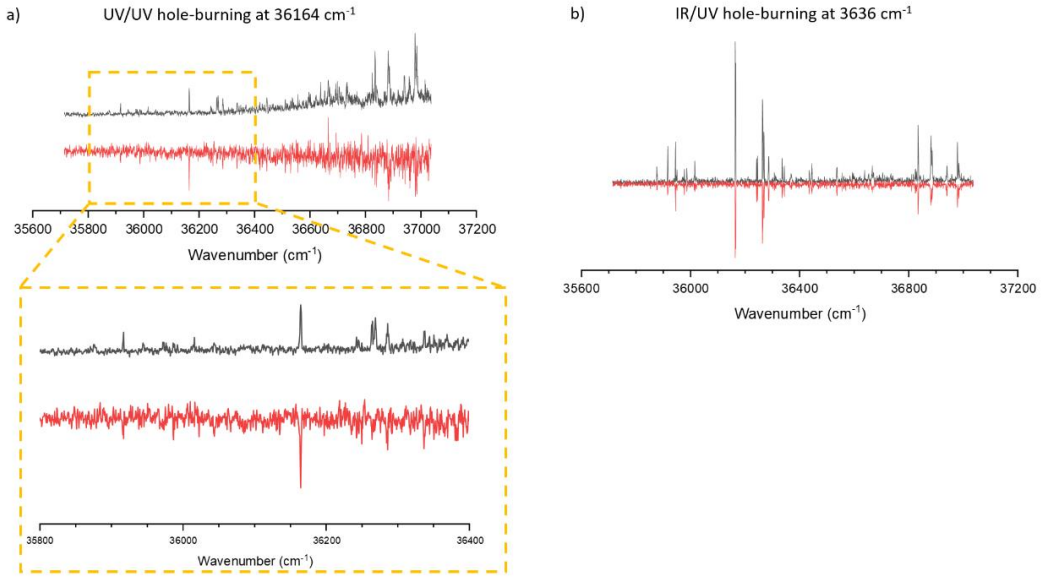

Figure S3. a) UV/UV and b) IR/UV hole burning spectra of carOH recorded probing the transitions at 36164, and 3636 cm^{-1} respectively.

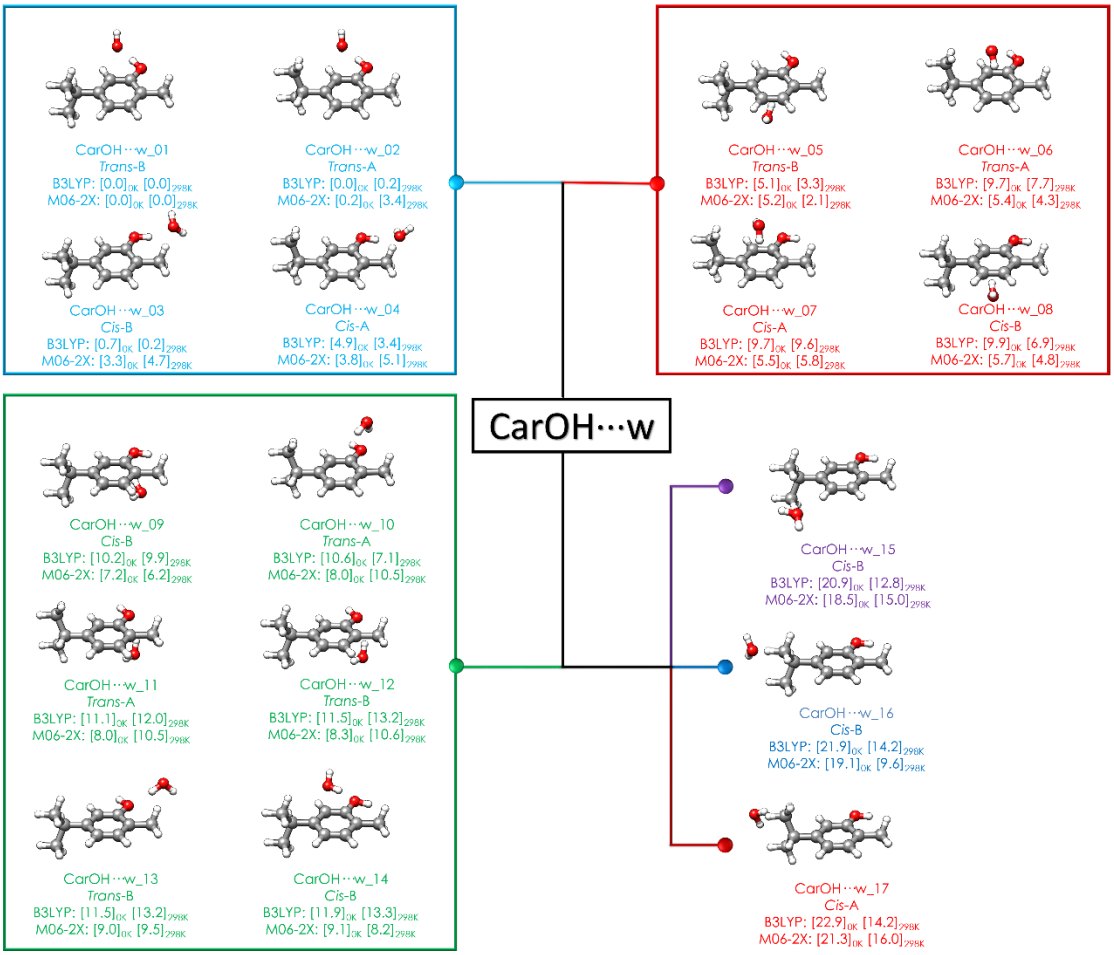

Figure S4. Summary of optimized geometries of carOH···w isomers with their relative energy values (kJ·mol^{-1}) at the B3LYP-D3BJ/def2-TZVP and M06-2X/6-311++G(d,p) levels at 0 and 298 K. All energies are BSSE and ZPE corrected. The conformers are grouped in families according to their interactions as explained in the main text.

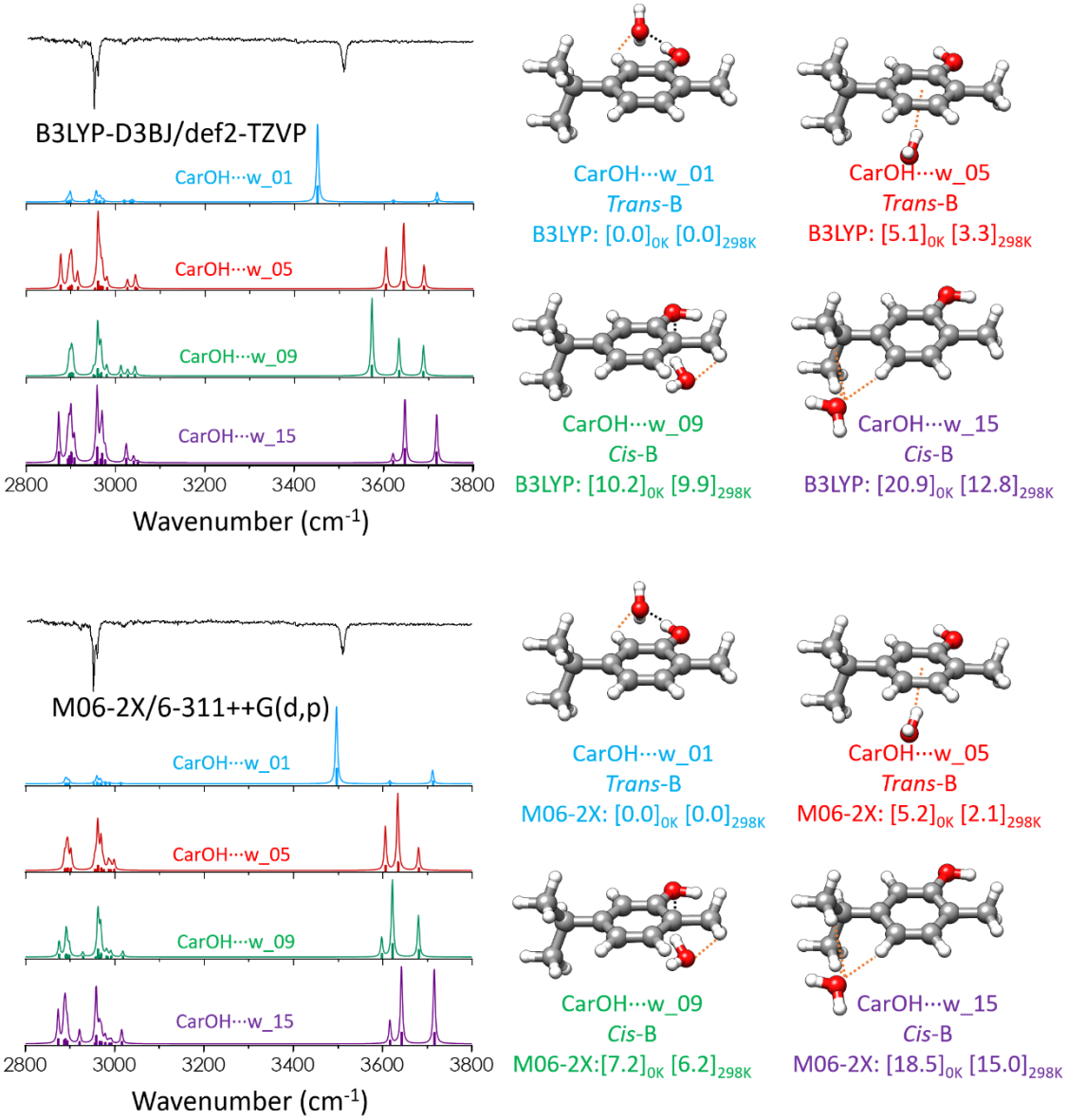

Figure S5. Experimental (black trace) and simulated (coloured traces) IDIR spectra for four representative carOH···w isomers, one from each family of interactions (Figure S4). The simulations were done based on a) B3LYP-D3BJ/def2-TZVP structures using a scaling factor of 0.957; and on b) M06-2X/6-311++G(d,p) structures using scaling factors of 0.946 and 0.932 for CH and OH stretching modes, respectively, to account for anharmonicity. The Gibbs free energies (kJ·mol^{-1}) are given at both levels of theory at 0 and 298 K. Panel b) is reproduced from Figure 3 from the main text for a better comparison of the simulations.

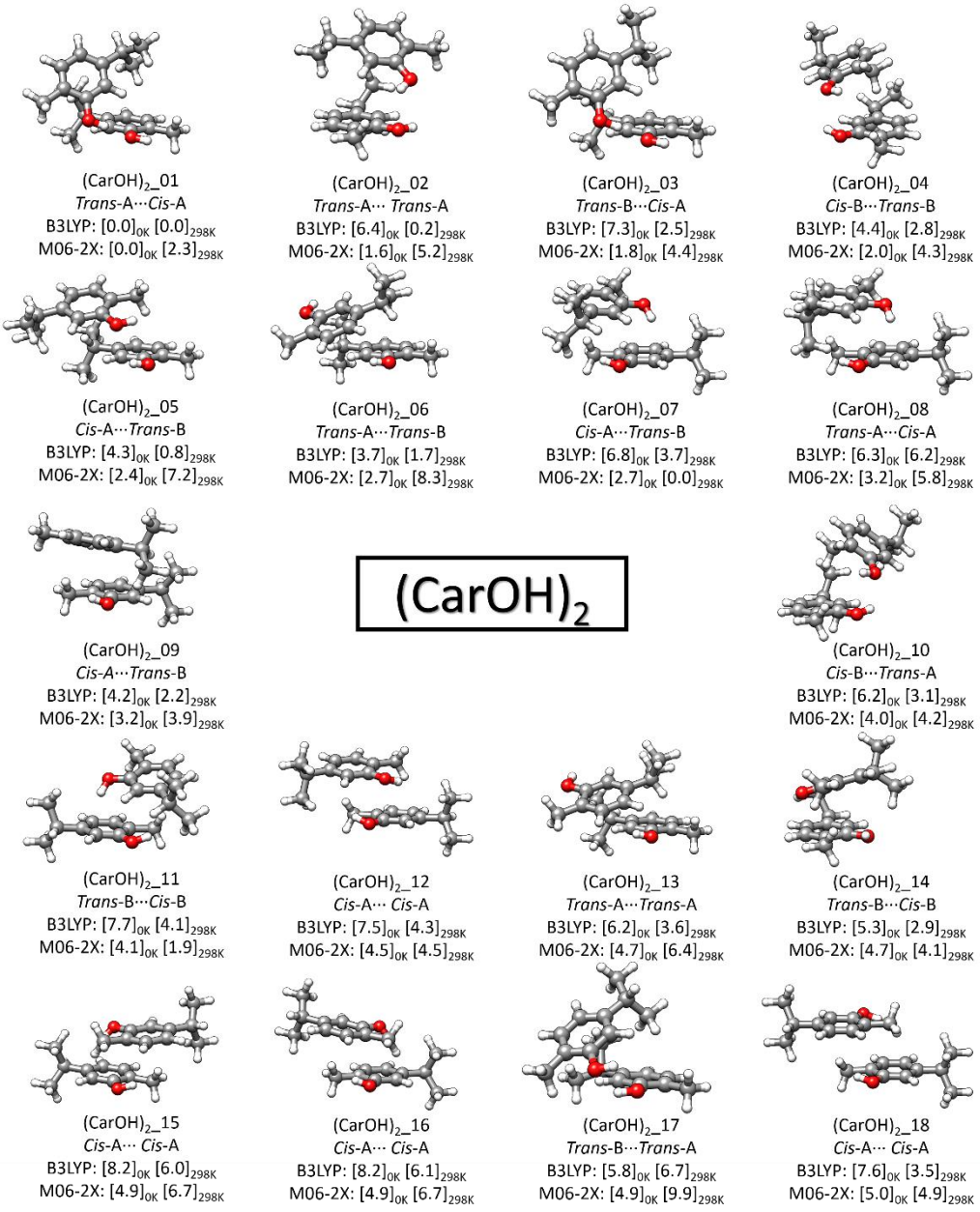

Figure S6. Summary of the optimized geometries of $(carOH)_2$ isomers with their relative energy values ($kJ \cdot mol^{-1}$) at the B3LYP-D3BJ/def2-TZVP and M06-2X/6-311++G(d,p) levels at 0 and 298 K. All energies are BSSE and ZPE corrected.

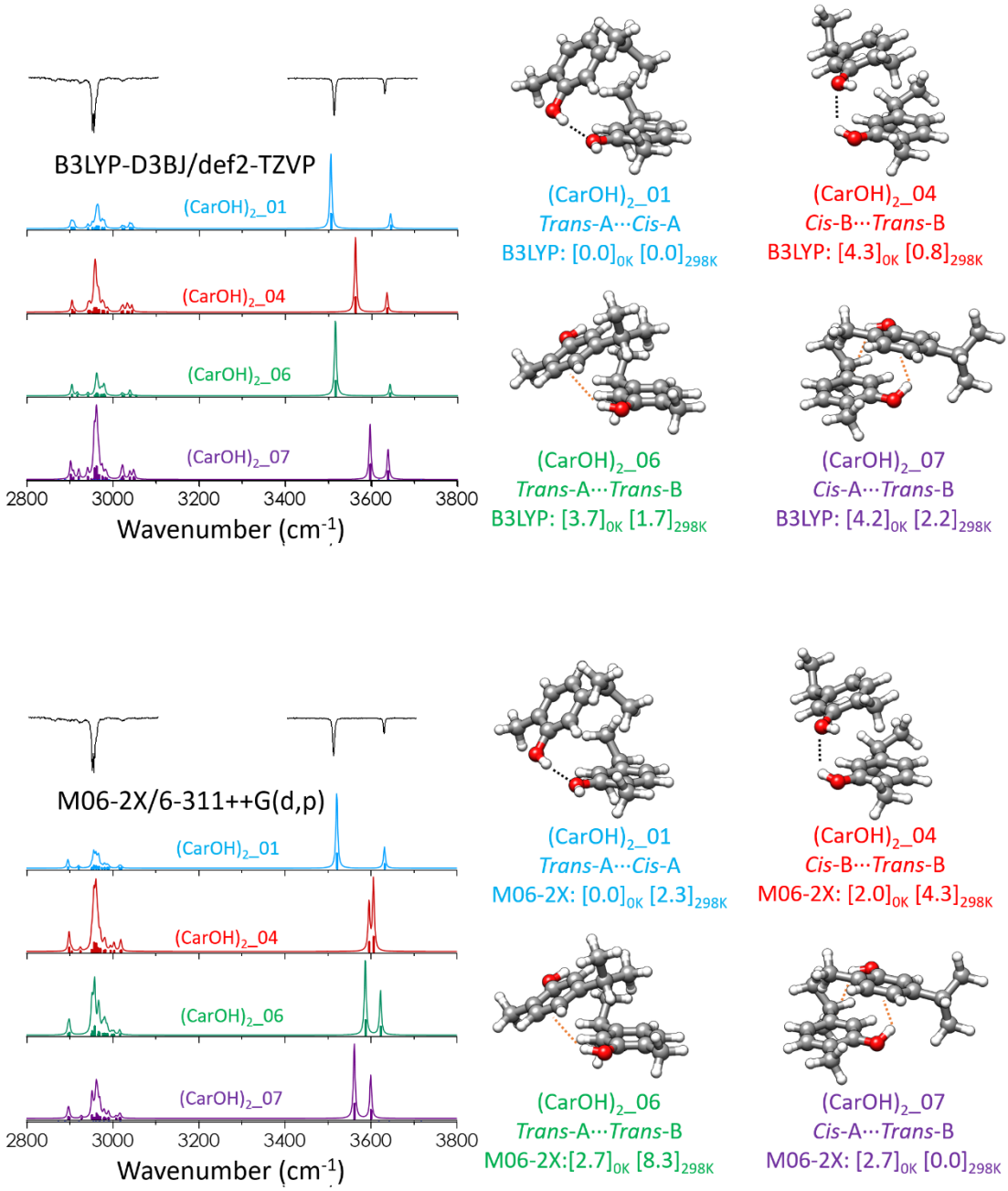

Figure S7. Experimental (black trace) and simulated (coloured traces) IDIR spectra for four representative $(carOH)_2$ isomers. The simulations were done based on a) B3LYP-D3BJ/def2-TZVP structures using a scaling factor of 0.957; and on b) M06-2X/6-311++G(d,p) structures using scaling factors of 0.946 and 0.932 for CH and OH stretching modes, respectively, to account for anharmonicity. The Gibbs free energies ($kJ \cdot mol^{-1}$) are given at both levels of theory at 0 and 298 K. Panel b) is reproduced from Figure 4 from the main text for a better comparison of the simulations.

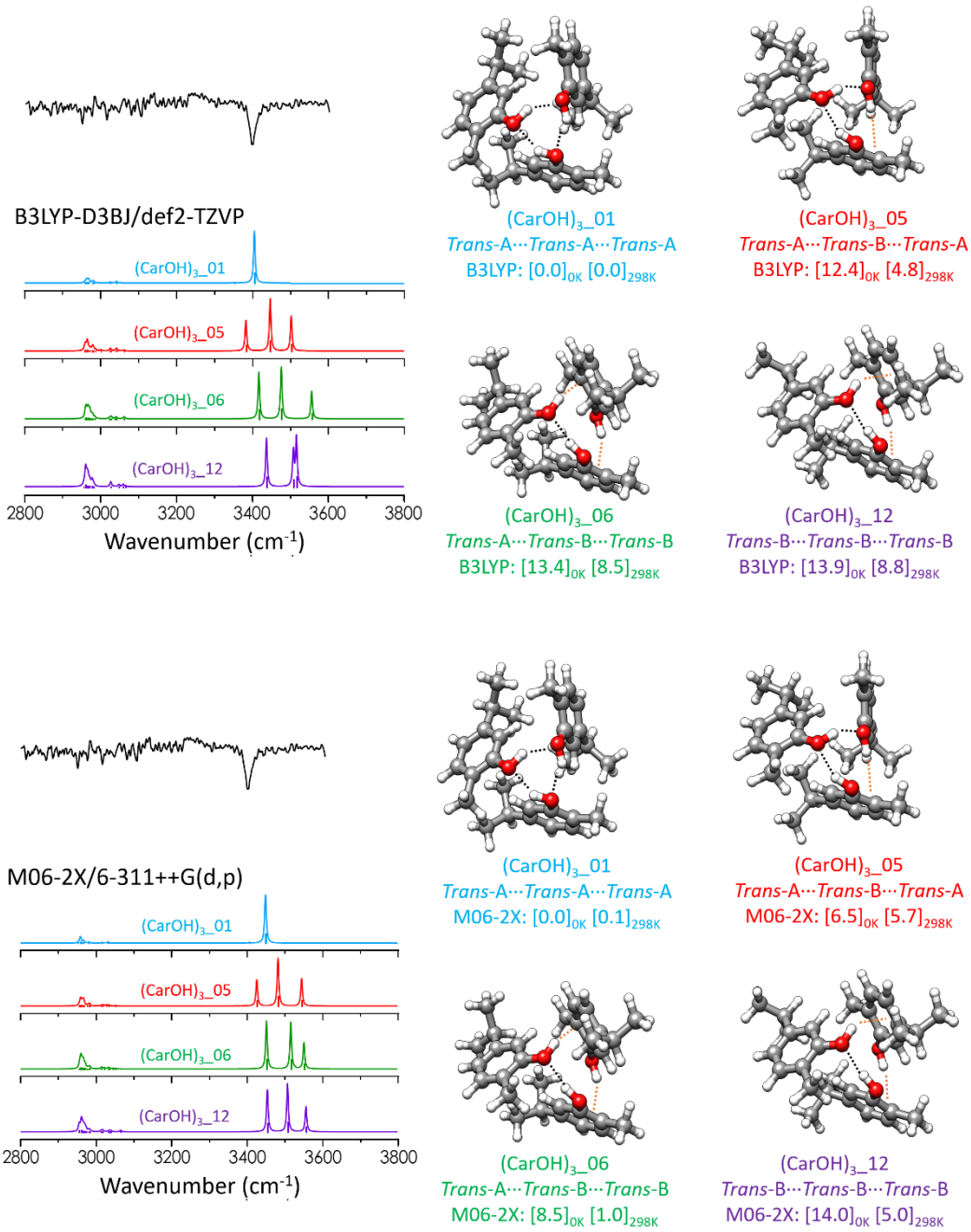

Figure S8. Experimental (black trace) and simulated (coloured traces) IDIR spectra for four representative $(carOH)_3$ isomers. The simulations were done based on a) B3LYP-D3BJ/def2-TZVP structures using a scaling factor of 0.957; and on b) M06-2X/6-311++G(d,p) structures using scaling factors of 0.946 and 0.932 for CH and OH stretching modes, respectively, to account for anharmonicity. The Gibbs free energies ($kJ \cdot mol^{-1}$) are given at both levels of theory at 0 and 298 K. Panel b) is reproduced from Figure 5 from the main text for a better comparison of the simulations.

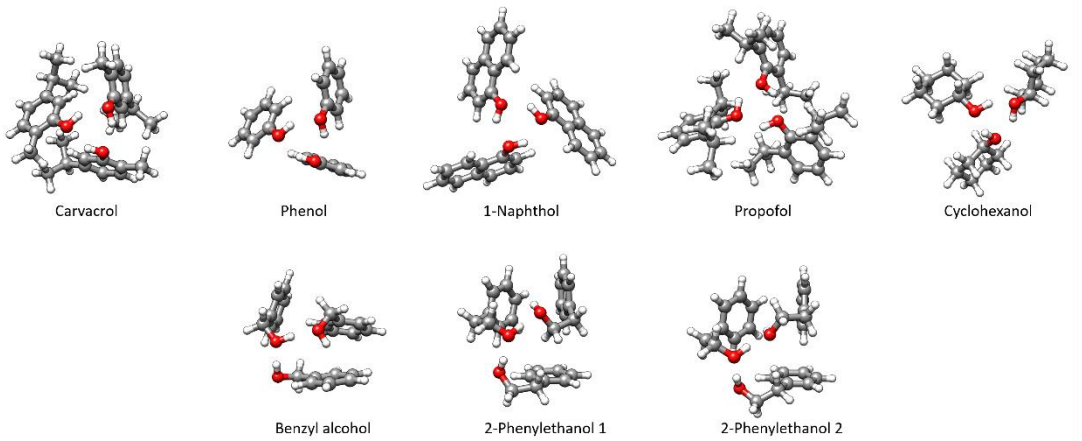

Figure S9. Experimentally observed trimers for carvacrol, 1-naphthol, phenol, propofol, cyclohexanol, benzyl alcohol, and 2-phenylethanol. The input geometry for each trimer was taken from the respective references and re-optimized at B3LYP-D3BJ/def2-TZVP, to display all of them at the same level of theory. The structures in the first row show five trimers having three hydrogen bonding each, in a cyclic arrangement. The trimer structures in the second row feature two hydrogen bonds and an OH···π interaction.

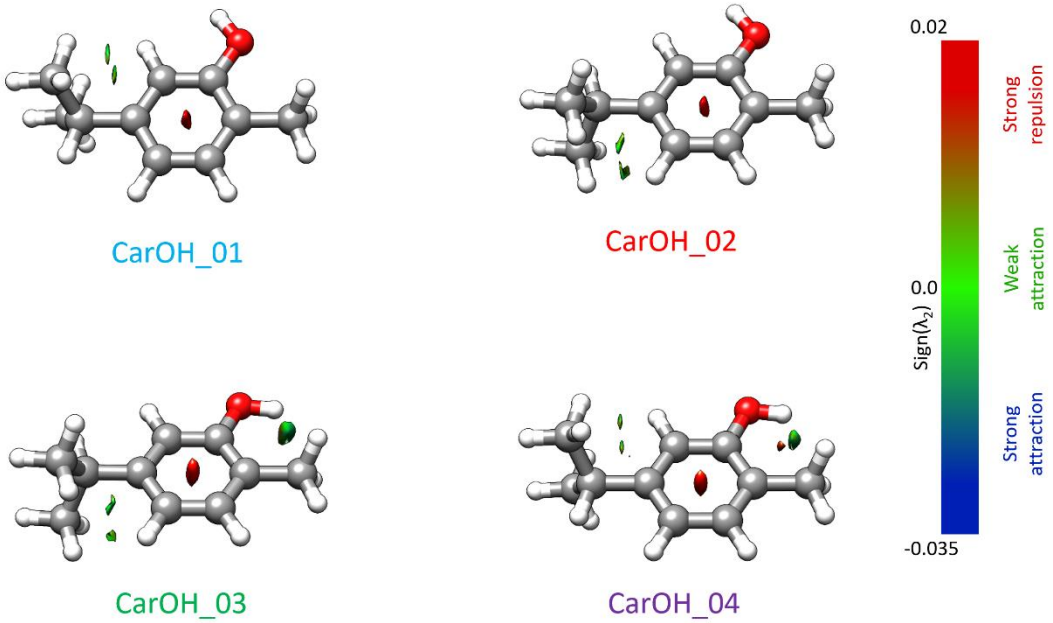

Figure S10. NCI plots for the four carOH isomers. λ_2 is the second eigenvalue of the electron density Hessian matrix. Its value indicates the type and strength of the interactions. Positive values (red areas) are associated with strong repulsions; negative values (blue areas) are associated with strong attractions; while values close to 0 (green surfaces) indicate the presence of weak interactions. Please note that the colour bar scale is not linear.

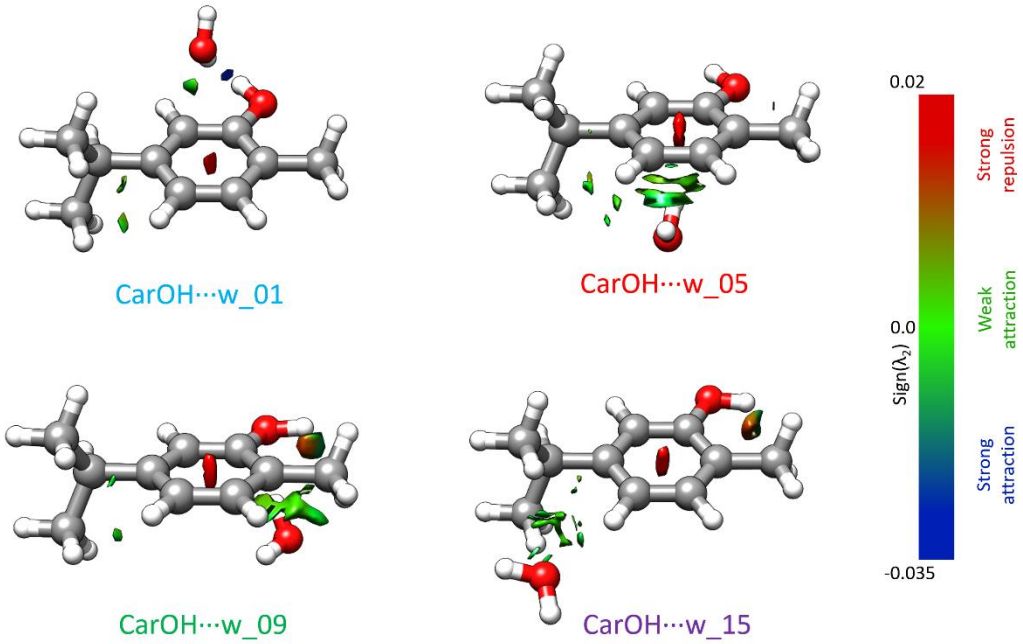

Figure S11. NCI plots for four representative carOH···w isomers. λ_2 is the second eigenvalue of the electron density Hessian matrix. Its value indicates the type and strength of the interactions. Positive values (red areas) are associated with strong repulsions; negative values (blue areas) are associated with strong attractions; while values close to 0 (green surfaces) indicate the presence of weak interactions. Please note that the colour bar scale is not linear.

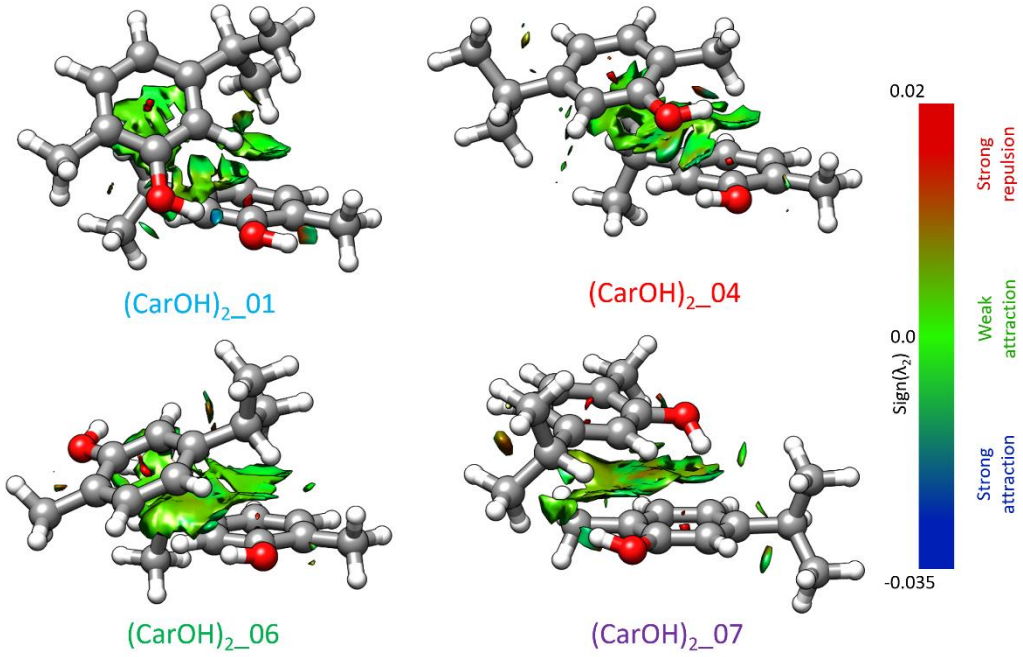

Figure S12. NCI plots for four representative $(carOH)_2$ isomers. λ_2 is the second eigenvalue of the electron density Hessian matrix. Its value indicates the type and strength of the interactions. Positive values (red areas) are associated with strong repulsions; negative values (blue areas) are associated with strong attractions; while values close to 0 (green surfaces) indicate the presence of weak interactions. Please note that the colour bar scale is not linear.

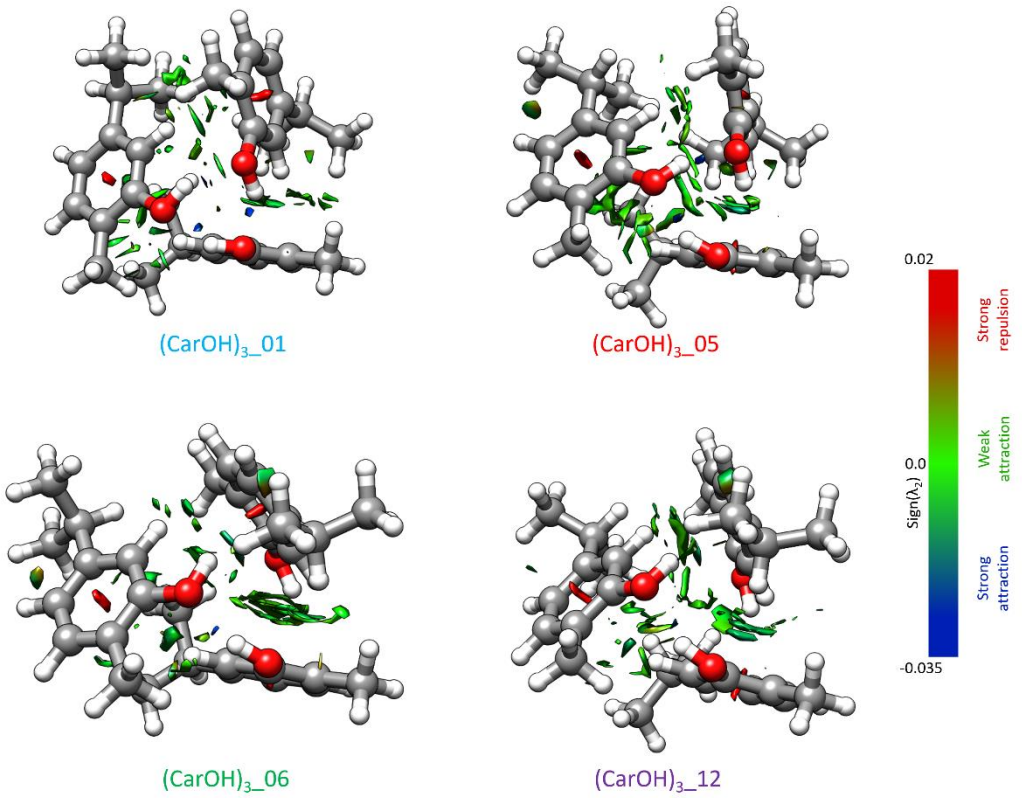

Figure S13. NCI plots for four representative $(carOH)_3$ isomers. λ_2 is the second eigenvalue of the electron density Hessian matrix. Its value indicates the type and strength of the interactions. Positive values (red areas) are associated with strong repulsions; negative values (blue areas) are associated with strong attractions; while values close to 0 (green surfaces) indicate the presence of weak interactions. Please note that the colour bar scale is not linear.