Supplementary Materials

Implicit and explicit solvent effect on the global reactivity and the density topological parameters of the preferred conformers of caespitate

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Table S1. Relative free energy (ΔG, kcal mol^{-1}) and population (%) of conformers of caespitate with free energies ≤ 2 kcal mol^{-1} calculated at the APFD/6-311+G(2d,p) level of theory in gas and solution phases.

Conformer	ΔG	Population
Gas		
G1	0.0000	24.60
G2	0.0063	23.65
G3	0.6903	19.88
G4	0.8063	6.73
G5	0.8120	6.31
G6	0.8860	5.66
G7	1.0084	5.60
G8	1.1107	4.95
G9	1.1163	4.02
G10	1.1370	3.38
G11	1.2149	3.35
G12	1.2218	3.24
G13	1.4502	2.84
G14	1.4590	2.81
G15	1.6824	1.91
G16	1.6880	1.88
G17	1.7275	1.29
G18	1.7551	1.28
G19	1.7583	1.20
G20	1.9578	1.14
G21	2.0124	1.13
G22	2.0626	0.81
G23	2.0771	0.74
G24	2.0852	0.68
Water		
W1	0.0000	26.50
W2	0.0454	17.19
W3	0.0554	15.18
W4	0.2789	14.10
W5	0.3094	10.72
W6	0.5990	7.08
W7	0.6498	6.50
W8	0.6815	6.16
W9	1.6346	1.23
W10	2.0400	0.16
Chloroform		
C1	0.0000	49.10
C2	0.0211	22.76
C3	0.3750	6.37
C4	0.3795	5.95
C5	0.4444	5.58
C6	0.4527	5.51
C7	0.4716	5.24
C8	0.6693	4.71
C9	0.7320	2.63
C10	1.0783	1.92
C11	1.2632	1.58
C12	1.3781	1.54

C13	1.3956	1.37
C14	1.4621	1.28
C15	1.5048	1.25
C16	1.5174	0.97
C17	1.6686	0.94
C18	1.6880	0.72
C19	1.8437	0.71
C20	1.8575	0.69
C21	1.8688	0.68
C22	1.8788	0.68
C23	1.8819	0.59
C24	1.9585	0.48
C25	2.0834	0.47
C26	2.0903	0.35
Acetonitrile		
A1	0.0000	20.25
A2	0.0076	15.54
A3	0.0128	14.94
A4	0.2904	14.34
A5	0.3806	11.96
A6	0.3883	5.64
A7	0.3966	5.56
A8	0.4489	5.09
A9	0.4516	5.07
A10	0.4620	4.98
A11	0.5045	4.64
A12	0.6295	3.75
A13	0.6562	3.59
A14	1.1510	1.56
A15	1.1881	1.46
A16	1.2583	1.30
A17	1.3318	1.15
A18	1.3512	1.11
A19	1.3650	1.09
A20	1.3832	1.05
A21	1.4296	0.97
A22	1.4359	0.96
A23	1.5112	0.85
A24	1.5376	0.81
A25	1.6850	0.63
A26	1.6995	0.62
A27	1.7516	0.57
A28	1.7603	0.56
A29	1.7672	0.55
A30	1.7999	0.52
A31	1.8156	0.51
A32	1.8306	0.49
A33	2.0728	0.33
DMSO		
D1	0.0000	23.62
D2	0.0905	21.66
D3	0.1074	13.10
D4	0.3467	7.18

D5	0.4277	7.09
D6	0.4340	6.20
D7	0.4421	5.41
D8	0.4694	5.35
D9	0.4857	5.28
D10	0.5242	5.04
D11	0.5266	4.91
D12	0.5410	4.60
D13	0.5475	4.58
D14	1.1495	4.47
D15	1.1564	4.42
D16	1.1827	1.60
D17	1.1915	1.58
D18	1.2411	1.51
D19	1.2706	1.49
D20	1.2825	1.37
D21	1.3038	1.30
D22	1.4155	1.28
D23	1.4620	1.23
D24	1.5002	1.02
D25	1.5128	0.94
D26	1.5266	0.89
D27	1.7795	0.87
D28	1.7876	0.85
D29	1.8485	0.55
D30	1.8560	0.54
D31	1.8749	0.49
D32	1.8981	0.49
D33	1.9150	0.47
D34	1.9765	0.45
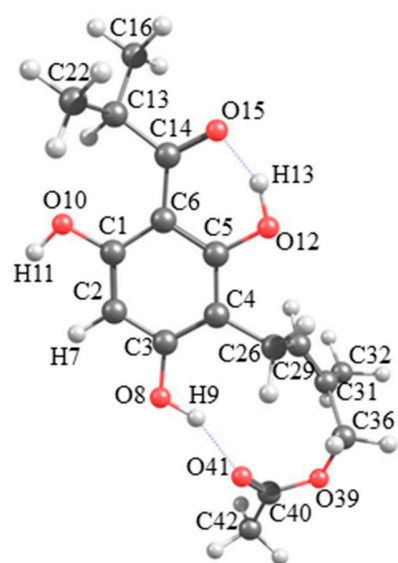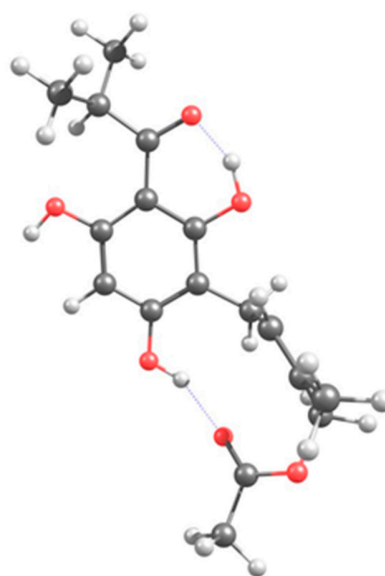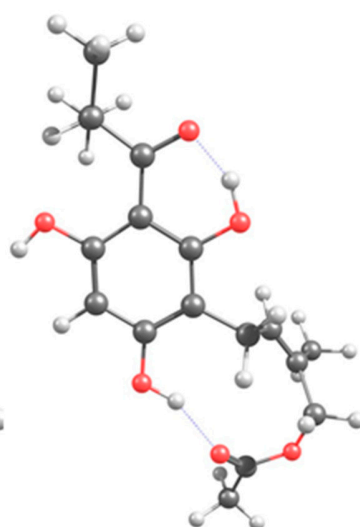
G1   **G2**   **G3**
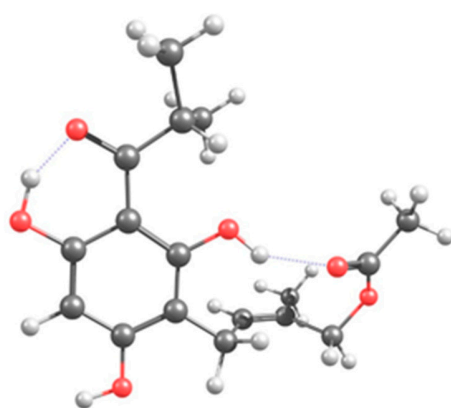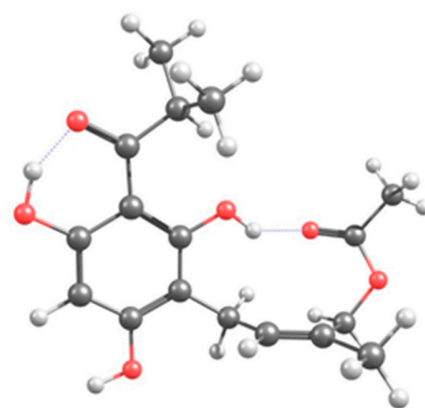
G4   **G5**

Gas
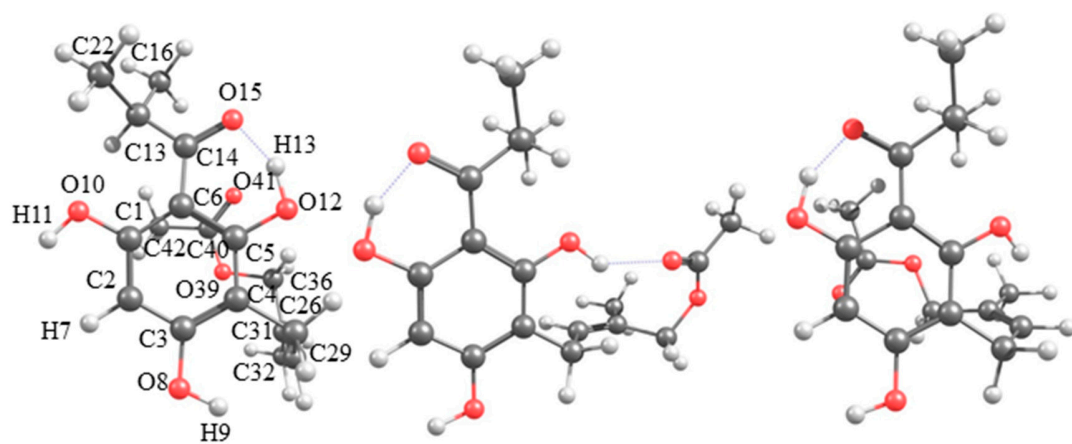
W1

W2

W3
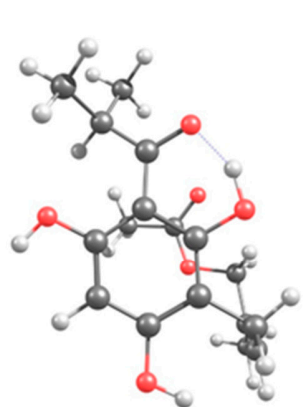
W4
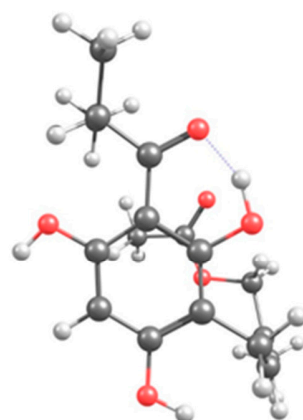
W5

Water
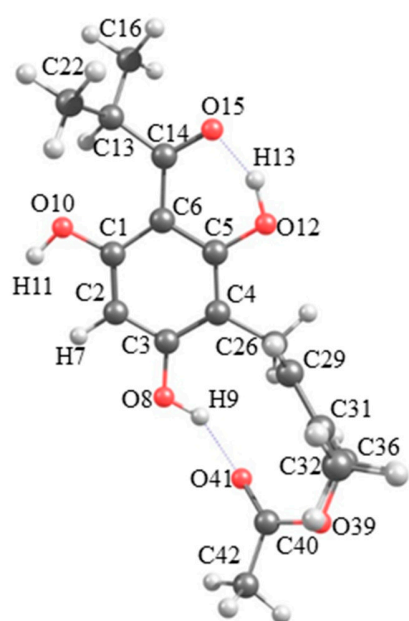
C1
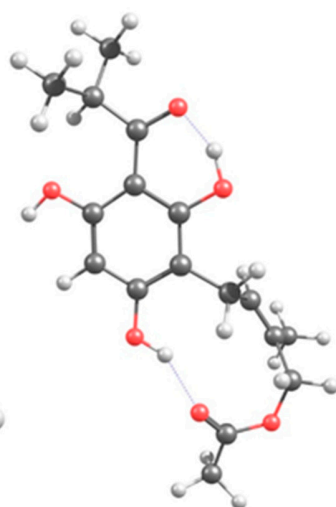
C2
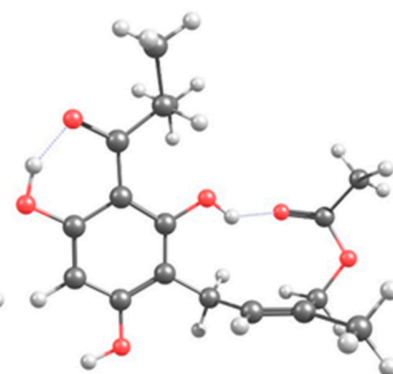
C3
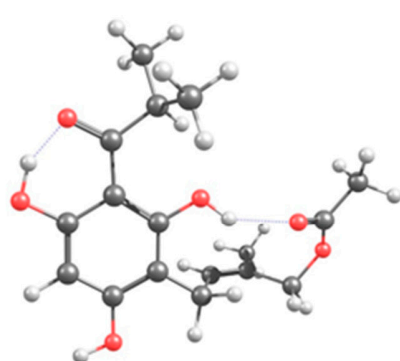
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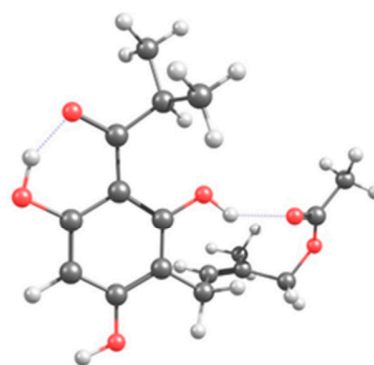
C5

Chloroform
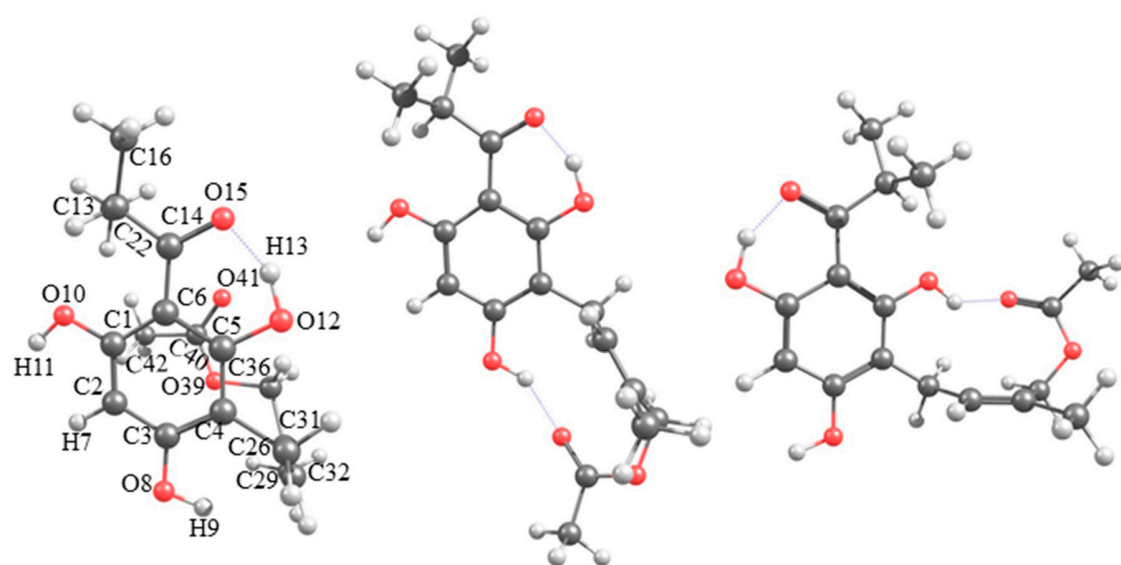
A1   A2   A3
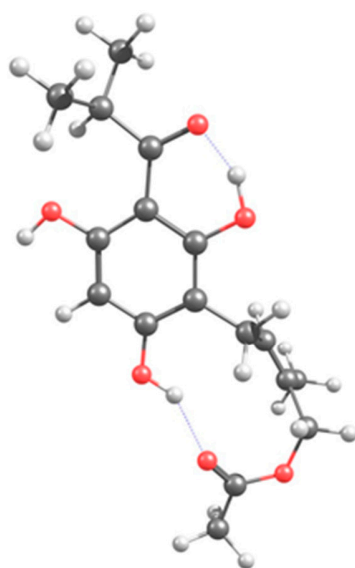
A4   A5

Acetonitrile

D1   **D2**   **D3**

D4   **D5**

DMSO

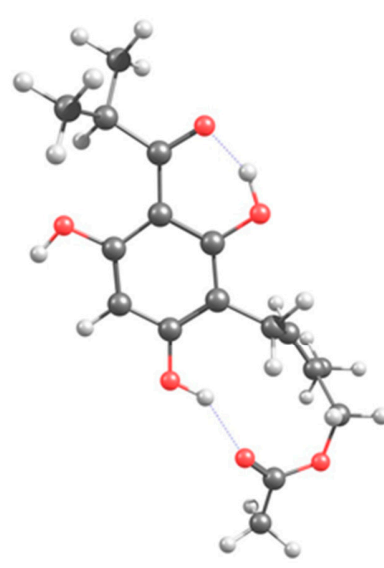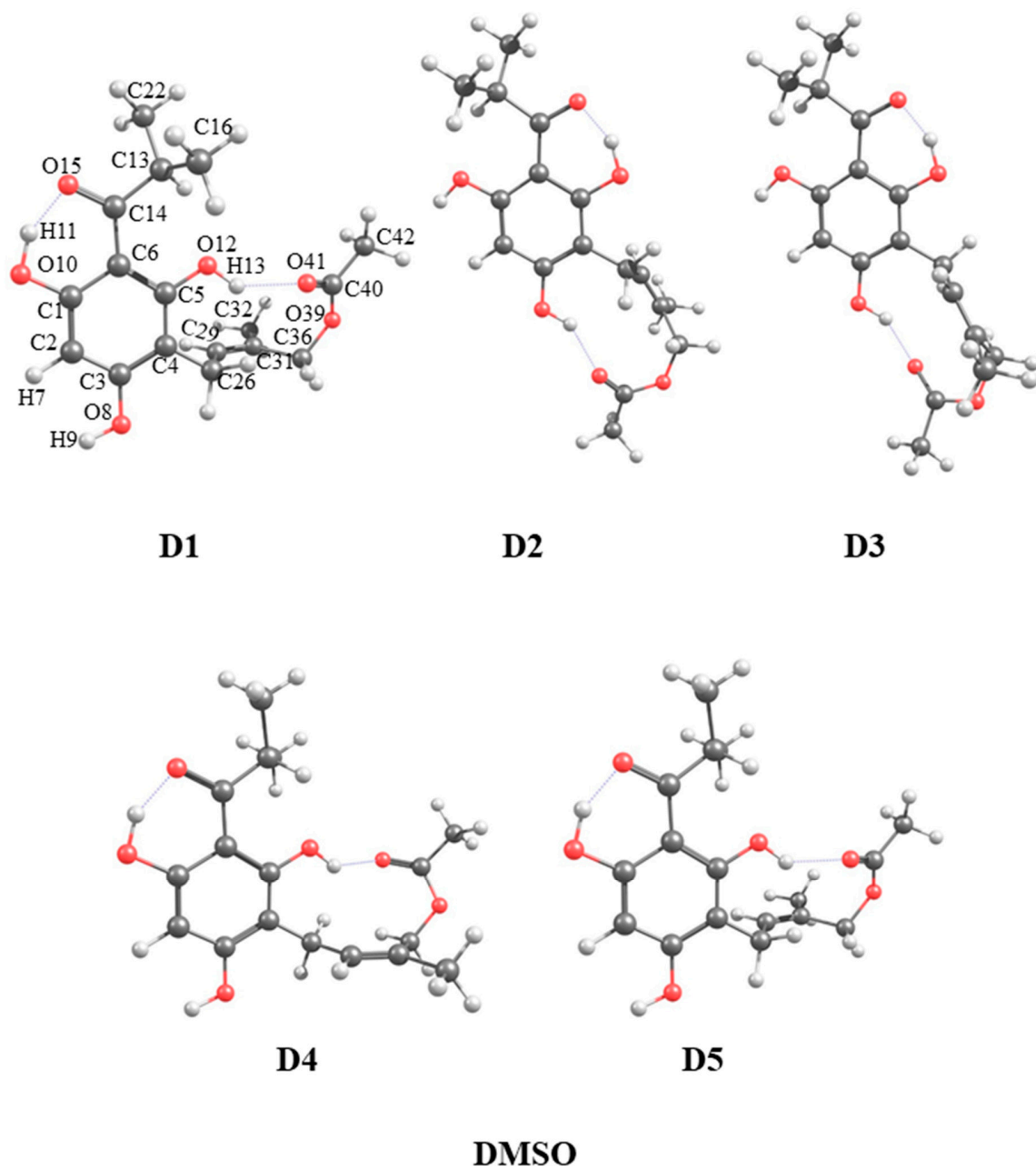**Figure S1.** Molecular structures of the five most stable conformers of caespitate calculated at the APFD/6-311+G(2d,p) level of theory in gas and solution phases. In gas (**G1-G5**), water (**W1-W5**), chloroform (**C1-C5**), acetonitrile (**A1-A5**), and DMSO (**D1-D5**) phases.
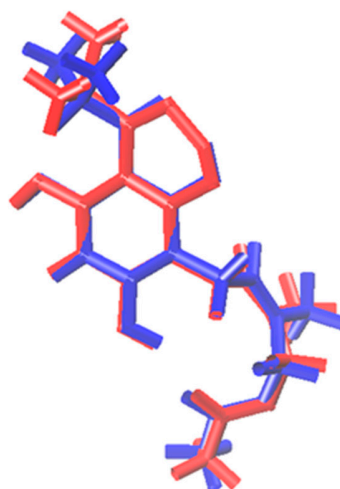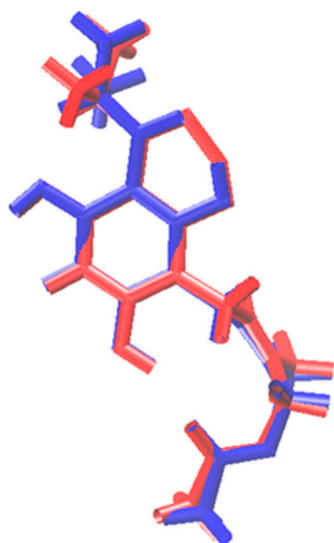
WG1E

CG1E

AG1E

DG1E
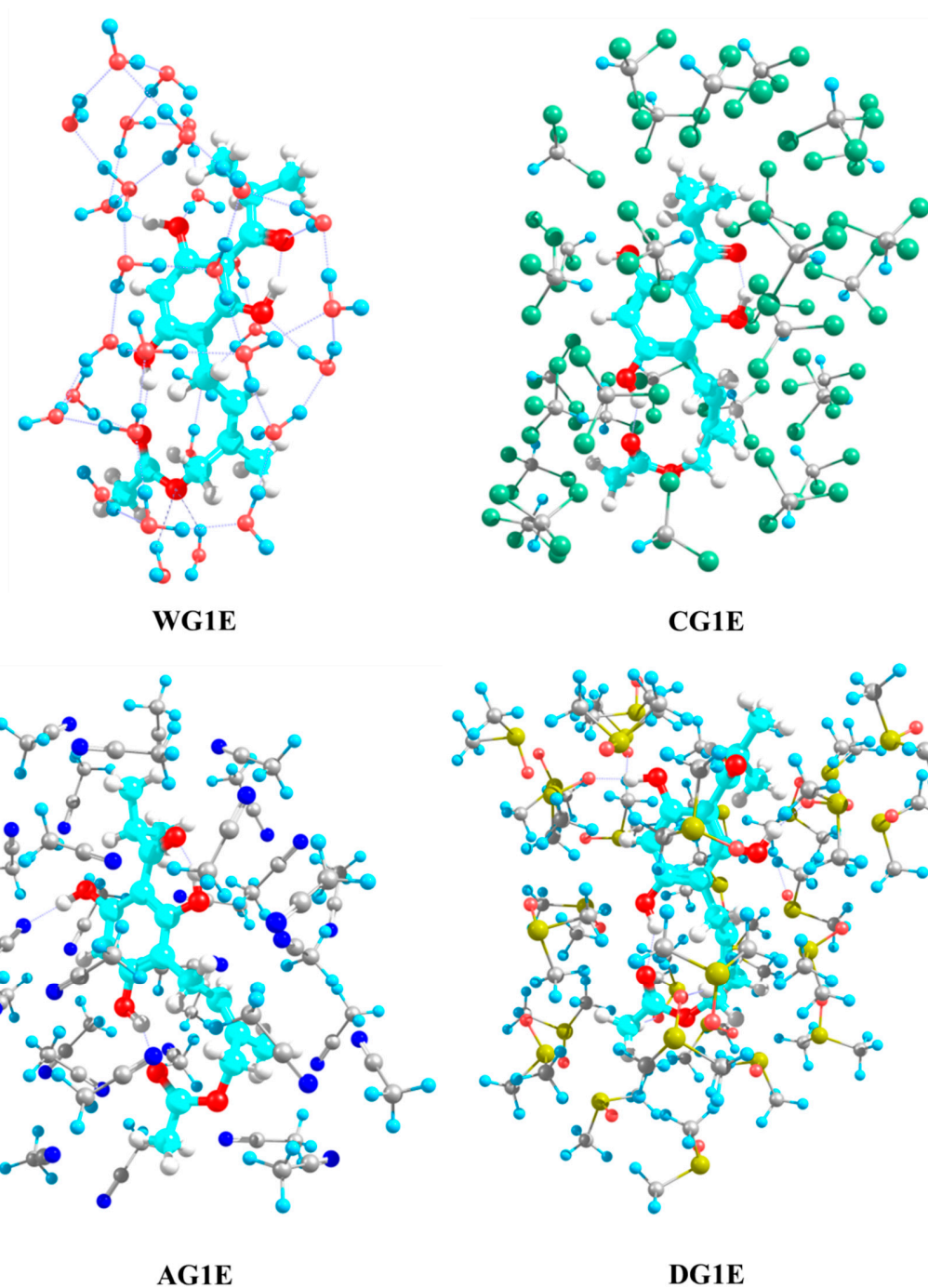
Figure S2. Optimized geometries of the caespitate–explicit solvent systems calculated at the ONIOM (ωB97X-D3/Def2-TZVP:XTB2) method obtained from the most stable conformer in gas phase (**G1**) surrounded by water (**WG1E**), chloroform (**CG1E**), acetonitrile (**AG1E**), and DMSO (**DG1E**) molecules.
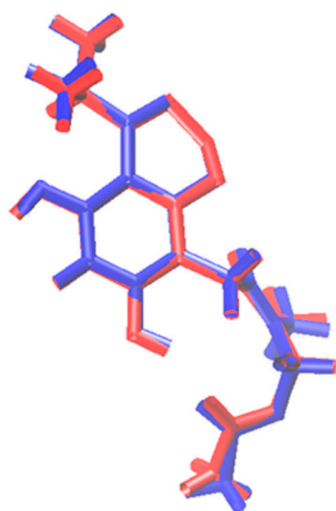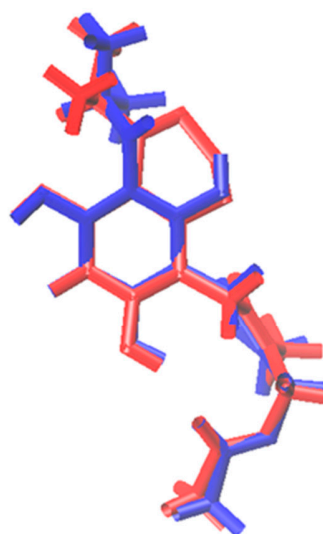
RMSD: 0.19 Å
G1/WG1E

RMSD: 0.48 Å
G1/CG1E

RMSD: 0.55 Å
G1/AG1E

RMSD: 0.79 Å
G1/DG1E

Figure S3. Comparison of the optimized structures of the most stable conformer in gas phase (**G1**) (in red color) surrounded of explicit solvent, in water (**WG1E**), in chloroform (**CG1E**), in acetonitrile (**AcG1E**), and in DMSO (**DG1E**) (in blue color).
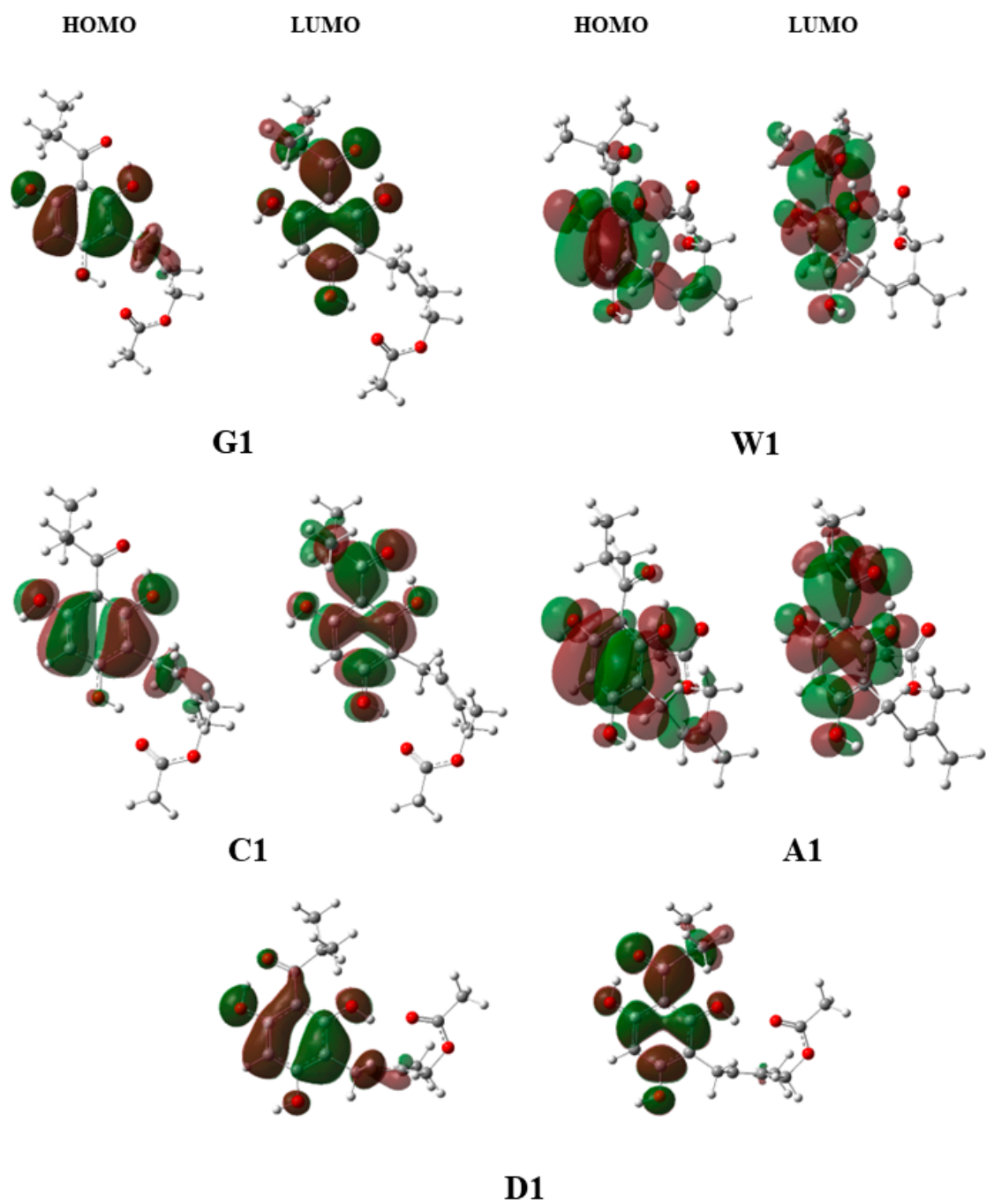
Figure S4. Isosurfaces of the frontier molecular orbitals HOMO and LUMO of the most stable caespitate conformers calculated at the APFD/6-311+G(2d,p) level of theory in gas and solution phases. In gas (**G1**), water (**W1**), chloroform (**C1**), acetonitrile (**A1**), and DMSO (**D1**) phases.
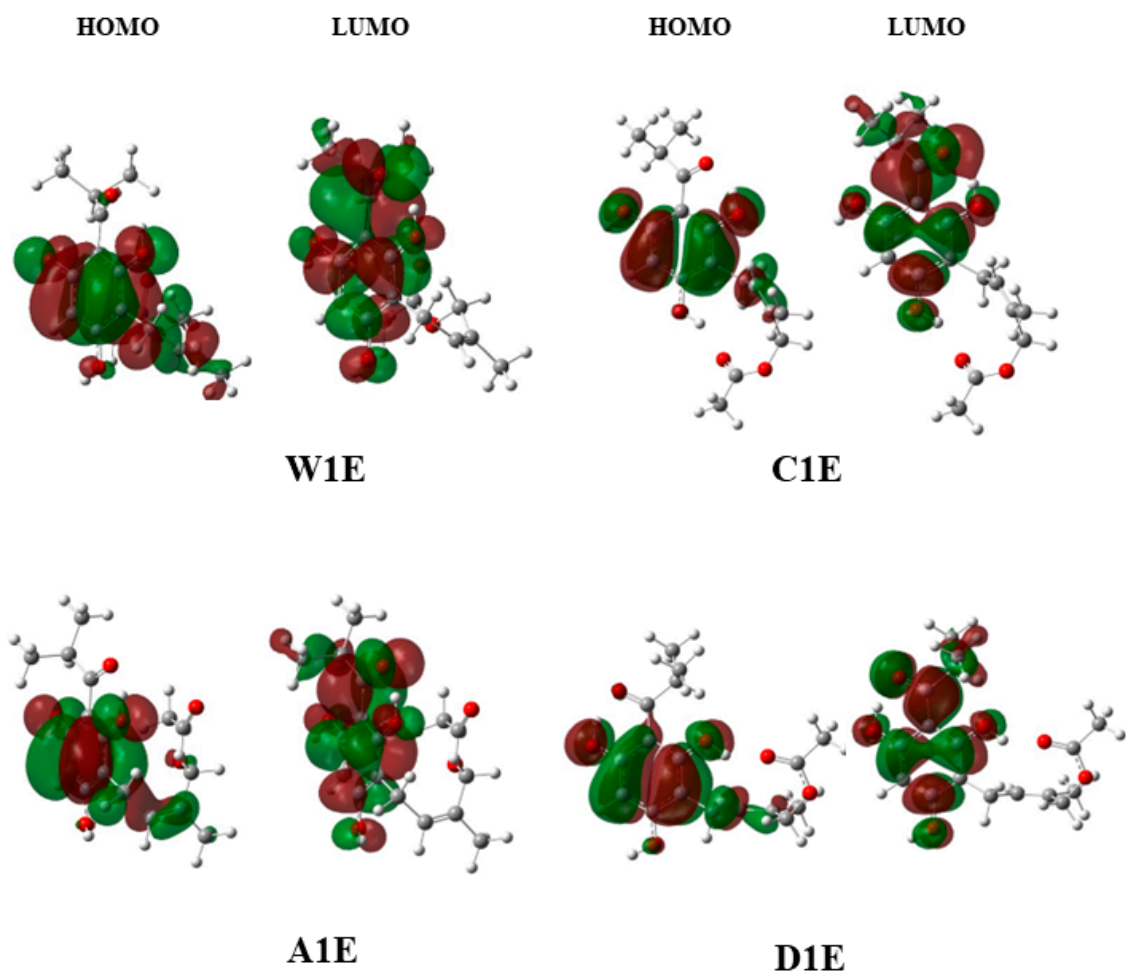
Figure S5. Isosurfaces of the frontier molecular orbitals HOMO and LUMO of the caespitate conformers calculated at the ONIOM (ωB97X-D3/Def2-TZVP:XTB2) method with explicit solvent obtained from the most stable conformers in implicit solution in water (**W1E**), in chloroform (**C1E**), in acetonitrile (**A1E**), and DMSO (**D1E**).
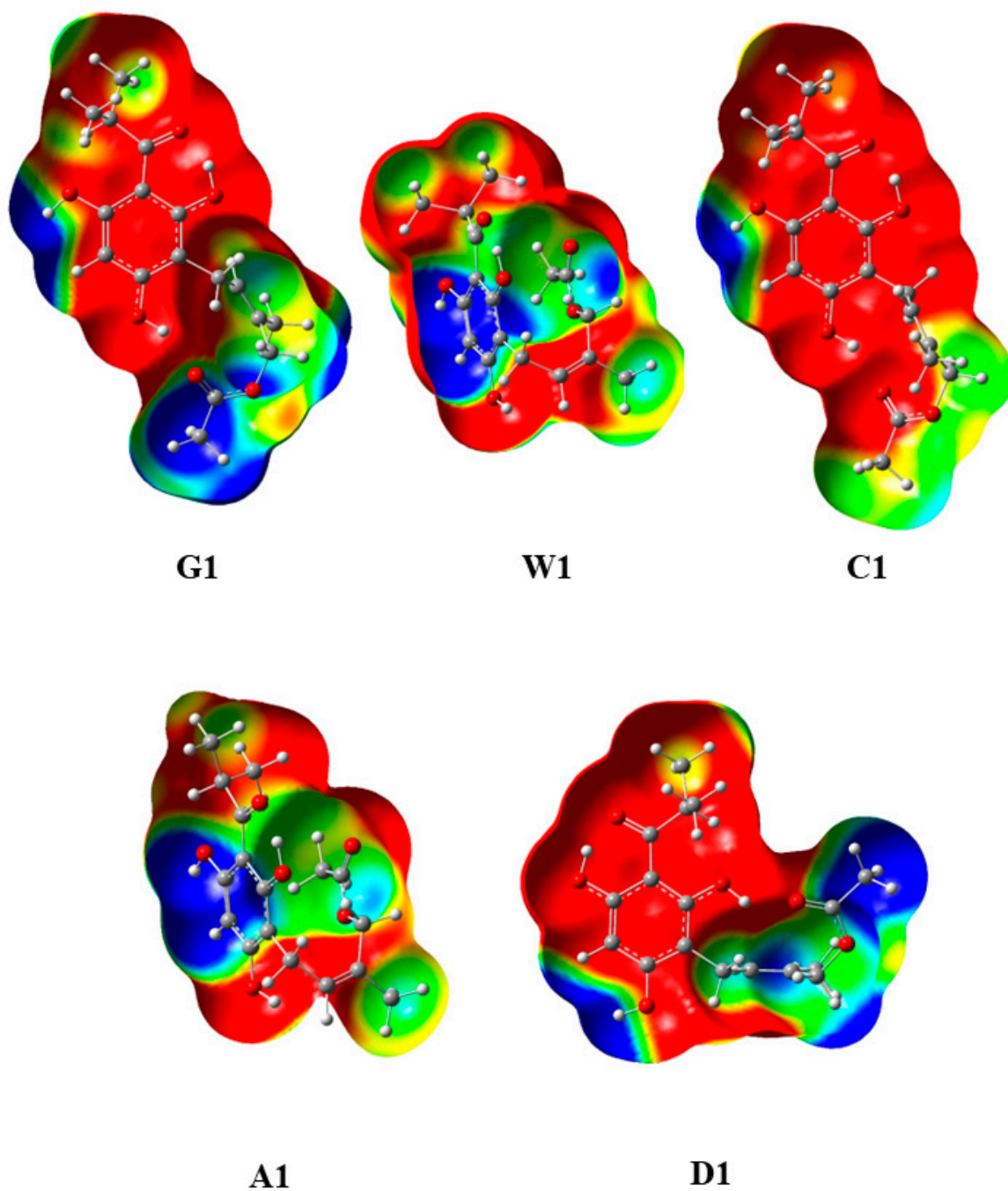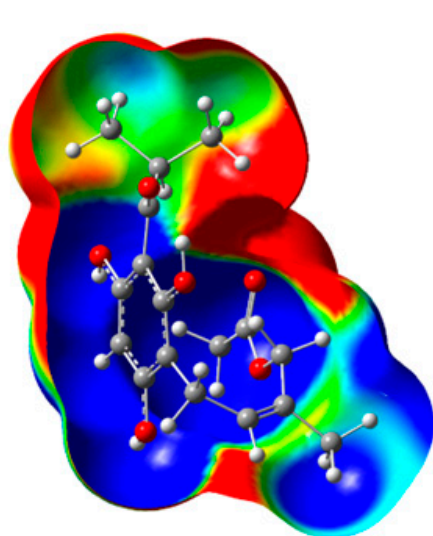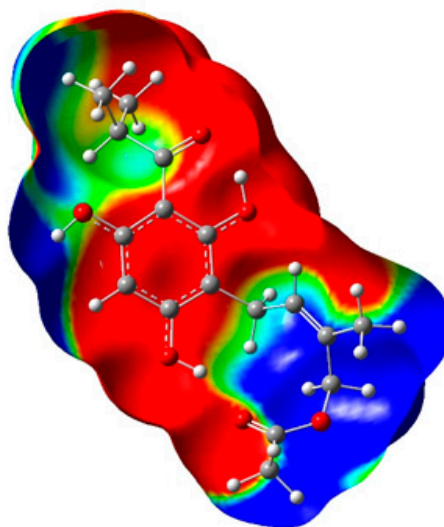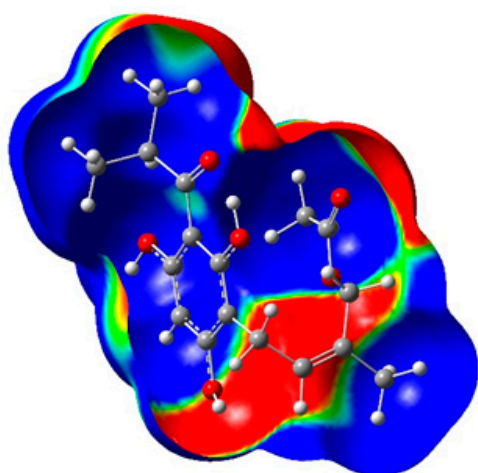
Figure S6. Molecular Electrostatic Potential (MEP) of the most stable caespitate conformers calculated at the APFD/6-311+G(2d,p) level of theory in gas and solution phases. In gas (**G1**), water (**W1**), chloroform (**C1**), acetonitrile (**A1**), and DMSO (**D1**) phases.
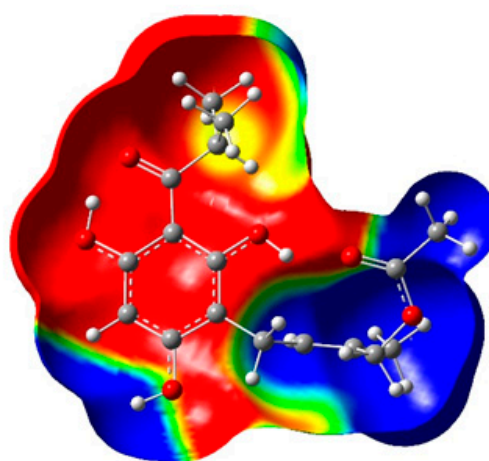
Figure S7. Molecular Electrostatic Potential (MEP) of the caespitate conformers calculated at the ONIOM (ωB97X-D3/Def2-TZVP:XTB2) method with explicit solvent obtained from the most stable conformers in implicit solution in water (**W1E**), in chloroform (**C1E**), in acetonitrile (**A1E**), and DMSO (**D1E**).