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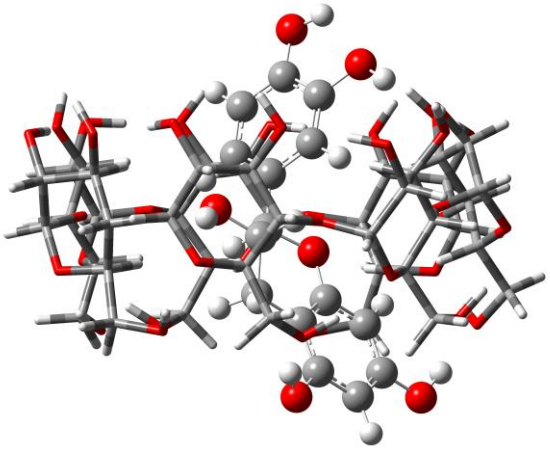
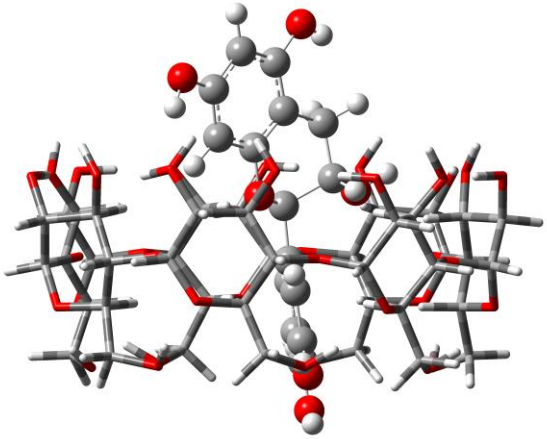
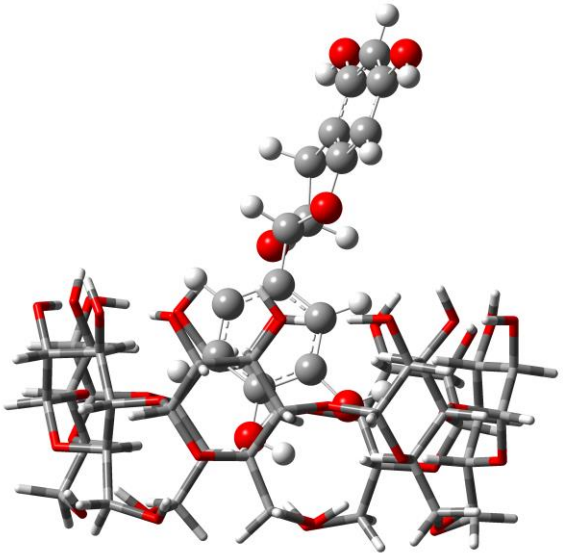
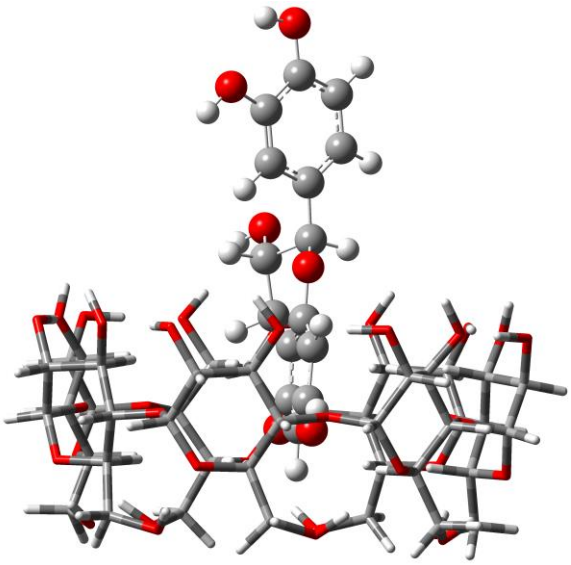
(a)		M1
(b)		M2
(c)		M3
(d)		M4

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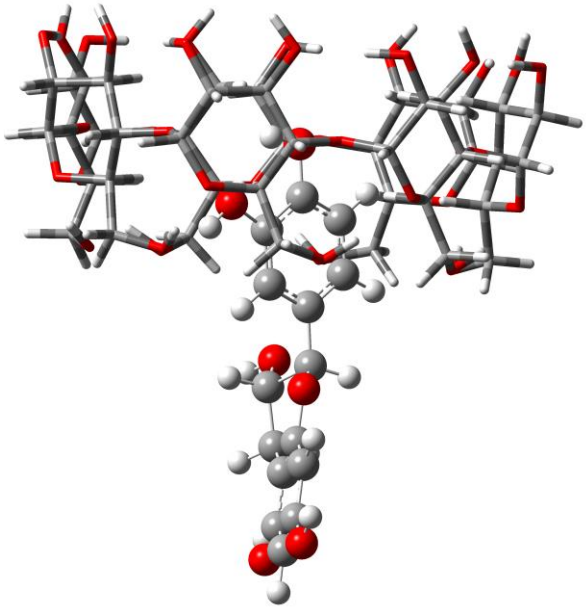

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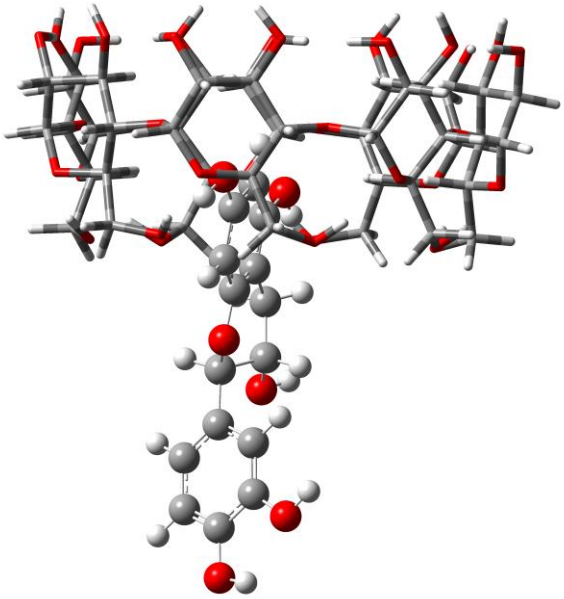

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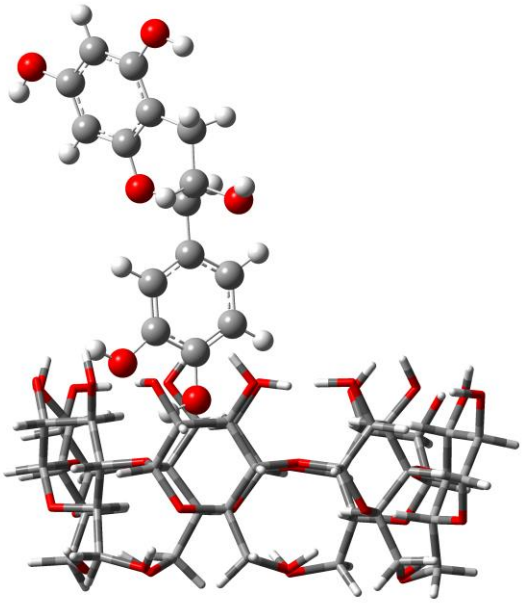

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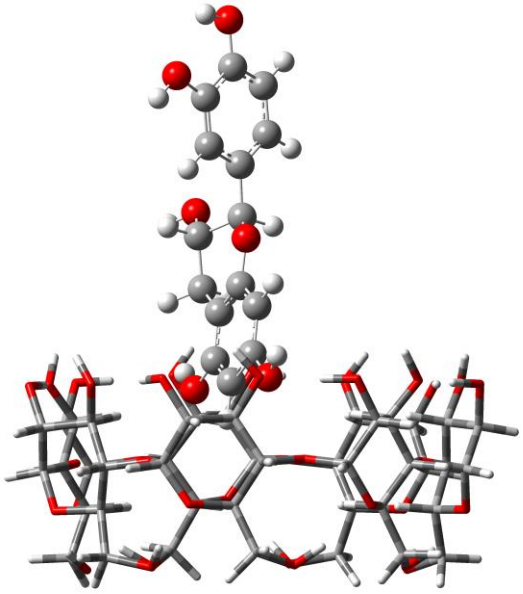

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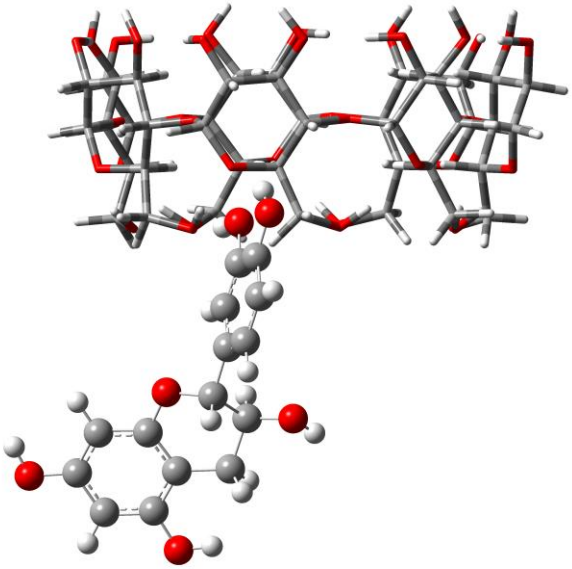

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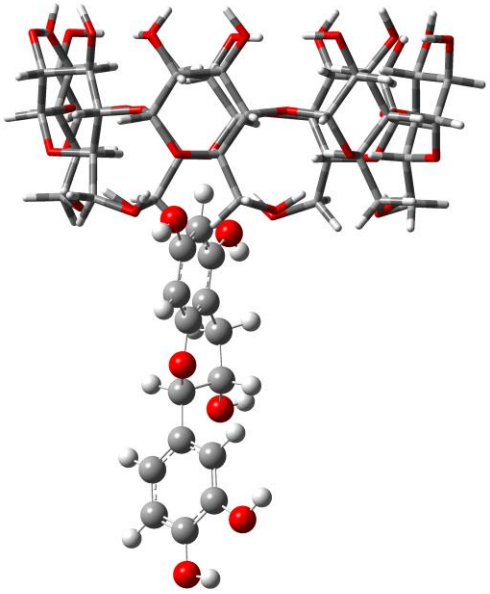
(j)



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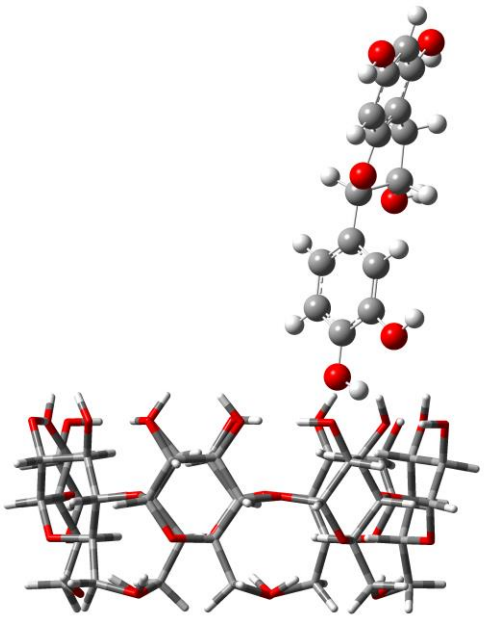

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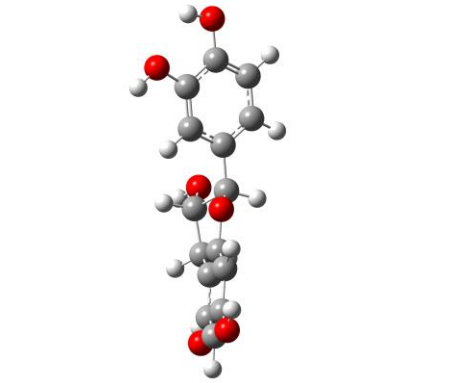

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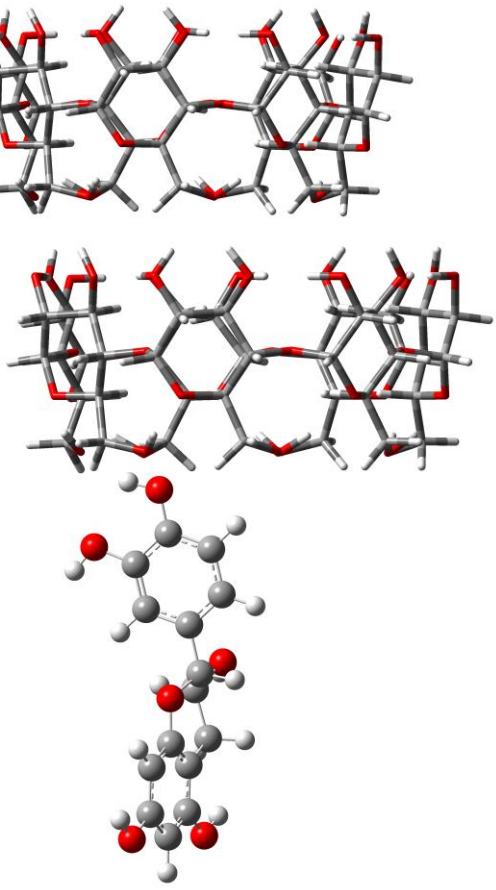

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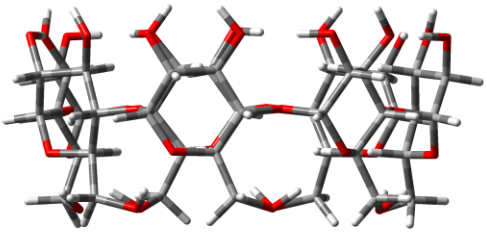

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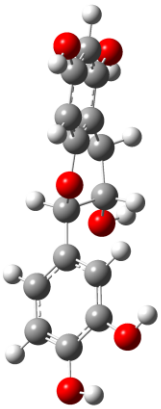

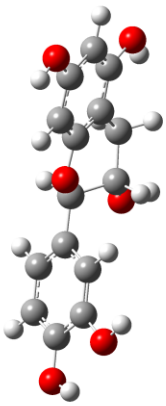

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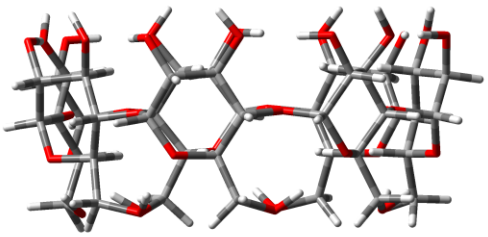

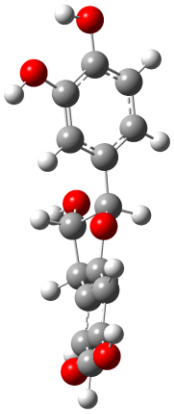

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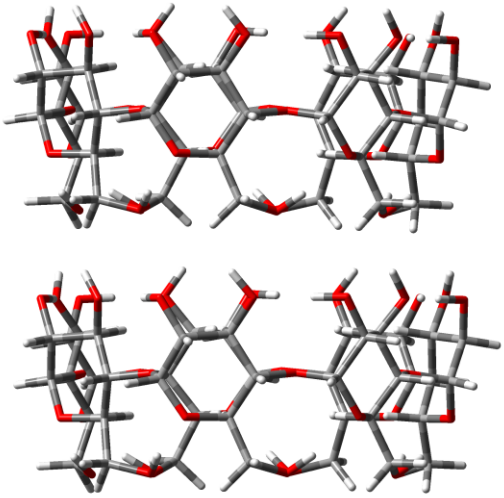

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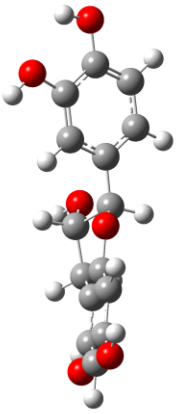

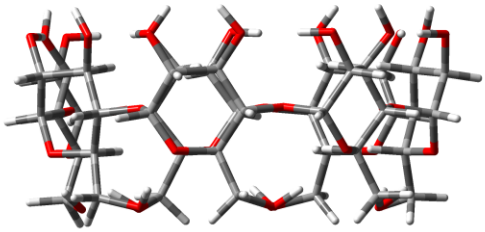

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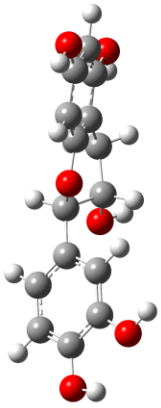

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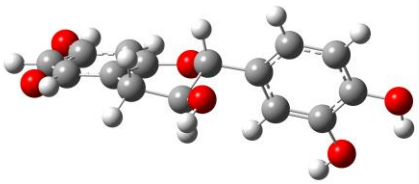

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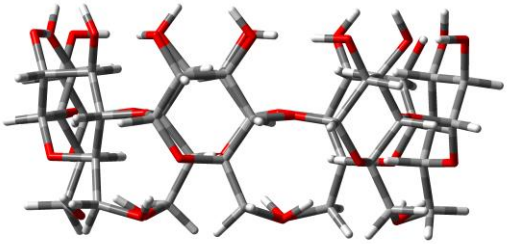

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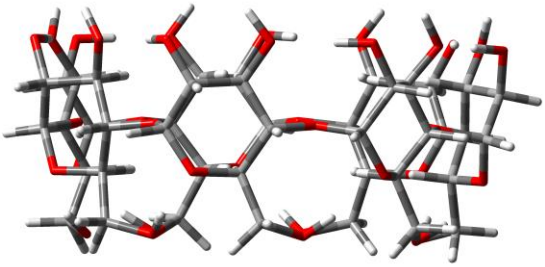

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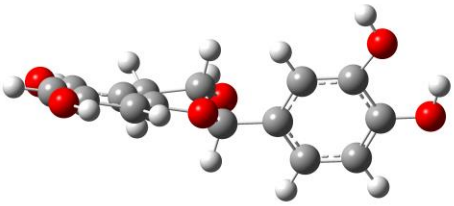

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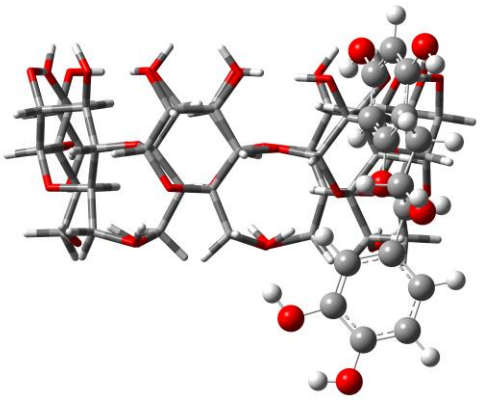
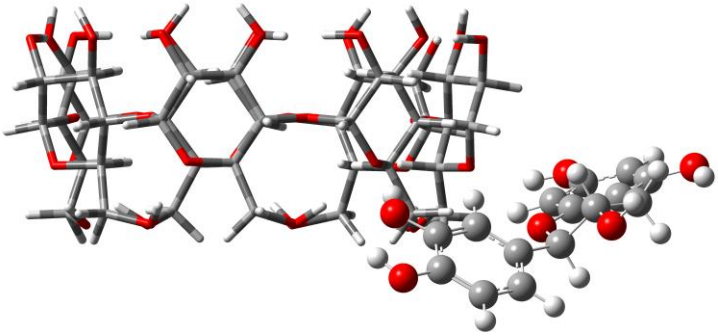
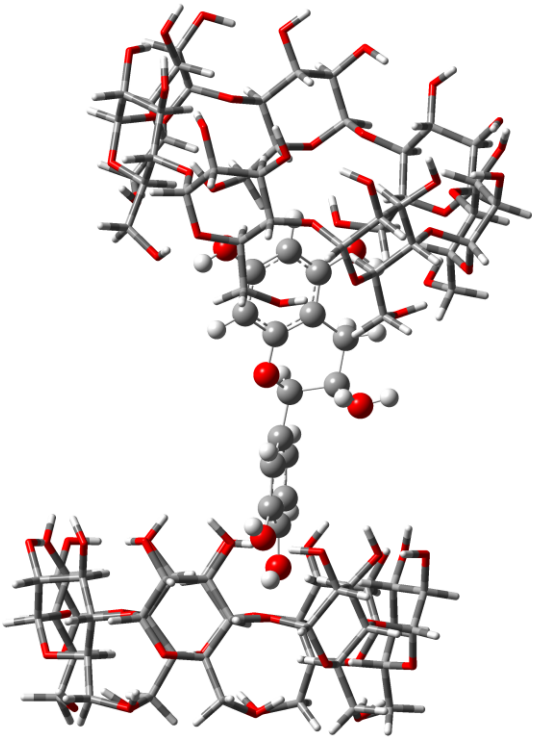
(u)  M21

(v)  M22

(w)  M23

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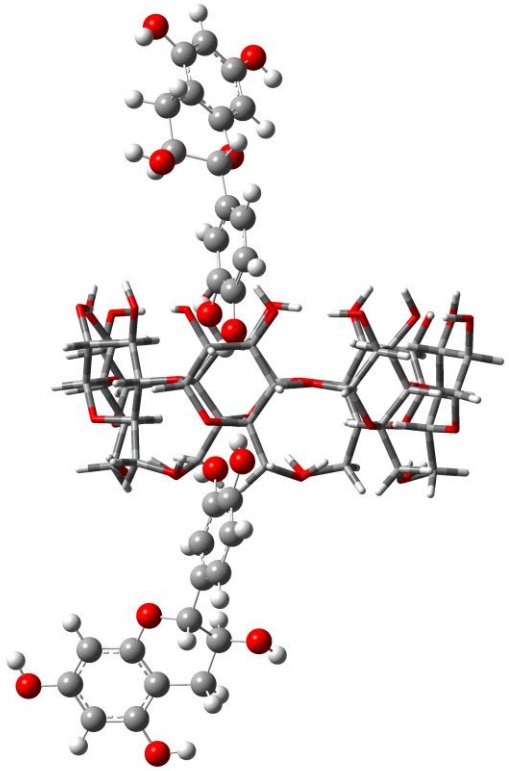

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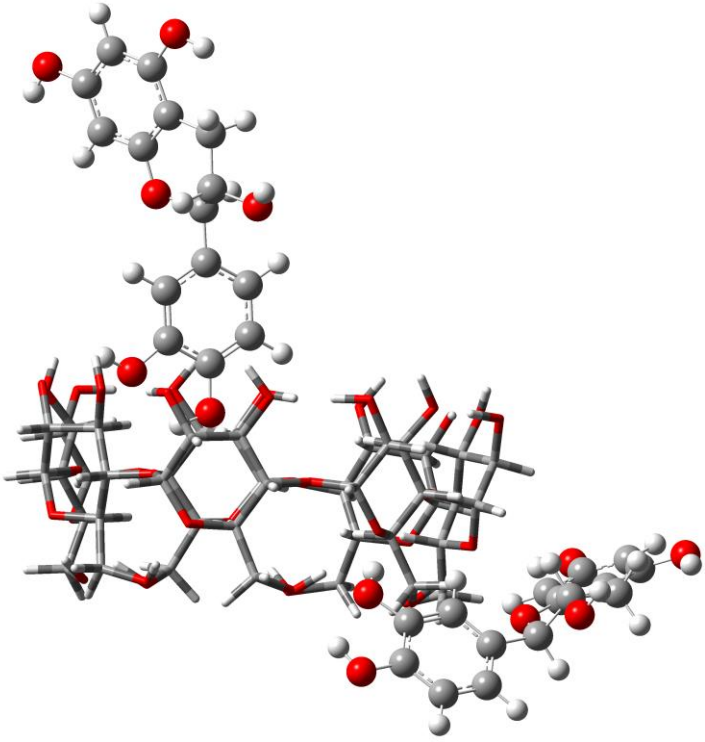

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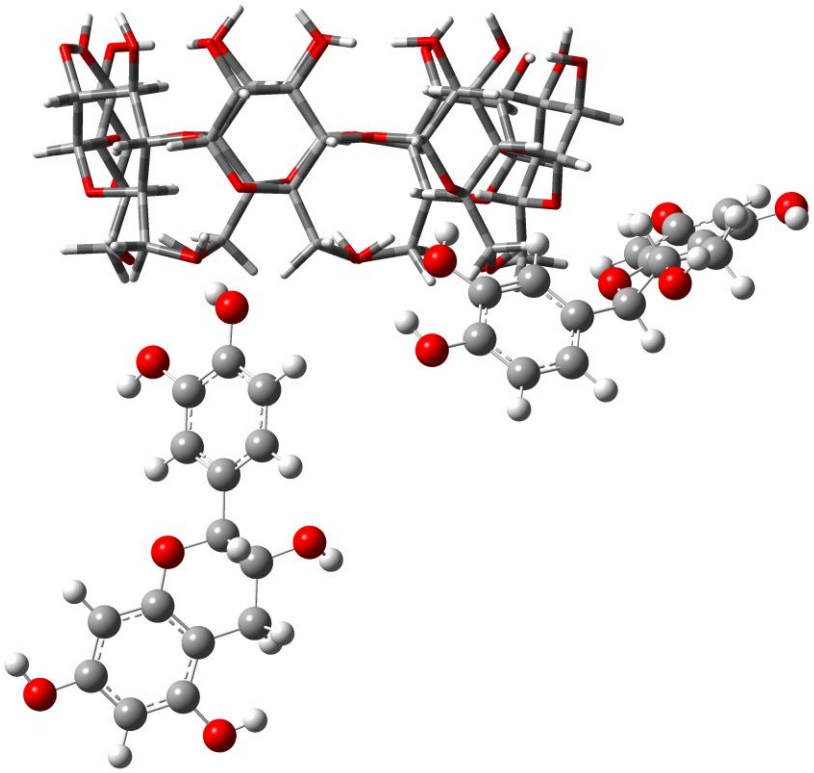

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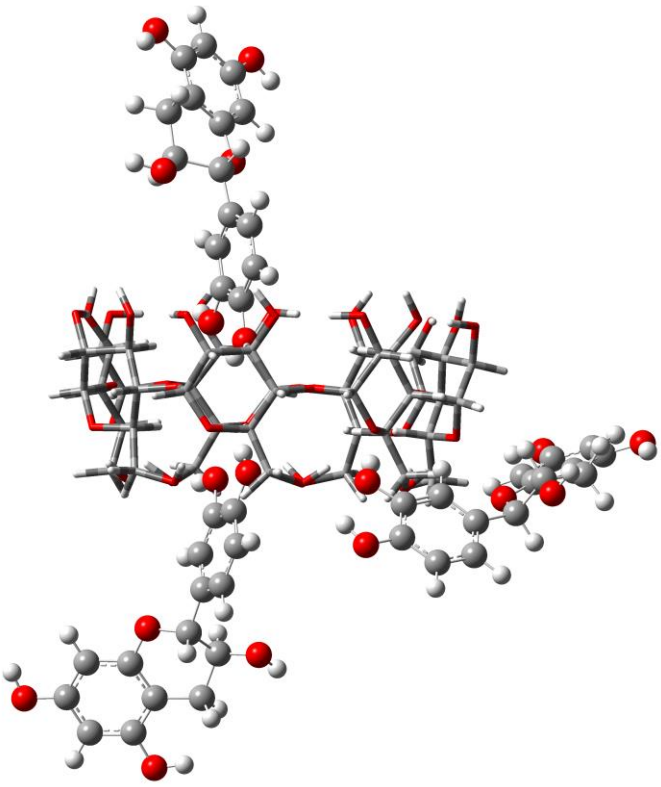

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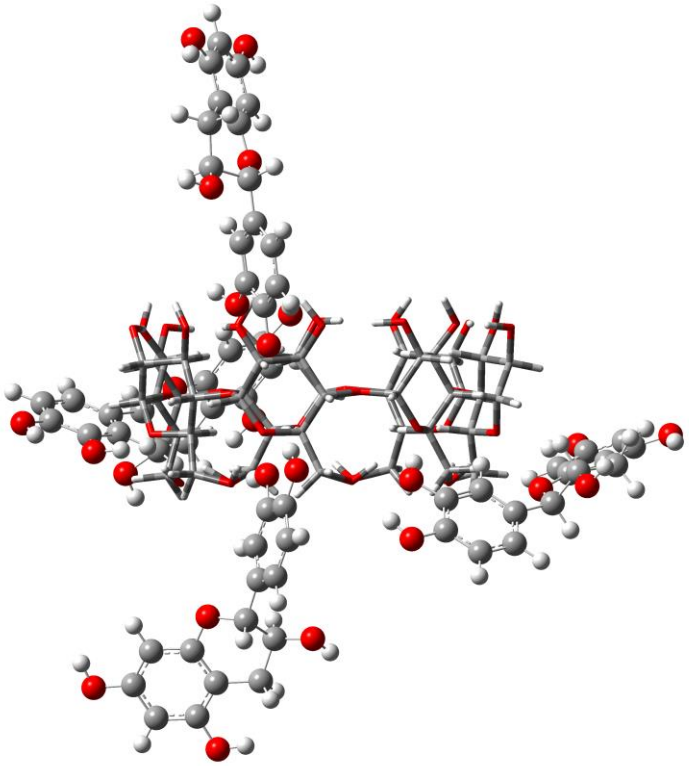

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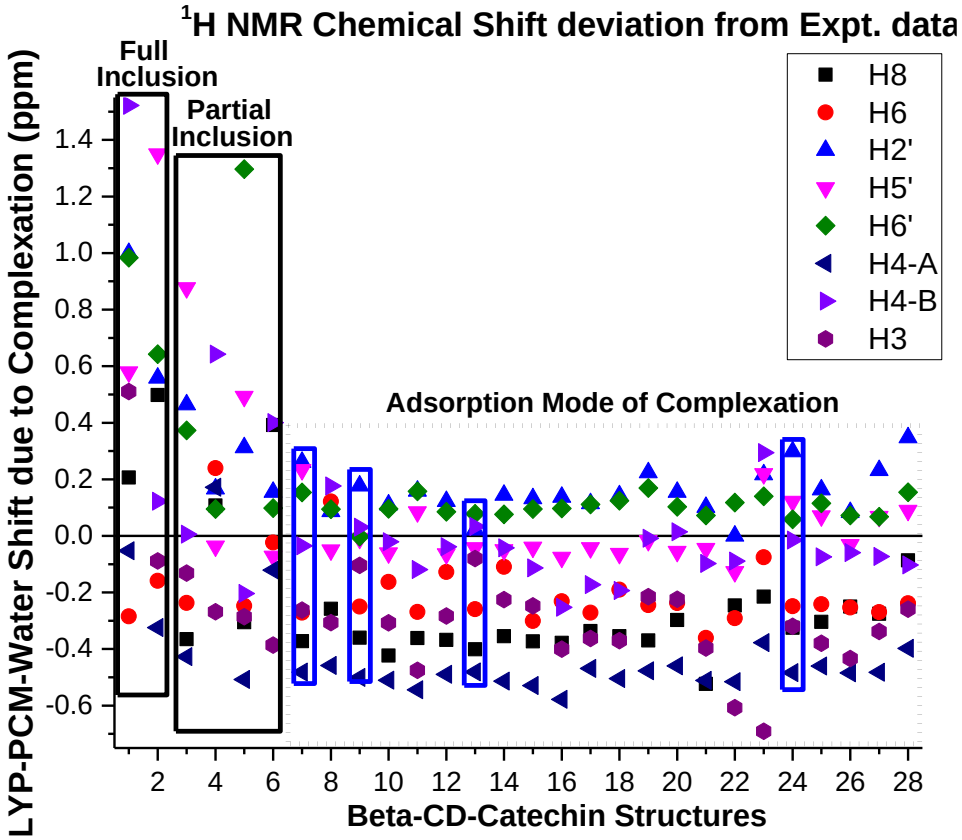

Figure S2. B3LYP/6-31G(d.p)-PCM-Water deviation from experimental 1H NMR chemical shifts[29] for all 28 ωB97x-D/6-31G(d,p)-PCM-Water optimized catechin-Beta-CD complex structures. The description of the complexes is given below, where Beta-CD Rim-A (Primary Rim) and Rim-B (Secondary Rim) mode of Catechin interaction are indicated, as well as A and B ring protons approaching Beta-CD-ring (through H6 and H5' respectively).
M1: Full-Incl-H5'-Rim-A; **M2**: Full-Incl-H5'-Rim-B**; M3**: Incl-H5'-Rim-A; **M4**: Incl-H6-Rim-A; **M5**: Incl-H5'-Rim-B; **M5**: Incl-H6-Rim-B; **M7**: Part-Incl-H5'-Rim-A**; M8**: Part-Incl-H6-Rim-A**; M9**: Part-Incl-H5'-Rim-B; **M10**: Part-Incl-H6-Rim-B; **M11**: Ads-Perp-H5'-Rim-A; **M12**: Ads-Perp-H6-Rim-A; **M13**: Ads-Perp-H5'-Rim-B**; M14**: Ads-Perp-H6-Rim-B**; M15**: Weak-Ads-Perp-H5'-Rim-A; **M16**: Weak-Ads-Perp-H6-Rim-A; **M17**: Weak-Ads-Perp-H5'-Rim-B**; M18**: Weak-Ads-Perp-H6-Rim-B**; M19**: Ads-Parallel-H2'-Rim-A; **M20**: Ads-Parallel-H2'-Rim-B; **M21**: Ads-Lateral-1; **M22**: Ads-Lateral-2; **M23**: Ads-CAT-(BCD)2; **M24:** Ads-(CAT)2-BCD-Perpendicular-Rim-A-and-Rim-B; **M25**: Ads-(CAT)2-BCD-Perp-Rim-A-and-Lateral-Approach; **M26**: (CAT)2-BCD-Perp-Rim-B-and-Lateral-Approach; **M27**: (CAT)3-BCD-Perp-Rim-A-Perp-Rim-B-and-Lateral-Approach; M28: (CAT)4-BCD-Perpendicular-Lateral

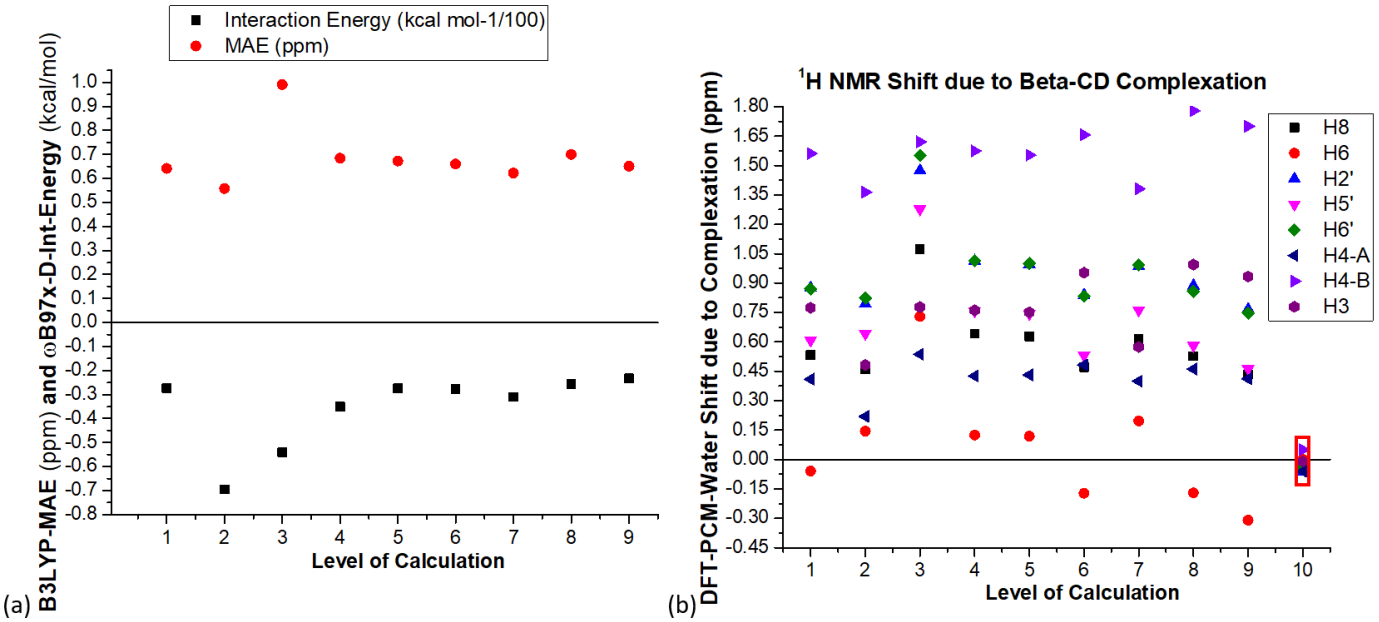

Figure S3. (a) Interaction energies (ΔE_{int} in kcal mol^{-1}) and MAE (ppm) values for structure M1 of Catechin-Beta-CD complex calculated with the 6-31G(d,p) basis set using various DFT functionals and PCM Model (water) (b) ^{1}H NMR chemical shift change due to complexation (ppm) values for structure M1 of Catechin-Beta-CD complex calculated with the 6-31G(d,p) basis set using various DFT functionals and PCM Model (water). Experimental data (in D_2O) are also given.

Method of Calculation:

(1) B3LYP/6-31G(d,p) (2) ωB97x-D/6-31G(d,p) (3) M06-2x/6-31G(d,p) (4) PBE1PBE/6-31G(d,p) (5) MPW1PW91/6-31G(d,p) (6) TPSSTPSS/6-31G(d,p) (7) BHandHLYP/6-31G(d,p) (8) BP86/6-31G(d,p) (9) BLYP/6-31G(d,p) (10) Experimental data.

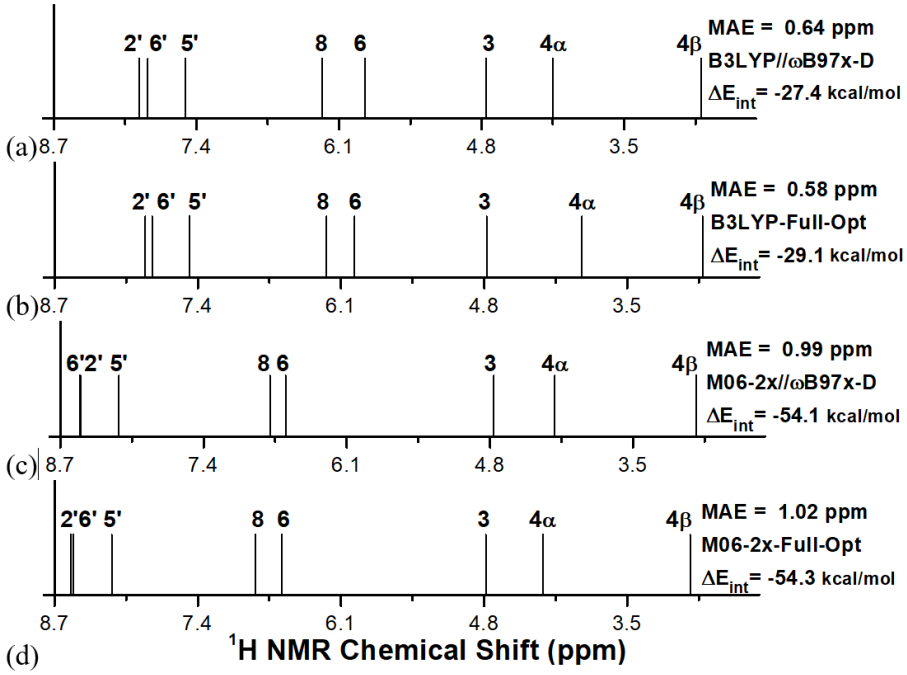

Figure S4. Comparison between DFT predictions of ^{1}H NMR spectrum for Catechin-Beta-CD structure M1 using single point B3LYP and M06-2x calculations at the geometry optimized with the ωB97x-D functional (named B3LYP//ωB97x-D and M06-2x//ωB97x-D) and using the fully optimized geometries (named B3LYP-Full-Opt and M06-2x-Full-Opt). The 6-31G(d,p) basis set was used.

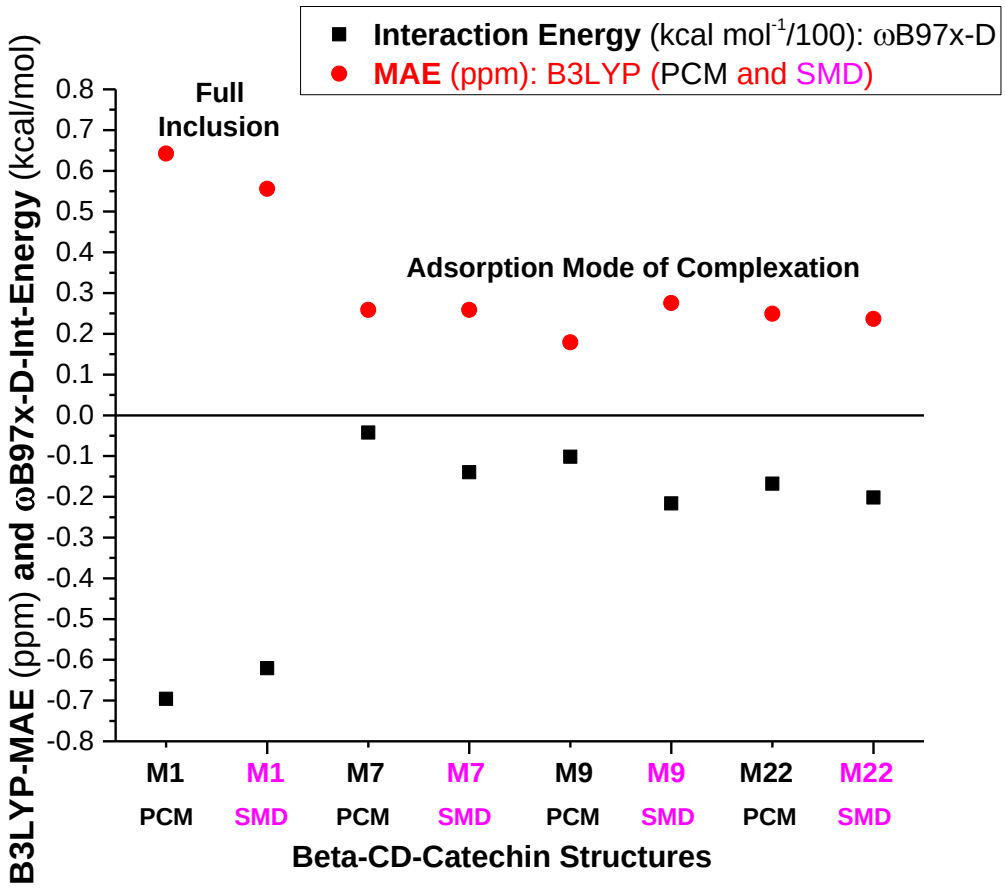

Figure S5. Comparison between-DFT-PCM-Water and DFT-SMD-Water interaction energy and MAE (^{1}H NMR) results for selected catechin-Beta-CD complex structures.

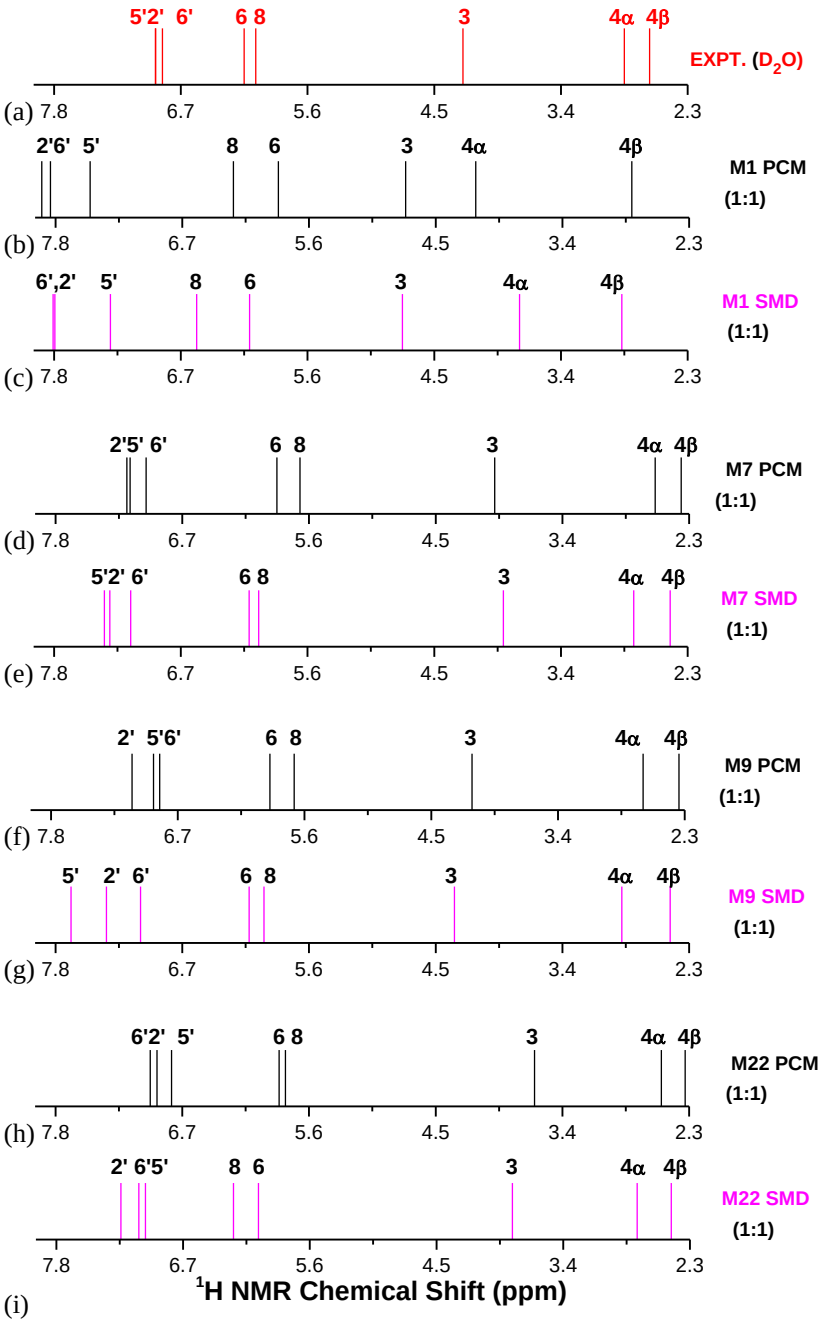

Figure S6. (a) Experimental (in D_2O) and (b-i) B3LYP/6-31G(d,p) ^1H NMR spectra calculated for representative optimized structures of catechin-Beta-CD complexes using the PCM and SMD solvation models in water.