Electronic Supplementary Material (ESI) for RSC Advances.

Insights into the Catalytic Mechanism of dTDP-Glucose 4,6-Dehydratase from Quantum Mechanics/Molecular Mechanics Simulations

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Table 1 Calculated QM/MM absolute and relative energies for all reaction species.

	Single-point energies E (a. u.)	**Entropic contributions S (J/mol/K)**	**TΔS (kcal/mol)**	**Relative energies ΔE[a] (kcal/mol)**	**Relative energies ΔG[b] (kcal/mol)**
R	-2573.52451	471.25	0.0	0.0	0.0
(R′)[c]	(-2748.25695)	(542.41)	0.0	(0.0)	(0.0)
TS1	-2573.49151	465.99	-0.4	20.7	21.1
(TS1′)	(-2748.22439)	(530.03)	-0.5	(20.4)	(20.9)
IM1	-2573.53011	481.20	0.7	-3.5	-4.2
(IM1′)	(-2748.26205)	(553.40)	0.8	(-3.2)	(-4.0)
TS2	-2573.50865	477.51	0.5	10.0	9.5
IM2	-2573.52466	483.24	0.8	-0.1	-0.9
TS3	-2573.51533	480.95	0.7	5.8	5.1
IM3	-2573.52950	493.88	1.7	-3.1	-4.8
TS4	-2573.51204	487.94	1.2	7.8	6.6
P′	-2573.54924	481.67	0.8	-15.5	-16.3
TS′	-2573.48713	483.00	0.9	23.5	22.6
P"	-2573.51313	488.94	1.2	7.1	5.9

[a] Relative single-point energies. [b] Relatvie Gibbs free energies, ΔG=ΔE-TΔS.

[c] Compared with R, the Lys155 was added to QM-region of R′.

Figure S1 Time dependence of RMSD (Å) from 15 ns MD simulation.

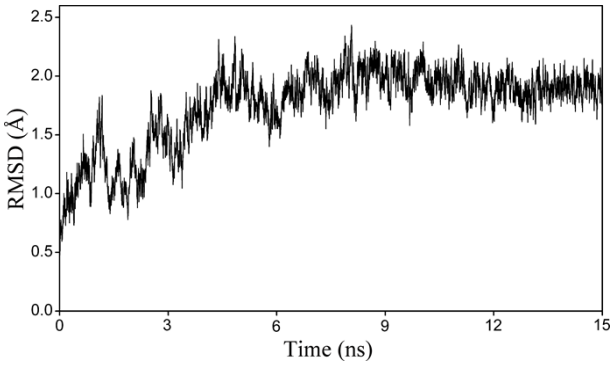

Figure S2 The superposition of the active sites of 11 optimized geometries. These structures were taken firstly from the snapshots of MD trajectories at intervals of 200 ps from 13 ns to 15 ns, and then optimized by QM/MM method at the B3LYP/6-31G(d,p)//CHARMM22 level. For clarity, the atoms included in QM region are shown in sticks.

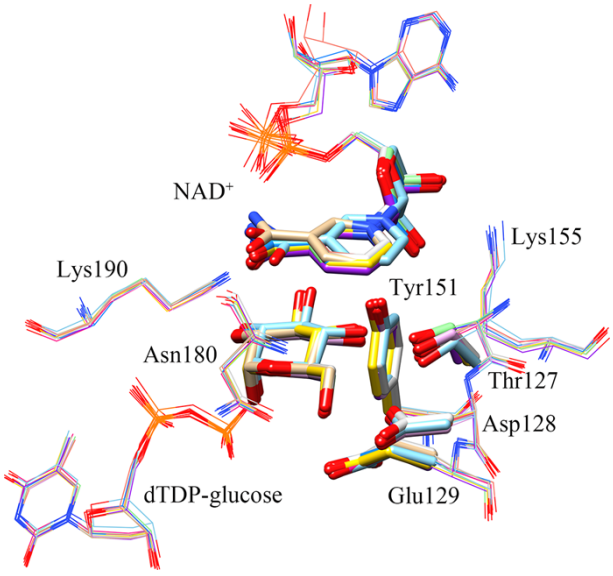

Figure S3 Optimized structures of reactant (R), transition state (TS) and product (P) for the four different enol-keto tautomerization models. Distances are given in Å.