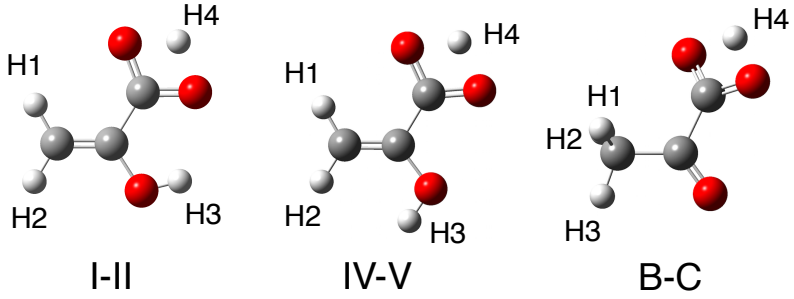
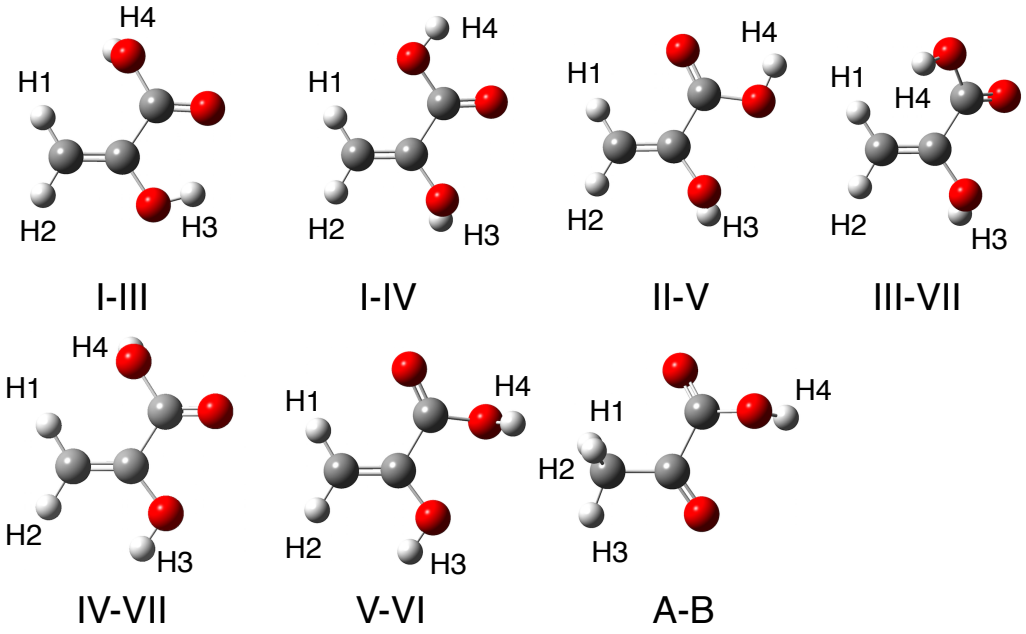
Electronic Supplementary Material (ESI) for RSC Advances.

Hydrogen transfer reactions



O-H rotational reactions



C-C rotational reactions

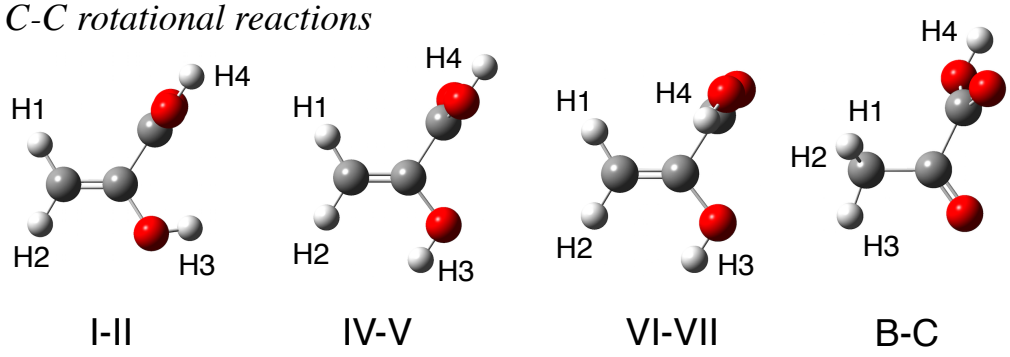


Figure S1. Optimized transition state structures of interconversion reactions of keto or enol forms themselves obtained by B3LYP/6-311++G(d,p) calculations.

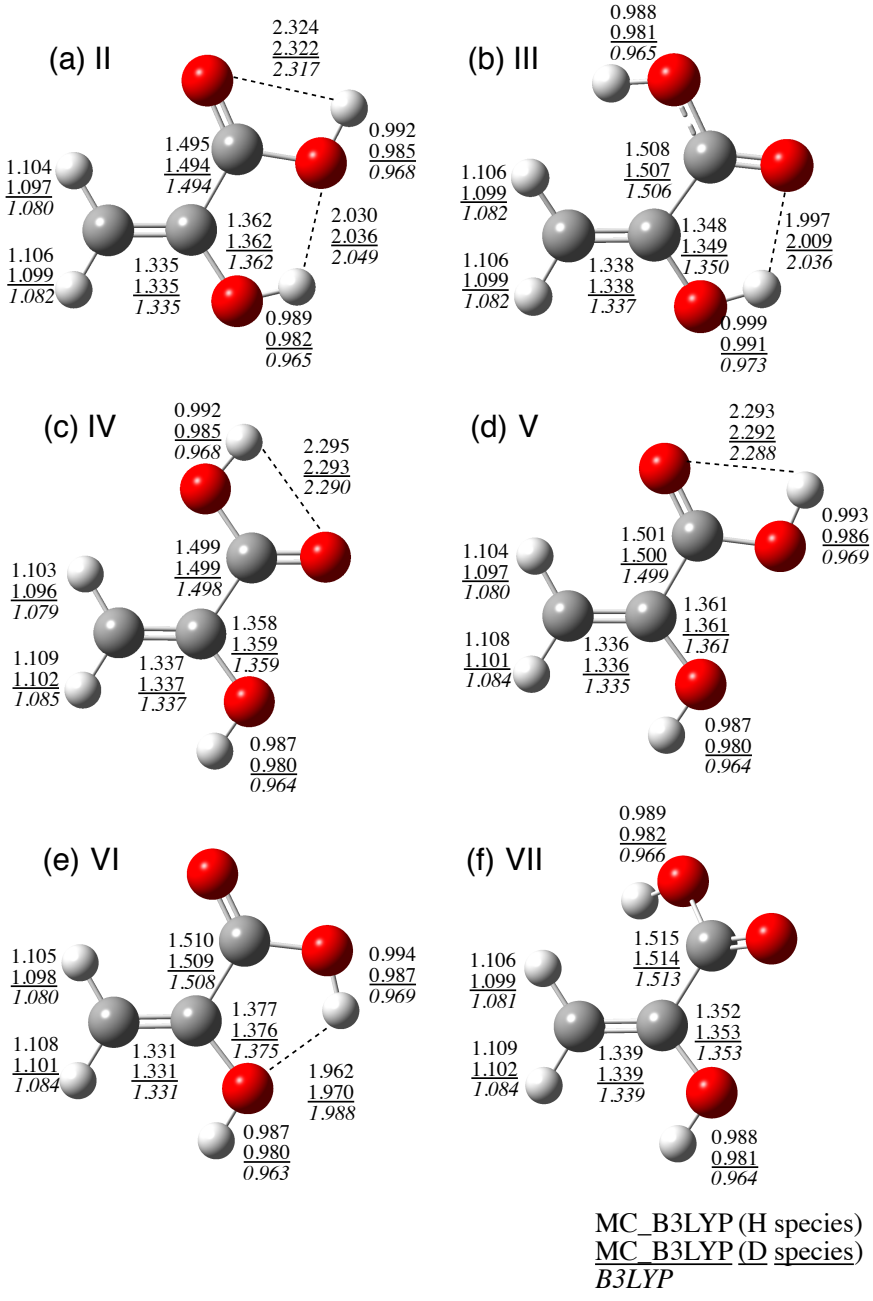


Figure S2. Optimized atomic distances [Å] of enol form structures II-VII.

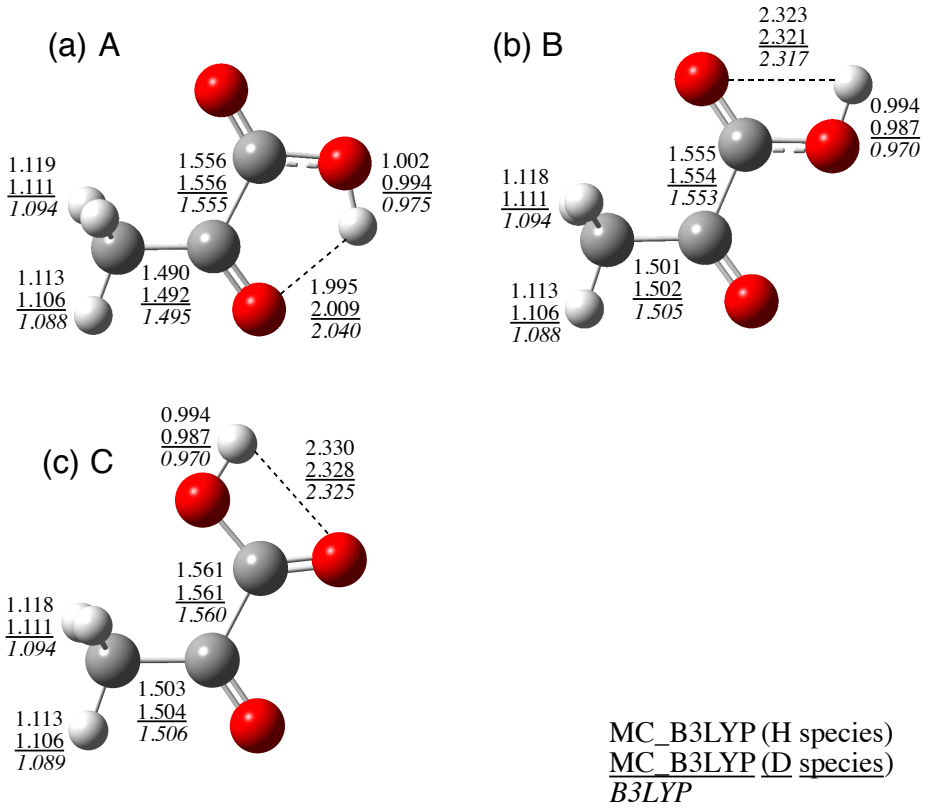
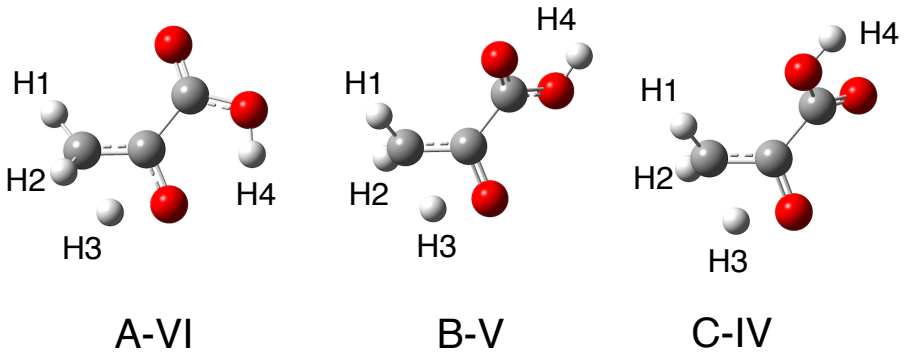


Figure S3. Optimized atomic distances [Å] of keto form structures A-C.

Keto-enol tautomerism reactions



A-VI B-V C-IV

Figure S4. Optimized transition state structures of keto-enol tautomerism reactions obtained by B3LYP/6-311++G(d,p) calculations.

Isomerization reactions

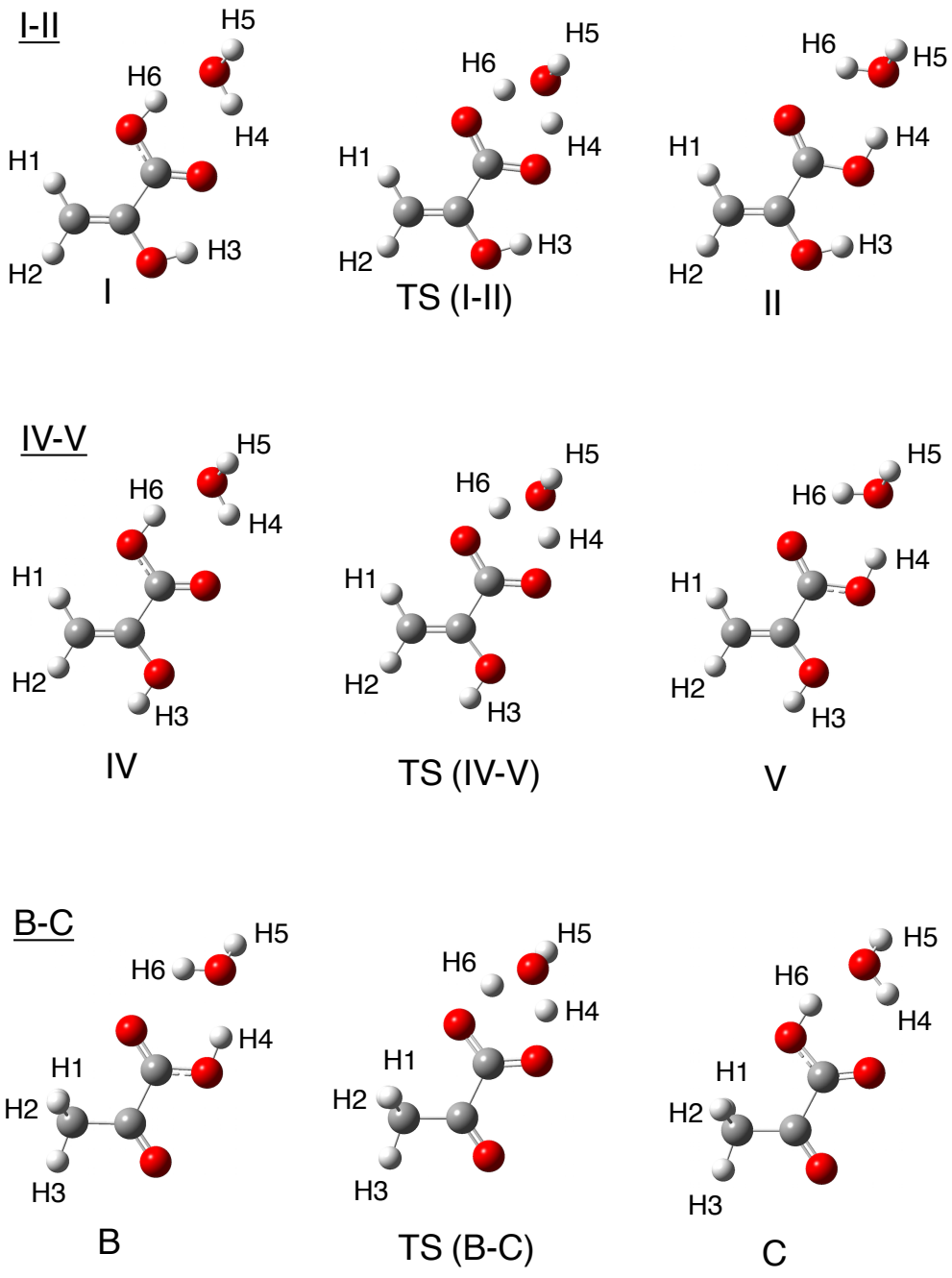


Figure S5. Optimized structures of reactant, transition state, and product systems of mono hydrated isomerization reactions obtained by B3LYP/6-311++G(d,p) calculations.

Keto-enol tautomerism reactions

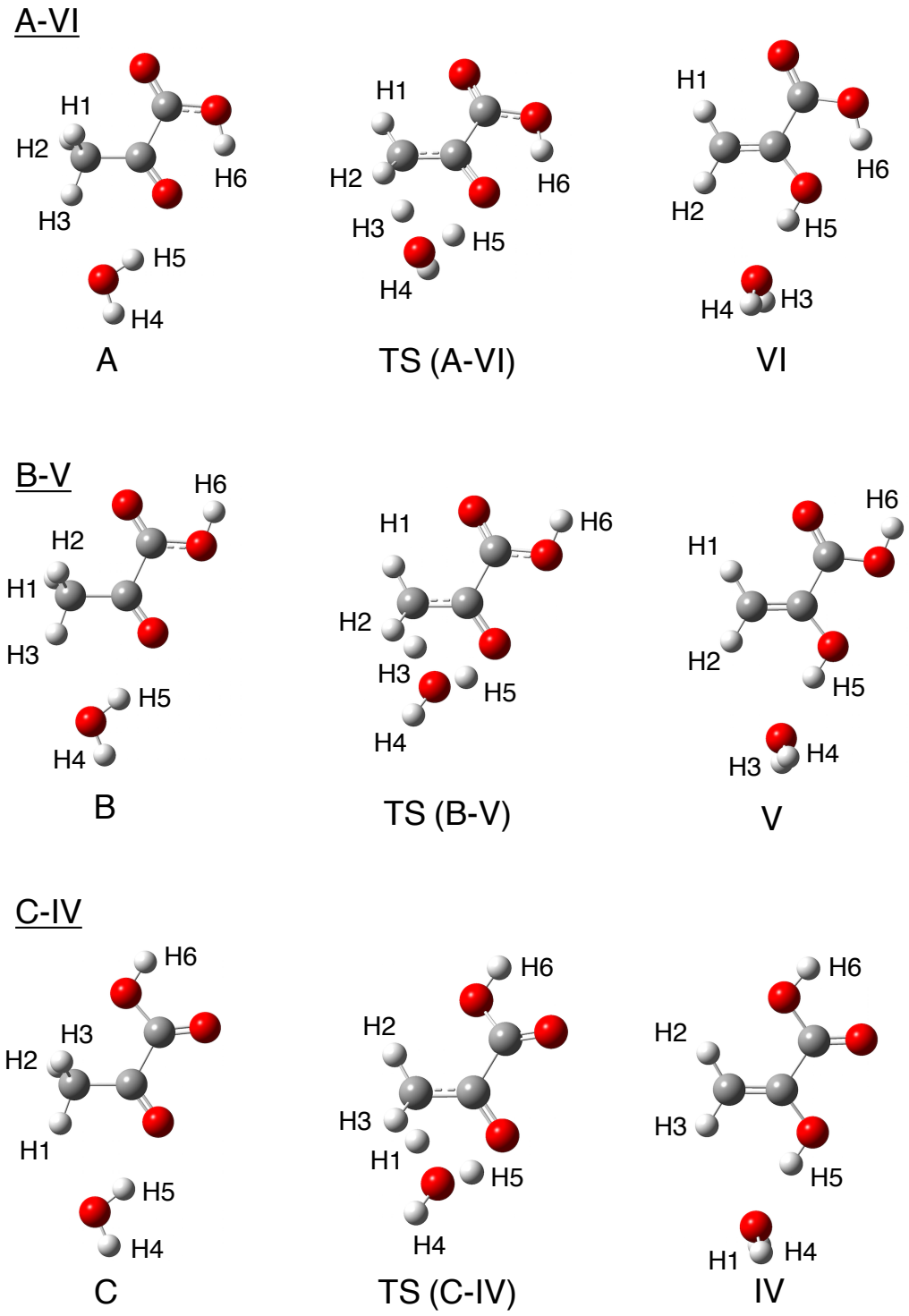


Figure S6. Optimized structures of reactant, transition state, and product systems of mono hydrated keto-enol tautomerism reactions obtained by B3LYP/6-311++G(d,p) calculations.

Table S1. Optimized exponent α (α_{opt}) values of quantum protons and deuterons in reactant molecule of isomerization and keto-enol tautomerism reactions catalyzed by a single water molecule optimized by MC_B3LYP/6-311++G(d,p) method.

	α_{opt} values for H species						α_{opt} values for D species					
	H1	H2	H3	H4	H5	H6	D1	D2	D3	D4	D5	D6
I-II	24.1	24.1	23.1	22.7	23.5	21.7	35.8	35.7	34.3	33.8	34.9	32.5
IV-V	24.1	24.2	23.6	22.5	23.5	21.8	35.7	35.8	35.0	33.7	34.9	32.7
B-C	24.0	24.0	24.2	21.7	23.5	22.7	35.6	35.6	35.9	32.5	34.9	33.9
A-VI	23.9	23.9	24.0	23.7	23.1	22.9	35.4	35.4	35.5	35.2	34.4	34.0
B-V	23.9	24.0	23.9	23.8	23.1	23.2	35.5	35.6	35.5	35.2	34.3	34.5
C-IV	23.9	24.0	24.0	23.8	23.1	23.2	35.5	35.5	35.6	35.2	34.3	34.4

Table S2. Optimized exponent α (α_{opt}) values of quantum protons and deuterons in product molecule of isomerization and keto-enol tautomerism reactions catalyzed by a single water molecule optimized by MC_B3LYP/6-311++G(d,p) method.

	α_{opt} values for H species						α_{opt} values for D species					
	H1	H2	H3	H4	H5	H6	D1	D2	D3	D4	D5	D6
I-II	24.1	24.1	23.2	21.5	23.5	22.6	35.7	35.8	34.5	32.3	34.9	33.7
IV-V	24.1	24.2	23.6	21.8	23.5	22.6	35.6	35.8	35.0	32.7	34.9	33.7
B-C	24.0	24.0	24.2	22.7	23.5	21.7	35.6	35.6	35.9	33.8	34.9	32.5
A-VI	24.1	24.2	23.4	23.4	22.3	23.0	35.6	35.8	34.8	34.8	33.3	34.3
B-V	24.1	24.2	23.4	23.4	22.6	23.3	35.7	35.8	34.8	34.8	33.7	34.6
C-IV	24.2	24.2	23.4	23.4	22.7	23.3	35.8	35.8	34.8	34.8	33.7	34.6