

Supporting Information for:
"Theoretical Studies of the Hydroxide-Catalyzed P-O
Cleavage Reactions of Neutral Phosphate Triesters and
Diesters in Aqueous Solution: Examination of the Changes
Induced by H/Me Substitution."

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Figure S1. Solution phase optimized structures of reactant and product states involved in the reaction of OH⁻ with TMP, DMNPP, DMHP, and DMP⁻.

Table S1. Selected Bond Lengths (in Å) and Valence Angles (in degrees) for Some Solution Phase Optimized Reactants and Products Involved in the Reaction of OH⁻ with TMP, DMNPP, DMHP, and DMP⁻.

Figures S2a-e. Enthalpy profiles in aqueous solution obtained from MPE geometry optimizations for the reaction shown in Scheme 1. Open symbols indicate fully optimized species.

Figure S3. Enthalpy profile in aqueous solution obtained from MPE geometry optimizations for the reaction shown in Scheme 2. Open diamonds indicate fully optimized species.

Figures S4a-b. Enthalpy profiles in aqueous solution obtained from MPE geometry optimizations for the reaction shown in Scheme 3. Open diamonds indicate fully optimized species.

Figure S5. Enthalpy profile in aqueous solution obtained from MPE geometry optimizations for the reaction shown in Scheme 4. Open symbols indicate fully optimized species.

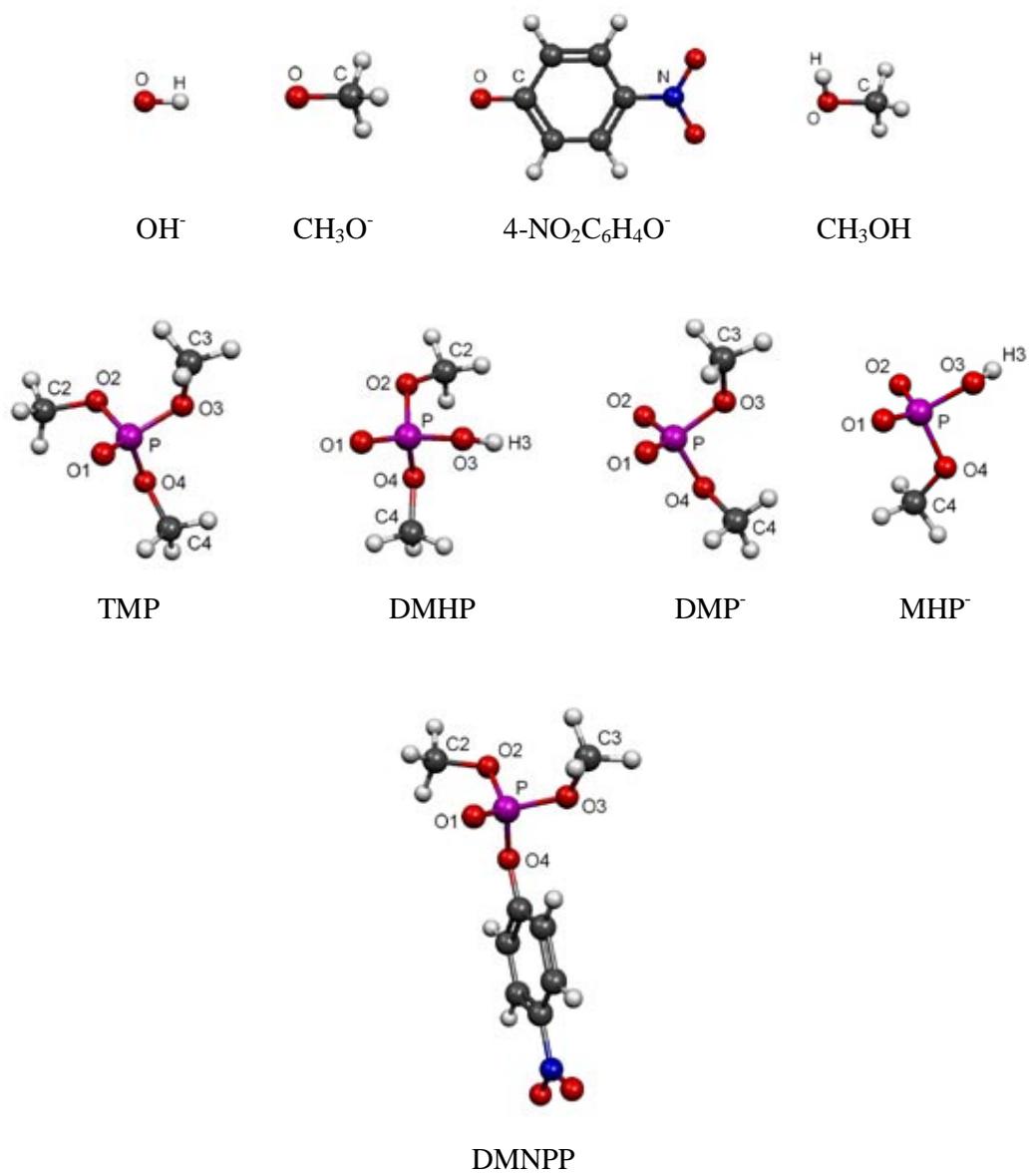


Figure S1

Table S1. Selected Bond Lengths (in Å) and Valence Angles (in degrees) for Some Solution Phase Optimized Reactants and Products Involved in the Reaction of OH⁻ with TMP, DMNPP, DMHP, and DMP^a

	TMP	DMHP	DMNPP	DMP ⁻	MHP ⁻
P-O1	1.489	1.484	1.485	1.514	1.512
P-O2	1.600	1.594	1.590	1.514	1.514
P-O3	1.600	1.616	1.591	1.653	1.650
P-O4	1.600	1.600	1.629	1.643	1.653
O1-P-O2	115.9	112.5	116.9	120.3	120.6
O2-P-O3	102.4	108.0	103.3	109.9	109.8
O3-P-O4	102.4	106.0	101.3	98.3	97.9
O4-P-O1	115.9	117.6	114.9	111.1	110.1

^a The corresponding optimized structures are shown in Figure S1.

Table S1

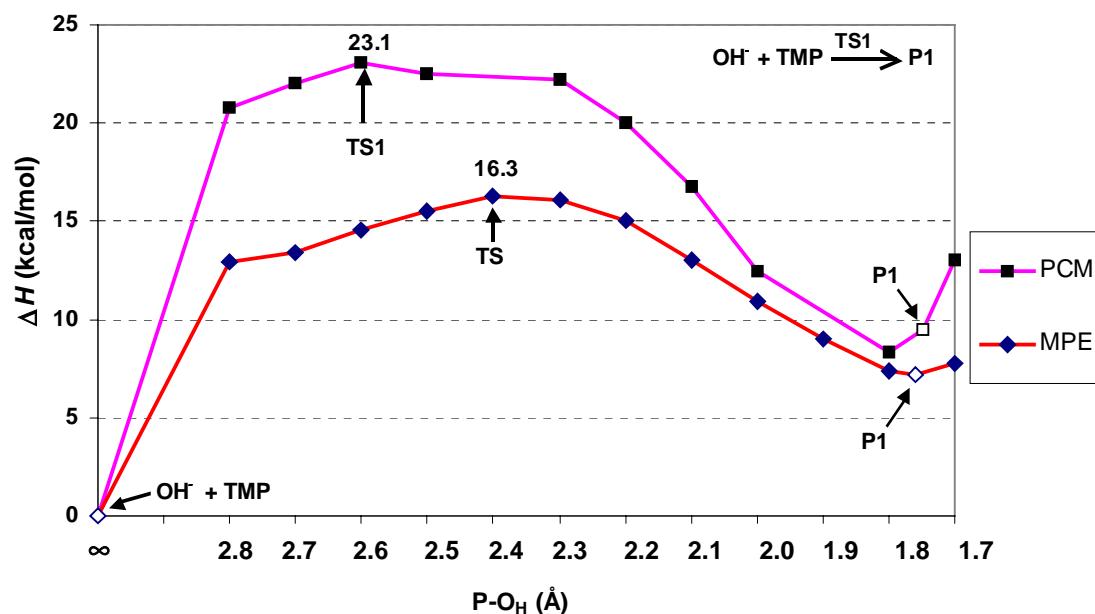


Figure S2a

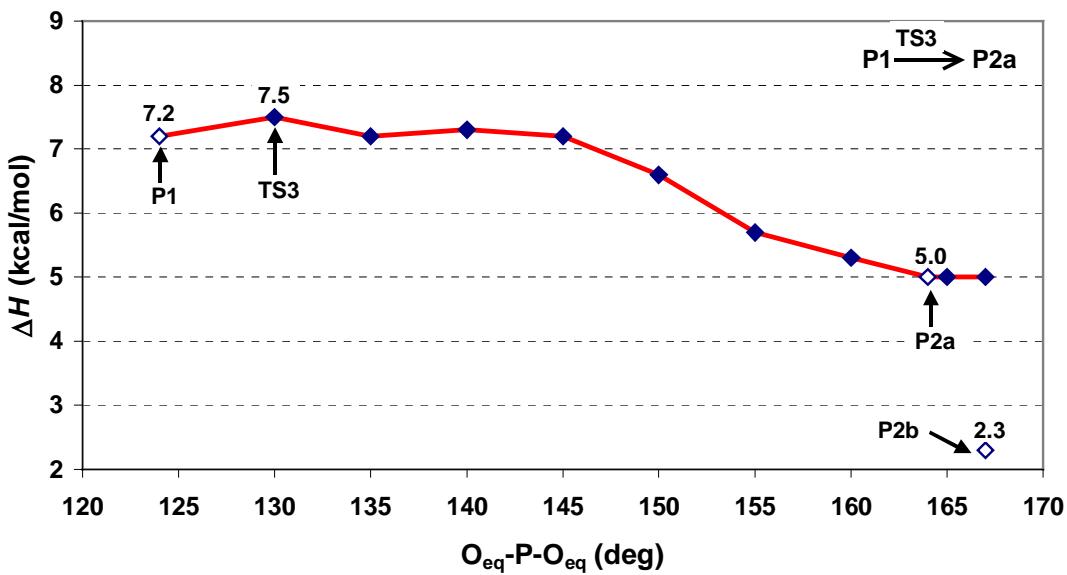


Figure S2b

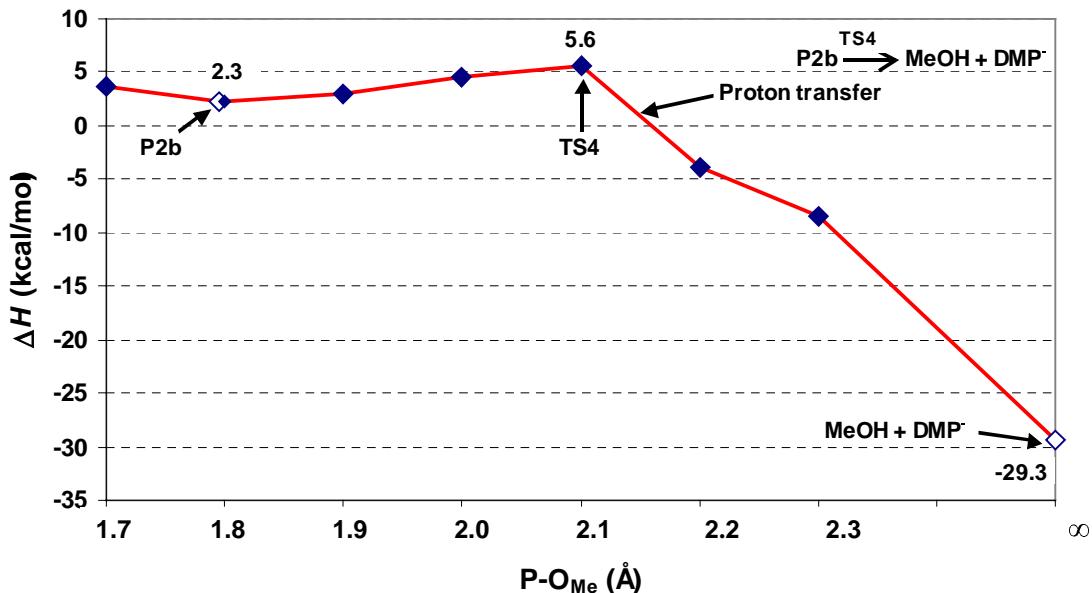


Figure S2c

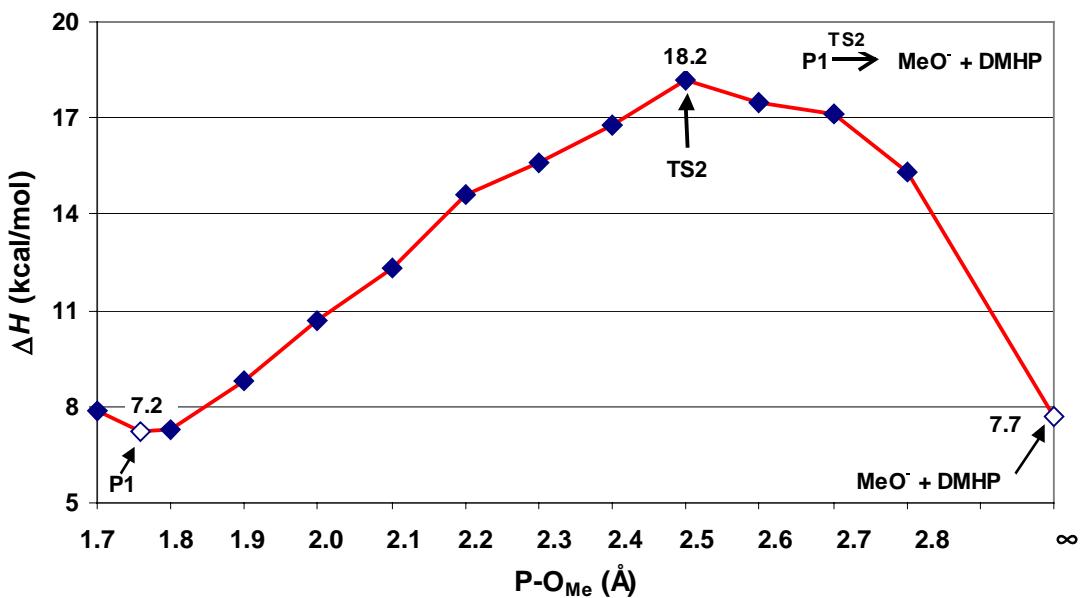


Figure S2d

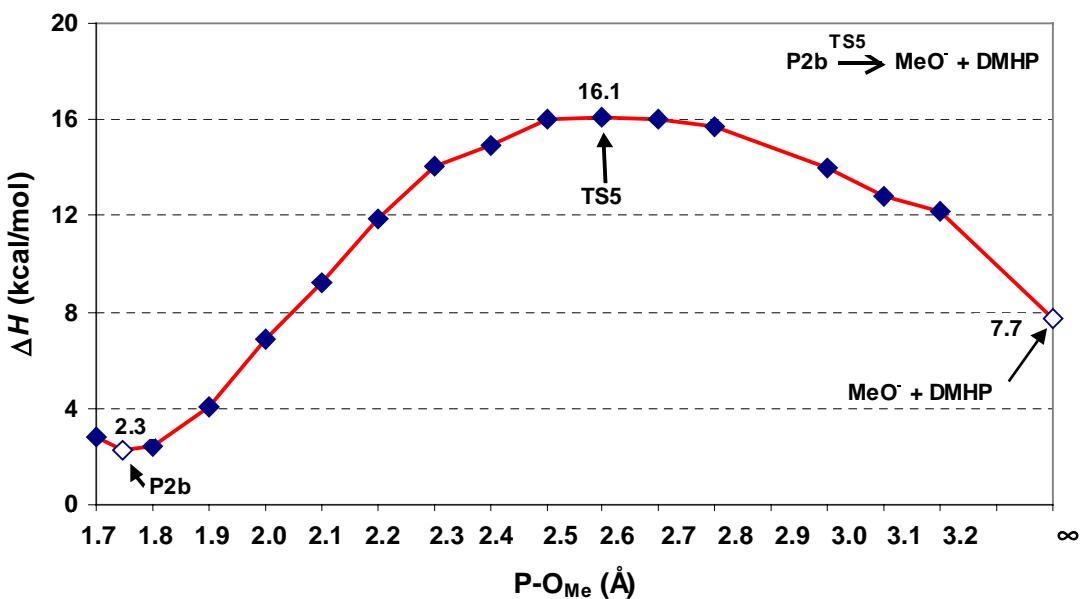


Figure S2e

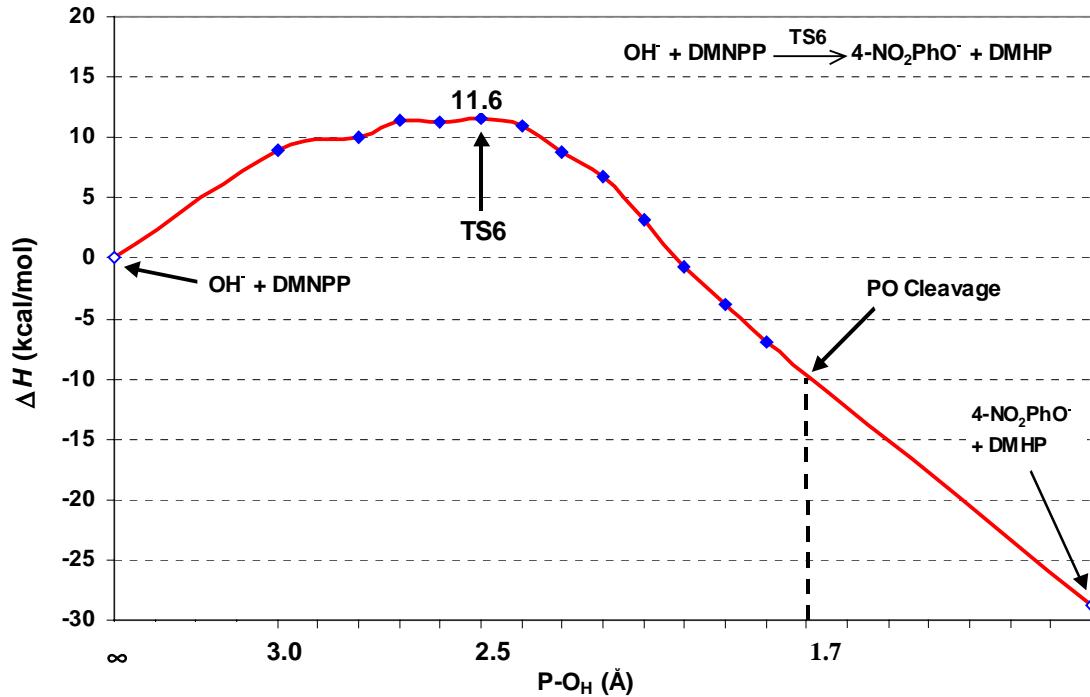


Figure S3

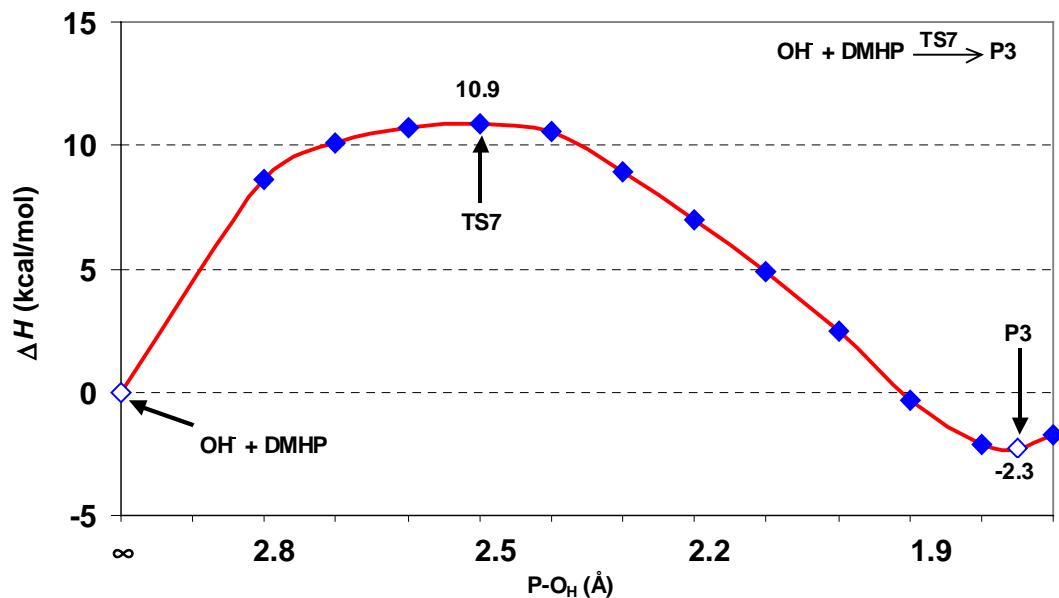


Figure S4a

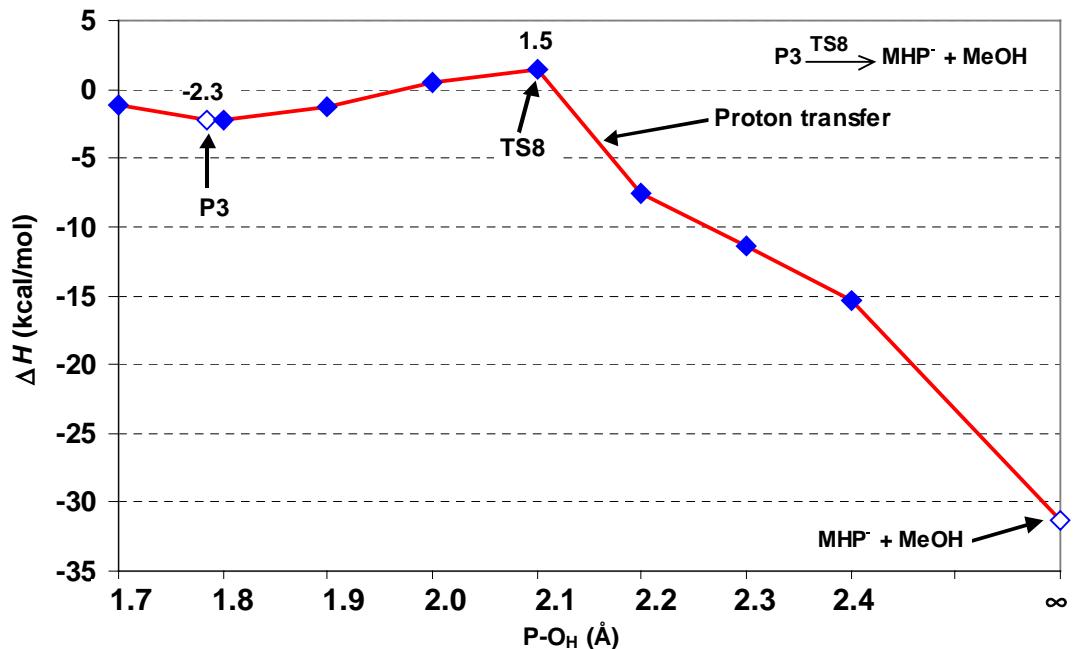


Figure S4b

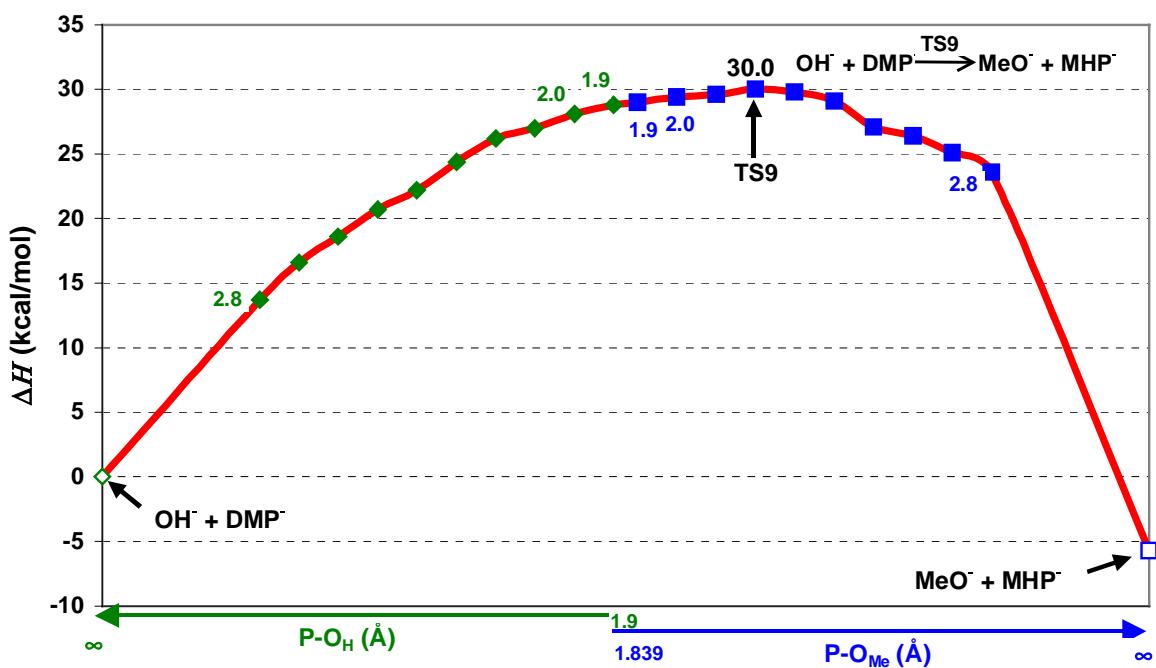


Figure S5