Electronic Supplementary Material for

Synthetic Efficiency in Enzyme Mechanisms Involving Carbocations: Aristolochene Synthase

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Tables

Table S1. Calculated free energy changes (ΔG) in kcal/mol at 298 K. No adjustments were made to the low energy vibrational modes.

Theory	**2 → TS1**	**TS1 → 3**	**3 → TS2**	**TS2 → 5**
AM1	18.5	-15.1	28.3	-47.0
PM3	17.7	-14.0	18.9	-37.2
mPW1PW	8.7	-4.5	25.6	-54.4
MPWB1K	9.5	-8.8	26.1	-59.0

Table S2. Calculated electronic energies (including nucar repulsion) in kcal/mol.

Theory	**2 →TS1**	**TS1→3**	**3 →TS2**	**TS2 →5**
AM1	11.4	-15.5	28.0	-49.8
PM3	11.5	-13.1	20.0	-39.6
mPW1PW	5.	-5.4	24.3	-58.3
MPWB1K	5.1	-8.9	26.1	-51.5
MP2[a]	4.2	-5.7	23.4	-60.4

[a] Determined by single-point energy calculations using theMPWB1K optimized structures. The 6-31+G(d,p) basis set is used in all computations.

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