Supplementary Materials: New Mechanistic Insights into the Claisen Rearrangement of Chorismate - A Unified Reaction Valley Approach Study

Marek Freindorf, Yuwen Tao, Daniel Sethio, Dieter Cremer,† Elfi Kraka[a]

[a] Computational and Theoretical Chemistry Group (CATCO), Department of Chemistry, Southern Methodist University, 3215 Daniel Ave, Dallas, Texas 75275-0314, USA

ARTICLE HISTORY
Compiled August 12, 2018

Contents

† In memoriam

1. Puckering parameters

For 6-membered rings the puckering analysis is based on the puckering amplitudes q_2 and q_3, the pseudo-rotation phase angle Φ_2, the hyperspherical angle Θ, and the total puckering amplitude Q. These parameters can be divided into the pseudo-rotational coordinate pair (q_2, Φ_2) describing the pseudo-rotation of boat and twistboat forms, and the crown puckering amplitude q_3, which describes the chair conformer. According to the Cremer-Pople puckering model, the percentage of the chair, boat, and twist-boat are derived from the formulas:

$$Chair : 100\% \ \frac{{q_3}^2}{Q^2}$$

$$Boat : 100\% \ \frac{{q_2}^2}{Q^2} cos^2(3\Phi_2)$$

$$TwistBoat : 100\% \ [1 - cos^2(3\Phi_2)] \frac{{q_2}^2}{Q^2}$$

2. Figure S1

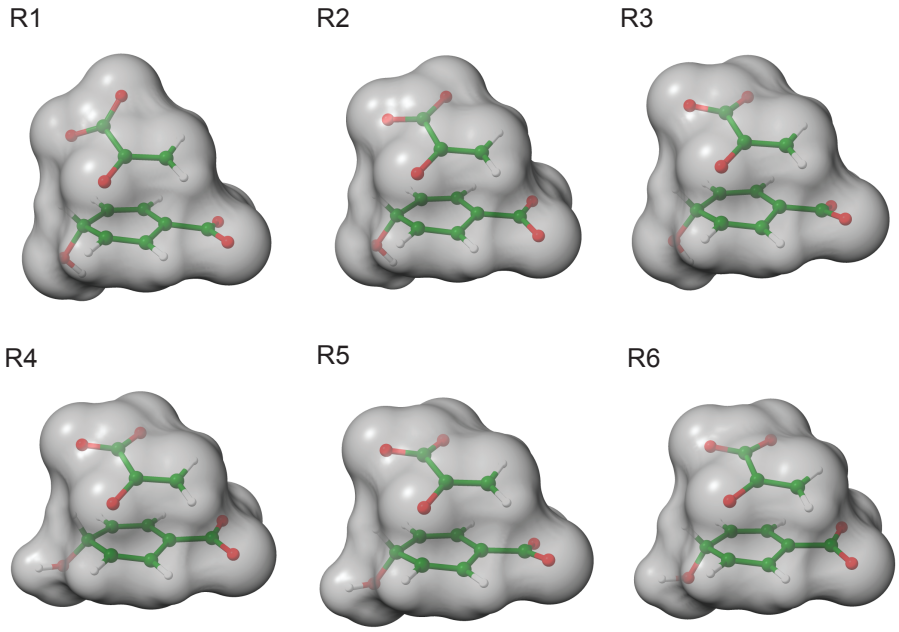


Figure S1. Connolly surface of TS for the reactions **R1** - **R6**.

3. Figure S2

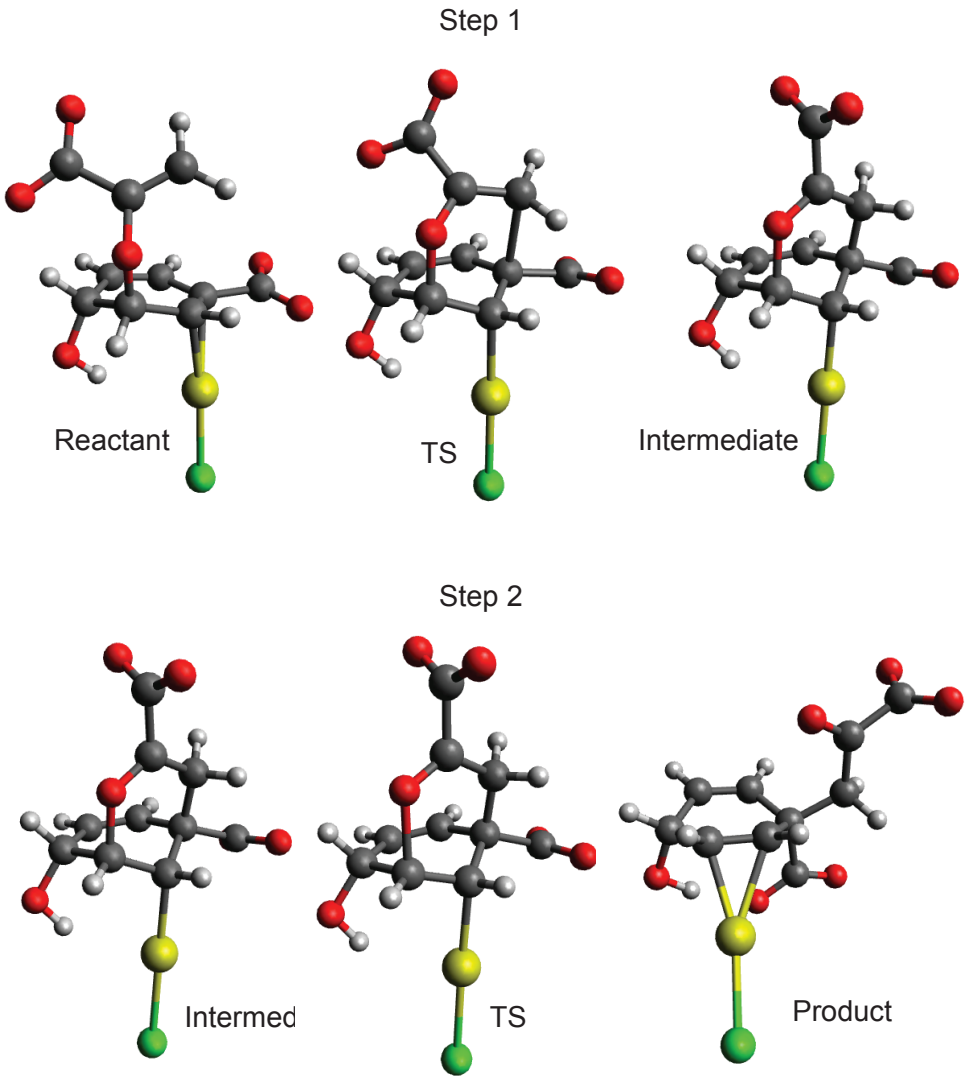
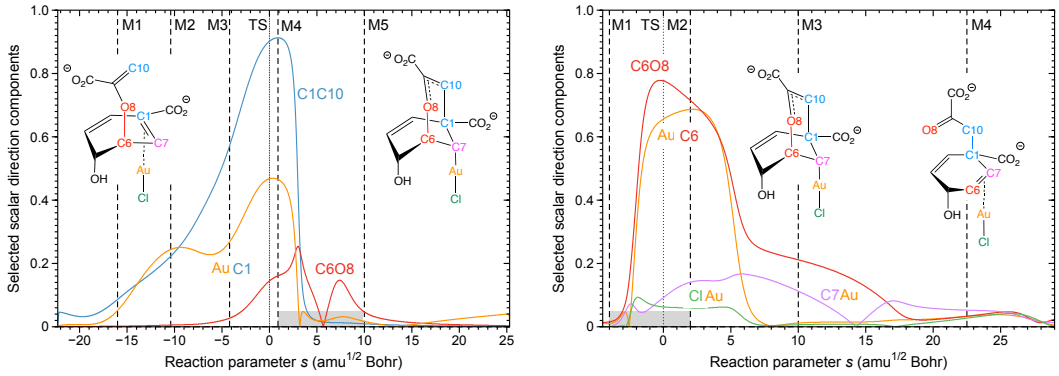


Figure S2. The reactant, intermediate, and TS of the reaction **R7** for Step 1 and Step 2.

4. Figure S3



(a) Step 1 (b) Step 2

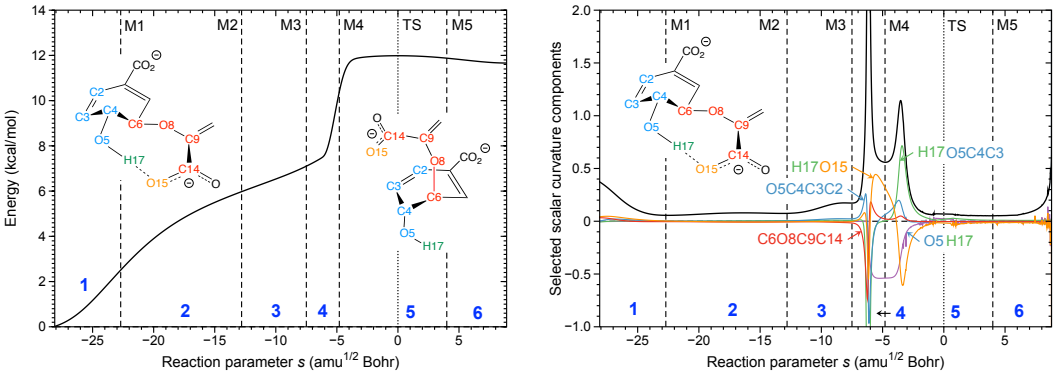
Figure S3. Components of the unit reaction path direction vector $\boldsymbol{\eta}$(s) as a function of the reaction path parameter s for the reactions **R7**. The borders of the reaction phases are indicated by vertical dashed lines at curvature points M1, M2, M3, etc. The TS at $s = 0$ amu$^{1/2}$ Bohr is also indicated by a vertical dotted line.

5. Table T1

Table S1. Puckering parameters of the pyran ring and the hexadienyl ring for Step 1 and Step 2 of the Au(I) catalyzed reaction **R7**.

Reaction	q_2 (Å)	q_3 (Å)	ϕ_2 (Deg)	Q (Å)	Chair (%)	Boat (%)	Tboat (%)
			Pyran Ring				
Chorismate	0.155	-0.734	308	0.75	95.7	3.6	0.6
TS1	0.261	-0.621	299	0.674	85	14.9	0.1
Intermediate	0.415	-0.364	341	0.552	43.4	16.6	40
TS2	0.425	-0.363	339.5	0.56	42	13.2	44.7
Prephenate	0.448	-0.378	334	0.586	41.6	2.5	56
			Cyclohexadienyl Ring				
Chorismate	0.193	0.132	150	0.234	32.1	0	67.9
TS1	0.331	0.26	84	0.42	38.1	6.7	55.2
Intermediate	0.395	0.306	66	0.5	37.6	55.8	6.7
TS2	0.343	0.231	57	0.414	31.1	66.7	2.2
Prephenate	0.411	0.008	182	0.411	0	98.8	1.2

6. Figure S4



(a) Step 1 (b) Step 2

Figure S4. **(a)** Energy profile, and **(b)** decomposition of the curvature into components as a function of the reaction parameter s for the reaction **1a** $\rightarrow$ **1b**. The borders of the reaction phases are indicated by vertical dashed lines at curvature points M1, M2, M3, etc. The TS at $s = 0$ amu$^{1/2}$ Bohr is also indicated by a vertical dotted line.