SUPPORTING INFORMATION

Mechanism of the Swern Oxidation: Significant Deviations from Transition State Theory

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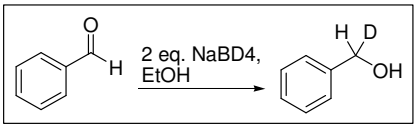
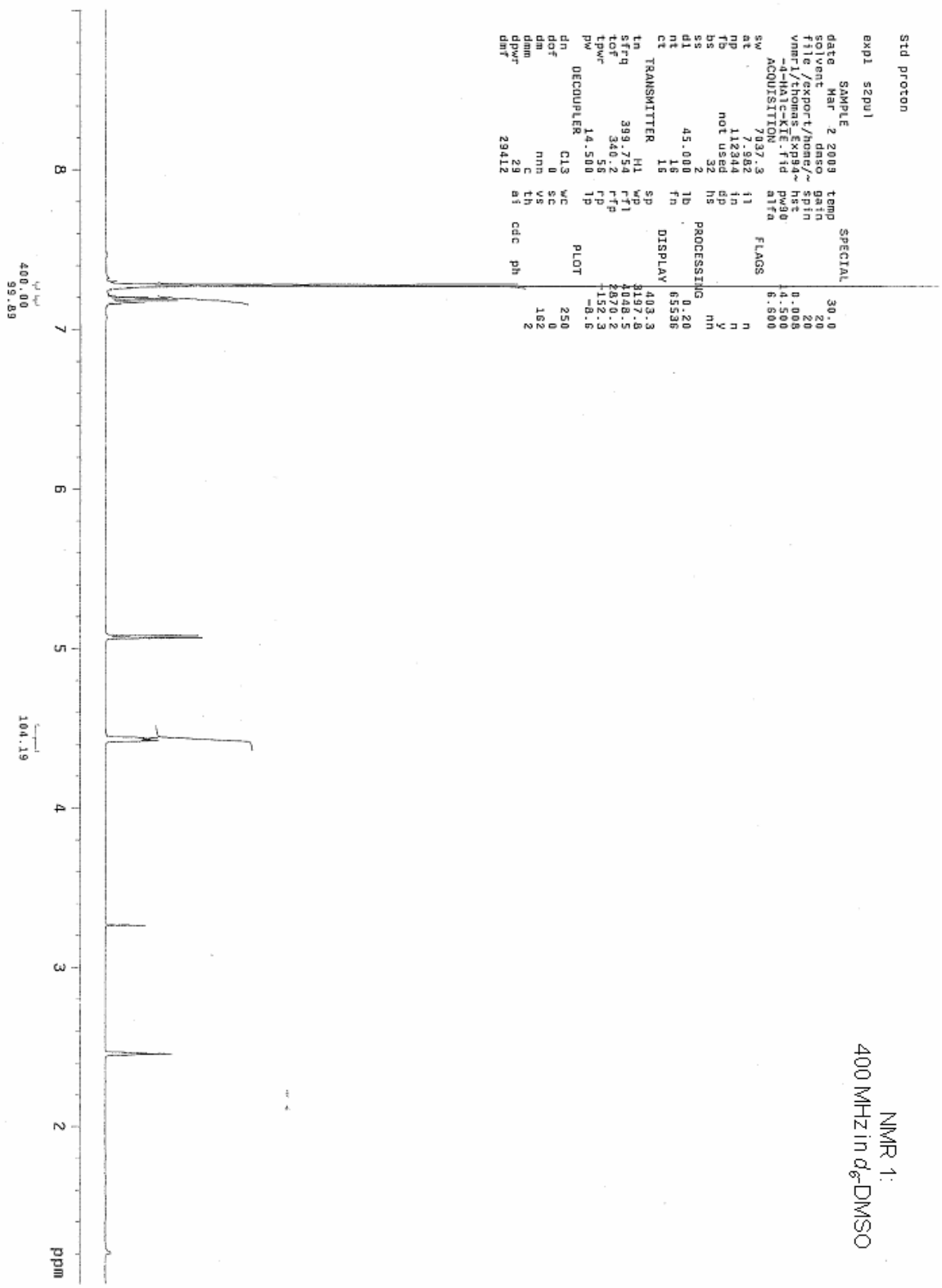


Synthesis of d_1-Benzyl Alcohol

A 500 mL Erlenmeyer flask with a 2" stir bar was charged with ethanol (200 mL, 3.43 mol) and benzaldehyde (10.9 g, 103.0 mmol). Sodium borodeuteride (2.2 g, 51.5 mmol) was added slowly in approximately 0.25 g portions to maintain the temperature at approximately 10 °C above room temperature. The resulting suspension was stirred for 2.0 hours at ambient temperature. The reaction was worked up by first dissolving the reaction in 1.5 volumes (300 mL) of ice water followed by extraction with 5×50 mL of diethyl ether. The collected organic layers were dried with $NaSO_4$ and filtered. The diethyl ether was removed using rotary evaporation to provide a clear liquid. The content was purified 1.5" (250 mL) column using 260-400 mesh silica as a stationary phase and 70:30 (hexanes:diethyl ether) mixture as the mobile phase.

^{1}H NMR (400MHz, d_6-DMSO): Spectrum 1



NMR 1:
400 MHz in d_6-DMSO

Procedure for Measuring Intramolecular ^{2}H KIEs

Intramolecular Competition Reaction. To a dried and purged 2-neck 50 mL RBF with a 3/4" stir bar, anhydrous dichloromethane (20.0 mL) and oxalyl chloride (1.2 mL, 1.7 g, 13.5 mmol) were added at ambient temperature. The flask was then placed in dry ice/acetone bath for 15 minutes to allow thermal equilibration to the bath temperature. Dimethyl sulfoxide (DMSO) (1.2 mL, 1.3 g, 16.2 mmol) was added via a 2 mL gastight syringe to the oxallyl chloride solution dropwise over a 2 minute period. After completing the addition and waiting for 10 minutes, d_1-benzyl alcohol (1.2 mL, 1.3 g, 9.0 mmol) was added to the reaction mixture in a dropwise fashion over a 2 minute period. The reaction mixture was stirred at -78 °C for 30 minutes after complete addition of the alcohol. Triethylamine (12.5 mL, 9.1 g, 90.3 mmol) was then added to the reaction mixture dropwise over a 10 minute period. The reaction was stirred for 30 minutes while maintaining a reaction temperature of -78 °C. The reaction was then quenched at -78°C with methanol (1.83 mL, 1.5 g, 45.1 mmol). After completing the dropwise addition of methanol to the reaction mixture and stirring the reaction for an additional 30 minutes at -78 °C, the reaction was allowed to come to room temperature. Once the reaction mixture reached room temperature, water (1.6 mL, 1.6 g, 90.3 mmol) was added to the reaction. The aqueous layer was removed, and the dichloromethane layer was dried using Na_2SO_4. Dichloromethane was removed using rotary evaporation at reduced temperature (10 °C) to provide a clear colorless liquid. The benzaldehyde isotopologs were purified using a flash chromatography using a 1.5" diameter column packed to a height of 12" of silica gel. The mobile phase to run the flash chromatography with was a mixture of ethyl ether and hexanes in 30:70 ratio. All fractions containing benzaldehyde were collected to obviate the possibility of spurious fractionation resulting from the separation process. Reactions performed at -63 °C, -47 °C, and -23 °C were equilibrated with slush baths of the following solvents: chloroform, *m*-xylene, and carbon tetrachloride but were otherwise carried out in an identical fashion to the experiments performed at -78 °C.

NMR Measurement and Calculation. Approximately 50 mg of sample was dissolved in 0.75 mL of d_6-DMSO and filled to the 5.0 cm mark in a standard 5 mm NMR tube. ^{1}H NMR spectra were recorded at 399.754 MHz on a Varian Unity 400 MHz NMR using a sweep width of 6419 Hz. A calibrated 90° pulse width and an acquisition time of 8.00 s were used to collect a total of 74442 points. A delay of 50.0 s (approximately 10 times the duration of the T_1 value for the longest relaxing peak) was used to ensure quantitative relative ^{1}H measurement. The *ortho*-aromatic and aldehydic peaks were integrated separately using an integration cut that achieved slightly greater (0.05 ppm) than full width integration. The *ortho*-aromatic peaks were assigned an integration of 200. A total of 8 integrated spectra are used to estimate the integrations of the benzyl peak on the reactant and the aldehydic peak on the product. The error associated with the KIE is reported as the standard deviation computed from the average integrations from five or six experiments. The relative integration of the aldehydic peak was corrected for contamination resulting from benzaldehyde produced from the oxidation of benzyl alcohol, which resulted from protium contamination of the deuteride source, $NaBD_4$.

Raw Data from Intramolecular ^{2}H KIE Experiments

Table S1. ^{1}H integrations and computed intramolecular ^{2}H KIEs at -78 °C resulting in a sample average value of 2.82 ± 0.06.

Stock d_1-Benzyl Alcohol for Experiments 1-5										
Benzyl Alcohol Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
benzylic	103.20	103.71	102.89	103.10	103.09	103.64	103.19	103.00	103.23	0.29
para-aromatic	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	0.00
Experiment 1 (Product Aldehyde): k_H/k_D = 2.72										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	28.35	28.37	28.33	28.36	28.33	28.33	28.33	28.33	28.34	0.02
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Experiment 2 (Product Aldehyde) : k_H/k_D = 2.82										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	27.69	27.69	27.63	27.70	27.70	27.70	27.74	27.73	27.70	0.04
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Experiment 3 (Product Aldehyde) : k_H/k_D = 2.83										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	27.72	27.69	27.65	27.66	27.64	27.61	27.67	27.56	27.65	0.05
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Experiment 4 (Product Aldehyde) : k_H/k_D = 2.88										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	27.31	27.36	27.32	27.34	27.30	27.31	27.29	27.33	27.32	0.02
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Experiment 5 (Product Aldehyde) : k_H/k_D = 2.84										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	27.55	27.60	27.58	27.56	27.56	27.57	27.55	27.55	27.57	0.02
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00

Table S2. ^{1}H integrations and computed intramolecular ^{2}H KIEs at -63 °C resulting in a sample average value of 2.37 ± 0.05.

Stock *d*$_1$-Benzyl Alcohol for Experiment 1										
Benzyl Alcohol Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
benzylic	103.20	103.71	102.89	103.10	103.09	103.64	103.19	103.00	103.23	0.29
para-aromatic	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	0.00
Experiment 1 (Product Aldehyde): k_H/k_D = 2.38										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	30.89	31.05	30.93	30.92	31.06	30.85	30.92	30.85	30.93	0.08
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Stock *d*$_1$-Benzyl Alcohol for Experiments 2-6										
Benzyl Alcohol Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
benzylic	101.26	101.33	101.27	101.37	101.28	101.20	101.38	101.26	101.29	0.06
para-aromatic	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	0.00
Experiment 2 (Product Aldehyde) : k_H/k_D = 2.43										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	29.86	29.80	29.76	29.69	29.65	29.54	29.52	29.49	29.66	0.14
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Experiment 3 (Product Aldehyde) : k_H/k_D = 2.32										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	30.78	30.73	30.73	30.69	30.66	30.70	30.58	30.55	30.68	0.08
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Experiment 4 (Product Aldehyde) : k_H/k_D = 2.39										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	29.98	30.02	30.05	30.05	30.03	30.05	30.02	30.02	20.03	0.02
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Experiment 5 (Product Aldehyde) : k_H/k_D = 2.32										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	30.79	30.76	30.69	30.71	30.61	30.62	30.60	30.55	30.67	0.08
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Experiment 6 (Product Aldehyde) : k_H/k_D = 2.40										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	30.04	30.02	29.97	29.98	29.94	29.91	N/A	29.78	29.95	0.09
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00

Table S3. ^{1}H integrations and computed intramolecular ^{2}H KIEs at -47 °C resulting in a sample average value of 2.22 ± 0.02.

Stock *d*$_1$-Benzyl Alcohol for Experiment 1										
Benzyl Alcohol Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
benzylic	100.83	100.67	100.81	100.82	100.78	100.76	100.75	100.78	100.78	0.05
para-aromatic	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	0.00
Experiment 1 (Product Aldehyde): k_H/k_D = 2.23										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	31.23	31.23	31.21	31.26	31.20	31.24	31.27	31.27	31.24	0.03
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Stock *d*$_1$-Benzyl Alcohol for Experiments 2-6										
Benzyl Alcohol Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
benzylic	101.26	101.33	101.27	101.37	101.28	101.20	101.38	101.26	101.29	0.06
para-aromatic	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	0.00
Experiment 2 (Product Aldehyde) : k_H/k_D = 2.21										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	31.62	31.62	31.63	31.64	31.64	31.63	N/A	31.61	31.63	0.01
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Experiment 3 (Product Aldehyde) : k_H/k_D = 2.25										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	31.65	31.63	31.62	31.64	31.66	31.64	31.61	31.68	31.64	0.01
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Experiment 4 (Product Aldehyde) : k_H/k_D = 2.21										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	31.24	31.25	31.22	31.26	31.25	31.24	31.23	31.22	31.24	0.02
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Experiment 5 (Product Aldehyde) : k_H/k_D = 2.19										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	31.86	31.90	31.81	31.88	31.87	31.80	31.77	31.70	31.82	0.07
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00

Table S4. ^{1}H integrations and computed intramolecular ^{2}H KIEs at -23 °C resulting in a sample average value of 2.08 ± 0.07.

Stock d_1-Benzyl Alcohol for Experiment 1										
Benzyl Alcohol Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
benzylic	100.83	100.67	100.81	100.82	100.78	100.76	100.75	100.78	100.78	0.05
para-aromatic	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	0.00
Experiment 1 (Product Aldehyde): k_H/k_D = 2.19										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	31.69	31.72	31.57	31.58	31.51	31.57	31.64	61.59	31.61	0.07
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Stock d_1-Benzyl Alcohol for Experiments 2-5										
Benzyl Alcohol Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
benzylic	100.32	100.30	100.29	100.23	100.26	100.27	100.25	100.31	100.28	0.03
para-aromatic	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	0.00
Experiment 2 (Product Aldehyde) : k_H/k_D = 2.02										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	33.28	33.25	33.25	33.19	33.19	33.19	33.20	33.16	33.21	0.04
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Experiment 3 (Product Aldehyde) : k_H/k_D = 2.09										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	32.41	32.43	32.46	32.46	32.48	32.46	32.47	32.45	32.45	0.02
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Experiment 4 (Product Aldehyde) : k_H/k_D = 2.03										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	33.14	33.17	33.14	33.15	33.12	33.12	33.09	33.09	33.13	0.03
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00
Experiment 5 (Product Aldehyde) : k_H/k_D = 2.06										
Benzaldehyde Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Ave.**	**Std. Dev.**
aldehydic	32.83	32.81	32.79	32.81	32.81	32.80	32.82	32.88	32.82	0.03
ortho-aromatic	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	0.00

Derivation of Equations

Eq. 1 is obvious by inspection under the assumption of facile inversion:

$$KIE_{Intra} = \frac{[\mathbf{4}]}{[\mathbf{5}]} = \frac{k_2 + k_4}{k_1 + k_3}$$

Eq. 2, which is an expression of the observed intramolecular KIE under the assumption of forbidden inversion of the ylide, is somewhat non-intuitive. We consider the four rate constants that describe the intramolecular KIE derived from the oxidation of (*S*)-d_1-benzyl alcohol (Scheme 3). An equivalent situation is operative for the oxidation of (*R*)-d_1-benzyl alcohol. We start from the definition of the observed KIE:

$KIE_{Intra} = \frac{[\mathbf{4}]}{[\mathbf{5}]} = \frac{[\mathbf{4}]_R + [\mathbf{4}]_S}{[\mathbf{5}]_R + [\mathbf{5}]_S}$, where $[\mathbf{4}]_R$ is *d*-benzaldehyde derived from the ylide with an *R*-configuration (**2**) about the sulfur atom; all other symbols are analogous. We assume that the amount of **2** and **3** formed is equivalent and independent of the label at the benzylic position, i.e. $[\mathbf{4}]_R + [\mathbf{5}]_R = [\mathbf{4}]_S + [\mathbf{5}]_S$.

Consider the ratios of rates for formation of **4** and **5** from **2** and **3**.

$$\frac{[\mathbf{4}]_R}{[\mathbf{5}]_R} = \frac{k_4}{k_1} \text{ and } \frac{[\mathbf{4}]_S}{[\mathbf{5}]_S} = \frac{k_2}{k_3}$$

Addition of 1 to each side of each equation yields:

$$\frac{[\mathbf{4}]_R + [\mathbf{5}]_R}{[\mathbf{5}]_R} = \frac{k_1 + k_4}{k_1} \text{ and } \frac{[\mathbf{4}]_S + [\mathbf{5}]_S}{[\mathbf{5}]_S} = \frac{k_3 + k_2}{k_3}$$

By our assumption of the equal formation of **2** and **3**:

$$\frac{k_3 + k_2}{k_3} = \frac{[\mathbf{4}]_R + [\mathbf{5}]_R}{[\mathbf{5}]_S}$$

Inversion yields:

$$\frac{[\mathbf{5}]_R}{[\mathbf{4}]_R + [\mathbf{5}]_R} = \frac{k_1}{k_1 + k_4} \text{ and } \frac{[\mathbf{5}]_S}{[\mathbf{4}]_R + [\mathbf{5}]_R} = \frac{k_3}{k_2 + k_3}$$

By similar manipulations:

$$\frac{[\mathbf{4}]_R}{[\mathbf{4}]_R + [\mathbf{5}]_R} = \frac{k_4}{k_1 + k_4} \text{ and } \frac{[\mathbf{4}]_S}{[\mathbf{4}]_S + [\mathbf{5}]_S} = \frac{k_2}{k_2 + k_3} = \frac{[\mathbf{4}]_S}{[\mathbf{4}]_R + [\mathbf{5}]_R}$$

Collecting over a common denominator:

$$\frac{[\mathbf{5}]_R + [\mathbf{5}]_S}{[\mathbf{4}]_R + [\mathbf{5}]_R} = \frac{k_1}{k_1 + k_4} + \frac{k_3}{k_3 + k_2} \text{ and } \frac{[\mathbf{4}]_R + [\mathbf{4}]_S}{[\mathbf{4}]_R + [\mathbf{5}]_R} = \frac{k_4}{k_1 + k_4} + \frac{k_2}{k_3 + k_2}$$

Taking the ratio to yield the observed intramolecular KIE:

$$KIE_{Intra} = \frac{[\mathbf{4}]_R + [\mathbf{4}]_S}{[\mathbf{5}]_R + [\mathbf{5}]_S} = \frac{\dfrac{k_4}{k_1 + k_4} + \dfrac{k_2}{k_3 + k_2}}{\dfrac{k_1}{k_1 + k_4} + \dfrac{k_3}{k_3 + k_2}} = \frac{k_1k_2 + \mathbf{2}k_2k_4 + k_3k_4}{k_1k_2 + \mathbf{2}k_1k_3 + k_3k_4}$$

Eq. 3 is the expression of the intramolecular KIE under the assumption of facile inversion as a function of the primary and secondary KIEs as computed from the *exo*-**TS1** and *endo*-**TS1** transition structures. This expression is arrived at by manipulating **Eq. 1**:

$$KIE_{Intra} = \frac{[\mathbf{4}]}{[\mathbf{5}]} = \frac{k_2 + k_4}{k_1 + k_3} = \frac{\dfrac{k_2}{k_{exo}^{H,H}} + \dfrac{k_4}{k_{endo}^{H,H}}\dfrac{k_{endo}^{H,H}}{k_{exo}^{H,H}}}{\dfrac{k_1}{k_{exo}^{H,H}} + \dfrac{k_3}{k_{endo}^{H,H}}\dfrac{k_{endo}^{H,H}}{k_{exo}^{H,H}}} = \frac{\dfrac{\mathbf{1}}{\mathbf{2}^o - KIE_{exo}} + \dfrac{\mathbf{1}}{\mathbf{2}^o - KIE_{endo}}\left(\dfrac{k_{endo}^{H,H}}{k_{exo}^{H,H}}\right)}{\dfrac{\mathbf{1}}{\mathbf{1}^o - KIE_{exo}} + \dfrac{\mathbf{1}}{\mathbf{1}^o - KIE_{endo}}\left(\dfrac{k_{endo}^{H,H}}{k_{exo}^{H,H}}\right)}$$

Eq. 4 is the expression of the intramolecular KIE under the assumption of forbidden stereoinversion of the ylide as a function of primary and secondary KIEs as computed from the *exo*-**TS1** and *endo*-**TS1** transition structures. This expression is arrived at by manipulating **Eq. 3**:

$$KIE_{Intra} = \frac{[\mathbf{4}]}{[\mathbf{5}]} = \frac{k_1k_2 + \mathbf{2}k_2k_4 + k_3k_4}{k_1k_2 + \mathbf{2}k_1k_3 + k_3k_4} = \frac{\dfrac{k_{exo}^{H,H}}{k_1}\dfrac{k_4}{k_{endo}^{H,H}}\left(\dfrac{k_{endo}^{H,H}}{k_{exo}^{H,H}}\right) + \mathbf{2}\dfrac{k_{endo}^{H,H}}{k_3}\dfrac{k_4}{k_{endo}^{H,H}}\dfrac{k_{exo}^{H,H}}{k_1}\dfrac{k_2}{k_{exo}^{H,H}} + \dfrac{k_{endo}^{H,H}}{k_3}\dfrac{k_2}{k_{exo}^{H,H}}\left(\dfrac{k_{exo}^{H,H}}{k_{endo}^{H,H}}\right)}{\dfrac{k_{exo}^{H,H}}{k_1}\dfrac{k_4}{k_{endo}^{H,H}}\left(\dfrac{k_{endo}^{H,H}}{k_{exo}^{H,H}}\right) + \mathbf{2} + \dfrac{k_{endo}^{H,H}}{k_3}\dfrac{k_2}{k_{exo}^{H,H}}\left(\dfrac{k_{exo}^{H,H}}{k_{endo}^{H,H}}\right)}$$

In terms of primary and secondary KIEs as computed from the *exo*-**TS1** and *endo*-**TS1** transition structures, this expression becomes **Eq. 4**:

$$KIE_{Intra} = \frac{[\mathbf{4}]}{[\mathbf{5}]} = \frac{\dfrac{\mathbf{1}^o - KIE_{exo}}{\mathbf{2}^o - KIE_{endo}}\left(\dfrac{k_{endo}^{H,H}}{k_{exo}^{H,H}}\right) + \mathbf{2}\dfrac{\mathbf{1}^o - KIE_{endo}}{\mathbf{2}^o - KIE_{endo}}\dfrac{\mathbf{1}^o - KIE_{exo}}{\mathbf{2}^o - KIE_{exo}} + \dfrac{\mathbf{1}^o - KIE_{endo}}{\mathbf{2}^o - KIE_{exo}}\left(\dfrac{k_{exo}^{H,H}}{k_{endo}^{H,H}}\right)}{\dfrac{\mathbf{1}^o - KIE_{exo}}{\mathbf{2}^o - KIE_{endo}}\left(\dfrac{k_{endo}^{H,H}}{k_{exo}^{H,H}}\right) + \mathbf{2} + \dfrac{\mathbf{1}^o - KIE_{endo}}{\mathbf{2}^o - KIE_{exo}}\left(\dfrac{k_{exo}^{H,H}}{k_{endo}^{H,H}}\right)}$$

Eq. 5 is arrived at by the following set of manipulations:

$$\frac{k_2 + k_4}{k_1 + k_3} = \frac{k_2}{k_1 + k_3} + \frac{k_4}{k_1 + k_3} = \frac{\mathbf{1}}{\dfrac{k_1}{k_2} + \dfrac{k_3}{k_2}} + \frac{\mathbf{1}}{\dfrac{k_1}{k_4} + \dfrac{k_3}{k_4}}$$

Eq. 6 is obtained by dividing the numerator and denominator of **Eq. 2** by k_1k_3:

$$KIE_{Intra} = \frac{k_1k_2 + \mathbf{2}k_2k_4 + k_3k_4}{k_1k_2 + \mathbf{2}k_1k_3 + k_3k_4} = \frac{\dfrac{k_2}{k_3} + \mathbf{2}\dfrac{k_2}{k_3}\dfrac{k_1}{k_4} + \dfrac{k_4}{k_1}}{\mathbf{2} + \dfrac{k_2}{k_3} + \dfrac{k_4}{k_1}}$$

Procedure for Computing KIEs

Calculation of KIEs from individual transition structures. Computing primary and secondary ^{2}H KIEs from *exo*-**TS1** and *endo*-**TS1** is accomplished using the Bigeleisen equation. Inputs from this equation were frequencies computed from the optimized reactant and transition structures. An example is shown below for the calculation of the primary ^{2}H KIE for the *exo*-**TS1** structure.

$$\frac{k_{exo}^{H,H}}{k_1} = \frac{Q_{exo}^{H,H}}{Q_{t,1}} \frac{\nu_{exo}^{\neq,H,H}}{\nu_1^{\neq}} \prod_i^{3N^{\neq}-7} \left(\frac{u_{i,exo}^{\neq,H,H}}{u_{i,1}^{\neq}} \right) \left(\frac{exp\left(u_{i,1}^{\neq}/2\right)}{exp\left(u_{i,exo}^{\neq,H,H}/2\right)} \right) \left(\frac{1-exp\left(u_{i,1}^{\neq}\right)}{1-exp\left(u_{i,exo}^{\neq,H,H}\right)} \right) \prod_i^{3N-6} \left(\frac{u_{i,1}}{u_{i,exo}^{H,H}} \right) \left(\frac{exp\left(u_{i,exo}^{H,H}/2\right)}{exp\left(u_{i,1}/2\right)} \right) \left(\frac{1-exp\left(u_{i,exo}^{H,H}\right)}{1-exp\left(u_{i,1}\right)} \right)$$

Computing KIEs using Eq. 5 and Eq. 6. Eqs. 5 and 6 in the manuscript express the observed intramolecular ^{2}H KIE as a function of four rate constant ratios under the assumption of facile and forbidden stereoinversion of the ylide intermediate. Ratios of rate constants involving the same transition structure, i. e. k_1/k_2 and k_3/k_4 are computed using an abbreviated version (Eq. 7) of the Bigeleisen equation, as the reactant structure and associated frequencies are equivalent. Ratios of rates involving different transition structures, i. e. k_3/k_2 and k_1/k_4 were computed using ratios of the electronic, rotational, and vibrational partition functions for the two transition structures (Eq. 8). Electronic energies, vibrational frequencies, and rotational temperatures were used as input into Eq. 8. It should be stated here that the ylide conformations leading to the *exo*-**TS1** and *endo*-**TS1** structures are slightly different; however, fractionation at the benzylic position is affected only slightly. For all intents and purposes, the reactant conformational equilibrium is likely quite rapid, and the ylide intermediate should probably be viewed as a weighted average between the two reactant conformers. However, since there is no material fractionation at the benzylic center, such considerations are moot. Eqs. 7 and 8 remain a reasonable means of computing rate constant ratios that can be substituted into Eq. 5 and Eq. 6.

Computed Structures [B3LYP/6-31+G(d,p)]

All quantum mechanical calculations below were performed with Gaussian03.[1] All structures were fully optimized using the B3LYP hybrid functional together with the 6-31+G(d,p) basis set. All reactant structures were found to have all real frequencies, and the transition structures were found to have exactly one imaginary frequency.

Solvent effects in the computed geometries and frequencies were taken into account by means of the IEFPCM solvation model as implemented in Gaussian03. All IEFPCM calculations were carried out at the B3LYP/6-31+G(d,p) level of theory. The solute cavities were generated using the United Atom Topological Model UA0 set of radii.

1. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Model Ylide Stereoinversion Transition Structure (gas phase)

E(RB+HF-LYP) = -592.313317908

Zero-point correction= 0.104950
(Hartree/Particle)
Thermal correction to Energy= 0.112304
Thermal correction to Enthalpy= 0.113248
Thermal correction to Gibbs Free Energy= 0.073163
Sum of electronic and zero-point Energies= -592.311521
Sum of electronic and thermal Energies= -592.304167
Sum of electronic and thermal Enthalpies= -592.303223
Sum of electronic and thermal Free Energies= -592.343308

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	70.472	24.013	84.366

S	0	0.397662	0.048435	-0.133404
O	0	-1.131600	-0.395857	-0.636260
C	0	1.623233	-1.199294	0.197580
H	0	1.797388	-1.772269	-0.689139
H	0	2.535074	-0.731050	0.504491
H	0	1.273956	-1.844602	0.976351
C	0	-2.068278	-0.159317	0.418057
H	0	-2.064607	0.880136	0.671869
H	0	-3.047888	-0.444226	0.095426
H	0	-1.793210	-0.736872	1.275768
C	0	0.802082	1.769719	0.071590
H	0	0.064602	2.519648	-0.124950
H	0	1.782670	2.054495	0.391357

Model Ylide (7; gas phase)

E(RB+HF-LYP) = -592.431335667

S	0	-0.597204	-0.088512	-0.468432
O	0	1.079585	-0.151634	-0.716551
C	0	1.912850	-0.087203	0.460483
H	0	2.946051	-0.141131	0.131435
H	0	1.758726	0.848101	0.995504
H	0	1.704978	-0.926501	1.120043
C	0	-0.802149	1.513639	0.349255
H	0	-1.833794	1.801773	0.184466
H	0	-0.610081	1.431869	1.416562
H	0	-0.137047	2.262723	-0.082282
C	0	-1.149254	-1.300860	0.499227
H	0	-0.670944	-1.539269	1.438234
H	0	-2.007994	-1.861765	0.169579

Endo-TS1 (gas phase)

E(RB+HF-LYP) = -823.533430085

Zero-point correction= 0.184780
(Hartree/Particle)
Thermal correction to Energy= 0.195834
Thermal correction to Enthalpy= 0.196778
Thermal correction to Gibbs Free Energy= 0.146752

```
 Sum of electronic and zero-point Energies=          -823.348650
 Sum of electronic and thermal Energies=             -823.337597
 Sum of electronic and thermal Enthalpies=           -823.336652
 Sum of electronic and thermal Free Energies=        -823.386678

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 122.887             41.598           105.289

 C             0       -3.190111   -0.861164   -0.574049
 C             0       -1.950192   -1.292976   -0.099070
 C             0       -1.033088   -0.382988    0.447513
 C             0       -1.386493    0.969341    0.516635
 C             0       -2.626712    1.406183    0.039238
 C             0       -3.532389    0.494126   -0.509127
 H             0       -3.889018   -1.579559   -0.994263
 H             0       -1.691231   -2.349200   -0.151046
 H             0       -0.683494    1.665463    0.963084
 H             0       -2.889846    2.458751    0.105607
 H             0       -4.497013    0.832477   -0.876799
 C             0        0.311143   -0.874903    0.973251
 H             0        0.816448   -1.408196    0.038347
 H             0        0.174562   -1.723280    1.672521
 O             0        1.165564    0.049468    1.417558
 S             0        2.862719   -0.004871   -0.044253
 C             0        2.287177    1.576323   -0.737567
 H             0        3.000895    1.927545   -1.485960
 H             0        1.294489    1.446137   -1.168780
 H             0        2.227439    2.275070    0.097262
 C             0        2.235939   -1.167279   -1.045529
 H             0        2.687642   -2.150943   -0.993151
 H             0        1.629472   -0.912054   -1.907016
```

Endo-TS1 (PCM – CH_2Cl_2)

```
E(RB+HF-LYP) =  -823.545644624

Zero-point correction=                           0.183984
(Hartree/Particle)
 Thermal correction to Energy=                    0.195176
 Thermal correction to Enthalpy=                  0.196120
 Thermal correction to Gibbs Free Energy=         0.145504
 Sum of electronic and zero-point Energies=          -823.362243
 Sum of electronic and thermal Energies=             -823.351051
 Sum of electronic and thermal Enthalpies=           -823.350107
 Sum of electronic and thermal Free Energies=        -823.400723

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 122.475             41.795           106.530

C             0       -3.190111   -0.861164   -0.574049
C             0       -1.950192   -1.292976   -0.099070
C             0       -1.033088   -0.382988    0.447513
C             0       -1.386493    0.969341    0.516635
C             0       -2.626712    1.406183    0.039238
C             0       -3.532389    0.494126   -0.509127
```

H	0	-3.889018	-1.579559	-0.994263
H	0	-1.691231	-2.349200	-0.151046
H	0	-0.683494	1.665463	0.963084
H	0	-2.889846	2.458751	0.105608
H	0	-4.497013	0.832477	-0.876799
C	0	0.311143	-0.874903	0.973251
H	0	0.816448	-1.408196	0.038347
H	0	0.174562	-1.723280	1.672521
O	0	1.165564	0.049468	1.417558
S	0	2.862719	-0.004871	-0.044253
C	0	2.287177	1.576323	-0.737566
H	0	3.000895	1.927545	-1.485959
H	0	1.294489	1.446137	-1.168780
H	0	2.227439	2.275070	0.097263
C	0	2.235939	-1.167279	-1.045529
H	0	2.687642	-2.150943	-0.993151
H	0	1.629472	-0.912053	-1.907016

Endo-TS1 (PCM – $CHCl_3$)

E(RB+HF-LYP) = -823.543514245

Zero-point correction= 0.184112
(Hartree/Particle)
Thermal correction to Energy= 0.195276
Thermal correction to Enthalpy= 0.196221
Thermal correction to Gibbs Free Energy= 0.145754
Sum of electronic and zero-point Energies= -823.359786
Sum of electronic and thermal Energies= -823.348622
Sum of electronic and thermal Enthalpies= -823.347677
Sum of electronic and thermal Free Energies= -823.398144

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	122.538	41.759	106.216

C	0	-3.190111	-0.861164	-0.574049
C	0	-1.950192	-1.292976	-0.099070
C	0	-1.033088	-0.382988	0.447513
C	0	-1.386493	0.969341	0.516635
C	0	-2.626712	1.406183	0.039238
C	0	-3.532389	0.494126	-0.509127
H	0	-3.889018	-1.579559	-0.994263
H	0	-1.691231	-2.349200	-0.151046
H	0	-0.683494	1.665463	0.963084
H	0	-2.889846	2.458751	0.105608
H	0	-4.497013	0.832477	-0.876799
C	0	0.311143	-0.874903	0.973251
H	0	0.816448	-1.408196	0.038347
H	0	0.174562	-1.723280	1.672521
O	0	1.165564	0.049468	1.417558
S	0	2.862719	-0.004871	-0.044253
C	0	2.287177	1.576323	-0.737566
H	0	3.000895	1.927545	-1.485959
H	0	1.294489	1.446137	-1.168780
H	0	2.227439	2.275070	0.097263
C	0	2.235939	-1.167279	-1.045529

H	0	2.687642	-2.150943	-0.993151
H	0	1.629472	-0.912053	-1.907016

Endo-TS1 (PCM – CCl_4)

E(RB+HF-LYP) = -823.539246853

Zero-point correction= 0.184385
(Hartree/Particle)
Thermal correction to Energy= 0.195501
Thermal correction to Enthalpy= 0.196445
Thermal correction to Gibbs Free Energy= 0.146193
Sum of electronic and zero-point Energies= -823.354962
Sum of electronic and thermal Energies= -823.343846
Sum of electronic and thermal Enthalpies= -823.342902
Sum of electronic and thermal Free Energies= -823.393154

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	122.679	41.691	105.764

C	0	-3.190111	-0.861164	-0.574049
C	0	-1.950192	-1.292976	-0.099070
C	0	-1.033088	-0.382988	0.447513
C	0	-1.386493	0.969341	0.516635
C	0	-2.626712	1.406183	0.039238
C	0	-3.532389	0.494126	-0.509127
H	0	-3.889018	-1.579559	-0.994263
H	0	-1.691231	-2.349200	-0.151046
H	0	-0.683494	1.665463	0.963084
H	0	-2.889846	2.458751	0.105608
H	0	-4.497013	0.832477	-0.876799
C	0	0.311143	-0.874903	0.973251
H	0	0.816448	-1.408196	0.038347
H	0	0.174562	-1.723280	1.672521
O	0	1.165564	0.049468	1.417558
S	0	2.862719	-0.004871	-0.044253
C	0	2.287177	1.576323	-0.737566
H	0	3.000895	1.927545	-1.485959
H	0	1.294489	1.446137	-1.168780
H	0	2.227439	2.275070	0.097263
C	0	2.235939	-1.167279	-1.045529
H	0	2.687642	-2.150943	-0.993151
H	0	1.629472	-0.912053	-1.907016

Endo-TS1 (PCM – dichloroethane)

E(RB+HF-LYP) = -823.545644624

Zero-point correction= 0.183984
(Hartree/Particle)
Thermal correction to Energy= 0.195176
Thermal correction to Enthalpy= 0.196120
Thermal correction to Gibbs Free Energy= 0.145504
Sum of electronic and zero-point Energies= -823.362243
Sum of electronic and thermal Energies= -823.351051
Sum of electronic and thermal Enthalpies= -823.350107
Sum of electronic and thermal Free Energies= -823.400723

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	122.475	41.795	106.530

C	0	-3.190111	-0.861164	-0.574049
C	0	-1.950192	-1.292976	-0.099070
C	0	-1.033088	-0.382988	0.447513
C	0	-1.386493	0.969341	0.516635
C	0	-2.626712	1.406183	0.039238
C	0	-3.532389	0.494126	-0.509127
H	0	-3.889018	-1.579559	-0.994263
H	0	-1.691231	-2.349200	-0.151046
H	0	-0.683494	1.665463	0.963084
H	0	-2.889846	2.458751	0.105608
H	0	-4.497013	0.832477	-0.876799
C	0	0.311143	-0.874903	0.973251
H	0	0.816448	-1.408196	0.038347
H	0	0.174562	-1.723280	1.672521
O	0	1.165564	0.049468	1.417558
S	0	2.862719	-0.004871	-0.044253
C	0	2.287177	1.576323	-0.737566
H	0	3.000895	1.927545	-1.485959
H	0	1.294489	1.446137	-1.168780
H	0	2.227439	2.275070	0.097263
C	0	2.235939	-1.167279	-1.045529
H	0	2.687642	-2.150943	-0.993151
H	0	1.629472	-0.912053	-1.907016

Endo-TS1 (PCM – chlorobenzene)

E(RB+HF-LYP) = -823.544083559

Zero-point correction= 0.184090
(Hartree/Particle)
Thermal correction to Energy= 0.195257
Thermal correction to Enthalpy= 0.196201
Thermal correction to Gibbs Free Energy= 0.145752
Sum of electronic and zero-point Energies= -823.360352
Sum of electronic and thermal Energies= -823.349185
Sum of electronic and thermal Enthalpies= -823.348241
Sum of electronic and thermal Free Energies= -823.398690

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	122.526	41.769	106.180

C	0	-3.190111	-0.861164	-0.574049
C	0	-1.950192	-1.292976	-0.099070
C	0	-1.033088	-0.382988	0.447513
C	0	-1.386493	0.969341	0.516635
C	0	-2.626712	1.406183	0.039238
C	0	-3.532389	0.494126	-0.509127
H	0	-3.889018	-1.579559	-0.994263
H	0	-1.691231	-2.349200	-0.151046
H	0	-0.683494	1.665463	0.963084
H	0	-2.889846	2.458751	0.105608

H	0	-4.497013	0.832477	-0.876799
C	0	0.311143	-0.874903	0.973251
H	0	0.816448	-1.408196	0.038347
H	0	0.174562	-1.723280	1.672521
O	0	1.165564	0.049468	1.417558
S	0	2.862719	-0.004871	-0.044253
C	0	2.287177	1.576323	-0.737566
H	0	3.000895	1.927545	-1.485959
H	0	1.294489	1.446137	-1.168780
H	0	2.227439	2.275070	0.097263
C	0	2.235939	-1.167279	-1.045529
H	0	2.687642	-2.150943	-0.993151
H	0	1.629472	-0.912053	-1.907016

Exo-TS1 (gas phase)

E(RB+HF-LYP) = -823.534276318

Zero-point correction= 0.184766
(Hartree/Particle)
Thermal correction to Energy= 0.195862
Thermal correction to Enthalpy= 0.196807
Thermal correction to Gibbs Free Energy= 0.146464
Sum of electronic and zero-point Energies= -823.349511
Sum of electronic and thermal Energies= -823.338414
Sum of electronic and thermal Enthalpies= -823.337470
Sum of electronic and thermal Free Energies= -823.387812

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	122.906	41.597	105.954

C	0	2.845770	-1.377503	0.254014
C	0	1.534998	-1.075635	-0.127906
C	0	1.159226	0.246776	-0.390073
C	0	2.119657	1.261339	-0.269483
C	0	3.429982	0.962564	0.109589
C	0	3.797366	-0.360957	0.375792
H	0	3.126352	-2.409161	0.449909
H	0	0.791198	-1.857342	-0.245216
H	0	1.840376	2.292705	-0.478511
H	0	4.164247	1.759262	0.194934
H	0	4.816618	-0.596543	0.668958
C	0	-0.270529	0.589061	-0.780347
H	0	-0.296918	1.403088	-1.530417
H	0	-0.724685	1.135573	0.172426
O	0	-1.079103	-0.434326	-1.073552
S	0	-2.551834	-0.495160	0.593261
C	0	-3.819973	-0.038567	-0.626974
H	0	-4.806179	-0.061090	-0.158549
H	0	-3.595103	0.950537	-1.026929
H	0	-3.752951	-0.771868	-1.430869
C	0	-2.118814	0.930048	1.317989
H	0	-1.585444	0.857369	2.258373
H	0	-2.581437	1.871890	1.046533

Exo-TS1 (PCM – CH_2Cl_2)

E(RB+HF-LYP) = -823.546858207

Zero-point correction= 0.183972
(Hartree/Particle)
Thermal correction to Energy= 0.195165
Thermal correction to Enthalpy= 0.196109
Thermal correction to Gibbs Free Energy= 0.145461
Sum of electronic and zero-point Energies= -823.362887
Sum of electronic and thermal Energies= -823.351693
Sum of electronic and thermal Enthalpies= -823.350749
Sum of electronic and thermal Free Energies= -823.401398

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	122.468	41.761	106.599

C	0	2.838748	-1.410177	0.034141
C	0	1.526105	-1.022098	-0.257467
C	0	1.176893	0.333948	-0.304644
C	0	2.169097	1.295762	-0.059474
C	0	3.481829	0.912119	0.231058
C	0	3.821728	-0.445285	0.280758
H	0	3.095388	-2.468243	0.064042
H	0	0.762743	-1.768183	-0.464641
H	0	1.912716	2.354956	-0.101557
H	0	4.240462	1.671800	0.413816
H	0	4.843765	-0.746676	0.503706
C	0	-0.254467	0.771905	-0.586800
H	0	-0.266808	1.769201	-1.069886
H	0	-0.706799	1.012762	0.470332
O	0	-1.057882	-0.124933	-1.185815
S	0	-2.599878	-0.638728	0.403154
C	0	-3.856980	0.215094	-0.596311
H	0	-4.834908	0.087510	-0.127076
H	0	-3.596178	1.270698	-0.682369
H	0	-3.840867	-0.249190	-1.582924
C	0	-2.138543	0.468461	1.535350
H	0	-1.574529	0.098037	2.385320
H	0	-2.560340	1.468078	1.567617

Exo-TS1 (PCM – $CHCl_3$)

E(RB+HF-LYP) = -823.544513714

Zero-point correction= 0.184070
(Hartree/Particle)
Thermal correction to Energy= 0.195267
Thermal correction to Enthalpy= 0.196211
Thermal correction to Gibbs Free Energy= 0.145495
Sum of electronic and zero-point Energies= -823.360444
Sum of electronic and thermal Energies= -823.349247
Sum of electronic and thermal Enthalpies= -823.348303
Sum of electronic and thermal Free Energies= -823.399019

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin

Total		122.532	41.743	106.741

C	0	2.833921	-1.409712	0.059633
C	0	1.522513	-1.028033	-0.244528
C	0	1.173030	0.326539	-0.316814
C	0	2.163452	1.293142	-0.085137
C	0	3.474986	0.915793	0.217273
C	0	3.815132	-0.440121	0.293118
H	0	3.091210	-2.466486	0.108932
H	0	0.760180	-1.776766	-0.443733
H	0	1.906724	2.350886	-0.147559
H	0	4.232361	1.678749	0.388903
H	0	4.836041	-0.736693	0.525570
C	0	-0.257307	0.757534	-0.611709
H	0	-0.270930	1.738955	-1.125953
H	0	-0.709680	1.033436	0.440294
O	0	-1.063221	-0.155961	-1.176905
S	0	-2.587878	-0.625466	0.427569
C	0	-3.851851	0.180305	-0.602256
H	0	-4.829648	0.061406	-0.130574
H	0	-3.600040	1.234143	-0.726990
H	0	-3.828938	-0.318269	-1.571822
C	0	-2.131040	0.527882	1.517074
H	0	-1.570818	0.191902	2.383313
H	0	-2.561669	1.523901	1.513831

Exo-TS1 (PCM – CCl_4)

E(RB+HF-LYP) = -823.540034523

Zero-point correction= 0.184291
(Hartree/Particle)
Thermal correction to Energy= 0.195444
Thermal correction to Enthalpy= 0.196388
Thermal correction to Gibbs Free Energy= 0.145852
Sum of electronic and zero-point Energies= -823.355744
Sum of electronic and thermal Energies= -823.344591
Sum of electronic and thermal Enthalpies= -823.343647
Sum of electronic and thermal Free Energies= -823.394183

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	122.643	41.690	106.362

C	0	2.843138	-1.389266	0.200109
C	0	1.533081	-1.063714	-0.166927
C	0	1.163859	0.270450	-0.376427
C	0	2.131727	1.273541	-0.217808
C	0	3.441383	0.951841	0.147154
C	0	3.801785	-0.383873	0.360167
H	0	3.117232	-2.430701	0.354968
H	0	0.785480	-1.838548	-0.310602
H	0	1.858641	2.314985	-0.385512
H	0	4.181273	1.740977	0.262288
H	0	4.821087	-0.637375	0.641826
C	0	-0.265686	0.639823	-0.746558
H	0	-0.285181	1.508600	-1.433660

H	0	-0.718953	1.113001	0.240556
O	0	-1.072463	-0.360255	-1.123209
S	0	-2.564226	-0.538641	0.551147
C	0	-3.837868	0.033776	-0.614124
H	0	-4.815259	0.006149	-0.127852
H	0	-3.591869	1.041395	-0.950772
H	0	-3.809259	-0.647881	-1.464669
C	0	-2.113369	0.815078	1.387324
H	0	-1.558293	0.661581	2.306149
H	0	-2.565878	1.782197	1.197137

Exo-TS1 (PCM – dichloroethane)

E(RB+HF-LYP) = -823.547193202

Zero-point correction= 0.183942
(Hartree/Particle)
Thermal correction to Energy= 0.195143
Thermal correction to Enthalpy= 0.196087
Thermal correction to Gibbs Free Energy= 0.145401
Sum of electronic and zero-point Energies= -823.363252
Sum of electronic and thermal Energies= -823.352050
Sum of electronic and thermal Enthalpies= -823.351106
Sum of electronic and thermal Free Energies= -823.401792

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	122.454	41.768	106.679

C	0	2.841358	-1.409304	0.036705
C	0	1.528250	-1.023313	-0.255863
C	0	1.177377	0.332227	-0.305821
C	0	2.168347	1.295688	-0.061797
C	0	3.481427	0.914160	0.230107
C	0	3.823090	-0.442773	0.282067
H	0	3.099260	-2.467084	0.068596
H	0	0.765960	-1.770856	-0.461501
H	0	1.910645	2.354570	-0.105508
H	0	4.238987	1.675164	0.412274
H	0	4.845466	-0.742539	0.506013
C	0	-0.254329	0.768472	-0.589315
H	0	-0.266942	1.764306	-1.075584
H	0	-0.706375	1.012386	0.466952
O	0	-1.057287	-0.130860	-1.185437
S	0	-2.601941	-0.637449	0.404785
C	0	-3.857756	0.215705	-0.596808
H	0	-4.835677	0.091191	-0.126721
H	0	-3.595197	1.270633	-0.685976
H	0	-3.843095	-0.251613	-1.582024
C	0	-2.139245	0.471684	1.534277
H	0	-1.575323	0.102545	2.384939
H	0	-2.559477	1.472093	1.564166

Exo-TS1 (PCM – chlorobenzene)

E(RB+HF-LYP) = -823.545138216

```
Zero-point correction=                           0.184010
(Hartree/Particle)
 Thermal correction to Energy=                    0.195233
 Thermal correction to Enthalpy=                  0.196177
 Thermal correction to Gibbs Free Energy=         0.145281
 Sum of electronic and zero-point Energies=           -823.361128
 Sum of electronic and thermal Energies=              -823.349905
 Sum of electronic and thermal Enthalpies=            -823.348961
 Sum of electronic and thermal Free Energies=         -823.399857

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 122.511             41.762           107.119

C             0        2.833775   -1.409445    0.065668
C             0        1.522980   -1.029431   -0.243669
C             0        1.172972    0.324731   -0.321696
C             0        2.162289    1.292676   -0.090424
C             0        3.473103    0.917025    0.217294
C             0        3.813799   -0.438536    0.298751
H             0        3.091385   -2.466029    0.119522
H             0        0.761595   -1.779661   -0.441496
H             0        1.905120    2.350171   -0.156987
H             0        4.229595    1.681042    0.388777
H             0        4.834244   -0.733791    0.535383
C             0       -0.256882    0.754096   -0.622305
H             0       -0.268935    1.730151   -1.146745
H             0       -0.709140    1.041158    0.425577
O             0       -1.063081   -0.164670   -1.180020
S             0       -2.586257   -0.622214    0.434138
C             0       -3.854041    0.173624   -0.598761
H             0       -4.829810    0.059601   -0.121690
H             0       -3.602560    1.226139   -0.734919
H             0       -3.835612   -0.334857   -1.563278
C             0       -2.129172    0.540254    1.513146
H             0       -1.563869    0.212761    2.379440
H             0       -2.560181    1.536141    1.502349
```

Ylide Preceding Endo-TS1 (gas phase)

```
E(RB+HF-LYP) =  -823.542959896

Zero-point correction=                           0.187448
(Hartree/Particle)
 Thermal correction to Energy=                    0.199328
 Thermal correction to Enthalpy=                  0.200272
 Thermal correction to Gibbs Free Energy=         0.146997
 Sum of electronic and zero-point Energies=           -823.355512
 Sum of electronic and thermal Energies=              -823.343632
 Sum of electronic and thermal Enthalpies=            -823.342688
 Sum of electronic and thermal Free Energies=         -823.395963

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 125.080             43.587           112.128

C             0       -3.039022    1.366693    0.365922
```

C	0	-1.729393	1.161523	-0.070580
C	0	-1.287577	-0.119251	-0.432835
C	0	-2.184857	-1.191033	-0.346999
C	0	-3.498316	-0.990393	0.087804
C	0	-3.928215	0.289492	0.446168
H	0	-3.368177	2.365214	0.640041
H	0	-1.039169	1.999150	-0.131258
H	0	-1.852163	-2.188585	-0.623083
H	0	-4.183311	-1.831713	0.145937
H	0	-4.948744	0.448360	0.782917
C	0	0.136375	-0.336737	-0.887442
H	0	0.441861	0.486569	-1.554061
H	0	0.209467	-1.276812	-1.456154
O	0	0.980524	-0.374961	0.258583
S	0	2.780203	-0.333867	-0.196603
C	0	3.138115	-0.248847	1.582955
H	0	4.212539	-0.381939	1.710982
H	0	2.815429	0.722999	1.960227
H	0	2.577906	-1.042613	2.075170
C	0	3.381566	1.061319	-0.804726
H	0	3.492615	1.099702	-1.881611
H	0	3.382239	1.984636	-0.233728

Ylide Preceding Endo-TS1 (PCM – CH_2Cl_2)

E(RB+HF-LYP) = -823.551090020

Zero-point correction= 0.186439
(Hartree/Particle)
Thermal correction to Energy= 0.198313
Thermal correction to Enthalpy= 0.199257
Thermal correction to Gibbs Free Energy= 0.146833
Sum of electronic and zero-point Energies= -823.364993
Sum of electronic and thermal Energies= -823.353119
Sum of electronic and thermal Enthalpies= -823.352175
Sum of electronic and thermal Free Energies= -823.404599

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	124.443	43.772	110.336

C	0	-3.039022	1.366693	0.365923
C	0	-1.729393	1.161523	-0.070580
C	0	-1.287577	-0.119251	-0.432835
C	0	-2.184857	-1.191033	-0.346999
C	0	-3.498316	-0.990393	0.087804
C	0	-3.928215	0.289492	0.446168
H	0	-3.368177	2.365214	0.640042
H	0	-1.039169	1.999150	-0.131257
H	0	-1.852163	-2.188585	-0.623084
H	0	-4.183311	-1.831713	0.145936
H	0	-4.948744	0.448360	0.782917
C	0	0.136375	-0.336737	-0.887442
H	0	0.441861	0.486570	-1.554061
H	0	0.209467	-1.276811	-1.456154
O	0	0.980524	-0.374961	0.258583
S	0	2.780203	-0.333867	-0.196603

C	0	3.138115	-0.248848	1.582955
H	0	4.212539	-0.381940	1.710982
H	0	2.815429	0.722998	1.960227
H	0	2.577906	-1.042614	2.075170
C	0	3.381566	1.061319	-0.804726
H	0	3.492615	1.099703	-1.881611
H	0	3.382239	1.984636	-0.233727

Ylide Preceding Endo-TS1 (PCM – $CHCl_3$)

E(RB+HF-LYP) = -823.549548977

Zero-point correction= 0.186600
(Hartree/Particle)
Thermal correction to Energy= 0.198492
Thermal correction to Enthalpy= 0.199437
Thermal correction to Gibbs Free Energy= 0.146711
Sum of electronic and zero-point Energies= -823.363180
Sum of electronic and thermal Energies= -823.351287
Sum of electronic and thermal Enthalpies= -823.350342
Sum of electronic and thermal Free Energies= -823.403069

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	124.556	43.751	110.971

C	0	-3.039022	1.366693	0.365923
C	0	-1.729393	1.161523	-0.070580
C	0	-1.287577	-0.119251	-0.432835
C	0	-2.184857	-1.191033	-0.346999
C	0	-3.498316	-0.990393	0.087804
C	0	-3.928215	0.289492	0.446168
H	0	-3.368177	2.365214	0.640042
H	0	-1.039169	1.999150	-0.131257
H	0	-1.852163	-2.188585	-0.623084
H	0	-4.183311	-1.831713	0.145936
H	0	-4.948744	0.448360	0.782917
C	0	0.136375	-0.336737	-0.887442
H	0	0.441861	0.486570	-1.554061
H	0	0.209467	-1.276811	-1.456154
O	0	0.980524	-0.374961	0.258583
S	0	2.780203	-0.333867	-0.196603
C	0	3.138115	-0.248848	1.582955
H	0	4.212539	-0.381940	1.710982
H	0	2.815429	0.722998	1.960227
H	0	2.577906	-1.042614	2.075170
C	0	3.381566	1.061319	-0.804726
H	0	3.492615	1.099703	-1.881611
H	0	3.382239	1.984636	-0.233727

Ylide Preceding Endo-TS1 (PCM – CCl_4)

E(RB+HF-LYP) = -823.546684090

Zero-point correction= 0.186960
(Hartree/Particle)
Thermal correction to Energy= 0.198852
Thermal correction to Enthalpy= 0.199796

```
 Thermal correction to Gibbs Free Energy=         0.146774
 Sum of electronic and zero-point Energies=           -823.359789
 Sum of electronic and thermal Energies=              -823.347897
 Sum of electronic and thermal Enthalpies=            -823.346953
 Sum of electronic and thermal Free Energies=         -823.399975

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 124.782             43.682           111.594

C             0       -3.039022    1.366693    0.365923
C             0       -1.729393    1.161523   -0.070580
C             0       -1.287577   -0.119251   -0.432835
C             0       -2.184857   -1.191033   -0.346999
C             0       -3.498316   -0.990393    0.087804
C             0       -3.928215    0.289492    0.446168
H             0       -3.368177    2.365214    0.640042
H             0       -1.039169    1.999150   -0.131257
H             0       -1.852163   -2.188585   -0.623084
H             0       -4.183311   -1.831713    0.145936
H             0       -4.948744    0.448360    0.782917
C             0        0.136375   -0.336737   -0.887442
H             0        0.441861    0.486570   -1.554061
H             0        0.209467   -1.276811   -1.456154
O             0        0.980524   -0.374961    0.258583
S             0        2.780203   -0.333867   -0.196603
C             0        3.138115   -0.248848    1.582955
H             0        4.212539   -0.381940    1.710982
H             0        2.815429    0.722998    1.960227
H             0        2.577906   -1.042614    2.075170
C             0        3.381566    1.061319   -0.804726
H             0        3.492615    1.099703   -1.881611
H             0        3.382239    1.984636   -0.233727
```

Ylide Preceding Endo-TS1 (PCM – dichloroethane)

```
E(RB+HF-LYP) =  -823.551212757

Zero-point correction=                           0.186424
(Hartree/Particle)
 Thermal correction to Energy=                    0.198294
 Thermal correction to Enthalpy=                  0.199238
 Thermal correction to Gibbs Free Energy=         0.146839
 Sum of electronic and zero-point Energies=           -823.365177
 Sum of electronic and thermal Energies=              -823.353307
 Sum of electronic and thermal Enthalpies=            -823.352363
 Sum of electronic and thermal Free Energies=         -823.404763

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 124.431             43.776           110.284

C             0       -3.039022    1.366693    0.365923
C             0       -1.729393    1.161523   -0.070580
C             0       -1.287577   -0.119251   -0.432835
C             0       -2.184857   -1.191033   -0.346999
C             0       -3.498316   -0.990393    0.087804
```

C	0	-3.928215	0.289492	0.446168
H	0	-3.368177	2.365214	0.640042
H	0	-1.039169	1.999150	-0.131257
H	0	-1.852163	-2.188585	-0.623084
H	0	-4.183311	-1.831713	0.145936
H	0	-4.948744	0.448360	0.782917
C	0	0.136375	-0.336737	-0.887442
H	0	0.441861	0.486570	-1.554061
H	0	0.209467	-1.276811	-1.456154
O	0	0.980524	-0.374961	0.258583
S	0	2.780203	-0.333867	-0.196603
C	0	3.138115	-0.248848	1.582955
H	0	4.212539	-0.381940	1.710982
H	0	2.815429	0.722998	1.960227
H	0	2.577906	-1.042614	2.075170
C	0	3.381566	1.061319	-0.804726
H	0	3.492615	1.099703	-1.881611
H	0	3.382239	1.984636	-0.233727

Ylide Preceding Endo-TS1 (PCM – chlorobenzene)

E(RB+HF-LYP) = -823.549808830

Zero-point correction= 0.186525
(Hartree/Particle)
Thermal correction to Energy= 0.198433
Thermal correction to Enthalpy= 0.199377
Thermal correction to Gibbs Free Energy= 0.146535
Sum of electronic and zero-point Energies= -823.363597
Sum of electronic and thermal Energies= -823.351688
Sum of electronic and thermal Enthalpies= -823.350744
Sum of electronic and thermal Free Energies= -823.403586

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	124.519	43.768	111.216

C	0	-3.039022	1.366693	0.365923
C	0	-1.729393	1.161523	-0.070580
C	0	-1.287577	-0.119251	-0.432835
C	0	-2.184857	-1.191033	-0.346999
C	0	-3.498316	-0.990393	0.087804
C	0	-3.928215	0.289492	0.446168
H	0	-3.368177	2.365214	0.640042
H	0	-1.039169	1.999150	-0.131257
H	0	-1.852163	-2.188585	-0.623084
H	0	-4.183311	-1.831713	0.145936
H	0	-4.948744	0.448360	0.782917
C	0	0.136375	-0.336737	-0.887442
H	0	0.441861	0.486570	-1.554061
H	0	0.209467	-1.276811	-1.456154
O	0	0.980524	-0.374961	0.258583
S	0	2.780203	-0.333867	-0.196603
C	0	3.138115	-0.248848	1.582955
H	0	4.212539	-0.381940	1.710982
H	0	2.815429	0.722998	1.960227
H	0	2.577906	-1.042614	2.075170

C	0	3.381566	1.061319	-0.804726
H	0	3.492615	1.099703	-1.881611
H	0	3.382239	1.984636	-0.233727

Ylide Preceding Exo-TS1 (gas phase)

E(RB+HF-LYP) = -823.543433402

Zero-point correction= 0.187404
(Hartree/Particle)
Thermal correction to Energy= 0.199121
Thermal correction to Enthalpy= 0.200066
Thermal correction to Gibbs Free Energy= 0.147978
Sum of electronic and zero-point Energies= -823.356030
Sum of electronic and thermal Energies= -823.344312
Sum of electronic and thermal Enthalpies= -823.343368
Sum of electronic and thermal Free Energies= -823.395455

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	124.951	43.611	109.627

C	0	-2.738067	-1.356628	-0.391884
C	0	-1.518085	-1.130746	0.249363
C	0	-1.123376	0.169016	0.594763
C	0	-1.974575	1.236980	0.281865
C	0	-3.198927	1.014390	-0.355351
C	0	-3.584159	-0.284929	-0.695250
H	0	-3.029891	-2.369762	-0.655243
H	0	-0.856221	-1.959825	0.480609
H	0	-1.676406	2.252418	0.534673
H	0	-3.845420	1.854738	-0.593095
H	0	-4.532285	-0.460987	-1.195380
C	0	0.182588	0.413977	1.333967
H	0	0.030214	0.278783	2.414015
H	0	0.493064	1.464554	1.195506
O	0	1.230010	-0.468409	0.984539
S	0	2.077040	0.029703	-0.616817
C	0	3.384178	-1.154808	-0.182710
H	0	4.029015	-1.270959	-1.054245
H	0	3.943159	-0.767916	0.670846
H	0	2.905733	-2.096657	0.082897
C	0	2.824684	1.483489	-0.634142
H	0	2.283707	2.289282	-1.114993
H	0	3.657055	1.713903	0.023427

Ylide Preceding Exo-TS1 (PCM – CH_2Cl_2)

E(RB+HF-LYP) = -823.551316504

Zero-point correction= 0.186190
(Hartree/Particle)
Thermal correction to Energy= 0.198060
Thermal correction to Enthalpy= 0.199004
Thermal correction to Gibbs Free Energy= 0.145417
Sum of electronic and zero-point Energies= -823.365388
Sum of electronic and thermal Energies= -823.353518
Sum of electronic and thermal Enthalpies= -823.352574

```
 Sum of electronic and thermal Free Energies=         -823.406161

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 124.284             43.864           112.784

C             0       -2.738067   -1.356628   -0.391884
C             0       -1.518085   -1.130746    0.249363
C             0       -1.123376    0.169016    0.594763
C             0       -1.974575    1.236980    0.281865
C             0       -3.198927    1.014390   -0.355351
C             0       -3.584159   -0.284929   -0.695250
H             0       -3.029891   -2.369762   -0.655243
H             0       -0.856221   -1.959825    0.480609
H             0       -1.676406    2.252418    0.534673
H             0       -3.845420    1.854738   -0.593095
H             0       -4.532285   -0.460987   -1.195380
C             0        0.182588    0.413977    1.333967
H             0        0.030214    0.278783    2.414015
H             0        0.493064    1.464554    1.195506
O             0        1.230010   -0.468409    0.984539
S             0        2.077040    0.029703   -0.616817
C             0        3.384178   -1.154808   -0.182710
H             0        4.029015   -1.270959   -1.054245
H             0        3.943159   -0.767916    0.670846
H             0        2.905733   -2.096657    0.082897
C             0        2.824684    1.483489   -0.634142
H             0        2.283707    2.289282   -1.114993
H             0        3.657055    1.713903    0.023427
```

Ylide Preceding Exo-TS1 (PCM – $CHCl_3$)

```
E(RB+HF-LYP) =  -823.549932178

Zero-point correction=                           0.186437
(Hartree/Particle)
 Thermal correction to Energy=                    0.198256
 Thermal correction to Enthalpy=                  0.199200
 Thermal correction to Gibbs Free Energy=         0.146405
 Sum of electronic and zero-point Energies=           -823.363640
 Sum of electronic and thermal Energies=              -823.351821
 Sum of electronic and thermal Enthalpies=            -823.350877
 Sum of electronic and thermal Free Energies=         -823.403672

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 124.408             43.808           111.117

C             0       -2.738067   -1.356628   -0.391884
C             0       -1.518085   -1.130746    0.249363
C             0       -1.123376    0.169016    0.594763
C             0       -1.974575    1.236980    0.281865
C             0       -3.198927    1.014390   -0.355351
C             0       -3.584159   -0.284929   -0.695250
H             0       -3.029891   -2.369762   -0.655243
H             0       -0.856221   -1.959825    0.480609
H             0       -1.676406    2.252418    0.534673
```

H	0	-3.845420	1.854738	-0.593095
H	0	-4.532285	-0.460987	-1.195380
C	0	0.182588	0.413977	1.333967
H	0	0.030214	0.278783	2.414015
H	0	0.493064	1.464554	1.195506
O	0	1.230010	-0.468409	0.984539
S	0	2.077040	0.029703	-0.616817
C	0	3.384178	-1.154808	-0.182710
H	0	4.029015	-1.270959	-1.054245
H	0	3.943159	-0.767916	0.670846
H	0	2.905733	-2.096657	0.082897
C	0	2.824684	1.483489	-0.634142
H	0	2.283707	2.289282	-1.114993
H	0	3.657055	1.713903	0.023427

Ylide Preceding Exo-TS1 (PCM – CCl_4)

E(RB+HF-LYP) = -823.547134630

Zero-point correction= 0.186863
(Hartree/Particle)
Thermal correction to Energy= 0.198635
Thermal correction to Enthalpy= 0.199579
Thermal correction to Gibbs Free Energy= 0.147161
Sum of electronic and zero-point Energies= -823.360325
Sum of electronic and thermal Energies= -823.348553
Sum of electronic and thermal Enthalpies= -823.347609
Sum of electronic and thermal Free Energies= -823.400027

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	124.645	43.724	110.322

C	0	-2.738067	-1.356628	-0.391884
C	0	-1.518085	-1.130746	0.249363
C	0	-1.123376	0.169016	0.594763
C	0	-1.974575	1.236980	0.281865
C	0	-3.198927	1.014390	-0.355351
C	0	-3.584159	-0.284929	-0.695250
H	0	-3.029891	-2.369762	-0.655243
H	0	-0.856221	-1.959825	0.480609
H	0	-1.676406	2.252418	0.534673
H	0	-3.845420	1.854738	-0.593095
H	0	-4.532285	-0.460987	-1.195380
C	0	0.182588	0.413977	1.333967
H	0	0.030214	0.278783	2.414015
H	0	0.493064	1.464554	1.195506
O	0	1.230010	-0.468409	0.984539
S	0	2.077040	0.029703	-0.616817
C	0	3.384178	-1.154808	-0.182710
H	0	4.029015	-1.270959	-1.054245
H	0	3.943159	-0.767916	0.670846
H	0	2.905733	-2.096657	0.082897
C	0	2.824684	1.483489	-0.634142
H	0	2.283707	2.289282	-1.114993
H	0	3.657055	1.713903	0.023427

Ylide Preceding Exo-TS1 (PCM – dichloroethane)

E(RB+HF-LYP) = -823.551531763

Zero-point correction=	0.186202
(Hartree/Particle)	
Thermal correction to Energy=	0.198043
Thermal correction to Enthalpy=	0.198987
Thermal correction to Gibbs Free Energy=	0.145989
Sum of electronic and zero-point Energies=	-823.365555
Sum of electronic and thermal Energies=	-823.353714
Sum of electronic and thermal Enthalpies=	-823.352770
Sum of electronic and thermal Free Energies=	-823.405768

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	124.274	43.853	111.543

C	0	-2.738067	-1.356628	-0.391884
C	0	-1.518085	-1.130746	0.249363
C	0	-1.123376	0.169016	0.594763
C	0	-1.974575	1.236980	0.281865
C	0	-3.198927	1.014390	-0.355351
C	0	-3.584159	-0.284929	-0.695250
H	0	-3.029891	-2.369762	-0.655243
H	0	-0.856221	-1.959825	0.480609
H	0	-1.676406	2.252418	0.534673
H	0	-3.845420	1.854738	-0.593095
H	0	-4.532285	-0.460987	-1.195380
C	0	0.182588	0.413977	1.333967
H	0	0.030214	0.278783	2.414015
H	0	0.493064	1.464554	1.195506
O	0	1.230010	-0.468409	0.984539
S	0	2.077040	0.029703	-0.616817
C	0	3.384178	-1.154808	-0.182710
H	0	4.029015	-1.270959	-1.054245
H	0	3.943159	-0.767916	0.670846
H	0	2.905733	-2.096657	0.082897
C	0	2.824684	1.483489	-0.634142
H	0	2.283707	2.289282	-1.114993
H	0	3.657055	1.713903	0.023427

Ylide Preceding Exo-TS1 (PCM – chlorobenzene)

E(RB+HF-LYP) = -823.550231557

Zero-point correction=	0.186390
(Hartree/Particle)	
Thermal correction to Energy=	0.198215
Thermal correction to Enthalpy=	0.199159
Thermal correction to Gibbs Free Energy=	0.146341
Sum of electronic and zero-point Energies=	-823.363985
Sum of electronic and thermal Energies=	-823.352160
Sum of electronic and thermal Enthalpies=	-823.351216
Sum of electronic and thermal Free Energies=	-823.404034

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin

Total		124.382	43.820	111.166
C	0	-2.738067	-1.356628	-0.391884
C	0	-1.518085	-1.130746	0.249363
C	0	-1.123376	0.169016	0.594763
C	0	-1.974575	1.236980	0.281865
C	0	-3.198927	1.014390	-0.355351
C	0	-3.584159	-0.284929	-0.695250
H	0	-3.029891	-2.369762	-0.655243
H	0	-0.856221	-1.959825	0.480609
H	0	-1.676406	2.252418	0.534673
H	0	-3.845420	1.854738	-0.593095
H	0	-4.532285	-0.460987	-1.195380
C	0	0.182588	0.413977	1.333967
H	0	0.030214	0.278783	2.414015
H	0	0.493064	1.464554	1.195506
O	0	1.230010	-0.468409	0.984539
S	0	2.077040	0.029703	-0.616817
C	0	3.384178	-1.154808	-0.182710
H	0	4.029015	-1.270959	-1.054245
H	0	3.943159	-0.767916	0.670846
H	0	2.905733	-2.096657	0.082897
C	0	2.824684	1.483489	-0.634142
H	0	2.283707	2.289282	-1.114993
H	0	3.657055	1.713903	0.023427

Transition Structure for Sulfoxide Thermolysis (gas phase)

E(RB+HF-LYP) = -823.504734379

C	0	-2.849189	-1.388131	-0.175293
C	0	-1.538578	-1.052482	0.177902
C	0	-1.172178	0.286729	0.353890
C	0	-2.141775	1.284069	0.176397
C	0	-3.451947	0.951689	-0.174154
C	0	-3.809976	-0.388818	-0.354158
H	0	-3.122406	-2.432253	-0.304061
H	0	-0.787561	-1.819354	0.338981
H	0	-1.869773	2.328715	0.318298
H	0	-4.193351	1.735607	-0.304338
H	0	-4.829072	-0.650430	-0.624942
C	0	0.257126	0.664182	0.712067
H	0	0.281497	1.523943	1.409319
H	0	0.700652	1.153284	-0.276251
S	0	2.538612	-0.486169	-0.606342
C	0	3.810630	0.056266	0.574066
H	0	4.793994	0.012142	0.101223
H	0	3.580073	1.066750	0.912628
H	0	3.754828	-0.625546	1.422881
O	0	2.126255	0.773772	-1.349308
C	0	1.115607	-0.380454	1.080401
H	0	2.059809	0.023101	1.381276
H	0	0.685152	-0.925733	1.894206

Computed Structures [B97D/6-31+G(d,p)]

All quantum mechanical calculations below were performed with Gaussian09.[2] All structures were fully optimized using the B97D hybrid functional together with the 6-31+G(d,p) basis set. All transition structures were found to have exactly one imaginary frequency.

Solvent effects in the computed geometries and frequencies were taken into account by means of the IEFPCM solvation model as implemented in Gaussian09. All IEFPCM calculations were carried out at the B97D/6-31+G(d,p) level of theory. The solute cavities were generated using the United Atom Topological Model UA0 set of radii.

2. Gaussian 09, Revision A.02,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci,
G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian,
A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada,
M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima,
Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr.,
J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers,
K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand,
K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi,
M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross,
V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann,
O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski,
R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth,
P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels,
O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski,
and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Endo-TS1 (gas phase)

E(B97D) = -823.2331667

Zero-point correction=	0.180116
(Hartree/Particle)	
Thermal correction to Energy=	0.191446
Thermal correction to Enthalpy=	0.192391
Thermal correction to Gibbs Free Energy=	0.141821
Sum of electronic and zero-point Energies=	-823.053051
Sum of electronic and thermal Energies=	-823.041720
Sum of electronic and thermal Enthalpies=	-823.040776
Sum of electronic and thermal Free Energies=	-823.091345

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	120.134	42.956	106.432

C	0	-3.053333	-0.887302	-0.665137
C	0	-1.825514	-1.320362	-0.139215
C	0	-0.962542	-0.418626	0.514913
C	0	-1.352414	0.927372	0.637817
C	0	-2.579405	1.366646	0.110429
C	0	-3.433412	0.462153	-0.544385
H	0	-3.710899	-1.597279	-1.170631
H	0	-1.529781	-2.368782	-0.237198
H	0	-0.682773	1.614673	1.155590
H	0	-2.872994	2.412949	0.217715
H	0	-4.386334	0.802421	-0.953108

C	0	0.374063	-0.913085	1.081351
H	0	0.865588	-1.500959	0.188570
H	0	0.211312	-1.720971	1.830908
O	0	1.238754	0.029149	1.507122
S	0	2.791440	0.116728	-0.129954
C	0	1.908576	1.565293	-0.819522
H	0	2.453794	1.945367	-1.694322
H	0	0.887628	1.262083	-1.077082
H	0	1.872295	2.314360	-0.020760
C	0	2.256769	-1.146124	-1.069391
H	0	2.805962	-2.083288	-1.004976
H	0	1.516411	-0.997208	-1.853579

Endo-TS1 (PCM – CH_2Cl_2)

E(RB97D) = -823.241536091

Zero-point correction= 0.180161
(Hartree/Particle)
Thermal correction to Energy= 0.191637
Thermal correction to Enthalpy= 0.192582
Thermal correction to Gibbs Free Energy= 0.141471
Sum of electronic and zero-point Energies= -823.062042
Sum of electronic and thermal Energies= -823.050566
Sum of electronic and thermal Enthalpies= -823.049622
Sum of electronic and thermal Free Energies= -823.100732

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	120.254	43.187	107.571

C	0	-3.163749	-0.808175	-0.642089
C	0	-1.939065	-1.311985	-0.173621
C	0	-1.000304	-0.463800	0.449623
C	0	-1.312435	0.899121	0.600870
C	0	-2.537155	1.409831	0.131987
C	0	-3.466806	0.559096	-0.492172
H	0	-3.879066	-1.477200	-1.124395
H	0	-1.705057	-2.373364	-0.293838
H	0	-0.584861	1.547974	1.088641
H	0	-2.766805	2.469870	0.257667
H	0	-4.416839	0.953809	-0.856138
C	0	0.331181	-1.044970	0.944113
H	0	0.808543	-1.524968	0.004206
H	0	0.137381	-1.927830	1.595252
O	0	1.209694	-0.170230	1.502217
S	0	2.818399	0.092056	-0.079545
C	0	2.012254	1.642170	-0.625659
H	0	2.621146	2.101113	-1.415159
H	0	1.003107	1.406475	-0.980039
H	0	1.956474	2.292951	0.253486
C	0	2.340698	-1.019042	-1.207082
H	0	2.845570	-1.983016	-1.205452
H	0	1.620747	-0.770339	-1.985070

Exo-TS1 (gas phase)

E(RB97D) = -823.232178620

Zero-point correction=	0.179996
(Hartree/Particle)	
Thermal correction to Energy=	0.191449
Thermal correction to Enthalpy=	0.192393
Thermal correction to Gibbs Free Energy=	0.141254
Sum of electronic and zero-point Energies=	-823.052182
Sum of electronic and thermal Energies=	-823.040730
Sum of electronic and thermal Enthalpies=	-823.039786
Sum of electronic and thermal Free Energies=	-823.090924

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	120.136	43.059	107.630

C	0	2.799901	-1.417547	0.146243
C	0	1.496475	-1.049048	-0.229436
C	0	1.158354	0.306680	-0.388958
C	0	2.144220	1.288881	-0.169523
C	0	3.447443	0.924616	0.204790
C	0	3.779117	-0.433254	0.366469
H	0	3.053468	-2.473407	0.261087
H	0	0.729008	-1.799507	-0.421388
H	0	1.887728	2.344537	-0.296354
H	0	4.203333	1.695349	0.367946
H	0	4.791955	-0.719570	0.655097
C	0	-0.265812	0.725898	-0.753367
H	0	-0.257002	1.607891	-1.433003
H	0	-0.698574	1.183131	0.236653
O	0	-1.099107	-0.253101	-1.174512
S	0	-2.508930	-0.576186	0.521032
C	0	-3.835287	0.039028	-0.577850
H	0	-4.809632	-0.086724	-0.086694
H	0	-3.636230	1.092193	-0.808654
H	0	-3.773113	-0.551990	-1.498354
C	0	-2.130302	0.731718	1.470320
H	0	-1.521967	0.547378	2.353179
H	0	-2.597896	1.702684	1.317941

Exo-TS1 (PCM – CH_2Cl_2)

E(RB97D) = -823.241252287

Zero-point correction=	0.180159
(Hartree/Particle)	
Thermal correction to Energy=	0.191683
Thermal correction to Enthalpy=	0.192627
Thermal correction to Gibbs Free Energy=	0.141125
Sum of electronic and zero-point Energies=	-823.061488
Sum of electronic and thermal Energies=	-823.049964
Sum of electronic and thermal Enthalpies=	-823.049020
Sum of electronic and thermal Free Energies=	-823.100522

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin

Total		120.283	43.174	108.394
C	0	2.766851	-1.426758	-0.221679
C	0	1.461269	-0.932213	-0.388377
C	0	1.181683	0.433499	-0.188081
C	0	2.232995	1.297005	0.179397
C	0	3.540468	0.807763	0.346019
C	0	3.811709	-0.558754	0.146791
H	0	2.970706	-2.487269	-0.382703
H	0	0.647610	-1.594236	-0.687956
H	0	2.024768	2.359722	0.329505
H	0	4.345787	1.490498	0.623946
H	0	4.826190	-0.941190	0.271297
C	0	-0.243382	0.973670	-0.319106
H	0	-0.218886	2.067888	-0.521200
H	0	-0.681178	0.918045	0.752128
O	0	-1.065505	0.297008	-1.170462
S	0	-2.569338	-0.723665	0.151846
C	0	-3.856124	0.403167	-0.496266
H	0	-4.830335	0.103570	-0.089298
H	0	-3.602614	1.430117	-0.209051
H	0	-3.839882	0.303018	-1.586788
C	0	-2.196537	-0.095658	1.634428
H	0	-1.586887	-0.706399	2.297259
H	0	-2.615428	0.848491	1.978266