Supporting Information for "Kinetics Study and Theoretical Modeling of the Diels-Alder Reactions of Cyclopentadiene and Cyclohexadiene with Methyl Vinyl Ketone. The Effects of A Novel Organotungsten Catalyst"

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Experimental Details

The kinetic study of the uncatalyzed DA reactions of CP and MVK were performed at three different temperatures of 0, 29, and 50 ^{o}C. The CP-to-MVK concentration ratios ([CP]/[MVK]) for each kinetic run are: [CP]/[MVK] = 1 M/0.5 M, 1 M/1 M, 0.5 M/1 M at 0 and 27 ^{o}C; [CP]/[MVK] = 0.5 M/0.25 M, 0.5 M/0.5 M, 0.25 M/0.5 M at 50 ^{o}C.

The uncatalyzed DA reactions of CH and MVK were performed at three different temperatures of 80, 90 and 100 ^{o}C. The [CH]/[MVK] concentration ratios ([CH]/[MVK]) for each kinetic run are: [CH]/[MVK] = 2.5 M/1.25 M, 2.5 M/2.5 M, 1.25 M/2.5 M at all three temperatures.

For the **1**-catalyzed DA reactions, both the CP/MVK and the CH/MVK systems, were performed at three different temperatures of 0, 27, and 50^{o}C. The concentration of organotungsten Lewis acid catalyst **1** was maintained at 0.0022 M in both CP/MVK and CH/MVK systems. The diene-to-MVK concentration ratios ([diene]/[MVK]) for each kinetic run are: For the CP/MVK systems, [CP]/[MVK] = 0.2 M/0.1 M, 0.1 M/0.1 M, 0.1 M/0.2 M at 0 ^{o}C; [CP]/[MVK] = 0.1 M/0.05 M, 0.1 M/0.1 M, 0.05 M/0.1 M at 27 and 50^{o}C. For the CH/MVK systems, [CH]/[MVK] = 0.25 M/0.5 M, 0.25 M/0.25 M, 0.5 M/0.25 M at all three temperatures. In addition, the concentration of catalyst **1** was also doubled from 0.0022 M to 0.0044 M to study the rate dependence on the catalyst concentration. The reactant concentrations and reaction temperatures for this series of kinetic runs are also listed as below. For the **1**-catalyzed CP/MVK systems, [CP]/[MVK] = 0.1 M/0.1 M at 0 ^{o}C; [CP]/[MVK] = 0.1 M/0.05 M, 0.1 M/0.1 M, 0.05 M/0.1 M at 27 ^{o}C; [CP]/[MVK] = 0.1 M/0.1 M at 50 ^{o}C. For the **1**-catalyzed CH/MVK systems, [CH]/[MVK] = 0.25 M/0.25 M at 0 ^{o}C; [CH]/[MVK] = 0.25 M/0.5 M, 0.25 M/0.25 M, 0.5 M/0.25 M at 27 ^{o}C; [CH]/[MVK] = 0.25 M/0.25 M at 50 ^{o}C.

A representative procedure for kinetics studies is as follows: **1** (16 mg, 0.0223 mmol) was added to a calibrated 10-mL flask containing a solution of CP (67 mg, 1.02 mmol) and durane (as an internal standard for ^{1}H NMR measurements, 20 mg, 0.15 mmol) in CH_3NO_2 (5 mL). Another solution of MVK (72 mg, 1.02 mmol) in CH_3NO_2 (3 mL) was then transferred to the flask. Continuous addition of CH_3NO_2 to the reaction mixture until the total volume is exactly 10.0 mL. The final solution (0.1 M CP and 0.1M MVK) was then stirred at 27 ^{o}C and a sample of the reaction mixture (0.1 mL) was collected in a double precision NMR tube equipped with a J-Young valve at 10-minute time intervals and diluted immediately with 0.9 mL of $CDCl_3$, which also

resulted in precipitation of the catalyst. (The deuterated chloroform was degassed and dried over 4 Å molecular sieves.) The diluted mixture was then subjected to ^{1}H NMR analysis for kinetics measurements. We noticed that when the **1**-catalyzed DA reactions were conducted entirely in the NMR tube without thoroughly stirring, the reactions became partially diffusion-controlled and the orders of the reaction could not be unambiguously determined.

A typical procedure for product identification and *endo/exo* ratios determination is as follows: A nitromethane solution containing 0.0022 M concentration of catalyst **1** and 0.1 M concentration of both CP and MVK were stirred at 27 °C for 6 hours. The solutions were then extracted twice with equal volumes of dry diethyl ether, and the extracts were analyzed by GC/MS on a ZB-5 column at 120 °C, on which the *endo*- and *exo*-products had a 2.2 and 2.0 minutes retention time, respectively. The *endo/exo* ratios were obtained from the average of three injections. Both GC peaks gave molecular ion at *m/z* 136.

The *endo/exo* product ratios of the ucatalyzed and catalyzed reactions were studied on a Fisons' make VG-Trio 2000 GC/MS spectrometer. The uncatalyzed DA reactions of CP and MVK were performed at three different temperatures of 0, 29, and 50 °C. The detailed CP-to-MVK concentration ratios ([CP]/[MVK]) and the resulting *endo/exo* product ratios are listed below. [CP]/[MVK] = 1 M/1 M at 0 °C to give *endo/exo* = 93.0/7.0; [CP]/[MVK] = 0.5 M/0.5 M at 29 °C to give *endo/exo* = 91.0/9.0; [CP]/[MVK] = 0.5 M/0.5 M at 50 °C to give *endo/exo* = 87.2/12.8. The **1**-catalyzed DA reactions of CP and MVK were performed at three different temperatures of 0, 27, and 50 °C. The concentration of organotungsten Lewis acid catalyst **1** was maintained at 0.0022 M.. The detailed CP-to-MVK concentration ratios and the resulting *endo/exo* product ratios are listed as following. [CP]/[MVK] = 0.1 M/0.1 M at 0 °C to give *endo/exo* = 99.2/1.8; [CP]/[MVK] = 0.1 M/0.1 M at 27 °C to give *endo/exo* = 98.5/1.5; [CP]/[MVK] = 0.1 M/0.1 M at 50 °C to give *endo/exo* = 95.8/4.2. The **1**-catalyzed DA reactions of CH and MVK were performed at three different temperatures of 0, 27, and 50 °C. The concentration of organotungsten Lewis acid catalyst **1** was maintained at 0.0022 M.. The CH-to-MVK concentration ratios were kept at [CH]/[MVK] = 0.25 M/0.5 M for all three temperatures. All the final reaction mixtures were then extracted twice with equal volumes of dry diethyl ether, and the extarcts were analyzed by GC/MS on a ZB-5 column, on which the *endo* adduct was obtained exclusively with a 2.2- and 2.9 min retention time at 150 and 120 °C, respectively.

The bimolecular rate constants were obtained from the plots $ln\,[b\,(a - x)\,/\,a\,(b - x)]$

/ (*a* *b*) against the elapsed time, where *a* and *b* are initial concentrations of the reactants, and *x* is the reactant concentration that is consumed at any given time, and by the very similar slope values of the plots at different initial reactant concentrations. When the initial concentrations of the two reactants are equal, *x* / *a* (*a* *x*) is plotted against time instead. Two such plots are shown in Figures S1 and S2. The bimolecular initial rate constants are equal to the slopes of these plots. The slopes were obtained using a linear least square fit to the first six data points.

Dynamics Method

The canonical variational theory (CVT) (Ref. 9) was used to calculate the variational effects, and the microcanonical optimized mulidimensional tunneling (OMT) approximation (Ref. 10) was applied to estimate the quantum effects. The low-level potential energy surface information was obtained using the PM3 method because it was found to predict reasonable transition-state geometry and reaction energies (within 5 kcal/mol of the MP2/6-31+G* values). The low-level reaction paths were calculated from –3.5 to 2.5 bohrs with the gradient and hessian step sizes of 0.005 and 0.05 bohrs, respectively in the mass-scaled coordinates with a scaling mass of 1 amu. The geometry optimized at MP2/6-31+G* level and the vibrational frequencies calculated at HF/6-31+G* level (scaled by 0.8929) were used for the high-level data. The SECKART (Ref. 8a) correction scheme was used in the dual-level rate constant calculation. The vibrational frequencies were corrected based on the ICL (Ref. 8c) scheme and the energies in the nonadiabatic region were corrected using linear interpolation (Ref. 8a). The effects of the solvent were not considered explicitly in the dynamics calculation, which is reasonable for the uncatalyzed systems but, as mentioned in the discussion, unreasonable for the catalyzed system due to the large changes in the entropic effects. The high-level classical barrier heights were obtained by fitting the calculated rate constants to experimental data at the middle temperature.

Table S1. The Calculated Bond Lengths (angstrom) of the Forming C C Bonds in the TS of the Uncatalyzed Reactions.

	CP + MVK			
	HF/6-31+G*	MP2/6-31+G*	B3LYP/6-31+G*	B3LYP/LANL2DZ
endo-cis	2.025, 2.401	2.149, 2.522	1.990, 2.690	1.970, 2.850
endo-trans	2.096, 2.276	2.179, 2.358	2.070, 2.430	2.067, 2.460
exo-cis	2.055, 2.378	2.162, 2.464	2.020, 2.580	2.023, 2.610
exo-trans	2.097, 2.304	2.168, 2.381	2.066, 2.460	2.066, 2.480

	CH + MVK			
	HF/6-31+G*	MP2/6-31+G*	B3LYP/6-31+G*	B3LYP/LANL2DZ
endo-cis	2.045, 2.425	2.152, 2.596	2.007, 2.720	1.984, 2.840
endo-trans	2.108, 2.322	2.207, 2.448	2.101, 2.490	2.111, 2.500
exo-cis	2.054, 2.446	2.182, 2.554	2.020, 2.730	2.028, 2.760
exo-trans	2.114, 2.331	2.219, 2.437	2.100, 2.501	2.105, 2.510

Table S2. Calculated Energy Barriers[a] (in kcal/mol) of the Catalyzed Reaction of CP and MVK

	Solvation = Onsager				Solvation = PCM			
	endo-cis	*endo-trans*	*exo-cis*	*exo-trans*	*endo-cis*	*endo-trans*	*exo-cis*	*exo-trans*
HF/LANL2DZ	2.3	0.8	0.9	2.2	15.3	13.4	10.5	12.6
B3LYP/LANL2DZ	7.1	13.3	6.5	12.1	2.0	3.0	3.7	2.4
	(5.4)[b]	(11.5)	(4.9)	(10.5)	(3.7)	(4.8)	(5.4)	(4.0)
MP2/LANL2DZ//B3LYP/LANL2DZ	1.2	5.6	1.2	2.6	8.2	11.2	10.2	11.0
	(0.5)[b]	(3.9)	(0.5)	(1.0)	(9.9)	(13.0)	(11.8)	(12.6)

[a]Born-Oppenheimer energy, not including ZPE. The MP2 and B3LYP results include the counterpoise correction for BSSE.

[b]Including ZPE calculated at B3LYP/LANL2DZ level.

Table S3. Calculated Energy Barriers[a] (in kcal/mol) of the Catalyzed Reaction of CH and MVK

	Solvation = Onsager				Solvation = PCM			
	endo-cis	*endo-trans*	*exo-cis*	*exo-trans*	*endo-cis*	*endo-trans*	*exo-cis*	*exo-trans*
HF/LANL2DZ	2.5	0.7	2.4	2.1	18.3	16.0	13.9	18.2
B3LYP/LANL2DZ	9.7	9.0	7.9	13.4	6.0	4.4	7.2	6.0
	(8.0)[b]	(7.6)	(6.5)	(12.0)	(7.7)	(5.9)	(8.6)	(7.4)
MP2/LANL2DZ//B3LYP/LANL2DZ	0.1	0.3	5.4	0.4	15.5	14.3	19.6	18.6
	(1.8)[b]	(1.1)	(6.8)	(1.1)	(17.2)	(15.8)	(21.0)	(20.1)

[a]Born-Oppenheimer energy, not including ZPE. The MP2 and B3LYP results include the counterpoise correction for BSSE.

[b]Including ZPE calculated at B3LYP/LANL2DZ level.

Table S4. The Calculated[a] Bond Lengths (angstrom) of the Forming C C bonds in the TS of the Catalyzed DA Reactions.

	CP + MVK		CH + MVK	
	HF/LANL2DZ	B3LYP/LANL2DZ	HF/LANL2DZ	B3LYP/LANL2DZ
endo-cis	(2.101, 3.277)	(2.115, 3.170)	(2.106, 3.561)	(2.019, 3.407)
endo-trans	(2.089, 3.276)	(2.053, 3.143)	(2.082, 3.582)	(2.094, 3.691)
exo-cis	(2.078, 3.309)	(2.150, 3.230)	(2.065, 3.940)	(1.968, 4.167)
exo-trans	(2.065, 3.316)	(2.050, 3.240)	(2.111, 3.696)	(1.986, 3.474)

[a]Solvent effects were considered with the Onsager model.

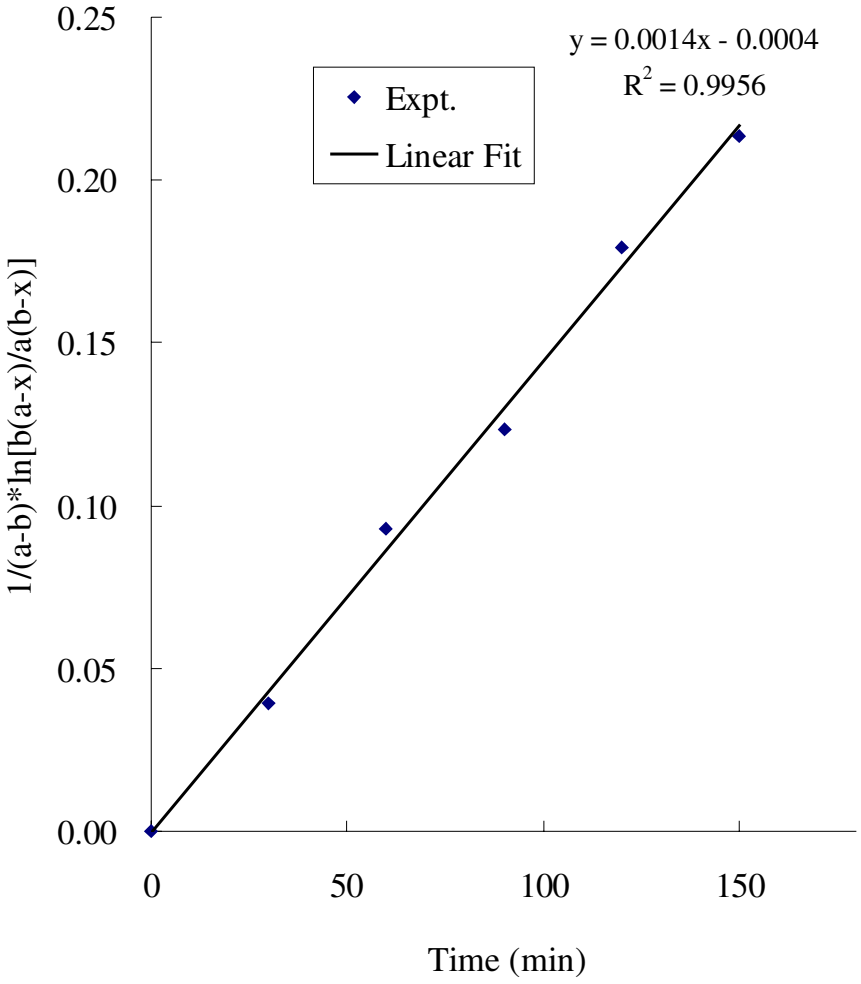

Figure S1. Graph method for obtaining the bimolecular rate constant [CP (0.5M) + MVK (1M) (0 C)].

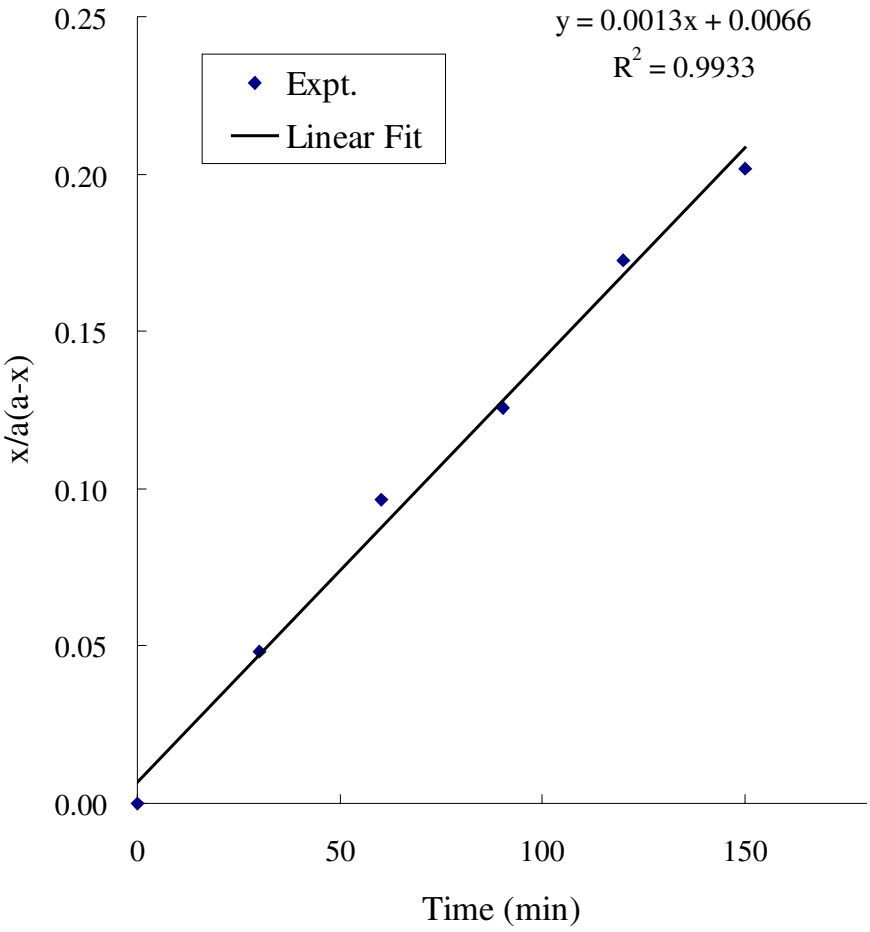

Figure S2. Graph method for obtaining the bimolecular rate constant [CP (1M) + MVK (1M) (0 C)].

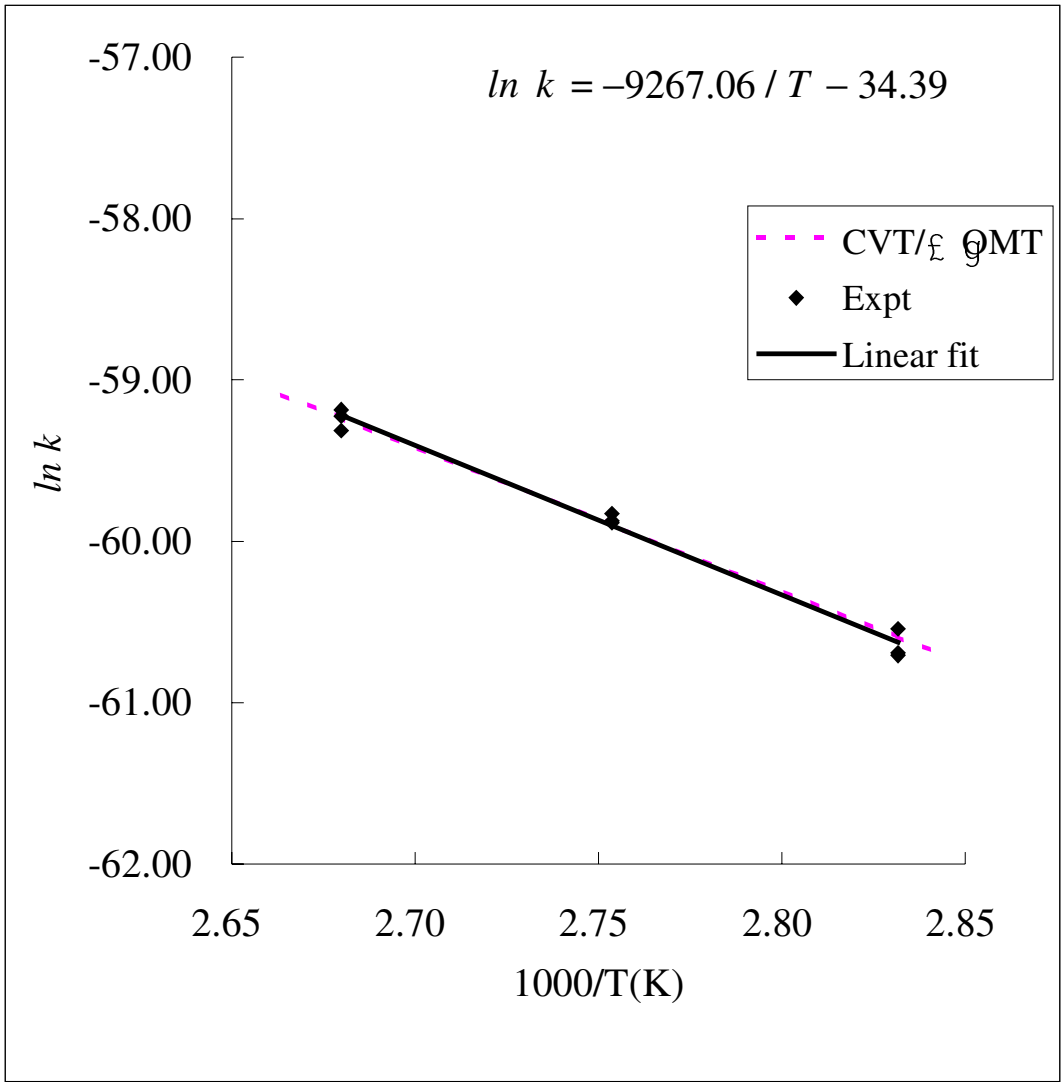

Figure S3. Arrhenius plot of the experimental and calculated rate constants of CH with MVK.

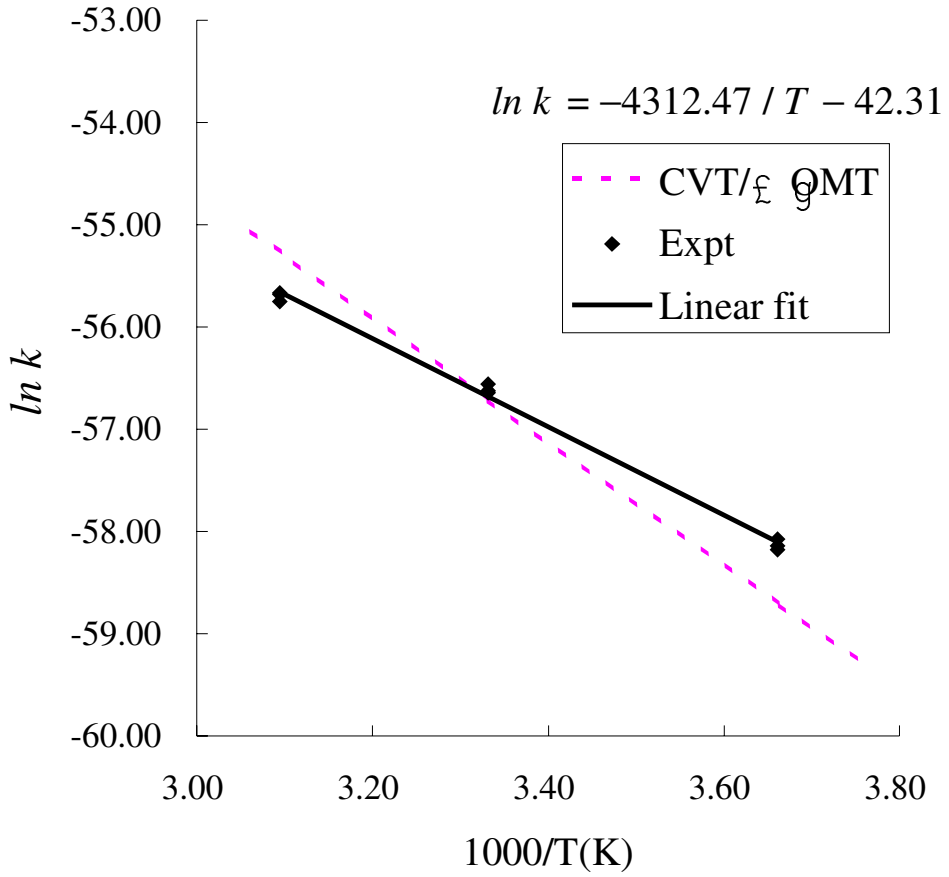

Figure S4. Arrhenius plot of the experimental and calculated catalyzed rate constants of CH with MVK.

Transition State Geometries and Energies

Name: CP+MVK endo-cis TS

OPT Level: B3LYP/6-31+G(d)

Number of imaginary frequency: 1

ZPE: 116.35 kcal/mol

Molecular geometry (in Å):

C,-0.9139198718,-1.3617701755,-0.6133885549

C,-1.9402761403,-0.3309495506,-0.9906059945

C,-1.9036576405,0.5688704863,0.2376658748

C,-1.433639957,-0.2391572382,1.2965873996

C,-0.79289735,-1.3775477555,0.7639173655

H,-0.5182597533,-2.1061446977,-1.2958667063

H,-2.9306783267,-0.8167344786,-1.0311157204

H,-1.7799139455,0.1666407082,-1.9499328

H,-2.6519614677,1.3418386883,0.3965756816

H,-1.4379511518,0.0379260023,2.3449446289

H,-0.2123251824,-2.0880655608,1.3415173943

C,-0.3267284345,1.6717602924,-0.2813050071

C,0.6534254029,0.820580506,-0.8160210672

C,1.6870957975,0.2701984566,0.0473855997

C,2.8212136532,-0.5253697507,-0.5854173913

O,1.6655120573,0.4449925755,1.2740276552

H,-0.1088845292,2.1186242428,0.6844321656

H,-0.8698559776,2.3175441719,-0.9685252443

H,0.7114172673,0.6375729127,-1.8850429344

H,3.0286578831,-1.4151399955,0.0178617063

H,2.6109092029,-0.8223995282,-1.6183657222

H,3.7310567647,0.0887053046,-0.5816130386

Single point energies (in hartrees) :

	Gas-Phase	PCM
B3LYP/6-31+G(d)	-425.33164	-425.33733
B3LYP/6-31+G(d) with BSSE[a]	-425.33013	-425.33582

[a]Estimate by counterpoise calculation.

Name: CP+MVK endo-trans TS

OPT Level: B3LYP/6-31+G*

Number of imaginary frequency: 1

ZPE: 116.57 kcal/mol

Molecular geometry (in Å):

C,-0.5285569223,-1.5444519003,-0.008304552

C,-0.5735018828,-1.4956033029,1.4958720505

C,0.8127195979,-1.5392496985,-0.3864909513

H,-1.3587225827,-1.8466935032,-0.6368514189

C,0.7404284773,-0.7878544006,1.7789075461

C,1.5941537972,-1.1216623182,0.7062176273

H,-0.4911266729,-2.5280830371,1.8780220851

H,-1.4673642289,-1.0486002345,1.9349330896

H,1.1814358202,-1.7225103901,-1.3904822887

H,1.1047216407,-0.6294340956,2.7906375429

H,2.6650547306,-0.9446552137,0.6812259319

C,0.0207077562,1.0770658946,1.2417934964

C,-0.863720516,0.8636407709,0.1714280186

H,0.9558287912,1.6003363456,1.0667486116

H,-0.4046246488,1.2697047269,2.2242699889

C,-0.6018600941,1.2241948749,-1.2317429328

H,-1.9159706512,0.6836175395,0.3748888023

C,0.7930808638,1.6864189914,-1.6317898737

O,-1.5054007418,1.1929394456,-2.0679639828

H,0.8654454643,1.699454961,-2.7218579428

H,0.9697325091,2.7036551681,-1.2576456774

H,1.5780892995,1.0446986999,-1.2155194366

Single point energies (in hartrees):

	Gas-Phase	PCM
B3LYP/6-31+G(d)	-425.32715	-425.33462
B3LYP/6-31+G(d) with BSSE	-425.32554	-425.33302

Name: CP+MVK exo-cis TS

OPT Level: B3LYP/6-31+G*

Number of imaginary frequency: 1

ZPE: 116.49 kcal/mol

Molecular geometry (in Å):

C,1.8074099231,-0.8598671525,0.1902562451

C,1.004727521,-0.2302586551,1.3138764722

C,0.7828689612,1.1438207188,0.7574180806

C,1.7809362826,1.406319114,-0.1759624336

C,2.4469582043,0.2057316269,-0.4831804358

H,2.2619101936,-1.8420926788,0.2917339011

H,1.6630477649,-0.1465043145,2.1966329347

H,0.1023717021,-0.7658103356,1.6166979486

H,0.1264031668,1.8821012102,1.2052431816

H,1.9617552621,2.3643515151,-0.6533625484

H,3.2247039827,0.0950552171,-1.2326526442

C,0.2234819425,-1.260949913,-1.0138512298

C,-0.6528147138,-0.1657405262,-0.9462276692

C,-1.8317258737,-0.1651821532,-0.0793943234

C,-2.8675505734,0.9271105527,-0.3129706531

O,-2.0225030856,-1.0220088445,0.7917973425

H,-0.0847229384,-2.1647857269,-0.4922310767

H,0.7648132002,-1.4360044133,-1.9383886794

H,-0.5829554915,0.6259183865,-1.6860406128

H,-3.4449356046,1.0905830083,0.6009693928

H,-2.4153482765,1.868328586,-0.644942219

H,-3.5627683195,0.5990286271,-1.0978226367

Single point energies (in hartrees):

	Gas-Phase	PCM
B3LYP/6-31+G(d)	-425.33157	-425.33648
B3LYP/6-31+G(d) with BSSE	-425.33002	-425.33493

Name: CP+MVK exo-trans TS

OPT Level: B3LYP/6-31+G*

Number of imaginary frequency: 1

ZPE: 116.46 kcal/mol

Molecular geometry (in Å):

C,1.748041238,-1.0032331564,0.193935205

C,0.9893615257,-0.3467033613,1.3329508017

C,2.4905529989,0.0329109283,-0.4144891114

H,2.1108518193,-2.0261830774,0.2558627627

C,0.8461803347,1.048811502,0.7925222294

C,1.9068297879,1.2686964118,-0.0841385258

H,1.6634626445,-0.3124439971,2.206665329

H,0.0681591277,-0.8366334547,1.6476026038

H,3.2844262476,-0.1107637215,-1.140984122

H,0.2204790698,1.8166748587,1.2331247366

H,2.1687271251,2.2252848084,-0.5247317545

C,0.1128491046,-1.1605753553,-1.0595823696

C,-0.6018516156,0.0436510094,-0.9334821764

H,0.6630374217,-1.3400675611,-1.9779304919

H,-0.2965592615,-2.0683003582,-0.6215303964

C,-1.8812206913,0.2253927928,-0.2293614999

H,-0.3822186924,0.861282945,-1.6123935829

C,-2.5161194559,-0.9262915841,0.546027705

O,-2.4941771209,1.2913822863,-0.3136431726

H,-3.1110654119,-0.5166804492,1.3668054904

H,-3.199519568,-1.4606531498,-0.1271378099

H,-1.8041029162,-1.6585302559,0.9374990681

Single point energies (in hartrees):

	Gas-Phase	PCM
B3LYP/6-31+G(d)	-425.32464	-425.33167
B3LYP/6-31+G(d) with BSSE	-425.32313	-425.33016

Name: CH+MVK endo-cis TS

OPT Level: B3LYP/6-31+G*

Number of imaginary frequency: 1

ZPE: 134.87 kcal/mol

Molecular geometry (in Å):

C,0.5648042449,1.3165496409,0.8492256397

C,1.628658971,1.5602212475,-0.1941881362

C,2.4089029903,0.2721769102,-0.5700434967

C,1.6896670563,-1.0031921458,-0.1428970672

C,1.1105159116,-1.0128806069,1.1341669207

C,0.5224905818,0.1761803659,1.6166797562

H,-0.0431740038,2.1742454255,1.132666712

H,2.331634444,2.3034469585,0.2109694778

H,1.1888635605,2.0373956216,-1.0778408979

H,3.3826650728,0.2773029864,-0.0624211113

H,2.6252370651,0.2508795183,-1.6445706302

H,2.1574756226,-1.9258449743,-0.4855457382

H,0.9082440673,-1.9522323025,1.640978009

H,-0.1249686208,0.1323773389,2.4881334708

C,0.1020424718,-1.0359382365,-1.3698865874

C,-0.8039171766,0.0059144681,-1.1151173138

C,-1.9215131198,-0.2163852583,-0.2110241329

C,-2.9942691862,0.8582093495,-0.0920929637

O,-2.016913833,-1.2609636523,0.4493849612

H,-0.240509966,-2.0346906773,-1.1142285022

H,0.7021860273,-0.974959672,-2.2759628421

H,-0.7490115495,0.9420046148,-1.6618453279

H,-3.2416656135,1.0180424498,0.9625780577

H,-2.6988350444,1.8091769507,-0.5480706187

H,-3.9071268684,0.5054305723,-0.5888554601

Single point energies (in hartrees):

	Gas-Phase	PCM
B3LYP/6-31+G(d)	-464.64245	-464.64837
B3LYP/6-31+G(d) with BSSE	-464.64090	-464.64682

Name: CH+MVK endo-trans TS

OPT Level: B3LYP/6-31+G*

Number of imaginary frequency: 1

ZPE: 135.09 kcal/mol

Molecular geometry (in Å):

C,-0.4344992764,-1.4748270999,0.1414048244

C,-0.4665366731,-1.4402591093,1.6521896791

C,0.7700384275,-1.4719989864,-0.5365340163

H,-1.3377220518,-1.8133501205,-0.3608528059

C,0.7417068345,-0.6735445828,2.2692726755

C,1.8662746133,-0.7914349624,0.0281649618

H,-0.4442635022,-2.4849664973,1.9952517141

H,-1.4211553454,-1.0371134279,2.0057201102

H,0.8134698768,-1.8040598073,-1.5714936771

C,0.4332956746,1.4921731232,0.5527972472

C,1.6639913069,-0.0775048656,1.2137021958

H,1.341724983,-1.3683626859,2.8708237711

H,0.3997470331,0.1060292073,2.9603753091

H,2.7592051606,-0.6166397023,-0.5688099718

C,-0.7892531573,0.9969132787,0.0823903529

H,1.1253971254,1.9497619028,-0.1477629892

H,0.4554241973,1.9380863918,1.5444994587

H,2.4925094492,0.5126676636,1.6037175087

C,-1.2108218649,0.9960575967,-1.3278473296

H,-1.6127225108,0.8620891722,0.7778185371

C,-0.1881603467,1.3239598081,-2.4080001616

O,-2.3838898779,0.7770936571,-1.6342454299

H,-0.59447294,1.0388929994,-3.3812875147

H,0.0081145597,2.4045411078,-2.4165319995

H,0.769649758,0.8184693376,-2.2427465872

Single point energies (in hartrees):

	Gas-Phase	PCM
B3LYP/6-31+G(d)	-464.63865	-464.64556
B3LYP/6-31+G(d) with BSSE	-464.63704	-464.64395

Name: CH+MVK exo-cis TS

OPT Level: B3LYP/6-31+G*

Number of imaginary frequency: 1

ZPE: 134.90 kcal/mol

Molecular geometry (in Å):

C,1.8240445369,-0.9200729664,-0.2255408978

C,1.3277530552,-0.9616921782,1.2153878898

C,0.5795107528,0.3313181211,1.6457100985

C,0.6458813499,1.429481063,0.6187056158

C,1.6427044289,1.4862941977,-0.3321549308

C,2.2979904527,0.3016086724,-0.7236436254

H,2.3303012644,-1.8264912313,-0.5572205088

H,2.2132670415,-1.1025519885,1.8493534431

H,0.6874558359,-1.8348695302,1.37129424

H,1.0270379389,0.7287244408,2.5693098919

H,-0.4609303217,0.1029758447,1.8976389792

H,0.0306304071,2.3093853324,0.7998224902

H,1.8077136199,2.4043397566,-0.8928545255

H,2.9774780794,0.3194458442,-1.5735140139

C,0.1108959243,-1.1640757374,-1.2864817732

C,-0.7968202967,-0.1052584629,-1.1214874308

C,-1.9319050144,-0.1751053553,-0.2099911025

C,-3.0189426512,0.8844820358,-0.350223841

O,-2.052731254,-1.0607115842,0.646936765

H,-0.1491811486,-2.1029834352,-0.8008175158

H,0.5843626831,-1.2732301268,-2.2577646073

H,-0.7791615577,0.721785426,-1.8248844379

H,-3.8930590221,0.4330946535,-0.8371368671

H,-3.338193172,1.2159995931,0.64346085

H,-2.7025468463,1.748191755,-0.9438615531

Single point energies (in hartrees):

	Gas-Phase	PCM
B3LYP/6-31+G(d)	-464.64083	-464.64563
B3LYP/6-31+G(d) with BSSE	-464.63933	-464.64413

Name: CH+MVK exo-trans TS

OPT Level: B3LYP/6-31+G*

Number of imaginary frequency: 1

ZPE: 135.02 kcal/mol

Molecular geometry (in Å):

C,0.7554155644,-0.9221612835,-1.1906458072

C,0.7656108804,-1.0536815471,0.2069904982

H,1.7067388413,-0.9556894914,-1.712096602

H,-0.0670424229,-1.3527640349,-1.7577641891

C,-0.2689756266,-1.7183790113,1.0161202428

H,1.7057298284,-0.9471480687,0.7379846271

C,0.250725061,1.2708134963,0.9740925687

O,-0.0917304952,-1.9120737038,2.2201079232

C,-1.5388402133,-2.2501242344,0.3593493559

C,-1.1276850241,1.2965402483,0.3551049826

H,0.3050955192,1.1118485919,2.0484010136

C,1.3314936231,1.8023683904,0.2962658977

H,-2.3165624343,-2.3520497109,1.120361424

H,-1.9054765009,-1.6274492448,-0.4619867612

H,-1.3335168699,-3.2475084391,-0.0517946059

C,-1.0982057819,1.1891142788,-1.1995488746

H,-1.5881770833,2.2535508667,0.6403662803

H,-1.7631546832,0.5258412556,0.8023612448

C,1.347294696,1.7401106113,-1.1102969021

H,2.2417556132,2.0589154356,0.8346018515

C,0.3118067935,1.0548043126,-1.7561082957

H,-1.7270215087,0.3635982626,-1.5523492512

H,-1.5323570395,2.099958358,-1.6315998725

H,2.2639942111,1.9743566948,-1.6479949944

H,0.3719986561,0.9346975864,-2.8372955487

Single point energies (in hartrees):

	Gas-Phase	PCM
B3LYP/6-31+G(d)	-464.63481	-464.64097
B3LYP/6-31+G(d) with BSSE	-464.63319	-464.63935

Name: CP+MVK endo-cis TS

OPT Level: MP2/6-31+G*

Molecular geometry (in Å):

C,-0.783252042,-1.273838546,-0.6538922722

C,-1.8672716649,-0.3182817746,-1.0597447852

C,-1.9771516579,0.5425311019,0.1756124571

C,-1.4906242999,-0.2188970856,1.2444389205

C,-0.7443622807,-1.3069777944,0.7311867332

H,-0.3470240032,-2.0177691077,-1.3159809117

H,-2.8088794884,-0.8873142979,-1.1508162692

H,-1.7058498,0.2147222857,-1.9997646488

H,-2.7235765922,1.3260655228,0.2861718905

H,-1.5436308766,0.0587842075,2.2931895764

H,-0.1464054882,-1.9853785625,1.3326680421

C,-0.2550355331,1.7154757359,-0.3496268364

C,0.6652250884,0.7840055964,-0.8056779914

C,1.6477139252,0.2275222841,0.1298507848

C,2.7571711734,-0.6273127852,-0.4433446031

O,1.5716553489,0.4499173833,1.3508219764

H,-0.1022493469,2.1355831643,0.6402912941

H,-0.7935866598,2.3354818807,-1.0628040933

H,0.7819624358,0.5764565161,-1.8678202129

H,3.3643969637,-1.0294210839,0.3702107691

H,2.3463386782,-1.4486879466,-1.0410914853

H,3.3907851354,-0.0232220396,-1.1036442059

Single point energies (in hartrees):

	Gas-Phase	PCM
MP2/6-31+G(d)	-423.93569	-423.93998
MP2/6-31+G(d) with BSSE	-423.92372	-423.92801

Name: CP+MVK endo-trans TS

OPT Level: MP2/6-31+G*

Molecular geometry (in Å):

C,-0.4830783657,-1.4895740895,0.0318335878

C,-0.445841003,-1.4597956654,1.5327831817

C,0.8353923402,-1.4306993773,-0.4119081895

H,-1.3259514016,-1.8422742969,-0.55703952

C,0.8589177353,-0.7409022473,1.7707605174

C,1.6610319524,-0.9996001727,0.651392173

H,-0.3139880911,-2.4978989841,1.8856422011

H,-1.325086849,-1.042201044,2.0274914272

H,1.158337837,-1.5782891972,-1.4390678548

H,1.2563167175,-0.5453647965,2.7644082606

H,2.7204638631,-0.7687611713,0.5698287801

C,-0.0557828458,1.1614022212,1.2309778805

C,-0.9239542601,0.8211740859,0.1964968709

H,0.8583647588,1.7095419741,1.0241867705

H,-0.4572457046,1.305718435,2.2314261584

C,-0.6670701018,1.1072832903,-1.2264053949

H,-1.9651081524,0.5894233362,0.414788775

C,0.6884089474,1.6488092715,-1.6310702067

O,-1.55865832,0.9469080391,-2.0738004546

H,0.7813592203,1.5813594256,-2.7170042053

H,0.767627274,2.7014536336,-1.3338639357

H,1.5060306947,1.1034444732,-1.1495557427

Single point energies (in hartrees):

	Gas-Phase	PCM
MP2/6-31+G(d)	-423.93167	-423.93825
MP2/6-31+G(d) with BSSE	-423.91958	-423.92616

Name: CP+MVK exo-cis TS

OPT Level: MP2/6-31+G*

Molecular geometry (in Å):

C,1.8749051262,-0.8513702186,0.1711215031

C,0.9932999333,-0.3133490909,1.2657531632

C,0.6833949277,1.0550885601,0.7456104395

C,1.6893984476,1.4059858646,-0.1516728063

C,2.4402206629,0.2554758283,-0.479209212

H,2.3462904591,-1.8304990632,0.2190735171

H,1.6260611284,-0.196238132,2.1636780148

H,0.1278782486,-0.923520115,1.5338717261

H,0.0083888959,1.7534359612,1.235137838

H,1.8198089712,2.3881554125,-0.5993063862

H,3.2254980076,0.2120247768,-1.2298071465

C,0.1738302971,-1.2675927701,-1.095553179

C,-0.6359416915,-0.1482787613,-0.9518379793

C,-1.7960054417,-0.139322809,-0.0495078313

C,-2.783024116,0.9965125638,-0.219231026

O,-1.9953698559,-1.0327572938,0.791015557

H,-0.1095249363,-2.1764020877,-0.5680451898

H,0.7461300615,-1.4007089925,-2.0084242116

H,-0.5638117924,0.6663286633,-1.6693412833

H,-3.4403768063,1.0409600342,0.6516185323

H,-2.2709134255,1.9544886187,-0.3567827317

H,-3.3929388379,0.8151382724,-1.1126355663

Single point energies (in hartrees):

	Gas-Phase	PCM
MP2/6-31+G(d)	-423.93448	-423.93888
MP2/6-31+G(d) with BSSE	-423.92270	-423.92710

Name: CP+MVK exo-trans TS

OPT Level: MP2/6-31+G*

Molecular geometry (in Å):

C,1.7772785848,-1.0080106559,0.2163210666

C,0.9539804359,-0.3528631906,1.2958053097

C,2.4903706033,0.0241732,-0.4115613239

H,2.1354700882,-2.0331639305,0.2838449158

C,0.7821781952,1.0254365569,0.729444878

C,1.8621576653,1.2546873485,-0.1203128626

H,1.6028386195,-0.2714668745,2.1857522208

H,0.0426788179,-0.8712978473,1.5933230777

H,3.2958440852,-0.1141911787,-1.128493393

H,0.1474208627,1.7950601567,1.1605956933

H,2.1076496709,2.2088808294,-0.5790775225

C,0.0662798863,-1.1781523313,-1.1044940972

C,-0.5943517835,0.0388526349,-0.9448312377

H,0.6529171791,-1.3470007892,-2.0022291996

H,-0.3281572571,-2.0819110318,-0.6456184971

C,-1.8370745852,0.2399678022,-0.1774545602

H,-0.3817408337,0.856048193,-1.6299435914

C,-2.5030833689,-0.9254917233,0.531296024

O,-2.3973795289,1.3477199033,-0.1754163484

H,-3.1183335719,-0.532773061,1.3438290308

H,-3.1610394271,-1.4335278041,-0.183847144

H,-1.8029258022,-1.668013737,0.9199160172

Single point energies (in hartrees):

	Gas-Phase	PCM
MP2/6-31+G(d)	-423.92752	-423.93356
MP2/6-31+G(d) with BSSE	-423.91585	-423.92190

Name: CH+MVK endo-cis TS

OPT Level: MP2/6-31+G*

Molecular geometry (in Å):

C,0.5023672925,1.3359700367,0.7210469175

C,1.6031793303,1.5072330156,-0.2975406862

C,2.4416664334,0.2249717047,-0.4755391298

C,1.6938496043,-1.0256502542,-0.0645674972

C,1.0065094089,-0.9929631245,1.1438085588

C,0.4221743055,0.2347017939,1.54468212

H,-0.0893392761,2.2212412362,0.9590008421

H,2.2638535624,2.3148237434,0.0468300384

H,1.1958711426,1.8546482634,-1.2542784851

H,3.330248407,0.2863464381,0.167142321

H,2.8077357695,0.1409784567,-1.5051271905

H,2.1140618369,-1.9749052144,-0.3970975165

H,0.711161872,-1.9129240144,1.6433466741

H,-0.2691929065,0.2428232746,2.385224395

C,0.0793722285,-0.9414571935,-1.484711854

C,-0.8044904586,0.0686611227,-1.1310056983

C,-1.8588734975,-0.2271703469,-0.1642877108

C,-2.9406518208,0.8037337827,0.0762477918

O,-1.870775991,-1.3129435871,0.4470185347

H,-0.2149862051,-1.9593595482,-1.2458317185

H,0.7231579627,-0.8092534877,-2.3520998228

H,-0.8010148181,1.0335783591,-1.6311645574

H,-3.2593480615,0.7583582112,1.120884913

H,-2.6088816604,1.816355614,-0.1713937573

H,-3.8077366566,0.5626541416,-0.5503812828

Single point energies (in hartrees):

	Gas-Phase	PCM
MP2/6-31+G(d)	-463.09727	-463.10159
MP2/6-31+G(d) with BSSE	-463.08476	-463.08908

Name: CH+MVK endo-trans TS

OPT Level: MP2/6-31+G*

Molecular geometry (in Å):

C,-0.3741071353,-1.4406643961,0.1529894876

C,-0.3589544462,-1.4138582831,1.660314003

C,0.8092000508,-1.3773863287,-0.5532921698

H,-1.2704395873,-1.8315833143,-0.3280931745

C,0.8048379417,-0.572003601,2.2485902332

C,1.9011458284,-0.6609035706,-0.0060989751

H,-0.2492724935,-2.4548049833,1.9942686281

H,-1.3276783083,-1.0790044229,2.045998862

H,0.833465423,-1.6807426034,-1.5989292831

C,0.3015538507,1.5849283595,0.5358003919

C,1.7120215965,0.0187038567,1.1908332782

H,1.4281839721,-1.2190997128,2.8785513407

H,0.4267915969,0.2167809883,2.9091026212

H,2.7591184234,-0.4244738589,-0.6351352945

C,-0.8615124145,0.9583530786,0.1073183928

H,0.9656981864,2.0517147207,-0.1855086315

H,0.3372681165,2.0095333585,1.5358730414

H,2.5125234101,0.6632642191,1.5559779036

C,-1.2560931572,0.846301331,-1.3068921997

H,-1.6707632781,0.7739599717,0.8110693946

C,-0.2534232225,1.2228311911,-2.3787791359

O,-2.4062267915,0.498855502,-1.617808675

H,-0.6043629135,0.8320886498,-3.3361996046

H,-0.1859514962,2.3152952553,-2.4493446895

H,0.7472199259,0.8384178915,-2.159861552

Single point energies (in hartrees):

	Gas-Phase	PCM
MP2/6-31+G(d)	-463.09294	-463.09827
MP2/6-31+G(d) with BSSE	-463.08081	-463.08614

Name: CH+MVK exo-cis TS

OPT Level: MP2/6-31+G*

Molecular geometry (in Å):

C,1.8808084078,-0.9084868833,-0.1504981051

C,1.2018637441,-0.9359405064,1.2024587498

C,0.568378738,0.4208178179,1.6001101368

C,0.5471625883,1.4222051186,0.4755063656

C,1.5942278249,1.4687177906,-0.4207907405

C,2.3350616449,0.2925503643,-0.6856840121

H,2.3831453134,-1.8301235511,-0.4474026815

H,1.9716337728,-1.1978458704,1.9398781084

H,0.4521812375,-1.7315107158,1.2386240831

H,1.1600251945,0.8733143575,2.4085900561

H,-0.43448164,0.2630764578,2.0081179758

H,-0.0984016609,2.2939660774,0.5881534356

H,1.7311193183,2.3438108102,-1.0556098852

H,3.0505445558,0.2828523208,-1.5075068987

C,0.0792363177,-1.1583318311,-1.3561993885

C,-0.7718621292,-0.0919460905,-1.1015280452

C,-1.8816473829,-0.2027521422,-0.1442301199

C,-2.9563073589,0.8617591565,-0.2181239254

O,-1.9724160594,-1.1381919689,0.6674777504

H,-0.1385720784,-2.1135869791,-0.8833067353

H,0.6051408228,-1.1978807625,-2.3053012196

H,-0.7970659391,0.7511065749,-1.7879278423

H,-3.5752760678,0.6937271381,-1.1079794381

H,-3.5902862382,0.7999215503,0.6688688384

H,-2.5219124826,1.8631515762,-0.303145293

Single point energies (in hartrees):

	Gas-Phase	PCM
MP2/6-31+G(d)	-463.09345	-463.09669
MP2/6-31+G(d) with BSSE	-463.08172	-463.08496

Name: CH+MVK exo-trans TS

OPT Level: MP2/6-31+G*

Molecular geometry (in Å):

C,0.776266294,-0.9843044803,-1.1860977625

C,0.7760508423,-1.0554394687,0.2038227825

H,1.7279276824,-0.9724565005,-1.7082977813

H,-0.056965088,-1.384574616,-1.758882586

C,-0.2997127274,-1.6518012474,1.0165045715

H,1.7147465646,-0.9553994293,0.7425730955

C,0.2755713903,1.1985021232,0.9703204463

O,-0.1713918131,-1.7507274612,2.2472961215

C,-1.5268332354,-2.2358946396,0.343713855

C,-1.1021978486,1.2425058136,0.359982146

H,0.3394242035,1.0247902176,2.0440774483

C,1.3427918415,1.7562166691,0.2958634883

H,-2.3063469815,-2.3654384662,1.097444092

H,-1.9010612914,-1.6182764374,-0.4761714023

H,-1.2731315413,-3.2189678966,-0.0704322296

C,-1.0898564399,1.1446611356,-1.1898531385

H,-1.5472628851,2.2043160153,0.6488734364

H,-1.7458121874,0.4779817681,0.8080538844

C,1.3418651144,1.7481161665,-1.1188558738

H,2.2662330633,1.9790564609,0.829396888

C,0.3039912447,1.0958802584,-1.7744580934

H,-1.6808356784,0.2928456082,-1.5446195059

H,-1.5782130347,2.0362440415,-1.6034400882

H,2.2616855266,1.978675633,-1.65569197

H,0.363127297,0.9763693082,-2.8569067825

Single point energies (in hartrees):

	Gas-Phase	PCM
MP2/6-31+G(d)	-463.08875	-463.09303
MP2/6-31+G(d) with BSSE	-463.07678	-463.08107

Name: Catalyzed CP+MVK endo-cis TS

OPT Level: B3LYP/LANL2DZ SCRF=(Dipole,Solvent=Nitromethane)

Number of imaginary frequency: 1

ZPE: 203.27 kcal/mol

Molecular geometry (in Å):

C,3.0288662952,0.8405156566,-1.8360013924

C,2.6053588474,1.594784092,-0.7129075837

C,1.3473791211,1.4935322481,-0.0897766447

C,1.0405540931,2.3252372105,1.1359561435

O,0.3942142474,0.7004137972,-0.5919612987

H,2.3013160619,0.2407913093,-2.3754515585

H,3.8243301847,1.2468908108,-2.4564931093

H,3.2791307304,2.3397623466,-0.30225269

H,0.1432176385,2.9400281817,0.9910718618

H,0.8605288773,1.6868366577,2.0096228506

H,1.8708312261,2.9953987799,1.3696271386

W,-1.4463420297,-0.087562069,-0.0129808076

N,-2.3059526792,1.7734237427,-1.0307269028

N,-1.6106492033,0.6586594495,1.6507211876

N,-0.7018891049,-1.5919149445,0.7185164381

N,-1.2886042084,-0.9338595147,-2.1225138426

O,-1.7026498708,1.1473677799,2.7592263484

N,-3.5545482883,-0.8773215041,0.0047588482

H,-3.0285439028,1.6034974028,-1.7436999248

H,-2.7207762449,2.4303012257,-0.3562003468

H,-3.6809398966,-1.4504928312,0.8494678908

H,-4.2714572405,-0.1404284311,0.0491442187

H,-1.5376169418,2.2707043917,-1.500321257

H,-3.7975098203,-1.4792925255,-0.793233926

H,-1.9886591435,-0.6188957414,-2.8066555781

H,-0.3692361278,-0.6130262835,-2.4531208797

H,-1.2917724515,-1.9612441801,-2.1512255973

O,-0.1373887926,-2.5598593427,1.1967087386

C,4.1577101163,-0.4462209364,1.1501830125

C,5.0476406871,-0.0521538651,-0.0040392706

C,4.3410117543,-0.690968158,-1.1992274978

C,3.4128393206,-1.6180107541,-0.6774459293

C,3.2572408392,-1.4136447381,0.7394915414

H,4.270900733,-0.0659733711,2.1602961572

H,6.0285026969,-0.5460682454,0.1128160775

H,5.2498269645,1.0193756598,-0.0804125816

H,4.8314027498,-0.8267596944,-2.1590895037

H,2.8770002924,-2.3579058917,-1.2632762379

H,2.5453270804,-1.9386194734,1.3654920774

Single point energies (in hartrees):

	Onsager	PCM
B3LYP/LANL2DZ	-922.24518	-922.44977
B3LYP/LANL2DZ with BSSE	-922.24246	-922.44705
MP2/LANL2DZ//B3LYP/LANL2DZ	-918.20334	-918.40512
MP2/LANL2DZ//B3LYP/LANL2DZ with BSSE	-918.18807	-918.38985

Name: Catalyzed CP+MVK endo-trans TS

OPT Level: B3LYP/LANL2DZ SCRF=(Dipole,Solvent=Nitromethane)

Number of imaginary frequency: 1

ZPE: 203.35 kcal/mol

Molecular geometry (in Å):

C,-3.1664034706,-1.2259725484,1.4250179049

C,-1.9100665607,-0.8300962261,0.8862899898

H,-3.6283972883,-2.1453004961,1.0748839311

H,-3.3164303174,-1.0432992139,2.4878362496

C,-4.6625956873,0.0977138655,0.9506694851

C,-1.3037301273,-1.4398218544,-0.2353140491

H,-1.3283506591,-0.0933523517,1.431330106

C,-3.9111896585,1.431963785,0.944225213

C,-4.929349348,-0.2183589346,-0.4048739587

H,-5.3454919017,-0.1736650676,1.7520202634

C,-1.9880071632,-2.4870135651,-1.0788809718

O,-0.0472881743,-1.1761717902,-0.5854359716

C,-3.4529649125,1.5374586981,-0.489043679

C,-4.1333827832,0.6109599626,-1.2651739745

H,-4.6383417927,2.2392589722,1.1429109365

H,-3.1159847028,1.5422320491,1.6853223761

H,-5.5915189064,-1.009639881,-0.7429666966

H,-1.5403795885,-2.5231114419,-2.0753666004

H,-1.8646723269,-3.482076662,-0.6280742778

H,-3.062249414,-2.2991202495,-1.1756370982

H,-2.7447616079,2.2784422982,-0.8459351775

H,-4.066982707,0.5118870486,-2.3422453872

W,1.5344579783,0.071215614,-0.0924369959

N,2.5721772433,-1.9284454572,0.2638977101

N,1.208292879,0.3008464904,1.6970286351

N,0.6521924821,1.6359782572,-0.4529108893

N,1.987388419,-0.2983947225,-2.2941912956

N,3.580259173,0.999657207,0.02025055

O,0.9649693777,0.4690073619,2.8771920715

H,3.456556641,-2.0877748758,-0.2380104578

H,2.7725375982,-2.0981277119,1.2585952064

H,3.5051640278,1.9203565227,0.4723982696

H,4.2479831535,0.4566868971,0.5847554233

H,1.9191502221,-2.6635316566,-0.0395940875

H,4.028306901,1.1612044166,-0.8917781718

H,2.8732969505,-0.7731462593,-2.5136971174

H,1.2272084682,-0.9075790742,-2.6254404132

H,1.9666076237,0.5569226392,-2.8643896204

O,0.0124220621,2.6489503207,-0.679580936

Single point energies (in hartrees)

	Onsager	PCM
B3LYP/LANL2DZ	-922.25448	-922.44756
B3LYP/LANL2DZ with BSSE	-922.25240	-922.44548
MP2/LANL2DZ//B3LYP/LANL2DZ	-918.21110	-918.40096
MP2/LANL2DZ//B3LYP/LANL2DZ with BSSE	-918.19518	-918.38504

Name: Catalyzed CP+MVK exo-cis TS

OPT Level: B3LYP/LANL2DZ SCRF=(Dipole,Solvent=Nitromethane)

Number of imaginary frequency: 1

ZPE: 203.24 kcal/mol

Molecular geometry (in Å):

C,3.185417904,-1.6316059584,-0.3874926596

C,2.7051789526,-0.6507299813,-1.2883997897

C,1.3966351333,-0.1317862287,-1.3137840078

C,1.0292660486,0.9352475676,-2.3207444006

O,0.4490176243,-0.5997224471,-0.4897593328

H,2.4842916894,-2.1190491711,0.2865378746

H,4.0330719956,-2.2434210418,-0.6801894387

H,3.3795759514,-0.2745145434,-2.0505156356

H,0.21976919,0.6009025998,-2.9821494233

H,0.6821895002,1.8469097471,-1.8189728421

H,1.8877477973,1.1924085971,-2.9446679806

W,-1.5120771459,-0.1441975874,0.0524764852

N,-2.0575688386,-1.6925932506,-1.5413956374

N,-1.8600201306,1.2470659442,-1.0849108179

N,-1.0179529022,1.0309842611,1.3686223119

N,-1.1292001916,-1.936696755,1.4089230927

O,-2.082787076,2.1776868533,-1.8334875577

N,-3.6607404497,-0.2766561867,0.7131097712

H,-1.1875566266,-2.1261415861,-1.8777286533

H,-2.6739747824,-2.4580830786,-1.2367555327

H,-3.9567468209,0.6531801063,1.038609218

H,-4.3105834746,-0.5360656893,-0.0413152668

H,-2.5145970725,-1.2639452486,-2.3572750545

H,-3.8358104624,-0.9254049291,1.4917850789

H,-0.1531576374,-2.1966785997,1.2175814177

H,-1.2026597644,-1.7090688736,2.4085460499

O,-0.6321013912,1.8066380277,2.2230730492

H,-1.7075544645,-2.7723477809,1.2536698232

C,4.2075296007,-0.6638214385,1.2380444845

C,3.3215981594,0.5424480547,1.5301894149

C,3.9254143586,1.6171425067,0.6615174955

C,5.1356701707,1.1815235609,0.1512938019

C,5.3440692243,-0.1861601184,0.5525056616

H,4.2242487654,-1.5487159654,1.8681720989

H,3.4433527188,0.8164414857,2.5927878803

H,2.2494010009,0.392800748,1.371844402

H,3.4871423023,2.6000934326,0.5223820911

H,5.8194152946,1.7613254041,-0.4573050323

H,6.2268107174,-0.7750994941,0.3238687008

Single point energies (in hartrees)

	Onsager	PCM
B3LYP/LANL2DZ	-922.24403	-922.44682
B3LYP/LANL2DZ with BSSE	-922.24156	-922.44435
MP2/LANL2DZ//B3LYP/LANL2DZ	-918.20235	-918.40100
MP2/LANL2DZ//B3LYP/LANL2DZ with BSSE	-918.18810	-918.38675

Name: Catalyzed CP+MVK exo-trans TS

OPT Level: B3LYP/LANL2DZ SCRF=(Dipole,Solvent=Nitromethane)

Number of imaginary frequency: 1

ZPE: 203.18 kcal/mol

Molecular geometry (in Å):

C,3.1840944249,1.4293272858,1.2245498442

C,1.9210108746,0.9848417709,0.7349809752

C,1.2110088561,1.588164109,-0.3244425863

C,1.7366878629,2.7045517454,-1.1939536537

O,-0.0499211688,1.2495723493,-0.6005784503

H,3.6006365156,2.3573043877,0.8375712316

H,3.3777535898,1.2816032323,2.2838520305

H,1.4134090149,0.2000654872,1.2874703958

H,1.584060454,2.4587519327,-2.251738454

H,1.1690805885,3.6247355209,-1.0018454666

H,2.7933585087,2.9244304405,-1.030573158

W,-1.5221831818,-0.1049055568,-0.0783661028

N,-2.6496275383,1.8106566033,0.4364679797

N,-1.0755218016,-0.3970883264,1.6749879967

N,-0.5911202113,-1.6062175587,-0.5658071066

N,-2.13016603,0.3375601208,-2.2301082926

O,-0.7527951143,-0.6042771703,2.8304724727

N,-3.5055140851,-1.1537583125,0.1010620671

H,-2.0565262426,2.5956556899,0.1354097968

H,-3.5684305408,1.9429135765,-0.0080443702

H,-3.359273223,-2.0658346291,0.5528929474

H,-4.190329294,-0.6514945604,0.6822389243

H,-2.8009355487,1.9202844176,1.4480093517

H,-3.9660124358,-1.3463711204,-0.7985528497

H,-3.053592541,0.7672070812,-2.3757156768

H,-1.4274699865,1.006632983,-2.5729181981

H,-2.09373493,-0.4872966536,-2.8428322415

O,0.0702481338,-2.5809212753,-0.8785349542

C,4.7462396526,0.2815313903,0.5570796035

C,4.4128646631,0.0152266787,-0.9107814663

C,3.6299400008,-1.2704140174,-0.842890913

C,3.7650828437,-1.8359324627,0.4158910449

C,4.5106993159,-0.9348189517,1.2472635093

H,5.533078085,0.9724278465,0.8505667581

H,5.3576301851,-0.1655903002,-1.45353449

H,3.9051175498,0.8215396048,-1.4446468541

H,3.0913995334,-1.701482517,-1.6803237656

H,3.3611211548,-2.7907647638,0.7298440165

H,4.7888369047,-1.1296306595,2.2786924807

Single point energies (in hartrees)

	Onsager	PCM
B3LYP/LANL2DZ	-922.25334	-922.44934
B3LYP/LANL2DZ with BSSE	-922.25047	-922.44646
MP2/LANL2DZ//B3LYP/LANL2DZ	-918.20582	-918.40087
MP2/LANL2DZ//B3LYP/LANL2DZ with BSSE	-918.19039	-918.38545

Name: CH+MVK endo-cis TS

OPT Level: B3LYP/LANL2DZ SCRF=(Dipole,Solvent=Nitromethane)

Number of imaginary frequency: 1

ZPE: 222.07 kcal/mol

Molecular geometry (in Å):

N,-2.6140973447,1.5369009509,-1.2902934951

H,-3.4070587919,1.2499379799,-1.8814777142

H,-2.9638698171,2.3081076626,-0.7056813398

H,-1.9063522846,1.93551972,-1.9212460509

W,-1.6573388718,-0.1241863621,-0.0413602755

O,0.1530112306,0.5550622952,-0.821848444

N,-1.731256692,0.8795771473,1.4893316335

N,-0.8338891396,-1.4774842303,0.8746354986

N,-1.6081769875,-1.2937580015,-1.993297154

N,-3.7485373383,-0.9113743037,0.2231216634

C,1.1010021113,1.4639632713,-0.5508370599

O,-1.7498867904,1.5411954884,2.5087653552

H,-3.8058439181,-1.4057053517,1.1235711143

H,-4.4640042976,-0.1718913403,0.2599617471

H,-4.0576604201,-1.5819221986,-0.4938338195

H,-2.3373349841,-1.0756317935,-2.6854935196

H,-0.7032833482,-1.0536025367,-2.418652274

H,-1.6314505897,-2.3125727076,-1.8578133203

O,-0.1939270623,-2.3350055606,1.4616557118

C,2.3896527645,1.3375453449,-1.090881307

C,0.7455804248,2.6605319067,0.3054771768

C,2.8343606587,0.248245065,-1.9014932992

H,3.0708805508,2.1632282973,-0.9107439773

H,-0.1166381723,3.2032736766,-0.103011524

H,0.4876713331,2.3561967863,1.3272332163

H,1.5811179319,3.3624943267,0.359608034

C,3.8715546076,0.008624666,1.6742976301

H,2.0801220882,-0.4448788095,-2.2670786809

H,3.6173526159,0.4657184593,-2.6275835145

C,5.0048038538,0.573931426,0.8469944282

C,3.0949213967,-1.0571372992,1.2858670995

H,3.6926863199,0.4706711128,2.6457308204

C,5.2892651251,-0.2190239169,-0.4609847777

C,3.2291140907,-1.6109154522,-0.0328140823

H,5.9109051196,0.595650751,1.4714568205

H,4.7848932566,1.6295018723,0.6352906037

H,2.3332585451,-1.4581407977,1.9481243291

C,4.095183083,-1.0303468365,-0.9793690754

H,6.0945517422,-0.9450614122,-0.2760488129

H,5.6622279775,0.4553445697,-1.2406065678

H,2.57432502,-2.4285398435,-0.3280699965

H,4.2920754314,-1.607465405,-1.8835835968

Single point energies (in hartrees)

	Onsager	PCM
B3LYP/LANL2DZ	-961.56043	-961.75504
B3LYP/LANL2DZ with BSSE	-961.55722	-961.75182
MP2/LANL2DZ//B3LYP/LANL2DZ	-957.31490	-957.50744
MP2/LANL2DZ//B3LYP/LANL2DZ with BSSE	-957.29801	-957.49055

Name: CH+MVK endo-trans TS

OPT Level: B3LYP/LANL2DZ SCRF=(Dipole,Solvent=Nitromethane)

Number of imaginary frequency: 1

ZPE: 221.79 kcal/mol

Molecular geometry (in Å):

C,0.1867303775,-0.5289810936,-3.4213087737
C,0.2120240435,-0.3451201164,-2.0071418244
H,1.1240509036,-0.6717502538,-3.9532963559
H,-0.6318261544,-1.1336675734,-3.808519111
C,1.3740053259,-0.1018496403,-1.2623347302
H,-0.7172640964,-0.494482302,-1.464177486
C,2.7291640528,0.1670411712,-1.8685428349
O,1.3748794043,-0.1532316271,0.0820653758
W,0.0742271297,-0.6026741252,1.6068090428
H,3.3225071045,0.7960724742,-1.1985760696
H,3.2808577739,-0.7737489547,-2.0073220862
H,2.6589675214,0.6583574575,-2.8429286885
N,1.8026325966,-1.9917890752,2.1651625876
N,-0.8463051777,-1.9868486146,0.8316157883
N,-1.2521289594,0.566963953,1.1368087583
N,1.3075012313,1.0435504181,2.5917683845
N,-0.759639033,-1.0300528015,3.661236407
O,-1.4575661267,-2.9008473639,0.3145255214
H,2.2092058051,-1.8897228454,3.10355491
H,1.5593926073,-2.9847617702,2.0559044918
H,-1.7829491934,-1.0924354912,3.5831816669
H,-0.4429536374,-1.9248222653,4.0565539207
H,2.5428536525,-1.7829708804,1.4817020454
H,-0.5625686834,-0.3038467134,4.361463271
H,1.8782910904,0.7798437308,3.4045010715
H,1.9501393907,1.3481867184,1.8481503412
H,0.7470170617,1.8575953416,2.8725326772
O,-2.1166525985,1.3455248303,0.7667109185
C,-0.6729659714,3.1755146952,-2.6752513801
C,-1.9162716785,2.3259111823,-2.775851966
C,0.4313469473,3.0101403122,-3.4773313615
H,-0.6684994695,3.9576680845,-1.9162018297
C,-1.9604685912,1.4157630935,-4.0349664389

C,0.4723135013,1.948566534,-4.446863381

H,-2.7956323648,2.984737265,-2.7604474041

H,-1.998494832,1.7419378621,-1.8464167332

H,1.2892914654,3.6682233431,-3.3733365474

C,-0.583827,1.0342869607,-4.5812394699

H,-2.4769566244,1.9498154035,-4.8471070244

H,-2.5628034047,0.5215283695,-3.834671923

H,1.3702722786,1.8243660545,-5.0509893202

H,-0.5877218719,0.4097897415,-5.474988028

Single point energies (in hartrees)

	Onsager	PCM
B3LYP/LANL2DZ	-961.55865	-961.75690
B3LYP/LANL2DZ with BSSE	-961.55604	-961.75429
MP2/LANL2DZ//B3LYP/LANL2DZ	-957.31376	-957.50758
MP2/LANL2DZ//B3LYP/LANL2DZ with BSSE	-957.29864	-957.49247

Name: CH+MVK exo-cis TS

OPT Level: B3LYP/LANL2DZ SCRF=(Dipole,Solvent=Nitromethane)

Number of imaginary frequency: 1

ZPE: 221.75 kcal/mol

Molecular geometry (in Å):

C,-2.7821758054,-1.4092604193,-1.242311961

C,-2.2843261081,-1.6390188333,0.0878917802

C,-1.0157833292,-1.2855790182,0.5497429008

C,-0.6269756296,-1.5624917241,1.9863866648

O,-0.0916167929,-0.7448607942,-0.2731508653

H,-2.0689188388,-0.9851764143,-1.9494873748

H,-3.396043484,-2.1882091584,-1.6888333715

H,-2.9246631622,-2.1589287099,0.7947238865

H,0.2425286916,-2.2283807711,2.04761863

H,-0.3606145868,-0.6327339588,2.5053789914

H,-1.4506948834,-2.0349892019,2.526819965

W,1.7988016351,0.0895384178,-0.1287197283

N,2.4640924045,-1.9805535721,-0.8436922445

N,2.2139112236,-0.3004714158,1.609572557

N,1.2201748858,1.7562437546,0.369126921

N,1.3479994502,0.5114047017,-2.3233299266

O,2.4809452364,-0.5467720245,2.770781134

N,3.905069374,0.7518351355,-0.5901004376

H,3.0472776987,-2.0105100779,-1.6908168431

H,2.9820758328,-2.4961598876,-0.1200071714

H,4.1756991588,1.4701341943,0.0943578393

H,4.6008136115,-0.0013581978,-0.5060436543

H,1.611072088,-2.5183455137,-1.0455948898

H,4.03538999,1.1729866531,-1.5193107391

H,1.9471117302,0.0534350102,-3.0221192987

H,0.392331393,0.1560763242,-2.4528372507

H,1.3448655116,1.5139201564,-2.5492063805

O,0.7894048565,2.8434810124,0.709812405

C,-4.0581738068,0.0890273307,-1.2857966968

C,-3.5397723408,1.2312871314,-0.391428018

C,-4.6121422579,1.8052877202,0.5695872929

C,-5.5398481078,0.750383142,1.1154924493

C,-5.8440673006,-0.3838611108,0.3985960071

C,-5.2440524579,-0.5786362528,-0.8911638677

H,-3.9348448345,0.213061286,-2.3633718506

H,-3.1475886004,2.0387170521,-1.0186153631

H,-2.7045411412,0.8556416014,0.2135752012

H,-5.2393320043,2.5544704646,0.0553300265

H,-4.1222725086,2.3469676932,1.3882610533

H,-6.0508336134,0.94656864,2.0582371474

H,-6.5978348553,-1.0833626702,0.7493882259

H,-5.6969990957,-1.2964910003,-1.5747456736

Single point energies (in hartrees)

	Onsager	PCM
B3LYP/LANL2DZ	-961.55725	-961.75273
B3LYP/LANL2DZ with BSSE	-961.55436	-961.74985
MP2/LANL2DZ//B3LYP/LANL2DZ	-957.30444	-957.49885
MP2/LANL2DZ//B3LYP/LANL2DZ with BSSE	-957.28963	-957.48404

Name: CH+MVK exo-trans TS

OPT Level: B3LYP/LANL2DZ SCRF=(Dipole,Solvent=Nitromethane)

Number of imaginary frequency: 1

ZPE: 221.79 kcal/mol

Molecular geometry (in Å):

C,0.6000340558,-0.5433315783,-3.4962716379

C,0.4651711855,-0.4192384568,-2.0710270519

H,1.606238564,-0.505635578,-3.9135170887

H,-0.0110594233,-1.3193643427,-3.9539873525

C,1.5099030166,-0.1107681309,-1.1838091404

H,-0.4835477081,-0.7171257497,-1.6344621468

C,2.8937572644,0.3317021269,-1.5933163939

O,1.3668731923,-0.2315774706,0.1417487299

H,3.1273319411,1.2974727295,-1.1260487856

H,3.6410908281,-0.3815099954,-1.2236276741

H,3.0184095253,0.4258029508,-2.6735367215

W,-0.052632085,-0.581536033,1.6026200245

N,1.2576033397,-2.401997616,2.0160827547

N,-1.256812494,-1.5714934281,0.6395260623

N,-1.0309333135,0.9306294047,1.2645785661

N,1.4936298753,0.5692759159,2.8183233167

N,-1.0354509487,-1.0296829772,3.5771898086

O,-2.0610181008,-2.1994719763,-0.0258900599

H,1.5932101896,-2.5194199562,2.9822902247

H,0.7962833572,-3.2864876044,1.7646644274

H,-2.0374041609,-0.8069823419,3.5124047955

H,-0.9800185743,-2.0201114393,3.8520734034

H,2.0913709693,-2.3191472417,1.4190446539

H,-0.6693768191,-0.4844398704,4.3695279888

H,1.938848179,0.069144193,3.5997437777

H,2.2375322074,0.805937087,2.1479872812

H,1.135667177,1.4516319282,3.2063603334

O,-1.6627832869,1.9354437923,0.982930268

C,-0.0527020976,0.9557542274,-4.6228167474

C,-1.4248100095,0.9544939776,-4.2861944615

H,0.2182392633,0.4634170985,-5.5588062393

C,0.7505857235,2.2268209643,-4.3171376843

C,0.3141370437,2.9604738255,-3.0158002615

C,-1.9291242638,1.7713613483,-3.2236571962

H,-2.0874940301,0.2177368767,-4.7390688486

H,1.8233396542,2.0070108052,-4.2844910945

H,0.6058487676,2.9005466984,-5.1747109161

C,-1.0921832889,2.6465712037,-2.5667473438

H,0.3908144085,4.0490454725,-3.1574293992

H,0.9967914038,2.7485540172,-2.1826096362

H,-2.9527692521,1.6366016634,-2.8859721804

H,-1.4540136048,3.1656781326,-1.6792581695

Single point energies (in hartrees)

	Onsager	PCM
B3LYP/LANL2DZ	-961.56495	-961.75357
B3LYP/LANL2DZ with BSSE	-961.56315	-961.75177
MP2/LANL2DZ//B3LYP/LANL2DZ	-957.31571	-957.50256
MP2/LANL2DZ//B3LYP/LANL2DZ with BSSE	-957.29876	-957.48561

Name: Catalyzed CP+MVK endo-cis TS2

OPT Level: HF/LANL2DZ

Number of imaginary frequency: 1

ZPE: 219.84 kcal/mol

Molecular geometry (in Å):

C,-2.8915406846,-0.5636831523,-2.1298702779

C,-2.9238235761,-0.7047087603,-0.6254220389

H,-1.8951760677,-0.6694166892,-2.5323849222

H,-3.5081896886,-1.3263941694,-2.5840405059

C,-3.5095605141,0.8544565566,-2.5208982897

C,-1.8247853186,-0.7537982599,0.2118344222

H,-3.8146566512,-1.126212299,-0.2012529005

C,-4.5818104346,1.0976816103,-1.4314234259

C,-2.5005886043,1.9115664452,-2.1698483724

H,-3.8530487516,0.8700375813,-3.5403887734

C,-3.6397009561,1.394708275,-0.2856675178

C,-1.9697431789,-1.0628206177,1.6810084889

O,-0.5951500609,-0.5224250963,-0.2453089361

C,-2.5437074744,2.165010237,-0.8362061697

H,-5.1549721132,1.9922860763,-1.6457208092

H,-5.2668885683,0.2840069371,-1.2699445827

H,-1.8145505166,2.342360688,-2.8712633085

H,-3.9193235138,1.3880421237,0.7482229547

H,-1.4137521264,-1.9568754137,1.9363816521

H,-1.580873871,-0.2516828228,2.284867065

H,-3.0015752133,-1.2256409665,1.9471231976

W,1.3171721361,-0.2390257463,0.3398052926

H,-1.8928747029,2.7929133231,-0.267990888

N,1.5394116714,-2.4039306116,-0.4598319949

N,1.2717085152,-0.8865192228,2.0337262152

N,1.1883917967,1.4908646956,0.8880925016

N,1.4532088796,0.5104059893,-1.838079208

N,3.5797719892,-0.2262440394,0.2728268632

O,1.2555651296,-1.3376965571,3.1218388087

H,2.2084621298,-2.554830779,-1.1987613497

H,1.7481682006,-3.065708314,0.2736985557

H,3.8923722902,0.336844372,1.0523986067

H,3.9889262569,-1.1403150286,0.395046284

H,0.626383573,-2.6353351841,-0.8239077861

H,3.978233586,0.1799778207,-0.5597418159

H,1.9638838414,-0.0559301484,-2.4968754543

H,0.4809720611,0.5037955337,-2.1093050363

H,1.7942180709,1.4566002966,-1.9178353486

O,1.0955397046,2.6259804795,1.1982078728

Single point energies (in hartrees)

	Gas-Phase	PCM
HF/LANL2DZ	-916.18330	-916.40580
MP2/LANL2DZ//HF/LANL2DZ	-918.18055	-918.39518
MP2/LANL2DZ//HF/LANL2DZ with BSSE	-918.15249	-918.36712

Name: Catalyzed CP+MVK endo-trans TS2

OPT Level: HF/LANL2DZ

Number of imaginary frequency: 1

ZPE: 219.71 kcal/mol

Molecular geometry (in Å):

C,3.4582146622,0.3923985835,1.4668870975

C,2.128385708,0.2284228781,0.7405417784

H,3.776016761,1.4204998008,1.5474787506

H,3.3617008382,0.0116105183,2.4738686659

C,4.5581889787,-0.4769209219,0.7152171024

C,1.4271109439,1.2748794105,0.145157847

H,1.5079730447,-0.5712303023,1.1016811943

C,3.7424051966,-1.6683839463,0.1632555136

C,4.9141193334,0.2433756735,-0.5560649524

H,5.3872812484,-0.7152182507,1.3576210785

C,2.022652646,2.6042142357,-0.2140654386

O,0.1347088655,1.1650549233,-0.1491866498

C,2.9871854166,-0.8987722686,-0.9033622998

C,3.9425122993,0.0319158065,-1.479665177

H,5.7616674543,0.8882297444,-0.6683042769

H,4.3846989606,-2.3937567708,-0.320830589

H,3.1319669937,-2.17903389,0.8883374299

H,1.5155146263,3.0247345119,-1.0698020835

H,1.8967582479,3.287634016,0.6200671773

H,3.0788211285,2.5351597277,-0.4193164893

W,-1.4801541825,-0.0244069602,-0.0319052533

H,2.1275316397,-1.2767202491,-1.4186032107

H,3.8523839353,0.4889522788,-2.4409053047

N,-2.3430792683,1.8453481065,1.0214515115

N,-1.223553333,-0.7930854581,1.5969899209

N,-0.8315875937,-1.4687648612,-0.9206812901

N,-1.9070705497,1.0073355351,-2.0540133994

N,-3.6385800323,-0.6908629937,-0.1603410119

O,-1.0833032641,-1.2716836897,2.6645416931

H,-3.1446794639,2.2885934437,0.6004646789

H,-2.5654375509,1.6788126574,1.9921543467

H,-3.6515105762,-1.6856633061,0.0204118368

H,-4.2365004093,-0.263602448,0.5308785717

H,-1.5802750833,2.5068349784,0.9960067207

H,-4.0659077432,-0.5534597423,-1.0635482908

H,-2.7115547529,1.6123729187,-2.1071422223

H,-1.0856117702,1.5793371475,-2.1889297189

H,-1.9610911244,0.3622786523,-2.828439872

O,-0.3921421727,-2.3842236572,-1.5270311178

Single point energies (in hartrees)

	Gas-Phase	PCM
HF/LANL2DZ	-916.18652	-916.40531
MP2/LANL2DZ//HF/LANL2DZ	-918.18317	-918.39579
MP2/LANL2DZ//HF/LANL2DZ with BSSE	-918.15433	-918.36695

Name: Catalyzed CP+MVK exo-cis TS2

OPT Level: HF/LANL2DZ

Number of imaginary frequency: 1

ZPE: 219.80 kcal/mol

Molecular geometry (in Å):

C,3.2241152888,-0.5628341062,-1.3853488957

C,2.7504067591,0.7784761518,-0.8607417474

H,2.3939577906,-1.2262831155,-1.5832961115

H,3.7719771826,-0.4415077608,-2.3078383788

C,4.1410297077,-1.2335504932,-0.2775530716

C,1.4319064673,1.0864952403,-0.5434754803

C,3.3581771126,-0.9612664199,1.0308001781

C,5.3510519788,-0.356247735,-0.0756890305

H,4.3579866264,-2.2633261202,-0.5037321202

H,3.3448301508,1.6336231421,-1.1112263068

C,1.0191157074,2.5013421249,-0.2251758161

O,0.4889442217,0.1501941704,-0.4931723514

C,3.6332286159,0.5216878973,1.1163708555

C,5.0152035184,0.7050123256,0.6968524724

H,6.2985397989,-0.5167789259,-0.5467631901

H,3.8165584906,-1.4586409445,1.8763745192

H,2.3126821547,-1.2205799207,0.9955831753

H,0.2904482741,2.8514776462,-0.9465450659

H,0.5614903053,2.557153587,0.7553310256

H,1.863273788,3.1708681945,-0.2516728015

W,-1.4564582285,-0.1654714415,-0.0226790213

H,5.6139342045,1.559039689,0.9255276283

H,3.1160289208,1.1988496081,1.7654106734

N,-1.6539246822,-0.2880470045,-2.3283932417

N,-2.1048966375,1.5274092684,-0.0762623533

N,-1.3197252127,-0.1603713317,1.7925777099

N,-0.7107009715,-2.3521823482,-0.044161946

N,-3.521043823,-1.0915562167,-0.014645214

O,-2.5381845981,2.6207487068,-0.1443396153

H,-0.7142213813,-0.1499504011,-2.6713688269

H,-1.992874531,-1.1550447688,-2.715532119

H,-4.0467277622,-0.6233255581,0.7113109175

H,-4.033134168,-0.9585171429,-0.8735601594

H,-2.2247287816,0.4539612387,-2.7068946446

H,-3.5378110387,-2.0760056771,0.203963859

H,0.2707056605,-2.2488402576,-0.2555479391

H,-0.7869860039,-2.8029247851,0.8557313638

O,-1.2209528948,-0.1941912298,2.9666016228

H,-1.1098462462,-2.9738307188,-0.7297666421

Single point energies (in hartrees)

	Gas-Phase	PCM
HF/LANL2DZ	-916.18252	-916.40270
MP2/LANL2DZ//HF/LANL2DZ	-918.18137	-918.39408
MP2/LANL2DZ//HF/LANL2DZ with BSSE	-918.15316	-918.36587

Name: Catalyzed CP+MVK exo-trans TS2

OPT Level: HF/LANL2DZ

Number of imaginary frequency: 1

ZPE: 219.79 kcal/mol

Molecular geometry (in Å):

C,-0.2462621863,-0.1230375483,-3.7860191682

C,-0.023817542,-0.1946192628,-2.2781309621

C,1.1587345214,0.076068995,-4.4907567953

H,-0.9107273874,0.6951850526,-4.0206761263

H,-0.6967466317,-1.0196450087,-4.1842479207

C,-0.2943428662,-1.3131049476,-1.4865722274

C,2.05813461,-0.9366871887,-3.7434966038

C,2.1154342738,-0.1934687484,-2.4261828977

C,1.7418584521,1.3824853341,-4.0148353556

H,1.0904963302,-0.0362027637,-5.5584986202

H,-0.1257163928,0.7390288601,-1.7602701646

C,-0.4433812615,-2.7287474038,-1.9664804962

O,-0.4196551309,-1.2002903873,-0.1667400862

C,2.2496617139,1.218510186,-2.7693542079

H,1.6858712528,2.3037844427,-4.5567407304

H,1.6699976898,-1.9395029064,-3.6947796736

H,3.0510571922,-0.9725300862,-4.1733610666

H,2.4805049221,-0.612603543,-1.5105478102

H,0.2968534154,-3.3579769769,-1.4864414041

H,-1.4187376588,-3.0969957751,-1.6710842776

H,-0.3529556277,-2.8313478061,-3.0328290175

W,-0.4332571791,0.0934304155,1.3750782935

H,2.6393650058,1.9697695431,-2.118285353

N,-2.498075647,-0.8881026801,1.7266984605

N,-1.2724429799,1.5211571213,0.6212831578

N,1.2129455511,0.8238100472,1.1471012497

N,0.527828437,-1.7344733759,2.4102746532

N,-0.6810091461,0.8825745097,3.4806704459

O,-1.844674626,2.4384634005,0.153248031

H,-2.5764653067,-1.5575646789,0.9746486333

H,-2.6350348247,-1.3863472347,2.5923213064

H,-0.3630493632,1.8424184142,3.4755202692

H,-1.6372925192,0.8962821046,3.801784609

H,-3.26238203,-0.2354793712,1.6296715229

H,-0.1310545448,0.3979456007,4.1735193621

H,0.0181962009,-2.1610535907,3.1682169483

H,0.5857292879,-2.4110011491,1.6625176985

H,1.4664166266,-1.5593008311,2.7376466748

O,2.2975627347,1.2693433753,0.9966042973

Single point energies (in hartrees)

	Gas-Phase	PCM
HF/LANL2DZ	-916.18523	-916.40516
MP2/LANL2DZ//HF/LANL2DZ	-918.18347	-918.39678
MP2/LANL2DZ//HF/LANL2DZ with BSSE	-918.15375	-918.36705

Name: Catalyzed CH+MVK endo-cis TS2

OPT Level: HF/LANL2DZ

Number of imaginary frequency: 1

ZPE: 239.44 kcal/mol

Molecular geometry (in Å):

C,3.3122053123,0.4293194172,1.2990802298

C,4.7263587439,0.744848284,0.8791643892

C,2.878085878,-0.9395084014,1.2875285271

H,2.8137076982,1.1329733566,1.9387673409

H,2.2113709603,-1.2980651218,2.0447521457

H,5.3219585049,0.5530483881,1.769348224

H,4.8459755562,1.7955796683,0.6679769933

C,5.2055465402,-0.1561386777,-0.2902858335

C,3.3198685219,-1.7018089219,0.2578104557

C,4.0560421577,-1.0229460936,-0.8579076038

H,3.0567761674,-2.7401072483,0.1815599214

H,5.614169361,0.4549378163,-1.0834111584

H,6.0025635551,-0.80200718,0.0466916863

C,3.0195471758,-0.1252913098,-1.6439621305

H,4.4588115108,-1.745839948,-1.550385836

C,2.5359189315,1.0671646861,-0.8541475088

H,2.1876511813,-0.7353469912,-1.9678619898

H,3.5230975161,0.2249114345,-2.5364737949

C,1.2456509257,1.3040610467,-0.4571259979

H,3.1722830438,1.9293507848,-0.8492095916

O,0.2834858134,0.3765439227,-0.6138714314

C,0.8251624491,2.6197953277,0.1530147215

W,-1.5662901778,-0.1393902301,-0.0511590165

H,0.0592605069,3.0890457295,-0.4533940241

H,0.4129735884,2.4784358123,1.1447336549

H,1.6568399176,3.3032370359,0.2207698557

N,-2.0915764611,0.6611673036,-2.1644359176

N,-2.1729252255,1.41002805,0.6709569187

N,-1.1858611306,-0.868903682,1.5728695388

N,-0.8923692442,-2.1138789341,-1.0404950911

N,-3.6433889876,-1.0451343182,-0.1503049745

H,-2.5440222215,0.0232411806,-2.8004051428

H,-2.6516940721,1.5004586001,-2.1307977728

H,-1.1978470406,0.9086792343,-2.563825662

O,-2.5848159669,2.424681902,1.1087113315

H,-4.0028906694,-1.0494561942,0.7946495811

H,-4.288442508,-0.5006975867,-0.7026570234

H,-3.6792463338,-1.9963138135,-0.4828223557

H,-1.3164810839,-2.3678075264,-1.9185145351

H,0.0831671098,-1.9187758854,-1.2109226034

H,-0.9512696557,-2.9131206253,-0.4278672363

O,-0.9145088354,-1.380151446,2.6046498162

Single point energies (in hartrees)

	Gas-Phase	PCM
HF/LANL2DZ	-955.21381	-955.43255
MP2/LANL2DZ//HF/LANL2DZ	-957.29324	-957.50454
MP2/LANL2DZ//HF/LANL2DZ with BSSE	-957.26399	-957.47529

Name: Catalyzed CH+MVK endo-trans TS2

OPT Level: HF/LANL2DZ

Number of imaginary frequency: 1

ZPE: 239.28 kcal/mol

Molecular geometry (in Å):

C,3.2577995928,0.7579394878,1.521335505

C,1.9569631778,0.4849426603,0.781928923

C,4.4923016829,-0.0530673687,0.9680427549

H,3.1244078004,0.4646166956,2.5551573938

H,3.5006087671,1.8103009715,1.5292502767

C,1.2134433593,1.4355531765,0.1156946399

H,1.4083757385,-0.37296218,1.1214043907

C,4.1449281969,-1.5561878982,0.8628175077

C,4.8235994435,0.4989386027,-0.3858048429

H,5.3125124053,0.084626763,1.6548567922

C,1.7092189999,2.7876680735,-0.3123960648

O,-0.0751678807,1.2230267585,-0.2067880492

C,3.102994375,-1.8201350881,-0.2568982672

C,3.9260799454,0.2923911366,-1.3790938544

H,5.67574144,1.1362288241,-0.5240925874

H,3.7634818985,-1.9001543564,1.8147660603

H,5.0461575076,-2.1177200869,0.6670375551

W,-1.6113865238,-0.0379208285,-0.0702021253

H,1.3096161338,3.0371751285,-1.2857486704

H,1.3595528742,3.5374106667,0.3901000072

H,2.7842130776,2.8430138449,-0.347923111

C,2.8204208776,-0.5741643987,-1.0668089152

H,3.9795011812,0.7816126509,-2.330120119

H,3.4974098985,-2.5311611734,-0.9785022436

H,2.1929845207,-2.2583172133,0.1211094002

N,-2.5508738833,1.7576571782,1.0484381658

N,-1.2819961703,-0.830601133,1.5334664805

N,-0.9262509517,-1.4358494706,-1.0080140814

N,-2.1470747991,1.0129293363,-2.0573747922

N,-3.7430773924,-0.8042286521,-0.1615225848

H,1.9709020049,-0.5940040594,-1.7227953374

O,-1.0955478616,-1.3278299968,2.5872856668

H,-3.3822724098,2.1698163805,0.6548595378

H,-2.7427752149,1.5563125445,2.0189105993

H,-3.7008303271,-1.8037085693,-0.0152214166

H,-4.3389496371,-0.4301536241,0.5613334744

H,-1.8216482586,2.4557524099,1.0227596463

H,-4.2031884323,-0.6576372708,-1.0468151133

H,-2.9805339348,1.579270143,-2.077331552

H,-1.3560465334,1.6264002597,-2.191839385

H,-2.1874754701,0.3846382322,-2.8460576627

O,-0.4681252329,-2.3224263595,-1.6464972796

Single point energies (in hartrees)

	Gas-Phase	PCM
HF/LANL2DZ	-955.21635	-955.43103
MP2/LANL2DZ//HF/LANL2DZ	-957.29690	-957.50569
MP2/LANL2DZ//HF/LANL2DZ with BSSE	-957.26642	-957.47521

Name: Catalyzed CH+MVK exo-cis TS2

OPT Level: HF/LANL2DZ

Number of imaginary frequency: 1

ZPE: 239.38 kcal/mol

Molecular geometry (in Å):

C,3.0673140339,-0.0175807278,-1.6212602216

C,2.5530749282,1.1312867393,-0.774189566

H,2.2532455496,-0.655886386,-1.9389993996

H,3.5183819276,0.3882520507,-2.51708129

C,4.1276837365,-0.934618013,-0.8987639771

C,1.2530492718,1.3140105872,-0.3649512226

H,3.1354534184,2.0307110815,-0.7935721898

C,3.4602279049,-1.7416212388,0.2387612731

C,5.2074398715,-0.0720360411,-0.3076768306

H,4.5357207103,-1.6119620743,-1.632968504

C,0.7972334329,2.6042885844,0.2706777911

O,0.3300649698,0.3486478672,-0.5007049823

C,2.9460937431,-0.8100851658,1.3661175416

C,4.8681903467,0.7220639048,0.7338850573

H,4.172646043,-2.4491854712,0.6376138702

H,2.6426453849,-2.3242073128,-0.1675018067

H,6.1779521664,-0.0169589286,-0.7606190404

H,0.0117286265,3.0612541875,-0.3192797995

H,0.3978851985,2.4280343577,1.2627306125

H,1.6078372552,3.3114435485,0.3453670585

W,-1.5669188642,-0.1489007771,-0.0598398226

C,3.5263162471,0.5769730534,1.2421265912

H,3.2737633479,-1.1731008365,2.3367318899

H,1.8689871892,-0.7692459847,1.4127813917

H,5.5104169992,1.4833393873,1.1269365458

N,-1.9137531535,0.488209209,-2.2633335342

N,-2.2387859179,1.4432091963,0.488709058

N,-1.3309060184,-0.7507613929,1.6431266271

N,-0.8015493079,-2.1842405742,-0.8391328746

N,-3.621955303,-1.0831498989,-0.2618883874

H,3.1278945304,1.344453056,1.8789004988

O,-2.6915152679,2.4826285498,0.8118428384

H,-2.2923223502,-0.2060042548,-2.8886153563

H,-2.4938925707,1.3109920866,-2.3399188969

H,-4.0796254575,-0.9701399624,0.6325873922

H,-4.2068767371,-0.6272492831,-0.9456515293

H,-0.9945729264,0.733567799,-2.6015025226

H,-3.6203400213,-2.0704546052,-0.4668710123

H,-1.1882252939,-2.5311092475,-1.7026284953

H,0.1761278314,-1.9872205296,-0.9939956822

H,-0.8667900478,-2.9238936097,-0.1558735004

O,-1.164441954,-1.1794923458,2.7312186188

Single point energies (in hartrees)

	Gas-Phase	PCM
HF/LANL2DZ	-955.20993	-955.42909
MP2/LANL2DZ//HF/LANL2DZ	-957.29267	-957.50458
MP2/LANL2DZ//HF/LANL2DZ with BSSE	-957.26292	-957.47483

Name: Catalyzed CH+MVK exo-trans TS2

OPT Level: HF/LANL2DZ

Number of imaginary frequency: 1

ZPE: 239.40 kcal/mol

Molecular geometry (in Å):

C,-3.9195041683,0.0073057239,-1.2570949562

H,-3.4910996233,-0.8107395042,-1.8141956636

H,-4.4207851629,0.6340220646,-1.9901112759

C,-4.9294681304,-0.4687033737,-0.1801101592

C,-2.8469091501,0.8884365668,-0.660439874

H,-5.8875379599,0.0048383947,-0.3358697939

H,-5.0931563414,-1.5343064552,-0.2653765754

C,-4.422097992,-0.1405009995,1.2430888373

C,-3.23414354,1.8062057704,0.3862222841

H,-2.0032175335,1.1372236482,-1.2755870502

C,-3.1325219732,-0.9826230542,1.5680248695

C,-4.0827341402,1.3209324558,1.3211913816

H,-5.1778615682,-0.4029470475,1.9667192544

H,-2.8033237621,2.785666159,0.4273267273

C,-1.8918772115,-0.5842389317,0.7715661557

H,-2.9003994443,-0.8679567608,2.6185780807

H,-3.3863831462,-2.0233942142,1.4242918728

H,-4.4201057012,1.923685724,2.1416362641

C,-1.1980576778,-1.4173926854,-0.0839722217

H,-1.2979860413,0.1868771827,1.22383095

C,-1.720400359,-2.6767685911,-0.7145271177

O,0.0674807874,-1.1481783984,-0.4457110799

H,-1.562700255,-2.6460246695,-1.7856081385

H,-1.1620322989,-3.5234915416,-0.3309074578

H,-2.7644462045,-2.8471501021,-0.516743476

W,1.6182990176,0.0726750793,-0.144311439

N,2.6328814462,-1.9182567806,0.459872839

N,1.41607492,0.4715467761,1.6194181374

N,0.8656310489,1.6366566156,-0.6799125731

N,1.9916884793,-0.4936364038,-2.3529268786

N,3.7383804696,0.8698813447,-0.2208345069

O,1.3145310552,0.7095690913,2.7697999792

H,3.4287229262,-2.2196266047,-0.0803485098

H,2.9014228691,-1.9401804577,1.4328282739

H,3.7126366188,1.8061076344,0.1599608472

H,4.389557218,0.3451620448,0.3432391511

H,1.9003961271,-2.6016776556,0.3329598484

H,4.1244202081,0.9428965134,-1.1496157403

H,2.8230224532,-1.0222604711,-2.5657302622

H,1.1948178891,-1.0783888337,-2.5609204409

H,1.9656910957,0.2969069136,-2.9796484903

O,0.3592271376,2.6383023096,-1.0596734284

Single point energies (in hartrees)

	Gas-Phase	PCM
HF/LANL2DZ	-955.21280	-955.42620
MP2/LANL2DZ//HF/LANL2DZ	-957.29501	-957.50195
MP2/LANL2DZ//HF/LANL2DZ with BSSE	-957.26410	-957.47103