Supplementary Information
Modeling Mechanochemistry: Pressure Dependence of Diels-Alder Cycloaddition Reaction Kinetics

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Computational Methods

Density functional theory calculations were performed with Gaussian 16[1]. Calculations were carried out using the B3LYP functional and 6-31G(d) basis set. Geometry optimizations were converged under *opt=verystrict* convergence criteria. The wavefunction is converged under *scf=tight* criteria. Additionally, Gaussian 16's *ultrafine* integration grid is used (*int=ultrafine*). Vibrational frequency analysis was performed on the optimized structures to verify the nature of the stationary points. The optimized transition state structure and reaction path were further verified with an Intrinsic Reaction Coordinate (IRC) calculation.

Transition states were generally found by step-wise extension of the mechanochemical coordinate (defined in section "IRC curvature and activation length analysis") from the product state, effectively pushing the diene and dienophile away from each other. The structure of highest energy was then optimized with the aforementioned convergence criteria.

Van der Waal bound initial state structures were defined as the endpoint of the IRC calculations and were not further optimized. These initial state structures are not well defined in general, and only served to estimate an activation length.

XP-PCM calculations were carried out with Gaussian 16 at the B3LYP/6-31G(d) level using a Julia script. A standard value of $\eta = 3$ was used for the empirical Pauli repulsion parameter. The range of scaling factors was 1.2 to 0.9, using steps of 0.01. For each reaction A+B in the XP-PCM calculations, structures A, B, the transition states for each pathway, and the products for each pathway were included. For example, a reaction with 4 pathways will contain 10 structures in the XP-PCM calculation [reactant A, reactant B, TS1, TS2, TS3, TS4, PS1, PS2, PS3, PS4]. Degenerate product states were included in XP-PCM calculations. Van der Waals' initial state structures were not used in XP-PCM calculations.

Reaction pathways and structures

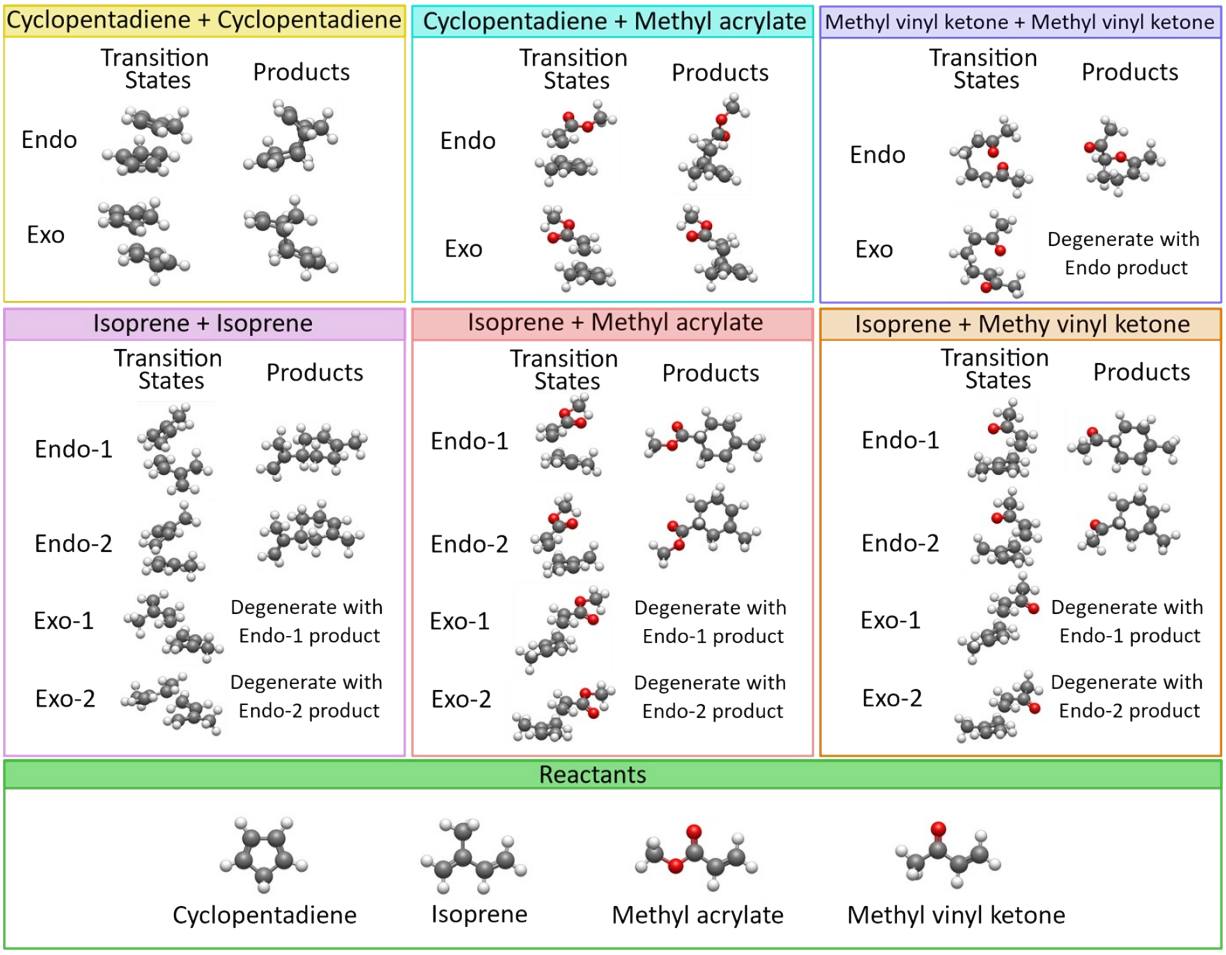


Figure S1. Molecular structures for the six Diels-alder cycloaddition reactions studied in this work.

XP-PCM analysis

A complete description of the XP-PCM computational protocol is found elsewhere.[2] Following the XP-PCM calculation, $\bar{P}$ and G_{tot} are fit to second-order polynomials $G_{tot}(P) = a + bP + cP^2$ for all structures in the calculation. For a reaction A+B, the activation volume is computed from the polynomials, $\Delta V^{\ddagger}(0) = \frac{\partial}{\partial P}\left(G_{tot}^{T}(P) - G_{tot}^{A}(P) - G_{tot}^{B}(P)\right)\Big|_{P=0}$. Polynomial fits are shown below for reactants and transition states.

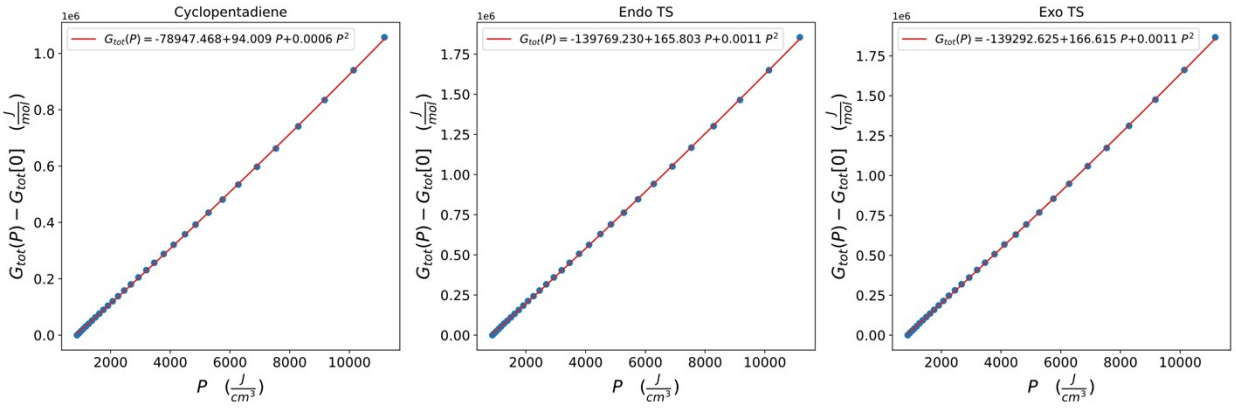


Figure S2. Cyclopentadiene dimerization $G_{tot}(P)$ fits

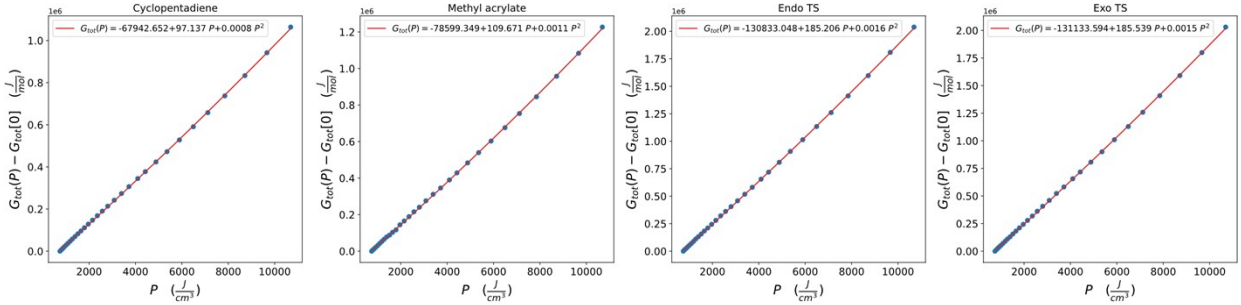


Figure S3. Cyclopentadiene + Methyl acrylate $G_{tot}(P)$ fits.

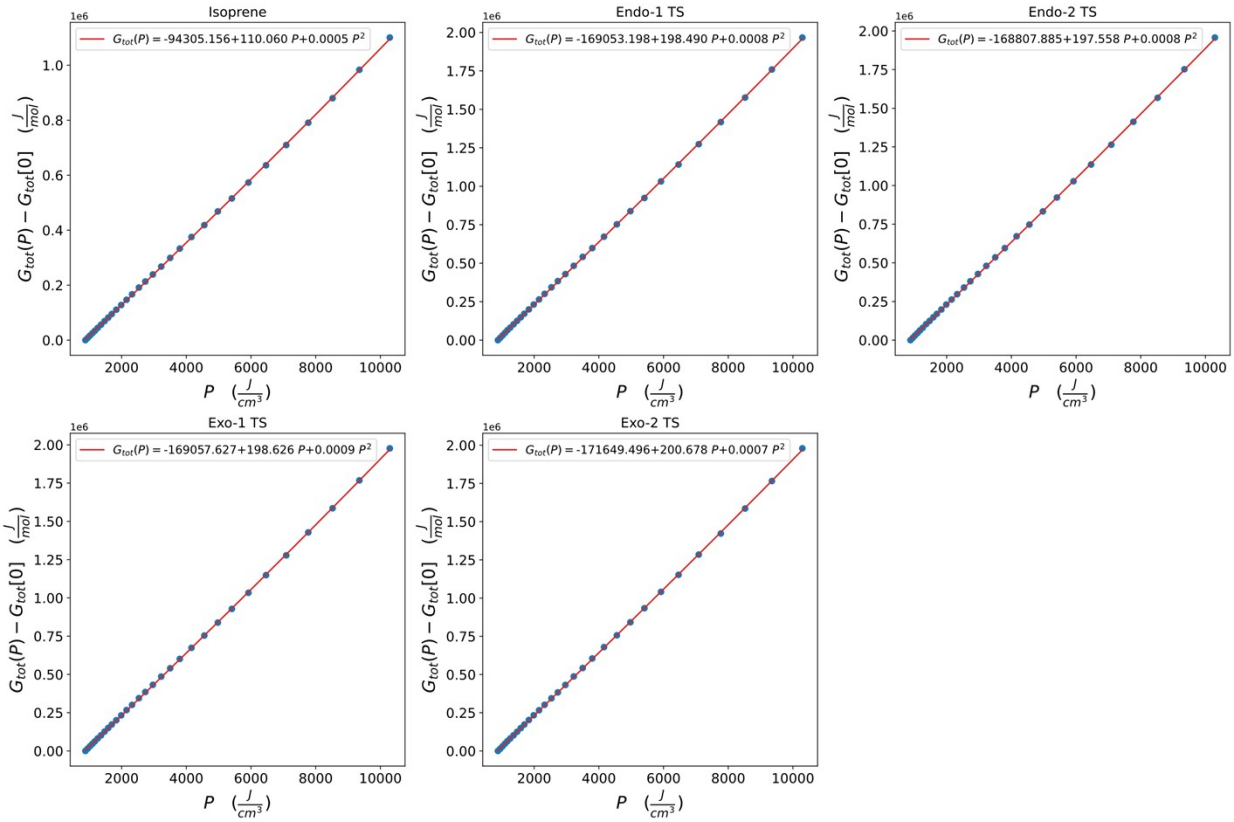


Figure S4. Isoprene dimerization $G_{tot}(P)$ fits.

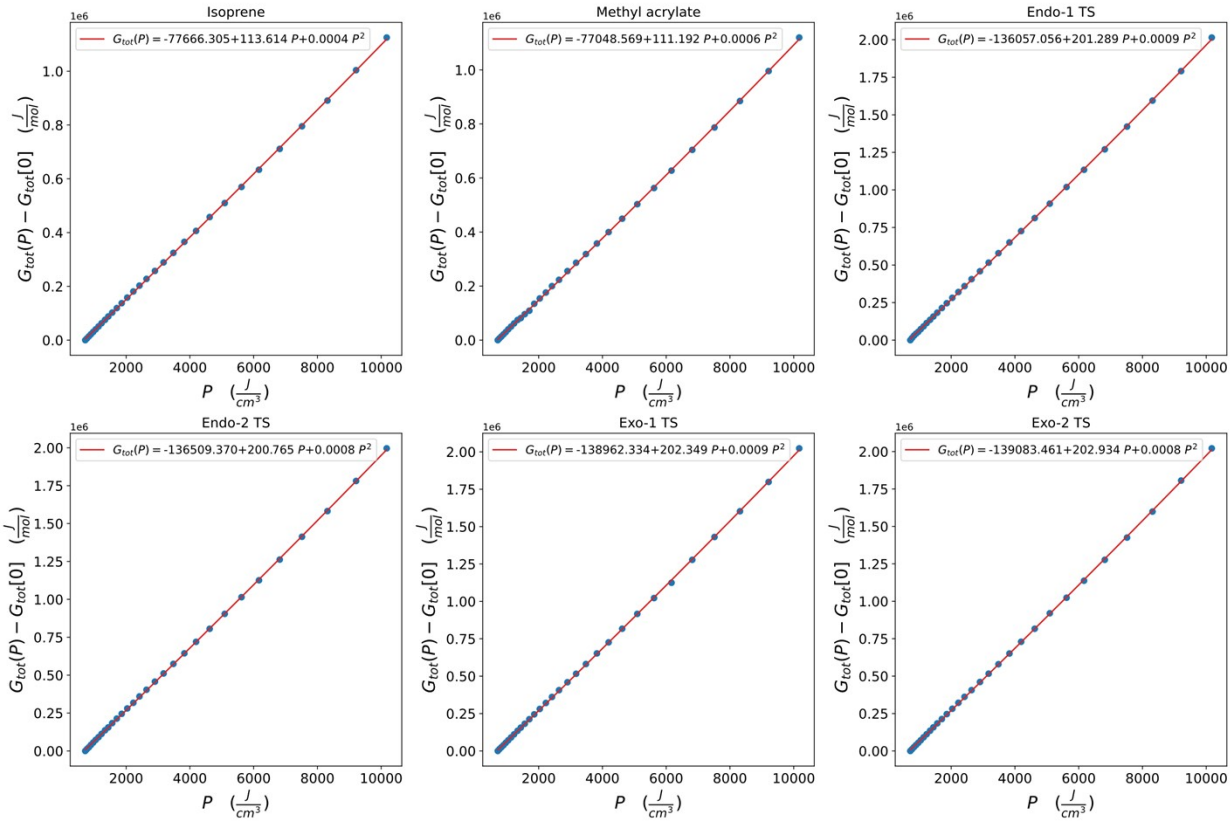


Figure S5. Isoprene + Methyl acrylate $G_{tot}(P)$ fits.

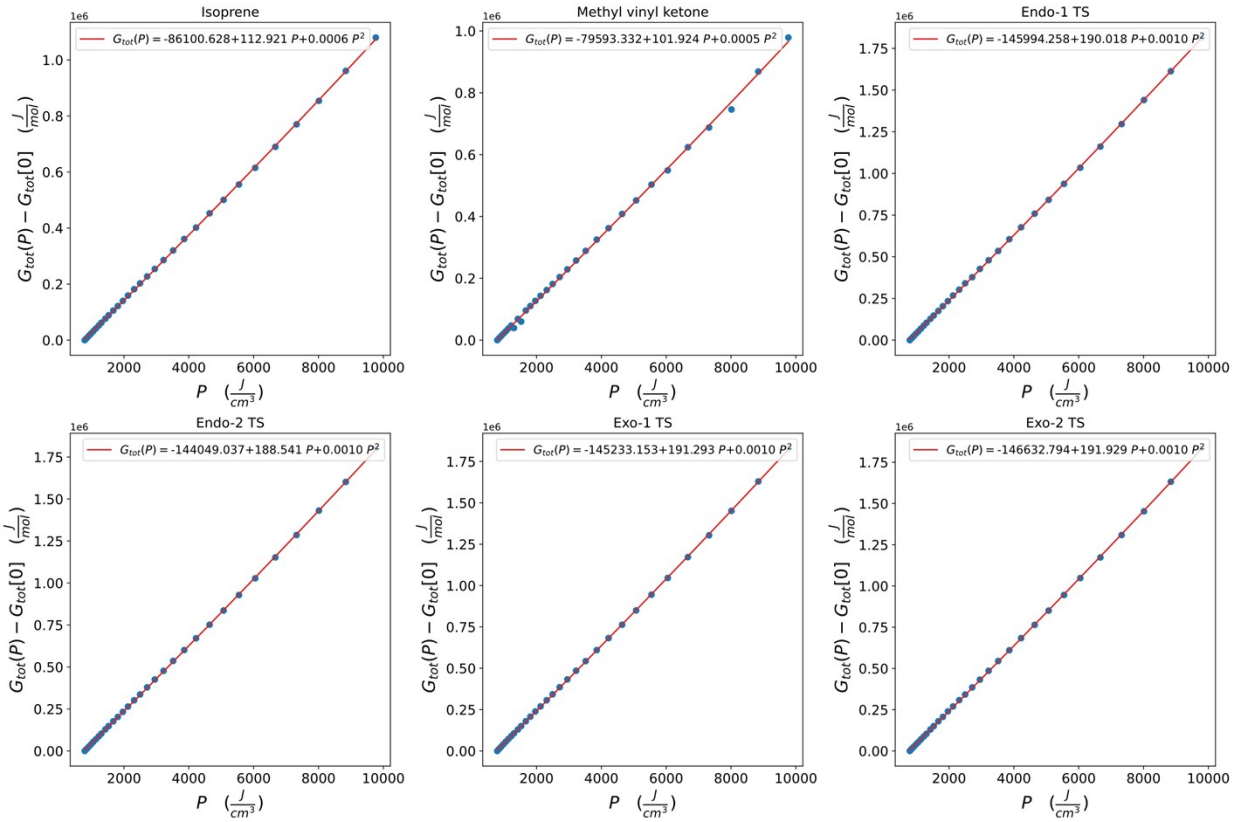


Figure S6. Isoprene + Methyl vinyl ketone $G_{tot}(P)$ fits.

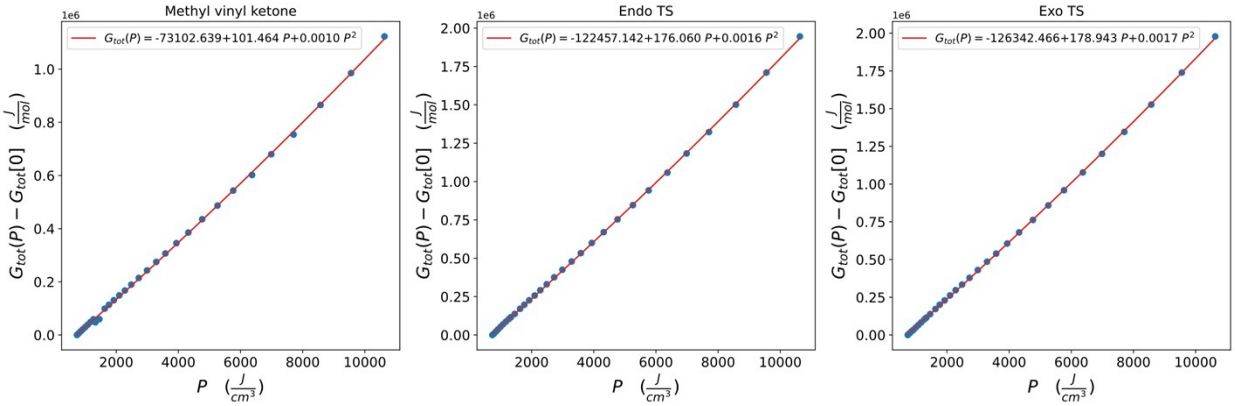
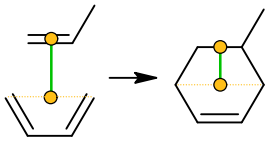


Figure S7. Methyl vinyl ketone dimerization $G_{tot}(P)$ fits.

IRC curvature and activation length analysis

For each structure connecting the transition state to the IRC endpoint (a van der Waals bound initial state), a mechanochemical coordinate was calculated. The mechanochemical coordinate is defined by the length of the vector between the centers of the two bond-forming atoms in both the diene and dienophile. A basic example is shown below where orange circles and green line represent the centroids and mechanochemical coordinate respectively:



The activation length is calculated directly from the transition state structure and IRC endpoint as the difference between the lengths of the mechanochemical coordinate, $\Delta x^{\ddagger} = x_{TS} - x_{IS}$. The curvature around the IRC endpoint and the transition state are determined by fitting $E = E_0 + \frac{1}{2}k(x - x_0)^2$, where E_0 and k are fitting parameters, x is the mechanochemical coordinate, and x_0 is the mechanochemical coordinate for the transition state or the IRC endpoint. For the transition state, the 5 points nearest to the transition state are used for the fit. For the IRC endpoint (van der Waals bound initial state), points up to $x_{IS} + \frac{\Delta x^{\ddagger}}{2}$ are used for the fit. Points used for the fits are shown as black circles in the figures below.

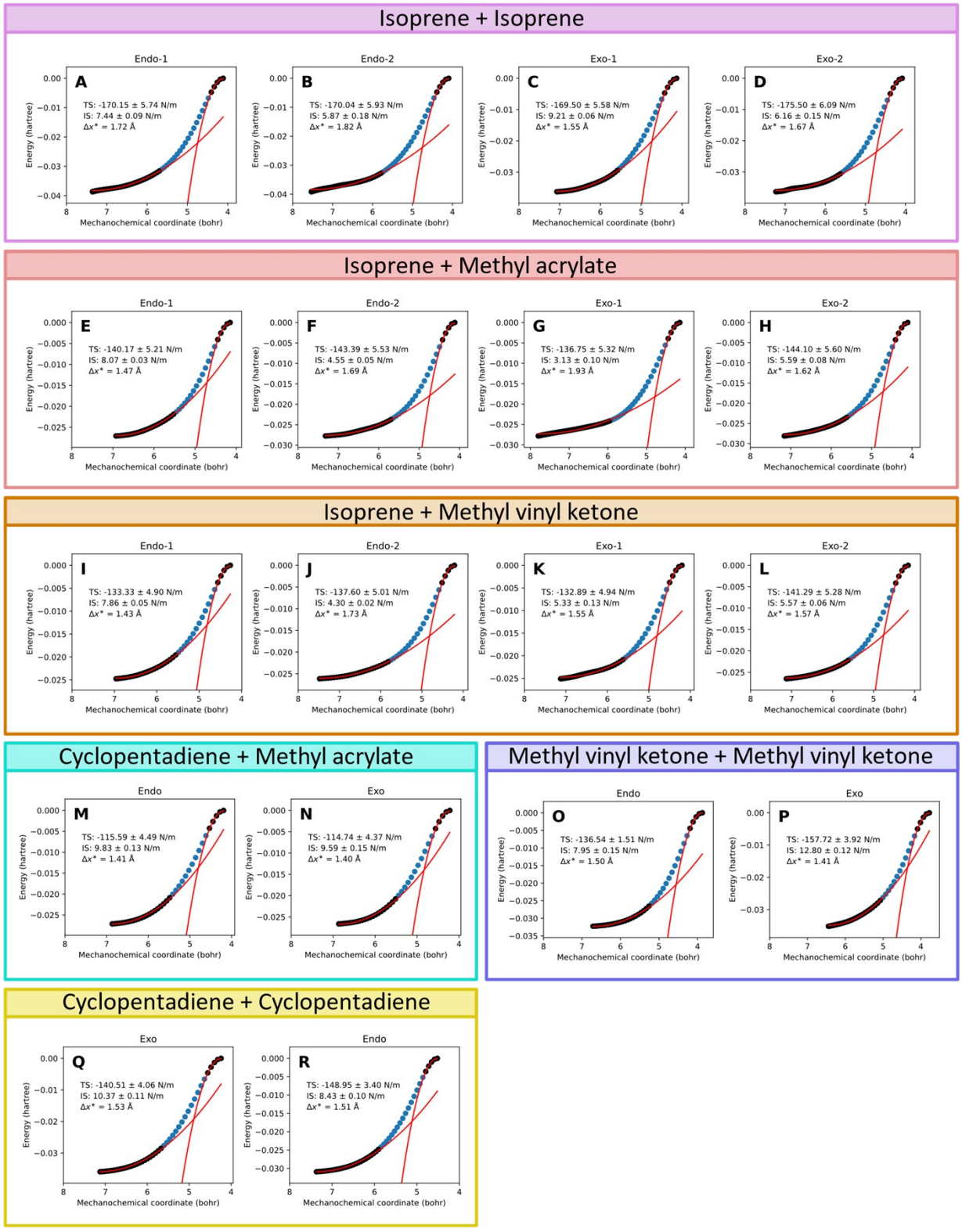


Figure S8. Transition state curvature, initial state curvature and activation lengths from IRC calculations for each reaction. Black circles represent the points used for the fits.

Activation energies of the gas-phase reactions

Reaction	$\Delta G^{\ddagger}$ (kJ/mol)	Relative $\Delta G^{\ddagger}$ (kJ/mol)
Cyclopentadiene + Cyclopentadiene		
Endo	142.7	0
Exo	155.4	12.7
Cyclopentadiene + Methyl acrylate		
Endo	135.0	7.7
Exo	127.3	0
Isoprene + Isoprene		
Endo-1	166.7	5.2
Endo-2	170.2	8.6
Exo-1	161.5	0
Exo-2	165.0	3.5
Isoprene + Methyl acrylate		
Endo-1	137.2	1.7
Endo-2	140.0	4.4
Exo-1	135.6	0
Exo-2	138.6	3.1
Isoprene + Methyl vinyl ketone		
Endo-1	130.4	0.5
Endo-2	133.4	3.6
Exo-1	129.8	0
Exo-2	133.8	4.0
Methyl vinyl ketone + Methyl vinyl ketone	135.4	0
Endo	142.2	6.8
Exo	**156.5	21.1
**	**163.5	28.1
**		

Table S1. Activation energies for each reaction pathway. **An additional endo and exo pathway were computed but were too high in energy to be thermodynamically relevant in the methyl vinyl ketone dimerization system. These were not included in any XP-PCM calculations or any analysis

Optimized gas-phase structural geometries

Reactants

Cyclopentadiene:

C	1.181164	-0.281706	0.000000
C	0.734959	0.991250	-0.000000
C	-0.734960	0.991250	-0.000000
C	-1.181163	-0.281706	0.000000
C	0.000000	-1.217365	-0.000000
H	2.214037	-0.610828	0.000000
H	1.347310	1.887344	-0.000000
H	-1.347311	1.887343	0.000000
H	-2.214037	-0.610829	0.000000
H	0.000000	-1.881684	-0.878153
H	0.000000	-1.881685	0.878152

Isoprene:

C	-1.986013	0.005080	0.000000
C	-0.833617	-0.679227	-0.000000
C	0.515858	-0.100690	0.000000
C	0.660150	1.402027	-0.000000
C	1.589105	-0.909872	0.000000
H	-2.019659	1.090965	0.000002
H	-2.943887	-0.506568	0.000000
H	-0.871636	-1.768653	-0.000002
H	0.180619	1.846231	0.881483
H	1.712859	1.698495	0.000000
H	0.180619	1.846231	-0.881484
H	1.485632	-1.992198	0.000000

H	2.602556	-0.518400	0.000001

Methyl acrylate:

C	2.128425	-0.884443	0.000000
O	0.700950	-1.033893	0.000000
C	0.000000	0.125328	0.000000
C	-1.459711	-0.147679	0.000000
C	-2.340475	0.854992	0.000000
O	0.518881	1.223638	0.000000
H	2.457994	-0.339968	0.889176
H	2.529880	-1.898307	0.000000
H	2.457994	-0.339968	-0.889176
H	-1.764183	-1.190084	0.000000
H	-1.998539	1.886134	0.000000
H	-3.411229	0.675043	0.000000

Methyl vinyl ketone:

C	1.167797	1.440286	0.000000
C	0.000000	0.470399	0.000000
O	-1.157550	0.857006	0.000000
C	0.346802	-0.985172	0.000000
C	-0.602382	-1.925662	0.000000
H	0.798543	2.467331	0.000000
H	1.801344	1.276483	0.881445
H	1.801344	1.276483	-0.881445
H	1.402375	-1.251617	0.000000
H	-0.366065	-2.985704	0.000000
H	-1.650440	-1.638138	0.000000

Transition states

Cyclopentadiene + Cyclopentadiene Endo TS:

(imaginary frequency = -382.1389 cm^{-1})

H	0.301060	0.190188	-2.341997
H	0.709084	-2.041848	-1.000433
C	-1.887531	-0.799952	-0.490936
C	0.758529	0.112267	-1.363756
C	0.807016	-1.052887	-0.556749
C	-1.942730	0.704274	-0.501277
C	-0.807017	-1.052888	0.556748
C	-1.401008	1.172922	0.665835
C	-0.758530	0.112266	1.363756
H	-2.481705	1.289052	-1.238313
H	-0.709085	-2.041849	1.000431
C	1.401008	1.172923	-0.665834
H	-2.844431	-1.200522	-0.113945
H	-1.705766	-1.266635	-1.463954
H	-1.401081	2.210029	0.987365
H	-0.301060	0.190186	2.341998
C	1.942731	0.704273	0.501277
C	1.887531	-0.799953	0.490935
H	1.705766	-1.266636	1.463953
H	2.844430	-1.200523	0.113944
H	1.401081	2.210029	-0.987363
H	2.481706	1.289050	1.238314

Cyclopentadiene + Cyclopentadiene Exo TS:

(imaginary frequency = -460.8566 cm^{-1})

C	1.873407	-1.111387	0.035200
C	1.761072	1.210196	-0.222193
C	2.444502	0.231897	0.415456
C	-0.808528	0.105529	1.322523

C	0.623508	-0.753682	-0.775401
C	0.652519	0.649118	-0.977276
C	-1.007081	-1.110912	0.438200
C	-1.354199	1.179894	0.428709
C	-2.102060	-0.810267	-0.401794
C	-2.264244	0.584780	-0.440181
H	-0.800796	-2.116051	0.797839
H	-1.298980	2.239357	0.653961
H	0.316121	-1.429482	-1.565102
H	0.155364	1.168283	-1.784600
H	2.573687	-1.657133	-0.616948
H	1.974802	2.273589	-0.161547
H	-1.462334	0.001607	2.205723
H	0.209291	0.270858	1.685325
H	-2.610860	-1.519506	-1.046677
H	3.270910	0.364620	1.105652
H	-2.931135	1.118021	-1.111277
H	1.690551	-1.765159	0.898185

Cyclopentadiene + Methyl acrylate Endo TS:

(imaginary frequency = -449.6370 cm^{-1})

C	2.192773	0.390939	0.712495
C	0.613301	-0.694819	1.530027
C	-0.097253	-1.216028	0.445249
H	0.121644	-2.206860	0.063462
C	1.271631	-0.226754	-1.323267
C	0.950811	1.102570	-1.074629
C	1.537029	1.495592	0.141275
C	2.419516	-0.592786	-0.420991
C	-1.383871	-0.692236	-0.021929

O	-2.115418	-1.244802	-0.825662
O	-1.698388	0.509557	0.547243
C	-2.943523	1.070593	0.119573
H	2.883051	0.480313	1.546740
H	1.267758	-1.363726	2.083161
H	0.153878	0.083203	2.128197
H	0.987051	-0.788441	-2.205590
H	0.266361	1.704565	-1.662200
H	1.380024	2.451198	0.630363
H	3.361176	-0.319387	-0.926867
H	2.488508	-1.644612	-0.137317
H	-2.939907	1.254386	-0.959093
H	-3.774213	0.398922	0.354335
H	-3.047360	2.009984	0.665346

Cyclopentadiene + Methyl acrylate Exo TS:

(imaginary frequency = -444.9278 cm^{-1})

C	-2.250457	-0.727766	0.386736
C	-2.845254	0.271192	-0.408235
C	-2.055276	1.431882	-0.349746
C	-1.000067	1.216226	0.530676
H	-3.688257	0.120946	-1.075285
H	-2.189714	2.314047	-0.967244
C	-1.311630	-0.011927	1.336972
H	-1.893118	0.292600	2.224161
H	-0.446620	-0.582993	1.677606
H	3.364578	0.846215	1.182996
C	3.538746	0.603490	0.130397
H	4.130588	1.385816	-0.347510
O	2.305117	0.555232	-0.594577

O	1.649124	-1.111992	0.793620
C	1.414060	-0.379940	-0.158241
C	0.191756	-0.370269	-0.961975
C	-0.735730	-1.410881	-0.854402
H	4.060871	-0.356267	0.076487
H	0.173853	0.311873	-1.802520
H	-0.251435	1.950164	0.807201
H	-0.461670	-2.256616	-0.229318
H	-1.347648	-1.658252	-1.714790
H	-2.762256	-1.645486	0.662786

Isoprene + Isoprene Endo-1 TS:

(imaginary frequency = -511.1588 cm^{-1})

C	1.982405	0.259670	-0.127646
C	3.179621	0.007803	0.436875
C	1.522017	1.681213	-0.352371
C	1.120989	-0.838469	-0.582327
C	-0.181064	-1.093110	1.538010
C	-1.113913	-0.096487	1.376556
C	-1.955586	0.007760	0.244733
C	-1.822814	-0.933343	-0.777886
C	0.104028	-0.715020	-1.539639
C	-2.724039	1.289808	0.013479
H	3.533004	-1.008078	0.597418
H	3.842310	0.808966	0.750950
H	2.234756	2.396096	0.069083
H	1.415656	1.905851	-1.421747
H	0.543958	1.858336	0.111328
H	1.525411	-1.834247	-0.411512
H	-0.294293	-2.063886	1.072216

H	0.542120	-1.046385	2.346508
H	-1.081137	0.753903	2.058214
H	-1.620826	-1.968189	-0.520204
H	-2.432732	-0.823538	-1.673214
H	-0.056271	0.252020	-2.007384
H	-0.049953	-1.554833	-2.212181
H	-3.046944	1.732258	0.962504
H	-2.109885	2.046532	-0.498801
H	-3.615029	1.126242	-0.601889

Isoprene + Isoprene Endo-2 TS:

(imaginary frequency = -517.8771 cm^{-1})

C	1.849830	-0.045770	-0.059065
C	2.827021	-0.633056	0.657454
C	1.651363	-0.384648	-1.518574
C	0.986152	0.980428	0.543114
C	0.253687	1.924638	-0.188870
C	-1.825200	1.612395	-0.117745
C	-2.040564	0.280869	-0.461759
C	-1.490552	-0.785324	0.285260
C	-0.756040	-0.516990	1.423461
C	-1.559880	-2.197056	-0.262423
H	3.494426	-1.368327	0.217261
H	2.990353	-0.392291	1.705341
H	0.610676	-0.659511	-1.726048
H	1.889544	0.471168	-2.163966
H	2.292975	-1.218102	-1.819210
H	1.218319	1.220234	1.578444
H	0.140464	2.915623	0.242275
H	0.333160	1.923523	-1.271129

H	-1.827318	1.899614	0.929552
H	-2.199678	2.390527	-0.779692
H	-2.422422	0.056992	-1.457355
H	-0.210218	-1.309237	1.928408
H	-0.930412	0.373614	2.013184
H	-1.586082	-2.213285	-1.358016
H	-0.703009	-2.794358	0.066507
H	-2.465678	-2.709095	0.089321

Isoprene + Isoprene Exo-1 TS:

(imaginary frequency = -499.8507 cm^{-1})

C	-2.239923	0.011534	0.201472
C	-3.114948	0.992486	0.501041
C	-2.616588	-1.070043	-0.788030
C	-0.923326	-0.046799	0.840624
C	0.309301	1.566512	-0.716556
C	1.600809	1.316049	-0.325940
C	2.173612	0.022988	-0.290238
C	1.381536	-1.081017	-0.624188
C	-0.078927	-1.166620	0.814596
C	3.493389	-0.185853	0.417178
H	-2.867582	1.778878	1.210022
H	-4.102805	1.034537	0.051597
H	-3.599184	-0.875755	-1.227290
H	-1.890204	-1.142318	-1.608283
H	-2.652309	-2.057922	-0.310742
H	-0.726231	0.725974	1.576507
H	-0.233389	0.905594	-1.379049
H	-0.133123	2.549161	-0.580671
H	2.160835	2.122702	0.148095

H	0.660536	-0.992577	-1.430536
H	1.823835	-2.073979	-0.552698
H	0.604598	-1.295515	1.648974
H	-0.482377	-2.104221	0.439435
H	4.038708	0.756884	0.531214
H	3.347912	-0.600744	1.426762
H	4.141166	-0.886126	-0.123097

Isoprene + Isoprene Exo-2 TS:

(imaginary frequency = -517.1903 cm^{-1})

C	-2.090680	-0.387441	0.130984
C	-2.636533	-1.609900	0.282090
C	-2.754523	0.641756	-0.757626
C	-0.860757	-0.018017	0.840704
C	-0.415068	1.301580	1.013555
C	1.042890	1.851003	-0.338507
C	2.095315	0.956463	-0.141322
C	1.948307	-0.435831	-0.333146
C	0.760343	-0.941729	-0.816577
C	3.029961	-1.366857	0.178381
H	-3.558723	-1.890251	-0.218598
H	-2.177888	-2.363661	0.917506
H	-3.092683	1.513130	-0.182095
H	-2.067573	1.019001	-1.526711
H	-3.625705	0.218578	-1.265708
H	-0.460015	-0.780564	1.500846
H	-1.080680	2.112701	0.728245
H	0.175582	1.517660	1.897581
H	0.367803	1.707866	-1.177044
H	1.206474	2.899509	-0.096242

H	2.961368	1.298337	0.424989
H	0.573554	-2.012097	-0.833111
H	0.100561	-0.352588	-1.438956
H	3.390767	-1.071920	1.171275
H	2.672638	-2.399808	0.239626
H	3.898992	-1.362057	-0.492820

Isoprene + Methyl acrylate Endo-1 TS:

(imaginary frequency = -465.8679 cm^{-1})

C	2.540415	-1.546553	-0.727887
C	2.088858	-0.458403	0.217129
C	1.137090	-0.780046	1.216544
C	0.436476	0.160295	1.925894
C	-0.493650	1.395510	-0.116757
C	0.637379	1.625815	-0.901317
C	2.363929	0.880857	-0.063793
H	-0.891261	2.151679	0.550190
C	-1.331430	0.235830	-0.411280
O	-1.024674	-0.688922	-1.150387
O	-2.529170	0.290851	0.238509
H	1.771715	-1.725484	-1.491862
H	2.693352	-2.492527	-0.196216
H	3.473482	-1.286527	-1.237610
H	0.816381	-1.818594	1.280820
H	0.791108	1.174876	2.054449
H	-0.385360	-0.132101	2.572859
C	-3.400927	-0.817349	-0.004587
H	1.021780	2.641090	-0.955730
H	0.720803	1.049831	-1.817571
H	3.091655	1.111393	-0.839280

H	2.344757	1.606141	0.743558
H	-4.308944	-0.608906	0.563785
H	-2.946787	-1.753773	0.334210
H	-3.630765	-0.908271	-1.070244

Isoprene + Methyl acrylate Endo-2 TS:

(imaginary frequency = -480.0474 cm^{-1})

C	-0.816785	2.454837	-0.321030
C	-1.352079	1.180226	0.298454
C	-0.804719	0.677310	1.457854
C	0.190567	-1.419710	0.483213
C	-0.844853	-1.997801	-0.251286
C	-2.600382	-0.909026	-0.098616
C	-2.261409	0.394802	-0.447968
H	0.425853	-1.746082	1.489747
C	1.186151	-0.600729	-0.210529
O	1.091429	-0.194296	-1.359240
O	2.268159	-0.339831	0.576874
H	-1.631450	3.067333	-0.724822
H	-0.134889	2.219805	-1.146924
H	-0.272917	3.061312	0.409844
H	-1.291194	-0.100331	2.032088
H	-0.006298	1.205351	1.971739
C	3.291772	0.447760	-0.039778
H	-1.303872	-2.903591	0.135786
H	-0.771887	-1.937363	-1.331883
H	-2.699661	-1.173596	0.949982
H	-3.269896	-1.463964	-0.752079
H	-2.517478	0.743337	-1.447656
H	4.094295	0.516886	0.696436

H	2.919806	1.446367	-0.289604
H	3.653308	-0.028462	-0.955621

Isoprene + Methyl acrylate Exo-1 TS:

(imaginary frequency = -464.9639 cm^{-1})

C	-3.897322	0.072057	0.258205
C	-2.489029	0.194207	-0.276240
C	-1.777735	1.405204	-0.084636
C	-0.458790	1.572696	-0.418489
C	0.476554	-0.410599	0.914752
C	-0.461825	-1.422989	0.711667
C	-1.817704	-0.931031	-0.757512
C	1.693032	-0.392651	0.104885
O	1.863071	-1.022012	-0.930602
O	2.638191	0.441421	0.620633
C	3.855123	0.518240	-0.130273
H	-4.051535	0.680590	1.157010
H	-4.629107	0.412360	-0.487909
H	-4.146910	-0.966662	0.500164
H	-2.263146	2.180187	0.508537
H	0.024829	0.970217	-1.176844
H	0.078422	2.466857	-0.115429
H	0.438741	0.235621	1.782163
H	-0.135984	-2.287032	0.139188
H	-1.167598	-1.636892	1.508173
H	-2.378164	-1.857519	-0.870309
H	-1.007143	-0.821588	-1.471180
H	4.492832	1.217121	0.413289
H	4.334757	-0.462638	-0.197003
H	3.666090	0.883298	-1.144241

Isoprene + Methyl acrylate Exo-2 TS:

(imaginary frequency = -481.9270 cm^{-1})

C	3.034897	-1.775275	0.304547
C	2.113795	-0.733316	-0.298400
C	0.826760	-1.057284	-0.666614
C	-0.418113	0.421974	0.951544
C	0.280862	1.629884	0.939561
C	1.667856	1.674678	-0.587128
C	2.532745	0.618215	-0.316510
C	-1.637418	0.297117	0.150635
O	-1.967221	1.049147	-0.755377
O	-2.375503	-0.787847	0.511339
C	-3.579795	-0.980601	-0.240058
H	3.912994	-1.935097	-0.334413
H	3.407698	-1.471677	1.290613
H	2.530267	-2.739850	0.415442
H	0.249224	-0.428449	-1.331365
H	0.447442	-2.066419	-0.529533
H	-0.232097	-0.334992	1.702513
H	-0.232056	2.492351	0.523112
H	0.951575	1.844096	1.765089
H	0.867034	1.558225	-1.311664
H	2.057829	2.688547	-0.525700
H	3.502543	0.848694	0.124424
H	-4.248357	-0.121731	-0.131225
H	-3.358609	-1.118240	-1.302618
H	-4.043233	-1.878211	0.172160

Isoprene + Methyl vinyl ketone Endo-1 TS:

(imaginary frequency = -433.7203 cm^{-1})

C	-2.402935	-0.893788	-1.076801
C	-1.760445	-0.281841	0.143689
C	-1.785232	1.102428	0.332735
C	-0.011935	1.799322	-0.361671
C	1.092237	1.143876	0.189705
C	-0.069083	-0.595563	1.905363
C	-0.913876	-1.088418	0.951355
H	-0.202290	2.826839	-0.059992
C	1.634550	-0.029238	-0.488055
O	1.035119	-0.567514	-1.423581
H	-2.652926	-1.946793	-0.907315
H	-1.701850	-0.858455	-1.921107
H	-3.316892	-0.365864	-1.367860
H	-1.638057	1.498104	1.332865
H	-2.472735	1.692123	-0.270327
C	2.990717	-0.556700	-0.035992
H	1.626171	1.563359	1.037346
H	3.784656	-0.043905	-0.594991
H	-0.174609	0.395862	2.326619
H	0.638314	-1.248693	2.408283
H	-0.821268	-2.137092	0.674454
H	-0.227252	1.574349	-1.402167
H	3.062097	-1.624173	-0.259626
H	3.171711	-0.386019	1.030495

Isoprene + Methyl acrylate Endo-2 TS:

(imaginary frequency = -445.5100 cm^{-1})

C	1.147211	-2.286125	-0.383765
C	1.271603	-0.935792	0.289633

C	0.639810	-0.686343	1.483163
C	-0.952290	1.203238	0.490422
C	-0.064608	2.078433	-0.142824
C	1.848182	1.452976	-0.008366
C	1.875830	0.123846	-0.432010
H	-1.288052	1.381467	1.507578
H	-2.654588	-1.708764	-0.007615
H	-3.652438	-0.252405	0.020583
H	2.109304	-2.610334	-0.797548
H	0.429896	-2.227417	-1.210795
H	0.806146	-3.056235	0.314944
H	0.829760	0.205491	2.065550
H	0.077607	-1.467115	1.988333
O	-1.193028	-0.114444	-1.440451
H	0.118462	3.046242	0.318581
H	-0.096351	2.078192	-1.227788
H	1.910724	1.666497	1.055119
H	2.349597	2.194834	-0.626064
H	2.193077	-0.086176	-1.451853
C	-1.559947	0.125386	-0.286048
C	-2.692565	-0.674620	0.345599
H	-2.668282	-0.654717	1.439758

Isoprene + Methyl vinyl ketone Exo-1 TS:

(imaginary frequency = -443.9152 cm^{-1})

C	2.110592	-0.221531	0.000575
C	3.249422	0.697593	0.423473
O	2.181658	-0.871379	-1.045571
C	0.946184	-0.310243	0.881813
C	-0.194822	1.654793	-0.496016

C	-1.476544	1.378749	-0.103179
C	-2.089353	0.105187	-0.234238
C	-1.341940	-0.979558	-0.699611
C	0.038000	-1.362906	0.732881
C	-3.470899	-0.106304	0.338787
H	3.907561	0.883403	-0.428297
H	2.879427	1.647688	0.824783
H	3.835816	0.216126	1.217311
H	0.886385	0.353921	1.737563
H	0.257672	2.613267	-0.256273
H	0.330947	1.054036	-1.226471
H	-2.014898	2.132984	0.471018
H	-1.841799	-1.942692	-0.787914
H	-0.555073	-0.828427	-1.432925
H	0.391368	-2.225730	0.173935
H	-0.625388	-1.593383	1.561539
H	-3.622766	0.457487	1.267266
H	-4.241897	0.231944	-0.367805
H	-3.664462	-1.164266	0.543926

Isoprene + Methyl vinyl ketone Exo-2 TS:

(imaginary frequency = -463.0644 cm^{-1})

C	2.957074	-1.398824	0.307741
C	1.875994	-0.515923	-0.283940
C	0.702854	-1.056661	-0.756151
C	-0.909553	0.150431	0.903700
C	-0.390102	1.446214	0.986617
C	0.990965	1.783581	-0.457887
C	2.029126	0.889903	-0.202355
C	-2.028925	-0.129766	-0.000666

C	-2.805512	-1.421484	0.216386
O	-2.342826	0.651836	-0.900209
H	3.896353	-1.290260	-0.249303
H	3.172198	-1.137304	1.351368
H	2.675269	-2.455571	0.274972
H	0.028924	-0.499419	-1.392480
H	0.536109	-2.130269	-0.717176
H	-0.622274	-0.606424	1.625935
H	-1.017223	2.242431	0.593588
H	0.196553	1.711704	1.860804
H	0.252717	1.563780	-1.224706
H	1.193865	2.846166	-0.340258
H	2.923023	1.268888	0.292943
H	-2.138460	-2.269771	0.406300
H	-3.455914	-1.317410	1.095008
H	-3.430045	-1.626053	-0.655990

Methyl vinyl ketone + Methyl vinyl ketone Endo TS:

(imaginary frequency = -375.1123 cm^{-1})

C	-1.513106	-0.116653	0.304400
C	-2.609104	0.727300	-0.314336
O	-1.047132	0.129652	1.421873
C	-0.946917	-1.215057	-0.476391
O	0.458398	0.574788	-1.287785
C	1.163429	0.897442	-0.294422
C	1.839020	-0.135508	0.412934
C	1.716417	-1.451083	-0.081164
C	-0.024082	-2.083701	0.134578
C	1.173248	2.328327	0.203035
H	-3.016961	1.409497	0.434712

H	-2.190329	1.305478	-1.145778
H	-3.413766	0.100298	-0.717040
H	-1.258218	-1.356682	-1.505875
H	2.261515	0.061342	1.394141
H	1.733541	-1.532298	-1.165739
H	2.286729	-2.225065	0.430860
H	-0.076775	-2.109525	1.220343
H	0.103937	-3.057483	-0.335625
H	0.283727	2.505148	0.818216
H	2.057352	2.539989	0.813410
H	1.145697	3.017381	-0.646130

Methyl vinyl ketone + Methyl vinyl ketone Exo TS:

(imaginary frequency = -447.0427 cm^{-1})

H	0.539600	-0.539100	1.673115
C	1.947286	-0.193358	-0.000650
O	2.374873	0.619105	-0.813893
C	0.877703	0.193057	0.949043
O	-0.591704	-0.945909	-0.410485
C	-1.747462	-0.462381	-0.241635
C	-1.929004	0.939237	-0.306416
C	-0.788499	1.738653	-0.508061
C	0.410714	1.512885	0.965592
C	-2.882061	-1.384182	0.164985
C	2.436705	-1.624009	0.047091
H	3.284370	-1.749777	-0.629224
H	1.617334	-2.285695	-0.256826
H	-2.906595	-2.256982	-0.495358
H	-2.862805	1.378884	0.035341
H	-0.054021	1.386647	-1.230378

H	-0.932055	2.818267	-0.512721
H	-0.176000	1.834988	1.821571
H	1.116204	2.251615	0.589707
H	-2.718749	-1.754951	1.185008
H	-3.853596	-0.881497	0.129067
H	2.728673	-1.907384	1.066035

Product states

Cyclopentadiene + Cyclopentadiene Endo PS:

H	0.320591	1.206037	-1.836760
H	0.391982	-1.171576	-1.812420
C	-1.916590	-0.044175	-0.787833
C	0.314445	0.803241	-0.814304
C	0.360610	-0.770022	-0.794163
C	-1.096329	1.117710	-0.173038
C	-1.025700	-1.141963	-0.152710
C	-1.054994	0.672830	1.280298
C	-1.017305	-0.666687	1.294060
H	-1.452924	2.134415	-0.357774
H	-1.325406	-2.181076	-0.314673
C	1.544966	1.213713	-0.051104
H	-2.950601	-0.073150	-0.429531
H	-1.906433	-0.053011	-1.885191
H	-0.961296	1.339477	2.131601
H	-0.895356	-1.308882	2.160559
C	2.251151	0.166686	0.384216
C	1.645771	-1.160215	-0.014137
H	1.428716	-1.783443	0.865095
H	2.338269	-1.744353	-0.636524
H	1.808578	2.254620	0.121830

H	3.167727	0.234229	0.966066

Cyclopentadiene + cyclopentadiene Exo PS:

C	1.763127	-1.166288	-0.104751
C	1.675133	1.202104	-0.136936
C	2.448804	0.154017	0.158731
C	-0.734648	0.014851	1.375029
C	0.350362	-0.773349	-0.627930
C	0.313333	0.803246	-0.645804
C	-0.840976	-1.124434	0.331629
C	-0.893817	1.131828	0.317617
C	-2.111845	-0.698919	-0.395564
C	-2.143355	0.640803	-0.403981
H	-0.821100	-2.151080	0.708055
H	-0.913388	2.164129	0.677325
H	0.177066	-1.199572	-1.619660
H	0.119055	1.221633	-1.640985
H	2.315298	-1.765675	-0.842235
H	1.709532	-1.783323	0.804788
H	1.968955	2.243109	-0.022036
H	-1.554739	0.000001	2.099257
H	0.223241	0.047082	1.904264
H	-2.790204	-1.376636	-0.905060
H	3.462052	0.217183	0.549330
H	-2.852481	1.279999	-0.921290

Cyclopentadiene + Methyl acrylate Endo PS:

C	2.079607	-0.866779	0.469857
C	0.641121	-1.424912	0.193531
C	0.023909	-0.316520	-0.730136
H	-0.156348	-0.744169	-1.725659

C	1.170943	0.747227	-0.820625
C	1.353579	1.326248	0.576912
C	1.898322	0.368834	1.340485
C	2.394180	-0.197977	-0.890157
C	-1.302864	0.255791	-0.276127
O	-1.568573	1.434029	-0.164182
O	-2.203191	-0.729246	-0.041150
C	-3.509927	-0.286232	0.358002
H	2.784674	-1.618252	0.833933
H	0.681347	-2.387848	-0.326484
H	0.070743	-1.570651	1.113980
H	1.038571	1.468499	-1.628867
H	0.987857	2.297146	0.889233
H	2.071787	0.400537	2.411818
H	3.345283	0.342634	-0.889216
H	2.366383	-0.893999	-1.738312
H	-3.454952	0.290163	1.285438
H	-3.959287	0.338221	-0.419086
H	-4.095163	-1.194634	0.505430

Cyclopentadiene + Methyl acrylate Exo PS:

C	-2.130472	-0.872239	0.012830
C	-2.837943	0.423768	-0.358236
C	-2.036169	1.437416	-0.003026
C	-0.785002	0.832289	0.615247
H	-3.768536	0.486030	-0.914065
H	-2.171380	2.494087	-0.211641
C	-1.380485	-0.424799	1.289712
H	-2.054779	-0.174685	2.114386
H	-0.623578	-1.141357	1.624103

H	3.632781	0.252404	1.177904
C	3.620668	0.446425	0.101839
H	4.203134	1.337891	-0.133497
O	2.285694	0.727776	-0.347439
O	1.678608	-1.328818	0.357919
C	1.385915	-0.265794	-0.151448
C	0.003633	0.166438	-0.596488
C	-0.924072	-1.025404	-0.977450
H	4.025934	-0.425731	-0.418228
H	0.120871	0.893828	-1.402633
H	-0.171319	1.499026	1.225121
H	-0.408315	-1.974347	-0.806154
H	-1.237369	-0.984186	-2.024394
H	-2.758306	-1.763227	0.087370

Isoprene + Isoprene Endo-1 PS:

C	-2.223346	0.010492	-0.173219
C	-3.051096	0.133281	-1.216890
C	-2.758645	-0.140058	1.232483
C	-0.716093	0.014891	-0.372151
C	-0.046706	1.293909	0.180554
C	1.459851	1.211489	0.158784
C	2.158832	0.081565	-0.012866
C	1.467554	-1.256856	-0.175459
C	-0.013593	-1.220718	0.226318
C	3.664779	0.065305	-0.064686
H	-2.679001	0.231920	-2.234157
H	-4.131773	0.139878	-1.094575
H	-3.850646	-0.071935	1.248013
H	-2.476613	-1.107559	1.667767

H	-2.364125	0.631680	1.905952
H	-0.530110	0.000265	-1.455390
H	-0.380878	2.160165	-0.406762
H	-0.388063	1.489346	1.209314
H	1.997687	2.151505	0.286478
H	1.566322	-1.589408	-1.221634
H	1.995994	-2.016084	0.419574
H	-0.087509	-1.189109	1.321713
H	-0.515935	-2.139559	-0.100778
H	4.086339	1.071434	0.028843
H	4.084788	-0.556588	0.738531
H	4.024298	-0.365749	-1.010096

Isoprene + Isoprene Endo-2 PS:

C	-2.060622	-0.247658	-0.155099
C	-2.869811	-0.504035	-1.188988
C	-2.560585	-0.343042	1.268295
C	-0.611379	0.152568	-0.382930
C	-0.227384	1.483010	0.295783
C	1.179527	1.923129	-0.133053
C	2.168967	0.785477	-0.094582
C	1.829991	-0.507029	0.001287
C	0.380896	-0.949467	0.052951
C	2.858582	-1.606821	0.067412
H	-3.907187	-0.798114	-1.046704
H	-2.525284	-0.428909	-2.217908
H	-1.957669	-1.036183	1.869104
H	-2.515480	0.629479	1.775382
H	-3.598306	-0.688744	1.299387
H	-0.478942	0.291175	-1.465284

H	-0.961190	2.260523	0.049822
H	-0.247315	1.356797	1.386669
H	1.145502	2.350061	-1.148535
H	1.529330	2.739872	0.513969
H	3.224753	1.052536	-0.147737
H	0.148851	-1.292499	1.073572
H	0.242568	-1.832344	-0.587361
H	3.879089	-1.210236	0.056638
H	2.738588	-2.208177	0.979987
H	2.753598	-2.302025	-0.777460

Isoprene + Isoprene Exo-1 PS: Degenerate with Isoprene+Isoprene Endo-1 PS via mirror symmetry

Isoprene + Isoprene Exo-2 PS: Degenerate with Isoprene+Isoprene Endo-2 PS via mirror symmetry

Isoprene + Methyl acrylate Endo-1 PS:

C	3.401148	-0.795674	-0.980377
C	2.259522	-0.387589	-0.091865
C	1.331592	-1.234475	0.372294
C	0.241086	-0.727132	1.280277
C	-0.383100	0.613076	0.764020
C	0.667918	1.553333	0.123674
C	2.123340	1.068178	0.304004
H	-0.856401	1.094809	1.627353
C	-1.516953	0.309132	-0.211967
O	-1.520268	0.512340	-1.406932
O	-2.567839	-0.247626	0.439544
H	3.368079	-0.260167	-1.939517

H	3.387436	-1.870318	-1.190306
H	4.369480	-0.551651	-0.520895
H	1.360364	-2.293340	0.121414
H	0.656179	-0.527486	2.279778
H	-0.547545	-1.470898	1.424228
C	-3.686087	-0.604100	-0.387486
H	0.561135	2.565552	0.530643
H	0.457419	1.616061	-0.947666
H	2.792483	1.702127	-0.289983
H	2.431666	1.197859	1.353753
H	-4.429323	-1.026124	0.290047
H	-3.390766	-1.340429	-1.140027
H	-4.086133	0.277798	-0.895157

Isoprene + Methyl acrylate Exo-1 PS:

C	4.045226	-0.362902	0.120108
C	2.549924	-0.206700	0.019677
C	1.748947	-1.216389	-0.345650
C	0.245289	-1.132890	-0.432412
C	-0.302985	0.120726	0.289121
C	0.535923	1.350809	-0.074259
C	1.993914	1.160007	0.364856
C	-1.771296	0.321645	-0.039870
O	-2.231131	1.211486	-0.723386
O	-2.531783	-0.651748	0.517912
C	-3.937672	-0.572376	0.234926
H	4.365028	-1.383753	-0.112581
H	4.563220	0.321904	-0.565920
H	4.401922	-0.118011	1.130718
H	2.191441	-2.179303	-0.601357

H	-0.066701	-1.115888	-1.489133
H	-0.209476	-2.033183	-0.001514
H	-0.232897	-0.063766	1.370009
H	0.486663	1.502270	-1.159181
H	0.111915	2.251569	0.382345
H	2.087432	1.321428	1.451191
H	2.621937	1.935859	-0.095973
H	-4.389195	-1.420723	0.750486
H	-4.352673	0.368233	0.607220
H	-4.118931	-0.636116	-0.841500

Isoprene + Methyl acrylate Exo-2 PS:

C	-2.874336	-1.981601	0.246535
C	-2.076579	-0.715828	0.065208
C	-0.575683	-0.855042	0.223589
C	0.197572	0.367835	-0.323289
C	-0.457207	1.670926	0.148137
C	-1.899799	1.761349	-0.368125
C	-2.650403	0.462539	-0.211159
C	1.658115	0.289927	0.084506
O	2.207817	1.002635	0.897012
O	2.291895	-0.715329	-0.567413
C	3.674132	-0.897639	-0.222100
H	-2.693431	-2.426428	1.235474
H	-3.949593	-1.800021	0.150286
H	-2.588830	-2.742709	-0.493214
H	-0.334603	-0.999112	1.289162
H	-0.228627	-1.763964	-0.284394
H	0.162578	0.316756	-1.420237
H	-0.447469	1.693166	1.244368

H	0.128109	2.534856	-0.184517
H	-2.433459	2.562007	0.162246
H	-1.903407	2.062713	-1.428247
H	-3.732953	0.505472	-0.332427
H	4.249514	0.004098	-0.448630
H	3.779352	-1.124875	0.842295
H	4.020239	-1.735201	-0.828783

Isoprene + Methyl acrylate Endo-1 PS: Degenerate with Isoprene + Methyl acrylate Exo-1 PS via mirror symmetry

Isoprene + Methyl acrylate Endo-2 PS: Degenerate with Isoprene + Methyl acrylate Exo-2 PS via mirror symmetry

Isoprene + Methyl vinyl ketone Exo-1 PS:

C	-2.211242	0.121612	-0.039748
C	-3.168536	-0.733245	0.774287
O	-2.608792	0.845404	-0.934500
C	-0.725838	0.018969	0.304964
C	-0.100083	-1.180166	-0.451338
C	1.406610	-1.179523	-0.365143
C	2.147809	-0.131307	0.016495
C	1.512599	1.193475	0.385317
C	0.042441	1.301414	-0.040596
C	3.649924	-0.201220	0.111509
H	-4.164227	-0.709995	0.326581
H	-2.814740	-1.768564	0.848114
H	-3.226134	-0.344162	1.799638
H	-0.630335	-0.184158	1.382049
H	-0.490165	-2.126518	-0.051766

H	-0.415170	-1.147004	-1.506107
H	1.903277	-2.110670	-0.638535
H	1.606383	1.344898	1.473142
H	2.089153	2.012179	-0.068990
H	-0.028282	1.467991	-1.121264
H	-0.429194	2.168519	0.436236
H	4.028468	-1.197731	-0.137972
H	4.124706	0.523381	-0.564739
H	3.994496	0.048547	1.125122

Isoprene + Methyl vinyl ketone Exo-2 PS:

C	-2.771053	-1.679327	0.209015
C	-1.792796	-0.544206	0.047857
C	-0.329439	-0.906171	0.211565
C	0.626156	0.185714	-0.330405
C	0.168525	1.566161	0.161342
C	-1.244436	1.883448	-0.346268
C	-2.182406	0.710400	-0.212362
C	2.056226	-0.137169	0.103658
C	2.883424	-1.001432	-0.832742
O	2.504478	0.267285	1.161020
H	-2.663459	-2.159226	1.192176
H	-3.806670	-1.337963	0.112258
H	-2.599342	-2.464819	-0.540559
H	-0.111726	-1.080350	1.276782
H	-0.133529	-1.863544	-0.292925
H	0.576518	0.156270	-1.428759
H	0.188770	1.567327	1.256758
H	0.874307	2.339764	-0.163523
H	-1.650760	2.744079	0.203092

H	-1.205729	2.204214	-1.400044
H	-3.245679	0.917101	-0.335431
H	2.325166	-1.892107	-1.146068
H	3.115706	-0.436680	-1.745505
H	3.815393	-1.296840	-0.346383

Isoprene + Methyl vinyl ketone Endo-1 PS: Degenerate with Isoprene + Methyl vinyl ketone Exo-1 PS via mirror symmetry

Isoprene + Methyl vinyl ketone Endo-2 PS: Degenerate with Isoprene + Methyl vinyl ketone Exo-2 PS via mirror symmetry

Methyl vinyl ketone + Methyl vinyl ketone Endo PS:

C	-1.627751	-0.534557	-0.052964
C	-1.322598	-1.937257	-0.533658
O	-2.639073	0.060817	-0.373167
C	-0.635009	0.130058	0.926003
O	0.626165	-0.548826	0.942560
C	1.545131	-0.161918	-0.012018
C	1.397991	0.919875	-0.790685
C	0.240176	1.874725	-0.656757
C	-0.486273	1.632805	0.673725
C	2.708085	-1.107142	-0.033372
H	-2.190830	-2.332267	-1.064809
H	-0.459509	-1.916117	-1.209803
H	-1.052185	-2.590913	0.302476
H	-1.049571	-0.041345	1.928501
H	2.170198	1.127656	-1.525514
H	0.599196	2.911282	-0.701085
H	-0.463462	1.764687	-1.494858

H	-1.479962	2.087504	0.676634
H	0.090813	2.061495	1.500786
H	2.382180	-2.126349	-0.275862
H	3.453791	-0.791436	-0.767342
H	3.184078	-1.149657	0.954096

Methyl vinyl ketone + Methyl vinyl ketone Exo PS:

H	1.049571	-0.041348	1.928500
C	1.627750	-0.534555	-0.052965
O	2.639067	0.060824	-0.373176
C	0.635008	0.130057	0.926003
O	-0.626165	-0.548828	0.942559
C	-1.545131	-0.161920	-0.012020
C	-1.397992	0.919875	-0.790684
C	-0.240178	1.874726	-0.656753
C	0.486271	1.632805	0.673728
C	-2.708084	-1.107145	-0.033376
C	1.322604	-1.937259	-0.533651
H	2.190837	-2.332267	-1.064801
H	0.459514	-1.916127	-1.209796
H	-2.382177	-2.126351	-0.275868
H	-2.170198	1.127657	-1.525513
H	0.463460	1.764691	-1.494854
H	-0.599200	2.911284	-0.701079
H	-0.090816	2.061492	1.500790
H	1.479959	2.087505	0.676638
H	-3.184077	-1.149662	0.954091
H	-3.453789	-0.791438	-0.767346
H	1.052195	-2.590912	0.302486

References

1. Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
2. B. Chen, R. Hoffmann and R. Cammi, *Angewandte Chemie International Edition*, 2017, **56**, 11126-11142.