Electronic Supplementary Information

Sigmatropic proton shifts: a quantum chemical study

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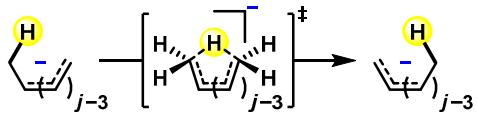
S1. Tunneling effect on sigmatropic proton shifts

Previously Grellmann and co-workers have observed a significant tunneling effect on the kinetics of [1,4] sigmatropic proton shifts.[1] To further assess the influence of proton tunneling, we carried out direct dynamics calculations with GAUSSRATE[2] as the interface between Gaussian 09[3] and POLYRATE.[4] Pruned integration grids with 99 radial shells and 590 angular points per shell were used. The ωB97XD functional[5] and the 6-31+G(d,p) basis set[6] were employed. The rate constants starting from the reactive conformers (not the most stable ones) were obtained using canonical variational transition state theory (CVT).[7] The local quadratic approximation (Page–McIver method) was employed to calculate the minimum energy path.[8] Quantum effects of multidimensional tunneling were calculated with small curvature tunneling (SCT) approximation.[9] As shown in Table S1, quantum tunneling increases the rate constants in a magnitude of 15–7000 at 298.15 K, corresponding to a decrease of 1.6–5.2 kcal/mol in terms of Gibbs energy of activation (according to the conventional transition state theory, in which $\kappa = 1$). However, these results did not change the relative ease of sigmatropic proton shifts.

Table S1 Theoretical rate constants and Gibbs energies of activation at 298.15 K



j	CVT		CVT/SCT	
	k [s^{-1}]	$\Delta G^{\ddagger}$ [kcal mol^{-1}]	k [s^{-1}]	$\Delta G^{\ddagger}$ [kcal mol^{-1}]
2	1.78×10^{-21}	45.7	1.31×10^{-17}	40.5
4	3.36×10^{-12}	33.1	4.44×10^{-10}	30.2
6	2.87×10^{1}	15.5	4.27×10^{2}	13.9

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S2. Formal sigmatropic proton shifts induced by water dimer

In the main text, we used one water molecule as an example to investigate the proton-shuttle-assisted pathways (Figs. 4 and 5). Here we provide the potential energy surfaces with water dimer as the proton shuttle (Figs. S1 and S2). These results do not change our conclusions.

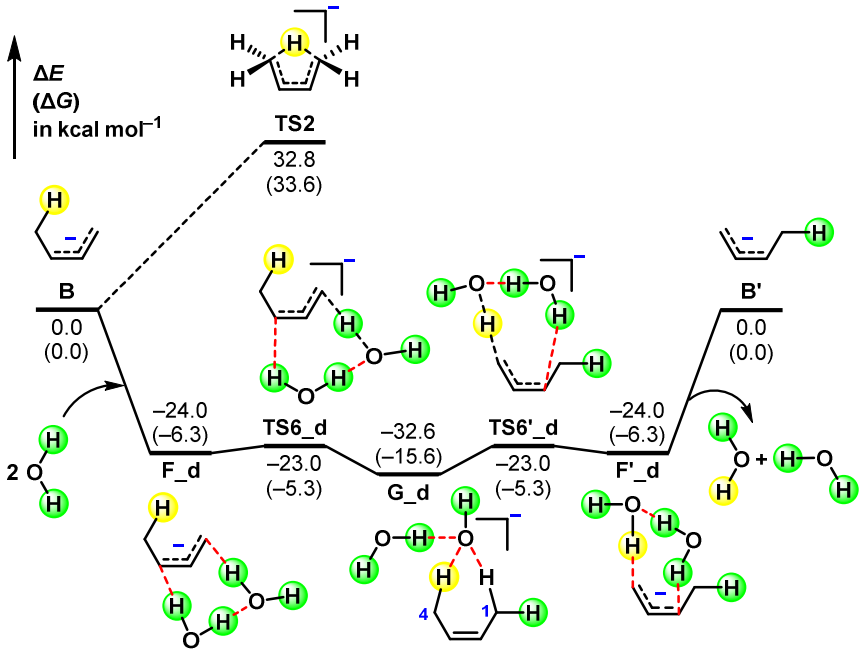

Fig. S1 Direct *versus* water-dimer-assisted pathways for [1,4] proton shift in carbanion **B**. Computed at the SCS-MP2/aug-cc-pVTZ//ωB97XD/6-311+G(d,p) level.

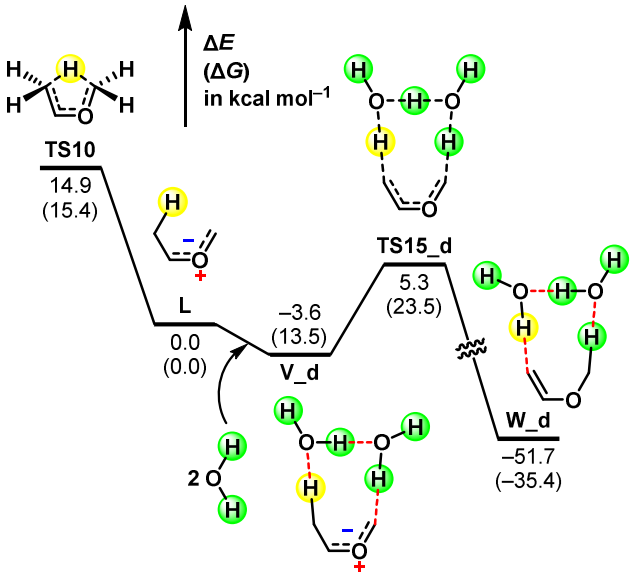

Fig. S2 Direct *versus* water-dimer-assisted mechanisms for [1,4] proton shift in carbonyl ylide **L**. Computed at the SCS-MP2/aug-cc-pVTZ//ωB97XD/6-311+G(d,p) level.

S3. Intermolecular proton transfer between propene and allyl anion

In the main text, we used the transition structure for intermolecular proton transfer between propene and allyl anion to estimate the ideal bond angle for sigmatropic proton shift (Fig. 3). Here we provide the complete energy profile for this process (Fig. S3). Although the considerations of orbital symmetry are absent in this intermolecular reaction (and any other intermolecular ones), this simple reaction shows that the C···H···C bond angle in the proton transfer transition structure between conjugated systems is very close to 180°.

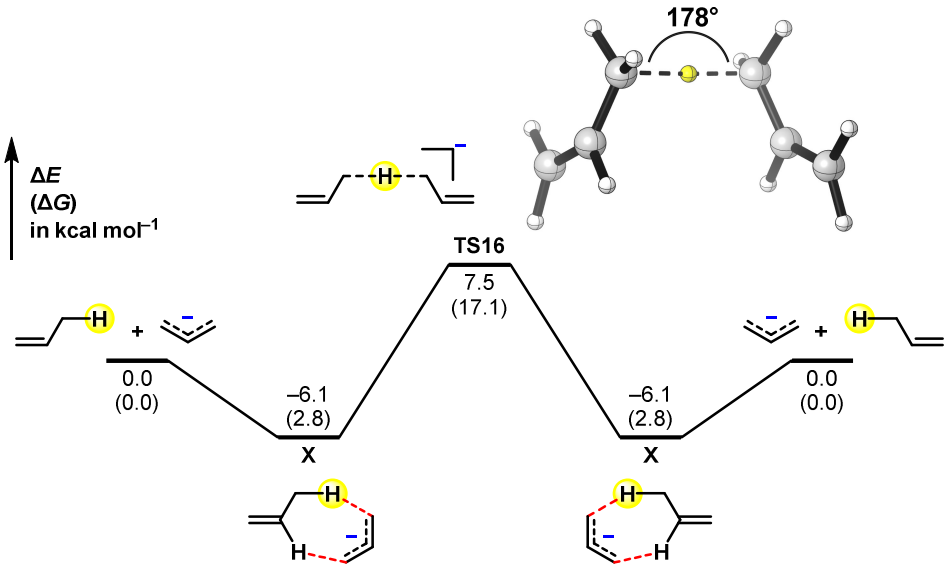

Fig. S3 Double-well potential energy surface for the intermolecular proton transfer between propene and allyl anion. Computed at the SCS-MP2/aug-cc-pVTZ//ωB97XD/6-311+G(d,p) level. Color scheme: C, gray; H, white; the migrating hydrogen, yellow.

S4. Computed energies of all stationary points

Table S2 Zero-point energies (ZPEs), thermal corrections to Gibbs energies (TCGs), and single-point energies (SPEs)

	ZPE[a] (a.u.)	TCG[a] (a.u.)	SPE[a] (a.u.)	SPE[b] (a.u.)
H_2O	0.021683	0.003399	−76.432257	−76.326121
(*Z*)-but-2-ene	0.108427	0.080436	−157.212626	−156.867774
hydroxyl anion	0.008765	−0.007481	−75.796177	−75.695732
propene	0.079923	0.054911	−117.897860	−117.640275
allyl anion	0.063653	0.038917	−117.260118	−117.003851
A	0.057831	0.034876	−79.136940	−78.961695
B and **B'**	0.092007	0.064755	−156.575101	−156.233047
C	0.126280	0.095394	−233.994065	−233.486683
C'	0.127042	0.096587	−233.983881	−233.476611
D	0.160266	0.125826	−311.406090	−310.734428
D'	0.161570	0.128986	−311.390775	−310.720902
E	0.194079	0.156080	−388.813560	−387.978043
E'	0.195724	0.160696	−388.788574	−387.956591
F and **F'**	0.117987	0.086516	−233.036518	−232.583861
F_d and **F'_d**	0.143450	0.107705	−309.494565	−308.931545
G and **G'**	0.117571	0.083610	−233.026805	−232.577485
G_d	0.143536	0.106873	−309.506362	−308.945416
H	0.172780	0.140640	−236.395846	−235.874395
H'	0.172753	0.141108	−236.390444	−235.866644
I	0.115646	0.088089	−157.769191	−157.421263
J	0.124288	0.094808	−212.504743	−212.071230
K	0.126062	0.097115	−212.550901	−212.111834
L	0.082663	0.055879	−193.024428	−192.670390
M	0.085695	0.059048	−193.105556	−192.745759
N	0.079677	0.051572	−516.030104	−515.302780
O	0.081658	0.053599	−516.092303	−515.356586
P	0.179272	0.145822	−404.201493	−403.376417
Q	0.181947	0.149239	−404.296430	−403.460342
R	0.138091	0.107202	−384.726164	−383.983219
S	0.141522	0.110556	−384.850773	−384.092646
T	0.135345	0.103536	−707.723789	−706.606851
U	0.138515	0.106828	−707.839670	−706.708762
V	0.107666	0.075878	−269.467196	−269.000327
V_d	0.133212	0.097126	−345.915806	−345.335520
W	0.109701	0.076698	−269.545310	−269.077733
W_d	0.135398	0.097966	−345.991431	−345.414333
X	0.144762	0.109114	−235.170932	−234.655018

continued	ZPE[a] (a.u.)	TCG[a] (a.u.)	SPE[a] (a.u.)	SPE[b] (a.u.)
TS1	0.053016	0.030185	−79.059236	−78.880060
TS2	0.088446	0.062348	−156.519743	−156.177169
TS3	0.123297	0.094661	−233.956590	−233.450244
TS4	0.157367	0.125438	−311.337728	−310.666968
TS5	0.192437	0.157840	−388.732119	−387.898230
TS6 and **TS6'**	0.113041	0.080222	−233.023228	−232.570631
TS6_d and **TS6'_d**	0.139429	0.103762	−309.490099	−308.925994
TS7	0.167397	0.136891	−236.372515	−235.844995
TS8	0.110132	0.083048	−157.739248	−157.386803
TS9	0.121631	0.093496	−212.470560	−212.031918
TS10	0.080847	0.054953	−193.005191	−192.644868
TS11	0.077104	0.050174	−515.998047	−515.266091
TS12	0.176189	0.143694	−404.175731	−403.348778
TS13	0.135653	0.105326	−384.715344	−383.965835
TS14	0.132410	0.101237	−707.706204	−706.587119
TS15	0.103678	0.074448	−269.450980	−268.971652
TS15_d	0.129027	0.094618	−345.905082	−345.317158
TS16	0.140537	0.106165	−235.148584	−234.629195

[a]Computed at the ωB97XD/6-311+G(d,p) level.

[b]Computed at the SCS-MP2/aug-cc-pVTZ//ωB97XD/6-311+G(d,p) level.

S5. Cartesian coordinates of all stationary points

H_2O

O	0.000000	0.116314	0.000000
H	0.760751	−0.465249	0.000000
H	−0.760751	−0.465265	0.000000

(*Z*)-but-2-ene

C	−1.584221	−0.522174	0.000000
C	−0.666048	0.663389	−0.000003
C	0.666048	0.663389	−0.000003
C	1.584221	−0.522174	−0.000001
H	−1.051571	−1.474041	−0.000086
H	−2.236611	−0.502129	−0.878951
H	−2.236482	−0.502220	0.879050
H	−1.163836	1.631097	0.000005
H	1.163836	1.631097	0.000008
H	2.236647	−0.502099	−0.878924
H	1.051571	−1.474041	−0.000141
H	2.236446	−0.502249	0.879077

hydroxyl anion

O	0.000000	0.000000	0.106827
H	0.000000	0.000000	−0.854620

propene

C	1.230952	−0.162496	0.000013
C	−0.134008	0.454346	−0.000084
C	−1.277192	−0.220990	−0.000136
H	1.801062	0.153499	0.879505
H	1.801106	0.153784	−0.879273
H	1.176328	−1.253588	0.000036
H	−0.167692	1.542529	0.000202
H	−2.235672	0.286048	0.000638
H	−1.293643	−1.307434	0.000132

allyl anion

C	1.270403	0.180433	−0.000098
C	−0.000025	−0.385538	−0.000045
C	−1.270361	0.180377	0.000137
H	2.158986	−0.443611	0.000188
H	1.414638	1.259376	0.000467
H	0.000113	−1.483317	−0.000078
H	−2.159148	−0.443408	0.000053
H	−1.414689	1.259329	−0.000592

A

C	−0.690397	0.000018	0.015424
C	0.832909	−0.000012	−0.146365
H	−1.141206	−0.875733	−0.478188
H	−1.141025	0.875331	−0.479014
H	−1.113250	0.000296	1.053386
H	1.270068	0.889197	0.344831
H	1.270336	−0.889128	0.344625

B and **B’**

C	−1.492387	−0.499381	0.000041
C	−0.614814	0.714313	−0.000104
C	0.763901	0.586417	0.000003
C	1.544851	−0.570824	−0.000079
H	−1.314804	−1.150731	−0.878217
H	−2.558214	−0.236434	0.000062
H	−1.314616	−1.150597	0.878365
H	−1.073274	1.698931	0.000198
H	1.322175	1.529027	0.000086
H	2.629083	−0.510626	0.000399
H	1.100342	−1.562725	−0.000058

C

C	2.496313	−0.820125	0.000019
C	1.933452	0.573113	−0.000085
C	0.586718	0.814173	0.000000
C	−0.482158	−0.111294	0.000064
C	−1.835764	0.288305	0.000039
C	−2.981770	−0.462635	−0.000039
H	2.171784	−1.402254	0.878659
H	3.592594	−0.813704	0.000317
H	2.172309	−1.402265	−0.878813
H	2.627775	1.408447	−0.000040
H	0.287221	1.867054	0.000030
H	−0.258814	−1.177534	−0.000057
H	−1.983989	1.374554	0.000068
H	−2.949148	−1.549855	−0.000082
H	−3.960475	0.006330	−0.000065

C’

C	−1.474440	−1.139770	0.410884
C	−1.600342	0.169559	−0.306603
C	−0.675343	1.171821	−0.242208

C	0.653346	1.169574	0.277354
C	1.616234	0.131314	0.223270
C	1.637688	−1.079305	−0.423359
H	−0.931880	−1.924188	−0.140460
H	−2.463965	−1.539712	0.667815
H	−0.902073	−0.999463	1.336847
H	−2.552198	0.382261	−0.790863
H	−1.024608	2.143343	−0.612335
H	1.040240	2.141417	0.583447
H	2.544697	0.378341	0.749932
H	0.821331	−1.417667	−1.049791
H	2.525598	−1.703496	−0.380628

D

C	−3.653683	0.909471	−0.000117
C	−3.148587	−0.507158	−0.000050
C	−1.825275	−0.817799	0.000111
C	−0.711070	0.069484	0.000294
C	0.606912	−0.376121	−0.000010
C	1.787552	0.355642	−0.000088
C	3.073355	−0.249565	0.000004
C	4.299027	0.340714	−0.000033
H	−3.305446	1.472803	−0.879054
H	−3.306226	1.472752	0.879165
H	−4.748242	0.946324	−0.000555
H	−3.881877	−1.308542	−0.000323
H	−1.573383	−1.881413	0.000001
H	−0.896556	1.142369	0.000526
H	0.732251	−1.465112	−0.000118
H	1.732099	1.444202	0.000090
H	3.061876	−1.343959	−0.000158
H	5.208944	−0.250018	−0.000215
H	4.407172	1.422586	−0.000024

D’

C	1.191888	1.019844	−1.296656
C	1.661583	0.804994	0.107491
C	1.491261	−0.346050	0.806916
C	0.697543	−1.487830	0.456918
C	−0.478657	−1.568442	−0.289665
C	−1.487553	−0.653478	−0.618187
C	−1.843703	0.591039	−0.013572
C	−1.349974	1.241391	1.075892
H	0.106594	1.175687	−1.366488
H	1.397755	0.126325	−1.901553
H	1.699054	1.877632	−1.752832
H	2.276085	1.584421	0.554009
H	2.063739	−0.433137	1.735084
H	1.098679	−2.445054	0.794943
H	−0.685149	−2.579047	−0.658980
H	−2.214816	−1.019161	−1.342519
H	−2.698504	1.073195	−0.497254
H	−1.816905	2.165904	1.405815
H	−0.520859	0.864417	1.654959

E

C	−4.856577	0.916386	0.000852
C	−4.354301	−0.501955	0.000788
C	−3.039352	−0.824951	0.000555
C	−1.918737	0.064879	0.000335
C	−0.611529	−0.376273	0.000077
C	0.569785	0.376994	−0.000155
C	1.845412	−0.204205	−0.000370
C	3.076563	0.415239	−0.000607
C	4.310520	−0.303675	−0.000820
C	5.570556	0.192493	−0.000818
H	−4.507862	1.475965	−0.878542
H	−4.507787	1.475926	0.880243
H	−5.950337	0.954143	0.000901
H	−5.092384	−1.298929	0.000949
H	−2.792057	−1.888573	0.000528
H	−2.106214	1.137167	0.000379
H	−0.474904	−1.462783	0.000057
H	0.493792	1.463776	−0.000162
H	1.862216	−1.299068	−0.000368
H	3.120558	1.503993	−0.000605
H	4.208720	−1.392282	−0.000806
H	6.435115	−0.462293	−0.000887
H	5.757099	1.263368	−0.000709

E’

C	2.266467	−0.523906	0.915829
C	1.553827	0.785192	1.060110
C	0.927714	1.454533	0.069784
C	0.665297	1.019658	−1.282261
C	0.370325	−0.241611	−1.762505
C	−0.078263	−1.427681	−1.136831
C	−0.644939	−1.672221	0.129032

C	−1.274430	−0.871537	1.070698
C	−1.906224	0.406728	0.922045
C	−2.201492	1.097792	−0.204345
H	1.598954	−1.379936	1.067904
H	3.091458	−0.595865	1.634664
H	2.670494	−0.628487	−0.096402
H	1.626888	1.277587	2.028205
H	0.603913	2.468812	0.303481
H	0.753451	1.803131	−2.036521
H	0.473118	−0.337246	−2.847856
H	0.067656	−2.326169	−1.738604
H	−0.583895	−2.724159	0.426269
H	−1.455707	−1.348228	2.034031
H	−2.235986	0.852432	1.863538
H	−1.949303	0.731729	−1.188893
H	−2.730729	2.044726	−0.139162

F and **F'**

O	−2.075558	−1.006894	−0.011960
C	1.447209	−0.951480	0.522842
C	0.965477	−0.224217	−0.700285
C	0.249479	0.956635	−0.585823
C	−0.256128	1.569868	0.562889
H	−1.251450	−1.134789	−0.505540
H	−1.885673	−0.126690	0.355094
H	2.117518	−0.333290	1.150811
H	1.993569	−1.866242	0.263071
H	0.616105	−1.246274	1.185609
H	1.337652	−0.533213	−1.673006
H	−0.003728	1.445898	−1.531366
H	−0.767594	2.525217	0.496445
H	0.011848	1.219696	1.556826

F_d and **F'_d**

O	1.448040	1.838652	−0.458539
O	2.244776	−0.765500	0.525024
C	−1.712271	0.649334	1.072303
C	−1.465022	0.500958	−0.401476
C	−0.889749	−0.634951	−0.916095
C	−0.378676	−1.755577	−0.222983
H	0.529129	1.534116	−0.542269
H	1.900074	1.022372	−0.193984
H	2.065579	−0.653605	1.459973
H	1.376614	−1.150200	0.183709
H	−2.386235	−0.129643	1.469336
H	−2.153058	1.622332	1.315227
H	−0.778842	0.560332	1.654006
H	−1.809225	1.283966	−1.071121
H	−0.747750	−0.643590	−2.000405
H	−0.153176	−2.652514	−0.796906
H	−0.711325	−1.937375	0.800063

G and **G'**

O	−3.231304	−0.053548	−0.413133
C	2.396111	−0.555496	−0.409290
C	1.555544	0.659011	−0.128702
C	0.314255	0.675329	0.367779
C	−0.572707	−0.461246	0.740676
H	−3.549708	0.088752	−1.307203
H	1.906660	−1.473123	−0.077986
H	3.368132	−0.491321	0.095982
H	2.601022	−0.658420	−1.482218
H	2.018482	1.612947	−0.381342
H	−0.151527	1.653348	0.485642
H	−0.839944	−0.391338	1.802997
H	−0.113888	−1.439306	0.565607
H	−1.548013	−0.378742	0.180811

G_d

O	−1.878984	0.070897	−1.481257
O	−1.922993	−0.037599	1.097687
C	0.724405	−1.597234	0.353841
C	1.683580	−0.641495	−0.294074
C	1.658267	0.692824	−0.243208
C	0.667569	1.563987	0.471673
H	−0.926952	0.016540	−1.577068
H	−1.998091	0.028672	−0.462629
H	−2.700854	−0.386304	1.532437
H	1.230780	−2.147141	1.159222
H	0.391655	−2.344668	−0.376226
H	−0.174709	−1.111153	0.763038
H	2.494638	−1.095207	−0.867865
H	2.449862	1.218644	−0.781560
H	0.244385	2.297601	−0.224110
H	1.176236	2.133666	1.261464
H	−0.174066	1.014480	0.912475

H

C	2.897017	0.542038	0.099265
C	1.765031	−0.419813	−0.258790
C	0.393441	0.065349	0.204796
C	−0.750937	−0.878485	−0.147292
C	−2.119376	−0.340490	0.306465
C	−2.509192	0.976637	−0.345980
H	2.722309	1.525878	−0.348213
H	3.871093	0.180570	−0.249262
H	2.959642	0.683022	1.184056
H	1.739609	−0.564840	−1.346053
H	1.972839	−1.406846	0.176721
H	0.411544	0.220178	1.294744
H	0.171513	1.037484	−0.251364
H	−0.781828	−1.001546	−1.238356
H	−0.553437	−1.867216	0.304757
H	−2.866335	−1.106422	0.048039
H	−2.080742	−0.345013	1.426691
H	−3.597570	1.135093	−0.296260
H	−2.024540	1.838243	0.143715

H'

C	−1.469432	1.304566	−0.304064
C	−1.640437	−0.019950	0.435278
C	−0.823655	−1.184920	−0.138763
C	0.685965	−1.197929	0.143058
C	1.534805	−0.072683	−0.495846
C	1.784777	1.100582	0.451884
H	−0.442933	1.665692	−0.133101
H	−2.172667	2.056143	0.076462
H	−1.655812	1.181051	−1.379273
H	−1.345836	0.129051	1.481215
H	−2.701572	−0.311824	0.435609
H	−1.247783	−2.120029	0.257148
H	−0.981280	−1.221350	−1.228059
H	0.843073	−1.162234	1.229244
H	1.056289	−2.178822	−0.196236
H	2.448885	−0.569005	−0.901340
H	1.003627	0.280646	−1.397059
H	2.435644	0.766010	1.281990
H	2.328222	1.906671	−0.075879

I

C	−1.504674	−0.565675	0.095225
C	−0.664410	0.654899	−0.271816
C	0.767187	0.563019	0.286396
C	1.565997	−0.612965	−0.252819
H	−1.025385	−1.462402	−0.309214
H	−2.526104	−0.503693	−0.301348
H	−1.569389	−0.675502	1.186146
H	−0.595798	0.724208	−1.364850
H	−1.163163	1.566830	0.099532
H	1.278004	1.500364	0.017060
H	0.649952	0.609965	1.400785
H	2.647758	−0.442243	−0.139010
H	1.319530	−1.553196	0.268979

J

N	−0.431572	0.051725	−0.017569
C	1.989153	−0.096158	0.008984
C	0.649336	−0.721025	−0.013200
C	−0.464215	1.391431	−0.004186
C	−1.736818	−0.622478	0.012929
H	2.141878	0.564645	−0.859711
H	2.770729	−0.856229	0.001472
H	2.129772	0.534932	0.901596
H	0.496162	−1.788059	−0.019279
H	−1.426423	1.875206	−0.011851
H	0.455613	1.948915	0.027956
H	−2.400193	−0.142098	−0.705426
H	−2.159092	−0.540384	1.014663
H	−1.612179	−1.669620	−0.253594

K

N	−0.418618	−0.020212	−0.261299
C	1.991080	−0.113449	0.117201
C	0.794152	−0.666064	−0.118836
C	−0.454009	1.399846	−0.001941
C	−1.603148	−0.753916	0.136801
H	2.870416	−0.742896	0.136674
H	2.133230	0.948180	0.274892
H	0.722006	−1.742752	−0.250883
H	0.276964	1.912319	−0.631864
H	−1.444870	1.786604	−0.246542
H	−0.232036	1.640213	1.050429
H	−2.485705	−0.317251	−0.337193
H	−1.756689	−0.749810	1.227207
H	−1.521442	−1.791614	−0.192977

L

O	0.721761	0.573517	0.000000
C	−1.417834	−0.495112	0.000000
C	−0.565046	0.702115	−0.000001
C	1.419404	−0.533057	0.000000
H	−1.216011	−1.129363	−0.880548
H	−2.472161	−0.221107	0.000002
H	−1.216008	−1.129361	0.880550
H	−0.899941	1.727014	0.000001
H	2.485395	−0.386817	0.000001
H	0.925491	−1.492179	−0.000004

M

O	0.601196	0.710208	0.000017
C	−1.440925	−0.567933	0.000002
C	−0.738140	0.563719	−0.000005
C	1.373428	−0.471553	−0.000015
H	−2.520623	−0.506647	−0.000003
H	−0.993341	−1.552961	0.000037
H	−1.217676	1.536358	−0.000029
H	1.170155	−1.072870	−0.893419
H	2.415722	−0.157858	0.000153
H	1.170019	−1.073087	0.893230

N

S	−0.758161	−0.564782	0.000022
C	1.757360	0.540504	0.000030
C	0.872299	−0.653920	−0.000065
C	−1.305903	0.976585	−0.000046
H	1.579659	1.174904	−0.880449
H	2.807337	0.246488	−0.000051
H	1.579778	1.174724	0.880656
H	1.252992	−1.665373	−0.000050
H	−2.378858	1.090451	0.000157
H	−0.652862	1.836306	−0.000117

O

S	−0.680313	−0.712806	−0.000003
C	1.764518	0.623692	−0.000003
C	1.059922	−0.505703	−0.000006
C	−1.262835	0.996350	0.000005
H	2.847062	0.581748	0.000025
H	1.308918	1.606527	−0.000022
H	1.563604	−1.467915	0.000041
H	−0.926136	1.523351	−0.894506
H	−2.351751	0.951881	−0.000107
H	−0.926318	1.523266	0.894634

P

N	−1.489234	−0.262275	−0.011339
C	−1.914193	1.010256	0.011823
C	−0.707484	1.894788	0.154103
C	0.382455	0.986103	−0.431642
C	1.788014	1.109388	0.066639
C	2.547233	−0.001292	0.188018
C	2.015062	−1.332169	0.013770
C	0.660370	−1.522513	−0.085071
C	−0.154548	−0.385160	−0.141689
C	−2.383617	−1.404355	0.106028
H	−2.928847	1.218080	0.318439
H	−0.782248	2.853344	−0.357862
H	−0.508473	2.091768	1.227990
H	0.348195	1.120897	−1.538666
H	2.202958	2.096344	0.243967
H	3.590929	0.095102	0.471438
H	2.681848	−2.183249	0.074246
H	0.236583	−2.521867	−0.057601
H	−2.253523	−2.060270	−0.755285
H	−2.150762	−1.954049	1.018907
H	−3.411764	−1.050453	0.141929

Q

N	−1.488907	−0.358271	0.278250
C	−1.955441	0.953703	−0.175385
C	−0.773533	1.889933	0.120199
C	0.394197	0.937637	0.037575
C	1.749479	1.166564	−0.075125
C	2.626836	0.077795	−0.100708
C	2.128513	−1.215461	−0.013560
C	0.758929	−1.459560	0.102248
C	−0.101091	−0.368926	0.137045
C	−2.258709	−1.505136	−0.137813
H	−2.875338	1.236264	0.341086
H	−0.713286	2.722018	−0.582922
H	−0.853615	2.304201	1.131520
H	−2.159257	0.929380	−1.259690
H	2.131598	2.179577	−0.151137
H	3.693501	0.242924	−0.196846

H	2.812846	−2.056394	−0.043531
H	0.387070	−2.475685	0.161055
H	−2.169888	−1.701111	−1.219226
H	−1.935272	−2.395467	0.404916
H	−3.311098	−1.337106	0.100161

R

O	−1.426982	−1.172843	0.025380
C	−2.338006	−0.188762	0.000809
C	−1.621932	1.114086	0.221441
C	−0.277097	0.743159	−0.404550
C	0.982730	1.439886	−0.021373
C	2.118992	0.721904	0.122840
C	2.142053	−0.718479	0.058496
C	0.977008	−1.440358	−0.006900
C	−0.205932	−0.709086	−0.094927
H	−3.297852	−0.493729	0.392463
H	−2.085517	1.976331	−0.253947
H	−1.514827	1.325201	1.308301
H	−0.443785	0.797786	−1.512073
H	0.987516	2.521696	0.054077
H	3.052374	1.235403	0.328948
H	3.090425	−1.233219	0.151053
H	0.960618	−2.520821	0.073119

S

O	−1.417271	−1.209257	0.089506
C	−2.354479	−0.147713	−0.170648
C	−1.615640	1.174017	0.110387
C	−0.180257	0.722083	0.020254
C	1.014000	1.418212	−0.017962
C	2.212661	0.703353	−0.041580
C	2.199736	−0.688134	−0.018436
C	1.002115	−1.400537	0.021654
C	−0.172142	−0.668584	0.038942
H	−2.654727	−0.215633	−1.221517
H	−3.225691	−0.313194	0.461935
H	−1.875784	1.946294	−0.615728
H	−1.839443	1.559208	1.110253
H	1.021557	2.503049	−0.028395
H	3.157002	1.233549	−0.077665
H	3.137453	−1.232317	−0.037082
H	0.981833	−2.483076	0.036478

T

S	−1.664806	−1.020554	0.052032
C	−2.264716	0.530818	0.001523
C	−1.156777	1.536760	0.169519
C	0.075888	0.847875	−0.415156
C	1.412341	1.378112	0.001870
C	2.459062	0.542865	0.141636
C	2.315031	−0.892000	0.037169
C	1.077566	−1.463731	−0.027037
C	−0.052170	−0.622657	−0.091379
H	−3.306622	0.686856	0.240299
H	−1.359309	2.483069	−0.334476
H	−0.999187	1.756974	1.245524
H	−0.021704	0.918692	−1.523755
H	1.530177	2.450673	0.117765
H	3.439249	0.942992	0.379629
H	3.196650	−1.517760	0.104536
H	0.960283	−2.540889	0.029101

U

S	−1.684585	−1.087582	0.100340
C	−2.233455	0.609084	−0.332259
C	−1.147082	1.554453	0.187341
C	0.160174	0.814887	0.055094
C	1.431724	1.365335	0.011193
C	2.546983	0.532214	−0.046673
C	2.385773	−0.848587	−0.056313
C	1.114254	−1.414335	−0.018410
C	0.010838	−0.574024	0.036411
H	−2.323774	0.673841	−1.418564
H	−3.207967	0.790485	0.119375
H	−1.149775	2.498756	−0.362532
H	−1.323822	1.783811	1.245042
H	1.556405	2.443368	0.023745
H	3.541153	0.962049	−0.086421
H	3.255367	−1.494287	−0.104942
H	0.990525	−2.490873	−0.039440

V

O	2.215012	−0.573076	−0.122382
O	−0.671027	0.910341	−0.463052
C	−1.001081	−1.270854	0.468860
C	−1.166024	−0.258730	−0.584082

C	0.073341	1.374791	0.556974
H	2.844543	−0.337749	−0.804117
H	1.742311	0.252425	0.098768
H	0.072846	−1.454019	0.633525
H	−1.488201	−2.203525	0.188683
H	−1.416644	−0.922834	1.426599
H	−1.647390	−0.428492	−1.537255
H	0.150562	2.451488	0.515430
H	−0.047327	0.873350	1.511320

V_d

O	2.169810	−1.322050	−0.039736
O	1.864071	1.409748	−0.136234
O	−1.511801	0.691633	−0.400390
C	−1.047551	−1.534708	0.357906
C	−1.564396	−0.558910	−0.608676
C	−0.934322	1.321484	0.663333
H	2.957761	−1.555222	0.450143
H	2.190116	−0.350471	−0.120097
H	1.932700	1.935768	−0.933588
H	0.919899	1.483888	0.156517
H	0.044098	−1.414942	0.470073
H	−1.252643	−2.550778	0.024621
H	−1.495594	−1.377022	1.349779
H	−1.982042	−0.817582	−1.573682
H	−1.341575	2.321770	0.743393
H	−0.871759	0.722748	1.568343

W

O	2.400014	0.314462	−0.056247
O	−1.100964	0.448980	−0.623410
C	−0.253923	−1.449710	0.592345
C	−0.794009	−0.847016	−0.470610
C	−0.845876	1.311395	0.474534
H	2.710013	0.437517	−0.953829
H	1.767943	−0.411101	−0.103597
H	−0.085314	−2.517384	0.551900
H	−0.005815	−0.933052	1.510592
H	−1.046482	−1.399672	−1.369793
H	−1.189349	2.297437	0.168040
H	−1.405454	0.985674	1.358112
H	0.224901	1.345027	0.698215

W_d

O	1.916062	−1.320558	−0.550703
O	2.205142	1.323320	0.315278
O	−1.700436	0.380449	−0.677683
C	−0.864252	−1.160843	0.969025
C	−1.521013	−0.832969	−0.150095
C	−1.179796	1.491003	0.044514
H	2.371153	−2.054196	−0.135509
H	2.274890	0.419874	−0.031899
H	2.809375	1.848829	−0.208318
H	0.992799	−1.394091	−0.267966
H	−0.855474	−2.198903	1.275903
H	−0.388119	−0.434171	1.614871
H	−1.998080	−1.586930	−0.768580
H	−1.460161	2.373656	−0.526951
H	−1.632011	1.540073	1.040971
H	−0.090153	1.437026	0.131678

X

C	−1.129391	0.905024	0.672784
C	−1.772147	−0.268824	0.014591
C	−2.992715	−0.293631	−0.518048
C	2.284033	1.046166	−0.392541
C	2.037326	−0.321998	−0.445080
C	1.707226	−1.237298	0.546221
H	−0.192560	1.156815	0.154723
H	−0.836846	0.645322	1.695705
H	−1.793868	1.775840	0.695422
H	−1.132880	−1.149805	−0.030087
H	−3.385003	−1.184828	−0.998904
H	−3.637792	0.582966	−0.502525
H	2.550961	1.598958	−1.287724
H	2.318883	1.582066	0.554603
H	2.082781	−0.748134	−1.454717
H	1.571434	−2.288891	0.311971
H	1.648891	−0.946944	1.593968

TS1

C	−0.793147	0.049353	0.027663
C	0.793141	−0.049347	0.027651
H	0.000033	−0.000010	1.050617
H	−1.244953	−0.946466	−0.007202

H	−1.277985	0.738235	−0.684053
H	1.277974	−0.738252	−0.684042
H	1.244969	0.946460	−0.007200

TS2

C	−1.289256	−0.600887	−0.064200
C	−0.684161	0.725934	0.059794
C	0.683957	0.726055	0.059984
C	1.289349	−0.600611	−0.064150
H	0.000450	−1.093155	−0.569140
H	−2.309084	−0.612824	−0.476784
H	−1.255764	−1.242058	0.828385
H	−1.256030	1.649985	−0.041085
H	1.255795	1.650200	−0.040061
H	2.308765	−0.612611	−0.477747
H	1.256528	−1.242481	0.827861

TS3

C	1.262910	−1.114192	−0.460812
C	1.531053	0.118088	0.220775
C	0.672008	1.205599	0.242923
C	−0.671972	1.205621	−0.242921
C	−1.531039	0.118110	−0.220780
C	−1.262967	−1.114145	0.460824
H	0.000037	−1.528147	0.000005
H	2.068417	−1.853318	−0.440029
H	0.839364	−0.990892	−1.464621
H	2.455526	0.200469	0.797861
H	1.070873	2.150520	0.620699
H	−1.070816	2.150548	−0.620700
H	−2.455495	0.200503	−0.797895
H	−0.839405	−0.990893	1.464626
H	−2.068463	−1.853279	0.440001

TS4

C	−1.346523	−1.615199	0.284062
C	−1.946942	−0.533935	−0.417882
C	−1.729062	0.819537	−0.256555
C	−0.696274	1.603859	0.340949
C	0.696277	1.603858	0.340949
C	1.729063	0.819535	−0.256555
C	1.946941	−0.533938	−0.417882
C	1.346520	−1.615200	0.284063
H	−0.000001	−1.748301	0.003902
H	−1.818653	−2.588382	0.132225
H	−1.150867	−1.416117	1.340419
H	−2.707820	−0.792838	−1.159161
H	−2.517361	1.448686	−0.680673
H	−1.077963	2.577253	0.661794
H	1.077967	2.577252	0.661792
H	2.517364	1.448683	−0.680674
H	2.707818	−0.792843	−1.159162
H	1.818649	−2.588384	0.132228
H	1.150863	−1.416116	1.340419

TS5

C	0.741560	1.458494	1.135277
C	2.018410	1.179248	0.597008
C	2.399323	0.113414	−0.188701
C	1.782987	−1.119861	−0.561417
C	0.639840	−1.864978	−0.334605
C	−0.639837	−1.864979	0.334603
C	−1.782985	−1.119863	0.561418
C	−2.399321	0.113412	0.188705
C	−2.018412	1.179246	−0.597006
C	−0.741564	1.458491	−1.135281
H	0.000001	1.738865	−0.000004
H	0.666225	2.316273	1.804396
H	0.114553	0.622549	1.438223
H	2.755760	1.980990	0.664701
H	3.407492	0.199628	−0.594035
H	2.484495	−1.704298	−1.160263
H	0.810015	−2.882440	−0.698774
H	−0.810012	−2.882443	0.698770
H	−2.484492	−1.704302	1.160264
H	−3.407489	0.199625	0.594042
H	−2.755762	1.980988	−0.664697
H	−0.114559	0.622546	−1.438230
H	−0.666233	2.316269	−1.804402

TS6 and **TS6'**

O	−2.717496	−0.649072	−0.253577
C	1.964675	−0.900065	0.264166
C	1.469440	0.259510	−0.558732
C	0.342422	0.948614	−0.288283
C	−0.657543	0.695626	0.746715
H	−2.347855	−1.217036	−0.933312
H	−1.658780	0.023946	0.234495

H	1.819787	−0.717032	1.335784
H	3.032222	−1.084785	0.097481
H	1.430326	−1.832232	0.034985
H	2.049591	0.522005	−1.441457
H	0.097007	1.751967	−0.986855
H	−1.114803	1.621087	1.115741
H	−0.281493	0.102543	1.588558

TS6_d and **TS6'_d**

O	1.458379	1.854769	−0.368451
O	2.265695	−0.630385	0.440420
C	−1.888084	0.595127	0.988812
C	−1.605934	0.342142	−0.468392
C	−0.840600	−0.687485	−0.896831
C	−0.110774	−1.649063	−0.089019
H	0.560244	1.565370	−0.559183
H	1.875576	1.011930	−0.068093
H	2.341459	−0.689555	1.394281
H	1.169284	−1.119902	0.184994
H	−2.344037	−0.280251	1.473752
H	−2.566796	1.442895	1.126772
H	−0.966653	0.814029	1.544997
H	−2.026183	1.033562	−1.194764
H	−0.680568	−0.750452	−1.975509
H	0.073376	−2.595520	−0.607163
H	−0.555945	−1.831510	0.896742

TS7

C	1.377929	1.255019	0.339224
C	1.608009	−0.070507	−0.381071
C	0.746946	−1.216789	0.179778
C	−0.747347	−1.216657	−0.179719
C	−1.608185	−0.070131	0.380942
C	−1.377368	1.255402	−0.339082
H	0.000156	1.475577	0.000161
H	2.009590	2.052710	−0.087137
H	1.629284	1.158212	1.410464
H	1.342740	0.053174	−1.445309
H	2.657585	−0.419582	−0.377809
H	1.165766	−2.176251	−0.163052
H	0.845701	−1.216180	1.275998
H	−0.846087	−1.216203	−1.275944
H	−1.166385	−2.175973	0.163249
H	−2.657888	−0.418809	0.377225
H	−1.343267	0.053331	1.445292
H	−1.627984	1.158779	−1.410505
H	−2.009115	2.053196	0.086939

TS8

C	1.333470	−0.686802	−0.117181
C	0.760070	0.685486	0.208818
C	−0.760070	0.685490	−0.208820
C	−1.333468	−0.686797	0.117185
H	−0.000027	−1.227769	0.000013
H	2.100088	−1.029388	0.590088
H	1.730507	−0.745926	−1.143091
H	0.803665	0.847854	1.297302
H	1.265303	1.549227	−0.251678
H	−1.265307	1.549227	0.251677
H	−0.803666	0.847854	−1.297304
H	−1.730524	−0.745925	1.143085
H	−2.100049	−1.029420	−0.590104

TS9

N	0.428210	0.007547	−0.094534
C	−1.862458	−0.198985	0.076870
C	−0.603890	−0.831662	−0.090727
C	0.092663	1.361402	0.065032
C	1.800789	−0.449380	0.023325
H	−1.258432	0.871673	0.662359
H	−2.656167	−0.837058	0.465049
H	−2.233113	0.432369	−0.733882
H	−0.399712	−1.891124	0.008472
H	0.934780	1.955556	0.418700
H	−0.404539	1.818251	−0.790949
H	2.284139	0.084614	0.844573
H	2.355919	−0.255621	−0.896703
H	1.817035	−1.519738	0.237118

TS10

O	0.661522	0.688865	0.035874
C	−1.250890	−0.572322	−0.047446
C	−0.637000	0.693373	0.076748
C	1.236455	−0.561628	−0.081317
H	−0.246536	−1.043590	−0.696205
H	−2.278978	−0.554112	−0.405655
H	−1.133054	−1.291032	0.768149
H	−1.083043	1.667670	−0.073815

H	2.281787	−0.439006	−0.348949
H	1.076257	−1.207384	0.781568

TS11

S	−0.800148	−0.594398	0.026739
C	1.584247	0.496199	−0.031111
C	0.873086	−0.726349	0.029224
C	−0.913661	1.124582	−0.078423
H	0.612137	1.173697	−0.594176
H	2.598889	0.424211	−0.420882
H	1.550725	1.153236	0.841826
H	1.293513	−1.712371	−0.121813
H	−1.882667	1.429583	−0.468186
H	−0.632256	1.675420	0.817266

TS12

N	1.493714	−0.296866	−0.111691
C	1.818588	1.010897	0.240980
C	0.745195	1.886168	−0.375534
C	−0.336700	0.949337	0.135815
C	−1.763382	1.127274	0.144465
C	−2.575406	0.028577	0.118861
C	−2.049392	−1.282964	−0.041667
C	−0.700080	−1.499647	−0.194795
C	0.145685	−0.383855	−0.161478
C	2.359536	−1.428455	0.143624
H	2.878449	1.250401	0.242681
H	0.692633	2.872101	0.083821
H	0.792943	1.977162	−1.476197
H	0.432157	1.036168	1.259944
H	−2.182027	2.125208	0.217915
H	−3.650641	0.151258	0.192405
H	−2.731144	−2.125405	−0.062210
H	−0.309322	−2.499903	−0.344954
H	2.226978	−1.797023	1.165915
H	2.133214	−2.230349	−0.560036
H	3.396505	−1.125552	0.000941

TS13

O	−1.413742	−1.201808	−0.035129
C	−2.261652	−0.133116	−0.282870
C	−1.656752	1.077392	0.397336
C	−0.286464	0.713532	−0.157383
C	0.959647	1.443009	−0.095754
C	2.131678	0.746054	−0.050931
C	2.159338	−0.675227	0.047896
C	1.003003	−1.417938	0.110808
C	−0.195526	−0.709377	0.056560
H	−3.297764	−0.443112	−0.199823
H	−2.029311	2.014189	−0.013396
H	−1.727461	1.088610	1.500672
H	−0.914573	0.556894	−1.265846
H	0.954937	2.526566	−0.126726
H	3.075293	1.280468	−0.061064
H	3.118329	−1.178451	0.088252
H	1.010857	−2.496678	0.204986

TS14

S	−1.685382	−1.040493	−0.016627
C	−2.130360	0.608048	−0.327176
C	−1.175066	1.508180	0.436598
C	0.062671	0.824347	−0.119601
C	1.401482	1.372672	−0.098169
C	2.481629	0.543664	−0.086808
C	2.328676	−0.867585	0.019700
C	1.087067	−1.443152	0.124075
C	−0.041807	−0.612540	0.086313
H	−3.202476	0.781673	−0.359746
H	−1.235761	2.539286	0.085160
H	−1.265747	1.483386	1.536762
H	−0.616444	0.845501	−1.216698
H	1.528861	2.449586	−0.122803
H	3.482676	0.958947	−0.125439
H	3.211846	−1.495807	0.030217
H	0.977394	−2.516490	0.228981

TS15

O	1.785055	−0.664199	−0.251614
O	−0.707531	0.974080	−0.375395
C	−0.794314	−1.290079	0.447984
C	−1.192383	−0.186549	−0.404124
C	0.407115	1.342436	0.461337
H	2.651614	−0.693294	−0.660137
H	1.329506	0.485803	0.070648
H	0.268212	−1.521286	0.120933
H	−1.459389	−2.143151	0.335424
H	−0.689934	−0.999317	1.497002
H	−1.922566	−0.312630	−1.201219

H	0.510759	2.415298	0.322342
H	0.169092	1.094681	1.499898

TS15_d

O	2.363300	−0.594676	−0.240111
O	1.102387	1.617237	0.085912
O	−1.554629	0.099810	−0.592512
C	−0.301069	−1.557191	0.651536
C	−1.028594	−1.030299	−0.493495
C	−1.420160	1.154591	0.392726
H	3.227159	−0.556190	0.168746
H	1.968542	0.329824	−0.151311
H	1.303265	2.390334	−0.442758
H	−0.169298	1.516635	0.261534
H	0.778280	−1.330068	0.450671
H	−0.400655	−2.642386	0.692347
H	−0.570389	−1.089799	1.597173
H	−1.128121	−1.623143	−1.401349
H	−2.180316	1.877990	0.107969
H	−1.617986	0.745225	1.386076

TS16

C	1.241677	0.979817	−0.693519
C	1.816804	−0.323822	−0.482701
C	2.585797	−0.748592	0.550174
C	−1.241736	0.979811	0.693535
C	−1.816897	−0.323768	0.482774
C	−2.585733	−0.748599	−0.550253
H	−0.000042	0.959813	−0.000013
H	0.997372	1.214530	−1.732290
H	1.765769	1.803890	−0.197604
H	1.494687	−1.092049	−1.190534
H	2.860285	−1.793221	0.660801
H	2.940269	−0.057731	1.312466
H	−0.997004	1.214650	1.732147
H	−1.765568	1.803983	0.197491
H	−1.495025	−1.091869	1.190864
H	−2.860256	−1.793224	−0.660611
H	−2.939962	−0.057854	−1.312775