Supporting information for:

Blocking deprotonation with retention of aromaticity in a plant *ent*-copalyl diphosphate synthase leads to product rearrangement

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Experimental Section

All reagents were purchased from Fisher Scientific unless noted otherwise.

The recombinant AtCPS used here was expressed as a previously described pseudomature construct.[1] Mutants were generated by whole plasmid PCR amplification with overlapping mutagenic primers of pENTR/SD/D-TOPO (Invitrogen) clones, and verified by complete gene sequencing prior to transfer by directional recombination to expression vectors, pDEST17 and the previously described pGG-DEST.[2] The resulting constructs were heterologously expressed in the C41 OverExpress strain of *Escherichia coli* (Lucigen), much as previously described.[3] Briefly, recombinant mutant clones were grown in liquid NZY media (10 g casein, 10 g NaCl, 5 g yeast extract, 1 g $MgSO_4$ (anhydrous) in 1 L H_2O, with pH adjusted to 7.0 using HCl) at 37 °C to OD_{600} = 0.6, then shifted to 16 °C for an hour prior to induction with 0.5 mM IPTG, followed by incubation at 16 °C.

Enzymatic products were investigated by expression from pGG-DEST based constructs in our previously described modular metabolic engineering system,[2] which couples production of GGPP in *E. coli* with further engineering to increase flux into isoprenoid metabolism.[4] Briefly, use of our metabolic engineering system involves, at the time of induction, supplementation with phosphate buffer (pH 7.0) to 100 mM, sodium pyruvate to 50 mM, and $MgCl_2$ to 1 mM (final concentrations), as previously described.[4] After induction and further incubation for 3 days, products (dephosphorylated by endogenous phosphatases) are extracted by addition of an equal volume of hexanes and gentle swirling, the organic solvent is separated and then dried under N_2, with the residue resuspended in fresh hexanes and analyzed by GC-MS.

Analysis of products by GC-MS was carried out much as previously described,[5] using a HP-5MS column (Agilent, 0.25 µm, 0.25ID, 30 m) on a 3900 GC with Saturn 2100T ion trap MS (Varian), with a 1.2 mL/min He flow rate, and the following oven temperature program: 50 °C for 3 min, 15 °C/min to 300 °C, hold 3 min. Samples (1 µL) underwent splitless injection at 250 °C.

To obtain a sufficient amount of (-)-kolavanol for NMR analysis, a total of 4 L of recombinant cultures were fermented and extracted as described above. (-)-Kolavenol was then purified much as previously described for other class II diterpene cyclase products.[6,7] After extraction, the phases were separated in a separatory funnel, and the pooled hexanes dried by rotary evaporation. The resulting extract was redissolved in 10 mL of fresh hexanes and fractionated over silica (4 g) using a Reveleris automated flash chromatography system (Grace, Deerfield, IL) with a 15 mL/min flow rate, 5 mL injections, UV detection at 200 nm, with the following stepwise gradient: 0%, 5%, 15%, 25% ethyl acetate/hexanes for 1 minute each and a final wash with 100% ethyl acetate for 3 minutes. The resulting fractions were analyzed by GC-MS, those containing the targeted (-)-kolavenol dried under N_2 and dissolved in 5 mL of 50% acetonitrile/dH_2O. This was then further purified via HPLC (Agilent 1200 system) equipped with a Kromasil 100-5-C8 (4.6 x 150mm, 5µm) column at a flow rate of 0.5 mL/min. The column was pre-equilibrated, sample injected and washed with 50% acetonitrile/dH_2O (0 - 2 minutes), eluted with 50 - 100% acetonitrile (2 - 7 minutes), and followed by a 100% acetonitrile wash (7 - 23 minutes). The purified (-)-kolavenol, with a final yield of ~1.5 mg, was dried under N_2 and redissolved in 0.5 mL CDCl3. This sample was analyzed by NMR carried out with a Bruker Avance 700 spectrometer equipped with a 5-mm HCN cryogenic probe for ^{1}H and ^{13}C detection using standard experiments from the Bruker TopSpin version 1.4 software. One-dimensional ^{1}H spectra were acquired at 700 MHz, and one-dimensional ^{13}C spectra acquired at 175 MHz. Chemical shifts were referenced using known chloroform

(^{13}C 77.23, ^{1}H 7.24 ppm) signals offset from TMS (Table S1), and compared to those previously reported for (-)-kolavenol.[8-11]

Optical rotation analysis was performed on a JASCO DIP-370 using a 0.5 dm cell. (-)-kolavenol was resuspended in hexanes to give a final concentration of 1 mg/mL and loaded into the cell. The observed rotation reading obtained was -0.024, using the following formula $[\alpha]_D^{23} = \frac{100*\alpha}{l*c}$ (c= 0.1 (g/100 mL), C_6H_{14}) gave a specific rotation of $[\alpha]_D^{23}$ = -48°, which was comparable to that previously reported for (-)-kolavenol.[8,9]

For in vitro assays, the enzymes were expressed as pDEST17 based 6xHis tagged constructs for ease of purification, which was accomplished much as previously described.[12] Briefly, cells from overnight incubation following induction were harvested by centrifugation for (5,000 *g* × 20 min at 4 °C), lysed by gentle sonification in 10 mL lysis buffer (50 mM Bis-Tris (pH 6.8), 150 mM KCl, 10 mM $MgCl_2$, 1 mM DTT, 10% glycerol), with the resulting lysate clarified by centrifugation (15,000 *g* x 20 min. at 4 °C). The tagged enzymes were purified over 5 mL of Ni-NTA His-bind resin (Novagen), in batch mode, with 30 minutes binding with mixing on a rotating disk mixer, followed by washing with 10 mL of 20mM imidazole and eluting with 5 mL of 250 mM imidazole in column buffer (50 mM Bis-Tris (pH 6.8), 1 mM DTT). Eluted protein was dialyzed using dialysis tubing (MW Cutoff = 12-14 kDa) against storage buffer (10 mM Bis-Tris (pH 6.8), 1 mM DTT, 10% glycerol).

In vitro assays for class II activity were carried out much as previously described.[13] Briefly, GGPP (Isoprenoids.com) was added to an assay tube and dried under N_2 gas. Then, assay buffer (50 mM HEPES (pH 7.75), 100 mM KCl, 0.1 mM $MgCl_2$, 10% glycerol) and purified enzymes were added for 1 mL total volume assays (50 µM GGPP and 200 nM enzyme). After incubation overnight at 30 °C, reactions were terminated by incubation in a boiling water bath for 5 minutes. After cooling to room temp (15 minutes), reaction products were dephosphorylated by adding 10 µL of a solution of 1 M $MgCl_2$ and 0.1 M $ZnCl_2$ to the assays, followed by the addition of 15 units calf intestinal alkaline phosphatase (Promega), and incubated at 37 °C overnight. Assays were extracted with 3x1 mL hexanes, with the organic extract dried under N_2 gas, resuspended in 50 µL fresh hexanes and analyzed by GC-MS.

Kinetic analyses were carried out much as previously described.[14] The enzyme concentrations and time were varied to achieve approximately 2-8% product formation. Catalytic rates were determined from the observed fractional turnover (i.e. the ratio of product to the sum of the product and substrate). This was quantified via GC-FID. The kinetic parameters were calculated by fitting the reaction rate data to the substrate inhibition equation (Kaleidagraph 4.0; Synergy Software, Reading, PA, USA). All curve fits exhibited $R^2 > 0.9$.

For the D_2O labeling assays, the pD for D_2O assay buffer was adjusted using the D_2O correction factor[15] of pD = pH + 0.4 with 5 M NaOH in D_2O. The solution of 1 M $MgCl_2$ and 0.1 M $ZnCl_2$ was prepared in D_2O as well. The purified enzymes were diluted (10-fold) and concentrated via ultrafiltration, using an Amicon Ultra centrifugal filter (MW cutoff = 10k Da), 3 times with D_2O assay buffer. Assays, dephosphorylation, and analysis by GC-MS were otherwise carried out as described above.

Quantum chemical calculations made use of several density functional methods; details and references can be found below.

Figure S1: GC-MS based comparison of dephosphorylated AtCPS, AtCPS:H263A, AtCPS:H263Y, AtCPS:H263F, and KgTPS products with structures shown below.

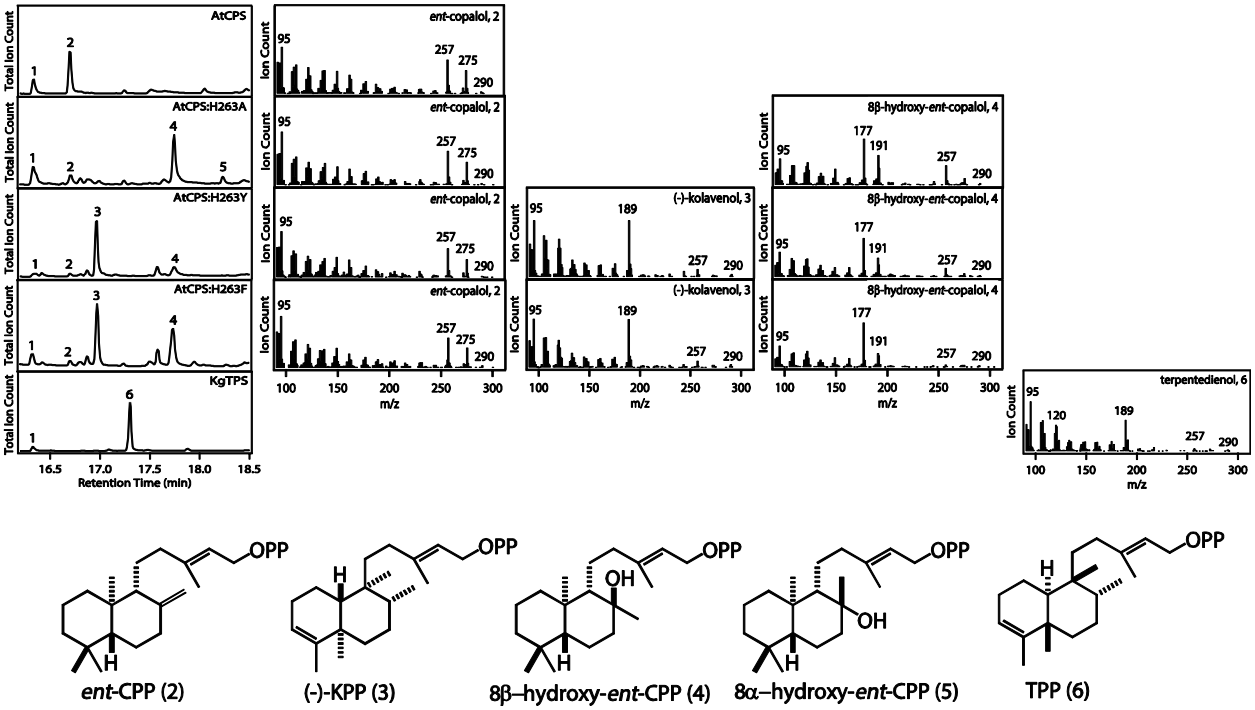


Table S1: ^{1}H and ^{13}C NMR data for (-)-kolavenol ($CDCl_3$, 700 MHz for ^{1}H NMR; 175 MHz for ^{13}C NMR)

Position	δ_H	δ_C
1a **1b**	1.50 (1H, m) 1.35 (1H, m)	18.8
2	1.94 (2H, m)	27.5
3	5.11 (1H,)	121.0
4		145.1
5		38.8
6	1.62 (1H, m) 1.09 (1H, m)	37.4
7	1.34 (2H, m)	28.1
8	1.39 (1H, m)	36.8
9		39.2
10	1.27 (1H, m)	47.0
11	1.39 (1H, m) 1.27 (1H, m)	37.3
12a **12b**	1.79 (1H, m) 1.73 (1H, m)	33.4
13		141.6
14a **14b**	5.31 (1H,)	123.4
15	4.06 (2H, dd, J = Hz)	60.1
16	1.59 (3H, s)	17.1
17	0.72 (3H, s)	16.6
18	0.63 (3H, s)	19.0
19	0.91 (3H, s)	20.5
20	1.50 (3H, s)	18.6

Figure S2: Labeled carbon structure of (-)-kolavenol based on ^{13}C data in Table S1.

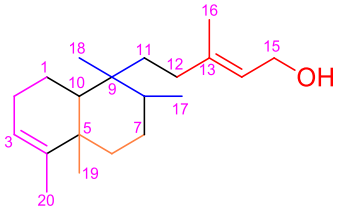


Figure S3: ^{1}H 1D spectrum obtained for (-)-kolavenol.

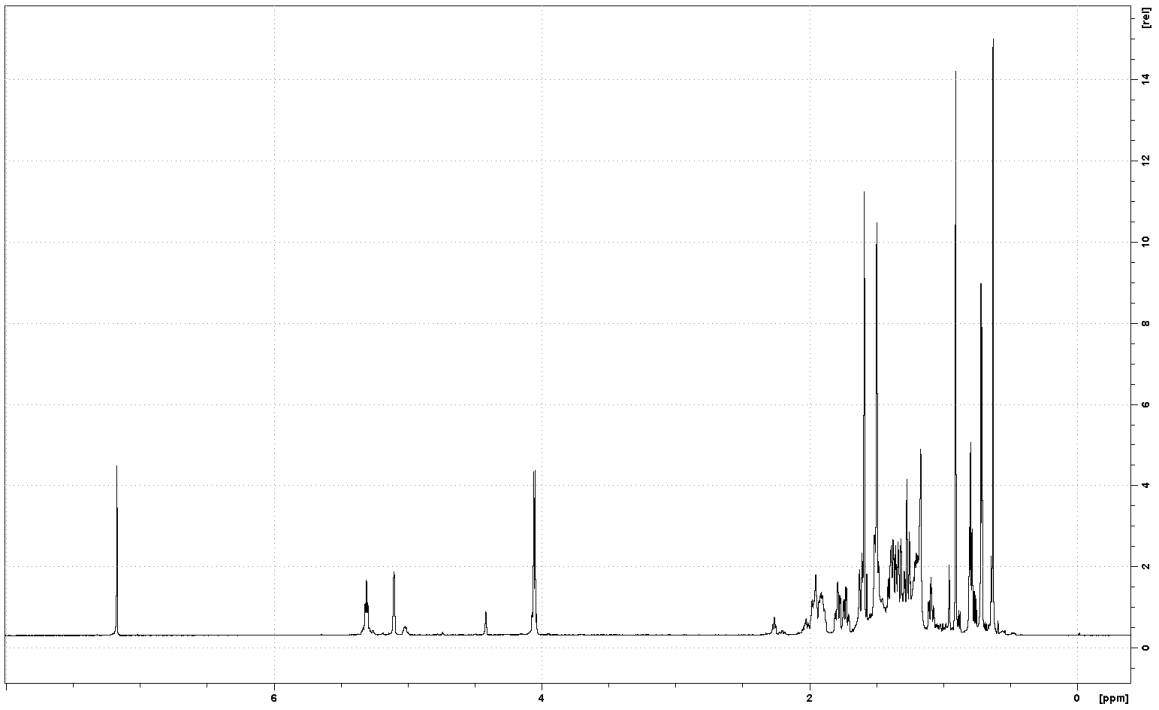


Figure S4: ^{13}C 1D spectrum obtained for (-)-kolavenol.

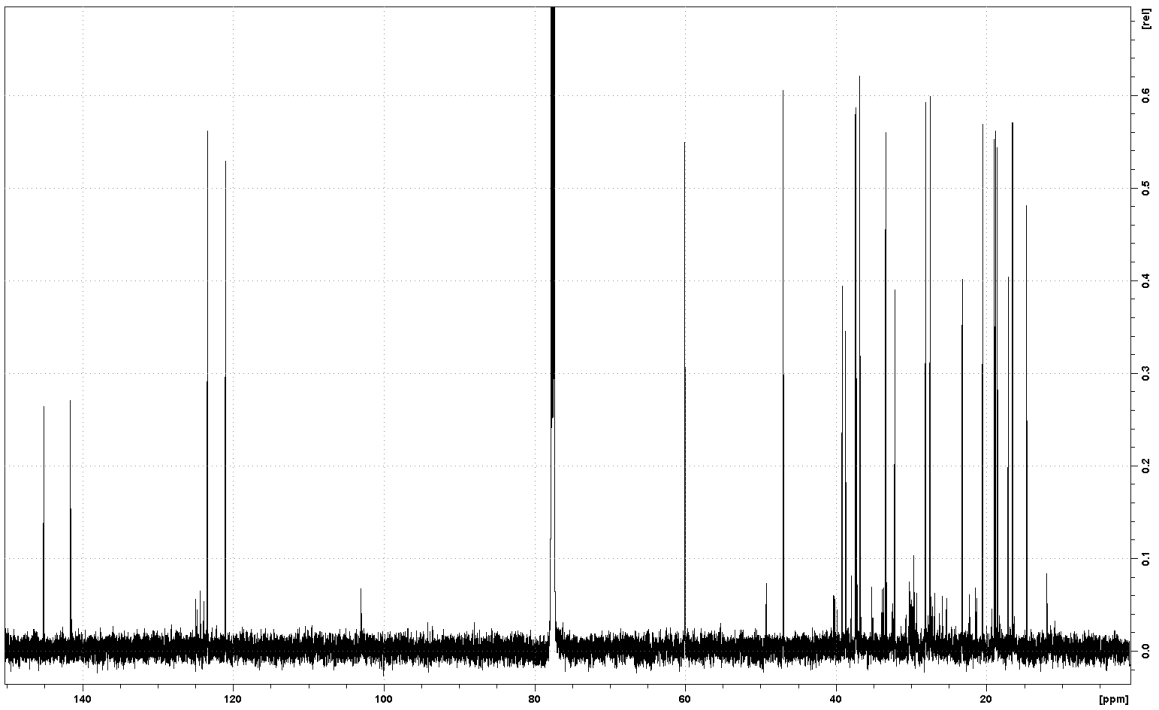


Figure S5: Part a) GC-MS comparison of dephosphorylated enzymatic products from overnight assays conducted in D_2O. Control assays with both Wild-type and AtCPS:H263Y are shown in **I** and **III**, respectively. Assays performed in D_2O for Wild-type and AtCPS:H263Y are shown in **II** and **IV**, respetively. Note (-)-kolavenol mass spectra is the same in both assays (**III** and **IV**), however the *ent*-copalol has a mass difference of +1 in the AtCPS in D_2O assay (**II**). **Part b**) Shown is the reaction scheme for the assays performed in D_2O.

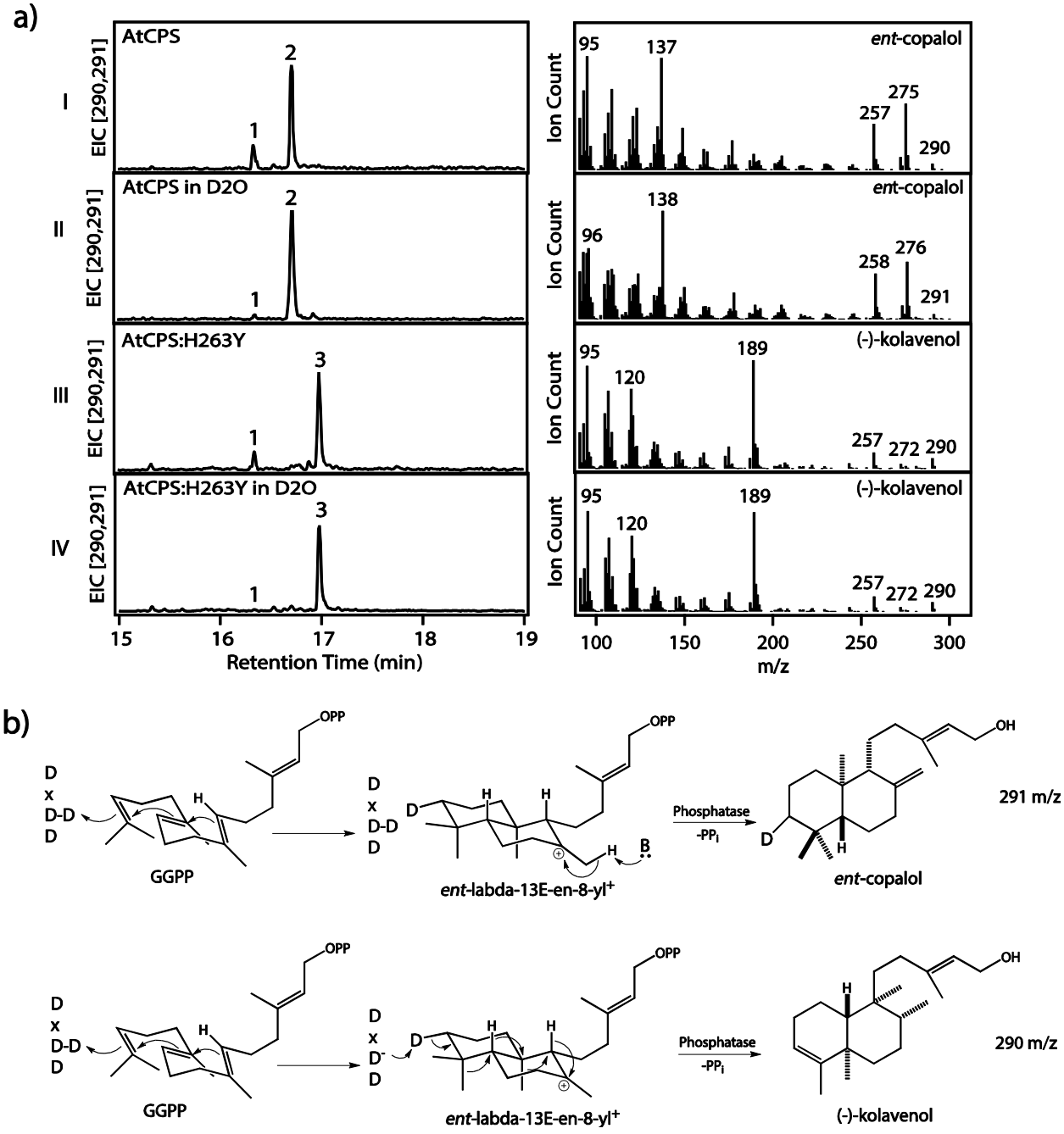


Table S2: Kinetic constants for wild-type (WT) and H263Y and H263F mutants of AtCPS.

	k_{cat} (s^{-1})	K_M (μM)	K_I (μM)	R^2
AtCPS (WT)	**0.3 ± 0.1**	**5 ± 3**	**5 ± 3**	**0.92**
AtCPS:H263Y	**0.01 ± 0.003**	**2.3 ± 0.8**	**26 ± 11**	**0.92**
AtCPS:H263F	**0.01 ± 0.002**	**3.1 ± 0.8**	**20 ± 6**	**0.96**

Scheme S1: All conformations of GGPP can be cyclized and further rearranged as illustrated here with halimadienyl diphosphate catalyzed by MtHPS, (-)-kolavenyl diphosphate catalyzed by AtCPS:H263Y and AtCPS:H263F, and terpentedienyl diphosphate catalyzed by KgTPS.

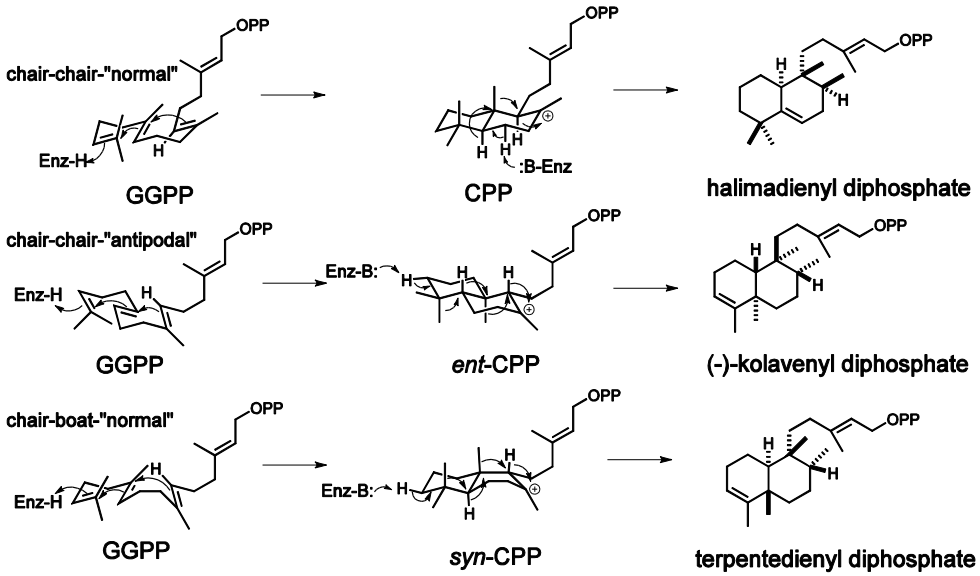


Figure S6: Overlay of the active sites of the wild-type enzyme (green) from the previously determined crystal structure, and AtCPS:H263Y mutant (cyan), generated via the mutagenesis feature in PyMol with choice of the rotamer most closely approximating the wild-type histidine. The DxDD motif is shown in stick representation on the left. The previously identified catalytic base group shown in stick representation (His263, Asn322 and ligated water molecule) of the wild-type enzyme on the right along with the overlay of the Tyr mutation and proposed hydrogen bond (red text) between Y263 and N322 in the AtCPS:H263Y mutant.

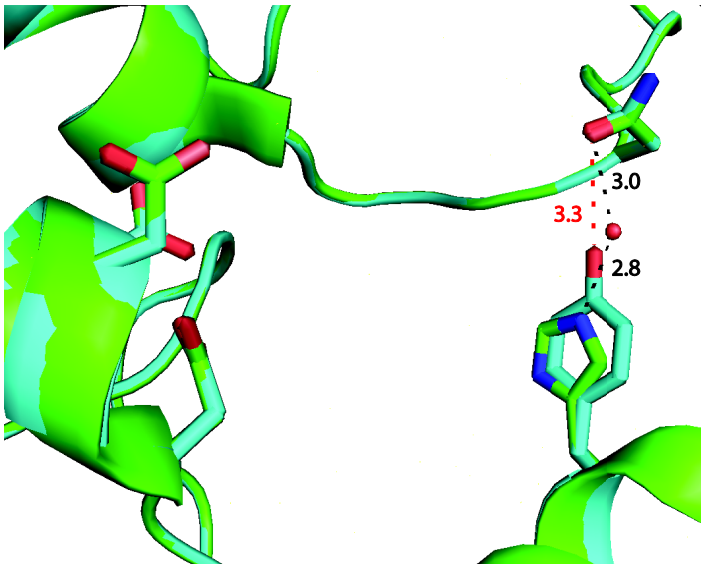


Figure S7. Theozyme calculations on bicyclization reaction.

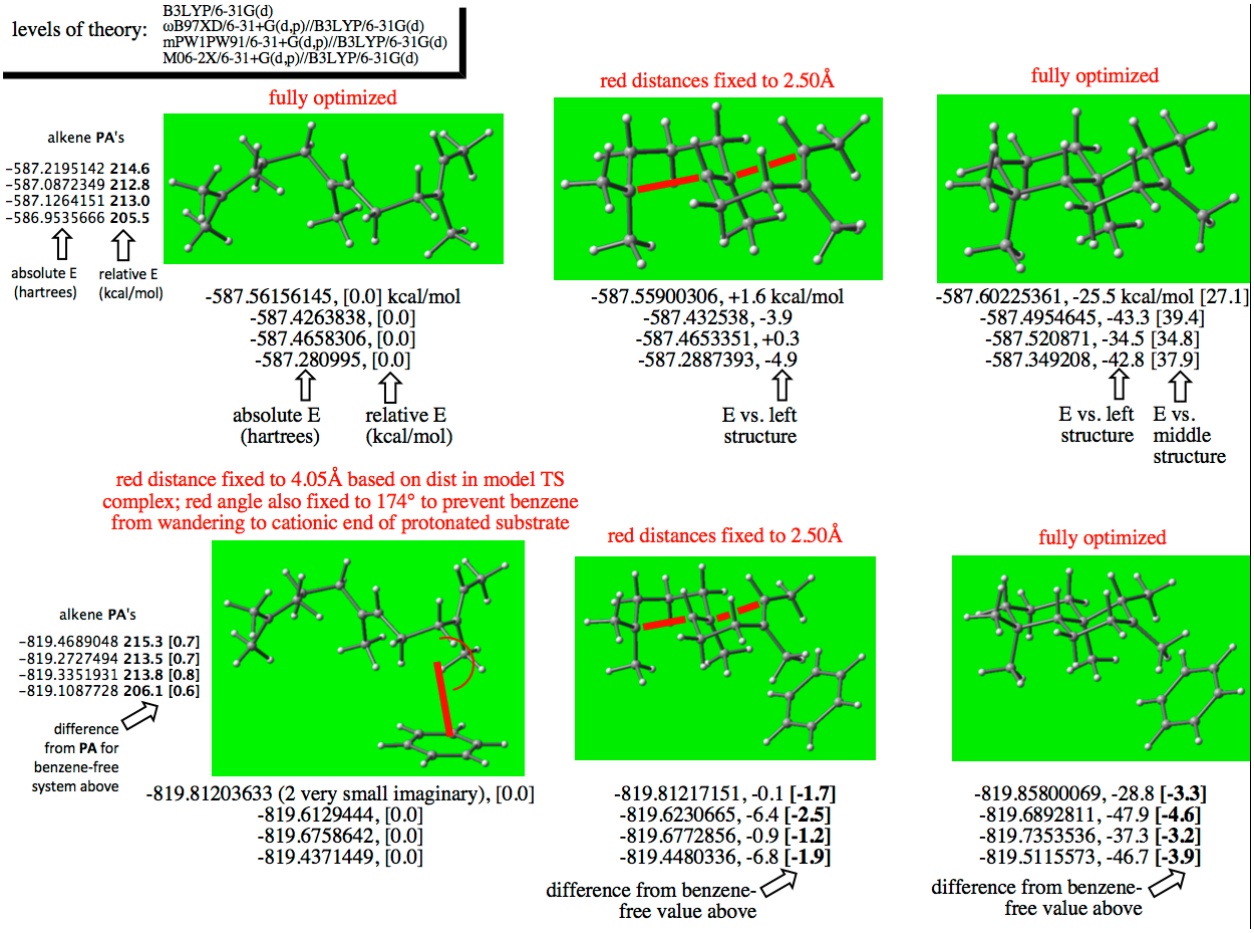
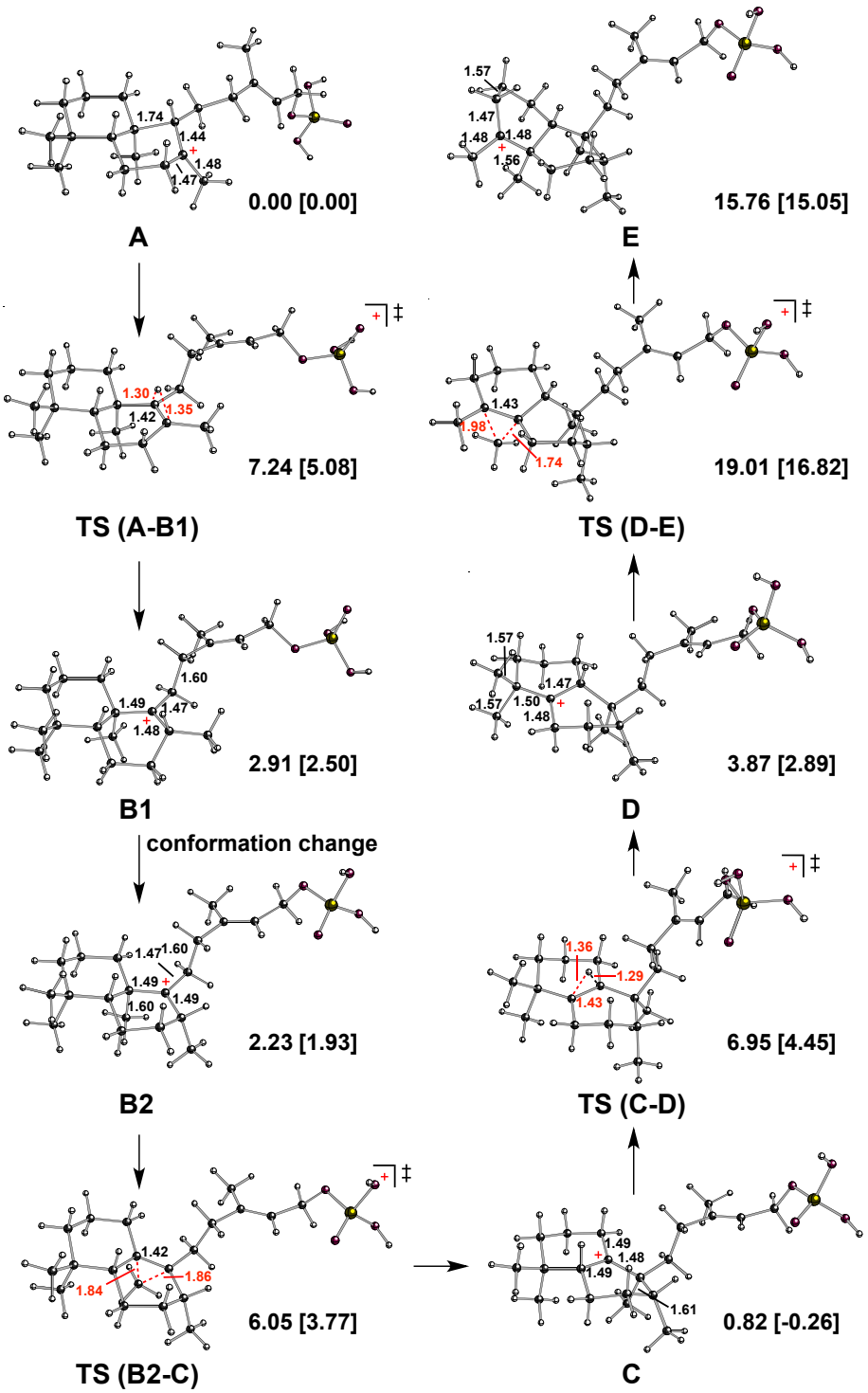


Figure S8. Carbocation minima and transitions state structures for hydride and methyl shifts. Note that a truncated model of the diphosphate group was used. Relative energies (B3LYP/6-31+G(d,p) and mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) [in brackets]) are shown in kcal/mol and distances are shown in Å.



Quantum Chemical Calculations

Calculations were performed with GAUSSIAN03[13] and GAUSSIAN09.[14] Geometries were optimized using the B3LYP method with the basis set of 6-31+G(d,p) in the absence and 6-31G(d) in the presence of theozymes.[15] All stationary points were characterized as minima or transition state structures using frequency calculations at the same level. All reported energies include zero-point energy corrections (unscaled) from the frequency calculations at the same level. Intrinsic reaction coordinate (IRC) calculations were used for further characterization of transition state structures.[16] mPW1PW91[17] single point energies are also shown, since it is known that B3LYP underestimates the relative energies of cyclic structures versus acyclic isomers.[17] The validity of this computational approach for examining terpene-forming carbocation rearrangements is well-established.[18] Structural images were created with *Ball&Stick*.[19]

References

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Coordinates and Energies

Figure 2

A

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.9572778 hartrees (-894802.451392278 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.538541 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.7068213 hartrees (-894645.287433963 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	5.475239	-0.510321	-0.382385
2	6	4.210632	0.295590	0.123653
3	6	2.831473	-0.320201	-0.260306
4	6	2.761327	-1.786969	0.213246
5	6	3.952230	-2.601885	-0.333596

6	6	5.294158	-1.984110	0.061107
7	1	4.271873	0.193912	1.217345
8	1	2.785463	-1.824895	1.309821
9	1	1.826072	-2.251781	-0.110690
10	1	3.875320	-3.617736	0.069765
11	1	3.876975	-2.706763	-1.421439
12	1	5.399816	-2.037462	1.153939
13	1	6.115809	-2.579167	-0.354507
14	6	1.673559	0.524957	0.720294
15	6	4.269600	1.793185	-0.176515
16	1	5.202478	2.240905	0.170688
17	1	4.193240	2.002901	-1.247250
18	6	3.113297	2.557838	0.585130
19	6	1.858196	1.871263	0.236281
20	6	5.724562	-0.421029	-1.903102
21	1	5.794794	0.615792	-2.247508
22	1	6.681041	-0.898800	-2.138141
23	1	4.963174	-0.922849	-2.502364
24	6	6.730676	0.042371	0.331794
25	1	6.585982	0.111522	1.416053
26	1	7.577400	-0.628951	0.156802
27	1	7.025118	1.028219	-0.041018
28	6	2.417691	-0.213351	-1.735963
29	1	2.924583	-0.974000	-2.329647
30	1	1.346150	-0.395456	-1.853382
31	1	2.649662	0.753736	-2.188539
32	1	2.134596	0.409631	1.705252
33	6	0.265292	-0.079339	0.717718
34	1	-0.201971	-0.020998	-0.269692
35	1	0.347455	-1.141536	0.955044
36	6	-0.663544	0.594481	1.758241
37	1	-0.761286	1.662718	1.531608
38	1	-0.197625	0.523213	2.751040
39	6	-2.044130	-0.039131	1.792373
40	6	-2.141874	-1.342544	2.547870
41	1	-3.101866	-1.843330	2.417451
42	1	-1.360865	-2.045780	2.234201
43	1	-1.998470	-1.171858	3.622633
44	6	-3.064007	0.580552	1.175366
45	6	-4.485273	0.125313	1.073873
46	1	-2.874096	1.533246	0.680992
47	1	-5.158384	0.863236	1.526837
48	1	3.317976	2.478160	1.657717
49	1	3.109248	3.609193	0.288616
50	1	-4.660740	-0.845306	1.542199
51	8	-6.146490	-0.290680	-2.386591
52	15	-6.332698	-0.109096	-0.797861
53	8	-7.276071	0.958773	-0.388379

54	8	-4.797806	0.021347	-0.344916
55	8	-6.686871	-1.587746	-0.248596
56	1	-6.633976	0.392234	-2.870903
57	1	-7.640243	-1.717805	-0.134340
58	6	0.942874	2.536766	-0.713724
59	1	1.496044	3.099536	-1.474169
60	1	0.199383	1.884705	-1.168733
61	1	0.406374	3.303888	-0.128034

TS (A-B1)

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.9430744 hartrees (-894793.538616744 kcal/mol)
Imaginary Frequencies: 1 (-424.0239 1/cm)
Zero-point correction = 0.535873 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.6960546 hartrees (-894638.531222046 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-5.518509	-0.107884	-0.288509
2	6	-4.096396	0.562523	-0.255108
3	6	-2.956924	-0.227243	0.485386
4	6	-2.926946	-1.681308	-0.061840
5	6	-4.296765	-2.366715	0.024828
6	6	-5.360458	-1.580383	-0.744748
7	1	-3.788804	0.550169	-1.316536
8	1	-2.620833	-1.658187	-1.117169
9	1	-2.182055	-2.279616	0.472795
10	1	-4.210100	-3.375947	-0.392118
11	1	-4.591339	-2.501825	1.071711
12	1	-5.097267	-1.590999	-1.812258
13	1	-6.331524	-2.082513	-0.665882
14	6	-1.598477	0.469129	0.246064
15	6	-4.096889	2.035084	0.182843
16	1	-4.911039	2.582813	-0.295442
17	1	-4.264453	2.118801	1.260370
18	6	-2.776245	2.712883	-0.191812
19	6	-1.537562	1.857257	-0.050522
20	6	-6.293587	-0.035351	1.046850
21	1	-6.326847	0.982181	1.448983
22	1	-7.329593	-0.346099	0.877702
23	1	-5.892487	-0.690286	1.823027
24	6	-6.374156	0.615378	-1.356238

25	1	-5.849885	0.687733	-2.316430
26	1	-7.298110	0.054564	-1.529507
27	1	-6.668514	1.623468	-1.048771
28	6	-3.080809	-0.243483	2.037996
29	1	-3.985801	-0.764298	2.343851
30	1	-2.238345	-0.771204	2.493818
31	1	-3.114392	0.760957	2.466862
32	1	-1.578178	0.891564	-0.987287
33	6	-0.301431	-0.290141	0.508016
34	1	0.394324	0.357264	1.048353
35	1	-0.534244	-1.122500	1.172839
36	6	0.407136	-0.841209	-0.767093
37	1	0.476217	-0.048353	-1.521770
38	1	-0.208806	-1.638613	-1.199668
39	6	1.802640	-1.358515	-0.465457
40	6	1.869483	-2.650302	0.311548
41	1	2.890077	-2.948604	0.552011
42	1	1.320980	-2.579755	1.258877
43	1	1.410900	-3.466155	-0.261602
44	6	2.860792	-0.657382	-0.905338
45	6	4.312824	-0.960935	-0.706496
46	1	2.683883	0.253528	-1.477131
47	1	4.817376	-1.073003	-1.673674
48	1	-2.800249	3.091664	-1.222887
49	1	-2.589776	3.601724	0.425158
50	1	4.489494	-1.857920	-0.109730
51	8	6.602758	1.661956	0.959224
52	15	6.482087	0.353895	0.029603
53	8	7.206261	0.421872	-1.261752
54	8	4.884078	0.181864	-0.010134
55	8	6.892478	-0.879596	0.989009
56	1	7.086587	2.367218	0.504013
57	1	7.820625	-1.137022	0.882550
58	6	-0.232361	2.606690	-0.147692
59	1	-0.026567	3.026059	0.846153
60	1	0.621435	1.992689	-0.429075
61	1	-0.320749	3.444745	-0.843029

B1

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.9528954 hartrees (-894799.701392454 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.538791 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.7030848 hartrees (-894642.942742848 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-5.432926	-0.005061	-0.545216
2	6	-3.994057	0.609051	-0.343312
3	6	-2.965742	-0.246441	0.472474
4	6	-2.978835	-1.732387	-0.008348
5	6	-4.395234	-2.315505	-0.068352
6	6	-5.289411	-1.482085	-0.986964
7	1	-3.579056	0.618972	-1.363423
8	1	-2.553604	-1.772020	-1.018842
9	1	-2.345430	-2.350185	0.635439
10	1	-4.325435	-3.342443	-0.443797
11	1	-4.824708	-2.392713	0.936927
12	1	-4.872335	-1.511695	-2.003917
13	1	-6.286830	-1.931287	-1.052187
14	6	-1.595572	0.344201	0.405950
15	6	-4.016052	2.074275	0.142956
16	1	-4.520406	2.682474	-0.610648
17	1	-4.616175	2.159096	1.052221
18	6	-2.609045	2.650753	0.409838
19	6	-1.437212	1.740329	-0.064472
20	6	-6.363242	0.083180	0.687129
21	1	-6.462565	1.105136	1.063605
22	1	-7.366405	-0.246597	0.398323
23	1	-6.055820	-0.553138	1.520189
24	6	-6.126255	0.762248	-1.696167
25	1	-5.496379	0.803683	-2.592409
26	1	-7.055959	0.254409	-1.971949
27	1	-6.391587	1.785848	-1.415824
28	6	-3.216674	-0.199507	2.038649
29	1	-4.225473	-0.567807	2.219801
30	1	-2.516247	-0.844187	2.572246
31	1	-3.153142	0.808005	2.453750
32	1	-1.598820	1.601612	-1.157300
33	6	-0.405002	-0.433596	0.785139
34	1	0.308532	0.208910	1.307087
35	1	-0.654866	-1.287731	1.413622
36	6	0.341315	-0.988255	-0.520304
37	1	0.365417	-0.216065	-1.292517
38	1	-0.251209	-1.824312	-0.902515
39	6	1.748985	-1.432908	-0.187871
40	6	1.865766	-2.633025	0.718328
41	1	2.900149	-2.914944	0.914930
42	1	1.392016	-2.448830	1.690814
43	1	1.362796	-3.502243	0.276323

44	6	2.777303	-0.755693	-0.728300
45	6	4.241206	-1.026959	-0.568611
46	1	2.564426	0.097286	-1.371686
47	1	4.688040	-1.289283	-1.535646
48	1	-2.481027	3.612899	-0.092245
49	1	-2.454600	2.844328	1.476762
50	1	4.457609	-1.822585	0.147388
51	8	6.606310	1.832515	0.497116
52	15	6.438200	0.376598	-0.163877
53	8	7.087773	0.189618	-1.482277
54	8	4.838116	0.207547	-0.093375
55	8	6.894583	-0.651517	0.993965
56	1	7.001790	2.458644	-0.127746
57	1	7.824816	-0.911565	0.914821
58	6	-0.075957	2.417488	0.142277
59	1	0.123169	2.584842	1.206103
60	1	0.758180	1.852659	-0.277619
61	1	-0.086269	3.395943	-0.344295

B2

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.95499 hartrees (-894801.0157749 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.539811 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.7050096 hartrees (-894644.150574096 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.974454	-0.016384	-1.053314
2	6	3.572789	-0.564546	-0.603780
3	6	2.831200	0.282320	0.505059
4	6	2.795175	1.780977	0.096143
5	6	4.184219	2.321104	-0.273690
6	6	4.834940	1.490972	-1.382049
7	1	2.938148	-0.426910	-1.493981
8	1	2.143436	1.893422	-0.778042
9	1	2.369491	2.392800	0.898371
10	1	4.070682	3.359290	-0.604293
11	1	4.833432	2.365271	0.608949
12	1	4.232987	1.594412	-2.296153
13	1	5.824480	1.897207	-1.620486
14	6	1.500014	-0.297502	0.835799

15	6	3.533050	-2.066529	-0.282502
16	1	4.044219	-2.625907	-1.069301
17	1	4.073912	-2.291524	0.643631
18	6	2.087015	-2.558101	-0.197546
19	6	1.249854	-1.770296	0.832002
20	6	6.100471	-0.250400	-0.021830
21	1	6.187760	-1.307128	0.250016
22	1	7.059398	0.047316	-0.458105
23	1	5.977793	0.323557	0.898658
24	6	5.386927	-0.731755	-2.361805
25	1	4.589824	-0.693858	-3.113287
26	1	6.265732	-0.238883	-2.790152
27	1	5.656363	-1.779647	-2.201090
28	6	3.480861	0.182556	1.960422
29	1	3.903222	-0.800272	2.155476
30	1	2.770951	0.423917	2.757816
31	1	0.180368	-1.890679	0.613934
32	6	0.351646	0.538247	1.217279
33	1	-0.290629	0.004917	1.923424
34	1	0.644932	1.503186	1.630824
35	6	-0.545290	0.806899	-0.083299
36	1	-0.772957	-0.148426	-0.562045
37	1	0.033003	1.412376	-0.786450
38	6	-1.829494	1.516317	0.290408
39	6	-1.696880	2.959786	0.708922
40	1	-2.659258	3.472593	0.748702
41	1	-1.246689	3.053871	1.706069
42	1	-1.054392	3.510967	0.012026
43	6	-2.978755	0.821436	0.217856
44	6	-4.364657	1.318334	0.514576
45	1	-2.950439	-0.224116	-0.084961
46	1	-4.435242	2.406064	0.539138
47	1	1.617126	-2.457908	-1.183428
48	1	2.044527	-3.621608	0.057993
49	1	-4.717330	0.935099	1.480927
50	8	-6.881860	-0.533229	0.717361
51	15	-5.880678	-0.583877	-0.542656
52	8	-4.887402	-1.689827	-0.536467
53	8	-5.289428	0.909846	-0.525571
54	8	-6.858824	-0.533145	-1.812182
55	1	-7.189399	-1.408684	0.996354
56	1	-6.499354	-1.009988	-2.574804
57	6	1.414951	-2.351367	2.282180
58	1	2.465596	-2.447187	2.558033
59	1	0.904048	-1.748857	3.037124
60	1	0.966333	-3.347193	2.280939
61	1	4.273259	0.929090	2.007903

TS (B2-C)
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.9485294 hartrees (-894796.961683794 kcal/mol)
Imaginary Frequencies: 1 (-286.3529 1/cm)
Zero-point correction = 0.539434 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.7017119 hartrees (-894642.081234369 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	5.163253	-0.032340	-0.840427
2	6	3.698426	-0.588533	-0.680705
3	6	2.722571	0.311385	0.094992
4	6	2.781742	1.776987	-0.316207
5	6	4.210666	2.328604	-0.406681
6	6	5.088976	1.446435	-1.297004
7	1	3.270474	-0.510853	-1.695814
8	1	2.326046	1.809480	-1.316025
9	1	2.158660	2.403252	0.324731
10	1	4.166731	3.345496	-0.809284
11	1	4.643551	2.420950	0.597140
12	1	4.699403	1.481814	-2.324112
13	1	6.104729	1.854783	-1.340878
14	6	1.581778	-0.229420	0.749289
15	6	3.587802	-2.069033	-0.288155
16	1	4.147620	-2.672263	-1.006014
17	1	4.051194	-2.259042	0.687864
18	6	2.125080	-2.514912	-0.279456
19	6	1.280112	-1.740219	0.749762
20	6	6.017294	-0.147146	0.442215
21	1	6.056007	-1.173708	0.820501
22	1	7.047555	0.145247	0.215990
23	1	5.678529	0.504715	1.252243
24	6	5.873625	-0.833789	-1.954202
25	1	5.276002	-0.869140	-2.872300
26	1	6.827235	-0.356378	-2.200563
27	1	6.097948	-1.860640	-1.651992
28	6	2.974136	0.173332	1.916331
29	1	3.826348	-0.495516	1.942651
30	1	2.271486	-0.138117	2.690868
31	1	0.233839	-1.778199	0.422736
32	6	0.388792	0.634063	1.136181
33	1	-0.167516	0.117969	1.925623

34	1	0.703943	1.596480	1.545564
35	6	-0.565250	0.866123	-0.070555
36	1	-0.780113	-0.089812	-0.558393
37	1	-0.059989	1.498317	-0.811937
38	6	-1.876531	1.515858	0.338433
39	6	-1.791305	2.962674	0.762629
40	1	-2.771443	3.430275	0.867972
41	1	-1.278745	3.074629	1.727202
42	1	-1.223318	3.547306	0.028205
43	6	-2.999409	0.779682	0.294250
44	6	-4.390552	1.208777	0.657962
45	1	-2.939615	-0.255780	-0.037420
46	1	-4.486339	2.284576	0.804804
47	1	1.703190	-2.368866	-1.281705
48	1	2.050006	-3.586146	-0.068747
49	1	-4.728439	0.710636	1.575025
50	8	-6.925553	-0.640370	0.689134
51	15	-5.917082	-0.583164	-0.566640
52	8	-4.937166	-1.697319	-0.655519
53	8	-5.320031	0.898317	-0.417696
54	8	-6.891533	-0.415753	-1.831387
55	1	-7.222163	-1.539569	0.894263
56	1	-6.531628	-0.833546	-2.627557
57	6	1.306721	-2.399783	2.145105
58	1	2.326846	-2.535657	2.517546
59	1	0.736585	-1.833916	2.889227
60	1	0.848990	-3.389751	2.077179
61	1	3.219317	1.216960	2.096203

C

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.9565209 hartrees (-894801.976429959 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.539085 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.7077731 hartrees (-894645.884697981 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	5.147733	-0.046203	-0.838009
2	6	3.658914	-0.592974	-0.714865
3	6	2.687733	0.312215	-0.038755
4	6	2.781549	1.763863	-0.354525

5	6	4.216461	2.320614	-0.466319
6	6	5.099820	1.419567	-1.325600
7	1	3.270570	-0.498015	-1.753241
8	1	2.301689	1.838889	-1.347286
9	1	2.162687	2.362115	0.314284
10	1	4.159809	3.326544	-0.892169
11	1	4.633928	2.435313	0.539870
12	1	4.741387	1.441898	-2.364133
13	1	6.121208	1.815469	-1.345749
14	6	1.679611	-0.189642	0.913204
15	6	3.505816	-2.072552	-0.336366
16	1	4.050366	-2.682578	-1.059828
17	1	3.958654	-2.274989	0.640512
18	6	2.027236	-2.456759	-0.333231
19	6	1.220327	-1.692736	0.734972
20	6	5.895168	-0.147660	0.507691
21	1	5.955342	-1.180049	0.863391
22	1	6.922900	0.206776	0.379013
23	1	5.439161	0.456089	1.297702
24	6	5.902188	-0.883551	-1.890196
25	1	5.367868	-0.912188	-2.846617
26	1	6.884326	-0.436777	-2.074032
27	1	6.073969	-1.911741	-1.561623
28	6	2.641595	-0.004145	2.194385
29	1	3.489587	-0.686073	2.205175
30	1	1.999484	-0.230377	3.048671
31	1	0.194926	-1.618604	0.361276
32	6	0.434553	0.709009	1.164952
33	1	-0.147922	0.196043	1.938630
34	1	0.729523	1.665534	1.608762
35	6	-0.483802	0.953534	-0.054558
36	1	-0.675543	0.007003	-0.570429
37	1	0.020155	1.610783	-0.776246
38	6	-1.815187	1.578980	0.329554
39	6	-1.764043	3.028573	0.750781
40	1	-2.753791	3.475107	0.857715
41	1	-1.250149	3.153061	1.712893
42	1	-1.210845	3.624289	0.013664
43	6	-2.923682	0.821280	0.280656
44	6	-4.323477	1.222779	0.640860
45	1	-2.840973	-0.213843	-0.047397
46	1	-4.440692	2.296246	0.789008
47	1	1.610276	-2.254052	-1.328935
48	1	1.913816	-3.532856	-0.171420
49	1	-4.655212	0.716868	1.555835
50	8	-6.821149	-0.664266	0.681794
51	15	-5.824670	-0.591423	-0.583509
52	8	-4.835105	-1.695980	-0.684277

53	8	-5.245826	0.896546	-0.437734
54	8	-6.811907	-0.432955	-1.840290
55	1	-7.096400	-1.568995	0.892101
56	1	-6.458734	-0.858377	-2.635348
57	6	1.132938	-2.483149	2.051711
58	1	2.115958	-2.724893	2.468826
59	1	0.554218	-1.959752	2.819205
60	1	0.619647	-3.429535	1.859489
61	1	2.992045	1.024011	2.307069

TS (C-D)

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.9446071 hartrees (-894794.500401321 kcal/mol)
Imaginary Frequencies: 1 (-314.3217 1/cm)
Zero-point correction = 0.536942 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.6981281 hartrees (-894639.832364031 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.506978	-0.353381	1.496115
2	6	3.426986	0.361746	0.664086
3	6	2.818233	-0.229386	-0.482705
4	6	3.187664	-1.658528	-0.891602
5	6	4.517186	-2.155346	-0.323441
6	6	4.589175	-1.862148	1.170308
7	1	2.262974	-0.339950	0.673725
8	1	2.372912	-2.323509	-0.578070
9	1	3.198433	-1.708625	-1.979589
10	1	4.606861	-3.229737	-0.508766
11	1	5.350850	-1.679972	-0.852653
12	1	3.768423	-2.384267	1.682374
13	1	5.515441	-2.253749	1.602103
14	6	1.851083	0.538208	-1.428946
15	6	3.042017	1.766610	1.065682
16	1	3.107767	1.872929	2.148998
17	1	3.809130	2.430837	0.647552
18	6	1.654010	2.164522	0.565587
19	6	1.549710	2.017252	-0.960457
20	6	5.845292	0.354583	1.131181
21	1	5.838730	1.409639	1.416366
22	1	6.653619	-0.130928	1.685877
23	1	6.079627	0.286817	0.065119

24	6	4.259480	-0.204635	3.016337
25	1	3.257983	-0.544968	3.302334
26	1	4.981479	-0.830047	3.549178
27	1	4.396368	0.818199	3.373990
28	6	2.508555	0.554906	-2.840301
29	1	3.518739	0.972632	-2.835908
30	1	1.895177	1.170677	-3.501523
31	1	0.508162	2.211788	-1.241096
32	6	0.520393	-0.275396	-1.587085
33	1	-0.075744	0.256656	-2.337046
34	1	0.757603	-1.247809	-2.031055
35	6	-0.351929	-0.485749	-0.335348
36	1	-0.630995	0.480391	0.093217
37	1	0.222117	-1.026977	0.437997
38	6	-1.624011	-1.272124	-0.612191
39	6	-1.440394	-2.726921	-0.974703
40	1	-2.375017	-3.289393	-0.951105
41	1	-1.018288	-2.846567	-1.980532
42	1	-0.747619	-3.213452	-0.275865
43	6	-2.804878	-0.638497	-0.515338
44	6	-4.170824	-1.209091	-0.756370
45	1	-2.815687	0.412066	-0.229393
46	1	-4.166531	-2.286635	-0.918847
47	1	0.903424	1.553925	1.079851
48	1	1.451149	3.200063	0.853402
49	1	-4.647501	-0.737761	-1.624136
50	8	-6.808877	0.434112	-0.529458
51	15	-5.736161	0.394415	0.674208
52	8	-4.861026	1.590370	0.788687
53	8	-5.024784	-1.017238	0.408935
54	8	-6.620272	0.064219	1.974303
55	1	-7.166775	1.321151	-0.683012
56	1	-6.284795	0.516254	2.762252
57	6	2.394705	3.120572	-1.634626
58	1	3.473003	2.988753	-1.493975
59	1	2.213289	3.189246	-2.708255
60	1	2.124456	4.089741	-1.203984
61	1	2.546739	-0.438532	-3.289476

D

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.9508299 hartrees (-894798.405270549 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.538255 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.7019277 hartrees (-894642.216651027 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.795403	-0.466244	-1.215530
2	6	3.607866	-0.659677	-0.323153
3	6	2.561538	0.351428	-0.125049
4	6	2.910685	1.806088	-0.551279
5	6	4.400200	2.019743	-0.818567
6	6	4.890129	0.961817	-1.802803
7	1	1.872985	-0.072876	-0.904569
8	1	2.349007	2.060944	-1.456049
9	1	2.562951	2.493031	0.221497
10	1	4.560824	3.023289	-1.223169
11	1	4.969568	1.966420	0.119430
12	1	4.286432	1.022122	-2.717583
13	1	5.926238	1.141398	-2.105737
14	6	1.737821	0.216816	1.232181
15	6	3.411489	-1.958613	0.353644
16	1	3.966551	-2.763302	-0.131549
17	1	3.891678	-1.822305	1.341093
18	6	1.931407	-2.301114	0.570728
19	6	1.190527	-1.254745	1.432743
20	6	6.078481	-0.782764	-0.372317
21	1	6.073784	-1.794883	0.036867
22	1	6.938695	-0.693763	-1.040964
23	1	6.209921	-0.071158	0.447188
24	6	4.715473	-1.495873	-2.390962
25	1	3.788025	-1.387312	-2.961126
26	1	5.548407	-1.280443	-3.066135
27	1	4.809815	-2.530638	-2.056908
28	6	2.681664	0.666933	2.374871
29	1	3.516875	-0.020276	2.542588
30	1	2.136445	0.745049	3.317763
31	1	0.156479	-1.251929	1.076694
32	6	0.512575	1.177912	1.216815
33	1	-0.086271	0.917299	2.098071
34	1	0.842667	2.208781	1.382075
35	6	-0.394862	1.114303	-0.032127
36	1	-0.525724	0.073232	-0.349617
37	1	0.091632	1.643233	-0.864445
38	6	-1.774015	1.717157	0.180440
39	6	-1.813960	3.215461	0.360932
40	1	-2.828054	3.618083	0.356279
41	1	-1.349210	3.517476	1.308332
42	1	-1.253975	3.713970	-0.440348

43	6	-2.840557	0.900497	0.203057
44	6	-4.276554	1.274040	0.420147
45	1	-2.688674	-0.167469	0.054928
46	1	-4.452316	2.349218	0.392853
47	1	1.458706	-2.398483	-0.414302
48	1	1.868813	-3.288232	1.036650
49	1	-4.645359	0.894476	1.380736
50	8	-6.622691	-0.784494	0.613582
51	15	-5.585844	-0.792274	-0.621816
52	8	-4.525346	-1.832588	-0.557709
53	8	-5.116426	0.738541	-0.645578
54	8	-6.532631	-0.859233	-1.918456
55	1	-6.836809	-1.675106	0.928687
56	1	-6.124240	-1.362943	-2.637547
57	6	1.128723	-1.701499	2.904333
58	1	2.121106	-1.848440	3.343983
59	1	0.589070	-0.984700	3.529610
60	1	0.593172	-2.653126	2.971569
61	1	3.100996	1.655682	2.167057

TS (D-E)

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.9273139 hartrees (-894783.648745389 kcal/mol)
Imaginary Frequencies: 1 (-151.2208 1/cm)
Zero-point correction = 0.538865 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.6803367 hartrees (-894628.668082617 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.811870	-0.135719	-1.369795
2	6	3.742142	-0.577499	-0.536542
3	6	2.672269	0.441423	-0.077668
4	6	3.090558	1.941283	-0.142908
5	6	4.583807	2.196823	-0.376459
6	6	5.123887	1.327479	-1.511944
7	1	1.955516	0.312440	-0.896513
8	1	2.534061	2.416274	-0.958785
9	1	2.782882	2.466348	0.762595
10	1	4.746686	3.249813	-0.622795
11	1	5.162129	2.008723	0.535859
12	1	4.642445	1.611020	-2.463378
13	1	6.198054	1.469730	-1.672525

14	6	1.851927	0.025413	1.208618
15	6	3.127144	-1.979599	-0.786642
16	1	3.107227	-2.161808	-1.866950
17	1	3.758853	-2.761368	-0.357759
18	6	1.695661	-2.108065	-0.236319
19	6	1.538905	-1.530956	1.182614
20	6	5.141679	-0.720024	0.491621
21	1	5.392512	-1.775557	0.519134
22	1	6.051772	-0.138922	0.317919
23	1	4.720260	-0.348844	1.421096
24	6	5.563173	-1.072633	-2.266451
25	1	5.112241	-0.976270	-3.264925
26	1	6.613492	-0.786954	-2.361247
27	1	5.487064	-2.120003	-1.976353
28	6	2.543826	0.441130	2.529439
29	1	3.452892	-0.117023	2.765252
30	1	1.863266	0.272896	3.369306
31	1	0.480998	-1.637632	1.449241
32	6	0.501966	0.822274	1.202642
33	1	-0.038584	0.527045	2.110323
34	1	0.724973	1.888553	1.327817
35	6	-0.461196	0.652008	0.008851
36	1	-0.694993	-0.406632	-0.139257
37	1	0.013721	1.009860	-0.917525
38	6	-1.767841	1.410060	0.184822
39	6	-1.661536	2.917098	0.175767
40	1	-2.630010	3.411567	0.085268
41	1	-1.188588	3.295038	1.090982
42	1	-1.040643	3.252100	-0.664901
43	6	-2.910148	0.716255	0.325979
44	6	-4.291893	1.265224	0.514598
45	1	-2.870090	-0.371528	0.301166
46	1	-4.335061	2.353041	0.470074
47	1	0.995689	-1.623997	-0.923447
48	1	1.424997	-3.169123	-0.234983
49	1	-4.715864	0.948509	1.474662
50	8	-6.941605	-0.391332	0.705224
51	15	-5.880208	-0.616303	-0.489674
52	8	-5.003194	-1.807273	-0.344130
53	8	-5.177776	0.820382	-0.558227
54	8	-6.783923	-0.591091	-1.819827
55	1	-7.283076	-1.225449	1.060167
56	1	-6.450440	-1.206218	-2.489104
57	6	2.305445	-2.403736	2.197560
58	1	3.391242	-2.397758	2.052064
59	1	2.112696	-2.100951	3.229058
60	1	1.974728	-3.443112	2.101199
61	1	2.792178	1.505812	2.541356

E

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.9325568 hartrees (-894786.938717568 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.538940 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -1425.6832333 hartrees (-894630.485728083 kcal/mol)

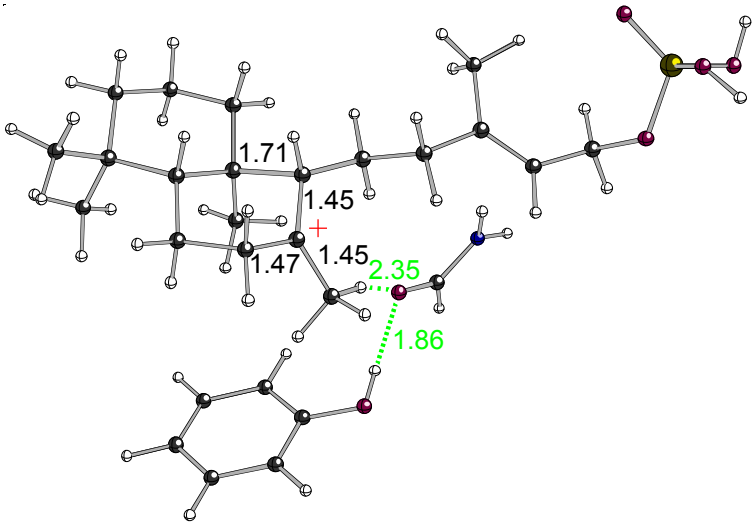
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.455492	-0.076492	-1.640864
2	6	3.846246	-0.544463	-0.381272
3	6	2.752766	0.453887	0.107990
4	6	3.349837	1.876031	0.182023
5	6	3.897205	2.331262	-1.193743
6	6	3.973400	1.170105	-2.245299
7	1	2.026723	0.484016	-0.711773
8	1	2.584932	2.579751	0.517096
9	1	4.147076	1.914950	0.929804
10	1	3.267929	3.107584	-1.635833
11	1	4.899612	2.757444	-1.097258
12	1	2.940732	0.957348	-2.574782
13	1	4.541746	1.452058	-3.134712
14	6	1.905388	-0.001011	1.350584
15	6	3.156748	-1.953261	-0.769939
16	1	3.151716	-2.122227	-1.852692
17	1	3.782561	-2.739642	-0.339694
18	6	1.708466	-2.029477	-0.261154
19	6	1.493616	-1.530901	1.181755
20	6	5.003151	-0.816742	0.635669
21	1	5.778408	-1.452193	0.203967
22	1	5.467137	0.110974	0.978324
23	1	4.599981	-1.337980	1.500473
24	6	5.552852	-0.801881	-2.310653
25	1	5.408446	-0.796613	-3.397529
26	1	6.469741	-0.208811	-2.145048
27	1	5.726196	-1.813027	-1.945862
28	6	2.620272	0.273649	2.695537
29	1	3.525247	-0.313271	2.852970
30	1	1.947833	0.053434	3.529506
31	1	0.410433	-1.573110	1.345077
32	6	0.595480	0.858323	1.421235

33	1	0.016194	0.463952	2.265019
34	1	0.858882	1.884459	1.703005
35	6	-0.332995	0.897057	0.188066
36	1	-0.499401	-0.115201	-0.193481
37	1	0.142050	1.471960	-0.621620
38	6	-1.688688	1.521270	0.477397
39	6	-1.678355	2.995642	0.803759
40	1	-2.676630	3.435867	0.823096
41	1	-1.219829	3.187338	1.782093
42	1	-1.086970	3.548104	0.062230
43	6	-2.784811	0.745070	0.430845
44	6	-4.202901	1.148884	0.699712
45	1	-2.672145	-0.306792	0.172557
46	1	-4.328420	2.222141	0.840146
47	1	1.055601	-1.484516	-0.949355
48	1	1.402142	-3.080411	-0.334553
49	1	-4.598319	0.642303	1.588036
50	8	-6.648470	-0.777780	0.597411
51	15	-5.623557	-0.655899	-0.643473
52	8	-4.637409	-1.762038	-0.761491
53	8	-5.059993	0.827704	-0.438465
54	8	-6.578938	-0.457307	-1.921690
55	1	-6.895324	-1.695119	0.786680
56	1	-6.226313	-0.907597	-2.702949
57	6	2.084581	-2.526859	2.199652
58	1	3.171628	-2.637720	2.137120
59	1	1.843780	-2.248513	3.227883
60	1	1.651862	-3.517754	2.026677
61	1	2.890105	1.330103	2.783573

Figure 3

A



B3LYP/6-31G(d)//B3LYP/6-31G(d):
HF = -1903.2544093 hartrees (-1194311.17437984 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.696350 (Hartree/Particle)

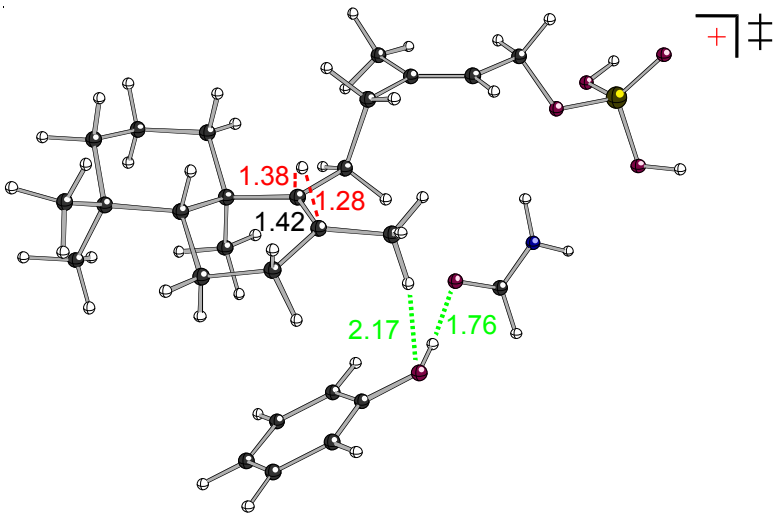
mPW1PW91/6-31+G(d,p)//B3LYP/6-31G(d):
HF = -1903.0143933 hartrees (-1194160.56193968 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-4.415968	-3.071344	0.029965
2	6	-3.189916	-2.335799	-0.641572
3	6	-2.151544	-1.720855	0.348506
4	6	-1.666871	-2.809567	1.331415
5	6	-2.850414	-3.491867	2.044915
6	6	-3.845625	-4.089403	1.049336
7	1	-2.650295	-3.153435	-1.144465
8	1	-1.099373	-3.573854	0.783807
9	1	-0.995058	-2.378608	2.080116
10	1	-2.447723	-4.281906	2.689649
11	1	-3.351498	-2.784276	2.715399
12	1	-3.347567	-4.898132	0.495177
13	1	-4.679731	-4.555380	1.588126
14	6	-0.793077	-1.325761	-0.608229
15	6	-3.584679	-1.344095	-1.737704
16	1	-4.247978	-1.799459	-2.476542
17	1	-4.104614	-0.468483	-1.337188
18	6	-2.310386	-0.867430	-2.538226
19	6	-1.354684	-0.360909	-1.536678
20	6	-5.436532	-2.132153	0.706224
21	1	-5.793033	-1.351571	0.025285
22	1	-6.312945	-2.714227	1.012117
23	1	-5.051110	-1.640765	1.602000
24	6	-5.168560	-3.873450	-1.056824
25	1	-4.485298	-4.483432	-1.660175
26	1	-5.884170	-4.553677	-0.582305
27	1	-5.741157	-3.228794	-1.731916
28	6	-2.602044	-0.468663	1.119101
29	1	-3.243553	-0.744869	1.957197
30	1	-1.742195	0.057866	1.543665
31	1	-3.157735	0.252426	0.514251
32	1	-0.617676	-2.275179	-1.125740
33	6	0.455420	-0.926782	0.191751
34	1	0.295152	0.003976	0.743998
35	1	0.643850	-1.707380	0.932365

36	6	1.708167	-0.785601	-0.702606
37	1	1.568244	0.029658	-1.422788
38	1	1.827624	-1.709030	-1.289625
39	6	2.988716	-0.562660	0.081501
40	6	3.387485	-1.671950	1.032774
41	1	4.472718	-1.773558	1.110215
42	1	2.976707	-1.516096	2.039524
43	1	2.999067	-2.633592	0.678131
44	6	3.713976	0.552140	-0.132123
45	6	5.039779	0.891684	0.487906
46	1	3.366378	1.268834	-0.876428
47	1	5.276234	0.243777	1.333929
48	1	-1.904132	-1.739742	-3.061855
49	1	-2.593387	-0.101771	-3.264960
50	1	5.059102	1.932260	0.827073
51	8	7.505230	-0.631775	-2.009631
52	15	7.115138	-0.433093	-0.464684
53	8	6.640518	-1.667821	0.191685
54	8	6.088176	0.804230	-0.517130
55	8	8.402825	0.272759	0.221514
56	1	7.924178	0.151813	-2.404164
57	1	9.006537	-0.395486	0.589538
58	6	-1.168757	1.091881	-1.429583
59	1	-2.137778	1.612082	-1.485497
60	1	-0.605946	1.433898	-0.563598
61	1	-0.646251	1.416560	-2.346989
62	6	0.867353	2.944870	2.213995
63	1	0.678419	3.793168	2.890723
64	8	0.015105	2.550152	1.411920
65	7	2.084146	2.398179	2.359882
66	1	2.390326	1.655597	1.735387
67	1	2.744983	2.777064	3.023967
68	1	-1.082202	3.675646	0.426200
69	6	-3.469828	3.232819	0.884570
70	6	-4.845440	2.993642	0.911459
71	6	-5.644445	3.299482	-0.192406
72	6	-5.052730	3.855945	-1.330354
73	6	-3.680975	4.100531	-1.372567
74	6	-2.881918	3.792930	-0.260756
75	1	-2.849639	3.007138	1.748515
76	1	-5.294619	2.576639	1.809284
77	1	-6.715090	3.121659	-0.161432
78	1	-5.664934	4.110423	-2.191437
79	1	-3.212930	4.548782	-2.243975
80	8	-1.547480	4.047051	-0.352887

TS (A-B1)



B3LYP/6-31G(d)//B3LYP/6-31G(d):
HF = -1903.2532378 hartrees (-1194310.43925188 kcal/mol)
Imaginary Frequencies: 1 (-464.2962 1/cm)
Zero-point correction = 0.695192 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31G(d):
HF = -1903.0157786 hartrees (-1194161.43122929 kcal/mol)

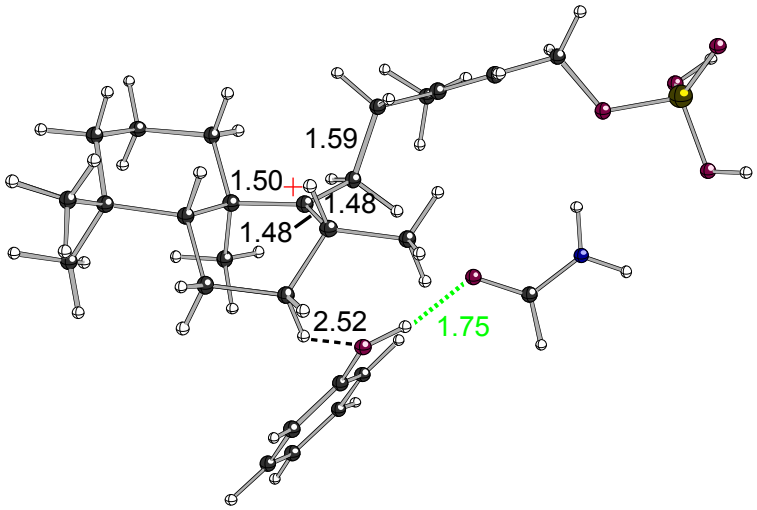
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	5.112135	-2.123341	-0.030569
2	6	3.866385	-1.385759	0.580684
3	6	2.557607	-1.365895	-0.287441
4	6	2.238509	-2.821229	-0.730157
5	6	3.426079	-3.487560	-1.437822
6	6	4.663676	-3.516983	-0.538097
7	1	3.604643	-2.014779	1.451396
8	1	1.989805	-3.418101	0.159505
9	1	1.361123	-2.844782	-1.385257
10	1	3.142092	-4.510512	-1.710619
11	1	3.642789	-2.974761	-2.382456
12	1	4.447123	-4.154922	0.331555
13	1	5.500758	-3.992239	-1.063756
14	6	1.392133	-0.773895	0.525078
15	6	4.155770	0.018270	1.129200
16	1	5.099616	0.036737	1.678715
17	1	4.259715	0.741899	0.315314
18	6	3.036353	0.464014	2.073552
19	6	1.635218	0.038343	1.666755
20	6	5.834729	-1.345580	-1.152856

21	1	6.038495	-0.307653	-0.868877
22	1	6.801159	-1.820087	-1.355966
23	1	5.287311	-1.332421	-2.098581
24	6	6.141645	-2.356369	1.100402
25	1	5.679558	-2.815901	1.982867
26	1	6.927262	-3.034338	0.749429
27	1	6.636040	-1.431843	1.416070
28	6	2.620247	-0.430187	-1.533776
29	1	3.408115	-0.755959	-2.210897
30	1	1.680797	-0.463987	-2.093935
31	1	2.808818	0.613557	-1.272518
32	1	1.524140	-1.228444	1.819878
33	6	-0.036746	-0.988323	0.048965
34	1	-0.588790	-0.045135	0.113613
35	1	0.012265	-1.250850	-1.008879
36	6	-0.826865	-2.107043	0.792559
37	1	-0.918251	-1.849024	1.853442
38	1	-0.264419	-3.047157	0.737630
39	6	-2.208389	-2.302444	0.191601
40	6	-2.252133	-3.110590	-1.081989
41	1	-3.229845	-3.100292	-1.566727
42	1	-1.521476	-2.743512	-1.813681
43	1	-1.992550	-4.157974	-0.877904
44	6	-3.274852	-1.776021	0.814107
45	6	-4.704318	-1.846313	0.381605
46	1	-3.123024	-1.230606	1.745415
47	1	-5.330620	-2.284144	1.166863
48	1	3.211976	0.111869	3.098378
49	1	2.996274	1.558538	2.138244
50	1	-4.852371	-2.406681	-0.543170
51	8	-6.702846	1.398504	-0.238101
52	15	-6.738428	-0.203115	0.003293
53	8	-7.639112	-0.648863	1.084026
54	8	-5.156090	-0.470449	0.162323
55	8	-6.999569	-0.837852	-1.455014
56	1	-7.263762	1.831636	0.428593
57	1	-7.936806	-1.066124	-1.580509
58	6	0.532524	0.725690	2.436063
59	1	0.476601	1.759809	2.066862
60	1	-0.449058	0.268199	2.321313
61	1	0.788246	0.766195	3.499260
62	6	-2.556724	2.688513	-0.586594
63	1	-2.600855	3.754168	-0.861436
64	8	-1.488743	2.151201	-0.255571
65	7	-3.734743	2.066484	-0.651950
66	1	-3.846355	1.095310	-0.373234
67	1	-4.583686	2.558156	-0.896014
68	1	-0.183920	3.166848	0.334278

69	6	1.718981	3.332266	-1.248303
70	6	2.913285	3.462181	-1.962114
71	6	4.073444	3.921314	-1.335116
72	6	4.026375	4.266205	0.019373
73	6	2.840324	4.147814	0.742980
74	6	1.680754	3.677230	0.110312
75	1	0.814128	2.979849	-1.737025
76	1	2.930253	3.209182	-3.019252
77	1	4.996126	4.027839	-1.897317
78	1	4.917064	4.643223	0.514967
79	1	2.785410	4.438801	1.788239
80	8	0.548964	3.566948	0.863591

B1



B3LYP/6-31G(d)//B3LYP/6-31G(d):
HF = -1903.2642515 hartrees (-1194317.35045876 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.697682 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31G(d):
HF = -1903.0219015 hartrees (-1194165.27341027 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	5.223500	-2.189662	0.163385
2	6	3.829309	-1.713097	0.714933
3	6	2.809782	-1.146298	-0.329451
4	6	2.696981	-2.126829	-1.548003
5	6	4.069874	-2.496305	-2.124503

6	6	4.977608	-3.110096	-1.057949
7	1	3.365724	-2.652552	1.056833
8	1	2.209978	-3.051843	-1.211989
9	1	2.066397	-1.691942	-2.329978
10	1	3.912111	-3.214200	-2.938333
11	1	4.542015	-1.621233	-2.585882
12	1	4.522456	-4.048582	-0.707976
13	1	5.942753	-3.384927	-1.500219
14	6	1.459918	-0.949267	0.292626
15	6	3.924662	-0.799395	1.955888
16	1	4.434608	-1.348882	2.751020
17	1	4.548746	0.072482	1.739791
18	6	2.542581	-0.327029	2.456271
19	6	1.337783	-1.043488	1.763278
20	6	6.206721	-1.059318	-0.213148
21	1	6.350414	-0.346366	0.604876
22	1	7.187463	-1.497010	-0.429973
23	1	5.912882	-0.492899	-1.100264
24	6	5.910689	-3.042946	1.255614
25	1	5.242374	-3.821562	1.643852
26	1	6.790321	-3.543842	0.836456
27	1	6.257755	-2.438945	2.100124
28	6	3.183243	0.290744	-0.857543
29	1	4.084297	0.204508	-1.463557
30	1	2.395539	0.711976	-1.484883
31	1	3.374020	0.994363	-0.048235
32	1	1.511247	-2.129207	1.930200
33	6	0.260804	-0.713942	-0.534846
34	1	-0.380694	0.032314	-0.056013
35	1	0.525308	-0.363387	-1.532767
36	6	-0.602247	-2.038138	-0.692631
37	1	-0.671149	-2.565974	0.261781
38	1	-0.080503	-2.697292	-1.394760
39	6	-1.990430	-1.721735	-1.210532
40	6	-2.046485	-1.053494	-2.561162
41	1	-3.057120	-0.992845	-2.967913
42	1	-1.659770	-0.027901	-2.499861
43	1	-1.425871	-1.591215	-3.289205
44	6	-3.053358	-2.050058	-0.457238
45	6	-4.495832	-1.851539	-0.800508
46	1	-2.885176	-2.509326	0.515948
47	1	-5.070708	-2.757213	-0.580760
48	1	2.433669	-0.509561	3.529179
49	1	2.394372	0.744132	2.297143
50	1	-4.662619	-1.568913	-1.841038
51	8	-6.635829	0.708749	1.129674
52	15	-6.604738	-0.653538	0.256564
53	8	-7.324533	-1.796715	0.850432

54	8	-5.008279	-0.771932	0.049323
55	8	-7.062776	-0.214523	-1.225347
56	1	-7.118402	0.548276	1.959002
57	1	-7.996690	-0.432928	-1.387798
58	6	0.005259	-0.649070	2.408703
59	1	-0.175261	0.423262	2.298781
60	1	-0.851739	-1.184148	1.992572
61	1	0.048633	-0.875284	3.478108
62	6	-2.578817	2.440217	0.707233
63	1	-2.532018	3.492144	1.028674
64	8	-1.558971	1.826141	0.357224
65	7	-3.804084	1.916136	0.732158
66	1	-3.977879	0.950459	0.459847
67	1	-4.606989	2.460755	1.015028
68	1	0.111848	2.265527	0.630001
69	6	0.969031	4.014008	-0.898105
70	6	1.578017	5.088890	-1.547396
71	6	2.844205	5.529830	-1.158916
72	6	3.498381	4.889363	-0.103641
73	6	2.897698	3.819457	0.558989
74	6	1.631232	3.378386	0.159889
75	1	-0.014200	3.664985	-1.203539
76	1	1.057240	5.581597	-2.364117
77	1	3.313564	6.365774	-1.668295
78	1	4.479501	5.230837	0.214952
79	1	3.387487	3.335633	1.399635
80	8	1.080769	2.305274	0.816515
