SUPPORTING INFORMATION

A Cytochrome P450 Serves as an Unexpected Terpene Cyclase during Fungal Meroterpenoid Biosynthesis

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Experimental Methods

Strains and culture conditions. *Penicillium aethiopicum* IBT 5753 was obtained from the IBT culture collection (Kgs. Lyngby, Denmark) and maintained on YMEG agar (4 g/L yeast extract, 10 g/L malt extract, and 16 g/L agar) or glucose minimal agar (GMM) at 30 ºC. *P. aethiopicum* Δ*gsfA*::*zeo*^{R}, which was blocked in griseofulvin biosynthesis, was obtained from previous study.[1] The *E. coli* strain XL-1 Blue (Stratagene) and TOP10 (Invitrogen) were used for DNA manipulation. *Saccharomyces cerevisiae* strain BJ5464 (*MATα ura3-52 his3-Δ200 leu2- Δ1 trp1 pep4::HIS3prb1 Δ1.6R can1 GAL*) was used as the yeast expression host. The *S. cerevisiae* strain was maintained on yeast peptone dextrose (YPD) agar.

General molecular biology methods. Genomic DNA from *P. aethiopicum* was prepared using the CTAB isolation buffer as described elsewhere or using ZYMO ZR fungal/bacterial DNA kit (Zymo Research) according to the manufacturer's protocol. PCR reactions were performed with Phusion high-fidelity DNA polymerase (New England Biolabs, NEB) or Platinum Pfx DNA polymerase (Invitrogen). PCR products were cloned into pCR-Blunt vector (Invitrogen) and confirmed by DNA sequencing. RNA extraction was performed using a RiboPure Yeast Kit (Ambion) and ImProm-II™ Reverse Transcription System (Promega) for reverse transcriptase-PCR (RT-PCR) was used to synthesize complementary DNA (cDNA) from total RNA. Primers used for molecular cloning were synthesized by Integrated DNA Technologies and are listed in Table S1.

Genetic manipulation of *P. aethiopicum*. Deletion of *vrtE* and *vrtK* were accomplished by a double homologous gene replacement cassette containing the *bar* resistance marker generated by fusion-PCR method described previously,[2,3] and the gene deletion strategy are illustrated in Figure S1. Transformation of *P. aethiopicum* was carried out using the polyethyelene-glycol method as described previously.[2] Diagnostic PCR was performed with miniprep genomic DNA from individual transformants prepared using a previously described toothpicks/alkaline lysis-based method.[2,4] The positive transformants were re-verified using higher quality genomic DNA extracted using ZYMO ZR fungal/bacterial DNA kit (Zymo Research). Primers used for the generation of gene deletion cassettes and diagnostic PCR are listed in Table S1 and shown in Figure S1.

Cloning and expression of *vrtK* in *S. cerevisiae*. The cDNA of *vrtK* was obtained as two overlapping fragments using RT-PCR from *P. aethiopicum* total RNA extracted after 4 days of growth in YMEG medium. The 5′ and 3′ primers for RT-PCR of *vrtK* (pESC-VrtK-F and pESC-VrtK-R) contained overhangs that overlap with the *GAL10* promoter cloning site of the pESC-Leu2d-AtCPR plasmid (Figure S2 and Table S1). The plasmid pESC-Leu2d-AtCPR is a gift from Dr. Dae-Kyun Ro at University of Calgary, and contained the *A. terreus* cytochrome P450 reductase (AtCPR) gene under the regulation of the *GAL1* promoter; it is PCR amplified as a linear fragment for cloning into the GAL10 promoter cloning site. Using a 3-way yeast *in vivo* recombination cloning approach, the complete cDNA of *vrtK* is cloned into pESC-

Leu2d-AtCPR plasmid under the regulation of *GAL10* promoter by transformation of *S. cerevisiae* BJ5464 with the 5′ and 3′ *vrtK* cDNA fragment along with the linear pESC-Leu2d-AtCPR plasmid using the S.c EasyComp Yeast Transformation Kit (Invitrogen) and selected on Synthetic Complete (SC) dropout agar medium lacking leucine (Figure S2). The strain *S. cerevisiae* BJ5464, which lacks vacuolar proteases,[5] was used for expression of VrtK and AtCPR. For biotransformation of **2** to **1** *in vivo* feeding, a 5 mL seed culture of the yeast strain harboring the pESC-Leu2d-AtCPR-VrtK plasmid growing in the appropriate yeast synthetic dropout medium was inoculated into 500 mL of galactose induction SC medium containing 0.2% glucose and 1.8% galactose and cultured for 8 hours or 24 hours at 30 °C, 250 rpm. After induction, the yeast cells were collected by centrifugation and replenished with 100 mL (1/5 volume) fresh liquid SC medium with 2% galactose to concentrate the cells 5 times. 1 mg of **2** dissolved in DMSO was added to 100 mL high density yeast cultures and incubated at 30 °C, 250 rpm. 5 mL of the high density yeast cultures were sampled after 24 and 48 hours and extracted twice with 5 mL of EtOAc/MeOH/AcOH (89:10:1) followed by drying *in vacuo*. The dried extracts were re-dissolved in 500 µL of MeOH and subjected to LCMS analysis.

LCMS analysis. All solvents and other chemicals used were of analytical grade. All LC-MS analyses were performed on a Shimadzu 2010 EV LC-MS (Phenomenex® Luna, 5µ, 2.0 × 100 mm, C18 column) using positive and negative mode electrospray ionization with a linear gradient of 5-95% MeCN-H_2O in 30 minutes followed by 95% MeCN for 15 minutes with a flow rate of 0.1 mL/min.

Compound extraction and purification. Compound **3** and **2** was purified from *P. aethiopicum* Δ*vrtE* and Δ*vrtK* mutants grown in stationary liquid YG culture for 5 days. The compound were extracted from the cultures using equal volume of EtOAc/MeOH/AcOH (89:10:1) twice followed by solvent partitioning using $CHCl_3$/H_2O ($CHCl_3$ fraction was retained and dried) and 90% MeOH/hexanes (90% MeOH fraction was retained and dried). This is followed by a chromatographic separation on a Sephadex LH-20 column using MeOH/$CHCl_3$ (1:1) as the mobile phase. Fractions collected were checked by TLC. Additional rounds of chromatographic separation using Sephadex LH-20 column was performed using a hexane/MeOH/$CHCl_3$ solvent system with decreasing ratio of hexane from 3:1:1 to 1:1:1. Further purification was carried out by reverse-phase HPLC using a Beckman Coulter System Gold LC coupled to a Phenomenex Luna 250 x 10mm 5 micron C18 column and a UV-Vis detector. The compounds were separated on a solvent gradient of 40-80% solvent B (acetonitrile with 0.1% TFA) at a flow rate of 3 ml/min over 30 mins. The HPLC fractions containing pure compounds were pooled and dried completely under vacuum before proceed to NMR analysis.

NMR characterizations. All ^{1}H, ^{13}C and 2D (HSQC and HMBC) NMR spectra were obtained on a Bruker DRX-500 spectrometer or a Bruker AV500 spectrometer with a 5 mm dual cryoprobe at the UCLA Molecular Instrumentation Center. DMSO-d_6 was used as the solvent for all compounds.

Computation methods. Calculations were performed with GAUSSIAN09.[7] Geometries were optimized using the B3LYP/6-31+G(d,p) method and all stationary points were characterized as minima or transition state structures using frequency calculations at the same level.[8] All reported energies include zero-point energy corrections (unscaled) from these B3LYP/6-31+G(d,p) frequency calculations. Intrinsic reaction coordinate (IRC) calculations were used for further characterization of transition state structures.[9] mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p)[10] and MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p)[11] and M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p)[12] energies are also shown to correct well-known shortcomings of B3LYP in predicting energies of cyclic structures[10] and dispersion interactions.[12] Truncated small model systems that lead to form 1a and 1a' are used to examine carbocationic rearrangements that begin with a secondary allylic carbocation A and A' resulted from hydrogen abstraction followed by electron transfer of 2a and 2a', respectively (Scheme 3). The numbering for the carbon atoms for model systems and all structures is adopted from that of viridicatumtoxin (**1**). Capital alphabets in bold are used to label carbocations and the following number is used to label different conformers and stereoisomers. The validity of this computational approach for examining terpene-forming carbocation rearrangements is well-established.[13] Structural drawings were created using *Ball & Stick.*[14]

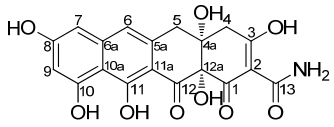
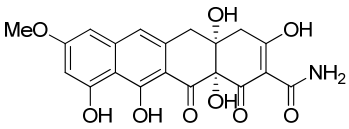
Supplementary Tables

Table S1. List of primers used in this study.

Primer Name	Sequence (5' to 3')	Remarks
VrtE-KO-P1*	ctactgctgcgttaccagtc	for *vrtE* deletion cassette
VrtE-KO-P2*	tatactcggccaggtcctgca	for *vrtE* deletion cassette
VrtE-KO-P3*	ctgcccgtcaccgagatttagctccatccagttgtgcgtgac	for *vrtE* deletion cassette
VrtE-KO-P4*	cttcaatatcatcttctgtcgaaggggctacaaagcatggca	for *vrtE* deletion cassette
VrtE-KO-P5*	caagaatggcgccgtggacatc	for *vrtE* deletion cassette
VrtE-KO-P6*	caggcagctgacgcacaggct	for *vrtE* deletion cassette
VrtK-KO-P1*	gatgattgcgcccgccatgag	for *vrtK* deletion cassette
VrtK-KO-P2*	gcctactctatcggccccatc	for *vrtK* deletion cassette
VrtK-KO-P3*	tgcccgtcaccgagatttaggagcttccaggtgagcaaggt	for *vrtK* deletion cassette
VrtK-KO-P4*	cttcaatatcatcttctgtcgcggtcccaatgctgtccgac	for *vrtK* deletion cassette
VrtK-KO-P5*	ccactggcctaacggactcag	for *vrtK* deletion cassette
VrtK-KO-P6*	gtctgtgagccgctagccatgt	for *vrtK* deletion cassette
PtrpC-F	gtcgacagaagatgatattga	for *bar* resistant marker in deletion cassette
bar-stp-R	cctaaatctcggtgacgggca	for *bar* resistant marker in deletion cassette
bar-F	agtaaccatgagcccagaacgac	for screening of targeted homologous recombination
bar-R	agaaacccacgtcatgccagttc	for screening of targeted homologous recombination
pESC-VrtK-F	gaaaattcgaattcaaccctcactaaagggcggcc atggctttctccacctatctagga	for cloning of *vrtK* cDNA into pESC-Leu2d-AtCPR
VrtK-RT-F2	cagtcaagagcgctggcgac	for cloning of *vrtK* cDNA into pESC-Leu2d-AtCPR
VrtK-RT-R2	agccggtgccgacaagtgtc	for cloning of *vrtK* cDNA into pESC-Leu2d-AtCPR
pESC-VrtK-R	ttatcgtcgtcatccttgtaatccatcgatactag ctttgtgttaatgcgcgcatgac	for cloning of *vrtK* cDNA into pESC-Leu2d-AtCPR
pESC-Gal10-iF	ggccgccctttagtgagggttg	for amplification of pESC-Leu2d-AtCPR plasmid as a linear fragment
pESC-FLAG-iR	ctagtatcgatggattacaag	for amplification of pESC-Leu2d-AtCPR plasmid as a linear fragment

* The designation of the primers P1 – P6 is following the fusion PCR primer design in Scewcyzk et al.[3] as shown in Figure S1.

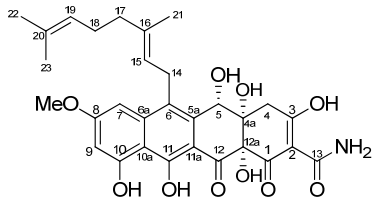
Table S2. NMR data of **3** in DMSO-d_6 measured on 500 MHz Bruker NMR spectrometer and mass spectra

3, $C_{19}H_{15}NO_9$				**anthrotainin**[6]	
a  desmethylanthrotainin **3**				 anthrotainin	
NO.	^{13}C δ(ppm) *a*/*b**	^{1}H δ(ppm) (m, J_{HH}(Hz)) *a*/*b**	HMBC *a*/*b**	^{13}C δ(ppm)	^{1}H 0δ(ppm)
1	194.3/170.8			192.1	
2	99.7/98.2			98.0	
3	197.99/196.4			194.3	
4	42.1/49.0	2.55 (m)/ 3.15 (m)		42.1	2.84 (s)
4a	72.5			72.3	
5	38.3	2.79 (m), 3.38 (m)		37.9	3.41 (br s)
5a	135.0			135.4	
6	117.0	6.8 (s, 1H)	7H	117.5	6.9 (s)
a	141.5			141.4	
7	102.3	6.47 (s, 1H)	9H	99.5	6.49 (d, 2.0)
8	162.4		9H	163.2	
9	102.0	6.33 (s, 1H)	7H	101.1	6.55 (d, 2.0)
10	159.8		9H	159.3	
10a	106.3		7H, 9H	108.2	
11	167.1			166.7	
11a	107.6			106.8	
12	200.8			196.6	
12a	82.1/81.0			82.1	
13	173.79			173.5	
13-NH_2		8.83 (br s, 1H), 9.03 (br s, 1H)			9.01 (s)
8-OCH_3	-	-	-	55.6	3.87 (s)
OH's		5.65 (br s, 1H), 9.81 (br s, 1H), 10.3 (br s, 1H), 14.7 (br s, 1H), 14.95/14.7 (br s, 1H), 18.2 (br s, 1H)			

* The additional carbon and proton signals appear to correlate with the 1,3 keto-enol tautomerization occurs at the A-ring. Similar to desmethyl-TAN-1612, **3** is highly unstable and decomposed gradually in DMSO and in light. The ^{1}H and ^{13}C-NMR data of anthrotainin in DMSO-d6 from previous report[6] is shown here for comparison. ^{1}H and ^{13}C-NMR spectra of **2** are shown in **Figure S3** and **S4**.

Table S3. NMR data of 2 in DMSO-d_6 measured on 500 MHz Bruker NMR spectrometer and mass spectrum.

2, $C_{30}H_{33}NO_{10}$ (MW = 567.58)



previridicatumtoxin, **2**

NO.	^{13}C δ(ppm)	^{1}H δ(ppm) (mult, J_{HH}(Hz))	HMBC
1	192.2		
2	99.57		
3	195.3		
4	41.9	2.71 (1H, d, 17.5) 2.80 (1H, d, 17.5)	
4a	73.2		5-H
5	70.8	4.75 (1H, brs)	6-H
5a	134.5		5-H, 14-H_2
6	129.1		7-H, 14-H_2, 15-H
6a	141.4		6-H
7	99.1	6.82 (1H, d, 1.9)	9-H
8	164.0		7-H, 9-H, 8-OCH_3
9	102.2	6.60 (1H, d, 1.9)	7-H
10	160.6		9-H
10a	109.2		7-H, 9-H
11	165.2		
11a	106.4		6-H
12	199.4		
12a	81.6		5-H
13	173.8		
14	28.3	3.67 (1H, dd, 4.4/16) 3.77 (1H, dd, 6.8/16)	15-H
15	124.9	5.03 (1H, m)	14-H_2, 17-H_2, 21-H_3
16	135.4		14-H_2, 15-H, 17-H, 21-H_3
17	40.1	2.01(2H, m)	21-H_3, 18-H_2
18	26.9	2.05 (2H, m)	17-H_2, 19-H
19	124.9	5.14 (1H, t, 5.8)	17-H_2, 18-H_2, 22-H_3, 23-H_3
20	131.7		22-H_3, 23-H_3
21	17.1	1.87 (3H, s)	15-H, 17-H_2
22	18.5	1.54 (3H, s)	19-H, 23-H_3
23	26.3	1.57 (3H, s)	19-H, 22-H_3
8-OCH3	56.3	3.9 (3H, s)	
13-NH_2		8.99 (2H, brs)	
-OH′s		5.29 (1H, brs), 5.73(1H, brs), 7.01(1H,s) 10.1 (1H, s), 15.26 (1H, brs), 18.22 (1H, brs),	

1H and 13C-NMR spectra of 2 are shown in **Figure S5** and **S6**.

Table S4 (i). Coordinates and Energies. Path 1: **A1→D1**

The coordinates below are those for the enantiomer of the structure presented in the main paper and Figure S10 (i).

A1

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2902722 hartrees (-558666.048708222 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.403251 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.005680	1.774219	-1.125771
2	6	1.373368	2.914706	-0.788426
3	6	1.814560	-0.561097	0.907947
4	6	3.171858	-0.768132	0.578903
5	6	3.853180	0.174279	-0.174625
6	6	3.448674	1.427903	-0.878547
7	1	1.457222	1.047484	-1.725494
8	1	4.924865	-0.008153	-0.264809
9	1	3.980462	2.240217	-0.358440
10	1	3.976808	1.379460	-1.848076
11	6	1.981122	4.043142	0.006746
12	1	1.998407	4.961412	-0.593034
13	1	1.366608	4.261915	0.888709
14	1	2.999454	3.850810	0.350838
15	6	-0.053138	3.152259	-1.221290
16	1	-0.702312	3.317669	-0.352277
17	1	-0.120053	4.056515	-1.838902
18	1	-0.453395	2.314894	-1.798719
19	6	0.964176	-1.447776	1.726765
20	1	0.393239	-0.913301	2.490111
21	1	1.502116	-2.271472	2.194802
22	6	0.072034	-1.928676	0.582541
23	6	-1.151903	-1.243239	0.248515
24	6	0.466428	-3.047908	-0.153995
25	6	-1.615507	-0.101887	0.930885
26	6	-1.949396	-1.778809	-0.823721
27	6	-0.324596	-3.559946	-1.194137
28	1	1.388570	-3.557805	0.107820
29	6	-2.825149	0.502011	0.588347
30	6	-3.176488	-1.141389	-1.145077

31	6	-1.512313	-2.928605	-1.523335
32	1	-0.007372	-4.449887	-1.726811
33	6	-3.615944	-0.027472	-0.463795
34	1	-3.784072	-1.553997	-1.945442
35	1	-2.129922	-3.316361	-2.328756
36	1	-4.559466	0.430514	-0.733209
37	6	3.931978	-1.958328	1.134960
38	1	3.853728	-2.013595	2.225187
39	1	3.554214	-2.901469	0.727535
40	1	4.992266	-1.897694	0.881874
41	8	-3.163738	1.591623	1.312391
42	6	-4.424293	2.235308	1.082292
43	1	-5.254948	1.544365	1.259640
44	1	-4.468155	3.050450	1.803475
45	1	-4.479970	2.640984	0.066530
46	1	-1.055470	0.346885	1.742797
47	1	1.331089	0.323803	0.504437

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0724437 hartrees (-558529.359146187 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.7964618 hartrees (-558356.177744118 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.856413105 hartrees (-558393.7978 kcal/mol)

TS $_{\mathbf{A1\text{-}E1}}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2768129 hartrees (-558657.602862879 kcal/mol)
Imaginary Frequencies: 1 (-86.0078 1/cm)
Zero-point correction = 0.403428 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.871226	0.738550	-1.087576
2	1	0.663952	-0.176153	-1.651082
3	1	1.509983	1.375366	-1.702272
4	6	-0.434416	1.445196	-0.727176
5	6	-1.589227	0.686245	-0.322740
6	6	-0.508710	2.830435	-0.796370
7	6	-1.609464	-0.724802	-0.254384

8	6	-2.789226	1.405774	0.009601
9	6	-1.696846	3.523441	-0.487252
10	1	0.356598	3.396250	-1.127434
11	6	-2.752228	-1.415344	0.134000
12	6	-3.937810	0.670322	0.403481
13	6	-2.812066	2.820331	-0.078720
14	1	-1.727165	4.604321	-0.574740
15	6	-3.933473	-0.705523	0.472008
16	1	-4.844895	1.214804	0.650020
17	1	-3.729069	3.345735	0.173053
18	1	-4.830416	-1.231497	0.774338
19	8	-2.646718	-2.767464	0.161458
20	6	-3.789475	-3.556882	0.512167
21	1	-4.612851	-3.392079	-0.190948
22	1	-3.458107	-4.592722	0.446816
23	1	-4.118658	-3.342715	1.534710
24	1	-0.743318	-1.320813	-0.517387
25	6	2.642778	-1.596863	0.651640
26	6	3.002267	-1.725518	-0.668108
27	6	1.497239	0.420060	0.233674
28	6	2.545951	1.208595	0.882130
29	6	3.441955	0.560366	1.659040
30	6	3.502255	-0.945736	1.718060
31	1	1.777290	-2.162390	0.988353
32	1	4.197336	1.121468	2.203829
33	1	4.549310	-1.261218	1.624834
34	1	3.183783	-1.287616	2.712702
35	6	4.271861	-1.136855	-1.209834
36	1	5.093769	-1.851899	-1.060191
37	1	4.203961	-0.948911	-2.284677
38	1	4.556980	-0.212300	-0.700094
39	6	2.172449	-2.535506	-1.618336
40	1	1.898797	-1.953911	-2.507806
41	1	2.770047	-3.379754	-1.988299
42	1	1.268011	-2.937776	-1.156306
43	6	2.633998	2.703533	0.644699
44	1	2.773192	2.933274	-0.417064
45	1	1.727615	3.215025	0.980197
46	1	3.486230	3.116323	1.187917
47	1	0.847141	-0.150005	0.889841

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0620826 hartrees (-558522.857452326 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):

HF = -889.7887715 hartrees (-558351.352003965 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8564131hartrees (-558393.7978 kcal/mol)

E1
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2871295 hartrees (-558664.076632545 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.404377 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.339085	1.090225	0.283067
2	6	-3.187770	1.354517	-0.865791
3	6	-1.521209	-0.227082	0.452620
4	6	-2.456764	-1.166828	1.207122
5	6	-3.543492	-0.521812	1.661431
6	6	-3.571356	0.941131	1.342858
7	1	-1.751495	1.974183	0.535498
8	1	-4.339621	-0.976608	2.243179
9	1	-4.551762	1.285085	0.980112
10	1	-3.315025	1.606065	2.176317
11	6	-3.888754	0.280400	-1.605240
12	1	-4.827537	0.622378	-2.046632
13	1	-3.231537	-0.021399	-2.435828
14	1	-4.036489	-0.613226	-0.992130
15	6	-3.402148	2.757849	-1.292815
16	1	-4.420600	2.944777	-1.643340
17	1	-3.104384	3.488736	-0.538410
18	1	-2.741805	2.911674	-2.165120
19	6	-0.876560	-0.757609	-0.871098
20	1	-0.775035	0.089869	-1.564113
21	1	-1.550606	-1.473372	-1.351959
22	6	0.475652	-1.408840	-0.686378
23	6	1.627700	-0.619861	-0.339317
24	6	0.623652	-2.773535	-0.867703
25	6	1.586455	0.788559	-0.198900
26	6	2.884893	-1.287412	-0.142150
27	6	1.865357	-3.424895	-0.685843
28	1	-0.237808	-3.367786	-1.162019
29	6	2.718050	1.518911	0.138492
30	6	4.021060	-0.512017	0.206325

31	6	2.972747	-2.693577	-0.317299
32	1	1.937225	-4.497134	-0.836387
33	6	3.954217	0.857255	0.351201
34	1	4.970477	-1.018343	0.356550
35	1	3.931379	-3.182344	-0.167108
36	1	4.845001	1.412894	0.616572
37	6	-2.117192	-2.600384	1.471857
38	1	-2.014231	-3.170812	0.542664
39	1	-1.155666	-2.680352	1.992061
40	1	-2.884077	-3.079570	2.084817
41	8	2.550185	2.866373	0.241853
42	6	3.677839	3.688357	0.555480
43	1	4.457397	3.600426	-0.209354
44	1	3.299569	4.710360	0.570783
45	1	4.089740	3.438211	1.539544
46	1	-0.689766	0.016518	1.126599
47	1	0.675413	1.348677	-0.374632

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0796788 hartrees (-558533.899243788 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8109502 hartrees (-558365.269360002 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.870561203 hartrees (-558402.6759 kcal/mol)

TS $_{\mathbf{E1\text{-}C1}}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2605113 hartrees (-558647.373445863 kcal/mol)
Imaginary Frequencies: 1 (-290.7141 1/cm)
Zero-point correction = 0.403653 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.935957	-1.695185	0.385274
2	6	2.790205	-1.107947	-0.679148
3	6	1.814108	0.050529	-0.202694
4	6	2.329349	0.761873	1.049521
5	6	2.546517	-0.064925	2.080814
6	6	2.262148	-1.532989	1.847548
7	1	1.168966	-2.407028	0.079498

8	1	2.937990	0.263182	3.037632
9	1	3.154737	-2.140105	2.062107
10	1	1.455898	-1.916391	2.482893
11	6	4.289095	-0.920661	-0.449151
12	1	4.790522	-1.888786	-0.539488
13	1	4.697881	-0.268327	-1.226198
14	1	4.539851	-0.493853	0.520696
15	6	2.521195	-1.684540	-2.073592
16	1	2.844108	-0.989721	-2.853556
17	1	3.099525	-2.605613	-2.193899
18	1	1.470420	-1.932463	-2.245229
19	6	1.013919	0.812264	-1.302182
20	1	0.785983	0.121564	-2.116115
21	1	1.723503	1.541611	-1.709247
22	6	-0.239545	1.517480	-0.827420
23	6	-1.385846	0.765007	-0.403549
24	6	-0.291996	2.899554	-0.809774
25	6	-1.460806	-0.648717	-0.488559
26	6	-2.518778	1.476055	0.119924
27	6	-1.427224	3.598498	-0.334909
28	1	0.561778	3.471014	-1.165661
29	6	-2.572076	-1.347157	-0.034962
30	6	-3.637118	0.731304	0.577206
31	6	-2.509678	2.896216	0.143958
32	1	-1.430275	4.683444	-0.339475
33	6	-3.672905	-0.645579	0.520220
34	1	-4.491469	1.269828	0.977618
35	1	-3.377853	3.419759	0.534265
36	1	-4.546135	-1.175946	0.879358
37	6	2.610306	2.236345	1.046448
38	1	3.286192	2.509729	0.227028
39	1	1.695019	2.821352	0.927628
40	1	3.083959	2.528780	1.986004
41	8	-2.521524	-2.699866	-0.170214
42	6	-3.673026	-3.481485	0.169267
43	1	-4.541895	-3.180582	-0.425557
44	1	-3.407694	-4.510833	-0.070228
45	1	-3.903887	-3.403597	1.237330
46	1	0.927789	-0.585785	0.282743
47	1	-0.695510	-1.227934	-0.993884

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0598432 hartrees (-558521.452206432 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):

HF = -889.7944069 hartrees (-558354.888273819 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.855047 hartrees (-558392.9405 kcal/mol)

C1
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.3109557 hartrees (-558679.027811307 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.406103 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.040189	1.509532	-0.002495
2	6	-2.699885	0.270357	-0.862614
3	6	-1.717616	-0.633941	-0.131178
4	6	-1.780589	-0.769349	1.290123
5	6	-2.627490	0.061084	1.994953
6	6	-3.431903	1.163712	1.431256
7	1	-3.843853	2.067395	-0.492043
8	1	-2.734265	-0.122650	3.063734
9	1	-4.489161	0.853310	1.511219
10	1	-3.363329	2.035086	2.096233
11	6	-3.972024	-0.620448	-1.091202
12	1	-4.710691	-0.021327	-1.632675
13	1	-3.738801	-1.495311	-1.704327
14	1	-4.420596	-0.966153	-0.156616
15	6	-2.224539	0.767472	-2.247437
16	1	-2.152655	-0.034438	-2.985451
17	1	-2.962017	1.480750	-2.626507
18	1	-1.262659	1.284893	-2.197878
19	6	-0.827576	-1.532629	-0.932155
20	1	-0.874579	-1.255572	-1.986194
21	1	-1.301858	-2.526933	-0.861585
22	6	0.634075	-1.714919	-0.517840
23	6	1.495376	-0.593853	-0.267798
24	6	1.152945	-2.997363	-0.489309
25	6	1.057428	0.749781	-0.281732
26	6	2.884010	-0.852244	0.010121
27	6	2.517887	-3.243157	-0.218150
28	1	0.501366	-3.844455	-0.689846
29	6	1.922930	1.806578	-0.044217
30	6	3.744674	0.250188	0.253849

31	6	3.365483	-2.186761	0.031353
32	1	2.888081	-4.262956	-0.213001
33	6	3.291795	1.550881	0.230135
34	1	4.792769	0.053762	0.461246
35	1	4.416435	-2.361682	0.243377
36	1	3.982112	2.364090	0.417191
37	6	-1.017924	-1.839375	2.044530
38	1	-1.135342	-2.824259	1.584737
39	1	0.052245	-1.623355	2.080658
40	1	-1.386504	-1.904650	3.070790
41	8	1.374582	3.050970	-0.089775
42	6	2.216533	4.193656	0.097228
43	1	2.999409	4.236685	-0.667643
44	1	1.561732	5.058559	-0.005879
45	1	2.666999	4.194745	1.095871
46	1	0.023368	1.000879	-0.487967
47	1	-2.165245	2.170617	0.016231

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.1034744 hartrees (-558548.831220744 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8347584 hartrees (-558380.209243584 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.897325 hartrees (-558419.4704 kcal/mol)

TS $_{\mathbf{C1\text{-}D1}}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2969743 hartrees (-558670.254342993 kcal/mol)
Imaginary Frequencies: 1 (-254.1549 1/cm)
Zero-point correction = 0.407105 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.123840	0.346593	-0.069968
2	6	-2.285369	-0.739656	-0.778356
3	6	-0.930786	-0.932877	-0.052762
4	6	-0.958606	-0.860679	1.418944
5	6	-2.076479	-0.427940	2.062979
6	6	-3.325192	0.064210	1.416658
7	1	-4.091127	0.432909	-0.576128

8	1	-2.080317	-0.477851	3.150732
9	1	-4.114687	-0.685885	1.582588
10	1	-3.679516	0.960169	1.942346
11	6	-3.013044	-2.120990	-0.700054
12	1	-4.030535	-2.003643	-1.085476
13	1	-2.513795	-2.873412	-1.316272
14	1	-3.077747	-2.506052	0.320506
15	6	-2.191779	-0.357038	-2.271509
16	1	-1.531470	-1.005840	-2.853788
17	1	-3.187207	-0.440559	-2.717533
18	1	-1.876478	0.682418	-2.410573
19	6	0.011097	-1.981176	-0.687644
20	1	-0.261466	-2.120872	-1.737643
21	1	-0.156733	-2.945245	-0.192514
22	6	1.459263	-1.561422	-0.567120
23	6	1.616636	-0.170598	-0.464673
24	6	2.566970	-2.383114	-0.436807
25	6	0.430410	0.635727	-0.639976
26	6	2.852443	0.390377	-0.057542
27	6	3.835678	-1.825041	-0.149408
28	1	2.464984	-3.462470	-0.510603
29	6	0.490557	1.999538	-0.226306
30	6	2.850771	1.767584	0.301694
31	6	3.976974	-0.466477	0.071547
32	1	4.693522	-2.481691	-0.048458
33	6	1.702352	2.540911	0.267935
34	1	3.775959	2.220116	0.649567
35	1	4.935388	-0.053149	0.371404
36	1	1.754844	3.578356	0.573319
37	6	0.222779	-1.321867	2.245805
38	1	0.541855	-2.337053	1.990455
39	1	1.094033	-0.672763	2.112617
40	1	-0.037284	-1.312679	3.306519
41	8	-0.616525	2.721914	-0.422742
42	6	-0.614712	4.145375	-0.186504
43	1	0.134569	4.636340	-0.813654
44	1	-1.611291	4.482093	-0.467006
45	1	-0.434405	4.360008	0.870434
46	1	-0.140845	0.494104	-1.551851
47	1	-2.614791	1.308691	-0.188657

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0938125 hartrees (-558542.768281875 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):

HF = -889.825113 hartrees (-558374.15665863 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8881748 hartrees (-558413.7286 kcal/mol)

D1
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.3106132 hartrees (-558678.812889132 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.408792 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.119072	0.005072	-0.482653
2	6	-2.027568	-1.026077	-0.848302
3	6	-0.707122	-0.782818	-0.001078
4	6	-1.021154	-0.460089	1.465582
5	6	-2.258823	-0.127936	1.874247
6	6	-3.475876	-0.019339	1.005296
7	1	-4.009612	-0.202483	-1.086833
8	1	-2.407612	0.064227	2.936244
9	1	-4.152717	-0.855652	1.233119
10	1	-4.040102	0.881945	1.277192
11	6	-2.586171	-2.441685	-0.533317
12	1	-3.596409	-2.530917	-0.944859
13	1	-1.988752	-3.236536	-0.987102
14	1	-2.646014	-2.637472	0.540497
15	6	-1.783756	-0.944535	-2.369282
16	1	-0.953218	-1.573941	-2.708403
17	1	-2.676972	-1.288581	-2.899980
18	1	-1.601113	0.082288	-2.709835
19	6	0.234992	-2.056515	-0.122012
20	1	0.033588	-2.583608	-1.059436
21	1	0.041939	-2.770202	0.683192
22	6	1.653472	-1.551350	-0.129184
23	6	1.658426	-0.183041	-0.339368
24	6	2.872493	-2.202250	0.070942
25	6	0.291291	0.361456	-0.577924
26	6	2.830274	0.591028	-0.256907
27	6	4.073810	-1.460973	0.075635
28	1	2.907082	-3.274278	0.244301
29	6	0.217173	1.827505	-0.296021
30	6	2.652719	2.001187	-0.217721

31	6	4.065252	-0.079002	-0.067310
32	1	5.015041	-1.978458	0.229013
33	6	1.397336	2.596817	-0.200425
34	1	3.527992	2.642595	-0.140712
35	1	4.988657	0.488858	-0.004266
36	1	1.332239	3.673144	-0.104867
37	6	0.111763	-0.482020	2.470076
38	1	0.623980	-1.449411	2.513924
39	1	0.884532	0.265308	2.242498
40	1	-0.264904	-0.261562	3.471660
41	8	-0.981180	2.348588	-0.272703
42	6	-1.197347	3.779706	-0.146342
43	1	-0.749016	4.300820	-0.995180
44	1	-2.278644	3.898428	-0.157557
45	1	-0.786910	4.136001	0.800674
46	1	0.135498	0.343493	-1.674244
47	1	-2.781790	1.006450	-0.760997

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.1123831 hartrees (-558554.421519081 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8488094 hartrees (-558389.0264 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.9103544 hartrees (-558427.6465 kcal/mol)

Table S4 (ii). Coordinates and Energies. Path 2: **A2→D2**
The coordinates below are those for the enantiomer of the structure presented in Figure S10 (ii).

A2
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2871372 hartrees (-558664.081464372 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.403528 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.750989	-0.154015	-0.870492
2	6	4.811611	0.322975	-0.190169
3	6	1.235240	-0.857099	0.806400
4	6	1.112592	-1.941058	-0.088365
5	6	2.173352	-2.249565	-0.926447
6	6	3.476619	-1.587710	-1.238425
7	1	3.054576	0.567742	-1.297781
8	1	2.062153	-3.191275	-1.465535
9	1	4.252895	-2.265803	-0.850004
10	1	3.585274	-1.699692	-2.332048
11	6	5.892521	-0.521407	0.437415
12	1	6.860101	-0.306785	-0.032813
13	1	6.003650	-0.271491	1.499596
14	1	5.717790	-1.596827	0.365154
15	6	5.006188	1.811308	-0.025377
16	1	5.057776	2.087125	1.035524
17	1	5.957988	2.124462	-0.471913
18	1	4.206699	2.387852	-0.498684
19	6	0.264681	-0.408757	1.831819
20	1	0.755944	-0.036835	2.733642
21	1	-0.477324	-1.155323	2.105431
22	6	-0.317281	0.739460	0.999225
23	6	-1.633901	0.680795	0.407732
24	6	0.477785	1.874342	0.805743
25	6	-2.546300	-0.370866	0.619476
26	6	-2.056863	1.801656	-0.393722
27	6	0.042023	2.964380	0.037598
28	1	1.452829	1.924696	1.282846
29	6	-3.819149	-0.354622	0.051200
30	6	-3.355702	1.782497	-0.966334
31	6	-1.200948	2.914858	-0.568745
32	1	0.676591	3.836870	-0.074130

33	6	-4.225378	0.734376	-0.761555
34	1	-3.671036	2.630292	-1.567686
35	1	-1.544757	3.746716	-1.177266
36	1	-5.211586	0.756940	-1.208032
37	6	-0.098698	-2.852004	-0.068891
38	1	-0.329902	-3.197371	0.943647
39	1	-0.982229	-2.338211	-0.456686
40	1	0.069220	-3.735007	-0.688920
41	8	-4.598706	-1.422078	0.331216
42	6	-5.941449	-1.474078	-0.168838
43	1	-5.953423	-1.485493	-1.263941
44	1	-6.354360	-2.408196	0.209749
45	1	-6.532703	-0.632840	0.207695
46	1	-2.303002	-1.222457	1.242007
47	1	2.148889	-0.275277	0.734917

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0694221 hartrees (-558527.463061971 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.7933907hartrees (-558354.2506 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8535017 hartrees (-558391.9709 kcal/mol)

TS $_{\mathbf{A2\text{-}E2}}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2712711 hartrees (-558654.125327961 kcal/mol)
Imaginary Frequencies: 1 (-136.8524 1/cm)
Zero-point correction = 0.402166 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.656113	-0.270071	-1.555783
2	6	3.219679	0.862908	-1.019513
3	6	1.352346	-0.784452	0.402873
4	6	2.242818	-1.875616	0.749861
5	6	3.082450	-2.356030	-0.200303
6	6	3.297892	-1.643868	-1.509010
7	1	1.805858	-0.139341	-2.220039
8	1	3.687222	-3.237548	0.000747
9	1	4.378182	-1.582340	-1.694431

10	1	2.904208	-2.268319	-2.324499
11	6	4.487608	0.802804	-0.219293
12	1	5.348681	0.742454	-0.900926
13	1	4.624082	1.695782	0.395094
14	1	4.535246	-0.084855	0.421036
15	6	2.645873	2.218328	-1.294245
16	1	2.492531	2.784112	-0.370023
17	1	3.371599	2.791992	-1.887905
18	1	1.704068	2.177484	-1.844370
19	6	0.808697	0.157638	1.425470
20	1	1.626442	0.660225	1.958025
21	1	0.375306	-0.513443	2.194109
22	6	-0.235196	1.147833	0.958654
23	6	-1.489345	0.693406	0.424512
24	6	0.001348	2.502793	1.091362
25	6	-1.851249	-0.675016	0.339522
26	6	-2.432970	1.680202	-0.025411
27	6	-0.941095	3.470116	0.667918
28	1	0.932488	2.840596	1.540076
29	6	-3.073011	-1.069105	-0.189528
30	6	-3.668983	1.241483	-0.567279
31	6	-2.128752	3.061554	0.105358
32	1	-0.720985	4.525608	0.789704
33	6	-3.991905	-0.094857	-0.659457
34	1	-4.380701	1.987251	-0.910169
35	1	-2.858563	3.792299	-0.231940
36	1	-4.947425	-0.389161	-1.075561
37	6	2.245264	-2.414055	2.169387
38	1	2.596169	-1.657352	2.879486
39	1	1.244580	-2.726718	2.485080
40	1	2.910522	-3.276217	2.245379
41	8	-3.308635	-2.407023	-0.214485
42	6	-4.569705	-2.889645	-0.687989
43	1	-4.723068	-2.631438	-1.741739
44	1	-4.524208	-3.973369	-0.583811
45	1	-5.394903	-2.499477	-0.082307
46	1	-1.210567	-1.463276	0.719464
47	1	0.745061	-0.896863	-0.487223

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0562 hartrees (-558519.1661 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.7824301 hartrees (-558347.3727 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8451418 hartrees (-558386.7249 kcal/mol)

E2
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2980938 hartrees (-558670.956840438 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.406030 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.524532	-0.553907	1.031399
2	6	-1.554008	0.934281	1.124889
3	6	-1.702271	-1.145628	-0.407411
4	6	-3.171181	-1.546021	-0.480251
5	6	-3.727309	-1.532011	0.739094
6	6	-2.757904	-1.148180	1.827762
7	1	-0.587888	-0.900356	1.470557
8	1	-4.747254	-1.833254	0.958975
9	1	-3.171421	-0.462436	2.575751
10	1	-2.406900	-2.027024	2.384535
11	6	-2.771104	1.700782	0.715892
12	1	-3.517798	1.553367	1.512476
13	1	-2.578763	2.773006	0.655796
14	1	-3.231853	1.337478	-0.201162
15	6	-0.637177	1.616856	2.070887
16	1	-0.237427	2.541542	1.631605
17	1	-1.220144	1.943115	2.946696
18	1	0.184683	0.984601	2.406761
19	6	-1.183313	-0.189145	-1.526013
20	1	-2.028351	0.331691	-1.985316
21	1	-0.730916	-0.786162	-2.326533
22	6	-0.195760	0.852036	-1.044772
23	6	1.131634	0.490056	-0.581404
24	6	-0.476298	2.211975	-1.249317
25	6	1.572140	-0.841733	-0.492049
26	6	2.049271	1.540882	-0.228495
27	6	0.426124	3.230765	-0.908162
28	1	-1.433111	2.484070	-1.684770
29	6	2.860397	-1.152423	-0.050710
30	6	3.346765	1.194847	0.230597
31	6	1.665818	2.894998	-0.386670
32	1	0.158086	4.269974	-1.067079

33	6	3.755233	-0.117863	0.325421
34	1	4.035310	1.990629	0.500278
35	1	2.375291	3.674387	-0.121180
36	1	4.755694	-0.347021	0.670673
37	6	-3.805166	-2.000932	-1.760342
38	1	-3.779673	-1.222617	-2.532531
39	1	-3.273492	-2.869025	-2.171215
40	1	-4.848266	-2.286809	-1.605625
41	8	3.167255	-2.465041	-0.017121
42	6	4.482891	-2.882627	0.374478
43	1	4.695283	-2.591949	1.408650
44	1	4.475608	-3.968786	0.295082
45	1	5.240760	-2.470294	-0.299509
46	1	0.940364	-1.668811	-0.789849
47	1	-1.111363	-2.071017	-0.445039

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0930611 hartrees (-558542.2968 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8265938 hartrees (-558375.0859 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8867459 hartrees (-558412.8319 kcal/mol)

TS $_{\mathbf{E2\text{-}C2}}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2603764 hartrees (-558647.288794764 kcal/mol)
Imaginary Frequencies: 1 (-234.9068 1/cm)
Zero-point correction = 0.403764 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.911813	-0.295190	-1.488132
2	6	2.850757	0.514550	-0.680562
3	6	1.788247	-0.107733	0.331086
4	6	2.161487	-1.528649	0.760196
5	6	2.310026	-2.368151	-0.272400
6	6	2.094864	-1.784885	-1.654342
7	1	1.187988	0.238648	-2.104441
8	1	2.584271	-3.411962	-0.163736
9	1	2.977200	-1.948332	-2.290892

10	1	1.240633	-2.237683	-2.170169
11	6	4.309493	0.085156	-0.530621
12	1	4.856907	0.365495	-1.435457
13	1	4.764044	0.624962	0.305160
14	1	4.447957	-0.981324	-0.362615
15	6	2.745902	2.022060	-0.912088
16	1	3.165375	2.572907	-0.065492
17	1	3.334079	2.286977	-1.795952
18	1	1.720784	2.361331	-1.067902
19	6	1.052908	0.864433	1.315110
20	1	1.780975	1.593086	1.677922
21	1	0.773463	0.238585	2.168491
22	6	-0.174410	1.579462	0.787252
23	6	-1.328728	0.836623	0.361795
24	6	-0.199859	2.962122	0.740480
25	6	-1.420685	-0.576873	0.451073
26	6	-2.448751	1.562595	-0.171993
27	6	-1.318744	3.673050	0.246453
28	1	0.663547	3.523144	1.088808
29	6	-2.549594	-1.258041	0.009722
30	6	-3.582171	0.833489	-0.616959
31	6	-2.414698	2.981637	-0.217811
32	1	-1.300975	4.757700	0.229487
33	6	-3.642498	-0.541305	-0.542867
34	1	-4.428065	1.383064	-1.020360
35	1	-3.274535	3.513738	-0.615032
36	1	-4.527966	-1.059657	-0.889356
37	6	2.339981	-1.875211	2.210380
38	1	3.055082	-1.202477	2.698153
39	1	1.399275	-1.808108	2.768591
40	1	2.710103	-2.897706	2.310522
41	8	-2.525176	-2.608045	0.153773
42	6	-3.690788	-3.371918	-0.175956
43	1	-3.925786	-3.296469	-1.243382
44	1	-3.440505	-4.403953	0.067930
45	1	-4.551916	-3.054046	0.421446
46	1	0.876124	-0.363817	-0.375293
47	1	-0.653946	-1.173066	0.934494

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0601792 hartrees (-558521.663 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.794978 hartrees (-558355.2466 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8559053 hartrees (-558393.4791 kcal/mol)

C2
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.3093959 hartrees (-558678.049021209 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.406539 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.631001	0.612667	-1.735391
2	6	-2.350731	-0.641080	-0.874125
3	6	-1.796624	-0.235049	0.479459
4	6	-2.256092	0.965842	1.111586
5	6	-3.073675	1.822245	0.402757
6	6	-3.464142	1.666889	-1.011988
7	1	-3.128738	0.300399	-2.658090
8	1	-3.477934	2.684927	0.931468
9	1	-4.541908	1.422647	-1.017617
10	1	-3.413607	2.645261	-1.508175
11	6	-3.690277	-1.398019	-0.552174
12	1	-4.140559	-1.697540	-1.503291
13	1	-3.503693	-2.305702	0.027215
14	1	-4.409100	-0.783614	-0.004681
15	6	-1.460661	-1.595986	-1.694480
16	1	-1.315327	-2.560023	-1.206690
17	1	-1.955293	-1.781139	-2.652778
18	1	-0.478724	-1.162855	-1.896809
19	6	-0.941004	-1.178498	1.273079
20	1	-1.551408	-2.087853	1.388053
21	1	-0.790810	-0.782868	2.278405
22	6	0.413660	-1.637735	0.713738
23	6	1.415753	-0.694650	0.312199
24	6	0.694762	-2.990585	0.695052
25	6	1.224801	0.707799	0.331265
26	6	2.685916	-1.203856	-0.132669
27	6	1.950098	-3.483468	0.268070
28	1	-0.061838	-3.702201	1.016604
29	6	2.217094	1.585333	-0.080651
30	6	3.679110	-0.278938	-0.547816
31	6	2.923418	-2.603486	-0.145913
32	1	2.133943	-4.552717	0.269230

33	6	3.465372	1.082073	-0.530075
34	1	4.636134	-0.663825	-0.888638
35	1	3.889386	-2.967969	-0.483717
36	1	4.251612	1.753297	-0.852520
37	6	-1.911965	1.310403	2.549680
38	1	-2.272476	0.550310	3.249784
39	1	-0.833367	1.417861	2.699772
40	1	-2.374679	2.259151	2.828772
41	8	1.909659	2.909393	-0.016862
42	6	2.906325	3.875733	-0.365803
43	1	3.202071	3.778758	-1.416276
44	1	2.438235	4.847335	-0.209564
45	1	3.785949	3.787063	0.280945
46	1	-1.670608	1.053919	-2.028038
47	1	0.304649	1.146440	0.696720

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.101875 hartrees (-558547.8276 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8333013 hartrees (-558379.2949 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.89553 hartrees (-558418.344 kcal/mol)

TS $_{C2\text{-}D2}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2956123 hartrees (-558669.399674373 kcal/mol)
Imaginary Frequencies: 1 (-234.6031 1/cm)
Zero-point correction = 0.407172 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.120263	-0.073149	-1.684817
2	6	-1.155948	-1.161317	-1.161325
3	6	-0.934980	-0.973181	0.357532
4	6	-2.134781	-0.631837	1.144914
5	6	-3.275013	-0.223333	0.527110
6	6	-3.455007	-0.049298	-0.941549
7	1	-2.283868	-0.232464	-2.755538
8	1	-4.147644	-0.033420	1.149831
9	1	-4.129658	-0.842084	-1.301130

10	1	-3.996583	0.885445	-1.134100
11	6	-1.803913	-2.572301	-1.351453
12	1	-2.110447	-2.675071	-2.396921
13	1	-1.089564	-3.373063	-1.143852
14	1	-2.682270	-2.726135	-0.720498
15	6	0.114349	-1.126804	-2.031212
16	1	0.852613	-1.876288	-1.739678
17	1	-0.170301	-1.334041	-3.067361
18	1	0.592037	-0.144106	-2.012547
19	6	0.112247	-1.883873	1.039924
20	1	-0.033219	-2.911844	0.690479
21	1	-0.062740	-1.901383	2.118531
22	6	1.521299	-1.409625	0.749834
23	6	1.587010	-0.029311	0.508768
24	6	2.662260	-2.180697	0.595487
25	6	0.375046	0.726085	0.724463
26	6	2.740507	0.553743	-0.068521
27	6	3.862726	-1.586318	0.136980
28	1	2.635230	-3.251266	0.779767
29	6	0.309094	2.045543	0.187724
30	6	2.615372	1.885290	-0.558905
31	6	3.899319	-0.250959	-0.224862
32	1	4.747107	-2.203340	0.016713
33	6	1.428260	2.595047	-0.487775
34	1	3.472683	2.348933	-1.040503
35	1	4.798824	0.179285	-0.655131
36	1	1.385434	3.596930	-0.896312
37	6	-2.126572	-0.747532	2.656374
38	1	-2.042908	-1.786988	2.992240
39	1	-1.299696	-0.195167	3.120647
40	1	-3.052330	-0.343338	3.070813
41	8	-0.807514	2.726252	0.456635
42	6	-0.929329	4.112429	0.076704
43	1	-0.886429	4.220094	-1.010863
44	1	-1.907248	4.422249	0.440996
45	1	-0.147530	4.709864	0.553967
46	1	-1.633128	0.902797	-1.582467
47	1	-0.098357	0.642779	1.697459

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0923695 hartrees (-558541.8628 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8244236 hartrees (-558373.7241 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8873451 hartrees (-558413.2079 kcal/mol)

D2
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.3073515 hartrees (-558676.766139765 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.408858 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.227726	-0.113935	-1.581804
2	6	-1.052350	-1.045067	-1.194449
3	6	-0.687428	-0.839116	0.340128
4	6	-1.947787	-0.791940	1.213854
5	6	-3.169596	-0.573758	0.697691
6	6	-3.486631	-0.365543	-0.751392
7	1	-2.444605	-0.257404	-2.646250
8	1	-4.016960	-0.562912	1.381642
9	1	-4.031914	-1.243506	-1.127331
10	1	-4.188729	0.471161	-0.858225
11	6	-1.499775	-2.510972	-1.442473
12	1	-1.998758	-2.574701	-2.414683
13	1	-0.652156	-3.200406	-1.481633
14	1	-2.198675	-2.873112	-0.684013
15	6	0.111729	-0.750898	-2.161989
16	1	0.973023	-1.404772	-2.005638
17	1	-0.231919	-0.911982	-3.189120
18	1	0.452971	0.289321	-2.104862
19	6	0.348517	-1.935398	0.839260
20	1	0.180699	-2.903446	0.367466
21	1	0.239471	-2.095613	1.916130
22	6	1.719722	-1.367107	0.558100
23	6	1.616250	0.006458	0.400396
24	6	2.971580	-1.959953	0.401619
25	6	0.230600	0.482167	0.635798
26	6	2.690443	0.814221	-0.006811
27	6	4.087850	-1.163024	0.055950
28	1	3.099844	-3.032202	0.521165
29	6	-0.000456	1.877834	0.174434
30	6	2.371552	2.159518	-0.341110
31	6	3.961075	0.201864	-0.165482
32	1	5.056094	-1.637103	-0.066870

33	6	1.077661	2.666986	-0.282102
34	1	3.164850	2.819163	-0.686367
35	1	4.816488	0.792483	-0.479274
36	1	0.908612	3.697403	-0.568224
37	6	-1.806188	-0.983233	2.710671
38	1	-1.580523	-2.021758	2.980327
39	1	-1.009668	-0.367964	3.152577
40	1	-2.735257	-0.711927	3.216843
41	8	-1.209905	2.344525	0.369632
42	6	-1.541532	3.735654	0.123280
43	1	-1.407575	3.972828	-0.934744
44	1	-2.590050	3.823785	0.399357
45	1	-0.927125	4.382779	0.753526
46	1	-1.924364	0.931474	-1.472391
47	1	0.120402	0.593683	1.732131

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.1092393 hartrees (-558552.4488 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8462327 hartrees (-558387.4095 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.9074548 hartrees (-558425.827 kcal/mol)

Table S4 (iii). Coordinates and Energies. **E2→F1** conversion
The coordinates below are those for the enantiomer of the structure presented in Figure S10 (iii).

TS $_{E2\text{-}F1}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2975642 hartrees (-558670.624511142 kcal/mol)
Imaginary Frequencies: 1 (-143.9420 1/cm)
Zero-point correction = 0.406847 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.494244	-0.637317	0.985720
2	6	-1.371575	0.870992	1.047236
3	6	-1.754618	-1.151516	-0.461865
4	6	-3.247324	-1.457471	-0.495807
5	6	-3.759062	-1.447468	0.743177
6	6	-2.729063	-1.155602	1.806113
7	1	-0.570109	-1.059347	1.385453
8	1	-4.789648	-1.687924	0.987690
9	1	-3.071147	-0.457619	2.578303
10	1	-2.438065	-2.071796	2.337241
11	6	-2.605932	1.707100	0.804066
12	1	-3.285347	1.533821	1.649740
13	1	-2.377505	2.773982	0.792143
14	1	-3.158362	1.430577	-0.093227
15	6	-0.445732	1.435128	2.079942
16	1	-0.132862	2.456449	1.839932
17	1	-1.006258	1.501061	3.025076
18	1	0.430468	0.809056	2.251832
19	6	-1.224987	-0.118177	-1.500167
20	1	-2.063303	0.427867	-1.942267
21	1	-0.725371	-0.626656	-2.332040
22	6	-0.271930	0.894460	-0.878424
23	6	1.091650	0.497944	-0.512353
24	6	-0.491928	2.275731	-1.131664
25	6	1.507733	-0.835728	-0.449971
26	6	2.056673	1.527201	-0.221395
27	6	0.450558	3.260435	-0.851112
28	1	-1.455371	2.572808	-1.533990
29	6	2.816854	-1.174286	-0.081294
30	6	3.372828	1.156921	0.165671
31	6	1.706953	2.883810	-0.381447
32	1	0.216140	4.306354	-1.017015

33	6	3.757305	-0.162254	0.243533
34	1	4.090129	1.940208	0.393371
35	1	2.452647	3.644394	-0.163770
36	1	4.768875	-0.415235	0.535041
37	6	-3.952558	-1.822691	-1.767547
38	1	-3.898010	-1.021320	-2.514824
39	1	-3.497183	-2.710661	-2.225300
40	1	-5.008041	-2.040609	-1.587264
41	8	3.092316	-2.488625	-0.065440
42	6	4.414264	-2.946268	0.263920
43	1	4.681317	-2.662332	1.286785
44	1	4.369386	-4.031297	0.184962
45	1	5.149343	-2.554985	-0.446228
46	1	0.844252	-1.651904	-0.704952
47	1	-1.219686	-2.101550	-0.601156

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.094627 hartrees (-558543.2794 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8287797 hartrees (-558376.4575 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8894347 hartrees (-558414.5192 kcal/mol)

F1
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.3029815 hartrees (-558674.023921065 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.408866 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.527546	-0.731729	0.940715
2	6	-1.218574	0.799064	0.952882
3	6	-1.788829	-1.132613	-0.538013
4	6	-3.291625	-1.371780	-0.603750
5	6	-3.820828	-1.389944	0.628499
6	6	-2.794668	-1.187857	1.716745
7	1	-0.647906	-1.242113	1.341886
8	1	-4.867954	-1.583638	0.843976
9	1	-3.115465	-0.490212	2.498196

10	1	-2.591157	-2.135659	2.234054
11	6	-2.488245	1.676660	0.920504
12	1	-3.106509	1.445744	1.790399
13	1	-2.238678	2.739011	0.989422
14	1	-3.108613	1.512218	0.037477
15	6	-0.373662	1.208838	2.163155
16	1	-0.063153	2.257773	2.109671
17	1	-0.975725	1.100059	3.071780
18	1	0.516114	0.585034	2.281192
19	6	-1.224950	0.013111	-1.425513
20	1	-2.044504	0.590576	-1.862749
21	1	-0.618098	-0.347971	-2.260252
22	6	-0.380932	0.956753	-0.506177
23	6	1.059918	0.516284	-0.338957
24	6	-0.496601	2.372954	-0.915133
25	6	1.443468	-0.811375	-0.288655
26	6	2.097805	1.514346	-0.219015
27	6	0.518342	3.287463	-0.850990
28	1	-1.477730	2.707635	-1.235139
29	6	2.789696	-1.186625	-0.069805
30	6	3.444176	1.117304	0.031233
31	6	1.803560	2.859862	-0.452061
32	1	0.349083	4.326989	-1.110094
33	6	3.799023	-0.207067	0.114090
34	1	4.202773	1.887366	0.137928
35	1	2.605106	3.590744	-0.371207
36	1	4.828141	-0.489004	0.295849
37	6	-3.994914	-1.636429	-1.901747
38	1	-3.879055	-0.806487	-2.610498
39	1	-3.585101	-2.528438	-2.393795
40	1	-5.065067	-1.797823	-1.749213
41	8	3.011107	-2.499366	-0.053248
42	6	4.340998	-3.020968	0.146742
43	1	4.725606	-2.723997	1.126499
44	1	4.229762	-4.102800	0.104905
45	1	5.008532	-2.683994	-0.651297
46	1	0.738100	-1.619612	-0.425556
47	1	-1.281033	-2.073973	-0.795938

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.1035357 hartrees (-558548.8697 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.839551 hartrees (-558383.2166 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8985877 hartrees (-558420.2628 kcal/mol)

Table S4 (iv). Coordinates and Energies. Path 3: **E3→D3**
The coordinates below are those for the enantiomer of the structure presented in Figure S10 (iv).

E3
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2981525 hartrees (-558670.993675275 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.405366 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.680727	0.616974	0.605092
2	6	2.576471	-0.110064	-0.800338
3	6	3.454418	-1.343827	-0.663738
4	6	4.086609	-1.373171	0.516467
5	6	3.811780	-0.176333	1.383947
6	1	2.990973	1.652694	0.456147
7	1	4.778614	-2.150968	0.826130
8	1	4.687972	0.477060	1.478783
9	1	3.525845	-0.446678	2.408502
10	6	1.126775	-0.415912	-1.249772
11	1	1.137565	-0.624839	-2.327657
12	1	0.800479	-1.342801	-0.774548
13	6	0.140401	0.697663	-0.959975
14	6	-1.229857	0.423206	-0.589235
15	6	0.503953	2.027316	-1.209976
16	6	-1.730397	-0.880947	-0.390234
17	6	-2.128925	1.532183	-0.397558
18	6	-0.384356	3.100474	-1.043189
19	1	1.511163	2.243607	-1.553539
20	6	-3.056363	-1.102535	-0.008155
21	6	-3.469472	1.272728	-0.003873
22	6	-1.682442	2.854177	-0.628017
23	1	-0.054688	4.113688	-1.248403
24	6	-3.936079	-0.007634	0.193858
25	1	-4.141532	2.114422	0.138033
26	1	-2.380183	3.675978	-0.491639
27	1	-4.965558	-0.168004	0.488607
28	6	3.594601	-2.326782	-1.787709
29	1	3.974228	-1.833419	-2.691734
30	1	2.632699	-2.780254	-2.055197
31	1	4.286108	-3.131223	-1.526430
32	8	-3.414420	-2.394084	0.138058

33	6	-4.765970	-2.727795	0.485439
34	1	-5.031089	-2.319244	1.466166
35	1	-4.792861	-3.815873	0.523818
36	1	-5.465366	-2.369787	-0.276931
37	1	-1.126758	-1.760170	-0.577991
38	6	1.441662	0.620011	1.422904
39	6	1.001340	1.868768	2.090748
40	1	1.189958	2.761916	1.493667
41	1	-0.046248	1.829168	2.401249
42	1	1.599812	1.962511	3.014400
43	6	0.837969	-0.649023	1.893946
44	1	0.741800	-0.625074	2.987797
45	1	-0.197842	-0.735397	1.524761
46	1	1.394458	-1.535374	1.588802
47	1	3.028746	0.563874	-1.541054

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0920925 hartrees (-558541.689 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8236614 hartrees (-558373.2458 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8837031 hartrees (-558410.9226 kcal/mol)

TS $_{E3\text{-}C3}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2558143 hartrees (-558644.426031393 kcal/mol)
Imaginary Frequencies: 1 (-265.3843 1/cm)
Zero-point correction = 0.403475 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.776490	0.141733	-1.419120
2	6	-2.181165	-0.206963	0.293117
3	6	-3.517192	-0.166892	1.037156
4	6	-4.545268	0.194314	0.258177
5	6	-4.226803	0.492690	-1.193661
6	1	-2.151180	0.767620	-2.056835
7	1	-5.569167	0.264478	0.609169
8	1	-4.436812	1.533287	-1.465219
9	1	-4.830573	-0.138762	-1.862838
10	6	-0.823209	-0.086263	1.049674

11	1	-1.091994	0.161023	2.081387
12	1	-0.372657	-1.077033	1.072294
13	6	0.150475	0.964555	0.530835
14	6	1.529626	0.651310	0.270943
15	6	-0.293742	2.267354	0.367747
16	6	2.099947	-0.630252	0.469757
17	6	2.383903	1.709549	-0.206310
18	6	0.551565	3.301461	-0.095165
19	1	-1.319801	2.528136	0.630286
20	6	3.438558	-0.878284	0.203888
21	6	3.747406	1.418087	-0.474527
22	6	1.867174	3.018231	-0.385460
23	1	0.162262	4.307955	-0.207366
24	6	4.275310	0.162011	-0.280460
25	1	4.387695	2.217714	-0.836109
26	1	2.532419	3.799256	-0.742678
27	1	5.321725	-0.019933	-0.491828
28	6	-3.598248	-0.515343	2.495364
29	1	-3.060850	0.207685	3.119301
30	1	-3.165518	-1.502330	2.696399
31	1	-4.639728	-0.525811	2.823570
32	8	3.866872	-2.145950	0.436016
33	6	5.245822	-2.470846	0.237213
34	1	5.537822	-2.338414	-0.810572
35	1	5.338759	-3.522016	0.508706
36	1	5.891438	-1.868493	0.885772
37	1	1.523390	-1.460517	0.859199
38	6	-2.222794	-1.159134	-0.985728
39	6	-0.859344	-1.491558	-1.594993
40	1	-0.191947	-0.629229	-1.648861
41	1	-0.357992	-2.274365	-1.020459
42	1	-1.007164	-1.875546	-2.609140
43	6	-3.118801	-2.394639	-0.922213
44	1	-3.241115	-2.796432	-1.932480
45	1	-2.631159	-3.167658	-0.321384
46	1	-4.106972	-2.210675	-0.503389
47	1	-2.216235	0.860932	-0.202460

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0549078 hartrees (-558518.3552 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.788893 hartrees (-558351.4282 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8490828 hartrees (-558389.198 kcal/mol)

C3

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.3154021 hartrees (-558681.817971771 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.407196 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.343916	-0.709620	-1.666435
2	6	-2.073617	-0.334291	0.470794
3	6	-3.227056	0.284727	1.047595
4	6	-4.440197	0.165775	0.403072
5	6	-4.651588	-0.476887	-0.912844
6	1	-3.494981	-1.425644	-2.479760
7	1	-5.323685	0.553462	0.909167
8	1	-5.359075	0.123939	-1.499268
9	1	-5.193578	-1.420789	-0.725776
10	6	-0.757857	-0.215094	1.166900
11	1	-0.869993	0.025216	2.226028
12	1	-0.244412	-1.175673	1.105040
13	6	0.089041	0.853278	0.454230
14	6	1.481735	0.613936	0.177004
15	6	-0.485175	2.065963	0.093089
16	6	2.163414	-0.571147	0.533077
17	6	2.227336	1.659499	-0.475057
18	6	0.256878	3.081567	-0.546704
19	1	-1.529306	2.260230	0.314913
20	6	3.519959	-0.737351	0.271308
21	6	3.606771	1.454565	-0.733798
22	6	1.588788	2.874506	-0.831935
23	1	-0.224884	4.019556	-0.801703
24	6	4.251176	0.289994	-0.376854
25	1	4.167396	2.248899	-1.218370
26	1	2.172268	3.646960	-1.324965
27	1	5.306471	0.172189	-0.589174
28	6	-3.162717	0.991917	2.389540
29	1	-2.404464	1.779399	2.406031
30	1	-2.930573	0.293232	3.200470
31	1	-4.123528	1.456086	2.621369
32	8	4.057459	-1.915267	0.668397
33	6	5.452230	-2.162682	0.458589
34	1	5.697648	-2.158841	-0.609020
35	1	5.635515	-3.154646	0.869959

36	1	6.066967	-1.427795	0.989461
37	1	1.665482	-1.395132	1.030646
38	6	-2.199173	-1.213852	-0.758898
39	6	-0.917247	-1.313735	-1.608946
40	1	-0.626038	-0.340016	-2.010183
41	1	-0.068617	-1.724231	-1.057796
42	1	-1.111293	-1.985033	-2.450734
43	6	-2.521895	-2.644713	-0.200753
44	1	-2.637153	-3.322810	-1.051957
45	1	-1.704604	-3.023285	0.418968
46	1	-3.439521	-2.673655	0.392165
47	1	-3.027059	0.232380	-2.130519

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.1074366 hartrees (-558551.3176 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8380938 hartrees (-558382.3022 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8993511 hartrees (-558420.7418 kcal/mol)

C4
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.3111114 hartrees (-558679.125514614 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.406825 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.753079	-0.033637	-1.158463
2	6	-1.894653	0.107630	0.539915
3	6	-2.318985	-1.159781	1.049853
4	6	-3.102347	-1.964404	0.244328
5	6	-3.715397	-1.552148	-1.033549
6	1	-4.026197	0.263107	-2.174945
7	1	-3.271185	-2.990308	0.571206
8	1	-4.714851	-1.999099	-1.112722
9	1	-3.140452	-2.028946	-1.847248
10	6	-0.954794	0.927109	1.379307
11	1	-1.587893	1.758064	1.735518
12	1	-0.676158	0.364235	2.270987
13	6	0.308203	1.548295	0.778306

14	6	1.386871	0.709792	0.337731
15	6	0.465460	2.921724	0.784183
16	6	1.324702	-0.703726	0.339270
17	6	2.592386	1.341790	-0.125792
18	6	1.656348	3.536874	0.330299
19	1	-0.337256	3.553777	1.155653
20	6	2.387590	-1.478824	-0.101013
21	6	3.660027	0.519776	-0.571842
22	6	2.696465	2.757967	-0.122000
23	1	1.741089	4.618302	0.348667
24	6	3.574827	-0.855399	-0.566193
25	1	4.569883	0.996611	-0.925361
26	1	3.616164	3.216642	-0.474009
27	1	4.413674	-1.446383	-0.912316
28	6	-1.875814	-1.692647	2.399857
29	1	-2.182903	-1.026608	3.212020
30	1	-0.791637	-1.823918	2.466952
31	1	-2.336000	-2.664985	2.587876
32	8	2.205365	-2.826022	-0.054092
33	6	3.274670	-3.691830	-0.448856
34	1	3.532752	-3.547416	-1.503799
35	1	2.898821	-4.704288	-0.303403
36	1	4.159700	-3.538760	0.178157
37	1	0.447488	-1.229248	0.697089
38	6	-2.408832	0.634649	-0.787455
39	6	-2.639176	2.165153	-0.757237
40	1	-3.328746	2.451881	0.043883
41	1	-1.710345	2.723112	-0.647231
42	1	-3.095370	2.462555	-1.705939
43	6	-1.336335	0.313435	-1.884045
44	1	-1.741727	0.639689	-2.846711
45	1	-0.407259	0.850674	-1.699047
46	1	-1.105744	-0.753131	-1.947213
47	1	-4.537604	0.351835	-0.494943

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.1038352 hartrees (-558549.0577 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8364235 hartrees (-558381.2541 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8982536 hartrees (-558420.0531 kcal/mol)

TS $_{C4\text{-}D3}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):

HF = -890.2904828 hartrees (-558666.180861828 kcal/mol)
Imaginary Frequencies: 1 (-205.6426 1/cm)
Zero-point correction = 0.406932 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.773741	-1.566559	-1.225165
2	6	1.161380	-0.657173	0.394934
3	6	2.270885	-0.009625	1.123132
4	6	3.524511	-0.040010	0.597554
5	6	3.905340	-0.692141	-0.688441
6	1	2.938365	-1.817460	-2.278196
7	1	4.330645	0.394069	1.186367
8	1	4.820984	-1.277826	-0.543218
9	1	4.176164	0.089503	-1.415131
10	6	0.346871	-1.698504	1.181933
11	1	0.742274	-2.688605	0.919705
12	1	0.531107	-1.571913	2.252990
13	6	-1.132581	-1.611657	0.868963
14	6	-1.544169	-0.316436	0.507397
15	6	-2.035418	-2.657597	0.794030
16	6	-0.588909	0.750420	0.652100
17	6	-2.809177	-0.100687	-0.094761
18	6	-3.343649	-2.433903	0.299503
19	1	-1.736196	-3.665640	1.068084
20	6	-0.878959	2.005982	0.054244
21	6	-3.048856	1.184539	-0.660086
22	6	-3.718308	-1.188657	-0.171510
23	1	-4.037987	-3.265700	0.242049
24	6	-2.105990	2.197503	-0.630515
25	1	-3.997948	1.368149	-1.157346
26	1	-4.696310	-1.040098	-0.619653
27	1	-2.337360	3.151340	-1.087941
28	6	2.075737	0.612455	2.492468
29	1	1.441682	0.018520	3.156960
30	1	1.625660	1.609649	2.406136
31	1	3.037290	0.736651	2.994708
32	8	0.017726	2.974438	0.269734
33	6	-0.240723	4.320261	-0.177303
34	1	-0.316245	4.357003	-1.267850
35	1	0.619577	4.900354	0.152170
36	1	-1.152065	4.710134	0.284959
37	1	-0.058645	0.835843	1.592452

38	6	1.376864	-0.867054	-1.118260
39	6	0.349159	-1.781783	-1.810200
40	1	0.300495	-2.779285	-1.364615
41	1	-0.655500	-1.355485	-1.807735
42	1	0.647735	-1.908651	-2.855363
43	6	1.426872	0.470949	-1.894754
44	1	1.864247	0.302301	-2.883639
45	1	0.416620	0.858614	-2.043687
46	1	2.013921	1.237858	-1.385199
47	1	2.751966	-2.516776	-0.676468

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0867056 hartrees (-558538.3087 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.818487 hartrees (-558369.9988 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8821463 hartrees (-558409.9456 kcal/mol)

D3
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.3090691 hartrees (-558677.843950941 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.409262 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.352654	-1.856456	-1.221070
2	6	0.815534	-0.601459	0.353709
3	6	2.061273	-0.350157	1.216038
4	6	3.286340	-0.731739	0.816235
5	6	3.612156	-1.387037	-0.491638
6	1	2.579987	-2.070052	-2.271470
7	1	4.122513	-0.556007	1.491026
8	1	4.288052	-2.233867	-0.320477
9	1	4.185190	-0.684064	-1.114358
10	6	0.007785	-1.845641	0.931211
11	1	0.342655	-2.783222	0.483500
12	1	0.190393	-1.935219	2.008719
13	6	-1.451327	-1.548125	0.664481
14	6	-1.591904	-0.193461	0.403642
15	6	-2.584296	-2.355792	0.583164

16	6	-0.312496	0.534322	0.586077
17	6	-2.793937	0.388616	-0.029659
18	6	-3.825259	-1.789586	0.207886
19	1	-2.525450	-3.422156	0.782937
20	6	-0.331841	1.921876	0.051703
21	6	-2.715445	1.746106	-0.450698
22	6	-3.940130	-0.443818	-0.115462
23	1	-4.698326	-2.430695	0.143810
24	6	-1.533680	2.480550	-0.434940
25	1	-3.614191	2.233700	-0.822654
26	1	-4.889459	-0.034948	-0.447992
27	1	-1.553183	3.506708	-0.779950
28	6	1.889584	0.272795	2.585737
29	1	1.135301	-0.238940	3.197598
30	1	1.602136	1.331573	2.527489
31	1	2.828524	0.229895	3.142348
32	8	0.775711	2.601002	0.222648
33	6	0.869466	4.007837	-0.121424
34	1	0.711101	4.140362	-1.194144
35	1	1.884463	4.292740	0.146909
36	1	0.146273	4.584980	0.459424
37	1	-0.239869	0.735769	1.672204
38	6	1.200653	-0.816373	-1.172761
39	6	0.047372	-1.357231	-2.044668
40	1	-0.313319	-2.336043	-1.717757
41	1	-0.808399	-0.675905	-2.084669
42	1	0.408431	-1.475020	-3.071525
43	6	1.695129	0.487768	-1.839374
44	1	2.168234	0.247913	-2.797038
45	1	0.862740	1.161640	-2.069405
46	1	2.420054	1.029113	-1.228706
47	1	2.014673	-2.804253	-0.786159

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.1111592 hartrees (-558553.6535 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8487782 hartrees (-558389.0068 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.9103238 hartrees (-558427.6273 kcal/mol)

Table S4 (v). Coordinates and Energies. Path 4: **E4→D4**

The coordinates below are those for the enantiomer of the structure presented in Figure S10 (V).

E4

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2877709 hartrees (-558664.479117459 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.403506 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.400785	-0.558202	0.362158
2	6	-2.035947	0.303271	0.687256
3	6	-1.467144	-0.536122	1.825348
4	6	-1.979334	-1.774263	1.834041
5	6	-3.032528	-1.998557	0.776910
6	1	-4.099313	-0.136773	1.097465
7	1	-1.688314	-2.553300	2.531197
8	1	-3.916344	-2.521224	1.161221
9	1	-2.647906	-2.608417	-0.051466
10	6	-1.129287	0.429698	-0.563294
11	1	-0.861498	-0.568300	-0.916181
12	1	-1.726052	0.893959	-1.365066
13	6	0.099293	1.276166	-0.333894
14	6	1.428223	0.720777	-0.301590
15	6	-0.065852	2.647807	-0.173185
16	6	1.704033	-0.657533	-0.449473
17	6	2.537537	1.619100	-0.106670
18	6	1.023085	3.517805	0.027012
19	1	-1.067226	3.070531	-0.220055
20	6	3.006575	-1.145538	-0.423618
21	6	3.853680	1.087342	-0.084071
22	6	2.305862	3.006690	0.058376
23	1	0.850915	4.582701	0.143646
24	6	4.098460	-0.259527	-0.239487
25	1	4.687181	1.769082	0.059800
26	1	3.156467	3.666418	0.205542
27	1	5.116738	-0.627360	-0.218718
28	6	-0.470081	0.028510	2.796892
29	1	-0.870955	0.923655	3.287748
30	1	0.459837	0.324501	2.302633
31	1	-0.231656	-0.706304	3.570009
32	8	3.138015	-2.486703	-0.580193

33	6	4.443995	-3.071385	-0.580543
34	1	5.053289	-2.676659	-1.400979
35	1	4.284528	-4.139082	-0.728140
36	1	4.951358	-2.907171	0.376532
37	6	-3.926837	-0.267662	-0.960976
38	6	-4.697656	0.977439	-1.180258
39	1	-4.678153	1.658812	-0.328343
40	1	-4.374889	1.491169	-2.093842
41	1	-5.747701	0.694035	-1.369489
42	6	-3.791581	-1.209401	-2.092864
43	1	-4.552675	-1.998252	-1.954881
44	1	-3.972841	-0.741335	-3.062192
45	1	-2.831472	-1.733970	-2.087492
46	1	-2.333594	1.304667	1.016095
47	1	0.913884	-1.386241	-0.581906

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0784368 hartrees (-558533.1198 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8058285 hartrees (-558362.0554 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8665476 hartrees (-558400.1573 kcal/mol)

TS $_{\mathbf{E4\text{-}C5}}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2562821 hartrees (-558644.719580571 kcal/mol)
Imaginary Frequencies: 1 (-276.0604 1/cm)
Zero-point correction = 0.403139 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.870263	0.452060	-0.290308
2	6	-2.119240	-0.167990	-0.138644
3	6	-2.060376	-0.347872	1.378859
4	6	-3.157231	0.087970	2.011223
5	6	-4.255903	0.673031	1.147059
6	1	-4.081180	1.222763	-1.032503
7	1	-3.297849	0.022335	3.084580
8	1	-4.441077	1.732633	1.356176
9	1	-5.206449	0.143854	1.318196

10	6	-0.825976	-0.156561	-0.991360
11	1	-0.413675	-1.161473	-0.872510
12	1	-1.088128	-0.063853	-2.047182
13	6	0.183687	0.918545	-0.614392
14	6	1.556798	0.594079	-0.335707
15	6	-0.216214	2.243127	-0.599726
16	6	2.079508	-0.722893	-0.366879
17	6	2.454748	1.674331	-0.014672
18	6	0.669438	3.299080	-0.287005
19	1	-1.242925	2.505815	-0.856723
20	6	3.413367	-0.981296	-0.086984
21	6	3.812404	1.372539	0.269951
22	6	1.983004	3.011906	0.006530
23	1	0.311185	4.323131	-0.285942
24	6	4.294005	0.083418	0.240042
25	1	4.485366	2.189686	0.513935
26	1	2.679415	3.809079	0.250842
27	1	5.337023	-0.106271	0.461201
28	6	-0.870159	-0.992321	2.025425
29	1	0.050643	-0.438207	1.822826
30	1	-0.722787	-2.012939	1.651377
31	1	-1.011277	-1.045411	3.106900
32	8	3.792919	-2.284257	-0.148925
33	6	5.160621	-2.631114	0.084432
34	1	5.821712	-2.147417	-0.643157
35	1	5.212027	-3.712182	-0.042422
36	1	5.468697	-2.369585	1.103007
37	6	-3.403633	-0.861758	-0.784602
38	6	-3.402374	-0.976892	-2.312618
39	1	-3.122174	-0.046846	-2.815169
40	1	-2.723980	-1.766605	-2.645715
41	1	-4.408772	-1.243916	-2.649421
42	6	-3.907236	-2.151833	-0.137887
43	1	-4.920797	-2.358707	-0.493692
44	1	-3.274431	-2.987069	-0.451108
45	1	-3.923360	-2.125280	0.950508
46	1	-2.412012	0.971764	-0.182645
47	1	1.467601	-1.578571	-0.626379

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0547798 hartrees (-558518.2749 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.788102 hartrees (-558350.9319 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):

HF = -889.848461 hartrees (-558388.8077 kcal/mol)

C5

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):

HF = -890.3153434 hartrees (-558681.781136934 kcal/mol)

Imaginary Frequencies: none found

Zero-point correction = 0.406531 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-4.507831	0.184581	-0.048118
2	6	-2.050399	-0.404124	-0.089167
3	6	-2.096289	-0.645004	1.317185
4	6	-3.328855	-0.788884	1.921437
5	6	-4.638260	-0.579914	1.265985
6	1	-3.344147	-1.120753	2.958910
7	1	-5.316032	-0.072597	1.964905
8	1	-5.094127	-1.575791	1.125363
9	6	-0.727910	-0.441578	-0.788286
10	1	-0.247274	-1.382363	-0.495690
11	1	-0.843865	-0.480737	-1.873021
12	6	0.178824	0.720175	-0.380857
13	6	1.590152	0.515393	-0.188020
14	6	-0.358739	1.991270	-0.227124
15	6	2.231317	-0.734540	-0.341323
16	6	2.394735	1.657877	0.160312
17	6	0.438155	3.101647	0.122458
18	1	-1.418777	2.151373	-0.395944
19	6	3.605785	-0.871379	-0.175782
20	6	3.792079	1.481574	0.329578
21	6	1.792188	2.932306	0.316462
22	1	-0.017097	4.081385	0.221607
23	6	4.397046	0.254139	0.168737
24	1	4.397535	2.346730	0.584577
25	1	2.419846	3.778964	0.580023
26	1	5.467425	0.160203	0.303157
27	6	-0.844648	-0.869153	2.138509
28	1	-0.241340	0.040369	2.198589
29	1	-0.208302	-1.652002	1.714191
30	1	-1.106621	-1.170410	3.154757
31	8	4.102439	-2.118298	-0.359688
32	6	5.509937	-2.344949	-0.227487
33	1	6.074774	-1.752421	-0.955304
34	1	5.653282	-3.405228	-0.432736

35	1	5.852226	-2.119900	0.788537
36	6	-3.319279	-0.287122	-0.913148
37	6	-3.199920	0.675175	-2.119150
38	1	-3.005392	1.703578	-1.803757
39	1	-2.428480	0.380423	-2.833030
40	1	-4.153784	0.672996	-2.654638
41	6	-3.564028	-1.732768	-1.468755
42	1	-4.466014	-1.711421	-2.088354
43	1	-2.734884	-2.066517	-2.098328
44	1	-3.706734	-2.468560	-0.672943
45	1	1.684750	-1.633785	-0.601707
46	1	-5.430624	0.105240	-0.630355
47	1	-4.370212	1.249268	0.178019

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.1070952 hartrees (-558551.1033 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8370249 hartrees (-558381.6315 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.898307 hartrees (-558420.0867 kcal/mol)

C6
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.3105636 hartrees (-558678.781764636 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.406260 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.018170	0.702426	0.188033
2	6	1.837898	-0.571937	-0.046867
3	6	1.720666	-0.528731	1.371900
4	6	2.401948	0.477629	2.032707
5	6	3.420969	1.360813	1.426685
6	1	4.675875	1.397153	-0.341536
7	1	2.154219	0.639529	3.081991
8	1	4.186801	1.593151	2.176959
9	1	2.948269	2.333364	1.204890
10	6	0.911838	-1.391109	-0.896137
11	1	0.932900	-0.989524	-1.915247

12	1	1.445598	-2.355813	-0.983267
13	6	-0.523909	-1.689377	-0.496388
14	6	-1.483993	-0.640856	-0.289015
15	6	-0.932334	-3.010013	-0.435059
16	6	-1.164826	0.735138	-0.362546
17	6	-2.842655	-1.011059	0.006431
18	6	-2.269809	-3.367182	-0.148212
19	1	-0.209840	-3.803235	-0.613291
20	6	-2.122311	1.717425	-0.155968
21	6	-3.797496	0.018268	0.215151
22	6	-3.205268	-2.381738	0.074347
23	1	-2.549387	-4.414750	-0.109688
24	6	-3.461334	1.352153	0.140440
25	1	-4.823507	-0.262083	0.436148
26	1	-4.236681	-2.640486	0.296605
27	1	-4.220659	2.107001	0.302506
28	6	0.825332	-1.446766	2.178463
29	1	0.913170	-2.483345	1.847794
30	1	-0.228499	-1.167985	2.107580
31	1	1.121674	-1.406939	3.229834
32	8	-1.689830	3.004025	-0.253274
33	6	-2.633441	4.071715	-0.116872
34	1	-3.415675	4.007730	-0.880982
35	1	-2.060650	4.987522	-0.260931
36	1	-3.084408	4.077778	0.881641
37	6	2.937376	0.184599	-0.784920
38	6	3.634788	-0.753316	-1.810998
39	1	4.022976	-1.656641	-1.330162
40	1	2.983270	-1.045838	-2.636470
41	1	4.483852	-0.213365	-2.240297
42	6	2.309421	1.384209	-1.563426
43	1	3.109345	1.881412	-2.119567
44	1	1.555992	1.058540	-2.283813
45	1	1.849258	2.122374	-0.901205
46	1	4.641899	-0.139919	0.512079
47	1	-0.163339	1.068424	-0.601882

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.103294 hartrees (-558548.718 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8354026 hartrees (-558380.6135 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8972783 hartrees (-558419.4411 kcal/mol)

TS $_{C6\text{-}D4}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2879297 hartrees (-558664.578766047 kcal/mol)
Imaginary Frequencies: 1 (-233.3395 1/cm)
Zero-point correction = 0.407138 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.540554	-1.028498	-0.236678
2	6	1.105943	-0.703496	-0.100390
3	6	1.183157	-0.745899	1.376803
4	6	2.403687	-0.780664	1.972833
5	6	3.718602	-0.799784	1.264055
6	1	4.451386	-0.766335	-0.785754
7	1	2.431888	-0.871081	3.057407
8	1	4.355890	-1.575450	1.705690
9	1	4.243669	0.147972	1.457148
10	6	0.339002	-1.853658	-0.788456
11	1	0.599265	-1.879114	-1.848565
12	1	0.687268	-2.798718	-0.353334
13	6	-1.155456	-1.715569	-0.630048
14	6	-1.577086	-0.387704	-0.462894
15	6	-2.077614	-2.747640	-0.551316
16	6	-0.576812	0.653058	-0.584800
17	6	-2.903734	-0.113053	-0.043470
18	6	-3.431180	-2.471481	-0.250914
19	1	-1.759781	-3.778567	-0.681293
20	6	-0.928077	1.954545	-0.105967
21	6	-3.189633	1.211792	0.388318
22	6	-3.836591	-1.179366	0.030959
23	1	-4.141481	-3.289429	-0.191050
24	6	-2.226831	2.202406	0.409086
25	1	-4.188805	1.442454	0.749077
26	1	-4.857761	-0.975795	0.339322
27	1	-2.490318	3.188977	0.768163
28	6	-0.051457	-0.891404	2.238502
29	1	-0.622906	-1.794735	2.004851
30	1	-0.727269	-0.039273	2.113377
31	1	0.232910	-0.942572	3.291652
32	8	-0.022250	2.918926	-0.269046
33	6	-0.333430	4.290575	0.050326
34	1	-1.179155	4.641988	-0.547252

35	1	0.562895	4.851441	-0.208842
36	1	-0.542309	4.399446	1.118141
37	6	2.370029	-0.171360	-0.818741
38	6	2.369873	-0.350786	-2.350506
39	1	2.420589	-1.398653	-2.660179
40	1	1.499936	0.107476	-2.835185
41	1	3.254473	0.145658	-2.759936
42	6	2.652388	1.319998	-0.520926
43	1	3.689767	1.548832	-0.784226
44	1	2.009089	1.965120	-1.120265
45	1	2.498673	1.582951	0.527153
46	1	3.353501	-2.092609	-0.428235
47	1	0.024581	0.676526	-1.490153

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0844818 hartrees (-558536.9132 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8163918 hartrees (-558368.684 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8800655 hartrees (-558408.6399 kcal/mol)

D4
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.3092784 hartrees (-558677.975288784 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.408866 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.122954	-1.557879	-0.332695
2	6	0.807366	-0.609121	0.024500
3	6	1.283528	-0.210798	1.427052
4	6	2.564692	-0.362714	1.805214
5	6	3.666603	-0.904980	0.941942
6	1	3.932813	-1.717937	-1.053357
7	1	2.831147	-0.102775	2.828727
8	1	4.251185	-1.632966	1.517994
9	1	4.374119	-0.099011	0.698153
10	6	0.034184	-2.002779	0.148560
11	1	0.352594	-2.702174	-0.626895

12	1	0.261811	-2.480196	1.106622
13	6	-1.436753	-1.699392	0.029843
14	6	-1.630084	-0.360021	-0.254916
15	6	-2.561670	-2.507698	0.227040
16	6	-0.352814	0.366928	-0.504242
17	6	-2.901896	0.241093	-0.255356
18	6	-3.853493	-1.949274	0.146032
19	1	-2.450897	-3.562602	0.462497
20	6	-0.488535	1.832676	-0.225449
21	6	-2.925719	1.664945	-0.285697
22	6	-4.035486	-0.587738	-0.073136
23	1	-4.717562	-2.588498	0.294427
24	6	-1.770491	2.432536	-0.235175
25	1	-3.885238	2.177518	-0.281100
26	1	-5.032360	-0.157159	-0.074380
27	1	-1.860638	3.509662	-0.174446
28	6	0.242923	0.215851	2.437421
29	1	-0.503218	-0.569133	2.612822
30	1	-0.316503	1.110880	2.132180
31	1	0.709375	0.443214	3.399041
32	8	0.620097	2.509645	-0.109952
33	6	0.632155	3.956718	0.023403
34	1	0.193200	4.416761	-0.864636
35	1	1.685115	4.217475	0.103952
36	1	0.097210	4.251420	0.928758
37	6	2.013232	-0.711472	-1.002480
38	6	1.616954	-1.388918	-2.334397
39	1	1.432465	-2.462051	-2.236895
40	1	0.730230	-0.940963	-2.801352
41	1	2.436224	-1.276172	-3.050992
42	6	2.597527	0.673708	-1.362296
43	1	3.522201	0.535421	-1.931924
44	1	1.918857	1.249560	-2.000655
45	1	2.826186	1.276281	-0.482803
46	1	2.726467	-2.551800	-0.090145
47	1	-0.226614	0.388058	-1.606984

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.1110984 hartrees (-558553.6154 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8483977 hartrees (-558388.7681 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.9098311 hartrees (-558427.3181 kcal/mol)

Table S4 (vi). Coordinates and Energies. *si→re* Facial 1,3-hydride shift
The coordinates below are those for the enantiomer of the structure presented in Figure S10 (vi).

Top
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2468963 hartrees (-558638.829897213 kcal/mol)
Imaginary Frequencies: 2 (-301.2649 1/cm) (-7.0672 1/cm)
Zero-point correction = 0.403220 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.272693	-0.751417	0.958059
2	6	-1.875218	-0.309269	1.201997
3	6	-1.977736	-0.447861	-0.382095
4	6	-2.651998	0.764915	-1.054410
5	6	-3.840489	1.086599	-0.524750
6	6	-4.355964	0.225526	0.605889
7	1	-3.521794	-1.781586	1.216734
8	1	-4.441284	1.917930	-0.877586
9	1	-4.554841	0.836006	1.500931
10	1	-5.295071	-0.277429	0.349794
11	6	-1.633552	1.078328	1.794810
12	1	-1.926777	1.069210	2.849244
13	1	-0.568186	1.311530	1.746579
14	1	-2.178692	1.876609	1.292088
15	6	-1.059506	-1.376433	1.939795
16	1	0.002758	-1.135511	1.936841
17	1	-1.396692	-1.405829	2.981319
18	1	-1.180506	-2.375749	1.514431
19	6	-0.976120	-1.343687	-1.217177
20	1	-0.913092	-0.802463	-2.168087
21	1	-1.470484	-2.286279	-1.464486
22	6	0.424709	-1.675192	-0.741519
23	6	1.393603	-0.685088	-0.361071
24	6	0.783082	-3.013401	-0.717955
25	6	1.137019	0.704994	-0.380395
26	6	2.702903	-1.127329	0.038652
27	6	2.074246	-3.442987	-0.333797
28	1	0.053350	-3.765404	-1.009531
29	6	2.105168	1.632922	-0.023522
30	6	3.669107	-0.154020	0.403705
31	6	3.014007	-2.512849	0.046398
32	1	2.312235	-4.501483	-0.339389

33	6	3.393092	1.195797	0.379020
34	1	4.657355	-0.490658	0.704098
35	1	4.009601	-2.824848	0.349164
36	1	4.160396	1.906819	0.659231
37	6	-2.060818	1.464886	-2.248453
38	1	-1.059626	1.860532	-2.056245
39	1	-1.988084	0.798167	-3.115009
40	1	-2.702274	2.301256	-2.534467
41	8	1.730172	2.939904	-0.085415
42	6	2.694784	3.958303	0.199810
43	1	3.544789	3.900281	-0.488671
44	1	2.173062	4.903733	0.053346
45	1	3.046354	3.892911	1.235466
46	1	-2.906979	-1.174057	-0.457357
47	1	0.177342	1.090662	-0.693067

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0455198 hartrees (-558512.4641 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.7804554 hartrees (-558346.1335 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8424394 hartrees (-558385.0292 kcal/mol)

bottom
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.2490992 hartrees (-558640.212238992 kcal/mol)
Imaginary Frequencies: 1 (-292.5912 1/cm)
Zero-point correction = 0.404061 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.672716	0.419144	-0.551633
2	6	2.385661	1.161006	-0.577130
3	6	1.974515	-0.365228	-0.337035
4	6	2.111804	-0.772531	1.142858
5	6	3.331236	-0.535069	1.648995
6	6	4.367369	0.080058	0.735441
7	1	4.184911	0.279998	-1.504680
8	1	3.586841	-0.738480	2.683285
9	1	4.750897	1.018269	1.165826
10	1	5.232855	-0.571890	0.572401

11	6	2.082805	2.173945	0.527661
12	1	2.704549	3.061831	0.377510
13	1	1.038473	2.488438	0.464238
14	1	2.262226	1.794550	1.532601
15	6	2.083294	1.746951	-1.961420
16	1	1.032700	2.027185	-2.063478
17	1	2.674221	2.659580	-2.087489
18	1	2.342097	1.071770	-2.782021
19	6	0.992512	-1.050663	-1.381321
20	1	1.516958	-1.889480	-1.844925
21	1	0.807335	-0.325097	-2.174430
22	6	-0.324140	-1.586940	-0.853764
23	6	-1.381978	-0.726523	-0.404607
24	6	-0.515505	-2.958989	-0.848597
25	6	-1.287827	0.683556	-0.411295
26	6	-2.601430	-1.326930	0.062991
27	6	-1.721883	-3.544564	-0.400949
28	1	0.281009	-3.610449	-1.200240
29	6	-2.328282	1.485647	0.033461
30	6	-3.647759	-0.479127	0.511996
31	6	-2.741494	-2.739725	0.056336
32	1	-1.835218	-4.623405	-0.420778
33	6	-3.527856	0.893776	0.507229
34	1	-4.569689	-0.932811	0.864709
35	1	-3.671598	-3.176169	0.409621
36	1	-4.349848	1.505982	0.856852
37	6	0.984345	-1.344229	1.956087
38	1	0.112898	-0.683118	1.947568
39	1	0.654463	-2.314250	1.577798
40	1	1.314849	-1.471014	2.989594
41	8	-2.110935	2.828222	-0.019741
42	6	-3.158678	3.723919	0.366570
43	1	-3.420830	3.595252	1.422512
44	1	-2.757968	4.725490	0.212303
45	1	-4.046593	3.586601	-0.259930
46	1	2.949851	-0.908837	-0.723978
47	1	-0.404456	1.179373	-0.788189

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -890.0476676 hartrees (-558513.8119 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.7823053 hartrees (-558347.2944 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -889.8442252 hartrees (-558386.1498 kcal/mol)

Table S4 (vii). Coordinates and Energies. Path 1: **A1'→D1'**
The coordinates below are those for the enantiomer of the structure presented in the Figure S10 (vii).

A1'
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.5178867 hartrees (-605872.129083117 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.407447 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.309368	1.547586	-1.242974
2	6	1.837770	2.766180	-0.917086
3	6	1.997742	-0.659942	0.919383
4	6	3.298871	-1.034415	0.513858
5	6	4.025616	-0.216913	-0.335048
6	6	3.717546	1.043991	-1.076119
7	1	1.639699	0.867694	-1.770144
8	1	5.058851	-0.530113	-0.489974
9	1	4.374383	1.810673	-0.636016
10	1	4.162280	0.891253	-2.075862
11	6	2.625715	3.843956	-0.214828
12	1	2.723898	4.724025	-0.862366
13	1	2.094434	4.179233	0.684343
14	1	3.629474	3.538242	0.087166
15	6	0.421319	3.154759	-1.266234
16	1	-0.143092	3.423707	-0.364469
17	1	0.415695	4.039606	-1.914911
18	1	-0.111123	2.351246	-1.781947
19	6	1.110158	-1.413480	1.827912
20	1	0.648454	-0.792616	2.599297
21	1	1.582019	-2.275359	2.298754
22	6	0.109410	-1.827796	0.752568
23	6	-1.055285	-1.024925	0.466577
24	6	0.343732	-3.002586	0.031937
25	6	-1.354306	0.169830	1.145258
26	6	-1.954277	-1.507537	-0.549095
27	6	-0.549396	-3.454250	-0.947186
28	1	1.221489	-3.598747	0.261973
29	6	-2.518295	0.881955	0.848521
30	6	-3.133698	-0.747406	-0.824430
31	6	-1.683416	-2.709229	-1.236262

32	1	-0.358213	-4.386108	-1.467982
33	6	-3.415844	0.423489	-0.142006
34	1	-2.382252	-3.046370	-1.993453
35	1	-4.321497	0.973387	-0.371094
36	6	3.959792	-2.277167	1.082170
37	1	3.948460	-2.275910	2.176562
38	1	3.456718	-3.189852	0.747075
39	1	5.001408	-2.345921	0.762363
40	8	-2.709615	2.013721	1.560225
41	6	-3.907636	2.778926	1.380460
42	1	-4.793975	2.180364	1.616021
43	1	-3.830512	3.606585	2.084380
44	1	-3.974758	3.171943	0.360180
45	1	-0.708818	0.579462	1.912221
46	1	1.589863	0.258342	0.507692
47	8	-3.951746	-1.246928	-1.782914
48	1	-4.741314	-0.699265	-1.892547

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.282833 hartrees (-605724.6305 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -964.9979769 hartrees (-605545.8805 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0610698 hartrees (-605585.4719 kcal/mol)

TS $_{\mathbf{A1'\text{-}E1'}}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.5038066 hartrees (-605863.293679566 kcal/mol)
Imaginary Frequencies: 1 (-92.5310 1/cm)
Zero-point correction = 0.407745 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.103616	-0.716186	-1.090746
2	1	-0.965823	0.215277	-1.647418
3	1	-1.720063	-1.382288	-1.697538
4	6	0.251189	-1.346220	-0.779414
5	6	1.365601	-0.520573	-0.391519
6	6	0.409662	-2.722753	-0.880886
7	6	1.289032	0.886620	-0.298687

8	6	2.611449	-1.177383	-0.105991
9	6	1.644324	-3.345114	-0.618011
10	1	-0.428667	-3.333790	-1.201023
11	6	2.400249	1.636435	0.071483
12	6	3.727966	-0.370815	0.275656
13	6	2.726469	-2.581887	-0.222926
14	1	1.741514	-4.419715	-0.729705
15	6	3.631376	1.006225	0.367527
16	1	3.680644	-3.048141	-0.006037
17	1	4.499357	1.586678	0.658567
18	8	2.216360	2.979344	0.127581
19	6	3.316104	3.832876	0.459523
20	1	4.127837	3.731814	-0.269134
21	1	2.919661	4.847013	0.421047
22	1	3.686857	3.625610	1.469497
23	1	0.381320	1.430446	-0.528114
24	6	-2.972116	1.446863	0.682396
25	6	-3.359547	1.565161	-0.632534
26	6	-1.716699	-0.451019	0.250533
27	6	-2.693042	-1.323473	0.915554
28	6	-3.625606	-0.746391	1.701891
29	6	-3.785848	0.752342	1.757888
30	1	-2.144657	2.070706	1.011311
31	1	-4.328573	-1.359143	2.260635
32	1	-4.850432	1.002490	1.665976
33	1	-3.484091	1.120856	2.747936
34	6	-4.594710	0.900201	-1.162944
35	1	-5.454067	1.570284	-1.014140
36	1	-4.521561	0.710403	-2.237201
37	1	-4.825773	-0.034985	-0.645882
38	6	-2.600320	2.436903	-1.585868
39	1	-2.306546	1.885136	-2.487556
40	1	-3.259985	3.243475	-1.934507
41	1	-1.716491	2.894017	-1.135264
42	6	-2.653142	-2.821844	0.690970
43	1	-2.787755	-3.073337	-0.366426
44	1	-1.700589	-3.249832	1.015631
45	1	-3.457862	-3.301736	1.251505
46	1	-1.073318	0.132023	0.903191
47	8	4.881330	-1.038792	0.535854
48	1	5.594903	-0.427480	0.763807

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.2721068 hartrees (-605717.8997 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -964.9899526 hartrees (-605540.8451 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0560879 hartrees (-605582.3457 kcal/mol)

E1'
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.5136882 hartrees (-605869.494482382 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.408276 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.659281	1.008858	0.309319
2	6	-3.523240	1.226966	-0.841293
3	6	-1.758956	-0.257498	0.460565
4	6	-2.624543	-1.256417	1.221512
5	6	-3.739995	-0.679572	1.697368
6	6	-3.855339	0.781946	1.390880
7	1	-2.118616	1.924545	0.554362
8	1	-4.498295	-1.184616	2.288193
9	1	-4.859068	1.074452	1.048482
10	1	-3.621067	1.449648	2.228796
11	6	-4.180867	0.117313	-1.568675
12	1	-5.143261	0.412353	-1.993560
13	1	-3.527476	-0.154224	-2.412484
14	1	-4.275623	-0.781133	-0.952289
15	6	-3.811830	2.616084	-1.271289
16	1	-4.848115	2.752135	-1.593203
17	1	-3.530109	3.364725	-0.528301
18	1	-3.188032	2.798314	-2.164659
19	6	-1.105233	-0.737585	-0.877341
20	1	-1.056815	0.123598	-1.559692
21	1	-1.749067	-1.479604	-1.359638
22	6	0.278708	-1.323201	-0.719420
23	6	1.395330	-0.481153	-0.380426
24	6	0.487674	-2.678688	-0.917773
25	6	1.279277	0.921520	-0.229451
26	6	2.679731	-1.099405	-0.207156
27	6	1.757885	-3.272209	-0.759703
28	1	-0.350793	-3.307889	-1.205836
29	6	2.383725	1.697243	0.098339

30	6	3.788072	-0.267180	0.137708
31	6	2.837414	-2.493844	-0.396732
32	1	1.879744	-4.337931	-0.923017
33	6	3.651444	1.101358	0.292663
34	1	3.818987	-2.933592	-0.263673
35	1	4.516580	1.700551	0.553031
36	6	-2.196477	-2.669046	1.471333
37	1	-2.078332	-3.228293	0.537102
38	1	-1.221978	-2.695348	1.972539
39	1	-2.922178	-3.195199	2.095844
40	8	2.160366	3.034499	0.214618
41	6	3.252044	3.906790	0.514941
42	1	4.023374	3.858301	-0.261918
43	1	2.827157	4.910082	0.539585
44	1	3.688812	3.673945	1.492775
45	1	-0.933535	0.033287	1.123360
46	1	0.342278	1.438629	-0.392596
47	8	4.980981	-0.899747	0.299398
48	1	5.681397	-0.268437	0.512455

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.2885428 hartrees (-605728.2135 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0102633 hartrees (-605553.5904 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0733364 hartrees (-605593.1693 kcal/mol)

TS $_{E1'-C1'}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.4875098 hartrees (-605853.067274598 kcal/mol)
Imaginary Frequencies: 1 (-291.4929 1/cm)
Zero-point correction = 0.407983 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.266108	1.566068	0.447372
2	6	-3.122301	0.932633	-0.589357
3	6	-2.038340	-0.151138	-0.179364
4	6	-2.436948	-0.922288	1.079254
5	6	-2.669379	-0.133185	2.136353

6	6	-2.512302	1.356198	1.919717
7	1	-1.573430	2.342420	0.122291
8	1	-2.989116	-0.507755	3.102766
9	1	-3.439238	1.886650	2.185334
10	1	-1.710368	1.792041	2.526006
11	6	-4.589984	0.626819	-0.294302
12	1	-5.167032	1.555034	-0.342514
13	1	-4.984686	-0.042558	-1.064154
14	1	-4.760267	0.166416	0.677498
15	6	-2.964918	1.551477	-1.982266
16	1	-3.272170	0.847381	-2.760302
17	1	-3.615303	2.428383	-2.056528
18	1	-1.944930	1.880264	-2.198105
19	6	-1.229063	-0.828021	-1.326136
20	1	-1.093504	-0.109012	-2.136182
21	1	-1.895165	-1.606294	-1.715886
22	6	0.096484	-1.434695	-0.917497
23	6	1.187390	-0.591731	-0.519683
24	6	0.265504	-2.807926	-0.933569
25	6	1.124494	0.824625	-0.578929
26	6	2.389197	-1.219765	-0.053302
27	6	1.471438	-3.415035	-0.516914
28	1	-0.550509	-3.442234	-1.271393
29	6	2.191158	1.603430	-0.149866
30	6	3.459989	-0.381811	0.385843
31	6	2.509015	-2.632185	-0.059678
32	1	1.568877	-4.495110	-0.546399
33	6	3.365726	0.999110	0.355740
34	1	3.431935	-3.081434	0.288076
35	1	4.198556	1.600995	0.701189
36	6	-2.604464	-2.413843	1.056768
37	1	-3.300042	-2.722706	0.266875
38	1	-1.655302	-2.924910	0.878168
39	1	-3.005011	-2.759280	2.012193
40	8	2.026353	2.949523	-0.255705
41	6	3.116643	3.821808	0.059053
42	1	3.986547	3.609296	-0.571731
43	1	2.755208	4.828278	-0.150230
44	1	3.391110	3.747485	1.117276
45	1	-1.179443	0.550194	0.275909
46	1	0.305578	1.340422	-1.066167
47	8	4.570538	-1.023633	0.832585
48	1	5.263195	-0.394364	1.075535

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):

HF = -965.2696886 hartrees (-605716.3823 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -964.9952194 hartrees (-605544.1501 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0592992 hartrees (-605584.3608 kcal/mol)

C1'
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.537271 hartrees (-605884.29292521 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.410170 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.287525	1.518264	0.018474
2	6	-2.959846	0.274610	-0.840042
3	6	-1.973601	-0.630608	-0.114915
4	6	-2.017752	-0.756033	1.307736
5	6	-2.853861	0.079822	2.018690
6	6	-3.665030	1.179591	1.457855
7	1	-4.094577	2.076775	-0.464831
8	1	-2.947490	-0.097463	3.089755
9	1	-4.721355	0.869396	1.549185
10	1	-3.589830	2.054628	2.117178
11	6	-4.237376	-0.611143	-1.053960
12	1	-4.978673	-0.011898	-1.591767
13	1	-4.013002	-1.489926	-1.664840
14	1	-4.679049	-0.950759	-0.113846
15	6	-2.493452	0.764990	-2.230374
16	1	-2.435757	-0.039405	-2.966996
17	1	-3.227889	1.484195	-2.604247
18	1	-1.525731	1.272261	-2.190153
19	6	-1.095483	-1.536126	-0.920052
20	1	-1.157742	-1.269887	-1.976123
21	1	-1.568351	-2.529771	-0.833482
22	6	0.372261	-1.716335	-0.528067
23	6	1.240934	-0.595519	-0.298448
24	6	0.886844	-3.002130	-0.511396
25	6	0.798594	0.746293	-0.292998
26	6	2.634180	-0.869259	-0.068256
27	6	2.254902	-3.253981	-0.279667

28	1	0.225463	-3.845367	-0.695879
29	6	1.682832	1.795449	-0.094228
30	6	3.513300	0.237783	0.143278
31	6	3.116485	-2.199889	-0.059271
32	1	2.622533	-4.274590	-0.284979
33	6	3.057655	1.543142	0.128869
34	1	4.171383	-2.373096	0.118423
35	1	3.755086	2.357635	0.288384
36	6	-1.247169	-1.823368	2.057869
37	1	-1.372621	-2.810607	1.605218
38	1	-0.176117	-1.609368	2.078374
39	1	-1.602173	-1.882489	3.089297
40	8	1.144149	3.044201	-0.119695
41	6	1.995809	4.182432	0.039415
42	1	2.750272	4.225475	-0.753818
43	1	1.341331	5.050296	-0.037594
44	1	2.481639	4.179974	1.021620
45	1	-0.243044	1.001132	-0.442516
46	1	-2.410432	2.176788	0.025519
47	8	4.819142	-0.075823	0.355025
48	1	5.353600	0.721125	0.472409

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.31237 hartrees (-605743.1653 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0344476 hartrees (-605568.7662 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.100491 hartrees (-605610.2091 kcal/mol)

TS $_{C1'-D1'}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.5303683 hartrees (-605879.961411933 kcal/mol)
Imaginary Frequencies: 1 (-181.6546 1/cm)
Zero-point correction = 0.411518 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.207132	0.932632	0.026570
2	6	-2.669890	-0.313065	-0.710905
3	6	-1.380289	-0.820172	-0.034228

4	6	-1.320269	-0.751675	1.426995
5	6	-2.281196	-0.074293	2.117997
6	6	-3.404902	0.698846	1.522150
7	1	-4.148969	1.241333	-0.438918
8	1	-2.251660	-0.129271	3.205078
9	1	-4.339971	0.153421	1.727796
10	1	-3.517363	1.650302	2.057920
11	6	-3.688625	-1.496328	-0.602994
12	1	-4.662016	-1.154223	-0.967400
13	1	-3.383220	-2.342872	-1.223960
14	1	-3.812893	-1.853071	0.422232
15	6	-2.550224	0.048123	-2.208264
16	1	-2.088283	-0.733870	-2.816714
17	1	-3.555898	0.205023	-2.609136
18	1	-2.003247	0.983415	-2.362944
19	6	-0.664103	-1.989705	-0.729664
20	1	-0.978058	-2.034285	-1.776200
21	1	-1.006027	-2.923559	-0.264862
22	6	0.843775	-1.880808	-0.631768
23	6	1.315594	-0.556844	-0.539262
24	6	1.733223	-2.934774	-0.516830
25	6	0.358484	0.504630	-0.708885
26	6	2.656415	-0.310353	-0.159875
27	6	3.099636	-2.687411	-0.249326
28	1	1.380979	-3.960717	-0.583538
29	6	0.744521	1.815069	-0.325531
30	6	2.994738	1.044138	0.169654
31	6	3.555117	-1.398397	-0.035618
32	1	3.784079	-3.524103	-0.156425
33	6	2.048703	2.070133	0.138027
34	1	4.584858	-1.213165	0.247340
35	1	2.350086	3.072524	0.420319
36	6	-0.247093	-1.482805	2.206657
37	1	-0.176333	-2.539153	1.930004
38	1	0.742601	-1.044835	2.047304
39	1	-0.463613	-1.433500	3.276090
40	8	-0.177354	2.773710	-0.509356
41	6	0.159491	4.155617	-0.293496
42	1	0.982929	4.458643	-0.947389
43	1	-0.738838	4.714832	-0.550388
44	1	0.415972	4.332948	0.755473
45	1	-0.314522	0.465461	-1.555530
46	1	-2.495227	1.752541	-0.119944
47	8	4.263803	1.255910	0.551798
48	1	4.427222	2.183868	0.775833

---

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.3089566 hartrees (-605741.0234 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0305983 hartrees (-605566.3508 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0969171 hartrees (-605607.9664 kcal/mol)

D1'
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.5502643 hartrees (-605892.446350893 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.414062 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.256725	0.522079	-0.473509
2	6	-2.390444	-0.699225	-0.855381
3	6	-1.041099	-0.726764	-0.016618
4	6	-1.284250	-0.377341	1.459951
5	6	-2.428108	0.192030	1.877969
6	6	-3.600088	0.559474	1.017116
7	1	-4.175946	0.495855	-1.070065
8	1	-2.535649	0.390268	2.943894
9	1	-4.433522	-0.121549	1.243318
10	1	-3.964706	1.555502	1.299450
11	6	-3.211771	-1.981489	-0.547209
12	1	-4.219848	-1.871996	-0.959171
13	1	-2.778550	-2.874800	-1.004546
14	1	-3.308470	-2.166435	0.525862
15	6	-2.146508	-0.650992	-2.378069
16	1	-1.461497	-1.429874	-2.731486
17	1	-3.094900	-0.802937	-2.902890
18	1	-1.763416	0.321865	-2.709683
19	6	-0.367422	-2.156826	-0.164569
20	1	-0.659132	-2.608215	-1.117439
21	1	-0.703945	-2.840090	0.619388
22	6	1.121984	-1.937090	-0.149098
23	6	1.394105	-0.589959	-0.336844
24	6	2.184376	-2.817011	0.055372
25	6	0.153504	0.203674	-0.589304

26	6	2.692290	-0.072351	-0.232292
27	6	3.504953	-2.324518	0.088457
28	1	2.004884	-3.877049	0.211909
29	6	0.361971	1.655667	-0.281282
30	6	2.789782	1.359094	-0.186275
31	6	3.770111	-0.964979	-0.031647
32	1	4.326070	-3.015693	0.247520
33	6	1.648702	2.183221	-0.163435
34	1	4.782477	-0.587118	0.054845
35	1	1.790136	3.252300	-0.052286
36	6	-0.188582	-0.663204	2.466989
37	1	0.092738	-1.721515	2.498683
38	1	0.733172	-0.105700	2.254810
39	1	-0.515022	-0.379820	3.470488
40	8	-0.721345	2.395632	-0.263521
41	6	-0.661536	3.832848	-0.097598
42	1	-0.109050	4.284704	-0.925481
43	1	-1.698851	4.160767	-0.116661
44	1	-0.206695	4.079894	0.864665
45	1	0.007759	0.220877	-1.684836
46	1	-2.732678	1.439171	-0.751201
47	8	4.013102	1.865586	-0.104551
48	1	4.019108	2.833814	-0.040860

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.3353572 hartrees (-605757.59 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0634789 hartrees (-605586.9836 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.1286412 hartrees (-605627.8736 kcal/mol)

Table S4 (viii). Coordinates and Energies. Path 2: **A2'→D2'**
The coordinates below are those for the enantiomer of the structure presented in Figure S10 (viii).

A2'
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.514531 hartrees (-605870.02334781 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.407772 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.902485	0.026465	-0.913698
2	6	4.957042	0.487544	-0.213452
3	6	1.493660	-0.978910	0.766215
4	6	1.403034	-1.984406	-0.220425
5	6	2.441461	-2.144245	-1.124379
6	6	3.688818	-1.374562	-1.421055
7	1	3.157015	0.749765	-1.244863
8	1	2.363661	-3.035921	-1.747660
9	1	4.520071	-2.040695	-1.141910
10	1	3.748485	-1.363737	-2.524016
11	6	6.098590	-0.356539	0.296505
12	1	7.041735	-0.031813	-0.159992
13	1	6.217901	-0.222832	1.378684
14	1	5.985428	-1.425365	0.103943
15	6	5.078733	1.958964	0.103580
16	1	5.155091	2.124123	1.185809
17	1	5.995385	2.370931	-0.336331
18	1	4.232798	2.535974	-0.279833
19	6	0.536809	-0.682461	1.858150
20	1	1.038230	-0.361681	2.773906
21	1	-0.152142	-1.491847	2.088413
22	6	-0.134491	0.496558	1.147089
23	6	-1.461814	0.408591	0.581126
24	6	0.586649	1.692310	1.044693
25	6	-2.297180	-0.713494	0.722256
26	6	-1.960546	1.571827	-0.108605
27	6	0.068898	2.816409	0.390441
28	1	1.568338	1.756945	1.506369
29	6	-3.582681	-0.720787	0.180206
30	6	-3.277877	1.519076	-0.663044
31	6	-1.184755	2.746640	-0.197431

32	1	0.644697	3.734495	0.348574
33	6	-4.076883	0.397530	-0.527855
34	1	-1.595010	3.603794	-0.719153
35	1	-5.073617	0.391986	-0.953901
36	6	0.252341	-2.971143	-0.239264
37	1	0.073107	-3.402543	0.750492
38	1	-0.672796	-2.488916	-0.565638
39	1	0.456995	-3.794889	-0.926390
40	8	-4.292893	-1.852395	0.379062
41	6	-5.640471	-1.945820	-0.097970
42	1	-5.678058	-1.865659	-1.189869
43	1	-5.986977	-2.932849	0.205562
44	1	-6.273433	-1.179149	0.361520
45	1	-1.989767	-1.597685	1.263919
46	1	2.368697	-0.338307	0.722331
47	8	-3.693532	2.635541	-1.311353
48	1	-4.605362	2.543428	-1.620143

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.2794796 hartrees (-605722.5262 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -964.9940559 hartrees (-605543.42 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0576046 hartrees (-605583.2975 kcal/mol)

TS $_{\mathbf{A2'\text{-}E2'}}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.4980468 hartrees (-605859.679347468 kcal/mol)
Imaginary Frequencies: 1 (-152.8606 1/cm)
Zero-point correction = 0.406641 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.013748	-0.056841	-1.494787
2	6	-3.692394	-0.984134	-0.740010
3	6	-1.573434	0.648102	0.255170
4	6	-2.373455	1.836708	0.496992
5	6	-3.207145	2.245191	-0.490407
6	6	-3.481236	1.375468	-1.692474
7	1	-2.222220	-0.421673	-2.143786

8	1	-3.750976	3.182797	-0.401001
9	1	-4.555248	1.412943	-1.915738
10	1	-2.989210	1.813063	-2.573414
11	6	-4.916865	-0.609016	0.039850
12	1	-4.801026	0.357178	0.546313
13	1	-5.770547	-0.494779	-0.643725
14	1	-5.184392	-1.369992	0.776070
15	6	-3.275118	-2.420839	-0.713520
16	1	-3.155261	-2.777828	0.316466
17	1	-4.076330	-3.033108	-1.150258
18	1	-2.353048	-2.607361	-1.266833
19	6	-1.039968	-0.227419	1.346079
20	1	-1.856506	-0.804668	1.801355
21	1	-0.724233	0.452949	2.156388
22	6	0.099222	-1.131680	0.928720
23	6	1.328557	-0.547405	0.472835
24	6	-0.026165	-2.505716	0.999901
25	6	1.546056	0.854423	0.443014
26	6	2.370643	-1.432696	0.041242
27	6	1.019492	-3.368423	0.597058
28	1	-0.946894	-2.939619	1.380977
29	6	2.744655	1.374821	-0.029312
30	6	3.586066	-0.855411	-0.437317
31	6	2.194383	-2.838098	0.111668
32	1	0.889887	-4.443150	0.669581
33	6	3.773310	0.515309	-0.482199
34	1	3.002411	-3.483647	-0.212330
35	1	4.710518	0.915528	-0.852034
36	6	-2.285349	2.549531	1.832715
37	1	-2.674990	1.922749	2.642514
38	1	-1.253345	2.813975	2.085013
39	1	-2.874489	3.468500	1.809471
40	8	2.853736	2.728368	-0.015654
41	6	4.078776	3.343996	-0.421681
42	1	4.300254	3.131157	-1.473670
43	1	3.922616	4.415014	-0.295558
44	1	4.912529	3.021062	0.211625
45	1	0.823417	1.561342	0.832246
46	1	-1.007915	0.616622	-0.669058
47	8	4.541036	-1.732778	-0.844336
48	1	5.339123	-1.268984	-1.131900

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.2659253 hartrees (-605714.0208 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -964.9836682 hartrees (-605536.9016 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.049725 hartrees (-605578.3529 kcal/mol)

E2'
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.5259195 hartrees (-605877.169745445 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.410267 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.768190	0.477096	1.041707
2	6	1.595954	-1.008773	1.091231
3	6	2.052266	1.055789	-0.383384
4	6	3.561047	1.268993	-0.417453
5	6	4.080507	1.173072	0.814401
6	6	3.043267	0.899878	1.874143
7	1	0.871354	0.932350	1.464915
8	1	5.124663	1.341217	1.061278
9	1	3.348960	0.155802	2.618042
10	1	2.796892	1.808759	2.439001
11	6	2.733590	-1.912047	0.724351
12	1	3.456553	-1.862549	1.553472
13	1	2.419628	-2.953558	0.638607
14	1	3.273478	-1.598110	-0.167684
15	6	0.588513	-1.580352	2.023265
16	1	0.138902	-2.494826	1.616180
17	1	1.111272	-1.893196	2.941449
18	1	-0.193811	-0.871008	2.293441
19	6	1.445327	0.168685	-1.513452
20	1	2.234254	-0.432219	-1.974763
21	1	1.055111	0.810857	-2.311553
22	6	0.355997	-0.771970	-1.040891
23	6	-0.942202	-0.271448	-0.613888
24	6	0.485357	-2.151864	-1.286622
25	6	-1.227506	1.096474	-0.508348
26	6	-1.975340	-1.230170	-0.320109
27	6	-0.531521	-3.068424	-1.002956
28	1	1.418904	-2.515892	-1.705122
29	6	-2.492808	1.533322	-0.101072

30	6	-3.250331	-0.748000	0.112108
31	6	-1.746155	-2.609125	-0.507787
32	1	-0.379229	-4.126769	-1.185674
33	6	-3.509235	0.607316	0.224123
34	1	-2.547173	-3.306357	-0.287412
35	1	-4.487682	0.943676	0.547401
36	6	4.278949	1.650951	-1.677014
37	1	4.174980	0.888237	-2.458397
38	1	3.871592	2.582600	-2.090942
39	1	5.345728	1.801389	-1.494748
40	8	-2.656861	2.869332	-0.045149
41	6	-3.930157	3.424640	0.310511
42	1	-4.211557	3.139875	1.329963
43	1	-3.798746	4.504459	0.257824
44	1	-4.703620	3.114497	-0.399848
45	1	-0.501353	1.855238	-0.766643
46	1	1.583475	2.048271	-0.431808
47	8	-4.178110	-1.694394	0.396889
48	1	-5.025049	-1.296500	0.641918

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.303968 hartrees (-605737.893 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0283216 hartrees (-605564.9221 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0920388 hartrees (-605604.9053 kcal/mol)

TS $_{E2'-C2'}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.4874165 hartrees (-605853.008727915 kcal/mol)
Imaginary Frequencies: 1 (-231.4732 1/cm)
Zero-point correction = 0.408053 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.035308	0.173754	-1.513360
2	6	-2.924037	-0.760775	-0.788596
3	6	-2.028182	-0.026094	0.303705
4	6	-2.613971	1.326858	0.714116
5	6	-2.787730	2.159014	-0.320529

6	6	-2.390972	1.631666	-1.684753
7	1	-1.203680	-0.254756	-2.072989
8	1	-3.203227	3.156608	-0.226561
9	1	-3.232313	1.694648	-2.390664
10	1	-1.561073	2.195915	-2.124853
11	6	-4.432746	-0.521118	-0.747639
12	1	-4.872120	-0.868653	-1.687389
13	1	-4.874341	-1.115749	0.057430
14	1	-4.719222	0.518537	-0.599493
15	6	-2.613639	-2.239644	-1.021323
16	1	-3.016172	-2.850650	-0.208419
17	1	-3.102271	-2.563772	-1.945139
18	1	-1.545655	-2.444699	-1.106885
19	6	-1.249421	-0.908227	1.337423
20	1	-1.918852	-1.704166	1.672023
21	1	-1.080096	-0.249334	2.194991
22	6	0.070392	-1.497153	0.884306
23	6	1.152108	-0.637836	0.490228
24	6	0.246870	-2.870052	0.874285
25	6	1.072602	0.778624	0.552952
26	6	2.358738	-1.254259	0.016635
27	6	1.454429	-3.462990	0.444448
28	1	-0.566726	-3.513786	1.199037
29	6	2.139384	1.566956	0.135256
30	6	3.426288	-0.405335	-0.409043
31	6	2.488314	-2.665512	0.003568
32	1	1.557528	-4.542863	0.453687
33	6	3.322508	0.973986	-0.365008
34	1	3.415396	-3.102872	-0.348287
35	1	4.154357	1.584718	-0.697023
36	6	-2.954248	1.618544	2.147213
37	1	-3.612103	0.848447	2.566893
38	1	-2.062500	1.663745	2.782404
39	1	-3.463330	2.581585	2.225026
40	8	1.968178	2.909035	0.247390
41	6	3.051263	3.790868	-0.063994
42	1	3.328429	3.720919	-1.121911
43	1	2.679919	4.793456	0.146234
44	1	3.922050	3.585586	0.568099
45	1	-1.101173	0.358060	-0.323979
46	1	0.239447	1.292840	1.018749
47	8	4.542858	-1.035530	-0.857653
48	1	5.233590	-0.399453	-1.088214

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):

HF = -965.270095 hartrees (-605716.6373 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -964.9957417 hartrees (-605544.4779 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0601947 hartrees (-605584.9227 kcal/mol)

C2'
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.5363118 hartrees (-605883.691017618 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.410744 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.785973	0.504530	-1.805632
2	6	-2.414077	-0.743370	-0.971773
3	6	-1.998667	-0.332976	0.430383
4	6	-2.627800	0.789023	1.063030
5	6	-3.498226	1.571154	0.332174
6	6	-3.789439	1.418291	-1.108091
7	1	-3.176666	0.177191	-2.773528
8	1	-4.027924	2.363542	0.859701
9	1	-4.823192	1.037290	-1.188788
10	1	-3.834558	2.411248	-1.574558
11	6	-3.668922	-1.668355	-0.778094
12	1	-4.026614	-1.961240	-1.769919
13	1	-3.407653	-2.581400	-0.237379
14	1	-4.486550	-1.176497	-0.245137
15	6	-1.361515	-1.545846	-1.763795
16	1	-1.123383	-2.503714	-1.301035
17	1	-1.770018	-1.750866	-2.758054
18	1	-0.432827	-0.984607	-1.887979
19	6	-1.141083	-1.238432	1.274193
20	1	-1.707454	-2.180240	1.348813
21	1	-1.086044	-0.840592	2.288675
22	6	0.271851	-1.608687	0.813598
23	6	1.207666	-0.588839	0.454974
24	6	0.660536	-2.934331	0.816723
25	6	0.885496	0.791512	0.484488
26	6	2.516113	-0.997920	0.036065
27	6	1.963832	-3.323079	0.431011

28	1	-0.051021	-3.703423	1.107372
29	6	1.803774	1.746849	0.063217
30	6	3.434220	0.017033	-0.376796
31	6	2.874967	-2.369229	0.034099
32	1	2.233658	-4.373837	0.435759
33	6	3.090369	1.359052	-0.376049
34	1	3.872747	-2.650432	-0.281624
35	1	3.815417	2.097467	-0.699190
36	6	-2.409710	1.122579	2.528400
37	1	-2.755841	0.319317	3.186668
38	1	-1.355930	1.308758	2.757012
39	1	-2.962686	2.025840	2.794101
40	8	1.389820	3.039017	0.123335
41	6	2.301933	4.088413	-0.214760
42	1	2.613370	4.019885	-1.263083
43	1	1.750309	5.015494	-0.061491
44	1	3.179525	4.074262	0.440849
45	1	-1.868297	1.069731	-2.008147
46	1	-0.043670	1.150518	0.904461
47	8	4.655356	-0.417688	-0.778199
48	1	5.221815	0.321452	-1.038771

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.3112794 hartrees (-605742.4809 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0335589 hartrees (-605568.2085 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0991317 hartrees (-605609.3561 kcal/mol)

TS $_{C2'-D2'}$
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.5289806 hartrees (-605879.090616306 kcal/mol)
Imaginary Frequencies: 1 (-174.4207 1/cm)
Zero-point correction = 0.411392 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.217958	0.464923	-1.739476
2	6	-1.631378	-0.866205	-1.218538
3	6	-1.452989	-0.789265	0.308511

4	6	-2.527546	-0.136857	1.063002
5	6	-3.474872	0.598940	0.417165
6	6	-3.523545	0.856356	-1.048578
7	1	-2.369097	0.386219	-2.820936
8	1	-4.284435	1.017634	1.012706
9	1	-4.382114	0.305003	-1.464154
10	1	-3.761648	1.913188	-1.224166
11	6	-2.638946	-2.032781	-1.490603
12	1	-2.880264	-2.040183	-2.557951
13	1	-2.199969	-3.004501	-1.249968
14	1	-3.570380	-1.930786	-0.929157
15	6	-0.356060	-1.173178	-2.025792
16	1	0.114416	-2.114890	-1.736881
17	1	-0.627200	-1.253899	-3.082928
18	1	0.384133	-0.374718	-1.934463
19	6	-0.685267	-1.922884	1.009028
20	1	-1.063950	-2.880263	0.631166
21	1	-0.908551	-1.910304	2.078500
22	6	0.812701	-1.833070	0.791478
23	6	1.284747	-0.519693	0.609823
24	6	1.685729	-2.899482	0.658627
25	6	0.348585	0.556862	0.806286
26	6	2.592611	-0.301490	0.117063
27	6	3.028774	-2.675638	0.277840
28	1	1.334319	-3.918396	0.797910
29	6	0.709935	1.846456	0.333644
30	6	2.908163	1.033429	-0.305771
31	6	3.473461	-1.400920	-0.027345
32	1	3.699667	-3.521458	0.169829
33	6	1.971235	2.066991	-0.252645
34	1	4.478927	-1.237570	-0.397646
35	1	2.252326	3.051673	-0.608699
36	6	-2.624071	-0.285978	2.569408
37	1	-2.852186	-1.314746	2.868834
38	1	-1.699024	0.000296	3.084478
39	1	-3.418474	0.352513	2.961129
40	8	-0.183287	2.819544	0.564555
41	6	0.136303	4.187325	0.254706
42	1	0.292547	4.316541	-0.820837
43	1	-0.731454	4.764017	0.570924
44	1	1.019599	4.512564	0.812847
45	1	-1.475438	1.254603	-1.579067
46	1	-0.240797	0.571066	1.714123
47	8	4.143199	1.215882	-0.797270
48	1	4.292093	2.129938	-1.080871

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.307472 hartrees (-605740.0918 kcal/mol)

MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0295455 hartrees (-605565.6901 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0957452 hartrees (-605607.2311 kcal/mol)

D2'
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.5469796 hartrees (-605890.385168796 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.414020 (Hartree/Particle)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.337872	0.367941	-1.609957
2	6	-1.415989	-0.821372	-1.242098
3	6	-1.060671	-0.767220	0.308748
4	6	-2.307556	-0.469508	1.156290
5	6	-3.430268	0.043293	0.625511
6	6	-3.646432	0.375401	-0.819234
7	1	-2.548368	0.321193	-2.684506
8	1	-4.274229	0.219881	1.290770
9	1	-4.362926	-0.340963	-1.247042
10	1	-4.137894	1.353046	-0.903911
11	6	-2.175465	-2.135102	-1.568346
12	1	-2.652226	-2.042530	-2.549409
13	1	-1.503613	-2.995670	-1.627914
14	1	-2.956019	-2.362095	-0.837575
15	6	-0.186440	-0.759325	-2.171318
16	1	0.504353	-1.592341	-2.021257
17	1	-0.525706	-0.805752	-3.211413
18	1	0.373388	0.176573	-2.064078
19	6	-0.327679	-2.097123	0.776378
20	1	-0.699603	-2.979325	0.255836
21	1	-0.506755	-2.271531	1.841730
22	6	1.146476	-1.854973	0.553902
23	6	1.371450	-0.487360	0.462347
24	6	2.224743	-2.721569	0.395065
25	6	0.121068	0.282323	0.696065

26	6	2.618870	0.048176	0.125476
27	6	3.506232	-2.198246	0.113821
28	1	2.090013	-3.797539	0.462095
29	6	0.239487	1.713740	0.291634
30	6	2.636901	1.459552	-0.138158
31	6	3.713412	-0.833109	-0.042221
32	1	4.340046	-2.880799	-0.013451
33	6	1.472387	2.251358	-0.080746
34	1	4.690581	-0.446846	-0.308659
35	1	1.559766	3.308570	-0.304786
36	6	-2.265317	-0.755393	2.644872
37	1	-2.306898	-1.828747	2.865253
38	1	-1.360049	-0.372137	3.135753
39	1	-3.118765	-0.290434	3.143573
40	8	-0.847391	2.434919	0.463300
41	6	-0.844347	3.868318	0.266147
42	1	-0.610250	4.107136	-0.774663
43	1	-1.857406	4.186309	0.503719
44	1	-0.132315	4.340282	0.948323
45	1	-1.809047	1.311151	-1.444409
46	1	0.008707	0.371980	1.792764
47	8	3.811546	1.980409	-0.468956
48	1	3.764038	2.929172	-0.666574

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mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.3321634 hartrees (-605755.5859 kcal/mol)

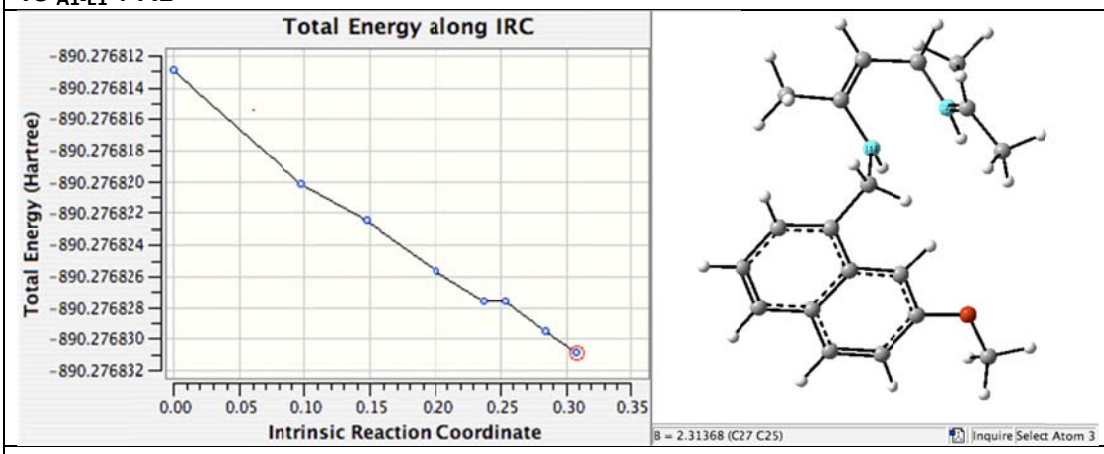
MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.0606896 hartrees (-605585.2333 kcal/mol)

M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -965.1256303 hartrees (-605625.9843 kcal/mol)

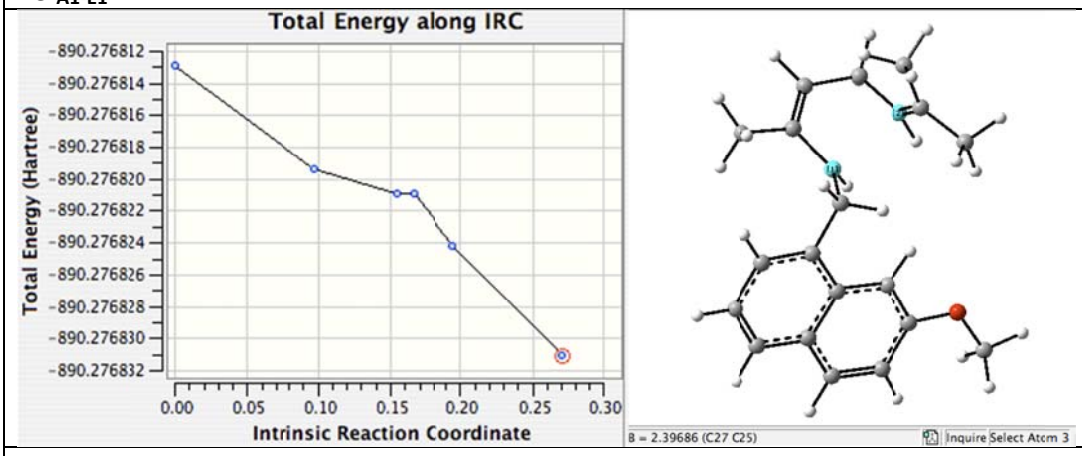
Table S5 (i). IRC plots. Path 1: **A1→D1**

Correspond to structures in Figure S10(i).

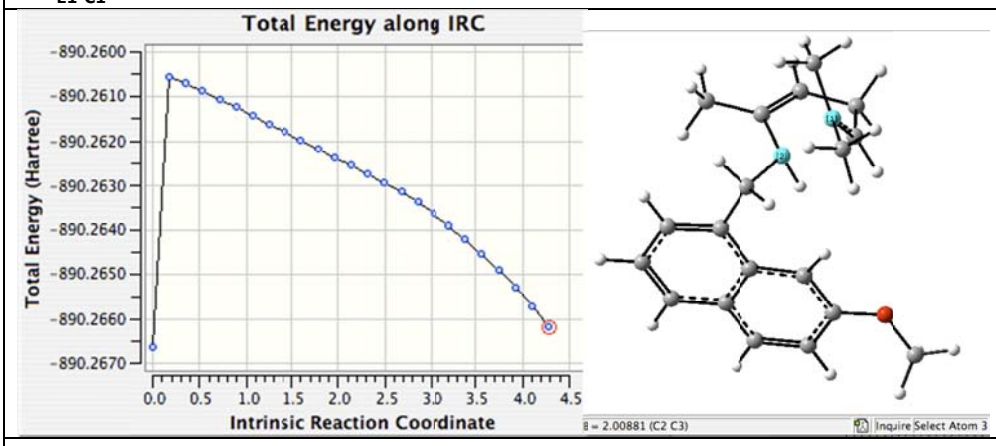
TS $_{A1\text{-}E1}$→A1



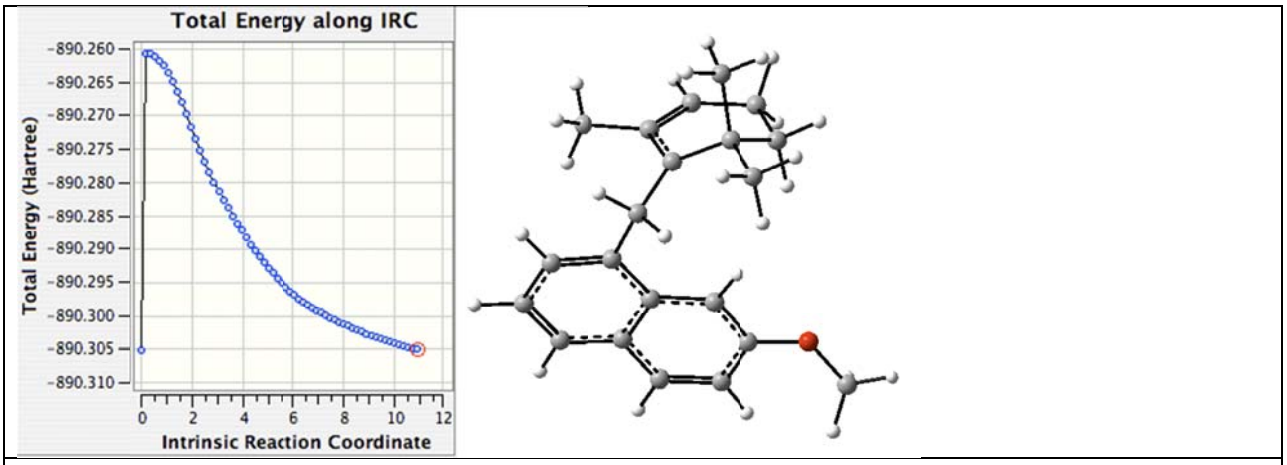
TS $_{A1\text{-}E1}$→E1



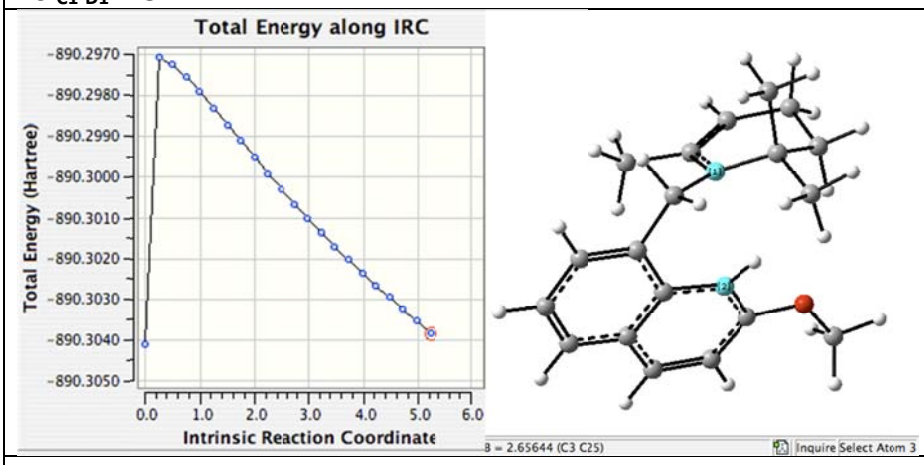
TS $_{E1\text{-}C1}$→E1



TS $_{E1\text{-}C1}$→C1



TS $_{C1\text{-}D1}$→C1



TS $_{C1\text{-}D1}$→D1

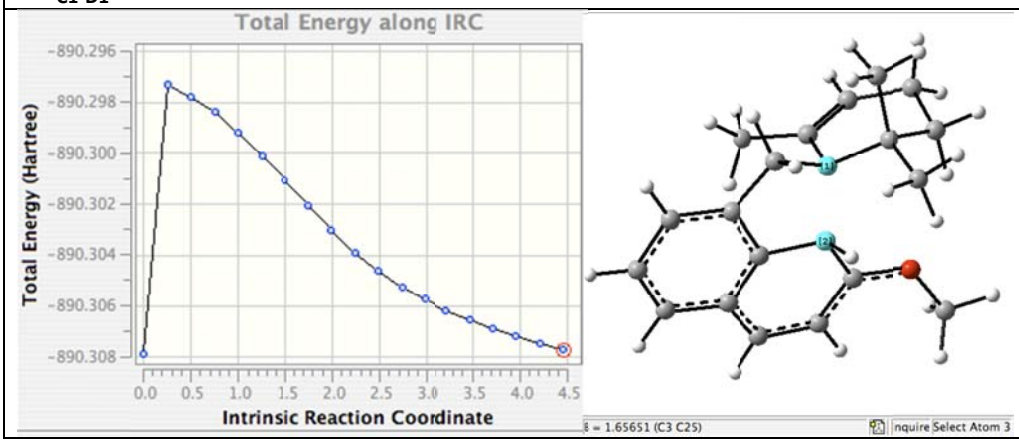
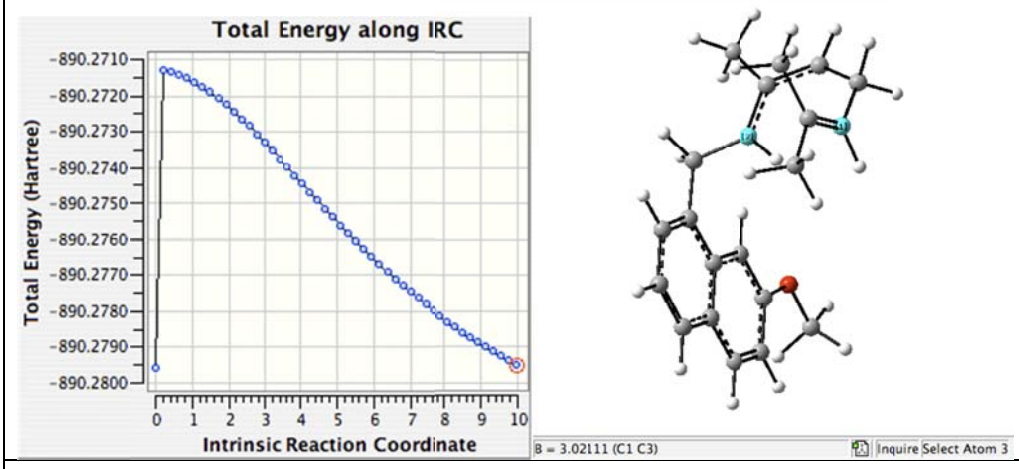


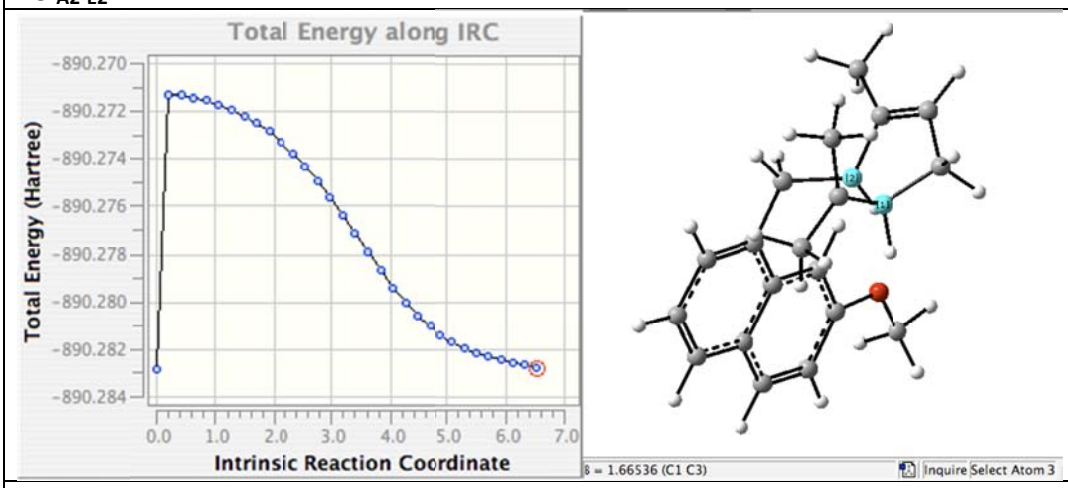
Table S5 (ii). IRC plots. Path 1: **A1→D1**

Correspond to structures in Figure S10(ii).

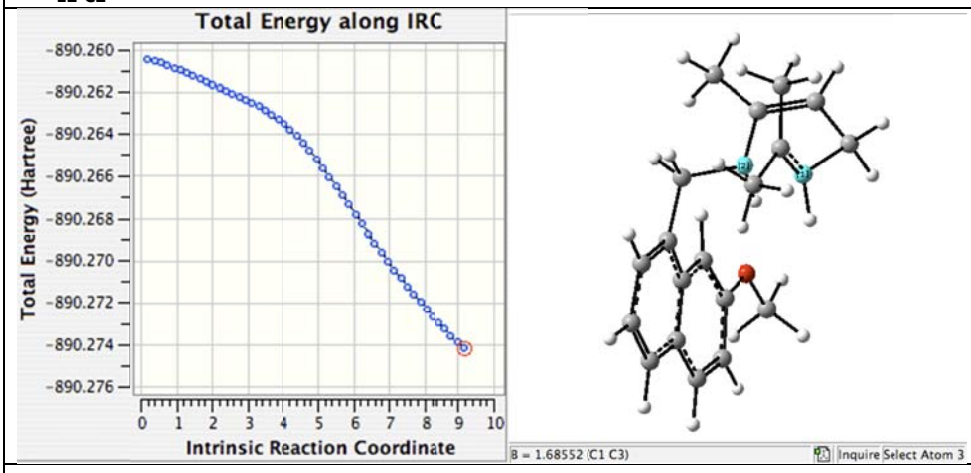
TS $_{A2\text{-}E2}$→A2



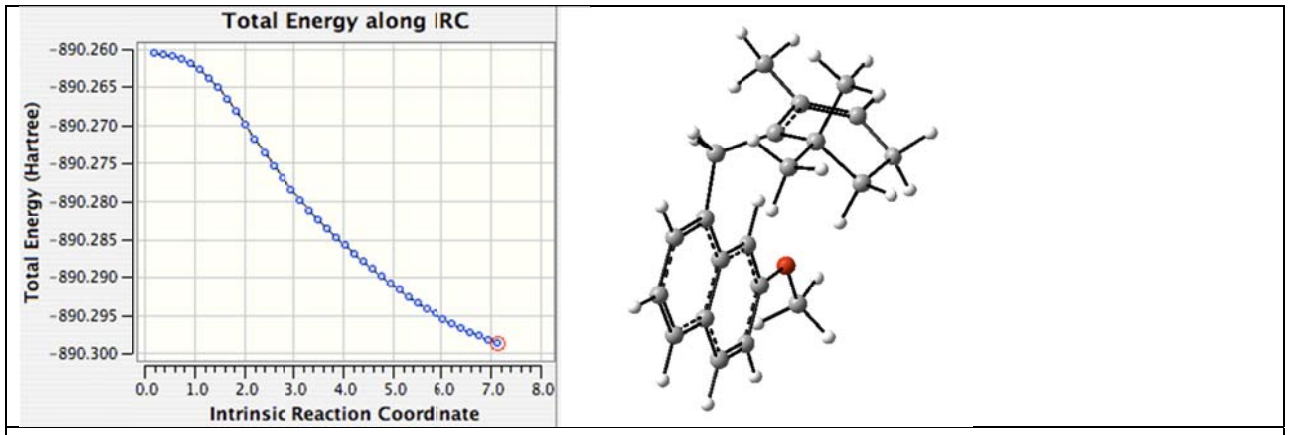
TS $_{A2\text{-}E2}$→E2



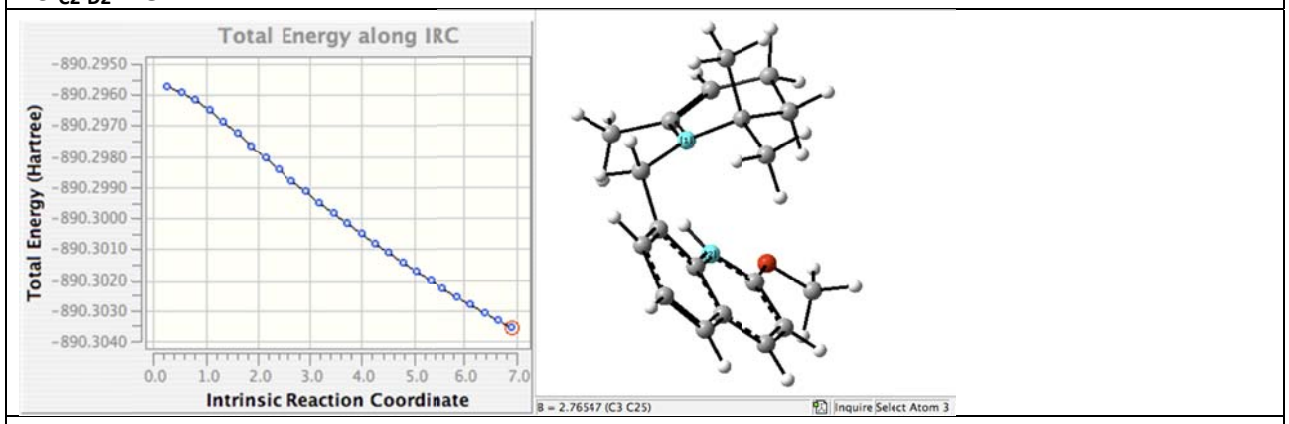
TS $_{E2\text{-}C2}$→E2



TS $_{E2\text{-}C2}$→C2



TS $_{C2\text{-}D2}$→C2



TS $_{C2\text{-}D2}$→D2

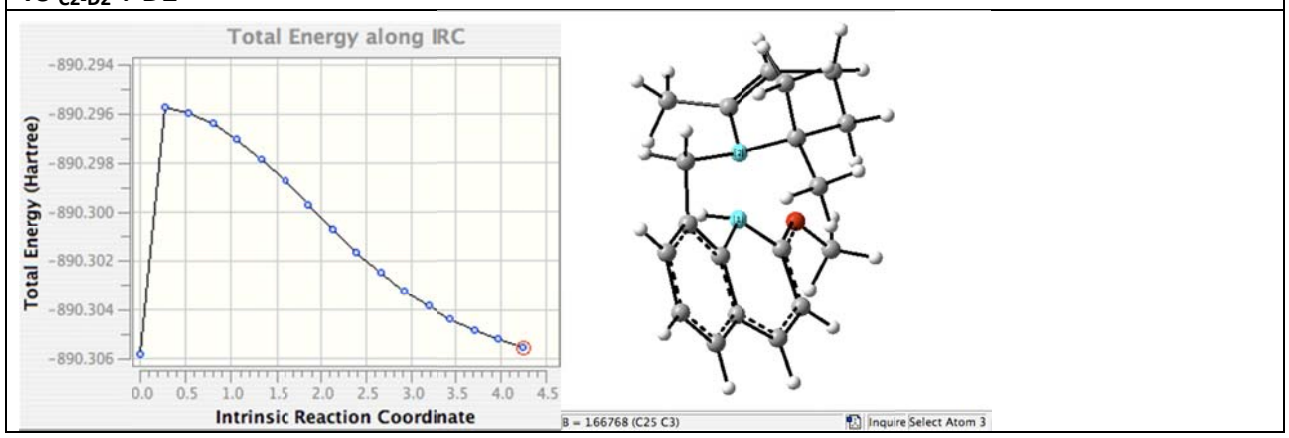
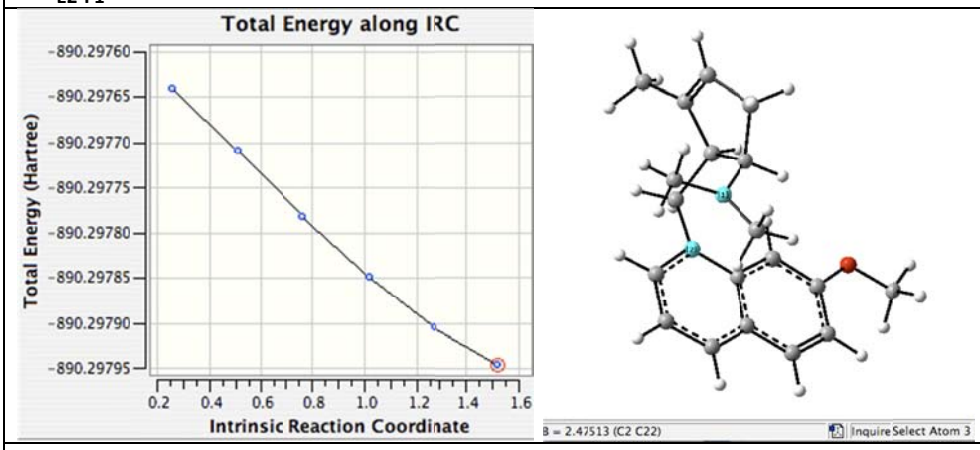


Table S5 (iii). IRC plots. **E2→F1** conversion

Correspond to structures in Figure S10(iii).

TS $_{E2\text{-}F1}$→E2



TS $_{E2\text{-}F1}$→F1

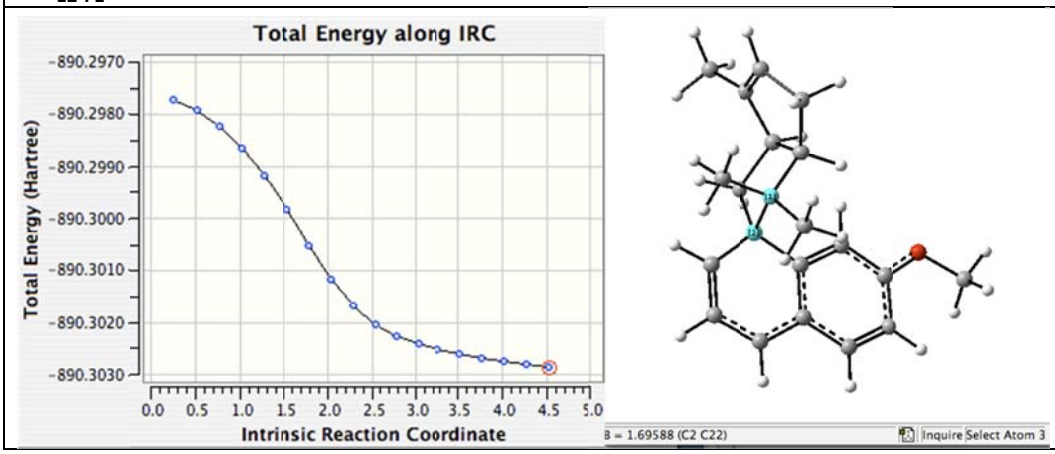
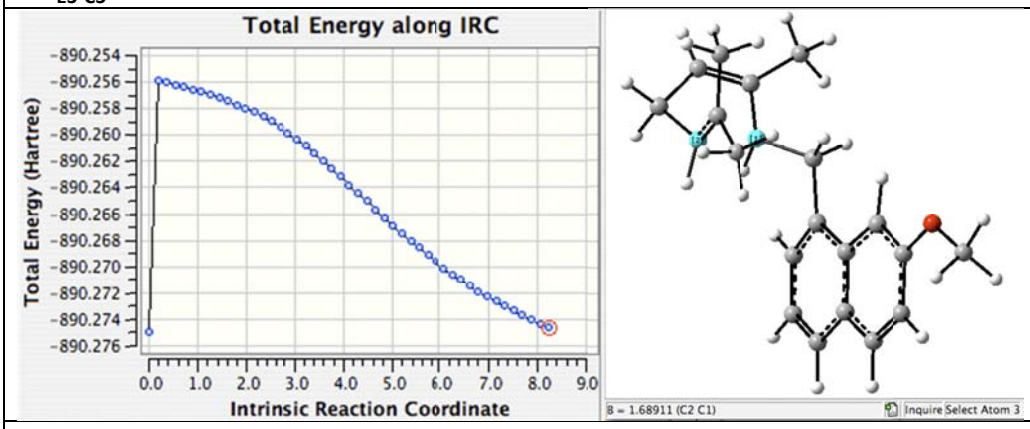


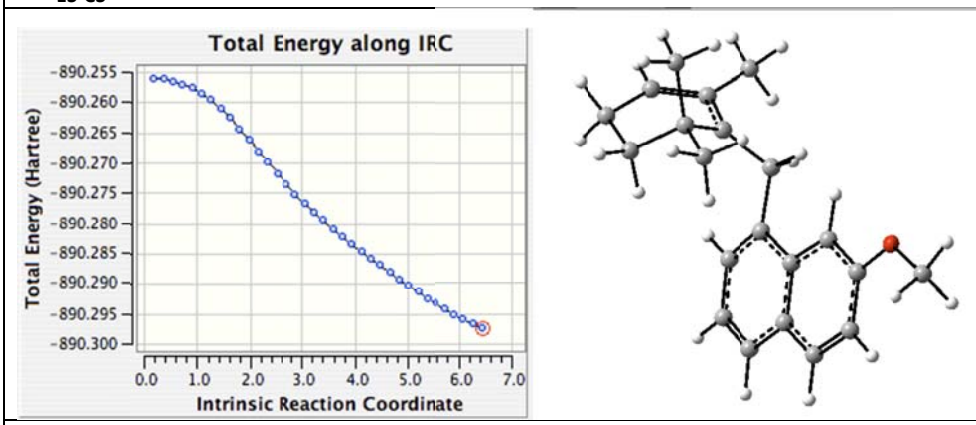
Table S5 (iv). IRC plots. Path 3: **E3→D3**

Correspond to structures in Figure S10(iv).

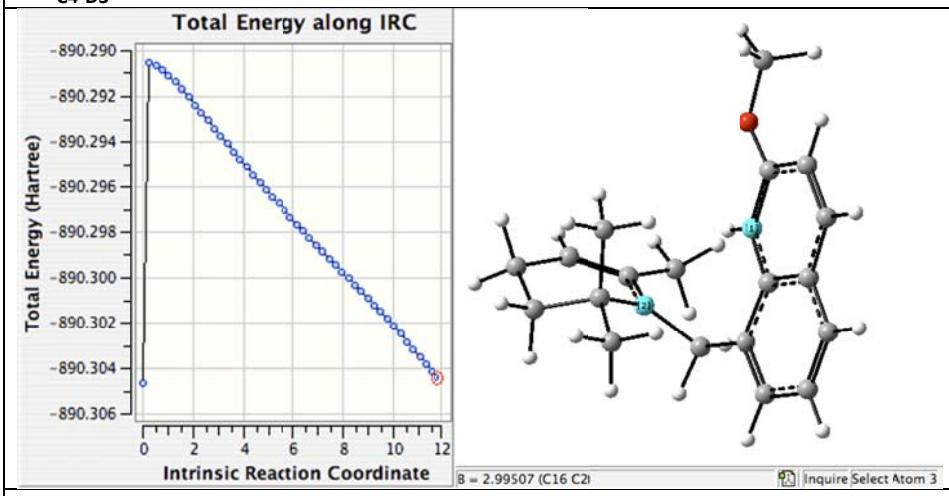
TS $_{E3\text{-}C3}$→E3



TS $_{E3\text{-}C3}$→C3



TS $_{C4\text{-}D3}$→C4



TS $_{C4\text{-}D3}$→D3

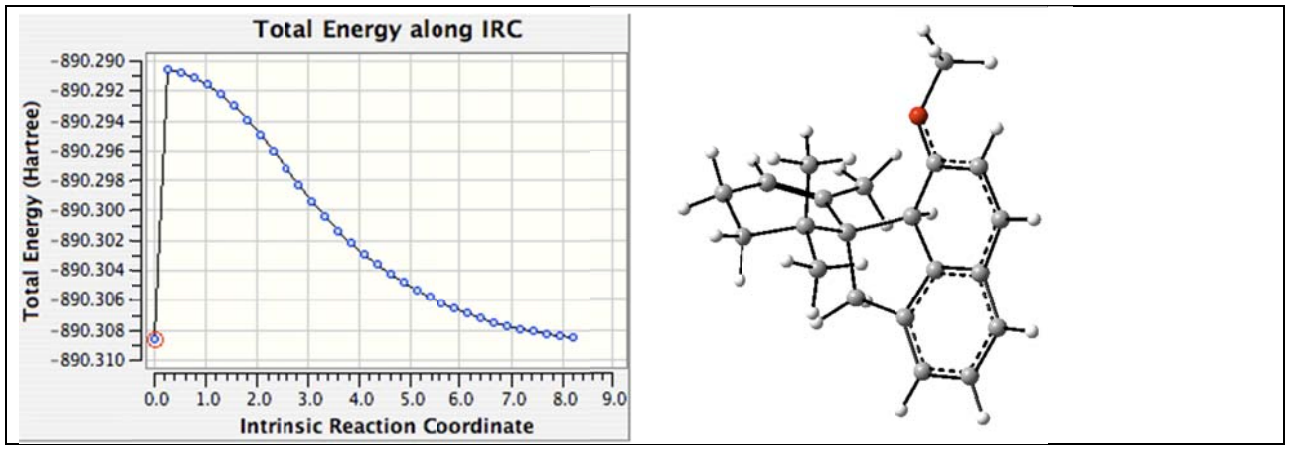
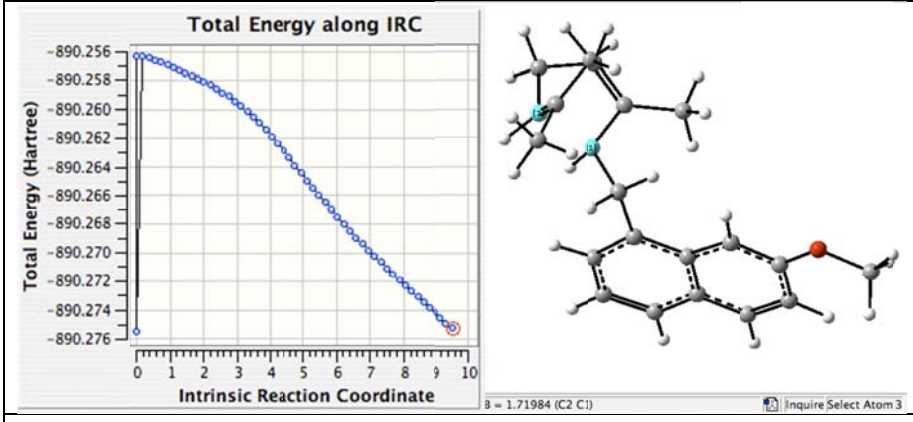

Total Energy along IRC
Total Energy (Hartree)
-890.290
-890.292
-890.294
-890.296
-890.298
-890.300
-890.302
-890.304
-890.306
-890.308
-890.310
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
Intrinsic Reaction Coordinate

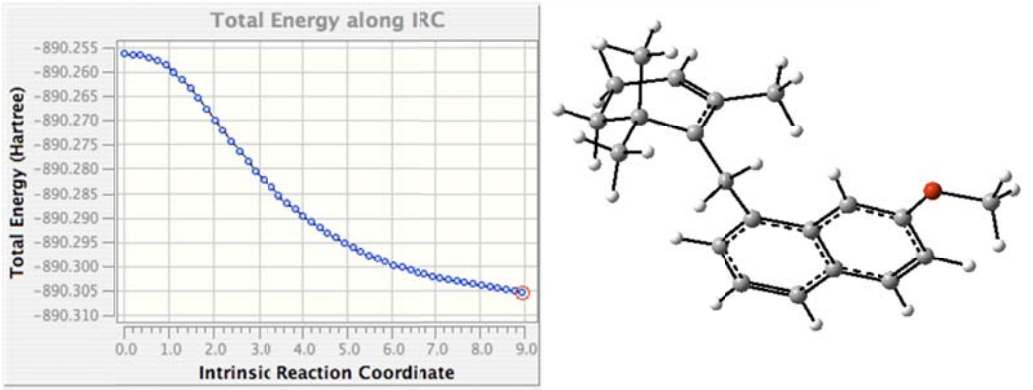
Table S5 (v). IRC plots. Path 4: **E4→D4**

Correspond to structures in Figure S10(v).

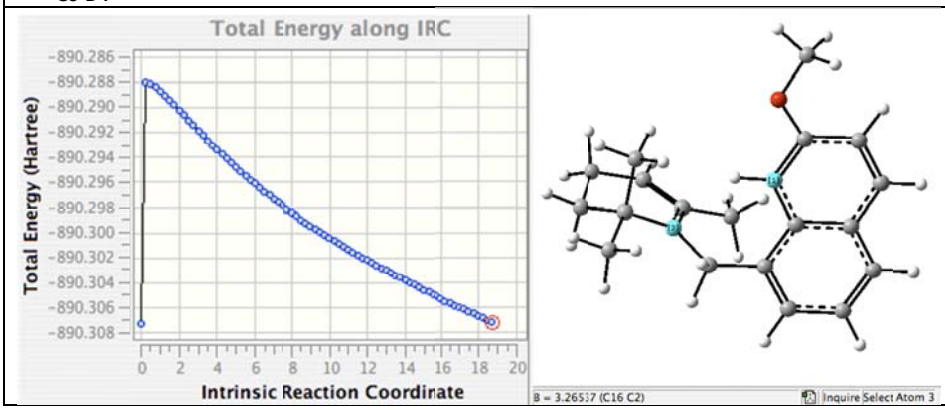
TS $_{E4\text{-}C5}$→E4



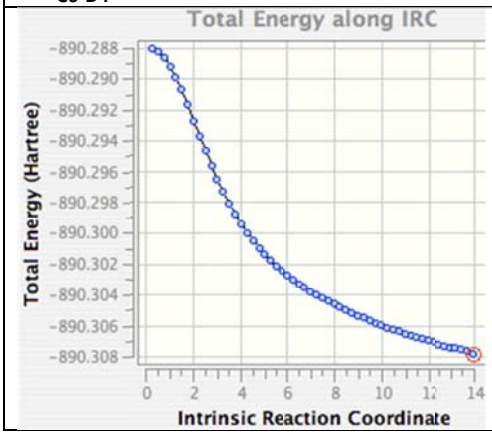
TS $_{E4\text{-}C5}$→C5



TS $_{C6\text{-}D4}$→C6



TS $_{C6\text{-}D4}$→D4



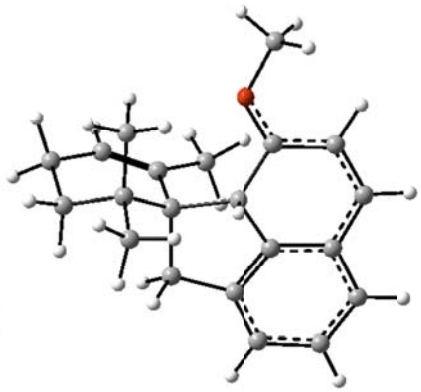
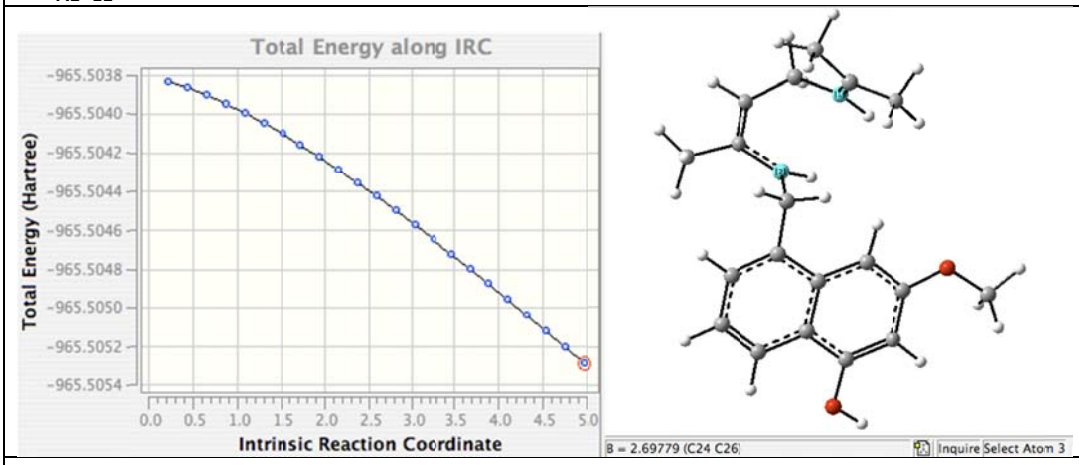


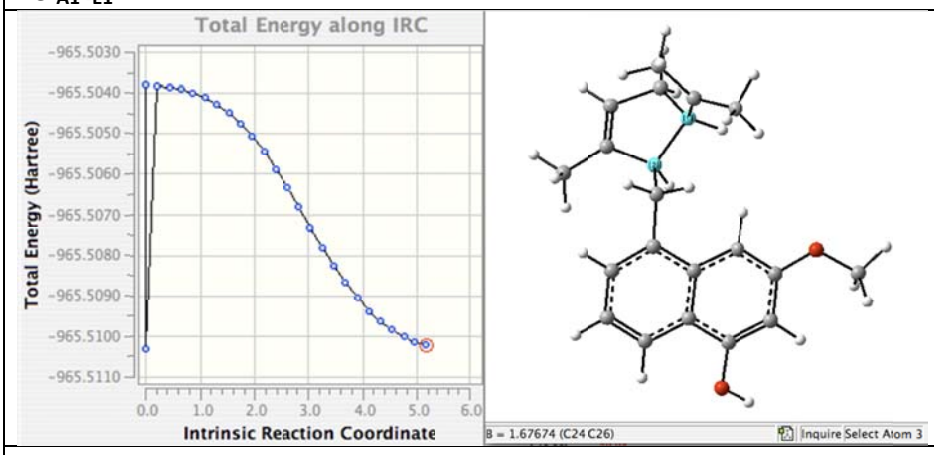
Table S5 (vi). IRC plots. Path 1: **A1'→D1'**

Correspond to structures in Figure S10(vii).

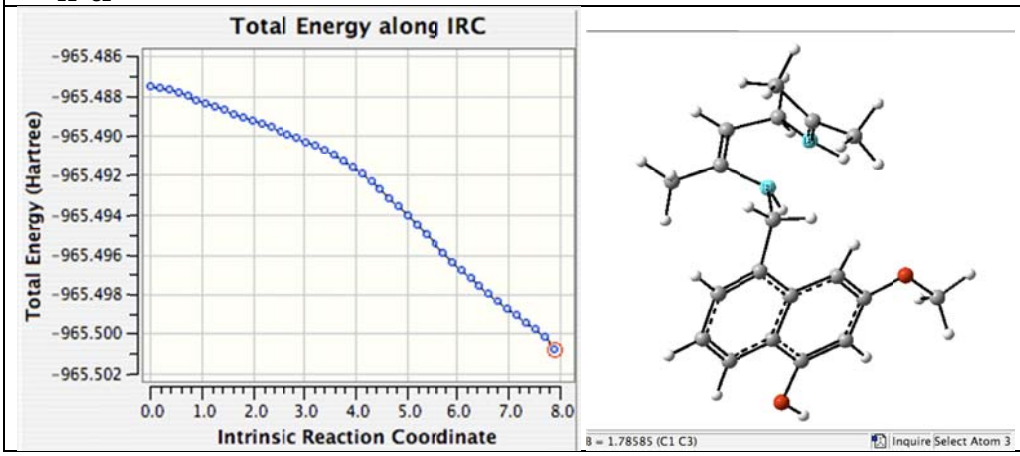
TS $_{A1'-E1'}$→A1'



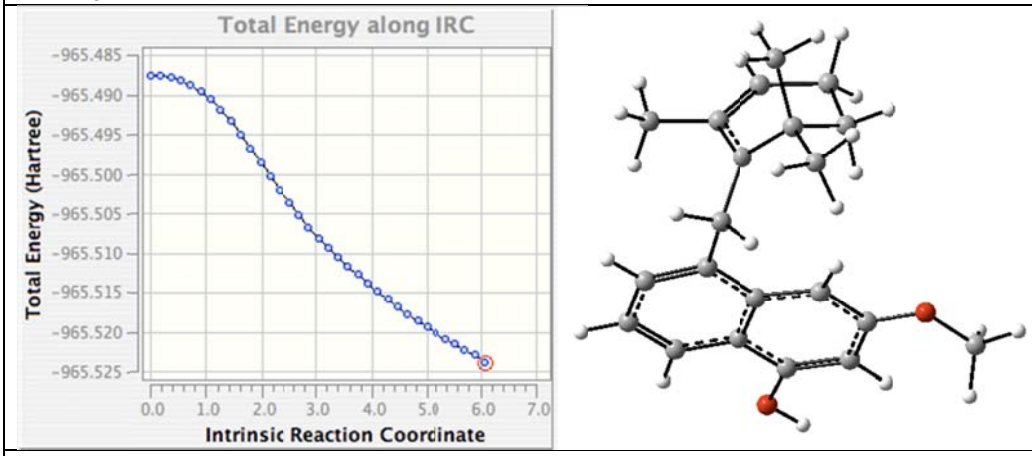
TS $_{A1'-E1'}$→E1'



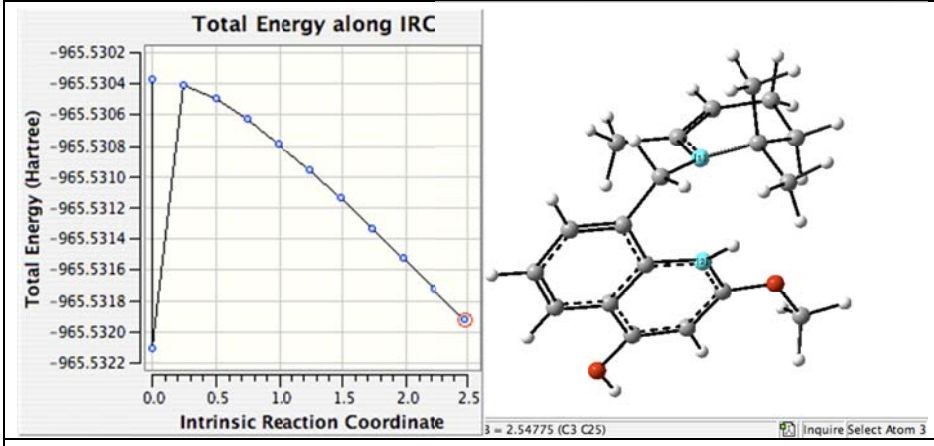
TS $_{E1'-C1'}$→E1'



TS $_{E1'\text{-}C1'}$→C1'



TS $_{C1'\text{-}D1'}$→C1'



TS $_{C1'\text{-}D1'}$→D1'

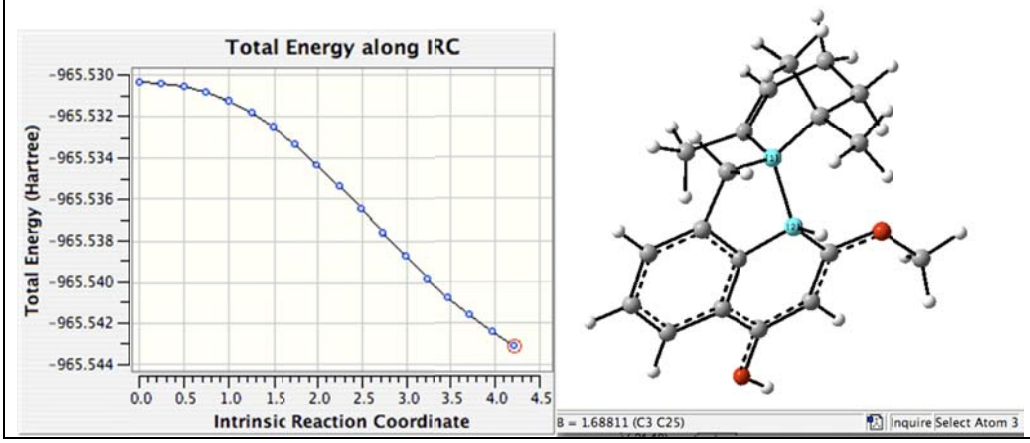
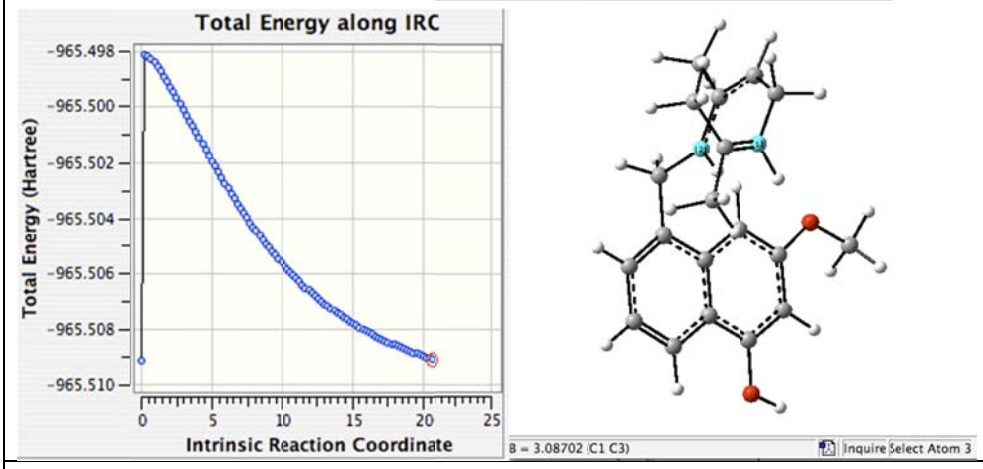


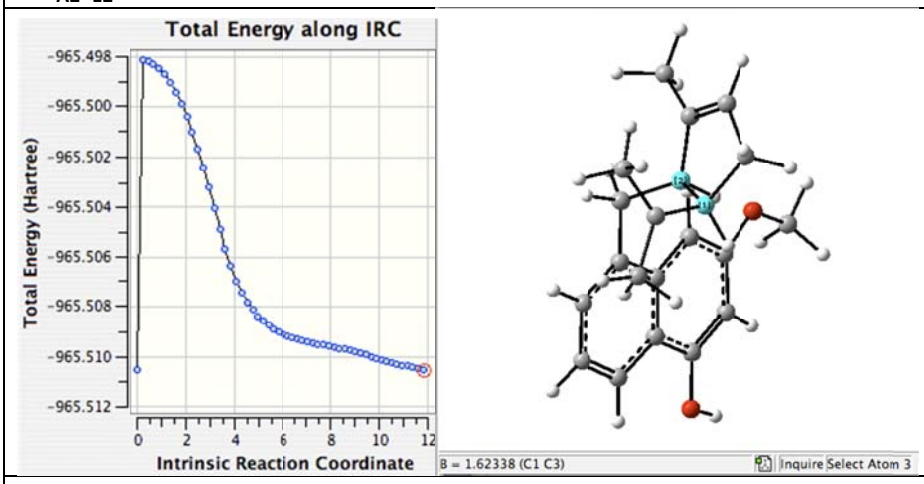
Table S5 (vii). IRC plots. Path 2: **A2'→D2'**

Correspond to structures in Figure S10(viii).

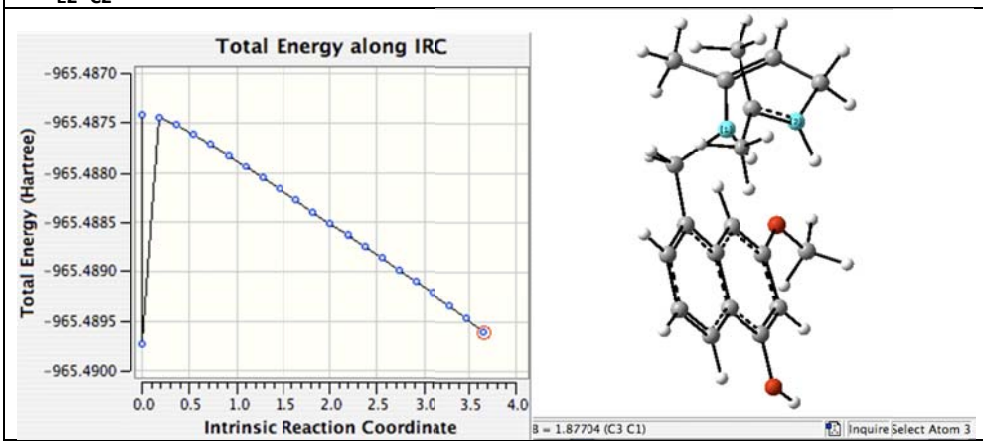
TS $_{A2'-E2'}$→A2'



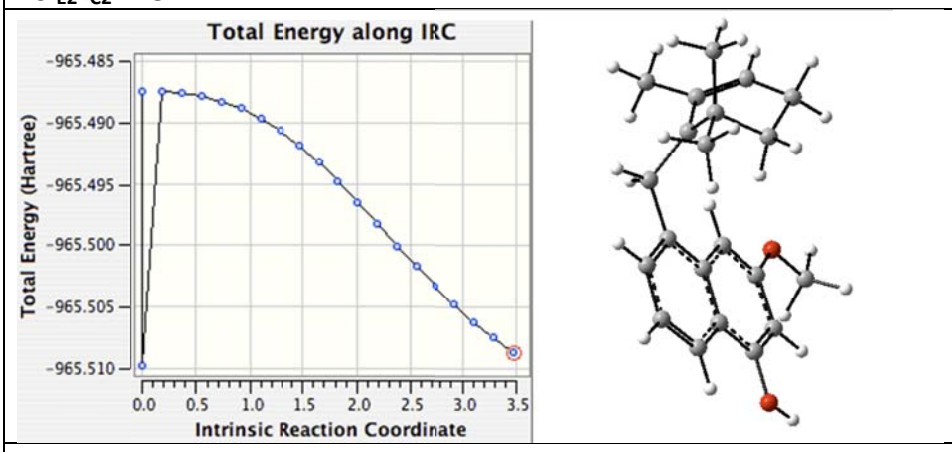
TS $_{A2'-E2'}$→E2'



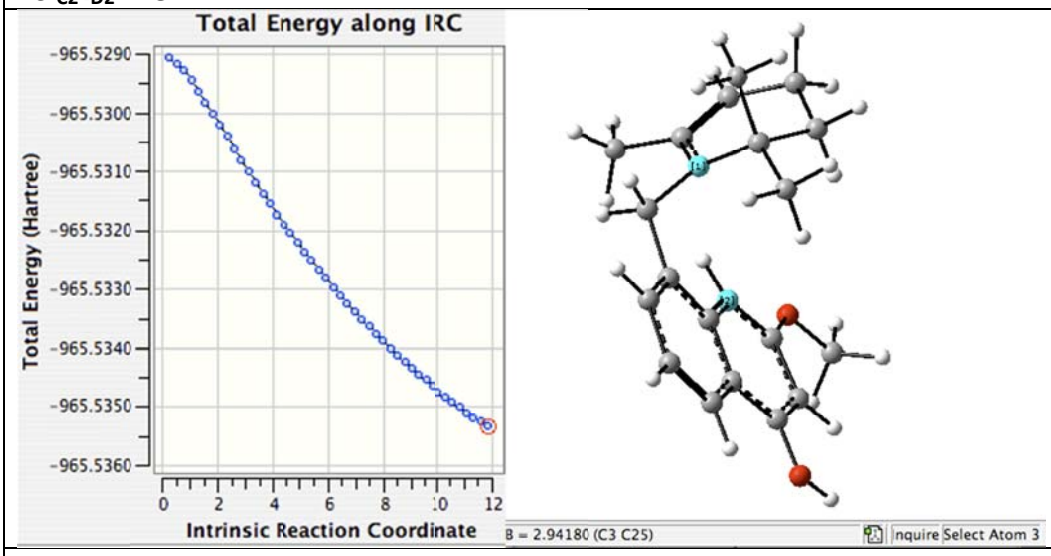
TS $_{E2'-C2'}$→E2'



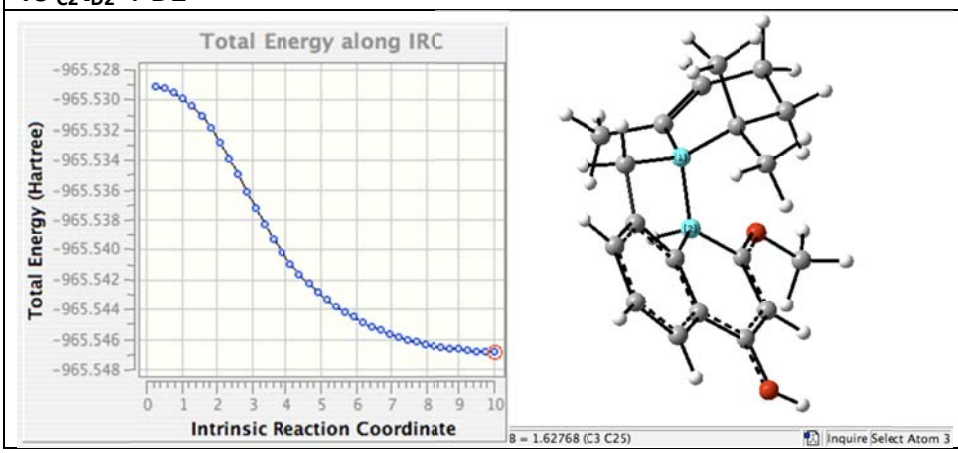
TS $_{E2'-C2'}$→C2'



TS $_{C2'-D2'}$→C2'



TS $_{C2'-D2'}$→D2'



Supplementary Figures

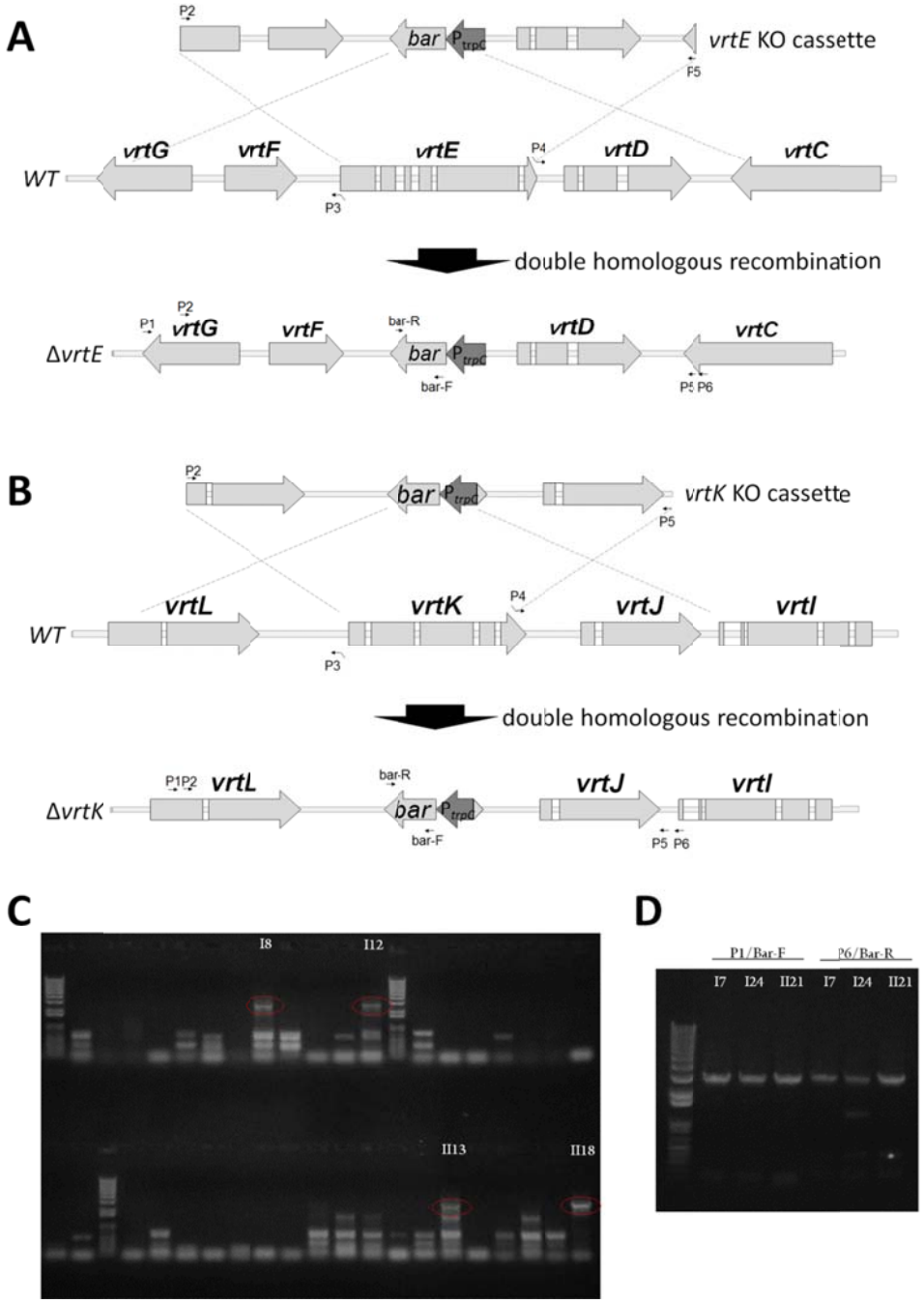


Figure S1. Gene deletion strategy for (A) *vrtE* and (B) *vrtK*, by double homologous replacement in *P. aethiopicum* Δ*gsfA*::*zeo*^{R}. Each of the flanking homologous region on the knockout (KO) cassette is about 2 kb in length. Primer pairs P1/bar-F and P6/bar-R were used for screening of positive transformants. 48 colonies from each transformation were first screened by P1/bar-F primers from genomic DNA extracted with a rapid toothpick/alkaline lysis miniprep method described previously,[2,4] (C) an example of gel electrophoresis for screening of Δ*vrtK* colonies using P1/bar-F (correct band size circled). Positive transformants is re-verified with both pair of primers using higher quality genomic DNA, e.g. (D) Δ*vrtE* positive transformants.

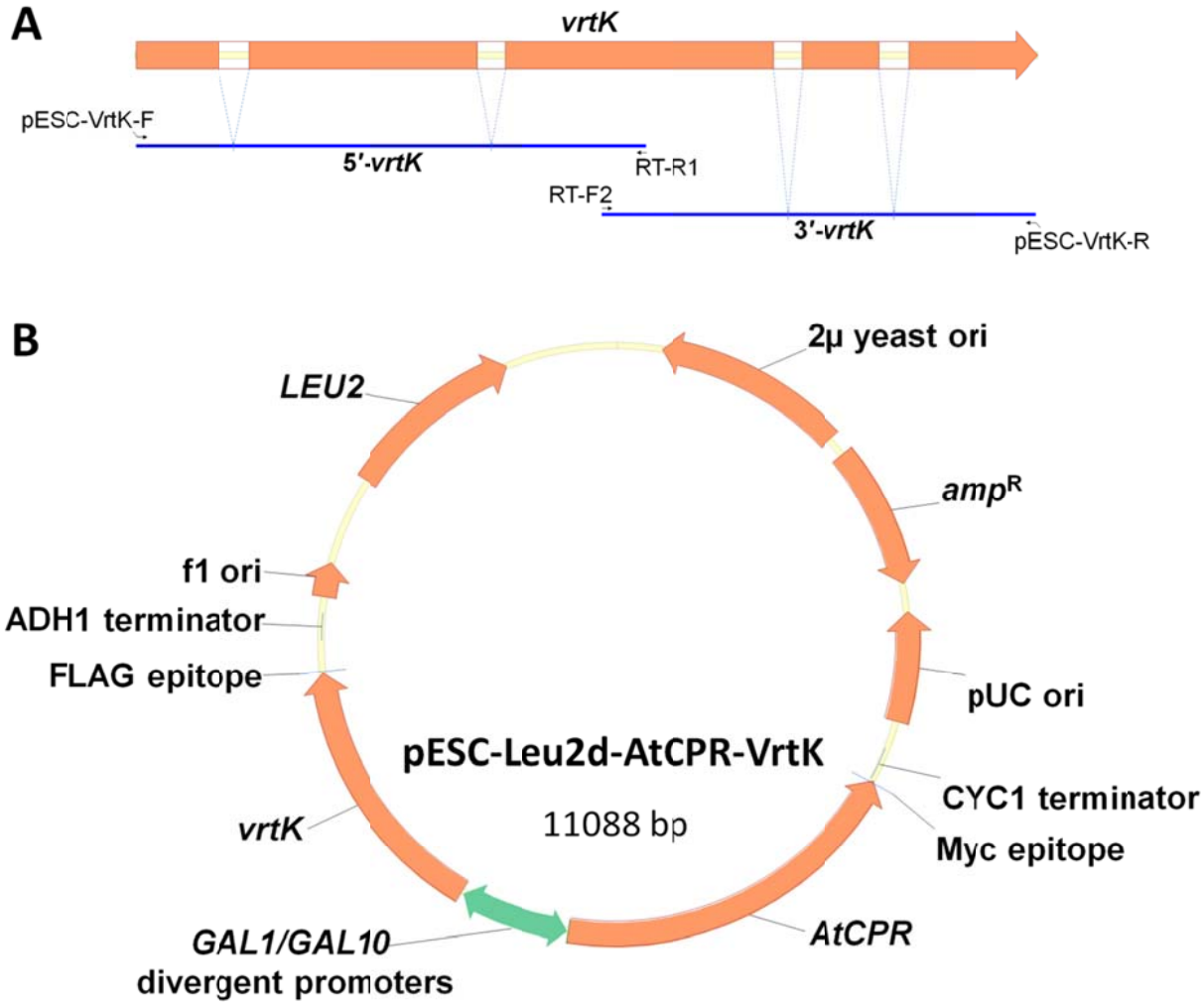


Figure S2. Construction of pESC-Leu2d-AtCPR-VrtK. (A) RT-PCR of overlapping 5'-*vrtK* and 3'-*vrtK* fragments. (B) The plasmid map of pESC-Leu2d-AtCPR-VrtK containing *A. terreus* cytochrome P450 reductase (AtCPR) gene and *vrtK* under the regulation of *GAL1/GAL10* divergent promoter.

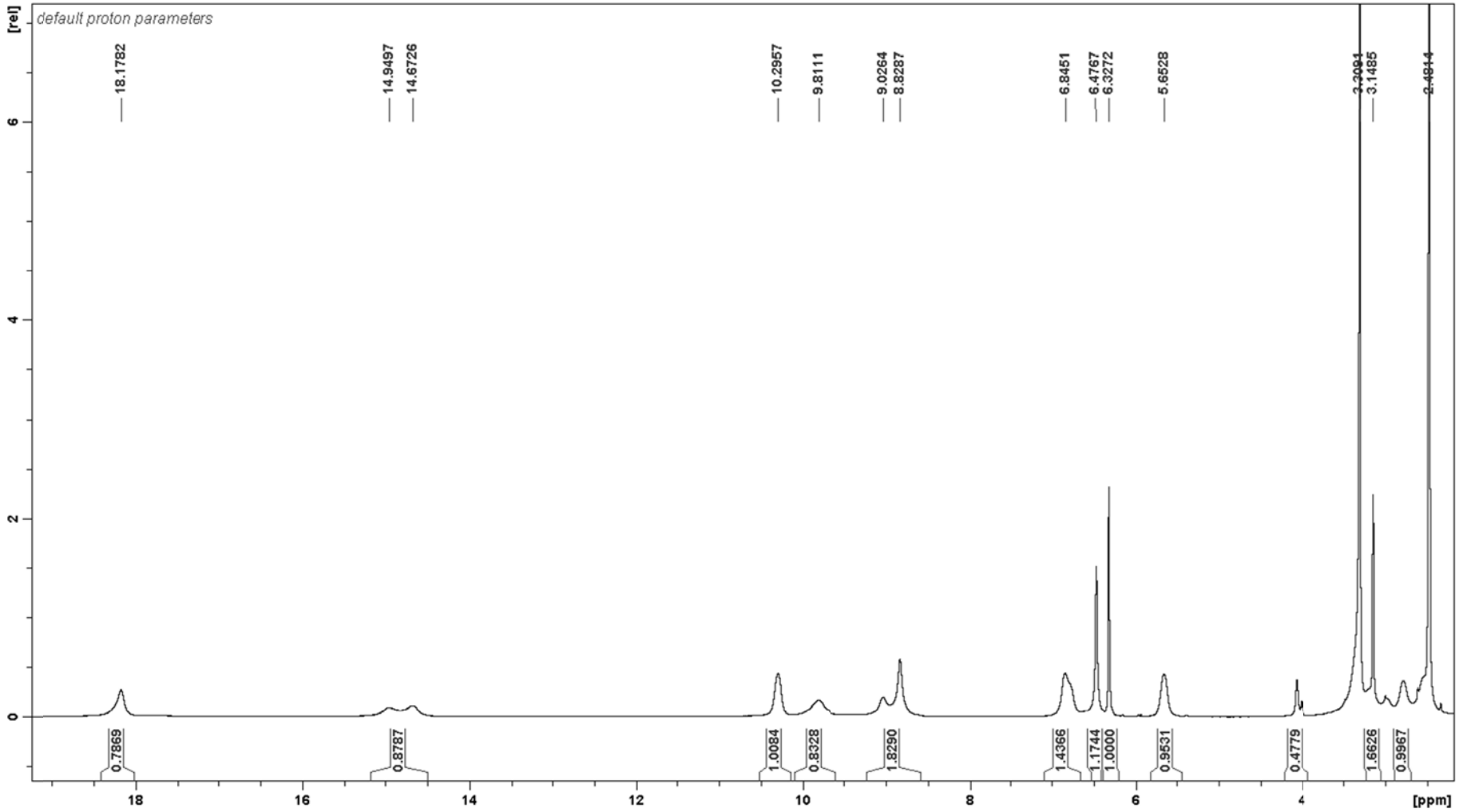


Figure S3. ^{1}H-NMR spectrum of compound **3** in DMSO-d6 measured on 500 MHz Bruker NMR spectrometer (see Table S2 for peak assignments).

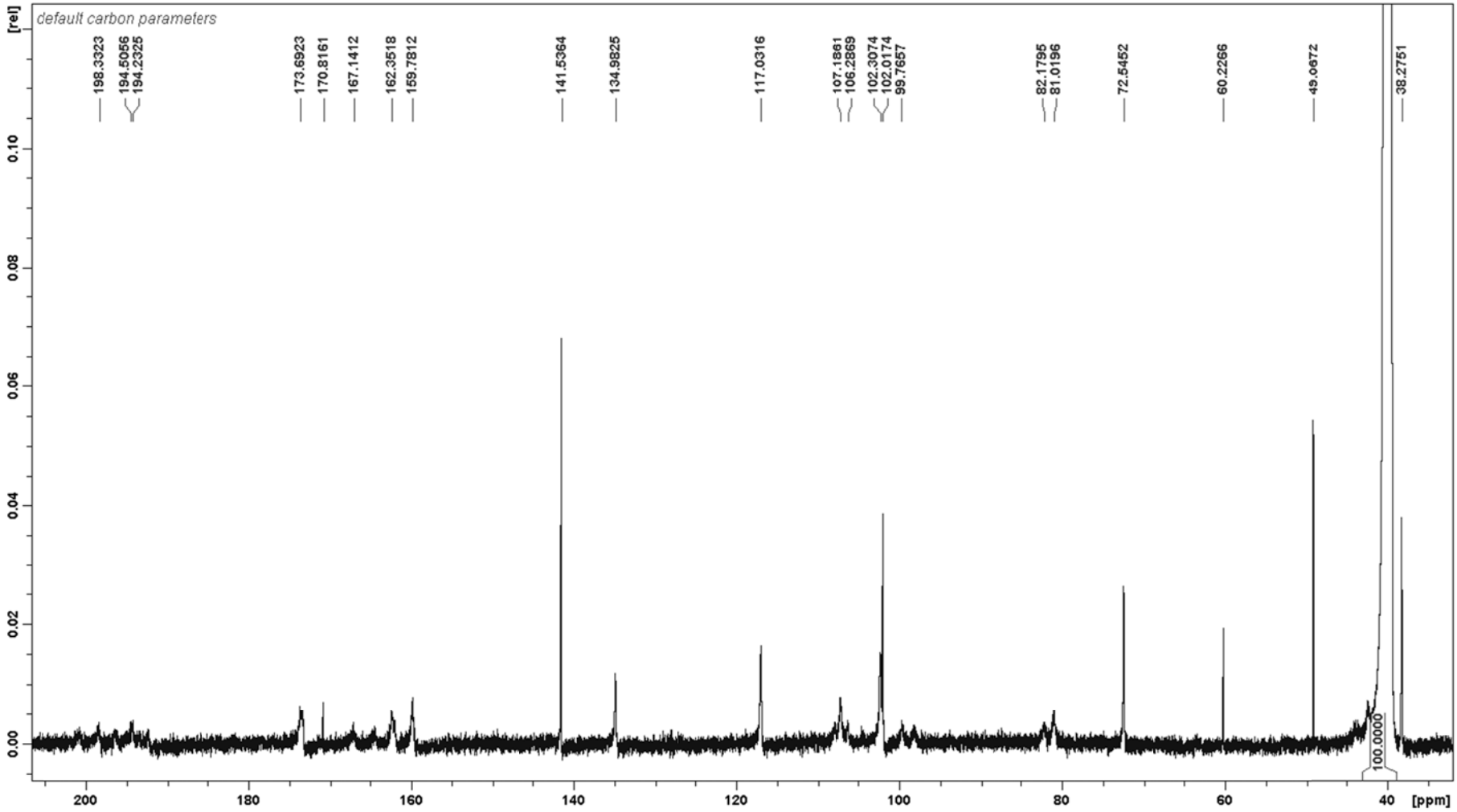


Figure S4. ^{13}C-NMR spectrum of compound **3** in DMSO-d6 measured on 500 MHz Bruker NMR spectrometer (see Table S2 for peak assignments).

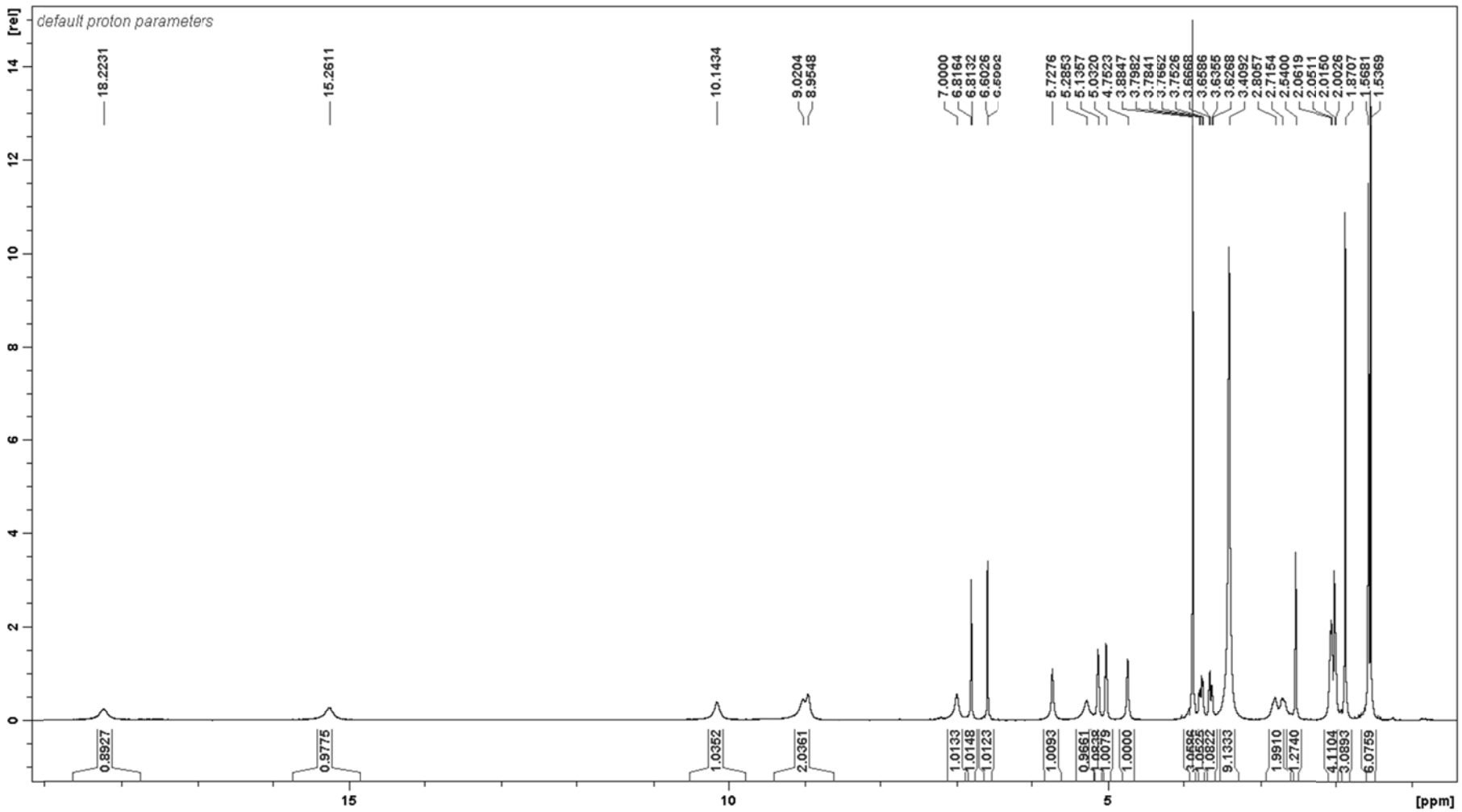


Figure S5. ^{1}H-NMR spectrum of compound **2** in DMSO-d6 measured on 500 MHz Bruker NMR spectrometer (see Table S3 for peak assignments).

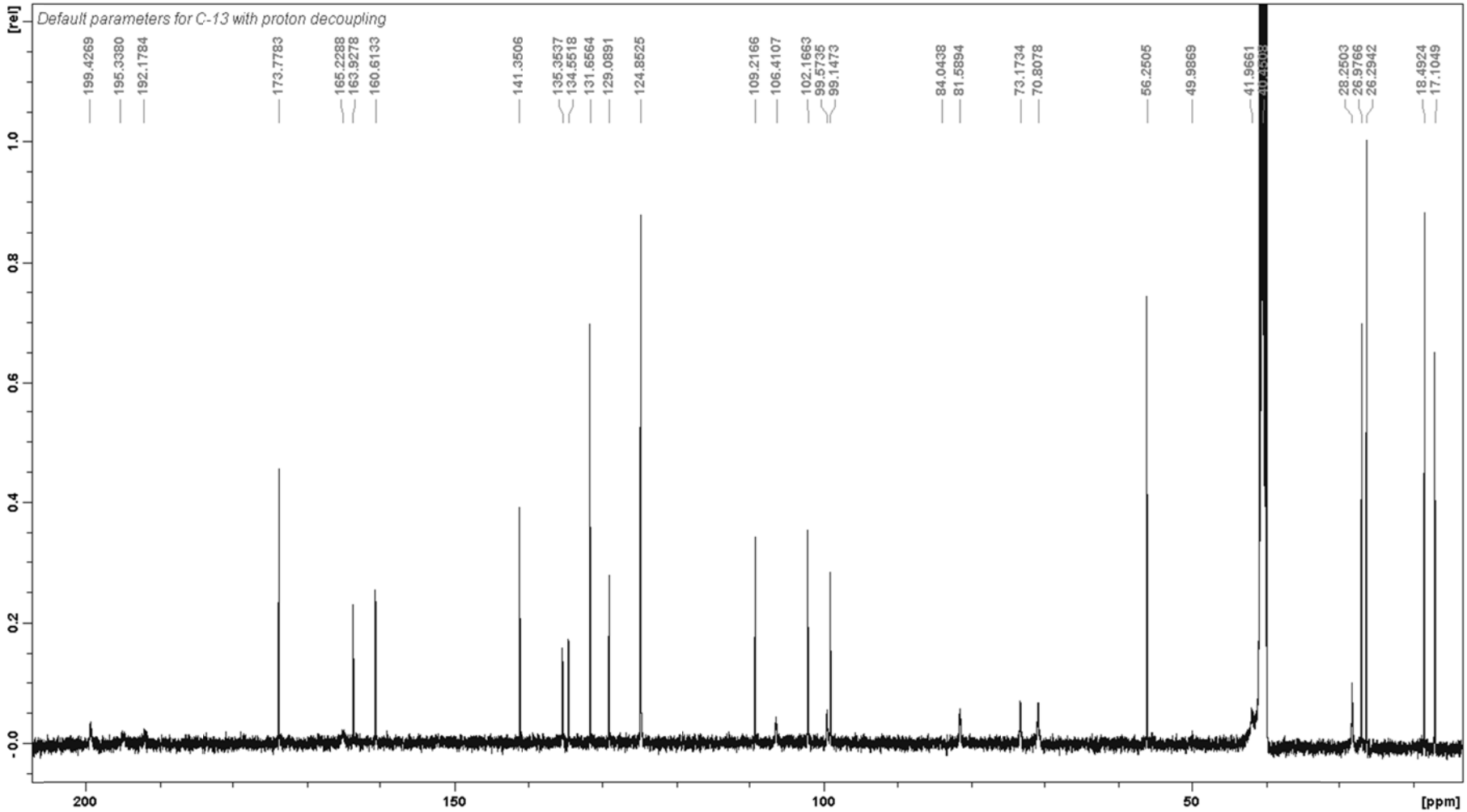


Figure S6. ^{13}C-NMR spectrum of compound **2** in DMSO-d6 measured on 500 MHz Bruker NMR spectrometer (see Table S3 for peak assignments).

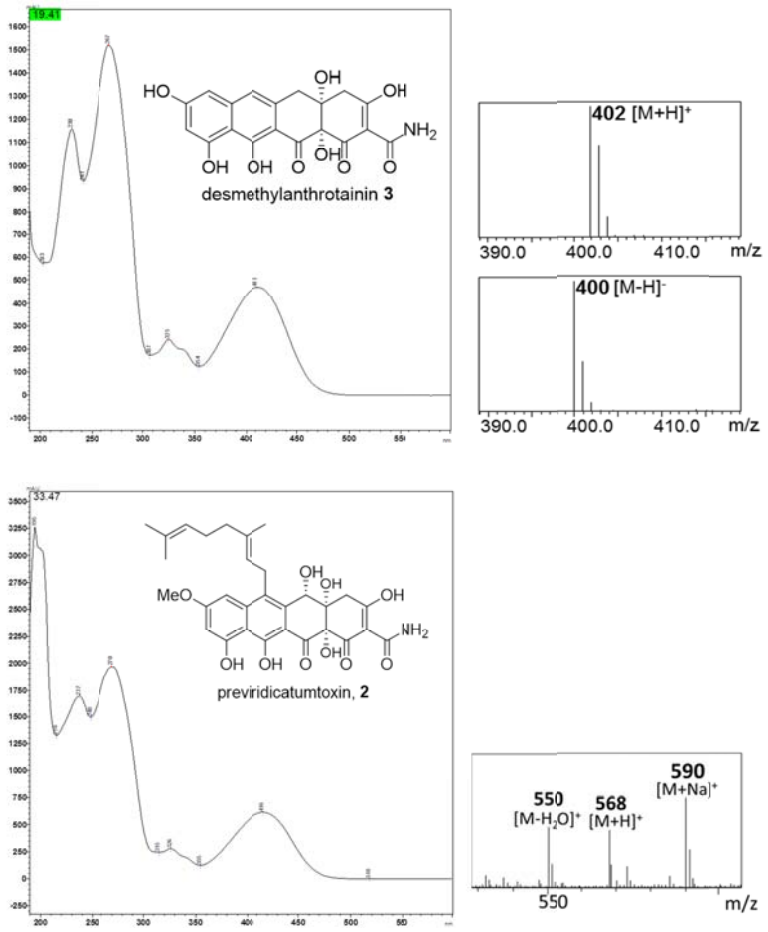


Figure S7. UV and mass spectra of **3** and **2**.

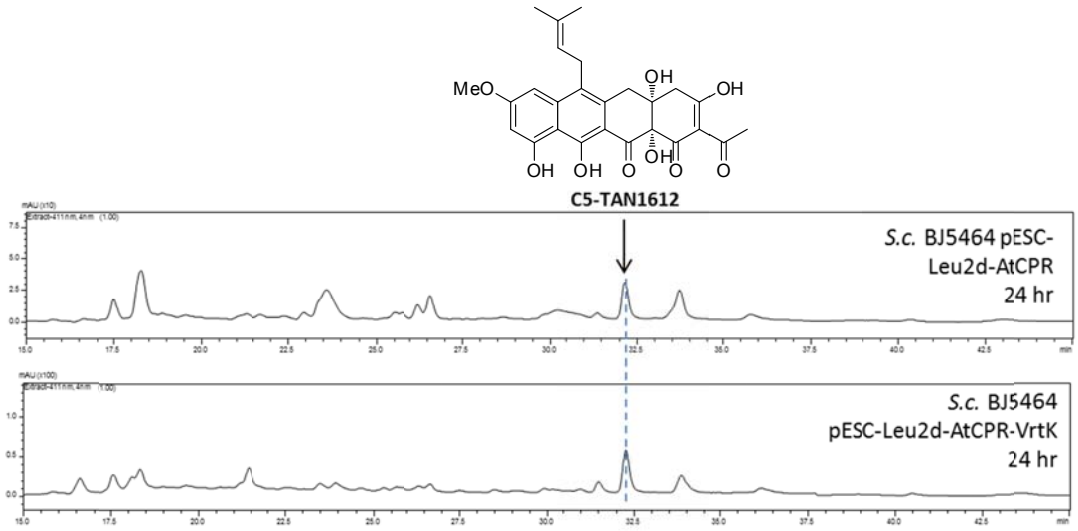


Figure S8. Feeding of dimethylallyl(C5)-TAN1612 substrate to high density yeast cultures. conversion of the substrate can be observed in both the experimental (pESC-Leu2d-AtCPR-V and negative control (pESC-Leu2d-AtCPR). Compound **2** can be converted to **1** in the sa experiment, as shown in Figure 2.

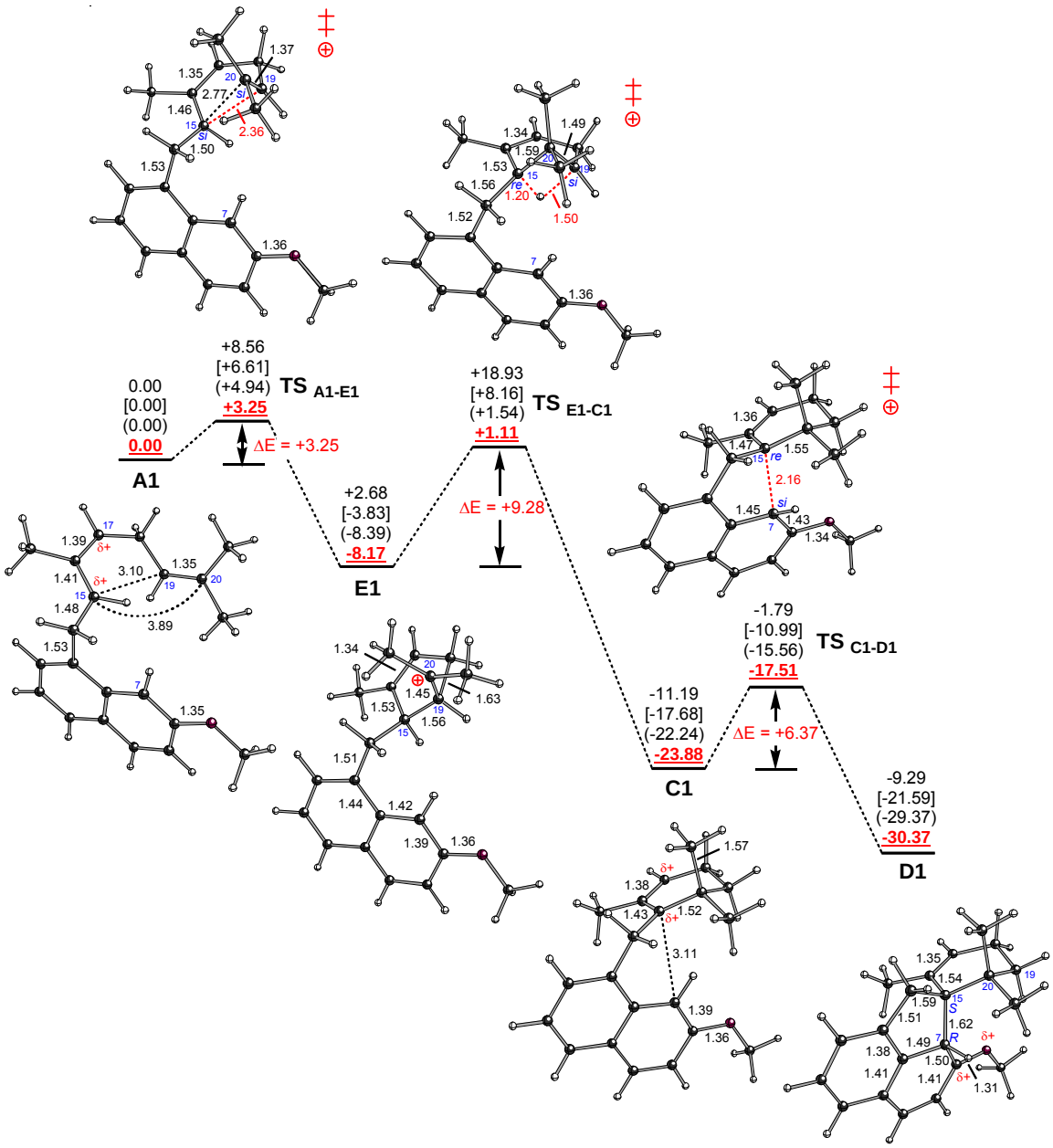


Figure S9 (i). Computed Reaction Pathways. Path 1: **A1→D1**.
Reaction energy diagram from M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p) calculations for **path 1**; Energies (in kcal/mol) from B3LYP (in normal texts), mPW1PW91 (in brackets), MPWB1K (in parentheses) are also shown. Overall the highest barrier (9.28 kcal/mol) is in the step involving hydride shift (**E1→C1**). Path 1 leads to (*7R,15S)*-**D1** and subsequent deprotonation will generate **1a**.

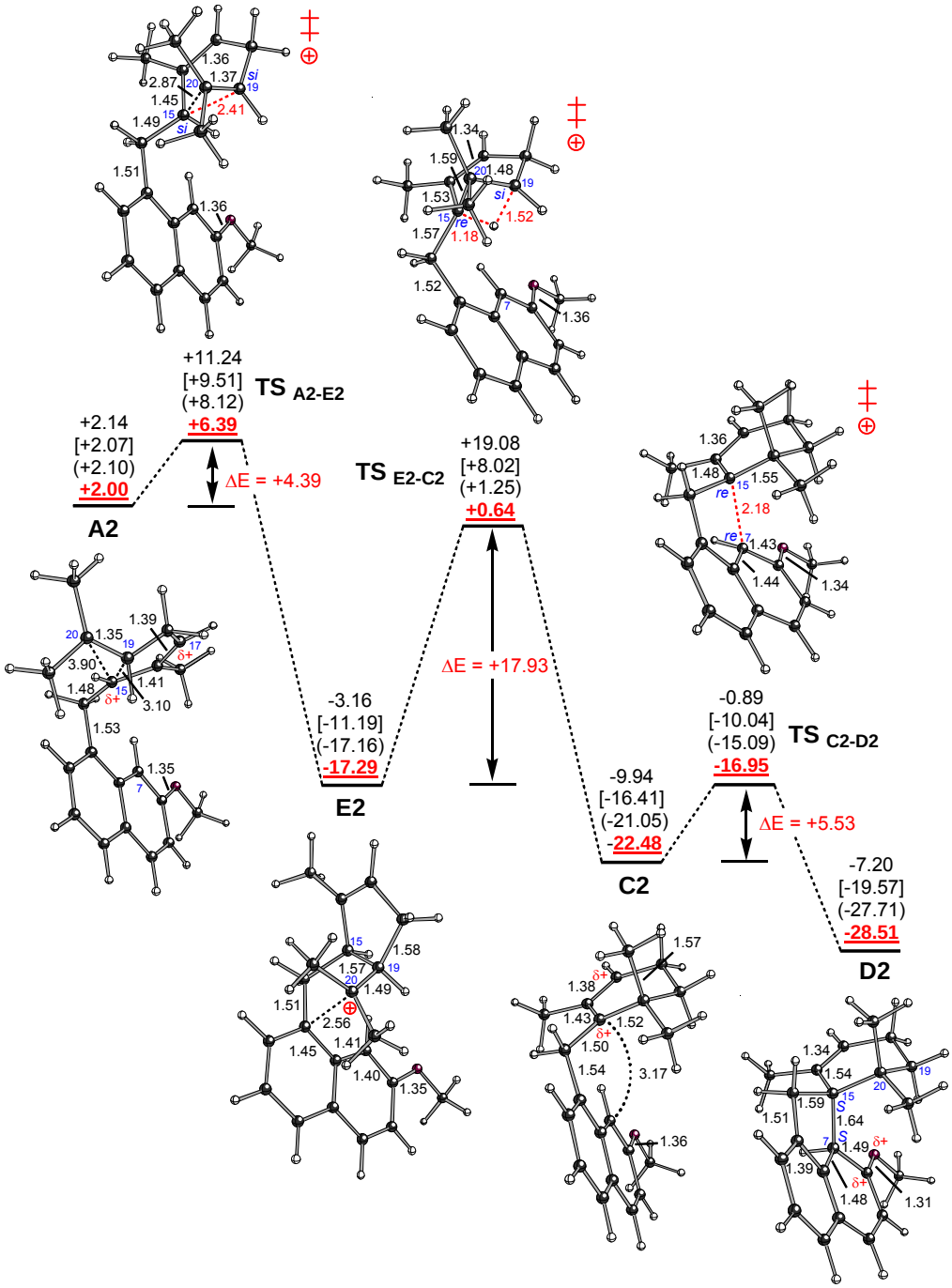


Figure S9 (ii). Computed Reaction Pathways. Path 2: **A2**→**D2**.
Reaction energy diagram from M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p) calculations for **path 2**; Energies (in kcal/mol) from B3LYP (in normal texts), mPW1PW91 (in brackets), MPWB1K (in parentheses) are also shown. The step involving hydride shift has overall the highest barrier (17.93 kcal/mol). **E2** is significantly more stable than **E1** (stabilization through cation-π interaction), which results in increase in the barrier for hydride transfer. Note **TS** $_{\mathbf{E2\text{-}C2}}$ has slightly lower energy than that of **TS** $_{\mathbf{E1\text{-}C1}}$. **D2** is a diastereomer of **D1** (Fig. S1). Deprotonation of **D2** will also generate **1a**. For an alternative conversion of **E2**, see Fig. S4.

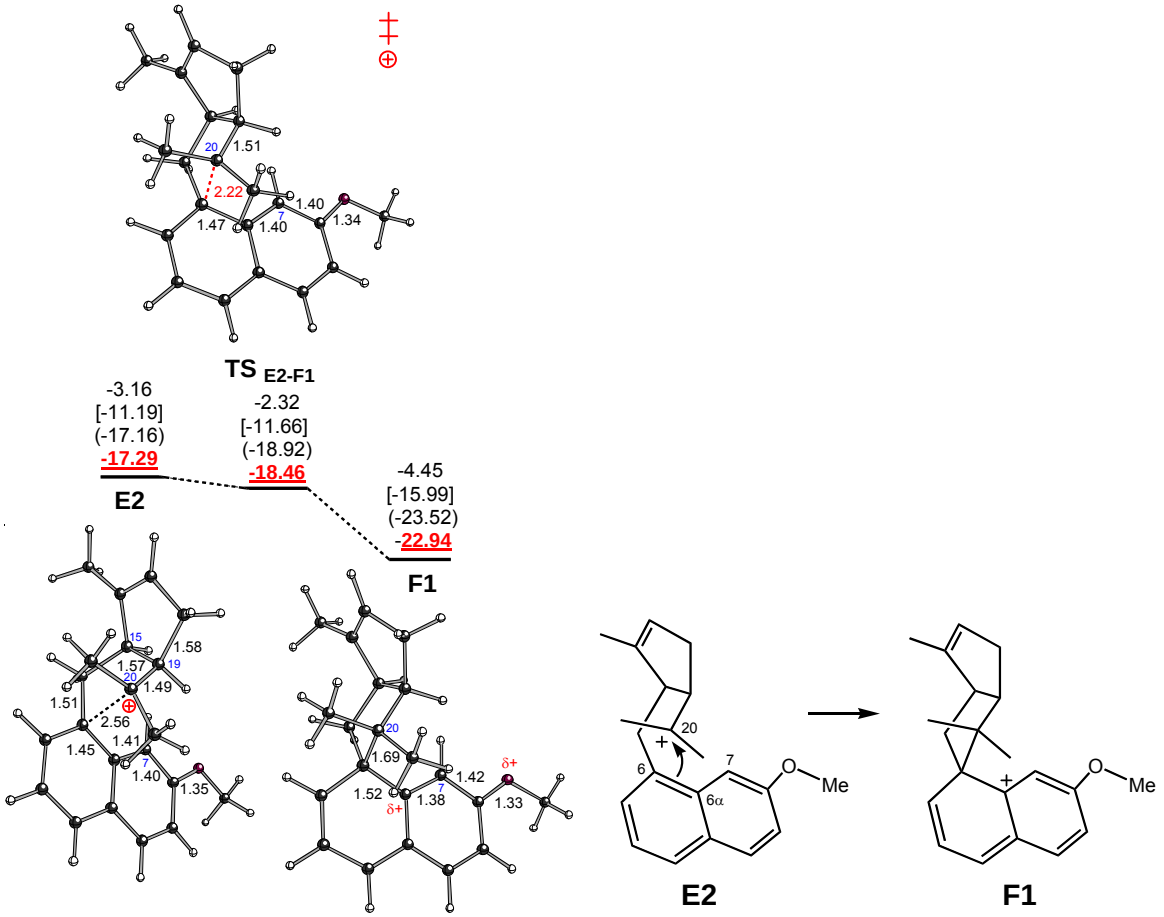


Figure S9 (iii). Computed Reaction Pathways. **E2→F1** conversion.
E2→F1 conversion (M06-2X/6-31+G(d,p) in red and underlined); Energies (in kcal/mol) from B3LYP (in normal texts), mPW1PW91 (in brackets) and MPWB1K (in parentheses) are also shown.

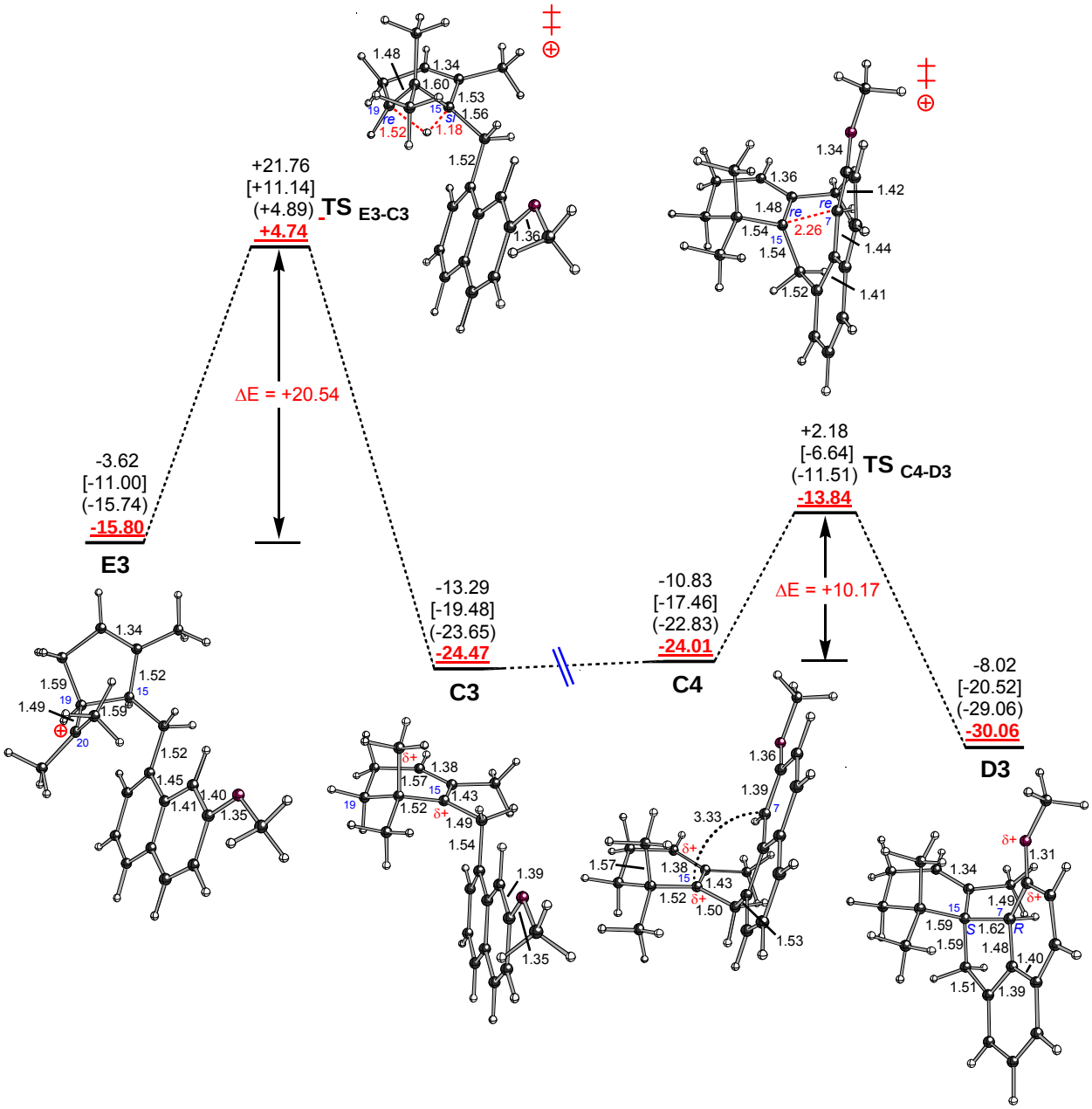


Figure S9(iv). Computed Reaction Pathways. Path 3: **E3**→**D3**.
Reaction energy diagram from M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p) calculations for **path 3**; Energies (in kcal/mol) from B3LYP (in normal texts), mPW1PW91 (in brackets), MPWB1K (in parentheses) are also shown. The step involving hydride shift has 20.54 kcal/mol barrier. Transition state structure for the hydride transfer for anti assembled **C** (such as **C4** conformation) could not be found due to steric clash (See Fig. S7, top). Conformation change of **C3** to **C4** may also experience steric clash. In addition, steric clash is expected in **C3** conformation in the case of full system. **E3** is significantly more stable than **E1** (Fig. S1, path 1) while energy of **TS** $_{\mathbf{E3\text{-}C3}}$ is ~4 kcal/mol higher than that of **TS** $_{\mathbf{E1\text{-}C1}}$ (Fig. S1, path 1). For the **C4**→**D3** has ~4kcal/mol higher barrier compared to corresponding reaction in path 1. Deprotonation of **D3** (conformation isomer of **D1** (Fig. S1)) will generate **1a**.

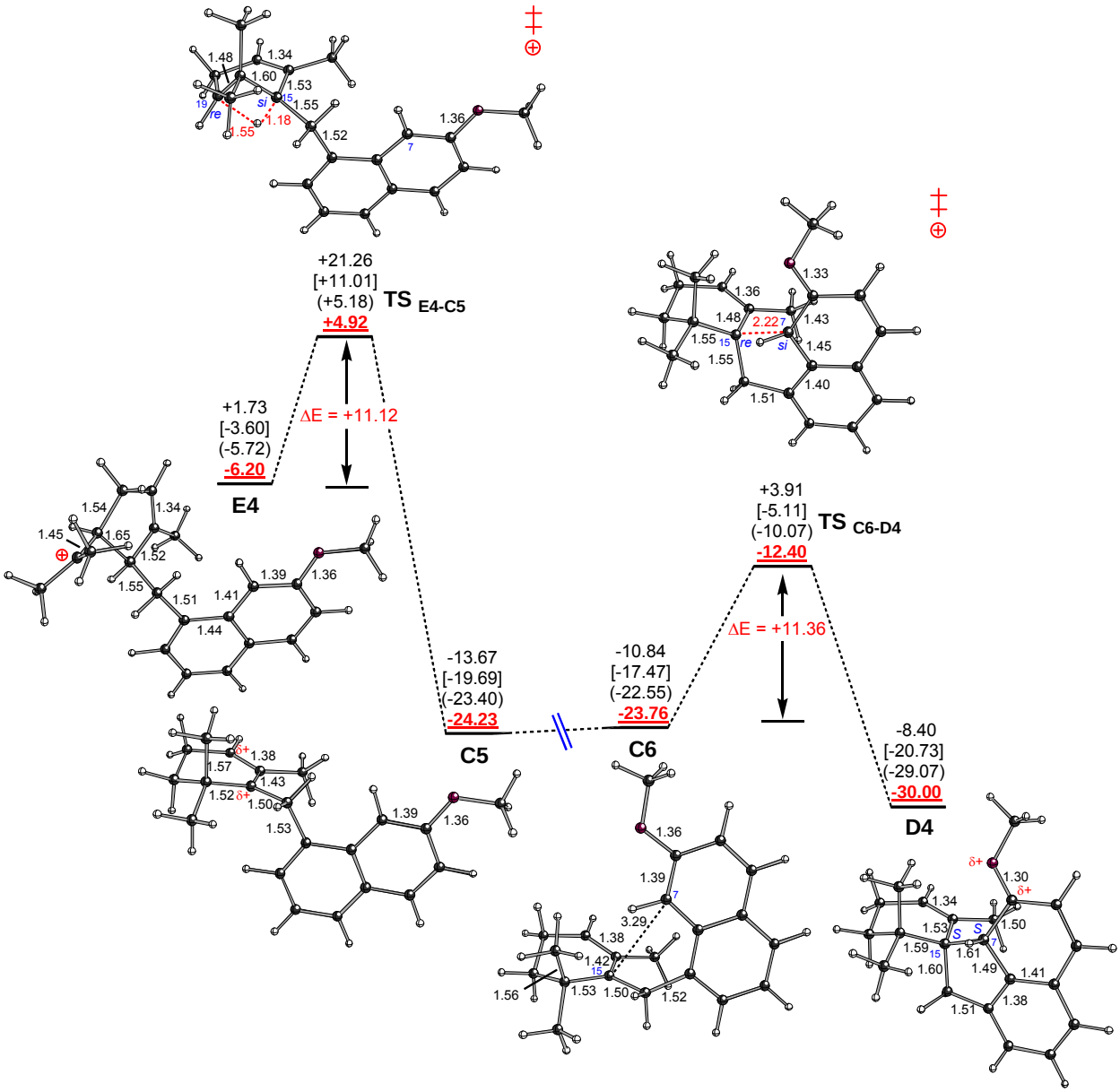


Figure S9 (v). Computed Reaction Pathways. Path 4: **E4**→**D4**.
Reaction energy diagram and computed transition state structures and carbocation structures from M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p) calculations for **path 4**; Energies (in kcal/mol) from B3LYP (in normal texts), mPW1PW91 (in brackets), MPWB1K (in parentheses) are also shown. The step involving hydride shift has 11.12 kcal/mol barrier. **TS** $_{\mathbf{C6\text{-}D4}}$ has ~5kcal/mol higher energy than that of **TS** $_{\mathbf{C1\text{-}D1}}$ (Fig. S1, path 1). Steric clash likely impedes hydride shift of *anti* assembly of **C** that may lead to **C6** (See Fig. S7, bottom). Deprotonation of **D4** (conformation isomer of **D2** (Fig. S2)) will generate **1a**.

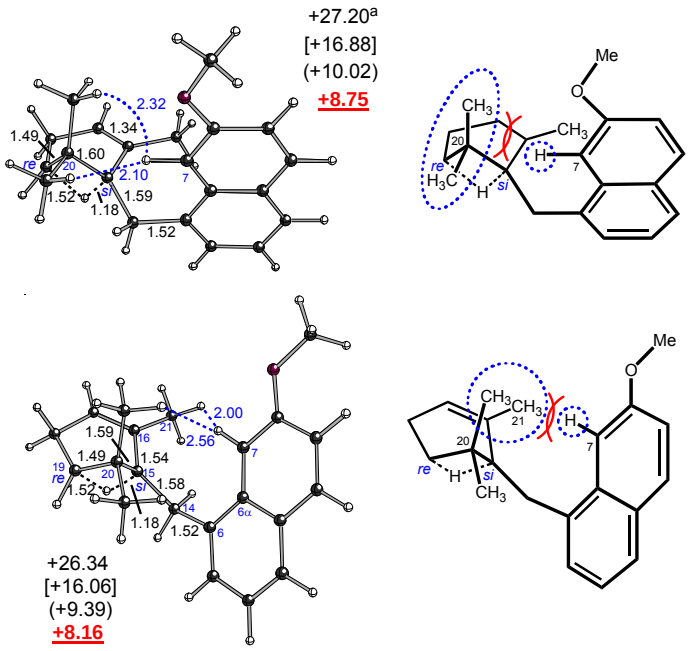


Figure S9 (vi). Computed Reaction Pathways. *si*→*re* Facial 1,3-hydride shift.
Computed geometries (***not stationary points***) for *si*→*re* facial 1,3-hydride shift (B3LYP/6-31+G(d,p); imaginary frequency corresponds to hydride shifting motion, distances C5-H-C19 and dihedral angle C15-C14-C6-C6α are constrained.). Energies (kcal/mol) are relative to that of **A1** (Fig. S1). B3LYP/6-31+G(d,p) in normal texts, mPW1PW91/6-31+G(d,p) in brackets, MPWB1K/6-31+G(d,p) in parentheses and M06-2X/6-31+G(d,p) in red and underlined. Aromatic ring (especially hydrogen at C7) clashes with methyl groups in cyclohexenyl ring. Full optimization of top and bottom structures without constrains led to transition state structures **TS** $_{\mathbf{E3\text{-}C3}}$ (Fig. S5) and **TS** $_{\mathbf{E4\text{-}C5}}$ (Fig. S6), respectively. [a] small additional imaginary frequency (-7.07 cm^{-1}) is associated with aromatic ring movement.

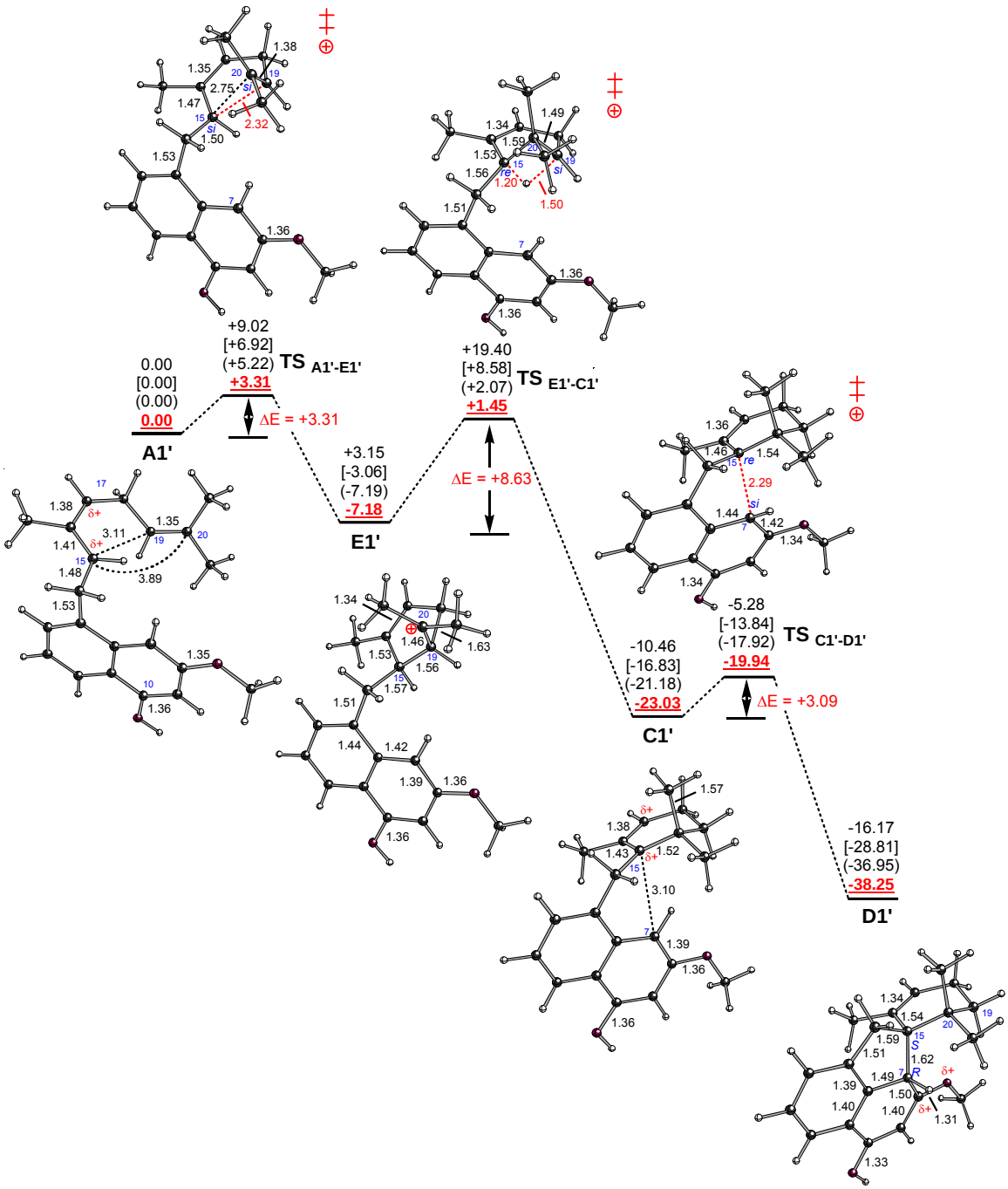


Figure S9 (vii). Computed Reaction Pathways. Path 1: **A1'→D1'**.
Reaction energy diagram from M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p) calculations for path 1 (Scheme 2; R=OH, Fig. 3 and Table 1); Energies (in kcal/mol) from B3LYP (in normal text), mPW1PW91 (in brackets), MPWB1K (in parentheses) are also shown. Overall the highest barrier (9.28 kcal/mol) is in the step involving hydride shift (**E1'→C1'**). Path 1 leads to (*7R,15S)*-**D1'** and subsequent deprotonation will generate **1a'**.

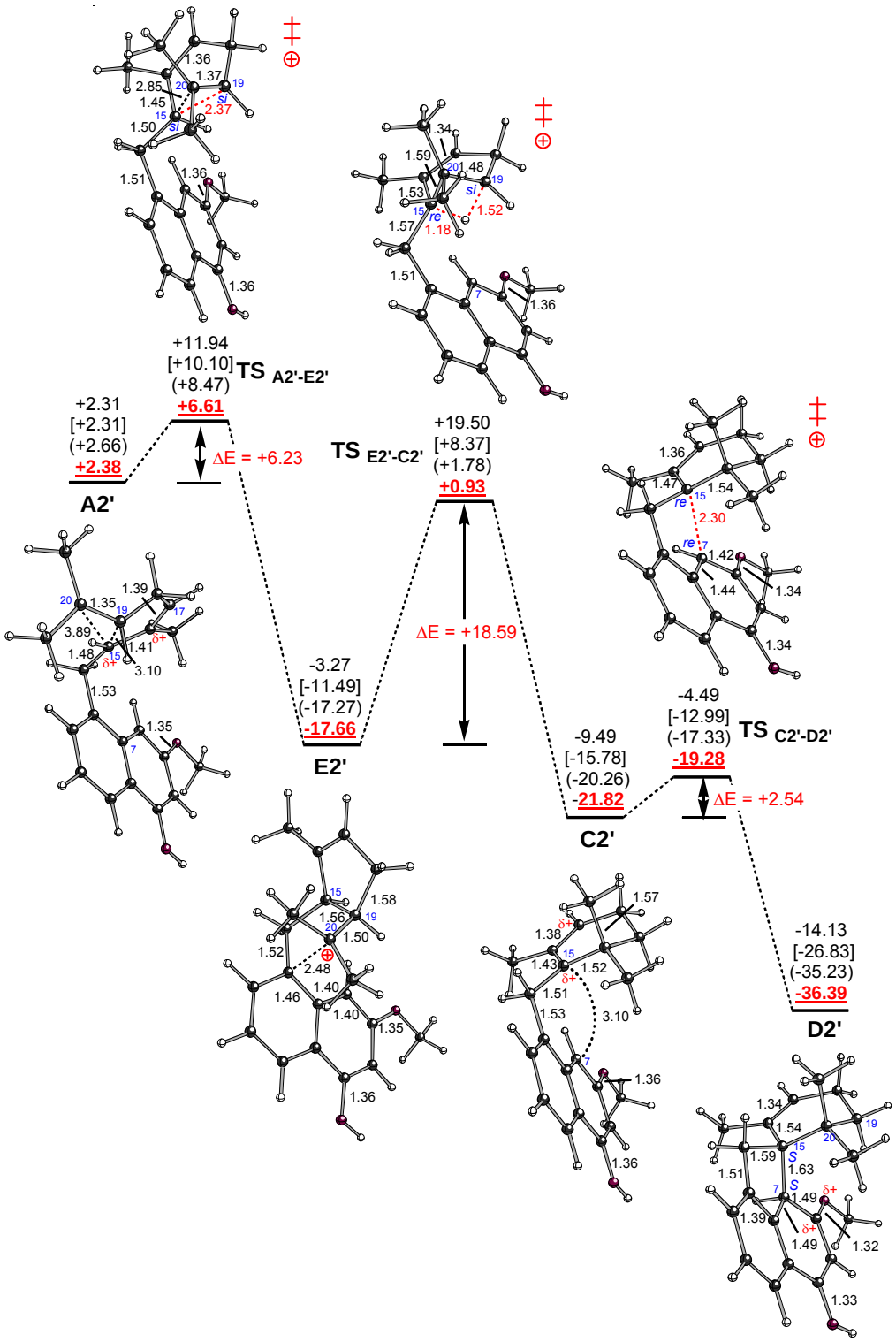


Figure S9 (viii). Computed Reaction Pathways. Path 2: **A2'→D2'**.
Reaction energy diagram from M06-2X/6-31+G(d,p)//B3LYP/6-31+G(d,p) calculations for path 2 (Scheme 2; R=OH, Fig. 3 and Table 1); Energies (in kcal/mol) from B3LYP (in normal texts), mPW1PW91 (in brackets), MPWB1K (in parentheses) are also shown. The step involving hydride shift has overall the highest barrier (17.93 kcal/mol). Deprotonation of **D2'** (a diatereomer of **D1'**) will also generate **1a'**

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