

Torsional Steering Controls the Stereoselectivity of Epoxidation in the Guanacastepene A Synthesis

Paul Ha-Yeon Cheong, Heedong Yun,[†] Samuel J. Danishefsky,[†] K. N. Houk,*

Contributions from the Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569, and the [†]Department of Chemistry, Columbia University, 3000 Broadway, New York, NY 10027

Gaussian03 Citation:

Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

Supporting Information

Computational Data:

Reactant - Acetone Optimization

Supporting Information: Acetone.output

Using Gaussian 98: x86-Linux-G98RevA.9 19-Apr-2000

=====

```
#b3lyp/6-31g* density=current ginput gfprint iop(6/7=1) iop(6/7=3)
scf=(maxcycle=300) opt=(maxcycle=150) pop=full fmm freq=noraman
#N Geom=AllCheck Guess=TCheck Test RB3LYP/6-31G(d) Freq
```

```
Pointgroup= CS Stoichiometry= C3H6O CS[SG(C3H2O),X(H4)] #Atoms= 10
Charge = 0 Multiplicity = 1
```

```
SCF Energy= -193.155694571 Predicted Change= -2.009967D-08
```

```
Optimization completed. {Found 2 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00002 || 0.00045 [ YES ] 0.00001 || 0.00030 [ YES ]
Displ 0.00023 || 0.00180 [ YES ] 0.00023 || 0.00180 [ YES ]
```

```
Atomic Coordinates (Angstroms)
Type X Y Z
```

C	0.000000	0.185249	0.000000
O	-0.000002	1.400933	0.000000
C	-1.293117	-0.614717	0.000000
H	-1.341543	-1.267377	0.880903
H	-2.148566	0.063615	0.000000
H	-1.341543	-1.267377	-0.880903
C	1.293118	-0.614724	0.000000
H	1.341551	-1.267388	0.880901
H	1.341551	-1.267388	-0.880901
H	2.148564	0.063610	0.000000

```
Statistical Thermodynamic Analysis
```

```
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
```

```
SCF Energy= -193.155694571 Predicted Change= -2.009967D-08
Zero-point correction (ZPE)= -193.0716 0.08407
Internal Energy (U)= -193.0661 0.08949
Enthalpy (H)= -193.0652 0.09044
Gibbs Free Energy (G)= -193.1002 0.05547
```

```
Frequencies -- 37.4559 135.1180 375.6749
```

Supporting Information

Reactant - Dimethyldioxirane Optimization
 Supporting Information: GS-Reactant-DMDO.output

Using Gaussian 03: A164T-G03RevC.01 3-Apr-2004

freq=norman b3lyp/6-31g(d) opt=(maxcycle=250) scf=(maxcycle=300,tight)
 #N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/6-31G(d) Freq

Pointgroup= C1 Stoichiometry= C3H6O2 C1[X(C3H6O2)] #Atoms= 11
 Charge = 0 Multiplicity = 1

SCF Energy= -268.268936220 Predicted Change= -1.587221D-07

Optimization completed.		{Found 2 times}	
Item	Max Val.	Criteria	Pass?
Force	0.00013	0.00045	[YES]
Displ	0.00063	0.00180	[YES]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	0.094164	0.000000	-0.000003
C	0.872193	-1.293753	-0.000007
H	0.179026	-2.137312	0.000025
H	1.514176	-1.353552	-0.885992
H	1.514229	-1.353528	0.885942
C	0.872193	1.293753	-0.000049
H	1.514181	1.353524	-0.886032
H	0.179025	2.137312	-0.000047
H	1.514224	1.353556	0.885902
O	-1.090361	0.000014	0.752654
O	-1.090409	-0.000014	-0.752585

Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -268.268936220 Predicted Change= -1.587221D-07
 Zero-point correction (ZPE)= -268.1802 0.08868
 Internal Energy (U)= -268.1746 0.09432
 Enthalpy (H)= -268.1736 0.09526
 Gibbs Free Energy (G)= -268.2085 0.06039

Frequencies -- 164.6433 213.1699 352.7729

Supporting Information

Reactant - Model Guanacastepene A precursor
Supporting Information: GS-Reactant-CP.output

Using Gaussian 03: A164T-G03RevC.01 3-Apr-2004

=====

freq=norman b3lyp/6-31g(d) opt=(maxcycle=250) scf=(maxcycle=300,tight)
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/6-31G(d) Freq

Pointgroup= C1 Stoichiometry= C12H18O2 C1[X(C12H18O2)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -618.54825539 Predicted Change= -1.497922D-10

=====

Optimization completed. {Found 2 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00000 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
Displ 0.00027 || 0.00180 [YES] 0.00027 || 0.00180 [YES]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	0.014591	-0.699735	-0.191622
C	1.404892	-0.157847	-0.466535
C	1.248630	1.380399	-0.174448
C	-0.251079	1.618069	-0.320878
C	-0.879400	0.304721	-0.160355
H	-0.227949	-1.748054	-0.122501
H	1.584188	-0.267736	-1.551175
C	1.687681	1.811355	1.239520
H	2.760751	1.669423	1.401455
H	1.461804	2.872544	1.387666
H	1.147817	1.246884	2.007855

C	2.579262	-0.890544	0.225018
H	2.522972	-0.703920	1.305876
C	3.928000	-0.362118	-0.292930
H	4.033049	0.719933	-0.161053
H	4.763196	-0.843714	0.228857
H	4.039240	-0.576294	-1.364128
C	2.509480	-2.412252	0.013193
H	2.486832	-2.662190	-1.055868
H	3.390207	-2.900363	0.446882
H	1.624970	-2.856173	0.480709
H	1.807856	1.972108	-0.907693
O	-2.258000	0.297920	-0.038698
C	-2.986842	-0.850740	0.095182
O	-2.518191	-1.962284	0.137874
C	-4.454571	-0.508641	0.183890
H	-4.636595	0.154491	1.035952
H	-4.773070	0.023878	-0.718343
H	-5.032513	-1.426288	0.296830
C	-0.877171	2.782416	-0.528570
H	-0.324418	3.710057	-0.648741
H	-1.959646	2.839833	-0.584789

Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

=====

SCF Energy= -618.54825539 Predicted Change= -1.497922D-10
Zero-point correction (ZPE)= -618.2704 0.27783
Internal Energy (U)= -618.2550 0.29323
Enthalpy (H)= -618.2540 0.29417
Gibbs Free Energy (G)= -618.3131 0.23513

Frequencies -- 36.3209 54.7110 65.6505

Supporting Information

Product Epoxidation Alpha (Chair) - Model Guanacastepene A precursor
 Supporting Information: GS-PROD-CHAIR-QF.output

Using Gaussian 03: A164T-G03RevC.01 3-Apr-2004

opt=maxcycle=150 freq=noraman b3lyp/6-31g(d) geom=connectivity
 scf=(direct,tight,maxcycle=300)
 #N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/6-31G(d) Freq

Pointgroup= C1 Stoichiometry= C12H18O3 C1[X(C12H18O3)] #Atoms= 33
 Charge = 0 Multiplicity = 1

SCF Energy= -693.742040024 Predicted Change= -1.101358D-08

Optimization completed.		{Found		1		times}	
Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?	
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]	
Displ	0.00311	0.00180	[NO]	0.00311	0.00180	[YES]	

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	0.266618	-0.832750	-0.731916
C	1.515075	0.012246	-0.460939
C	0.926589	1.389640	0.041065
C	-0.490422	1.451402	-0.529577
C	-0.902298	0.044024	-0.831823
H	0.177208	-1.878330	-0.454797
H	1.963195	0.189176	-1.449144
C	0.826210	1.504015	1.577996
H	1.807625	1.457690	2.060130
H	0.366745	2.462179	1.843291
H	0.194938	0.709706	1.988540

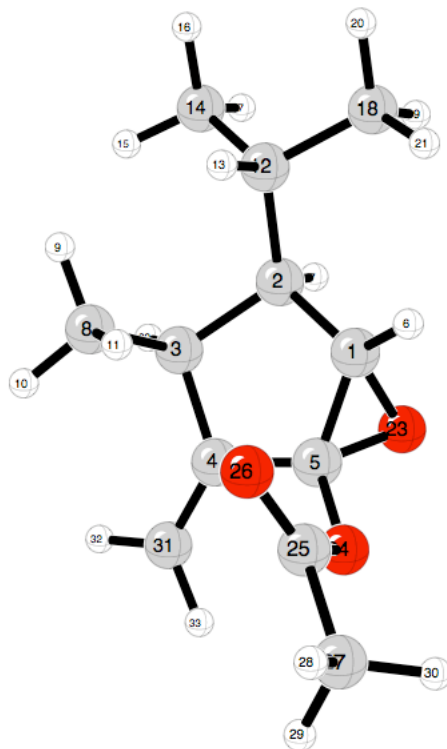
C	2.607080	-0.640870	0.414292
H	2.220325	-0.765374	1.434532
C	3.859274	0.251656	0.472932
H	3.642250	1.256063	0.849838
H	4.622300	-0.190780	1.123735
H	4.299100	0.361232	-0.527027
C	3.001755	-2.032084	-0.112115
H	3.343562	-1.976458	-1.153690
H	3.822353	-2.447298	0.484342
H	2.174856	-2.748491	-0.070420
H	1.532465	2.221499	-0.335641
O	-0.339788	-0.489637	-2.013078
O	-2.239157	-0.346864	-0.638837
C	-2.616134	-0.712092	0.622557
O	-1.864417	-0.750302	1.567877
C	-4.085410	-1.052009	0.647241
H	-4.358512	-1.409707	1.640382
H	-4.675668	-0.163465	0.398673
H	-4.310931	-1.814201	-0.105131
C	-1.258240	2.526817	-0.696482
H	-0.898896	3.527143	-0.468460
H	-2.276602	2.443881	-1.066234

Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-693.742040024	Predicted Change=	-1.101358D-08
Zero-point correction (ZPE)=	-693.4595	0.28248	
Internal Energy (U)=		-693.4435	0.29845
Enthalpy (H)=	-693.4426	0.29939	
Gibbs Free Energy (G)=		-693.5026	0.23934

Frequencies --	48.0897	52.8762	67.3978
----------------	---------	---------	---------

Supporting Information



Name	Definition	Value						
R1	R(1,2)	1.5284	R17	R(8,11)	1.0976	A1	A(2,1,5)	108.0379
R2	R(1,5)	1.5061	R18	R(12,13)	1.1153	A2	A(2,1,6)	121.204
R3	R(1,6)	1.1014	R19	R(12,14)	1.5184	A3	A(2,1,23)	113.8889
R4	R(1,23)	1.4568	R20	R(12,18)	1.5179	A4	A(5,1,6)	124.9255
R5	R(2,3)	1.5633	R21	R(14,15)	1.0976	A5	A(6,1,23)	115.0589
R6	R(2,7)	1.1186	R22	R(14,16)	1.0975	A6	A(1,2,3)	104.6293
R7	R(2,12)	1.5197	R23	R(14,17)	1.0987	A7	A(1,2,7)	108.5392
R8	R(3,4)	1.5093	R24	R(18,19)	1.0981	A8	A(1,2,12)	113.2773
R9	R(3,8)	1.5182	R25	R(18,20)	1.0981	A9	A(3,2,7)	107.916
R10	R(3,22)	1.1111	R26	R(18,21)	1.0974	A10	A(3,2,12)	115.0059
R11	R(4,5)	1.5029	R27	R(24,25)	1.3726	A11	A(7,2,12)	107.235
R12	R(4,31)	1.3248	R28	R(25,26)	1.2129	A12	A(2,3,4)	106.3244
R13	R(5,23)	1.4233	R29	R(25,27)	1.5126	A13	A(2,3,8)	114.1671
R14	R(5,24)	1.4044	R30	R(27,28)	1.0958	A14	A(2,3,22)	109.196
R15	R(8,9)	1.0966	R31	R(27,29)	1.098	A15	A(4,3,8)	107.9723
R16	R(8,10)	1.0982	R32	R(27,30)	1.0976	A16	A(4,3,22)	110.459
			R33	R(31,32)	1.0853	A17	A(8,3,22)	108.6895
			R34	R(31,33)	1.0857	A18	A(3,4,5)	107.1988
						A19	A(3,4,31)	126.7311
						A20	A(5,4,31)	126.0378
						A21	A(1,5,4)	108.5713
						A22	A(1,5,24)	127.4963
						A23	A(4,5,23)	116.2789
						A24	A(4,5,24)	120.1519
						A25	A(23,5,24)	109.4756
						A26	A(3,8,9)	111.445
						A27	A(3,8,10)	110.1332
						A28	A(3,8,11)	111.4512
						A29	A(9,8,10)	107.7808
						A30	A(9,8,11)	108.0789
						A31	A(10,8,11)	107.8019
						A32	A(2,12,13)	109.4774
						A33	A(2,12,14)	109.7535
						A34	A(2,12,18)	110.5864
						A35	A(13,12,14)	109.5073
						A36	A(13,12,18)	108.8089

Supporting Information

A37	A(14, 12, 18)	108.6848	A53	A(26, 25, 27)	126.9939	D7	D(1, 2, 3, 4)	-22.7944	D23	D(3, 4, 31, 33)	179.9174
A38	A(12, 14, 15)	111.4861	A54	A(25, 27, 28)	110.5119	D8	D(1, 2, 3, 8)	96.1415	D24	D(5, 4, 31, 32)	-178.0365
A39	A(12, 14, 16)	110.8833	A55	A(25, 27, 29)	110.546	D9	D(7, 2, 3, 4)	92.6568	D25	D(1, 5, 24, 25)	69.7182
A40	A(12, 14, 17)	111.2835	A56	A(25, 27, 30)	111.0171	D10	D(1, 2, 12, 13)	-66.2604	D26	D(4, 5, 24, 25)	-85.7742
A41	A(15, 14, 16)	107.7068	A57	A(28, 27, 29)	108.4608	D11	D(1, 2, 12, 14)	173.5178	D27	D(2, 12, 14, 15)	59.2575
A42	A(15, 14, 17)	107.6161	A58	A(28, 27, 30)	108.5824	D12	D(3, 2, 12, 13)	54.0072	D28	D(2, 12, 14, 16)	179.259
A43	A(16, 14, 17)	107.6861	A59	A(29, 27, 30)	107.6271	D13	D(2, 3, 4, 5)	21.4836	D29	D(13, 12, 14, 15)	-60.9462
A44	A(12, 18, 19)	111.4406	A60	A(4, 31, 32)	122.0487	D14	D(2, 3, 4, 31)	-156.5414	D30	D(2, 12, 18, 19)	56.1584
A45	A(12, 18, 20)	110.7344	A61	A(4, 31, 33)	122.0533	D15	D(8, 3, 4, 5)	-101.4377	D31	D(2, 12, 18, 20)	175.9793
A46	A(12, 18, 21)	111.6869	A62	A(32, 31, 33)	115.8975	D16	D(2, 3, 8, 9)	66.1244	D32	D(13, 12, 18, 19)	176.4369
A47	A(19, 18, 20)	107.667	D1	D(5, 1, 2, 3)	15.6832	D17	D(2, 3, 8, 10)	-174.3082	D33	D(5, 24, 25, 26)	-3.1064
A48	A(19, 18, 21)	107.6226	D2	D(5, 1, 2, 7)	-99.3325	D18	D(4, 3, 8, 9)	-175.8776	D34	D(5, 24, 25, 27)	177.4348
A49	A(20, 18, 21)	107.4956	D3	D(6, 1, 2, 3)	-138.6326	D19	D(3, 4, 5, 1)	-11.8143	D35	D(24, 25, 27, 28)	176.9702
A50	A(5, 24, 25)	119.5148	D4	D(2, 1, 5, 4)	-2.8457	D20	D(3, 4, 5, 23)	-76.3351	D36	D(24, 25, 27, 29)	-62.9451
A51	A(24, 25, 26)	121.2804	D5	D(2, 1, 5, 24)	-160.6117	D21	D(31, 4, 5, 1)	166.2282	D37	D(26, 25, 27, 28)	-2.4507
A52	A(24, 25, 27)	111.7232	D6	D(6, 1, 5, 4)	150.2732	D22	D(3, 4, 31, 32)	-0.3699			

Supporting Information

Product Epoxidation Beta (Boat) - Model Guanacastepene A precursor
Supporting Information: GS-PROD-BOAT-QF.output

Using Gaussian 03: A164T-G03RevC.01 3-Apr-2004

opt=(gdiis,maxcycle=150) freq=noraman b3lyp/6-31g(d) geom=connectivity
scf=(direct,tight,maxcycle=300)
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/6-31G(d) Freq

Pointgroup= C1 Stoichiometry= C12H18O3 C1[X(C12H18O3)] #Atoms= 33
Charge = 0 Multiplicity = 1

SCF Energy= -693.747159314 Predicted Change= -2.917488D-09

Optimization completed.						
			{Found	2	times}	
Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00145	0.00180	[YES]	0.00145	0.00180	[YES]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	0.136546	-0.785060	0.446474
C	1.313084	-0.260898	-0.363806
C	1.076422	1.299101	-0.411178
C	-0.431024	1.460145	-0.210465
C	-0.897745	0.247153	0.517877
H	-0.116659	-1.840730	0.473247
H	1.137444	-0.646936	-1.380775
O	-0.133377	-0.061578	1.679470
C	1.848254	2.120130	0.642365
H	2.931395	2.046063	0.501175
H	1.573582	3.176983	0.555740
H	1.604987	1.789273	1.655246

C	2.712566	-0.742062	0.076675
H	2.953508	-0.265803	1.035792
C	3.780511	-0.335812	-0.952495
H	3.799109	0.744690	-1.129881
H	4.780293	-0.634952	-0.616833
H	3.594088	-0.826378	-1.916980
C	2.748582	-2.264248	0.293974
H	2.441860	-2.802867	-0.612479
H	3.763762	-2.592746	0.545034
H	2.090564	-2.577165	1.111602
H	1.351617	1.676233	-1.402599
O	-2.270024	0.006245	0.655544
C	-2.883858	-0.727235	-0.328210
O	-2.307890	-1.183541	-1.284989
C	-4.354995	-0.862423	-0.025074
H	-4.496686	-1.307836	0.964752
H	-4.825374	0.126423	-0.007270
H	-4.826991	-1.482498	-0.787658
C	-1.211051	2.449004	-0.642400
H	-0.813780	3.278675	-1.221158
H	-2.276150	2.463790	-0.429566

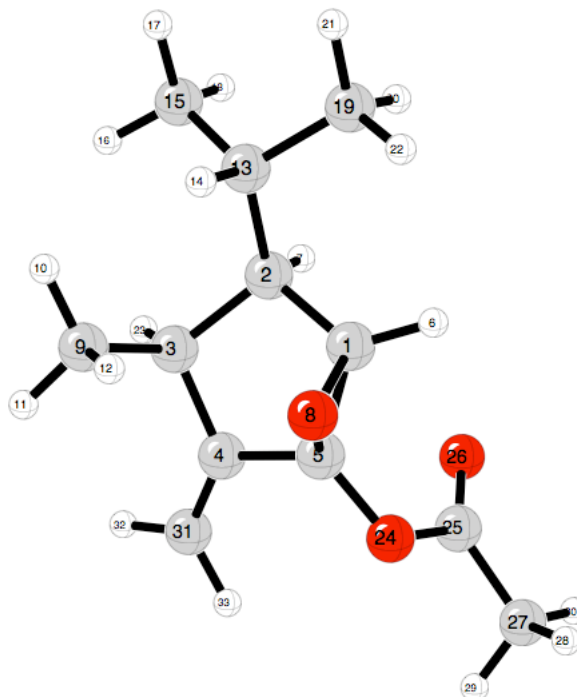
Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-693.747159314	Predicted Change=	-2.917488D-09
Zero-point correction (ZPE)=	-693.4647	0.28238	
Internal Energy (U)=		-693.4487	0.29843
Enthalpy (H)=	-693.4477	0.29937	
Gibbs Free Energy (G)=		-693.5081	0.23900

Frequencies --	44.1965	62.4807	64.1970
----------------	---------	---------	---------

Supporting Information



Name	Definition	Value	R17	R(9,12)	1.0971	A1	A(2,1,5)	107.5191	A19	A(3,4,31)	125.9292
R1	R(1,2)	1.5245	R18	R(13,14)	1.1154	A2	A(2,1,6)	119.8454	A20	A(5,4,31)	126.1695
R2	R(1,5)	1.5084	R19	R(13,15)	1.517	A3	A(2,1,8)	117.7165	A21	A(1,5,4)	108.6961
R3	R(1,6)	1.1026	R20	R(13,19)	1.5174	A4	A(5,1,6)	125.3061	A22	A(1,5,24)	126.9173
R4	R(1,8)	1.4507	R21	R(15,16)	1.0975	A5	A(6,1,8)	113.9747	A23	A(4,5,8)	115.8341
R5	R(2,3)	1.5633	R22	R(15,17)	1.0973	A6	A(1,2,3)	106.1167	A24	A(4,5,24)	120.3515
R6	R(2,7)	1.1174	R23	R(15,18)	1.0987	A7	A(1,2,7)	105.0374	A25	A(8,5,24)	110.4143
R7	R(2,13)	1.5194	R24	R(19,20)	1.0981	A8	A(1,2,13)	114.6672	A26	A(3,9,10)	111.1768
R8	R(3,4)	1.5132	R25	R(19,21)	1.0977	A9	A(3,2,7)	107.0755	A27	A(3,9,11)	110.0952
R9	R(3,9)	1.5162	R26	R(19,22)	1.097	A10	A(3,2,13)	116.0387	A28	A(3,9,12)	111.9054
R10	R(3,23)	1.1127	R27	R(24,25)	1.3755	A11	A(7,2,13)	107.1373	A29	A(10,9,11)	107.7337
R11	R(4,5)	1.508	R28	R(25,26)	1.2124	A12	A(2,3,4)	105.661	A30	A(10,9,12)	107.9699
R12	R(4,31)	1.3255	R29	R(25,27)	1.5116	A13	A(2,3,9)	114.9778	A31	A(11,9,12)	107.8004
R13	R(5,8)	1.4299	R30	R(27,28)	1.0978	A14	A(2,3,23)	108.8956	A32	A(2,13,14)	109.5572
R14	R(5,24)	1.4031	R31	R(27,29)	1.0979	A15	A(4,3,9)	109.275	A33	A(2,13,15)	109.4943
R15	R(9,10)	1.0971	R32	R(27,30)	1.0957	A16	A(4,3,23)	109.8413	A34	A(2,13,19)	110.2891
R16	R(9,11)	1.0978	R33	R(31,32)	1.0852	A17	A(9,3,23)	108.1228	A35	A(14,13,15)	109.7665
			R34	R(31,33)	1.0858	A18	A(3,4,5)	107.797	A36	A(14,13,19)	109.0197

Supporting Information

A37	A(15,13,19)	108.6977	A52	A(24,25,27)	111.6009	D5	D(2,1,5,24)	154.4497	D20	D(3,4,5,8)	53.477
A38	A(13,15,16)	111.4845	A53	A(26,25,27)	127.3478	D6	D(6,1,5,4)	-152.3519	D21	D(31,4,5,1)	165.9403
A39	A(13,15,17)	110.9236	A54	A(25,27,28)	110.8779	D7	D(1,2,3,4)	-20.5387	D22	D(3,4,31,32)	-0.0498
A40	A(13,15,18)	111.2743	A55	A(25,27,29)	110.5866	D8	D(1,2,3,9)	100.0453	D23	D(3,4,31,33)	178.4135
A41	A(16,15,17)	107.7753	A56	A(25,27,30)	110.5493	D9	D(7,2,3,4)	91.2555	D24	D(5,4,31,32)	-175.8777
A42	A(16,15,18)	107.5592	A57	A(28,27,29)	107.5741	D10	D(1,2,13,14)	-71.9682	D25	D(1,5,24,25)	-61.8281
A43	A(17,15,18)	107.6432	A58	A(28,27,30)	108.6275	D11	D(1,2,13,15)	167.6025	D26	D(4,5,24,25)	92.9334
A44	A(13,19,20)	111.4486	A59	A(29,27,30)	108.5323	D12	D(3,2,13,14)	52.3895	D27	D(2,13,15,16)	59.0258
A45	A(13,19,21)	110.7979	A60	A(4,31,32)	121.9887	D13	D(2,3,4,5)	19.0798	D28	D(2,13,15,17)	179.1403
A46	A(13,19,22)	111.516	A61	A(4,31,33)	122.1568	D14	D(2,3,4,31)	-157.3837	D29	D(14,13,15,16)	-61.276
A47	A(20,19,21)	107.5854	A62	A(32,31,33)	115.838	D15	D(9,3,4,5)	-105.1582	D30	D(2,13,19,20)	55.0019
A48	A(20,19,22)	107.6858	D1	D(5,1,2,3)	14.3245	D16	D(2,3,9,10)	65.426	D31	D(2,13,19,21)	174.7677
A49	A(21,19,22)	107.6199	D2	D(5,1,2,7)	-98.8859	D17	D(2,3,9,11)	-175.2622	D32	D(14,13,19,20)	175.3292
A50	A(5,24,25)	118.9072	D3	D(6,1,2,3)	165.9477	D18	D(4,3,9,10)	-175.9939	D33	D(5,24,25,26)	1.1255
A51	A(24,25,26)	121.0455	D4	D(2,1,5,4)	-2.6926	D19	D(3,4,5,1)	-10.5124	D34	D(5,24,25,27)	-179.6885
D35	D(24,25,27,28)	-56.2028									
D36	D(24,25,27,29)	63.0369									
D37	D(26,25,27,28)	122.9199									

Supporting Information

Transition Structure Epoxidation Alpha (Chair) - Model Guanacastepene A precursor
Supporting Information: GS-TS-CHAIR-QF.output

Using Gaussian 03: A164T-G03RevC.01 3-Apr-2004

```
# opt=(gdiis,modredundant,maxcycle=250) b3lyp/6-31g(d) geom=connectivity
scf=(direct,maxcycle=300,tight)
```

```
Modredundant Input: B 1 5 1.3800 F
Modredundant Input: B 1 24 2.0300 F
Modredundant Input: B 5 24 2.0300 F
Modredundant Input: B 8 24 1.8900 F
Modredundant Input: B 24 25 1.4900 F
Modredundant Input: B 8 25 1.3300 F
```

```
# opt=(modredundant,maxcycle=250,gdiis) b3lyp/6-31g(d) geom=check
guess=read scf=(direct,maxcycle=300,tight)
```

```
Modredundant Input: B 1 5 A
Modredundant Input: B 1 24 2.0300 F
Modredundant Input: B 5 24 2.0300 F
Modredundant Input: B 8 24 1.8900 F
Modredundant Input: B 24 25 A
Modredundant Input: B 8 25 A
```

```
# opt=(modredundant,maxcycle=250,gdiis,ts,noeigentest,calcfc)
```

```
b3lyp/6-31g(d) freq=noraman geom=check guess=read
```

```
scf=(direct,maxcycle=300,tight)
```

```
Modredundant Input: B 1 5 A
Modredundant Input: B 1 24 A
Modredundant Input: B 5 24 A
Modredundant Input: B 8 24 A
Modredundant Input: B 24 25 A
Modredundant Input: B 8 25 A
```

```
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/6-31G(d) Freq
```

Pointgroup= C1 Stoichiometry= C15H24O4 C1[X(C15H24O4)] #Atoms= 43

Charge = 0 Multiplicity = 1

SCF Energy= -886.793001547 Predicted Change= -6.348942D-08

```
Optimization completed. {Found 3 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00001 || 0.00045 [ YES ] 0.00000 || 0.00030 [ YES ]
Displ 0.00759 || 0.00180 [ NO ] 0.00759 || 0.00180 [ NO ]
```

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	-0.336416	0.112450	0.356505
C	-1.775502	0.203317	-0.148816
C	-2.034639	-1.198274	-0.818790
C	-0.634164	-1.757053	-1.045617
C	0.243514	-1.057510	-0.127483
H	0.015886	0.630844	1.232199

H	-1.749081	0.948669	-0.953203
O	1.157389	2.641857	-1.842225
C	-2.824186	-2.203593	0.044988
H	-3.844940	-1.865742	0.244392
H	-2.884338	-3.167910	-0.470920
H	-2.328587	-2.375341	1.007607
C	-2.828693	0.698441	0.870932
H	-2.989497	-0.077802	1.631758
C	-4.167005	0.969899	0.160251
H	-4.538276	0.099347	-0.390253
H	-4.938206	1.260347	0.882860
H	-4.058128	1.792124	-0.558413
C	-2.375189	1.977607	1.595632
H	-2.114083	2.764900	0.877573
H	-3.182208	2.360192	2.231223
H	-1.507057	1.809376	2.241074
H	-2.558838	-1.069991	-1.771628
O	0.522462	1.094295	-0.973951
C	1.679077	1.985033	-0.800175
C	3.000626	1.275113	-1.092528
H	3.780537	2.026735	-1.261826
H	3.327427	0.639133	-0.261975
H	2.892661	0.674118	-1.998690
C	1.663163	2.738334	0.530472
H	1.899095	2.090131	1.381279
H	2.413825	3.536327	0.496290
H	0.681998	3.198291	0.675834
O	1.477261	-1.592715	0.099498
C	2.218277	-1.316501	1.233394
O	1.856639	-0.572906	2.108536
C	3.501991	-2.102054	1.194298
H	4.099187	-1.859095	2.073422
H	3.282927	-3.174997	1.177921
H	4.060483	-1.867032	0.282888
C	-0.270551	-2.756750	-1.865503
H	-0.990635	-3.248449	-2.512985
H	0.758021	-3.099173	-1.916645

Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -886.793001547 Predicted Change= -6.348942D-08

Zero-point correction (ZPE)= -886.4261 0.36686

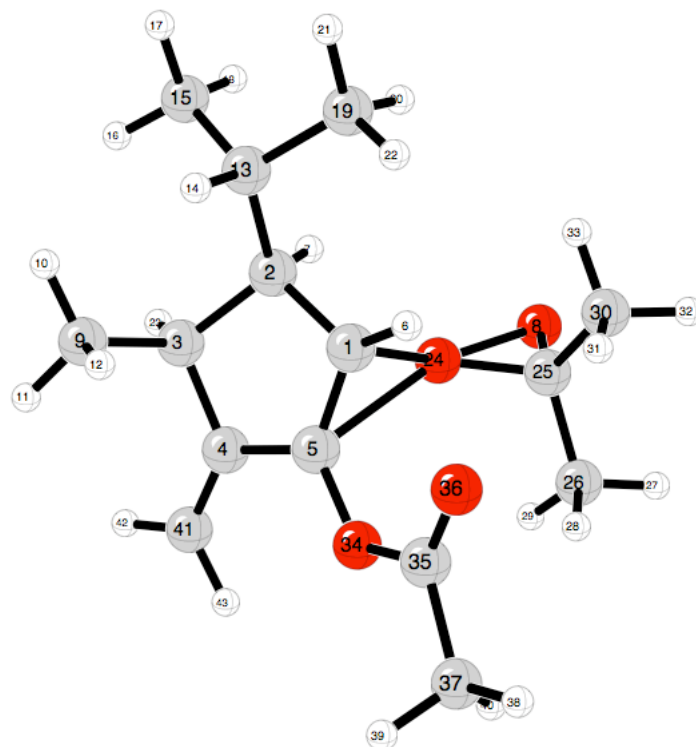
Internal Energy (U)= -886.4042 0.38875

Enthalpy (H)= -886.4033 0.38969

Gibbs Free Energy (G)= -886.4769 0.31610

Frequencies -- -449.6357 26.9797 32.9479

Supporting Information



Name	Definition	Value									
R1	R(1,2)	1.5211	R16	R(7,24)	2.3008	R33	R(26,27)	1.0972	A4	A(5,1,6)	124.8876
R2	R(1,5)	1.3918	R17	R(8,25)	1.3126	R34	R(26,28)	1.0964	A5	A(1,2,3)	104.7136
R3	R(1,6)	1.0969	R18	R(9,10)	1.097	R35	R(26,29)	1.0967	A6	A(1,2,7)	105.0705
R4	R(1,24)	1.8384	R19	R(9,11)	1.0984	R36	R(30,31)	1.0963	A7	A(1,2,13)	114.7042
R5	R(2,3)	1.5615	R20	R(9,12)	1.0977	R37	R(30,32)	1.097	A8	A(3,2,7)	108.1749
R6	R(2,7)	1.1147	R21	R(13,14)	1.1135	R38	R(30,33)	1.0974	A9	A(3,2,13)	115.9352
R7	R(2,13)	1.5275	R22	R(13,15)	1.5223	R39	R(34,35)	1.3852	A10	A(7,2,13)	107.5817
R8	R(3,4)	1.5106	R23	R(13,19)	1.5207	R40	R(35,36)	1.208	A11	A(2,3,4)	104.2745
R9	R(3,9)	1.5203	R24	R(15,16)	1.0976	R41	R(35,37)	1.51	A12	A(2,3,9)	115.2222
R10	R(3,23)	1.1099	R25	R(15,17)	1.0976	R42	R(37,38)	1.0955	A13	A(2,3,23)	109.7485
R11	R(4,5)	1.4694	R26	R(15,18)	1.0987	R43	R(37,39)	1.0981	A14	A(4,3,9)	107.9567
R12	R(4,41)	1.3325	R27	R(19,20)	1.0983	R44	R(37,40)	1.0983	A15	A(4,3,23)	110.8497
R13	R(5,24)	2.2936	R28	R(19,21)	1.0985	R45	R(41,42)	1.0854	A16	A(9,3,23)	108.71
R14	R(5,34)	1.3614	R29	R(19,22)	1.0974	R46	R(41,43)	1.0861	A17	A(3,4,5)	106.6322
R15	R(6,24)	2.3112	R30	R(24,25)	1.4096	A1	A(2,1,5)	109.0311	A18	A(3,4,41)	126.6356
			R31	R(25,26)	1.5366	A2	A(2,1,6)	121.3351	A19	A(5,4,41)	126.7077
			R32	R(25,30)	1.5335	A3	A(2,1,24)	101.0884	A20	A(1,5,4)	111.361

Supporting Information

A21	A(1,5,34)	131.638	A52	A(5,24,6)	57.3758	A83	A(38,37,39)	108.6077	D26	D(3,4,41,42)	-0.9413
A22	A(4,5,24)	108.6803	A53	A(5,24,7)	80.1129	A84	A(38,37,40)	108.8332	D27	D(3,4,41,43)	-177.8092
A23	A(4,5,34)	117.0009	A54	A(5,24,25)	126.8902	A85	A(39,37,40)	107.6864	D28	D(5,4,41,42)	-178.8988
A24	A(24,5,34)	108.307	A55	A(6,24,7)	75.6818	A86	A(4,41,42)	121.7255	D29	D(4,5,24,6)	129.9362
A25	A(2,7,24)	92.5986	A56	A(6,24,25)	100.5057	A87	A(4,41,43)	122.1059	D30	D(4,5,24,7)	50.6844
A26	A(3,9,10)	111.5906	A57	A(7,24,25)	146.0079	A88	A(42,41,43)	116.0999	D31	D(34,5,24,6)	-101.991
A27	A(3,9,11)	110.1349	A58	A(8,25,11)	67.1305	D1	D(5,1,2,3)	9.0727	D32	D(1,5,34,35)	25.4339
A28	A(3,9,12)	111.6907	A59	A(8,25,26)	117.5018	D2	D(5,1,2,7)	-104.7991	D33	D(4,5,34,35)	-154.667
A29	A(10,9,11)	107.7733	A60	A(8,25,30)	119.6349	D3	D(6,1,2,3)	-147.6166	D34	D(2,7,24,1)	-8.3776
A30	A(10,9,12)	107.9297	A61	A(24,25,26)	114.2418	D4	D(2,1,5,4)	3.6273	D35	D(2,7,24,5)	25.3913
A31	A(11,9,12)	107.5481	A62	A(24,25,30)	114.842	D5	D(2,1,5,34)	-176.4692	D36	D(2,13,15,16)	57.3741
A32	A(2,13,14)	109.6616	A63	A(26,25,30)	114.7412	D6	D(6,1,5,4)	159.2935	D37	D(2,13,15,17)	177.4403
A33	A(2,13,15)	109.614	A64	A(25,26,27)	109.8532	D7	D(2,1,24,7)	6.2399	D38	D(14,13,15,16)	-62.7665
A34	A(2,13,19)	111.2189	A65	A(25,26,28)	111.6377	D8	D(2,1,24,25)	146.0106	D39	D(2,13,19,20)	53.5122
A35	A(14,13,15)	109.1783	A66	A(25,26,29)	111.3088	D9	D(1,2,3,4)	-17.6129	D40	D(2,13,19,21)	173.3458
A36	A(14,13,19)	108.523	A67	A(27,26,28)	107.4634	D10	D(1,2,3,9)	100.5181	D41	D(14,13,19,20)	174.2249
A37	A(15,13,19)	108.6072	A68	A(27,26,29)	107.8353	D11	D(7,2,3,4)	94.0504	D42	D(1,24,25,8)	-151.4297
A38	A(13,15,16)	111.7088	A69	A(28,26,29)	108.5911	D12	D(1,2,7,24)	9.0827	D43	D(1,24,25,26)	97.488
A39	A(13,15,17)	110.9507	A70	A(25,30,31)	111.1753	D13	D(3,2,7,24)	-102.3401	D44	D(5,24,25,8)	161.3639
A40	A(13,15,18)	111.2058	A71	A(25,30,32)	110.0394	D14	D(1,2,13,14)	-70.5752	D45	D(8,25,26,27)	84.1953
A41	A(16,15,17)	107.6039	A72	A(25,30,33)	111.3949	D15	D(1,2,13,15)	169.5794	D46	D(8,25,26,28)	-156.6953
A42	A(16,15,18)	107.5634	A73	A(31,30,32)	107.6157	D16	D(3,2,13,14)	51.7427	D47	D(24,25,26,27)	159.949
A43	A(17,15,18)	107.6153	A74	A(31,30,33)	108.4264	D17	D(2,3,4,5)	19.9371	D48	D(8,25,30,31)	154.7402
A44	A(13,19,20)	111.4756	A75	A(32,30,33)	108.057	D18	D(2,3,4,41)	-158.354	D49	D(8,25,30,32)	-86.1322
A45	A(13,19,21)	110.6184	A76	A(5,34,35)	123.9663	D19	D(9,3,4,5)	-103.0654	D50	D(24,25,30,31)	77.9986
A46	A(13,19,22)	111.8358	A77	A(34,35,36)	121.9709	D20	D(2,3,9,10)	64.6525	D51	D(5,34,35,36)	1.1714
A47	A(20,19,21)	107.7203	A78	A(34,35,37)	110.2414	D21	D(2,3,9,11)	-175.6944	D52	D(5,34,35,37)	179.0889
A48	A(20,19,22)	107.5787	A79	A(36,35,37)	127.7496	D22	D(4,3,9,10)	-179.2968	D53	D(34,35,37,38)	177.5579
A49	A(21,19,22)	107.4133	A80	A(35,37,38)	110.302	D23	D(3,4,5,1)	-15.3499	D54	D(34,35,37,39)	-62.3163
A50	A(1,24,7)	59.9547	A81	A(35,37,39)	110.5368	D24	D(3,4,5,24)	-72.2842	D55	D(36,35,37,38)	-4.6765
A51	A(1,24,25)	126.8792	A82	A(35,37,40)	110.7982	D25	D(41,4,5,1)	162.9397			

Supporting Information

Transition Structure Epoxidation Beta (Boat) - Model Guanacastepene A precursor
Supporting Information: GS-TS-B0AT-QF.output

Using Gaussian 03: A164T-G03RevC.01 3-Apr-2004

```
# opt=(gdiis,modredundant,maxcycle=250) b3lyp/6-31g(d) geom=connectivity
scf=(direct,maxcycle=300,tight)
```

```
Modredundant Input: B 1 5 1.3800 F
Modredundant Input: B 1 8 2.0300 F
Modredundant Input: B 5 8 2.0300 F
Modredundant Input: B 8 24 1.8900 F
Modredundant Input: B 8 25 1.4900 F
Modredundant Input: B 24 25 1.3300 F
```

```
# opt=(modredundant,maxcycle=250,gdiis,) b3lyp/6-31g(d) geom=check
guess=read scf=(direct,maxcycle=300,tight)
```

```
Modredundant Input: B 1 5 A
Modredundant Input: B 1 8 2.0300 F
Modredundant Input: B 5 8 2.0300 F
Modredundant Input: B 8 24 1.8900 F
Modredundant Input: B 8 25 A
Modredundant Input: B 24 25 A
```

```
# opt=(modredundant,maxcycle=250,gdiis,ts,noeigentest,calcf)
b3lyp/6-31g(d) freq=noraman geom=check guess=read
```

```
scf=(direct,maxcycle=300,tight)
```

```
Modredundant Input: B 1 5 A
Modredundant Input: B 1 8 A
Modredundant Input: B 5 8 A
Modredundant Input: B 8 24 A
Modredundant Input: B 8 25 A
Modredundant Input: B 24 25 A
```

```
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/6-31G(d) Freq
```

Pointgroup= C1 Stoichiometry= C15H24O4 C1[X(C15H24O4)] #Atoms= 43

Charge = 0 Multiplicity = 1

SCF Energy= -886.799840173 Predicted Change= -4.309436D-08

```
Optimization completed. {Found 3 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00001 || 0.00045 [ YES ] 0.00000 || 0.00030 [ YES ]
Displ 0.00677 || 0.00180 [ NO ] 0.00677 || 0.00180 [ YES ]
```

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	-0.214104	-0.169678	-0.770488
C	-1.650034	-0.668151	-0.708086
C	-1.636697	-1.695910	0.484027
C	-0.168855	-2.100158	0.577091
C	0.598266	-1.107539	-0.150594
H	0.132750	0.502773	-1.537538

H	-1.785638	-1.256591	-1.632699
O	-0.164234	0.995078	0.749553
C	-2.130929	-1.156936	1.842589
H	-3.190811	-0.887593	1.804370
H	-2.013597	-1.934329	2.606331
H	-1.560994	-0.278006	2.149714
C	-2.761688	0.403635	-0.715295
H	-2.711687	0.956163	0.228738
C	-4.144777	-0.257057	-0.847456
H	-4.342342	-0.985789	-0.054576
H	-4.937637	0.498597	-0.806967
H	-4.236534	-0.780253	-1.808918
C	-2.566028	1.411396	-1.858885
H	-2.530419	0.907053	-2.834329
H	-3.399047	2.123087	-1.886332
H	-1.645929	1.990227	-1.739610
H	-2.242685	-2.570799	0.221195
O	-0.280665	2.543617	1.754743
C	0.733335	2.117487	0.978256
C	1.992617	1.709752	1.739375
H	2.713767	1.189033	1.098952
H	2.482679	2.605381	2.138501
H	1.713659	1.060521	2.572637
C	1.003363	2.955110	-0.269260
H	1.505186	3.884770	0.023181
H	1.645928	2.435712	-0.988093
H	0.053923	3.215090	-0.744284
O	1.959790	-1.218229	-0.126742
C	2.779897	-0.662723	-1.091760
O	2.382954	-0.001092	-2.015881
C	4.211092	-1.028649	-0.799658
H	4.491576	-0.686905	0.201765
H	4.330793	-2.117011	-0.819113
H	4.859256	-0.570429	-1.546903
C	0.347410	-3.180941	1.186347
H	-0.289046	-3.908707	1.680860
H	1.416883	-3.364826	1.202506

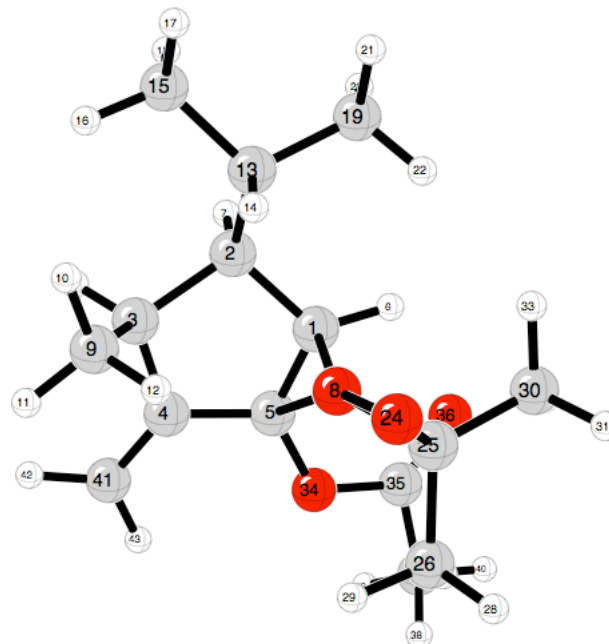
Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

```
SCF Energy= -886.799840173 Predicted Change= -4.309436D-08
Zero-point correction (ZPE)= -886.4329 0.36688
Internal Energy (U)= -886.4110 0.38878
Enthalpy (H)= -886.4101 0.38972
Gibbs Free Energy (G)= -886.4831 0.31670
```

Frequencies -- -406.0339 30.7022 51.4423

Supporting Information



Name	Definition	Value									
R1	R(1,2)	1.5195	R16	R(8,12)	2.3825	R33	R(26,27)	1.0964	A4	A(5,1,6)	125.2532
R2	R(1,5)	1.3846	R17	R(8,25)	1.3999	R34	R(26,28)	1.0968	A5	A(1,2,3)	104.3212
R3	R(1,6)	1.0966	R18	R(9,10)	1.0972	R35	R(26,29)	1.0969	A6	A(1,2,7)	105.4774
R4	R(1,8)	1.9034	R19	R(9,11)	1.098	R36	R(30,31)	1.0969	A7	A(1,2,13)	115.8454
R5	R(2,3)	1.5629	R20	R(9,12)	1.0996	R37	R(30,32)	1.0961	A8	A(3,2,7)	107.1568
R6	R(2,7)	1.1178	R21	R(13,14)	1.1128	R38	R(30,33)	1.0977	A9	A(3,2,13)	116.7831
R7	R(2,13)	1.527	R22	R(13,15)	1.5213	R39	R(34,35)	1.3839	A10	A(7,2,13)	106.4555
R8	R(3,4)	1.5124	R23	R(13,19)	1.5219	R40	R(35,36)	1.2081	A11	A(2,3,4)	103.5425
R9	R(3,9)	1.5205	R24	R(15,16)	1.0973	R41	R(35,37)	1.51	A12	A(2,3,9)	115.5945
R10	R(3,23)	1.1109	R25	R(15,17)	1.0976	R42	R(37,38)	1.0981	A13	A(2,3,23)	109.5112
R11	R(4,5)	1.4712	R26	R(15,18)	1.0988	R43	R(37,39)	1.098	A14	A(4,3,9)	109.6123
R12	R(4,41)	1.333	R27	R(19,20)	1.0983	R44	R(37,40)	1.0954	A15	A(4,3,23)	109.9866
R13	R(5,8)	2.3788	R28	R(19,21)	1.0979	R45	R(41,42)	1.0853	A16	A(9,3,23)	108.4639
R14	R(5,34)	1.3641	R29	R(19,22)	1.0978	R46	R(41,43)	1.086	A17	A(3,4,5)	107.1919
R15	R(6,8)	2.3318	R30	R(24,25)	1.3238	A1	A(2,1,5)	108.1395	A18	A(3,4,41)	126.4532
			R31	R(25,26)	1.5347	A2	A(2,1,6)	121.4995	A19	A(5,4,41)	126.3288
			R32	R(25,30)	1.5312	A3	A(2,1,8)	102.8025	A20	A(1,5,4)	111.588

Supporting Information

A21	A(1,5,34)	131.283	A52	A(13,19,20)	111.6338	A83	A(38,37,39)	107.6813	D26	D(5,4,41,42)	-177.7844
A22	A(4,5,8)	104.7851	A53	A(13,19,21)	110.6403	A84	A(38,37,40)	108.7941	D27	D(4,5,8,6)	-133.185
A23	A(4,5,34)	117.1288	A54	A(13,19,22)	111.6075	A85	A(39,37,40)	108.6821	D28	D(4,5,8,12)	-0.0625
A24	A(8,5,34)	111.6932	A55	A(20,19,21)	107.4729	A86	A(4,41,42)	121.689	D29	D(34,5,8,6)	99.0408
A25	A(1,8,12)	95.9435	A56	A(20,19,22)	107.8788	A87	A(4,41,43)	122.202	D30	D(1,5,34,35)	-23.7809
A26	A(1,8,25)	128.0564	A57	A(21,19,22)	107.4075	A88	A(42,41,43)	116.1004	D31	D(4,5,34,35)	156.0658
A27	A(5,8,6)	55.8754	A58	A(8,25,24)	65.4923	D1	D(5,1,2,3)	21.0404	D32	D(1,8,12,9)	-5.8912
A28	A(5,8,12)	85.9772	A59	A(8,25,26)	114.8012	D2	D(5,1,2,7)	-91.7024	D33	D(5,8,12,9)	-40.1017
A29	A(5,8,25)	121.5436	A60	A(8,25,30)	115.0857	D3	D(6,1,2,3)	176.978	D34	D(1,8,25,24)	156.2926
A30	A(6,8,12)	121.676	A61	A(24,25,26)	117.5779	D4	D(2,1,5,4)	-11.2706	D35	D(1,8,25,26)	-93.2307
A31	A(6,8,25)	103.8406	A62	A(24,25,30)	119.391	D5	D(2,1,5,34)	168.5826	D36	D(5,8,25,24)	-160.7039
A32	A(12,8,25)	134.4328	A63	A(26,25,30)	115.0875	D6	D(6,1,5,4)	-166.0741	D37	D(3,9,12,8)	13.4131
A33	A(3,9,10)	110.919	A64	A(25,26,27)	111.3144	D7	D(2,1,8,12)	34.4006	D38	D(10,9,12,8)	-109.0524
A34	A(3,9,11)	109.8167	A65	A(25,26,28)	109.9816	D8	D(2,1,8,25)	-158.3356	D39	D(2,13,15,16)	58.5006
A35	A(3,9,12)	111.9538	A66	A(25,26,29)	111.3564	D9	D(1,2,3,4)	-22.2817	D40	D(2,13,15,17)	178.4324
A36	A(10,9,11)	107.7228	A67	A(27,26,28)	107.4493	D10	D(1,2,3,9)	97.5986	D41	D(14,13,15,16)	-61.4162
A37	A(10,9,12)	108.1038	A68	A(27,26,29)	108.4883	D11	D(7,2,3,4)	89.2527	D42	D(2,13,19,20)	55.6165
A38	A(11,9,12)	108.187	A69	A(28,26,29)	108.1136	D12	D(1,2,13,14)	-68.3851	D43	D(2,13,19,21)	175.257
A39	A(8,12,9)	125.0786	A70	A(25,30,31)	110.2654	D13	D(1,2,13,15)	171.4377	D44	D(14,13,19,20)	175.576
A40	A(2,13,14)	109.1468	A71	A(25,30,32)	110.9689	D14	D(3,2,13,14)	55.1459	D45	D(8,25,26,27)	78.9193
A41	A(2,13,15)	109.8788	A72	A(25,30,33)	111.2653	D15	D(2,3,4,5)	16.3068	D46	D(8,25,26,28)	-162.1098
A42	A(2,13,19)	110.7769	A73	A(31,30,32)	107.9136	D16	D(2,3,4,41)	-161.9192	D47	D(24,25,26,27)	153.0057
A43	A(14,13,15)	109.5753	A74	A(31,30,33)	108.0729	D17	D(9,3,4,5)	-107.5794	D48	D(8,25,30,31)	164.7076
A44	A(14,13,19)	108.764	A75	A(32,30,33)	108.236	D18	D(2,3,9,10)	65.1697	D49	D(8,25,30,32)	-75.7784
A45	A(15,13,19)	108.6773	A76	A(5,34,35)	123.641	D19	D(2,3,9,11)	-175.8736	D50	D(24,25,30,31)	89.8961
A46	A(13,15,16)	111.7385	A77	A(34,35,36)	122.1877	D20	D(4,3,9,10)	-178.3228	D51	D(5,34,35,36)	0.7357
A47	A(13,15,17)	110.7432	A78	A(34,35,37)	110.2405	D21	D(3,4,5,1)	-3.6976	D52	D(5,34,35,37)	-177.3718
A48	A(13,15,18)	111.4292	A79	A(36,35,37)	127.5406	D22	D(3,4,5,8)	52.0392	D53	D(34,35,37,38)	-57.3354
A49	A(16,15,17)	107.5935	A80	A(35,37,38)	110.7153	D23	D(41,4,5,1)	174.5313	D54	D(34,35,37,39)	61.9527
A50	A(16,15,18)	107.6095	A81	A(35,37,39)	110.6162	D24	D(3,4,41,42)	0.1119	D55	D(36,35,37,38)	124.6846
A51	A(17,15,18)	107.5294	A82	A(35,37,40)	110.2769	D25	D(3,4,41,43)	179.0046			

Supporting Information

Reactant - ONIOM Full Guanacastepene A precursor
Supporting Information: GS-Reactant-CP-ONIOM.output

Using Gaussian 03: IA32L-G03RevC.02 12-Jun-2004

oniom(b3lyp/6-31g(d):pm3) scf=(direct,maxcycle=300,tight)
geom=connectivity freq=noraman guess=read

Pointgroup= C1 Stoichiometry= C24H34O4 C1[X(C24H34O4)] #Atoms= 62
Charge = 0 Multiplicity = 1

SCF Energy= -657.976751383922 Predicted Change= -1.134563D-08

Optimization incomplete.

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00459	0.00180	[NO]	0.00459	0.00180	[YES]

Atomic Coordinates (Angstroms)

Atomic Type	X	Y	Z
-------------	---	---	---

C	1.206420	-2.098978	-0.347320
C	1.334720	-0.598127	-0.168140
C	0.254869	0.371332	-0.078275
C	-0.054583	-2.702729	0.294210
C	-1.078859	0.212982	0.079105
C	-1.375302	-2.277919	-0.321611
C	-1.954300	-1.011039	0.344232
H	0.561971	1.416663	-0.222306
H	-0.054862	-2.471789	1.383909
H	-2.097716	-3.106627	-0.225693
C	-2.011778	1.339598	-0.046719
C	-3.279015	0.936461	-0.233906
H	-4.117074	1.591911	-0.404704
C	-3.352947	-0.577261	-0.267617
H	-3.356570	-0.890670	-1.327045
C	2.391561	-2.781336	0.392857
H	2.277167	-2.578168	1.477460
C	3.790892	-2.365839	-0.038396
H	4.497584	-2.518430	0.801832
C	3.834831	-0.926553	-0.536112
C	2.609258	-0.137192	-0.182474
H	3.992681	-0.903315	-1.642974
H	2.302807	-3.881072	0.282290
H	4.150470	-3.031056	-0.848373
H	0.021876	-3.807814	0.222125
H	-1.247148	-2.094545	-1.410752
C	1.226712	-2.444262	-1.837021
H	2.064047	-1.964493	-2.359526
H	1.314255	-3.527599	-1.993183
H	0.292416	-2.112971	-2.319815
C	-2.066190	-1.172196	1.884031
H	-2.457720	-0.260851	2.346227
H	-2.719544	-2.006184	2.158259
H	-1.072346	-1.369374	2.311788
C	-4.655722	-1.155428	0.352247
H	-4.684611	-0.883560	1.416032

C	-4.750448	-2.687422	0.243435
H	-4.676141	-3.010919	-0.803126
H	-3.970634	-3.205149	0.808916
H	-5.716418	-3.036436	0.627153
C	-5.900148	-0.539486	-0.315933
H	-6.812968	-0.987772	0.093311
H	-5.969865	0.541109	-0.161453
H	-5.897833	-0.725181	-1.398194
O	4.903197	-0.170823	0.045980
O	2.994874	1.141604	0.162140
C	4.441488	1.172146	0.267949
C	4.835611	1.612693	1.679544
H	5.927328	1.618756	1.791892
H	4.469469	2.626449	1.886179
H	4.424761	0.945711	2.448331
C	5.005862	2.121539	-0.795131
H	4.625079	3.140447	-0.650099
H	6.101006	2.159447	-0.736082
H	4.737961	1.806051	-1.811802
C	-1.281778	4.949067	-0.140551
H	-0.753854	4.974525	0.818328
H	-0.524089	4.886301	-0.928719
H	-1.871959	5.857337	-0.265129
O	-3.389181	3.780257	-0.373897
O	-1.461044	2.609000	-0.025486
C	-2.194870	3.748110	-0.200896

Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-657.976751383922	Predicted Change=	-1.134563D-08
Zero-point correction (ZPE)=	-657.4379		0.53884
Internal Energy (U)=		-657.4096	0.56710
Enthalpy (H)=	-657.4087	0.56805	
Gibbs Free Energy (G)=		-657.4963	0.48041

Frequencies -- 18.1091 31.4184 43.2152

Supporting Information

Transition Structure Epoxidation Alpha (Chair) - ONIOM Full Guanacastepene A precursor

Supporting Information: GS-TS-CHAIR-ONIOM.output

Using Gaussian 03: IA32L-G03RevC.02 12-Jun-2004

```
# oniom(b3lyp/6-31g(d):pm3) scf=(direct,maxcycle=300,tight) geom=check
guess=read opt=(gdiis,maxcycle=250,ts,noeigentest,readfc) freq=noraman
#N Geom=AllCheck Guess=Read SCRF=Check GenChk
ONIOM(B3LYP/6-31G(d):PM3/ZDO) Freq
```

Pointgroup= C1 Stoichiometry= C27H40O6 C1[X(C27H40O6)] #Atoms= 73
Charge = 0 Multiplicity = 1

SCF Energy= -926.224346847678 Predicted Change= -8.801157D-08

```
Optimization completed. {Found 1 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00007 || 0.00045 [ YES ] 0.00000 || 0.00030 [ YES ]
Displ 0.00628 || 0.00180 [ NO ] 0.00628 || 0.00180 [ YES ]
```

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	-2.143006	-2.044304	0.552630
C	-2.041932	-0.590799	0.128887
C	-0.841298	0.133257	-0.240128
C	-1.113151	-2.967431	-0.121754
C	0.420303	-0.301610	-0.500252
C	0.337285	-2.724730	0.254405
C	1.021742	-1.694646	-0.669310
H	-0.941640	1.227439	-0.241082
H	-1.233206	-2.901285	-1.227161
H	0.885370	-3.681251	0.204198
C	1.512247	0.631342	-0.682732
C	2.746233	0.032250	-0.473664
H	3.677392	0.474667	-0.783316
C	2.548562	-1.469697	-0.297497
H	2.652155	-1.665627	0.777427
C	-3.523973	-2.591056	0.091838
H	-3.542586	-2.579622	-1.017359
C	-4.752355	-1.857387	0.610750
H	-5.597161	-2.006125	-0.091364
C	-4.482135	-0.375474	0.836500
C	-3.207504	0.101027	0.204034
H	-4.465809	-0.145052	1.930973
H	-3.605357	-3.658090	0.382358
H	-5.084334	-2.305320	1.568427
H	-1.368682	-4.014067	0.145502
H	0.408884	-2.373261	1.306487
C	-1.995893	-2.148799	2.071043
H	-2.651282	-1.443699	2.597910
H	-2.241475	-3.158732	2.425122
H	-0.956716	-1.934282	2.371837
C	0.864407	-2.065667	-2.169172

H	1.330635	-1.313882	-2.814935
H	1.312524	-3.036819	-2.397592
H	-0.202524	-2.118957	-2.431376
C	3.626076	-2.330701	-1.011518
H	3.550709	-2.171082	-2.096136
C	3.461137	-3.835674	-0.733530
H	3.500851	-4.037766	0.344429
H	2.521529	-4.243492	-1.115894
H	4.275631	-4.398361	-1.204288
C	5.043654	-1.913162	-0.574347
H	5.790483	-2.566744	-1.039671
H	5.291444	-0.886150	-0.858033
H	5.157536	-1.995798	0.513590
O	-5.481448	0.467334	0.250325
O	-3.420049	1.352406	-0.325868
C	-4.839519	1.654435	-0.242823
C	-5.368145	1.967228	-1.643777
H	-6.446792	2.167961	-1.612814
H	-4.871844	2.854567	-2.057077
H	-5.203756	1.136088	-2.341614
C	-5.051599	2.830282	0.716676
H	-4.525581	3.725064	0.360379
H	-6.118456	3.075476	0.794906
H	-4.686280	2.607791	1.727718
C	1.420447	4.153951	-1.707206
H	2.128873	4.857530	-2.144788
H	0.550060	4.044565	-2.362856
H	1.060856	4.531289	-0.744823
O	3.437112	0.909785	3.062059
O	2.772676	0.551891	1.360173
C	3.543645	1.640739	1.938186
C	4.954720	1.760193	1.363380
H	5.548167	2.425811	2.000838
H	5.428074	0.774896	1.360547
H	4.956043	2.175344	0.349573
C	2.775191	2.961481	1.969506
H	1.743651	2.769939	2.274876
H	3.240185	3.628718	2.704589
H	2.787315	3.475034	1.001571
C	2.094424	2.819965	-1.521713
O	1.208176	1.938513	-0.935448
O	3.219503	2.534222	-1.842684

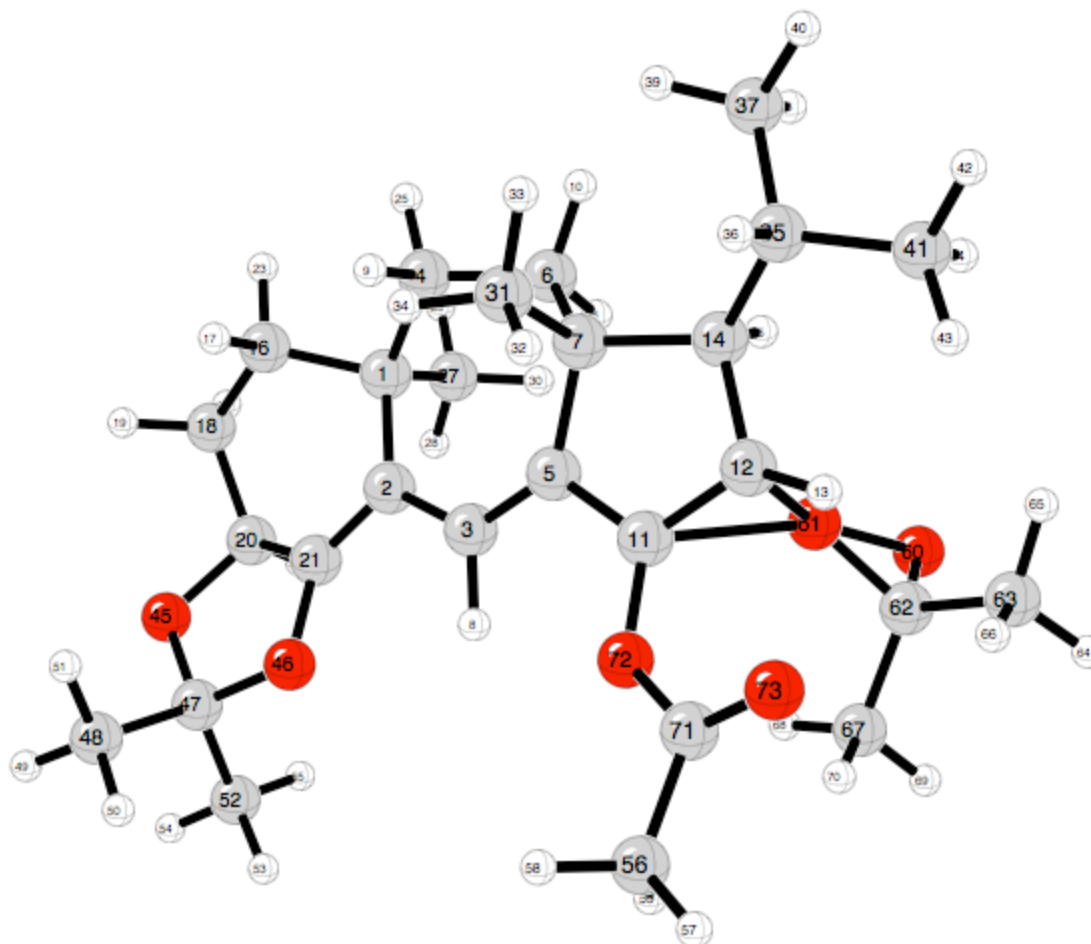
Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

```
SCF Energy= -926.224346847678 Predicted Change= -8.801157D-08
Zero-point correction (ZPE)= -925.5967 0.62759
Internal Energy (U)= -925.5618 0.66245
Enthalpy (H)= -925.5609 0.66339
Gibbs Free Energy (G)= -925.6629 0.56136
```

Frequencies -- -446.8516 17.4467 25.1167

Supporting Information



Supporting Information

Name	Definition	Value	R55	R(46, 47)	1.4544	A32	A(6, 7, 31)	111.2629	A88	A(37, 35, 41)	108.3136
R1	R(1, 2)	1.5143	R56	R(47, 48)	1.53	A33	A(14, 7, 31)	111.3022	A89	A(35, 37, 38)	111.3007
R2	R(1, 4)	1.5388	R57	R(47, 52)	1.5327	A34	A(5, 11, 12)	111.5294	A90	A(35, 37, 39)	111.8435
R3	R(1, 16)	1.5556	R58	R(48, 49)	1.0977	A35	A(5, 11, 61)	107.3544	A91	A(35, 37, 40)	110.6867
R4	R(1, 27)	1.5289	R59	R(48, 50)	1.0975	A36	A(5, 11, 72)	117.595	A92	A(38, 37, 39)	107.7827
R5	R(2, 3)	1.4461	R60	R(48, 51)	1.0976	A37	A(12, 11, 72)	130.8258	A93	A(38, 37, 40)	107.6066
R6	R(2, 21)	1.3585	R61	R(52, 53)	1.0974	A38	A(61, 11, 72)	108.0433	A94	A(39, 37, 40)	107.4266
R7	R(3, 5)	1.3467	R62	R(52, 54)	1.0976	A39	A(11, 12, 13)	125.0537	A95	A(35, 41, 42)	110.8578
R8	R(3, 8)	1.1019	R63	R(52, 55)	1.0977	A40	A(11, 12, 14)	109.1489	A96	A(35, 41, 43)	111.7842
R9	R(4, 6)	1.519	R64	R(56, 57)	1.0953	A41	A(13, 12, 14)	121.254	A97	A(35, 41, 44)	111.3646
R10	R(4, 9)	1.1139	R65	R(56, 58)	1.0981	A42	A(14, 12, 61)	100.6246	A98	A(42, 41, 43)	107.4852
R11	R(4, 25)	1.1101	R66	R(56, 59)	1.0984	A43	A(7, 14, 12)	104.0689	A99	A(42, 41, 44)	107.766
R12	R(5, 7)	1.5155	R67	R(56, 71)	1.511	A44	A(7, 14, 15)	108.5513	A100	A(43, 41, 44)	107.3821
R13	R(5, 11)	1.4708	R68	R(60, 62)	1.3214	A45	A(7, 14, 35)	117.548	A101	A(20, 45, 47)	108.371
R14	R(6, 7)	1.5206	R69	R(61, 62)	1.3977	A46	A(11, 14, 15)	106.214	A102	A(21, 46, 47)	108.6063
R15	R(6, 10)	1.1082	R70	R(62, 63)	1.5338	A47	A(12, 14, 35)	111.9381	A103	A(45, 47, 46)	106.4601
R16	R(6, 26)	1.1132	R71	R(62, 67)	1.537	A48	A(15, 14, 35)	107.9314	A104	A(45, 47, 48)	109.1687
R17	R(7, 14)	1.5737	R72	R(63, 64)	1.0969	A49	A(14, 15, 61)	92.9503	A105	A(45, 47, 48)	110.9306
R18	R(7, 31)	1.5288	R73	R(63, 65)	1.0975	A50	A(1, 16, 17)	107.947	A106	A(46, 47, 48)	109.2429
R19	R(11, 12)	1.3877	R74	R(63, 66)	1.0965	A51	A(1, 16, 18)	116.4761	A107	A(46, 47, 52)	109.3772
R20	R(11, 61)	2.3745	R75	R(67, 68)	1.0967	A52	A(1, 16, 23)	109.0449	A108	A(48, 47, 52)	111.5202
R21	R(11, 72)	1.3646	R76	R(67, 69)	1.0971	A53	A(17, 16, 18)	108.7696	A109	A(47, 48, 49)	110.545
R22	R(12, 13)	1.0971	R77	R(67, 70)	1.0966	A54	A(17, 16, 23)	105.7309	A110	A(47, 48, 50)	110.7491
R23	R(12, 14)	1.5177	R78	R(71, 72)	1.3825	A55	A(18, 16, 23)	108.3528	A111	A(47, 48, 51)	112.1017
R24	R(12, 61)	1.8838	R79	R(71, 73)	1.2085	A56	A(16, 18, 19)	109.5674	A112	A(49, 48, 50)	107.8469
R25	R(13, 61)	2.3192	A1	A(2, 1, 4)	113.522	A57	A(16, 18, 20)	112.1354	A113	A(49, 48, 51)	107.6543
R26	R(14, 15)	1.1147	A2	A(2, 1, 16)	108.2411	A58	A(16, 18, 24)	110.0062	A114	A(50, 48, 51)	107.7773
R27	R(14, 35)	1.5296	A3	A(2, 1, 27)	109.551	A59	A(19, 18, 20)	111.0411	A115	A(47, 52, 53)	110.8649
R28	R(15, 61)	2.3232	A4	A(4, 1, 16)	105.1663	A60	A(19, 18, 24)	105.3384	A116	A(47, 52, 54)	110.5239
R29	R(16, 17)	1.1094	A5	A(4, 1, 27)	109.4335	A61	A(20, 18, 24)	108.5245	A117	A(47, 52, 55)	112.0636
R30	R(16, 18)	1.5227	A6	A(16, 1, 27)	110.8583	A62	A(18, 20, 21)	113.3513	A118	A(53, 52, 54)	107.8359
R31	R(16, 23)	1.1088	A7	A(1, 2, 3)	126.9802	A63	A(18, 20, 22)	110.3878	A119	A(53, 52, 55)	107.7501
R32	R(18, 19)	1.1086	A8	A(1, 2, 21)	114.6744	A64	A(18, 20, 45)	112.8288	A120	A(54, 52, 55)	107.6328
R33	R(18, 20)	1.5232	A9	A(3, 2, 21)	118.1865	A65	A(21, 20, 22)	109.5475	A121	A(57, 56, 58)	108.6424
R34	R(18, 24)	1.1082	A10	A(2, 3, 5)	132.1647	A66	A(21, 20, 45)	103.5621	A122	A(57, 56, 59)	108.8011
R35	R(20, 21)	1.5006	A11	A(2, 3, 8)	112.9527	A67	A(22, 20, 45)	106.7718	A123	A(57, 56, 71)	110.4244
R36	R(20, 22)	1.1186	A12	A(5, 3, 8)	114.8697	A68	A(2, 21, 20)	126.1654	A124	A(58, 56, 59)	107.6027
R37	R(20, 45)	1.4328	A13	A(1, 4, 6)	115.6343	A69	A(2, 21, 46)	125.224	A125	A(58, 56, 71)	110.5148
R38	R(21, 46)	1.3761	A14	A(1, 4, 9)	109.0918	A70	A(20, 21, 46)	108.5865	A126	A(59, 56, 71)	110.7745
R39	R(27, 28)	1.0975	A15	A(1, 4, 25)	107.7758	A71	A(1, 27, 28)	112.0066	A127	A(11, 61, 13)	56.1255
R40	R(27, 29)	1.0979	A16	A(6, 4, 9)	109.9053	A72	A(1, 27, 29)	111.2178	A128	A(11, 61, 15)	78.3163
R41	R(27, 30)	1.1028	A17	A(6, 4, 25)	108.2773	A73	A(1, 27, 30)	110.3642	A129	A(11, 61, 62)	125.4776
R42	R(31, 32)	1.0969	A18	A(9, 4, 25)	105.6697	A74	A(28, 27, 29)	107.6116	A130	A(12, 61, 15)	59.4045
R43	R(31, 33)	1.0976	A19	A(3, 5, 7)	132.2036	A75	A(28, 27, 30)	107.8533	A131	A(12, 61, 62)	126.5907
R44	R(31, 34)	1.1019	A20	A(3, 5, 11)	122.2135	A76	A(29, 27, 30)	107.6076	A132	A(13, 61, 15)	75.3678
R45	R(35, 36)	1.1138	A21	A(7, 5, 11)	105.4975	A77	A(7, 31, 32)	111.2184	A133	A(13, 61, 62)	100.5993
R46	R(35, 37)	1.5197	A22	A(4, 6, 7)	112.961	A78	A(7, 31, 33)	111.2571	A134	A(15, 61, 62)	149.085
R47	R(35, 41)	1.5238	A23	A(4, 6, 10)	109.3146	A79	A(7, 31, 34)	110.3682	A135	A(60, 62, 61)	66.233
R48	R(37, 38)	1.0984	A24	A(4, 6, 26)	110.1717	A80	A(32, 31, 33)	108.2144	A136	A(60, 62, 63)	119.4152
R49	R(37, 39)	1.0981	A25	A(7, 6, 10)	108.3722	A81	A(32, 31, 34)	107.9595	A137	A(60, 62, 67)	117.4764
R50	R(37, 40)	1.0988	A26	A(7, 6, 26)	109.4505	A82	A(33, 31, 34)	107.686	A138	A(61, 62, 63)	115.2704
R51	R(41, 42)	1.0987	A27	A(10, 6, 26)	106.3393	A83	A(14, 35, 36)	109.3607	A139	A(61, 62, 67)	114.902
R52	R(41, 43)	1.0982	A28	A(5, 7, 6)	111.8894	A84	A(14, 35, 37)	111.5307	A140	A(63, 62, 67)	114.6882
R53	R(41, 44)	1.0983	A29	A(5, 7, 14)	103.765	A85	A(14, 35, 41)	110.0413	A141	A(62, 63, 64)	110.2363
R54	R(45, 47)	1.4368	A30	A(5, 7, 31)	107.3916	A86	A(36, 35, 37)	108.9816	A142	A(62, 63, 65)	111.4133
			A31	A(6, 7, 14)	110.9506	A87	A(36, 35, 41)	108.5534	A143	A(62, 63, 66)	110.9701

Supporting Information

A144	A(64,63,65)	108.307	D17	D(1,2,21,46)	-168.538	D46	D(5,11,72,71)	-156.1522	D75	D(36,35,37,38)	-177.2575
A145	A(64,63,66)	107.6177	D18	D(3,2,21,20)	-166.2697	D47	D(12,11,72,71)	26.662	D76	D(14,35,41,42)	177.2484
A146	A(65,63,66)	108.1687	D19	D(2,3,5,7)	5.6525	D48	D(11,12,14,7)	9.624	D77	D(14,35,41,43)	-62.8486
A147	A(62,67,68)	111.2629	D20	D(2,3,5,11)	-170.47	D49	D(11,12,14,15)	-104.8609	D78	D(36,35,41,42)	-63.1041
A148	A(62,67,69)	110.062	D21	D(8,3,5,7)	-175.7755	D50	D(13,12,14,7)	-147.5871	D79	D(20,45,47,46)	17.1477
A149	A(62,67,70)	111.5324	D22	D(1,4,6,7)	-89.9148	D51	D(14,12,61,15)	4.8996	D80	D(20,45,47,48)	134.9575
A150	A(68,67,69)	107.9116	D23	D(1,4,6,10)	149.3405	D52	D(14,12,61,62)	148.255	D81	D(21,46,47,45)	-5.3149
A151	A(68,67,70)	108.2648	D24	D(9,4,6,7)	34.1132	D53	D(7,14,15,61)	-104.0684	D82	D(21,46,47,48)	-123.0757
A152	A(69,67,70)	107.6641	D25	D(3,5,7,6)	-32.5266	D54	D(12,14,15,61)	7.3158	D83	D(45,47,48,49)	62.1575
A153	A(56,71,72)	109.9907	D26	D(3,5,7,14)	-152.2073	D55	D(7,14,35,36)	56.2271	D84	D(45,47,48,50)	-178.3719
A154	A(56,71,73)	127.6901	D27	D(11,5,7,6)	144.0696	D56	D(7,14,35,37)	-64.387	D85	D(46,47,48,49)	178.2027
A155	A(72,71,73)	122.307	D28	D(3,5,11,12)	157.1454	D57	D(12,14,35,36)	-64.149	D86	D(45,47,52,53)	177.7156
A156	A(11,72,71)	124.4835	D29	D(3,5,11,61)	101.4061	D58	D(14,15,61,11)	26.2219	D87	D(45,47,52,54)	-62.7666
D1	D(4,1,2,3)	-32.1946	D30	D(7,5,11,12)	-19.8749	D59	D(14,15,61,12)	-6.5716	D88	D(46,47,52,53)	60.5797
D2	D(4,1,2,21)	152.508	D31	D(4,6,7,5)	66.484	D60	D(1,16,18,19)	154.7229	D89	D(57,56,71,72)	177.4844
D3	D(16,1,2,3)	-148.5465	D32	D(4,6,7,14)	-178.1491	D61	D(1,16,18,20)	30.9468	D90	D(57,56,71,73)	-3.77
D4	D(2,1,4,6)	65.8644	D33	D(10,6,7,5)	-172.2363	D62	D(17,16,18,19)	32.5257	D91	D(58,56,71,72)	-62.2812
D5	D(2,1,4,9)	-58.5868	D34	D(5,7,14,12)	-20.7726	D63	D(16,18,20,21)	13.7471	D92	D(11,61,62,60)	159.7149
D6	D(16,1,4,6)	-175.9917	D35	D(5,7,14,15)	92.0413	D64	D(16,18,20,22)	-109.5684	D93	D(11,61,62,63)	-87.6069
D7	D(2,1,16,17)	64.8173	D36	D(6,7,14,12)	-141.0913	D65	D(19,18,20,21)	-109.2009	D94	D(12,61,62,60)	-155.7047
D8	D(2,1,16,18)	-57.8098	D37	D(5,7,31,32)	56.2742	D66	D(18,20,21,2)	-37.6126	D95	D(60,62,63,64)	-85.8007
D9	D(4,1,16,17)	-56.832	D38	D(5,7,31,33)	176.9925	D67	D(18,20,21,46)	140.6699	D96	D(60,62,63,65)	34.4753
D10	D(2,1,27,28)	49.4425	D39	D(6,7,31,32)	179.0328	D68	D(22,20,21,2)	86.1633	D97	D(61,62,63,64)	-161.5915
D11	D(2,1,27,29)	169.9054	D40	D(5,11,12,13)	162.2279	D69	D(18,20,45,47)	-144.1893	D98	D(60,62,67,68)	-36.6375
D12	D(4,1,27,28)	174.4999	D41	D(5,11,12,14)	6.0875	D70	D(21,20,45,47)	-21.2374	D99	D(60,62,67,69)	82.9297
D13	D(1,2,3,5)	12.4556	D42	D(72,11,12,13)	-20.4531	D71	D(2,21,46,47)	170.3273	D100	D(61,62,67,68)	38.3279
D14	D(1,2,3,8)	-166.1375	D43	D(5,11,61,13)	131.3156	D72	D(20,21,46,47)	-7.9753	D101	D(56,71,72,11)	179.4495
D15	D(21,2,3,5)	-172.393	D44	D(5,11,61,15)	51.2121	D73	D(14,35,37,38)	-56.4216	D102	D(73,71,72,11)	0.6239
D16	D(1,2,21,20)	9.469	D45	D(72,11,61,13)	-100.9348	D74	D(14,35,37,39)	64.2055			

Supporting Information

Transition Structure Epoxidation Beta (Boat) - ONIOM Full Guanacastepene A precursor
Supporting Information: GS-TS-BOAT-ONIOM.output

Using Gaussian 03: IA32L-G03RevC.02 12-Jun-2004

```
# opt=(readfc,gdiis,ts,maxcycle=250,noeigentest) freq=noraman
oniom(b3lyp/6-31g(d):pm3) geom=check guess=read
scf=(direct,maxcycle=250,tight)
#N Geom=AllCheck Guess=Read SCRF=Check GenChk
ONIOM(B3LYP/6-31G(d):PM3/ZDO) Freq
```

Pointgroup= C1 Stoichiometry= C27H40O6 C1[X(C27H40O6)] #Atoms= 73
Charge = 0 Multiplicity = 1

SCF Energy= -926.228695002638 Predicted Change= -2.105761D-07

```
Optimization completed. {Found 1 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00002 || 0.00045 [ YES ] 0.00000 || 0.00030 [ YES ]
Displ 0.01334 || 0.00180 [ NO ] 0.01334 || 0.00180 [ NO ]
```

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	2.350809	-2.090453	-0.268537
C	2.163640	-0.588702	-0.160011
C	0.917474	0.148143	-0.249510
C	1.177510	-2.915400	0.287185
C	-0.377954	-0.266242	-0.197031
C	-0.141417	-2.770223	-0.449077
C	-1.011824	-1.620844	0.114051
H	1.032118	1.217925	-0.471461
H	1.038265	-2.669564	1.364629
H	-0.699909	-3.718002	-0.369235
C	-1.447563	0.627520	-0.589940
C	-2.655549	-0.025971	-0.742648
H	-3.482010	0.382985	-1.299037
C	-2.413771	-1.523127	-0.625589
H	-2.251345	-1.873181	-1.660438
C	3.567677	-2.496286	0.610311
H	3.308285	-2.285088	1.668209
C	4.894742	-1.824506	0.288196
H	5.532951	-1.811654	1.194486
C	4.705557	-0.419391	-0.268119
C	3.318647	0.118270	-0.071784
H	4.966250	-0.394172	-1.355524
H	3.707509	-3.594584	0.549052
H	5.453667	-2.426492	-0.455554
H	1.472744	-3.985269	0.260446
H	0.043769	-2.602841	-1.533079
C	2.581941	-2.472984	-1.731199
H	3.345592	-1.844557	-2.206701
H	2.907517	-3.517654	-1.822418
H	1.647039	-2.364950	-2.306002
C	-1.190735	-1.740935	1.651697

H	-1.804801	-0.929523	2.043637
H	-1.661846	-2.692317	1.918029
H	-0.206870	-1.708381	2.143633
C	-3.621615	-2.331050	-0.080327
H	-3.814870	-2.006484	0.946660
C	-3.381258	-3.850485	-0.087708
H	-3.140629	-4.211924	-1.096554
H	-2.573122	-4.158914	0.581288
H	-4.287646	-4.373246	0.239236
C	-4.886820	-2.029619	-0.904094
H	-5.725691	-2.636548	-0.545130
H	-5.188542	-0.981871	-0.826784
H	-4.738467	-2.266741	-1.966612
O	5.536842	0.551914	0.377535
O	3.405968	1.454814	0.244243
C	4.801952	1.782874	0.479193
C	4.955126	2.346082	1.893186
H	6.007487	2.574194	2.105706
H	4.379283	3.273523	2.006382
H	4.605905	1.640153	2.657769
C	5.270029	2.785184	-0.581501
H	4.681792	3.710230	-0.531300
H	6.324028	3.047577	-0.424394
H	5.175459	2.382946	-1.598474
C	-1.203384	4.113210	-1.725457
H	-1.757594	4.748883	-2.416184
H	-1.207443	4.554001	-0.723417
H	-0.158452	4.037677	-2.044250
O	-3.299544	0.429822	1.044605
O	-4.426197	0.770012	2.448543
C	-4.079797	1.585697	1.428863
C	-5.203142	1.929724	0.454392
H	-4.825610	2.365389	-0.476852
H	-5.778271	1.027634	0.230693
H	-5.876071	2.658615	0.920570
C	-3.217509	2.777534	1.834722
H	-2.418572	2.433427	2.495710
H	-2.777599	3.282667	0.967799
H	-3.832879	3.506687	2.374301
O	-2.777223	2.377542	-2.344889
O	-1.147642	1.947395	-0.798261
C	-1.832607	2.744886	-1.694771

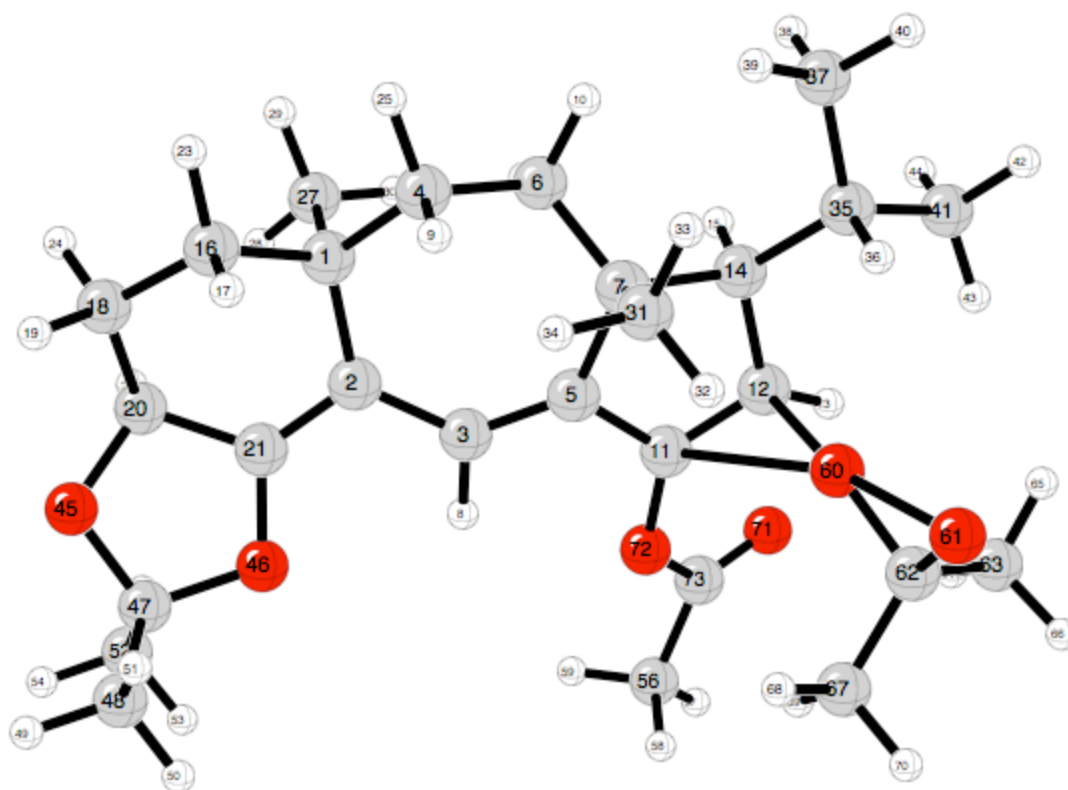
Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

```
SCF Energy= -926.228695002638 Predicted Change= -2.105761D-07
Zero-point correction (ZPE)= -925.6009 0.62778
Internal Energy (U)= -925.5661 0.66259
Enthalpy (H)= -925.5651 0.66353
Gibbs Free Energy (G)= -925.6667 0.56196
```

Frequencies -- -417.5695 16.9765 29.1222

Supporting Information



Supporting Information

Name	Definition	Value	R53	R(41,43)	1.098	A27	A(10,6,26)	106.2926	A81	A(33,31,34)	107.6579
R1	R(1,2)	1.5144	R54	R(41,44)	1.0981	A28	A(5,7,6)	110.678	A82	A(31,32,60)	131.056
R2	R(1,4)	1.5393	R55	R(45,47)	1.4373	A29	A(5,7,14)	103.3233	A83	A(14,35,36)	109.1264
R3	R(1,16)	1.5556	R56	R(46,47)	1.4538	A30	A(5,7,31)	108.8775	A84	A(14,35,37)	111.6863
R4	R(1,27)	1.5297	R57	R(47,48)	1.5299	A31	A(6,7,14)	110.8575	A85	A(14,35,41)	109.8464
R5	R(2,3)	1.4467	R58	R(47,52)	1.533	A32	A(6,7,31)	111.1136	A86	A(36,35,37)	109.8049
R6	R(2,21)	1.3581	R59	R(48,49)	1.0977	A33	A(14,7,31)	111.7194	A87	A(36,35,41)	108.0661
R7	R(3,5)	1.3471	R60	R(48,50)	1.0975	A34	A(5,11,12)	112.0902	A88	A(37,35,41)	108.2385
R8	R(3,8)	1.1019	R61	R(48,51)	1.0976	A35	A(5,11,60)	109.2224	A89	A(35,36,60)	106.1539
R9	R(4,6)	1.5196	R62	R(52,53)	1.0974	A36	A(5,11,72)	117.7519	A90	A(35,37,38)	111.5002
R10	R(4,9)	1.1138	R63	R(52,54)	1.0976	A37	A(12,11,72)	130.1539	A91	A(35,37,39)	111.9632
R11	R(4,25)	1.1102	R64	R(52,55)	1.0977	A38	A(60,11,72)	108.6152	A92	A(35,37,40)	110.4907
R12	R(5,7)	1.5165	R65	R(56,57)	1.0954	A39	A(11,12,13)	125.1059	A93	A(38,37,39)	107.7208
R13	R(5,11)	1.4724	R66	R(56,58)	1.0982	A40	A(11,12,14)	108.6089	A94	A(38,37,40)	107.4956
R14	R(6,7)	1.526	R67	R(56,59)	1.0981	A41	A(13,12,14)	121.3173	A95	A(39,37,40)	107.4653
R15	R(6,10)	1.1083	R68	R(56,73)	1.5104	A42	A(14,12,60)	103.8045	A96	A(35,41,42)	110.7599
R16	R(6,26)	1.1131	R69	R(60,62)	1.3945	A43	A(7,14,12)	103.8059	A97	A(35,41,43)	111.6011
R17	R(7,14)	1.5774	R70	R(61,62)	1.3299	A44	A(7,14,15)	107.2747	A98	A(35,41,44)	111.6928
R18	R(7,31)	1.5279	R71	R(62,63)	1.5317	A45	A(7,14,35)	118.7908	A99	A(42,41,43)	107.2025
R19	R(11,12)	1.3801	R72	R(62,67)	1.535	A46	A(12,14,15)	106.2531	A100	A(42,41,44)	107.5472
R20	R(11,60)	2.4518	R73	R(63,64)	1.0963	A47	A(12,14,35)	113.4632	A101	A(43,41,44)	107.8263
R21	R(11,72)	1.3683	R74	R(63,65)	1.0977	A48	A(15,14,35)	106.5121	A102	A(20,45,47)	108.4269
R22	R(12,13)	1.0964	R75	R(63,66)	1.097	A49	A(1,16,17)	107.8514	A103	A(21,46,47)	108.5668
R23	R(12,14)	1.5172	R76	R(67,68)	1.0971	A50	A(1,16,18)	116.5674	A104	A(45,47,46)	106.5868
R24	R(12,60)	1.9457	R77	R(67,69)	1.0967	A51	A(1,16,23)	109.0624	A105	A(45,47,48)	109.2284
R25	R(13,60)	2.322	R78	R(67,70)	1.0967	A52	A(17,16,18)	108.7163	A106	A(45,47,52)	110.8022
R26	R(14,15)	1.1181	R79	R(71,73)	1.2087	A53	A(17,16,23)	105.7535	A107	A(46,47,48)	109.253
R27	R(14,35)	1.5327	R80	R(72,73)	1.3815	A54	A(18,16,23)	108.3647	A108	A(46,47,52)	109.3455
R28	R(16,17)	1.1095	A1	A(2,1,4)	113.7139	A55	A(16,18,19)	109.5517	A109	A(48,47,52)	111.4923
R29	R(16,18)	1.5229	A2	A(2,1,16)	108.2036	A56	A(16,18,20)	112.1435	A110	A(47,48,49)	110.5798
R30	R(16,23)	1.1087	A3	A(2,1,27)	109.5326	A57	A(16,18,24)	110.046	A111	A(47,48,50)	110.7334
R31	R(18,19)	1.1086	A4	A(4,1,16)	105.1794	A58	A(19,18,20)	111.02	A112	A(47,48,51)	112.0606
R32	R(18,20)	1.5231	A5	A(4,1,27)	109.2863	A59	A(19,18,24)	105.3154	A113	A(49,48,50)	107.8722
R33	R(18,24)	1.1082	A6	A(16,1,27)	110.8584	A60	A(20,18,24)	108.5356	A114	A(49,48,51)	107.6805
R34	R(20,21)	1.5004	A7	A(1,2,3)	126.9003	A61	A(18,20,21)	113.3605	A115	A(50,48,51)	107.7497
R35	R(20,22)	1.1186	A8	A(1,2,21)	114.6733	A62	A(18,20,22)	110.3233	A116	A(47,52,53)	110.866
R36	R(20,45)	1.4325	A9	A(3,2,21)	118.1673	A63	A(18,20,45)	112.9144	A117	A(47,52,54)	110.5168
R37	R(21,46)	1.3768	A10	A(2,3,5)	132.38	A64	A(21,20,22)	109.5795	A118	A(47,52,55)	112.0885
R38	R(27,28)	1.0975	A11	A(2,3,8)	112.6341	A65	A(21,20,45)	103.6103	A119	A(53,52,54)	107.8114
R39	R(27,29)	1.098	A12	A(5,3,8)	114.9295	A66	A(22,20,45)	106.6611	A120	A(53,52,55)	107.7713
R40	R(27,30)	1.1027	A13	A(1,4,6)	115.8825	A67	A(2,21,20)	126.2312	A121	A(54,52,55)	107.6155
R41	R(31,32)	1.098	A14	A(1,4,9)	108.9741	A68	A(2,21,46)	125.2136	A122	A(57,56,58)	108.8563
R42	R(31,33)	1.0979	A15	A(1,4,25)	107.6881	A69	A(20,21,46)	108.5402	A123	A(57,56,59)	108.6203
R43	R(31,34)	1.1013	A16	A(6,4,9)	109.8689	A70	A(1,27,28)	112.092	A124	A(57,56,73)	110.3513
R44	R(32,60)	2.2755	A17	A(6,4,25)	108.2936	A71	A(1,27,29)	111.2454	A125	A(58,56,59)	107.6516
R45	R(35,36)	1.1133	A18	A(9,4,25)	105.6224	A72	A(1,27,30)	110.2725	A126	A(58,56,73)	110.7378
R46	R(35,37)	1.5187	A19	A(3,5,7)	131.7033	A73	A(28,27,29)	107.5644	A127	A(59,56,73)	110.5464
R47	R(35,41)	1.5249	A20	A(3,5,11)	121.5666	A74	A(28,27,30)	107.9213	A128	A(11,60,13)	54.847
R48	R(36,60)	2.4878	A21	A(7,5,11)	106.4936	A75	A(29,27,30)	107.5632	A129	A(11,60,32)	80.7542
R49	R(37,38)	1.0984	A22	A(4,6,7)	113.1273	A76	A(7,31,32)	111.1534	A130	A(11,60,36)	101.7018
R50	R(37,39)	1.0978	A23	A(4,6,10)	109.2605	A77	A(7,31,33)	110.7148	A131	A(11,60,62)	120.4746
R51	R(37,40)	1.0989	A24	A(4,6,26)	109.8355	A78	A(7,31,34)	110.438	A132	A(12,60,32)	91.7239
R52	R(41,42)	1.0982	A25	A(7,6,10)	108.2874	A79	A(32,31,33)	108.3964	A133	A(12,60,36)	78.2261
			A26	A(7,6,26)	109.7955	A80	A(32,31,34)	108.3693	A134	A(12,60,62)	127.7623

Supporting Information

A135	A(13,60,32)	118.4983	D30	D(7,5,11,12)	-7.9453	D87	D(45,47,48,49)	62.0684
A136	A(13,60,36)	85.04	D31	D(4,6,7,5)	69.1745	D88	D(45,47,48,50)	-178.4171
A137	A(13,60,62)	103.8081	D32	D(4,6,7,14)	-176.7843	D89	D(46,47,48,49)	178.3044
A138	A(32,60,36)	62.8445	D33	D(10,6,7,5)	-169.566	D90	D(45,47,52,53)	177.7308
A139	A(32,60,62)	136.698	D34	D(5,7,14,12)	-23.5454	D91	D(45,47,52,54)	-62.7859
A140	A(36,60,62)	134.0179	D35	D(5,7,14,15)	88.6793	D92	D(46,47,52,53)	60.5352
A141	A(60,62,61)	64.6802	D36	D(6,7,14,12)	-142.1369	D93	D(57,56,73,71)	4.0974
A142	A(60,62,63)	115.5911	D37	D(5,7,31,32)	57.368	D94	D(57,56,73,72)	-178.4634
A143	A(60,62,67)	115.1662	D38	D(5,7,31,33)	177.9057	D95	D(58,56,73,71)	124.6971
A144	A(61,62,63)	119.2435	D39	D(6,7,31,32)	179.5141	D96	D(11,60,62,61)	-161.8632
A145	A(61,62,67)	117.6101	D40	D(5,11,12,13)	-163.1042	D97	D(11,60,62,63)	86.2587
A146	A(63,62,67)	115.0142	D41	D(5,11,12,14)	-7.9966	D98	D(12,60,62,61)	157.4475
A147	A(62,63,64)	110.9141	D42	D(72,11,12,13)	16.1389	D99	D(60,62,63,64)	-76.5201
A148	A(62,63,65)	111.5711	D43	D(5,11,60,13)	-131.3501	D100	D(60,62,63,65)	44.4952
A149	A(62,63,66)	110.1478	D44	D(5,11,60,32)	3.5505	D101	D(61,62,63,64)	-150.5397
A150	A(64,63,65)	108.4434	D45	D(72,11,60,13)	99.0215	D102	D(60,62,67,68)	-42.2767
A151	A(64,63,66)	107.5085	D46	D(5,11,72,73)	149.0116	D103	D(60,62,67,69)	78.2662
A152	A(65,63,66)	108.1208	D47	D(12,11,72,73)	-30.1959	D104	D(61,62,67,68)	31.0141
A153	A(62,67,68)	111.3235	D48	D(11,12,14,7)	19.8315	D105	D(11,72,73,56)	-176.6746
A154	A(62,67,69)	111.1823	D49	D(11,12,14,15)	-93.1328	D106	D(11,72,73,71)	0.9195
A155	A(62,67,70)	110.2447	D50	D(13,12,14,7)	176.061			
A156	A(68,67,69)	108.0602	D51	D(14,12,60,32)	39.4056			
A157	A(68,67,70)	108.2541	D52	D(14,12,60,36)	-22.3847			
A158	A(69,67,70)	107.6442	D53	D(7,14,35,36)	58.7655			
A159	A(11,72,73)	123.5705	D54	D(7,14,35,37)	-62.8248			
A160	A(56,73,71)	127.4821	D55	D(12,14,35,36)	-63.6033			
A161	A(56,73,72)	110.098	D56	D(1,16,18,19)	154.3285			
A162	A(71,73,72)	122.3694	D57	D(1,16,18,20)	30.5852			
D1	D(4,1,2,3)	-33.1045	D58	D(17,16,18,19)	32.2357			
D2	D(4,1,2,21)	152.8964	D59	D(16,18,20,21)	13.9745			
D3	D(16,1,2,3)	-149.5603	D60	D(16,18,20,22)	-109.3405			
D4	D(2,1,4,6)	64.2749	D61	D(19,18,20,21)	-108.9435			
D5	D(2,1,4,9)	-60.2168	D62	D(18,20,21,2)	-37.3972			
D6	D(16,1,4,6)	-177.5146	D63	D(18,20,21,46)	141.2527			
D7	D(2,1,16,17)	64.8678	D64	D(22,20,21,2)	86.3254			
D8	D(2,1,16,18)	-57.6767	D65	D(18,20,45,47)	-143.7851			
D9	D(4,1,16,17)	-56.9946	D66	D(21,20,45,47)	-20.7421			
D10	D(2,1,27,28)	48.7115	D67	D(2,21,46,47)	169.5115			
D11	D(2,1,27,29)	169.1919	D68	D(20,21,46,47)	-9.1555			
D12	D(4,1,27,28)	173.8978	D69	D(7,31,32,60)	22.4067			
D13	D(1,2,3,5)	14.4268	D70	D(33,31,32,60)	-99.49			
D14	D(1,2,3,8)	-162.6408	D71	D(31,32,60,11)	-48.3261			
D15	D(21,2,3,5)	-171.7595	D72	D(31,32,60,12)	-15.8246			
D16	D(1,2,21,20)	8.9832	D73	D(14,35,36,60)	35.4788			
D17	D(1,2,21,46)	-169.4499	D74	D(37,35,36,60)	158.2027			
D18	D(3,2,21,20)	-165.575	D75	D(14,35,37,38)	-56.7361			
D19	D(2,3,5,7)	6.9094	D76	D(14,35,37,39)	64.0345			
D20	D(2,3,5,11)	-166.6975	D77	D(36,35,37,38)	-177.9334			
D21	D(8,3,5,7)	-176.0752	D78	D(14,35,41,42)	176.4918			
D22	D(1,4,6,7)	-89.5022	D79	D(14,35,41,43)	-64.1502			
D23	D(1,4,6,10)	149.7892	D80	D(36,35,41,42)	-64.5519			
D24	D(9,4,6,7)	34.5263	D81	D(35,36,60,11)	-33.3051			
D25	D(3,5,7,6)	-36.1632	D82	D(35,36,60,12)	-8.2763			
D26	D(3,5,7,14)	-154.8794	D83	D(20,45,47,46)	15.9503			
D27	D(11,5,7,6)	138.1584	D84	D(20,45,47,48)	133.8729			
D28	D(3,5,11,12)	167.0809	D85	D(21,46,47,45)	-3.8398			
D29	D(3,5,11,60)	-136.6997	D86	D(21,46,47,48)	-121.746			