$AlCl_3$-Catalyzed Ring-Expansion Cascades of Bicyclic Cyclobutenamides Involving Highly Strained *Cis*,*Trans*-Cycloheptadienone Intermediates

Xiao-Na Wang,[†,‡] Elizabeth H. Krenske,[*,§] Ryne C. Johnston,[§,¶] K. N. Houk,[*,^] and Richard P. Hsung[*,‡]

[†] School of Pharmaceutical Sciences, Zhengzhou University, Zhengzhou, Henan, 450001 P. R. China

[‡] Division of Pharmaceutical Sciences and Department of Chemistry, University of Wisconsin, Madison, WI 53705 USA

[§] School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, QLD 4072, Australia

[^] Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095 USA

Supporting Information Part 3 – Computational Data

Contents **Page**

$AlCl_3$-Catalyzed Ring Opening of α,β-Unsaturated 4,6- and 4,5-Fused Cyclobutenamides to Monocyclic 2-Amidodienes

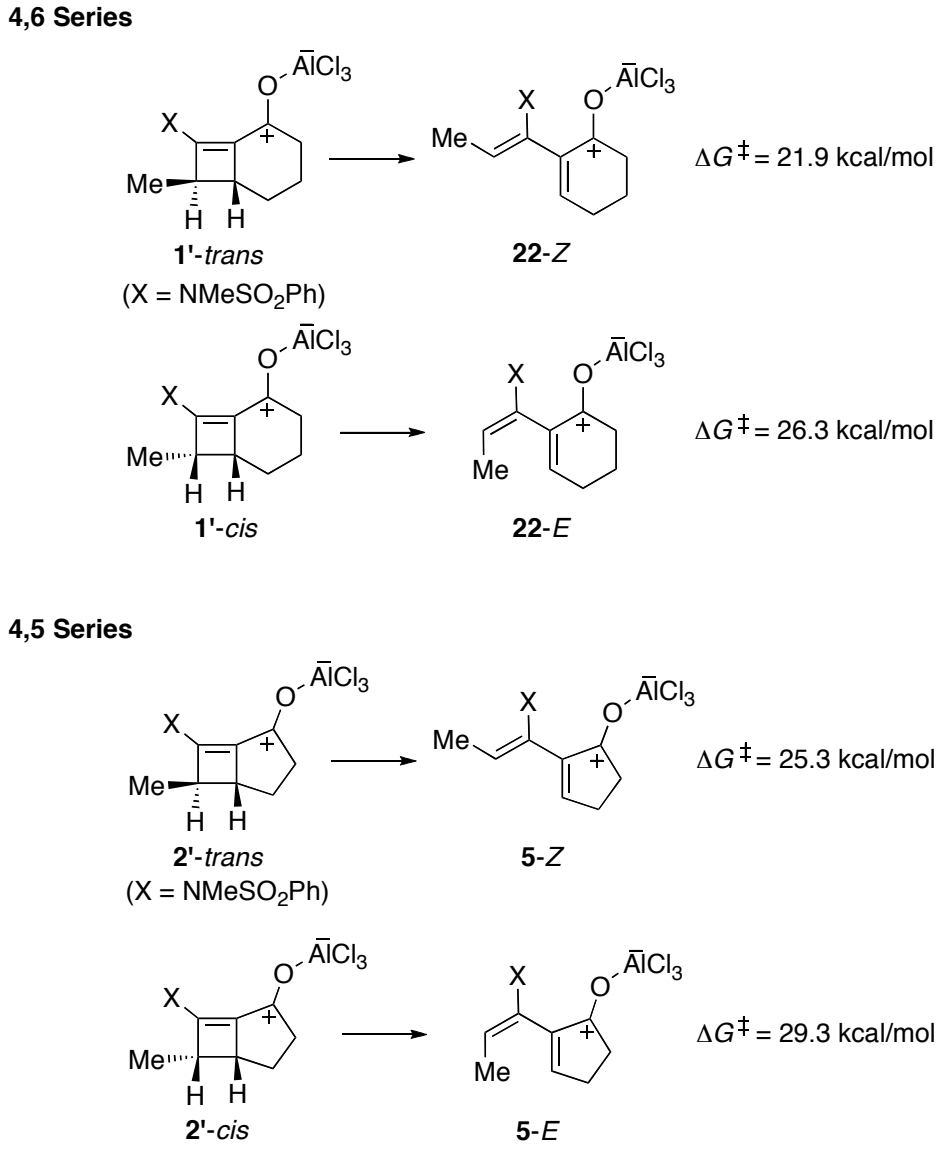


Figure S1. Computed activation energies for $AlCl_3$-catalyzed ring opening of α,β-unsaturated 4,6- and 4,5-fused cyclobutenamides to monocyclic 2-amidodienes in toluene. Barriers are calculated relative to the respective β,γ-unsaturated cyclobutenamides (**1** or **2**), which are the precursors to **1'** and **2'**.

Prins Cascade from 4,6-Fused Cyclobutenamides

The computed free energy profile for the cascade of reactions leading from **16** to aza-tricycle **21** is shown in Figure S2. The structures of **TS9** and **18** are shown in Figure S3, along with the structures of the first transition state and intermediate in a model intermolecular reaction (**16'** + propene).

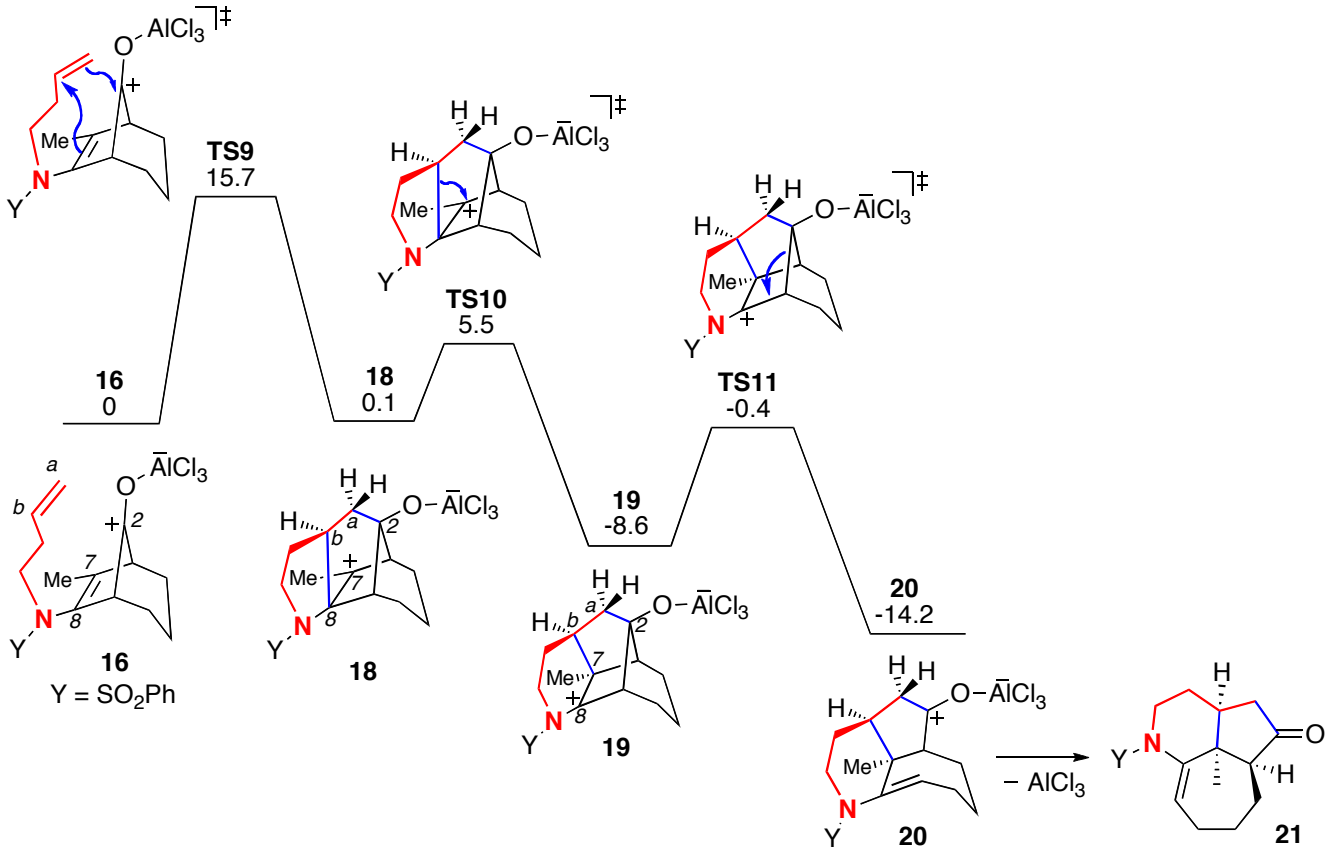


Figure S2. Computed free energy profile for the cascade leading from $AlCl_3$-coordinated [3.2.1]-bicyclic ketone **16** (derived from 4,6-fused cyclobutenamide **1**) to aza-tricycle **21**. ΔG in kcal/mol.

Starting from **16**, the first step in the cascade gives **18**, in which two new C–C bonds have formed: C(a)–C(2) and C(b)–C(8). A subsequent 1,2-alkyl shift gives **19**, in which C(b) is bonded to C(7) (albeit weakly: 1.69 Å). The initial formation of a bond between C(b) and C(8) is unexpected, because it would be expected that the polarization of the enamide in **16** would instead favor bond formation between C(b) and C(7). Calculations (Figure S3) reveal that the regioselectivity of the first step results from geometrical constraints imposed by the tether. As shown in Figure S3(b), an intermolecular Prins-type reaction (**16'** + propene) leads directly to **19'**, with bond formation between C(b) and C(7). In the intermolecular transition state (**TS9'**), C(b) lies 0.15 Å closer to C(7) than to C(8). In contrast, in the intramolecular TS (**TS9**), C(b) lies 0.12 Å closer to C(8) than to C(7); this geometry is constrained by the tether. After the C(b)–C(8) bond has formed, an inversion of configuration at nitrogen occurs, which allows the tether to adopt a appropriate geometry for the 1,2-alkyl shift leading to the more stable C(b)–C(7) bound intermediate, **19**.

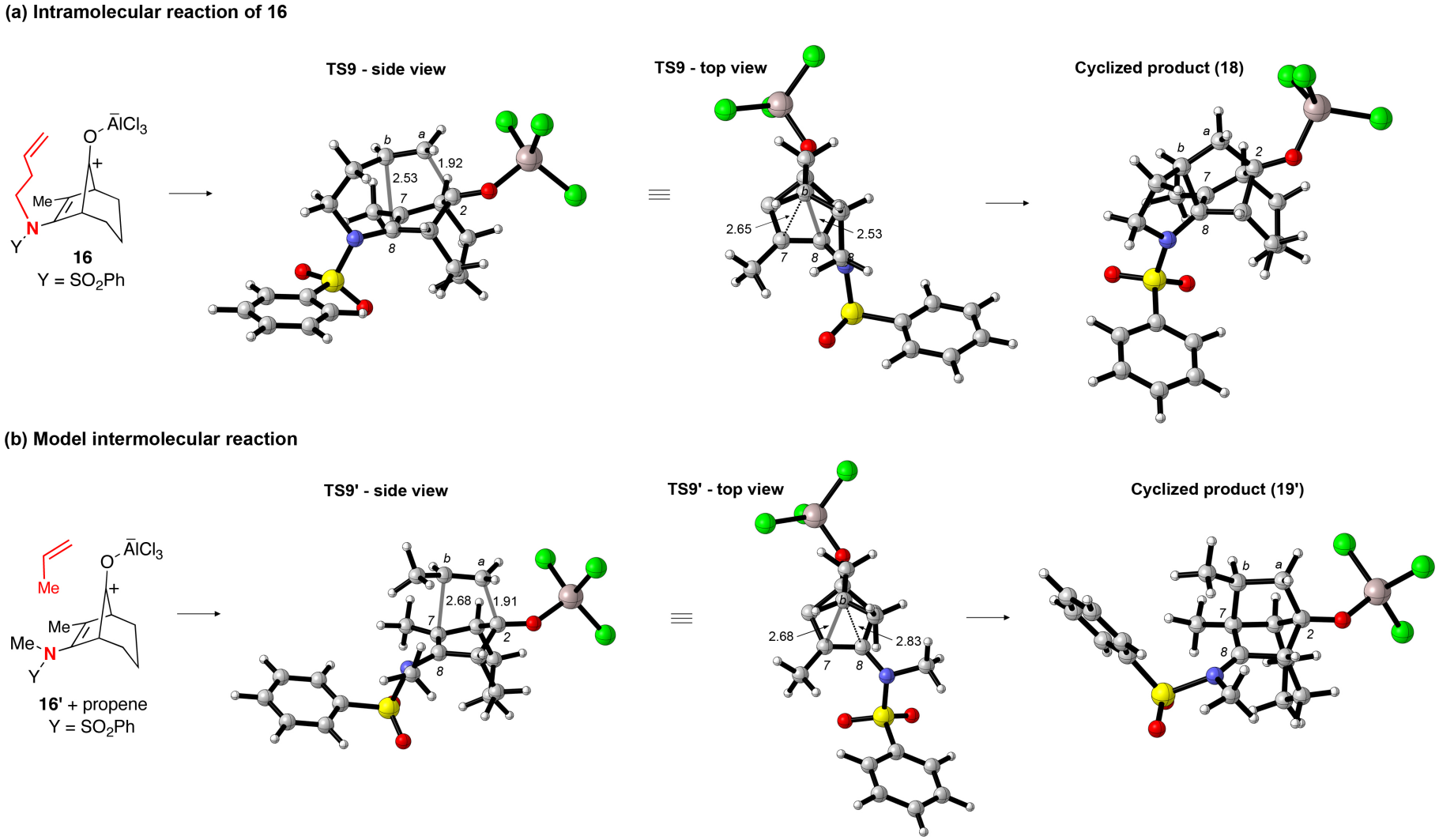


Figure S3. Geometries of the transition state and intermediate of the first step in (a) the Prins cascade from **16** and (b) the intermolecular reaction of **16'** with propene. Side and top views of the transition states are shown. In the top views, some atoms have been omitted for clarity. Distances in Å. The regioselectivity of bond formation by C(b) in the first step differs between the intra- and intermolecular reactions.

Computational Methods

Geometry optimizations were performed in the gas phase at the B3LYP/6-31G(d) level of theory. Vibrational frequency calculations indicated the nature of each stationary point (local minimum or first-order saddle point) and the computed frequencies were also used to derive unscaled zero-point energy and thermochemical corrections. Solvation energies were computed by means of single-point calculations with B3LYP/6-31G(d) in implicit toluene using the SMD continuum method. Single-point energies were computed at the M06-2X/6-311+G(d,p) level of theory in the gas phase. Free energies in solution were calculated by adding the B3LYP zero-point energy, thermochemical corrections, and solvation energy to the M06-2X potential energy. A standard state of 298.15 K and 1 mol/L was used.

Underneath the Cartesian coordinates for the optimized geometries below are listed the following energies:

B3LYP gas-phase electronic energy (`E`)
B3LYP gas-phase Gibbs free energy at 298.15 K and 1 mol/L (`G`) and/or B3LYP gas-phase enthalpy at 298.15 K (`H`)
M06-2X/6-311+G(d,p) gas-phase potential energy (E_{M06-2X})
Sum of B3LYP/6-31G(d) potential energy and free energy of solvation in toluene at 298.15 K and 1 mol/L (E_{solv})

All energies are given in Hartree.

Computed Geometries and Energies

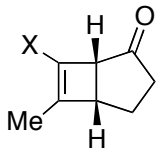
In the structures below, X represents $NMeSO_2Ph$.

Part 1 – 4,5-Fused Series

$AlCl_3$

```
Al    0.000000    0.000000    0.000000
Cl    0.000000    2.087290    0.000000
Cl    1.807646   -1.043645    0.000000
Cl   -1.807646   -1.043645    0.000000
0 imaginary frequencies
E = -1623.233266
G = -1623.254789
E_M06-2X = -1623.219865
E_solv = -1623.239524
```

4,5-Bicyclic cyclobutenamide 2

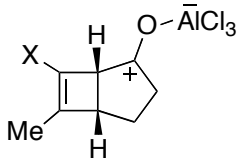



```
C     1.492145    0.600116   -0.057487
C     2.742552    1.033596    0.223536
C     3.380512    2.101783    1.048278
H     3.981094    2.767780    0.413706
H     4.067730    1.676152    1.793297
H     2.650676    2.719570    1.578300
C     3.396115   -0.045137   -0.638592
C     1.950177   -0.576974   -0.917898
H     1.570121   -0.628620   -1.939015
H     3.933461    0.340477   -1.512787
C     4.164939   -1.176881    0.083018
C     3.085332   -2.073759    0.718919
C     1.840739   -1.894791   -0.160192
O     0.909609   -2.673982   -0.218483
H     3.356402   -3.131321    0.783525
H     2.827837   -1.750235    1.736259
H     4.887076   -0.794949    0.813312
H     4.734024   -1.753026   -0.656916
N     0.202656    0.908603    0.400516
C     0.042256    1.662628    1.649225
S    -1.046384    1.161836   -0.754568
H     0.240335    2.733041    1.527362
H    -0.979689    1.536741    2.016744
H     0.728285    1.238746    2.386260
O    -1.520531    2.544576   -0.625580
O    -0.543405    0.654503   -2.031084
C    -2.349240    0.082316   -0.154712
C    -3.558752    0.651269    0.246667
C    -4.400720   -1.571247    0.692786
C    -3.183006   -2.123865    0.283899
C    -2.144245   -1.300820   -0.147921
H    -1.195221   -1.728321   -0.459486
H    -3.038602   -3.200231    0.299843
```

H	-5.204721	-2.221956	1.026031
H	-5.536614	0.239513	0.988447
H	-3.682390	1.728262	0.215544
C	-4.589079	-0.188565	0.673843

0 imaginary frequencies
E = -1260.328932
G = -1260.075980
E_{M06-2X} = -1260.200982
E_{solv} = -1260.349318

4,5-Bicyclic cyclobutenamide $AlCl_3$ complex 9

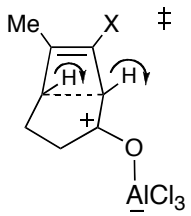


C	0.950793	2.045653	0.796948
C	1.045156	3.230765	0.157254
C	2.081968	3.914052	-0.661459
H	2.144761	4.976561	-0.396422
H	1.837840	3.851117	-1.730155
H	3.065482	3.455096	-0.527173
C	-0.381880	3.639493	0.504056
C	-0.512771	2.270245	1.255939
H	-0.732613	2.229586	2.326303
H	-0.469933	4.533036	1.130741
C	-1.412739	3.604956	-0.652366
C	-1.716012	2.111296	-0.900631
C	-1.410345	1.438297	0.412317
O	-1.799193	0.308196	0.772391
Al	-2.956200	-1.012346	0.050639
Cl	-2.141589	-1.421299	-1.889959
Cl	-4.837413	0.000642	0.002673
Cl	-2.785943	-2.615060	1.434236
H	-2.747005	1.908143	-1.206927
H	-1.068314	1.655550	-1.662932
H	-1.046574	4.110451	-1.550578
H	-2.329874	4.116707	-0.340990
N	1.721144	0.891699	0.947866
C	2.228483	0.570035	2.291122
S	2.695917	0.396389	-0.386502
H	1.409092	0.696774	3.003614
H	2.542477	-0.475615	2.321912
H	3.067537	1.214266	2.577293
O	1.975853	0.849330	-1.579127
O	4.085097	0.804266	-0.142014
C	2.608832	-1.387971	-0.278748
C	1.442840	-2.032240	-0.700665
C	2.478377	-4.148353	-0.153072
C	3.641946	-3.490301	0.250852
C	3.716713	-2.097872	0.189472
H	4.615189	-1.566118	0.483508
H	4.494751	-4.058620	0.610521
H	2.425456	-5.232183	-0.101085
H	0.480125	-3.932775	-0.951026
H	0.603320	-1.465609	-1.088153
C	1.383011	-3.422576	-0.630343

0 imaginary frequencies

E = -2883.619087
G = -2883.372163
E_{M06-2X} = -2883.487800
E_{solv} = -2883.647030

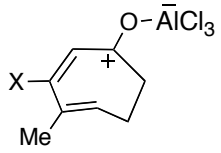
TS2 (Cyclobutene ring opening)



C	2.675218	-1.284711	1.531048
C	3.133238	-1.157047	0.216038
C	3.385340	-2.274347	-0.584059
C	3.161575	-3.545353	-0.053883
C	2.692486	-3.687798	1.253500
C	2.454419	-2.561264	2.045450
S	3.363312	0.482746	-0.471178
O	3.650964	1.405609	0.625200
N	1.809098	0.930475	-1.083987
C	1.355969	0.182032	-2.272082
C	0.851029	1.444766	-0.195987
C	-0.476086	0.860004	-0.058415
H	-0.575316	-0.223246	0.013149
C	-1.713743	1.547669	-0.281241
O	-2.821078	0.924132	-0.311446
C	0.918440	2.575436	0.569233
C	-0.288852	2.502532	1.380609
H	-0.365930	1.794161	2.200260
C	-1.395376	3.501312	1.136278
C	-1.832688	3.075601	-0.290995
C	1.828334	3.763431	0.474763
O	4.225117	0.374648	-1.646430
H	2.589741	3.737367	1.260935
H	2.352390	3.771723	-0.484619
H	1.267254	4.699172	0.583753
H	-1.051735	4.541117	1.167652
H	-2.212451	3.381835	1.852443
H	-1.163203	3.507582	-1.041765
H	-2.861132	3.350618	-0.530402
H	1.038382	-0.840979	-2.039201
H	2.171428	0.160879	-2.995263
H	0.511349	0.718907	-2.709331
H	2.517238	-0.401312	2.140113
H	2.099291	-2.676316	3.065092
H	2.515310	-4.679593	1.659136
H	3.355979	-4.423079	-0.662990
Al	-3.384918	-0.849716	-0.132633
Cl	-5.479441	-0.768828	-0.480585
Cl	-2.264047	-1.938253	-1.611250
Cl	-2.807366	-1.337227	1.880233
H	3.767301	-2.145219	-1.590870

1 imaginary frequency
E = -2883.573391
G = -2883.327445
E_{M06-2X} = -2883.438578
E_{solv} = -2883.604482

Cycloheptadienone $AlCl_3$ complex 10



C	-3.717905	-2.150620	0.345588
C	-3.025653	-1.142563	-0.329532
C	-2.104340	-1.428554	-1.342145
C	-1.864565	-2.760810	-1.672097
C	-2.547948	-3.781722	-1.005240
C	-3.475174	-3.478849	-0.006098
S	-3.298304	0.562203	0.140516
O	-3.256021	1.403934	-1.051646
N	-1.861982	0.949002	1.070483
C	-1.739370	0.208796	2.338074
C	-0.731569	1.413362	0.419821
C	0.540969	0.956583	0.761357
C	1.775232	1.600316	0.391720
O	2.852581	0.915514	0.362966
Al	3.236378	-0.895577	0.141877
Cl	2.122155	-1.388534	-1.638560
Cl	2.493728	-1.906295	1.889520
Cl	5.348213	-0.965843	-0.085753
C	-0.735018	2.569603	-0.468342
C	0.328545	2.564608	-1.325863
C	1.430499	3.585752	-1.264187
C	2.009518	3.116905	0.112193
C	-1.548560	3.794044	-0.118401
O	-4.401714	0.621380	1.095447
H	-2.555648	3.695166	-0.534786
H	-1.651950	3.925883	0.964257
H	-1.099041	4.695044	-0.545898
H	0.666742	1.601313	-1.705925
H	2.154098	3.473367	-2.075264
H	1.111646	4.629502	-1.215349
H	3.088206	3.277487	0.192540
H	1.504758	3.676679	0.907984
H	0.660292	0.025858	1.308838
H	-1.397724	-0.822369	2.190058
H	-2.712759	0.207292	2.828771
H	-1.022035	0.736643	2.969855
H	-4.435590	-1.892801	1.116726
H	-4.008721	-4.275180	0.504207
H	-2.354569	-4.818126	-1.266196
H	-1.140156	-2.998328	-2.444468
H	-1.590090	-0.629498	-1.865114

0 imaginary frequencies

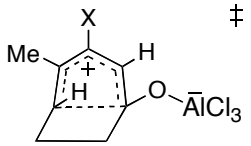
E = -2883.592977

G = -2883.345851

$E_{M06\text{-}2X}$ = -2883.458016

E_{solv} = -2883.622135

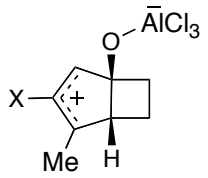
TS3 (Nazarov-like ring closure)



C	-1.746809	-1.599509	-0.930767
C	-2.869315	-1.023793	-0.327346
C	-3.852798	-1.796978	0.296615
C	-3.699954	-3.183074	0.315273
C	-2.577475	-3.773315	-0.270888
C	-1.604861	-2.985650	-0.891777
S	-3.037503	0.755775	-0.327473
O	-2.486249	1.288231	-1.574182
N	-1.952538	1.315377	0.919104
C	-2.255510	0.820695	2.271947
C	-0.618012	1.536725	0.566528
C	-0.200234	2.511242	-0.393917
C	1.183532	2.321097	-0.730163
H	1.409331	1.514797	-1.437310
C	1.765965	1.532405	0.736310
C	0.487708	1.019779	1.227183
C	2.307125	3.009593	0.962142
H	1.637613	3.572217	1.619286
H	3.313800	2.953624	1.382088
C	2.189617	3.459111	-0.508997
H	3.109027	3.302522	-1.075476
H	1.833168	4.477389	-0.675286
C	-1.006188	3.708750	-0.767298
O	2.771489	0.663534	0.653670
O	-4.374703	1.105155	0.145652
H	0.451209	0.203964	1.943537
H	-1.442031	3.553225	-1.761388
H	-1.831695	3.874516	-0.070494
H	-0.374314	4.600948	-0.822833
H	-3.327464	0.927947	2.441444
H	-1.963662	-0.226583	2.417848
H	-1.724576	1.448763	2.991922
H	-0.998586	-0.990721	-1.426476
H	-0.729430	-3.440900	-1.343085
H	-2.459557	-4.852753	-0.244177
H	-4.458196	-3.800176	0.788279
H	-4.720717	-1.318929	0.737587
Al	2.864550	-1.029549	0.047127
Cl	1.730578	-2.299833	1.383470
Cl	4.925362	-1.549383	-0.092949
Cl	1.873689	-0.945699	-1.902431

1 imaginary frequency
E = -2883.578762
G = -2883.330566
E_{M06-2X} = -2883.448221
E_{solv} = -2883.609117

5,4-Bicyclic intermediate 11



C	3.277521	0.870329	1.389567
C	3.517163	0.548732	0.049902
C	4.096192	1.469037	-0.829193
C	4.420963	2.740716	-0.356634
C	4.173724	3.079279	0.975919
C	3.610504	2.144860	1.848486
S	3.045727	-1.072211	-0.559176
O	2.874501	-1.953235	0.600288
N	1.475258	-0.904849	-1.225185
C	1.352001	-0.088848	-2.448101
C	0.396718	-0.891538	-0.303408
C	-0.193497	-2.057283	0.213257
C	-1.244346	-1.712205	1.188290
C	-1.280547	-0.146278	1.220178
C	-0.244001	0.233563	0.220169
H	0.066538	1.259957	0.061548
C	-0.601256	-0.205044	2.679516
H	0.395224	0.232481	2.770922
H	-1.287892	0.290911	3.367723
C	-0.680488	-1.737429	2.676267
H	-1.425406	-2.141066	3.364312
H	0.260763	-2.275452	2.806233
C	0.236902	-3.441174	-0.084868
H	0.971930	-3.762537	0.666263
H	0.740480	-3.492959	-1.053914
H	-0.611352	-4.131082	-0.048041
O	-2.459925	0.530272	1.218193
O	3.918544	-1.409154	-1.680420
H	-2.196523	-2.225007	1.038803
H	1.451997	0.987275	-2.255456
H	2.121165	-0.411978	-3.150471
H	0.367533	-0.275439	-2.880018
H	2.871958	0.120138	2.059730
H	3.439323	2.404274	2.889115
H	4.430748	4.070360	1.338343
H	4.875143	3.463242	-1.028073
H	4.310683	1.182720	-1.853141
Al	-3.525493	0.686210	-0.199309
Cl	-4.904431	2.283607	0.084224
Cl	-4.437690	-1.227073	-0.621451
Cl	-2.051975	1.125194	-1.799263

0 imaginary frequencies

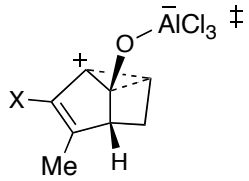
E = -2883.579980

G = -2883.333662

E_{M06-2X} = -2883.449511

E_{solv} = -2883.612494

TS4 (1,2-Alkyl Shift)



C	3.181570	-1.683106	-0.959375
C	3.767779	-0.682008	-0.179178
C	4.976025	-0.884561	0.489410
C	5.603919	-2.126926	0.380088
C	5.026563	-3.138589	-0.388430
C	3.819096	-2.917160	-1.058735
S	2.963431	0.913851	-0.061454
O	2.419053	1.288562	-1.373465
N	1.591936	0.575518	0.892259
C	1.794842	0.353544	2.333096
C	0.348158	1.101841	0.453117
C	-0.013603	2.434504	0.315233
C	-1.352433	2.519178	-0.318608
C	-1.825417	1.052136	-0.419223
C	-0.704856	0.264983	0.011642
H	-0.654848	-0.814659	-0.067888
C	-1.186062	2.613599	-1.902099
H	-0.292356	3.138626	-2.243541
H	-2.081275	3.086858	-2.310278
C	0.843594	3.627083	0.547567
H	1.779246	3.376862	1.051405
H	0.299994	4.381794	1.128381
H	1.103291	4.091135	-0.414485
O	-3.106489	0.746864	-0.349885
O	3.864309	1.815814	0.666480
H	-2.051225	3.238559	0.109265
H	1.991485	1.284398	2.877652
H	0.895985	-0.122521	2.732335
H	2.636153	-0.329498	2.476021
H	2.250874	-1.495450	-1.484416
H	3.375772	-3.704753	-1.660527
H	5.518903	-4.103401	-0.469891
H	6.544979	-2.299963	0.893636
H	5.411834	-0.079251	1.070441
Al	-3.755705	-0.858715	0.183671
Cl	-2.736867	-1.200561	2.077331
Cl	-3.035418	-2.278825	-1.286117
Cl	-5.872862	-0.705658	0.323335
C	-1.213238	1.113550	-2.109360
H	-0.263463	0.635840	-2.340375
H	-2.042757	0.675894	-2.661256

1 imaginary frequency

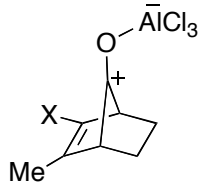
E = -2883.572794

G = -2883.328795

E_{M06-2X} = -2883.441329

E_{solv} = -2883.605908

Bicyclic ketone $AlCl_3$ complex 12



C	-4.674254	-1.364483	0.917016
C	-4.076636	-0.359847	0.154101
C	-4.578341	0.010455	-1.096403
C	-5.695154	-0.655991	-1.596161
C	-6.298397	-1.672447	-0.849206
C	-5.792903	-2.023185	0.403708
S	-2.658152	0.511663	0.817540
O	-2.524556	0.155549	2.236644
N	-1.347858	-0.186777	-0.092480
C	-1.038155	-1.577789	0.297296
C	-0.239385	0.685188	-0.228525
C	-0.068125	1.603248	-1.210827
C	1.207296	2.381522	-0.875745
C	1.923013	1.191357	-0.286484
C	0.918393	0.807639	0.777830
H	1.140722	-0.064492	1.388226
C	0.778213	2.166366	1.537627
H	1.562966	2.252366	2.295728
H	-0.190334	2.226865	2.037982
C	0.949461	3.236628	0.411326
H	0.058949	3.856263	0.284292
H	1.801597	3.894719	0.607866
C	-0.936368	1.901523	-2.384660
H	-1.484739	2.840264	-2.233443
H	-1.666329	1.101952	-2.533993
H	-0.337287	2.011455	-3.296555
O	2.983708	0.678981	-0.666950
O	-2.719057	1.917536	0.405919
H	1.696737	2.885183	-1.709324
H	-0.259819	-1.949419	-0.372055
H	-0.699725	-1.664020	1.336040
H	-1.934005	-2.188565	0.162127
H	-4.274289	-1.609067	1.895098
H	-6.269766	-2.805912	0.986170
H	-7.169534	-2.187578	-1.243957
H	-6.098744	-0.378734	-2.565527
H	-4.111707	0.815287	-1.653961
Al	3.951819	-0.874239	-0.106994
Cl	4.045817	-0.651463	2.017586
Cl	5.793907	-0.689391	-1.137745
Cl	2.668182	-2.456101	-0.765567

0 imaginary frequencies

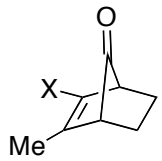
E = -2883.624490

G = -2883.376841

$E_{M06\text{-}2X}$ = -2883.495185

E_{solv} = -2883.652070

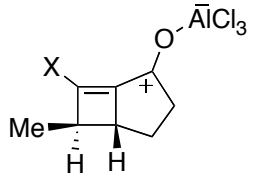
Bicyclic ketone 8



C	-2.776040	1.259268	0.306514
C	-2.507656	-0.109017	0.214829
C	-3.486345	-1.020423	-0.183244
C	-4.757221	-0.545421	-0.513833
C	-5.035745	0.820013	-0.438120
C	-4.048509	1.720117	-0.025248
S	-0.876769	-0.710485	0.666624
O	-0.961248	-2.172832	0.795349
N	0.059405	-0.283958	-0.720506
C	-0.164520	-1.170603	-1.875950
C	1.423234	0.029039	-0.438385
C	1.920223	1.278488	-0.291640
C	3.395480	1.136613	0.039254
C	3.678417	-0.127861	-0.803706
C	2.539504	-0.984940	-0.211458
H	2.402219	-1.980928	-0.632354
C	2.952430	-0.935344	1.296388
H	3.720258	-1.689823	1.500052
H	2.098503	-1.128924	1.948173
C	3.517817	0.513188	1.471205
H	2.948616	1.092899	2.202659
H	4.565917	0.500057	1.788926
C	1.202116	2.584690	-0.365903
H	1.139061	3.054854	0.624864
H	0.185293	2.450387	-0.744893
H	1.733272	3.287569	-1.020480
O	4.507358	-0.359133	-1.643681
O	-0.365346	0.109760	1.768845
H	4.023482	2.007716	-0.154176
H	0.203645	-2.190571	-1.713511
H	-1.234329	-1.212235	-2.098142
H	0.347516	-0.728078	-2.733700
H	-2.004814	1.941131	0.648593
H	-4.272490	2.780707	0.044304
H	-6.026587	1.185144	-0.693747
H	-5.529053	-1.244252	-0.823211
H	-3.253243	-2.079381	-0.214135

0 imaginary frequencies
E = -1260.337583
G = -1260.084942
E_{M06-2X} = -1260.213411
E_{solv} = -1260.358273

α,β-Unsaturated 4,5-bicyclic cyclobutenamide $AlCl_3$ complex 2'-*trans*



C	-1.374018	3.016418	0.484101
C	-2.524416	3.943905	0.095631
H	-1.505920	2.642666	1.504495
H	-3.487385	3.436734	0.187922
H	-2.528947	4.814936	0.760529
H	-2.412357	4.306043	-0.932630
C	-1.013480	1.865412	-0.469821
C	0.298218	2.320354	-0.634090
C	0.102442	3.535649	0.237328
H	0.112518	4.499810	-0.284708
C	1.244184	3.408260	1.274757
H	0.907715	2.830048	2.143869
H	1.619416	4.368457	1.640338
C	2.338546	2.591662	0.521724
H	2.977689	1.993123	1.175676
H	2.997074	3.245896	-0.068348
C	1.545438	1.707165	-0.438161
O	1.898125	0.561307	-0.866032
Al	2.943000	-0.812398	-0.207848
Cl	2.330005	-0.939514	1.864105
Cl	4.987693	-0.253078	-0.458546
Cl	2.292528	-2.495410	-1.357667
N	-1.645818	0.789819	-0.958377
C	-1.069246	-0.001784	-2.067436
S	-3.129215	0.153834	-0.239846
H	-1.886103	-0.331933	-2.711977
H	-0.401184	0.651658	-2.629815
H	-0.503176	-0.858841	-1.697145
O	-3.404703	1.010853	0.909362
O	-4.081370	0.002313	-1.335556
C	-2.587289	-1.460150	0.297495
C	-3.188677	-2.586207	-0.268953
C	-2.771309	-3.847532	0.156583
C	-1.763396	-3.966657	1.115390
C	-1.169537	-2.828168	1.668576
C	-1.586416	-1.560763	1.269090
H	-1.126250	-0.675740	1.695888
H	-0.371813	-2.920673	2.398062
H	-1.430793	-4.951752	1.428918
H	-3.227934	-4.735298	-0.270330
H	-3.959893	-2.469172	-1.022199

0 imaginary frequencies

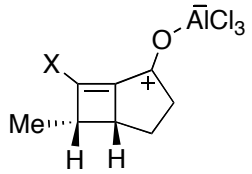
E = -2883.619644

G = -2883.371454

E_{M06-2X} = -2883.484687

E_{solv} = -2883.648031

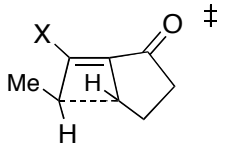
α,β-Unsaturated 4,5-bicyclic cyclobutenamide $AlCl_3$ complex 2'-*cis*



C	-1.028618	2.938186	0.200862
C	-0.753485	1.621437	-0.556500
C	0.621848	1.858763	-0.588738
C	0.520292	3.232000	0.013804
H	0.681692	4.049996	-0.699327
H	-1.687628	3.622833	-0.342688
C	-1.503990	2.809485	1.650119
H	-0.942095	2.044721	2.197272
H	-1.355591	3.766598	2.162069
H	-2.567161	2.565915	1.689041
C	1.607452	3.219070	1.112231
H	1.213189	2.836785	2.059859
H	2.046872	4.201343	1.308570
C	2.656254	2.205712	0.553529
H	3.225014	1.681023	1.326271
H	3.386363	2.697075	-0.105878
C	1.835252	1.221980	-0.278072
O	2.152800	0.019163	-0.541154
Al	3.536038	-1.120440	-0.037394
Cl	3.412766	-1.193173	2.108270
Cl	5.323013	-0.192660	-0.765000
Cl	2.997935	-2.948988	-1.001120
N	-1.490645	0.587328	-0.994616
C	-0.876542	-0.513453	-1.771444
S	-3.251620	0.588149	-0.983956
H	-1.266880	-1.468897	-1.413829
H	-1.111475	-0.392879	-2.831118
H	0.200334	-0.501869	-1.610510
O	-3.638948	0.259426	-2.351589
O	-3.655865	1.832660	-0.339510
C	-3.633646	-0.802681	0.071948
C	-4.030996	-2.004110	-0.520476
C	-4.336007	-3.087397	0.304299
C	-4.243425	-2.960058	1.691358
C	-3.852827	-1.747649	2.267657
C	-3.546379	-0.655354	1.459488
H	-3.253349	0.292844	1.896559
H	-3.789299	-1.651748	3.347215
H	-4.479367	-3.807612	2.328114
H	-4.647119	-4.028226	-0.139216
H	-4.109686	-2.077481	-1.599588

0 imaginary frequencies
E = -2883.615808
G = -2883.367885
E_{M06-2X} = -2883.478155
E_{solv} = -2883.646656

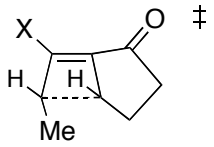
TS for ring opening of 2'-*trans* (leads to 5-*Z*)



C	-0.173925	3.588007	-0.111686
H	-0.698344	4.306516	-0.731668
C	1.112431	3.957112	0.602323
C	2.057431	2.755667	0.280562
C	1.158631	1.660150	-0.271216
C	-0.136737	2.200414	-0.440701
H	0.965017	4.036052	1.687026
H	1.521542	4.915640	0.268398
H	2.621020	2.381301	1.141215
H	2.796922	3.025310	-0.483762
O	1.494904	0.455282	-0.478943
Al	3.029182	-0.539011	-0.120394
Cl	2.663170	-2.406308	-1.083148
Cl	3.056882	-0.631715	2.028407
Cl	4.649754	0.588961	-0.955353
C	-1.465179	1.749774	-0.250837
C	-2.032796	2.758993	0.604919
H	-1.551816	2.854158	1.575089
C	-3.431790	3.304397	0.517555
H	-3.414187	4.383238	0.715682
H	-4.088776	2.840333	1.260235
H	-3.869057	3.140854	-0.472082
N	-2.113485	0.751795	-0.932036
C	-1.502544	0.175306	-2.145269
S	-3.263707	-0.286544	-0.109641
H	-0.673235	-0.498369	-1.907428
H	-1.133576	1.000070	-2.758551
H	-2.275244	-0.357238	-2.701295
O	-3.606369	0.405279	1.130430
O	-4.267579	-0.635264	-1.111530
C	-2.295972	-1.739442	0.276021
C	-1.350596	-1.669525	1.304769
C	-0.572465	-2.792250	1.576752
C	-0.752502	-3.964689	0.836262
C	-1.712538	-4.023650	-0.175265
C	-2.491378	-2.903816	-0.469352
H	-3.242107	-2.927055	-1.251662
H	-1.852183	-4.938366	-0.743442
H	-0.136291	-4.833226	1.047951
H	0.179970	-2.747300	2.357581
H	-1.230085	-0.759640	1.883257

1 imaginary frequency
E = -2883.583266
G = -2883.338450
$E_{M06\text{-}2X}$ = -2883.444138
E_{solv} = -2883.612517

TS for ring opening of 2'-*cis* (leads to 5-*E*)



C	1.314286	1.535039	-0.438755
C	0.076081	2.192614	-0.609443
C	0.171784	3.577909	-0.303799
H	-0.346673	4.332485	-0.882976
C	1.506633	3.853394	0.351535
H	1.393764	4.006380	1.433790
H	1.992275	4.751172	-0.044264
C	2.323024	2.551488	0.074205
H	2.845482	2.151094	0.948867
H	3.086361	2.713575	-0.697448
O	1.523364	0.295899	-0.607399
Al	2.890291	-0.871193	-0.127655
Cl	4.670932	-0.062462	-1.004150
Cl	2.261957	-2.741147	-0.939339
Cl	2.871397	-0.779960	2.022251
C	-1.285711	1.858513	-0.389386
C	-1.749787	2.867745	0.528719
H	-2.757797	3.258041	0.366388
C	-1.340960	2.896753	1.986306
H	-1.341035	3.918833	2.381093
H	-0.355997	2.451425	2.155762
H	-2.075177	2.324746	2.569320
N	-2.044266	0.975336	-1.104264
C	-1.486661	0.325662	-2.305358
S	-3.371833	0.123459	-0.325897
H	-2.308895	-0.090651	-2.887469
H	-0.766148	-0.457175	-2.047556
H	-0.985394	1.094327	-2.897720
O	-4.301966	-0.203654	-1.402367
O	-3.756771	0.951953	0.814539
C	-2.599557	-1.375534	0.262885
C	-1.829670	-1.329044	1.429654
C	-1.180786	-2.487754	1.850295
C	-2.096866	-3.703632	-0.037961
C	-2.746984	-2.550441	-0.478022
C	-1.310676	-3.669760	1.114995
H	-0.791902	-4.565807	1.441637
H	-2.199454	-4.625593	-0.602098
H	-3.364520	-2.556297	-1.369508
H	-1.747632	-0.409060	1.998592
H	-0.566664	-2.465318	2.744931

1 imaginary frequency

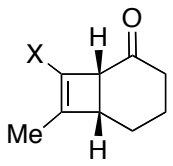
E = -2883.577411

G = -2883.331596

E_{M06-2X} = -2883.438642

E_{solv} = -2883.606644

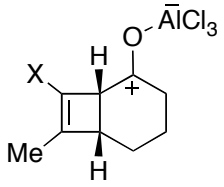
4,6-Bicyclic cyclobutenamide 1



C	-2.248864	1.106298	-0.388227
C	-2.541819	1.997627	-1.543934
H	-2.516971	1.444295	-2.492712
H	-3.549924	2.423623	-1.449251
H	-1.810798	2.804791	-1.618262
C	-1.259688	0.975558	0.520682
C	-1.926709	-0.176565	1.286796
H	-2.204248	0.063061	2.320867
C	-3.085840	-0.007514	0.233994
H	-4.003193	0.381881	0.697975
C	-1.118771	-1.467363	1.298386
O	-0.203620	-1.607300	2.093408
C	-1.477432	-2.565039	0.305654
H	-0.564894	-3.129447	0.088789
H	-2.149870	-3.253344	0.843293
C	-2.182432	-2.068737	-0.965179
H	-2.464688	-2.927426	-1.585752
H	-1.486777	-1.464874	-1.561035
C	-3.424744	-1.240999	-0.614115
H	-4.131361	-1.874585	-0.058951
H	-3.945454	-0.924506	-1.527372
N	-0.059695	1.650870	0.809358
C	0.316712	1.738478	2.232349
S	1.191685	1.709778	-0.349792
H	0.451524	0.746317	2.676845
H	1.229725	2.327074	2.314370
H	-0.482001	2.268456	2.760279
O	2.199775	2.614304	0.206865
O	0.551171	1.966807	-1.640451
C	1.920726	0.069123	-0.440809
C	1.549546	-0.782213	-1.483689
C	2.105572	-2.061045	-1.543913
C	3.015831	-2.476124	-0.569622
C	3.385264	-1.610627	0.463164
C	2.842535	-0.328728	0.531007
H	3.140697	0.360364	1.313675
H	0.859220	-0.429464	-2.241828
H	1.834281	-2.727980	-2.357557
H	3.446078	-3.472514	-0.619771
H	4.101598	-1.931518	1.213732

0 imaginary frequencies
E = -1299.646787
G = -1299.366531
E_{M06-2X} = -1299.515289
E_{solv} = -1299.667226

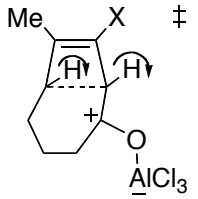
4,6-Bicyclic cyclobutenamide $AlCl_3$ complex 13



C	-1.362429	3.233130	-0.640665
C	-2.545945	4.066037	-0.291141
H	-2.328392	4.699915	0.577749
H	-2.815163	4.739381	-1.116111
H	-3.411807	3.444507	-0.045017
C	-1.152978	1.924597	-0.869913
C	0.355542	2.070989	-1.154854
H	0.641749	1.815327	-2.180822
C	0.101943	3.601540	-0.863472
H	0.268204	4.208078	-1.762903
C	1.240335	1.327303	-0.211212
O	1.659500	0.209815	-0.593922
Al	2.924156	-1.096816	-0.077945
Cl	4.763246	-0.069188	-0.449131
Cl	2.463546	-2.691253	-1.422658
Cl	2.574496	-1.565043	1.975182
C	1.660064	1.907309	1.103054
H	1.566564	1.123450	1.863144
H	2.743833	2.085644	0.994506
C	0.933385	3.196834	1.502749
H	1.460489	3.649112	2.349142
H	-0.073247	2.944086	1.851924
C	0.862953	4.187867	0.332479
H	1.879567	4.456650	0.013682
H	0.380484	5.120541	0.650484
N	-1.951580	0.762223	-0.923471
C	-3.061469	0.740018	-1.891869
S	-2.301061	0.092575	0.620629
H	-3.864598	1.440369	-1.635581
H	-2.654944	0.989771	-2.874705
H	-3.472014	-0.272112	-1.937911
O	-3.613117	0.558541	1.090120
O	-1.095575	0.365397	1.415504
C	-2.418319	-1.656301	0.261440
C	-3.586902	-2.334338	0.613659
C	-3.654066	-3.711075	0.394142
C	-2.566979	-4.385731	-0.165020
C	-1.403492	-3.691820	-0.510818
C	-1.320720	-2.317872	-0.296693
H	-0.421943	-1.775966	-0.567433
H	-4.415699	-1.789347	1.052026
H	-4.555069	-4.254310	0.663774
H	-2.624239	-5.457934	-0.330620
H	-0.553655	-4.213025	-0.940295

0 imaginary frequencies
E = -2922.938658
G = -2922.663738
E_{M06-2X} = -2922.800785
E_{solv} = -2922.967119

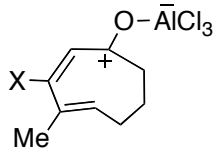
TS6 (Cyclobutene ring opening)



C	0.648025	1.698736	0.523879
C	0.033499	2.883001	0.803718
C	0.591647	4.276151	0.867233
H	0.676091	4.637741	1.900450
H	1.581662	4.323482	0.406329
H	-0.053483	4.983738	0.335479
C	-1.377676	2.506048	0.946561
H	-1.680497	1.936273	1.821026
C	-2.466671	3.258653	0.218893
H	-2.187650	4.319820	0.210818
H	-3.410577	3.172834	0.763653
C	-2.666961	2.779486	-1.257823
H	-3.576858	2.175583	-1.316715
H	-2.807342	3.635621	-1.924935
C	-1.477494	1.921391	-1.747349
H	-1.697957	1.515800	-2.739042
H	-0.553796	2.498899	-1.805127
C	-1.339586	0.766063	-0.792043
O	-2.219401	-0.154053	-0.926386
C	-0.398328	0.717123	0.276581
H	-0.362969	-0.230745	0.816166
N	2.003320	1.352940	0.554595
C	2.924751	1.959988	1.525397
H	3.691834	1.229427	1.798751
H	2.351774	2.203010	2.422382
H	3.416572	2.857623	1.140095
S	2.736546	0.659646	-0.846858
O	1.665000	0.526357	-1.835259
O	3.938878	1.450659	-1.118507
C	3.251621	-0.967968	-0.308385
C	4.587882	-1.171403	0.044913
C	4.982014	-2.439342	0.474414
C	4.050212	-3.477145	0.543242
C	2.719516	-3.259186	0.175424
C	2.310267	-1.999622	-0.257989
H	1.281648	-1.833587	-0.558134
H	1.994417	-4.065724	0.222172
H	4.362632	-4.461972	0.878944
H	6.018046	-2.615448	0.748701
H	5.299600	-0.357188	-0.037163
Al	-2.923012	-1.519456	0.096387
Cl	-1.310163	-2.896173	0.490073
Cl	-4.498896	-2.337826	-1.073520
Cl	-3.571181	-0.500868	1.886501

1 imaginary frequency
E = -2922.902879
G = -2922.628863
E_{M06-2X} = -2922.761749
E_{solv} = -2922.932900

Cyclooctadienone $AlCl_3$ complex 14



C	-0.667218	1.387233	0.587997
C	-0.532164	2.563215	-0.276032
C	-1.334827	3.803502	0.047248
H	-2.353599	3.694119	-0.334929
H	-1.402123	3.974370	1.127615
H	-0.900407	4.689716	-0.420895
C	0.492317	2.505462	-1.171116
H	0.840474	1.519608	-1.477668
C	1.431768	3.613509	-1.499772
H	1.024245	4.597050	-1.250359
H	1.737734	3.626664	-2.551356
C	2.677867	3.306962	-0.599131
H	3.317358	2.567549	-1.093028
H	3.278551	4.214036	-0.469739
C	2.264591	2.752470	0.791914
H	3.144854	2.774670	1.445769
H	1.488056	3.378646	1.240172
C	1.829396	1.291010	0.772264
O	2.806451	0.470531	0.653037
C	0.507965	0.775696	0.997307
H	0.474487	-0.208662	1.456594
N	-1.889501	0.990164	1.111875
C	-1.940712	0.217204	2.364795
H	-2.952890	0.283163	2.764938
H	-1.246209	0.674127	3.072613
H	-1.669551	-0.835427	2.221604
S	-3.251497	0.703802	0.043325
O	-4.439795	0.875250	0.875691
O	-3.018206	1.514553	-1.148427
C	-3.082968	-1.028248	-0.376038
C	-2.035283	-1.428609	-1.211592
C	-1.900540	-2.782359	-1.513124
C	-2.809657	-3.709442	-0.995444
C	-3.856632	-3.291635	-0.171210
C	-3.998044	-1.941806	0.152257
H	-4.802747	-1.594426	0.790945
H	-4.563055	-4.015146	0.224822
H	-2.698278	-4.763131	-1.234419
H	-1.080134	-3.106933	-2.144988
H	-1.336021	-0.706484	-1.618990
Al	2.952098	-1.304131	0.134827
Cl	5.041882	-1.639441	-0.067637
Cl	1.867525	-1.350405	-1.736297
Cl	2.002928	-2.486002	1.661457

0 imaginary frequencies

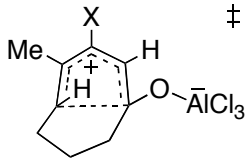
E = -2922.937871

G = -2922.660887

E_{M06-2X} = -2922.797285

E_{solv} = -2922.966427

TS7 (Nazarov-like ring closure)



C	-2.067646	-1.489407	-0.898467
C	-3.119453	-0.764653	-0.329315
C	-4.225309	-1.394818	0.248616
C	-4.271785	-2.788690	0.253896
C	-3.223273	-3.528002	-0.299306
C	-2.125387	-2.881919	-0.873169
S	-3.034270	1.020987	-0.313435
O	-2.392519	1.483654	-1.546209
N	-1.898846	1.415107	0.947902
C	-2.262481	0.933123	2.289424
C	-0.546430	1.475420	0.596063
C	-0.018379	2.405980	-0.364891
C	1.302371	2.019948	-0.771793
H	1.315759	1.087742	-1.347753
C	1.827477	1.217817	0.762865
C	0.486724	0.817907	1.227442
C	2.520103	2.494827	1.300020
C	3.343096	3.039580	0.120775
C	2.381794	3.044305	-1.106044
C	-0.680392	3.703219	-0.684865
O	2.711864	0.230719	0.614651
O	-4.317477	1.550551	0.142256
H	0.367278	-0.000382	1.931405
H	1.763569	3.219158	1.624381
H	3.140466	2.221934	2.159330
H	4.179381	2.360373	-0.066804
H	3.759062	4.030031	0.330436
H	2.908617	2.777580	-2.025553
H	1.956904	4.040864	-1.256967
H	-0.966943	3.725989	-1.742538
H	-1.578075	3.854641	-0.083874
H	0.014356	4.534226	-0.518762
H	-1.666169	1.482694	3.022305
H	-3.316154	1.158153	2.459061
H	-2.091870	-0.143277	2.415129
H	-1.221618	-0.989882	-1.357494
H	-1.307396	-3.453237	-1.299721
H	-3.261645	-4.613430	-0.283841
H	-5.127263	-3.295392	0.690801
H	-5.031317	-0.801188	0.665861
Al	2.626434	-1.471912	0.041361
Cl	1.579239	-1.351156	-1.876198
Cl	1.435524	-2.605505	1.449010
Cl	4.627504	-2.175721	-0.160255

1 imaginary frequency

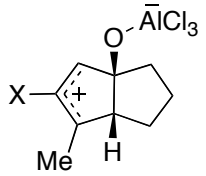
E = -2922.920375

G = -2922.643161

E_{M06-2X} = -2922.781972

E_{solv} = -2922.951099

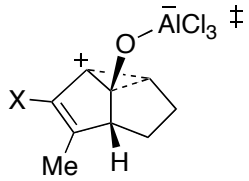
5,5-Bicyclic intermediate 15



C	-4.281006	-1.141634	0.328454
C	-3.126214	-0.643928	-0.283408
C	-2.129818	-1.487265	-0.784664
C	-2.296438	-2.865455	-0.655021
C	-3.443059	-3.379966	-0.045471
C	-4.434305	-2.522882	0.439959
S	-2.915071	1.125634	-0.414738
O	-4.174807	1.776630	-0.062083
N	-1.804027	1.570023	0.852739
C	-2.234149	1.211646	2.213419
C	-0.434304	1.538771	0.555303
C	0.196304	2.405506	-0.392236
C	1.576460	1.970468	-0.628635
C	1.913009	1.153534	0.757832
C	0.543176	0.843048	1.239962
H	0.364636	0.098137	2.009001
C	2.689210	2.291028	1.492969
C	3.616313	2.844850	0.400834
C	2.701430	3.002386	-0.843685
C	-0.428176	3.631789	-0.939509
H	-0.738101	3.436524	-1.974773
H	0.289884	4.456968	-0.966666
H	-1.321279	3.917029	-0.379524
O	2.718833	0.065538	0.632480
O	-2.198340	1.432313	-1.654548
H	1.560261	1.153131	-1.368681
H	2.307497	4.022235	-0.897914
H	3.240943	2.818008	-1.775843
H	4.403488	2.112993	0.198899
H	4.097543	3.783684	0.692333
H	3.217525	1.874615	2.354442
H	1.989496	3.062450	1.839030
H	-3.279318	1.502410	2.327801
H	-2.126221	0.140929	2.427346
H	-1.635482	1.786450	2.924996
H	-5.043220	-0.458252	0.686315
H	-5.328520	-2.928071	0.904394
H	-3.565087	-4.455010	0.051059
H	-1.522667	-3.529028	-1.026437
H	-1.245799	-1.089758	-1.271992
Al	2.468640	-1.576112	-0.015091
Cl	4.367370	-2.533110	-0.175467
Cl	1.503230	-1.294808	-1.964911
Cl	1.080891	-2.614642	1.296004

0 imaginary frequencies
E = -2922.921157
G = -2922.643845
E_{M06-2X} = -2922.783299
E_{solv} = -2922.952863

TS8 (1,2-Alkyl Shift)



C	5.113068	-0.780708	0.385800
C	3.845934	-0.699628	-0.193623
C	3.283117	-1.776330	-0.885393
C	4.005780	-2.962526	-0.985047
C	5.273869	-3.062106	-0.403455
C	5.826384	-1.976117	0.276864
S	2.938735	0.841574	-0.092092
O	2.340343	1.146266	-1.398550
N	1.617405	0.427423	0.904723
C	1.901499	0.205232	2.332578
C	0.354606	0.988383	0.558427
C	-0.078814	2.282147	0.697898
C	-1.495736	2.409245	0.172393
C	-1.846388	0.975511	-0.260496
C	-0.693018	0.181602	-0.002680
H	-0.631944	-0.887965	-0.166421
C	-1.170527	1.000481	-1.973382
C	-0.761896	2.455112	-2.145474
C	-1.556373	3.271638	-1.110056
C	0.707106	3.447695	1.189172
H	1.739142	3.183500	1.427913
H	0.225540	3.877299	2.078089
H	0.728563	4.243688	0.434129
O	-3.109235	0.588819	-0.259129
O	3.796147	1.824432	0.584080
H	-2.197333	2.745101	0.943120
H	-1.164660	4.283290	-0.965865
H	-2.606834	3.358045	-1.408885
H	-0.965493	2.771443	-3.175853
H	0.315749	2.560555	-1.987892
H	-2.124052	0.704366	-2.410568
H	-0.400542	0.286889	-2.271063
H	1.040040	-0.303867	2.771231
H	2.770716	-0.451073	2.425226
H	2.096855	1.136201	2.877455
H	5.526339	0.079634	0.900722
H	6.813768	-2.054687	0.722045
H	5.832535	-3.990115	-0.484854
H	3.580983	-3.807957	-1.517777
H	2.302841	-1.684597	-1.341018
Al	-3.692511	-1.069672	0.174703
Cl	-2.643194	-1.498108	2.033169
Cl	-2.937176	-2.368532	-1.388732
Cl	-5.813211	-1.006011	0.337161

1 imaginary frequency

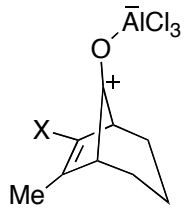
E = -2922.904625

G = -2922.631150

E_{M06-2X} = -2922.768292

E_{solv} = -2922.937724

Bicyclic ketone $AlCl_3$ complex 16



C	4.807054	-0.671027	1.188578
C	4.553702	-0.161996	-0.088030
C	5.454238	-0.335764	-1.140150
C	6.629412	-1.052739	-0.908190
C	6.890321	-1.578249	0.358428
C	5.983439	-1.385503	1.405110
S	3.060935	0.791798	-0.363287
O	3.165336	1.432095	-1.683581
N	1.842687	-0.440682	-0.399639
C	1.926503	-1.314048	-1.585532
C	0.534011	0.005616	-0.059809
C	0.006410	-0.001014	1.181561
C	-1.413852	0.565589	1.123377
C	-1.721687	0.277557	-0.315724
C	-0.468096	0.589160	-1.070337
H	-0.452927	0.150136	-2.070634
C	-0.408001	2.158254	-1.137414
H	-1.268970	2.502916	-1.724745
H	0.496069	2.445751	-1.684486
C	-0.411718	2.783840	0.273095
C	-1.437344	2.136631	1.226160
C	0.642234	-0.436340	2.457959
H	0.900650	0.428793	3.082229
H	1.560207	-0.995022	2.259738
H	-0.043100	-1.066628	3.037442
O	-2.780314	-0.115545	-0.831350
O	2.781656	1.592707	0.832573
H	-2.115067	0.112862	1.828215
H	-1.228725	2.415611	2.264804
H	-2.458122	2.470167	1.006014
H	-0.621845	3.856260	0.191114
H	0.589994	2.693874	0.701328
H	2.927203	-1.749449	-1.638757
H	1.208687	-2.126640	-1.450539
H	1.718525	-0.787428	-2.524581
H	4.104058	-0.493530	1.995258
H	6.196180	-1.786093	2.391850
H	7.806761	-2.134306	0.534526
H	7.341073	-1.194466	-1.716146
H	5.237433	0.096159	-2.111210
Al	-4.488840	-0.636143	-0.144195
Cl	-5.505532	-1.311618	-1.878375
Cl	-5.224172	1.174868	0.722210
Cl	-3.985009	-2.151896	1.280726

0 imaginary frequencies

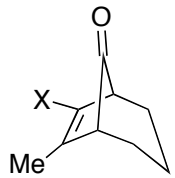
E = -2922.953753

G = -2922.676694

E_{M06-2X} = -2922.817044

E_{solv} = -2922.982382

Bicyclic ketone 17



C	3.307622	0.071901	0.741336
C	2.293320	-0.030989	-0.214140
C	1.980104	1.035494	-1.062349
C	2.689813	2.229462	-0.936826
C	3.701809	2.347596	0.019581
C	4.013159	1.270688	0.852551
S	1.345718	-1.555304	-0.328625
O	2.128732	-2.613260	0.315375
N	-0.043795	-1.346309	0.659232
C	0.203799	-1.376830	2.107647
C	-1.051698	-0.456065	0.193188
C	-1.992731	-0.762726	-0.728514
C	-2.851830	0.468287	-0.989774
C	-1.860127	1.562641	-0.588985
C	-1.203830	0.989949	0.671656
H	-0.269615	1.497373	0.927022
C	-2.272205	1.163627	1.797672
H	-2.477976	2.237490	1.901467
H	-1.870134	0.826763	2.760833
C	-3.572137	0.397707	1.472245
C	-4.041023	0.587237	0.013340
C	-2.223227	-2.062959	-1.426058
H	-3.284768	-2.341440	-1.386325
H	-1.624393	-2.862441	-0.985030
H	-1.945518	-1.989259	-2.485010
O	-1.645691	2.621255	-1.130881
O	0.863791	-1.675487	-1.703612
H	-3.198089	0.565817	-2.024138
H	-4.813745	-0.151976	-0.230926
H	-4.496983	1.577449	-0.118200
H	-4.367061	0.706949	2.160990
H	-3.407984	-0.670614	1.652115
H	0.882407	-2.200338	2.330414
H	0.629425	-0.438184	2.490990
H	-0.750007	-1.564729	2.607822
H	3.549355	-0.782628	1.364113
H	4.809670	1.359958	1.585883
H	4.253502	3.279150	0.110606
H	2.453147	3.064383	-1.589633
H	1.204280	0.925128	-1.812075

0 imaginary frequencies

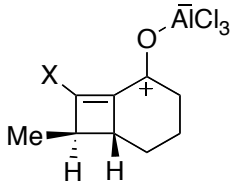
E = -1299.665775

G = -1299.383245

E_{M06-2X} = -1299.537328

E_{solv} = -1299.686708

α,β-Unsaturated 4,6-bicyclic cyclobutenamide $AlCl_3$ complex 1'-*trans*



C	-3.338951	-2.400817	-0.293381
C	-2.807840	-1.283009	0.353064
C	-2.009738	-1.394316	1.496230
C	-1.727132	-2.664894	1.990883
C	-2.249502	-3.795738	1.355582
C	-3.056688	-3.665216	0.224244
S	-3.151404	0.338202	-0.309745
O	-4.030413	0.211304	-1.468058
N	-1.561380	0.787333	-0.935910
C	-1.017612	-0.100368	-1.988216
C	-0.870251	1.826963	-0.444488
C	-1.256694	3.114288	0.291335
H	-1.501822	2.902731	1.337503
C	-2.313650	4.024031	-0.334909
C	0.489469	2.159431	-0.468120
C	0.255434	3.533159	0.128374
H	0.343167	4.339659	-0.612069
C	1.186510	3.802043	1.307664
C	2.623467	3.505172	0.829255
C	2.822583	2.034793	0.398504
O	-3.429705	1.274682	0.775201
H	0.930059	3.145155	2.150739
H	1.109032	4.835914	1.663648
H	3.348019	3.736155	1.617462
H	2.858979	4.169714	-0.012388
H	-3.312925	3.593226	-0.241610
H	-2.104492	4.205035	-1.395415
H	-2.308749	4.992072	0.178689
H	-0.598624	-1.016936	-1.570600
H	-0.232387	0.443835	-2.511437
H	-1.827817	-0.328175	-2.684105
H	-3.957406	-2.275911	-1.175319
H	-3.460786	-4.546800	-0.263831
H	-2.019583	-4.783676	1.743249
H	-1.091591	-2.771112	2.864026
H	-1.614279	-0.510519	1.985735
C	1.660276	1.403675	-0.335609
H	3.726405	1.912913	-0.212490
H	2.986217	1.398714	1.280990
O	1.710525	0.170314	-0.687718
Al	2.694316	-1.321705	-0.252277
Cl	4.695863	-1.001878	-0.941614
Cl	1.648095	-2.894336	-1.268425
Cl	2.521526	-1.458373	1.893935

0 imaginary frequencies

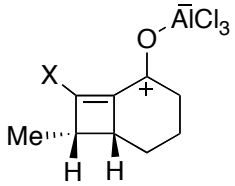
E = -2922.952997

G = -2922.675827

E_{M06-2X} = -2922.809223

E_{solv} = -2922.982463

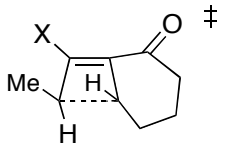
α,β-Unsaturated 4,6-bicyclic cyclobutenamide $AlCl_3$ complex 1'-*cis*



C	-3.196927	-0.662877	1.532251
C	-3.315016	-0.840122	0.150533
C	-3.526108	-2.098450	-0.419324
C	-3.609376	-3.206991	0.422819
C	-3.483280	-3.049181	1.804267
C	-3.282493	-1.781544	2.357881
S	-3.174620	0.577309	-0.925712
O	-3.674610	0.223245	-2.249413
N	-1.420721	0.726176	-1.117271
C	-0.788924	-0.303832	-1.974444
C	-0.703363	1.716482	-0.569543
C	-1.033069	3.051134	0.117481
H	-1.733026	3.672388	-0.450853
C	-1.472527	2.985435	1.584236
C	0.677224	1.964611	-0.541418
C	0.496952	3.402349	-0.099106
H	0.592380	4.104575	-0.938310
C	1.477306	3.799300	1.001607
C	2.884454	3.402710	0.504296
C	3.033054	1.884262	0.260906
O	-3.610631	1.783676	-0.232090
H	1.254932	3.271766	1.937401
H	1.440323	4.874112	1.214386
H	3.648079	3.715243	1.224564
H	3.095926	3.945335	-0.426469
H	-2.522537	2.700088	1.661999
H	-1.354017	3.973932	2.040712
H	-0.865675	2.275300	2.156033
H	0.115948	0.125140	-2.402028
H	-1.486561	-0.553469	-2.773990
H	-0.522077	-1.191577	-1.398310
H	-3.050894	0.326921	1.950404
H	-3.191910	-1.663543	3.433287
H	-3.542234	-3.917384	2.453930
H	-3.770405	-4.192591	-0.002691
H	-3.632579	-2.200196	-1.493604
C	1.830917	1.198131	-0.348515
H	3.908611	1.663047	-0.363715
H	3.218815	1.357712	1.208763
O	1.844820	-0.069828	-0.545149
Al	2.856384	-1.529368	-0.070149
Cl	4.740039	-1.335075	-1.072933
Cl	1.650025	-3.163564	-0.766544
Cl	2.997777	-1.441974	2.076088

0 imaginary frequencies
E = -2922.949020
G = -2922.672325
E_{M06-2X} = -2922.804978
E_{solv} = -2922.979407

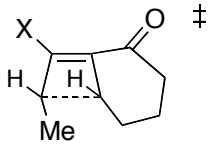
TS for ring opening of 1'-*trans* (leads to 2-amidodiene 22-*Z*)



C	-1.480990	-1.701611	1.519508
C	-2.250151	-1.776458	0.353976
C	-2.346298	-2.951887	-0.392933
C	-1.646141	-4.078066	0.040530
C	-0.862593	-4.016006	1.193593
C	-0.781249	-2.832435	1.933268
S	-3.142870	-0.323635	-0.183709
O	-4.050381	-0.699805	-1.265774
N	-1.913816	0.677094	-0.923854
C	-1.232412	0.075405	-2.085410
C	-1.376071	1.747871	-0.249031
C	-2.102341	2.782216	0.419419
H	-1.716153	3.064082	1.395102
C	-3.512615	3.210152	0.128741
C	-0.038449	2.233873	-0.313992
C	-0.193626	3.654115	-0.254661
H	-0.766041	4.135363	-1.040454
C	0.825098	4.506366	0.458887
C	1.821788	3.636304	1.238327
C	2.344425	2.460177	0.391187
O	-3.599723	0.405668	0.997750
H	0.331952	5.231973	1.119445
H	1.354875	5.110339	-0.295560
H	1.338238	3.235733	2.138379
H	2.668150	4.241439	1.578067
H	-3.574235	4.305268	0.168879
H	-4.213583	2.811230	0.868966
H	-3.842016	2.880352	-0.861218
H	-1.989585	-0.364821	-2.736554
H	-0.498849	-0.679328	-1.789329
H	-0.724502	0.875890	-2.626450
H	-1.442260	-0.781658	2.093012
H	-0.167303	-2.787862	2.827220
H	-0.307384	-4.891283	1.517053
H	-1.708416	-5.000523	-0.528687
H	-2.964649	-2.979999	-1.283362
C	1.209548	1.595519	-0.110741
H	2.912336	2.823024	-0.478221
H	3.033153	1.836846	0.968867
O	1.346689	0.343853	-0.305439
Al	2.747019	-0.878952	-0.241156
Cl	1.939417	-2.598954	-1.218404
Cl	3.132106	-1.132430	1.856337
Cl	4.364209	0.033023	-1.316174

1 imaginary frequency
E = -2922.908790
G = -2922.634716
E_{M06-2X} = -2922.763743
E_{solv} = -2922.938573

TS for ring opening of 1'-*cis* (leads to 2-amidodiene 22-*E*)

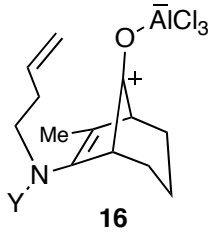


C	-1.472672	3.093464	0.281739
H	-2.432613	3.474640	-0.071175
C	-1.202227	3.431112	1.729498
H	-1.144986	4.514773	1.886419
H	-2.039187	3.063498	2.338813
C	-0.951956	1.941054	-0.386348
C	0.461206	2.131927	-0.451487
C	0.609551	3.550137	-0.465196
H	0.111563	4.110779	-1.248086
N	-1.695537	1.041140	-1.106935
C	-1.102117	0.238396	-2.191595
H	-0.594914	-0.652627	-1.810610
H	-1.894792	-0.040036	-2.886738
H	-0.377455	0.866242	-2.714064
S	-3.227405	0.452515	-0.490662
O	-3.638547	1.399586	0.544709
O	-4.044586	0.192108	-1.672953
C	-2.805835	-1.102302	0.281034
C	-3.017185	-2.289674	-0.422945
C	-2.663550	-3.496681	0.180105
C	-2.105595	-3.504573	1.459271
C	-1.908744	-2.307571	2.153971
C	-2.260579	-1.093607	1.568675
H	-2.128835	-0.158203	2.101862
H	-1.478850	-2.319547	3.150775
H	-1.819501	-4.446371	1.917691
H	-2.817700	-4.428925	-0.354412
H	-3.458191	-2.263218	-1.413256
C	1.550839	1.255705	-0.235544
O	1.401879	-0.007069	-0.321048
Al	2.490845	-1.504810	-0.158905
Cl	2.959483	-1.601801	1.933230
Cl	4.187575	-1.114761	-1.412489
Cl	1.242578	-3.087810	-0.869423
C	1.780670	4.209278	0.208400
H	1.430414	4.994260	0.894886
H	2.369832	4.735369	-0.559294
C	2.869944	1.891547	0.141007
H	3.428443	2.098021	-0.783830
H	3.465572	1.170913	0.708077
H	-0.282925	2.971493	2.102532
C	2.653095	3.184130	0.953345
H	3.625173	3.625191	1.195116
H	2.182372	2.921338	1.908537

1 imaginary frequency
E = -2922.903269
G = -2922.628776
E_{M06-2X} = -2922.756931
E_{solv} = -2922.933166

$AlCl_3$-coordinated [3.2.1]-bicyclic ketone 16

In this and subsequent structures, Y represents SO_2Ph.



16

Y = SO_2Ph

C	1.582652	-2.786340	-0.077342
C	1.537038	-1.400847	0.669870
C	1.822669	-0.385823	-0.395233
C	0.565760	-0.273137	-1.198249
C	0.527620	-1.565959	-2.089151
C	0.557667	-2.846474	-1.228415
C	-0.434582	-0.333711	-0.029382
C	0.110673	-0.975416	1.025328
N	-1.761244	0.180391	-0.087332
C	-1.909287	1.540990	-0.658445
C	-0.509772	-1.295681	2.342852
O	2.867199	0.246141	-0.622832
Al	4.573113	0.356828	0.233839
Cl	4.059499	0.861424	2.249598
S	-2.936884	-0.953966	-0.674166
O	-2.603528	-2.235374	-0.043798
C	-4.457748	-0.333692	0.047229
C	-4.676244	-0.499579	1.417581
C	-5.875311	-0.049346	1.966009
C	-6.839219	0.550047	1.149381
C	-6.612192	0.696947	-0.219979
C	-5.414676	0.251858	-0.783101
O	-3.050821	-0.853732	-2.137373
Cl	5.551304	1.883053	-0.867474
Cl	5.355057	-1.617941	-0.007648
H	0.534449	0.629654	-1.812764
H	1.385907	-1.529507	-2.772556
H	-0.379303	-1.535544	-2.702133
H	-0.763423	-2.361577	2.408107
H	-1.428511	-0.721718	2.486626
H	0.183934	-1.070886	3.161960
H	2.240120	-1.379816	1.505619
H	1.386607	-3.576463	0.655644
H	2.606068	-2.935784	-0.440555
H	0.784953	-3.706111	-1.868950
H	-0.439834	-3.018772	-0.816551
H	-2.979947	1.762193	-0.695775
C	-1.208725	2.590517	0.218776
H	-1.537707	1.587582	-1.690167
H	-3.928357	-0.986125	2.034268
H	-6.060650	-0.171709	3.029067
H	-7.773006	0.896863	1.582801
H	-7.367306	1.152873	-0.853454
H	-5.221674	0.341284	-1.846742
C	-1.449965	3.984450	-0.297243
H	-1.593378	2.488974	1.242945
H	-0.131447	2.392426	0.261860

C	-0.499740	4.807013	-0.741665
H	-2.489274	4.317755	-0.303142
H	-0.731694	5.804685	-1.104084
H	0.549738	4.519369	-0.750934

0 imaginary frequencies

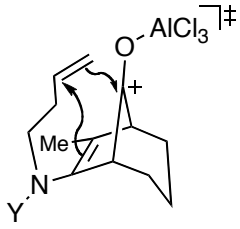
E = -3039.659920

G = -3039.326098

E_{M06-2X} = -3039.501357

E_{solv} = -3039.690565

TS9 (Prins-like addition of tethered alkene to carbocation in $AlCl_3$-coordinated [3.2.1]-bicyclic ketone 16)



C	-4.342882	1.485884	-1.133765
C	-4.568438	0.351883	-0.348079
C	-5.742706	0.191573	0.389054
C	-6.706686	1.200969	0.346880
C	-6.491208	2.343138	-0.425488
C	-5.313148	2.484751	-1.166114
S	-3.340519	-0.954400	-0.330500
O	-2.821524	-1.158523	-1.685084
N	-2.058670	-0.230582	0.536807
C	-0.717636	-0.544538	0.146798
C	0.236871	0.045238	2.410749
C	-1.082142	0.744663	2.554515
C	-2.256637	-0.071315	1.993206
C	1.412312	0.608056	1.920960
C	1.540670	0.087475	0.079178
C	1.422995	-1.458769	0.044251
C	-0.018495	-1.683954	0.420627
C	0.168446	0.485792	-0.506686
C	0.308783	0.267140	-2.048466
C	0.626667	-1.200508	-2.397554
C	1.669306	-1.838594	-1.457684
O	2.598671	0.691494	-0.368426
Al	4.401666	0.634097	-0.107855
Cl	4.897021	2.566551	0.675986
C	-0.515316	-2.982147	0.969081
Cl	5.256596	0.186589	-2.018907
Cl	4.745987	-0.934501	1.353418
O	-3.896401	-2.073849	0.443204
H	-0.133077	1.516055	-0.300445
H	1.106479	0.934109	-2.391849
H	-0.622162	0.570996	-2.537624
H	0.032057	-3.264641	1.878063
H	-0.329750	-3.781316	0.239268
H	-1.587875	-2.969831	1.175961
H	2.140673	-1.986416	0.677951
H	1.647709	-2.930551	-1.549336
H	2.681615	-1.512774	-1.715896
H	0.989476	-1.257254	-3.429817
H	-0.303846	-1.775657	-2.359799

H	-2.323358	-1.043241	2.500462
H	-3.198499	0.460059	2.160638
H	-5.894355	-0.711683	0.969909
H	-7.626422	1.089552	0.913534
H	-7.245054	3.124650	-0.456724
H	-5.153833	3.370803	-1.773425
H	-3.430201	1.575584	-1.713556
H	-1.049999	1.735703	2.090060
H	-1.261082	0.895623	3.630445
H	0.284888	-0.946861	2.857018
H	1.437534	1.685376	1.770709
H	2.352653	0.172642	2.252137

1 imaginary frequency

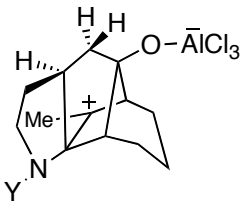
E = -3039.631150

G = -3039.290405

E_{M06-2X} = -3039.478772

E_{solv} = -3039.666359

$AlCl_3$-coordinated intermediate 18



C	1.541066	-1.116254	1.257482
C	1.550719	-0.037040	0.128306
C	1.288399	-0.803785	-1.258191
C	-0.050346	-1.365574	-1.066209
C	-0.654763	-0.690666	0.062973
C	0.127300	-1.670983	1.196179
C	0.149412	0.626506	0.267603
C	-0.045817	1.760338	-0.742905
C	0.112014	1.306397	-2.205356
C	1.260622	0.304232	-2.378989
C	-0.842363	-1.474070	2.372978
C	-2.240465	-1.490283	1.750904
N	-2.044043	-0.817224	0.444278
O	2.597586	0.812895	0.095056
Al	4.348619	0.516403	0.322131
Cl	5.370450	2.147348	-0.625681
C	-0.592970	-2.524845	-1.801584
S	-3.329571	-0.794891	-0.652107
O	-4.025720	-2.082870	-0.562876
Cl	4.775692	-1.396910	-0.649335
Cl	4.733346	0.372379	2.445722
O	-2.758332	-0.328770	-1.921198
C	-4.428020	0.463844	-0.006081
C	-5.491388	0.081130	0.814770
C	-6.334290	1.068719	1.326818
C	-6.114171	2.410845	1.011576
C	-5.055299	2.775844	0.175210
C	-4.202861	1.801749	-0.341179
H	-0.014972	1.002880	1.281453
H	0.721566	2.504712	-0.501268
H	-1.019325	2.242796	-0.595773
H	0.197262	-3.241066	-2.048044
H	-0.995828	-2.141307	-2.751131

H	-1.425919	-3.011984	-1.287295
H	2.045959	-1.547084	-1.524541
H	1.207577	-0.189250	-3.355073
H	2.234825	0.793913	-2.289198
H	0.297148	2.176161	-2.845413
H	-0.825089	0.856140	-2.549743
H	-2.609214	-2.510941	1.597622
H	-2.973209	-0.945731	2.354880
H	-5.663372	-0.968638	1.026445
H	-7.166936	0.786408	1.964186
H	-6.774653	3.175187	1.410736
H	-4.896071	3.819152	-0.080285
H	-3.390724	2.067725	-1.008841
H	-0.646609	-0.518589	2.867358
H	-0.714461	-2.269142	3.114189
H	0.080358	-2.717012	0.877637
H	1.750849	-0.618460	2.208463
H	2.309986	-1.874831	1.093999

0 imaginary frequencies

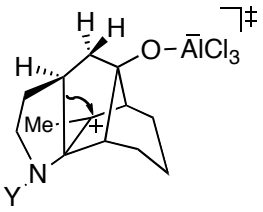
E = -3039.646171

G = -3039.302815

E_{M06-2X} = -3039.501256

E_{solv} = -3039.686355

TS10 (1,2-Alkyl shift in $AlCl_3$-coordinated intermediate 18)



C	-1.487022	2.472585	0.500017
C	-1.331386	1.071147	1.167117
C	-1.620944	-0.027040	0.059785
C	-0.300251	0.141022	-0.782558
C	-0.404467	1.460360	-1.579381
C	-0.499073	2.688431	-0.659499
C	0.681829	0.136104	0.393802
C	0.099750	0.813558	1.478491
N	2.074901	-0.234736	0.394426
C	2.306454	-1.566296	1.020828
C	0.784913	1.248748	2.724589
O	-2.755521	0.153100	-0.640172
Al	-4.456674	-0.270819	-0.288371
Cl	-4.732869	0.040547	1.860593
S	2.967072	0.066878	-1.054637
O	2.669942	1.455591	-1.406039
C	4.649224	-0.038866	-0.445479
C	5.125466	0.953701	0.415913
C	6.451666	0.894204	0.838590
C	7.284513	-0.137670	0.394024
C	6.798019	-1.112830	-0.478235
C	5.470672	-1.068241	-0.908242
O	2.757804	-1.022352	-2.015638
Cl	-4.724587	-2.365047	-0.759718
Cl	-5.680586	1.042685	-1.459872
H	-0.124048	-0.700238	-1.458772
H	-1.319528	1.366870	-2.173172

H	0.438766	1.565681	-2.262970
H	0.745468	2.346157	2.759636
H	1.831972	0.940436	2.757796
H	0.255217	0.897590	3.617859
H	-1.994245	1.001344	2.034976
H	-1.375353	3.253666	1.261345
H	-2.519255	2.506862	0.138541
H	-0.806884	3.563791	-1.241707
H	0.500842	2.918990	-0.266801
H	2.576829	-1.418469	2.073340
C	0.996577	-2.340642	0.892247
H	0.839897	-2.646880	-0.146438
H	4.472568	1.759285	0.735029
H	6.838722	1.657535	1.507012
H	8.318727	-0.175551	0.723907
H	7.450711	-1.905766	-0.830881
H	5.074664	-1.805676	-1.598354
H	1.007395	-3.241630	1.519020
H	3.138786	-2.076788	0.533784
C	-0.114147	-1.424765	1.353777
C	-1.476536	-1.429780	0.755859
H	-0.077189	-1.265540	2.432935
H	-1.593697	-2.200490	-0.010558
H	-2.263697	-1.549662	1.504395

1 imaginary frequency

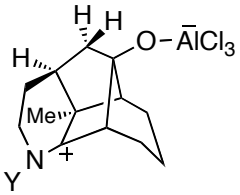
E = -3039.635772

G = -3039.292664

$E_{M06\text{-}2X}$ = -3039.490927

E_{solv} = -3039.677338

$AlCl_3$-coordinated intermediate 19

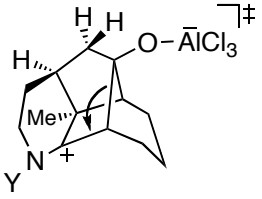


C	1.561468	2.006792	-1.452709
C	1.351057	0.488589	-1.447247
C	1.485718	-0.185326	-0.051570
C	0.173892	0.519935	0.655053
C	0.473806	2.024863	0.828400
C	0.598604	2.749662	-0.515191
C	-0.786656	0.143757	-0.399086
C	-0.074989	-0.048826	-1.723076
N	-1.958206	-0.451081	-0.212282
C	-2.374811	-1.531816	-1.143125
C	-0.715335	0.415544	-3.029032
O	2.565032	0.032615	0.716468
Al	4.329670	-0.105338	0.498374
Cl	4.657091	-1.186135	-1.372025
S	-2.900933	-0.316399	1.325506
O	-2.365729	0.846422	2.017739
C	-4.516658	0.071617	0.673725
C	-4.772306	1.377609	0.242916
C	-6.046421	1.684221	-0.229432
C	-7.040477	0.700992	-0.256351
C	-6.771427	-0.593728	0.192605
C	-5.500228	-0.920716	0.665178

O	-2.914620	-1.656629	1.900806
Cl	5.125544	-1.175502	2.183868
Cl	5.117147	1.905792	0.352088
H	-0.053843	0.066528	1.620663
H	1.412541	2.085604	1.386918
H	-0.317727	2.463292	1.444176
H	-0.030889	0.181023	-3.851167
H	-0.865611	1.499580	-3.025173
H	-1.674347	-0.053606	-3.261813
H	2.051342	0.025432	-2.151259
H	1.476982	2.394091	-2.476045
H	2.593888	2.192327	-1.135787
H	0.945677	3.776173	-0.354264
H	-0.397398	2.832166	-0.979435
H	-2.817907	-1.084309	-2.033635
C	-1.148666	-2.416351	-1.475208
H	-1.056850	-3.190973	-0.707492
H	-3.998080	2.136050	0.293272
H	-6.266071	2.692455	-0.566752
H	-8.032766	0.949278	-0.621319
H	-7.551303	-1.348894	0.183479
H	-5.276045	-1.914096	1.038894
H	-1.361999	-2.926270	-2.420274
H	-3.151199	-2.113386	-0.645480
C	0.169281	-1.614878	-1.570474
C	1.131463	-1.675337	-0.344496
H	0.716217	-1.911796	-2.471449
H	0.681975	-2.161986	0.529291
H	2.052427	-2.208857	-0.588545

0 imaginary frequencies
E = -3039.662559
G = -3039.317764
E_{M06-2X} = -3039.514859
E_{solv} = -3039.704386

TS11 (retro-aldol-like C–C cleavage in $AlCl_3$-coordinated intermediate 19)



C	-1.593544	-0.610653	0.100175
C	-0.036530	0.456088	-0.787002
H	0.110068	0.192997	-1.832180
C	-0.587099	1.862524	-0.622505
H	0.043766	2.507748	-1.248404
H	-1.594766	1.900452	-1.051804
C	-0.598298	2.367907	0.818368
H	0.436067	2.440562	1.185832
H	-1.013479	3.380904	0.849755
H	-1.213823	1.659532	2.779242
C	-1.420703	1.445693	1.723458
H	-2.487404	1.645809	1.578842
C	-1.184403	-0.044588	1.466828
H	-1.761913	-0.606481	2.216820
O	-2.649864	-0.287647	-0.554355
Al	-4.405905	0.148217	-0.337010

Cl	-5.458399	-0.878339	-1.887799
Cl	-4.872050	-0.572116	1.648707
Cl	-4.549137	2.290993	-0.486613
C	-1.107101	-2.061101	0.068781
H	-0.741888	-2.351813	-0.921338
H	-1.965795	-2.703515	0.296073
C	-0.023871	-2.125287	1.178549
H	-0.479275	-2.522769	2.092725
C	1.228537	-2.952778	0.827825
H	1.557697	-3.540271	1.690956
H	3.041147	-1.789597	1.224951
C	0.266625	-0.592202	1.465819
C	1.077152	-0.307040	2.729112
H	1.181042	0.770226	2.892315
H	0.561949	-0.727585	3.599885
H	2.082914	-0.734411	2.703464
H	0.981458	-3.667904	0.036686
C	2.418009	-2.085644	0.374817
H	3.048517	-2.637379	-0.323162
C	0.835264	-0.191467	0.111171
N	1.933408	-0.880493	-0.330918
S	3.032110	-0.228474	-1.549198
O	3.484625	-1.384753	-2.317449
O	2.366980	0.913742	-2.163344
C	4.394163	0.372824	-0.554330
C	4.296998	1.640380	0.027994
C	5.361344	2.106253	0.797427
C	6.500773	1.315218	0.972353
C	6.587030	0.056808	0.373498
C	5.529532	-0.425727	-0.398722
H	5.587736	-1.389941	-0.891946
H	7.480183	-0.547963	0.498448
H	7.328099	1.686380	1.570271
H	5.305256	3.090785	1.251976
H	3.417356	2.253308	-0.138216

1 imaginary frequency

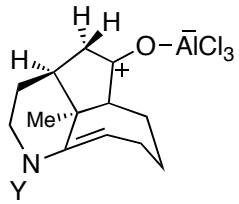
E = -3039.655330

G = -3039.312474

E_{M06-2X} = -3039.505806

E_{solv} = -3039.691180

$AlCl_3$-coordinated tricyclic product 20

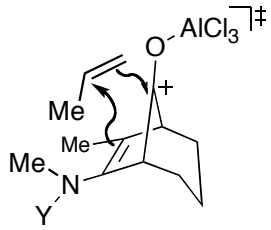


C	-1.174187	1.651799	0.256248
C	-0.969470	0.246641	0.845044
C	-1.921694	-0.849596	0.473205
C	0.599104	-0.294334	-1.713660
C	-0.488094	0.702506	-2.048390
C	-0.529882	1.918451	-1.114411
C	1.091156	-0.631549	-0.505392
C	0.438784	-0.433144	0.866885
N	2.308236	-1.402148	-0.444609
C	2.489322	-2.391521	0.638439

C	1.338079	0.343204	1.849353
O	-3.094975	-0.740934	0.085172
Al	-4.703175	0.256223	-0.005390
Cl	-4.658737	1.287789	1.871539
S	3.753955	-0.837852	-1.171316
O	3.419638	-0.287251	-2.483377
C	4.342346	0.527242	-0.161784
C	3.937683	1.829307	-0.469358
C	4.367892	2.879923	0.341590
C	5.192495	2.626787	1.440868
C	5.602500	1.322593	1.727978
C	5.181088	0.262263	0.924681
O	4.701111	-1.944403	-1.017271
Cl	-6.188569	-1.253800	-0.160351
Cl	-4.479893	1.487832	-1.733553
H	1.131874	-0.700220	-2.566612
H	-1.480791	0.231292	-2.105367
H	-0.292459	1.052629	-3.068368
H	0.893387	0.343977	2.852119
H	1.448232	1.383532	1.527468
H	2.343256	-0.071103	1.930914
H	-1.234045	0.333138	1.920413
H	-0.802191	2.382453	0.982541
H	-2.250588	1.830538	0.194378
H	-1.090134	2.728472	-1.594451
H	0.496841	2.280548	-0.981488
H	2.974515	-1.950782	1.520731
C	1.127749	-2.970930	1.007425
H	0.773766	-3.558108	0.152325
H	3.320657	2.009664	-1.342643
H	4.068153	3.897486	0.107730
H	5.527203	3.449217	2.066810
H	6.260570	1.130724	2.570616
H	5.515599	-0.752159	1.114074
H	1.257728	-3.674019	1.837007
H	3.145968	-3.178768	0.268299
C	0.079342	-1.891929	1.366480
C	-1.294595	-2.186128	0.727211
H	-0.040647	-1.838846	2.456297
H	-1.184585	-2.679022	-0.249046
H	-1.963489	-2.820617	1.319170

0 imaginary frequencies
E = -3039.674131
G = -3039.332486
E_{M06-2X} = -3039.530371
E_{solv} = -3039.706224

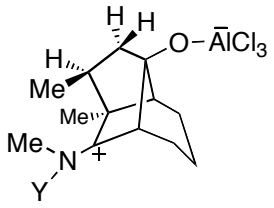
TS9' (Prins-like addition of propene to carbocation in $AlCl_3$-coordinated [3.2.1]-bicyclic ketone 16')



C	1.389277	-1.645565	1.428605
C	1.164750	-0.107721	1.236290

```
C     1.641301    0.179466   -0.204104
C     0.435732   -0.330691   -1.009709
C     0.603355   -1.890850   -1.020844
C     0.600422   -2.486555    0.403364
C    -0.731497    0.059143   -0.129090
C    -0.307711    0.230408    1.159514
N    -2.065240    0.152503   -0.605983
C    -2.240376    0.457758   -2.041395
C    -1.102233    0.604119    2.369709
O     2.818689   -0.184411   -0.628105
Al    4.561537    0.009919   -0.154221
Cl    4.556063    1.060197    1.748527
S    -3.165327   -1.124857   -0.114994
O    -2.764392   -1.538819    1.229433
C    -4.733692   -0.258130   -0.014081
C    -5.028970    0.487543    1.130148
C    -6.257512    1.140706    1.208612
C    -7.174166    1.041002    0.157739
C    -6.872122    0.278856   -0.971992
C    -5.645910   -0.382040   -1.063877
O    -3.259411   -2.100416   -1.207600
Cl    5.427772    1.213120   -1.705246
Cl    5.351547   -1.973515   -0.003538
H     0.399767    0.040715   -2.036902
H     1.547205   -2.101115   -1.533758
H    -0.208898   -2.330355   -1.611000
H    -1.385448   -0.284282    2.945168
H    -2.026921    1.122064    2.097032
H    -0.514201    1.252150    3.031202
H     1.709828    0.437313    2.011189
H     1.095709   -1.921438    2.447750
H     2.464153   -1.832517    1.341753
H     1.019633   -3.498144    0.367703
H    -0.433065   -2.590581    0.746916
H    -3.287448    0.712116   -2.221572
H    -1.638638    1.332315   -2.285813
H    -1.961665   -0.376748   -2.692596
H    -4.320625    0.532233    1.949982
H    -6.503277    1.719907    2.093786
H    -8.130991    1.550691    0.226046
H    -7.592428    0.189512   -1.779747
H    -5.401899   -1.000255   -1.921073
C     1.666294    2.081779   -0.336183
H     2.544637    2.175246    0.299771
H     1.858768    2.213832   -1.399572
C     0.482506    2.597856    0.181045
H     0.400253    2.694085    1.261806
C    -0.600450    3.255583   -0.601441
H    -1.599026    2.923796   -0.295286
H    -0.552983    4.336501   -0.396336
H    -0.475075    3.120721   -1.679102
1 imaginary frequency
E = -3040.831507
```

$AlCl_3$-coordinated intermediate 19'



C	1.416709	-1.415618	1.715092
C	1.070953	-0.057748	1.095052
C	1.550396	0.087252	-0.379322
C	0.566813	-0.942536	-1.030379
C	0.996985	-2.384159	-0.595025
C	0.844138	-2.600197	0.919171
C	-0.746725	-0.637135	-0.359234
C	-0.437027	0.247917	0.816254
N	-1.886761	-1.045124	-0.904943
C	-1.884043	-1.580042	-2.295507
C	-1.300738	0.397095	2.059369
O	2.840482	-0.209749	-0.693086
Al	4.417818	0.388033	-0.141641
Cl	4.063464	2.037361	1.253031
S	-3.469826	-1.391881	-0.000880
O	-3.076165	-1.793252	1.340603
C	-4.389067	0.138167	0.038141
C	-4.789502	0.639768	1.278724
C	-5.583107	1.787235	1.307241
C	-5.962583	2.408077	0.115792
C	-5.567555	1.879374	-1.117132
C	-4.783986	0.728998	-1.165828
O	-4.140838	-2.310745	-0.912883
Cl	5.530582	1.053864	-1.863428
Cl	5.397100	-1.252778	0.879364
H	0.548510	-0.873971	-2.120686
H	2.047921	-2.453447	-0.892740
H	0.432843	-3.140296	-1.152890
H	-1.439470	-0.550885	2.580640
H	-2.282837	0.823953	1.850276
H	-0.784285	1.085615	2.736586
H	1.479050	0.744262	1.717935
H	1.076447	-1.459875	2.756986
H	2.510089	-1.485226	1.738637
H	1.349716	-3.527961	1.207660
H	-0.218034	-2.743000	1.167234
H	-2.903251	-1.817585	-2.585172
H	-1.473903	-0.821834	-2.963828
H	-1.288895	-2.492210	-2.352103
H	-4.494948	0.136820	2.192700
H	-5.905507	2.190804	2.261990
H	-6.576974	3.302946	0.145565
H	-5.876764	2.357450	-2.041320
H	-4.495405	0.300929	-2.119974
C	1.049887	1.496781	-0.781676
H	1.804777	2.240684	-0.518271
H	0.873915	1.562438	-1.862681
C	-0.237727	1.676540	0.046111
H	-0.022257	2.327176	0.901658
C	-1.432073	2.261916	-0.700720
H	-2.322964	2.345617	-0.069372

```
H   -1.175728    3.271614   -1.040971
H   -1.696918    1.683772   -1.594116
0 imaginary frequencies
E = -3040.860600
```

Part 3 – Calculation of Strain Energies

H_2

```
H     0.000000     0.000000     0.128559
H     0.000000     0.000000     0.871441
0 imaginary frequencies
E = -1.175482
H = -1.162036
```
E_{M06-2X} = -1.168294

Z-Cyclohexene

```
C   -0.005260    0.668458    1.306093
H   -0.019281    1.204708    2.254607
C    0.005260    1.503008    0.047896
C    0.371521    0.671524   -1.192292
H   -0.983001    1.970642   -0.089950
H    0.709314    2.338873    0.163910
C   -0.371521   -0.671524   -1.192292
H    0.149800    1.236654   -2.105966
H    1.454199    0.482476   -1.192786
C   -0.005260   -1.503008    0.047896
H   -1.454199   -0.482476   -1.192786
H   -0.149800   -1.236654   -2.105966
C    0.005260   -0.668458    1.306093
H   -0.709314   -2.338873    0.163910
H    0.983001   -1.970642   -0.089950
H    0.019281   -1.204708    2.254607
0 imaginary frequencies
E = -234.648289
H = -234.494841
```
E_{M06-2X} = -234.590077

Cyclohexane

```
C   -0.229233    0.733686    1.270339
H    0.146241    1.249078    2.163835
C    0.229233   -0.733686    1.270339
H   -1.327581    0.767811    1.328928
C   -0.229233   -1.467698    0.000000
H    1.327581   -0.767811    1.328928
H   -0.146241   -1.249078    2.163835
C    0.229233   -0.733686   -1.270339
H    0.147594   -2.498717    0.000000
H   -1.327442   -1.537183    0.000000
C   -0.229233    0.733686   -1.270339
H    1.327581   -0.767811   -1.328928
H   -0.146241   -1.249078   -2.163835
C    0.229233    1.467698    0.000000
H    0.146241    1.249078   -2.163835
H   -1.327581    0.767811   -1.328928
H    1.327442    1.537183    0.000000
H   -0.147594    2.498717    0.000000
0 imaginary frequencies
```

E = -235.880452
H = -235.702633
E_{M06-2X} = -235.816340

E-Cycloheptene

C	0.568768	-1.252886	0.448342
C	-1.399430	0.880805	-0.171603
C	-0.487852	-1.314273	-0.373118
C	1.301204	0.929269	-0.314253
C	-0.028051	1.384574	0.383055
C	1.806984	-0.535890	-0.020848
H	-0.305171	-1.297526	-1.451757
C	-1.745868	-0.628427	0.071753
H	-1.422120	1.069953	-1.254224
H	-2.194212	1.503752	0.263315
H	2.086120	1.648968	-0.044997
H	1.153635	1.028907	-1.397830
H	0.026034	1.175994	1.460354
H	-0.054982	2.479552	0.300216
H	2.233448	-0.965960	-0.935166
H	2.596310	-0.535655	0.739187
H	-2.654098	-0.900659	-0.480324
H	-1.932278	-0.794636	1.140478
H	0.372780	-1.191716	1.520776

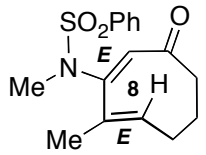
0 imaginary frequencies
E = -273.907882
H = -273.725107
E_{M06-2X} = -273.841925

Cycloheptane

C	0.000000	1.315329	0.970248
C	0.850588	-1.332684	-0.314039
C	0.000000	0.000000	1.777177
C	-0.124577	0.757940	-1.543691
C	0.124577	-0.757940	-1.543691
C	-0.850588	1.332684	-0.314039
C	0.000000	-1.315329	0.970248
H	1.031668	1.574999	0.694197
H	-0.333943	2.118632	1.640108
H	1.802600	-0.806038	-0.151838
H	1.118233	-2.373448	-0.539972
H	-0.874958	-0.014305	2.441390
H	0.874958	0.014305	2.441390
H	-0.697486	1.009190	-2.447083
H	0.839329	1.279456	-1.643448
H	-0.839329	-1.279456	-1.643448
H	0.697486	-1.009190	-2.447083
H	-1.118233	2.373448	-0.539972
H	-1.802600	0.806038	-0.151838
H	0.333943	-2.118632	1.640108
H	-1.031668	-1.574999	0.694197

0 imaginary frequencies
E = -275.183553
H = -274.975427
E_{M06-2X} = -275.110684

3



C	-0.779597	-0.492615	0.580140
C	-1.605818	-0.888807	-0.576488
C	-1.994877	-2.341887	-0.719440
H	-1.106294	-2.944984	-0.924092
H	-2.454296	-2.731226	0.198672
H	-2.694693	-2.488656	-1.545885
C	-2.153958	0.138222	-1.264899
H	-1.689929	1.116707	-1.143709
C	-3.553306	0.195608	-1.781076
H	-3.980344	-0.802270	-1.921277
H	-3.654420	0.740981	-2.726889
C	-4.327966	0.950831	-0.650841
H	-4.171203	2.031325	-0.754217
H	-5.405013	0.775829	-0.762751
C	-3.873660	0.534005	0.773925
H	-4.634868	0.875572	1.484881
H	-3.809897	-0.557043	0.848462
C	-2.571077	1.210619	1.259069
O	-2.634500	2.373315	1.646354
C	-1.259977	0.507085	1.376860
H	-0.647838	0.911152	2.179064
N	0.368332	-1.239605	0.947642
C	0.831002	-1.192024	2.342955
H	1.315756	-0.240457	2.600806
H	1.531337	-2.010175	2.505071
H	-0.042263	-1.327879	2.984526
S	1.631715	-1.444511	-0.213755
O	2.593350	-2.352178	0.413103
O	0.998148	-1.760718	-1.491728
C	2.398648	0.171781	-0.360113
C	3.513376	0.472470	0.426262
C	4.084676	1.741663	0.327909
C	3.543229	2.688491	-0.544151
C	2.431935	2.370892	-1.329452
C	1.850828	1.106459	-1.243137
H	1.000173	0.836207	-1.859718
H	2.019777	3.106359	-2.014125
H	3.992069	3.675110	-0.617260
H	4.956377	1.986938	0.927708
H	3.933062	-0.284195	1.080349

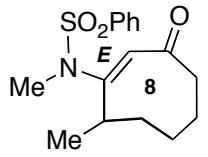
0 imaginary frequencies

E = -1299.633850

H = -1299.286070

E_{M06-2X} = -1299.500766

Partially saturated derivative of 3



C	2.513294	-0.869227	-1.406632
C	1.077975	0.718953	1.159716
C	1.013976	-0.551699	0.694533
C	2.161187	-1.323134	0.038964
C	3.686159	1.419938	-0.905670
C	3.572606	1.431575	0.639979
C	2.168056	1.731639	1.143562
O	1.892310	2.859069	1.540562
C	1.983571	-2.849546	0.078136
N	-0.206534	-1.284157	0.951903
S	-1.339966	-1.455131	-0.311784
C	-0.794005	-1.212894	2.300203
O	-0.566026	-1.571725	-1.549300
O	-2.274529	-2.496949	0.116645
C	-2.252991	0.091282	-0.383065
C	-1.756721	1.146841	-1.153601
C	-2.455207	2.353613	-1.177120
C	-3.632880	2.498060	-0.439767
C	-4.124117	1.433072	0.318463
C	-3.435425	0.220196	0.351401
C	2.608162	0.638673	-1.676577
H	1.764459	-1.292165	-2.082780
H	3.473469	-1.340911	-1.659339
H	0.184873	1.141390	1.613035
H	3.034826	-1.107311	0.662825
H	4.679918	1.034530	-1.170026
H	3.657146	2.461791	-1.248419
H	4.212513	2.225102	1.037292
H	3.932207	0.486071	1.058014
H	1.776216	-3.209006	1.090972
H	1.171301	-3.176840	-0.574436
H	2.909299	-3.325208	-0.265963
H	0.019628	-1.301365	3.022644
H	-1.337421	-0.277793	2.493383
H	-1.474365	-2.056738	2.423734
H	-0.854637	1.012022	-1.739583
H	-2.080623	3.179522	-1.774648
H	-4.172397	3.440733	-0.462098
H	-5.047839	1.542216	0.879413
H	-3.816761	-0.625412	0.913527
H	1.629675	1.103337	-1.502454
H	2.807815	0.769992	-2.748264

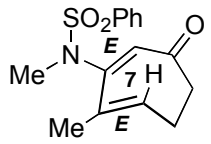
0 imaginary frequencies

E = -1300.866079

H = -1300.493528

E_{M06-2X} = -1300.730726

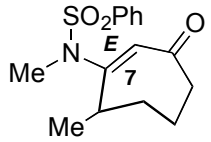
6



C	1.768364	1.060684	-1.226215
C	2.229500	0.130430	-0.290451
C	3.301250	0.414340	0.559160
C	3.917542	1.663165	0.471490
C	3.462404	2.606163	-0.452403
C	2.393450	2.304761	-1.300451
S	1.407718	-1.460194	-0.162464
O	0.857253	-1.789643	-1.474670
N	0.072476	-1.192721	0.905212
C	0.418545	-1.181375	2.333972
C	-1.008184	-0.406331	0.452355
C	-1.624322	0.520756	1.256381
C	-2.936206	1.218018	1.040660
O	-3.181232	2.180574	1.758485
C	-1.724151	-0.682333	-0.803145
C	-2.233749	0.450901	-1.345726
C	-3.709251	0.687638	-1.469053
C	-4.062875	0.741861	0.059975
C	-2.232635	-2.077681	-1.077508
O	2.294467	-2.379517	0.551017
H	-1.407759	-2.714659	-1.410579
H	-2.665626	-2.542614	-0.182461
H	-2.989024	-2.068121	-1.868017
H	-1.687980	1.371092	-1.140703
H	-3.942357	1.632120	-1.969764
H	-4.273099	-0.110365	-1.960757
H	-4.913927	1.398242	0.264390
H	-4.333253	-0.275076	0.374903
H	-1.175595	0.824722	2.198333
H	0.874974	-0.233902	2.651126
H	1.106161	-2.001811	2.532308
H	-0.502929	-1.336894	2.899530
H	0.949635	0.803393	-1.889999
H	2.049723	3.036403	-2.025840
H	3.946319	3.576650	-0.517223
H	4.757027	1.895144	1.120463
H	3.654896	-0.339468	1.254326

0 imaginary frequencies
E = -1260.293844
H = -1259.976672
E_{M06-2X} = -1260.167396

Partially saturated derivative of 6



C	-3.014006	-0.392351	-1.437095
C	-1.224736	0.872217	0.835053
C	-1.124274	-0.384519	0.349405
C	-2.128219	-1.185079	-0.461195
C	-3.300431	1.949115	-0.402839
C	-2.297135	1.898014	0.738919
O	-2.292430	2.792774	1.576736
C	-2.951129	-2.071066	0.504299
N	-0.008495	-1.191208	0.793667
S	1.249191	-1.504170	-0.326724
C	0.442118	-1.085108	2.191677
O	2.044447	-2.586345	0.254184
O	0.628997	-1.625255	-1.647529
C	2.270972	-0.025084	-0.341500
C	3.380478	0.046423	0.504936
C	4.156897	1.205785	0.506109
C	3.822437	2.274217	-0.328496
C	2.714761	2.187074	-1.175637
C	1.930231	1.034358	-1.187636
C	-3.973219	0.641270	-0.833445
H	-3.602083	-1.132700	-1.994530
H	-2.370615	0.102446	-2.177863
H	-0.434154	1.225581	1.491539
H	-1.534302	-1.866796	-1.075534
H	-2.757822	2.364846	-1.267144
H	-4.046275	2.695802	-0.113217
H	-3.561996	-1.474953	1.190716
H	-3.619055	-2.725852	-0.067278
H	-2.290095	-2.705093	1.103066
H	1.030875	-1.971694	2.430371
H	1.042567	-0.187748	2.394099
H	-0.446728	-1.062684	2.825060
H	3.638818	-0.803306	1.127503
H	5.026537	1.270098	1.153730
H	4.430563	3.174465	-0.324858
H	2.464082	3.014895	-1.832570
H	1.081108	0.942581	-1.855483
H	-4.527323	0.208642	0.009343
H	-4.728284	0.895661	-1.587488

0 imaginary frequencies
E = -1261.559943
H = -1261.217770
E_{M06-2X} = -1261.430278