Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Computational Studies on the Mechanism of the Gold(I)-Catalysed Rearrangement of Cyclopropenes

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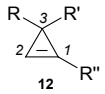
Contents

Computed Cartesian Coordinates (Å) and energies (SCF, Enthalpies at 0 K and 298.15 K and Free Energies at 298.15 K/1 atm) for all structures; unique negative frequencies for all transition states. Solvation energies (tolune and dichloromethane, PCM approach) are included for the reactions of 3-phenylcyclopropene-3-methylcarboxylate at $\{Au(PPh_3)^+\}$.

(i) Small Models@{Au(PH$_3$)$^+$}

1. 

R=R′=R″=H

13$_{H/H}$

BP86 Energy = -260.676914170
Enthalpy 0K= -260.593706
Enthalpy 298K= -260.585480
Free Energy 298K= -260.629230

C	-2.72910	0.85080	0.00209
C	-2.06149	-0.33796	0.67881
Au	0.07845	-0.07136	0.00018
P	2.41068	0.19793	-0.00063
C	-2.06139	-0.33308	-0.68282
H	-2.26970	1.84299	0.00572
H	2.92930	1.03649	-1.02878
H	2.95271	0.79164	1.17544
H	3.19618	-0.98225	-0.13929
H	-2.11389	-0.98026	1.56072
H	-2.11266	-0.96864	-1.56965
H	-3.82749	0.84991	0.00237

TS(13-14)$_{H/H}$

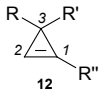
BP86 Energy = -260.665071404
Enthalpy 0K= -260.583273
Enthalpy 298K= -260.575403
Free Energy 298K= -260.618762
Nimag=1 (-164.9357cm-1)

C	2.80013	0.93073	-0.06495
C	1.93958	-0.42202	-0.32321
Au	-0.14135	-0.07126	-0.06493
P	-2.43344	0.18888	0.17805
C	2.83076	-0.30808	0.70026
H	2.19621	1.79016	0.23161
H	-2.95574	1.49296	-0.06286
H	-3.24184	-0.61662	-0.67546
H	-2.96869	-0.11176	1.46410
H	1.98366	-1.24380	-1.05810
H	3.51791	-0.90372	1.30925
H	3.71421	1.18534	-0.62241

14$_{H/H}$

BP86 Energy = -260.693592844
Enthalpy 0K= -260.610370
Enthalpy 298K= -260.602726
Free Energy 298K= -260.644528

C	2.95584	1.32928	-0.00015
C	1.75073	-0.78990	0.00094
Au	-0.14810	-0.16308	-0.00043
P	-2.45404	0.45065	0.00084
C	2.96346	-0.04822	0.00130
H	2.00619	1.87853	-0.00141
H	-2.90592	1.26498	-1.07906
H	-3.40073	-0.61462	-0.03749
H	-2.91972	1.19780	1.12263
H	1.90160	-1.88406	0.00180
H	3.92491	-0.57815	0.00257
H	3.88427	1.91203	-0.00016

2. 

R=H; R′=Me; R″=H

13$_{H/Me}$

BP86 Energy = -299.997557239
Enthalpy 0K= -299.887350
Enthalpy 298K= -299.877514
Free Energy 298K= -299.924901

C	-2.51266	0.58005	0.00248
C	-1.73576	-0.55012	0.67790
Au	0.36734	-0.09561	0.00068
P	2.67136	0.35633	-0.00118
C	-1.73565	-0.54103	-0.68715
H	-2.08740	1.58995	0.00935
H	3.12859	1.21975	-1.03805
H	3.16791	1.00352	1.16689
H	3.54766	-0.76000	-0.12552
H	-1.74813	-1.21760	1.54373
H	-1.74573	-1.19616	-1.56239
C	-4.03005	0.51698	0.00122
H	-4.43361	1.03421	-0.88549
H	-4.40082	-0.52137	-0.00661
H	-4.43437	1.02101	0.89517

TS(13-14)$_{H/Me}$

BP86 Energy = -299.987762140
Enthalpy 0K= -299.878726
Enthalpy 298K= -299.869249
Free Energy 298K= -299.916546
Nimag=1 (-180.7736cm-1)

C	2.59315	0.47105	0.33163
C	1.62408	-0.57711	-0.45032
Au	-0.41367	-0.08588	-0.07542
P	-2.67611	0.36318	0.18363
C	2.30994	-0.92723	0.67505
H	2.03585	1.28012	0.81072
H	-3.35563	-0.35845	1.20794
H	-3.03074	1.70956	0.48927
H	-3.49306	0.09684	-0.95331
H	1.65225	-1.12074	-1.40808
H	2.79228	-1.78722	1.15254
C	3.99820	0.82181	-0.11971
H	4.57477	1.24873	0.71816
H	4.54290	-0.04906	-0.51804
H	3.95071	1.58607	-0.91562

14$_{H/Me}$

BP86 Energy = -300.030038112
Enthalpy 0K= -299.919679
Enthalpy 298K= -299.909646
Free Energy 298K= -299.958001

C	2.87871	0.62231	-0.00013
C	1.26820	-1.21436	0.00190
Au	-0.47369	-0.21543	-0.00086
P	-2.60799	0.83711	0.00182

```
C    2.59247 -0.74128  0.00248
H    2.01662  1.30787 -0.00246
H   -2.91690  1.68255  1.10848
H   -2.91152  1.70432 -1.08940
H   -3.74795 -0.01983 -0.00946
H    1.18844 -2.31525  0.00400
H    3.43014 -1.45244  0.00490
C    4.22497  1.21526 -0.00004
H    4.32826  1.89522  0.87126
H    5.03833  0.47637  0.00236
H    4.33001  1.89148 -0.87403
```

13$_{Me/H}$

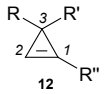
```
BP86 Energy =  -299.997008140
Enthalpy 0K=  -299.886986
Enthalpy 298K=  -299.877225
Free Energy 298K=  -299.924948

C   -2.72007  0.15696  0.00100
C   -1.79867 -0.84484  0.68332
Au   0.25915 -0.15950 -0.00065
P    2.52499  0.45982  0.00094
C   -1.79893 -0.84601 -0.68018
C   -2.53420  1.66113 -0.00039
H    2.92886  1.32468 -1.05687
H    2.96349  1.17504  1.15259
H    3.48309 -0.59109 -0.08470
H   -1.68613 -1.47733  1.56791
H   -1.68807 -1.48058 -1.56351
H   -3.77508 -0.16266  0.00154
H   -3.00067  2.10972 -0.89314
H   -3.00049  2.11142  0.89160
H   -1.46123  1.93083 -0.00079
```

TS(13-14)$_{Me/H}$

```
BP86 Energy =  -299.984301820
Enthalpy 0K=  -299.875383
Enthalpy 298K=  -299.866035
Free Energy 298K=  -299.912954
Nimag=1 (-169.6826cm-1)

C    2.81231  0.32021 -0.17814
C    1.67567 -0.87608 -0.26883
Au  -0.30915 -0.16524 -0.05832
P   -2.55237  0.39712  0.15724
C    2.65438 -0.83278  0.68371
C    2.34487  1.74853  0.04569
H   -2.89185  1.77114 -0.01413
H   -3.44905 -0.23731 -0.75106
H   -3.15805  0.10506  1.41399
H    1.55271 -1.78249 -0.89001
H    3.27802 -1.51561  1.27159
H    3.73721  0.26593 -0.78080
H    3.16453  2.33024  0.50242
H    2.08263  2.22142 -0.91344
H    1.46855  1.77926  0.71563
```

14$_{Me/H}$

```
BP86 Energy =  -300.023342747
Enthalpy 0K=  -299.912902
Enthalpy 298K=  -299.902915
Free Energy 298K=  -299.951373

C    3.21796  0.58612  0.00254
C    1.43087 -1.17047  0.00181
Au  -0.34966 -0.24519 -0.00143
P   -2.54844  0.66677  0.00329
C    2.77041 -0.73959  0.00409
C    2.44868  1.84009 -0.00186
H   -2.90385  1.53157 -1.07412
H   -3.62620 -0.26634 -0.03139
H   -2.91987  1.46832  1.12333
H    1.35024 -2.27150  0.00321
H    3.55624 -1.50669  0.00724
H    4.31116  0.71333  0.00482
H    2.75690  2.45102  0.87162
H    2.76048  2.44704 -0.87685
H    1.35684  1.70493 -0.00390
```

3. 

R=H; R′=Ph; R″=H

13$_{H/Ph}$

```
BP86 Energy =  -491.735820170
Enthalpy 0K=  -491.574016
Enthalpy 298K=  -491.561070
Free Energy 298K=  -491.617620

C   -2.83046  0.26922 -0.00023
C   -1.35126  0.44272 -0.00053
C   -0.52048 -0.64616 -0.68578
C   -0.52016 -0.64560  0.68542
H   -0.99573  1.47776 -0.00108
Au   1.54545 -0.09624 -0.00004
P    3.82328  0.45863  0.00020
H    4.26454  1.26578 -1.08815
H    4.27653  1.20986  1.12312
H    4.75328 -0.62034 -0.03191
H   -0.57176 -1.32953  1.53774
H   -0.57183 -1.33051 -1.53777
C   -3.65962  1.41348 -0.00017
C   -5.05196  1.27629  0.00012
C   -5.63582 -0.00463  0.00036
C   -4.82128 -1.14820  0.00031
C   -3.42567 -1.01646  0.00005
H   -3.20628  2.41083 -0.00038
H   -5.68623  2.16780  0.00017
H   -6.72501 -0.10862  0.00061
H   -5.27282 -2.14473  0.00052
H   -2.80419 -1.91882  0.00007
```

TS(13-14)$_{H/Ph}$

```
BP86 Energy =  -491.730342499
Enthalpy 0K=  -491.569351
Enthalpy 298K=  -491.556947
Free Energy 298K=  -491.612715
Nimag=1 (-104.7215cm-1)

C    2.85266  0.24727  0.11604
C    1.40002  0.32105  0.39847
C    0.88183 -0.80819  1.21165
C    0.40755 -0.84948 -0.07233
```

H	0.96402	1.32086	0.46749
Au	-1.58364	-0.10654	-0.03958
P	-3.80415	0.56954	-0.15348
H	-4.50779	0.19060	-1.33379
H	-4.68074	0.09397	0.86574
H	-4.05377	1.97269	-0.11285
H	0.49432	-1.67156	-0.79966
H	1.21125	-1.44935	2.03500
C	3.64010	1.42341	0.17682
C	5.01659	1.35891	-0.05101
C	5.63112	0.12084	-0.33260
C	4.86199	-1.05188	-0.39321
C	3.47953	-0.99427	-0.17099
H	3.16220	2.38401	0.39714
H	5.61817	2.27198	-0.01441
H	6.70960	0.07695	-0.51199
H	5.33747	-2.01053	-0.62002
H	2.88671	-1.91220	-0.24047

14$_{H/Ph}$

BP86 Energy = -491.786319188
Enthalpy 0K= -491.623125
Enthalpy 298K= -491.610131
Free Energy 298K= -491.667409

C	3.10908	0.03835	0.00002
C	1.71084	-0.24398	0.00001
C	1.07819	-1.50304	0.00007
C	-0.30944	-1.62776	0.00001
H	1.03288	0.62296	-0.00007
Au	-1.74686	-0.21471	-0.00009
P	-3.54318	1.33664	0.00024
H	-4.86552	0.80013	-0.01507
H	-3.64640	2.23693	1.10328
H	-3.62963	2.25807	-1.08667
H	-0.66919	-2.67000	0.00003
H	1.69463	-2.41131	0.00013
C	3.51834	1.41009	-0.00015
C	4.86992	1.74691	-0.00016
C	5.84048	0.72437	0.00002
C	5.46070	-0.63662	0.00020
C	4.11314	-0.98279	0.00019
H	2.75259	2.19305	-0.00028
H	5.17812	2.79602	-0.00029
H	6.90314	0.98729	0.00002
H	6.22749	-1.41628	0.00034
H	3.82437	-2.03736	0.00034

13$_{Ph/H}$

BP86 Energy = -491.734076805
Enthalpy 0K= -491.572544
Enthalpy 298K= -491.559640
Free Energy 298K= -491.615478

H	-1.85096	2.91879	0.13692
C	-1.24609	1.99793	0.10544
C	0.12760	2.10695	0.75954
C	0.09813	2.16828	-0.59723
C	-2.02256	0.71066	0.08713
Au	1.02455	0.15830	-0.00151
P	2.16040	-1.87490	-0.24788
H	2.40593	-2.58740	0.96179
H	1.51214	-2.86518	-1.04114
H	3.46075	-1.83150	-0.82893
H	0.58292	2.58593	-1.48213
H	0.65638	2.46855	1.64446
C	-2.85772	0.39902	-1.00527
C	-3.56888	-0.81061	-1.02580
C	-3.45977	-1.71555	0.04534
C	-2.64276	-1.40595	1.14409
C	-1.92907	-0.19383	1.16800
H	-2.95195	1.10389	-1.83871
H	-4.21378	-1.04591	-1.87804
H	-4.02432	-2.65280	0.02926
H	-2.58042	-2.09138	1.99524
H	-1.33518	0.07345	2.05100

TS(13-14)$_{Ph/H}$

BP86 Energy = -491.720590716
Enthalpy 0K= -491.560572
Enthalpy 298K= -491.547889
Free Energy 298K= -491.603741
Nimag=1 (-265.6089cm-1)

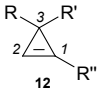
H	-2.06720	2.70812	-0.76192
C	-1.44792	2.01143	-0.17122
C	-0.56456	2.68234	0.77562
C	0.20381	2.14274	-0.20645
C	-2.04199	0.63998	-0.03978
Au	1.01735	0.16801	-0.06379
P	2.18967	-1.82609	-0.01177
H	1.44950	-3.01661	-0.27194
H	3.26508	-1.94935	-0.93903
H	2.83458	-2.15282	1.21685
H	0.95789	2.71776	-0.77046
H	-0.57997	3.52983	1.46968
C	-2.71678	0.07293	-1.13959
C	-3.27084	-1.21251	-1.03828
C	-3.16777	-1.93535	0.16239
C	-2.51862	-1.36385	1.27013
C	-1.95788	-0.07996	1.17492
H	-2.80587	0.63579	-2.07510
H	-3.79248	-1.64539	-1.89726
H	-3.61409	-2.93114	0.24243
H	-2.47625	-1.90289	2.22192
H	-1.49176	0.37842	2.05443

14$_{Ph/H}$

BP86 Energy = -491.774369718
Enthalpy 0K= -491.611336
Enthalpy 298K= -491.598494
Free Energy 298K= -491.654668

H	-2.66214	2.55887	-1.03295
C	-1.97351	1.95975	-0.41942
C	-0.79350	2.61599	-0.00048
C	0.42917	2.05012	0.35268
C	-2.41237	0.63861	-0.11416
Au	1.17758	0.20243	0.03605
P	2.29458	-1.83390	-0.43438
H	2.27825	-2.29121	-1.78640
H	3.69653	-1.86928	-0.17069
H	1.88202	-3.02501	0.23674
H	1.15635	2.78375	0.73848

H	-0.83979	3.71520	-0.05342
C	-3.43239	0.05690	-0.93481
C	-3.85466	-1.25066	-0.71202
C	-3.31445	-1.98710	0.36549
C	-2.34995	-1.41664	1.22021
C	-1.89719	-0.11571	0.99175
H	-3.85011	0.64148	-1.76120
H	-4.61735	-1.69973	-1.35435
H	-3.67937	-3.00034	0.56241
H	-1.98693	-1.97799	2.08605
H	-1.23190	0.37359	1.70739



4. **R=H; R′=CO_2Me; R″=H**

$13_{H/CO2ME}$

BP86 Energy = -488.557358070
Enthalpy 0K= -488.433049
Enthalpy 298K= -488.419997
Free Energy 298K= -488.477327

C	-1.75779	0.30154	-0.01944
C	-0.88656	-0.71288	0.71980
Au	1.15783	-0.09068	0.01234
P	3.40726	0.57415	-0.04496
C	-0.88796	-0.79431	-0.63497
C	-3.22786	-0.06102	-0.02562
H	-1.49230	1.36101	-0.07434
H	3.77001	1.41921	-1.13287
H	3.84915	1.32637	1.08125
H	4.38090	-0.46272	-0.12226
H	-0.86215	-1.30173	1.63920
H	-0.85944	-1.47942	-1.48451
O	-4.00065	1.03364	0.01016
O	-3.60212	-1.22854	-0.06449
C	-5.43942	0.77714	-0.00048
H	-5.90605	1.76898	0.02860
H	-5.71702	0.23497	-0.91659
H	-5.72079	0.18078	0.88016

TS(13-14)$_{H/CO2Me}$

BP86 Energy = -488.546108296
Enthalpy 0K= -488.422819
Enthalpy 298K= -488.410367
Free Energy 298K= -488.465825
Nimag=1 (-93.3135cm-1)

C	1.81049	-0.21337	0.59782
C	0.69188	-1.06705	-0.28913
Au	-1.17103	-0.10130	-0.07079
P	-3.29740	0.81000	0.09390
C	1.45667	-1.63235	0.68107
C	3.21188	-0.04898	0.07851
H	1.35846	0.56118	1.21990
H	-3.38055	2.22590	0.23580
H	-4.16258	0.57436	-1.01376
H	-4.09110	0.35836	1.18787
H	0.70549	-1.47327	-1.31621
H	1.97252	-2.56601	0.91827
O	3.70277	1.17922	0.26688
O	3.78279	-1.00904	-0.44007
C	5.07716	1.37881	-0.19549
H	5.28231	2.44229	-0.02613
H	5.76007	0.74524	0.38960
H	5.15482	1.12103	-1.26212

$14_{H/CO2Me}$

BP86 Energy = -488.575228493
Enthalpy 0K= -488.450652
Enthalpy 298K= -488.437473
Free Energy 298K= -488.495962

C	2.11336	-0.18887	0.01376
C	0.11608	-1.59133	-0.07846
Au	-1.33355	-0.21433	-0.01335
P	-3.15106	1.32832	0.05832
C	1.52410	-1.43864	-0.02626
C	3.60290	-0.05191	0.05252
H	1.49829	0.72061	0.02825
H	-3.19422	2.32628	-0.95974
H	-4.46412	0.78081	-0.03716
H	-3.27193	2.13134	1.23080
H	-0.21139	-2.64192	-0.16790
H	2.18982	-2.31255	-0.03500
O	3.94780	1.24447	-0.07834
O	4.35972	-1.00563	0.19483
C	5.38453	1.50155	-0.06573
H	5.48699	2.57662	-0.25285
H	5.79965	1.22468	0.91596
H	5.87719	0.90537	-0.84949

$13_{CO2Me/H}$

BP86 Energy = -488.571303971
Enthalpy 0K= -488.446783
Enthalpy 298K= -488.433901
Free Energy 298K= -488.490847

C	1.96399	1.36574	-0.00034
C	0.67902	1.83069	0.67055
Au	-0.80316	0.13546	0.00040
P	-2.78416	-1.07640	-0.00147
C	0.67975	1.83074	-0.67221
H	2.82088	2.05105	-0.00024
C	2.31499	-0.10034	-0.00003
H	-2.92546	-2.03826	-1.04396
H	-3.01644	-1.87706	1.15471
H	-4.00968	-0.35622	-0.10465
H	0.30253	2.28456	1.58831
H	0.30363	2.28349	-1.59065
O	3.62967	-0.29145	-0.00032
O	1.46585	-1.00380	0.00040
C	4.08735	-1.68243	-0.00014
H	5.18161	-1.61779	-0.00080
H	3.72068	-2.19450	0.90141
H	3.71962	-2.19511	-0.90092

TS(13-14)$_{CO2Me/H}$

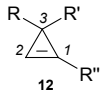
BP86 Energy = -488.547400946
Enthalpy 0K= -488.424123
Enthalpy 298K= -488.411609
Free Energy 298K= -488.467097
Nimag=1 (-347.0884cm-1)

C	-2.26273	1.29232	-0.13876
C	-0.39030	1.83591	-0.12502
Au	0.88144	0.21023	-0.05891
P	2.67634	-1.27117	0.07456
C	-1.50889	2.26104	0.55038
H	-3.12374	1.66352	-0.71519
C	-2.31894	-0.21440	0.06532
H	2.38762	-2.64183	0.34348
H	3.51342	-1.38533	-1.07385
H	3.63812	-0.99022	1.08851
H	0.10150	2.64700	-0.69874
H	-1.82409	3.25630	0.88523
O	-3.56166	-0.57926	-0.28424
O	-1.46293	-0.96064	0.52248
C	-3.90199	-1.98300	-0.05116
H	-4.91387	-2.09701	-0.45708
H	-3.18273	-2.62970	-0.57519
H	-3.88156	-2.19529	1.02795

14$_{CO2Me/H}$

BP86 Energy = -488.572258687
Enthalpy 0K= -488.447725
Enthalpy 298K= -488.434863
Free Energy 298K= -488.490965

C	2.52794	-1.31835	0.40621
C	0.16394	-1.88761	-0.25398
Au	-0.96308	-0.25567	-0.04335
P	-2.49512	1.53832	0.23570
C	1.45960	-2.17455	0.24821
H	3.45702	-1.68809	0.85275
C	2.53553	0.09770	-0.05062
H	-2.07553	2.84349	-0.15959
H	-3.73739	1.42973	-0.45529
H	-2.94508	1.79174	1.56491
H	-0.28465	-2.73797	-0.79974
H	1.65958	-3.23420	0.48022
O	3.70272	0.67262	0.28826
O	1.60562	0.67076	-0.63054
C	3.85658	2.07515	-0.07941
H	4.91223	2.30441	0.10764
H	3.59166	2.21567	-1.13850
H	3.20409	2.69745	0.55236

5. 

R=Ph; R′=CO_2Me; R″=H

13$_{Ph/CO2ME}$

BP86 Energy = -719.612319345
Enthalpy 0K= -719.410080
Enthalpy 298K= -719.392099
Free Energy 298K= -719.462049

C	-1.48764	-0.55927	0.00573
C	-0.52386	-1.53424	0.69313
Au	1.41159	-0.58015	0.01474
P	3.56592	0.32564	-0.08072
C	-0.53628	-1.56256	-0.66083
C	-2.91429	-1.10230	-0.03698
C	-1.22945	0.92473	-0.00183
H	3.67722	1.64919	-0.59616
H	4.23525	0.44231	1.17194
H	4.52728	-0.38079	-0.85970
H	-0.42386	-2.16048	1.58206
H	-0.43437	-2.19591	-1.54347
C	-1.31333	1.65359	-1.20680
C	-1.06680	3.03566	-1.21300
C	-0.74159	3.70095	-0.01804
C	-0.66426	2.98199	1.18659
C	-0.90963	1.59837	1.19690
H	-1.57911	1.13970	-2.13720
H	-1.13681	3.59507	-2.15107
H	-0.55868	4.77988	-0.02465
H	-0.42832	3.49908	2.12200
H	-0.87459	1.04103	2.14001
O	-3.83152	-0.14899	0.17775
O	-3.13506	-2.29027	-0.25231
C	-5.21747	-0.60849	0.14304
H	-5.82047	0.29321	0.30395
H	-5.43836	-1.06547	-0.83302
H	-5.38900	-1.34660	0.94085

TS(13-14)$_{Ph/CO2Me}$

BP86 Energy = -719.599671109
Enthalpy 0K= -719.398423
Enthalpy 298K= -719.380995
Free Energy 298K= -719.448028
Nimag=1 (-187.0008cm-1)

C	1.63245	-0.44202	0.49245
C	0.37423	-1.61018	0.50726
Au	-1.40898	-0.62868	-0.03830
P	-3.49681	0.22216	-0.56237
C	1.18881	-1.34439	1.56494
C	2.98170	-0.95080	0.02675
C	1.22200	0.99018	0.35069
H	-3.58655	1.62341	-0.81111
H	-4.13270	-0.31184	-1.72122
H	-4.51271	0.04581	0.42202
H	0.30935	-2.64730	0.12950
H	1.67433	-1.87369	2.38938
C	0.96445	1.75148	1.51263
C	0.61001	3.10551	1.40408
C	0.52150	3.70891	0.13979
C	0.79161	2.95713	-1.01961
C	1.14234	1.60420	-0.91909
H	1.06021	1.28541	2.49953
H	0.41885	3.69008	2.30922
H	0.25737	4.76756	0.05569
H	0.74005	3.43151	-2.00455
H	1.36809	1.02515	-1.81956
O	3.63693	-0.13876	-0.80520
O	3.37776	-2.04120	0.44637
C	4.94934	-0.61948	-1.23939
H	5.30152	0.12923	-1.95866
H	5.62468	-0.68510	-0.37372
H	4.85062	-1.61014	-1.70767

14$_{Ph/CO2Me}$

BP86 Energy = -719.646971715
Enthalpy 0K= -719.442941
Enthalpy 298K= -719.425365

Free Energy 298K= -719.492685

C	1.95614	-0.59337	0.27863
C	-0.22525	-1.72761	0.84499
Au	-1.66392	-0.56067	0.04760
P	-3.49669	0.55473	-0.95887
C	1.16228	-1.67783	0.72838
C	3.33031	-1.01407	-0.22092
C	1.53082	0.78108	0.30085
H	-3.40589	0.85786	-2.35076
H	-4.74951	-0.12758	-0.92883
H	-3.89295	1.82944	-0.45113
H	-0.59057	-2.62999	1.36322
H	1.72044	-2.60825	0.91073
C	0.58792	1.23062	1.28729
C	0.16438	2.56405	1.30883
C	0.64115	3.46646	0.34268
C	1.56082	3.04152	-0.64205
C	2.02456	1.72887	-0.65149
H	0.31527	0.55585	2.10261
H	-0.50921	2.90766	2.09934
H	0.32205	4.51326	0.37034
H	1.92334	3.75055	-1.39196
H	2.73856	1.40632	-1.41161
O	4.24507	-0.02885	-0.11766
O	3.54627	-2.14612	-0.63419
C	5.59282	-0.40444	-0.53889
H	6.21378	0.47378	-0.32579
H	5.93052	-1.28154	0.03359
H	5.59783	-0.64720	-1.61227

13$_{CO2Me/Ph}$

BP86 Energy = -719.620228465
Enthalpy 0K= -719.417906
Enthalpy 298K= -719.399999
Free Energy 298K= -719.469315

C	3.41105	-0.77402	-1.18437
C	2.75130	-0.40844	0.00510
C	3.46900	-0.36954	1.21745
C	4.83406	-0.69179	1.23713
C	5.48888	-1.05537	0.04888
C	4.77706	-1.09463	-1.16101
C	1.27843	-0.07697	-0.00844
C	0.85828	1.38613	-0.04939
O	-0.32635	1.75765	-0.04740
C	0.32282	-1.09197	-0.64497
C	0.33723	-1.05532	0.69851
Au	-1.76947	-0.29736	0.00710
P	-4.08760	-0.18130	0.03355
O	1.89553	2.21441	-0.09070
C	1.58368	3.64228	-0.13656
H	-4.67110	0.78473	0.90520
H	-4.69654	0.16383	-1.20849
H	-4.81374	-1.35609	0.38655
H	0.20786	-1.71660	-1.53213
H	0.23053	-1.61872	1.62668
H	2.55942	4.14102	-0.16967
H	0.99248	3.86703	-1.03643
H	1.02107	3.93112	0.76343
H	2.96208	-0.08258	2.14565
H	5.38615	-0.65893	2.18134
H	6.55314	-1.30903	0.06594
H	5.28490	-1.37424	-2.08908
H	2.86160	-0.79948	-2.13226

TS(13-14)$_{CO2Me/Ph}$

BP86 Energy = -719.608789736
Enthalpy 0K= -719.407201
Enthalpy 298K= -719.389892
Free Energy 298K= -719.456767
Nimag=1 (-274.1924cm-1)

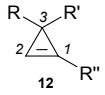
C	3.21926	0.26962	-1.02008
C	2.62001	-0.33431	0.11613
C	3.21693	-1.50305	0.66047
C	4.39149	-2.02566	0.11092
C	4.98101	-1.40779	-1.00541
C	4.38692	-0.26551	-1.57166
C	1.37798	0.19511	0.71273
C	0.82793	1.55754	0.25009
O	-0.30171	1.81373	-0.15530
C	-0.01413	-0.84924	1.24389
C	0.94289	-0.26396	2.01399
Au	-1.68599	-0.36779	0.06493
P	-3.76249	-0.29121	-0.96433
O	1.79188	2.46927	0.43105
C	1.42647	3.85171	0.11278
H	-4.08407	0.86208	-1.74077
H	-4.07500	-1.33099	-1.88913
H	-4.89561	-0.35372	-0.10075
H	-0.15211	-1.94126	1.38749
H	1.49603	-0.56250	2.91081
H	2.33563	4.43199	0.30989
H	1.12597	3.92734	-0.94261
H	0.59982	4.17567	0.76174
H	2.74803	-2.02172	1.50266
H	4.84043	-2.92426	0.54389
H	5.89362	-1.82367	-1.44289
H	4.83690	0.20903	-2.44857
H	2.77920	1.16513	-1.46558

14$_{CO2Me/Ph}$

BP86 Energy = -719.652299442
Enthalpy 0K= -719.448403
Enthalpy 298K= -719.430478
Free Energy 298K= -719.499298

C	-3.81664	0.99931	0.14391
C	-3.15457	-0.26267	0.01214
C	-3.94515	-1.45447	0.07989
C	-5.32317	-1.37918	0.26223
C	-5.95373	-0.12221	0.37600
C	-5.19721	1.06504	0.31706
C	-1.72378	-0.31023	-0.17091
C	-0.95205	0.97123	0.07843
O	-0.52418	1.24709	1.19143
C	0.36457	-1.63207	-0.60747
C	-1.01723	-1.48727	-0.52958
Au	1.91879	-0.47165	-0.06364
P	3.87073	0.67155	0.64355
O	-0.86845	1.72554	-1.02969
C	-0.18003	3.00669	-0.87730
H	4.35496	1.75688	-0.14841
H	3.84314	1.29154	1.92889

```
H    5.06396 -0.10280  0.75816
H    0.66400 -2.63252 -0.96091
H   -1.63238 -2.35858 -0.78516
H   -0.39776  3.55864 -1.79941
H   -0.55461  3.53933  0.00911
H    0.90157  2.83057 -0.77792
H   -3.47008 -2.43663  0.02031
H   -5.91591 -2.29614  0.32303
H   -7.03812 -0.06974  0.51528
H   -5.69203  2.03602  0.40635
H   -3.23735  1.92431  0.08464
```

6. 

R=R′=H; R″=Me

13_{Me}

```
BP86 Energy =  -300.008055166
Enthalpy 0K=  -299.897705
Enthalpy 298K=  -299.887819
Free Energy 298K=  -299.935560

C    2.43737 -1.03999  0.74669
C    2.15244  0.28100  0.07846
Au  -0.26709 -0.10813 -0.08578
P   -2.54845  0.30675  0.22739
C    1.72269 -0.83003 -0.59876
H    1.89286 -1.38401  1.63102
H   -3.42010 -0.65711 -0.35720
H   -3.01131  0.34090  1.57480
H   -3.06618  1.52663 -0.29725
C    2.59422  1.68793  0.03878
H    1.74398 -1.24354 -1.61116
H    3.49022 -1.35735  0.70962
H    2.21401  2.23229 -0.83850
H    2.34018  2.22224  0.96962
H    3.70247  1.66750 -0.00622
```

$TS(13\text{-}14)_{Me}^{\alpha}$

```
BP86 Energy =  -299.984241270
Enthalpy 0K=  -299.875431
Enthalpy 298K=  -299.865607
Free Energy 298K=  -299.913546
Nimag=1 (-304.7588cm-1)

C   -2.39406 -1.32416 -0.52019
C   -1.85587  0.20215  0.03360
Au   0.26898 -0.00127 -0.00550
P    2.58936 -0.02691  0.02885
C   -2.50143 -0.73221  0.79278
H   -1.56297 -1.93881 -0.86208
H    3.23556 -0.93491 -0.86030
H    3.23159  1.20325 -0.29647
H    3.20191 -0.35399  1.27376
C   -2.30210  1.64498 -0.16769
H   -3.25310 -0.74914  1.59099
H   -3.34206 -1.49587 -1.05573
H   -2.15938  2.21140  0.76946
H   -1.74377  2.14480 -0.97079
H   -3.37664  1.67232 -0.41828
```

14_{Me}^{α}

```
BP86 Energy =  -300.026928919
Enthalpy 0K=  -299.917154
Enthalpy 298K=  -299.906838
Free Energy 298K=  -299.956338

C    2.38305  1.98231  0.00792
C    1.74320 -0.39175 -0.00529
Au  -0.26087 -0.07168 -0.00388
P   -2.62368  0.21165  0.00703
C    2.72489  0.65607 -0.00163
H    1.33085  2.29105  0.01198
H   -3.15346  1.39187 -0.59391
H   -3.39924 -0.79410 -0.64201
H   -3.25338  0.25476  1.28618
C    2.23905 -1.78912  0.00494
H    3.78853  0.37819 -0.00750
H    3.14437  2.77011  0.01101
H    1.90878 -2.26199  0.95606
H    1.72409 -2.39180 -0.76836
H    3.33233 -1.89557 -0.08828
```

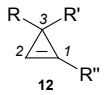
$TS(13\text{-}14)_{Me}^{\beta}$

```
BP86 Energy =  -300.003567433
Enthalpy 0K=  -299.894748
Enthalpy 298K=  -299.885102
Free Energy 298K=  -299.932623
Nimag=1 (-157.7745cm-1)

C   -2.36703  1.33515  0.10755
C   -2.77315 -0.02215  0.25719
Au   0.42707 -0.02866 -0.09679
P    2.71813 -0.04741  0.31061
C   -1.60993 -0.16445 -0.47437
H   -1.59052  1.80543  0.70854
H    3.53012 -0.70200 -0.66148
H    3.37130  1.21564  0.41829
H    3.14538 -0.68669  1.51105
C   -4.07270 -0.70704  0.37006
H   -1.75739 -0.70385 -1.42948
H   -3.02643  2.01691 -0.45076
H   -4.09373 -1.67019 -0.16079
H   -4.25559 -0.89984  1.44670
H   -4.89703 -0.04889  0.04285
```

14_{Me}^{β}

```
BP86 Energy =  -300.015158128
Enthalpy 0K=  -299.905044
Enthalpy 298K=  -299.894783
Free Energy 298K=  -299.943740

C   -2.50283  1.57705 -0.00040
C   -2.69525  0.20581  0.00040
Au   0.41845 -0.13923 -0.00033
P    2.76222  0.29732  0.00065
C   -1.52560 -0.61624 -0.00027
H   -1.49002  1.99495 -0.00070
H    3.62730 -0.82974 -0.11934
H    3.26612  1.14339 -1.03096
H    3.29694  0.93339  1.15977
```

```
C  -4.07641 -0.41834  0.00120
H  -1.75089 -1.69911 -0.00111
H  -3.34460  2.27978 -0.00101
H  -4.21222 -1.05903 -0.88647
H  -4.21218 -1.05656  0.89066
H  -4.87059  0.34266  0.00018
```

7. 

R=R′=H; R″=C_2H_3

13_{Vi}

```
BP86 Energy =  -338.091987156
Enthalpy 0K=  -337.976551
Enthalpy 298K=  -337.965869
Free Energy 298K=  -338.016924

C   2.07986 -1.74149  0.44656
C   2.41435 -0.32385  0.21571
Au -0.52996 -0.11099 -0.11034
P  -2.71552  0.57151  0.33300
C   1.39974 -0.81122 -0.61156
H   1.49701 -2.06086  1.31540
H  -3.44225 -0.18629  1.29821
H  -2.90495  1.89784  0.82260
H  -3.61815  0.55268 -0.77088
C   3.38825  0.67920  0.48491
H   1.46334 -0.87432 -1.70755
H   2.85101 -2.46212  0.13467
C   3.36745  1.88031 -0.16234
H   4.14703  0.46396  1.24549
H   4.11134  2.65434  0.05092
H   2.59770  2.11293 -0.90642
```

TS(13-14)$_{Vi}^{\alpha}$

```
BP86 Energy =  -338.063041105
Enthalpy 0K=  -337.949155
Enthalpy 298K=  -337.938627
Free Energy 298K=  -337.988690
Nimag=1 (-296.4102cm-1)

C  -1.97222 -1.89543 -0.37894
C  -1.72278 -0.22622 -0.05178
Au  0.40974 -0.05607 -0.02138
P   2.69460  0.29852  0.10072
C  -2.31231 -1.12589  0.79438
H  -1.02188 -2.40461 -0.53001
H   3.51840 -0.53914 -0.70674
H   3.15183  1.59717 -0.26871
H   3.28885  0.13638  1.38616
C  -2.23276  1.08510 -0.53341
H  -3.16310 -1.13603  1.48387
H  -2.81135 -2.29441 -0.97183
C  -2.97270  1.93222  0.21494
H  -1.91880  1.37055 -1.54384
H  -3.28511  2.90071 -0.18560
H  -3.27040  1.70216  1.24352
```

14_{Vi}^{α}

```
BP86 Energy =  -338.113617894
Enthalpy 0K=  -337.997672
Enthalpy 298K=  -337.986852
Free Energy 298K=  -338.037318

C   1.80591  2.42771  0.06294
C   1.60524 -0.01912 -0.09738
Au -0.43010 -0.04319 -0.01794
P  -2.80011 -0.15806  0.07300
C   2.37980  1.19439 -0.07696
H   0.71932  2.53485  0.16182
H  -3.53459  0.71898 -0.77947
H  -3.40477 -1.40969 -0.24721
H  -3.41281  0.11965  1.33118
C   2.28219 -1.29557 -0.18280
H   3.46904  1.13921 -0.20616
H   2.40997  3.34095  0.07771
C   3.56881 -1.51579  0.22971
H   1.68596 -2.16144 -0.49312
H   3.98815 -2.52704  0.23292
H   4.20727 -0.72224  0.63132
```

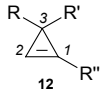
TS(13-14)$_{Vi}^{\beta}$

```
BP86 Energy =  -338.086923053
Enthalpy 0K=  -337.972396
Enthalpy 298K=  -337.962151
Free Energy 298K=  -338.011297
Nimag=1 (-235.6132cm-1)

C   2.02271  1.73000 -0.15415
C   2.53808  0.41756 -0.22994
Au -0.61559 -0.00841  0.09911
P  -2.90516 -0.24350 -0.32112
C   1.39830  0.04648  0.49562
H   1.10335  2.04436 -0.64516
H  -3.27392 -1.06490 -1.42689
H  -3.69349 -0.81493  0.72091
H  -3.64470  0.94278 -0.60474
C   3.89335 -0.07182 -0.28788
H   1.65027 -0.42575  1.46269
H   2.62160  2.51359  0.33273
C   4.17638 -1.39399 -0.16965
H   4.68143  0.65595 -0.51223
H   5.20105 -1.76471 -0.26278
H   3.39061 -2.13864 -0.00170
```

14_{Vi}^{β}

```
BP86 Energy =  -338.092587829
Enthalpy 0K=  -337.977532
Enthalpy 298K=  -337.966546
Free Energy 298K=  -338.018450

C  -2.10970  1.88602  0.04804
C  -2.45192  0.53799  0.00452
Au  0.61122 -0.10872 -0.04019
P   2.98001  0.07207  0.13623
C  -1.36657 -0.37501 -0.18835
H  -1.05936  2.19308  0.06982
H   3.51434  0.20045  1.45227
H   3.74899 -1.01722 -0.36890
H   3.60161  1.17586 -0.51895
C  -3.87049  0.11662  0.01947
H  -1.68990 -1.38921 -0.48361
```

H -2.87229 2.67385 0.02181
C -4.30481 -1.14667 0.19719
H -4.60313 0.92560 -0.08784
H -5.37449 -1.37109 0.21197
H -3.63154 -1.99752 0.34988

8.  **R=R′=H; R″=Ph**

13$_{Ph}$

BP86 Energy = -491.761664478
Enthalpy 0K= -491.599326
Enthalpy 298K= -491.586372
Free Energy 298K= -491.643638

C -0.78665 2.29939 0.09651
C -1.42037 0.99544 -0.17655
Au 1.43637 0.08372 -0.10937
P 3.32360 -1.07884 0.61901
C -0.19471 1.19262 -0.83562
H -0.28766 2.50241 1.04898
H 4.11874 -0.45826 1.62827
H 3.13271 -2.37283 1.18980
H 4.31756 -1.36589 -0.36339
C -2.61432 0.25597 -0.04281
H -0.11355 1.26295 -1.93043
H -1.28754 3.17413 -0.34398
C -2.79876 -0.96768 -0.75940
C -3.99516 -1.66789 -0.63191
C -5.01616 -1.16375 0.20454
C -4.84818 0.03999 0.92036
C -3.65311 0.74810 0.80622
H -1.99372 -1.33753 -1.40198
H -4.14866 -2.60350 -1.17692
H -5.95448 -1.71965 0.30041
H -5.65142 0.41134 1.56275
H -3.49495 1.68264 1.35313

TS(13-14)$_{Ph}^{\alpha}$

BP86 Energy = -491.726770441
Enthalpy 0K= -491.566230
Enthalpy 298K= -491.553375
Free Energy 298K= -491.609303
Nimag=1 (-338.6643cm-1)

C -0.27172 2.62925 0.95522
C -0.74584 1.19986 0.07426
Au 1.04436 0.04275 -0.00767
P 2.93196 -1.27512 -0.27617
C -0.62336 2.47155 -0.43117
H 0.72087 2.47095 1.37148
H 3.86326 -1.30392 0.80334
H 2.71081 -2.66693 -0.49365
H 3.78372 -0.95090 -1.37278
C -1.91356 0.29051 0.03253
H -1.18596 3.10602 -1.12463
H -0.94553 3.24289 1.57560
C -2.94575 0.45952 -0.92347
C -4.02876 -0.42441 -0.94740
C -4.10810 -1.47465 -0.01115
C -3.09650 -1.64526 0.94789
C -1.99615 -0.77792 0.96323
H -2.89553 1.27794 -1.64883
H -4.82240 -0.29123 -1.68860
H -4.96446 -2.15557 -0.02888
H -3.16229 -2.45510 1.68038
H -1.20800 -0.89546 1.71530

14$_{Ph}^{\alpha}$

BP86 Energy = -491.780913259
Enthalpy 0K= -491.618621
Enthalpy 298K= -491.605211
Free Energy 298K= -491.664648

C 0.33572 3.15300 -0.01833
C -0.76836 0.94475 -0.00992
Au 1.04576 -0.02354 -0.00224
P 3.13907 -1.13307 0.02307
C -0.79583 2.38933 -0.01998
H 1.33080 2.69253 -0.00883
H 3.84234 -1.16996 1.26450
H 3.16386 -2.51676 -0.32599
H 4.16311 -0.63476 -0.83731
C -2.00274 0.19812 -0.00250
H -1.75578 2.91924 -0.03447
H 0.28478 4.24662 -0.02617
C -3.29919 0.81589 0.04052
C -4.45760 0.04453 0.04572
C -4.37135 -1.36362 0.00420
C -3.11618 -2.00305 -0.03865
C -1.95468 -1.23529 -0.03868
H -3.39637 1.90312 0.07689
H -5.43699 0.52995 0.08208
H -5.28749 -1.96296 0.00675
H -3.05628 -3.09450 -0.07013
H -0.97160 -1.71897 -0.07109

TS(13-14)$_{Ph}^{\beta}$

BP86 Energy = -491.750332403
Enthalpy 0K= -491.589062
Enthalpy 298K= -491.576527
Free Energy 298K= -491.631730
Nimag=1 (-41.0400cm-1)

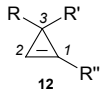
C -1.05755 1.87057 -0.44667
C -1.49137 0.57445 -0.15245
Au 1.58295 -0.09671 -0.05946
P 3.90431 -0.04015 0.40072
C -0.39012 -0.28032 -0.42022
H -0.01283 2.16062 -0.30569
H 4.69822 0.85378 -0.37744
H 4.30135 0.32667 1.72053
H 4.62334 -1.25961 0.22856
C -2.90256 0.17453 -0.02791
H -0.67580 -1.20263 -0.95959
H -1.72802 2.59735 -0.92201
C -3.30436 -1.17801 -0.14542
C -4.65173 -1.52803 -0.00825
C -5.61461 -0.53839 0.25861
C -5.22455 0.80442 0.40155
C -3.87786 1.15860 0.26451
H -2.56930 -1.96385 -0.34836
H -4.95337 -2.57491 -0.10565

```
H  -6.66690 -0.81659  0.37051
H  -5.96869  1.57256  0.63076
H  -3.57751  2.20181  0.41201
```

14_{Ph}^{β}

```
BP86 Energy =  -491.751719136
Enthalpy 0K=  -491.590132
Enthalpy 298K=  -491.576870
Free Energy 298K=  -491.633954

C   1.08486  1.79500  0.79728
C   1.46392  0.55093  0.29679
Au -1.57336 -0.12081 -0.03015
P  -3.94599  0.05172 -0.14140
C   0.41294 -0.37274  0.02353
H   0.02869  2.08280  0.82279
H  -4.67113 -1.15565 -0.36511
H  -4.61691  0.56310  1.00874
H  -4.48712  0.88779 -1.16255
C   2.89308  0.18127  0.10651
H   0.77114 -1.39588 -0.19002
H   1.82097  2.49954  1.20032
C   3.36192 -1.11911  0.40507
C   4.71484 -1.43696  0.23076
C   5.60910 -0.46916 -0.25725
C   5.14992  0.82282 -0.56604
C   3.79973  1.14872 -0.38398
H   2.68125 -1.87480  0.81303
H   5.07262 -2.44032  0.47950
H   6.66290 -0.72400 -0.40466
H   5.84158  1.57350 -0.95940
H   3.43975  2.14754 -0.65596
```

(ii) Large Models@{Au(PPh$_3$)$^+$}

1. 

R=CO$_2$Me; R′=Ph; R″=H

(a) Butenolide Pathway

15$_{CO2Me/Ph}$ (O-bound form)

BP86 Energy = -1412.80374610
Enthalpy 0K= -1412.360102
Enthalpy 298K= -1412.327628
Free Energy 298K= -1412.431517
PCM(toluene) = -1412.83406442
PCM(CH_2Cl_2) = -1412.85291004

C	6.42959	0.72343	1.66598
C	5.20336	0.22372	1.20597
C	4.76550	0.49834	-0.10674
C	5.57433	1.29167	-0.94264
C	6.80367	1.78887	-0.48489
C	7.23444	1.50519	0.82062
C	3.41848	0.00909	-0.58821
C	2.79125	0.57701	-1.86385
C	2.25331	0.99087	-0.74767
C	3.06870	-1.42972	-0.30812
O	4.11883	-2.23171	-0.22113
C	3.86794	-3.65489	-0.00204
O	1.90437	-1.91010	-0.21325
Au	0.05055	-0.82624	-0.12467
P	-2.00539	0.15109	0.06893
C	-3.09465	-0.25315	-1.36143
C	-2.88050	-0.37483	1.60258
C	-1.84646	1.98984	0.14512
H	1.65275	1.71531	-0.20123
H	2.90352	0.60159	-2.94514
H	4.86536	-4.10699	0.05108
H	3.31676	-3.79868	0.93890
H	3.29016	-4.06740	-0.84213
H	5.23902	1.52722	-1.95923
H	7.42432	2.39832	-1.14911
H	8.19157	1.89527	1.18030
H	6.75621	0.50461	2.68749
H	4.58443	-0.38584	1.87444
C	-1.00339	2.55346	1.13026
C	-0.85698	3.94564	1.20980
C	-1.53969	4.77862	0.30506
C	-2.37411	4.21892	-0.67459
C	-2.53268	2.82503	-0.75823
H	-0.47542	1.90617	1.84042
H	-0.21033	4.38086	1.97815
H	-1.42036	5.86470	0.36646
H	-2.90776	4.86577	-1.37770
H	-3.18689	2.39263	-1.52122
C	-3.70578	0.52482	2.31001
C	-4.39884	0.08200	3.44803
C	-4.27098	-1.24798	3.88027
C	-3.44743	-2.14330	3.17636
C	-2.74916	-1.71063	2.04008
H	-3.80078	1.56447	1.98170
H	-5.03649	0.78068	3.99830
H	-4.80963	-1.58666	4.77065
H	-3.34256	-3.17817	3.51616
H	-2.10012	-2.40529	1.49493
C	-4.49366	-0.33622	-1.19869
C	-5.30530	-0.61723	-2.30876
C	-4.72905	-0.81605	-3.57420
C	-3.33561	-0.73530	-3.73612
C	-2.51582	-0.45770	-2.63256
H	-4.94553	-0.19301	-0.21220
H	-6.38991	-0.68656	-2.18123
H	-5.36638	-1.04120	-4.43486
H	-2.88524	-0.89773	-4.72014
H	-1.42779	-0.40618	-2.75347

15$_{CO2Me/Ph}$ (η^2-alkene form)

BP86 Energy = -1412.80006908
Enthalpy 0K= -1412.356833
Enthalpy 298K= -1412.324133
Free Energy 298K= -1412.430044
PCM(toluene) = -1412.83077190

C	-6.81224	-1.21545	1.15233
C	-5.45302	-0.86719	1.17660
C	-4.78949	-0.51969	-0.01611
C	-5.50052	-0.52633	-1.23280
C	-6.85900	-0.87551	-1.25476
C	-7.51623	-1.22145	-0.06269
C	-3.32201	-0.15823	-0.00248
C	-2.36729	-1.12181	-0.71294
Au	-0.27457	-0.44515	-0.03283
P	2.04229	-0.07719	-0.00944
C	-2.94570	1.31787	0.03961
O	-4.02331	2.10211	0.14898
C	-3.76262	3.53490	0.20707
C	-2.35800	-1.16426	0.63319
O	-1.78595	1.74026	-0.01554
C	2.51026	1.15073	-1.30263
C	2.56681	0.60628	1.62317
C	3.03564	-1.60138	-0.30102
H	-2.26276	-1.79725	1.51598
H	-2.28722	-1.69461	-1.63735
H	-4.75168	3.99925	0.30155
H	-3.13159	3.76898	1.07765
H	-3.25919	3.86490	-0.71413
H	-4.99173	-0.25229	-2.16401
H	-7.40423	-0.87731	-2.20371
H	-8.57538	-1.49612	-0.08067
H	-7.32137	-1.48142	2.08390
H	-4.90982	-0.85742	2.12838
C	3.74337	1.05260	-1.98039
C	4.08638	2.01968	-2.93827
C	3.20693	3.07769	-3.22088
C	1.97732	3.17269	-2.54725
C	1.62131	2.21044	-1.59045
H	4.42715	0.22503	-1.76783
H	5.04172	1.94216	-3.46633
H	3.47766	3.82644	-3.97176
H	1.28928	3.99368	-2.77139
H	0.65812	2.28124	-1.07233
C	4.28920	-1.78030	0.32129
C	5.04422	-2.93082	0.04214
C	4.55588	-3.89753	-0.85179
C	3.30660	-3.71984	-1.47068
C	2.54371	-2.57629	-1.19483
H	4.66988	-1.03281	1.02429

H	6.01459	-3.07138	0.52813
H	5.14677	-4.79425	-1.06237
H	2.92266	-4.47567	-2.16265
H	1.56480	-2.44002	-1.66851
C	3.31195	1.79885	1.71223
C	3.69704	2.28360	2.97324
C	3.34276	1.58508	4.13800
C	2.59945	0.39484	4.04877
C	2.20616	-0.09484	2.79577
H	3.58943	2.34486	0.80575
H	4.27625	3.20955	3.04170
H	3.64431	1.96787	5.11788
H	2.32265	-0.15071	4.95618
H	1.62750	-1.02316	2.72832

TS(15-16)$_{CO2Me/Ph}$

BP86 Energy = -1412.78300314
Enthalpy 0K= -1412.340934
Enthalpy 298K= -1412.308624
Free Energy 298K= -1412.412697
Nimag=1 (-279.0893cm-1)
PCM(toluene) = -1412.83077190
PCM(CH_2Cl_2) = -1412.83164821

C	-5.83403	-0.92547	1.81947
C	-4.83668	-0.18608	1.17687
C	-4.48414	-0.47056	-0.16792
C	-5.14287	-1.53759	-0.83339
C	-6.14779	-2.26578	-0.18932
C	-6.49795	-1.96067	1.13760
C	-3.43128	0.29421	-0.86057
C	-3.19554	0.12448	-2.27634
C	-2.04853	-0.46034	-1.84682
Au	-0.26566	-0.14944	-0.77338
P	1.90323	-0.11328	0.10746
C	-2.93004	1.61322	-0.24451
O	-4.00659	2.40608	-0.08961
C	-3.72814	3.75155	0.40724
O	-1.78107	1.95070	0.00683
C	1.91369	-0.56940	1.89842
C	3.02921	-1.30367	-0.74390
C	2.68850	1.55166	-0.02853
H	-1.82723	-1.46041	-2.27696
H	-3.87725	-0.05661	-3.11395
H	-4.71063	4.23403	0.47618
H	-3.24250	3.69785	1.39315
H	-3.07513	4.28398	-0.30013
H	-4.85438	-1.81089	-1.85327
H	-6.65120	-3.08095	-0.71738
H	-7.27747	-2.53796	1.64407
H	-6.09567	-0.69520	2.85645
H	-4.33600	0.62248	1.71592
C	2.67881	0.15216	2.83689
C	2.67571	-0.23975	4.18582
C	1.91517	-1.34481	4.59939
C	1.15012	-2.06355	3.66421
C	1.14279	-1.67639	2.31679
H	3.27053	1.01570	2.51805
H	3.26983	0.32251	4.91293
H	1.91492	-1.64535	5.65179
H	0.55430	-2.92370	3.98528
H	0.54158	-2.23321	1.58881
C	4.07575	1.68852	-0.24430
C	4.64569	2.96960	-0.31424
C	3.83920	4.11037	-0.17104
C	2.45684	3.97395	0.04045
C	1.87618	2.69870	0.10796
H	4.70624	0.80227	-0.36572
H	5.72155	3.07423	-0.48549
H	4.28754	5.10702	-0.23100
H	1.82665	4.86277	0.14438
H	0.79626	2.59338	0.25915
C	4.00272	-2.03198	-0.02948
C	4.86212	-2.90449	-0.71717
C	4.75552	-3.05028	-2.10952
C	3.78570	-2.32422	-2.82225
C	2.91986	-1.45540	-2.14307
H	4.08477	-1.92582	1.05668
H	5.61410	-3.47246	-0.16065
H	5.42522	-3.73416	-2.64015
H	3.69844	-2.44008	-3.90702
H	2.15620	-0.89625	-2.69592

16$_{CO2Me/Ph}$

BP86 Energy = -1412.82587275
Enthalpy 0K= -1412.381163
Enthalpy 298K= -1412.348460
Free Energy 298K= -1412.453179
PCM(toluene) = -1412.85648310
PCM(CH_2Cl_2) = -1412.87469641

C	-6.97549	1.27130	0.37200
C	-5.61914	1.03437	0.15470
C	-5.12341	-0.29758	0.00434
C	-6.05251	-1.37976	0.09873
C	-7.40520	-1.13500	0.32388
C	-7.87206	0.18878	0.45640
C	-3.71233	-0.52280	-0.23037
C	-3.16498	-1.77550	-0.58815
C	-1.80481	-2.05762	-0.74160
Au	-0.11186	-1.02602	-0.37290
P	1.97911	0.01866	0.09016
C	-2.79118	0.66398	-0.02075
O	-2.59466	1.35119	-1.15713
C	-1.77513	2.55794	-1.04478
O	-2.37400	0.94814	1.09539
C	2.25360	1.52595	-0.94886
C	2.12647	0.54967	1.85319
C	3.40987	-1.09958	-0.24824
H	-1.63603	-3.09796	-1.06974
H	-3.88276	-2.58474	-0.77200
H	-1.99554	3.13696	-1.94988
H	-2.04203	3.11584	-0.13528
H	-0.71182	2.27531	-1.01750
H	-5.70540	-2.41295	0.02323
H	-8.10408	-1.97241	0.40360
H	-8.93644	0.37517	0.63049
H	-7.34119	2.29655	0.47697
H	-4.93091	1.88075	0.08396
C	2.74857	2.72772	-0.40300
C	2.95825	3.83882	-1.23721
C	2.67816	3.75534	-2.61058
C	2.18185	2.55865	-3.15668
C	1.96394	1.44656	-2.33014
H	2.96955	2.79531	0.66676
H	3.34482	4.76968	-0.81050

H	2.84585	4.62268	-3.25678
H	1.96306	2.49066	-4.22703
H	1.57733	0.51404	-2.75736
C	3.36760	0.52314	2.52309
C	3.44662	0.94710	3.85896
C	2.29476	1.39394	4.52734
C	1.05807	1.41743	3.86129
C	0.96688	0.99291	2.52686
H	4.26451	0.16431	2.00846
H	4.40974	0.92273	4.37822
H	2.36006	1.71762	5.57088
H	0.15783	1.75632	4.38344
H	-0.00303	1.00136	2.01646
C	4.62985	-0.60790	-0.75694
C	5.70107	-1.49019	-0.97137
C	5.55985	-2.85702	-0.68138
C	4.34400	-3.34870	-0.17692
C	3.26783	-2.47510	0.03655
H	4.74072	0.45521	-0.99258
H	6.64619	-1.10718	-1.36870
H	6.39637	-3.54137	-0.85367
H	4.23035	-4.41455	0.04397
H	2.31674	-2.85944	0.42270

TS(16-17)$_{CO2Me/Ph}$

BP86 Energy = -1412.81563975
Enthalpy 0K= -1412.371797
Enthalpy 298K= -1412.340100
Free Energy 298K= -1412.442516
Nimag=1 (-147.8497cm-1)
PCM(toluene) = -1412.84566506

C	-7.35472	-0.24893	0.62555
C	-6.11287	-0.58517	0.07904
C	-5.11096	0.41001	-0.10180
C	-5.40470	1.74898	0.28558
C	-6.64214	2.07475	0.84030
C	-7.62336	1.07668	1.00876
C	-3.81508	0.10221	-0.69309
C	-3.07524	1.00043	-1.46450
C	-1.75323	0.82235	-1.92894
Au	-0.03845	0.42148	-0.93345
P	2.04442	0.07171	0.15613
C	-3.15763	-1.24275	-0.61336
O	-3.61716	-2.02846	0.37654
C	-2.97306	-3.33252	0.49262
O	-2.22628	-1.56011	-1.36832
C	1.85802	-0.79505	1.77889
C	3.19013	-0.95157	-0.86801
C	2.92399	1.65703	0.51151
H	-1.61087	1.17660	-2.96842
H	-3.60238	1.88639	-1.84876
H	-3.54856	-3.86421	1.26028
H	-3.00884	-3.86097	-0.47212
H	-1.92631	-3.20566	0.80639
H	-4.63671	2.52193	0.17768
H	-6.84770	3.10372	1.14975
H	-8.59619	1.33545	1.43817
H	-8.12016	-1.02074	0.74817
H	-5.91541	-1.61394	-0.22837
C	2.72666	-1.83394	2.16994
C	2.55740	-2.45079	3.42068
C	1.52927	-2.03436	4.28124
C	0.66141	-0.99904	3.89240
C	0.81916	-0.38267	2.64269
H	3.52859	-2.16191	1.50138
H	3.23290	-3.25787	3.72100
H	1.40213	-2.51731	5.25517
H	-0.14101	-0.67300	4.56172
H	0.14033	0.42268	2.33871
C	4.58550	-0.74833	-0.83373
C	5.42655	-1.56123	-1.61018
C	4.88239	-2.57208	-2.41942
C	3.49229	-2.77314	-2.45752
C	2.64423	-1.96389	-1.68715
H	5.01192	0.04589	-0.21282
H	6.50869	-1.39968	-1.58517
H	5.54189	-3.19957	-3.02698
H	3.06622	-3.55447	-3.09450
H	1.55892	-2.11351	-1.72595
C	3.64718	1.84776	1.70683
C	4.32651	3.05771	1.92347
C	4.28667	4.07407	0.95543
C	3.56417	3.88562	-0.23524
C	2.87914	2.68255	-0.45815
H	3.67556	1.06028	2.46636
H	4.88611	3.20461	2.85250
H	4.81522	5.01632	1.13033
H	3.52813	4.67854	-0.98872
H	2.31029	2.53807	-1.38374

17$_{CO2Me/Ph}$

BP86 Energy = -1412.86405548
Enthalpy 0K= -1412.416916
Enthalpy 298K= -1412.385344
Free Energy 298K= -1412.488867
PCM(toluene) = -1412.89447718

C	-7.17209	0.96709	0.64534
C	-6.14521	0.08859	0.27407
C	-4.91545	0.59296	-0.20839
C	-4.74020	1.99343	-0.30252
C	-5.77062	2.86582	0.06846
C	-6.99063	2.35556	0.54294
C	-3.82790	-0.30484	-0.63743
C	-2.80895	-0.06510	-1.56090
C	-1.88830	-1.17688	-1.61172
Au	-0.01689	-0.52417	-0.78929
P	2.03715	0.17150	0.11784
C	-3.56784	-1.63858	-0.19378
O	-4.25053	-2.31512	0.70366
C	-3.83016	-3.68446	1.00344
O	-2.49277	-2.19011	-0.75436
C	2.05940	0.01396	1.95773
C	3.46014	-0.81123	-0.52594
C	2.39449	1.94058	-0.27278
H	-1.63534	-1.64043	-2.57743
H	-2.69936	0.83220	-2.17251
H	-4.54514	-4.03451	1.75695
H	-3.88514	-4.30153	0.09401
H	-2.80606	-3.68256	1.40490
H	-3.78506	2.40097	-0.65135
H	-5.61848	3.94697	-0.00637
H	-7.79488	3.03791	0.83448
H	-8.12092	0.56316	1.01162
H	-6.30341	-0.99058	0.34627

C	3.19115	-0.47600	2.64090
C	3.17439	-0.56292	4.04267
C	2.03766	-0.16244	4.76268
C	0.90826	0.32542	4.08253
C	0.91374	0.40971	2.68297
H	4.07803	-0.79202	2.08319
H	4.05320	-0.94593	4.57058
H	2.02923	-0.23353	5.85477
H	0.02029	0.63579	4.64208
H	0.03064	0.78421	2.15251
C	4.72209	-0.21696	-0.73576
C	5.79063	-0.99986	-1.20115
C	5.60543	-2.36822	-1.45710
C	4.34792	-2.96074	-1.25075
C	3.27388	-2.18555	-0.78996
H	4.86786	0.85089	-0.54536
H	6.76820	-0.53671	-1.36701
H	6.44031	-2.97308	-1.82433
H	4.20064	-4.02538	-1.45698
H	2.28985	-2.64395	-0.63845
C	2.93554	2.81545	0.69123
C	3.21474	4.14724	0.34238
C	2.95788	4.60584	-0.95944
C	2.41805	3.73397	-1.92097
C	2.13109	2.40456	-1.58034
H	3.13369	2.46158	1.70765
H	3.63341	4.82578	1.09207
H	3.17539	5.64492	-1.22551
H	2.21544	4.09095	-2.93552
H	1.70656	1.72510	-2.32838

(b) Indene Pathway

15$_{Ph/CO2Me}$

BP86 Energy = -1412.79521225
Enthalpy 0K= -1412.352115
Enthalpy 298K= -1412.319332
Free Energy 298K= -1412.425575
PCM(toluene) = -1412.82730659
PCM(CH_2Cl_2) = -1412.84695023

C	3.33595	1.47783	-1.14868
C	3.13349	0.71722	0.02121
C	2.73652	1.36758	1.20791
C	2.53263	2.75740	1.22214
C	2.73125	3.50858	0.05183
C	3.13391	2.86633	-1.13261
C	3.35848	-0.77250	0.00653
C	4.78167	-1.32671	-0.01187
O	5.00744	-2.52853	-0.11118
C	2.39338	-1.75150	-0.67512
C	2.38855	-1.75158	0.67620
Au	0.40638	-0.86667	0.00541
P	-1.79755	-0.03976	-0.01769
O	5.70941	-0.35919	0.09426
C	7.08815	-0.83237	0.08692
C	-2.20780	0.76027	1.59260
C	-2.00105	1.22481	-1.34272
C	-3.04330	-1.36589	-0.30153
H	2.30534	-2.37084	-1.56831
H	2.29761	-2.38696	1.55831
H	2.60063	0.78382	2.12551
H	2.23176	3.25343	2.15029
H	2.58369	4.59305	0.06498
H	3.30067	3.44913	-2.04413
H	3.65963	0.98196	-2.07021
H	7.70192	0.07307	0.16859
H	7.26179	-1.50547	0.94011
H	7.29904	-1.37080	-0.84939
C	-2.82307	2.02729	1.64215
C	-3.14284	2.59414	2.88703
C	-2.85238	1.90377	4.07435
C	-2.23797	0.64000	4.02429
C	-1.91098	0.06721	2.78737
H	-3.04918	2.56863	0.71851
H	-3.62076	3.57784	2.92539
H	-3.10269	2.35065	5.04140
H	-2.01020	0.10140	4.94926
H	-1.43349	-0.91889	2.74999
C	-4.31766	-1.29392	0.29974
C	-5.26452	-2.29703	0.03925
C	-4.94542	-3.36568	-0.81450
C	-3.67572	-3.43771	-1.41273
C	-2.72197	-2.44226	-1.15634
H	-4.56644	-0.46646	0.97141
H	-6.25168	-2.24340	0.50831
H	-5.68558	-4.14756	-1.01033
H	-3.42485	-4.27320	-2.07329
H	-1.72904	-2.50134	-1.61674
C	-3.15356	1.24183	-2.15482
C	-3.28993	2.22890	-3.14408
C	-2.28550	3.19353	-3.32259
C	-1.13677	3.17470	-2.51266
C	-0.98582	2.19040	-1.52553
H	-3.93660	0.48963	-2.01988
H	-4.18319	2.24041	-3.77601
H	-2.39490	3.95899	-4.09704
H	-0.35087	3.92275	-2.65398
H	-0.08435	2.17751	-0.90192

TS(15-16)$_{Ph/CO2Me}$

BP86 Energy = -1412.77798604
Enthalpy 0K= -1412.336226
Enthalpy 298K= -1412.303785
Free Energy 298K= -1412.408168
Nimag=1 (-205.0944cm-1)
PCM(toluene) = -1412.80921942
PCM(CH_2Cl_2) = -1412.82827791

C	-3.07531	1.38955	0.89559
C	-3.18789	0.82869	-0.39647
C	-2.99902	1.65347	-1.52854
C	-2.68687	3.01194	-1.37287
C	-2.57399	3.56274	-0.08666
C	-2.77270	2.74922	1.04471
C	-3.56541	-0.60145	-0.59732
C	-4.79523	-1.21623	0.05175
O	-5.16522	-2.34294	-0.27404
C	-2.23411	-1.70748	-0.90251
C	-3.21914	-1.38930	-1.77906
Au	-0.41867	-0.80743	-0.30239
P	1.76006	-0.05689	0.09632
O	-5.40377	-0.42047	0.94456
C	-6.60582	-0.98682	1.54907
C	2.30355	1.15152	-1.18674
C	1.95017	0.75855	1.73962

C	2.95060	-1.46472	0.05119
H	-2.08916	-2.78199	-0.67805
H	-3.81218	-1.91546	-2.53228
H	-3.11743	1.22842	-2.53127
H	-2.55082	3.64248	-2.25681
H	-2.34712	4.62631	0.03624
H	-2.70427	3.18079	2.04833
H	-3.23652	0.76233	1.77653
H	-6.94808	-0.23047	2.26568
H	-7.36462	-1.16820	0.77333
H	-6.36491	-1.93477	2.05353
C	3.05181	2.29663	-0.84478
C	3.47929	3.17356	-1.85527
C	3.16518	2.91188	-3.19841
C	2.41819	1.77061	-3.53914
C	1.98229	0.89231	-2.53738
H	3.29696	2.50481	0.20112
H	4.05922	4.06262	-1.58903
H	3.49985	3.59914	-3.98161
H	2.17038	1.56690	-4.58546
H	1.39477	0.00586	-2.80228
C	4.22914	-1.31737	-0.52581
C	5.12373	-2.39971	-0.51638
C	4.74868	-3.62223	0.06374
C	3.47435	-3.76952	0.63835
C	2.57246	-2.69604	0.62992
H	4.52295	-0.36768	-0.98325
H	6.11448	-2.28546	-0.96684
H	5.44808	-4.46394	0.06395
H	3.17918	-4.72337	1.08622
H	1.57496	-2.81287	1.06894
C	3.06048	0.47701	2.56248
C	3.19321	1.13162	3.79761
C	2.22601	2.06093	4.21194
C	1.11871	2.33951	3.39183
C	0.97313	1.68822	2.15865
H	3.81406	-0.24918	2.24336
H	4.05439	0.91146	4.43590
H	2.33168	2.56621	5.17695
H	0.36325	3.06151	3.71702
H	0.10403	1.89970	1.52536

16$_{Ph/CO2Me}$

BP86 Energy = -1412.82179351
Enthalpy 0K= -1412.376928
Enthalpy 298K= -1412.344519
Free Energy 298K= -1412.448299
PCM(toluene) = -1412.85071302
PCM(CH_2Cl_2) = -1412.86963957

C	2.91658	3.13924	0.68591
C	3.52729	1.88895	0.74266
C	3.30403	0.93284	-0.29932
C	2.48045	1.31360	-1.41248
C	1.88838	2.58029	-1.45933
C	2.09845	3.49054	-0.41105
C	3.90569	-0.37749	-0.28190
C	3.36435	-1.50307	-0.95323
C	2.02873	-1.71447	-1.30423
Au	0.31715	-0.85456	-0.65495
P	-1.80273	-0.10238	0.12931
C	5.19063	-0.60757	0.48575
O	6.07519	-1.31562	-0.24147
C	7.33871	-1.60411	0.43376
O	5.36399	-0.21884	1.63506
C	-1.80534	0.28274	1.93570
C	-2.38322	1.42146	-0.74497
C	-3.11636	-1.37563	-0.13278
H	1.89602	-2.59094	-1.96280
H	4.08133	-2.31578	-1.14088
H	7.96220	-2.09055	-0.32579
H	7.79832	-0.66922	0.78751
H	7.16058	-2.27299	1.28912
H	2.42705	0.65419	-2.28196
H	1.28848	2.86772	-2.32709
H	1.64824	4.48726	-0.45647
H	3.07596	3.85517	1.49776
H	4.14234	1.60033	1.59743
C	-2.95419	0.07362	2.72708
C	-2.92616	0.39094	4.09425
C	-1.75848	0.91282	4.67471
C	-0.61215	1.11835	3.88874
C	-0.63092	0.80156	2.52231
H	-3.86177	-0.34452	2.28035
H	-3.81765	0.22427	4.70676
H	-1.73918	1.15246	5.74242
H	0.30112	1.51544	4.34290
H	0.26588	0.95003	1.91004
C	-4.41880	-1.02483	-0.54364
C	-5.39073	-2.02546	-0.70701
C	-5.06957	-3.37008	-0.46145
C	-3.77178	-3.72106	-0.05198
C	-2.79374	-2.72915	0.10886
H	-4.67215	0.02109	-0.74252
H	-6.40006	-1.75117	-1.02925
H	-5.82945	-4.14649	-0.59373
H	-3.51809	-4.76904	0.13539
H	-1.77992	-3.00441	0.42174
C	-2.95910	2.50503	-0.05185
C	-3.40119	3.63301	-0.76341
C	-3.27287	3.68336	-2.16062
C	-2.69862	2.60355	-2.85402
C	-2.24935	1.47644	-2.15062
H	-3.06381	2.46887	1.03692
H	-3.85025	4.47157	-0.22195
H	-3.62150	4.56297	-2.71079
H	-2.60107	2.63855	-3.94374
H	-1.80438	0.63441	-2.69353

TS(16-17)$_{Ph/CO2Me}$

BP86 Energy = -1412.81255467
Enthalpy 0K= -1412.368764
Enthalpy 298K= -1412.337153
Free Energy 298K= -1412.438712
Nimag=1 (-190.6903cm-1)
PCM(toluene) = -1412.84425873

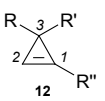
C	3.83157	-1.59230	0.88978
C	3.60960	-0.88270	-0.32399
C	2.85042	-1.53379	-1.36772
C	2.23037	-2.79186	-1.14104
C	2.43022	-3.43539	0.07576
C	3.23671	-2.83631	1.08147
C	3.95568	0.49709	-0.57010
C	5.08834	1.29212	0.01433
O	5.33527	2.44073	-0.33316

C	3.17059	1.11485	-1.54131
C	1.98197	0.51661	-2.02442
Au	0.25832	0.19141	-0.96117
P	-1.82348	0.12996	0.15134
O	5.79285	0.60015	0.94234
C	6.90599	1.33725	1.52649
C	-1.66534	-0.29414	1.94270
C	-2.67412	1.76692	0.07226
C	-2.98133	-1.10553	-0.58607
H	1.81306	0.62271	-3.11330
H	3.52709	2.05653	-1.98528
H	3.06578	-1.26486	-2.41220
H	1.67912	-3.27829	-1.95077
H	2.00493	-4.42922	0.24628
H	3.38087	-3.35859	2.03243
H	4.42248	-1.12440	1.67870
H	7.37073	0.64184	2.23636
H	7.61611	1.63188	0.73931
H	6.53778	2.23944	2.03821
C	-4.36053	-0.83882	-0.70806
C	-5.21280	-1.81374	-1.25162
C	-4.69611	-3.04973	-1.67224
C	-3.32137	-3.31626	-1.55280
C	-2.46286	-2.34653	-1.01534
H	-4.76563	0.12601	-0.38770
H	-6.28236	-1.60322	-1.34840
H	-5.36385	-3.80458	-2.09885
H	-2.91718	-4.27731	-1.88592
H	-1.38910	-2.54899	-0.92871
C	-2.60035	-1.12906	2.58830
C	-2.46254	-1.39871	3.95981
C	-1.40016	-0.83868	4.68721
C	-0.46663	-0.00735	4.04429
C	-0.59285	0.26221	2.67393
H	-3.42896	-1.56844	2.02430
H	-3.18891	-2.04767	4.45883
H	-1.29752	-1.05135	5.75590
H	0.36242	0.42937	4.60994
H	0.13749	0.90676	2.17125
C	-3.41686	2.26243	1.16385
C	-4.07332	3.49908	1.05431
C	-3.99178	4.24048	-0.13535
C	-3.25016	3.74848	-1.22299
C	-2.58811	2.51652	-1.12148
H	-3.47710	1.69192	2.09583
H	-4.64680	3.88337	1.90352
H	-4.50200	5.20547	-0.21386
H	-3.18054	4.32742	-2.14907
H	-2.00345	2.13743	-1.96746

17$_{Ph/CO2Me}$

BP86 Energy = -1412.84677786
Enthalpy 0K= -1412.401523
Enthalpy 298K= -1412.369587
Free Energy 298K= -1412.473823
PCM(toluene) = -1412.88294031

C	4.60210	-1.21078	0.93511
C	3.84744	-0.78945	-0.19911
C	3.11939	-1.82422	-1.02948
C	2.85795	-3.13828	-0.36523
C	3.55528	-3.45854	0.76350
C	4.45282	-2.50799	1.38916
C	3.54320	0.48553	-0.70523
C	4.01551	1.83053	-0.29689
O	3.51601	2.87114	-0.71626
C	2.56947	0.34135	-1.75284
C	2.15957	-1.01123	-1.90257
Au	0.31537	-0.32171	-0.86106
P	-1.75923	0.10749	0.13893
O	5.05122	1.77429	0.58255
C	5.55211	3.07174	1.00745
C	-2.37304	-1.34877	1.09148
C	-1.68505	1.53002	1.31061
C	-3.03604	0.50514	-1.13060
H	1.78354	-1.40616	-2.85388
H	2.27764	1.17176	-2.40243
H	3.88706	-2.11690	-1.79981
H	2.20632	-3.86346	-0.86335
H	3.44226	-4.44838	1.21606
H	4.99916	-2.82530	2.28352
H	5.21798	-0.48547	1.47123
H	6.38500	2.85198	1.68729
H	5.89801	3.65011	0.13732
H	4.76143	3.63673	1.52489
C	-4.02589	1.48064	-0.88984
C	-5.00282	1.73353	-1.86632
C	-4.99515	1.02066	-3.07610
C	-4.00750	0.05009	-3.31726
C	-3.02547	-0.20660	-2.35017
H	-4.03162	2.04279	0.04909
H	-5.76868	2.49267	-1.67999
H	-5.75621	1.22537	-3.83539
H	-3.99700	-0.50184	-4.26216
H	-2.24984	-0.95727	-2.54097
C	-3.72651	-1.73978	1.03713
C	-4.16384	-2.83833	1.79519
C	-3.25956	-3.54326	2.60522
C	-1.91008	-3.15334	2.66013
C	-1.46283	-2.06176	1.90248
H	-4.43361	-1.19453	0.40459
H	-5.21408	-3.14238	1.74944
H	-3.60484	-4.39994	3.19221
H	-1.20399	-3.70350	3.28987
H	-0.40951	-1.76133	1.94139
C	-2.39289	1.50640	2.53019
C	-2.34206	2.62070	3.38322
C	-1.59007	3.75131	3.02533
C	-0.88216	3.77334	1.81119
C	-0.92376	2.66471	0.95378
H	-2.97517	0.62444	2.81399
H	-2.89070	2.60179	4.32996
H	-1.55160	4.61576	3.69542
H	-0.29107	4.65111	1.53266
H	-0.36504	2.68122	0.01133

2. 

R=CO_2Me; R′=Ph; R″=Ph

(a) Butenolide Pathway

18$_{Ph}$ (O-bound)

BP86 Energy = -1643.87179601
Enthalpy 0K= -1643.348821
Enthalpy 298K= -1643.311474

Free Energy 298K= -1643.426937
PCM(toluene) = -1643.90066273

C	-2.23517	2.58875	-0.73628
C	-3.10561	1.51966	-0.43292
C	-4.50130	1.68924	-0.55163
C	-5.01824	2.92726	-0.96433
C	-4.15156	3.99221	-1.25998
C	-2.76142	3.82274	-1.14558
P	-2.39883	-0.08409	0.13985
C	-2.31100	-0.02360	1.98395
C	-1.66798	-1.08489	2.66065
C	-1.59046	-1.07601	4.06054
C	-2.14342	-0.00788	4.78945
C	-2.77889	1.04793	4.11785
C	-2.86694	1.04467	2.71529
Au	-0.34157	-0.48731	-0.77001
O	1.43507	-1.00420	-1.89134
C	2.60002	-1.05384	-1.40772
O	3.61311	-1.44730	-2.16927
C	3.30919	-1.82625	-3.54713
C	2.99598	-0.63471	-0.01807
C	1.86717	-0.14070	0.88913
C	2.60768	0.80812	0.34329
C	4.22850	-1.28064	0.57599
C	4.40648	-2.67850	0.49734
C	5.51260	-3.29230	1.10151
C	6.45610	-2.51827	1.79688
C	6.28293	-1.12834	1.88796
C	5.17523	-0.51425	1.28422
C	-3.61655	-1.40118	-0.28819
C	-4.59282	-1.81983	0.64034
C	-5.53268	-2.79446	0.26770
C	-5.50163	-3.34983	-1.02160
C	-4.52812	-2.93351	-1.94596
C	-3.58314	-1.96363	-1.58263
H	1.26050	-0.47408	1.72836
C	3.00619	2.17527	0.11928
H	4.27358	-2.13054	-3.97114
H	2.59147	-2.65968	-3.55873
H	2.89117	-0.96591	-4.09040
H	5.04596	0.57008	1.36606
H	7.01231	-0.51758	2.42936
H	7.31956	-2.99747	2.26863
H	5.63544	-4.37785	1.03266
H	3.67540	-3.29395	-0.03941
H	-1.23909	-1.91918	2.09321
H	-1.09777	-1.90211	4.58278
H	-2.07784	-0.00060	5.88183
H	-3.21091	1.87901	4.68387
H	-3.36482	1.86877	2.19537
H	-4.61566	-1.39612	1.64923
H	-6.28740	-3.12108	0.98974
H	-6.23344	-4.11241	-1.30548
H	-4.49902	-3.37012	-2.94898
H	-2.81728	-1.64564	-2.29913
H	-5.17985	0.85828	-0.33480
H	-6.10071	3.05577	-1.06068
H	-4.55956	4.95325	-1.58811
H	-2.08453	4.64842	-1.38591
H	-1.15046	2.45094	-0.66163
C	2.34738	3.23048	0.80180
C	2.73114	4.55572	0.57330
C	3.77072	4.84555	-0.33028
C	4.42934	3.80516	-1.00850
C	4.05179	2.47520	-0.78881
H	1.54750	2.99609	1.51158
H	2.22505	5.36801	1.10413
H	4.06920	5.88423	-0.50278
H	5.23983	4.03261	-1.70746
H	4.56360	1.65708	-1.30573

18_{Ph} (η^1-C-bound form)

BP86 Energy = -1643.87050196
Enthalpy 0K= -1643.348025
Enthalpy 298K= -1643.310421
Free Energy 298K= -1643.428083
PCM(toluene) = -1643.89934168

C	-2.34199	3.20506	-0.76851
C	-2.95260	2.15109	-0.03121
C	-3.88682	2.45697	0.99750
C	-4.20987	3.78845	1.27113
C	-3.60376	4.82263	0.53262
C	-2.67106	4.53089	-0.48404
C	-2.63417	0.79001	-0.31952
C	-1.94744	-0.15614	-1.03503
C	-3.04724	-0.62582	-0.03349
C	-4.36742	-1.13636	-0.56958
C	-5.40435	-0.27346	-0.97516
C	-6.58957	-0.79164	-1.52055
C	-6.75254	-2.17735	-1.66897
C	-5.72141	-3.04504	-1.27235
C	-4.53752	-2.52932	-0.72841
C	-2.53697	-1.24748	1.25921
O	-3.54198	-1.61793	2.06777
C	-3.14545	-2.20822	3.33952
O	-1.34436	-1.36793	1.55532
Au	0.10191	-0.15805	-0.28241
P	2.43008	-0.09992	-0.08873
C	3.12983	-1.79738	0.10228
C	4.36098	-2.15329	-0.48656
C	4.87350	-3.44705	-0.29833
C	4.16437	-4.38233	0.47248
C	2.93669	-4.02808	1.05777
C	2.41355	-2.74012	0.87208
C	2.98206	0.87581	1.38054
C	2.29924	2.07064	1.69420
C	2.71510	2.84842	2.78401
C	3.80466	2.43389	3.56930
C	4.48056	1.24201	3.26261
C	4.07358	0.45901	2.17000
C	3.25812	0.64959	-1.55983
C	2.75178	0.35538	-2.84431
C	3.38390	0.87664	-3.98212
C	4.51486	1.69993	-3.84390
C	5.01518	1.99975	-2.56692
C	4.39194	1.47656	-1.42197
H	-1.86682	-0.36412	-2.10764
H	-4.08775	-2.43553	3.85310
H	-2.56303	-3.12566	3.16577
H	-2.54150	-1.49385	3.91939
H	-3.73676	-3.21341	-0.42590
H	-5.83785	-4.12720	-1.38825
H	-7.67716	-2.58026	-2.09355
H	-7.38732	-0.10805	-1.82770
H	-5.29275	0.80983	-0.86603

H	1.86360	-0.27821	-2.94934
H	2.98964	0.64546	-4.97659
H	5.00289	2.11167	-4.73278
H	5.89303	2.64411	-2.45735
H	4.78332	1.71633	-0.42838
H	4.91210	-1.42871	-1.09412
H	5.82713	-3.72327	-0.75882
H	4.56564	-5.39089	0.61274
H	2.38047	-4.75864	1.65338
H	1.45000	-2.46727	1.31731
H	4.59867	-0.47233	1.93647
H	5.32650	0.91579	3.87561
H	4.12335	3.03814	4.42439
H	2.18391	3.77443	3.02541
H	1.44277	2.38588	1.08740
H	-4.34773	1.63827	1.55895
H	-4.93106	4.02692	2.05820
H	-3.85758	5.86479	0.75088
H	-2.20750	5.34417	-1.05016
H	-1.61810	2.96126	-1.55249

TS(18-19)$_{Ph}^{\beta}$ (from O-bound form)

BP86 Energy = -1643.85983023
Enthalpy 0K= -1643.338510
Enthalpy 298K= -1643.301275
Free Energy 298K= -1643.416627
Nimag=1 (-208.1324cm-1)
PCM(toluene) = -1643.88864993

C	2.41688	2.40544	0.99326
C	2.95051	1.10687	1.13837
C	3.89172	0.84272	2.15492
C	4.30002	1.87725	3.01249
C	3.77410	3.17018	2.86101
C	2.83332	3.43363	1.85066
P	2.41058	-0.20887	-0.04175
C	3.48618	-0.04564	-1.53404
C	3.02747	-0.57299	-2.76052
C	3.83771	-0.49583	-3.90270
C	5.10159	0.11390	-3.82856
C	5.55663	0.64606	-2.61116
C	4.75359	0.56952	-1.46192
Au	0.11690	-0.10261	-0.56464
O	-1.78951	-0.49300	1.97725
C	-2.94364	-0.51915	1.55981
O	-4.03906	-0.67324	2.33298
C	-3.77334	-0.83520	3.75675
C	-3.31270	-0.36873	0.09585
C	-1.90312	-0.19102	-1.05100
C	-2.76893	0.78894	-0.58706
C	-4.38842	-1.20826	-0.49551
C	-4.56547	-2.55266	-0.09274
C	-5.57768	-3.33219	-0.66401
C	-6.42044	-2.78829	-1.64994
C	-6.25031	-1.45556	-2.05834
C	-5.24382	-0.66752	-1.48410
C	2.82941	-1.82263	0.75292
C	4.00838	-2.52586	0.43231
C	4.29204	-3.73963	1.07961
C	3.40716	-4.25085	2.04233
C	2.23081	-3.55044	2.36075
C	1.93523	-2.34071	1.71616
H	-2.16548	-1.00806	-1.72728
C	-2.78614	2.20258	-0.35781
H	-4.76226	-0.92111	4.22372
H	-3.17748	-1.74414	3.93038
H	-3.22698	0.03811	4.14446
H	-5.12909	0.37955	-1.78447
H	-6.91127	-1.02314	-2.81584
H	-7.21119	-3.40112	-2.09328
H	-5.70828	-4.37016	-0.34290
H	-3.90852	-2.98626	0.66809
H	2.03615	-1.03686	-2.81874
H	3.47851	-0.90500	-4.85209
H	5.72990	0.17962	-4.72232
H	6.53868	1.12583	-2.55365
H	5.10876	0.99259	-0.51698
H	4.69824	-2.13243	-0.32060
H	5.20633	-4.28587	0.82752
H	3.63144	-5.19854	2.54186
H	1.53776	-3.95052	3.10750
H	1.01232	-1.80038	1.95666
H	4.29854	-0.16548	2.28109
H	5.02902	1.66889	3.80180
H	4.09290	3.97232	3.53393
H	2.41803	4.43975	1.73535
H	1.67492	2.60696	0.21236
C	-1.89437	3.06182	-1.05811
C	-1.98440	4.44257	-0.88420
C	-2.95726	4.98083	-0.01512
C	-3.84684	4.13950	0.67976
C	-3.76891	2.75517	0.50892
H	-1.14568	2.62209	-1.72566
H	-1.30482	5.10979	-1.42263
H	-3.02422	6.06560	0.11570
H	-4.60101	4.56932	1.34522
H	-4.46192	2.08481	1.02783

TS(18-19)$_{Ph}^{\beta}$ (from C-bound form)

BP86 Energy = -1643.85871208
Enthalpy 0K= -1643.337143
Enthalpy 298K= -1643.300071
Free Energy 298K= -1643.414348
Nimag=1 (-203.9840cm-1)

C	-2.92154	-0.81332	-2.80793
C	-3.43305	-0.86674	-1.49301
C	-4.66713	-1.50071	-1.24199
C	-5.38510	-2.07153	-2.30570
C	-4.87796	-2.01232	-3.61359
C	-3.64678	-1.38240	-3.86441
P	-2.46344	-0.06392	-0.14127
C	-2.90782	1.72769	-0.15934
C	-4.13512	2.16852	-0.69835
C	-4.45455	3.53520	-0.67255
C	-3.55578	4.45985	-0.11557
C	-2.33178	4.02091	0.41640
C	-2.00068	2.65767	0.39386
Au	-0.14972	-0.39525	-0.38826
C	1.85175	-0.79267	-0.70199
C	3.03666	-0.83202	0.02374
C	2.83552	0.56197	0.34846
C	1.85471	0.93135	1.45406
O	1.30757	2.02002	1.58414
C	3.70540	1.61246	-0.20735
C	3.90380	2.84618	0.46931

C	4.76864	3.81049	-0.06175
C	5.43457	3.57916	-1.27630
C	5.23287	2.36879	-1.96588
C	4.38276	1.39540	-1.43799
C	-3.10284	-0.76091	1.44699
C	-4.06662	-0.07655	2.21539
C	-4.54927	-0.65241	3.40213
C	-4.07615	-1.90569	3.82289
C	-3.11365	-2.58837	3.05884
C	-2.62205	-2.01818	1.87556
O	1.77670	-0.08549	2.35014
C	0.90267	0.16118	3.48679
H	1.97965	-1.09311	-1.76236
C	4.21679	-1.66603	-0.04279
H	1.10236	-0.66132	4.18488
H	1.13551	1.13542	3.94166
H	-0.14975	0.14636	3.16181
H	4.22076	0.46461	-1.99006
H	5.73489	2.18991	-2.92142
H	6.10108	4.34157	-1.69113
H	4.91741	4.75211	0.47525
H	3.38162	3.04478	1.40663
H	-4.43452	0.90192	1.89126
H	-5.29642	-0.11823	3.99733
H	-4.45482	-2.35066	4.74838
H	-2.74205	-3.56443	3.38641
H	-1.86776	-2.54809	1.28242
H	-4.83257	1.45161	-1.14299
H	-5.40538	3.87658	-1.09355
H	-3.80677	5.52517	-0.10297
H	-1.62582	4.74073	0.84205
H	-1.03790	2.32410	0.79849
H	-5.06265	-1.55537	-0.22295
H	-6.34168	-2.56546	-2.10875
H	-5.43975	-2.46156	-4.43843
H	-3.24774	-1.33927	-4.88259
H	-1.95834	-0.32725	-3.00121
C	5.40587	-1.29671	0.63944
C	6.51647	-2.14374	0.61895
C	6.45583	-3.36802	-0.07392
C	5.27682	-3.75163	-0.74127
C	4.16122	-2.91123	-0.72305
H	5.44453	-0.34575	1.17928
H	7.43173	-1.85692	1.14504
H	7.32706	-4.03039	-0.08538
H	5.23147	-4.71030	-1.26637
H	3.23436	-3.21382	-1.22231

19_{Ph}^{β} (from O-bound form)

BP86 Energy = -1643.87389506
Enthalpy 0K= -1643.350736
Enthalpy 298K= -1643.313166
Free Energy 298K= -1643.429989
PCM(toluene) = -1643.90066433

C	-2.81042	-0.73915	2.68809
C	-3.46023	0.00278	1.67774
C	-4.71250	0.59691	1.93735
C	-5.31113	0.43925	3.19775
C	-4.66574	-0.30447	4.19895
C	-3.41578	-0.89358	3.94372
P	-2.64292	0.15515	0.02605
C	-3.16829	-1.31910	-0.95712
C	-2.37296	-1.70909	-2.05630
C	-2.75879	-2.80094	-2.84767
C	-3.93050	-3.51317	-2.54066
C	-4.71784	-3.13321	-1.44146
C	-4.34163	-2.03762	-0.64779
Au	-0.27472	0.37657	0.18885
O	5.03134	-1.06746	1.95391
C	5.12104	-0.72898	0.78107
O	6.08431	-1.08875	-0.08359
C	7.06180	-2.03923	0.44494
C	4.11809	0.24012	0.18824
C	1.71802	0.69068	0.25772
C	2.76616	-0.21612	0.03016
C	4.56904	1.58481	-0.07945
C	5.71280	2.11218	0.59469
C	6.13140	3.41929	0.35501
C	5.44862	4.21925	-0.58494
C	4.34133	3.70717	-1.28638
C	3.90125	2.40481	-1.04271
C	-3.41444	1.62630	-0.78801
C	-4.46553	1.49553	-1.71785
C	-5.03458	2.64394	-2.29266
C	-4.56139	3.91853	-1.94238
C	-3.51235	4.05034	-1.01626
C	-2.93432	2.90878	-0.44269
H	2.05339	1.69748	0.55002
C	2.53977	-1.66706	-0.22811
H	7.74894	-2.23290	-0.38743
H	7.59276	-1.59860	1.30181
H	6.55297	-2.96180	0.76209
H	3.08802	1.97664	-1.63556
H	3.83934	4.31929	-2.04127
H	5.79570	5.23784	-0.78475
H	6.99116	3.82432	0.89640
H	6.22604	1.50224	1.34422
H	-1.45217	-1.16104	-2.28697
H	-2.14001	-3.09987	-3.69955
H	-4.22719	-4.36872	-3.15549
H	-5.62756	-3.69082	-1.19769
H	-4.95411	-1.74844	0.21215
H	-4.83466	0.50319	-1.99480
H	-5.84922	2.53943	-3.01609
H	-5.00716	4.81033	-2.39391
H	-3.13948	5.04290	-0.74459
H	-2.11147	3.01049	0.27432
H	-5.21300	1.18585	1.16238
H	-6.28257	0.90245	3.39694
H	-5.13407	-0.42033	5.18134
H	-2.90784	-1.46739	4.72514
H	-1.83153	-1.19144	2.49193
C	1.61049	-2.41700	0.52912
C	1.41104	-3.77744	0.26054
C	2.12984	-4.40772	-0.77047
C	3.05742	-3.67371	-1.52715
C	3.26815	-2.31405	-1.25410
H	1.07177	-1.93167	1.34923
H	0.70030	-4.35142	0.86323
H	1.96894	-5.46976	-0.98041
H	3.61438	-4.15782	-2.33545
H	3.98250	-1.74138	-1.85499

19_{Ph}^{β} (from η^1-C-bound form)

BP86 Energy = -1643.87179002

Enthalpy 0K= -1643.348769
Enthalpy 298K= -1643.311245
Free Energy 298K= -1643.426673

C	3.16254	2.68594	-1.00101
C	3.66723	1.55764	-0.31926
C	4.98963	1.56509	0.17117
C	5.80027	2.69421	-0.02757
C	5.29799	3.81325	-0.71162
C	3.98000	3.80841	-1.19859
P	2.56961	0.08440	-0.12514
C	2.84509	-0.98259	-1.60718
C	4.02287	-0.88481	-2.37748
C	4.20328	-1.73082	-3.48318
C	3.21534	-2.66970	-3.82295
C	2.04062	-2.76388	-3.05819
C	1.84795	-1.92095	-1.95313
Au	0.28001	0.68666	0.14615
C	-1.61448	1.36581	0.30238
C	-2.90005	0.79418	0.21572
C	-3.06780	-0.62367	0.14519
C	-1.89601	-1.51844	0.50907
O	-1.27405	-2.14753	-0.33931
C	-4.25387	-1.33639	-0.28830
C	-4.43126	-2.70390	0.09051
C	-5.53930	-3.42847	-0.34499
C	-6.47962	-2.82340	-1.20110
C	-6.31082	-1.48537	-1.61046
C	-5.22682	-0.74053	-1.14977
C	3.22634	-0.85302	1.33043
C	4.03526	-1.99706	1.17654
C	4.52370	-2.66446	2.31236
C	4.20903	-2.19674	3.59832
C	3.40015	-1.05769	3.75447
C	2.90442	-0.38806	2.62582
O	-1.72799	-1.58716	1.84260
C	-0.66387	-2.47450	2.30642
H	-1.67481	2.46641	0.37039
C	-4.08395	1.71605	0.23879
H	-0.88843	-2.66455	3.36326
H	-0.66093	-3.40561	1.72087
H	0.30508	-1.96172	2.20275
H	-5.10130	0.29400	-1.47403
H	-7.03343	-1.02605	-2.29105
H	-7.34319	-3.39617	-1.55370
H	-5.67264	-4.46648	-0.02756
H	-3.70572	-3.18022	0.75570
H	4.28179	-2.36592	0.17606
H	5.15315	-3.55136	2.18885
H	4.59311	-2.71961	4.47982
H	3.15357	-0.69019	4.75564
H	2.27495	0.50089	2.74953
H	4.79061	-0.14780	-2.12162
H	5.11634	-1.65153	-4.08146
H	3.35863	-3.32378	-4.68882
H	1.26553	-3.48863	-3.32641
H	0.92515	-1.99036	-1.36628
H	5.38207	0.69798	0.71181
H	6.82515	2.69893	0.35647
H	5.93228	4.69262	-0.86056
H	3.58500	4.68210	-1.72626
H	2.13136	2.68382	-1.37270
C	-5.09038	1.55596	1.21842
C	-6.15501	2.46431	1.29427
C	-6.23700	3.53527	0.38798
C	-5.24250	3.70203	-0.58951
C	-4.16740	2.80319	-0.66026
H	-5.02483	0.72913	1.93352
H	-6.91942	2.34010	2.06768
H	-7.07112	4.24114	0.44745
H	-5.30108	4.53448	-1.29759
H	-3.39513	2.93282	-1.42693

TS(19-20)$_{Ph}^{\beta}$

BP86 Energy = -1643.85730859
Enthalpy 0K= -1643.335052
Enthalpy 298K= -1643.298306
Free Energy 298K= -1643.411609
Nimag=1 (-86.0644cm-1)
PCM(toluene) = -1643.88587265

C	-3.01983	2.78466	-0.68591
C	-3.34565	1.46405	-1.06470
C	-4.25305	1.23677	-2.11994
C	-4.83394	2.32847	-2.78557
C	-4.51388	3.64123	-2.40344
C	-3.60837	3.86860	-1.35304
P	-2.58144	0.06639	-0.12907
C	-3.63471	-0.21300	1.36132
C	-4.98872	0.18149	1.38958
C	-5.76075	-0.06263	2.53646
C	-5.18819	-0.69411	3.65287
C	-3.83838	-1.08330	3.62769
C	-3.05863	-0.84185	2.48689
Au	-0.32220	0.50866	0.47480
C	1.55556	1.02911	0.99080
C	2.84361	0.58544	0.57568
C	3.19823	-0.76024	0.38438
C	2.15898	-1.74544	0.85934
O	1.39520	-1.49699	1.79845
C	4.53336	-1.21778	-0.04220
C	4.70713	-2.33078	-0.91061
C	5.98936	-2.73770	-1.29523
C	7.12629	-2.08383	-0.79184
C	6.97128	-0.99928	0.09107
C	5.69535	-0.55727	0.44665
C	-2.75663	-1.43003	-1.20117
C	-3.77833	-2.37923	-0.99606
C	-3.88100	-3.48864	-1.85194
C	-2.97230	-3.65255	-2.90965
C	-1.95230	-2.70716	-3.11491
C	-1.83900	-1.60039	-2.26134
O	2.14522	-2.90811	0.17715
C	1.20726	-3.90920	0.66883
H	1.61443	1.96808	1.57310
C	3.72004	1.76475	0.23128
H	1.43284	-4.81579	0.09356
H	1.36060	-4.07378	1.74579
H	0.17347	-3.57947	0.48721
H	5.59208	0.28140	1.13872
H	7.85062	-0.49666	0.50496
H	8.12725	-2.41868	-1.08089
H	6.10076	-3.57766	-1.98769
H	3.83353	-2.85103	-1.30397
H	-4.48753	-2.25452	-0.17183
H	-4.67486	-4.22449	-1.68994
H	-3.05741	-4.51803	-3.57421

H	-1.24323	-2.83281	-3.93928
H	-1.04276	-0.86404	-2.42066
H	-5.43472	0.68603	0.52648
H	-6.81025	0.24702	2.55795
H	-5.79273	-0.87642	4.54681
H	-3.38819	-1.56670	4.50030
H	-2.00236	-1.13458	2.47265
H	-4.50024	0.21515	-2.42505
H	-5.53633	2.15003	-3.60572
H	-4.96653	4.48867	-2.92760
H	-3.35383	4.89109	-1.05724
H	-2.30786	2.96207	0.12815
C	4.07672	1.99777	-1.11572
C	4.86346	3.10853	-1.44951
C	5.28666	4.00273	-0.45101
C	4.91672	3.78651	0.88765
C	4.12416	2.68209	1.22873
H	3.74429	1.30201	-1.89248
H	5.14082	3.28012	-2.49410
H	5.89525	4.87236	-0.71690
H	5.24237	4.48106	1.66803
H	3.83908	2.51384	2.27344

20_{Ph}^{β}

BP86 Energy = -1643.92049120
Enthalpy 0K= -1643.395046
Enthalpy 298K= -1643.358435
Free Energy 298K= -1643.474102
PCM(toluene) = -1643.95323363

C	3.08158	2.20512	-1.30227
C	3.20611	1.60465	-0.02962
C	3.89966	2.27307	0.99954
C	4.46897	3.53313	0.75156
C	4.35089	4.12535	-0.51580
C	3.65882	3.46014	-1.54280
P	2.45662	-0.06517	0.22982
C	3.62952	-1.28179	-0.51482
C	4.97483	-0.94407	-0.76952
C	5.84460	-1.90617	-1.30810
C	5.37903	-3.19984	-1.59237
C	4.03784	-3.53691	-1.34132
C	3.16147	-2.58108	-0.80794
Au	0.30682	-0.19678	-0.71641
C	-1.61056	-0.32653	-1.65283
C	-2.70658	0.29945	-0.90055
C	-3.57505	-0.71019	-0.43758
C	-3.05978	-1.91226	-0.99312
O	-1.97195	-1.74667	-1.73807
C	-4.73854	-0.64470	0.47596
C	-5.92131	-1.36286	0.18879
C	-7.01192	-1.31304	1.06867
C	-6.93652	-0.55043	2.24505
C	-5.76325	0.16460	2.53972
C	-4.67087	0.11925	1.66391
O	-3.54165	-3.12219	-0.79999
C	-2.87692	-4.24080	-1.46355
C	2.45938	-0.37486	2.05028
C	3.54260	-1.01915	2.68352
C	3.52332	-1.20883	4.07460
C	2.43094	-0.75980	4.83441
C	1.34943	-0.12100	4.20448
C	1.35843	0.06847	2.81485
H	-1.45945	0.03428	-2.68263
C	-2.86974	1.75614	-0.78929
H	-3.46324	-5.12172	-1.17685
H	-2.89362	-4.09784	-2.55468
H	-1.84019	-4.32887	-1.10589
H	-3.75678	0.67385	1.89811
H	-5.69672	0.75617	3.45819
H	-7.78832	-0.51395	2.93118
H	-7.92373	-1.87019	0.83215
H	-5.98902	-1.95502	-0.72885
H	4.39274	-1.37699	2.09436
H	4.36363	-1.71157	4.56338
H	2.41925	-0.91291	5.91803
H	0.49445	0.22373	4.79441
H	0.51079	0.55688	2.32072
H	5.34009	0.06531	-0.55600
H	6.88745	-1.64074	-1.50757
H	6.05973	-3.94512	-2.01538
H	3.67213	-4.54322	-1.56821
H	2.11330	-2.84022	-0.61978
H	3.99338	1.81506	1.98896
H	5.00572	4.05061	1.55276
H	4.79572	5.10745	-0.70410
H	3.56424	3.92092	-2.53109
H	2.53716	1.68983	-2.10204
C	-1.75144	2.62679	-0.76468
C	-1.92769	4.01553	-0.74280
C	-3.22186	4.56229	-0.75204
C	-4.33996	3.71103	-0.78329
C	-4.17074	2.32214	-0.79581
H	-0.73941	2.20275	-0.73262
H	-1.05305	4.67255	-0.71152
H	-3.35899	5.64792	-0.73286
H	-5.35008	4.13133	-0.80171
H	-5.04462	1.66710	-0.83841

$TS(18\text{-}19)_{Ph}^{\alpha}$

BP86 Energy = -1643.84232417
Enthalpy 0K= -1643.321629
Enthalpy 298K= -1643.284211
Free Energy 298K= -1643.400114
Nimag=1 (-192.9140cm-1)
PCM(toluene) = -1643.87094160

C	3.68116	2.37837	0.37066
C	2.48287	1.75715	-0.09367
C	1.81282	2.29579	-1.22887
C	2.33980	3.40772	-1.88850
C	3.52493	4.01269	-1.42801
C	4.18645	3.49574	-0.30026
C	1.98835	0.62334	0.61201
C	2.10789	-0.49761	1.34990
C	3.05699	-1.14373	0.42355
C	4.49055	-0.89770	0.61140
C	5.40144	-0.83916	-0.47706
C	6.76121	-0.59688	-0.25384
C	7.24366	-0.39151	1.05075
C	6.35388	-0.42720	2.13876
C	4.99355	-0.67445	1.92271
C	2.48167	-1.98536	-0.64260
O	3.38626	-2.81393	-1.21018
C	2.86652	-3.69550	-2.24117
O	1.28256	-1.97234	-0.98515

Au	-0.09593	-0.16426	0.32070
P	-2.41440	-0.02278	0.08761
C	-3.10665	-1.34772	-0.99019
C	-4.45463	-1.74668	-0.85938
C	-4.97486	-2.72630	-1.71874
C	-4.15728	-3.30960	-2.70144
C	-2.81351	-2.91961	-2.82400
C	-2.28200	-1.94233	-1.96859
C	-2.89112	1.60158	-0.65044
C	-2.32123	2.77782	-0.11349
C	-2.68254	4.02841	-0.63395
C	-3.60025	4.11147	-1.69593
C	-4.15949	2.94260	-2.23556
C	-3.81003	1.68501	-1.71594
C	-3.27916	-0.15039	1.71334
C	-2.84330	-1.13004	2.63194
C	-3.50095	-1.27688	3.86104
C	-4.58813	-0.44526	4.18139
C	-5.01999	0.53144	3.27027
C	-4.36971	0.68350	2.03434
H	1.64664	-0.82131	2.29434
H	3.72932	-4.28974	-2.56772
H	2.07982	-4.34499	-1.82754
H	2.45464	-3.10976	-3.07767
H	4.31106	-0.72472	2.77826
H	6.72401	-0.27472	3.15735
H	8.30879	-0.20500	1.21929
H	7.44983	-0.56131	-1.10376
H	5.03546	-0.99348	-1.49455
H	-1.99358	-1.77673	2.38410
H	-3.16133	-2.03684	4.57154
H	-5.09606	-0.55708	5.14427
H	-5.86471	1.18112	3.51937
H	-4.70631	1.45026	1.32977
H	-5.09012	-1.30328	-0.08602
H	-6.01903	-3.03734	-1.61570
H	-4.56671	-4.07657	-3.36626
H	-2.17325	-3.38314	-3.58083
H	-1.22714	-1.65699	-2.04745
H	-4.24911	0.77686	-2.13957
H	-4.87147	3.00494	-3.06434
H	-3.87630	5.08863	-2.10426
H	-2.24294	4.93812	-0.21325
H	-1.59997	2.71312	0.70903
H	0.88688	1.82594	-1.57580
H	1.82186	3.81197	-2.76346
H	3.92629	4.89079	-1.94282
H	5.10314	3.96961	0.06373
H	4.19089	1.97780	1.25032

19$_{Ph}^{\alpha}$

BP86 Energy = -1643.88006129
Enthalpy 0K= -1643.356941
Enthalpy 298K= -1643.319494
Free Energy 298K= -1643.436393

C	-3.36039	2.45540	-1.57851
C	-2.23527	2.10599	-0.76348
C	-1.57686	3.14334	-0.03054
C	-2.05594	4.45135	-0.06571
C	-3.16104	4.77158	-0.88201
C	-3.80208	3.77717	-1.64802
C	-1.72498	0.76403	-0.75233
C	-2.49236	-0.37886	-1.13051
C	-3.61682	-0.96974	-0.57437
C	-4.37642	-0.55221	0.62461
C	-4.45753	-1.45177	1.72039
C	-5.12499	-1.09066	2.89538
C	-5.75394	0.16258	2.99391
C	-5.70444	1.05296	1.90928
C	-5.01724	0.70499	0.73861
C	-3.92952	-2.30348	-1.23337
O	-5.10034	-2.81755	-0.79872
C	-5.49515	-4.06044	-1.44249
O	-3.23006	-2.81887	-2.10303
Au	0.23091	0.32686	-0.31143
P	2.50749	-0.20237	0.12700
C	3.09741	-1.61346	-0.90909
C	4.39891	-1.63761	-1.45148
C	4.81236	-2.73832	-2.21936
C	3.93487	-3.81050	-2.44829
C	2.63679	-3.78638	-1.91046
C	2.21423	-2.68981	-1.14535
C	2.80716	-0.67607	1.88715
C	2.09802	0.00440	2.90094
C	2.32324	-0.31424	4.24791
C	3.24769	-1.31628	4.58863
C	3.94840	-1.99955	3.58159
C	3.73152	-1.68417	2.23052
C	3.62559	1.22181	-0.23892
C	3.34568	2.01560	-1.37293
C	4.18696	3.08813	-1.70192
C	5.30269	3.37907	-0.89835
C	5.57878	2.59528	0.23358
C	4.74445	1.51578	0.56734
H	-2.00410	-1.05950	-1.85536
H	-6.43300	-4.35160	-0.95322
H	-5.64794	-3.89649	-2.52029
H	-4.71809	-4.82741	-1.30133
H	-5.01547	1.39230	-0.10999
H	-6.21509	2.01926	1.96864
H	-6.29171	0.43751	3.90660
H	-5.16223	-1.79251	3.73423
H	-3.97423	-2.43050	1.64893
H	2.47181	1.79293	-1.99626
H	3.96838	3.69984	-2.58279
H	5.95525	4.22001	-1.15299
H	6.44540	2.82297	0.86205
H	4.95985	0.90978	1.45308
H	5.08237	-0.79967	-1.28223
H	5.82189	-2.75406	-2.64174
H	4.26033	-4.66351	-3.05181
H	1.94876	-4.61738	-2.09414
H	1.19878	-2.66811	-0.73328
H	4.27319	-2.22492	1.44818
H	4.66498	-2.78367	3.84523
H	3.41754	-1.56845	5.63999
H	1.77133	0.21477	5.03111
H	1.37003	0.77949	2.63538
H	-0.70388	2.87877	0.57563
H	-1.56466	5.23315	0.52079
H	-3.51439	5.80652	-0.93345
H	-4.64127	4.04273	-2.29772
H	-3.83331	1.67714	-2.18556

TS(19-20)$_{Ph}^{\alpha}$

BP86 Energy = -1643.87648923
Enthalpy 0K= -1643.354113
Enthalpy 298K= -1643.317330
Free Energy 298K= -1643.431735
Nimag=1 (-270.7910cm-1)

C	-3.68446	3.07734	-0.62592
C	-2.45149	2.56054	-0.14194
C	-1.46146	3.47958	0.29445
C	-1.68022	4.85954	0.22076
C	-2.89836	5.35023	-0.28211
C	-3.90033	4.45668	-0.70443
C	-2.21117	1.10451	-0.08435
C	-2.99328	0.21923	-0.91639
C	-3.44165	-0.98929	-0.39675
C	-3.17541	-1.10314	1.01529
C	-2.95722	-2.29357	1.75460
C	-2.38028	-2.21752	3.02116
C	-2.02276	-0.96908	3.61068
C	-2.27967	0.21602	2.94315
C	-2.89264	0.17902	1.64418
C	-4.07421	-1.97979	-1.31939
O	-4.47667	-3.10855	-0.67627
C	-5.11848	-4.09172	-1.53505
O	-4.22193	-1.77967	-2.51972
Au	-0.20352	0.43535	-0.00043
P	2.04676	-0.21755	-0.14203
C	2.25115	-1.80446	-1.06413
C	3.36936	-2.03573	-1.89190
C	3.50159	-3.26611	-2.55545
C	2.52543	-4.26330	-2.39726
C	1.40964	-4.03289	-1.57483
C	1.26757	-2.80532	-0.91183
C	2.84349	-0.45789	1.50892
C	2.59977	0.49785	2.51982
C	3.21193	0.36349	3.77399
C	4.05936	-0.72837	4.03063
C	4.29683	-1.68366	3.02988
C	3.69281	-1.55259	1.76831
C	3.06065	1.04487	-1.03074
C	2.48645	1.71223	-2.13484
C	3.23976	2.65271	-2.85224
C	4.56151	2.93664	-2.46807
C	5.13187	2.27845	-1.36658
C	4.38638	1.33199	-0.64476
H	-3.22493	0.49166	-1.95369
H	-5.39480	-4.92006	-0.87045
H	-6.00963	-3.65532	-2.01104
H	-4.42193	-4.42896	-2.31815
H	-3.62851	0.97393	1.47084
H	-2.09076	1.18280	3.41976
H	-1.58698	-0.95367	4.61419
H	-2.17874	-3.14171	3.57256
H	-3.19296	-3.25724	1.29889
H	1.45273	1.49597	-2.42812
H	2.79209	3.16843	-3.70746
H	5.14577	3.67534	-3.02556
H	6.15976	2.50171	-1.06424
H	4.83211	0.82570	0.21719
H	4.12769	-1.25774	-2.02433
H	4.36807	-3.44211	-3.20038
H	2.63080	-5.21871	-2.92057
H	0.64486	-4.80689	-1.45671
H	0.39273	-2.61753	-0.27882
H	3.88082	-2.30009	0.99161
H	4.95465	-2.53572	3.22765
H	4.53219	-0.83466	5.01194
H	3.02417	1.10922	4.55294
H	1.93530	1.34708	2.32377
H	-0.51317	3.08642	0.67978
H	-0.90349	5.55510	0.55267
H	-3.07149	6.42956	-0.33780
H	-4.85113	4.83976	-1.08729
H	-4.47465	2.38503	-0.93804

20_{Ph}^{α}

BP86 Energy = -1643.90030561
Enthalpy 0K= -1643.376399
Enthalpy 298K= -1643.339490
Free Energy 298K= -1643.452755

C	-2.76954	3.00605	-1.78039
C	-2.44215	2.50753	-0.49605
C	-2.02855	3.42427	0.50173
C	-1.94585	4.79501	0.22237
C	-2.27205	5.27540	-1.05697
C	-2.68133	4.37666	-2.05683
C	-2.53605	1.05421	-0.20398
C	-2.41501	0.00548	-1.15532
C	-2.96073	-1.24371	-0.64666
C	-3.46769	-1.02427	0.63556
C	-3.93150	-1.92503	1.64328
C	-4.04757	-1.47404	2.94163
C	-3.71122	-0.11558	3.32397
C	-3.32857	0.81429	2.40226
C	-3.36920	0.45716	0.94738
C	-2.81616	-2.48928	-1.43133
O	-3.53957	-3.52100	-0.91989
C	-3.42302	-4.76674	-1.65910
O	-2.11083	-2.57171	-2.43671
Au	-0.31912	0.26946	-0.18041
P	1.95424	-0.16614	0.10545
C	2.67106	-0.72890	-1.49793
C	3.97651	-0.35705	-1.88172
C	4.49984	-0.82102	-3.09924
C	3.72801	-1.64882	-3.93066
C	2.42655	-2.01694	-3.54888
C	1.89221	-1.55743	-2.33644
C	2.26157	-1.49679	1.34602
C	1.54330	-1.47019	2.56124
C	1.77988	-2.45245	3.53307
C	2.72444	-3.46592	3.29424
C	3.43518	-3.49579	2.08392
C	3.20850	-2.51335	1.10608
C	2.91309	1.31127	0.65236
C	2.56231	2.57997	0.14193
C	3.30725	3.70935	0.51058
C	4.39359	3.57973	1.39295
C	4.73844	2.31908	1.90628
C	4.00185	1.18119	1.53941
H	-2.13774	0.13363	-2.20670
H	-4.08722	-5.47209	-1.14365
H	-3.73943	-4.62229	-2.70336
H	-2.38246	-5.12679	-1.64429

H	-4.37395	0.85610	0.63758
H	-3.13039	1.85009	2.69117
H	-3.77234	0.16022	4.38142
H	-4.36589	-2.16953	3.72487
H	-4.11306	-2.97012	1.38290
H	1.70909	2.68199	-0.53824
H	3.03504	4.69203	0.11325
H	4.96914	4.46391	1.68408
H	5.58165	2.21780	2.59647
H	4.26947	0.20070	1.94531
H	4.57740	0.29509	-1.24029
H	5.51148	-0.52986	-3.39835
H	4.13885	-2.00254	-4.88141
H	1.81992	-2.65488	-4.19879
H	0.87145	-1.83756	-2.05111
H	3.76104	-2.54070	0.16194
H	4.16833	-4.28615	1.89567
H	2.90319	-4.23534	4.05175
H	1.22299	-2.43016	4.47493
H	0.80287	-0.68343	2.74520
H	-1.74104	3.05645	1.49158
H	-1.62352	5.48945	1.00451
H	-2.21341	6.34661	-1.27277
H	-2.94692	4.74608	-3.05217
H	-3.11879	2.31725	-2.55639

(b) Indene Pathway

η^2-alkene Reactant

BP86 Energy = -1643.86515184
Enthalpy 0K= -1643.342840
Enthalpy 298K= -1643.305142
Free Energy 298K= -1643.422612

C	-4.18499	-2.12439	-0.74227
C	-3.12553	-1.32490	-1.21913
C	-2.77035	-1.36432	-2.58516
C	-3.47868	-2.19162	-3.46797
C	-4.53566	-2.98705	-2.99242
C	-4.88619	-2.95327	-1.63332
P	-2.20458	-0.18312	-0.09966
C	-2.55864	-0.73111	1.62770
C	-1.87760	-1.86075	2.13252
C	-2.14652	-2.31640	3.43073
C	-3.08402	-1.64279	4.23321
C	-3.75528	-0.51484	3.73537
C	-3.49682	-0.05459	2.43370
Au	0.09062	-0.15127	-0.57986
C	2.10149	-0.02015	-1.33213
C	3.01165	0.92572	-0.45898
C	2.38868	1.89030	0.51967
C	2.88636	-0.56429	-0.33980
C	3.43097	-1.70902	0.31039
C	3.05971	-3.01854	-0.10957
C	3.62670	-4.13161	0.51058
C	4.56743	-3.95572	1.54708
C	4.94263	-2.66596	1.96996
C	4.37495	-1.54367	1.36262
C	4.31617	1.38164	-1.10979
C	-2.95246	1.48958	-0.30333
C	-4.27400	1.64133	-0.77385
C	-4.82699	2.92645	-0.88881
C	-4.06808	4.05541	-0.53938
C	-2.75109	3.90356	-0.07354
C	-2.18744	2.62452	0.04311
H	2.11334	-0.15952	-2.41826
H	-1.94269	-0.74807	-2.95476
H	-3.20163	-2.21971	-4.52634
H	-5.08326	-3.63687	-3.68204
H	-5.70704	-3.57414	-1.26118
H	-4.45850	-2.10455	0.31720
H	-4.86415	0.76354	-1.05540
H	-5.85094	3.04374	-1.25681
H	-4.50158	5.05573	-0.63604
H	-2.15598	4.78236	0.19264
H	-1.15706	2.51103	0.39959
H	-4.02100	0.82554	2.04928
H	-4.48347	0.01206	4.35974
H	-3.28780	-1.99611	5.24880
H	-1.61972	-3.19382	3.81869
H	-1.14026	-2.38042	1.51009
H	4.65116	-0.53319	1.67992
H	5.67403	-2.54369	2.77396
H	5.01037	-4.83315	2.02895
H	3.34735	-5.14000	0.19154
H	2.33195	-3.13505	-0.91891
C	2.00222	1.46294	1.80697
C	1.38656	2.35326	2.70232
C	1.16030	3.68548	2.32286
C	1.55164	4.12098	1.04438
C	2.16284	3.23251	0.14755
H	2.18858	0.42857	2.11714
H	1.09829	2.00680	3.69982
H	0.69358	4.38503	3.02350
H	1.39278	5.16247	0.74677
H	2.48226	3.58427	-0.83708
O	4.78627	0.42571	-1.96209
O	4.86192	2.45343	-0.90927
C	6.02882	0.77401	-2.63344
H	6.29156	-0.10760	-3.23183
H	5.87868	1.65396	-3.27762
H	6.81265	0.99890	-1.89417

Ring-opening TS (Ph^{β})

BP86 Energy = -1643.85448797
Enthalpy 0K= -1643.333269
Enthalpy 298K= -1643.295977
Free Energy 298K= -1643.411546
Nimag=1 (-231.7434cm-1)

C	-4.27272	-2.39769	0.01152
C	-3.16336	-1.83462	-0.65208
C	-2.65664	-2.44412	-1.82065
C	-3.26366	-3.60253	-2.32587
C	-4.37028	-4.16236	-1.66450
C	-4.87158	-3.56150	-0.49874
P	-2.35286	-0.28584	-0.05110
C	-2.90709	-0.04958	1.69531
C	-2.24038	-0.76466	2.71435
C	-2.65725	-0.63613	4.04694
C	-3.73055	0.21192	4.37020
C	-4.38984	0.92906	3.35914
C	-3.98340	0.80083	2.02075
Au	-0.01885	-0.43774	-0.25747

C	1.99961	-0.83625	-0.45637
C	2.98206	0.84004	-0.27343
C	2.19363	1.84748	0.46346
C	3.18748	-0.52255	0.18473
C	4.38861	-1.23541	0.53664
C	4.40135	-2.65562	0.57379
C	5.56192	-3.33269	0.95065
C	6.71766	-2.60586	1.30263
C	6.71196	-1.19844	1.28499
C	5.55307	-0.51248	0.91215
C	3.89518	1.32324	-1.38857
C	-3.08260	1.09492	-1.03714
C	-4.32811	0.94972	-1.68323
C	-4.86913	2.02720	-2.40266
C	-4.17338	3.24439	-2.48092
C	-2.93114	3.38837	-1.83983
C	-2.38099	2.31690	-1.12097
H	2.12604	-1.63326	-1.21671
H	-1.78820	-2.01150	-2.33058
H	-2.86864	-4.07208	-3.23215
H	-4.83901	-5.07057	-2.05600
H	-5.73072	-3.99868	0.01952
H	-4.66290	-1.93538	0.92361
H	-4.86847	-0.00063	-1.63146
H	-5.83432	1.91174	-2.90550
H	-4.59638	4.08012	-3.04705
H	-2.38595	4.33509	-1.90617
H	-1.40898	2.42758	-0.62676
H	-4.49911	1.36276	1.23592
H	-5.22409	1.59183	3.60941
H	-4.05074	0.31550	5.41168
H	-2.14026	-1.19401	4.83405
H	-1.39857	-1.42013	2.46323
H	5.53064	0.58262	0.91671
H	7.60916	-0.64264	1.57258
H	7.62395	-3.14122	1.60277
H	5.57500	-4.42626	0.97632
H	3.49629	-3.21068	0.30543
C	1.96331	1.66576	1.85053
C	1.26218	2.62796	2.58613
C	0.79149	3.79152	1.95291
C	1.02968	3.98876	0.58035
C	1.72277	3.02690	-0.16409
H	2.35877	0.77487	2.34938
H	1.10316	2.48236	3.65891
H	0.25735	4.55195	2.53106
H	0.68255	4.90384	0.09056
H	1.91426	3.19154	-1.22687
O	4.18957	0.31544	-2.24755
O	4.29881	2.47290	-1.49352
C	5.07972	0.69246	-3.33554
H	5.20465	-0.21823	-3.93432
H	4.62736	1.49848	-3.93316
H	6.04509	1.03793	-2.93470

Ring-opened intermediate (Ph^{β})

BP86 Energy = -1643.87007007
Enthalpy 0K= -1643.347275
Enthalpy 298K= -1643.309651
Free Energy 298K= -1643.426804

C	-4.64065	1.92585	-0.48195
C	-3.33475	1.87181	0.04829
C	-2.73116	3.04427	0.55345
C	-3.43477	4.25733	0.53567
C	-4.73643	4.30886	0.00866
C	-5.33638	3.14554	-0.49979
P	-2.38372	0.28909	0.12927
C	-3.18193	-0.83871	-1.10338
C	-2.89463	-0.63894	-2.47237
C	-3.49860	-1.45283	-3.44186
C	-4.38186	-2.47510	-3.05219
C	-4.66220	-2.68047	-1.69202
C	-4.06624	-1.86480	-0.71522
Au	-0.07146	0.63673	-0.30505
C	1.85798	1.14928	-0.64003
C	3.13813	-0.88211	-0.00872
C	2.24114	-1.90857	-0.46277
C	3.08182	0.49292	-0.42394
C	4.36880	1.24629	-0.51958
C	4.48601	2.57208	-0.03922
C	5.68800	3.27455	-0.18382
C	6.79216	2.66742	-0.80948
C	6.68958	1.35174	-1.28818
C	5.48839	0.64293	-1.14336
C	4.27515	-1.30766	0.90575
C	-2.71751	-0.43707	1.79569
C	-3.88002	-0.11031	2.52420
C	-4.10583	-0.69982	3.77822
C	-3.17815	-1.61137	4.30838
C	-2.01732	-1.93495	3.58597
C	-1.78255	-1.34735	2.33401
H	2.01014	2.20127	-0.94001
H	-1.71249	3.00594	0.95606
H	-2.96313	5.16430	0.92655
H	-5.28099	5.25800	-0.01062
H	-6.34825	3.18497	-0.91503
H	-5.10930	1.02349	-0.88701
H	-4.60020	0.60747	2.11913
H	-5.00707	-0.44167	4.34295
H	-3.35639	-2.06438	5.28864
H	-1.28933	-2.63817	4.00273
H	-0.87176	-1.58820	1.77368
H	-4.29009	-2.02568	0.34387
H	-5.35038	-3.47487	-1.38635
H	-4.85170	-3.10999	-3.80994
H	-3.28154	-1.28762	-4.50207
H	-2.20720	0.15858	-2.77756
H	5.40778	-0.37387	-1.54221
H	7.54161	0.87838	-1.78564
H	7.72868	3.22169	-0.92505
H	5.76827	4.29703	0.19805
H	3.63896	3.04003	0.47355
C	1.49933	-1.75143	-1.67959
C	0.61563	-2.74699	-2.10481
C	0.45241	-3.91428	-1.33807
C	1.18790	-4.09902	-0.14655
C	2.08367	-3.12251	0.27995
H	1.70211	-0.88704	-2.31592
H	0.06971	-2.62655	-3.04446
H	-0.22767	-4.69991	-1.68220
H	1.06506	-5.01773	0.43425
H	2.66237	-3.27429	1.19431
O	4.33407	-0.52608	2.00024
O	5.00785	-2.25698	0.65700
C	5.42827	-0.83092	2.91516

```
H    5.26474 -0.18168  3.78369
H    5.40438 -1.89325  3.20110
H    6.38904 -0.60407  2.42847
```

C-C bond formation TS (Ph^{β})

```
BP86 Energy =  -1643.86483770
Enthalpy 0K=  -1643.342685
Enthalpy 298K=  -1643.305937
Free Energy 298K=  -1643.420517
Nimag=1 (-99.2970cm-1)


C  -4.30102  2.29470 -0.22170
C  -2.98564  2.01484  0.20138
C  -2.15999  3.05869  0.67354
C  -2.65309  4.37011  0.72934
C  -3.96459  4.64785  0.30731
C  -4.78495  3.61226 -0.16760
P  -2.30452  0.29685  0.17936
C  -3.43570 -0.69004 -0.90033
C  -3.28391 -0.58150 -2.30063
C  -4.14217 -1.28841 -3.15506
C  -5.14590 -2.11377 -2.61890
C  -5.29265 -2.22947 -1.22741
C  -4.44164 -1.51933 -0.36432
Au -0.07083  0.23920 -0.60647
C   1.84031  0.40657 -1.29561
C   3.28634 -1.07077  0.02322
C   2.49223 -2.15167 -0.49244
C   3.05803  0.19137 -0.56741
C   4.05496  1.29297 -0.59489
C   3.62785  2.63637 -0.47016
C   4.55067  3.68617 -0.57108
C   5.90794  3.40973 -0.80296
C   6.34236  2.07836 -0.93104
C   5.42596  1.02532 -0.82740
C   4.29209 -1.33668  1.11105
C  -2.49478 -0.35966  1.89484
C  -3.46297  0.16163  2.77828
C  -3.59506 -0.38101  4.06643
C  -2.76697 -1.43880  4.47625
C  -1.79972 -1.95677  3.59854
C  -1.65844 -1.41762  2.31141
H   1.95943  1.05399 -2.18424
H  -1.13492  2.84358  0.99617
H  -2.01078  5.17683  1.09610
H  -4.34511  5.67330  0.34481
H  -5.80544  3.82712 -0.49960
H  -4.94223  1.49169 -0.59796
H  -4.10375  0.99223  2.46581
H  -4.34461  0.02760  4.75124
H  -2.87106 -1.85579  5.48279
H  -1.14905 -2.77616  3.91990
H  -0.89706 -1.81283  1.62918
H  -4.55980 -1.61260  0.71969
H  -6.07258 -2.87291 -0.80836
H  -5.81228 -2.66818 -3.28706
H  -4.02569 -1.19716 -4.23958
H  -2.49954  0.06020 -2.71864
H   5.76389 -0.00841 -0.95675
H   7.39834  1.86111 -1.11937
H   6.62815  4.22982 -0.88283
H   4.21144  4.72091 -0.46247
H   2.57485  2.84938 -0.25647
C   1.87509 -1.97484 -1.78423
C   0.89376 -2.88166 -2.24935
C   0.58983 -4.00637 -1.48518
C   1.24903 -4.23604 -0.24666
C   2.19148 -3.33947  0.24269
H   2.36445 -1.32229 -2.51777
H   0.44487 -2.73910 -3.23622
H  -0.12519 -4.74482 -1.86108
H   1.00502 -5.13182  0.33286
H   2.68531 -3.51177  1.20109
O   4.47041 -0.24952  1.89791
O   4.83396 -2.42299  1.28903
C   5.42800 -0.43341  2.97644
H   5.43388  0.51886  3.52096
H   5.11293 -1.26166  3.62955
H   6.42441 -0.65847  2.56559
```

Indene precursor (Ph^{β})

```
BP86 Energy =  -1643.90110221
Enthalpy 0K=  -1643.377082
Enthalpy 298K=  -1643.340412
Free Energy 298K=  -1643.453529


C  -4.66347 -0.82653 -0.72662
C  -3.47478 -0.14629 -1.06194
C  -3.28100  0.32953 -2.37745
C  -4.27628  0.13409 -3.34569
C  -5.46127 -0.54333 -3.00997
C  -5.65258 -1.02273 -1.70422
P  -2.15625  0.16465  0.19301
C  -2.47647 -0.98959  1.59874
C  -1.94427 -2.29578  1.53867
C  -2.20157 -3.20411  2.57554
C  -2.98029 -2.81240  3.67788
C  -3.50379 -1.51108  3.74313
C  -3.25483 -0.59615  2.70741
Au -0.01306 -0.11925 -0.71219
C   1.90947 -0.48084 -1.65471
C   3.48476 -0.89084  0.07516
C   3.08611 -2.15865 -0.39700
C   2.86760  0.12349 -0.73724
C   3.23201  1.54424 -0.80232
C   2.27597  2.53050 -1.15592
C   2.65342  3.86819 -1.31264
C   3.99683  4.24556 -1.13901
C   4.95859  3.27776 -0.80188
C   4.58217  1.94204 -0.62466
C   4.30257 -0.74309  1.31286
C  -2.43249  1.87151  0.84221
C  -3.65810  2.54152  0.64984
C  -3.83985  3.82641  1.18711
C  -2.80727  4.44166  1.91283
C  -1.58490  3.77435  2.10420
C  -1.39243  2.49341  1.56738
H   1.82321 -0.00170 -2.64176
H  -2.35344  0.85076 -2.64078
H  -4.12383  0.50508 -4.36400
H  -6.23398 -0.70096 -3.76881
H  -6.57331 -1.55331 -1.44250
H  -4.81444 -1.20488  0.28911
H  -4.46329  2.06469  0.08259
```

H	-4.79101	4.34613	1.03555
H	-2.95309	5.44417	2.32701
H	-0.77807	4.25411	2.66692
H	-0.43718	1.97537	1.71052
H	-3.65929	0.41917	2.76565
H	-4.10621	-1.20291	4.60327
H	-3.17433	-3.52074	4.48928
H	-1.78790	-4.21623	2.52702
H	-1.32784	-2.59652	0.68375
H	5.34217	1.19131	-0.39203
H	6.00745	3.56510	-0.68076
H	4.29323	5.29144	-1.26606
H	1.89973	4.61958	-1.56737
H	1.22431	2.23907	-1.26913
C	2.25702	-1.98946	-1.63724
C	1.33828	-3.12015	-1.96876
C	1.50834	-4.32752	-1.35327
C	2.49819	-4.49838	-0.31063
C	3.27190	-3.45470	0.16531
H	3.00305	-2.06046	-2.47608
H	0.62377	-2.99093	-2.78845
H	0.89918	-5.18780	-1.64697
H	2.60866	-5.49041	0.14038
H	3.96523	-3.58115	0.99984
O	4.10163	0.45477	1.92343
O	5.02974	-1.62598	1.76008
C	4.85077	0.63394	3.15577
H	4.60197	1.64596	3.49933
H	4.54852	-0.11924	3.89975
H	5.93100	0.53614	2.96713

Ring-opening TS (Ph$^{\alpha}$)

BP86 Energy = -1643.83583439
Enthalpy 0K= -1643.315105
Enthalpy 298K= -1643.277649
Free Energy 298K= -1643.393539
Nimag=1 (-302.0193cm-1)

C	3.72750	2.24831	1.01903
C	2.65379	1.93545	0.15988
C	2.03070	2.95512	-0.59252
C	2.48796	4.27695	-0.49121
C	3.55785	4.58805	0.36545
C	4.17412	3.57596	1.11889
P	2.05919	0.19892	-0.03531
C	2.65751	-0.74262	1.43376
C	1.88193	-0.72918	2.61280
C	2.34373	-1.38812	3.76112
C	3.57236	-2.06990	3.73478
C	4.34028	-2.09323	2.55916
C	3.88820	-1.43171	1.40598
Au	-0.26992	0.15138	-0.25678
C	-2.88587	-0.22271	-1.51213
C	-3.11342	-1.18019	-0.43858
C	-2.19567	-2.26426	-0.00577
C	-2.37586	0.53155	-0.49023
C	-2.81071	1.86513	-0.03802
C	-3.85064	2.55639	-0.71339
C	-4.24873	3.82655	-0.28366
C	-3.62966	4.42336	0.83023
C	-2.61030	3.74372	1.51846
C	-2.20369	2.47447	1.08982
C	-4.57159	-1.31693	-0.02809
C	2.92742	-0.50148	-1.50699
C	3.99884	0.17806	-2.12184
C	4.64259	-0.39822	-3.22937
C	4.22251	-1.64349	-3.72249
C	3.15374	-2.32044	-3.10918
C	2.50143	-1.75204	-2.00627
H	-3.43056	-0.02959	-2.44448
H	1.18832	2.71372	-1.25084
H	2.00314	5.06504	-1.07565
H	3.90822	5.62152	0.44885
H	5.00474	3.81740	1.78931
H	4.20862	1.46319	1.61031
H	4.32759	1.14983	-1.74150
H	5.47352	0.13068	-3.70632
H	4.72553	-2.08658	-4.58758
H	2.82495	-3.29040	-3.49523
H	1.66519	-2.27663	-1.53038
H	4.48693	-1.45632	0.49017
H	5.29445	-2.62874	2.53578
H	3.92859	-2.58861	4.63024
H	1.74064	-1.37549	4.67428
H	0.91762	-0.20892	2.62785
H	-1.41579	1.93313	1.62459
H	-2.13528	4.20239	2.39093
H	-3.95060	5.41405	1.16699
H	-5.05040	4.35222	-0.81170
H	-4.34970	2.08703	-1.56615
C	-2.16391	-2.72844	1.32868
C	-1.34039	-3.80729	1.67594
C	-0.55196	-4.44560	0.70223
C	-0.59002	-3.99974	-0.62928
C	-1.40410	-2.91441	-0.98528
H	-2.79327	-2.24963	2.08211
H	-1.32294	-4.16052	2.71157
H	0.07662	-5.29811	0.97758
H	-0.00736	-4.51561	-1.39939
H	-1.46098	-2.58578	-2.02840
O	-5.35230	-0.52086	-0.80623
O	-4.98303	-2.01415	0.88596
C	-6.77867	-0.57988	-0.51151
H	-7.25181	0.09307	-1.23736
H	-7.14820	-1.60952	-0.62953
H	-6.96282	-0.24085	0.51902

Ring-opened intermediate (Ph$^{\alpha}$)

BP86 Energy = -1643.89236942
Enthalpy 0K= -1643.368620
Enthalpy 298K= -1643.331265
Free Energy 298K= -1643.446261

C	3.80394	-0.02629	2.43496
C	2.73324	0.63050	1.79279
C	2.20636	1.81819	2.34314
C	2.75419	2.34978	3.51996
C	3.82400	1.69709	4.15487
C	4.34610	0.51091	3.61341
P	2.01683	-0.01782	0.21547
C	2.38025	-1.83135	0.22304
C	1.56176	-2.67043	1.01026
C	1.83445	-4.04392	1.08554
C	2.91413	-4.58806	0.36848

C	3.72220	-3.75697	-0.42358
C	3.46073	-2.37862	-0.49821
Au	-0.28596	0.51846	-0.00411
C	-3.27137	0.17005	0.39542
C	-3.29686	-1.20512	0.15710
C	-2.49026	-1.85308	-0.87075
C	-2.26496	1.10550	0.00293
C	-2.64024	2.49658	-0.18738
C	-4.00446	2.89961	-0.34188
C	-4.33610	4.23718	-0.55410
C	-3.32149	5.21449	-0.61336
C	-1.96979	4.84612	-0.47442
C	-1.63399	3.50648	-0.27478
C	-4.23211	-2.03228	1.00723
C	3.02110	0.71244	-1.15505
C	4.30620	1.24869	-0.93356
C	5.03536	1.78157	-2.00907
C	4.48971	1.78178	-3.30286
C	3.20824	1.24982	-3.52589
C	2.47171	0.72038	-2.45603
H	-4.10205	0.55103	1.00519
H	1.36380	2.31832	1.85262
H	2.34005	3.26913	3.94567
H	4.24642	2.10941	5.07649
H	5.17497	-0.00241	4.11072
H	4.20510	-0.95749	2.02241
H	4.73355	1.25849	0.07392
H	6.03133	2.19954	-1.83234
H	5.06058	2.20098	-4.13725
H	2.77869	1.25434	-4.53268
H	1.46789	0.31437	-2.62663
H	4.09488	-1.73414	-1.11494
H	4.56233	-4.17887	-0.98418
H	3.12437	-5.66066	0.42688
H	1.20249	-4.68961	1.70344
H	0.71736	-2.24808	1.56668
H	-0.58629	3.20108	-0.17474
H	-1.18559	5.60699	-0.52788
H	-3.58673	6.26413	-0.77567
H	-5.38330	4.52862	-0.67831
H	-4.79757	2.14596	-0.31632
C	-2.06780	-3.21137	-0.77575
C	-1.29823	-3.78038	-1.79174
C	-0.94902	-3.03382	-2.93552
C	-1.37511	-1.70252	-3.06099
C	-2.14018	-1.11510	-2.04502
H	-2.33689	-3.78413	0.11344
H	-0.96565	-4.81841	-1.69727
H	-0.36844	-3.50123	-3.73716
H	-1.14836	-1.13243	-3.96706
H	-2.56849	-0.12071	-2.19685
O	-5.39248	-1.37846	1.25481
O	-3.95976	-3.14501	1.44450
C	-6.32414	-2.09924	2.11259
H	-7.22794	-1.47810	2.14056
H	-6.53862	-3.09175	1.68855
H	-5.89664	-2.21926	3.11988