ELECTRONIC SUPPLEMENTARY INFORMATION

Concerted, highly asynchronous, enzyme-catalyzed [4+2] cycloaddition in the biosynthesis of spinosyn A; computational evidence

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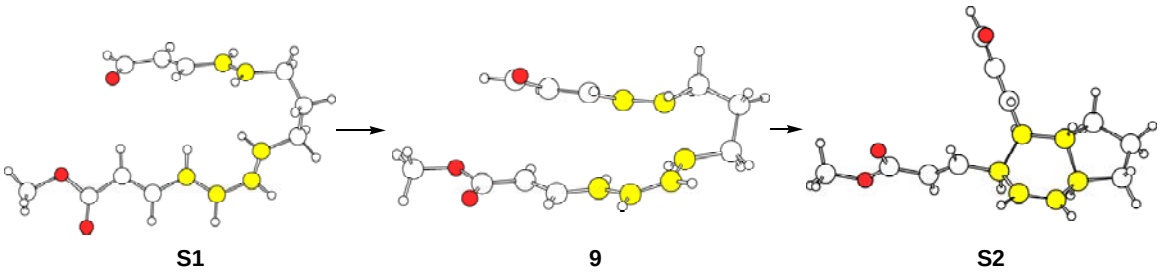
Transition structure **9**, a conformer transition structure **6** was found, which by way of its IRC was shown to link **S1** with a Diels-Alder product (**S2**).



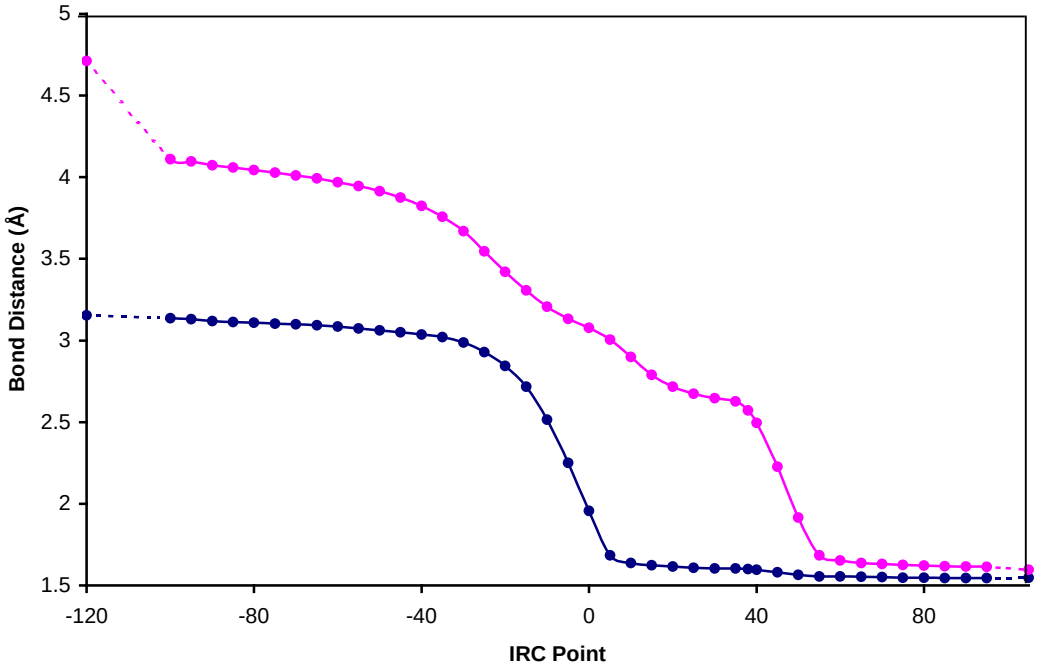


Figure S1 | A plot of the bond distances of the two forming sigma bonds vs. the IRC point. Point 0 is the TS (**9**). The points at -120 and +120 reactant (**S1**) and product (**S2**) respectively.

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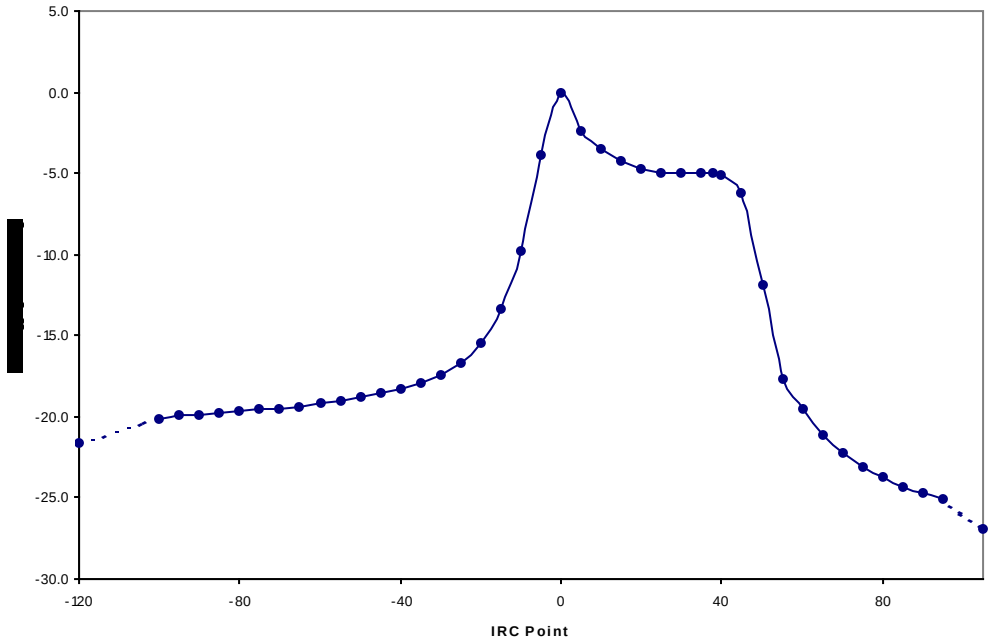

Figure S2 | A plot of the energies of the IRC points. Point 0 is the TS (**9**). The points at -120 and +120 represent reactant (**S1**) and product (**S2**) respectively.

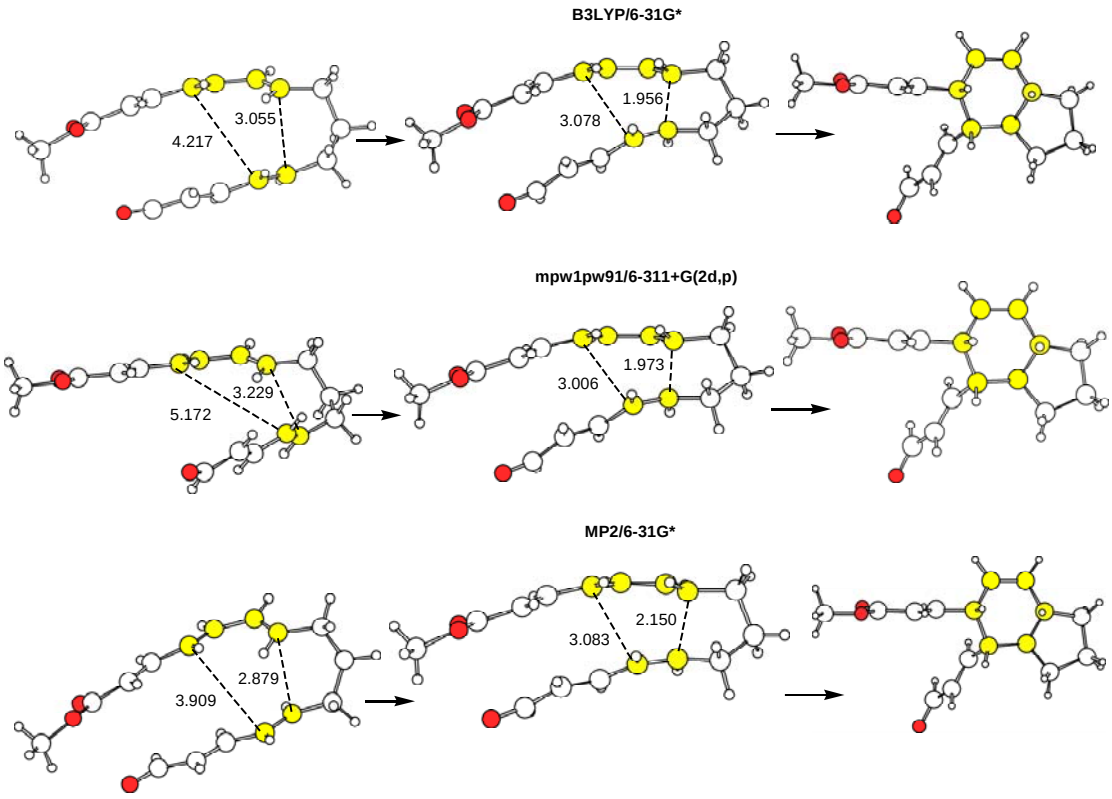

Figure S3 | Optimized geometries of reactant (**S1**), transition structure (**9**) and product (**S2**). Bond distances are in Ångstroms

7 → 6 → 8 (energies)

	B3LYP	with ZPE	MPW[1]+ZPE	MPW	with ZPE	MP2	with ZPE[2]
reactant	-847.344683	-847.018986	-847.049883	-847.377418	-847.052321	-844.615128	-844.289157
TS	-847.311372	-846.984846	-847.018110	-847.346858	-847.020892	-844.599140723	-844.272703
product	-847.354736	-847.024206	-847.069463	-847.402078	-847.071644	-844.651564	-844.232024
Eact =	**20.9**	**21.4**	**19.9**	**19.2**	**19.7**	**10.0**	**10.3**
Ereact=	**-6.3**	**-3.3**	**-12.3**	**-15.5**	**-12.1**	**-22.9**	**-20.0**

[1]Single point at B3LYP geometry. [2]ZPE from B3LYP

S1 → 9 → S2 (energies)

	B3LYP/6-31G*	with ZPE	MPW[1]+ZPE	
reactant	-847.343943	-847.017972	-847.046335	a.u.
TS	-847.309580	-846.983143	-847.016091	a.u.
+product	-847.352544	-847.022000	-847.065781	a.u.
Eact =	**21.6**	**21.9**	**19.0**	kcal/mol
Ereact=	**-5.4**	**-2.5**	**-12.2**	kcal/mol

[1]Single point at B3LYP geometry

13 → 12 → 14 (energies)

	B3LYP/6-31G*	with ZPE	MPW[1]+ZPE	
reactant	1042.716885	-1042.267200	-1042.306021	a.u.
TS	-1042.679490	-1042.228935	-1042.271610	a.u.
product	-1042.721558	-1042.266874	-1042.320384	a.u.
Eact =	**23.5**	**24**	**21.6**	kcal/mol
Ereact=	**-2.9**	**0.2**	**-9**	kcal/mol

[1]Single point at B3LYP geometry

REACTANT DFT (7)

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#6-31G* B3LYP freq(noraman) nopop
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1	6	0	2.315545	-2.066701	-0.477061
2	6	0	-0.763487	-1.797964	-0.241153
3	6	0	1.436563	-3.027066	-0.131098
4	6	0	0.005988	-2.862598	0.094709
5	6	0	3.672477	0.672729	0.662133
6	6	0	3.143295	1.683104	-0.055688
7	6	0	4.878454	-0.130150	0.271404
8	6	0	4.717584	-1.663432	0.357628
9	6	0	3.782458	-2.309016	-0.693858
10	6	0	2.001368	2.460296	0.375749
11	6	0	1.448116	3.481565	-0.316111
12	6	0	0.291700	4.215389	0.200925
13	8	0	-0.250130	5.144384	-0.372539
14	6	0	-2.978694	-0.692466	-0.259232
15	6	0	-2.172844	-1.731476	0.050281
16	6	0	-4.409745	-0.724335	0.088451
17	8	0	-4.988609	-1.633459	0.656167
18	8	0	-5.028283	0.416633	-0.309925
19	6	0	-6.429192	0.485759	-0.013693
20	1	0	1.968654	-1.041892	-0.594666
21	1	0	-0.322648	-0.947943	-0.760858
22	1	0	1.817065	-4.038818	0.014375
23	1	0	-0.490638	-3.703373	0.579399
24	1	0	3.217691	0.421254	1.622516
25	1	0	3.587197	1.947794	-1.015733
26	1	0	5.701319	0.147094	0.949495
27	1	0	5.204354	0.154458	-0.737908
28	1	0	4.375751	-1.942104	1.363288
29	1	0	5.714613	-2.105723	0.236280
30	1	0	3.967803	-3.390535	-0.698950
31	1	0	4.073781	-1.938601	-1.689051
32	1	0	1.562580	2.190171	1.338532
33	1	0	1.840286	3.799176	-1.280263
34	1	0	-0.079586	3.860431	1.190022
35	1	0	-2.607637	0.193075	-0.767291
36	1	0	-2.624640	-2.581666	0.560501
37	1	0	-6.761715	1.453839	-0.390210
38	1	0	-6.600088	0.413634	1.064168
39	1	0	-6.969703	-0.325453	-0.509801

```
SCF Done:  E(RB3LYP) =  -847.344683209     A.U. after   15 cycles

Frequencies --    11.0126                15.6022                29.5137

Zero-point correction=                           0.325697 (Hartree/Particle)
Thermal correction to Energy=                    0.347099
Thermal correction to Enthalpy=                  0.348043
Thermal correction to Gibbs Free Energy=         0.270245
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Sum of electronic and zero-point Energies=           -847.018987
Sum of electronic and thermal Energies=              -846.997584
Sum of electronic and thermal Enthalpies=            -846.996640
Sum of electronic and thermal Free Energies=         -847.074438
Displacement     0.001103     0.001200     YES

SCF Done:  E(RmPW1PW91) =  -847.375579884
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TS DFT (6)

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#6-31g* b3lyp nopop freq(noraman) guess=read geom=check
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1	6	0	3.496167	1.372180	0.016152
2	6	0	0.553879	1.811842	-0.289710
3	6	0	2.888777	2.096172	-1.040050
4	6	0	1.511239	2.258747	-1.195310
5	6	0	3.185289	-0.532248	-0.309398
6	6	0	1.899464	-0.928976	0.134860
7	6	0	4.426003	-0.978641	0.460055
8	6	0	5.573521	-0.042022	0.081784
9	6	0	5.018645	1.397059	0.184447
10	6	0	0.815117	-1.277612	-0.693751
11	6	0	-0.406526	-1.740426	-0.259609
12	6	0	-1.449621	-2.128101	-1.193877
13	8	0	-2.537402	-2.597724	-0.881596
14	6	0	-1.692388	0.967550	0.163062
15	6	0	-0.814947	1.656304	-0.618970
16	6	0	-3.062520	0.676682	-0.301373
17	8	0	-3.525675	1.009872	-1.377598
18	8	0	-3.737197	-0.037894	0.624420
19	6	0	-5.025300	-0.520235	0.208909
20	1	0	2.963563	1.400881	0.964682
21	1	0	0.861683	1.508837	0.707148
22	1	0	3.525443	2.394826	-1.872302
23	1	0	1.154094	2.667130	-2.140127
24	1	0	3.319955	-0.586156	-1.391755
25	1	0	1.753788	-1.032474	1.212194
26	1	0	4.659144	-2.023980	0.220769
27	1	0	4.225039	-0.935258	1.539117
28	1	0	5.877586	-0.247846	-0.952645
29	1	0	6.458914	-0.192119	0.708623
30	1	0	5.479203	2.049241	-0.565750
31	1	0	5.258642	1.826497	1.164507
32	1	0	0.961815	-1.177070	-1.770949
33	1	0	-0.606846	-1.898542	0.797809
34	1	0	-1.193027	-1.964607	-2.266343
35	1	0	-1.417626	0.617779	1.152555
36	1	0	-1.161514	1.984925	-1.597779
37	1	0	-5.440245	-1.027931	1.080242
38	1	0	-4.904861	-1.221651	-0.619480
39	1	0	-5.667693	0.309550	-0.097610

```
SCF Done:  E(RB3LYP) =  -847.311372168     A.U. after    1 cycles

Frequencies --  -422.5258                27.7151                54.8006
Zero-point correction=                          0.326526 (Hartree/Particle)
Thermal correction to Energy=                   0.345826
Thermal correction to Enthalpy=                 0.346770
Thermal correction to Gibbs Free Energy=        0.278282
Sum of electronic and zero-point Energies=          -846.984846
Sum of electronic and thermal Energies=             -846.965546
Sum of electronic and thermal Enthalpies=           -846.964602
Sum of electronic and thermal Free Energies=        -847.033090

SCF Done:  E(RmPW1PW91) =  -847.344635917
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PRODUCT DFT (8)

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#6-31G* B3LYP FREQ(NORAMAN) GUESS=READ GEOM=CHECK nopop
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1	6	0	3.127776	1.272992	0.282707
2	6	0	0.359196	0.985968	0.161920
3	6	0	2.368055	2.182131	-0.640798
4	6	0	1.045724	1.999774	-0.739941
5	6	0	2.666808	-0.183073	0.034486
6	6	0	1.146813	-0.399490	0.246116
7	6	0	3.646148	-1.008645	0.883276
8	6	0	4.996436	-0.236620	0.768124
9	6	0	4.655244	1.160167	0.161842
10	6	0	0.640299	-1.419337	-0.733621
11	6	0	0.182540	-2.643676	-0.427385
12	6	0	-0.247674	-3.583507	-1.472307
13	8	0	-0.653252	-4.710995	-1.259258
14	6	0	-2.110846	0.969574	0.664078
15	6	0	-1.091253	0.800640	-0.185628
16	6	0	-3.509011	0.766130	0.218928
17	8	0	-3.863028	0.465983	-0.904728
18	8	0	-4.370696	0.962153	1.246305
19	6	0	-5.757532	0.783699	0.922451
20	1	0	2.879810	1.526342	1.328833
21	1	0	0.405401	1.386582	1.185502
22	1	0	2.888884	2.928490	-1.237793
23	1	0	0.431769	2.599604	-1.408130
24	1	0	2.889311	-0.379499	-1.024706
25	1	0	0.972322	-0.785054	1.257970
26	1	0	3.723614	-2.049037	0.551271
27	1	0	3.305400	-1.029315	1.926673
28	1	0	5.707675	-0.772102	0.131086
29	1	0	5.471075	-0.138442	1.749867
30	1	0	4.942323	1.197285	-0.896804
31	1	0	5.181281	1.977845	0.665570
32	1	0	0.687464	-1.133933	-1.787697
33	1	0	0.113986	-2.992746	0.601259

34	1	0	-0.175858	-3.187885	-2.511545
35	1	0	-1.958494	1.258322	1.700791
36	1	0	-1.333272	0.513892	-1.208548
37	1	0	-6.301789	0.973352	1.848205
38	1	0	-5.942088	-0.234550	0.569332
39	1	0	-6.064919	1.487941	0.144414

SCF Done: E(RB3LYP) = -847.354735632 A.U. after 1 cycles

Frequencies -- 15.5271 22.7259 37.3837

Zero-point correction= 0.330529 (Hartree/Particle)
Thermal correction to Energy= 0.349548
Thermal correction to Enthalpy= 0.350492
Thermal correction to Gibbs Free Energy= 0.280133
Sum of electronic and zero-point Energies= -847.024207
Sum of electronic and thermal Energies= -847.005188
Sum of electronic and thermal Enthalpies= -847.004243
Sum of electronic and thermal Free Energies= -847.074603

SCF Done: E(RmPW1PW91) = **-847.399992204**

REACTANT MPW (7)

#6-311+G(2d,p) mpw1pw91 nopop guess=read freq(noraman)

1	6	0	2.312279	-2.063397	-0.441268
2	6	0	-0.742178	-1.803442	-0.255217
3	6	0	1.440768	-3.014467	-0.089390
4	6	0	0.023534	-2.827737	0.162869
5	6	0	3.661938	0.665893	0.634493
6	6	0	3.095690	1.658766	-0.061807
7	6	0	4.851355	-0.120444	0.202656
8	6	0	4.713817	-1.642071	0.316697
9	6	0	3.763232	-2.307111	-0.689205
10	6	0	1.962265	2.409060	0.412452
11	6	0	1.360636	3.406824	-0.255651
12	6	0	0.213938	4.101554	0.312835
13	8	0	-0.376791	5.006708	-0.227856
14	6	0	-2.932483	-0.687961	-0.314347
15	6	0	-2.135156	-1.694918	0.070300
16	6	0	-4.347248	-0.668430	0.073502
17	8	0	-4.910815	-1.501555	0.741206
18	8	0	-4.964244	0.421534	-0.417253
19	6	0	-6.346132	0.531007	-0.091015
20	1	0	1.964342	-1.039594	-0.538584
21	1	0	-0.312243	-1.021165	-0.874399
22	1	0	1.814912	-4.026386	0.048362
23	1	0	-0.462265	-3.611496	0.738679
24	1	0	3.245808	0.416074	1.609333
25	1	0	3.494478	1.923868	-1.037873

26	1	0	5.693413	0.178584	0.839991
27	1	0	5.127969	0.156072	-0.819037
28	1	0	4.406689	-1.907631	1.332925
29	1	0	5.707640	-2.074727	0.173719
30	1	0	3.947895	-3.384552	-0.681007
31	1	0	4.022895	-1.955594	-1.695688
32	1	0	1.568485	2.134914	1.389929
33	1	0	1.701700	3.731754	-1.233082
34	1	0	-0.102562	3.738057	1.313472
35	1	0	-2.568448	0.136180	-0.915748
36	1	0	-2.578918	-2.482759	0.673384
37	1	0	-6.686781	1.453229	-0.553959
38	1	0	-6.481902	0.572800	0.989366
39	1	0	-6.900510	-0.321423	-0.482849

SCF Done: E(RmPW1PW91) = -847.377417379 A.U. after 14 cycles

Frequencies -- 4.2476 11.1089 26.8683

Zero-point correction= 0.325097 (Hartree/Particle)
Thermal correction to Energy= 0.346569
Thermal correction to Enthalpy= 0.347513
Thermal correction to Gibbs Free Energy= 0.268270
Sum of electronic and zero-point Energies= -847.052320
Sum of electronic and thermal Energies= -847.030848
Sum of electronic and thermal Enthalpies= -847.029904
Sum of electronic and thermal Free Energies= -847.109147

TS MPW (6)

#6-311+G(2d,p) mpw1pw91 freq(noraman) guess=read geom=check nopop

1	6	0	3.482526	1.390014	0.018180
2	6	0	0.558178	1.728907	-0.286530
3	6	0	2.867813	2.075601	-1.036757
4	6	0	1.490295	2.195137	-1.190297
5	6	0	3.190849	-0.532800	-0.312159
6	6	0	1.914291	-0.924585	0.112264
7	6	0	4.416660	-0.937115	0.478697
8	6	0	5.550224	-0.002838	0.100574
9	6	0	4.989996	1.422825	0.186242
10	6	0	0.851580	-1.288143	-0.732223
11	6	0	-0.344615	-1.796965	-0.317317
12	6	0	-1.349757	-2.213766	-1.269666
13	8	0	-2.400726	-2.752077	-0.986590
14	6	0	-1.681953	0.898328	0.165459
15	6	0	-0.808301	1.574240	-0.610653
16	6	0	-3.061152	0.660806	-0.283797
17	8	0	-3.517256	1.004713	-1.347265
18	8	0	-3.758232	-0.002606	0.647496
19	6	0	-5.082483	-0.369863	0.266398

20	1	0	2.939943	1.384406	0.957133
21	1	0	0.870913	1.436745	0.709099
22	1	0	3.495033	2.388072	-1.866757
23	1	0	1.119354	2.585195	-2.133634
24	1	0	3.343250	-0.572551	-1.388874
25	1	0	1.756082	-1.041841	1.183278
26	1	0	4.663618	-1.980464	0.263587
27	1	0	4.198133	-0.876349	1.549408
28	1	0	5.859691	-0.215432	-0.926682
29	1	0	6.430540	-0.140435	0.730075
30	1	0	5.443570	2.069317	-0.566966
31	1	0	5.223442	1.862066	1.159143
32	1	0	1.005618	-1.171310	-1.803646
33	1	0	-0.549105	-1.978676	0.732344
34	1	0	-1.095904	-2.007860	-2.331544
35	1	0	-1.407500	0.530858	1.145561
36	1	0	-1.157963	1.916137	-1.580753
37	1	0	-5.509947	-0.867313	1.132568
38	1	0	-5.049788	-1.049508	-0.583809
39	1	0	-5.663332	0.513692	0.003767

SCF Done: E(RmPW1PW91) = -847.346857843 A.U. after 2 cycles

Frequencies -- -433.4136 26.9705 34.7686

Zero-point correction= 0.325966 (Hartree/Particle)
Thermal correction to Energy= 0.345399
Thermal correction to Enthalpy= 0.346343
Thermal correction to Gibbs Free Energy= 0.276926
Sum of electronic and zero-point Energies= -847.020892
Sum of electronic and thermal Energies= -847.001459
Sum of electronic and thermal Enthalpies= -847.000515
Sum of electronic and thermal Free Energies= -847.069932

PRODUCT MPW (8)

#6-311+G(2d,p) mpw1pw91 nopop freq(noraman) guess=read geom=check

1	6	0	3.104094	1.261072	0.270039
2	6	0	0.366301	0.977277	0.143281
3	6	0	2.359823	2.148975	-0.668732
4	6	0	1.045644	1.968750	-0.769234
5	6	0	2.649322	-0.186855	0.042551
6	6	0	1.138817	-0.395903	0.236324
7	6	0	3.608321	-0.989782	0.914623
8	6	0	4.950897	-0.228474	0.799053
9	6	0	4.620552	1.145930	0.167390
10	6	0	0.642996	-1.402518	-0.746341
11	6	0	0.182529	-2.618648	-0.450420
12	6	0	-0.235593	-3.539727	-1.505784
13	8	0	-0.640760	-4.660051	-1.313609

14	6	0	-2.080888	0.969451	0.664337
15	6	0	-1.077508	0.791436	-0.187874
16	6	0	-3.476977	0.760464	0.236305
17	8	0	-3.837191	0.455339	-0.872064
18	8	0	-4.323193	0.957755	1.260640
19	6	0	-5.701949	0.771852	0.948806
20	1	0	2.843117	1.531412	1.305014
21	1	0	0.421803	1.392041	1.156861
22	1	0	2.880604	2.883579	-1.273807
23	1	0	0.438980	2.555584	-1.449761
24	1	0	2.886441	-0.400740	-1.006986
25	1	0	0.951938	-0.783795	1.241306
26	1	0	3.688290	-2.033906	0.609562
27	1	0	3.254655	-0.984451	1.949697
28	1	0	5.664697	-0.775695	0.182374
29	1	0	5.414546	-0.112889	1.779507
30	1	0	4.915067	1.161586	-0.885602
31	1	0	5.141630	1.969574	0.657275
32	1	0	0.698002	-1.117005	-1.797007
33	1	0	0.102671	-2.972351	0.572447
34	1	0	-0.155208	-3.135374	-2.536943
35	1	0	-1.917792	1.269517	1.693080
36	1	0	-1.332322	0.492438	-1.201660
37	1	0	-6.241591	0.960731	1.872761
38	1	0	-5.880251	-0.245339	0.601856
39	1	0	-6.014875	1.469701	0.172851

SCF Done: E(RmPW1PW91) = -847.402078008 A.U. after 2 cycles

Zero-point correction= 0.330434 (Hartree/Particle)
Thermal correction to Energy= 0.349429
Thermal correction to Enthalpy= 0.350373
Thermal correction to Gibbs Free Energy= 0.279988
Sum of electronic and zero-point Energies= -847.071644
Sum of electronic and thermal Energies= -847.052649
Sum of electronic and thermal Enthalpies= -847.051705
Sum of electronic and thermal Free Energies= -847.122090

REACTANT MP2 (7)

#6-31g* mp2 nopop guess=read geom=check opt(readfc)

1	6	0	2.645240	-2.110581	-0.720342
2	6	0	-0.334373	-1.769625	-0.349851
3	6	0	1.880874	-2.827206	0.133714
4	6	0	0.492861	-2.508259	0.435437
5	6	0	3.155908	0.385263	0.621803
6	6	0	2.203034	1.173924	0.075443
7	6	0	4.506346	0.111287	0.030345
8	6	0	4.907398	-1.371456	0.072135
9	6	0	4.122192	-2.278835	-0.895284

10	6	0	0.909243	1.379737	0.687379
11	6	0	-0.086924	2.134331	0.163502
12	6	0	-1.377355	2.250942	0.841543
13	8	0	-2.318559	2.921820	0.414307
14	6	0	-2.384751	-0.435142	-0.614213
15	6	0	-1.618095	-1.293904	0.095187
16	6	0	-3.611978	0.130698	-0.022846
17	8	0	-4.004938	-0.065813	1.120274
18	8	0	-4.237966	0.934012	-0.911964
19	6	0	-5.344097	1.671777	-0.353132
20	1	0	2.184216	-1.285552	-1.257045
21	1	0	-0.004349	-1.463748	-1.342901
22	1	0	2.344445	-3.629573	0.709607
23	1	0	0.110124	-2.849270	1.398961
24	1	0	2.949443	-0.081272	1.587494
25	1	0	2.388370	1.656440	-0.885849
26	1	0	5.258765	0.677749	0.598484
27	1	0	4.548129	0.488470	-1.000095
28	1	0	4.762541	-1.745103	1.093908
29	1	0	5.978986	-1.460204	-0.146813
30	1	0	4.415042	-3.320785	-0.716051
31	1	0	4.407776	-2.037623	-1.926900
32	1	0	0.727559	0.866987	1.634828
33	1	0	0.030760	2.670640	-0.776700
34	1	0	-1.472253	1.682398	1.790030
35	1	0	-2.105125	-0.100422	-1.609846
36	1	0	-1.964819	-1.583587	1.088040
37	1	0	-5.746370	2.247603	-1.184384
38	1	0	-4.975509	2.330084	0.434020
39	1	0	-6.094784	0.989810	0.048714

SCF Done: E(RHF) = -842.036390688 A.U. after 1 cycles

E2 = -0.2578739123D+01 EUMP2 = -0.84461512981037D+03

Maximum Force	0.000018	0.000450	YES
RMS Force	0.000004	0.000300	YES
Maximum Displacement	0.001421	0.001800	YES
RMS Displacement	0.000339	0.001200	YES

TS MP2 (6)

#6-31g* mp2 nopop opt(TS,noeigentest,READFC) guess=read geom=check

1	6	0	3.501214	1.457319	0.057896
2	6	0	0.576438	1.763076	-0.349635
3	6	0	2.925221	2.091506	-1.045400
4	6	0	1.539513	2.192954	-1.253106
5	6	0	3.162207	-0.635942	-0.299809
6	6	0	1.892384	-0.975930	0.169349
7	6	0	4.425758	-0.975614	0.451513

8	6	0	5.523496	-0.004911	0.034906
9	6	0	4.997586	1.420842	0.273273
10	6	0	0.773061	-1.211534	-0.661136
11	6	0	-0.467597	-1.614074	-0.226929
12	6	0	-1.514310	-1.947993	-1.181733
13	8	0	-2.599175	-2.455262	-0.883777
14	6	0	-1.637663	0.881096	0.110044
15	6	0	-0.781830	1.586335	-0.690235
16	6	0	-3.008380	0.573318	-0.332734
17	8	0	-3.471871	0.832214	-1.436580
18	8	0	-3.686657	-0.067507	0.645960
19	6	0	-4.987223	-0.543477	0.239623
20	1	0	2.903631	1.409894	0.965717
21	1	0	0.876066	1.488008	0.661030
22	1	0	3.585022	2.366288	-1.870028
23	1	0	1.192325	2.545298	-2.225502
24	1	0	3.272568	-0.626050	-1.387480
25	1	0	1.763208	-1.115718	1.246720
26	1	0	4.718444	-2.011690	0.233439
27	1	0	4.243933	-0.916234	1.533047
28	1	0	5.726607	-0.143283	-1.034192
29	1	0	6.464641	-0.186249	0.565946
30	1	0	5.499634	2.136910	-0.387352
31	1	0	5.216932	1.726617	1.303013
32	1	0	0.914640	-1.067136	-1.735761
33	1	0	-0.660622	-1.833932	0.822033
34	1	0	-1.274920	-1.711868	-2.241904
35	1	0	-1.363989	0.607880	1.125314
36	1	0	-1.130687	1.872656	-1.683194
37	1	0	-5.394532	-1.032526	1.122399
38	1	0	-4.873613	-1.252402	-0.580147
39	1	0	-5.617875	0.291679	-0.069230

SCF Done: E(RHF) = -841.973033111 A.U. after 8 cycles

E2 = -0.2626106461D+01 EUMP2 = -0.84459913957242D+03

Maximum Force	0.000039	0.000450	YES
RMS Force	0.000006	0.000300	YES
Maximum Displacement	0.000513	0.001800	YES
RMS Displacement	0.000116	0.001200	YES

PRODUCT MP2 (8)

#6-31g* b3lyp nopop freq(noraman)

1	6	0	3.106629	1.264254	0.245461
2	6	0	0.383297	0.996562	0.098233
3	6	0	2.396779	2.100775	-0.771114
4	6	0	1.067082	1.922056	-0.880421

5	6	0	2.651367	-0.194868	0.071345
6	6	0	1.130603	-0.385623	0.214924
7	6	0	3.569078	-0.954915	1.027638
8	6	0	4.926173	-0.210751	0.910941
9	6	0	4.627514	1.130316	0.185965
10	6	0	0.649466	-1.360238	-0.810636
11	6	0	0.141141	-2.579079	-0.548441
12	6	0	-0.265455	-3.475451	-1.636978
13	8	0	-0.718261	-4.604461	-1.464755
14	6	0	-2.057804	0.979713	0.683342
15	6	0	-1.067354	0.800340	-0.204609
16	6	0	-3.463150	0.741491	0.287974
17	8	0	-3.850105	0.414655	-0.824590
18	8	0	-4.291518	0.936359	1.345289
19	6	0	-5.684296	0.717752	1.044133
20	1	0	2.818274	1.584769	1.262123
21	1	0	0.465075	1.451275	1.098363
22	1	0	2.943765	2.778743	-1.424822
23	1	0	0.468378	2.460437	-1.613072
24	1	0	2.934894	-0.461732	-0.958257
25	1	0	0.896132	-0.785428	1.211753
26	1	0	3.644806	-2.020888	0.789244
27	1	0	3.173913	-0.878118	2.048177
28	1	0	5.655719	-0.801883	0.349371
29	1	0	5.359758	-0.037089	1.900485
30	1	0	4.941602	1.076813	-0.863486
31	1	0	5.149315	1.980462	0.637023
32	1	0	0.756718	-1.049947	-1.854456
33	1	0	0.014792	-2.944389	0.469004
34	1	0	-0.135867	-3.064117	-2.660947
35	1	0	-1.870254	1.295347	1.706422
36	1	0	-1.343261	0.483789	-1.211029
37	1	0	-6.209093	0.908663	1.978069
38	1	0	-5.843845	-0.308755	0.710726
39	1	0	-6.016365	1.404121	0.263725

SCF Done: E(RHF) = -842.066546261 A.U. after 11 cycles

E2 = -0.2585018132D+01 EUMP2 = -0.84465156439327D+03

Maximum	Force	0.000014	0.000450	YES
RMS	Force	0.000002	0.000300	YES
Maximum	Displacement	0.001019	0.001800	YES
RMS	Displacement	0.000230	0.001200	YES

REACTANT C-CH=O CONF. DFT (S1)

#b3lyp 6-31g* freq(noraman) guess=read geom=check nopop

1	6	0	2.473781	-2.099282	-0.614483
2	6	0	-0.536236	-1.637833	-0.063636
3	6	0	1.566593	-3.011260	-0.215758
4	6	0	0.122138	-2.819889	-0.149295
5	6	0	3.444102	0.597154	0.699880
6	6	0	2.923587	1.560346	-0.087673
7	6	0	4.767173	-0.078650	0.497483
8	6	0	4.716224	-1.621465	0.552870
9	6	0	3.961669	-2.320728	-0.605540
10	6	0	1.611808	2.123498	0.128556
11	6	0	1.012773	3.049593	-0.655491
12	6	0	-0.356369	3.507931	-0.381008
13	8	0	-1.080725	3.053516	0.492479
14	6	0	-2.670754	-0.391296	0.110592
15	6	0	-1.974097	-1.542360	-0.010571
16	6	0	-4.144306	-0.425173	0.153683
17	8	0	-4.840163	-1.424183	0.095522
18	8	0	-4.654997	0.826502	0.268180
19	6	0	-6.084422	0.898540	0.324103
20	1	0	2.125762	-1.130138	-0.963464
21	1	0	0.024720	-0.705379	-0.014386
22	1	0	1.923600	-4.001197	0.073130
23	1	0	-0.476775	-3.731054	-0.142210
24	1	0	2.862688	0.263160	1.561277
25	1	0	3.486468	1.910500	-0.953570
26	1	0	5.450657	0.252574	1.295445
27	1	0	5.215398	0.250192	-0.449524
28	1	0	4.272180	-1.935957	1.506620
29	1	0	5.750345	-1.989562	0.554531
30	1	0	4.164700	-3.396981	-0.534492
31	1	0	4.394320	-1.981052	-1.558323
32	1	0	1.042271	1.755319	0.982271
33	1	0	1.524495	3.478351	-1.515431
34	1	0	-0.723373	4.323914	-1.039510
35	1	0	-2.187346	0.579491	0.186806
36	1	0	-2.543322	-2.469666	-0.069876
37	1	0	-6.321746	1.959451	0.412882
38	1	0	-6.466415	0.346705	1.187959
39	1	0	-6.529673	0.479923	-0.583227

SCF Done: E(RB3LYP) = -847.343943626 A.U. after 1 cycles

Frequencies -- 20.4892 25.1475 32.0135

Zero-point correction= 0.325971 (Hartree/Particle)
Thermal correction to Energy= 0.347201
Thermal correction to Enthalpy= 0.348145
Thermal correction to Gibbs Free Energy= 0.272126
Sum of electronic and zero-point Energies= -847.017973
Sum of electronic and thermal Energies= -846.996743
Sum of electronic and thermal Enthalpies= -846.995798
Sum of electronic and thermal Free Energies= -847.071818

SCF Done: E(RmPW1PW91) = **-847.372306**

TS DFT Conf. (C-CH=O)(9)

```
---------------------------------------------------
#b3lyp 6-31g* freq(noraman) guess=read geom=check nopop
---------------------------------------------------
```

1	6	0	3.702157	-0.544037	0.080948
2	6	0	0.902095	-1.478217	0.561404
3	6	0	3.249828	-1.178801	1.264283
4	6	0	1.932114	-1.581304	1.490508
5	6	0	3.039015	1.295880	0.080049
6	6	0	1.691060	1.353437	-0.352033
7	6	0	4.153376	1.811615	-0.826479
8	6	0	5.468628	1.196252	-0.346599
9	6	0	5.200341	-0.312341	-0.137088
10	6	0	0.584644	1.626836	0.473673
11	6	0	-0.718758	1.747327	0.049118
12	6	0	-1.791221	2.081580	0.979850
13	8	0	-1.640713	2.307895	2.175074
14	6	0	-1.480420	-1.237641	0.061227
15	6	0	-0.468002	-1.592355	0.902576
16	6	0	-2.885180	-1.310332	0.497912
17	8	0	-3.276445	-1.725733	1.572790
18	8	0	-3.718547	-0.849467	-0.472068
19	6	0	-5.112857	-0.878106	-0.136077
20	1	0	3.183163	-0.837636	-0.829391
21	1	0	1.137373	-1.257333	-0.475699
22	1	0	3.934259	-1.204282	2.111437
23	1	0	1.667623	-1.902399	2.497249
24	1	0	3.183042	1.573161	1.126105
25	1	0	1.502909	1.226816	-1.420686
26	1	0	4.183913	2.908169	-0.795911
27	1	0	3.943855	1.526675	-1.866516
28	1	0	5.751856	1.656867	0.608418
29	1	0	6.293147	1.379135	-1.043753
30	1	0	5.776613	-0.698331	0.710877
31	1	0	5.519450	-0.880824	-1.018928
32	1	0	0.760993	1.767439	1.539710
33	1	0	-0.975792	1.645933	-1.003359
34	1	0	-2.805579	2.123512	0.526245
35	1	0	-1.290273	-0.938425	-0.963725
36	1	0	-0.733920	-1.880875	1.918328
37	1	0	-5.633035	-0.475526	-1.006182
38	1	0	-5.309380	-0.264493	0.747456
39	1	0	-5.440071	-1.901849	0.066704

```
SCF Done:  E(RB3LYP) =  -847.309580047     A.U. after    1 cycles

Frequencies --  -421.6272                30.0756                38.4409

Zero-point correction=                           0.326437 (Hartree/Particle)
Thermal correction to Energy=                    0.345828
Thermal correction to Enthalpy=                  0.346772
Thermal correction to Gibbs Free Energy=         0.277432
```

```
Sum of electronic and zero-point Energies=           -846.983143
Sum of electronic and thermal Energies=              -846.963753
Sum of electronic and thermal Enthalpies=            -846.962808
Sum of electronic and thermal Free Energies=         -847.032148

SCF Done:  E(RmPW1PW91) =  -847.3425276
```

PRODUCT - C-CH=O CONF DFT (S2)

```
---------------------------------------------------------
#b3lyp 6-31g* freq(noraman) guess=read geom=check nopop
---------------------------------------------------------
```

1	6	0	3.109656	-1.299684	0.005837
2	6	0	0.357956	-0.963276	0.077610
3	6	0	2.358170	-1.950891	1.131629
4	6	0	1.038080	-1.738010	1.194696
5	6	0	2.670942	0.181670	-0.093569
6	6	0	1.145537	0.370496	-0.305228
7	6	0	3.634739	0.760832	-1.140810
8	6	0	4.977882	0.010876	-0.880291
9	6	0	4.639657	-1.181607	0.067335
10	6	0	0.675278	1.561778	0.476163
11	6	0	0.173507	2.695039	-0.040532
12	6	0	-0.224750	3.828469	0.820758
13	8	0	-0.100328	3.858343	2.032435
14	6	0	-2.100123	-1.089342	-0.449600
15	6	0	-1.097394	-0.707986	0.350584
16	6	0	-3.508606	-0.797200	-0.097847
17	8	0	-3.892254	-0.230286	0.906507
18	8	0	-4.345714	-1.253341	-1.062867
19	6	0	-5.740248	-1.017924	-0.820594
20	1	0	2.838347	-1.792048	-0.945127
21	1	0	0.421657	-1.583611	-0.828854
22	1	0	2.882374	-2.531744	1.888170
23	1	0	0.425416	-2.147222	1.994720
24	1	0	2.929124	0.622898	0.880028
25	1	0	0.940415	0.548526	-1.368212
26	1	0	3.736487	1.848449	-1.066410
27	1	0	3.263179	0.541124	-2.150328
28	1	0	5.721660	0.671606	-0.423584
29	1	0	5.411720	-0.342769	-1.821424
30	1	0	4.946743	-0.951117	1.095536
31	1	0	5.150178	-2.106458	-0.221233
32	1	0	0.777999	1.511260	1.561323
33	1	0	0.038116	2.815439	-1.114535
34	1	0	-0.663420	4.695867	0.280906
35	1	0	-1.924999	-1.623550	-1.379942
36	1	0	-1.355599	-0.178370	1.267053
37	1	0	-6.262981	-1.438892	-1.680199
38	1	0	-5.940765	0.053696	-0.735423
39	1	0	-6.059744	-1.509900	0.102289

SCF Done: E(RB3LYP) = -847.352544035 A.U. after 1 cycles

Frequencies -- 17.9165 26.4636 43.9703

Zero-point correction= 0.330540 (Hartree/Particle)
Thermal correction to Energy= 0.349584
Thermal correction to Enthalpy= 0.350528
Thermal correction to Gibbs Free Energy= 0.280238
Sum of electronic and zero-point Energies= -847.022004
Sum of electronic and thermal Energies= -847.002960
Sum of electronic and thermal Enthalpies= -847.002016
Sum of electronic and thermal Free Energies= -847.072306

SCF Done: E(RmPW1PW91) = **-847.3963208**

C21 TS DFT (12)

#6-31g* b3lyp guess=read geom=check nopop FREQ(NORAMAN)

1	6	0	4.354973	-0.972703	-0.069757
2	6	0	1.518010	-1.721799	0.404697
3	6	0	3.846809	-1.442261	1.168487
4	6	0	2.503575	-1.756255	1.384104
5	6	0	3.771967	0.826566	-0.347614
6	6	0	2.401849	0.917689	-0.705336
7	6	0	4.843347	1.124404	-1.398089
8	6	0	6.170966	0.569569	-0.874143
9	6	0	5.865746	-0.823615	-0.267577
10	6	0	1.397353	1.464780	0.125548
11	6	0	0.114774	1.765463	-0.248882
12	6	0	-0.806143	2.415268	0.698115
13	8	0	-0.467792	2.696718	1.847066
14	6	0	-0.853393	-1.683271	-0.234049
15	6	0	0.128663	-1.841435	0.692367
16	6	0	-2.272769	-1.856256	0.115057
17	8	0	-2.704019	-2.147157	1.216196
18	8	0	-3.051269	-1.654268	-0.984710
19	6	0	-4.472327	-1.882825	-0.870170
20	6	0	-3.067199	1.413366	0.156068
21	6	0	-4.548419	1.668095	-0.141767
22	6	0	-5.451082	0.423312	-0.063901
23	6	0	-5.294344	-0.632087	-1.187884
24	6	0	-2.224845	2.703001	0.217110
25	1	0	3.861206	-1.383241	-0.950224
26	1	0	1.798876	-1.632901	-0.639914
27	1	0	4.501464	-1.390609	2.037267
28	1	0	2.186367	-1.954901	2.407085
29	1	0	4.001311	1.278626	0.619902
30	1	0	2.128343	0.657266	-1.729747
31	1	0	4.899775	2.203482	-1.586656
32	1	0	4.565749	0.648134	-2.348161
33	1	0	6.555783	1.237077	-0.093381

34	1	0	6.936395	0.526033	-1.655918
35	1	0	6.389625	-0.958439	0.685149
36	1	0	6.215470	-1.622186	-0.932880
37	1	0	1.667149	1.718919	1.150513
38	1	0	-0.229085	1.572996	-1.263208
39	1	0	-0.622669	-1.472366	-1.273877
40	1	0	-0.173540	-2.037196	1.720326
41	1	0	-4.695453	-2.664825	-1.604513
42	1	0	-4.689032	-2.263917	0.130556
43	1	0	-2.979209	0.889004	1.116906
44	1	0	-2.649330	0.744606	-0.602435
45	1	0	-4.653328	2.131813	-1.134364
46	1	0	-4.928649	2.406434	0.578178
47	1	0	-6.490336	0.775983	-0.079967
48	1	0	-5.315686	-0.060621	0.913310
49	1	0	-4.899165	-0.169222	-2.102243
50	1	0	-6.293454	-1.005157	-1.451338
51	1	0	-2.200701	3.175395	-0.775560
52	1	0	-2.668300	3.413432	0.922482

SCF Done: E(RB3LYP) = -1042.67949021 A.U. after 1 cycles

Frequencies -- -403.0844 14.0335 35.2049

Zero-point correction= 0.450555 (Hartree/Particle)
Thermal correction to Energy= 0.474074
Thermal correction to Enthalpy= 0.475018
Thermal correction to Gibbs Free Energy= 0.396528
Sum of electronic and zero-point Energies= -1042.228935
Sum of electronic and thermal Energies= -1042.205417
Sum of electronic and thermal Enthalpies= -1042.204472
Sum of electronic and thermal Free Energies= -1042.282962

SCF Done: E(RmPW1PW91) = -1042.722165 A.U. after 15 cycles

C21 - Reactant - DFT (13)

#6-31g* b3lyp nopop freq(noraman)

1	6	0	-4.198203	1.356193	-0.560376
2	6	0	-1.252345	2.165594	-0.229715
3	6	0	-3.737220	2.477445	0.027133
4	6	0	-2.337194	2.798160	0.281679
5	6	0	-4.200846	-1.673101	0.470596
6	6	0	-3.112428	-2.115037	-0.189353
7	6	0	-5.576545	-1.509096	-0.106781
8	6	0	-6.203910	-0.111629	0.107701
9	6	0	-5.647890	1.031021	-0.778640
10	6	0	-1.799048	-2.191547	0.413668
11	6	0	-0.653129	-2.465114	-0.245865
12	6	0	0.662403	-2.397428	0.439336

13	8	0	0.755421	-2.283286	1.654982
14	6	0	1.188424	1.820779	-0.315505
15	6	0	0.102677	2.485159	0.138596
16	6	0	2.539065	2.143320	0.173003
17	8	0	2.827325	3.040592	0.943968
18	8	0	3.454457	1.274457	-0.336716
19	6	0	4.800876	1.418260	0.162287
20	6	0	3.156777	-1.877606	0.203826
21	6	0	4.340090	-1.792151	-0.770096
22	6	0	5.586585	-1.062991	-0.216507
23	6	0	5.719978	0.436670	-0.553558
24	6	0	1.895308	-2.437541	-0.458160
25	1	0	-3.485259	0.601678	-0.882597
26	1	0	-1.385628	1.350027	-0.939069
27	1	0	-4.461878	3.212130	0.379708
28	1	0	-2.159766	3.629046	0.964659
29	1	0	-4.090767	-1.398036	1.521348
30	1	0	-3.196909	-2.385564	-1.243038
31	1	0	-6.241039	-2.240620	0.379236
32	1	0	-5.571712	-1.760259	-1.176013
33	1	0	-6.100875	0.172445	1.163436
34	1	0	-7.280820	-0.189729	-0.089324
35	1	0	-6.255627	1.927283	-0.599319
36	1	0	-5.803148	0.752821	-1.832500
37	1	0	-1.716262	-1.963058	1.476127
38	1	0	-0.663118	-2.675007	-1.314682
39	1	0	1.097121	0.997820	-1.018615
40	1	0	0.263862	3.293812	0.850622
41	1	0	5.124964	2.450011	-0.008564
42	1	0	4.794580	1.252390	1.246142
43	1	0	3.422693	-2.499305	1.067057
44	1	0	2.928186	-0.884874	0.600722
45	1	0	4.017954	-1.295294	-1.695862
46	1	0	4.625135	-2.813082	-1.061194
47	1	0	6.482777	-1.552138	-0.619485
48	1	0	5.640913	-1.197185	0.873667
49	1	0	5.614424	0.583153	-1.637166
50	1	0	6.743524	0.748883	-0.302808
51	1	0	1.671434	-1.885542	-1.382946
52	1	0	2.047078	-3.482057	-0.777032

SCF Done: E(RB3LYP) = -1042.71688523 A.U. after 15 cycles

Frequencies -- 28.1880 29.9404 35.8439

Zero-point correction= 0.449686
(Hartree/Particle)
Thermal correction to Energy= 0.474991
Thermal correction to Enthalpy= 0.475935
Thermal correction to Gibbs Free Energy= 0.392498
Sum of electronic and zero-point Energies= -1042.267199
Sum of electronic and thermal Energies= -1042.241894
Sum of electronic and thermal Enthalpies= -1042.240950
Sum of electronic and thermal Free Energies= -1042.324387

SCF Done: E(RmPW1PW91) = -1042.75570757 A.U. after 15 cycles

C21 DFT PRODUCT (14)

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#6-31G* B3LYP FREQ(NORAMAN) GUESS=READ GEOM=CHECK nopop
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1	6	0	4.408443	-0.917846	-0.076816
2	6	0	1.663423	-1.403650	0.151414
3	6	0	3.926616	-1.727440	1.093206
4	6	0	2.606917	-1.903505	1.228182
5	6	0	3.540592	0.358617	-0.187733
6	6	0	2.036434	0.072590	-0.379689
7	6	0	4.265036	1.180969	-1.266493
8	6	0	5.776764	0.871557	-1.040334
9	6	0	5.835683	-0.348781	-0.071578
10	6	0	1.194611	1.138641	0.260623
11	6	0	0.145846	1.744339	-0.314014
12	6	0	-0.717441	2.689770	0.447591
13	8	0	-0.323863	3.256020	1.457444
14	6	0	-0.771496	-1.880530	-0.282672
15	6	0	0.215539	-1.513759	0.543550
16	6	0	-2.185644	-1.880292	0.158068
17	8	0	-2.575106	-1.814034	1.308441
18	8	0	-3.001270	-1.944192	-0.924934
19	6	0	-4.429907	-2.028266	-0.712667
20	6	0	-2.916481	1.495421	0.097471
21	6	0	-4.434962	1.637614	-0.054926
22	6	0	-5.211672	0.325585	0.166997
23	6	0	-5.152167	-0.706405	-0.992419
24	6	0	-2.154438	2.833551	-0.038405
25	1	0	4.268179	-1.497671	-1.006541
26	1	0	1.815035	-2.040103	-0.732954
27	1	0	4.631270	-2.109186	1.829703
28	1	0	2.186420	-2.448068	2.071178
29	1	0	3.661861	0.877534	0.774231
30	1	0	1.801894	0.054010	-1.451506
31	1	0	4.038358	2.250369	-1.205910
32	1	0	3.950672	0.843120	-2.262838
33	1	0	6.300683	1.732546	-0.612922
34	1	0	6.271922	0.646701	-1.990822
35	1	0	6.092765	-0.018479	0.943030
36	1	0	6.588180	-1.086878	-0.368864
37	1	0	1.430117	1.411106	1.290273
38	1	0	-0.159849	1.478236	-1.325005
39	1	0	-0.583831	-2.138904	-1.321921
40	1	0	-0.051817	-1.240337	1.563929
41	1	0	-4.758935	-2.789563	-1.426376
42	1	0	-4.616861	-2.383257	0.303884
43	1	0	-2.705175	1.062750	1.083598
44	1	0	-2.534177	0.777734	-0.638611
45	1	0	-4.679046	2.048450	-1.046126
46	1	0	-4.788668	2.378062	0.675696

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   47          1             0       -6.263099    0.586640    0.339008
   48          1             0       -4.860977   -0.142241    1.095369
   49          1             0       -4.710097   -0.259013   -1.892545
   50          1             0       -6.177581   -0.980434   -1.273242
   51          1             0       -2.167420    3.164509   -1.087149
   52          1             0       -2.628085    3.610932    0.569680
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 SCF Done:  E(RB+HF-LYP) =  -1042.72155834     A.U. after    1 cycles

 Frequencies --    18.7200                33.8895
52.7876

 Zero-point correction=                           0.454684
(Hartree/Particle)
 Thermal correction to Energy=                    0.477692
 Thermal correction to Enthalpy=                  0.478636
 Thermal correction to Gibbs Free Energy=         0.400949
 Sum of electronic and zero-point Energies=          -1042.266874
 Sum of electronic and thermal Energies=             -1042.243867
 Sum of electronic and thermal Enthalpies=           -1042.242923
 Sum of electronic and thermal Free Energies=        -1042.320609

 SCF Done:  E(RmPW1PW91) =  -1042.77506855     A.U. after   15 cycles
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