Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Theoretical Calculations on Carbocations Involved in the Biosynthesis of Bergamotenes and Related Terpenes – The Same and Not the Same

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1. References for Methods

1.1. Gaussian03 Full Reference

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1.2. B3LYP

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1.3. mPW1PW91

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1.4. mPWB1K

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1.5. IRC

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1.6. *Ball & Stick*

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2. **A**→**C** conversion

2.1. R_1=prenyl/CH_3, R_2=CH_3/prenyl

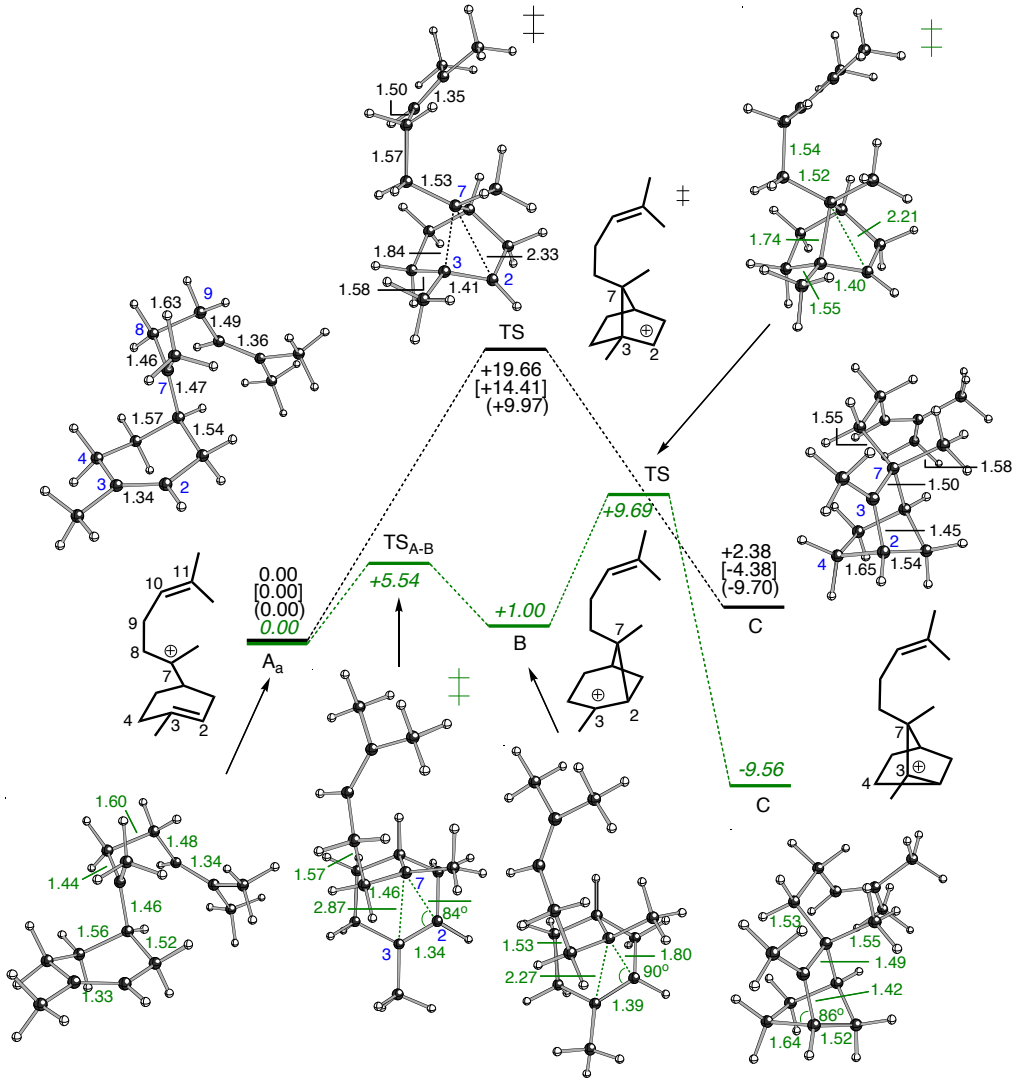


Fig. S1 Concerted **A**→**C** conversion (B3LYP). Computed geometries (selected distances in Å) and energies (kcal/mol, Table 1) for structures (B3LYP/6-31+G(d,p) + ZPE (B3LYP/6-31+G(d,p)) in normal text, mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in brackets, mPWB1k/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in parentheses, MPWB1K/6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)) in green) involved in the **A$_a$**→**C** conversion for the "aligned" bergamotene/santalene system (R_1=prenyl, R_2=CH_3).

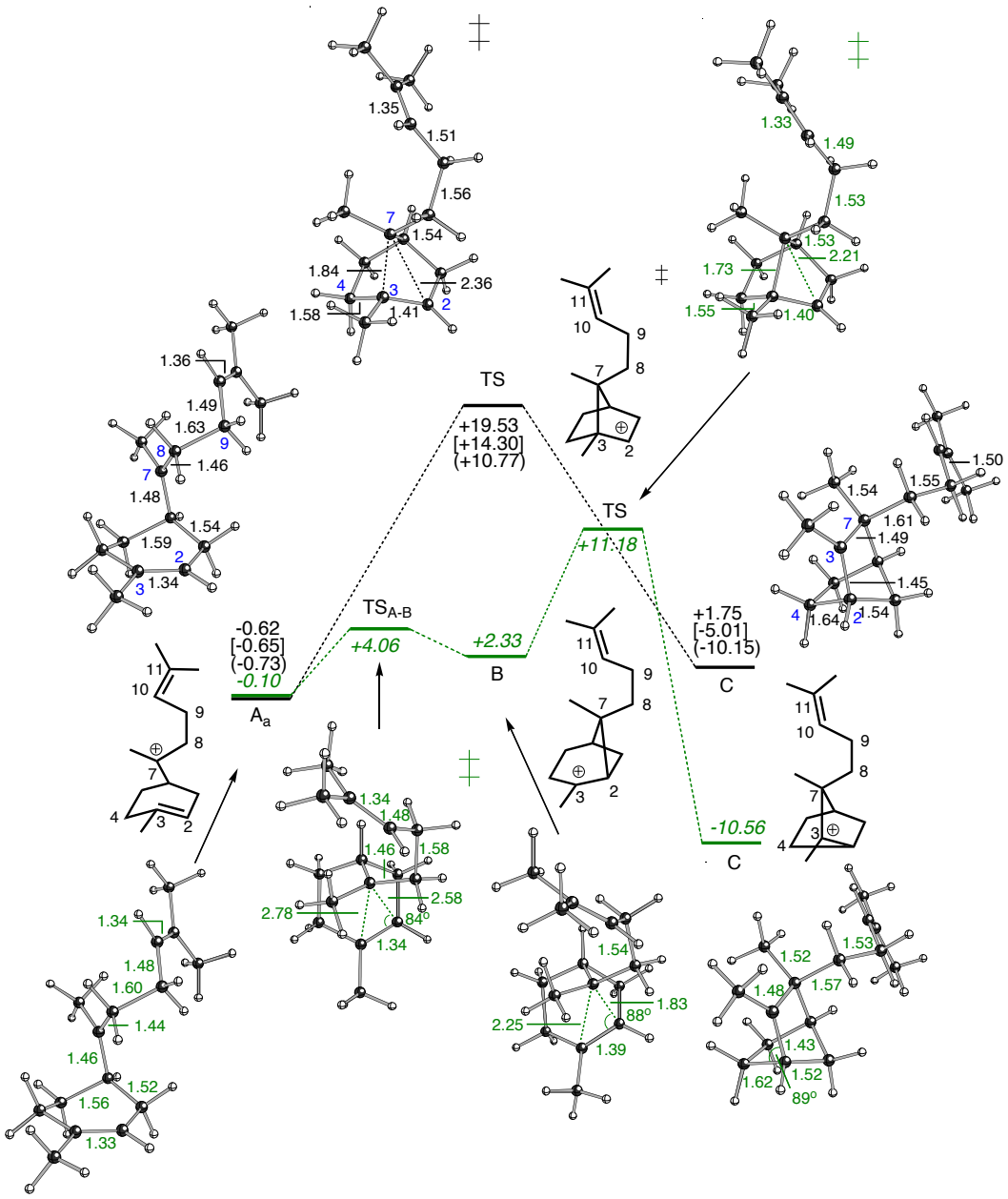


Fig. S2 Concerted **A**→**C** conversion (B3LYP). Computed geometries (selected distances in Å) and energies (kcal/mol, Fig. 3 and Table 1) for structures (B3LYP/6-31+G(d,p) + ZPE (B3LYP/6-31+G(d,p)) in normal text, mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in brackets, mPWB1k/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in parentheses, MPWB1K/6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)) in green) involved in the **A$_a$**→**C** conversion for the "aligned" bergamotene/santalene system (R_1=CH_3, R_2=prenyl).

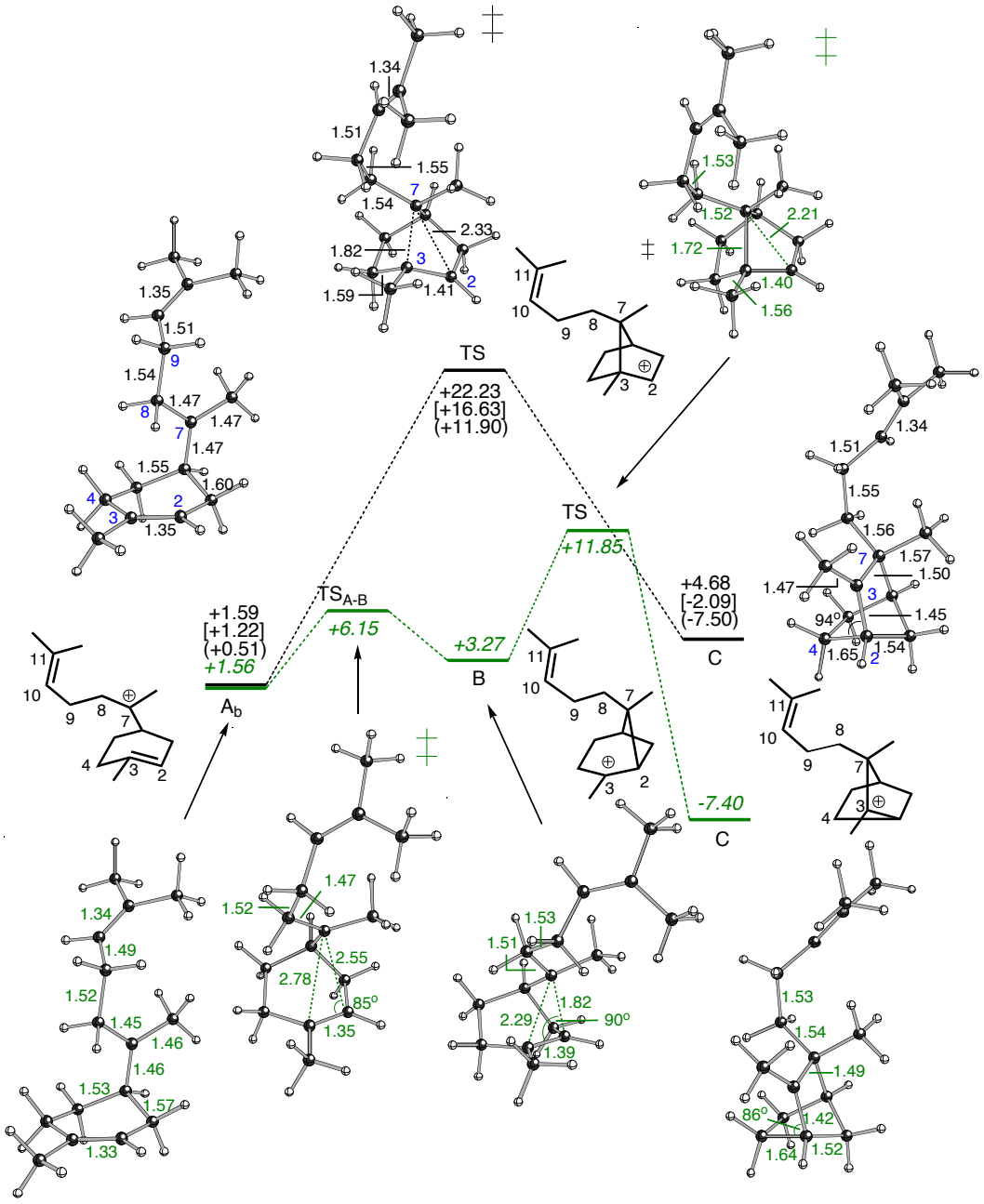


Fig. S3 Concerted **A**→**C** conversion (B3LYP). Computed geometries (selected distances in Å) and energies (kcal/mol, Fig. 4 and Table 2) for structures (B3LYP/6-31+G(d,p) + ZPE (B3LYP/6-31+G(d,p)) in normal text, mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in brackets, mPWB1k/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in parentheses, MPWB1K/6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)) in green) involved in the **A$_a$**→**C** conversion for the "extended" bergamotene/santalene system (R_1=prenyl, R_2=CH_3).

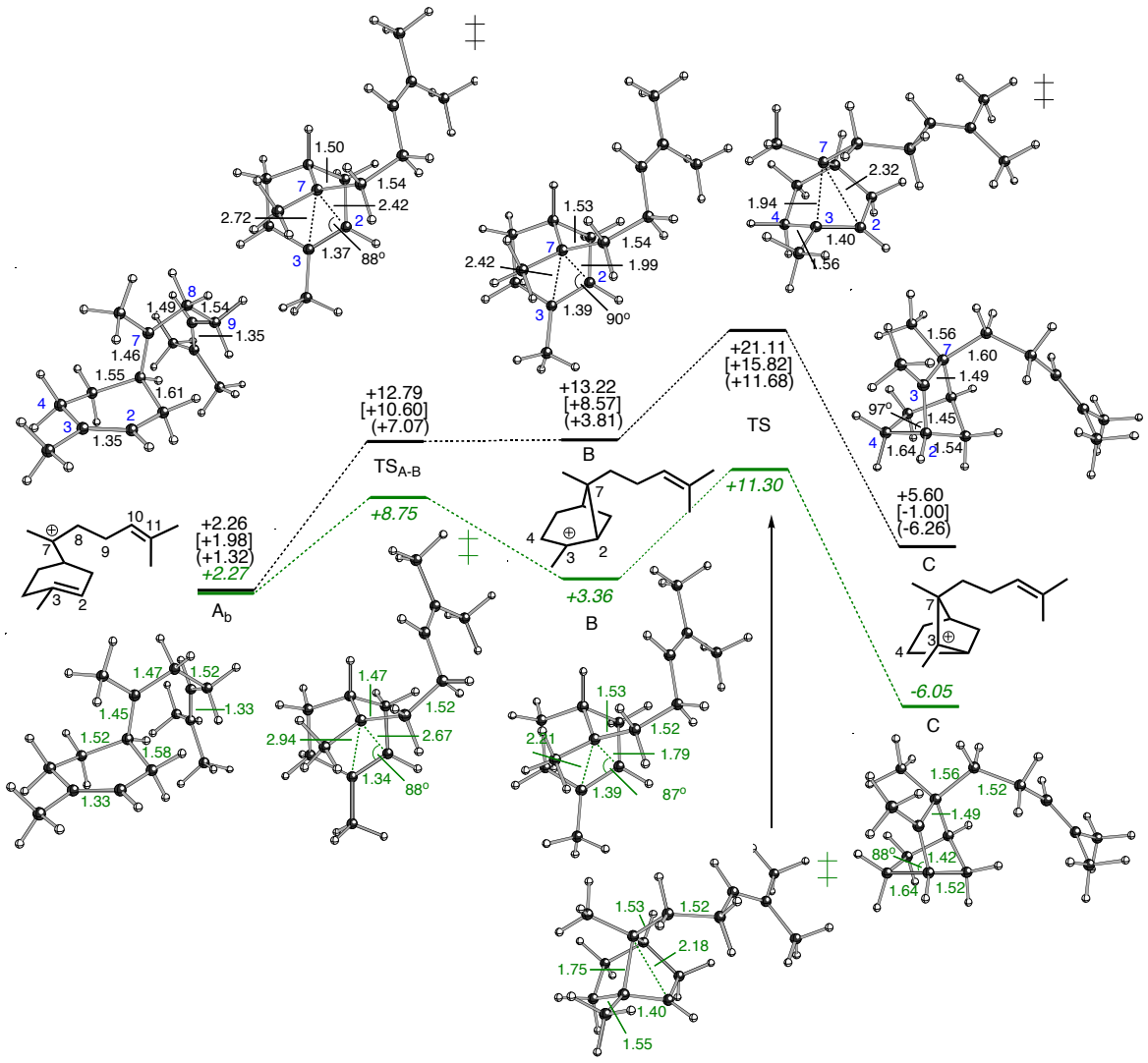


Fig. S4 Stepwise **A**→**C** conversion (B3LYP). Computed geometries (selected distances in Å) and energies (kcal/mol, Table 2) for structures (B3LYP/6-31+G(d,p) + ZPE (B3LYP/6-31+G(d,p)) in normal text, mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in brackets, mPWB1k/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in parentheses, MPWB1K/6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)) in green) involved in the $\mathbf{A_a}$→**C** conversion for the "extended" bergamotene/santalene system (R_1=CH_3, R_2=prenyl).

2.2. R_1=C_2H_6/CH_3, R_2=C_2H_6/CH_3

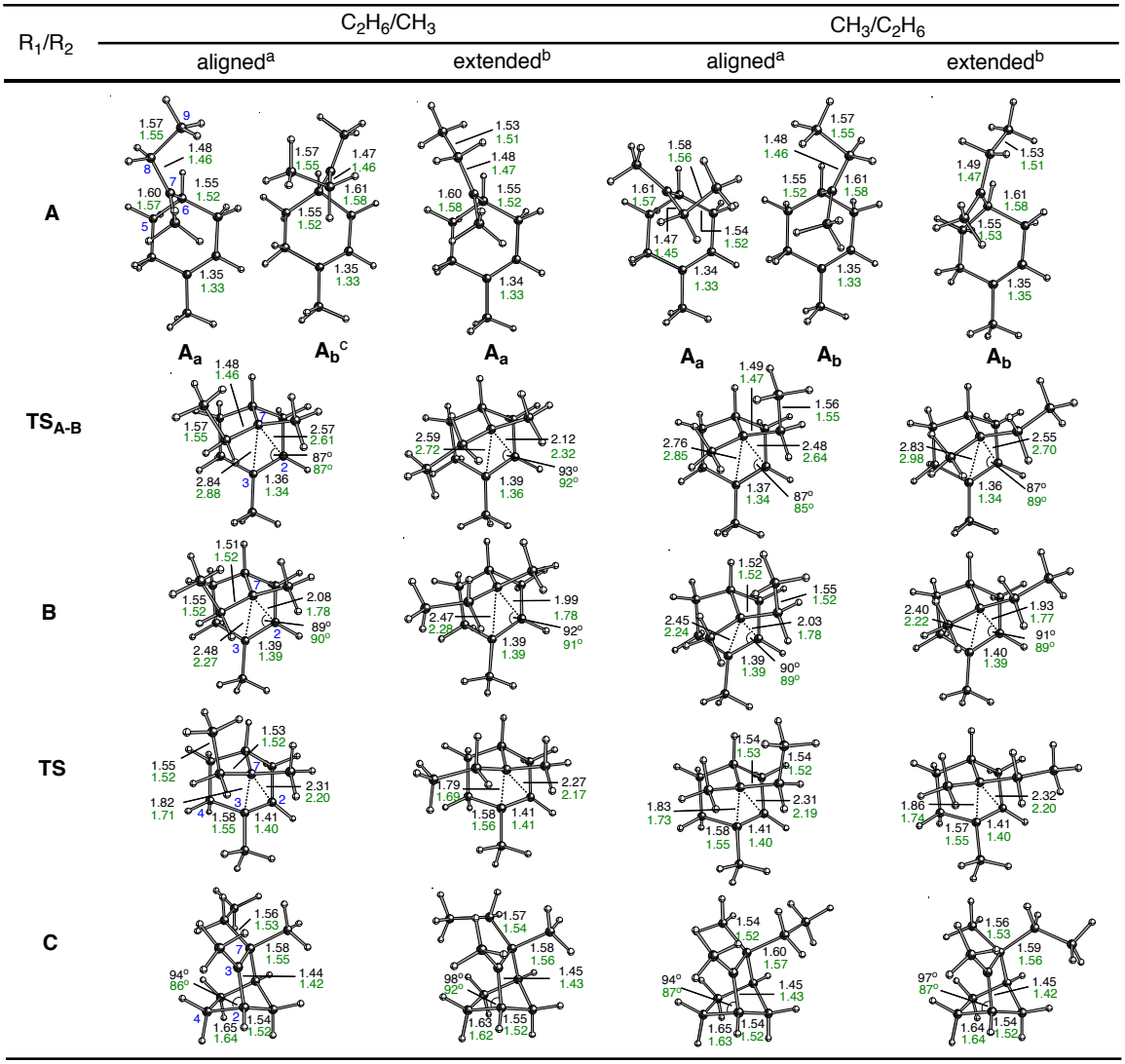


Fig. S5 Computed geometries for structures (selected distances in Å, B3LYP/6-31+G(d,p) in black, and MPWB1K/6-31+G(d,p) in green. See Tables 1[a] and 2[b] for energies) involved in the **A**→**C** conversion for R_1= C_2H_6/CH_3, R_2=C_2H_6/CH_3, R_3=H/H system. [c] We were unable to locate the conformer $\mathbf{A_b}$ at mPWB1K level of theory. The structure shown has an imaginary frequency (-48.2697 1/cm) corresponding to ethyl (R_1) group movement.

2.3. R_1/R_2= –$(CH_2)_5$–

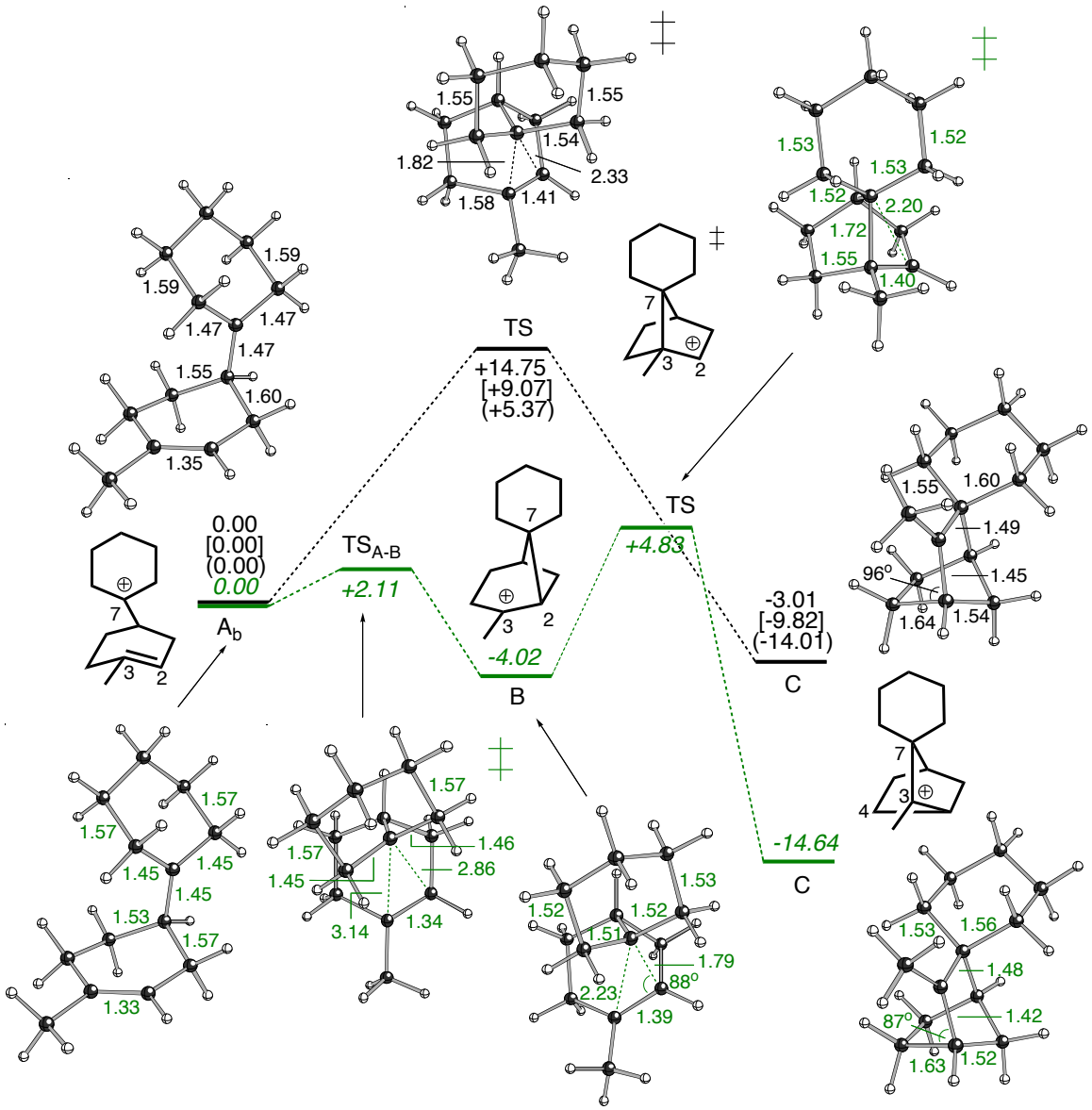


Fig. S6 Computed geometries (selected distances in Å) and energies (kcal/mol, Table 1) for structures (B3LYP/6-31+G(d,p) + ZPE (B3LYP/6-31+G(d,p)) in normal text, mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in brackets, mPWB1k/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in parentheses, MPWB1K/6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)) in green) involved in the **A**→**C** conversion for R_1/R_2=–$(CH_2)_5$– system.

2.4. R_1=CH_3, R_2=Ph

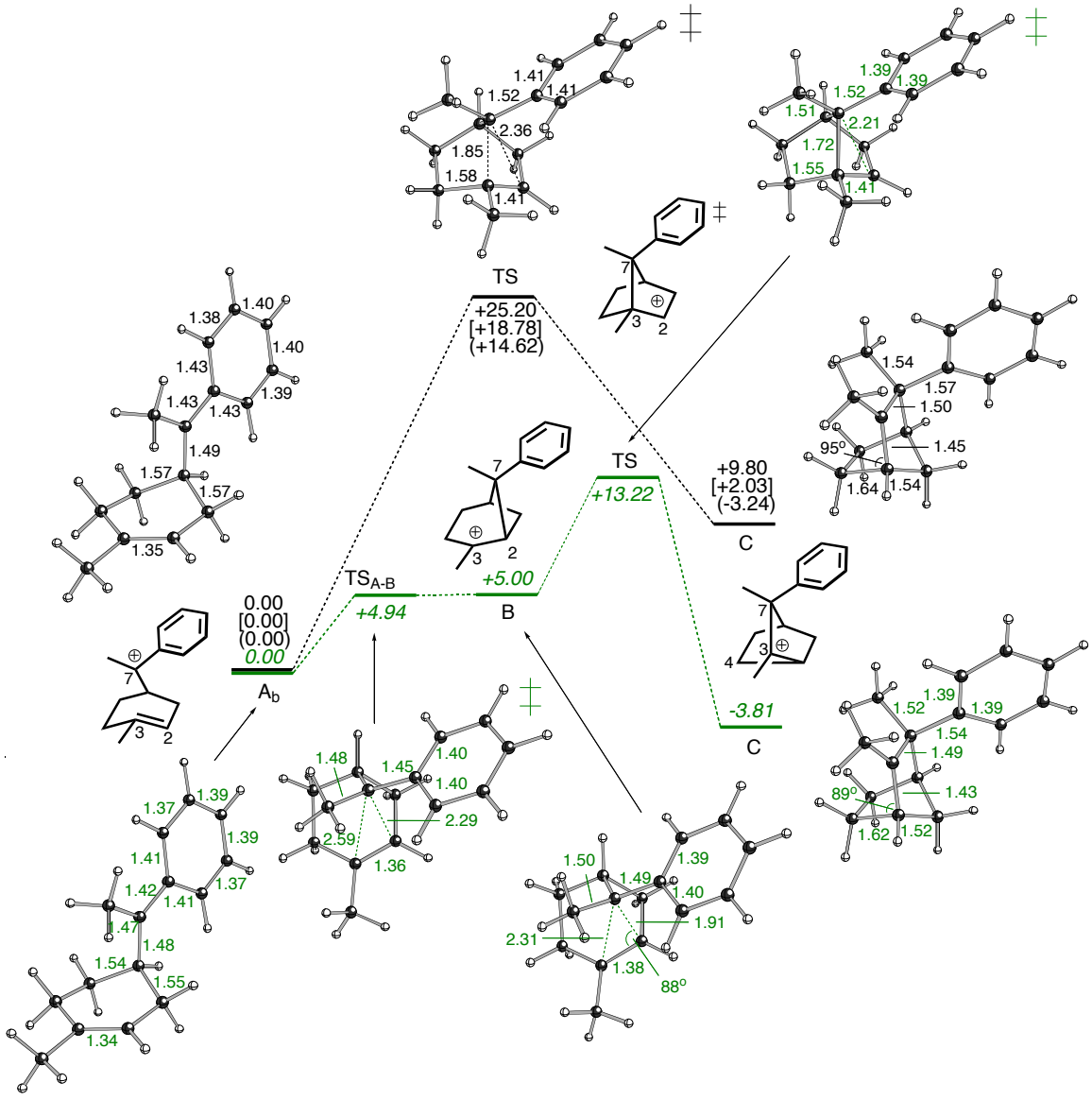


Fig. S7 Computed geometries (selected distances in Å) and energies (kcal/mol, Table 1) for structures (B3LYP/6-31+G(d,p) + ZPE (B3LYP/6-31+G(d,p)) in normal text, mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in brackets, mPWB1k/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in parentheses, MPWB1K/6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)) in green) involved in the **A**→**C** conversion for R_1=CH_3, R_2=Ph system.

2.5. R_1=CH_3, R_2=cyclopropyl

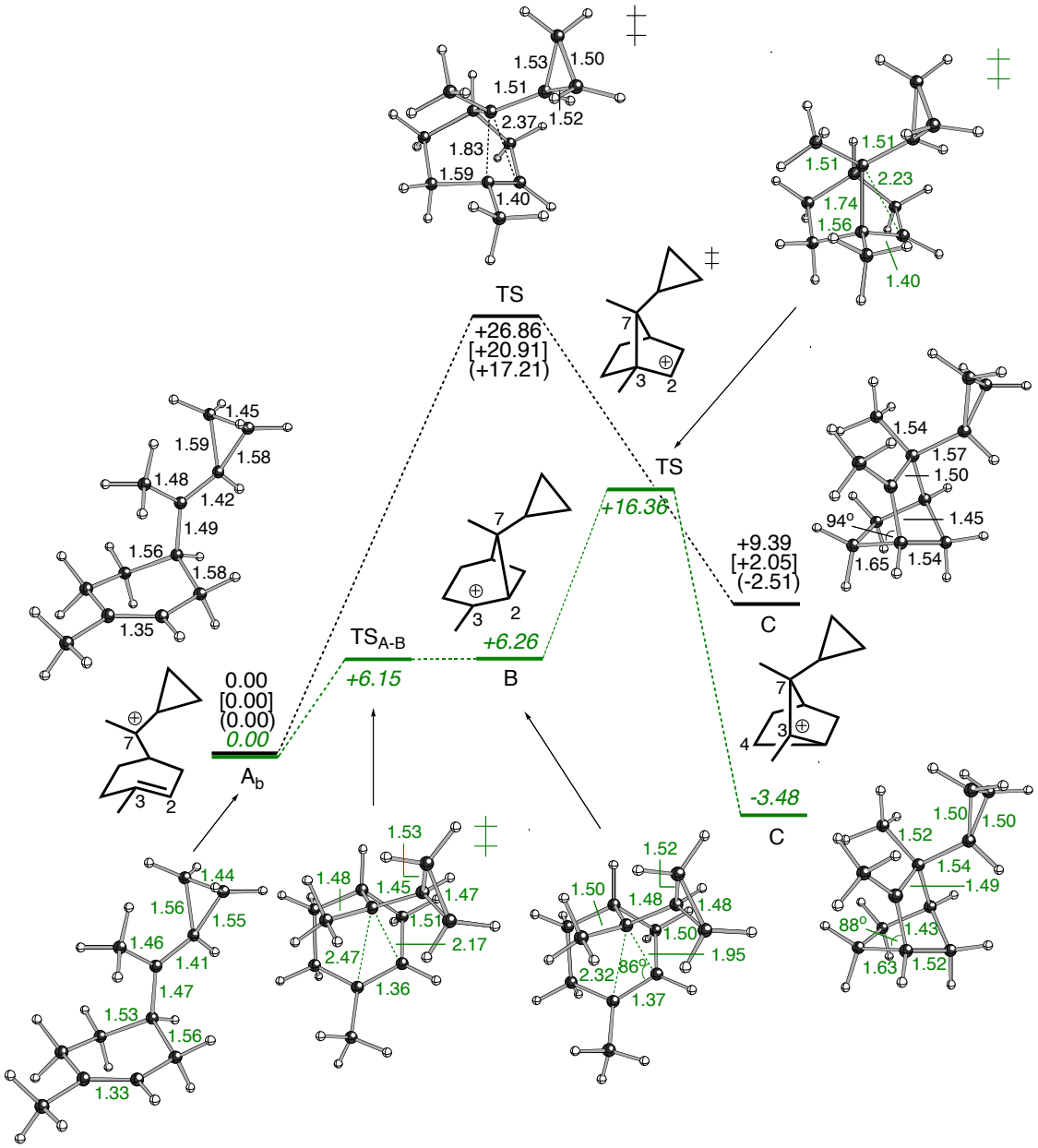


Fig. S8 Computed geometries (selected distances in Å) and energies (kcal/mol, Table 1) for structures (B3LYP/6-31+G(d,p) + ZPE (B3LYP/6-31+G(d,p)) in normal text, mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in brackets, mPWB1k/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in parentheses, MPWB1K/6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)) in green) involved in the **A**→**C** conversion for R_1=CH_3, R_2=cyclopropyl system.

2.6. R_1=CH_3, R_2=$(CH_2)_2$–Ph

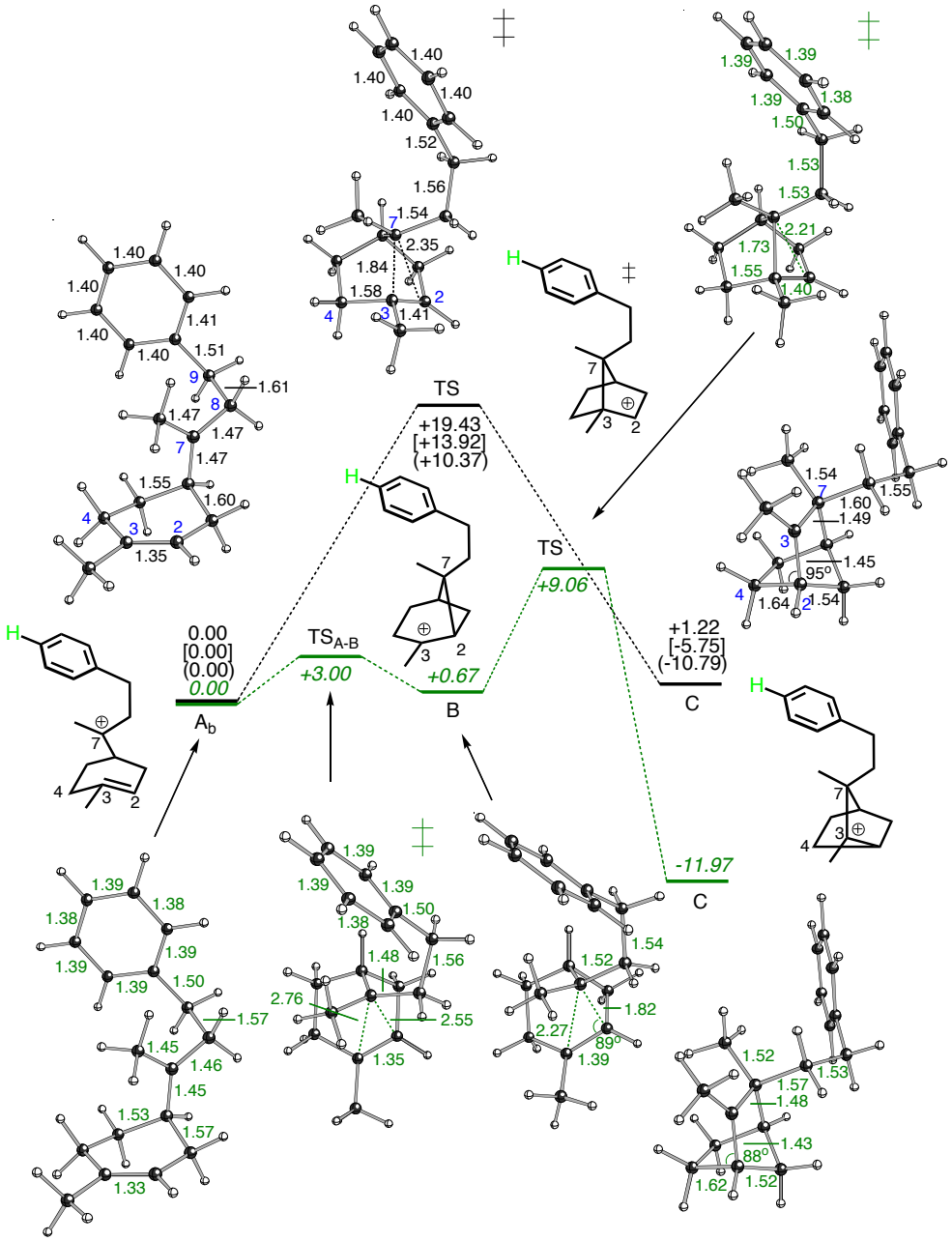


Fig. S9 Computed geometries (selected distances in Å) and energies (kcal/mol, Table 1) for structures (B3LYP/6-31+G(d,p) + ZPE (B3LYP/6-31+G(d,p)) in normal text, mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in brackets, mPWB1k/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in parentheses, MPWB1K/6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)) in green) involved in the "aligned" **A**→**C** conversion for R_1=CH_3, R_2=$(CH_2)_2$–Ph system.

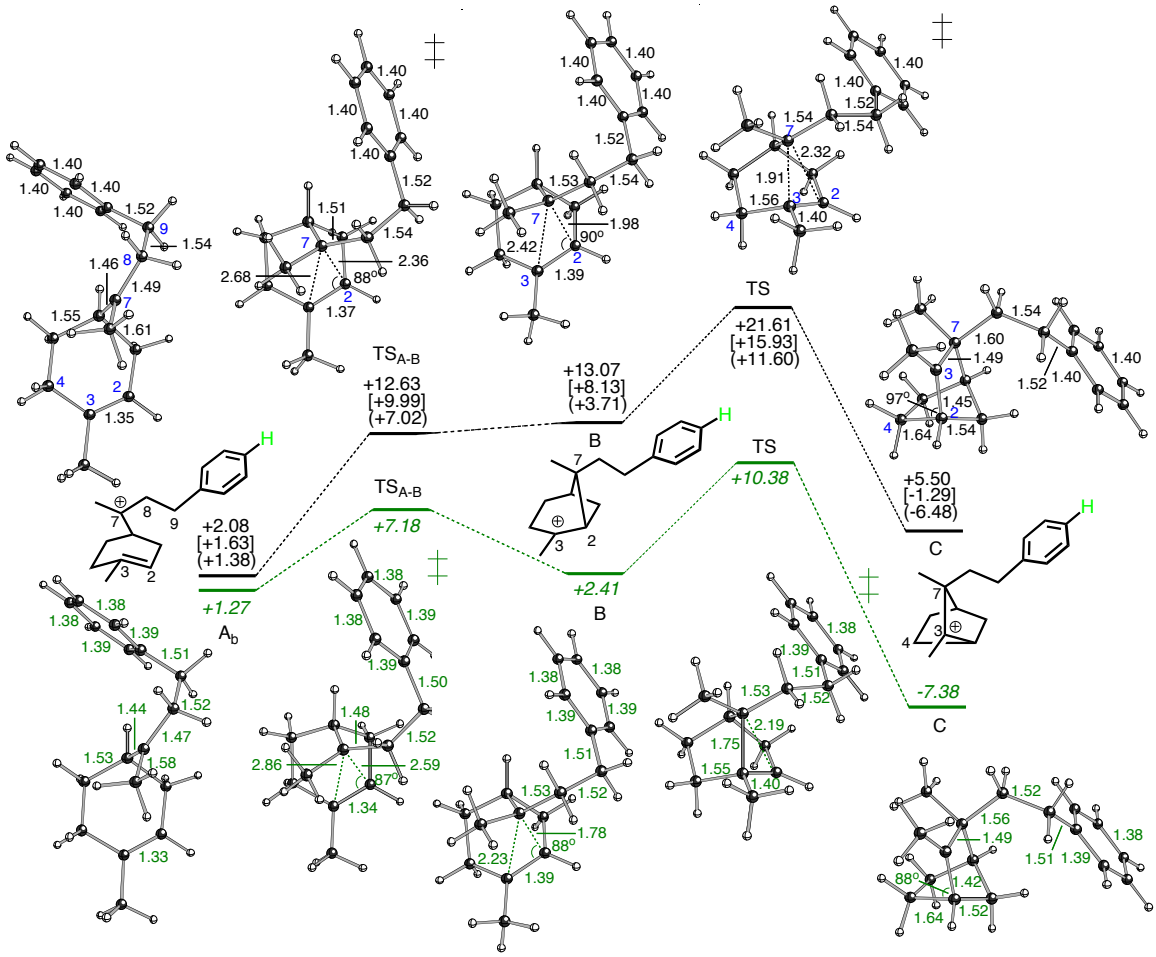


Fig. S10 Computed geometries (selected distances in Å) and energies (kcal/mol, Table 2) for structures (B3LYP/6-31+G(d,p) + ZPE (B3LYP/6-31+G(d,p)) in normal text, mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in brackets, mPWB1k/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in parentheses, MPWB1K/6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)) in green) involved in the "extended" **A→C** conversion for R_1=CH_3, R_2=$(CH_2)_2$–Ph system. We were unable to locate **TS$_{A-B}$** at mPWB1K level of theory. The structure shown has two imaginary frequencies: -87.9 cm^{-1} corresponding to C2–C7 bond making breaking and -10.0 cm^{-1} corresponding to a conformational change of the sidechain.

2.7. R_1=CH_3, R_2=$(CH_2)_2$–*p*–NH_2–Ph

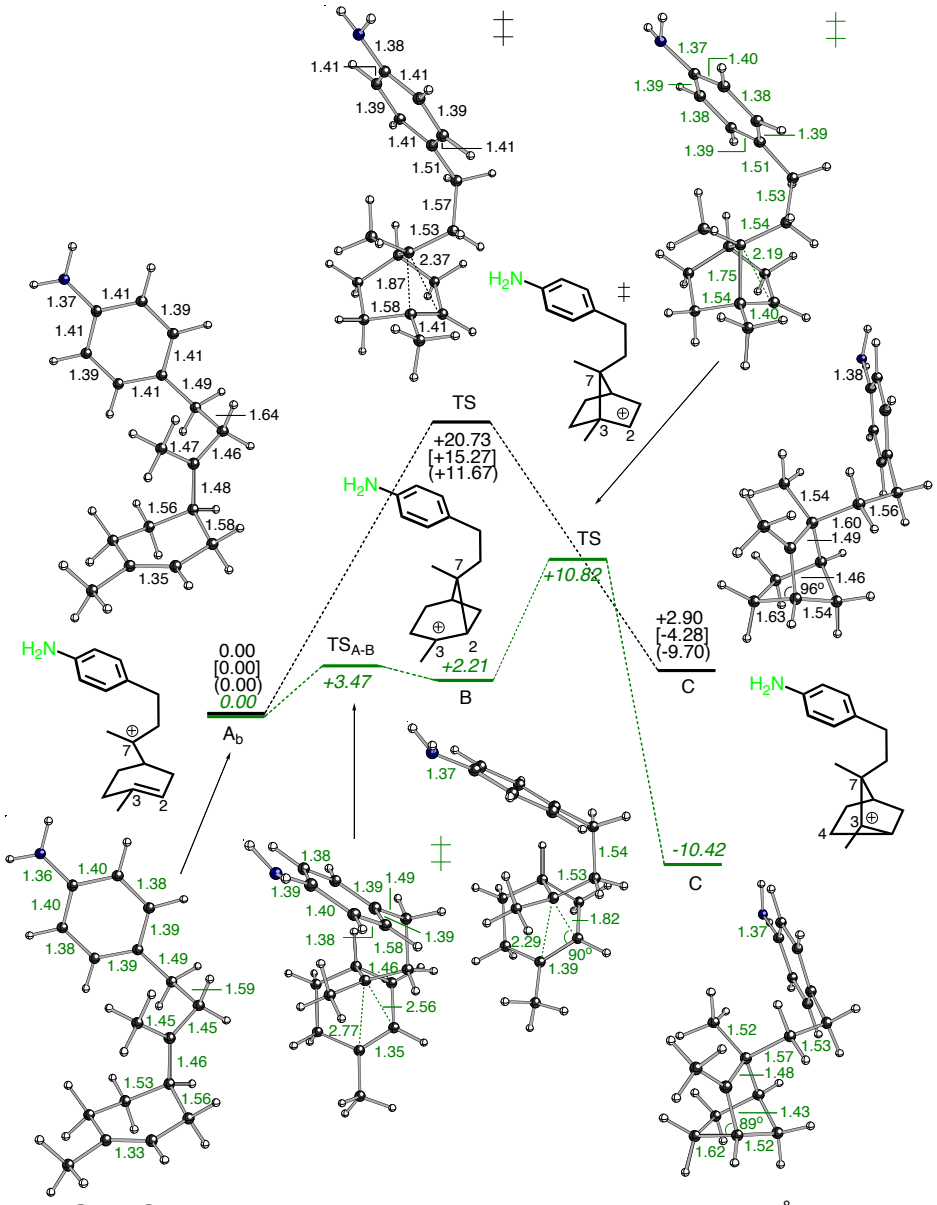


Fig. S11 Computed geometries (selected distances in Å) and energies (kcal/mol, Table 1) for structures (B3LYP/6-31+G(d,p) + ZPE (B3LYP/6-31+G(d,p)) in normal text, mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in brackets, mPWB1k/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in parentheses, MPWB1K/6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)) in green) involved in the "aligned" **A**→**C** conversion for R_1=CH_3, R_2=$(CH_2)_2$–*p*–NH_2–Ph system.

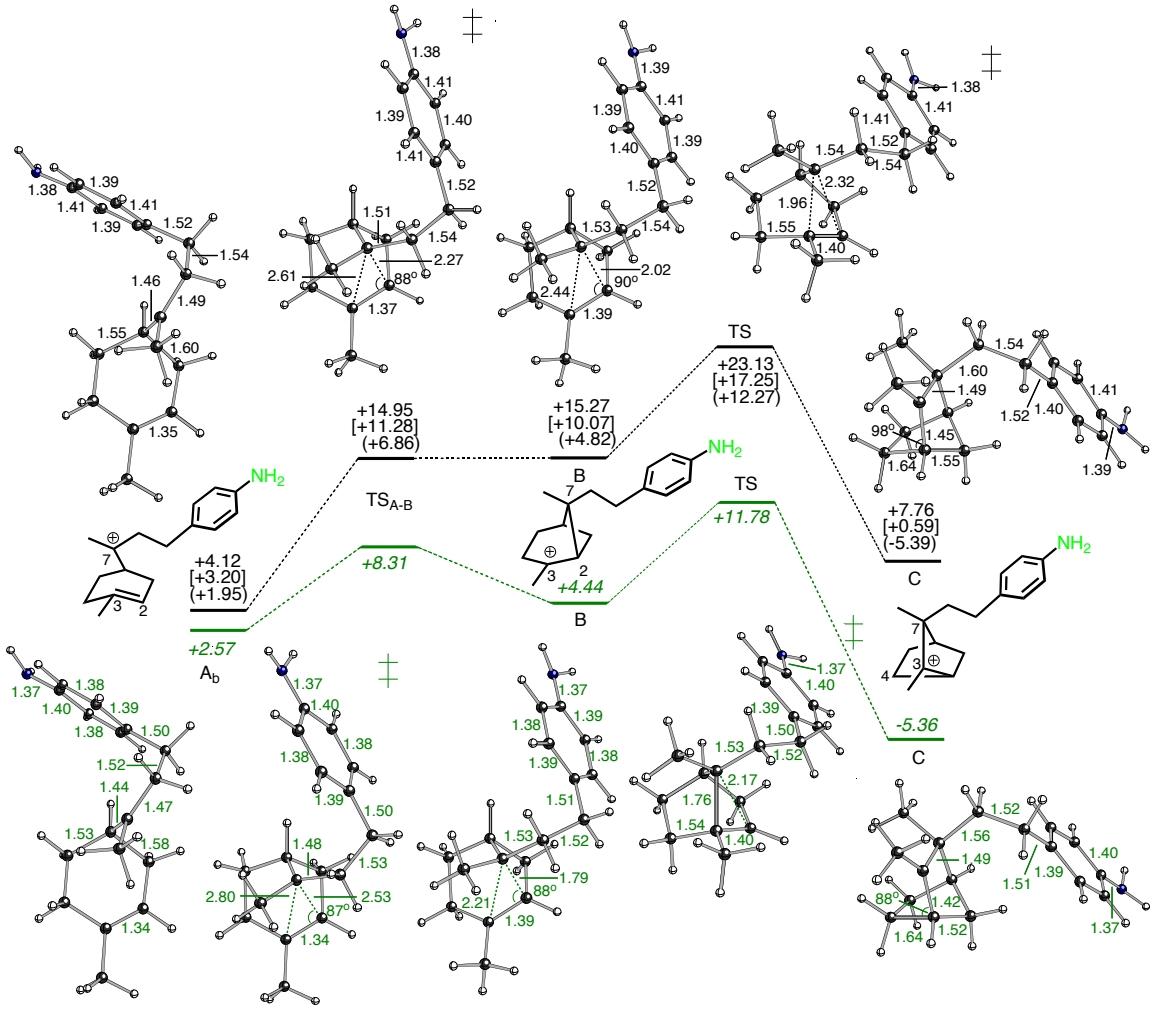


Fig. S12 Computed geometries (selected distances in Å) and energies (kcal/mol, Table 2) for structures (B3LYP/6-31+G(d,p) + ZPE (B3LYP/6-31+G(d,p)) in normal text, mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in brackets, mPWB1k/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in parentheses, MPWB1K/6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)) in green) involved in the "extended" **A**→**C** conversion for R_1=CH_3, R_2=$(CH_2)_2$–*p*–NH_2–Ph system.

2.8. R_1=CH_3, R_2=$(CH_2)_2$–*p*–NO_2–Ph

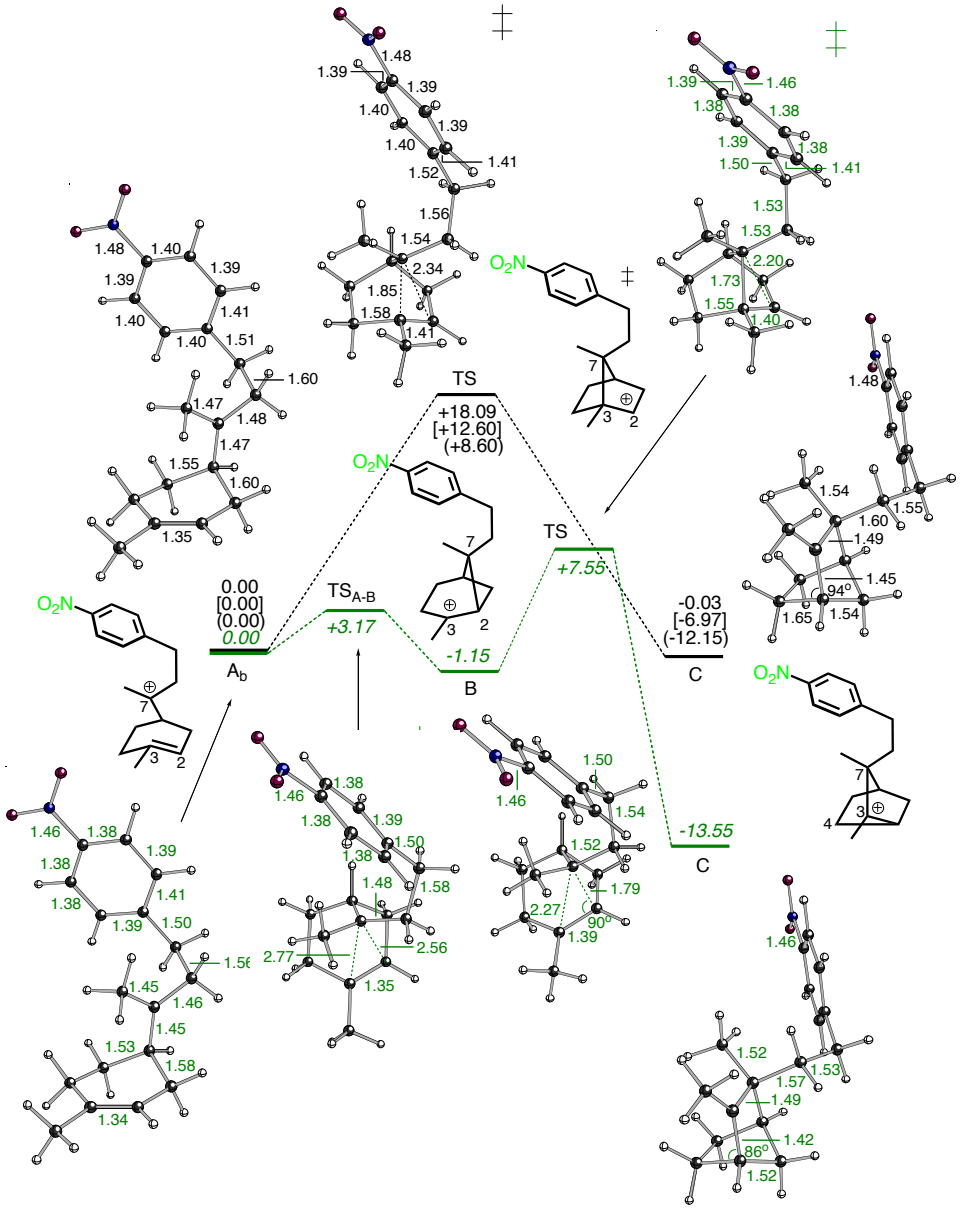


Fig. S13 Computed geometries (selected distances in Å) and energies (kcal/mol, Table 1) for structures (B3LYP/6-31+G(d,p) + ZPE (B3LYP/6-31+G(d,p)) in normal text, mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in brackets, mPWB1k/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in parentheses, MPWB1K/6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)) in green) involved in the "aligned" **A**→**C** conversion for R_2=$(CH_2)_2$–*p*–NO_2–Ph system.

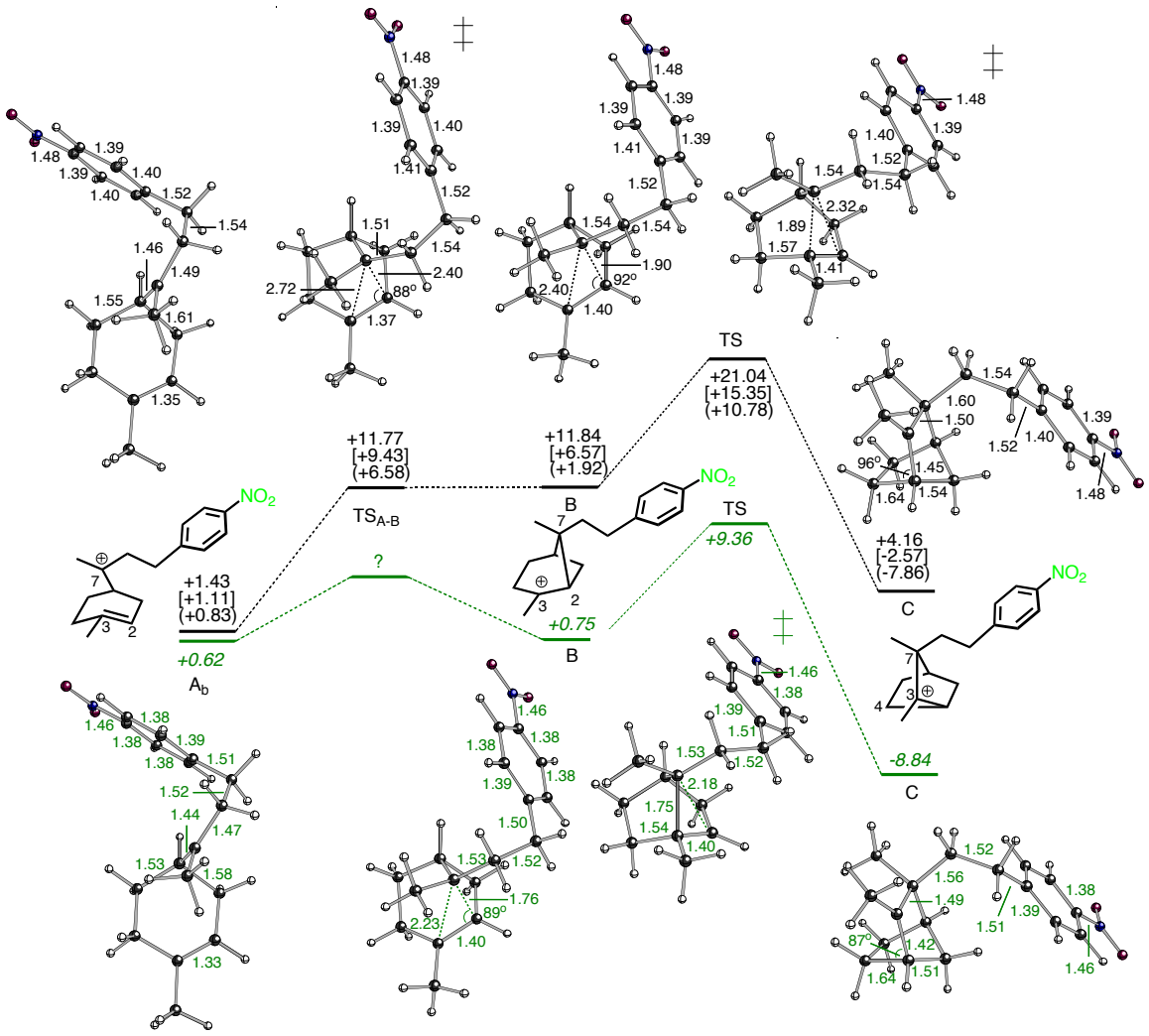


Fig. S14 Computed geometries (selected distances in Å) and energies (kcal/mol, Table 2) for structures (B3LYP/6-31+G(d,p) + ZPE (B3LYP/6-31+G(d,p)) in normal text, mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in brackets, mPWB1k/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p) in parentheses, MPWB1K/6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)) in green) involved in the "extended" **A**→**C** conversion for R_2=$(CH_2)_2$–*p*–NO_2–Ph system.

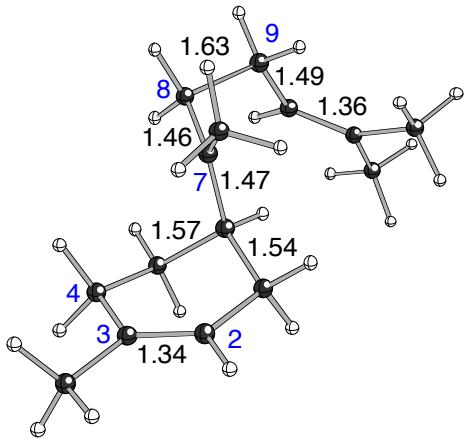
3. Coordinates and Energies

3.1. R_1=prenyl/CH_3, R_2=CH_3/prenyl

Table 1: R_1/R_2=prenyl/CH_3 (aligned) (Fig. S1)

B3LYP

A_a




```
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.4129745 hartrees (-367980.005628495 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.362806 (Hartree/Particle)

Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
     -586.096864 hartrees (-367781.64312864 kcal/mol)

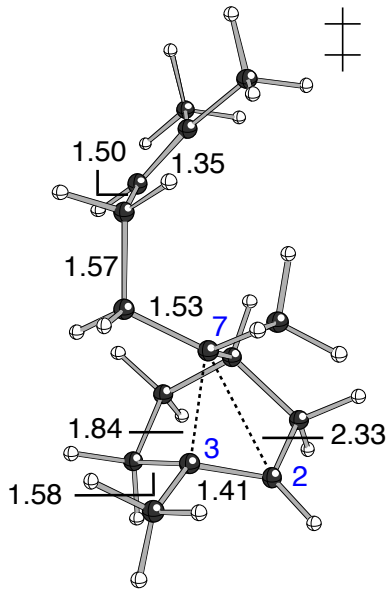
mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.2744621 hartrees (-367893.087712371 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.0581056 hartrees (-367757.321845056 kcal/mol)

Coordinates (from last standard orientation):
 ---------------------------------------------------------------------
 Center     Atomic                   Coordinates (Angstroms)
 Number     Number                X           Y           Z
 ---------------------------------------------------------------------
    1          6              -2.584320   -0.942469    1.039211
    2          6              -3.296246   -0.514132   -0.016354
    3          6              -2.624374   -0.132770   -1.320767
    4          6              -1.156794   -0.567383   -1.408423
    5          6              -0.396605   -0.278295   -0.061612
    6          6              -1.077964   -1.083908    1.056827
    7          1              -3.173259   -0.587005   -2.155630
    8          1              -3.105026   -1.235129    1.948633
```

9	1	-1.093926	-1.649773	-1.556723
10	1	-0.656363	-0.099099	-2.259125
11	1	-0.800984	-2.139045	0.924639
12	1	-0.683223	-0.810330	2.042084
13	1	-2.716830	0.954216	-1.476405
14	6	-4.796774	-0.388253	0.016150
15	1	-5.259645	-1.046816	-0.729183
16	1	-5.204349	-0.645310	0.997001
17	1	-5.114218	0.633529	-0.228985
18	1	0.644087	-0.642394	-0.239669
19	6	-0.171570	1.158554	0.170674
20	6	0.668310	1.904230	-0.759631
21	1	0.596950	1.559802	-1.791953
22	1	0.478652	2.977414	-0.702652
23	6	-0.665106	1.841981	1.382856
24	1	-0.388305	1.293468	2.292169
25	1	-0.345901	2.881559	1.456606
26	1	-1.766148	1.789549	1.367877
27	6	2.218530	1.672084	-0.311189
28	1	2.721606	2.504340	-0.815073
29	1	2.320245	1.839037	0.762631
30	6	2.786400	0.377383	-0.772591
31	6	3.337990	-0.604556	-0.016897
32	1	2.814776	0.250972	-1.854877
33	6	3.975677	-1.800476	-0.675392
34	1	5.040850	-1.852415	-0.417991
35	1	3.525572	-2.732702	-0.312455
36	1	3.889001	-1.771421	-1.764030
37	6	3.426474	-0.586729	1.486582
38	1	3.058402	-1.531930	1.902579
39	1	4.475955	-0.505153	1.796473
40	1	2.880310	0.233062	1.957400

TS



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.3830163 hartrees (-367961.206558413 kcal/mol)
Imaginary Frequencies: 1 (-315.1968 1/cm)
Zero-point correction = 0.364183 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-586.062539 hartrees (-367760.10384789 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.2528762 hartrees (-367879.542344262 kcal/mol)

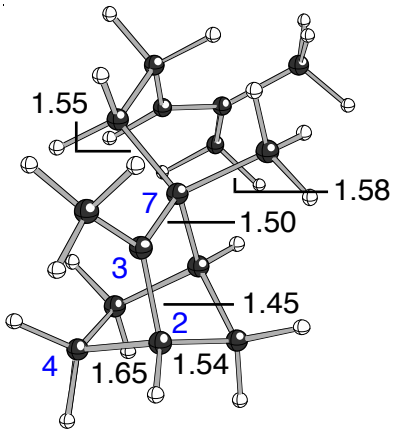
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.043592 hartrees (-367748.21441592 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.702726	0.461875	1.122044
2	6	2.520179	-0.122345	-0.147600
3	6	2.244276	0.992043	-1.231433
4	6	0.964201	1.756565	-0.815390
5	6	0.525007	1.057740	0.484244
6	6	1.597856	1.353708	1.549765
7	1	3.125048	1.635689	-1.296756
8	1	3.511835	0.180838	1.799532
9	1	1.156062	2.818969	-0.645131
10	1	0.192905	1.694282	-1.584937
11	1	1.926661	2.403227	1.618547
12	1	1.292995	1.091143	2.571122
13	1	2.148828	0.484683	-2.193880
14	6	3.421382	-1.260024	-0.581410
15	1	4.401511	-0.875368	-0.884107
16	1	3.576855	-1.990819	0.217222
17	1	3.001241	-1.779857	-1.446176
18	1	-0.493666	1.297663	0.794148
19	6	0.754045	-0.463226	0.235453
20	6	0.153713	-1.106774	-1.015516
21	1	0.333906	-0.506463	-1.907785
22	1	0.645662	-2.072507	-1.175150
23	6	0.563092	-1.391111	1.437606
24	1	-0.505528	-1.465607	1.658338
25	1	0.917631	-2.400227	1.207994
26	1	1.054758	-1.065573	2.355185
27	6	-1.385701	-1.387864	-0.940983
28	1	-1.595580	-1.948435	-1.863220
29	1	-1.607531	-2.074180	-0.121818
30	6	-2.265325	-0.169161	-0.907109
31	6	-3.294376	0.092876	-0.077227
32	1	-2.077328	0.550072	-1.706186
33	6	-4.125780	1.340944	-0.255841

34	1	-5.171094	1.081500	-0.465409
35	1	-4.135307	1.943121	0.661836
36	1	-3.762321	1.966276	-1.075754
37	6	-3.750687	-0.802560	1.048882
38	1	-3.786895	-0.246293	1.993948
39	1	-4.773189	-1.152842	0.860325
40	1	-3.125107	-1.685406	1.195205

C



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.4119164 hartrees (-367979.341660164 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.365536 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-586.090942 hartrees (-367777.92701442 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.2841772 hartrees (-367899.184034772 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):HF = -586.0762967 hartrees (-367768.736942217 kcal/mol)

Coordinates (from last standard orientation):

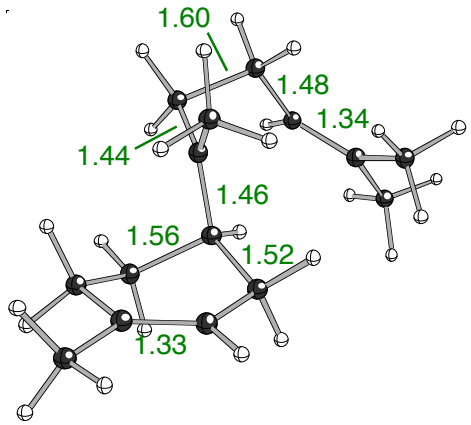
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.782801	0.772895	0.532822
2	6	2.328337	-0.498222	0.018734
3	6	2.366505	1.600543	-0.832534
4	6	0.841546	1.794541	-0.679469
5	6	0.509158	0.903808	0.542005
6	6	1.674867	1.270631	1.482114
7	1	2.957849	2.516896	-0.749465

8	1	3.838467	0.882407	0.776325
9	1	0.603529	2.836791	-0.452129
10	1	0.293485	1.523183	-1.581633
11	1	1.752980	2.344127	1.669785
12	1	1.679572	0.753792	2.443425
13	1	2.669053	1.107840	-1.760630
14	6	3.200184	-1.512276	-0.600179
15	1	4.239813	-1.190753	-0.675262
16	1	3.160259	-2.409792	0.037819
17	1	2.824171	-1.834818	-1.577022
18	1	-0.499067	1.026280	0.934191
19	6	0.842056	-0.586924	0.165408
20	6	0.112708	-1.210780	-1.057159
21	1	0.303863	-0.599657	-1.946930
22	1	0.569475	-2.187608	-1.253922
23	6	0.645382	-1.529681	1.416360
24	1	-0.365921	-1.373036	1.797029
25	1	0.753233	-2.573802	1.113262
26	1	1.342226	-1.339394	2.234998
27	6	-1.412182	-1.431124	-0.918175
28	1	-1.699842	-2.035901	-1.790402
29	1	-1.622570	-2.060262	-0.049304
30	6	-2.251745	-0.178666	-0.909520
31	6	-3.258073	0.145310	-0.076358
32	1	-2.048200	0.509669	-1.731932
33	6	-4.043355	1.420090	-0.278400
34	1	-5.102088	1.197512	-0.461336
35	1	-4.010693	2.050995	0.619339
36	1	-3.670327	2.004104	-1.124237
37	6	-3.728503	-0.697321	1.084763
38	1	-3.731142	-0.110633	2.012217
39	1	-4.765120	-1.018415	0.922909
40	1	-3.131133	-1.596465	1.250431

Table 1: R_1/R_2=prenyl/CH_3 (aligned) (Fig. S1)

mPWB1K

A_a



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0642091 hartrees (-367761.151852341 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.372426 (Hartree/Particle)

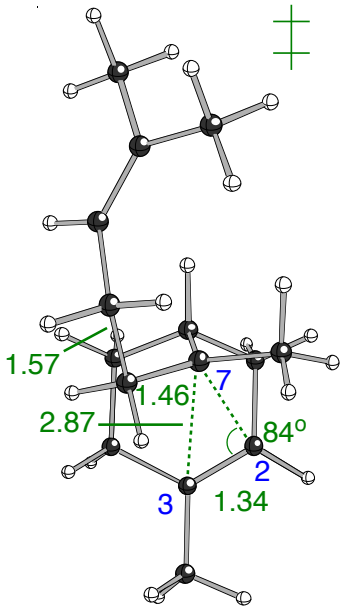
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.737248 hartrees (-367555.98049248 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.340728	-1.321637	0.563836
2	6	-3.175286	-0.489365	-0.054391
3	6	-2.690904	0.465342	-1.103510
4	6	-1.303614	0.139729	-1.610025
5	6	-0.328898	-0.196230	-0.439427
6	6	-0.868384	-1.398765	0.313422
7	1	-3.382124	0.450023	-1.945979
8	1	-2.737571	-2.014874	1.292764
9	1	-1.330925	-0.761335	-2.218698
10	1	-0.909166	0.938798	-2.230950
11	1	-0.638875	-2.290199	-0.272485
12	1	-0.335395	-1.534772	1.254466
13	1	-2.740006	1.490513	-0.720735
14	6	-4.636334	-0.452343	0.240084
15	1	-5.212992	-0.728881	-0.641416
16	1	-4.901756	-1.129639	1.045269
17	1	-4.954660	0.551711	0.519438
18	1	0.638357	-0.413640	-0.913354
19	6	-0.094916	1.024197	0.321570
20	6	0.758327	2.040856	-0.246020
21	1	0.802370	2.012472	-1.329621
22	1	0.497011	3.031789	0.111493
23	6	-0.648707	1.226431	1.654846
24	1	-0.493247	0.350629	2.284293
25	1	-0.296451	2.129694	2.137915
26	1	-1.738053	1.269255	1.535658
27	6	2.223035	1.707099	0.295159
28	1	2.745821	2.652314	0.169653
29	1	2.188727	1.513101	1.362766
30	6	2.914441	0.647765	-0.473678
31	6	3.200741	-0.591581	-0.057354
32	1	3.258143	0.941844	-1.457378
33	6	3.995526	-1.518345	-0.914287
34	1	4.907990	-1.817055	-0.400143
35	1	3.440717	-2.433550	-1.116359
36	1	4.271892	-1.063446	-1.859752
37	6	2.796347	-1.149186	1.266499

38	1	2.343144	-2.130954	1.138242
39	1	3.672322	-1.296158	1.897400
40	1	2.100856	-0.521445	1.817157

TS_{A-B}



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0564365 hartrees (-367756.274468115 kcal/mol)
Imaginary Frequencies: 1 (-52.5369 1/cm)
Zero-point correction = 0.373475 (Hartree/Particle)

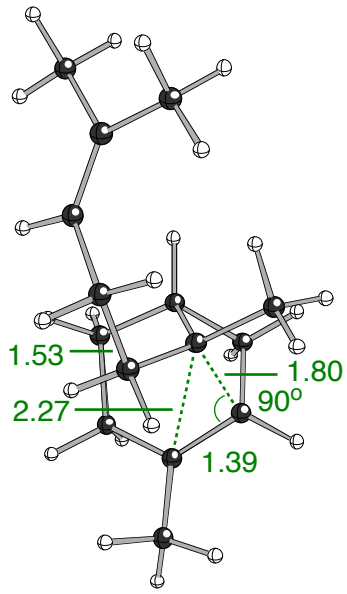
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.725881 hartrees (-367548.84758631 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.680517	0.010568	1.227972
2	6	3.065580	0.011116	-0.059374
3	6	2.482996	0.963453	-1.057852
4	6	1.194339	1.645342	-0.589768
5	6	0.564472	0.866638	0.553898
6	6	1.544354	0.859408	1.717441
7	1	3.239047	1.717505	-1.277557
8	1	3.214981	-0.607175	1.936697
9	1	1.404261	2.643046	-0.214951
10	1	0.502283	1.777595	-1.417980
11	1	1.858479	1.872697	1.964461

12	1	1.107937	0.453891	2.624610
13	1	2.338929	0.435937	-2.001394
14	6	4.168521	-0.860033	-0.551923
15	1	4.989639	-0.253792	-0.932028
16	1	4.556638	-1.505610	0.228892
17	1	3.833102	-1.481393	-1.381516
18	1	-0.413667	1.299219	0.811087
19	6	0.266698	-0.550855	0.214843
20	6	-0.015057	-0.974139	-1.152146
21	1	0.342107	-0.270009	-1.890799
22	1	0.427968	-1.952707	-1.330640
23	6	-0.083539	-1.507211	1.267013
24	1	-1.132061	-1.262263	1.493937
25	1	-0.057060	-2.535504	0.924518
26	1	0.468940	-1.390865	2.188725
27	6	-1.568332	-1.135950	-1.308956
28	1	-1.703833	-1.388021	-2.359813
29	1	-1.896053	-1.994817	-0.732970
30	6	-2.328520	0.096355	-0.965367
31	6	-3.345863	0.208813	-0.107115
32	1	-2.037340	0.985785	-1.513838
33	6	-4.033942	1.521799	0.079323
34	1	-5.081084	1.444350	-0.209343
35	1	-4.023310	1.821228	1.126443
36	1	-3.578153	2.310014	-0.511788
37	6	-3.930200	-0.911249	0.690829
38	1	-3.947561	-0.656815	1.749829
39	1	-4.968130	-1.066034	0.399796
40	1	-3.418196	-1.860602	0.572722

B



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):

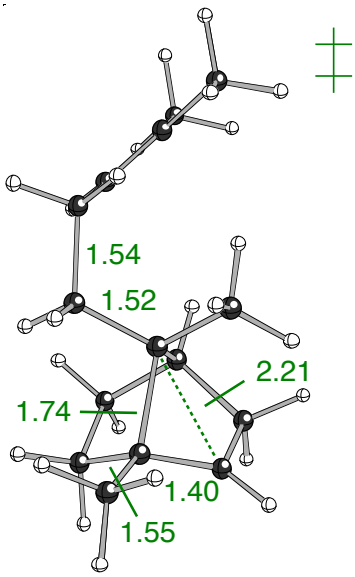
HF = -586.065779 hartrees (-367762.13698029 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.375585 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.732178 hartrees (-367552.79901678 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.228453	-0.186169	1.087748
2	6	2.693197	-0.101388	-0.219557
3	6	2.452824	1.160327	-0.950385
4	6	1.072339	1.770002	-0.611385
5	6	0.531412	1.105349	0.630417
6	6	1.649021	1.080403	1.677968
7	1	3.237864	1.837886	-0.600219
8	1	2.564065	-1.017033	1.694134
9	1	1.168123	2.839261	-0.449329
10	1	0.399055	1.631594	-1.452157
11	1	2.320908	1.935545	1.673734
12	1	1.295013	0.923105	2.688601
13	1	2.605054	1.034858	-2.018237
14	6	3.397582	-1.212319	-0.873686
15	1	4.427141	-0.887555	-1.043414
16	1	3.420031	-2.114592	-0.272952
17	1	2.979634	-1.415929	-1.857532
18	1	-0.435194	1.506689	0.921427
19	6	0.555174	-0.418078	0.479144
20	6	0.260781	-1.091926	-0.847369
21	1	0.654083	-0.513013	-1.681951
22	1	0.762608	-2.059632	-0.866826
23	6	-0.081850	-1.176487	1.618115
24	1	-1.156866	-1.019189	1.534818
25	1	0.112533	-2.242779	1.540814
26	1	0.223921	-0.832589	2.598552
27	6	-1.236325	-1.327069	-1.080414
28	1	-1.327369	-1.756903	-2.078632
29	1	-1.599401	-2.088482	-0.396762
30	6	-2.055726	-0.082341	-0.995658
31	6	-3.142595	0.137296	-0.253838
32	1	-1.742789	0.720404	-1.655025
33	6	-3.859661	1.446707	-0.327935
34	1	-4.882923	1.303316	-0.672262
35	1	-3.926699	1.910475	0.655733
36	1	-3.370643	2.141193	-1.004593
37	6	-3.771340	-0.856790	0.667348
38	1	-3.854359	-0.447425	1.673873
39	1	-4.788261	-1.070474	0.340974
40	1	-3.245248	-1.803828	0.724151

TS



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0505486 hartrees (-367752.579751986 kcal/mol)
Imaginary Frequencies: 1 (-309.6472 1/cm)
Zero-point correction = 0.374209 (Hartree/Particle)

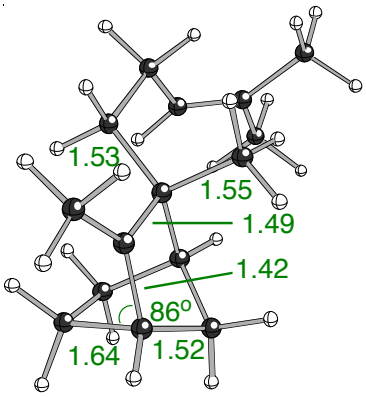
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.718311 hartrees (-367544.09733561 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.468124	0.451819	1.229194
2	6	2.409043	-0.232965	0.007714
3	6	2.418532	0.750104	-1.193054
4	6	1.183634	1.645544	-1.075151
5	6	0.536756	1.180386	0.216117
6	6	1.477149	1.526943	1.362141
7	1	3.351539	1.305866	-1.183182
8	1	3.079836	0.118753	2.062921
9	1	1.439851	2.699864	-1.034552
10	1	0.515202	1.515388	-1.920638
11	1	1.955130	2.510460	1.304940
12	1	1.016326	1.486201	2.348158
13	1	2.421202	0.148191	-2.096816
14	6	3.211549	-1.490405	-0.153187
15	1	4.270088	-1.255260	-0.237023
16	1	3.080492	-2.166750	0.687501
17	1	2.927991	-2.013381	-1.061086

18	1	-0.482147	1.522059	0.357190
19	6	0.687642	-0.353635	0.201741
20	6	0.197737	-1.118883	-1.017363
21	1	0.457810	-0.595113	-1.931566
22	1	0.703094	-2.083132	-1.048078
23	6	0.220380	-1.062296	1.459996
24	1	-0.861729	-0.971298	1.516033
25	1	0.462710	-2.121570	1.416462
26	1	0.622439	-0.668302	2.388326
27	6	-1.313942	-1.387498	-1.017879
28	1	-1.518805	-1.891746	-1.963815
29	1	-1.567289	-2.104785	-0.243759
30	6	-2.150328	-0.157190	-0.922305
31	6	-3.153821	0.087820	-0.078182
32	1	-1.928238	0.607011	-1.661038
33	6	-3.916979	1.370825	-0.155091
34	1	-4.968960	1.178610	-0.361609
35	1	-3.881593	1.902892	0.795290
36	1	-3.536292	2.026087	-0.933001
37	6	-3.639421	-0.855478	0.973912
38	1	-3.649600	-0.368509	1.948602
39	1	-4.668863	-1.144917	0.766778
40	1	-3.056526	-1.767167	1.052337

C



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0825825 hartrees (-367772.681344575 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.375571 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.749370 hartrees (-367563.5871687 kcal/mol)

Coordinates (from last standard orientation):

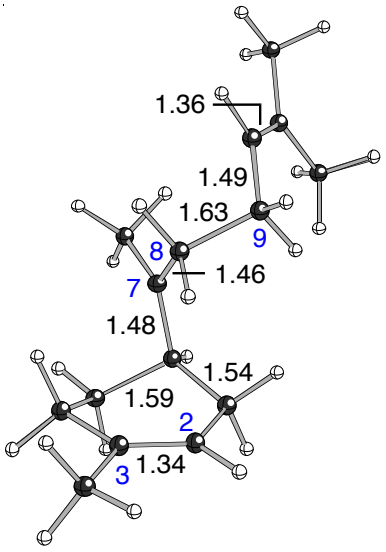
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z

1	6	2.720039	0.679052	0.676297
2	6	2.217447	-0.555121	0.184559
3	6	2.553638	1.224540	-0.858686
4	6	1.115271	1.720786	-0.904166
5	6	0.521597	1.032524	0.319709
6	6	1.572063	1.389937	1.361965
7	1	3.333379	1.978715	-0.928637
8	1	3.738835	0.735914	1.033230
9	1	1.073884	2.799094	-0.783166
10	1	0.621650	1.475762	-1.837742
11	1	1.739310	2.459776	1.439954
12	1	1.387863	0.999201	2.357451
13	1	2.780442	0.494273	-1.636712
14	6	3.040971	-1.705353	-0.195638
15	1	4.102066	-1.486618	-0.170579
16	1	2.836354	-2.478876	0.550427
17	1	2.755943	-2.125733	-1.155298
18	1	-0.502769	1.295281	0.549791
19	6	0.731019	-0.490574	0.132704
20	6	0.122340	-1.145566	-1.108650
21	1	0.395217	-0.571245	-1.993499
22	1	0.576564	-2.128254	-1.232485
23	6	0.282254	-1.262719	1.395952
24	1	-0.751016	-0.992738	1.598864
25	1	0.333841	-2.333778	1.218901
26	1	0.868073	-1.036608	2.281966
27	6	-1.389959	-1.345472	-1.073551
28	1	-1.659742	-1.824269	-2.016156
29	1	-1.641882	-2.064305	-0.298744
30	6	-2.176677	-0.087857	-0.919700
31	6	-3.160619	0.162873	-0.054882
32	1	-1.932663	0.695857	-1.630674
33	6	-3.872294	1.477398	-0.071855
34	1	-4.933819	1.335851	-0.270390
35	1	-3.802940	1.970893	0.897409
36	1	-3.474899	2.146445	-0.829442
37	6	-3.670207	-0.798565	0.969243
38	1	-3.626520	-0.355761	1.964138
39	1	-4.719819	-1.020298	0.780694
40	1	-3.138642	-1.743876	0.990890

Table 1: R_1/R_2=CH_3/prenyl (aligned) (Fig. 3 and Fig. S2)

B3LYP

A_a



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.4144521 hartrees (-367980.932837271 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.363297 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-586.096825 hartrees (-367781.61865575 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.2759895 hartrees (-367894.046171145 kcal/mol)

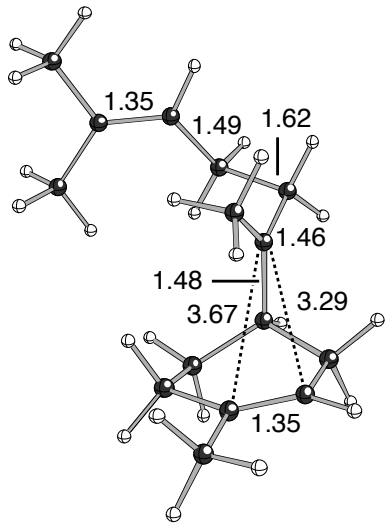
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.0597582 hartrees (-367758.358868082 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.705786	-1.043124	0.865184
2	6	3.417473	-0.481321	-0.124698
3	6	3.104877	0.914217	-0.623127
4	6	2.211917	1.718281	0.323600
5	6	0.992291	0.868719	0.892216
6	6	1.546096	-0.393687	1.583216
7	1	4.043186	1.468405	-0.755178
8	1	2.976383	-2.038076	1.213353
9	1	2.776557	2.007595	1.216011
10	1	1.856011	2.639234	-0.146354
11	1	1.858158	-0.099130	2.594940
12	1	0.746256	-1.127740	1.740843
13	1	2.666845	0.856396	-1.631802
14	6	4.563930	-1.186038	-0.800708

15	1	5.503010	-0.640278	-0.646250
16	1	4.695357	-2.202890	-0.422552
17	1	4.408949	-1.241927	-1.885936
18	1	0.510774	1.531000	1.624902
19	6	0.036682	0.690800	-0.219588
20	6	-0.834609	1.810771	-0.594844
21	1	-1.875834	1.443140	-0.447599
22	1	-0.674309	2.721916	-0.017989
23	1	-0.788401	2.016508	-1.671264
24	6	-0.145641	-0.573333	-0.922119
25	1	-0.358270	-0.429665	-1.984959
26	1	0.701871	-1.244641	-0.787567
27	6	-1.458803	-1.311476	-0.301992
28	1	-1.325815	-2.334233	-0.671615
29	1	-1.378093	-1.351776	0.785134
30	6	-2.757649	-0.762568	-0.774491
31	6	-3.790845	-0.312440	-0.019373
32	6	-5.085727	0.096061	-0.672823
33	1	-5.350719	1.126323	-0.404869
34	1	-5.045085	0.018052	-1.761729
35	1	-5.907478	-0.536206	-0.314338
36	6	-3.787164	-0.228930	1.485017
37	1	-4.129599	0.759000	1.814279
38	1	-4.500494	-0.952885	1.898761
39	1	-2.816125	-0.427058	1.943112
40	1	-2.904821	-0.796649	-1.854170

A_b



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.4130061 hartrees (-367980.025457811 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.363052 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =

-586.096391 hartrees (-367781.34631641 kcal/mol)

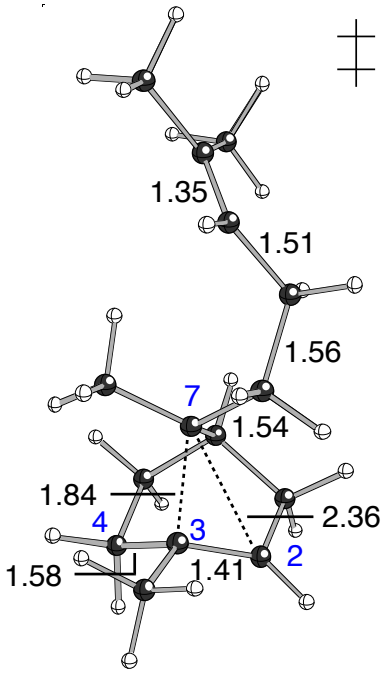
mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.2739852 hartrees (-367892.788452852 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.0576771 hartrees (-367757.052957021 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.279387	0.477510	-0.433623
2	6	-3.132740	-0.830505	-0.153310
3	6	-2.008466	-1.325508	0.724402
4	6	-1.277190	-0.224331	1.500675
5	6	-1.058956	1.120852	0.746913
6	6	-2.431859	1.590712	0.107555
7	1	-2.409583	-2.045204	1.449895
8	1	-4.082555	0.789187	-1.098820
9	1	-1.873152	0.044029	2.379772
10	1	-0.319131	-0.592810	1.881015
11	1	-2.951341	2.119935	0.918031
12	1	-2.268578	2.351974	-0.667727
13	1	-1.310334	-1.914275	0.111122
14	6	-4.055625	-1.880504	-0.711495
15	1	-4.587253	-2.395872	0.097903
16	1	-4.799201	-1.451946	-1.387701
17	1	-3.496186	-2.650400	-1.257987
18	1	-0.772279	1.871799	1.488784
19	6	-0.068350	1.170205	-0.345255
20	6	-0.060803	0.191463	-1.437207
21	1	0.633351	-0.609106	-1.099977
22	1	-1.036829	-0.266056	-1.612617
23	1	0.373582	0.587590	-2.357267
24	6	0.992233	2.175085	-0.309797
25	1	1.316589	2.481039	-1.307213
26	1	0.707115	3.047511	0.282782
27	6	2.281113	1.524605	0.427379
28	1	2.908948	2.407834	0.592740
29	1	1.983396	1.156412	1.411009
30	6	3.023968	0.516538	-0.381749
31	6	3.346989	-0.749450	-0.031704
32	6	4.201639	-1.596029	-0.941568
33	1	3.691496	-2.532824	-1.198120
34	1	4.461694	-1.077415	-1.867454
35	1	5.132819	-1.880070	-0.435986
36	6	2.967169	-1.411479	1.268842
37	1	2.510417	-2.390800	1.082164
38	1	3.867207	-1.603543	1.866189
39	1	2.284795	-0.824914	1.887657
40	1	3.396599	0.882932	-1.338542

TS



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.3825505 hartrees (-367960.914264255 kcal/mol)
Imaginary Frequencies: 1 (-310.2609 1/cm)
Zero-point correction = 0.363506 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-586.062823 hartrees (-367760.28206073 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.2523718 hartrees (-367879.225828218 kcal/mol)

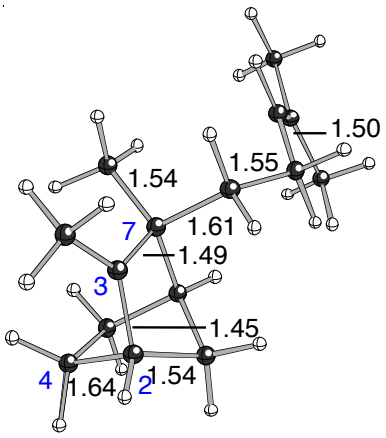
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.041641 hartrees (-367746.99014391 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.731046	-0.167771	1.117751
2	6	-2.478861	0.613396	-0.026431
3	6	-2.827335	-0.204644	-1.335065
4	6	-1.953805	-1.481990	-1.349363
5	6	-1.087696	-1.342729	-0.083138
6	6	-2.027108	-1.471861	1.130231
7	1	-3.899110	-0.416979	-1.336878
8	1	-3.269354	0.203298	1.992085

9	1	-2.555684	-2.393682	-1.315091
10	1	-1.343474	-1.541345	-2.252887
11	1	-2.727908	-2.320937	1.099445
12	1	-1.499639	-1.581824	2.087761
13	1	-2.629236	0.459427	-2.179348
14	6	-2.873825	2.075628	-0.039855
15	1	-3.952016	2.180406	-0.203181
16	1	-2.622592	2.578021	0.898274
17	1	-2.373990	2.603935	-0.856209
18	1	-0.238582	-2.028903	-0.054201
19	6	-0.692570	0.165249	-0.021497
20	6	-0.061213	0.776037	-1.255285
21	1	0.994291	0.464566	-1.256426
22	1	-0.502018	0.474817	-2.203646
23	1	-0.052140	1.868076	-1.197683
24	6	0.037427	0.653484	1.241200
25	1	0.102549	1.747254	1.205689
26	1	-0.529948	0.419488	2.146147
27	6	1.469253	0.071126	1.440727
28	1	1.710060	0.269672	2.495411
29	1	1.442293	-1.018756	1.345666
30	6	2.559948	0.675329	0.596641
31	6	3.548425	0.043961	-0.068732
32	6	4.609064	0.834569	-0.796019
33	1	4.641546	0.563958	-1.859100
34	1	4.445770	1.912700	-0.719222
35	1	5.603236	0.611286	-0.388892
36	6	3.724894	-1.452668	-0.140550
37	1	3.793937	-1.782184	-1.184788
38	1	4.669056	-1.744232	0.336440
39	1	2.925523	-2.017281	0.343937
40	1	2.574118	1.766522	0.593020

C



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.4131827 hartrees (-367980.136276077 kcal/mol)
Imaginary Frequencies: none found

Zero-point correction = 0.365796 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-586.091088 hartrees (-367778.01863088 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.2854371 hartrees (-367899.974634621 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.0772684 hartrees (-367769.346693684 kcal/mol)

Coordinates (from last standard orientation):

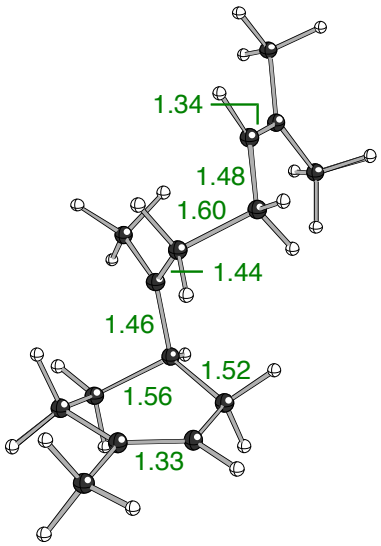
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.799964	0.414168	-0.673948
2	6	-2.164052	-0.756687	-0.100501
3	6	-3.017302	1.169481	0.764627
4	6	-1.615440	1.741683	1.081632
5	6	-0.733287	1.107312	-0.022778
6	6	-1.652863	1.269500	-1.249737
7	1	-3.776844	1.925685	0.546213
8	1	-3.733520	0.277756	-1.218353
9	1	-1.608780	2.829880	0.979113
10	1	-1.285503	1.507663	2.094748
11	1	-1.963447	2.302802	-1.422018
12	1	-1.254758	0.868113	-2.183806
13	1	-3.426203	0.521596	1.544934
14	6	-2.849016	-2.025809	0.199499
15	1	-3.935617	-1.945037	0.133137
16	1	-2.527981	-2.748554	-0.569478
17	1	-2.543444	-2.450324	1.160102
18	1	0.267336	1.530426	-0.097902
19	6	-0.737055	-0.448233	0.186527
20	6	-0.216074	-0.953042	1.545048
21	1	0.799455	-0.588342	1.705389
22	1	-0.839099	-0.609814	2.375044
23	1	-0.182912	-2.045246	1.578506
24	6	0.003785	-1.215490	-1.013035
25	1	0.076402	-2.263372	-0.702863
26	1	-0.611958	-1.208897	-1.919536
27	6	1.404073	-0.681215	-1.401986
28	1	1.681897	-1.278535	-2.284046
29	1	1.328924	0.348671	-1.759166
30	6	2.475146	-0.836584	-0.357510
31	6	3.379090	0.074976	0.049856
32	6	4.436485	-0.294467	1.062746
33	1	4.381889	0.358561	1.943286
34	1	4.343998	-1.331394	1.396561
35	1	5.440371	-0.161910	0.640441
36	6	3.465937	1.495981	-0.450781
37	1	3.431754	2.202837	0.387910

38	1	4.428007	1.661135	-0.951601
39	1	2.679874	1.766583	-1.159154
40	1	2.553384	-1.839732	0.064590

Table 1: R_1/R_2=CH_3/prenyl (aligned) (Fig. 3 and Fig. S2)

mPWB1K

A_a



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0646367 hartrees (-367761.420175617 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.372700 (Hartree/Particle)

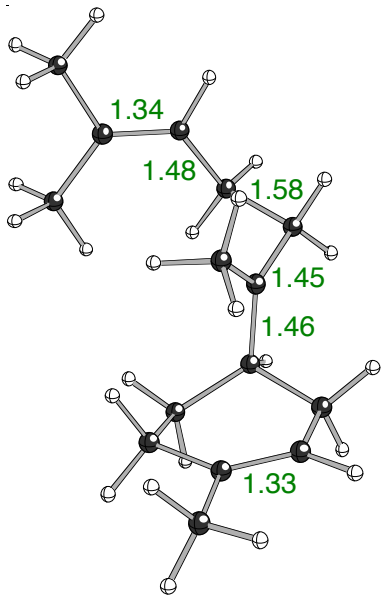
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.737656 hartrees (-367556.23651656 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.661013	-0.947103	0.932541
2	6	3.325612	-0.442453	-0.103696
3	6	2.957345	0.886773	-0.687342
4	6	2.096308	1.715566	0.238876
5	6	0.919251	0.888158	0.850153
6	6	1.489397	-0.304128	1.603787
7	1	3.867775	1.444608	-0.904540
8	1	2.977258	-1.895103	1.345877

9	1	2.681342	2.036425	1.098306
10	1	1.726441	2.611828	-0.252203
11	1	1.781583	0.042121	2.595926
12	1	0.713764	-1.048936	1.783575
13	1	2.476070	0.741711	-1.659790
14	6	4.474376	-1.146489	-0.741222
15	1	5.386808	-0.559851	-0.646041
16	1	4.648856	-2.119542	-0.293694
17	1	4.302143	-1.287175	-1.807748
18	1	0.401134	1.572647	1.524122
19	6	0.021662	0.624400	-0.273956
20	6	-0.829309	1.693546	-0.760842
21	1	-1.860418	1.321925	-0.607835
22	1	-0.691319	2.642024	-0.256581
23	1	-0.757428	1.802326	-1.841912
24	6	-0.107785	-0.682232	-0.873002
25	1	-0.320688	-0.639250	-1.936979
26	1	0.757678	-1.303706	-0.670374
27	6	-1.377281	-1.347050	-0.171644
28	1	-1.246635	-2.401693	-0.406651
29	1	-1.297422	-1.259175	0.906733
30	6	-2.676236	-0.873309	-0.693063
31	6	-3.672829	-0.306396	0.002305
32	6	-4.968422	0.014993	-0.663810
33	1	-5.207162	1.072142	-0.557978
34	1	-4.960333	-0.236354	-1.719177
35	1	-5.780612	-0.533475	-0.189087
36	6	-3.620746	0.017011	1.457967
37	1	-3.952039	1.039822	1.628091
38	1	-4.313253	-0.621945	2.004299
39	1	-2.640501	-0.103553	1.906891
40	1	-2.847182	-1.065551	-1.745533

A_b



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.06302 hartrees (-367760.4056802 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.373519 (Hartree/Particle)

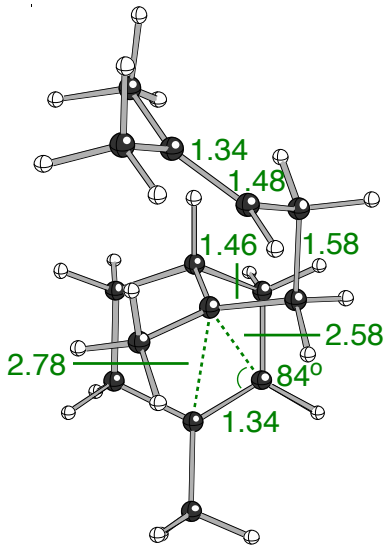
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.733763 hartrees (-367553.79362013 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.127037	0.562440	-0.528081
2	6	-3.102543	-0.728742	-0.195784
3	6	-2.100891	-1.268476	0.770772
4	6	-1.344538	-0.206336	1.546053
5	6	-0.982300	1.063612	0.780249
6	6	-2.241075	1.617868	0.028789
7	1	-2.610527	-1.916573	1.483502
8	1	-3.853353	0.903734	-1.253027
9	1	-1.966966	0.129235	2.373223
10	1	-0.447863	-0.628290	1.996051
11	1	-2.768716	2.221268	0.768305
12	1	-1.961449	2.322118	-0.758350
13	1	-1.422460	-1.935849	0.234146
14	6	-4.052678	-1.717249	-0.779557
15	1	-4.682235	-2.143685	-0.000012
16	1	-4.696629	-1.266231	-1.527264
17	1	-3.519394	-2.547912	-1.240191
18	1	-0.670894	1.827133	1.489514
19	6	0.003212	1.017991	-0.291894
20	6	0.037109	-0.084853	-1.233944
21	1	0.389505	-0.967829	-0.686926
22	1	-0.986333	-0.324419	-1.540526
23	1	0.683792	0.087472	-2.083398
24	6	0.977383	2.085600	-0.395245
25	1	1.268848	2.290535	-1.421006
26	1	0.640814	2.990166	0.101972
27	6	2.254173	1.553426	0.376014
28	1	2.844855	2.456154	0.522665
29	1	1.966197	1.211433	1.366118
30	6	3.047088	0.549210	-0.374310
31	6	3.279075	-0.719274	-0.026555
32	6	4.170672	-1.583142	-0.855475
33	1	3.645517	-2.477298	-1.188818
34	1	4.549507	-1.059464	-1.727121
35	1	5.021390	-1.924473	-0.267329
36	6	2.726799	-1.381213	1.193082
37	1	2.255304	-2.327742	0.930876
38	1	3.531381	-1.625674	1.885470

39	1	2.005672	-0.777098	1.735241
40	1	3.517347	0.918105	-1.277787

TS_{A-B}



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0580126 hartrees (-367757.263486626 kcal/mol)
Imaginary Frequencies: 1 (-67.0213 1/cm)
Zero-point correction = 0.372696 (Hartree/Particle)

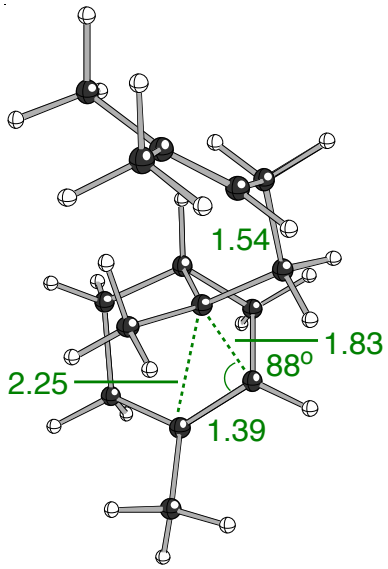
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.730080 hartrees (-367551.4825008 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.717482	0.997155	-0.313972
2	6	3.018151	-0.050494	0.473371
3	6	2.704552	-1.453598	0.056198
4	6	1.623719	-1.560963	-1.028088
5	6	0.899733	-0.235871	-1.197175
6	6	1.930286	0.818730	-1.578599
7	1	3.630951	-1.904174	-0.300984
8	1	3.057729	1.984844	-0.034709
9	1	2.067139	-1.808665	-1.988189
10	1	0.932063	-2.368817	-0.801837
11	1	2.544215	0.481519	-2.412654
12	1	1.473171	1.750131	-1.896375
13	1	2.441347	-2.031539	0.942023
14	6	3.754172	0.107602	1.756826
15	1	4.683355	-0.460113	1.735009

16	1	3.993472	1.145105	1.965228
17	1	3.169916	-0.288793	2.587238
18	1	0.101734	-0.337077	-1.940064
19	6	0.279132	0.253717	0.079051
20	6	-0.105403	-0.653467	1.141643
21	1	-1.204423	-0.733051	0.999097
22	1	0.331815	-1.639592	1.104599
23	1	-0.004801	-0.200556	2.124420
24	6	-0.286364	1.599303	0.165854
25	1	-0.361156	1.928561	1.197844
26	1	0.278298	2.326110	-0.402212
27	6	-1.744013	1.564818	-0.440262
28	1	-1.988807	2.619282	-0.555314
29	1	-1.713387	1.146494	-1.441507
30	6	-2.769300	0.925819	0.417753
31	6	-3.482938	-0.175260	0.146559
32	6	-4.558859	-0.630480	1.075045
33	1	-4.382044	-1.653307	1.404631
34	1	-4.641616	0.007383	1.949006
35	1	-5.520336	-0.632697	0.563416
36	6	-3.315864	-1.013504	-1.077405
37	1	-3.224034	-2.064003	-0.806000
38	1	-4.201429	-0.937441	-1.707116
39	1	-2.457661	-0.742836	-1.684435
40	1	-2.992423	1.452189	1.338102

B



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0635549 hartrees (-367760.741335299 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.375481 (Hartree/Particle)

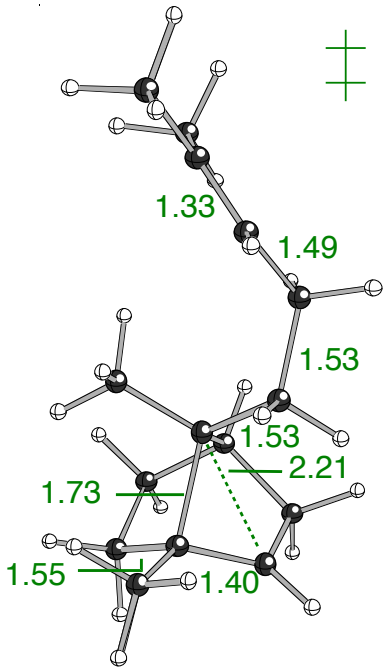
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =
-585.730807 hartrees (-367551.93870057 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.240932	-0.124726	-1.092033
2	6	2.595721	0.869725	-0.196255
3	6	2.980692	0.455266	1.173922
4	6	2.117193	-0.720322	1.686715
5	6	1.373978	-1.322223	0.517842
6	6	2.374058	-1.552460	-0.616080
7	1	4.020833	0.128074	1.089735
8	1	2.129628	0.136237	-2.135748
9	1	2.745968	-1.470524	2.156184
10	1	1.424250	-0.363600	2.443732
11	1	3.376458	-1.836218	-0.304354
12	1	2.033262	-2.256675	-1.364093
13	1	2.978472	1.301238	1.855242
14	6	2.601998	2.293691	-0.565027
15	1	3.636365	2.640953	-0.518652
16	1	2.225229	2.475210	-1.565259
17	1	2.052351	2.888796	0.161873
18	1	0.752762	-2.163434	0.815691
19	6	0.629767	-0.221144	-0.239441
20	6	-0.001987	0.905954	0.525474
21	1	-0.901516	0.501700	0.989098
22	1	0.613024	1.319511	1.317297
23	1	-0.328711	1.704007	-0.135324
24	6	-0.248404	-0.671658	-1.392425
25	1	-0.395318	0.163888	-2.075639
26	1	0.245634	-1.458703	-1.952283
27	6	-1.622544	-1.179967	-0.916412
28	1	-1.925946	-1.947906	-1.628540
29	1	-1.523433	-1.693874	0.038176
30	6	-2.682317	-0.130312	-0.876269
31	6	-3.509971	0.168779	0.125084
32	6	-4.562126	1.215868	-0.044460
33	1	-4.445754	2.007345	0.695256
34	1	-4.534685	1.662491	-1.033555
35	1	-5.553383	0.791028	0.108315
36	6	-3.497449	-0.485034	1.468359
37	1	-3.440097	0.266373	2.255491
38	1	-4.428191	-1.027021	1.631276
39	1	-2.683715	-1.189890	1.608612
40	1	-2.810727	0.412367	-1.806483

TS



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0483186 hartrees (-367751.180404686 kcal/mol)
Imaginary Frequencies: 1 (-308.1262 1/cm)
Zero-point correction = 0.374351 (Hartree/Particle)

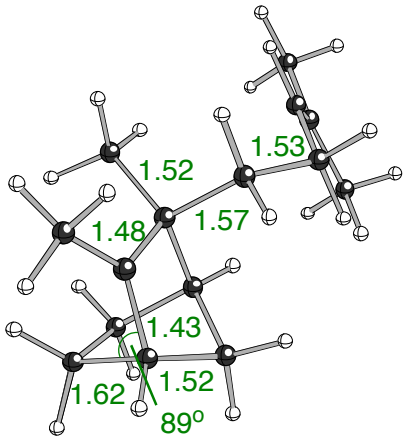
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.716403 hartrees (-367542.90004653 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.636989	0.283297	1.082309
2	6	-2.239399	0.797696	-0.159531
3	6	-2.786799	-0.075891	-1.319591
4	6	-2.170534	-1.471109	-1.188825
5	6	-1.380599	-1.376636	0.103764
6	6	-2.368464	-1.151995	1.242836
7	1	-3.871882	-0.084385	-1.272394
8	1	-2.964737	0.909230	1.907431
9	1	-2.921412	-2.253891	-1.145569
10	1	-1.520119	-1.697682	-2.027812
11	1	-3.295393	-1.731056	1.173763
12	1	-1.973362	-1.352510	2.236906
13	1	-2.519365	0.421727	-2.247233
14	6	-2.239644	2.279592	-0.384828
15	1	-3.247295	2.635084	-0.586606
16	1	-1.852155	2.823662	0.472035

17	1	-1.631148	2.526797	-1.250259
18	1	-0.697617	-2.203565	0.269389
19	6	-0.709514	0.010284	0.033675
20	6	0.090348	0.306972	-1.208597
21	1	0.896209	-0.425817	-1.261616
22	1	-0.477345	0.238588	-2.128754
23	1	0.560382	1.283435	-1.150809
24	6	0.055021	0.453811	1.276316
25	1	0.187459	1.535408	1.228214
26	1	-0.525704	0.265685	2.178822
27	6	1.426861	-0.213138	1.437723
28	1	1.637829	-0.245020	2.507530
29	1	1.375267	-1.253844	1.122359
30	6	2.549016	0.509535	0.767097
31	6	3.470957	0.014744	-0.057925
32	6	4.566785	0.883541	-0.584041
33	1	4.552982	0.909872	-1.673212
34	1	4.490573	1.901562	-0.214582
35	1	5.540391	0.489917	-0.294890
36	6	3.527283	-1.403230	-0.525064
37	1	3.582922	-1.442350	-1.612593
38	1	4.430755	-1.886359	-0.155021
39	1	2.682666	-2.005684	-0.205656
40	1	2.634132	1.556361	1.038650

C



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0839868 hartrees (-367773.562556868 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.375376 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.751408 hartrees (-367564.86603408 kcal/mol)

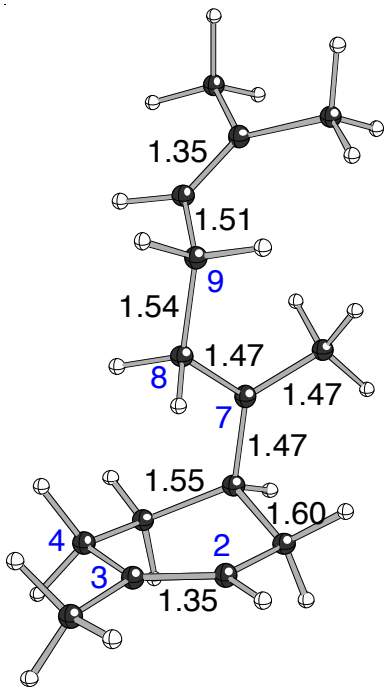
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.617563	0.568597	-0.721705
2	6	-2.148231	-0.631828	-0.107526
3	6	-2.761713	1.222859	0.756173
4	6	-1.357005	1.731535	1.063108
5	6	-0.529943	1.030534	-0.009865
6	6	-1.388137	1.293636	-1.239426
7	1	-3.520130	1.990176	0.622027
8	1	-3.549875	0.552182	-1.269524
9	1	-1.299589	2.808066	0.932434
10	1	-1.043509	1.506307	2.076332
11	1	-1.576792	2.349477	-1.408167
12	1	-1.013988	0.855163	-2.160227
13	1	-3.153674	0.544117	1.513712
14	6	-2.955285	-1.810108	0.202811
15	1	-4.017070	-1.646891	0.059552
16	1	-2.636864	-2.583993	-0.502715
17	1	-2.745803	-2.198604	1.195839
18	1	0.510224	1.331507	-0.059464
19	6	-0.710656	-0.486612	0.196321
20	6	-0.292389	-1.030862	1.551784
21	1	0.730153	-0.739434	1.766412
22	1	-0.928242	-0.656230	2.350791
23	1	-0.338875	-2.116444	1.569931
24	6	-0.075963	-1.312233	-0.980642
25	1	-0.045903	-2.349680	-0.650367
26	1	-0.718205	-1.296142	-1.863528
27	6	1.314861	-0.852411	-1.408689
28	1	1.608451	-1.520093	-2.221254
29	1	1.255537	0.139252	-1.848889
30	6	2.339592	-0.911505	-0.328671
31	6	3.188830	0.045504	0.048111
32	6	4.189327	-0.209852	1.128599
33	1	4.075823	0.507107	1.941230
34	1	4.100011	-1.211614	1.537877
35	1	5.202717	-0.089226	0.748200
36	6	3.264287	1.412009	-0.550944
37	1	3.150821	2.173730	0.220385
38	1	4.247290	1.570263	-0.992479
39	1	2.528508	1.595776	-1.327178
40	1	2.418913	-1.870348	0.172446

Table 2: R_1/R_2=prenyl/CH_3 (extended) (Fig. 4 and Fig. S3)

<u>B3LYP</u>

A_b



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.4100515 hartrees (-367978.171416765 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.362412 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-586.093330 hartrees (-367779.4255083 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.2721174 hartrees (-367891.616389674 kcal/mol)

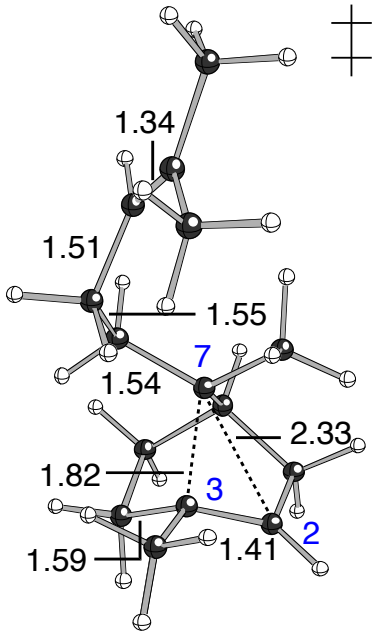
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.0568957 hartrees (-367756.562620707 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.030175	0.306246	-1.056619
2	6	-3.308925	-0.693288	-0.195875
3	6	-2.808063	-0.674565	1.226393
4	6	-2.118866	0.627339	1.672632
5	6	-1.357396	1.421194	0.583862
6	6	-2.296112	1.562904	-0.707151
7	1	-3.651379	-0.867474	1.902405
8	1	-3.369594	0.229521	-2.087577
9	1	-2.881492	1.320081	2.043830
10	1	-1.452137	0.433821	2.519795

11	1	-2.990319	2.366475	-0.429236
12	1	-1.740878	1.942285	-1.573465
13	1	-2.149124	-1.543944	1.369287
14	6	-4.109719	-1.900520	-0.603555
15	1	-5.033309	-1.962964	-0.015169
16	1	-4.381969	-1.871364	-1.661167
17	1	-3.555318	-2.828057	-0.413997
18	1	-1.190549	2.440410	0.944580
19	6	-0.084620	0.925265	0.042392
20	6	0.126121	-0.509862	-0.184867
21	1	-0.160348	-1.034583	0.740856
22	1	-0.715622	-0.790022	-0.860268
23	6	0.950684	1.896888	-0.344050
24	1	1.818096	1.701651	0.313298
25	1	1.340440	1.692033	-1.348526
26	1	0.639789	2.937195	-0.248788
27	6	1.477026	-1.026794	-0.711869
28	1	1.325641	-2.089004	-0.945886
29	1	1.722200	-0.549135	-1.665071
30	6	2.596486	-0.890776	0.293988
31	6	3.856278	-0.463710	0.084262
32	1	2.347811	-1.244435	1.296327
33	6	4.863655	-0.465360	1.209273
34	1	5.708888	-1.121570	0.967595
35	1	5.283064	0.536808	1.362813
36	1	4.429153	-0.806016	2.152731
37	6	4.400782	0.006160	-1.242537
38	1	4.856439	0.999183	-1.143445
39	1	5.201041	-0.665239	-1.577656
40	1	3.656556	0.047619	-2.040946

TS



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.3782177 hartrees (-367958.195388927 kcal/mol)
Imaginary Frequencies: 1 (-323.9269 1/cm)
Zero-point correction = 0.363472 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-586.058341 hartrees (-367757.46956091 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.2486258 hartrees (-367876.875175758 kcal/mol)

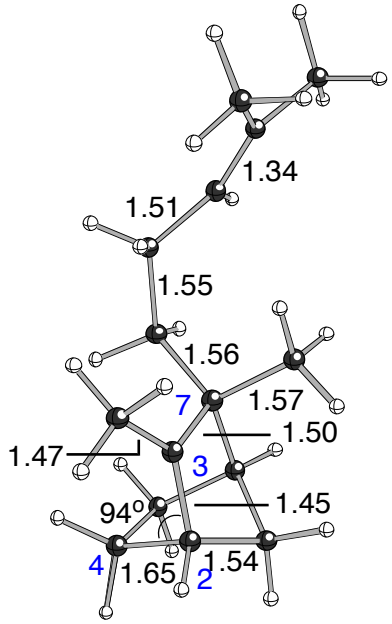
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.0398054 hartrees (-367745.838286554 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.512859	0.619477	1.292843
2	6	-1.915165	0.978246	0.065823
3	6	-2.811985	0.451163	-1.130036
4	6	-2.864285	-1.092869	-1.043521
5	6	-2.034323	-1.406143	0.215004
6	6	-2.795521	-0.827609	1.423019
7	1	-3.797397	0.918724	-1.062415
8	1	-2.639113	1.311908	2.128207
9	1	-3.886564	-1.467493	-0.949428
10	1	-2.436042	-1.559099	-1.933279
11	1	-3.880634	-1.022794	1.432634
12	1	-2.443553	-1.187095	2.398082
13	1	-2.349771	0.816295	-2.050125
14	6	-1.344890	2.371957	-0.105508
15	1	-2.152358	3.105812	-0.204495
16	1	-0.721165	2.667686	0.742695
17	1	-0.741134	2.433447	-1.013853
18	1	-1.770700	-2.460895	0.325730
19	6	-0.797853	-0.451732	0.138099
20	6	0.014149	-0.523897	-1.164573
21	1	0.211605	-1.602481	-1.287448
22	1	-0.604588	-0.254911	-2.021213
23	6	0.118549	-0.451718	1.359968
24	1	0.776107	-1.324464	1.304622
25	1	0.771318	0.423225	1.365005
26	1	-0.404658	-0.486081	2.317517
27	6	1.364426	0.232207	-1.266991
28	1	1.527249	0.415156	-2.338393
29	1	1.287415	1.224650	-0.813095
30	6	2.554975	-0.529277	-0.733402
31	6	3.586374	-0.067743	-0.004407
32	1	2.592408	-1.574859	-1.045293
33	6	4.729940	-0.978953	0.374265

34	1	5.678369	-0.598842	-0.025684
35	1	4.849213	-1.027153	1.464361
36	1	4.587576	-1.995860	-0.001084
37	6	3.734062	1.353481	0.482385
38	1	3.902062	1.374677	1.566648
39	1	4.615619	1.820977	0.025884
40	1	2.875165	1.989923	0.256607

C



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.4081304 hartrees (-367976.965907304 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.365418 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-586.086729 hartrees (-367775.28331479 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.2804075 hartrees (-367896.818510325 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.072675 hartrees (-367766.46428925 kcal/mol)

Coordinates (from last standard orientation):

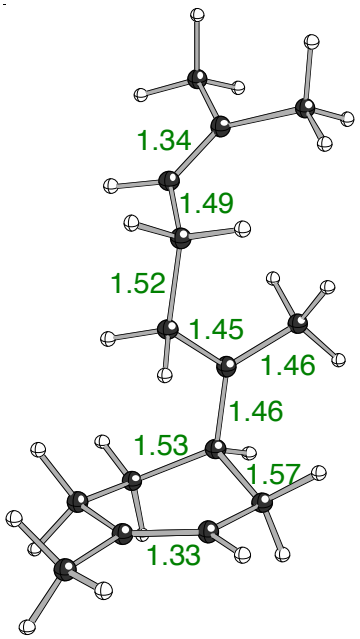
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.923744	0.671236	0.675429

2	6	-1.587186	0.995511	0.230792
3	6	-3.418441	0.169911	-0.818233
4	6	-2.845038	-1.260727	-0.921513
5	6	-1.917400	-1.334533	0.315447
6	6	-2.821510	-0.692173	1.384898
7	1	-4.508216	0.225714	-0.744927
8	1	-3.547007	1.474654	1.065551
9	1	-3.640831	-2.004626	-0.832108
10	1	-2.333861	-1.439284	-1.868146
11	1	-3.795676	-1.179176	1.471578
12	1	-2.386483	-0.617975	2.382670
13	1	-3.117716	0.836372	-1.631245
14	6	-1.142928	2.354247	-0.122837
15	1	-1.968929	3.064733	-0.189895
16	1	-0.486025	2.687627	0.698279
17	1	-0.527941	2.377102	-1.026568
18	1	-1.525652	-2.327894	0.539886
19	6	-0.777230	-0.258694	0.137120
20	6	0.050510	-0.427735	-1.174668
21	1	0.171001	-1.508372	-1.320393
22	1	-0.564545	-0.085333	-2.014059
23	6	0.151100	-0.251834	1.405886
24	1	0.635511	-1.229310	1.463948
25	1	0.929050	0.505388	1.311545
26	1	-0.391347	-0.079905	2.337119
27	6	1.446956	0.232115	-1.290996
28	1	1.639106	0.340325	-2.368145
29	1	1.435691	1.253777	-0.897326
30	6	2.572849	-0.573962	-0.686131
31	6	3.647100	-0.131530	-0.008885
32	1	2.517670	-1.644166	-0.892813
33	6	4.713332	-1.093687	0.458507
34	1	5.686323	-0.837497	0.020856
35	1	4.838915	-1.042194	1.547686
36	1	4.482010	-2.127381	0.187960
37	6	3.919773	1.314138	0.329690
38	1	4.093660	1.433600	1.406628
39	1	4.836707	1.653122	-0.168646
40	1	3.119722	1.996996	0.033532

Table 2: R_1/R_2=prenyl/CH_3 (extended) (Fig. 4 and Fig. S3)

mPWB1K

A_b



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0617866 hartrees (-367759.631709366 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.372485 (Hartree/Particle)

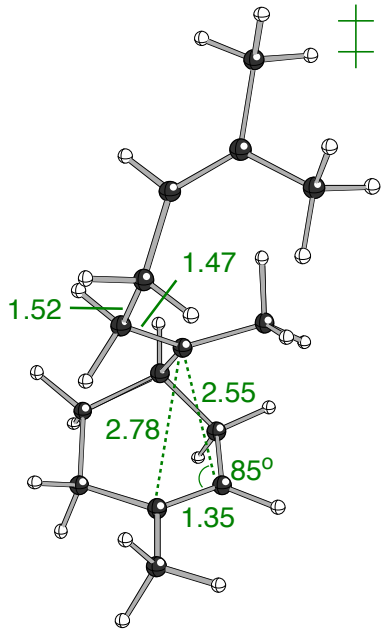
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.734100 hartrees (-367554.005091 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.926058	0.409359	-1.041229
2	6	-3.257261	-0.597970	-0.232121
3	6	-2.783836	-0.659521	1.181661
4	6	-2.067657	0.586179	1.679300
5	6	-1.263648	1.371679	0.649350
6	6	-2.126838	1.597339	-0.646938
7	1	-3.641484	-0.844091	1.828802
8	1	-3.270229	0.395286	-2.066226
9	1	-2.810474	1.287891	2.052681
10	1	-1.432730	0.345328	2.530186
11	1	-2.772807	2.439610	-0.397608
12	1	-1.518910	1.941156	-1.484696
13	1	-2.167559	-1.553695	1.297964
14	6	-4.103066	-1.736481	-0.689709
15	1	-5.028654	-1.774379	-0.117411
16	1	-4.357760	-1.653131	-1.741077
17	1	-3.598308	-2.688606	-0.531586

18	1	-1.041650	2.361182	1.042941
19	6	-0.032073	0.827359	0.097249
20	6	0.111336	-0.602453	-0.110503
21	1	-0.145398	-1.079610	0.842567
22	1	-0.772735	-0.856593	-0.727653
23	6	1.021915	1.751081	-0.297322
24	1	1.822637	1.587153	0.438149
25	1	1.479899	1.478313	-1.245413
26	1	0.720578	2.791434	-0.276455
27	6	1.404526	-1.157095	-0.685002
28	1	1.226693	-2.212153	-0.891512
29	1	1.613917	-0.702220	-1.649741
30	6	2.555381	-1.029790	0.260441
31	6	3.737820	-0.452066	0.041958
32	1	2.405939	-1.508848	1.221968
33	6	4.796676	-0.466151	1.096203
34	1	5.679522	-0.994717	0.739703
35	1	5.118579	0.545617	1.339865
36	1	4.458081	-0.949318	2.007341
37	6	4.136817	0.227583	-1.226822
38	1	4.408320	1.265565	-1.033204
39	1	5.025941	-0.245820	-1.640013
40	1	3.374397	0.210338	-1.998667

$TS_{A\text{-}B}$



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0553111 hartrees (-367755.568268361 kcal/mol)
Imaginary Frequencies: 1 (-50.3219 1/cm)
Zero-point correction = 0.373325 (Hartree/Particle)

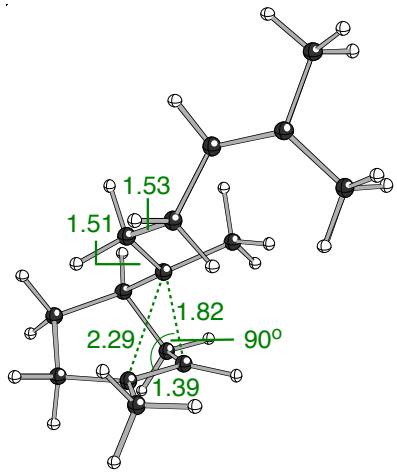
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =
-585.724553 hartrees (-367548.01425303 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.471370	0.242018	1.315704
2	6	-2.754640	0.849982	0.149732
3	6	-3.046117	0.042980	-1.075766
4	6	-2.402364	-1.354287	-1.080550
5	6	-1.487808	-1.530972	0.120601
6	6	-2.303654	-1.248375	1.375074
7	1	-4.129985	-0.054412	-1.149981
8	1	-2.369745	0.831213	2.216558
9	1	-3.162691	-2.126972	-1.019165
10	1	-1.879726	-1.525999	-2.017995
11	1	-3.253446	-1.780676	1.349240
12	1	-1.803873	-1.560364	2.285014
13	1	-2.762206	0.614402	-1.959772
14	6	-2.881463	2.326443	0.026579
15	1	-3.876882	2.593495	-0.325594
16	1	-2.706177	2.832526	0.970035
17	1	-2.180530	2.714018	-0.713540
18	1	-1.037764	-2.530973	0.104672
19	6	-0.353568	-0.553394	0.142972
20	6	0.142769	-0.000321	-1.124893
21	1	0.204388	-0.870377	-1.793994
22	1	-0.675659	0.574035	-1.567102
23	6	0.462671	-0.378827	1.337239
24	1	1.390266	-0.923257	1.104247
25	1	0.794226	0.650460	1.450136
26	1	0.033303	-0.756392	2.252721
27	6	1.443836	0.788857	-1.150230
28	1	1.504126	1.245676	-2.138183
29	1	1.394560	1.618312	-0.449330
30	6	2.654834	-0.062552	-0.940305
31	6	3.647241	0.118493	-0.067250
32	1	2.743163	-0.897858	-1.626817
33	6	4.815356	-0.812594	-0.040866
34	1	5.734928	-0.274374	-0.265662
35	1	4.944779	-1.247379	0.949532
36	1	4.710540	-1.618632	-0.760383
37	6	3.717125	1.228771	0.929143
38	1	3.758064	0.828479	1.942439
39	1	4.636170	1.795613	0.790045
40	1	2.893088	1.932113	0.869765

B



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0620685 hartrees (-367759.808604435 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.375504 (Hartree/Particle)

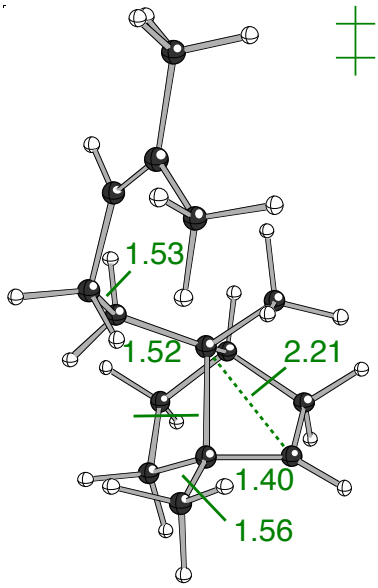
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.729027 hartrees (-367550.82173277 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.714020	0.060367	1.280897
2	6	-2.092586	1.051079	0.386916
3	6	-3.080671	0.693742	-0.656422
4	6	-2.882936	-0.743331	-1.185722
5	6	-1.975906	-1.492726	-0.239334
6	6	-2.468172	-1.248090	1.188085
7	1	-4.049439	0.759776	-0.151102
8	1	-1.140635	0.345510	2.152563
9	1	-3.841007	-1.248436	-1.260641
10	1	-2.460049	-0.710153	-2.186033
11	1	-3.545982	-1.158500	1.302321
12	1	-2.105844	-1.970769	1.907163
13	1	-3.098714	1.433928	-1.451198
14	6	-1.562918	2.421242	0.446060
15	1	-2.408315	3.091867	0.613903
16	1	-0.840027	2.567250	1.239950
17	1	-1.136740	2.713822	-0.512858
18	1	-1.822421	-2.524203	-0.547203
19	6	-0.684073	-0.709401	-0.009087
20	6	-0.058794	0.043749	-1.160330
21	1	0.227736	-0.742246	-1.866113
22	1	-0.795039	0.640133	-1.692963
23	6	0.350409	-1.412294	0.830976

24	1	0.906514	-2.073354	0.166002
25	1	1.071003	-0.717384	1.249944
26	1	-0.078312	-2.009530	1.626415
27	6	1.172589	0.892958	-0.829065
28	1	1.189296	1.733413	-1.524450
29	1	1.068249	1.331336	0.162262
30	6	2.463889	0.151050	-0.957845
31	6	3.463743	0.074776	-0.080687
32	1	2.599044	-0.347434	-1.911526
33	6	4.708840	-0.682399	-0.410787
34	1	5.577305	-0.025952	-0.376962
35	1	4.887006	-1.472728	0.317665
36	1	4.661328	-1.130281	-1.398503
37	6	3.468753	0.712285	1.270160
38	1	3.660014	-0.033615	2.041411
39	1	4.278102	1.437888	1.339464
40	1	2.548042	1.231626	1.517607

TS



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0463296 hartrees (-367749.932287296 kcal/mol)
Imaginary Frequencies: 1 (-323.8039 1/cm)
Zero-point correction = 0.373428 (Hartree/Particle)

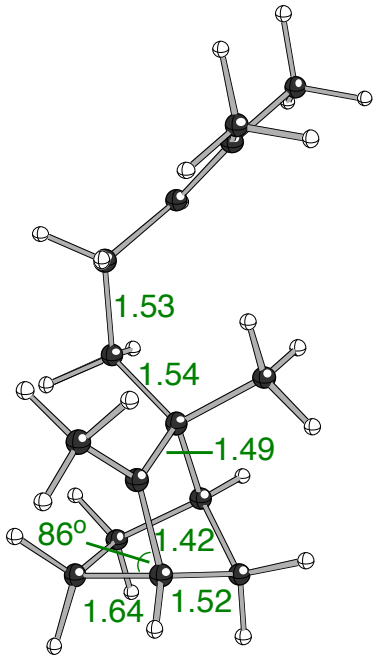
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.715697 hartrees (-367542.45702447 kcal/mol)

Coordinates (from last standard orientation):

Center	Atomic	Coordinates (Angstroms)

Number	Number	X	Y	Z
1	6	-2.329899	0.605166	1.325253
2	6	-1.847835	0.940422	0.049832
3	6	-2.820273	0.414368	-1.044287
4	6	-2.820380	-1.113551	-0.970746
5	6	-1.958117	-1.392206	0.246999
6	6	-2.670686	-0.815004	1.465280
7	1	-3.802897	0.849309	-0.885916
8	1	-2.312569	1.287960	2.170171
9	1	-3.819346	-1.523855	-0.859571
10	1	-2.391728	-1.555225	-1.864923
11	1	-3.758208	-0.948833	1.472767
12	1	-2.327472	-1.196560	2.424962
13	1	-2.461156	0.794734	-1.996486
14	6	-1.270268	2.304018	-0.187189
15	1	-2.057304	3.054291	-0.208071
16	1	-0.554071	2.583310	0.581314
17	1	-0.769222	2.333982	-1.150234
18	1	-1.661421	-2.430210	0.360402
19	6	-0.780160	-0.403644	0.117922
20	6	-0.022355	-0.467925	-1.201801
21	1	0.166816	-1.536941	-1.350038
22	1	-0.671118	-0.176558	-2.021783
23	6	0.178328	-0.395337	1.291938
24	1	0.843082	-1.250778	1.209583
25	1	0.810248	0.488489	1.273761
26	1	-0.304984	-0.439332	2.264047
27	6	1.306956	0.282780	-1.315215
28	1	1.457007	0.491479	-2.375395
29	1	1.241946	1.256286	-0.835253
30	6	2.488444	-0.488476	-0.821643
31	6	3.462301	-0.077107	-0.010972
32	1	2.569409	-1.492204	-1.225671
33	6	4.604309	-0.979337	0.328150
34	1	5.548931	-0.537956	0.013009
35	1	4.675109	-1.128916	1.405189
36	1	4.509737	-1.950490	-0.147921
37	6	3.535192	1.274828	0.620165
38	1	3.610663	1.184665	1.703777
39	1	4.434998	1.794177	0.293086
40	1	2.690200	1.915194	0.387075

C



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0793051 hartrees (-367770.624743301 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.375726 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.745711 hartrees (-367561.29110961 kcal/mol)

Coordinates (from last standard orientation):

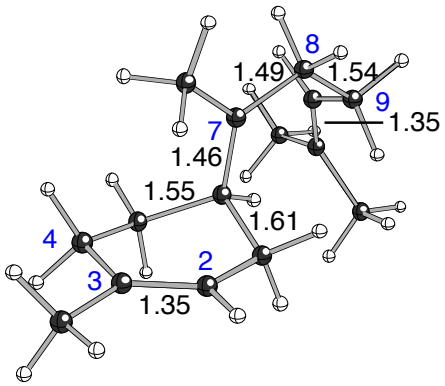
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.821494	0.647674	0.731583
2	6	-1.556403	0.970612	0.169788
3	6	-3.238937	0.130887	-0.764474
4	6	-2.754252	-1.312221	-0.794173
5	6	-1.797413	-1.329181	0.393722
6	6	-2.669544	-0.674744	1.455321
7	1	-4.315724	0.279533	-0.773355
8	1	-3.462696	1.439438	1.093404
9	1	-3.576360	-2.001330	-0.626794
10	1	-2.288658	-1.572124	-1.738176
11	1	-3.621472	-1.180055	1.587046
12	1	-2.207293	-0.557463	2.429543
13	1	-2.849854	0.733724	-1.585518
14	6	-1.153489	2.299279	-0.292950
15	1	-1.973090	3.008578	-0.303728
16	1	-0.411697	2.651729	0.430218
17	1	-0.649941	2.266086	-1.255218

18	1	-1.378440	-2.298501	0.639930
19	6	-0.718477	-0.255860	0.111051
20	6	0.026170	-0.461624	-1.215522
21	1	0.164074	-1.536429	-1.337457
22	1	-0.634080	-0.157347	-2.028864
23	6	0.242148	-0.126859	1.312391
24	1	0.776821	-1.066224	1.417122
25	1	0.979256	0.650535	1.140304
26	1	-0.271318	0.085485	2.244779
27	6	1.383629	0.221242	-1.392157
28	1	1.553431	0.312334	-2.465983
29	1	1.360467	1.241706	-1.014490
30	6	2.520257	-0.549568	-0.802247
31	6	3.484832	-0.114654	0.007216
32	1	2.569094	-1.585097	-1.121379
33	6	4.573465	-1.033574	0.458328
34	1	5.547021	-0.659144	0.144814
35	1	4.600997	-1.099582	1.545679
36	1	4.450985	-2.034807	0.056914
37	6	3.595289	1.278690	0.534368
38	1	3.613833	1.272571	1.624388
39	1	4.534270	1.728663	0.215121
40	1	2.795680	1.937126	0.208236

Table 2: R_1/R_2=CH_3/prenyl (extended) (Fig. S4)

<u>B3LYP</u>

A_b



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.4090742 hartrees (-367977.558151242 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.362509 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-586.092898 hartrees (-367779.15442398 kcal/mol)

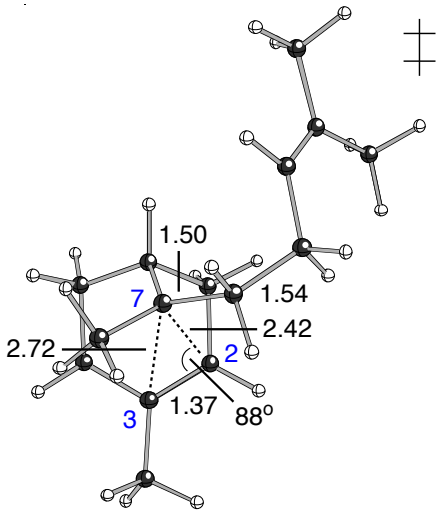
mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.2710044 hartrees (-367890.917971044 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.0557019 hartrees (-367755.813499269 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.369712	-0.134610	0.025923
2	6	-1.425109	1.979264	-0.928686
3	1	-1.279572	3.055357	-1.029430
4	1	-2.331080	1.758336	-0.336952
5	1	-1.636060	1.541142	-1.915675
6	6	-0.280949	1.282319	-0.322550
7	6	0.913524	2.101247	0.002336
8	6	3.546059	-0.589828	-0.048573
9	6	2.159550	1.462788	0.635257
10	1	1.179278	2.601200	-0.947945
11	1	0.543110	2.948839	0.606217
12	6	2.925824	0.574396	-0.317762
13	1	1.887377	0.940237	1.557716
14	1	2.798944	2.298563	0.951219
15	6	-1.180306	-0.121550	1.411527
16	6	-1.051032	-1.137534	-0.943071
17	6	-2.666168	-0.200210	1.257613
18	6	-2.575664	-1.032727	-1.089944
19	6	-3.317511	-0.645217	0.164161
20	1	-0.565103	-1.080516	-1.922526
21	1	-0.802547	-2.125088	-0.540136
22	1	-2.953183	-2.000967	-1.444116
23	1	-3.241990	0.124146	2.122270
24	1	-0.904711	0.735469	2.039468
25	1	-0.784470	-1.001765	1.934926
26	6	-4.817686	-0.747461	0.112888
27	1	-5.284241	-0.372532	1.026811
28	1	-5.124875	-1.791643	-0.023345
29	1	-5.224987	-0.188543	-0.738789
30	6	4.328155	-1.309745	-1.120704
31	1	5.380181	-1.411576	-0.826916
32	1	4.292973	-0.785940	-2.079520
33	1	3.947057	-2.328125	-1.268128
34	6	3.564817	-1.263446	1.301735
35	1	4.589150	-1.288102	1.694123
36	1	3.244241	-2.309247	1.217579
37	1	2.942653	-0.771099	2.052654
38	1	3.027992	0.975192	-1.327736
39	1	0.632840	-0.500441	0.245254
40	1	-2.855723	-0.329009	-1.887927

TS_{A-B}



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.393065 hartrees (-367967.51221815 kcal/mol)
Imaginary Frequencies: 1 (-70.8221 1/cm)
Zero-point correction = 0.363279 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-586.073491 hartrees (-367766.97633741 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.2580483 hartrees (-367882.787888733 kcal/mol)

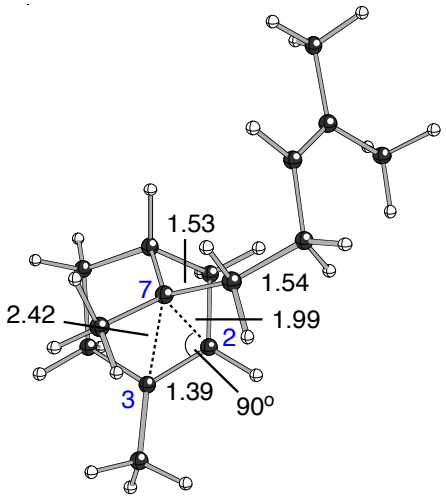
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.0468381 hartrees (-367750.251376131 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.489701	-0.363234	0.974849
2	6	1.812300	1.885774	1.005299
3	1	1.989023	2.796319	0.429625
4	1	2.755348	1.383524	1.213178
5	1	1.408169	2.189655	1.987404
6	6	0.761450	1.017544	0.399041
7	6	-0.210684	1.803593	-0.434124
8	6	-3.417127	-0.195393	-0.017991
9	6	-1.546347	1.273110	-0.984884
10	1	-0.436676	2.659330	0.230602
11	1	0.369990	2.276927	-1.238194
12	6	-2.513351	0.797607	0.073632
13	1	-1.376137	0.524561	-1.762643
14	1	-1.985672	2.132748	-1.511615

15	6	0.284458	-1.234744	-0.280287
16	6	1.695890	-0.927952	1.737236
17	6	1.413808	-0.721436	-1.154458
18	6	2.917689	-1.121771	0.775029
19	6	2.673121	-0.626448	-0.631346
20	1	1.974489	-0.290095	2.580752
21	1	1.399480	-1.888160	2.166572
22	1	3.147428	-2.193629	0.699954
23	1	1.239314	-0.481919	-2.201241
24	1	-0.690363	-1.091299	-0.735833
25	1	0.378212	-2.302092	-0.047006
26	6	3.841919	-0.118299	-1.417403
27	1	3.564149	0.179825	-2.430928
28	1	4.613774	-0.895569	-1.486469
29	1	4.315778	0.734245	-0.913382
30	6	-4.360921	-0.485549	1.124311
31	1	-5.403200	-0.363465	0.804704
32	1	-4.189851	0.174000	1.979378
33	1	-4.259767	-1.524498	1.462757
34	6	-3.615800	-1.069658	-1.232258
35	1	-4.617418	-0.906689	-1.649466
36	1	-3.566278	-2.131075	-0.959608
37	1	-2.897812	-0.886322	-2.034881
38	1	-2.514592	1.390952	0.990272
39	1	-0.398208	-0.303337	1.622381
40	1	3.824190	-0.662805	1.183808

B



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):HF = -586.3936201 hartrees (-367967.860548951 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.364518 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =

-586.073251 hartrees (-367766.82573501 kcal/mol)

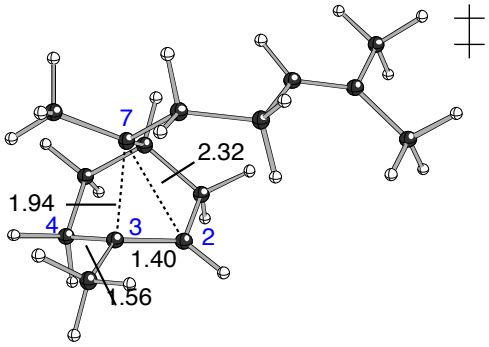
mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.2625116 hartrees (-367885.588654116 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.0537524 hartrees (-367754.590168524 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.894837	0.680198	-0.635016
2	6	-0.508268	-0.806675	-0.783345
3	6	-0.227223	-1.049104	0.715490
4	6	2.471971	0.686300	-0.430900
5	6	1.499684	1.552422	0.335238
6	6	0.143337	1.772973	-0.361691
7	1	-0.414999	-2.074463	1.050526
8	1	0.330501	-0.965522	-1.468971
9	1	0.356523	2.156978	-1.373325
10	1	-0.383345	2.597197	0.134050
11	6	-1.986853	1.257291	-1.515226
12	1	-1.548712	1.365771	-2.517511
13	1	-2.287863	2.255468	-1.187240
14	1	-2.874407	0.637796	-1.628284
15	6	3.419967	-0.131415	0.062367
16	6	-1.731696	-1.646085	-1.163548
17	1	-2.104781	-1.383196	-2.156794
18	1	-1.446368	-2.700240	-1.201574
19	6	-1.272360	-0.043981	1.183706
20	1	-1.060028	0.697996	1.950443
21	6	-2.864471	-1.438815	-0.095227
22	1	-2.901379	-2.322276	0.559395
23	1	-3.854030	-1.360008	-0.553327
24	6	-2.592125	-0.270985	0.808861
25	6	-3.716470	0.583884	1.277810
26	1	-4.391054	-0.032766	1.888678
27	1	-4.321150	0.943032	0.436577
28	1	-3.383196	1.428940	1.883392
29	6	3.670627	-0.370463	1.531909
30	1	4.663410	0.006184	1.808575
31	1	2.946586	0.114742	2.190723
32	1	3.676963	-1.444412	1.756243
33	6	4.361990	-0.866280	-0.861174
34	1	5.402484	-0.585930	-0.655295
35	1	4.296704	-1.951020	-0.707512
36	1	4.156594	-0.654240	-1.913915
37	1	0.779164	-0.770624	1.009985
38	1	1.925389	2.562395	0.427938
39	1	2.433479	0.809448	-1.514837
40	1	1.363875	1.213163	1.366552

TS



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.3802295 hartrees (-367959.457813545 kcal/mol)
Imaginary Frequencies: 1 (-298.1820 1/cm)
Zero-point correction = 0.363709 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-586.059600 hartrees (-367758.259596 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.2501592 hartrees (-367877.837399592 kcal/mol)

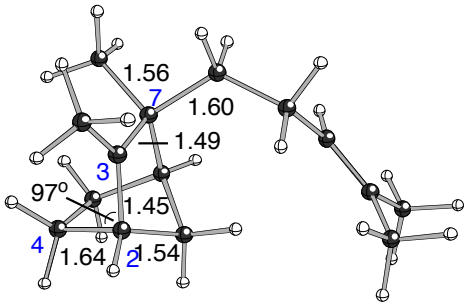
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.0403898 hartrees (-367746.205003398 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.154963	-0.000997	0.866451
2	6	-0.834549	1.345271	0.154322
3	6	-0.158963	0.867029	-1.146117
4	6	2.271143	-0.073700	0.705790
5	6	1.283826	-1.217908	0.637275
6	6	-0.061195	-0.972185	1.341385
7	1	-0.236612	1.570046	-1.989438
8	1	-0.211642	2.014271	0.755010
9	1	0.162176	-0.645817	2.367976
10	1	-0.557690	-1.941649	1.468768
11	6	-2.220469	0.034003	1.955927
12	1	-1.815618	0.655468	2.767368
13	1	-2.404957	-0.959283	2.371432
14	1	-3.171866	0.472511	1.665662
15	6	3.409397	0.056098	-0.005338
16	6	-2.197744	1.947915	-0.221198
17	1	-2.699138	2.387429	0.644076
18	1	-2.077251	2.747806	-0.955864

19	6	-0.895147	-0.398584	-1.400936
20	1	-0.450041	-1.220215	-1.963264
21	6	-3.001420	0.748094	-0.794084
22	1	-3.284226	0.904026	-1.839312
23	1	-3.928110	0.558747	-0.247698
24	6	-2.119834	-0.533547	-0.730759
25	6	-2.840806	-1.860557	-0.706862
26	1	-3.497260	-1.948735	-1.580025
27	1	-3.478964	-1.941243	0.178161
28	1	-2.150815	-2.708712	-0.715264
29	6	3.870575	-0.934588	-1.044985
30	1	4.822932	-1.384316	-0.737177
31	1	3.164497	-1.749505	-1.219623
32	1	4.064639	-0.433266	-2.001479
33	6	4.340925	1.219926	0.224731
34	1	5.329950	0.864694	0.539675
35	1	4.496384	1.787449	-0.701552
36	1	3.966819	1.904809	0.990315
37	1	0.912448	0.673523	-1.016304
38	1	1.714458	-2.095097	1.140032
39	1	2.061253	0.683683	1.461798
40	1	1.123976	-1.554246	-0.396882

C



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.4067804 hartrees (-367976.118768804 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.365540 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-586.084973 hartrees (-367774.18140723 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.278788 hartrees (-367895.80225788 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -586.0708116 hartrees (-367765.294987116 kcal/mol)

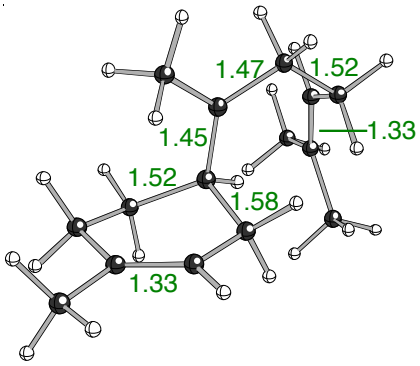
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.222128	-0.577913	-0.599274
2	6	0.732481	0.886020	-0.885349
3	6	0.200982	1.337326	0.489691
4	6	-2.278296	-0.657163	-0.573439
5	6	-1.271225	-1.564463	0.094461
6	6	0.080208	-1.696715	-0.635652
7	1	0.039486	2.416457	0.553099
8	1	0.033042	0.954036	-1.718507
9	1	-0.115542	-1.824998	-1.706693
10	1	0.564269	-2.621216	-0.303886
11	6	2.310713	-1.104933	-1.577929
12	1	1.952174	-0.964547	-2.601798
13	1	2.493344	-2.172172	-1.432930
14	1	3.264559	-0.582283	-1.480615
15	6	-3.262893	0.055531	0.003255
16	6	1.984714	1.791949	-1.006128
17	1	2.673995	1.496395	-1.797876
18	1	1.675472	2.819834	-1.211255
19	6	1.457622	0.902178	1.274033
20	1	1.552490	1.085734	2.343881
21	6	2.611936	1.680236	0.403462
22	1	2.724808	2.634130	0.926160
23	1	3.585322	1.182578	0.426930
24	6	1.751194	-0.428267	0.786037
25	6	2.501860	-1.444314	1.538656
26	1	3.197938	-0.998801	2.254983
27	1	3.000718	-2.184537	0.911410
28	1	1.749277	-1.978844	2.146073
29	6	-3.522032	0.116620	1.489361
30	1	-4.498955	-0.326932	1.719471
31	1	-2.777963	-0.411048	2.090920
32	1	-3.569861	1.157418	1.833749
33	6	-4.235213	0.848757	-0.836675
34	1	-5.261834	0.495717	-0.678025
35	1	-4.224748	1.909433	-0.554833
36	1	-4.012902	0.774354	-1.904506
37	1	-0.705493	0.831910	0.813825
38	1	-1.678681	-2.587097	0.092665
39	1	-2.230407	-0.654122	-1.663611
40	1	-1.135594	-1.320492	1.154311

Table 2: R_1/R_2=CH_3/prenyl (extended) (Fig. S4)

mPWB1K

A_b



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0611192 hartrees (-367759.212909192 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.372956 (Hartree/Particle)

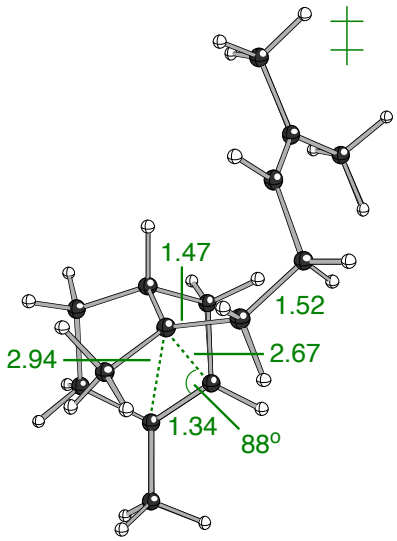
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.732184 hartrees (-367552.80278184 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.282153	-0.127161	-0.146966
2	6	-1.383438	2.016828	-0.877428
3	1	-1.269999	3.094053	-0.878985
4	1	-2.269888	1.716693	-0.303157
5	1	-1.575349	1.651499	-1.888589
6	6	-0.238485	1.305969	-0.327987
7	6	0.911376	2.103030	0.115677
8	6	3.358296	-0.619199	-0.019540
9	6	2.089704	1.425820	0.796986
10	1	1.237568	2.611515	-0.804001
11	1	0.509766	2.931440	0.707821
12	6	2.954744	0.646328	-0.140674
13	1	1.740013	0.818759	1.629532
14	1	2.683781	2.221151	1.247064
15	6	-0.961353	-0.177369	1.278252
16	6	-1.033874	-1.022053	-1.124945
17	6	-2.441773	-0.286396	1.240672
18	6	-2.545536	-0.890296	-1.151950
19	6	-3.171054	-0.628052	0.177494
20	1	-0.618509	-0.889993	-2.122086
21	1	-0.781476	-2.038193	-0.829225
22	1	-2.963011	-1.810204	-1.561176
23	1	-2.942935	-0.073707	2.175146
24	1	-0.668304	0.667420	1.906287
25	1	-0.507230	-1.048005	1.753541
26	6	-4.655166	-0.744963	0.240354

27	1	-5.042399	-0.468317	1.215388
28	1	-4.963174	-1.767828	0.029232
29	1	-5.129325	-0.114213	-0.510402
30	6	4.285030	-1.221946	-1.024043
31	1	5.209622	-1.540924	-0.545045
32	1	4.537181	-0.522796	-1.814945
33	1	3.845733	-2.110859	-1.474985
34	6	2.968228	-1.536757	1.093571
35	1	3.844809	-1.809250	1.679783
36	1	2.567353	-2.468344	0.694855
37	1	2.240472	-1.115493	1.781447
38	1	3.330052	1.210866	-0.986941
39	1	0.731449	-0.493003	-0.029836
40	1	-2.873471	-0.114972	-1.847565

TS_{A-B}



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0500016 hartrees (-367752.236504016 kcal/mol)
Imaginary Frequencies: 1 (-83.2650 1/cm)
Zero-point correction = 0.372159 (Hartree/Particle)

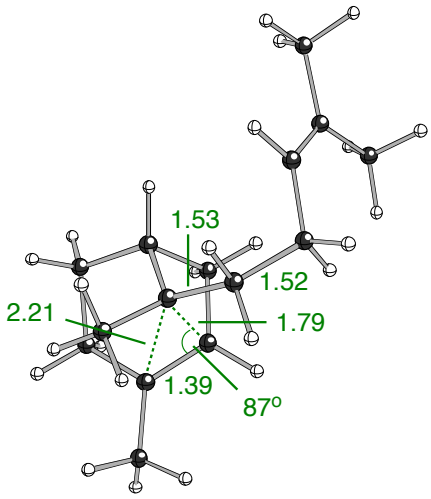
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.721001 hartrees (-367545.78533751 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.386424	-0.100019	0.880058
2	6	1.613821	2.126313	0.663970
3	1	1.746568	2.982786	0.013138

4	1	2.560975	1.647789	0.884514
5	1	1.235070	2.486358	1.630080
6	6	0.596601	1.189888	0.184193
7	6	-0.290521	1.744467	-0.850489
8	6	-3.275707	-0.281947	0.032363
9	6	-1.613827	1.125967	-1.275187
10	1	-0.462811	2.771870	-0.503933
11	1	0.364134	1.913030	-1.714240
12	6	-2.515625	0.802195	-0.129339
13	1	-1.452405	0.277006	-1.930474
14	1	-2.088752	1.881961	-1.902877
15	6	0.282143	-1.183514	-0.190511
16	6	1.506448	-0.481394	1.830778
17	6	1.525471	-1.012756	-1.013255
18	6	2.816880	-0.778838	1.074775
19	6	2.701796	-0.767820	-0.420008
20	1	1.668812	0.284014	2.586598
21	1	1.175950	-1.364357	2.369646
22	1	3.181973	-1.765153	1.363251
23	1	1.472963	-1.119808	-2.087989
24	1	-0.619222	-1.085779	-0.778397
25	1	0.231826	-2.160168	0.290865
26	6	3.963566	-0.567560	-1.183312
27	1	3.805781	-0.637232	-2.254545
28	1	4.703497	-1.314195	-0.898312
29	1	4.404515	0.404109	-0.960144
30	6	-4.165076	-0.413066	1.225936
31	1	-5.206730	-0.489835	0.917969
32	1	-4.074061	0.434114	1.898974
33	1	-3.938846	-1.322748	1.781024
34	6	-3.357117	-1.421822	-0.929137
35	1	-4.376328	-1.516692	-1.300905
36	1	-3.124911	-2.361551	-0.429499
37	1	-2.707090	-1.321194	-1.791946
38	1	-2.592189	1.578407	0.625983
39	1	-0.571783	0.014093	1.406677
40	1	3.611417	-0.097379	1.379546

B



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.061619 hartrees (-367759.52653869 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.375198 (Hartree/Particle)

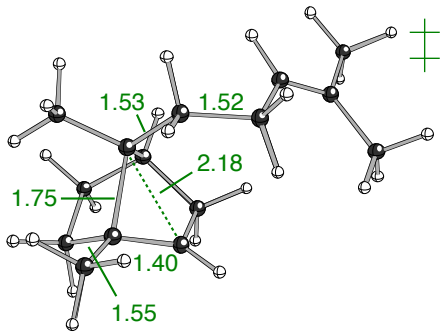
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.728444 hartrees (-367550.45589444 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.924525	0.602917	-0.565432
2	6	-0.439105	-0.839770	-0.728569
3	6	-0.143239	-0.999215	0.761923
4	6	2.391182	0.725616	-0.467079
5	6	1.423421	1.601744	0.261954
6	6	0.076011	1.747952	-0.428803
7	1	-0.349888	-1.984412	1.174625
8	1	0.394708	-0.965308	-1.413778
9	1	0.265566	2.048452	-1.462964
10	1	-0.463804	2.584469	0.014156
11	6	-2.031133	1.096266	-1.474407
12	1	-1.588461	1.227635	-2.460932
13	1	-2.403130	2.066789	-1.156551
14	1	-2.873658	0.424946	-1.593853
15	6	3.300815	-0.100278	0.050285
16	6	-1.621244	-1.722678	-1.056166
17	1	-2.008533	-1.513335	-2.049408
18	1	-1.323465	-2.766598	-1.039956
19	6	-1.164094	0.055029	1.116610
20	1	-0.976966	0.842246	1.835673
21	6	-2.724924	-1.470258	-0.000256
22	1	-2.694824	-2.270904	0.744491

23	1	-3.723512	-1.479733	-0.427077
24	6	-2.479356	-0.227368	0.770024
25	6	-3.597177	0.648373	1.152446
26	1	-4.187081	0.109065	1.897425
27	1	-4.263495	0.834193	0.313211
28	1	-3.270101	1.582917	1.594808
29	6	3.502111	-0.335536	1.512152
30	1	4.484321	0.025798	1.814488
31	1	2.770244	0.159029	2.143561
32	1	3.486243	-1.401741	1.735678
33	6	4.240744	-0.852324	-0.834808
34	1	5.273166	-0.591322	-0.606208
35	1	4.149854	-1.926382	-0.675867
36	1	4.064816	-0.643265	-1.885673
37	1	0.861245	-0.709456	1.027927
38	1	1.832322	2.613567	0.298234
39	1	2.379892	0.838074	-1.546306
40	1	1.307620	1.312464	1.305052

TS



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0478244 hartrees (-367750.870289244 kcal/mol)
Imaginary Frequencies: 1 (-306.9713 1/cm)
Zero-point correction = 0.374050 (Hartree/Particle)

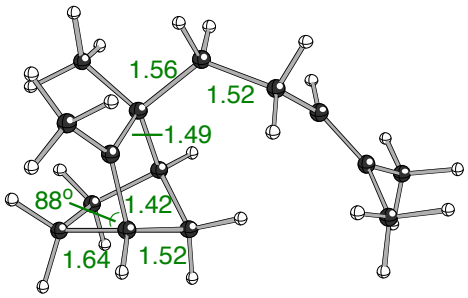
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-585.715286 hartrees (-367542.19911786 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.114871	-0.278484	0.717652
2	6	-0.595636	1.153527	0.482758
3	6	-0.052440	1.032944	-0.939669
4	6	2.216566	-0.548064	0.677250
5	6	1.208520	-1.510390	0.134473
6	6	-0.142237	-1.451132	0.835019

7	1	-0.173195	1.935740	-1.547551
8	1	0.140510	1.489993	1.205924
9	1	0.054140	-1.546131	1.903945
10	1	-0.713087	-2.345524	0.582446
11	6	-2.112111	-0.448788	1.847991
12	1	-1.607876	-0.132919	2.762113
13	1	-2.384481	-1.492951	1.970330
14	1	-3.018858	0.134791	1.754511
15	6	3.239197	0.013946	0.029529
16	6	-1.857479	1.992731	0.417141
17	1	-2.276938	2.159799	1.404350
18	1	-1.664148	2.969001	-0.016401
19	6	-0.907889	-0.048496	-1.443956
20	1	-0.583775	-0.751085	-2.205568
21	6	-2.790235	1.144783	-0.456425
22	1	-3.007394	1.615466	-1.411480
23	1	-3.748453	0.944434	0.013745
24	6	-2.098540	-0.210512	-0.726732
25	6	-2.988346	-1.381917	-1.008683
26	1	-3.608771	-1.182816	-1.879335
27	1	-3.657975	-1.560517	-0.171834
28	1	-2.423031	-2.290543	-1.196984
29	6	3.539103	-0.197122	-1.418914
30	1	4.474965	-0.743960	-1.528528
31	1	2.776674	-0.760231	-1.949148
32	1	3.681883	0.756147	-1.926407
33	6	4.207952	0.895721	0.746657
34	1	5.215033	0.485889	0.682959
35	1	4.246338	1.884615	0.291212
36	1	3.954965	1.008969	1.796249
37	1	1.000588	0.771846	-0.986976
38	1	1.572580	-2.526415	0.298249
39	1	2.126923	-0.344135	1.738731
40	1	1.114060	-1.431949	-0.949097

C



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -586.0772039 hartrees (-367769.306219289 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.375784 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =
-585.743823 hartrees (-367560.10637073 kcal/mol)

Coordinates (from last standard orientation):

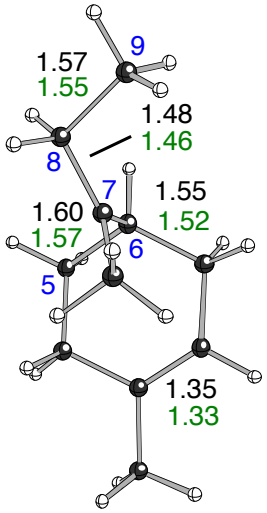
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.175575	0.581900	-0.567931
2	6	-0.623512	-0.819559	-0.913018
3	6	-0.118331	-1.345228	0.424149
4	6	2.231307	0.791501	-0.474099
5	6	1.196717	1.561895	0.283865
6	6	-0.121102	1.728901	-0.461755
7	1	0.050716	-2.417926	0.411300
8	1	0.091331	-0.821054	-1.727623
9	1	0.100348	1.984734	-1.497982
10	1	-0.653578	2.589032	-0.056789
11	6	-2.237986	1.100508	-1.539710
12	1	-1.856136	1.022911	-2.554361
13	1	-2.460772	2.147130	-1.351906
14	1	-3.169571	0.543531	-1.487580
15	6	3.176267	-0.013355	0.010944
16	6	-1.840696	-1.722796	-1.101618
17	1	-2.486468	-1.439251	-1.924754
18	1	-1.522436	-2.746864	-1.270841
19	6	-1.356204	-0.974270	1.216135
20	1	-1.486878	-1.246415	2.254586
21	6	-2.526597	-1.587429	0.253107
22	1	-2.780904	-2.517706	0.754708
23	1	-3.447166	-1.004039	0.221309
24	6	-1.745218	0.319618	0.778410
25	6	-2.605205	1.242056	1.516398
26	1	-3.183439	0.750399	2.291134
27	1	-3.238062	1.841791	0.870393
28	1	-1.917233	1.929691	2.020702
29	6	3.352282	-0.338428	1.458607
30	1	4.301449	0.058240	1.817133
31	1	2.573519	0.066718	2.097907
32	1	3.395521	-1.416902	1.607729
33	6	4.179618	-0.647138	-0.896615
34	1	5.189375	-0.344909	-0.622183
35	1	4.147468	-1.733145	-0.815085
36	1	4.016309	-0.375306	-1.934975
37	1	0.772373	-0.859972	0.796446
38	1	1.571706	2.576459	0.434652
39	1	2.235847	0.975656	-1.543267
40	1	1.042104	1.168147	1.288136

3.2. R_1=C_2H_6/CH_3, R_2=C_2H_6/CH_3

Table 1: R_1/R_2=C_2H_6/CH_3 (aligned) (Fig. S5)

B3LYP (distances in black), mPWB1K (distances in green)

A_a



B3LYP

```
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3668613 hartrees (-270059.509134363 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.273979 (Hartree/Particle)

Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
     -430.131229 hartrees (-269911.64750979 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2657233 hartrees (-269996.044027983 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.1054668 hartrees (-269895.481471668 kcal/mol)


Coordinates (from last standard orientation):
 ---------------------------------------------------------------------
 Center     Atomic                  Coordinates (Angstroms)
 Number     Number                 X           Y           Z
 ---------------------------------------------------------------------
    1          6              -1.645461   -1.198914   -0.397239
    2          6              -2.243129   -0.089175    0.070782
    3          6              -1.573750    1.262894   -0.021275
    4          6              -0.371622    1.314724   -0.961543
    5          6               0.567416    0.022619   -0.894987
```

6	6	-0.300277	-1.249587	-1.066786
7	1	-2.302209	2.001334	-0.383804
8	1	-2.161684	-2.152899	-0.311376
9	1	-0.709852	1.319240	-2.002655
10	1	0.216589	2.225074	-0.813660
11	1	-0.424761	-1.391869	-2.149610
12	1	0.258196	-2.132458	-0.728354
13	1	-1.317856	1.614323	0.990612
14	6	-3.598216	-0.115009	0.725579
15	1	-4.319667	0.479235	0.151468
16	1	-3.987909	-1.132055	0.811265
17	1	-3.560189	0.323939	1.730882
18	1	1.252708	0.130265	-1.743137
19	6	1.365457	0.106396	0.330090
20	6	2.717609	0.691240	0.259899
21	1	2.794062	1.408404	-0.563166
22	1	2.989865	1.172314	1.204455
23	6	0.870225	-0.344513	1.637537
24	1	0.115755	-1.131655	1.580905
25	1	1.681465	-0.587841	2.328991
26	1	0.357950	0.535879	2.072486
27	6	3.734207	-0.476909	-0.008403
28	1	4.731406	-0.033453	-0.053795
29	1	3.719102	-1.215622	0.795923
30	1	3.532268	-0.974750	-0.959356

mPWB1K

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1089892 hartrees (-269897.691812892 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.281281 (Hartree/Particle)

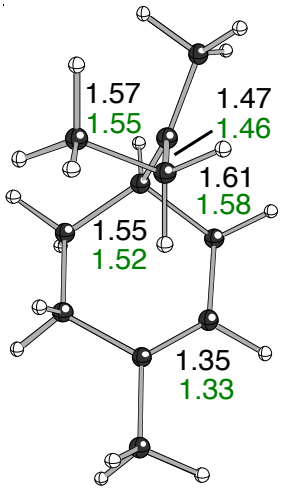
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.865638 hartrees (-269744.98650138 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.651483	-1.119351	-0.507435
2	6	-2.179081	-0.047858	0.080213
3	6	-1.473534	1.271589	0.084700
4	6	-0.305361	1.343795	-0.869728
5	6	0.561760	0.034514	-0.912163
6	6	-0.329944	-1.165666	-1.196747
7	1	-2.181773	2.050705	-0.199874
8	1	-2.212856	-2.043623	-0.506218
9	1	-0.667181	1.436287	-1.891489
10	1	0.317238	2.213528	-0.674979
11	1	-0.471006	-1.217303	-2.277261

12	1	0.194636	-2.086117	-0.936400
13	1	-1.185828	1.534446	1.106561
14	6	-3.503945	-0.081274	0.762002
15	1	-4.207905	0.587851	0.269632
16	1	-3.929529	-1.079282	0.763448
17	1	-3.420891	0.255802	1.794806
18	1	1.273191	0.197242	-1.722185
19	6	1.316377	0.014341	0.328092
20	6	2.602176	0.702142	0.370869
21	1	2.644007	1.510060	-0.355055
22	1	2.825426	1.073518	1.367462
23	6	0.840439	-0.642062	1.533565
24	1	0.174737	-1.477754	1.351355
25	1	1.648795	-0.883260	2.217803
26	1	0.234169	0.125030	2.038236
27	6	3.653860	-0.369252	-0.012360
28	1	4.627714	0.108613	0.007280
29	1	3.665390	-1.194333	0.692655
30	1	3.484087	-0.756912	-1.011830

A_b



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3639653 hartrees (-270057.691865403 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.273928 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.128910 hartrees (-269910.1923141 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.262921 hartrees (-269994.28555671 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.102893 hartrees (-269893.86638643 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.476339	-1.019741	-0.803550
2	6	2.041103	0.024553	-0.170020
3	6	1.403043	0.646184	1.048534
4	6	0.283189	-0.190709	1.677635
5	6	-0.653227	-0.955452	0.705386
6	6	0.232608	-1.739069	-0.382706
7	1	2.174006	0.809931	1.812366
8	1	1.942400	-1.406704	-1.707843
9	1	0.736892	-0.975011	2.292755
10	1	-0.321072	0.415985	2.359488
11	1	0.459463	-2.690814	0.116437
12	1	-0.356558	-2.021015	-1.266835
13	1	1.054841	1.656360	0.790333
14	6	3.319551	0.656832	-0.649367
15	1	4.104998	0.556773	0.109789
16	1	3.679417	0.200452	-1.574283
17	1	3.188492	1.732317	-0.823138
18	1	-1.190233	-1.714799	1.280505
19	6	-1.613194	-0.267881	-0.155434
20	6	-2.971051	-0.842667	-0.282220
21	1	-3.500328	-0.525533	-1.182081
22	1	-2.970996	-1.933077	-0.187654
23	1	-3.541259	-0.478334	0.591908
24	6	-1.296797	0.963134	-0.902200
25	1	-0.221166	1.063425	-1.060847
26	1	-1.811960	0.962143	-1.867793
27	6	-1.821506	2.196430	-0.082308
28	1	-1.548229	3.097281	-0.635961
29	1	-2.908506	2.170577	0.019805
30	1	-1.370545	2.250360	0.910542

mPWB1K

We were unable to locate the structure $\mathbf{A}_b$ at mPWB1K level of theory. The structure (energy in Table 1 in the main paper) shown has an imaginary frequency corresponding to ethyl (R_1) group movement.

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1069264 hartrees (-269896.397385264 kcal/mol)
Imaginary Frequencies: 1 (-48.2697 1/cm)
Zero-point correction = 0.280844 (Hartree/Particle)

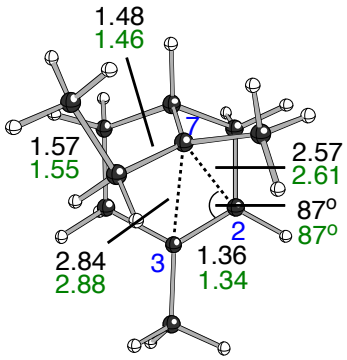
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =

-429.863100 hartrees (-269743.393881 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.395262	-1.090060	-0.710758
2	6	1.994542	-0.025146	-0.178912
3	6	1.383803	0.731418	0.955425
4	6	0.294646	-0.033269	1.676993
5	6	-0.667253	-0.840114	0.816755
6	6	0.110879	-1.691287	-0.268330
7	1	2.162430	0.977975	1.676519
8	1	1.858686	-1.590850	-1.549838
9	1	0.766853	-0.764712	2.329514
10	1	-0.277870	0.622894	2.329042
11	1	0.246052	-2.667256	0.198844
12	1	-0.502859	-1.907540	-1.151099
13	1	1.031663	1.698800	0.590859
14	6	3.294737	0.488422	-0.693389
15	1	4.060188	0.422426	0.078263
16	1	3.635988	-0.067837	-1.560170
17	1	3.216787	1.539577	-0.967908
18	1	-1.210617	-1.534653	1.450570
19	6	-1.578506	-0.259227	-0.138693
20	6	-2.905536	-0.863754	-0.291162
21	1	-3.319573	-0.751629	-1.287097
22	1	-2.942856	-1.894815	0.045318
23	1	-3.549501	-0.296292	0.393396
24	6	-1.241591	0.914224	-0.946051
25	1	-0.169192	0.966278	-1.112208
26	1	-1.755712	0.886442	-1.902282
27	6	-1.711437	2.157645	-0.158622
28	1	-1.401757	3.039612	-0.709472
29	1	-2.792529	2.181798	-0.065642
30	1	-1.273455	2.206663	0.833849

TS_{A-B}



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3571621 hartrees (-270053.422789371 kcal/mol)
Imaginary Frequencies: 1 (-45.1264 1/cm)
Zero-point correction = 0.274202 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.119685 hartrees (-269904.40353435 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2581431 hartrees (-269991.287376681 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.1001173 hartrees (-269892.124606923 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.457591	1.082503	-0.283418
2	6	-1.732889	-0.251770	-0.323739
3	6	-1.374178	-1.140263	0.844335
4	6	-0.190040	-0.612159	1.712545
5	6	0.437605	0.646773	1.092742
6	6	-0.684302	1.682886	0.874506
7	1	-2.271005	-1.232583	1.471752
8	1	-1.831171	1.731562	-1.072408
9	1	-0.541191	-0.341224	2.711433
10	1	0.552732	-1.401212	1.859083
11	1	-1.294747	1.805053	1.777005
12	1	-0.300374	2.673521	0.627205
13	1	-1.181607	-2.157223	0.482690
14	6	-2.478295	-0.882745	-1.463011
15	1	-3.409918	-1.335699	-1.100906
16	1	-2.729630	-0.161389	-2.243717
17	1	-1.895838	-1.698238	-1.910325
18	1	1.248771	1.021257	1.740188
19	6	1.023360	0.413919	-0.286310
20	6	1.488948	-0.925701	-0.719215
21	1	0.809642	-1.715966	-0.398221
22	1	1.593589	-0.965453	-1.806495
23	6	1.497232	1.555687	-1.108698
24	1	2.590581	1.597915	-0.959739
25	1	1.354938	1.369233	-2.177117
26	1	1.092881	2.526292	-0.832434
27	6	2.890353	-1.207409	-0.071484
28	1	3.195914	-2.211421	-0.374849
29	1	3.643561	-0.498686	-0.422312
30	1	2.851649	-1.176073	1.019655

mPWB1K

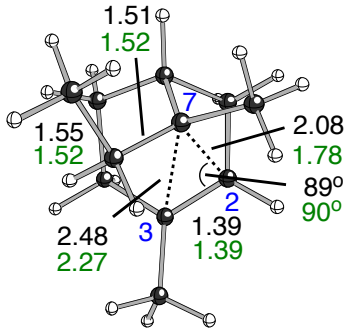
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1028311 hartrees (-269893.827543561 kcal/mol)
Imaginary Frequencies: 1 (-93.4205 1/cm)
Zero-point correction = 0.281539 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.857656 hartrees (-269739.97771656 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.431207	1.096651	-0.303221
2	6	-1.735141	-0.210629	-0.303308
3	6	-1.366986	-1.084844	0.854315
4	6	-0.186711	-0.570117	1.696979
5	6	0.468154	0.640270	1.061086
6	6	-0.601212	1.700520	0.792675
7	1	-2.252205	-1.172392	1.485070
8	1	-1.813362	1.734331	-1.088399
9	1	-0.527494	-0.268149	2.682932
10	1	0.534499	-1.367246	1.863188
11	1	-1.172306	1.901258	1.698157
12	1	-0.170928	2.646423	0.481152
13	1	-1.185876	-2.098064	0.496448
14	6	-2.531640	-0.845034	-1.387958
15	1	-3.443650	-1.280964	-0.982348
16	1	-2.808271	-0.134802	-2.159948
17	1	-1.977812	-1.662892	-1.848618
18	1	1.271924	1.029286	1.698289
19	6	1.077741	0.381632	-0.270669
20	6	1.403720	-0.959503	-0.737949
21	1	0.677315	-1.699017	-0.423007
22	1	1.519494	-0.982007	-1.817956
23	6	1.609424	1.504241	-1.056603
24	1	2.526179	1.211423	-1.563111
25	1	0.891875	1.721430	-1.851262
26	1	1.760144	2.407540	-0.477934
27	6	2.770815	-1.288999	-0.079272
28	1	3.041683	-2.294137	-0.385573
29	1	3.551217	-0.610655	-0.408010
30	1	2.715836	-1.266493	1.004466

B



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3578235 hartrees (-270053.837824485 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.275605 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.119120 hartrees (-269904.0489912 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.262909 hartrees (-269994.27802659 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.1072543 hartrees (-269896.603145793 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.097702	0.712778	-0.945805
2	6	-1.528539	-0.451080	-0.331473
3	6	-1.600724	-0.470581	1.169775
4	6	-0.438413	0.340653	1.840424
5	6	0.300058	1.166540	0.783157
6	6	-0.757425	1.908664	-0.066661
7	1	-2.562253	-0.006404	1.434018
8	1	-1.163576	0.799367	-2.027724
9	1	-0.840919	1.013155	2.601816
10	1	0.242915	-0.342883	2.353817
11	1	-1.605347	2.292532	0.509368
12	1	-0.348229	2.734208	-0.647965
13	1	-1.651224	-1.496845	1.543720
14	6	-1.940901	-1.658271	-1.101147
15	1	-2.991897	-1.883618	-0.873808
16	1	-1.841653	-1.528451	-2.180590
17	1	-1.371440	-2.540166	-0.782146
18	1	1.079960	1.789831	1.236761
19	6	0.847695	0.272322	-0.344177

20	6	1.304419	-1.143900	-0.078838
21	1	0.620618	-1.677693	0.582194
22	1	1.352138	-1.696822	-1.022743
23	6	1.601105	0.937390	-1.469537
24	1	2.636365	1.063789	-1.122218
25	1	1.639213	0.304844	-2.360157
26	1	1.235482	1.926486	-1.740389
27	6	2.709024	-1.152455	0.583714
28	1	2.965472	-2.184315	0.836969
29	1	3.482987	-0.771510	-0.085770
30	1	2.729805	-0.567863	1.508247

mPWB1K

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1145872 hartrees (-269901.204613872 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.283146 (Hartree/Particle)

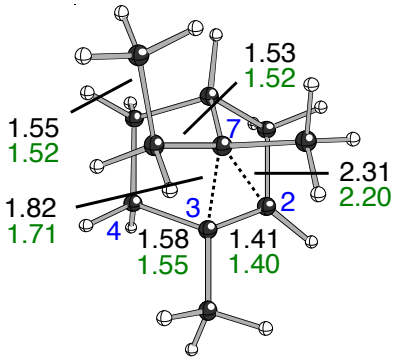
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.867490 hartrees (-269746.1486499 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.879526	0.596479	-1.031907
2	6	-1.421291	-0.478988	-0.333369
3	6	-1.633761	-0.307703	1.119522
4	6	-0.498338	0.511097	1.776803
5	6	0.277429	1.230564	0.699216
6	6	-0.722390	1.886443	-0.256052
7	1	-2.569122	0.255954	1.196271
8	1	-0.900928	0.561041	-2.113032
9	1	-0.915368	1.224544	2.480784
10	1	0.149494	-0.155971	2.340174
11	1	-1.634946	2.263079	0.199679
12	1	-0.291274	2.669282	-0.866242
13	1	-1.803827	-1.260350	1.612036
14	6	-1.764604	-1.744503	-0.993922
15	1	-2.853977	-1.833531	-0.967843
16	1	-1.446606	-1.783313	-2.029581
17	1	-1.380305	-2.598347	-0.440019
18	1	1.067611	1.854988	1.107538
19	6	0.731070	0.231509	-0.368098
20	6	1.176034	-1.156572	0.050152
21	1	0.466243	-1.622474	0.729776
22	1	1.240261	-1.798119	-0.828126
23	6	1.638419	0.790781	-1.439451
24	1	2.623841	0.935849	-1.001044

25	1	1.742378	0.093135	-2.265740
26	1	1.314789	1.748248	-1.829367
27	6	2.526778	-1.101777	0.752774
28	1	2.759045	-2.075384	1.172733
29	1	3.333761	-0.838817	0.077064
30	1	2.520008	-0.383797	1.570928

TS



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3421056 hartrees (-270043.974685056 kcal/mol)
Imaginary Frequencies: 1 (-310.4350 1/cm)
Zero-point correction = 0.274946 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.102592 hartrees (-269893.67750592 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2500018 hartrees (-269986.178629518 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.0957773 hartrees (-269889.401213523 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.750031	0.004386	0.784544
2	6	-1.087799	0.621984	-0.296999
3	6	-1.026678	-0.362150	-1.531457
4	6	-0.212638	-1.609433	-1.108801
5	6	0.126196	-1.336129	0.367273
6	6	-1.198063	-1.319630	1.157541
7	1	-2.048773	-0.601920	-1.834963
8	1	-2.504342	0.508548	1.392922
9	1	-0.784110	-2.534092	-1.221428

10	1	0.690471	-1.718560	-1.713056
11	1	-1.902678	-2.132091	0.915927
12	1	-1.073720	-1.373821	2.246311
13	1	-0.571856	0.188757	-2.357579
14	6	-1.365205	2.076852	-0.614436
15	1	-2.310516	2.175294	-1.158911
16	1	-1.428596	2.691290	0.288004
17	1	-0.581402	2.488862	-1.255560
18	1	0.875507	-2.010993	0.786287
19	6	0.522718	0.172732	0.414232
20	6	1.600369	0.663611	-0.562852
21	1	1.309749	0.513971	-1.603372
22	1	1.734201	1.741380	-0.425105
23	6	0.775906	0.778394	1.797414
24	1	1.781603	0.502365	2.127415
25	1	0.744862	1.870978	1.750940
26	1	0.084001	0.454787	2.577002
27	6	2.957612	-0.044350	-0.341109
28	1	3.677131	0.349079	-1.064748
29	1	3.365451	0.133114	0.656693
30	1	2.888698	-1.124538	-0.498878

mPWB1K

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1010005 hartrees (-269892.678823755 kcal/mol)
Imaginary Frequencies: 1 (-314.2291 1/cm)
Zero-point correction = 0.282638 (Hartree/Particle)

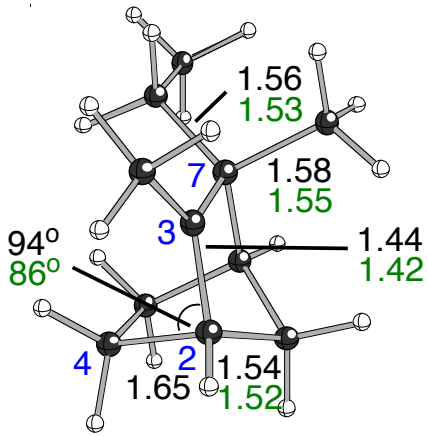
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.853056 hartrees (-269737.09117056 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.694618	0.049967	0.775277
2	6	-1.030592	0.597088	-0.334851
3	6	-0.998526	-0.424254	-1.503697
4	6	-0.160323	-1.621215	-1.050212
5	6	0.127196	-1.305321	0.406012
6	6	-1.199578	-1.278900	1.157932
7	1	-2.017376	-0.693894	-1.766300
8	1	-2.390962	0.612975	1.390662
9	1	-0.687459	-2.563558	-1.162582
10	1	0.759271	-1.698926	-1.622822
11	1	-1.915884	-2.057012	0.872466
12	1	-1.111379	-1.350571	2.240637
13	1	-0.580269	0.086281	-2.366161
14	6	-1.267003	2.031635	-0.702586

15	1	-2.228186	2.146488	-1.197667
16	1	-1.252372	2.682826	0.167370
17	1	-0.504163	2.372349	-1.396932
18	1	0.877356	-1.940294	0.865502
19	6	0.463349	0.198476	0.401071
20	6	1.559054	0.654195	-0.552956
21	1	1.275117	0.499000	-1.589444
22	1	1.709330	1.724385	-0.425062
23	6	0.687981	0.837590	1.760403
24	1	1.693912	0.611631	2.101278
25	1	0.609645	1.919638	1.687035
26	1	0.006900	0.504141	2.538349
27	6	2.866849	-0.082543	-0.292368
28	1	3.624503	0.282700	-0.979499
29	1	3.241161	0.074593	0.714559
30	1	2.768115	-1.153056	-0.455543

C



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3724191 hartrees (-270062.996709441 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.276197 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.132545 hartrees (-269912.47331295 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2823016 hartrees (-270006.447077016 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.1291063 hartrees (-269910.315494313 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.816363	0.295308	0.221672
2	6	-0.617990	1.018119	-0.135851
3	6	-1.724192	-0.714645	-1.079715
4	6	-0.673605	-1.761346	-0.646905
5	6	-0.104297	-1.142640	0.653581
6	6	-1.404754	-0.680612	1.341093
7	1	-2.745977	-1.095431	-1.164200
8	1	-2.758865	0.839855	0.254752
9	1	-1.149349	-2.720035	-0.425267
10	1	0.078780	-1.939647	-1.416600
11	1	-2.132302	-1.485631	1.468396
12	1	-1.270155	-0.184598	2.303817
13	1	-1.493685	-0.207078	-2.020466
14	6	-0.596036	2.312430	-0.836622
15	1	-1.564410	2.578095	-1.264971
16	1	-0.362315	3.070903	-0.069422
17	1	0.199117	2.381107	-1.583622
18	1	0.539396	-1.802803	1.235307
19	6	0.579068	0.222371	0.277531
20	6	1.708991	0.164877	-0.788203
21	1	1.285184	-0.125613	-1.756139
22	1	2.110870	1.175527	-0.921832
23	6	1.118176	0.951020	1.566597
24	1	1.828458	0.282127	2.057431
25	1	1.638110	1.870369	1.287233
26	1	0.342291	1.202279	2.292336
27	6	2.858567	-0.788915	-0.438351
28	1	3.608230	-0.763155	-1.233970
29	1	3.362321	-0.507602	0.490580
30	1	2.518908	-1.824465	-0.342324

mPWB1K

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1340572 hartrees (-269913.422233572 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.284140 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.885209 hartrees (-269757.26749959 kcal/mol)

Coordinates (from last standard orientation):

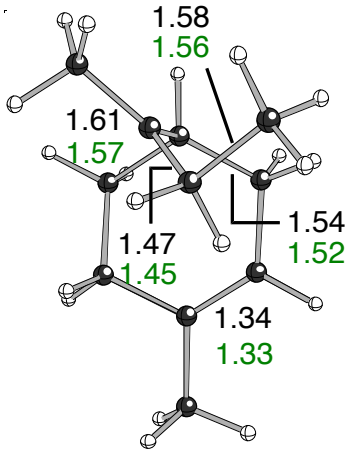
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.818986	0.180120	0.245275

2	6	-0.686038	0.956318	-0.115165
3	6	-1.533663	-0.668185	-1.125458
4	6	-0.533901	-1.730855	-0.691460
5	6	-0.037441	-1.150755	0.628573
6	6	-1.363642	-0.812774	1.296596
7	1	-2.527207	-1.018469	-1.393728
8	1	-2.799327	0.635524	0.258318
9	1	-1.028401	-2.682801	-0.523728
10	1	0.248199	-1.888346	-1.426327
11	1	-2.028079	-1.668331	1.368847
12	1	-1.283137	-0.357612	2.278495
13	1	-1.192092	-0.074733	-1.974471
14	6	-0.716233	2.251022	-0.795299
15	1	-1.694015	2.496871	-1.193397
16	1	-0.477860	2.991121	-0.024788
17	1	0.052925	2.338964	-1.556979
18	1	0.634671	-1.785593	1.194075
19	6	0.548258	0.241851	0.303278
20	6	1.661600	0.268876	-0.747315
21	1	1.248598	0.019404	-1.725709
22	1	2.036951	1.288292	-0.827823
23	6	1.011955	0.970331	1.584100
24	1	1.781936	0.369434	2.058464
25	1	1.439690	1.937572	1.335782
26	1	0.220308	1.124964	2.310710
27	6	2.807435	-0.670754	-0.430712
28	1	3.581129	-0.584860	-1.187392
29	1	3.266545	-0.443939	0.527794
30	1	2.483095	-1.708630	-0.412630

Table 1: $R_1/R_2=CH_3/C_2H_6$ (aligned) (Fig. S5)

B3LYP (distances in black), mPWB1K (distances in green)

A_a



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.363851 hartrees (-270057.62014101 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.273895 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.129098 hartrees (-269910.31028598 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2628912 hartrees (-269994.266856912 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.1032354 hartrees (-269894.081245854 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.471890	-0.925653	0.834744
2	6	2.051551	-0.241042	-0.164320
3	6	1.501482	1.092235	-0.626851
4	6	0.518255	1.726169	0.355083
5	6	-0.536804	0.669676	0.952087
6	6	0.243339	-0.491320	1.598117
7	1	2.332295	1.797385	-0.761946
8	1	1.910809	-1.868696	1.153986
9	1	1.046333	2.077815	1.246676
10	1	0.000541	2.584991	-0.078589
11	1	0.530431	-0.161259	2.606156
12	1	-0.418118	-1.349770	1.762807
13	1	1.057533	0.983709	-1.628545
14	6	3.274872	-0.738581	-0.887563
15	1	4.118439	-0.051885	-0.745350
16	1	3.578775	-1.727764	-0.537034
17	1	3.097718	-0.798202	-1.969086
18	1	-1.083701	1.250359	1.707238
19	6	-1.482078	0.367701	-0.123323
20	6	-2.465840	1.397212	-0.521158
21	1	-2.564738	2.218245	0.189443
22	1	-2.136382	1.805801	-1.491636
23	1	-3.443712	0.947088	-0.728962
24	6	-1.495868	-0.912335	-0.849536
25	1	-1.770924	-0.756672	-1.898146
26	1	-0.532295	-1.419099	-0.780348
27	6	-2.603596	-1.831575	-0.206607
28	1	-3.600723	-1.406015	-0.334046
29	1	-2.562195	-2.788617	-0.731137
30	1	-2.423311	-2.012340	0.854482

mPWB1K

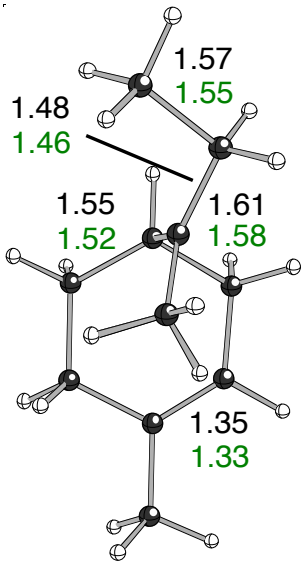
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1070905 hartrees (-269896.500359655 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.280844 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.864864 hartrees (-269744.50080864 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.419156	-1.009148	0.743332
2	6	1.979043	-0.244530	-0.190710
3	6	1.444325	1.120674	-0.501904
4	6	0.521679	1.644787	0.574424
5	6	-0.529713	0.564578	1.006476
6	6	0.211142	-0.646320	1.547470
7	1	2.277227	1.814540	-0.611555
8	1	1.858570	-1.972352	0.963275
9	1	1.085648	1.850771	1.481206
10	1	0.031616	2.568199	0.279151
11	1	0.501347	-0.424588	2.575266
12	1	-0.455698	-1.504928	1.622674
13	1	0.954506	1.111430	-1.481708
14	6	3.174223	-0.675255	-0.970016
15	1	4.018761	-0.016190	-0.774157
16	1	3.471082	-1.689280	-0.722974
17	1	2.980263	-0.627540	-2.041026
18	1	-1.136195	1.049153	1.775976
19	6	-1.399723	0.365930	-0.145214
20	6	-2.235055	1.474699	-0.600147
21	1	-2.405003	2.239658	0.148676
22	1	-1.677055	1.929091	-1.429717
23	1	-3.167173	1.128283	-1.039102
24	6	-1.468972	-0.887718	-0.874200
25	1	-1.706262	-0.726354	-1.922754
26	1	-0.557306	-1.465136	-0.764285
27	6	-2.658060	-1.655082	-0.224149
28	1	-3.602136	-1.151061	-0.400688
29	1	-2.695078	-2.632513	-0.693668
30	1	-2.525392	-1.796881	0.843235

A_b



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3679718 hartrees (-270060.205984218 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.274037 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.131959 hartrees (-269912.10559209 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2669973 hartrees (-269996.843475723 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.1060184 hartrees (-269895.827606184 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.609008	1.230371	-0.081261
2	6	2.232977	0.048489	0.101248
3	6	1.611547	-1.248891	-0.351045
4	6	0.362645	-1.107466	-1.234813
5	6	-0.570069	0.090720	-0.929347
6	6	0.316183	1.423879	-0.807873
7	1	2.360696	-1.829784	-0.904569
8	1	2.065631	2.137615	0.309224
9	1	0.679192	-0.960487	-2.272860
10	1	-0.219245	-2.035074	-1.224899
11	1	0.480339	1.708486	-1.855509
12	1	-0.251827	2.253964	-0.368600

13	1	1.404869	-1.860697	0.539759
14	6	3.564607	-0.054648	0.793621
15	1	4.323404	-0.445490	0.104610
16	1	3.908424	0.913723	1.164223
17	1	3.520184	-0.753414	1.638129
18	1	-1.237787	0.245501	-1.781952
19	6	-1.372981	0.130014	0.293375
20	6	-0.826239	-0.313358	1.579382
21	6	-2.748606	0.665907	0.236564
22	1	-2.886922	1.319882	-0.629030
23	1	-2.994910	1.208209	1.154894
24	1	-0.520054	-1.367735	1.525103
25	1	0.128833	0.225208	1.739257
26	1	-1.499195	-0.156818	2.422201
27	6	-3.730800	-0.550821	0.104452
28	1	-4.745428	-0.148589	0.056175
29	1	-3.541869	-1.121036	-0.808270
30	1	-3.663959	-1.218643	0.966289

mPWB1K

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.109583 hartrees (-269898.06442833 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.280927 (Hartree/Particle)

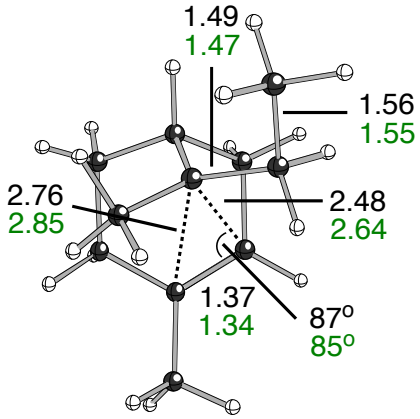
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.866680 hartrees (-269745.6403668 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.550861	1.225150	-0.115580
2	6	2.189405	0.074439	0.103198
3	6	1.601556	-1.236838	-0.297110
4	6	0.385410	-1.142319	-1.200284
5	6	-0.565066	0.022111	-0.942636
6	6	0.248347	1.370945	-0.812068
7	1	2.364807	-1.820527	-0.811641
8	1	2.000609	2.149250	0.220780
9	1	0.723304	-1.010718	-2.225980
10	1	-0.174977	-2.074907	-1.186465
11	1	0.379422	1.698841	-1.843780
12	1	-0.340210	2.161658	-0.340975
13	1	1.391665	-1.812039	0.607178
14	6	3.516113	0.020218	0.779072
15	1	4.269159	-0.377536	0.100519
16	1	3.841708	1.000446	1.110847
17	1	3.489377	-0.644731	1.641241
18	1	-1.234937	0.143763	-1.790425

19	6	-1.343084	0.111411	0.273849
20	6	-0.807724	-0.334391	1.547482
21	6	-2.685500	0.690151	0.218298
22	1	-2.815139	1.313464	-0.661931
23	1	-2.905122	1.260101	1.117408
24	1	-0.552128	-1.393996	1.494261
25	1	0.162745	0.167797	1.680765
26	1	-1.460407	-0.137768	2.388720
27	6	-3.657914	-0.510161	0.137579
28	1	-4.666519	-0.113812	0.083594
29	1	-3.480596	-1.109180	-0.750385
30	1	-3.587176	-1.144400	1.015472

TS_{A-B}



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3573258 hartrees (-270053.525512758 kcal/mol)
Imaginary Frequencies: 1 (-58.8599 1/cm)
Zero-point correction = 0.274425 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.119387 hartrees (-269904.21653637 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2589084 hartrees (-269991.767610084 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.1010018 hartrees (-269892.679639518 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.910403	-0.282829	-1.349590

2	6	-1.729713	-0.470257	-0.272686
3	6	-1.975784	0.665065	0.691785
4	6	-0.793283	1.680970	0.794348
5	6	0.379109	1.249017	-0.098776
6	6	-0.160020	1.023742	-1.525517
7	1	-2.877397	1.190803	0.348824
8	1	-0.829021	-1.062001	-2.104254
9	1	-1.112691	2.673015	0.465618
10	1	-0.479772	1.793908	1.836172
11	1	-0.804438	1.847715	-1.853118
12	1	0.632503	0.933416	-2.269495
13	1	-2.243962	0.262027	1.675046
14	6	-2.476599	-1.749911	-0.045276
15	1	-3.557391	-1.559194	-0.041332
16	1	-2.263486	-2.497856	-0.812049
17	1	-2.239251	-2.173832	0.938986
18	1	1.189569	1.993435	-0.040378
19	6	0.947518	-0.107474	0.288644
20	6	0.823579	-0.613313	1.677811
21	1	1.463918	0.040752	2.296743
22	1	-0.177553	-0.513718	2.098269
23	1	1.183334	-1.637246	1.790074
24	6	1.992099	-0.762873	-0.548529
25	1	1.910234	-1.850491	-0.457793
26	1	1.916651	-0.492064	-1.600546
27	6	3.405295	-0.335668	-0.029762
28	1	3.585863	-0.673555	0.992792
29	1	4.149882	-0.801603	-0.679603
30	1	3.542214	0.747672	-0.078671

mPWB1K

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1032625 hartrees (-269894.098251375 kcal/mol)
Imaginary Frequencies: 1 (-80.5515 1/cm)
Zero-point correction = 0.281124 (Hartree/Particle)

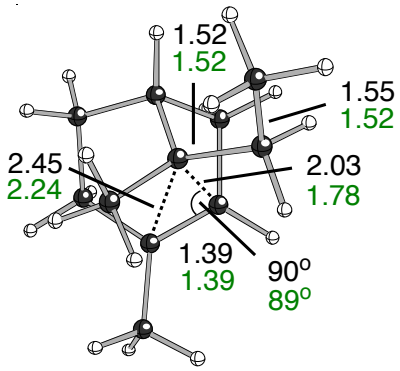
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.858773 hartrees (-269740.67864523 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.982194	-0.892372	1.063261
2	6	1.748392	-0.510585	0.026411
3	6	1.872903	0.928908	-0.360354
4	6	0.739535	1.821314	0.159061
5	6	-0.416886	0.978879	0.682015
6	6	0.103980	0.081692	1.790962

7	1	2.827596	1.291556	0.022223
8	1	1.007957	-1.923762	1.387241
9	1	1.081147	2.435349	0.986940
10	1	0.417908	2.514615	-0.614221
11	1	0.648688	0.660585	2.535627
12	1	-0.693368	-0.423549	2.326524
13	1	1.974353	1.000860	-1.444232
14	6	2.591306	-1.473728	-0.733539
15	1	3.641535	-1.193076	-0.668048
16	1	2.486079	-2.488136	-0.363820
17	1	2.335604	-1.462943	-1.793169
18	1	-1.231713	1.641930	1.003616
19	6	-1.008156	0.096176	-0.362327
20	6	-0.949874	0.498530	-1.766645
21	1	-1.142348	1.567049	-1.866337
22	1	0.078971	0.366307	-2.112459
23	1	-1.608420	-0.078060	-2.404909
24	6	-1.887922	-1.027697	-0.034240
25	1	-1.842002	-1.774754	-0.822562
26	1	-1.659712	-1.490398	0.916261
27	6	-3.322086	-0.445987	0.008230
28	1	-3.603843	0.021311	-0.930296
29	1	-4.003518	-1.270162	0.192506
30	1	-3.435225	0.274491	0.812107

B



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3579574 hartrees (-270053.921848074 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.275417 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.119634 hartrees (-269904.37153134 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2636231 hartrees (-269994.726131481 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.107951 hartrees (-269897.04033201 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.618055	-0.145455	-1.288551
2	6	-1.595612	-0.474198	-0.358551
3	6	-2.059829	0.600336	0.581362
4	6	-0.898101	1.559677	1.016854
5	6	0.330057	1.321640	0.134346
6	6	-0.136078	1.299784	-1.339885
7	1	-2.814206	1.179352	0.028050
8	1	-0.368115	-0.862456	-2.067013
9	1	-1.216036	2.600518	0.918741
10	1	-0.661465	1.401018	2.072371
11	1	-0.918765	2.025763	-1.580866
12	1	0.675040	1.429205	-2.055371
13	1	-2.582457	0.170910	1.440464
14	6	-2.192750	-1.834985	-0.275467
15	1	-3.270633	-1.759339	-0.476391
16	1	-1.757415	-2.535289	-0.990858
17	1	-2.108122	-2.241130	0.740110
18	1	1.139388	2.017244	0.383189
19	6	0.772536	-0.154916	0.183928
20	6	0.608247	-0.968554	1.441831
21	1	1.391861	-0.633524	2.136016
22	1	-0.339738	-0.835499	1.961029
23	1	0.775128	-2.033674	1.260266
24	6	1.998187	-0.565930	-0.621721
25	1	1.952887	-1.642096	-0.819801
26	1	2.034657	-0.057379	-1.585839
27	6	3.310300	-0.252334	0.141254
28	1	3.416384	-0.851080	1.048492
29	1	4.153400	-0.488916	-0.513186
30	1	3.384794	0.805984	0.408195

mPWB1K

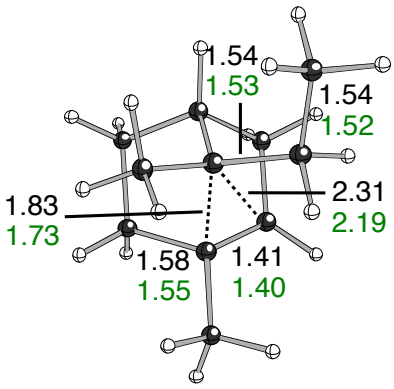
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.114894 hartrees (-269901.39713394 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.283869 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.866674 hartrees (-269745.63660174 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.485045	0.111821	-1.245432
2	6	1.495399	0.482528	-0.365003
3	6	2.033124	-0.560301	0.536577
4	6	0.923810	-1.513036	1.040851
5	6	-0.302903	-1.330522	0.179264
6	6	0.130358	-1.357897	-1.287781
7	1	2.737080	-1.126575	-0.080831
8	1	0.219374	0.802406	-2.034870
9	1	1.266455	-2.542102	0.995076
10	1	0.701591	-1.294283	2.081748
11	1	0.955935	-2.023731	-1.526587
12	1	-0.681035	-1.550821	-1.977647
13	1	2.611590	-0.125267	1.346221
14	6	2.019474	1.853911	-0.309030
15	1	3.053459	1.817778	-0.661029
16	1	1.470628	2.545791	-0.937713
17	1	2.064098	2.218268	0.715322
18	1	-1.114767	-1.988840	0.476821
19	6	-0.667982	0.154654	0.112625
20	6	-0.507157	1.010339	1.343113
21	1	-1.292629	0.722894	2.039498
22	1	0.433216	0.884106	1.868842
23	1	-0.644438	2.064530	1.115224
24	6	-1.958264	0.499501	-0.619899
25	1	-1.924442	1.549254	-0.907558
26	1	-2.038566	-0.077083	-1.536154
27	6	-3.192926	0.245554	0.233535
28	1	-3.271951	0.937264	1.066055
29	1	-4.079315	0.375954	-0.380035
30	1	-3.214162	-0.768868	0.624694

TS



B3LYP

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

HF = -430.3418905 hartrees (-270043.839707655 kcal/mol)
Imaginary Frequencies: 1 (-305.5864 1/cm)
Zero-point correction = 0.274560 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.102913 hartrees (-269893.87893663 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.249694 hartrees (-269985.98548194 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.095257 hartrees (-269889.07472007 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.870345	-0.043733	-1.516902
2	6	1.049718	0.691348	-0.327863
3	6	1.949189	-0.109046	0.692645
4	6	1.233068	-1.441950	1.023913
5	6	-0.045158	-1.388762	0.168711
6	6	0.379104	-1.428058	-1.312936
7	1	2.934825	-0.254419	0.243529
8	1	0.940836	0.402400	-2.511369
9	1	1.843458	-2.312822	0.772397
10	1	0.998826	-1.516586	2.088077
11	1	1.154060	-2.171441	-1.560779
12	1	-0.441085	-1.634547	-2.011521
13	1	2.090168	0.531966	1.565790
14	6	1.283105	2.186253	-0.392069
15	1	2.333573	2.399641	-0.617366
16	1	0.667371	2.668760	-1.156013
17	1	1.060946	2.651963	0.572058
18	1	-0.785769	-2.146357	0.435048
19	6	-0.557666	0.079472	0.299712
20	6	-0.730698	0.634829	1.705627
21	1	-1.494039	0.026069	2.206867
22	1	0.160622	0.594969	2.328876
23	1	-1.097210	1.664155	1.684395
24	6	-1.751788	0.494998	-0.581384
25	1	-1.787073	1.590373	-0.611068
26	1	-1.622733	0.171004	-1.618521
27	6	-3.107358	-0.035927	-0.078691
28	1	-3.388364	0.387168	0.888419
29	1	-3.888533	0.238404	-0.792865
30	1	-3.111053	-1.127246	0.009467

mPWB1K

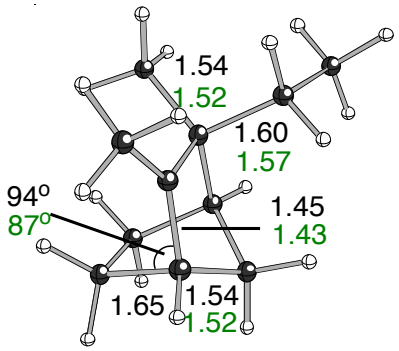
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1003431 hartrees (-269892.266298681 kcal/mol)
Imaginary Frequencies: 1 (-306.8358 1/cm)
Zero-point correction = 0.281989 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.853430 hartrees (-269737.3258593 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.766520	-0.054512	-1.507884
2	6	0.986155	0.689805	-0.339803
3	6	1.943143	-0.051219	0.628049
4	6	1.267818	-1.358969	1.046307
5	6	0.001438	-1.376269	0.208739
6	6	0.404919	-1.457361	-1.260255
7	1	2.895915	-0.205816	0.130025
8	1	0.706755	0.396535	-2.494345
9	1	1.889616	-2.227610	0.853257
10	1	1.033906	-1.363876	2.106370
11	1	1.250717	-2.119794	-1.472676
12	1	-0.388871	-1.769086	-1.936094
13	1	2.134183	0.614541	1.464675
14	6	1.144754	2.178033	-0.427466
15	1	2.154277	2.435464	-0.738602
16	1	0.447378	2.623752	-1.131472
17	1	0.982997	2.630267	0.547200
18	1	-0.722699	-2.126011	0.510899
19	6	-0.507772	0.077268	0.271023
20	6	-0.685988	0.671570	1.647428
21	1	-1.398159	0.045557	2.184528
22	1	0.219992	0.709497	2.240048
23	1	-1.105900	1.671934	1.590492
24	6	-1.722842	0.410479	-0.592136
25	1	-1.767135	1.493881	-0.705006
26	1	-1.623880	0.009000	-1.600312
27	6	-3.029576	-0.090051	-0.002001
28	1	-3.278404	0.415704	0.925701
29	1	-3.842179	0.093645	-0.697991
30	1	-2.999932	-1.160231	0.191298

C



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3728191 hartrees (-270063.247713441 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.276265 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.133055 hartrees (-269912.79334305 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2826051 hartrees (-270006.637526301 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.1290868 hartrees (-269910.303257868 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.422782	0.157400	-1.019636
2	6	0.464491	0.991219	-0.327868
3	6	2.256308	-0.219189	0.349794
4	6	1.388293	-1.316280	1.005947
5	6	0.102258	-1.285908	0.143186
6	6	0.708260	-1.186337	-1.270236
7	1	3.220455	-0.565153	-0.033731
8	1	2.056304	0.617100	-1.776886
9	1	1.868364	-2.294368	0.919955
10	1	1.209891	-1.131975	2.066170
11	1	1.416416	-1.987887	-1.492665
12	1	-0.017295	-1.132181	-2.084114
13	1	2.458798	0.640588	0.994512
14	6	0.526722	2.459834	-0.253594
15	1	1.502663	2.856430	-0.541133
16	1	-0.200305	2.832178	-0.996603
17	1	0.208573	2.855824	0.714059
18	1	-0.581958	-2.114173	0.324460
19	6	-0.562136	0.126200	0.320519

20	6	-0.930675	0.518323	1.765168
21	1	-1.542660	-0.267376	2.214666
22	1	-0.049923	0.650272	2.398567
23	1	-1.509074	1.445603	1.794615
24	6	-1.846015	0.305564	-0.615541
25	1	-2.228609	1.314281	-0.429071
26	1	-1.569987	0.268825	-1.673954
27	6	-2.948439	-0.725815	-0.349301
28	1	-3.274683	-0.724252	0.693716
29	1	-3.816399	-0.473749	-0.966309
30	1	-2.641660	-1.740046	-0.616887

mPWB1K

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1338897 hartrees (-269913.317125647 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.283393 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.886781 hartrees (-269758.25394531 kcal/mol)

Coordinates (from last standard orientation):

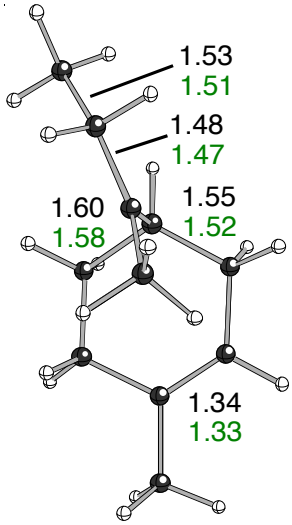
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.352598	0.021006	-1.074075
2	6	0.508058	0.927673	-0.371741
3	6	2.140575	-0.209097	0.333351
4	6	1.329132	-1.296194	1.025558
5	6	0.034064	-1.268580	0.221082
6	6	0.588057	-1.285231	-1.196137
7	1	3.141976	-0.486824	0.013923
8	1	1.994238	0.392056	-1.861235
9	1	1.811174	-2.263671	0.922462
10	1	1.196378	-1.106122	2.084544
11	1	1.245162	-2.128525	-1.384309
12	1	-0.161873	-1.248287	-1.980679
13	1	2.263149	0.689485	0.939280
14	6	0.642058	2.383247	-0.353260
15	1	1.587797	2.725938	-0.757220
16	1	-0.150052	2.754531	-1.012128
17	1	0.454648	2.808979	0.627890
18	1	-0.677893	-2.044753	0.474529
19	6	-0.539135	0.159712	0.337080
20	6	-0.843866	0.635971	1.746619
21	1	-1.523791	-0.057146	2.233159
22	1	0.050403	0.703771	2.360552
23	1	-1.320053	1.612691	1.738977
24	6	-1.789547	0.368352	-0.581582

25	1	-2.166514	1.368834	-0.377052
26	1	-1.513074	0.356901	-1.635680
27	6	-2.877149	-0.658723	-0.340497
28	1	-3.157433	-0.715000	0.707625
29	1	-3.764450	-0.382066	-0.902486
30	1	-2.578857	-1.649609	-0.670542

Table 2: $R_1/R_2=C_2H_6/CH_3$ (extended) (Fig. S5)

B3LYP (distances in black), mPWB1K (distances in green)

A_a



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3651555 hartrees (-270058.438727805 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.273129 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.130789 hartrees (-269911.37140539 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2643404 hartrees (-269995.176244404 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.1043098 hartrees (-269894.755442598 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z

1	6	-1.786708	0.452020	1.084376
2	6	-2.226526	-0.101812	-0.059489
3	6	-1.328279	-0.976476	-0.902046
4	6	-0.057778	-1.452281	-0.201393
5	6	0.643195	-0.347465	0.717308
6	6	-0.418000	0.264888	1.673964
7	1	-1.883377	-1.873656	-1.209648
8	1	-2.462291	1.080220	1.661476
9	1	-0.300528	-2.245457	0.512881
10	1	0.657316	-1.874647	-0.912673
11	1	-0.469998	-0.414508	2.536447
12	1	-0.049399	1.214197	2.085175
13	1	-1.107011	-0.463779	-1.851313
14	6	-3.618835	0.122816	-0.585127
15	1	-4.173429	-0.822300	-0.633844
16	1	-4.182795	0.815863	0.043452
17	1	-3.596434	0.525876	-1.605851
18	1	1.389207	-0.893331	1.299159
19	6	1.344751	0.612605	-0.136562
20	6	2.804483	0.516483	-0.367453
21	1	3.020817	0.867483	-1.386618
22	1	3.187242	1.351422	0.258922
23	6	0.636759	1.706580	-0.820875
24	1	-0.259507	2.042379	-0.294663
25	1	1.299297	2.533669	-1.089345
26	1	0.277253	1.275635	-1.774666
27	6	3.562200	-0.770669	-0.031681
28	1	4.613964	-0.638779	-0.295721
29	1	3.524103	-1.016898	1.032448
30	1	3.183996	-1.623533	-0.601755

mPWB1K

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1082702 hartrees (-269897.240633202 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.280783 (Hartree/Particle)

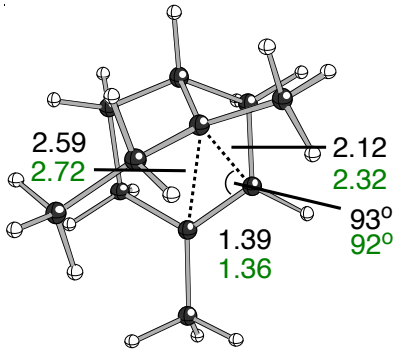
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.865043 hartrees (-269744.61313293 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.784504	0.483108	1.020267
2	6	-2.135410	-0.146355	-0.098474
3	6	-1.190070	-1.060612	-0.811208
4	6	0.039595	-1.424600	-0.014882

5	6	0.639426	-0.228610	0.821606
6	6	-0.456109	0.375520	1.690200
7	1	-1.710635	-1.989941	-1.047588
8	1	-2.509441	1.117074	1.512052
9	1	-0.217063	-2.148171	0.755865
10	1	0.797517	-1.885659	-0.641837
11	1	-0.537792	-0.248427	2.581307
12	1	-0.139588	1.352502	2.057760
13	1	-0.937042	-0.644862	-1.790786
14	6	-3.482760	0.008664	-0.717018
15	1	-4.011393	-0.943199	-0.733023
16	1	-4.092055	0.725439	-0.176521
17	1	-3.403221	0.340624	-1.751905
18	1	1.419303	-0.678580	1.431604
19	6	1.275711	0.640433	-0.145255
20	6	2.666628	0.425513	-0.551824
21	1	2.693389	0.482160	-1.645576
22	1	3.148542	1.373839	-0.269070
23	6	0.559980	1.735288	-0.790092
24	1	-0.134512	2.228523	-0.115782
25	1	1.222652	2.435967	-1.286518
26	1	-0.074295	1.277219	-1.559197
27	6	3.448163	-0.749945	-0.014532
28	1	4.444614	-0.738897	-0.443358
29	1	3.562660	-0.704779	1.064806
30	1	2.994472	-1.701252	-0.274959

TS_{A-B}



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3456048 hartrees (-270046.170468048 kcal/mol)
Imaginary Frequencies: 1 (-49.1930 1/cm)
Zero-point correction = 0.275099 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.106732 hartrees (-269896.27539732 kcal/mol)

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

HF = -430.2498787 hartrees (-269986.101383037 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.0936276 hartrees (-269888.052255276 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.254179	-1.158592	-0.954126
2	6	1.318177	-0.376037	-0.535803
3	6	1.627068	-0.347253	0.935522
4	6	0.348913	-0.445905	1.835075
5	6	-0.874780	-0.813804	0.990353
6	6	-0.459645	-2.002418	0.092751
7	1	2.260314	-1.227793	1.123273
8	1	0.090213	-1.310273	-2.018514
9	1	0.487839	-1.224978	2.589334
10	1	0.193314	0.485627	2.380595
11	1	0.197719	-2.720437	0.593751
12	1	-1.296535	-2.557370	-0.327119
13	1	2.240783	0.519658	1.189419
14	6	2.228431	0.298312	-1.509857
15	1	3.115883	-0.341365	-1.630847
16	1	1.775784	0.410955	-2.498049
17	1	2.593860	1.263961	-1.153595
18	1	-1.756515	-0.968250	1.626392
19	6	-1.175796	0.183833	-0.140544
20	6	-1.070502	1.694466	-0.031674
21	1	-1.375196	2.114154	-0.995761
22	6	-2.324548	-0.169107	-1.063718
23	1	-3.226148	0.286763	-0.628988
24	1	-2.198234	0.277093	-2.053321
25	1	-2.520425	-1.233453	-1.169314
26	1	-1.922133	1.901892	0.644575
27	6	0.136018	2.492397	0.474618
28	1	0.423974	2.263548	1.499889
29	1	1.003986	2.373217	-0.174889
30	1	-0.133584	3.551700	0.447581

mPWB1K

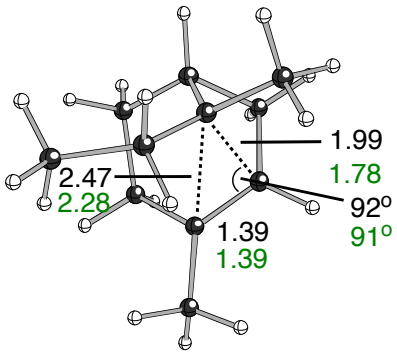
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.097053 hartrees (-269890.20172803 kcal/mol)
Imaginary Frequencies: 1 (-109.3683 1/cm)
Zero-point correction = 0.282587 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.849560 hartrees (-269734.8973956 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.598067	-0.938825	-1.080902
2	6	1.413392	-0.051634	-0.454848
3	6	1.624250	-0.244934	1.008433
4	6	0.328151	-0.616679	1.755233
5	6	-0.728025	-1.115033	0.783842
6	6	-0.049665	-2.008088	-0.246115
7	1	2.333145	-1.070172	1.108512
8	1	0.509118	-0.930885	-2.158264
9	1	0.530193	-1.404646	2.474591
10	1	-0.029568	0.233657	2.330492
11	1	0.676981	-2.680672	0.208376
12	1	-0.742428	-2.618862	-0.811744
13	1	2.107727	0.619015	1.455245
14	6	2.229704	0.945304	-1.189933
15	1	3.253936	0.573604	-1.247489
16	1	1.878339	1.097101	-2.205601
17	1	2.276576	1.899339	-0.673189
18	1	-1.558408	-1.567764	1.336059
19	6	-1.283962	-0.017612	-0.077134
20	6	-1.513087	1.347871	0.469388
21	1	-2.400144	1.750438	-0.013994
22	6	-2.130981	-0.335643	-1.244566
23	1	-3.155589	-0.339058	-0.854371
24	1	-2.099075	0.464329	-1.979805
25	1	-1.948134	-1.290821	-1.714838
26	1	-1.739311	1.220070	1.530084
27	6	-0.401342	2.382088	0.329940
28	1	0.475229	2.123995	0.912955
29	1	-0.115853	2.505392	-0.709989
30	1	-0.771744	3.335047	0.692939

B



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3471139 hartrees (-270047.117443389 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.275781 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.108023 hartrees (-269897.08551273 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.253022 hartrees (-269988.07383522 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.0981549 hartrees (-269890.893181299 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.131391	-1.179154	-0.943735
2	6	1.251764	-0.413423	-0.632498
3	6	1.713597	-0.425027	0.793438
4	6	0.512303	-0.430935	1.800831
5	6	-0.787936	-0.765916	1.063320
6	6	-0.484813	-2.006120	0.181466
7	1	2.280367	-1.360997	0.912528
8	1	-0.122924	-1.341675	-1.988574
9	1	0.679636	-1.192368	2.567195
10	1	0.455748	0.526969	2.314773
11	1	0.202790	-2.725039	0.637495
12	1	-1.369651	-2.548622	-0.145589
13	1	2.418487	0.384434	0.994767
14	6	1.994128	0.365182	-1.659998
15	1	3.016195	-0.034190	-1.728669
16	1	1.537068	0.307600	-2.649760
17	1	2.105340	1.414066	-1.361352
18	1	-1.631165	-0.848329	1.758878
19	6	-1.091557	0.169440	-0.131381
20	6	-0.856983	1.679360	-0.227350
21	1	-1.868473	2.105583	-0.166814
22	1	-0.554873	1.884522	-1.263049
23	6	-2.360038	-0.158627	-0.909585
24	1	-3.197133	0.222791	-0.307986
25	1	-2.387024	0.367157	-1.867468
26	6	0.022887	2.481503	0.738985
27	1	-0.345510	2.434305	1.766356
28	1	1.074862	2.191902	0.731412
29	1	-0.019718	3.531508	0.435292
30	1	-2.542480	-1.217314	-1.080393

mPWB1K

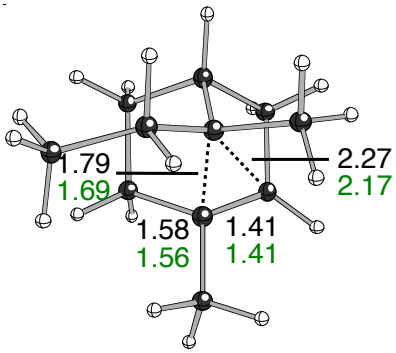
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1044992 hartrees (-269894.874292992 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.284425 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.854779 hartrees (-269738.17237029 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.480414	-0.846563	-1.050678
2	6	0.874010	-0.759981	-0.733447
3	6	1.281606	-1.264155	0.594065
4	6	0.251150	-0.890972	1.684316
5	6	-1.041432	-0.475437	1.018707
6	6	-1.351726	-1.550724	-0.031502
7	1	1.289807	-2.352849	0.476326
8	1	-0.769924	-0.715947	-2.085203
9	1	0.062694	-1.753183	2.317405
10	1	0.654377	-0.112534	2.318744
11	1	-1.030810	-2.557506	0.226513
12	1	-2.387449	-1.587643	-0.339955
13	1	2.294456	-0.971443	0.849539
14	6	1.858962	-0.217798	-1.678376
15	1	2.502699	-1.048117	-1.980831
16	1	1.405273	0.199457	-2.570216
17	1	2.511187	0.510444	-1.201972
18	1	-1.817256	-0.239706	1.742452
19	6	-0.838061	0.587056	-0.068363
20	6	0.059082	1.819575	0.012487
21	1	-0.623915	2.635592	0.248829
22	1	0.384522	2.036563	-1.006368
23	6	-2.132885	1.047124	-0.718562
24	1	-2.639847	1.693163	-0.002674
25	1	-1.927681	1.639211	-1.606045
26	6	1.233289	1.943048	0.965742
27	1	0.912238	1.959033	2.002233
28	1	1.990870	1.173932	0.854420
29	1	1.722051	2.894480	0.775389
30	1	-2.814786	0.250011	-0.984914

TS



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3313316 hartrees (-270037.213892316 kcal/mol)
Imaginary Frequencies: 1 (-288.1143 1/cm)
Zero-point correction = 0.274822 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.091706 hartrees (-269886.84643206 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2394098 hartrees (-269979.532043598 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.0854651 hartrees (-269882.930204901 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.712908	0.227389	0.707159
2	6	0.369921	-0.062262	1.044440
3	6	0.044152	-1.575000	0.723243
4	6	0.212724	-1.782972	-0.801510
5	6	0.697009	-0.411904	-1.297344
6	6	2.090170	-0.172956	-0.670473
7	1	0.717541	-2.202287	1.312972
8	1	2.372978	0.823928	1.341133
9	1	0.939231	-2.566148	-1.033116
10	1	-0.724134	-2.073537	-1.276742
11	1	2.745169	-1.060038	-0.654162
12	1	2.688550	0.610007	-1.148494
13	1	-0.966618	-1.777863	1.071084
14	6	-0.201158	0.504068	2.329768
15	1	0.117661	-0.099763	3.186086
16	1	0.123017	1.534144	2.503271
17	1	-1.293114	0.489149	2.313325
18	1	0.673326	-0.291343	-2.383101

19	6	-0.148464	0.649217	-0.516495
20	6	-1.692935	0.688363	-0.652531
21	1	-2.022497	1.620727	-0.182683
22	6	0.303582	2.110064	-0.722897
23	1	-0.126750	2.479720	-1.659123
24	1	-0.078592	2.749719	0.077665
25	1	1.381999	2.262077	-0.785689
26	1	-1.811476	0.860445	-1.735477
27	6	-2.687909	-0.403380	-0.234130
28	1	-2.526149	-1.368472	-0.715746
29	1	-2.726095	-0.549529	0.847841
30	1	-3.684055	-0.064692	-0.534419

mPWB1K

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.0903091 hartrees (-269885.969863341 kcal/mol)
Imaginary Frequencies: 1 (-304.7884 1/cm)
Zero-point correction = 0.282248 (Hartree/Particle)

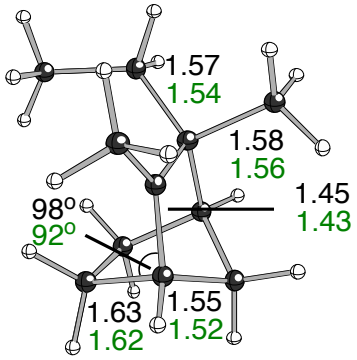
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.842934 hartrees (-269730.73951434 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.635843	-0.421275	0.679273
2	6	-0.282052	-0.187319	0.995752
3	6	-0.016245	1.345288	1.058816
4	6	-0.233497	1.905046	-0.348558
5	6	-0.749581	0.701852	-1.114497
6	6	-2.096393	0.326956	-0.495994
7	1	-0.683747	1.786088	1.793962
8	1	-2.236022	-1.189318	1.159740
9	1	-0.950751	2.720413	-0.360719
10	1	0.682636	2.287607	-0.780862
11	1	-2.706259	1.181384	-0.180389
12	1	-2.748455	-0.282646	-1.116955
13	1	0.991771	1.496439	1.424224
14	6	0.359927	-1.047161	2.046101
15	1	0.085276	-0.704827	3.040717
16	1	0.061683	-2.088146	1.952010
17	1	1.441402	-1.001093	1.973612
18	1	-0.777288	0.825869	-2.192252
19	6	0.101240	-0.488109	-0.618291
20	6	1.618790	-0.504223	-0.841574
21	1	1.950658	-1.511963	-0.596237
22	6	-0.375925	-1.846163	-1.136777
23	1	0.018286	-1.996512	-2.138671

24	1	0.014565	-2.648543	-0.515746
25	1	-1.453363	-1.967730	-1.198405
26	1	1.692294	-0.441871	-1.931803
27	6	2.621260	0.459634	-0.234474
28	1	2.452378	1.499927	-0.484875
29	1	2.695801	0.368800	0.844390
30	1	3.599047	0.198967	-0.630400

C



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3662837 hartrees (-270059.146684587 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.276432 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.125976 hartrees (-269908.35119976 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2757887 hartrees (-270002.360167137 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.1225785 hartrees (-269906.219234535 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.405272	-0.474959	0.882497
2	6	0.027059	-0.694747	0.782985
3	6	-1.370631	1.157214	0.954378
4	6	-1.155743	1.579788	-0.518622
5	6	-0.840904	0.230730	-1.207515
6	6	-1.926318	-0.657586	-0.564474
7	1	-2.349877	1.423572	1.361760
8	1	-1.929088	-0.924013	1.725804

9	1	-2.072859	2.000288	-0.939226
10	1	-0.373350	2.327223	-0.637415
11	1	-2.934846	-0.253516	-0.679594
12	1	-1.937537	-1.700174	-0.885278
13	1	-0.615899	1.544014	1.643890
14	6	0.873418	-1.174344	1.886011
15	1	0.607570	-0.682512	2.829470
16	1	0.617692	-2.235927	2.042031
17	1	1.943190	-1.092605	1.697241
18	1	-0.822390	0.264966	-2.298061
19	6	0.477810	-0.367121	-0.593936
20	6	1.799796	0.462225	-0.727728
21	1	2.637141	-0.242467	-0.695990
22	6	0.776977	-1.771485	-1.262558
23	1	1.050561	-1.565263	-2.301309
24	1	1.622333	-2.260153	-0.773668
25	1	-0.071656	-2.455382	-1.262271
26	1	1.792707	0.861529	-1.749082
27	6	2.107943	1.595396	0.264673
28	1	1.400759	2.425005	0.219780
29	1	2.157932	1.247564	1.301284
30	1	3.092809	2.007175	0.026369

mPWB1K

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1272787 hartrees (-269909.168657037 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.283894 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.879230 hartrees (-269753.5156173 kcal/mol)

Coordinates (from last standard orientation):

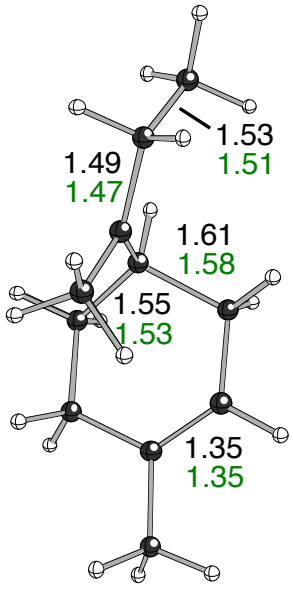
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.400741	-0.427091	0.894538
2	6	0.005131	-0.670496	0.771488
3	6	-1.161939	1.167909	0.980428
4	6	-1.075357	1.597757	-0.480844
5	6	-0.861460	0.260888	-1.180450
6	6	-1.962110	-0.555294	-0.514613
7	1	-2.025767	1.538660	1.526128
8	1	-1.923541	-0.829981	1.751801
9	1	-2.012856	2.036848	-0.809156
10	1	-0.295801	2.324416	-0.667412
11	1	-2.938374	-0.088342	-0.601231
12	1	-2.047221	-1.586820	-0.838102
13	1	-0.285530	1.451884	1.562194

14	6	0.871131	-1.156245	1.841564
15	1	0.620585	-0.700265	2.796909
16	1	0.633277	-2.218586	1.957850
17	1	1.927998	-1.055923	1.627903
18	1	-0.874040	0.297763	-2.264282
19	6	0.424845	-0.380456	-0.609583
20	6	1.754098	0.379433	-0.779429
21	1	2.555629	-0.357185	-0.758903
22	6	0.629829	-1.794425	-1.223433
23	1	0.878466	-1.648505	-2.271541
24	1	1.461453	-2.303497	-0.745229
25	1	-0.245491	-2.431545	-1.169086
26	1	1.749139	0.771283	-1.796184
27	6	2.122595	1.488044	0.194546
28	1	1.474226	2.354993	0.142625
29	1	2.146617	1.149109	1.228137
30	1	3.125106	1.835556	-0.037694

Table 2: R_1/R_2=CH_3/C_2H_6 (extended) (Fig. S5)

B3LYP (distances in black), mPWB1K (distances in green)

A_b



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3669517 hartrees (-270059.565861267 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.273314 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =

-430.131558 hartrees (-269911.85396058 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2664584 hartrees (-269996.505310584 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.1060199 hartrees (-269895.828547449 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.349625	-0.816214	-1.028979
2	6	2.194333	-0.157860	-0.209026
3	6	1.778105	0.264250	1.177392
4	6	0.437348	-0.305164	1.666561
5	6	-0.663971	-0.519268	0.595784
6	6	-0.020746	-1.288266	-0.662226
7	1	2.557656	-0.034317	1.890393
8	1	1.668113	-1.049072	-2.043066
9	1	0.609504	-1.299063	2.092859
10	1	0.037234	0.307077	2.481489
11	1	-0.011081	-2.333717	-0.327541
12	1	-0.683094	-1.269597	-1.536820
13	1	1.785336	1.363590	1.218896
14	6	3.583580	0.230267	-0.636419
15	1	4.330161	-0.262268	-0.001520
16	1	3.783832	-0.046102	-1.674090
17	1	3.744984	1.309987	-0.527705
18	1	-1.420927	-1.189888	1.004343
19	6	-1.332188	0.621638	-0.024649
20	6	-0.572836	1.818154	-0.410807
21	1	-0.121783	2.278108	0.480351
22	1	0.297213	1.495889	-1.012850
23	1	-1.163289	2.558074	-0.952083
24	6	-2.778775	0.593356	-0.356842
25	1	-3.190420	1.464407	0.189766
26	1	-2.873454	0.918949	-1.406039
27	6	-3.611725	-0.657401	-0.081123
28	1	-3.245175	-1.524887	-0.637710
29	1	-3.639982	-0.910850	0.982444
30	1	-4.641325	-0.477267	-0.399115

mPWB1K

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1097496 hartrees (-269898.168971496 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.280538 (Hartree/Particle)

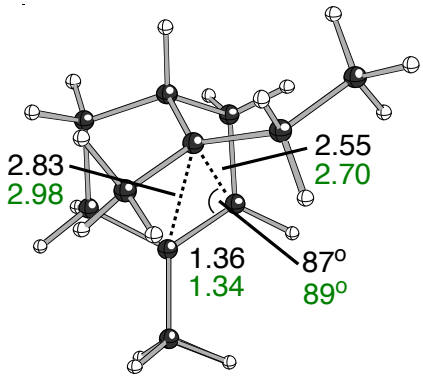
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =
-429.866504 hartrees (-269745.52992504 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.265105	-1.102314	-0.697723
2	6	2.138625	-0.242903	-0.170460
3	6	1.778741	0.633730	0.981536
4	6	0.475176	0.274923	1.672108
5	6	-0.652940	-0.241655	0.785490
6	6	-0.111332	-1.352733	-0.203133
7	1	2.579795	0.590249	1.719201
8	1	1.559477	-1.692035	-1.555091
9	1	0.667986	-0.527789	2.380564
10	1	0.111696	1.113308	2.263010
11	1	-0.168225	-2.271875	0.380450
12	1	-0.785220	-1.516845	-1.047767
13	1	1.785616	1.671359	0.641212
14	6	3.517585	-0.084720	-0.711777
15	1	4.252866	-0.366032	0.040465
16	1	3.680044	-0.698337	-1.591561
17	1	3.718684	0.953359	-0.972840
18	1	-1.407343	-0.719638	1.400930
19	6	-1.302477	0.608584	-0.184233
20	6	-0.549348	1.619983	-0.908980
21	1	-0.117205	2.328540	-0.199883
22	1	0.318123	1.122878	-1.364644
23	1	-1.130165	2.140237	-1.660797
24	6	-2.719972	0.432573	-0.525087
25	1	-3.157184	1.402168	-0.241530
26	1	-2.799643	0.452197	-1.615364
27	6	-3.499527	-0.708717	0.083990
28	1	-3.058535	-1.673267	-0.155188
29	1	-3.580382	-0.622808	1.163729
30	1	-4.508206	-0.706170	-0.315279

TS_{A-B}



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3519597 hartrees (-270050.158231347 kcal/mol)
Imaginary Frequencies: 1 (-65.4690 1/cm)
Zero-point correction = 0.273974 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.114228 hartrees (-269900.97921228 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2535232 hartrees (-269988.388343232 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.095833 hartrees (-269889.43616583 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.506225	-1.185900	-0.747316
2	6	-1.585703	-0.723889	-0.056502
3	6	-2.059464	0.695578	-0.274504
4	6	-0.931231	1.697592	-0.688004
5	6	0.435022	0.997069	-0.757072
6	6	0.271749	-0.249362	-1.652689
7	1	-2.820331	0.664519	-1.066275
8	1	-0.234118	-2.237739	-0.691335
9	1	-1.136851	2.109659	-1.678978
10	1	-0.911844	2.550702	-0.003813
11	1	-0.273004	0.001310	-2.571080
12	1	1.219505	-0.681757	-1.959198
13	1	-2.595981	1.046735	0.614381
14	6	-2.390625	-1.591055	0.864529
15	1	-3.433409	-1.637001	0.525749
16	1	-2.002884	-2.610793	0.918482
17	1	-2.418829	-1.170422	1.878331
18	1	1.205140	1.698864	-1.120869
19	6	0.899885	0.469793	0.585501
20	6	0.337297	1.029745	1.843021
21	1	0.691608	2.075216	1.889660
22	1	-0.750400	1.090987	1.855661
23	1	0.698103	0.515340	2.735093
24	6	2.170977	-0.283767	0.797398
25	1	2.759714	0.458530	1.373803
26	1	1.973053	-1.055745	1.554592
27	6	3.049069	-0.834377	-0.325894
28	1	2.625293	-1.731572	-0.782330
29	1	3.248085	-0.095788	-1.107178
30	1	4.012643	-1.119604	0.104500

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mPWB1K

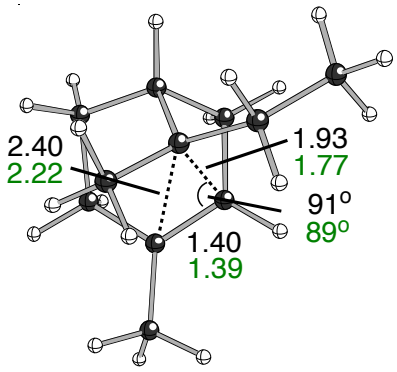
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.0982887 hartrees (-269890.977142137 kcal/mol)
Imaginary Frequencies: 1 (-82.7406 1/cm)
Zero-point correction = 0.280240 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.854828 hartrees (-269738.20311828 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.703580	-1.393082	-0.212838
2	6	-1.714761	-0.601186	0.164324
3	6	-1.978414	0.687991	-0.553866
4	6	-0.759912	1.301078	-1.271472
5	6	0.514998	0.524027	-0.998789
6	6	0.245697	-0.956691	-1.289536
7	1	-2.764548	0.494787	-1.284507
8	1	-0.586200	-2.372304	0.229893
9	1	-0.913125	1.286966	-2.346453
10	1	-0.648450	2.349112	-1.001511
11	1	-0.180893	-1.048492	-2.288286
12	1	1.150046	-1.547222	-1.284314
13	1	-2.423377	1.402175	0.139390
14	6	-2.675297	-0.972402	1.238172
15	1	-3.692243	-0.994324	0.848965
16	1	-2.452598	-1.945011	1.664099
17	1	-2.668361	-0.233269	2.039665
18	1	1.340353	0.897496	-1.619582
19	6	0.997775	0.606968	0.398243
20	6	0.406996	1.555949	1.339597
21	1	0.741114	2.541241	0.985103
22	1	-0.675545	1.584849	1.294935
23	1	0.759993	1.427234	2.356347
24	6	2.215612	-0.059212	0.875381
25	1	2.760359	0.756718	1.368377
26	1	1.898118	-0.654548	1.740157
27	6	3.142648	-0.834800	-0.035335
28	1	2.827285	-1.862854	-0.171013
29	1	3.249041	-0.369988	-1.011838
30	1	4.128464	-0.864404	0.417290

B



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3535303 hartrees (-270051.143798553 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.275526 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.114462 hartrees (-269901.12604962 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2604907 hartrees (-269992.760519157 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.1060323 hartrees (-269895.836328573 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.128698	-0.238421	-1.157594
2	6	-1.399781	-0.461543	-0.622573
3	6	-2.090394	0.704412	0.017750
4	6	-1.090893	1.643905	0.784451
5	6	0.345877	1.309607	0.370963
6	6	0.366809	1.206240	-1.172708
7	1	-2.542773	1.269813	-0.811475
8	1	0.324102	-1.014770	-1.770947
9	1	-1.305395	2.687394	0.541236
10	1	-1.232471	1.532566	1.862552
11	1	-0.300185	1.904316	-1.687940
12	1	1.356085	1.293307	-1.610056
13	1	-2.919716	0.376696	0.649864
14	6	-2.062693	-1.790037	-0.667206
15	1	-2.975697	-1.696172	-1.273378
16	1	-1.435395	-2.565718	-1.110205
17	1	-2.399424	-2.100948	0.328794
18	1	1.071533	1.981932	0.841561

19	6	0.643056	-0.189822	0.604538
20	6	0.004180	-0.905037	1.785015
21	1	0.542153	-0.574025	2.683306
22	1	-1.048917	-0.684878	1.953117
23	1	0.131883	-1.988771	1.717502
24	6	2.061950	-0.741217	0.415556
25	1	2.500477	-0.616661	1.418724
26	1	1.980132	-1.826333	0.281671
27	6	3.057302	-0.176383	-0.601079
28	1	2.768432	-0.373096	-1.637503
29	1	3.225444	0.896951	-0.476388
30	1	4.019438	-0.671830	-0.443107

mPWB1K

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1117195 hartrees (-269899.405103445 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.283954 (Hartree/Particle)

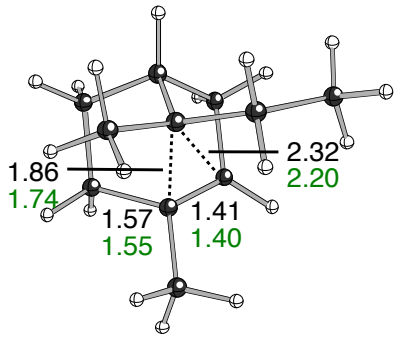
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.862897 hartrees (-269743.26649647 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.036206	-0.187603	-1.121717
2	6	-1.315588	-0.437109	-0.630526
3	6	-2.038433	0.701658	-0.019919
4	6	-1.094680	1.607509	0.807897
5	6	0.331764	1.291656	0.422033
6	6	0.397318	1.261392	-1.106891
7	1	-2.424445	1.272532	-0.870058
8	1	0.429877	-0.938767	-1.746853
9	1	-1.315486	2.651686	0.609038
10	1	-1.262020	1.437748	1.867789
11	1	-0.282869	1.942052	-1.614178
12	1	1.387225	1.396210	-1.513679
13	1	-2.901519	0.365724	0.546822
14	6	-1.935581	-1.766399	-0.710194
15	1	-2.729255	-1.699590	-1.459297
16	1	-1.242078	-2.537362	-1.027417
17	1	-2.420330	-2.042610	0.222861
18	1	1.053512	1.909398	0.950721
19	6	0.561456	-0.218226	0.540967
20	6	-0.115927	-0.968138	1.669800
21	1	0.408497	-0.702408	2.586499
22	1	-1.163060	-0.733958	1.827053
23	1	-0.018242	-2.043406	1.544258

24	6	1.981761	-0.761882	0.430428
25	1	2.365576	-0.677135	1.449866
26	1	1.907932	-1.832219	0.241023
27	6	2.993424	-0.148280	-0.511473
28	1	2.738252	-0.289097	-1.559138
29	1	3.142936	0.911910	-0.324600
30	1	3.949651	-0.638180	-0.353145

TS



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3379298 hartrees (-270041.354328798 kcal/mol)
Imaginary Frequencies: 1 (-284.5976 1/cm)
Zero-point correction = 0.274810 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.098307 hartrees (-269890.98862557 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2457484 hartrees (-269983.509578484 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.0915632 hartrees (-269886.756823632 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.026449	-0.205946	-1.529677
2	6	0.687580	0.671319	-0.693437
3	6	2.034419	0.020252	-0.206434
4	6	1.700927	-1.272011	0.585425
5	6	0.167301	-1.364857	0.496550
6	6	-0.184411	-1.580515	-0.991115
7	1	2.654397	-0.173578	-1.085696
8	1	-0.531027	0.121206	-2.440292
9	1	2.174652	-2.154908	0.149585

10	1	2.043105	-1.208541	1.620329
11	1	0.478483	-2.288116	-1.515323
12	1	-1.196512	-1.947803	-1.173329
13	1	2.563346	0.765299	0.391622
14	6	0.723878	2.152706	-0.998611
15	1	1.488126	2.366288	-1.753948
16	1	-0.234779	2.521675	-1.373405
17	1	0.989023	2.725846	-0.105811
18	1	-0.272327	-2.105152	1.170229
19	6	-0.333506	0.091989	0.748721
20	6	0.234428	0.802949	1.977333
21	1	-0.109149	0.239973	2.855921
22	1	1.319396	0.847972	2.032641
23	1	-0.159774	1.817453	2.069102
24	6	-1.830680	0.438994	0.692419
25	1	-2.204346	0.195982	1.697178
26	1	-1.894513	1.532560	0.634988
27	6	-2.812029	-0.153101	-0.321376
28	1	-2.556919	0.085040	-1.361530
29	1	-2.922606	-1.237280	-0.230441
30	1	-3.797326	0.285410	-0.140611

mPWB1K

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.0967856 hartrees (-269890.033931856 kcal/mol)
Imaginary Frequencies: 1 (-293.3646 1/cm)
Zero-point correction = 0.283054 (Hartree/Particle)

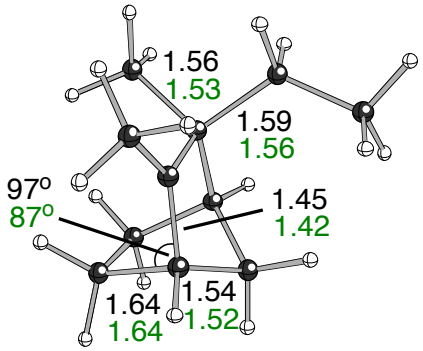
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.848086 hartrees (-269733.97244586 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.091365	-0.296544	-1.466420
2	6	0.687716	0.585178	-0.708738
3	6	1.999574	-0.097837	-0.243885
4	6	1.630314	-1.260032	0.684027
5	6	0.116406	-1.301466	0.590266
6	6	-0.238227	-1.627460	-0.859876
7	1	2.549332	-0.422822	-1.122736
8	1	-0.645184	0.012095	-2.347635
9	1	2.077526	-2.197273	0.368052
10	1	1.957992	-1.077393	1.702475
11	1	0.444498	-2.338417	-1.338300
12	1	-1.236166	-2.020629	-1.018624
13	1	2.610430	0.658054	0.240606
14	6	0.774737	2.029788	-1.095944

15	1	1.484248	2.163097	-1.909089
16	1	-0.185618	2.425452	-1.415132
17	1	1.129761	2.623951	-0.258398
18	1	-0.361981	-1.944639	1.322565
19	6	-0.294398	0.183409	0.672852
20	6	0.301681	0.975600	1.820845
21	1	-0.027567	0.495577	2.743011
22	1	1.382871	1.014016	1.840213
23	1	-0.079783	1.992176	1.828735
24	6	-1.768196	0.568353	0.616377
25	1	-2.106708	0.519147	1.651666
26	1	-1.802637	1.629334	0.365996
27	6	-2.781074	-0.172504	-0.230341
28	1	-2.589544	-0.110265	-1.301141
29	1	-2.868886	-1.220213	0.045075
30	1	-3.755593	0.279842	-0.072312

C



B3LYP

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.3675857 hartrees (-270059.963702607 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.276331 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-430.127526 hartrees (-269909.32384026 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.2770876 hartrees (-270003.175239876 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -430.1235144 hartrees (-269906.806521144 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z

1	6	0.999818	-0.003003	-1.284704
2	6	0.043891	0.837230	-0.594104
3	6	2.238222	0.216338	-0.230457
4	6	1.886986	-0.733178	0.939457
5	6	0.437424	-1.161679	0.594579
6	6	0.594458	-1.446453	-0.914661
7	1	3.119198	-0.079283	-0.806999
8	1	1.271124	0.264748	-2.305396
9	1	2.540789	-1.608931	0.936655
10	1	1.988801	-0.255873	1.914520
11	1	1.394490	-2.157753	-1.134228
12	1	-0.307261	-1.772027	-1.429311
13	1	2.380872	1.259824	0.063892
14	6	-0.318090	2.200922	-1.004757
15	1	0.476066	2.689562	-1.576066
16	1	-1.162708	2.080881	-1.707846
17	1	-0.665172	2.833653	-0.186528
18	1	0.042750	-1.974716	1.206226
19	6	-0.462836	0.125028	0.614644
20	6	-0.332227	0.996374	1.896177
21	1	-0.480728	0.354093	2.769106
22	1	0.644553	1.474817	1.992462
23	1	-1.095833	1.777075	1.924122
24	6	-2.023641	-0.166818	0.477131
25	1	-2.291640	-0.592026	1.450607
26	1	-2.515577	0.810389	0.425091
27	6	-2.577989	-1.067119	-0.629679
28	1	-2.353179	-0.703574	-1.638159
29	1	-2.234576	-2.100685	-0.545130
30	1	-3.668068	-1.086018	-0.534773

mPWB1K

mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -430.1285045 hartrees (-269909.937858795 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.283909 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-429.880322 hartrees (-269754.20085822 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.880309	-0.215122	-1.317601
2	6	0.044765	0.727159	-0.661998
3	6	2.074413	0.274951	-0.309082
4	6	1.887434	-0.605240	0.920670

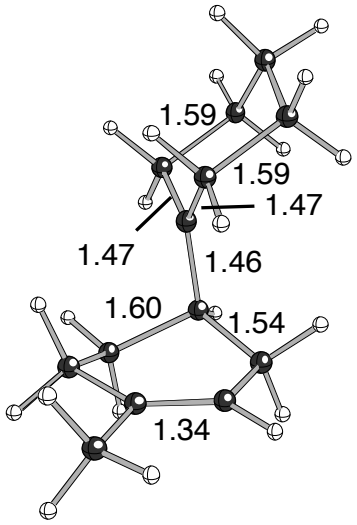
5	6	0.457541	-1.102682	0.714381
6	6	0.562535	-1.575610	-0.731763
7	1	2.968584	0.095442	-0.900640
8	1	1.130291	-0.074785	-2.360103
9	1	2.580641	-1.440617	0.905977
10	1	2.042725	-0.064545	1.846988
11	1	1.376515	-2.279411	-0.877486
12	1	-0.336090	-1.998397	-1.159263
13	1	2.077696	1.341776	-0.082607
14	6	-0.290905	2.059485	-1.159287
15	1	0.361053	2.390831	-1.959739
16	1	-1.296743	1.955992	-1.581912
17	1	-0.356867	2.802302	-0.370517
18	1	0.111110	-1.831376	1.438995
19	6	-0.427504	0.161069	0.628703
20	6	-0.248300	1.136000	1.792465
21	1	-0.371915	0.599024	2.729354
22	1	0.729595	1.609029	1.803920
23	1	-0.998936	1.920485	1.763429
24	6	-1.960386	-0.101031	0.526920
25	1	-2.243919	-0.460844	1.514714
26	1	-2.427691	0.877648	0.422741
27	6	-2.523103	-1.031720	-0.527834
28	1	-2.220531	-0.763580	-1.539412
29	1	-2.258982	-2.069454	-0.351173
30	1	-3.607333	-0.973084	-0.496707

3.3. R_1/R_2= –$(CH_2)_5$–

Table 1: R_1/R_2= –$(CH_2)_5$– (Fig. S6)

<u>B3LYP</u>

A_a



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -507.7977382 hartrees (-318648.158697882 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.312285 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-507.524695 hartrees (-318476.82135945 kcal/mol)

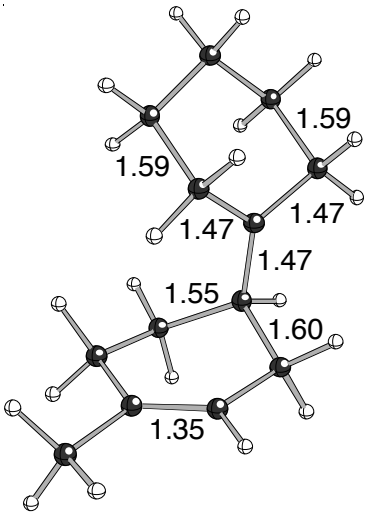
mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -507.6853221 hartrees (-318577.616470971 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -507.5031343 hartrees (-318463.291804593 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.097788	-0.748973	0.996290
2	6	2.652214	-0.314507	-0.146624
3	6	2.107253	0.895305	-0.876946
4	6	1.169964	1.757149	-0.032680
5	6	0.131410	0.897821	0.833602
6	6	0.909195	-0.125593	1.685842
7	1	2.944469	1.530709	-1.194836
8	1	2.530967	-1.610651	1.500132
9	1	1.738744	2.302272	0.727440
10	1	0.644610	2.499464	-0.639683
11	1	1.240708	0.399371	2.592640
12	1	0.231007	-0.909163	2.047645
13	1	1.624806	0.575469	-1.813025
14	6	3.841637	-0.988603	-0.777661
15	1	4.699431	-0.306062	-0.820117
16	1	4.143925	-1.880233	-0.222941
17	1	3.625449	-1.285685	-1.811923
18	1	-0.369103	1.640774	1.468473
19	6	-0.862150	0.392248	-0.115942
20	6	-1.989999	1.252094	-0.514566
21	1	-1.875815	2.282498	-0.170968
22	1	-2.125149	1.235243	-1.602380
23	6	-0.887710	-0.984017	-0.625049
24	1	-1.041554	-0.987576	-1.710731
25	1	0.006806	-1.551881	-0.372352
26	6	-3.291549	0.606216	0.121053
27	1	-4.135345	1.221476	-0.203503
28	1	-3.233693	0.686098	1.212586
29	6	-2.181132	-1.657791	0.013782
30	1	-2.222796	-2.674246	-0.387395
31	1	-2.042582	-1.742685	1.097013
32	6	-3.436856	-0.851719	-0.312620
33	1	-4.296495	-1.298503	0.200641
34	1	-3.648779	-0.904469	-1.387599

A_b



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -507.7720774 hartrees (-318632.056289274 kcal/mol)
Imaginary Frequencies: 1 (-307.2629 1/cm)
Zero-point correction = 0.312442 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-507.495859 hartrees (-318458.72648109 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -507.6685436 hartrees (-318567.087794436 kcal/mol)

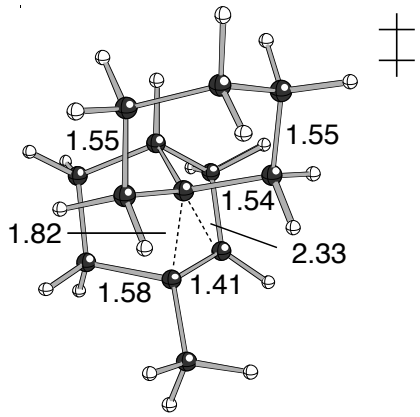
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -507.4919658 hartrees (-318456.283459158 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.844846	1.019108	0.727582
2	6	1.523163	-0.351378	0.658334
3	6	2.042456	-0.966920	-0.704547
4	6	1.349601	-0.213720	-1.865243
5	6	0.448319	0.807057	-1.145773
6	6	1.368140	1.813344	-0.428100
7	1	3.131711	-0.884309	-0.729149
8	1	2.276839	1.490401	1.613112
9	1	2.067554	0.285730	-2.520677
10	1	0.767559	-0.891978	-2.492664
11	1	2.206597	2.205583	-1.025991
12	1	0.847835	2.707704	-0.060697

13	1	1.802371	-2.031859	-0.678803
14	6	1.699785	-1.222760	1.884912
15	1	2.757480	-1.468796	2.028653
16	1	1.339532	-0.732935	2.793679
17	1	1.164297	-2.168563	1.769356
18	1	-0.291966	1.279328	-1.794183
19	6	-0.154696	0.030175	0.067699
20	6	-0.860198	-1.298699	-0.210416
21	1	-0.295385	-1.947322	-0.879880
22	1	-0.987691	-1.839672	0.734681
23	6	-1.006266	0.835905	1.062514
24	1	-1.095272	0.256058	1.989746
25	1	-0.549662	1.790672	1.338059
26	6	-2.266955	-1.041886	-0.815475
27	1	-2.727908	-2.015740	-1.012117
28	1	-2.165909	-0.543972	-1.788425
29	6	-2.424146	1.100329	0.503728
30	1	-2.995702	1.651187	1.257979
31	1	-2.354946	1.758071	-0.372882
32	6	-3.137246	-0.200697	0.122925
33	1	-4.100344	0.018740	-0.349712
34	1	-3.357808	-0.777475	1.031083

TS



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -507.7720774 hartrees (-318632.056289274 kcal/mol)
Imaginary Frequencies: 1 (-307.2629 1/cm)
Zero-point correction = 0.312442 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-507.495859 hartrees (-318458.72648109 kcal/mol)

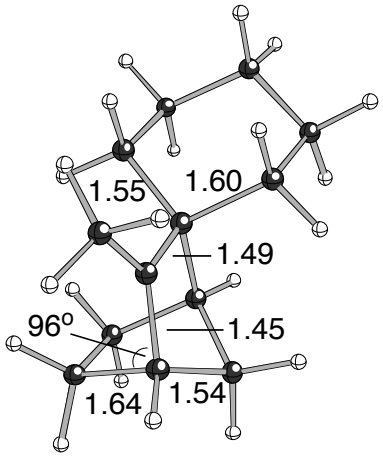
mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -507.6685436 hartrees (-318567.087794436 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -507.4919658 hartrees (-318456.283459158 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.844846	1.019108	0.727582
2	6	1.523163	-0.351378	0.658334
3	6	2.042456	-0.966920	-0.704547
4	6	1.349601	-0.213720	-1.865243
5	6	0.448319	0.807057	-1.145773
6	6	1.368140	1.813344	-0.428100
7	1	3.131711	-0.884309	-0.729149
8	1	2.276839	1.490401	1.613112
9	1	2.067554	0.285730	-2.520677
10	1	0.767559	-0.891978	-2.492664
11	1	2.206597	2.205583	-1.025991
12	1	0.847835	2.707704	-0.060697
13	1	1.802371	-2.031859	-0.678803
14	6	1.699785	-1.222760	1.884912
15	1	2.757480	-1.468796	2.028653
16	1	1.339532	-0.732935	2.793679
17	1	1.164297	-2.168563	1.769356
18	1	-0.291966	1.279328	-1.794183
19	6	-0.154696	0.030175	0.067699
20	6	-0.860198	-1.298699	-0.210416
21	1	-0.295385	-1.947322	-0.879880
22	1	-0.987691	-1.839672	0.734681
23	6	-1.006266	0.835905	1.062514
24	1	-1.095272	0.256058	1.989746
25	1	-0.549662	1.790672	1.338059
26	6	-2.266955	-1.041886	-0.815475
27	1	-2.727908	-2.015740	-1.012117
28	1	-2.165909	-0.543972	-1.788425
29	6	-2.424146	1.100329	0.503728
30	1	-2.995702	1.651187	1.257979
31	1	-2.354946	1.758071	-0.372882
32	6	-3.137246	-0.200697	0.122925
33	1	-4.100344	0.018740	-0.349712
34	1	-3.357808	-0.777475	1.031083

C



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -507.8021335 hartrees (-318650.916792585 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.314198 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-507.524892 hartrees (-318476.94497892 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -507.7004103 hartrees (-318587.084467353 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -507.5246075 hartrees (-318476.766452325 kcal/mol)

Coordinates (from last standard orientation):

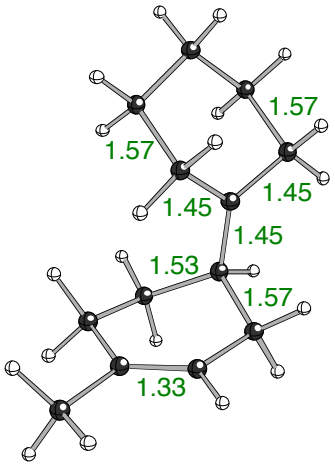
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.178674	0.332617	0.567171
2	6	-1.070287	1.035868	-0.050869
3	6	-2.505490	-0.616726	-0.726003
4	6	-1.419354	-1.714599	-0.645853
5	6	-0.486351	-1.183488	0.472369
6	6	-1.527823	-0.706077	1.503491
7	1	-3.523260	-0.970969	-0.539080
8	1	-3.041084	0.917738	0.884676
9	1	-1.854039	-2.669496	-0.339741
10	1	-0.915699	-1.876724	-1.599761
11	1	-2.232790	-1.488006	1.795673
12	1	-1.115252	-0.260212	2.410235
13	1	-2.523935	-0.072688	-1.674537
14	6	-1.173833	2.383732	-0.633372
15	1	-2.199866	2.631916	-0.917275
16	1	-0.905285	3.085348	0.176127
17	1	-0.482572	2.563695	-1.458145

18	1	0.246074	-1.905435	0.829834
19	6	0.138557	0.173984	-0.021194
20	6	0.958392	0.127574	-1.340666
21	1	0.345088	-0.272116	-2.153865
22	1	1.229466	1.150871	-1.626435
23	6	1.086045	0.830617	1.088092
24	1	1.330856	1.845311	0.753803
25	1	0.573472	0.921289	2.048490
26	6	2.247182	-0.694930	-1.184354
27	1	2.779814	-0.694570	-2.141143
28	1	2.000597	-1.742848	-0.970644
29	6	2.383624	0.019435	1.246322
30	1	3.002587	0.537390	1.988153
31	1	2.160094	-0.967214	1.668633
32	6	3.144858	-0.125739	-0.077258
33	1	4.021904	-0.764759	0.065727
34	1	3.522756	0.857878	-0.387976

Table 1: R_1/R_2=–$(CH_2)_5$– (Fig. S6)

mPWB1K

A_b



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -507.505434 hartrees (-318464.73488934 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.320953 (Hartree/Particle)

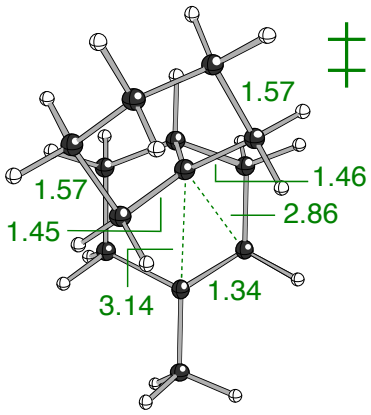
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-507.222683 hartrees (-318287.30580933 kcal/mol)

Coordinates (from last standard orientation):

Center	Atomic	Coordinates (Angstroms)

Number	Number	X	Y	Z
1	6	-2.189901	0.851824	-0.756474
2	6	-2.522421	-0.259257	-0.100708
3	6	-1.730405	-0.744437	1.070998
4	6	-0.768737	0.284632	1.626141
5	6	-0.040137	1.152759	0.601074
6	6	-1.062555	1.761080	-0.417280
7	1	-2.417023	-1.035303	1.865747
8	1	-2.782596	1.155044	-1.608730
9	1	-1.328898	0.988815	2.238275
10	1	-0.042025	-0.179312	2.289967
11	1	-1.419194	2.677925	0.054072
12	1	-0.569178	2.098231	-1.332948
13	1	-1.219011	-1.671478	0.799547
14	6	-3.687677	-1.097429	-0.501440
15	1	-4.426619	-1.129939	0.297672
16	1	-4.170492	-0.716061	-1.395212
17	1	-3.383289	-2.126612	-0.688696
18	1	0.435714	1.976575	1.126841
19	6	0.934630	0.579293	-0.311602
20	6	0.757257	-0.686984	-1.002911
21	1	-0.272978	-1.016200	-1.039396
22	1	1.181551	-0.651511	-2.003789
23	6	2.241738	1.198610	-0.459345
24	1	2.612380	1.156489	-1.479988
25	1	2.285830	2.210277	-0.070563
26	6	1.637196	-1.662172	-0.151364
27	1	1.553062	-2.642458	-0.612375
28	1	1.226126	-1.744196	0.854256
29	6	3.133883	0.248243	0.415071
30	1	4.140469	0.656348	0.378507
31	1	2.808987	0.295673	1.454244
32	6	3.067089	-1.169647	-0.105727
33	1	3.658302	-1.821238	0.534469
34	1	3.509130	-1.220176	-1.100490

$TS_{A\text{-}B}$



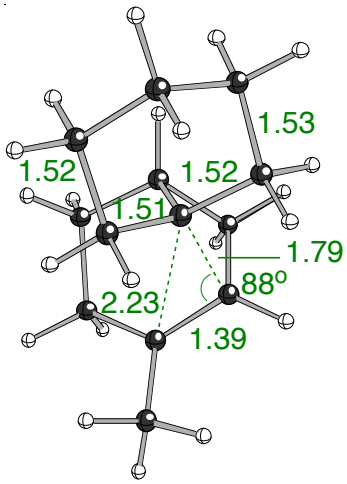
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -507.5014519 hartrees (-318462.236081769 kcal/mol)
Imaginary Frequencies: 1 (-51.0544 1/cm)
Zero-point correction = 0.320328 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-507.218915 hartrees (-318284.94135165 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.009971	1.121781	-0.525275
2	6	-2.425634	-0.137418	-0.372800
3	6	-2.070556	-0.943426	0.838499
4	6	-0.946585	-0.361249	1.707973
5	6	-0.137757	0.707113	0.993964
6	6	-1.094143	1.784165	0.456330
7	1	-2.971957	-1.042524	1.443795
8	1	-2.368793	1.706357	-1.360653
9	1	-1.369073	0.109951	2.591283
10	1	-0.300857	-1.156671	2.076949
11	1	-1.632839	2.216646	1.299390
12	1	-0.552480	2.601567	-0.008143
13	1	-1.845962	-1.964523	0.527550
14	6	-3.338825	-0.798245	-1.347368
15	1	-4.270244	-1.088232	-0.863045
16	1	-3.578868	-0.146135	-2.180657
17	1	-2.895130	-1.711845	-1.741639
18	1	0.566640	1.186944	1.685432
19	6	0.683122	0.242022	-0.143493
20	6	0.867952	-1.154267	-0.479499
21	1	0.091906	-1.805994	-0.104730
22	1	1.012494	-1.296272	-1.547106
23	6	1.597045	1.167801	-0.800859
24	1	1.659967	0.968368	-1.868069
25	1	1.360092	2.209911	-0.624244
26	6	2.233110	-1.486895	0.227377
27	1	2.406840	-2.546201	0.058804
28	1	2.134758	-1.344812	1.303292
29	6	2.993424	0.841932	-0.169665
30	1	3.712043	1.492226	-0.660415
31	1	2.979080	1.116584	0.884286
32	6	3.333008	-0.619264	-0.335397
33	1	4.268241	-0.836512	0.177263
34	1	3.489011	-0.853134	-1.388065

B



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -507.513035 hartrees (-318469.50459285 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.322152 (Hartree/Particle)

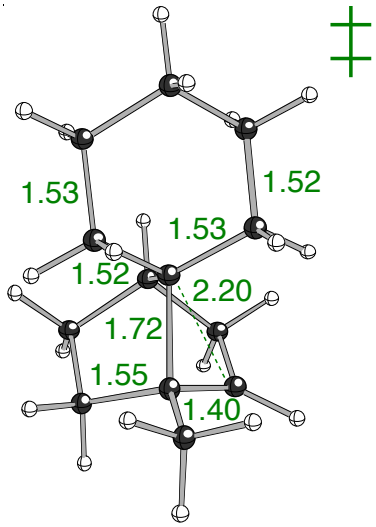
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-507.227461 hartrees (-318290.30405211 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.246042	0.622839	-1.094833
2	6	-1.868285	-0.456532	-0.481859
3	6	-2.275806	-0.301399	0.933574
4	6	-1.235392	0.500392	1.748032
5	6	-0.304808	1.198804	0.785950
6	6	-1.147708	1.895722	-0.285300
7	1	-3.212733	0.262178	0.895294
8	1	-1.114240	0.598257	-2.168300
9	1	-1.735310	1.224893	2.383364
10	1	-0.683735	-0.172205	2.399884
11	1	-2.099402	2.300243	0.051184
12	1	-0.613222	2.668158	-0.823307
13	1	-2.509176	-1.261682	1.383878
14	6	-2.120410	-1.719642	-1.190045
15	1	-3.203388	-1.835933	-1.273753
16	1	-1.696481	-1.739790	-2.187597
17	1	-1.770272	-2.570398	-0.608484
18	1	0.443547	1.796374	1.299327
19	6	0.251184	0.185234	-0.216082
20	6	0.615562	-1.207931	0.246539
21	1	-0.139499	-1.650241	0.892184
22	1	0.724475	-1.860034	-0.621005

23	6	1.319050	0.700830	-1.165157
24	1	1.386620	0.024690	-2.017522
25	1	1.071971	1.686054	-1.548973
26	6	1.944866	-1.142224	0.995483
27	1	2.183873	-2.135734	1.366732
28	1	1.837282	-0.499869	1.872174
29	6	2.667974	0.744265	-0.450715
30	1	3.414046	1.101988	-1.156698
31	1	2.631781	1.476561	0.356788
32	6	3.047482	-0.612859	0.102814
33	1	3.982597	-0.547730	0.653340
34	1	3.215262	-1.310776	-0.718908

TS



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -507.4977386 hartrees (-318459.905948886 kcal/mol)
Imaginary Frequencies: 1 (-314.8568 1/cm)
Zero-point correction = 0.320947 (Hartree/Particle)

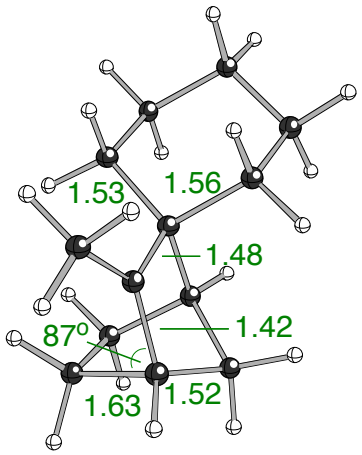
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-507.212660 hartrees (-318281.0162766 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.732009	0.961124	-0.831705
2	6	-1.472401	-0.398750	-0.605250
3	6	-2.032389	-0.847357	0.773499
4	6	-1.301869	-0.051043	1.856157
5	6	-0.416478	0.885885	1.055035

6	6	-1.314096	1.835032	0.271485
7	1	-3.107657	-0.695784	0.783806
8	1	-2.061207	1.352077	-1.790428
9	1	-1.983585	0.494487	2.501427
10	1	-0.708899	-0.698580	2.494993
11	1	-2.182045	2.224339	0.814098
12	1	-0.803697	2.712069	-0.124738
13	1	-1.865426	-1.917745	0.848865
14	6	-1.634137	-1.373748	-1.733416
15	1	-2.687790	-1.567536	-1.919900
16	1	-1.187337	-1.010400	-2.654776
17	1	-1.173273	-2.323926	-1.480584
18	1	0.344723	1.388813	1.641463
19	6	0.116373	0.012183	-0.098487
20	6	0.809876	-1.283234	0.278016
21	1	0.215568	-1.885962	0.956201
22	1	0.971875	-1.872673	-0.624256
23	6	0.978724	0.727797	-1.133135
24	1	1.083422	0.074937	-2.000879
25	1	0.528212	1.650567	-1.495534
26	6	2.164651	-0.966210	0.906505
27	1	2.627817	-1.900706	1.215061
28	1	2.020835	-0.378299	1.814718
29	6	2.360105	1.034677	-0.566859
30	1	2.954598	1.521633	-1.336178
31	1	2.267165	1.753784	0.248832
32	6	3.051014	-0.217918	-0.068047
33	1	3.999607	0.035500	0.398787
34	1	3.282912	-0.867234	-0.913761

C



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -507.5304577 hartrees (-318480.437511327 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.322645 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-507.244269 hartrees (-318300.85124019 kcal/mol)

Coordinates (from last standard orientation):

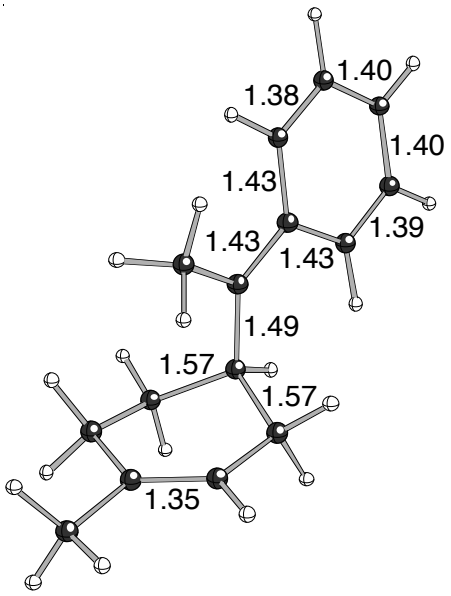
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.136414	0.226206	0.662928
2	6	-1.100932	0.984714	0.047072
3	6	-2.363808	-0.487221	-0.786564
4	6	-1.358210	-1.629818	-0.784529
5	6	-0.435483	-1.220017	0.359480
6	6	-1.461730	-0.892865	1.433777
7	1	-3.412958	-0.770832	-0.759297
8	1	-3.021136	0.730733	1.025968
9	1	-1.844036	-2.572557	-0.551599
10	1	-0.856332	-1.745558	-1.738645
11	1	-2.138602	-1.717559	1.634586
12	1	-1.050837	-0.548270	2.377035
13	1	-2.258459	0.177773	-1.644435
14	6	-1.243457	2.346787	-0.467183
15	1	-2.276809	2.670437	-0.517375
16	1	-0.731787	2.990031	0.255814
17	1	-0.740481	2.489862	-1.418797
18	1	0.314803	-1.953637	0.625275
19	6	0.133454	0.173318	-0.001081
20	6	0.924896	0.264204	-1.304118
21	1	0.312388	-0.046268	-2.149187
22	1	1.193166	1.307049	-1.478779
23	6	1.037295	0.747142	1.134566
24	1	1.277004	1.780123	0.879945
25	1	0.522204	0.764934	2.091605
26	6	2.198145	-0.557949	-1.221030
27	1	2.731672	-0.488180	-2.165799
28	1	1.952587	-1.612484	-1.085527
29	6	2.326504	-0.052238	1.234817
30	1	2.940630	0.394364	2.014106
31	1	2.109599	-1.068296	1.563106
32	6	3.077320	-0.072461	-0.083256
33	1	3.963385	-0.696198	0.003255
34	1	3.428524	0.935713	-0.310536

3.4. R_1=CH_3, R_2=Ph

Table 1: R_1/R_2=CH_3/Ph (Fig. S7)

B3LYP

A_b

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B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -582.8134759 hartrees (-365721.284262009 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.299795 (Hartree/Particle)

Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
     -582.555259 hartrees (-365559.25057509 kcal/mol)

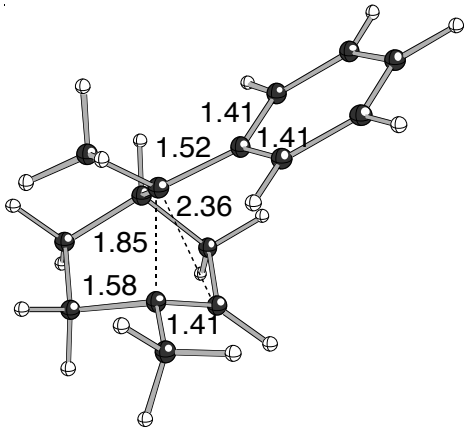
mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -582.675614 hartrees (-365634.77454114 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -582.4838655 hartrees (-365514.450439905 kcal/mol)


Coordinates (from last standard orientation):
 ---------------------------------------------------------------------
 Center     Atomic                   Coordinates (Angstroms)
 Number     Number                X           Y           Z
 ---------------------------------------------------------------------
    1          6               2.699003   -0.582604   -1.135062
    2          6               3.369388    0.051542   -0.153857
    3          6               2.781029    0.205825    1.226223
    4          6               1.542583   -0.655278    1.501208
```

5	6	0.557067	-0.860375	0.303294
6	6	1.365338	-1.254110	-0.986427
7	1	3.544279	-0.053272	1.972279
8	1	3.145236	-0.643072	-2.125968
9	1	1.872174	-1.667190	1.760276
10	1	0.995820	-0.280889	2.373005
11	1	1.499446	-2.343545	-0.928526
12	1	0.760121	-1.089980	-1.888398
13	1	2.583001	1.273116	1.406444
14	6	4.722607	0.671710	-0.375602
15	1	5.475224	0.196344	0.265527
16	1	5.049954	0.575166	-1.413564
17	1	4.717321	1.737574	-0.113791
18	1	-0.056324	-1.716086	0.577925
19	6	-0.338305	0.293602	0.003349
20	6	0.311586	1.596401	-0.284720
21	1	0.675385	2.032366	0.658349
22	1	1.217338	1.430798	-0.882938
23	1	-0.326033	2.323722	-0.781147
24	6	-1.763984	0.157289	-0.023077
25	6	-2.403542	-1.120945	0.006524
26	6	-2.604699	1.312766	-0.067009
27	6	-3.783809	-1.229847	-0.019961
28	1	-1.816806	-2.030317	0.012827
29	6	-3.984410	1.195318	-0.061735
30	1	-2.170569	2.304392	-0.066671
31	6	-4.578563	-0.074725	-0.046302
32	1	-4.248873	-2.209861	-0.018586
33	1	-4.603710	2.085869	-0.072545
34	1	-5.660719	-0.164541	-0.055584

TS



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -582.7721395 hartrees (-365695.345257645 kcal/mol)
Imaginary Frequencies: 1 (-337.1038 1/cm)
Zero-point correction = 0.298619 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =
-582.511968 hartrees (-365532.08503968 kcal/mol)

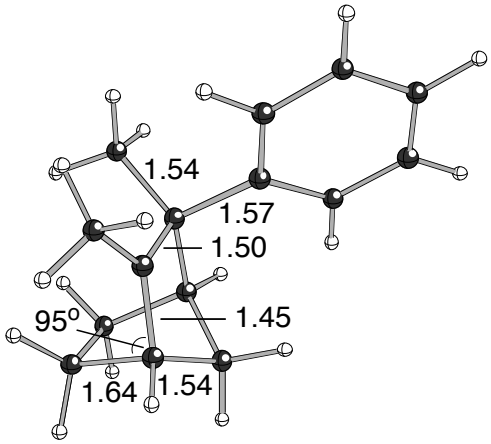
mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -582.6445024 hartrees (-365615.251701024 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -582.4593888 hartrees (-365499.091065888 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.194874	0.033967	-1.616664
2	6	1.565773	0.821351	-0.507077
3	6	2.913418	0.268239	0.112114
4	6	2.676046	-1.191210	0.556597
5	6	1.196380	-1.439477	0.217441
6	6	1.044723	-1.400984	-1.315219
7	1	3.702406	0.365754	-0.637684
8	1	0.904411	0.450970	-2.582984
9	1	3.322434	-1.895821	0.027230
10	1	2.869685	-1.323282	1.623400
11	1	1.724840	-2.035736	-1.903396
12	1	0.031778	-1.691263	-1.638922
13	1	3.175602	0.934223	0.937195
14	6	1.481843	2.331477	-0.591704
15	1	2.376012	2.728968	-1.084598
16	1	0.607791	2.670028	-1.152702
17	1	1.447225	2.774657	0.407687
18	1	0.795338	-2.346753	0.673240
19	6	0.445859	-0.135501	0.617955
20	6	0.662882	0.410747	2.025470
21	1	0.121400	-0.257889	2.707442
22	1	1.701860	0.447379	2.348761
23	1	0.217779	1.400926	2.144127
24	6	-1.031356	-0.072824	0.272573
25	6	-1.793417	-1.247229	0.138030
26	6	-1.697825	1.162516	0.183632
27	6	-3.170358	-1.187057	-0.098859
28	1	-1.330210	-2.222325	0.248933
29	6	-3.068356	1.222408	-0.067103
30	1	-1.150864	2.090416	0.314290
31	6	-3.811156	0.046253	-0.210820
32	1	-3.736719	-2.108488	-0.191066
33	1	-3.557644	2.188558	-0.141426
34	1	-4.879106	0.093619	-0.397709

C



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -582.799021 hartrees (-365712.21366771 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.300952 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-582.536773 hartrees (-365547.65042523 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -582.6735395 hartrees (-365633.472771645 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -582.4901788 hartrees (-365518.412098788 kcal/mol)

Coordinates (from last standard orientation):

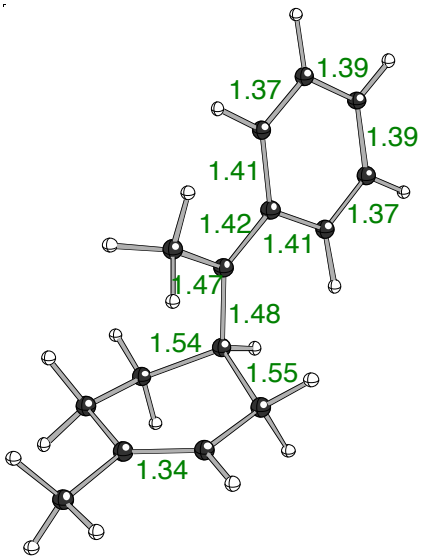
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.848992	0.004104	-1.324156
2	6	1.041958	0.889589	-0.505609
3	6	3.145760	0.016242	-0.322839
4	6	2.732676	-0.959512	0.803340
5	6	1.245605	-1.238840	0.479258
6	6	1.317905	-1.413926	-1.053755
7	1	3.962587	-0.342507	-0.955853
8	1	2.101092	0.330997	-2.332501
9	1	3.300510	-1.891084	0.738123
10	1	2.898636	-0.547982	1.799660
11	1	2.029396	-2.182931	-1.364091
12	1	0.362874	-1.593580	-1.548139
13	1	3.425053	1.013171	0.027900
14	6	0.975001	2.346555	-0.735051
15	1	1.889377	2.707338	-1.215910
16	1	0.168537	2.527033	-1.462287
17	1	0.760998	2.926496	0.163597
18	1	0.817125	-2.060436	1.052998

19	6	0.443752	0.106722	0.630578
20	6	0.541641	0.773438	2.018564
21	1	0.188223	0.065844	2.773839
22	1	1.565420	1.061245	2.270578
23	1	-0.086175	1.663306	2.085452
24	6	-1.066549	-0.046644	0.224561
25	6	-1.664799	-1.307344	0.053006
26	6	-1.882963	1.095353	0.125790
27	6	-3.033723	-1.417316	-0.197319
28	1	-1.086187	-2.217929	0.139456
29	6	-3.248586	0.983522	-0.135279
30	1	-1.474711	2.087383	0.284363
31	6	-3.829764	-0.275096	-0.302563
32	1	-3.475488	-2.402837	-0.306040
33	1	-3.856449	1.880524	-0.197881
34	1	-4.892247	-0.365141	-0.504420

Table 1: R_1/R_2=CH_3/Ph (Fig. S7)

mPWB1K

A_b



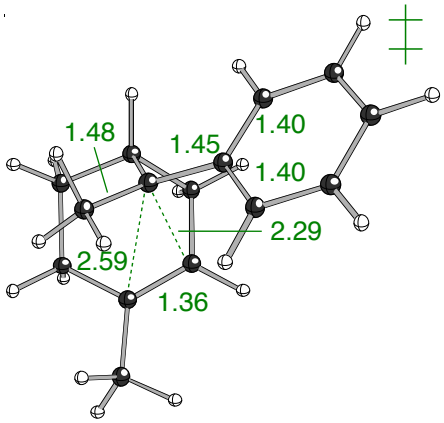
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -582.4879282 hartrees (-365516.999824782 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.308595 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-582.219861 hartrees (-365348.78497611 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.654494	-0.632401	-1.101699
2	6	3.323288	0.043866	-0.167998
3	6	2.746187	0.275114	1.189141
4	6	1.538946	-0.583247	1.507665
5	6	0.553118	-0.842851	0.351780
6	6	1.318532	-1.263100	-0.928236
7	1	3.511958	0.066763	1.937079
8	1	3.104107	-0.761369	-2.077041
9	1	1.889858	-1.572908	1.793238
10	1	1.002276	-0.193340	2.370185
11	1	1.426202	-2.347759	-0.875763
12	1	0.709007	-1.084501	-1.816757
13	1	2.539151	1.340726	1.309303
14	6	4.671192	0.627327	-0.419686
15	1	5.411055	0.178976	0.241796
16	1	4.993349	0.471307	-1.444101
17	1	4.677604	1.697800	-0.217129
18	1	-0.055168	-1.678841	0.669458
19	6	-0.331486	0.287992	0.014916
20	6	0.317240	1.567778	-0.296360
21	1	0.584191	2.051527	0.648242
22	1	1.264006	1.381976	-0.803918
23	1	-0.289556	2.249353	-0.875769
24	6	-1.742923	0.151922	-0.023046
25	6	-2.370291	-1.113609	0.024545
26	6	-2.567249	1.298004	-0.094350
27	6	-3.738124	-1.221788	-0.009333
28	1	-1.785615	-2.016704	0.046991
29	6	-3.934777	1.184224	-0.091614
30	1	-2.129808	2.281633	-0.109930
31	6	-4.521799	-0.075130	-0.057458
32	1	-4.202770	-2.194106	0.004700
33	1	-4.550586	2.068301	-0.120297
34	1	-5.597361	-0.163450	-0.069894

$TS_{A\text{-}B}$



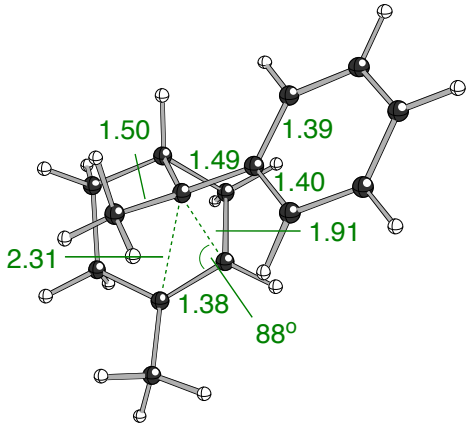
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -582.4793799 hartrees (-365511.635681049 kcal/mol)
Imaginary Frequencies: 1 (-69.9641 1/cm)
Zero-point correction = 0.307912 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-582.209753 hartrees (-365342.44210503 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.127372	0.162739	-1.347853
2	6	2.166615	0.710004	-0.673376
3	6	3.088655	-0.193906	0.078042
4	6	2.369950	-1.396920	0.724897
5	6	0.921640	-1.447386	0.285709
6	6	0.882427	-1.314470	-1.235333
7	1	3.826429	-0.554922	-0.640725
8	1	0.508069	0.780370	-1.982195
9	1	2.845650	-2.326419	0.426960
10	1	2.446758	-1.347883	1.808225
11	1	1.642249	-1.918222	-1.729192
12	1	-0.079681	-1.577807	-1.658806
13	1	3.656420	0.372894	0.813197
14	6	2.459560	2.161873	-0.681412
15	1	3.470201	2.338137	-1.048047
16	1	1.766121	2.722480	-1.299176
17	1	2.433537	2.558373	0.335050
18	1	0.440327	-2.339609	0.688115
19	6	0.166781	-0.198776	0.698476
20	6	0.643630	0.615948	1.834601
21	1	0.337646	0.054250	2.724952
22	1	1.718817	0.729267	1.884744
23	1	0.160374	1.582411	1.902687
24	6	-1.218782	-0.039647	0.312828
25	6	-1.991850	-1.156505	-0.033268
26	6	-1.835054	1.219807	0.342000
27	6	-3.333884	-1.018852	-0.317251
28	1	-1.553997	-2.141550	-0.032423
29	6	-3.166997	1.356526	0.024663
30	1	-1.256627	2.101424	0.567832
31	6	-3.921128	0.236230	-0.297110
32	1	-3.923842	-1.889820	-0.553205
33	1	-3.623269	2.333268	0.029301
34	1	-4.968780	0.343372	-0.530971

B



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -582.480169 hartrees (-365512.13084919 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.308801 (Hartree/Particle)

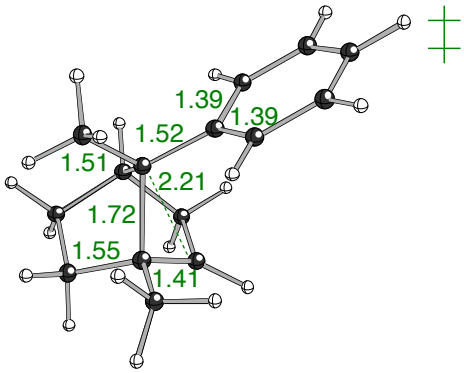
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-582.210155 hartrees (-365342.69436405 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.982238	0.179852	-1.207319
2	6	2.085872	0.735622	-0.595705
3	6	3.087309	-0.185085	-0.001889
4	6	2.424578	-1.408916	0.664414
5	6	0.971886	-1.474968	0.253795
6	6	0.890859	-1.323636	-1.264880
7	1	3.706978	-0.518267	-0.838511
8	1	0.324629	0.817767	-1.779502
9	1	2.927255	-2.322056	0.360959
10	1	2.519870	-1.340532	1.744666
11	1	1.691688	-1.804583	-1.821961
12	1	-0.063675	-1.631570	-1.674485
13	1	3.751140	0.345386	0.675203
14	6	2.296131	2.192429	-0.528554
15	1	3.208045	2.434629	-1.076913
16	1	1.476481	2.757014	-0.959429
17	1	2.471011	2.510615	0.498522
18	1	0.481597	-2.337334	0.697821
19	6	0.280708	-0.145297	0.544148
20	6	0.675019	0.645171	1.755265
21	1	0.192843	0.153881	2.601742
22	1	1.741258	0.669560	1.950623
23	1	0.296871	1.661418	1.729397
24	6	-1.172093	-0.037340	0.241054

25	6	-1.957181	-1.174695	0.071417
26	6	-1.782838	1.215021	0.175311
27	6	-3.319989	-1.060828	-0.140275
28	1	-1.519510	-2.158460	0.129540
29	6	-3.137987	1.326752	-0.054855
30	1	-1.194814	2.114668	0.282742
31	6	-3.912507	0.186658	-0.208196
32	1	-3.916738	-1.952176	-0.251254
33	1	-3.593237	2.302622	-0.111926
34	1	-4.973728	0.272973	-0.379613

TS



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -582.4655267 hartrees (-365502.942659517 kcal/mol)
Imaginary Frequencies: 1 (-315.1909 1/cm)
Zero-point correction = 0.307267 (Hartree/Particle)

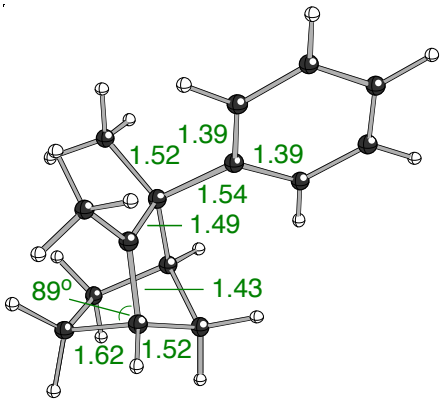
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-582.196283 hartrees (-365333.98954533 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.008800	-0.000438	-1.554269
2	6	1.495431	0.792124	-0.497895
3	6	2.872030	0.277822	0.004037
4	6	2.675973	-1.140375	0.535388
5	6	1.211859	-1.413846	0.249544
6	6	1.009677	-1.434371	-1.261095
7	1	3.588331	0.337521	-0.810381
8	1	0.545760	0.411596	-2.446038
9	1	3.319098	-1.862336	0.041637
10	1	2.886840	-1.201855	1.598431
11	1	1.778762	-1.950932	-1.845595
12	1	0.059182	-1.862104	-1.579787

13	1	3.206636	0.975180	0.766759
14	6	1.392418	2.286623	-0.597929
15	1	2.270176	2.680086	-1.105443
16	1	0.514136	2.610001	-1.147057
17	1	1.370242	2.735142	0.392188
18	1	0.826387	-2.289286	0.760380
19	6	0.492397	-0.094000	0.586523
20	6	0.714698	0.480677	1.966576
21	1	0.217244	-0.187334	2.669956
22	1	1.757629	0.562314	2.249711
23	1	0.242788	1.452978	2.067253
24	6	-0.989501	-0.069617	0.268452
25	6	-1.734529	-1.240516	0.185095
26	6	-1.655788	1.146908	0.153762
27	6	-3.100712	-1.196093	-0.040034
28	1	-1.261103	-2.202616	0.309881
29	6	-3.018048	1.192322	-0.078590
30	1	-1.117131	2.074293	0.272792
31	6	-3.745396	0.018727	-0.181328
32	1	-3.659225	-2.116952	-0.099613
33	1	-3.512863	2.146627	-0.167151
34	1	-4.808746	0.052009	-0.357344

C



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -582.4956414 hartrees (-365521.839934914 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.310241 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-582.223076 hartrees (-365350.80242076 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z

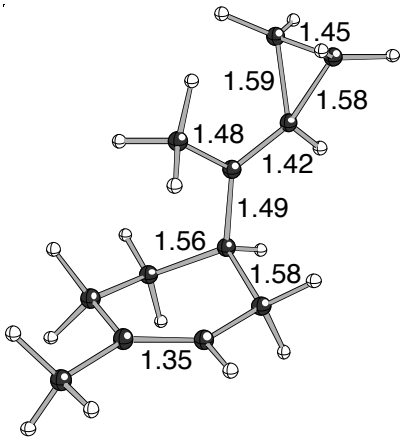
1	6	1.799818	-0.062824	-1.337818
2	6	1.038581	0.841114	-0.538884
3	6	3.022629	0.088975	-0.281127
4	6	2.690789	-0.934957	0.796572
5	6	1.226596	-1.233136	0.497239
6	6	1.297449	-1.453842	-1.010502
7	1	3.904941	-0.122799	-0.880189
8	1	2.072981	0.227850	-2.343222
9	1	3.281795	-1.836865	0.669522
10	1	2.872721	-0.563050	1.798345
11	1	2.009231	-2.224576	-1.290030
12	1	0.347742	-1.652555	-1.495110
13	1	3.161060	1.095790	0.112420
14	6	0.956406	2.280460	-0.798291
15	1	1.811134	2.628672	-1.370080
16	1	0.080533	2.426461	-1.435126
17	1	0.825045	2.872816	0.100902
18	1	0.805184	-2.032899	1.094522
19	6	0.449915	0.099480	0.614226
20	6	0.590718	0.813413	1.952094
21	1	0.286149	0.140222	2.748361
22	1	1.613259	1.130168	2.141613
23	1	-0.046705	1.689735	2.004532
24	6	-1.040201	-0.046243	0.237729
25	6	-1.636577	-1.290526	0.063786
26	6	-1.842669	1.089231	0.154443
27	6	-2.993340	-1.392711	-0.187718
28	1	-1.061026	-2.197032	0.144744
29	6	-3.195778	0.987357	-0.107381
30	1	-1.426240	2.070184	0.326250
31	6	-3.776111	-0.256616	-0.283935
32	1	-3.437568	-2.368567	-0.304285
33	1	-3.797150	1.881005	-0.161529
34	1	-4.832446	-0.339610	-0.484235

3.5. R_1=CH_3, R_2=cyclopropyl

Table 1: R_1/R_2=CH_3/cyclopropyl (Fig. S8)

B3LYP

A_b

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B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -468.4564796 hartrees (-293961.125513796 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.280919 (Hartree/Particle)

Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
     -468.214114 hartrees (-293809.03867614 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -468.3505403 hartrees (-293894.647543653 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -468.1850656 hartrees (-293790.810514656 kcal/mol)


Coordinates (from last standard orientation):
 ---------------------------------------------------------------------
 Center     Atomic                   Coordinates (Angstroms)
 Number     Number                X           Y           Z
 ---------------------------------------------------------------------
    1          6                1.818399   -0.358651    1.227409
    2          6                2.484023   -0.294084    0.059006
    3          6                2.016009    0.594412   -1.067201
    4          6                0.894105    1.579092   -0.703207
    5          6               -0.143687    1.084434    0.344273
    6          6                0.616545    0.466049    1.584052
    7          1                2.869572    1.175124   -1.441124
    8          1                2.172733   -1.035548    2.002411
    9          1                1.340510    2.471511   -0.251989
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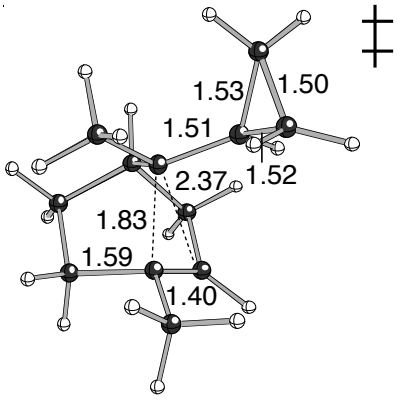
10	1	0.378225	1.923743	-1.605981
11	1	0.912596	1.330396	2.194045
12	1	-0.070479	-0.110655	2.216769
13	1	1.733577	-0.042131	-1.919613
14	6	3.714148	-1.118406	-0.211703
15	1	4.579773	-0.470760	-0.397339
16	1	3.955958	-1.776144	0.626581
17	1	3.587932	-1.736233	-1.109957
18	1	-0.684795	1.960822	0.711383
19	6	-1.160911	0.096738	-0.105173
20	6	-0.734469	-1.109241	-0.845428
21	1	-0.322001	-0.800137	-1.816545
22	1	0.114984	-1.571540	-0.320298
23	1	-1.519213	-1.845012	-1.016857
24	6	-2.515516	0.339158	0.234809
25	6	-3.677617	-0.146863	-0.729117
26	1	-4.451835	0.606120	-0.836696
27	6	-3.517697	-0.843655	0.534693
28	1	-2.729678	1.258728	0.767918
29	1	-3.359532	-0.621728	-1.650638
30	1	-3.088733	-1.839456	0.550539
31	1	-4.179584	-0.610995	1.362913

TS



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -468.4131756 hartrees (-293933.951820756 kcal/mol)
Imaginary Frequencies: 1 (-344.4630 1/cm)
Zero-point correction = 0.280426 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-468.168896 hartrees (-293780.66392896 kcal/mol)

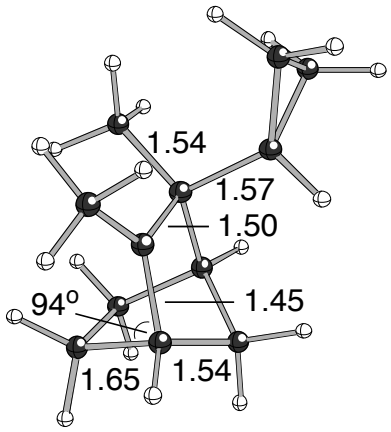
mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -468.3167218 hartrees (-293873.426096718 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -468.1571434 hartrees (-293773.289054934 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.011985	0.405783	-1.499419
2	6	0.886829	0.950588	-0.205865
3	6	2.097294	0.415074	0.678898
4	6	1.969736	-1.122886	0.784382
5	6	0.720899	-1.434980	-0.060608
6	6	1.061740	-1.073958	-1.519176
7	1	3.035452	0.737784	0.221482
8	1	0.955182	0.995974	-2.416511
9	1	2.851624	-1.637174	0.394698
10	1	1.846251	-1.446958	1.819763
11	1	2.037354	-1.440036	-1.878624
12	1	0.343706	-1.451521	-2.258916
13	1	2.022405	0.926081	1.641421
14	6	0.536555	2.412882	-0.027898
15	1	1.403000	3.047027	-0.245543
16	1	-0.284095	2.716913	-0.682371
17	1	0.242724	2.615346	1.005763
18	1	0.337369	-2.450559	0.062186
19	6	-0.311873	-0.323049	0.321728
20	6	-0.571687	-0.131422	1.809740
21	1	-0.989458	-1.069395	2.195668
22	1	0.317345	0.081753	2.399019
23	1	-1.298373	0.659022	2.004568
24	6	-1.582381	-0.304867	-0.495783
25	6	-2.925600	-0.766515	0.059544
26	1	-3.534682	-1.378265	-0.598305
27	6	-2.723662	0.678818	-0.279220
28	1	-1.450004	-0.567364	-1.541108
29	1	-2.996866	-1.037025	1.106796
30	1	-2.657738	1.386430	0.540735
31	1	-3.200197	1.079146	-1.168654

C



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -468.4428288 hartrees (-293952.559500288 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.282237 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-468.197235 hartrees (-293798.44693485 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -468.3485949 hartrees (-293893.426785699 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -468.1903876 hartrees (-293794.150122876 kcal/mol)

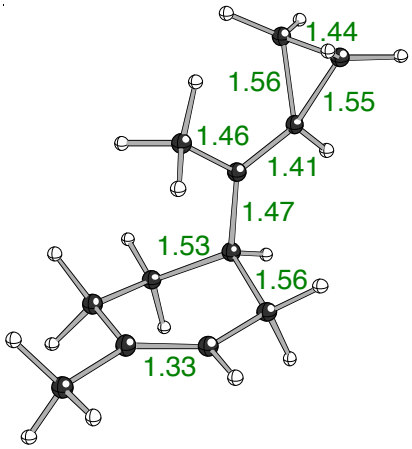
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.544781	0.606380	-0.972816
2	6	0.403322	1.013873	-0.182421
3	6	2.481193	0.273843	0.341872
4	6	1.989412	-1.123260	0.789333
5	6	0.723605	-1.322235	-0.078842
6	6	1.245522	-0.830658	-1.445150
7	1	3.496012	0.294165	-0.065879
8	1	2.004154	1.339167	-1.634665
9	1	2.729559	-1.890344	0.548464
10	1	1.801366	-1.176674	1.862381
11	1	2.152178	-1.348666	-1.766371
12	1	0.527151	-0.864387	-2.265348
13	1	2.435760	1.038564	1.122372
14	6	0.041554	2.406141	0.123053
15	1	0.828441	3.116986	-0.135605
16	1	-0.834096	2.633148	-0.509343
17	1	-0.290624	2.542413	1.155869
18	1	0.294458	-2.324746	-0.052395
19	6	-0.311507	-0.204369	0.315599
20	6	-0.678121	-0.156964	1.810857
21	1	-0.954568	-1.158005	2.150901
22	1	0.160753	0.178869	2.424623
23	1	-1.517152	0.512018	2.011405
24	6	-1.578487	-0.298765	-0.602248
25	6	-2.824444	-1.036817	-0.152394
26	1	-3.298252	-1.686869	-0.880846
27	6	-2.863605	0.457576	-0.360814
28	1	-1.341086	-0.440216	-1.650619
29	1	-2.883594	-1.396104	0.868975
30	1	-2.967555	1.070679	0.529334
31	1	-3.382262	0.851534	-1.229427

Table 1: R_1/R_2=CH_3/cyclopropyl (Fig. S8)

mPWB1K

A_b



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -468.1888106 hartrees (-293793.160539606 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.289130 (Hartree/Particle)

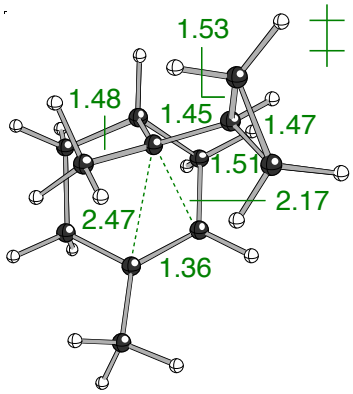
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-467.937892 hartrees (-293635.70660892 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.754619	-0.392976	1.210611
2	6	2.425335	-0.310809	0.062440
3	6	1.996405	0.610210	-1.031980
4	6	0.905645	1.595252	-0.645356
5	6	-0.138208	1.095366	0.357487
6	6	0.568139	0.427310	1.573186
7	1	2.863155	1.177976	-1.371250
8	1	2.094938	-1.084707	1.969170
9	1	1.368744	2.452355	-0.160753
10	1	0.410289	1.986161	-1.532084
11	1	0.861035	1.249208	2.227639
12	1	-0.137194	-0.165338	2.157671
13	1	1.716559	0.010812	-1.901245
14	6	3.632857	-1.140160	-0.212601
15	1	4.507326	-0.505577	-0.348073
16	1	3.839490	-1.832462	0.597102

17	1	3.515288	-1.711947	-1.132322
18	1	-0.678949	1.958273	0.737503
19	6	-1.140199	0.126693	-0.113614
20	6	-0.718970	-1.010241	-0.930071
21	1	-0.339841	-0.627024	-1.879442
22	1	0.143683	-1.481913	-0.451061
23	1	-1.493271	-1.741014	-1.127015
24	6	-2.477014	0.311218	0.280530
25	6	-3.601987	-0.130109	-0.709423
26	1	-4.398151	0.594884	-0.762379
27	6	-3.416667	-0.900866	0.491961
28	1	-2.698945	1.184680	0.871153
29	1	-3.268416	-0.523802	-1.655508
30	1	-2.957935	-1.874649	0.439200
31	1	-4.087528	-0.751241	1.322671

TS_{A-B}



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -468.178788 hartrees (-293786.87125788 kcal/mol)
Imaginary Frequencies: 1 (-88.4199 1/cm)
Zero-point correction = 0.288914 (Hartree/Particle)

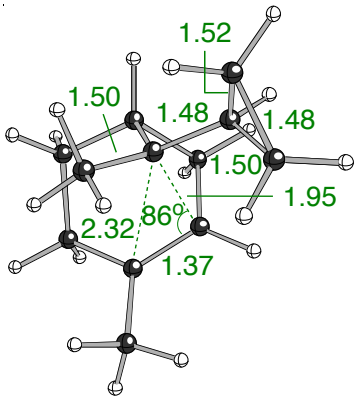
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-467.925938 hartrees (-293628.20535438 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.677643	0.311013	-1.309494
2	6	1.463599	0.855336	-0.342578
3	6	2.339386	-0.054942	0.452469
4	6	1.663439	-1.405105	0.772599
5	6	0.372492	-1.524217	-0.006401
6	6	0.665024	-1.184862	-1.465893

7	1	3.231465	-0.228931	-0.152022
8	1	0.116819	0.953288	-1.973247
9	1	2.314563	-2.230029	0.500304
10	1	1.481478	-1.494461	1.840395
11	1	1.610050	-1.593979	-1.818385
12	1	-0.108182	-1.510246	-2.151372
13	1	2.688128	0.443912	1.353649
14	6	1.526727	2.311691	-0.085951
15	1	2.545938	2.664868	-0.241092
16	1	0.864820	2.877438	-0.732780
17	1	1.287096	2.529402	0.955182
18	1	-0.112754	-2.484140	0.171768
19	6	-0.566769	-0.375816	0.323016
20	6	-0.512127	0.270307	1.657164
21	1	-0.943403	-0.451414	2.356658
22	1	0.492738	0.471352	2.005081
23	1	-1.101593	1.179364	1.714804
24	6	-1.825869	-0.317627	-0.397324
25	6	-3.130704	-0.186156	0.388169
26	1	-3.932573	-0.811966	0.031436
27	6	-2.675681	0.932945	-0.439831
28	1	-1.889814	-0.947620	-1.268621
29	1	-3.070130	-0.097627	1.460089
30	1	-2.287414	1.811863	0.051024
31	1	-3.170190	1.123529	-1.378546

B



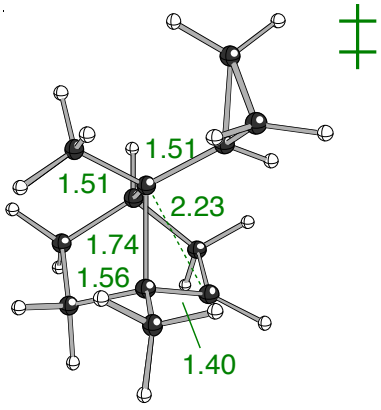
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -468.1789615 hartrees (-293786.980130865 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.289251 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-467.926814 hartrees (-293628.75505314 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.557631	0.235789	-1.263937
2	6	1.400460	0.855344	-0.374352
3	6	2.355094	0.002358	0.383622
4	6	1.721087	-1.340695	0.813071
5	6	0.417679	-1.527143	0.074219
6	6	0.669279	-1.258982	-1.409671
7	1	3.185782	-0.190715	-0.299378
8	1	-0.047466	0.837589	-1.926633
9	1	2.391132	-2.163799	0.585224
10	1	1.561911	-1.350683	1.887893
11	1	1.636896	-1.600185	-1.771073
12	1	-0.095696	-1.656721	-2.064469
13	1	2.775946	0.544677	1.225990
14	6	1.407025	2.317751	-0.179089
15	1	2.374748	2.703750	-0.503013
16	1	0.631606	2.820346	-0.746800
17	1	1.319911	2.572780	0.876057
18	1	-0.067007	-2.466690	0.331522
19	6	-0.484090	-0.315251	0.294657
20	6	-0.450437	0.395147	1.610350
21	1	-0.918834	-0.276566	2.331073
22	1	0.545905	0.602891	1.980570
23	1	-1.019924	1.319826	1.602381
24	6	-1.808096	-0.366162	-0.358559
25	6	-3.076927	-0.237179	0.457587
26	1	-3.874962	-0.908399	0.184659
27	6	-2.698401	0.839904	-0.476664
28	1	-1.874617	-1.062989	-1.178383
29	1	-2.996678	-0.046429	1.514678
30	1	-2.345879	1.770118	-0.057751
31	1	-3.244598	0.945907	-1.399951

TS



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -468.1626745 hartrees (-293776.759875495 kcal/mol)

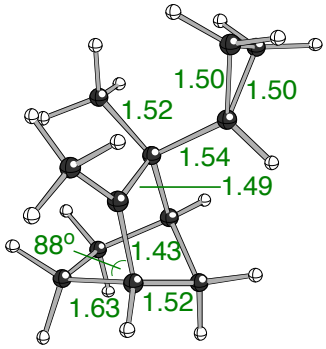
Imaginary Frequencies: 1 (-335.3411 1/cm)
Zero-point correction = 0.289072 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-467.908690 hartrees (-293617.3820619 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.851085	0.310992	-1.513067
2	6	0.816406	0.931525	-0.256632
3	6	2.073525	0.529979	0.567024
4	6	2.010304	-0.978492	0.816730
5	6	0.783691	-1.403504	0.029793
6	6	1.066536	-1.139816	-1.444510
7	1	2.963882	0.834063	0.024532
8	1	0.593899	0.818165	-2.438561
9	1	2.903952	-1.491744	0.475535
10	1	1.898021	-1.203809	1.872648
11	1	2.078866	-1.396025	-1.776090
12	1	0.402592	-1.651828	-2.138879
13	1	2.052580	1.116452	1.481219
14	6	0.370107	2.357684	-0.142564
15	1	1.171121	3.035004	-0.429146
16	1	-0.494868	2.559343	-0.767168
17	1	0.108317	2.586067	0.887442
18	1	0.438641	-2.410562	0.240494
19	6	-0.256280	-0.301562	0.325521
20	6	-0.503844	-0.011138	1.785127
21	1	-0.824546	-0.941886	2.252496
22	1	0.372888	0.331775	2.319355
23	1	-1.291695	0.721030	1.930147
24	6	-1.537441	-0.408003	-0.455945
25	6	-2.835748	-0.799474	0.183223
26	1	-3.469218	-1.470043	-0.374219
27	6	-2.653200	0.585832	-0.318488
28	1	-1.423600	-0.790559	-1.460465
29	1	-2.868923	-0.946242	1.250113
30	1	-2.556296	1.373827	0.412286
31	1	-3.166463	0.882829	-1.219003

C



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -468.1956713 hartrees (-293797.465697463 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.290445 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-467.940974 hartrees (-293637.64059474 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.507673	0.596176	-0.996633
2	6	0.396786	0.979630	-0.192172
3	6	2.336095	0.353512	0.386560
4	6	1.972035	-1.072357	0.783296
5	6	0.743241	-1.321763	-0.084967
6	6	1.264224	-0.837457	-1.432112
7	1	3.367436	0.515386	0.082868
8	1	1.973761	1.325746	-1.644458
9	1	2.766452	-1.763298	0.518346
10	1	1.789326	-1.173607	1.847195
11	1	2.183305	-1.334530	-1.726974
12	1	0.563804	-0.902214	-2.257534
13	1	2.139593	1.085295	1.170531
14	6	0.006926	2.350343	0.127162
15	1	0.784921	3.072798	-0.092876
16	1	-0.838404	2.563977	-0.535422
17	1	-0.357933	2.457735	1.144092
18	1	0.342735	-2.328637	-0.053119
19	6	-0.295356	-0.241468	0.296338
20	6	-0.651352	-0.192200	1.773381
21	1	-0.860913	-1.194981	2.133946
22	1	0.162464	0.210287	2.370747
23	1	-1.526421	0.422479	1.962705
24	6	-1.537478	-0.338838	-0.606381
25	6	-2.790440	-0.990886	-0.111346
26	1	-3.308578	-1.641769	-0.796490
27	6	-2.772892	0.472903	-0.380556

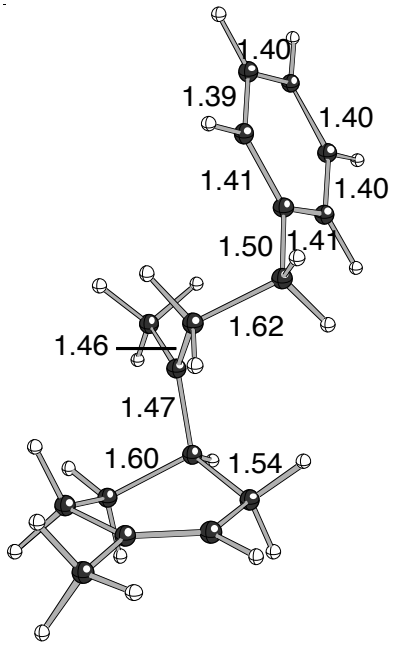
28	1	-1.311522	-0.532746	-1.642659
29	1	-2.834999	-1.303292	0.919415
30	1	-2.823012	1.129870	0.475122
31	1	-3.288792	0.845933	-1.250863

3.6. R_1=CH_3, R_2=$(CH_2)_2$–Ph

Table 1: R_1/R_2=CH_3/$(CH_2)_2$–Ph (aligned) (Fig. S9)

B3LYP

A_a



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.4348863 hartrees (-415057.005502113 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.355297 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-661.125172 hartrees (-414862.65668172 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.2807556 hartrees (-414960.286946556 kcal/mol)

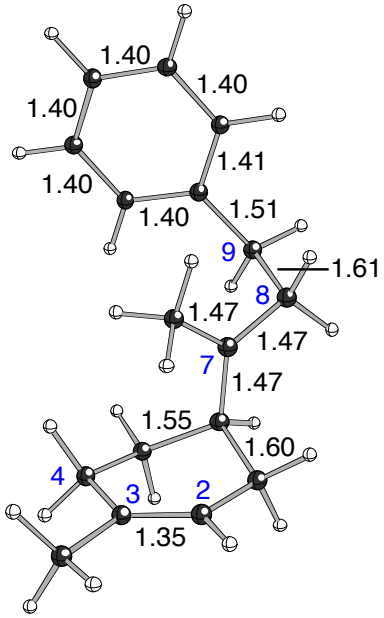
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.0583759 hartrees (-414820.741461009 kcal/mol)

Coordinates (from last standard orientation):

Center	Atomic	Coordinates (Angstroms)

Number	Number	X	Y	Z
1	6	3.186561	-0.513410	1.181035
2	6	3.760546	-0.595280	-0.029749
3	6	3.399667	0.372242	-1.137329
4	6	2.664139	1.620611	-0.647726
5	6	1.523941	1.292051	0.419317
6	6	2.149755	0.506452	1.589159
7	1	4.317300	0.700103	-1.642816
8	1	3.489136	-1.211597	1.959082
9	1	3.353350	2.273014	-0.101829
10	1	2.258752	2.201459	-1.480475
11	1	2.605944	1.243880	2.264302
12	1	1.368041	0.025813	2.189312
13	1	2.821666	-0.152957	-1.913503
14	6	4.792476	-1.637996	-0.369781
15	1	5.750745	-1.169132	-0.625584
16	1	4.962404	-2.326899	0.461314
17	1	4.488035	-2.226216	-1.245152
18	1	1.174084	2.277352	0.756657
19	6	0.412184	0.675480	-0.325584
20	6	-0.484376	1.546577	-1.098532
21	1	-1.476120	1.477242	-0.602327
22	1	-0.175633	2.591981	-1.128958
23	1	-0.667581	1.157471	-2.106431
24	6	0.122613	-0.756694	-0.286981
25	1	-0.253802	-1.117907	-1.246890
26	1	0.994174	-1.332193	0.026517
27	6	-1.046589	-1.049339	0.797589
28	1	-0.986903	-2.135802	0.912720
29	1	-0.766940	-0.606901	1.755994
30	6	-2.431259	-0.633089	0.394228
31	6	-3.091628	0.410746	1.067691
32	6	-3.111020	-1.306967	-0.636859
33	6	-4.398864	0.768835	0.724378
34	1	-2.593214	0.924784	1.886688
35	6	-4.411678	-0.946425	-0.983535
36	1	-2.628530	-2.131208	-1.157555
37	6	-5.058649	0.093858	-0.304035
38	1	-4.899487	1.566379	1.264320
39	1	-4.928040	-1.482463	-1.773727
40	1	-6.074296	0.367888	-0.571379

A_b



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.4353689 hartrees (-415057.308338439 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.355432 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-661.125736 hartrees (-414863.01059736 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.2810824 hartrees (-414960.492016824 kcal/mol)

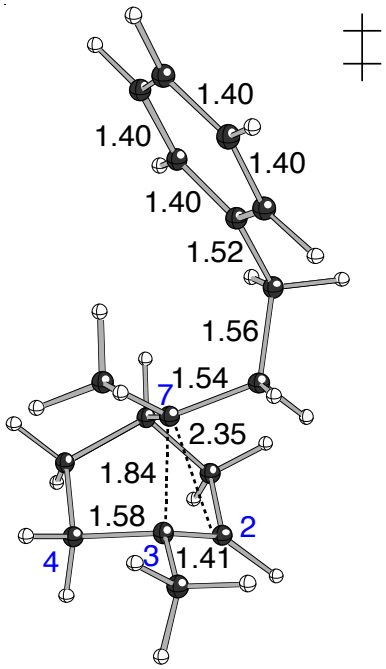
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.058461 hartrees (-414820.79486211 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.558201	0.404177	-0.782222
2	6	-3.572009	-0.838116	-0.259379
3	6	-2.692791	-1.211326	0.907819
4	6	-1.995258	-0.031827	1.600815
5	6	-1.549849	1.140624	0.687986
6	6	-2.767785	1.560431	-0.252421
7	1	-3.296827	-1.741123	1.655904
8	1	-4.172580	0.618509	-1.654521
9	1	-2.690958	0.418091	2.317332
10	1	-1.141355	-0.385019	2.188166
11	1	-3.386329	2.204980	0.386306
12	1	-2.436355	2.205760	-1.076648

13	1	-1.965266	-1.963431	0.567967
14	6	-4.436175	-1.934799	-0.820514
15	1	-5.166054	-2.267560	-0.072259
16	1	-4.983324	-1.609713	-1.708452
17	1	-3.837630	-2.815226	-1.086014
18	1	-1.332011	2.006295	1.320630
19	6	-0.422629	0.963937	-0.240726
20	6	-0.291340	-0.246103	-1.056774
21	1	-0.085787	-1.101107	-0.391672
22	1	-1.270139	-0.482222	-1.509907
23	1	0.492717	-0.185472	-1.809766
24	6	0.583526	2.026064	-0.349953
25	1	1.006125	2.084143	-1.355809
26	1	0.173738	2.995339	-0.052420
27	6	1.791497	1.715568	0.663784
28	1	2.379844	2.638393	0.635714
29	1	1.385750	1.623384	1.675265
30	6	2.647961	0.527254	0.312708
31	6	2.606100	-0.641167	1.088867
32	6	3.526935	0.579571	-0.781795
33	6	3.419905	-1.734573	0.778593
34	1	1.957771	-0.687389	1.961546
35	6	4.335787	-0.512913	-1.096981
36	1	3.595527	1.484947	-1.381160
37	6	4.282462	-1.673936	-0.318283
38	1	3.388229	-2.624847	1.399216
39	1	5.017146	-0.454194	-1.940096
40	1	4.918951	-2.519735	-0.558470

TS



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.4049768 hartrees (-415038.236991768 kcal/mol)
Imaginary Frequencies: 1 (-316.7231 1/cm)
Zero-point correction = 0.356008 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-661.091867 hartrees (-414841.75746117 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.2594694 hartrees (-414946.929643194 kcal/mol)

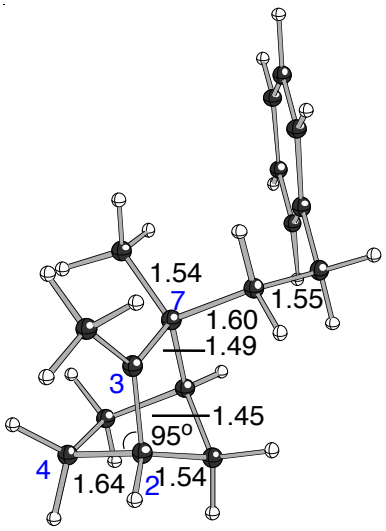
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.0425088 hartrees (-414810.784697088 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.080868	0.323063	1.030492
2	6	-2.647676	0.808440	-0.218418
3	6	-3.151838	-0.142439	-1.377385
4	6	-2.570448	-1.554640	-1.127724
5	6	-1.724006	-1.378263	0.146758
6	6	-2.693021	-1.080579	1.305855
7	1	-4.244276	-0.124270	-1.390566
8	1	-3.532635	0.955595	1.797495
9	1	-3.353469	-2.302615	-0.979207
10	1	-1.964980	-1.894669	-1.970412
11	1	-3.570096	-1.743522	1.374792
12	1	-2.226089	-1.134417	2.298761
13	1	-2.812826	0.302008	-2.315785
14	6	-2.704735	2.292820	-0.512455
15	1	-3.726762	2.594571	-0.766371
16	1	-2.374704	2.894427	0.338880
17	1	-2.074950	2.539482	-1.371523
18	1	-1.048252	-2.213157	0.344499
19	6	-1.006230	-0.003628	-0.025382
20	6	-0.233013	0.226324	-1.308394
21	1	0.683243	-0.376585	-1.245999
22	1	-0.752807	-0.062089	-2.220034
23	1	0.093385	1.265327	-1.397107
24	6	-0.220168	0.539677	1.183418
25	1	0.077710	1.571010	0.966429
26	1	-0.851257	0.595664	2.074820
27	6	1.042062	-0.280564	1.585310
28	1	1.292158	0.048655	2.601975
29	1	0.778154	-1.340645	1.673263
30	6	2.278564	-0.136659	0.719204
31	6	2.841370	-1.250831	0.079237
32	6	2.911904	1.108263	0.575254
33	6	3.996244	-1.124637	-0.699823
34	1	2.384449	-2.230395	0.202216

35	6	4.062326	1.238784	-0.203983
36	1	2.514900	1.982227	1.087205
37	6	4.606608	0.121954	-0.847543
38	1	4.419958	-2.000469	-1.181838
39	1	4.541623	2.208444	-0.299800
40	1	5.505081	0.222919	-1.448227

C



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.4359368 hartrees (-415057.664701368 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.357949 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-661.121348 hartrees (-414860.25708348 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.2927629 hartrees (-414967.821647379 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.0781796 hartrees (-414833.168480796 kcal/mol)

Coordinates (from last standard orientation):

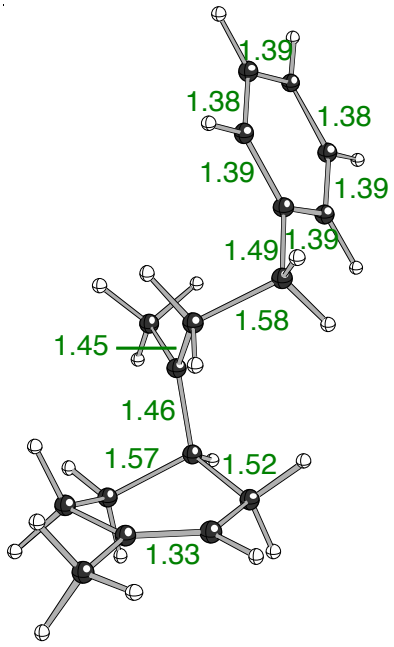
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.265448	0.009534	0.499179
2	6	-2.325873	0.918068	-0.126456
3	6	-3.475733	-0.904814	-0.848799
4	6	-2.213195	-1.797576	-0.872626
5	6	-1.345119	-1.183929	0.253364

6	6	-2.410501	-0.956558	1.344085
7	1	-4.409071	-1.439799	-0.651195
8	1	-4.202948	0.416679	0.875748
9	1	-2.464879	-2.831499	-0.622747
10	1	-1.723772	-1.807441	-1.847457
11	1	-2.959299	-1.863957	1.606880
12	1	-2.042032	-0.497503	2.263718
13	1	-3.629380	-0.318709	-1.759194
14	6	-2.676071	2.234625	-0.685910
15	1	-3.754261	2.384817	-0.767270
16	1	-2.294628	2.989181	0.022687
17	1	-2.177714	2.434815	-1.638666
18	1	-0.480548	-1.784958	0.529859
19	6	-0.977290	0.285077	-0.161414
20	6	-0.220226	0.446910	-1.494345
21	1	0.689113	-0.155036	-1.482883
22	1	-0.827111	0.131430	-2.347088
23	1	0.079351	1.484904	-1.658745
24	6	-0.222000	1.071005	1.014595
25	1	0.101631	2.023508	0.583676
26	1	-0.918806	1.322718	1.822444
27	6	0.983797	0.347023	1.665252
28	1	1.282383	0.996334	2.499019
29	1	0.655095	-0.590810	2.123147
30	6	2.184583	0.097459	0.776658
31	6	2.583951	-1.206619	0.451652
32	6	2.941861	1.172408	0.283714
33	6	3.696674	-1.434250	-0.363960
34	1	2.034634	-2.055468	0.852657
35	6	4.052101	0.949987	-0.532327
36	1	2.673741	2.192243	0.551612
37	6	4.429475	-0.355553	-0.863743
38	1	3.995127	-2.451651	-0.598118
39	1	4.630584	1.792711	-0.898712
40	1	5.296858	-0.529285	-1.492870

Table 1: R_1/R_2=$CH_3/(CH_2)_2$–Ph (aligned) (Fig. S9)

mPWB1K

A_a



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -661.0638879 hartrees (-414824.200296129 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.365225 (Hartree/Particle)

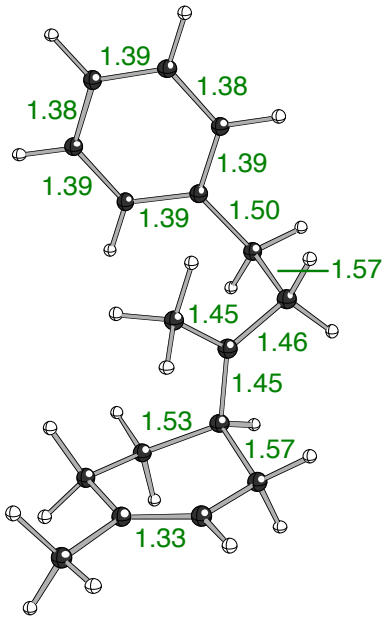
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-660.742514 hartrees (-414622.53496014 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.143032	-0.367646	1.200102
2	6	3.649903	-0.565523	-0.013763
3	6	3.207187	0.265242	-1.178813
4	6	2.540595	1.554457	-0.757111
5	6	1.454828	1.334565	0.355449
6	6	2.099772	0.645566	1.549720
7	1	4.072232	0.512046	-1.793632
8	1	3.505538	-0.966741	2.024268
9	1	3.269718	2.211092	-0.286392
10	1	2.123372	2.089348	-1.606154
11	1	2.544035	1.422865	2.172731
12	1	1.338198	0.184985	2.178329
13	1	2.555667	-0.327403	-1.828705
14	6	4.681538	-1.603203	-0.297223
15	1	5.604734	-1.142463	-0.645665
16	1	4.908886	-2.195789	0.582963
17	1	4.350274	-2.277243	-1.086646

18	1	1.102579	2.333404	0.615473
19	6	0.373421	0.650207	-0.340752
20	6	-0.548889	1.441173	-1.135390
21	1	-1.478543	1.446390	-0.537049
22	1	-0.234133	2.467500	-1.285264
23	1	-0.832509	0.955805	-2.065155
24	6	0.164180	-0.781954	-0.234499
25	1	-0.195907	-1.202376	-1.169172
26	1	1.069002	-1.283471	0.095598
27	6	-0.955228	-1.039989	0.853644
28	1	-0.893816	-2.112359	1.024160
29	1	-0.683674	-0.556553	1.787363
30	6	-2.333768	-0.647045	0.441560
31	6	-3.012491	0.358408	1.121562
32	6	-2.964650	-1.280730	-0.624384
33	6	-4.295070	0.725644	0.744882
34	1	-2.544892	0.843500	1.967421
35	6	-4.241590	-0.913083	-1.003648
36	1	-2.462498	-2.079997	-1.152335
37	6	-4.908550	0.093948	-0.321218
38	1	-4.813126	1.499681	1.288893
39	1	-4.723528	-1.418425	-1.825828
40	1	-5.906937	0.375975	-0.615905

A_b



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -661.0640218 hartrees (-414824.284319718 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.366021 (Hartree/Particle)

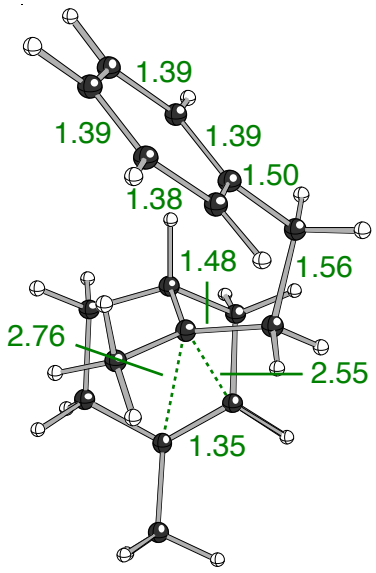
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =

-660.742109 hartrees (-414622.28081859 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.433082	0.406408	-0.772292
2	6	-3.453337	-0.824420	-0.258956
3	6	-2.584461	-1.208721	0.891525
4	6	-1.913362	-0.043084	1.594220
5	6	-1.468117	1.118707	0.711525
6	6	-2.625841	1.543368	-0.261824
7	1	-3.185785	-1.749640	1.622076
8	1	-4.058152	0.629293	-1.626211
9	1	-2.618849	0.390442	2.300180
10	1	-1.068837	-0.389853	2.187177
11	1	-3.238391	2.233731	0.319012
12	1	-2.251574	2.138403	-1.098515
13	1	-1.855720	-1.944791	0.544677
14	6	-4.324606	-1.899814	-0.810790
15	1	-5.051012	-2.217597	-0.064308
16	1	-4.865219	-1.570633	-1.691968
17	1	-3.740253	-2.780638	-1.073634
18	1	-1.249652	1.980098	1.338701
19	6	-0.370441	0.953462	-0.226816
20	6	-0.213029	-0.265916	-0.993823
21	1	-0.008517	-1.083949	-0.295539
22	1	-1.183891	-0.516720	-1.440480
23	1	0.571437	-0.216605	-1.737237
24	6	0.580839	2.044748	-0.386283
25	1	0.995460	2.077981	-1.389511
26	1	0.136494	3.000831	-0.122384
27	6	1.751430	1.767363	0.623253
28	1	2.365807	2.663937	0.573138
29	1	1.352243	1.713401	1.633712
30	6	2.561403	0.550801	0.304964
31	6	2.541310	-0.556392	1.141470
32	6	3.345105	0.513127	-0.842719
33	6	3.289401	-1.683308	0.838240
34	1	1.957820	-0.530565	2.052182
35	6	4.087484	-0.612014	-1.150701
36	1	3.392715	1.376138	-1.493096
37	6	4.059414	-1.714182	-0.310849
38	1	3.277717	-2.530733	1.505806
39	1	4.699438	-0.625097	-2.038996
40	1	4.646058	-2.588239	-0.545644

TS_{A-B}



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -661.0585573 hartrees (-414820.855291323 kcal/mol)
Imaginary Frequencies: 1 (-69.4041 1/cm)
Zero-point correction = 0.365334 (Hartree/Particle)

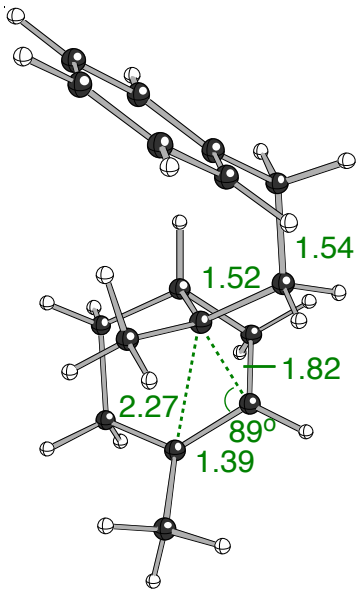
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-660.735671 hartrees (-414618.24090921 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.950345	-0.790431	-0.632721
2	6	-3.315239	0.014410	0.383736
3	6	-2.956623	1.466530	0.393496
4	6	-1.767015	1.820809	-0.507507
5	6	-1.052577	0.562649	-0.968826
6	6	-2.039191	-0.312227	-1.725065
7	1	-3.839686	2.021726	0.075865
8	1	-3.333944	-1.801205	-0.665764
9	1	-2.100612	2.346788	-1.397337
10	1	-1.085533	2.496890	0.002779
11	1	-2.561155	0.246221	-2.500627
12	1	-1.548623	-1.145206	-2.221336
13	1	-2.789594	1.782029	1.423193
14	6	-4.178503	-0.463340	1.497027
15	1	-5.097863	0.119086	1.538383
16	1	-4.442337	-1.510129	1.389658
17	1	-3.682085	-0.324821	2.457085
18	1	-0.165367	0.830076	-1.552690
19	6	-0.584350	-0.292429	0.164822

20	6	-0.267270	0.274496	1.463436
21	1	0.816961	0.472347	1.361097
22	1	-0.755092	1.207748	1.703807
23	1	-0.348526	-0.451692	2.266356
24	6	-0.058579	-1.650219	-0.089483
25	1	0.172473	-2.138203	0.852273
26	1	-0.778100	-2.261903	-0.622705
27	6	1.223901	-1.576290	-0.967728
28	1	1.572757	-2.603489	-1.051077
29	1	0.945415	-1.251637	-1.968277
30	6	2.303349	-0.694438	-0.421288
31	6	2.627245	0.493562	-1.063454
32	6	2.983310	-1.031312	0.745318
33	6	3.601844	1.334993	-0.551623
34	1	2.138739	0.750618	-1.993364
35	6	3.957113	-0.192278	1.258991
36	1	2.764606	-1.964436	1.246486
37	6	4.264886	0.995617	0.613864
38	1	3.851377	2.247001	-1.070888
39	1	4.485200	-0.472366	2.157099
40	1	5.029256	1.643955	1.012023

B



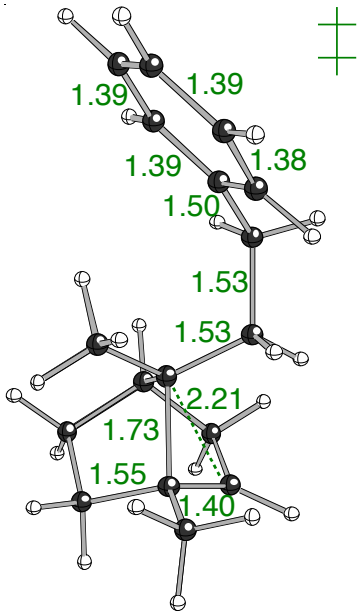
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -661.0647067 hartrees (-414824.714101317 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.367766 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-660.739703 hartrees (-414620.77102953 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.574405	-0.087479	-1.013184
2	6	2.955946	0.823720	-0.040844
3	6	3.205790	0.309670	1.324359
4	6	2.212945	-0.810828	1.708943
5	6	1.510173	-1.295758	0.463314
6	6	2.559346	-1.546667	-0.619388
7	1	4.218161	-0.103492	1.289194
8	1	2.568526	0.240176	-2.044021
9	1	2.743246	-1.632824	2.179849
10	1	1.497338	-0.433262	2.434041
11	1	3.512468	-1.939495	-0.273601
12	1	2.199972	-2.170101	-1.428792
13	1	3.227242	1.116652	2.051028
14	6	3.102761	2.257631	-0.329533
15	1	4.145594	2.529427	-0.154051
16	1	2.844846	2.513615	-1.350781
17	1	2.517081	2.853677	0.369107
18	1	0.813810	-2.099864	0.684117
19	6	0.900720	-0.112989	-0.291177
20	6	0.309892	1.038315	0.471170
21	1	-0.657301	0.709838	0.848991
22	1	0.895909	1.367618	1.323062
23	1	0.120156	1.887866	-0.179682
24	6	0.077615	-0.456394	-1.527215
25	1	-0.187654	0.471715	-2.030535
26	1	0.662343	-1.039722	-2.231473
27	6	-1.195616	-1.264703	-1.233274
28	1	-1.567364	-1.582940	-2.206974
29	1	-0.936638	-2.178936	-0.702564
30	6	-2.292226	-0.546257	-0.505449
31	6	-2.739515	-0.990820	0.730926
32	6	-2.889766	0.576215	-1.067183
33	6	-3.753625	-0.323155	1.399995
34	1	-2.301227	-1.875317	1.172068
35	6	-3.899914	1.246423	-0.402026
36	1	-2.573652	0.923197	-2.041571
37	6	-4.332709	0.799691	0.836855
38	1	-4.094610	-0.686259	2.357082
39	1	-4.359855	2.110970	-0.854965
40	1	-5.125716	1.317775	1.352730

TS



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -661.0495327 hartrees (-414815.192264577 kcal/mol)
Imaginary Frequencies: 1 (-309.3334 1/cm)
Zero-point correction = 0.365976 (Hartree/Particle)

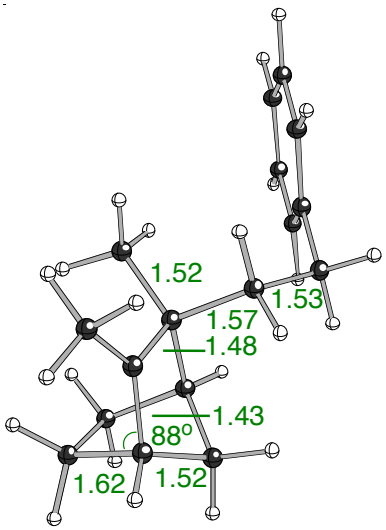
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-660.725464 hartrees (-414611.83591464 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.903467	0.458203	1.059798
2	6	-2.418251	0.933625	-0.166150
3	6	-3.099422	0.206352	-1.354420
4	6	-2.740057	-1.278691	-1.265073
5	6	-1.952739	-1.365224	0.029911
6	6	-2.892313	-1.006850	1.175815
7	1	-4.169347	0.387744	-1.310094
8	1	-3.114269	1.106233	1.905719
9	1	-3.618607	-1.916211	-1.242903
10	1	-2.139508	-1.595182	-2.111953
11	1	-3.905201	-1.413660	1.089748
12	1	-2.540962	-1.303032	2.162513
13	1	-2.741078	0.676948	-2.265317
14	6	-2.153968	2.398164	-0.343022
15	1	-3.079584	2.931266	-0.546459
16	1	-1.693100	2.839302	0.536466
17	1	-1.494645	2.558910	-1.191546
18	1	-1.426382	-2.304307	0.167205

19	6	-1.049439	-0.115254	0.006472
20	6	-0.204129	0.080932	-1.225508
21	1	0.476817	-0.768154	-1.290683
22	1	-0.767999	0.123442	-2.149550
23	1	0.417173	0.967738	-1.142517
24	6	-0.227536	0.156148	1.263723
25	1	0.094475	1.197131	1.238296
26	1	-0.837898	0.056831	2.160695
27	6	0.996780	-0.748243	1.434418
28	1	1.244956	-0.747993	2.495529
29	1	0.732572	-1.778443	1.195112
30	6	2.223206	-0.354793	0.658304
31	6	2.855702	-1.270009	-0.171197
32	6	2.764980	0.919414	0.777270
33	6	3.991370	-0.919325	-0.882356
34	1	2.461376	-2.273345	-0.258143
35	6	3.898664	1.274712	0.067804
36	1	2.312172	1.641184	1.443397
37	6	4.512500	0.357292	-0.769305
38	1	4.470456	-1.645378	-1.520568
39	1	4.309761	2.266430	0.176406
40	1	5.397537	0.633819	-1.320254

C



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -661.0851288 hartrees (-414837.529173288 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.368049 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-660.759091 hartrees (-414632.93719341 kcal/mol)

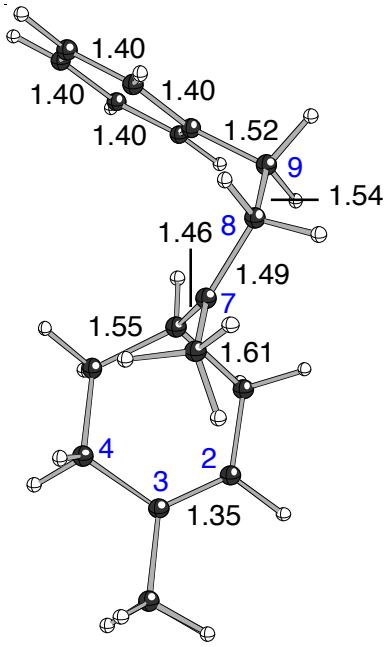
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.154423	-0.093732	0.486123
2	6	-2.274918	0.850408	-0.121734
3	6	-3.214149	-0.868316	-0.940427
4	6	-1.986235	-1.770282	-0.911199
5	6	-1.190459	-1.169964	0.241862
6	6	-2.280946	-1.036455	1.295168
7	1	-4.176504	-1.373319	-0.915037
8	1	-4.125649	0.232783	0.831801
9	1	-2.264435	-2.793942	-0.678753
10	1	-1.452956	-1.779766	-1.855079
11	1	-2.781292	-1.975711	1.510122
12	1	-1.958398	-0.593445	2.233278
13	1	-3.245883	-0.211749	-1.810638
14	6	-2.658104	2.149016	-0.672575
15	1	-3.731850	2.278920	-0.742929
16	1	-2.279066	2.892861	0.035567
17	1	-2.172236	2.354607	-1.622279
18	1	-0.304295	-1.727306	0.518210
19	6	-0.901345	0.299963	-0.127211
20	6	-0.147745	0.513969	-1.431882
21	1	0.736954	-0.113355	-1.465387
22	1	-0.767790	0.270587	-2.292565
23	1	0.181470	1.544387	-1.533578
24	6	-0.261297	1.092340	1.065993
25	1	0.055440	2.054191	0.665574
26	1	-1.007952	1.313865	1.830983
27	6	0.913801	0.396572	1.747925
28	1	1.226408	1.048637	2.563355
29	1	0.577357	-0.528367	2.213000
30	6	2.075302	0.125586	0.838991
31	6	2.468626	-1.171099	0.541462
32	6	2.766573	1.181969	0.256241
33	6	3.510872	-1.411675	-0.340428
34	1	1.969429	-2.005503	1.014664
35	6	3.806981	0.947354	-0.623530
36	1	2.495990	2.200457	0.500023
37	6	4.176050	-0.352825	-0.932134
38	1	3.807398	-2.426247	-0.556887
39	1	4.337420	1.777944	-1.062718
40	1	4.988940	-0.537501	-1.616599

Table 2: R_1/R_2=$CH_3/(CH_2)_2$–Ph (extended) (Fig. S10)

<u>B3LYP</u>

A_b



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.4314957 hartrees (-415054.877866707 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.354877 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-661.122450 hartrees (-414860.9485995 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.277923 hartrees (-414958.50946173 kcal/mol)

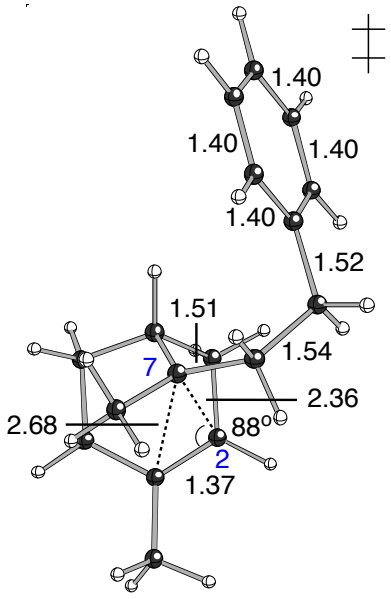
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.0557112 hartrees (-414819.069335112 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.719299	-0.098306	0.286439
2	6	-1.599332	1.661196	-1.328950
3	1	-1.435887	2.679625	-1.682967
4	1	-2.588276	1.566790	-0.845623
5	1	-1.654984	0.975128	-2.187318
6	6	-0.569993	1.186440	-0.392749
7	6	0.557876	2.110950	-0.109278
8	6	1.692964	1.708631	0.845455
9	1	0.955857	2.380285	-1.103090
10	1	0.096280	3.062453	0.209979
11	1	1.283644	1.484202	1.836700

12	1	2.310933	2.604906	0.981539
13	6	-1.741594	0.230467	1.480797
14	6	-1.240509	-1.337702	-0.489384
15	6	-3.183749	0.070023	1.118309
16	6	-2.722714	-1.332421	-0.890186
17	6	-3.653940	-0.660915	0.087154
18	1	-0.604924	-1.507923	-1.364183
19	1	-1.058870	-2.182006	0.183884
20	1	-3.043208	-2.373094	-1.030808
21	1	-3.888323	0.587046	1.766877
22	1	-1.561793	1.222876	1.913531
23	1	-1.442143	-0.483828	2.258908
24	6	-5.126805	-0.819810	-0.175156
25	1	-5.731893	-0.246287	0.530810
26	1	-5.417476	-1.874515	-0.095884
27	1	-5.385134	-0.500304	-1.192442
28	1	0.230665	-0.362958	0.748791
29	1	-2.870559	-0.872021	-1.878572
30	6	2.569178	0.555344	0.379356
31	6	2.901900	-0.476716	1.269152
32	6	3.101918	0.516346	-0.918617
33	6	3.736978	-1.525362	0.873334
34	1	2.520106	-0.453710	2.287659
35	6	3.936108	-0.531394	-1.317803
36	1	2.892262	1.316023	-1.625439
37	6	4.253497	-1.557531	-0.423934
38	1	3.987220	-2.310657	1.580126
39	1	4.346392	-0.538875	-2.323066
40	1	4.905226	-2.368575	-0.733041

TS_{A-B}



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

HF = -661.4157206 hartrees (-415044.978833706 kcal/mol)
Imaginary Frequencies: 1 (-68.3745 1/cm)
Zero-point correction = 0.355915 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-661.102964 hartrees (-414848.72093964 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.2656424 hartrees (-414950.803262424 kcal/mol)

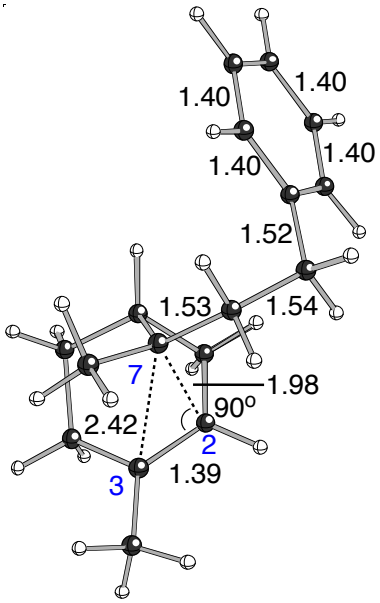
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.0477503 hartrees (-414814.073790753 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.655353	-0.713184	0.527977
2	6	1.686068	1.485872	1.501289
3	1	1.942327	2.511559	1.226638
4	1	2.569810	0.959839	1.855564
5	1	0.994678	1.543239	2.360862
6	6	0.914783	0.785044	0.432023
7	6	0.075495	1.747560	-0.371944
8	6	-1.104223	1.338353	-1.275121
9	1	-0.309100	2.432521	0.401996
10	1	0.768882	2.390393	-0.931996
11	1	-0.754093	0.803871	-2.161836
12	1	-1.508998	2.284984	-1.656624
13	6	0.873440	-1.172416	-0.928578
14	6	1.698904	-1.426624	1.396455
15	6	2.097509	-0.342927	-1.273136
16	6	3.129878	-1.281823	0.772011
17	6	3.175580	-0.367839	-0.429279
18	1	1.692596	-1.048045	2.422267
19	1	1.421263	-2.481693	1.458397
20	1	3.472962	-2.268723	0.431559
21	1	2.148731	0.212887	-2.206960
22	1	0.031248	-0.947569	-1.575261
23	1	1.052315	-2.252024	-0.993899
24	6	4.421277	0.422339	-0.679182
25	1	4.360144	1.022896	-1.589481
26	1	5.280300	-0.254883	-0.770397
27	1	4.645904	1.081480	0.169649
28	1	-0.362118	-0.879743	0.909168
29	1	3.862865	-0.962851	1.519985
30	6	-2.223418	0.561547	-0.599203
31	6	-2.755819	-0.587432	-1.200872
32	6	-2.787107	1.003498	0.608988
33	6	-3.811123	-1.286888	-0.607217
34	1	-2.358260	-0.932237	-2.152817
35	6	-3.839592	0.306149	1.206474

36	1	-2.426465	1.913669	1.083015
37	6	-4.352139	-0.845325	0.601954
38	1	-4.212666	-2.170318	-1.094238
39	1	-4.267699	0.669742	2.135780
40	1	-5.173814	-1.384412	1.062799

B



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.416082 hartrees (-415045.20561582 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.356967 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-661.102871 hartrees (-414848.66258121 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.2696595 hartrees (-414953.324032845 kcal/mol)

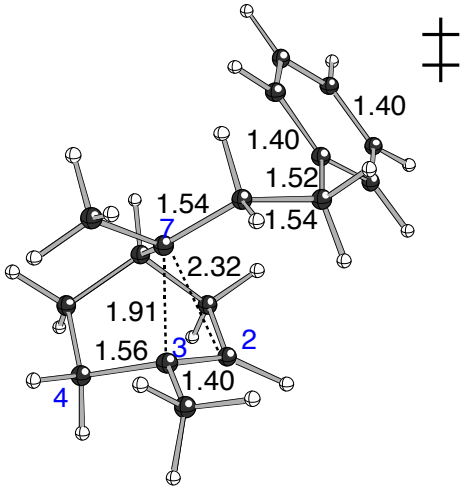
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.054076 hartrees (-414818.04323076 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.088862	0.661576	0.472079
2	6	0.663343	-0.820508	0.550022
3	6	0.723626	-1.073028	-0.973242
4	6	-1.058258	1.540932	-0.966060

5	6	0.143015	1.762099	-0.026694
6	1	0.976745	-2.100625	-1.253403
7	1	-0.307046	-0.965299	1.035012
8	1	-0.240353	2.193829	0.909885
9	1	0.770393	2.557694	-0.446513
10	6	1.963947	1.245318	1.565864
11	1	1.315062	1.373660	2.443463
12	1	2.341350	2.235859	1.298358
13	1	2.798461	0.622842	1.883895
14	6	1.766038	-1.663669	1.197003
15	1	1.913762	-1.393642	2.245885
16	1	1.470590	-2.715559	1.179391
17	6	1.850557	-0.070991	-1.195955
18	1	1.821962	0.665241	-1.996566
19	6	3.109029	-1.475096	0.403218
20	1	3.276356	-2.362514	-0.225657
21	1	3.975426	-1.406222	1.066469
22	6	3.055958	-0.311003	-0.542025
23	6	4.263947	0.530468	-0.754709
24	1	5.054108	-0.099567	-1.187489
25	1	4.664771	0.897838	0.197525
26	1	4.085777	1.368891	-1.430953
27	1	-0.187251	-0.793662	-1.491222
28	1	-1.453923	2.548302	-1.153497
29	1	-0.729890	1.185352	-1.948379
30	6	-2.193991	0.669206	-0.450352
31	6	-2.811121	-0.258667	-1.302020
32	6	-2.700664	0.814751	0.851139
33	6	-3.891080	-1.031782	-0.866008
34	1	-2.458669	-0.367919	-2.325595
35	6	-3.778670	0.042814	1.291825
36	1	-2.274043	1.550305	1.528897
37	6	-4.374961	-0.887261	0.435820
38	1	-4.355913	-1.739563	-1.545680
39	1	-4.159631	0.177189	2.299813
40	1	-5.215489	-1.483382	0.776939

TS



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.4017869 hartrees (-415036.235297619 kcal/mol)
Imaginary Frequencies: 1 (-294.3791 1/cm)
Zero-point correction = 0.356295 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-661.087714 hartrees (-414839.15141214 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.2565628 hartrees (-414945.105722628 kcal/mol)

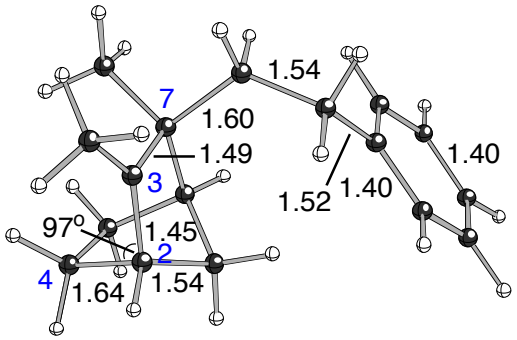
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.0408348 hartrees (-414809.734245348 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.319996	0.239745	0.762372
2	6	-0.865691	1.203235	-0.373560
3	6	-0.466033	0.217867	-1.489116
4	6	0.820311	-1.472450	0.800237
5	6	-0.360381	-0.741165	1.462111
6	1	-0.542220	0.623074	-2.510346
7	1	-0.059915	1.879203	-0.076264
8	1	0.026280	-0.180197	2.322683
9	1	-1.000670	-1.507031	1.916591
10	6	-2.197905	0.841240	1.856435
11	1	-1.579686	1.584134	2.379922
12	1	-2.493393	0.090290	2.592660
13	1	-3.089169	1.358376	1.510149
14	6	-2.146370	1.921732	-0.831733
15	1	-2.444608	2.707807	-0.134458
16	1	-1.994576	2.402266	-1.801326
17	6	-1.431884	-0.885677	-1.260081
18	1	-1.222316	-1.910153	-1.571684
19	6	-3.208399	0.791200	-0.902876
20	1	-3.604528	0.657241	-1.913461
21	1	-4.067584	0.972347	-0.253239
22	6	-2.543771	-0.554519	-0.468529
23	6	-3.467508	-1.634100	0.046880
24	1	-4.239736	-1.857480	-0.697690
25	1	-3.985319	-1.301677	0.951298
26	1	-2.937156	-2.563123	0.273746
27	1	0.563775	-0.142764	-1.397444
28	1	1.149394	-2.213445	1.541466
29	1	0.474307	-2.080632	-0.046914
30	6	2.037705	-0.664554	0.377317
31	6	2.835874	-1.131988	-0.681381
32	6	2.446527	0.495090	1.054105

33	6	4.000419	-0.459522	-1.058514
34	1	2.552293	-2.042267	-1.206013
35	6	3.611068	1.170746	0.678162
36	1	1.876113	0.872140	1.898285
37	6	4.390180	0.698471	-0.380896
38	1	4.603530	-0.843271	-1.875702
39	1	3.914059	2.061022	1.221015
40	1	5.296247	1.222050	-0.668873

C



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.4289547 hartrees (-415053.283363797 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.357786 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-661.114450 hartrees (-414855.9285195 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.2854865 hartrees (-414963.255633615 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -661.0711439 hartrees (-414828.753508689 kcal/mol)

Coordinates (from last standard orientation):

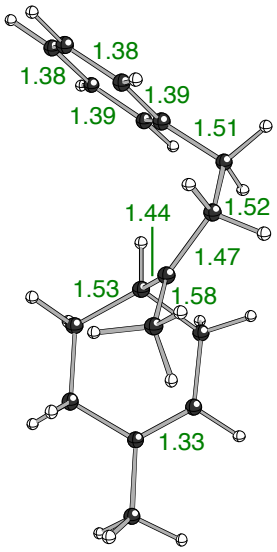
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.403627	-0.596777	0.517782
2	6	-0.820745	0.835669	0.792343
3	6	-0.633136	1.400601	-0.630127
4	6	0.833637	-1.553159	-0.805807
5	6	-0.323009	-1.728953	0.197770
6	1	-0.463364	2.480044	-0.643060
7	1	0.063780	0.829454	1.428671
8	1	0.090016	-1.971236	1.181569
9	1	-0.900032	-2.609137	-0.105532

10	6	-2.246189	-1.192260	1.683256
11	1	-1.657195	-1.128983	2.602849
12	1	-2.479156	-2.245163	1.508182
13	1	-3.186242	-0.661784	1.848823
14	6	-1.982767	1.733107	1.290761
15	1	-2.462059	1.374980	2.202499
16	1	-1.607415	2.739140	1.493789
17	6	-2.053350	1.038472	-1.113891
18	1	-2.404381	1.313956	-2.107929
19	6	-2.940630	1.741312	0.076352
20	1	-3.157913	2.735533	-0.323933
21	1	-3.900254	1.248181	0.254205
22	6	-2.249663	-0.327777	-0.681480
23	6	-3.184702	-1.273564	-1.308629
24	1	-4.020751	-0.766987	-1.799122
25	1	-3.537740	-2.060533	-0.640421
26	1	-2.613574	-1.761137	-2.119336
27	1	0.150758	0.924409	-1.214193
28	1	1.199479	-2.574203	-0.984704
29	1	0.466789	-1.213883	-1.782158
30	6	2.024963	-0.704344	-0.384800
31	6	2.655946	0.128539	-1.320806
32	6	2.575375	-0.790513	0.903338
33	6	3.791489	0.868514	-0.979680
34	1	2.267416	0.189248	-2.335500
35	6	3.708626	-0.050085	1.249874
36	1	2.139148	-1.452890	1.646668
37	6	4.318636	0.785786	0.310726
38	1	4.264865	1.502598	-1.723247
39	1	4.120927	-0.135947	2.250792
40	1	5.201769	1.356940	0.579205

Table 2: R_1/R_2=$CH_3/(CH_2)_2$–Ph (extended) (Fig. S10)

mPWB1K

A_b



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -661.0610072 hartrees (-414822.392628072 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.365030 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-660.740483 hartrees (-414621.26048733 kcal/mol)

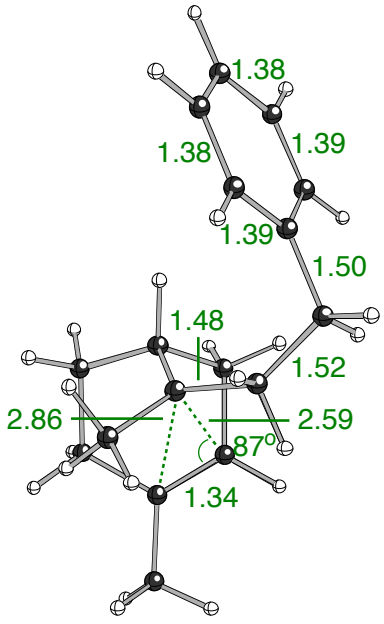
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.707006	-0.206461	0.220155
2	6	-1.512517	1.547839	-1.395543
3	1	-1.330309	2.556547	-1.745592
4	1	-2.510879	1.463669	-0.945652
5	1	-1.530632	0.847215	-2.233373
6	6	-0.547134	1.081454	-0.413613
7	6	0.519271	2.010861	-0.014770
8	6	1.572594	1.565496	0.982844
9	1	0.974947	2.327918	-0.959621
10	1	0.010590	2.926922	0.309226
11	1	1.096791	1.215538	1.898555
12	1	2.138497	2.451789	1.266462
13	6	-1.654354	0.202165	1.419165
14	6	-1.306964	-1.387913	-0.534268
15	6	-3.101561	0.114063	1.099373
16	6	-2.775461	-1.288375	-0.907988
17	6	-3.629487	-0.569506	0.082934
18	1	-0.699391	-1.596821	-1.412437
19	1	-1.173433	-2.240436	0.128289
20	1	-3.165422	-2.297852	-1.038380

21	1	-3.758755	0.647480	1.772474
22	1	-1.413341	1.189850	1.816561
23	1	-1.379323	-0.495783	2.210588
24	6	-5.100438	-0.638559	-0.145165
25	1	-5.649537	-0.031930	0.567373
26	1	-5.448726	-1.666447	-0.057116
27	1	-5.356436	-0.306461	-1.150382
28	1	0.241770	-0.503411	0.653400
29	1	-2.914007	-0.821290	-1.885360
30	6	2.512099	0.512870	0.456875
31	6	2.775454	-0.633740	1.194939
32	6	3.160991	0.683585	-0.760254
33	6	3.658331	-1.592330	0.725643
34	1	2.300415	-0.771366	2.157154
35	6	4.042310	-0.272826	-1.233009
36	1	3.006546	1.581720	-1.342065
37	6	4.290471	-1.416027	-0.492847
38	1	3.855482	-2.473305	1.316316
39	1	4.545018	-0.119147	-2.175067
40	1	4.980545	-2.159980	-0.858176

TS_{A-B}

We were unable to locate **TS_{A-B}** at mPWB1K level of theory. The structure shown has two imaginary frequencies: -87.9 cm^{-1} corresponding to C2–C7 bond making breaking and -10.0 cm^{-1} corresponding to a conformational change of the sidechain.



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):

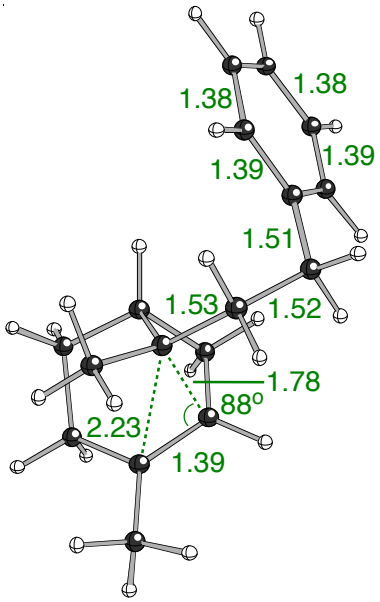
HF = -661.0511216 hartrees (-414816.189315216 kcal/mol)
Imaginary Frequencies: 2 (-87.8633 1/cm) (-10.0408 1/cm)
Zero-point correction = 0.364569 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-660.727522 hartrees (-414613.12733022 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.543442	-0.628232	0.352326
2	6	1.478452	1.380908	1.636556
3	1	1.714487	2.433667	1.524898
4	1	2.350395	0.804619	1.919170
5	1	0.769448	1.290599	2.472853
6	6	0.738062	0.837364	0.497496
7	6	0.024430	1.865175	-0.291732
8	6	-1.162205	1.558877	-1.198372
9	1	-0.270539	2.608774	0.455297
10	1	0.809665	2.395247	-0.842636
11	1	-0.834838	1.161163	-2.154165
12	1	-1.611085	2.524604	-1.429369
13	6	0.862441	-0.935011	-1.109116
14	6	1.469027	-1.450564	1.226553
15	6	2.199447	-0.283740	-1.318300
16	6	2.942970	-1.279148	0.808218
17	6	3.157716	-0.399466	-0.385122
18	1	1.339697	-1.203216	2.277890
19	1	1.166581	-2.488444	1.125381
20	1	3.364179	-2.255328	0.564628
21	1	2.399207	0.251935	-2.236148
22	1	0.113193	-0.542015	-1.781337
23	1	0.887423	-2.013309	-1.264558
24	6	4.492018	0.243707	-0.515504
25	1	4.585595	0.806420	-1.438477
26	1	5.279253	-0.508659	-0.492643
27	1	4.683615	0.914063	0.322835
28	1	-0.509486	-0.825777	0.588671
29	1	3.550494	-0.919067	1.638252
30	6	-2.193927	0.655224	-0.586173
31	6	-2.616733	-0.481994	-1.259361
32	6	-2.732586	0.928783	0.666807
33	6	-3.545358	-1.338988	-0.690640
34	1	-2.225285	-0.698246	-2.243668
35	6	-3.659191	0.073934	1.238515
36	1	-2.445968	1.827666	1.196151
37	6	-4.062458	-1.067177	0.563305
38	1	-3.866816	-2.216061	-1.230318
39	1	-4.076021	0.304835	2.206521
40	1	-4.786479	-1.731386	1.008032

B



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -661.0620743 hartrees (-414823.062243993 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.367919 (Hartree/Particle)

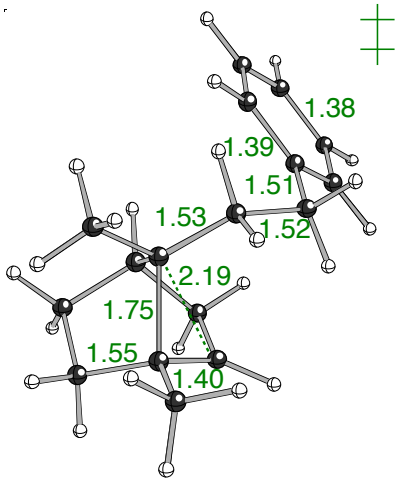
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-660.735913 hartrees (-414618.39276663 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.124935	0.582528	0.446859
2	6	0.594053	-0.854534	0.475020
3	6	0.627547	-0.983227	-1.047717
4	6	-0.990739	1.635815	-0.820294
5	6	0.194727	1.750380	0.125033
6	1	0.901150	-1.966045	-1.426002
7	1	-0.368627	-0.976417	0.964015
8	1	-0.175680	2.061513	1.103502
9	1	0.825885	2.574792	-0.206110
10	6	2.021915	1.038668	1.579192
11	1	1.383033	1.160457	2.453049
12	1	2.467805	2.007360	1.368454
13	1	2.808700	0.347417	1.859684
14	6	1.664320	-1.764140	1.031135
15	1	1.834909	-1.574920	2.087186
16	1	1.356354	-2.800883	0.936559
17	6	1.719107	0.055193	-1.148593

18	1	1.709514	0.855411	-1.877812
19	6	2.974013	-1.527416	0.239937
20	1	3.086011	-2.317358	-0.508842
21	1	3.858075	-1.568745	0.869562
22	6	2.927189	-0.270413	-0.542019
23	6	4.119709	0.580759	-0.663038
24	1	4.850573	0.027615	-1.257826
25	1	4.585775	0.752884	0.304678
26	1	3.919071	1.521497	-1.163474
27	1	-0.287876	-0.671704	-1.526037
28	1	-1.383405	2.648783	-0.916763
29	1	-0.668618	1.366951	-1.825875
30	6	-2.112214	0.731806	-0.381581
31	6	-2.734434	-0.104418	-1.299571
32	6	-2.588882	0.747205	0.924597
33	6	-3.790201	-0.918188	-0.924505
34	1	-2.399316	-0.110061	-2.328461
35	6	-3.643310	-0.065031	1.304625
36	1	-2.153882	1.411069	1.657951
37	6	-4.244097	-0.905502	0.382395
38	1	-4.260843	-1.556655	-1.655883
39	1	-4.002845	-0.033727	2.321507
40	1	-5.067605	-1.536136	0.678084

TS



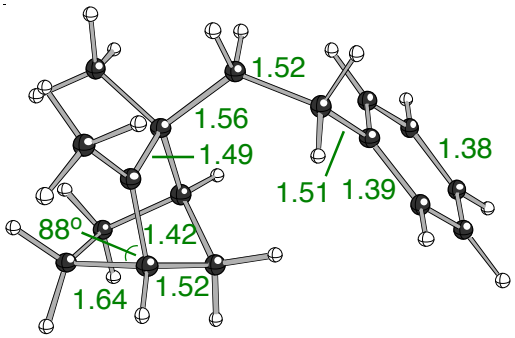
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -661.0480738 hartrees (-414814.276790238 kcal/mol)
Imaginary Frequencies: 1 (-304.8409 1/cm)
Zero-point correction = 0.366610 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-660.722679 hartrees (-414610.08829929 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.271514	-0.004425	0.696799
2	6	-0.725145	1.161855	-0.149768
3	6	-0.492799	0.461466	-1.485785
4	6	0.781090	-1.693906	0.252393
5	6	-0.389462	-1.193693	1.084669
6	1	-0.661180	1.090983	-2.366010
7	1	0.159688	1.641541	0.254838
8	1	-0.011775	-0.958629	2.078263
9	1	-1.069138	-2.029453	1.256007
10	6	-2.016292	0.383641	1.959161
11	1	-1.307108	0.924604	2.587171
12	1	-2.333205	-0.497602	2.509164
13	1	-2.876162	1.023410	1.809612
14	6	-1.921364	2.080476	-0.320823
15	1	-2.112462	2.656872	0.579073
16	1	-1.762263	2.791618	-1.125501
17	6	-1.508942	-0.594944	-1.400475
18	1	-1.403894	-1.554266	-1.898357
19	6	-3.067435	1.108798	-0.622705
20	1	-3.462765	1.227692	-1.627734
21	1	-3.908641	1.218821	0.055407
22	6	-2.526867	-0.332018	-0.475963
23	6	-3.526479	-1.395187	-0.138384
24	1	-4.315080	-1.422624	-0.886633
25	1	-3.998366	-1.180739	0.816842
26	1	-3.076483	-2.382735	-0.085741
27	1	0.505770	0.048693	-1.602595
28	1	1.104453	-2.620893	0.727523
29	1	0.466773	-2.002532	-0.746572
30	6	1.973925	-0.781934	0.141387
31	6	2.782811	-0.837935	-0.989596
32	6	2.335170	0.084010	1.166332
33	6	3.913634	-0.046997	-1.098222
34	1	2.534387	-1.523252	-1.789403
35	6	3.465740	0.876166	1.061410
36	1	1.747919	0.138799	2.070868
37	6	4.256998	0.816875	-0.072657
38	1	4.528778	-0.111381	-1.982188
39	1	3.733219	1.535580	1.872410
40	1	5.139127	1.432022	-0.153091

C



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -661.0776091 hartrees (-414832.810486341 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.367853 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-660.751987 hartrees (-414628.47936237 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.366311	-0.568784	0.514396
2	6	-0.761517	0.827128	0.785047
3	6	-0.553655	1.403326	-0.610486
4	6	0.776449	-1.520794	-0.838213
5	6	-0.355548	-1.705577	0.161170
6	1	-0.389236	2.476569	-0.594325
7	1	0.109648	0.811367	1.429497
8	1	0.058172	-2.001410	1.122907
9	1	-0.959205	-2.554587	-0.159072
10	6	-2.203429	-1.132502	1.665599
11	1	-1.620868	-1.085557	2.581995
12	1	-2.456262	-2.174235	1.488550
13	1	-3.128792	-0.587060	1.828200
14	6	-1.918285	1.706024	1.256803
15	1	-2.373819	1.384362	2.186261
16	1	-1.577720	2.727790	1.393315
17	6	-1.927808	1.043765	-1.136879
18	1	-2.276371	1.348089	-2.114288
19	6	-2.872992	1.609451	0.072392
20	1	-3.230095	2.553269	-0.331976
21	1	-3.763919	1.014273	0.274409
22	6	-2.207221	-0.269399	-0.672493
23	6	-3.195625	-1.178344	-1.248551
24	1	-3.925147	-0.668610	-1.868366
25	1	-3.677521	-1.809993	-0.509294
26	1	-2.621965	-1.837674	-1.909620
27	1	0.240883	0.946695	-1.184221

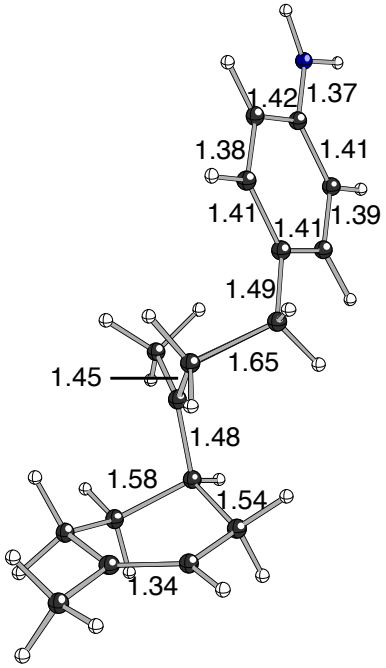
28	1	1.128400	-2.527276	-1.069386
29	1	0.405604	-1.130208	-1.787288
30	6	1.965328	-0.709084	-0.393436
31	6	2.630139	0.091382	-1.314312
32	6	2.469669	-0.782882	0.899203
33	6	3.756953	0.810726	-0.956109
34	1	2.268633	0.144116	-2.332820
35	6	3.595430	-0.062900	1.263088
36	1	2.002803	-1.418842	1.637069
37	6	4.240866	0.739771	0.338557
38	1	4.258687	1.422324	-1.689708
39	1	3.974017	-0.138325	2.270713
40	1	5.119408	1.297087	0.622799

3.7. R_1=CH_3, R_2=$(CH_2)_2$–*p*–NH_2–Ph

Table 1: R_1/R_2=$CH_3/(CH_2)_2$–*p*–NH_2–Ph (aligned) (Fig. S11)

B3LYP

A_a



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.8064851 hartrees (-449803.237465101 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.371713 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.481800 hartrees (-449599.494318 kcal/mol)

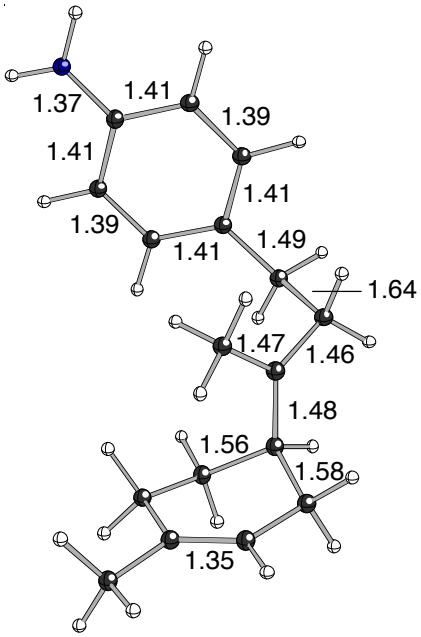
mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.6398947 hartrees (-449698.700323197 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.4013321 hartrees (-449548.999906071 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.668947	-0.559285	1.083788
2	6	4.212061	-0.533970	-0.143863
3	6	3.802188	0.508733	-1.163773
4	6	3.039875	1.690032	-0.557862
5	6	1.939599	1.228996	0.480831
6	6	2.618114	0.401243	1.589120
7	1	4.698907	0.897248	-1.663482
8	1	4.008452	-1.307343	1.797896
9	1	3.725561	2.321710	0.016556
10	1	2.598913	2.318425	-1.336717
11	1	3.074640	1.108589	2.295662
12	1	1.869746	-0.139970	2.180826
13	1	3.216279	0.028741	-1.963441
14	6	5.256372	-1.523612	-0.588784
15	1	6.198362	-1.015276	-0.829666
16	1	5.461039	-2.272035	0.180996
17	1	4.941277	-2.047594	-1.500442
18	1	1.534191	2.163907	0.896891
19	6	0.827928	0.593672	-0.268505
20	6	-0.078392	1.448854	-1.050239
21	1	-1.092581	1.305680	-0.618952
22	1	0.179334	2.508367	-1.036439
23	1	-0.181443	1.091850	-2.082408
24	6	0.515350	-0.821304	-0.192173
25	1	0.118627	-1.212962	-1.130974
26	1	1.361953	-1.417604	0.146752
27	6	-0.686707	-1.044695	0.915753
28	1	-0.619168	-2.124775	1.074161
29	1	-0.394758	-0.557142	1.848022
30	6	-2.057859	-0.648516	0.496524
31	6	-2.740800	0.417685	1.121913
32	6	-2.758664	-1.376599	-0.490357
33	6	-4.050979	0.737374	0.796895
34	1	-2.243269	0.987153	1.903745
35	6	-4.061873	-1.064608	-0.833875
36	1	-2.277169	-2.217140	-0.985167
37	6	-4.741983	0.001622	-0.192182
38	1	-4.553047	1.552445	1.309959
39	1	-4.577469	-1.648697	-1.590861
40	7	-6.023928	0.317858	-0.538347
41	1	-6.552038	-0.278154	-1.156415
42	1	-6.547907	0.995851	-0.007332

A_b



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.8048313 hartrees (-449802.199689063 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.371555 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.481041 hartrees (-449599.01803791 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.637823 hartrees (-449697.40031073 kcal/mol)

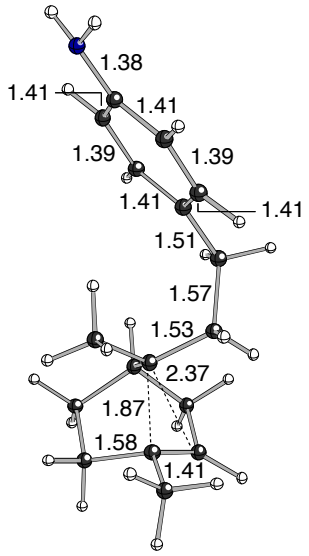
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.3992038 hartrees (-449547.664376538 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.968502	0.038994	-0.823743
2	6	3.717996	1.195194	-0.184006
3	6	2.739595	1.262030	0.964906
4	6	2.327289	-0.104794	1.522676
5	6	2.121253	-1.237168	0.470790
6	6	3.383981	-1.299894	-0.474050
7	1	3.184094	1.844948	1.782212
8	1	4.661266	0.038632	-1.663370

9	1	3.123654	-0.474533	2.177985
10	1	1.434252	-0.012049	2.149347
11	1	4.120675	-1.912092	0.064203
12	1	3.160173	-1.863869	-1.389618
13	1	1.862474	1.848541	0.653016
14	6	4.368989	2.493320	-0.581318
15	1	4.976339	2.890049	0.241623
16	1	5.015066	2.374304	-1.454511
17	1	3.617112	3.258959	-0.812410
18	1	2.076103	-2.183725	1.017852
19	6	0.916565	-1.165374	-0.388318
20	6	0.587739	0.028858	-1.176798
21	1	-0.097705	0.623957	-0.534009
22	1	1.455060	0.650743	-1.405100
23	1	0.011646	-0.204463	-2.074912
24	6	-0.034709	-2.265748	-0.381863
25	1	-0.564235	-2.380360	-1.329112
26	1	0.429389	-3.208440	-0.083807
27	6	-1.182212	-1.967593	0.756427
28	1	-1.660833	-2.948064	0.835263
29	1	-0.678821	-1.771685	1.706193
30	6	-2.179594	-0.911477	0.426804
31	6	-2.199743	0.324975	1.103947
32	6	-3.177048	-1.134600	-0.545003
33	6	-3.165067	1.287925	0.839398
34	1	-1.467281	0.522175	1.883955
35	6	-4.140511	-0.181153	-0.828644
36	1	-3.210058	-2.082847	-1.076990
37	6	-4.156838	1.055664	-0.138540
38	1	-3.165011	2.221950	1.393976
39	1	-4.901272	-0.386355	-1.576443
40	7	-5.095698	2.007058	-0.432662
41	1	-5.885627	1.776105	-1.015139
42	1	-5.203710	2.813760	0.162425

TS



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.7721427 hartrees (-449781.687265677 kcal/mol)
Imaginary Frequencies: 1 (-323.9289 1/cm)
Zero-point correction = 0.371910 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.445498 hartrees (-449576.71444998 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.6138479 hartrees (-449682.355695729 kcal/mol)

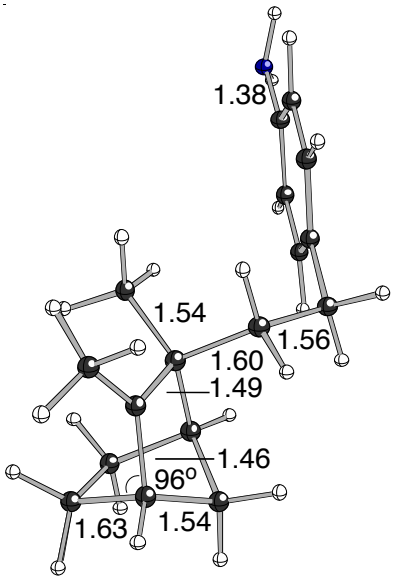
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.3809621 hartrees (-449536.217527371 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.544721	0.245395	0.895466
2	6	-3.038676	0.799732	-0.296800
3	6	-3.397850	-0.105658	-1.534528
4	6	-2.804985	-1.514628	-1.288640
5	6	-2.055077	-1.368154	0.048909
6	6	-3.112481	-1.152365	1.148731
7	1	-4.484374	-0.114992	-1.652056
8	1	-4.060077	0.833103	1.656553
9	1	-3.579950	-2.282502	-1.220632
10	1	-2.134476	-1.814160	-2.096972
11	1	-3.952987	-1.863060	1.133370
12	1	-2.704833	-1.219937	2.167143
13	1	-2.984777	0.381702	-2.420711
14	6	-3.124603	2.293747	-0.527329
15	1	-4.133519	2.574390	-0.849351
16	1	-2.885187	2.863673	0.374690
17	1	-2.438445	2.602564	-1.320849
18	1	-1.370382	-2.193579	0.257339
19	6	-1.364762	0.027371	-0.017412
20	6	-0.508731	0.331176	-1.226659
21	1	0.454841	-0.175741	-1.064776
22	1	-0.906574	-0.008021	-2.181174
23	1	-0.276952	1.397509	-1.294080
24	6	-0.677048	0.539826	1.253242
25	1	-0.367804	1.577806	1.090605
26	1	-1.366079	0.562590	2.101253
27	6	0.563282	-0.292172	1.720246
28	1	0.746009	0.035962	2.752085
29	1	0.282816	-1.349292	1.790948
30	6	1.852561	-0.164832	0.941237
31	6	2.447729	-1.277844	0.322488
32	6	2.541222	1.059773	0.865815

33	6	3.657813	-1.179556	-0.357367
34	1	1.963295	-2.249798	0.385779
35	6	3.746951	1.177510	0.187226
36	1	2.134877	1.940490	1.358339
37	6	4.331359	0.055415	-0.442293
38	1	4.090181	-2.061531	-0.821839
39	1	4.253704	2.137974	0.147318
40	7	5.507481	0.177009	-1.149767
41	1	6.078565	0.996540	-1.006969
42	1	6.017848	-0.659176	-1.391644

C



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.8027642 hartrees (-449800.902563142 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.374115 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.473807 hartrees (-449594.47863057 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.6472056 hartrees (-449703.287986056 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.4172174 hartrees (-449558.968090674 kcal/mol)

Coordinates (from last standard orientation):

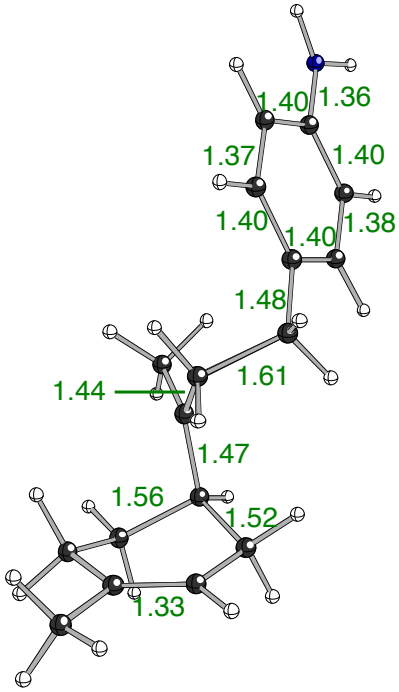
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z

1	6	-3.663740	0.057094	0.308045
2	6	-2.654569	0.876641	-0.347932
3	6	-3.797716	-1.045241	-0.884295
4	6	-2.533656	-1.921559	-0.703451
5	6	-1.745939	-1.160737	0.393165
6	6	-2.891028	-0.777574	1.352411
7	1	-4.736070	-1.565145	-0.670262
8	1	-4.615983	0.524636	0.557179
9	1	-2.800851	-2.917689	-0.341249
10	1	-1.974720	-2.051393	-1.631280
11	1	-3.471947	-1.637731	1.694072
12	1	-2.589405	-0.195260	2.225223
13	1	-3.896200	-0.600887	-1.878635
14	6	-2.938223	2.111715	-1.100021
15	1	-3.990282	2.189257	-1.384826
16	1	-2.735365	2.956928	-0.420879
17	1	-2.286124	2.241760	-1.967182
18	1	-0.915863	-1.722270	0.819749
19	6	-1.323852	0.234743	-0.188938
20	6	-0.450232	0.204859	-1.459357
21	1	0.440204	-0.400350	-1.286150
22	1	-0.990231	-0.217538	-2.310819
23	1	-0.112493	1.206372	-1.736651
24	6	-0.664718	1.180959	0.925571
25	1	-0.318486	2.076355	0.399871
26	1	-1.420376	1.519876	1.643281
27	6	0.503695	0.567228	1.749061
28	1	0.701629	1.314051	2.530098
29	1	0.157764	-0.328351	2.274092
30	6	1.778317	0.275426	0.998752
31	6	2.237093	-1.036635	0.805918
32	6	2.564891	1.318178	0.478431
33	6	3.411278	-1.306787	0.108435
34	1	1.675992	-1.870534	1.222221
35	6	3.738192	1.067504	-0.222346
36	1	2.264895	2.352209	0.635881
37	6	4.184382	-0.255948	-0.425660
38	1	3.741663	-2.334370	-0.016854
39	1	4.326712	1.896464	-0.606259
40	7	5.326559	-0.513441	-1.157168
41	1	5.979538	0.241828	-1.305481
42	1	5.755040	-1.423333	-1.071695

Table 1: R_1/R_2=$CH_3/(CH_2)_2$–*p*–NH_2–Ph (aligned) (Fig. S11)

mPWB1K

A_a



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -716.407221 hartrees (-449552.69524971 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.381513 (Hartree/Particle)

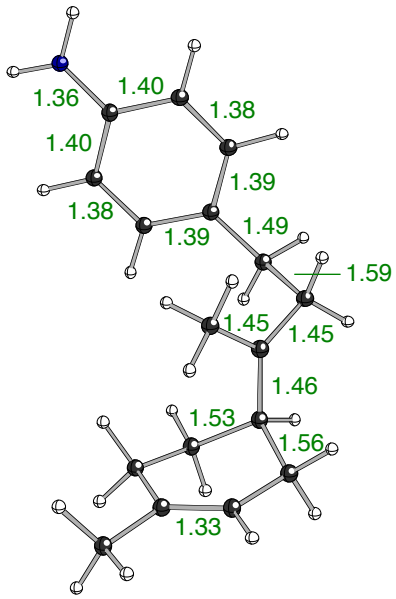
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.071959 hartrees (-449342.31499209 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.602871	-0.490153	1.065508
2	6	4.088645	-0.473484	-0.173292
3	6	3.619440	0.534279	-1.178715
4	6	2.884056	1.695527	-0.546679
5	6	1.834764	1.213075	0.496577
6	6	2.547549	0.431677	1.587461
7	1	4.479605	0.919732	-1.725374
8	1	3.991829	-1.212093	1.770804
9	1	3.581389	2.315077	0.013341
10	1	2.421119	2.328571	-1.298839
11	1	2.994526	1.151848	2.274312
12	1	1.833503	-0.127333	2.192185
13	1	3.002232	0.038079	-1.934681
14	6	5.129229	-1.433876	-0.638612
15	1	6.040066	-0.908184	-0.921518
16	1	5.380025	-2.157987	0.129891

17	1	4.792663	-1.975905	-1.521821
18	1	1.376638	2.121600	0.897080
19	6	0.786549	0.518965	-0.260120
20	6	-0.116316	1.302462	-1.082324
21	1	-1.114023	1.145046	-0.630350
22	1	0.108306	2.361460	-1.115592
23	1	-0.219907	0.883878	-2.081926
24	6	0.543175	-0.895743	-0.146356
25	1	0.157940	-1.329437	-1.063594
26	1	1.417435	-1.432671	0.205259
27	6	-0.609188	-1.072026	0.958886
28	1	-0.557040	-2.139149	1.161518
29	1	-0.317076	-0.560873	1.871717
30	6	-1.972154	-0.675426	0.537056
31	6	-2.640347	0.384104	1.150763
32	6	-2.655030	-1.373807	-0.459996
33	6	-3.924182	0.734506	0.796643
34	1	-2.151865	0.935597	1.942551
35	6	-3.932507	-1.032340	-0.830510
36	1	-2.181678	-2.214776	-0.948452
37	6	-4.598835	0.032109	-0.206122
38	1	-4.416476	1.552842	1.299511
39	1	-4.436911	-1.595216	-1.601250
40	7	-5.850884	0.382510	-0.585941
41	1	-6.376825	-0.214024	-1.191252
42	1	-6.375585	1.037260	-0.042951

A_b



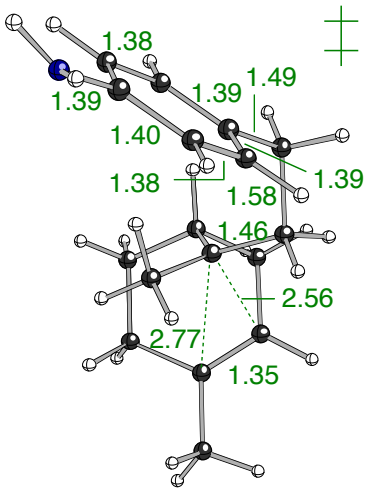
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -716.4058325 hartrees (-449551.823952075 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.382197 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.069552 hartrees (-449340.80457552 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.808604	0.004585	-0.763253
2	6	3.555310	1.185650	-0.199717
3	6	2.564717	1.325514	0.909037
4	6	2.145951	0.009508	1.532960
5	6	1.963998	-1.164384	0.567926
6	6	3.211528	-1.296222	-0.359488
7	1	2.992284	1.954521	1.689720
8	1	4.516853	-0.045345	-1.579114
9	1	2.921482	-0.311874	2.225495
10	1	1.242471	0.136755	2.126816
11	1	3.930447	-1.893487	0.202735
12	1	2.985712	-1.892387	-1.246826
13	1	1.703340	1.889788	0.543948
14	6	4.219379	2.440733	-0.652250
15	1	4.814981	2.868371	0.152873
16	1	4.871233	2.268758	-1.502484
17	1	3.482828	3.193577	-0.930799
18	1	1.890651	-2.079736	1.151144
19	6	0.837699	-1.138800	-0.361316
20	6	0.505803	0.049661	-1.119997
21	1	-0.050848	0.688142	-0.413648
22	1	1.399439	0.606824	-1.399852
23	1	-0.148933	-0.142623	-1.960826
24	6	-0.011632	-2.305170	-0.461304
25	1	-0.497646	-2.393052	-1.427127
26	1	0.521507	-3.217039	-0.207229
27	6	-1.138341	-2.107783	0.641253
28	1	-1.643810	-3.071301	0.644858
29	1	-0.665955	-1.994474	1.614612
30	6	-2.094597	-0.999246	0.377836
31	6	-2.148935	0.119916	1.201327
32	6	-2.975751	-1.050540	-0.698801
33	6	-3.040392	1.147170	0.968488
34	1	-1.498951	0.182075	2.064318
35	6	-3.865531	-0.030998	-0.948751
36	1	-2.981585	-1.913900	-1.350656
37	6	-3.917247	1.092272	-0.116173
38	1	-3.067571	1.996390	1.634525
39	1	-4.540517	-0.101597	-1.788395
40	7	-4.772701	2.119163	-0.382303
41	1	-5.532641	1.958721	-1.012887
42	1	-4.959245	2.787559	0.338260

TS_{A-B}



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -716.4001992 hartrees (-449548.288999992 kcal/mol)
Imaginary Frequencies: 1 (-56.4865 1/cm)
Zero-point correction = 0.382098 (Hartree/Particle)

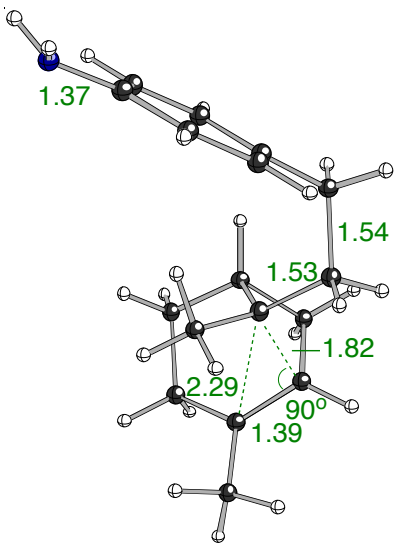
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.063232 hartrees (-449336.83871232 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.489270	0.658961	-0.588991
2	6	-3.590950	-0.679117	-0.500816
3	6	-3.355999	-1.387428	0.796736
4	6	-2.494481	-0.602522	1.797895
5	6	-1.875861	0.616418	1.138005
6	6	-3.003508	1.473624	0.574308
7	1	-4.332461	-1.595568	1.235238
8	1	-3.772461	1.154611	-1.507330
9	1	-3.099176	-0.248413	2.627740
10	1	-1.733834	-1.245076	2.234528
11	1	-3.776594	1.646718	1.321776
12	1	-2.660741	2.453183	0.257163
13	1	-2.932030	-2.369759	0.589913
14	6	-4.022634	-1.521388	-1.648367
15	1	-4.923413	-2.078183	-1.393757
16	1	-4.226026	-0.930322	-2.535182
17	1	-3.260021	-2.261794	-1.889785
18	1	-1.248629	1.154619	1.855953
19	6	-1.023468	0.267558	-0.046612

20	6	-0.409413	-1.038597	-0.187567
21	1	0.591230	-0.875233	0.264160
22	1	-0.892544	-1.844848	0.344730
23	1	-0.201896	-1.295629	-1.221336
24	6	-0.475034	1.322810	-0.896285
25	1	-0.177885	0.929728	-1.863316
26	1	-1.166917	2.142613	-1.038807
27	6	0.808908	1.928609	-0.202914
28	1	1.037988	2.793613	-0.822123
29	1	0.538335	2.309955	0.778677
30	6	1.989694	1.028639	-0.116718
31	6	2.464661	0.562921	1.106414
32	6	2.677236	0.635910	-1.263619
33	6	3.570609	-0.257519	1.189831
34	1	1.974344	0.867496	2.021372
35	6	3.777284	-0.187050	-1.197924
36	1	2.354808	0.993795	-2.232124
37	6	4.249912	-0.651527	0.035426
38	1	3.919543	-0.591679	2.155222
39	1	4.291490	-0.469701	-2.104214
40	7	5.318178	-1.492938	0.100694
41	1	5.913521	-1.579784	-0.698426
42	1	5.770018	-1.631583	0.982270

B



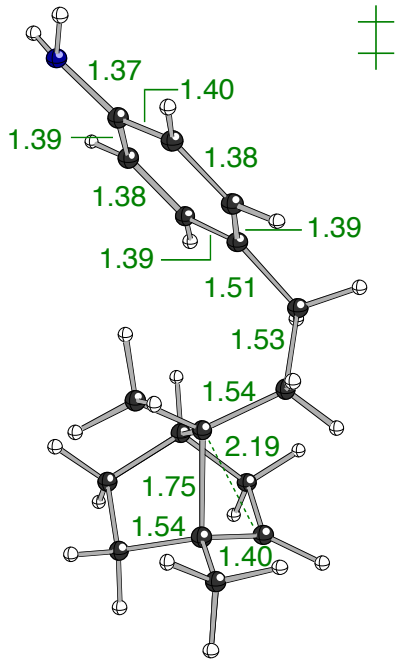
mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -716.404752 hartrees (-449551.14592752 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.384643 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.063972 hartrees (-449337.30306972 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.978854	0.694941	-0.392972
2	6	-3.230635	-0.661337	-0.528445
3	6	-3.194039	-1.495427	0.693328
4	6	-2.080586	-1.045259	1.664140
5	6	-1.596063	0.325454	1.259140
6	6	-2.809209	1.223049	1.013592
7	1	-4.167642	-1.341319	1.168061
8	1	-3.185605	1.336107	-1.238922
9	1	-2.460459	-1.019600	2.680909
10	1	-1.264346	-1.761847	1.644107
11	1	-3.660571	1.062097	1.670746
12	1	-2.563657	2.278458	1.011005
13	1	-3.133257	-2.551727	0.448009
14	6	-3.505653	-1.278491	-1.833696
15	1	-4.517390	-1.688259	-1.803309
16	1	-3.441373	-0.576764	-2.657366
17	1	-2.844087	-2.126356	-2.005230
18	1	-0.828736	0.692812	1.933869
19	6	-1.200209	0.337968	-0.216837
20	6	-0.548858	-0.863256	-0.840078
21	1	0.501436	-0.843095	-0.552674
22	1	-0.958274	-1.817434	-0.523947
23	1	-0.581562	-0.806125	-1.925374
24	6	-0.594835	1.639462	-0.738264
25	1	-0.335678	1.492779	-1.785208
26	1	-1.309895	2.455954	-0.703410
27	6	0.649207	2.105361	0.038451
28	1	0.945448	3.045814	-0.425544
29	1	0.364203	2.353979	1.059388
30	6	1.804724	1.154888	0.047916
31	6	2.176342	0.466740	1.194437
32	6	2.527059	0.901763	-1.113230
33	6	3.209462	-0.451295	1.186869
34	1	1.660075	0.658015	2.125649
35	6	3.558737	-0.012080	-1.138392
36	1	2.284369	1.435337	-2.022407
37	6	3.919156	-0.711568	0.015798
38	1	3.477868	-0.964827	2.098198
39	1	4.102940	-0.182892	-2.055445
40	7	4.912692	-1.655416	-0.014350
41	1	5.567404	-1.611153	-0.770432
42	1	5.325480	-1.917530	0.859235

TS



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -716.3901114 hartrees (-449541.958804614 kcal/mol)
Imaginary Frequencies: 1 (-290.6407 1/cm)
Zero-point correction = 0.383716 (Hartree/Particle)

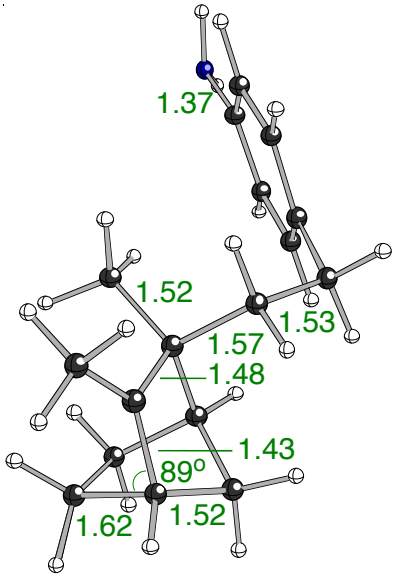
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.049238 hartrees (-449328.05733738 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.263461	-0.496275	-0.677342
2	6	-2.942186	-0.162280	0.642603
3	6	-3.084930	1.352324	0.909737
4	6	-2.124975	2.087735	-0.029074
5	6	-1.507625	0.972065	-0.850383
6	6	-2.599097	0.330855	-1.695707
7	1	-4.123035	1.636447	0.762685
8	1	-3.815961	-1.394279	-0.937622
9	1	-2.635425	2.810220	-0.658788
10	1	-1.365306	2.629900	0.525054
11	1	-3.299115	1.020398	-2.176529
12	1	-2.219894	-0.312088	-2.490791
13	1	-2.862423	1.519375	1.959451
14	6	-3.345787	-1.083754	1.753313
15	1	-4.397809	-0.952224	1.995388
16	1	-3.182292	-2.126905	1.495763

17	1	-2.777965	-0.860203	2.651907
18	1	-0.627231	1.272956	-1.408103
19	6	-1.258293	-0.166518	0.152120
20	6	-0.476602	0.173967	1.394613
21	1	0.545164	0.389515	1.082397
22	1	-0.851238	1.037784	1.930125
23	1	-0.432522	-0.672215	2.073642
24	6	-0.769695	-1.494665	-0.452071
25	1	-0.506684	-2.158010	0.370489
26	1	-1.556402	-2.016786	-0.996284
27	6	0.421455	-1.370066	-1.405893
28	1	0.629565	-2.374725	-1.773487
29	1	0.125481	-0.789228	-2.280798
30	6	1.664064	-0.774695	-0.816485
31	6	2.152131	0.453520	-1.237522
32	6	2.361305	-1.429526	0.193560
33	6	3.273366	1.024658	-0.666005
34	1	1.658773	0.977876	-2.045084
35	6	3.478920	-0.872608	0.776376
36	1	2.028026	-2.400891	0.533745
37	6	3.956039	0.372353	0.358662
38	1	3.629638	1.980423	-1.020542
39	1	3.999506	-1.406220	1.557774
40	7	5.038210	0.950246	0.969150
41	1	5.652046	0.351209	1.485312
42	1	5.509855	1.683409	0.477215

C



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -716.4251303 hartrees (-449563.933514553 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.384891 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.083801 hartrees (-449349.74596551 kcal/mol)

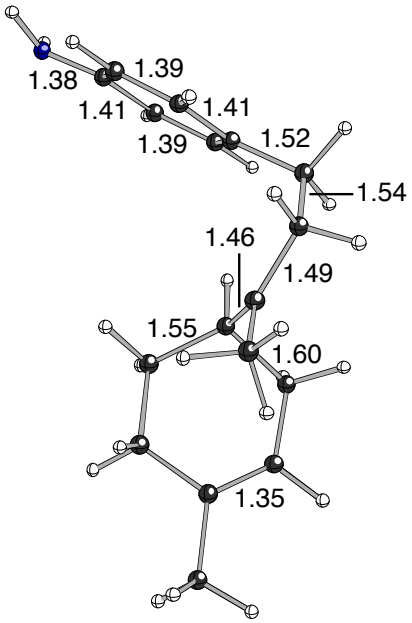
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.501459	-0.123374	0.285202
2	6	-2.595098	0.737426	-0.406839
3	6	-3.379618	-1.180422	-0.937530
4	6	-2.117085	-1.969803	-0.607665
5	6	-1.481072	-1.099754	0.470572
6	6	-2.685380	-0.823584	1.357961
7	1	-4.310538	-1.739771	-0.888742
8	1	-4.515644	0.209462	0.459476
9	1	-2.366456	-2.945790	-0.202033
10	1	-1.482551	-2.123044	-1.473370
11	1	-3.167917	-1.728957	1.713214
12	1	-2.486551	-0.178324	2.208998
13	1	-3.357163	-0.722190	-1.926577
14	6	-2.963889	1.872604	-1.250063
15	1	-4.026196	1.916702	-1.460711
16	1	-2.701812	2.766705	-0.675328
17	1	-2.376872	1.912653	-2.163407
18	1	-0.609200	-1.531553	0.944448
19	6	-1.211867	0.278120	-0.167167
20	6	-0.334334	0.269091	-1.411359
21	1	0.562409	-0.317061	-1.239689
22	1	-0.860996	-0.157246	-2.263140
23	1	-0.018389	1.273640	-1.678764
24	6	-0.733252	1.333743	0.891588
25	1	-0.418116	2.211344	0.328814
26	1	-1.561994	1.660176	1.523308
27	6	0.400265	0.864084	1.803131
28	1	0.608416	1.693897	2.479215
29	1	0.053090	0.044930	2.431195
30	6	1.641754	0.460596	1.070609
31	6	2.100193	-0.848931	1.074053
32	6	2.355082	1.386064	0.316152
33	6	3.199824	-1.235243	0.332054
34	1	1.598329	-1.591287	1.679972
35	6	3.452948	1.018251	-0.430685
36	1	2.049945	2.424146	0.311071
37	6	3.893170	-0.307731	-0.444181
38	1	3.531510	-2.262619	0.358572
39	1	3.985684	1.760931	-1.005986
40	7	4.950079	-0.690288	-1.227391
41	1	5.578172	0.024295	-1.538680
42	1	5.401177	-1.555834	-1.005129

Table 2: R_1/R_2=CH_3/$(CH_2)_2$–*p*–NH_2–Ph (extended) (Fig. S12)

B3LYP

A_b



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.7981347 hartrees (-449797.997505597 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.371425 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.474156 hartrees (-449594.69763156 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.6325961 hartrees (-449694.120378711 kcal/mol)

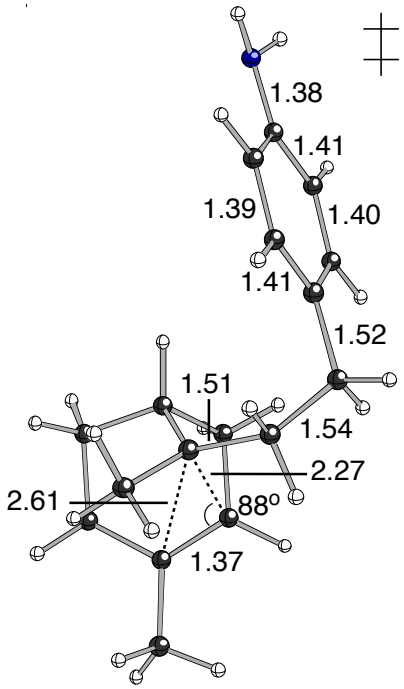
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.3959677 hartrees (-449545.633691427 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.059098	0.050039	0.383404
2	6	-2.011101	1.392349	-1.563059
3	1	-1.939454	2.354463	-2.071754
4	1	-3.014536	1.247831	-1.127507
5	1	-1.918669	0.581422	-2.301801
6	6	-0.993274	1.201259	-0.518025

7	6	0.016294	2.279423	-0.363384
8	6	1.160504	2.141265	0.651004
9	1	0.411189	2.456934	-1.377596
10	1	-0.564505	3.204299	-0.186394
11	1	0.751199	2.020466	1.660681
12	1	1.679019	3.108897	0.663373
13	6	-2.205989	0.446174	1.428460
14	6	-1.366955	-1.362656	-0.185538
15	6	-3.585225	0.030746	1.023123
16	6	-2.798854	-1.611437	-0.678414
17	6	-3.879909	-0.917039	0.110938
18	1	-0.640213	-1.602141	-0.968025
19	1	-1.154645	-2.045837	0.643438
20	1	-2.983159	-2.693689	-0.661475
21	1	-4.396931	0.546340	1.532855
22	1	-2.184114	1.516206	1.672212
23	1	-1.890227	-0.064842	2.347687
24	6	-5.297011	-1.313448	-0.203285
25	1	-6.021732	-0.716493	0.355277
26	1	-5.462445	-2.369620	0.042312
27	1	-5.511023	-1.204731	-1.273970
28	1	-0.124093	-0.010536	0.937264
29	1	-2.914054	-1.337989	-1.737913
30	6	2.144854	1.020220	0.360830
31	6	2.575732	0.164367	1.386237
32	6	2.707528	0.832363	-0.912657
33	6	3.511055	-0.841356	1.157948
34	1	2.185437	0.292561	2.393923
35	6	3.643637	-0.168444	-1.157689
36	1	2.437599	1.488777	-1.737194
37	6	4.063911	-1.029626	-0.124439
38	1	3.819955	-1.485767	1.976551
39	1	4.060415	-0.282815	-2.154701
40	7	4.953272	-2.058644	-0.372763
41	1	5.519597	-2.003045	-1.206775
42	1	5.425888	-2.475385	0.416141

TS_{A-B}



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.781821 hartrees (-449787.76049571 kcal/mol)
Imaginary Frequencies: 1 (-49.8431 1/cm)
Zero-point correction = 0.372363 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.454569 hartrees (-449582.40659319 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.6206596 hartrees (-449686.630105596 kcal/mol)

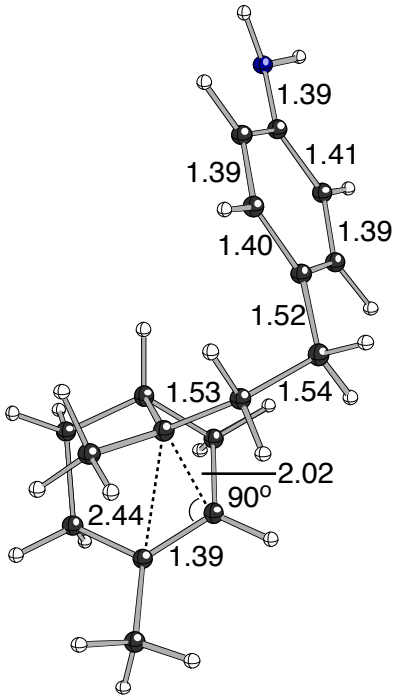
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.3890829 hartrees (-449541.313410579 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.897770	-0.807640	0.301210
2	6	2.114384	0.909287	1.868123
3	1	2.494700	1.933219	1.890876
4	1	2.919748	0.209456	2.079910
5	1	1.392230	0.813572	2.696829
6	6	1.326861	0.622849	0.626058
7	6	0.591460	1.856748	0.149624
8	6	-0.572537	1.852742	-0.862069
9	1	0.211375	2.279090	1.094769
10	1	1.348535	2.591429	-0.156257

11	1	-0.218560	1.592386	-1.863808
12	1	-0.877379	2.905445	-0.937828
13	6	1.127268	-0.833501	-1.224314
14	6	1.844513	-1.839479	0.924625
15	6	2.408344	-0.019341	-1.265593
16	6	3.298438	-1.651942	0.365367
17	6	3.458738	-0.405540	-0.469683
18	1	1.846899	-1.773771	2.016040
19	1	1.474119	-2.837308	0.677008
20	1	3.541100	-2.500590	-0.289593
21	1	2.531605	0.802346	-1.967696
22	1	0.323602	-0.366004	-1.783498
23	1	1.248922	-1.851787	-1.610934
24	6	4.763434	0.322926	-0.437486
25	1	4.774054	1.194823	-1.095207
26	1	5.570828	-0.353205	-0.747658
27	1	5.012293	0.639143	0.583827
28	1	-0.141482	-0.968483	0.616708
29	1	4.044425	-1.676394	1.165638
30	6	-1.775507	1.002510	-0.492624
31	6	-2.359006	0.129588	-1.422410
32	6	-2.390346	1.100921	0.766796
33	6	-3.484544	-0.630820	-1.112131
34	1	-1.941148	0.049486	-2.423839
35	6	-3.513840	0.346833	1.094299
36	1	-2.008317	1.795630	1.512221
37	6	-4.082146	-0.541569	0.159246
38	1	-3.908518	-1.294958	-1.860475
39	1	-3.965180	0.452487	2.077232
40	7	-5.166111	-1.333985	0.497199
41	1	-5.726311	-1.049057	1.287580
42	1	-5.704449	-1.736473	-0.256465

B



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.78194 hartrees (-449787.8351694 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.373006 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.454966 hartrees (-449582.65571466 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.6232291 hartrees (-449688.242492541 kcal/mol)

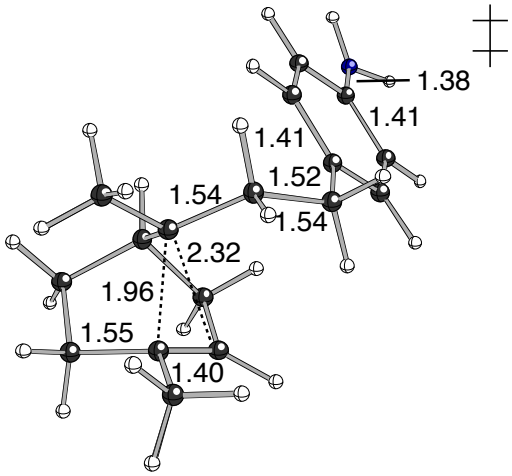
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.3929744 hartrees (-449543.755365744 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.440670	0.571726	0.589370
2	6	0.900736	-0.853648	0.358492
3	6	1.030803	-0.836019	-1.180834
4	6	-0.548284	1.876792	-0.742450
5	6	0.628776	1.824475	0.252134
6	1	1.204068	-1.820921	-1.626880
7	1	-0.108345	-0.993140	0.759735
8	1	0.243295	2.127246	1.238104
9	1	1.344492	2.615960	-0.002900

10	6	2.300643	0.858225	1.803192
11	1	1.618339	0.864431	2.665431
12	1	2.760706	1.848336	1.750377
13	1	3.069638	0.119041	2.018975
14	6	1.887806	-1.897607	0.888440
15	1	1.994289	-1.833696	1.974512
16	1	1.504718	-2.896740	0.666941
17	6	2.256405	0.067562	-1.185536
18	1	2.333454	0.934705	-1.838004
19	6	3.286816	-1.699640	0.200821
20	1	3.418533	-2.478229	-0.565155
21	1	4.113420	-1.825645	0.905375
22	6	3.389329	-0.387829	-0.524125
23	6	4.675847	0.361605	-0.524053
24	1	5.438787	-0.251580	-1.023952
25	1	5.042791	0.520267	0.497109
26	1	4.610178	1.318596	-1.045706
27	1	0.179200	-0.383860	-1.677386
28	1	-0.848458	2.933748	-0.757346
29	1	-0.206810	1.672024	-1.762631
30	6	-1.759484	1.018738	-0.417673
31	6	-2.392659	0.261732	-1.414522
32	6	-2.339446	1.003040	0.861388
33	6	-3.532127	-0.495962	-1.152883
34	1	-2.002667	0.274757	-2.430554
35	6	-3.476363	0.249160	1.141278
36	1	-1.917276	1.604025	1.663984
37	6	-4.094431	-0.522276	0.137165
38	1	-3.993592	-1.068465	-1.953053
39	1	-3.898086	0.263487	2.142854
40	7	-5.192059	-1.317796	0.422751
41	1	-5.723728	-1.099505	1.253135
42	1	-5.762741	-1.620710	-0.353448

TS



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

HF = -716.7690663 hartrees (-449779.756793913 kcal/mol)
Imaginary Frequencies: 1 (-311.2134 1/cm)
Zero-point correction = 0.372645 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.440082 hartrees (-449573.31585582 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.6114251 hartrees (-449680.835364501 kcal/mol)

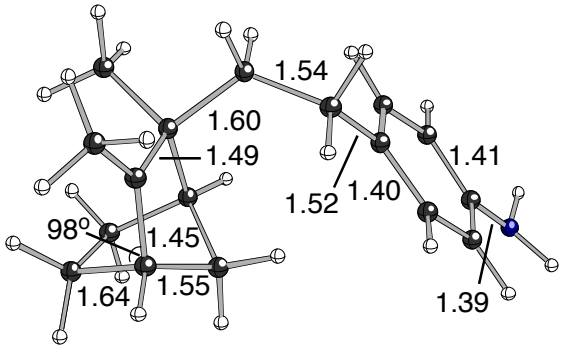
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.3807447 hartrees (-449536.081106697 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.671216	0.093201	0.801249
2	6	-1.114810	1.234610	-0.095052
3	6	-0.740020	0.474750	-1.382716
4	6	0.347530	-1.742411	0.512656
5	6	-0.811094	-1.086152	1.284577
6	1	-0.731622	1.092648	-2.293174
7	1	-0.275021	1.766665	0.360457
8	1	-0.424922	-0.755989	2.258683
9	1	-1.519425	-1.883150	1.541835
10	6	-2.560744	0.503425	1.968255
11	1	-1.923019	1.069882	2.662154
12	1	-2.938544	-0.365195	2.512686
13	1	-3.399179	1.146515	1.713231
14	6	-2.317133	2.136424	-0.415958
15	1	-2.585225	2.772626	0.430800
16	1	-2.084986	2.803265	-1.249961
17	6	-1.798230	-0.568692	-1.415293
18	1	-1.638495	-1.533774	-1.897152
19	6	-3.462743	1.146342	-0.765660
20	1	-3.820797	1.280261	-1.790979
21	1	-4.334348	1.261862	-0.117196
22	6	-2.936836	-0.309180	-0.639501
23	6	-3.961326	-1.390047	-0.390824
24	1	-4.721273	-1.376819	-1.180519
25	1	-4.485158	-1.220389	0.554802
26	1	-3.515825	-2.388361	-0.366706
27	1	0.254191	0.018377	-1.324885
28	1	0.596216	-2.642968	1.091384
29	1	-0.009156	-2.137131	-0.449193
30	6	1.621568	-0.946804	0.289602
31	6	2.461435	-1.269499	-0.792625
32	6	2.070797	0.050604	1.170777
33	6	3.677252	-0.627733	-0.998079
34	1	2.163856	-2.052947	-1.486885
35	6	3.285979	0.702602	0.980137

36	1	1.482411	0.321165	2.043434
37	6	4.116107	0.377523	-0.111984
38	1	4.297121	-0.904911	-1.846343
39	1	3.603264	1.465122	1.686393
40	7	5.299175	1.052452	-0.331554
41	1	5.701183	1.578292	0.430344
42	1	5.975423	0.644009	-0.959688

C



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.7948434 hartrees (-449795.932181934 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.373938 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.465894 hartrees (-449589.51314394 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.6392699 hartrees (-449698.308254949 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -716.4101818 hartrees (-449554.553181318 kcal/mol)

Coordinates (from last standard orientation):

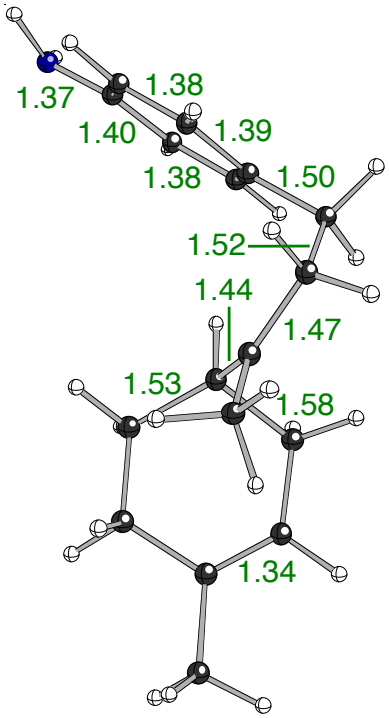
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.776100	-0.495182	0.584626
2	6	-1.052540	0.894095	0.696628
3	6	-0.871553	1.294563	-0.781011
4	6	0.326325	-1.786263	-0.679705
5	6	-0.813809	-1.753130	0.357165
6	1	-0.597571	2.344569	-0.911084
7	1	-0.145898	0.864780	1.300192
8	1	-0.397007	-1.932673	1.353274
9	1	-1.477487	-2.601149	0.156085
10	6	-2.630485	-0.888221	1.826250

11	1	-2.005369	-0.793643	2.718917
12	1	-2.969550	-1.924829	1.764169
13	1	-3.507722	-0.252081	1.959817
14	6	-2.102142	1.947573	1.137520
15	1	-2.580329	1.727942	2.092699
16	1	-1.620866	2.924173	1.232148
17	6	-2.341604	1.032185	-1.177297
18	1	-2.703176	1.238674	-2.184474
19	6	-3.099331	1.941147	-0.045625
20	1	-3.224472	2.911771	-0.533487
21	1	-4.098098	1.574668	0.206706
22	6	-2.638038	-0.267077	-0.608877
23	6	-3.670551	-1.181794	-1.118451
24	1	-4.497359	-0.645888	-1.594315
25	1	-4.038372	-1.895716	-0.380234
26	1	-3.186793	-1.758118	-1.927571
27	1	-0.163596	0.683173	-1.334692
28	1	0.595783	-2.850935	-0.745430
29	1	-0.041681	-1.530844	-1.681011
30	6	1.588517	-0.994159	-0.382984
31	6	2.257275	-0.308090	-1.408323
32	6	2.190986	-0.993058	0.885184
33	6	3.452701	0.370196	-1.184025
34	1	1.846300	-0.313267	-2.416242
35	6	3.383180	-0.316349	1.128598
36	1	1.741618	-1.542913	1.708706
37	6	4.038025	0.384623	0.096182
38	1	3.939406	0.890845	-2.004383
39	1	3.819904	-0.337122	2.123566
40	7	5.196009	1.101782	0.344563
41	1	5.721289	0.872161	1.175805
42	1	5.773827	1.347595	-0.446215

Table 2: R_1/R_2=$CH_3/(CH_2)_2$–*p*–NH_2–Ph (extended) (Fig. S12)

mPWB1K

A_b



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -716.4014291 hartrees (-449549.060774541 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.381884 (Hartree/Particle)

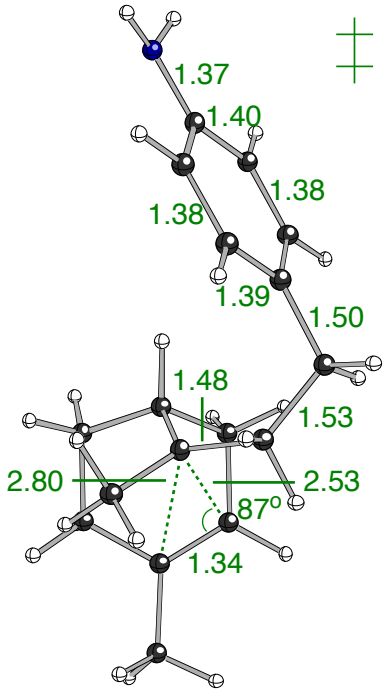
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.066040 hartrees (-449338.6007604 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.966747	-0.083036	0.176067
2	6	-2.037227	1.440489	-1.518908
3	1	-2.001134	2.441994	-1.930270
4	1	-3.001571	1.253893	-1.029233
5	1	-1.984226	0.698501	-2.318323
6	6	-0.987419	1.166477	-0.548842
7	6	-0.023889	2.240405	-0.275411
8	6	1.061220	2.046258	0.767603
9	1	0.408342	2.456122	-1.261559
10	1	-0.613863	3.143986	-0.085846
11	1	0.603535	1.817216	1.730377
12	1	1.545721	3.013490	0.898480
13	6	-1.937871	0.288523	1.366085
14	6	-1.416715	-1.380602	-0.486255
15	6	-3.363031	-0.041272	1.111119

16	6	-2.891734	-1.503067	-0.823166
17	6	-3.812624	-0.861554	0.160304
18	1	-0.803482	-1.562463	-1.366498
19	1	-1.156109	-2.163442	0.222753
20	1	-3.140441	-2.561577	-0.898510
21	1	-4.072471	0.427501	1.779450
22	1	-1.842546	1.334821	1.665162
23	1	-1.543273	-0.279793	2.208856
24	6	-5.261960	-1.169242	0.001338
25	1	-5.873904	-0.609386	0.700869
26	1	-5.442833	-2.230630	0.164070
27	1	-5.601111	-0.945629	-1.009260
28	1	0.020372	-0.222031	0.602087
29	1	-3.115691	-1.103999	-1.814967
30	6	2.080877	0.991868	0.434874
31	6	2.460360	0.053880	1.386720
32	6	2.702988	0.927935	-0.806354
33	6	3.404720	-0.915305	1.117561
34	1	2.016060	0.084662	2.372748
35	6	3.648223	-0.035970	-1.092076
36	1	2.471120	1.654092	-1.573800
37	6	4.017267	-0.981397	-0.134149
38	1	3.674162	-1.628461	1.882191
39	1	4.114619	-0.055122	-2.065787
40	7	4.916240	-1.969570	-0.429706
41	1	5.517389	-1.832800	-1.218160
42	1	5.349012	-2.450288	0.334055

$TS_{A\text{-}B}$



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -716.3918624 hartrees (-449543.057574624 kcal/mol)
Imaginary Frequencies: 1 (-94.5183 1/cm)
Zero-point correction = 0.381465 (Hartree/Particle)

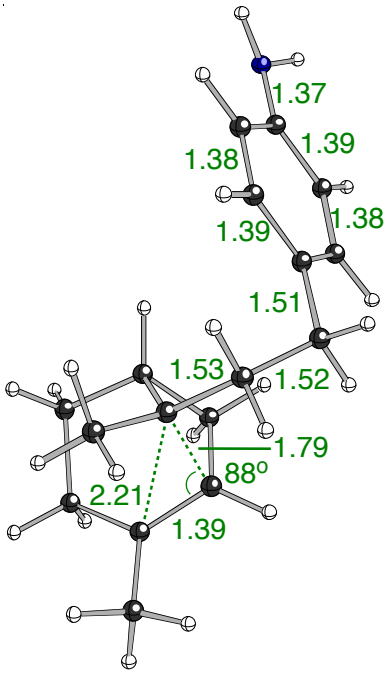
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.055661 hartrees (-449332.08783411 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.804370	-0.677968	-0.075440
2	6	1.669598	0.548955	2.004713
3	1	2.031461	1.519386	2.328377
4	1	2.411328	-0.224411	2.154799
5	1	0.814869	0.294071	2.649618
6	6	1.077399	0.582241	0.667182
7	6	0.544461	1.911607	0.280018
8	6	-0.629547	2.073530	-0.684253
9	1	0.299356	2.396517	1.227783
10	1	1.413225	2.484158	-0.062004
11	1	-0.312337	1.978798	-1.717847
12	1	-0.949030	3.110230	-0.577614
13	6	1.308109	-0.400375	-1.489368
14	6	1.557409	-1.872102	0.474392
15	6	2.678111	0.165114	-1.242502
16	6	3.081502	-1.694041	0.318095
17	6	3.489223	-0.411631	-0.339573
18	1	1.298096	-2.053394	1.514895
19	1	1.220583	-2.746832	-0.073700
20	1	3.479443	-2.504961	-0.293213
21	1	3.019249	1.022821	-1.805895
22	1	0.675995	0.298526	-2.020019
23	1	1.325780	-1.319338	-2.074515
24	6	4.836483	0.121726	-0.008632
25	1	5.076849	1.011974	-0.580505
26	1	5.600934	-0.628621	-0.205763
27	1	4.906403	0.359164	1.053499
28	1	-0.278702	-0.838933	-0.039421
29	1	3.592308	-1.792458	1.275258
30	6	-1.774298	1.144461	-0.409649
31	6	-2.273755	0.307271	-1.397539
32	6	-2.360483	1.069897	0.849526
33	6	-3.303653	-0.578152	-1.145825
34	1	-1.856466	0.348003	-2.394695
35	6	-3.387779	0.189093	1.117817
36	1	-2.029668	1.728210	1.642340
37	6	-3.880142	-0.657422	0.121753
38	1	-3.670035	-1.212708	-1.938946
39	1	-3.827239	0.161948	2.103889
40	7	-4.866575	-1.565666	0.394472

41	1	-5.429581	-1.412092	1.207694
42	1	-5.368844	-1.953603	-0.379613

B



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -716.4017424 hartrees (-449549.257373424 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.385183 (Hartree/Particle)

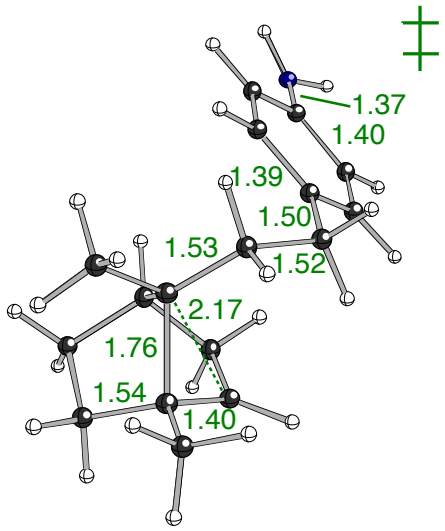
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.060094 hartrees (-449334.86958594 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.487226	-0.474249	0.542254
2	6	-0.825798	0.883881	0.293532
3	6	-0.906268	0.739407	-1.225990
4	6	0.474206	-1.942528	-0.556246
5	6	-0.687141	-1.769099	0.410565
6	1	-1.101006	1.660089	-1.772125
7	1	0.163812	0.993763	0.728489
8	1	-0.314494	-1.943017	1.421923
9	1	-1.407459	-2.569683	0.241822
10	6	-2.369488	-0.634546	1.762815
11	1	-1.703473	-0.659887	2.624428

12	1	-2.906714	-1.579299	1.742910
13	1	-3.080333	0.164512	1.939818
14	6	-1.784988	1.978102	0.698889
15	1	-1.927038	2.001301	1.775775
16	1	-1.390231	2.946026	0.405838
17	6	-2.091051	-0.188845	-1.115389
18	1	-2.178344	-1.107403	-1.681625
19	6	-3.142568	1.725830	-0.003107
20	1	-3.214469	2.374233	-0.881011
21	1	-3.992643	1.961944	0.630211
22	6	-3.235928	0.347097	-0.539486
23	6	-4.499832	-0.402018	-0.467615
24	1	-5.196532	0.075965	-1.160365
25	1	-4.952729	-0.329836	0.518382
26	1	-4.391677	-1.439899	-0.763094
27	1	-0.040372	0.258287	-1.652826
28	1	0.764232	-2.990740	-0.469066
29	1	0.145264	-1.832946	-1.589878
30	6	1.677265	-1.074256	-0.308345
31	6	2.352795	-0.478050	-1.365201
32	6	2.196743	-0.876576	0.966050
33	6	3.476929	0.298691	-1.169316
34	1	2.001732	-0.632597	-2.377380
35	6	3.317789	-0.100745	1.180575
36	1	1.734330	-1.346576	1.822935
37	6	3.980046	0.507691	0.113689
38	1	3.973362	0.746742	-2.017210
39	1	3.693137	0.030997	2.184644
40	7	5.062155	1.322158	0.326087
41	1	5.551654	1.221208	1.193502
42	1	5.662007	1.502993	-0.454744

TS



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):

HF = -716.3885811 hartrees (-449540.998526061 kcal/mol)
Imaginary Frequencies: 1 (-310.0818 1/cm)
Zero-point correction = 0.383717 (Hartree/Particle)

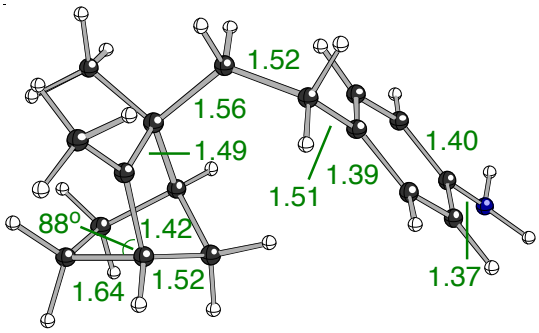
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.047472 hartrees (-449326.94915472 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.622157	-0.016765	0.692068
2	6	-0.946065	1.136269	-0.076664
3	6	-0.743268	0.479600	-1.440462
4	6	0.291057	-1.859244	0.214710
5	6	-0.854347	-1.293260	1.040866
6	1	-0.833150	1.161868	-2.291660
7	1	-0.028324	1.500190	0.373353
8	1	-0.480785	-1.130719	2.051155
9	1	-1.606409	-2.074038	1.163814
10	6	-2.368919	0.373773	1.953035
11	1	-1.634310	0.827314	2.620079
12	1	-2.769449	-0.501746	2.455290
13	1	-3.169967	1.088112	1.813369
14	6	-2.043190	2.172769	-0.223489
15	1	-2.206428	2.713157	0.703956
16	1	-1.793464	2.908896	-0.981300
17	6	-1.852005	-0.483976	-1.416133
18	1	-1.809046	-1.444186	-1.920570
19	6	-3.268509	1.335575	-0.610310
20	1	-3.610627	1.542913	-1.620794
21	1	-4.119938	1.501204	0.043282
22	6	-2.880642	-0.153635	-0.527641
23	6	-3.983968	-1.130682	-0.262086
24	1	-4.746537	-1.055780	-1.033755
25	1	-4.465284	-0.910906	0.687182
26	1	-3.627028	-2.156676	-0.238023
27	1	0.218382	-0.015335	-1.548232
28	1	0.524128	-2.823910	0.668018
29	1	-0.031930	-2.114160	-0.797070
30	6	1.547957	-1.036972	0.142193
31	6	2.383861	-1.134519	-0.966988
32	6	1.966125	-0.207517	1.175987
33	6	3.567836	-0.433608	-1.053285
34	1	2.109188	-1.788713	-1.784341
35	6	3.148228	0.500928	1.105965
36	1	1.373985	-0.110169	2.074472
37	6	3.975101	0.404312	-0.014157
38	1	4.187882	-0.535840	-1.931342
39	1	3.441645	1.134166	1.930060
40	7	5.122680	1.141249	-0.111397
41	1	5.512585	1.516640	0.730297

42	1		5.803544	0.860686	-0.789116

C



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -716.4172033 hartrees (-449558.959242783 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.385023 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-716.075696 hartrees (-449344.65999696 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.729747	-0.449829	0.597814
2	6	-0.991674	0.906896	0.664113
3	6	-0.781242	1.268961	-0.800271
4	6	0.271751	-1.765076	-0.666335
5	6	-0.835889	-1.711167	0.376196
6	1	-0.516726	2.313404	-0.935752
7	1	-0.102241	0.892987	1.282888
8	1	-0.413677	-1.911102	1.359009
9	1	-1.523063	-2.536728	0.190927
10	6	-2.573414	-0.771935	1.834304
11	1	-1.959459	-0.648021	2.722641
12	1	-2.917825	-1.802203	1.813600
13	1	-3.444236	-0.129779	1.935167
14	6	-2.044762	1.947548	1.038997
15	1	-2.493006	1.801118	2.015067
16	1	-1.607100	2.940984	1.023164
17	6	-2.200534	0.976398	-1.241182
18	1	-2.555948	1.181622	-2.241701
19	6	-3.047807	1.781921	-0.096192
20	1	-3.338248	2.691499	-0.615712
21	1	-3.977610	1.301119	0.208829
22	6	-2.581561	-0.231757	-0.599054
23	6	-3.669240	-1.111424	-1.021826

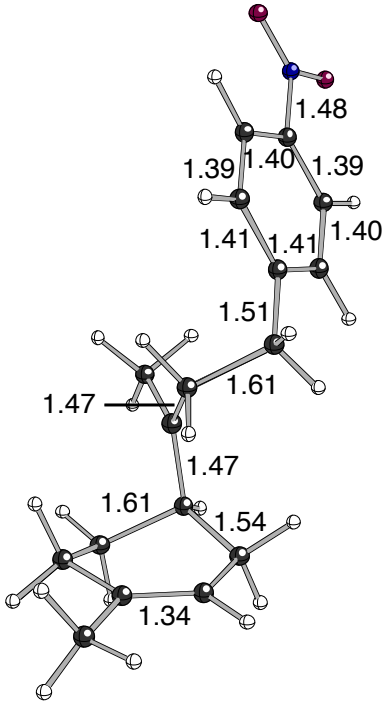
24	1	-4.369334	-0.624467	-1.691779
25	1	-4.182035	-1.584282	-0.190391
26	1	-3.181939	-1.909189	-1.593398
27	1	-0.053282	0.662180	-1.321110
28	1	0.522946	-2.822743	-0.764044
29	1	-0.103098	-1.477304	-1.650440
30	6	1.532843	-0.998842	-0.368523
31	6	2.237931	-0.386969	-1.397865
32	6	2.086540	-0.929159	0.903689
33	6	3.424969	0.280361	-1.176343
34	1	1.856109	-0.439426	-2.409390
35	6	3.271941	-0.263085	1.143798
36	1	1.604823	-1.414254	1.740766
37	6	3.965505	0.359381	0.106305
38	1	3.940908	0.745544	-2.003181
39	1	3.671863	-0.228993	2.146433
40	7	5.115078	1.066421	0.346992
41	1	5.607225	0.871823	1.196704
42	1	5.715762	1.247929	-0.433006

3.8. R_1=CH_3, R_2=$(CH_2)_2$–*p*–NO_2–Ph

Table 1: R_1/R_2=$CH_3/(CH_2)_2$–*p*–NO_2–Ph (aligned) (Fig. S13)

B3LYP

A_a



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

HF = -865.9321957 hartrees (-543381.112123707 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.357677 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.624595 hartrees (-543188.08960845 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.7277482 hartrees (-543252.819272982 kcal/mol)

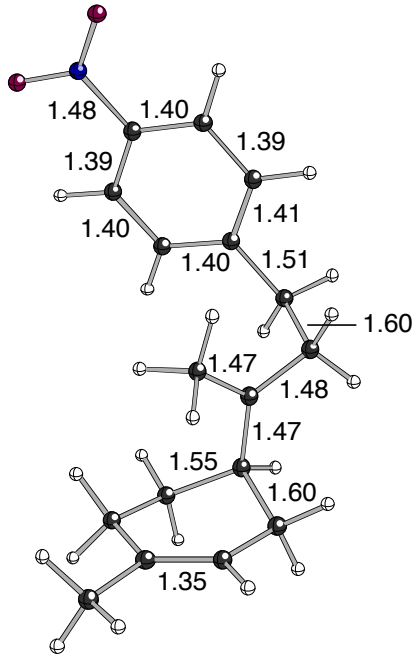
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.4699745 hartrees (-543091.063698495 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.278795	-0.284170	1.142998
2	6	4.780599	-0.552922	-0.072764
3	6	4.333829	0.221513	-1.295314
4	6	3.609547	1.526431	-0.968555
5	6	2.540766	1.375912	0.218897
6	6	3.248849	0.776861	1.451094
7	1	5.213079	0.474996	-1.902027
8	1	4.641029	-0.845546	2.001889
9	1	4.317220	2.262903	-0.574459
10	1	3.143654	1.964621	-1.854832
11	1	3.729028	1.612027	1.979687
12	1	2.510796	0.386056	2.161840
13	1	3.722468	-0.426308	-1.942340
14	6	5.811521	-1.625036	-0.307782
15	1	6.744380	-1.191173	-0.688416
16	1	6.041289	-2.174815	0.608114
17	1	5.469457	-2.344417	-1.062807
18	1	2.215852	2.406047	0.415652
19	6	1.398282	0.660569	-0.359808
20	6	0.440134	1.412722	-1.185602
21	1	-0.518858	1.409396	-0.630015
22	1	0.731444	2.446490	-1.374162
23	1	0.208619	0.889366	-2.120452
24	6	1.155101	-0.769594	-0.130177
25	1	0.748113	-1.249019	-1.024390
26	1	2.068803	-1.273018	0.188799
27	6	0.074064	-0.977006	1.042863
28	1	0.186859	-2.035946	1.294753
29	1	0.376644	-0.406039	1.923396
30	6	-1.355123	-0.677662	0.675801
31	6	-2.034180	0.403727	1.263687
32	6	-2.046416	-1.500779	-0.231570
33	6	-3.370167	0.666943	0.954923
34	1	-1.527315	1.032365	1.991346
35	6	-3.376934	-1.249542	-0.554243

36	1	-1.549865	-2.358545	-0.677938
37	6	-4.015859	-0.162732	0.043836
38	1	-3.908096	1.490991	1.408005
39	1	-3.924097	-1.879353	-1.245418
40	7	-5.430743	0.114553	-0.299739
41	8	-5.971334	-0.639453	-1.104797
42	8	-5.961434	1.081408	0.241327

A_b



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.934365 hartrees (-543382.47338115 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.357649 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.626698 hartrees (-543189.40926198 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.7297563 hartrees (-543254.079375813 kcal/mol)

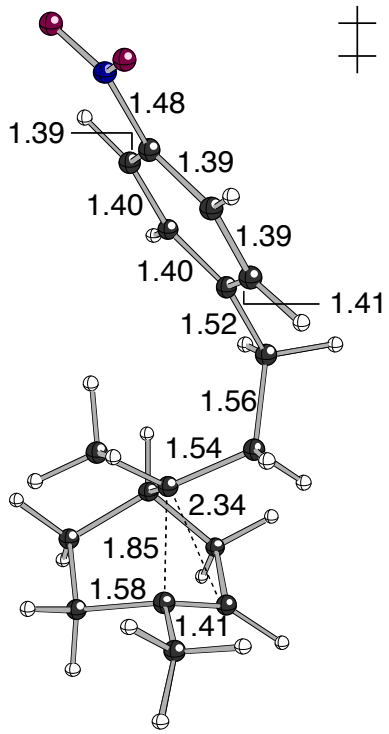
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.4713516 hartrees (-543091.927842516 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z

1	6	4.391188	0.218002	-0.902342
2	6	4.179595	1.393731	-0.274907
3	6	3.329175	1.479951	0.966972
4	6	2.935867	0.131701	1.588463
5	6	2.685465	-1.038575	0.602368
6	6	3.912249	-1.115948	-0.424884
7	1	3.863922	2.065595	1.726154
8	1	4.964637	0.206062	-1.827051
9	1	3.752570	-0.212697	2.231750
10	1	2.066064	0.252918	2.242466
11	1	4.688650	-1.639565	0.148536
12	1	3.689422	-1.771571	-1.276486
13	1	2.442471	2.089272	0.736546
14	6	4.744035	2.688992	-0.790944
15	1	5.436127	3.123113	-0.058998
16	1	5.283979	2.553269	-1.730807
17	1	3.952318	3.431569	-0.950387
18	1	2.696464	-1.977308	1.164362
19	6	1.506292	-1.040688	-0.269320
20	6	1.074334	0.173892	-0.963548
21	1	0.808983	0.950935	-0.230820
22	1	1.954855	0.599607	-1.484667
23	1	0.249382	0.018209	-1.656498
24	6	0.775830	-2.304991	-0.480597
25	1	0.347773	-2.351668	-1.485585
26	1	1.430620	-3.165489	-0.314170
27	6	-0.418479	-2.436408	0.567630
28	1	-0.771314	-3.464446	0.436474
29	1	-0.013023	-2.365233	1.581025
30	6	-1.557000	-1.462895	0.375870
31	6	-1.774938	-0.427135	1.297228
32	6	-2.429493	-1.593506	-0.717761
33	6	-2.828289	0.472561	1.130915
34	1	-1.133071	-0.332159	2.169380
35	6	-3.484761	-0.702599	-0.901906
36	1	-2.297992	-2.406959	-1.426813
37	6	-3.661369	0.323233	0.025564
38	1	-3.013828	1.271128	1.839122
39	1	-4.168278	-0.795406	-1.737296
40	7	-4.772767	1.282173	-0.168109
41	8	-5.497034	1.115706	-1.146557
42	8	-4.890411	2.183007	0.660023

TS



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.906161 hartrees (-543364.77508911 kcal/mol)
Imaginary Frequencies: 1 (-304.9548 1/cm)
Zero-point correction = 0.358274 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.595621 hartrees (-543169.90813371 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.7103073 hartrees (-543241.874933823 kcal/mol)

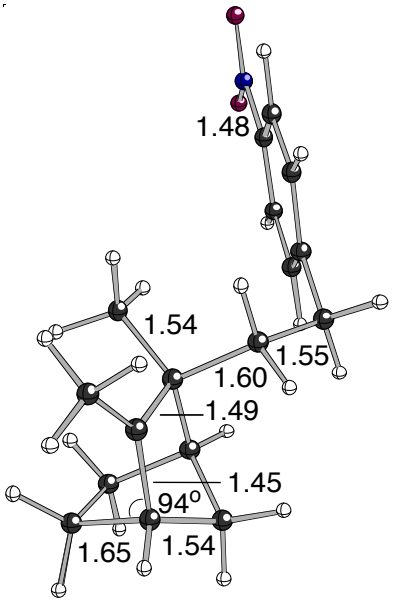
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.4582635 hartrees (-543083.714928885 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-4.120570	0.264313	0.802105
2	6	-3.508984	0.949311	-0.265368
3	6	-3.893902	0.288015	-1.645508
4	6	-3.421381	-1.186216	-1.624548
5	6	-2.761626	-1.337989	-0.242138
6	6	-3.869921	-1.197283	0.818879
7	1	-4.972946	0.388602	-1.785889
8	1	-4.613501	0.772328	1.633805

9	1	-4.251550	-1.887069	-1.742557
10	1	-2.716751	-1.393668	-2.432480
11	1	-4.789108	-1.771174	0.620242
12	1	-3.563707	-1.501694	1.828299
13	1	-3.414791	0.881737	-2.427019
14	6	-3.440240	2.461680	-0.250382
15	1	-4.396318	2.889809	-0.570835
16	1	-3.209227	2.855492	0.743220
17	1	-2.679424	2.821113	-0.948580
18	1	-2.167922	-2.248965	-0.138458
19	6	-1.954015	-0.020850	-0.026072
20	6	-0.995516	0.402849	-1.122592
21	1	-0.150843	-0.298594	-1.106205
22	1	-1.408062	0.384547	-2.129418
23	1	-0.578050	1.393705	-0.928584
24	6	-1.321728	0.202962	1.362807
25	1	-0.971594	1.239193	1.419148
26	1	-2.064516	0.098889	2.158122
27	6	-0.150359	-0.755194	1.732473
28	1	-0.040552	-0.680326	2.821685
29	1	-0.444340	-1.791910	1.535109
30	6	1.204052	-0.485834	1.105616
31	6	1.843092	-1.467593	0.332905
32	6	1.865898	0.734003	1.325293
33	6	3.099404	-1.239405	-0.230257
34	1	1.363079	-2.429950	0.175722
35	6	3.118394	0.982405	0.769213
36	1	1.409746	1.498405	1.948935
37	6	3.713753	-0.010212	-0.008811
38	1	3.600935	-1.991927	-0.826698
39	1	3.638660	1.918233	0.933917
40	7	5.038590	0.249396	-0.611362
41	8	5.551441	1.346742	-0.398834
42	8	5.537627	-0.647033	-1.289122

C



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.9369612 hartrees (-543384.102522612 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.360194 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.624576 hartrees (-543188.07768576 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.7434122 hartrees (-543262.648589622 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.4932641 hartrees (-543105.678155391 kcal/mol)

Coordinates (from last standard orientation):

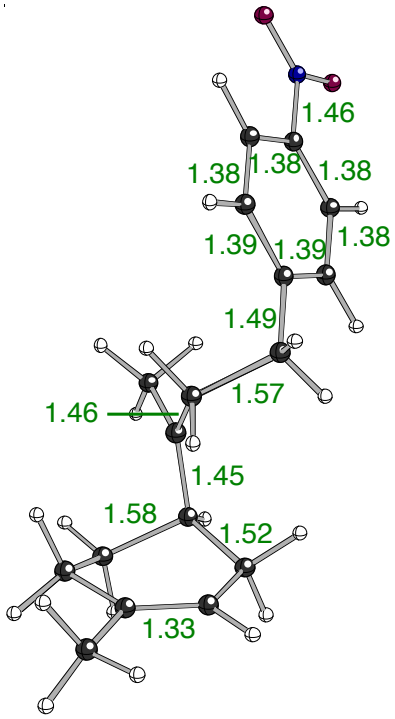
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-4.239449	-0.060117	0.141342
2	6	-3.247380	0.770403	-0.503316
3	6	-4.173766	-1.228568	-1.020016
4	6	-2.898733	-2.021894	-0.655295
5	6	-2.261092	-1.142327	0.447538
6	6	-3.504265	-0.785385	1.286042
7	1	-5.110748	-1.773498	-0.873366
8	1	-5.244871	0.338023	0.270388
9	1	-3.155580	-3.001869	-0.245043
10	1	-2.247579	-2.187683	-1.514307
11	1	-4.055738	-1.661939	1.633612
12	1	-3.317002	-0.134723	2.142909

13	1	-4.186830	-0.839242	-2.041778
14	6	-3.545638	1.922446	-1.370153
15	1	-4.600702	1.985671	-1.642587
16	1	-3.304987	2.825353	-0.783168
17	1	-2.906459	1.960805	-2.256842
18	1	-1.434837	-1.616215	0.975542
19	6	-1.883704	0.241209	-0.194937
20	6	-0.933847	0.186171	-1.408597
21	1	-0.027908	-0.363552	-1.150277
22	1	-1.394908	-0.310987	-2.265934
23	1	-0.630724	1.187658	-1.723890
24	6	-1.348664	1.284377	0.893520
25	1	-1.011294	2.164110	0.336455
26	1	-2.168320	1.627072	1.534662
27	6	-0.221367	0.789557	1.833607
28	1	-0.086178	1.595896	2.566259
29	1	-0.563694	-0.077247	2.406094
30	6	1.116724	0.486817	1.190613
31	6	1.642493	-0.813673	1.202970
32	6	1.871739	1.513127	0.598122
33	6	2.875742	-1.099080	0.616117
34	1	1.093315	-1.615887	1.688528
35	6	3.103635	1.248814	0.004469
36	1	1.503804	2.535897	0.609681
37	6	3.582507	-0.060907	0.015220
38	1	3.291674	-2.099356	0.622608
39	1	3.695456	2.032541	-0.452823
40	7	4.883290	-0.354416	-0.623703
41	8	5.480525	0.584041	-1.147712
42	8	5.278408	-1.518508	-0.594073

Table 1: R_1/R_2=$CH_3/(CH_2)_2$–*p*–NO_2–Ph (aligned) (Fig. S13)

mPWB1K

A_a



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -865.4773571 hartrees (-543095.696353821 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.368006 (Hartree/Particle)

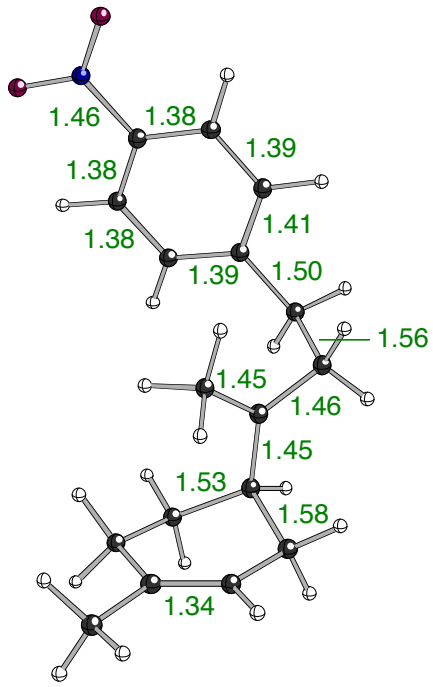
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.158168 hartrees (-542895.40200168 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.180210	-0.134153	1.146086
2	6	4.645811	-0.474783	-0.052653
3	6	4.128259	0.180408	-1.296836
4	6	3.423683	1.488217	-1.022255
5	6	2.393877	1.387889	0.167639
6	6	3.118948	0.886213	1.407865
7	1	4.961909	0.379815	-1.969570
8	1	4.597301	-0.606669	2.024788
9	1	4.140027	2.229235	-0.672738
10	1	2.950446	1.889764	-1.914031
11	1	3.564428	1.754843	1.894468
12	1	2.404631	0.497411	2.132861
13	1	3.484671	-0.516346	-1.842998
14	6	5.703403	-1.507995	-0.240783
15	1	5.984852	-1.970318	0.699683

16	1	5.368217	-2.291273	-0.919809
17	1	6.595502	-1.068610	-0.684528
18	1	2.020186	2.403157	0.303322
19	6	1.320832	0.587612	-0.394060
20	6	0.345959	1.239064	-1.255068
21	1	-0.580615	1.263040	-0.658598
22	1	0.606039	2.256897	-1.521543
23	1	0.093340	0.640575	-2.126984
24	6	1.180249	-0.835928	-0.116582
25	1	0.802369	-1.367428	-0.985952
26	1	2.127921	-1.255338	0.209474
27	6	0.146270	-1.040626	1.051468
28	1	0.252489	-2.091792	1.309707
29	1	0.451598	-0.471728	1.924316
30	6	-1.273344	-0.733133	0.699867
31	6	-1.948101	0.294416	1.350054
32	6	-1.939788	-1.473133	-0.272726
33	6	-3.263434	0.589327	1.037333
34	1	-1.450775	0.861903	2.123246
35	6	-3.250561	-1.190254	-0.599854
36	1	-1.439028	-2.291193	-0.770631
37	6	-3.885592	-0.156607	0.060733
38	1	-3.806949	1.376671	1.532754
39	1	-3.787762	-1.754180	-1.344311
40	7	-5.269702	0.155887	-0.288498
41	8	-5.783725	-0.516176	-1.147923
42	8	-5.792897	1.066320	0.304822

A_b



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):

HF = -865.479166 hartrees (-543096.83145666 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.369414 (Hartree/Particle)

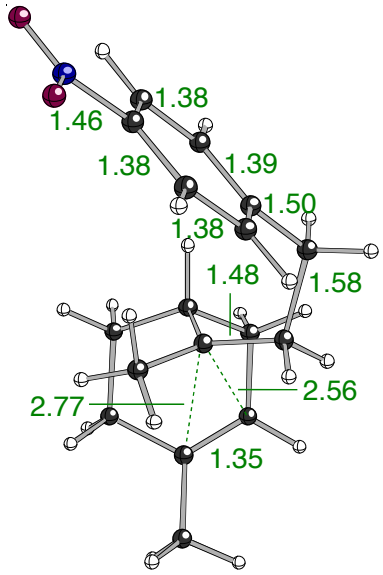
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.157558 hartrees (-542895.01922058 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-4.193727	-0.288258	-0.786351
2	6	-3.857062	-1.466064	-0.256669
3	6	-2.897493	-1.566632	0.881226
4	6	-2.581119	-0.247619	1.560272
5	6	-2.491360	0.978224	0.656347
6	6	-3.735954	1.038949	-0.306417
7	1	-3.306821	-2.246724	1.628089
8	1	-4.865441	-0.266112	-1.633512
9	1	-3.374392	-0.020741	2.269445
10	1	-1.667437	-0.330203	2.146061
11	1	-4.506862	1.538964	0.281065
12	1	-3.560697	1.701667	-1.157662
13	1	-1.993316	-2.068608	0.530032
14	6	-4.394262	-2.753007	-0.780324
15	1	-4.985236	-3.254524	-0.015480
16	1	-5.022930	-2.604658	-1.651933
17	1	-3.587566	-3.433799	-1.048672
18	1	-2.518685	1.878340	1.266415
19	6	-1.417928	1.111747	-0.308227
20	6	-0.939634	-0.027455	-1.066072
21	1	-0.488009	-0.735590	-0.362869
22	1	-1.806869	-0.563693	-1.475690
23	1	-0.223510	0.230466	-1.835071
24	6	-0.819627	2.431757	-0.513919
25	1	-0.417744	2.534017	-1.517752
26	1	-1.539568	3.222085	-0.313670
27	6	0.343415	2.586745	0.517331
28	1	0.726605	3.592947	0.363276
29	1	-0.064284	2.551150	1.524854
30	6	1.435023	1.573845	0.357739
31	6	1.600261	0.567018	1.300364
32	6	2.281288	1.617248	-0.744735
33	6	2.583050	-0.393945	1.146921
34	1	0.971271	0.543085	2.179145
35	6	3.267400	0.665399	-0.915310
36	1	2.184068	2.410249	-1.472467
37	6	3.392968	-0.329745	0.033327
38	1	2.734431	-1.177212	1.870971
39	1	3.938339	0.684499	-1.758043
40	7	4.424030	-1.347888	-0.146186
41	8	5.125162	-1.254504	-1.123129

42	8	4.494215	-2.212951	0.692349

TS_{A-B}



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -865.4728241 hartrees (-543092.851850991 kcal/mol)
Imaginary Frequencies: 1 (-57.5275 1/cm)
Zero-point correction = 0.368131 (Hartree/Particle)

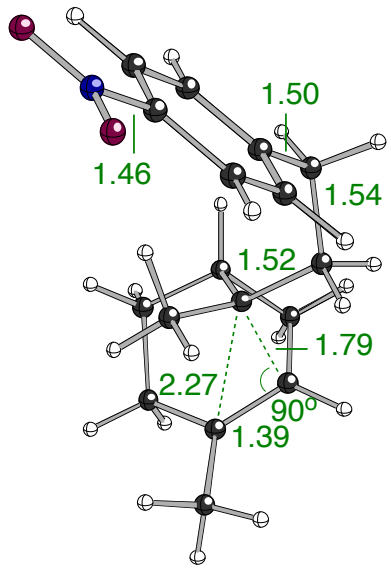
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.151947 hartrees (-542891.49826197 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.050639	0.643925	-0.173993
2	6	4.203950	-0.543574	0.437426
3	6	3.614812	-1.800786	-0.120581
4	6	2.540623	-1.565658	-1.185260
5	6	2.011671	-0.141796	-1.109120
6	6	3.162272	0.818965	-1.369796
7	1	4.429712	-2.387565	-0.544960
8	1	4.599974	1.498640	0.196896
9	1	2.954974	-1.695250	-2.181059
10	1	1.741349	-2.297474	-1.098008
11	1	3.666207	0.583871	-2.306244
12	1	2.821188	1.847190	-1.459169
13	1	3.242095	-2.409414	0.703714
14	6	5.057053	-0.699111	1.647733

15	1	5.878905	-1.384648	1.445876
16	1	5.476147	0.246498	1.975041
17	1	4.489300	-1.131110	2.470890
18	1	1.183168	-0.014960	-1.818438
19	6	1.458427	0.218614	0.226597
20	6	0.904880	-0.784800	1.116259
21	1	-0.176960	-0.723151	0.895137
22	1	1.226834	-1.800079	0.938775
23	1	0.989518	-0.500537	2.161474
24	6	1.156325	1.623896	0.560022
25	1	0.855849	1.704431	1.600075
26	1	2.024973	2.254821	0.404582
27	6	0.017082	2.165919	-0.350665
28	1	-0.132475	3.198240	-0.041881
29	1	0.359705	2.186952	-1.382597
30	6	-1.262882	1.397799	-0.235931
31	6	-1.736811	0.645791	-1.303947
32	6	-1.979091	1.404693	0.958722
33	6	-2.896793	-0.099753	-1.187793
34	1	-1.213590	0.659665	-2.249141
35	6	-3.137528	0.665385	1.093155
36	1	-1.638146	2.005638	1.789631
37	6	-3.568759	-0.081691	0.014963
38	1	-3.286243	-0.683400	-2.005394
39	1	-3.710533	0.661939	2.005642
40	7	-4.785853	-0.877955	0.153779
41	8	-5.346836	-0.841021	1.220873
42	8	-5.135189	-1.519167	-0.806378

B



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -865.4821264 hartrees (-543098.689137264 kcal/mol)
Imaginary Frequencies: none found

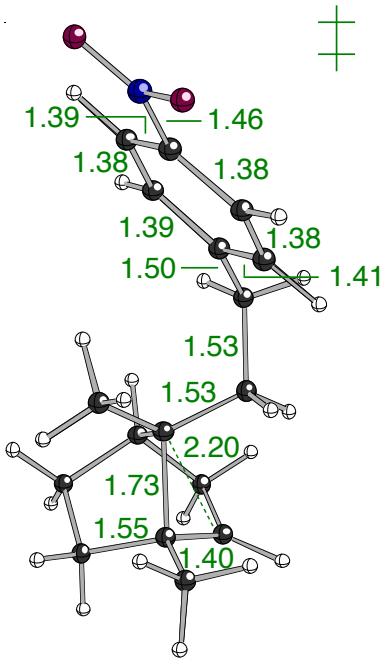
Zero-point correction = 0.370548 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.158554 hartrees (-542895.64422054 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.500596	-0.011764	-0.931384
2	6	3.627502	1.202449	-0.265024
3	6	3.980212	1.158454	1.170089
4	6	3.301624	-0.025359	1.896564
5	6	2.786760	-1.005479	0.868176
6	6	3.895714	-1.249582	-0.155960
7	1	5.064747	1.011077	1.184165
8	1	3.434252	0.007042	-2.011297
9	1	4.013762	-0.515231	2.553339
10	1	2.492778	0.344854	2.520362
11	1	4.910276	-1.242517	0.234938
12	1	3.758772	-2.149462	-0.741840
13	1	3.791983	2.111786	1.654980
14	6	3.404654	2.489298	-0.935573
15	1	4.358003	3.023618	-0.938071
16	1	3.068941	2.384058	-1.960842
17	1	2.715815	3.112843	-0.368406
18	1	2.329164	-1.874984	1.332780
19	6	1.908206	-0.275091	-0.151080
20	6	1.011759	0.842482	0.309229
21	1	0.182612	0.391438	0.851372
22	1	1.476226	1.554925	0.983232
23	1	0.582312	1.380272	-0.532122
24	6	1.227412	-1.142471	-1.203149
25	1	0.885294	-0.498154	-2.011556
26	1	1.941666	-1.834448	-1.637608
27	6	0.051529	-1.976651	-0.676004
28	1	-0.127616	-2.745965	-1.427041
29	1	0.347725	-2.510483	0.225216
30	6	-1.239260	-1.251444	-0.427336
31	6	-1.881950	-1.370935	0.798299
32	6	-1.827961	-0.476784	-1.421930
33	6	-3.077339	-0.720651	1.044041
34	1	-1.449208	-1.987042	1.572768
35	6	-3.018499	0.184181	-1.194760
36	1	-1.364894	-0.396625	-2.394676
37	6	-3.618709	0.055505	0.041920
38	1	-3.588152	-0.804590	1.988668
39	1	-3.490221	0.786390	-1.953324
40	7	-4.868579	0.763524	0.293282
41	8	-5.307915	1.442710	-0.603037
42	8	-5.373045	0.625987	1.381196

TS



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -865.4674009 hartrees (-543089.448738759 kcal/mol)
Imaginary Frequencies: 1 (-309.5897 1/cm)
Zero-point correction = 0.369673 (Hartree/Particle)

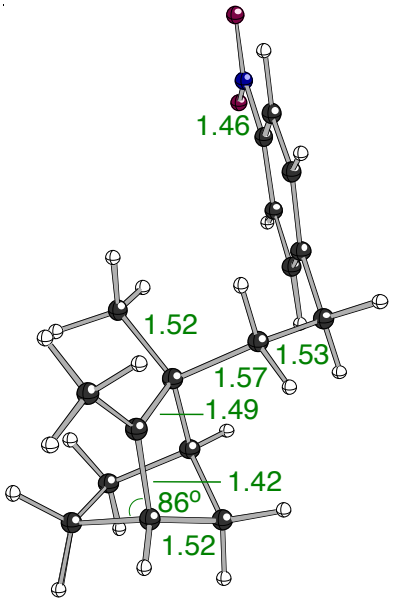
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.143569 hartrees (-542886.24098319 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.880118	0.408415	-0.965514
2	6	3.211759	1.113289	0.045206
3	6	3.823782	0.812465	1.437505
4	6	3.636204	-0.680123	1.721902
5	6	3.023632	-1.200838	0.434364
6	6	4.049924	-1.023594	-0.680454
7	1	4.866697	1.115819	1.433869
8	1	4.106423	0.839036	-1.936872
9	1	4.572925	-1.178721	1.950768
10	1	2.974241	-0.844401	2.566177
11	1	5.084050	-1.243132	-0.394898
12	1	3.863018	-1.614210	-1.575105
13	1	3.317136	1.449792	2.156152
14	6	2.773407	2.525210	-0.202990

15	1	3.611796	3.208612	-0.091804
16	1	2.358938	2.655700	-1.198931
17	1	2.020193	2.818899	0.522709
18	1	2.621913	-2.206458	0.508795
19	6	1.996268	-0.120062	0.042479
20	6	0.993550	0.272877	1.097393
21	1	0.412697	-0.616218	1.343825
22	1	1.434781	0.637249	2.017075
23	1	0.292043	1.012450	0.722523
24	6	1.301465	-0.305518	-1.304665
25	1	0.890514	0.656623	-1.609988
26	1	2.015700	-0.583501	-2.078319
27	6	0.186401	-1.357531	-1.301796
28	1	0.082806	-1.719643	-2.324094
29	1	0.490464	-2.222813	-0.713125
30	6	-1.162017	-0.883082	-0.836889
31	6	-1.837073	-1.551814	0.175935
32	6	-1.769362	0.215199	-1.436086
33	6	-3.079259	-1.125919	0.607619
34	1	-1.390930	-2.422428	0.634760
35	6	-3.009095	0.657305	-1.019145
36	1	-1.281733	0.728672	-2.252135
37	6	-3.638736	-0.018862	0.006230
38	1	-3.613757	-1.632536	1.393804
39	1	-3.494535	1.504254	-1.474444
40	7	-4.941035	0.450357	0.463938
41	8	-5.401081	1.423496	-0.083010
42	8	-5.465662	-0.163503	1.361151

C



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -865.5022713 hartrees (-543111.330263463 kcal/mol)

Imaginary Frequencies: none found
Zero-point correction = 0.370924 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.177732 hartrees (-542907.67860732 kcal/mol)

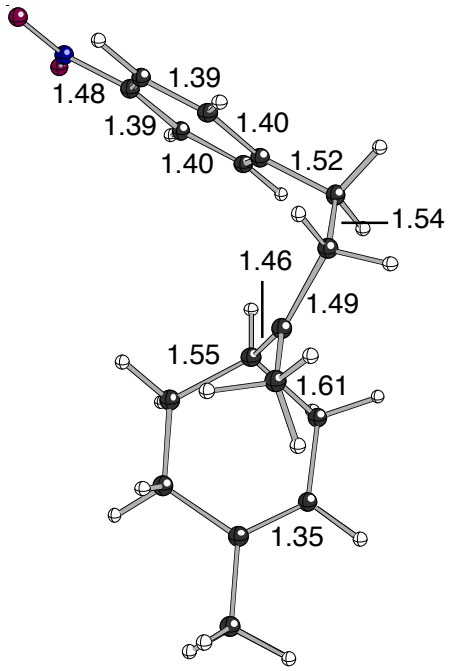
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.091490	0.167860	0.135864
2	6	3.159435	-0.676507	-0.525423
3	6	3.841484	1.200223	-1.108744
4	6	2.639349	2.015140	-0.657321
5	6	2.078897	1.133163	0.452433
6	6	3.341421	0.862711	1.257021
7	1	4.790701	1.723779	-1.190173
8	1	5.124327	-0.137248	0.228610
9	1	2.951734	2.972030	-0.250011
10	1	1.940339	2.208915	-1.463189
11	1	3.839184	1.769090	1.586824
12	1	3.205155	0.210140	2.114919
13	1	3.689141	0.723897	-2.078897
14	6	3.487689	-1.802914	-1.400463
15	1	4.531062	-1.819314	-1.694254
16	1	3.299753	-2.701575	-0.804674
17	1	2.834952	-1.861339	-2.266509
18	1	1.238348	1.559346	0.986179
19	6	1.780580	-0.244177	-0.176966
20	6	0.820054	-0.223551	-1.357110
21	1	-0.077197	0.332152	-1.104407
22	1	1.268629	0.243753	-2.231182
23	1	0.512426	-1.228273	-1.634160
24	6	1.375013	-1.312261	0.892731
25	1	1.043508	-2.194386	0.346764
26	1	2.242497	-1.628097	1.473950
27	6	0.297002	-0.871930	1.879117
28	1	0.171337	-1.686678	2.591813
29	1	0.648618	-0.019666	2.456616
30	6	-1.024629	-0.550185	1.248398
31	6	-1.570445	0.723148	1.344569
32	6	-1.720543	-1.530062	0.546833
33	6	-2.771438	1.030854	0.731092
34	1	-1.060630	1.485845	1.915149
35	6	-2.919171	-1.243594	-0.072962
36	1	-1.328390	-2.535384	0.490451
37	6	-3.417424	0.041412	0.021860
38	1	-3.210393	2.012614	0.795639
39	1	-3.472937	-1.988870	-0.619182
40	7	-4.675163	0.360664	-0.644789
41	8	-5.212103	-0.525421	-1.264127
42	8	-5.086472	1.490252	-0.536165

Table 2: R_1/R_2=$CH_3/(CH_2)_2$–*p*–NO_2–Ph (extended) (Fig. S14)

B3LYP

A_b



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.9314943 hartrees (-543380.671988193 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.357065 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.625062 hartrees (-543188.38265562 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.7274102 hartrees (-543252.607174602 kcal/mol)

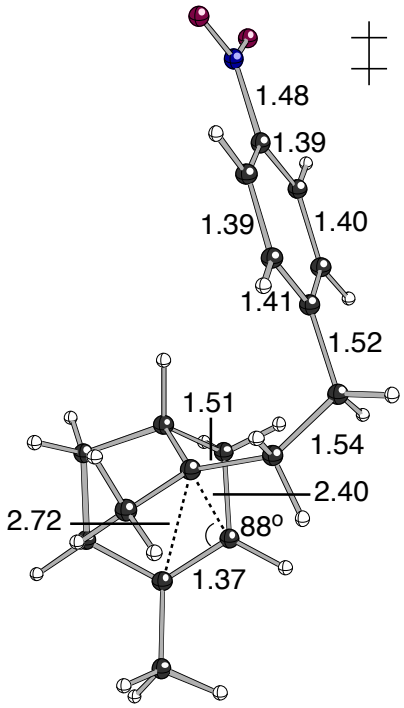
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.469444 hartrees (-543090.73080444 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.625434	0.031528	0.339577
2	6	-2.713180	1.289316	-1.585650

3	1	-2.737353	2.253708	-2.094146
4	1	-3.696325	1.054744	-1.138050
5	1	-2.560269	0.486542	-2.322920
6	6	-1.683959	1.194301	-0.541333
7	6	-0.788622	2.370675	-0.374859
8	6	0.329305	2.379688	0.681509
9	1	-0.381231	2.560479	-1.382709
10	1	-1.455084	3.240096	-0.235993
11	1	-0.092098	2.200373	1.676350
12	1	0.716818	3.405612	0.709483
13	6	-2.797858	0.319864	1.401797
14	6	-1.813741	-1.400069	-0.232412
15	6	-4.137754	-0.204064	0.995979
16	6	-3.223522	-1.774541	-0.710366
17	6	-4.355018	-1.176274	0.085776
18	1	-1.080148	-1.570469	-1.026797
19	1	-1.529818	-2.065752	0.589350
20	1	-3.311694	-2.868691	-0.691487
21	1	-4.988155	0.246675	1.503740
22	1	-2.863398	1.384164	1.661935
23	1	-2.429214	-0.178398	2.307995
24	6	-5.734429	-1.691925	-0.220022
25	1	-6.505265	-1.153063	0.335582
26	1	-5.809116	-2.755743	0.036760
27	1	-5.958920	-1.613015	-1.290949
28	1	-0.687822	0.053728	0.893162
29	1	-3.371731	-1.513673	-1.768951
30	6	1.484585	1.422870	0.432359
31	6	1.947580	0.594622	1.466594
32	6	2.142449	1.381693	-0.808103
33	6	3.026923	-0.267459	1.273100
34	1	1.472146	0.631291	2.443431
35	6	3.220978	0.524719	-1.021718
36	1	1.834081	2.035783	-1.619280
37	6	3.641631	-0.293981	0.024274
38	1	3.392763	-0.907944	2.066577
39	1	3.738563	0.488950	-1.972753
40	7	4.777309	-1.215782	-0.197799
41	8	5.290896	-1.219911	-1.314697
42	8	5.126917	-1.918926	0.747853

$TS_{A\text{-}B}$



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.9158495 hartrees (-543370.854719745 kcal/mol)
Imaginary Frequencies: 1 (-74.0872 1/cm)
Zero-point correction = 0.357889 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.605939 hartrees (-543176.38278189 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.7149678 hartrees (-543244.799444178 kcal/mol)

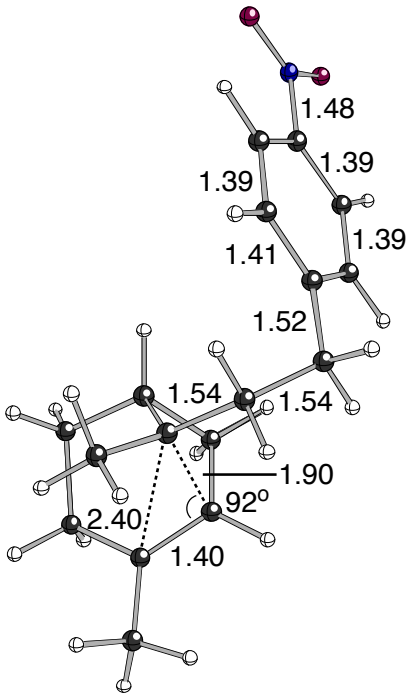
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.4611124 hartrees (-543085.502642124 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.404319	-0.773926	0.158914
2	6	2.517300	0.750153	1.968513
3	1	2.928532	1.751596	2.114881
4	1	3.269955	-0.003692	2.189179
5	1	1.716756	0.617342	2.719182
6	6	1.836163	0.598972	0.651879
7	6	1.251070	1.903979	0.168152
8	6	0.131117	2.022883	-0.886238
9	1	0.899820	2.379699	1.097502

10	1	2.095805	2.545772	-0.119662
11	1	0.492536	1.754832	-1.881179
12	1	-0.091579	3.096151	-0.943596
13	6	1.790651	-0.731264	-1.334484
14	6	2.204221	-1.909704	0.810726
15	6	3.155522	-0.073450	-1.235448
16	6	3.724199	-1.802728	0.445733
17	6	4.074473	-0.568848	-0.350858
18	1	2.074051	-1.917311	1.896439
19	1	1.796014	-2.856510	0.448863
20	1	4.006022	-2.668061	-0.170214
21	1	3.428242	0.738493	-1.906120
22	1	1.103974	-0.145913	-1.938978
23	1	1.827475	-1.735670	-1.772402
24	6	5.439370	0.021689	-0.184120
25	1	5.601958	0.887311	-0.830060
26	1	6.203200	-0.731064	-0.418212
27	1	5.616066	0.315665	0.858827
28	1	0.327149	-0.896541	0.344972
29	1	4.355542	-1.868322	1.337933
30	6	-1.156053	1.277795	-0.575644
31	6	-1.737050	0.430265	-1.530813
32	6	-1.816045	1.457647	0.652486
33	6	-2.931453	-0.242421	-1.269432
34	1	-1.264726	0.301334	-2.500812
35	6	-3.008087	0.792830	0.933575
36	1	-1.417118	2.141376	1.397295
37	6	-3.542959	-0.057322	-0.032808
38	1	-3.387685	-0.896460	-2.002782
39	1	-3.527361	0.929368	1.874530
40	7	-4.800907	-0.777489	0.262445
41	8	-5.247867	-1.515826	-0.612743
42	8	-5.310737	-0.593709	1.366055

B



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.9171441 hartrees (-543371.667094191 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.359303 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.605639 hartrees (-543176.19452889 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.7209355 hartrees (-543248.544235605 kcal/mol)

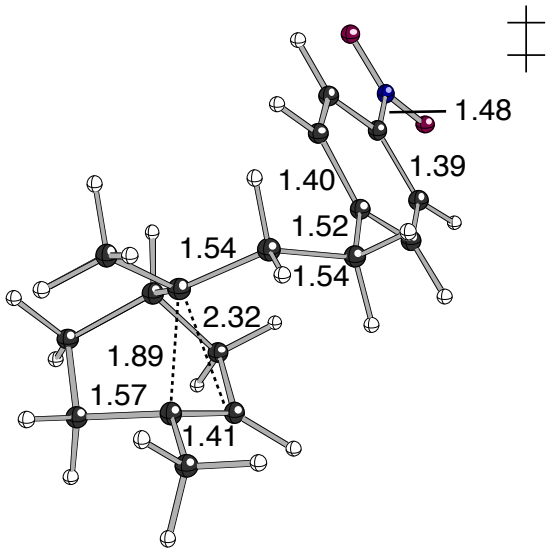
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.4699422 hartrees (-543091.043429922 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.086097	0.496118	0.613877
2	6	1.415281	-0.875139	0.358275
3	6	1.513456	-0.759199	-1.180209
4	6	0.179790	2.048038	-0.593312
5	6	1.320869	1.819169	0.418151
6	1	1.630965	-1.708325	-1.712146
7	1	0.415272	-0.970878	0.791366
8	1	0.929647	2.030305	1.423779
9	1	2.074703	2.598046	0.253919

10	6	2.991858	0.666503	1.826280
11	1	2.338301	0.720222	2.706729
12	1	3.551407	1.604875	1.783408
13	1	3.691047	-0.148781	2.006053
14	6	2.340310	-2.016638	0.790726
15	1	2.490722	-2.021916	1.873368
16	1	1.882038	-2.973210	0.528357
17	6	2.783213	0.087396	-1.102870
18	1	2.924003	0.982581	-1.705937
19	6	3.727401	-1.878338	0.064532
20	1	3.757570	-2.589150	-0.776163
21	1	4.566365	-2.140483	0.714237
22	6	3.914552	-0.527510	-0.551496
23	6	5.251488	0.117274	-0.551437
24	1	5.923601	-0.495911	-1.170418
25	1	5.694109	0.118874	0.451526
26	1	5.239130	1.129153	-0.960583
27	1	0.686144	-0.217984	-1.625667
28	1	-0.042159	3.121752	-0.526890
29	1	0.526814	1.899917	-1.621057
30	6	-1.121128	1.291692	-0.373947
31	6	-1.806533	0.742810	-1.469342
32	6	-1.702805	1.182186	0.900498
33	6	-3.024098	0.082429	-1.306496
34	1	-1.394807	0.842990	-2.470431
35	6	-2.917757	0.524361	1.084983
36	1	-1.222173	1.627930	1.766628
37	6	-3.556610	-0.025380	-0.024733
38	1	-3.557799	-0.341604	-2.148487
39	1	-3.374246	0.438935	2.063750
40	7	-4.838226	-0.737479	0.163898
41	8	-5.276117	-0.819954	1.310150
42	8	-5.378305	-1.204999	-0.836839

TS



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.9016121 hartrees (-543361.920608871 kcal/mol)
Imaginary Frequencies: 1 (-296.4871 1/cm)
Zero-point correction = 0.358431 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.590057 hartrees (-543166.41666807 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.7060762 hartrees (-543239.219876262 kcal/mol)

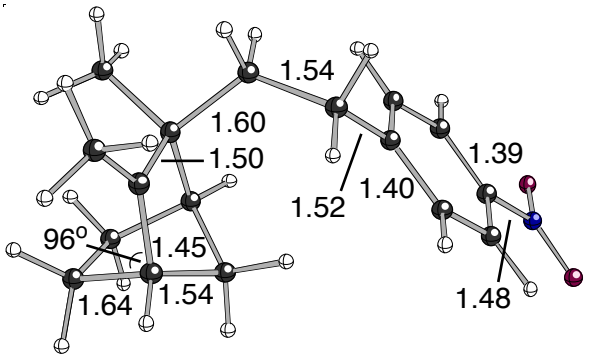
mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.4549554 hartrees (-543081.639063054 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.264208	0.195528	0.757288
2	6	-1.603471	1.241586	-0.189483
3	6	-1.243300	0.381545	-1.416839
4	6	-0.364874	-1.786687	0.674314
5	6	-1.484890	-0.988278	1.366188
6	1	-1.195875	0.934440	-2.368552
7	1	-0.748073	1.757755	0.253680
8	1	-1.090541	-0.601465	2.314522
9	1	-2.245771	-1.714105	1.677050
10	6	-3.141590	0.749236	1.877762
11	1	-2.476848	1.313680	2.546587
12	1	-3.591521	-0.051262	2.469425
13	1	-3.927104	1.431410	1.562691
14	6	-2.747147	2.180927	-0.610707
15	1	-3.000325	2.892782	0.177754
16	1	-2.463793	2.769386	-1.486672
17	6	-2.349957	-0.606839	-1.413916
18	1	-2.248209	-1.590545	-1.875641
19	6	-3.928394	1.219727	-0.911931
20	1	-4.257354	1.277386	-1.953172
21	1	-4.808185	1.416595	-0.295539
22	6	-3.464575	-0.250621	-0.635860
23	6	-4.549604	-1.262989	-0.347346
24	1	-5.266929	-1.293043	-1.174986
25	1	-5.111424	-0.986497	0.549476
26	1	-4.151124	-2.271888	-0.208493
27	1	-0.275660	-0.121610	-1.330687
28	1	-0.192292	-2.657482	1.321567
29	1	-0.718758	-2.224282	-0.268794
30	6	0.982735	-1.120990	0.444492
31	6	1.788134	-1.559478	-0.621982
32	6	1.491499	-0.131817	1.301683

33	6	3.055984	-1.024098	-0.841830
34	1	1.426966	-2.341990	-1.284859
35	6	2.757772	0.416541	1.097257
36	1	0.915208	0.212875	2.154387
37	6	3.518996	-0.034424	0.021967
38	1	3.680862	-1.359967	-1.660656
39	1	3.159734	1.176331	1.756764
40	7	4.857177	0.552439	-0.207032
41	8	5.234450	1.420932	0.577127
42	8	5.499066	0.135468	-1.168747

C



B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.9301507 hartrees (-543379.828865757 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.360071 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.617843 hartrees (-543183.85266093 kcal/mol)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.7362767 hartrees (-543258.170992017 kcal/mol)

mPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -865.4862985 hartrees (-543101.307171735 kcal/mol)

Coordinates (from last standard orientation):

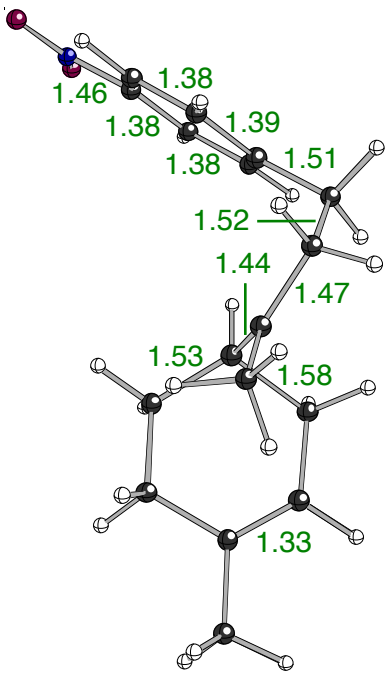
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.358504	-0.426810	0.611800
2	6	-1.556682	0.921298	0.700790
3	6	-1.356952	1.293878	-0.782336
4	6	-0.382732	-1.866873	-0.686502
5	6	-1.477946	-1.738750	0.391929
6	1	-1.029691	2.326676	-0.924890
7	1	-0.654405	0.851145	1.308141

8	1	-1.038792	-1.922077	1.377109
9	1	-2.194522	-2.551376	0.233990
10	6	-3.223115	-0.750789	1.865388
11	1	-2.590085	-0.668663	2.753758
12	1	-3.613890	-1.770159	1.827451
13	1	-4.067519	-0.070100	1.990545
14	6	-2.546729	2.035858	1.128933
15	1	-3.027555	1.859163	2.091464
16	1	-2.015866	2.988310	1.200664
17	6	-2.836517	1.101513	-1.176948
18	1	-3.191035	1.319973	-2.183755
19	6	-3.551897	2.056788	-0.045503
20	1	-3.639468	3.021787	-0.552546
21	1	-4.564058	1.738649	0.218708
22	6	-3.214813	-0.161142	-0.583602
23	6	-4.314805	-1.010030	-1.064578
24	1	-5.093580	-0.431249	-1.569622
25	1	-4.741435	-1.663298	-0.302011
26	1	-3.872995	-1.656068	-1.844782
27	1	-0.684055	0.643386	-1.336141
28	1	-0.194907	-2.946560	-0.769508
29	1	-0.757911	-1.572658	-1.673507
30	6	0.958855	-1.196243	-0.431691
31	6	1.653998	-0.599977	-1.495982
32	6	1.571106	-1.226184	0.831899
33	6	2.910995	-0.025538	-1.310814
34	1	1.216029	-0.592179	-2.490985
35	6	2.826153	-0.655487	1.038664
36	1	1.083958	-1.712746	1.671573
37	6	3.474350	-0.054012	-0.037956
38	1	3.451391	0.435989	-2.128426
39	1	3.305770	-0.676282	2.009825
40	7	4.798961	0.566320	0.176086
41	8	5.340527	1.092858	-0.794152
42	8	5.268635	0.519531	1.311576

Table 2: R_1/R_2=$CH_3/(CH_2)_2$–*p*–NO_2–Ph (extended) (Fig. S14)

mPWB1K

A_b



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -865.4766893 hartrees (-543095.277302643 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.367929 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.157921 hartrees (-542895.24700671 kcal/mol)

Coordinates (from last standard orientation):

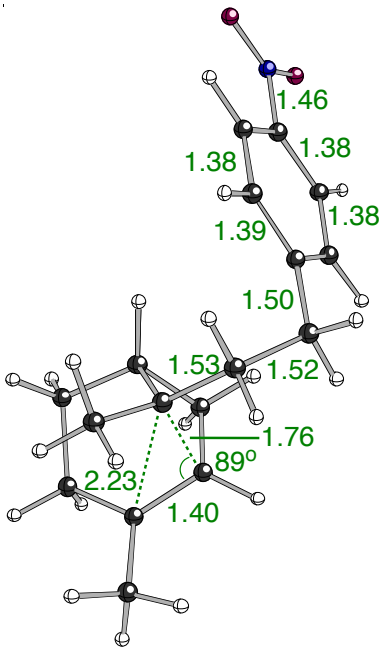
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.511758	-0.048966	0.205797
2	6	-2.688553	1.238583	-1.609811
3	1	-2.753545	2.213184	-2.078210
4	1	-3.642694	0.966377	-1.139006
5	1	-2.525294	0.465056	-2.363891
6	6	-1.646718	1.140704	-0.599680
7	6	-0.816091	2.334509	-0.372835
8	6	0.257389	2.322109	0.699497
9	1	-0.398120	2.562132	-1.360859
10	1	-1.511049	3.168075	-0.225532
11	1	-0.189754	2.083087	1.663780
12	1	0.626288	3.342811	0.792606
13	6	-2.565423	0.296344	1.337557
14	6	-1.797743	-1.433350	-0.367174
15	6	-3.936638	-0.197221	1.058356
16	6	-3.237209	-1.738275	-0.740275

17	6	-4.260179	-1.126912	0.157800
18	1	-1.135189	-1.613391	-1.211256
19	1	-1.485489	-2.128270	0.409355
20	1	-3.369174	-2.820149	-0.736616
21	1	-4.717527	0.244435	1.662172
22	1	-2.590036	1.363548	1.569552
23	1	-2.144441	-0.174729	2.226422
24	6	-5.662341	-1.594288	-0.028658
25	1	-6.357657	-1.052733	0.603942
26	1	-5.741244	-2.654274	0.207642
27	1	-5.977740	-1.480707	-1.064875
28	1	-0.535583	-0.052958	0.676972
29	1	-3.460865	-1.446727	-1.768585
30	6	1.419184	1.400501	0.443158
31	6	1.916430	0.619476	1.480404
32	6	2.033463	1.333716	-0.802598
33	6	2.994290	-0.222800	1.285479
34	1	1.463187	0.676659	2.459553
35	6	3.110317	0.494684	-1.017787
36	1	1.693068	1.953597	-1.618831
37	6	3.565686	-0.274876	0.031926
38	1	3.393627	-0.833486	2.078119
39	1	3.602335	0.432461	-1.974199
40	7	4.693134	-1.174585	-0.191856
41	8	5.164803	-1.200426	-1.302266
42	8	5.067738	-1.831515	0.748241

TS_{A-B}

We were unable to locate **TS_{A-B}** at this level of theory.

B



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -865.4791084 hartrees (-543096.795312084 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.370550 (Hartree/Particle)

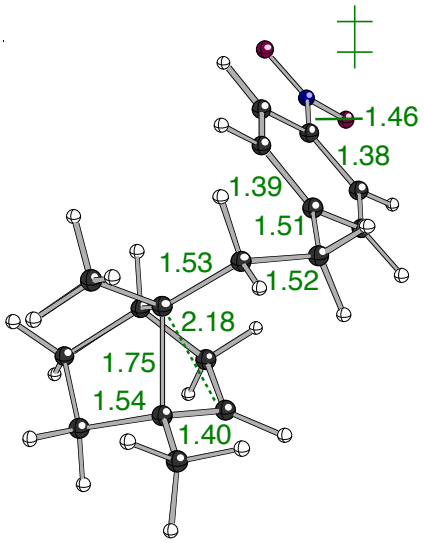
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.154937 hartrees (-542893.37451687 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.078382	0.438496	0.564046
2	6	1.319577	-0.869360	0.310477
3	6	1.406174	-0.703331	-1.206962
4	6	0.233962	2.072016	-0.509919
5	6	1.351106	1.780126	0.481434
6	1	1.533533	-1.622853	-1.774036
7	1	0.330591	-0.924515	0.757201
8	1	0.964318	1.928097	1.491167
9	1	2.116916	2.546116	0.364916
10	6	2.989608	0.517299	1.773285
11	1	2.348245	0.587791	2.650607
12	1	3.604781	1.413323	1.750586
13	1	3.635030	-0.340658	1.925694
14	6	2.200904	-2.037560	0.689619
15	1	2.354715	-2.084241	1.764038
16	1	1.730816	-2.969563	0.391474
17	6	2.655029	0.138262	-1.070646
18	1	2.818688	1.048737	-1.633727
19	6	3.565882	-1.884190	-0.025608
20	1	3.572326	-2.517710	-0.918384
21	1	4.401463	-2.205538	0.589071
22	6	3.768750	-0.512943	-0.540869
23	6	5.091833	0.120988	-0.483933
24	1	5.731070	-0.416187	-1.189832
25	1	5.552795	-0.002358	0.493546
26	1	5.075413	1.165781	-0.773288
27	1	0.582084	-0.150396	-1.629784
28	1	0.020763	3.136024	-0.400068
29	1	0.576856	1.962027	-1.537923
30	6	-1.056450	1.321575	-0.319983
31	6	-1.739468	0.824608	-1.424259
32	6	-1.620268	1.156157	0.941609
33	6	-2.940573	0.155831	-1.283721
34	1	-1.335022	0.973324	-2.415674
35	6	-2.818634	0.488714	1.104145
36	1	-1.137142	1.564272	1.816486
37	6	-3.452795	-0.009892	-0.014927
38	1	-3.480131	-0.233709	-2.130901

39	1	-3.269608	0.354026	2.073257
40	7	-4.710360	-0.730144	0.149254
41	8	-5.131209	-0.856411	1.273600
42	8	-5.238053	-1.153784	-0.850092

TS



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -865.4641502 hartrees (-543087.408892002 kcal/mol)
Imaginary Frequencies: 1 (-304.2534 1/cm)
Zero-point correction = 0.369316 (Hartree/Particle)

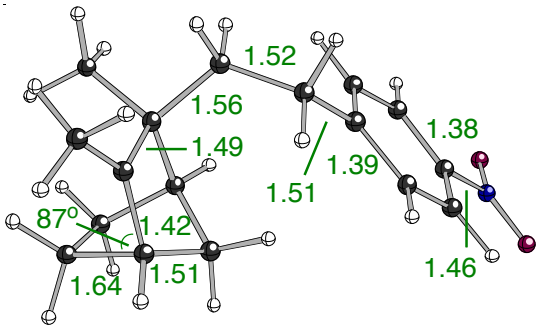
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.140319 hartrees (-542884.20157569 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.210416	0.104377	0.686298
2	6	-1.440941	1.148540	-0.147429
3	6	-1.195942	0.361243	-1.432273
4	6	-0.398649	-1.892277	0.488272
5	6	-1.517258	-1.155331	1.209261
6	1	-1.210214	0.966432	-2.344927
7	1	-0.536151	1.523605	0.319286
8	1	-1.156733	-0.889456	2.202288
9	1	-2.312332	-1.875723	1.404428
10	6	-3.008220	0.642907	1.858911
11	1	-2.294592	1.117031	2.533969
12	1	-3.489517	-0.162247	2.406115
13	1	-3.755573	1.381629	1.602760

14	6	-2.481262	2.209590	-0.455197
15	1	-2.668229	2.843740	0.405655
16	1	-2.159618	2.858703	-1.263545
17	6	-2.348840	-0.548296	-1.393671
18	1	-2.331400	-1.540510	-1.834234
19	6	-3.719636	1.386300	-0.829419
20	1	-4.000925	1.508109	-1.871825
21	1	-4.596277	1.642696	-0.241916
22	6	-3.399991	-0.105076	-0.584536
23	6	-4.557118	-1.013309	-0.302153
24	1	-5.260487	-0.994973	-1.131318
25	1	-5.095438	-0.681616	0.581422
26	1	-4.242868	-2.042191	-0.148480
27	1	-0.258238	-0.186247	-1.453709
28	1	-0.236741	-2.808240	1.058220
29	1	-0.716721	-2.245338	-0.494371
30	6	0.932094	-1.203392	0.350271
31	6	1.755944	-1.554171	-0.716509
32	6	1.393829	-0.266928	1.267847
33	6	2.999760	-0.978555	-0.882520
34	1	1.423676	-2.298013	-1.426874
35	6	2.636527	0.321603	1.117999
36	1	0.795304	0.008837	2.122452
37	6	3.414008	-0.038982	0.038278
38	1	3.645459	-1.240374	-1.704072
39	1	3.008883	1.047703	1.821585
40	7	4.716529	0.595075	-0.135058
41	8	5.045263	1.413347	0.689010
42	8	5.368450	0.260586	-1.093771

C



mPWB1K/6-31+G(d,p)//mPWB1K/6-31+G(d,p):
HF = -865.4949143 hartrees (-543106.713672393 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.371070 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-865.169791 hartrees (-542902.69555041 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.289898	-0.391646	0.615997
2	6	-1.463855	0.913794	0.662086
3	6	-1.261699	1.263765	-0.807339
4	6	-0.420346	-1.843024	-0.699626
5	6	-1.489302	-1.709190	0.376084
6	1	-0.937545	2.290463	-0.948130
7	1	-0.567965	0.848152	1.268374
8	1	-1.056239	-1.939275	1.347055
9	1	-2.233321	-2.487671	0.209983
10	6	-3.119612	-0.657891	1.874434
11	1	-2.475934	-0.581310	2.746992
12	1	-3.537771	-1.660597	1.860988
13	1	-3.939332	0.043976	2.000678
14	6	-2.442277	2.018807	1.055926
15	1	-2.874702	1.902785	2.042978
16	1	-1.946821	2.984249	1.024965
17	6	-2.704148	1.057195	-1.220934
18	1	-3.067152	1.287842	-2.212917
19	6	-3.480064	1.908398	-0.053792
20	1	-3.734666	2.829427	-0.572028
21	1	-4.427734	1.481367	0.275855
22	6	-3.156574	-0.114262	-0.561635
23	6	-4.313485	-0.917324	-0.954755
24	1	-4.989273	-0.387164	-1.616787
25	1	-4.844131	-1.343312	-0.109274
26	1	-3.898128	-1.754349	-1.526718
27	1	-0.585555	0.617880	-1.350620
28	1	-0.243632	-2.914230	-0.807329
29	1	-0.794609	-1.522761	-1.672441
30	6	0.912819	-1.194133	-0.437218
31	6	1.619932	-0.629298	-1.493630
32	6	1.495254	-1.198962	0.825367
33	6	2.863916	-0.060776	-1.302355
34	1	1.196147	-0.640561	-2.488007
35	6	2.738724	-0.634694	1.038301
36	1	0.993426	-1.659484	1.662515
37	6	3.397693	-0.065561	-0.031071
38	1	3.420345	0.381306	-2.112039
39	1	3.202756	-0.632918	2.010527
40	7	4.701879	0.548698	0.187772
41	8	5.242326	1.050498	-0.767804
42	8	5.145952	0.517515	1.309795

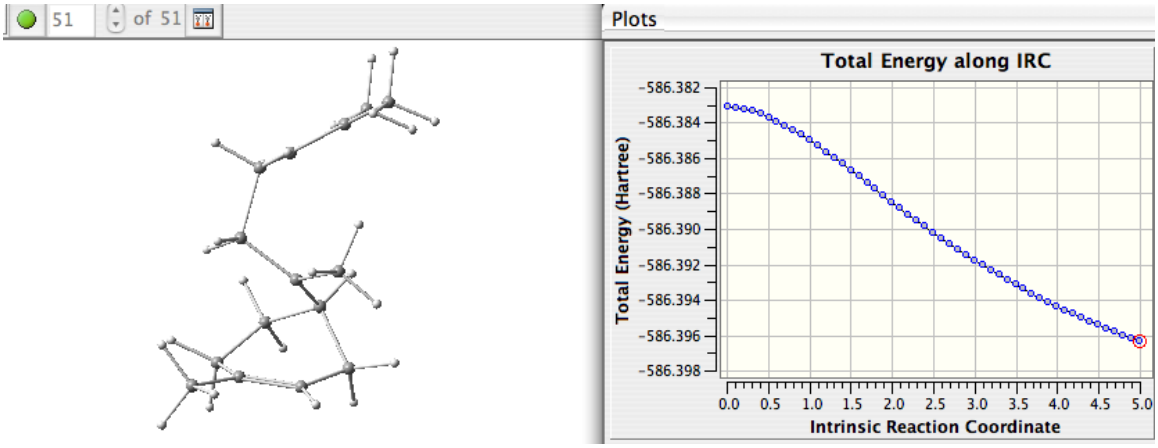
4. IRC Plots

4.1. R_1=prenyl/CH_3, R_2=CH_3/prenyl

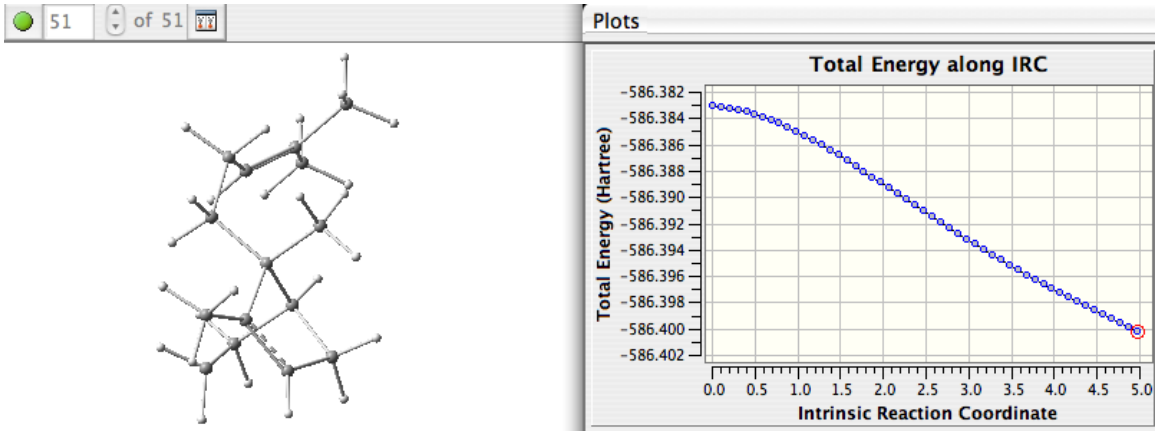
Table 1: R_1/R_2=prenyl/CH_3 (aligned) (Fig. S1)

B3LYP

A→TS

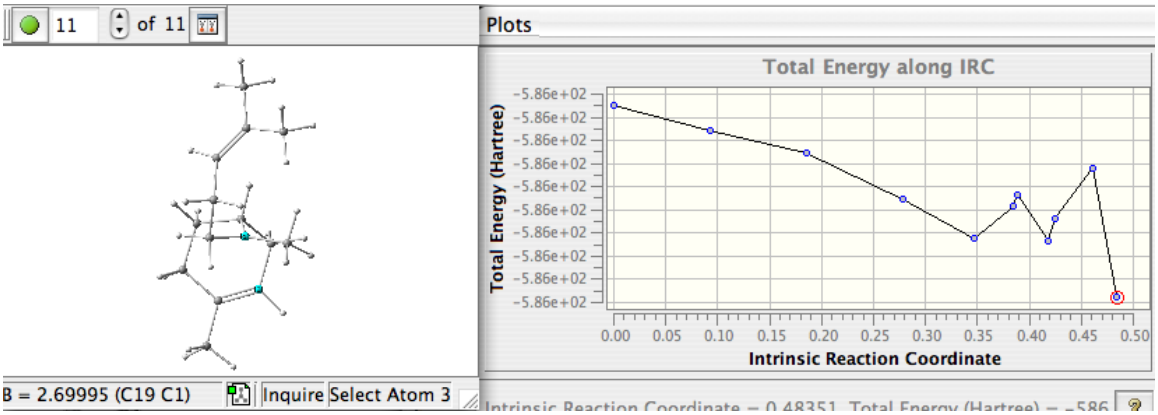


TS→C

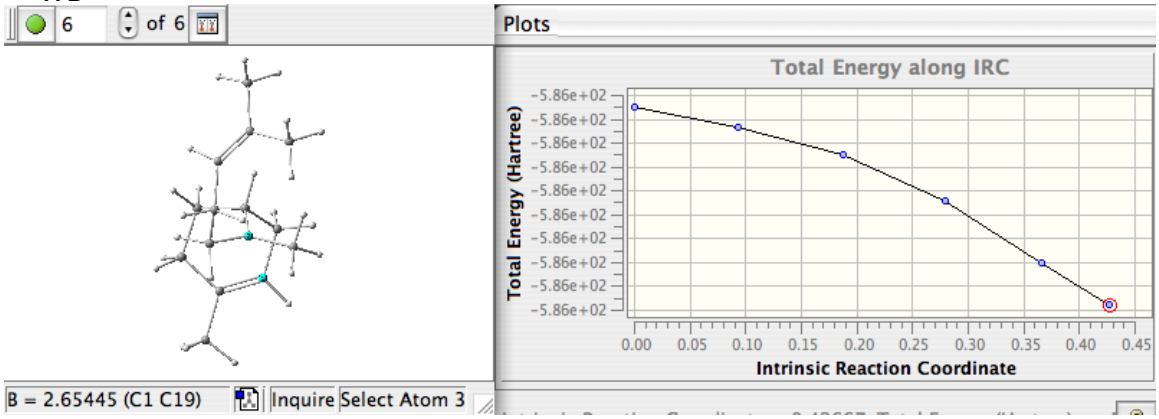


mPWB1K

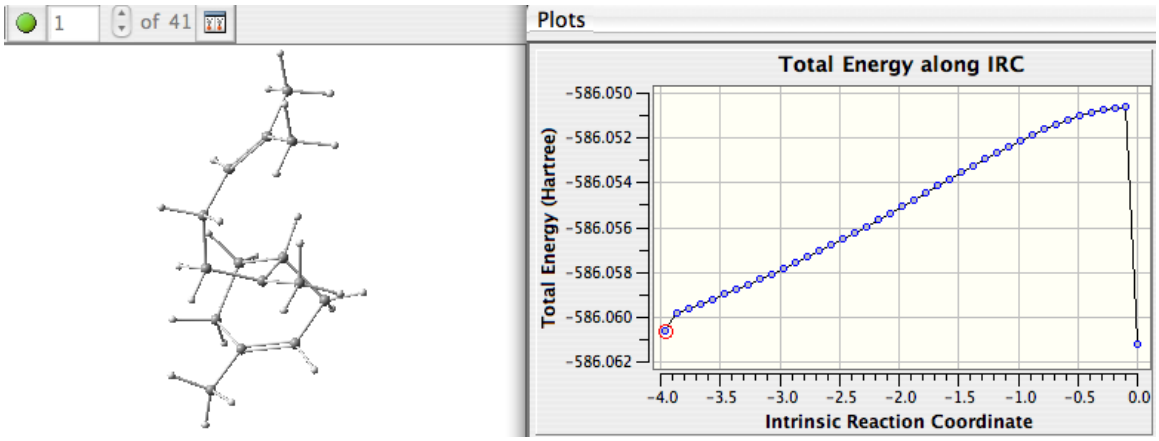
A→TS_{A-B}



TS_{A-B}→B



B→TS



TS→C

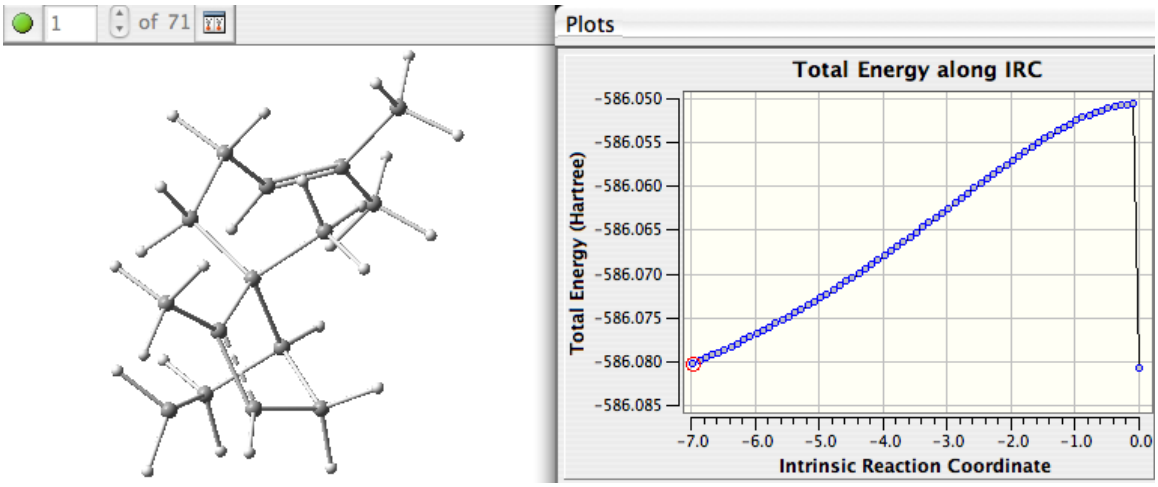
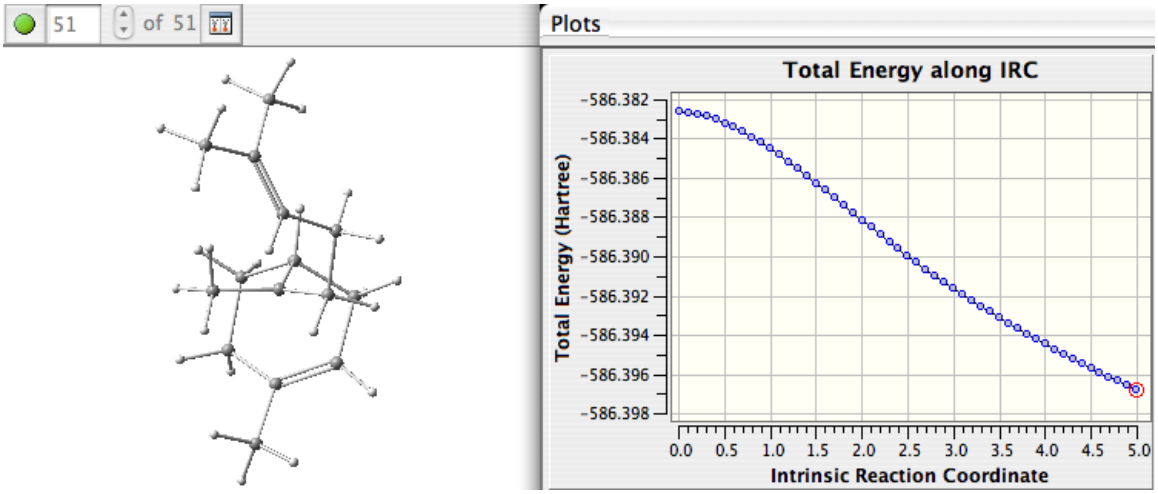


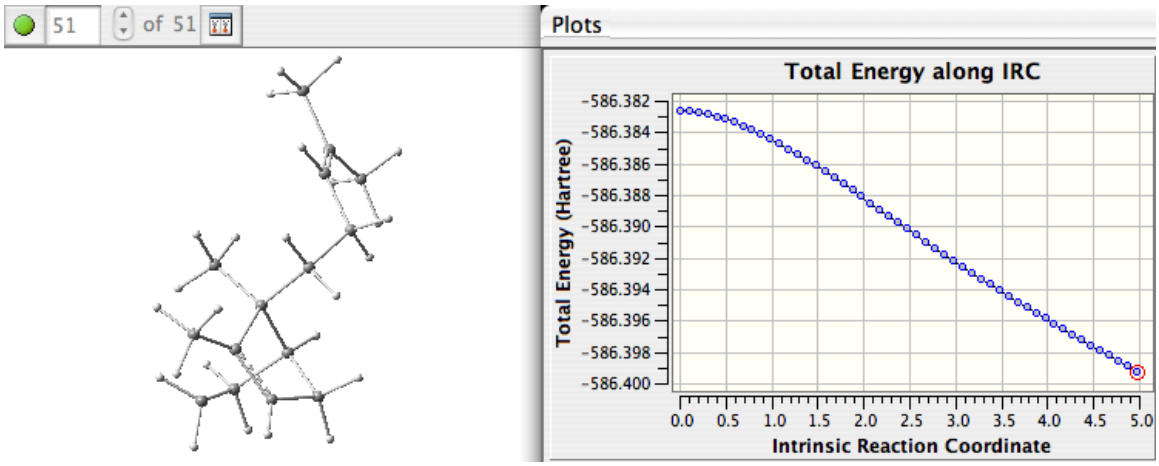
Table 1: R_1/R_2=CH_3/prenyl (aligned) (Fig. 3 and Fig. S2)

<u>B3LYP</u>

A→TS

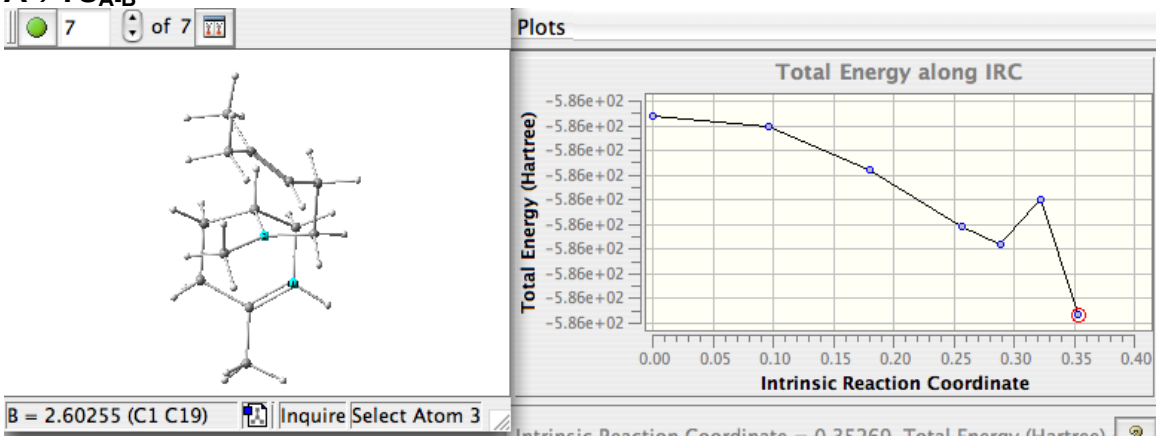


TS→C

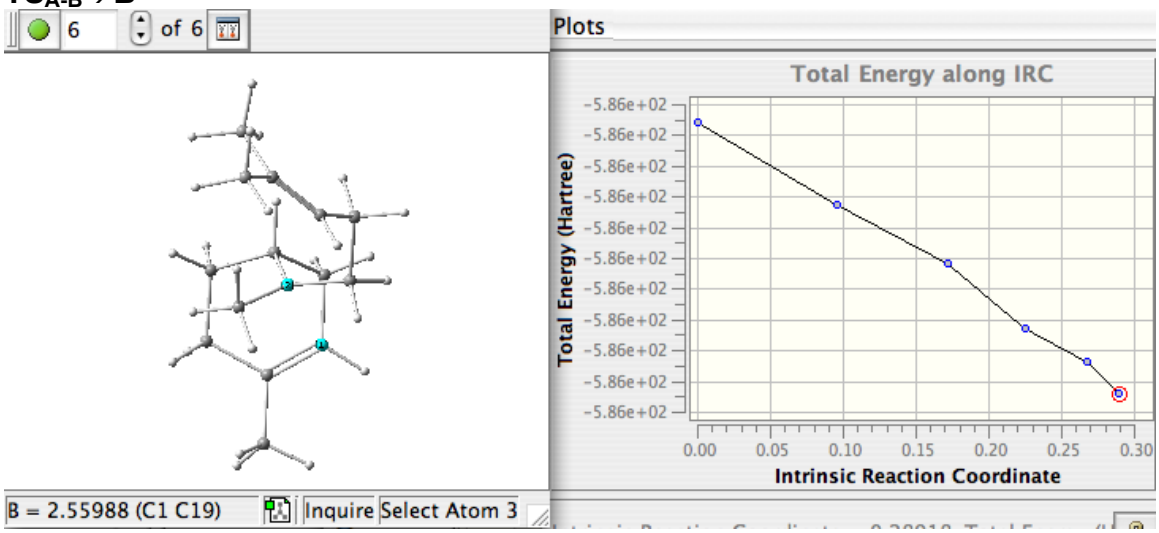


mPWB1K

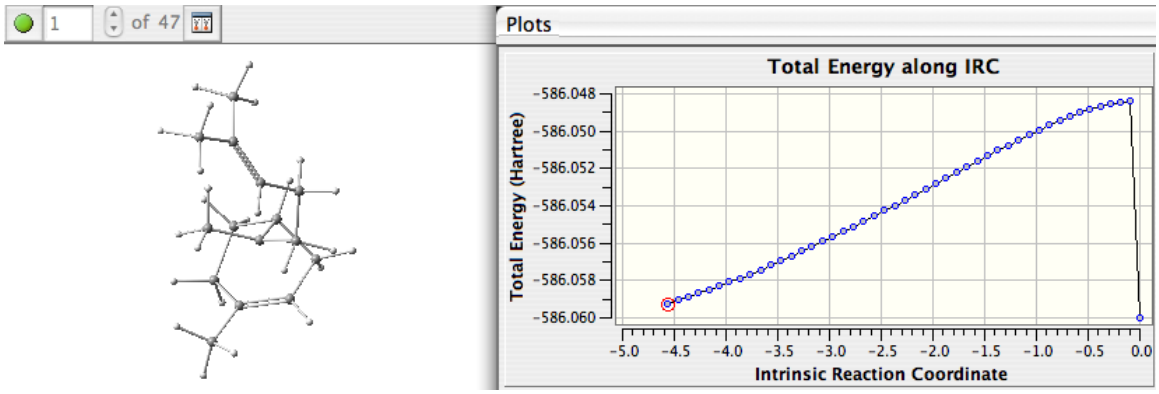
A→TS_{A-B}



TS_{A-B}→B



B→TS



TS→C

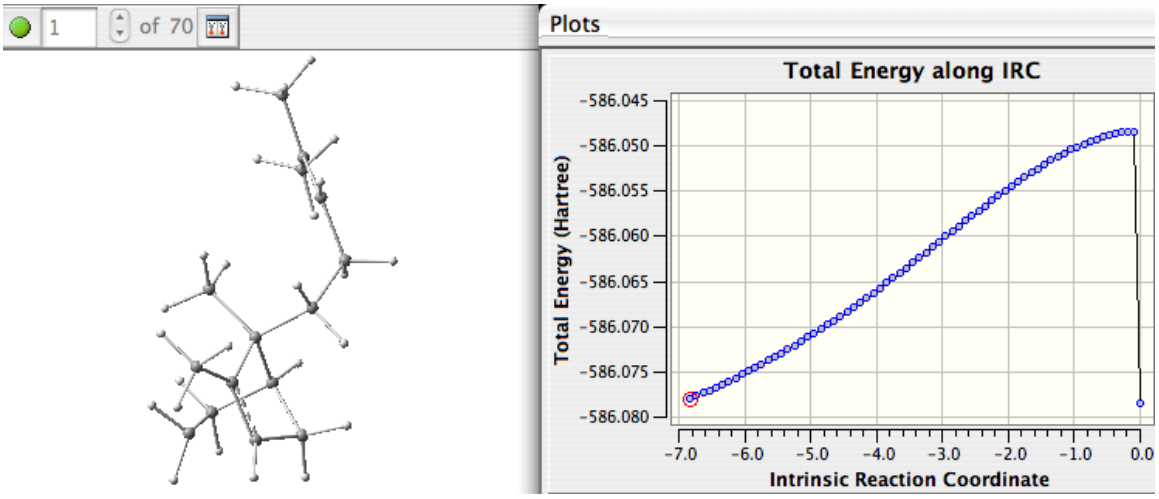
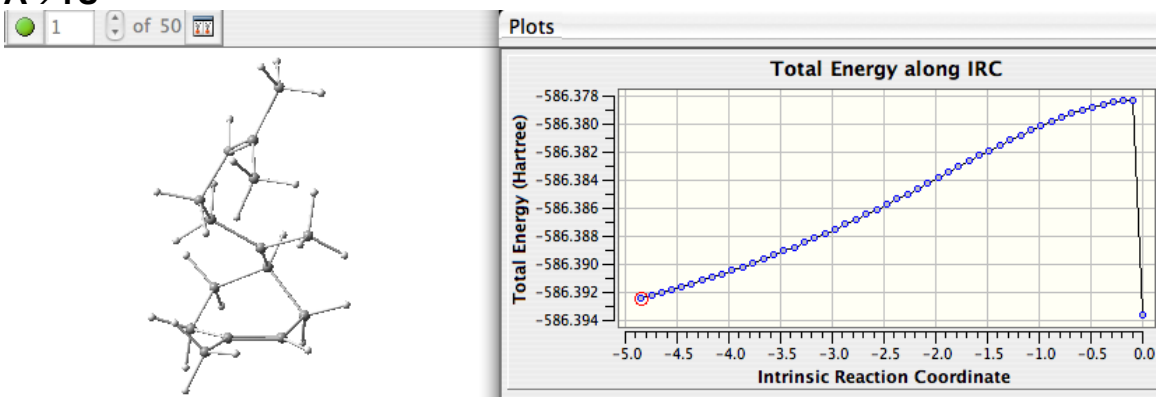


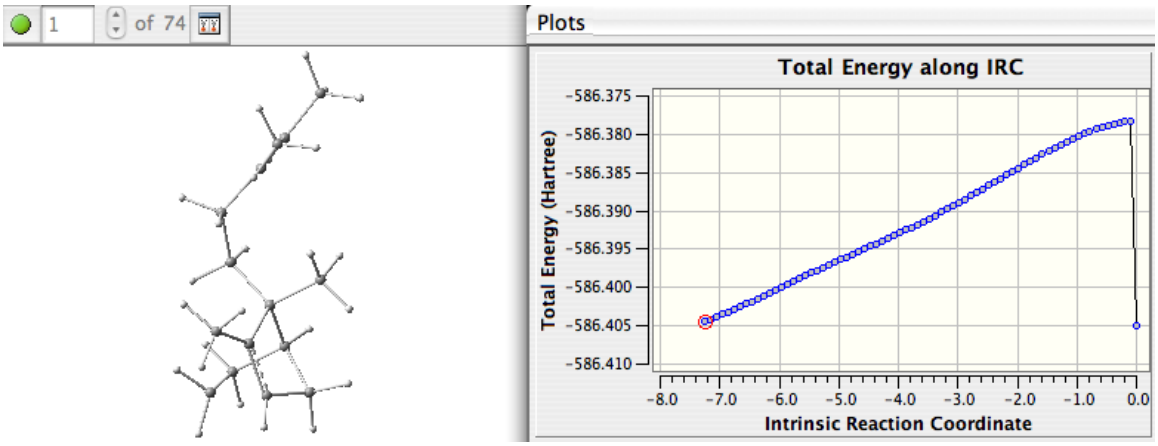
Table 2: R_1/R_2=prenyl/CH_3 (extended) (Fig. 4 and Fig. S3)

<u>B3LYP</u>

A→TS

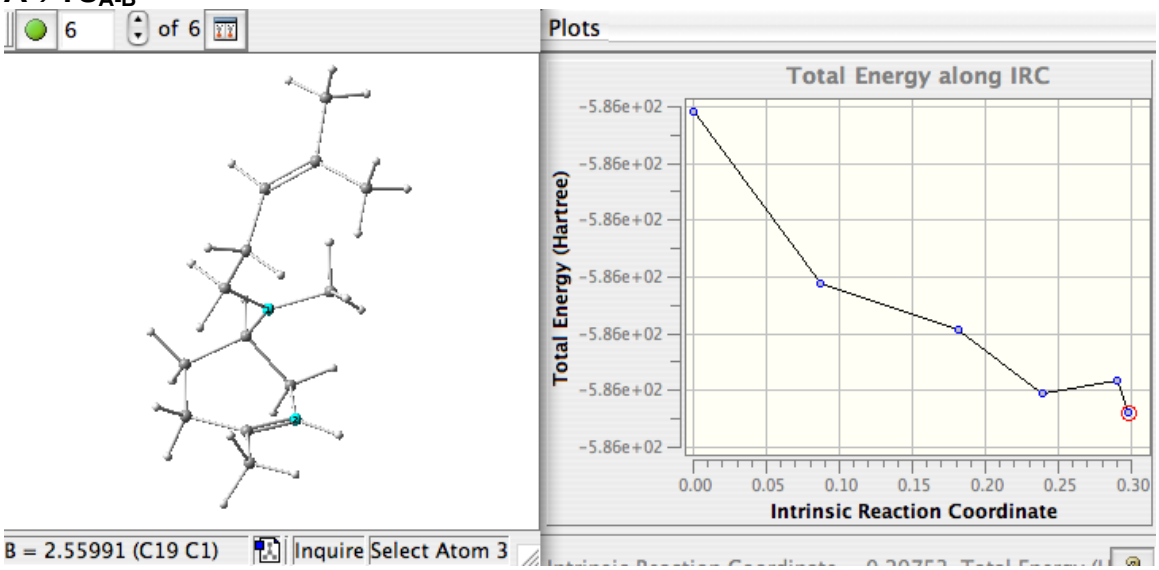


TS→C

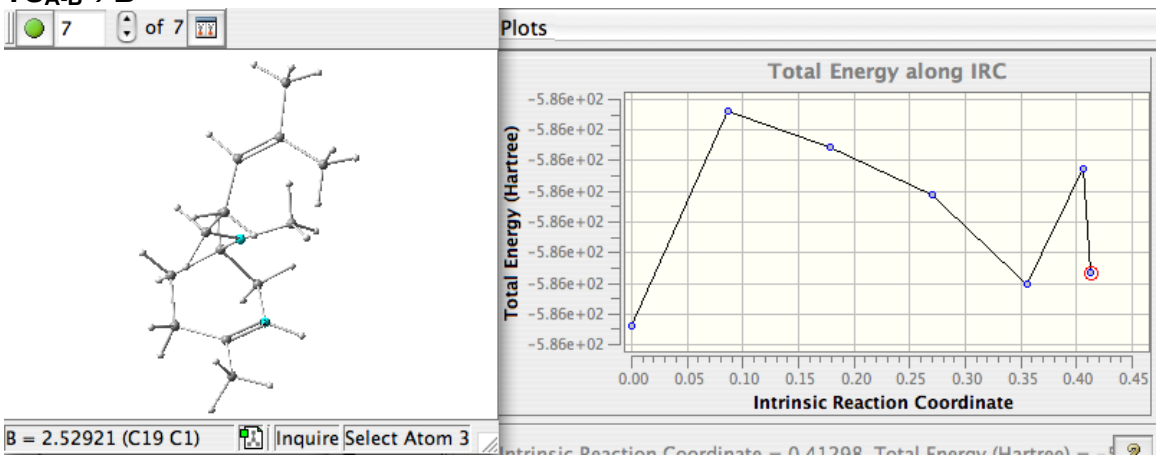


mPWB1K

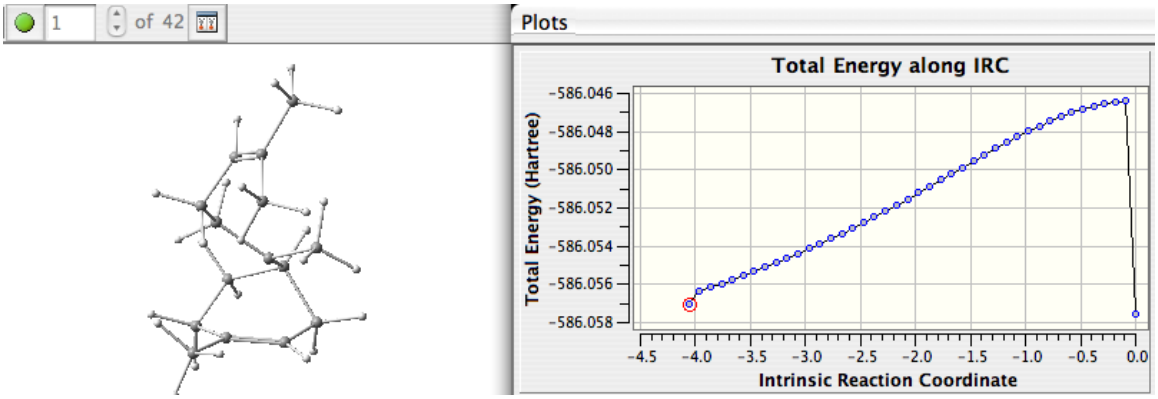
A→TS_{A-B}



TS_{A-B}→B



B→TS



TS→C

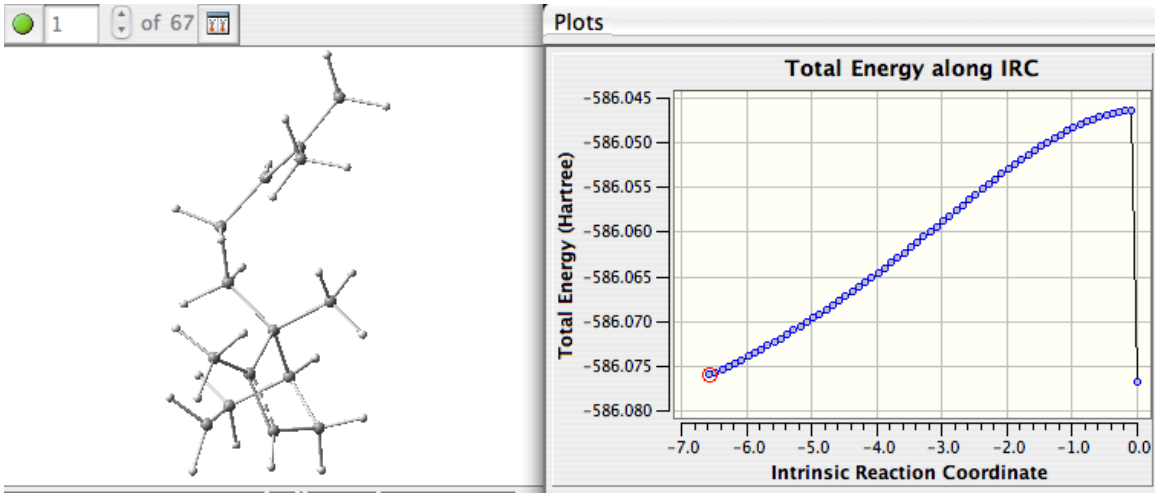
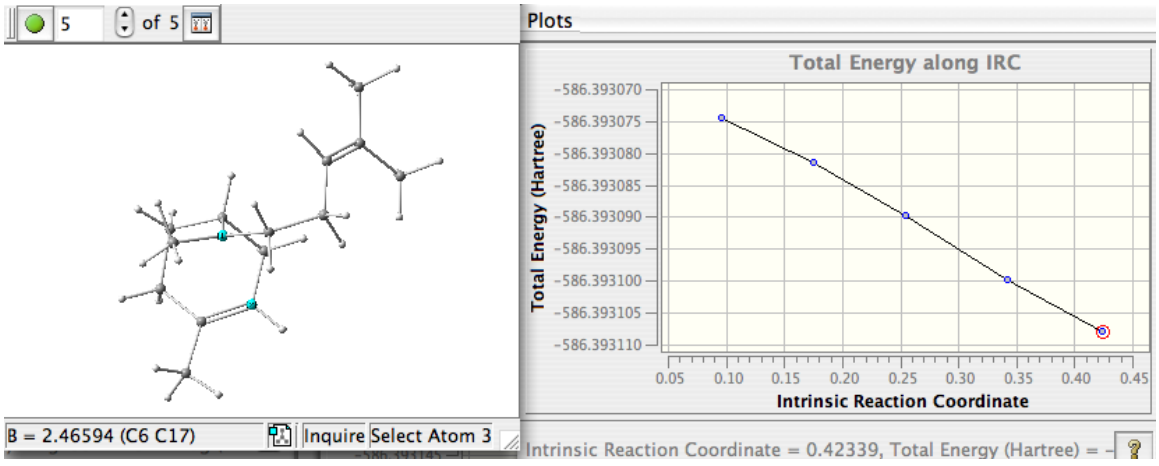


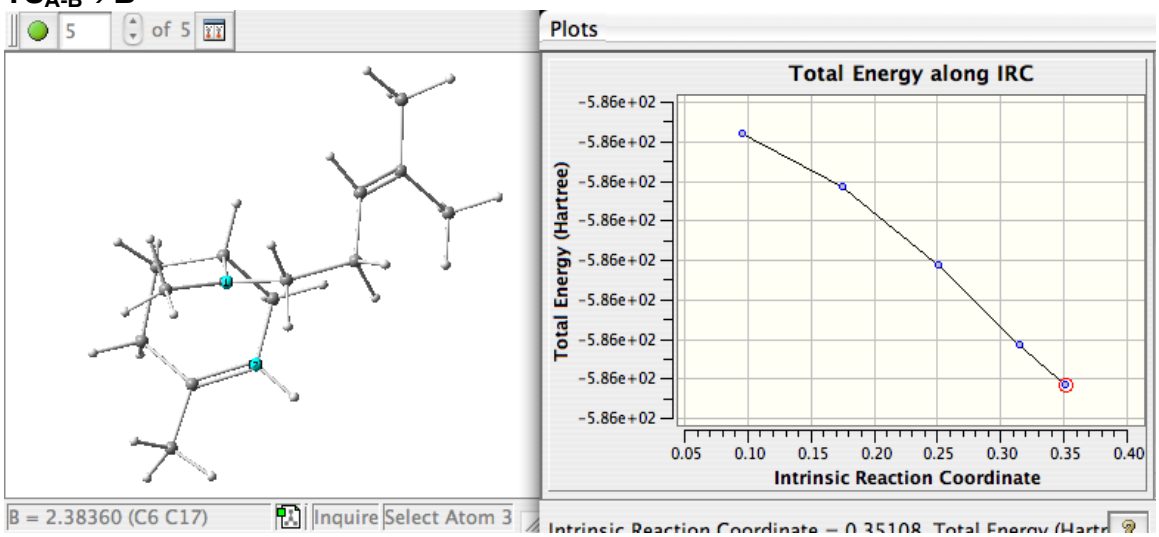
Table 2: R_1/R_2=CH_3/prenyl (extended) (Fig. S4)

<u>B3LYP</u>

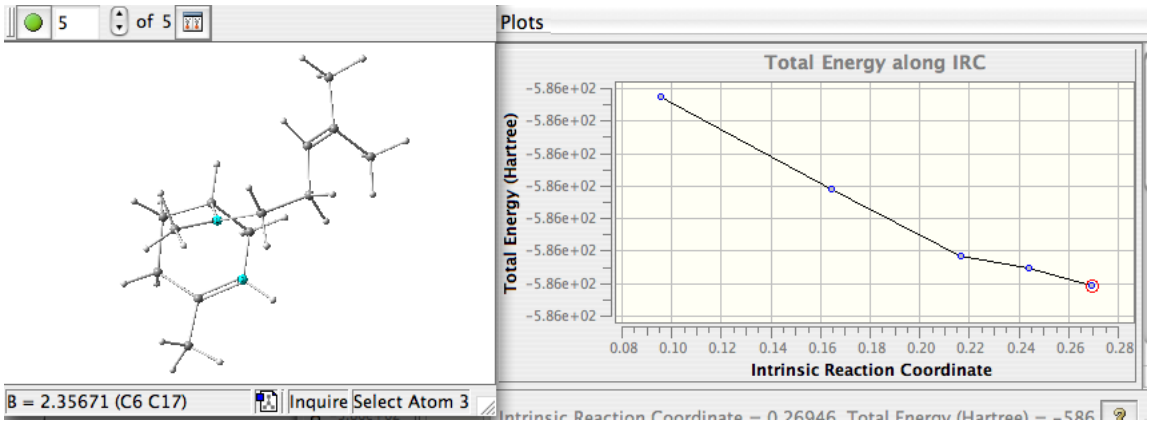
A→TS_{A-B}



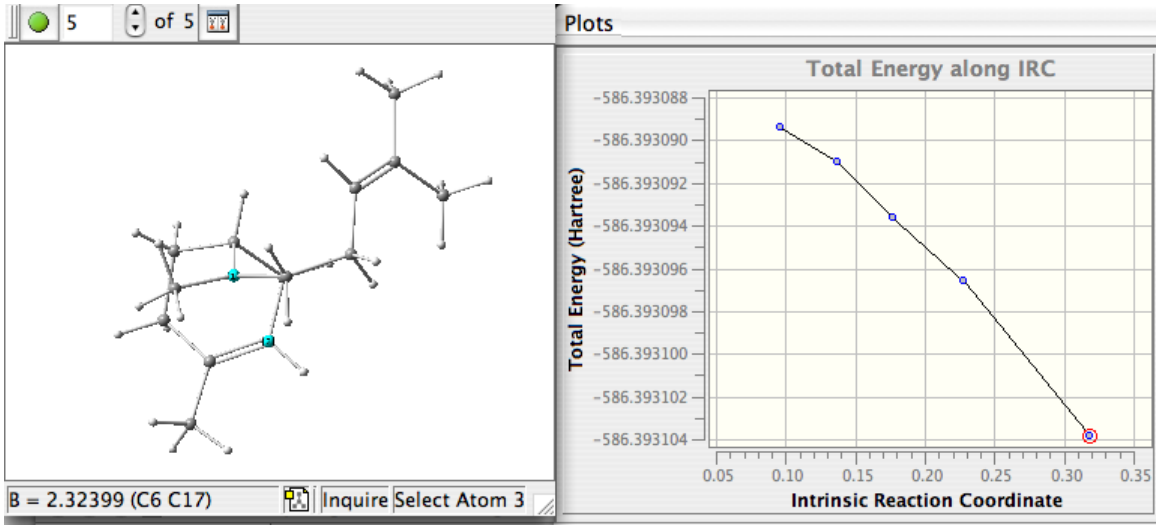
$TS_{A\text{-}B} \rightarrow B$



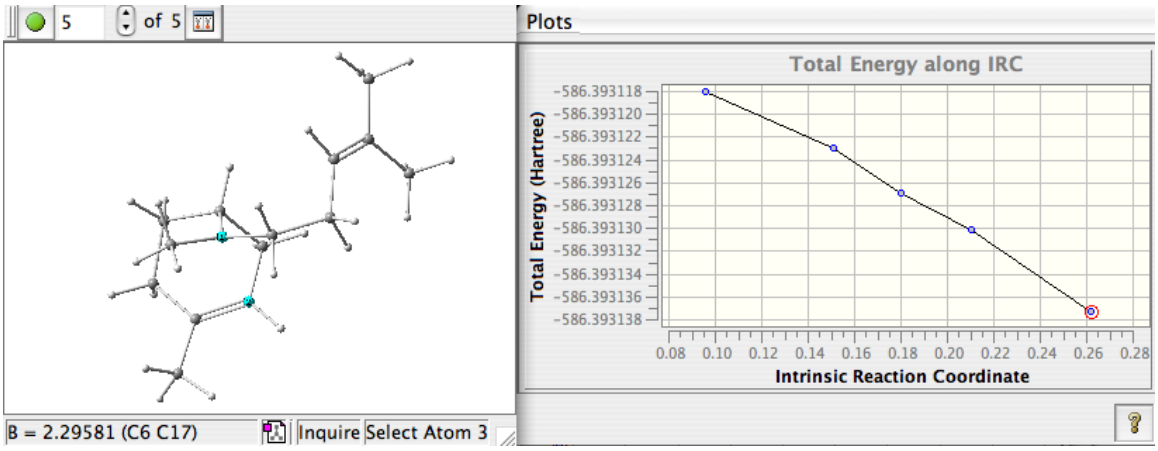
Extended IRC calculation



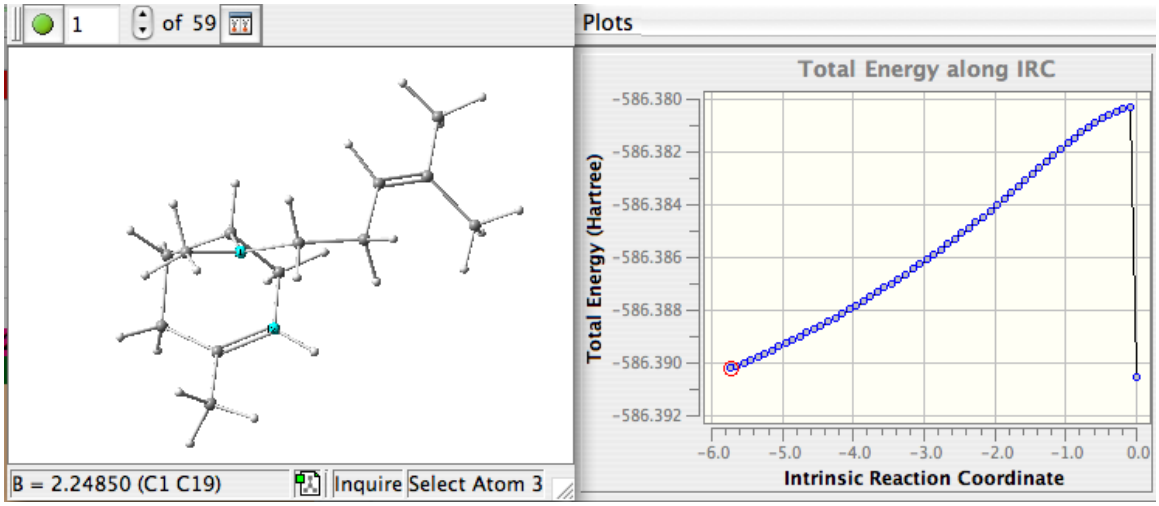
Extended IRC calculation



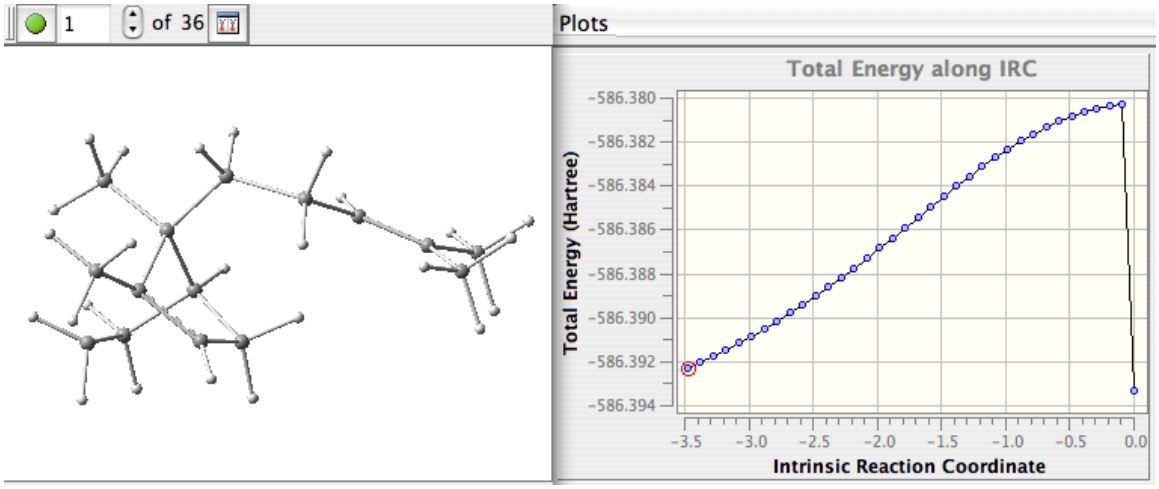
Extended IRC calculation



B→TS

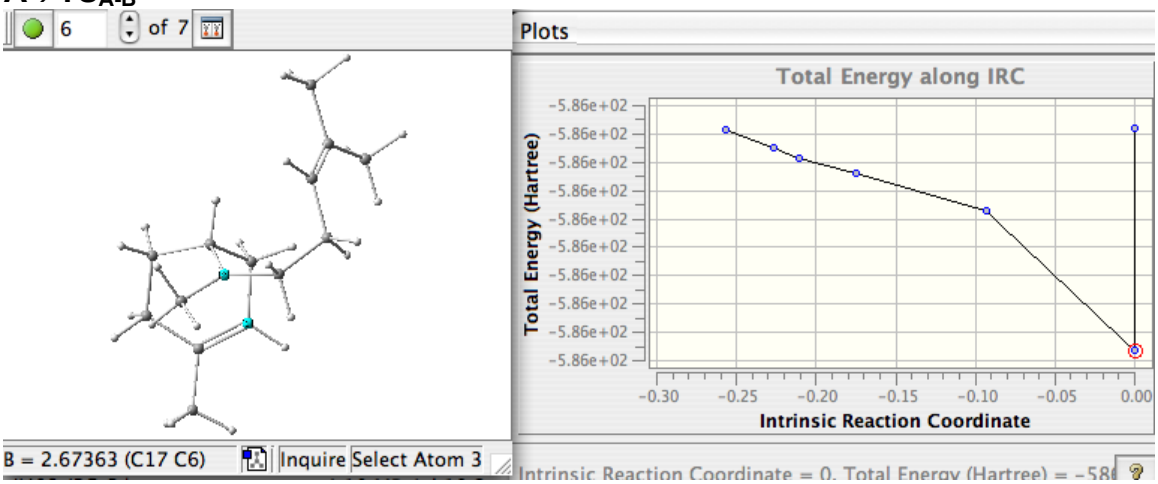


TS→C

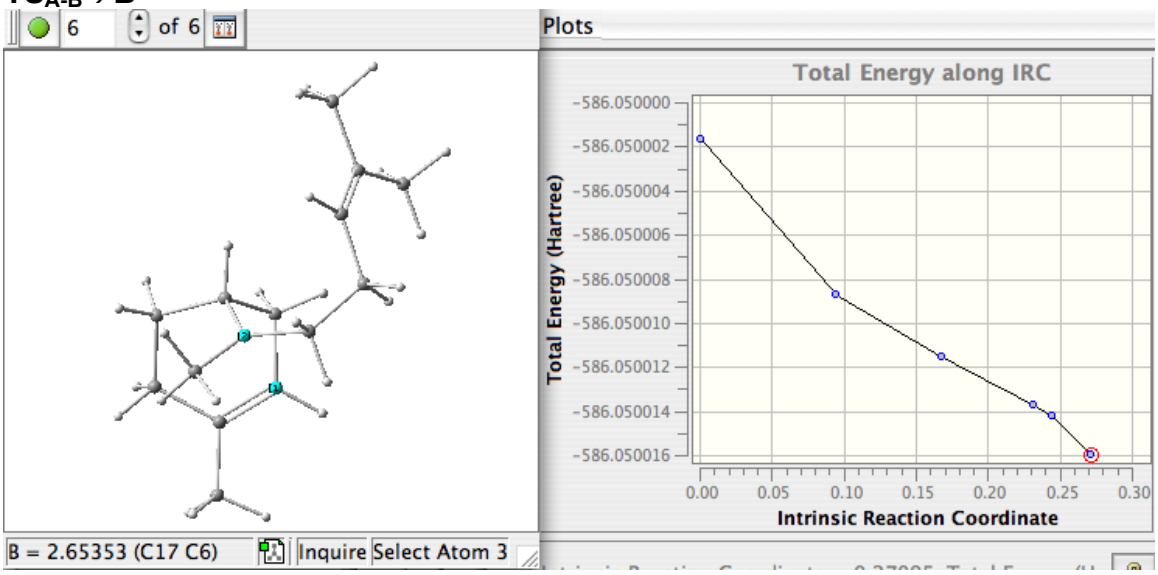


<u>mPWB1K</u>

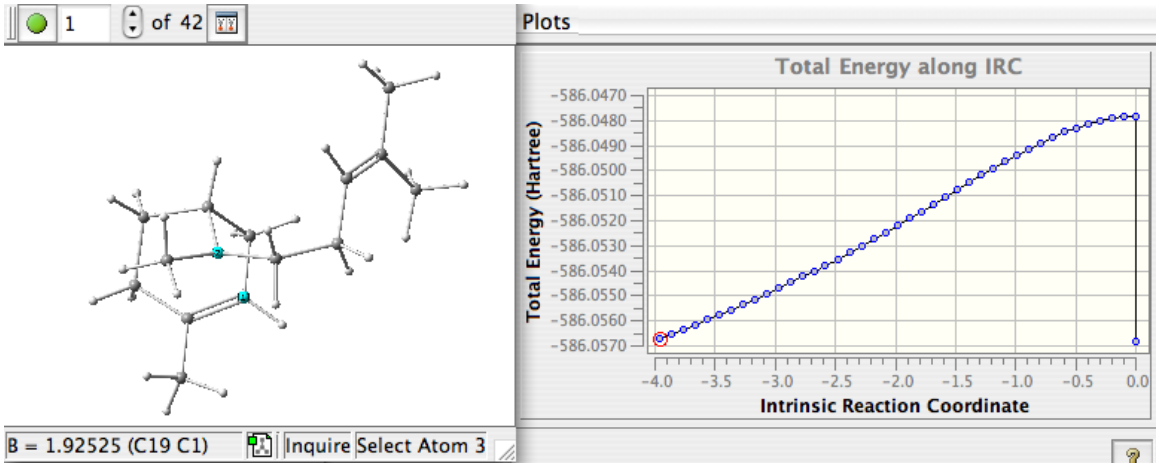
A→TS$_{A-B}$



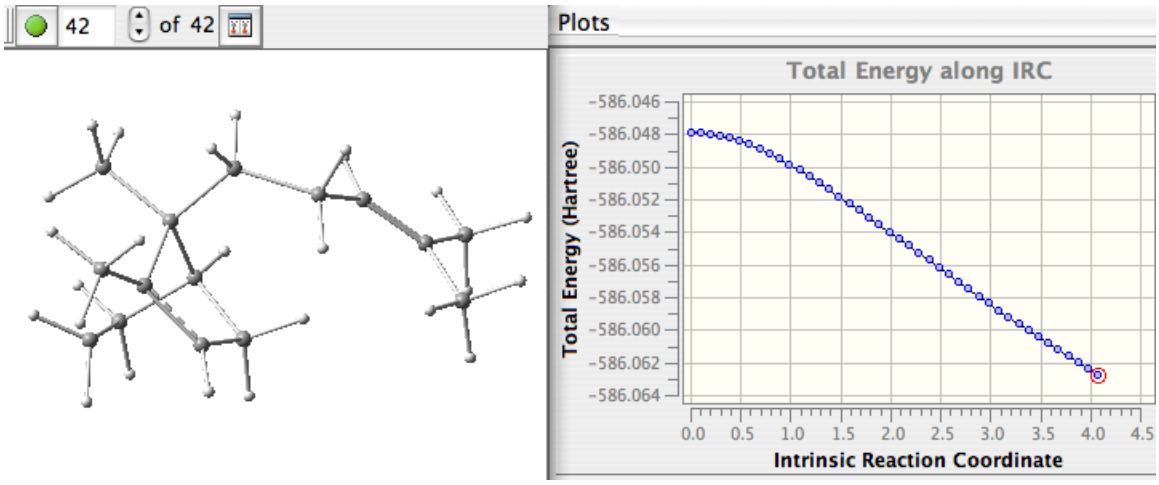
TS$_{A-B}$→B



B→TS



TS→C

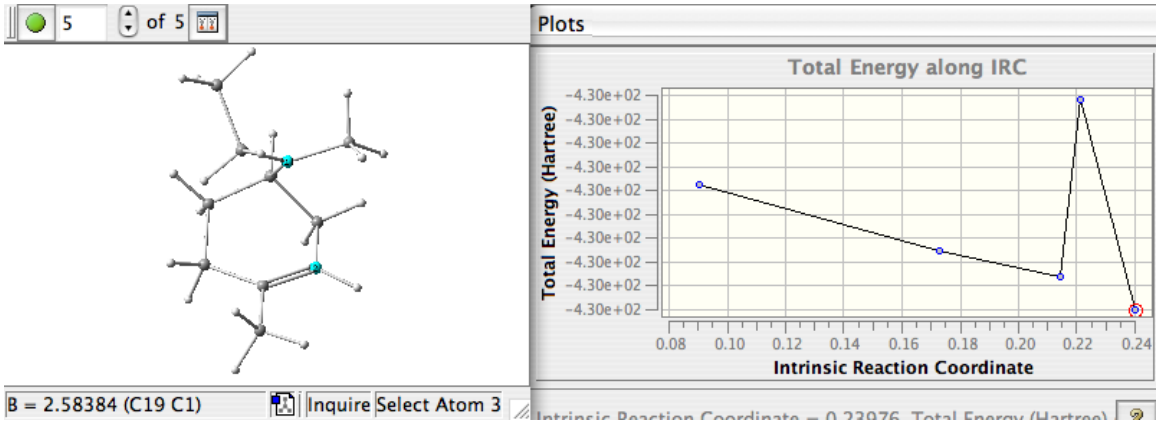


4.2. R_1=C_2H_6/CH_3, R_2=C_2H_6/CH_3

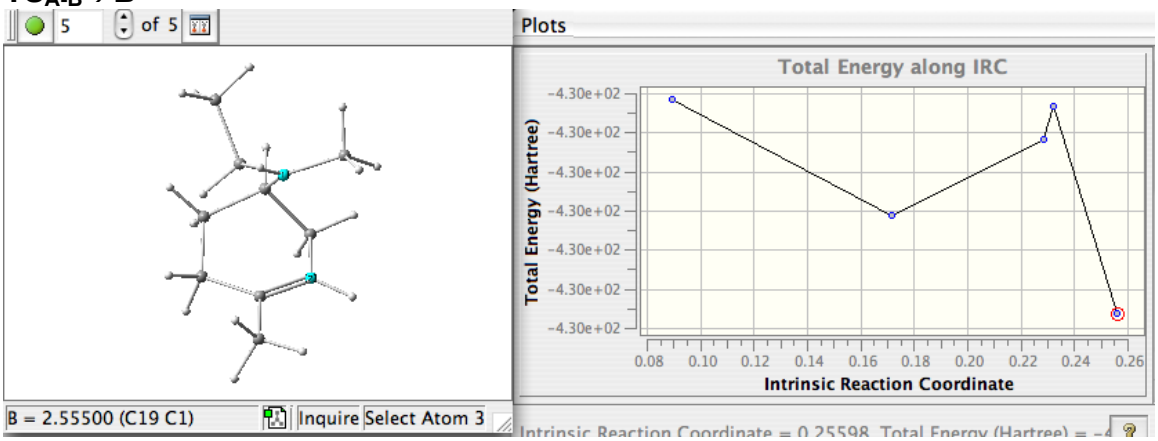
Table 1: R_1/R_2=C_2H_6/CH_3 (aligned) (Fig. S5)

<u>B3LYP</u>

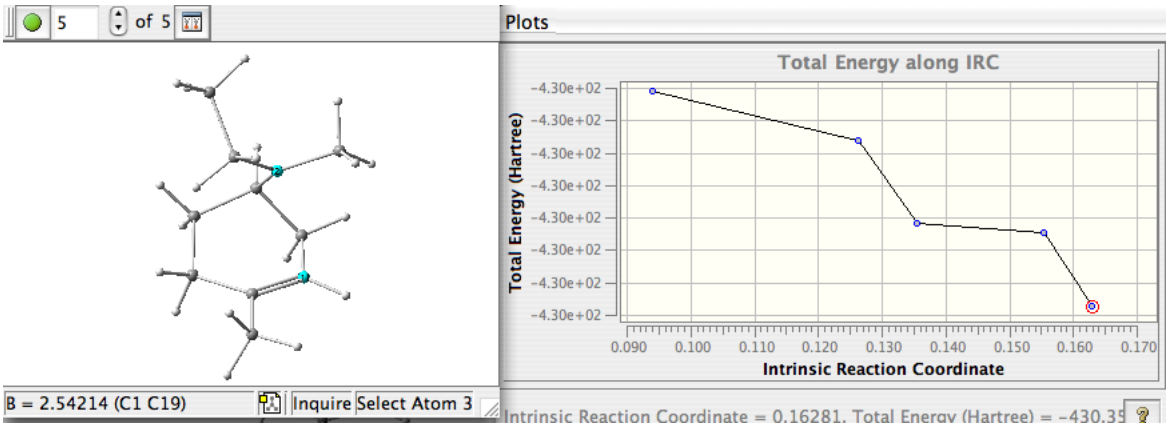
A→TS_{A-B}



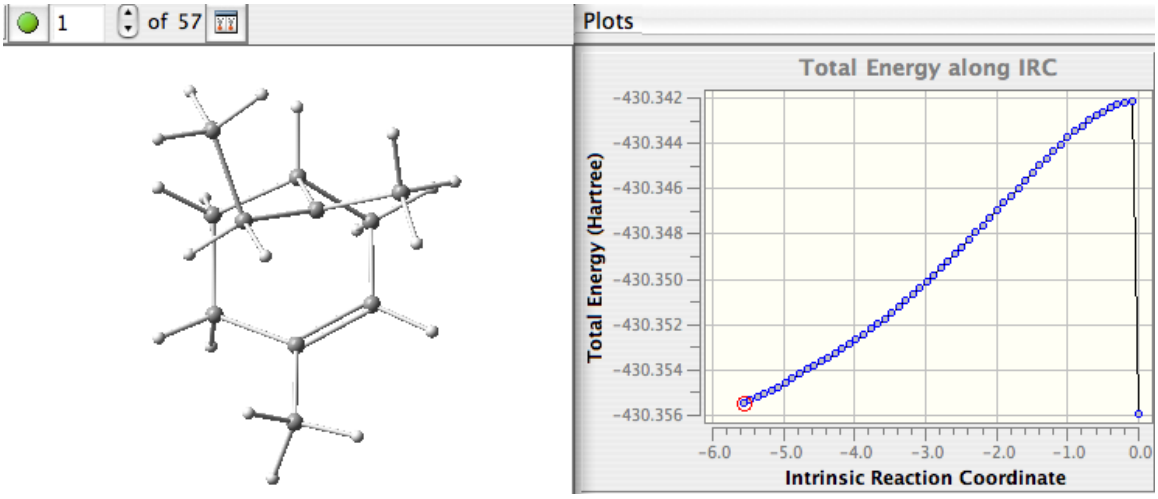
TS_{A-B}→B



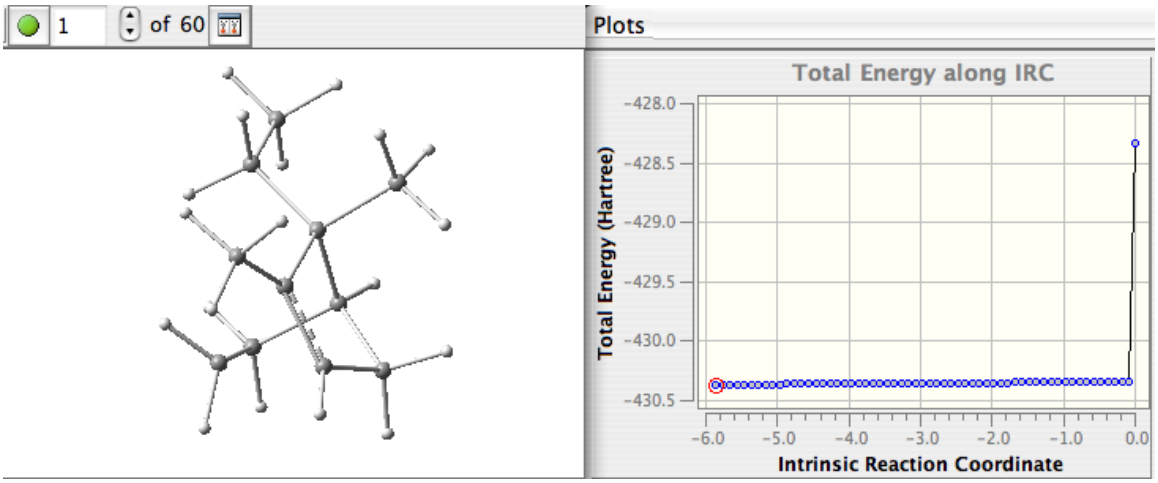
Extended IRC calculation



B→TS

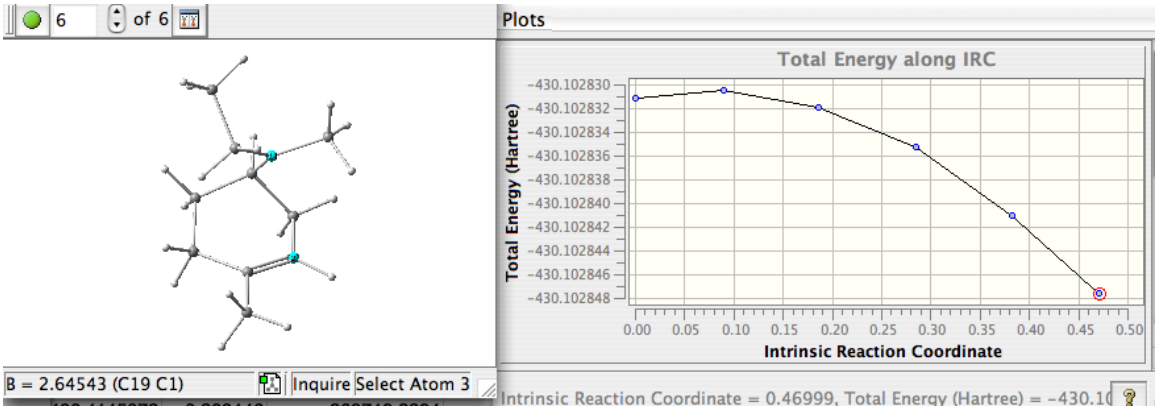


TS→C

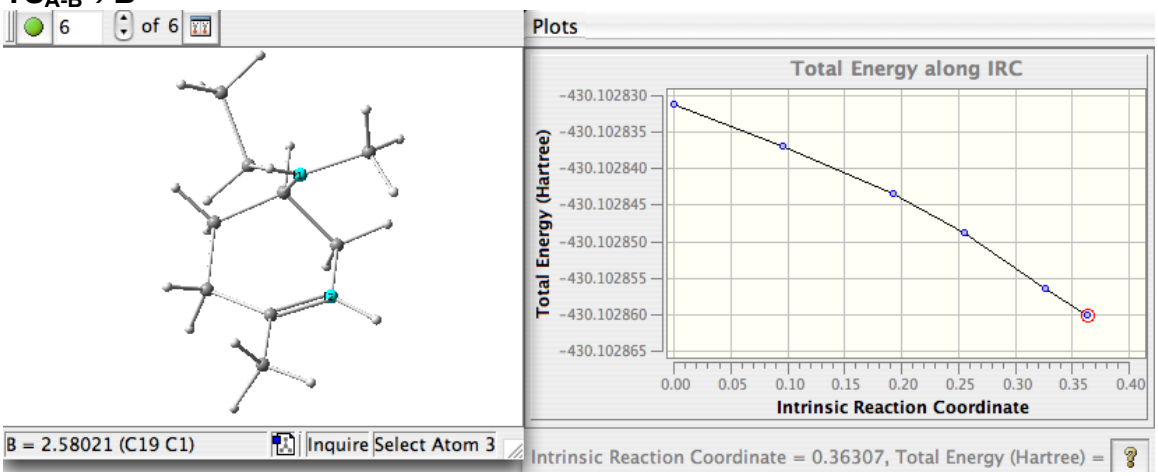


mPWB1K

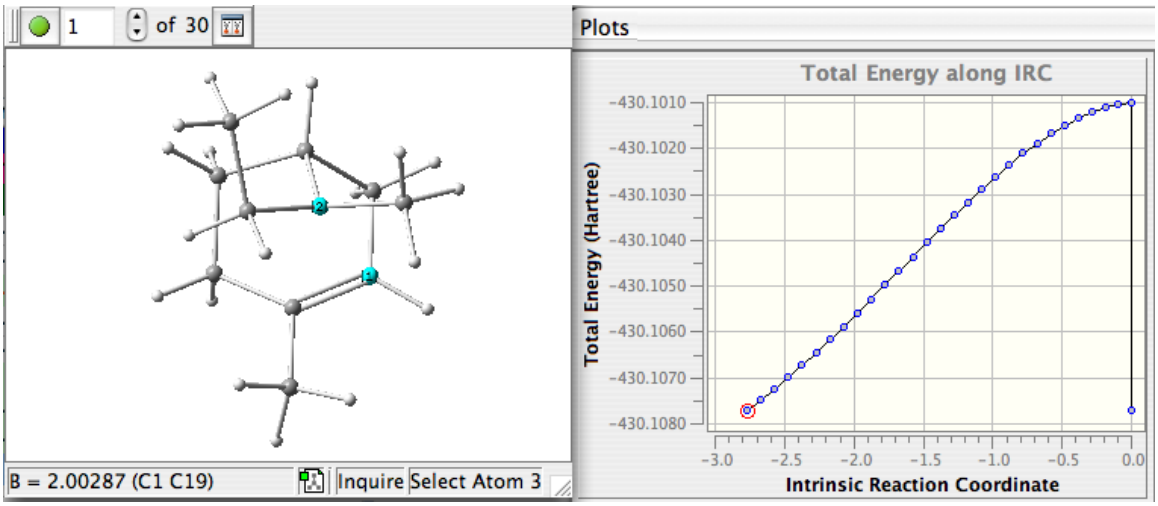
A→TS$_{A-B}$



TS$_{A-B}$→B



B→TS



TS→C

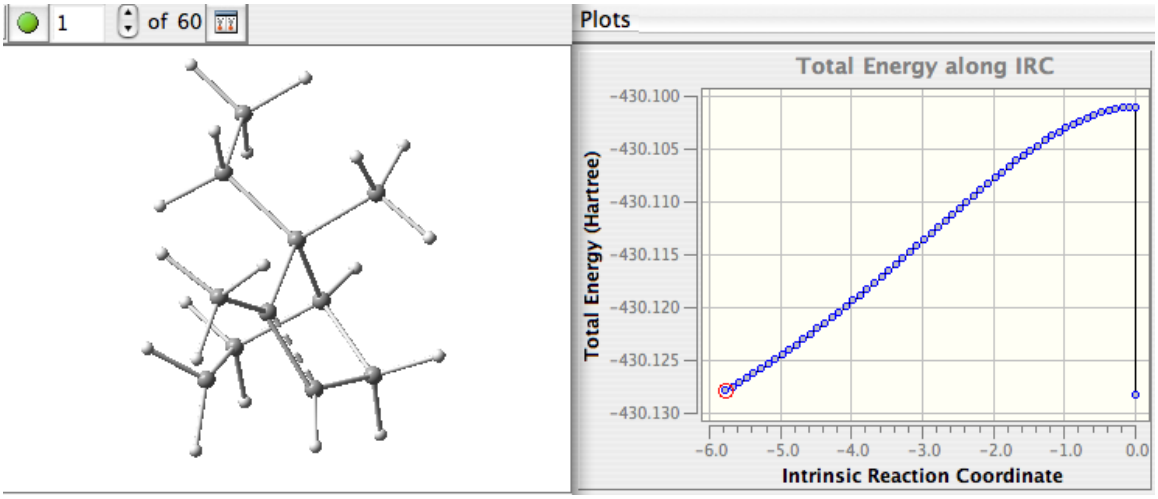
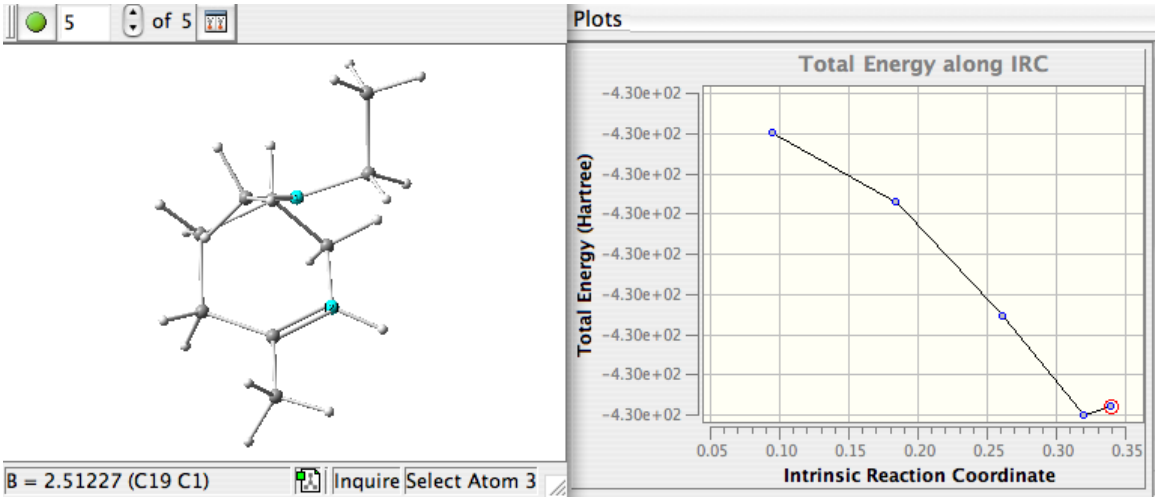


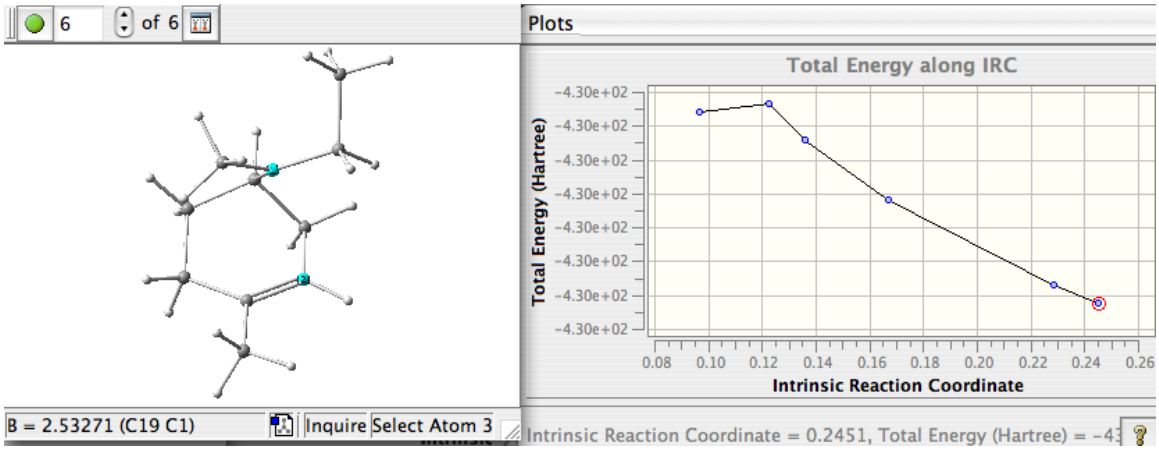
Table 1: R_1/R_2=CH_3/C_2H_6 (aligned) (Fig. S5)

<u>B3LYP</u>

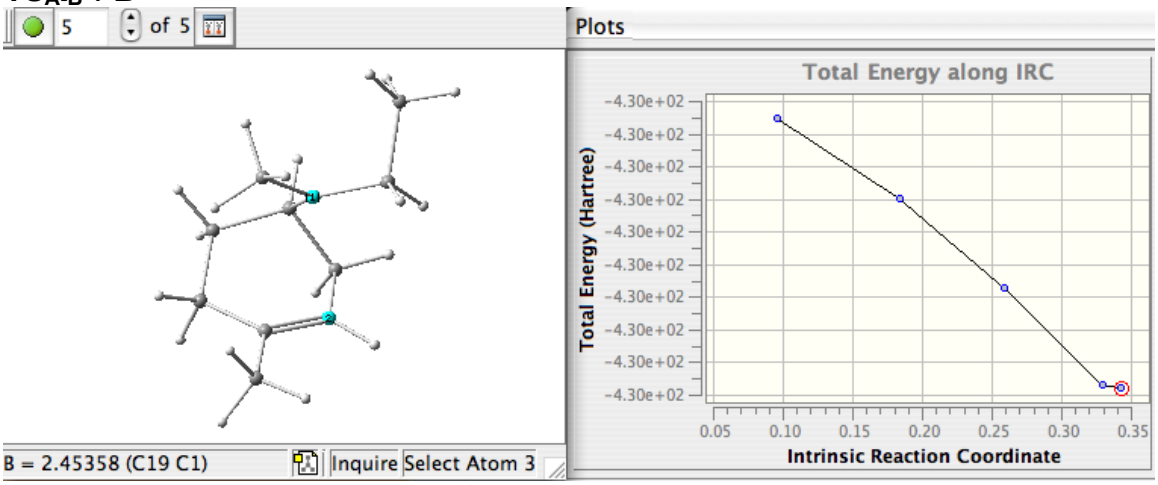
A→TS_{A-B}



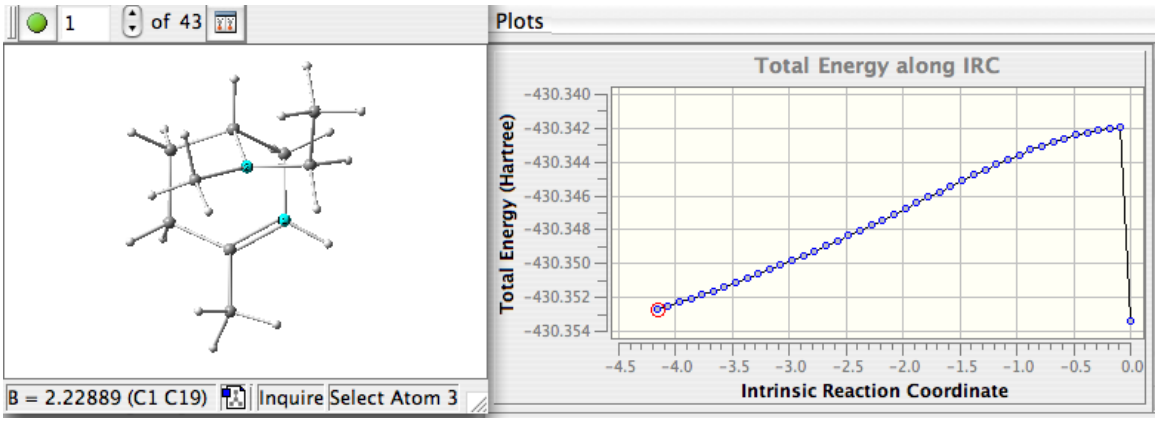
Extended IRC calculation



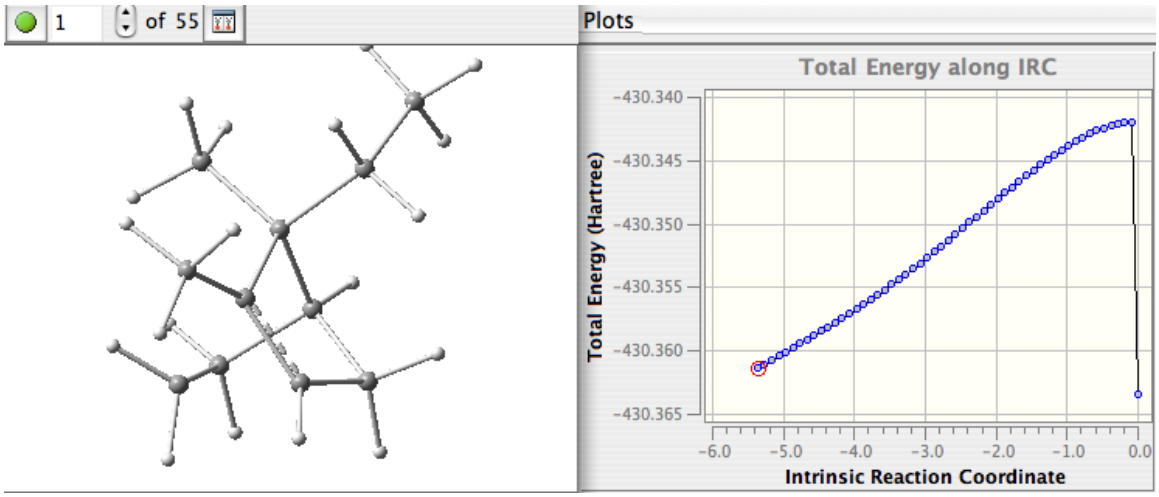
TS_{A-B}→B



B→TS

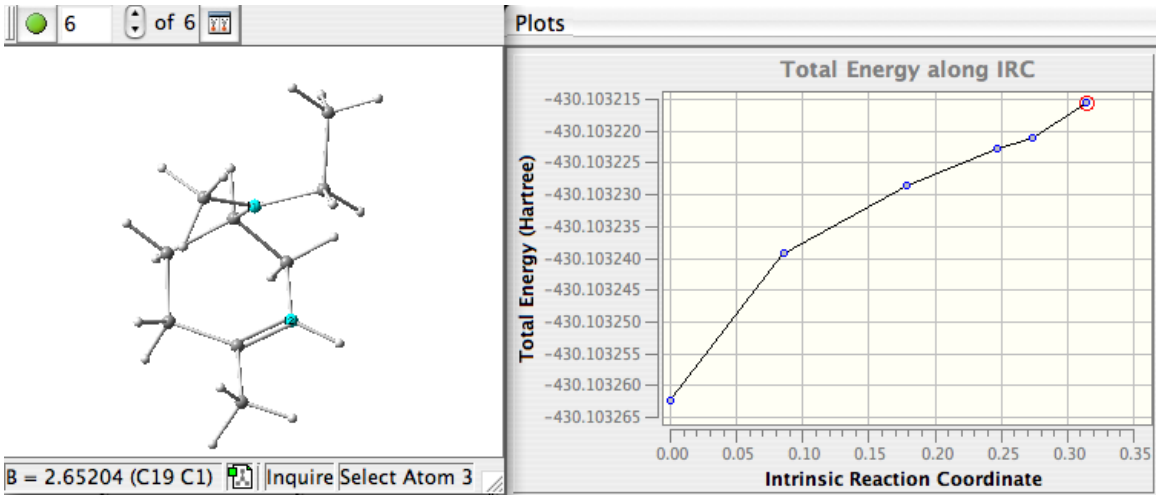


TS→C

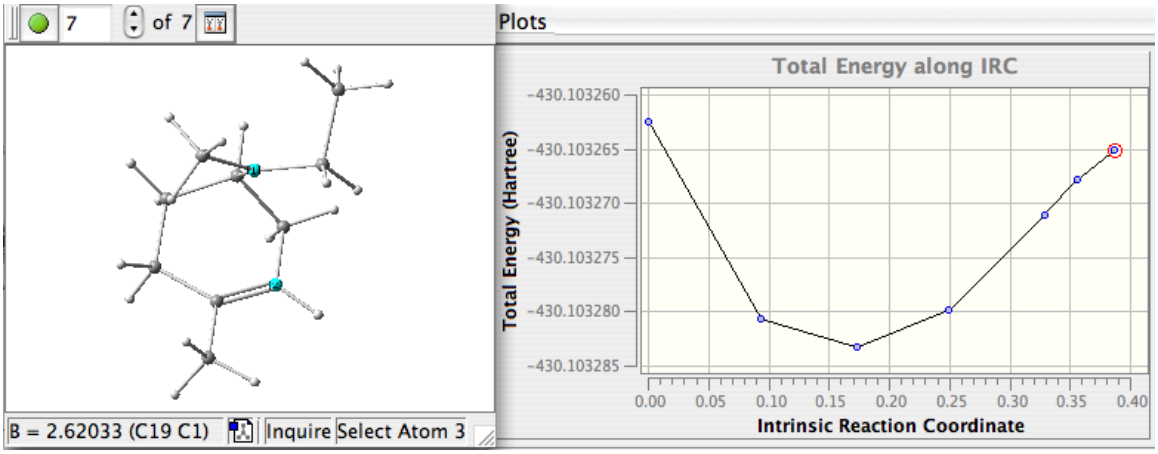


mPWB1K

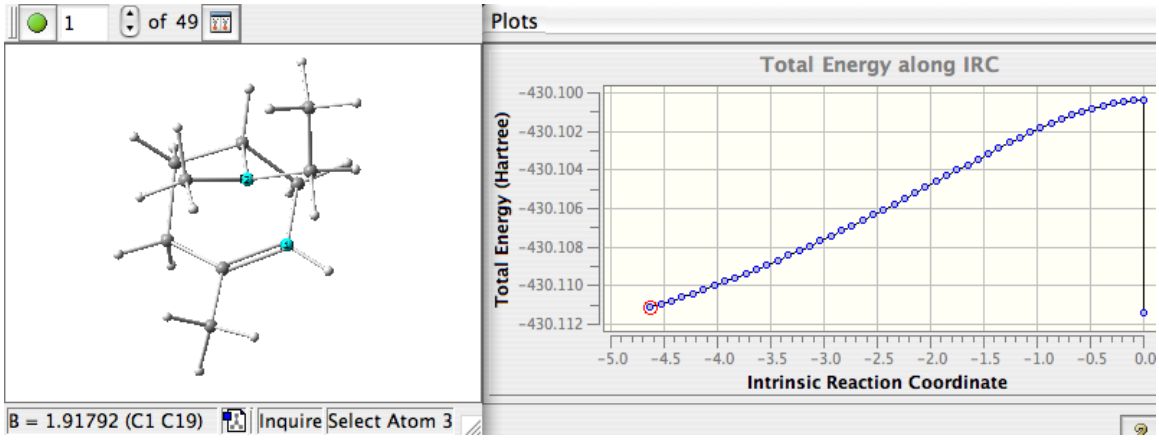
A→TS_{A-B}



TS_{A-B}→B



B→TS



TS→C

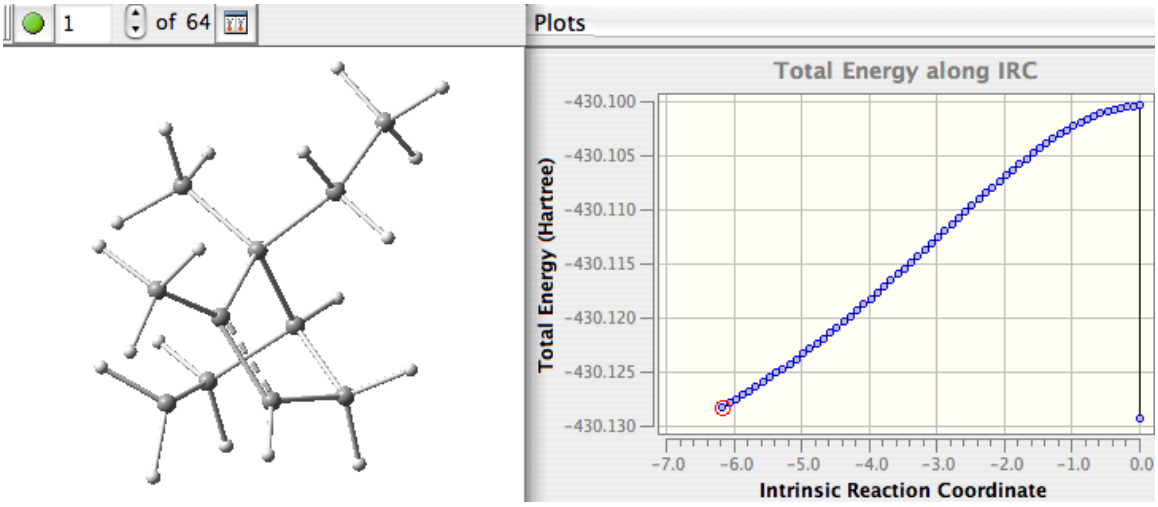
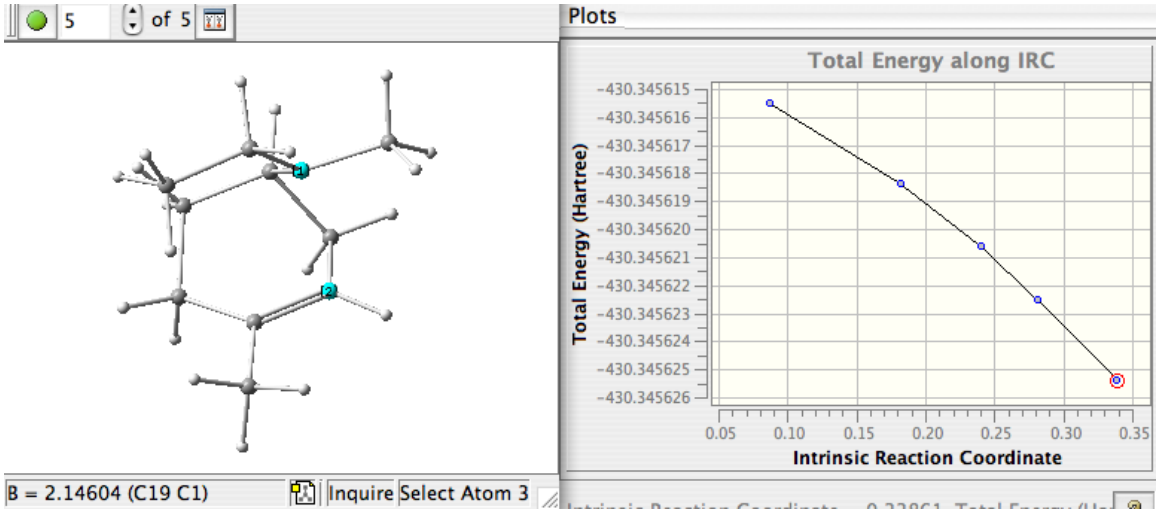


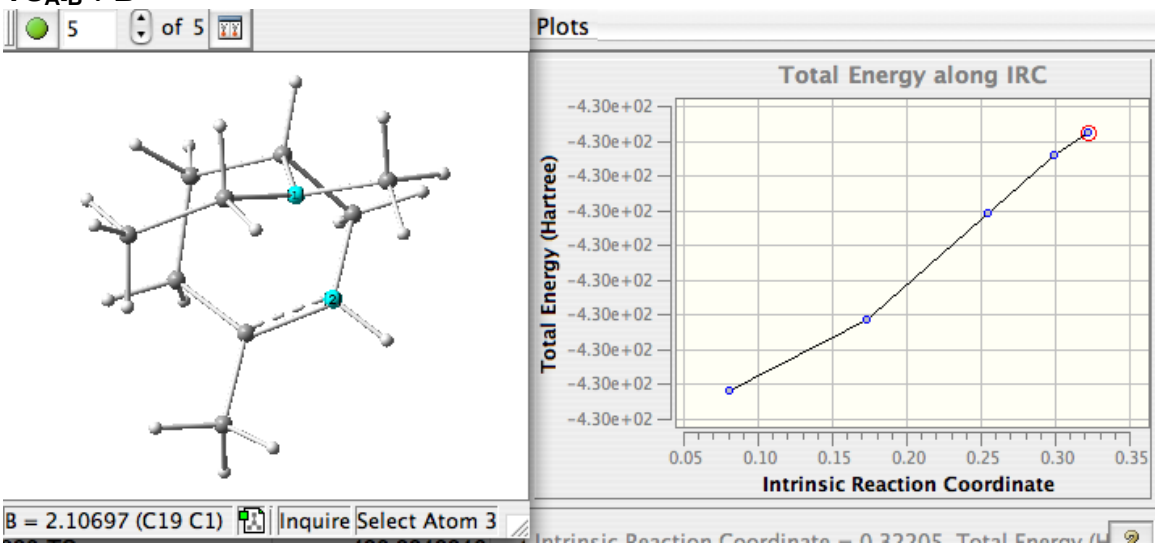
Table 2: R_1/R_2=C_2H_6/CH_3 (extended) (Fig. S5)

<u>B3LYP</u>

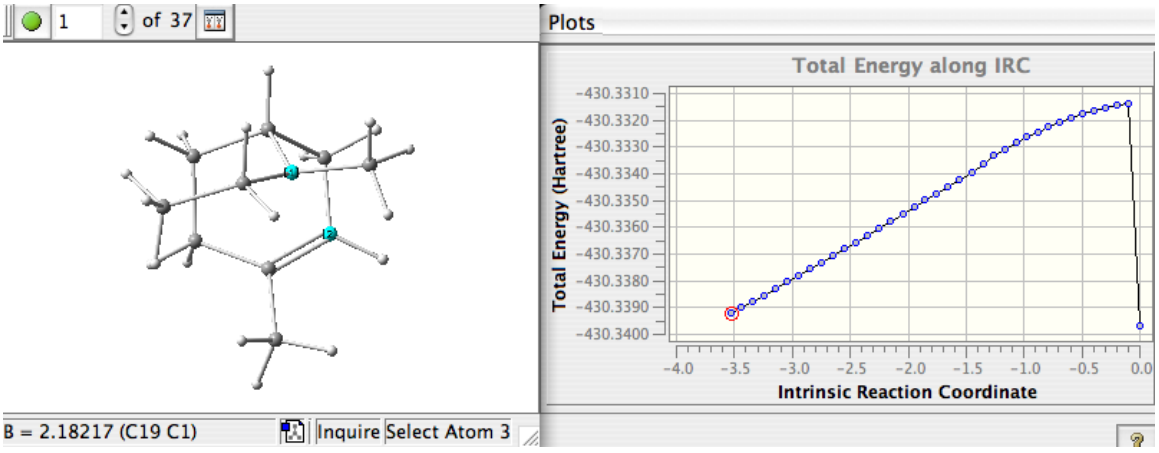
A→TS_{A-B}



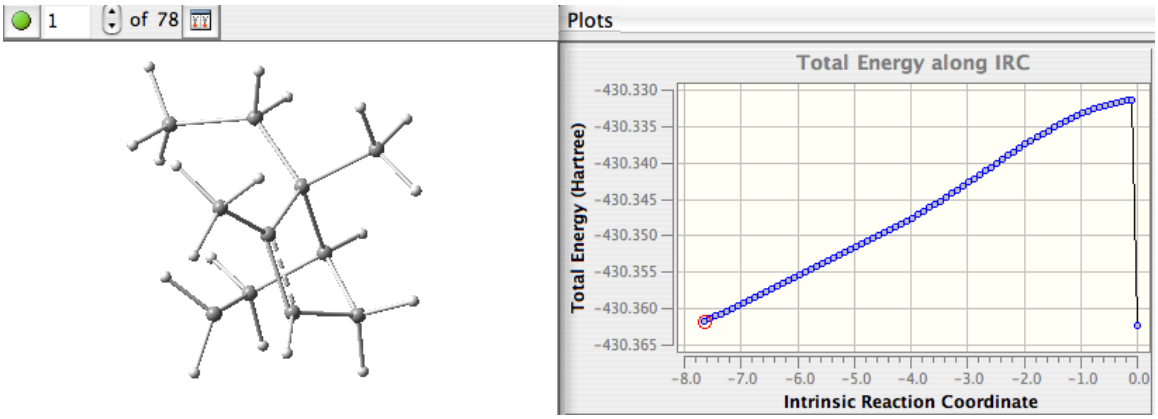
TS_{A-B}→B



B→TS

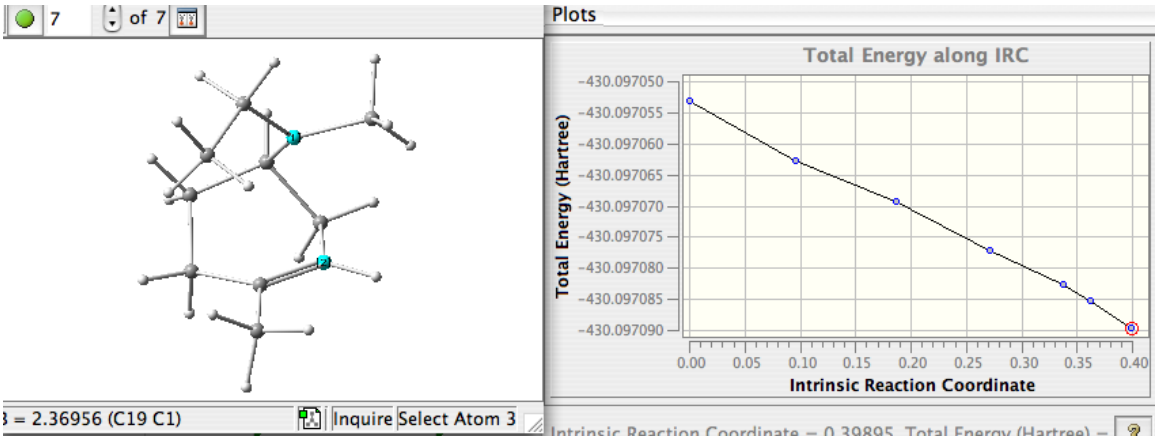


TS→C

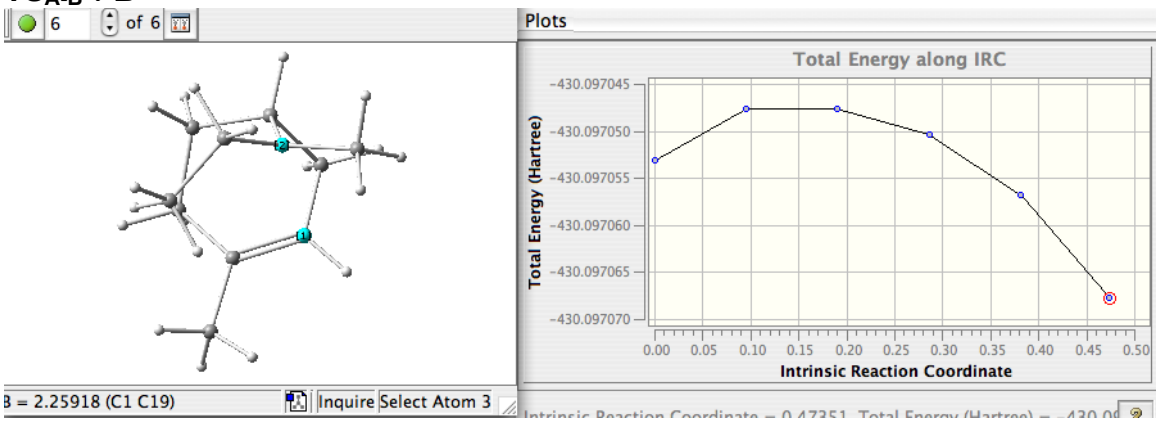


mPWB1K

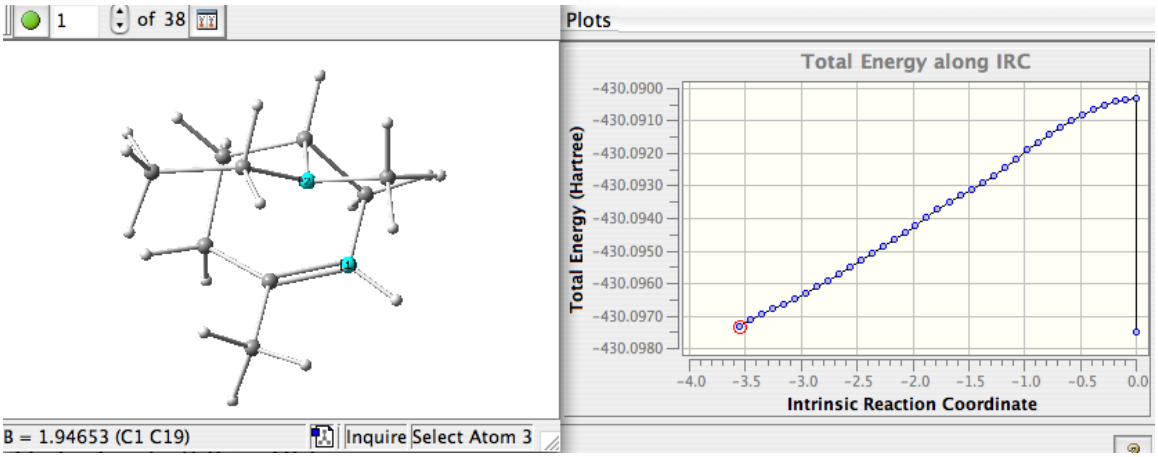
A→TS_{A-B}



TS_{A-B}→B



B→TS



TS→C

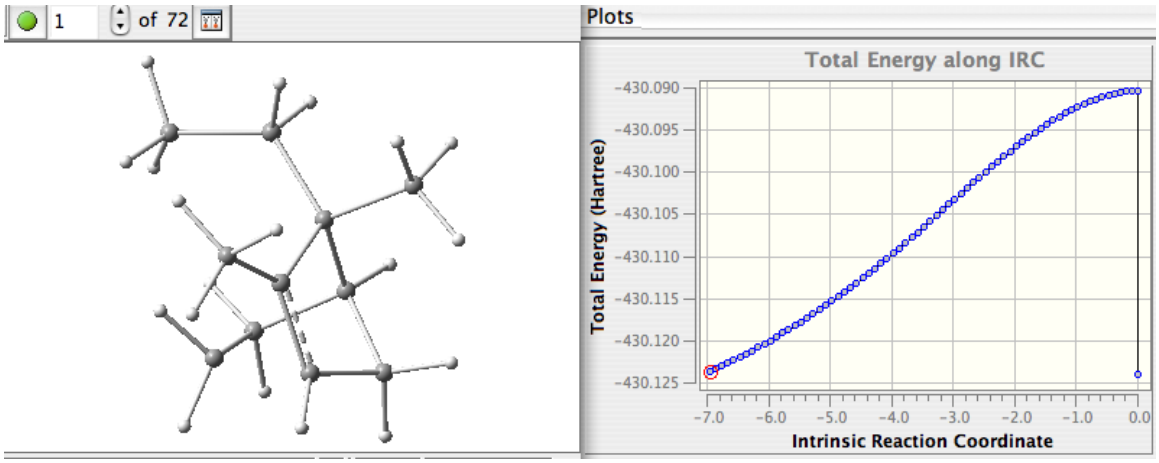
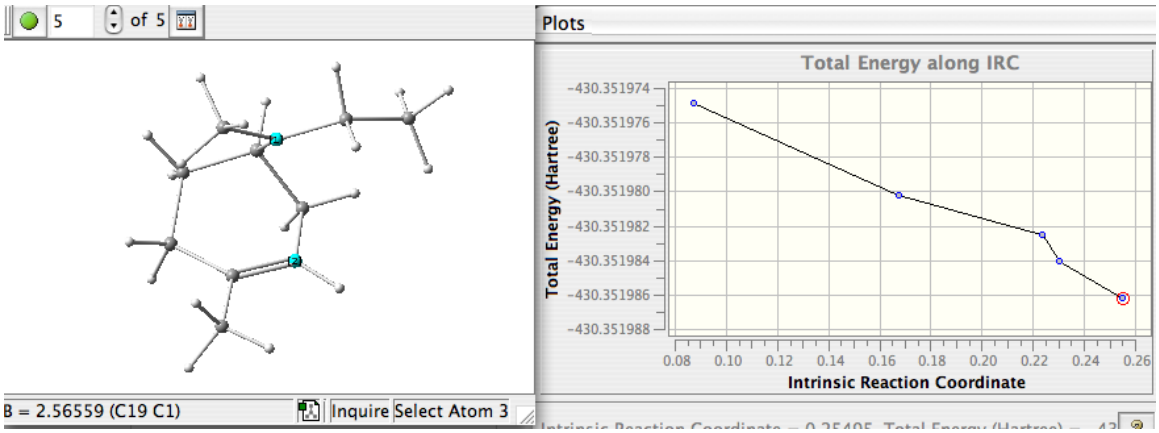


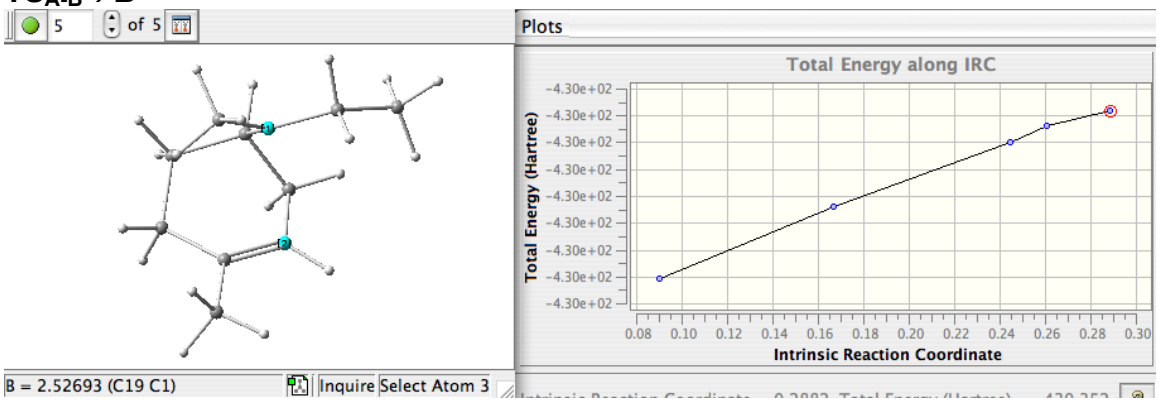
Table 2: R_1/R_2=CH_3/C_2H_6 (extended) (Fig. S5)

<u>B3LYP</u>

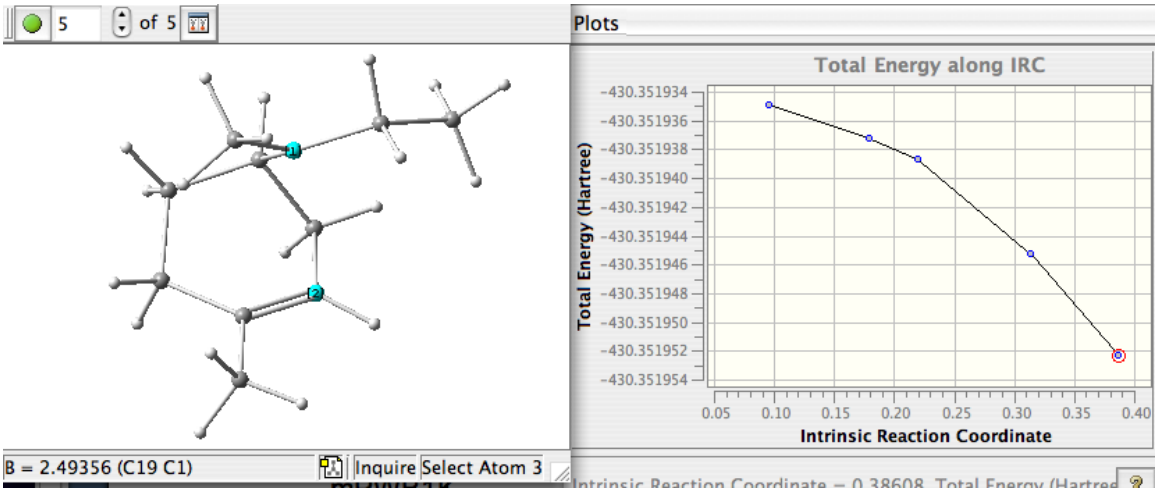
A→TS_{A-B}



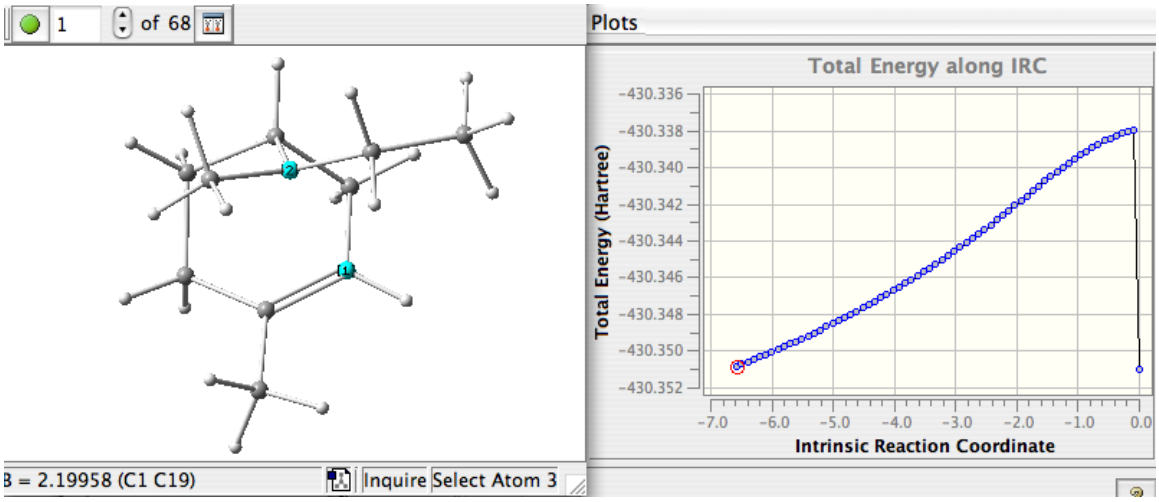
TS_{A-B}→B



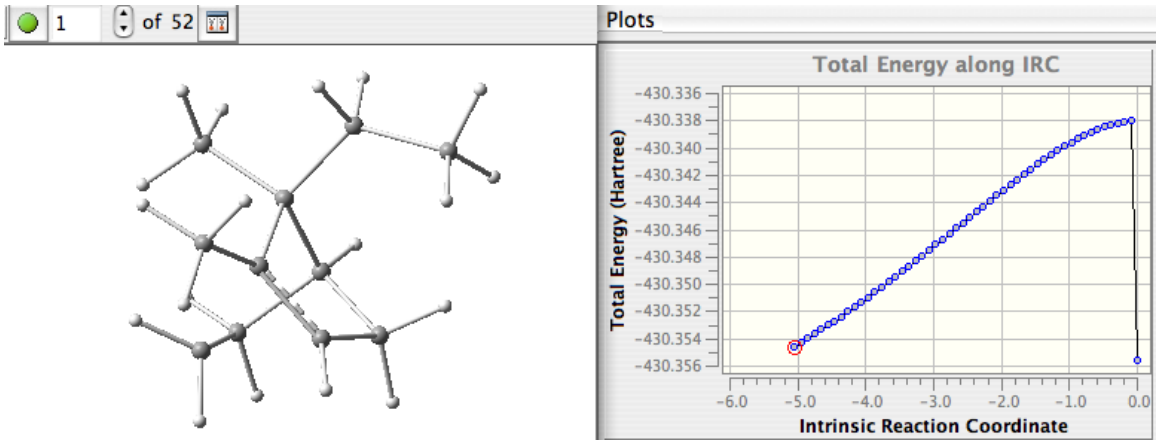
Extended IRC calculation



B→TS

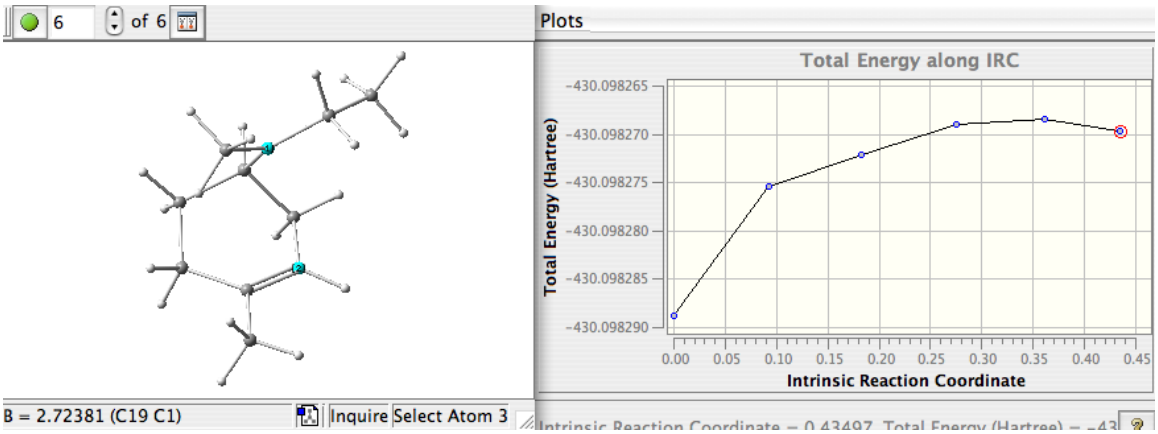


TS→C

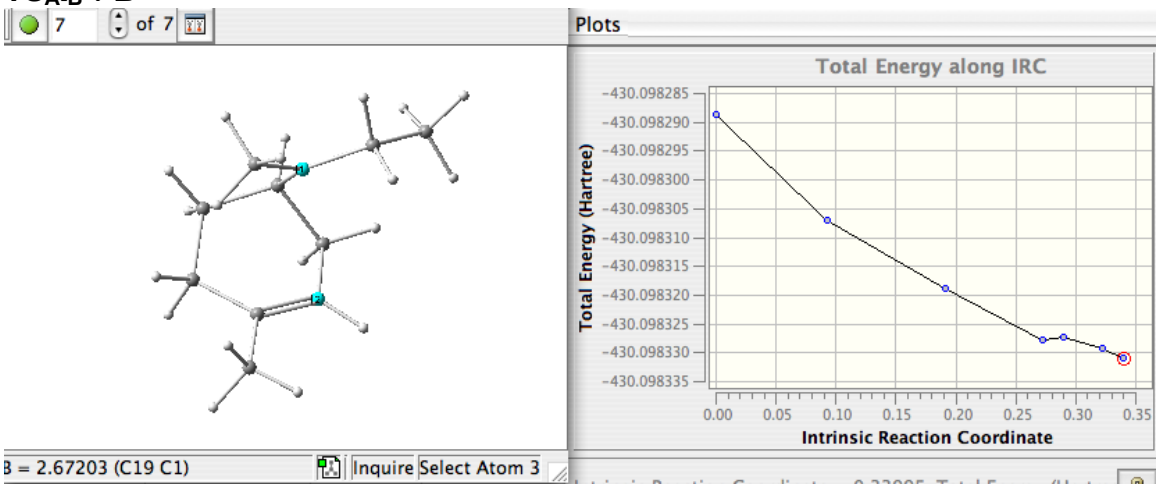


mPWB1K

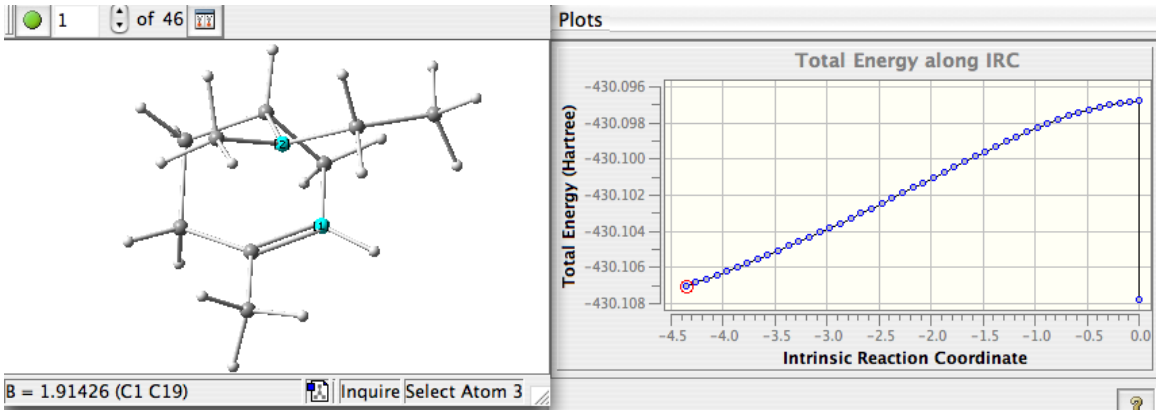
A→TS_{A-B}



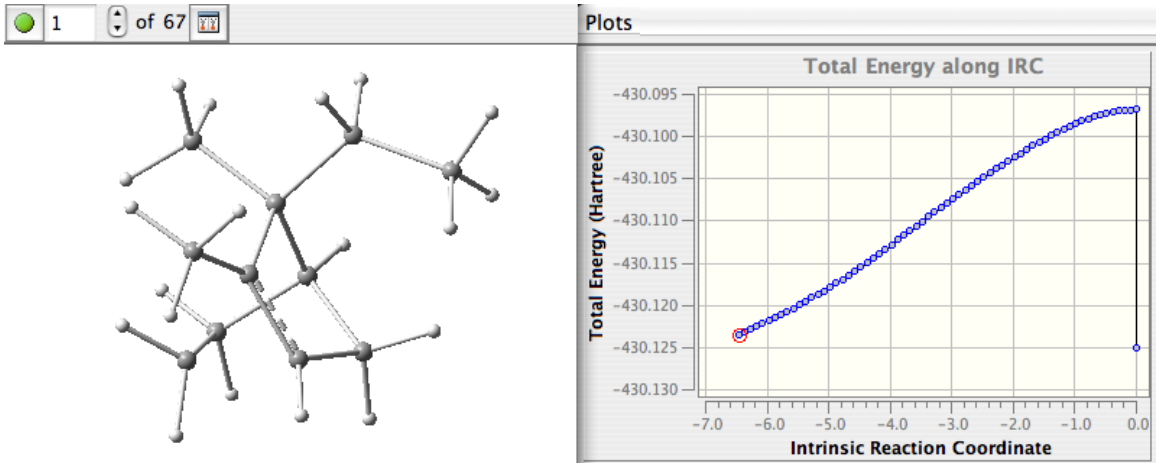
TS_{A-B}→B



B→TS



TS→C

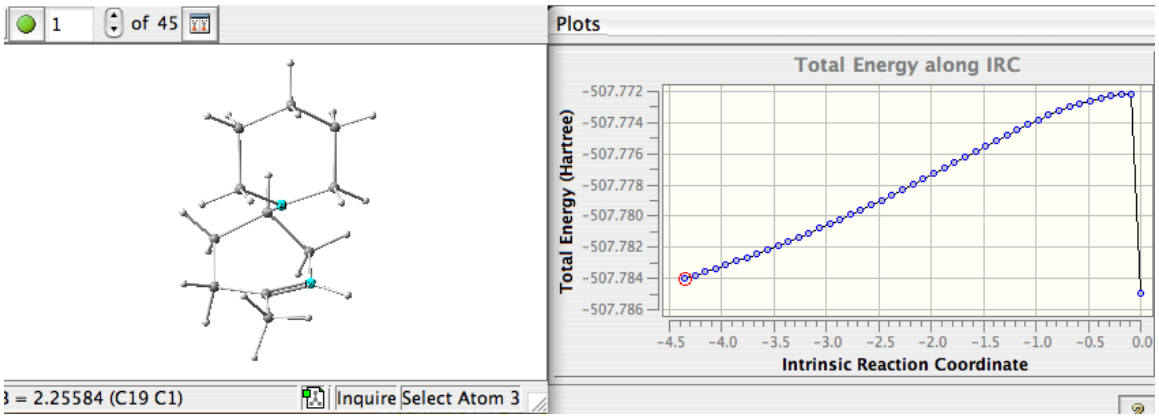


4.3. R_1/R_2= –$(CH_2)_5$–

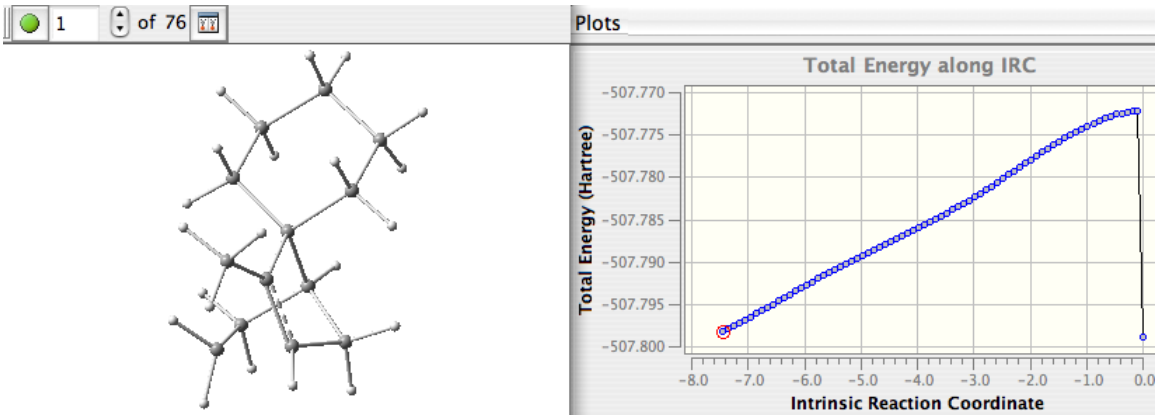
Table 1: R_1/R_2=–$(CH_2)_5$– (Fig. S6)

<u>B3LYP</u>

A→TS

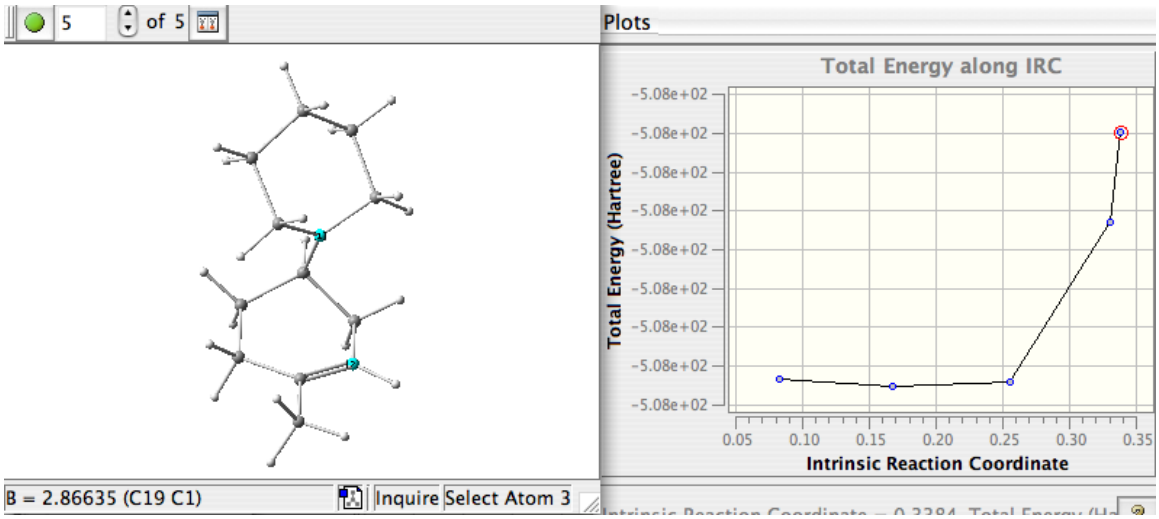


TS→C

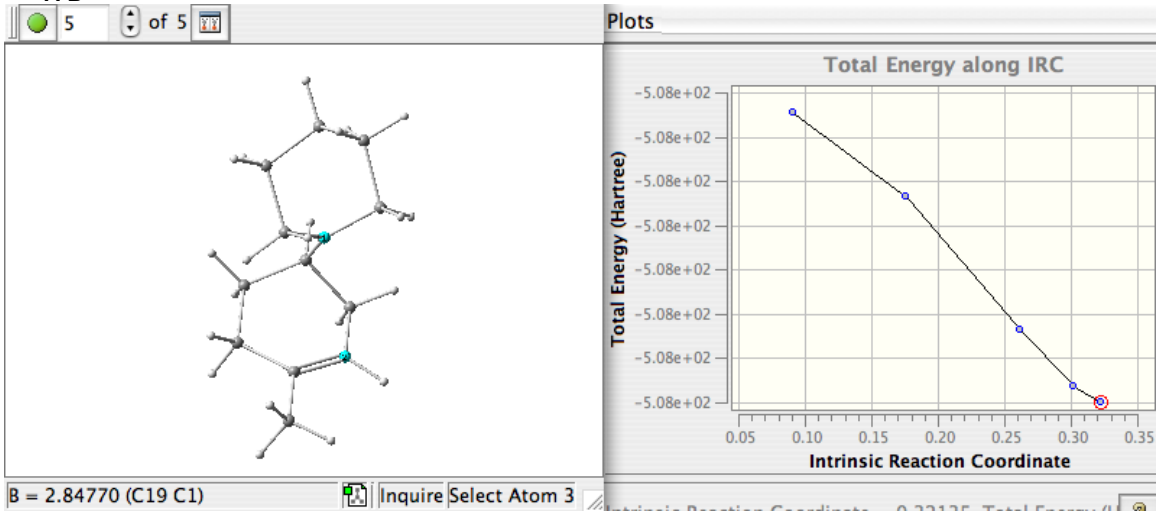


mPWB1K

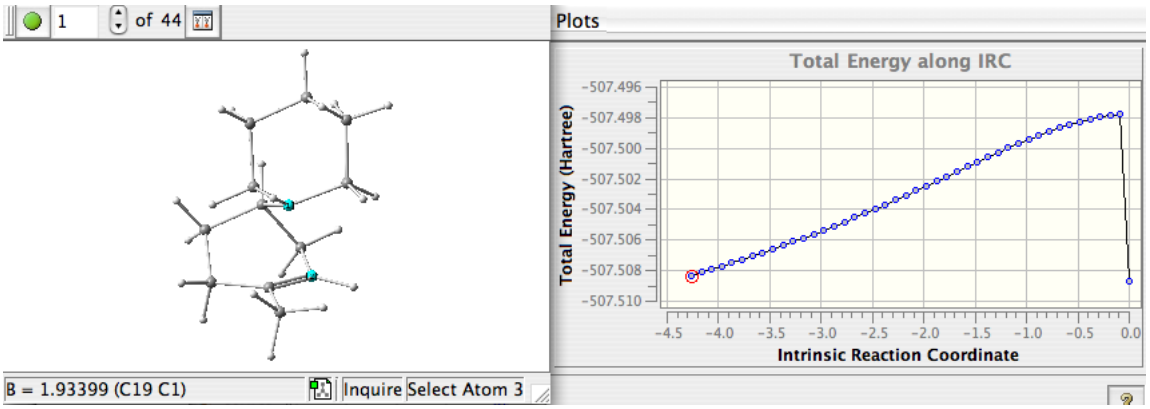
A→TS_{A-B}



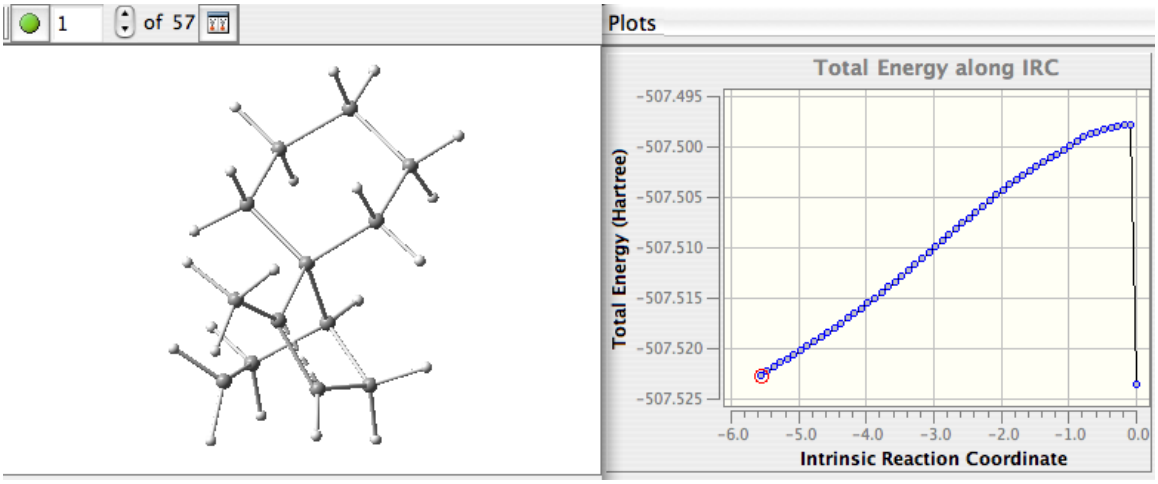
TS_{A-B}→B



B→TS



TS→C

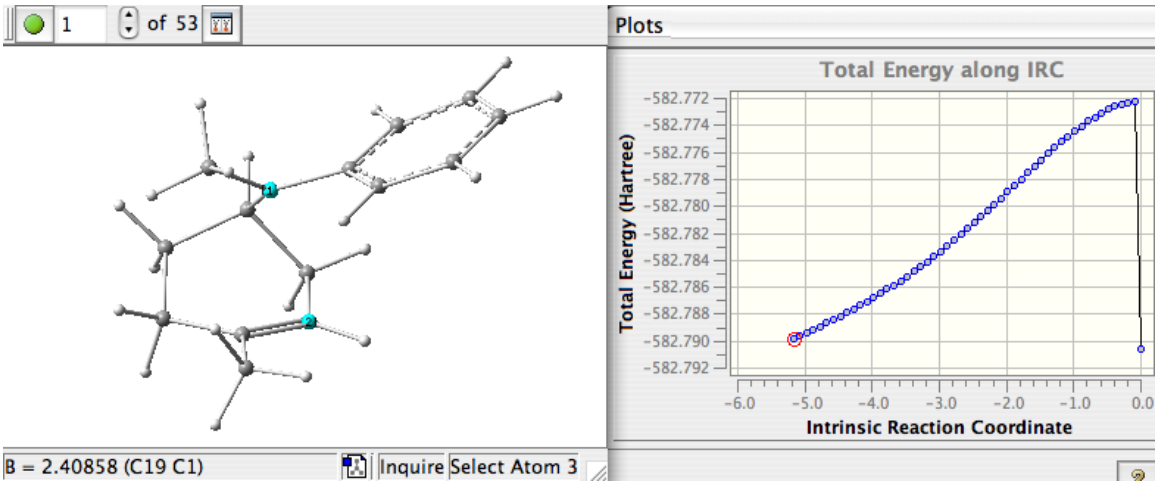


4.4. R_1=CH_3, R_2=Ph

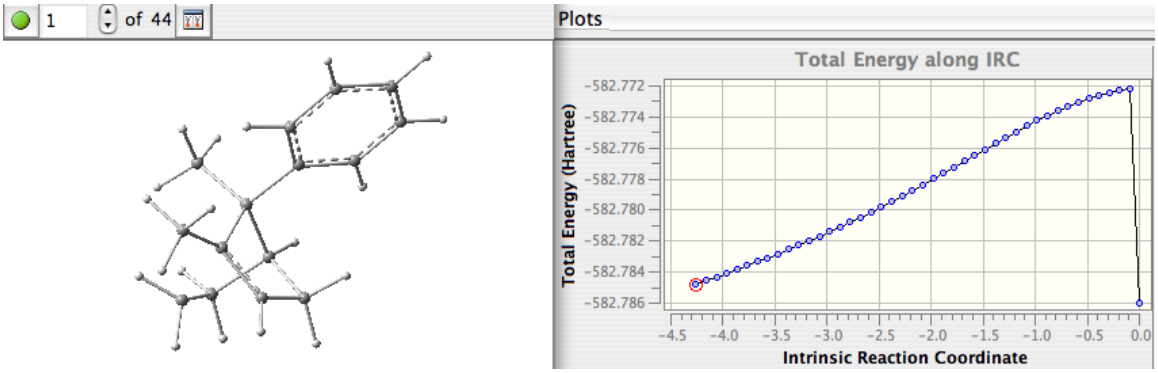
Table 1: R_1/R_2=CH_3/Ph (Fig. S7)

<u>B3LYP</u>

A→TS

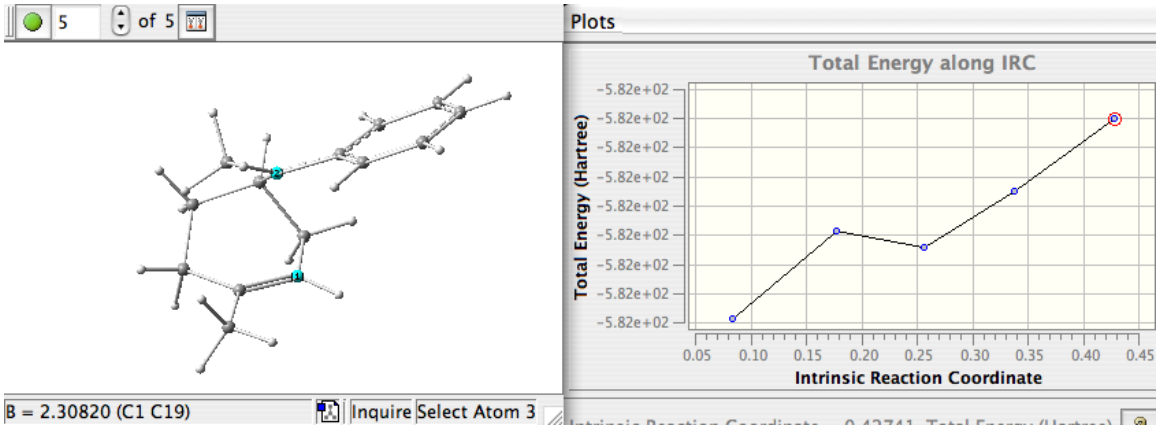


TS→C

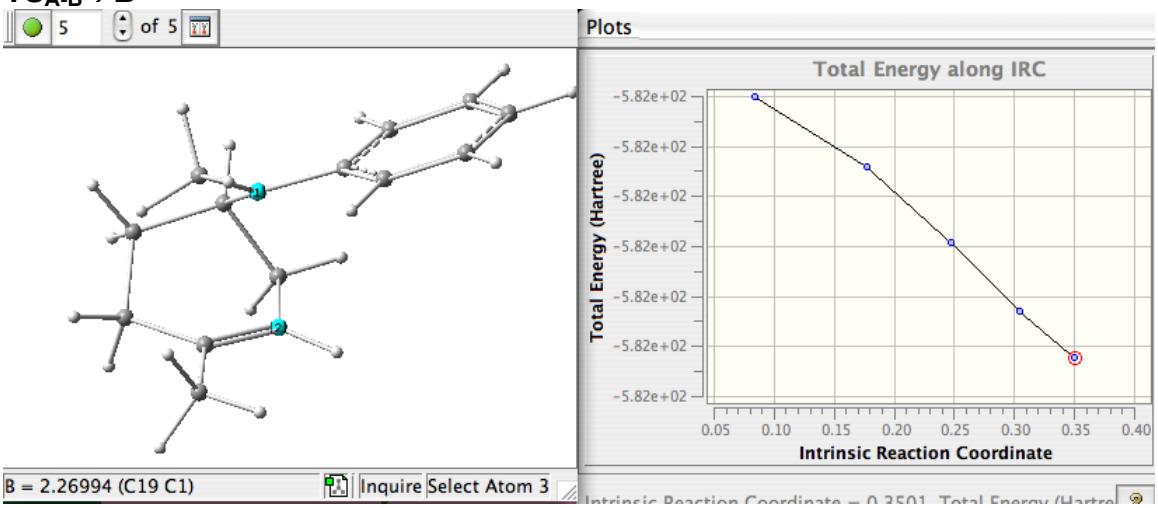


mPWB1K

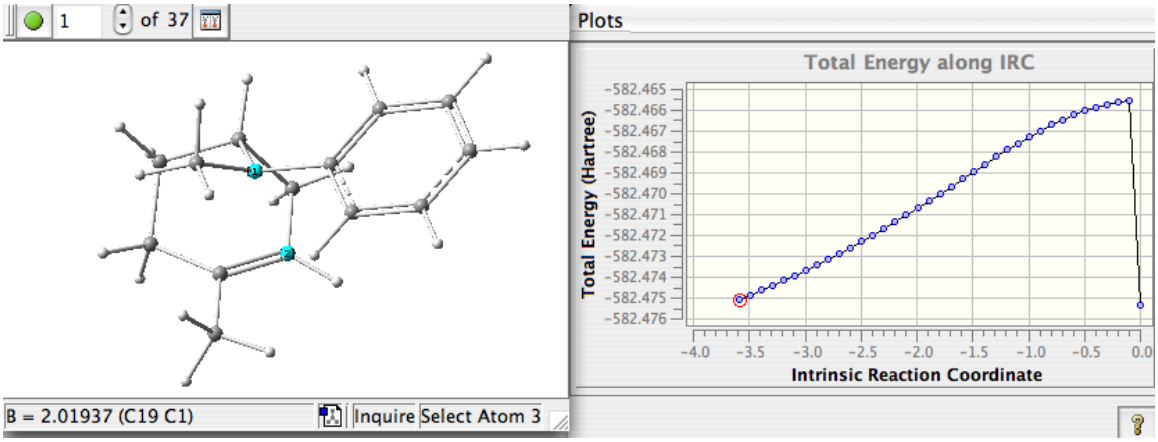
A→TS$_{A-B}$



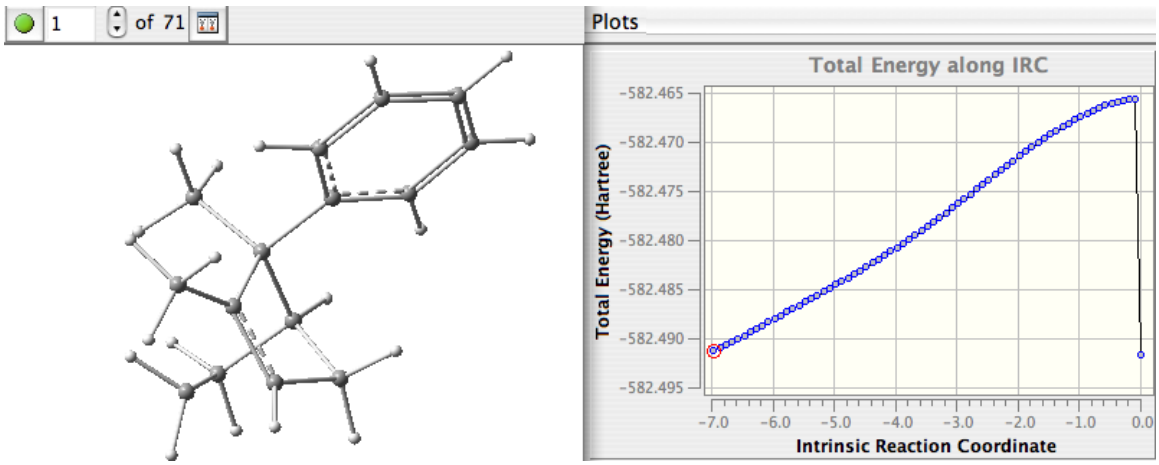
TS_{A-B}→B



B→TS



TS→C

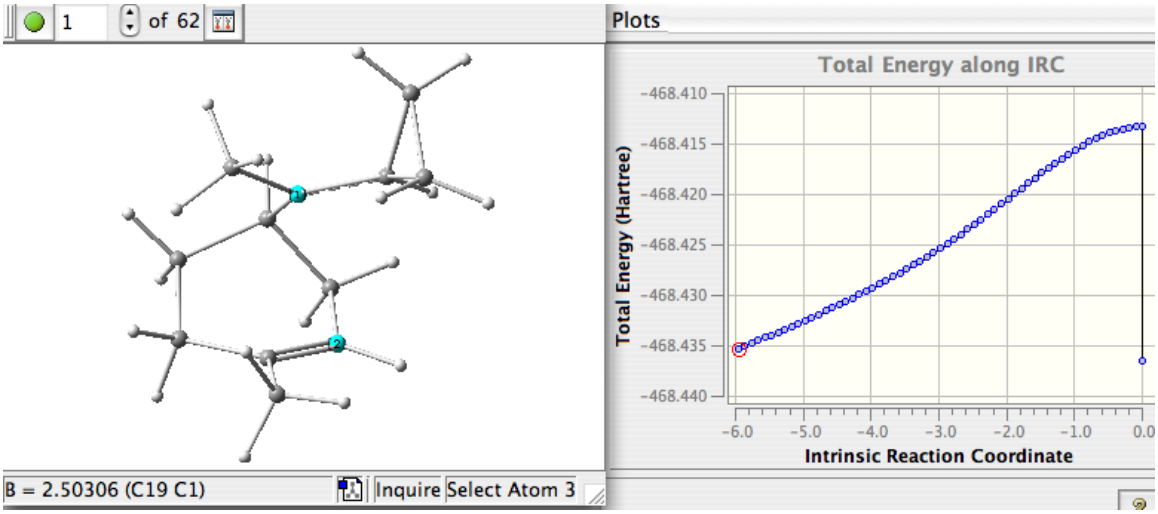


4.5. R_1=CH_3, R_2=cyclopropyl

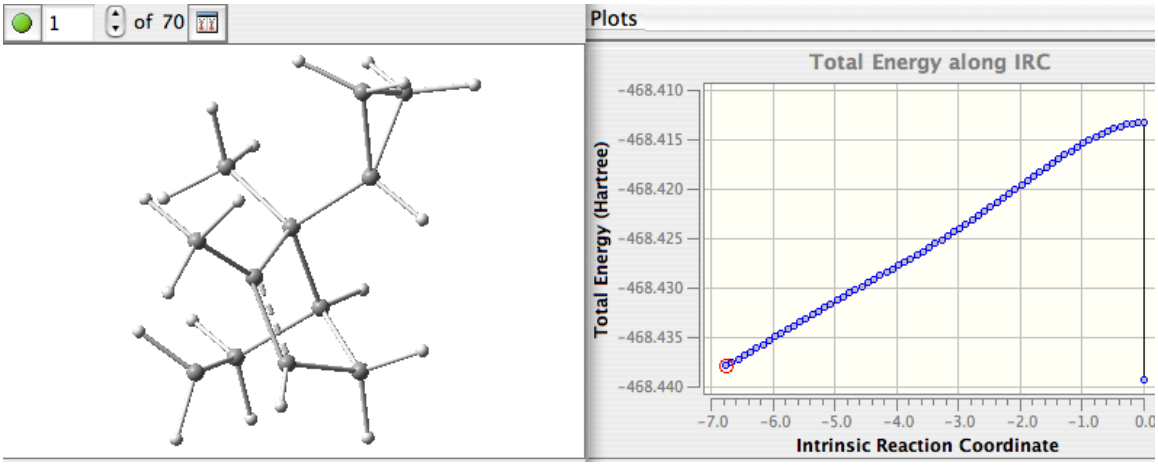
Table 1: R_1/R_2=CH_3/cyclopropyl (Fig. S8)

B3LYP

A→TS

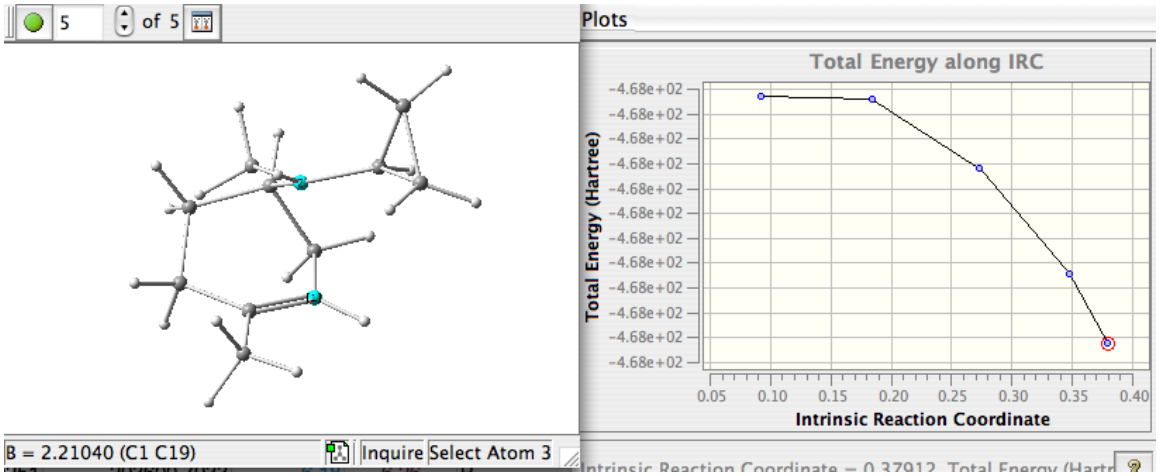


TS→C

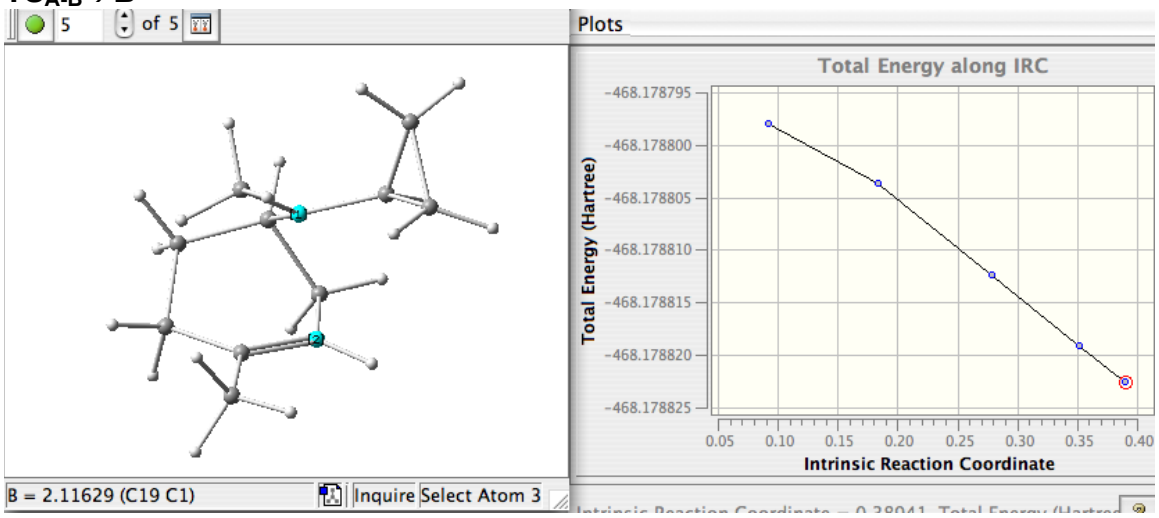


mPWB1K

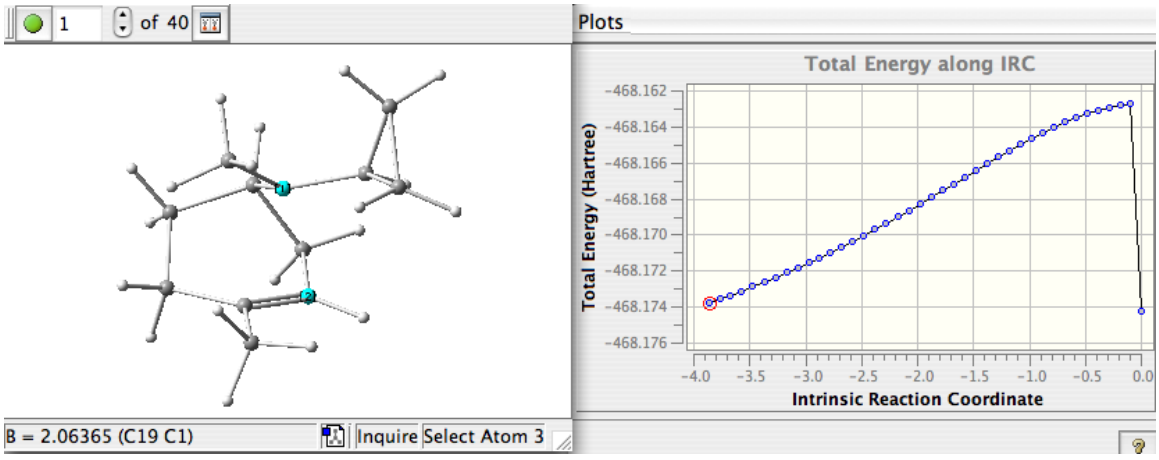
A→TS_{A-B}



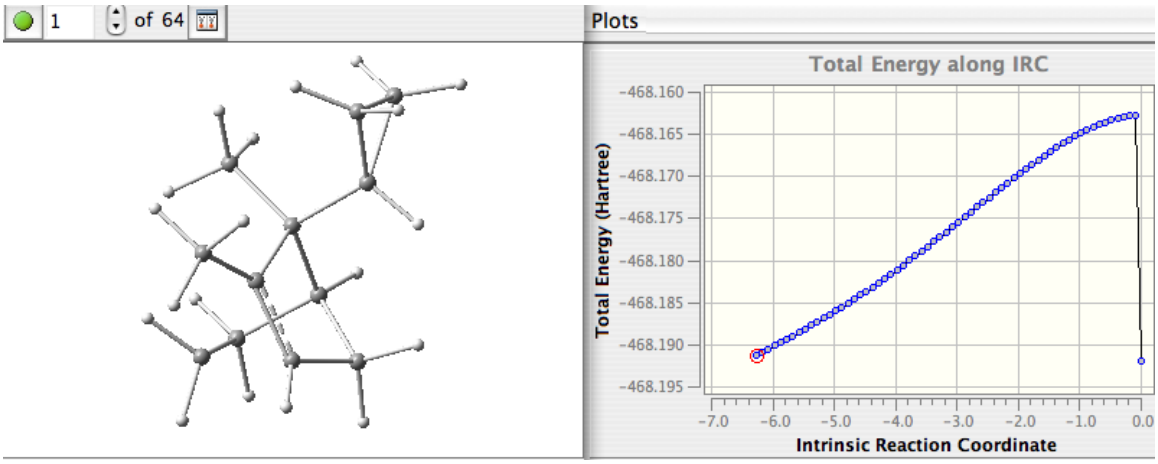
TS_{A-B}→B



B→TS



TS→C

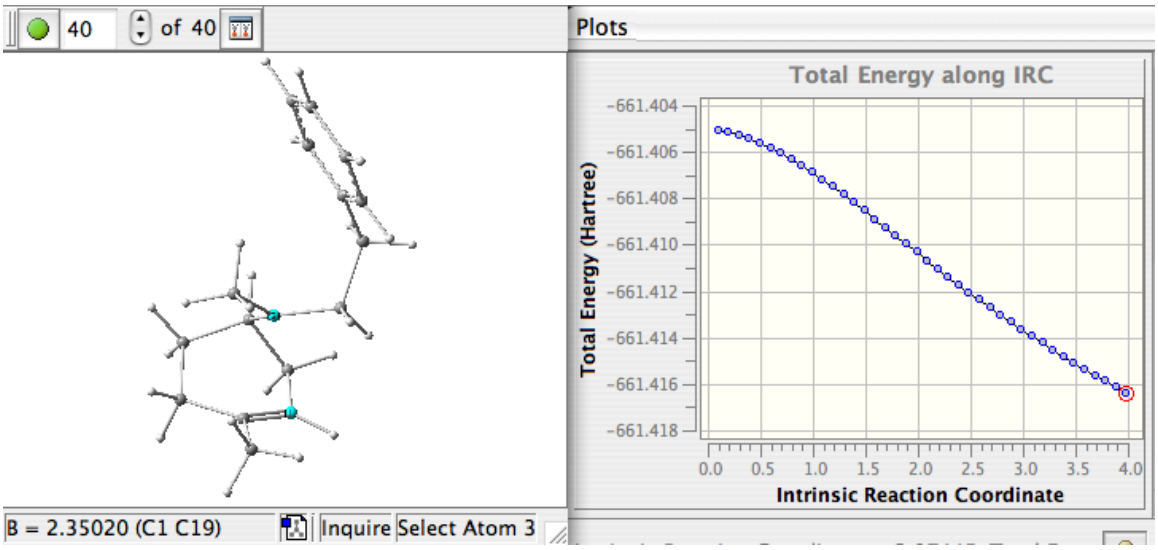


4.6. R_1=CH_3, R_2=$(CH_2)_2$–Ph

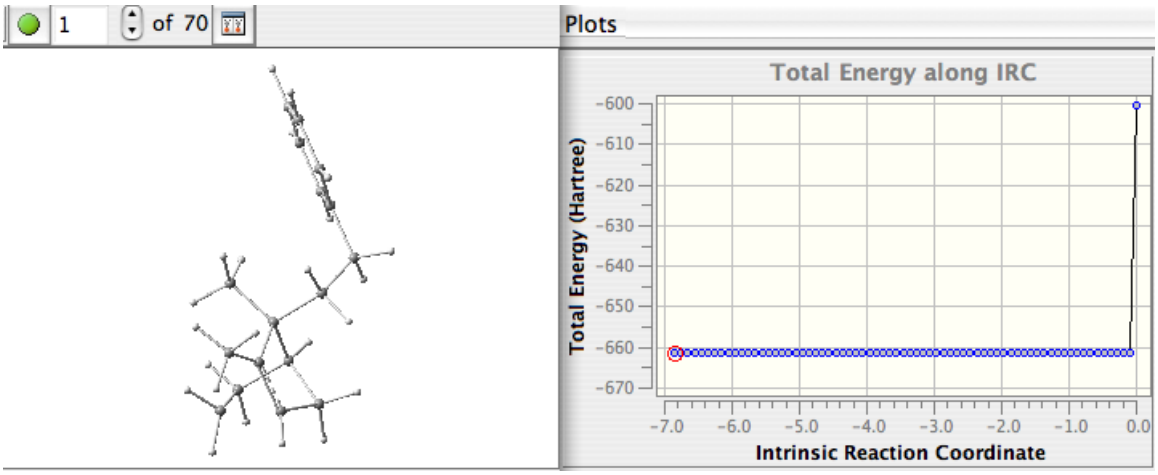
Table 1: R_1/R_2=$CH_3/(CH_2)_2$–Ph (aligned) (Fig. S9)

<u>B3LYP</u>

A→TS

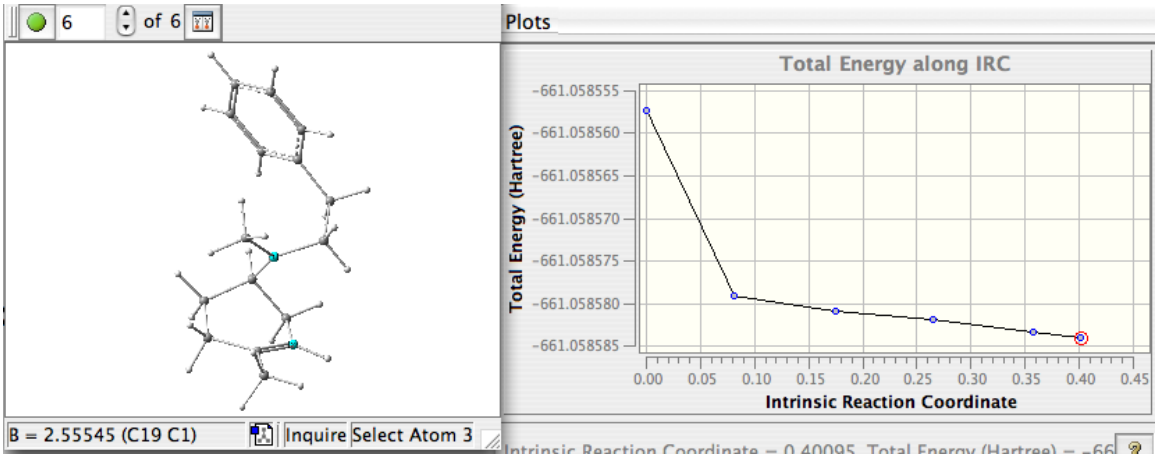


TS→C

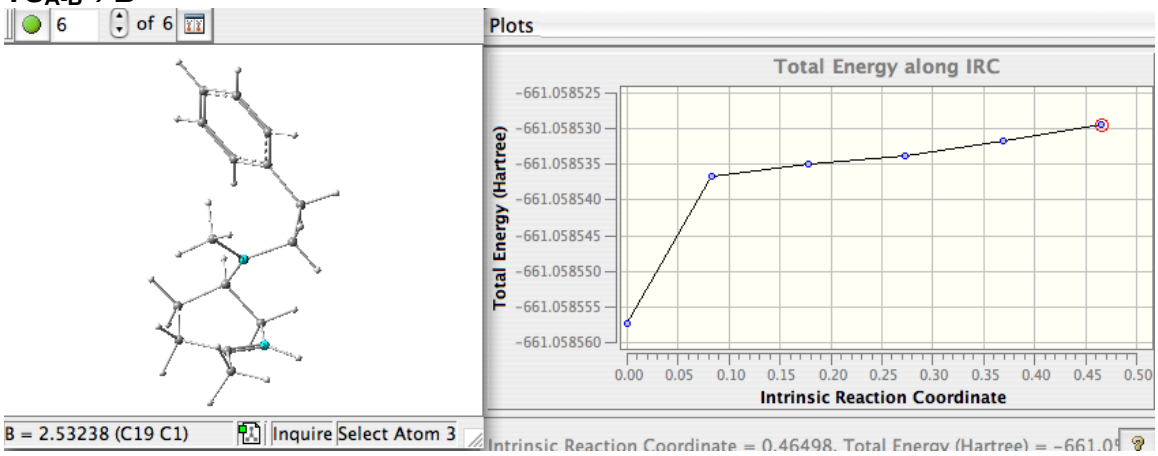


mPWB1K

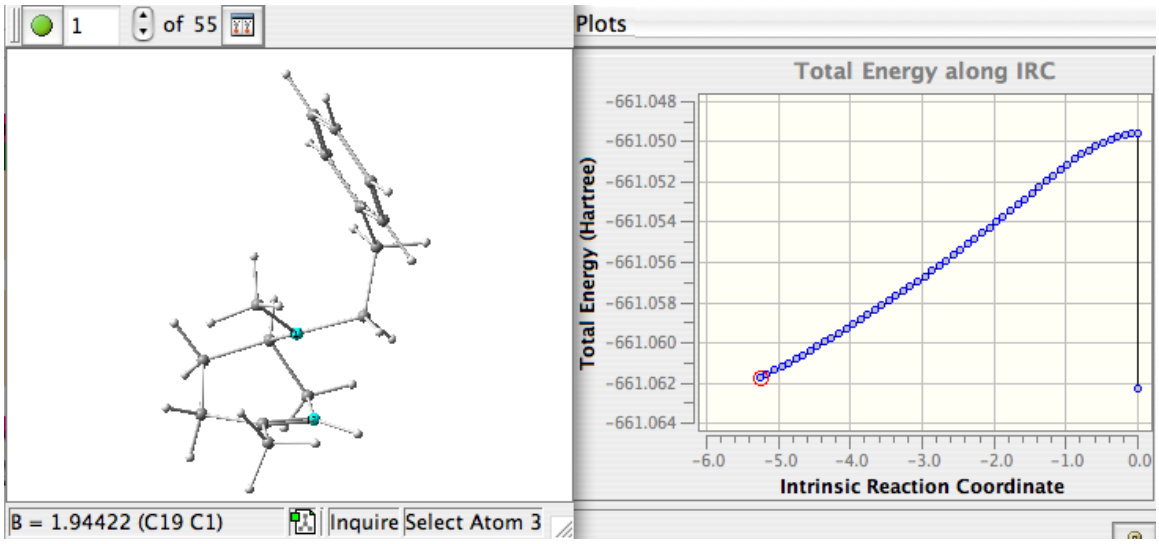
A→TS_{A-B}



TS_{A-B}→B



B→TS



TS→C

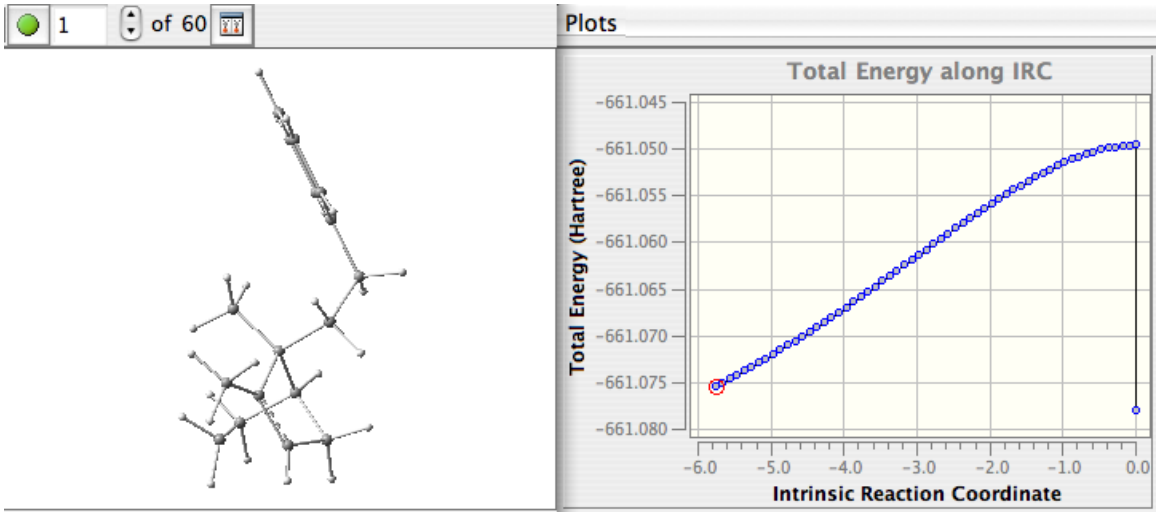
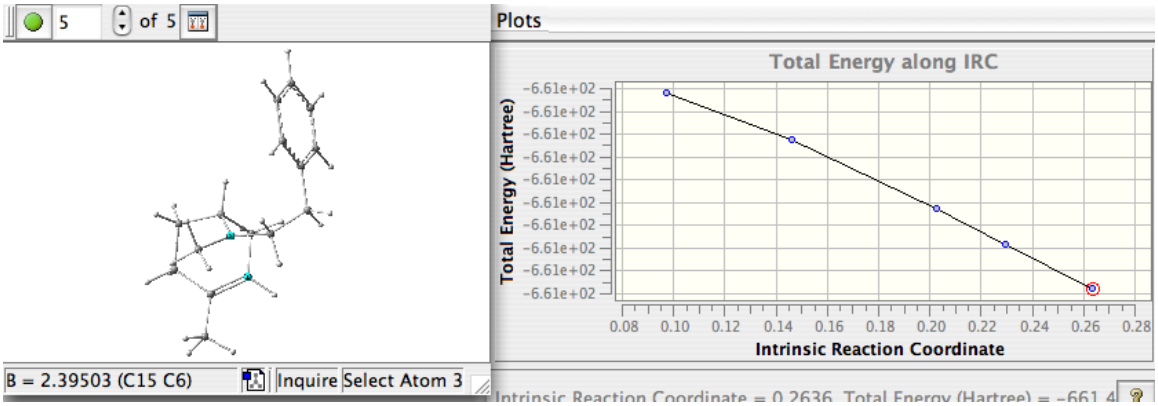


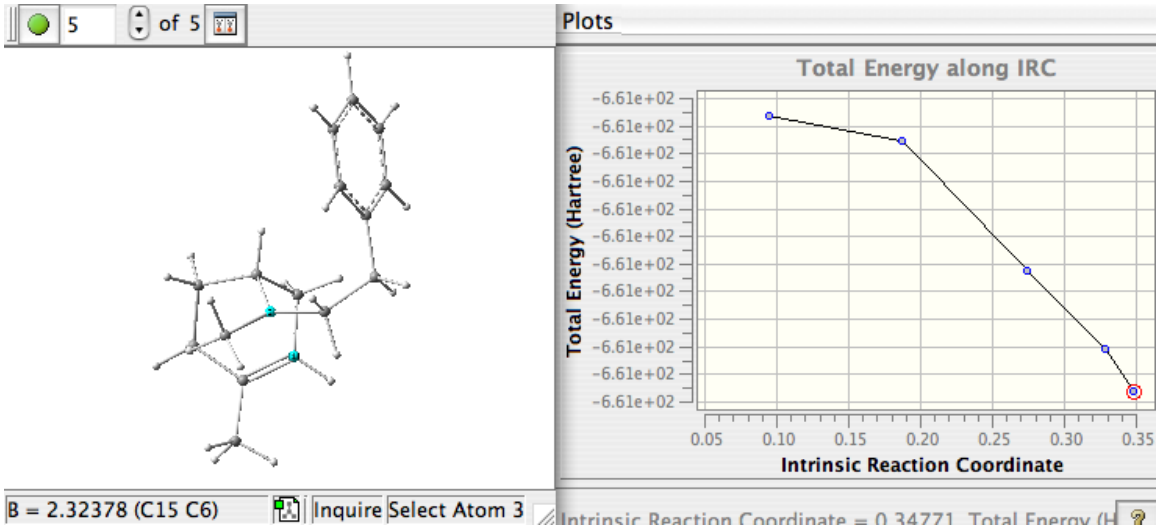
Table 2: R_1/R_2=$CH_3/(CH_2)_2$–Ph (extended) (Fig. S10)

<u>B3LYP</u>

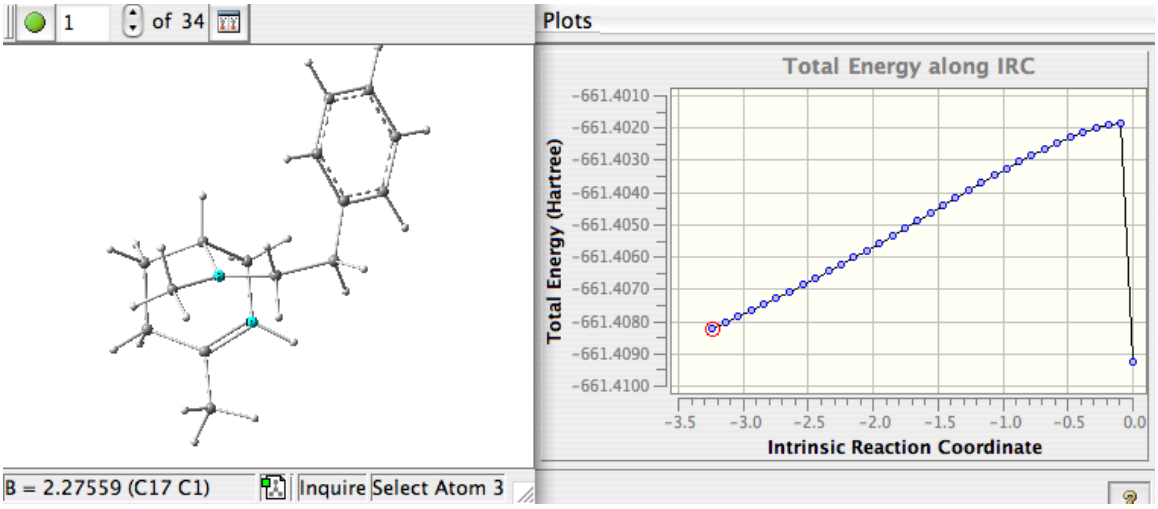
A→TS_{A-B}



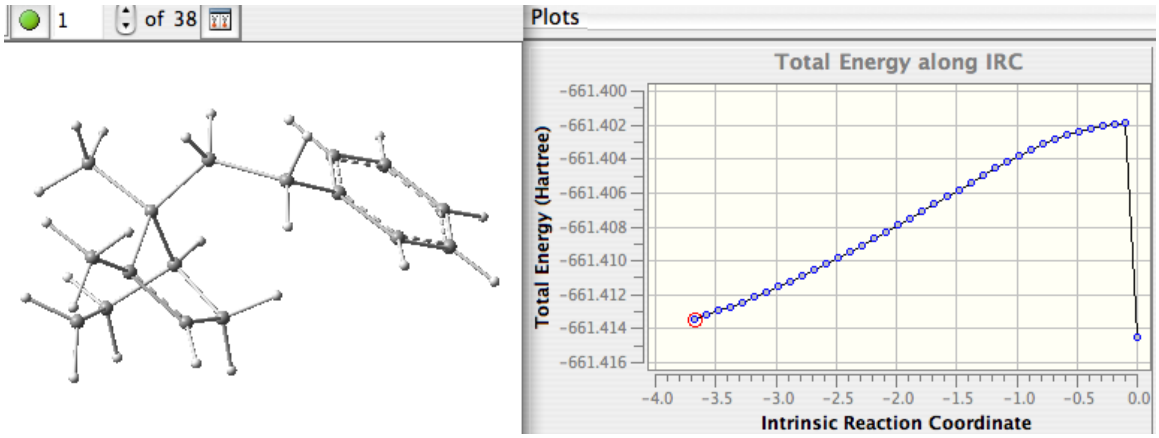
TS_{A-B}→B



B→TS



TS→C

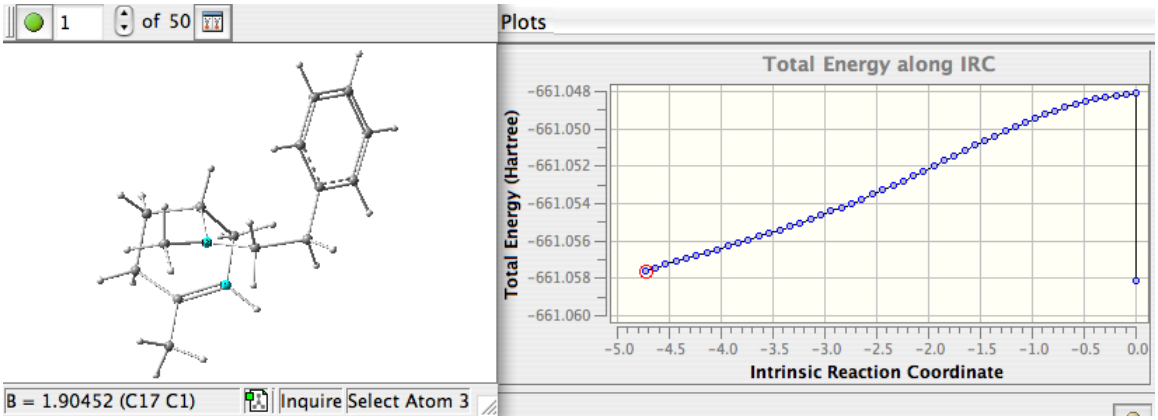


mPWB1K

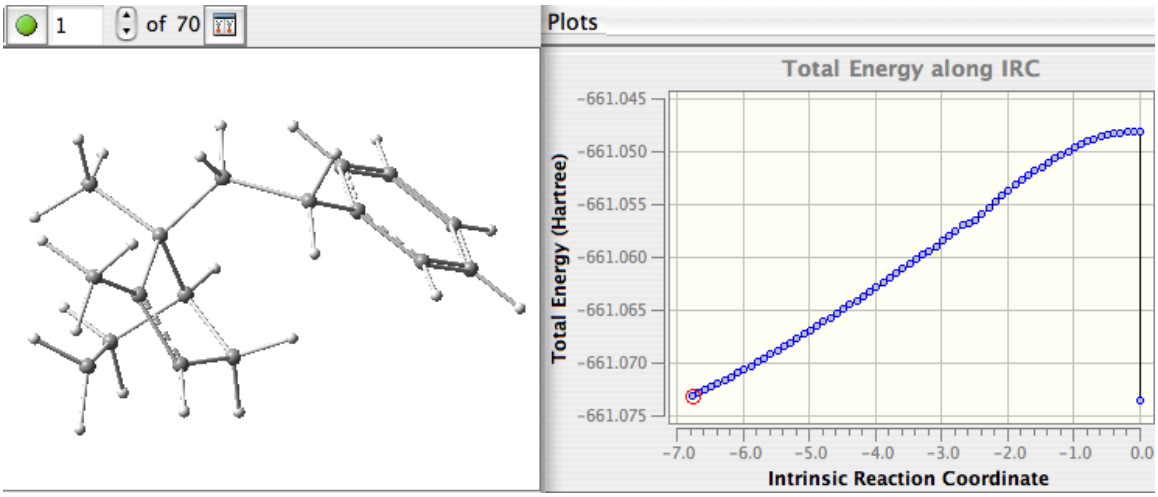
TS_{A-B}

We were unable to locate **TS_{A-B}** at this level of theory.

B→TS



TS→C

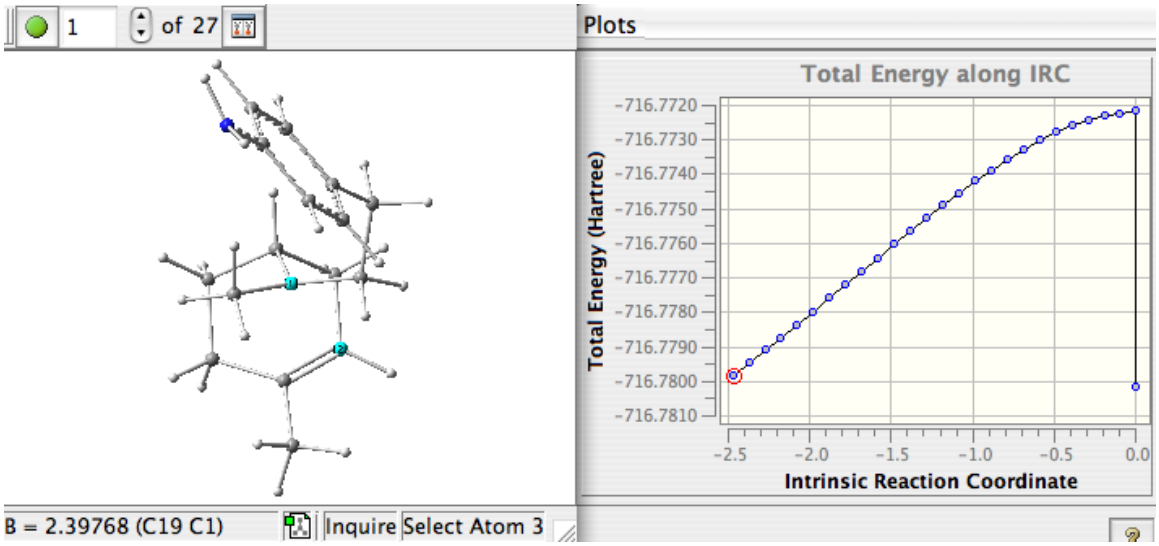


4.7. R_1=CH_3, R_2=$(CH_2)_2$–*p*–NH_2–Ph

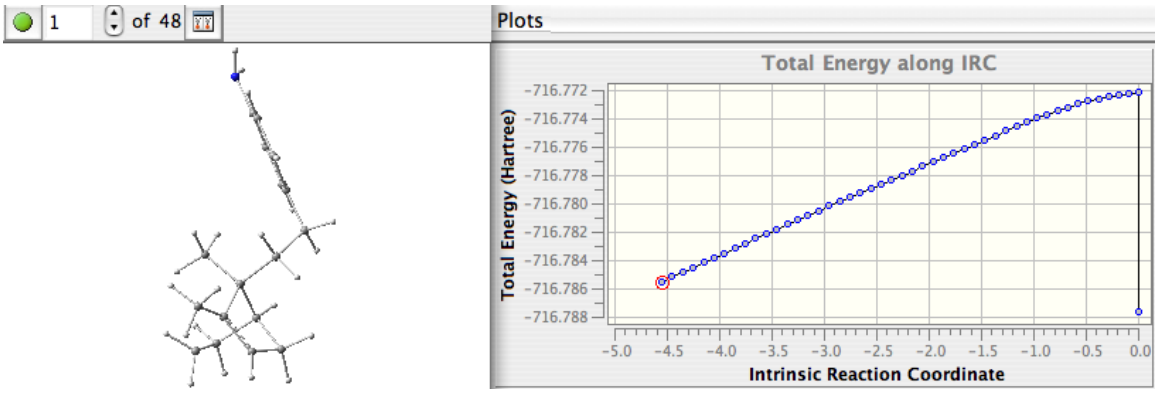
Table 1: R_1/R_2=$CH_3/(CH_2)_2$–*p*–NH_2–Ph (aligned) (Fig. S11)

<u>B3LYP</u>

A→TS

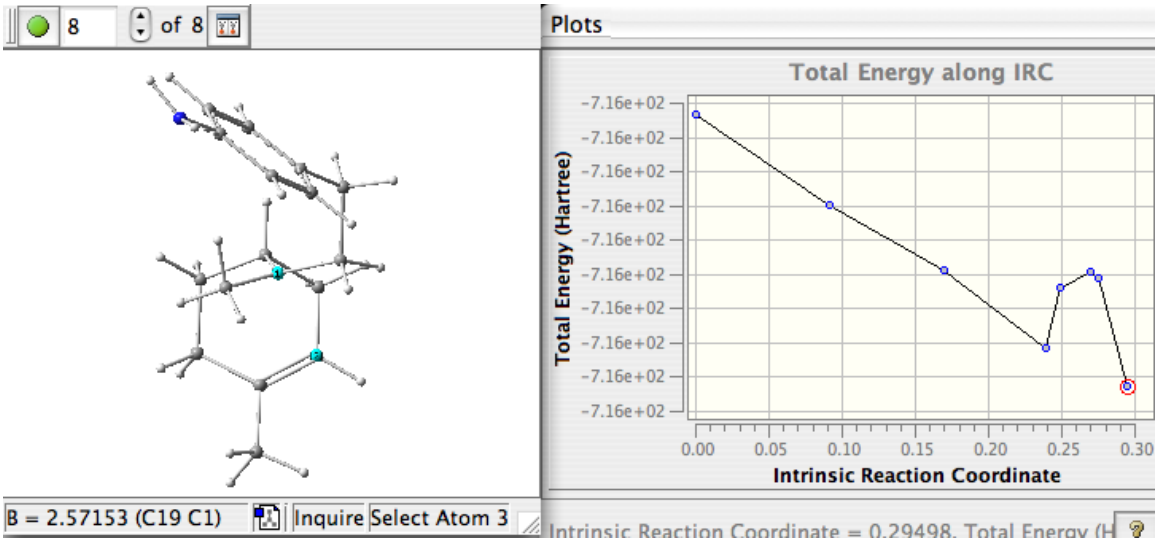


TS→C

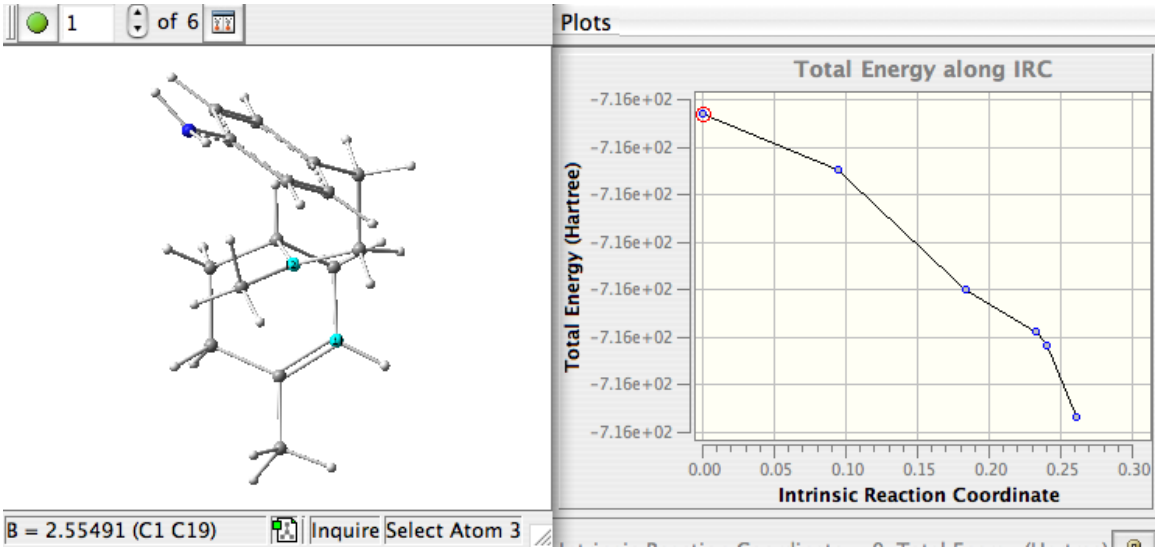


mPWB1K

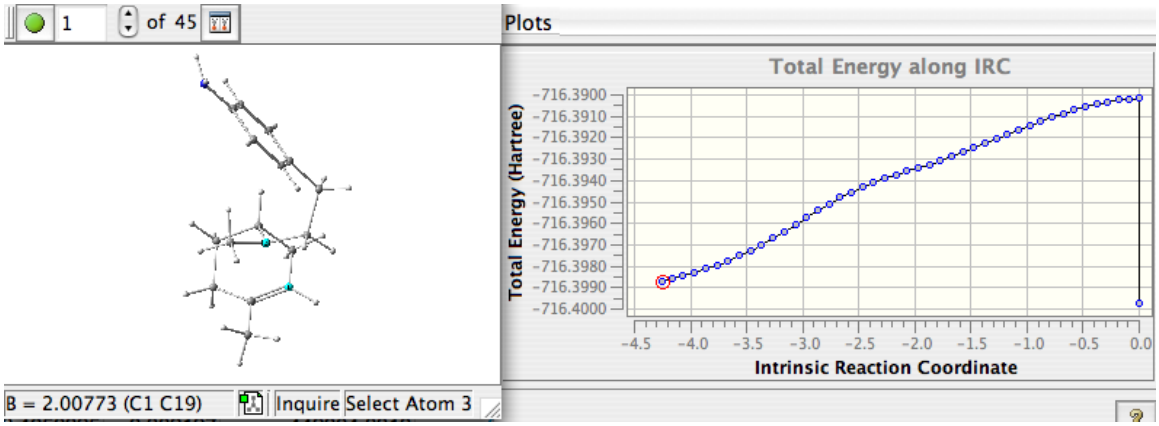
A→TS$_{A-B}$



TS$_{A-B}$→B



B→TS



TS→C

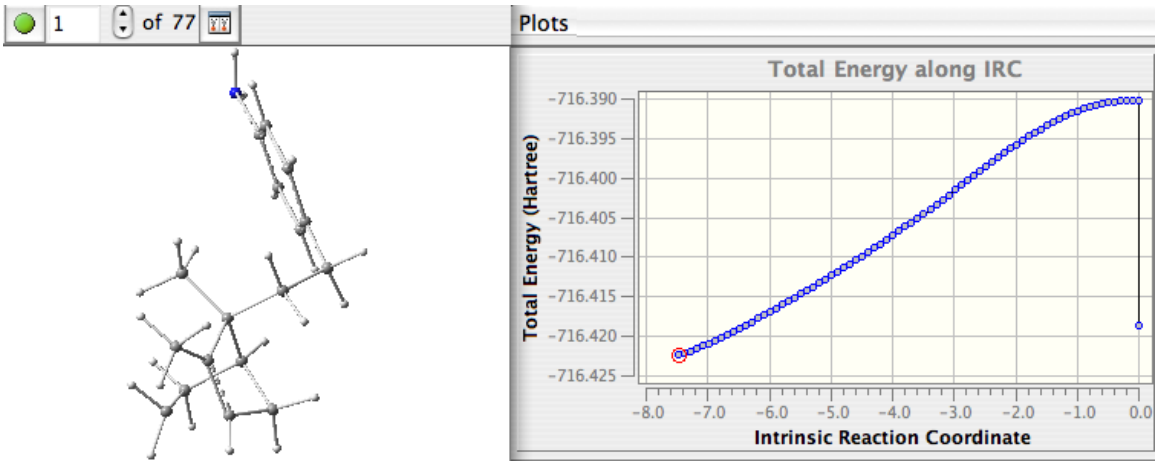
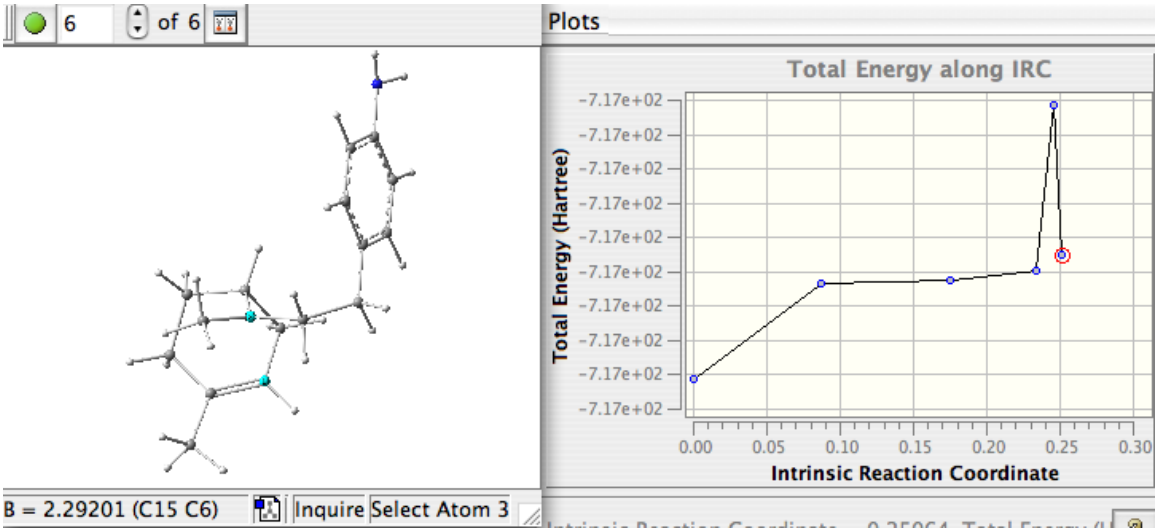


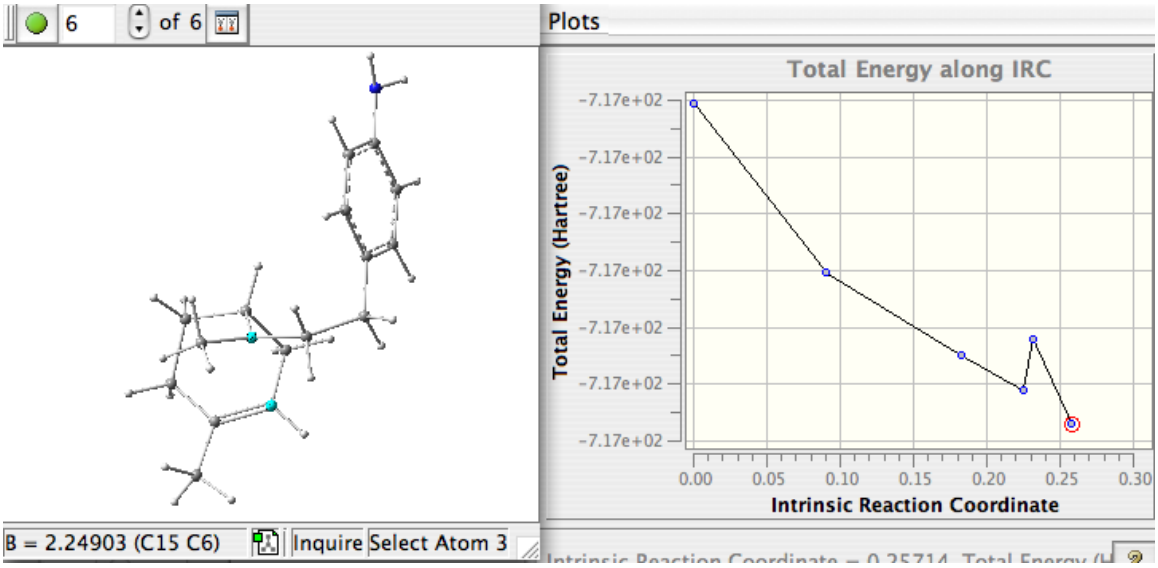
Table 2: R_1/R_2=CH_3/$(CH_2)_2$–*p*–NH_2–Ph (extended) (Fig. S12)

<u>B3LYP</u>

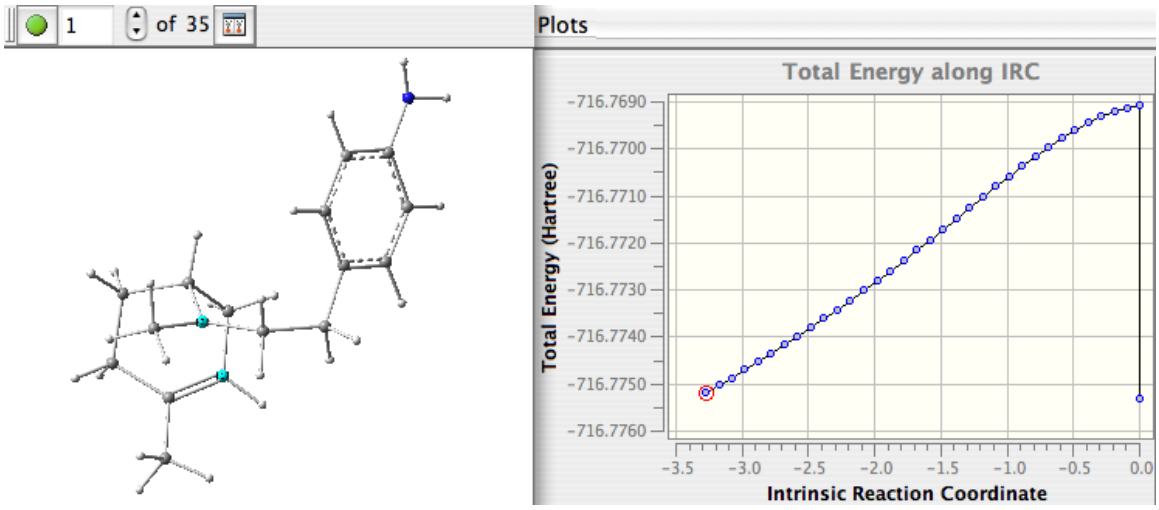
A→TS_{A-B}


6
of 6
Plots
Total Energy along IRC
Total Energy (Hartree)
-7.17e+02
-7.17e+02
-7.17e+02
-7.17e+02
-7.17e+02
-7.17e+02
-7.17e+02
-7.17e+02
-7.17e+02
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Intrinsic Reaction Coordinate
B = 2.29201 (C15 C6)
Inquire
Select Atom 3

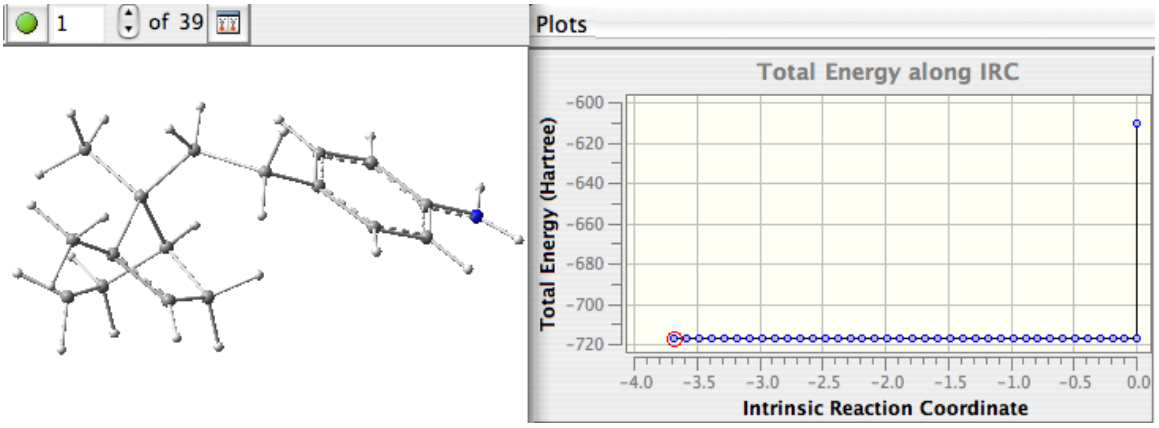
TS_{A-B}→B


6
of 6
Plots
Total Energy along IRC
Total Energy (Hartree)
-7.17e+02
-7.17e+02
-7.17e+02
-7.17e+02
-7.17e+02
-7.17e+02
-7.17e+02
-7.17e+02
-7.17e+02
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Intrinsic Reaction Coordinate
B = 2.24903 (C15 C6)
Inquire
Select Atom 3

B→TS

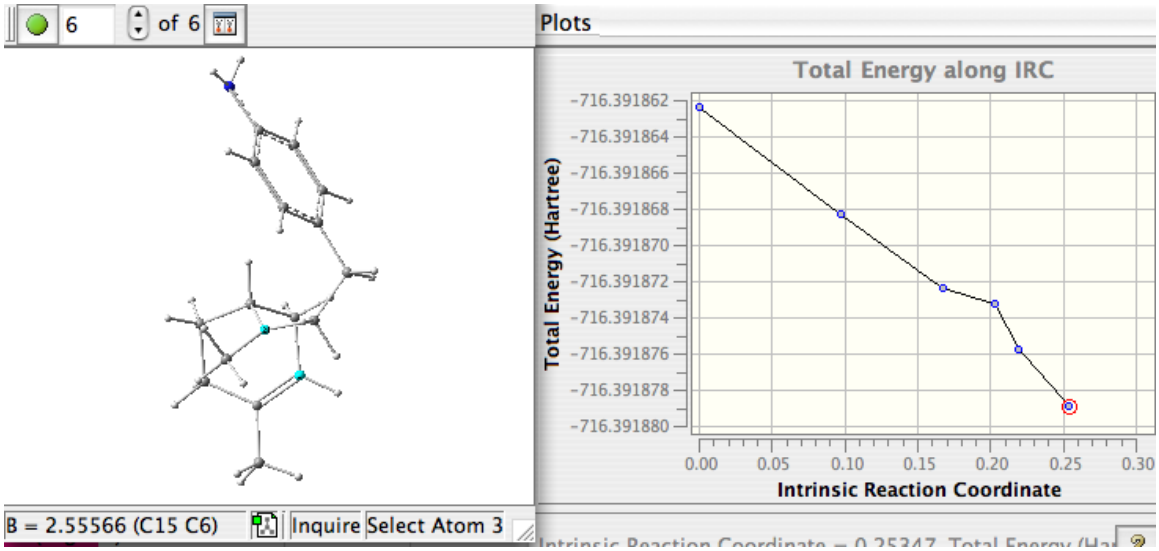


TS→C

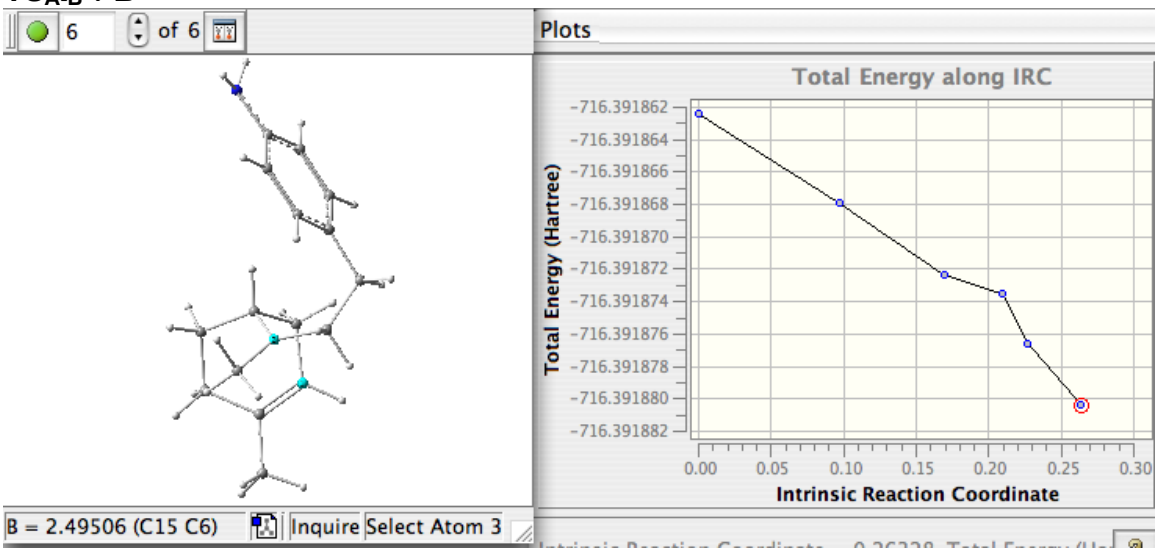


mPWB1K

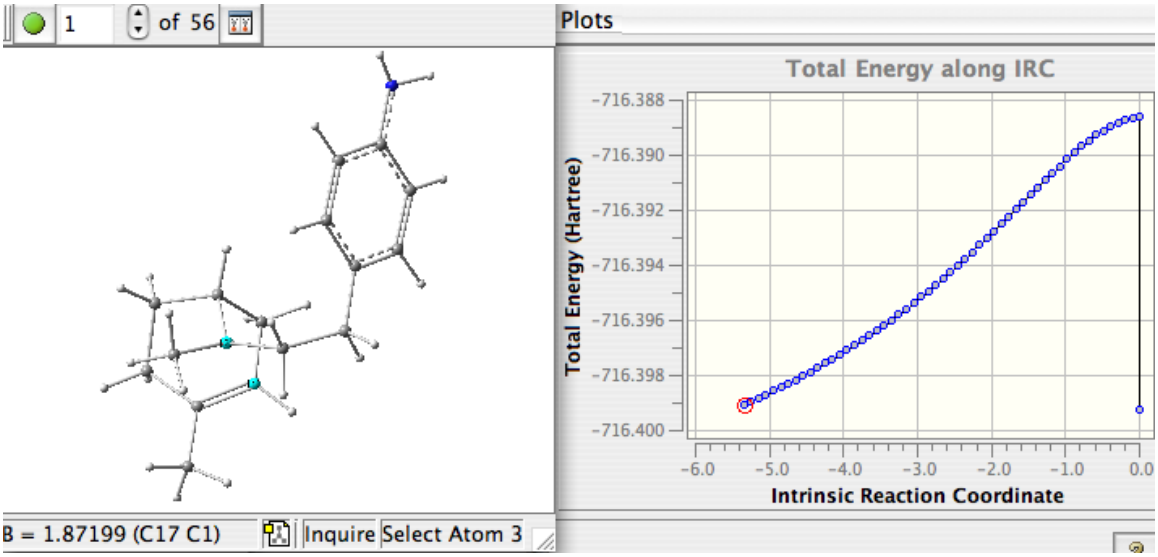
A→TS$_{A-B}$



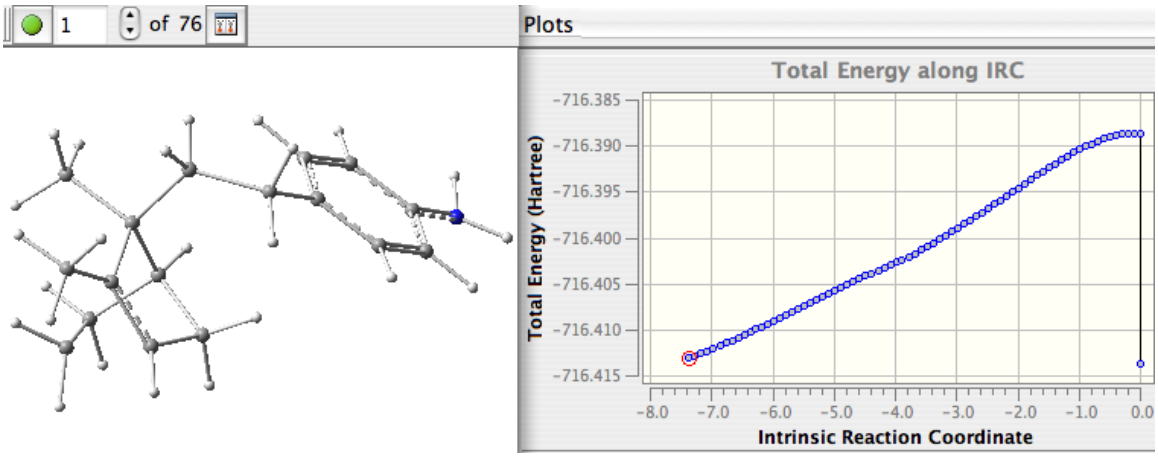
$TS_{A\text{-}B} \rightarrow B$



$B \rightarrow TS$



TS→C

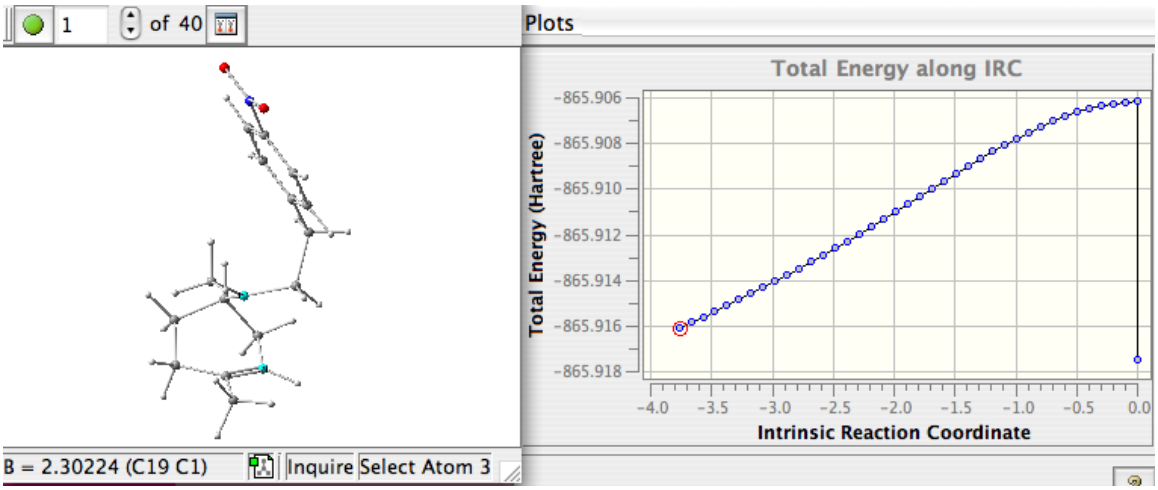


4.8. R_1=CH_3, R_2=$(CH_2)_2$–*p*–NO_2–Ph

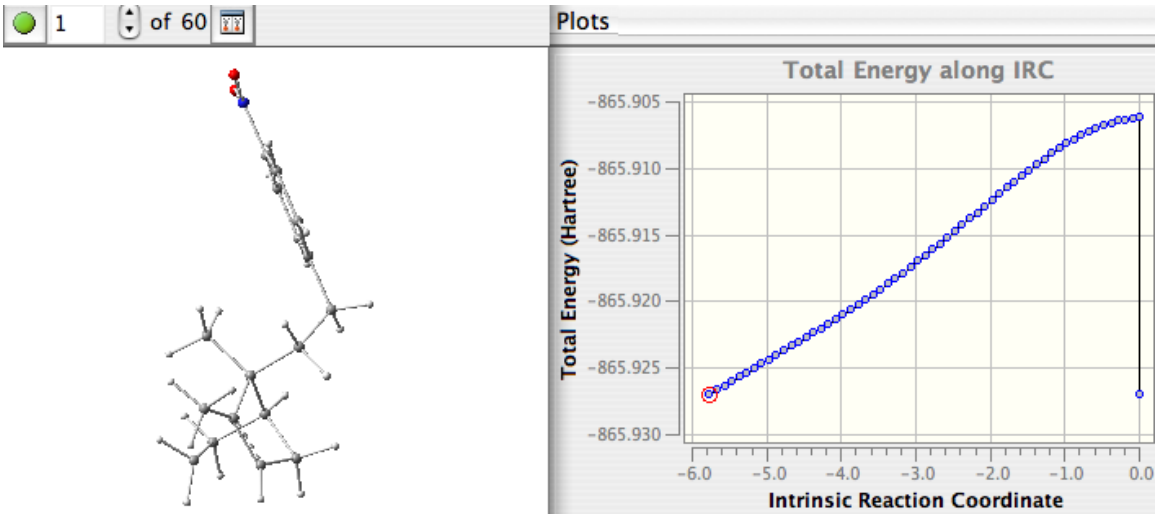
Table 1: R_1/R_2=$CH_3/(CH_2)_2$–*p*–NO_2–Ph (aligned) (Fig. S13)

B3LYP

A→TS

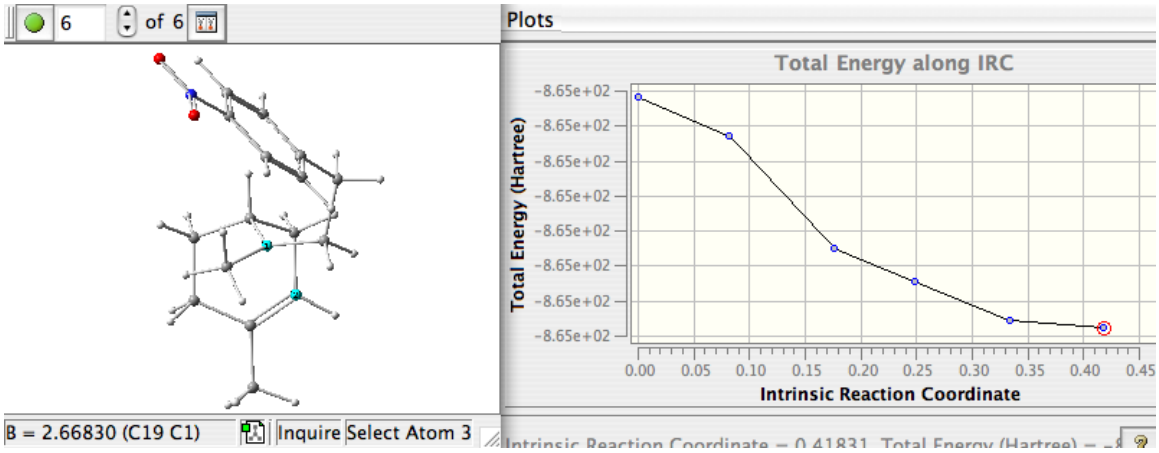


TS→C

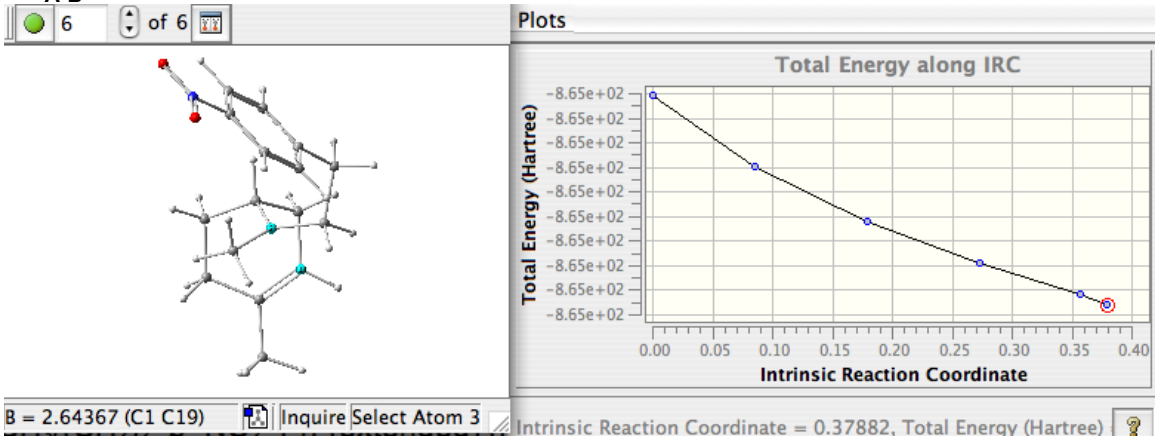


mPWB1K

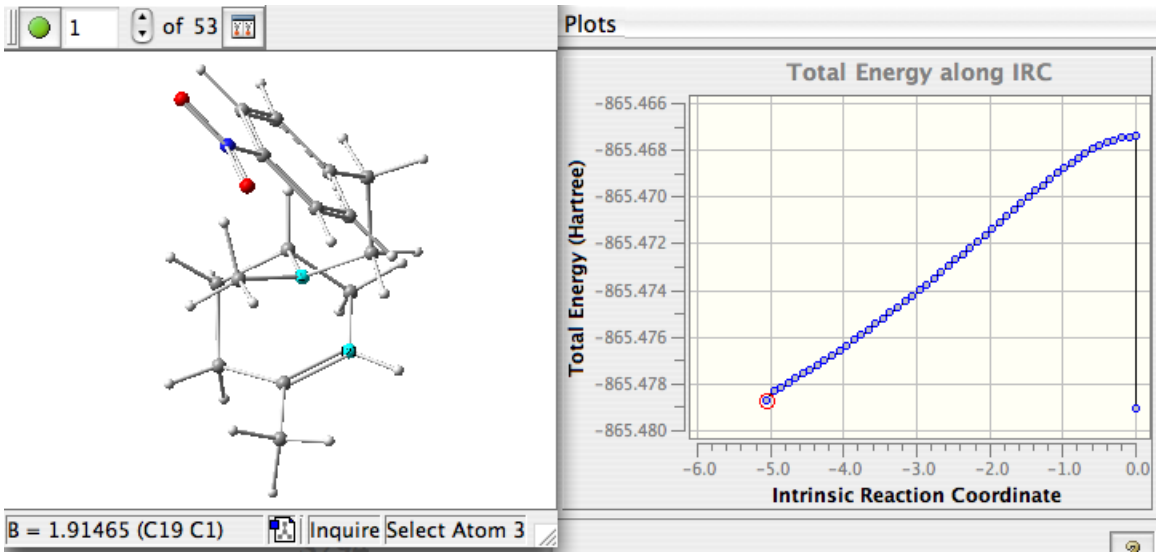
A→TS_{A-B}



TS_{A-B}→B



B→TS



TS→C

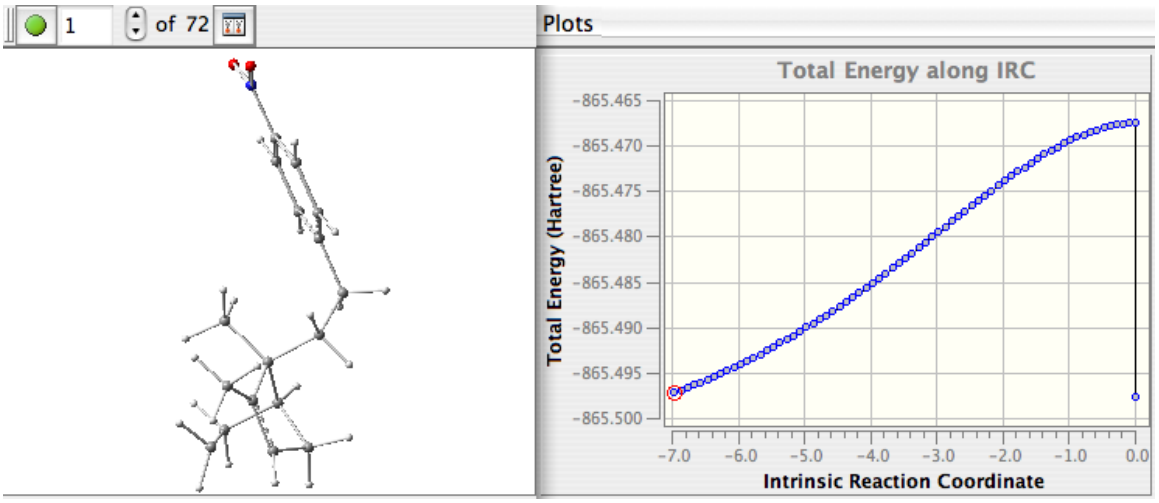
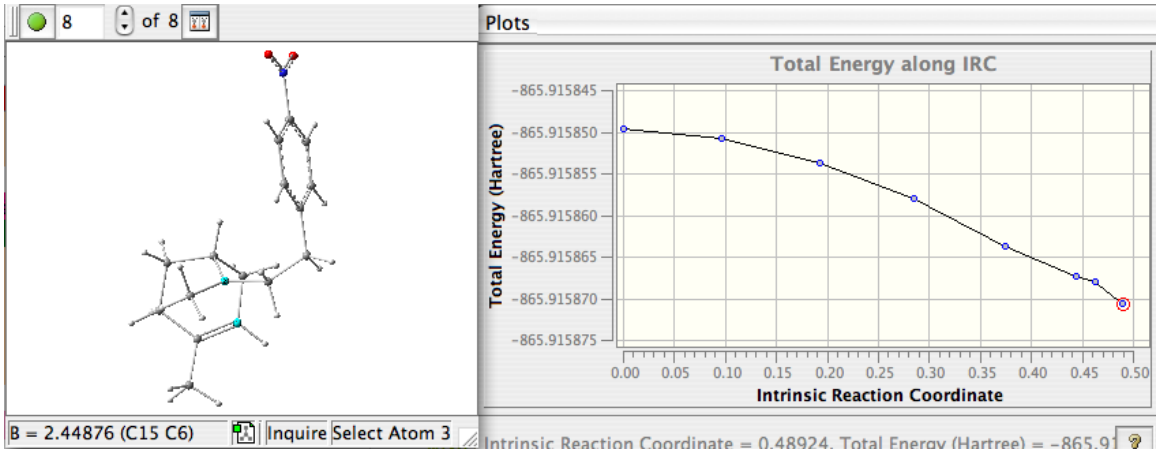


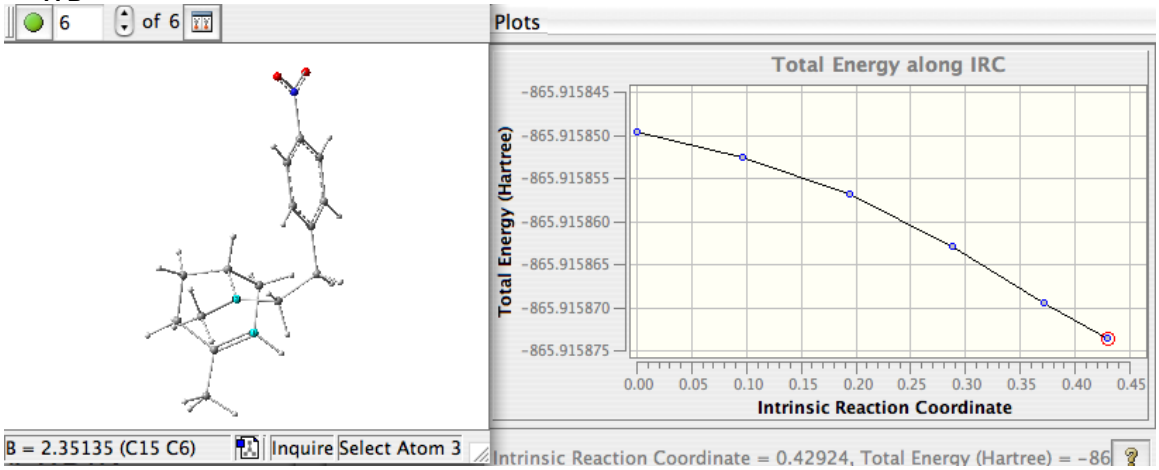
Table 2: R_1/R_2=$CH_3/(CH_2)_2$–*p*–NO_2–Ph (extended) (Fig. S14)

<u>B3LYP</u>

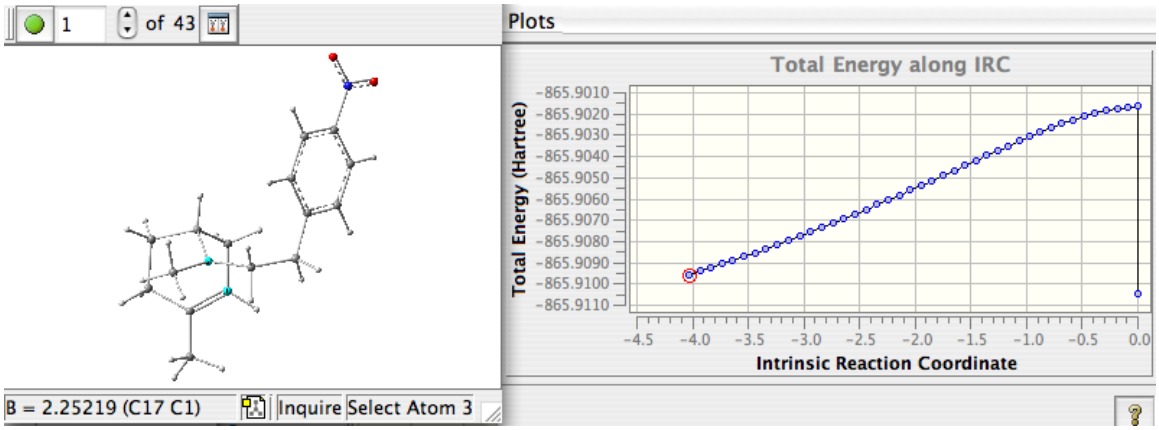
A→TS_{A-B}



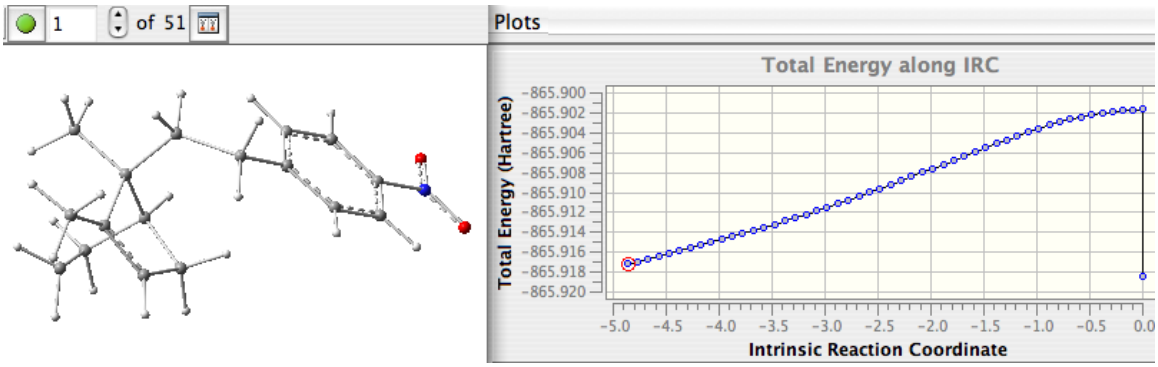
TS_{A-B}→B



B→TS



TS→C

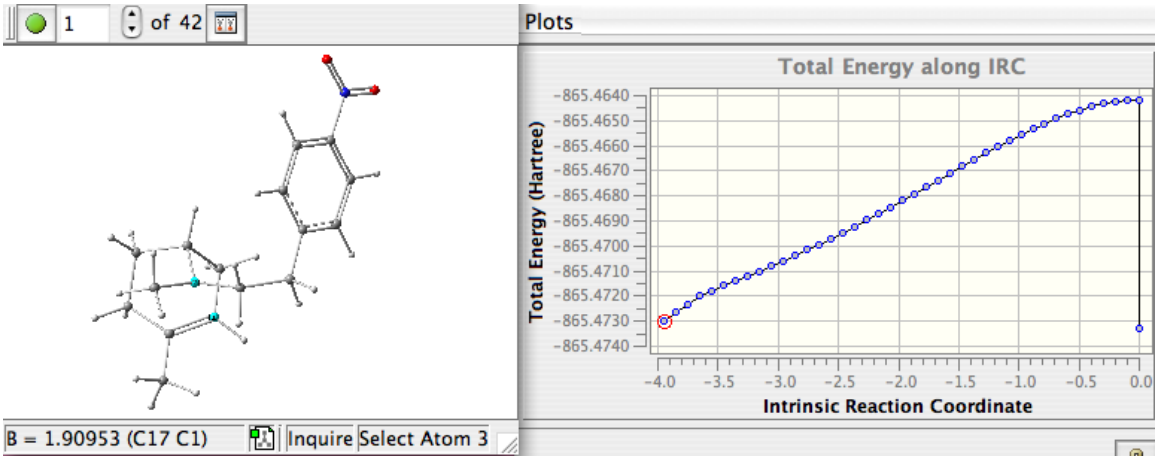


<u>mPWB1K</u>

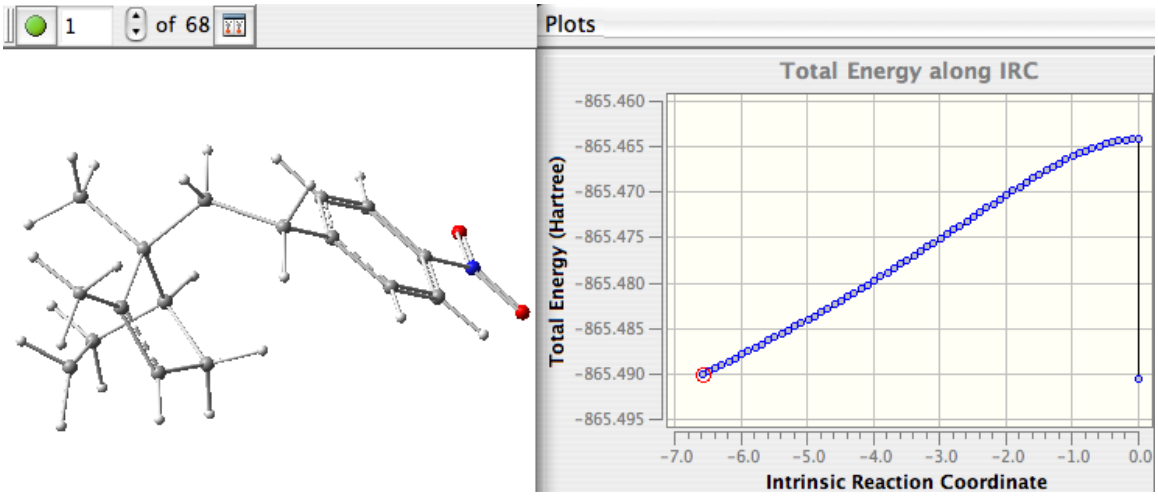
TS_{A-B}

We were unable to locate **TS_{A-B}** at this level of theory.

B→TS



TS→C



5. Table of energies for extended systems

Energies (kcal/mol, relative to the same species as in Table 1) of stationary points with "extended" rather than "aligned" (as in Table 1) conformations.

R_1/R_2[a]	Method	$\mathbf{A_a}$[g]	$\mathbf{A_b}$[g]	$\mathbf{TS_{A\text{-}B}}$	**B**	**TS**	**C**
CH_3/homo-prenyl	B3LYP[b]	–	+2.0	+10.6	+8.6	+15.8	-1.0
	MPWB1K[c]	–	*+2.3*	*+8.7*	*+3.4*	*+11.3*	*-6.0*
homoprenyl /CH_3	B3LYP[b]	–	+1.2	–	–	+16.6	-2.1
	MPWB1K[c]	–	*+1.6*	*+6.1*	*+3.3*	*+11.8*	*-7.4*
CH_3/ C_2H_5	B3LYP[b]	–	-0.9	+7.7	+4.3	+13.1	-5.7
	MPWB1K[c]	–	-0.9	+6.1	0.0	+8.8	-10.6
C_2H_5/ CH_3	B3LYP[b]	+0.3	–	+10.6	+9.1	+17.0	-4.8
	MPWB1K[c]	+0.1	–	+8.3	+4.8	+12.3	-9.8
CH_3/$(CH_2)_2$-Ph	B3LYP[b]	–	+1.6	+10.0	+8.1	+15.9	-1.3
	MPWB1K[c]	–	*+1.3*	*+7.2*[d]	*+2.4*	*+10.4*	*-7.4*
CH_3/$(CH_2)_2$ -*p*-NH_2-Ph	B3LYP[b]	–	+3.2	+11.3	+10.1	+17.2	+0.6
	MPWB1K[c]	–	*+2.6*	*+8.3*	*+4.4*	*+11.8*	*-5.4*
CH_3/$(CH_2)_2$ -*p*-NO_2-Ph	B3LYP[b]	–	+1.1	+9.4	+6.6	+15.3	-2.6
	MPWB1K[c]	–	*+0.6*	*e*	*+0.7*	*+9.4*	*-8.8*

[a] For all but the sativene system, R_3=H; see Fig. 1. [b] mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p)).‡ [c] MPWB1K/6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)).‡ [d] We were unable to locate $\mathbf{TS_{A\text{-}B}}$ at this level of theory. The energy shown corresponds to a structure with two imaginary frequencies: -88 cm^{-1} corresponding to C2–C7 bond making breaking and -10 cm^{-1} corresponding to a conformational change of the sidechain. [e] We were unable to locate $\mathbf{TS_{A\text{-}B}}$ at this level of theory. [g] Two distinct conformers of **A** that differ in their R_1/R_2–C^+–C–C dihedral angles.

6. "Table" 1 mentioned in the manuscript

Table 1. Relative energies (kcal/mol) of stationary points involved in the lowest energy paths from **A** to **C** (Scheme 1).

R_1/R_2[a]	Method	$\mathbf{A_a}$[d]	$\mathbf{A_b}$[d]	$\mathbf{TS_{A-B}}$	**B**	**TS**	**C**
CH_3/ CH_3[3]	B3LYP[b]	0.0	–	+3.9	+0.1	+8.4	-10.5
	MPWB1K[c]	*0.0*	–	*+3.4*	*-3.3*	*+4.6*	*-14.6*
sativene[4]	B3LYP[b]	0.0	–	+1.3	+0.5	+8.2	-11.4
CH_3/	B3LYP[b]	-0.7	+0.5	–	–	+14.3	-5.0
homoprenyl	*MPWB1K*[c]	*-0.1*	*+1.4*	*+4.1*	*+2.3*	*+11.2*	*-10.6*
homoprenyl	B3LYP[b]	0.0	–	–	–	+14.4	-4.4
/CH_3	*MPWB1K*[c]	*0.0*	–	*+5.5*	*+1.0*	*+9.7*	*-9.6*
CH_3/ C_2H_5	B3LYP[b]	+1.7	-0.8	+4.6	+2.2	+10.4	-9.2
	MPWB1K[c]	+0.9	-0.6	+3.5	-2.1	+5.9	-14.3
C_2H_5/ CH_3	B3LYP[b]	0.0	+1.7	+4.9	+2.8	+10.5	-9.0
	MPWB1K[c]	0.0	+1.0[e]	+4.0	-2.3	+5.9	-13.9
$-(CH_2)_5-$	B3LYP[b]	-1.6	0.0	–	–	+9.1	-9.8
	MPWB1K[c]	–	*0.0*	*+2.1*	*-4.0*	*+4.8*	*-14.6*
CH_3/Ph	B3LYP[b]	–	0.0	–	–	+18.8	+2.0
	MPWB1K[c]	–	*0.0*	*+4.9*[e]	*+5.0*[f]	*+13.2*	*-3.8*
CH_3/cyclo-	B3LYP[b]	–	0.0	–	–	+20.9	+2.0
propyl	*MPWB1K*[c]	–	*0.0*	*+6.2*[e]	*+6.3*[f]	*+16.4*	*-3.5*
$CH_3/(CH_2)_2$	B3LYP[b]	+0.1	0.0	–	–	+13.9	-5.8
-Ph							
	MPWB1K[c]	-0.4	*0.0*	*+3.0*	*+0.7*	*+9.1*	*-12.0*
$CH_3/(CH_2)_2$	B3LYP[b]	-1.2	0.0	–	–	+15.3	-4.3
-*p*-NH_2-Ph							
	MPWB1K[c]	-1.3	*0.0*	*+3.5*	*+2.2*	*+10.8*	*-10.4*
$CH_3/(CH_2)_2$	B3LYP[b]	+1.3	0.0	–	–	+12.6	-7.0
-*p*-NO_2-Ph							
	MPWB1K[c]	+0.3	*0.0*	*+3.2*	*-1.1*	*+7.5*	*-13.6*

[a] For all but the sativene system, R_3=H; see Fig. 1. [b] mPW1PW91/6-31+ G(d,p)//B3LYP/6-31+G(d,p) + ZPE (B3LYP//6-31+G(d,p)). [c] MPWB1K /6-31+G(d,p) + ZPE (MPWB1K//6-31+G(d,p)).‡ [d] Two distinct conformers of **A** that differ in their R_1/R_2–C^+–C–C dihedral angles; see earlier. [e] This structure has a small imaginary frequency (-48 cm^{-1}, small movement of the ethyl group). [f] **B** is slightly higher in energy than $\mathbf{TS_{A-B}}$ due to the inclusion of ZPE corrections in the relative energies, suggesting that even though a minimum was located for **B** in these cases, **B** is not truly a minimum on the enthalpy surface for the **A**→**C** reaction.