Energetic and Spectroscopic Properties of the Low-Lying Isomers of C_5H: A High-Level ab Initio Study

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Table S1: Optimized geometries of the C_5H isomers (**1**-**14**) along with their cationic and anionic forms in Cartesian coordinates (in Angstrom units) obtained at UB3LYP/6-311+G(d,p) level of theory.

1-c (singlet)

C	-2.688829000	0.010849000	0.001746000
C	-1.373226000	-0.000148000	-0.002446000
C	-0.120816000	-0.010380000	-0.000625000
C	1.196100000	-0.024564000	0.001822000
C	2.411514000	0.011588000	-0.000255000
H	3.482441000	0.011634000	-0.000269000

1-c (triplet)

C	0.000000000	0.000000000	2.647769000
C	0.000000000	0.000000000	1.404789000
C	0.000000000	0.000000000	0.117065000
C	0.000000000	0.000000000	-1.179160000
C	0.000000000	0.000000000	-2.410128000
H	0.000000000	0.000000000	-3.482006000

1

C	-2.696840000	-0.000834000	-0.000124000
C	-1.388649000	-0.000053000	0.000188000
C	-0.121531000	0.001181000	0.000007000
C	1.200868000	0.001020000	-0.000085000
C	2.424716000	-0.001110000	0.000020000
H	3.488621000	-0.001225000	-0.000033000

1-a (singlet)

C	0.000000000	0.000000000	2.694617000
C	0.000000000	0.000000000	1.411453000
C	0.000000000	0.000000000	0.110910000
C	0.000000000	0.000000000	-1.193925000
C	0.000000000	0.000000000	-2.439934000
H	0.000000000	0.000000000	-3.498727000

1-a (triplet)

C	0.000000000	0.000000000	2.696889000
C	0.000000000	0.000000000	1.411969000
C	0.000000000	0.000000000	0.111515000
C	0.000000000	0.000000000	-1.195931000
C	0.000000000	0.000000000	-2.441095000
H	0.000000000	0.000000000	-3.500085000

2-c (singlet)

C	0.0000000	0.641826000	-1.637721000
C	0.0000000	0.000000000	-0.387281000
C	0.0000000	0.000000000	0.954753000
C	0.0000000	-0.641826000	-1.637721000
C	0.0000000	0.000000000	2.167794000
H	0.0000000	0.000000000	3.241058000

2-c (triplet)

C	0.000000000	0.674822000	-1.632863000
C	0.000000000	0.000000000	-0.394109000
C	0.000000000	0.000000000	0.955205000
C	0.000000000	-0.674822000	-1.632863000
C	0.000000000	0.000000000	2.165251000
H	0.000000000	0.000000000	3.236270000

2

C	1.629838000	-0.679092000	-0.000234000
C	0.413706000	-0.000129000	0.000367000
C	-0.963257000	0.000147000	0.000542000
C	1.630498000	0.679015000	-0.000234000
C	-2.171507000	0.000062000	-0.000275000
H	-3.235669000	-0.000015000	-0.000995000

2-a (singlet)

C	0.000000000	0.722622000	-1.616388000
C	0.000000000	0.000000000	-0.427920000
C	0.000000000	0.000000000	0.953705000
C	0.000000000	-0.722622000	-1.616388000
C	0.000000000	0.000000000	2.168897000
H	0.000000000	0.000000000	3.228564000

2-a (triplet)

C	0.000000000	0.653587000	-1.686831000
C	0.000000000	0.000000000	-0.352386000
C	0.000000000	0.000000000	0.965804000
C	0.000000000	-0.653587000	-1.686831000
C	0.000000000	0.000000000	2.214623000
H	0.000000000	0.000000000	3.273722000

3-c (singlet)

Not Available

3-c (triplet)

C	-1.029961000	-2.092771000	0.000000000
C	-0.566428000	-0.971764000	0.000000000
C	0.000000000	0.260449000	0.000000000
C	1.197209000	1.010783000	0.000000000
C	0.019958000	1.638955000	0.000000000
H	2.275337000	0.926090000	0.000000000

3

C	-1.035940000	2.142112000	0.000000000
C	-0.535958000	0.964598000	0.000000000
C	0.000000000	-0.242138000	0.000000000
C	1.177752000	-1.022466000	0.000000000
C	0.018977000	-1.689461000	0.000000000
H	2.251017000	-0.915867000	0.000000000

3-a (singlet)

C	-0.416907000	-2.336996000	0.000000000
C	-0.227026000	-1.102709000	0.000000000
C	0.000000000	0.246236000	0.000000000
C	0.840926000	1.305145000	0.000000000
C	-0.506303000	1.608299000	0.000000000
H	1.855861000	1.680147000	0.000000000

3-a (triplet)

C	-1.818343000	-1.568239000	0.000000000
C	-0.938599000	-0.635478000	0.000000000
C	0.000000000	0.286792000	0.000000000
C	1.582857000	0.454623000	0.000000000
C	0.761388000	1.484680000	0.000000000
H	2.476185000	-0.134272000	0.000000000

4-c (singlet)

Not Available

4-c (triplet)

C	0.771840000	-0.636797000	0.000000000
C	0.000000000	0.625320000	0.000000000
C	0.002520000	-1.728550000	0.000000000
C	-0.770562000	-0.639535000	0.000000000
C	-0.002183000	1.886456000	0.000000000
H	-0.009697000	2.958632000	0.000000000

4

C	0.620615000	0.745758000	0.000000000
C	-0.632609000	0.039074000	0.000000000
C	1.809754000	-0.025275000	0.000000000
C	0.593327000	-0.765420000	0.000000000
C	-1.919489000	0.086104000	0.000000000
H	-2.829595000	-0.481450000	0.000000000

4-a (singlet)

C	0.000000000	0.428054000	0.000000000
C	0.000890000	-0.953751000	0.000000000
C	-0.723439000	1.615785000	0.000000000
C	0.721695000	1.617005000	0.000000000
C	0.000571000	-2.168984000	0.000000000
C	0.001702000	-3.228658000	0.000000000

4-a (triplet)

Not Available

5-c (singlet)

C	0.000000000	1.932490000	-0.686511000
C	0.000000000	0.762446000	-0.039318000
C	0.000000000	0.000000000	1.089328000
C	0.000000000	-0.762446000	-0.039318000
C	0.000000000	-1.932490000	-0.686511000
H	0.000000000	0.000000000	2.173968000

5-c (triplet)

C	0.000000000	2.315840000	-0.490773000
C	0.000000000	1.208536000	0.012727000
C	0.000000000	0.000000000	0.663603000
C	0.000000000	-1.208536000	0.012727000
C	0.000000000	-2.315840000	-0.490773000
H	0.000000000	0.000000000	1.754931000

5

C	-2.251713000	0.592278000	0.000000000
C	-1.134827000	-0.037658000	0.000000000
C	0.000000000	-0.795229000	0.000000000
C	1.134838000	-0.037687000	0.000000000
C	2.251710000	0.592275000	0.000000000
H	-0.000048000	-1.883875000	0.000000000

5-a (singlet)

C	0.000000000	2.414696000	-0.436969000
C	0.000000000	1.237353000	0.000941000
C	0.000000000	0.000000000	0.591100000
C	0.000000000	-1.237353000	0.000941000
C	0.000000000	-2.414696000	-0.436969000
H	0.000000000	0.000000000	1.685738000

5-a (triplet)

C	0.000000000	2.249261000	-0.604368000
C	0.000000000	1.152962000	0.041348000
C	0.000000000	0.000000000	0.810418000
C	0.000000000	-1.152962000	0.041348000
C	0.000000000	-2.249261000	-0.604368000
H	0.000000000	0.000000000	1.893726000

6-c (singlet)

Not Available

6-c (triplet)

C	1.638122000	0.505767000	0.000000000
C	0.288590000	0.131142000	0.000000000
C	-1.948881000	-0.540185000	-0.000001000
C	-1.074106000	0.457690000	0.000001000
C	1.334700000	-0.803044000	-0.000001000
H	-1.430554000	1.491782000	0.000001000

6

C	1.646443000	-0.537030000	-0.000002000
C	0.327313000	-0.081729000	0.000003000
C	-2.046476000	0.468825000	-0.000001000
C	-1.070841000	-0.405687000	0.000000000
C	1.376220000	0.797776000	0.000000000
H	-1.395951000	-1.452927000	-0.000002000

6-a (singlet)

C	1.482270000	-0.462432000	-0.001697000
C	0.005388000	0.126453000	-0.000179000
C	-1.429589000	0.648247000	-0.002182000
C	-1.130888000	-0.659253000	0.002251000
C	1.334932000	0.836893000	0.002022000
H	-1.425405000	-1.700681000	-0.000215000

6-a (triplet)

C	-0.164775000	1.742224000	0.000000000
C	0.000000000	0.310603000	0.000000000
C	0.017311000	-2.151373000	0.000000000
C	-0.624826000	-0.948782000	0.000000000
C	1.059965000	1.196106000	0.000000000
H	-1.726048000	-0.892669000	0.000000000

7-c (singlet)

C	0.433917000	-0.782868000	0.000103000
C	0.433402000	0.782239000	0.000103000
C	-2.095765000	0.000335000	-0.000205000
C	-0.758767000	-0.000286000	0.000111000
C	1.549390000	0.000338000	0.000131000
C	2.626940000	0.001457000	-0.001456000

7-c (triplet)

C	-0.045358000	-0.717604000	0.018900000
C	0.581184000	0.849245000	-0.176241000
C	-1.389578000	-0.472422000	-0.108909000
C	-0.822119000	0.714143000	0.189063000
C	1.294531000	-0.260484000	0.069681000
H	2.288036000	-0.677269000	0.045040000

7

C	0.070658000	-0.704491000	0.057290000
C	-0.665815000	0.880242000	0.131291000
C	1.532708000	-0.373288000	0.041086000
C	0.712531000	0.670529000	-0.132252000
C	-1.276678000	-0.341870000	-0.107519000
H	-2.240421000	-0.786732000	0.060629000

7-a (singlet)

C	-0.122132000	-0.786259000	-0.142310000
C	0.703786000	0.919253000	-0.171526000
C	-1.486340000	-0.331819000	-0.002711000
C	-0.641353000	0.730953000	0.144804000
C	1.190567000	-0.390076000	0.184793000
H	2.132827000	-0.852309000	-0.078292000

7-a (triplet)

C	-0.269700000	-0.911123000	-0.000148000
C	0.887087000	0.921365000	-0.000290000
C	-1.523921000	-0.125738000	-0.000086000
C	-0.536712000	0.744332000	0.000273000
C	1.108910000	-0.452868000	0.000304000
H	2.006008000	-1.055811000	-0.000315000

8-c (singlet)

C	2.491273000	-0.276567000	-0.005313000
C	0.095852000	0.000342000	0.002996000
C	-2.286628000	0.471081000	-0.002314000
C	-1.211166000	-0.333439000	-0.000184000
C	1.317151000	0.312233000	0.005967000
H	-1.569773000	-1.384423000	-0.001154000

8-c (triplet)

C	1.294073000	0.261083000	0.070394000
C	-0.822841000	-0.713958000	0.188850000
C	-0.045103000	0.717075000	0.018353000
C	-1.389159000	0.472558000	-0.108626000
C	0.581528000	-0.849154000	-0.176284000
H	2.289008000	0.674372000	0.043883000

8

C	0.781711000	0.687171000	0.101002000
C	-0.090490000	-0.737019000	0.142358000
C	-0.647016000	0.715619000	-0.335212000
C	-1.469246000	-0.257375000	0.143196000
C	1.231281000	-0.643263000	-0.187389000
H	1.162559000	1.409194000	0.816269000

8-a (singlet)

C	0.734833000	0.742151000	0.019138000
C	-0.010389000	-0.723101000	0.232822000
C	-0.672476000	0.673941000	-0.214040000
C	-1.532704000	-0.299527000	0.028618000
C	1.297711000	-0.634713000	-0.193681000
H	1.098151000	1.447491000	0.762867000

8-a (triplet)

C	1.109736000	0.452835000	-0.000063000
C	-0.537812000	-0.744547000	0.000160000
C	-0.268859000	0.909372000	0.000353000
C	-1.524084000	0.127761000	-0.000327000
C	0.886516000	-0.921311000	0.000001000
H	2.007014000	1.055342000	-0.000743000

9-c (singlet)

C	-0.000250000	1.089666000	0.000000000
C	0.000086000	-0.038918000	0.762547000
C	0.000086000	-0.038918000	-0.762547000
C	0.000086000	-0.687106000	1.931886000
C	0.000086000	-0.687106000	-1.931886000
H	-0.000571000	2.174295000	0.000000000

9-c (triplet)

Not Available

9

C	0.001123000	1.239844000	0.000000000
C	-0.000343000	0.125031000	0.808134000
C	-0.000343000	0.125031000	-0.808134000
C	-0.000343000	-0.937807000	1.578834000
C	-0.000343000	-0.937807000	-1.578834000
H	0.001485000	2.314244000	0.000000000

9-a (singlet)

C	0.084149000	1.343054000	0.000000000
C	0.014121000	0.126156000	0.777273000
C	0.014121000	0.126156000	-0.777273000
C	0.014121000	-0.957666000	1.477016000
C	0.014121000	-0.957666000	-1.477016000
H	-0.843790000	1.919791000	0.000000000

9-a (triplet)

C	0.000047000	0.809035000	0.000000000
C	-0.000017000	0.040754000	1.153701000
C	-0.000017000	0.040754000	-1.153701000
C	-0.000017000	-0.602962000	2.251131000
C	-0.000017000	-0.602962000	-2.251131000
C	0.000130000	1.892278000	0.000000000

10-c (singlet)

C	-0.545313000	0.956712000	-0.118081000
C	0.529190000	0.035607000	0.023295000
C	-1.164493000	-0.141273000	0.417433000
C	-0.557884000	-1.139586000	-0.313954000
C	1.863240000	-0.031186000	0.087194000
H	-0.748443000	1.918363000	-0.575321000

10-c (triplet)

Not Available

10

C	0.479130000	0.850861000	0.092001000
C	-0.641711000	-0.058495000	0.098922000
C	1.371030000	-0.094712000	-0.446777000
C	0.610022000	-0.947995000	0.334436000
C	-1.919355000	-0.044128000	-0.188341000
H	0.605301000	1.766817000	0.658554000

10-a (singlet)

C	0.203822000	0.610157000	0.179857000
C	-1.153901000	0.479329000	0.020353000
C	1.180367000	-0.358642000	0.110153000
C	2.073421000	-1.244613000	0.046407000
C	-2.380989000	0.362235000	-0.168340000
H	0.581697000	1.623882000	0.360365000

10-a (triplet)

C	-0.518979000	0.798874000	0.080877000
C	0.751311000	-0.042441000	0.043187000
C	-1.664303000	-0.177105000	0.105296000
C	-0.521245000	-0.804786000	-0.151553000
C	2.053689000	-0.049631000	0.022160000
H	-0.602840000	1.650531000	-0.599798000

11-c (singlet)

C	0.481736000	0.734439000	-0.000082000
C	1.750101000	-0.204701000	0.000626000
C	0.510459000	-0.694772000	-0.000404000
C	-0.761665000	-0.094723000	-0.000709000
H	0.659044000	1.811144000	-0.000438000
C	-2.090471000	-0.042101000	0.000642000

11-c (triplet)

C	0.579196000	0.808872000	0.061748000
C	1.463115000	-0.175221000	-0.367929000
C	0.464595000	-0.886340000	0.310009000
C	-0.654396000	-0.066469000	0.070410000
H	0.708716000	1.758134000	0.578448000
C	-1.970630000	0.026136000	-0.170646000

11

C	0.501445000	0.769262000	0.038844000
C	1.564763000	-0.129973000	-0.322162000
C	0.548907000	-0.805814000	0.277044000
C	-0.719276000	-0.111540000	0.086205000
H	0.559461000	1.725258000	0.554610000
C	-1.989083000	-0.009479000	-0.172366000

11-a (singlet)

C	0.286191000	0.610036000	0.088308000
C	1.289949000	-0.300637000	0.004779000
C	1.938995000	-1.359216000	0.213232000
C	-1.126445000	0.440052000	0.045876000
H	0.392863000	1.657897000	0.383655000
C	-2.315337000	0.389582000	-0.273675000

11-a (triplet)

C	0.553009000	0.797825000	-0.088470000
C	1.663600000	-0.183891000	-0.094929000
C	0.496835000	-0.799247000	0.143836000
C	-0.757750000	-0.067471000	-0.039163000
H	0.609770000	1.643914000	0.602172000
C	-2.057323000	-0.021201000	-0.021636000

12-c (singlet)

C	-0.032720000	0.782197000	0.092516000
C	0.703011000	-0.703510000	0.164334000
C	-1.343792000	0.311749000	0.239887000
C	-0.725884000	-0.696553000	-0.438909000
C	1.233500000	0.540729000	-0.214878000
H	0.995309000	-1.407672000	0.942291000

12-c (triplet)

C	-0.573199000	0.772134000	0.085519000
C	0.711400000	-0.000004000	0.383297000
C	-1.587636000	0.000001000	-0.300321000
C	-0.573197000	-0.772134000	0.085508000
C	1.843851000	0.000005000	-0.491439000
H	1.072684000	-0.000018000	1.424618000

12

C	-0.554310000	0.754820000	0.066317000
C	0.718337000	0.000001000	0.343167000
C	-1.698988000	-0.000009000	-0.256873000
C	-0.554337000	-0.754800000	0.066336000
C	1.909080000	-0.000015000	-0.450186000
H	1.081305000	0.000016000	1.387437000

12-a (singlet)

C	-0.610934000	0.807402000	0.147881000
C	0.768799000	0.000826000	0.283038000
C	-1.642896000	0.000953000	-0.339060000
C	-0.613993000	-0.808163000	0.148471000
C	1.891624000	-0.001143000	-0.454350000
H	1.244400000	0.000749000	1.284117000

12-a (triplet)

C	-0.548350000	0.752520000	0.127651000
C	0.748739000	0.000087000	0.422735000
C	-1.626420000	0.000063000	-0.362871000
C	-0.548513000	-0.752613000	0.127809000
C	1.805957000	-0.000099000	-0.563469000
H	1.011521000	0.000247000	1.488867000

13-c (singlet)

C	-0.577447000	1.060208000	-0.000446000
C	-0.092011000	0.000386000	0.960382000
C	0.989992000	0.001571000	0.000017000
C	-0.091965000	-0.000579000	-0.960387000
C	-0.573990000	-1.062078000	0.000428000
H	2.072525000	0.002949000	0.000042000

13-c (triplet)

C	0.159392000	-0.000004000	-0.971038000
C	-0.134378000	0.936295000	0.151219000
C	1.001268000	0.000002000	0.323258000
C	-0.134379000	-0.936296000	0.151224000
C	-1.234910000	0.000003000	0.254777000
H	2.058045000	0.000003000	0.543359000

13

C	-0.115954000	1.159079000	0.002841000
C	0.094181000	-0.091866000	-0.896260000
C	-0.970929000	-0.472084000	-0.001088000
C	0.094452000	-0.096758000	0.895739000
C	1.238641000	-0.403542000	-0.001048000
H	-2.042342000	-0.568976000	-0.001108000

13-a (singlet)

C	-0.056096000	0.000801000	-1.002958000
C	-0.051700000	0.869251000	0.502348000
C	1.018902000	-0.000027000	-0.001396000
C	-0.051765000	-0.870018000	0.500981000
C	-1.208908000	0.000003000	0.001538000
H	2.097399000	-0.000061000	-0.003076000

13-a (triplet)

C	0.081807000	0.000330000	-1.038486000
C	-0.105929000	1.058891000	0.165529000
C	0.910201000	-0.000141000	0.344564000
C	-0.106009000	-1.058981000	0.165114000
C	-1.111470000	-0.000067000	0.295488000
H	1.988405000	-0.000200000	0.406748000

14-c (singlet)

C	2.154857000	1.475815000	0.000000000
C	1.119052000	0.657712000	0.000000000
C	0.129207000	-0.088840000	0.000000000
C	-0.944786000	-0.898857000	0.000000000
C	-2.271115000	-0.737695000	0.000000000
H	-0.802346000	-2.005959000	0.000000000

14-c (triplet)

Not Available

14

C	2.290311000	1.333146000	0.000000000
C	1.142888000	0.672183000	0.000000000
C	0.000000000	0.129691000	0.000000000
C	-1.001114000	-0.823381000	0.000000000
C	-2.309059000	-0.992074000	0.000000000
H	-0.738156000	-1.917390000	0.000000000

14-a (singlet)

C	0.509263000	2.625821000	0.000000000
C	0.257976000	1.383265000	0.000000000
C	0.000000000	0.092126000	0.000000000
C	-0.211777000	-1.160564000	0.000000000
C	-0.591873000	-2.414882000	0.000000000
H	0.218463000	-3.154596000	0.000000000

14-a (triplet)

Not Available

Table S2: Geometries of transition states involved in the rearrangement scheme in Cartesian coordinates (in Angstrom units) obtained at UB3LYP/6-311+G(d,p) level of theory.

16ᶻ

C	0.6136850	0.756814000	-0.000040000
C	-0.6356800	0.000801000	0.000388000
C	1.8141350	0.000931000	0.000075000
C	0.6132280	-0.758917000	-0.000042000
C	-1.9096710	0.000817000	-0.000912000
H	-2.9741740	-0.002673000	0.003189000

15ᶻ

C	-1.5539380	-0.00248600	-0.035201000
C	-0.4577410	0.808674000	0.026131000
C	-0.4434770	-0.802856000	0.026274000
C	0.7889140	-0.004746000	0.022329000
C	2.1037510	0.003745000	-0.032245000
H	-2.6250630	-0.013986000	-0.043729000

TS1

C	2.50913700	0.726004000	0.00000000
C	1.2427100	0.371577000	0.000000000
C	0.0000000	0.135660000	0.000000000
C	-1.1517580	-0.657290000	0.000000000
C	-2.4128270	-0.281508000	0.000000000
H	-1.1235790	-1.766663000	0.000000000

TS2

C	2.50899300	0.726582000	0.000000000
C	1.24256900	0.372069000	0.000000000
C	0.00000000	0.135718000	0.000000000
C	-1.15156200	-0.657460000	0.000000000
C	-2.41280200	-0.282429000	0.000000000
H	-1.12318900	-1.766877000	0.000000000

TS3

C	-0.79260400	0.920476000	-0.098493000
C	0.74540800	-0.300897000	-0.066957000
C	-1.33325500	-0.141794000	0.417591000
C	-0.36834700	-1.081632000	-0.286375000
C	1.87937200	0.315260000	0.168970000
H	-0.78344200	1.731518000	-0.808415000

TS4

C	-0.52309300	0.877537000	-0.081550000
C	0.69853100	0.217512000	-0.064627000
C	-1.33602600	-0.167162000	0.410657000
C	-0.62664300	-1.056560000	-0.322616000
C	1.91814600	-0.176523000	0.145964000
H	-0.78548500	1.831178000	-0.526973000

TS5

C	2.4264920	0.048210000	0.000008000
C	1.1418760	-0.035124000	-0.000008000
C	-0.1890430	-0.015027000	-0.000005000
C	-1.3997030	-0.706501000	0.000002000
C	-1.9045500	0.515433000	0.000005000
H	-0.4504350	1.158054000	-0.000012000

TS6

C	0.59090900	0.755781000	0.039921000
C	1.60827200	-0.132484000	-0.293408000
C	0.49003300	-0.781899000	0.234980000
C	-0.77478700	-0.202985000	0.119777000
H	0.50202500	1.715551000	0.536606000
C	-1.99809700	0.075663000	-0.190704000

TS7

C	-1.80967200	-0.087461000	-0.000192000
C	-0.56933900	-0.681976000	-0.000156000
C	-0.72395600	0.845892000	0.000036000
C	0.68081100	-0.108940000	0.000036000
C	1.94556200	-0.051545000	0.000213000
H	2.85956100	0.504182000	0.000372000

TS8

C	-0.569466000	1.6487800	0.000000000
C	0.0000000	0.379857000	0.000000000
C	0.1222950	-2.269563000	0.000000000
C	-0.1367820	-1.015887000	0.000000000
C	0.7810820	1.515310000	0.000000000
H	-1.1827790	-1.550990000	0.000000000

TS9

C	-0.22184100	-0.563224000	0.000002000
C	1.1628950	0.852106000	-0.000008000
C	-1.58804700	-0.342571000	-0.00000800
C	-0.84885200	0.772360000	0.00001000
C	1.1685360	-0.511881000	0.000004000
H	1.96385300	-1.240736000	0.00000300

TS10

C	-0.585023000	0.761374000	0.012872000
C	0.686201000	-0.000064000	0.048657000
C	-1.778394000	0.000016000	-0.064409000
C	-0.58506400	-0.761361000	0.012914000
C	2.029288000	0.000001000	-0.188206000
H	1.39796200	0.000203000	1.069027000

TS11

C	-0.67905100	0.831514000	0.068742000
C	0.765199000	-0.061533000	0.343962000
C	-1.69504400	-0.117041000	-0.251041000
C	-0.49064600	-0.690221000	0.059547000
C	1.91592700	0.041276000	-0.453339000
H	1.101700000	-0.023969000	1.39277200

Table S3: Point Group, relative zero-point corrected energy (ΔE_0 in kJ mol^{-1}), dipole moments (in Debye) and rotational constants (in MHz) of C_5H isomers of **1-14** in their ground electronic states calculated at the UB3LYP/6-311+G(d,p) level of theory.

Isomer	Point group	ΔE_0 (kJmol^{-1})	$\|\mu\|$ (Debye)	Rotational Constants (in MHz)		
				A_e	B_e	C_e
1	$C_{\infty v}$	0	5.21	2400.64	2400.64	0
2	C_{2v}	45	3.68	45666.48	3511.17	3260.48
3	C_S	105	4.79	37334.32	3635.19	3312.64
4	C_S	206	4.01	36025.46	4807.4	4241.4
5	C_{2v}	222	3.01	25835.77	3311.94	2935.61
6	C_S	249	2.26	28321.5	4124.46	3600.16
7	C_1	260	2.99	20315.34	7787.44	5708.13
8	C_1	318	2.51	17425.72	8290.86	6014.3
9	C_1	320	4.56	11170.93	6693.84	4185.69
10	C_1	333	2.76	18357.79	6013.25	4949.45
11	C_S	336	1.72	23929.85	5440.15	4667.71
12	C_S	422	2.92	24897.01	5066.38	4732.01
13	C_1	428	2.61	12494.76	9427.41	9102.76
14	C_S	369	3.06	150775.51	2497.43	2456.73

Table S4: Point Group, relative zero-point corrected energy (ΔE_0 in kJ mol^{-1}), dipole moments (in Debye) and rotational constants (in MHz) of **cationic counterpart of C_5H** isomers of **1-14** in their singlet ground electronic states calculated at the UB3LYP/6-311+G(d,p) level of theory.

Isomer	Point group	ΔE_0 (kJmol^{-1})	$\|\mu\|$ (Debye)	Rotational Constants (in MHz)		
				A_e	B_e	C_e
1	$C_{\infty v}$	0	3.89	0	2424.0217	2424.0217
2	C_{2v}	116	2.52	51117.71	3511.56	3285.84
3	-	-	-	-	-	-
4	-	-	-	-	-	-
5	C_{2v}	377	2.87	16693.11	4879.11	3775.57
6	-	-	-	-	-	-
7	C_1	230	3.07	34385.67	5064.95	4414.67
8	C_1	373	1.85	16572.96	8710.06	6394.64
9	C_1	377	2.87	16677.06	4881.58	3776.23
10	C_1	424	3.20	14736.66	6920.62	5.069.75
11	C_S	406	1.53	31325.19	4929.77	4259.44
12	C_S	373	1.85	16559.75	8710.27	6395.0
13	C_1	477	2.04	10911.83	10280.12	9870.04
14	-	-	-	-	-	-

Table S5: Point Group, relative zero-point corrected energy (ΔE_0 in kJ mol^{-1}), dipole moments (in Debye) and rotational constants (in MHz) of **anionic counterpart of C_5H** isomers of **1-14** in their singlet ground electronic states calculated at the UB3LYP/6-311+G(d,p) level of theory.

Isomer	Point group	ΔE_0 ($kJmol^{-1}$)	$\|\mu\|$ (Debye)	Rotational Constants (in MHz)		
				A_e	B_e	C_e
1	$C_{\infty v}$	0	5.78	0	2385.33	2385.33
2	C_{2v}	-13	6.14	40325.85	3543.95	3257.65
3	C_S	-40	6.02	36158.12	3639.95	3307.04
4	C_S	-13	6.14	40331.95	3543.74	3257.52
5	C_{2v}	-47	3.46	43591.53	2860.37	2684.24
6	C_1	118	3.95	21414.24	5601.81	4440.28
7	C_1	209	2.61	17430.55	8358.85	5813.74
8	C_1	250	3.28	17744.24	7926.01	5750.06
9	C_S	247	3.31	10421.46	7470.26	4411.59
10	-	-	-	-	-	-
11	-	-	-	-	-	-
12	C_1	374	2.23	22351.59	5056.85	4651.45
13	C_1	252	4.32	13937.06	9613.24	9606.09
14	C_S	-45	3.52	602046.3	2410.3	2400.69

Table S6: Point Group, relative zero-point corrected energy (ΔE_0 in kJ mol^{-1}), dipole moments (in Debye) and rotational constants (in MHz) of **cationic counterpart of C_5H** isomers of **1-14** in their triplet ground electronic states calculated at the UB3LYP/6-311+G(d,p) level of theory.

Isomer	Point group	ΔE_0 ($kJmol^{-1}$)	$\|\mu\|$ (Debye)	Rotational Constants (in MHz)		
				A_e	B_e	C_e
1	$C_{\infty v}$	0	6.37	0	23819.44	2381.944
2	C_{2v}	171	3.50	49294.59	3358.99	3144.7
3	C_s	224	5.73	36284.2	3516.49	3205.8
4	-	-	-	-	-	-
5	C_{2v}	187	3.69	24963.15	3296.15	2911.69
6	C_s	281		28668.91	4020.32	3525.88
7	C_1	307	2.07	16623.64	8347.91	5557.23
8	C_1	307	2.07	16640.34	8344.02	5557.37
9	C_s	187	3.68	25055.00	3290.94	2908.86
10	C_1	360	2.67	26026.44	5140.92	4353.16
11	C_1	359	2.61	26226.99	5121.26	4341.73
12	C_1	432	3.57	21336.16	5266.24	5081.01
13	C_1	473	2.42	11727.24	11163.52	9024.51
14	-	-	-	-	-	-

Table S7: Point Group, relative zero-point corrected energy (ΔE_0 in kJ mol^{-1}), dipole moments (in Debye) and rotational constants (in MHz) of **anionic counterpart of C_5H** isomers of **1-14** in their triplet ground electronic states calculated at the UB3LYP/6-311+G(d,p) level of theory.

Isomer	Point group	ΔE_0 ($kJmol^{-1}$)	$\|\mu\|$ (Debye)	Rotational Constants (in MHz)		
				A_e	B_e	C_e
1	$C_{\infty v}$	0	0.84	0	2448.696	2448.696
2	C_{2v}	17	0.84	46241.09	3523.06	3273.65
3	C_S	79	1.77	37291.38	3732.12	3392.59
4	C_S	149	1.66	35405.3	4968.99	4357.44
5	C_{2v}	240	0.47	35783.87	3085.94	2840.94
6	C_1	241	1.90	26336.91	4353.82	3736.18
7	C_1	185	1.67	19556.77	8185.91	5906.54
8	C_1	186	1.67	19566.52	8186.74	5907.77
9	-	-	-	-	-	-
10	-	-	-	-	-	-
11	C_1	298	1.91	20788.04	5738.46	4795.82
12	C_1	386	1.50	22754.71	5372.05	5029.5
13	C_1	412	1.12	14370.05	10218.22	8965.58
14	-	-	-	-	-	-

Table S8: Point Group, relative zero-point corrected energy (ΔE_0 in kJ mol^{-1}), dipole moments (in Debye) and rotational constants (in MHz) of C_5H isomers of **1-14** in their ground electronic states calculated at the UωB97XD/6-311+G(d,p) level of theory.

Isomer	Point group	ΔE_0 ($kJmol^{-1}$)	$\|\mu\|$ (Debye)	Rotational Constants (in MHz)		
				A_e	B_e	C_e
1	$C_{\infty v}$	0	3.52	0	2430.59	2430.59
2	C_{2v}	96	2.25	51373.08	3519.8	3294.11
3	C_s	-1	3.52	99174.29	2430.96	2430.96
4	-	-	-	-	-	-
5	C_{2v}	353	2.92	16758.43	4933.95	3811.72
6	-	-	-	-	-	-
7	C_1	183	3.09	35178.78	5060.45	4424.05
8	C_1	328	1.91	16327.18	8847.45	6485.99
9	C_s	353	2.92	16776.45	4931.82	3811.38
10	C_1	381	3.55	14416.41	7088.69	5104.17
11	-	-	-	-	-	-
12	C_1	329	1.91	16341.8	8844.39	6485.52
13	C_1	427	2.13	10856.86	10301.3	9771.37
14	-	-	-	-	-	-

Table S9: Point Group, relative zero-point corrected energy (ΔE_0 in kJ mol-1), dipole moments (in Debye) and rotational constants (in MHz) of **cationic counterpart of C_5H** isomers of **1-14** in their singlet ground electronic states calculated at the UωB97XD/6-311+G(d,p) level of theory.

Isomer	Point group	ΔE_0 ($kJmol^{-1}$)	$\lvert\mu\rvert$ (Debye)	Rotational Constants (in MHz)		
				A_e	B_e	C_e
1	$C_{\infty v}$	0	5.10	0	2402.355	2402.355
2	C_{2v}	18	3.62	45743.59	3518.23	3266.96
3	C_s	87	4.75	37394.19	3649.39	3324.9
4	C_s	169	4.04	36843.01	4815.12	4258.55
5	C_{2v}	221	3.97	18479.81	3881.74	3207.91
6	C_s	214	2.28	27890.76	4190.06	3642.8
7	C_1	247	3.21	20672.79	7747.7	5718.67
8	C_1	277	3.11	17050.58	8414.56	5993.23
9	C_s	-	-	-	-	-
10	C_1	299	2.92	18180.39	6091.22	5001.5
11	C_1	299	1.72	24078.83	5435.9	4671.26
12	C_1	380	3.05	25276.97	5080.87	4770.67
13	C_1	386	2.74	12572.83	9431.37	9136.37
14	C_s	360	3.16	150775.7	2497.43	2456.73

Table S10: Point Group, relative zero-point corrected energy (ΔE_0 in kJ mol-1), dipole moments (in Debye) and rotational constants (in MHz) of **anionic counterpart of C_5H** isomers of **1-14** in their singlet ground electronic states calculated at the UωB97XD/6-311+G(d,p) level of theory.

Isomer	Point group	ΔE_0 ($kJmol^{-1}$)	$\lvert\mu\rvert$ (Debye)	Rotational Constants (in MHz)		
				A_e	B_e	C_e
1	C_1	0	0.26	845742.88	2465.14	2458.2
2	C_{2v}	-1	0.41	46399.69	3539.28	3288.45
3	C_s	54	1.88	37428.44	3742.04	3401.92
4	C_s	121	1.64	36002.72	4967.21	4364.99
5	C_{2v}	233	0.55	33343.49	3144.87	2873.82
6	C_1	209	2.01	25892.63	4440.17	3790.21
7	C_1	148	1.66	19711.41	8178.18	5913.82
8	C_1	148	1.66	19723.99	8182.8	5917.7
9	C_s	282	2.89	14095.66	4733.26	3567.41
10	C_1	267	2.02	20273.96	5822.13	4862.72
11	C_s	182	2.09	21182.92	7605.27	5596.11
12	C_1	351	1.58	23329.77	5347.23	5017.2
13	C_1	330	1.55	13481.62	10537.56	9479.3
14	-	-	-	-	-	-

Table S11: Point Group, relative zero-point corrected energy (ΔE_0 in kJ mol-1), dipole moments (in Debye) and rotational constants (in MHz) of **cationic counterpart of C_5H** isomers of **1-14** in their triplet ground electronic states calculated at the UωB97XD/6-311+G(d,p) level of theory.

Isomer	Point group	ΔE_0 (kJmol^{-1})	$\|\mu\|$ (Debye)	Rotational Constants (in MHz)		
				A_e	B_e	C_e
1	$C_{\infty v}$	0	6.02	0	2389.25	2389.25
2	C_{2v}	-45	6.57	40101.87	3553.05	3263.87
3	C_s	-74	6.25	36171.24	3654.43	3319.09
4	-	-	-	-	-	-
5	C_{2v}	-58	3.58	42885.56	2881.35	2699.95
6	-	-	-	-	-	-
7	C_1	163	2.84	17878.56	8267.65	5831.49
8	C_1	198	3.41	17768.96	7912.77	5757.66
9	C_s	-58	3.58	42826.26	2882.76	2700.95
10	C_1	-58	3.72	38824.52	2931.17	2725.64
11	-	-	-	-	-	-
12	-	-	-	-	-	-
13	C_1	187	4.46	13927.33	9622.22	9620.93
14	C_s	444	4.36	150775.68	2497.43	2456.73

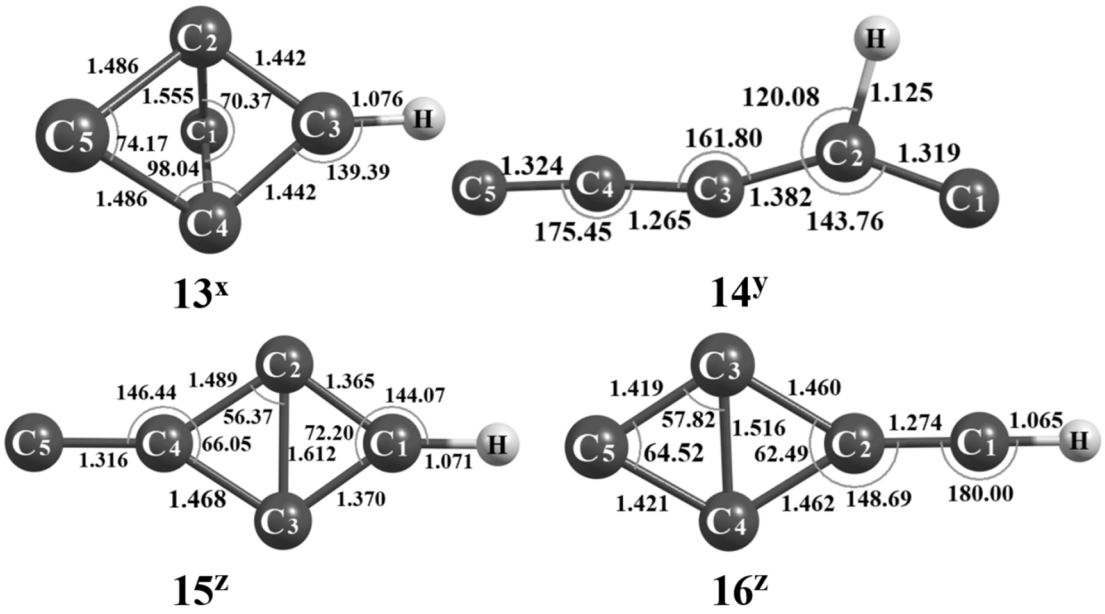
Table S12: Point Group, relative zero-point corrected energy (ΔE_0 in kJ mol-1), dipole moments (in Debye) and rotational constants (in MHz) of **anionic counterpart of C_5H** isomers of **1-14** in their triplet ground electronic states calculated at the UωB97XD/6-311+G(d,p) level of theory.

Isomer	Point group	ΔE_0 (kJmol^{-1})	$\|\mu\|$ (Debye)	Rotational Constants (in MHz)		
				A_e	B_e	C_e
1	$C_{\infty v}$	0	6.71	0	2383.11	2383.11
2	C_{2v}	155	3.81	49528.57	3356.48	3143.45
3	C_s	212	5.93	39660.42	3418.05	3146.84
4	C_s	312	4.46	27755.89	4894.65	4160.89
5	C_{2v}	187	4.53	19.63624	3699.07	3112.7
6	C_s	257	2.98	28568.2	4049.78	3546.97
7	C_1	272	2.09	16667.4	8382.96	5577.65
8	C_1	272	2.09	16661.09	8383.54	5577.2
9	C_s	187	3.60	29043.43	3077.83	2783.64
10	C_1	330	2.84	25890.05	5149.14	4360.12
11	C_1	330	2.84	25875.33	5148.48	4359.3
12	C_1	395	3.85	22148.85	5224.17	5035.78
13	C_1	423	2.38	11794.18	11260.81	9058.1
14	C_s	426	4.73	150775.68	2497.43	2456.73

Table S13: Ionization Potential (IP, in eV) and Electron Affinity (EA, in eV) of Isomer **6** to **14** calculated at different level of theory.

Energy Parameter	Methods	6-c	6-a	7-c	7-a	8-c	8-a	9-c	9-a	10-c	10-a	11-c	11-a	12-c	12-a	13-c	13-a	14-c	14-a
IP	**UB3LYP/ 6-311+G(d,p)**	---	---	7.97	---	8.85	---	8.88	---	9.22	---	9.02	---	7.77	---	8.79	---	---	---
	UωB97XD/ 6-311+G(d,p)	---	---	7.99	---	8.88	---	9.71	---	9.19	---	---	---	7.82	---	8.78	---	---	---
EA	**UB3LYP/ 6-311+G(d,p)**	---	3.49	---	2.68	---	2.85	---	2.90	---	---	---	---	---	2.65	---	3.98	---	6.44
	UωB97XD/ 6-311+G(d,p)	---	---	---	2.68	---	2.92	---	5.00	---	5.81	---	---	---	---	---	4.17	---	1.24

Figure S1: Optimized geometries of isomers **13** to **16** of the C_5H radicals.

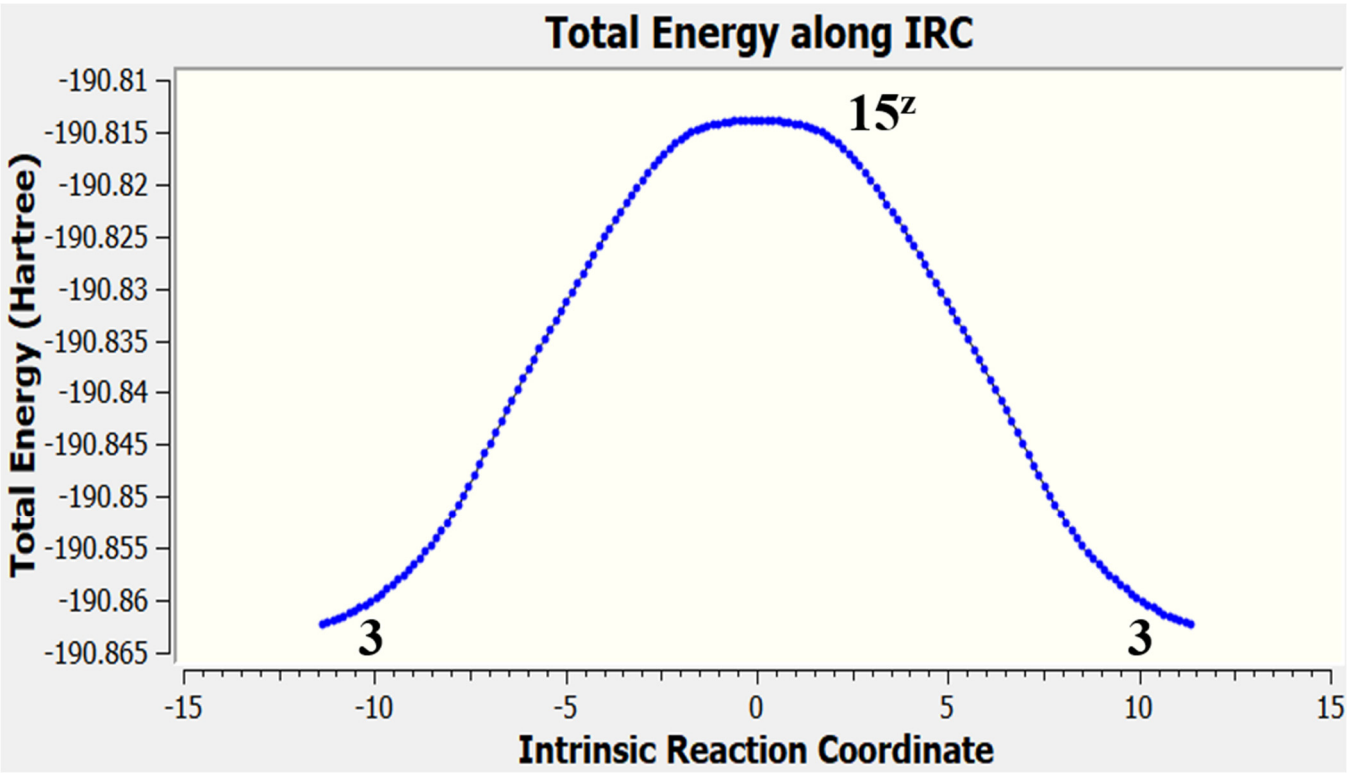


[x] represents the isomer calculated at UB3LYP/6-311+G(d,p) level of theory.

[y] represents the isomer calculated at UB3LYP/6-31+G level of theory.

[z] represents the transition state calculated at UB3LYP/6-311+G(d,p) level of theory.

Figure S2: Intrinsic Reaction Coordinate for the transition state **15^z** and **16^z** calculated at UB3LYP/6-311+G(d,p) level of theory.



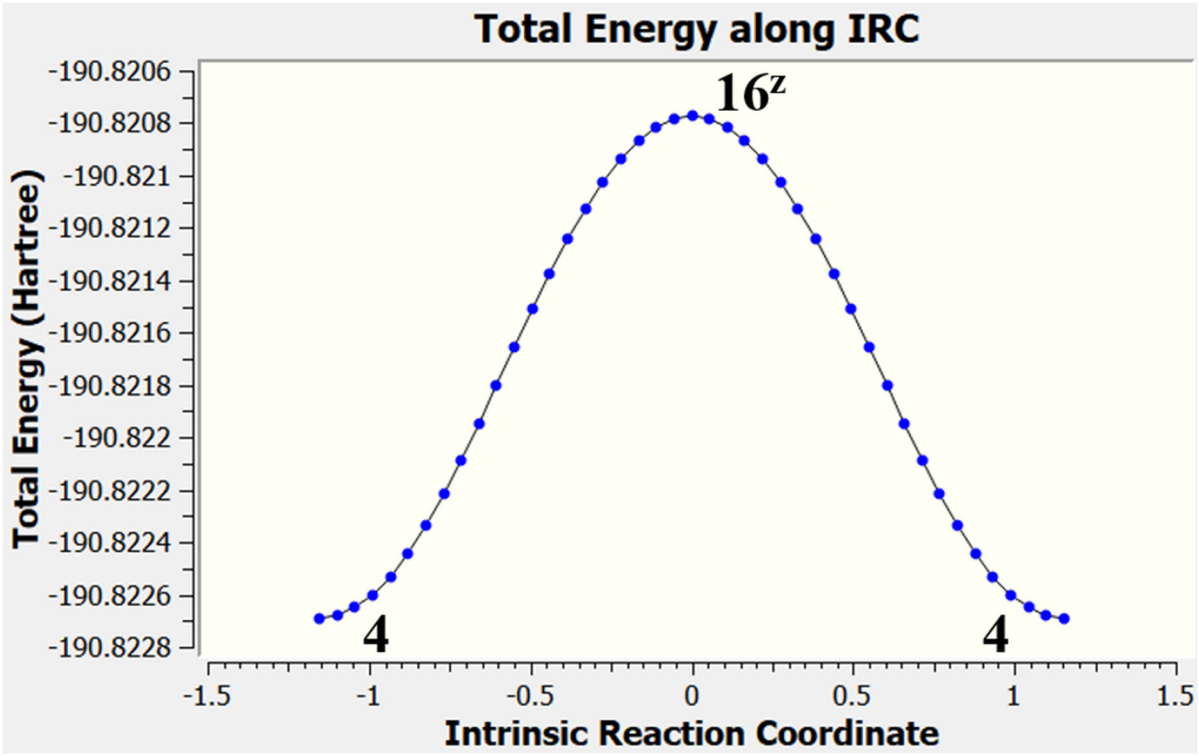
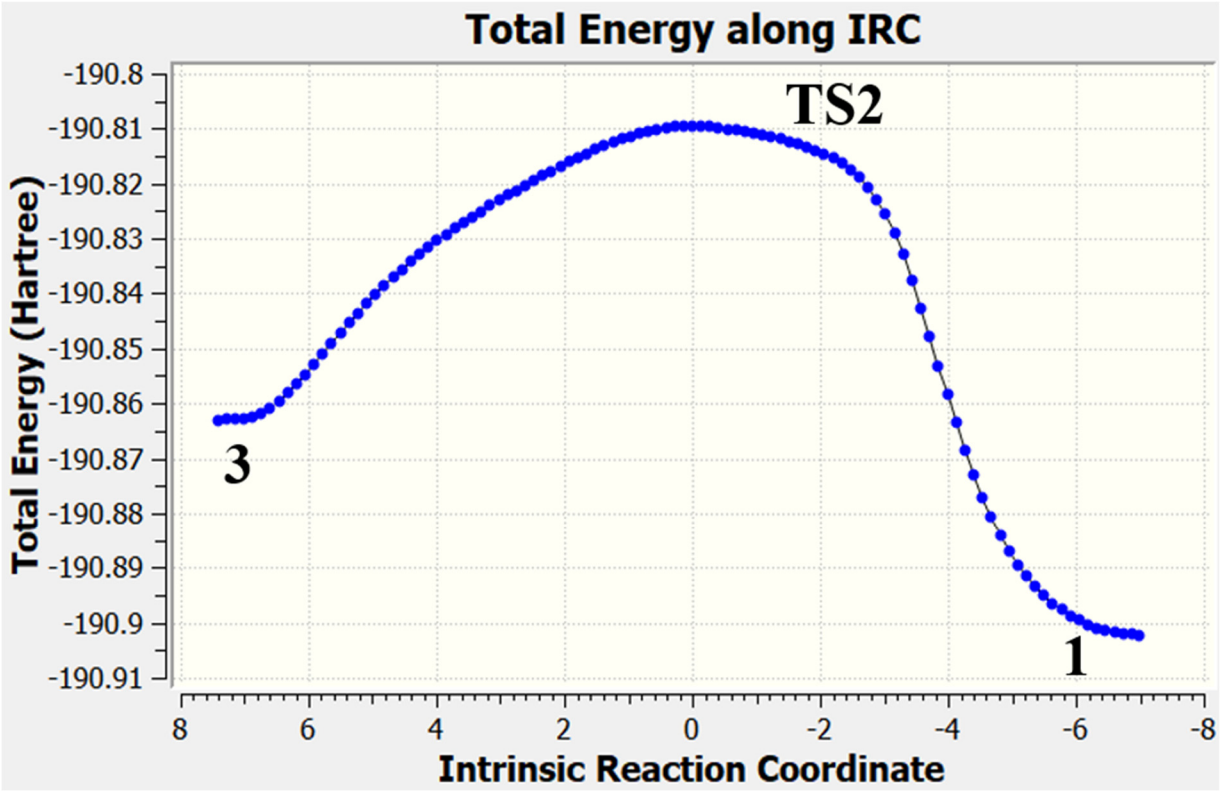


Figure S3: Intrinsic Reaction Coordinate for the rearrangement from **3** to **1** and **10** to **1** calculated at UB3LYP/6-311+G(d,p) level of theory.



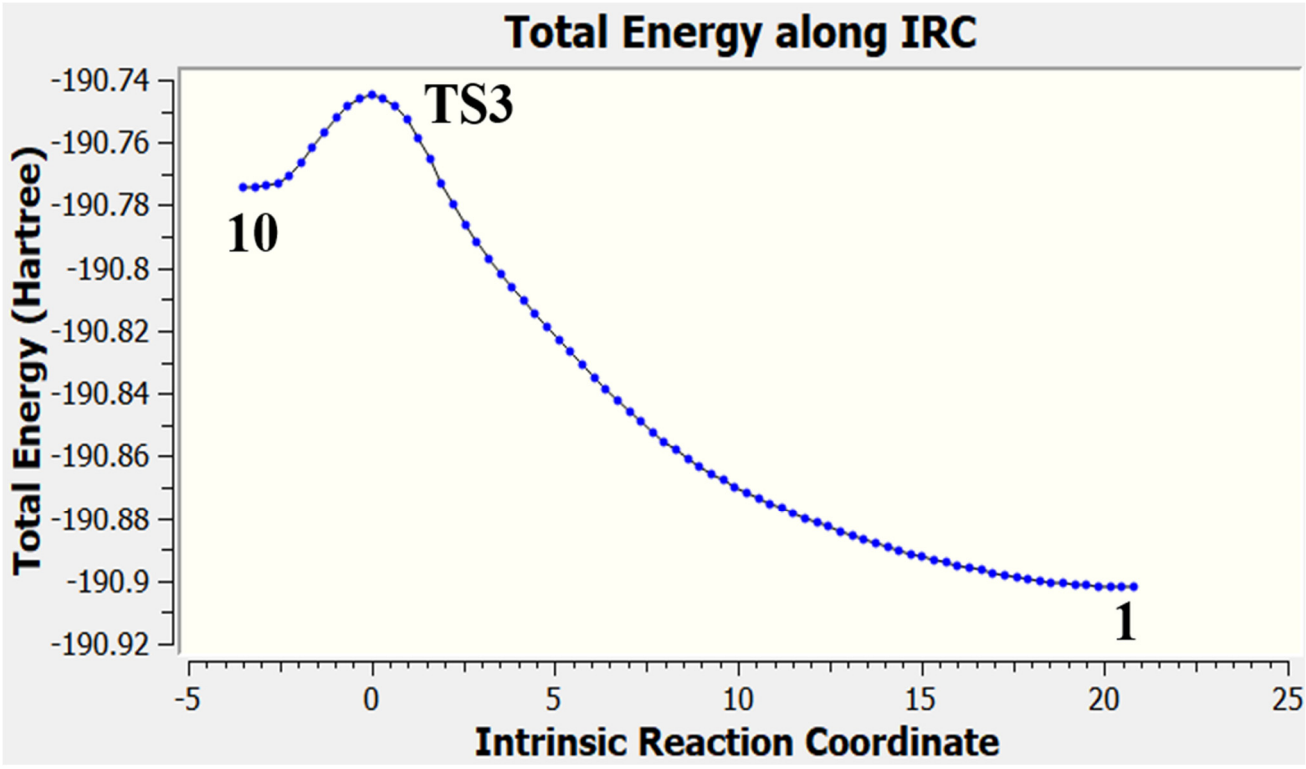
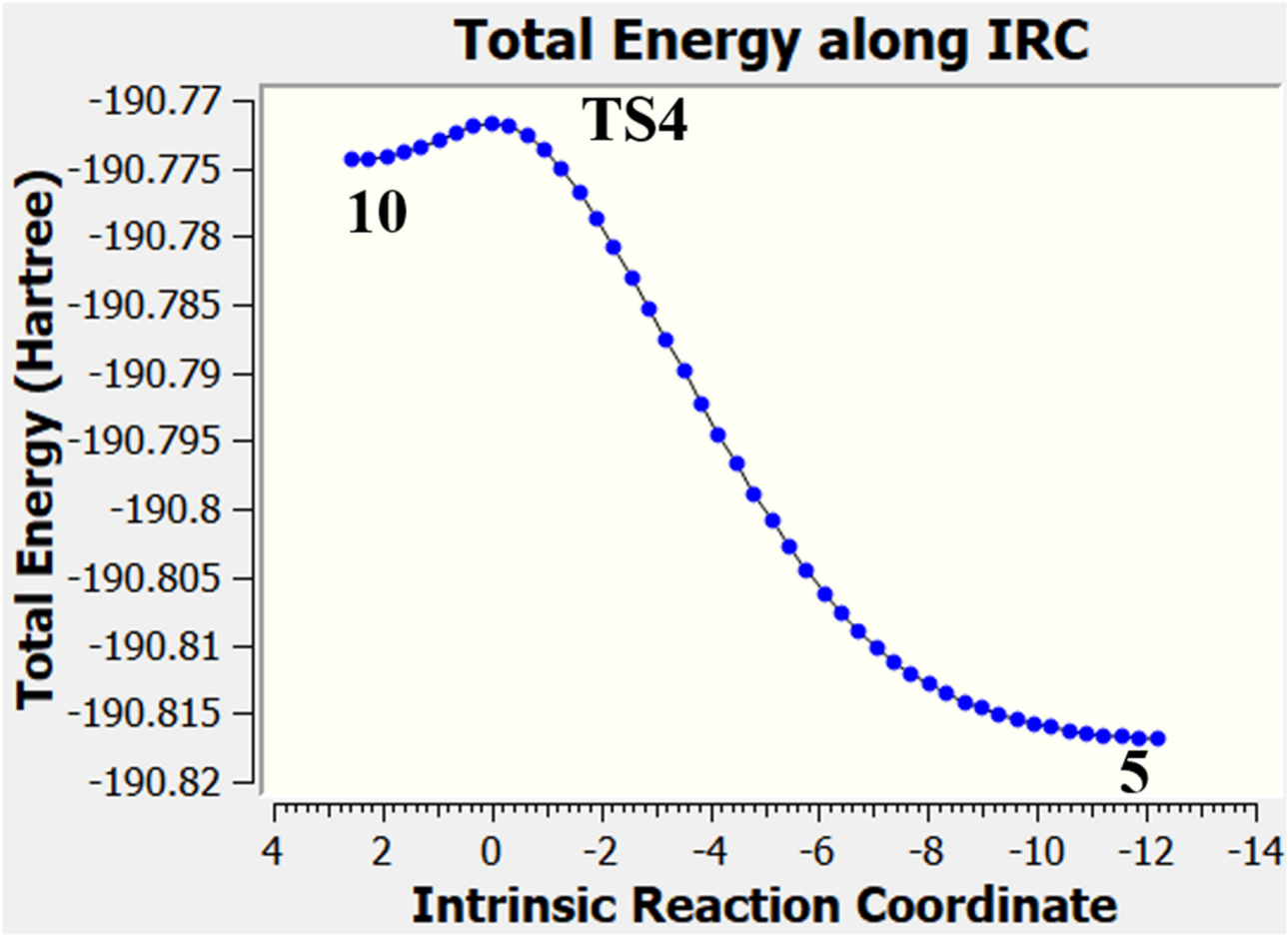


Figure S4: Intrinsic Reaction Coordinate for the rearrangement from **10** to **5** and **5** to **3** calculated at UB3LYP/6-311+G(d,p) level of theory.



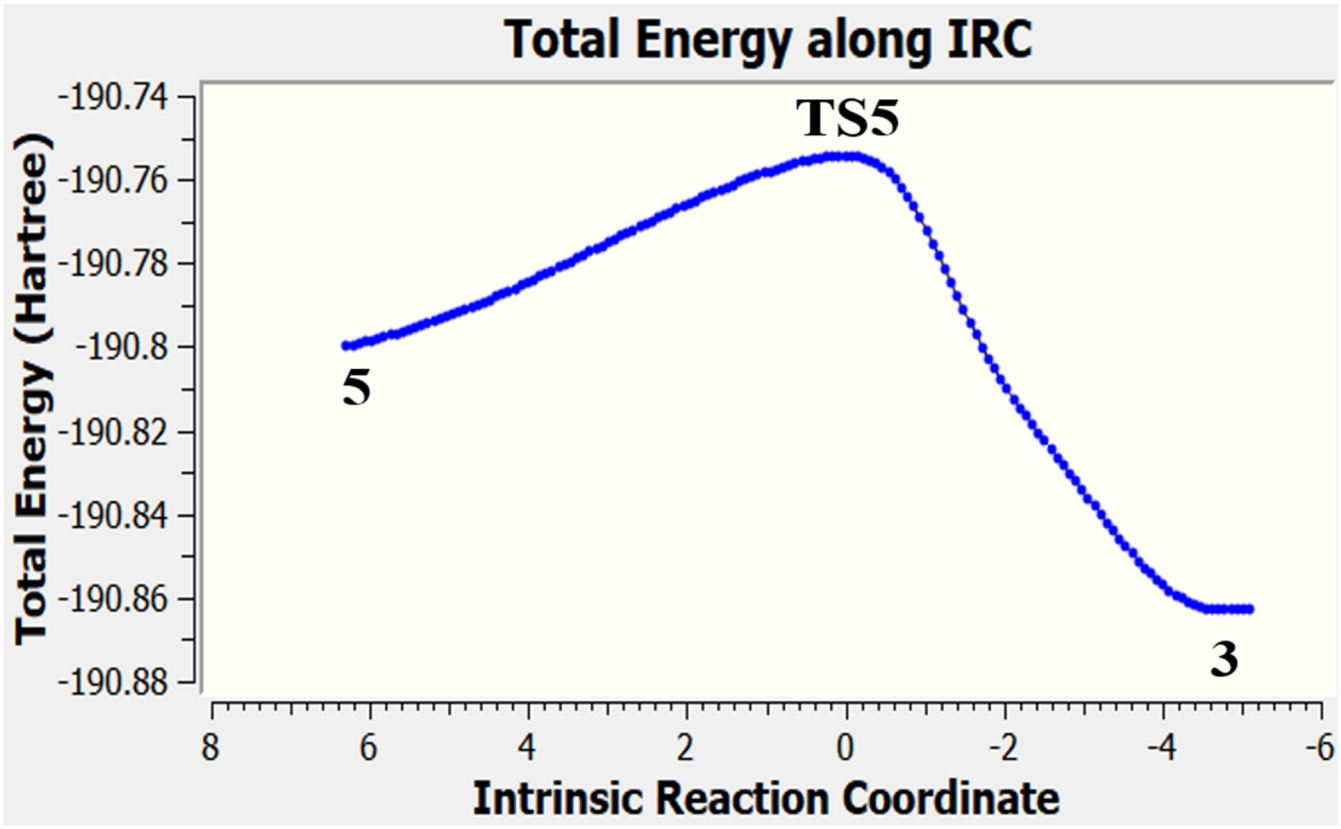
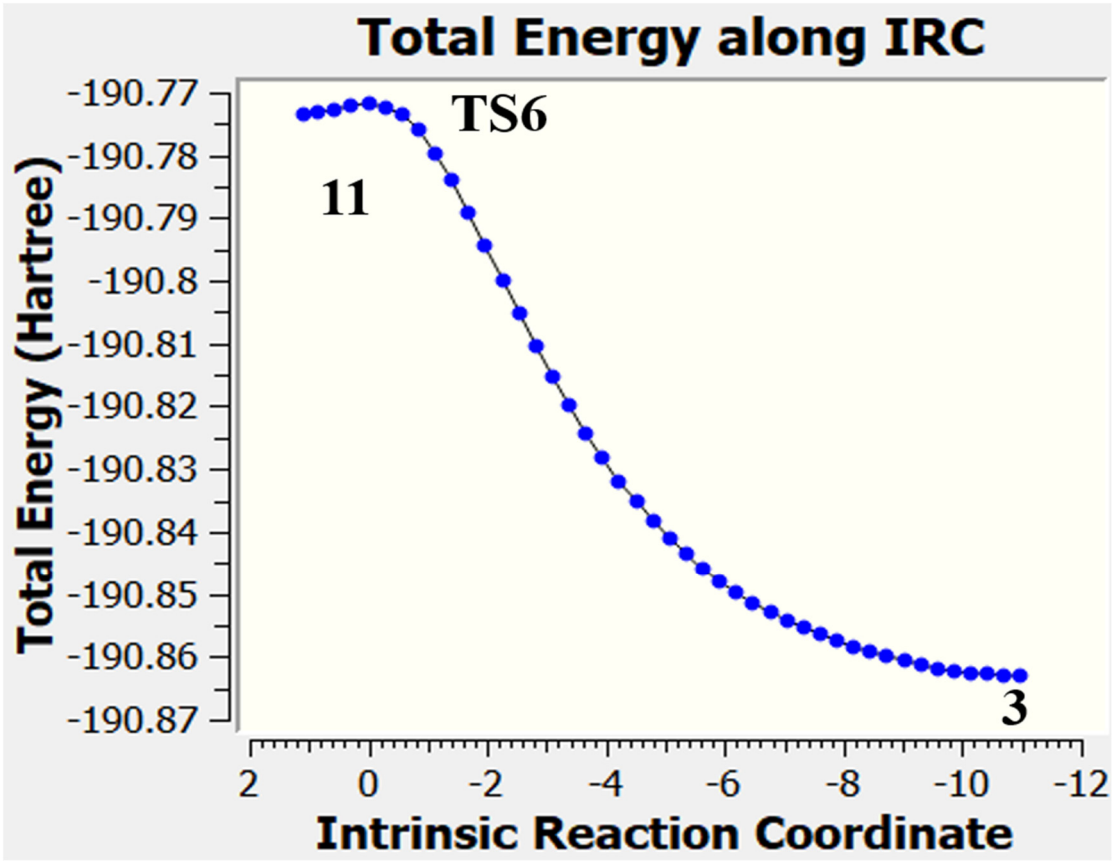


Figure S5: Intrinsic Reaction Coordinate for the rearrangement from **10** to **5** and **4** to **2** calculated at UB3LYP/6-311+G(d,p) level of theory.



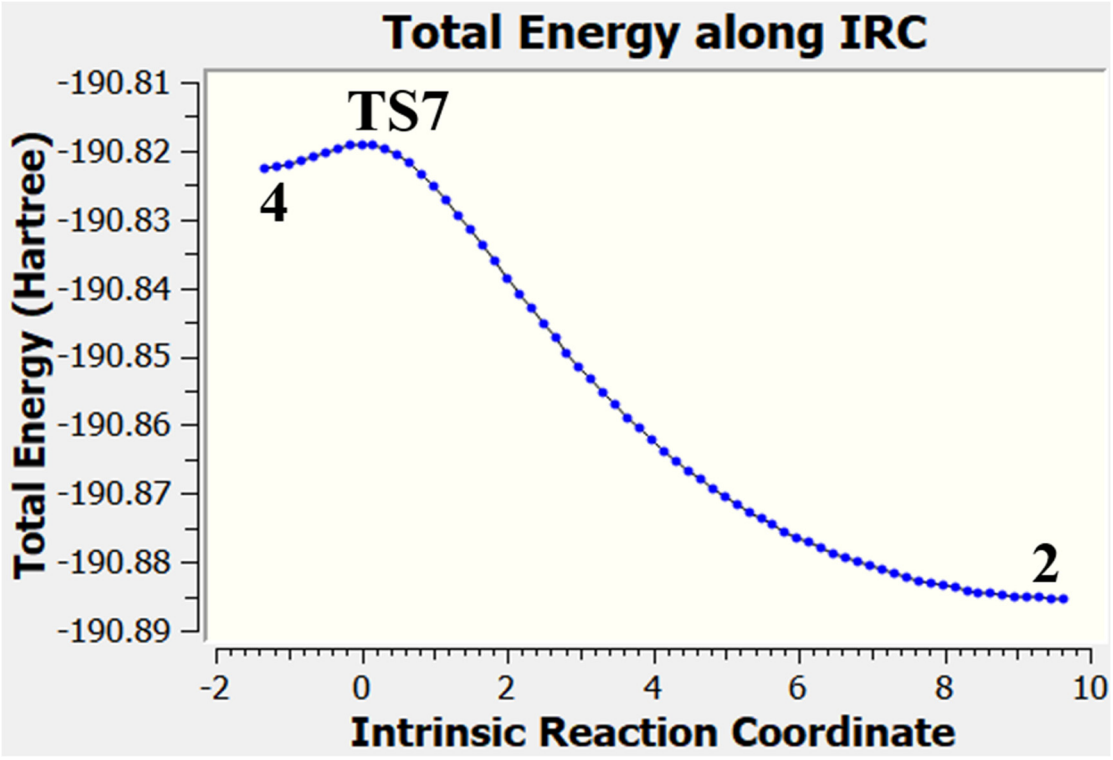
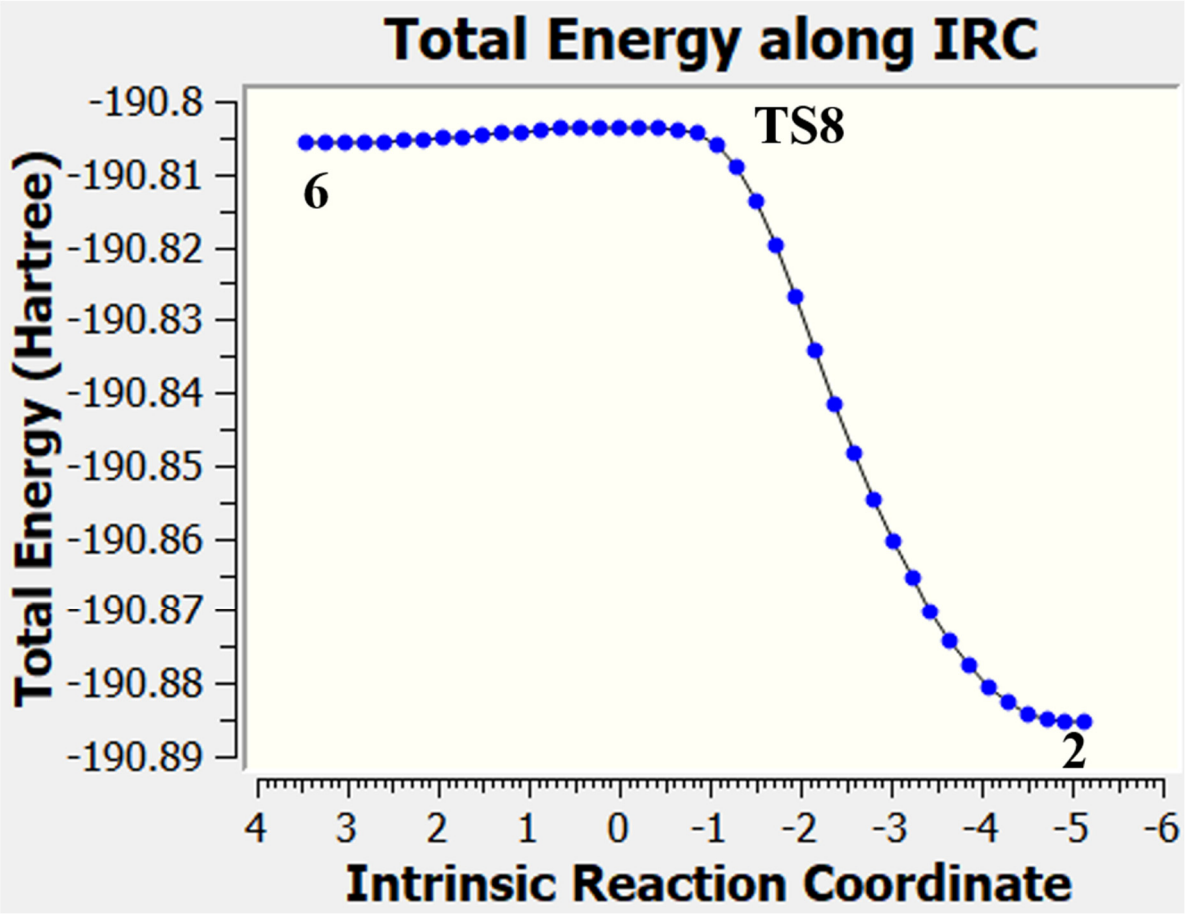


Figure S6: Intrinsic Reaction Coordinate for the rearrangement from **6** to **2** and **10** to **5** calculated at UB3LYP/6-311+G(d,p) level of theory.



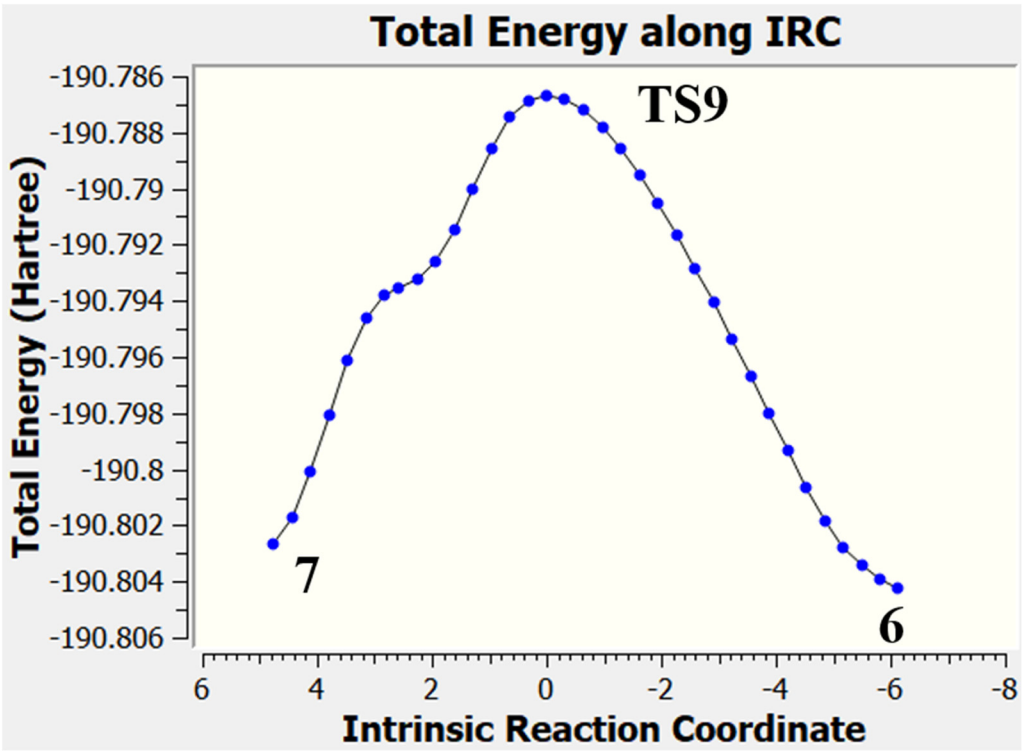
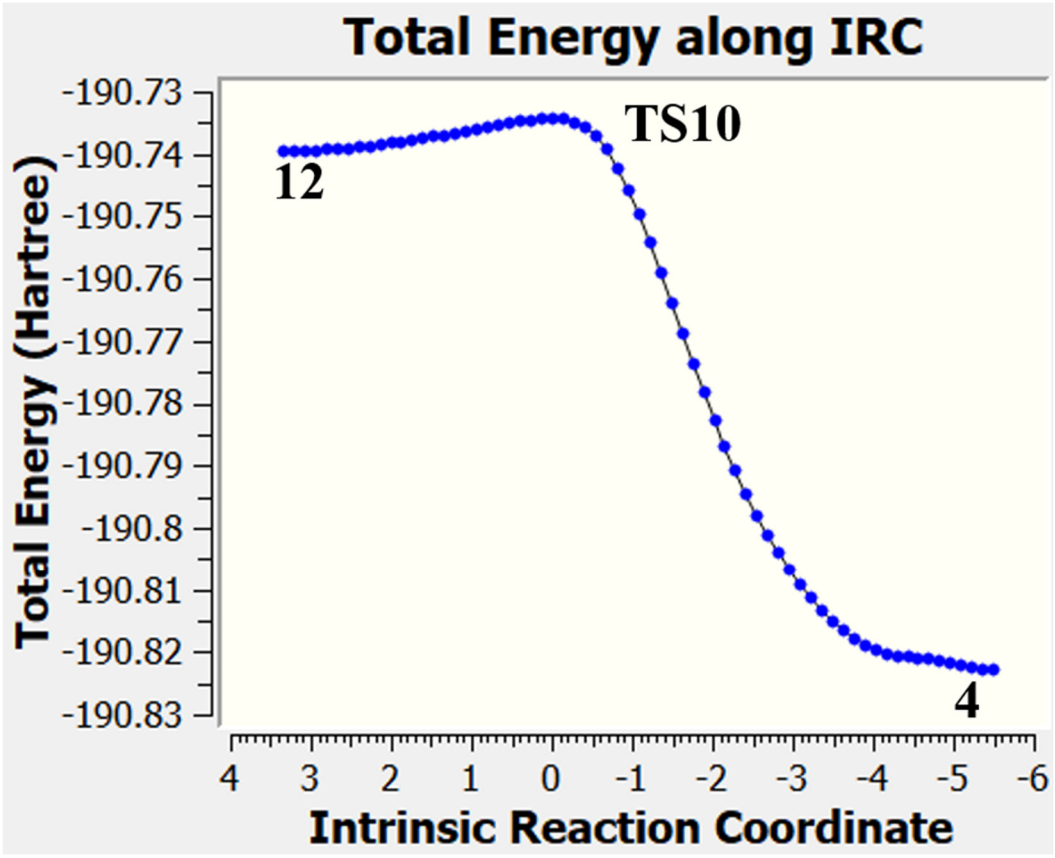


Figure S7: Intrinsic Reaction Coordinate for the rearrangement from **12** to **4** and **10** to **5** calculated at UB3LYP/6-311+G(d,p) level of theory.



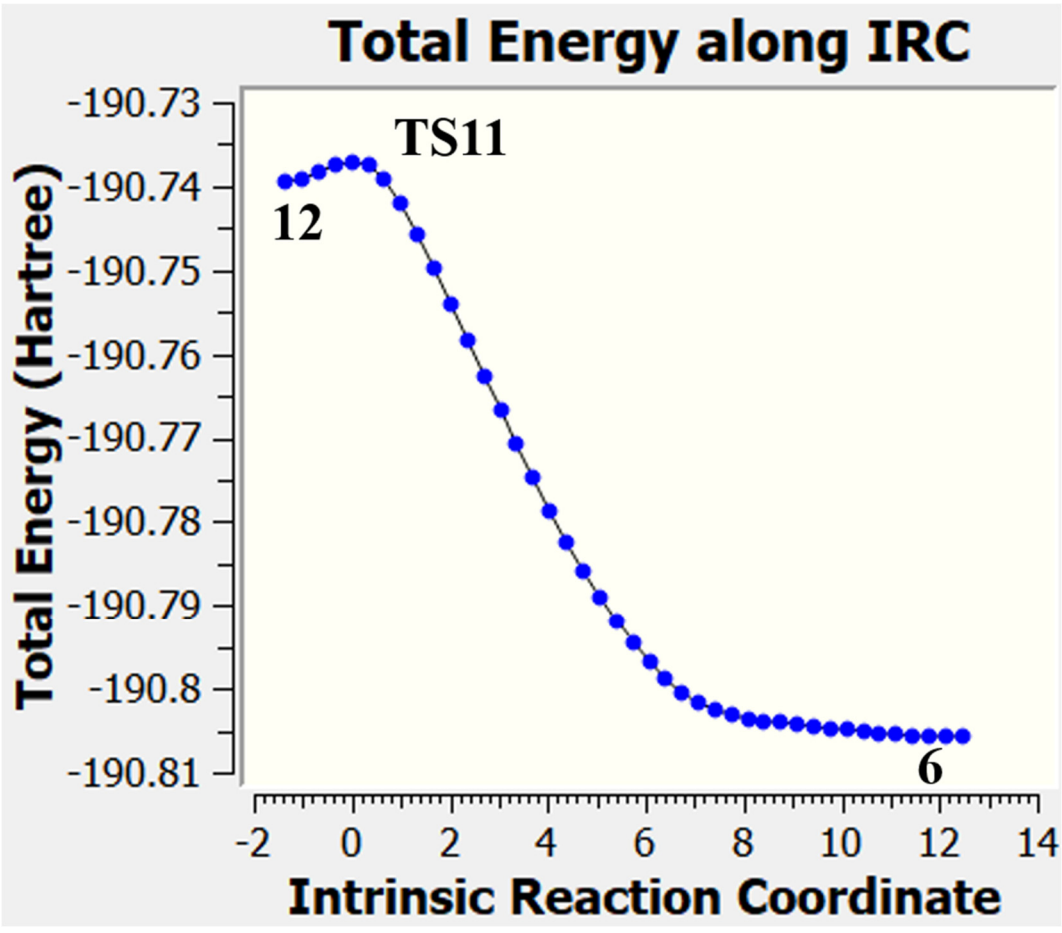


Figure S8: Energy evolution of isomer **6** - **14** of C_5H obtained from the AIMD simulation carried out at 298.15K temperatures and 1 atm pressure for 2500 fs at the B3LYP/6-311+G(d,p) level of theory.