

Kinetic and mechanistic investigations of thermal decomposition of methyl-substituted cycloalkyl radicals

Long Chen ^a, Wenliang Wang ^{a,*}, Weina Wang ^a, Chunying Li ^b, Fengyi Liu ^a, Jian Lü ^{b,*}

^a School of Chemistry and Chemical Engineering, Key Laboratory for Macromolecular Science of Shaanxi Province, Shaanxi Normal University, Xi'an, Shaanxi 710062, People's Republic of China

^b Xi'an Modern Chemistry Research Institute, Xi'an 710065, People's Republic of China

Corresponding authors. Tel: +86-29-81530815, Fax: +86-29-81530727.
e-mail: wlwang@snnu.edu.cn (W. L. Wang), lujian204@263.net (J. Lü).

Eight sections of the supporting information

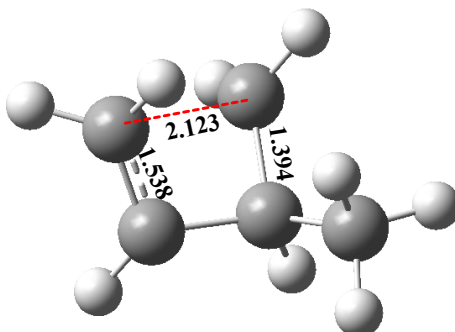
- A.** The geometries of all of transition states involved in the thermal decomposition of 2-Me-cyclobutyl radical at the CBS-QB3 level (Fig. S1)
- B.** The geometries of all of transition states involved in the thermal decomposition of 2-Me-cyclopentyl radical at the CBS-QB3 level (Fig. S2)
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Fig. S1. The geometries of all of transition states involved in the thermal decomposition of 2-Me-cyclobutyl radical at the CBS-QB3 level.

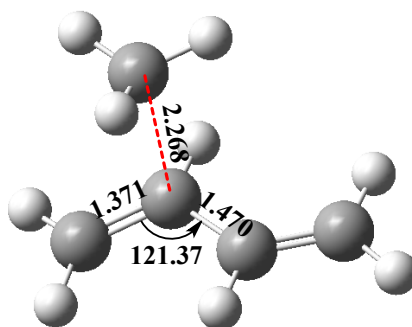
1. TS1a



Cartesian Coordinates (Å)

At	X	Y	Z
C	-0.22466300	1.30126300	-0.11856200
C	-1.49832700	-0.25541800	0.56013000
H	-1.07479000	-0.04329000	1.53698700
C	-0.72319800	-0.84210500	-0.43890000
C	0.51672800	0.02077900	-0.53926600
H	-2.58374500	-0.35435300	0.57676500
H	-0.76716100	1.82484100	-0.89872100
C	1.68495300	-0.34635400	0.38713300
H	2.10702600	-1.31682200	0.11434500
H	2.48120200	0.40157200	0.32447700
H	1.36038400	-0.40434400	1.43017300
H	0.89586900	0.06425100	-1.56847300
H	-1.14477700	-1.37655800	-1.28197600
H	0.19303700	1.93571400	0.66320900

2. TS1b

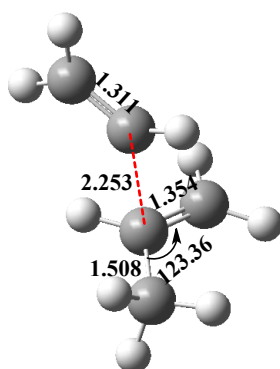


Cartesian Coordinates (Å)

At	X	Y	Z
C	-0.33156200	-0.42928600	-0.37758800
C	-1.31605100	-1.30575800	0.00013300
H	-0.30635600	-0.09839300	-1.41198200

H	-2.18129900	-1.48760100	-0.62505600
H	-1.29756800	-1.78480800	0.97307100
C	0.94014700	-0.34450200	0.35525200
C	2.08309300	0.12669100	-0.14647700
C	-1.14733900	1.62222100	0.14220500
H	-1.14836400	1.57839500	1.22430800
H	-0.37998700	2.23597500	-0.31387000
H	-2.11773900	1.61248500	-0.33966900
H	0.92202400	-0.72311900	1.37557200
H	2.14377500	0.50994200	-1.16058200
H	2.99578600	0.14093300	0.43705900

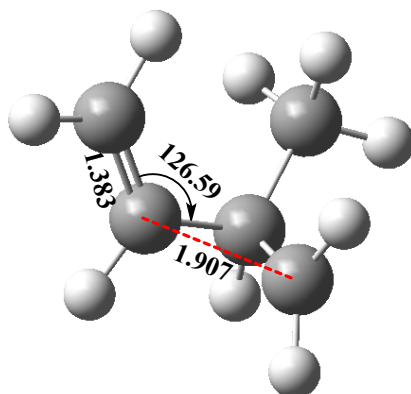
3. TS1c



Cartesian Coordinates (Å)

At	X	Y	Z
C	-2.36280500	-0.01570500	-0.23249300
H	-3.37423100	-0.12441900	0.16600300
H	-2.29780300	0.24603200	-1.28683000
C	-1.29962400	-0.19444000	0.51390000
H	-1.17830800	-0.43077500	1.56373400
C	0.83484500	0.16226800	-0.40940100
H	0.30343600	0.17047500	-1.35703000
C	1.18557800	1.34924400	0.14035200
H	1.80757600	1.39783500	1.02863800
H	0.80156600	2.28626600	-0.24446000
C	1.47368600	-1.14840800	-0.02439100
H	1.87521400	-1.11108400	0.99148700
H	0.76754900	-1.97844900	-0.08688500
H	2.30492600	-1.37362900	-0.70246200

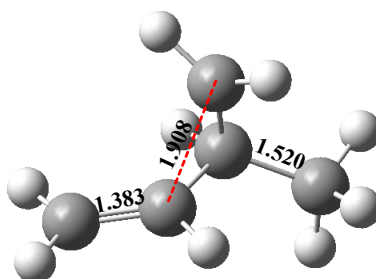
4. TS1d-cis



Cartesian Coordinates (Å)

At	X	Y	Z
C	-0.63542800	0.25414700	-0.45024000
C	-0.29957100	1.34730800	0.49654600
H	-0.20428000	2.37283900	0.16828400
H	-0.24051400	1.13754000	1.55538900
C	0.86469700	0.18848000	-0.47221100
H	1.34451300	0.85155600	-1.18362000
C	1.66047800	-0.71141600	0.21280300
H	1.24666800	-1.46971200	0.86558400
H	2.73926200	-0.64641100	0.15180800
H	-1.04243500	0.61225800	-1.39682700
C	-1.41854300	-0.93564300	0.07874000
H	-2.47359700	-0.67226100	0.19182600
H	-1.34634200	-1.78707200	-0.60366400
H	-1.05308000	-1.25599300	1.05739100

5. TS1d-trans

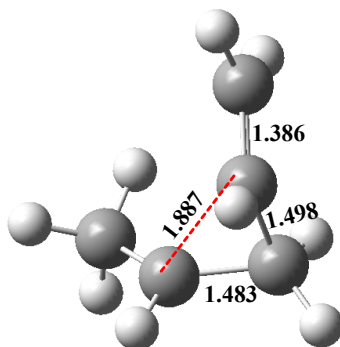


Cartesian Coordinates (Å)

At	X	Y	Z
C	1.80858700	-0.62541000	0.04037900
C	0.50227300	0.00345000	-0.41578400
H	2.65814600	-0.17450200	-0.48064100
H	1.95880300	-0.47717900	1.11416600
H	1.81533500	-1.70131700	-0.15479600
C	0.18213800	1.37441500	0.04841800

H	0.62262100	1.76307200	0.95737900
H	-0.42132100	2.03583700	-0.55538800
C	-0.72485400	-0.26693100	0.39829200
H	-0.55608600	-0.42590200	1.45869300
C	-1.99601900	-0.46169000	-0.10961800
H	-2.19329400	-0.40149700	-1.17419500
H	-2.84197600	-0.61925600	0.54711600
H	0.32502000	-0.14226200	-1.48245700

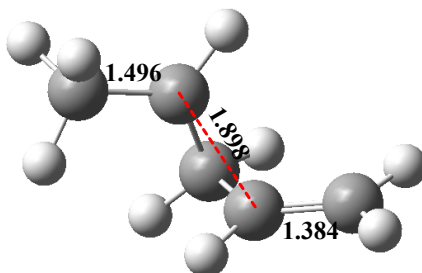
6. TS1e-cis



Cartesian Coordinates (Å)

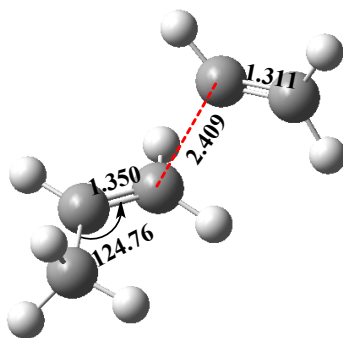
At	X	Y	Z
C	-0.85741500	0.41015300	-0.39347100
C	0.09497100	1.13560700	0.48110200
H	0.17501200	2.21274000	0.34373400
H	0.05807300	0.87066400	1.53720000
C	1.02460000	0.29183700	-0.33590400
H	1.33135600	0.70899800	-1.28835900
C	1.64125300	-0.86753900	0.10644400
H	1.46834600	-1.26009600	1.10169300
H	2.27702800	-1.44472500	-0.55290100
C	-1.65960900	-0.76245300	0.07236000
H	-2.58700600	-0.43643000	0.56439800
H	-1.94273500	-1.41560000	-0.75761500
H	-1.10326500	-1.36636400	0.79430100
H	-1.13961000	0.88518200	-1.32563400

7. TS1e-trans



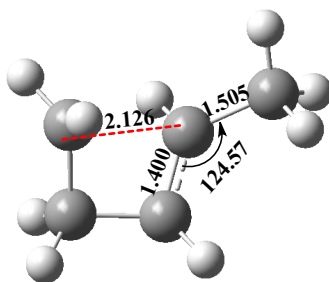
Cartesian Coordinates (Å)			
At	X	Y	Z
C	-1.98158200	-0.48447200	-0.07244500
C	-0.72744800	0.06225000	0.53346300
H	-2.86528700	0.07015900	0.27798800
H	-1.97039700	-0.40300100	-1.16367000
H	-2.13962100	-1.53567900	0.18596800
C	0.08482500	1.12014500	-0.11492500
H	-0.38598900	1.64474700	-0.94564400
H	0.60116500	1.81055400	0.55019600
C	0.87068000	-0.10150400	-0.47741800
H	0.54586400	-0.62791900	-1.36822300
C	2.04128000	-0.50138600	0.14213800
H	2.46048800	0.05833700	0.97082900
H	2.53670800	-1.42124000	-0.14115400
H	-0.50945800	-0.16615900	1.56883300

8. TS1f



Cartesian Coordinates (Å)			
At	X	Y	Z
C	2.45842100	-0.53735700	-0.19257300
H	3.38304200	-0.94003400	0.22868600
H	2.26346300	-0.79665200	-1.23131500
C	1.64395700	0.21235800	0.50918400
H	1.66590600	0.55771400	1.53478200
C	-0.40520500	0.95877000	-0.51422600
H	-0.05904700	1.97681700	-0.38618300
H	-0.05512700	0.43802600	-1.39883900
C	-1.43572300	0.47631200	0.21153800
H	-1.82620500	1.07794600	1.02980100
C	-2.04877300	-0.87742700	0.02877600
H	-3.13166300	-0.80575700	-0.12496200
H	-1.61563800	-1.40168500	-0.82621800
H	-1.90079600	-1.50231200	0.91805700

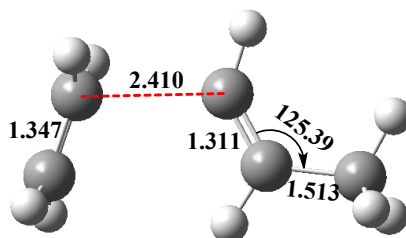
9. TS1g



Cartesian Coordinates (Å)

At	X	Y	Z
C	-2.08315200	0.13536800	-0.10385800
C	-0.65909700	-0.00047800	0.36387400
H	-2.24024100	-0.35062000	-1.06931700
C	1.10631900	1.03965300	-0.20260900
H	0.98355900	1.29352300	-1.25103000
C	1.59581000	-0.38068000	0.08858400
H	2.00587200	-0.46136500	1.10291000
C	0.22712300	-0.99515600	-0.06701500
H	1.40244100	1.86659500	0.44208300
H	2.35218900	-0.77517100	-0.59823800
H	-0.47307400	0.44299100	1.34102200
H	-2.35418800	1.18989500	-0.20620000
H	-2.77851400	-0.30235400	0.62246500
H	-0.02005900	-1.69573400	-0.85755100

10. TS1h

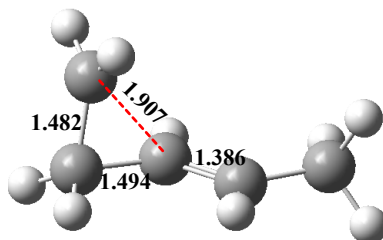


Cartesian Coordinates (Å)

At	X	Y	Z
C	1.11911200	-0.24566100	0.00001300
H	0.63590600	-1.22389800	-0.00009300
C	0.36368900	0.82615500	0.00018900
H	0.56915000	1.88996100	0.00031600
C	-2.02937300	0.54424400	-0.00022200
H	-2.02196500	1.11552200	0.92037200
H	-2.02148900	1.11495200	-0.92116500
C	-2.31789800	-0.77161800	0.00011000
H	-2.41745500	-1.33077000	0.92386300
H	-2.41699800	-1.33133900	-0.92334800
C	2.63162100	-0.25668200	-0.00004700
H	3.01341700	-0.78382000	0.88093700

H	3.01334900	-0.78361000	-0.88118900
H	3.04317600	0.75438300	0.00005000

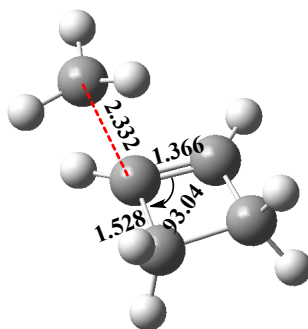
11. TS1i



Cartesian Coordinates (Å)

At	X	Y	Z
C	1.57140400	-0.63722100	0.01653900
C	1.67377100	0.82801100	-0.18205100
H	2.06268800	1.46995200	0.59588900
H	1.46617700	1.26027100	-1.14955900
C	0.20203900	-0.21427200	0.43845700
H	0.09320400	0.08572500	1.47576200
C	-0.93783200	-0.31296000	-0.34311300
H	-0.84347700	-0.71159700	-1.35096800
H	1.60041900	-1.24163100	-0.88869100
H	2.19577800	-1.06638300	0.79805500
C	-2.28164800	0.20043100	0.06912000
H	-3.06299000	-0.55747700	-0.06270100
H	-2.28807300	0.50799900	1.11837000
H	-2.59012900	1.06920700	-0.52986800

12. TS1j



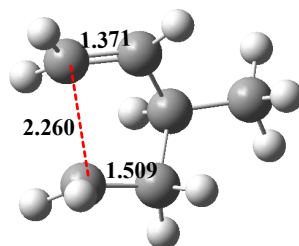
Cartesian Coordinates (Å)

At	X	Y	Z
C	0.61350800	1.06519500	-0.15742200
C	-0.16467100	0.13687200	-0.78832200
C	0.63452100	-1.03650000	-0.22312600
C	1.43124200	0.03993100	0.59800300
H	1.24879900	-1.55724100	-0.96297500
H	0.08254300	-1.77589100	0.36088000
H	2.51056900	0.05743100	0.41380700
H	1.27029500	0.00076500	1.68137500

H	-0.79553800	0.20388300	-1.66557500
C	-2.17190400	-0.02839500	0.38733300
H	-2.64500800	0.91169200	0.13301400
H	-2.56406800	-0.92129400	-0.08528100
H	-1.80133600	-0.13046000	1.39948800
H	0.63757300	2.14850100	-0.17352800

Fig. S2. The geometries of all of transition states involved in the thermal decomposition of 2-Me-cyclopentyl radical at the CBS-QB3 level.

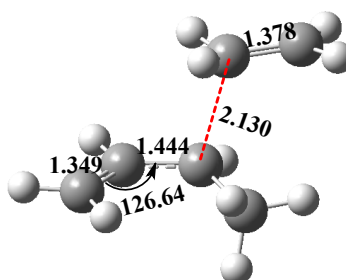
1. TS2a



Cartesian Coordinates (Å)

At	X	Y	Z
C	-1.44310700	-1.18763500	0.12967300
C	-1.51165200	1.06432300	-0.05246700
H	-2.11254700	1.24274800	-0.93649800
C	-0.01416600	1.23414800	-0.13632200
H	0.32799000	2.09399200	0.45195100
H	-2.00422100	1.30888400	0.88348000
H	0.28413900	1.41935700	-1.17386300
C	-0.12506100	-1.16398500	-0.24840200
H	0.18149600	-1.58223100	-1.20468900
H	-2.18271600	-1.73310600	-0.44826300
C	2.19481300	-0.09892400	-0.01652900
H	2.72253300	0.76704600	0.39357200
H	2.68057900	-0.99998300	0.36763500
H	2.32672500	-0.08400500	-1.10358800
C	0.71267600	-0.06926300	0.35144200
H	0.61606700	-0.10711300	1.44506300
H	-1.72106300	-0.99756700	1.16083000

2. TS2b

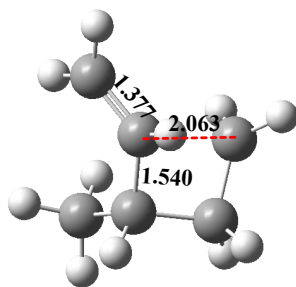


Cartesian Coordinates (Å)

At	X	Y	Z
C	-1.37107900	-0.57212000	0.45796800
C	-0.21146800	0.27126200	0.62831400
C	1.33410600	-0.87190100	-0.28968100
C	2.55298300	-0.24517400	-0.15072400
H	3.17944200	-0.41326800	0.71814800
H	2.88399700	0.51173200	-0.85238100

H	-1.44282500	-1.41779600	1.13979400
H	0.23051300	0.23574800	1.61937300
H	1.13286500	-1.75893900	0.30149300
H	0.82950900	-0.84524500	-1.24962200
C	-2.33431000	-0.43752300	-0.47753300
H	-2.33962800	0.37911800	-1.19044200
H	-3.15407100	-1.14286400	-0.54125400
C	-0.13259600	1.61317200	-0.04808900
H	0.84971300	2.06602800	0.09950300
H	-0.30943000	1.54012200	-1.12526400
H	-0.88589900	2.29906900	0.35912100

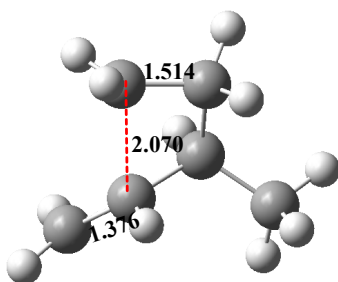
3. TS2c-cis



Cartesian Coordinates (Å)

At	X	Y	Z
C	-2.01337500	-0.30296600	0.10263700
C	-0.78771100	-0.48096100	-0.49814400
H	-2.20629900	0.51920300	0.78152100
C	0.70343000	-1.36894400	0.61694900
H	0.47691100	-1.12793600	1.65012800
C	1.50258600	-0.36087100	-0.18491400
H	1.94388300	-0.83184000	-1.06734400
C	0.33387700	0.57053500	-0.58406900
H	0.79058600	-2.43150900	0.41367400
H	2.31002400	0.13532500	0.36484400
H	-0.73978700	-1.22808300	-1.28837200
H	-2.79547200	-1.04603300	-0.00049900
C	0.16411800	1.75411200	0.36759300
H	1.02800200	2.42093000	0.29615200
H	-0.72896500	2.33695500	0.12663400
H	0.08001300	1.42934400	1.40924600
H	0.42355400	0.95821100	-1.60629700

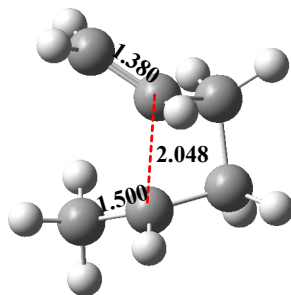
4. TS2c-trans



Cartesian Coordinates (Å)

At	X	Y	Z
C	-1.69189100	-1.29731500	-0.14105100
C	-0.70950700	-0.48345400	0.37509400
H	-1.70427400	-1.56336200	-1.19314100
C	-0.87892000	1.55314300	0.04524300
H	-1.44769800	1.63475600	-0.87552200
C	0.61860000	1.36189500	-0.07471500
H	1.11313100	1.57576800	0.87852700
C	0.60521800	-0.15636500	-0.34078900
H	0.44851300	-0.32328400	-1.41326000
H	-1.30841500	2.07990500	0.89137000
H	1.10951100	1.96442700	-0.84623300
C	1.82098900	-0.95732600	0.12176600
H	2.72709000	-0.63362800	-0.39992200
H	1.98978800	-0.82631000	1.19568800
H	1.68395600	-2.02559200	-0.06840900
H	-0.66011000	-0.39324700	1.46009200
H	-2.53842300	-1.61290000	0.45752000

5. TS2d-cis

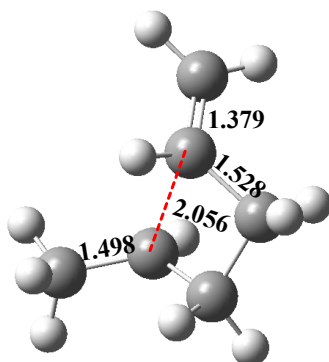


Cartesian Coordinates (Å)

At	X	Y	Z
C	-1.88149200	-0.88986200	-0.06653600
C	-1.08442000	0.13600900	0.39951900
H	-1.93638500	-1.12437300	-1.12446100
C	-0.50149900	1.23552000	-0.48924900
H	-0.53537100	0.92140100	-1.53636900
C	0.93986400	1.21815300	0.05203500
H	1.06393100	1.93404900	0.86912600

C	0.92610200	-0.21195000	0.57788800
H	-1.02624900	2.19371800	-0.41522400
H	1.71844600	1.42298400	-0.69086300
H	-2.39234000	-1.56177400	0.61342500
H	-1.22078600	0.42467800	1.44048700
H	1.14511700	-0.36299200	1.63268500
C	1.37844700	-1.32160400	-0.32383300
H	2.47631700	-1.35843300	-0.37581700
H	1.03366400	-2.29550700	0.03434900
H	1.01164600	-1.19135200	-1.34627900

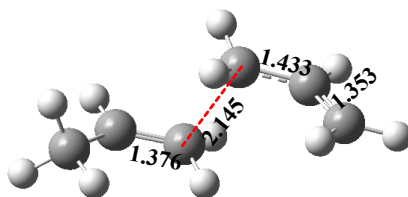
6. TS2d-trans



Cartesian Coordinates (Å)

At	X	Y	Z
C	-1.88632600	-1.15204900	-0.15027600
C	-0.98094300	-0.27806800	0.41406600
H	-2.43772500	-0.88765100	-1.04670700
C	-0.90728800	1.21280700	0.08649900
H	-1.39492700	1.40234600	-0.87459600
C	0.62086200	1.32935700	-0.04007700
H	1.07501600	1.52813400	0.93634300
C	0.87503100	-0.10925200	-0.45521000
H	0.64417800	-0.32274200	-1.49698200
H	-1.37740300	1.86073100	0.83347200
H	0.98470300	2.09250200	-0.73677600
C	1.98451600	-0.92677700	0.13142100
H	2.96238200	-0.62551500	-0.27483300
H	2.04137100	-0.80785000	1.21825000
H	1.85860900	-1.99047900	-0.09106200
H	-1.99587600	-2.16651200	0.21497200
H	-0.59544400	-0.53906800	1.39938100

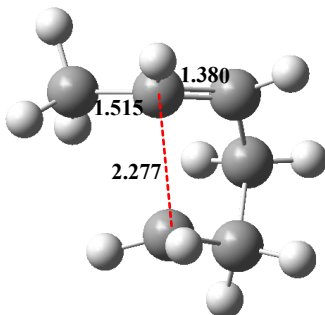
7. TS2e



Cartesian Coordinates (Å)

At	X	Y	Z
C	-2.07868900	-0.34308200	0.17517200
C	-0.80301000	-0.28455400	0.82541700
C	0.67381100	-0.53962500	-0.70976800
C	1.93431300	-0.50602200	-0.15811100
H	2.37479400	-1.43518300	0.19632000
H	-2.49878400	-1.33481000	0.01504900
H	-0.46339400	0.68124000	1.18499600
H	-0.50419600	-1.12470300	1.44031700
H	0.27245500	-1.48882000	-1.04601400
H	0.30457400	0.32787900	-1.24727600
C	-2.76489100	0.72071300	-0.30177600
H	-2.39743200	1.73429100	-0.17393700
H	-3.71132300	0.60215400	-0.81502600
C	2.69153700	0.75037600	0.13433900
H	3.71817800	0.69515500	-0.24637800
H	2.21127600	1.62371500	-0.31467900
H	2.77543200	0.93223700	1.21499400

8. TS2f

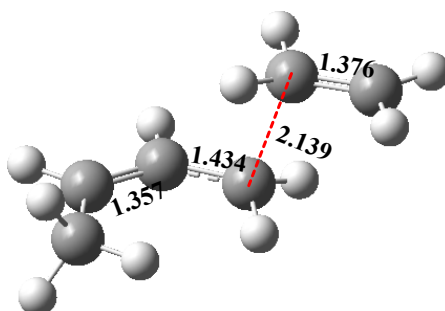


Cartesian Coordinates (Å)

At	X	Y	Z
C	-0.53448100	1.37647600	0.31075400
C	-1.61601300	0.43361500	-0.16723900
H	-2.35539400	0.28483600	0.62528400
C	-0.98426400	-0.95800200	-0.52280800
H	-0.54777900	-0.91978100	-1.52530700
C	0.05846900	-1.13800700	0.54057900
H	-2.15334600	0.84086500	-1.03102700
H	-1.73859400	-1.74782500	-0.52688600
C	1.07551300	-0.20672500	0.60072900

H	1.57998200	-0.10335300	1.56107500
H	-0.63844100	1.83557000	1.28754000
H	-0.26116000	-1.60865800	1.46742700
C	1.93597200	0.22938600	-0.56804900
H	2.31053200	1.24720300	-0.43303200
H	2.80986600	-0.42950200	-0.64146500
H	1.41087500	0.18725000	-1.52336500
H	-0.02772100	1.99292800	-0.42403800

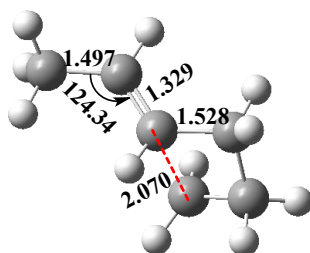
9. TS2g



Cartesian Coordinates (Å)

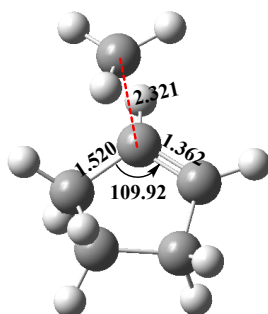
At	X	Y	Z
C	-0.82806500	-1.05974900	-0.02507100
C	0.30989200	-0.65391200	0.74738000
C	1.74870600	0.13268800	-0.62608800
C	2.87911800	0.53041300	0.04921600
H	3.68726500	-0.16176700	0.25700900
H	2.95547800	1.51722500	0.49185900
H	-0.78153600	-2.06012900	-0.45090300
H	0.23137100	0.22142600	1.38056600
H	0.93938400	-1.43529300	1.15495800
H	1.77763600	-0.77809800	-1.21397700
H	1.05240200	0.88101600	-0.98717800
C	-1.92533100	-0.32053000	-0.32883700
H	-2.68514100	-0.78390300	-0.95317600
C	-2.22212000	1.07786100	0.12075600
H	-2.33016500	1.75093300	-0.73828400
H	-3.17285700	1.11948300	0.66548100
H	-1.44703700	1.48847900	0.76950400

10. TS2h



Cartesian Coordinates (Å)			
At	X	Y	Z
C	1.36879200	-0.37466000	-0.33428800
C	0.17235200	-0.28246700	0.34558900
H	1.36942800	-0.83569100	-1.32038400
C	-1.09012500	-1.05743900	-0.02895100
H	-1.01435300	-1.39953300	-1.06575300
C	-2.10327100	0.09381400	0.09237600
H	-2.48236600	0.16826700	1.11565200
C	-1.13563300	1.22530800	-0.20101000
H	-1.28154000	-1.93449800	0.59871600
H	-2.96799800	0.02933800	-0.57628000
H	0.22696600	0.01595700	1.39239800
H	-1.09360200	2.10092800	0.43991000
C	2.64824000	0.25564700	0.11906600
H	3.47715300	-0.46226900	0.10246300
H	2.94762900	1.08623500	-0.53462300
H	2.56390300	0.64866300	1.13570200
H	-0.90734500	1.42138600	-1.24449300

11. TS2i

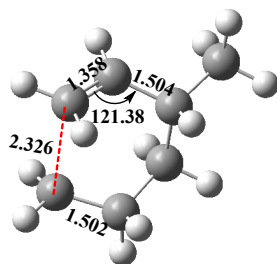


Cartesian Coordinates (Å)			
At	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.62430370	1.36537609	0.23782382
C	0.80719912	-0.97406914	0.50586141
C	2.12100985	1.03054282	0.43860259
C	2.14000060	-0.43171433	0.95329733
H	-1.06568749	-0.12521332	-0.14409800
H	0.19458236	1.80836483	1.14624813
H	0.45508498	2.07662450	-0.57350853
H	0.53687681	-2.02038283	0.58734679
H	2.62360216	1.72497382	1.11476930
H	2.63626926	1.08303549	-0.52438522
H	2.99315471	-1.00203731	0.56886495
H	2.21806648	-0.47029289	2.04966224
C	0.13176829	-0.15096249	-2.31224332

H	-0.14483511	-1.18479142	-2.47748730
H	-0.60726354	0.59742023	-2.57532550
H	1.16835735	0.10488474	-2.49367974

Fig. S3. The geometries of all of transition states involved in the thermal decomposition of 2-Me-cyclohexyl radical at the CBS-QB3 level.

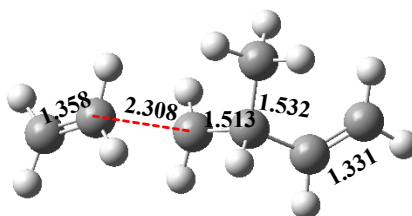
1. TS3a



Cartesian Coordinates (Å)

At	X	Y	Z
C	2.11366400	-0.11039300	0.33068100
C	1.28173900	-1.21710000	-0.25284000
C	-0.19842800	-1.23106100	0.17904500
C	-1.01649000	-0.00697200	-0.31588200
C	-0.38040400	1.24319400	0.22657000
C	0.79467300	1.71011500	-0.26746400
H	-0.67024500	-2.14530500	-0.19914100
H	1.33521500	-1.18071400	-1.34883500
H	1.72021700	-2.19004500	0.02461200
H	2.10907700	0.01186300	1.40965100
H	3.05726600	0.12805800	-0.15139100
H	-0.93852500	0.00774500	-1.41156600
H	-0.73145800	1.59699000	1.19422500
H	1.09901600	1.48250600	-1.28356200
H	1.31077600	2.54036600	0.20166600
H	-0.25875100	-1.27871400	1.27400200
C	-2.49611600	-0.13374600	0.06518400
H	-3.07269400	0.71582200	-0.31055100
H	-2.93446400	-1.04832700	-0.34409300
H	-2.61725900	-0.16446100	1.15322100

2. TS3b

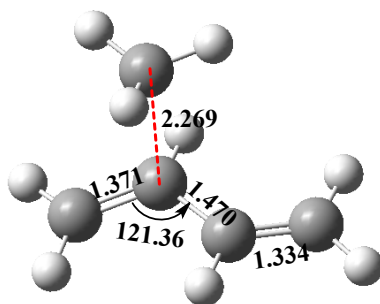


Cartesian Coordinates (Å)

At	X	Y	Z
C	-3.06527700	-0.44879000	0.30357400
C	-1.92510300	-0.75899200	-0.30968600
C	-0.68062500	0.10566300	-0.42317400

C	0.43361700	-0.60553500	0.31218700
C	2.45764100	0.35830500	-0.23535700
C	3.47656700	-0.43195600	0.18930600
H	-3.88666100	-1.15545400	0.34482600
H	-3.22929300	0.51071300	0.78067600
H	-1.82929600	-1.74274200	-0.76587600
H	-0.41870500	0.13523900	-1.49163500
H	0.47039700	-0.47663500	1.39036800
H	0.68986300	-1.60425400	-0.02635700
H	2.18468600	1.24401700	0.32555800
H	3.89991700	-0.32714700	1.18190400
H	3.85832800	-1.24306500	-0.42070700
C	-0.87983200	1.54485800	0.06209900
H	0.02112200	2.13718500	-0.10859600
H	-1.70542400	2.02962200	-0.46475100
H	-1.09917700	1.57267000	1.13356100
H	2.14231600	0.33853400	-1.27267000

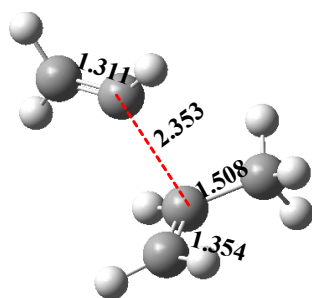
3. TS3c



Cartesian Coordinates (Å)

At	X	Y	Z
C	-1.31530100	-1.30621400	0.00051600
C	-0.33132000	-0.42955600	-0.37794200
C	-1.14858700	1.62182400	0.14186800
H	-2.18020400	-1.48946300	-0.62474600
H	-1.29687900	-1.78392200	0.97411500
H	-0.30576200	-0.10011500	-1.41279700
H	-0.38153700	2.23540900	-0.31490300
H	-1.14917400	1.57828500	1.22397100
H	-2.11920300	1.61150100	-0.33955100
C	0.94015100	-0.34349300	0.35524800
C	2.08344200	0.12717900	-0.14623000
H	0.92174300	-0.72135300	1.37586300
H	2.99574500	0.14176100	0.43791500
H	2.14496200	0.50946100	-1.16062800

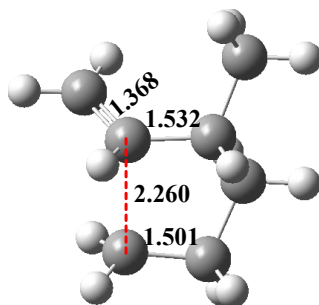
4. TS3d



Cartesian Coordinates (Å)

At	X	Y	Z
C	1.29900000	-0.21267300	0.51003600
C	-0.83401300	0.16652500	-0.40809200
C	-1.17673400	1.35184900	0.15024300
H	1.17796200	-0.48892200	1.55015400
H	-0.30362600	0.17796500	-1.35625700
H	-0.78726800	2.28908000	-0.22851400
C	2.36164900	-0.01033100	-0.23099900
H	2.29523700	0.29287300	-1.27412800
H	3.37374200	-0.13937800	0.15963200
C	-1.48062800	-1.14281000	-0.03179000
H	-0.77970500	-1.97679200	-0.10079800
H	-1.88124300	-1.11021300	0.98461200
H	-2.31364300	-1.35815500	-0.71086800
H	-1.79710000	1.39818600	1.03978100

5. TS3e-cis

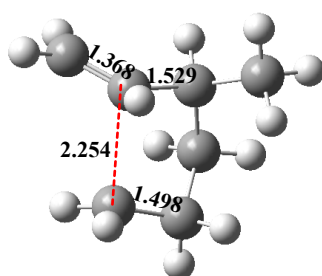


Cartesian Coordinates (Å)

At	X	Y	Z
C	-0.36972500	0.98451600	-0.48220100
C	-0.83281600	1.85641500	0.46509100
H	-1.21966200	1.51807400	1.42024900
C	1.84251300	0.71460500	-0.10927400
H	2.30187900	1.15479700	-0.98851000
C	1.79531500	-0.77896400	0.02938900
H	2.54846000	-1.13901800	0.74360000
C	0.38997100	-1.20339700	0.48661300
H	0.27545300	-2.29273600	0.47357000

H	1.94942900	1.30336400	0.79531400
H	2.01790500	-1.25583100	-0.93119300
C	-0.63752500	-0.52333700	-0.43547600
H	-0.46041900	-0.90855500	-1.44747100
H	-0.15032600	1.39704500	-1.46270500
H	-0.74872600	2.92803500	0.32784100
H	0.22142700	-0.87356700	1.51929200
C	-2.08385800	-0.87272300	-0.05237000
H	-2.79899100	-0.39411900	-0.72582100
H	-2.24331500	-1.95423900	-0.09936300
H	-2.31636100	-0.54593900	0.96456700

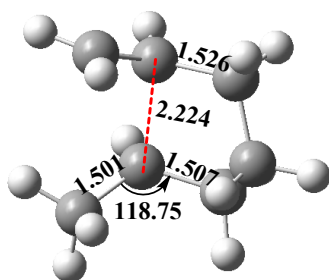
6. TS3e-trans



Cartesian Coordinates (Å)

At	X	Y	Z
C	1.10561100	0.18398700	-0.31562100
C	2.29445300	-0.06191500	0.31450200
H	2.39618900	0.04066800	1.39038000
C	-0.01620900	-1.75670300	-0.54882200
H	0.13028000	-2.01628800	-1.59235000
C	-1.33174800	-1.19790000	-0.10046200
H	-1.97120500	-1.97631500	0.34004000
C	-1.06748100	-0.09829700	0.94074000
H	-1.99202700	0.40133600	1.25032800
H	0.52868400	-2.38108100	0.15174000
H	-1.88496800	-0.78853900	-0.95126100
C	-0.04870800	0.91453300	0.37158000
H	1.12038500	0.23919800	-1.40132700
H	3.15086000	-0.45029900	-0.22431000
H	-0.63984500	-0.56227300	1.83677100
C	-0.70268700	1.92560200	-0.58332300
H	-1.49609700	2.48464500	-0.07904000
H	0.03300900	2.64569100	-0.95216700
H	-1.14359500	1.43120800	-1.45444500
H	0.36894600	1.47620500	1.21407400

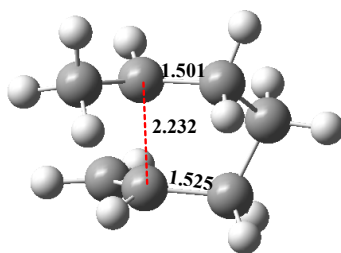
7. TS3f-cis



Cartesian Coordinates (Å)

At	X	Y	Z
C	-1.13140200	0.49335200	0.52649800
C	-1.47870800	1.57740300	-0.24160400
H	-1.70081500	1.47447100	-1.29921800
C	-1.37020500	-0.93571300	0.04786600
H	-1.64094100	-1.56060600	0.90598900
C	-0.11758900	-1.51874400	-0.62301800
H	0.02033200	-1.05419500	-1.60577800
C	1.08530100	-1.18832800	0.27512600
H	1.01492900	-1.77317700	1.19864200
H	-2.22021300	-0.96199700	-0.64011000
H	-0.21384000	-2.59629500	-0.79081500
C	1.08220700	0.28495700	0.59137800
H	1.24676800	0.55437100	1.63203100
H	-1.11929100	0.64133400	1.60265100
H	-1.46009000	2.58466000	0.15794200
H	2.02214100	-1.48364400	-0.21886700
C	1.68130200	1.23771500	-0.40138100
H	1.40247600	2.27232200	-0.18606300
H	2.77971200	1.18248200	-0.38147500
H	1.36338900	1.01642100	-1.42412300

8. TS3f-trans

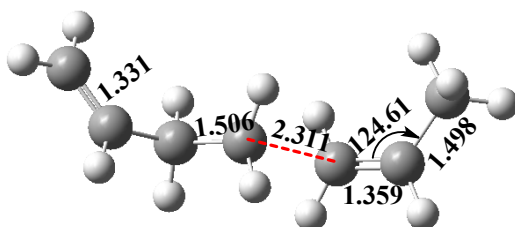


Cartesian Coordinates (Å)

At	X	Y	Z
C	-0.82647600	0.85383700	0.41494700
C	-1.34509000	1.80351700	-0.42700500
H	-2.08173000	1.54735400	-1.18209400
C	-1.46145000	-0.52434800	0.56501800
H	-1.42020400	-0.82337800	1.61803600

C	-0.73502800	-1.58054900	-0.28743900
H	-1.00569900	-1.44373500	-1.34093500
C	0.77418400	-1.36241900	-0.12578800
H	1.07733600	-1.60679600	0.90009800
H	-2.52002700	-0.47925200	0.29371000
H	-1.03475600	-2.59590300	-0.00917800
C	1.08837800	0.07432100	-0.42668900
H	-0.24969600	1.21115200	1.26395900
H	-0.98115500	2.82445400	-0.42284600
H	1.33226300	-2.04182600	-0.78761400
H	0.92779600	0.36623200	-1.46215800
C	2.22792600	0.76758700	0.25686300
H	3.20052400	0.40439700	-0.10948600
H	2.20613800	1.84707900	0.08003800
H	2.21454400	0.59855100	1.33903700

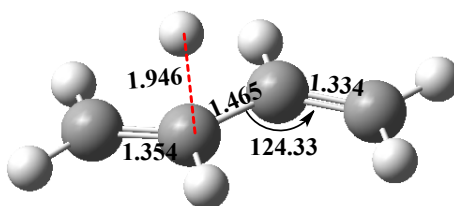
9. TS3g



Cartesian Coordinates (Å)

At	X	Y	Z
C	-2.77448900	-0.12723200	0.31986800
C	-1.44623400	-0.54264300	-0.27005800
C	-0.29689800	-0.06693200	0.57947100
C	1.61456800	-0.76891000	-0.51418300
C	2.72538700	-0.37561500	0.16212500
C	3.39845900	0.95145400	-0.00642300
H	3.32276100	1.55933700	0.90454800
H	2.95948600	1.52297000	-0.82823700
H	4.46920800	0.83304300	-0.20992000
H	-3.01488400	-0.56062100	1.28909900
H	-1.41671600	-1.63657300	-0.35509900
H	-1.36472900	-0.13894500	-1.28526700
H	-0.10433900	1.00107200	0.59495400
H	-0.12884800	-0.56846100	1.52749600
H	1.25899300	-1.78946300	-0.43592400
H	1.28070300	-0.21449900	-1.38521400
H	3.12373700	-1.02674800	0.93722100
C	-3.62311300	0.73301900	-0.23730000
H	-3.41744900	1.19140200	-1.20030800
H	-4.55400700	1.00863300	0.24565700

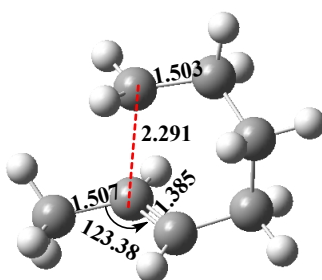
10. TS3h



Cartesian Coordinates (Å)

At	X	Y	Z
C	1.8255260	-0.18430200	-0.11810900
C	0.5924920	0.37358500	-0.06456800
H	2.7073470	0.41093500	-0.31926000
H	1.9760690	-1.23839100	0.08893500
C	-0.6374340	-0.40745100	0.08891300
H	0.6448110	1.12851500	1.72847400
H	0.4703550	1.41223800	-0.36084900
C	-1.8660840	0.07914300	-0.09683600
H	-0.5089160	-1.45409100	0.35568600
H	-2.7452980	-0.54485400	0.00826400
H	-2.0313680	1.11980000	-0.35765200

11. TS3i

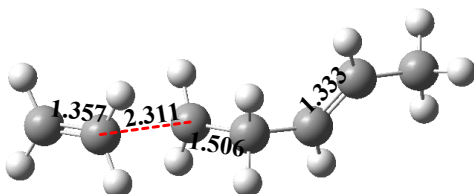


Cartesian Coordinates (Å)

At	X	Y	Z
C	0.08156900	1.57082100	0.21240100
C	1.44469900	1.12069500	-0.23330000
C	1.87211800	-0.26253600	0.29322200
C	0.96353600	-1.40905900	-0.21771100
C	-0.45672100	-1.18104800	0.20890100
C	-1.22274000	-0.21724000	-0.37946000
H	2.90671000	-0.45989300	-0.00790700
H	1.49056500	1.11443600	-1.33038400
H	2.20170200	1.85657500	0.08466800
H	-0.11521000	1.58903200	1.28101200
H	-0.39298600	2.37317900	-0.34641300
H	1.03306600	-1.44602400	-1.31197100
H	1.33979400	-2.36560800	0.15803900
H	-0.76619800	-1.58447500	1.17120600

H	-0.98034800	0.07004200	-1.40062500
H	1.86021100	-0.25424900	1.38990800
C	-2.61839800	0.12411800	0.07421800
H	-2.82176300	1.19371700	-0.02198600
H	-3.36348800	-0.40252300	-0.53310900
H	-2.77643900	-0.15871900	1.11793800

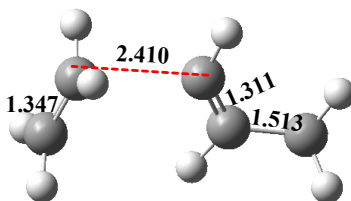
12. TS3j



Cartesian Coordinates (Å)

At	X	Y	Z
C	-3.96722700	-0.46264200	-0.19027600
C	-2.98292900	0.47093100	-0.18985500
C	-0.92986200	-0.48840400	0.26348900
C	0.06417900	0.64211700	0.22312100
C	1.46960600	0.14919800	0.48538200
C	2.45961900	0.14968500	-0.40664200
C	3.84885400	-0.36216900	-0.16052500
H	4.10389500	-1.16728800	-0.85916100
H	3.95973300	-0.74829900	0.85560300
H	4.59459400	0.42736000	-0.30720300
H	-4.48909900	-0.73772600	0.71945700
H	-2.56724500	0.83133900	-1.12384100
H	-2.83309500	1.11168300	0.67169900
H	-1.17303300	-0.91613300	1.23108700
H	-0.89922900	-1.20533600	-0.55052000
H	0.03600500	1.13831500	-0.75317900
H	-0.20172100	1.39664900	0.97444900
H	1.65179900	-0.25746500	1.47967000
H	2.26579400	0.55299600	-1.40046200
H	-4.22183300	-1.01838900	-1.08576700

13. TS3k

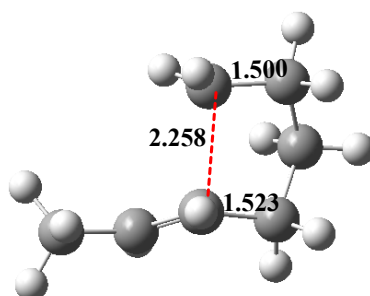


Cartesian Coordinates (Å)

At	X	Y	Z
C	-1.11911200	-0.24566100	-0.00001300
H	-0.63590600	-1.22389800	0.00009300

C	-0.36368900	0.82615500	-0.00018900
H	-0.56915000	1.88996100	-0.00031900
C	2.02937300	0.54424400	0.00022200
H	2.02196500	1.11552200	-0.92037200
H	2.02148900	1.11495200	0.92116500
C	2.31789800	-0.77161800	-0.00011000
H	2.41745500	-1.33077000	-0.92386300
H	2.41699800	-1.33133900	0.92334800
C	-2.63162100	-0.25668200	0.00004700
H	-3.01341700	-0.78382000	-0.88093700
H	-3.01334900	-0.78361100	0.88118900
H	-3.04317600	0.75438300	-0.00005000

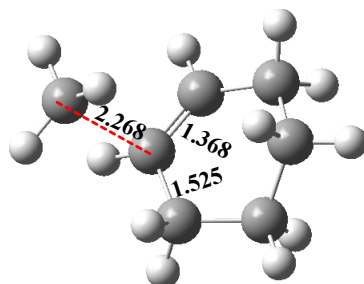
14. TS3I



Cartesian Coordinates (Å)

At	X	Y	Z
C	-0.52517000	-0.38013900	0.53293800
C	-1.60616400	-0.44076400	-0.30719500
H	-1.51811700	-1.01308300	-1.22959200
C	0.68001700	-1.29655100	0.36799500
H	1.09747600	-1.52236200	1.35514400
C	1.77002100	-0.64759100	-0.50149500
H	1.43110900	-0.61789400	-1.54378200
C	1.98421700	0.78920500	-0.00056000
H	2.44772900	0.76303200	0.99198700
H	0.36788600	-2.25129500	-0.06584000
H	2.69821300	-1.22837700	-0.48145800
C	0.65719300	1.48485400	0.06368000
H	0.44336500	2.14967300	0.89453800
H	-0.69622800	0.02536000	1.52692400
H	2.68619400	1.31652200	-0.66243100
C	-2.87664300	0.32506300	-0.10889200
H	-2.99176800	1.12085800	-0.85770000
H	-3.75637900	-0.32145700	-0.20860700
H	-2.91187000	0.79367500	0.87816100
H	0.20156000	1.78088700	-0.87616900

15. TS3m



Cartesian Coordinates (Å)

At	X	Y	Z
C	0.15469900	1.36640400	-0.34573500
C	-1.33478200	1.14114500	-0.04034400
C	-1.53363100	-0.12764300	0.79644600
C	-1.06542200	-1.36515700	0.01555500
C	0.21095600	-1.12233900	-0.73924500
C	0.85897900	0.08236600	-0.77049600
H	-0.95765100	-0.03921600	1.72518800
H	-1.74591600	2.01434100	0.47529200
H	-1.89038900	1.03855600	-0.98041800
H	0.26092700	2.10589700	-1.14734100
H	0.64337500	1.80494700	0.53000900
H	-0.94452000	-2.22025800	0.69427300
H	-1.84787900	-1.67307200	-0.69442100
H	0.66778600	-1.97916800	-1.22730200
H	1.67535900	0.19406200	-1.47574000
H	-2.58201200	-0.24173700	1.08767600
C	2.50003900	-0.09110200	0.78508600
H	1.92724700	-0.16886300	1.70166900
H	3.03034500	-0.98565400	0.48027800
H	3.01830000	0.84812500	0.62324300

Table S1 Relative Energies (ΔE and ΔG) (in kcal·mol⁻¹), imaginary frequencies (ν , cm⁻¹) of transition states, $\langle S^2 \rangle$ value after spin annihilation and T_1 diagnostic values in 2-Me-cyclobutyl radical reactions

Species	ΔE	ΔG^a	ν^c	$\langle S^2 \rangle^c$	T_1^b
R (2-Me-cyclobutyl)	0.00	0.00		0.750	0.010
TS1a	27.87 ^a ; 30.97 ^b	28.28	854 <i>i</i>	0.750	0.031
TS1b	26.04 ^a ; 29.97 ^b	25.87	480 <i>i</i>	0.750	0.038
TS1c	35.40 ^a ; 38.30 ^b	34.42	344 <i>i</i>	0.750	0.036
TS1d-cis	9.40 ^a ; 11.84 ^b	10.38	564 <i>i</i>	0.750	0.022
TS1d-trans	8.47 ^a ; 10.74 ^b	9.38	562 <i>i</i>	0.750	0.022
TS1e-cis	5.87 ^a ; 7.88 ^b	5.94	560 <i>i</i>	0.750	0.022
TS1e-trans	7.02 ^a ; 9.12 ^b	7.08	561 <i>i</i>	0.750	0.022
TS1f	35.55 ^a ; 38.07 ^b	34.11	272 <i>i</i>	0.750	0.036
TS1g	25.53 ^a ; 28.84 ^b	25.66	729 <i>i</i>	0.750	0.031
TS1h	35.95 ^a ; 38.70 ^b	34.94	257 <i>i</i>	0.750	0.036
TS1i	10.40 ^a ; 12.73 ^b	11.20	601 <i>i</i>	0.750	0.022
TS1j	32.03 ^a ; 34.73 ^b	31.65	430 <i>i</i>	0.750	0.027
P1 (2-CH ₃ -3-C ₄ H ₆ -1)	-4.58 ^a ; -3.32 ^b	-5.24		0.750	0.015
P2 (1,3-C ₄ H ₆ +CH ₃)	17.51 ^a ; 18.17 ^b	7.60		0.00; 0.750	0.011; 0.007
P3 (C ₃ H ₆ +C ₂ H ₃)	31.63 ^a ; 32.20 ^b	20.94		0.00; 0.750	0.009; 0.012
P4 (2-CH ₃ -c-C ₃ H ₄ -CH ₂ -cis)	3.12 ^a ; 3.56 ^b	3.72		0.750	0.010
P5 (2-CH ₃ -c-C ₃ H ₄ -CH ₂ -trans)	2.13 ^a ; 2.47 ^b	2.76		0.750	0.010
P6 (4-C ₅ H ₉ -2)	-4.53 ^a ; -4.61 ^b	-5.82		0.750	0.013
P7 (3-C ₅ H ₉ -1)	-5.56 ^a ; -4.22 ^b	-6.48		0.750	0.011
P8 (1-C ₃ H ₅ -1+C ₂ H ₄)	33.34 ^a ; 33.81 ^b	23.18		0.750; 0.00	0.013; 0.010
P9 (2-C ₂ H ₅ -C ₃ H ₄)	3.47 ^a ; 3.78 ^b	3.70		0.750	0.010
P10 (c-C ₄ H ₈ +CH ₃)	25.57 ^a ; 25.99 ^b	15.53		0.00; 0.750	0.009; 0.007

^a at the CBS-QB3 level; ^b at the CCSD(T)/6-311G(2d,d,p)//B3LYP/6-311G(2d,d,p) level; ^c at the B3LYP/6-311G(2d,d,p) level

Table S2 Relative Energies (ΔE and ΔG) (in kcal·mol⁻¹), imaginary frequencies (ν , cm⁻¹) of transition states, $\langle S^2 \rangle$ value after spin annihilation and T_1 diagnostic values in 2-Me-cyclopentyl radical reactions

Species	ΔE	ΔG^a	ν^c	$\langle S^2 \rangle^c$	T_1^b
R (2-Me-cyclopentyl)	0.00	0.00		0.750	0.009
TS2a	32.41 ^a ; 35.21 ^b	32.43	568i	0.750	0.026
TS2b	18.64 ^a ; 23.68 ^b	18.54	590i	0.750	0.031
TS2c-cis	16.20 ^a ; 18.15 ^b	17.46	635i	0.750	0.022
TS2c-trans	14.82 ^a ; 16.45 ^b	15.91	619i	0.750	0.022
TS2d-cis	10.44 ^a ; 13.48 ^b	10.53	611i	0.750	0.022
TS2d-trans	11.86 ^a ; 14.96 ^b	12.13	599i	0.750	0.022
TS2e	19.49 ^a ; 24.07 ^b	19.76	594i	0.750	0.031
TS2f	35.59 ^a ; 38.22 ^b	35.61	567i	0.750	0.027
TS2g	20.00 ^a ; 25.19 ^b	20.00	602i	0.750	0.031
TS2h	15.31 ^a ; 17.00 ^b	16.71	637i	0.750	0.022
TS2i	29.78 ^a ; 32.12 ^b	29.10	437i	0.750	0.024
P1 (3-CH ₃ -4-C ₅ H ₈ -1)	17.38 ^a ; 18.16 ^b	16.18		0.750	0.010
P2 (3-C ₄ H ₇ -2+C ₂ H ₄)	6.28 ^a ; 9.20 ^b	-4.35		0.750; 0.00	0.024; 0.010
P3 (2-CH ₃ -c-C ₄ H ₆ -CH ₂ -cis)	3.60 ^a ; 2.55 ^b	4.46		0.750	0.009
P4 (2-CH ₃ -c-C ₄ H ₆ -CH ₂ -trans)	1.94 ^a ; 0.75 ^b	-1.85		0.750	0.009
P5 (5-C ₆ H ₁₁ -2)	-4.52 ^a ; -3.07 ^b	-6.34		0.750	0.010
P6 (2-C ₃ H ₅ -1+C ₃ H ₆)	7.64 ^a ; 10.00 ^b	-2.51		0.750; 0.00	0.028; 0.009
P7 (4-C ₆ H ₁₁ -1)	17.07 ^a ; 17.89 ^b	15.15		0.750	0.010
P8 (2-C ₄ H ₇ -1+C ₂ H ₄)	6.60 ^a ; 9.47 ^b	-3.33		0.750; 0.00	0.024; 0.010
P9 (2-C ₂ H ₅ -C ₄ H ₆)	3.18 ^a ; 2.36 ^b	4.05		0.750	0.009
P10 (c-C ₅ H ₈ +CH ₃)	23.25 ^a ; 23.26 ^b	12.75		0.00; 0.750	0.009; 0.007

^a at the CBS-QB3 level; ^b at the CCSD(T)/6-311G(2d,d,p)//B3LYP/6-311G(2d,d,p) level; ^c at the B3LYP/6-311G(2d,d,p) level

Table S3 Relative Energies (ΔE and ΔG) (in kcal·mol⁻¹), imaginary frequencies (ν , cm⁻¹) of transition states, $\langle S^2 \rangle$ value after spin annihilation and T_1 diagnostic values in 2-Me-cyclohexyl radical reactions

Species	ΔE	ΔG^a	ν^c	$\langle S^2 \rangle^c$	T_1^b
R (2-Me-cyclohexyl)	0.00	0.00		0.750	0.009
TS3a	27.77 ^a ; 30.50 ^b	27.64	436i	0.750	0.024
TS3b	28.20 ^a ; 31.58 ^b	28.19	379i	0.750	0.025
TS3c	26.04 ^a ; 29.97 ^b	25.87	480i	0.750	0.028
TS3d	35.39 ^a ; 38.29 ^b	34.43	345i	0.750	0.026
TS3e-cis	8.09 ^a ; 10.06 ^b	10.18	462i	0.750	0.022
TS3e-trans	7.84 ^a ; 9.86 ^b	9.68	474i	0.750	0.022
TS3f-cis	20.74 ^a ; 24.15 ^b	20.98	475i	0.750	0.022
TS3f-trans	20.58 ^a ; 23.88 ^b	20.79	468i	0.750	0.022
TS3g	28.20 ^a ; 30.88 ^b	27.82	383i	0.750	0.024
TS3h	31.66 ^a ; 35.35 ^b	32.20	728i	0.750	0.035
TS3i	27.13 ^a ; 29.89 ^b	26.85	467i	0.750	0.023
TS3j	27.93 ^a ; 30.88 ^b	27.41	375i	0.750	0.024
TS3k	35.95 ^a ; 38.70 ^b	34.94	257i	0.750	0.036
TS3l	7.52 ^a ; 9.45 ^b	9.14	477i	0.750	0.022
TS3m	29.84 ^a ; 32.37 ^b	29.08	485i	0.750	0.022
P1 (4-CH ₃ -5-C ₆ H ₁₀ -1)	20.07 ^a ; 20.76 ^b	17.52		0.750	0.010
P2 (2-CH ₃ -3-C ₄ H ₆ -1+C ₂ H ₄)	21.64 ^a ; 22.56 ^b	11.40		0.750; 0.00	0.015; 0.010
P3 (1,3-C ₄ H ₆ +CH ₃)	17.51 ^a ; 18.18 ^b	8.02		0.00; 0.750	0.011; 0.007
P4 (C ₃ H ₆ + C ₂ H ₃)	31.63 ^a ; 32.20 ^b	20.94		0.00; 0.750	0.009; 0.032
P5 (2-CH ₃ -c-C ₅ H ₈ -CH ₂ -cis)	-14.80 ^a ; -15.89 ^b	-13.14		0.750	0.009
P6 (2-CH ₃ -c-C ₅ H ₈ -CH ₂ -trans)	-14.85 ^a ; -15.76 ^b	-13.29		0.750	0.009
P7 (6-C ₇ H ₁₃ -2)	12.88 ^a ; 14.47 ^b	10.76		0.750	0.010
P8 (3-C ₄ H ₇ -1+C ₃ H ₆)	22.75 ^a ; 23.34 ^b	11.95		0.750; 0.00	0.012; 0.009
P9 (1,3-C ₄ H ₆ +H)	27.96 ^a ; 28.12 ^b	22.61		0.00; 0.750	0.011; 0.00
P10 (5-C ₇ H ₁₃ -1)	18.71 ^a ; 19.55 ^b	16.07		0.750	0.009
P11 (3-C ₅ H ₉ -1+C ₂ H ₄)	22.03 ^a ; 22.86 ^b	11.61		0.750; 0.00	0.011; 0.010
P12 (1-C ₃ H ₅ -1+C ₂ H ₄)	33.76 ^a ; 34.30 ^b	23.56		0.750; 0.00	0.034; 0.010
P13 (2-C ₂ H ₅ -C ₅ H ₈)	-14.55 ^a ; -15.49 ^b	-13.76		0.750	0.009
P14 (c-C ₆ H ₁₀ +CH ₃)	20.91 ^a ; 21.05 ^b	11.16		0.00; 0.750	0.008; 0.007

^a at the CBS-QB3 level; ^b at the CCSD(T)/6-311G(2d,d,p)//B3LYP/6-311G(2d,d,p) level; ^c at the B3LYP/6-311G(2d,d,p) level

Table S4 The theoretical rate coefficients expression of 2-Me-cyclobutyl radical pyrolysis

Reactions	log <i>A</i>	n	<i>E_a</i> /R	Reactions	log <i>A</i>	n	<i>E_a</i> /R
2-CH ₃ -cyclobutyl → 2-CH ₃ -3-C ₄ H ₆ -1 (R _{1a})	12.32	0.24	13491	2-CH ₃ -3-C ₄ H ₆ -1 → 1,3-C ₄ H ₆ + CH ₃ (R _{1b})	12.90	0.29	12479
2-CH ₃ -3-C ₄ H ₆ -1 → C ₃ H ₆ + C ₂ H ₃ (R _{1c})	13.77	0.23	17204	2-CH ₃ -3-C ₄ H ₆ -1 → 2-CH ₃ -c-C ₃ H ₄ -CH ₂ (R _{1d-cis})	11.83	0.06	4566
2-CH ₃ -3-C ₄ H ₆ -1 → 2-CH ₃ -c-C ₃ H ₄ -CH ₂ (R _{1d-trans})	11.87	0.08	4024	2-CH ₃ -c-C ₃ H ₄ -CH ₂ → 4-C ₅ H ₉ -2 (R _{1e-cis})	12.86	0.06	2678
2-CH ₃ -c-C ₃ H ₄ -CH ₂ → 4-C ₅ H ₉ -2 (R _{1e-trans})	12.89	0.05	3277	4-C ₅ H ₉ -2 → C ₃ H ₆ + C ₂ H ₃ (R _{1f})	14.15	0.26	17359
2-CH ₃ -cyclobutyl → 3-C ₅ H ₉ -1 (R _{1g})	12.71	0.20	12358	3-C ₅ H ₉ -1 → 1-C ₃ H ₅ -1 + C ₂ H ₄ (R _{1h})	13.87	0.20	17732
3-C ₅ H ₉ -1 → 2-C ₂ H ₅ -c-C ₃ H ₄ (R _{1i})	12.00	0.05	5090	3-C ₅ H ₉ -1 → c-C ₄ H ₆ + CH ₃ (R _{1j})	13.15	0.33	15462

The ring opening reactions include R_{1a}, R_{1e} and R_{1g}; exocyclization reaction contain R_{1d} and R_{1i}; the remain reactions are C-C bond scission; the unit of s⁻¹

Table S5 The theoretical rate coefficients expression of 2-Me-cyclopentyl radical pyrolysis

Reactions	log <i>A</i>	n	<i>E_a</i> /R	Reactions	log <i>A</i>	n	<i>E_a</i> /R
2-CH ₃ -cyclopentyl → 3-CH ₃ -4-C ₅ H ₈ -1 (R _{2a})	12.83	0.26	15799	3-CH ₃ -4-C ₅ H ₈ -1 → 3-C ₄ H ₇ -2 + C ₂ H ₄ (R _{2b})	12.98	0.15	9086
3-CH ₃ -4-C ₅ H ₈ -1 → 2-CH ₃ -c-C ₄ H ₆ -CH ₂ (R _{2c-cis})	11.42	0.04	7961	3-CH ₃ -4-C ₅ H ₈ -1 → 2-CH ₃ -c-C ₄ H ₆ -CH ₂ (R _{2c-trans})	11.60	0.06	7225
2-CH ₃ -c-C ₄ H ₆ -CH ₂ → 5-C ₆ H ₁₁ -2 (R _{2d-cis})	12.81	0.11	4895	2-CH ₃ -c-C ₄ H ₆ -CH ₂ → 5-C ₆ H ₁₁ -2 (R _{2d-trans})	12.63	0.10	5621
5-C ₆ H ₁₁ -2 → C ₃ H ₆ + 2-C ₃ H ₅ -1 (R _{2e})	12.51	0.24	9393	2-CH ₃ -cyclopentyl → 4-C ₆ H ₁₁ -1 (R _{2f})	12.91	0.19	17548
4-C ₆ H ₁₁ -1 → 2-C ₄ H ₇ -1 + C ₂ H ₄ (R _{2g})	12.65	0.22	9633	4-C ₆ H ₁₁ -1 → 2-C ₂ H ₅ -c-C ₄ H ₆ (R _{2h})	11.19	0.07	7362
2-CH ₃ -cyclopentyl → c-C ₅ H ₈ + CH ₃ (R _{2i})	13.48	0.32	14378				

The ring opening reactions include R_{2a}, R_{2d} and R_{2f}; exocyclization reaction contain R_{2c} and R_{2h}; the remain reactions are C-C bond scission; the unit of s⁻¹

