Electronic Supplementary Material (ESI) for Chemical Science.
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Supporting information for

Bouncing Off Walls – Widths of Exit Channels from Shallow Minima Can Dominate Selectivity Control

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DFT calculations
Cartesian Coordinates of Computed Structures

[B3LYP-D3/6-311+G(d,p)] level of theory

Rc

Sum of electronic and thermal Free Energies= -272.996261 Hartrees

C	-0.10338600	-1.07208900	-0.29822500
C	0.64294800	-0.28498700	0.69579800

C	1.92160200	0.29957800	0.56789000
C	-1.61338200	-0.98852900	-0.03350900
C	2.67326900	0.19207400	-0.56066200
C	-2.09783900	0.42922700	0.01151900
C	-1.36125300	1.51519800	-0.25764700
H	0.16058300	-0.80881700	-1.32461700
H	0.19107100	-0.22879100	1.68473500
H	2.31631300	-0.31347700	-1.45120000
H	-1.83118500	-1.46443400	0.93004800
H	0.22002100	-2.11860900	-0.15568200
H	-0.36403000	1.46615100	-0.67916100
H	-1.76211900	2.51210900	-0.12009200
H	2.32474400	0.81547300	1.43203600
H	-2.16974200	-1.56522200	-0.77872200
H	3.67614400	0.60277600	-0.60195500
H	-3.13354900	0.56001200	0.31363400

TS-a

Sum of electronic and thermal Free Energies= -272.992492 Hartrees

C	-0.09541100	-1.16808300	-0.40236200
C	0.84182200	-0.74726800	0.62056800
C	1.99088300	0.05439200	0.47653900
C	-1.60548800	-0.90697900	-0.04860500
C	2.31368100	0.67574500	-0.69273600
C	-1.99349200	0.54011900	-0.18699500
C	-1.33229300	1.57440600	0.32895300
H	0.13759700	-0.80274200	-1.40064700
H	0.64235700	-1.12605600	1.62285200
H	1.70933000	0.58331500	-1.58746700
H	-1.80494900	-1.27498200	0.96198500
H	-0.00429800	-2.27012100	-0.40931900
H	-0.39768600	1.46322300	0.87217200
H	-1.71329300	2.58572600	0.25333800
H	2.61881700	0.19882400	1.34860000
H	-2.19214700	-1.52405800	-0.72895000
H	3.19353200	1.30645700	-0.76073800
H	-2.90746800	0.72642000	-0.74399900

Prod-1

Sum of electronic and thermal Free Energies= -273.011649 Hartrees

C	-1.49472300	0.40355000	0.43210500

C	-0.67147900	1.46663000	-0.18387400
C	0.67333000	1.46587200	-0.18390500
C	-1.27069200	-1.05249500	-0.35178400
C	1.49539900	0.40171300	0.43194000
C	-0.00099600	-1.47428400	0.15031200
C	1.26925700	-1.05399300	-0.35159800
H	-1.29659600	0.24576800	1.49217900
H	-1.19532600	2.23362800	-0.74381900
H	1.29739500	0.24424600	1.49207200
H	-1.30687400	-0.84756500	-1.41842000
H	-2.56157800	0.57981800	0.30624400
H	1.30569000	-0.84929700	-1.41828300
H	2.09185200	-1.68661900	-0.02154700
H	1.19805100	2.23230000	-0.74379800
H	-2.09412600	-1.68404200	-0.02176700
H	2.56241200	0.57663400	0.30558800
H	-0.00147200	-1.98682100	1.11237300

TS-b

Sum of electronic and thermal Free Energies= -272.988653 Hartrees

C	-0.32029300	-1.18364300	-0.04726000
C	0.34408500	0.02141600	0.60904100
C	1.74679800	0.37940000	0.44819300
C	-1.81720800	-0.81815700	-0.02745800
C	2.58059500	-0.23921800	-0.40190700
C	-1.83091600	0.67129800	-0.05019100
C	-0.68375700	1.32300300	-0.46134200
H	0.04322700	-1.32186800	-1.06630100
H	-0.01755200	0.21077800	1.61752600
H	2.25662700	-1.02107300	-1.07934400
H	-2.29857000	-1.14959700	0.89929400
H	-0.09918400	-2.09708900	0.50798900
H	-0.15551900	0.95529200	-1.33317700
H	-0.55964200	2.38196600	-0.26315700
H	2.12658000	1.14869500	1.11204400
H	-2.41473200	-1.25224800	-0.83838000
H	3.63590100	0.00534500	-0.41568600
H	-2.63295600	1.21520100	0.44473800

Prod-2

Sum of electronic and thermal Free Energies= -273.000366 Hartrees

C	-0.26701600	-1.13474300	0.07509400
C	0.31720200	0.21904700	0.52632600
C	1.75964900	0.49436800	0.20685500
C	-1.78283400	-0.86307600	-0.00214000
C	2.60775500	-0.36304700	-0.35129700
C	-1.91958100	0.54683000	-0.26867200
C	-0.66540100	1.23381700	-0.13190000
H	0.09187000	-1.39725900	-0.92384400
H	0.17799700	0.32241700	1.61142600
H	2.32690400	-1.37069800	-0.63632200
H	-2.22097900	-0.87717300	1.03278800
H	-0.02427400	-1.95364000	0.74873300
H	-0.39944400	1.30800400	-1.22288000
H	-0.70474700	2.27151300	0.20794500
H	2.11222800	1.48137800	0.49589100
H	-2.43710200	-1.52899800	-0.57115600
H	3.63831900	-0.08410000	-0.53213800
H	-2.85942000	1.02937800	-0.53603800

[M06-2X/6-311+G(d,p)] level of theory

Rc

Sum of electronic and thermal Free Energies= -272.815254 Hartrees

C	-0.08948200	-1.04416600	-0.34085700
C	0.67528700	-0.33842900	0.69156900
C	1.94706400	0.26402300	0.58718900
C	-1.59255800	-0.99280700	-0.04993700
C	2.64757700	0.25782600	-0.57537500
C	-2.10968800	0.41408000	0.03418200
C	-1.40909200	1.52071000	-0.21060200
H	0.15941000	-0.71812800	-1.35254200
H	0.22986600	-0.34728600	1.68788700
H	2.25097000	-0.17030700	-1.49051500
H	-1.78977300	-1.50455300	0.89841100
H	0.24648700	-2.09504800	-0.25698900
H	-0.39095600	1.51184300	-0.58690700
H	-1.85502200	2.49993500	-0.08759300
H	2.37630500	0.70402400	1.47957000
H	-2.13786900	-1.55371300	-0.81340400
H	3.64675300	0.67873000	-0.62548800
H	-3.15081700	0.50707900	0.33055900

TS-a

Sum of electronic and thermal Free Energies= -272.812237 Hartrees

C	-0.09845400	-1.15996100	-0.37809500
C	0.81920900	-0.68635300	0.64119500
C	2.00452000	0.05665700	0.47606200
C	-1.59982300	-0.91476600	-0.05530300
C	2.32245600	0.63939500	-0.70998100
C	-1.99010500	0.53385400	-0.21231700
C	-1.34136700	1.55837600	0.32645000
H	0.15282600	-0.84424400	-1.38901000
H	0.57714000	-0.99000600	1.66146200
H	1.69012900	0.55905100	-1.58763000
H	-1.81970700	-1.26856100	0.95643500
H	0.04165800	-2.25848500	-0.32202300
H	-0.44091000	1.43718100	0.92629700
H	-1.70124700	2.57471400	0.22286600
H	2.64231100	0.20372300	1.34005000
H	-2.17435900	-1.53998300	-0.73780000
H	3.22197000	1.23928300	-0.80693800
H	-2.88842700	0.72411600	-0.79177800

Prod-1

Sum of electronic and thermal Free Energies= -272.837283 Hartrees

C	-1.48383100	0.38223300	0.43565300
C	-0.67332800	1.45783600	-0.18729100
C	0.66512200	1.46132800	-0.18719200
C	-1.26779600	-1.04707100	-0.35807900
C	1.48109200	0.39021700	0.43616200
C	0.00431900	-1.44917400	0.15207500
C	1.27396700	-1.04076400	-0.35845500
H	-1.27124300	0.22985300	1.49487200
H	-1.20622900	2.23071200	-0.73027700
H	1.26863900	0.23631500	1.49516500
H	-1.29674800	-0.83820800	-1.42427600
H	-2.55272800	0.55823300	0.32811900
H	1.30185500	-0.83102800	-1.42450100
H	2.09112000	-1.68074100	-0.02900800
H	1.19415600	2.23693600	-0.73007400
H	-2.08096200	-1.69224400	-0.02879800
H	2.54909700	0.57178200	0.32916900

H	0.00577400	-1.94924200	1.12236400

TS-b

Sum of electronic and thermal Free Energies= -272.809369 Hartrees

C	-0.24174200	-1.18291500	-0.18412800
C	0.42689800	-0.14933100	0.66958600
C	1.74970300	0.37000100	0.51687800
C	-1.73782700	-0.88227700	-0.03849200
C	2.58107800	-0.08582900	-0.44075600
C	-1.83918600	0.61608300	0.05645500
C	-0.91182800	1.44053000	-0.48149600
H	0.09034000	-1.12601300	-1.22098300
H	-0.01407200	-0.01242300	1.65499300
H	2.26560100	-0.80178900	-1.19262900
H	-2.11820500	-1.31668000	0.88942000
H	0.02725100	-2.17632100	0.19397300
H	-0.22563600	1.11815100	-1.25445700
H	-0.93595500	2.50451400	-0.27512900
H	2.10399600	1.07296400	1.26207200
H	-2.34706400	-1.28913100	-0.84917000
H	3.61843700	0.22860100	-0.46992600
H	-2.62726400	1.04055700	0.67355400

Prod-2

Sum of electronic and thermal Free Energies= -272.828064 Hartrees

C	-0.25703300	-1.12559100	0.05434400
C	0.31227900	0.22221200	0.52216500
C	1.75269000	0.50444200	0.20080500
C	-1.77251300	-0.86857000	0.01025600
C	2.59903600	-0.36515500	-0.33491900
C	-1.92011200	0.53881800	-0.26040100
C	-0.66691900	1.22872500	-0.13594500
H	0.08767000	-1.35542300	-0.95833300
H	0.16969600	0.31522500	1.60753800
H	2.31371300	-1.37943300	-0.59301700
H	-2.16894200	-0.84436000	1.06245400
H	0.00675400	-1.95661300	0.70499000
H	-0.42250900	1.25792900	-1.23590700
H	-0.69735800	2.27288300	0.17909500
H	2.10101900	1.49909400	0.46731600
H	-2.44029000	-1.54498900	-0.52555000

H	3.62940700	-0.09045200	-0.52266100
H	-2.86372700	1.01684800	-0.52376300

[M06-2X/6-311G(d)] level of theory

Rc

Sum of electronic and thermal Free Energies= -272.800285 Hartrees

C	-0.09078100	-1.04698800	-0.33390700
C	0.66855700	-0.32320800	0.69282600
C	1.94000500	0.27804900	0.58479300
C	-1.59343800	-0.99476500	-0.04411000
C	2.65320200	0.24017300	-0.56956400
C	-2.10538300	0.41441600	0.03624100
C	-1.40488500	1.51618800	-0.22871900
H	0.15474400	-0.72719100	-1.34841100
H	0.21974900	-0.31710500	1.68699800
H	2.26860200	-0.21176900	-1.47829400
H	-1.79255700	-1.50538800	0.90422900
H	0.24894200	-2.09565800	-0.24771700
H	-0.39385300	1.50280400	-0.62501700
H	-1.84493900	2.49869900	-0.10906400
H	2.36236800	0.73920300	1.46991000
H	-2.13945800	-1.55732200	-0.80583100
H	3.65413500	0.65600600	-0.62064200
H	-3.14140000	0.51453100	0.34848500

TS-a

Sum of electronic and thermal Free Energies= -272.796982 Hartrees

C	-0.10491100	-1.15430500	-0.39602300
C	0.82349200	-0.70903100	0.62719400
C	2.00680000	0.03867700	0.47334400
C	-1.60281200	-0.91093500	-0.05435700
C	2.31574400	0.65841800	-0.69637400
C	-1.99388200	0.53881600	-0.19150000
C	-1.32725800	1.56139200	0.32766100
H	0.13684300	-0.81458900	-1.40140900
H	0.59187300	-1.04260900	1.64017400
H	1.67843400	0.60934100	-1.57254700
H	-1.81404100	-1.27919900	0.95396700
H	0.03011400	-2.25410100	-0.37313100
H	-0.40749900	1.44145300	0.89793300

H	-1.69098200	2.57810400	0.24038600
H	2.65279900	0.15901900	1.33557200
H	-2.18494600	-1.52863100	-0.73733400
H	3.21455200	1.26060000	-0.78187700
H	-2.91018600	0.73241800	-0.74141200

Prod-1

Sum of electronic and thermal Free Energies= -272.823942 Hartrees

C	-1.48481800	0.38449800	0.43390800
C	-0.67074200	1.45924100	-0.18645500
C	0.66734500	1.46064300	-0.18630500
C	-1.27006500	-1.04520300	-0.35688800
C	1.48349400	0.38766400	0.43437900
C	0.00192200	-1.44982100	0.15228700
C	1.27273300	-1.04214600	-0.35736800
H	-1.28011400	0.23309100	1.49460000
H	-1.20228200	2.23417200	-0.72832000
H	1.27832000	0.23554400	1.49488800
H	-1.30179800	-0.83952000	-1.42363400
H	-2.55306600	0.56276800	0.32357900
H	1.30365200	-0.83586300	-1.42399600
H	2.08859200	-1.68467400	-0.02931000
H	1.19741100	2.23661400	-0.72812600
H	-2.08415900	-1.68964000	-0.02819300
H	2.55143200	0.56849700	0.32513500
H	0.00279200	-1.95024500	1.12203400

TS-b

Sum of electronic and thermal Free Energies= -272.795023 Hartrees

C	-0.23697300	-1.18355400	-0.19268600
C	0.43500800	-0.16404600	0.67406800
C	1.75114300	0.36607800	0.52253700
C	-1.73308400	-0.88564800	-0.04295900
C	2.58203700	-0.07048800	-0.44556300
C	-1.83942400	0.61247500	0.06699600
C	-0.93042000	1.44907700	-0.47951400
H	0.09389000	-1.11636900	-1.22922000
H	-0.00751300	-0.03463400	1.65944700
H	2.27109000	-0.77821700	-1.20718700
H	-2.11400200	-1.33392800	0.87764700
H	0.03196700	-2.18279900	0.17047500

H	-0.24379900	1.13905500	-1.25773800
H	-0.96428900	2.51249300	-0.27134500
H	2.10547000	1.06018700	1.27623500
H	-2.33883700	-1.28540700	-0.85955300
H	3.61746800	0.25001000	-0.47514500
H	-2.62116300	1.02624300	0.69910400

Prod-2

Sum of electronic and thermal Free Energies= -272.813153 Hartrees

C	-0.25703800	-1.12441000	0.05151300
C	0.31209600	0.22259100	0.52156600
C	1.75256900	0.50398400	0.20111300
C	-1.77293200	-0.86921800	0.01171100
C	2.59886200	-0.36546600	-0.33325800
C	-1.92115700	0.53959300	-0.25807900
C	-0.66632700	1.22940900	-0.13830600
H	0.08692400	-1.35353800	-0.96114300
H	0.16784800	0.31421100	1.60659300
H	2.31665000	-1.38137000	-0.59052800
H	-2.17309600	-0.86633900	1.06089300
H	0.00940700	-1.95658600	0.69959800
H	-0.41301600	1.27136000	-1.23396000
H	-0.70023900	2.27168200	0.18327800
H	2.10167700	1.49840500	0.46880000
H	-2.43741000	-1.54145000	-0.53402900
H	3.63025500	-0.09283600	-0.52000400
H	-2.86543600	1.01757100	-0.51706400

[PCM(DMSO)-M06-2X/6-311G(d)] level of theory

Rc

Sum of electronic and thermal Free Energies= -272.879440 Hartrees

C	-0.05917600	-1.00335500	-0.37361500
C	0.73088600	-0.37840600	0.68955500
C	1.98702100	0.24090200	0.59445000
C	-1.55726800	-1.00632100	-0.06548200
C	2.64643200	0.33436300	-0.59031700
C	-2.15340300	0.36791500	0.04261700
C	-1.51944300	1.51991600	-0.15529800
H	0.16920700	-0.61425800	-1.36645300
H	0.31260100	-0.45924200	1.69248200
H	2.22564800	-0.02664100	-1.52191400

H	-1.73046700	-1.54637100	0.87096400
H	0.29260100	-2.05158400	-0.36884200
H	-0.48246500	1.58401000	-0.46966000
H	-2.03250000	2.46613000	-0.03059700
H	2.44199500	0.61424700	1.50274000
H	-2.07870300	-1.57643000	-0.83852500
H	3.63691200	0.77146300	-0.63946800
H	-3.20512000	0.38858900	0.31781700

TS-a

Sum of electronic and thermal Free Energies= -272.876778 Hartrees

C	-0.07624200	-1.15628500	-0.36361000
C	0.83069400	-0.65161100	0.65708100
C	2.00377900	0.09913800	0.48765900
C	-1.57470700	-0.93495700	-0.04484400
C	2.34720000	0.62170600	-0.71984600
C	-2.00821700	0.49940000	-0.22961900
C	-1.40931000	1.55468300	0.30759100
H	0.16916100	-0.84186100	-1.37554200
H	0.58303700	-0.93493600	1.67986500
H	1.74637400	0.48169700	-1.61049900
H	-1.78519500	-1.27365100	0.97352600
H	0.09526700	-2.24786400	-0.30449400
H	-0.52756400	1.47667800	0.94013500
H	-1.78989100	2.55786100	0.15436300
H	2.61631100	0.29647600	1.35823500
H	-2.13930000	-1.58446200	-0.71209800
H	3.24226500	1.22401800	-0.82415200
H	-2.88964600	0.65360100	-0.84581700

Prod-1

Sum of electronic and thermal Free Energies= -272.902854 Hartrees

C	-1.48616600	0.37833000	0.43048300
C	-0.66896200	1.45888900	-0.18132200
C	0.66770600	1.45941700	-0.18129200
C	-1.27064800	-1.03764900	-0.35793500
C	1.48572500	0.37954100	0.43059700
C	0.00067900	-1.44501300	0.15384700
C	1.27159700	-1.03665900	-0.35803500
H	-1.28456000	0.22552500	1.49103500
H	-1.20038200	2.23475000	-0.72158000

H	1.28411300	0.22652300	1.49111500
H	-1.29578900	-0.83304100	-1.42445100
H	-2.55237200	0.56092700	0.31647900
H	1.29653100	-0.83182200	-1.42451000
H	2.08115600	-1.68537300	-0.03029100
H	1.19856000	2.23568600	-0.72152400
H	-2.07956200	-1.68715300	-0.03013900
H	2.55180000	0.56297900	0.31673000
H	0.00091600	-1.95013500	1.11907900

TS-b

Sum of electronic and thermal Free Energies= -272.870026 Hartrees

C	-0.25659900	-1.19902300	-0.18240800
C	0.41421100	-0.17593400	0.68074800
C	1.73118400	0.35303400	0.52544200
C	-1.74702900	-0.86038500	-0.06126300
C	2.55486500	-0.08596200	-0.44483900
C	-1.79305200	0.64001900	0.08028200
C	-0.88036100	1.44999300	-0.49712800
H	0.09145700	-1.15479800	-1.21318200
H	-0.02596500	-0.04466300	1.66579600
H	2.23783400	-0.79063100	-1.20528700
H	-2.16330100	-1.31176000	0.84039700
H	-0.01182800	-2.19336100	0.20616500
H	-0.23112200	1.12118500	-1.29901400
H	-0.85701800	2.50749100	-0.26196000
H	2.08460500	1.04889300	1.27656600
H	-2.33861400	-1.21667300	-0.90653300
H	3.58917300	0.23474200	-0.47765600
H	-2.51452700	1.06912400	0.76970800

Prod-2

Sum of electronic and thermal Free Energies= -272.897884 Hartrees

C	-0.25384400	-1.12527100	0.04516300
C	0.31047000	0.22526300	0.51006200
C	1.74823000	0.50995200	0.18691000
C	-1.76762200	-0.87464700	0.01165100
C	2.60800700	-0.36613700	-0.31687400
C	-1.92349800	0.53202200	-0.25146200
C	-0.67162800	1.23073900	-0.13336700
H	0.08558100	-1.35275100	-0.96878600

H	0.17523900	0.31302500	1.59530700
H	2.32848700	-1.38931100	-0.54702400
H	-2.17559200	-0.88037100	1.05522600
H	0.01671000	-1.95353100	0.69603000
H	-0.43763400	1.31688400	-1.22600700
H	-0.72195200	2.25742200	0.22884600
H	2.08263400	1.51926600	0.41697400
H	-2.42448600	-1.54049900	-0.54747300
H	3.63768300	-0.08860400	-0.50997100
H	-2.86735800	1.00693800	-0.50561500

[ωB97X-D/6-311G(d)] level of theory

Rc

Sum of electronic and thermal Free Energies= -272.847446 Hartrees

C	-0.08784600	-1.05023800	-0.33931400
C	0.68215300	-0.34634700	0.69080800
C	1.95114300	0.25628400	0.58540100
C	-1.59222000	-0.99184700	-0.05686300
C	2.65480700	0.27232300	-0.57498600
C	-2.11274100	0.41218800	0.03635600
C	-1.42417500	1.52600000	-0.20362400
H	0.16296200	-0.73200500	-1.35357200
H	0.24303200	-0.35687400	1.68859200
H	2.27049900	-0.14575800	-1.49993000
H	-1.80080000	-1.51401300	0.88382400
H	0.24070800	-2.10311400	-0.26018300
H	-0.40840700	1.53415300	-0.58970200
H	-1.87700900	2.50154300	-0.07127500
H	2.37989400	0.69193000	1.48096600
H	-2.13325500	-1.54816200	-0.82764400
H	3.64910000	0.70496600	-0.61646600
H	-3.15345500	0.49715300	0.33871900

TS-a

Sum of electronic and thermal Free Energies= -272.844743 Hartrees

C	-0.09553700	-1.16405900	-0.39667400
C	0.83778600	-0.71818400	0.62199900
C	2.00700400	0.04821300	0.47182300
C	-1.59233500	-0.91581700	-0.05044200
C	2.31646800	0.67712000	-0.69246600

C	-1.99656500	0.52920700	-0.19412500
C	-1.35617500	1.56560200	0.33019300
H	0.13984100	-0.82184900	-1.40363900
H	0.61828300	-1.06354200	1.63327000
H	1.68874300	0.62304200	-1.57541100
H	-1.80239000	-1.28152500	0.95968800
H	0.03656400	-2.26317500	-0.38158700
H	-0.44243500	1.46624400	0.91493500
H	-1.73584500	2.57581200	0.22920500
H	2.64853200	0.17388200	1.33716900
H	-2.17593000	-1.53970100	-0.72779700
H	3.20850100	1.29055100	-0.76940800
H	-2.90773500	0.70777200	-0.75827600

Prod-1

Sum of electronic and thermal Free Energies= -272.870251 Hartrees

C	-1.49855500	0.38344600	0.41851300
C	-0.67120700	1.46209700	-0.17831000
C	0.66629600	1.46416200	-0.17821000
C	-1.27000400	-1.04833400	-0.35101900
C	1.49688200	0.38815600	0.41886200
C	0.00260800	-1.45146900	0.15929000
C	1.27371500	-1.04442500	-0.35135300
H	-1.32506300	0.23909800	1.48638500
H	-1.19762400	2.25172800	-0.70431700
H	1.32330400	0.24300500	1.48660800
H	-1.30240800	-0.85857400	-1.42139100
H	-2.56359000	0.56572200	0.28209300
H	1.30546300	-0.85415600	-1.42164100
H	2.08708700	-1.69036200	-0.02151800
H	1.19042000	2.25536700	-0.70414700
H	-2.08100900	-1.69723900	-0.02115500
H	2.56141700	0.57381500	0.28304500
H	0.00358700	-1.95021000	1.12939700

TS-b

Sum of electronic and thermal Free Energies= -272.841334 Hartrees

C	-0.29462700	-1.21425900	-0.14289300
C	0.38190700	-0.14045300	0.66553700
C	1.72331700	0.34507400	0.50871600
C	-1.78071400	-0.83059600	-0.07373000

C	2.55762400	-0.13077800	-0.43081900
C	-1.75702100	0.66743700	0.08232900
C	-0.81249900	1.43358400	-0.51314400
H	0.07215200	-1.23961100	-1.16949200
H	-0.03264200	0.00256100	1.66079100
H	2.25009300	-0.85076200	-1.18213100
H	-2.25753700	-1.27857400	0.79988000
H	-0.07759900	-2.19068700	0.30251100
H	-0.23069000	1.08481900	-1.35777700
H	-0.72274700	2.48748600	-0.27410600
H	2.08188900	1.05492200	1.24635600
H	-2.35461400	-1.14959700	-0.94700500
H	3.59937200	0.16933700	-0.45001100
H	-2.43560400	1.13004700	0.79500500

Prod-2

Sum of electronic and thermal Free Energies= -272.861778 Hartrees

C	-0.26223200	-1.12821300	0.05727000
C	0.31441800	0.22124700	0.51604500
C	1.75268000	0.50413500	0.18789100
C	-1.77611400	-0.86904100	0.00255600
C	2.61105300	-0.36457100	-0.32715400
C	-1.92220300	0.54085600	-0.25496300
C	-0.67016200	1.23066900	-0.12833300
H	0.08849800	-1.37750000	-0.94854000
H	0.18323200	0.31418200	1.60297800
H	2.34593900	-1.38993500	-0.56656900
H	-2.20549500	-0.89862900	1.03769100
H	-0.00363500	-1.95300000	0.71857400
H	-0.41979800	1.31419800	-1.22074500
H	-0.71308500	2.26536400	0.21921100
H	2.09332800	1.50736600	0.43544200
H	-2.42825700	-1.53112700	-0.57204000
H	3.64038400	-0.08266100	-0.51479800
H	-2.86575800	1.02126500	-0.51107200

[CCSD(T)-F12a/AVDZ] level of theory

Rc

CCSD(T)-F12A/aug-cc-pVDZ energy= -272.566087241980 Hartrees

CCSD(T)-F12A	RHF-SCF
-272.56608724	-271.19227112

TS-a

CCSD(T)-F12A/aug-cc-pVDZ energy= -272.563007622833 Hartrees

CCSD(T)-F12A	RHF-SCF
-272.56300762	-271.18842617

Prod-1

CCSD(T)-F12A/aug-cc-pVDZ energy= -272.593670488936 Hartrees

CCSD(T)-F12A	RHF-SCF
-272.59367049	-271.20439960

TS-b

CCSD(T)-F12A/aug-cc-pVDZ energy= -272.564859638283 Hartrees

CCSD(T)-F12A	RHF-SCF
-272.56485964	-271.18219563

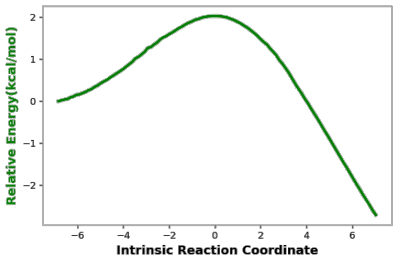
Prod-2

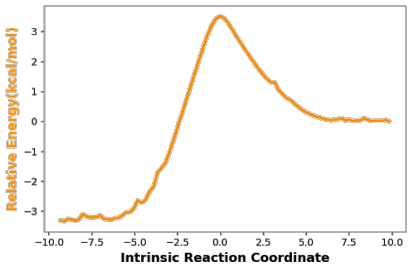
CCSD(T)-F12A/aug-cc-pVDZ energy= -272.580537149087 Hartrees

CCSD(T)-F12A	RHF-SCF
-272.58053715	-271.20177873

Intrinsic Reaction Coordinates (IRCs)

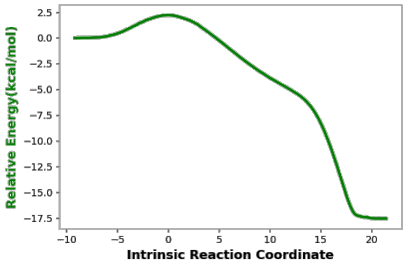
[B3LYP-D3/6-311+G(d,p)] level of theory

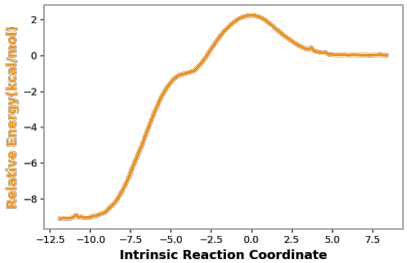




TS-a TS-b

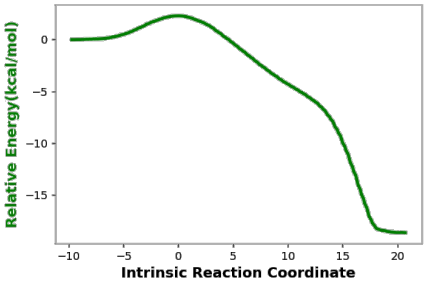
[M06-2X/6-311+G(d,p)] level of theory

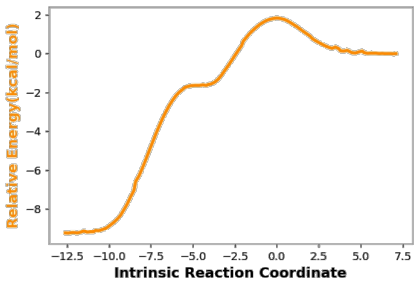




TS-a TS-b

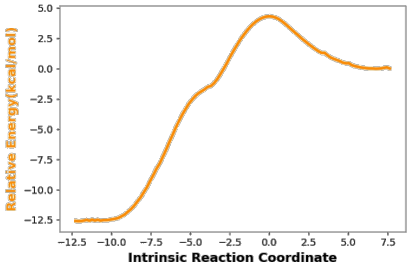
[M06-2X/6-311G(d)] level of theory





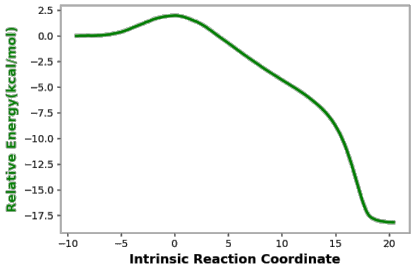
TS-a TS-b

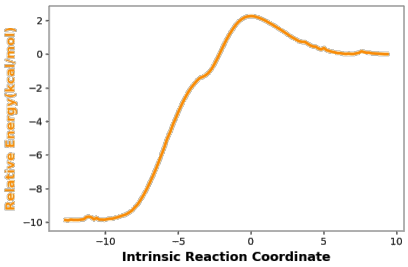
[PCM(DMSO)-M06-2X/6-311G(d)] level of theory



TS-a **TS-b**

[ωB97X-D/6-311G(d)] level of theory





TS-a **TS-b**

PES

Projections of trajectories onto PES

Projections of trajectories onto the PCM(DMSO)-M06-2X/6-311G(d) PES

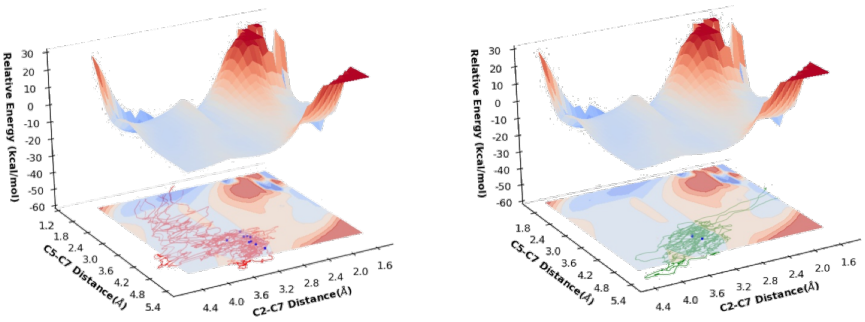
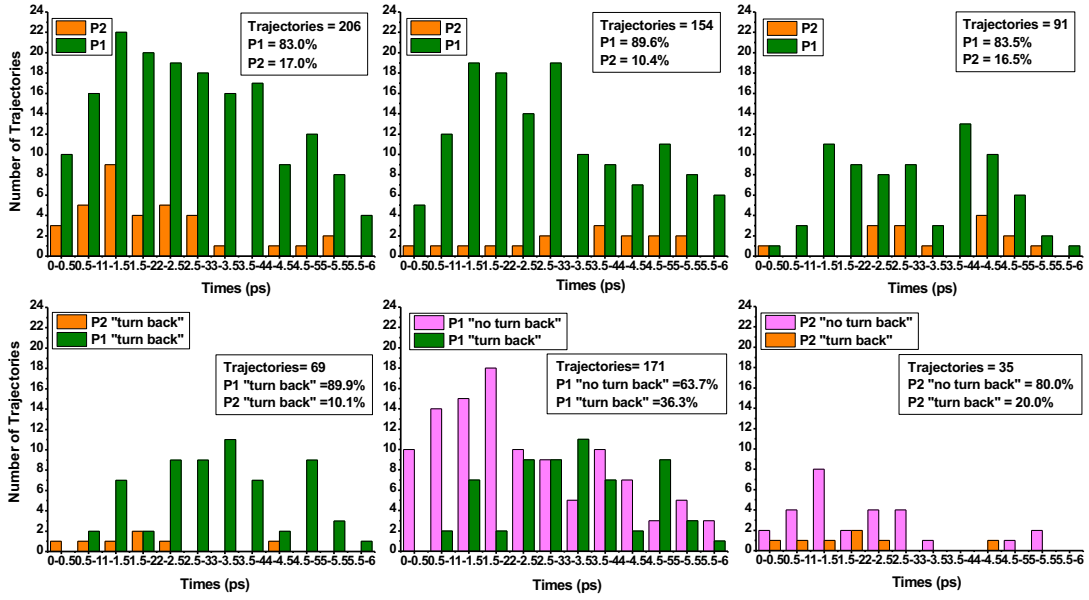


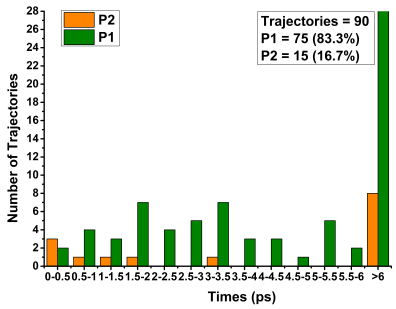
Figure. S1. Projections of trajectories onto the potential energy surface at PCM(DMSO)-M06-2X/6-311G(d) level of theory. The left and right plots demonstrate (4+3) and (2+3) addition trajectories, respectively.

Dynamic calculations

Timing of reactions



(a/quasi-classical)



(b/classical)

Figure S2. (a) Histograms that bin (top) uphill trajectories (bin widths of 0.5 ps) based on the timing of formation for **Prod-1** and **Prod-2** calculated at three different levels of theory. (left to right: M06-2X/6-311G(d), ωB97X-D/6-311G(d) and PCM(DMSO)-M06-2X/6-311G(d)). Green bins correspond to **Prod-1** (P1) formation (i.e., when the C5−C7 distance drops below 1.7 Å) while yellow bins correspond to **Prod-2** (P2) formation (i.e., when the C2−C7 distance drops below 1.6 Å). (2) Histograms that bin (bottom) uphill trajectories based on the timing of product-forming "turn back" trajectories discussed at M06-2X/6-311G(d) level of theory. Green bins correspond to **Prod-1**-forming "turn back" trajectories and yellow bins correspond to **Prod-2**-forming "turn back" trajectories. Pink bins correspond to "no turn back" trajectories. (b) Histograms that bin classical uphill trajectories (bin widths of 0.5 ps) based on the timing of formation for **Prod-1** and **Prod-2** calculated at M06-2X/6-311G(d) level of theory.

Results of "turn back" trajectories in uphill dynamics simulations

Table. S1 Results of "turn back" trajectories in uphill dynamics simulations in M06-2X/6-311G(d) level of theory.

	Total	Turn back toward Prod-1	Turn back toward Prod-2
Turn back	69	62 (89.9%)	7 (10.1%)
Prod-1	171	62 (36.3%)	

Prod-2	35	7 (20.0%)

Molecular Dynamics Trajectory Configuration Files

Downhill dynamics (used for TS-a and TS-b)

method m062x/6-311G(d)
method2 restricted
charge 1
multiplicity 1
processors 16
memory 60GB
killcheck 1
diagnostics 0
title my dynamic test TS
initialdis 2
timestep 1E-15
scaling 1.0
temperature 298.15
methodfile 0
numimag 1
searchdir positive
classical 0
keepevery 1
highlevel 999
boxon 0
boxsize 7.5
etolerance 1
damping 1
reversetraj true

Uphill dynamic in M06-2X/6-311G(d)) level of theory

method m062x/6-311G(d)
method2 restricted
charge 1
multiplicity 1
processors 16

memory 60GB
killcheck 1
diagnostics 0
title my dynamic test TS
initialdis 2
timestep 1E-15
scaling 1.0
temperature 298.15
methodfile 0
numimag 0
searchdir positive
classical 0
keepevery 1
highlevel 999
boxon 0
boxsize 7.5
etolerance 1
damping 1

Uphill dynamic in ωB97X-D/6-311G(d)) level of theory

method wb97xd/6-311G(d)
method2 restricted
charge 1
multiplicity 1
processors 16
memory 60GB
killcheck 1
diagnostics 0
title my dynamic test TS
initialdis 2
timestep 1E-15
scaling 1.0
temperature 298.15
methodfile 0
numimag 0
searchdir positive
classical 0
keepevery 1
highlevel 999

boxon 0
boxsize 7.5
etolerance 1
damping 1

Uphill dynamic in PCM(DMSO)-M06-2X/6-311G(d)) level of theory

method m062x/6-311G(d)
method2 restricted
charge 1
multiplicity 1
processors 16
memory 60GB
killcheck 1
diagnostics 0
title my dynamic test TS
initialdis 2
timestep 1E-15
scaling 1.0
temperature 298.15
method4 scrf = (pcm, solvent=DMSO)
methodfile 0
numimag 0
searchdir positive
classical 0
keepevery 1
highlevel 999
boxon 0
boxsize 7.5
etolerance 1
damping 1

VTS calculations

PATH-a

c7h11tr1.dat
*General

TITLE

```
C3H5 + C4H6    -> C7H11
 END

 ATOMS
    1       C
    2       H
    3       C
    4       C
    5       H
    6       H
    7       H
    8       H
    9       C
    10      C
    11      H
    12      H
    13      H
    14      C
    15      C
    16      H
    17      H
    18      H
 END

 NOSUPERMOL

 INPUNIT AU

 MDMOVIE ON

 *OPTIMIZATION

    OPTMIN    OHOOK
    OPTTS     OHOOK

 *SECOND
    HESSCAL HHOOK

 *REACT1
 STATUS 0
 INITGEO    HOOKS
```

```
    SPECIES NONLINRP
    GEOM
      1
      2
      3
      4
      5
      6
      7
      8
      9
      10
      11
      12
      13
      14
      15
      16
      17
      18
    END
# end of react1 section

    *PROD1
    STATUS 0
    INITGEO    HOOKS
    SPECIES NONLINRP
    GEOM
      1
      2
      3
      4
      5
      6
      7
      8
      9
      10
      11
      12
      13
```

```
    14
    15
    16
    17
    18
  END
# end of prod1 section

  *START
  STATUS 0
  INITGEO   HOOKS
  SPECIES NONLINRP
  GEOM
    1
    2
    3
    4
    5
    6
    7
    8
    9
    10
    11
    12
    13
    14
    15
    16
    17
    18
  END
# end of start section

  *PATH
  SCALEMASS   1.00
  INTMU 3
  SSTEP     0.01
  INH       9

  SRANGE
```

```
   SLP      2.0
   SLM    -2.5
END

RPM pagem

RODS ON

SIGN REACTANT

IDIRECT 1

COORD CURV3

INTDEF
2-1 3-1 4-3 5-1 6-4 7-4 8-3 9-1 10-9
11-9 12-10 13-10 14-9 15-14 16-15 17-14 18-15
3-1-2 4-3-1 5-1-3 6-4-3 7-4-3 8-3-1 9-1-3
10-9-1 11-9-1 12-10-9 13-10-9
14-9-1 15-14-9 16-15-14 17-14-9 18-15-14
4-3-1-2 5-1-3-4 6-4-3-1 7-4-3-1 8-3-1-4
9-1-3-4 10-9-1-3 11-9-1-3 12-10-9-1 13-10-9-1
14-9-1-3 15-14-9-1 16-15-14-9 17-14-9-1 18-15-14-9
END

PRPATH
COORD       1 11
INTERVAL 1
XMOL
END

*TUNNEL

  QUAD
    NQE 40
    NQTH 40
  END

    SCT

  *RATE
```

```
      FORWARDK

      SIGMAF 1
      CVT
      CUS 2
      PRDELG ON
      #PRGIGT ON
      #ICVT ON
      # MUVT ON
      # MUVTOPT
      # prenergy 4
      # niter 30
      # END

      TEMP
         298.15
      END



c7h11tr1.70
*GRGENERAL

   GRRESTART
   RSTTOL 0.00000001

   *GRREACT1

    CHARGE 1
    MULTIPLICITY 1

   *GRPROD1

    CHARGE 1
    MULTIPLICITY 1

   *GRSTART

    CHARGE 1
    MULTIPLICITY 1
```

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*GRCOMMON

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   END

   GRFIRST
   #p m062x/6-311G(d) FORCE UNITS=AU FCHK NOSYMM SCF=(tight)
   END

   GRSEC
   #p m062x/6-311G(d) FREQ=NORAMAN UNITS=AU FCHK NOSYMM SCF=(tight)
   END

   GRLINK0
        %chk=g09.chk
        %nproc=16
        %mem=4gb
    END


c7h11tr1.71
%chk=g09.chk
%mem=1000MB
%nproc=16
# opt M062x/6-311G(d) FCHK NOSYMM SCF=(tight)

rc

1 1
 C                  -1.59343800    -0.99476500    -0.04411000
 H                  -1.79255700    -1.50538800     0.90422900
 C                  -2.10538300     0.41441600     0.03624100
 C                  -1.40488500     1.51618800    -0.22871900
 H                  -2.13945800    -1.55732200    -0.80583100
 H                  -0.39385300     1.50280400    -0.62501700
 H                  -1.84493900     2.49869900    -0.10906400
 H                  -3.14140000     0.51453100     0.34848500
 C                   0.66855700    -0.32320800     0.69282600
 C                  -0.09078100    -1.04698800    -0.33390700
```

H	0.21974900	-0.31710500	1.68699800
H	0.15474400	-0.72719100	-1.34841100
H	0.24894200	-2.09565800	-0.24771700
C	1.94000500	0.27804900	0.58479300
C	2.65320200	0.24017300	-0.56956400
H	2.26860200	-0.21176900	-1.47829400
H	2.36236800	0.73920300	1.46991000
H	3.65413500	0.65600600	-0.62064200

c7h11tr1.73
%chk=g09.chk
%mem=1000MB
%nproc=16
opt M062x/6-311G(d) FCHK NOSYMM SCF=(tight)

prod1

1 1

C	1.27273300	-1.04214600	-0.35736800
H	1.30365200	-0.83586300	-1.42399600
C	0.00192200	-1.44982100	0.15228700
C	-1.27006500	-1.04520300	-0.35688800
H	2.08859200	-1.68467400	-0.02931000
H	-1.30179800	-0.83952000	-1.42363400
H	-2.08415900	-1.68964000	-0.02819300
H	0.00279200	-1.95024500	1.12203400
C	0.66734500	1.46064300	-0.18630500
C	1.48349400	0.38766400	0.43437900
H	1.19741100	2.23661400	-0.72812600
H	1.27832000	0.23554400	1.49488800
H	2.55143200	0.56849700	0.32513500
C	-0.67074200	1.45924100	-0.18645500
C	-1.48481800	0.38449800	0.43390800
H	-1.28011400	0.23309100	1.49460000
H	-1.20228200	2.23417200	-0.72832000
H	-2.55306600	0.56276800	0.32357900

c7h11tr1.75
%chk=g09.chk

%mem=1000MB
%nproc=16
M062x/6-311G(d) FCHK NOSYMM opt=(calcfc,ts,noeigen) SCF=(tight)

ts1

1 1

C	-1.60281200	-0.91093500	-0.05435700
H	-1.81404100	-1.27919900	0.95396700
C	-1.99388200	0.53881600	-0.19150000
C	-1.32725800	1.56139200	0.32766100
H	-2.18494600	-1.52863100	-0.73733400
H	-0.40749900	1.44145300	0.89793300
H	-1.69098200	2.57810400	0.24038600
H	-2.91018600	0.73241800	-0.74141200
C	0.82349200	-0.70903100	0.62719400
C	-0.10491100	-1.15430500	-0.39602300
H	0.59187300	-1.04260900	1.64017400
H	0.13684300	-0.81458900	-1.40140900
H	0.03011400	-2.25410100	-0.37313100
C	2.00680000	0.03867700	0.47334400
C	2.31574400	0.65841800	-0.69637400
H	1.67843400	0.60934100	-1.57254700
H	2.65279900	0.15901900	1.33557200
H	3.21455200	1.26060000	-0.78187700

PATH-b

c7h11tr1.dat
*General

TITLE
C3H5 + C4H6 -> C7H11
END

ATOMS
1 C
2 H
3 C
4 C
5 H

```
   6      H
   7      H
   8      H
   9      C
   10     C
   11     H
   12     H
   13     H
   14     C
   15     C
   16     H
   17     H
   18     H
END

NOSUPERMOL

INPUNIT AU

MDMOVIE ON

*OPTIMIZATION

   OPTMIN    OHOOK
   OPTTS     OHOOK

*SECOND
   HESSCAL HHOOK

*REACT1
  STATUS 0
INITGEO    HOOKS
SPECIES NONLINRP

GEOM
  1
  2
  3
  4
  5
  6
```

```
    7
    8
    9
    10
    11
    12
    13
    14
    15
    16
    17
    18
   END
# end of react1 section

   *PROD1
   STATUS 0
   INITGEO    HOOKS
   SPECIES NONLINRP
   GEOM
    1
    2
    3
    4
    5
    6
    7
    8
    9
    10
    11
    12
    13
    14
    15
    16
    17
    18
   END
# end of prod1 section
```

```
   *START
   STATUS 0
   INITGEO    HOOKS
   SPECIES NONLINRP
   GEOM
     1
     2
     3
     4
     5
     6
     7
     8
     9
     10
     11
     12
     13
     14
     15
     16
     17
     18
   END
# end of start section

   *PATH
   SCALEMASS    1.00
   INTMU 3
   SSTEP      0.01
   INH         9

   SRANGE
      SLP      1.6
      SLM    -2.0
   END

   RPM pagem

   RODS ON
```

```
SIGN REACTANT

IDIRECT 1

COORD CURV3

INTDEF
2-1 3-1 4-3 5-1 6-4 7-4 8-3 9-1 10-9
11-9 12-10 13-10 14-9 15-14 16-15 17-14 18-15
3-1-2 4-3-1 5-1-3 6-4-3 7-4-3 8-3-1 9-1-3
10-9-1 11-9-1 12-10-9 13-10-9
14-9-1 15-14-9 16-15-14 17-14-9 18-15-14
4-3-1-2 5-1-3-4 6-4-3-1 7-4-3-1 8-3-1-4
9-1-3-4 10-9-1-3 11-9-1-3 12-10-9-1 13-10-9-1
14-9-1-3 15-14-9-1 16-15-14-9 17-14-9-1 18-15-14-9
END

PRPATH
COORD       1 11
INTERVAL 1
XMOL
END

*TUNNEL

 QUAD
  NQE 40
  NQTH 40
 END

  SCT

 *RATE

  FORWARDK

  SIGMAF 1
  CVT
  CUS 2
  PRDELG ON
  #PRGIGT ON
```

```
      #ICVT ON
      # MUVT ON
      # MUVTOPT
      # prenergy 4
      # niter 30
      # END

      TEMP
         298.15
      END



c7h11tr1.70
*GRGENERAL

   GRRESTART
   RSTTOL 0.00000001

   *GRSTART

    CHARGE 1
    MULTIPLICITY 1

   *GRREACT1

    CHARGE 1
    MULTIPLICITY 1

   *GRPROD1

    CHARGE 1
    MULTIPLICITY 1

*GRCOMMON

   GRENER
   #p m062x/6-311G(d) UNITS=AU FCHK NOSYMM SCF=(tight)
   END

   GRFIRST
```

```
  #p m062x/6-311G(d) FORCE UNITS=AU FCHK NOSYMM SCF=(tight)
  END

  GRSEC
  #p m062x/6-311G(d) FREQ=NORAMAN UNITS=AU FCHK NOSYMM SCF=(tight)
  END

  GRLINK0
       %chk=g09.chk
       %nproc=16
       %mem=4gb
   END


c7h11tr1.71
%chk=g09.chk
%mem=1000MB
%nproc=16
# opt M062x/6-311G(d) FCHK NOSYMM SCF=(tight)

rc

1 1
 C                  -1.59343800    -0.99476500    -0.04411000
 H                  -1.79255700    -1.50538800     0.90422900
 C                  -2.10538300     0.41441600     0.03624100
 C                  -1.40488500     1.51618800    -0.22871900
 H                  -2.13945800    -1.55732200    -0.80583100
 H                  -0.39385300     1.50280400    -0.62501700
 H                  -1.84493900     2.49869900    -0.10906400
 H                  -3.14140000     0.51453100     0.34848500
 C                   0.66855700    -0.32320800     0.69282600
 C                  -0.09078100    -1.04698800    -0.33390700
 H                   0.21974900    -0.31710500     1.68699800
 H                   0.15474400    -0.72719100    -1.34841100
 H                   0.24894200    -2.09565800    -0.24771700
 C                   1.94000500     0.27804900     0.58479300
 C                   2.65320200     0.24017300    -0.56956400
 H                   2.26860200    -0.21176900    -1.47829400
 H                   2.36236800     0.73920300     1.46991000
 H                   3.65413500     0.65600600    -0.62064200
```

c7h11tr1.73
%chk=g09.chk
%mem=1000MB
%nproc=16
opt M062x/6-311G(d) FCHK NOSYMM SCF=(tight)

prod2

1 1

C	-1.77293200	-0.86921800	0.01171100
H	-2.17309600	-0.86633900	1.06089300
C	-1.92115700	0.53959300	-0.25807900
C	-0.66632700	1.22940900	-0.13830600
H	-2.43741000	-1.54145000	-0.53402900
H	-0.70023900	2.27168200	0.18327800
H	-0.41301600	1.27136000	-1.23396000
H	-2.86543600	1.01757100	-0.51706400
C	0.31209600	0.22259100	0.52156600
C	-0.25703800	-1.12441000	0.05151300
H	0.16784800	0.31421100	1.60659300
H	0.08692400	-1.35353800	-0.96114300
H	0.00940700	-1.95658600	0.69959800
C	1.75256900	0.50398400	0.20111300
C	2.59886200	-0.36546600	-0.33325800
H	2.31665000	-1.38137000	-0.59052800
H	2.10167700	1.49840500	0.46880000
H	3.63025500	-0.09283600	-0.52000400

c7h11tr1.75
%chk=g09.chk
%mem=1000MB
%nproc=16
M062x/6-311G(d) FCHK NOSYMM opt=(calcfc,ts,noeigen) SCF=(tight)

ts2

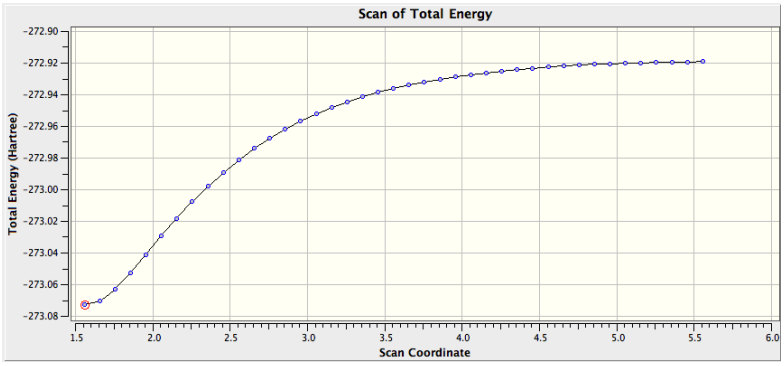
1 1

C	-1.73308400	-0.88564800	-0.04295900

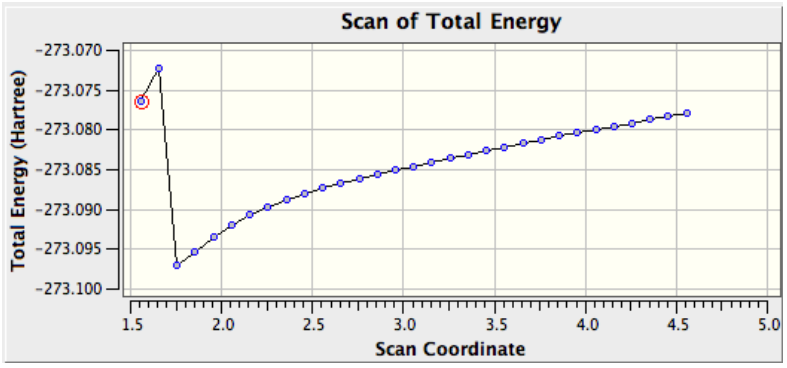
H	-2.11400200	-1.33392800	0.87764700
C	-1.83942400	0.61247500	0.06699600
C	-0.93042000	1.44907700	-0.47951400
H	-2.33883700	-1.28540700	-0.85955300
H	-0.24379900	1.13905500	-1.25773800
H	-0.96428900	2.51249300	-0.27134500
H	-2.62116300	1.02624300	0.69910400
C	0.43500800	-0.16404600	0.67406800
C	-0.23697300	-1.18355400	-0.19268600
H	-0.00751300	-0.03463400	1.65944700
H	0.09389000	-1.11636900	-1.22922000
H	0.03196700	-2.18279900	0.17047500
C	1.75114300	0.36607800	0.52253700
C	2.58203700	-0.07048800	-0.44556300
H	2.27109000	-0.77821700	-1.20718700
H	2.10547000	1.06018700	1.27623500
H	3.61746800	0.25001000	-0.47514500

Search for addition TSS

Both rigid…



and relaxed scans…



in which the length of the putative forming C–C was varied were carried out in pursuit of a TSS for addition of the two separate reactants (B3LYP/6-311G(d)). As shown in the scan plots, this addition appears to be barrierless at the level of theory used.