

Supplementary Material

A Computational and Conceptual DFT Study on the Mechanism of Hydrogen Activation by Novel Frustrated Lewis Pairs

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ω B97X-D/6-311G(d,p) gas phase total energies (in au), unique imaginary frequency (in cm^{-1}), and cartesian coordinates of the structures involved in the activation of molecular hydrogen by the FLP models and the corresponding for the hydrogenation of acetylene.....S2

Table S1. ω B97X-D/6-311G(d,p) total energies (E, in au), enthalpies (H, in au), entropies (S, in cal/mol K) and Gibbs free energies (G, in au), computed at 120°C and 1 atm in toluene, of the stationary points involved in the activation of molecular hydrogen **1** by the three FLP models **2**, **3** and **4** and for the hydrogenation of acetylene **8** by the three FLP models **2**, **3** and **4** to yield ethylene **9**.....S18

Table S2. ω B97X-D/6-311G(d,p) total energies (E, in au) and enthalpies (H, in au), entropies (S, in cal/mol K) and Gibbs free energies (G, in au), in gas phase and computed at 120°C and 1 atm in toluene, for open-chain (O) and four-membered ring (R) forms of **2**, **3** and **4**.....S19

1, H₂, Total Energy = -1.176071 a.u.

H	0.00000000	0.00000000	0.37258000
H	0.00000000	0.00000000	-0.37258000

2, Total Energy = -1535.576750 a.u.

C	-2.60511800	-0.06481200	-0.32574400
C	-3.48241000	1.01743700	-0.15615600
C	-4.85001600	0.75587200	-0.12186100
C	-5.33945800	-0.53366500	-0.25640600
C	-4.45714800	-1.58341600	-0.46289200
C	-3.08391700	-1.36919200	-0.51930900
H	-5.53890600	1.58481600	0.00325600
H	-6.40724900	-0.71654400	-0.22449100
H	-4.83652700	-2.59061000	-0.60023200
N	-1.20865900	0.14150400	-0.43743400
C	-0.50870800	0.51552300	0.53356800
N	0.92013200	0.70281500	0.22699500
B	1.78566300	-0.38487500	0.09066700
C	-0.88473400	0.78882200	1.95495600
H	-1.93463200	0.55355200	2.12462900
H	-0.26346600	0.18214500	2.61546900
H	-0.70602900	1.83962500	2.19648400
C	-2.98294000	2.43612000	-0.06879100
H	-2.54896800	2.66195300	0.90965700
H	-2.21328800	2.63277700	-0.81767100
H	-3.80315300	3.13671500	-0.23091600
C	-2.13688900	-2.50617600	-0.78569800
H	-1.34228900	-2.19801500	-1.46887700
H	-1.65443300	-2.85017700	0.13121900
H	-2.66791200	-3.35195700	-1.22544000
C	1.31099300	2.07148800	0.01055800
F	1.93215300	2.24022100	-1.14669800
F	2.11643800	2.49828000	0.98477800
F	0.23506700	2.86262800	0.01416600
C	1.38576900	-1.85506600	0.62993900
C	3.25584400	-0.28536300	-0.58788100
F	3.97930400	-1.40389900	-0.42772000
F	4.00195700	0.72582500	-0.10724600
F	3.12247600	-0.10267900	-1.91639300
F	1.30652300	-2.74876100	-0.36812700
F	0.22465600	-1.92760500	1.31664800
F	2.33482800	-2.27685000	1.48847600

3, Total Energy = -2863.261202 a.u.

C	-3.34568000	-1.48751200	0.14071100
C	-3.46153800	-2.71703800	0.81560800
C	-4.66886300	-3.40893400	0.75106400
C	-5.75294500	-2.90096100	0.05976000
C	-5.64025000	-1.66284900	-0.55087800
C	-4.45715500	-0.92718700	-0.51799500
H	-4.75621000	-4.36425200	1.25742900
H	-6.68539000	-3.45146500	0.01358700
H	-6.49760200	-1.23973600	-1.06418300
C	-4.47873900	0.45907400	-1.13984600
C	-3.55270500	0.62226800	-2.34762300
C	-4.26215400	1.53404800	-0.07192900
H	-5.49700200	0.59402300	-1.51908900
H	-3.78035400	-0.12529600	-3.11231500
H	-3.68216000	1.61219500	-2.79455500
H	-2.50240300	0.52201500	-2.08125500
H	-5.01362900	1.44430800	0.71605800
H	-3.27983700	1.43140200	0.39068900
H	-4.34716200	2.53186300	-0.51083500
C	-2.31865000	-3.30430600	1.62781200
C	-1.78760700	-4.59729300	0.99777600
C	-2.72804800	-3.53610400	3.08696800
H	-1.50708400	-2.57891300	1.64192200
H	-1.49011700	-4.44132300	-0.04243700
H	-0.91833300	-4.96570700	1.54819400
H	-2.55192300	-5.38044400	1.00627300
H	-3.10390300	-2.61479900	3.53761700
H	-3.50926800	-4.29726000	3.17229900
H	-1.86745600	-3.87650400	3.66954600
N	-2.08648700	-0.82203100	0.22135000
C	-1.17196700	-1.12599500	-0.59289000
N	0.14257000	-0.57253500	-0.38017700
C	1.22807400	-1.43342500	-0.71410600
C	2.01920500	-1.16262400	-1.82563000
C	1.54235800	-2.54628500	0.05709300
C	3.10126400	-1.96080600	-2.15379800
C	2.61228200	-3.36502200	-0.26647700
C	3.39494200	-3.06797900	-1.37178500
B	0.44591600	0.72763900	0.08212000
C	-1.28598400	-2.03140100	-1.78936700
H	-0.74338400	-2.96693600	-1.63837600
H	-2.33131300	-2.26729200	-1.97682600
H	-0.86191100	-1.53283300	-2.66457400
F	0.81284900	-2.84399700	1.12210700
F	2.89334600	-4.42358900	0.47980700
F	3.84951500	-1.67909400	-3.21094800
F	1.74563100	-0.10982600	-2.58641700

F	4.42245800	-3.84170800	-1.68099800
C	1.94105700	1.06599000	0.48090500
C	2.65353900	2.05969500	-0.17754100
C	2.58726900	0.42986600	1.53231900
C	3.95219300	2.39612500	0.16780000
C	3.88150800	0.74407500	1.91072300
C	4.56525000	1.73418900	1.22086700
C	-0.57969200	1.91652700	0.12218000
C	-0.94715600	2.50646100	1.31952000
C	-1.00665500	2.53009200	-1.04338800
C	-1.72945300	3.64736900	1.37161300
C	-1.78943000	3.67083200	-1.03168600
C	-2.15097000	4.22808400	0.18441300
F	-0.53668800	1.96082600	2.46721600
F	-2.08606900	4.18103100	2.53360800
F	-2.92725500	5.30231500	0.21253100
F	-2.22013900	4.21436800	-2.16507700
F	-0.64900700	2.02225900	-2.22711700
F	1.95287000	-0.52286400	2.21917800
F	2.09515300	2.71141600	-1.19859600
F	4.61076400	3.33903600	-0.49388600
F	5.80448200	2.04556300	1.56684900
F	4.46814000	0.11503100	2.92161800

4, Total Energy = -2459.341635 a.u.

C	3.16684700	1.65993300	0.30634100
C	3.15865500	3.03572400	0.63146500
C	4.37320500	3.70948500	0.70753600
C	5.57448300	3.05935500	0.47727100
C	5.56570800	1.70934000	0.18088300
C	4.37898800	0.98099000	0.09756400
H	4.38341500	4.76457000	0.95018100
H	6.51117600	3.60095000	0.53873800
H	6.50419700	1.19166000	0.01139900
C	4.48660200	-0.49955800	-0.22342200
C	3.99600800	-0.81838200	-1.63886900
C	3.84854800	-1.38422000	0.84947600
H	5.55841400	-0.72376500	-0.21319600
H	4.54208200	-0.22356900	-2.37567900
H	4.15423900	-1.87429800	-1.87438000
H	2.93441500	-0.60488100	-1.76134100
H	4.28761700	-1.17423000	1.82770800
H	2.77532700	-1.21248400	0.92405100
H	4.02305800	-2.43962400	0.62189500
C	1.85774900	3.75478900	0.96221400
C	1.93670500	5.27790200	0.85726400
C	1.36717100	3.33788700	2.35601000
H	1.10440700	3.44204600	0.23504000
H	2.33437100	5.59824300	-0.10911500

H	0.93672600	5.70508000	0.96987000
H	2.56118900	5.70899600	1.64502000
H	1.21171500	2.25837800	2.41782400
H	2.10578100	3.61756700	3.11245900
H	0.42786600	3.84305100	2.60450500
N	1.91261000	0.98610500	0.30617300
C	1.12392400	1.10675000	-0.67270100
N	-0.21965000	0.60162300	-0.52634500
C	-1.23405200	1.59508100	-0.76263600
C	-1.99571800	1.54760400	-1.92499800
C	-1.45165600	2.58901700	0.18385800
C	-2.97663600	2.50002400	-2.14654700
C	-2.42814900	3.54669500	-0.03373000
C	-3.19089800	3.50592700	-1.20209800
B	-0.59970000	-0.68174300	-0.11671200
C	1.40182500	1.77674800	-1.98907200
H	0.83980000	2.70985200	-2.07978800
H	2.46338000	1.99728200	-2.08684900
H	1.08729000	1.11626400	-2.80022300
C	-2.12246500	-0.93974500	0.23384900
C	-2.92242300	-1.70990000	-0.59346500
C	-2.71308500	-0.42529000	1.37705300
C	-4.25572200	-1.96040100	-0.31767800
C	-4.04207600	-0.65598000	1.69063900
C	-4.81387800	-1.42925900	0.83599100
C	0.37312600	-1.91459600	-0.08935000
C	0.52351400	-2.68847700	1.05171300
C	1.00852200	-2.35975900	-1.23639800
C	1.29321400	-3.83816700	1.07085300
C	1.78457400	-3.50517000	-1.25828600
C	1.92895900	-4.24209000	-0.09368900
F	-0.06915000	-2.30790300	2.18530800
F	1.44584700	-4.54187900	2.18556700
F	2.69427000	-5.32375800	-0.08772700
F	2.40296500	-3.89082800	-2.36899300
F	0.87424100	-1.67276000	-2.37886200
F	-1.99018400	0.32131800	2.21694400
F	-2.40502100	-2.20872500	-1.72374400
F	-4.99996200	-2.69058900	-1.13979200
F	-6.08726600	-1.65840300	1.12011200
F	-4.58098500	-0.15056800	2.79345600
H	-0.87529700	2.58638300	1.09943300
H	-2.61065200	4.31959400	0.70238800
H	-1.81639500	0.75924300	-2.64658600
H	-3.57646300	2.47031500	-3.04753700
C	-4.20179800	4.49708800	-1.43039200
N	-5.01161200	5.29411000	-1.61447900

TS2/H₂ Total Energy = -1536.749127 a.u.

Imaginary frequency : 383.4 cm⁻¹

C	-2.53029100	0.07191800	0.28523500
C	-3.17313300	-0.93603500	1.01743400
C	-4.56008400	-0.89281300	1.12166600
C	-5.28927200	0.12180000	0.51925700
C	-4.63130600	1.11287800	-0.19286400
C	-3.24431000	1.11063600	-0.32092600
H	-5.07048000	-1.66660800	1.68545500
H	-6.36887500	0.14427000	0.61197600
H	-5.19820200	1.91112400	-0.66035600
N	-1.11267400	0.04520000	0.23724800
H	0.25475100	0.46026700	1.55534800
C	-0.49236500	-0.65134400	-0.61807700
N	0.93835200	-0.67557200	-0.46859300
B	1.56907100	0.43649000	0.22359300
C	-1.12147800	-1.41564400	-1.74530100
H	-2.18797400	-1.20037200	-1.76837100
H	-0.66249100	-1.12153000	-2.68935200
H	-0.98334500	-2.49120400	-1.62618300
H	0.92988600	0.53892300	1.92626300
C	-2.37894200	-2.03261800	1.67647100
H	-1.86909800	-2.66485300	0.94302600
H	-1.60679900	-1.62200900	2.33304400
H	-3.02865600	-2.67368300	2.27360100
C	-2.53376500	2.19008900	-1.08783400
H	-1.79636000	2.69581700	-0.46212400
H	-1.99256400	1.78414100	-1.94638500
H	-3.24481500	2.93152300	-1.45485900
C	1.56920500	-1.91670000	-0.76184400
F	2.85867600	-1.89275400	-0.47861100
F	1.46401200	-2.22679400	-2.06312000
F	1.00870700	-2.93000400	-0.07957800
C	1.21545500	1.93457900	-0.32802100
C	2.99626500	0.35396900	1.00500300
F	3.13002900	1.43166000	1.81062800
F	4.05235100	0.35264500	0.18082500
F	3.10005100	-0.72074600	1.81309600
F	0.50126900	2.70884500	0.50444200
F	0.54951000	1.89274200	-1.50388500
F	2.36251100	2.59552400	-0.58833200

TS3/H₂ Total Energy = -2864.428559 a.u.

Imaginary frequency : 426.7cm⁻¹

C	3.14757500	-1.78498000	-0.31836000
C	2.99560300	-3.01558000	-0.98841000
C	4.11533100	-3.82767500	-1.15196400
C	5.35597300	-3.44629900	-0.67211100
C	5.49384100	-2.21755700	-0.04825400
C	4.41112000	-1.35835000	0.12915600
H	4.01241200	-4.77489700	-1.66927100
H	6.21542300	-4.09436200	-0.79945500

H	6.46996600	-1.90251000	0.30622000
C	4.67772300	-0.00022100	0.75703800
C	4.00735900	0.18585200	2.12094300
C	4.36523900	1.14082400	-0.21653200
H	5.75740400	0.03226100	0.93818800
H	4.32124600	-0.59823100	2.81543100
H	4.28560300	1.15052100	2.55445200
H	2.92143100	0.16083300	2.05018800
H	4.93168100	1.02117600	-1.14317400
H	3.30520800	1.16029200	-0.46967600
H	4.63536000	2.10359600	0.22702500
C	1.67810500	-3.42960400	-1.62504000
C	1.31742300	-4.89484600	-1.36599700
C	1.70498900	-3.11959700	-3.12744000
H	0.87725600	-2.82957600	-1.19882100
H	1.35352200	-5.13028700	-0.29894300
H	0.30570400	-5.09880000	-1.72527300
H	1.99356600	-5.58075700	-1.88394300
H	1.91076800	-2.06044500	-3.30283700
H	2.48392500	-3.69971200	-3.63162600
H	0.74303900	-3.36224600	-3.58779200
N	1.99551100	-0.96061700	-0.19071100
H	0.97488300	-0.19718400	-1.42513000
C	1.08565100	-1.24743800	0.66181500
N	-0.11947700	-0.54760300	0.55449200
C	-1.29721700	-1.07678600	1.12784100
C	-2.08874800	-0.28471300	1.95945900
C	-1.77513500	-2.35226200	0.83139700
C	-3.29220100	-0.73760300	2.47392800
C	-2.96141700	-2.83188700	1.36038600
C	-3.72697000	-2.02032300	2.18134200
B	-0.22033800	0.64072900	-0.32969600
C	1.22046800	-2.27983300	1.74396300
H	0.87070100	-3.25282000	1.39220600
H	2.27178200	-2.38097500	2.00970100
H	0.64695800	-1.99499100	2.62656700
F	-1.09182400	-3.15541300	0.02039100
F	-3.37443800	-4.05742600	1.06724200
F	-4.02455200	0.04942900	3.24965700
F	-1.71562800	0.95681900	2.24260700
F	-4.86884300	-2.46642500	2.68023500
H	0.34712800	0.12127600	-1.80401100
C	-1.67402900	0.92540700	-0.92920300
C	-2.37193100	2.10437300	-0.69234400
C	-2.33478800	-0.03074500	-1.69399800
C	-3.65404300	2.32009800	-1.17597900
C	-3.61025100	0.14982100	-2.19641700
C	-4.27342800	1.33863300	-1.93204400
C	0.75621700	1.87087100	-0.07696600
C	1.09922400	2.73427300	-1.10894200
C	1.26824900	2.18446700	1.17458100

C	1.92684600	3.82894400	-0.93565300
C	2.10008100	3.27070200	1.38838800
C	2.43322300	4.09382000	0.32677300
F	0.62685800	2.50683100	-2.34119700
F	2.24189300	4.61739700	-1.95673100
F	3.24721100	5.12306700	0.51411300
F	2.60040000	3.51325500	2.59589700
F	0.98944300	1.42882400	2.24102400
F	-1.72604300	-1.19000000	-1.97509100
F	-1.83567900	3.07982900	0.03991900
F	-4.29181800	3.45515600	-0.91872900
F	-5.49637600	1.53311300	-2.40012600
F	-4.19904900	-0.79323300	-2.92211700

TS4/H₂ Total Energy = -2860.507170 a.u.

Imaginary frequency : 450.6 cm⁻¹

C	3.04052400	-1.78187900	-0.31446100
C	2.89512200	-3.02952000	-0.95344500
C	4.03194500	-3.80783600	-1.15815800
C	5.28020000	-3.37820000	-0.74105400
C	5.40663700	-2.14016600	-0.13174900
C	4.30517100	-1.31509200	0.08464400
H	3.93840000	-4.76608900	-1.65693500
H	6.15400000	-3.99893300	-0.90203800
H	6.38636300	-1.79362400	0.18112200
C	4.53838700	0.04942600	0.71330500
C	3.87780400	0.21165200	2.08637100
C	4.16862900	1.18727700	-0.24426400
H	5.61885400	0.11670400	0.88014900
H	4.20092400	-0.57819400	2.76986100
H	4.15338100	1.17306100	2.52887900
H	2.79070900	0.18018400	2.02110400
H	4.71538600	1.09428700	-1.18565200
H	3.10212100	1.17362100	-0.46939300
H	4.41764800	2.15487700	0.20155600
C	1.55955000	-3.49708200	-1.51553600
C	1.25673000	-4.96648500	-1.20779300
C	1.49824200	-3.21794400	-3.02270100
H	0.76257500	-2.90660900	-1.06172600
H	1.35670100	-5.17958900	-0.13989900
H	0.23618100	-5.21293200	-1.51447600
H	1.92708900	-5.64207600	-1.74585700
H	1.66279200	-2.15720900	-3.22717500
H	2.26851800	-3.78542900	-3.55343200
H	0.52264900	-3.49828700	-3.43013300
N	1.88232900	-0.98135900	-0.15075400
H	0.81189400	-0.23882200	-1.36457500
C	0.99195200	-1.31029600	0.71070800
N	-0.22300000	-0.64182700	0.65324200
C	-1.37280500	-1.22718500	1.26348000

C	-2.04035800	-0.52953600	2.26599800
C	-1.85879700	-2.45831900	0.82910600
C	-3.19282900	-1.05322900	2.82836200
C	-3.00380800	-2.99210900	1.39371900
C	-3.67665700	-2.28847300	2.39487800
B	-0.40252900	0.53827700	-0.21236700
C	1.16860400	-2.37198900	1.76139600
H	0.77986800	-3.33362000	1.41797100
H	2.23000800	-2.49634400	1.97119900
H	0.64008900	-2.09984400	2.67526100
H	0.17122700	0.06512300	-1.72635800
C	-1.88295000	0.75657500	-0.76945100
C	-2.66732000	1.83489900	-0.38396800
C	-2.48203800	-0.15946300	-1.62525200
C	-3.96942800	2.00786400	-0.82601100
C	-3.77628300	-0.02025400	-2.09278500
C	-4.52310300	1.07625000	-1.68963800
C	0.52325300	1.81367400	0.01447200
C	0.84761600	2.67480700	-1.02463500
C	1.01506100	2.15718700	1.26543100
C	1.65233700	3.78854600	-0.85754200
C	1.82712300	3.25820500	1.47396500
C	2.15042900	4.07490000	0.40335300
F	0.39088200	2.42290200	-2.25714800
F	1.95702800	4.57220700	-1.88500700
F	2.94269400	5.12215700	0.58322600
F	2.30888200	3.52815300	2.68289100
F	0.71724200	1.41746100	2.34351100
F	-1.79636100	-1.23677100	-2.03324800
F	-2.19195300	2.73830700	0.47901900
F	-4.69049600	3.04752100	-0.42399400
F	-5.76514200	1.22791200	-2.12240000
F	-4.30570600	-0.91911600	-2.91407600
H	-1.35239800	-2.98121800	0.02671400
H	-3.39066700	-3.94450600	1.05326600
H	-1.64582800	0.42248600	2.59891100
H	-3.71769300	-0.51220100	3.60576900
C	-4.86828400	-2.83557400	2.97479000
N	-5.82442900	-3.27632500	3.44030600

5, Total Energy = -1536.812453 a.u.

C	-2.71025400	0.13915100	0.27039700
C	-3.31021800	-0.47467100	1.37202100
C	-4.70034500	-0.45076300	1.44410900
C	-5.44937300	0.17406300	0.45686400
C	-4.82407400	0.78763300	-0.61926200
C	-3.43632600	0.78298500	-0.73343200
H	-5.19567200	-0.91932300	2.28717400
H	-6.53058200	0.18991800	0.53186600

H	-5.41633200	1.28207200	-1.38118900
N	-1.27777900	0.15703400	0.19041200
H	-0.80289700	0.97162500	0.56252300
C	-0.51898000	-0.75910400	-0.38185600
N	0.80893600	-0.61709600	-0.34625700
B	1.49752400	0.48040800	0.59982000
C	-1.21662800	-1.90779400	-1.04854100
H	-2.18553100	-2.06614300	-0.57977100
H	-1.38291600	-1.66800600	-2.10023800
H	-0.63081700	-2.81997700	-0.99164300
H	0.73270400	0.66730400	1.51143100
C	-2.47556500	-1.14411900	2.43009500
H	-1.96864800	-2.03099100	2.03609800
H	-1.69957700	-0.47526700	2.80984300
H	-3.09611600	-1.46105300	3.26856200
C	-2.73624000	1.44398600	-1.89011700
H	-1.96979700	2.14373100	-1.55056300
H	-2.23392000	0.70714400	-2.52449600
H	-3.44774000	1.98778200	-2.51184800
C	1.59107400	-1.47070900	-1.19202700
F	2.82823200	-1.03732600	-1.26851800
F	1.09638400	-1.50483500	-2.44283300
F	1.61890100	-2.73818200	-0.75446900
C	1.65037300	1.86798300	-0.22362400
C	2.86645800	-0.01802600	1.32164700
F	2.99990100	0.58018100	2.52916800
F	4.02477100	0.22685200	0.67264000
F	2.84850500	-1.35773400	1.57316900
F	0.39791500	2.40667200	-0.49317300
F	2.23809700	1.76492100	-1.43390600
F	2.30759600	2.82455100	0.44974600

6, Total Energy = -2864.478830 a. u.

C	3.32246500	-1.69479300	-0.28470700
C	3.18177200	-2.93687500	-0.92381100
C	4.31499700	-3.73923900	-1.03970000
C	5.53979000	-3.31479300	-0.55381300
C	5.65824600	-2.06614900	0.03548800
C	4.55855300	-1.22208000	0.17785000
H	4.23853000	-4.70365100	-1.52737600
H	6.41105100	-3.95277200	-0.64883000
H	6.62573400	-1.72911400	0.39156400
C	4.77896200	0.15216100	0.79144300
C	4.08884800	0.32787400	2.14736200
C	4.45125500	1.29213600	-0.18117100
H	5.85574000	0.21149500	0.98067500
H	4.40285700	-0.45127300	2.84735800
H	4.35162100	1.29604500	2.58066900
H	3.00376500	0.30004300	2.06136100

H	4.96693600	1.15483800	-1.13459700
H	3.38079200	1.37065800	-0.37528700
H	4.77184000	2.24697400	0.24426800
C	1.87407600	-3.37239400	-1.56588000
C	1.55205200	-4.85131200	-1.33777700
C	1.89364300	-3.02928900	-3.06154200
H	1.05312300	-2.80297700	-1.13187000
H	1.60921500	-5.11535700	-0.27826600
H	0.53940800	-5.06522900	-1.68643000
H	2.23273600	-5.50812700	-1.88615500
H	2.05743000	-1.96017600	-3.21900300
H	2.69236000	-3.57276400	-3.57519400
H	0.93991500	-3.29486400	-3.52406200
N	2.14566400	-0.87548100	-0.15256200
H	1.91993600	-0.25994600	-0.92725000
C	1.11264800	-1.19308100	0.62735100
N	-0.04769700	-0.59104700	0.42774200
C	-1.20496200	-1.06054800	1.09492000
C	-2.00173200	-0.21276100	1.86160800
C	-1.68115600	-2.35148500	0.87176500
C	-3.21495400	-0.63569400	2.38162600
C	-2.87988800	-2.79469200	1.40096600
C	-3.65464500	-1.92986100	2.15654200
B	-0.18382400	0.56711100	-0.67472800
C	1.32803200	-2.19438800	1.71591000
H	1.15824200	-3.20372900	1.33548900
H	2.35539100	-2.13267000	2.07115200
H	0.64360800	-2.00750400	2.54164700
F	-0.97864100	-3.20285400	0.12575400
F	-3.29168600	-4.03507000	1.17683800
F	-3.95478100	0.19762800	3.09864100
F	-1.63727000	1.03893400	2.08282300
F	-4.80593200	-2.33936500	2.66369300
H	0.34099000	0.11903400	-1.67905500
C	-1.74603500	0.79342300	-1.03017500
C	-2.49362900	1.92909400	-0.75121500
C	-2.43050000	-0.22344400	-1.68577700
C	-3.83552400	2.04861800	-1.08833200
C	-3.76812300	-0.15071800	-2.03053400
C	-4.47589400	1.00274600	-1.72975100
C	0.65508800	1.89091600	-0.23335400
C	0.96049500	2.81930600	-1.22270000
C	1.17064800	2.18407800	1.02038300
C	1.73010100	3.94923600	-1.00454900
C	1.95290000	3.29839400	1.28305000
C	2.23641600	4.18732500	0.26343200
F	0.49809900	2.63030700	-2.46470800
F	1.99410100	4.79968100	-1.99274200
F	3.00018600	5.25035000	0.49267800
F	2.45935400	3.49937700	2.49935700
F	0.97482900	1.35885700	2.06623400

F	-1.78866900	-1.36516600	-1.98721500
F	-1.94921700	2.97385600	-0.12033500
F	-4.51237100	3.15574500	-0.79631200
F	-5.76033600	1.10045500	-2.05212600
F	-4.37672700	-1.16485100	-2.64178900

7, Total Energy = -2460.559495 a.u.

C	3.25288600	-1.64836500	-0.19579300
C	3.20047000	-2.86432300	-0.89429900
C	4.38019400	-3.59628300	-1.01657800
C	5.56495400	-3.13006200	-0.47251400
C	5.59456600	-1.91182800	0.18981600
C	4.44485800	-1.13864600	0.33890300
H	4.37285300	-4.53807000	-1.55380500
H	6.47447900	-3.71125300	-0.57532500
H	6.52989600	-1.54438300	0.59842900
C	4.56106300	0.21013400	1.03544200
C	3.75477600	0.30663300	2.33554800
C	4.26758400	1.38109600	0.08781400
H	5.61589000	0.29684400	1.31717600
H	3.99972800	-0.51928600	3.01013700
H	3.98954900	1.24274500	2.85082200
H	2.67973600	0.30156700	2.15449000
H	4.87811000	1.31643800	-0.81697600
H	3.21596900	1.41255100	-0.20750000
H	4.49164600	2.33051900	0.58496200
C	1.93077300	-3.35377000	-1.57518900
C	1.63435400	-4.82957200	-1.29037300
C	2.00796500	-3.07892200	-3.08265900
H	1.08199200	-2.77722300	-1.20105400
H	1.60870800	-5.03454300	-0.21660500
H	0.66539000	-5.10419800	-1.71573300
H	2.38351300	-5.48935900	-1.73672000
H	2.16223500	-2.01471400	-3.27906100
H	2.83650800	-3.63045600	-3.53809200
H	1.07950100	-3.38239500	-3.57356400
N	2.03946700	-0.89151300	-0.06640200
H	1.81131600	-0.24953600	-0.81726800
C	1.00018500	-1.27566200	0.68180300
N	-0.16913900	-0.70918300	0.49200500
C	-1.31104300	-1.21211600	1.19342700
C	-1.90875200	-0.46666300	2.20367800
C	-1.86608000	-2.42210200	0.78671100
C	-3.05606800	-0.94182800	2.81821700
H	-1.48021400	0.48388300	2.49038100
C	-3.01111400	-2.90139800	1.39913900
H	-1.41502900	-2.96362300	-0.03696600
C	-3.60854100	-2.16121100	2.42135400
H	-3.53076100	-0.36694700	3.60396800

H	-3.45429000	-3.83710000	1.08097700
C	-4.79491700	-2.65297200	3.05966000
N	-5.74400400	-3.05197000	3.57502300
B	-0.37254600	0.42230200	-0.61460800
C	1.21658900	-2.32440800	1.72789500
H	0.87472900	-3.29630500	1.36083600
H	2.27440600	-2.40209800	1.97475300
H	0.64268000	-2.07996400	2.62217000
H	0.16423100	-0.00451900	-1.61863700
C	-1.94933100	0.57672300	-0.93087300
C	-2.77759000	1.55132500	-0.39689600
C	-2.56908300	-0.33854700	-1.77094600
C	-4.13026800	1.63932500	-0.68863200
C	-3.91643300	-0.29323800	-2.08494300
C	-4.70130800	0.71144400	-1.54269300
C	0.40064700	1.79966400	-0.21173700
C	0.82277200	2.17842200	1.05291300
C	0.74305600	2.68211100	-1.23076200
C	1.56902400	3.31673000	1.30543800
C	1.47349300	3.84212700	-1.02514800
C	1.89822100	4.15633100	0.25550100
F	-1.86170200	-1.35576400	-2.28907200
F	-4.46513900	-1.20213000	-2.88797700
F	-5.99610900	0.77508800	-1.82904000
F	-4.88391300	2.59250800	-0.14726100
F	-2.29501200	2.44625800	0.47693900
F	0.37203500	2.41747200	-2.48891700
F	1.77734900	4.64813500	-2.04030400
F	2.62700300	5.24569500	0.47207000
F	1.99329100	3.59378700	2.53765100
F	0.54533900	1.41202400	2.13008100

TS2-H₂/8 Total Energy = -1614.079313 a.u.

Imaginary frequency : 1506.0cm⁻¹

C	-2.71047400	-0.07097200	-0.11390900
C	-3.37922900	-0.11787000	-1.34054200
C	-4.77134800	-0.13410700	-1.32668600
C	-5.46792300	-0.13261700	-0.12660500
C	-4.78086400	-0.12053500	1.07874400
C	-3.38857900	-0.09654300	1.10793200
H	-5.31022900	-0.15763700	-2.26781800
H	-6.55177300	-0.15166200	-0.13072700
H	-5.32837200	-0.13595900	2.01508500
N	-1.28059900	-0.12114200	-0.12124900
H	-1.04385600	-1.37850000	-0.15344100
C	-0.55929100	0.95792100	-0.04060200
N	0.79991200	0.87132400	-0.05727700
B	1.54498200	-0.50064600	-0.12058500

C	-1.24221700	2.29826300	0.06329800
H	-2.27029300	2.21232700	-0.27768600
H	-1.24812300	2.62254800	1.10494700
H	-0.73307800	3.05731000	-0.52359000
H	0.75427700	-1.31770700	-0.71926700
C	-0.88132600	-2.70292100	-0.37541500
C	0.31330000	-2.72933000	-0.75095700
H	-1.67068700	-3.42869900	-0.27301800
C	-2.60157800	-0.11929200	-2.62885900
H	-2.07308500	0.82830000	-2.77427300
H	-1.84655700	-0.90970200	-2.63444300
H	-3.26462700	-0.26786000	-3.48206100
C	-2.62986300	-0.09382900	2.40757500
H	-1.84072300	-0.84806300	2.41062900
H	-2.14559900	0.87151700	2.58535900
H	-3.30079700	-0.28692700	3.24551700
C	1.56066800	2.06687800	0.11296800
F	2.84290800	1.78226200	0.24789400
F	1.19159800	2.75515200	1.20652500
F	1.44499100	2.90773200	-0.92926100
C	1.81792600	-1.08817300	1.36708500
C	2.83533700	-0.57461400	-1.12376300
F	2.91749100	-1.80611800	-1.71197400
F	4.03728700	-0.38077100	-0.55704600
F	2.73551900	0.30480400	-2.14766400
F	2.39364300	-2.31137500	1.35446300
F	0.66458400	-1.21975200	2.08071400
F	2.61308200	-0.29675800	2.11633900
H	1.25625300	-3.12745800	-1.07410600

TS3-H₂/8 Total Energy = -2941.751243 a.u.

Imaginary frequency : 995.5 cm⁻¹

C	3.42529600	-1.46100400	-0.22554200
C	3.46629300	-2.76220100	-0.75485400
C	4.68855900	-3.43169600	-0.76605400
C	5.83888000	-2.82610900	-0.29590000
C	5.78362100	-1.52458700	0.17497900
C	4.58929300	-0.80696300	0.21145800
H	4.73905500	-4.43699500	-1.16872400
H	6.78297300	-3.35852600	-0.31264800
H	6.69125600	-1.04140600	0.52050500
C	4.64928700	0.61986800	0.73686900
C	4.01196400	0.74871100	2.12298400
C	4.13331300	1.66928700	-0.25302300
H	5.71624700	0.82672300	0.86957400
H	4.47148900	0.04786100	2.82547600
H	4.14872100	1.75944100	2.51507400
H	2.94150800	0.55274000	2.09948200

H	4.62949100	1.56744600	-1.22077600
H	3.06051100	1.59029300	-0.42397600
H	4.33995700	2.67137600	0.13418500
C	2.25297900	-3.44681700	-1.36565200
C	2.00034600	-4.83129400	-0.75830900
C	2.40303300	-3.53487000	-2.88957400
H	1.36723300	-2.84202800	-1.17680200
H	1.94256200	-4.79058100	0.33262400
H	1.05765400	-5.23805900	-1.13183500
H	2.79228900	-5.53796700	-1.02161800
H	2.52724300	-2.54151300	-3.32506400
H	3.27000700	-4.14292500	-3.16575700
H	1.51276100	-3.99088500	-3.33096600
N	2.15813500	-0.77520700	-0.25918800
H	2.06518500	-0.26030800	-1.25564000
C	1.18357600	-1.06491700	0.56734000
N	-0.06301500	-0.58468300	0.37272000
C	-1.13894300	-1.19945100	1.05997300
C	-1.98291100	-0.47913100	1.90344000
C	-1.47151700	-2.53089500	0.81529800
C	-3.10480200	-1.05839500	2.47443700
C	-2.57373400	-3.13154200	1.39747300
C	-3.39814300	-2.38954600	2.22796900
B	-0.37943800	0.64383700	-0.52620300
C	1.45579300	-1.94058700	1.75472900
H	2.50799100	-1.88167900	2.02376700
H	0.84196400	-1.63454800	2.60071300
H	1.23136100	-2.98103700	1.51017000
F	-0.71539500	-3.26605900	0.00393300
F	-2.84872200	-4.40542000	1.15276900
F	-3.89444000	-0.34171000	3.26149800
F	-1.75587500	0.80260400	2.14952300
F	-4.46071600	-2.95012100	2.78287700
H	0.16399200	0.31721600	-1.70284700
C	-1.93320700	0.73058100	-0.92446700
C	-2.77976600	1.78607800	-0.60551100
C	-2.51594000	-0.30927800	-1.64281800
C	-4.11985600	1.80670600	-0.96575900
C	-3.84767400	-0.32817200	-2.01711100
C	-4.65566500	0.74490800	-1.67469900
C	0.36821300	1.99386500	-0.07889700
C	0.49489700	3.04661600	-0.97897000
C	0.92623700	2.22078300	1.17224000
C	1.18189200	4.21398700	-0.69773900
C	1.61100900	3.37950900	1.50001300
C	1.75403000	4.37678100	0.55317000
F	-0.09029200	2.96500500	-2.17871500
F	1.28687500	5.17950500	-1.60481200
F	2.43008800	5.48150000	0.84221300
F	2.15034800	3.53016300	2.70802300
F	0.84339300	1.30169900	2.14937300

F	-1.77295600	-1.37134700	-1.98766000
F	-2.33928900	2.83451000	0.09078400
F	-4.89434700	2.83338900	-0.63264800
F	-5.93483800	0.75221400	-2.02271900
F	-4.35422600	-1.35363800	-2.69478400
C	2.01457100	0.17859100	-2.79098900
C	0.77231800	0.37002700	-2.90196400
H	2.78475000	0.14715400	-3.54776800
H	-0.10077000	0.59457600	-3.49500000

TS4-H₂/8 Total Energy = -2537.830553 a.u.

Imaginary frequency : 977.0 cm⁻¹

C	3.31818900	-1.49391900	-0.21385200
C	3.35582500	-2.78827800	-0.75813800
C	4.58521000	-3.44268900	-0.81027500
C	5.73921000	-2.82928000	-0.35660700
C	5.68125200	-1.53856300	0.14508200
C	4.47942600	-0.83746600	0.22142000
H	4.64009300	-4.44150500	-1.22880300
H	6.68863200	-3.34997400	-0.40630100
H	6.59065200	-1.05444300	0.48483800
C	4.51258000	0.57511300	0.78766500
C	3.83511300	0.66623200	2.15857100
C	4.00080100	1.64493300	-0.18364900
H	5.57358300	0.79063700	0.95177600
H	4.26742300	-0.05629100	2.85628300
H	3.96505400	1.66512000	2.58238000
H	2.76423500	0.47758300	2.09486900
H	4.50878800	1.57299600	-1.14784400
H	2.93027600	1.55802500	-0.36847800
H	4.19213900	2.63887700	0.23178700
C	2.12995100	-3.47378100	-1.34550600
C	1.89292900	-4.86195400	-0.73978900
C	2.24298000	-3.55144500	-2.87307700
H	1.24815500	-2.86657900	-1.13366400
H	1.84697600	-4.82711000	0.35200600
H	0.95247900	-5.27963800	-1.11008700
H	2.68803700	-5.56103800	-1.01275600
H	2.35702700	-2.55463100	-3.30302100
H	3.10394000	-4.15680700	-3.17235000
H	1.34372700	-4.00512900	-3.29872900
N	2.05096800	-0.81742400	-0.21399400
H	1.93856800	-0.28329600	-1.19812100
C	1.08543100	-1.15390300	0.61063700
N	-0.16781600	-0.71054200	0.43481800
C	-1.22103900	-1.33760700	1.17399400
C	-1.93731000	-0.62453200	2.13086800
C	-1.57318500	-2.64987300	0.87157400
C	-2.99802900	-1.22462300	2.78807500
C	-2.62562400	-3.25861300	1.53293900

C	-3.34252000	-2.54540900	2.49509200
B	-0.53973100	0.50952800	-0.43916000
C	1.39038400	-2.04260700	1.78307700
H	2.45348500	-2.01153200	2.00907500
H	0.81549500	-1.72569300	2.65246900
H	1.12178000	-3.07633400	1.55763700
H	0.00307200	0.22426100	-1.63562000
C	-2.10088800	0.54114200	-0.80560000
C	-2.99164100	1.50474200	-0.35319900
C	-2.64818800	-0.45768200	-1.60241000
C	-4.33965600	1.49365100	-0.67687900
C	-3.98711700	-0.50647900	-1.94813000
C	-4.83823300	0.48408100	-1.48363200
C	0.16268200	1.88740300	0.00541100
C	0.28043200	2.94098100	-0.89489300
C	0.70245400	2.12867700	1.26122700
C	0.96427900	4.11127600	-0.61323100
C	1.38621400	3.28661300	1.59009700
C	1.53409700	4.27900500	0.63804600
F	-0.30220300	2.85677400	-2.09437900
F	1.06859400	5.07473200	-1.52188500
F	2.20628400	5.38607000	0.92557100
F	1.90974200	3.44585300	2.80348400
F	0.57798200	1.22385500	2.25282400
F	-1.86481600	-1.44882500	-2.05448300
F	-2.58036500	2.47750900	0.46877800
F	-5.15756900	2.43271400	-0.21289900
F	-6.12474600	0.45907600	-1.80214000
F	-4.46140300	-1.48605500	-2.71129600
C	1.85158800	0.17522300	-2.72489700
C	0.59855600	0.30937700	-2.82533000
H	2.60234200	0.18627400	-3.50254200
H	-0.28016100	0.49624300	-3.42366100
C	-4.43790700	-3.16975200	3.17757500
N	-5.31534800	-3.67349500	3.72666800
H	-3.56203500	-0.67344200	3.53007400
H	-1.66422500	0.39862700	2.35240700
H	-2.90451700	-4.27839500	1.29907900
H	-1.03396900	-3.17950700	0.09495000

8, Total Energy = -77.318631 a.u.

C	0.00000000	0.00000000	0.59821900
C	0.00000000	0.00000000	-0.59821900
H	0.00000000	0.00000000	1.66217600
H	0.00000000	0.00000000	-1.66217600

9, Total Energy = -78.578844 a.u.

C	-0.66219500	0.00000000	0.00000000
C	0.66219500	0.00000000	0.00000000

H	-1.23108700	-0.92410300	0.00000000
H	-1.23108600	0.92410300	0.00000000
H	1.23108700	0.92410300	0.00000000
H	1.23108600	-0.92410300	0.00000000

Table S1. ω B97X-D/6-311G(d,p) total energies (E, in au), enthalpies (H, in au), entropies (S, in cal/mol K) and Gibbs free energies (G, in au), computed at 120°C and 1 atm in toluene, of the stationary points involved in the activation of molecular hydrogen **1** by the three FLP models **2**, **3** and **4** and for the hydrogenation of acetylene **8** by the three FLP models **2**, **3** and **4** to yield ethylene **9**.

	E	H	S	G
1	-1.176144	-1.161685	33.1	-1.182391
2	-1535.579977	-1535.287075	195.6	-1535.409570
3	-2863.265642	-2862.713703	318.8	-2.862.913368
4	-2459.348201	-2458.760987	306.3	-2458.952800
TS2/H₂	-1536.752218	-1536.443029	195.2	-1536.565286
TS3/H₂	-2864.432675	-2863.864797	319.9	-2.864.065167
TS4/H₂	-2460.513553	-2459.910776	309.4	-2460.104548
5	-1536.820217	-1536.505014	195.1	-1536.627229
6	-2864.484861	-2863.910049	318.1	-2.864.109259
7	-2460.567962	-2459.959379	306.5	-2460.151347
8	-77.320353	-77.287807	50.7	-77.319561
TS2- H₂/8	-1614.084333	-1613.740713	209.0	-1613.871585
TS3- H₂/8	-2941.756186	-2941.153721	329.1	-2941.359844
TS4- H₂/8	-253.837780	-2537.199933	318.6	-2537.39945
9	-78.580125	-78.523287	56.7	-78.558809

Table S2. ω B97X-D/6-311G(d,p) total energies (E, in au) and enthalpies (H, in au), entropies (S, in cal/mol K) and Gibbs free energies (G, in au), in gas phase and computed at 120°C and 1 atm in toluene, for open-chain (**O**) and four-membered ring (**R**) forms of **2**, **3** and **4**.

	E	ΔE	E	ΔE	H	ΔH	S	ΔS	G	ΔG
	Gas phase	Ⓢ		Ⓢ	Toluene	Ⓢ		Ⓢ		Ⓢ
2										
O	-1535.579948		-1535.579977		-1535.287075		195.6		-1535.409570	
R	-1535.623057	-27.1	-1535.627946	-30.1	-1535.334533	-29.8	195.0	-0.6	-1535.456627	-29.5
3										
O	-2863.261203		-2863.265642		-2862.713703		318.8		-2862.913368	
R	-2863.283474	-14.0	-2863.288090	-14.1	-2862.736714	-14.4	320.2	1.4	-2862.937239	-15.0
4										
O	-2459.341634		-2459.348201		-2458.760987		306.3		-2458.952799	
R	-2459.363721	-13.9	-2459.371775	-14.8	-2458.785992	-15.7	298.0	-8.2	-2458.972654	-12.5