

Electronic Supplementary Information

How the mechanism of a [3+2] cycloaddition reaction involving a stabilized N-lithiated azomethine ylide toward a π -deficient alkene is turned into stepwise by the solvent polarity? What is the origin of the regio- and *endo* stereospecificity? A DFT study using NBO, QTAIM, and NCI analyses

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- S3 Table S1.** Absolute Gibbs free energy values, G in a.u., obtained *via* MPWB1K/6-31G(d) frequency calculation, total electronic energy, $E_{\text{MPWB1K/6-31+G(d)}}^{\text{ele}}$ in a.u., attained through MPWB1K/6-31+G(d) single-point energy calculation over the MPWB1K/6-31G(d) optimized structures, and absolute Gibbs free energy values, $G_{\text{(corrected)}}$ in a.u. calculated using equation (1) given in the text, of the stationary points involved in the studied 32CA reaction in THF.
- S4 Scheme S1.** The relative corrected Gibbs free energy profile, ΔG (corrected) obtained employing equation (1) given in the text, associated with the reaction paths involved in the studied 32CA reaction in THF.
- S6** MPWB1K/6-31G(d) computed total electronic energies (E , in a.u.) and Cartesian coordinates of the optimized structures involved in the studied 32CA reaction in THF

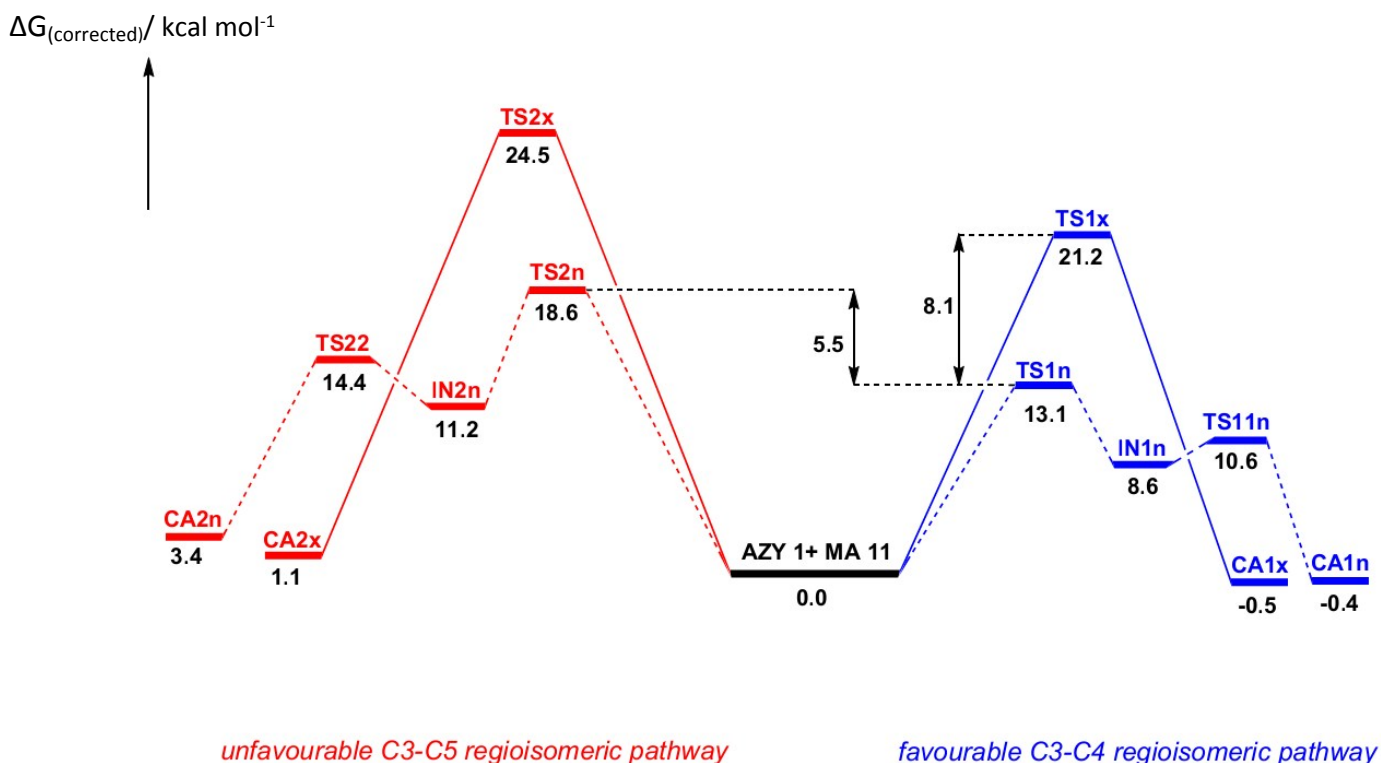
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(see Scheme 9 in the text for details). While the unique imaginary frequency of TSs is also given in cm^{-1} , the selected bond distances in the given optimized structures are in Å.

Table S1. Absolute Gibbs free energy values, G in a.u., obtained *via* MPWB1K/6-31G(d) frequency calculation, total electronic energy, $E_{\text{MPWB1K/6-31+G(d)}}^{\text{ele}}$ in a.u., attained through MPWB1K/6-31+G(d) single-point energy calculation over the MPWB1K/6-31G(d) optimized structures, and corrected Gibbs free energy values, $G_{\text{(corrected)}}$ in a.u., calculated using equation (1) of the stationary points involved in the studied 32CA reaction in THF

Stationary point	G	$E_{\text{MPWB1K/6-31+G(d)}}^{\text{ele}}$	G (corrected)
AZY 1	-1304.023015	-1304.327848	-1304.049373
MA 11	-306.249799	-306.328967	-306.261321
TS1x	-1610.241110	-1610.646419	-1610.276884
CA1x	-1610.278697	-1610.687619	-1610.311535
TS1n	-1610.257241	-1610.661669	-1610.289894
IN1n	-1610.264540	-1610.674480	-1610.296918
TS11n	-1610.262532	-1610.672628	-1610.293849
CA1n	-1610.280948	-1610.690218	-1610.311275
TS2x	-1610.234819	-1610.645027	-1610.271723
CA2x	-1610.275704	-1610.684686	-1610.309019
TS2n	-1610.248844	-1610.657384	-1610.281029
IN2n	-1610.259550	-1610.669238	-1610.292767
TS22n	-1610.256287	-1610.666021	-1610.287799
CA2n	-1610.274711	-1610.687837	-1610.305223



Scheme S1. The relative corrected Gibbs free energy profile, ΔG (corrected) obtained using equation (1) given in the text, of the studied 32CA reaction in THF. The values of ΔG (corrected) associated with each of the stationary point can easily be calculated employing values given in the last column of Table S1.

When the profile given in scheme S1 is compared with that of sketched in Fig. 5 of the main text some appealing and important conclusions about the impact of diffuse functions, included *via* 6-31+G(d) basis set among the computations, on the energetics of the studied 32CA reaction can be pointed out:

- Inclusion of diffuse functions results to an increase in the activation barriers by *ca.* 1.0 to 4.0 kcal/mol while the exergonic character of reaction along generation of cycloadducts is strongly decreased as a consequence of the more stabilization of reagents than TSs as well as cycloadducts.
- The selectivities (regio- and stereoselectivity) of the reaction are not considerably affected by the inclusion of diffuse functions, *i.e.* the reaction still displays a C3-C4

regiospecificity and an *endo*-stereospecificity. Considering a large increase (from 9.8 into 13.1 kcal/mol) experienced by the RDS of reaction (conversion of reagents into **IN1n**) formation of **IN1n** should be ruled out by the inclusion of diffuse functions. In the other words, a barrier of 13.1 kcal/mol (compared with 9.8 kcal/mol in the absence of diffuse functions) is significantly large and cannot easily (at least in comparison with 9.8 kcal/mol) be achieved in the reaction conditions. Note that this reaction experimentally takes place at the ambient temperature.

- Finally, inclusion of diffuse functions makes the reaction thermodynamically very unfavourable, *i.e.* the equilibrium constant K_{eq} of the overall reaction becomes less than 2.0 (see equation 6 in the main text). Taking such very slight equilibrium constant, the presence of **CA1n** (located just 0.4 kcal/mol below reagents) as a sufficiently stable species is strongly questioned. On the other hand, without using diffuse functions, K_{eq} is 5500 indicating a very favourable thermodynamically situation introducing CA1n as an actual and separable species in the reaction medium.

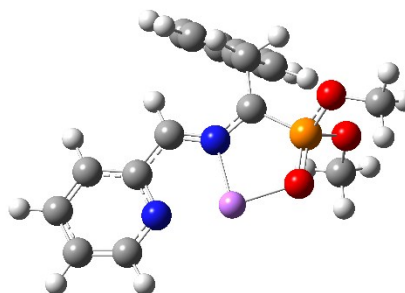
As explained, inclusion of diffuse functions not only cannot modify the selectivities but also leads to the increase of the barrier together with the decrease of exergonicity of reaction. Paying attention to abovementioned justifications particularly for the reactions taking place under kinetics control (such as the studied reaction which experimentally takes place at ambient temperature) is very important. Based on the results obtained *via* inclusion of diffuse functions if, for example, we experimentally increase the temperature while the barriers may be overcome, the cycloadducts become more elusive as well. Considering a similar justification on the failure of diffuse functions to modify selectivities provided by Nacereddine and co-workers (see Ref. 48 in the main text) it seems one may conclude that inclusion of diffuse functions, at least in 32CA reactions independent of the involved mechanistic aspects, should be avoided since the experimental finding cannot properly and reliably be justified by the computation outcomes.

MPWB1K/6-31G(d) computed total electronic energies (E , in a.u.) and Cartesian coordinates of the optimized structures involved in the studied 32CA reaction in THF (see Scheme 7 in the text for details). While the unique imaginary frequency of TSs is given in cm^{-1} , the selected bond distances in the given optimized structures are in Å.

AZY 1

$E(\text{RmPW+HF-B95}) = -1304.30149118$ a.u.

C	4.38631700	-1.42058100	0.74003300
C	2.94391300	0.07342800	-0.25360600
C	4.01169300	0.94719300	-0.49875500
C	5.28005000	0.60096300	-0.10265300
C	5.48648500	-0.61474600	0.53732700
H	4.49820300	-2.37735200	1.23209500
H	3.82089500	1.88600500	-0.99581800
H	6.10754200	1.26989200	-0.28708500
H	6.46400500	-0.92695900	0.86588500
N	3.15377800	-1.10692600	0.36457000
C	1.60512300	0.40670200	-0.65209100
H	1.43085900	1.34772800	-1.16063800
N	0.66044600	-0.44470600	-0.37529600
C	-0.62927400	-0.38645900	-0.66469900
P	-1.44963700	-1.79420800	-0.08547500
O	-0.50708200	-2.80725800	0.49253300
O	-2.36123800	-2.32038300	-1.27955000
O	-2.61794900	-1.45409700	0.97083200
C	-3.31286700	-3.34935400	-1.04669400
H	-4.08641700	-2.99948600	-0.37047900

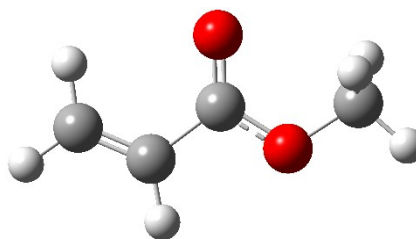


H	-3.74506900	-3.59750000	-2.00843200
H	-2.82806300	-4.22745900	-0.62894300
C	-2.21744300	-1.10982400	2.28493400
H	-3.11596600	-0.85426700	2.83443400
H	-1.71979700	-1.94939300	2.76211900
H	-1.54937600	-0.24976300	2.26656700
C	-1.28301200	0.72307600	-1.42866000
H	-0.69649800	0.92391800	-2.33030700
H	-2.26396700	0.39164600	-1.76918300
C	-1.43248200	2.00706900	-0.65248500
C	-0.72439600	3.14689000	-1.00194100
C	-2.29390000	2.07219700	0.43683300
C	-0.86001400	4.32110600	-0.27907900
H	-0.06016300	3.11594100	-1.85514000
C	-2.43655300	3.24188200	1.15948200
H	-2.86606500	1.19557200	0.70699300
C	-1.71552000	4.37188700	0.80595300
H	-0.29677200	5.19640800	-0.56683100
H	-3.11533100	3.27494600	1.99885900
H	-1.82475300	5.28521500	1.37102600
Li	1.31104400	-2.15507700	0.50606000

MA 11

E(RmPW+HF-B95)= -306.31744541 a.u.

C	2.46017900	0.00022600	0.00001500
H	2.47843500	1.07986000	0.00000500
H	3.40423100	-0.52100200	0.00003800
C	1.30604400	-0.64671400	-0.00000600



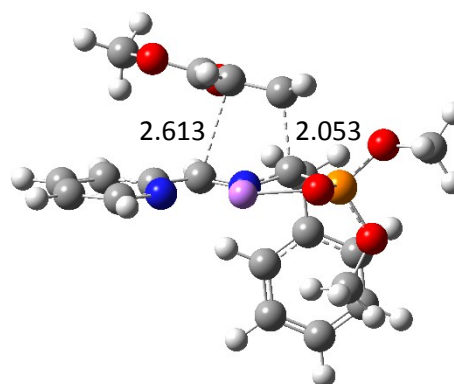
H	1.24120200	-1.72333900	0.00000200
C	0.03938200	0.10308600	-0.00004500
O	-0.06189900	1.30373300	-0.00000400
O	-1.00623800	-0.71521700	-0.00000500
C	-2.27263500	-0.08064000	0.00002500
H	-3.00541100	-0.87687600	0.00001700
H	-2.38557900	0.53871800	0.88423000
H	-2.38559900	0.53876000	-0.88414700

TS1x

E(RmPW+HF-B95)= -1610.61064732 a.u.

1 imaginary frequency= 355.6 cm⁻¹

C	-3.32442900	-0.75937800	-3.06039000
C	-2.45608200	0.27595800	-1.20990200
C	-3.60488700	1.04830400	-1.07230800
C	-4.63277300	0.89380800	-1.97823700
C	-4.49486900	-0.02709100	-3.00222400
H	-3.17987100	-1.49384500	-3.84017900
H	-3.67620700	1.75090000	-0.25623700
H	-5.53120100	1.48522700	-1.88836800
H	-5.27085000	-0.18013000	-3.73409900
N	-2.33043400	-0.62442700	-2.19639900
C	-1.35172300	0.38994100	-0.26851300
H	-1.43375700	1.13191000	0.51876700
N	-0.28454700	-0.29864500	-0.50344300
C	0.68082800	-0.50846400	0.42532800
P	1.85298000	-1.61747000	-0.31032900
O	1.22074400	-2.43517500	-1.39281700



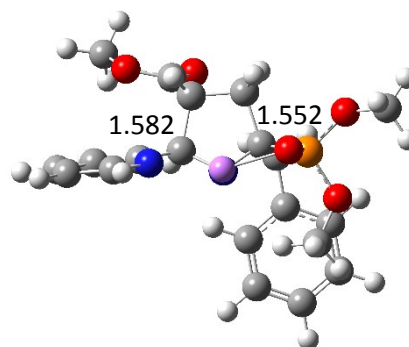
O	2.44362100	-2.44377200	0.90613900
O	3.18939300	-0.90430200	-0.82375900
C	3.48538000	-3.38486000	0.68026700
H	4.38594200	-2.87480800	0.35346400
H	3.66356600	-3.88317500	1.62481200
H	3.18130400	-4.11372200	-0.06551200
C	3.12384900	-0.10215400	-1.99283100
H	4.09618400	0.36058200	-2.10893300
H	2.89827400	-0.71846700	-2.85881600
H	2.37192800	0.67648500	-1.88003500
C	1.18012400	0.57185400	1.36921800
H	0.32050100	0.96884900	1.90857900
H	1.81241100	0.09600500	2.11807000
C	1.95476000	1.66881400	0.69552100
C	1.31511400	2.63789100	-0.07073400
C	3.33906000	1.72201000	0.79776700
C	2.03988900	3.61214500	-0.73497700
H	0.23852500	2.63059500	-0.14939800
C	4.06812700	2.69575000	0.13786400
H	3.85192800	0.97874100	1.39118200
C	3.42076800	3.64202400	-0.63728700
H	1.52331100	4.35422200	-1.32539500
H	5.14390800	2.71489900	0.23064400
H	3.98681800	4.40271000	-1.15345000
Li	-0.47930800	-1.69221500	-1.96996400
C	-0.37906700	-1.64546400	1.76759400
H	-0.08397100	-2.63001800	1.43528400
H	0.17445700	-1.28362300	2.62338000
C	-1.72128100	-1.31155800	1.67900900

H	-2.40043400	-1.88603300	1.06980100
C	-2.28218200	-0.23669800	2.42789500
O	-1.69317400	0.55568100	3.14708700
O	-3.61986700	-0.13731100	2.25374100
C	-4.23379700	0.92493300	2.94360100
H	-5.29366100	0.85217900	2.72851600
H	-4.06523500	0.84779700	4.01406900
H	-3.85236500	1.88536500	2.60447700

CA1x

E(RmPW+HF-B95)= -1610.65478214 a.u.

C	-3.32867800	-2.00587300	-2.34865500
C	-2.52514900	-0.28405200	-1.06697100
C	-3.65122400	0.47681400	-1.34241500
C	-4.64093400	-0.04556600	-2.14953400
C	-4.48103400	-1.31840400	-2.66760800
H	-3.15863000	-3.00054600	-2.73555100
H	-3.73952700	1.46497600	-0.91965700
H	-5.52401800	0.53261600	-2.37555900
H	-5.22461700	-1.76684600	-3.30620100
N	-2.37347900	-1.50928600	-1.57097300
C	-1.43185200	0.21615500	-0.15857500
H	-1.48481000	1.32250500	-0.17958300
N	-0.16992300	-0.32763500	-0.50657400
C	0.61816300	-0.29156600	0.68147700
P	1.79641400	-1.63562500	0.42432100
O	1.14734200	-2.82256000	-0.21367100
O	2.43224600	-1.91447000	1.85217300



O	3.08127200	-1.15486800	-0.38392800
C	3.41708300	-2.92899200	1.99982300
H	4.30210400	-2.67901100	1.42243800
H	3.66538600	-2.97175200	3.05297000
H	3.02298000	-3.88829200	1.67709900
C	2.96014300	-0.91269300	-1.78123100
H	3.88084800	-0.43545500	-2.09418500
H	2.82947900	-1.85426300	-2.30798400
H	2.12040200	-0.25097900	-1.97469100
C	1.28109900	1.05764000	1.06106600
H	0.46111100	1.70010300	1.38878600
H	1.91439000	0.90525100	1.93605900
C	2.05429100	1.74706700	-0.01575100
C	1.40370300	2.29510200	-1.11656300
C	3.43601500	1.86704300	0.05701100
C	2.11739400	2.92004200	-2.12447000
H	0.32948800	2.21643600	-1.18232100
C	4.15441600	2.49438400	-0.94581400
H	3.95607200	1.45005100	0.90780000
C	3.49646400	3.01867900	-2.04535700
H	1.59434700	3.33587400	-2.97319100
H	5.22867800	2.57465900	-0.86745900
H	4.05309500	3.50863200	-2.83037000
Li	-0.40670200	-2.12439000	-1.20053800
C	-0.34081600	-0.69128500	1.83419400
H	-0.35445700	-1.77010600	1.97280700
H	-0.06962600	-0.23405200	2.78261700
C	-1.69995400	-0.22348600	1.33756100
H	-2.42922800	-1.02907000	1.33745900

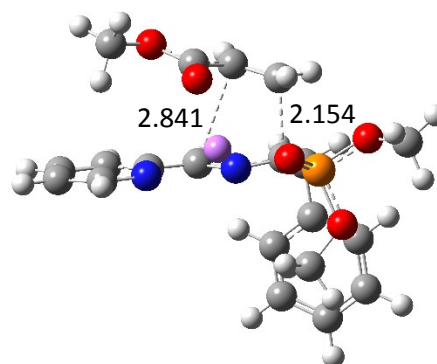
C	-2.26774100	0.91630600	2.11501200
O	-1.64691100	1.68654000	2.80291200
O	-3.57627200	1.03938600	1.90911500
C	-4.19263500	2.14486400	2.54592900
H	-5.24051000	2.09646200	2.27925300
H	-4.07328300	2.07746500	3.62262500
H	-3.75591200	3.07603800	2.19887200

TS1n

E(RmPW+HF-B95)= -1610.62901700 a.u.

1 imaginary frequency= -296.4 cm⁻¹

C	3.53664100	1.11702000	2.07423400
C	2.26063900	1.32462400	0.18340900
C	3.16433400	2.23804600	-0.35554700
C	4.28066600	2.58920600	0.37103600
C	4.47605200	2.02423200	1.62064900
H	3.65721800	0.64343100	3.03856100
H	2.97788100	2.66062800	-1.33075900
H	4.99050100	3.29742300	-0.02861400
H	5.33118300	2.27395300	2.22726200
N	2.46281100	0.76467300	1.38482400
C	1.06815700	0.92580600	-0.54538000
H	0.89036900	1.37619800	-1.51616600
N	0.25019900	0.11543100	0.03746000
C	-0.79693300	-0.50119000	-0.53723600
P	-1.53208700	-1.50794700	0.71022500
O	-0.49226600	-2.01972500	1.65353700
O	-2.33748000	-2.61182800	-0.09552600



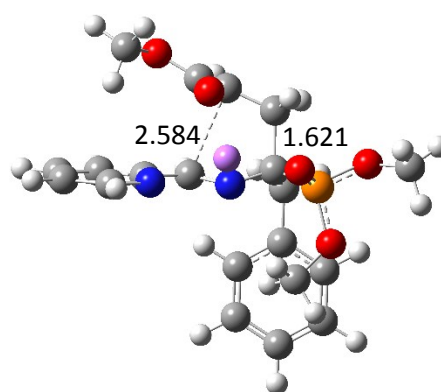
O	-2.74194700	-0.80030300	1.48399000
C	-3.14980800	-3.54794400	0.60056600
H	-3.97263300	-3.03712400	1.09082200
H	-3.53229100	-4.23897400	-0.14015900
H	-2.55983700	-4.08945100	1.33432300
C	-2.47244300	0.37724000	2.22933400
H	-3.40503300	0.67276800	2.69444700
H	-1.72657200	0.18117100	2.99556900
H	-2.13057300	1.17176500	1.56822600
C	-1.60666500	0.09622800	-1.66392100
H	-0.91677800	0.45172300	-2.43084100
H	-2.20435100	-0.69147300	-2.12016500
C	-2.51251300	1.20193000	-1.20110200
C	-2.05733200	2.50762300	-1.06083400
C	-3.82384400	0.91629900	-0.84132500
C	-2.88472800	3.49534100	-0.55343800
H	-1.04805400	2.75637300	-1.35360400
C	-4.65379500	1.89980300	-0.33499900
H	-4.18692700	-0.09667800	-0.94352200
C	-4.18445600	3.19372800	-0.18445900
H	-2.51340300	4.50407800	-0.45065800
H	-5.66895200	1.65633300	-0.05898200
H	-4.82953500	3.96386300	0.21071600
Li	1.24718700	-1.06191000	1.38403800
C	0.28732100	-2.02021900	-1.61361300
H	0.30742500	-2.71099500	-0.78313600
H	-0.50010000	-2.18048400	-2.33481700
C	1.48322700	-1.47416500	-2.00789700
H	1.63259900	-1.02155300	-2.97401000

C	2.56993100	-1.50539300	-1.09248500
O	2.50721500	-1.89594900	0.07760700
O	3.73000400	-1.08756300	-1.61231700
C	4.83908800	-1.08270800	-0.74005700
H	5.67939600	-0.73874000	-1.33124100
H	4.67424900	-0.40932300	0.09547500
H	5.03744500	-2.08078800	-0.36013300

IN1n

E(RmPW+HF-B95)= -1610.64210395 a.u.

C	3.45257800	1.16910500	2.08742600
C	2.23356000	1.26196500	0.16226800
C	3.14345500	2.13127000	-0.41991800
C	4.24890500	2.52634800	0.30784200
C	4.40770600	2.04141100	1.59194800
H	3.55033800	0.76137500	3.08335100
H	2.98013000	2.48538300	-1.42583900
H	4.97276500	3.20264700	-0.11975700
H	5.25181900	2.32358900	2.20002400
N	2.39479300	0.77895100	1.39743600
C	1.05264100	0.79687000	-0.57369900
H	0.93445600	1.15537200	-1.58996500
N	0.18757800	0.09514800	0.05721400
C	-0.74572000	-0.66414400	-0.69014300
P	-1.58276800	-1.54192300	0.65328800
O	-0.57219600	-2.08023700	1.60840100
O	-2.47937600	-2.61704000	-0.08404000



O	-2.69369600	-0.66570500	1.37854400
C	-3.21512700	-3.56959300	0.67622500
H	-3.96769300	-3.06797600	1.27692700
H	-3.69298400	-4.23105000	-0.03501200
H	-2.54622500	-4.13759200	1.31532200
C	-2.32259000	0.44793400	2.18144300
H	-3.19274500	0.70762600	2.77200900
H	-1.49793400	0.18336200	2.83760200
H	-2.04389300	1.28456600	1.54546600
C	-1.61971500	0.07098900	-1.71166000
H	-0.95377800	0.40452400	-2.50971200
H	-2.28679100	-0.66476600	-2.15879900
C	-2.41876800	1.22604000	-1.18698900
C	-1.84541100	2.48228900	-1.02564900
C	-3.75336700	1.06281600	-0.83873200
C	-2.57210200	3.53438600	-0.49604500
H	-0.82060100	2.64359500	-1.32305900
C	-4.48490600	2.11087800	-0.30973200
H	-4.21629000	0.09479200	-0.96646400
C	-3.89336600	3.34974800	-0.12891100
H	-2.10607000	4.50092100	-0.37624600
H	-5.51934200	1.96001300	-0.03974800
H	-4.46234100	4.16858500	0.28477000
Li	1.17137300	-1.08843400	1.41381900
C	0.09179000	-1.80290000	-1.48298300
H	0.19835400	-2.64400500	-0.79908400
H	-0.54807300	-2.11755200	-2.30453500
C	1.41489600	-1.36928000	-1.93509500
H	1.59603200	-1.05883600	-2.95055400

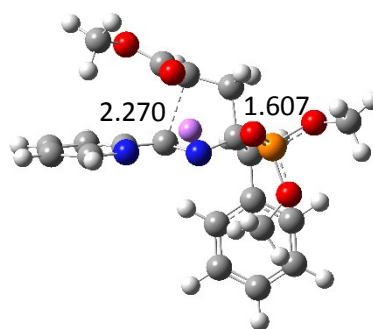
C	2.47678200	-1.52656600	-1.06348300
O	2.39521400	-1.89742700	0.13155400
O	3.69901700	-1.23299100	-1.58184500
C	4.77204300	-1.26665100	-0.67680600
H	5.65959000	-1.03276100	-1.25539800
H	4.64985600	-0.52843700	0.11321700
H	4.88080300	-2.24820700	-0.22261200

TS11n

E(RmPW+HF-B95)= -1610.64131267 a.u.

1 imaginary frequency= -172.3 cm⁻¹

C	3.47563800	1.17101100	2.04266800
C	2.26370700	1.22794100	0.10791400
C	3.17788000	2.08983000	-0.48134800
C	4.27661100	2.50023800	0.24632600
C	4.42905100	2.03940700	1.54126000
H	3.56671100	0.77994400	3.04599800
H	3.01892000	2.42936000	-1.49309500
H	5.00010700	3.17302100	-0.18773800
H	5.26630700	2.33832900	2.15086100
N	2.42370600	0.76419300	1.35054200
C	1.07163000	0.75815300	-0.61816700
H	0.89420700	1.23406500	-1.57880900
N	0.15401000	0.15091700	0.07900800
C	-0.74903300	-0.61679500	-0.69504500
P	-1.56449800	-1.57473400	0.60284400



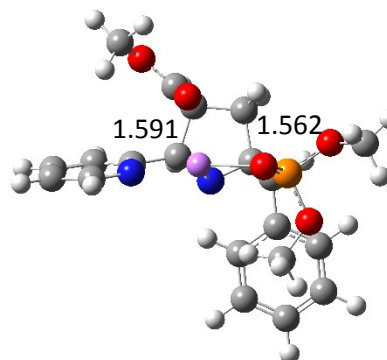
O	-0.55708900	-2.11030600	1.56333900
O	-2.40504600	-2.66585200	-0.18013000
O	-2.72446000	-0.75858600	1.32208200
C	-3.11144700	-3.66590100	0.54476400
H	-3.91034600	-3.21353700	1.12465500
H	-3.52835400	-4.34508800	-0.18799300
H	-2.43475300	-4.20412000	1.20147900
C	-2.40671500	0.31492000	2.19891800
H	-3.34773800	0.67820700	2.59364800
H	-1.77619600	-0.03769300	3.01049900
H	-1.90320700	1.10696800	1.65244400
C	-1.66229100	0.11758200	-1.68739600
H	-1.01497100	0.49650300	-2.48071300
H	-2.31199000	-0.62264200	-2.15307500
C	-2.48546200	1.23740900	-1.12659100
C	-1.91790800	2.47975000	-0.86651800
C	-3.83435300	1.05987200	-0.84889600
C	-2.66919800	3.50576900	-0.32115900
H	-0.87726600	2.64840900	-1.09845300
C	-4.59098500	2.08241900	-0.30452900
H	-4.29251900	0.10198100	-1.04983800
C	-4.00864700	3.30888100	-0.03347200
H	-2.20829300	4.46263600	-0.12651100
H	-5.63783800	1.92136100	-0.09448800
H	-4.59736600	4.10859100	0.39005900
Li	1.15266200	-1.05195900	1.40627100
C	0.14649100	-1.65570600	-1.53405500
H	0.26267500	-2.55246300	-0.92755200
H	-0.41344500	-1.92395900	-2.42687400

C	1.47231700	-1.10238900	-1.85543100
H	1.70518800	-0.76657700	-2.85282100
C	2.53220400	-1.43430900	-1.00510600
O	2.40715500	-1.89674800	0.14233600
O	3.75829700	-1.15417300	-1.49129400
C	4.81894500	-1.24611500	-0.56965500
H	5.72018100	-1.01697300	-1.12700900
H	4.69405400	-0.52732600	0.23689100
H	4.88994600	-2.24437300	-0.14744900

CA1n

E(RmPW+HF-B95)= -1610.65989290 a.u.

C	3.53335100	1.37466600	1.89892800
C	2.32247000	1.33865900	-0.04268900
C	3.13513500	2.31462600	-0.59913000
C	4.18286200	2.82484500	0.14171500
C	4.39059100	2.34706300	1.42275800
H	3.65812900	0.97390600	2.89500200
H	2.93693100	2.66722600	-1.59967500
H	4.82490800	3.58758300	-0.27186500
H	5.19199200	2.71772100	2.04117700
N	2.52689500	0.88003700	1.19218800
C	1.17889600	0.71896500	-0.80471100
H	0.90278100	1.43222400	-1.60343100
N	0.13856200	0.33162800	0.06628200
C	-0.69043300	-0.54026700	-0.69811400
P	-1.42896800	-1.59147400	0.57478300
O	-0.44091100	-1.98392700	1.62204500



O	-2.07582500	-2.80653900	-0.22221800
O	-2.73256700	-0.92334300	1.19812800
C	-2.74000000	-3.84129500	0.48957700
H	-3.61061100	-3.44463000	1.00358900
H	-3.05013500	-4.57595300	-0.24330600
H	-2.06570300	-4.30133900	1.20603400
C	-2.58275900	0.18325600	2.08251800
H	-3.50954800	0.74389000	2.03743300
H	-2.40957600	-0.17930500	3.09191500
H	-1.76244300	0.81759900	1.75969500
C	-1.73232700	0.11194300	-1.64547500
H	-1.14820500	0.58622800	-2.43787800
H	-2.31124100	-0.67820200	-2.12541300
C	-2.65406300	1.12892300	-1.05237700
C	-2.16941500	2.35600800	-0.61375900
C	-4.01636600	0.88175500	-0.94036300
C	-3.01885300	3.29535400	-0.05458900
H	-1.11416400	2.56255000	-0.70139300
C	-4.87141300	1.82012100	-0.38938500
H	-4.40904500	-0.06591300	-1.28128400
C	-4.37297100	3.03040500	0.06266000
H	-2.62243000	4.24053500	0.28640600
H	-5.92707700	1.60529200	-0.31210400
H	-5.03612800	3.76487200	0.49500700
Li	1.10406100	-0.73466400	1.44232900
C	0.26814100	-1.39331300	-1.58931900
H	0.41601300	-2.38998900	-1.18030500
H	-0.12244400	-1.51139800	-2.59753600
C	1.57784400	-0.61190400	-1.58084200

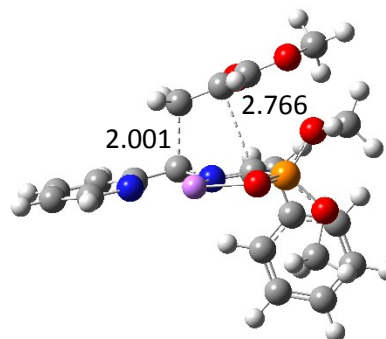
H	1.96887200	-0.39992100	-2.57076900
C	2.61604900	-1.31257100	-0.78294600
O	2.39775500	-1.86499600	0.27673800
O	3.82795200	-1.22183700	-1.29720400
C	4.87890700	-1.76952600	-0.51630500
H	5.77959300	-1.64077700	-1.10180400
H	4.96078800	-1.23745600	0.42629700
H	4.69776900	-2.82143800	-0.32264000

TS2x

E(RmPW+HF-B95)= -1610.60812379 a.u.

1 imaginary frequency= -397.8 cm⁻¹

C	-4.73373300	-1.04105000	1.31382300
C	-3.21795500	-0.46555200	-0.30892200
C	-4.19645000	-0.58994800	-1.29235900
C	-5.47422700	-0.95573400	-0.93294400
C	-5.75855100	-1.19133100	0.40272000
H	-4.91092900	-1.21332800	2.36626100
H	-3.93937200	-0.40381300	-2.32376200
H	-6.24201400	-1.06063800	-1.68456500
H	-6.74305200	-1.48192200	0.73058000
N	-3.49812700	-0.68543800	0.98402700
C	-1.87166800	-0.00590300	-0.63823500
H	-1.59951300	-0.06467700	-1.68744100
N	-0.95181500	-0.23116500	0.31615500
C	0.30542100	0.05816200	0.19520600
P	1.09008800	0.02188000	1.78422200
O	0.10710300	-0.28915400	2.86576900



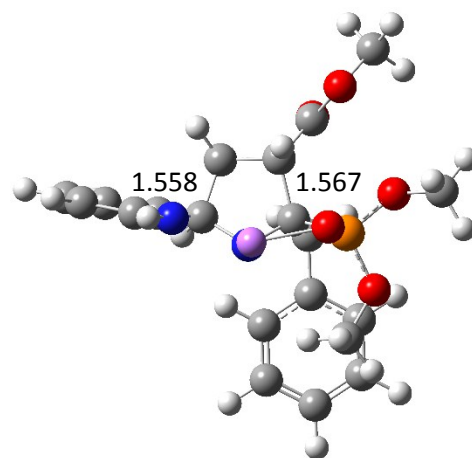
O	1.82319800	1.41956800	1.89391900
O	2.35220500	-0.95150200	1.81924000
C	2.68779600	1.69047400	2.99089000
H	3.54480900	1.02504300	2.96560300
H	3.01205100	2.71736500	2.88007200
H	2.15567100	1.57489700	3.93075700
C	2.15914000	-2.35722900	1.88022600
H	3.11033400	-2.79082200	2.16387500
H	1.40823600	-2.60279900	2.62606200
H	1.86263300	-2.73630000	0.90530700
C	1.12076700	0.16757000	-1.06178500
H	0.48895400	0.51012500	-1.87884100
H	1.88318600	0.93320800	-0.92358100
C	1.77477400	-1.14621900	-1.39586100
C	1.00237000	-2.25342800	-1.73030600
C	3.15149900	-1.29730000	-1.31921200
C	1.59189500	-3.48087700	-1.97388300
H	-0.07242700	-2.15149000	-1.78936300
C	3.74570200	-2.52506600	-1.55834200
H	3.76262900	-0.44655800	-1.05394700
C	2.96751900	-3.62180100	-1.88359600
H	0.97681000	-4.32975100	-2.23285300
H	4.81858500	-2.62426200	-1.48756500
H	3.42860100	-4.58017500	-2.06868000
Li	-1.70288000	-0.51530200	2.19063300
C	-0.79172500	2.57086100	-0.16960400
H	-0.50324100	2.74966200	0.85317200
C	-2.00790900	1.98605800	-0.49679300
H	-2.36905000	2.13201500	-1.50611900

H	-2.78669000	1.98243800	0.25404200
C	0.09420200	2.99024200	-1.19825300
O	-0.06832500	2.85796800	-2.40290900
O	1.21862000	3.57341900	-0.71996300
C	2.12630100	4.00814400	-1.70333000
H	1.67403000	4.74931000	-2.35724900
H	2.96220800	4.44669500	-1.17013800
H	2.47105600	3.17686100	-2.31322400

CA2x

E(RmPW+HF-B95)= -1610.65137259 a.u.

C	-4.52700300	-0.61676000	1.59617200
C	-3.15685600	-0.71458200	-0.24071800
C	-4.23942500	-1.03788300	-1.05054800
C	-5.49827200	-1.13517900	-0.49828100
C	-5.65211300	-0.91751400	0.86085300
H	-4.59678900	-0.44930500	2.66149600
H	-4.08006000	-1.20806300	-2.10460200
H	-6.34920800	-1.38103100	-1.11543700
H	-6.61554700	-0.98573500	1.33926300
N	-3.31050500	-0.51609200	1.06709000
C	-1.77666600	-0.53898000	-0.83025700
H	-1.71492200	-1.26960900	-1.65624400
N	-0.74551200	-0.67195100	0.15150200
C	0.28020500	0.24716900	-0.20319900
P	1.07975500	0.61327500	1.37536200
O	0.07820200	0.77848100	2.47298500
O	1.97478100	1.88926700	1.08623000
O	2.19632500	-0.45805100	1.74295300



C	2.69422900	2.51419400	2.14057800
H	3.46014000	1.84485600	2.52095900
H	3.15571000	3.39913000	1.72052900
H	2.01894600	2.79864200	2.94195900
C	1.81610600	-1.75887000	2.17605100
H	2.73434300	-2.31660000	2.31424300
H	1.27498800	-1.69406500	3.11652600
H	1.20511700	-2.24016700	1.41778900
C	1.28348800	-0.17290800	-1.30736300
H	0.73575800	-0.13474400	-2.24956700
H	2.06814300	0.57830900	-1.39264500
C	1.88641100	-1.53120000	-1.14395100
C	1.11102500	-2.67414900	-1.30533600
C	3.23268100	-1.68800200	-0.84162600
C	1.66090600	-3.93393500	-1.14379300
H	0.06610000	-2.56753000	-1.55175200
C	3.78856800	-2.94528500	-0.68038400
H	3.84937200	-0.80944200	-0.71561700
C	3.00157800	-4.07460800	-0.82593900
H	1.04129300	-4.80958500	-1.27042200
H	4.83763400	-3.04220700	-0.44243500
H	3.43116500	-5.05743200	-0.70083600
Li	-1.44701100	-0.30051300	1.93021400
C	-0.52323800	1.51930500	-0.64270900
H	-0.94731400	1.95696500	0.25827900
C	-1.61883800	0.87135600	-1.47423500
H	-1.29890700	0.79753000	-2.51138700
H	-2.53777900	1.45256200	-1.45485500
C	0.20838000	2.59198000	-1.38402900

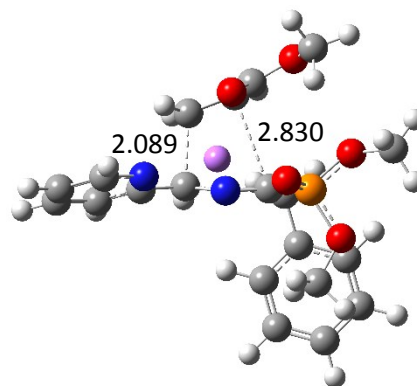
O	0.67633500	2.48279800	-2.48987700
O	0.27878800	3.72141400	-0.68770000
C	0.97957200	4.77877400	-1.31557500
H	0.53252800	5.01588300	-2.27584400
H	0.90658900	5.62517600	-0.64479300
H	2.01966600	4.50637000	-1.46681400

TS2n

E(RmPW+HF-B95)= -1610.62520083 a.u.

1 imaginary frequency= -378.6 cm⁻¹

C	-4.33820900	-0.91657500	1.52765200
C	-2.76651300	-1.48950400	-0.04257000
C	-3.54273200	-2.56838900	-0.45577000
C	-4.74706000	-2.81078600	0.16758600
C	-5.16051500	-1.97280100	1.18979800
H	-4.62539800	-0.22959400	2.31139000
H	-3.18779000	-3.20824500	-1.24899100
H	-5.35702100	-3.64856200	-0.13513600
H	-6.09340700	-2.12636000	1.70690500
N	-3.17997600	-0.66600000	0.93268000
C	-1.51150600	-1.14385100	-0.69981200
H	-1.13789300	-1.84995200	-1.43288800
N	-0.67480100	-0.41079400	0.04503900
C	0.48155300	0.03349200	-0.33354000
P	1.15389400	1.09765300	0.91555900
O	0.11924700	1.49758700	1.90903700
O	1.85424700	2.27253600	0.11469500
O	2.44350400	0.44618600	1.59796700



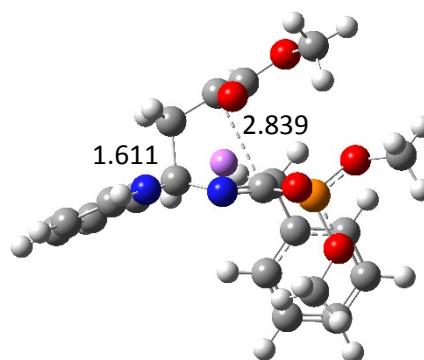
C	2.61186800	3.25109500	0.81334400
H	3.49254800	2.79601900	1.25588200
H	2.90545900	3.99526400	0.08344600
H	2.00803500	3.71803400	1.58682700
C	2.29876500	-0.73917800	2.36420300
H	3.25431000	-0.92239100	2.84035500
H	1.53079400	-0.61323300	3.12282200
H	2.05117200	-1.57594600	1.71408500
C	1.30401300	-0.44256100	-1.50014100
H	0.63191700	-0.83136300	-2.26385400
H	1.82569200	0.40535000	-1.93911300
C	2.30125800	-1.48824300	-1.07953800
C	1.90232700	-2.79708300	-0.83410600
C	3.62914100	-1.14778000	-0.86210700
C	2.80719200	-3.73919700	-0.37850900
H	0.87191800	-3.08002600	-0.99659000
C	4.53699900	-2.08626200	-0.40378400
H	3.95048100	-0.13190300	-1.04310300
C	4.12840000	-3.38532900	-0.15862000
H	2.48033600	-4.75187500	-0.19550300
H	5.56548600	-1.80176600	-0.23930700
H	4.83490200	-4.11962000	0.19766400
Li	-1.71791000	0.89706000	1.22430100
C	-1.24756400	1.36759700	-2.13404700
H	-0.52639400	1.45362600	-2.92980500
C	-2.14593000	0.32416500	-2.04443600
H	-2.26720200	-0.34024800	-2.88769300
H	-3.03979200	0.49086300	-1.46015700
C	-1.29915300	2.38001900	-1.14335400

O	-1.97880600	2.33160900	-0.11095500
O	-0.55888000	3.46133200	-1.41433400
C	-0.54077400	4.45819900	-0.41725300
H	-0.32339700	4.02736200	0.55458400
H	0.23698300	5.15626600	-0.70496300
H	-1.49683100	4.97370100	-0.36844400

IN2n

E(RmPW+HF-B95)= -1610.63602155 a.u.

C	-4.41377700	-0.80148900	1.44810700
C	-2.92977500	-1.27139600	-0.22559400
C	-3.64926900	-2.39293400	-0.59711300
C	-4.79679700	-2.71439200	0.10260900
C	-5.19071900	-1.90521300	1.15040200
H	-4.68807300	-0.14066800	2.25791700
H	-3.30727100	-3.00470800	-1.41749700
H	-5.37212400	-3.58769000	-0.16440100
H	-6.07642500	-2.11828700	1.72642600
N	-3.31279900	-0.48378200	0.78185900
C	-1.71107500	-0.81343700	-0.96926900
H	-1.29902800	-1.62513600	-1.56878500
N	-0.79759000	-0.29848400	-0.02197900
C	0.39964800	0.00533700	-0.31620600
P	1.13917200	0.86312800	1.09189500
O	0.09900700	1.39927600	2.00352200
O	2.12051000	1.89866800	0.41850500
O	2.16879400	-0.10185700	1.82772300
C	2.86383700	2.80623400	1.22673000



H	3.57687300	2.26238200	1.83829100
H	3.38667700	3.46619300	0.54678600
H	2.19398300	3.38311200	1.85723600
C	1.67210800	-1.15080100	2.64732400
H	2.51958900	-1.54817800	3.19166300
H	0.92932900	-0.77092100	3.34245000
H	1.23987400	-1.93310800	2.02800300
C	1.22953600	-0.36587800	-1.51063300
H	0.58172300	-0.76560200	-2.28699700
H	1.67996600	0.53922000	-1.90892700
C	2.30058500	-1.35442100	-1.13524000
C	1.96325300	-2.66642300	-0.82575100
C	3.63058600	-0.96947600	-1.06064800
C	2.93729700	-3.57796900	-0.46113300
H	0.92853000	-2.97794900	-0.87678000
C	4.60793800	-1.87904400	-0.69513400
H	3.89909700	0.05250600	-1.28790100
C	4.26396300	-3.18564100	-0.39566000
H	2.66163800	-4.59599700	-0.23048900
H	5.63988500	-1.56581600	-0.64486700
H	5.02600300	-3.89590400	-0.11293100
Li	-1.78114600	1.10669900	1.15879200
C	-1.18210000	1.45702100	-2.17411000
H	-0.56296300	1.51127200	-3.05377600
C	-2.15012700	0.37458100	-1.96513200
H	-2.42897100	-0.11857900	-2.89434900
H	-3.05748700	0.77783300	-1.51593600
C	-1.12376600	2.43725300	-1.21823800
O	-1.79211100	2.45973600	-0.14716400

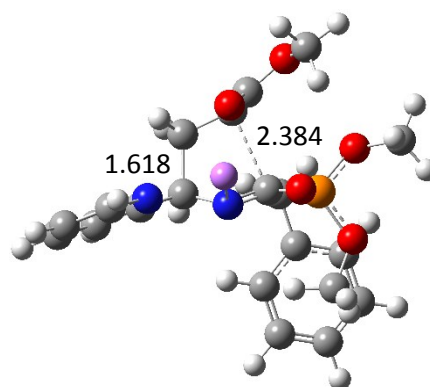
O	-0.26890800	3.47263300	-1.46626300
C	-0.16711700	4.42962900	-0.44589400
H	0.07197400	3.96908000	0.50903900
H	0.63176900	5.10242800	-0.74206800
H	-1.08969000	4.99645600	-0.33314700

TS22n

E(RmPW+HF-B95)= -1610.63451015 a.u.

1 imaginary frequency= -167.5 cm⁻¹

C	-4.36519500	-0.81877000	1.46115300
C	-2.83483400	-1.34496500	-0.15504300
C	-3.59001400	-2.43136300	-0.56138600
C	-4.77892700	-2.70413400	0.08740600
C	-5.17948700	-1.88281500	1.12349600
H	-4.64132500	-0.15057300	2.26433000
H	-3.24269200	-3.05394200	-1.37139000
H	-5.38195500	-3.54862500	-0.20956300
H	-6.09783800	-2.05696300	1.66018900
N	-3.22429000	-0.54867200	0.84226600
C	-1.56589000	-0.94534200	-0.84578100
H	-1.17566400	-1.78917000	-1.41900100
N	-0.67031600	-0.40822200	0.09646400
C	0.41702700	0.10260500	-0.39728300
P	1.19831300	1.10633600	0.87734400
O	0.21865100	1.53061900	1.91049300
O	1.93974500	2.25455900	0.08358300
O	2.45092800	0.32381600	1.47462900
C	2.71160900	3.21879900	0.78814100



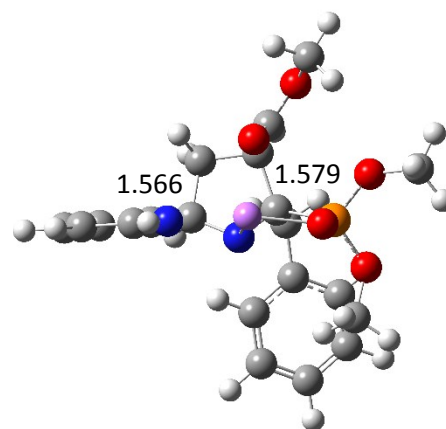
H	3.62579600	2.76518800	1.15840900
H	2.94665400	4.00391300	0.08051200
H	2.14202800	3.63296300	1.61546800
C	2.24316600	-0.82493900	2.28522300
H	3.06528200	-1.50332500	2.08478900
H	2.23610000	-0.53426300	3.33090300
H	1.30853300	-1.32083800	2.03468800
C	1.27154900	-0.46183200	-1.51154000
H	0.61865100	-0.84328500	-2.29446000
H	1.85962700	0.34007000	-1.94986500
C	2.18172800	-1.55560000	-1.01626700
C	1.65671700	-2.74664300	-0.52873200
C	3.55984000	-1.39346300	-1.02212600
C	2.48675500	-3.74945200	-0.06133500
H	0.58560800	-2.88645500	-0.50563900
C	4.39497200	-2.39330100	-0.55317900
H	3.98268300	-0.47089800	-1.39356400
C	3.86083400	-3.57578000	-0.07107900
H	2.05979300	-4.66839600	0.31166000
H	5.46475800	-2.24775700	-0.56632400
H	4.51030100	-4.35751900	0.29281100
Li	-1.67866800	0.93055200	1.24113000
C	-0.88388600	1.31989100	-1.92653600
H	-0.25814800	1.48002900	-2.78925000
C	-1.88129500	0.23739500	-1.90472700
H	-1.99730500	-0.22646000	-2.88115000
H	-2.84774900	0.63556500	-1.59880900
C	-1.11616500	2.39537600	-1.06467100
O	-1.87195700	2.35699300	-0.07566400
O	-0.44034800	3.52686200	-1.34647600

C	-0.48292800	4.52258300	-0.35299300
H	-0.16220600	4.12579700	0.60643600
H	0.19714100	5.30186900	-0.67940600
H	-1.48413200	4.93234700	-0.24538200

CA2n

E(RmPW+HF-B95)= -1610.65732724 a.u.

C	-4.10166900	-1.30007400	1.59979600
C	-2.61736000	-1.64233800	-0.11154200
C	-3.42112700	-2.64766700	-0.63298200
C	-4.60586900	-2.96754400	-0.00160400
C	-4.96082700	-2.27813600	1.14405200
H	-4.33473600	-0.74032900	2.49470200
H	-3.10736800	-3.17049500	-1.52376300
H	-5.24138700	-3.74718600	-0.39374300
H	-5.87392200	-2.49437400	1.67464200
N	-2.96284600	-0.98650800	0.99515500
C	-1.33591000	-1.22364300	-0.79229900
H	-0.97695800	-2.11455300	-1.33963900
N	-0.40646900	-0.68407400	0.14112800
C	0.37874900	0.24507700	-0.57322200
P	1.08564100	1.28601300	0.74224500
O	0.16455000	1.47028600	1.89896900
O	1.47684600	2.62686800	-0.02007300
O	2.51850500	0.77431200	1.20343700
C	2.04371700	3.70888000	0.70598600
H	3.01496700	3.42682400	1.10155300
H	2.15541500	4.52911200	0.00782500
H	1.38676700	4.00548700	1.51866100



C	2.64319300	-0.23567900	2.19722800
H	3.63635100	-0.13560200	2.61874400
H	1.89665800	-0.09385700	2.97266400
H	2.53246100	-1.21455100	1.74087600
C	1.47726300	-0.29034300	-1.54477900
H	0.93378000	-0.73106100	-2.38416900
H	2.03480800	0.55551100	-1.94863900
C	2.42358600	-1.30925600	-0.99826100
C	1.97283200	-2.56745200	-0.61554000
C	3.77777100	-1.02720700	-0.86789100
C	2.84834500	-3.50577000	-0.09474000
H	0.92570500	-2.80373500	-0.71780900
C	4.65641300	-1.96109500	-0.34896000
H	4.14273800	-0.05328500	-1.16130800
C	4.19244400	-3.20461200	0.04558500
H	2.47856900	-4.47647600	0.20113900
H	5.70406000	-1.71731200	-0.25202500
H	4.87460500	-3.93612900	0.45246300
Li	-1.45400500	0.41518500	1.41966900
C	-0.62902700	1.01542300	-1.51476500
H	-0.13410500	1.45012300	-2.37779700
C	-1.58569500	-0.12374900	-1.87920100
H	-1.36582000	-0.49777400	-2.87625600
H	-2.62079900	0.20976500	-1.88111100
C	-1.38172800	2.08711600	-0.80852300
O	-2.07571600	1.89970900	0.16982600
O	-1.24741200	3.27736400	-1.35876900
C	-1.91839500	4.34203200	-0.70343200
H	-1.51569700	4.47629200	0.29538400
H	-1.73583300	5.22173000	-1.30629400

H -2.98207600 4.13810300 -0.63932400