Supporting Information

The potential of pnicogen bonding for catalysis – A computational study

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1 Computational Details

For the computational investigations, the conformational space for each structure was explored using the OPLS-2005 force field[S1] and a modified Monte Carlo search algorithm implemented in MacroModel 10.6.[S2] An energy cut-off of 20 kcal mol^{-1} was employed for the conformational analysis, and structures with heavy-atom root-mean-square deviations (RMSD) up to 1.0 Å after the initial force field optimizations were considered to be the same conformer. The remaining structures were subsequently optimized with the dispersion-corrected M06-2X functional[S3] with Grimme's dispersion correction D3 (zero-damping),[S4] the triple-z basis set 6-311+G(d,p) and the integral equation formalism polarizable continuum model (IEFPCM)[S5] for dichloromethane. Vibrational analysis verified that each structure was a minimum or transition state. Thermal corrections were obtained from unscaled harmonic vibrational frequencies at the same level of theory for a standard state of 1 mol L^{-1} and 298.15 K. Entropic contributions to the reported free energies were derived from partition functions evaluated with the quasiharmonic approximation by Truhlar and coworkers.[S6] Electronic energies were subsequently obtained from single point calculations of the M06-2X-D3 geometries employing the meta-hybrid M06-2X functional, Grimme's dispersion-correction D3 (zero-damping), the large quadruple-z basis set def2-QZVP,[S7] and the integral equation formalism polarizable continuum model (IEFPCM) for dichloromethane, a level expected to give accurate energies. An ultrafine grid was used throughout this study for numerical integration of the density. All density functional theory calculations were performed with Gaussian 09[S8] and natural population analysis used the NBO 6.0 program[S9] in combination with Gaussian 09.

2 Validation of the computational method

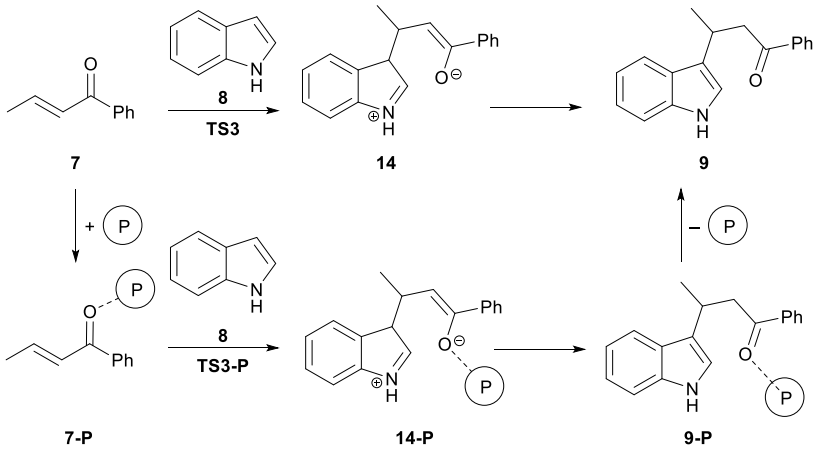

Table S1. Comparison of the calculated free-energies of M062X-D3/def2-QZVP/IEFPCM//M062X-D3/6-311+G(d,p)/IEFPCM with B3LYP-D3BJ/6-311+G(d,p)/IEFPCM and ωB97XD/6-311+G(d,p)/IEFPCM.

Method	7 + 8	7-P14	7-P15	TS3	TS3-P14	TS3-P15	14	14-P14	14-P15	9	9-P14	P-P15
M062X-D3	0.0	–26.7	–9.6	+37.7	–14.8	+6.3	+38.7	–27.9	–6.6	–8.0	–29.4	–17.9
B3LYP-D3BJ	0.0	–23.4	–6.5	-	–13.5	+6.7	+41.6	–21.3	–3.0	–6.4	–24.6	–13.8
ωB97XD	0.0	–22.0	–5.3	-	–8.8	+10.9	+39.8	–24.5	–5.4	–10.7	–29.7	–16.8

Table S2. RMSD-values of all structures calculated with B3LYP-D3BJ/6-311+G(d,p)/IEFPCM and ωB97XD/6-311+G(d,p)/IEFPCM in comparison with M062X-D3/6-311+G(d,p)/IEFPCM.

Method	7	8	P14	P15	7-P14	7-P15	TS3	TS3-P14	TS3-P15	14	14-P14	14-P15	9	9-P14	P-P15
B3LYP-D3BJ	0.05	0.01	0.00	0.01	0.06	0.91	-	0.08	1.42	3.02	2.75	3.34	0.50	0.05	1.63
ωB97XD	0.02	0.00	0.00	0.00	0.04	0.08	-	0.49	1.37	2.98	2.74	3.33	0.04	0.09	1.63

3 Energy Profile for the exo-Diels-Alder-Reaction

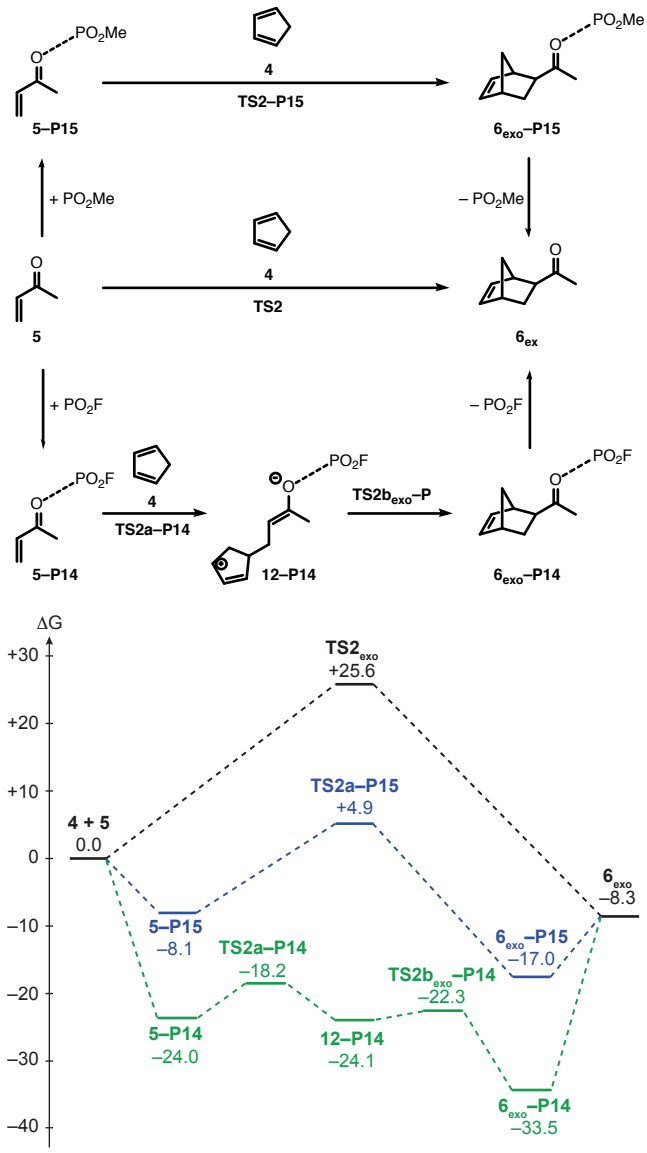

Figure S1: Gibbs free energy profile for the exo-Diels-Alder reaction between cyclopentadiene (4) and methyl vinyl ketone (5).

4 Energies and geometries for the CCSD(T) comparison

4.1 CCSD(T) Reference Calculations

General

All CCSD(T) calculations were performed employing the triple-ζ basis set aug-cc-pVTZ using MOLPRO2015.[S10 S11]

Ethyne

SCF energy: –77.19219737 hartree

Cartesian Coordinates

C	-0.8300039956	-0.1886792400	0.0000000000
H	-1.8939611404	-0.1886792400	0.0000000000
C	0.3802607156	-0.1886792400	0.0000000000
H	1.4442178604	-0.1886792400	0.0000000000

Formaldehyde

SCF energy: –114.34293364 hartree

Cartesian Coordinates

O	0.0000000000	-2.3181262540	0.1515595596
C	0.0000000000	-3.0057484799	1.1491099498
H	0.0000000000	-2.5622690060	2.1590923308
H	0.0000000000	-4.1074262602	1.0939681598

PFH_2

SCF energy: –441.86185998 hartree

Cartesian Coordinates

P	-1.0168526503	0.1128384837	0.0320369472
H	-0.2694603299	-1.0970789837	-0.0144705860
H	-0.2694384868	0.6775071248	-1.0390279199
F	-0.2084604029	0.8160667152	1.2500806386

PO_2F

SCF energy: –590.98744811 hartree

Cartesian Coordinates

P	0.1487321700	-0.0533366736	1.0269703695
F	0.1487321700	-0.1245689245	2.5758828347
O	1.5036608419	-0.0279271409	0.4772798179
O	-1.2061965019	-0.0279271409	0.4772798179

PFH_2-Ethyne Complex

SCF energy: –519.05985477 hartree

Cartesian Coordinates

C	-2.3951379409	0.6133110013	-0.0000456987
H	-2.4744189447	1.6752447984	-0.0000642510
C	-2.3138317708	-0.5954626085	-0.0002623286
H	-2.2558086774	-1.6587521134	0.0003292823
P	0.7637194360	-0.1798120396	0.0000188470
H	0.4005464582	0.7299687491	-1.0290355843
H	0.4005015638	0.7300881586	1.0289341843
F	2.3626158757	0.1249920540	-0.0001354509

PH_2F-Formaldehyde Complex

SCF energy: –556.21367171 hartree

Cartesian Coordinates

P	-5.5999328619	0.9579504495	-0.3758270415
H	-5.0293020812	1.0233600269	-1.6728070194
F	-6.0035618000	-0.6229430424	-0.4072557271
H	-6.8470471643	1.4704372857	-0.8164129364
O	-5.1668102706	3.5812619610	-0.8269236289
C	-4.5963127202	4.0611421372	0.1328511631
H	-4.3214727707	5.1265583883	0.1577560093
H	-4.3361833310	3.4453857936	1.0081391809

PO_2F-Formaldehyd Complex

SCF energy: –705.36400951 hartree

Cartesian Coordinates

P	0.5645997309	0.1227558700	0.1162602179
F	0.9115564179	-0.2998733997	-1.3471471186
O	1.2043162584	-0.7444266336	1.1081468180
O	0.1366776112	1.5323010022	0.1723800390
O	-1.1709782273	-0.7413178095	-0.0696306156

C	-2.1615660314	-0.0219425917	0.0726981541
H	-2.0305246700	1.0509972705	0.2398999653
H	-3.1455240899	-0.4906767084	0.0254315398

4.2 M062X Calculations

Ethyne

SCF energy:	–77.335577 hartree
Zero-point correction:	+0.027503 hartree
Enthalpy correction:	+0.031172 hartree
Free energy correction:	+0.008580 hartree
Quasiharmonic free energy correction:	+0.008580 hartree

Cartesian Coordinates

C	0.00000	0.00000	0.59924
H	0.00000	0.00000	1.66541
C	0.00000	0.00000	-0.59924
H	0.00000	0.00000	-1.66541

Formaldehyde

SCF energy:	–114.513576 hartree
Zero-point correction:	+0.027135 hartree
Enthalpy correction:	+0.030945 hartree
Free energy correction:	+0.005483 hartree
Quasiharmonic free energy correction:	+0.005483 hartree

Cartesian Coordinates

O	-0.00000	0.67317	0.00000
C	-0.00000	-0.52860	-0.00000
H	-0.93830	-1.10688	-0.00000
H	0.93832	-1.10685	-0.00000

PFH_2

SCF energy:	–442.423067 hartree
Zero-point correction:	+0.019903 hartree
Enthalpy correction:	+0.023880 hartree
Free energy correction:	–0.003820 hartree
Quasiharmonic free energy correction:	–0.003820 hartree

Cartesian Coordinates

P	-0.07377	-0.55794	-0.00000
H	0.88520	-0.72147	1.02771
H	0.88520	-0.72147	-1.02771
F	-0.07377	1.09023	0.00000

PO_2F

SCF energy:	–591.762320 hartree
Zero-point correction:	+0.011060 hartree
Enthalpy correction:	+0.015791 hartree
Free energy correction:	–0.015701 hartree
Quasiharmonic free energy correction:	–0.015701 hartree

Cartesian Coordinates

P	0.00000	0.13085	-0.00000
F	-0.00000	-1.42179	0.00000
O	0.00000	0.67708	1.34213
O	0.00000	0.67708	-1.34213

PFH_2-Ethyne-Complex

SCF energy:	–519.764305 hartree
Zero-point correction:	+0.048996 hartree
Enthalpy correction:	+0.056691 hartree
Free energy correction:	+0.018322 hartree
Quasiharmonic free energy correction:	+0.018322 hartree

Cartesian Coordinates

C	-2.34357	0.63517	0.00338
H	-2.34548	1.70202	0.00554
C	-2.35241	-0.56467	0.00065
H	-2.37669	-1.63110	-0.00154
P	0.73150	-0.20488	-0.01236
H	0.38162	0.75865	-0.98601
H	0.38256	0.63258	1.07185
F	2.35126	0.13200	0.00793

PH_2F-Formaldehyde-Complex

SCF energy:	–556.944310 hartree
Zero-point correction:	+0.049266 hartree
Enthalpy correction:	+0.057175 hartree
Free energy correction:	+0.017997 hartree
Quasiharmonic free energy correction:	+0.018688 hartree

Cartesian Coordinates

P	0.78106	0.09353	-0.00019
H	0.63354	-0.85908	-1.03147
F	2.44463	0.08675	0.00009
H	0.63334	-0.85796	1.03210
O	-1.75654	-0.54793	0.00020
C	-2.52581	0.37981	-0.00000
H	-3.61320	0.21799	0.00009
H	-2.16408	1.41994	-0.00027

PO_2F-Formaldehyde Complex

SCF energy:	–706.323113 hartree
Zero-point correction:	+0.042991 hartree
Enthalpy correction:	+0.050191 hartree
Free energy correction:	+0.012730 hartree
Quasiharmonic free energy correction:	+0.012730 hartree

Cartesian Coordinates

P	-0.52963	0.11792	-0.11481
F	-0.88856	-0.34800	1.34857
O	-1.22517	-0.70076	-1.10516
O	-0.18525	1.54321	-0.13143
O	1.12884	-0.70109	0.00184
C	2.16226	-0.03989	-0.06061
H	2.11151	1.04769	-0.15413
H	3.10905	-0.57603	-0.01907

5 Energies and Geometries for all Phosphorous Compounds

P1

SCF energy:	–568.963242 hartree
Zero-point correction:	+0.042819 hartree
Enthalpy correction:	+0.049494 hartree
Free energy correction:	+0.014291 hartree
Quasiharmonic free energy correction:	+0.014291 hartree

Cartesian Coordinates

P	-0.02113	-0.02615	-0.53501
O	0.39186	1.33141	0.31883
O	-1.42089	-0.42167	0.22072
O	1.07697	-0.99562	0.18725
H	0.07774	2.15267	-0.07477
H	1.28718	-0.77281	1.10505
H	-1.43152	-0.30057	1.18056

P2

SCF energy:	–461.092918 hartree
Zero-point correction:	+0.113162 hartree

Enthalpy correction:	+0.120736 hartree
Free energy correction:	+0.083959 hartree
Quasiharmonic free energy correction:	+0.083959 hartree

Cartesian Coordinates

P	0.00001	-0.00005	-0.60619
C	-0.89957	-1.35236	0.28003
C	1.62107	-0.10276	0.28001
C	-0.72151	1.45520	0.27999
H	2.13721	-1.02087	-0.00660
H	1.48456	-0.09362	1.36484
H	2.24958	0.74220	-0.00730
H	-1.76752	1.57689	-0.00731
H	-0.18464	2.36127	-0.00684
H	-0.66108	1.33251	1.36483
H	-0.48148	-2.31904	-0.00668
H	-1.95262	-1.34095	-0.00713
H	-0.82400	-1.23813	1.36483

P3

SCF energy:	–641.060614 hartree
Zero-point correction:	+0.008226 hartree
Enthalpy correction:	+0.013225 hartree
Free energy correction:	–0.018949 hartree
Quasiharmonic free energy correction:	–0.018949 hartree

Cartesian Coordinates

P	-0.00015	0.00005	-0.52403
F	0.83650	1.08567	0.29109
F	-1.35877	0.18118	0.29123
F	0.52251	-1.26693	0.29106

P4

SCF energy:	–619.886337 hartree
Zero-point correction:	+0.026579 hartree
Enthalpy correction:	+0.034935 hartree
Free energy correction:	–0.005746 hartree
Quasiharmonic free energy correction:	–0.005746 hartree

Cartesian Coordinates

P	-0.00003	-0.00007	0.84960
C	-1.12452	1.05988	-0.07217
C	1.48053	0.44403	-0.07175
C	-0.35541	-1.50320	-0.07296
N	-1.88612	1.77887	-0.54493
N	2.48392	0.74325	-0.54521
N	-0.59826	-2.52257	-0.54452

P5

SCF energy:	–497.041903 hartree
Zero-point correction:	+0.089453 hartree
Enthalpy correction:	+0.096962 hartree
Free energy correction:	+0.060079 hartree
Quasiharmonic free energy correction:	+0.060079 hartree

Cartesian Coordinates

P	0.00002	0.09931	-0.56117
C	1.38989	-0.79930	0.23494
O	0.00058	1.46624	0.42171
C	-1.39059	-0.79807	0.23494
H	-1.41159	-1.82631	-0.13352
H	-1.27242	-0.80529	1.32108
H	1.40960	-1.82783	-0.13276
H	1.27200	-0.80556	1.32112
H	-2.33581	-0.31973	-0.02407
H	2.33558	-0.32222	-0.02466
H	0.00190	2.27157	-0.10259

P6

SCF energy:	–536.334116 hartree
Zero-point correction:	+0.118167 hartree
Enthalpy correction:	+0.127017 hartree
Free energy correction:	+0.086313 hartree
Quasiharmonic free energy correction:	+0.086803 hartree

Cartesian Coordinates

P	-0.36179	-0.01937	-0.55849
C	-1.62125	-1.09140	0.22993
O	0.91765	-0.49641	0.42009
C	-0.80460	1.57860	0.24614
C	2.21555	-0.08487	0.01226
H	2.93129	-0.55779	0.68315
H	2.32826	1.00162	0.08497
H	2.42376	-0.39677	-1.01577
H	-0.04005	2.32784	0.03368
H	-1.74969	1.93694	-0.16927
H	-1.45042	-2.13082	-0.05128
H	-2.61127	-0.79453	-0.12278
H	-0.90517	1.45650	1.32701
H	-1.57927	-0.99516	1.31701

P7

SCF energy:	–686.842025 hartree
Zero-point correction:	+0.129488 hartree

Enthalpy correction:	+0.140592 hartree
Free energy correction:	+0.093145 hartree
Quasiharmonic free energy correction:	+0.094384 hartree

Cartesian Coordinates

P	0.00650	-0.45604	-0.56769
O	-1.17856	-0.70360	0.54377
O	1.19350	-0.68663	0.54483
O	-0.00679	1.17528	-0.71517
C	-2.52566	-0.60245	0.07834
C	-0.03066	2.03588	0.43103
C	2.54026	-0.57306	0.08138
H	3.18313	-0.90821	0.89189
H	2.77747	0.46522	-0.16443
H	2.70905	-1.20112	-0.79754
H	-3.16724	-0.92897	0.89337
H	-2.69126	-1.24346	-0.79173
H	-2.76798	0.43118	-0.18219
H	0.81340	1.82125	1.08866
H	-0.96183	1.90605	0.98511
H	0.03893	3.05600	0.06036

P8

SCF energy:	–536.387507 hartree
Zero-point correction:	+0.117631 hartree
Enthalpy correction:	+0.126115 hartree
Free energy correction:	+0.086980 hartree
Quasiharmonic free energy correction:	+0.086980 hartree

Cartesian Coordinates

P	-0.00014	-0.00007	0.16911
C	1.18351	-1.17122	-0.54483
C	-1.60604	-0.43841	-0.54608
C	0.42360	1.61016	-0.54460
H	-1.88775	-1.43581	-0.20555
H	-1.56254	-0.42602	-1.63638
H	-2.35554	0.27710	-0.20490
H	1.41780	1.90108	-0.20245
H	-0.29968	2.35268	-0.20453
H	0.41346	1.56605	-1.63489
H	0.93691	-2.17868	-0.20663
H	2.18731	-0.91785	-0.20085
H	1.15432	-1.13695	-1.63514
O	-0.00107	-0.00047	1.67597

P9

SCF energy:	–572.348780 hartree
Zero-point correction:	+0.094693 hartree
Enthalpy correction:	+0.102775 hartree

Free energy correction:	+0.064488 hartree
Quasiharmonic free energy correction:	+0.064488 hartree

Cartesian Coordinates

P	0.00700	-0.08870	0.12462
C	1.40480	1.00931	-0.17163
O	0.13066	-0.87025	1.39002
O	-0.09415	-1.01668	-1.20630
H	2.32237	0.41911	-0.18132
H	1.46371	1.74093	0.63505
H	1.29248	1.52360	-1.12643
H	0.50219	-1.77498	-1.19516
C	-1.49850	0.87629	-0.04034
H	-2.35500	0.21038	0.06815
H	-1.53484	1.36347	-1.01494
H	-1.52577	1.62972	0.74732

P10

SCF energy:	–611.641988 hartree
Zero-point correction:	+0.123587 hartree
Enthalpy correction:	+0.133144 hartree
Free energy correction:	+0.090662 hartree
Quasiharmonic free energy correction:	+0.091206 hartree

Cartesian Coordinates

P	0.37187	0.00101	0.16753
C	1.65833	-1.00598	-0.57747
O	0.30900	-0.04241	1.65894
O	-0.93921	-0.61498	-0.55889
H	1.52624	-2.03834	-0.25253
H	2.63096	-0.64457	-0.24228
H	1.60167	-0.95374	-1.66479
C	-2.23557	-0.16966	-0.14324
H	-2.96081	-0.79278	-0.66036
H	-2.39074	0.87485	-0.42349
H	-2.35018	-0.28549	0.93539
C	0.52958	1.67812	-0.47983
H	0.50870	1.67353	-1.57008
H	1.47188	2.10375	-0.13276
H	-0.28805	2.29182	-0.09917

P11

SCF energy:	–608.311338 hartree
Zero-point correction:	+0.071607 hartree
Enthalpy correction:	+0.079312 hartree
Free energy correction:	+0.041603 hartree
Quasiharmonic free energy correction:	+0.041603 hartree

Cartesian Coordinates

P	-0.05161	0.12393	-0.00000
O	-0.53816	-0.72037	1.28096
O	-0.53816	1.52361	-0.00000
O	-0.53816	-0.72037	-1.28096
H	-1.36467	-0.40593	1.66751
H	-1.36467	-0.40593	-1.66751
C	1.70625	-0.17109	0.00000
H	1.89950	-1.24375	0.00000
H	2.14112	0.28014	0.89098
H	2.14112	0.28014	-0.89098

P12

SCF energy:	–686.896157 hartree
Zero-point correction:	+0.129350 hartree
Enthalpy correction:	+0.140079 hartree
Free energy correction:	+0.093854 hartree
Quasiharmonic free energy correction:	+0.095163 hartree

Cartesian Coordinates

P	-0.03395	-0.43242	-0.17555
O	1.42809	0.01323	-0.63107
O	-0.64720	-1.37956	-1.13095
O	-0.76826	0.99424	-0.07526
C	2.18587	0.99747	0.08861
H	2.49707	0.60113	1.05667
H	1.59676	1.90515	0.22147
H	3.06406	1.20986	-0.51492
C	-2.18538	1.04918	0.14052
H	-2.70599	0.47454	-0.62619
H	-2.43591	0.66475	1.13157
H	-2.46872	2.09616	0.07579
C	0.08911	-1.04062	1.50978
H	-0.90221	-1.33628	1.85516
H	0.48582	-0.27306	2.17481
H	0.73978	-1.91539	1.52367

P13

SCF energy:	–762.151241 hartree
Zero-point correction:	+0.135173 hartree
Enthalpy correction:	+0.147103 hartree
Free energy correction:	+0.097067 hartree
Quasiharmonic free energy correction:	+0.098846 hartree

Cartesian Coordinates

P	0.00023	-0.00038	0.11856
O	-0.76628	-1.21021	-0.56307

O	0.00199	0.00028	1.59486
O	-0.66508	1.26735	-0.56401
C	-2.06546	-1.58850	-0.07275
H	-2.77690	-0.77944	-0.24307
H	-2.00932	-1.82604	0.98943
H	-2.36054	-2.46666	-0.63964
C	-0.34531	2.58193	-0.07307
H	-0.58005	2.65139	0.98891
H	0.71094	2.79505	-0.24226
H	-0.95866	3.27596	-0.64026
O	1.42983	-0.05951	-0.56586
C	2.40990	-0.99128	-0.07315
H	3.31405	-0.81373	-0.64812
H	2.06374	-2.01359	-0.23085
H	2.59485	-0.81344	0.98603

P14

SCF energy:	–591.762313 hartree
Zero-point correction:	+0.011062 hartree
Enthalpy correction:	+0.015792 hartree
Free energy correction:	–0.015045 hartree
Quasiharmonic free energy correction:	–0.015045 hartree

Cartesian Coordinates

P	0.00000	-0.00000	0.13127
F	-0.00000	0.00000	-1.42157
O	0.00000	1.34238	0.67656
O	-0.00000	-1.34238	0.67656

P15

SCF energy:	–531.797652 hartree
Zero-point correction:	+0.045514 hartree
Enthalpy correction:	+0.051460 hartree
Free energy correction:	+0.016745 hartree
Quasiharmonic free energy correction:	+0.017690 hartree

Cartesian Coordinates

P	0.17822	0.00219	-0.00170
O	0.74166	1.35439	0.00107
O	0.86927	-1.28931	0.00111
C	-1.61291	-0.06351	-0.00074
H	-1.96414	0.38732	0.92846
H	-1.97567	0.53557	-0.83588
H	-1.94348	-1.09524	-0.08000

Acetophenone (10)

SCF energy:	–384.910825 hartree
Zero-point correction:	+0.138630 hartree
Enthalpy correction:	+0.147391 hartree
Free energy correction:	+0.105709 hartree
Quasiharmonic free energy correction:	+0.106429 hartree

Cartesian Coordinates

O	-2.20981	-1.30395	0.00018
C	-1.69637	-0.20424	-0.00000
C	-0.20302	-0.06324	-0.00003
C	0.42011	1.18688	0.00003
C	1.80864	1.27637	0.00008
C	2.58015	0.11848	0.00002
C	0.57907	-1.22193	-0.00009
H	-0.16949	2.09560	0.00008
H	2.28639	2.24849	0.00015
C	1.96383	-1.13229	-0.00007
H	3.66149	0.18910	0.00006
H	2.56525	-2.03334	-0.00011
H	0.08369	-2.18517	-0.00015
C	-2.53903	1.04703	-0.00012
H	-2.31955	1.65344	-0.88175
H	-2.31956	1.65359	0.88142
H	-3.58993	0.76748	-0.00006

Imine 11

SCF energy:	–365.011200 hartree
Zero-point correction:	+0.151028 hartree
Enthalpy correction:	+0.159979 hartree
Free energy correction:	+0.118135 hartree
Quasiharmonic free energy correction:	+0.118353 hartree

Cartesian Coordinates

N	2.28918	-0.43573	-0.00011
C	3.68337	-0.03401	-0.00001
C	1.41558	0.47965	0.00006
C	-0.03643	0.20600	0.00004
C	-0.53415	-1.10115	0.00005
C	-1.90348	-1.32496	0.00002
C	-2.79097	-0.24758	-0.00003
C	-0.92849	1.27935	0.00000
H	0.16620	-1.92751	0.00008
H	-2.28493	-2.33924	0.00003
C	-2.30241	1.05466	-0.00004
H	-3.85976	-0.42617	-0.00006
H	-2.98807	1.89349	-0.00007
H	-0.54362	2.29407	0.00000
H	4.17628	-0.45630	-0.87850
H	3.81852	1.05420	0.00014
H	4.17622	-0.45654	0.87840
H	1.69677	1.54232	0.00022

6 Energies and Geometries for the Aza-Diels-Alder

6.1 Uncatalysed Aza-Diels-Alder reaction

Butadiene (1)

SCF energy:	–155.985969 hartree
Zero-point correction:	+0.085613 hartree
Enthalpy correction:	+0.091189 hartree
Free energy correction:	+0.059162 hartree
Quasiharmonic free energy correction:	+0.059162 hartree

Cartesian Coordinates

C	-1.83903	-0.11131	-0.00000
C	-0.60862	0.40479	0.00000
C	0.60862	-0.40479	0.00000
C	1.83903	0.11131	-0.00000
H	0.47312	-1.48411	0.00000
H	-0.47313	1.48411	0.00000
H	2.71900	-0.52007	-0.00000
H	1.99613	1.18541	-0.00000
H	-1.99612	-1.18542	-0.00000
H	-2.71901	0.52007	-0.00000

Methanimine (2)

SCF energy:	–94.634120 hartree
Zero-point correction:	+0.040419 hartree
Enthalpy correction:	+0.044279 hartree
Free energy correction:	+0.018513 hartree
Quasiharmonic free energy correction:	+0.018513 hartree

Cartesian Coordinates

H	-0.84757	1.19653	0.00000
C	0.05691	0.58337	0.00000
H	1.00874	1.11414	0.00000
N	0.05691	-0.68192	0.00000
H	-0.90100	-1.03745	0.00000

Uncatalysed Transition State $TS1_{endo}$

SCF energy:	–250.586997 hartree
Zero-point correction:	+0.130288 hartree
Enthalpy correction:	+0.137365 hartree
Free energy correction:	0.100997 hartree
Quasiharmonic free energy correction:	+0.100997 hartree

Imaginary Frequency:	501.2 *i*cm^{-1}

Cartesian Coordinates

C	-1.02130	-1.00012	-0.23080
C	-1.40120	0.35356	-0.33044
C	0.03463	-1.37779	0.58632
N	1.51959	-0.39899	-0.27865
H	0.39415	-2.39938	0.55152
H	0.21697	-0.87799	1.52984
C	1.42363	0.90076	-0.13744
C	-0.82811	1.35128	0.41680
H	-0.40200	1.14707	1.39005
H	-1.07050	2.38877	0.21859
H	1.34507	1.56699	-0.99126
H	1.72517	1.33543	0.81004
H	1.33010	-0.67388	-1.24162
H	-1.37593	-1.69487	-0.98436
H	-2.04602	0.63460	-1.15891

Uncatalysed Transition State TS1$_{exo}$

SCF energy:	–250.582296 hartree
Zero-point correction:	+0.130350 hartree
Enthalpy correction:	+0.137336 hartree
Free energy correction:	+0.101191 hartree
Quasiharmonic free energy correction:	+0.101191 hartree
Imaginary Frequency:	537.3 *i*cm^{-1}

Cartesian Coordinates

C	-1.27522	-0.71980	-0.29803
C	-1.29387	0.68040	-0.19604
C	-0.32953	-1.45347	0.39053
N	1.51343	-0.64834	-0.15756
H	-0.19436	-2.50441	0.16697
H	-0.04038	-1.15933	1.39273
C	1.40036	0.63597	-0.43888
C	-0.38625	1.38854	0.56753
H	0.04129	0.96226	1.46723
H	-0.38685	2.47203	0.52720
H	1.07187	0.90802	-1.43683
H	1.97766	1.38408	0.10030
H	1.97895	-0.75964	0.74365
H	-1.82810	-1.18646	-1.10559
H	-1.90703	1.23197	-0.90344

Uncatalysed Aza-Diels-Alder Product 3

SCF energy:	–250.675791 hartree
Zero-point correction:	+0.136004 hartree

Enthalpy correction:	+0.142244 hartree
Free energy correction:	+0.107610 hartree
Quasiharmonic free energy correction:	+0.107610 hartree

Cartesian Coordinates

C	-0.55273	1.32831	0.06481
C	0.77056	1.23511	-0.04854
C	-1.45365	0.12371	0.07318
N	-0.73515	-1.05915	-0.39650
H	-2.30807	0.30324	-0.58507
H	-1.85828	-0.00860	1.09140
C	0.54060	-1.21614	0.30266
C	1.47935	-0.09160	-0.12258
H	2.36232	-0.07701	0.52315
H	1.83727	-0.26709	-1.14290
H	0.96494	-2.18881	0.04941
H	0.41017	-1.17892	1.39662
H	-1.31074	-1.88088	-0.25240
H	-1.03102	2.29862	0.15526
H	1.37467	2.13717	-0.07715

6.2 Pnicogen-bonded Aza-Diels-Alder reaction with P14

Pnicogen-bonded Imine Complex 2-P14

SCF energy:	–686.477480 hartree
Zero-point correction:	+0.056708 hartree
Enthalpy correction:	+0.063855 hartree
Free energy correction:	+0.026448 hartree
Quasiharmonic free energy correction:	+0.026448 hartree

Cartesian Coordinates

N	1.14383	0.65017	0.00628
C	2.22000	-0.02401	-0.03358
P	-0.50818	-0.10337	-0.12502
O	-0.23965	-1.54762	-0.21432
O	-1.24571	0.75609	-1.06266
F	-0.92826	0.27082	1.36560
H	3.18150	0.47541	-0.00044
H	2.14428	-1.10485	-0.10369
H	1.20722	1.66753	0.06245

Pnicogen-bonded Transition State TS1-P14$_{endo}$

SCF energy:	–842.459394 hartree
Zero-point correction:	+0.145293 hartree
Enthalpy correction:	+0.156792 hartree
Free energy correction:	+0.108710 hartree

Quasiharmonic free energy correction:	+0.109673 hartree
Imaginary Frequency:	298.0 *i*cm^{-1}

Cartesian Coordinates

N	0.15953	-0.35123	-0.90090
C	-0.57274	-1.45652	-0.65902
C	-1.52946	1.71599	0.25527
C	-2.54428	1.01574	-0.29266
H	-1.33621	2.74016	-0.04103
H	-0.90173	1.30974	1.04068
C	-2.75669	-0.37142	-0.01942
C	-1.90089	-1.17230	0.71172
H	-1.14497	-1.84845	-1.48980
H	-0.09307	-2.20184	-0.03166
H	-1.20060	-0.74459	1.42308
H	-2.22088	-2.18724	0.91821
H	-3.19319	1.48695	-1.02161
H	-3.58478	-0.85233	-0.53328
H	-0.05798	0.20586	-1.71798
P	1.45288	0.18852	0.12253
O	1.79808	1.56207	-0.30401
O	1.09976	-0.24148	1.49926
F	2.60724	-0.80345	-0.40172

Pnicogen-bonded Transition State TS1-P14$_{exo}$

SCF energy:	–842.457402 hartree
Zero-point correction:	+0.144912 hartree
Enthalpy correction:	+0.156525 hartree
Free energy correction:	+0.108361 hartree
Quasiharmonic free energy correction:	+0.109095 hartree
Imaginary Frequency:	304.0 *i*cm^{-1}

Cartesian Coordinates

N	0.22693	-0.71952	-0.88684
C	-0.59675	-1.66567	-0.40557
C	-1.52473	1.68536	-0.77150
C	-1.76618	1.24968	0.47919
H	-1.77195	1.10471	-1.65199
H	-1.08571	2.66042	-0.94117
C	-2.21936	-0.07738	0.76979
C	-2.44275	-1.05840	-0.17216
H	-0.38392	-2.00008	0.60154
H	-0.92564	-2.42277	-1.10882
H	-2.89348	-1.98808	0.15484
H	-2.62547	-0.78852	-1.20606
H	-1.51972	1.88168	1.32304
H	-2.27465	-0.35564	1.81805
H	0.26182	-0.56941	-1.88801
P	1.32143	0.16777	0.13283
O	1.68584	1.42494	-0.55662

O	0.78920	0.02630	1.51049
F	2.58967	-0.82375	0.00940

Pnicogen-bonded Aza-Diels-Alder Product-P14

SCF energy:	–842.530016 hartree
Zero-point correction:	+0.152049 hartree
Enthalpy correction:	+0.162411 hartree
Free energy correction:	+0.116816 hartree
Quasiharmonic free energy correction:	+0.117511 hartree

Cartesian Coordinates

N	-0.19609	-0.02318	-0.29062
C	-0.91228	-1.17294	0.36721
C	-0.80484	1.28618	0.11304
C	-2.30145	1.23897	0.01488
H	-0.39012	2.05179	-0.54262
H	-0.46379	1.49034	1.13092
C	-2.99359	0.11252	-0.11904
C	-2.34350	-1.24292	-0.13575
H	-0.87062	-0.97506	1.43904
H	-0.35005	-2.07837	0.14453
H	-2.89717	-1.93156	0.50618
H	-2.37601	-1.66879	-1.14429
H	-2.80057	2.20050	0.04901
H	-4.07236	0.15305	-0.21960
H	-0.30305	-0.13044	-1.30470
P	1.60373	-0.12209	0.06335
O	1.73566	0.18279	1.49786
O	2.06859	-1.31869	-0.65779
F	1.94894	1.18206	-0.79300

6.3 Pnicogen-bonded Aza-Diels-Alder reaction with P15

Pnicogen-bonded Imine Complex 2-P15

SCF energy:	–626.484293 hartree
Zero-point correction:	+0.091134 hartree
Enthalpy correction:	+0.099300 hartree
Free energy correction:	+0.060106 hartree
Quasiharmonic free energy correction:	+0.060106 hartree

Cartesian Coordinates

N	1.18376	0.35629	0.58247
C	2.25721	0.16398	-0.06508
H	3.21788	0.45020	0.34971
H	2.17874	-0.30153	-1.04377
H	1.24980	0.77432	1.51038
P	-0.49281	-0.22315	-0.03493
O	-0.11877	-0.87809	-1.32011

O	-1.03764	-0.93800	1.15161
C	-1.25785	1.39114	-0.27490
H	-2.28056	1.22739	-0.61887
H	-1.28961	1.94045	0.66607
H	-0.71528	1.96043	-1.02906

Pnicogen-bonded Transition State TS1-P15

SCF energy:	–782.459707 hartree
Zero-point correction:	+0.179992 hartree
Enthalpy correction:	+0.192286 hartree
Free energy correction:	+0.143123 hartree
Quasiharmonic free energy correction:	+0.143748 hartree
Imaginary Frequency:	326.4 *i*cm^{-1}

Cartesian Coordinates

N	0.10353	-0.32666	-0.86361
C	-0.61072	-1.45172	-0.61317
C	-1.51371	1.64633	0.18016
C	-2.58653	0.97777	-0.31147
H	-1.27276	2.64430	-0.16669
H	-0.89973	1.25245	0.98137
C	-2.81233	-0.38904	-0.01313
C	-1.91212	-1.19308	0.68257
H	-0.08959	-2.18606	-0.00307
H	-1.14540	-1.87544	-1.45521
H	-1.24004	-0.75236	1.41387
H	-2.23802	-2.20232	0.91007
H	-3.23789	1.45579	-1.03387
H	-3.65632	-0.87197	-0.49849
H	-0.10103	0.19222	-1.70811
P	1.45607	0.22009	0.14342
O	1.65825	1.65425	-0.24351
O	1.05125	-0.19216	1.53292
C	2.82171	-0.81099	-0.45243
H	3.71627	-0.56293	0.12148
H	2.59460	-1.86832	-0.31010
H	3.01036	-0.61238	-1.50777

Pnicogen-bonded Aza-Diels-Alder Product-P15

SCF energy:	–782.535689 hartree
Zero-point correction:	+0.186843 hartree
Enthalpy correction:	+0.198068 hartree
Free energy correction:	+0.151083 hartree
Quasiharmonic free energy correction:	+0.151729 hartree

Cartesian Coordinates

N	-0.23202	0.00650	-0.31177

C	-0.97067	-1.16202	0.26935
C	-0.81876	1.29200	0.16341
C	-2.31883	1.28248	0.08451
H	-0.41158	2.09347	-0.45444
H	-0.46452	1.44107	1.18754
C	-3.03325	0.18077	-0.12149
C	-2.40333	-1.17973	-0.23621
H	-0.92873	-1.03363	1.35153
H	-0.42214	-2.06211	-0.00380
H	-2.96927	-1.90463	0.35334
H	-2.44225	-1.52995	-1.27356
H	-2.80057	2.24777	0.19232
H	-4.11238	0.24702	-0.20629
H	-0.32665	-0.04521	-1.32985
P	1.61622	-0.18208	0.07557
O	1.63216	-0.14903	1.56574
O	1.97153	-1.38047	-0.73730
C	2.24749	1.34295	-0.65687
H	1.94200	2.21586	-0.08162
H	3.33670	1.27441	-0.63243
H	1.93485	1.43896	-1.69759

7 Energies and Geometries for the Diels-Alder Reaction

7.1 Uncatalysed Diels-Alder reaction

Cyclopentadiene (4)

SCF energy:	–194.100690 hartree
Zero-point correction:	+0.092965 hartree
Enthalpy correction:	+0.098059 hartree
Free energy correction:	+0.066367 hartree
Quasiharmonic free energy correction:	+0.066367 hartree

Cartesian Coordinates

C	-0.73549	-0.98876	0.00000
C	0.73549	-0.98876	-0.00000
C	-1.17597	0.28134	-0.00000
C	-0.00000	1.21425	-0.00000
C	1.17597	0.28134	0.00000
H	-0.00001	1.87277	0.87685
H	-0.00001	1.87277	-0.87685
H	-1.35016	-1.87939	0.00000
H	-2.20672	0.60838	-0.00000
H	1.35017	-1.87938	-0.00000
H	2.20672	0.60839	0.00000

Methyl vinyl ketone (5)

SCF energy:	–231.245569 hartree
Zero-point correction:	+0.090139 hartree
Enthalpy correction:	+0.096798 hartree
Free energy correction:	+0.061404 hartree
Quasiharmonic free energy correction:	+0.061404 hartree

Cartesian Coordinates

C	0.86963	-0.64858	0.00004
C	1.92128	0.16698	-0.00004
H	1.81301	1.24602	0.00010
H	2.93209	-0.22313	-0.00026
C	-0.54415	-0.18539	0.00038
H	0.99071	-1.72723	-0.00012
O	-1.44025	-1.00628	-0.00014
C	-0.83295	1.29529	-0.00006
H	-0.39388	1.76748	0.88139
H	-0.39341	1.76709	-0.88148
H	-1.90941	1.45020	-0.00039

Uncatalysed Transition State $TS2_{endo}$

SCF energy:	–425.328151 hartree
Zero-point correction:	+0.186212 hartree
Enthalpy correction:	+0.196683 hartree
Free energy correction:	+0.151296 hartree
Quasiharmonic free energy correction:	+0.151830 hartree
Imaginary Frequency:	436.7 *i*cm^{-1}

Cartesian Coordinates

C	-1.44198	-0.07472	1.29953
C	-0.69316	-1.20211	0.92060
C	-1.95484	0.54450	0.15357
C	-0.34395	1.63522	-0.48866
C	-0.74727	-1.33310	-0.45333
C	-1.86415	-0.47240	-0.96109
H	-2.72227	1.30785	0.18732
H	-1.73839	-0.07166	-1.96450
H	-2.78634	-1.07068	-0.94324
C	1.64761	0.28279	0.02489
O	1.69272	0.69294	1.18066
C	2.66632	-0.72721	-0.45943
H	2.42865	-1.69752	-0.01435
H	3.65912	-0.43735	-0.11385
H	2.66495	-0.83187	-1.54426
H	-1.51015	0.31985	2.30461
H	-0.07599	-1.79054	1.58627
C	0.60013	0.69990	-0.89776
H	-0.27682	-2.11821	-1.03123
H	-0.14984	2.17927	0.42687
H	-0.91574	2.16930	-1.23883
H	0.66880	0.38088	-1.93003

Uncatalysed Transition State $TS2_{exo}$

SCF energy:	–425.326506 hartree
Zero-point correction:	+0.186230 hartree
Enthalpy correction:	+0.196643 hartree
Free energy correction:	+0.151479 hartree
Quasiharmonic free energy correction:	+0.151896 hartree
Imaginary Frequency:	445.6 *i*cm^{-1}

Cartesian Coordinates

C	-2.41326	0.23075	-0.47741
C	-1.67654	1.39230	-0.20310
C	-1.84680	-0.84418	0.21852
C	-0.22470	-1.28371	-1.01519
C	-0.66951	1.08232	0.70038
C	0.60999	-0.17570	-0.93165
H	-0.78888	-1.46014	-1.92075

H	0.05870	-2.17199	-0.46021
C	-0.98089	-0.25217	1.29962
H	0.02140	1.79381	1.13524
H	-2.31894	-1.81433	0.31008
H	-0.12183	-0.84507	1.60541
H	-1.61785	-0.08200	2.17997
C	1.79099	-0.15877	-0.06537
H	0.55100	0.60790	-1.67630
O	2.02660	-1.03345	0.75966
C	2.74908	0.99688	-0.25620
H	2.21538	1.93022	-0.44151
H	3.37108	0.79167	-1.13255
H	3.39463	1.09464	0.61509
H	-3.20311	0.14991	-1.21287
H	-1.80458	2.34668	-0.69638

Uncatalysed Diels-Alder Product 6_{endo}

SCF energy:	–425.386988 hartree
Zero-point correction:	+0.191246 hartree
Enthalpy correction:	+0.200815 hartree
Free energy correction:	+0.157495 hartree
Quasiharmonic free energy correction:	+0.158000 hartree

Cartesian Coordinates

C	-1.51467	0.10734	1.34415
C	-0.66528	-0.91091	1.18029
C	-1.90337	0.61227	-0.03321
C	-0.63621	1.32634	-0.60108
C	-0.46725	-1.09724	-0.31500
C	-1.86179	-0.70361	-0.83429
H	-2.81388	1.20490	-0.08959
H	-1.88980	-0.55020	-1.91590
H	-2.63355	-1.41223	-0.53105
C	1.67857	0.28716	-0.07260
O	1.99287	1.28009	0.54597
C	2.59149	-0.91453	-0.14295
H	3.59836	-0.63904	0.16476
H	2.60065	-1.34204	-1.14723
H	2.21013	-1.68390	0.53543
H	-1.79395	0.57923	2.27783
H	-0.11504	-1.43443	1.95240
C	0.35608	0.15783	-0.79946
H	-0.05876	-2.05153	-0.64148
H	-0.24206	2.07740	0.08250
H	-0.86636	1.80963	-1.55207
H	0.59581	0.01352	-1.85848

Uncatalysed Diels-Alder Product 6_{exo}

SCF energy:	–425.386395 hartree
Zero-point correction:	+0.191125 hartree
Enthalpy correction:	+0.200776 hartree

Free energy correction:	+0.157300 hartree
Quasiharmonic free energy correction:	+0.157661 hartree

Cartesian Coordinates

C	2.41577	0.52777	-0.32241
C	1.87852	-0.35052	-1.17352
C	1.54794	0.54381	0.92424
C	0.21215	1.23816	0.52019
C	0.64218	-0.93358	-0.50948
C	-0.39733	0.22605	-0.50944
H	0.36491	2.22704	0.08838
H	-0.42923	1.34561	1.39949
C	1.08826	-0.92555	0.96614
H	0.26016	-1.86784	-0.91392
H	2.00125	0.95450	1.82417
H	0.26718	-1.10402	1.66275
H	1.90790	-1.61884	1.15810
C	-1.78978	-0.19492	-0.08731
H	-0.48032	0.69051	-1.49573
O	-2.02561	-1.28370	0.38924
C	-2.87893	0.82736	-0.30609
H	-3.10686	0.86126	-1.37563
H	-2.54215	1.82447	-0.01542
H	-3.77694	0.55157	0.24355
H	3.24736	1.19598	-0.50753
H	2.17884	-0.54205	-2.19609

7.2 Pnicogen-bonded Diels-Alder reaction with P14

Pnicogen-bonded Methyl vinyl ketone 5-P14

SCF energy:	–823.066364 hartree
Zero-point correction:	+0.104477 hartree
Enthalpy correction:	+0.115265 hartree
Free energy correction:	+0.068524 hartree
Quasiharmonic free energy correction:	+0.069618 hartree

Cartesian Coordinates

C	2.43103	-0.82207	-0.03819
C	3.66215	-0.30059	-0.00197
C	1.22915	-0.01673	-0.01586
O	0.15448	-0.69466	-0.03656
P	-1.51458	-0.11520	-0.11953
F	-1.44893	0.61355	1.29753
O	-2.29874	-1.34740	-0.00706
O	-1.53978	0.90111	-1.18185
H	4.52777	-0.95133	-0.01967
H	3.85358	0.76365	0.04680
H	2.26784	-1.89202	-0.08404
C	1.19836	1.46090	0.03040
H	2.18822	1.90085	0.04018
H	0.64358	1.76854	0.92137

H	0.62625	1.81485	-0.83212

Pnicogen-bonded Transition State TS2a-P14

SCF energy:	–1017.179484 hartree
Zero-point correction:	+0.200071 hartree
Enthalpy correction:	+0.214888 hartree
Free energy correction:	+0.158964 hartree
Quasiharmonic free energy correction:	+0.160579 hartree
Imaginary Frequency:	188.3 *i*cm^{-1}

Cartesian Coordinates

C	-1.69030	-1.56921	0.12913
C	-1.34739	-0.98828	-1.14274
C	-2.81832	-0.96548	0.62116
C	-1.64817	0.68442	1.80534
C	-2.27593	-0.04972	-1.45970
C	-3.37431	-0.06141	-0.44448
H	-3.37338	-1.29049	1.49081
H	-3.69923	0.92392	-0.10775
H	-4.25710	-0.54643	-0.88472
C	0.04266	1.25923	0.18461
O	0.71552	0.22850	0.60123
C	0.58745	2.11655	-0.90012
H	0.82799	1.49951	-1.77024
H	1.52313	2.56659	-0.55500
H	-0.12381	2.89117	-1.17420
H	-1.11912	-2.34084	0.62925
H	-0.45469	-1.22876	-1.70546
C	-1.18070	1.52278	0.82364
H	-2.27980	0.57043	-2.34660
H	-0.99158	-0.04260	2.26268
H	-2.56581	0.91919	2.33059
H	-1.75995	2.36341	0.46740
P	2.20236	-0.32219	-0.06315
F	2.31663	-1.48664	1.01445
O	3.21710	0.71035	0.21582
O	1.89466	-0.90957	-1.38214

Pnicogen-bonded Zwitterion 12-P14

SCF energy:	–1017.191574 hartree
Zero-point correction:	+0.202915 hartree
Enthalpy correction:	+0.217733 hartree
Free energy correction:	+0.161162 hartree
Quasiharmonic free energy correction:	+0.163394 hartree

Cartesian Coordinates

C	-1.36989	-1.32934	-0.15802
C	-1.88732	-1.01384	-1.41997

C	-2.12336	-0.66095	0.91828
C	-1.25454	0.39827	1.69533
C	-2.97799	-0.20528	-1.24180
C	-3.31174	-0.02246	0.18783
H	-3.50129	1.02287	0.43935
H	-4.24083	-0.56790	0.39776
C	0.11152	1.38978	-0.10220
O	0.53768	0.09838	-0.32872
C	0.70840	2.42503	-0.99137
H	0.26380	3.40053	-0.79965
H	0.55995	2.15369	-2.03900
H	1.78579	2.48347	-0.81217
H	-0.55708	-2.02605	0.02505
H	-1.47800	-1.34228	-2.36352
C	-0.81329	1.55063	0.84609
H	-3.56514	0.22316	-2.04648
H	-1.23883	2.53355	1.00519
P	1.98820	-0.52365	0.17203
F	2.83995	-0.19232	-1.15382
O	2.53181	0.30607	1.27167
O	1.77727	-1.99117	0.21884
H	-1.86671	0.74665	2.52626
H	-2.41622	-1.40952	1.66141
H	-0.39305	-0.12981	2.11028

Pnicogen-bonded Transition State TS2b$_{endo}$-P14

SCF energy:	–1017.192402 hartree
Zero-point correction:	+0.203137 hartree
Enthalpy correction:	+0.216868 hartree
Free energy correction:	+0.163484 hartree
Quasiharmonic free energy correction:	+0.164870 hartree
Imaginary Frequency:	110.5 *i*cm^{-1}

Cartesian Coordinates

C	1.51360	-1.57377	0.04560
C	1.21707	-0.95540	1.23823
C	2.58259	-0.85744	-0.66222
C	1.90396	0.28521	-1.58799
C	2.09618	0.12346	1.37280
C	3.26079	-0.06549	0.46801
H	3.21357	-1.47794	-1.29428
H	3.76460	0.84854	0.16259
H	3.98294	-0.71098	0.98236
C	0.03511	1.26702	-0.27742
O	-0.64276	0.16565	-0.60868
C	-0.62254	2.30359	0.57069
H	-1.51861	2.67609	0.06945
H	0.06388	3.12569	0.76153
H	-0.93858	1.86199	1.52008
H	0.96829	-2.40998	-0.37603
H	0.35591	-1.15766	1.85993
C	1.31408	1.34735	-0.74413
H	2.03722	0.88315	2.14378

H	1.16593	-0.19213	-2.22934
H	2.71644	0.67491	-2.19937
H	1.87033	2.25155	-0.53389
P	-2.13183	-0.28339	0.04351
F	-2.17399	-1.63970	-0.80175
O	-1.92813	-0.62594	1.47056
O	-3.17205	0.63376	-0.46751

Pnicogen-bonded Transition State $TS2b_{exo}$-P14

SCF energy:	–1017.190452 hartree
Zero-point correction:	+0.203309 hartree
Enthalpy correction:	+0.216883 hartree
Free energy correction:	+0.164326 hartree
Quasiharmonic free energy correction:	+0.165047 hartree
Imaginary Frequency:	105.8 *i*cm^{-1}

Cartesian Coordinates

C	-3.51583	-0.22191	0.20683
C	-2.86674	0.28078	1.30133
C	-2.57104	-0.95951	-0.65163
C	-1.84155	0.09823	-1.62598
C	-1.53648	-0.20128	1.27006
C	-1.17630	1.15498	-0.82949
H	-2.58937	0.51993	-2.29584
H	-1.12295	-0.48011	-2.20521
C	-1.46557	-1.34817	0.34079
H	-0.73465	0.06227	1.95134
H	-3.00439	-1.75352	-1.25448
H	-0.48901	-1.54727	-0.08829
H	-1.78323	-2.23566	0.90392
C	0.13712	1.17924	-0.47284
H	-1.75686	2.02053	-0.53591
O	0.93932	0.17593	-0.88083
C	0.75545	2.30712	0.28742
H	1.17889	1.94408	1.22645
H	0.01560	3.07717	0.49523
H	1.57255	2.73128	-0.30075
H	-4.54544	-0.01759	-0.06143
H	-3.26247	0.98214	2.02138
P	2.09595	-0.53345	0.09734
F	3.20873	0.62163	0.00629
O	2.58310	-1.71262	-0.64400
O	1.56372	-0.54245	1.48332

Pnicogen-bonded Diels-Alder Product 6_{endo}-P14

SCF energy:	–1017.211362 hartree
Zero-point correction:	+0.205071 hartree
Enthalpy correction:	+0.219107 hartree
Free energy correction:	+0.163434 hartree

Quasiharmonic free energy correction:	+0.166635 hartree

Cartesian Coordinates

C	2.13717	-1.55965	0.59037
C	1.69094	-0.57201	1.37149
C	2.92396	-0.93858	-0.54586
C	1.87343	-0.25093	-1.47618
C	2.17409	0.72997	0.77135
C	3.51809	0.29204	0.16290
H	3.61261	-1.59507	-1.07164
H	3.94397	1.02805	-0.52203
H	4.23871	0.02965	0.93745
C	-0.05836	0.98447	-0.28745
O	-0.73421	-0.07102	-0.42606
C	-0.66173	2.21199	0.28126
H	-1.50703	2.50901	-0.34771
H	0.06540	3.01565	0.34928
H	-1.07056	1.97647	1.26987
H	1.89295	-2.61108	0.67009
H	1.00680	-0.65251	2.20659
C	1.37065	0.92893	-0.61725
H	2.15566	1.61531	1.40199
H	1.07198	-0.92923	-1.76334
H	2.34934	0.12855	-2.38088
H	1.66593	1.90366	-1.00878
P	-2.42961	-0.26273	0.06075
F	-2.45212	-1.74965	-0.47698
O	-2.41103	-0.25355	1.53064
O	-3.19502	0.61356	-0.83748

Pnicogen-bonded Diels-Alder Product 6_{exo}-P14

SCF energy:	–1017.209868 hartree
Zero-point correction:	+0.205254 hartree
Enthalpy correction:	+0.219190 hartree
Free energy correction:	+0.164438 hartree
Quasiharmonic free energy correction:	+0.166653 hartree

Cartesian Coordinates

C	3.92343	-0.18927	-0.03767
C	3.28360	-0.46366	-1.17712
C	2.90162	-0.23326	1.08430
C	2.00359	1.02902	0.91747
C	1.81940	-0.68637	-0.83423
C	1.30103	0.73717	-0.46938
H	2.56236	1.96237	0.88562
H	1.28309	1.08395	1.73780
C	1.95131	-1.32528	0.56218
H	1.21317	-1.20113	-1.57552
H	3.29115	-0.34613	2.09338
H	1.01035	-1.38234	1.11228
H	2.42148	-2.30722	0.52009
C	-0.15684	0.86536	-0.28346
H	1.59704	1.49513	-1.19898

O	-0.83378	-0.19358	-0.20588
C	-0.79156	2.19902	-0.17516
H	-1.43631	2.23204	0.70740
H	-1.43904	2.32951	-1.04980
H	-0.04364	2.98639	-0.14043
H	4.95677	0.11074	0.07822
H	3.68015	-0.42842	-2.18336
P	-2.59159	-0.26074	0.06895
F	-2.58808	-1.83352	-0.08985
O	-3.18939	0.37026	-1.11570
O	-2.76976	0.10852	1.47986

7.3 Pnicogen-bonded Diels-Alder reaction with P15

Pnicogen-bonded methyl vinyl ketone 5-P15

SCF energy:	–763.076154 hartree
Zero-point correction:	+0.138508 hartree
Enthalpy correction:	+0.150844 hartree
Free energy correction:	+0.099853 hartree
Quasiharmonic free energy correction:	+0.102185 hartree

Cartesian Coordinates

C	-1.69799	0.84728	0.00021
C	-2.98802	1.19197	0.00003
C	-1.28568	-0.55282	0.00006
O	-0.07674	-0.87407	-0.00017
P	1.40908	0.28989	-0.00009
C	2.59390	-1.05751	0.00060
H	2.46646	-1.66485	0.89539
H	3.59374	-0.62099	0.00121
H	2.46754	-1.66491	-0.89429
O	1.27588	0.97240	-1.31111
O	1.27531	0.97310	1.31052
H	-3.27700	2.23574	0.00004
H	-3.78821	0.46106	-0.00016
H	-0.91679	1.59625	0.00044
C	-2.27338	-1.66991	-0.00004
H	-2.91273	-1.59796	0.88197
H	-1.74624	-2.61978	0.00052
H	-2.91161	-1.59849	-0.88293

Pnicogen-bonded Transition State TS2a-P15

SCF energy:	–957.183590 hartree
Zero-point correction:	+0.235064 hartree
Enthalpy correction:	+0.250756 hartree
Free energy correction:	+0.193511 hartree
Quasiharmonic free energy correction:	+0.194855 hartree
Imaginary Frequency:	244.2 *i*cm^{-1}

Cartesian Coordinates

C	-1.63885	-1.58255	-0.11838
C	-1.32914	-0.81573	-1.28412
C	-2.75723	-1.06070	0.50310
C	-1.73702	0.33365	1.82239
C	-2.27880	0.14882	-1.43407
C	-3.37290	-0.05523	-0.43668
H	-3.30849	-1.56468	1.28593
H	-3.75927	0.85568	0.01948
H	-4.21819	-0.54161	-0.94403
C	-0.01446	1.22744	0.37523
O	0.68193	0.16632	0.62750
C	0.51488	2.27658	-0.54164
H	-0.22394	3.05918	-0.69695
H	0.79224	1.82041	-1.49530
H	1.42933	2.69283	-0.11179
H	-1.05284	-2.41530	0.24863
H	-0.43252	-0.93763	-1.87820
C	-1.26278	1.34635	1.00562
H	-2.30001	0.90596	-2.20721
H	-1.04582	-0.39652	2.22048
H	-2.64810	0.48899	2.38768
H	-1.86072	2.21844	0.77904
P	2.23177	-0.26259	-0.12828
C	2.48521	-1.73781	0.87276
O	1.88454	-0.58711	-1.54495
H	2.54556	-1.46996	1.92714
H	3.42584	-2.19704	0.56575
H	1.67402	-2.44706	0.71122
O	3.16513	0.84356	0.23332

Pnicogen-bonded Diels-Alder Product 6_{endo}-P15

SCF energy:	–957.220539 hartree
Zero-point correction:	+0.239604 hartree
Enthalpy correction:	+0.254765 hartree
Free energy correction:	+0.197438 hartree
Quasiharmonic free energy correction:	+0.199965 hartree

Cartesian Coordinates

C	-2.15309	-1.50012	-0.75370
C	-1.74232	-0.41815	-1.42076
C	-2.93729	-1.03227	0.45668
C	-1.88915	-0.42586	1.44402
C	-2.24490	0.79521	-0.66401
C	-3.57120	0.25604	-0.10041
H	-3.60272	-1.76143	0.91234
H	-4.00496	0.89619	0.67084
H	-4.29737	0.06579	-0.89090
C	0.01972	0.95121	0.37091
O	0.73341	-0.06687	0.47674
C	0.55729	2.22324	-0.17981
H	-0.15873	3.03408	-0.07575

H	0.78841	2.05221	-1.23717
H	1.50227	2.46443	0.31230
H	-1.88636	-2.52938	-0.95732
H	-1.06877	-0.38445	-2.26790
C	-1.41822	0.84682	0.70775
H	-2.25942	1.74459	-1.19386
H	-1.07078	-1.11385	1.64926
H	-2.36322	-0.15711	2.38869
H	-1.70771	1.76515	1.22302
P	2.51891	-0.20281	-0.07969
C	2.59944	-1.96183	0.26792
O	2.42628	0.11475	-1.52771
H	2.42210	-2.13974	1.32766
H	3.59858	-2.31202	0.00549
H	1.86246	-2.49065	-0.33530
O	3.23293	0.63993	0.91251

Pnicogen-bonded Diels-Alder Product 6_{exo}-P15

SCF energy:	–957.219586 hartree
Zero-point correction:	+0.239749 hartree
Enthalpy correction:	+0.254879 hartree
Free energy correction:	+0.197655 hartree
Quasiharmonic free energy correction:	+0.200122 hartree

Cartesian Coordinates

C	-3.92840	-0.39254	-0.11142
C	-3.54192	0.75474	0.45149
C	-2.71842	-1.30646	-0.17651
C	-1.77613	-0.70105	-1.26436
C	-2.06887	0.62114	0.78493
C	-1.34655	0.64995	-0.64792
H	-2.28184	-0.55800	-2.21818
H	-0.91290	-1.34836	-1.42071
C	-1.97408	-0.88048	1.10191
H	-1.66446	1.32781	1.50695
H	-2.91915	-2.36682	-0.30862
H	-0.95129	-1.25817	1.15389
H	-2.51544	-1.13409	2.01316
C	0.10154	0.83223	-0.38460
H	-1.69660	1.52165	-1.20077
O	0.82966	-0.17913	-0.29952
C	0.64467	2.19876	-0.16637
H	-0.15202	2.93619	-0.11365
H	1.30988	2.42373	-1.00694
H	1.25958	2.21317	0.73612
H	-4.89328	-0.61025	-0.55104
H	-4.11237	1.66762	0.56061
P	2.65822	-0.17064	0.13207
C	2.82216	-1.94496	-0.08421
H	2.57993	-2.21775	-1.11043
H	2.16711	-2.46546	0.61322
H	3.85799	-2.21519	0.12530
O	2.64943	0.25953	1.55325

O	3.24186	0.62655	-0.97594

8 Energies and Geometries for the Friedel-Crafts Reaction

8.1 Uncatalysed Friedel-Crafts reaction

trans-Crotonophenone (7)

SCF energy:	–462.308969 hartree
Zero-point correction:	+0.172288 hartree
Enthalpy correction:	+0.183349 hartree
Free energy correction:	+0.135763 hartree
Quasiharmonic free energy correction:	+0.137021 hartree

Cartesian Coordinates

C	3.03848	0.72487	0.22218
C	1.71252	1.13209	0.18065
C	3.35887	-0.62045	0.04485
C	2.35025	-1.55438	-0.16990
C	1.01910	-1.14952	-0.19418
C	0.69234	0.19754	-0.02036
C	-0.72162	0.69302	-0.07381
H	3.82357	1.45224	0.39008
H	1.44684	2.17459	0.30717
H	4.39431	-0.93879	0.07244
H	2.59827	-2.59834	-0.31818
H	0.24522	-1.88563	-0.37360
O	-0.94552	1.86935	-0.29865
C	-1.81912	-0.27795	0.16854
C	-3.09089	0.05735	-0.06210
H	-1.57168	-1.26198	0.54988
C	-4.26408	-0.83511	0.16349
H	-3.28949	1.05630	-0.44444
H	-4.81462	-0.97914	-0.77019
H	-4.95959	-0.37059	0.86799
H	-3.96368	-1.80832	0.55192

Indole (8)

SCF energy:	–363.836276 hartree
Zero-point correction:	+0.130689 hartree
Enthalpy correction:	+0.137834 hartree
Free energy correction:	+0.100437 hartree
Quasiharmonic free energy correction:	+0.100437 hartree

Cartesian Coordinates

C	-2.15316	0.69014	0.00003

C	-0.98259	1.42640	0.00003
C	-2.12730	-0.71965	0.00001
C	-0.93195	-1.41635	-0.00001
C	0.24913	-0.66744	-0.00002
C	0.24813	0.74898	0.00000
C	1.62316	1.16595	0.00001
N	1.56129	-1.07657	-0.00004
C	2.38055	0.02853	-0.00001
H	3.45256	-0.09024	-0.00002
H	1.99837	2.17705	0.00002
H	-3.10880	1.20083	0.00005
H	-1.01158	2.51026	0.00005
H	-3.06206	-1.26760	0.00002
H	-0.90995	-2.49986	-0.00002
H	1.87664	-2.03384	-0.00007

Uncatalysed Transition State TS3

SCF energy:	–826.107661 hartree
Zero-point correction:	+0.304981 hartree
Enthalpy correction:	+0.322321 hartree
Free energy correction:	+0.259780 hartree
Quasiharmonic free energy correction:	+0.262897 hartree
Imaginary Frequency:	460.2 *i*cm^{-1}

Cartesian Coordinates

C	-5.06285	-1.41485	0.20169
C	-3.69805	-1.29779	-0.04009
C	-5.86077	-0.27507	0.26464
C	-5.28373	0.97969	0.08245
C	-3.91697	1.09432	-0.15096
C	-3.10657	-0.04351	-0.20744
C	-1.62133	0.02920	-0.45651
H	-5.50580	-2.39483	0.33807
H	-3.06797	-2.17690	-0.10339
H	-6.92538	-0.36351	0.44713
H	-5.90099	1.87010	0.11497
H	-3.48234	2.07431	-0.31040
O	-1.04116	-1.00008	-0.90292
C	-0.92391	1.19500	-0.12950
C	0.48536	1.26069	-0.37695
H	-1.40507	2.01068	0.39591
C	1.09499	2.64766	-0.34295
H	0.62958	3.24440	-1.13109
H	2.16822	2.63731	-0.52391
H	0.89611	3.14164	0.61125
C	3.04251	-1.09151	0.05721
C	2.85283	0.21105	0.54015
C	3.93240	1.09326	0.52693
C	5.14726	0.65648	0.00998
C	5.29617	-0.64016	-0.49888
C	4.24046	-1.54293	-0.48003

H	6.25261	-0.94921	-0.90214
H	4.34876	-2.55320	-0.85472
H	3.83548	2.09569	0.92623
H	5.99616	1.32915	0.00328
C	0.93726	-1.00699	0.83076
N	1.84789	-1.79213	0.27266
H	-0.02681	-1.39120	1.11597
H	1.68442	-2.75381	0.00590
H	0.80686	0.66097	-1.22820
C	1.43608	0.33324	0.93965
H	1.14326	0.93725	1.78894

Uncatalysed Zwitterion 14

SCF energy:	–826.106523 hartree
Zero-point correction:	+0.305514 hartree
Enthalpy correction:	+0.323155 hartree
Free energy correction:	+0.259407 hartree
Quasiharmonic free energy correction:	+0.263345 hartree

Cartesian Coordinates

C	4.52368	0.71095	1.20429
C	3.33977	-0.01662	1.14101
C	5.14291	1.14755	0.03459
C	4.57173	0.84095	-1.19765
C	3.39064	0.10688	-1.25747
C	2.75110	-0.32130	-0.09126
C	1.46139	-1.09706	-0.21499
H	4.96948	0.93067	2.16787
H	2.87965	-0.36790	2.05742
H	6.06584	1.71361	0.08451
H	5.04950	1.17115	-2.11331
H	2.94232	-0.14944	-2.20989
O	1.21795	-1.66373	-1.33348
C	0.57501	-1.10619	0.84451
C	-0.73707	-1.76644	0.68019
H	0.73231	-0.48787	1.71952
C	-1.58522	-1.75544	1.94518
H	-2.54681	-2.25696	1.80678
H	-1.77403	-0.73062	2.27663
H	-1.04817	-2.27041	2.74438
C	-3.33988	0.41613	-0.33108
C	-1.94491	0.36080	-0.29537
C	-1.23459	1.51950	-0.00016
C	-1.95233	2.68555	0.25604
C	-3.35114	2.70818	0.21675
C	-4.07897	1.56141	-0.08187
H	-3.87679	3.63314	0.41832
H	-5.16111	1.56520	-0.11877
H	-0.15224	1.50768	0.02703
H	-1.41717	3.59828	0.48833
C	-2.79295	-1.70229	-0.82438
N	-3.79747	-0.88288	-0.65743
H	-2.95835	-2.74409	-1.06579

H	-4.77373	-1.14639	-0.73776
H	-0.61626	-2.78776	0.30593
C	-1.52297	-1.04192	-0.56499
H	-0.77302	-1.19225	-1.36143

Uncatalysed Friedel-Crafts Product 9

SCF energy:	–826.183428 hartree
Zero-point correction:	+0.307665 hartree
Enthalpy correction:	+0.325101 hartree
Free energy correction:	+0.263827 hartree
Quasiharmonic free energy correction:	+0.265842 hartree

Cartesian Coordinates

C	1.44334	1.81814	-1.92040
C	0.22053	1.79000	-1.25644
C	2.63077	1.82240	-1.19583
C	2.59637	1.81497	0.19817
C	1.37729	1.79669	0.85993
C	0.17819	1.77581	0.13970
C	-1.10150	1.67761	0.91723
H	1.46673	1.82972	-3.00355
H	-0.69064	1.77292	-1.83927
H	3.58234	1.83129	-1.71455
H	3.51997	1.81407	0.76464
H	1.33432	1.77214	1.94179
O	-1.09936	1.85558	2.12031
C	-2.38945	1.27293	0.23000
C	-2.58413	-0.26704	0.27146
C	-3.90812	-0.63048	-0.40049
H	-3.90030	-0.33866	-1.45435
H	-4.74069	-0.11470	0.08244
H	-4.08509	-1.70602	-0.34590
C	0.69858	-1.84670	-0.63382
C	-0.20448	-1.36443	0.34304
C	0.20040	-1.32678	1.68720
C	1.47187	-1.76108	2.01482
C	2.35773	-2.23313	1.02443
C	1.98672	-2.28386	-0.30784
H	3.34943	-2.56149	1.31257
H	2.66689	-2.64472	-1.07045
H	-0.46712	-0.94838	2.45425
H	1.79936	-1.73414	3.04738
C	-1.19970	-1.25181	-1.66823
N	0.06314	-1.77148	-1.84818
H	0.44885	-2.06703	-2.73055
H	-2.63749	-0.55350	1.32755
C	-1.40963	-0.97714	-0.34364
H	-1.84935	-1.10500	-2.51778
H	-2.42501	1.60349	-0.80898
H	-3.20790	1.74905	0.77385

8.2 Pnicogen-bonded Friedel-Crafts reaction with P14

Pnicogen-bonded *trans*-Crotonophenone complex 7-P14

SCF energy:	–1054.135547 hartree
Zero-point correction:	+0.186524 hartree
Enthalpy correction:	+0.201718 hartree
Free energy correction:	+0.144255 hartree
Quasiharmonic free energy correction:	+0.146059 hartree

Cartesian Coordinates

C	0.15474	3.88528	-0.43281
C	-0.30267	2.47698	-0.36932
H	-0.60842	4.53314	0.00890
H	0.24940	4.19144	-1.47868
H	1.10356	4.03422	0.07916
C	0.40446	1.48309	0.20634
H	-1.24462	2.24727	-0.85978
C	-0.04863	0.12049	0.16922
H	1.38960	1.66683	0.62136
O	0.77918	-0.86290	0.18874
C	-1.45217	-0.26642	0.10085
C	-1.78779	-1.48020	-0.52021
C	-2.45254	0.53016	0.67829
C	-3.77700	0.12347	0.61142
C	-4.10758	-1.06506	-0.03417
C	-3.11461	-1.86592	-0.59934
H	-3.37928	-2.79029	-1.09663
H	-5.14398	-1.37597	-0.08907
H	-2.18841	1.43206	1.21524
H	-4.54903	0.72688	1.07132
H	-1.00573	-2.09118	-0.95271
P	2.52165	-0.81408	0.16300
O	2.94589	0.06396	1.26699
O	2.90170	-2.21090	-0.07833
F	2.60452	0.00715	-1.20499

Pnicogen-bonded Transition State TS3-P14

SCF energy:	–1417.975444 hartree
Zero-point correction:	+0.318808 hartree
Enthalpy correction:	+0.340506 hartree
Free energy correction:	+0.268060 hartree
Quasiharmonic free energy correction:	+0.272088 hartree
Imaginary Frequency:	253.0 *i*cm^{-1}

Cartesian Coordinates

C	-5.61582	-0.79644	-0.30008
C	-5.52408	0.56454	-0.64525
C	-4.57069	-1.44786	0.33374
C	-3.40955	-0.72163	0.63130

C	-3.34793	0.64702	0.29287
C	-4.39124	1.30741	-0.35451
H	-6.52241	-1.34079	-0.53488
H	-6.35884	1.04249	-1.14327
H	-4.64919	-2.49626	0.59828
H	-4.31858	2.35694	-0.61163
C	-2.13473	-1.06163	1.21580
C	-1.41789	0.13207	1.28460
N	-2.12128	1.13110	0.72206
C	-0.87763	-1.55133	-0.74420
C	-1.66253	-2.76017	-1.11882
H	-1.42717	-3.61051	-0.47787
H	-1.35702	-3.02109	-2.14048
H	-2.73385	-2.57575	-1.13432
C	0.48135	-1.69259	-0.42192
C	1.36000	-0.63275	-0.43028
C	2.79736	-0.80715	-0.19692
C	3.25196	-1.75338	0.72899
C	4.61377	-1.92764	0.92854
C	5.52795	-1.17443	0.19495
C	5.07890	-0.24048	-0.73555
C	3.71818	-0.04751	-0.92761
H	3.36741	0.67244	-1.65583
H	2.54032	-2.32222	1.31544
H	4.96287	-2.64523	1.66058
H	6.59096	-1.31441	0.35029
H	5.79000	0.33896	-1.31109
H	-1.86900	-1.97936	1.71760
H	-1.21313	-0.59264	-1.12994
H	0.87816	-2.68344	-0.24038
O	0.88693	0.57735	-0.73892
P	1.19810	1.99874	0.11746
O	1.82899	1.63246	1.40168
O	-0.03667	2.80748	-0.02267
F	2.29046	2.62033	-0.86460
H	-0.42919	0.30959	1.68585
H	-1.68628	2.02484	0.48204

Pnicogen-bonded Zwitterion 14-P14

SCF energy:	–1418.000220 hartree
Zero-point correction:	+0.322222 hartree
Enthalpy correction:	+0.343763 hartree
Free energy correction:	+0.271510 hartree
Quasiharmonic free energy correction:	+0.275906 hartree

Cartesian Coordinates

C	-5.29485	-0.85029	-0.48962
C	-5.44102	0.45158	-0.01006
C	-4.10993	-1.56567	-0.30809
C	-3.06574	-0.95060	0.36559
C	-3.25464	0.34171	0.85483
C	-4.41047	1.07806	0.68698
H	-6.11957	-1.31768	-1.01311

H	-6.37120	0.98106	-0.17226
H	-4.02431	-2.58009	-0.67538
H	-4.50992	2.08252	1.07797
C	-1.65716	-1.37627	0.69941
C	-1.19212	-0.23259	1.53149
N	-2.07202	0.70624	1.55383
C	-0.71590	-1.47104	-0.56296
C	-1.05888	-2.72073	-1.37655
H	-0.93011	-3.62423	-0.77471
H	-0.39171	-2.78312	-2.23743
H	-2.08297	-2.68694	-1.74845
C	0.73016	-1.49385	-0.15263
C	1.61781	-0.53551	-0.43872
C	3.05767	-0.58124	-0.09317
C	3.70872	-1.79522	0.15503
C	5.05163	-1.81656	0.50833
C	5.76912	-0.62657	0.61043
C	5.13406	0.58281	0.34793
C	3.78926	0.60698	-0.00701
H	3.30515	1.55300	-0.21375
H	3.17228	-2.73065	0.04989
H	5.54272	-2.76488	0.69146
H	6.81778	-0.64465	0.88223
H	5.68561	1.51286	0.41701
H	-1.58923	-2.31673	1.25639
H	-0.90869	-0.58070	-1.16567
H	1.07125	-2.36440	0.39887
O	1.24254	0.59401	-1.13765
P	0.42639	1.84119	-0.44380
O	0.66094	1.83274	1.02856
O	-0.93685	1.92816	-1.02558
F	1.31914	3.00772	-1.08742
H	-0.22301	-0.09971	1.99092
H	-1.88740	1.62390	1.95318

Pnicogen-bonded Friedel-Crafts Product 9-P14

SCF energy:	–1418.004737 hartree
Zero-point correction:	+0.321638 hartree
Enthalpy correction:	+0.343559 hartree
Free energy correction:	+0.271051 hartree
Quasiharmonic free energy correction:	+0.275156 hartree

Cartesian Coordinates

C	0.24448	-2.71656	-0.43773
C	-0.54331	-1.58532	-0.32393
C	1.14480	-3.04627	0.57491
C	1.26708	-2.24053	1.70364
C	0.51182	-1.08434	1.81038
C	-0.41004	-0.75482	0.80342
C	-1.11180	0.51330	0.85340
H	0.16683	-3.33769	-1.32106
H	-1.20520	-1.31026	-1.13636
H	1.75951	-3.93355	0.47945

H	1.96611	-2.50093	2.48794
H	0.61847	-0.45629	2.68553
O	-2.25084	0.70987	0.32721
C	-0.47915	1.75171	1.38643
C	0.08992	2.54184	0.16085
C	0.81499	3.79627	0.64715
H	1.16770	4.37192	-0.21005
H	0.14587	4.42549	1.23768
H	1.67977	3.54336	1.26324
C	2.44084	0.02648	-1.34282
C	2.13377	0.92332	-0.29004
C	2.95342	0.92445	0.85292
C	4.02546	0.05300	0.91384
C	4.30548	-0.83271	-0.14505
C	3.52224	-0.85723	-1.28498
H	5.15069	-1.50601	-0.06540
H	3.73228	-1.53876	-2.10101
H	2.75502	1.59225	1.68356
H	4.66084	0.04654	1.79144
C	0.59670	1.15624	-1.91964
N	1.49551	0.20092	-2.32395
H	1.46086	-0.29524	-3.20045
H	-0.77168	2.84494	-0.44095
C	0.93889	1.63086	-0.68136
H	-0.24820	1.41647	-2.54025
H	0.33468	1.51509	2.06942
H	-1.23305	2.35583	1.89297
P	-3.50215	-0.39098	-0.24388
F	-4.62853	0.66976	0.10539
O	-3.55371	-1.50270	0.71566
O	-3.33215	-0.45728	-1.70372

8.3 Pnicogen-bonded Friedel-Crafts reaction with P15

Pnicogen-bonded *trans*-Crotonophenone Complex 7-P15

SCF energy:	–994.143834 hartree
Zero-point correction:	+0.221031 hartree
Enthalpy correction:	+0.237407 hartree
Free energy correction:	+0.177534 hartree
Quasiharmonic free energy correction:	+0.179622 hartree

Cartesian Coordinates

C	-0.04150	3.93825	-0.42588
C	-0.44216	2.50992	-0.35867
H	0.03806	4.24746	-1.47192
H	0.90602	4.12155	0.07801
H	-0.82208	4.55932	0.02279
C	0.30854	1.54555	0.20231
H	-1.38302	2.24473	-0.83335
C	-0.08033	0.15299	0.15975
H	1.28783	1.76657	0.61359
O	0.78654	-0.76998	0.17531

C	-1.47907	-0.28686	0.09215
C	-1.77111	-1.48904	-0.56668
C	-2.50328	0.44428	0.70690
C	-3.81065	-0.01962	0.64686
C	-4.10006	-1.19920	-0.03311
C	-3.08139	-1.93278	-0.64089
H	-3.31201	-2.85019	-1.16762
H	-5.12252	-1.55390	-0.08412
H	-2.27169	1.34506	1.26082
H	-4.60121	0.53524	1.13598
H	-0.96859	-2.04855	-1.03082
P	2.61210	-0.54253	0.04298
O	2.97212	0.14762	1.31052
O	2.77304	0.07208	-1.30092
C	2.95255	-2.30612	0.07122
H	2.58885	-2.74045	1.00145
H	4.03353	-2.43985	0.01066
H	2.48241	-2.79105	-0.78323

Pnicogen-bonded Transition State TS3-P15

SCF energy:	–1357.977967 hartree
Zero-point correction:	+0.353449 hartree
Enthalpy correction:	+0.376057 hartree
Free energy correction:	+0.302134 hartree
Quasiharmonic free energy correction:	+0.306246 hartree
Imaginary Frequency:	276.0 *i*cm^{-1}

Cartesian Coordinates

C	5.38028	-0.83584	0.37348
C	5.27754	0.56647	0.37031
C	4.36881	-1.63083	-0.14224
C	3.23580	-1.00746	-0.67889
C	3.16711	0.40017	-0.69590
C	4.17040	1.20715	-0.16396
H	6.26646	-1.29984	0.78914
H	6.08226	1.15807	0.78953
H	4.45322	-2.71159	-0.13246
H	4.08694	2.28683	-0.17347
C	1.98351	-1.48694	-1.22184
C	1.29718	-0.34525	-1.65024
N	1.97516	0.76257	-1.31359
C	0.69036	-1.40206	0.66794
C	1.37919	-2.50077	1.40945
H	1.12554	-3.48205	1.00562
H	1.00514	-2.45919	2.43996
H	2.45783	-2.37031	1.44545
C	-0.68614	-1.56912	0.38455
C	-1.50855	-0.53539	0.01015
C	-2.96988	-0.67458	-0.12122
C	-3.67592	-1.65268	0.59052
C	-5.05264	-1.75872	0.44963
C	-5.73715	-0.89500	-0.40298
C	-5.04174	0.08270	-1.11009

C	-3.66580	0.19915	-0.96536
H	-3.11725	0.95396	-1.51472
H	-3.15564	-2.30867	1.27770
H	-5.59426	-2.50887	1.01258
H	-6.81173	-0.98088	-0.51115
H	-5.57221	0.75483	-1.77343
H	1.74252	-2.49963	-1.50723
H	1.05211	-0.39183	0.83505
H	-1.11771	-2.55538	0.50257
O	-1.00346	0.63494	-0.36202
P	-0.55143	2.00751	0.58803
O	0.29223	2.77963	-0.38673
O	0.01099	1.46361	1.86101
C	-2.15865	2.78569	0.83903
H	-2.59045	3.07655	-0.11809
H	-2.01706	3.67483	1.45517
H	-2.82930	2.09782	1.35585
H	0.33488	-0.27490	-2.13041
H	1.52367	1.68397	-1.22497

Pnicogen-bonded Zwitterion 14-P15

SCF energy:	–1358.002371 hartree
Zero-point correction:	+0.357130 hartree
Enthalpy correction:	+0.379469 hartree
Free energy correction:	+0.306246 hartree
Quasiharmonic free energy correction:	+0.310075 hartree

Cartesian Coordinates

C	5.43729	-1.27963	0.39186
C	5.85299	-0.09277	-0.21160
C	4.09751	-1.66967	0.38398
C	3.16613	-0.83829	-0.22344
C	3.62027	0.32717	-0.83996
C	4.93993	0.73713	-0.85715
H	6.17015	-1.91599	0.87219
H	6.89961	0.18337	-0.18891
H	3.80598	-2.60882	0.83433
H	5.24673	1.65104	-1.34994
C	1.67648	-0.94843	-0.46464
C	1.40461	0.31207	-1.21941
N	2.50181	0.95415	-1.44910
C	0.71242	-1.16267	0.73998
C	1.09623	-2.41700	1.53129
H	0.32832	-2.61750	2.27997
H	2.04265	-2.28264	2.05498
H	1.17173	-3.29246	0.87915
C	-0.69564	-1.30088	0.23026
C	-1.71019	-0.45626	0.45159
C	-3.10464	-0.72730	0.01925
C	-3.59274	-2.03426	-0.08468
C	-4.89463	-2.27134	-0.51015
C	-5.73227	-1.20529	-0.82863
C	-5.25926	0.09885	-0.71272

C	-3.95737	0.33758	-0.28617
H	-3.58420	1.35102	-0.21080
H	-2.95968	-2.86939	0.19162
H	-5.25999	-3.28923	-0.57906
H	-6.74849	-1.39001	-1.15622
H	-5.90555	0.93415	-0.95575
H	1.48576	-1.76829	-1.17708
H	0.78891	-0.28349	1.37825
H	-0.91096	-2.20380	-0.33483
O	-1.55770	0.72725	1.13023
P	-0.75847	2.02651	0.41997
O	-1.18231	2.08037	-1.02519
O	0.71686	1.87602	0.70502
C	-1.49149	3.34195	1.41107
H	-1.04697	4.29196	1.11234
H	-1.28752	3.16770	2.46754
H	-2.56840	3.38024	1.24646
H	0.44792	0.66492	-1.59228
H	2.53977	1.84565	-1.93275

Pnicogen-bonded Friedel-Crafts Product 9-P15

SCF energy:	–1358.019270 hartree
Zero-point correction:	+0.356490 hartree
Enthalpy correction:	+0.379448 hartree
Free energy correction:	+0.305298 hartree
Quasiharmonic free energy correction:	+0.309051 hartree

Cartesian Coordinates

C	1.84325	2.71911	-1.12523
C	0.63125	2.10499	-0.86362
C	2.78237	2.08331	-1.93830
C	2.50501	0.83868	-2.49619
C	1.29362	0.21429	-2.23298
C	0.34875	0.84214	-1.41040
C	-0.90398	0.18297	-1.03574
H	2.06525	3.68525	-0.68987
H	-0.09555	2.57547	-0.21425
H	3.73377	2.56236	-2.13765
H	3.23308	0.35277	-3.13339
H	1.09512	-0.75371	-2.67107
O	-1.74651	0.89499	-0.42880
C	-1.15742	-1.26572	-1.28050
C	-0.64120	-2.16751	-0.10235
C	-0.83842	-3.62683	-0.50787
H	-0.23206	-3.87709	-1.38275
H	-1.88389	-3.82125	-0.75464
H	-0.54649	-4.28566	0.31137
C	2.58159	-0.69775	1.10404
C	1.17115	-0.78684	1.15569
C	0.45007	0.09929	1.97295
C	1.15012	1.04806	2.69666
C	2.55669	1.12741	2.62593
C	3.29152	0.25840	1.83763

H	3.07425	1.88283	3.20547
H	4.37244	0.31833	1.78798
H	-0.63346	0.03580	2.03052
H	0.61412	1.74244	3.33299
C	1.93303	-2.35314	-0.26484
N	3.01857	-1.67037	0.23789
H	3.98104	-1.86917	0.01619
H	-1.27944	-1.94368	0.75587
C	0.77676	-1.84282	0.26134
H	2.07866	-3.15181	-0.97640
H	-0.65667	-1.57884	-2.19601
H	-2.23152	-1.41876	-1.39755
P	-3.39084	0.40274	0.27105
C	-3.76899	2.06979	0.82214
O	-4.16994	-0.02095	-0.92097
O	-3.01085	-0.50998	1.38159
H	-4.74361	2.04823	1.31165
H	-3.80890	2.74634	-0.03041
H	-3.01609	2.40203	1.53619

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