

Hydrophosphorylation of aliphatic alkynes catalyzed by CuNPs/ZnO for the synthesis of vinyl phosphonates. A DFT study on the reaction mechanism

Leandro Fortunato, Yanina Moglie, Viviana Dorn* and Gabriel Radivoy*

*Instituto de Química del Sur (INQUISUR-CONICET), Depto. de Química, Universidad Nacional del Sur, Av. Alem
1253, B8000CPB Bahía Blanca, Argentina.*

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Computational procedure

The calculations were performed with the Gaussian09 program.¹ The reactive system was simplified. Ethynylcyclohexane and dimethyl phosphite were chosen as model starting materials for the theoretical study of the process. The initial conformational analysis of phosphorous-containing structures (mainly by scanning the two main torsion angles of the methoxy groups) and ACN- or DMSO-containing structures (mainly by scanning the rotation angles to optimize the methyl groups), were performed with the semi empirical PM6 method. The geometry of the most stable conformers thus obtained was then refined within the B3LYP DFT functional, and the 6-31+G* basis set for all atoms. Zero point energy was computed at the 6-31+G* level. The characterization of all stationary points was done by Hessian matrix calculations of geometries, obtained with full optimization for the minimums that have zero imaginary frequencies. The transition states were obtained using the QST2 or QST3 methodologies, characterized by have one imaginary frequency (only the first frequency is a negative value). The first frequency for all the structures is provided in the SI. All the gas-phase geometries were used as the starting point for the solution-phase calculations. Energies in solution (ACN, DMSO) were obtained within the Tomasi's polarized continuum model (PCM) as implemented in Gaussian09. Dispersion corrections were computed for the optimized geometries applying the D2 Grimme's dispersion corrections with the B3LYP-D functional [additional keyword: IOp(3/124=3)] as implemented in Gaussian09 Rev. C.01. The Merz-Singh-Kollman (MK) charges of IN4, TS3, IN7 and TS4 were calculated by using the keyword pop=MK as implemented in Gaussian09. The structures' figures were built with the VMD program.

¹ Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

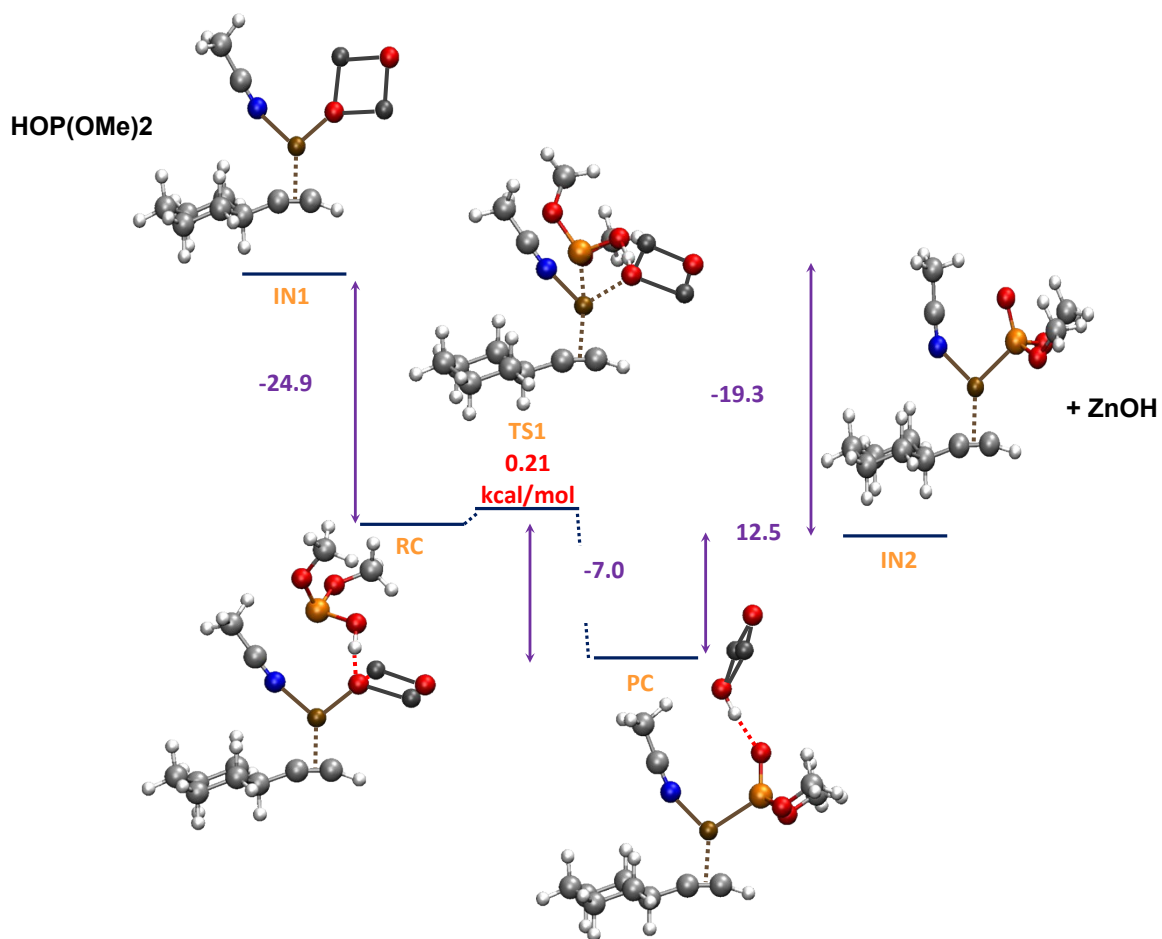


Figure S11. B3LYP-D/6-31+G* potential energy profile for initial RC and PC complexes together IN1 and IN2 (*E* isomer, ACN)

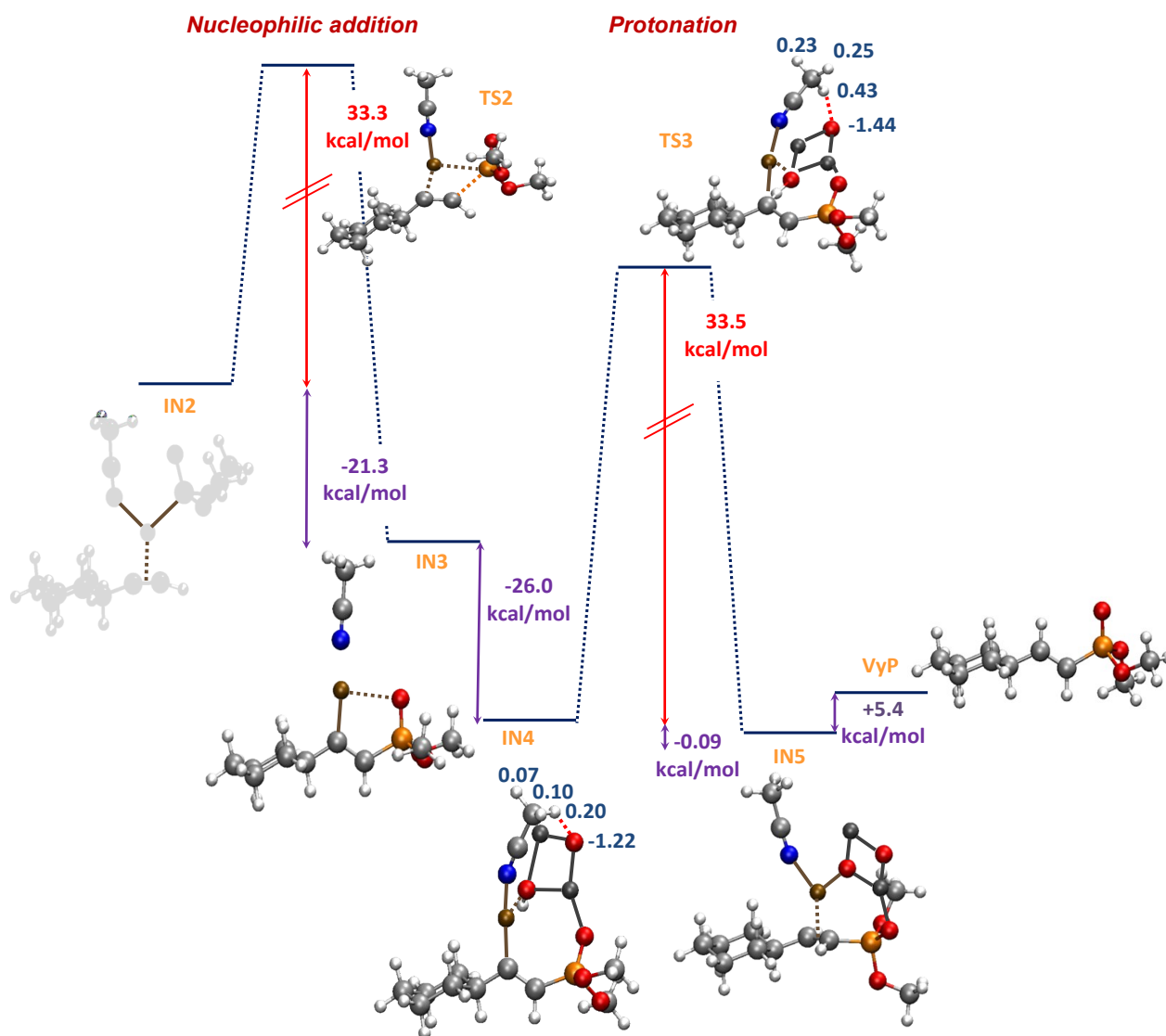


Figure S12. B3LYP-D/6-31+G* potential energy profile for the nucleophilic addition and protonation steps in the formation of *E* vinyl phosphonate (ACN) and MK charges (in blue).

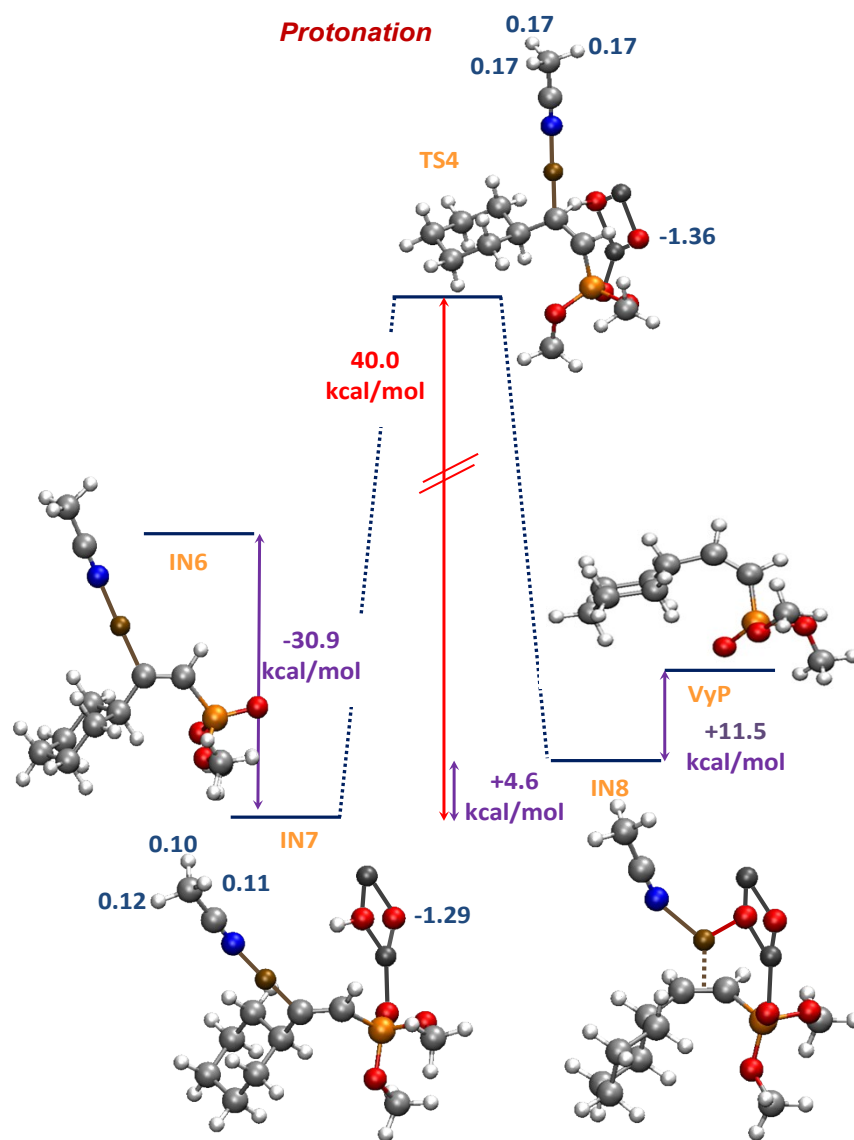


Figure SI3. B3LYP-D/6-31+G* potential energy profile for the protonation step corresponding to Z vinyl phosphonate (ACN) and MK charges (in blue).

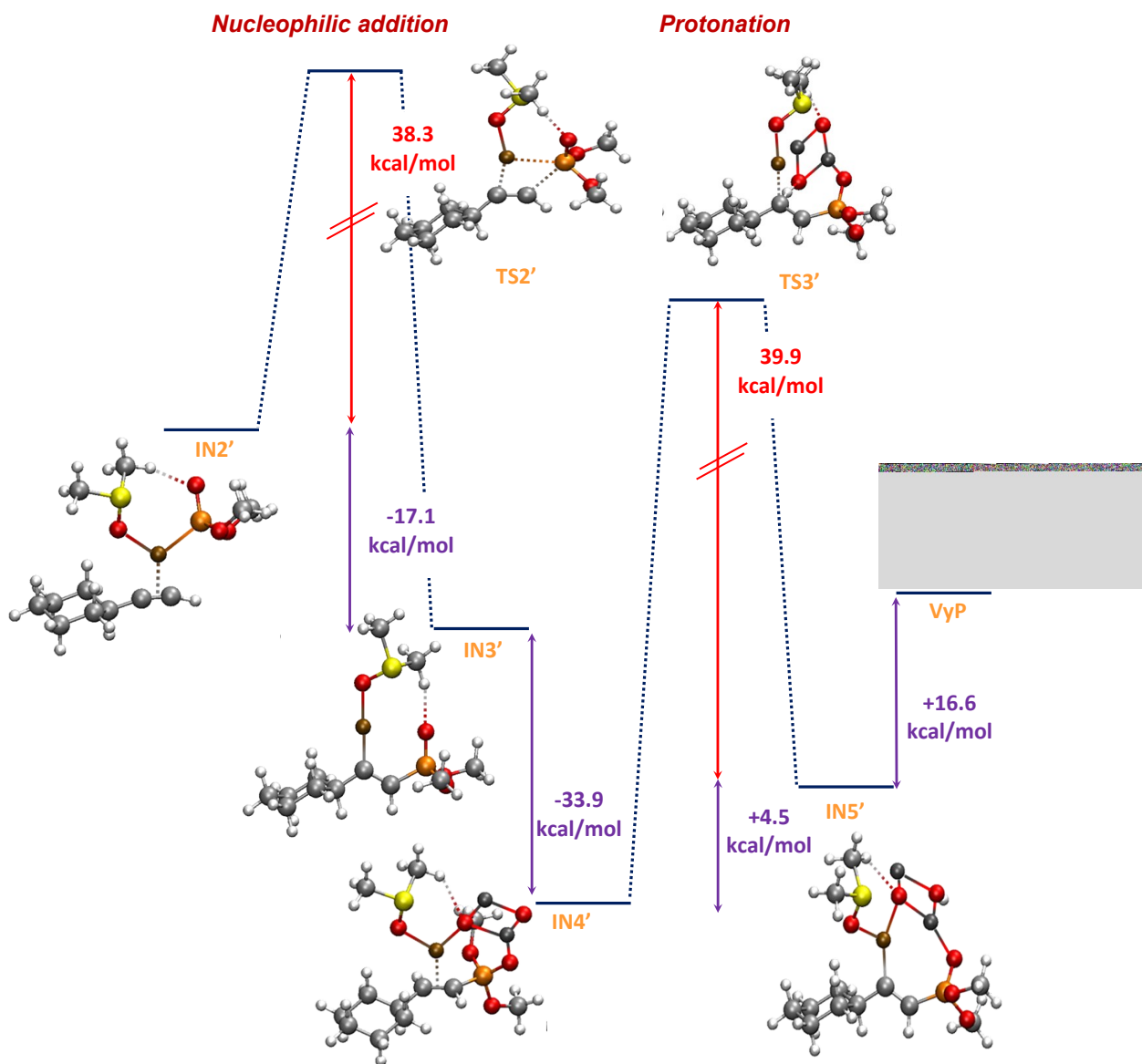


Figure SI4. B3LYP-D/6-31+G* potential energy profile for the nucleophilic addition and protonation steps in the formation of *E* vinyl phosphonate (DMSO)

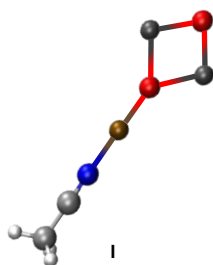
Cartesians coordinates

CuLn complexes

I (24.15)

11
 B3LYP/6-31+G*
 ZPE: -5481.900964 a.u.
 SCRF(PCM,solvent=acetonitrile)
 HF: -5482.014158 a.u.
 B3LYP-D/6-31+G*
 SCRF(PCM,solvent=acetonitrile)
 HF: -5482.028638 a.u.

0 2

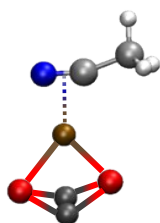


O	2.909178	0.170163	-1.399717
Zn	1.503649	0.098551	-0.161525
Zn	2.862519	-1.699765	-1.394482
O	1.393545	-1.875917	-0.107756
Cu	0.432257	-3.210472	0.589292
N	-0.543225	-4.594493	1.287872
C	-1.154381	-5.479000	1.716035
C	-1.922540	-6.594767	2.252447
H	-2.563059	-7.017811	1.471662
H	-1.245400	-7.373752	2.617798
H	-2.550813	-6.252571	3.081215

II (45.30)

11
 B3LYP/6-31+G*
 ZPE: -5481.857073 a.u.
 SCRF(PCM,solvent=acetonitrile)
 HF: -5481.976756 a.u.
 B3LYP-D/6-31+G*
 SCRF(PCM,solvent=acetonitrile)
 HF: -5481.984008 a.u.

0 2

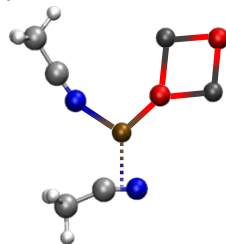


O	0.915840	-0.361898	-0.598179
Zn	0.189076	0.454491	0.996861
Zn	2.365681	-0.880968	0.575482
O	1.006317	-1.050177	1.990159
Cu	0.098237	-2.057443	0.507729
N	-0.961455	-3.536634	-0.264551
C	-0.829973	-3.836872	0.880277
C	-0.911904	-4.600399	2.136276
H	0.076346	-4.998076	2.387249
H	-1.234068	-3.950139	2.953749
H	-1.619298	-5.428743	2.019598

III (20.93)

17
 B3LYP/6-31+G*
 ZPE: -5614.598637 a.u.
 SCRF(PCM,solvent=acetonitrile)
 HF: -5614.762597 a.u.
 B3LYP-D/6-31+G*
 SCRF(PCM,solvent=acetonitrile)
 HF: -5614.778735 a.u.

0 2



C	0.682342	1.033513	-2.001478
Cu	-0.766031	1.644001	-3.356774
N	-2.277130	2.302212	-2.250206
C	-3.311737	2.755421	-1.994929
C	-4.625900	3.330505	-1.739506
H	-4.531523	4.244522	-1.144807
H	-5.100744	3.573446	-2.697320
H	-5.254285	2.614836	-1.200014
O	-2.238857	2.385508	-7.814574

Zn	-2.925934	2.710412	-6.075065
Zn	-0.791686	1.633951	-6.927446
O	-1.356898	1.905707	-5.124144
C	0.682263	1.065192	-0.528734
H	-0.143122	0.461629	-0.139981
H	1.630299	0.668911	-0.148564
H	0.552417	2.092129	-0.175073
N	1.067158	0.843523	-3.109650

IV (2.51)

17

B3LYP/6-31+G*

ZPE: -5614.606461 a.u.

SCRF(PCM, solvent=acetonitrile)

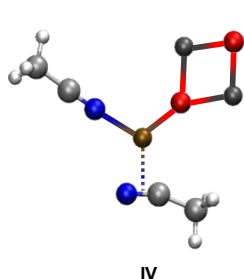
HF: -5614.767294 a.u.

B3LYP-D/6-31+G*

SCRF(PCM, solvent=acetonitrile)

HF: -5614.783449 a.u.

0 2



C	0.950438	0.991580	-3.279220
Cu	-0.905115	1.761314	-3.680553
N	-2.486323	2.433734	-2.602303
C	-3.427359	2.831807	-2.060795
C	-4.619313	3.338056	-1.389978
H	-4.419923	4.330630	-0.973699
H	-5.446121	3.411633	-2.103884
H	-4.907948	2.663538	-0.577775
O	-2.123806	2.273150	-8.225234
Zn	-2.735448	2.724303	-6.516990
Zn	-0.678270	1.474784	-7.329311
O	-1.269978	1.932451	-5.505674
C	1.997431	0.577748	-4.228199
H	1.628980	-0.239189	-4.855383
H	2.258840	1.414163	-4.882415
H	2.885664	0.247390	-3.678184
N	0.406841	1.199811	-2.242441

V (9.24)

21

B3LYP/6-31+G*

ZPE: -9323.369687 a.u.

SCRF(PCM, solvent=acetonitrile)

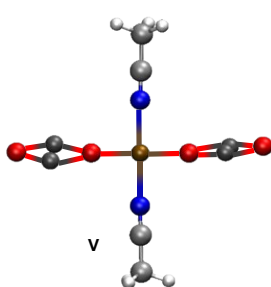
HF: -9323.591363 a.u.

B3LYP-D/6-31+G*

SCRF(PCM, solvent=acetonitrile)

HF: -9323.618084 a.u.

0 2

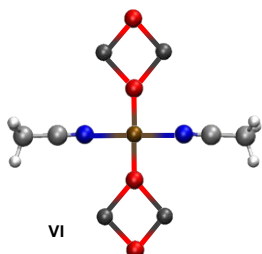


C	-0.059899	0.058943	-0.082211
C	0.008850	0.045273	1.374015
N	0.058008	0.035210	2.528071
Cu	0.108945	0.021903	4.630185
O	-1.761726	0.183393	4.671912
Zn	-3.293416	0.246450	3.442962
O	-4.629185	0.291700	4.751673
Zn	-3.220607	0.238697	5.978972
O	1.977363	-0.143706	4.586938
Zn	3.431081	-0.195196	3.274243
Zn	3.513906	-0.222777	5.810602
O	4.844106	-0.261931	4.495730
N	0.152667	0.021723	6.731348
C	0.144864	0.029098	7.886431
C	0.124586	0.040542	9.344147
H	-1.094237	0.218298	-0.404216
H	0.566360	0.864858	-0.477819
H	0.295425	-0.896384	-0.481277
H	0.436029	-0.935561	9.729261
H	0.808976	0.807056	9.721272
H	-0.887951	0.258266	9.699725

VI (9.06)

21
 B3LYP/6-31+G*
 ZPE: -9323.370833 a.u.
 SCRF(PCM,solvent=acetonitrile)
 HF: -9323.587221 a.u.
 B3LYP-D/6-31+G*
 SCRF(PCM,solvent=acetonitrile)
 HF: -9323.609274 a.u.

0 2

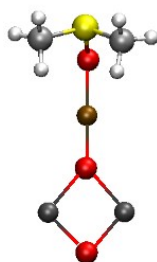


C	0.063089	0.055067	0.040884
C	0.008319	0.059104	1.498320
N	-0.032098	0.061698	2.652320
Cu	-0.019012	0.106569	4.744931
O	1.658870	-0.718987	4.754309
Zn	2.425557	-2.503206	4.563178
O	4.214119	-1.950384	4.488509
Zn	3.552439	-0.206123	4.681223
N	-0.012814	0.158884	6.830476
C	0.000072	0.144563	7.984830
C	0.017194	0.125748	9.443067
O	-1.698122	0.933877	4.730560
Zn	-3.580984	0.479445	4.427062
O	-4.260887	2.204174	4.688345
Zn	-2.484174	2.709515	4.990276
H	-0.626003	0.803764	-0.362281
H	1.079512	0.284480	-0.294361
H	-0.220545	-0.931543	-0.338991
H	0.905885	-0.403906	9.800377
H	0.032459	1.150080	9.828568
H	-0.877345	-0.380426	9.819450

I' (7.86)

15
 B3LYP/6-31+G*
 ZPE: -5902.301822 a.u.
 SCRF(PCM,solvent=dimethylsulfoxide)
 HF: -5902.433559 a.u.
 B3LYP-D/6-31+G*
 SCRF(PCM,solvent=dimethylsulfoxide)
 HF: -5902.450645 a.u.

0 2



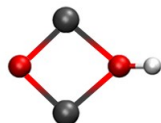
O	2.04818500	-0.34582500	-1.60820000
Zn	0.67694300	-0.48953900	-0.33870700
Zn	2.37890600	-2.16075400	-1.28526400
O	0.94053300	-2.39774300	0.03007500
Cu	0.36845900	-3.68632500	1.13337600
O	-0.23450700	-5.05364400	2.30445600
S	-1.46181900	-5.97292200	2.05300100
C	-2.87221500	-4.86318500	1.72602900
C	-1.26008900	-6.64784800	0.36976900
H	-3.74382200	-5.46708200	1.45431200
H	-3.07112800	-4.31841400	2.65193100
H	-2.60599100	-4.16422200	0.92704200
H	-0.38115900	-7.29647600	0.38873800
H	-2.14929200	-7.23200000	0.11203500
H	-1.10553200	-5.82399900	-0.33404500

ZnOH (171.8)

5
 B3LYP/6-31+G*
 ZPE: -3709.368740 a.u.
 SCRF(PCM,solvent=acetonitrile)
 HF: -3709.441301 a.u.
 SCRF(PCM,solvent=dimethylsulfoxide)
 HF: -3709.442001 a.u.
 B3LYP-D/6-31+G*
 SCRF(PCM,solvent=acetonitrile)

HF: -3709.444289 a.u.
 SCRF(PCM,solvent=dimethylsulfoxide)
 HF: -3709.444989 a.u.

0 2

**ZnOH**

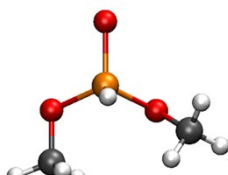
O	-0.073030	0.216890	0.000550
Zn	-0.020170	-0.350240	1.939610
Zn	1.853870	-0.358190	0.053590
O	1.795400	-0.739870	1.868900
H	-0.757290	0.135090	-0.683370

H-P(O)(OCH₃)₂ (64.18)

13

B3LYP/6-31+G*
 ZPE: -647.401190 a.u.
 SCRF(PCM,solvent=acetonitrile)
 HF: -647.514268 a.u.
 SCRF(PCM,solvent=dimethylsulfoxide)
 HF: -647.514411 a.u.
 B3LYP-D/6-31+G*
 SCRF(PCM,solvent=acetonitrile)
 HF: -647.524448 a.u.
 SCRF(PCM,solvent=dimethylsulfoxide)
 HF: -647.524591 a.u.

0 1

**H-P(O)(OCH₃)₂**

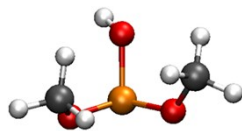
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.442205
P	1.399774	0.000000	2.259446
O	0.920151	0.438782	3.727602
C	-0.172724	-0.220178	4.394292
O	2.501929	0.807444	1.690820
H	1.693458	-1.372658	2.397160
H	0.340191	-0.968939	-0.383134
H	-1.034719	0.169572	-0.301986
H	0.641611	0.798174	-0.381830
H	-0.185802	0.172620	5.411970
H	-1.115321	0.005976	3.888633
H	-0.015978	-1.305402	4.424020

HO-P(OCH₃)₂ (28.67)

13

B3LYP/6-31+G*
 ZPE: -647.392293 a.u.
 SCRF(PCM,solvent=acetonitrile)
 HF: -647.500243 a.u.
 SCRF(PCM,solvent=dimethylsulfoxide)
 HF: -647.500336 a.u.
 B3LYP-D/6-31+G*
 SCRF(PCM,solvent=acetonitrile)
 HF: -647.511087 a.u.
 SCRF(PCM,solvent=dimethylsulfoxide)
 HF: -647.511181 a.u.

0 1

**HO-P(OCH₃)₂**

C	-0.082559	-0.028498	0.006368
O	0.055488	0.164325	1.423668
P	1.402398	-0.050608	2.342272
O	1.414431	-1.658615	2.710201
C	1.273463	-2.729201	1.764679
O	2.520057	0.013942	1.075930
H	0.737556	0.452892	-0.532374
H	-1.034311	0.431261	-0.269602
H	-0.107966	-1.094596	-0.244018
H	0.228259	-2.817292	1.448348
H	3.403227	0.248016	1.402121
H	1.919202	-2.571293	0.894373
H	1.571194	-3.645662	2.279784

(ZnO)₂-HO-P(OCH₃)₂ (3.71)

17

B3LYP/6-31+G*

ZPE: -4356.147101 a.u.

SCRF(PCM,solvent=acetonitrile)

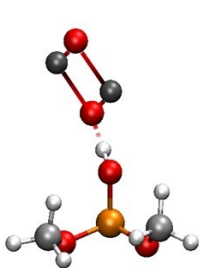
HF: -4356.361950 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -4356.376096 a.u.

0 1



C	-0.026044	0.025233	0.025660
O	0.247316	0.277479	1.409166
P	1.583224	-0.225137	2.256356
O	1.203390	-1.777308	2.717959
C	0.874694	-2.837007	1.814070
O	2.601292	-0.483591	0.982078
H	0.881078	0.124524	-0.577441
H	-0.765332	0.768624	-0.285812
H	-0.447520	-0.977859	-0.112912
H	-0.171448	-2.754964	1.494922
H	3.558537	-0.319624	1.236079
H	1.532918	-2.828055	0.938042
H	1.006611	-3.776112	2.359627
O	7.977672	0.442389	2.074007
Zn	6.302509	1.271087	2.314988
Zn	6.809748	-0.880752	1.414879
O	5.129187	-0.054316	1.648800

Cyclohexylacetylene (113.1)

20

B3LYP/6-31+G*

ZPE: -311.850660 a.u.

SCRF(PCM,solvent=acetonitrile)

HF: -312.033389 a.u.

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -312.033428 a.u.

B3LYP-D/6-31+G*

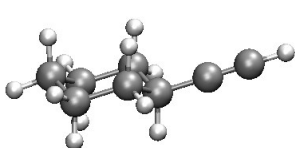
SCRF(PCM,solvent=acetonitrile)

HF: -312.057708 a.u.

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -312.057747 a.u.

0 1



C	-0.022230	0.007285	0.043299
C	0.036510	0.062893	1.577342
C	1.500458	0.060330	2.086134
C	2.304239	1.217490	1.440771
C	2.236677	1.157745	-0.092713
C	0.785623	1.145795	-0.599400
C	1.564695	0.109407	3.549737
H	1.962703	-0.886343	1.762038
H	1.890104	2.171884	1.795400
H	3.345141	1.177192	1.783778
H	2.782705	2.009039	-0.519970
H	2.751222	0.250041	-0.443871
H	0.309689	2.108270	-0.357092
H	0.766243	1.054020	-1.693375
H	-1.068332	0.047845	-0.287491
H	0.376035	-0.959787	-0.300266
H	-0.457864	0.976188	1.937564
H	-0.505397	-0.783799	2.015848
C	1.614554	0.161310	4.758493
H	1.662906	0.203283	5.823820

IN1 (18.47)

31

B3LYP/6-31+G*

ZPE: -5793.749198 a.u.

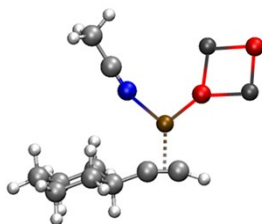
SCRF(PCM,solvent=acetonitrile)

HF: -5794.04183430 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)
HF: -5794.085694 a.u.

0 2



C	0.677793	2.615325	0.016526
C	0.740990	2.631153	1.551608
C	-0.307999	1.696372	2.173865
C	-0.179266	0.267408	1.622896
C	-0.247826	0.241340	0.088318
C	0.813597	1.176850	-0.537829
C	0.782433	1.142907	-2.018877
C	1.128413	0.966687	-3.201717
Cu	-0.690378	1.700664	-3.327099
N	-2.296836	2.377348	-2.340072
C	-3.334214	2.805249	-2.057875
C	-4.651409	3.349178	-1.752073
H	1.717976	0.705022	-4.059988
H	-0.104688	-0.779749	-0.285696
H	-1.242731	0.565381	-0.246050
H	-0.967384	-0.374457	2.037637
H	0.778024	-0.163615	1.953015
H	-1.314761	2.081114	1.949008
H	-0.211939	1.692056	3.267399
H	0.601802	3.657735	1.914811
H	1.744416	2.319533	1.878916
H	1.466331	3.248787	-0.407678
H	-0.280488	3.032691	-0.320934
H	-4.556281	4.246259	-1.132167
H	-5.159192	3.612542	-2.686838
H	-5.251769	2.606601	-1.217016
O	-2.330431	2.297564	-7.762764
Zn	-2.868580	2.720752	-6.002360
Zn	-0.845038	1.526424	-6.939931
O	-1.301992	1.910074	-5.106647
H	1.806339	0.798755	-0.243000

RC (6.22)

44

B3LYP/6-31+G*

ZPE: -6441.167025 a.u.

SCRF(PCM,solvent=acetonitrile)

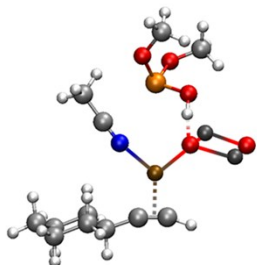
HF: -6441.568249 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -6441.636497 a.u.

0 2



C	0.926850	3.740650	0.242150
C	1.150230	3.998180	1.740580
C	0.685340	2.810820	2.598000
C	1.352110	1.501260	2.148550
C	1.129630	1.231630	0.652360
C	1.607740	2.426060	-0.207220
C	1.443870	2.172680	-1.657210
C	1.701200	1.984810	-2.859640
Cu	-0.265640	1.860260	-2.748450
N	-1.866510	1.973530	-1.564740
C	-2.900910	1.895510	-1.052320
C	-4.218560	1.768690	-0.445930
H	2.260920	1.872590	-3.768690
H	1.656860	0.320900	0.343610
H	0.062280	1.061570	0.457930
H	0.968440	0.656260	2.734620
H	2.432300	1.555620	2.352270
H	-0.407510	2.708850	2.513290
H	0.899870	3.001240	3.657520
H	0.623600	4.914210	2.037990
H	2.219840	4.181820	1.923460
H	1.312660	4.577280	-0.353050
H	-0.148740	3.669700	0.032150

H	-4.132090	1.332010	0.554110
H	-4.692370	2.752700	-0.369750
H	-4.823770	1.111590	-1.083690
O	-0.890650	2.659610	-7.074170
Zn	-1.840010	3.004710	-5.499180
Zn	-0.174080	1.190160	-6.175020
O	-1.108250	1.467610	-4.450380
H	2.692150	2.540160	-0.044810
H	-2.196650	0.310840	-4.393200
O	-2.896520	-0.432430	-4.496230
P	-3.503650	-1.021220	-3.099770
O	-4.955140	-0.173830	-2.962230
O	-3.982370	-2.516810	-3.618560
C	-5.872320	-0.001950	-4.052250
C	-4.171280	-2.924850	-4.981650
H	-5.340040	0.244920	-4.976690
H	-6.542360	0.821590	-3.787400
H	-6.465480	-0.912870	-4.193760
H	-5.174130	-2.652380	-5.331180
H	-3.421860	-2.469400	-5.634120
H	-4.069930	-4.013390	-4.995030

TS1 (-37.36)

44

B3LYP/6-31+G*

ZPE:-6441.162276 a.u.

SCRF(PCM,solvent=acetonitrile)

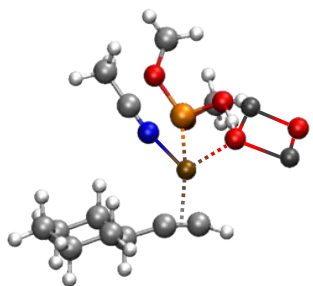
HF: -6441.568038 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -6441.636154 a.u.

0 2



C	0.138380	-0.799391	-0.380063
C	-0.334076	-0.500942	1.063252
C	0.901502	0.397393	-0.967807
H	-0.724388	-1.053314	-1.006500
H	0.784127	-1.686840	-0.364245
C	0.853472	-0.086765	1.964683
C	-1.118545	-1.617153	1.631842
H	-1.030719	0.352518	1.017739
C	2.077440	0.820256	-0.073575
H	1.257739	0.145159	-1.974754
H	0.211994	1.247206	-1.086152
C	1.613503	1.105806	1.363252
H	0.487081	0.158134	2.969204
H	1.530589	-0.944596	2.072226
C	-2.019389	-2.332419	2.089810
Cu	-0.439216	-3.559052	2.016953
H	2.574854	1.704250	-0.493221
H	0.960794	1.991982	1.364598
H	2.472280	1.352523	2.000854
H	2.828883	0.015807	-0.058588
H	-2.976622	-2.678886	2.427172
N	1.513689	-3.795233	1.672596
P	-0.663302	-5.523036	-0.328899
C	2.436335	-4.218818	1.115475
O	0.815694	-6.123920	-0.950294
O	-1.093863	-6.575644	0.756831
O	-1.695545	-5.799274	-1.624884
C	3.517207	-4.799146	0.334205
C	0.917481	-7.496975	-1.340990
C	-2.522792	-6.960553	-1.740638
H	4.098458	-5.498700	0.943336
H	3.044339	-5.342150	-0.494137
H	4.175696	-4.014482	-0.051806
H	1.982258	-7.744746	-1.422456
H	0.445921	-7.654173	-2.319352
H	0.450876	-8.153521	-0.597394
H	-2.735242	-7.391846	-0.757210

H	-3.455651	-6.649409	-2.222782
H	-2.034547	-7.717469	-2.368798
H	-1.031425	-5.933921	2.011121
O	-0.945690	-5.328859	2.905361
Cu	0.153371	-6.210844	4.355019
Zn	-2.415222	-5.742315	4.265743
O	-1.255152	-6.443280	5.538721

PC (2.71)

44

B3LYP/6-31+G*

ZPE: -6441.183580 a.u.

SCRF(PCM,solvent=acetonitrile)

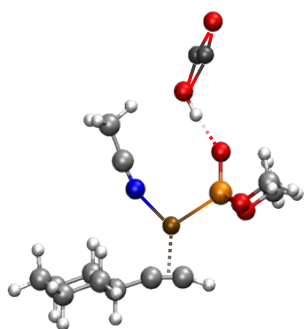
HF: -6441.586030 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -6441.647239 a.u.

0 2



C	0.073740	-0.212420	-0.091460
C	-0.025140	-0.195710	1.452700
C	1.381440	-0.127060	2.093890
C	2.174440	1.078980	1.566990
C	2.265130	1.074720	0.032920
C	0.871410	0.994580	-0.609110
C	-0.822670	-1.32690	1.975660
C	-1.696960	-2.012110	2.527620
Cu	-0.418080	-3.381040	1.837660
P	-1.167630	-5.461270	2.434810
O	-0.647610	-6.746060	1.786040
N	1.215470	-3.763980	0.802220
C	2.025020	-4.376810	0.244960
C	2.996580	-5.222560	-0.430130
O	-2.828530	-5.444570	2.288480
C	-3.593650	-6.652050	2.184760
O	-0.923280	-5.556900	4.080620
C	-1.005990	-6.802430	4.782920
O	1.374160	-7.845910	0.385430
Zn	2.187520	-9.447960	1.294930
O	1.627700	-10.655480	-0.009710
Zn	0.721390	-9.269530	-0.856710
H	-0.489620	-6.664210	5.737100
H	-0.526900	-7.606290	4.214240
H	-2.052730	-7.067930	4.978400
H	-3.837990	-7.039640	3.182050
H	-4.521440	-6.398510	1.663590
H	-3.045500	-7.413940	1.621800
H	-2.577680	-2.326790	3.053840
H	-0.933250	-0.222870	-0.525960
H	0.565400	-1.144580	-0.401220
H	0.957050	0.936320	-1.701900
H	0.316240	1.919360	-0.390200
H	2.863950	0.210130	-0.291990
H	2.793270	1.970610	-0.318240
H	3.178880	1.079330	2.009570
H	1.687690	2.008320	1.899830
H	1.286840	-0.077930	3.185470
H	1.918170	-1.057030	1.862140
H	3.985580	-5.095890	0.022200
H	2.658220	-6.264860	-0.310560
H	3.051060	-4.963700	-1.492510
H	-0.569430	0.718230	1.742440
H	0.658410	-7.372980	0.900760

IN2 (12.41)

39

B3LYP/6-31+G*

ZPE: -2731.795969 a.u.

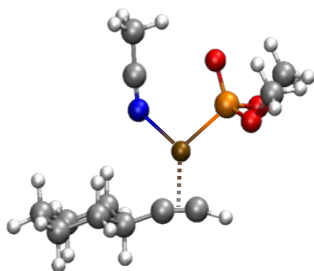
SCRF(PCM,solvent=acetonitrile)

HF: -2732.13079908 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)
HF: -2732.183041 a.u.

0 1



C	0.518243	2.661675	0.129062
C	0.908717	2.602063	1.613870
C	-0.006171	1.653519	2.404034
C	-0.034427	0.251582	1.775698
C	-0.428941	0.300015	0.291234
C	0.501788	1.248651	-0.502580
C	0.164232	1.286958	-1.942684
C	0.190174	1.195665	-3.179060
Cu	-1.615433	1.965813	-2.814110
P	-2.927063	2.434325	-4.634126
O	-2.031236	3.364845	-5.695374
C	-2.661782	4.216278	-6.657910
N	-2.959624	2.599814	-1.429964
C	-4.023188	3.065463	-1.415636
C	-5.353885	3.642797	-1.510906
O	-4.276854	3.103450	-4.395280
O	-3.154233	1.009306	-5.476603
C	-4.214322	0.875053	-6.428850
H	-1.942971	5.002138	-6.909719
H	-3.574203	4.662612	-6.248608
H	-2.908795	3.655474	-7.569101
H	-3.927061	1.312614	-7.394093
H	-4.388975	-0.196666	-6.563695
H	-5.128400	1.358865	-6.068294
H	0.495232	1.005336	-4.190040
H	-0.393051	-0.703987	-0.149060
H	-1.462198	0.657733	0.190208
H	-0.733542	-0.396677	2.319709
H	0.959507	-0.211245	1.873956
H	-1.027054	2.064104	2.418672
H	0.322663	1.593388	3.449738
H	0.873473	3.611845	2.042977
H	1.951593	2.261811	1.705015
H	1.212079	3.305012	-0.425784
H	-0.481626	3.103404	0.025415
H	-5.375640	4.637705	-1.055188
H	-5.572127	3.710792	-2.585541
H	-6.087859	2.999858	-1.014956
H	1.524909	0.842140	-0.441067

TS2 (-257.0)

39

B3LYP/6-31+G*

ZPE: -2731.740984 a.u.

SCRF(PCM,solvent=acetonitrile)

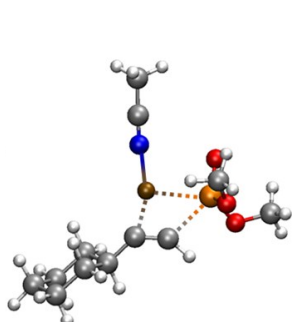
HF: -2732.078579 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -2732.129964 a.u.

0 1



C	-0.076463	-0.041502	0.223883
C	0.188733	0.119826	1.737430
C	1.681941	-0.021229	2.072375
C	2.539313	0.965927	1.264702
C	2.277541	0.826982	-0.243432
C	0.783305	0.963912	-0.575089
C	-1.533724	0.131587	-0.098097
Cu	-3.049011	1.324923	-0.208392
N	-4.055768	2.879522	0.041929
C	-4.800872	3.734394	0.266797
C	-5.764704	4.787366	0.554490
C	-2.404629	-0.612615	-0.700707
P	-4.711758	-0.343493	-1.100210
O	-5.882783	0.257047	-0.358070
O	-4.848964	-0.125414	-2.746476

C	-5.168295	1.173237	-3.247682
O	-4.744487	-1.984611	-1.104094
C	-5.996804	-2.653589	-1.332674
H	-5.814576	-3.713833	-1.142543
H	-6.319097	-2.512624	-2.369952
H	-6.764456	-2.276750	-0.649676
H	-2.523338	-1.573513	-1.188174
H	0.244029	-1.057854	-0.066250
H	-0.172716	1.110691	2.049369
H	-0.399871	-0.618991	2.296284
H	1.837825	0.131324	3.148921
H	2.009961	-1.049037	1.853209
H	2.299913	1.993400	1.579931
H	3.604981	0.812133	1.482017
H	2.852539	1.579046	-0.800671
H	2.638146	-0.155738	-0.584126
H	0.439963	1.981491	-0.336953
H	0.616558	0.819107	-1.650265
H	-5.549187	5.242000	1.526920
H	-5.718262	5.562009	-0.217662
H	-6.773761	4.362027	0.574288
H	-4.370127	1.893710	-3.020128
H	-5.257947	1.074871	-4.332635
H	-6.113983	1.533178	-2.827465

IN3 (20.07)

39

B3LYP/6-31+G*

ZPE: -2731.825696 a.u.

SCRF(PCM,solvent=acetonitrile)

HF: -2732.164767 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -2732.216951 a.u.

0 1

C	0.001266	0.002299	0.001710
C	0.003263	0.001319	1.538353
C	1.433511	-0.000940	2.102779
C	2.275371	-1.177360	1.558937
C	2.262643	-1.160438	0.012907
C	0.834223	-1.162594	-0.555564
C	3.694246	-1.140720	2.092550
C	4.131697	-2.206859	2.808882
P	5.780049	-2.214160	3.470684
O	6.595170	-0.983896	3.174150
Cu	4.944858	0.308667	1.797113
N	6.035876	1.786997	1.400815
C	6.773566	2.652795	1.191436
C	7.708750	3.739701	0.929753
O	5.704311	-2.531335	5.077258
C	5.432199	-1.455899	5.987197
O	6.415496	-3.613991	2.963346
C	7.755384	-3.975497	3.338967
H	7.984491	-4.895749	2.797619
H	7.814008	-4.154532	4.417435
H	8.460650	-3.189253	3.050642
H	3.518528	-3.089147	3.024450
H	1.781164	-2.112844	1.880772
H	2.795757	-0.261124	-0.331967
H	2.826290	-2.021827	-0.368817
H	0.868216	-1.115009	-1.652839
H	0.341511	-2.113429	-0.300327
H	0.424145	0.953023	-0.358649
H	-1.028156	-0.047158	-0.379046
H	-0.548498	0.871522	1.920190
H	-0.532773	-0.889988	1.899382
H	1.936965	0.941426	1.837632
H	1.408618	-0.041981	3.200045
H	7.658598	4.034244	-0.123475

H	7.461345	4.605551	1.552468
H	8.729019	3.416732	1.160873
H	4.427571	-1.049608	5.818762
H	5.488414	-1.882256	6.991467
H	6.174503	-0.659333	5.875289

IN4 (14.26)

44

B3LYP/6-31+G*

ZPE: -6441.252112 a.u.

SCRF(PCM,solvent=acetonitrile)

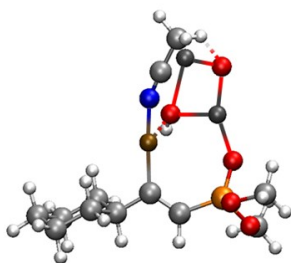
HF: -6441.626658 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -6441.702744 a.u.

0 2



C	0.186440	-0.141120	-0.206846
C	0.063447	-0.101846	1.325060
C	1.447761	-0.036222	2.012073
C	2.248127	1.170439	1.468294
C	2.374958	1.134293	-0.063171
C	0.998906	1.048716	-0.741478
C	1.311921	0.029726	3.524836
Cu	0.427846	1.561265	4.310360
Zn	1.544900	1.886125	7.025910
O	0.960466	3.341810	7.951991
Zn	1.646249	4.624142	6.722233
O	1.996871	2.939871	5.341737
C	1.832821	-1.026044	4.210442
P	1.789139	-1.231375	5.958156
O	0.507283	-2.127791	6.316072
C	0.234379	-2.538920	7.674023
O	2.992268	-2.231241	6.377747
C	4.349295	-1.753975	6.452921
O	1.856657	0.009648	6.855350
N	-0.992229	2.558406	5.149645
C	-1.553224	3.105927	6.003502
C	-2.140005	3.786106	7.147429
H	0.164336	-1.666841	8.330493
H	-0.724059	-3.058709	7.639045
H	1.016972	-3.216797	8.026066
H	4.438446	-0.981262	7.222044
H	4.958000	-2.619220	6.720326
H	4.674324	-1.359012	5.484274
H	2.292236	-1.887546	3.709839
H	2.833417	2.819216	4.864325
H	-1.346324	3.822324	7.909676
H	-2.439803	4.803022	6.874769
H	-3.010974	3.237728	7.520220
H	1.997905	-0.951689	1.724995
H	1.741243	2.098774	1.773799
H	3.243992	1.192077	1.931500
H	2.917848	2.022636	-0.413187
H	2.979383	0.262817	-0.358329
H	0.444224	1.980280	-0.550760
H	1.115564	0.971720	-1.830892
H	-0.814062	-0.152488	-0.660023
H	0.676451	-1.079303	-0.509514
H	-0.523963	0.778615	1.626154
H	-0.486315	-0.980453	1.686766

TS3 (-1015.9)

44

B3LYP/6-31+G*

ZPE: -6441.182888 a.u.

SCRF(PCM,solvent=acetonitrile)

HF: -6441.571480 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -6441.649435 a.u.

0 2



C	-0.284800	-0.556750	0.008180
C	0.105150	-0.217730	1.466700
C	1.628060	0.001320	1.568730
C	2.421360	-1.196960	1.025750
C	2.020490	-1.541190	-0.417100
C	0.504080	-1.758080	-0.537600
C	-0.686490	0.967730	2.019530
C	-2.047330	0.757480	2.285960
P	-3.104850	1.835630	3.170260
O	-2.585550	3.255340	3.439580
Zn	-0.843840	3.897730	4.027160
O	0.533570	2.498460	3.891590
Zn	1.637700	4.006730	4.437480
O	0.272750	5.355450	4.382850
Cu	-0.366200	2.751620	1.144800
N	-0.110000	4.595710	0.794500
C	0.068890	5.675480	1.181310
C	0.322540	6.951440	1.821060
O	-3.580810	1.146340	4.561790
C	-2.648340	1.00370	5.655120
O	-4.497010	1.858670	2.376360
C	-5.658730	2.534180	2.910370
H	-5.430600	3.587470	3.097330
H	-6.428750	2.449280	2.142450
H	-5.987360	2.045660	3.831370
H	-2.478470	1.973700	6.132530
H	-3.118230	0.320230	6.364030
H	-1.696550	0.589840	5.307880
H	-2.530210	-0.189670	2.033760
H	-0.065240	1.645110	2.841290
H	0.369340	6.702610	2.908970
H	1.276060	7.367980	1.481150
H	-0.485190	7.660370	1.613900
H	-0.142090	-1.103080	2.080110
H	1.892230	0.904730	0.993830
H	1.903410	0.210460	2.609040
H	3.498220	-0.988600	1.081750
H	2.241610	-2.071840	1.669870
H	2.321150	-0.716850	-1.082190
H	2.560850	-2.433270	-0.761400
H	0.226510	-1.941640	-1.584420
H	0.221730	-2.662400	0.023250
H	-0.090100	0.326820	-0.621020
H	-1.363670	-0.748980	-0.058280

IN5 (22.51)

44

B3LYP/6-31+G*

ZPE: -6441.235399 a.u.

SCRF(PCM,solvent=acetonitrile)

HF: -6441.627848 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -6441.702881 a.u.

0 2



C	0.028274	0.012708	-0.016630
C	0.032938	0.027072	1.519302
C	1.462218	0.015949	2.088602
C	2.285609	-1.166940	1.543326
C	2.272790	-1.173355	-0.000269
C	0.843080	-1.169671	-0.562803
C	3.704066	-1.265111	2.079892
C	4.115660	-0.873858	3.359508
P	5.497686	-1.559785	4.264301
O	6.114564	-0.625869	5.297302
Zn	6.612567	1.278865	4.905958
O	7.256759	2.961539	5.161483

Zn	6.908351	3.345080	3.309843
O	6.214684	1.408287	2.991998
Cu	4.890167	0.458506	2.100020
N	4.927948	1.454968	0.383987
C	5.259414	2.364791	-0.250630
C	5.725710	3.538799	-0.974250
O	4.863167	-2.858828	4.960206
C	5.624632	-3.632001	5.917285
O	6.559937	-2.176668	3.232510
C	7.806059	-1.509417	2.872672
H	5.972432	-2.990625	6.731318
H	4.938364	-4.388570	6.299353
H	6.471859	-4.113579	5.419856
H	7.617222	-0.458398	2.633399
H	8.512894	-1.596879	3.701875
H	8.179545	-2.053226	2.003825
H	6.288856	4.168970	-0.273601
H	6.379733	3.240846	-1.799899
H	4.878114	4.105864	-1.371728
H	3.416894	-0.354200	4.016123
H	4.339649	-1.975204	1.545793
H	1.780150	-2.095006	1.870060
H	1.968841	0.956404	1.823600
H	1.414436	-0.017721	3.184546
H	2.822564	-2.050011	-0.370360
H	2.813301	-0.287814	-0.362364
H	-1.002465	-0.028478	-0.392228
H	0.460920	0.953864	-0.388952
H	0.874671	-1.137851	-1.659771
H	0.341816	-2.111652	-0.292405
H	-0.511151	-0.854397	1.891344
H	-0.506051	0.906194	1.895121

(E)-VyP (23.07)

33

B3LYP/6-31+G*

ZPE: -959.314931 a.u.

SCRF(PCM,solvent=acetonitrile)

HF: -959.614070 a.u.

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -959.614226 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -959.665652 a.u.

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -959.663432 a.u.

0 1

C	-0.035268	-0.096845	-0.101801
C	-0.073751	-0.009380	1.431726
C	1.339346	0.050123	2.033008
C	2.211235	-1.143930	1.573003
C	2.243652	-1.219595	0.027119
C	0.829095	-1.276994	-0.571597
C	3.599632	-1.033818	2.136749
C	4.169603	-1.907068	2.980135
P	5.834273	-1.636522	3.591589
O	5.638168	-1.990792	5.169529
C	6.662000	-1.606880	6.109311
O	6.448104	-0.319124	3.287608
O	6.773137	-2.843551	3.028971
C	6.437109	-4.225937	3.212139
H	7.305724	-4.798306	2.879946
H	6.231315	-4.446651	4.265362
H	5.570134	-4.499544	2.599461
H	3.629244	-2.787849	3.326467
H	4.174240	-0.156139	1.833428
H	1.749917	-2.069313	1.951310
H	1.828166	0.987519	1.726634
H	1.288184	0.067760	3.129050

H	2.769877	-0.334683	-0.362129
H	2.827550	-2.094118	-0.287595
H	-0.648762	0.870215	1.749600
H	-0.601187	-0.888417	1.832523
H	0.891628	-1.292008	-1.667611
H	0.347605	-2.220952	-0.273751
H	-1.053266	-0.188934	-0.502642
H	0.377888	0.839076	-0.507808
H	6.262415	-1.831067	7.100040
H	7.578184	-2.183343	5.939803
H	6.877877	-0.538667	6.020818

IN1' (23.67)

35

B3LYP/6-31+G*

ZPE:-6214.164718 a.u.

SCRF(PCM,solvent=dimethylsulfoxide)

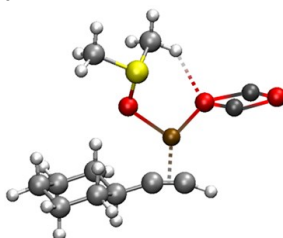
HF: -6214.488203 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -6214.541326 a.u

0 2



C	0.901847	2.569544	-0.079895
C	1.133699	2.638026	1.437361
C	0.040635	1.888371	2.215094
C	-0.091263	0.435598	1.731378
C	-0.327197	0.359725	0.215027
C	0.786812	1.102828	-0.561176
C	0.593121	1.016780	-2.026923
C	0.776034	0.765235	-3.234256
Cu	-0.932204	1.717231	-3.143506
H	1.238255	0.399668	-4.132453
H	-0.369777	-0.686155	-0.113829
H	-1.291744	0.818131	-0.039036
H	-0.912898	-0.068380	2.257165
H	0.826281	-0.116547	1.986926
H	-0.921106	2.404840	2.075334
H	0.256844	1.911895	3.291357
H	1.176677	3.687889	1.755845
H	2.114941	2.200119	1.677075
H	1.718541	3.069706	-0.615210
H	-0.026067	3.093588	-0.343372
O	-1.661524	2.402667	-7.549909
Zn	-1.397404	3.435758	-6.011875
Zn	-2.201838	1.056128	-6.354384
O	-1.981634	2.113749	-4.693081
H	1.743769	0.599258	-0.345139
O	-2.272553	2.582715	-1.792776
S	-3.422237	3.393213	-2.461262
C	-4.302847	4.073536	-1.014710
C	-4.674277	2.171509	-2.969332
H	-5.576710	2.700221	-3.293319
H	-4.225157	1.633773	-3.805724
H	-4.886820	1.500854	-2.131778
H	-5.215946	4.575147	-1.351029
H	-4.533976	3.266648	-0.313795
H	-3.635878	4.798279	-0.541841

IN2' (18.07)

43

B3LYP/6-31+G*

ZPE:-3152.207548 a.u.

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -3152.580219 a.u.

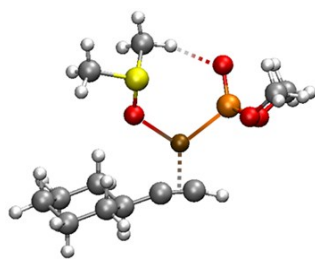
B3LYP-D/6-31+G*

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -3152.641344 a.u

0 1

C	-0.091940	-0.197390	-0.031750
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C	-0.106280	-0.121320	1.502850
C	1.319370	0.096820	2.064850
C	2.281230	-1.006340	1.561580
C	2.286700	-1.079470	0.026650
C	0.872160	-1.281220	-0.539120
C	1.319020	0.203480	3.540190
Cu	0.739050	-1.236760	4.937760
O	0.068170	-2.812570	3.807840
S	-0.180380	-4.213700	4.452350
C	-0.428180	-5.274930	2.991300
C	1.432770	0.614740	4.705370
P	0.402000	-1.744340	7.132610
O	1.876750	-2.186070	7.782870
C	1.953690	-2.860030	9.042880
O	-0.645890	-2.787980	7.512270
O	0.053260	-0.312520	7.929230
C	-0.682650	-0.304740	9.156760
C	-1.889230	-4.188360	5.073850
H	2.922980	-3.366870	9.076520
H	1.146430	-3.593350	9.144930
H	1.900500	-2.140830	9.870920
H	-0.008810	-0.438790	10.013330
H	-1.165990	0.674130	9.235630
H	-1.439290	-1.096270	9.163710
H	1.613260	1.223730	5.570380
H	-0.762170	0.690970	1.839790
H	-0.505650	-1.053830	1.922360
H	-1.108480	-0.388510	-0.400070
H	0.209610	0.777800	-0.444120
H	0.497940	-2.269670	-0.232130
H	0.899070	-1.282250	-1.636830
H	2.948380	-1.892230	-0.300780
H	2.711520	-0.149740	-0.382120
H	3.292660	-0.813230	1.939910
H	1.957340	-1.967080	1.982720
H	-2.178240	-5.214020	5.326520
H	-1.855670	-3.575490	5.982580
H	-2.543240	-3.768860	4.303710
H	-0.715910	-6.277580	3.322270
H	-1.199540	-4.836630	2.352090
H	0.523430	-5.319820	2.456630
H	1.688510	1.063630	1.683610

TS2' (-263.2)

43

B3LYP/6-31+G*

ZPE: -3152.152734 a.u.

SCRF(PCM,solvent=dimethylsulfoxide)

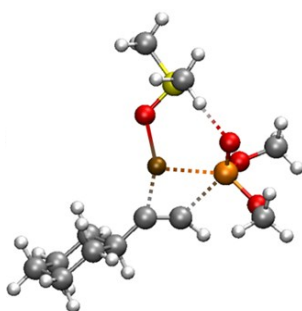
HF: -3152.521527 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -3152.580224 a.u

0 1



C	0.166149	0.154283	0.133097
C	0.564426	0.028360	1.621217
C	2.090126	-0.010686	1.804294
C	2.770587	1.207749	1.160901
C	2.379059	1.346309	-0.318585
C	0.853032	1.386550	-0.497337
C	-1.326454	0.232587	-0.009249
Cu	-2.965166	1.058592	0.620542
C	-2.224369	-0.553367	-0.507519
P	-4.532801	-0.263051	-0.807768
O	-5.431983	0.938210	-1.062276
O	-4.514203	-1.222861	-2.168683
C	-4.344732	-0.599388	-3.447134
O	-5.169042	-1.364809	0.229762
C	-6.478001	-1.917568	-0.003491
H	-6.723077	-2.507339	0.883006

H	-6.465880	-2.561720	-0.888183
H	-7.217285	-1.120230	-0.135263
H	-2.355118	-1.518452	-0.986212
H	0.541895	-0.743594	-0.389923
H	0.145142	0.886234	2.166696
H	0.105303	-0.871379	2.050548
H	2.334041	-0.062026	2.874184
H	2.489985	-0.930143	1.349660
H	2.466935	2.117803	1.700861
H	3.861871	1.132514	1.261753
H	2.827929	2.252156	-0.748393
H	2.792171	0.496418	-0.883644
H	0.444141	2.290267	-0.022773
H	0.594683	1.448049	-1.562592
H	-3.348306	-0.146467	-3.533224
H	-4.445803	-1.391233	-4.193822
H	-5.108854	0.167411	-3.609962
O	-3.990943	2.395011	1.563386
S	-5.549658	2.532113	1.492721
C	-5.876329	3.710990	0.145283
C	-5.859841	3.644582	2.902189
H	-6.926106	4.017730	0.195750
H	-5.206436	4.568841	0.252935
H	-5.687215	3.157979	-0.776162
H	-6.914643	3.936524	2.905881
H	-5.624816	3.085933	3.811052
H	-5.208593	4.519223	2.822509

IN3' (19.12)

43

B3LYP/6-31+G*

ZPE: -3152.235393 a.u.

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -3152.607635 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -3152.668592 a.u.

0 1

C	0.088160	0.654680	0.204090
C	-0.248060	0.506570	1.696850
C	0.895740	-0.166230	2.471720
C	1.280820	-1.512200	1.837610
C	1.612370	-1.359650	0.344300
C	0.458890	-0.699730	-0.444250
C	0.808240	-0.524780	-1.911320
C	-0.012690	-1.107490	-2.822310
P	0.252730	-1.005600	-4.573870
O	1.424450	-0.192050	-5.056270
Cu	2.321660	0.483910	-2.485400
O	-1.187510	-0.544210	-5.154390
C	-1.408140	-0.460080	-6.571400
O	3.832440	1.527360	-3.085700
S	4.357540	1.283650	-4.536660
C	3.263990	2.242780	-5.630430
C	5.824210	2.363080	-4.588890
O	0.289640	-2.532030	-5.173600
C	1.497530	-3.296540	-5.057490
H	-2.400500	-0.022600	-6.699170
H	-0.657480	0.183130	-7.042930
H	-1.380560	-1.457470	-7.021680
H	1.303000	-4.254690	-5.544890
H	1.749320	-3.466910	-4.003860
H	2.327450	-2.785310	-5.556250
H	-0.894050	-1.694280	-2.537640
H	-0.423960	-1.358970	-0.350930
H	0.935810	1.346370	0.083000
H	-0.757620	1.101060	-0.335080
H	-0.472280	1.491540	2.129120
H	-1.162290	-0.097140	1.805810

H	1.773510	0.498530	2.469000
H	0.612990	-0.307000	3.524050
H	2.136700	-1.951920	2.368190
H	0.444760	-2.218950	1.955220
H	2.515510	-0.741300	0.227650
H	1.847020	-2.338510	-0.095130
H	3.698460	2.254840	-6.635500
H	2.312300	1.704530	-5.633260
H	3.156970	3.255410	-5.231100
H	6.227280	2.374310	-5.606190
H	5.541710	3.368480	-4.264790
H	6.560060	1.941160	-3.900460

IN4' (12.58)

48

B3LYP/6-31+G*

ZPE: -6861.677057 a.u.

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -6862.085494 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -6862.167577 a.u

0 2

C	2.132598	-0.895780	-0.537485
C	0.675678	-0.730655	-0.997375
C	-0.075986	0.307755	-0.147807
C	-0.014921	-0.038214	1.361328
C	1.455424	-0.195335	1.808310
C	2.207345	-1.233058	0.959707
C	-0.753723	1.010943	2.179534
C	-1.976088	0.624584	2.649303
P	-3.078394	1.601897	3.610153
O	-2.496005	2.627782	4.601291
Zn	-0.764706	3.475582	4.600136
O	0.468770	4.352090	3.416752
Zn	1.808377	4.510121	4.809399
O	0.325137	3.886426	6.151665
Cu	0.068334	2.740564	2.388059
O	-4.140158	2.295674	2.624927
C	-5.212636	3.113042	3.142552
O	-4.043518	0.598966	4.441154
C	-3.552897	-0.066962	5.620212
H	-4.810845	3.925621	3.754608
H	-5.723979	3.519909	2.268955
H	-5.902519	2.501083	3.730639
H	-3.274232	0.666519	6.382456
H	-4.375604	-0.687062	5.980209
H	-2.692642	-0.699862	5.376345
H	-2.404682	-0.361022	2.427381
H	1.777704	5.816105	2.022501
H	-0.506637	-1.021153	1.489200
H	0.354759	1.305064	-0.304268
H	-1.125770	0.366502	-0.464710
H	1.492798	-0.472285	2.870687
H	1.956068	0.780733	1.722148
H	2.633973	-1.673936	-1.129326
H	2.677471	0.042305	-0.722884
H	3.254948	-1.292594	1.285148
H	1.771338	-2.230028	1.129392
H	0.163329	-1.702967	-0.926906
H	0.642555	-0.437242	-2.055749
S	0.329501	5.179690	0.276398
O	0.630511	3.672138	0.366975
C	1.786669	6.042756	0.954511
C	0.597355	5.589443	-1.486509
H	1.681717	7.119687	0.785442
H	0.428111	3.359112	6.957103
H	2.692051	5.652673	0.479658
H	-0.184616	5.082812	-2.057309

H	0.519794	6.672534	-1.627770
H	1.580219	5.222017	-1.795639

TS3' (-1223.3)

48

B3LYP/6-31+G*

ZPE: -6861.591053 a.u.

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -6862.020502 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -6862.103614 a.u.

0 2

C	2.06669	-1.74680	-0.26028
C	0.54640	-1.84655	-0.45963
C	-0.17452	-0.58619	0.04595
C	0.16251	-0.27423	1.52325
C	1.69024	-0.17545	1.70571
C	2.41668	-1.43240	1.20260
C	-0.56165	0.97130	2.04188
C	-1.95715	0.86068	2.19266
P	-2.97247	1.99640	3.03797
O	-2.33579	3.35727	3.37187
Zn	-0.55489	3.70305	4.05249
O	0.79730	4.95633	4.36483
Zn	1.83148	3.38911	4.75776
O	0.54283	2.05795	4.25182
Cu	-0.02098	2.69303	1.20853
O	-4.30969	2.17575	2.16892
C	-5.44993	2.90183	2.67898
O	-3.59884	1.33527	4.38323
C	-2.75276	1.10850	5.53495
H	-5.15759	3.91663	2.96492
H	-6.16886	2.93821	1.85909
H	-5.87919	2.37499	3.53522
H	-2.67368	2.03218	6.11653
H	-3.24935	0.33874	6.12819
H	-1.75365	0.77477	5.23820
H	-2.48646	-0.04699	1.89341
H	1.30415	6.00427	2.77039
H	-0.18361	-1.13620	2.12237
H	0.12034	0.27792	-0.57080
H	-1.25987	-0.69569	-0.07825
H	1.92231	0.01175	2.76058
H	2.05361	0.70332	1.14663
H	2.55471	-2.67796	-0.57898
H	2.46300	-0.94802	-0.90630
H	3.50230	-1.30830	1.31532
H	2.13613	-2.28984	1.83404
H	0.16729	-2.72466	0.08578
H	0.31041	-2.01241	-1.51975
S	-0.04443	5.76185	0.83706
O	0.49084	4.35363	0.39442
C	1.29972	6.51980	1.78971
C	0.09191	6.71128	-0.70966
H	1.05979	7.57992	1.92601
H	0.02719	1.49252	3.00256
H	2.23743	6.39244	1.24011
H	-0.63014	6.29280	-1.41459
H	-0.14528	7.76004	-0.50701
H	1.10712	6.60628	-1.10195

IN5' (19.91)

48

B3LYP/6-31+G*

ZPE: -6861.650516 a.u.

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -6862.076403 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=dimethylsulfoxide)

HF: -6862.160377 a.u

0 2

C	-0.00755	-0.29879	-0.13001
C	0.00753	-0.10822	1.39409
C	1.44096	-0.06958	1.95083
C	2.24627	-1.31859	1.54208
C	2.22293	-1.50484	0.00925
C	0.78912	-1.54636	-0.54107
C	3.67230	-1.35831	2.06706
C	4.09434	-0.84927	3.30563
P	5.50495	-1.42493	4.22793
O	6.19333	-0.35245	5.06165
Zn	6.52121	1.52304	4.43003
O	7.02155	3.25090	4.72768
Zn	6.63586	3.64972	2.90596
O	6.08925	1.57198	2.52165
Cu	4.80612	0.35415	1.89803
O	4.91922	-2.60001	5.14745
C	5.73218	-3.20960	6.17815
O	6.51410	-2.19039	3.23723
C	7.73888	-1.57678	2.75089
H	6.10453	-2.44608	6.86599
H	5.07372	-3.90289	6.70248
H	6.56443	-3.75614	5.72444
H	7.53841	-0.57165	2.36865
H	8.47319	-1.53563	3.55946
H	8.09385	-2.23232	1.95439
H	3.39712	-0.28900	3.92982
H	4.30377	-2.11518	1.59645
H	1.73675	-2.19587	1.98325
H	1.95617	0.82573	1.57202
H	1.40180	0.02645	3.04359
H	2.75437	-2.42986	-0.25576
H	2.77868	-0.67876	-0.45388
H	-1.04154	-0.36960	-0.49268
H	0.43416	0.58764	-0.61015
H	0.81260	-1.64113	-1.63478
H	0.27658	-2.44389	-0.16147
H	-0.54273	-0.93570	1.86763
H	-0.52018	0.81402	1.66962
S	5.39119	2.27024	-0.33869
O	4.73046	0.87630	-0.05253
C	7.17730	1.94461	-0.45242
C	5.04474	2.48086	-2.11707
H	7.68229	2.85322	-0.79426
H	7.47740	1.70525	0.57036
H	7.34725	1.10784	-1.13678
H	3.96584	2.61507	-2.22400
H	5.56617	3.37328	-2.47708
H	5.36809	1.58975	-2.66199

IN6 (19.17)

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B3LYP/6-31+G*

ZPE: -2731,812806 a.u.

SCRF(PCM,solvent=acetonitrile)

HF: -2732,158949 a.u.

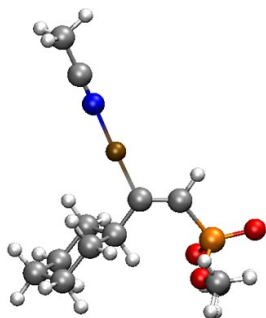
B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -2732.210377 a.u

0 1

C	0.120680	4.090710	0.112580
C	-0.315170	3.299520	1.355880
C	0.168490	1.841590	1.297170
C	-0.297910	1.125960	0.009120
C	0.150810	1.931540	-1.232300
C	-0.330510	3.390610	-1.178850
C	0.227640	-0.297220	-0.050490



C	-0.595460	-1.373280	-0.120660
P	-2.394310	-1.459090	-0.133000
O	-2.923210	-2.856930	-0.128550
Cu	2.121210	-0.610650	-0.052870
N	3.967860	-0.959530	-0.062990
C	5.102980	-1.181510	-0.072870
C	6.533150	-1.460340	-0.085420
O	-3.001860	-0.553660	1.097170
C	-3.088280	-1.137250	2.405110
O	-2.854890	-0.530520	-1.384380
C	-4.249540	-0.462990	-1.731310
H	-4.301580	0.078600	-2.678280
H	-4.807380	0.080880	-0.961600
H	-4.664920	-1.468310	-1.853190
H	-0.188350	-2.383270	-0.173310
H	-1.396070	1.130610	0.015450
H	1.251410	1.910990	-1.292600
H	-0.222520	1.439840	-2.139360
H	0.037590	3.938790	-2.057250
H	-1.429300	3.411300	-1.236070
H	1.218390	4.182710	0.109360
H	-0.278340	5.113610	0.152000
H	0.062850	3.783910	2.267000
H	-1.413230	3.313680	1.426900
H	1.269890	1.818640	1.339420
H	-0.187950	1.287390	2.175460
H	7.013450	-0.912130	-0.902300
H	6.982490	-1.151380	0.863870
H	6.703020	-2.532450	-0.227740
H	-2.087700	-1.265810	2.836670
H	-3.660020	-0.436580	3.018450
H	-3.598830	-2.104380	2.364610

IN7 (9.61)

44

B3LYP/6-31+G*

ZPE: -6441,228094 a.u.

SCRF(PCM,solvent=acetonitrile)

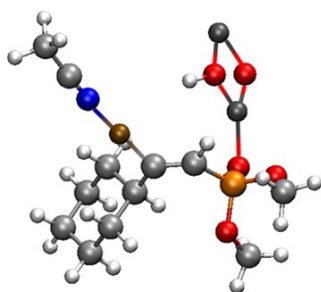
HF: -6441,625752 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -6441,703928 a.u.

0 2



C	0.907865	0.865812	-1.374979
C	0.575209	0.488720	0.077474
C	1.750699	0.792689	1.036260
C	2.169117	2.276399	0.908213
C	2.506160	2.652893	-0.543166
C	1.342820	2.334711	-1.495353
C	1.381193	0.447737	2.464936
Cu	0.057378	1.492504	3.382968
Zn	6.021481	2.587192	5.383895
O	7.023173	1.500428	4.190546
Zn	5.584031	0.507833	3.697512
O	4.294706	1.275386	4.999045
C	2.004190	-0.542048	3.155127
P	3.412668	-1.518986	2.656888
O	4.759554	-0.821201	2.508367
O	3.610859	-2.672861	3.769748
C	2.579644	-3.629413	4.077146
O	3.031621	-2.265812	1.277771
N	-1.137610	2.560723	4.361823
C	-1.805384	3.255593	5.000675
C	-2.638246	4.136549	5.808131
H	2.300951	-4.197947	3.184176
H	3.006169	-4.297474	4.826920
H	1.695784	-3.130858	4.487961
H	1.749039	-0.743477	4.195568
H	3.414557	1.585716	4.736045

H	-3.125455	3.563760	6.603680
H	-2.019413	4.918742	6.259797
H	-3.405040	4.603896	5.182124
H	2.605203	0.187974	0.696337
H	1.342506	2.910381	1.267812
H	3.025789	2.479148	1.563126
H	2.765403	3.718288	-0.599420
H	3.401243	2.098774	-0.863066
H	0.488101	2.985468	-1.252905
H	1.625256	2.563919	-2.531513
H	0.039016	0.671085	-2.018224
H	1.718360	0.217306	-1.740940
H	-0.309175	1.054439	0.410951
H	0.311209	-0.574370	0.145270
C	4.060274	-2.906398	0.484927
H	4.488328	-3.754580	1.028373
H	3.561075	-3.256136	-0.419757
H	4.846546	-2.189931	0.236283

TS4 (-1158.7)

44

B3LYP/6-31+G*

ZPE: -6441,163839 a.u.

SCRF(PCM,solvent=acetonitrile)

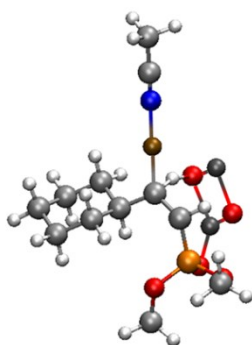
HF: -6441,560345 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -6441,640151 a.u.

0 2



C	1.288400	0.950950	-1.063190
C	0.953060	0.604910	0.396710
C	2.067540	1.046770	1.374330
C	2.351210	2.551440	1.191040
C	2.692600	2.906800	-0.264590
C	1.595100	2.446800	-1.236960
C	1.737940	0.686300	2.829570
Cu	0.291660	1.678880	3.670330
Zn	5.373250	2.350600	4.918800
O	6.596300	0.998960	4.559900
Zn	5.095980	0.172030	3.765880
O	3.786450	1.671200	4.157690
C	1.828270	-0.697230	3.227700
P	3.037750	-1.815370	2.671360
O	4.519190	-1.389960	2.797210
O	2.920390	-3.189940	3.524510
C	1.718990	-3.980330	3.492210
O	2.775270	-2.223320	1.126090
N	-1.061220	2.666580	4.517600
C	-1.898080	3.282870	5.025900
C	-2.954660	4.058630	5.662590
H	1.468900	-4.264310	2.464780
H	1.930380	-4.873340	4.083960
H	0.881290	-3.431350	3.934530
H	1.533910	-0.956090	4.246030
H	2.540650	1.310320	3.572380
H	-2.805530	5.124960	5.464420
H	-3.930740	3.756420	5.269240
H	-2.939750	3.892810	6.744630
H	2.986730	0.515870	1.064850
H	1.456130	3.118420	1.500900
H	3.160550	2.852960	1.865710
H	2.855540	3.989360	-0.360310
H	3.644110	2.425870	-0.540210
H	0.678110	3.026430	-1.045500
H	1.888100	2.659690	-2.274490
H	0.458900	0.654050	-1.720570
H	2.163440	0.363440	-1.381970
H	0.017610	1.110810	0.686480
H	0.773740	-0.470890	0.503540

C	3.819470	-2.839960	0.341450
H	4.081640	-3.820640	0.752210
H	3.408470	-2.955500	-0.663010
H	4.706230	-2.201880	0.319230

IN8 (20.40)

44

B3LYP/6-31+G*

ZPE: -6441,220880 a.u.

SCRF(PCM,solvent=acetonitrile)

HF: -6441,620534 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -6441,696493 a.u.

0 2

C	-0.757424	0.240496	2.020441
C	-0.249777	-0.903633	1.129056
C	1.129619	-1.409612	1.582886
C	2.161740	-0.252696	1.661188
C	1.642995	0.872263	2.577731
C	0.269639	1.379904	2.107342
C	3.546571	-0.795453	1.965311
C	4.204075	-1.022553	3.189890
P	3.704033	-0.840845	4.907233
O	3.571651	0.529492	5.535516
Zn	4.892370	2.047300	5.343627
O	5.525093	3.735805	5.629116
Zn	6.512172	3.577540	3.984856
O	5.884401	1.616560	3.718256
Cu	4.936927	0.669657	2.441533
N	5.234212	1.817457	0.843340
C	5.664190	2.743306	0.297667
C	6.237515	3.934475	-0.312734
O	2.317496	-1.658841	5.016636
C	1.520676	-1.576548	6.225269
O	4.794685	-1.655170	5.768385
C	5.091819	-3.050974	5.577573
H	1.279110	-0.534467	6.446470
H	0.613284	-2.145587	6.019504
H	2.059991	-2.021411	7.067024
H	4.175773	-3.634344	5.441042
H	5.755006	-3.183685	4.716840
H	5.607329	-3.374242	6.483279
H	6.724091	4.520997	0.477332
H	6.979518	3.655284	-1.067517
H	5.453685	4.537891	-0.781352
H	5.066344	-1.689394	3.137065
H	3.976424	-1.348065	1.127323
H	2.233965	0.171619	0.646887
H	1.050346	-1.877933	2.573309
H	1.491471	-2.184714	0.893530
H	2.361700	1.701593	2.602966
H	1.547935	0.509285	3.608143
H	-1.715018	0.620483	1.640894
H	-0.953862	-0.147459	3.031706
H	-0.086475	2.164069	2.787372
H	0.375699	1.850119	1.117737
H	-0.180663	-0.549112	0.089294
H	-0.967389	-1.734860	1.127210

(Z) -VyP (26.01)

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B3LYP/6-31+G*

ZPE: -959.305677 a.u.

SCRF(PCM,solvent=acetonitrile)

HF: -959.602694 a.u.

B3LYP-D/6-31+G*

SCRF(PCM,solvent=acetonitrile)

HF: -959.649634 a.u.

