Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A 1,2,4-Diazaphospholyl Radical and Its Nitrogen-Phosphorus Coupled Dimer: Synthesis, X-Ray Structural Characterization, EPR Analysis, and Computational Studies

Jing Su,[a] Binqiang Wang,[a] Dongling Liu,[a] Libo Du,[b] Yang Liu,[b] Jihu Su,[c] and Wenjun Zheng,[a,d,*]

[a]*Institute of Organic Chemistry & College of Chemical and Materials Science Shanxi Normal Univeristy, Gongyuan Street 1, Linfen, Shanxi Province, 041004, PR China*

[b]*Beijing Institute of Chemistry, Chinese Academy of Science, Zhongguancun North First Street 2, Beijing 100190, PR China*

[c]*Department of Morden Physics, University of Science and Technology of China, Hefei 230026, PR China*

[d]*Key Laboratory of Magnetic Molecules and Magnetic Information Material, Ministry of Education, Linfen, Shanxi Province, 041004, PR China*

Email: wjzheng@sxnu.edu.cn

Table of Content

SI-1. General consideration and spectroscopic measurement for [DMPO]**2**$^{\bullet}$ and **2**(*N*)–**2**(*P*)

All manipulations were carried out in an argon atmosphere under anaerobic conditions using standard Schlenk-line, vacuumline and glovebox techniques. The solvents were thoroughly dired before use. The single-crystal X-ray diffraction data of 2(N)-2(P) were collected using a Bruker SMART CCD diffractometer operating at 50 kV and 20 mA using Mo Ka radiation (k = 0.71073 Å). Empirical absorption correction was applied using the SADABS program. The structures were solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package. The hydrogen atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All non-hydrogen atoms were found from the difference Fourier syntheses. All calculations were per-formed using the Bruker Smart program.

Cyclic voltammetries were carried out at room temperature under nitrogen with a LK98II Microcomputer-based Electrochemical System (LAN-LIKE, Tianjin, China) and performed using a three-electrode system consisted of a Pt disk electrode (diameter 1 mm) as the working electrode, the $Ag/AgNO_3$ (a silver wire in a 0.1 M $AgNO_3$ CH_3CN solution) reference electrode and a platinum wire as the auxiliary electrode. Cyclic voltammetries were carried out with a scan rate of 100 mV/s in a 0.2M Bu_4NPF_6/DMF solution. Ferrocene was added to the electrolyte solution at the end of a series of experiments. The Fc/Fc couple served as internal standard. Bu_4NPF_6 was recrystallized three times from 95% ethanol and dried at 125°C in vacuo for 24 h prior to use.

The ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra were recorded with a Bruker DRX-600 spectrometer.

EPR measurements were carried out on a Bruker ESP-300 spectrometer at the X-band with a high sensitivity resonator at –10°C. General instrument settings are as follows: microwave frequency 9.5 GHz; microwave power, 12.9 mW; modulation amplitude, 0.5–1.5 G; modulation frequency, 100 kHz; receiver gain 1.04–1.06 × 10^5; time constant, 164 ms; and conversion time, 82 ms. DMPO, $FeCl_3$, and $CuCl_2$ were all commercially obtained. All solutions for spin trapping were prepared using anhydrous toluene. The total volume

of each solution used for EPR measurement was 0.5 mL, and it was loaded into a 50μL micropipette.

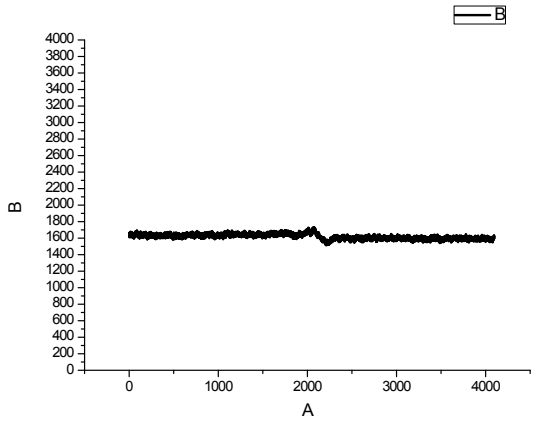
SI-2. Crystal data and structure refinements for **2**(*N*)–**2**(*P*)

Compound	**2**(*N*)–**2**(*P*)
CCDC number	1056795
Empirical formula	$C_{20}H_{36}N_4P_2$
Formula weight	394.47
Crystal system	Orthorhombic
Space group	*Pnma*
a, Å	9.2644(8)
b, Å	14.3849(12)
c, Å	17.7198(12)
α, º	90
β, º	90
γ, º	90
Volume, Å^3	2361.5(3)
Z	4
ρ, Mg/m^3	1.110
Absorption coefficient, mm^{-1}	0.195
F(000)	856
Crystal size, mm^3	0.211 × 0.157 × 0.123
Θ range, º	2.83 to 26.0
Limiting indices	-11 ≤ h ≤ 7
	-17 ≤ k ≤ 15
	-21 ≤ l ≤ 18
Reflections collected / unique	6173/ 2414
Data / restraints / parameters	2414 /36 / 171
GooF on F^2	1.049
R_1, wR_2 [I>2sigma(I)]	0.0473, 0.1142

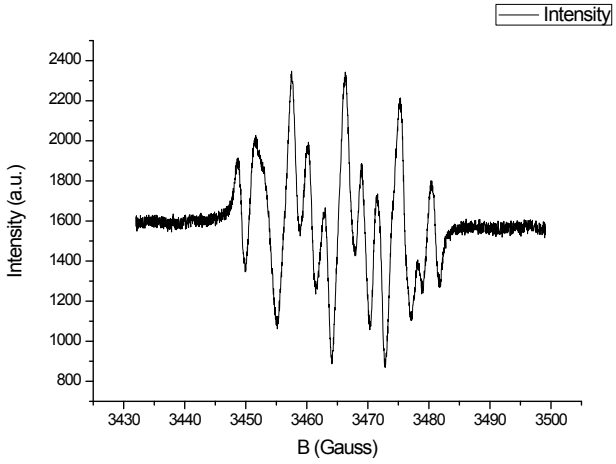
R_1, wR_2 (all data)	0.0769, 0.1287
Largest diff. peak and hole, e·A^{-3}	0.290 and -0.235

SI-3. EPR spectra for DMPO[**2**•]

SI-3-1 EPR spectrum of sole DMPO

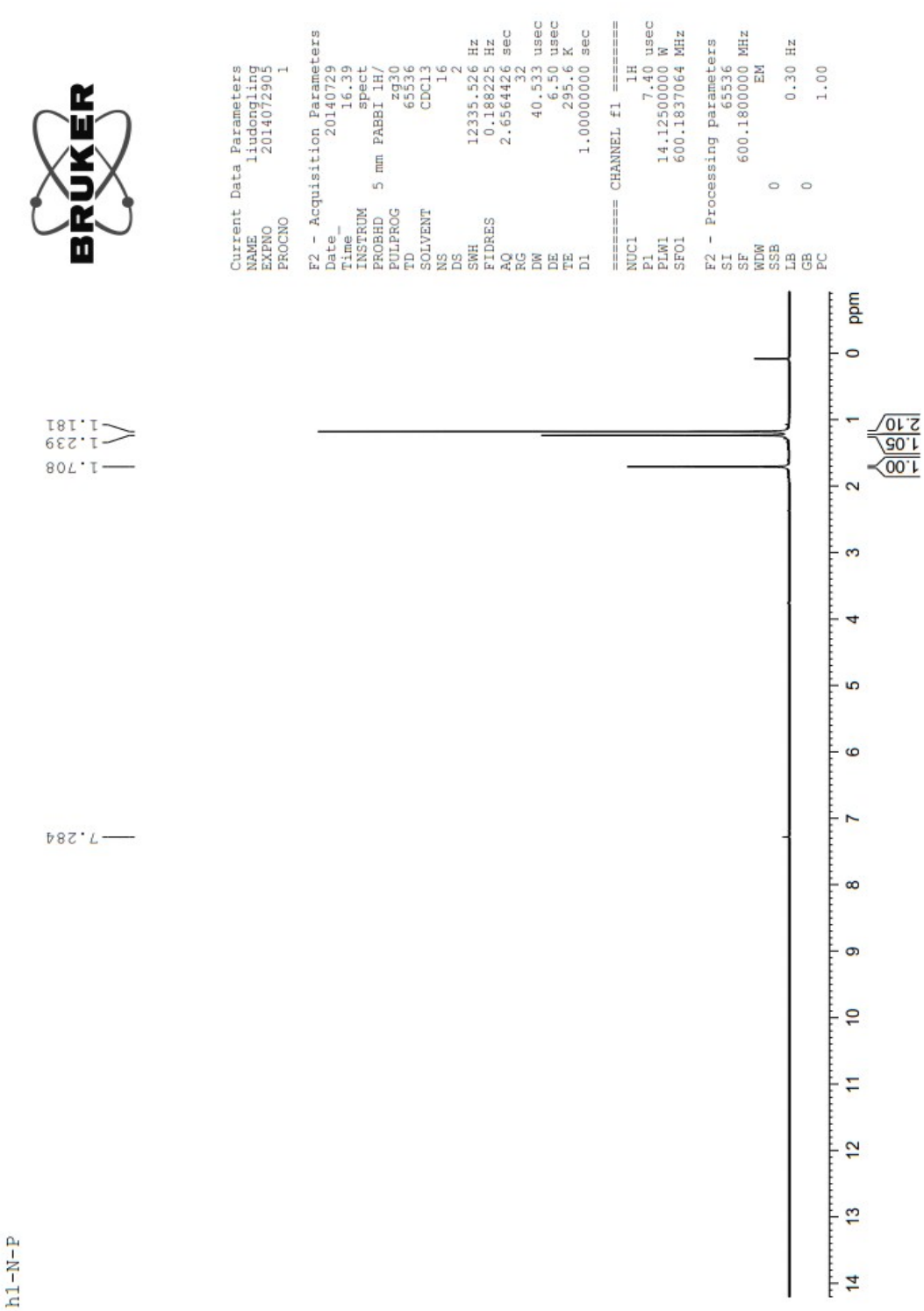


SI-3-2 EPR spectrum of DMPO[**2**•] in the presence of K^+[**2**$^-$] and $CuCl_2$

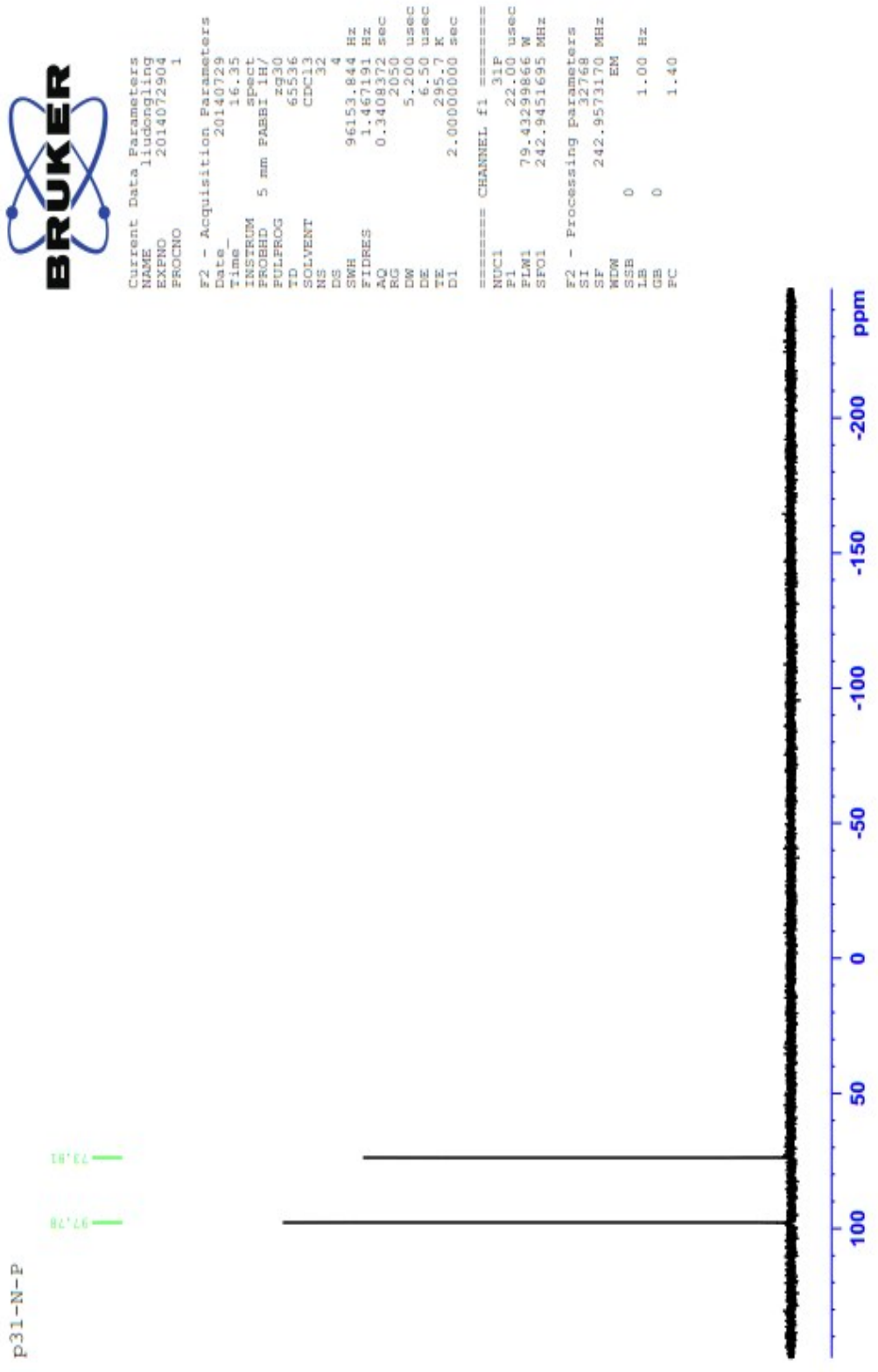


SI-4. ^{1}H, $^{31}P\{^{1}H\}$, and $^{13}C\{^{1}H\}$ spectra of **2**(*N*)–**2**(*P*)

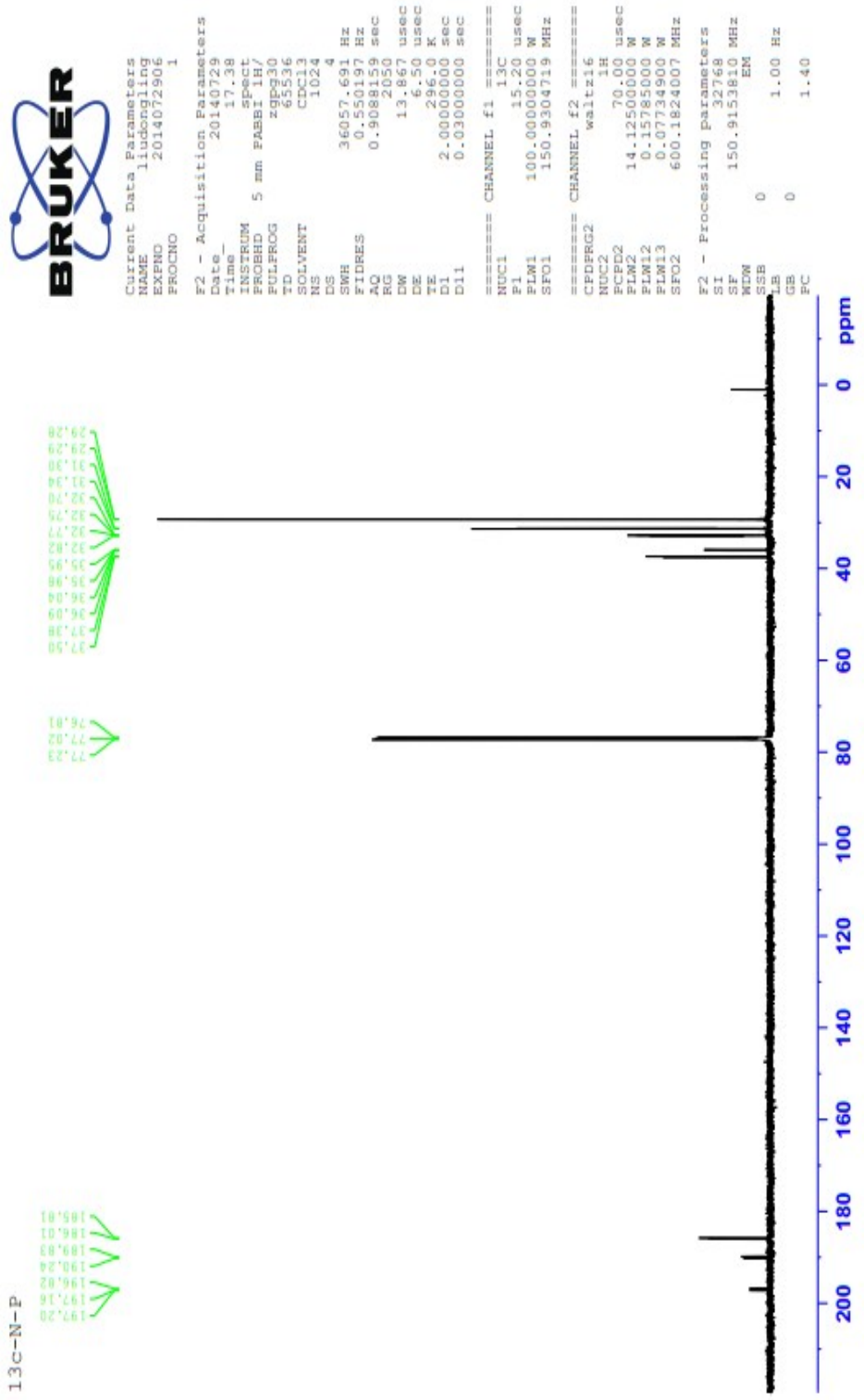
1. ^{1}H NMR spectrum of **2**(*N*)–**2**(*P*)



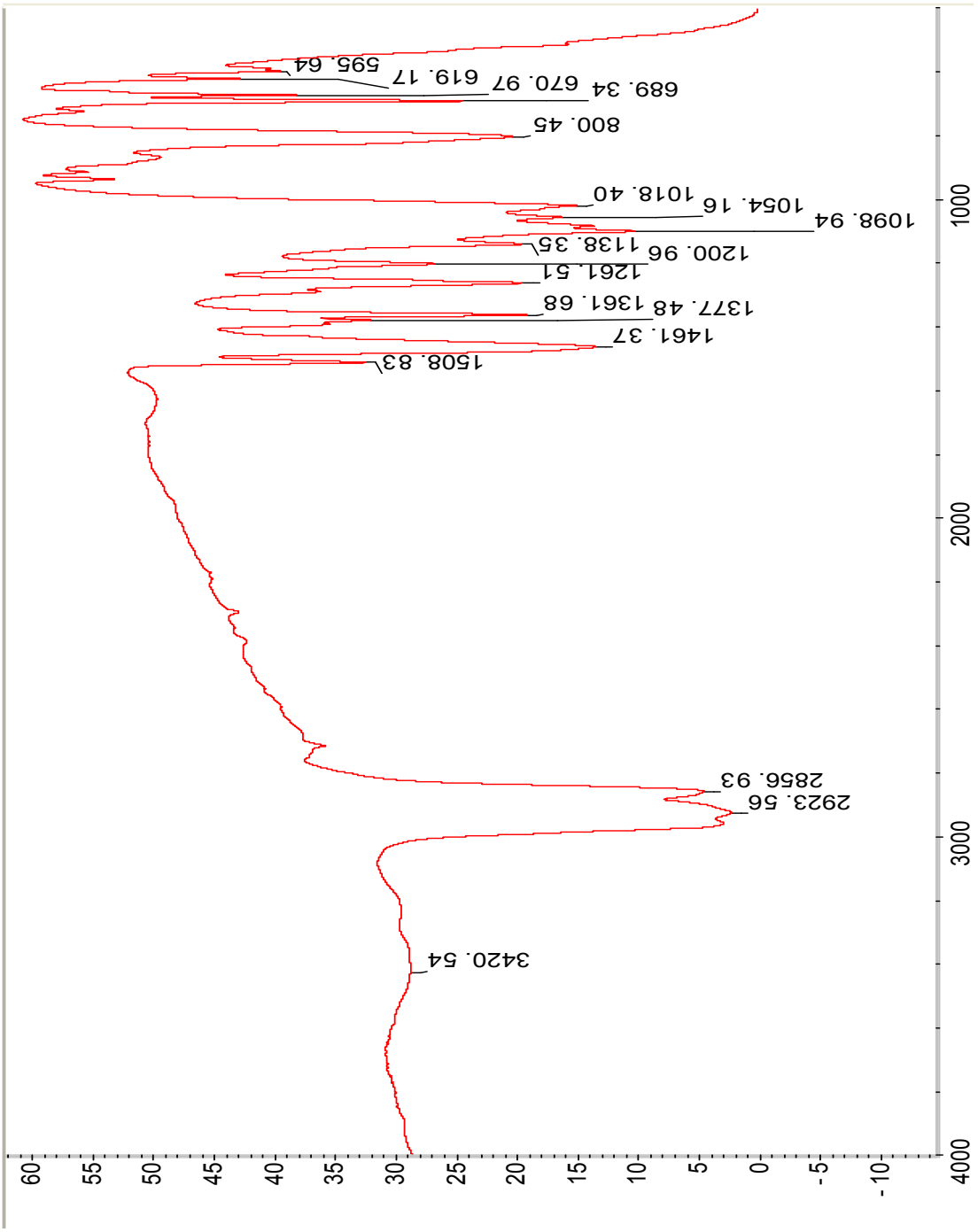
2. $^{31}P\{^{1}H\}$ spectrum of **2**(*N*)–**2**(*P*)



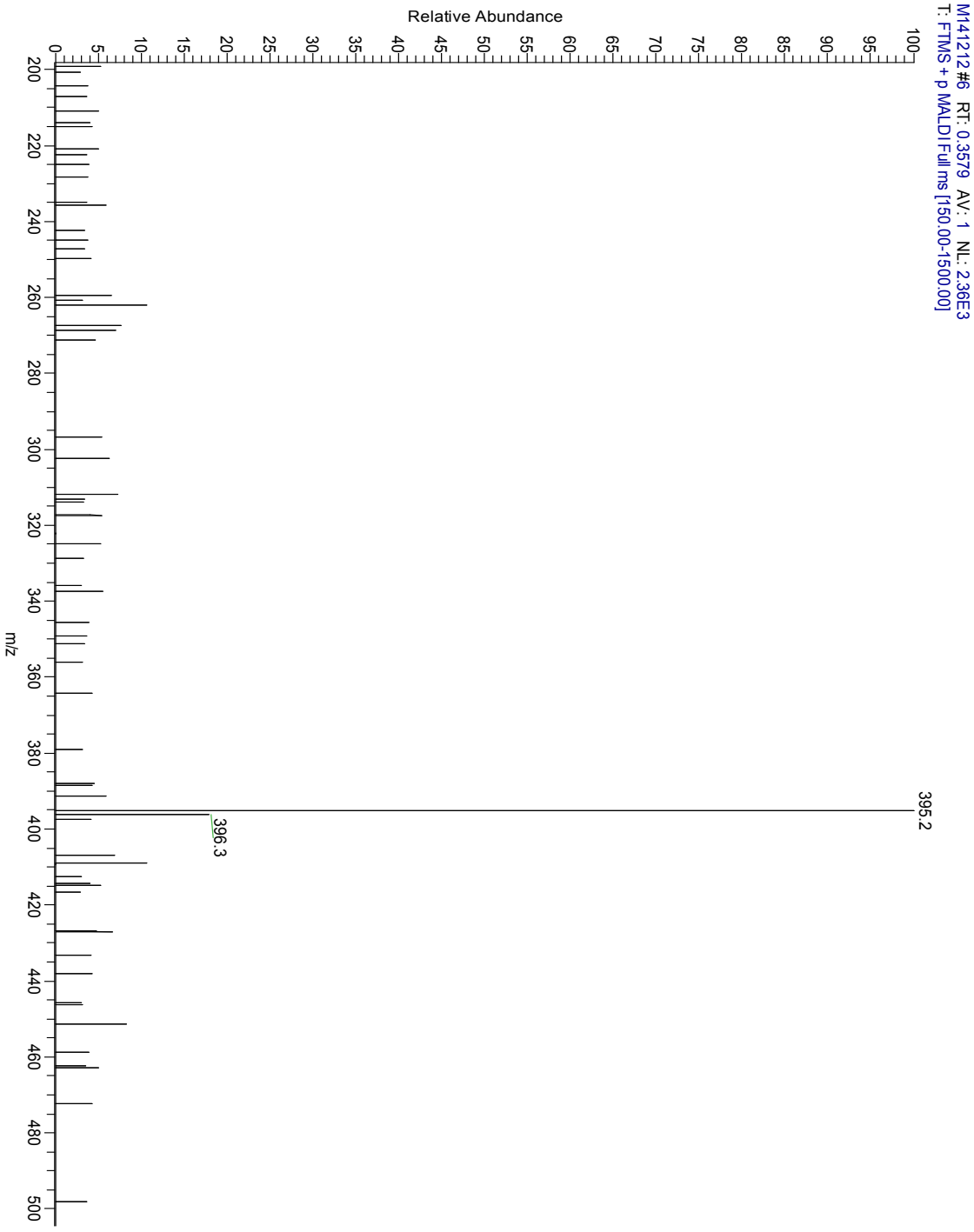
3. $^{13}C\{^{1}H\}$ NMR spectrum of **2**(*N*)–**2**(*P*)



SI-5. IR spectrum of **2**(*N*)–**2**(*P*)



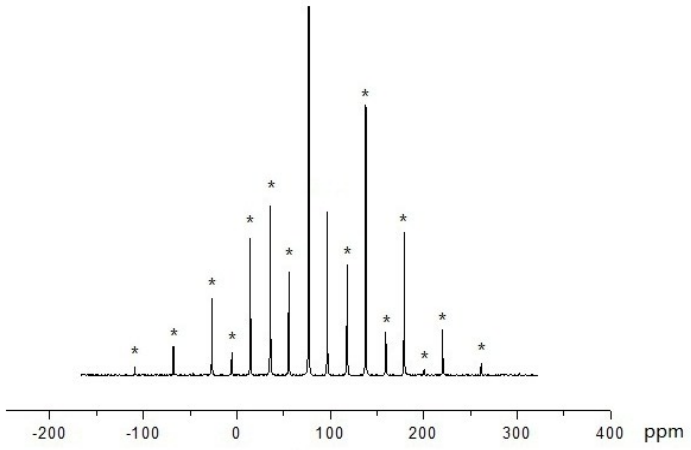
SI–6. Mass spectrum of **2**(*N*)–**2**(*P*)



SI–7. ^{31}P MAS NMR of **2**(*N*)–**2**(*P*) (* = Spinning side bands)

^{31}P MAS NMR experiments were performed on a Bruker AVANCE III 500WB spectrometer at a resonance frequency of 202.3 MHz using a 4 mm double-resonance MAS probe at a sample spinning rate of 12 kHz. The chemical shift of ^{31}P was referenced to $(NH_4)_2HPO_4$. ^{31}P MAS NMR spectra were recorded by using a recycle delay of 30s.

δ = 97.0(s), 77.0(s) ppm



SI-8. The data of DFT calculations for [DMPO]**2**$^{\bullet}$ and **2**(*N*1)–**2**(*P*2)

To understand the self-association of radical **2**$^{\bullet}$, we address aromaticity, the spin density distribution of **2**$^{\bullet}$, and the **2**(*N*)–**2**(*P*) formation computationally by analyzing compounds models sequentially using density functional theory (DFT). These included **2**$^{-}$, **2**$^{\bullet}$, the possible product models **2**(*N1*)–**2**(*N3*), **2**(*N1*)–**2**(*P2*), **2**(*P1*)–**2**(*P2*), and the supposed intermediates **2**$^{\bullet}$(*N1*)–**2**$^{\bullet}$(*N3*), **2**$^{\bullet}$(*N1*)–**2**•(*P2*), and **2**$^{\bullet}$(*P1*)–**2**$^{\bullet}$(*P2*). All structures were fully optimized without any symmetry constraint, and the harmonic frequencies were calculated to insure that they are indeed minima on potential energy surface. Geometry optimization and frequency calculation were carried out at the B3LYP/6-31+G(d), and the single point energies were calculated at the cam-B3LYP/6-311++G(d,p) level. The nucleus independent chemical shifts (NICSs), Mulliken atomic charges and spin densities of **2**$^{\bullet}$ and **2**(*N*1)–**2**(*P*2) were calculated at the cam-B3LYP/6-311++G(d,p) level. The zero point energies (ZPE) correction were obtained from the calculations of harmonic frequency at B3LYP/6-31+G(d) level. All calculations were carried out using Gaussian 09 program package.

Figure SI-8-1. The optimized geometries of **2**$^{-}$, **2**$^{\bullet}$, **2**$^{\bullet}$(*N*1)–**2**$^{\bullet}$(*N*3), **2**$^{\bullet}$(*N*1)–**2**$^{\bullet}$(*P*2), **2**$^{\bullet}$(*P*1)–**2**$^{\bullet}$(*P*2), **2**(*N*1)–**2**(*N*3), **2**(*N*1)–**2**(*P*2), and **2**(*P*1)–**2**(*P*2) at the B3LYP/6-31+G(d) level.

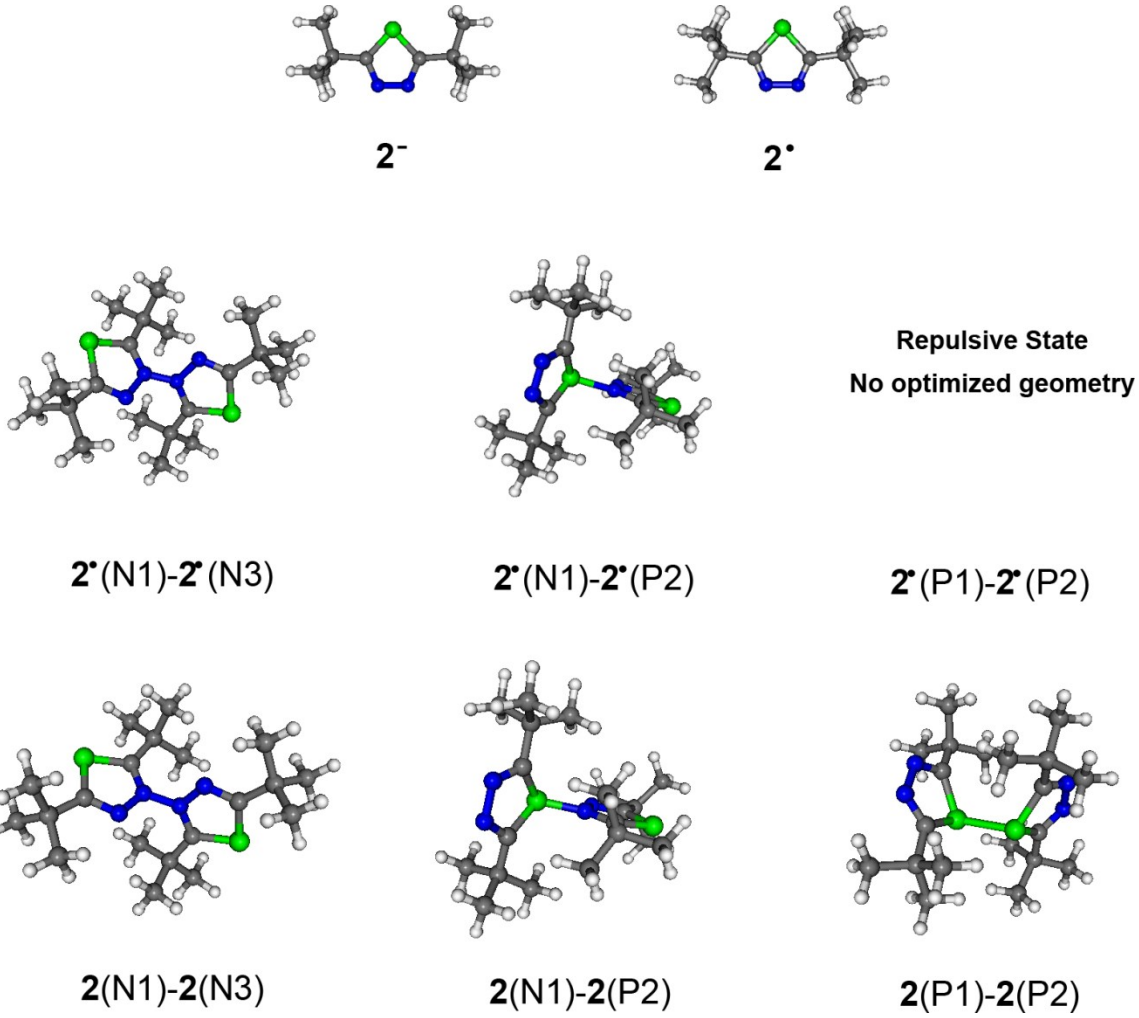


Table SI-8-2. The values of nucleus independent chemical shifts (NICSs) and P–C, C–N, and N–N bond lengths (in Å), Mulliken atomic charges and spin densities of **2**$^-$ and **2**$^\bullet$.

		Bond length[b]			Charge[c]			Spin density		
	NICS(1)[a]	P–C	C–N	N–N	P	C	N	P	C	N
2$^-$	–11.3	1.781	1.335	1.356	–0.416	–0.229	–0.096			
2$^\bullet$	–1.3	1.844	1.295	1.420	0.013	–0.268	0.059	0.892	–0.110	0.127

[a] NICS at 1.0 Å above the centers of five member rings of **2**$^-$ and **2**$^\bullet$. The NICS values of **2**$^-$(–11.3) and **2**$^\bullet$(–1.3) and the bond lengths are all indicative of **2**$^-$ being aromatic but **2**$^\bullet$ nonaromatic. [H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta and P. von R. Schleyer, *Org. Lett.* 2006, ***8***, 863–866.]

[b] C–N bond length of **2**$^-$ is close to the C–N bonds in aromatic rings such as pyrroles, and that of **2**$^\bullet$ is close to the typical C=N double bond in imines. Likewise, N–N bond length in **2**$^\bullet$ is close to the N–N single bond in N_2H_4, and that in **2**$^-$ falls in between N–N single and double bonds. These data of bond length support that **2**$^-$ is aromatic but **2**$^\bullet$ is nonaromatic.

[c] As the anion **2**$^-$ was oxidized toward **2**$^\bullet$, charge differences ($\Delta q = q(\mathbf{2}^\bullet) - q(\mathbf{2}^-)$) at the corresponding atom of the ring are 0.429(P), –0.039(C), and 0.155(N), respectively, suggesting that charge loss occurs mostly at P- and N-atoms. Consequnently, the remained unpaired electron localizes largely at P- and N-atoms.

Figure SI-8-3. The singly occupied molecular orbital (SOMO) of the radical**2**• illustrates the remained unpaired electron localizes largely at P- and N-atoms.

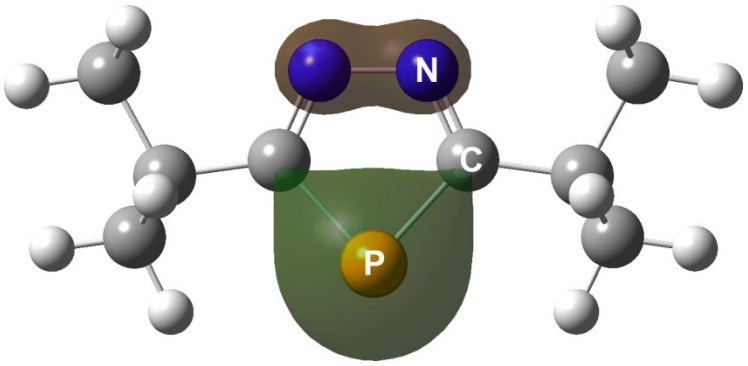


Table SI-8-4. The relative energies with ZPE correction (E_{ZPE}), distances (R) and dihedral angles (DA) between two diazaphospholyl radical **2**• for **2**$^-$, **2**•, possible oxidation products **2**(*N*1)–**2**(*N*3), **2**(*N*1)–**2**(*P*2), and **2**(*P*1)–**2**(*P*2), their reaction intermediates **2**•(*N*1)–**2**•(*N*3) and **2**•(*N*1)–**2**•(*P*2), and the enthalpies of dissociation (ΔH) of **2**(*N*1)–**2**(*N*3), **2**(*N*1)–**2**(*P*2), and **2**(*P*1)–**2**(*P*2) (in kcal·mol^{-1} for energy and enthalpy, Å for distance and degree for angle).

	2$^-$	**2**•	**2**•(*N*1)–**2**•(*N*3)	**2**•(*N*1)–**2**•(*P*2)	**2**(*N*1)–**2**(*N*3)	**2**(*N*1)–**2**(*P*2)	**2**(*P*1)–**2**(*P*2)
E_{ZPE}	0.0	69.7	186.8	144.9	94.3	97.5	102.2
R	–	–	1.348	1.884	1.391	1.779	2.233
DA	–	–	61.8	90.0	78.1	90.0	46.8
ΔH[a]					46.2	42.3	37.5

[a] The energies of dissociation of **2**(*N*1)–**2**(*N*3), **2**(*N*1)–**2**(*P*2), and **2**(*P*1)–**2**(*P*2) to **2**• were calculated at the cam-B3LYP/6-311++G(d,p) level, and the corrections from energy to enthalpy were obtained by the harmonic frequency calculations at the B3LYP/6-31+G(d) level. The C-C bond dissociation enthalpy (ΔH) of bis(pentamethylcyclopentadienyl) was calculated to be 18.1 kcal·mol^{-1} at the same level, close to the experimental value of 18.8 kcal·mol^{-1}, which was reported to slightly dissociate thermally (less than one in million) to pentamethylcyclopentadienyl radicals at 92 ºC [Culshaw, P. N.; Walton, J. C.; Hughes, L.; Ingold, K. U., *J. Chem. Soc., Perkin Trans. 2* **1993**, 879-886]. The larger P-N bond dissociation enthalpy, 42.3 kcal·mol^{-1}, ensures the stability of **2**(*N*1)–**2**(*P*2) upto 90 ºC.

Figure SI-8-5. The relative energies with ZPE correction of the reactant, products, and the intermediates involved in the oxidation of $\mathbf{2}^-$.

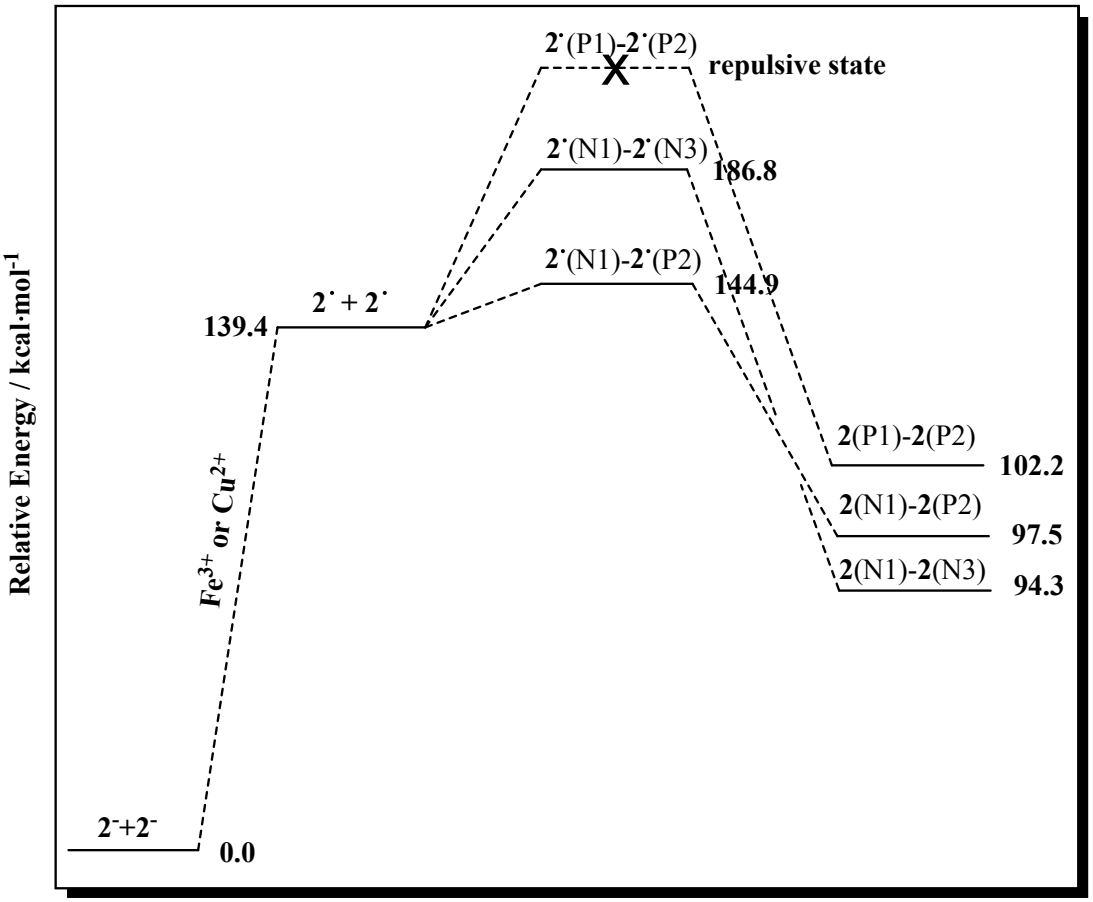


Figure SI-8-6. The relative energies with ZPE correction of the reactant, products and their intermediates of oxidation reaction of 2- for the simplified models in which tertiary butyls are substituted by H atoms. All calculations about the simplified models were carried out at the cam-B3LYP/6-311++G(d,p) level. When the steric hindrance was excluded by substituting tBu with H atoms, the intermediate 2•(P1)–2•(P2) is still higher in energy than 2•(N1)–2•(P2).

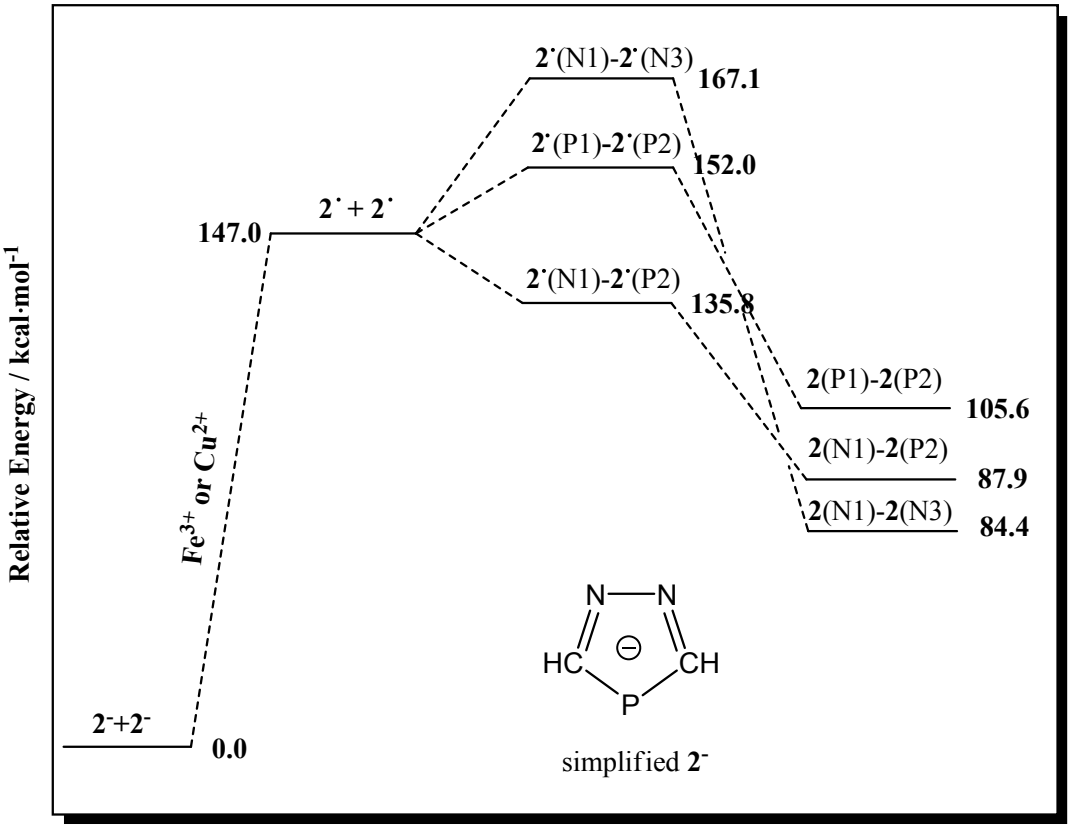


Figure SI-8-7. Several important molecular orbitals of **2**• and **2**(*N*)–**2**(*P*). SOMO and SOMO-1 of two radicals **2**• are arranged to highlight the symmetry-adaptation in **2**(*N*)–**2**(*P*). For **2**•, SOMO is a typical π orbital and SOMO-1 is a σ orbital. The σ orbita of **2**•(*N1*) is symmetry-adapted with the π orbital of **2**•(*P2*) as their orientations are vertical to each other in **2**(*N1*)–**2**(*P2*). Different from the previously reported π-π interaction via a P-P σ bond in 1,1'-diphosphole[C. Fave, M. Hissler, T. Kárpáti, J. Rault-Berthelot, V. Deborde, L. Toupet, L. Nyulászi and R. Réau, *J. Am. Chem. Soc.* 2004, **126**, 6058–6063.], a σ-π interaction via a P-N σ bond can be observed in **2**(*N1*)-**2**(*P2*).

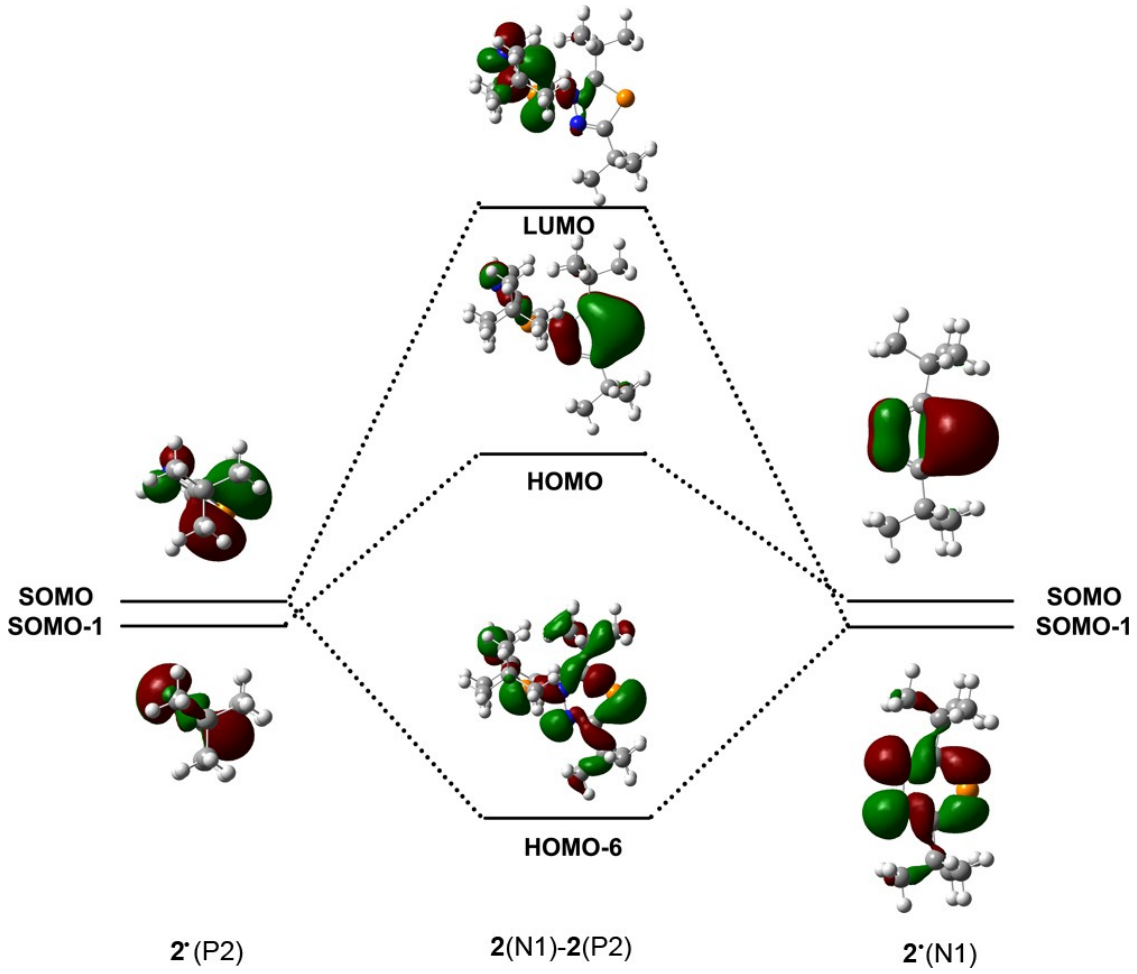


Table SI-8-8. Natural bond orbitals (NBOs) with their natural hybrid orbital compositions for two phosphorus atoms *P*1 and *P*2 in **2**(*N*1)-**2**(*P*2) at the cam-B3LYP/6-311++G(d,p) level.

NBO	Occupancy	Coefficient	Hybrid	Compositions		
*P*1[a]						
Lone Pair	1.96		$sp^{0.56}d^{0.00}$	s(64.25%)	p(35.72%)	d(0.03%)
*P*1-*C*1	1.96	0.6024	$sp^{4.78}d^{0.05}$	s(17.17%)	p(82.03%)	d(0.79%)
*P*1-*C*2	1.95	0.5926	$sp^{4.15}d^{0.04}$	s(19.27%)	p(79.94%)	d(0.79%)
Σ				s(100.69%)	p(197.69%)	d(1.61%)
*P*1-*C*2	1.81	0.7208	p_z	s(0.00%)	p(99.57%)	d(0.43%)
*P*2[b]						
Lone Pair	1.80		$sp^{1.04}d^{0.00}$	s(49.08%)	p(50.90%)	d(0.03%)
*P*2-*N*1	1.96	0.4950	$sp^{5.49}d^{0.08}$	s(15.21%)	p(83.51%)	d(1.28%)
*P*2-*C*3	1.96	0.6209	$sp^{4.53}d^{0.05}$	s(17.94%)	p(81.22%	d(0.83%)
*P*2-*C*4	1.96	0.6209	$sp^{4.53}d^{0.05}$	s(17.94%)	p(81.22%	d(0.83%)
Σ				s(100.17%)	p(296.85%)	d(2.97%)

[a] The hybridization of the *P*1 atom involves one s-rich ($sp^{0.56}$) lone pair orbital and two p-rich ($sp^{4.78}$ and $sp^{4.15}$) orbitals. The unhybridized pure p-orbital confirms an inequivalent sp^2 hybridized *P*1 atom.

[b] The hybridization of the *P*2 atom involves one s-rich ($sp^{1.04}$) lone pair orbital and three p-rich ($sp^{5.49}$, $sp^{4.53}$ and $sp^{4.53}$) orbitals. The summation of the compositions shows that these four hybrid orbitals are mostly consisting of one s orbital and three p orbitals, indicating an inequivalent sp^3 hybridized *P*2 atom.

SI-8-9. Coordinates and zero point energies of the structures in **Figure SI-8-2** optimized at the B3LYP/6-31+G* level.

2^{-}, ZPE = 166.9 kcal·mol^{-1}

1\1\GINC-C2B6\FOpt\RB3LYP\6-31+G(d)\C10H18N2P1(1-)\LIBT\11-Sep-2014\0\

\# opt freq b3lyp 6-31+G*\\C4H4N4P2-PN + tBu\\-1,1\P,-0.8502601212,-0.

0000084414,-0.5931398993\C,-2.1456418357,-1.2070843967,-0.7842355334\C

,-2.145986826,1.206674405,-0.7843785439\N,-3.3590851234,0.6776355988,-

0.963284313\N,-3.3588864593,-0.6784136319,-0.963236012\C,-2.0305801517

,-2.7343072814,-0.7670666007\C,-0.5749064896,-3.1901823919,-0.55350172

25\H,0.0791512862,-2.8182448056,-1.3514627138\H,-0.1776015822,-2.81835

16222,0.3987535861\H,-0.5159776134,-4.2890469691,-0.5448939299\C,-2.90

36959683,-3.3030883049,0.3761898004\H,-3.9428850117,-2.982054832,0.252

6109493\H,-2.8678503774,-4.4040809675,0.38898823\H,-2.5516737924,-2.93

59302243,1.3487702542\C,-2.5387159637,-3.3037938429,-2.1126558336\H,-2

.5009020048,-4.4047785035,-2.1139751826\H,-3.5695130119,-2.9825886565,

-2.292926335\H,-1.9220529513,-2.9371557766,-2.94328485\C,-2.0313825729

,2.7339321946,-0.7672494556\C,-2.5396811182,3.3032367035,-2.1128536143

\H,-3.5703818405,2.9817223956,-2.2931220038\H,-2.5021917975,4.40423248

77,-2.1141971347\H,-1.922905955,2.9367621634,-2.9434714941\C,-0.575847

3703,3.190248594,-0.5536831408\H,-0.1784316293,2.8185436353,0.39857535

32\H,0.0783240692,2.8185038618,-1.3516404806\H,-0.5172506099,4.2891309

808,-0.5450808586\C,-2.9046758519,3.3024764271,0.3759898947\H,-2.86916

60655,4.4034802111,0.3887623714\H,-3.9437669758,2.9811242944,0.2524135

417\H,-2.5525462848,2.9354486954,1.3485806709\\Version=EM64L-G09RevC.0

1\State=1-A\HF=-842.8238745\RMSD=3.942e-09\RMSF=1.657e-05\Dipole=0.625

4095,0.0000948,0.0926284\Quadrupole=-2.4518862,-3.7286475,6.1805337,0.

0001445,-1.302441,0.0001336\PG=C01 [X(C10H18N2P1)]\\@

2$^{\bullet}$, ZPE = 167.0 kcal·mol^{-1}

1\1\GINC-C11B2\FOpt\UB3LYP\6-31+G(d)\C10H18N2P1(2)\LIBT\11-Sep-2014\0\

\# opt freq b3lyp 6-31+G*\\C4H4N4P2-PN + tBu\\0,2\P,-1.2973888059,-0.0

001028293,-1.6223085381\C,-2.2071208728,-1.2433881149,-0.6096791595\C,

-2.2074857339,1.2429696222,-0.6097455223\N,-2.9964382108,0.7097922692,

0.2683268245\N,-2.9962301284,-0.7103954205,0.2683644427\C,-2.068873907

3,-2.7514341143,-0.7629421968\C,-0.5938262878,-3.1492243351,-0.5156816

189\H,0.0838796287,-2.6705654153,-1.2331892787\H,-0.2742127111,-2.8699

189723,0.4950210747\H,-0.4775322021,-4.2348750636,-0.6208207788\C,-2.9

73879384,-3.4855071738,0.2439285714\H,-4.0268113794,-3.2266357547,0.09

5791965\H,-2.8595040286,-4.5690987273,0.1171552\H,-2.7150993959,-3.226

1701861,1.2751447021\C,-2.4710017006,-3.1498161137,-2.2033271674\H,-2.

378339889,-4.2354700652,-2.3297761929\H,-3.5100138048,-2.8710029399,-2

.4140455381\H,-1.8296318116,-2.6711078452,-2.9534577636\C,-2.069678919

6,2.751047922,-0.7630869429\C,-2.4719279126,3.1492378213,-2.2034911519

\H,-3.510859269,2.8701102807,-2.4141914684\H,-2.3795835555,4.234912234

9,-2.3299966812\H,-1.8304207953,2.6706780008,-2.9535991318\C,-0.594746

5763,3.1492813777,-0.5158520963\H,-0.2750479128,2.8701215819,0.4948639

126\H,0.083096496,2.670783136,-1.2333373746\H,-0.4787695769,4.23496055

71,-0.6210477836\C,-2.974895129,3.4849090772,0.2437488584\H,-2.8608361

536,4.5685273848,0.1169191088\H,-4.0277520332,3.2257228803,0.095629169

3\H,-2.7160360369,3.2257009251,1.2749775563\\Version=EM64L-G09RevC.01\

State=2-A\HF=-842.7132083\S2=0.756719\S2-1=0.\S2A=0.750035\RMSD=7.248e

-09\RMSF=6.983e-06\Dipole=0.740398,0.0000871,-0.823717\Quadrupole=-2.7

992875,6.3532084,-3.5539209,-0.0012444,3.5267087,0.0002555\PG=C01 [X(C

10H18N2P1)]\\@

2$^{\bullet}$(*N*1)–**2**$^{\bullet}$(*N*3), ZPE = 337.3 kcal·mol^{-1}

1\1\GINC-HOST01\FOpt\UB3LYP\6-31+G(d)\C20H36N4P2(3)\WBQ\08-Jan-2015\0\

\# opt freq b3lyp/6-31+g(d)\\C4R4N4P2-NN + tBu sigma-sigma triplet\\0,
3\N,0.6337570654,-0.2299834954,-0.1938897943\N,1.5435876636,0.57979955
54,0.5273071314\C,2.6484130023,-0.0703033542,0.7342996011\C,1.05820454
22,-1.4753260393,-0.6040539386\P,2.7071115542,-1.7710570482,0.07843240
47\N,-0.6338807017,0.2297409568,-0.1940435842\N,-1.5438169717,-0.57971
59851,0.5273888903\C,-2.6485951349,0.0705586421,0.7341118615\C,-1.0581
831147,1.4750011475,-0.6045936433\P,-2.7070861952,1.7711172349,0.07772
4411\C,3.7790893068,0.5791591226,1.5286356555\C,0.3029482043,-2.470537
5501,-1.4760732432\C,-0.3424459314,-3.568387547,-0.5865072394\H,-0.857
8178468,-4.307014331,-1.2152517569\H,0.420897915,-4.0958319273,-0.0023
624669\H,-1.0631675886,-3.1292739648,0.1068957772\C,1.324989535,-3.156
9238193,-2.4214336781\H,0.8092105691,-3.900755838,-3.0408507542\H,1.80
37451179,-2.428983278,-3.0864748913\H,2.1124991596,-3.6789442944,-1.86
69753487\C,-0.7898920747,-1.8351922571,-2.3645315418\H,-1.6269043129,-
1.4403994506,-1.7860537644\H,-0.3846261483,-1.0318764475,-2.9885951356
\H,-1.1876564779,-2.6073238388,-3.0339247258\C,-3.7793382853,-0.578491
9673,1.5286923871\C,-3.4411857813,-2.0334528156,1.9020870113\H,-4.2638
1603,-2.4610597221,2.4878452117\H,-3.300167197,-2.6531735858,1.0104251
354\H,-2.5253309722,-2.0930372277,2.4985013647\C,-5.0719497941,-0.5560
45809,0.678952915\H,-4.94092914,-1.1156958298,-0.2545492801\H,-5.89425
43411,-1.0171988045,1.2398633681\H,-5.3713861629,0.4661672616,0.421452
5047\C,-4.0049766502,0.2400895149,2.8231958189\H,-3.1045756449,0.24316
64402,3.4482538417\H,-4.2689980222,1.2809788717,2.6046882979\H,-4.8236
114033,-0.2019930774,3.4044323708\C,-0.3027071849,2.4698956463,-1.4767
808263\C,0.3429374499,3.5677341537,-0.5873840884\H,0.8584799142,4.3061
448798,-1.2162420036\H,-0.4202826986,4.0954439449,-0.0033182466\H,1.06
35623609,3.1285626576,0.1060872414\C,0.7900091685,1.8341433286,-2.3650
977816\H,1.1880097211,2.6060765565,-3.0345794749\H,1.6268880274,1.4392
106914,-1.7865199305\H,0.3845660475,1.0308447955,-2.9890680624\C,-1.32

45769197,3.1563557749,-2.4222758591\H,-1.8034762622,2.4284140673,-3.08
72120855\H,-2.1119858215,3.6786361671,-1.8679197676\H,-0.8086205594,3.
8999761903,-3.0417993608\C,5.0716913612,0.5565676733,0.6788854982\H,4.
9405874917,1.1158655485,-0.2548161028\H,5.8939470377,1.0180246529,1.23
9617467\H,5.3712510102,-0.4657007433,0.4217479963\C,3.4407599861,2.034
2115591,1.9015138216\H,4.2633637732,2.4621463335,2.4870697561\H,3.2996
050694,2.6535851872,1.0096316155\H,2.5249292477,2.0938894583,2.4979556
479\C,4.0048422415,-0.238934784,2.8234276038\H,3.1044449948,-0.2419090
286,3.4484914282\H,4.2690004407,-1.2798665518,2.6052883878\H,4.8234213
904,0.2034623986,3.4045029532\\Version=EM64L-G09RevA.01\State=3-A\HF=-
1685.3651353\S2=2.014951\S2-1=0.\S2A=2.000126\RMSD=6.357e-09\RMSF=1.93
3e-06\Dipole=0.0000559,-0.0000139,-0.1299029\Quadrupole=2.3841754,-3.4
298204,1.045645,5.7096097,-0.0011529,0.0014677\PG=C01 [X(C20H36N4P2)]\
\@

2$^{\bullet}$(*N*1)–**2**$^{\bullet}$(*P*2), ZPE = 335.6 kcal·mol^{-1}

1\1\GINC-HOST01\FOpt\UB3LYP\6-31+G(d)\C20H36N4P2(3)\WBQ\06-Jan-2015\0\
\# opt freq b3lyp/6-31+g(d)\\C4H4N4P2-PN + tBu sigma-pi triplet\\0,3\N
,0.6429358062,0.0000620703,0.0906218492\N,1.6819975518,0.0003138226,-0
.8143736435\C,2.8528429578,0.0013869524,-0.2197551913\P,2.7641976871,0
.0022271662,1.5632248311\C,1.0190969918,0.0008814139,1.4169469193\P,-0
.8600753391,-0.0004783771,-1.0450380871\C,-2.0714320568,-1.2300712893,
-0.4876224486\C,-2.0718811893,1.2288372815,-0.4879437129\N,-3.29742224
51,0.6362123658,-0.0830748506\N,-3.2972179376,-0.6377432573,-0.0829066
073\C,0.0836117478,0.0005683537,2.6331734828\C,0.9167665705,0.00108232
08,3.9367270109\H,1.5553024938,-0.8854991415,4.0149624602\H,1.55453632
57,0.8882323529,4.01477359\H,0.2356912233,0.0008938599,4.7959536541\C,
-0.8015080633,1.2656392562,2.6580660417\H,-0.1857629699,2.1724044922,2
.6580607714\H,-1.4758256861,1.3082933383,1.8007898424\H,-1.4194689976,
1.2719770515,3.5643964103\C,-0.8002999009,-1.2653304674,2.6583021875\H

,-1.474633299,-1.3087762769,1.8010766734\H,-0.183703154,-2.1715185205,
2.6584151936\H,-1.4181986568,-1.2721011648,3.5646704736\C,4.1313516265
,0.0010424853,-1.0564181318\C,4.9632589725,1.2592630194,-0.7122966245\
H,5.237084777,1.2840104453,0.3488929746\H,5.8896176169,1.2734554053,-1
.3005916684\H,4.4024364414,2.1741002958,-0.9371471478\C,4.9588430061,-
1.2614888464,-0.7171942828\H,5.8851543101,-1.2766914709,-1.3055474491\
H,5.2324845394,-1.2912148371,0.3439097379\H,4.3947436407,-2.1734303888
,-0.9455707071\C,3.8112487254,0.0045477939,-2.5634744266\H,3.228782459
,-0.8765606126,-2.8516827895\H,3.2322112457,0.8890739378,-2.8482096601
\H,4.7466517312,0.0039009208,-3.1368240808\C,-2.0592354257,-2.71483956
96,-0.7591970539\C,-0.615235517,-3.255050093,-0.8095356502\H,-0.019450
5233,-2.7552419557,-1.5820330554\H,-0.1035032333,-3.1235726907,0.14981
74962\H,-0.6303704031,-4.3267329574,-1.0403893518\C,-2.8724606183,-3.4
863642574,0.3058060643\H,-3.9027320915,-3.1241920473,0.3610116916\H,-2
.8910131238,-4.551676998,0.0464064983\H,-2.4223785179,-3.390264253,1.2
993713259\C,-2.7303452869,-2.9330018306,-2.1496342396\H,-2.746774041,-
4.0058782888,-2.3796928841\H,-3.7608948725,-2.5630774475,-2.1496090011
\H,-2.1743834449,-2.4207734316,-2.9429169795\C,-2.0601106716,2.7135497
572,-0.7598807689\C,-2.7308208892,2.9311324986,-2.1506018378\H,-3.7612
367277,2.5608334569,-2.1508461553\H,-2.747565986,4.0039466408,-2.38092
44802\H,-2.1743912665,2.4189197237,-2.9435658989\C,-0.6162698187,3.254
2265037,-0.8098797096\H,-0.1048166394,3.1231758468,0.1496813385\H,-0.0
200595033,2.7544105089,-1.5820434292\H,-0.6316801732,4.325844394,-1.04
10203174\C,-2.8739419156,3.4850716386,0.3046512792\H,-2.8927199924,4.5
503203896,0.0450044044\H,-3.9041252104,3.122607309,0.359578754\H,-2.42
41860594,3.3893334017,1.2983993661\\Version=EM64L-G09RevA.01\State=3-A
\HF=-1685.4161402\S2=2.017696\S2-1=0.\S2A=2.000166\RMSD=7.369e-09\RMSF
=2.084e-06\Dipole=-0.2395013,-0.0005637,-0.1259749\Quadrupole=-9.04610
26,7.9170563,1.1290462,-0.0055328,-0.2194102,-0.0019236\PG=C01 [X(C20H

36N4P2)]\\@

2(*N*1)–**2**(*N*3), ZPE = 339.6 kcal·mol^{-1}

1\1\GINC-C6B2\FOpt\RB3LYP\6-31+G(d)\C20H36N4P2\LIBT\06-Sep-2014\0\\# o
pt b3lyp 6-31+G*\\C4H4N4P2-NN + tBu\\0,1\N,0.6545732622,-0.23429542,-0
.0749777368\N,1.5029129199,0.4626843019,0.7268454669\C,2.6969612508,-0
.0923813505,0.6976912665\C,1.1226974889,-1.3512846656,-0.7151507717\P,
2.8206537168,-1.5476774003,-0.3413880179\N,-0.654680287,0.2341646947,-
0.0749462754\N,-1.5030359166,-0.4628662738,0.7268158859\C,-2.697045311
9,0.0922929805,0.697792272\C,-1.1227505499,1.3512762244,-0.7149373123\
P,-2.8206813874,1.5477326824,-0.3410942706\C,3.8262375973,0.4949143285
,1.5425867057\C,0.2844841986,-2.3482883157,-1.526275425\C,-0.310776904
,-3.3918443959,-0.5425675688\H,-0.9067976862,-4.1242078831,-1.10187904
65\H,0.4862595388,-3.9281483813,-0.0161069967\H,-0.9527487053,-2.91150
42757,0.1999168588\C,1.2167762824,-3.0860865457,-2.516273863\H,0.63771
40922,-3.8343645808,-3.0698766082\H,1.6614448568,-2.3937760076,-3.2400
454355\H,2.029830901,-3.6106764199,-2.0036223608\C,-0.8617765048,-1.72
15150158,-2.3524667981\H,-1.6516631072,-1.2905415223,-1.735094978\H,-0
.493570532,-0.951288197,-3.0373175829\H,-1.3185709935,-2.5102811152,-2
.9618216681\C,-3.8263173911,-0.4950055666,1.54269347\C,-3.412395451,-1
.8392985082,2.1709918198\H,-4.2368785545,-2.2277614051,2.7811451992\H,
-3.17648196,-2.5842059948,1.4033408765\H,-2.531220785,-1.7299520431,2.
8107551735\C,-5.0766960577,-0.7094983707,0.6591979577\H,-4.8690707989,
-1.4115039015,-0.1569885982\H,-5.8966480243,-1.1202940617,1.2612857115
\H,-5.4256400651,0.2299317554,0.2148998656\C,-4.1691297182,0.507053164
6,2.6725060012\H,-3.2986171405,0.6866684246,3.3138951178\H,-4.49606227
88,1.4718476341,2.2680375163\H,-4.9788941453,0.1090167079,3.2969235271
\C,-0.2844492011,2.3483702537,-1.5258536523\C,0.3109770334,3.391602888
8,-0.541902806\H,0.9070715458,4.1240335268,-1.1010471721\H,-0.48597385

68,3.9278716759,-0.0152772086\H,0.9529175997,2.9109921283,0.2004361034
\C,0.861717848,1.7216399244,-2.3522073258\H,1.3186323621,2.5104953949,
-2.961355867\H,1.651535936,1.2903878185,-1.7349400687\H,0.4934006725,0
.9516445519,-3.0372583816\C,-1.2166713021,3.0865211447,-2.515657107\H,
-1.6614477681,2.3944366003,-3.2395785204\H,-2.0296452838,3.6110956993,
-2.0028624184\H,-0.6375271476,3.8348537488,-3.0691006801\C,5.076564557
9,0.7095501309,0.6590522862\H,4.8688589984,1.4116018217,-0.1570740362\
H,5.8965178445,1.1203531471,1.2611331036\H,5.4255479086,-0.2298257646,
0.2146703644\C,3.4122616279,1.8391332252,2.1710070513\H,4.2367565016,2
.2276125945,2.7811340826\H,3.1762448665,2.584076956,1.4034220124\H,2.5
311360086,1.7296793182,2.8108192512\C,4.1691551755,-0.5072156038,2.672
3040822\H,3.2986803067,-0.6869322753,3.3137161671\H,4.4961238312,-1.47
19590921,2.2677432279\H,4.978924085,-0.1091850954,3.2967201348\\Versio
n=EM64L-G09RevC.01\State=1-A\HF=-1685.4973426\RMSD=6.217e-09\RMSF=7.43
2e-06\Dipole=0.0000725,-0.0000147,-0.4174885\Quadrupole=-0.7380839,-0.
1227179,0.8608019,4.9174403,0.0002325,0.0004857\PG=C01 [X(C20H36N4P2)]
\\@

2(*N*1)–**2**(*P*2), ZPE = 337.5 kcal·mol^{-1}

1\1\GINC-C5B5\FOpt\RB3LYP\6-31+G(d)\C20H36N4P2\LIBT\06-Sep-2014\0\\# o
pt b3lyp 6-31+G*\\C4H4N4P2-PN + tBu\\0,1\N,0.5668496635,-0.0004941968,
0.0401497066\N,1.6038256661,-0.0005368094,-0.8822964236\C,2.7749666547
,-0.0027417053,-0.2955367198\P,2.6997244242,-0.0050395442,1.4902081784
\C,0.95718287,-0.0027605662,1.3705382432\P,-0.9045030251,0.0023039684,
-0.9598462168\C,-2.1455289402,-1.2599084352,-0.4811231868\C,-2.1428340
851,1.2659516109,-0.4779665474\N,-3.2986877481,0.7102701407,-0.2838706
836\N,-3.3001891331,-0.7022451388,-0.285633976\C,0.0479763617,-0.00323
75506,2.6111220748\C,0.9205209941,-0.0057770574,3.8901683182\H,1.55830
24867,-0.8940938377,3.9514585317\H,1.5602629024,0.8809749859,3.9536414

453\H,0.2625097978,-0.0061347257,4.7668248515\C,-0.8355424685,1.262188
8459,2.671185093\H,-0.2209484273,2.1692396554,2.6614311362\H,-1.545455
4769,1.3110821118,1.845100057\H,-1.4167392744,1.257709852,3.6012140476
\C,-0.8384098869,-1.2668094279,2.6681285711\H,-1.5483895072,-1.3121263
341,1.8418970801\H,-0.2258576393,-2.1752139768,2.6562321354\H,-1.41963
82288,-1.2632378675,3.5981409896\C,4.0481449613,-0.0031684282,-1.13967
73516\C,4.8797211458,1.2563332926,-0.7992859009\H,5.1597609705,1.28186
25348,0.2602708565\H,5.8026826707,1.2699765496,-1.3923538225\H,4.31780
42812,2.1707963046,-1.0224455951\C,4.8767591933,-1.2654769758,-0.80247
69507\H,5.7996950974,-1.279779996,-1.3955689772\H,5.1567253211,-1.2943
51787,0.2570137212\H,4.3127035693,-2.1780510637,-1.0279606748\C,3.7194
130062,-0.0008761844,-2.644827879\H,3.1370626043,-0.8829963278,-2.9301
44142\H,3.139145061,0.8833335335,-2.9279089462\H,4.6519663284,-0.00124
49318,-3.2222686505\C,-2.0346214685,-2.7646568755,-0.7232605084\C,-0.5
808009806,-3.2516532658,-0.56703898\H,0.0947544464,-2.7544073547,-1.27
38313785\H,-0.1989188477,-3.0811004519,0.4442288807\H,-0.530440518,-4.
3285765345,-0.7667290766\C,-2.9563856056,-3.5279143261,0.251267665\H,-
3.9902407741,-3.1831096256,0.1639991034\H,-2.9228840243,-4.6004507319,
0.0245961415\H,-2.6394668159,-3.3921252258,1.2912024231\C,-2.502390864
1,-3.0357640205,-2.1772287601\H,-2.4353147475,-4.1093266804,-2.3941101
396\H,-3.5402247904,-2.7160713846,-2.3157131193\H,-1.8772420054,-2.503
9926395,-2.9041780143\C,-2.0287362157,2.7710714096,-0.7163263324\C,-2.
4960582293,3.0468204373,-2.1695629041\H,-3.5345814113,2.7296845951,-2.
3087562026\H,-2.4267141553,4.1207769717,-2.3837639335\H,-1.8721070116,
2.5155421996,-2.8979021978\C,-0.5738713951,3.2545833938,-0.5590238127\
H,-0.1922522617,3.0806601469,0.4517693222\H,0.1005560559,2.7576919571,
-1.2671412833\H,-0.5212452543,4.3318992368,-0.7559918064\C,-2.94879166
08,3.5338415367,0.2602010307\H,-2.9131041873,4.6068581485,0.0361502038
\H,-3.9833669983,3.1913863835,0.1722214877\H,-2.6320104702,3.394859182

7,1.2997547989\\Version=EM64L-G09RevC.01\State=1-A\HF=-1685.4916271\RM
SD=8.958e-09\RMSF=1.192e-06\Dipole=0.7090663,-0.000961,0.1576944\Quadr
upole=-10.2045376,7.4802953,2.7242423,0.0214538,-1.9842208,0.008733\PG
=C01 [X(C20H36N4P2)]\\@

2(*P*1)–**2**(*P*2), ZPE = 337.3 kcal·mol^{-1}

1|1|UNPC-PC-201005241613|FOpt|RB3LYP|6-31+G(d)|C20H36N4P2|ADMINISTRATO
R|07-Sep-2014|0||# b3lyp 6-31+g* opt geom=checkpoint guess=read||C4H4N
4P2-PP + tBu||0,1|P,0.4834153867,-0.608860833,1.0065637714|C,2.2888315
332,-0.7790901039,0.6794021622|N,2.9494299698,0.2170023165,1.178801046
9|N,2.1650296774,1.2351731044,1.741707705|C,0.8829572704,1.0619661233,
1.6807885776|P,-0.483206679,-0.6093677125,-1.0062669899|C,-2.288572548
4,-0.7800964895,-0.6790735733|N,-2.9494998505,0.2155821189,-1.1788598|
N,-2.1654344286,1.2338222697,-1.742110339|C,-0.8833041875,1.0610823713
,-1.6810939408|C,0.0549542896,2.011949504,-2.4228551814|C,-3.026323912
4,-1.9789640717,-0.0792348196|C,-3.3099917916,-1.6966564013,1.41688433
98|H,-3.8665118833,-2.5361244436,1.8516816201|H,-2.3833187245,-1.57780
22013,1.9891663599|H,-3.9114432,-0.7890265238,1.5339995529|C,-2.182570
9779,-3.2641304619,-0.2032468124|H,-2.7402097099,-4.1136097617,0.20866
25463|H,-1.9485535542,-3.4923298805,-1.2496855346|H,-1.2410315966,-3.1
902293318,0.3526310935|C,-4.3686309392,-2.1818403552,-0.8153041058|H,-
4.9021942539,-3.0328949028,-0.3745529006|H,-5.0005115662,-1.2932491684
,-0.7423397365|H,-4.2076218084,-2.3909908026,-1.8790183936|C,1.5028113
954,1.9000727678,-1.9157786347|H,1.9014048981,0.8872627271,-2.04343503
21|H,2.1468219333,2.5772019724,-2.4891711064|H,1.5929917577,2.17350415
28,-0.8603021274|C,-0.441154912,3.4646311963,-2.2574817667|H,0.2057158
535,4.1408961214,-2.8292094711|H,-1.4685999807,3.5745731603,-2.6136820
544|H,-0.411093325,3.7758321378,-1.2070368548|C,0.0107908044,1.6262958
728,-3.9239822268|H,-1.006004676,1.719583215,-4.3186770029|H,0.6707115

718,2.2894166522,-4.4971690471|H,0.3489645397,0.5950758696,-4.0823762122|C,-0.0556222286,2.0127987516,2.4221874813|C,-0.0113681684,1.6276988957,3.9234538442|H,-0.6715179986,2.2908107276,4.4963872608|H,-0.3492097375,0.5964260381,4.0822117891|H,1.0053878045,1.7214593534,4.3181386517|C,0.4400226353,3.465580472,2.2563018893|H,0.4098812937,3.7763938236,1.2057445341|H,-0.207076939,4.1418423763,2.8277741094|H,1.4674253399,3.5759809292,2.6124822901|C,-1.5034318606,1.900274391,1.9151167285|H,-2.1476744824,2.5773993926,2.4882535298|H,-1.5936767166,2.1733007477,0.8595404404|H,-1.9016995824,0.8873809754,2.0431246705|C,3.026983876,-1.9778867303,0.079911511|C,2.1836205098,-3.2632808025,0.2041800976|H,1.242088374,-3.1898011808,-0.3517648621|H,2.7415425406,-4.1126854168,-0.2074998305|H,1.9496198758,-3.4913081525,1.2506605691|C,3.3106628809,-1.6958551273,-1.416257436|H,3.911828311,-0.7880600695,-1.5335551011|H,3.8674774832,-2.5352521155,-1.8508146171|H,2.3839871408,-1.5774369966,-1.9886273641|C,4.3693040063,-2.1801692902,0.8161243792|H,4.9031570955,-3.0311733874,0.3756264521|H,5.0009170894,-1.2914032194,0.7429755196|H,4.2082840824,-2.3891005935,1.879880352||Version=IA32W-G09RevA.02|State=1-A|HF=-1685.4877052|RMSD=5.651e-009|RMSF=2.595e-006|Dipole=0.0001663,-0.9785757,0.0001778|Quadrupole=-9.5295369,6.5997494,2.9297875,-0.0045533,-10.2312976,-0.00226|PG=C01 [X(C20H36N4P2)]||@