Supplementary Information

A DFT study of the active role of the phosphate group of an internal aldimine in a transamination reaction

Shinichi Yamabe,[a] Noriko Tsuchida,[b] and Shoko Yamazaki*[a]

[a]*Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630-8528, Japan*

[b]*Department of Liberal Arts, Faculty of Medicine, Saitama Medical University, 38 Morohongo, Moroyama-machi, Iruma-gun, Saitama 350-0495, Japan*

email: yamazaks@cc.nara-edu.ac.jp

Precursor

$\Delta(E_T+ZPE) = 0$ kcal/mol

$\Delta G^o = 0$ kcal/mol

$[\Delta G^o = 0$ kcal/mol]

$<\Delta G^o = 0$ kcal/mol>

Figure S1-1

⇩

TS1

2.114 Å

$\Delta(E_T+ZPE)^{\ddagger} = +14.11$ kcal/mol

$\Delta G^{\ddagger} = +12.00$ kcal/mol

$[\Delta G^{\ddagger} = +12.70$ kcal/mol]

$<\Delta G^{\ddagger} = +12.00$ kcal/mol>

$\nu^{\ddagger} = 153.0955i$ cm^{-1}

Figure S1-2

⇩

Int1

$\Delta(E_T+ZPE) = +4.58$ kcal/mol

$\Delta G^o = +3.10$ kcal/mol

$[\Delta G^o = +3.52$ kcal/mol]

$<\Delta G^o = +4.34$ kcal/mol>

Figure S1-3

⇩
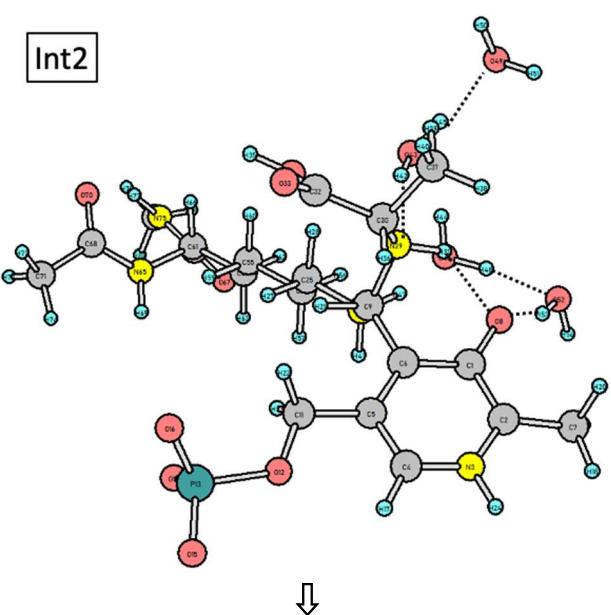
Figure S1. The optimized geometries of species in Scheme 4a (from Precursor to TS3). At TSs, red and blue broken lines stand for covalent bonds cleaved and formed, respectively. All the Cartesian

coordinates and energies corresponding to those geometries are shown at the end of Supplementary Information. ΔG, [ΔG] and <ΔG> values are by DFT = wB97X-D, M06-2X and APF-D in DFT/6-311+G(d,p) SCRF=(PCM,solvent=water)//wB97X-D/6-311+G(d,p) SCRF=(PCM,solvent=water), respectively.

a) The optimized geometry of TS3 by wB97x-D/6-311+G(d,p) SCRF=(PCM,solvent=water) could not be obtained in spite of many attempts. Alternatively, by B3LYP/6-31G(d) SCRF=(PCM,solvent=water), it was successfully obtained. Then, a single-point calclation of wB97x-D/6-311+G(d,p) SCRF=(PCM,solvent=water)//B3LYP/6-31G(d) SCRF=(PCM,solvent=water) was carried out. The (E_T + ZPE) and G values of TS3 were obtained by the sum of wB97x-D/6-311+G(d,p) electronic energy (E_T) and B3LYP/6-31G(d) zero-point vibrational energy (ZPE) and by that of E_T and B3LYP/6-31G(d) thermal correction, respectively.

TS3 in **Figure S1-6**

$\Downarrow$

Int3

2.560 Å
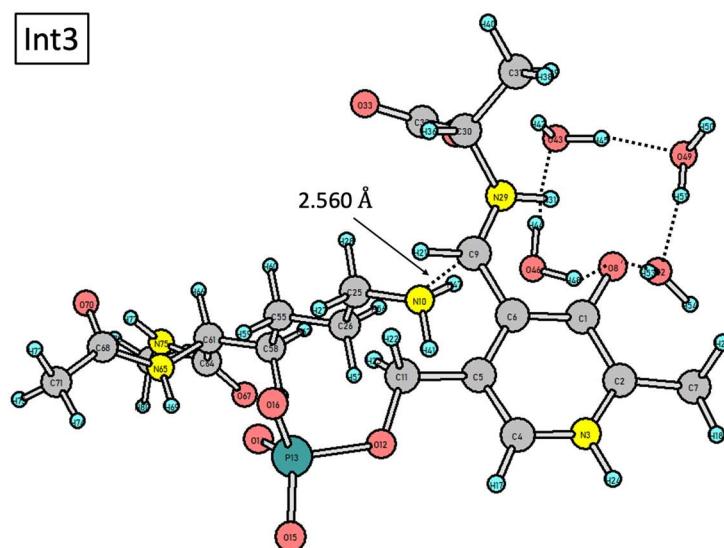
$\Delta(E_T+ZPE) = +15.64$ kcal/mol

$\Delta G^\circ = +13.68$ kcal/mol

$[\Delta G^\circ = +15.22$ kcal/mol$]$

$<\Delta G^\circ = +14.81$ kcal/mol$>$

Figure S2-1

$\Downarrow$

TS4

1.181 Å   1.322 Å

1.092 Å

1.574 Å
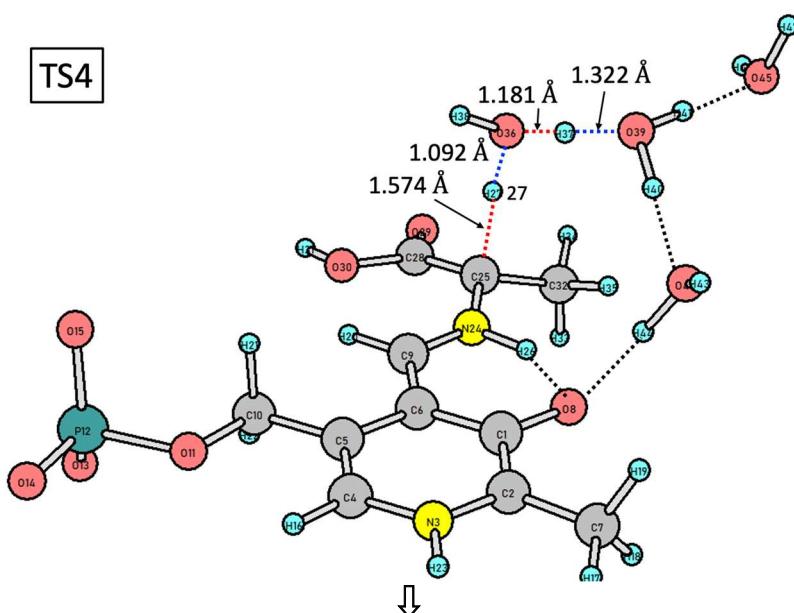
$\Delta(E_T+ZPE)^\ddagger = +45.65$ kcal/mol

$\Delta G^\ddagger = +43.20$ kcal/mol

$[\Delta G^\ddagger = +42.84$ kcal/mol$]$

$<\Delta G^\ddagger = +39.18$ kcal/mol$>$

$\nu^\ddagger = 741.2181i$ cm^{-1}

Figure S2-2

$\Downarrow$

Int4
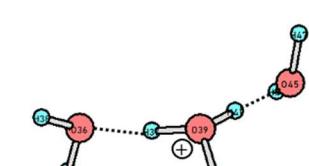
$\Delta(E_T+ZPE) = +42.17$ kcal/mol

$\Delta G^\circ = +39.96$ kcal/mol

$[\Delta G^\circ = +38.81$ kcal/mol$]$

$<\Delta G^\circ = +35.06$ kcal/mol$>$

Figure S2-3

Int3 in **Figure S2-1**

⇩

TS5
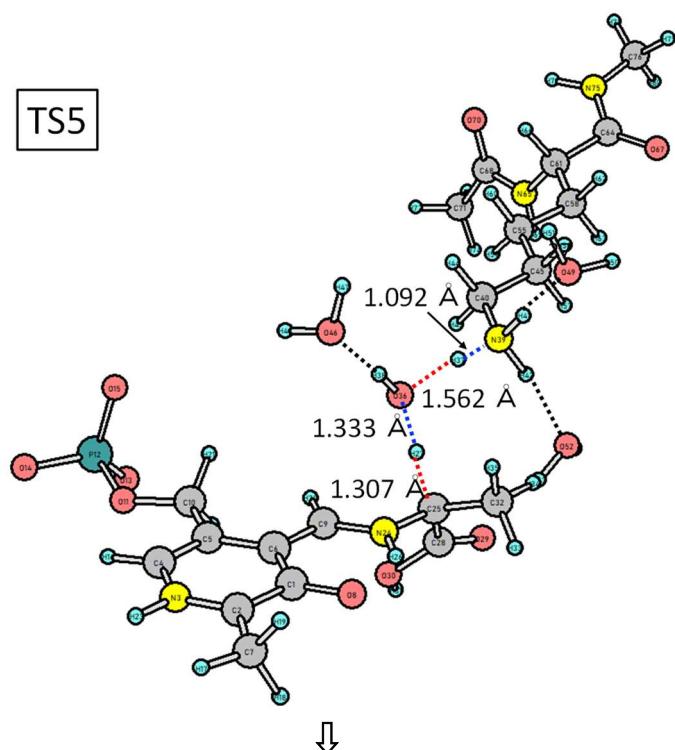
$\Delta(E_T+ZPE)^{\ddagger} = +23.61$ kcal/mol

$\Delta G^{\ddagger} = +20.93$ kcal/mol

$[\Delta G^{\ddagger} = +21.95$ kcal/mol$]$

$<\Delta G^{\ddagger} = +18.12$ kcal/mol$>$

$\nu^{\ddagger} = 1154.0598i$ cm^{-1}

Figure S2-4

⇩

Int5
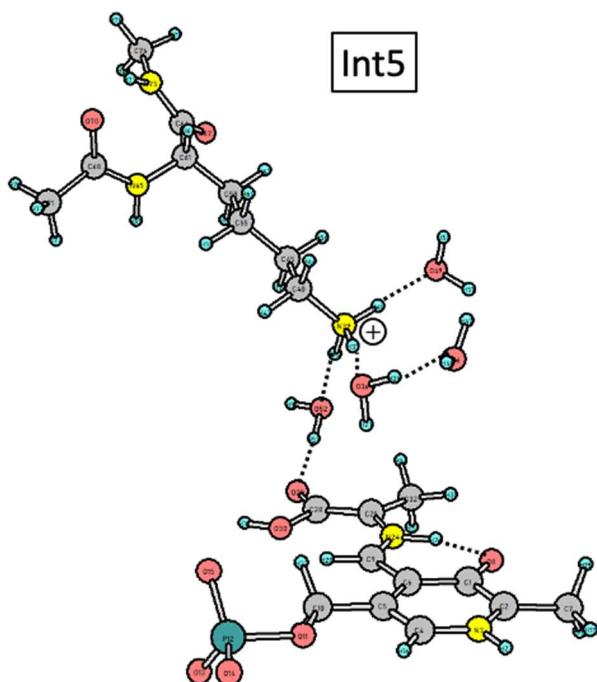
$\Delta(E_T+ZPE) = +11.73$ kcal/mol

$\Delta G^{o} = +11.92$ kcal/mol

$[\Delta G^{o} = +12.80$ kcal/mol$]$

$<\Delta G^{o} = +7.17$ kcal/mol$>$

Figure S2-5

Int3 in **Figure S2-1**

⇩

TS6

1.006 Å 1.595 Å 1.017 Å
1.555 Å
1.346 Å
1.283 Å
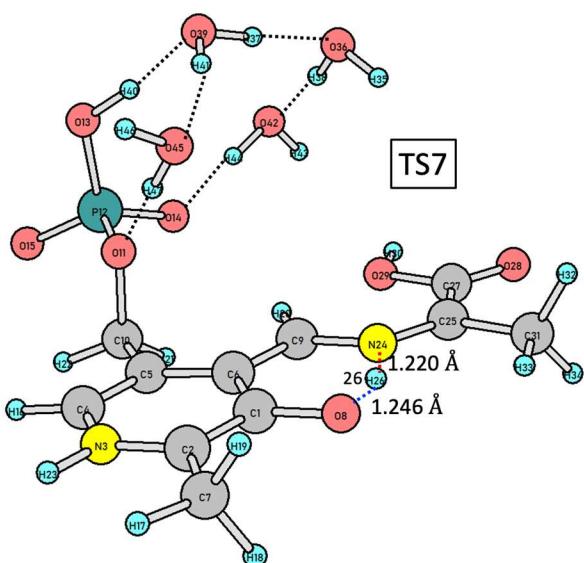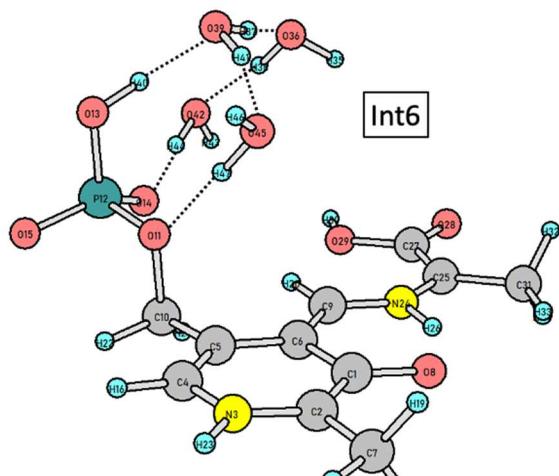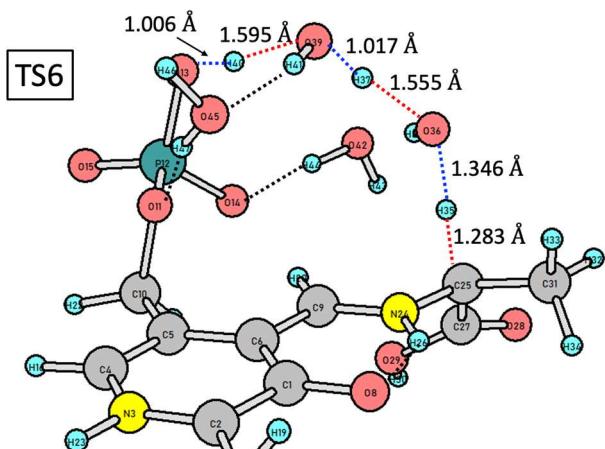
$\Delta(E_T + ZPE)^{\ddagger} = +19.00$ kcal/mol

$\Delta G^{\ddagger} = +20.40$ kcal/mol

[$\Delta G^{\ddagger} = +19.73$ kcal/mol]

<$\Delta G^{\ddagger} = +16.11$ kcal/mol>

$v^{\ddagger} = 1006.6264i$ cm^{-1}

Figure S2-6

⇩

Int6

$\Delta(E_T + ZPE) = +1.31$ kcal/mol

$\Delta G^{\circ} = +1.89$ kcal/mol

[$\Delta G^{\circ} = -1.59$ kcal/mol]

<$\Delta G^{\circ} = -5.07$ kcal/mol>

Figure S2-7

⇩

TS7

1.220 Å
1.246 Å

$\Delta(E_T + ZPE)^{\ddagger} = -0.07$ kcal/mol

$\Delta G^{\ddagger} = +0.48$ kcal/mol

[$\Delta G^{\ddagger} = -4.62$ kcal/mol]

<$\Delta G^{\ddagger} = -6.99$ kcal/mol>

$v^{\ddagger} = 1076.4290i$ cm^{-1}

Figure S2-8

Figure S2. The optimized geometries of species in Scheme 4b (from Int3 to TS7).

⇓

Int7

$\Delta(E_T+ZPE)$ = -1.49 kcal/mol

ΔG^o = -1.83 kcal/mol

[ΔG^o = -7.13 kcal/mol]

<ΔG^o = -7.18 kcal/mol>

Figure S3-1

⇓

TS8

1.004 Å

1.624 Å

1.596 Å

1.009 Å

1.208 Å

1.412 Å

26
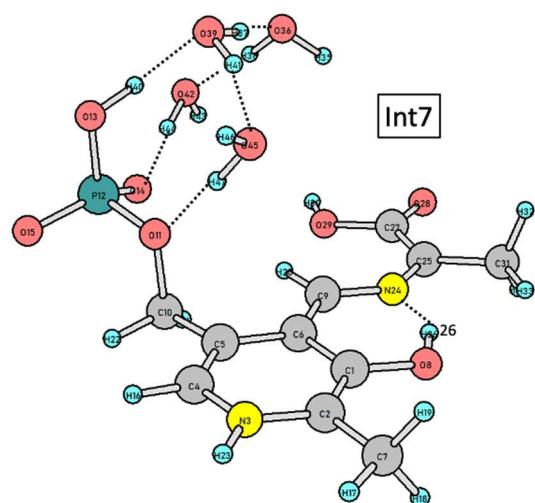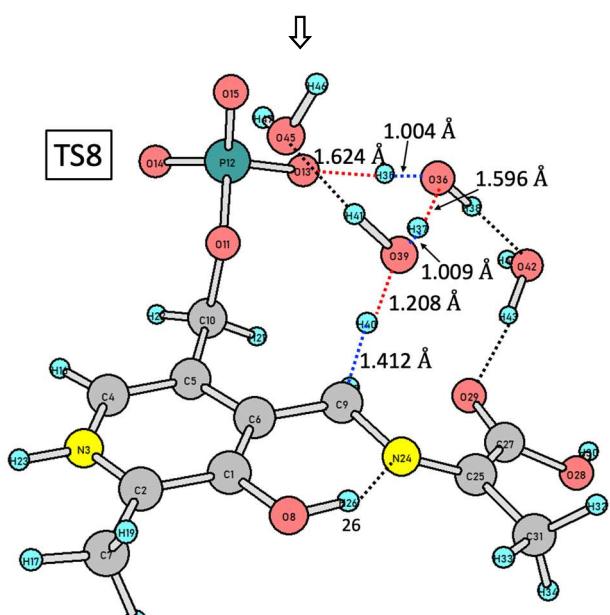
$\Delta(E_T+ZPE)^{\ddagger}$ = +25.42 kcal/mol

$\Delta G^{\ddagger}$ = +26.85 kcal/mol

[$\Delta G^{\ddagger}$ = +24.26 kcal/mol]

<$\Delta G^{\ddagger}$ = +21.46 kcal/mol>

$v^{\ddagger}$ = 1394.2219i cm^{-1}

Figure S3-2

⇓

Int8
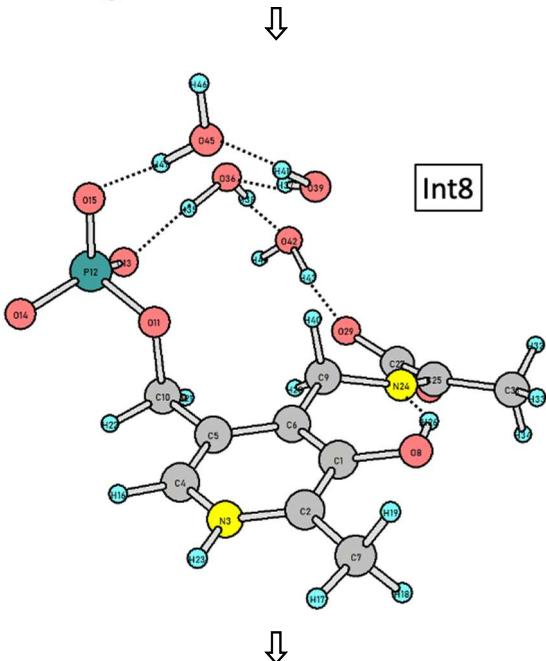
$\Delta(E_T+ZPE)$ = +13.50 kcal/mol

ΔG^o = +11.87 kcal/mol

[ΔG^o = +11.80 kcal/mol]

<ΔG^o = +13.64 kcal/mol>

Figure S3-3

⇓

TS9
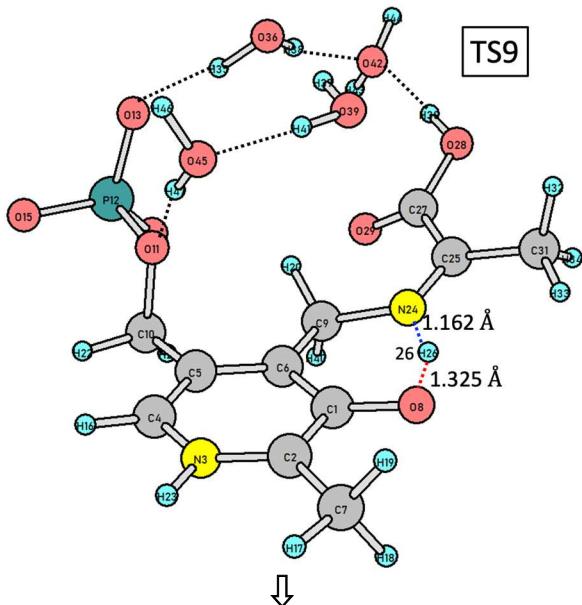
$\Delta(E_T+ZPE)^{\ddagger} = +12.38$ kcal/mol

$\Delta G^{\ddagger} = +11.91$ kcal/mol

$[\Delta G^{\ddagger} = +10.64$ kcal/mol$]$

$<\Delta G^{\ddagger} = +11.58$ kcal/mol$>$

$\nu^{\ddagger} = 573.7087i$ cm^{-1}

Figure S3-4
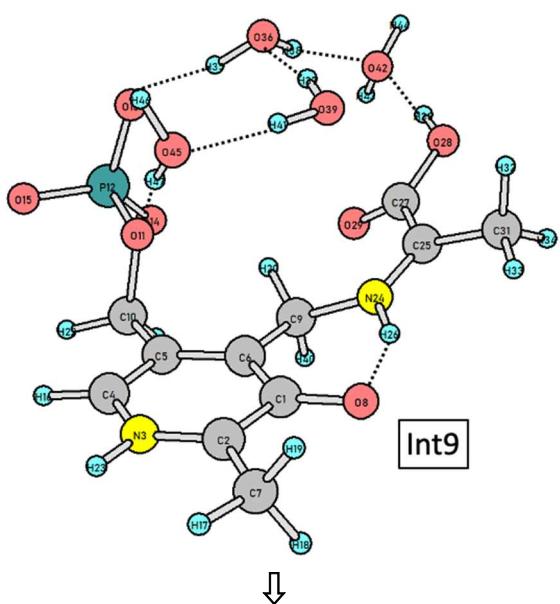
$\Delta(E_T+ZPE) = +13.84$ kcal/mol

$\Delta G^{o} = +13.28$ kcal/mol

$[\Delta G^{o} = +12.66$ kcal/mol$]$

$<\Delta G^{o} = +13.16$ kcal/mol$>$

Figure S3-5

Int9
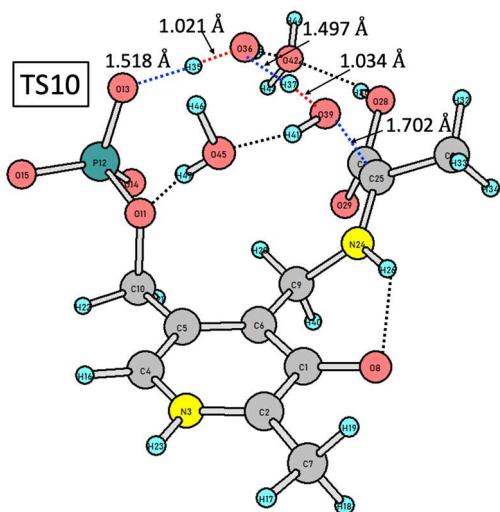
TS10

$\Delta(E_T+ZPE)^{\ddagger} = +23.59$ kcal/mol

$\Delta G^{\ddagger} = +25.38$ kcal/mol

$[\Delta G^{\ddagger} = +21.87$ kcal/mol$]$

$<\Delta G^{\ddagger} = +22.18$ kcal/mol$>$

$\nu^{\ddagger} = 161.4793i$ cm^{-1}

Figure S3-6

Figure S3. The optimized geometries of species in Scheme 4c (from Int7 to TS10).

TS10 in **Figure S3-6**

⇩

Int10
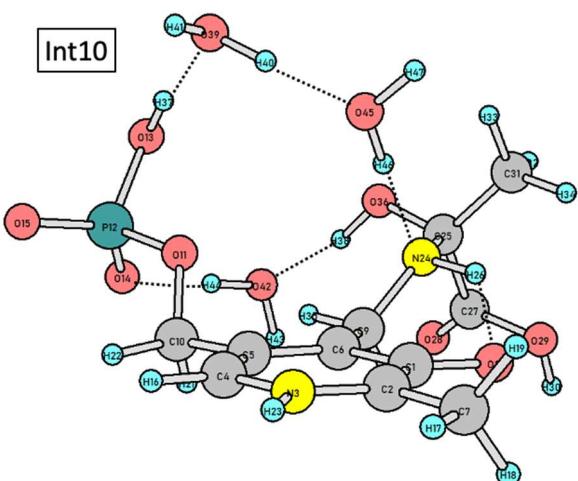
$\Delta(E_T+ZPE)$ = -3.19 kcal/mol

$\Delta G°$ = -3.02 kcal/mol

[$\Delta G°$ = -6.72 kcal/mol]

<$\Delta G°$ = -3.07 kcal/mol>

Figure S4-1

⇩

TS11

1.438 Å   1.230 Å

1.179 Å

1.050 Å

1.515 Å

1.093 Å
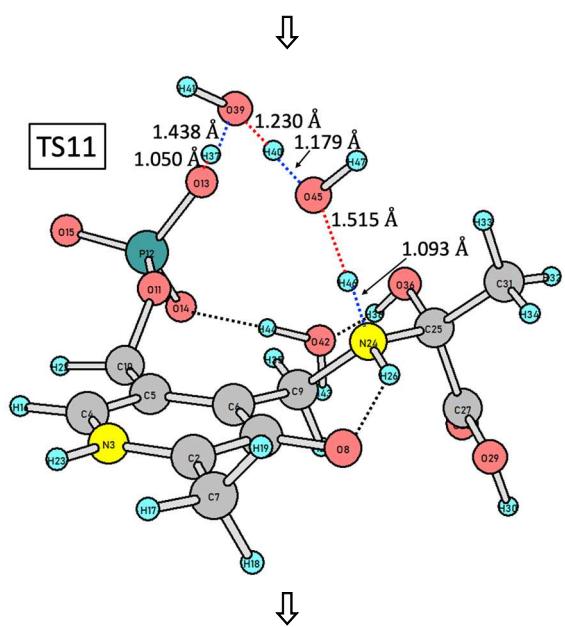
$\Delta(E_T+ZPE)^{\ddagger}$ = +5.83 kcal/mol

$\Delta G^{\ddagger}$ = +7.96 kcal/mol

[$\Delta G^{\ddagger}$ = +4.13 kcal/mol]

<$\Delta G^{\ddagger}$ = +4.69 kcal/mol>

$\nu^{\ddagger}$ = 828.6060i cm^{-1}

Figure S4-2

⇩

Int11
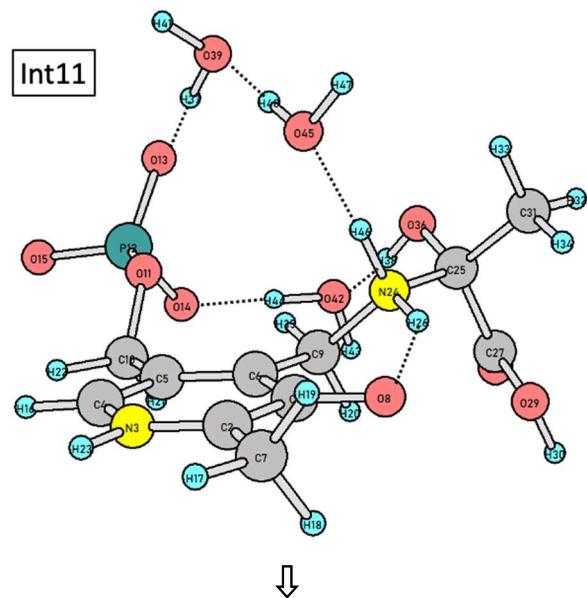
$\Delta(E_T+ZPE)$ = +1.71 kcal/mol

$\Delta G°$ = +2.54 kcal/mol

[$\Delta G°$ = +0.97 kcal/mol]

<$\Delta G°$ = +1.34 kcal/mol>

Figure S4-3

⇩

TS12

1.346 Å

1.084 Å

1.357 Å

1.089 Å
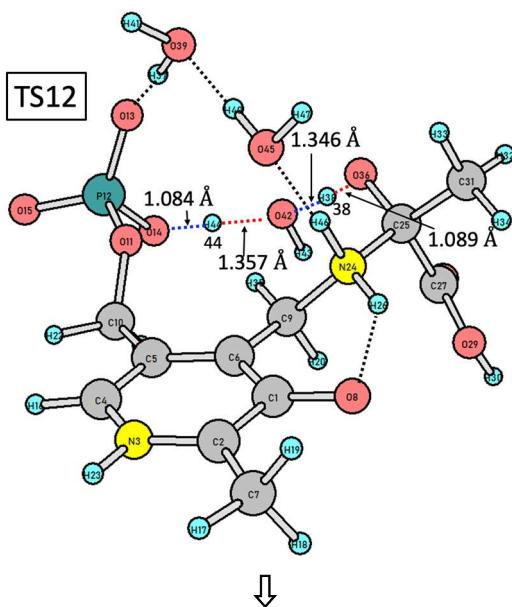
$\Delta(E_T+ZPE)^{\ddagger} = +2.75$ kcal/mol

$\Delta G^{\ddagger} = +4.43$ kcal/mol

$[\Delta G^{\ddagger} = +0.69$ kcal/mol]

$<\Delta G^{\ddagger} = +1.75$ kcal/mol>

$\nu^{\ddagger} = 401.4243i$ cm^{-1}

Figure S4-4

⇩

Int12

1.311 Å

1.566 Å
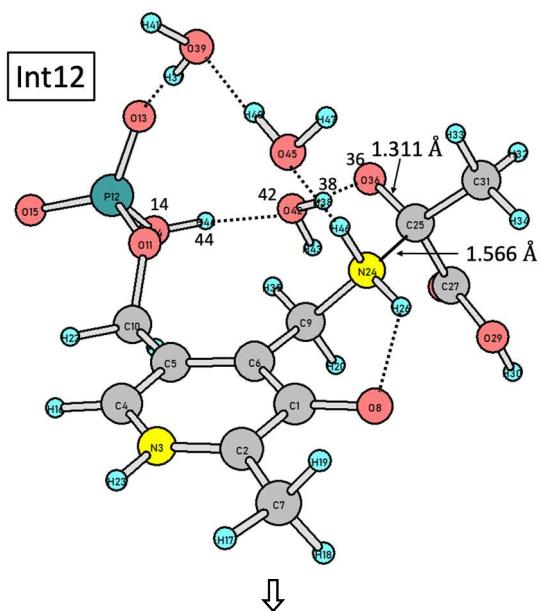
$\Delta(E_T+ZPE) = +1.80$ kcal/mol

$\Delta G^{\circ} = +2.93$ kcal/mol

$[\Delta G^{\circ} = +0.76$ kcal/mol]

$<\Delta G^{\circ} = +1.97$ kcal/mol>

Figure S4-5

⇩

TS13

2.115 Å
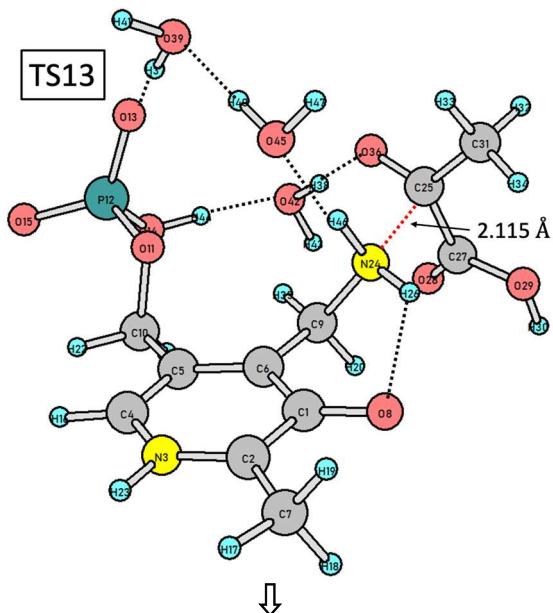
$\Delta(E_T+ZPE)^{\ddagger} = +6.19$ kcal/mol

$\Delta G^{\ddagger} = +6.00$ kcal/mol

$[\Delta G^{\ddagger} = +4.65$ kcal/mol]

$<\Delta G^{\ddagger} = +5.39$ kcal/mol>

$\nu^{\ddagger} = 108.4551i$ cm^{-1}

Figure S4-6

⇩

S11

Int13

2.490 Å
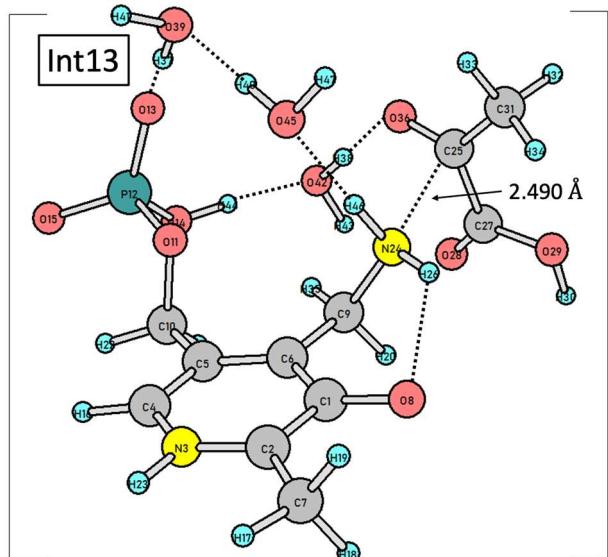
$\Delta(E_T+ZPE) = +5.45$ kcal/mol

$\Delta G^{\circ} = +3.33$ kcal/mol

$[\Delta G^{\circ} = +2.29$ kcal/mol]

$<\Delta G^{\circ} = +4.46$ kcal/mol>

Figure S4-7

⇩

Int14

O(in PO$_3$)-protonated PMP

pyruvic acid
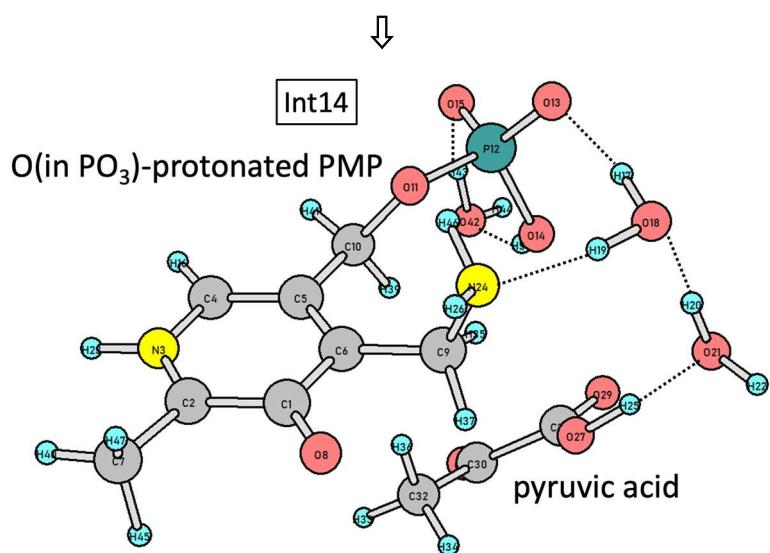
$\Delta(E_T+ZPE) = -0.79$ kcal/mol

$\Delta G^{\circ} = -2.17$ kcal/mol

$[\Delta G^{\circ} = -3.39$ kcal/mol]

$<\Delta G^{\circ} = -1.21$ kcal/mol>

Figure S4-8

Figure S4. The optimized geometries of species in Scheme 4d (from Int10 to Int14).
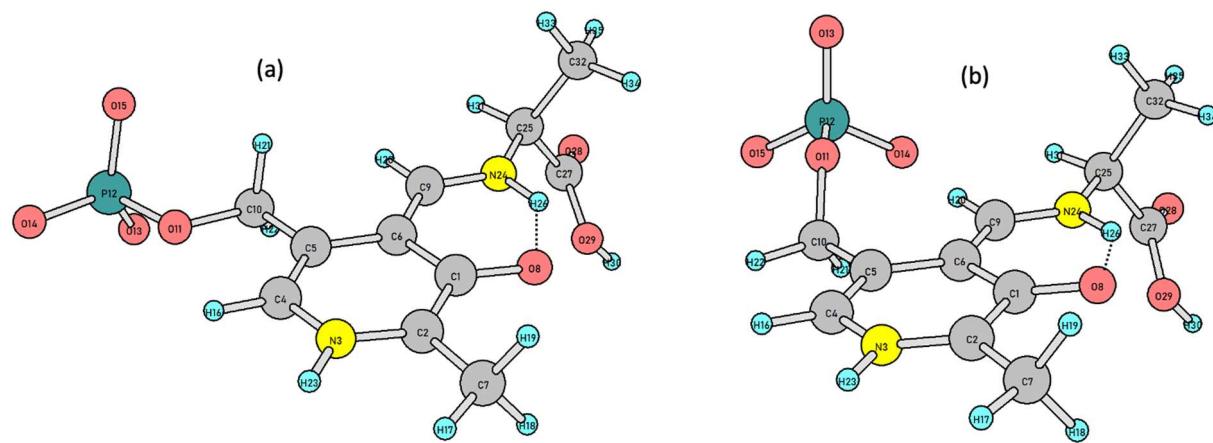
Figure S5. Two conformations (a) and (b) of the external aldimine in Int3 of Scheme 4b. (b) is 2.85 kcal/mol in (E_T + ZPE) or 2.22 kcal/mol in G^o more stable than (a).

TS (Int 3 → Int9)

1.214 Å

85.0°

1.482 Å
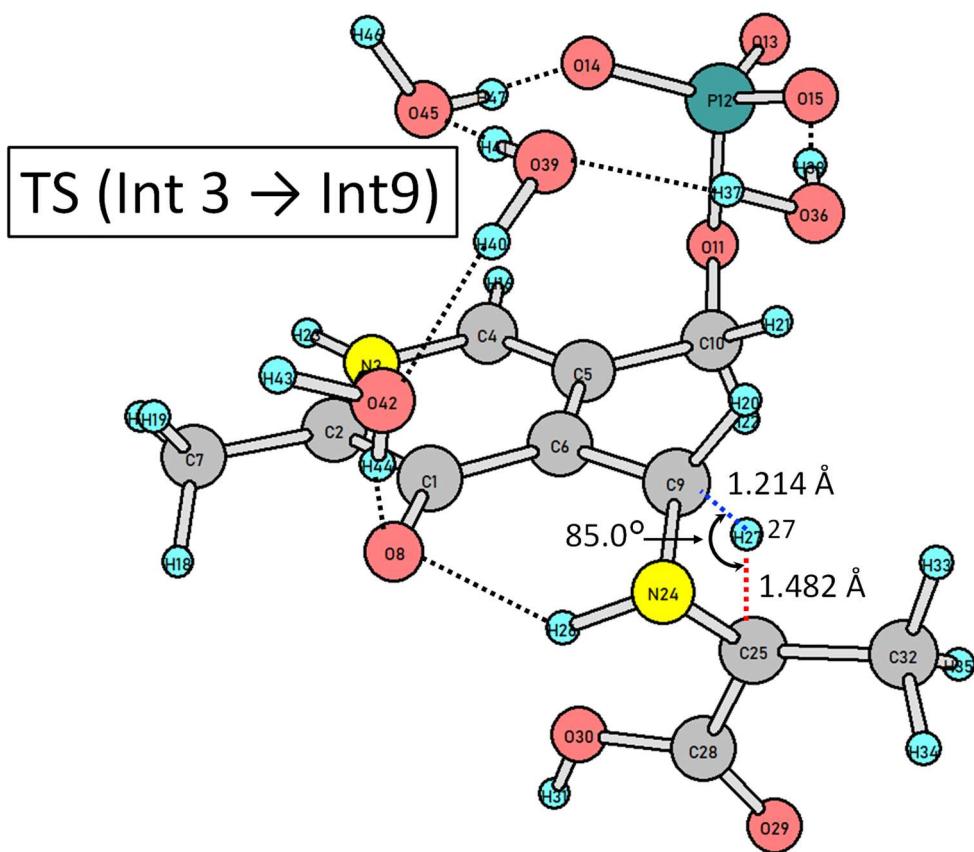
$\Delta G^{\ddagger} = +70.78$ kcal/mol

$\nu^{\ddagger} = 464.3921i$ cm^{-1}

Figure S6. The direct proton-transfer TS, TS (Int 3 → Int9), where Int3 is the external aldimine <C> and Int9 is the ketimine <E> in Scheme 2.

Cartesian coordinates and energies calculated by wb97x-D/6-311+G(d,p) with SCRF=(PCM, solvent=water)

```
=========== [PLP-model] defined in Scheme 3=====

The energy "Sum of electronic and zero-point Energies
= -668.870782 a.u."
of this [PLP-model] was added to (ET + ZPE)s of systems
with stoichiometry C11H22N2O11P(1-),
C11H22N2O11P(1-) + C9H19N3O2 =  C20H41N5O13P(1-),
in order to show overall energy changes in Scheme 4.

  plp.high.log

Stoichiometry   C9H19N3O2

                    Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic            Coordinates (Angstroms)
Number     Number      Type         X           Y           Z
---------------------------------------------------------------------
    1          7          0        5.795430   -0.224373   -0.040477
    2          6          0        4.461286    0.279400   -0.369902
    3          6          0        3.295769   -0.589415    0.103513
    4          1          0        4.363566    1.282319    0.059367
    5          1          0        4.404929    0.400665   -1.456987
    6          1          0        5.883325   -0.334853    0.964467
    7          1          0        5.922026   -1.149764   -0.437278
    8          6          0        1.935356   -0.006576   -0.270108
    9          1          0        3.398803   -1.592458   -0.329131
   10          1          0        3.358251   -0.708561    1.192485
   11          6          0        0.776081   -0.882769    0.198683
   12          1          0        1.842966    0.997592    0.159023
   13          1          0        1.876929    0.115522   -1.358679
   14          6          0       -0.587011   -0.319038   -0.178525
   15          1          0        0.863004   -1.877414   -0.246723
   16          1          0        0.822859   -1.028309    1.283626
   17          6          0       -1.734219   -1.302274    0.127661
   18          7          0       -0.824729    0.950607    0.499211
   19          1          0       -0.608798   -0.108861   -1.251978
   20          8          0       -1.592055   -2.282522    0.850886
   21          6          0       -1.566352    1.946286   -0.027822
   22          1          0       -0.396051    1.088880    1.401300
   23          8          0       -2.157448    1.819858   -1.101483
   24          6          0       -1.635688    3.224620    0.766388
   25          1          0       -1.235050    4.034155    0.153403
   26          1          0       -2.682521    3.450159    0.976135
   27          1          0       -1.081812    3.179743    1.704010
   28          7          0       -2.897958   -0.984998   -0.463907
   29          6          0       -4.113733   -1.738111   -0.228234
   30          1          0       -2.938167   -0.114494   -0.980887
   31          1          0       -4.903424   -1.328252   -0.855649
   32          1          0       -3.969256   -2.789639   -0.484012
   33          1          0       -4.423691   -1.676501    0.818585
---------------------------------------------------------------------

Standard basis: 6-311+G(d,p) (6D, 7F)

  436 basis functions
   55 alpha electrons       55 beta electrons
      nuclear repulsion energy      930.0262684235 Hartrees.
NAtoms=   33

Force inversion solution in PCM.
--------------------------------------------------------
Polarizable Continuum Model (PCM)
=================================
Model              : PCM.

Solvent : Water, Eps=  78.355300 Eps(inf)=   1.777849
------------------------------------------------------

SCF Done:  E(RwB97XD) =  -669.161984902  A.U. after 1 cycles
        NFock=  1  Conv=0.12D-08     -V/T= 2.0051

Zero-point correction=                      0.291203 (a.u.)
Thermal correction to Energy=               0.308530
Thermal correction to Enthalpy=             0.309474
```

```
Thermal correction to Gibbs Free Energy=        0.243867
Sum of electronic and zero-point Energies=          -668.870782
Sum of electronic and thermal Energies=             -668.853455
Sum of electronic and thermal Enthalpies=           -668.852511
Sum of electronic and thermal Free Energies=        -668.918118

                 E (Thermal)          CV                 S
                  KCal/Mol       Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              193.605           60.116            138.082

        Item              Value     Threshold  Converged?
Maximum Force            0.000028    0.000450     YES
RMS     Force            0.000004    0.000300     YES
Maximum Displacement     0.001906    0.001800     NO
RMS     Displacement     0.000420    0.001200     YES

Normal termination of Gaussian 16 at Sat Nov 13 17:58:48 2021.

 =========== Figure S1 in Scheme 4a==========

   -------Figure S1-1, Precursor----------

vita-b6fora.plp.high.log

Stoichiometry   C20H41N5O13P(1-)

                   Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic          Coordinates (Angstroms)
Number     Number      Type         X           Y           Z
---------------------------------------------------------------------
   1          6          0        3.697722    2.384209   -0.476932
   2          6          0        5.012210    2.450505    0.092809
   3          7          0        5.759686    1.354809    0.082258
   4          6          0        5.396476    0.154617   -0.427494
   5          6          0        4.154935    0.007315   -0.985843
   6          6          0        3.292165    1.124900   -1.012110
   7          6          0        5.529546    3.711060    0.687713
   8          8          0        2.959733    3.421689   -0.477225
   9          6          0        1.953469    0.975814   -1.534189
  10          7          0        1.113409    1.954950   -1.585727
  11          6          0        3.777716   -1.342363   -1.564932
  12          8          0        4.626846   -2.365185   -1.126904
  13         15          0        4.099938   -3.282489    0.220604
  14          8          0        2.897713   -4.078254   -0.294745
  15          8          0        5.343225   -4.106577    0.535353
  16          8          0        3.725683   -2.236455    1.278136
  17          1          0        6.104486   -0.653529   -0.343039
  18          1          0        6.556139    3.602337    1.037796
  19          1          0        5.486143    4.512444   -0.053118
  20          1          0        4.896958    4.012765    1.526288
  21          1          0        1.604108    0.017259   -1.900394
  22          1          0        2.734798   -1.564335   -1.320257
  23          1          0        3.851271   -1.272883   -2.657126
  24          1          0        6.684040    1.417634    0.495374
  25          6          0       -0.279264    1.791092   -1.992561
  26          6          0       -1.150940    1.500859   -0.774011
  27          1          0       -0.587656    2.702217   -2.507142
  28          1          0       -0.324416    0.958493   -2.695888
  29          7          0        1.214182   -0.883826    0.537277
  30          6          0        0.380523   -2.061126    0.338230
  31          1          0        2.116254   -1.192790    0.911600
  32          6          0       -0.407324   -1.948713   -0.959401
  33          8          0        0.006341   -1.448296   -1.981910
  34          8          0       -1.616024   -2.526876   -0.912759
  35          1          0       -2.007121   -2.470118   -1.794485
  36          1          0        1.067422   -2.897871    0.125952
  37          6          0       -0.479747   -2.424451    1.549872
  38          1          0        0.177402   -2.565924    2.410855
  39          1          0       -1.182208   -1.621742    1.792609
  40          1          0       -1.045565   -3.343957    1.391582
  41          1          0        1.456783    2.845109   -1.198401
  42          1          0        0.777020   -0.240435    1.195739
  43          8          0       -0.184461    1.026586    2.513708
  44          1          0       -0.306155    1.960678    2.274998
  45          1          0       -1.064958    0.701588    2.765913
  46          8          0       -0.436849    3.776450    1.881354
  47          1          0        0.447769    4.192246    1.832612
  48          1          0       -0.916950    4.271388    2.548113
  49          8          0       -2.663819    0.065318    3.425332
```

S16

```
50          1          0        -3.403493  -0.223790   2.856781
51          1          0        -2.544058  -0.640674   4.063520
52          8          0         2.113431   4.798653   1.679893
53          1          0         2.503511   4.361214   0.894009
54          1          0         2.227535   5.740665   1.540020
55          6          0        -2.554283   1.044232  -1.155099
56          1          0        -0.660476   0.714831  -0.196121
57          1          0        -1.191598   2.378736  -0.122457
58          6          0        -3.290917   0.481627   0.057740
59          1          0        -3.117756   1.871224  -1.599628
60          1          0        -2.487102   0.263771  -1.922665
61          6          0        -4.674036  -0.051478  -0.283117
62          1          0        -2.709413  -0.342335   0.479275
63          1          0        -3.366371   1.239655   0.845479
64          6          0        -5.294861  -0.853351   0.874673
65          7          0        -5.560078   1.034023  -0.684084
66          1          0        -4.599263  -0.729281  -1.139085
67          8          0        -4.830380  -0.849604   2.016876
68          6          0        -6.565783   0.879699  -1.570586
69          1          0        -5.389934   1.947814  -0.293144
70          8          0        -6.852600  -0.222495  -2.040228
71          6          0        -7.321694   2.124191  -1.954442
72          1          0        -7.223085   2.268897  -3.031881
73          1          0        -8.379276   1.973138  -1.732316
74          1          0        -6.969259   3.018313  -1.440637
75          7          0        -6.380473  -1.557079   0.543300
76          6          0        -7.132707  -2.328007   1.514779
77          1          0        -6.722671  -1.467546  -0.407163
78          1          0        -7.936356  -2.847634   0.996335
79          1          0        -6.489240  -3.063211   2.001649
80          1          0        -7.563356  -1.680570   2.282566
```

Standard basis: 6-311+G(d,p) (6D, 7F)

 1151 basis functions
  158 alpha electrons   158 beta electrons
     nuclear repulsion energy   5325.0957163069 Hartrees.
NAtoms= 80 NActive= 80

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
=================================
Model   : PCM.
Atomic radii   : UFF (Universal Force Field).
Polarization charges : Total charges.

Solvent : Water, Eps= 78.355300 Eps(inf)= 1.777849

SCF Done: E(RwB97XD) = -2380.27550752 A.U. after 2 cycles
        NFock= 2 Conv=0.11D-08   -V/T= 2.0042

Zero-point correction=   0.660637 (a.u.)
Thermal correction to Energy=   0.710682
Thermal correction to Enthalpy=   0.711626
Thermal correction to Gibbs Free Energy=   0.570386
Sum of electronic and zero-point Energies=   -2379.614871
Sum of electronic and thermal Energies=   -2379.564826
Sum of electronic and thermal Enthalpies=   -2379.563882
Sum of electronic and thermal Free Energies=   -2379.705122

              E (Thermal)   CV   S
              KCal/Mol   Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total   445.960   177.136   297.265

       Item   Value   Threshold Converged?
Maximum Force   0.000112   0.000450   YES
RMS   Force   0.000013   0.000300   YES
Maximum Displacement   0.010445   0.001800   NO
RMS   Displacement   0.002306   0.001200   NO

Normal termination of Gaussian 16 at Sun Jan 2 03:32:03 2022.

    ----------Figure S1-2, TS1----------------

 vita-b6tsa.plp.high.log

Stoichiometry   C20H41N5O13P(1-)

```
                 Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic           Coordinates (Angstroms)
Number     Number     Type          X          Y          Z
---------------------------------------------------------------------
   1          6          0       -2.422486  -2.204615  -1.905761
   2          6          0       -3.605193  -2.622692  -2.591026
   3          7          0       -4.612743  -1.763154  -2.714430
   4          6          0       -4.623249  -0.498040  -2.243775
   5          6          0       -3.530156  -0.029694  -1.556997
   6          6          0       -2.431073  -0.887011  -1.368180
   7          6          0       -3.717460  -3.991320  -3.161603
   8          8          0       -1.439184  -3.014826  -1.799183
   9          6          0       -1.268205  -0.415274  -0.596612
  10          7          0       -0.073360  -0.911654  -0.828447
  11          6          0       -3.538275   1.398218  -1.063765
  12          8          0       -4.754707   2.006861  -1.368355
  13         15          0       -4.994097   3.601138  -0.789235
  14          8          0       -3.872977   4.416980  -1.437715
  15          8          0       -6.397216   3.899055  -1.309394
  16          8          0       -4.877570   3.479748   0.732154
  17          1          0       -5.502157   0.097065  -2.429585
  18          1          0       -4.688435  -4.156930  -3.629142
  19          1          0       -2.931161  -4.148415  -3.903511
  20          1          0       -3.567766  -4.732969  -2.373666
  21          1          0       -1.295629   0.583238  -0.179858
  22          1          0       -3.360248   1.417721   0.018395
  23          1          0       -2.701910   1.937745  -1.532112
  24          1          0       -5.439859  -2.080087  -3.207840
  25          6          0        1.127125  -0.436123  -0.158100
  26          6          0        2.343452  -0.529990  -1.067386
  27          1          0        0.953975   0.597618   0.152008
  28          1          0        1.286161  -1.033137   0.745814
  29          7          0       -1.823453  -1.196683   1.287670
  30          6          0       -3.081829  -0.841480   1.942344
  31          1          0       -1.811509  -2.200062   1.096253
  32          6          0       -3.001847   0.527512   2.599583
  33          8          0       -3.770170   0.914771   3.441972
  34          8          0       -2.004966   1.280194   2.122266
  35          1          0       -2.039070   2.144671   2.553321
  36          1          0       -3.849067  -0.736259   1.162434
  37          6          0       -3.552253  -1.901032   2.938331
  38          1          0       -3.694109  -2.849107   2.416110
  39          1          0       -2.810405  -2.042073   3.727959
  40          1          0       -4.500123  -1.608157   3.390291
  41          1          0       -0.067361  -1.830257  -1.273733
  42          1          0       -1.026263  -1.014569   1.909684
  43          8          0        0.414503  -1.100487   3.217742
  44          1          0        0.727118  -1.970588   2.913255
  45          1          0       -0.052694  -1.250894   4.055131
  46          8          0        1.150616  -3.417255   1.883476
  47          1          0        0.352110  -3.757861   1.436027
  48          1          0        1.593881  -4.182093   2.254879
  49          8          0       -1.103009  -1.403177   5.580559
  50          1          0       -0.661178  -1.613782   6.406571
  51          1          0       -1.659477  -0.645820   5.777978
  52          8          0       -1.196947  -4.089344   0.622147
  53          1          0       -1.283600  -3.849206  -0.328098
  54          1          0       -1.690794  -4.900108   0.757089
  55          6          0        3.614250  -0.087986  -0.347947
  56          1          0        2.456896  -1.564623  -1.411023
  57          1          0        2.180538   0.087832  -1.956626
  58          6          0        4.848861  -0.196710  -1.238925
  59          1          0        3.492596   0.943526   0.000334
  60          1          0        3.759827  -0.703991   0.547335
  61          6          0        6.123251   0.250602  -0.536374
  62          1          0        4.984572  -1.233752  -1.556612
  63          1          0        4.712066   0.389300  -2.154399
  64          6          0        7.387386  -0.058595  -1.362518
  65          7          0        6.064634   1.674106  -0.224275
  66          1          0        6.216042  -0.275086   0.418644
  67          8          0        7.344756  -0.365930  -2.548929
  68          6          0        6.666591   2.223497   0.850715
  69          1          0        5.537817   2.269227  -0.844883
  70          8          0        7.372256   1.558911   1.611251
  71          6          0        6.432304   3.694724   1.074461
  72          1          0        5.960690   3.824242   2.050367
  73          1          0        7.397718   4.202786   1.099247
  74          1          0        5.803455   4.152691   0.311119
```

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```
  75        7        0      8.532223    0.043283   -0.667234
  76        6        0      9.830609   -0.125431   -1.289027
  77        1        0      8.471524    0.371563    0.289409
  78        1        0     10.596912   -0.048841   -0.519483
  79        1        0      9.904407   -1.105487   -1.764541
  80        1        0     10.010947    0.641193   -2.047548
 ----------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

 1151 basis functions
  158 alpha electrons   158 beta electrons
     nuclear repulsion energy   5026.2244026406 Hartrees.
NAtoms= 80 NActive= 80

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
=================================
Model   : PCM.
Atomic radii   : UFF (Universal Force Field).

Solvent : Water, Eps= 78.355300 Eps(inf)= 1.777849

SCF Done: E(RwB97XD) = -2380.25149952 A.U. after 2 cycles
        NFock= 2 Conv=0.10D-08   -V/T= 2.0043

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman
               1   2   3
               A   A   A
Frequencies -- -153.0995   6.0451   13.3164

Zero-point correction=   0.659110 (a.u.)
Thermal correction to Energy=   0.709644
Thermal correction to Enthalpy=   0.710588
Thermal correction to Gibbs Free Energy=   0.565498
Sum of electronic and zero-point Energies=   -2379.592389
Sum of electronic and thermal Energies=   -2379.541855
Sum of electronic and thermal Enthalpies=   -2379.540911
Sum of electronic and thermal Free Energies=   -2379.686002

                E (Thermal)   CV   S
                 KCal/Mol   Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total   445.309   176.444   305.369

       Item   Value   Threshold Converged?
Maximum Force   0.000002   0.000450   YES
RMS   Force   0.000000   0.000300   YES
Maximum Displacement   0.002833   0.001800   NO
RMS   Displacement   0.000579   0.001200   YES

 Normal termination of Gaussian 16 at Fri Jan 14 06:11:59 2022.

 ----------Figure S1-3, Int1-------------------

vita-b6for1.plp.high.log

 Stoichiometry   C20H41N5O13P(1-)

                   Standard orientation:

Center   Atomic   Atomic   Coordinates (Angstroms)
Number   Number   Type   X   Y   Z
 ----
     1   6   0   -3.990711   -0.787574   -1.260375
     2   6   0   -5.033598   -0.218912   -2.041578
     3   7   0   -5.137367   1.109714   -2.099979
     4   6   0   -4.330335   1.982532   -1.466432
     5   6   0   -3.306327   1.499725   -0.685771
     6   6   0   -3.135219   0.113990   -0.580409
     7   6   0   -5.984985   -1.076314   -2.798453
     8   8   0   -3.870818   -2.070237   -1.189637
     9   6   0   -1.961366   -0.416890   0.215682
    10   7   0   -0.801534   -0.605856   -0.629402
    11   6   0   -2.388361   2.470076   0.018276
    12   8   0   -2.700284   3.778815   -0.341063
    13   15   0   -1.692926   5.018382   0.281456
    14   8   0   -0.296704   4.674301   -0.243338
    15   8   0   -2.331413   6.258326   -0.336605
```

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```
16          8          0      -1.831852    4.902430    1.801034
17          1          0      -4.521918    3.034154   -1.605151
18          1          0      -6.769671   -0.488274   -3.274798
19          1          0      -5.449650   -1.638804   -3.567540
20          1          0      -6.440097   -1.804469   -2.124054
21          1          0      -1.734574    0.258460    1.046447
22          1          0      -2.487325    2.329662    1.105546
23          1          0      -1.345588    2.235542   -0.242777
24          1          0      -5.882094    1.495545   -2.669624
25          6          0       0.476801   -0.398717    0.068417
26          6          0       1.651037   -0.592602   -0.876956
27          1          0       0.515728    0.605067    0.515726
28          1          0       0.535906   -1.123858    0.884419
29          7          0      -2.315164   -1.739027    0.837195
30          6          0      -3.166652   -1.666744    2.047617
31          1          0      -2.878671   -2.215227    0.075963
32          6          0      -2.439991   -1.065759    3.241142
33          8          0      -3.019297   -0.631996    4.200023
34          8          0      -1.115121   -1.114399    3.117454
35          1          0      -0.703218   -0.736508    3.906425
36          1          0      -4.009892   -1.009957    1.824293
37          6          0      -3.679058   -3.064594    2.392619
38          1          0      -4.263135   -3.456384    1.558659
39          1          0      -2.849681   -3.745113    2.596981
40          1          0      -4.320705   -3.011477    3.271510
41          1          0      -0.867142    0.009197   -1.432877
42          1          0      -1.461372   -2.322424    1.009846
43          8          0      -0.254094   -3.575765    0.967463
44          1          0      -0.263774   -3.735203    0.004121
45          1          0      -0.548212   -4.397779    1.396130
46          8          0      -0.483357   -3.292754   -1.752247
47          1          0      -0.648789   -2.356280   -1.538182
48          1          0      -1.290854   -3.592497   -2.209173
49          8          0      -1.133050   -5.874581    2.289913
50          1          0      -1.083571   -5.896572    3.248497
51          1          0      -1.975543   -6.276742    2.065698
52          8          0      -2.951369   -3.921750   -2.894514
53          1          0      -3.409870   -3.222980   -2.381370
54          1          0      -3.093281   -3.707841   -3.818558
55          6          0       2.986979   -0.377026   -0.171662
56          1          0       1.612923   -1.601922   -1.299488
57          1          0       1.563037    0.108990   -1.715450
58          6          0       4.172860   -0.566927   -1.113845
59          1          0       3.010041    0.628424    0.262456
60          1          0       3.074217   -1.080089    0.665271
61          6          0       5.514970   -0.381371   -0.419986
62          1          0       4.149835   -1.574358   -1.537789
63          1          0       4.101803    0.124010   -1.960968
64          6          0       6.700850   -0.757078   -1.330082
65          7          0       5.664290    0.989535    0.054768
66          1          0       5.559243   -1.024400    0.463981
67          8          0       6.586323   -0.898120   -2.542897
68          6          0       6.367148    1.319633    1.157753
69          1          0       5.204020    1.720153   -0.465950
70          8          0       6.995806    0.479915    1.804161
71          6          0       6.344772    2.771426    1.559097
72          1          0       5.929552    2.844940    2.565920
73          1          0       7.370936    3.141212    1.592220
74          1          0       5.758159    3.395509    0.885148
75          7          0       7.863866   -0.910614   -0.675363
76          6          0       9.109399   -1.179118   -1.366366
77          1          0       7.874527   -0.696816    0.315005
78          1          0       9.893093   -1.326989   -0.625297
79          1          0       9.023291   -2.081820   -1.974354
80          1          0       9.390145   -0.348090   -2.019337
----------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

 1151 basis functions
  158 alpha electrons   158 beta electrons
     nuclear repulsion energy   5080.6583122480 Hartrees.
 NAtoms=   80

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
=================================
Model   : PCM.

```
Solvent : Water, Eps=  78.355300 Eps(inf)=   1.777849
----------------------------------------------------

SCF Done:  E(RwB97XD) =  -2380.27039183 A.U. after  1 cycles
         NFock=  1 Conv=0.59D-08     -V/T= 2.0043

Zero-point correction=                           0.662812 (a.u.)
Thermal correction to Energy=                    0.712405
Thermal correction to Enthalpy=                  0.713349
Thermal correction to Gibbs Free Energy=         0.570211
Sum of electronic and zero-point Energies=          -2379.607580
Sum of electronic and thermal Energies=             -2379.557987
Sum of electronic and thermal Enthalpies=           -2379.557043
Sum of electronic and thermal Free Energies=        -2379.700180

                E (Thermal)          CV                S
                 KCal/Mol        Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total             447.041           173.978          301.259


        Item               Value     Threshold  Converged?
Maximum Force            0.000024     0.000450     YES
RMS     Force            0.000005     0.000300     YES
Maximum Displacement     0.004393     0.001800     NO
RMS     Displacement     0.000708     0.001200     YES

Normal termination of Gaussian 16 at Wed Jan 12 07:46:02 2022.

    ---------Figure S1-4, TS2-------------

 vita-b6ts1.plp.high.log

  Stoichiometry    C20H41N5O13P(1-)

                      Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic          Coordinates (Angstroms)
Number     Number     Type         X           Y           Z
---------------------------------------------------------------------
    1          6          0      -4.029656   -0.799019   -1.233978
    2          6          0      -5.062481   -0.216067   -2.022754
    3          7          0      -5.132382    1.113266   -2.119092
    4          6          0      -4.295088    1.978194   -1.516008
    5          6          0      -3.277529    1.483932   -0.732165
    6          6          0      -3.139032    0.097393   -0.584691
    7          6          0      -6.046951   -1.064789   -2.747639
    8          8          0      -3.954101   -2.077431   -1.137574
    9          6          0      -1.983122   -0.447371    0.241042
   10          7          0      -0.831162   -0.700154   -0.635199
   11          6          0      -2.329773    2.454052   -0.064942
   12          8          0      -2.624001    3.762063   -0.447947
   13         15          0      -1.610221    5.001376    0.155704
   14          8          0      -0.216237    4.647842   -0.369822
   15          8          0      -2.244826    6.238554   -0.473266
   16          8          0      -1.742284    4.906204    1.677812
   17          1          0      -4.457283    3.030878   -1.681180
   18          1          0      -6.793657   -0.465720   -3.269463
   19          1          0      -5.530844   -1.698652   -3.473073
   20          1          0      -6.550850   -1.729860   -2.042832
   21          1          0      -1.699408    0.311938    0.979188
   22          1          0      -2.412463    2.342352    1.026467
   23          1          0      -1.294951    2.196910   -0.336519
   24          1          0      -5.870828    1.503453   -2.693277
   25          6          0       0.454150   -0.505201    0.056379
   26          6          0       1.630218   -0.703285   -0.886781
   27          1          0       0.499060    0.499396    0.501339
   28          1          0       0.504888   -1.220153    0.881596
   29          7          0      -2.324437   -1.655091    1.006864
   30          6          0      -3.012151   -1.358457    2.262282
   31          1          0      -2.969383   -2.183675    0.407504
   32          6          0      -2.067035   -0.811611    3.321436
   33          8          0      -2.417616   -0.065491    4.201603
   34          8          0      -0.821649   -1.278134    3.210671
   35          1          0      -0.292245   -0.913246    3.932225
   36          1          0      -3.783042   -0.589433    2.129723
   37          6          0      -3.676896   -2.626815    2.802615
   38          1          0      -4.405436   -2.993896    2.077142
   39          1          0      -2.936303   -3.409656    2.982130
   40          1          0      -4.198372   -2.415316    3.736709
   41          1          0      -0.879943   -0.060793   -1.423012
   42          1          0      -1.168301   -2.901125    1.123256
---------------------------------------------------------------------
```

S21

```
43          8          0      -0.591598   -3.699425    0.885478
44          1          0      -0.598110   -3.638656   -0.280665
45          1          0      -1.037686   -4.512179    1.228560
46          8          0      -0.623086   -3.286293   -1.469381
47          1          0      -0.754184   -2.299687   -1.342411
48          1          0      -1.424417   -3.615990   -1.954150
49          8          0      -1.806975   -5.884730    1.808280
50          1          0      -1.721754   -6.097936    2.741079
51          1          0      -2.738569   -5.989810    1.598607
52          8          0      -2.908549   -3.956203   -2.634497
53          1          0      -3.418871   -3.234072   -2.192561
54          1          0      -3.002440   -3.820162   -3.579372
55          6          0       2.965020   -0.481055   -0.181271
56          1          0       1.598255   -1.713667   -1.307471
57          1          0       1.541936   -0.004918   -1.727936
58          6          0       4.152612   -0.667657   -1.121937
59          1          0       2.983074    0.525787    0.249890
60          1          0       3.054835   -1.181012    0.657989
61          6          0       5.492902   -0.461248   -0.430428
62          1          0       4.139955   -1.678952   -1.536987
63          1          0       4.074190    0.014935   -1.975202
64          6          0       6.682397   -0.833921   -1.337084
65          7          0       5.627868    0.916145    0.029682
66          1          0       5.544067   -1.094521    0.460187
67          8          0       6.568688   -0.989832   -2.548152
68          6          0       6.327072    1.265758    1.128954
69          1          0       5.159437    1.636123   -0.498526
70          8          0       6.964742    0.439965    1.784442
71          6          0       6.289105    2.721539    1.514349
72          1          0       5.871933    2.801748    2.519854
73          1          0       7.311328    3.102311    1.544541
74          1          0       5.696832    3.332164    0.833057
75          7          0       7.847438   -0.966897   -0.681473
76          6          0       9.095807   -1.228203   -1.370109
77          1          0       7.856101   -0.741754    0.306392
78          1          0       9.880746   -1.362434   -0.627762
79          1          0       9.018809   -2.136422   -1.971003
80          1          0       9.368453   -0.399551   -2.029521
 ---------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

 1151 basis functions
  158 alpha electrons   158 beta electrons
      nuclear repulsion energy   5101.1101928482 Hartrees.
NAtoms= 80 NActive= 80

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
 =================================
Model   : PCM.
Atomic radii   : UFF (Universal Force Field).

Solvent : Water, Eps= 78.355300 Eps(inf)= 1.777849

SCF Done: E(RwB97XD) = -2380.25333338 A.U. after 2 cycles
          NFock= 2 Conv=0.63D-09   -V/T= 2.0043
DoSCS=F DFT=T ScalE2(SS,OS)= 1.000000 1.000000
Range of M.O.s used for correlation: 1 1147

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman
                1   2   3
                A   A   A
Frequencies -- -551.7132   8.7245   10.2489

Zero-point correction=   0.658602 (a.u.)
Thermal correction to Energy=   0.706500
Thermal correction to Enthalpy=   0.707444
Thermal correction to Gibbs Free Energy=   0.568183
Sum of electronic and zero-point Energies=   -2379.594732
Sum of electronic and thermal Energies=   -2379.546833
Sum of electronic and thermal Enthalpies=   -2379.545889
Sum of electronic and thermal Free Energies=   -2379.685151

                E (Thermal)   CV   S
                 KCal/Mol   Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total   443.335   169.415   293.100

```
     Item              Value    Threshold Converged?
Maximum Force          0.000009   0.000450    YES
RMS     Force          0.000001   0.000300    YES
Maximum Displacement   0.001315   0.001800    YES
RMS     Displacement   0.000244   0.001200    YES
```

Normal termination of Gaussian 16 at Wed Dec 29 16:27:32 2021.

----------Figure S1-5, Int2--------------

vita-b6rev1.plp.high.log

Stoichiometry   C20H41N5O13P(1-)

Standard orientation:
```
---------------------------------------------------------------------
Center    Atomic    Atomic          Coordinates (Angstroms)
Number    Number    Type         X           Y           Z
---------------------------------------------------------------------
   1        6         0       -3.633745   -1.409761   -1.382163
   2        6         0       -4.774140   -1.152343   -2.199972
   3        7         0       -5.227319    0.098052   -2.288093
   4        6         0       -4.701533    1.166382   -1.656650
   5        6         0       -3.599916    0.992802   -0.848815
   6        6         0       -3.062490   -0.293345   -0.715716
   7        6         0       -5.449137   -2.247677   -2.946619
   8        8         0       -3.170880   -2.592984   -1.262802
   9        6         0       -1.846949   -0.545599    0.156349
  10        7         0       -0.629138   -0.747067   -0.712040
  11        6         0       -3.014000    2.196106   -0.145360
  12        8         0       -3.715194    3.349962   -0.493076
  13       15         0       -3.096295    4.836749    0.090922
  14        8         0       -1.664579    4.890533   -0.447980
  15        8         0       -4.065321    5.832451   -0.538697
  16        8         0       -3.183600    4.719588    1.614469
  17        1         0       -5.169722    2.123299   -1.818424
  18        1         0       -6.320752   -1.889001   -3.494808
  19        1         0       -4.750329   -2.704118   -3.651990
  20        1         0       -5.761031   -3.030544   -2.251416
  21        1         0       -1.627724    0.339821    0.752411
  22        1         0       -3.055526    2.033254    0.942080
  23        1         0       -1.954322    2.300055   -0.418425
  24        1         0       -6.036020    0.261468   -2.877346
  25        6         0        0.651371   -0.389063   -0.029716
  26        6         0        1.845589   -0.585222   -0.947291
  27        1         0        0.567334    0.651701    0.287691
  28        1         0        0.718654   -1.013903    0.860040
  29        7         0       -1.955802   -1.683078    1.047713
  30        6         0       -2.709009   -1.410746    2.267857
  31        1         0       -2.421368   -2.422997    0.517924
  32        6         0       -1.918990   -0.597857    3.284380
  33        8         0       -2.440799   -0.019349    4.204401
  34        8         0       -0.600916   -0.608795    3.079670
  35        1         0       -0.179623   -0.082828    3.772833
  36        1         0       -3.616235   -0.825206    2.069039
  37        6         0       -3.128141   -2.734117    2.912627
  38        1         0       -3.773046   -3.286374    2.226313
  39        1         0       -2.255033   -3.348743    3.143989
  40        1         0       -3.683459   -2.547202    3.831660
  41        1         0       -0.730087   -0.182825   -1.556340
  42        1         0       -0.421015   -2.864408    1.466340
  43        8         0        0.261165   -3.554430    1.385481
  44        1         0        0.140642   -3.674126   -0.426769
  45        1         0       -0.030070   -4.278973    1.964644
  46        8         0        0.028027   -3.336485   -1.335531
  47        1         0       -0.560139   -1.753077   -1.025714
  48        1         0       -0.654474   -3.883617   -1.767639
  49        8         0       -0.597167   -5.627101    3.059189
  50        1         0       -0.567607   -5.495289    4.009770
  51        1         0       -1.450075   -6.031340    2.883034
  52        8         0       -2.107744   -4.611151   -2.583360
  53        1         0       -2.658109   -3.873987   -2.237579
  54        1         0       -2.143206   -4.545992   -3.539388
  55        6         0        3.137863   -0.191384   -0.235933
  56        1         0        1.893126   -1.629516   -1.267210
  57        1         0        1.722419    0.027162   -1.847596
  58        6         0        4.362965   -0.377690   -1.127194
  59        1         0        3.068419    0.851464    0.091405
  60        1         0        3.254803   -0.797004    0.670094
  61        6         0        5.654013    0.044206   -0.439064
```

```
    62           1           0        4.457480   -1.428402   -1.412488
    63           1           0        4.245987    0.185015   -2.059840
    64           6           0        6.905452   -0.339960   -1.252686
    65           7           0        5.648374    1.478530   -0.174651
    66           1           0        5.727396   -0.452223    0.533129
    67           8           0        6.850616   -0.690606   -2.426445
    68           6           0        6.268527    2.040454    0.883567
    69           1           0        5.149925    2.073007   -0.818941
    70           8           0        6.946894    1.375319    1.667938
    71           6           0        6.089658    3.526096    1.057050
    72           1           0        5.631607    3.706771    2.031207
    73           1           0        7.073120    3.999049    1.056710
    74           1           0        5.471335    3.979888    0.282700
    75           7           0        8.053736   -0.251024   -0.561518
    76           6           0        9.344868   -0.488359   -1.175943
    77           1           0        8.005404    0.111699    0.383323
    78           1           0       10.114624   -0.402323   -0.410898
    79           1           0        9.386849   -1.490147   -1.608127
    80           1           0        9.547788    0.238234   -1.967390
 ---------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

 1151 basis functions
  158 alpha electrons   158 beta electrons
     nuclear repulsion energy 5050.8290753958 Hartrees.
  NAtoms=   80

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
================================
Model   : PCM.
Atomic radii   : UFF (Universal Force Field).

Solvent : Water, Eps= 78.355300 Eps(inf)= 1.777849

SCF Done: E(RwB97XD) = -2380.26888388 A.U. after 1 cycles
         NFock= 1 Conv=0.57D-08   -V/T= 2.0043

Zero-point correction=   0.664519 (a.u.)
Thermal correction to Energy=   0.713888
Thermal correction to Enthalpy=   0.714832
Thermal correction to Gibbs Free Energy=   0.572955
Sum of electronic and zero-point Energies=   -2379.604365
Sum of electronic and thermal Energies=   -2379.554996
Sum of electronic and thermal Enthalpies=   -2379.554052
Sum of electronic and thermal Free Energies=   -2379.695929

                   E (Thermal)   CV   S
                     KCal/Mol   Cal/Mol-Kelvin Cal/Mol-Kelvin
 Total   447.971   173.744   298.605

        Item   Value   Threshold Converged?
 Maximum Force   0.000016   0.000450   YES
 RMS   Force   0.000002   0.000300   YES
 Maximum Displacement   0.004216   0.001800   NO
 RMS   Displacement   0.000464   0.001200   YES

 Normal termination of Gaussian 16 at Wed Jan 12 09:33:52 2022.

   ---------Figure S1-6, TS3----------------

 vita-b6tsb.plp.log
  .. ..
 The optimized geometry of TS3 by wB97x-D/6-311+G(d,p)
SCRF=(PCM,solvent=water) could not be obtained
in spite of many attempts. Alternatively, by B3LYP/6-31G(d)
SCRF=(PCM,solvent=water), it was successfully obtained.
Then, a single-point calclation of wB97x-D/6-311+G(d,p)
SCRF=(PCM,solvent=water)//B3LYP/6-31G(d) SCRF=(PCM,solvent=water)
was carried out. The (ET + ZPE) value of TS3 was obtained
by the sum of wB97x-D/6-311+G(d,p) electronic energy (ET) and
B3LYP/6-31G(d) zero-point vibrational energy(ZPE)
  ....
 Stoichiometry   C20H41N5O13P(1-)

                    Standard orientation:

```
Center     Atomic    Atomic           Coordinates (Angstroms)
Number     Number    Type         X           Y           Z
---------------------------------------------------------------------
   1         6         0       -4.438148   -0.213492   -0.601266
   2         6         0       -5.321168    0.414118   -1.546126
   3         7         0       -5.124241    1.704484   -1.840804
   4         6         0       -4.156903    2.497686   -1.314996
   5         6         0       -3.286057    1.974877   -0.381770
   6         6         0       -3.425636    0.613605   -0.010602
   7         6         0       -6.441660   -0.325668   -2.198290
   8         8         0       -4.591341   -1.459425   -0.310685
   9         6         0       -2.567128    0.074301    1.042365
  10         7         0       -0.764519   -0.343112   -0.325569
  11         6         0       -2.230050    2.883858    0.218852
  12         8         0       -2.341760    4.179057   -0.316619
  13        15         0       -1.104598    5.322453    0.087413
  14         8         0        0.190438    4.722410   -0.500809
  15         8         0       -1.628216    6.577638   -0.633583
  16         8         0       -1.122173    5.394330    1.629037
  17         1         0       -4.121906    3.523828   -1.646029
  18         1         0       -7.138475    0.356156   -2.692916
  19         1         0       -6.059938   -1.025533   -2.951330
  20         1         0       -6.984468   -0.914484   -1.453321
  21         1         0       -1.924840    0.761370    1.578192
  22         1         0       -2.353056    2.909382    1.312251
  23         1         0       -1.232606    2.465186    0.015297
  24         1         0       -5.757892    2.131857   -2.512670
  25         6         0        0.591226   -0.234802    0.241744
  26         6         0        1.720979   -0.556506   -0.747081
  27         1         0        0.715332    0.783011    0.630662
  28         1         0        0.649918   -0.913458    1.099280
  29         7         0       -2.862103   -1.045935    1.677828
  30         6         0       -2.355089   -1.383066    3.007794
  31         1         0       -3.543778   -1.651022    1.202724
  32         6         0       -1.050109   -2.181728    3.009381
  33         8         0       -0.181215   -2.022953    3.842419
  34         8         0       -0.972335   -3.106689    2.033355
  35         1         0       -0.118813   -3.576419    2.126956
  36         1         0       -2.124805   -0.449355    3.526322
  37         6         0       -3.431191   -2.149993    3.795356
  38         1         0       -4.330745   -1.534040    3.876246
  39         1         0       -3.686374   -3.091270    3.298695
  40         1         0       -3.068327   -2.373028    4.801928
  41         1         0       -0.861423    0.283168   -1.125397
  42         1         0       -1.856205   -4.699904    0.889201
  43         8         0       -1.649914   -5.232174    0.102566
  44         1         0       -1.281797   -3.829564   -1.082571
  45         1         0       -2.521579   -5.559035   -0.231195
  46         8         0       -1.296045   -3.065811   -1.704115
  47         1         0       -0.949343   -1.292213   -0.676973
  48         1         0       -2.218562   -3.071317   -2.034939
  49         8         0       -4.063292   -5.906942   -1.074819
  50         1         0       -4.818494   -6.085513   -0.492490
  51         1         0       -4.228471   -5.017252   -1.473515
  52         8         0       -4.119954   -3.369570   -2.149030
  53         1         0       -4.409594   -2.656791   -1.514742
  54         1         0       -4.607602   -3.229837   -2.976212
  55         6         0        3.109544   -0.432071   -0.104819
  56         1         0        1.581603   -1.575177   -1.133825
  57         1         0        1.649127    0.121734   -1.608777
  58         6         0        4.240122   -0.776859   -1.083780
  59         1         0        3.242599    0.588204    0.278273
  60         1         0        3.169884   -1.100023    0.766054
  61         6         0        5.634050   -0.677481   -0.458784
  62         1         0        4.110806   -1.801188   -1.450280
  63         1         0        4.189527   -0.128528   -1.968180
  64         6         0        6.742516   -1.235986   -1.387218
  65         7         0        5.941281    0.708742   -0.088618
  66         1         0        5.660666   -1.256482    0.470674
  67         8         0        6.561616   -1.442313   -2.597112
  68         6         0        6.746110    1.051890    0.942012
  69         1         0        5.539625    1.443903   -0.656581
  70         8         0        7.332739    0.196203    1.632613
  71         6         0        6.900570    2.531434    1.218191
  72         1         0        6.554477    2.737254    2.236050
  73         1         0        7.961977    2.793213    1.170325
  74         1         0        6.344461    3.162762    0.520870
  75         7         0        7.912074   -1.471696   -0.763283
  76         6         0        9.102927   -1.925718   -1.467079
  77         1         0        7.982571   -1.194906    0.212845
```

```
  78      1       0       9.891750   -2.100707   -0.734028
  79      1       0       8.900331   -2.858571   -2.001647
  80      1       0       9.448154   -1.180073   -2.192348
 ---------------------------------------------------------------------

 SCF Done:  E(RB3LYP) =  -2380.25869196 A.U. after  1 cycles


 Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman
                1                      2                      3
                A                      A                      A
 Frequencies --   -45.9492                8.2534                11.2515


 Zero-point correction=                           0.656092 (a.u.)
 Thermal correction to Energy=                    0.705780
 Thermal correction to Enthalpy=                  0.706724
 Thermal correction to Gibbs Free Energy=         0.564119
 Sum of electronic and zero-point Energies=          -2379.602600
 Sum of electronic and thermal Energies=             -2379.552912
 Sum of electronic and thermal Enthalpies=           -2379.551968
 Sum of electronic and thermal Free Energies=        -2379.694573


                    E (Thermal)           CV                S
                     KCal/Mol        Cal/Mol-Kelvin   Cal/Mol-Kelvin
 Total                442.884           175.674           300.139


         Item               Value     Threshold  Converged?
 Maximum Force            0.000003     0.000450     YES
 RMS     Force            0.000001     0.000300     YES
 Maximum Displacement     0.001733     0.001800     YES
 RMS     Displacement     0.000270     0.001200     YES
 Predicted change in Energy=-7.072559D-09
 Optimization completed.

 ......................................................
  The single-point electronic energy of TS3 by
 wb97x-D/ 6-311+G(d,p) SCRF=(PCM,solvent=water)
 = -2380.243213 a.u..
 Then, the splicing ET + ZPE= -2380.243213 + 0.656092
  = -2379.587121 a.u.
 ......................................................


   =================Figure S2 in Scheme 4b============

    ----------Figure S2-1,  Int3-------------

  vita-b6forb.plp.high.log

  Stoichiometry    C20H41N5O13P(1-)


                   Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic           Coordinates (Angstroms)
 Number     Number     Type         X           Y           Z
 ---------------------------------------------------------------------
     1        6         0       -4.483017    0.234368   -0.714304
     2        6         0       -5.065599    0.929685   -1.829133
     3        7         0       -4.603337    2.133395   -2.134332
     4        6         0       -3.615949    2.792922   -1.480356
     5        6         0       -3.027648    2.208091   -0.392794
     6        6         0       -3.467648    0.925239    0.004792
     7        6         0       -6.153581    0.322199   -2.639907
     8        8         0       -4.888287   -0.935175   -0.415912
     9        6         0       -2.876573    0.308343    1.169864
    10        7         0       -0.792263   -0.327680   -0.172843
    11        6         0       -1.928801    2.944421    0.332607
    12        8         0       -1.643046    4.141114   -0.320706
    13       15         0       -0.316448    5.057173    0.261118
    14        8         0        0.892945    4.134478    0.093160
    15        8         0       -0.352202    6.256119   -0.681423
    16        8         0       -0.671873    5.360592    1.718387
    17        1         0       -3.336886    3.765249   -1.851347
    18        1         0       -6.666788    1.068975   -3.245723
    19        1         0       -5.742828   -0.438905   -3.308762
    20        1         0       -6.871088   -0.168898   -1.981861
    21        1         0       -2.160085    0.863538    1.761871
    22        1         0       -2.245698    3.132021    1.369112
    23        1         0       -1.039227    2.300362    0.377782
    24        1         0       -5.023744    2.606463   -2.927688
    25        6         0        0.571998   -0.273124    0.349593
    26        6         0        1.652789   -0.736117   -0.625038
```

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```
27          1          0        0.777921    0.756953    0.659747
28          1          0        0.619228   -0.878788    1.259553
29          7          0       -3.303687   -0.813363    1.662369
30          6          0       -2.837675   -1.362271    2.932823
31          1          0       -4.001715   -1.305493    1.086769
32          6          0       -1.441047   -1.965118    2.814760
33          8          0       -0.542007   -1.702789    3.567608
34          8          0       -1.336133   -2.835637    1.809457
35          1          0       -0.431269   -3.177119    1.784519
36          1          0       -2.748773   -0.542768    3.646383
37          6          0       -3.836376   -2.395031    3.446095
38          1          0       -4.804771   -1.918698    3.602808
39          1          0       -3.953697   -3.213619    2.733317
40          1          0       -3.492297   -2.804112    4.396250
41          1          0       -0.864560    0.258667   -0.999287
42          1          0       -2.269881   -4.670277    1.052870
43          8          0       -2.190729   -5.175274    0.239132
44          1          0       -1.735379   -3.750302   -0.922361
45          1          0       -3.109793   -5.352858   -0.041103
46          8          0       -1.697645   -2.984828   -1.520526
47          1          0       -1.037901   -1.272304   -0.476931
48          1          0       -2.608295   -2.914121   -1.843705
49          8          0       -4.732032   -5.429272   -0.789348
50          1          0       -5.499685   -5.457005   -0.215045
51          1          0       -4.776777   -4.573387   -1.258397
52          8          0       -4.522451   -3.005284   -2.066294
53          1          0       -4.778778   -2.228008   -1.521223
54          1          0       -4.935623   -2.898298   -2.925497
55          6          0        3.053105   -0.647761   -0.025233
56          1          0        1.442225   -1.768274   -0.929737
57          1          0        1.601249   -0.121766   -1.532330
58          6          0        4.135949   -1.097568   -1.002828
59          1          0        3.242535    0.383231    0.294224
60          1          0        3.103149   -1.266407    0.879144
61          6          0        5.538432   -1.009559   -0.416643
62          1          0        3.958922   -2.134998   -1.298802
63          1          0        4.087693   -0.504347   -1.922757
64          6          0        6.600928   -1.638954   -1.339173
65          7          0        5.887653    0.376615   -0.126319
66          1          0        5.568587   -1.546085    0.536413
67          8          0        6.380263   -1.913997   -2.513797
68          6          0        6.702872    0.741553    0.884142
69          1          0        5.476560    1.094323   -0.703013
70          8          0        7.274054   -0.089540    1.592389
71          6          0        6.878563    2.221441    1.104576
72          1          0        6.511709    2.467022    2.103090
73          1          0        7.943433    2.456816    1.071726
74          1          0        6.350762    2.832098    0.372141
75          7          0        7.785270   -1.852838   -0.742200
76          6          0        8.934669   -2.356071   -1.467742
77          1          0        7.895245   -1.525530    0.210423
78          1          0        9.757266   -2.488501   -0.767021
79          1          0        8.706194   -3.318529   -1.929921
80          1          0        9.244944   -1.661007   -2.252766
 ---------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

 1151 basis functions
  158 alpha electrons   158 beta electrons
     nuclear repulsion energy   5000.6277874191 Hartrees.
NAtoms= 80 NActive= 80

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
=================================
Model   : PCM.
Atomic radii   : UFF (Universal Force Field).

Solvent : Water, Eps= 78.355300 Eps(inf)= 1.777849

SCF Done: E(RwB97XD) = -2380.24952346 A.U. after 2 cycles

Zero-point correction=   0.659573 (a.u.)
Thermal correction to Energy=   0.710173
Thermal correction to Enthalpy=   0.711117
Thermal correction to Gibbs Free Energy=   0.566202
Sum of electronic and zero-point Energies=   -2379.589951

```
Sum of electronic and thermal Energies=          -2379.539351
Sum of electronic and thermal Enthalpies=        -2379.538406
Sum of electronic and thermal Free Energies=     -2379.683321

                   E (Thermal)         CV              S
                    KCal/Mol       Cal/Mol-Kelvin  Cal/Mol-Kelvin
Total               445.640          177.743          304.999

Maximum Force            0.000014    0.000450     YES
RMS     Force            0.000003    0.000300     YES
Maximum Displacement     0.004526    0.001800     NO
RMS     Displacement     0.000899    0.001200     YES

Normal termination of Gaussian 16 at Wed Jan 12 12:49:45 2022.

  ----------Figure S2-2, TS4-----------

  vita-b6ts4.high.log

Stoichiometry    C11H22N2O11P(1-)

                       Standard orientation:
-----------------------------------------------------------------
Center     Atomic     Atomic           Coordinates (Angstroms)
Number     Number     Type         X           Y           Z
-----------------------------------------------------------------
   1          6          0      -0.414940    2.064786   -0.637004
   2          6          0       0.225201    3.335063   -0.558903
   3          7          0       1.536464    3.374609   -0.331279
   4          6          0       2.333361    2.295435   -0.161550
   5          6          0       1.788728    1.039993   -0.222815
   6          6          0       0.403312    0.910223   -0.463936
   7          6          0      -0.540359    4.599336   -0.729305
   8          8          0      -1.677354    2.000660   -0.861303
   9          6          0      -0.185016   -0.411785   -0.518256
  10          6          0       2.681720   -0.161797   -0.029557
  11          8          0       3.991266    0.245528    0.223836
  12         15          0       5.147063   -0.983449    0.519150
  13          8          0       5.198428   -1.784465   -0.784149
  14          8          0       6.392792   -0.155406    0.820042
  15          8          0       4.580142   -1.762957    1.708213
  16          1          0       3.380962    2.473545    0.017999
  17          1          0       0.116629    5.468889   -0.753408
  18          1          0      -1.117456    4.558422   -1.654896
  19          1          0      -1.251831    4.720537    0.091127
  20          1          0       0.414615   -1.293776   -0.351829
  21          1          0       2.298013   -0.765228    0.805485
  22          1          0       2.635587   -0.789747   -0.931466
  23          1          0       1.976010    4.286726   -0.281618
  24          7          0      -1.452530   -0.562323   -0.757837
  25          6          0      -2.317860   -1.672746   -0.772308
  26          1          0      -1.911801    0.367795   -0.888921
  27          1          0      -2.736511   -1.727771    0.743648
  28          6          0      -1.811975   -3.017861   -0.935898
  29          8          0      -2.494599   -3.976705   -1.257625
  30          8          0      -0.502857   -3.176499   -0.626395
  31          1          0      -0.290951   -4.111947   -0.732191
  32          6          0      -3.652094   -1.363021   -1.420747
  33          1          0      -3.580911   -1.291041   -2.511697
  34          1          0      -4.372149   -2.145237   -1.181744
  35          1          0      -4.053787   -0.418196   -1.043345
  36          8          0      -3.113458   -1.666265    1.766723
  37          1          0      -3.765839   -0.784259    1.863362
  38          1          0      -2.368297   -1.609670    2.374674
  39          8          0      -4.593167    0.242765    1.949105
  40          1          0      -4.254048    1.079632    1.545924
  41          1          0      -5.468845    0.050596    1.550476
  42          8          0      -3.710565    2.500218    0.840620
  43          1          0      -3.496773    3.215860    1.442446
  44          1          0      -2.942287    2.405667    0.237551
  45          8          0      -6.992812   -0.315114    0.810565
  46          1          0      -6.977395   -0.953020    0.092728
  47          1          0      -7.709425   -0.591876    1.386872
-----------------------------------------------------------------

Standard basis: 6-311+G(d,p) (6D, 7F)

  715 basis functions
 103 alpha electrons     103 beta electrons
    nuclear repulsion energy    2561.3035828000 Hartrees.
```

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```
NAtoms=  47 NActive=  47

Force inversion solution in PCM.
------------------------------------------------
Polarizable Continuum Model (PCM)
=================================
Model            : PCM.
Atomic radii     : UFF (Universal Force Field).

Solvent : Water, Eps= 78.355300 Eps(inf)=  1.777849
-------------------------------------------------------

SCF Done:  E(RwB97XD) =  -1711.02987648 A.U. after  1 cycles
        NFock=  1 Conv=0.36D-08     -V/T= 2.0039

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman
                1                     2                     3
                A                     A                     A
Frequencies --  -741.2181             13.0739               26.4608

Zero-point correction=                           0.358533 (a.u.)
Thermal correction to Energy=                    0.389766
Thermal correction to Enthalpy=                  0.390710
Thermal correction to Gibbs Free Energy=         0.292561
Sum of electronic and zero-point Energies=          -1710.671344
Sum of electronic and thermal Energies=             -1710.640111
Sum of electronic and thermal Enthalpies=           -1710.639166
Sum of electronic and thermal Free Energies=        -1710.737316

                 E (Thermal)           CV                S
                  KCal/Mol        Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              244.582          109.999          206.573


        Item              Value     Threshold  Converged?
Maximum Force          0.000027     0.000450     YES
RMS     Force          0.000004     0.000300     YES
Maximum Displacement   0.002778     0.001800      NO
RMS     Displacement   0.000644     0.001200     YES
Predicted change in Energy=-2.073107D-08

Normal termination of Gaussian 16 at Tue Jan 11 17:32:30 2022.

   ------------Figure S2-3, Int4-----------

 vita-b6ts4.rev.high.log

 Stoichiometry   C11H22N2O11P(1-)

                  Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic          Coordinates (Angstroms)
Number     Number      Type         X           Y           Z
---------------------------------------------------------------------
    1         6         0        -0.517461    1.888467   -0.635218
    2         6         0         0.016689    3.188454   -0.536186
    3         7         0         1.326155    3.332271   -0.283337
    4         6         0         2.188782    2.311546   -0.109621
    5         6         0         1.738202    1.019366   -0.185325
    6         6         0         0.369801    0.782541   -0.448599
    7         6         0        -0.832392    4.403773   -0.691444
    8         8         0        -1.777455    1.718062   -0.896717
    9         6         0        -0.112755   -0.573457   -0.512543
   10         6         0         2.713534   -0.115002    0.013857
   11         8         0         3.996038    0.386419    0.245725
   12        15         0         5.267179   -0.741769    0.434187
   13         8         0         5.296644   -1.515821   -0.886482
   14         8         0         6.457341    0.185412    0.664290
   15         8         0         4.861564   -1.588006    1.644067
   16         1         0         3.220236    2.558567    0.084341
   17         1         0        -0.230575    5.289070   -0.900704
   18         1         0        -1.545353    4.256453   -1.503292
   19         1         0        -1.403162    4.589185    0.223221
   20         1         0         0.539780   -1.412276   -0.336355
   21         1         0         2.378732   -0.732991    0.860214
   22         1         0         2.702650   -0.758800   -0.877811
   23         1         0         1.693568    4.273445   -0.221296
   24         7         0        -1.384625   -0.805792   -0.772289
   25         6         0        -2.162230   -1.917051   -0.847489
   26         1         0        -1.879368    0.110065   -0.919326
   27         1         0        -2.722010   -1.629423    1.224379
```

```
28          6          0       -1.665987   -3.252199   -0.705642
29          8          0       -2.342254   -4.260950   -0.869099
30          8          0       -0.360931   -3.348364   -0.346022
31          1          0       -0.154918   -4.287790   -0.270149
32          6          0       -3.573863   -1.719939   -1.330295
33          1          0       -3.673494   -1.929732   -2.401131
34          1          0       -4.261504   -2.384114   -0.803707
35          1          0       -3.903030   -0.691637   -1.161061
36          8          0       -3.085852   -1.291361    2.059156
37          1          0       -4.094758   -0.096810    1.867717
38          1          0       -2.330816   -1.128754    2.631144
39          8          0       -4.773723    0.635931    1.740879
40          1          0       -4.386301    1.422648    1.173260
41          1          0       -5.604606    0.266277    1.317144
42          8          0       -3.896359    2.508123    0.364486
43          1          0       -3.782006    3.342940    0.823572
44          1          0       -3.043750    2.300993   -0.112027
45          8          0       -6.947490   -0.248091    0.645557
46          1          0       -6.873459   -0.904301   -0.052506
47          1          0       -7.638356   -0.561639    1.235263
 --------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

  715 basis functions
  103 alpha electrons   103 beta electrons
      nuclear repulsion energy   2556.5495731576 Hartrees.
NAtoms=   47 NActive=   47

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
 =================================
Model   : PCM.
Atomic radii   : UFF (Universal Force Field).

Solvent : Water, Eps= 78.355300 Eps(inf)=   1.777849

SCF Done: E(RwB97XD) = -1711.03939183 A.U. after 1 cycles
          NFock= 1 Conv=0.45D-08   -V/T= 2.0039

Zero-point correction=   0.362499 (a.u.)
Thermal correction to Energy=   0.394177
Thermal correction to Enthalpy=   0.395121
Thermal correction to Gibbs Free Energy=   0.296915
Sum of electronic and zero-point Energies=   -1710.676893
Sum of electronic and thermal Energies=   -1710.645215
Sum of electronic and thermal Enthalpies=   -1710.644270
Sum of electronic and thermal Free Energies=   -1710.742477

                E (Thermal)   CV   S
                 KCal/Mol   Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total   247.350   112.008   206.694

        Item   Value   Threshold Converged?
Maximum Force   0.000039   0.000450   YES
RMS   Force   0.000008   0.000300   YES
Maximum Displacement 0.006359   0.001800   NO
RMS   Displacement 0.001174   0.001200   YES

Normal termination of Gaussian 16 at Tue Jan 11 16:55:44 2022.

  -----------Figure S2-4, TS5--------------

  vita-b6ts4c.plp.high.log

 Stoichiometry   C20H41N5O13P(1-)

                  Standard orientation:

 Center   Atomic   Atomic   Coordinates (Angstroms)
 Number   Number   Type   X   Y   Z
 ----
     1   6   0   6.150888   -1.434645   -0.540834
     2   6   0   7.426276   -0.881969   -0.943343
     3   7   0   7.683707   0.383673   -0.663276
     4   6   0   6.856912   1.241505   -0.006880
     5   6   0   5.639927   0.797986   0.424909
     6   6   0   5.276660   -0.546130   0.167826
```

```
   7          6          0       8.419233    -1.710820    -1.673104
   8          8          0       5.868341    -2.626655    -0.828870
   9          6          0       3.981318    -1.011422     0.562145
  10          6          0       4.743785     1.756599     1.185606
  11          8          0       5.151541     3.086521     1.038375
  12         15          0       4.281036     4.044782    -0.073920
  13          8          0       2.941570     4.328210     0.600354
  14          8          0       5.202252     5.241397    -0.251042
  15          8          0       4.148303     3.146962    -1.320669
  16          1          0       7.201703     2.253798     0.124651
  17          1          0       9.333851    -1.157018    -1.885477
  18          1          0       8.663243    -2.596248    -1.081946
  19          1          0       7.985170    -2.062345    -2.612108
  20          1          0       3.294322    -0.349991     1.075889
  21          1          0       3.707811     1.628549     0.856963
  22          1          0       4.785618     1.489924     2.248633
  23          1          0       8.577988     0.754525    -0.966707
  24          7          0       3.543123    -2.204662     0.322399
  25          6          0       2.199252    -2.633920     0.658695
  26          1          0       4.204731    -2.814139    -0.181256
  27          1          0       1.501048    -1.536330     0.511333
  28          6          0       2.018172    -3.004092     2.062378
  29          8          0       1.041175    -3.600468     2.498330
  30          8          0       2.968628    -2.555853     2.894713
  31          1          0       2.696754    -2.769989     3.795740
  32          6          0       1.675766    -3.631364    -0.358552
  33          1          0       2.287566    -4.538552    -0.412875
  34          1          0       0.657728    -3.926697    -0.105738
  35          1          0       1.650951    -3.169438    -1.348272
  36          8          0       0.882949    -0.415380     0.249238
  37          1          0      -0.442670    -0.941855    -0.247321
  38          1          0       1.420603     0.091084    -0.377749
  39          7          0      -1.410691    -1.395248    -0.473782
  40          6          0      -2.508680    -0.427291    -0.261473
  41          1          0      -1.412498    -1.731042    -1.445972
  42          1          0      -1.514781    -2.208464     0.153731
  43          1          0      -2.430654    -0.060902     0.764216
  44          1          0      -2.337203     0.417872    -0.931395
  45          6          0      -3.873721    -1.049001    -0.512789
  46          8          0       2.706812     0.975670    -1.577157
  47          1          0       3.270000     0.370914    -2.062700
  48          1          0       3.250265     1.808331    -1.459099
  49          8          0      -1.517123    -2.215754    -3.258183
  50          1          0      -2.209689    -2.824798    -3.525173
  51          1          0      -1.542089    -1.504911    -3.903154
  52          8          0      -1.492827    -3.588806     1.387492
  53          1          0      -0.615979    -3.636233     1.812859
  54          1          0      -2.129622    -3.543019     2.103476
  55          6          0      -5.000754    -0.037615    -0.324757
  56          1          0      -3.904631    -1.452004    -1.531306
  57          1          0      -4.017614    -1.894331     0.169789
  58          6          0      -6.376469    -0.659759    -0.550515
  59          1          0      -4.942226     0.386236     0.683577
  60          1          0      -4.861399     0.796880    -1.021969
  61          6          0      -7.509884     0.347401    -0.413469
  62          1          0      -6.428080    -1.087974    -1.555073
  63          1          0      -6.538387    -1.489926     0.145669
  64          6          0      -8.873919    -0.249801    -0.811933
  65          7          0      -7.571321     0.873844     0.945203
  66          1          0      -7.318357     1.201213    -1.070172
  67          8          0      -9.057588    -1.455645    -0.939108
  68          6          0      -7.986779     2.123741     1.237202
  69          1          0      -7.277301     0.270034     1.697254
  70          8          0      -8.413704     2.886451     0.369001
  71          6          0      -7.903017     2.540114     2.682493
  72          1          0      -7.262844     3.421550     2.750627
  73          1          0      -8.900212     2.823613     3.023312
  74          1          0      -7.507579     1.760837     3.333813
  75          7          0      -9.836937     0.667234    -1.001230
  76          6          0     -11.206643     0.297638    -1.297881
  77          1          0      -9.608477     1.634056    -0.802128
  78          1          0     -11.784733     1.206222    -1.457402
  79          1          0     -11.252452    -0.313276    -2.201626
  80          1          0     -11.653130    -0.267918    -0.475451
 ---------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

 1151 basis functions
  158 alpha electrons   158 beta electrons

```
      nuclear repulsion energy      4766.4775565358 Hartrees.
NAtoms=  80 NActive=  80

Force inversion solution in PCM.
--------------------------------------------------
Polarizable Continuum Model (PCM)
=================================
Model               : PCM.
Atomic radii        : UFF (Universal Force Field).

Solvent : Water, Eps=  78.355300 Eps(inf)=   1.777849
--------------------------------------------------------

SCF Done:  E(RwB97XD) =  -2380.23042567  A.U. after  2 cycles
          NFock=  2 Conv=0.81D-09    -V/T= 2.0043
DoSCS=F DFT=T ScalE2(SS,OS)=  1.000000  1.000000
Range of M.O.s used for correlation:     1  1148

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman
                 1                      2                      3
                 A                      A                      A
Frequencies --  -1154.0598            10.2205                11.1655

Zero-point correction=                           0.653172 (a.u.)
Thermal correction to Energy=                    0.703808
Thermal correction to Enthalpy=                  0.704752
Thermal correction to Gibbs Free Energy=         0.558664
Sum of electronic and zero-point Energies=          -2379.577254
Sum of electronic and thermal Energies=             -2379.526618
Sum of electronic and thermal Enthalpies=           -2379.525673
Sum of electronic and thermal Free Energies=        -2379.671762

                  E (Thermal)          CV               S
                   KCal/Mol        Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total               441.646          176.140          307.468
Electronic            0.000            0.000            0.000

        Item              Value     Threshold  Converged?
Maximum Force            0.000003   0.000450     YES
RMS     Force            0.000001   0.000300     YES
Maximum Displacement     0.003725   0.001800     NO
RMS     Displacement     0.000268   0.001200     YES

Normal termination of Gaussian 16 at Mon Jan 10 04:45:10 2022.

   ------------Figure S2-5, Int5-------------

 vita-b6rev4b.plp.high.log

 Stoichiometry    C20H41N5O13P(1-)

                  Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic            Coordinates (Angstroms)
Number     Number     Type         X           Y           Z
---------------------------------------------------------------------
    1         6          0       4.402119    1.015646    0.546944
    2         6          0       5.170915    2.069075    0.006629
    3         7          0       4.545828    3.174215   -0.421498
    4         6          0       3.211332    3.366132   -0.378967
    5         6          0       2.401102    2.388483    0.136349
    6         6          0       2.984283    1.194257    0.616472
    7         6          0       6.652955    1.971033   -0.108415
    8         8          0       4.983898   -0.064443    0.958624
    9         6          0       2.136115    0.156148    1.143004
   10         6          0       0.907310    2.599870    0.160142
   11         8          0       0.584205    3.832846   -0.409596
   12        15          0      -1.074092    4.193311   -0.613091
   13         8          0      -1.644957    4.201069    0.808303
   14         8          0      -1.005384    5.560480   -1.288003
   15         8          0      -1.609787    3.062581   -1.495079
   16         1          0       2.829789    4.297397   -0.765882
   17         1          0       7.095136    2.915738   -0.426401
   18         1          0       7.082520    1.680397    0.852015
   19         1          0       6.925261    1.199432   -0.833229
   20         1          0       1.071323    0.293070    1.238704
   21         1          0       0.421288    1.781019   -0.390678
   22         1          0       0.549917    2.544825    1.199437
   23         1          0       5.114733    3.918143   -0.806008
   24         7          0       2.663246   -1.002045    1.489751
```

S32

```
   25         6       0      2.169179  -2.188175   1.922666
   26         1       0      3.706876  -0.957254   1.361920
   27         1       0      3.572177  -0.745156  -2.085662
   28         6       0      0.798592  -2.416314   2.194904
   29         8       0      0.307913  -3.521032   2.470346
   30         8       0     -0.006266  -1.327815   2.141436
   31         1       0     -0.898269  -1.627521   2.353326
   32         6       0      3.166345  -3.301045   2.081197
   33         1       0      2.812945  -4.023354   2.817157
   34         1       0      3.342343  -3.842323   1.145402
   35         1       0      4.127200  -2.911446   2.428066
   36         8       0      3.733481  -1.691218  -2.071290
   37         1       0      2.325962  -2.716981  -1.737489
   38         1       0      4.592969  -1.805261  -1.613780
   39         7       0      1.367575  -3.098062  -1.623480
   40         6       0      0.427237  -1.984094  -1.333040
   41         1       0      1.091518  -3.564754  -2.503403
   42         1       0      1.349369  -3.810514  -0.870338
   43         1       0      0.835176  -1.417781  -0.495298
   44         1       0      0.420744  -1.329824  -2.206310
   45         6       0     -0.967243  -2.497266  -1.021170
   46         8       0      6.055117  -1.887868  -0.651955
   47         1       0      6.888682  -1.644910  -1.059240
   48         1       0      5.824040  -1.163103  -0.028398
   49         8       0      0.337589  -4.131833  -4.058696
   50         1       0      0.845145  -4.072952  -4.871732
   51         1       0     -0.087180  -4.992697  -4.081709
   52         8       0      1.047307  -5.120782   0.363537
   53         1       0      0.767060  -4.706231   1.202985
   54         1       0      0.337204  -5.717523   0.116765
   55         6       0     -1.958834  -1.353607  -0.824598
   56         1       0     -1.306407  -3.141929  -1.839399
   57         1       0     -0.932883  -3.118789  -0.119464
   58         6       0     -3.344537  -1.874553  -0.451658
   59         1       0     -1.585556  -0.674038  -0.051185
   60         1       0     -2.026025  -0.766442  -1.747517
   61         6       0     -4.382263  -0.770915  -0.302293
   62         1       0     -3.696145  -2.562983  -1.224628
   63         1       0     -3.294881  -2.456784   0.475338
   64         6       0     -5.808048  -1.335523  -0.138861
   65         7       0     -4.053775   0.099002   0.819764
   66         1       0     -4.376633  -0.141993  -1.197583
   67         8       0     -6.029082  -2.515238   0.115924
   68         6       0     -4.376243   1.410847   0.866090
   69         1       0     -3.569857  -0.307349   1.604866
   70         8       0     -5.049629   1.939761  -0.021821
   71         6       0     -3.847696   2.190991   2.034376
   72         1       0     -3.071366   2.872168   1.656105
   73         1       0     -4.657090   2.790535   2.453969
   74         1       0     -3.425618   1.554234   2.813283
   75         7       0     -6.778501  -0.420822  -0.296894
   76         6       0     -8.177942  -0.738241  -0.094714
   77         1       0     -6.492585   0.543782  -0.424822
   78         1       0     -8.772162   0.141641  -0.335591
   79         1       0     -8.483563  -1.559358  -0.746180
   80         1       0     -8.375716  -1.027366   0.941272
 ---------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

 1151 basis functions
  158 alpha electrons   158 beta electrons
     nuclear repulsion energy   5250.8476205590 Hartrees.
NAtoms= 80 NActive= 80

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
================================
Model   : PCM.
Atomic radii   : UFF (Universal Force Field).

Solvent : Water, Eps= 78.355300 Eps(inf)= 1.777849

SCF Done: E(RwB97XD) = -2380.25564482 A.U. after 2 cycles
        NFock= 2 Conv=0.47D-09   -V/T= 2.0043

Zero-point correction=   0.659469 (a.u.)

```
Thermal correction to Energy=                      0.710227
Thermal correction to Enthalpy=                    0.711171
Thermal correction to Gibbs Free Energy=           0.569522
Sum of electronic and zero-point Energies=          -2379.596176
Sum of electronic and thermal Energies=             -2379.545418
Sum of electronic and thermal Enthalpies=           -2379.544474
Sum of electronic and thermal Free Energies=        -2379.686123

                 E (Thermal)            CV                 S
                  KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              445.674           178.605           298.126


        Item              Value     Threshold  Converged?
Maximum Force            0.000026    0.000450     YES
RMS     Force            0.000003    0.000300     YES
Maximum Displacement     0.005157    0.001800     NO
RMS     Displacement     0.000772    0.001200     YES


Normal termination of Gaussian 16 at Sat Jan 15 02:04:17 2022.

 ------------Figure S2-6, TS6-----------------------

 vita-b6ts5h.high.log

  Stoichiometry    C11H22N2O11P(1-)

                     Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic            Coordinates (Angstroms)
Number     Number      Type          X           Y           Z
---------------------------------------------------------------------
    1         6          0       -2.905372   -1.015889    0.047844
    2         6          0       -4.210144   -0.400519   -0.069250
    3         7          0       -4.295714    0.839168   -0.520095
    4         6          0       -3.244442    1.613999   -0.901900
    5         6          0       -1.979545    1.106069   -0.828687
    6         6          0       -1.787835   -0.212264   -0.348808
    7         6          0       -5.434894   -1.147304    0.311095
    8         8          0       -2.817653   -2.196075    0.478051
    9         6          0       -0.458943   -0.759332   -0.263039
   10         6          0       -0.832132    1.974482   -1.276466
   11         8          0       -0.019997    2.302280   -0.151313
   12        15          0        1.620829    2.494137   -0.427662
   13         8          0        2.085619    2.837492    1.058025
   14         8          0        2.110647    1.137085   -0.882853
   15         8          0        1.833170    3.682237   -1.311016
   16         1          0       -3.484169    2.606657   -1.250467
   17         1          0       -6.337556   -0.558189    0.150988
   18         1          0       -5.495264   -2.069036   -0.271882
   19         1          0       -5.373979   -1.437679    1.362485
   20         1          0        0.413777   -0.157791   -0.515826
   21         1          0       -0.239126    1.446037   -2.029716
   22         1          0       -1.214813    2.891579   -1.729212
   23         1          0       -5.220783    1.249521   -0.589855
   24         7          0       -0.246662   -1.983506    0.098375
   25         6          0        1.051594   -2.608036    0.200582
   26         1          0       -1.103233   -2.501784    0.355373
   27         6          0        1.821262   -2.630970   -1.060037
   28         8          0        2.930940   -3.127127   -1.150891
   29         8          0        1.254517   -2.003016   -2.100354
   30         1          0        1.887539   -2.005631   -2.829159
   31         6          0        0.947700   -3.968554    0.875054
   32         1          0        1.941307   -4.409230    0.950290
   33         1          0        0.555519   -3.853261    1.887990
   34         1          0        0.302151   -4.662299    0.325386
   35         1          0        1.764204   -1.905619    1.003678
   36         8          0        2.507786   -1.257984    1.919852
   37         1          0        1.936180    0.074797    2.480811
   38         1          0        3.259583   -0.985457    1.380299
   39         8          0        1.643239    0.985744    2.825928
   40         1          0        1.966448    2.093124    1.724460
   41         1          0        0.674462    1.004072    2.841628
   42         8          0        4.289387   -0.428152   -0.437369
   43         1          0        4.069054   -1.295008   -0.792547
   44         1          0        3.507042    0.136045   -0.615866
   45         8          0       -1.069301    1.666117    2.380270
   46         1          0       -1.339920    2.445509    2.869764
   47         1          0       -0.774544    1.993057    1.513383
---------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

   715 basis functions
   103 alpha electrons   103 beta electrons
       nuclear repulsion energy   2813.2215890403 Hartrees.
NAtoms=   47 NActive=   47

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
=================================
Model   : PCM.

Solvent   : Water, Eps= 78.355300 Eps(inf)= 1.777849

SCF Done: E(RwB97XD) = -1711.07475349   A.U. after 1 cycles
         NFock= 1 Conv=0.22D-08   -V/T= 2.0039

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman
                   1   2   3
                   A   A   A
Frequencies -- -1006.6264   31.1109   42.4377

Zero-point correction=   0.360938 (a.u.)
Thermal correction to Energy=   0.390763
Thermal correction to Enthalpy=   0.391707
Thermal correction to Gibbs Free Energy=   0.301093
Sum of electronic and zero-point Energies=   -1710.713815
Sum of electronic and thermal Energies=   -1710.683991
Sum of electronic and thermal Enthalpies=   -1710.683047
Sum of electronic and thermal Free Energies=   -1710.773661

                  E (Thermal)   CV   S
                   KCal/Mol   Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total   245.207   108.946   190.713

       Item   Value   Threshold Converged?
Maximum Force   0.000014   0.000450   YES
RMS   Force   0.000002   0.000300   YES
Maximum Displacement   0.000513   0.001800   YES
RMS   Displacement   0.000127   0.001200   YES
Predicted change in Energy=-1.018149D-08

Normal termination of Gaussian 16 at Wed Dec 29 02:06:17 2021.

    ----------Figure S2-7, Int6--------------------

 vita-b6rev5h.high.log

 Stoichiometry   C11H22N2O11P(1-)

                     Standard orientation:

Center   Atomic   Atomic   Coordinates (Angstroms)
Number   Number   Type   X   Y   Z
----
     1   6   0   -3.263830   -0.762140   -0.049605
     2   6   0   -4.422573   0.028438   0.119079
     3   7   0   -4.352621   1.359507   -0.068848
     4   6   0   -3.229668   2.019261   -0.412708
     5   6   0   -2.065859   1.321588   -0.611857
     6   6   0   -2.057749   -0.084115   -0.450630
     7   6   0   -5.722064   -0.581120   0.517477
     8   8   0   -3.305342   -2.029342   0.149150
     9   6   0   -0.842147   -0.807498   -0.649253
    10   6   0   -0.824357   2.081971   -0.987473
    11   8   0   0.108717   2.033957   0.099149
    12   15   0   1.609127   2.710280   -0.155593
    13   8   0   2.211323   2.565133   1.321034
    14   8   0   2.341495   1.826468   -1.138634
    15   8   0   1.436676   4.160731   -0.476563
    16   1   0   -3.311607   3.091345   -0.515853
    17   1   0   -6.524053   0.157910   0.545095
    18   1   0   -5.994031   -1.373679   -0.183215
    19   1   0   -5.634817   -1.041994   1.504803
    20   1   0   0.067055   -0.306401   -0.931899
    21   1   0   -0.363629   1.650760   -1.883094
    22   1   0   -1.074110   3.123821   -1.202250
    23   1   0   -5.197321   1.900631   0.063879

```
   24      7       0      -0.798817   -2.108135   -0.388132
   25      6       0       0.189568   -3.022828   -0.360588
   26      1       0      -1.761716   -2.431143   -0.103784
   27      6       0       1.546721   -2.706732   -0.680987
   28      8       0       2.502884   -3.450081   -0.427020
   29      8       0       1.721970   -1.527065   -1.287369
   30      1       0       2.670205   -1.281880   -1.366612
   31      6       0      -0.144850   -4.390095    0.158559
   32      1       0       0.206417   -4.534413    1.186496
   33      1       0      -1.225039   -4.552220    0.149931
   34      1       0       0.316444   -5.167709   -0.454248
   35      1       0       3.738699   -2.449037    0.631286
   36      8       0       4.222321   -1.699992    1.016875
   37      1       0       3.106585   -0.580715    1.893881
   38      1       0       4.387909   -1.124097    0.251019
   39      8       0       2.623788    0.145979    2.333394
   40      1       0       2.447352    1.645642    1.604494
   41      1       0       1.681841   -0.091863    2.377189
   42      8       0       4.025838   -0.156683   -1.274583
   43      1       0       4.632227   -0.012538   -2.003167
   44      1       0       3.448224    0.651539   -1.201642
   45      8       0      -0.145795    0.265436    2.310320
   46      1       0      -0.455800    0.779557    3.058749
   47      1       0      -0.167824    0.875983    1.553581
 ---------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

  715 basis functions
  103 alpha electrons   103 beta electrons
     nuclear repulsion energy   2770.0600367239 Hartrees.
NAtoms= 47 NActive= 47

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
=================================
Model   : PCM.
Atomic radii   : UFF (Universal Force Field).

Solvent: Water, Eps= 78.355300 Eps(inf)= 1.777849

SCF Done: E(RwB97XD) = -1711.10773553 A.U. after 1 cycles
        NFock= 1 Conv=0.23D-08   -V/T= 2.0039

Zero-point correction=   0.365737 (a.u.)
Thermal correction to Energy=   0.396265
Thermal correction to Enthalpy=   0.397209
Thermal correction to Gibbs Free Energy=   0.304588
Sum of electronic and zero-point Energies=   -1710.741998
Sum of electronic and thermal Energies=   -1710.711470
Sum of electronic and thermal Enthalpies=   -1710.710526
Sum of electronic and thermal Free Energies=   -1710.803148

                E (Thermal)   CV   S
                 KCal/Mol   Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total   248.660   111.001   194.938

        Item   Value   Threshold Converged?
Maximum Force   0.000030   0.000450   YES
RMS   Force   0.000005   0.000300   YES
Maximum Displacement   0.002715   0.001800   NO
RMS   Displacement   0.000496   0.001200   YES

Normal termination of Gaussian 16 at Tue Jan 11 19:35:21 2022.

   -------------Figure S2-8, TS7-------------------

  vita-b6h26miga.high.log

 Stoichiometry   C11H22N2O11P(1-)

              Standard orientation:

 Center   Atomic   Atomic   Coordinates (Angstroms)
 Number   Number   Type   X   Y   Z
 ----
    1   6   0   3.211485   0.674295   -0.057938
    2   6   0   4.360970   -0.080008   0.137722
```

```
   3        7        0      4.303932   -1.424716   -0.042144
   4        6        0      3.183731   -2.082354   -0.395548
   5        6        0      2.019087   -1.397622   -0.617012
   6        6        0      2.001397    0.014901   -0.469157
   7        6        0      5.652757    0.538297    0.555285
   8        8        0      3.222761    1.974054    0.127427
   9        6        0      0.820345    0.765136   -0.682586
  10        6        0      0.780838   -2.155376   -0.997518
  11        8        0     -0.157553   -2.101841    0.086338
  12       15        0     -1.693487   -2.669945   -0.203263
  13        8        0     -2.293605   -2.562149    1.278157
  14        8        0     -2.366914   -1.693537   -1.140559
  15        8        0     -1.611725   -4.110538   -0.597776
  16        1        0      3.266841   -3.155924   -0.490327
  17        1        0      6.465828   -0.189028    0.550537
  18        1        0      5.911710    1.359260   -0.116332
  19        1        0      5.566732    0.956876    1.561491
  20        1        0     -0.105722    0.292734   -0.966966
  21        1        0      0.325155   -1.720402   -1.894026
  22        1        0      1.025128   -3.199041   -1.210054
  23        1        0      5.147995   -1.960650    0.104881
  24        7        0      0.869398    2.076376   -0.413054
  25        6        0     -0.056870    3.021099   -0.379831
  26        1        0      2.032458    2.273363   -0.101658
  27        6        0     -1.454522    2.778581   -0.677383
  28        8        0     -2.360773    3.542477   -0.341466
  29        8        0     -1.692791    1.651304   -1.344830
  30        1        0     -2.650031    1.427179   -1.384096
  31        6        0      0.332037    4.384009    0.116719
  32        1        0     -0.077146    4.580403    1.113534
  33        1        0      1.418357    4.469886    0.174311
  34        1        0     -0.039090    5.171168   -0.544728
  35        1        0     -3.603538    2.537970    0.764407
  36        8        0     -4.090660    1.782601    1.128109
  37        1        0     -3.011455    0.598140    1.968291
  38        1        0     -4.283132    1.241683    0.342573
  39        8        0     -2.563013   -0.162160    2.386188
  40        1        0     -2.473563   -1.643968    1.603420
  41        1        0     -1.609939    0.027372    2.428161
  42        8        0     -4.006883    0.325214   -1.220553
  43        1        0     -4.660241    0.188759   -1.908920
  44        1        0     -3.446824   -0.497732   -1.169283
  45        8        0      0.199221   -0.405631    2.339560
  46        1        0      0.471859   -0.979945    3.058291
  47        1        0      0.185553   -0.974661    1.550546
 ------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

  715 basis functions
  103 alpha electrons   103 beta electrons
     nuclear repulsion energy   2772.8251991583 Hartrees.
NAtoms= 47 NActive= 47

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
=================================
Model   : PCM.
Atomic radii   : UFF (Universal Force Field).

Solvent : Water, Eps= 78.355300 Eps(inf)=   1.777849

SCF Done: E(RwB97XD) = -1711.10507713 A.U. after 1 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman
               1   2   3
               A   A   A
Frequencies -- -1076.4290   27.5005   40.9218

Zero-point correction=   0.360875 (a.u.)
Thermal correction to Energy=   0.391282
Thermal correction to Enthalpy=   0.392226
Thermal correction to Gibbs Free Energy=   0.299673
Sum of electronic and zero-point Energies=   -1710.744202
Sum of electronic and thermal Energies=   -1710.713795
Sum of electronic and thermal Enthalpies=   -1710.712851
Sum of electronic and thermal Free Energies=   -1710.805404

```
              E (Thermal)          CV              S
               KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total            245.533          110.465         194.795


        Item             Value    Threshold  Converged?
Maximum Force          0.000025    0.000450      YES
RMS     Force          0.000005    0.000300      YES
Maximum Displacement   0.014528    0.001800      NO
RMS     Displacement   0.001712    0.001200      NO


Normal termination of Gaussian 16 at Wed Jan 12 18:29:19 2022.

  ============== Figure S3 in Scheme 4c ================

  --------------Figure S3-1, Int7----------------------

  vita-b6h26miga.for.high.log

 Stoichiometry   C11H22N2O11P(1-)

                    Standard orientation:
---------------------------------------------------------------------
Center   Atomic    Atomic          Coordinates (Angstroms)
Number   Number    Type        X           Y           Z
---------------------------------------------------------------------
   1        6        0      3.321209    0.592204   -0.034313
   2        6        0      4.399985   -0.224756    0.168273
   3        7        0      4.252751   -1.570939   -0.019147
   4        6        0      3.079448   -2.124797   -0.389066
   5        6        0      1.971963   -1.360686   -0.602727
   6        6        0      2.037958    0.067217   -0.430521
   7        6        0      5.743120    0.293717    0.568816
   8        8        0      3.493469    1.918944    0.145214
   9        6        0      0.910301    0.864355   -0.623840
  10        6        0      0.702164   -2.036513   -1.024582
  11        8        0     -0.248071   -2.006213    0.052899
  12       15        0     -1.750499   -2.652263   -0.238845
  13        8        0     -2.357786   -2.584065    1.241931
  14        8        0     -2.479225   -1.715494   -1.175951
  15        8        0     -1.595278   -4.085432   -0.639119
  16        1        0      3.076989   -3.200333   -0.503799
  17        1        0      6.387367   -0.511062    0.926330
  18        1        0      6.236792    0.778700   -0.277819
  19        1        0      5.640648    1.037568    1.359836
  20        1        0     -0.027361    0.396481   -0.884605
  21        1        0      0.270384   -1.535758   -1.898395
  22        1        0      0.902256   -3.077318   -1.291042
  23        1        0      5.050850   -2.169178    0.130350
  24        7        0      0.977169    2.197998   -0.381389
  25        6        0      0.021648    3.080072   -0.369858
  26        1        0      2.596650    2.329651    0.000544
  27        6        0     -1.403439    2.790040   -0.631761
  28        8        0     -2.308770    3.487926   -0.189058
  29        8        0     -1.628046    1.721066   -1.380278
  30        1        0     -2.582735    1.467640   -1.408271
  31        6        0      0.336869    4.489111    0.051385
  32        1        0     -0.110251    4.722093    1.023163
  33        1        0      1.417249    4.615164    0.127969
  34        1        0     -0.052326    5.220198   -0.663260
  35        1        0     -3.628973    2.490669    0.813598
  36        8        0     -4.162432    1.740081    1.115577
  37        1        0     -3.144573    0.535101    1.983184
  38        1        0     -4.310105    1.235712    0.296446
  39        8        0     -2.698402   -0.223320    2.408072
  40        1        0     -2.565643   -1.678455    1.585673
  41        1        0     -1.748209   -0.022440    2.466693
  42        8        0     -3.946787    0.416682   -1.297418
  43        1        0     -4.574844    0.330316   -2.017007
  44        1        0     -3.442279   -0.442551   -1.232534
  45        8        0      0.069467   -0.393635    2.363997
  46        1        0      0.351123   -1.003877    3.048829
  47        1        0      0.072569   -0.915880    1.542783
---------------------------------------------------------------------

Standard basis: 6-311+G(d,p) (6D, 7F)

  715 basis functions
  103 alpha electrons     103 beta electrons
     nuclear repulsion energy    2756.2783999044 Hartrees.
NAtoms=  47 NActive=  47
```

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
================================
Model   : PCM.
Atomic radii   : UFF (Universal Force Field).

Solvent : Water, Eps= 78.355300 Eps(inf)= 1.777849

SCF Done: E(RwB97XD) = -1711.11121947 A.U. after 1 cycles
        NFock= 1 Conv=0.46D-08   -V/T= 2.0038

Zero-point correction=   0.364755 (a.u.)
Thermal correction to Energy=   0.395569
Thermal correction to Enthalpy=   0.396513
Thermal correction to Gibbs Free Energy=   0.302142
Sum of electronic and zero-point Energies=   -1710.746465
Sum of electronic and thermal Energies=   -1710.715651
Sum of electronic and thermal Enthalpies=   -1710.714706
Sum of electronic and thermal Free Energies=   -1710.809077

                E (Thermal)   CV   S
                 KCal/Mol   Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total   248.223   111.725   198.620

        Item   Value   Threshold Converged?
Maximum Force   0.000006   0.000450   YES
RMS   Force   0.000001   0.000300   YES
Maximum Displacement   0.001077   0.001800   YES
RMS   Displacement   0.000156   0.001200   YES

Normal termination of Gaussian 16 at Wed Jan 12 04:55:02 2022.

   ---------Figure S3-2, TS8 -----------------

 vita-b6ts5jy.high.log

 Stoichiometry   C11H22N2O11P(1-)

               Standard orientation:

Center   Atomic   Atomic   Coordinates (Angstroms)
Number   Number   Type   X   Y   Z
----
   1   6   0   2.686303   -1.477387   0.066554
   2   6   0   2.999183   -2.812891   -0.134220
   3   7   0   2.096014   -3.593192   -0.759319
   4   6   0   0.903007   -3.142147   -1.182729
   5   6   0   0.551360   -1.828815   -1.012888
   6   6   0   1.459044   -0.933266   -0.393763
   7   6   0   4.292633   -3.402253   0.316549
   8   8   0   3.606182   -0.740893   0.710253
   9   6   0   1.105631   0.471978   -0.215256
  10   6   0   -0.847018   -1.420470   -1.395075
  11   8   0   -1.588353   -1.351419   -0.197858
  12   15   0   -3.269131   -1.305645   -0.235199
  13   8   0   -3.631263   0.132344   -0.646403
  14   8   0   -3.720115   -2.364017   -1.226874
  15   8   0   -3.578106   -1.603912   1.240473
  16   1   0   0.253229   -3.869055   -1.648983
  17   1   0   4.384341   -4.444639   0.011502
  18   1   0   5.126964   -2.836029   -0.101705
  19   1   0   4.371863   -3.345750   1.404452
  20   1   0   0.397531   0.861086   -0.943150
  21   1   0   -0.853244   -0.457445   -1.920449
  22   1   0   -1.277860   -2.167099   -2.070161
  23   1   0   2.325498   -4.567016   -0.910150
  24   7   0   2.159204   1.307832   0.157327
  25   6   0   2.253717   2.584545   0.083292
  26   1   0   3.277566   0.200162   0.670475
  27   6   0   1.206100   3.438527   -0.541831
  28   8   0   1.557147   4.725258   -0.576296
  29   8   0   0.145033   3.041144   -0.982944
  30   1   0   0.850872   5.232567   -0.996937
  31   6   0   3.477993   3.266062   0.630899
  32   1   0   3.212608   3.982398   1.412769
  33   1   0   4.151570   2.520021   1.051085
  34   1   0   4.003977   3.819800   -0.150711

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```
35        1        0       -3.071823    1.271467    0.333869
36        8        0       -2.674596    1.962131    0.945195
37        1        0       -1.297846    1.331449    1.447608
38        1        0       -2.618809    2.774465    0.415749
39        8        0       -0.492979    0.847258    1.815937
40        1        0        0.237885    0.573284    0.893578
41        1        0       -0.857849    0.014321    2.231589
42        8        0       -2.372159    4.192491   -0.771646
43        1        0       -1.494038    3.884990   -1.047922
44        1        0       -2.921732    4.150468   -1.557035
45        8        0       -1.632345   -1.256298    2.919295
46        1        0       -2.028789   -1.061360    3.770517
47        1        0       -2.396740   -1.421885    2.283689
 ----------------------------------------------------------------

Standard basis: 6-311+G(d,p)  (6D, 7F)

  715 basis functions
  103 alpha electrons      103 beta electrons
      nuclear repulsion energy    2736.7900942579 Hartrees.
NAtoms=   47 NActive=   47

Force inversion solution in PCM.
 --------------------------------------------------------
Polarizable Continuum Model (PCM)
 ===============================
Model          : PCM.

Solvent : Water, Eps= 78.355300 Eps(inf)=  1.777849
 --------------------------------------------------------

SCF Done:  E(RwB97XD) =  -1711.06384110 A.U. after   1 cycles
         NFock=  1 Conv=0.19D-08     -V/T= 2.0039

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering
                   1                2                3
                   A                A                A
Frequencies --  -1394.2219         -14.3640           27.0951


                E (Thermal)          CV              S
                 KCal/Mol        Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total            244.076            105.697          188.234


       Item              Value     Threshold  Converged?
Maximum Force           0.000004    0.000450      YES
RMS     Force           0.000001    0.000300      YES
Maximum Displacement    0.003486    0.001800      NO
RMS     Displacement    0.000793    0.001200      YES

Normal termination of Gaussian 16 at Thu Nov 11 21:16:02 2021.

  ----------Figure S3-3,  Int8 --------------------

  vita-b6for5j.high.log

Stoichiometry    C11H22N2O11P(1-)

                  Standard orientation:
 ----------------------------------------------------------------------
Center    Atomic    Atomic           Coordinates (Angstroms)
Number    Number    Type        X           Y           Z
 ----------------------------------------------------------------------
    1        6        0        3.122156   -0.250922    0.366866
    2        6        0        4.050414   -1.254124    0.072649
    3        7        0        3.649007   -2.266408   -0.705768
    4        6        0        2.413504   -2.378112   -1.218917
    5        6        0        1.472194   -1.409256   -0.965173
    6        6        0        1.821808   -0.309850   -0.161866
    7        6        0        5.442795   -1.227370    0.598998
    8        8        0        3.556227    0.724681    1.171838
    9        6        0        0.797754    0.761111    0.144868
   10        6        0        0.077630   -1.612336   -1.497955
   11        8        0       -0.741776   -1.950236   -0.406163
   12       15        0       -2.388584   -2.220277   -0.686286
   13        8        0       -2.996311   -0.826515   -0.902462
   14        8        0       -2.464183   -3.124940   -1.906188
   15        8        0       -2.803753   -2.869375    0.639143
   16        1        0        2.219880   -3.253252   -1.821690
   17        1        0        6.040107   -2.042115    0.190621
   18        1        0        5.914062   -0.275972    0.346195
```

```
  19        1        0        5.430717   -1.307523    1.688272
  20        1        0        0.067705    0.821655   -0.664121
  21        1        0       -0.279114   -0.704392   -2.001998
  22        1        0        0.083071   -2.414677   -2.243097
  23        1        0        4.319443   -2.996154   -0.917905
  24        7        0        1.457265    2.025170    0.426350
  25        6        0        1.044085    3.155560    0.038698
  26        1        0        2.889164    1.459345    1.115792
  27        6        0       -0.247299    3.334873   -0.738448
  28        8        0       -0.080386    4.098449   -1.805787
  29        8        0       -1.297862    2.854191   -0.393121
  30        1        0       -0.924957    4.202768   -2.266775
  31        6        0        1.799476    4.408193    0.355370
  32        1        0        1.152328    5.120596    0.874025
  33        1        0        2.659037    4.174528    0.981214
  34        1        0        2.134230    4.884631   -0.569029
  35        1        0       -3.427477    0.085942    0.405745
  36        8        0       -3.666080    0.650590    1.189776
  37        1        0       -2.110342    0.534540    2.138693
  38        1        0       -3.890243    1.514892    0.814859
  39        8        0       -1.287800    0.336493    2.626456
  40        1        0        0.232051    0.469600    1.044553
  41        1        0       -1.346045   -0.621108    2.796394
  42        8        0       -4.084510    3.173365   -0.126021
  43        1        0       -3.163737    3.186684   -0.423132
  44        1        0       -4.611722    3.117267   -0.925613
  45        8        0       -1.605616   -2.436871    2.921894
  46        1        0       -2.237653   -2.694269    3.594982
  47        1        0       -2.056363   -2.615436    2.046773
 ----------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

  715 basis functions
  103 alpha electrons   103 beta electrons
      nuclear repulsion energy   2694.6971958144 Hartrees.
NAtoms= 47 NActive= 47

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
================================
Model   : PCM.
Atomic radii   : UFF (Universal Force Field).

Solvent : Water, Eps= 78.355300 Eps(inf)= 1.777849

SCF Done: E(RwB97XD) = -1711.08797455 A.U. after 2 cycles
        NFock= 2 Conv=0.69D-09   -V/T= 2.0039

Zero-point correction=   0.365398 (a.u.)
Thermal correction to Energy=   0.396706
Thermal correction to Enthalpy=   0.397650
Thermal correction to Gibbs Free Energy=   0.300720
Sum of electronic and zero-point Energies=   -1710.722577
Sum of electronic and thermal Energies=   -1710.691269
Sum of electronic and thermal Enthalpies=   -1710.690324
Sum of electronic and thermal Free Energies=   -1710.787254

                 E (Thermal)   CV   S
                  KCal/Mol   Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total   248.937   111.405   204.006

       Item   Value   Threshold Converged?
Maximum Force   0.000035   0.000450   YES
RMS   Force   0.000007   0.000300   YES
Maximum Displacement   0.006286   0.001800   NO
RMS   Displacement   0.000965   0.001200   YES

Normal termination of Gaussian 16 at Wed Jan 12 11:00:45 2022.

  -----------Figure S3-4, TS9 ------------

 vita-b6tsohx1.high.log

 Stoichiometry   C11H22N2O11P(1-)

                Standard orientation:

```
Center     Atomic      Atomic              Coordinates (Angstroms)
Number     Number       Type           X           Y           Z
---------------------------------------------------------------------
    1         6           0        -3.019713   -0.998976   -0.202120
    2         6           0        -4.265676   -0.401539    0.101810
    3         7           0        -4.371129    0.930977    0.049593
    4         6           0        -3.366521    1.765891   -0.270392
    5         6           0        -2.129881    1.247308   -0.576439
    6         6           0        -1.945370   -0.140356   -0.541860
    7         6           0        -5.449219   -1.225546    0.468495
    8         8           0        -2.912579   -2.293901   -0.162784
    9         6           0        -0.583391   -0.695973   -0.890429
   10         6           0        -1.006738    2.189570   -0.932165
   11         8           0        -0.008534    2.121845    0.064689
   12        15           0         1.469789    2.954620   -0.220019
   13         8           0         2.293452    2.457153    0.973640
   14         8           0         1.937578    2.458537   -1.581932
   15         8           0         1.104775    4.432052   -0.160228
   16         1           0        -3.593548    2.821577   -0.267269
   17         1           0        -6.326737   -0.609971    0.667468
   18         1           0        -5.679379   -1.923176   -0.339876
   19         1           0        -5.223331   -1.822978    1.354650
   20         1           0         0.191275   -0.153769   -0.347105
   21         1           0        -0.577737    1.911835   -1.902540
   22         1           0        -1.396536    3.209372   -1.019805
   23         1           0        -5.271484    1.340652    0.269559
   24         7           0        -0.525899   -2.119115   -0.576732
   25         6           0         0.512341   -2.833739   -0.412102
   26         1           0        -1.614716   -2.465897   -0.367518
   27         6           0         1.893819   -2.263775   -0.685483
   28         8           0         2.839183   -2.930659   -0.062479
   29         8           0         2.071679   -1.333675   -1.431874
   30         1           0         3.704426   -2.475901   -0.221476
   31         6           0         0.396631   -4.254376    0.010801
   32         1           0         0.901036   -4.372801    0.972173
   33         1           0        -0.646411   -4.552164    0.101334
   34         1           0         0.906630   -4.901507   -0.706218
   35         1           0         3.012658    1.016442    1.224629
   36         8           0         3.412705    0.147951    1.507993
   37         1           0         1.985272   -0.886873    1.831511
   38         1           0         3.964168   -0.169291    0.783954
   39         8           0         1.144777   -1.368807    1.960561
   40         1           0        -0.384895   -0.550890   -1.956877
   41         1           0         0.503316   -0.665108    2.156115
   42         8           0         5.032743   -1.426992   -0.401239
   43         1           0         5.149789   -1.100048   -1.297806
   44         1           0         5.906305   -1.680758   -0.090841
   45         8           0        -0.537281    0.855093    2.413604
   46         1           0        -0.197676    1.366390    3.150758
   47         1           0        -0.325734    1.382792    1.615145
---------------------------------------------------------------------

Standard basis: 6-311+G(d,p) (6D, 7F)

  715 basis functions
  103 alpha electrons     103 beta electrons
     nuclear repulsion energy   2780.4405357676 Hartrees.
NAtoms=  47 NActive=  47

Force inversion solution in PCM.
-----------------------------------------------------------
Polarizable Continuum Model (PCM)
=================================
Model             : PCM.
Atomic radii      : UFF (Universal Force Field).

Solvent : Water, Eps= 78.355300 Eps(inf)=  1.777849
------------------------------------------------------

SCF Done:  E(RwB97XD) =  -1711.08630605 A.U. after 2 cycles
        NFock=  2  Conv=0.32D-09     -V/T= 2.0039

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman
               1                    2                    3
               A                    A                    A
Frequencies --  -573.7087            24.5837              34.2348

Zero-point correction=                      0.361950 (a.u.)
Thermal correction to Energy=               0.392880
Thermal correction to Enthalpy=             0.393824
```

```
Thermal correction to Gibbs Free Energy=        0.299120
Sum of electronic and zero-point Energies=          -1710.724356
Sum of electronic and thermal Energies=             -1710.693426
Sum of electronic and thermal Enthalpies=           -1710.692482
Sum of electronic and thermal Free Energies=        -1710.787186

                  E (Thermal)             CV                S
                    KCal/Mol        Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total                246.536           110.379          199.320

          Item              Value     Threshold  Converged?
Maximum Force            0.000001     0.000450     YES
RMS     Force            0.000000     0.000300     YES
Maximum Displacement     0.000315     0.001800     YES
RMS     Displacement     0.000053     0.001200     YES

Normal termination of Gaussian 16 at Thu Jan 13 05:38:04 2022.

  ------------Figure S3-5,  Int9 ------------

  vita-b6revohx1.high.log

   Stoichiometry    C11H22N2O11P(1-)

                     Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic          Coordinates (Angstroms)
Number     Number     Type         X           Y           Z
---------------------------------------------------------------------
    1         6         0       -3.053420   -1.003826   -0.238481
    2         6         0       -4.275752   -0.370413    0.117108
    3         7         0       -4.348905    0.963848    0.096806
    4         6         0       -3.333713    1.782096   -0.234386
    5         6         0       -2.119051    1.237758   -0.582199
    6         6         0       -1.966480   -0.153781   -0.580727
    7         6         0       -5.471520   -1.169934    0.497701
    8         8         0       -2.985633   -2.290809   -0.237101
    9         6         0       -0.621595   -0.719494   -0.980013
   10         6         0       -0.983114    2.163575   -0.942492
   11         8         0        0.019101    2.075505    0.049677
   12        15         0        1.482599    2.941372   -0.207822
   13         8         0        2.301391    2.449844    0.991921
   14         8         0        1.979223    2.467746   -1.567585
   15         8         0        1.084980    4.409954   -0.139215
   16         1         0       -3.534127    2.842560   -0.203854
   17         1         0       -6.316990   -0.535498    0.765268
   18         1         0       -5.762943   -1.819569   -0.331006
   19         1         0       -5.228513   -1.817980    1.342701
   20         1         0        0.179822   -0.149429   -0.511469
   21         1         0       -0.564167    1.885508   -1.917108
   22         1         0       -1.356074    3.190053   -1.022240
   23         1         0       -5.231849    1.390633    0.351965
   24         7         0       -0.523120   -2.126060   -0.599738
   25         6         0        0.522223   -2.821873   -0.386400
   26         1         0       -1.523674   -2.507182   -0.413787
   27         6         0        1.898192   -2.246861   -0.677970
   28         8         0        2.848173   -2.903620   -0.054586
   29         8         0        2.063521   -1.327920   -1.439805
   30         1         0        3.712562   -2.448883   -0.222940
   31         6         0        0.415019   -4.221611    0.094712
   32         1         0        0.919372   -4.289998    1.060819
   33         1         0       -0.624758   -4.527098    0.196208
   34         1         0        0.934935   -4.891666   -0.593396
   35         1         0        3.005452    1.006000    1.247017
   36         8         0        3.398353    0.132351    1.526333
   37         1         0        1.972751   -0.908887    1.812857
   38         1         0        3.969228   -0.170492    0.811294
   39         8         0        1.130841   -1.395014    1.918661
   40         1         0       -0.487277   -0.637988   -2.063446
   41         1         0        0.485237   -0.695261    2.117280
   42         8         0        5.035768   -1.404819   -0.401571
   43         1         0        5.149653   -1.064312   -1.293531
   44         1         0        5.909815   -1.666666   -0.099253
   45         8         0       -0.538597    0.824392    2.397576
   46         1         0       -0.183886    1.329549    3.131896
   47         1         0       -0.321093    1.346809    1.597000
---------------------------------------------------------------------

Standard basis: 6-311+G(d,p) (6D, 7F)
```

```
   715 basis functions
   103 alpha electrons     103 beta electrons
      nuclear repulsion energy    2781.6610447787 Hartrees.
NAtoms=  47 NActive=  47

Force inversion solution in PCM.
---------------------------------------------------------
Polarizable Continuum Model (PCM)
=================================
Model               : PCM.
Atomic radii        : UFF (Universal Force Field).

Solvent: Water, Eps= 78.355300 Eps(inf)=  1.777849
---------------------------------------------------------

SCF Done:  E(RwB97XD) =  -1711.08655986 A.U. after  2 cycles
         NFock=  2 Conv=0.45D-09     -V/T= 2.0039

Zero-point correction=                           0.364524 (a.u.)
Thermal correction to Energy=                    0.395749
Thermal correction to Enthalpy=                  0.396693
Thermal correction to Gibbs Free Energy=         0.301559
Sum of electronic and zero-point Energies=          -1710.722035
Sum of electronic and thermal Energies=             -1710.690811
Sum of electronic and thermal Enthalpies=           -1710.689867
Sum of electronic and thermal Free Energies=        -1710.785001

                 E (Thermal)           CV              S
                  KCal/Mol        Cal/Mol-Kelvin  Cal/Mol-Kelvin
Total             248.336           111.578          200.226

          Item            Value    Threshold  Converged?
Maximum Force          0.000012     0.000450     YES
RMS     Force          0.000003     0.000300     YES
Maximum Displacement   0.001237     0.001800     YES
RMS     Displacement   0.000303     0.001200     YES

Normal termination of Gaussian 16 at Wed Jan 12 13:27:20 2022.

  --------Figure S3-6,  TS10-----------

    vita-b6tsohx.high.log

 Stoichiometry    C11H22N2O11P(1-)

                    Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic          Coordinates (Angstroms)
Number     Number      Type          X           Y           Z
---------------------------------------------------------------------
     1        6          0       -3.146670   -0.958237   -0.353453
     2        6          0       -4.354830   -0.286880    0.012200
     3        7          0       -4.380554    1.048612    0.056797
     4        6          0       -3.330250    1.843655   -0.215163
     5        6          0       -2.127353    1.268194   -0.565145
     6        6          0       -2.017032   -0.124741   -0.625892
     7        6          0       -5.591179   -1.054650    0.324526
     8        8          0       -3.126051   -2.229760   -0.421711
     9        6          0       -0.711635   -0.764366   -1.053263
    10        6          0       -0.960730    2.181677   -0.849068
    11        8          0       -0.020397    2.067365    0.203627
    12       15          0        1.529631    2.764497   -0.022991
    13        8          0        2.220564    2.276627    1.262953
    14        8          0        2.058816    2.136672   -1.303718
    15        8          0        1.293138    4.265306   -0.072719
    16        1          0       -3.493047    2.908253   -0.139221
    17        1          0       -6.419757   -0.400140    0.598198
    18        1          0       -5.884539   -1.656461   -0.539200
    19        1          0       -5.399124   -1.749375    1.145588
    20        1          0        0.114961   -0.077638   -0.879313
    21        1          0       -0.485283    1.915006   -1.799530
    22        1          0       -1.311692    3.215652   -0.929899
    23        1          0       -5.253105    1.495002    0.313424
    24        7          0       -0.463453   -2.011488   -0.340254
    25        6          0        0.709255   -2.453736    0.142636
    26        1          0       -1.321596   -2.508881   -0.105797
    27        6          0        1.949404   -2.183717   -0.724483
    28        8          0        3.052431   -2.618761   -0.140655
    29        8          0        1.906143   -1.655217   -1.803929
    30        1          0        3.831208   -2.214720   -0.584581
```

```
    31          6          0        0.647760   -3.858180    0.697201
    32          1          0        1.558021   -4.095325    1.241734
    33          1          0       -0.207439   -3.947519    1.368062
    34          1          0        0.529138   -4.563403   -0.128165
    35          1          0        2.825014    0.886543    1.339614
    36          8          0        3.191489   -0.060957    1.439434
    37          1          0        2.035145   -1.011848    1.451470
    38          1          0        3.835990   -0.194334    0.731965
    39          8          0        1.165348   -1.567017    1.522328
    40          1          0       -0.751961   -0.951970   -2.133173
    41          1          0        0.449812   -0.906722    1.760137
    42          8          0        4.937304   -0.844567   -0.821759
    43          1          0        4.806269   -0.339390   -1.629108
    44          1          0        5.887964   -0.934020   -0.713869
    45          8          0       -0.468163    0.352440    2.216522
    46          1          0       -0.160780    0.729139    3.044367
    47          1          0       -0.307034    1.043649    1.532786
 ----------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

  715 basis functions
  103 alpha electrons   103 beta electrons
     nuclear repulsion energy   2831.8398641268 Hartrees.
NAtoms= 47 NActive= 47

Nuclear repulsion after empirical dispersion term =
 2831.7987957203 Hartrees.
Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
================================
Model   : PCM.

Solvent: Water, Eps= 78.355300 Eps(inf)= 1.777849

SCF Done: E(RwB97XD) = -1711.07230209 A.U. after 2 cycles
         NFock= 2 Conv=0.86D-09   -V/T= 2.0039
DoSCS=F DFT=T ScalE2(SS,OS)= 1.000000 1.000000
Range of M.O.s used for correlation: 1   713

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman
                  1   2   3
                  A   A   A
 Frequencies -- -161.4793   29.4588   36.2553

Zero-point correction=   0.365799 (a.u.)
Thermal correction to Energy=   0.394869
Thermal correction to Enthalpy=   0.395813
Thermal correction to Gibbs Free Energy=   0.306582
Sum of electronic and zero-point Energies=   -1710.706503
Sum of electronic and thermal Energies=   -1710.677433
Sum of electronic and thermal Enthalpies=   -1710.676489
Sum of electronic and thermal Free Energies=   -1710.765720

                E (Thermal)   CV   S
                 KCal/Mol   Cal/Mol-Kelvin   Cal/Mol-Kelvin
 Total   247.784   106.832   187.803

       Item   Value   Threshold Converged?
 Maximum Force   0.000081   0.000450   YES
 RMS   Force   0.000018   0.000300   YES
 Maximum Displacement 0.002210   0.001800   NO
 RMS   Displacement 0.000540   0.001200   YES

 Normal termination of Gaussian 16 at Fri Nov 12 10:36:25 2021.

  ============= Figure S4 in Scheme 4d ===========

  ---------Figure S4-1, Int10------------------

 vita-b6forhh.high.log

 Stoichiometry   C11H22N2O11P(1-)

                 Standard orientation:

 Center   Atomic   Atomic   Coordinates (Angstroms)
 Number   Number   Type   X   Y   Z

```
-------------------------------------------------------------------
    1          6           0       -2.698591    1.157043   -0.296845
    2          6           0       -3.104124    2.526185   -0.201089
    3          7           0       -2.212382    3.492886   -0.440353
    4          6           0       -0.924388    3.289444   -0.773119
    5          6           0       -0.459169    1.994663   -0.882281
    6          6           0       -1.328119    0.929778   -0.639614
    7          6           0       -4.502684    2.890174    0.154180
    8          8           0       -3.528316    0.221386   -0.085651
    9          6           0       -0.886705   -0.506013   -0.738926
   10          6           0        0.981958    1.788201   -1.271804
   11          8           0        1.664948    1.167888   -0.191554
   12         15           0        3.280691    0.884923   -0.340120
   13          8           0        3.485925   -0.012041    0.978505
   14          8           0        3.512149   -0.009707   -1.537250
   15          8           0        4.020051    2.188722   -0.270885
   16          1           0       -0.320283    4.169064   -0.936458
   17          1           0       -4.638932    3.970290    0.224261
   18          1           0       -5.193839    2.493622   -0.594028
   19          1           0       -4.772746    2.434254    1.109736
   20          1           0       -1.427647   -0.971998   -1.578161
   21          1           0        1.048328    1.155419   -2.164225
   22          1           0        1.441412    2.752851   -1.509741
   23          1           0       -2.529266    4.452304   -0.366331
   24          7           0       -1.162868   -1.203380    0.526273
   25          6           0       -0.694954   -2.592054    0.588807
   26          1           0       -2.175093   -1.170108    0.652478
   27          6           0       -1.231861   -3.384587   -0.628628
   28          8           0       -0.550881   -3.886797   -1.484734
   29          8           0       -2.567236   -3.426001   -0.638139
   30          1           0       -2.856854   -3.906642   -1.424657
   31          6           0       -1.212485   -3.218902    1.879528
   32          1           0       -0.932153   -4.272669    1.923014
   33          1           0       -0.751316   -2.698925    2.720607
   34          1           0       -2.297102   -3.137226    1.955280
   35          1           0        0.179852   -0.572004   -0.943128
   36          8           0        0.692544   -2.657364    0.616912
   37          1           0        3.084106    0.373747    1.792400
   38          1           0        1.093213   -2.521333   -0.268948
   39          8           0        2.241334    0.890561    3.182925
   40          1           0        1.290643    0.688234    3.040296
   41          1           0        2.285915    1.836551    3.336066
   42          8           0        2.100319   -2.249398   -1.676567
   43          1           0        1.584741   -2.258479   -2.484663
   44          1           0        2.619096   -1.405259   -1.673971
   45          8           0       -0.376668    0.312903    2.747560
   46          1           0       -0.604884   -0.230895    1.951751
   47          1           0       -0.897434   -0.046004    3.468551
-------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

   715 basis functions
   103 alpha electrons   103 beta electrons
      nuclear repulsion energy   2811.3768338519 Hartrees.
NAtoms=   47 NActive=   47

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
=================================
Model   : PCM.
Atomic radii   : UFF (Universal Force Field).

Solvent : Water, Eps= 78.355300 Eps(inf)=   1.777849

SCF Done: E(RwB97XD) = -1711.11768876 A.U. after   1 cycles
        NFock= 1 Conv=0.27D-08   -V/T= 2.0039

Zero-point correction=   0.368513 (a.u.)
Thermal correction to Energy=   0.398423
Thermal correction to Enthalpy=   0.399368
Thermal correction to Gibbs Free Energy=   0.306706
Sum of electronic and zero-point Energies=   -1710.749175
Sum of electronic and thermal Energies=   -1710.719265
Sum of electronic and thermal Enthalpies=   -1710.718321
Sum of electronic and thermal Free Energies=   -1710.810983

                E (Thermal)   CV   S

```
                KCal/Mol        Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              250.014         108.652          195.023

        Item               Value    Threshold  Converged?
Maximum Force            0.000004   0.000450     YES
RMS     Force            0.000001   0.000300     YES
Maximum Displacement     0.001284   0.001800     YES
RMS     Displacement     0.000281   0.001200     YES
```

Normal termination of Gaussian 16 at Wed Jan 12 22:45:27 2022.

    ---------Figure S4-2, TS11 -------------

 vita-b6tshh.high.log

 Stoichiometry   C11H22N2O11P(1-)

```
                Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic           Coordinates (Angstroms)
Number     Number     Type         X           Y           Z
---------------------------------------------------------------------
    1          6          0      -2.624236    1.117875   -0.171397
    2          6          0      -3.158623    2.441703   -0.099324
    3          7          0      -2.362741    3.479606   -0.368086
    4          6          0      -1.060398    3.390832   -0.701373
    5          6          0      -0.474917    2.146883   -0.788520
    6          6          0      -1.247154    1.013000   -0.525915
    7          6          0      -4.584305    2.675055    0.255357
    8          8          0      -3.360368    0.107159    0.069512
    9          6          0      -0.676350   -0.374315   -0.656271
   10          6          0       0.982813    2.056571   -1.163189
   11          8          0       1.681880    1.485659   -0.072390
   12         15          0       3.245176    0.976434   -0.268240
   13          8          0       3.357221    0.003890    0.977501
   14          8          0       3.306551    0.157536   -1.546822
   15          8          0       4.159544    2.166894   -0.175366
   16          1          0      -0.541350    4.319707   -0.883167
   17          1          0      -4.831530    3.736979    0.279791
   18          1          0      -5.233449    2.175243   -0.467703
   19          1          0      -4.797521    2.236081    1.232878
   20          1          0      -1.078880   -0.841080   -1.562004
   21          1          0       1.108405    1.435143   -2.057189
   22          1          0       1.369859    3.054862   -1.391956
   23          1          0      -2.768158    4.407077   -0.316369
   24          7          0      -1.078127   -1.205671    0.507960
   25          6          0      -0.624578   -2.638041    0.467208
   26          1          0      -2.114685   -1.118908    0.538070
   27          6          0      -1.213072   -3.304792   -0.796873
   28          8          0      -0.562690   -3.913619   -1.600548
   29          8          0      -2.531565   -3.137916   -0.861779
   30          1          0      -2.872405   -3.574062   -1.654249
   31          6          0      -1.163255   -3.332276    1.713364
   32          1          0      -0.901051   -4.389929    1.676103
   33          1          0      -0.693586   -2.882454    2.588927
   34          1          0      -2.246346   -3.234657    1.788985
   35          1          0       0.407778   -0.366546   -0.713119
   36          8          0       0.744822   -2.705909    0.481215
   37          1          0       2.827393    0.239773    1.853022
   38          1          0       1.151643   -2.525164   -0.402520
   39          8          0       2.091298    0.416164    3.075284
   40          1          0       0.899166    0.165157    2.906443
   41          1          0       2.171097    1.316490    3.394043
   42          8          0       2.070058   -2.142636   -1.756250
   43          1          0       1.591296   -2.157590   -2.586735
   44          1          0       2.539264   -1.264287   -1.706767
   45          8          0      -0.232074   -0.092163    2.708208
   46          1          0      -0.696702   -0.760221    1.430832
   47          1          0      -0.614763   -0.451102    3.510239
---------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

 715 basis functions
 103 alpha electrons   103 beta electrons
    nuclear repulsion energy 2835.6629903179 Hartrees.
NAtoms= 47 NActive= 47

Force inversion solution in PCM.

```
Polarizable Continuum Model (PCM)
=================================
Model              : PCM.
Atomic radii       : UFF (Universal Force Field).

Solvent: Water, Eps= 78.355300 Eps(inf)=  1.777849
--------------------------------------------------

SCF Done:  E(RwB97XD) =  -1711.09705601 A.U. after  1 cycles
         NFock=  1 Conv=0.21D-08    -V/T= 2.0039
DoSCS=F DFT=T ScalE2(SS,OS)= 1.000000 1.000000
Range of M.O.s used for correlation:    1   712

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman
                 1                   2                   3
                 A                   A                   A
Frequencies --  -828.6060            29.6838             38.3851

Zero-point correction=                          0.362265 (a.u.)
Thermal correction to Energy=                   0.390552
Thermal correction to Enthalpy=                 0.391497
Thermal correction to Gibbs Free Energy=        0.303575
Sum of electronic and zero-point Energies=         -1710.734791
Sum of electronic and thermal Energies=            -1710.706504
Sum of electronic and thermal Enthalpies=          -1710.705559
Sum of electronic and thermal Free Energies=       -1710.793481

                E (Thermal)             CV                S
                 KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total             245.075            104.541           185.047

        Item              Value     Threshold  Converged?
Maximum Force            0.000006     0.000450     YES
RMS     Force            0.000001     0.000300     YES
Maximum Displacement     0.000967     0.001800     YES
RMS     Displacement     0.000132     0.001200     YES

Normal termination of Gaussian 16 at Tue Dec 28 20:16:43 2021.

   ---------Figure S4-3, Int11 --------------------

 vita-b6revhh.high.log

 Stoichiometry    C11H22N2O11P(1-)

                  Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic         Coordinates (Angstroms)
Number     Number      Type         X           Y           Z
---------------------------------------------------------------------
    1         6          0       -2.592706    1.203547   -0.180332
    2         6          0       -3.096439    2.534206   -0.064287
    3         7          0       -2.266723    3.560633   -0.265320
    4         6          0       -0.958797    3.450530   -0.569628
    5         6          0       -0.400079    2.197407   -0.694170
    6         6          0       -1.209365    1.075821   -0.497237
    7         6          0       -4.525014    2.789063    0.262805
    8         8          0       -3.363814    0.201393   -0.003732
    9         6          0       -0.664254   -0.320573   -0.653192
   10         6          0        1.058764    2.085639   -1.061192
   11         8          0        1.757758    1.458400   -0.008576
   12        15          0        3.323053    0.915080   -0.327403
   13         8          0        3.653593    0.171672    0.970253
   14         8          0        3.173688   -0.014510   -1.545641
   15         8          0        4.166580    2.146582   -0.607191
   16         1          0       -0.412759    4.372366   -0.701762
   17         1          0       -4.748644    3.855187    0.312745
   18         1          0       -5.166447    2.325741   -0.490540
   19         1          0       -4.772452    2.326918    1.221473
   20         1          0       -1.020036   -0.749341   -1.595206
   21         1          0        1.161184    1.501221   -1.984443
   22         1          0        1.463693    3.084889   -1.256591
   23         1          0       -2.649084    4.495631   -0.182363
   24         7          0       -1.181718   -1.171426    0.454535
   25         6          0       -0.791344   -2.627691    0.429637
   26         1          0       -2.219911   -1.015590    0.421538
   27         6          0       -1.303115   -3.247928   -0.889852
   28         8          0       -0.632419   -3.928555   -1.614370
   29         8          0       -2.585535   -2.958355   -1.092533
   30         1          0       -2.885186   -3.374270   -1.912244
```

```
      31        6         0      -1.478664   -3.303072    1.611881
      32        1         0      -1.261216   -4.370964    1.587749
      33        1         0      -1.074352   -2.883937    2.534573
      34        1         0      -2.558498   -3.155925    1.585615
      35        1         0       0.422221   -0.341424   -0.633266
      36        8         0       0.562757   -2.754040    0.568187
      37        1         0       2.819466    0.040467    2.304428
      38        1         0       1.059353   -2.596896   -0.280952
      39        8         0       2.320972   -0.075420    3.168798
      40        1         0       0.646320   -0.033980    2.961309
      41        1         0       2.662228    0.598288    3.759298
      42        8         0       2.037514   -2.305309   -1.549940
      43        1         0       1.598721   -2.409600   -2.395845
      44        1         0       2.482637   -1.396210   -1.552870
      45        8         0      -0.329527   -0.025516    2.805024
      46        1         0      -0.842613   -0.778817    1.365598
      47        1         0      -0.737802   -0.296817    3.629467
 ----------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

  715 basis functions
  103 alpha electrons   103 beta electrons
    nuclear repulsion energy   2815.0097566279 Hartrees.
NAtoms= 47 NActive= 47

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
=================================
Model   : PCM.

Solvent : Water, Eps= 78.355300 Eps(inf)=   1.777849

SCF Done: E(RwB97XD) = -1711.11059629 A.U. after 1 cycles
        NFock= 1 Conv=0.22D-08   -V/T= 2.0039

Zero-point correction=   0.369228 (a.u.)
Thermal correction to Energy=   0.398384
Thermal correction to Enthalpy=   0.399328
Thermal correction to Gibbs Free Energy=   0.308488
Sum of electronic and zero-point Energies=   -1710.741369
Sum of electronic and thermal Energies=   -1710.712212
Sum of electronic and thermal Enthalpies=   -1710.711268
Sum of electronic and thermal Free Energies=   -1710.802108

```
                  E (Thermal)             CV                S
                   KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total                249.990           106.477           191.188
```

```
         Item              Value     Threshold  Converged?
Maximum Force            0.000012     0.000450     YES
RMS     Force            0.000002     0.000300     YES
Maximum Displacement     0.000511     0.001800     YES
RMS     Displacement     0.000086     0.001200     YES
```

Normal termination of Gaussian 16 at Wed Jan 12 18:27:08 2022.

  ---------------Figure S4-4, TS12 ---------------------

  vita-b6ts7.high.log

 Stoichiometry   C11H22N2O11P(1-)

```
                  Standard orientation:
 ----------------------------------------------------------------------
 Center     Atomic      Atomic           Coordinates (Angstroms)
 Number     Number      Type         X           Y           Z
 ----------------------------------------------------------------------
      1        6         0       2.693570   -1.059171   -0.191411
      2        6         0       3.246257   -2.369036   -0.047441
      3        7         0       2.456314   -3.430180   -0.228819
      4        6         0       1.146307   -3.377430   -0.538715
      5        6         0       0.543179   -2.148297   -0.695058
      6        6         0       1.307842   -0.992629   -0.522417
      7        6         0       4.681654   -2.565754    0.289773
      8        8         0       3.420234   -0.025579   -0.029642
      9        6         0       0.721198    0.380359   -0.713367
     10        6         0      -0.915252   -2.103550   -1.073237
```

```
    11           8           0       -1.643894   -1.466862   -0.037574
    12          15           0       -3.244181   -1.111415   -0.306256
    13           8           0       -3.639341   -0.358870    0.949501
    14           8           0       -3.210239   -0.163859   -1.574774
    15           8           0       -3.972683   -2.382274   -0.648382
    16           1           0        0.636120   -4.322143   -0.651063
    17           1           0        4.948648   -3.622183    0.335763
    18           1           0        5.308550   -2.071452   -0.455940
    19           1           0        4.903089   -2.099889    1.253165
    20           1           0        1.123853    0.822476   -1.629385
    21           1           0       -1.038555   -1.551960   -2.012931
    22           1           0       -1.288716   -3.119501   -1.232696
    23           1           0        2.874484   -4.347684   -0.125652
    24           7           0        1.132337    1.255783    0.418533
    25           6           0        0.576445    2.673392    0.412627
    26           1           0        2.172242    1.211338    0.412741
    27           6           0        1.034765    3.354049   -0.900972
    28           8           0        0.328875    4.033855   -1.592860
    29           8           0        2.329779    3.134902   -1.140427
    30           1           0        2.588797    3.600275   -1.947001
    31           6           0        1.226441    3.401728    1.590379
    32           1           0        0.886250    4.437693    1.593594
    33           1           0        0.897611    2.924352    2.515041
    34           1           0        2.315796    3.383128    1.536128
    35           1           0       -0.363515    0.376118   -0.765541
    36           8           0       -0.764350    2.649509    0.557730
    37           1           0       -2.787582   -0.175772    2.323554
    38           1           0       -1.334436    2.382552   -0.331079
    39           8           0       -2.292232   -0.043950    3.176542
    40           1           0       -0.597895   -0.015252    2.947242
    41           1           0       -2.604293   -0.732085    3.766772
    42           8           0       -2.144149    2.020253   -1.343255
    43           1           0       -1.810174    2.363664   -2.172814
    44           1           0       -2.730701    0.802009   -1.463251
    45           8           0        0.373192    0.019171    2.782585
    46           1           0        0.815232    0.822087    1.315427
    47           1           0        0.771398    0.331894    3.597277
 ---------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

  715 basis functions
 103 alpha electrons   103 beta electrons
    nuclear repulsion energy   2823.3802694244 Hartrees.
NAtoms= 47 NActive= 47

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
 =================================
Model   : PCM.

Solvent : Water, Eps= 78.355300 Eps(inf)= 1.777849

SCF Done: E(RwB97XD) = -1711.10355475 A.U. after 1 cycles
        NFock= 1 Conv=0.24D-08   -V/T= 2.0039

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman
                 1   2   3
                 A   A   A
Frequencies -- -401.4243   28.5113   32.6512

Zero-point correction=   0.363855 (a.u.)
Thermal correction to Energy=   0.392462
Thermal correction to Enthalpy=   0.393406
Thermal correction to Gibbs Free Energy=   0.304452
Sum of electronic and zero-point Energies=   -1710.739699
Sum of electronic and thermal Energies=   -1710.711093
Sum of electronic and thermal Enthalpies=   -1710.710149
Sum of electronic and thermal Free Energies=   -1710.799103

               E (Thermal)   CV   S
                KCal/Mol   Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total   246.273   104.844   187.219

       Item   Value   Threshold Converged?
Maximum Force   0.000006   0.000450   YES
RMS   Force   0.000001   0.000300   YES
Maximum Displacement 0.000600   0.001800   YES

RMS   Displacement   0.000088   0.001200   YES

Normal termination of Gaussian 16 at Tue Dec 28 20:32:48 2021.

    ---------------Figure S4-5, Int12-----------------

  vita-b6revpmp.high.log

 Stoichiometry   C11H22N2O11P(1-)

                     Standard orientation:

Center   Atomic   Atomic   Coordinates (Angstroms)
Number   Number   Type   X   Y   Z
----
    1   6   0   2.805440   -0.881213   -0.231066
    2   6   0   3.426950   -2.159398   -0.071929
    3   7   0   2.692385   -3.263926   -0.225781
    4   6   0   1.378902   -3.285897   -0.523254
    5   6   0   0.709698   -2.091894   -0.687821
    6   6   0   1.410292   -0.893763   -0.534903
    7   6   0   4.874377   -2.276276   0.250866
    8   8   0   3.479384   0.188991   -0.103101
    9   6   0   0.746713   0.445501   -0.711060
   10   6   0   -0.749639   -2.136315   -1.061120
   11   8   0   -1.514917   -1.515630   -0.037230
   12   15   0   -3.145395   -1.376715   -0.242461
   13   8   0   -3.590711   -0.572198   0.954483
   14   8   0   -3.272135   -0.511905   -1.595897
   15   8   0   -3.738018   -2.725357   -0.513875
   16   1   0   0.919334   -4.258112   -0.617293
   17   1   0   5.183463   -3.316113   0.364595
   18   1   0   5.470677   -1.812525   -0.538775
   19   1   0   5.092182   -1.735461   1.174813
   20   1   0   1.123213   0.919706   -1.622760
   21   1   0   -0.908054   -1.612950   -2.011132
   22   1   0   -1.068215   -3.173992   -1.193991
   23   1   0   3.159422   -4.155826   -0.109622
   24   7   0   1.086461   1.335337   0.425938
   25   6   0   0.332796   2.707669   0.435735
   26   1   0   2.116331   1.412263   0.419086
   27   6   0   0.776217   3.400050   -0.892770
   28   8   0   0.019621   3.862095   -1.705499
   29   8   0   2.108383   3.444855   -1.028580
   30   1   0   2.325516   3.886609   -1.860260
   31   6   0   0.934397   3.480805   1.622441
   32   1   0   0.502816   4.483185   1.636144
   33   1   0   0.645424   2.969008   2.542736
   34   1   0   2.022226   3.564851   1.577003
   35   1   0   -0.335861   0.374270   -0.761761
   36   8   0   -0.960437   2.513005   0.520582
   37   1   0   -2.738426   -0.225798   2.328187
   38   1   0   -1.861464   2.230104   -0.699168
   39   8   0   -2.251610   -0.014673   3.165120
   40   1   0   -0.537311   -0.024519   2.965065
   41   1   0   -2.585775   -0.630241   3.819995
   42   8   0   -2.495602   2.008654   -1.458538
   43   1   0   -2.086984   2.395799   -2.235224
   44   1   0   -2.969377   0.431500   -1.519461
   45   8   0   0.434116   -0.007479   2.811959
   46   1   0   0.817477   0.867159   1.315002
   47   1   0   0.820942   0.343469   3.616526

Standard basis: 6-311+G(d,p) (6D, 7F)

  715 basis functions
  103 alpha electrons   103 beta electrons
     nuclear repulsion energy   2808.8714265044 Hartrees.
NAtoms= 47 NActive= 47

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
=================================
Model   : PCM.

Solvent : Water, Eps= 78.355300 Eps(inf)= 1.777849

```
SCF Done:  E(RwB97XD) =   -1711.10995294 A.U. after  2 cycles
        NFock=  2 Conv=0.67D-09     -V/T= 2.0039


Zero-point correction=                           0.368739 (a.u.)
Thermal correction to Energy=                    0.398223
Thermal correction to Enthalpy=                  0.399167
Thermal correction to Gibbs Free Energy=         0.308462
Sum of electronic and zero-point Energies=          -1710.741214
Sum of electronic and thermal Energies=             -1710.711730
Sum of electronic and thermal Enthalpies=           -1710.710786
Sum of electronic and thermal Free Energies=        -1710.801491

                 E (Thermal)             CV                S
                  KCal/Mol        Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              249.889           107.785          190.905

          Item              Value     Threshold  Converged?
Maximum Force            0.000133     0.000450     YES
RMS     Force            0.000016     0.000300     YES
Maximum Displacement     0.000574     0.001800     YES
RMS     Displacement     0.000105     0.001200     YES

Normal termination of Gaussian 16 at Wed Jan 12 22:18:50 2022.

  -----------------Figure S4-6, TS13 ----------------------

 vita-b6tspmp.high.log

 Stoichiometry    C11H22N2O11P(1-)

                 Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic          Coordinates (Angstroms)
Number     Number      Type        X           Y           Z
---------------------------------------------------------------------
    1          6          0       3.102566   -0.153931   -0.247248
    2          6          0       3.984045   -1.255721   -0.008918
    3          7          0       3.512670   -2.504035   -0.096638
    4          6          0       2.243103   -2.830057   -0.401691
    5          6          0       1.332525   -1.820812   -0.643226
    6          6          0       1.744283   -0.489951   -0.553572
    7          6          0       5.416929   -1.035511    0.328442
    8          8          0       3.526338    1.039350   -0.185280
    9          6          0       0.806304    0.671082   -0.770793
   10          6          0      -0.067937   -2.213202   -1.037631
   11          8          0      -0.990864   -1.745525   -0.061133
   12         15          0      -2.580564   -2.139723   -0.228502
   13          8          0      -3.272325   -1.339027    0.847581
   14          8          0      -2.951620   -1.563053   -1.690464
   15          8          0      -2.735280   -3.628248   -0.285995
   16          1          0       2.009096   -3.883276   -0.442485
   17          1          0       5.947793   -1.974670    0.490842
   18          1          0       5.909172   -0.485011   -0.477099
   19          1          0       5.496937   -0.421344    1.228786
   20          1          0       1.149112    1.245993   -1.636476
   21          1          0      -0.316220   -1.780481   -2.013310
   22          1          0      -0.136868   -3.301246   -1.127802
   23          1          0       4.160808   -3.262990    0.077852
   24          7          0       0.773244    1.571881    0.385350
   25          6          0      -0.855228    2.920897    0.427756
   26          1          0       1.708258    1.959001    0.509258
   27          6          0      -0.301342    3.554780   -0.860118
   28          8          0      -0.700960    3.267568   -1.960337
   29          8          0       0.657921    4.452444   -0.637328
   30          1          0       0.967205    4.790478   -1.488130
   31          6          0      -0.498541    3.566695    1.742751
   32          1          0      -1.136018    4.448022    1.864977
   33          1          0      -0.718148    2.865852    2.547974
   34          1          0       0.541300    3.882558    1.791696
   35          1          0      -0.211621    0.336144   -0.966947
   36          8          0      -1.874397    2.232555    0.320670
   37          1          0      -2.690862   -0.905189    2.330988
   38          1          0      -2.457131    1.547078   -1.136508
   39          8          0      -2.344079   -0.626393    3.216093
   40          1          0      -0.676754   -0.112952    3.077520
   41          1          0      -2.490797   -1.373604    3.798737
   42          8          0      -2.778092    1.096054   -1.949808
   43          1          0      -2.194791    1.435996   -2.632974
   44          1          0      -2.884333   -0.580588   -1.764481
```

S52

```
     45           8           0       0.250501    0.181661    2.955194
     46           1           0       0.536989    1.055057    1.238708
     47           1           0       0.456532    0.711389    3.727373
 ---------------------------------------------------------------------

Standard basis: 6-311+G(d,p) (6D, 7F)

  715 basis functions
  103 alpha electrons      103 beta electrons
     nuclear repulsion energy    2770.8113263616 Hartrees.
NAtoms=  47 NActive=  47

Force inversion solution in PCM.
 ----------------------------------------------------
Polarizable Continuum Model (PCM)
 =================================
Model            : PCM.

Solvent: Water, Eps= 78.355300 Eps(inf)=  1.777849
 --------------------------------------------------

SCF Done:  E(RwB97XD) =  -1711.10068062 A.U. after 2 cycles
         NFock= 2 Conv=0.76D-09    -V/T= 2.0039

Harmonic frequencies (cm**-1), IR intensities (KM/Mole),
                  1                      2                      3
                  A                      A                      A
Frequencies --  -108.4551              19.5864                28.5878

Zero-point correction=                           0.366462 (a.u.)
Thermal correction to Energy=                    0.396754
Thermal correction to Enthalpy=                  0.397699
Thermal correction to Gibbs Free Energy=         0.304083
Sum of electronic and zero-point Energies=        -1710.734219
Sum of electronic and thermal Energies=           -1710.703926
Sum of electronic and thermal Enthalpies=         -1710.702982
Sum of electronic and thermal Free Energies=      -1710.796597


                E (Thermal)            CV                 S
                 KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total             248.967           109.241           197.030


        Item              Value     Threshold  Converged?
Maximum Force            0.000025    0.000450     YES
RMS     Force            0.000003    0.000300     YES
Maximum Displacement     0.005086    0.001800     NO
RMS     Displacement     0.000938    0.001200     YES

Normal termination of Gaussian 16 at Thu Jan 13 04:00:16 2022.

   -----------Figure S4-7, Int13----------

 vita-b6forpmp.high.log

  Stoichiometry    C11H22N2O11P(1-)

                   Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic            Coordinates (Angstroms)
 Number     Number      Type         X           Y           Z
 ---------------------------------------------------------------------
     1          6           0       3.138999    0.577676   -0.262913
     2          6           0       4.236997   -0.284917    0.047947
     3          7           0       4.065055   -1.611386    0.005147
     4          6           0       2.913885   -2.228497   -0.315774
     5          6           0       1.806740   -1.461909   -0.623465
     6          6           0       1.900804   -0.069498   -0.585686
     7          6           0       5.570835    0.265501    0.414380
     8          8           0       3.281240    1.837176   -0.244389
     9          6           0       0.725301    0.837670   -0.858490
    10          6           0       0.544386   -2.180105   -1.024737
    11          8           0      -0.472606   -1.947139   -0.055174
    12         15           0      -1.906229   -2.736757   -0.227237
    13          8           0      -2.780871   -2.163048    0.860232
    14          8           0      -2.424552   -2.249332   -1.678033
    15          8           0      -1.668963   -4.212891   -0.313897
    16          1           0       2.925582   -3.308132   -0.316207
    17          1           0       6.288645   -0.523903    0.642612
    18          1           0       5.962811    0.874459   -0.404131
    19          1           0       5.477216    0.921928    1.283027
```

```
   20          1         0        0.962413    1.474537   -1.716770
   21          1         0        0.204448   -1.824822   -2.003679
   22          1         0        0.739527   -3.253169   -1.108556
   23          1         0        4.862650   -2.194597    0.228886
   24          7         0        0.412237    1.708444    0.275818
   25          6         0       -1.817337    2.805305    0.431608
   26          1         0        1.232168    2.281969    0.459647
   27          6         0       -1.287162    3.324896   -0.916834
   28          8         0       -1.539407    2.805493   -1.975181
   29          8         0       -0.582693    4.446722   -0.793835
   30          1         0       -0.285779    4.722925   -1.670823
   31          6         0       -1.472517    3.558200    1.680177
   32          1         0       -2.143344    4.421578    1.746095
   33          1         0       -1.643484    2.915802    2.542863
   34          1         0       -0.449039    3.925014    1.668858
   35          1         0       -0.167805    0.265831   -1.109271
   36          8         0       -2.628592    1.901308    0.416933
   37          1         0       -2.384752   -1.528781    2.328724
   38          1         0       -3.013927    0.833226   -0.995666
   39          8         0       -2.160412   -1.126835    3.205611
   40          1         0       -0.679135   -0.191234    3.083957
   41          1         0       -2.127966   -1.857584    3.825418
   42          8         0       -3.073010    0.352314   -1.841459
   43          1         0       -2.519766    0.898913   -2.409436
   44          1         0       -2.654102   -1.291056   -1.713755
   45          8         0        0.142067    0.330200    2.968113
   46          1         0        0.244590    1.152706    1.116454
   47          1         0        0.118251    0.998671    3.654917
 ----------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

   715 basis functions
   103 alpha electrons   103 beta electrons
      nuclear repulsion energy   2744.4546944680 Hartrees.
 NAtoms=   47

Force inversion solution in PCM.

 Polarizable Continuum Model (PCM)
 =================================
 Model   : PCM.
 Atomic radii   : UFF (Universal Force Field).

 Solvent: Water, Eps= 78.355300 Eps(inf)=   1.777849

 SCF Done: E(RwB97XD) = -1711.10138150 A.U. after 2 cycles
          NFock= 2 Conv=0.56D-09   -V/T= 2.0039

 Zero-point correction=   0.365973 (a.u.)
 Thermal correction to Energy=   0.397651
 Thermal correction to Enthalpy=   0.398596
 Thermal correction to Gibbs Free Energy=   0.300532
 Sum of electronic and zero-point Energies=   -1710.735409
 Sum of electronic and thermal Energies=   -1710.703730
 Sum of electronic and thermal Enthalpies=   -1710.702786
 Sum of electronic and thermal Free Energies=   -1710.800849

                 E (Thermal)   CV   S
                  KCal/Mol   Cal/Mol-Kelvin   Cal/Mol-Kelvin
 Total   249.530   112.166   206.392

         Item   Value   Threshold Converged?
 Maximum Force   0.000007   0.000450   YES
 RMS   Force   0.000001   0.000300   YES
 Maximum Displacement   0.002031   0.001800   NO
 RMS   Displacement   0.000483   0.001200   YES

 Normal termination of Gaussian 16 at Thu Jan 13 00:05:19 2022.

  -----------Figure S4-8, Int14----------

  vita-b6int13q.high.log

  Stoichiometry   C11H22N2O11P(1-)

                 Standard orientation:

 Center   Atomic   Atomic   Coordinates (Angstroms)
```

Number	Number	Type	X	Y	Z
1	6	0	-3.421996	-0.155082	0.742043
2	6	0	-4.430595	-0.195390	-0.276287
3	7	0	-4.102661	0.094286	-1.539803
4	6	0	-2.868135	0.425996	-1.961459
5	6	0	-1.836329	0.447148	-1.044459
6	6	0	-2.091862	0.136662	0.293391
7	6	0	-5.842138	-0.532824	0.053648
8	8	0	-3.716284	-0.375596	1.951238
9	6	0	-1.019149	0.174258	1.350627
10	6	0	-0.453949	0.785349	-1.539594
11	8	0	0.082145	1.852698	-0.763486
12	15	0	1.703332	2.095986	-0.755235
13	8	0	1.946238	3.078304	0.351104
14	8	0	2.273639	0.646017	-0.291664
15	8	0	2.175764	2.370935	-2.161226
16	1	0	-2.758597	0.655042	-3.010755
17	1	0	1.839370	2.407962	2.016185
18	8	0	1.627248	1.972717	2.867466
19	1	0	0.668526	1.763579	2.768256
20	1	0	2.421496	0.505751	2.997095
21	8	0	2.849680	-0.388075	3.053078
22	1	0	2.878372	-0.618667	3.983861
23	1	0	-4.841777	0.072676	-2.232579
24	7	0	-1.002057	1.445421	2.094119
25	1	0	2.122238	-1.425082	2.086361
26	1	0	-1.865618	1.533148	2.620309
27	8	0	1.548445	-2.011790	1.501527
28	6	0	2.190329	-2.457198	0.450894
29	8	0	3.365621	-2.320958	0.216635
30	6	0	1.249067	-3.219149	-0.526714
31	8	0	1.748262	-3.784423	-1.465832
32	6	0	-0.222262	-3.192842	-0.248460
33	1	0	-0.754784	-3.750158	-1.017028
34	1	0	-0.421800	-3.618025	0.737945
35	1	0	-0.029725	0.013401	0.924457
36	1	0	-0.578661	-2.159770	-0.218698
37	1	0	-1.203693	-0.628429	2.066188
38	1	0	2.636081	0.144312	-1.045643
39	1	0	0.193211	-0.094488	-1.452738
40	1	0	-6.472519	-0.569716	-0.836001
41	1	0	-0.487929	1.071568	-2.594203
42	8	0	3.052737	-0.094191	-2.865291
43	1	0	2.830933	0.859383	-2.898047
44	1	0	3.984753	-0.158751	-3.082372
45	1	0	-5.883826	-1.499932	0.560372
46	1	0	-0.987293	2.204863	1.418581
47	1	0	-6.251569	0.206918	0.746601

Standard basis: 6-311+G(d,p) (6D, 7F)

715 basis functions
103 alpha electrons   103 beta electrons
    nuclear repulsion energy   2768.2749367387 Hartrees.
NAtoms= 47 NActive= 47

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
=================================
Model   : PCM.
Atomic radii   : UFF (Universal Force Field).

Solvent: Water, Eps= 78.355300 Eps(inf)= 1.777849

SCF Done: E(RwB97XD) = -1711.11222211 A.U. after 2 cycles
        NFock= 2 Conv=0.20D-08   -V/T= 2.0038

Zero-point correction=   0.366871 (a.u.)
Thermal correction to Energy=   0.397813
Thermal correction to Enthalpy=   0.398758
Thermal correction to Gibbs Free Energy=   0.302594
Sum of electronic and zero-point Energies=   -1710.745351
Sum of electronic and thermal Energies=   -1710.714409
Sum of electronic and thermal Enthalpies=   -1710.713465
Sum of electronic and thermal Free Energies=   -1710.809628

```
                    E (Thermal)           CV              S
                     KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total                 249.632         109.831          202.393


       Item              Value     Threshold  Converged?
Maximum Force          0.000025     0.000450     YES
RMS    Force           0.000006     0.000300     YES
Maximum Displacement   0.005832     0.001800     NO
RMS    Displacement    0.000975     0.001200     YES


Normal termination of Gaussian 16 at Sun Jan 23 21:07:04 2022.

  =================== Figure S5 ================

 Two conformations (a) and (b) of the external aldimine
 in Int3 of Scheme 4b.

  ------------------(a)-------------------

 vita-b6.ext-ald.high.log

 Stoichiometry   C11H14N2O7P(1-)

                   Standard orientation:
---------------------------------------------------------------------
Center    Atomic    Atomic        Coordinates (Angstroms)
Number    Number     Type        X          Y          Z
---------------------------------------------------------------------
    1        6         0      -1.302098   2.073847    0.085399
    2        6         0      -0.575849   3.320973   -0.056866
    3        7         0       0.742066   3.269861   -0.136735
    4        6         0       1.509282   2.141209   -0.099754
    5        6         0       0.909483   0.922123    0.034368
    6        6         0      -0.508832   0.870533    0.131857
    7        6         0      -1.285158   4.622111   -0.112879
    8        8         0      -2.558223   2.094062    0.162080
    9        6         0      -1.168279  -0.380959    0.284289
   10        6         0       1.760417  -0.325276    0.069987
   11        8         0       3.118580  -0.004335   -0.021058
   12       15         0       4.224072  -1.311472   -0.049052
   13        8         0       3.870204  -2.089551   -1.314619
   14        8         0       5.553513  -0.571466   -0.096405
   15        8         0       3.952468  -2.074126    1.245602
   16        1         0       2.572303   2.273659   -0.179722
   17        1         0      -0.592967   5.452094   -0.233599
   18        1         0      -1.994878   4.623786   -0.940751
   19        1         0      -1.866149   4.769454    0.798270
   20        1         0      -0.591766  -1.295292    0.334902
   21        1         0       1.557942  -0.872586    0.998700
   22        1         0       1.462711  -0.981385   -0.757752
   23        1         0       1.234221   4.151431   -0.235105
   24        7         0      -2.460296  -0.494744    0.374934
   25        6         0      -3.172306  -1.752942    0.556156
   26        1         0      -2.966572   0.405584    0.322234
   27        6         0      -4.048396  -2.101565   -0.647544
   28        8         0      -4.507255  -3.202693   -0.810597
   29        8         0      -4.268729  -1.065033   -1.460880
   30        1         0      -4.853069  -1.347681   -2.182279
   31        1         0      -2.433802  -2.548582    0.636513
   32        6         0      -4.026676  -1.714684    1.830004
   33        1         0      -3.385879  -1.556285    2.694352
   34        1         0      -4.762351  -0.912902    1.783304
   35        1         0      -4.547202  -2.662107    1.946234
---------------------------------------------------------------------

Standard basis: 6-311+G(2df,2p) (6D, 7F)

  890 basis functions
   83 alpha electrons      83 beta electrons
     nuclear repulsion energy   1829.7059307346 Hartrees.
NAtoms=  35 NActive=  35

Force inversion solution in PCM.
-----------------------------------------------------------
Polarizable Continuum Model (PCM)
=================================
Model            : PCM.
Atomic radii     : UFF (Universal Force Field).

Solvent: Water, Eps= 78.355300 Eps(inf)=  1.777849
```

```
          ----------------------------------------------------

SCF Done:  E(RB3LYP) =  -1405.73830722 A.U. after  1 cycles
         NFock=  1 Conv=0.25D-08     -V/T= 2.0040

Zero-point correction=                           0.261676 (a.u.)
Thermal correction to Energy=                    0.282658
Thermal correction to Enthalpy=                  0.283602
Thermal correction to Gibbs Free Energy=         0.208919
Sum of electronic and zero-point Energies=          -1405.476631
Sum of electronic and thermal Energies=             -1405.455650
Sum of electronic and thermal Enthalpies=           -1405.454705
Sum of electronic and thermal Free Energies=        -1405.529388

                E (Thermal)          CV                S
                 KCal/Mol       Cal/Mol-Kelvin  Cal/Mol-Kelvin
Total             177.370          76.446          157.183

        Item              Value    Threshold  Converged?
Maximum Force         0.000016     0.000450     YES
RMS     Force         0.000002     0.000300     YES
Maximum Displacement  0.001207     0.001800     YES
RMS     Displacement  0.000283     0.001200     YES

Normal termination of Gaussian 16 at Fri Nov 26 14:32:38 2021.

   --------------------(b)---------------------

 vita-b6.ext-aldb.high.log

 Stoichiometry    C11H14N2O7P(1-)

                 Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic          Coordinates (Angstroms)
Number     Number     Type         X           Y           Z
---------------------------------------------------------------------
    1          6          0      2.543233   -0.068003    0.224583
    2          6          0      3.576771   -1.082403    0.132628
    3          7          0      3.227922   -2.307875   -0.223895
    4          6          0      1.961902   -2.723790   -0.517432
    5          6          0      0.927036   -1.833702   -0.456153
    6          6          0      1.202308   -0.491964   -0.084528
    7          6          0      4.993958   -0.761169    0.428871
    8          8          0      2.856842    1.105625    0.556943
    9          6          0      0.128245    0.449227   -0.019966
   10          6          0     -0.470366   -2.309198   -0.787521
   11          8          0     -1.299124   -2.219502    0.353634
   12         15          0     -2.914318   -1.708191    0.138123
   13          8          0     -3.450423   -1.794471    1.557878
   14          8          0     -2.771920   -0.280495   -0.408153
   15          8          0     -3.523586   -2.688558   -0.856778
   16          1          0      1.855209   -3.760834   -0.785625
   17          1          0      5.637642   -1.630079    0.314579
   18          1          0      5.341461    0.032520   -0.233376
   19          1          0      5.083535   -0.380020    1.446729
   20          1          0     -0.903232    0.146226   -0.232996
   21          1          0     -0.869854   -1.707879   -1.609030
   22          1          0     -0.416027   -3.341847   -1.141760
   23          1          0      3.963311   -3.004362   -0.279632
   24          7          0      0.314414    1.692980    0.308364
   25          6          0     -0.767780    2.666000    0.402101
   26          1          0      1.289665    1.952801    0.517088
   27          6          0     -0.669819    3.752674   -0.667098
   28          8          0     -1.550439    4.553258   -0.855066
   29          8          0      0.480331    3.733062   -1.348965
   30          1          0      0.473352    4.457890   -1.994126
   31          1          0     -1.698881    2.131386    0.212753
   32          6          0     -0.808660    3.301529    1.796844
   33          1          0     -0.979464    2.530340    2.544537
   34          1          0      0.127354    3.810999    2.023313
   35          1          0     -1.620046    4.023443    1.844507
---------------------------------------------------------------------

Standard basis: 6-311+G(2df,2p) (6D, 7F)

  890 basis functions
   83 alpha electrons       83 beta electrons
      nuclear repulsion energy    1911.8204155953 Hartrees.
NAtoms=  35 NActive=  35
```

```
Force inversion solution in PCM.
-------------------------------------------------
Polarizable Continuum Model (PCM)
=================================
Model            : PCM.
Atomic radii     : UFF (Universal Force Field).
Polarization charges : Total charges.

Solvent : Water, Eps= 78.355300 Eps(inf)=  1.777849
-------------------------------------------------------

SCF Done:  E(RB3LYP) = -1405.74333803 A.U. after 1 cycles
        NFock=  1 Conv=0.11D-08     -V/T= 2.0040

Zero-point correction=                           0.262161 (a.u.)
Thermal correction to Energy=                    0.282859
Thermal correction to Enthalpy=                  0.283803
Thermal correction to Gibbs Free Energy=         0.210419
Sum of electronic and zero-point Energies=         -1405.481177
Sum of electronic and thermal Energies=            -1405.460479
Sum of electronic and thermal Enthalpies=          -1405.459535
Sum of electronic and thermal Free Energies=       -1405.532919

                E (Thermal)          CV              S
                KCal/Mol        Cal/Mol-Kelvin  Cal/Mol-Kelvin
Total             177.497           76.120          154.450

       Item              Value     Threshold  Converged?
Maximum Force          0.000035     0.000450     YES
RMS     Force          0.000007     0.000300     YES
Maximum Displacement   0.003507     0.001800     NO
RMS     Displacement   0.000688     0.001200     YES

Normal termination of Gaussian 16 at Fri Nov 26 15:02:43 2021.

   ===================Figure S6=====================

   ----- TS(Int3 -> Int9), TS of the H[1,3]migration-----

 vita-b6ts.int3-9a.high.log

 Stoichiometry    C11H22N2O11P(1-)

                  Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic          Coordinates (Angstroms)
Number     Number      Type         X           Y           Z
---------------------------------------------------------------------
    1         6           0       -1.387106    1.492134   -0.499156
    2         6           0       -0.748317    2.422650   -1.377961
    3         7           0        0.363351    2.058927   -2.009165
    4         6           0        0.972008    0.863470   -1.892453
    5         6           0        0.425493   -0.084497   -1.065983
    6         6           0       -0.752848    0.224591   -0.368811
    7         6           0       -1.309548    3.784312   -1.581006
    8         8           0       -2.450139    1.839253    0.115240
    9         6           0       -1.275037   -0.784455    0.595381
   10         6           0        1.092847   -1.442757   -0.965379
   11         8           0        2.437366   -1.434081   -1.349980
   12        15           0        3.622429   -0.987780   -0.210169
   13         8           0        4.880737   -1.603894   -0.790436
   14         8           0        3.621076    0.548564   -0.204380
   15         8           0        3.135750   -1.593757    1.112037
   16         1           0        1.892447    0.716468   -2.432442
   17         1           0       -0.722497    4.362278   -2.295293
   18         1           0       -2.339233    3.711276   -1.937891
   19         1           0       -1.337733    4.317164   -0.627437
   20         1           0       -0.567486   -1.164642    1.350561
   21         1           0        0.998482   -1.830576    0.053825
   22         1           0        0.560564   -2.131444   -1.633432
   23         1           0        0.801641    2.744400   -2.613765
   24         7           0       -2.634466   -0.625621    1.149911
   25         6           0       -2.778256   -1.821318    0.443899
   26         1           0       -3.044385    0.197626    0.686894
   27         1           0       -1.389622   -1.791111   -0.073350
   28         6           0       -3.473943   -1.846135   -0.925987
   29         8           0       -4.013094   -2.835317   -1.327498
   30         8           0       -3.410733   -0.673441   -1.523902
   31         1           0       -3.854753   -0.710252   -2.382690
```

```
32            6            0        -2.759579    -3.097501     1.211587
33            1            0        -2.080841    -3.017872     2.059414
34            1            0        -3.775698    -3.224669     1.599471
35            1            0        -2.513807    -3.951794     0.584390
36            8            0         0.951029    -1.256084     2.618411
37            1            0         0.855135    -0.302225     2.794529
38            1            0         1.773124    -1.345612     2.077292
39            8            0         0.604814     1.496802     2.905114
40            1            0        -0.292785     1.868065     2.847984
41            1            0         1.088922     1.844316     2.127840
42            8            0        -1.980443     2.583377     2.672319
43            1            0        -2.007325     3.539073     2.749794
44            1            0        -2.220541     2.386844     1.742121
45            8            0         2.031595     2.374076     0.739224
46            1            0         2.627734     3.098032     0.937919
47            1            0         2.612074     1.641257     0.377610
---------------------------------------------------------------------
```

Standard basis: 6-311+G(d,p) (6D, 7F)

  715 basis functions
  103 alpha electrons   103 beta electrons
      nuclear repulsion energy   2820.6819496994 Hartrees.
NAtoms=   47 NActive=   47

Force inversion solution in PCM.

Polarizable Continuum Model (PCM)
=================================
Model   : PCM.
Atomic radii   : UFF (Universal Force Field).

Solvent : Water, Eps= 78.355300 Eps(inf)= 1.777849

SCF Done: E(RwB97XD) = -1710.99408514 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman
                 1   2   3
                 A   A   A
Frequencies -- -464.3921   24.2984   30.4606

Zero-point correction=   0.362479 (a.u.)
Thermal correction to Energy=   0.392463
Thermal correction to Enthalpy=   0.393408
Thermal correction to Gibbs Free Energy=   0.300720
Sum of electronic and zero-point Energies=   -1710.631607
Sum of electronic and thermal Energies=   -1710.601622
Sum of electronic and thermal Enthalpies=   -1710.600678
Sum of electronic and thermal Free Energies=   -1710.693365

                  E (Thermal)   CV   S
                   KCal/Mol   Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total   246.274   108.996   195.078

       Item   Value   Threshold Converged?
Maximum Force   0.000020   0.000450   YES
RMS   Force   0.000004   0.000300   YES
Maximum Displacement   0.008472   0.001800   NO
RMS   Displacement   0.001405   0.001200   NO

Normal termination of Gaussian 16 at Sun Jun 5 05:49:49 2022.
```