Supporting Information
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Catalytic Zinc Complexes for Phosphate Diester Hydrolysis**
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## Supporting information

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Synthesis

6-Methyl-2-pyridinemethanol was purchased from Maybridge and used without further purification. It was converted to 6-methyl-2-(bromomethyl)-pyridine according to the method of Lippard et al.\(^1\)

\[ \text{L2} \]

3-(bis ((6-methylpyridin-2-yl) methyl) amino) propan-1-ol (L2)\(^2\)

To a solution of 6-methyl-2-(bromomethyl)-pyridine\(^1\) (535 mg, 2.89 mmol) in dry DMF (30 mL) were added 3-amino-1-propanol (100 µL, 1.32 mmol) and then \(N,N\)-Diisopropylethylamine (690 µL, 3.96 mmol). The reaction was stirred for 16 h at 70 °C. The solution was poured into 40 mL H\(_2\)O and the organic component was extracted with CH\(_2\)Cl\(_2\) (3 × 30 mL) and dried over MgSO\(_4\). The solvent was removed under reduce pressure and the product was purified using silica gel chromatography (EtOAc : MeOH - 9:1) to yield 350 mg of L2\(^2\) as a yellow oil (92%).

\[ \delta_H (400 \text{ MHz, CDCl}_3): 7.53 (2 \text{ H, t}, 7.5, \text{ Py-H}), 7.23 (2 \text{ H, d}, 7.5, \text{ Py-H}), 7.00 (2 \text{ H, d}, 7.4, \text{ Py-H}), 3.75 (4 \text{ H, s, Py-CH}_2), 2.73 (2 \text{ H, t}, 7.1, \text{ CH}_2\text{-O}), 2.56 (2 \text{ H, s, CH}_2\text{-N}), 2.55 (6 \text{ H, s, CH}_3), 1.70 (2 \text{ H, qn}, 7.6, \text{ C-CH}_2\text{-C}); \delta_C (101 \text{ MHz, CDCl}_3): 157.8 (\text{Py-N}), 136.9 (\text{Py}), 121.7 (\text{Py}), 120.0 (\text{Py}), 62.0 (\text{C-O}), 59.8 (\text{C-N}), 52.7 (\text{C-N}), 28.7 (\text{CH}_3), 24.2 (\text{CH}_3); \text{HRMS (TOF mode) calculated for C}_{17}\text{H}_{24}\text{N}_3\text{O (MH}^+\text{), 286.1919, found 286.1915} \]

3-(bis ((6-methylpyridin-2-yl)methyl)amino)-2,2-dimethylpropan-1-ol (L3)

To a solution of 3-amino-2,2-dimethyl-1-propanol (0.350 g, 3.39 mmol) in dry DMF (50 mL) were added 6-methyl-2-(bromomethyl)-pyridine\(^1\) (1.4 g, 7.57 mmol) and then \(N,N\)-Diisopropylethylamine (1.80 mL, 10.2 mmol). The reaction was stirred for 16 h at 70 °C. The solution was poured into 60 mL of H\(_2\)O and the organic component was extracted with CH\(_2\)Cl\(_2\) (3 × 40 mL) and dried over MgSO\(_4\). The solvent was removed under reduce pressure and the product was purified using silica gel chromatography (hexane: EtOAc - 1:9) to yield 0.73 g of L3 as a pale yellow oil (68%).

\[ \delta_H (400 \text{ MHz, CDCl}_3): 7.52 (2 \text{ H, t}, 7.5, \text{ Py-H}), 7.20 (2 \text{ H, d}, 7.5, \text{ Py-H}), 7.01 (2 \text{ H, d}, 7.4, \text{ Py-H}), 3.85 (4 \text{ H, s, Py-CH}_2), 3.35 (2 \text{ H, s, CH}_2\text{-O}), 2.60 (s, 2H, CH\text{-N}), 2.59 (s, 6H, CH\text{_3}), 0.91 (s, 6H, CH\text{_3}); \delta_C (101 \text{ MHz, CDCl}_3): 158.4 (\text{Py-N}), 157.7 (\text{Py-N}), 136.7 (\text{Py}), 121.6 (\text{Py}), 120.2 (\text{Py}), 71.3 (\text{C-O}), 64.3 (\text{C-N}), 62.7 (\text{C-N}), 36.8 (\text{C-CH}_3), 24.8 (\text{CH}_3), 24.3 (\text{CH}_3); \text{HRMS (TOF mode) calculated for C}_{19}\text{H}_{32}\text{N}_3\text{O (MH}^+\text{), 314.2232, found 314.2242} \]

S2
3-(bis (6-methylpyridin-2-yl) methyl amino)-2, 2-dimethylpropan-1-ol (L4)
A solution of Dess Martin periodinanone (0.83 g, 1.97 mmol) in 20 mL dry CH$_2$Cl$_2$ was added to a solution of 3-(bis(6-methylpyridin-2-yl)methylamino)-2,2-dimethylpropan-1-ol (L3) (0.56 g, 1.79 mmol) in 20 mL of dry CH$_2$Cl$_2$ at 0 °C under a nitrogen atmosphere. After 2 h at room temperature, 40 mL of H$_2$O was added to the reaction mixture and the organic component was extracted with CH$_2$Cl$_2$ (3 × 20 mL). The extract was dried over MgSO$_4$ and the solvent removed under reduced pressure. The product was purified using silica gel chromatography (EtOAc) to yield 0.36 g of L4 as a pale yellow oil (64%).

δ$_{H}$ (400 MHz, CDCl$_3$): 9.26 (1 H, s, O=C-H), 7.56 (2 H, t, 7.5, Py-H), 7.29 (2 H, d, 7.5, Py-H), 7.05 (2 H, d, 7.4, Py-H), 3.78 (4 H, s, Py-CH$_2$), 2.91 (2 H, s, CH$_2$-N), 2.55 (6 H, s, CH$_3$), 1.01 (6 H, s, CH$_3$); δ$_{C}$ (101 MHz, CDCl$_3$): 206.2 (C=O), 158.8 (Py-N), 157.5 (Py-N), 136.7 (Py), 121.6 (Py), 120.0 (Py), 62.1 (C-N), 61.5 (C-N), 41.1 (C-C), 24.3 (CH$_3$), 20.4 (CH$_3$); HRMS (TOF mode) calculated for C$_{19}$H$_{26}$N$_3$O (MH$^+$), 312.2076, found 312.2068

3-(bis(6-methylpyridin-2-yl)methyl)amino)-2,2-dimethylpropane (L5)
To a solution of 2,2-dimethylpropan-1-amine (0.60 mL, 0.44 g, 4.9 mmol) in dry DMF (50 mL) was added 6-methyl-2-(bromomethyl)-pyridine$^1$ (2.00 g, 10.8 mmol) and K$_2$CO$_3$ (1.49 g, 10.8 mmol). The solution was stirred at 40 °C for 16 h. The organic component was extracted into CH$_2$Cl$_2$ (3 × 40 mL), the extract dried over MgSO$_4$, filtered and the solvent was removed under reduced pressure. The product was purified using silica gel chromatography (Hexane : EtOAc - 10:1) to yield 1.28 g of L5 as a pale yellow solid (88%).

δ$_{H}$ (400 MHz, CDCl$_3$): 7.57 (2 H, t, 7.5, Py-H), 7.41 (2 H, d, 7.5, Py-H), 7.00 (2 H, d, 7.4, Py-H), 3.85 (4 H, s, Py-CH$_2$), 2.55 (6 H, s, CH$_3$), 2.54 (2 H, s, CH$_2$-N), 0.80 (9 H, s, CH$_3$); δ$_{C}$ (101 MHz, CDCl$_3$): 159.9 (Py-N), 157.4 (Py-N), 136.4 (Py), 121.2 (Py), 119.9 (Py), 66.6 (C-N), 63.1 (C-N), 33.1 (q C-C), 28.2 (CH$_3$), 24.5 (CH$_3$); HRMS (TOF mode) calculated for C$_{19}$H$_{26}$N$_3$ (MH$^+$), 298.2283, found 298.2278

Zn complex of L4 [4',(NO$_3$)$_2$]
A solution of Zn(NO$_3$)$_2$(H$_2$O)$_6$ (24 mg, 0.081 mmol in 2 mL MeOH) was added to a solution of L4 (23 mg, 0.074 mmol in 2 mL MeOH). After 10 min stirring, the solution was filtered and the volume reduced to 1 mL. Et$_2$O was introduced by slow diffusion and colourless crystals of X-ray quality were collected after two days (27 mg, 70% yield).
Crystallographic details for Zn complex of L4 [4'(NO₃)₂]

Figure S1. Representation of the X-ray crystal structure of 4'(NO₃)₂ (50% probability ellipsoids; hydrogen atoms and non-coordinated nitrate omitted for clarity). Selected bond distances: Zn(1)-N(1) = 2.131 Å; Zn(1)-N(2) = 2.149 Å; Zn(1)-N(3) = 2.062 Å; Zn(1)-O(1) = 2.534 Å; Zn(1)-O(2) = 2.045 Å; Zn(1)-O(3) = 2.076 Å

Empirical formula
C₂₀H₂₉N₅O₈Zn

Formula weight
532.85

Temperature
100(2) K

Wavelength
0.71073 Å

Crystal system
Orthorhombic

Space group
Pbca

Unit cell dimensions
a = 14.9370(4) Å  α = 90°.
b = 16.1280(4) Å  β = 90°.
c = 19.7011(5) Å  γ = 90°.

Volume
4746.1(2) Å³

Z
8

Density (calculated)
1.491 Mg/m³

Absorption coefficient
1.090 mm⁻¹

F(000)
2224

Crystal size
0.32 x 0.21 x 0.18 mm³

Theta range for data collection
2.07 to 27.87°.

Index ranges
-19<=h<=19, -21<=k<=21, -25<=l<=25

Reflections collected
101826

Independent reflections
5588 [R(int) = 0.0495]

Completeness to theta = 27.87°
98.7 %

Absorption correction
Semi-empirical from equivalents

Max. and min. transmission
0.8280 and 0.7218

Refinement method
Full-matrix least-squares on F²

Data / restraints / parameters
5588 / 0 / 315

Goodness-of-fit on F²
0.887

Final R indices [I>2sigma(I)]
R1 = 0.0310, wR2 = 0.0910

R indices (all data)
R1 = 0.0362, wR2 = 0.0963

Largest diff. peak and hole
0.520 and -0.412 e Å⁻³
Kinetic data for Zn complex 2.

Figure S2. pH rate profile for the transesterification of BNPP catalysed by Zn complex 2 (50 mM buffer; 0.1 M ionic strength (NaNO₃); 25 °C). The solid line is the least squares fit of equation 1 (main text) to the data.

Titration data and speciation curves of L2 and Zn complex 2.

Figure S3. left: titration of 10 mL of 2 mM L2 and 4 mM HCl with 10 µL aliquots of 0.2 mM NaOH; right: speciation diagram of 1mM L2. The theoretical fit and speciation were carried out with Hyperquad and HySS software and gave pKₐs of 3.85 and 6.99.

Figure S4. left: titration of 10 mL of 2 mM Zn complex 2 and 4 mM HCl with 10 µL aliquots of 0.2 mM NaOH; right: speciation diagram of 1 mM 2. The theoretical fit and speciation were carried out with Hyperquad and HySS software using formation constants for Zn(OH) (10⁻⁷.84) and Zn(OH)₂ (10⁻¹⁶.85) taken from literature. The fit gives pKₐs for the Zn complex 2 of 7.84 and 9.02, and log Kₐ as 4.85.
Kinetic data for Zn complex 3.

Figure S5. Plots of observed rate constants for the transesterification of BNPP (2 mM) against concentration of Zn complex 3. Left: pH from 6.74 to 7.99; right: pH from 8.63 to 9.91. The solid lines are the least squares fit of equation S1 to the data.

Observed rate constants \( (k_{\text{obs}}) \) were obtained by the initial rate method over the first 30 minutes of the reaction. Equation S1 is derived from Scheme S1, and fitted to the data in Tables S1 to S8 to give the values of \( k_2 \) used in Figure S5.

\[
k_{\text{obs}} = k_2 \times \frac{1}{2} \left\{ (K_d + [\text{Zn}]_T + [\text{L}]_T) - \sqrt{(K_d + [\text{Zn}]_T + [\text{L}]_T)^2 - 4[\text{Zn}]_T[\text{L}]_T} \right\}
\]

Equation S1

Zn + L \rightleftharpoons \text{ZnL} \quad K_d \quad \text{BNPP} \quad k_2 \quad \text{products}

Scheme S1

| [3] mM | \( k_{\text{obs}} \) s\(^{-1}\) at pH 6.74 | \( k_{\text{obs}} \) s\(^{-1}\) at pH 7.23 | \( k_{\text{obs}} \) s\(^{-1}\) at pH 7.62 | \( k_{\text{obs}} \) s\(^{-1}\) at pH 7.99 |
|--------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 0.2    | 6.6±0.4×10\(^{-9}\)            | 2.04±0.01×10\(^{-7}\)            | 4.59±0.02×10\(^{-7}\)            | 9.9±0.2×10\(^{-7}\)            |
| 0.4    | 1.83±0.08×10\(^{-7}\)          | 5.11±0.02×10\(^{-7}\)            | 1.074±0.002×10\(^{-6}\)          | 2.233±0.007×10\(^{-6}\)        |
| 0.6    | 3.03±0.03×10\(^{-7}\)          | 8.42±0.02×10\(^{-7}\)            | 1.722±0.009×10\(^{-6}\)          | 3.479±0.005×10\(^{-6}\)        |
| 0.8    | 4.50±0.01×10\(^{-7}\)          | 1.183±0.002×10\(^{-6}\)          | 2.42±0.01×10\(^{-6}\)            | 4.780±0.004×10\(^{-6}\)        |
| 1.0    | 5.72±0.06×10\(^{-7}\)          | 1.530±0.001×10\(^{-6}\)          | 3.10±0.02×10\(^{-6}\)            | 6.072±0.005×10\(^{-6}\)        |

| [3] mM | \( k_{\text{obs}} \) s\(^{-1}\) at pH 8.63 | \( k_{\text{obs}} \) s\(^{-1}\) at pH 9.12 | \( k_{\text{obs}} \) s\(^{-1}\) at pH 9.52 | \( k_{\text{obs}} \) s\(^{-1}\) at pH 9.91 |
|--------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 0.2    | 1.63±0.01×10\(^{-6}\)          | 1.070±0.007×10\(^{-6}\)         | 5.7±0.1×10\(^{-7}\)            | 2.34±0.05×10\(^{-7}\)          |
| 0.4    | 3.35±0.02×10\(^{-6}\)          | 2.084±0.002×10\(^{-6}\)         | 1.07±0.01×10\(^{-7}\)          | 4.50±0.07×10\(^{-7}\)          |
| 0.6    | 5.023±0.02×10\(^{-6}\)         | 3.105±0.009×10\(^{-6}\)         | 1.60±0.03×10\(^{-6}\)          | 6.5±0.4×10\(^{-7}\)            |
| 0.8    | 6.61±0.08×10\(^{-6}\)          | 4.12±0.02×10\(^{-6}\)           | 2.13±0.01×10\(^{-6}\)          | 8.1±0.3×10\(^{-7}\)            |
| 1.0    | 8.28±0.08×10\(^{-6}\)          | 5.22±0.04×10\(^{-6}\)           | 2.78±0.02×10\(^{-6}\)          | 1.11±0.04×10\(^{-6}\)          |

Table S1. Observed rate constants for the cleavage of BNPP in the presence of Zn complex 3 (50 mM buffer; 0.1 M ionic strength (NaNO\(_3\)); 25 °C)
Figure S6. pH rate profile for the transesterification of BNPP catalysed by Zn complex 3 (50 mM buffer; 0.1 M ionic strength (NaNO₃); 25 °C). The solid line is the least squares fit of equation 1 (main text) to the data.

Figure S7. Plots of the dependence of the change in absorbance at 400 nm on BNPP concentration in the presence of 1 mM Zn complex 3 (25 °C, 50 mM buffer, 0.1 M ionic strength (NaNO₃), pH = 8.1), demonstrating first order dependence of rate on [BNPP]. The solid line is the linear least squares fit to the data.

Figure S8. Plots of the dependence of the limiting second order rate constant $k_2$ for the transesterification of BNPP (2 mM) on buffer concentration in the presence of Zn complex 3 (25 °C, 0.1 M ionic strength (NaNO₃), pH = 8.1), demonstrating the absence of buffer catalysis.
Titration data and speciation curves of L3 and Zn complex 3.

Figure S9. left: titration of 10 mL of 2 mM L3 and 4 mM HCl with 10 µL aliquots of 0.2 mM NaOH; right: speciation diagram of 1mM L3. The theoretical fit and speciation were carried out with Hyperquad and HySS software and gave pK_a values of 3.58 and 6.71.

Figure S10. left: titration of 10 mL of 2 mM Zn complex 3 and 4 mM HCl with 10 µL aliquots of 0.2 mM NaOH; right: speciation diagram of 1 mM Zn complex 3. The theoretical fit and speciation were carried out with Hyperquad and HySS software using formation constants for Zn(OH) (10^{-7.84}) and Zn(OH)_2 (10^{-16.86}) taken from literature. The fit gives pK_a values for the Zn complex 2 of 8.17 and 8.46, and log K_d as 3.80.
Kinetic data for Zn complex 4.

![Graphs showing observed rate constants for the transesterification of BNPP in the presence of Zn complex 4.](image)

Figure S11. Plots of observed rate constants for the transesterification of BNPP (2 mM) against concentration of Zn complex 4. Left: pH from 6.76 to 8.03; right: pH from 8.62 to 9.91. The solid lines are the least squares fit of equation S1 to the data.

Observed rate constants ($k_{obs}$) were obtained by the initial rate method over the first 30 minutes of the reaction. Equation S1 derived from Scheme S1 was fitted to the data in Tables S10 to S17 to give the values of $k_2$ used in Figure S12.

| [4] mM     | $k_{obs}$ s$^{-1}$ at pH 6.76 | $k_{obs}$ s$^{-1}$ at pH 7.27 | $k_{obs}$ s$^{-1}$ at pH 7.63 | $k_{obs}$ s$^{-1}$ at pH 8.03 |
|------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 0.2        | 1.40±0.02×10$^{-7}$           | 3.76±0.07×10$^{-7}$           | 7.33±0.09×10$^{-7}$           | 1.46±0.08×10$^{-7}$           |
| 0.4        | 3.33±0.3×10$^{-7}$            | 1.001±0.001×10$^{-6}$         | 2.004±0.001×10$^{-6}$         | 3.71±0.01×10$^{-6}$           |
| 0.6        | 6.55±0.01×10$^{-7}$           | 1.778±0.007×10$^{-6}$         | 3.49±0.01×10$^{-6}$           | 6.21±0.01×10$^{-6}$           |
| 0.8        | 9.77±0.04×10$^{-7}$           | 2.630±0.004×10$^{-6}$         | 5.08±0.03×10$^{-6}$           | 8.79±0.01×10$^{-6}$           |
| 1.0        | 1.35±0.002×10$^{-6}$          | 3.546±0.007×10$^{-6}$         | 6.74±0.03×10$^{-6}$           | 1.139±0.002×10$^{-5}$         |

| [4] mM     | $k_{obs}$ s$^{-1}$ at pH 8.62 | $k_{obs}$ s$^{-1}$ at pH 9.11 | $k_{obs}$ s$^{-1}$ at pH 9.47 | $k_{obs}$ s$^{-1}$ at pH 9.91 |
|------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 0.2        | 1.98±0.09×10$^{-6}$           | 1.01±0.01×10$^{-6}$           | 5.30±0.06×10$^{-7}$           | 2.00±0.07×10$^{-7}$           |
| 0.4        | 4.14±0.05×10$^{-6}$           | 2.12±0.04×10$^{-6}$           | 1.055±0.004×10$^{-6}$         | 3.52±0.1×10$^{-7}$            |
| 0.6        | 6.27±0.1×10$^{-6}$            | 3.09±0.03×10$^{-6}$           | 1.53±0.04×10$^{-6}$           | 5.4±0.5×10$^{-7}$             |
| 0.8        | 8.36±0.1×10$^{-6}$            | 4.13±0.01×10$^{-6}$           | 1.99±0.01×10$^{-6}$           | 6.80±0.1×10$^{-7}$            |
| 1.0        | 1.08±0.01×10$^{-5}$           | 5.28±0.03×10$^{-6}$           | 2.60±0.01×10$^{-6}$           | 9.56±0.08×10$^{-7}$           |

Table S2. Observed rate constants for the cleavage of BNPP in the presence of Zn complex 4 (50 mM buffer; 0.1 M ionic strength (NaNO$_3$); 25 °C)
Figure S12. pH rate profile for the transesterification of BNPP catalysed by Zn complex 4 (50 mM buffer; 0.1 M ionic strength (NaNO₃); 25 °C). The solid line is the least squares fit of equation 1 (main text) to the data.

| pH   | k₂ M⁻¹ s⁻¹ | Standard deviation | log(k₂) M⁻¹ s⁻¹ |
|------|-------------|--------------------|-----------------|
| 6.76 | 3.01x10⁻²   | 0.3x10⁻³           | -2.52           |
| 7.26 | 6.57x10⁻³   | 0.2x10⁻³           | -2.18           |
| 7.63 | 1.15x10⁻²   | 0.005x10⁻²         | -1.94           |
| 8.03 | 1.64x10⁻²   | 0.02x10⁻²          | -1.79           |
| 8.62 | 1.10x10⁻²   | 0.02x10⁻²          | -1.96           |
| 9.11 | 5.27x10⁻³   | 0.08x10⁻³          | -2.28           |
| 9.47 | 2.34x10⁻²   | 0.07x10⁻²          | -2.60           |
| 9.91 | 9.20x10⁻⁴   | 0.6x10⁻³           | -3.04           |

Figure S13. Plot of the dependence of the change in absorbance at 400 nm on BNPP concentration in the presence of 1 mM Zn complex 4 (25 °C, 50 mM buffer, 0.1 M ionic strength (NaNO₃), pH = 8.0), demonstrating first order dependence of rate on [BNPP].

| [BNPP] mM | gradient Abs |
|-----------|--------------|
| 0.4       | 6.90 x 10⁻⁴ |
| 0.8       | 1.32 x 10⁻⁴ |
| 1.2       | 1.90 x 10⁻⁴ |
| 1.6       | 2.46 x 10⁻⁴ |
| 2         | 2.98 x 10⁻⁴ |

Figure S14. Plots of the dependence of the limiting second order rate constant k₂ for the transesterification of BNPP (2 mM) on buffer concentration in the presence of Zn complex 4 (25 °C, 0.1 M ionic strength (NaNO₃), pH = 8.1), demonstrating the absence of buffer catalysis.

| [buffer] mM | k₂ M⁻¹ s⁻¹ |
|-------------|------------|
| 50          | 1.64±0.01 x 10⁻² |
| 75          | 1.60±0.01 x 10⁻² |
| 100         | 1.49±0.02 x 10⁻² |
| 125         | 1.51±0.01 x 10⁻² |
Figure S15. Dependence of $k_{obs}$ on the Zn:ligand ratio; left: pH 6.72; right: pH 7.44. [L4] = 0.2 mM; 0.1 M ionic strength (NaNO$_3$); 25 °C. Solid lines are from linear least squares fitting equation S2 (derived from scheme S1) to the data and yield to $K_d^{app} = 1.2 \pm 0.3$ mM and $k_2 = 3.1 \pm 0.1 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}$ at pH = 6.72 and $K_d^{app} = 0.48 \pm 0.06$ mM and $k_2 = 4.1 \pm 0.1 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}$ at pH = 7.44.

$$k_{obs} = k_2 \times \frac{1}{2} \left\{ (K_d^{app} + [\text{Zn}])_T + [L4]_T \right\} - \frac{\left\{ (K_d^{app} + [\text{Zn}])_T + [L4]_T \right\}^2 - 4[\text{Zn}]_T[L4]_T}{4}$$

Equation S2

The values of the conditional dissociation constant $K_d^{app}$ differ by a factor of ~2.6 fold, which is in good agreement with variation expected at these pHs based on the $pK_a$ of L4 (6.91) and the first $pK_a$ of the Zn complex of 4 (8.09) established by potentiometric titration. The limiting second rate constants agree well with the data obtained at constant Zn:ligand ratio; the $K_d$ values are about 4 fold greater than obtained from potentiometric titration (0.12 mM).
Titration data and speciation curves of L4 and Zn complex 4.

Figure S16. left: titration of 10 mL of 2 mM L4 and 4 mM HCl with 10 µL aliquots of 0.2 mM NaOH; right: speciation diagram of 1mM L4. The theoretical fit and speciation were carried out with Hyperquad and HySS software and gave pKₘₙ₃s of 4.23 and 6.91.

Figure S17. left: titration of 10 mL of 2 mM Zn complex 4 and 4 mM HCl with 10 µL aliquots of 0.2 mM NaOH; right: speciation diagram of 1 mM 4. The theoretical fit and speciation were carried out with Hyperquad and HySS software using formation constants for Zn(OH) (10⁻⁷.84) and Zn(OH)₂ (10⁻₁₆.86) taken from literature. The fit gives pKₘₙ₃s for the Zn complex 2 of 8.09 and 8.23, and log Kₘₙ₃ as 3.94.
Product analysis of the cleavage of BNPP by Zn complexes 3, 4 and 5.

Figure S18. $^{31}$P NMR spectra for the reaction of 5 mM BNPP with 1 mM Zn complex 3 (pH 8.5) at 25 °C. The slow appearance of 4-nitrophenyl phosphate is accounted for by the background reaction of BNPP.

Figure S19. $^{31}$P NMR spectra for the reaction of 5 mM BNPP with 1 mM Zn complex 4 (pH 8.5) at 25 °C.

Figure S20. $^{31}$P NMR spectra for the reaction of 5 mM BNPP with 1 mM Zn complex 5 (pH 7.0) at 25 °C.
Cleavage of BNPP in methanol by Zn complexes 2, 3 and 4'.
The reactions in dry methanol led to the loss of both leaving groups from BNPP, with the second reaction much slower than the first. Thus, a sequential reaction scheme (scheme 2) was used to fit the appearance of both equivalents of 4-nitrophenol (equation S3). This yielded the observed rate constant for the initial reaction between the complex and BNPP, given in tables S3, S4 and S5. Plots of $k_{obs}$ against [complex] show an upward curvature that is very similar to the behaviour of the complexes in water at lower pH. However, in methanol, it can be explained by cooperativity between two complexes as described by Mohamed et al.\textsuperscript{5} This reaction scheme is given in scheme 3, and leads to equation S4. The $k_2$ values have been obtained by fitting equation S4 to the data in tables S3, S4 and S5 derived by Mohamed et al.\textsuperscript{5} Although the active species may be involve a second metal ion complex, the variation in the nucleophile structure is the only change between each complex.

![Figure S21. Typical kinetic trace for the cleavage of BNPP (50 µM) in MeOH in the presence of the triflate salt of Zn complex 3 (3mM) at 25 °C (50 mM buffer). The red line is the linear least squares fit of equation S3 to the data.](image)

$$\text{BNPP} \xrightarrow{k_1} 1 + 4\text{-nitrophenol} \xrightarrow{k_2} P + 4\text{-nitrophenol}$$

Scheme S2.

$$\text{Abs} = \epsilon_P [A]_0 \left( \frac{1}{k_2 - k_1} \right) \left\{ \left( 2k_2 - k_1 \right) \left( 1 - e^{-k_1 t} \right) - k_1 \left( 1 - e^{-k_2 t} \right) \right\} + \epsilon_P [B]_0 \left( 1 - e^{-k_1 t} \right) + \epsilon_P [P]_0$$

Equation S3

$$\text{Complex} + \text{BNPP} \xleftrightarrow{K_d} \text{Complex.BNPP} \xrightarrow{k} \text{products}$$

Scheme S3.

$$k_{obs} = k \times \frac{1}{2} \left\{ (k_d + [\text{Complex}]_T + [\text{BNPP}]_T) - \sqrt{(k_d + [\text{Complex}]_T + [\text{BNPP}]_T)^2 - 4[\text{Complex}]_T[\text{BNPP}]_T} \right\}$$

Equation S4
| [2] mM | $s_pH = 8.01$ | $s_pH = 8.43$ | $s_pH = 8.81$ | $s_pH = 9.01$ | $s_pH = 10.25$ | $s_pH = 10.73$ | $s_pH = 11.03$ |
|-------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 0.5   | $1.826 \times 10^{-5}$ | $5.882 \times 10^{-5}$ | $2.095 \times 10^{-4}$ | $2.944 \times 10^{-4}$ | $3.759 \times 10^{-4}$ | $3.061 \times 10^{-4}$ | $3.730 \times 10^{-4}$ |
| 1     | $7.366 \times 10^{-5}$ | $2.655 \times 10^{-4}$ | $7.836 \times 10^{-4}$ | $1.280 \times 10^{-3}$ | $8.089 \times 10^{-4}$ | $6.680 \times 10^{-4}$ | $6.922 \times 10^{-4}$ |
| 1.5   | $1.990 \times 10^{-4}$ | $2.656 \times 10^{-4}$ | $1.537 \times 10^{-3}$ | $2.379 \times 10^{-3}$ | $1.312 \times 10^{-3}$ | $1.033 \times 10^{-3}$ | $1.017 \times 10^{-3}$ |
| 2     | $3.140 \times 10^{-4}$ | $9.328 \times 10^{-4}$ | $2.498 \times 10^{-3}$ | $3.519 \times 10^{-3}$ | $2.088 \times 10^{-3}$ | $1.413 \times 10^{-3}$ | $1.424 \times 10^{-3}$ |
| 2.5   | $5.104 \times 10^{-4}$ | $1.373 \times 10^{-3}$ | $3.570 \times 10^{-3}$ | $4.936 \times 10^{-3}$ | $2.851 \times 10^{-3}$ | $1.962 \times 10^{-3}$ | $1.778 \times 10^{-3}$ |
| 3     | $6.768 \times 10^{-4}$ | $1.822 \times 10^{-3}$ | $4.212 \times 10^{-3}$ | $6.205 \times 10^{-3}$ | $3.798 \times 10^{-3}$ | $2.429 \times 10^{-3}$ | $2.102 \times 10^{-3}$ |

Table S3. Observed rate constants for the cleavage of BNPP (50 μM) catalysed by the triflate salt of Zn complex 2 (50 mM buffer; 25 °C).

| [3] mM | $s_pH = 8.03$ | $s_pH = 8.41$ | $s_pH = 8.61$ | $s_pH = 8.99$ | $s_pH = 9.33$ | $s_pH = 10.33$ | $s_pH = 10.64$ |
|-------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 0.5   | $1.536 \times 10^{-4}$ | $3.225 \times 10^{-5}$ | $1.232 \times 10^{-4}$ | $2.190 \times 10^{-4}$ | $3.161 \times 10^{-4}$ | $2.290 \times 10^{-4}$ | $2.030 \times 10^{-4}$ |
| 1     | $9.123 \times 10^{-5}$ | $1.841 \times 10^{-4}$ | $1.301 \times 10^{-3}$ | $1.346 \times 10^{-3}$ | $1.666 \times 10^{-3}$ | $1.170 \times 10^{-3}$ | $9.140 \times 10^{-4}$ |
| 1.5   | $1.680 \times 10^{-4}$ | $6.374 \times 10^{-5}$ | $2.005 \times 10^{-3}$ | $2.060 \times 10^{-3}$ | $3.532 \times 10^{-3}$ | $2.240 \times 10^{-3}$ | $1.430 \times 10^{-3}$ |
| 2     | $2.860 \times 10^{-4}$ | $7.551 \times 10^{-5}$ | $2.874 \times 10^{-3}$ | $3.580 \times 10^{-3}$ | $5.557 \times 10^{-3}$ | $3.730 \times 10^{-3}$ | $2.360 \times 10^{-3}$ |
| 2.5   | $4.080 \times 10^{-4}$ | $1.051 \times 10^{-3}$ | $3.958 \times 10^{-3}$ | $4.970 \times 10^{-3}$ | $7.577 \times 10^{-3}$ | $5.890 \times 10^{-3}$ | $3.260 \times 10^{-3}$ |
| 3     | $5.170 \times 10^{-4}$ | $1.470 \times 10^{-3}$ | $6.360 \times 10^{-3}$ | $1.119 \times 10^{-2}$ | $7.270 \times 10^{-3}$ | $4.150 \times 10^{-3}$ | |

Table S4. Observed rate constants for the cleavage of BNPP (50 μM) catalysed by the triflate salt of Zn complex 3 (50 mM buffer; 25 °C).

| [4] mM | $s_pH = 8.05$ | $s_pH = 8.37$ | $s_pH = 8.52$ | $s_pH = 8.89$ | $s_pH = 9.24$ | $s_pH = 10.16$ |
|-------|--------------|--------------|--------------|--------------|--------------|--------------|
| 0.5   | $4.130 \times 10^{-6}$ | $6.784 \times 10^{-6}$ | $1.153 \times 10^{-5}$ | $1.344 \times 10^{-5}$ | $2.171 \times 10^{-5}$ | $7.617 \times 10^{-6}$ |
| 1     | $1.232 \times 10^{-5}$ | $2.003 \times 10^{-5}$ | $2.562 \times 10^{-5}$ | $3.336 \times 10^{-5}$ | $4.210 \times 10^{-5}$ | $1.956 \times 10^{-5}$ |
| 1.5   | $2.021 \times 10^{-5}$ | $3.264 \times 10^{-5}$ | $3.948 \times 10^{-5}$ | $5.321 \times 10^{-5}$ | $7.363 \times 10^{-5}$ | $2.909 \times 10^{-5}$ |
| 2     | $2.769 \times 10^{-5}$ | $4.167 \times 10^{-5}$ | $6.065 \times 10^{-5}$ | $8.287 \times 10^{-5}$ | $8.945 \times 10^{-5}$ | $4.117 \times 10^{-5}$ |
| 2.5   | $3.741 \times 10^{-5}$ | $6.147 \times 10^{-5}$ | $7.288 \times 10^{-5}$ | $1.035 \times 10^{-4}$ | $1.316 \times 10^{-4}$ | $5.137 \times 10^{-5}$ |
| 3     | $4.529 \times 10^{-5}$ | $7.365 \times 10^{-5}$ | $8.813 \times 10^{-5}$ | $1.260 \times 10^{-4}$ | $1.490 \times 10^{-4}$ | $5.880 \times 10^{-5}$ |

Table S5. Observed rate constants for the cleavage of BNPP (50 μM) catalysed by the triflate salt of Zn complex 4’ (50 mM buffer; 25 °C).

| 2     | 3     | 4’    |
|-------|-------|-------|
| $s_pH$ | Log $k_2$ M$^{-1}$ s$^{-1}$ | $s_pH$ | Log $k_2$ M$^{-1}$ s$^{-1}$ | $s_pH$ | Log $k_2$ M$^{-1}$ s$^{-1}$ |
| 8.01  | 0.324 | 8.03  | -0.275 | 8.05  | -1.674 |
| 8.43  | 0.423 | 8.41  | 0.117  | 8.37  | -1.444 |
| 8.81  | 0.516 | 8.61  | 0.478  | 8.52  | -1.450 |
| 9.09  | 0.645 | 8.99  | 0.745  | 8.89  | -1.22  |
| 10.25 | 0.437 | 9.33  | 1.263  | 9.24  | -1.221 |
| 10.73 | 0.042 | 10.33 | 0.994  | 10.16 | -1.635 |
| 11.03 | -0.150| 10.64 | 0.498  |       |       |

Table S6. Dependence of the limiting rate constant $k_2$ for the cleavage of BNPP in dry methanol catalysed by the triflate salts of Zn complexes 2, 3 and 4’ on the $s_pH$ (50 mM buffer; 25 °C).
Figure S22. pH rate profile for the cleavage of BNPP in dry methanol (50 mM buffer, 25 °C) catalysed by triflate salts of the Zn complexes 2 (green); 3 (red) and 4' (blue). The solid line is the least squares fit of equation 1 (main text) to the data.
Computational Methods.
Initial geometry optimizations were performed at the Hartree Fock (HF) level of theory using the 6-31+G* basis set. Hay and Wadt’s effective core potential with the double-ζ valence basis set (LANL2DZ$^6$,$^7$) was used to describe zinc. The resulting structures were characterised by frequency calculations. Single point energy calculations on the optimized structures were performed at the DFT level of theory using the dispersion corrected M06-2X functional$^8$ with a larger (6-311+G**) basis set, and the metal center described as before. For both optimization and single point calculations, solvation was implicitly accounted for by the SMD continuum solvation model.$^9$

All quantum chemical calculations were performed using the Gaussian 09 simulation package.$^{10}$ The computational methodology used here is at a similar level to that used by Ohanessian et al. for their study of biomimetic Zn complexes.$^{11}$ In this study, it was demonstrated that reliable results in terms of geometry and chemical accuracy could be reached by simply performing a HF geometry optimization, followed by a B3LYP energy calculation with a larger basis set. In this work, we used the M06-2X functional (instead of the popular B3LYP) as it also includes dispersion correction.
Computational Results.
Using the crystal structure of 4' as a starting point, three different Zn-complex structures were generated (Fig. S23). Complex 1-1 is closely related to the crystal structure, with a water molecule replacing the nitrate group coordinated to the Zn ion in the crystal structure, and the methoxy group converted to a hydroxyl. From this optimized structure, two further conformations were generated. By rotating the nucleophile side chain dihedral angles N₁-C₁-C₂-C₃ and C₁-C₂-C₃-O₂, complex 1-2 was generated. Complex 1-3 was obtained by changing the propeller like arrangement of the ligand around the zinc. It was found that all structures are very similar in energy (Table S7). Conformations 1-1 and 1-3 show that the non-coordinated oxygen can readily be positioned close to the free coordination site on the Zn ion, and are almost mirror images as the coordinated water leads to a more symmetrical coordination sphere than when nitrate is coordinated.

![Figure S23: Optimised structures of water-bound zinc-complexes using HF method and 6-31+G* / LANL2DZ basis set.](image)

| Zn-Complex | Distance | ΔE (kcal mol⁻¹) |
|------------|----------|----------------|
|            | 1-1      | 1-2            | 1-3            |
| O₁-Zn      | 3.612    | 4.424          | 3.113          |
| O₁-H₂O     | 4.591    | 4.747          | 3.671          |
| O₂-Zn      | 2.274    | 2.300          | 2.347          |
| N₁-Zn      | 2.349    | 2.31           | 2.268          |
| N₂-Zn      | 2.285    | 2.249          | 2.284          |
| N₃-Zn      | 2.258    | 2.269          | 2.263          |
| ΔE         | 0.0      | -0.40          | -0.36          |

Table S7: Selected distances (in Å) of the optimised structure and relative energy (in kcal mol⁻¹) of the three conformers 1-1, 1-2 and 1-3. The energies were obtained by single point calculation on the optimised structure at M062X and 6-311+G**/ LANL2DZ level of theory using SMD solvent model.
Similar calculations were performed on the monodeprotonated forms (at the non-coordinated hydroxyl) of these complexes. Once again, all the structures show similar energies. In these structures, the deprotonated non-bound oxygen shows a very similar distance to the substrate binding site compared to the protonated forms.

Figure S24: Optimised structure of monodeprotonated water-bound zinc-complexes using HF method and 6-31+G* / LANL2DZ basis set.

| Distance | 2-1 | 2-2 | 2-3 |
|----------|-----|-----|-----|
| O1-Zn    | 3.559 | 4.363 | 3.106 |
| O1-OH2   | 4.664 | 4.934 | 3.669 |
| O2-Zn    | 2.200 | 2.142 | 2.285 |
| N1-Zn    | 2.296 | 2.327 | 2.259 |
| N2-Zn    | 2.294 | 2.283 | 2.290 |
| N3-Zn    | 2.327 | 2.301 | 2.274 |
| ΔE       | 0.0  | -0.02 | +0.32 |

Table S8: Selected distances (in Å) of the optimised structure and relative energy (in kcal mol⁻¹) of the three monodeprotonated conformers 2-1, 2-2 and 2-3. The energies were obtained by single point calculation on the optimised structure using M062X and 6-311+G**/LANL2DZ basis set using SMD solvent model.
Finally, to explore the possibility of the non-coordinated oxygen acting as a nucleophile towards a coordinated phosphate diester, we replaced the water in the monodeprotonated complexes with methyl-p-nitrophenylphosphate. As before, we explored the same three different conformations of the complex system. The presence of the phosphate diester reintroduces the asymmetry between 3-1 and 3-3, where it is evident that the non-coordinated oxygen can be either remote or close to the substrate.

3-1 reflects the original crystal structure, and shows a large distance between the non-bound oxygen atom and the phosphate centre (5.60Å). However, once the rotation of the side chain and the propellor inversion have taken place, the non-bound oxygen is much closer to the phosphate centre, reaching a value of 4.06Å with an angle to the leaving group PO bond of 164°.

![Optimised structure of monodeprotonated zinc complexes with phosphate bound using HF method and 6-31+G* / LANL2DZ basis set.](image)

**Figure S25**: Optimised structure of monodeprotonated zinc complexes with phosphate bound using HF method and 6-31+G* / LANL2DZ basis set.

| Distance      | 3-1   | 3-2   | 3-3   |
|---------------|-------|-------|-------|
| O1-Zn         | 2.193 | 4.359 | 3.115 |
| O1-P          | 3.436 | 4.790 | 4.062 |
| O1-P-O<sub>LG</sub> | 165°  | 139°  | 164°  |
| O2-Zn         | 3.947 | 2.157 | 2.239 |
| O2-P          | 5.604 | 3.449 | 3.721 |
| O2-P-O<sub>LG</sub> | 163°  | 137°  | 154°  |
| ΔE            | 0.0   | -0.66 | +0.92 |

Table S9: Selected distances (in Å) and angles (in degrees) of the optimised structures and relative energies (in kcal mol<sup>-1</sup>) of the three monodeprotonated complexes with the phosphate diester bound. The energies were obtained by single point calculation on the minimised structure using M062X and 6-31+G*/* / LANL2DZ basis set.
Finally we performed a transition state optimization for the nucleophile attack reaction of the non-coordinated oxygen for conformation 3-2 (Figure S26). The resulting structure was characterized by frequency calculations, and the minimum energy path connecting reactants to products through this transition state was evaluated by calculating the intrinsic reaction coordinate\(^{13,14}\) (IRC=\(\xi\)) in both the forward and reverse directions in order to identify the corresponding reactant. Our results not only confirm this is a viable pathway for the phosphoryl transfer reaction, but comparison of the reactant stated optimized from the IRC calculation (RS) and the optimized complexes (3-1, 3-2 and 3-3) show almost no difference in energy.

![Figure S26: Reactant (RS), last reverse IRC point (IRC), Transition state (TS) and product (PS) state for the phosphoryl transfer reaction. Full optimization of the PS was not possible as the separation between the leaving group and the complex leads to the formation of two independent solvent cavities, so the last point of the IRC is shown here.](image)

| Zn-Complex  | Distance     | RS  | IRC | TS  | PS  |
|-------------|--------------|-----|-----|-----|-----|
| O1-Zn       | 4.336        | 4.008| 3.415| 3.582|
| O1-P        | 5.031        | 3.600| 2.057| 1.603|
| P-O\(_{LG}\) | 1.626        | 1.628| 1.857| 3.377|
| O1-P-O\(_{LG}\)| 160°        | 169°| 174°| 172°|
| O2-Zn       | 2.168        | 2.183| 2.210| 2.378|
| O2-P        | 3.756        | 3.749| 3.431| 3.08|
| O2-P-O\(_{LG}\)| 149°        | 146°| 138°|       |
| \(\Delta E\) | 0.0          | +2.25| +16.26|       |

Table S10: Selected distances (in Å) and angles (in degrees) of the structures and relative energies (in kcal mol\(^{-1}\)) for the phosphoryl transfer reaction. The energies were obtained by single point calculation on the structure using M062X and 6-311+G**/ LANL2DZ basis set.
Structure: 1-1

M062X-Energy = -1196.592169/HF-Energy = -1187.789623127/lower frequency = 25.6358 cm⁻¹; Cartesian coordinates:

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| Zn      | 11.92721  | 2.76164   | 5.43229   |
| N       | 11.89765  | 2.25761   | 3.23117   |
| N       | 12.32371  | 0.44839   | 5.33336   |
| N       | 10.16083  | 1.83081   | 6.54308   |
| O       | 13.76857  | 2.75723   | 6.76658   |
| O       | 13.09382  | 1.64552   | 8.66337   |
| O       | 12.24100  | 5.00031   | 5.64791   |
| C       | 11.41704  | 3.05444   | 2.26922   |
| C       | 11.44089  | 2.66868   | 0.93925   |
| H       | 11.04954  | 3.32491   | 0.18521   |
| C       | 11.96521  | 1.42996   | 0.60701   |
| H       | 11.99160  | 1.10890   | -0.41839  |
| C       | 12.43785  | 0.60591   | 1.61141   |
| H       | 12.83301  | -0.36911  | 1.39614   |
| C       | 12.38598  | 1.06117   | 2.91932   |
| C       | 12.94125  | 0.19685   | 4.02922   |
| H       | 12.83447  | -0.84774  | 3.75023   |
| H       | 13.99701  | 0.39790   | 4.09250   |
| C       | 10.96232  | -0.10731  | 5.32503   |
| H       | 10.98643  | -1.18361  | 5.46186   |
| H       | 10.51536  | 0.07516   | 4.35600   |
| C       | 10.05506  | 0.51872   | 6.35731   |
| C       | 9.10957   | -0.24364  | 7.02104   |
| H       | 9.05417   | -1.30281  | 6.85420   |
| C       | 8.24717   | 0.39593   | 7.89542   |
| H       | 7.49904   | -0.16390  | 8.42678   |
| C       | 8.35982   | 1.76383   | 8.08122   |
| H       | 7.70608   | 2.28574   | 8.75388   |
| C       | 9.33849   | 2.45890   | 7.38596   |
| C       | 13.08446  | -0.20771  | 6.42457   |
| H       | 13.34959  | -1.20903  | 6.09160   |
| H       | 12.39409  | -0.33094  | 7.24568   |
| C       | 14.36434  | 0.43344   | 7.01576   |
| C       | 14.10933  | 1.77284   | 7.71470   |
| H       | 15.01662  | 2.09536   | 8.20595   |
| C       | 10.85625  | 4.38828   | 2.67067   |
| H       | 10.22638  | 4.29256   | 3.54790   |
| H       | 10.26988  | 4.81271   | 1.86610   |
| H       | 11.66042  | 5.07933   | 2.90163   |
| C       | 9.51504   | 3.94151   | 7.55149   |
| H       | 10.49509  | 4.16026   | 7.96197   |
| H       | 9.43175   | 4.44289   | 6.59372   |
| C       | 14.84764  | -0.56541  | 8.08703   |
| H       | 15.16826  | -1.48868  | 7.61575   |
| H       | 14.07002  | -0.80697  | 8.80210   |
| H       | 15.69423  | -0.16000  | 8.63225   |
| C       | 15.52326  | 0.62503   | 6.02399   |
| H       | 15.33480  | 1.39492   | 5.28859   |
| H       | 15.73694  | -0.30381  | 5.50527   |
| H       | 16.41987  | 0.91126   | 6.56698   |
| H       | 8.76599   | 4.34650   | 8.21990   |
| H       | 13.88215  | 3.62272   | 7.14698   |
| H       | 12.13521  | 5.21540   | 6.57082   |
| H       | 11.54297  | 5.46939   | 5.20093   |
| H       | 13.12890  | 2.37925   | 9.26837   |
Structure: 1-2
M062X-Energy = -1196.592808/HF-Energy = -1187.7883587/lower frequency = 33.5338 cm⁻¹; Cartesian coordinates:

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| Zn   | 12.06086| 2.67945 | 5.44699 |
| N    | 11.86405| 2.19718 | 3.23896 |
| N    | 12.34917| 0.39124 | 5.31957 |
| O    | 14.77224| 2.03882 | 8.88396 |
| H    | 14.41194| 2.42800 | 9.67446 |
| O    | 12.96768| 2.47163 | 7.55035 |
| C    | 11.32393| 2.98848 | 2.30728 |
| C    | 11.23503| 2.58088 | 0.98476 |
| H    | 10.79256| 3.23026 | 0.25329 |
| C    | 11.71490| 1.33081 | 0.63257 |
| H    | 11.65277| 0.99243 | -0.38575|
| C    | 12.25966| 0.51500 | 1.60915 |
| H    | 12.62390| -0.46827| 1.37780 |
| C    | 12.31643| 0.99072 | 2.90797 |
| C    | 12.93497| 0.14257 | 3.99710 |
| H    | 12.83971| -0.90538| 3.72854 |
| H    | 13.99034| 0.36433 | 4.03213 |
| C    | 10.98597| -0.16167| 5.34904 |
| H    | 11.00562| -1.22546| 5.55883 |
| H    | 10.53947| -0.04550| 4.36964 |
| C    | 10.07914| 0.54447 | 6.32763 |
| C    | 9.11710 | -0.15322| 7.03670 |
| H    | 9.04929 | -1.22136| 6.95083 |
| C    | 8.25292 | 0.56282 | 7.84865 |
| H    | 7.49175 | 0.05510 | 8.41277 |
| C    | 8.38005 | 1.93941 | 7.92863 |
| H    | 7.72530 | 2.52031 | 8.55007 |
| C    | 9.37778 | 2.56649 | 7.19616 |
| C    | 13.16538| -0.24971| 6.38155 |
| H    | 13.57713| -1.16561| 5.96896 |
| H    | 12.48785| -0.55067| 7.16947 |
| C    | 14.31969| 0.54167 | 7.05415 |
| C    | 13.73963| 1.45806 | 8.14152 |
| H    | 13.10541| 0.88558 | 8.0683 |
| C    | 10.82529| 4.34170 | 2.72912 |
| H    | 10.33961| 4.29207 | 3.69501 |
| H    | 10.12054| 4.73010 | 2.00475 |
| H    | 11.65170| 5.04259 | 2.79693 |
| C    | 9.57612 | 4.05462 | 7.25415 |
| H    | 10.53368| 4.29069 | 7.70648 |
| H    | 9.56254 | 4.47904 | 6.25669 |
| C    | 15.18905| -0.52001| 7.75162 |
| H    | 15.58630| -1.21431| 7.01891 |
| H    | 14.61332| -1.09153| 8.47522 |
| H    | 16.02550| -0.06828| 8.26940 |
| C    | 15.19445| 1.33909 | 6.07853 |
| H    | 14.62776| 2.07081 | 5.51445 |
| H    | 15.68163| 0.67167 | 5.37622 |
| H    | 15.97344| 1.86668 | 6.61730 |
| H    | 12.38762| 2.86242 | 8.19599 |
| H    | 8.79707 | 4.52405 | 7.84098 |
| H    | 13.59839| 4.77086 | 6.02250 |
| O    | 12.76110| 4.77311 | 5.56582 |
| H    | 12.94413| 5.12077 | 4.69756 |
Structure: 1-3

M062X-Energy = -1196.592735/HF-Energy = -1187.75426644/lower frequency = 39.2026 cm⁻¹; Cartesian coordinates:

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| Zn   | 12.18530| 2.59708 | 5.34350 |
| N    | 14.08651| 2.21639 | 4.17615 |
| N    | 12.31371| 0.33231 | 5.33154 |
| N    | 10.34188| 1.96903 | 4.15034 |
| O    | 13.79212| 2.13691 | 7.96967 |
| O    | 11.53692| 2.09308 | 7.54231 |
| O    | 12.00965| 4.68418 | 6.01746 |
| C    | 15.05477| 3.09587 | 3.90727 |
| C    | 16.24768| 2.69052 | 3.32711 |
| H    | 17.01350| 3.41256 | 3.11661 |
| C    | 16.43064| 1.34985 | 3.03236 |
| H    | 17.35008| 1.01254 | 2.58943 |
| C    | 15.41740| 0.44874 | 3.13141 |
| H    | 15.52280| -0.59770| 3.09732 |
| C    | 14.25111| 0.93015 | 3.88164 |
| C    | 13.07073| 0.01587 | 4.10925 |
| H    | 12.41577| 0.13054 | 3.25482 |
| H    | 13.39989| -1.01747| 4.11900 |
| C    | 10.94095| -0.15919| 5.18527 |
| H    | 10.44728| -0.10428| 6.13969 |
| H    | 10.93370| -1.19966| 4.87543 |
| C    | 10.11441| 0.65974 | 4.21528 |
| C    | 9.11699 | 0.05049 | 3.47251 |
| H    | 8.96545 | -1.01052| 3.53819 |
| C    | 8.33308 | 0.84104 | 2.65049 |
| H    | 7.55010 | 0.40092 | 2.06002 |
| C    | 8.57373 | 2.20393 | 2.58920 |
| H    | 7.98605 | 2.84135 | 1.95628 |
| C    | 9.59692 | 2.74150 | 3.35502 |
| C    | 13.03267| -0.28894| 6.47366 |
| H    | 14.06771| -0.00798| 6.34430 |
| H    | 12.98524| -1.36925| 6.35527 |
| C    | 12.66554| 0.01565 | 7.95162 |
| C    | 12.58356| 1.50754 | 8.27881 |
| H    | 12.37096| 1.63712 | 9.33092 |
| C    | 14.80407| 4.53717 | 4.24702 |
| H    | 13.89257| 4.88327 | 3.77232 |
| H    | 15.62483| 5.15762 | 3.91092 |
| H    | 14.69624| 4.66157 | 5.31838 |
| C    | 9.90013 | 4.21287 | 3.32910 |
| H    | 9.65555 | 4.66375 | 4.28473 |
| H    | 10.95278| 4.38261 | 3.13338 |
| C    | 11.37325| -0.66418| 8.44317 |
| H    | 11.35211| -0.65802| 9.52902 |
| H    | 11.34550| -1.69931| 8.11892 |
| H    | 10.46835| -0.17857| 8.10702 |
| C    | 13.81906| -0.59198| 8.77588 |
| H    | 14.78647| -0.21091| 8.47293 |
| H    | 13.83148| -1.67105| 8.65901 |
| H    | 13.68546| -0.37560| 9.83122 |
| H    | 9.32112 | 4.70851 | 2.56046 |
| H    | 13.81115| 3.00271 | 8.36451 |
| H    | 11.14217| 4.81600 | 6.39090 |
| H    | 12.05453| 5.26566 | 5.26320 |
| H    | 11.28340| 2.92121 | 7.93904 |
Structure: 2-1

M062X-Energy = -1196.11255/HF-Energy = -1187.3018448/lower frequency = 41.4151 cm⁻¹; Cartesian coordinates:

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| Zn   | 12.00264 | 2.74535 | 5.47305 |
| N    | 11.90998 | 2.26102 | 3.19890 |
| N    | 12.32302 | 0.47722 | 5.32329 |
| N    | 10.18978 | 1.85267 | 6.55873 |
| O    | 13.78561 | 2.80590 | 6.76002 |
| O    | 13.11716 | 1.76631 | 8.70862 |
| O    | 12.03279 | 4.99894 | 5.52643 |
| C    | 11.43033 | 3.04075 | 2.22277 |
| C    | 11.45746 | 2.63473 | 0.89821 |
| H    | 11.06738 | 3.27929 | 0.13348 |
| C    | 11.98151 | 1.39102 | 0.58454 |
| H    | 12.00916 | 1.05452 | -0.43594 |
| C    | 12.45088 | 0.58286 | 1.60261 |
| H    | 12.84481 | -0.39640 | 1.40449 |
| C    | 12.39721 | 1.06051 | 2.90318 |
| C    | 12.94878 | 0.21060 | 4.02601 |
| H    | 12.84355 | -0.83765 | 3.76034 |
| H    | 14.00413 | 0.41247 | 4.09419 |
| C    | 10.95971 | -0.07408 | 5.30656 |
| H    | 10.98152 | -1.15098 | 5.43937 |
| H    | 10.51645 | 0.11351 | 4.33688 |
| C    | 10.05237 | 0.54967 | 6.33957 |
| C    | 9.08145 | -0.20635 | 6.97444 |
| H    | 9.00191 | -1.25932 | 6.78006 |
| C    | 8.22813 | 0.43118 | 7.85841 |
| H    | 7.46132 | -0.12276 | 8.36895 |
| C    | 8.37647 | 1.78979 | 8.08389 |
| H    | 7.73362 | 2.30985 | 8.76846 |
| C    | 9.37807 | 2.47759 | 7.41508 |
| C    | 13.07277 | -0.17555 | 6.42878 |
| H    | 13.32725 | -1.18206 | 6.10107 |
| H    | 12.37291 | -0.28550 | 7.24349 |
| C    | 14.34512 | 0.46627 | 7.03064 |
| C    | 14.07472 | 1.79407 | 7.78219 |
| H    | 15.03611 | 2.11621 | 8.19256 |
| C    | 10.85828 | 4.37748 | 2.59881 |
| H    | 10.17729 | 4.28011 | 3.43635 |
| H    | 10.32082 | 4.80813 | 1.76371 |
| H    | 11.64944 | 5.06285 | 2.88126 |
| C    | 9.58833 | 3.94980 | 7.62720 |
| H    | 10.59758 | 4.14013 | 7.97479 |
| H    | 9.44446 | 4.49076 | 6.69863 |
| C    | 14.82537 | -0.55128 | 8.08600 |
| H    | 15.14869 | -1.47183 | 7.60865 |
| H    | 14.04528 | -0.80087 | 8.79665 |
| H    | 15.66961 | -0.15429 | 8.64226 |
| C    | 15.50723 | 0.65603 | 6.04223 |
| H    | 15.32151 | 1.42072 | 5.30018 |
| H    | 15.73478 | -0.27286 | 5.52665 |
| H    | 16.40052 | 0.95114 | 6.58707 |
| H    | 8.89183 | 4.33569 | 8.36065 |
| H    | 13.72698 | 3.64297 | 7.20831 |
| H    | 12.15932 | 5.24746 | 6.43813 |
| H    | 11.18353 | 5.35753 | 5.28625 |
Structure: 2-2

M062X-Energy = -1196.112576/HF-Energy = -1187.30067724/lower frequency = 40.7123 cm⁻¹; Cartesian coordinates:

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| Zn      | 11.96078  | 2.76559   | 5.45559   |
| N       | 11.87680  | 2.27416   | 3.20930   |
| N       | 12.33581  | 0.47338   | 5.31480   |
| N       | 10.18247  | 1.82845   | 6.53875   |
| O       | 15.02253  | 2.26937   | 8.52357   |
| O       | 13.66985  | 2.72879   | 6.74547   |
| C       | 11.36171  | 3.04646   | 2.24715   |
| C       | 11.37992  | 2.64788   | 0.91949   |
| H       | 10.95916  | 3.28444   | 0.16430   |
| C       | 11.93544  | 1.42226   | 0.59228   |
| H       | 11.95771  | 1.09156   | -0.43022  |
| C       | 12.44317  | 0.62099   | 1.59904   |
| H       | 12.86124  | -0.34541  | 1.38801   |
| C       | 12.39357  | 1.08768   | 2.90257   |
| C       | 12.97752  | 0.24873   | 4.01823   |
| H       | 12.92198  | -0.79965  | 3.73761   |
| H       | 14.02230  | 0.49954   | 4.09652   |
| C       | 10.97848  | -0.09039  | 5.28780   |
| H       | 11.00575  | -1.16816  | 5.41346   |
| H       | 10.53510  | 0.10069   | 4.31896   |
| C       | 10.06549  | 0.52177   | 6.32443   |
| C       | 9.10902   | -0.24429  | 6.96826   |
| H       | 9.04432   | -1.29959  | 6.78127   |
| C       | 8.24884   | 0.38651   | 7.85128   |
| H       | 7.49334   | -0.17667  | 8.36852   |
| C       | 8.37307   | 1.74949   | 8.06550   |
| H       | 7.72139   | 2.26368   | 8.74611   |
| C       | 9.36186   | 2.44857   | 7.38898   |
| C       | 13.08479  | -0.19163  | 6.41135   |
| H       | 13.33917  | -1.19308  | 6.06948   |
| H       | 12.37773  | -0.31557  | 7.22103   |
| C       | 14.35526  | 0.43186   | 7.04734   |
| C       | 14.03839  | 1.75899   | 7.77939   |
| H       | 13.12375  | 1.60474   | 8.35909   |
| C       | 10.76532  | 4.36800   | 2.64025   |
| H       | 10.19158  | 4.27610   | 3.55400   |
| H       | 10.11667  | 4.73853   | 1.85661   |
| H       | 11.54847  | 5.10130   | 2.80153   |
| C       | 9.55459   | 3.92602   | 7.58318   |
| H       | 10.53894  | 4.12674   | 7.99265   |
| H       | 9.47175   | 4.44775   | 6.63587   |
| C       | 14.76088  | -0.59641  | 8.12191   |
| H       | 14.93641  | -1.57018  | 7.67360   |
| H       | 13.98723  | -0.71357  | 8.87686   |
| H       | 15.67222  | -0.29507  | 8.62293   |
| C       | 15.54252  | 0.59368   | 6.08786   |
| H       | 15.40115  | 1.38760   | 5.36562   |
| H       | 15.72682  | -0.33017  | 5.54615   |
| H       | 16.44185  | 0.82614   | 6.64805   |
| H       | 13.78994  | 3.59056   | 7.12912   |
| H       | 8.81283   | 4.32602   | 8.26267   |
| H       | 12.72950  | 5.36088   | 4.81101   |
| O       | 12.22936  | 5.05746   | 5.56308   |
| H       | 11.37198  | 5.46320   | 5.47178   |
Structure: 2-3

M062X-Energy = -1196.11203282/ HF-Energy = -1187.29514110/ lower frequency = 39.0754 cm⁻¹; Cartesian coordinates:

Zn  12.18370  2.57462  5.36677
N  14.09512  2.21476  4.18841
N  12.31945  0.32049  5.31901
N  10.34080  1.95648  4.15629
O  13.78410  2.20632  8.00318
O  11.53838  2.10650  7.50766
O  11.97198  4.68359  5.99246
C  15.06645  3.09450  3.93181
C  16.26013  2.69378  3.34987
H  17.02808  3.41672  3.15032
C  16.44138  1.35628  3.03997
H  17.36134  1.02210  2.59566
C  15.42576  0.45454  3.30878
H  15.52983 -0.58985  3.08224
C  14.25878  0.93183  3.87997
C  13.07830  0.01508  4.09716
H  12.42520  0.13632  3.24183
H  13.40902 -1.01816  4.09895
C  10.95229 -0.18141  5.16870
H  10.46328 -0.15721  6.12665
H  10.95469 -1.21475  4.83444
C  10.11051  0.64783  4.22061
C  9.09753  0.04346  3.49381
H  8.94404  1.01730  3.56027
C  8.30246  0.83760  2.68706
H  7.50753  0.40153  2.10967
C  8.54884  2.19957  2.62250
H  7.95449  2.83988  1.99871
C  9.58656  2.73201  3.37195
C  13.03797 -0.29585  6.46530
H  14.07280 -0.01515  6.33338
H  12.99047 -1.37720  6.34619
C  12.67134  0.02770  7.93675
C  12.65508  1.53853  8.26155
H  12.34915  1.63258  9.30756
C  14.81827  4.53237  4.28668
H  13.92399  4.89300  3.79002
H  15.65330  5.15131  3.98453
H  14.67876  4.64094  5.35596
C  9.89606  4.20211  3.33661
H  9.65324  4.66200  4.28853
H  10.94939  4.36630  3.14043
C  11.36729 -0.63049  8.42791
H  11.34237 -0.61754  9.51428
H  11.31633 -1.66957  8.11461
H  10.46983 -0.13191  8.08964
C  13.80706 -0.60924  8.76357
H  14.78329 -0.24561  8.46541
H  13.80272 -1.69005  8.65074
H  13.67624 -0.38934  9.81926
H  9.31920  4.69438  2.56409
H  11.07692  4.80934  6.29567
H  12.06489  5.25810  5.23772
H  11.37790  2.97674  7.85665
Structure: 3-1
M062X-Energy = -2238.184225/HF-Energy = -2224.93557423/lower frequency = 17.4505 cm⁻¹; Cartesian coordinates:

Zn  11.85964  2.49047  5.99650
N  11.90558  2.57551  3.68411
N  12.31916  0.31565  5.25333
N  9.95391  1.32559  6.43576
O  12.93697  1.92328  7.82100
O  12.42251  0.03812  9.03827
O  12.14311  4.53088  6.49164
C  11.40454  3.54902  2.91627
C  11.59878  3.55329  1.54295
H  11.18232  4.34321  0.94688
C  12.32025  2.52431  0.96135
H  12.48173  2.50636 -0.10127
C  12.80954  1.50783  1.76155
H  13.34760  0.67708  1.34477
C  12.57568  1.57217  3.12573
C  13.10209  0.47631  4.02556
H  13.12755 -0.45394  3.46380
H  14.12184  0.71456  4.28285
C  10.99878 -0.23326  4.90488
H  11.05369 -1.30823  4.76850
H  10.67826  0.18357  3.95930
C  9.92970  0.10242  5.91680
C  8.93397 -0.80776  6.22804
H  8.94666 -1.79232  5.79989
H  7.93454 -0.41413  7.10210
H  7.14538 -1.09447  7.36637
C  7.96477  0.86274  7.63769
H  7.20683  1.19410  8.32190
C  9.00163  1.71450  7.28585
C  12.98779 -0.63179  6.18406
H  13.43716 -1.41946  5.58211
H  12.20743 -1.10031  6.76422
C  14.03892 -0.12648  7.19449
C  13.40237  0.65433  8.37128
H  14.22553  0.94191  9.03246
C  10.61903  4.64741  3.57652
H  10.01684  4.25832  4.38755
H  9.96830  5.12850  2.85699
H  11.28622  5.39982  3.98212
C  9.10242  3.10281  7.85119
H  10.00945  3.20395  8.43780
H  9.13474  3.83754  7.05442
C  14.67201 -1.39664  7.79360
H  15.25259 -1.92532  7.04326
H  13.92386 -2.08125  8.17848
H  15.34152 -1.14273  8.61085
C  15.17539  0.70171  6.57804
H  14.83540  1.62749  6.13249
H  15.70449  0.13358  5.81823
H  15.89672  0.96097  7.34909
H  15.16995  7.84808  6.08729
H  16.19662  9.87310  7.04269
C  14.68320  8.38039  6.88116
C  15.25785  9.51731  7.41608
O  12.87047  6.84189  6.81279
|   | X      | Y      | Z      |
|---|--------|--------|--------|
| O | 16.25362 | 11.74379 | 8.56662 |
| C | 13.46672 | 7.93313  | 7.37681 |
| C | 14.59688 | 10.18291 | 8.43659 |
| N | 15.19611 | 11.37597 | 8.99778 |
| P | 13.14283 | 5.31043  | 7.28241 |
| C | 12.81002 | 8.60744  | 8.39660 |
| O | 14.61867 | 5.02426  | 6.77371 |
| C | 13.37878 | 9.74503  | 8.93492 |
| O | 13.15315 | 5.22600  | 8.75917 |
| O | 14.61318 | 11.95328 | 9.87310 |
| H | 11.86725 | 8.24429  | 8.75833 |
| H | 12.88279 | 10.27526 | 9.72241 |
| C | 14.95213 | 4.95489  | 5.38766 |
| H | 14.49269 | 5.76481  | 4.83891 |
| H | 14.63467 | 4.00659  | 4.98085 |
| H | 16.02600 | 5.03762  | 5.32513 |
| H | 8.25554  | 3.32119  | 8.48928 |
| H | 12.53461 | 2.40836  | 8.53371 |
Structure: 3-2

M062X-Energy = -2238.185274/HF-Energy = -2224.93680032/lower frequency = 21.6397 \text{cm}^{-1}; \text{Cartesian coordinates:}

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| Zn   | 12.08144   | 2.52978    | 5.60869    |
| N    | 12.34182   | 2.04998    | 3.31200    |
| N    | 12.20501   | 0.27072    | 5.48555    |
| O    | 10.00525   | 1.87711    | 6.23727    |
| O    | 13.93941   | 1.76511    | 9.47664    |
| O    | 12.69645   | 2.38493    | 7.67142    |
| O    | 12.77495   | 4.60704    | 5.54940    |
| C    | 12.09007   | 2.83872    | 2.26288    |
| C    | 12.32374   | 2.40557    | 0.96583    |
| H    | 12.11272   | 3.05637    | 0.13832    |
| C    | 12.81516   | 1.12733    | 0.76055    |
| H    | 13.00016   | 0.76955    | -0.23614   |
| C    | 13.04035   | 0.30836    | 1.85213    |
| H    | 13.39311   | -0.69900   | 1.73280    |
| C    | 12.78655   | 0.81310    | 3.11767    |
| H    | 12.91080   | -1.09711   | 4.04593    |
| H    | 14.08142   | 0.06146    | 4.60463    |
| C    | 10.82210   | -0.15560   | 5.21265    |
| H    | 10.71797   | -1.22705   | 5.34718    |
| H    | 10.58611   | 0.05708    | 4.17785    |
| C    | 9.80739    | 0.57446    | 6.06174    |
| C    | 8.69654    | -0.07462   | 6.57112    |
| H    | 8.56793    | -1.12996   | 6.42080    |
| C    | 7.76584    | 0.67394    | 7.27369    |
| H    | 6.89053    | 0.20416    | 7.68433    |
| C    | 7.97390    | 2.03231    | 7.44411    |
| H    | 7.26861    | 2.63660    | 7.98250    |
| C    | 9.11727    | 2.60968    | 6.90942    |
| C    | 12.69361   | -0.44750   | 6.69517    |
| H    | 13.04350   | -1.42318   | 6.36772    |
| H    | 11.82869   | -0.63170   | 7.31895    |
| C    | 13.77045   | 0.18548    | 7.61349    |
| C    | 13.14349   | 1.28298    | 8.51653    |
| H    | 12.21097   | 0.87307    | 8.91460    |
| C    | 11.54310   | 4.21562    | 2.51798    |
| H    | 10.83782   | 4.20621    | 3.33937    |
| H    | 11.04417   | 4.59138    | 1.63327    |
| H    | 12.34445   | 4.90165    | 2.76869    |
| C    | 9.40298    | 4.07688    | 7.05995    |
| H    | 10.30324   | 4.22828    | 7.64517    |
| H    | 9.55427    | 4.53374    | 6.08810    |
| C    | 14.21157   | -0.96530   | 8.53713    |
| H    | 14.61158   | -1.79190   | 7.95719    |
| H    | 13.37813   | -1.34553   | 9.12394    |
| H    | 14.98161   | -0.64101   | 9.22630    |
| C    | 15.00315   | 0.71671    | 6.87416    |
| H    | 14.76391   | 1.51582    | 6.18157    |
| H    | 15.49537   | -0.07589   | 6.31776    |
| H    | 15.72286   | 1.10658    | 7.58580    |
| H    | 13.23473   | 3.14271    | 7.89218    |
| H    | 12.36077   | 7.62696    | 8.65120    |
| H    | 13.17917   | 9.59507    | 9.89555    |
| C    | 13.12130   | 8.25897    | 8.23438    |
| C    | 13.57870   | 9.36134    | 8.92942    |
| Element | X-coordinates | Y-coordinates | Z-coordinates |
|---------|---------------|---------------|---------------|
| O       | 13.15752      | 6.91448       | 6.27780       |
| O       | 14.57969      | 11.53984      | 10.16246      |
| C       | 13.65247      | 7.97252       | 6.98476       |
| C       | 14.55911      | 10.15473      | 8.35250       |
| N       | 15.04093      | 11.31088      | 9.07907       |
| P       | 13.73878      | 5.40134       | 6.36479       |
| C       | 14.62955      | 8.77418       | 6.41250       |
| O       | 15.14682      | 5.49955       | 5.63875       |
| C       | 15.09105      | 9.87878       | 7.10253       |
| O       | 13.99026      | 5.02759       | 7.77586       |
| O       | 15.88359      | 11.99741      | 8.57110       |
| H       | 15.01829      | 8.53691       | 5.44104       |
| H       | 15.84487      | 10.50693      | 6.67275       |
| C       | 15.26832      | 5.67360       | 4.22713       |
| H       | 14.64670      | 6.48918       | 3.88516       |
| H       | 14.99595      | 4.75948       | 3.72008       |
| H       | 16.30499      | 5.90308       | 4.03585       |
| H       | 8.58266       | 4.58072       | 7.55528       |
Structure: 3-3

M062X-Energy = -2238.18275013/ HF-Energy = -2224.93493333; lower frequency = 25.6358 cm⁻¹; Cartesian coordinates:

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| Zn   | 12.99939  | 2.64079   | 5.85831   |
| N    | 15.24029  | 2.31036   | 5.05926   |
| N    | 13.31954  | 0.35352   | 5.85963   |
| N    | 11.56106  | 1.80606   | 4.20121   |
| O    | 14.09234  | 2.30118   | 8.75574   |
| O    | 12.00816  | 2.08986   | 7.78854   |
| C    | 16.23289  | 3.20026   | 4.99982   |
| C    | 17.53851  | 2.80939   | 4.73275   |
| H    | 18.31875  | 3.54548   | 4.68816   |
| C    | 17.81131  | 1.46787   | 4.53205   |
| H    | 18.81562  | 1.14074   | 4.33204   |
| C    | 16.77386  | 0.55270   | 4.59157   |
| H    | 16.94341  | -0.49660  | 4.43872   |
| C    | 15.49751  | 1.02232   | 4.85160   |
| C    | 14.31918  | 0.08016   | 4.81888   |
| H    | 13.85389  | 0.19347   | 3.84806   |
| H    | 14.66768  | -0.94581  | 4.88295   |
| C    | 12.04060  | -0.23024  | 5.45090   |
| H    | 11.35074  | -0.17322  | 6.27422   |
| H    | 12.15817  | -1.28123  | 5.20119   |
| C    | 11.39634  | 0.48974   | 4.28652   |
| C    | 10.62133  | -0.21841  | 3.38164   |
| H    | 10.51668  | -1.28294  | 3.47611   |
| C    | 9.99968   | 0.47884   | 2.36125   |
| H    | 10.54094  | -0.03722  | 1.64098   |
| C    | 10.18212  | 1.84866   | 2.27001   |
| H    | 9.72392   | 2.41655   | 1.48253   |
| C    | 10.97763  | 2.48683   | 3.21020   |
| C    | 13.81893  | -0.22434  | 7.13186   |
| H    | 14.83855  | 0.12105   | 7.21986   |
| H    | 13.86423  | -1.30656  | 7.01524   |
| C    | 13.12847  | 0.07310   | 8.48643   |
| C    | 12.96685  | 1.58275   | 8.77456   |
| H    | 12.43515  | 1.66787   | 9.72677   |
| C    | 15.89627  | 4.64529   | 5.22972   |
| H    | 15.07752  | 4.95260   | 4.59024   |
| C    | 16.75324  | 5.27381   | 5.02216   |
| H    | 15.59780  | 4.80441   | 6.25880   |
| C    | 11.20111  | 3.97119   | 3.14605   |
| H    | 10.69021  | 4.46609   | 3.96447   |
| C    | 12.25655  | 4.20437   | 3.21990   |
| C    | 11.78661  | -0.65537  | 8.69899   |
| H    | 11.53878  | -0.65519  | 9.75710   |
| H    | 11.85320  | -1.69258  | 8.38217   |
| H    | 10.95312  | -0.19897  | 8.18432   |
| C    | 14.09220  | -0.50159  | 9.54466   |
| H    | 15.09267  | -0.09586  | 9.45271   |
| H    | 14.15864  | -1.58245  | 9.45231   |
| H    | 13.73239  | -0.27964  | 10.54534  |
| H    | 10.82129  | 4.37272   | 2.21515   |
| H    | 11.65390  | 2.90572   | 8.12409   |
| H    | 9.91096   | 4.49043   | 6.90251   |
| H    | 9.23425   | 5.42734   | 8.23944   |
| C    | 9.95361   | 5.42912   | 7.43556   |
| H    | 9.74349   | 6.24770   | 6.76069   |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| O       | 11.23502| 5.59853 | 8.03986 |
| O       | 12.56044| 4.68968 | 6.09621 |
| O       | 12.37994| 7.11549 | 6.36867 |
| P       | 12.56419| 5.71863 | 7.17902 |
| H       | 14.41517| 8.48812 | 5.58647 |
| C       | 12.71116| 8.34222 | 6.86450 |
| C       | 13.82497| 8.98004 | 6.33595 |
| C       | 11.92124| 8.94976 | 7.83027 |
| C       | 14.16363| 10.24152| 6.78296 |
| H       | 11.05719| 8.44582 | 8.21824 |
| H       | 15.02281| 10.74315| 6.38564 |
| C       | 13.37479| 10.83803| 7.75567 |
| C       | 12.25772| 10.21058| 8.28491 |
| O       | 13.70027| 5.83142 | 8.11708 |
| O       | 14.67743| 12.70785| 7.74421 |
| N       | 13.72903| 12.15816| 8.23202 |
| H       | 11.65868| 10.69105| 9.03175 |
| O       | 13.06249| 12.65451| 9.09750 |
Structure: RS

M062X-Energy = -2238.18312031/HF-Energy = -2224.93484844/lower frequency =18.9483; Cartesian coordinates:

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| Zn   | -1.07084600 | -1.10856400 | 0.04378400 |
| N    | -1.27144500 | -1.05608200 | -2.22383200 |
| N    | -1.26753700 | -3.28665100 | -0.57865600 |
| N    | -3.24164600 | -1.67226500 | 0.64960400 |
| O    | 0.96721600  | -2.91259400 | 3.41950500 |
| O    | -0.44112000 | -1.84120700 | 1.98419600 |
| O    | -0.22793400 | 0.77723000  | 0.48086100 |
| C    | -1.56441800 | -0.00401700 | -2.99570200 |
| C    | -1.47864300 | -0.08174700 | -4.37764500 |
| H    | -1.72347000 | 0.77467600  | -4.97711700 |
| C    | -1.08240400 | -1.27262700 | -4.96333000 |
| C    | -1.00917500 | -1.35488000 | -6.03260800 |
| C    | -0.80046600 | -2.35995500 | -4.15640500 |
| H    | -0.51140100 | -3.30696700 | -4.57242900 |
| C    | -0.90762300 | -2.20636600 | -2.78414300 |
| C    | -0.58412700 | -3.37080600 | -1.87349300 |
| H    | -0.83921100 | -4.29712100 | -2.38076200 |
| H    | 0.48192200  | -3.38274200 | -1.71071700 |
| C    | -2.70359600 | -3.53863700 | -0.78903400 |
| H    | -2.90007090 | -4.60415700 | -0.83564500 |
| H    | -2.99824700 | -3.12676500 | -1.74503900 |
| C    | -3.58362200 | -2.89247400 | 0.25304800 |
| C    | -4.73397300 | -3.51905500 | 0.70217000 |
| H    | -4.97714500 | -4.51043000 | 0.36874200 |
| C    | -5.55313900 | -2.83113600 | 1.58196200 |
| H    | -6.45601300 | -3.28389300 | 1.94993100 |
| C    | -5.19659800 | -1.55478700 | 1.98412600 |
| H    | -5.81280700 | -0.99731300 | 2.66387700 |
| C    | -4.01967700 | -1.00099700 | 1.49946600 |
| C    | -0.74106000 | -4.31104200 | 0.36401000 |
| H    | -0.51662600 | -5.19932900 | -0.22096600 |
| H    | -1.55927600 | -4.57905100 | 1.01979500 |
| C    | 0.47041700  | -3.99972200 | 1.27779800 |
| C    | 0.03400700  | -3.13034800 | 2.48790200 |
| H    | -0.86635700 | -3.59317500 | 2.90179800 |
| C    | -1.98295100 | 1.27663200  | -2.32950300 |
| H    | -2.60552600 | 1.08105600  | -1.46596400 |
| H    | -2.53369300 | 1.89929000  | -3.02336900 |
| C    | -1.11157300 | 1.83141800  | -1.99860600 |
| C    | -3.57253900 | 0.37283100  | 1.91339400 |
| H    | -4.32393700 | 0.85318800  | 2.52752100 |
| H    | -2.65157000 | 0.31217900  | 2.48308000 |
| C    | 0.89110200  | -5.36880300 | 1.84290400 |
| H    | 1.17067400  | -6.04644300 | 1.04162000 |
| H    | 0.08188500  | -5.83355900 | 2.40206900 |
| H    | 1.74090100  | -5.27214700 | 2.50769000 |
| C    | 1.66893100  | -3.38515000 | 0.54755800 |
| H    | 1.44261500  | -2.42332500 | 0.10350200 |
| H    | 2.02132800  | -4.04529100 | -0.24027100 |
| H    | 2.49240900  | -3.24101200 | 1.23838400 |
| H    | 0.08644100  | -1.18297300 | 2.42290300 |
| H    | 0.79694800  | 4.75085600  | -1.42595100 |
| H    | 2.48726100  | 6.46877700  | -1.94285300 |
| C    | 1.76453900  | 4.72320500  | -0.96229100 |
| C    | 2.71050900  | 5.68285800  | -1.25001300 |
Structure: TS
M062X-Energy = -2238.15721268/HF-Energy = -2224.88307557/lower frequency = -355.9064; Cartesian coordinates:

Zn  12.06251300  2.31927000  5.57481900
N   11.91689000  2.10216000  3.36802800
N   12.08176900  0.05285900  5.24247900
N   10.00591700  1.72031400  6.30779300
O   14.77235400  2.23984600  7.71099100
O   12.55659900  1.60330900  7.60687300
O   13.48678600  3.74251100  6.01486500
C   11.57659400  3.09660200  2.54116000
C   11.38827400  2.86809900  1.18808000
H   11.11154300  3.67784400  0.53987900
C   11.55636500  1.58312200  0.69504400
H   11.40837900  1.38072800  2.25918900
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| O       | 14.79561100 | 5.70555600 | 5.90282700 |
| O       | 18.33682400 | 10.69717700 | 5.05015200 |
| C       | 15.70757900 | 6.64054600 | 5.93478600 |
| C       | 17.55728700 | 8.72525000 | 5.86099700 |
| N       | 18.51393600 | 9.78149600 | 5.81455400 |
| P       | 14.81013600 | 4.01543000 | 6.67234100 |
| C       | 16.85257900 | 6.61554800 | 6.75613500 |
| O       | 16.16417500 | 3.65374100 | 6.17680500 |
| C       | 17.76422900 | 7.64519000 | 6.71418700 |
| O       | 14.79141500 | 4.67469800 | 8.12558200 |
| O       | 19.47723800 | 9.73283300 | 6.53857600 |
| H       | 17.02912100 | 5.79199900 | 7.41947200 |
| H       | 18.63313800 | 7.60681300 | 7.34081100 |
| H       | 9.29035500  | 4.37358300 | 6.05514200 |
| C       | 13.61441500 | 5.22865400 | 8.69288800 |
| H       | 13.92256700 | 5.74493800 | 9.58977500 |
| H       | 13.14918000 | 5.93042800 | 8.01494000 |
| H       | 12.91411700 | 4.44637200 | 8.95373300 |
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