Frustrated Lewis Pair Stabilized Phosphoryl Nitride (NPO), a Mono Phosphorus Analogue of Nitrous Oxide (N\textsubscript{2}O)

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General Remarks

All manipulations were performed in a Vacuum Atmospheres model MO-40M glovebox under an inert atmosphere of purified N\textsubscript{2}. All solvents were obtained anhydrous and oxygen-free by bubble degassing (N\textsubscript{2}) and purification through columns of alumina and Q5, and storage over molecular sieves. Literature procedures were followed for the preparation of MgA\textsubscript{3}THF, Me\textsubscript{2}NP\textsubscript{A}, CIPA\textsubscript{A}, N\textsubscript{3}PA (A = C\textsubscript{14}H\textsubscript{10}, anthracene), and 2,4,6-trimethylbenzonitrile N-oxide (MesCNO). Deuterated solvents were purchased from Cambridge Isotope Labs, degassed, and stored over molecular sieves for at least 48 h prior to use. Activated Charcoal Norit CA1 (Aldrich) and Celite 435 (EM Science) were dried by heating above 200 °C under dynamic vacuum for at least 48 h. All glassware was oven dried for at least 3 h at temperatures greater than 150 °C. NMR spectra were obtained on a Bruker Avance-III HD Nanobay spectrometer operating at 400.09 MHz equipped with a 5mm liquid-nitrogen cooled Prodigy broad band observe cryoprobe or on a Bruker Avance Neo spectrometer operating at 500.34 MHz equipped with a 5mm liquid-nitrogen cooled Prodigy broad band observe cryoprobe. ¹H and ¹³C NMR spectra were referenced to residual protiated solvent resonances; ³¹P NMR spectra were referenced externally to 85% aqueous H\textsubscript{3}PO\textsubscript{4} (δ = 0 ppm). Elemental analyses were performed by Midwest Microlab (Indianapolis, IN). High resolution mass spectral (HRMS) data were collected using a Jeol AccuTOF 4G LC-Plus mass spectrometer equipped with an Ion-Sense DART source. Data were calibrated to a sample of PEG-600 and were collected in positive ion. Samples were prepared in THF (ca. 10 μM concentration) and were briefly exposed to air (<5 s) before being placed in front of the DART source.

Synthesis of N\textsubscript{3}P(O)A

\textit{Attention: Solid N\textsubscript{3}PA is explosive.}

Inside the glovebox, a 20 mL vial was charged with solid, colorless N\textsubscript{3}PA (195 mg, 0.78 mmol, 1.0 equiv), 2,4,6-trimethylbenzonitrile N-oxide (MesCNO, 125 mg, 0.78 mmol, 1 equiv) and 4 mL diethyl ether. The solution turned homogeneous after addition of 1 mL THF within a few minutes and was further stirred for 30 min at room temperature under aluminum foil in the dark. After adding 15 mL hexanes, the reaction mixture was placed in the freezer at –20 °C for one hour. A colorless precipitate developed, which was filtered and washed with a minimal amount of pentane and further dried in the glovebox in the dark for 30 min. Yields varied depending on how much anthracene was produced during the course of the reaction, giving up to 154 mg (74%) of clean product. The identity of the product was confirmed by NMR and IR spectroscopy as well as by an X-ray diffraction study performed on a crystal grown from diethyl ether at –20 °C (Figure 2). The crystalline compound turns red-brown at 60 °C and does melt at around 220 °C. DART HRMS(Q-TOF) m/z: [M + H]\textsuperscript{+} Calcd for C\textsubscript{14}H\textsubscript{11}N\textsubscript{3}PO 268.0634; Found 268.0648. ¹H NMR (benzene-\textit{d}_6, 400 MHz, 25 °C) δ 7.09 (m, 2H), 6.92 (m, 6H), 4.09 (d, 2H, 2H,
$J_{\text{PH}} = 11.1$ Hz ppm. $^{13}$C{\text{\textsuperscript{1}H}} NMR (benzene-$d_6$, 101 MHz, 25 °C) δ 138.3 (d, $J = 13.1$ Hz), 134.3 (d, $J = 12.0$ Hz), 127.2 (d, $J = 1.7$ Hz), 127.1 (d, $J = 1.5$ Hz), 124.2 (d, $J = 9.0$ Hz), 123.3 (d, $J = 8.8$ Hz), 53.4 (d, $J = 69.9$ Hz) ppm. $^{31}$P{\text{\textsuperscript{1}H}} NMR (benzene-$d_6$, 162 MHz, 25 °C) δ 76 ppm.

**Figure S1:** $^1$H NMR (benzene-$d_6$, 400 MHz, 25 °C) spectrum of N₃P(O)A.
Figure S2: $^{13}$C{\textsuperscript{1}H} NMR (benzene-$d_6$, 101 MHz, 25 °C) spectrum of N$_3$PA.

Figure S3: $^{31}$P{\textsuperscript{1}H} and $^{31}$P (inset) NMR (benzene-$d_6$, 162 MHz, 25 °C) spectrum of N$_3$P(O)A.
Figure S4: ATR-IR spectrum of solid N$_3$P(O)A.

Figure S5: $^{31}$P($^1$H) NMR (benzene-$d_6$, 162 MHz, 25 °C) spectrum of N$_3$P(O)A after thermolysis for 60 minutes at 70 °C.
Synthesis of Cy$_3$P=NP(O)A

Inside the glovebox, a 20 mL vial was charged with solid, colorless N$_3$P(O)A (155 mg, 0.58 mmol, 1.0 equiv), tricyclohexylphosphine (PCy$_3$, 162 mg, 0.78 mmol, 1.0 equiv) and 10 mL diethyl ether. The heterogeneous solution was stirred for 30 min at room temperature. Gas evolution occurred and a colorless precipitate formed that was filtered and washed with a minimal amount of pentane and further dried in the glovebox for 30 min, giving up to 246 mg (82%) clean product. The identity of the product was confirmed by NMR as well as by an X-ray diffraction study performed on a crystal grown from diethyl ether at −20 °C (Figure 4A). Crystals for elemental analysis were grown from a chloroform/pentane solution. One molecule of pentane and two molecules of chloroform are included in the elemental analysis result. Anal. Calcd for C$_{39}$H$_{57}$Cl$_6$NOP$_2$: C, 56.40; H, 6.92; N, 1.69. Found: C, 55.11; H, 6.91; N, 2.19. $^1$H NMR (benzene-$d_6$, 400 MHz, 25 °C) δ 7.41 (m, 2H), 7.27 (m, 2H), 7.08 (m, 2H), 7.01 (m, 2H), 4.67 (d, 2H, $^2$J$_{PH}$= 8.8 Hz), 1.63 (m, 18H), 1.12 (m, 15H) ppm. $^{13}$C{$^1$H} NMR (benzene-$d_6$, 101 MHz, 25 °C) δ 144.7 (d, $^1$J$_{CH}$= 8.7 Hz), 142.9 (d, $^1$J$_{CH}$= 10.1 Hz), 125.6, 124.9, 123.8 (d, $^1$J$_{CH}$= 8.4 Hz), 122.9 (d, $^1$J$_{CH}$= 7.9 Hz), 57.9 (dd, $^1$J$_{CH}$= 76.3, 3.0 Hz), 35.5 (d, $^1$J$_{CH}$= 1.9 Hz), 34.9 (d, $^1$J$_{CH}$= 1.9 Hz), 27.1, 27.0 26.7, 26.6, 26.3 ppm. $^{31}$P{$^1$H} NMR (benzene-$d_6$, 162 MHz, 25 °C) δ 82.9 (d, $^1$J$_{PH}$= 21.4 Hz), 82.3 (d, $^1$J$_{PH}$= 21.4 Hz) ppm.

Figure S6: $^1$H NMR (benzene-$d_6$, 400 MHz, 25 °C) spectrum of Cy$_3$P=NP(O)A.
Figure S7: $^{13}$C{\textsuperscript{1}H} NMR (benzene-$d_6$, 101 MHz, 25 °C) spectrum of Cy$_3$P=NP(O)A.

Figure S8: $^{31}$P{\textsuperscript{1}H} and $^{31}$P (inset) NMR (benzene-$d_6$, 162 MHz, 25 °C) spectrum of Cy$_3$P=NP(O)A.
Synthesis of Cy$_3$P-NP(A)O-B(C$_6$F$_5$)$_3$

Inside the glovebox, a 20 mL vial was charged with solid, colorless Cy$_3$PNP(O)A (50.8 mg, 0.098 mmol, 1.0 equiv), tris(pentafluorophenyl)borane (B(C$_6$F$_5$)$_3$, 50.0 mg, 0.098 mmol, 1.0 equiv) and 5 mL dichloromethane. The solution was stirred for 10 min at room temperature and all volatile materials were removed under reduced pressure, yielding Cy$_3$P-NP(A)O-B(C$_6$F$_5$)$_3$ quantitatively. The identity of the product was confirmed by NMR as well as by an X-ray diffraction study performed on a crystal grown from diethyl ether at -20 °C (Figure 4B). Crystals for elemental analysis were grown from a chloroform/pentane solution. One molecule of pentane and two molecules of chloroform are included in the elemental analysis. Anal. Caled for C$_{57}$H$_{57}$BCl$_6$F$_{15}$NOP$_2$: C, 51.00; H, 4.28; N, 1.04. Found: C, 50.66; H, 4.02; N, 1.34. $^1$H NMR (chloroform-$d$, 500 MHz, 25 °C) δ 7.36 (m, 2H), 7.17 (m, 4H), 6.93 (m, 2H), 4.68 (d, 2H, $^2$J$_{PH}$ = 12.2 Hz), 1.73 (m, 9H), 1.47 (m, 6H), 1.27 (m, 3H), 1.04 (m, 15H) ppm. $^{13}$C{$^1$H} NMR (chloroform-$d$, 126 MHz, 25 °C) δ 148.8 (b), 146.9 (b), 141.3 (d, $^J$= 15.3 Hz), 140.3 (b), 140.1 (d, $J$ = 11.2 Hz), 138.3 (b), 137.7 (b), 135.7 (b), 126.5, 126.0, 124.4 (d, $J$ = 10.4 Hz), 123.5 (d, $J$ = 9.2 Hz), 54.8 (d, $J$ = 89.1 Hz), 35.8, 35.3, 26.6, 26.5, 26.3, 26.2, 25.8 ppm. $^{31}$P{$^1$H} NMR (chloroform-$d$, 203 MHz, 25 °C) δ 82.5 (d, $J$ = 16.7 Hz), 32.9 (d, $J$ = 16.9 Hz) ppm. $^{19}$F NMR (chloroform-$d$, 471 MHz, 25 °C) δ −133.4 (m), −160.4 (t, $J$ = 20.5 Hz), −165.5 (m) ppm. $^{11}$B NMR (chloroform-$d$, 161 MHz, 25 °C) δ −3.88 (b, $\nu_{1/2} = 341$ Hz) ppm.

![Figure S9: $^1$H NMR (chloroform-$d$, 500 MHz, 25 °C) spectrum of Cy$_3$P-NP(A)O-B(C$_6$F$_5$)$_3$.](image)
Figure S10: $^{13}$C\{H\} NMR (chloroform-$d$, 126 MHz, 25 °C) spectrum of Cy$_3$P-NP(A)O-B(C$_6$F$_5$)$_3$.

Figure S11: $^{31}$P\{H\} and $^{31}$P (inset) NMR (chloroform-$d$, 203 MHz, 25 °C) spectrum of Cy$_3$P-NP(A)O-B(C$_6$F$_5$)$_3$. 
**Figure S12:** $^{19}$F NMR (chloroform-$d$, 471 MHz, 25 °C) spectrum of Cy$_3$P-NP(A)O-B(C$_6$F$_5$)$_3$.

**Figure S13:** $^{11}$B NMR (chloroform-$d$, 161 MHz, 25 °C) spectrum of Cy$_3$P-NP(A)O-B(C$_6$F$_5$)$_3$.
Synthesis of Cy$_3$P-NPO-B(C$_6$F$_5$)$_3$

Inside the glovebox, a quartz NMR tube with a J young valve was charged with solid, colorless Cy$_3$P-NP(A)O-B(C$_6$F$_5$)$_3$ (100 mg, 0.192 mmol) and 5 mL benzene or toluene. The homogeneous solution was irradiated for 220 min with 254 nm light in a photoreactor outside the glovebox and the reaction followed by NMR spectroscopy. The tube was brought back inside the glovebox and the colorless precipitate that was formed during the irradiation filtered off. The filtrate was layered with pentane and placed in the freezer (–20 °C) over night, yielding 35.3 mg crystalline Cy$_3$P-NPO-B(C$_6$F$_5$)$_3$ in 42% yield. The identity of the product was confirmed by NMR as well as by an X-ray diffraction study performed on a crystal directly grown from an irradiated benzene/pentane solution at –20 °C (Figure 4C). The compound did not pass elemental analysis probably due to the poor thermal stability of the molecule.

$^1$H NMR (chloroform-$d$, 500 MHz, 25 °C) δ 2.16 (m, 2H), 1.80 (m, 15H), 1.28 (m, 16H) ppm. $^{13}$C($^1$H) NMR (chloroform-$d$, 126 MHz, 25 °C) δ 148.9 (b), 147.0 (b), 140.7(b), 138.7 (b), 138.0 (b), 136.1 (b), 34.2 (d, $J$ = 2.4 Hz), 33.8 (d, $J$ = 2.4 Hz), 26.6, 26.5, 26.4, 26.3, 25.6 ppm. $^{31}$P($^1$H) NMR (chloroform-$d$, 203 MHz, 25 °C) δ 271.1 (dp, $J$ = 77.4, 25.5 Hz), 44.1 (d, $J$ = 78.2 Hz) ppm. $^{19}$F NMR (chloroform-$d$, 471 MHz, 25 °C) δ −133.4 (td, $J$ = 24.8, 8.5 Hz), −158.9 (t, $J$ = 20.3 Hz), 164.78 (td, $J$ = 22.9, 8.4 Hz) ppm. $^{11}$B NMR (chloroform-$d$, 161 MHz, 25 °C) δ −3.06 (b, $\nu_{1/2}$ = 381 Hz) ppm.

![Figure S14: $^1$H NMR (chloroform-$d$, 500 MHz, 25 °C) spectrum of Cy$_3$P-NPO-B(C$_6$F$_5$)$_3$.](image-url)
Figure S15: $^{13}$C{$^1$H} NMR (chloroform-$d$, 126 MHz, 25 °C) spectrum of Cy$_3$P-NPO-B(C$_6$F$_5$)$_3$.

Figure S16: $^{31}$P{$^1$H} and enlarged $^{31}$P{$^1$H} (inset left) as well as $^{31}$P{$^1$H, $^{19}$F} (inset right) NMR (chloroform-$d$, 203 MHz, 25 °C) spectrum of Cy$_3$P-NPO-B(C$_6$F$_5$)$_3$. 
**Figure S17:** $^{19}$F NMR (chloroform-<i>d</i>, 471 MHz, 25 °C) spectrum of Cy$_3$P-NPO-B(C$_6$F$_5$)$_3$.

**Figure S18:** $^{11}$B NMR (chloroform-<i>d</i>, 161 MHz, 25 °C) spectrum of Cy$_3$P-NPO-B(C$_6$F$_5$)$_3$. 
Figure S19: $^{31}$P{¹H} NMR (benzene-$d_6$, 203 MHz, 25 °C) spectrum after thermolysis of Cy$_3$P-NPO-B(C$_6$F$_5$)$_3$ at 80 °C for 3h.
Monitoring the Decay of N$_3$P(O)A by $^1$H NMR Spectroscopy

A standard NMR tube was charged with 10 mg of N$_3$P(O)A and 5 mg acenaphthene as an internal standard. The tube was filled with 0.6 mL benzene-$d_6$ and placed into the NMR spectrometer. All kinetic studies were performed by $^1$H NMR spectroscopy on a Bruker Avance Neo500 spectrometer ($^1$H 500 MHz). Temperatures were calibrated with an ethylene glycol thermometer. Eight-scan spectra were acquired continuously over a period of 3-5 half-lives depending on the temperature. Integrals of the N$_3$P(O)A bridgehead protons were normalized against the methylene protons of internal standard acenaphthene at 2.99 ppm. The integral of the bridgehead protons (A) at 3.72 and 3.75 ppm was evaluated according to a zero-order ($A = A_0 - kt$, Figure S20), first-order ($\ln(A) = \ln(A_0) - kt$, Figure S21) and second-order ($A^{-1} - A_0^{-1} = kt$, Figure S22) kinetics. All experiments were performed three times at a given temperature and averaged. The measurements are summarized in Table S1–S2 and the associated Eyring plot is depicted in Figure S23. All error bars were calculated according to total derivatives.

Figure S20: Decay of N$_3$P(O)A according to a zero-order kinetics ($A = A_0 - kt$) at 60.0 °C.
Figure S21: Decay of $\text{N}_3\text{P(O)A}$ according to a first-order kinetics ($\ln(A) = \ln(A_0) - kt$) at 60.0 °C.

Figure S22: Decay of $\text{N}_3\text{P(O)A}$ according to a second-order kinetics ($A^{-1} - A_0^{-1} = kt$) 60.0 °C.
As only the evaluation according to a first order kinetic profile results in a linear plot, N₃P(O)A decays following first-order kinetics. The experiment was repeated three times.

**Table S1:** Rate constant $k$ and half-life of the decay of N₃P(O)A according to a first-order kinetics at 60.0 °C.

| Experiment | Rate constant / s⁻¹ |
|------------|---------------------|
| #01        | $(1.29 \pm 0.01) \cdot 10^{-3}$ |
| #02        | $(1.02 \pm 0.01) \cdot 10^{-3}$ |
| #03        | $(1.35 \pm 0.03) \cdot 10^{-3}$ |
| average    | $(1.22 \pm 0.02) \cdot 10^{-3}$ |

The same set of experiments was repeated at 52.5, 67.5 and 75.0 °C and an Eyring plot (Figure S23) prepared based on these data.

**Table 2:** Rate constants $k$ of the decay of N₃P(O)A according to a first-order kinetics at 25, 35, 45 and 55 °C

| Exp / T in °C | 52.5   | 60.0   | 67.5   | 70.0   |
|---------------|--------|--------|--------|--------|
| #01           | $(3.45 \pm 0.02) \cdot 10^{-4}$ | $(1.29 \pm 0.01) \cdot 10^{-3}$ | $(3.22 \pm 0.06) \cdot 10^{-3}$ | $(7.40 \pm 0.12) \cdot 10^{-3}$ |
| #02           | $(3.53 \pm 0.09) \cdot 10^{-4}$ | $(1.02 \pm 0.01) \cdot 10^{-3}$ | $(3.30 \pm 0.03) \cdot 10^{-3}$ | $(8.06 \pm 0.31) \cdot 10^{-3}$ |
| #03           | $(6.64 \pm 0.09) \cdot 10^{-4}$ | $(1.35 \pm 0.03) \cdot 10^{-3}$ | $(3.07 \pm 0.04) \cdot 10^{-3}$ | $(7.13 \pm 0.29) \cdot 10^{-3}$ |
| average       | $(4.54 \pm 0.07) \cdot 10^{-4}$ | $(1.22 \pm 0.02) \cdot 10^{-3}$ | $(3.20 \pm 0.05) \cdot 10^{-3}$ | $(7.53 \pm 0.24) \cdot 10^{-3}$ |

**Figure S23:** Eyring plot for the decay of N₃P(O)A using rate constants from monitoring N₃P(O)A decay by ¹H NMR spectroscopy.
Molecular Beam Mass Spectrometry (MBMS)

The molecular beam mass spectrometer (MBMS) apparatus has been previously described elsewhere. Briefly, the apparatus consists of two high vacuum chambers designated the source and detection chamber. The source chamber consists of a sample holder suspended in the middle of the vacuum chamber. The sample holder is a ceramic cup directed at a 1 mm diameter skimmer from the source chamber to the detection chamber. The ceramic cup is loaded with 10 to 15 mg of sample, restrained with a stainless steel screen (98% open area, Unique Wire Weaving Co.), and resistively heated with Nichrome wire wrapped around the cup. The temperature is monitored with a thermocouple reader, the placement of which on the sample holder may have some effect on the temperature reading. Experience has indicated that temperature readings are generally consistent within 5 °C between runs. Once gases are evolved from the sample, they pass unimpeded through a 1 mm diameter skimmer between the source chamber and the detection chamber, creating a molecular beam. The molecular beam is then sent to the entrance of an axially oriented Extrel MAX600 Mass Spectrometer (Extrel Core Mass Spectrometers), where the beam is ionized by EI (70 eV), mass separated by a quadrupole, and detected by a Faraday cup. The masses of interest are monitored as a function of temperature and are baseline corrected for background signal. Where depicted, literature fragmentation data were taken from the AIST SDBS.

Figure S24: Molecular Beam Mass Spectrum (MBMS) of $\text{N}_3\text{P(0)A}$ with the major detected decomposition products that were assigned to $\text{N}_2^+\ (m/z = 28)$, $\text{P}^+\ (m/z = 31)$, $\text{PN}^+\ (m/z = 45)$, anthracene$^+\ (A, m/z = 178)$ and $\text{CPO}^+\ or\ \text{PN}_2^+\ at\ m/z = 59$. 

S18
X-Ray Diffraction Studies

Diffraction-quality, colorless crystals of \( \text{N}_3\text{P(O)A} \), \( \text{Cy}_3\text{P=NP(O)A} \), \( \text{Cy}_3\text{P-NP(A)O-B(C}_6\text{F}_5)_3 \) and \( \text{Cy}_3\text{P-NPO-B(C}_6\text{F}_5)_3 \) were grown at \(-20\, ^\circ\text{C}\) from saturated solutions as described in the experimental procedure. Low-temperature (\(-100\, ^\circ\text{C}\)) diffraction data were collected on a Bruker-AXS X8 Kappa Duo diffractometer with \( I_\mu S \) micro-sources, coupled to a Photon 3 CPAD detector and a Smart APEX2 CCD detector, respectively, performing \( \phi \) - and \( \omega \)-scans. Cu \( K_\alpha \) radiation (\( \lambda = 1.54178 \, \text{Å} \)) was used for \( \text{N}_3\text{P(O)A} \) and Mo \( K_\alpha \) radiation (\( \lambda = 0.71073 \, \text{Å} \)) was used for the other three structures. The structures were solved by dual-space methods using SHELXT\(^{12}\) and refined against \( F^2 \) on all data by full-matrix least squares with SHELXL-2017\(^{13}\) following established refinement strategies.\(^{14}\) All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the \( U \)-value of the atoms they are linked to. Details of the data quality and a summary of the residual values of the refinement are listed in Tables S3–S5. All .cif files are available from the CCDC CSD.

\( \text{N}_3\text{P(O)A} \) crystallizes in the monoclinic centrosymmetric space group \( P2_1/c \) with two molecules of \( \text{N}_3\text{P(O)A} \) per asymmetric unit. In addition, the asymmetric unit contains one half molecule of highly disordered diethyl ether. This solvent was modelled as disordered over six positions (three of them crystallographically unique); however this model did not lead to a stable refinement. Therefore, SQUEEZE\(^{15}\) as implemented in Platon\(^{16}\) was used to address the diffuse solvent electron density. SQUEEZE accounted for ca. 80 electrons, which corresponds to just below two \( \text{Et}_2\text{O} \) molecules per unit cell. This lines up well with the half ether molecule per asymmetric unit that was modelled unsuccessfully as disordered over three independent positions near the crystallographic inversion center. The disorder model is still contained in the SHELXL instruction file as a comment. Since the SHELXL instruction file is part of the CIF file, the attempted solvent disorder can be examined by those interested.

\( \text{Cy}_3\text{P=NP(O)A} \) crystallizes in the monoclinic space group \( P2_1/n \) with one molecule of \( \text{Cy}_3\text{P=NP(O)A} \) and one molecule of diethyl ether in the asymmetric unit. The molecules exhibit no disorder.

\( \text{Cy}_3\text{P-NP(A)O-B(C}_6\text{F}_5)_3 \) crystallizes in the triclinic space group \( P1 \) with two molecules of \( \text{Cy}_3\text{P-NP(A)O-B(C}_6\text{F}_5)_3 \) and four molecules of diethyl ether in the asymmetric unit. Two of the four diethyl ethers were refined as disordered over two positions with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters. The disorder ratios were refined freely and converged at 0.558(5) and 0.661(4).

\( \text{Cy}_3\text{P-NPO-B(C}_6\text{F}_5)_3 \) crystallizes in the monoclinic space group \( C2/c \) with one molecule of \( \text{Cy}_3\text{P-NPO-B(C}_6\text{F}_5)_3 \) in the asymmetric unit. The molecule exhibits no disorder.
Table S3: Crystallographic data for N$_3$P(O)A.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| CSD identification code                       | 2113855                                    |
| Reciprocal net code                           | P8_20123                                   |
| Empirical formula                             | C$_{14}$H$_{10}$N$_3$OP                    |
| Formula weight (g mol$^{-1}$)                 | 267.22                                     |
| Temperature (K)                               | 100(2)                                     |
| Wavelength (Å)                                | 1.54178                                    |
| Crystal system                                | Monoclinic                                 |
| Space group                                   | P2$_1$/$c$                                  |
| Unit cell dimensions (Å, °)                   | a = 7.1500(3), b = 20.8990(7), c = 18.2161(6), α = 90, β = 161.204(2), γ = 90 |
| Volume (Å$^3$)                                 | 2721.39(17)                                |
| Z                                             | 8                                          |
| Density (calc., g cm$^{-3}$)                  | 1.304                                      |
| Absorption coefficient (mm$^{-1}$)            | 1.754                                      |
| $F$(000)                                      | 1104                                       |
| Crystal size (mm$^3$)                         | 0.230 x 0.015 x 0.010                      |
| Theta range for data collection (°)           | 3.219 to 75.352                            |
| Index ranges                                  | −8 ≤ h ≤ 7, −24 ≤ k ≤ 26, −22 ≤ l ≤ 22    |
| Reflections collected                         | 34065                                      |
| Independent reflections, $R_{int}$            | 5566, 0.0771                               |
| Completeness to Θ$_{max}$ (%)                 | 100.0                                      |
| Absorption correction                         | Semi-empirical from equivalents            |
| Max. and min. transmission                    | 0.5542 and 0.4355                          |
| Refinement method                             | Full-matrix least-squares on $F^2$         |
| Data / restraints / parameters                | 5566 / 0 / 343                             |
| Goodness-of-fit on $F^2$                      | 1.049                                      |
| Final $R$ indices [$I > 2σ(I)$]               | $R_1 = 0.0432$, $ωR_2 = 0.1112$            |
| $R$ indices (all data)                        | $R_1 = 0.0602$, $ωR_2 = 0.1228$            |
| Largest diff. peak and hole (e Å$^{-3}$)      | 0.312 and −0.484                           |
### Table S4: Crystallographic data for Cy$_3$P=NP(O)A.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| CSD identification code                       | 2113617                                    |
| Reciprocal net code                           | X8_21042                                   |
| Empirical formula                             | C$_{36}$H$_{53}$NO$_2$P$_2$                |
| Formula weight (g mol$^{-1}$)                 | 597.73                                     |
| Temperature (K)                               | 100(2)                                     |
| Wavelength (Å)                                | 0.71073                                    |
| Crystal system                                | Monoclinic                                 |
| Space group                                   | $P2_1/n$                                   |
| Unit cell dimensions (Å, °)                   | $a = 11.6601(5)$, $\alpha = 90$           |
|                                              | $b = 18.2594(7)$, $\beta = 91.9110(10)$   |
|                                              | $c = 15.1712(6)$, $\gamma = 90$           |
| Volume (Å$^3$)                                 | 3228.3(2)                                  |
| $Z$                                           | 4                                          |
| Density (calc., g cm$^{-3}$)                  | 1.222                                      |
| Absorption coefficient (mm$^{-1}$)            | 0.167                                      |
| $F$(000)                                      | 1288                                       |
| Crystal size (mm$^3$)                         | 0.230 x 0.140 x 0.125                      |
| Theta range for data collection (°)           | 1.746 to 31.511                            |
| Index ranges                                  | $-17 \leq h \leq 17, -26 \leq k \leq 24, -22 \leq l \leq 22$ |
| Reflections collected                         | 122510                                     |
| Independent reflections, $R_{int}$            | 10744, 0.0517                              |
| Completeness to $\Theta_{max}$ (%)            | 100.0                                      |
| Absorption correction                         | Semi-empirical from equivalents            |
| Max. and min. transmission                    | 0.7462 and 0.6662                          |
| Refinement method                             | Full-matrix least-squares on $F^2$         |
| Data / restraints / parameters                 | 10744 / 0 / 372                            |
| Goodness-of-fit on $F^2$                      | 1.037                                      |
| Final $R$ indices [$I > 2\sigma(I)$]          | $R_1 = 0.0345$, $\omega R_2 = 0.0874$      |
| $R$ indices (all data)                        | $R_1 = 0.0423$, $\omega R_2 = 0.0921$      |
| Largest diff. peak and hole (e Å$^{-3}$)      | 0.453 and $-0.352$                         |
Table S5: Crystallographic data for Cy3P-NP(A)-O-B(C6F5)3.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| CSD identification code                       | 2113618                                    |
| Reciprocal net code                           | X8_21037                                   |
| Empirical formula                             | C₅₈H₆₃BF₁₅NO₃P₂                           |
| Formula weight (g mol⁻¹)                      | 1179.84                                    |
| Temperature (K)                               | 100(2)                                     |
| Wavelength (Å)                                | 0.71073                                    |
| Crystal system                                | Triclinic                                  |
| Space group                                   | P1                                         |
| Unit cell dimensions (Å, °)                   | a = 12.1132(6), α= 72.9230(10)             |
|                                           | b = 20.5429(9), β= 78.6680(10)             |
|                                           | c = 23.5935(10), γ = 89.9210(10)           |
| Volume (Å³)                                   | 5492.8(4)                                  |
| Z                                             | 4                                          |
| Density (calc., g cm⁻³)                       | 1.427                                      |
| Absorption coefficient (mm⁻¹)                 | 0.176                                      |
| F(000)                                        | 2448                                       |
| Crystal size (mm³)                            | 0.380 x 0.265 x 0.205                      |
| Theta range for data collection (°)           | 1.039 to 30.526                            |
| Index ranges                                  | 202912                                     |
| Reflections collected                         | 33559, 0.0474                              |
| Completeness to Θ max (%)                    | 99.9                                       |
| Absorption correction                         | Semi-empirical from equivalents            |
| Max. and min. transmission                    | 0.7461 and 0.7121                          |
| Refinement method                             | Full-matrix least-squares on F²            |
| Data / restraints / parameters                | 33559 / 3024 / 1544                        |
| Goodness-of-fit on F²                         | 1.034                                      |
| Final R indices [I > 2σ(I)]                   | R₁ = 0.0456, ωR₂ = 0.1234                  |
|                                           | R₁ = 0.0695, ωR₂ = 0.1381                  |
| R indices (all data)                          | R₁ = 0.0695, ωR₂ = 0.1381                  |
| Largest diff. peak and hole (e Å⁻³)           | 0.530 and −0.585                           |
| Property                                      | Value                                                                 |
|-----------------------------------------------|----------------------------------------------------------------------|
| CSD identification code                       | 2113616                                                              |
| Reciprocal net code                           | P8_21108                                                             |
| Empirical formula                             | C₃₆H₃₃BF₁₅NOP₂                                                        |
| Formula weight (g mol⁻¹)                      | 853.38                                                               |
| Temperature (K)                               | 101(2)                                                              |
| Wavelength (Å)                                | 0.71073                                                              |
| Crystal system                                | Monoclinic                                                           |
| Space group                                   | C2/c                                                                 |
| Unit cell dimensions (Å, °)                   |                                                                      |
| a                                             | 28.1151(10), α = 90                                                  |
| b                                             | 13.2645(4), β = 125.0510(10)                                         |
| c                                             | 23.6665(8), γ = 90                                                  |
| Volume (Å³)                                   | 7225.3(4)                                                            |
| Z                                             | 8                                                                   |
| Density (calc., g cm⁻³)                       | 1.569                                                               |
| Absorption coefficient (mm⁻¹)                 | 0.231                                                               |
| F(000)                                        | 3472                                                                |
| Crystal size (mm³)                            | 0.380 x 0.195 x 0.125                                               |
| Theta range for data collection (°)           | 1.770 to 33.216                                                      |
| Index ranges                                  |                                                                      |
| Reflections collected                         | 229148                                                              |
| Independent reflections, Rint                 | 13862, 0.0600                                                        |
| Completeness to Θmax (%)                      | 100.0                                                               |
| Absorption correction                         | Semi-empirical from equivalents                                     |
| Max. and min. transmission                    |                                                                      |
| Max. and min. transmission                    | 0.7465 and 0.7017                                                   |
| Refinement method                             | Full-matrix least-squares on F²                                      |
| Data / restraints / parameters                 |                                                                      |
| Goodness-of-fit on F²                         | 1.037                                                               |
| Final R indices [I > 2σ(I)]                    | R₁ = 0.0371, ωR₂ = 0.0943                                           |
| R indices (all data)                           | R₁ = 0.0487, ωR₂ = 0.1018                                           |
| Largest diff. peak and hole (e Å⁻³)            | 0.544 and −0.425                                                    |
**Computational Studies**

Unless otherwise indicated, all calculations were performed with the Gaussian 16 Rev C.01 quantum chemistry package. All geometries were optimized at PBE0-D3(BJ)/cc-pVTZ level of theory\(^\text{17-20}\). In all cases, computed electronic energies were corrected for thermal energy to obtain the corresponding free energy (all free energies reported at 298.15 K within this SI). To disclose the nature of all stationary points we computed the corresponding frequencies (Nimag=0 for minima and 1 for transition states). All transition states were also confirmed by PBE0-D3(BJ)/cc-pVTZ IRC computations employing Gaussian 16. All electronic energies were augmented with higher level DLPNO-CCSD(T)/cc-pVTZ energies with TightPNO settings\(^\text{21}\).

Cartesian coordinates (in Å) and energies in (Hartree)

\[
\begin{align*}
A & \ (D_{2h}) \\
C & \quad -0.000000 \quad -1.405559 \quad 0.000000 \\
H & \quad -0.000000 \quad 2.501134 \quad 2.476017 \\
C & \quad -0.000000 \quad -0.722400 \quad 1.223935 \\
H & \quad -0.000000 \quad 1.249925 \quad 4.614267 \\
C & \quad -0.000000 \quad 0.722400 \quad 1.223935 \\
H & \quad -0.000000 \quad -1.249925 \quad 4.614267 \\
C & \quad -0.000000 \quad 1.405559 \quad -0.000000 \\
H & \quad -0.000000 \quad -2.501134 \quad 2.476017 \\
C & \quad -0.000000 \quad 0.722400 \quad -1.223935 \\
H & \quad -0.000000 \quad 2.501134 \quad -2.476017 \\
C & \quad -0.000000 \quad -0.722400 \quad -1.223935 \\
H & \quad -0.000000 \quad 1.249925 \quad -4.614267 \\
C & \quad -0.000000 \quad 1.408446 \quad 2.480280 \\
H & \quad -0.000000 \quad -1.249925 \quad -4.614267 \\
C & \quad -0.000000 \quad 0.714121 \quad 3.662715 \\
H & \quad -0.000000 \quad -2.501134 \quad -2.476017 \\
C & \quad -0.000000 \quad -0.714121 \quad 3.662715 \\
H & \quad -0.000000 \quad 2.498816 \quad -0.000000 \\
C & \quad -0.000000 \quad -1.408446 \quad 2.480280 \\
H & \quad -0.000000 \quad -2.498816 \quad 0.000000 \\
C & \quad -0.000000 \quad 1.408446 \quad -2.480280 \\
C & \quad -0.000000 \quad 0.714121 \quad -3.662715 \\
C & \quad -0.000000 \quad -0.714121 \quad -3.662715 \\
C & \quad -0.000000 \quad -1.408446 \quad -2.480280 \\
\end{align*}
\]

\[E = -539.6167286\]

Zero-point correction = 0.194035
Thermal correction to Energy = 0.203449
Thermal correction to Enthalpy = 0.204393
Thermal correction to Gibbs Free Energy = 0.160588

\[E[DLPNO-CCSD(T)/cc-pVTZ] = -538.4969642\]
Cyc-ONPA (C₆)

\[
\begin{aligned}
&\text{E} = -1010.0935786 \\
&\text{Zero-point correction} = 0.204611 \\
&\text{Thermal correction to Energy} = 0.217126 \\
&\text{Thermal correction to Enthalpy} = 0.218071 \\
&\text{Thermal correction to Gibbs Free Energy} = 0.165651 \\
&[\text{DLPNO-CCSD(T)/cc-pVTZ}] = -1009.0859480
\end{aligned}
\]

ONPA (C₆)

\[
\begin{aligned}
&\text{E} = -1010.0935786 \\
&\text{Zero-point correction} = 0.204611 \\
&\text{Thermal correction to Energy} = 0.217126 \\
&\text{Thermal correction to Enthalpy} = 0.218071 \\
&\text{Thermal correction to Gibbs Free Energy} = 0.165651 \\
&[\text{DLPNO-CCSD(T)/cc-pVTZ}] = -1009.0859480
\end{aligned}
\]
S26

C   0.093023  -1.565647   2.281418
H   2.392779   0.109168  -4.122230
C   0.965189  -1.274112   3.325792
H   2.187180   1.695143  -2.228809
C   1.718375  -0.111652   3.304097
H  -1.456168  -1.802579   0.000000
C   1.607071   0.779751   2.241005
H   1.113780   2.258785   0.000000
C   0.093023  -1.565647  -2.281418
C   0.965189  -1.274112  -3.325792
C   1.718375  -0.111652  -3.304097
C   1.607071   0.779751  -2.241005
P  -1.919595   0.636026   0.000000
N  -0.937055   1.836596   0.000000
O  -3.386675   0.578355   0.000000

E = -1010.2081621
Zero-point correction= 0.207282
Thermal correction to Energy = 0.219193
Thermal correction to Enthalpy = 0.220137
Thermal correction to Gibbs Free Energy = 0.169141
[DLNCCD(T)/cc-pVTZ] = -1009.1995262

$N_3P(O)A$ (C3)

C  -0.059635   0.166721   1.230610
H   2.210454  -1.095407  -2.486346
C   1.184960  -0.488303   0.700429
H   4.082623  -2.121010  -1.230443
C   1.184960  -0.488303  -0.700429
H   4.082623  -2.121010   1.230443
C  -0.059635   0.166721  -1.230610
H   2.210454  -1.095407   2.486346
C  -0.110353   1.576787  -0.700208
H  -0.203749   2.763842  -2.486684
C  -0.110353   1.576787   0.700208
H  -0.302212   4.896097  -1.230256
C   2.216125  -1.082096  -1.402961
H  -0.302212   4.896097   1.230256
C   3.261469  -1.661265  -0.694343
H  -0.203749   2.763842   2.486684
C   3.261469  -1.661265   0.694343
H  -0.268913   0.039138  -2.288323
C   2.216125  -1.082096  -1.402961
H  -0.268913   0.039138   2.288323
C  -0.188685   2.763272  -1.403433
C  -0.248594   3.956523  -0.694252
C  -0.248594   3.956523   0.694252
C  -0.188685   2.763272   1.403433
P  -1.286830  -0.537167   0.000000
O  -2.708173  -0.144564   0.000000
N  -1.050133  -2.234653   0.000000

S26
\[ \begin{array}{cccc}
N & -2.055721 & -2.935122 & 0.000000 \\
N & -2.914614 & -3.653912 & 0.000000 \\
\end{array} \]

\( E = -1119.6208165 \)
Zero-point correction= 0.216013
Thermal correction to Energy = 0.230371
Thermal correction to Enthalpy = 0.231315
Thermal correction to Gibbs Free Energy = 0.174005
\[ \text{[DLPNO-CCSD(T)/cc-pVTZ]} = -1118.5209577 \]

\( \text{N}_3\text{P(O)}\text{A}_2 (C_1) \)

\[ \begin{array}{cccc}
C & -0.236708 & 0.261232 & 1.232101 \\
H & 1.470140 & -1.697679 & -2.486630 \\
C & 0.706711 & -0.779362 & 0.701448 \\
H & 2.870023 & -3.307546 & -1.230372 \\
C & 0.706711 & -0.779362 & -0.701448 \\
H & 2.870023 & -3.307546 & 1.230372 \\
C & -0.236708 & 0.261232 & -1.232101 \\
H & 1.470140 & -1.697679 & 2.486630 \\
C & 0.199221 & 1.601761 & -0.700205 \\
H & 0.511611 & 2.750713 & -2.486706 \\
C & 0.199221 & 1.601761 & 0.700205 \\
H & 1.144050 & 4.789427 & -1.230253 \\
C & 1.477418 & -1.688679 & -1.403185 \\
H & 1.144050 & 4.789427 & 1.230253 \\
C & 2.258554 & -2.592175 & -0.694609 \\
H & 0.511611 & 2.750713 & 2.486706 \\
C & 2.258554 & -2.592175 & 0.694609 \\
H & -0.474239 & 0.215717 & -2.290647 \\
C & 1.477418 & -1.688679 & 1.403185 \\
H & -0.474239 & 0.215717 & 2.290647 \\
C & 0.527289 & 2.744637 & -1.403492 \\
C & 0.876024 & 3.887272 & -0.694264 \\
C & 0.876024 & 3.887272 & 0.694264 \\
C & 0.527289 & 2.744637 & 1.403492 \\
P & -1.642236 & 0.028961 & 0.000000 \\
O & -2.800596 & 0.932810 & 0.000000 \\
N & -2.214346 & -1.575195 & 0.000000 \\
N & -1.548855 & -2.600364 & 0.000000 \\
N & -1.070444 & -3.614894 & 0.000000 \\
\end{array} \]

\( E = -1119.6186116 \)
Zero-point correction= 0.216124
Thermal correction to Energy = 0.230352
Thermal correction to Enthalpy = 0.231296
Thermal correction to Gibbs Free Energy = 0.174774
\[ \text{[DLPNO-CCSD(T)/cc-pVTZ]} = -1118.5183251 \]

\textbf{Complex (C_1)}


\[
\begin{array}{cccc}
C & 0.551951 & -1.738719 & 0.679656 \\
H & -1.986481 & 0.330484 & -2.533409 \\
C & -0.655717 & -1.537142 & 0.017733 \\
H & -4.013936 & -0.851564 & -1.813034 \\
C & -0.704488 & -0.616796 & -1.079296 \\
H & -3.927308 & -2.465683 & 0.067398 \\
C & 0.460164 & 0.056348 & -1.451653 \\
H & -1.809686 & -2.894620 & 1.238671 \\
C & 1.673496 & -0.157443 & -0.792313 \\
H & 2.829415 & 1.213967 & -1.993575 \\
C & 1.716334 & -1.073962 & 0.306373 \\
H & 4.928888 & 0.824126 & -0.780628 \\
C & -1.945639 & -0.390191 & -1.726216 \\
H & 5.003743 & -0.761799 & 1.125732 \\
C & -3.069368 & -1.042455 & -1.319210 \\
H & 2.974741 & -1.964496 & 1.818170 \\
C & -3.020837 & -1.961267 & -0.243263 \\
H & 0.432220 & 0.725019 & -2.305649 \\
C & -1.849270 & -2.200582 & 0.407117 \\
H & 0.585746 & -2.431928 & 1.513870 \\
C & 2.864598 & 0.517476 & -1.163803 \\
C & 4.026624 & 0.300934 & -0.488346 \\
C & 4.069863 & -0.604989 & 0.600264 \\
C & 2.947949 & -1.271856 & 0.984802 \\
P & -0.268517 & 2.434264 & 0.053484 \\
O & -1.619021 & 2.612007 & -0.526735 \\
N & -2.452473 & 0.641304 & 2.197364 \\
N & -1.474900 & 1.070325 & 1.858837 \\
N & -0.380375 & 1.520694 & 1.529671 \\
\end{array}
\]

\[E = -1119.6067191\]
Zero-point correction= 0.213403  
Thermal correction to Energy = 0.229545  
Thermal correction to Enthalpy = 0.230489  
Thermal correction to Gibbs Free Energy = 0.167751  
[DLPNO-CCSD(T)/cc-pVTZ] = –1118.5098217

\[N_2 (D_{\infty h})\]

\[
\begin{array}{ccc}
N & 0.000000 & 0.000000 & 0.545035 \\
N & 0.000000 & 0.000000 & -0.545035 \\
\end{array}
\]

\[E = -109.4418010\]
Zero-point correction= 0.005655  
Thermal correction to Energy = 0.008016  
Thermal correction to Enthalpy = 0.008960  
Thermal correction to Gibbs Free Energy = –0.012768  
[DLPNO-CCSD(T)/cc-pVTZ] = –109.3726900

S28
NPO ($C_{ss}$)

|  | Ox | Px | Np |
|---|---|---|---|
| O | 0.000000 | 0.000000 | -1.423504 |
| P | 0.000000 | 0.000000 | 0.043840 |
| N | 0.000000 | 0.000000 | 1.532728 |

$E = -471.0393259$

Zero-point correction= 0.007155
Thermal correction to Energy = 0.010488
Thermal correction to Enthalpy = 0.011432
Thermal correction to Gibbs Free Energy = -0.015606

$[\text{DLPNO-CCSD(T)/cc-pVTZ}] = -470.6325644$

Cyc-NPO ($C_s$)

|  | Px | Ox | Np | Cx |
|---|---|---|---|---|
| P | -0.007902 | 0.671551 | 0.000000 |
| O | -0.771959 | -0.744000 | 0.000000 |
| N | 0.892562 | -0.614677 | 0.000000 |

$E = -470.9945224$

Zero-point correction= 0.005717
Thermal correction to Energy = 0.008920
Thermal correction to Enthalpy = 0.009864
Thermal correction to Gibbs Free Energy = -0.019181

$[\text{DLPNO-CCSD(T)/cc-pVTZ}] = -470.5863607$

TS1 ($C_1$)

|  | Ox | Px | Np | Np | Np |
|---|---|---|---|---|---|
| O | -1.373553 | -1.451997 | 0.000000 |
| P | -1.280973 | 0.024772 | -0.000000 |
| N | 0.005107 | 0.944045 | -0.000000 |
| N | 1.632268 | 0.231869 | -0.000000 |
| N | 2.709624 | 0.421970 | -0.000000 |

$E = -580.4409043$

Zero-point correction= 0.013016
Thermal correction to Energy = 0.018765
Thermal correction to Enthalpy = 0.019710
Thermal correction to Gibbs Free Energy = -0.018144

$[\text{DLPNO-CCSD(T)/cc-pVTZ}] = -579.9516027$

$\nu = 544.7 \text{ cm}^{-1}$

TS2 ($C_1$)

|  | Ox | Px | Np | Cx |
|---|---|---|---|---|
| C | -0.605143 | -0.922745 | -1.328482 |
| H | 1.826580 | -1.302166 | 2.512062 |
| C | 0.476443 | -1.504706 | -0.615955 |
| H | 3.434727 | -2.855736 | 1.476266 |
| C | 0.618323 | -1.131237 | 0.741676 |
\[ H \quad 3.197573 \quad -3.504942 \quad -0.897672 \\
C \quad -0.296657 \quad -0.120997 \quad 1.201415 \\
H \quad 1.333300 \quad -2.621973 \quad -2.248217 \\
C \quad -1.651062 \quad -0.162934 \quad 0.710475 \\
H \quad -2.646052 \quad 0.626625 \quad 2.444493 \\
C \quad -1.793614 \quad -0.547183 \quad -0.643274 \\
H \quad -4.861727 \quad 0.676525 \quad 1.365421 \\
C \quad 1.706093 \quad -1.610106 \quad 1.480309 \\
H \quad -5.119350 \quad -0.003788 \quad -0.997224 \\
C \quad 2.606209 \quad -2.467699 \quad 0.896725 \\
H \quad -3.159917 \quad -0.747325 \quad -2.297536 \\
C \quad 2.471704 \quad -2.836752 \quad -0.451278 \\
H \quad -0.139097 \quad 0.282339 \quad 2.197939 \\
C \quad 1.434437 \quad -2.350253 \quad -1.204037 \\
H \quad -0.648646 \quad -1.057693 \quad -2.404366 \\
C \quad -2.763661 \quad 0.302205 \quad 1.417558 \\
C \quad -3.996504 \quad 0.337442 \quad 0.809370 \\
C \quad -4.142841 \quad -0.047669 \quad -0.531316 \\
C \quad -3.055403 \quad -0.465592 \quad -1.256333 \\
P \quad 0.344935 \quad 1.368627 \quad -0.315355 \\
O \quad -0.163070 \quad 2.750153 \quad -0.153773 \\
N \quad 3.224949 \quad 3.386511 \quad -0.013245 \\
N \quad 2.659348 \quad 2.418844 \quad -0.075091 \\
N \quad 2.092164 \quad 1.336093 \quad -0.141685 \\

E = -1119.5801459 \\
Zero-point correction= 0.213264 \\
Thermal correction to Energy = 0.228256 \\
Thermal correction to Enthalpy = 0.229200 \\
Thermal correction to Gibbs Free Energy = 0.169786 \\
[DLPNO-CCSD(T)/cc-pVTZ] = -1118.4766742 \\
\nu_i = 255.5 \text{ cm}^{-1}

TS3 (C_i)

C \quad -0.081584 \quad -0.369760 \quad 1.066997 \\
H \quad 1.198418 \quad 2.245304 \quad -2.409763 \\
C \quad 0.753497 \quad 0.806035 \quad 0.640863 \\
H \quad 2.726727 \quad 3.641103 \quad -1.049337 \\
C \quad 0.595878 \quad 1.052584 \quad -0.730278 \\
H \quad 3.008571 \quad 3.203721 \quad 1.355752 \\
C \quad -0.354725 \quad 0.061285 \quad -1.342422 \\
H \quad 1.761546 \quad 1.365373 \quad 2.452391 \\
C \quad -1.677924 \quad 0.186316 \quad -0.626819 \\
H \quad -3.047061 \quad 0.645346 \quad -2.214926 \\
C \quad -1.522252 \quad -0.061640 \quad 0.742423 \\
H \quad -4.998284 \quad 0.736943 \quad -0.691410 \\
C \quad 1.307581 \quad 2.062437 \quad -1.347503 \\
H \quad -4.724996 \quad 0.299499 \quad 1.714176 \\
C \quad 2.169506 \quad 2.838940 \quad -0.581340 \\
H \quad -2.494405 \quad -0.236990 \quad 2.648431
C   2.328597   2.592497   0.775305
H  -0.393146   0.024754  -2.426797
C   1.626805   1.565160   1.395987
H   0.110870  -0.777039   2.055215
C  -2.922966   0.466911  -1.153625
C  -4.015458   0.512786  -0.295544
C  -3.861286   0.265936   1.061647
C   2.675975  -1.800089   0.160898
N   3.460714  -2.011999   0.935920

E = –1119.6178212
Zero-point correction= 0.215991
Thermal correction to Energy = 0.229456
Thermal correction to Enthalpy = 0.230401
Thermal correction to Gibbs Free Energy = 0.175806

[DLRNO-CCSD(T)/cc-pVTZ] = –1118.5171377
\nu_i = 27.7 \text{ cm}^{-1}

TS4 (C_i)

C   -0.112227  -0.038211   1.215788
H   1.008857   2.245884  -2.542817
C   0.532000   1.183133   0.650988
H   2.098985   4.099599  -1.310262
C   0.473507   1.201673  -0.746592
H   2.187705   4.074124   1.150425
C  -0.220315  -0.016809  -1.266562
H   1.203235   2.191745   2.422798
C  -1.606481  -0.061604  -0.664905
H  -2.889066  -0.069615  -2.384161
C  -1.531305  -0.117516   0.732906
H  -4.949654  -0.216299  -1.017090
C   1.042309   2.238458  -1.459530
H  -4.816991  -0.338358   1.436444
C   1.656340   3.275385  -0.764665
H  -2.616803  -0.299484   2.577841
C   1.706267   3.260395   0.621904
H  -0.168337  -0.196078  -2.336815
C   1.149095   2.208898   1.340904
H   0.051776  -0.251508   2.265231
C  -2.828549  -0.097746  -1.303110
C  -3.982180  -0.187311  -0.531102
C  -3.907972  -0.257591   0.853458
C  -2.677559  -0.234614   1.498215
P   0.454943  -1.405291  -0.184229
N   1.798580  -1.202038   0.676959
N   3.169314  -2.200281  -0.002997
\[ E = -1119.5305926 \]
Zero-point correction = 0.211384
Thermal correction to Energy = 0.226499
Thermal correction to Enthalpy = 0.227443
Thermal correction to Gibbs Free Energy = 0.168476
\[
[DLPNO-CCSD(T)/cc-pVTZ] = -1118.4443840
\]
\[ \nu_i = 549.1 \text{ cm}^{-1} \]

**TS5 (C₅)**

|   |  X    |  Y    |  Z    |
|---|-------|-------|-------|
| C | -1.165540 | 1.166096 | 0.000000 |
| H | 0.501466  | -2.293288 | -2.464148 |
| C | -1.006826 | 0.505994  | -1.230682 |
| H | -0.449644 | -1.389307 | -4.547632 |
| C | -0.278184 | -0.708475 | -1.239371 |
| H | -1.697094 | 0.745316  | -4.542183 |
| C | 0.342157  | -1.106624 | 0.000000 |
| H | -2.030829 | 1.976268  | -2.425837 |
| C | -0.278184 | -0.708475 | 1.239371 |
| H | 0.501466  | -2.293288 | 2.464148 |
| C | -1.006826 | 0.505994  | 1.230682 |
| H | -0.449644 | -1.389307 | 4.547632 |
| C | -0.072487 | -1.374676 | -2.451542 |
| H | -1.697094 | 0.745316  | 4.542183 |
| C | -0.595949 | -0.859588 | -3.614222 |
| H | -2.030829 | 1.976268  | 2.425837 |
| C | -1.307887 | 0.350865  | -3.612298 |
| H | 0.872895  | -2.052930 | 0.000000 |
| C | -1.498126 | 1.033026  | -2.439912 |
| H | -1.587851 | 2.165072  | -0.000000 |
| C | -0.072487 | -1.374676 | 2.451542 |
| C | -0.595949 | -0.859588 | 3.614222 |
| C | -1.307887 | 0.350865  | 3.612298 |
| C | -1.498126 | 1.033026  | 2.439912 |
| P | 1.954129  | 0.287763  | 0.000000 |
| N | 1.474912  | 1.722755  | 0.000000 |
| O | 3.116665  | -0.635331 | 0.000000 |

\[ E = -1010.1346504 \]
Zero-point correction = 0.203712
Thermal correction to Energy = 0.216526
Thermal correction to Enthalpy = 0.217471
Thermal correction to Gibbs Free Energy = 0.164146
\[
[DLPNO-CCSD(T)/cc-pVTZ] = -1009.1248146
\]
\[ \nu_i = 211.3 \text{ cm}^{-1} \]

**TS6 (C₅)**

|   |  X    |  Y    |  Z    |
|---|-------|-------|-------|
| P | 1.954129 | 0.287763 | 0.000000 |
| N | 1.474912 | 1.722755 | 0.000000 |
| O | 3.116665 | -0.635331 | 0.000000 |
|    | X       | Y       | Z       |
|----|---------|---------|---------|
| C  | -0.180912 | 0.312209 | 1.233575 |
| H  | 1.562931  | -1.613192 | -2.486728 |
| C  | 0.795873  | -0.698477 | 0.701126  |
| H  | 2.980901  | -3.208052 | -1.230665 |
| C  | 0.178402  | 1.671250  | -0.700630 |
| H  | 0.417677  | 2.840020  | 2.486836  |

E = -1119.5332198
Zero-point correction= 0.211292
Thermal correction to Energy = 0.226628
Thermal correction to Enthalpy = 0.227572
Thermal correction to Gibbs Free Energy = 0.167740

[DLPNO-CCSD(T)/cc-pVTZ] = -1118.4517421

νᵢ = 302.3 cm⁻¹

TS7 (C₅)

|    | X       | Y       | Z       |
|----|---------|---------|---------|
| C  | -0.203514 | 0.172993 | 1.387072 |
| H  | -0.351331 | 2.624823 | -2.452568 |
| C  | -0.395153 | 1.441051 | 0.743357 |
| H  | -0.712745 | 4.741887 | -1.237264 |
| C  | -0.331293 | 1.431390 | -0.664898 |
| H  | -0.826127 | 4.762478 | 1.230765 |
| C  | -0.016298 | 0.144950 | -1.251425 |
| H  | -0.586940 | 2.662614 | 2.505526 |
| C  | -0.649256 | -1.011922 | -0.662773 |
| H  | -0.934608 | -2.186086 | -2.443088 |
C  -0.712104  -1.000025   0.753083
H  -1.800962  -4.141806  -1.218082
C  -0.422926   2.631474  -1.371368
H  -1.912079  -4.126280   1.250116
C  -0.616752   3.813016  -0.688843
H  -1.170993  -2.146952  -2.519660
C  -0.681107   3.824840   0.708836
H   0.194599   0.111088  -2.315891
C  -0.552762   2.655241   1.422429
H  -0.053403   0.154463   2.461423
C  -1.016375  -2.167733  -1.363385
C  -1.488224  -3.258038  -0.676130
C  -1.551131  -3.249558   0.727125
C  -1.145043  -2.149330   1.436649
P   1.761061  -0.253436  -0.064625
O   2.190364  -1.779948  -0.170106
N   3.245766  -0.513734  -0.565594

E = –1010.0641472
Zero-point correction= 0.202208
Thermal correction to Energy = 0.215148
Thermal correction to Enthalpy = 0.216092
Thermal correction to Gibbs Free Energy = 0.162240

[DLPNO-CCSD(T)/cc-pVTZ] = –1009.0548443
νi = 293.5 cm⁻¹
Full Citations for Electronic Structure Codes

**Gaussian 16**

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, D. J. Fox, Gaussian 16 Revision C.01, 2016, Gaussian Inc., Wallingford.

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Chemcraft – graphical software for visualization of quantum chemistry computations. https://www.chemcraftprog.com.

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