Diazaphosphinanes as Hydride, Hydrogen-atom, Proton or Electron Donors under Transition-metal-free Conditions: Thermodynamics, Kinetics and Synthetic Applications

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1. General information.

Chemicals: 1a, 1a-D, 1b-D and 1b-[P]+ were synthesized in this work and the methods were shown below. 1a-[P]+ and 1b2 were synthesized according to literature procedures, and all 1H NMR as well as 31P NMR spectra were shown in the NMR part of Supporting Information. N-methylacridinium iodide A1+, 3 phenanthridinium trifluoromethanesulfonate A2+, benzimidazolium perchlorate A3+, 5 3,5-bis(ethoxycarbonyl)-1,2,6-trimethylpyridin-1-ium tetrafluoroborate A4+, 6 and 2,4,6-tri-tert-butylphenol O•7 were prepared as described before.

CH3CN was purchased from J&K Chemical (99.9 %, Extra dry, water < 10 ppm, J&K seal). THF, n-pentane and toluene were distilled by standard solvent treatment methods. Unless otherwise mentioned, all chemicals were purchased from commercial sources and used without further purification. Reaction temperature refers to temperature of an aluminum heating block or a silicon oil bath, which was controlled by an electronic temperature modulator from IKA.

Reactions and characterizations: All reactions involving 1a and 1b were carried out in very dried glass wares under an argon atmosphere using Schlenk technique until the end of the reactions. 1H and 13C NMR spectra were recorded in acetonitrile-d3 (δH 1.94, δc 118.26), toluene-d8 δH 7.09, 7.01, 6.97, 2.08, δc 137.48, 128.87, 127.96, 125.13, 20.43) and C6D6 (δH 7.16, δc 128.06) on 400 MHz NMR instrument at Center of Basic Molecular Science (CBMS) of Tsinghua University. Data for 1H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad).

Electrochemical: All samples were prepared and all electrochemical experiments were performed in an inert Ar atmosphere. The supporting electrolyte was [Bu4N]PF6, which was recrystallized three times by EtOH and dried about 12 hours before use, and the concentration is about 0.1 M in acetonitrile. A standard three-electrode cell consists of a glassy carbon disk as work electrode, a platinum wire as a counter electrode, and 0.1 M AgNO3/Ag (in 0.1 M [Bu4N]PF6-acetonitrile) as reference electrode. Ferrocene (Fc0/+ ) was used as an external reference and was found to be 0.04 V with respect to our reference electrode. The sample concentrations of 1a, 1b, 1a-[P]+ and 1b-[P]+ are about 1.0 mM. The scan rate was 100 mV/s. All potentials are reported in volts (V) vs. Fc0/+.

Kinetics: The rates of all reactions were determined by UV/Vis spectroscopy in CH3CN by using Stopped-flow apparatus. The temperature of the solutions was maintained at 20 ± 0.2 ºC by using circulating bath cryostats. 1a and 1b are air-sensitive compounds, so all solutions used for measurement were prepared in glove box. Concentrations of approximate 10−5 M were used for the acceptors A+ and O• to achieve an initial absorbance A0 of approximate 1.0. In order to satisfy pseudo first-order kinetics with kobs = k2[1]0 + C, the concentrations of nucleophiles 1 were selected by the criterion [1]0/[A+ or O•]> 10. All concentrations are specified in the Tables below. Pseudo-first order rate constants kobs (s−1) were obtained by fitting the monoexponential function Ai = A0exp(−kobsτ) + C to the observed time-dependent absorbance Ai. To obtain the second-order rate constants kHT and kHAT (M−1 s−1), each acceptor-donor combination was measured in 3 to 5 different concentrations of 1a or 1b. For hydride transfers, kobs = kHT[1] and for hydrogen-atom
transfers, \( k_{\text{obs}} = 2k_{\text{HAT}} \). As for the measurements for Arrhenius and Eyring correlations, kinetics were performed at 5 different temperatures from 292 K to 322 K. Kinetic runs were reported three times at each temperature.

**Acidity estimation:** \( N \)-heterocyclic phosphines with strong hydricity are generally too low to be determined or synthetically used. Although the hydricity of phosphines have been extensively exploited for synthetic applications, their acidic properties remain elusive. This stimulated us to identify the feasibility of 1a and 1b as proton donors. We first chose several strong bases, such as 1,8-diazabicyclo[5,4,0]-7-undecene (DBU, \( pK_a = 24.34 \) in acetonitrile), 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine (TBD, \( pK_a = 26.03 \)) and \((\text{tert-butylimino})\text{tris}(\text{pyrrolidino})\)-phosphorane (BTPP, \( pK_a = 28.42 \)) to deprotonate 1a and 1b. Disappointingly, only negative results were obtained. When stoichiometric ‘BuOK was added to the CD\(_3\)CN solution of 1a, it is pleasant to find that a fast H/D exchange of P-H hydrogen was completed in about 10 minutes. Such a result definitely confirmed the acidic reactivity of P-H hydrides. Reversibly, combing ‘BuOK with 1a-D in CH\(_3\)CN resulted in an almost quantitative recover of 1a after 8 hours. According to the acidities of CH\(_3\)CN (\( pK_a = 31.3 \)) and ‘BuOH (\( pK_a = 32.3 \)) in DMSO solution, the ‘BuOK may be a very strong base in CH\(_3\)CN which could react with solvent CH\(_3\)CN or 1a. Present results indicated that a reaction between 1a and ‘BuOK was established in CH\(_3\)CN (Eq. S1), and, a complete conversion of P-H into P-D demonstrates that 1a may reach the limited value of acidity in CH\(_3\)CN.

\[
\begin{align*}
\text{1a} & \quad \text{BuOK} \quad \text{CD}_3\text{CN} \\
\text{1a-D} & \quad \text{CD}_3\text{CN}
\end{align*}
\]

2. The synthesis of 1a, 1a-D and 1b-D.

**Preparation of 1,3-diisopropyl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaphosphinine 1a.**

A yellow solution of 2-chloro-1,3-diisopropyl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaphosphinine \( 1, 9.1 \) (1.6 g, 5.0 mmol) in THF (20 mL) was cooled to 0 °C, and 1.0 M LiAlH\(_4\) solution in THF (1.25 mL, 1.25 mmol) was slowly added into the mixture. The mixture was stirred for 10 min at 0 °C and then warmed to room temperature for 1 hour. All solvents were evaporated in vacuum, and the residue was extracted with n-hexane (50 mL) and then filtered under Ar atmosphere. The filtrate was evaporated, producing 1e as yellow solid, 1.1 g (80%).

\(^1H\) NMR (400 MHz, CD\(_3\)CN) \( \delta 7.35 \text{–} 7.17 \) (m, 4H), 6.86 (dd, \( J = 5.9, 2.9 \) Hz, 2H), 5.64 (d, \( J = 224.7 \) Hz, 1H), 4.30 – 4.20 (m, 2H), 1.38 (dd, \( J = 8.5, 6.7 \) Hz, 12H). \(^13C\) NMR (101 MHz, CD\(_3\)CN) \( \delta 146.38 \) (d, \( J = 4.8 \) Hz), 136.62, 125.79, 120.77, 119.51, 107.94, 50.23 (d, \( J = 23.3 \) Hz), 22.22 (d, \( J = 14.6 \) Hz), 22.05 (d, \( J = 12.3 \) Hz). \(^31P\) NMR (162 MHz, CD\(_3\)CN) \( \delta 25.66 \) (dt, \( J = 225.0, 13.6 \) Hz). ESI-HR calcd for C\(_{10}\)H\(_8\)N\(_2\)P (M-H\(^+\)) 273.1515, found 273.1504.

**Preparation of 1,3-diisopropyl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaphosphinine-2-d 1a-D.**

The preparation of 1a-D was the same as 1a. A yellow solution of 2-chloro-1,3-
diisopropyl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaphosphinine\(^1, 9\) (1.6 g, 5.0 mmol) in THF (20 mL) was cooled to 0 °C, and 2.0 M LiAlD\(_4\) solution in THF (0.6 mL, 1.25 mmol) was slowly added into the mixture. The mixture was stirred for 10 min at 0 °C and then warmed to room temperature for 1 hour. All solvents were evaporated in vacuum, and the residue was extracted with n-hexane (50 mL) and then filtered under Ar atmosphere. The filtrate was evaporated, producing 1a-D as yellow solid, 1.0 g (73%).

\(^1\)H NMR (400 MHz, CD\(_3\)CN) \(\delta\) 7.35 – 7.18 (m, 4H), 6.85 (dd, \(J = 5.6, 3.0\) Hz, 2H), 4.29 – 4.19 (m, 2H), 1.39 – 1.36 (m, 12H).

\(^31\)P NMR (162 MHz, CD\(_3\)CN) \(\delta\) 24.44 (tt, \(J = 48.6, 13.0\) Hz).

Preparation of 1,3-di-tert-butyl-1,3,2-diazaphosphinane-2-d 1b-D.

A solution of 1,3-di-tert-butyl-2-chloro-1,3,2-diazaphosphinane\(^2\) (2.5 g, 10.0 mmol) in THF (40 mL) was cooled to 0 °C, and 2.0 M LiAlD\(_4\) solution (1.3 mL, 2.5 mmol) was slowly added. The mixture was stirred for 10 min at 0 °C and then warmed to room temperature for 3 hours. All solvents were evaporated in vacuum. Then the residue was extracted with n-hexane (50 mL) and filtered. The solvent of filtrate was removed and produced 1b-D yellow oil 1.6 g (74%).

\(^1\)H NMR (400 MHz, toluene-\(d_8\)) \(\delta\) 3.42 – 3.26 (m, 2H), 2.88 – 2.82 (m, 2H), 1.81 – 1.72 (m, 1H), 1.34 – 1.31 (m, 1H), 1.22 (s, 18H).

\(^31\)P NMR (162 MHz, toluene-\(d_8\)) \(\delta\) 48.53 (t, \(J = 34.0\) Hz).

3. The synthesis of 1a-[P]+ and 1b-[P]+.

Preparation of 1a-[P]+.

AgSO\(_3\)CF\(_3\) (AgOTf) (0.51 g, 2.0 mmol) was added into the solution of 2-chloro-1,3-diisopropyl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaphosphinine\(^1, 9\) (0.61 g, 2.0 mmol) in 10 mL of acetonitrile. After 1 hours stirring, the reaction mixture was filtered through a glass frit packed with Celite. The filtrate was concentrated to yield red solid 1a-[P]+ 0.78 g (93%).

\(^1\)H NMR (400 MHz, CD\(_3\)CN) \(\delta\) 7.47 – 7.33 (m, 4H), 6.94 (dd, \(J = 5.7, 2.9\) Hz, 2H), 4.40 – 4.31 (m, 2H), 1.54 (dd, \(J = 6.7, 1.1\) Hz, 1H), 1.18 – 1.72 (m, 1H), 1.34 – 1.31 (m, 1H), 1.22 (s, 18H).

\(^{13}\)C NMR (101 MHz, CD\(_3\)CN) \(\delta\) 137.22, 135.78, 126.75, 121.43, 119.48, 108.95, 51.13 (d, \(J = 27.6\) Hz), 21.33 (d, \(J = 17.5\) Hz).

\(^1\)H NMR (400 MHz, toluene-\(d_8\)) \(\delta\) 7.19 (d, \(J = 8.0\) Hz, 2H), 7.12 – 7.08 (m, 2H), 6.51 (d, \(J = 7.7\) Hz, 2H), 3.89 (tt, \(J = 13.5, 6.6\) Hz, 2H), 1.32 (dd, \(J = 6.6, 2.2\) Hz, 12H).

\(^31\)P NMR (162 MHz, toluene-\(d_8\)) \(\delta\) 141.26 (s).

The NMR spectroscopic data are in good agreement with those in the literature.\(^1\)

Preparation of 1b-[P]+.

The preparation of 1b-[P]+ was the same as 1a-[P]+. AgSO\(_3\)CF\(_3\) (AgOTf) (0.51 g, 2.0 mmol) was added into the solution of 1,3-di-tert-butyl-2-chloro-1,3,2-diazaphosphinane\(^2\) (0.50 g, 2.0 mmol) in 10 mL of acetonitrile. After 1 hours stirring, the reaction mixture was filtered through a glass frit packed with Celite. The filtrate was concentrated to yield white solid 1b-[P]+ 0.67 g (92%).

\(^1\)H NMR (400 MHz, CD\(_3\)CN) \(\delta\) 3.39 (dd, \(J = 11.3, 5.8\) Hz, 4H), 3.10 – 1.99 (m, 2H), 1.45 (d, \(J = 3.1\) Hz, 18H).

\(^{13}\)C NMR (101 MHz, CD\(_3\)CN) \(\delta\) 62.63 (d, \(J = 18.7\) Hz), 43.98 (d, \(J = 7.8\) Hz), 28.52 (d, \(J = 18.7\) Hz).
14.6 Hz), 24.43. $^{31}$P NMR (162 MHz, CD$_3$CN) δ 248.59 (s). ESI-HR calcd for C$_{11}$H$_{24}$N$_2$P (M$^+$) 215.1672, found 215.1667.

4. Cyclic voltammetry.

Figure S1. 1) Cyclic voltammetry for the oxidation of a) 1.2 mM 1a, b) 1.2 mM 1b, and the reduction of c) 3 mM 1a-[P]$^+$ and d) 1 mM 1b-[P]$^+$ in acetonitrile at 20 °C with 0.1 M [Bu$_4$N]PF$_6$ as supporting electrolytes and Ferrocene (Fc$^{0/+}$) as an external reference at a scan rate of 100 mV/s. 2) Cyclic voltammetry for the oxidation of 1.2 mM 1a at different sweep rates from 50 mV to 1000 mV.

5. Kinetics for the reactions of 1a and 1a-D with A1$^+$. 

Table S1. Kinetics of the reaction of 1a with A1$^+$ in CH$_3$CN at 20 °C (Stopped-flow, $\lambda = 430$ nm).
Table S2. Kinetics of the reaction of 1a-D with A1⁺ in CH₃CN at 20 °C (Stopped-flow, λ = 430 nm).

| [A1⁺] / M | [1a-D] / M | kₕobs / s⁻¹ |
|-----------|-----------|-------------|
| ≈ 5.00 × 10⁻⁵ | 7.33 × 10⁻³ | 1.33 × 10⁻² |
| ≈ 5.00 × 10⁻⁵ | 1.14 × 10⁻² | 2.44 × 10⁻² |
| ≈ 5.00 × 10⁻⁵ | 1.51 × 10⁻² | 3.35 × 10⁻² |
| ≈ 5.00 × 10⁻⁵ | 1.96 × 10⁻² | 4.19 × 10⁻² |

kᵢH₂ = 2.34 ± 0.15 M⁻¹s⁻¹

6. Kinetics for the reactions of 1a and 1a-D with 2,4,6-tri-tert-butylphenol O⁻.

Table S3. Kinetics of the reaction of 1a with O⁻ in CH₃CN at 20 °C (Stopped-flow, λ = 630 nm).

| [A1⁺] / M | [1a] / M | kₕobs / s⁻¹ |
|-----------|-----------|-------------|
| ≈ 5.00 × 10⁻⁵ | 3.03 × 10⁻³ | 1.68 × 10⁻² |
| ≈ 5.00 × 10⁻⁵ | 5.06 × 10⁻³ | 3.18 × 10⁻² |
| ≈ 5.00 × 10⁻⁵ | 8.27 × 10⁻³ | 5.27 × 10⁻² |
| ≈ 5.00 × 10⁻⁵ | 1.14 × 10⁻² | 6.63 × 10⁻² |

kᵢH₁ = 5.94 ± 0.46 M⁻¹s⁻¹

k₁c = 5.04(1a) = 7.02 × 10⁻⁷ M⁻¹s⁻¹

kᵢH₁ = 2.54(1a-D) = 0.300/μM
Table S4. Kinetics of the reaction of 1a-D with O• in CH₃CN at 20 °C (Stopped-flow, λ = 630 nm).

| [O•] / M  | [1a] / M  | \(k_{obs} / \text{s}^{-1}\) |
|-----------|-----------|---------------------------|
| ≈ 2.00 × 10⁻⁴ | 5.74 × 10⁻³ | 8.78 × 10⁻³ |
| ≈ 2.00 × 10⁻⁴ | 7.81 × 10⁻² | 1.05 × 10⁻² |
| ≈ 2.00 × 10⁻⁴ | 1.05 × 10⁻² | 1.52 × 10⁻² |
| ≈ 2.00 × 10⁻⁴ | 1.31 × 10⁻² | 1.86 × 10⁻² |

\(2k_{HAT} = 1.39 ± 0.11 \text{ M}^{-1}\text{s}^{-1}\)

Table S5. Kinetics of the reaction of 1b with O• in CH₃CN at 20 °C (Stopped-flow, λ = 630 nm).

| [O•] / M  | [1a-D] / M | \(k_{obs} / \text{s}^{-1}\) |
|-----------|------------|---------------------------|
| ≈ 2.00 × 10⁻⁴ | 2.65 × 10⁻² | 1.00 × 10⁻³ |
| ≈ 2.00 × 10⁻⁴ | 3.97 × 10⁻² | 1.55 × 10⁻³ |
| ≈ 5.00 × 10⁻⁴ | 4.76 × 10⁻² | 1.86 × 10⁻³ |
| ≈ 5.00 × 10⁻⁴ | 6.30 × 10⁻² | 2.64 × 10⁻³ |

\(2k_{HAT} = 0.0448 ± 0.0020 \text{ M}^{-1}\text{s}^{-1}\)
Table S6. Kinetics of the reaction of 1b-D with O• in CH3CN at 20 °C (Stopped-flow, λ = 630 nm).

| [O•]/M | [1b]/M | \( k_{obs} \)/ s⁻¹ |
|--------|--------|-----------------|
| \( \approx 2.00 \times 10^{-4} \) | \( 6.69 \times 10^{-3} \) | \( 8.00 \times 10^{-3} \) |
| \( \approx 2.00 \times 10^{-4} \) | \( 8.62 \times 10^{-3} \) | \( 1.14 \times 10^{-2} \) |
| \( \approx 2.00 \times 10^{-4} \) | \( 1.00 \times 10^{-2} \) | \( 1.35 \times 10^{-2} \) |
| \( \approx 2.00 \times 10^{-4} \) | \( 1.15 \times 10^{-2} \) | \( 1.53 \times 10^{-2} \) |
| \( \approx 2.00 \times 10^{-4} \) | \( 1.35 \times 10^{-2} \) | \( 1.82 \times 10^{-2} \) |

\[ 2k_{liq} = 1.47 \pm 0.059 \text{ M}^{-1}\text{s}^{-1} \]

Table S7. Kinetics of the reaction of 1a with O• in CH3CN at different temperatures (Stopped-flow, λ = 630 nm).

7. Kinetics for the reactions of 1a and 1a-D with 2,4,6-tri-tert-butylphenol O• at 292 K – 320 K.

Table S7. Kinetics of the reaction of 1a with O• in CH3CN at different temperatures (Stopped-flow, λ = 630 nm).
Table S8. Kinetics of the reaction of 1a-D with O• in CH₃CN at different temperatures (Stopped-flow, λ = 630 nm).

| [1a-D] = 0.0397 M |
|-------------------|
| T / K  | 294.2   | 301.4   | 309.3   | 316.8   | 322     |
| 1/T    | 0.003399| 0.003318| 0.003233| 0.003157| 0.003106|
| kobs (s⁻¹) | 0.00185 | 0.00248 | 0.00392 | 0.00661 | 0.00757 |
| k_HAT (1a-D) | 0.0233  | 0.031234| 0.04937 | 0.083249| 0.09534 |
| lnk_HAT    | -3.75931| -3.46624 | -3.00841| -2.48591| -2.35031 |

8. Kinetics for the reactions of 1b and 1b-D with 2,4,6-tri-tert-butylphenol O• at 292 K – 322 K.

Table S9. Kinetics of the reaction of 1b with O• in CH₃CN at different temperatures (Stopped-flow, λ = 630 nm).
Table S10. Kinetics of the reaction of 1b-D with O• in CH₃CN at different temperatures (Stopped-flow, λ = 630 nm).

| T / K  | 293  | 298  | 303  | 310.5 | 317.5 |
|--------|------|------|------|-------|-------|
| 1/T    | 0.003413 | 0.003356 | 0.0033 | 0.003221 | 0.00315 |
| $k_{\text{obs}}$ (s⁻¹) | 0.0114 | 0.0131 | 0.0158 | 0.0203 | 0.025 |
| $k_{\text{HAT (1b)}}$ | 0.661253 | 0.759861 | 0.916473 | 1.177494 | 1.450116 |
| $\ln k_{\text{HAT}}$ | -0.41362 | -0.27462 | -0.08722 | 0.163389 | 0.371644 |
9. Kinetics for the reactions of 1b and 1b-D with 2,4,6-tri-tert-butylphenol O• at 292 K – 322 K.

### Table S11

|          | ΔHǂ[^a] | ΔSǂ[^d] | ΔGǂ[^c] | E₀[^d] | lnA  |
|----------|---------|---------|---------|--------|------|
| 1a       | 4.97    | -41.45  | 17.11   | 5.58   | 9.62 |
| 1a-D     | 9.50    | -33.78  | 19.40   | 10.11  | 13.49|
| 1b       | 5.43    | -40.81  | 17.39   | 6.04   | 9.94 |
| 1b-D     | 5.81    | -43.26  | 18.49   | 6.42   | 8.72 |

[^a]: In units of kcal/mol.  
[^d]: In units of cal/mol/K.  
[^c]: At 293 K, in units of kcal/mol.  
[^d]: In units of kcal/mol.

10. The reactions of 1a and 1a-D with N-methylacridinium ion A1⁺ in CD₃CN.

A1⁺ (0.02 mmol) was added into the CD₃CN (0.5 mL) solution of 1a (0.02 mmol), and the
mixture was checked by NMR spectrum after 10 minutes.

(1) $^1$H NMR in CD$_3$CN

(2) $^{31}$P NMR in CD$_3$CN

Figure S3. $^1$H and $^{31}$P NMR spectra comparison for the stoichiometric reaction between 1a and A1$^+$. 
A1⁺ (0.02 mmol) was added into the CD₃CN (0.5 mL) solution of 1a-D (0.02 mmol), and the mixture was checked by NMR spectra after 10 minutes.

(1) $^1$H NMR in CD₃CN

(2) $^{31}$P NMR in CD₃CN
**Figure S4.** $^1$H and $^{31}$P NMR spectra comparison for the stoichiometric reaction between 1a-D and A1$^+$. Deuterated ratio > 95% based on the analysis of $^1$H NMR.

11. The equilibrium between 1a and A2$^+$ in CD$_3$CN.

Equilibrium for 1a (0.013 mmol) and A2$^+$ (0.013 mmol) was established about 24 hours in acetonitrile-$d_3$ (0.5 mL) at 20 °C. All the four components in the mixture can be well monitored by $^1$H NMR and $^{31}$P NMR, albeit slight oxidative deterioration of 1a. The equilibrium constant was obtained by the concentration ratio of corresponding four components and calculated by the following equation:

$$K_{eq}(1a) = \frac{[1a-[P]^+][A2^H]}{[1a][A2^+]} = 0.48$$

$$\Delta G_{rxn} = -RT\ln K_{eq} = 0.43 \text{ kcal/mol}$$

$$\Delta G_{rxn} = \Delta G_{Hr}(1a) - \Delta G_{Hr}(A2H)$$

Referenced to the hydricity of 5-methyl-5,6-dihydrophenanthridine A2H ($\Delta G_{Hr}(A2H) = 61.4 \text{ kcal/mol}$), the hydricity $\Delta G_{Hr}$ of 1a can be obtained as 61.8 kcal/mol.

(1) $^1$H NMR in CD$_3$CN

(2) $^{31}$P NMR in CD$_3$CN
Figure S5. Construction of equilibrium for the reaction of 1a (0.013 mmol) and A2⁺ (0.013 mmol) in CD₃CN at 20 °C.

A. The verification of the hydricity ΔG_H⁺ of 1a by the reaction of 1a-[P]⁺ with A2H:

Equilibrium for 1a-[P]⁺ (0.01 mmol) and A2H (0.015 mmol) was established in about 24 hours in acetonitrile-d₃ (0.5 mL) at 20 °C. All the four components in the mixture can be well monitored by ¹H NMR and ³¹P NMR, albeit slight deterioration. The equilibrium constant was obtained from the concentration ratio of the corresponding four components by using the following equation:

\[
K_{eq} = \frac{[1a\cdot[P]⁺]}{[1a][A2H]} = 3.6
\]

\[
\Delta G_{rxn} = -RT\ln K_{eq} = -0.75 \text{ kcal/mol}
\]

\[
\Delta G_{rxn} = \Delta G_{H⁺}(A2H) - \Delta G_{H⁺}(1a)
\]

Referenced to the hydricity of 5-methyl-5,6-dihydrophenanthridine A2H (ΔG_H⁺(A2H) = 61.4 kcal/mol), the hydricity ΔG_H⁺ of 1a can be obtained as 62.1 kcal/mol.

(1) ¹H NMR in CD₃CN
Figure S6. The equilibrium for the reaction of 1a-[P]+ (0.015 mmol) with A2H (0.015 mmol) in CD$_3$CN at 20 °C.

B. The verification of the hydricity $\Delta G_{H^+}$ of 1a by the reaction of 1a with A4$^+$:
Equilibrium for 1a (0.015 mmol) and A4⁺ (0.015 mmol) was established in about 24 hours in acetonitrile-d₃ (0.5 mL) at 20 °C. All the four components in the mixture can be well monitored by ¹H NMR and ³¹P NMR, albeit slight deterioration. The equilibrium constant was obtained by the concentration ratio of their corresponding four components by using the following equation:

\[
K_{eq}(1a) = \frac{[1a-P][A4]}{[1a][A4⁺]} = 0.13
\]

\[
\Delta G_{rxn} = -RT\ln K_{eq} = 1.2 \text{ kcal/mol}
\]

\[
\Delta G_{rxn} = \Delta G_{HF}(1a) - \Delta G_{HF}(A4H)
\]

Reference to the hydricity of diethyl 1,2,6-trimethyl-1,4-dihydropyridine-3,5-dicarboxylate A4H (ΔG_{HF}(A4H) = 61.5 kcal/mol)¹⁰, the hydricity ΔG_{HF} of 1a can be obtained as 62.7 kcal/mol.

(1) ¹H NMR in CD₃CN

(2) ³¹P NMR in CD₃CN
Figure S7. The equilibrium for the reaction of 1a (0.015 mmol) with A4+ (0.015 mmol) in CD3CN at 20 °C.

12. The equilibrium between 1b and A3+ in CD3CN.

The weak equilibrium for the reaction of 1b (0.010 mmol) with A3+ (0.010 mmol) was established in about 48 hours in acetonitrile-d3 (0.5 mL) at 20 °C. The three components (1b, A3+ and A3H) in the mixture can be well monitored by ¹H NMR. The 1b-[P]+ could not be well monitored by ¹H NMR due to the overlap of spectrum, but it could be estimated by the concentration of A3H. The equilibrium was obtained by the concentration ratio of corresponding four components by using the following equation:

\[
K_{eq}(1b) = \frac{[1b-P]^+[A3H]}{[1b][A3^+]} = 0.0016
\]

\[
\Delta G_{rxn} = -RT\ln K_{eq} = 3.75 \text{ kcal/mol}
\]

\[
\Delta G_{rxn} = \Delta G_{H-H}^{(1b)} - \Delta G_{H-H}^{(A3H)}
\]

Reference to the hydricity of 1,3-dimethyl-2,3-dihydro-1H-benzo[d]imidazole A3H (\(\Delta G_{H-H}^{(A3H)} = 45.0 \text{ kcal/mol}\)), the hydricity \(\Delta G_{H-H}^{(1b)}\) of 1b was obtained as 48.8.
13. The reactions of 1a with HOTf and HBF₄•Et₂O in CD₃CN.

Excess HBF₄•Et₂O was added into the CD₃CN (0.5 mL) solution of 1b (0.02 mmol), and the mixture was checked by NMR spectrum immediately.

a) 1a

b) 1a + HBF₄

c) 1a + HBF₄ + pyridine

Figure S9. 1) (a) The ³¹P NMR spectrum of 1a. (b) The ³¹P NMR spectrum of 1aH⁺ generated by the reaction of HBF₄•Et₂O and 1a in CD₃CN, which is almost same with generated by HOTf, and the ¹H NMR spectrum was not shown here due to the effect of Et₂O. (c) The ³¹P NMR spectrum of the mixture that adding pyridine to the reaction of 1a and HBF₄•Et₂O in CD₃CN.
Excess HOTf (purity > 98%) was added into the CD$_3$CN (0.5 mL) solution of 1b (0.02 mmol), and the mixture was checked by NMR spectrum immediately.

Analysis: We thought the position of proton is on the nitrogen atom of 1a, because a doublet peak was detected in the $^{31}$P NMR (a triplet peak will be detected if the position of proton is on the phosphorus atom) and the unsymmetrical peaks of naphthyl ring and isopropyl group were also shown in the $^1$H NMR.

$1a^+$: $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 8.41 (s, 1H), 8.08 (d, $J$ = 8.3 Hz, 1H), 7.77 (d, $J$ = 8.2 Hz, 1H), 7.65 (t, $J$ = 8.0 Hz, 1H), 7.58 (t, $J$ = 7.9 Hz, 1H), 7.49 (d, $J$ = 7.9 Hz, 1H), 7.46 (d, $J$ = 7.4 Hz, 1H), 6.26 (d, $J$ = 236.1 Hz, 1H), 4.58 – 4.49 (m, 1H), 3.87 – 3.51 (m, 1H), 1.68 (d, $J$ = 6.5 Hz, 3H), 1.58 (d, $J$ = 6.6 Hz, 3H), 1.54 (d, $J$ = 6.6 Hz, 3H), 1.06 (d, $J$ = 6.5 Hz, 3H). $^{31}$P NMR (162 MHz, CD$_3$CN) $\delta$ 79.12 (d, $J$ = 236.2 Hz).

(1) $^1$H NMR of 1a$^+$ in CD$_3$CN

(2) $^{31}$P NMR of 1a$^+$ in CD$_3$CN
Figure S10. 1) $^1$H and 2)$^{31}$P NMR spectra comparison for the reaction between 1a and HOTf in CD$_3$CN.

14. The reactions of 1a and 1b with O$^\cdot$ in toluene-$d_8$.

O$^\cdot$ (0.02 mmol) was added into the toluene-$d_8$ (0.5 mL) solution of 1a (0.01 mmol), and the mixture was checked by NMR spectra after 10 minutes.

(1) $^1$HNMR in toluene-$d_8$
(2) $^{31}$P NMR in toluene-$d_8$

Figure S11. $^1$H and $^{31}$P NMR spectra for the reaction between 1a and O'. The integrations of $^1$H NMR spectrum are assigned to the structure shown in the spectra, and the shift of 4.76 ppm in $^1$H NMR spectrum is OH of product 2,4,6-tri-tert-butylphenol, other hydrogen shifts of 2,4,6-tri-tert-butylphenol are not be marked.

O' (0.02 mmol) was added into the toluene-$d_8$ (0.5 mL) solution of 1b (0.01 mmol), and the mixture was checked by NMR spectrum after 10 minutes.

(1) $^1$H NMR in toluene-$d_8$
(2) $^{31}$P NMR in toluene-$d_8$

![Figure S12](image)

Figure S12. $^1$H and $^{31}$P NMR spectra for the reaction between 1b and O'. The integrations of $^1$H NMR spectrum are assigned to the structure shown in the spectra, and the shift of 4.76 ppm in $^1$H NMR spectrum is OH of product 2,4,6-tri-tert-butylphenol OH, other hydrogen shifts of 2,4,6-tri-tert-butylphenol are not be marked.

15. The reaction of 1a and 1a-D with 'BuOK.

$^1$BuOK (1.2 mmol, 1.2 eq.) was added into CD$_3$CN (1.0 mL) solution of 1a (1.0 mmol) at room temperature. After 10 minutes, the solvent was rotary-evaporated, and the residue was extracted with n-hexane (20 mL) and then filtered under Ar atmosphere. The filtrate was evaporated to dryness, producing 1a-D as a yellowish solid, 265 mg (97%).

However, when the same reaction was performed in the more acidic MeOH solution (with other conditions identical), the P-H species didn’t change at all. Similar phenomenon was also observed in the toluene solution.

(1) $^1$H NMR in CD$_3$CN
(2) $^{31}$P NMR in CD$_3$CN

Figure S13. $^1$H and $^{31}$P NMR spectra for the reaction mixture between 1a and tBuOK in CD$_3$CN.
'BuOK (0.04 mmol, 2.0 eq.) was added into the CH$_3$CN (0.5 mL) solution of 1a (0.02 mmol) at room temperature, and the mixture was checked by $^{31}$P NMR spectra.

$^{31}$P NMR of the reaction mixture in CH$_3$CN:

![Figure S14, $^{31}$P NMR spectra for the reaction mixture between 1a-D and 'BuOK in CH$_3$CN.](image)

16. The reaction of 1a-[P]$^+$ with substituted pyridine.

15 mol% load of catalyst and 1.5 equivalents of HBpin were added into the solution of 3-CN-pyridine (2.0 mmol) in 1.0 mL CD$_3$CN. The mixture was heated to 80 °C for 36 hours. The solvent concentrated in the vacuum. Purification of the residues by flash column chromatography under Ar atmosphere (eluent: n-hexane/CH$_3$CN: 50/1) gave 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine-3-carbonitrile a yellow solid (0.186 g, 40%). And the NMR spectra of mixture and product were shown as below:
$^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 6.86 (d, $J$ = 0.9 Hz, 1H), 6.09 (ddd, $J$ = 8.3, 3.1, 1.8 Hz, 1H), 4.83 (dt, $J$ = 8.2, 3.4 Hz, 1H), 3.03 – 2.95 (m, 2H), 1.25 (s, 12H). $^{13}$C NMR (101 MHz, CD$_3$CN) $\delta$ 141.02, 125.52, 120.48, 104.19, 85.83, 85.26, 24.40, 23.46. $^1$B NMR (128 MHz, CD$_3$CN) $\delta$ 23.70.

The NMR spectroscopic data of the product are in good agreement with those in the literature.$^{11}$

(1) $^1$H NMR of the mixture in CD$_3$CN

(2) $^1$H NMR of the isolated product in CD$_3$CN
(3) $^{13}$C NMR of the isolated product in CD$_3$CN

(4) $^{11}$B NMR of the isolated product in CD$_3$CN
**Figure S15.** The NMR spectra of the catalytic reaction of 1a-[P] with substituted pyridine.

17. **The reactions of 1a and 1b with AIBN in C₆D₆.**

AIBN (0.03 mmol, 1.5 eq.) was added into the C₆D₆ (0.5 mL) solution of 1a (0.02 mmol), and the mixture was heated at 80 °C for 3 hours. The reaction was monitored by NMR spectrum.

(1) **¹H NMR in C₆D₆**
(2) $^{31}$P NMR in C$_6$D$_6$

![Diagram of 1a-[$P_2$]](image)

Figure S16. $^1$H and $^{31}$P NMR spectra comparison for the reaction between 1a and AIBN. The integrations of $^1$H NMR spectrum are assigned to the structure shown in the spectra and the byproduct (CNC(CH$_3$)$_2$)$_2$ was not marked.

The synthesis of 1a-[$P_2$] using the reaction of 1a with AIBN.

AIBN (0.3 mmol, 1.5 eq.) was added into the toluene (1.0 mL) solution of 1a (0.2 mmol), and the mixture was stirred at 80 °C for about 3 hours. The solvent was rotary-evaporated, and the residue was washed with pentane (5 mL) and then filtered, producing 1a-[$P_2$] as a yellow solid (50 mg, 92%).

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 7.33 (d, $J = 8.0$ Hz, 4H), 7.26 (t, $J = 7.8$ Hz, 4H), 6.77 (d, $J = 7.6$ Hz, 4H), 3.99 - 3.88 (m, 4H), 1.04 (d, $J = 6.7$ Hz, 12H), 0.95 (d, $J = 6.4$ Hz, 12H). $^{31}$P NMR (162 MHz, C$_6$D$_6$) $\delta$ 38.77.

$^{13}$C NMR (101 MHz, C$_6$D$_6$) $\delta$ 143.77, 136.50, 125.41, 122.99 (t, $J = 4.1$ Hz), 120.05, 110.70, 52.21 (t, $J = 12.1$ Hz), 23.22 (t, $J = 9.6$ Hz), 22.62 (t, $J = 5.6$ Hz).

AIBN (0.03 mmol, 1.5 eq.) was added into the C$_6$D$_6$ (0.5 mL) solution of 1b (0.02 mmol), and the mixture was heated at 80 °C for 3 hours. The reaction was monitored by NMR spectrum. The NMR spectroscopic data of 1b-[$P_2$] are in good agreement with those reported in the literature.
(1) $^1$H NMR in C$_6$D$_6$

![1H NMR spectrum](image1)

Figure S17. $^1$H and $^{31}$P NMR spectra for the reaction between 1b and AIBN. The integrations of $^1$H NMR spectrum are assigned to the structure shown in the spectrum and the byproduct (CNC(CH$_3$)$_2$)$_2$ was not marked.

18. The hydrodehalogenation reaction of bromobenzene.

```
Bromobenzene (0.1 mmol), AIBN (15 mol%), 1b (0.15 mmol) and toluene-$d_8$ (0.5 mL) were mixed in a Schlenk tube under argon and stirred at 90 °C for 5 hours. The $^1$H NMR yield was given using 1,3,5-trimethoxybenzene (0.11 mmol) as internal standard.
```
Figure S18. The NMR spectra of the mixture solution of hydrodehalogenation reaction of bromobenzene.

19. DFT Calculations.

Quantum calculations were conducted by using Gaussian 09\textsuperscript{13}. Geometry optimizations and frequency computations were performed using the M06-2X\textsuperscript{14} density functional in conjunction with the 6-31+G(d) basis set and an ultrafine integration grid. The SMD\textsuperscript{15} model was used to account for the solvation effects of toluene, the solvent used experimentally. All of the optimized geometries were characterized as minima structures by frequency calculations. Thermal free energy corrections were obtained at 293.15 K. To obtain more accurate electronic energies, single-point energy calculations were performed at the (SMD)-M06-2X/6-311++G(2df,2p) level of
theory with the (SMD)-M06-2X/6-31+G(d) optimized structure.

The difference of bond dissociation free energies of P-Br bonds of 1a-Br and 1b-Br was calculated on the basis of reaction Gibbs free energy changes of Eq. S1 and S2 through DFT calculations. The result showed 1a-[P]' and 1b-[P]' should have a comparable ability (with an energy difference of 1.3 kcal/mol) in abstracting bromine atom. This failed to explain the disparate yields of <10% for 1a-[P]' and 90% for 1b-[P]'. Hence, the bromine abstraction pathway seems unlikely.

\[
\Delta G_{\text{rxn}} = -1.3 \text{ kcal/mol}
\]

(S1)

\[
\Delta G_{\text{rxn}} = \text{BDFE}_{1b-\text{Br}(\text{P-Br})} - \text{BDFE}_{1a-\text{Br}(\text{P-Br})} = 1.3 \text{ kcal/mol}
\]

(S2)
20. NMR spectra.

$^1$H NMR

$^1$C NMR
$^1$H NMR in toluene-$d_8$

1a-[$P]^*$

$^{31}$P NMR in toluene-$d_8$

1a-[$P]^*$
$^{31}$P NMR in CD$_3$CN

$^1$H NMR in C$_6$D$_6$
$^{31}$P NMR in C$_6$D$_6$

1a-[P$_2$]

$^{13}$C NMR in C$_6$D$_6$

1a-[P$_2$]
21. Crystal data of 1a.

The crystal structure of 1a could be obtained by the volatilization of solution of 1a in hexane at -30 °C. Crystallographic data of 1a structure including CIF file have been deposited with the Cambridge Crystallographic Data Centre with the numbers of 1947293. Copies of these data can be requested from, free of charge, the CCDC website at https://www.ccdc.cam.ac.uk/structures/.

22. SMD-M06-2X/6-31+G(d) calculated cartesian coordinates and energies.

```
21. Crystal data of 1a.

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22. SMD-M06-2X/6-31+G(d) calculated cartesian coordinates and energies.

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| Element | X          | Y          | Z          |
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| H       | -2.7516440 | -2.7731810 | -0.7361830 |
| H       | -3.4229500 | -2.2637170 | 0.8273180  |
| H       | -4.3517890 | -2.0026390 | -0.6494620 |
| H       | -3.0357740 | 1.4376750  | 0.1829330  |
| H       | -4.5020550 | 0.5580660  | -0.3023840 |
| H       | -3.7740060 | 0.2403930  | 1.2719490  |
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| C       | 2.6396650  | -0.6491660 | -0.4200310 |
| C       | 2.6872670  | 0.0952480  | -1.7592030 |
| C       | 3.3417670  | 0.2070910  | 0.6431300  |
| C       | 3.3552250  | -1.9938170 | -0.5957660 |
| H       | 2.1829470  | -0.4653500 | -2.5535920 |
| H       | 2.2476000  | 1.0962060  | -1.6947210 |
| H       | 3.7359430  | 0.2181790  | -2.0491890 |
| H       | 3.3753370  | -0.2941170 | 1.6165090  |
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| H       | 2.8265240  | 1.1651600  | 0.7620040  |
| H       | 4.3879640  | -1.8251650 | -0.9196220 |
| H       | 3.3952560  | -2.5717990 | 0.3327290  |
| H       | 2.8481660  | -2.5981570 | -1.3559460 |
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Thermal correction to Enthalpy= 0.368994
Thermal correction to Gibbs Free Energy= 0.304532
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Sum of electronic and thermal Enthalpies= -3455.698338
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| C    | 3.17567400  | -0.64581300 | 1.31863000  |
| C    | 2.62706300  | -1.69038300 | -0.89481000 |
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| H    | 3.82970800  | 1.48604400 | -0.26348100 |
| H    | 4.60785200  | 0.05696600 | -0.94170400 |
| H    | 2.53510200  | -1.37274500 | 1.83147600 |
| H    | 4.19451000  | -1.05009900 | 1.29453800 |
| H    | 3.19315300  | 0.27255500 | 1.91628500 |
| H    | 3.64515000  | -2.07617100 | -1.01732500 |
| H    | 2.03859700  | -2.46140900 | -0.38981400 |
| H    | 2.19278300  | -1.52717000 | -1.88733800 |
| C    | -2.68135600 | -0.35637700 | 0.04606700 |
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| C    | -3.28704500 | 0.39190500 | 1.15187700 |
| C    | -3.51385900 | -0.10375200 | -1.31123500 |
| H    | -2.24903600 | -2.43045500 | -0.56759700 |
| H    | -2.22459400 | -2.11926100 | 1.18268000 |
| H    | -3.76488800 | -2.18169300 | 0.32187900 |
| H    | -3.31235500 | 1.47481000 | 0.98578400 |
| H    | -4.31709100 | 0.06201200 | 1.33111700 |
| H    | -2.70063800 | 0.19598500 | 2.05705600 |
| H    | -4.53134200 | -0.48559000 | -1.17120000 |
| H    | -3.59574600 | 0.95966600 | -1.55590500 |
| H    | -3.06505900 | 0.61927700 | -2.16718800 |

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Thermal correction to Enthalpy= 0.364449
Thermal correction to Gibbs Free Energy= 0.303085
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Sum of electronic and thermal Enthalpies= -883.819567
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![Chemical Structure Diagram]

C                  2.99007800  2.41605600 -0.17082000
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| C       | 2.95386800 | 0.00010400 | -0.16339100 |
| C       | 1.54409100 | 0.00005100 | -0.38478700 |
| C       | 0.86806500 | 1.26609400 | -0.48653500 |
| C       | 1.59261000 | 2.43865900 | -0.35783300 |
| H       | 4.73739100 | -1.19964600 | 0.07426500 |
| H       | 3.52295800 | 3.35925800 | -0.08825400 |
| H       | 4.73729400 | 1.19998900 | 0.07430300 |
| C       | 3.66175100 | -1.22734100 | -0.07717900 |
| C       | 0.86815800 | -1.26604100 | -0.48656300 |
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| C       | 1.59280100 | -2.43855200 | -0.35789500 |
| C       | 2.99026800 | -2.41584200 | -0.17088700 |
| H       | 1.09853300 | -3.40118200 | -0.38834700 |
| N       | -0.52240000 | 1.28187100 | -0.71888200 |
| N       | -0.52231400 | -1.28190900 | -0.71889300 |
| P       | -1.49521300 | -0.00005400 | -0.19651400 |
| C       | -1.21012600 | 2.57020200 | -0.97796400 |
| C       | -1.59289300 | 3.29541500 | 0.31251500 |
| C       | -2.42041700 | 2.37869800 | -1.89149200 |
| H       | -0.48779300 | 3.16850100 | -1.53950500 |
| H       | -0.75117700 | 3.36228600 | 1.00809600 |
| H       | -1.94101000 | 4.30963700 | 0.08777500 |
| H       | -2.40645400 | 2.76618100 | 0.82285200 |
| H       | -2.15168100 | 1.79536300 | -2.77831900 |
| H       | -3.24978200 | 1.87839100 | -1.38195200 |
| H       | -2.77975000 | 3.36010800 | -2.21977500 |
| C       | -1.20997200 | -2.57027200 | -0.97799300 |
| C       | -2.42037100 | -2.37878200 | -1.89137600 |
| C       | -1.59255800 | -3.29559500 | 0.31247800 |
| H       | -0.48766500 | -3.16848600 | -1.53965700 |
| H       | -2.15176700 | -1.79536800 | -2.77819200 |
| H       | -2.77790200 | -3.36019200 | -2.21968800 |
| H       | -3.24971300 | -1.87856100 | -1.38177100 |
| H       | -0.75076100 | -3.36246500 | 1.00796000 |
| H       | -2.40609300 | -2.76644100 | 0.82293900 |
| H       | -1.94064100 | -4.30982100 | 0.08770700 |
| Br      | -1.00308800 | -0.00004200 | 2.08284100 |

Zero-point correction= 0.333962 (Hartree/Particle)
Thermal correction to Energy= 0.353733
Thermal correction to Enthalpy= 0.354677
Thermal correction to Gibbs Free Energy= 0.285126
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Sum of electronic and thermal Energies = -3643.807671
Sum of electronic and thermal Enthalpies = -3643.806727
Sum of electronic and thermal Free Energies = -3643.876278

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  C     3.49766900  1.05090900  -0.07218600
  C     2.71999600 -0.13693100  -0.06054600
  C     1.29293600 -0.06567000  -0.05911000
  C     0.67201100  1.23715500  -0.08094500
  C     1.47670300  2.36952800  -0.08887100
  H     4.46162800 -1.41907400  -0.06776700
  H     3.46897200  3.18678800  -0.09255800
  H     4.58078700  0.96550600  -0.07012900
  C     3.37532800 -1.39616400  -0.06943100
  C     0.54515100 -1.30014500  -0.07951500
  H     1.03878900  3.35847500  -0.07328400
  C     1.23283500 -2.50702600  -0.08310600
  C     2.64038000 -2.55051600  -0.08282000
  H     0.69922300 -3.44796200  -0.06498200
  H     3.13402900 -3.51866700  -0.08411600
  N    -0.72621400  1.33880000  -0.10992100
  N    -0.85635400 -1.26036200  -0.11263000
  P    -1.73070800  0.08567600  0.50285100
  C    -1.35525300  2.67125400  -0.24728900
  C    -1.46008600  3.39294200  1.09823900
  C    -2.71809700  2.58750100  -0.93430600
  H    -0.70587100  3.23866300  -0.91995000
  H    -0.49665100  3.43113300  1.61540800
  H    -1.81855700  4.41875400  0.95768200
  H    -2.17158000  2.87320400  1.75101200
  H    -2.65937500  1.99728200  -1.85439400
  H    -3.48549100  2.14840900  -0.28922500
  H    -3.04325200  3.60040300  -1.19455500
  C    -1.61703500 -2.52286300  -0.24814000
  C    -2.95962400 -2.30323800  -0.94484500
  C    -1.80210700 -3.22175800  1.10128400
  H    -1.02509200 -3.15706200  -0.91390500
  H    -2.83251200 -1.72775200  -1.86730400
  H    -3.38673700 -3.27837300  -1.20212900
  H    -3.68168100 -1.78291200  -0.30774500
  H    -0.85015100  3.34813600  1.62588700
```
Zero-point correction= 0.333028 (Hartree/Particle)
Thermal correction to Energy= 0.350802
Thermal correction to Enthalpy= 0.351746
Thermal correction to Gibbs Free Energy= 0.287505

Sum of electronic and zero-point Energies= -1071.950951
Sum of electronic and thermal Energies= -1071.933178
Sum of electronic and thermal Enthalpies= -1071.932233
Sum of electronic and thermal Free Energies= -1071.996475

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