Electronic Supplementary Information

for

Synthesis and reactivity of NHC-coordinated phosphinidene oxide

Debabrata Dhara,[a] Pradeep Kumar Pal,[b] Ramapada Dolai,[a] Nicolas Chrysochos,[c] Hemant Rawat,[a] Benedict J. Elvers,[c] Ivo Krummenacher,[d] Holger Braunschweig,*[d] Carola Schulzke,*[c] Vadapalli Chandrasekhar,*[a,e] U. Deva Priyakumar,*[b] and Anukul Jana*[a]

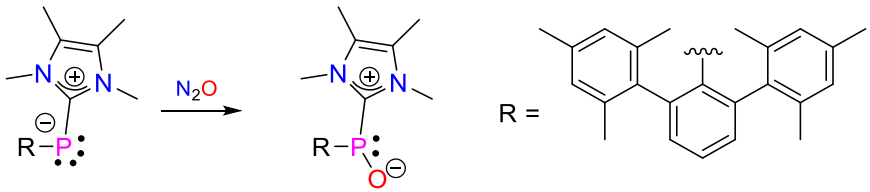
[a] Tata Institute of Fundamental Research Hyderabad
Gopanpally, Hyderabad-500107
Telangana, India
E-mail: ajana@tifrh.res.in
[b] International Institute of Information Technology, Gachibowli, Hyderabad-500032, India
E-mail: deva@iiit.ac.in
[c] Institut für Biochemie, Universität Greifswald, Felix-Hausdorff-Straße 4, D-17489 Greifswald
E-mail: carola.schulzke@uni-greifswald.de
[d] Institute of Inorganic Chemistry and Institute for Sustainable Chemistry & Catalysis with Boron (ICB), Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
E-mail: h.braunschweig@uni-wuerzburg.de
[e] Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016, India
E-mail: vc@iitk.ac.in

Experimental Details and Analytical Data

General considerations

All experiments were carried out under argon or nitrogen atmosphere using standard Schlenk techniques, PL-HE-2GB Innovative Technology GloveBox, and MBraun Unilab GloveBox. Hexane, diethyl ether, THF, and toluene were dried by PS-MD-5 Innovative Technology solvent purification system. Benzene was refluxed over sodium/benzophenone then distilled and stored under argon or nitrogen gas. CH_3CN was refluxed over CaH_2 and then distilled under vacuum followed by freeze-pump-thaw and eventually stored under argon or nitrogen gas. Compound **1** was prepared according to our reported literature procedure.[S1] N_2O gas was dried by passing through P_4O_{10} before passed into the reaction mixture. $NOSbF_6$ was purchased from Sigma Aldrich and used as received. Benzene-d_6, THF-d_8, and toluene-d_8 were dried and distilled over potassium under argon or nitrogen. CD_3CN was dried using CaH_2 and degassed by freeze-pump-thaw cycling. NMR spectra were recorded with a Bruker NanoBay 300 MHz NMR spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the peaks of residual protons of the deuterated solvent (^1H) or the deuterated solvent itself $^{13}C\{^1H\}$. $^{31}P\{^1H\}$ and ^{31}P spectra were referenced to the peaks of H_3PO_4. ^{19}F spectrum was referenced to external tol-CF_3. UV/Vis spectra were acquired using a Jasco V-670 spectrometer using quartz cells with a path length of 0.1 cm. FT-IR spectra were recorded on a Bruker-Alpha spectrometer. Elemental analyses were performed on an Elemental Analyzer from Elementar (Vario Micro Cube). Melting points were determined in closed NMR tubes under argon atmosphere and are reported without correction.

Synthesis of 2



1 **2**

The argon atmosphere of a Schlenk flask containing toluene solution of **1** (0.300 g, 0.640 mmol, in 15 mL of toluene) was exchanged with N_2O gas using standard Schlenk line technique at room temperature. The reaction mixture was stirred for 10 minutes and an appearance of yellow turbidity was observed. Subsequently, the ^{31}P NMR spectrum of an aliquot from the reaction

mixture with 2 drops of C_6D_6 shows complete conversion of **1** into **2**. Then the reaction mixture was evaporated to dryness and washed with hexane to obtain compound **2** as a yellow powder. **Yield**: 0.295 g (95 %). Single crystals suitable for X-ray diffraction were grown from the saturated solution of CH_3CN. **M.P.:** 145 °C (decomposed). **^{1}H NMR (300 MHz, CD_3CN, 298 K):** δ = 1.88 (s, 6H, C*H*$_3$ of Mes), 1.95 (s, 6H, CC*H*$_3$, NHC^{Me4} mixed with CD_3CN residual signal), 2.08 (s, 6H, C*H*$_3$ of Mes), 2.27 (s, 6H, C*H*$_3$ of Mes), 3.13 (s, 6H, N-C*H*$_3$, NHC^{Me4}), 6.74 (s, 2H, Ar-*H*), 6.85-6.87 (m, 4H, Ar-*H*), 7.33 (t, $^3J_{(^{31}P,\ ^1H)}$ = 7.5 Hz, 1H, Ar-*H*) ppm. **^{13}C{^{1}H} NMR (75.43 MHz, CD_3CN, 298 K):** δ = 8.5 (2C, *C*H$_3$C, NHC^{Me4}), 21.4 (1C, *C*H$_3$-Mes), 21.5 (1C, *C*H$_3$-Mes), 21.7 (2C, *C*H$_3$-Mes), 21.9 (1C, *C*H$_3$-Mes), 22.1 (1C, *C*H$_3$-Mes), 31.8 (2C, N-*C*H$_3$, NHC^{Me4}), 128.7 (2C, Ar-*C*H), 129.2 (2C, Ar-*C*H), 129.7 (1C, Ar-*C*H), 129.9 (2C, CH$_3$*C*-*C*CH$_3$, NHC^{Me4}), 130.7 (2C, Ar-*C*H), 136.9 (3C, Ar-C_{quat}), 137.2 (2C, Ar-C_{quat}), 137.8 (2C, Ar-C_{quat}), 140.1 (1C, Ar-C_{quat}), 141.7 (2C, Ar-C_{quat}), 146.7 (1C, d, $^1J_{(^{31}P,\ ^{13}C)}$ = 18 Hz, Ar-C_{ipso}), 159.0 (1C, d, $^1J_{(^{31}P,\ ^{13}C)}$ = 113 Hz, N-*C*-N, NHC^{Me4}) ppm. **^{31}P NMR (121.5 MHz, CD_3CN, 298 K):** δ = 89.6 ppm. **IR (KBr, cm^{-1}):** $\bar{\upsilon}$ (cm^{-1}) = 2407 (vw), 1977 (vw), 1782 (vw), 1736 (vw), 1650 (s), 1608 (s), 1565 (s), 1480(s), 1434 (s), 1402 (s), 1370 (m), 1264 (mw), 1232 (m), 1186 (m) 1111 (m), 1083 (m), 1022(vs), 895 (w), 852 (vs), 806 (vs), 724 (vs), 695 (m), 671 (w), 525(s). **UV/Vis (CH_3CN):** $\lambda_{max}(\varepsilon)$ = 329 (6410), 285 (4397) nm (Lmol^{-1}cm^{-1}). **Elemental Analysis:** Calcd. for ($C_{31}H_{37}N_2OP$): C, 76.83; H, 7.70; N, 5.78; Found: C, 76.82; H, 7.55; N, 5.74.

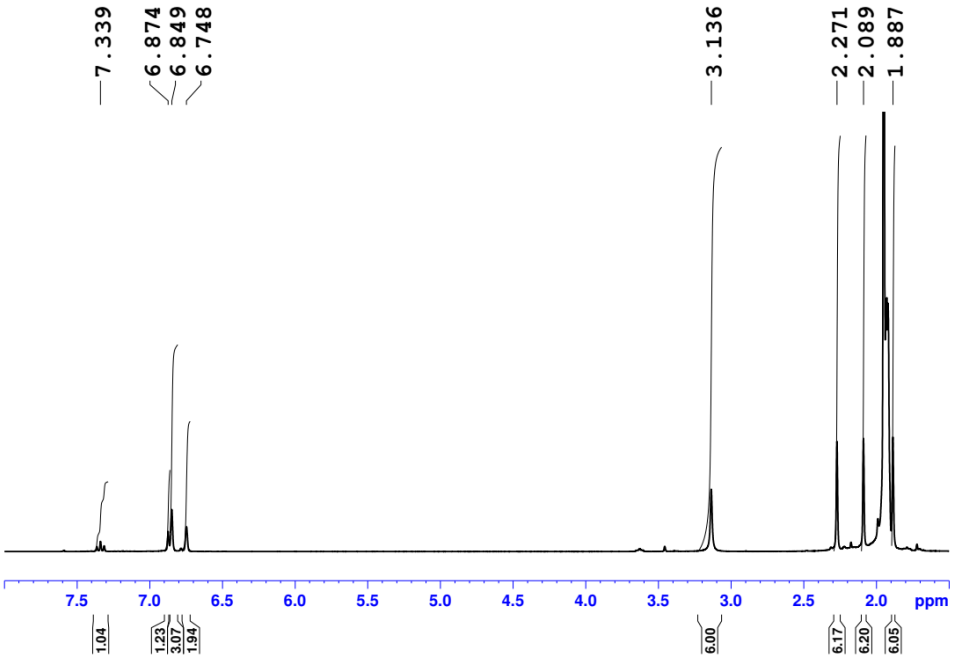


Fig. S1 ^{1}H NMR spectrum of **2** in CD_3CN at RT.

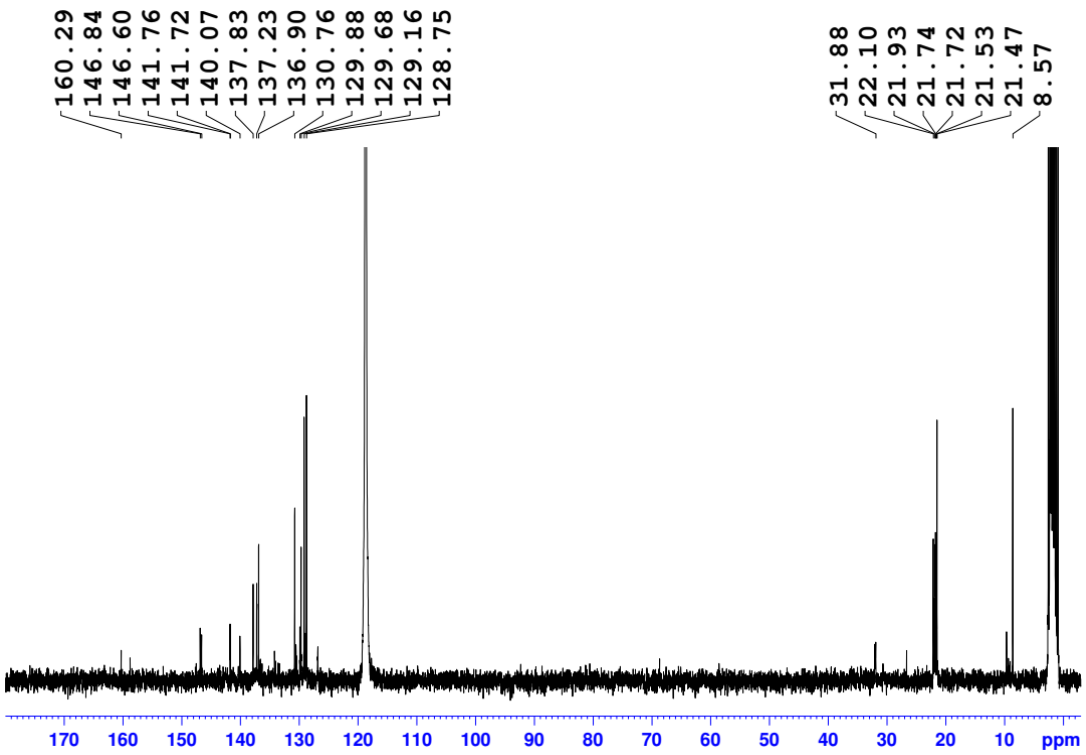


Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum of **2** in CD_3CN at RT.

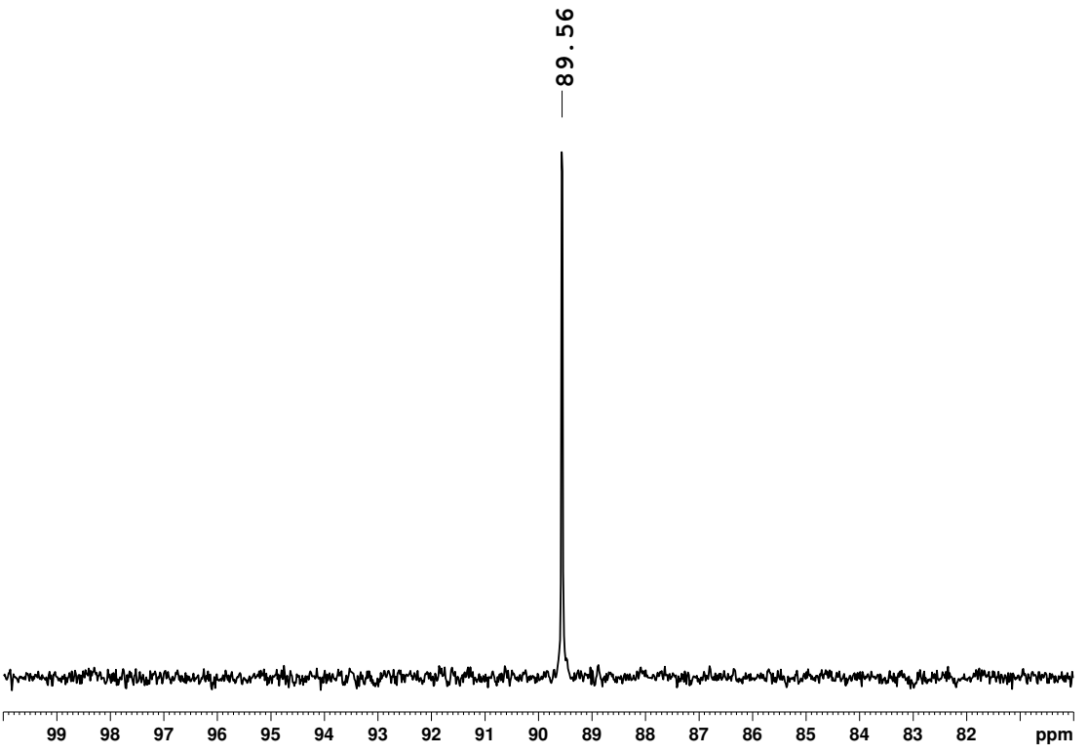
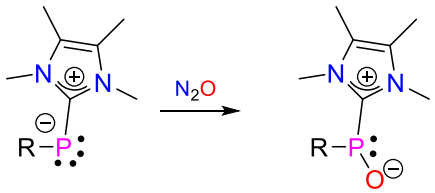


Fig. S3 ^{31}P NMR spectrum of **2** in CD_3CN at RT.

VT-^{31}P NMR study from the synthesis of 2 from of 1 and N_2O



1 **2**

In a NMR tube 0.017 g (0.036 mmol) of compound **1** was taken and dissolved in normal THF (0.4 mL) and into that tube 0.1 mL THF-d_8 was added. The NMR tube was degassed (for removing argon in the tube) by applying the freeze-pump-thaw method and finally filled with N_2O at −78 °C. Then the NMR was recorded with a precooled probe at −70 °C and slowly brought to room temperature while recording ^{31}P in 10 °C intervals. The VT NMR shows the formation of only **2** which started already at −70 °C and at room temperature **1** was fully converted to **2**.

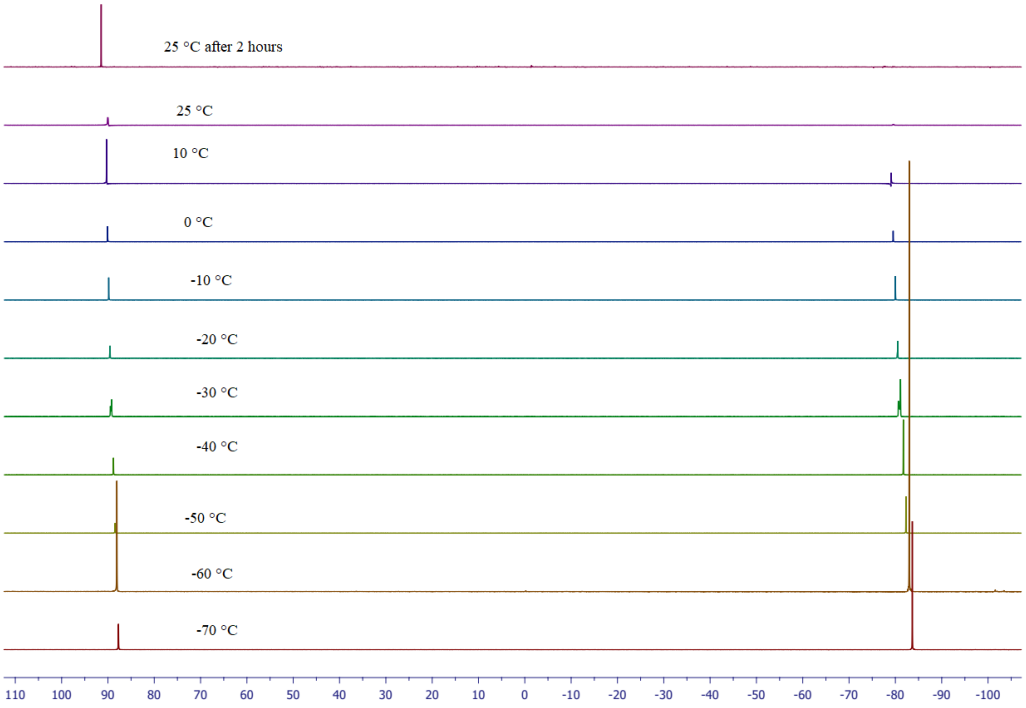


Fig. S4 VT-^{31}P NMR study of **1** with N_2O in THF/THF-d_8 (4:1).

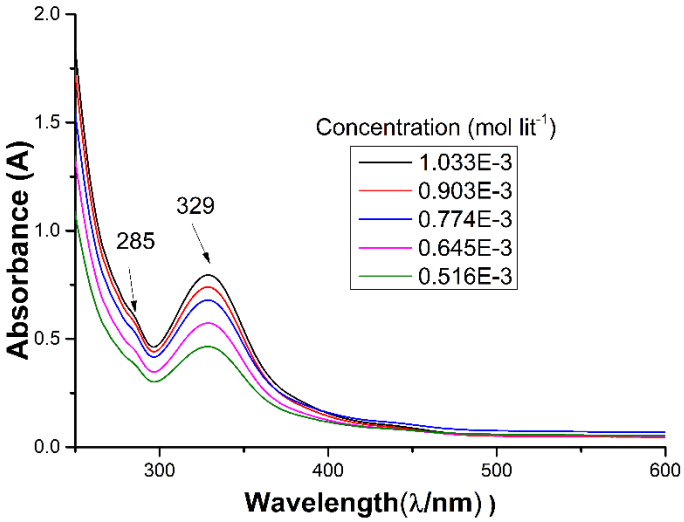


Fig. S5 UV/Vis spectrum of compound **2** in THF at RT.

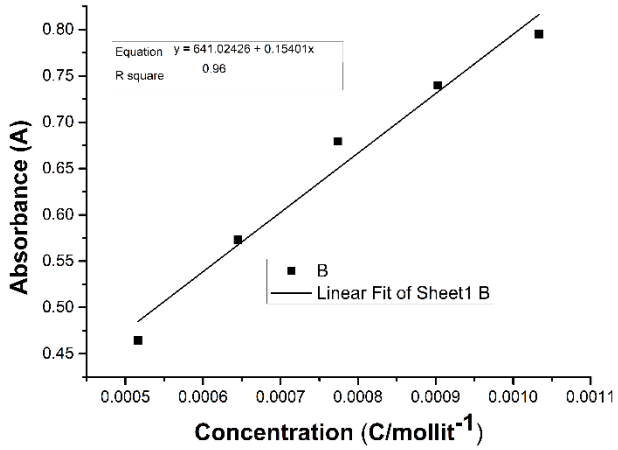


Fig. S6 Linear regression of compound **2** at 329 nm.

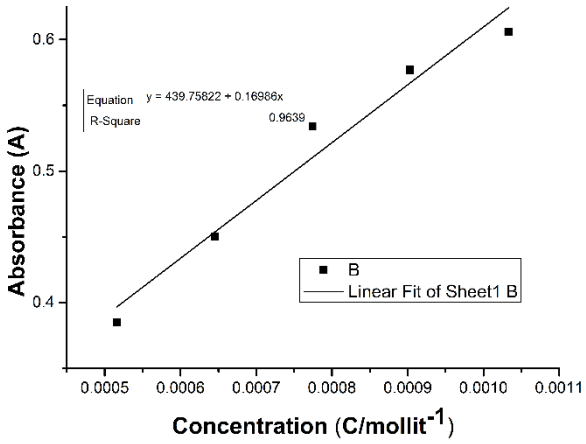
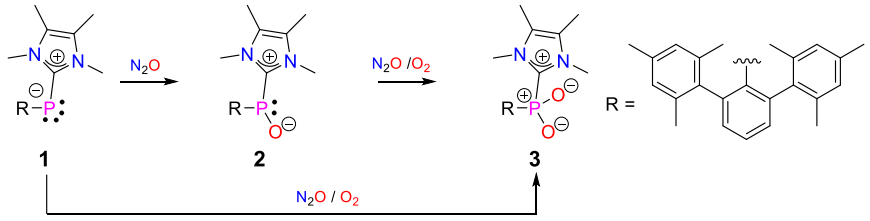


Fig. S7 Linear regression of compound **2** at 285 nm.

Synthesis of 3



Path-1: Using **2** and N_2O

The Ar atmosphere of a Schlenk flask containing turbid toluene solution of **2** (0.480 g, 99 mmol, in 15 mL of toluene) was exchanged with N_2O gas using standard Schlenk line technique at room temperature. The reaction mixture was stirred for 2 hrs, during the course of reaction the yellow solution of **1** turned into colourless and the appearance of a white precipitate was observed. Subsequently, the ^{31}P NMR spectrum of an aliquot from the reaction mixture with 2 drops of C_6D_6 shows complete conversion of **2** into **3**. Then the reaction mixture was filtered and residue solid was collected as compound **3** and dried. **Yield:** 0.470 g (95 %).

Path-2: Using **2** and O_2The Ar atmosphere of a Schlenk flask containing turbid toluene solution of **2** (0.200 g, 41 mmol, in 15 mL of toluene) was exchanged with O_2 gas using standard Schlenk line technique at room temperature. The reaction mixture was stirred for 1 hr, during the course of reaction the yellow solution of **1** turned into colourless and the appearance of a white precipitate was observed. Subsequently, the ^{31}P NMR spectrum of an aliquot from the reaction mixture with 2 drops of C_6D_6 shows complete conversion of **2** into **3** quantitatively. Then the reaction mixture was filtered and residue solid was collected as compound **3**.

Path-3: Using **1** and N_2O

The Ar atmosphere of a Schlenk flask containing turbid toluene solution of **1** (0.2 g, 42 mmol, in 15 mL of toluene) was exchanged with N_2O gas using standard Schlenk line technique at room temperature. The reaction mixture was stirred for 3 hrs, during the course of reaction the yellow solution of **1** turned into colourless and the appearance of a white precipitate was observed. Subsequently, the ^{31}P NMR spectrum of an aliquot from the reaction mixture with 2 drops of C_6D_6 shows complete conversion of **1** into **3**.

Path-4: Using **1** and O_2

The Ar atmosphere of a Schlenk flask containing toluene solution of **1** (0.500 g, 1 mmol, in 15 mL of toluene) was exchanged with O_2 gas using standard Schlenk line technique at room temperature. The reaction mixture was stirred for 1 hour, during the course of reaction the yellow solution of **1** turned into colourless and the appearance of a white precipitate was observed. Subsequently, the ^{31}P NMR spectrum of an aliquot from the reaction mixture with 2 drops of C_6D_6 shows complete conversion of **1** into **3**. Then the reaction mixture was filtered and residue solid was collected as compound **3** and dried. **Yield:** 0.525 g (98 %). Single crystals suitable for X-ray diffraction were grown from the saturated solution of CH_3CN at 0 °C on standing overnight.

M.P.: 150 °C, decomposed. **^{1}H NMR (300 MHz, CD_3CN, 298 K):** δ = 2.03 (s, 18H, CH_3 of Mes), 2.32 (s, 6H, CCH_3, NHC^{Me4}), 3.50 (s, 6H, N-CH_3, NHC^{Me4}), 6.83 (s, 4H, Ar-*H*), 6.88-6.92 (m, 2H, Ar–*H*), 7.45 (t, $^3J_{(^1H, ^1H)}$ = 7.5 Hz. 1H, Ar–*H*) ppm. **^{13}C{^{1}H} NMR (75.43 MHz, CD_3CN, 298 K):** δ = 9.0 (2C, *C*H_3, C*C*H_3, NHC^{Me4}), 21.5 (2C, *C*H_3-Mes), 21.8 (4C, *C*H_3-Mes), 34.4 (2C, N-*C*H_3, NHC^{Me4}), 128.2 (2C, *C*CH$_3$, NHC^{Me4}), 129.0 (4C, Ar-*C*H), 130.8 (1C, Ar-*C*H), 130.8 (1C, Ar-*C*H), 31.4 (1C, Ar-*C*H), 131.5 (1C, Ar-*C*H), 136.9 (2C, Ar-C_{quat}), 137.2 (4C, Ar-C_{quat}), 138.5 (1C, Ar-C_{quat}), 40.4 (1C, Ar-C_{quat}), 141.4 (1C, Ar-C_{quat}), 141.4 (1C, Ar-C_{quat}), 145.3 (1C, d, $^1J_{(^{31}P, ^{13}C)}$ = 9.7 Hz), 147.3 (1C, d, $^1J_{(^{31}P, ^{13}C)}$ = 105 Hz. N-*C*-N, NHC^{Me4}) ppm. **^{31}P NMR (121.5 MHz, CD_3CN, 298 K):** δ = −0.8 ppm. **IR (KBr, cm^{-1}):** ῡ (cm^{-1}) = 2737 (w), 2409 (vw), 1969 (w), 1730 (vw), 1645 (mw), 1566 (m), 1459 (vs), 1366 (w), 1260 (s), 1233 (s), 1184 (m), 1131 (s), 1077 (s), 1042 (s) 859 (m), 847 (vs), 816 (s), 758 (vs), 723 (s), 598 (s), 562 (vs). **Elemental Analysis:** Calcd. for ($C_{31}H_{37}N_2O_2P$): C, 74.38; H, 7.45; N, 5.60; Found: C, 74.40: 12; H, 7.38; N, 5.60.

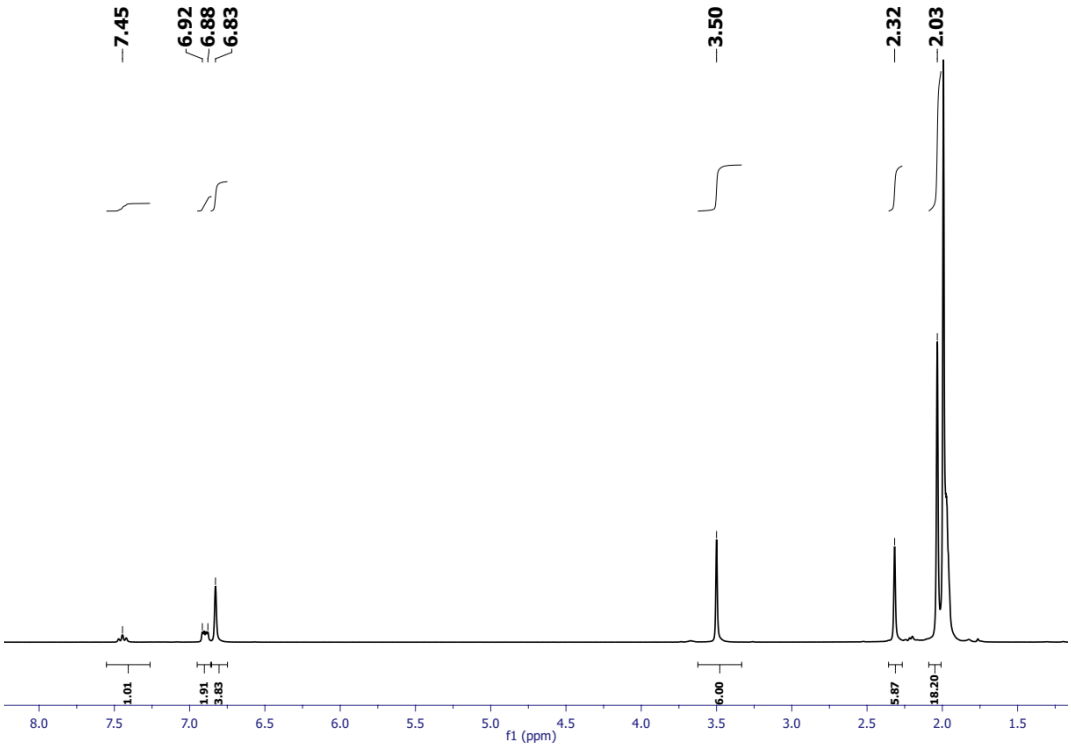


Fig. S8 ^{1}H NMR spectrum of **3** in CD_3CN at RT.

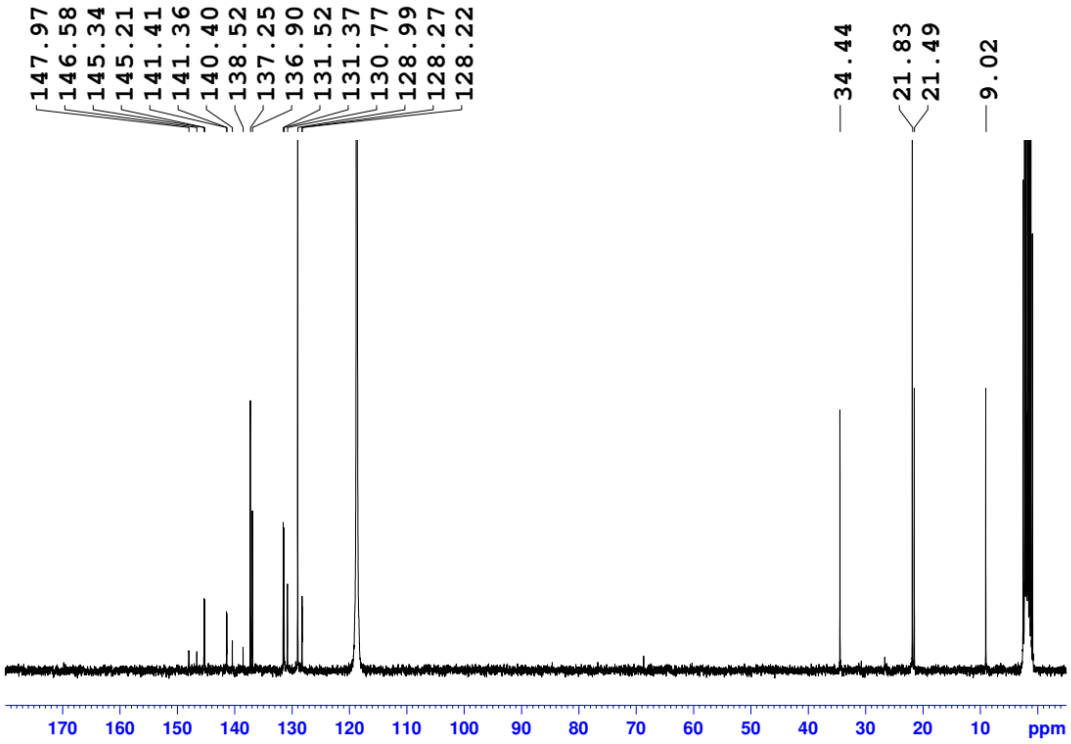


Fig. S9 $^{13}C\{^{1}H\}$ NMR spectrum of **3** in CD_3CN at RT.

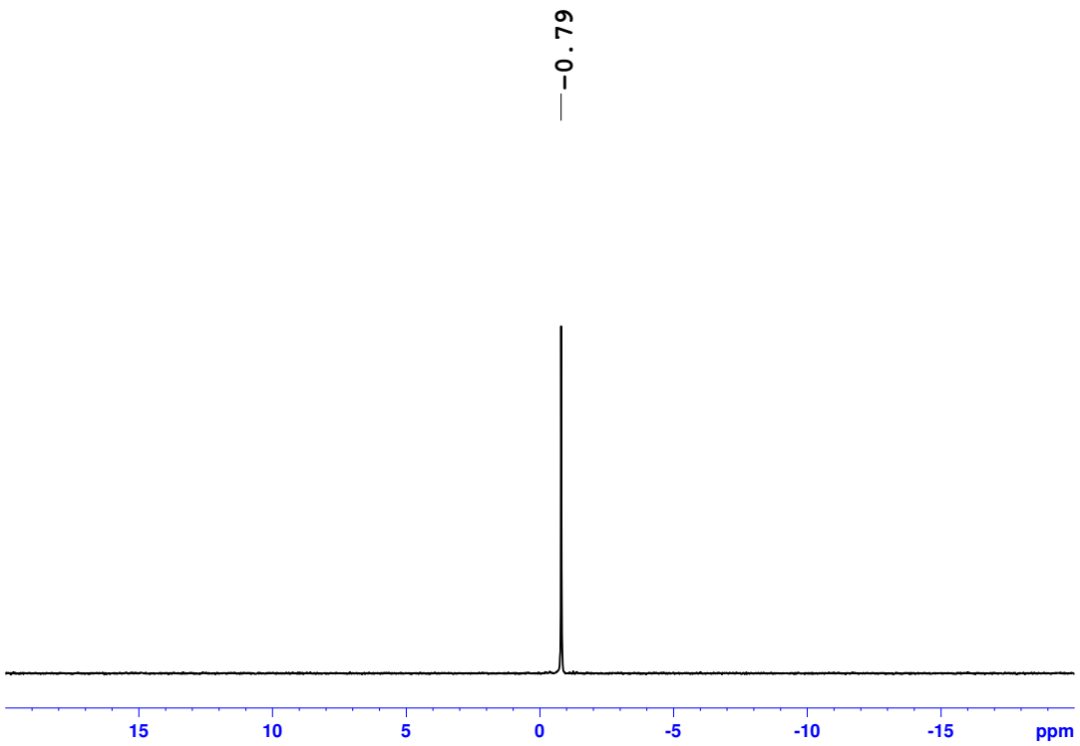
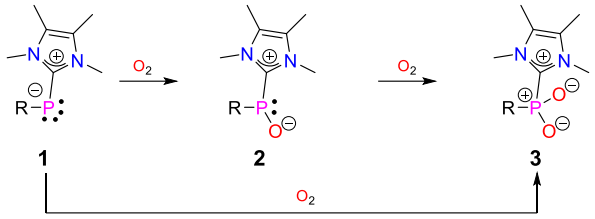


Fig. S10 ^{31}P NMR spectrum of **3** in CD_3CN at RT.

VT NMR of 1 with O_2



In a NMR tube 0.020 g (0.042 mmol) of compound **1** was taken and dissolved in normal THF (0.4 mL) and into that tube 0.1 mL THF-D8 was added. The NMR tube was degassed (for removing argon in the tube) by applying the Freeze-pump-thaw method and finally filled with O_2 at −78 °C. Then the NMR was recorded with a precooled probe at −70 °C and slowly brought to room temperature while recording ^{31}P spectra in 10 °C intervals. The VT NMR shows the formation of **3** started already at −70 °C. At that temperature am signal for compound **2** was also observed. Up to room temperature signals for both 2, and 3 are present. This suggests that the formation of **3** occurs stepwise through the formation of **2**.

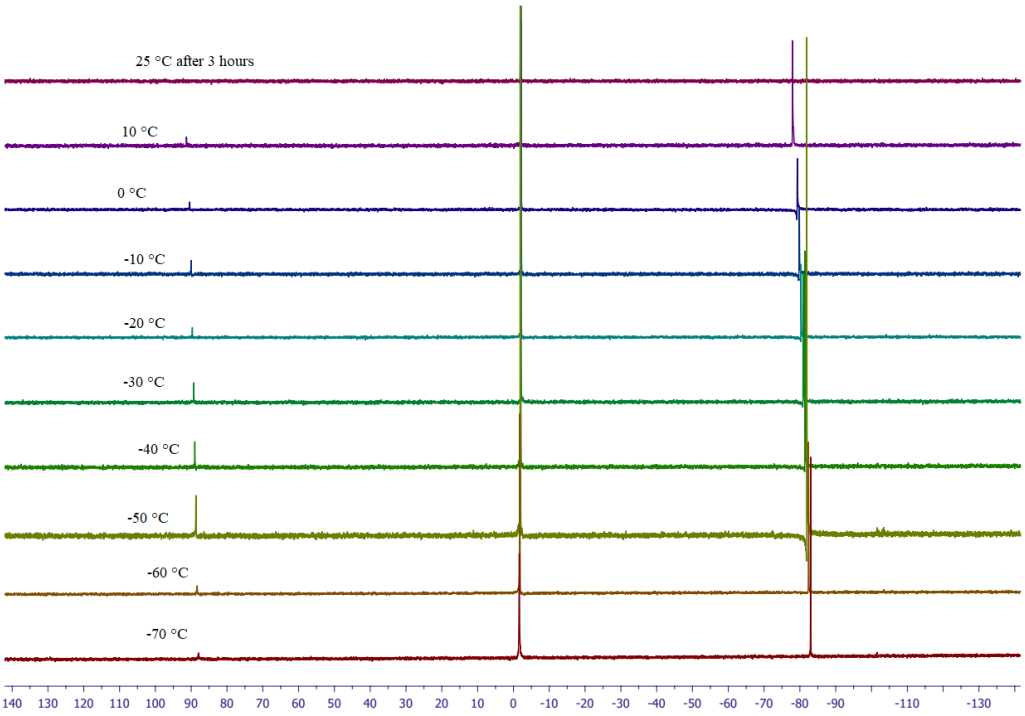
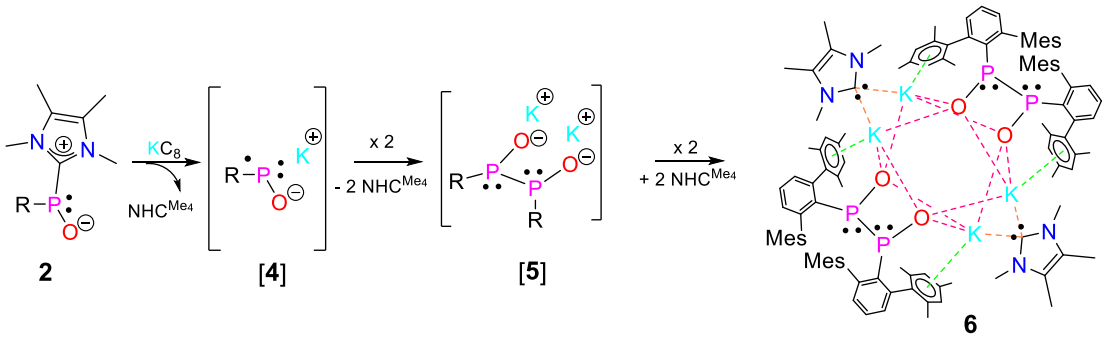


Fig. S11 Variable temperatures ^{31}P NMR of **1** with O_2 in THF/THF-D_8.

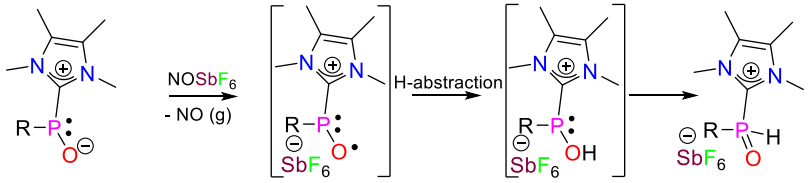
Synthesis of 6



2 [**4**] [**5**] **6**

10 mL of C_6H_6 was added to a Schlenk flask containing 0.250 g (0.515 mmol) of **2** and 0.091 g (0.670 mmol) of KC_8 at 0 °C. Then the reaction mixture was slowly brought to room temperature over 6 hrs and the resulting red coloured reaction mixture was filtered. Then the obtained filtrate was concentrated to about 5 mL and dark red crystals of **6** were obtained by a slow diffusion of hexane onto the solution over two days at room temperature. **Yield:** 0.087g (25-35 %). Compound **6** is very much air and moisture sensitive and not stable in solution which hindered us to get any further analytical or spectroscopic data.

Synthesis of 9



20 mL of CH_3CN was added to a Schlenk flask containing 0.290 g (0.598 mmol) of **2** and 0.159 g (0.598 mmol) of $NOSbF_6$ at −78 °C. The reaction mixture was then slowly brought to room temperature over 3 hrs. The yellow colour of the solution became light brown around −30 to −20 °C to colourless around 0 °C. Subsequently, the ^{31}P NMR spectrum of an aliquot from the reaction mixture with 2 drops of C_6D_6 showed complete consumption of **2**. After that all the volatiles were removed under vacuum. The resulting colourless solid was washed with hexane to isolate pure compound **9** as solid powder. Single crystals suitable for X-ray diffraction study were obtained from its saturated solution in CH_3CN on standing overnight at room temperature. **Yield:** 0.400 g (92 %). **M.P.**: >180 °C. **^{1}H NMR (300 MHz, CD_3CN, 298 K):** δ = 1.87 (s, 6H, CH_3 of Mes), 2.11 (s, 6H, CH_3 of Mes), 2.16 (s, 6H, CCH_3, NHC^{Me4}), 2.35 (s, 6H, CH_3 of Mes), 3.29, (s, 6H, N-CH_3, NHC^{Me4}), 6.71 (s, 2H, Ar-*H*), 6.91 (s, 2H, Ar-*H*), 7.35-7.39 (m, 2H, Ar-*H*), 7.91 (t, $^3J_{(^1H,\ ^1H)}$ = 7.5 Hz, 1H, Ar-*H*), 7.62 (d, $^1J_{(^{31}P,\ ^1H)}$ = 547 Hz, 1H, P-*H*) ppm. **^{13}C{^{1}H} NMR (75.43 MHz, CD_3CN, 298 K):** δ = 9.2 (2C, *C*H_3, CH_3*C*-*C*CH_3, NHC^{Me4}), 21.3 (2C, *C*H_3-Mes), 21.5 (2C, *C*H_3-Mes), 21.7 (2C, *C*H_3-Mes), 34.4 (2C, N-*C*H_3, NHC^{Me4}), 127.8 (1C, CH_3*C*-*C*CH_3, NHC^{Me4}), 128.0 (1C, CH_3*C*-*C*CH_3, NHC^{Me4}), 129.8 (2C, Ar-*C*H), 130.4 (2C, Ar-*C*H), 132.4 (1C, Ar-*C*H), 132.6 (2C, Ar-*C*H), 135.7 (1C, Ar-C_{quat}), 135.8 (1C, Ar-C_{quat}), 136.4 (1C, Ar-C_{quat}), 136.4 (1C, Ar-C_{quat}), 138.0 (2C, Ar-C_{quat}), 138.0 (2C, Ar-C_{quat}), 140.1 (3C, Ar-C_{quat}), 147.5 (d, $^1J_{(^{31}P,\ ^{13}C)}$ = 12.7 Hz, N-*C*-N of NHC^{Me4}) ppm. **^{31}P NMR (121.5 MHz, CD_3CN, 298 K):** δ = −7.0 (d, $^1J_{(^{31}P,\ ^1H)}$ = 547 Hz) ppm. **^{31}P{^{1}H} NMR (121.5 MHz, CD_3CN, 298 K):** δ = −7.0 (s) ppm. **^{19}F NMR (282.4 MHz, CH_3CN, 298 K):** δ = −124.0 [m, 6F, (sex, $^1J_{(^{121}Sb,\ ^{19}F)}$ = 1930 Hz, oct, $^1J_{(^{123}Sb,\ ^{19}F)}$ = 1056 Hz.)] ppm. **IR (KBr, cm^{-1}):** ῡ (cm^{-1}) = 2971 (s), 2961 (s), 2854 (m), 2361(m, P-*H*), 1637 (mw), 1604 (mw), 1567 (m), 1456 (vs), 1376 (s), 1261 (m), 1116 (m), 985 (w), 937 (s), 851 (s), 814 (s), 773 (w), 657 (s), 519 (m). **Elemental Analysis:** Calcd. for ($C_{31}H_{38}N_2OPSbF_6$): C, 51.61; H, 5.31; N, 3.88; Found: C, 49.67; H, 5.17; N 3.74 (the deviation of the elemental analysis result is most likely due to the presence of very minor amount of unassigned impurity, which can be seen in the ^{1}H NMR spectrum).

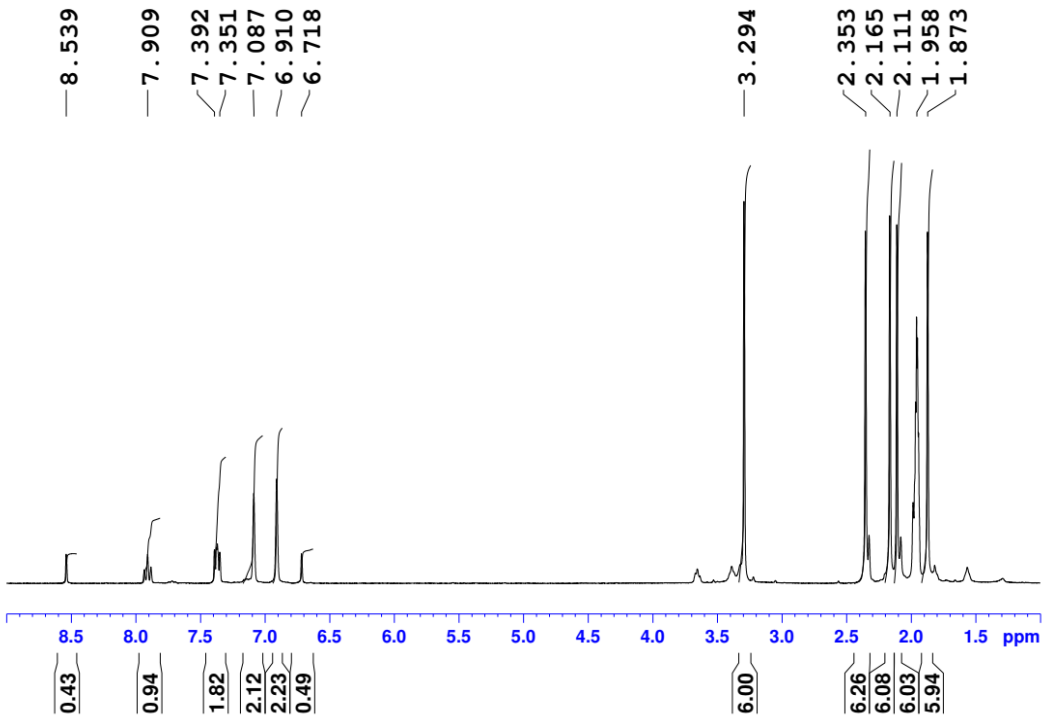


Fig. 12 ^{1}H NMR spectrum of **9** in CD_3CN at RT.

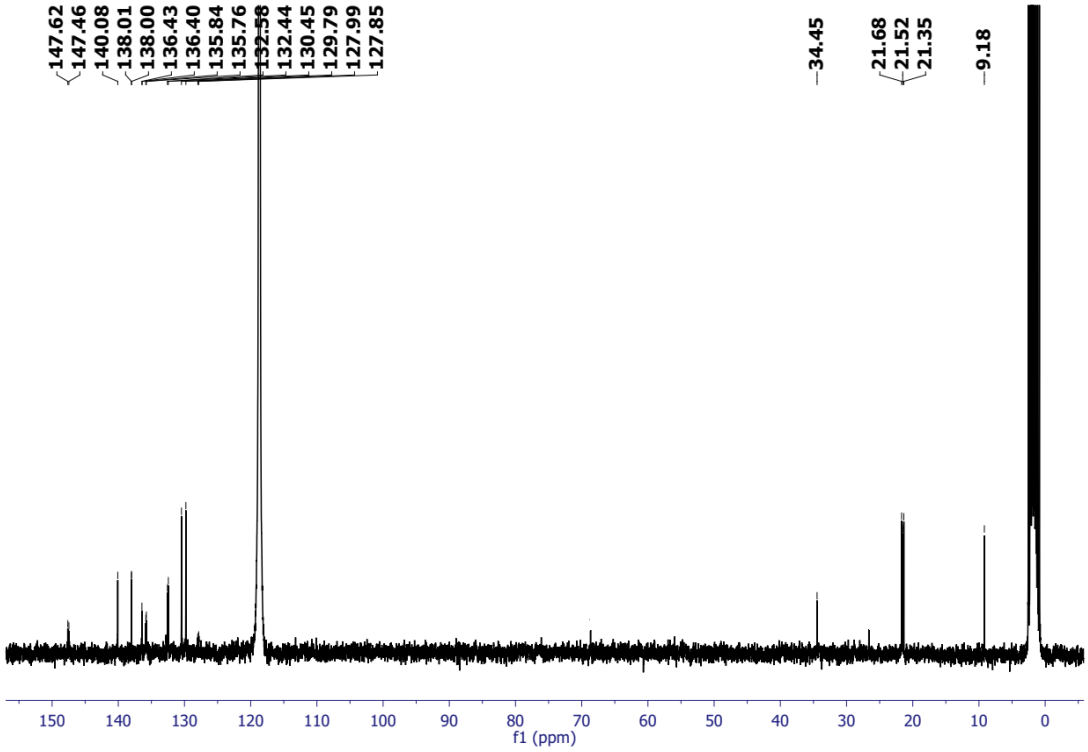


Fig. S13 $^{13}C\{^{1}H\}$ NMR spectrum of **9** in CD_3CN at RT.

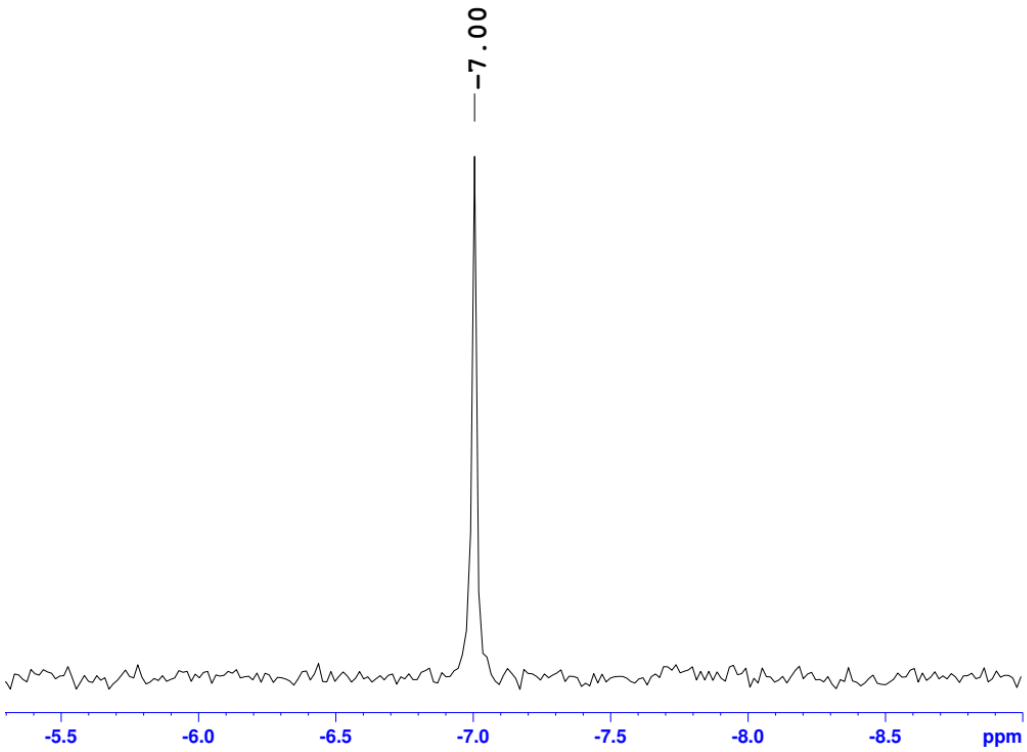


Fig. S14 $^{31}P\{^{1}H\}$ NMR spectrum of **9** in CD_3CN at RT.

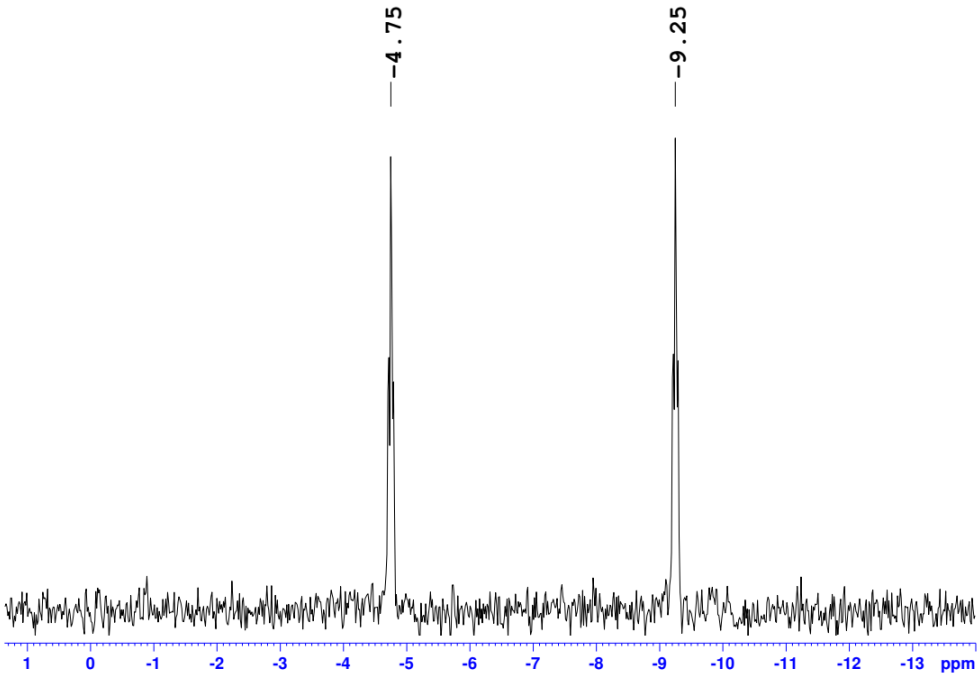


Fig. S15 ^{31}P NMR spectrum of **9** in CD_3CN at RT.

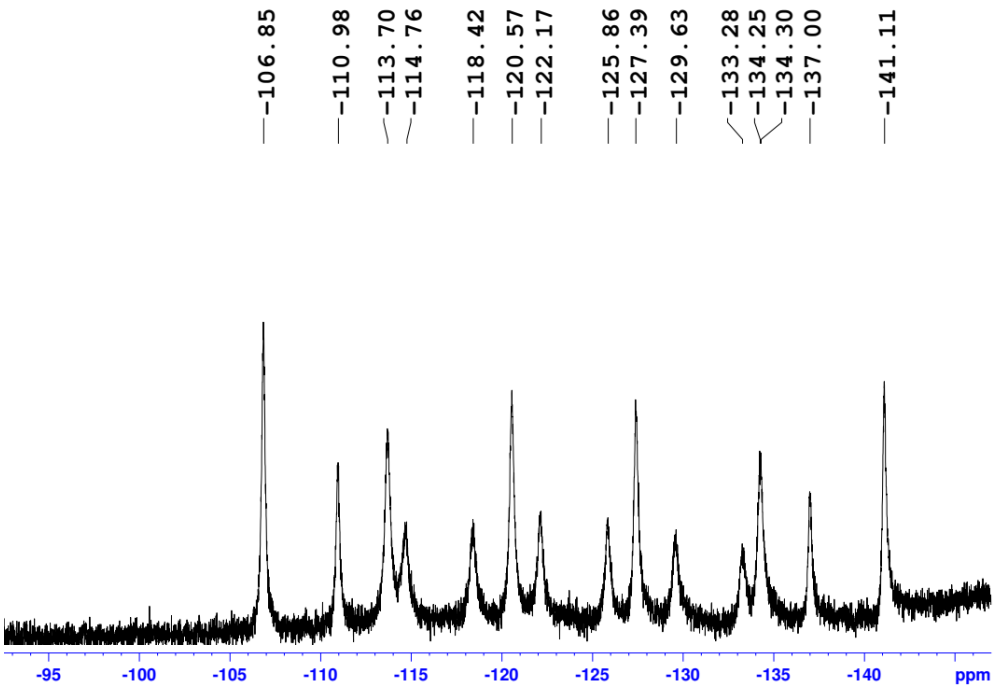
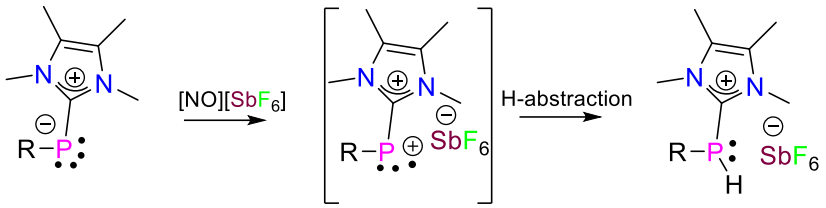


Fig. S16 ^{19}F NMR spectrum of **9** in CD_3CN at RT.

Synthesis of 11



1 **[10]** **11**

15 mL of CH_3CN was added to a Schlenk flask containing 0.350 g (0.746 mmol) of **1** and 0.198 g (0.746 mmol) of $NOSbF_6$ at −78 °C. The reaction mixture was then slowly brought to room temperature over 3 hrs. The orange solution become light brown to colourless again. Subsequently, the ^{31}P NMR spectrum of an aliquot from the reaction mixture with 2 drops of C_6D_6 shows complete consumption of **1**. After that all the volatilities were removed under vacuum. The resulting colourless solid was washed with hexane and a white solid was obtained which consists mostly of compound **11** along with a small amount of unidentified impurity as revealed by ^{31}P NMR data. Single crystals suitable for a X-ray diffraction study of **11** were obtained from its saturated solution in CH_3CN upon standing overnight at room temperature. We were unable to fully purify compound **11** not even after repeated re-crystallization. As a result, we cannot report the $^{13}C\{^1H\}$ NMR data here and in the ^1H, $^{31}P\{^1H\}$, and ^{31}P NMR spectra some unidentified resonances remain. **Yield:** 0.490 g (93 %). **^{1}H NMR (300 MHz, CD_3CN, 298 K):** δ = 1.86 (s, 6H, C*H*$_3$ of Mes), 2.10 (s, 6H, *C*H$_3$, *C*H$_3$C-C*C*H$_3$, NHC^{Me4}), 2.18 (s, 6H, C*H*$_3$ of Mes), 2.35 (s, 6H, C*H*$_3$ of Mes), 3.23 (s, 6H, N-C*H*$_3$ of NHC^{Me4}), 4.72 (d, $^1J_{(^{31}P,\ ^1H)}$ = 260 HZ. 1H, P-*H*), 6.91 (s, 2H, Ar-*H*), 7.09 (s, 2H, Ar-*H*), 7.19-7.23 (m, 2H, Ar-*H*), 7.6-7.7 (m, 1H, Ar-*H*) ppm. **$^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN, 298 K):** δ = −103.6 ppm. **^{31}P NMR (121.5 MHz, CD_3CN, 298 K):** δ = −103.6 (d, $^1J_{(^{31}P,\ ^1H)}$ = 260 Hz., *P*-H) ppm. **^{19}F NMR (282.4 MHz, CD_3CN, 298 K):** −123.97 (m, 6F, (sex, $^1J_{(^{121}Sb,\ ^{19}F)}$ = 1942 Hz & oct, $^1J_{(^{123}Sb,\ ^{19}F)}$ = 1032 Hz.)) ppm.

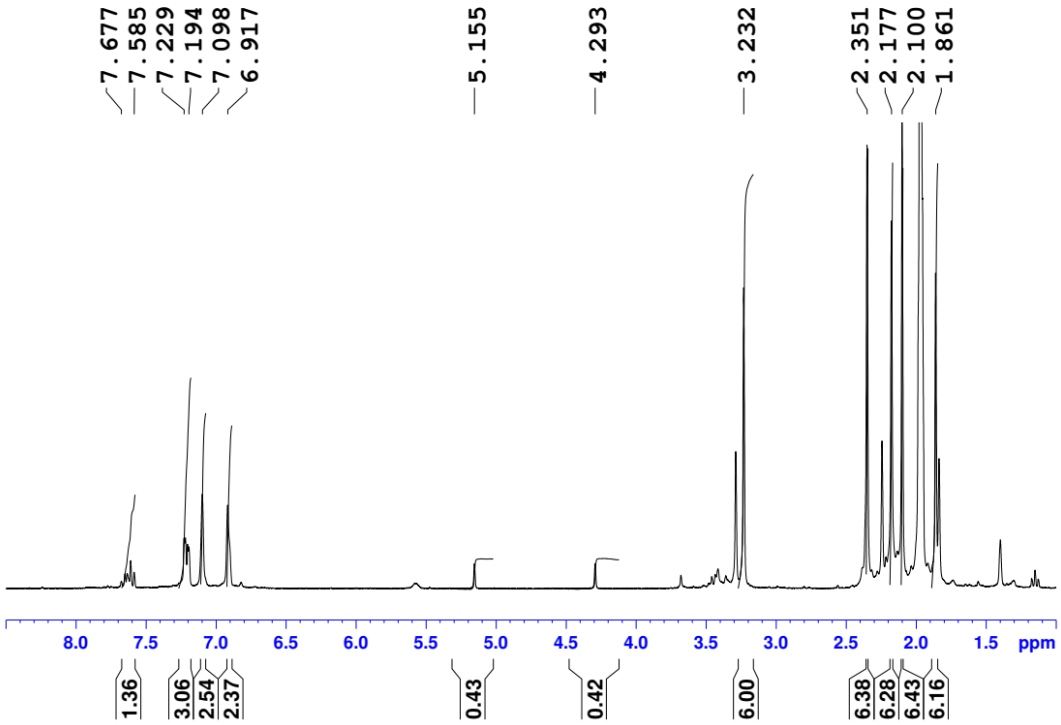


Fig. 17 ^{1}H NMR spectrum of **11** in CD_3CN at RT.

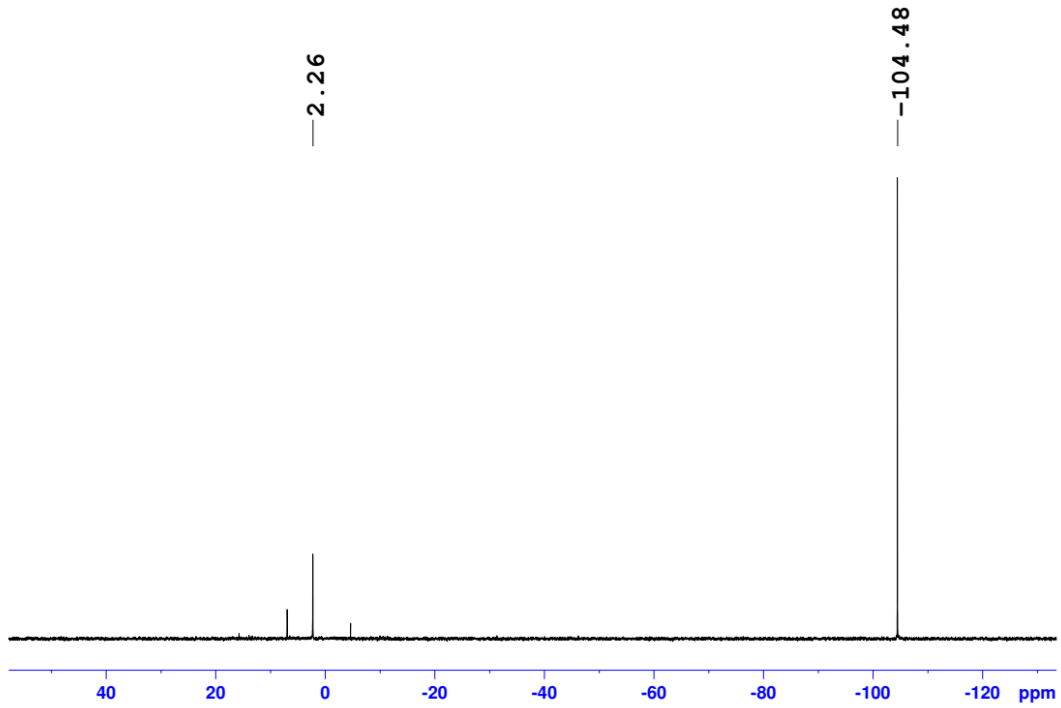


Fig. S18 $^{31}P\{^{1}H\}$ NMR spectrum of **11** in CD_3CN at RT.

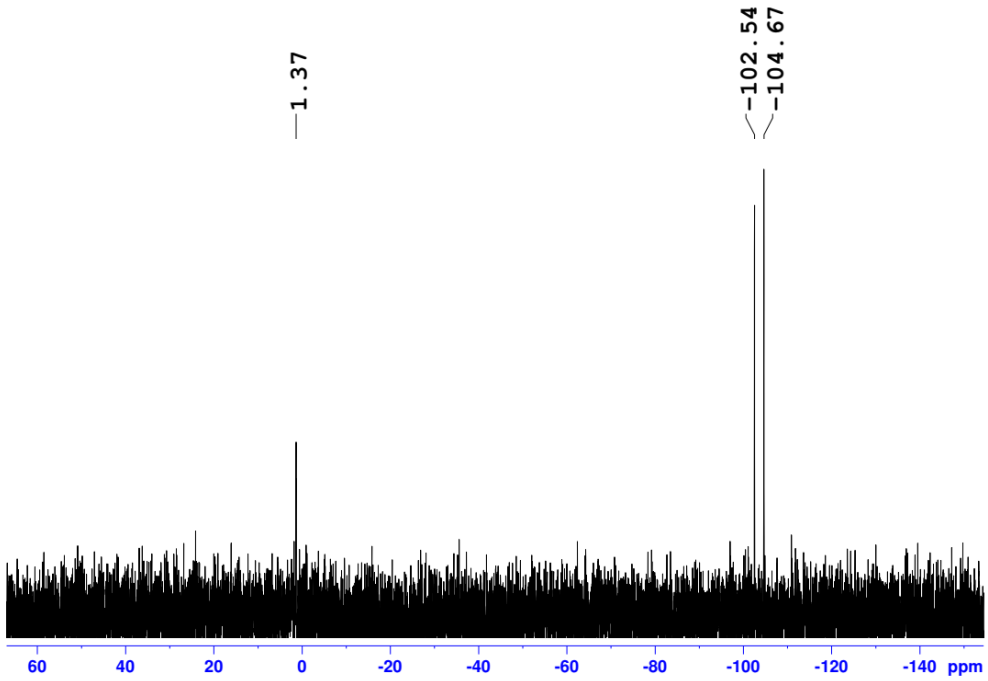


Fig. S19 ^{31}P NMR spectrum of **11** in CD_3CN at RT.

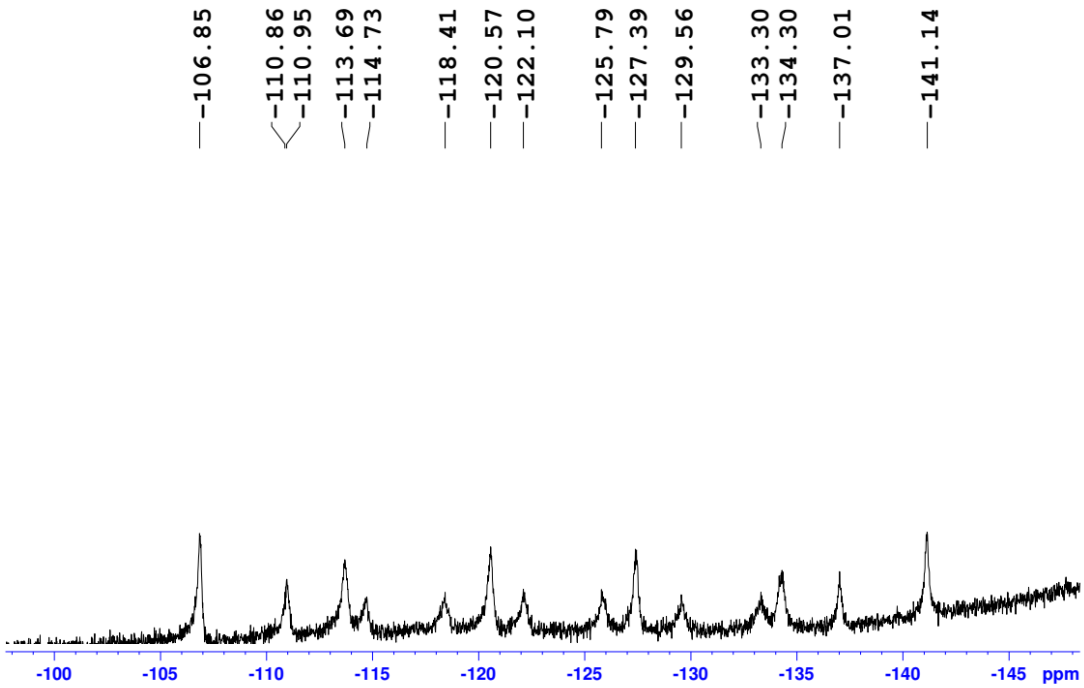
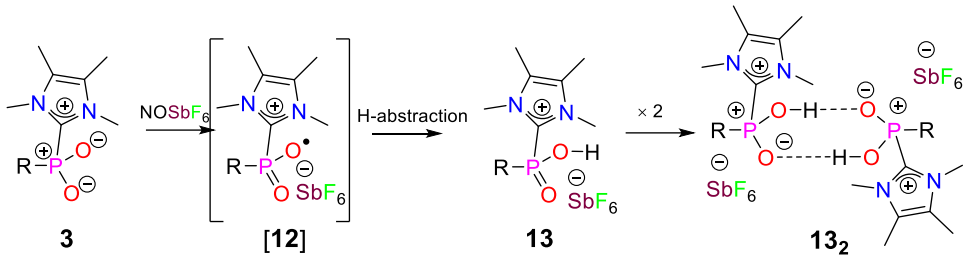


Fig. S20 ^{19}F NMR spectrum of **11** in CD_3CN at RT

Synthesis of 13



15 mL of CH_3CN was added to a Schlenk flask containing 0.200 g (0.40 mmol) of **3** and 0.106 g (0.4 mmol) of $NOSbF_6$ at −78 °C. The reaction mixture was then slowly brought to room temperature over 3 hrs. The colourless solution turned light brown to colourless. Subsequently, the ^{31}P NMR spectrum of an aliquot from the reaction mixture with 2 drops of C_6D_6 shows complete consumption of **3**. After that, all the volatilities were removed under vacuum. The resulting colourless solid was washed with hexane to yield pure compound **13** as solid powder. Single crystals suitable for a X-ray diffraction study were obtained from its saturated solution in DCM on standing overnight at room temperature. **Yield:** 0.275 g (93 %). **M.P.:** >180 °C. **^{1}H NMR (300 MHz, CD_3CN, 298 K):** δ = 1.90 (s, br, 12H, CH_3 of Mes), 2.04 (s, 6H, s, 6H, C–CCH_3, NHC^{Me}$_4$), 2.27 (s, 6H, CH_3 of Mes), 3.33 (s, 6H, N-CH_3 of NHC^{Me}$_4$), 5.60 (S, br, 1H, PO-*H*)), 7.10 (s, 4H, Ar-*H*), 7.12-7.15 (m, 2H, Ar-*H*), 7.70 (t, 1H, $^3J_{(^1H,\ ^1H)}$ = 7.8 Hz) ppm. **^{13}C{^{1}H} NMR (75.43 MHz, CD_3CN, 298 K):** δ = 9.3 (2C, *C*H_3, *C*H_3C-C*C*H_3, NHC^{Me}$_4$), 21.5 (2C, *C*H_3-Mes), 21.6 (4C, *C*H_3-Mes), 35.5 (2C, N-*C*H_3, NHC^{Me}$_4$), 129.7 (4C, Ar-*C*H), 131.5 (2C, CH_3*C*-*C*CH_3, NHC^{Me}$_4$), 132.6 (1C, Ar-*C*H), 132.8 (1C, Ar-*C*H), 134.6 (1C, Ar-*C*H), 137.3 (6C, Ar-C_{quat}), 138.4 (2C, Ar-C_{quat}), 138.8 (3C, Ar-C_{quat}), 146.7 (d, $^1J_{(^{31}P,\ ^{13}C)}$ = 12.0 Hz., N-*C*-N of NHC^{Me}$_4$) ppm. **^{31}P NMR (121.5 MHz, CD_3CN, 298 K):** δ = 8.1 ppm. **^{19}F NMR (282.4 MHz, CD_3CN, 298 K):** −123.94 (m, 6F, (sex, $^1J_{(^{121}Sb,\ ^{19}F)}$ = 1936 Hz & oct, $^1J_{(^{123}Sb,\ ^{19}F)}$ = 1050 Hz.)) ppm. **FT-IR (KBr, cm^{-1}):** ῡ (cm^{-1}) = 2958(s), 2967 (s), 2856 (vs), 2732 (vw), 2231 (w, br, P-*H*), 1630 (w), 1612 (w), 1563 (w), 1488 (m), 1451 (m), 1350 (w), 1235 (s), 1185 (vs), 1118 (s), 1094 (w), 1062 (m), 1029 (s), 974 (m, br), 857 (vs), 809 (s), 772 (s), 759 (mw), 732 (w), 663 (vs), 607 (s), 556(s), 537 (s). **Elemental Analysis:** Calcd. for ($C_{31}H_{38}N_2O_2PSbF_6$): C, 50.49; H, 5.19; N, 3.80; Found: C, 49.10; H, 5.40; N 3.80 (the deviation of the elemental analysis result is most likely due to the presence of very minor amount of unassigned impurity, which can be seen in the ^{1}H NMR spectrum).

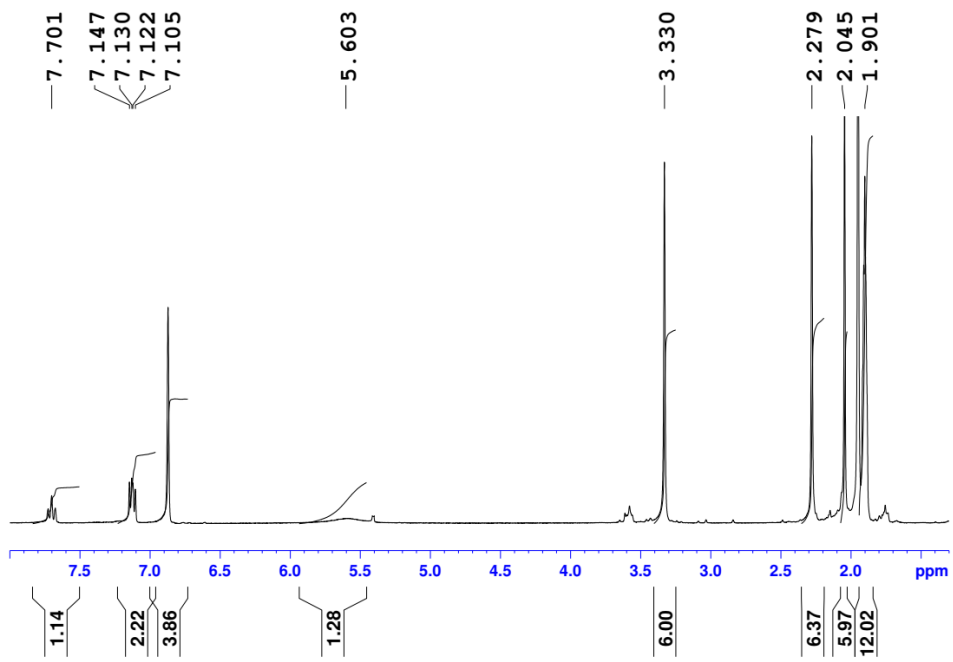


Fig. 21 ^{1}H NMR spectrum of **13** in CD_3CN at RT.

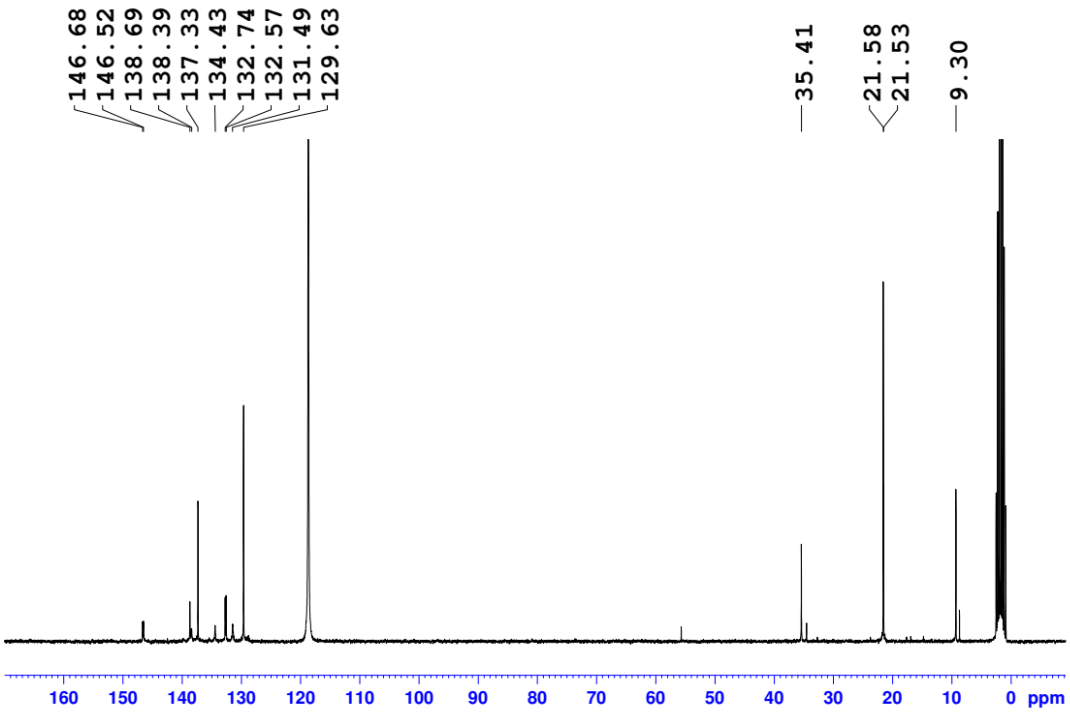


Fig. S22 $^{13}C\{^{1}H\}$ NMR spectrum of **13** in CD_3CN at RT.

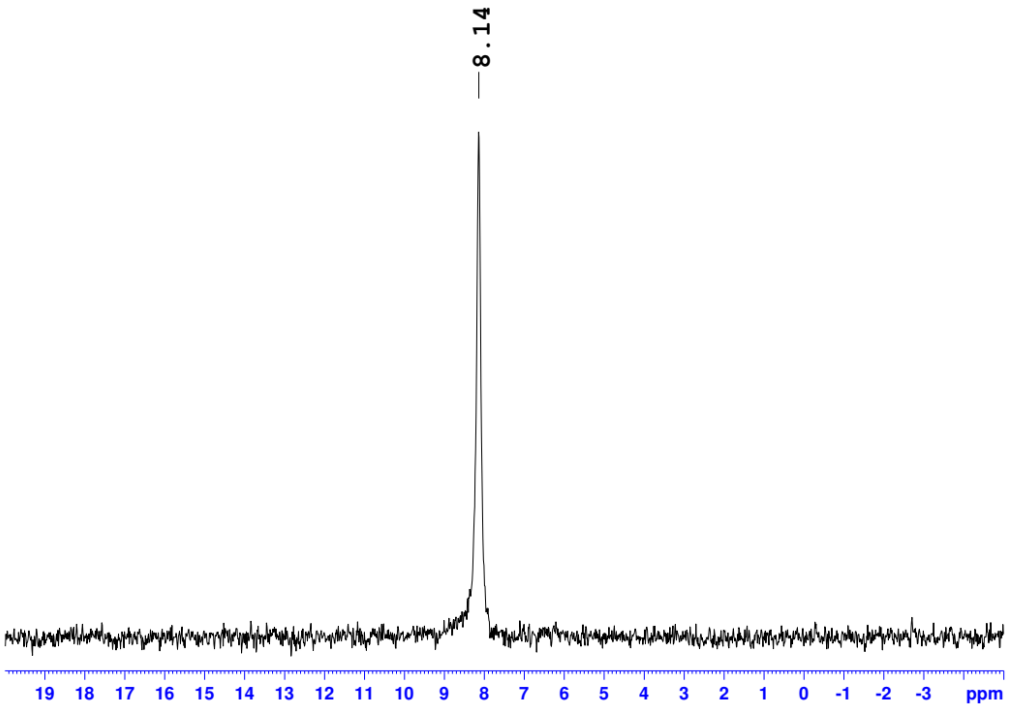


Fig. S23 $^{31}P\{^{1}H\}$ NMR spectrum of **13** in CD_3CN at RT.

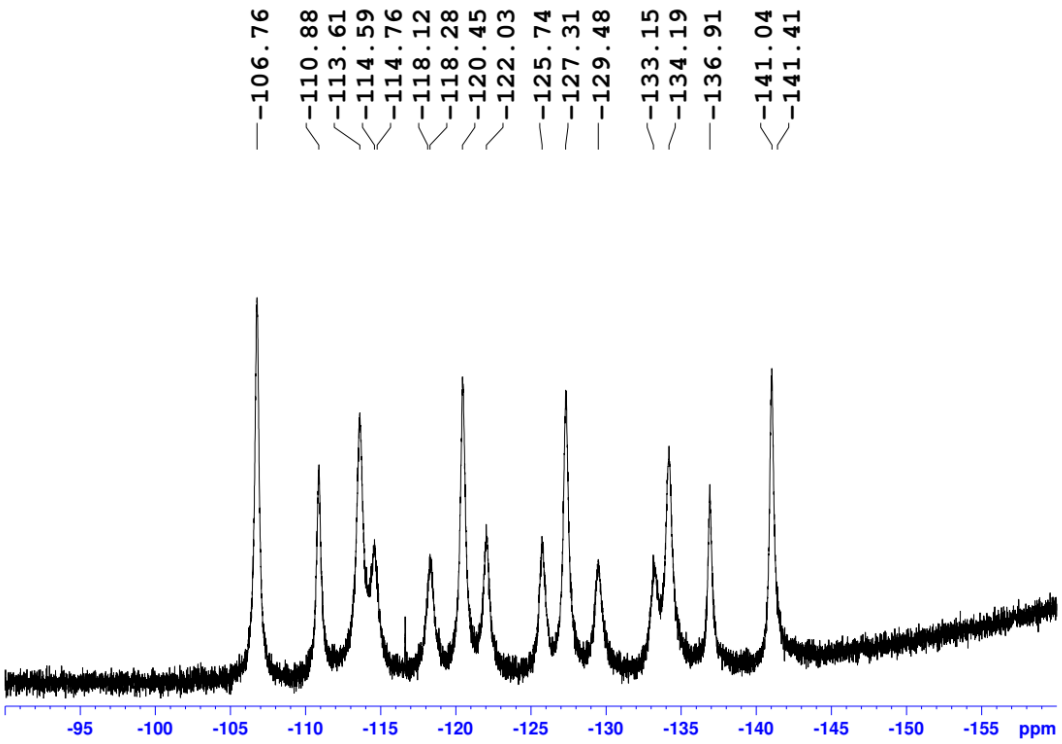


Fig. S24 ^{19}F NMR spectrum of **13** in CD_3CN at RT.

Molecular Structures of 9, 11, and 13·DCM

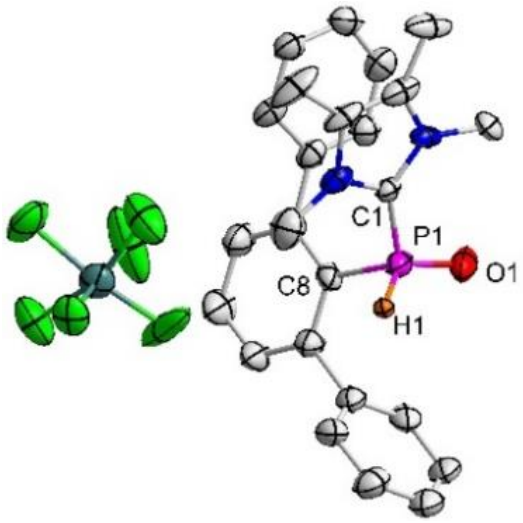


Fig. S25 Molecular structure of **9**, all hydrogen atoms except those at the P1-centre and all mesityl methyl groups are omitted for clarity.

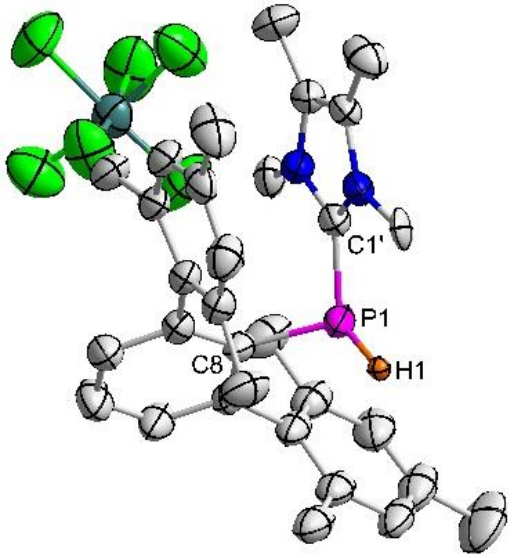


Fig. S26 Molecular structure of **11**, all hydrogen atoms except those at the P1-centre and all mesityl methyl groups are omitted for clarity.

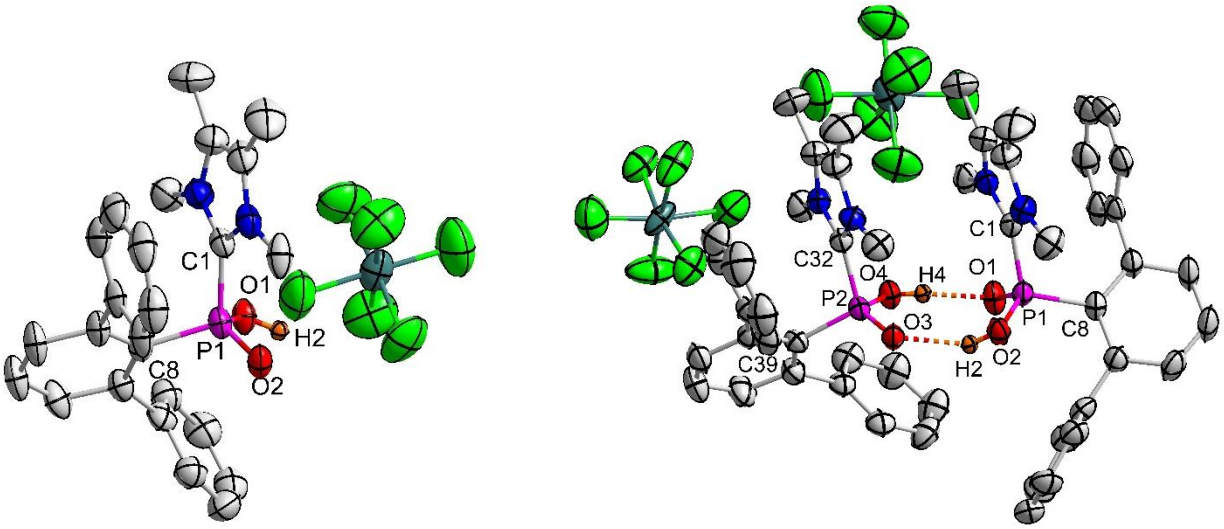


Fig. S27 Monomeric (left) and H-bonded dimeric (right) molecular structure of **13·DCM**; all hydrogen atoms except at O1 (for the monomeric structure) and O2 and O4 (for H-bonded dimeric structure) and all mesityl methyl groups are omitted for clarity.

Crystallographic Details

Single crystal X-ray data of **2** and **3** were collected at 298 K and those for **9**, **11** and **13·DCM** were collected at 293 K using a Rigaku XtaLAB AFC12 (RINC): Kappa single diffractometer with graphite-monochromated Mo *K*α radiation, λ = 0.71073 Å. Single crystal X-ray data of **6·3C$_6$H$_6$** were collected at 170 K using a STOE-IPDS 2T diffractometer with graphite-monochromated molybdenum *K*α radiation, λ = 0.71073 Å. The unit cell parameters and the data reduction were obtained with the CrysAlisPro software from Rigaku Oxford Diffraction or with X-AREA from STOE.[S2] A multi-scan absorption correction was applied to the collected reflections during data processing with SCALE3 ABSPACK also integrated in the CrysAlisPro software.[S3] For **6·3C$_6$H$_6$** a numerical absorption correction was carried out with X-Red32 and X-Shape from STOE. The structures were solved with SHELXT[S4] structure solution program using Intrinsic phasing and refined by full matrix least-squares methods based on F^2 using the SHELXL[S4] refinement programme in the Olex-2 GUI.[S5] All non-hydrogen-atoms were refined with anisotropic displacement parameters. Hydrogens were placed in geometrically calculated positions or found in the Fourier difference map and included in the refinement process using the riding model. The program Diamond (version 3.2k) was used for creating the crystallographic figures.[S6] In the refinement of **6·3C$_6$H$_6$** two of the three benzene solvent molecules did not behave well due to disorder. The carbon atoms were fixed to form ideal hexagons and their displacement parameters were constrained to be almost the same for all six carbon atoms of each ring (AFIX, SIMU, DELU). In compound **11** the SbF_6^- anion is disordered over two positions involving all six F atoms. This was modelled with SAME, SIMU and DELU constraints. The occupancies are roughly 60% and 40%. The imidazole-like heterocyclic substituent on P is disordered entirely (i.e. all N and all C appear in two positions). This was also modelled with SAME, SIMU and DELU constraints. The respective occupancies are roughly 58% and 42%. The hydrogen atom on P was refined freely with regard to location and its U_{iso} constrained to 1.5 times that of P. The crystal of **13·DCM** was a non-merohedral twin (presence of a minor domain accounting for ca. 17%) and the data were refined using a hklf5 file. The lattice dichloromethane is disordered over two positions. This was refined with SADI, SIMU and DELU constraints. The occupancies are roughly 80% and 20%. Both SbF_6^- anions are disordered and both were treated with SAME, SIMU and DELU constraints. The occupancies for Sb1 are 72% and 28% and those for Sb2 are 57% and 43%. Clear outliers were omitted from the refinement (OMIT). Because it was not possible to refine them, the oxygen bound hydrogen atoms were fixed.

Table S1. Crystal data and structure refinement for **2** (CCDC: 1985944)

Identification code	AJ1010
Empirical formula	$C_{31}H_{37}N_2OP$
Formula weight	484.59
Temperature/K	298.16(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.0570(6)
b/Å	14.0475(13)
c/Å	12.2644(9)
α/°	90
β/°	95.457(6)
γ/°	90
Volume/Å^3	1381.80(19)
Z	2
ρ_{calc}g/cm^3	1.165
μ/mm^{-1}	0.125
F(000)	520.0
Crystal size/mm^3	0.34 × 0.23 × 0.19
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.8 to 57.916
Index ranges	-9 ≤ h ≤ 10, -18 ≤ k ≤ 15, -15 ≤ l ≤ 16
Reflections collected	15907
Independent reflections	5547 [R_{int} = 0.1035, R_{sigma} = 0.0980]
Data/restraints/parameters	5547/1/326
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0681, wR_2 = 0.1850
Final R indexes [all data]	R_1 = 0.0876, wR_2 = 0.1970
Largest diff. peak/hole / e Å^{-3}	0.52/-0.20

Table S2. Crystal data and structure refinement for **3** (CCDC: 2082008)

Identification code	aj1003
Empirical formula	$C_{31}H_{37}N_2O_2P$
Formula weight	500.59
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.0017(10)
b/Å	14.1141(8)
c/Å	14.6959(11)
α/°	90
β/°	109.903(8)
γ/°	90
Volume/Å^3	2730.8(3)
Z	4
ρ_{calc}g/cm^3	1.218
μ/mm^{-1}	0.131
F(000)	1072.0
Crystal size/mm^3	0.250 × 0.190 × 0.140
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.948 to 58.042
Index ranges	-18 ≤ h ≤ 17, -19 ≤ k ≤ 17, -17 ≤ l ≤ 18
Reflections collected	18615
Independent reflections	5983 [R_{int} = 0.0580, R_{sigma} = 0.0722]
Data/restraints/parameters	5983/0/335
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0609, wR_2 = 0.1371
Final R indexes [all data]	R_1 = 0.1066, wR_2 = 0.1558
Largest diff. peak/hole / e Å^{-3}	0.29/-0.27

Table S3. Crystal data and structure refinement for **6**·**3C$_6$H$_6$** (CCDC: 1985948)

Identification code	DD 1155 B
Empirical formula	C_{128} H_{142} K_4 N_4 O_4 P_4
Formula weight	2080.73
Temperature/K	170.15(2) K
Crystal system	triclinic
Space group	P-1
a/Å	13.406(3)
b/Å	14.783(3)
c/Å	30.449(6)
α/°	99.67(3)
β/°	102.51(3)
γ/°	96.47(3)
Volume/Å^3	5737(2)
Z	2
ρ_{calc}g/cm^3	1.204
μ/mm^{-1}	0.265
F(000)	2212
Crystal size/mm^3	0.389 x 0.333 x 0.272
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.102 to 52.744
Index ranges	-16<=h<=16, -18<=k<=18, -38<=l<=38
Reflections collected	48722
Independent reflections	23376 [R(int) = 0.0781]
Data/restraints/parameters	23376 / 96 / 1306
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R1 = 0.0656, wR2 = 0.1632
Final R indexes [all data]	R1 = 0.1286, wR2 = 0.1940
Largest diff. peak/hole / e Å^{-3}	hole 0.68 and -0.45

Table S4. Crystal data and structure refinement for **9** (CCDC: 1985946)

Identification code	AJ1015
Empirical formula	$C_{31}H_{38}F_6N_2OPSb$
Formula weight	721.35
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pnn2
a/Å	38.5155(18)
b/Å	9.8022(5)
c/Å	8.6041(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3248.4(3)
Z	4
ρ_{calc}g/cm^3	1.475
μ/mm^{-1}	0.959
F(000)	1464.0
Crystal size/mm^3	0.17 × 0.14 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.186 to 50.044
Index ranges	-45 ≤ h ≤ 42, -11 ≤ k ≤ 10, -10 ≤ l ≤ 10
Reflections collected	38805
Independent reflections	5736 [R_{int} = 0.1669, R_{sigma} = 0.0811]
Data/restraints/parameters	5736/1/394
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0701, wR_2 = 0.1827
Final R indexes [all data]	R_1 = 0.0881, wR_2 = 0.1949
Largest diff. peak/hole / e Å^{-3}	0.83/-0.49

Table S5. Crystal data and structure refinement for **11** (CCDC: 2082011)

Identification code	aj1026
Empirical formula	$C_{31}H_{38}F_6N_2PSb$
Formula weight	705.35
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pnn2
a/Å	38.1631(19)
b/Å	9.9045(6)
c/Å	8.5781(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3242.4(3)
Z	4
ρ_{calc}g/cm^3	1.445
μ/mm^{-1}	0.957
F(000)	1432.0
Crystal size/mm^3	0.250 × 0.210 × 0.160
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.728 to 57.818
Index ranges	-51 ≤ h ≤ 47, -11 ≤ k ≤ 12, -11 ≤ l ≤ 11
Reflections collected	24941
Independent reflections	7122 [R_{int} = 0.1157, R_{sigma} = 0.0863]
Data/restraints/parameters	7122/922/515
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0624, wR_2 = 0.1564
Final R indexes [all data]	R_1 = 0.0940, wR_2 = 0.1737
Largest diff. peak/hole / e Å^{-3}	0.66/-0.46
Flack parameter	0.00(3)

Table S6. Crystal data and structure refinement for **13·DCM** (CCDC: 2082009)

Identification code	AJ1028
Empirical formula	$C_{63}H_{78}Cl_2F_{12}N_4O_4P_2Sb_2$
Formula weight	1559.63
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Triclinic
Space group	P-1
a/Å	12.6743(2)
b/Å	14.2432(3)
c/Å	20.3249(7)
α/°	93.375(2)
β/°	91.737(2)
γ/°	108.005(2)
Volume	3478.82(16) A^3
Z, Calculated density	2, 1.489 Mg/m^3
Absorption coefficient	0.978 mm^-1
F(000)	1580
Crystal size	0.260 x 0.180 x 0.140 mm
Theta range for data collection	2.561 to 24.999 deg.
Limiting indices	-15<=h<=15, -16<=k<=16, -2<=l<=24
Reflections collected / unique	12154 / 12154 [R(int) = ?]
Completeness to theta = 24.999	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.84588
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12154 / 876 / 978
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	R1 = 0.0886, wR2 = 0.2396
R indices (all data)	R1 = 0.1003, wR2 = 0.2498
Extinction coefficient	n/a
Largest diff. peak and hole	0.641 and -0.630 e.A^-3

EPR Spectroscopy

EPR measurements at X-band (9.38 GHz) were carried out using a Bruker ELEXSYS E580 CW EPR spectrometer equipped with an Oxford Instruments helium cryostat (ESR900) and a MercuryiTC temperature controller. The spectral simulations were performed using MATLAB 9.8 (R2020a) and the EasySpin 5.2.28 toolbox.[S7]

In Situ Reduction Study of 2

To a cooled toluene solution of **2** at −30 ºC was added KC_8. After filtering, the resulting deep red solution was probed by EPR spectroscopy at ambient temperature.

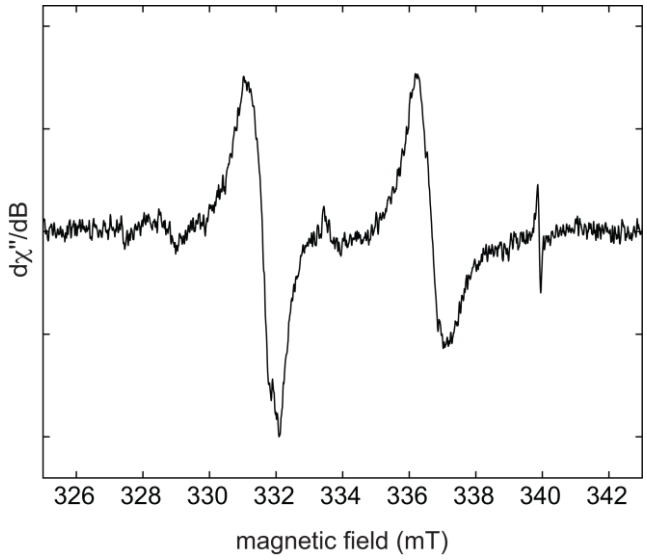


Fig. **S28** Experimental CW EPR spectrum of the putative radical anion of **2** in toluene. The broad doublet has an isotropic *g*-value of 2.0059 with a phosphorus hyperfine coupling of $a(^{31}P)$ = 143 MHz (51 G). The spectrum is stable over several hours at room temperature.

In Situ Oxidation Study of 2, 1, and 3

General Procedure for Sample Preparation: The phosphorus compound (**2**, **1**, or **3**) and the nitrosonium hexafluoroantimonate, [NO][SbF_6], were each dissolved in acetonitrile solution and cooled to −30 ºC. The solutions were mixed in the cold, transferred into an EPR tube and immediately frozen by using an acetone/liquid nitrogen bath. The EPR response was constantly monitored during thawing of the frozen solutions in the spectrometer cavity.

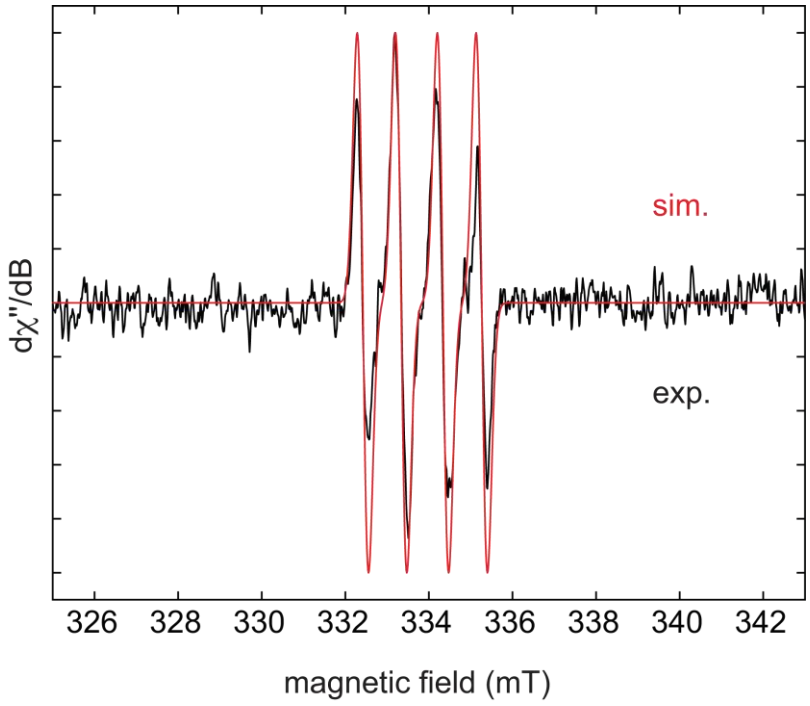


Fig. S29 Experimental and simulated CW EPR spectra of [**7**] (radical cation of **2**) in acetonitrile. Simulation parameters: g_{iso} = 2.0064, $a(^{31}P)$ = 54 MHz, and $a(^{1}H$ or $^{19}F)$ = 26 MHz.

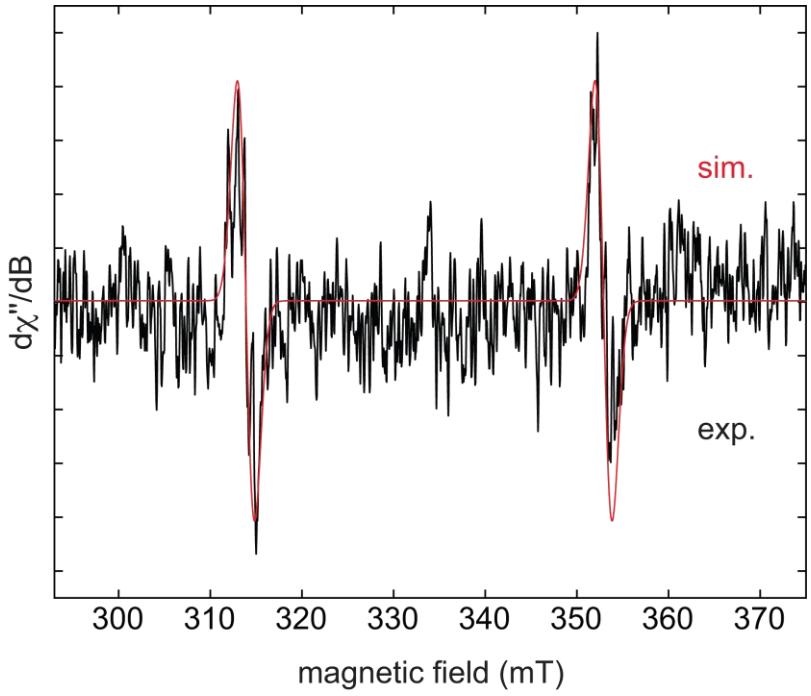


Fig. 30 Experimental and simulated CW EPR spectra of [**10**] (radical cation of **1**) in acetonitrile. Simulation parameters: g_{iso} = 2.0021 and $a(^{31}P)$ = 1090 MHz (389 G).

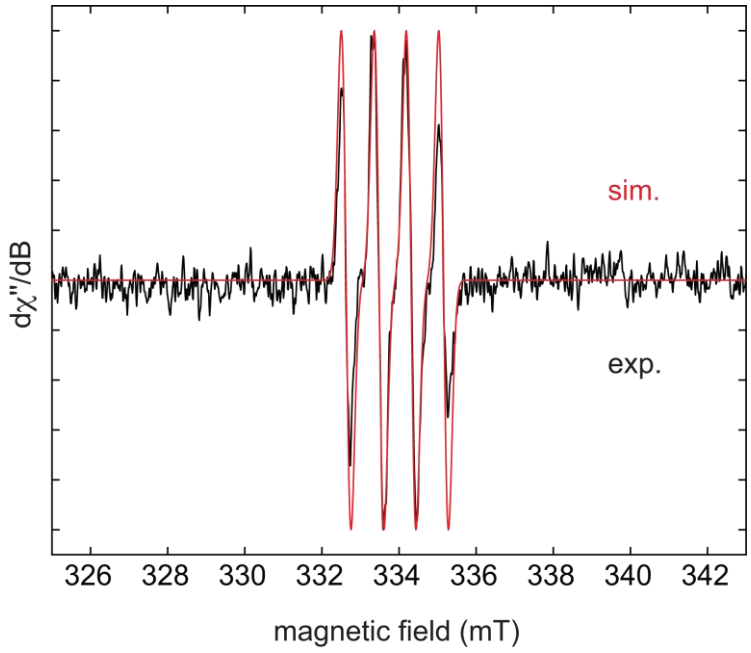


Fig. S31 Experimental (black) and simulated (red) CW EPR spectra of [**12**] (radical cation of **3**) in acetonitrile. Simulation parameters: g_{iso} = 2.0069, $a(^{31}P)$ = 47 MHz, and $a(^{1}H$ or $^{19}F)$ = 24 MHz.

Computational Details

Compounds **1**-**5** and **7**-**13** were optimized at the M06[S8]/cc-pVDZ level of theory using the Gaussian 16 program.[S9] The energy difference between singlet and triplet states was calculated for selected molecules and the singlet state was found to be more stable. Therefore, all energies reported here for the neutral molecules correspond to singlet states. Doublet states were considered for the negatively and positively charged species considered here. The images of the frontier orbitals and the spin densities were prepared using the GaussView program.[S10] TD-DFT calculation was performed at the M06/cc-pVDZ level on molecule **2** to calculate the absorption spectrum. EPR calculation was performed at b3lyp[S11]/cc-pVDZ level on radicals 7, 10 and 12. Coordinates of these radicals, in the presence and absence of coordinated NHC are also added. Natural Resonance Theory (NRT)[12] calculations were done using NBO 5.9[S13] in Gamess[S14].

Bonding Analysis of 2, 2-H, $Ph_2P\text{-}O^-$, and $H_2P\text{-}O^-$

Table S7. Wiberg bond orders (WBO) of **2** at the HF/6-31G* level of theory.

Bond	WBO
P-O	1.0313
P-C (NHC)	0.7093
P-C (R)	0.7716

Table S8. Orbital contribution in hybridized MO in each bond involving phosphorus of **2** at the HF/6-31G* level of theory.

Bond	Atom	*s*-orbital %	*p*-orbital %	*d*-orbital %
P-O	P	21.4	76.73	1.87
	O	38.48	61.01	0.51
P-C (NHC)	P	10.3	87.62	2.07
	C	39.75	60.23	0.02
P-C (R)	P	15.09	82.98	1.94
	C	29.29	70.68	0.03

Table S9. Wiberg bond orders (WBO) of **Ph_2P-O^-** at the HF/6-31G* level of theory.

Bond	WBO
P-O	1.0380
P-C	0.7488
P-C	0.7488

Table S10. Orbital contribution in hybridized MO in each bond involving phosphorus of **2-H** at the HF/6-31G* level of theory.

Bond	Atom	*s*-orbital %	*p*-orbital %	*d*-orbital %
P-O	P	20.93	76.80	2.27
	O	37.69	62.22	0.09
P-C	P	14.27	83.67	2.06
	C	30.32	69.66	0.02
P-C	P	14.27	83.67	2.06
	C	30.32	69.66	0.02

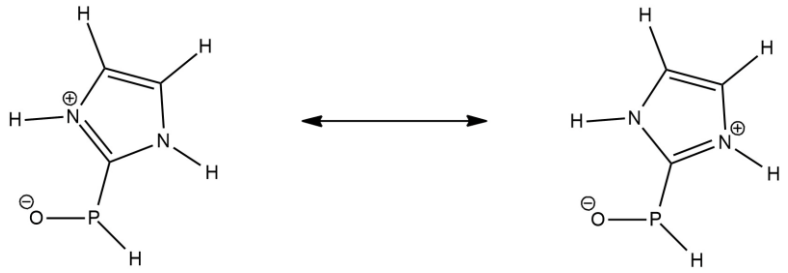


Fig. S32 The two most dominant resonance structures of **2-H** obtained using natural resonance theory (NRT) analysis at HF/6-31G* level of theory (R group and CH_3 in NHC ring has been replaced with H to avoid calculating too many possible resonance structures in NRT calculations).

Table S11. Selected Natural Bond Order (NBO) of **2-H** involving bonds with phosphorus calculated using NRT analysis at the HF/6-31G* level of theory.

Bond	**Bond Order**
P-O	0.98947
P-H	0.94374
P-C	0.92817

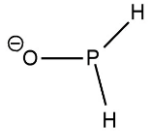


Fig. S33 The most dominant resonance structure of **H_2P-O^-** obtained using NRT analysis at HF/6-31G* level of theory (benzene rings have been replaced with H to avoid calculating too many possible resonance structures in NRT calculations).

Table S12. Natural Bond Order (NBO) of H_2P-O^- calculated using NRT analysis at the HF/6-31G* level of theory.

Bond	**Bond Order**
P-O	0.99276
P-H (both)	0.94996

Table S13. Wiberg bond orders (WBO) of **2-H** at the HF/6-31G* level of theory.

Bond	WBO
P-O	1.0648
P-C (NHC)	0.7055
P-H	0.8719

Table S14. Orbital contribution in hybridized MO in each bond involving phosphorus of **2-H** at the HF/6-31G* level of theory.

Bond	Atom	*s*-orbital %	*p*-orbital %	*d*-orbital %
P-O	P	21.38	76.43	2.19
	O	35.04	64.86	0.1
P-C (NHC)	P	10.05	87.64	2.31
	C	39.75	60.23	0.02
P-H	P	13.39	84.32	2.29
	H	100		

Table S15. Wiberg bond orders (WBO) of **H_2P-O^-** at the HF/6-31G* level of theory.

Bond	WBO
P-O	1.0502
P-H	0.8722
P-H	0.8722

Table S16. Orbital contribution in hybridized MO in each bond involving phosphorus of **H_2P-O^-** at the HF/6-31G* level of theory.

Bond	Atom	*s*-orbital %	*p*-orbital %	*d*-orbital %
P-O	P	22.77	75.39	1.84
	O	36.07	63.72	0.22
P-H	P	13.45	84.46	2.10
	H	100		
P-H	P	13.45	84.46	2.10
	H	100		

Calculation of EPR Parameters

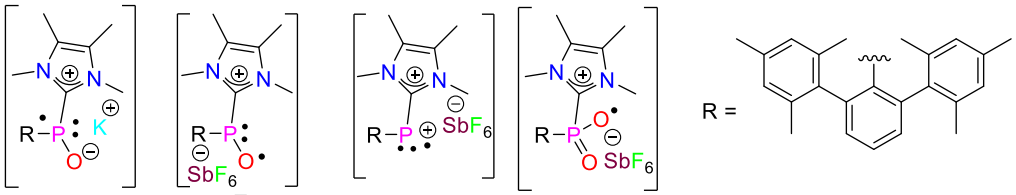
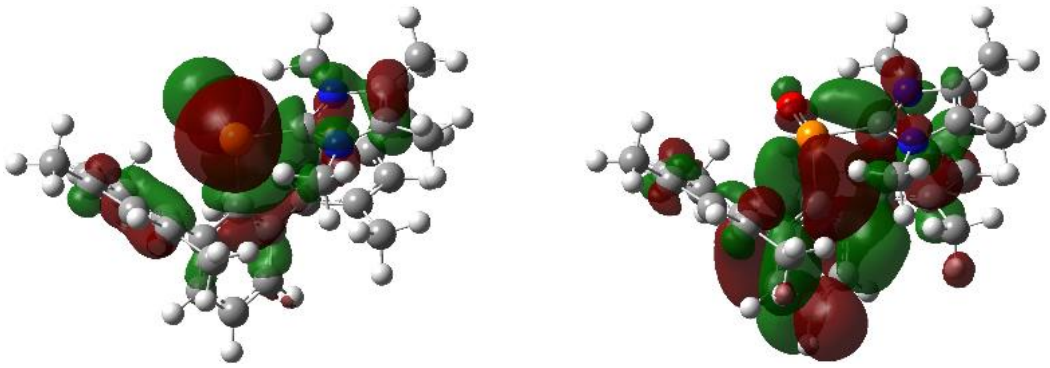


Table S17. Calculated EPR parameters for radicals [**4**], [**7**], [**10**] and [**12**] in presence and absence of coordinated NHC^{Me4} considering the presence and absence of CH_3CN, as a solvent at the b3lyp/cc-pVDZ level of theory (the entries in blue are the best compared values).

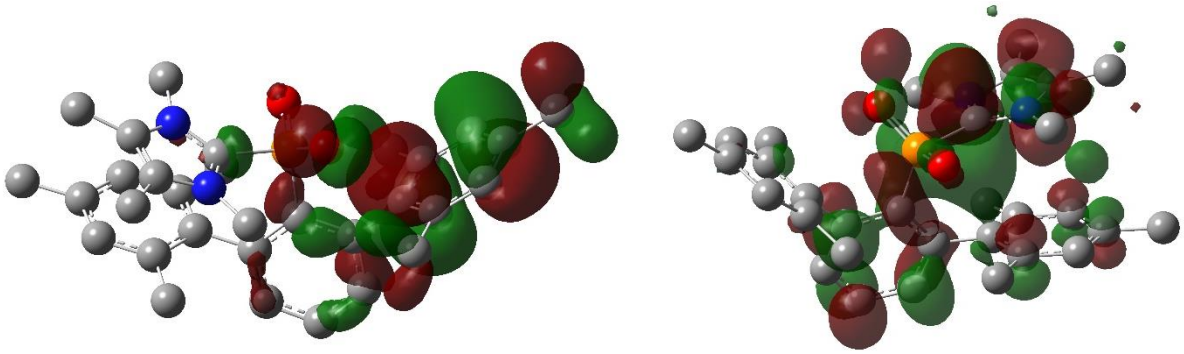
Solvent	Radical Ion	NHC	$a(^{31}P)$(exp.)	$a(^{31}P)$calc.	$a(^{19}F)$ exp.	$a(^{19}F)$ calc.
Toluene	[**4**]	Present	143 MHz	−27.45 MHz	-	-
Toluene	[**4**]	Absent	143 MHz	154.48 MHz		-
THF	[**4**]	Present	143 MHz	−26.84 MHz	-	-
THF	[**4**]	Absent	143 MHz	158.21 MHz	-	-
None	[**7**]	Present	54 MHz	1257 MHz	26 MHz	113 MHz
None	[**10**]	Present	1090 MHz	214 MHz	None	None
None	[**12**]	Present	47 MHz	−34 MHz	24 MHz	None
CH_3CN	[**7**]	Present	54 MHz	1106 MHz	26 MHz	27 MHz
CH_3CN	[**10**]	Present	1090 MHz	227 MHz	None	None
CH_3CN	[**12**]	Present	47 MHz	−34 MHz	24 MHz	None
None	[**7**]	Absent	54 MHz	1327 MHz	26 MHz	144 MHz
None	[**10**]	Absent	1090 MHz	216 MHz	None	60 MHz
None	[**12**]	Absent	47 MHz	−29 MHz	24 MHz	1.73 MHz*
CH_3CN	[**7**]	Absent	54 MHz	177 MHz	26 MHz	27 MHz
CH_3CN	[**10**]	Absent	1090 MHz	157 MHz	None	67 MHz
CH_3CN	[**12**]	Absent	47 MHz	−19 MHz	24 MHz	−3 MHz

*the F atom is bonded to P radical centre with a bond length of 1.8 A.



HOMO LUMO

Fig. S34 Frontier orbitals of **2** calculated at M06/cc-pVDZ level of theory.



HOMO LUMO

Fig. S35 Frontier orbitals of **3** calculated at M06/cc-pVDZ level of theory.

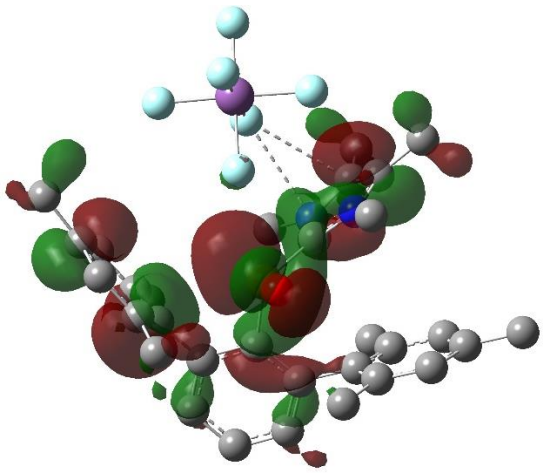


Fig. S36 Single occupied molecular orbital (SOMO) surfaces of [**7**].

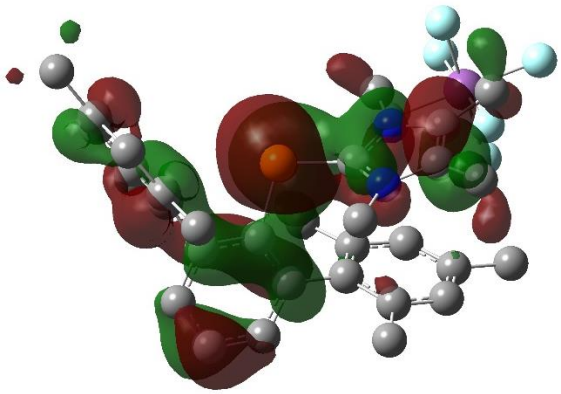


Fig. S37 Single occupied molecular orbital (SOMO) surfaces of [**10**].

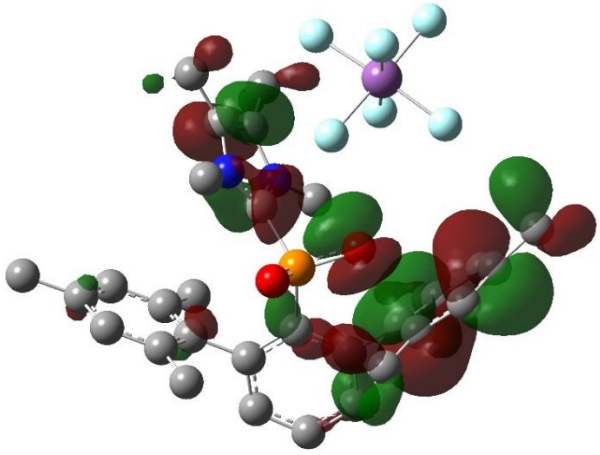


Fig. S38 Single occupied molecular orbital (SOMO) surfaces of [**12**].

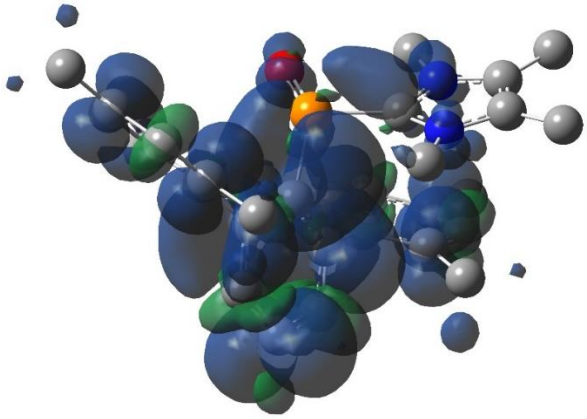


Fig. 39 Spin density plot of **4** (with NHC^{Me_4}) at M06/cc-pVDZ level of theory.

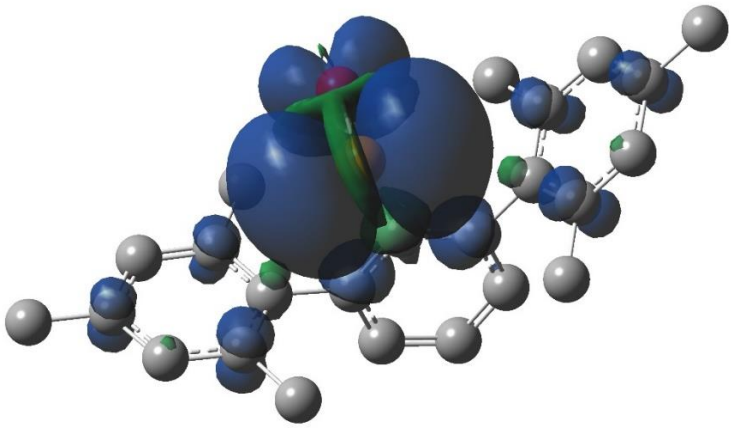


Fig. S40 Spin density plot of **4** (without NHC^{Me_4}) at M06/cc-pVDZ level of theory.

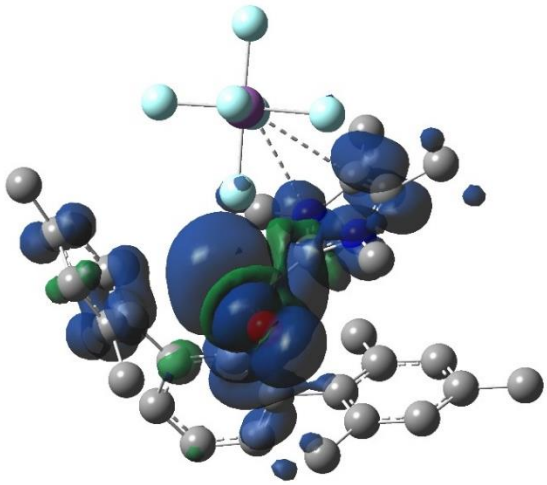


Fig. S41 Spin density plot of **7** (with NHC^{Me_4}) at M06/cc-pVDZ level of theory.

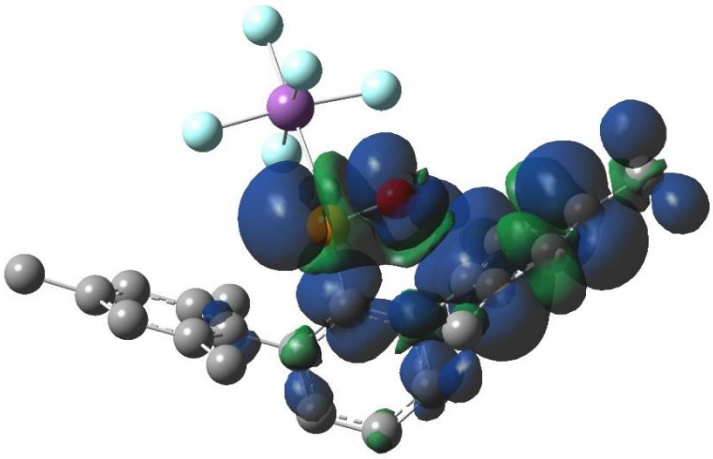


Fig. S42 Spin density plot of **7** (without NHC^{Me_4}) at M06/cc-pVDZ level of theory.

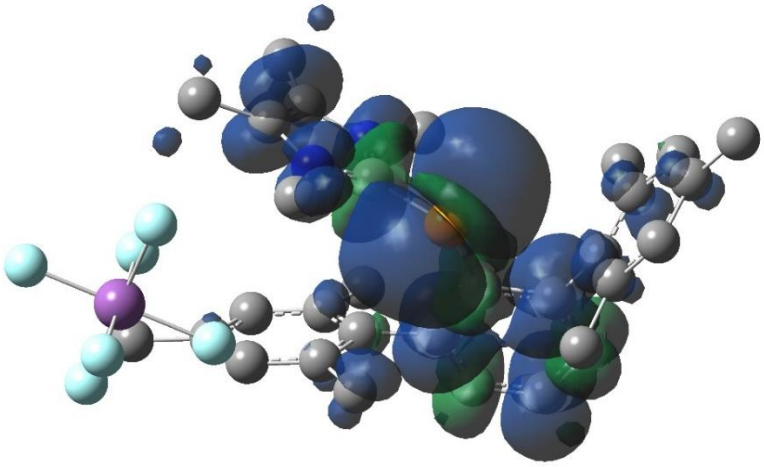


Fig. S43 Spin density plot of **10** (with NHC^{Me_4}) at M06/cc-pVDZ level of theory.

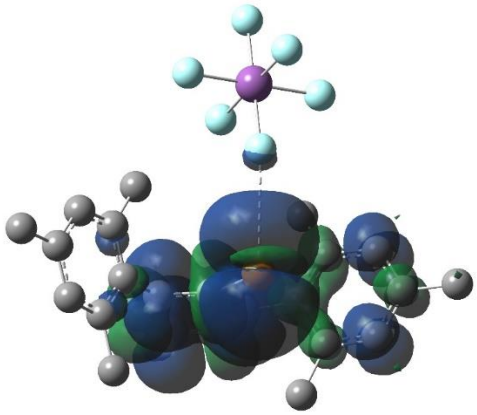


Fig. S44 Spin density plot of **10** (without NHC^{Me_4}) at M06/cc-pVDZ level of theory.

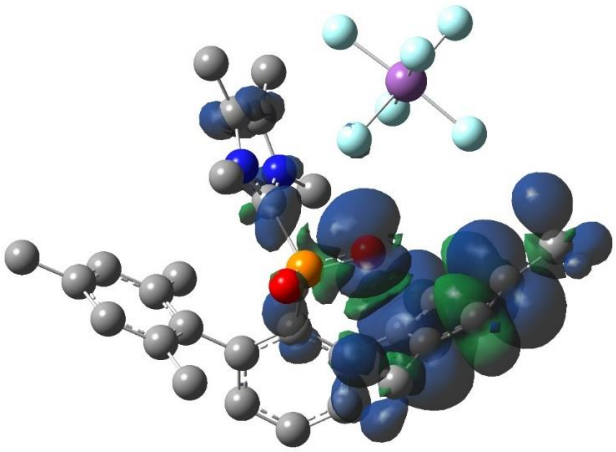


Fig. S45 Spin density plot of **12** (with NHC^{Me_4}) at M06/cc-pVDZ level of theory.

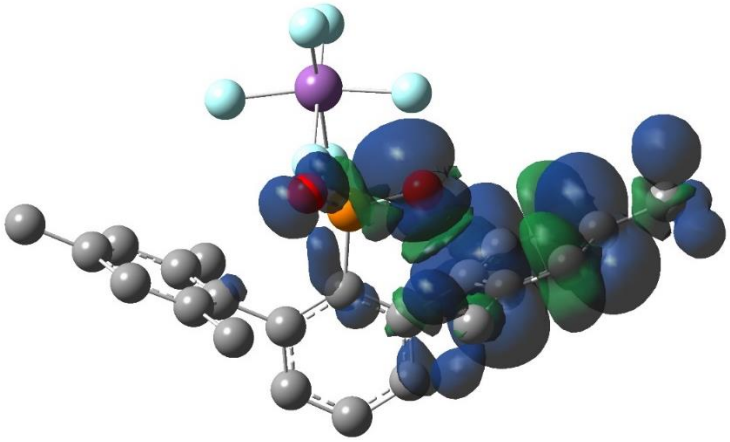


Fig. S46 Spin density plot of **12** (without NHC^{Me_4}) at M06/cc-pVDZ level of theory.

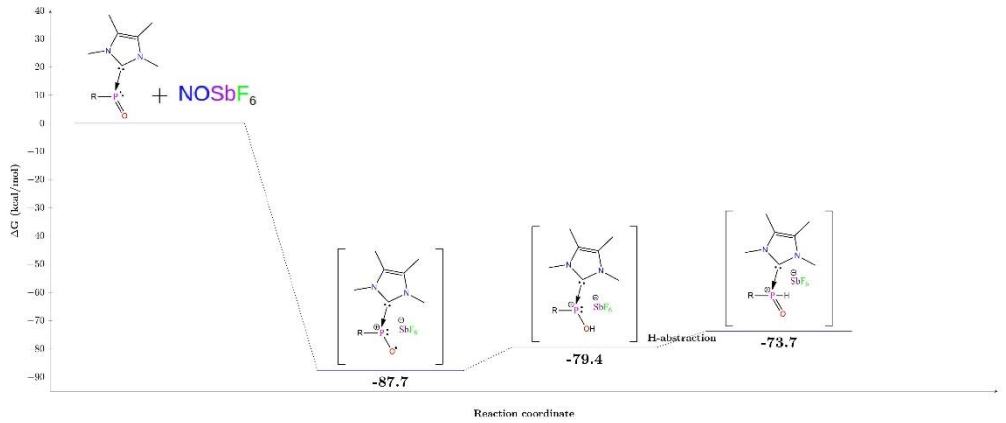


Fig. S47 Reaction free energy profile for **2** to **9** at M06/cc-pVDZ level of theory.

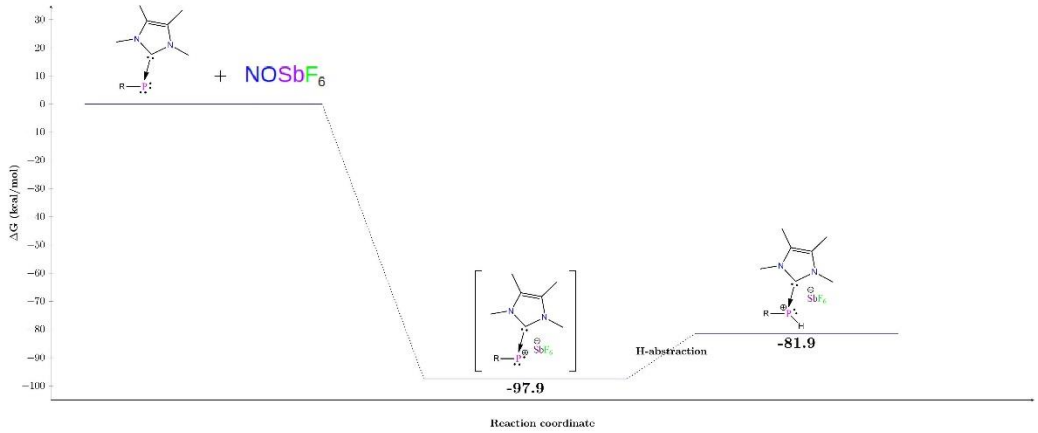


Fig. S48 Reaction free energy profile for **1** to **11** at M06/cc-pVDZ level of theory.

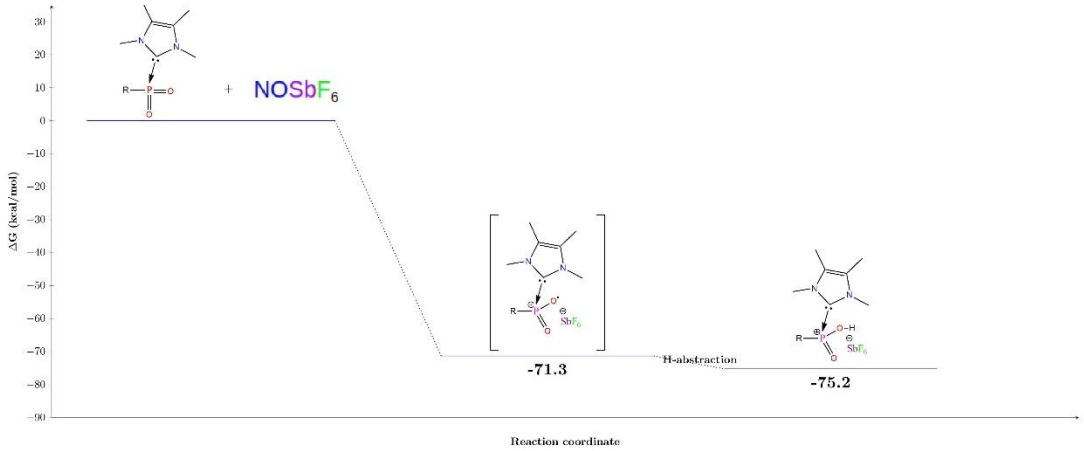


Fig. S49 Reaction free energy profile for **3** to **13** at M06/cc-pVDZ level of theory.

Coordinates of optimized geometries of radicals (at b3lyp/cc-PVDZ level of theory)

Table S18. Cartesian coordinates and energy values of [**7**] (with NHC^{Me_4})

C	0.620889	-0.939867	0.247980
N	0.509937	-2.179038	-0.288205
C	0.172257	-3.087645	0.700540
C	0.052066	-2.377227	1.873632
N	0.327349	-1.057840	1.566534
C	-0.044881	-4.532572	0.417397
C	-0.357568	-2.817498	3.235490
C	0.638434	-2.559883	-1.698502
C	0.119050	0.046336	2.499992
P	0.768177	0.660224	-0.663503
O	0.923899	0.402042	-2.174674
H	-0.199364	-5.082415	1.354265
H	0.814870	-4.980503	-0.103931
H	-0.940418	-4.664169	-0.210135
H	-0.470720	-3.908487	3.261659
H	-1.324965	-2.366718	3.508956
H	0.382836	-2.534072	3.999519
H	-0.959516	0.236949	2.584050
H	0.627990	0.939327	2.129340
H	0.536609	-0.215956	3.478867
H	-0.317169	-2.996074	-2.019035
H	1.443447	-3.298543	-1.805119
H	0.854875	-1.666699	-2.288406
F	-2.671895	-0.991933	1.425627
F	-5.040885	-2.042445	0.551182
F	-4.409939	-1.328144	-2.025273
F	-4.379918	0.566811	-0.041791
F	-2.020698	-0.304286	-1.141597
F	-2.675551	-2.879894	-0.576056
Sb	-3.549288	-1.163882	-0.304186
C	2.125048	1.718340	0.024540
C	1.754579	3.064006	0.284191
C	3.467027	1.281128	0.158331
C	2.748210	3.966953	0.688766
C	4.422897	2.220846	0.575285
C	4.071015	3.547235	0.834406
H	2.475723	5.004778	0.889022
H	5.460722	1.900410	0.687503
H	4.836182	4.259417	1.150437
C	0.324333	3.504499	0.145881
C	-0.488869	3.647348	1.298191
C	-0.222167	3.768866	-1.136985

C	-1.856271	3.901580	1.134533
C	-1.594108	4.033113	-1.246632
C	-2.438290	4.057865	-0.129973
H	-2.487404	3.971552	2.025127
H	-2.015133	4.214125	-2.239528
C	3.910984	-0.125820	-0.128361
C	4.065476	-1.048224	0.930516
C	4.253729	-0.503105	-1.450500
C	4.494216	-2.352975	0.641038
C	4.687647	-1.812998	-1.689272
C	4.801561	-2.759985	-0.661423
H	4.600005	-3.065922	1.463640
H	4.951966	-2.099367	-2.711358
C	0.071137	3.579488	2.702390
H	0.327536	4.592370	3.059084
H	-0.669161	3.167796	3.404499
H	0.990789	2.984143	2.773911
C	-3.931617	4.209168	-0.280479
H	-4.197843	4.704702	-1.226105
H	-4.406968	3.212404	-0.278833
H	-4.368671	4.783488	0.550990
C	0.633040	3.776063	-2.384667
H	1.617392	4.232939	-2.201662
H	0.811343	2.754521	-2.758222
H	0.134753	4.340990	-3.185970
C	3.835605	-0.654907	2.372426
H	3.635735	-1.538588	2.995785
H	4.727842	-0.154359	2.787576
H	3.002407	0.050585	2.492241
C	4.186789	0.482505	-2.594052
H	4.594360	0.039011	-3.514003
H	3.147186	0.786804	-2.790181
H	4.760297	1.397101	-2.372446
C	5.242572	-4.173045	-0.959551
H	6.113458	-4.187485	-1.634289
H	5.509617	-4.715546	-0.040709
H	4.439485	-4.740595	-1.460975

Zero-point correction= 0.617472 (Hartree/Particle)
Thermal correction to Energy= 0.665963
Thermal correction to Enthalpy= 0.666907
Thermal correction to Gibbs Free Energy= 0.530289
Sum of electronic and zero-point Energies= -2568.700441
Sum of electronic and thermal Energies= -2568.651950
Sum of electronic and thermal Enthalpies= -2568.651006

Sum of electronic and thermal Free Energies= -2568.787624

Table S19. Cartesian coordinates and energy values of [**7**] (without NHC^{Me_4})

P	0.373151	0.548384	-1.107853
C	0.792062	1.625684	0.317934
C	2.117242	1.577599	0.818609
C	-0.190625	2.476583	0.869754
C	2.435489	2.400962	1.909665
C	0.170737	3.283775	1.958076
C	1.468581	3.241612	2.470554
H	3.446146	2.385859	2.320893
H	-0.572388	3.949862	2.400034
H	1.738237	3.876099	3.317227
C	3.188297	0.708932	0.244435
C	3.452205	-0.583979	0.819947
C	4.100671	1.265388	-0.723169
C	4.562494	-1.292938	0.378960
C	5.190070	0.509440	-1.122011
C	5.442220	-0.775480	-0.591136
H	4.764675	-2.278274	0.804290
H	5.880057	0.920803	-1.862281
C	-1.583981	2.524981	0.310814
C	-1.866307	3.352203	-0.803384
C	-2.614789	1.772397	0.918623
C	-3.173518	3.388770	-1.304060
C	-3.905534	1.835489	0.375064
C	-4.206919	2.630946	-0.736377
H	-3.389656	4.030377	-2.162927
H	-4.697518	1.240440	0.837660
6	2.538975	-1.174356	1.857890
H	2.295916	-0.449092	2.649060
H	1.586323	-1.487649	1.402377
H	2.998561	-2.058015	2.321145
C	3.867452	2.635195	-1.297446
H	2.901344	2.680729	-1.825949
H	3.834252	3.404209	-0.509428
H	4.659998	2.901038	-2.009589
C	6.625491	-1.566506	-1.064435
H	6.807584	-2.449196	-0.436663
H	6.459466	-1.912005	-2.100402
H	7.534479	-0.944164	-1.083488
C	-0.793572	4.198920	-1.450600
H	-0.267728	4.825447	-0.712628
H	-0.023407	3.582629	-1.945104
H	-1.226281	4.859264	-2.215259

C	-5.598101	2.657585	-1.322169
H	-6.356251	2.378063	-0.575401
H	-5.850050	3.653884	-1.717174
H	-5.684729	1.944762	-2.161079
C	-2.366723	0.932169	2.150065
H	-1.429888	0.364574	2.079829
H	-2.302467	1.563505	3.053071
H	-3.182447	0.211297	2.299817
O	1.733997	-0.107057	-1.429991
Sb	-1.521502	-2.609542	-0.044071
F	-0.864201	-2.547526	-1.856979
F	-2.488606	-4.243459	-0.339852
F	0.069068	-3.551143	0.508422
F	-2.079976	-2.485352	1.796462
F	-0.470537	-0.902350	0.253136
F	-3.022234	-1.517871	-0.558557

Zero-point correction= 0.430699 (Hartree/Particle)
Thermal correction to Energy= 0.467458
Thermal correction to Enthalpy= 0.468402
Thermal correction to Gibbs Free Energy= 0.357892
Sum of electronic and zero-point Energies= -2185.339205
Sum of electronic and thermal Energies= -2185.302447
Sum of electronic and thermal Enthalpies= -2185.301503
Sum of electronic and thermal Free Energies= -2185.412013

Table S20. Cartesian coordinates and energy values of [**12**] (with NHC^{Me_4})

C	-0.614333	-1.103812	0.048553
N	-0.127971	-1.288560	1.298021
C	0.423470	-2.550956	1.410788
C	0.248651	-3.163286	0.192033
F	-0.398859	-2.256138	-0.626401
C	1.157223	-3.008571	2.622845
C	0.748902	-4.478286	-0.295585
C	-0.009205	-0.262437	2.330656
C	-0.622944	-2.502810	-2.053953
P	-1.011762	0.543452	-0.719067
O	0.277709	1.345006	-0.281759
O	-1.391842	0.340485	-2.176046
H	1.529254	-4.029230	2.471634
H	0.524396	-3.000575	3.525585
H	2.028492	-2.355503	2.785071
H	1.021238	-5.117198	0.554407
H	1.660484	-4.326988	-0.896215
H	0.000414	-5.012561	-0.899531

H	0.357723	-2.632943	-2.532103
H	-1.125010	-1.632808	-2.486657
H	-1.229763	-3.410794	-2.172542
H	0.987552	0.190396	2.254151
H	-0.145957	-0.731195	3.313174
H	-0.787514	0.489804	2.183248
Sb	3.754474	-0.977772	-0.178002
F	2.825522	-0.509894	1.485891
F	5.408442	-1.055109	0.801767
F	4.005614	0.910003	-0.539744
F	3.378196	-2.845529	0.242250
F	4.632723	-1.474644	-1.815643
F	2.043174	-0.948846	-1.113877
C	-2.311230	1.519225	0.157190
C	-1.907256	2.852921	0.421365
C	-3.641684	1.107601	0.391654
C	-2.842384	3.765588	0.928868
C	-4.544408	2.044617	0.922135
C	-4.153720	3.358778	1.182873
H	-2.542220	4.798051	1.121153
H	-5.572550	1.731914	1.117483
H	-4.876605	4.073399	1.582694
C	-0.497312	3.305709	0.145453
C	0.409807	3.540140	1.246285
C	-0.123604	3.766527	-1.178396
C	1.714736	3.885235	0.955906
C	1.195551	4.133823	-1.398566
C	2.154779	4.106071	-0.370865
H	2.440396	3.961632	1.769015
H	1.508848	4.399253	-2.410744
C	-4.128572	-0.284944	0.097354
C	-4.182238	-1.248083	1.128595
C	-4.606380	-0.607687	-1.196570
C	-4.657000	-2.535593	0.837949
C	-5.079611	-1.903255	-1.436199
C	-5.105168	-2.886619	-0.438648
H	-4.685275	-3.279916	1.638958
H	-5.446142	-2.148044	-2.437499
C	-3.785428	-0.913686	2.549013
H	-2.846559	-0.344797	2.600183
H	-4.552649	-0.291184	3.041217
H	-3.667286	-1.827066	3.150359
C	-5.622333	-4.273538	-0.737854
H	-5.058095	-4.743539	-1.560719
H	-5.549772	-4.931583	0.140646

H	-6.679686	-4.245768	-1.051165
C	-4.621281	0.412840	-2.309018
H	-5.114070	1.347297	-1.995564
H	-3.591417	0.661478	-2.610284
H	-5.156999	0.024083	-3.187297
C	-0.032416	3.377441	2.676376
H	-0.618525	4.252862	3.007200
H	-0.681720	2.503402	2.820093
H	0.834841	3.286270	3.345467
C	3.615110	4.247568	-0.664563
H	4.147292	4.785422	0.135336
H	4.042335	3.227294	-0.717801
H	3.800356	4.746696	-1.626588
C	-1.111865	3.752904	-2.310425
H	-1.317278	2.717023	-2.632422
H	-2.074568	4.200541	-2.017585
H	-0.715011	4.304046	-3.174425

Zero-point correction= 0.622276 (Hartree/Particle)
Thermal correction to Energy= 0.670993
Thermal correction to Enthalpy= 0.671937
Thermal correction to Gibbs Free Energy= 0.537031
Sum of electronic and zero-point Energies= -2643.888260
Sum of electronic and thermal Energies= -2643.839544
Sum of electronic and thermal Enthalpies= -2643.838599
Sum of electronic and thermal Free Energies= -2643.973505

Table S21. Cartesian coordinates and energy values of [**12**] (without NHC^{Me_4})

C	-0.212082	-1.675314	0.382838
C	-1.490884	-1.892320	0.934955
C	0.949466	-2.222333	0.969142
C	-1.615003	-2.675615	2.090598
C	0.788013	-2.995710	2.129720
C	-0.474334	-3.222761	2.681796
H	-2.601038	-2.855307	2.524674
H	1.675590	-3.422613	2.600809
H	-0.571854	-3.830462	3.584201
C	-2.729972	-1.325554	0.300740
C	-3.358488	-0.157983	0.888500
C	-3.474947	-2.142286	-0.640015
C	-4.619156	0.207199	0.444999
C	-4.732788	-1.726190	-1.027514
C	-5.320185	-0.543753	-0.518708
H	-5.084783	1.103856	0.859612
H	-5.290616	-2.323060	-1.753062

C	2.326418	-1.994093	0.416138
C	2.833949	-2.844481	-0.592458
C	3.127695	-0.960588	0.949060
C	4.138048	-2.638329	-1.053763
C	4.422223	-0.784451	0.442254
C	4.946590	-1.608117	-0.558330
H	4.528914	-3.298092	-1.833701
H	5.034525	0.027017	0.844931
C	-2.653781	0.640640	1.941733
H	-2.399397	0.017645	2.814527
H	-1.710538	1.060171	1.565563
H	-3.278946	1.478011	2.279267
C	-2.865844	-3.390558	-1.212346
H	-1.985013	-3.145403	-1.829299
H	-2.521398	-4.076829	-0.423004
H	-3.585904	-3.921324	-1.850066
C	-6.660538	-0.091867	-1.017524
H	-7.159194	0.579508	-0.303910
H	-6.535706	0.466644	-1.963502
H	-7.322106	-0.944784	-1.233567
C	1.992935	-3.943073	-1.198631
H	1.471354	-4.541081	-0.434355
H	1.230685	-3.507291	-1.864960
H	2.612697	-4.625142	-1.798817
C	6.330821	-1.374774	-1.113427
H	6.982993	-0.876997	-0.379709
H	6.810224	-2.319034	-1.415575
H	6.290724	-0.728377	-2.007826
C	2.643907	-0.062447	2.064141
H	1.588427	0.217510	1.957358
H	2.754227	-0.554860	3.046866
H	3.223880	0.870205	2.086513
O	-1.715065	-0.243373	-1.291097
Sb	0.501256	2.918624	-0.046146
F	0.742781	3.147656	-1.927483
F	0.450676	4.770539	0.407944
F	-1.394512	2.738479	-0.302115
F	0.230932	2.277384	1.758274
F	0.559087	0.796491	-0.478596
F	2.389608	2.704779	0.200371
P	-0.236489	-0.695405	-1.143333
O	0.623316	-1.086385	-2.298710

Zero-point correction= 0.436262 (Hartree/Particle)
Thermal correction to Energy= 0.474347

Thermal correction to Enthalpy= 0.475291
Thermal correction to Gibbs Free Energy= 0.360941
Sum of electronic and zero-point Energies= -2260.548575
Sum of electronic and thermal Energies= -2260.510489
Sum of electronic and thermal Enthalpies= -2260.509545
Sum of electronic and thermal Free Energies= -2260.623895

Table S22. Cartesian coordinates and energy values of [**10**] (with NHC^{Me_4})

C	0.959665	0.574130	1.442883
N	1.210732	1.746880	2.080956
C	0.143257	2.079200	2.900457
C	-0.792296	1.075710	2.764946
N	-0.259600	0.155823	1.875628
C	0.128186	3.312837	3.736740
C	-2.132297	0.918178	3.399101
C	2.474215	2.480738	2.063402
C	-0.927860	-1.070536	1.427132
P	2.077072	-0.521541	0.480960
H	-0.800479	3.362974	4.318594
H	0.189315	4.221141	3.115855
H	0.972925	3.332196	4.443715
H	-2.369518	1.806690	3.997958
H	-2.156900	0.043579	4.069598
H	-2.916195	0.787870	2.638361
H	-0.234410	-1.917263	1.513961
H	-1.264151	-0.966418	0.388611
H	-1.801467	-1.255163	2.058041
H	2.274952	3.553586	1.962389
H	3.077486	2.144876	1.215826
H	3.021176	2.298596	3.000021
F	-3.840700	0.233897	0.693066
F	-6.295467	-0.974446	0.820082
F	-3.999170	-2.397429	1.360752
F	-5.445711	-2.897992	-0.935660
F	-5.233760	-0.229892	-1.610457
F	-2.991290	-1.698511	-1.079366
Sb	-4.650646	-1.335314	-0.125772
C	2.781878	0.494082	-0.883922
C	4.116875	0.123914	-1.226585
C	2.074976	1.428534	-1.700964
C	4.740628	0.724397	-2.327491
C	2.745338	2.000046	-2.793728
C	4.064661	1.666551	-3.103071
H	5.766291	0.442382	-2.574068
H	2.206074	2.709744	-3.424278

H	4.558492	2.128660	-3.960415
C	0.633005	1.807862	-1.512218
C	-0.393840	0.896120	-1.863546
C	0.288592	3.118716	-1.100683
C	-1.732865	1.290767	-1.734960
C	-1.064724	3.465188	-0.980097
C	-2.093176	2.566218	-1.284580
H	-2.515379	0.574810	-1.989394
H	-1.318690	4.474693	-0.642234
C	4.878819	-0.925000	-0.460740
C	5.741540	-0.572029	0.600338
C	4.783209	-2.281710	-0.869162
C	6.466065	-1.581945	1.254516
C	5.519460	-3.252825	-0.183933
C	6.365251	-2.926298	0.887275
H	7.134958	-1.300824	2.073095
H	5.437848	-4.296272	-0.501900
C	-0.095190	-0.470516	-2.441656
H	0.528969	-1.086235	-1.774732
H	-1.027995	-1.023090	-2.616700
H	0.451613	-0.388937	-3.396203
C	1.327372	4.186999	-0.832176
H	0.984042	4.880442	-0.049438
H	2.299127	3.775355	-0.532890
H	1.507264	4.790966	-1.738727
C	-3.543765	2.964280	-1.151705
H	-4.207539	2.101299	-1.293496
H	-3.747763	3.393211	-0.156966
H	-3.811575	3.736448	-1.893682
C	5.910299	0.856892	1.065713
H	5.719731	1.585057	0.265681
H	5.219173	1.087042	1.894599
H	6.928954	1.023899	1.446757
C	3.905047	-2.692782	-2.029035
H	2.840888	-2.479286	-1.832839
H	4.168920	-2.151026	-2.951401
H	3.998026	-3.770083	-2.226627
C	7.141689	-4.001199	1.609048
H	6.463817	-4.687694	2.144464
H	7.724927	-4.615337	0.903386
H	7.836868	-3.572410	2.345460

Zero-point correction= 0.613468 (Hartree/Particle)
Thermal correction to Energy= 0.661074
Thermal correction to Enthalpy= 0.662018

Thermal correction to Gibbs Free Energy= 0.526070
Sum of electronic and zero-point Energies= -2493.474228
Sum of electronic and thermal Energies= -2493.426623
Sum of electronic and thermal Enthalpies= -2493.425679
Sum of electronic and thermal Free Energies= -2493.561627

Table S23. Cartesian coordinates and energy values of [**10**] (without NHC^{Me_4})

P	-1.200861	1.176093	-1.070014
C	-1.995475	0.740157	0.485159
C	-1.766431	1.926415	1.207163
C	-2.695849	-0.356785	1.032195
C	-2.213898	2.082036	2.511801
C	-3.140250	-0.186243	2.352696
C	-2.905968	0.996805	3.075954
H	-2.040417	2.998595	3.078226
H	-3.684519	-1.001464	2.834483
H	-3.273564	1.070667	4.101311
C	-1.009483	2.847084	0.268827
C	0.444874	2.933164	0.357287
C	-1.734266	3.870541	-0.482574
C	1.103273	3.862814	-0.440023
C	-1.007964	4.773294	-1.242500
C	0.403853	4.777542	-1.247627
H	2.193853	3.898116	-0.416902
H	-1.542285	5.515050	-1.839177
C	-2.954670	-1.609629	0.254463
C	-4.210768	-1.804655	-0.366625
C	-1.945642	-2.593216	0.145759
C	-4.432972	-2.984882	-1.087525
C	-2.216467	-3.760537	-0.583196
C	-3.451339	-3.978553	-1.205432
H	-5.402336	-3.129736	-1.573183
H	-1.434110	-4.520356	-0.664922
6	1.211779	2.063880	1.304468
H	1.134192	2.493153	2.319638
H	0.818449	1.041548	1.361744
H	2.270991	2.011944	1.026760
C	-3.231274	3.946668	-0.417492
H	-3.702985	2.962077	-0.552338
H	-3.541614	4.310019	0.576961
H	-3.623144	4.635988	-1.176240
C	1.143219	5.753935	-2.111386
H	2.188066	5.872204	-1.795027
H	1.144328	5.389805	-3.154244
H	0.646264	6.735510	-2.116431

C	-5.304514	-0.764501	-0.274278
H	-5.642638	-0.618987	0.764733
H	-4.962085	0.219276	-0.634970
H	-6.177236	-1.060424	-0.873678
C	-3.730366	-5.254503	-1.963380
H	-2.799226	-5.757057	-2.264693
H	-4.303248	-5.965481	-1.342367
H	-4.328765	-5.062821	-2.867802
C	-0.593763	-2.406183	0.791832
H	-0.058149	-1.542593	0.372159
H	-0.681460	-2.231213	1.876574
H	0.047106	-3.283875	0.634265
Sb	3.262491	-1.164625	0.039053
F	4.169194	-1.285877	-1.664291
F	4.793432	-1.929841	0.937777
F	4.000851	0.613203	0.301478
F	2.328762	-1.025127	1.735988
F	1.714936	-0.377598	-0.842857
F	2.524664	-2.936244	-0.224736

Zero-point correction= 0.427612 (Hartree/Particle)
Thermal correction to Energy= 0.463255
Thermal correction to Enthalpy= 0.464200
Thermal correction to Gibbs Free Energy= 0.354428
Sum of electronic and zero-point Energies= -2110.092477
Sum of electronic and thermal Energies= -2110.056833
Sum of electronic and thermal Enthalpies= -2110.055889
Sum of electronic and thermal Free Energies= -2110.165660

Table S24. Cartesian coordinates and energy values of [**4**] (with NHC^{Me_4})

C	2.275030	3.174512	0.057999
N	1.076677	2.478245	0.229196
C	0.993914	1.433934	-0.646068
N	2.133012	1.494719	-1.385739
C	2.942502	2.551370	-0.962389
C	2.478514	0.564894	-2.458770
C	0.020498	2.838627	1.164567
P	-0.629186	0.483150	-0.983481
O	-0.335774	-0.320103	-2.334971
C	4.271239	2.838533	-1.577624
C	2.654738	4.353765	0.890022
C	-0.721880	-0.594444	0.505046
C	0.376556	-1.228764	1.247245
C	0.146753	-1.683829	2.549311
C	-1.123473	-1.658779	3.156930

C	-2.221355	-1.209868	2.381654
C	-2.055136	-0.716679	1.090572
C	1.742345	-1.492748	0.696787
C	1.941576	-2.416283	-0.372116
C	3.238158	-2.738651	-0.786891
C	4.381966	-2.172866	-0.196792
C	4.178930	-1.262309	0.844816
C	2.896181	-0.917131	1.303241
C	-3.307928	-0.361192	0.343088
C	-3.752234	-1.134387	-0.768679
C	-4.962815	-0.822002	-1.397055
C	-5.774966	0.246242	-0.978138
C	-5.335702	0.993242	0.117824
C	-4.132180	0.710389	0.786385
C	-2.951148	-2.305639	-1.284400
C	-7.068450	0.563614	-1.691168
C	-3.754683	1.577704	1.968735
C	0.771271	-3.083266	-1.048815
C	5.766889	-2.540254	-0.675882
C	2.794802	0.069202	2.447345
H	0.983208	-2.137382	3.092945
H	-1.273572	-2.072419	4.157387
H	-3.236321	-1.292166	2.785242
H	-5.291121	-1.441979	-2.238349
H	-5.946339	1.832263	0.468543
H	-4.093708	1.145264	2.926877
H	-4.216093	2.575167	1.884762
H	-2.665754	1.697391	2.053038
H	-2.058997	-1.951460	-1.826937
H	-3.559695	-2.927728	-1.959728
H	-2.587198	-2.937054	-0.458422
H	-7.606632	1.389987	-1.202136
H	-7.743534	-0.309640	-1.715633
H	-6.893311	0.854831	-2.742023
H	3.362053	-3.471423	-1.591997
H	5.049042	-0.800075	1.323771
H	0.196622	-2.329197	-1.614137
H	0.083273	-3.529840	-0.311365
H	1.113057	-3.877082	-1.732493
H	5.940889	-3.629363	-0.621128
H	6.545853	-2.046846	-0.074372
H	5.926107	-2.250197	-1.729755
H	1.922549	0.728403	2.334879
H	3.701911	0.691892	2.506560
H	2.681237	-0.431041	3.425310

H	1.536856	0.087000	-2.775430
H	3.178806	-0.198295	-2.089172
H	2.943761	1.122371	-3.284038
H	4.936112	1.960288	-1.531853
H	4.765804	3.664855	-1.049662
H	4.180400	3.126712	-2.638401
H	1.967662	5.203880	0.741953
H	3.664198	4.694483	0.623516
H	2.653928	4.111409	1.965524
H	-0.947287	2.623464	0.689510
H	0.089117	3.907834	1.398930
H	0.093796	2.256885	2.095402

Zero-point correction= 0.597169 (Hartree/Particle)
Thermal correction to Energy= 0.635021
Thermal correction to Enthalpy= 0.635966
Thermal correction to Gibbs Free Energy= 0.526811
Sum of electronic and zero-point Energies= -1729.227583
Sum of electronic and thermal Energies= -1729.189731
Sum of electronic and thermal Enthalpies= -1729.188786
Sum of electronic and thermal Free Energies= -1729.297941

Table S25. Cartesian coordinates and energy values of [**4**] (without NHC^{Me_4})

P	0.005878	-0.931986	-1.320770
O	0.059771	-2.424222	-0.731085
C	-0.001549	0.187743	0.228126
C	1.215853	0.617262	0.816136
C	1.200543	1.422522	1.969179
C	-0.006450	1.817079	2.549754
C	-1.210675	1.416539	1.968221
C	-1.221660	0.611545	0.814403
C	2.562312	0.253700	0.245611
C	3.192335	-0.960243	0.611845
C	4.480833	-1.234113	0.134274
C	5.170783	-0.343654	-0.700876
C	4.529372	0.848191	-1.055700
C	3.241173	1.163720	-0.594814
C	-2.566893	0.242463	0.244312
C	-3.171671	-0.996116	0.569929
C	-4.460640	-1.273915	0.095873
C	-5.175777	-0.364626	-0.696776
C	-4.559520	0.851181	-1.011872
C	-3.271983	1.172061	-0.552404
C	-2.427124	-2.031443	1.377846
C	-6.565052	-0.695996	-1.190327

C	-2.652384	2.495224	-0.942744
C	2.470238	-1.976268	1.463558
C	6.560500	-0.669179	-1.197209
C	2.590894	2.457369	-1.029958
H	2.148385	1.740905	2.412576
H	-0.008425	2.439446	3.448323
H	-2.160295	1.728779	2.412159
H	-4.919865	-2.233617	0.353877
H	-5.093248	1.575946	-1.634258
H	-2.422629	3.118569	-0.063445
H	-3.324705	3.067257	-1.599187
H	-1.698774	2.345087	-1.476219
H	-1.556367	-2.390282	0.797949
H	-3.078472	-2.884554	1.622522
H	-2.040297	-1.611796	2.321177
H	-6.982777	0.120068	-1.798696
H	-7.256981	-0.879266	-0.350608
H	-6.565069	-1.610863	-1.806994
H	4.959362	-2.175580	0.422637
H	5.043351	1.557453	-1.711677
H	1.592801	-2.353254	0.906537
H	2.098988	-1.533513	2.402499
H	3.130231	-2.819708	1.718254
H	7.267586	-0.795103	-0.359504
H	6.951796	0.124376	-1.851217
H	6.572795	-1.613516	-1.767505
H	1.651536	2.263107	-1.574939
H	3.256591	3.031685	-1.691141
H	2.327393	3.095671	-0.171206

Zero-point correction= 0.416259 (Hartree/Particle)
Thermal correction to Energy= 0.443039
Thermal correction to Enthalpy= 0.443983
Thermal correction to Gibbs Free Energy= 0.356563
Sum of electronic and zero-point Energies= -1345.971153
Sum of electronic and thermal Energies= -1345.944373
Sum of electronic and thermal Enthalpies= -1345.943429
Sum of electronic and thermal Free Energies= -1346.030848

Coordinates of optimized geometries of other molecules: (at M06/cc-pVDZ level)

Table S26. Cartesian coordinates and energy values of **1**

P	-0.558818	0.259228	-1.148985
N	2.017687	1.409696	-1.432802
N	1.057917	2.011972	0.417152
C	-0.777813	-0.707662	0.428711
C	0.287110	-1.374575	1.096487
C	0.031604	-2.118163	2.254172
H	0.870624	-2.620152	2.748771
C	-1.258351	-2.271032	2.749117
H	-1.441572	-2.868374	3.646046
C	-2.313938	-1.681456	2.063551
H	-3.343322	-1.816464	2.413224
C	-2.094035	-0.909808	0.918807
C	-3.292227	-0.344981	0.230395
C	-3.770518	-0.941835	-0.952251
C	-4.904431	-0.415205	-1.570879
H	-5.273545	-0.888653	-2.488597
C	-5.581519	0.690249	-1.056660
C	-5.109533	1.249117	0.129037
H	-5.637028	2.106663	0.564092
C	-3.986322	0.743591	0.787255
C	-3.570061	1.354586	2.094012
H	-3.945510	2.385356	2.188415
H	-2.477646	1.363993	2.220387
H	-3.970558	0.783058	2.950044
C	-3.088198	-2.134064	-1.555573
H	-2.167806	-1.837537	-2.090697
H	-3.744341	-2.638514	-2.280822
H	-2.787279	-2.867666	-0.790052
C	-6.769656	1.264955	-1.766983
H	-7.428961	1.814836	-1.077674
H	-7.366558	0.480236	-2.258024
H	-6.460183	1.973148	-2.555309
C	1.686315	-1.414392	0.569387
C	1.977318	-2.222354	-0.553683
C	3.280422	-2.264241	-1.045909
H	3.493890	-2.892804	-1.919748
C	4.319846	-1.535898	-0.461560
C	4.027705	-0.795968	0.679704
H	4.832030	-0.242658	1.181084
C	2.737701	-0.747833	1.221934
C	0.914202	-3.040387	-1.220016
H	0.279842	-3.562276	-0.484976
H	1.356058	-3.790354	-1.893309
H	0.242526	-2.393054	-1.812685
C	5.702195	-1.579856	-1.041287
H	6.110385	-2.604655	-1.035337
H	6.400558	-0.940166	-0.479936

H	5.711951	-1.246880	-2.093998
C	2.537006	-0.015037	2.516559
H	1.545629	0.453657	2.592371
H	3.308239	0.760153	2.655128
H	2.617517	-0.702759	3.377044
C	0.896380	1.210272	-0.679637
C	2.880875	2.299532	-0.801434
C	2.281808	2.677620	0.361217
C	2.301483	0.724843	-2.671662
H	1.576779	-0.099009	-2.766674
H	3.322734	0.313625	-2.650981
H	2.191687	1.398438	-3.536956
C	4.201989	2.649277	-1.371963
H	4.873573	1.773187	-1.410715
H	4.695464	3.419519	-0.763015
H	4.113973	3.041120	-2.399090
C	2.738626	3.601638	1.425567
H	2.119556	4.513577	1.485948
H	3.773308	3.921385	1.237599
H	2.710974	3.121541	2.418551
C	-0.011256	2.292561	1.345322
H	-0.956480	2.312033	0.775064
H	0.163921	3.262990	1.828864
H	-0.105753	1.512407	2.119884

Zero-point correction= 0.596846 (Hartree/Particle)
Thermal correction to Energy= 0.632595
Thermal correction to Enthalpy= 0.633539
Thermal correction to Gibbs Free Energy= 0.531765
Sum of electronic and zero-point Energies= -1652.862700
Sum of electronic and thermal Energies= -1652.826951
Sum of electronic and thermal Enthalpies= -1652.826007
Sum of electronic and thermal Free Energies= -1652.927781

Table S27. Cartesian coordinates and energy values of **2**

P	-0.687750	0.373393	-1.080796
O	-0.328662	-0.548316	-2.283503
N	2.099456	1.338946	-1.323319
N	1.013467	2.263929	0.292770
C	0.949858	1.268457	-0.623974
C	0.313435	-1.359060	1.159110
C	1.718542	-1.397849	0.650381
C	-0.759584	-0.707977	0.505586
C	2.236459	2.925339	0.212582
C	2.606770	4.023163	1.135041
H	1.979673	4.920044	0.993886
H	3.650605	4.325006	0.970919
H	2.508250	3.715078	2.190121
C	0.071827	-2.106068	2.319218

H	0.917161	-2.602726	2.808240
C	2.921887	2.336065	-0.808367
C	2.041309	-2.304929	-0.381830
C	-3.279235	-0.359287	0.322789
C	2.465640	0.205382	2.470561
H	1.512656	0.748071	2.382935
H	3.275680	0.936912	2.621805
H	2.390893	-0.393486	3.395186
C	-2.066601	-0.898851	1.010223
C	-3.975158	0.735503	0.864678
C	-2.277947	-1.664616	2.162887
H	-3.302997	-1.803453	2.522616
C	-0.086882	2.622387	1.161572
H	-1.029660	2.374687	0.645033
H	-0.060439	3.701642	1.363857
H	-0.050471	2.075152	2.118108
C	0.982034	-3.134804	-1.037877
H	0.339348	-3.636710	-0.295049
H	1.427445	-3.902847	-1.687772
H	0.332235	-2.479992	-1.648307
C	2.740012	-0.666293	1.279863
C	2.449559	0.495272	-2.458471
H	3.269368	-0.183829	-2.181055
H	2.764409	1.135447	-3.296637
H	1.550995	-0.083206	-2.730619
C	3.372582	-2.421928	-0.785116
H	3.619755	-3.134864	-1.581163
C	-4.923629	-0.504083	-1.438793
H	-5.304460	-1.007317	-2.335373
C	-3.770622	-1.003209	-0.830298
C	-1.212528	-2.254388	2.828690
H	-1.383165	-2.850070	3.729628
C	-3.530107	1.389409	2.141138
H	-3.876872	0.826452	3.025762
H	-3.933957	2.410102	2.227655
H	-2.433568	1.436201	2.224835
C	-5.603750	0.607602	-0.943254
C	-5.117086	1.208387	0.216841
H	-5.647124	2.071862	0.636711
C	4.054115	-0.783194	0.816143
H	4.841405	-0.190126	1.298634
C	4.391576	-1.655148	-0.217332
C	4.282849	2.577839	-1.338429
H	4.901408	1.665953	-1.273512
H	4.785981	3.369152	-0.765520
H	4.266914	2.890378	-2.395702
C	-6.812496	1.146659	-1.646681
H	-6.527097	1.844271	-2.453262
H	-7.471849	1.698172	-0.958653
H	-7.401389	0.341617	-2.113609
C	-3.080506	-2.199599	-1.416352

H	-2.176864	-1.896937	-1.977768
H	-3.748203	-2.734608	-2.108396
H	-2.751715	-2.906452	-0.636585
C	5.797349	-1.751280	-0.729430
H	6.082442	-2.794833	-0.937798
H	6.523156	-1.335727	-0.013530
H	5.917109	-1.196917	-1.678398

Zero-point correction= 0.600687 (Hartree/Particle)
Thermal correction to Energy= 0.637565
Thermal correction to Enthalpy= 0.638509
Thermal correction to Gibbs Free Energy= 0.533572
Sum of electronic and zero-point Energies= -1728.068856
Sum of electronic and thermal Energies= -1728.031977
Sum of electronic and thermal Enthalpies= -1728.031033
Sum of electronic and thermal Free Energies= -1728.135971

Table S28. Cartesian coordinates and energy values of **3**

P	0.585697	0.562707	-0.811370
O	1.403346	1.796384	-0.496633
O	0.519059	-0.133744	-2.161745
N	-2.229191	1.259266	-1.331369
N	-1.470359	2.080939	0.514447
C	-1.165402	1.257540	-0.508669
C	-0.231305	-1.473219	1.092019
C	-2.754246	2.586515	0.355516
C	-3.235274	2.059459	-0.808524
C	-1.639880	-1.489465	0.589772
C	0.808854	-0.698833	0.531383
C	2.132840	-0.900976	0.982163
C	-2.677601	-0.901014	1.333428
C	0.050974	-2.355025	2.142270
H	-0.768695	-2.947706	2.562219
C	3.338784	-0.313047	0.321667
C	-2.328092	0.572448	-2.613999
H	-2.569373	1.309490	-3.394364
H	-3.118661	-0.191335	-2.564957
H	-1.350668	0.113716	-2.825123
C	-1.944951	-2.230010	-0.573418
C	-0.544979	2.498405	1.557836
H	-1.120177	2.799047	2.443718
H	0.080128	3.326259	1.194713
H	0.123460	1.668915	1.819921
C	-3.378489	3.520943	1.321039
H	-3.481796	3.074805	2.324658
H	-4.384264	3.802352	0.980098
H	-2.793567	4.449002	1.431184
C	-2.417461	-0.228798	2.649887
H	-2.416167	-0.963926	3.474006
H	-3.202175	0.509125	2.884040

H	-1.436426	0.266726	2.687346
C	3.855143	-0.949777	-0.819163
C	2.376646	-1.791895	2.033295
H	3.411060	-1.932410	2.363611
C	4.012491	0.785129	0.883252
C	1.343237	-2.503076	2.628323
H	1.548491	-3.195965	3.448753
C	-4.552048	2.197608	-1.469901
H	-4.460937	2.588290	-2.496497
H	-5.197197	2.885876	-0.906931
H	-5.069115	1.224317	-1.530224
C	-3.991006	-0.975951	0.857935
H	-4.790368	-0.485893	1.428126
C	-3.273683	-2.310183	-0.990734
H	-3.507380	-2.890868	-1.892017
C	-4.310462	-1.674528	-0.303856
C	5.044943	-0.472747	-1.376962
H	5.447966	-0.973708	-2.264937
C	-0.873291	-2.932690	-1.348592
H	-0.211714	-2.198840	-1.842876
H	-1.308627	-3.588457	-2.117251
H	-0.236971	-3.547322	-0.689874
C	5.196099	1.225926	0.297782
H	5.716392	2.085563	0.737162
C	3.429213	1.523449	2.047386
H	2.538116	2.071166	1.695113
H	4.142282	2.251349	2.462687
H	3.109529	0.851253	2.860460
C	5.729959	0.611525	-0.836571
C	3.146580	-2.106678	-1.460125
H	2.826283	-2.860420	-0.721053
H	3.793658	-2.604164	-2.198073
H	2.239084	-1.753204	-1.982009
C	-5.721564	-1.770701	-0.802512
H	-6.402918	-1.121870	-0.230827
H	-6.105142	-2.802268	-0.727052
H	-5.794543	-1.487970	-1.867039
C	6.990913	1.127334	-1.461558
H	7.737149	1.404071	-0.699291
H	6.796430	2.032966	-2.061938
H	7.447359	0.382879	-2.131671

Zero-point correction= 0.607703 (Hartree/Particle)
Thermal correction to Energy= 0.644586
Thermal correction to Enthalpy= 0.645530
Thermal correction to Gibbs Free Energy= 0.542318
Sum of electronic and zero-point Energies= -1803.304026
Sum of electronic and thermal Energies= -1803.267144
Sum of electronic and thermal Enthalpies= -1803.266200
Sum of electronic and thermal Free Energies= -1803.369411

Table S29. Cartesian coordinates and energy values of [**4**]

C	2.514421	2.597305	-0.578966
N	1.219316	2.153657	-0.325209
C	0.959128	1.017976	-1.029850
N	2.080834	0.772660	-1.753436
C	3.056793	1.719852	-1.469993
C	2.244730	-0.345185	-2.666768
C	0.234236	2.788711	0.520945
P	-0.747675	0.226303	-1.128047
O	-0.594053	-0.943731	-2.169877
C	4.423261	1.620418	-2.031176
C	3.103670	3.782833	0.085095
C	-0.772595	-0.355780	0.640070
C	0.350937	-0.652039	1.528277
C	0.141772	-0.589764	2.913534
C	-1.108178	-0.373886	3.483695
C	-2.226830	-0.248899	2.626574
C	-2.071263	-0.241350	1.249943
C	1.689055	-1.069563	1.063739
C	1.849715	-2.213010	0.227509
C	3.119500	-2.604540	-0.184007
C	4.279477	-1.892623	0.159214
C	4.120404	-0.787486	0.991759
C	2.869893	-0.375887	1.463100
C	-3.317435	-0.151726	0.431959
C	-3.766852	-1.257700	-0.324467
C	-4.980408	-1.173799	-1.007430
C	-5.768363	-0.021838	-0.990083
C	-5.307327	1.065452	-0.252777
C	-4.103414	1.019963	0.455341
C	-2.960170	-2.514775	-0.423727
C	-7.052018	0.040592	-1.763533
C	-3.655458	2.244003	1.200811
C	0.671294	-3.034922	-0.186633
C	5.618718	-2.311147	-0.366933
C	2.831622	0.818102	2.372133
H	0.993311	-0.804247	3.572239
H	-1.234725	-0.392817	4.570493
H	-3.239740	-0.197709	3.045316
H	-5.322842	-2.047110	-1.578093
H	-5.899825	1.989722	-0.232412
H	-3.772694	2.146384	2.293112
H	-4.229469	3.129270	0.879956
H	-2.585539	2.439409	1.024649
H	-2.138626	-2.368149	-1.150379
H	-3.586183	-3.358276	-0.757930
H	-2.493359	-2.774432	0.540375
H	-7.647899	0.926738	-1.491338
H	-7.676999	-0.852254	-1.588233
H	-6.870738	0.088784	-2.852497

H	3.212410	-3.509754	-0.800525
H	5.008636	-0.210807	1.288070
H	0.101195	-2.510304	-0.979322
H	-0.021084	-3.188025	0.659202
H	0.995356	-4.018679	-0.565022
H	5.857132	-3.360240	-0.110539
H	6.428445	-1.679654	0.035580
H	5.669359	-2.247021	-1.471630
H	1.961241	1.462859	2.163550
H	3.754455	1.415904	2.267959
H	2.745245	0.545849	3.440164
H	1.242728	-0.799151	-2.795848
H	2.935752	-1.089149	-2.238019
H	2.640589	0.023753	-3.627444
H	4.898130	0.670468	-1.724509
H	5.054138	2.445822	-1.670041
H	4.428400	1.651077	-3.134254
H	2.564655	4.715521	-0.158009
H	4.148692	3.913855	-0.231750
H	3.100768	3.676609	1.184550
H	-0.654733	3.050870	-0.080425
H	0.663570	3.696629	0.966061
H	-0.093132	2.093634	1.313036

Zero-point correction= 0.594787 (Hartree/Particle)
Thermal correction to Energy= 0.632035
Thermal correction to Enthalpy= 0.632979
Thermal correction to Gibbs Free Energy= 0.527011
Sum of electronic and zero-point Energies= -1728.062451
Sum of electronic and thermal Energies= -1728.025203
Sum of electronic and thermal Enthalpies= -1728.024259
Sum of electronic and thermal Free Energies= -1728.130227

Table S30. Cartesian coordinates and energy values of [**5**]

C	-4.394664	1.393680	1.886850
C	-4.188603	1.893353	0.603686
C	-2.958486	2.428458	0.207704
C	-1.896902	2.440986	1.126280
C	-2.082659	1.941482	2.431132
C	-3.332890	1.436528	2.789480
C	-0.572372	3.041643	0.778683
C	0.467068	2.347518	0.118332
C	1.716038	2.991703	0.017060
C	1.908666	4.295229	0.491526
C	0.860295	4.990499	1.082081
C	-0.366981	4.352713	1.230900
P	0.394032	0.727797	-0.947352
O	-0.439823	1.244909	-2.196054
C	2.910782	2.310276	-0.572299

C	3.720942	1.505781	0.250793
C	4.910481	0.993965	-0.277067
C	5.299610	1.231539	-1.594101
C	4.457290	1.999463	-2.403060
C	3.270493	2.544070	-1.912750
C	3.262795	1.118341	1.620069
C	2.329378	3.283539	-2.817079
C	6.583541	0.672146	-2.134733
C	-2.771279	2.958900	-1.178847
C	-0.939000	1.855618	3.397027
C	-5.711098	0.804014	2.299840
P	-0.717650	-0.568154	0.693199
C	-0.478283	-2.152592	-0.299036
C	-1.584559	-2.604214	-1.065844
C	-1.529158	-3.806760	-1.773774
C	-0.394902	-4.615359	-1.729051
C	0.690078	-4.192242	-0.968861
C	0.673713	-2.982714	-0.260053
C	-2.892374	-1.872884	-1.131692
C	-3.850689	-2.062307	-0.115867
C	-5.124472	-1.509865	-0.257457
C	-5.476662	-0.753492	-1.374282
C	-4.518976	-0.576349	-2.369667
C	-3.236632	-1.128482	-2.279431
C	1.932708	-2.708796	0.508552
C	3.097727	-2.319001	-0.178310
C	4.315031	-2.275674	0.510272
C	4.412252	-2.591915	1.861933
C	3.245031	-2.969108	2.528137
C	2.013666	-3.033047	1.877157
C	-3.509601	-2.821925	1.127738
C	-2.256698	-0.900612	-3.386673
C	-6.833829	-0.124230	-1.487776
C	3.050157	-1.887237	-1.612564
C	0.778585	-3.381197	2.645680
C	5.721765	-2.482747	2.586751
O	0.474114	-0.487917	1.744136
H	-2.409162	-4.113989	-2.353790
H	1.595198	-4.811258	-0.912257
H	-0.362546	-5.567665	-2.269060
H	2.899649	4.755075	0.387660
H	-1.197974	4.865257	1.732646
H	1.001584	6.015754	1.442083
H	-5.865838	-1.675369	0.535643
H	-4.774119	0.011285	-3.261663
H	5.217184	-1.975668	-0.039035
H	3.291650	-3.218242	3.597033
H	5.538486	0.362902	0.365467
H	4.722466	2.162399	-3.456618
H	-5.008875	1.862590	-0.124841
H	-3.470530	1.032794	3.801639

H	1.020651	-3.804950	3.634879
H	0.211920	-2.438414	2.769139
H	0.134809	-4.091599	2.099319
H	6.575497	-2.693288	1.919682
H	5.878988	-1.465837	2.993462
H	5.777056	-3.180473	3.440160
H	4.060821	-1.662420	-1.993636
H	2.579459	-2.639242	-2.267285
H	2.439342	-0.964988	-1.695375
H	-3.024756	-3.787915	0.905732
H	-2.779715	-2.232491	1.717290
H	-4.404438	-3.005186	1.745888
H	-1.721980	-1.824192	-3.660938
H	-2.766761	-0.510637	-4.283746
H	-1.492083	-0.154706	-3.067060
H	-7.586898	-0.668997	-0.892949
H	-6.828734	0.919723	-1.119185
H	-7.183842	-0.089962	-2.533716
H	4.046344	0.560195	2.159816
H	2.967244	1.994972	2.223377
H	2.353749	0.470192	1.561470
H	6.928006	-0.190899	-1.540266
H	6.468574	0.334036	-3.179276
H	7.402069	1.417198	-2.129137
H	1.356687	2.752737	-2.864060
H	2.113466	4.300210	-2.445182
H	2.739877	3.366992	-3.837066
H	-0.235778	1.071826	3.039644
H	-0.374511	2.800070	3.469957
H	-1.294935	1.579945	4.403902
H	-2.425584	4.008795	-1.160409
H	-1.986713	2.371767	-1.708358
H	-3.714100	2.913472	-1.750054
H	-5.618411	-0.280950	2.490296
H	-6.090531	1.261017	3.231945
H	-6.479945	0.935387	1.520135

Zero-point correction= 0.830646 (Hartree/Particle)
Thermal correction to Energy= 0.882311
Thermal correction to Enthalpy= 0.883255
Thermal correction to Gibbs Free Energy= 0.749010
Sum of electronic and zero-point Energies= -2690.142752
Sum of electronic and thermal Energies= -2690.091088
Sum of electronic and thermal Enthalpies= -2690.090143
Sum of electronic and thermal Free Energies= -2690.224388

Table S31. Cartesian coordinates and energy values of [**7**]

P	-0.558615	0.119008	-0.958027
N	1.919962	1.581558	-1.207353
N	0.648819	2.288344	0.400450

C	-0.702158	-0.968002	0.511359
C	0.403393	-1.616045	1.099691
C	0.162417	-2.433937	2.206820
H	1.010142	-2.945741	2.672857
C	-1.127549	-2.621424	2.696061
H	-1.290682	-3.274588	3.556839
C	-2.210573	-1.998769	2.084978
H	-3.227310	-2.162848	2.453257
C	-2.016156	-1.164398	0.981859
C	-3.169178	-0.513724	0.301040
C	-3.617382	-1.019063	-0.942613
C	-4.666829	-0.367418	-1.587599
H	-5.019277	-0.760151	-2.547847
C	-5.293678	0.754508	-1.041932
C	-4.867789	1.201031	0.209345
H	-5.373658	2.055982	0.671996
C	-3.832127	0.574973	0.904208
C	-3.501832	1.044956	2.292695
H	-4.157981	0.556358	3.034070
H	-3.665976	2.129286	2.398543
H	-2.470878	0.810107	2.597131
C	-3.017140	-2.246179	-1.566502
H	-2.137043	-2.002115	-2.187124
H	-3.748401	-2.737499	-2.224490
H	-2.692109	-2.979610	-0.811777
6	-6.400564	1.440176	-1.779560
H	-6.921912	2.173399	-1.147857
H	-7.143039	0.714999	-2.147796
H	-6.014253	1.974206	-2.663752
C	1.793387	-1.507817	0.571919
C	2.184809	-2.329145	-0.506970
C	3.507692	-2.269620	-0.946942
H	3.815699	-2.914954	-1.777513
C	4.449472	-1.422082	-0.358247
C	4.038752	-0.627077	0.712508
H	4.767579	0.028340	1.204502
C	2.731190	-0.672715	1.204273
C	1.216211	-3.266668	-1.162875
H	0.464763	-2.712810	-1.751240
H	0.667183	-3.870015	-0.421461
H	1.734824	-3.955403	-1.844470
C	5.861654	-1.388693	-0.857716
H	6.403292	-2.305704	-0.571681
H	6.423068	-0.536093	-0.447093
H	5.901343	-1.332593	-1.957684
C	2.372874	0.130605	2.420784
H	1.377567	0.597302	2.342524
H	3.116979	0.919368	2.611424
H	2.338436	-0.505506	3.321988
C	0.758515	1.354176	-0.567413
C	2.587012	2.630915	-0.598420

C	1.784329	3.079912	0.419232
C	2.459656	0.845979	-2.348671
H	1.693866	0.157418	-2.722409
H	3.350358	0.286262	-2.027896
H	2.728686	1.564569	-3.135157
C	3.922854	3.079327	-1.049897
H	4.650720	2.251440	-1.026361
H	4.299654	3.879856	-0.400058
H	3.896621	3.470398	-2.079858
C	1.977715	4.164001	1.408147
H	1.249703	4.981018	1.274094
H	2.980693	4.598864	1.307664
H	1.875067	3.790044	2.440165
C	-0.500014	2.464714	1.273176
H	-1.388704	2.016932	0.803635
H	-0.684980	3.537597	1.414850
H	-0.325780	1.993273	2.253248
O	-0.227536	-0.545098	-2.292872

Zero-point correction= 0.601799 (Hartree/Particle)
Thermal correction to Energy= 0.637253
Thermal correction to Enthalpy= 0.638198
Thermal correction to Gibbs Free Energy= 0.536120
Sum of electronic and zero-point Energies= -1727.859234
Sum of electronic and thermal Energies= -1727.823780
Sum of electronic and thermal Enthalpies= -1727.822836
Sum of electronic and thermal Free Energies= -1727.924913

Table S32. Cartesian coordinates and energy values of [**8**]

N	1.874038	1.626101	-1.122748
N	1.426150	1.844524	0.982609
C	-0.836113	-0.865212	0.372974
C	0.253891	-1.730330	0.621182
C	-0.006525	-2.970189	1.218298
H	0.836509	-3.642646	1.405479
C	-1.297605	-3.368603	1.544064
H	-1.467232	-4.343288	2.007870
C	-2.371419	-2.537137	1.249575
H	-3.398233	-2.850712	1.461159
C	-2.155618	-1.289233	0.665143
C	-3.329602	-0.454516	0.269738
C	-3.891886	-0.642776	-1.010743
C	-4.972027	0.154620	-1.394008
H	-5.408588	0.010822	-2.388952
C	-5.528962	1.107184	-0.537831
C	-4.973988	1.250996	0.734347
H	-5.402917	1.986439	1.424053
C	-3.887678	0.485273	1.156352
C	-3.301546	0.705411	2.517066
H	-3.046583	-0.239854	3.021369

H	-3.992629	1.264153	3.164181
H	-2.370445	1.298495	2.449053
C	-3.367273	-1.695948	-1.942874
H	-2.288365	-1.578598	-2.138571
H	-3.894655	-1.669058	-2.907306
H	-3.500303	-2.705910	-1.520408
C	-6.713852	1.920172	-0.957505
H	-6.723321	2.906738	-0.470585
H	-7.653767	1.413864	-0.679323
H	-6.739319	2.070323	-2.047098
H	1.670686	-1.481992	0.219215
H	2.046119	-1.715804	-1.119112
H	3.391751	-1.599535	-1.474696
H	3.682854	-1.806120	-2.512152
C	4.378353	-1.257542	-0.546895
C	3.984137	-1.044682	0.773550
H	4.744330	-0.796603	1.524616
C	2.653751	-1.180135	1.179582
C	1.031968	-2.117409	-2.149878
H	0.279796	-1.329242	-2.325714
H	0.470168	-3.012450	-1.833067
H	1.514592	-2.346200	-3.111467
C	5.821171	-1.174986	-0.942866
H	6.336916	-2.130942	-0.750317
H	6.358530	-0.403676	-0.368908
H	5.941489	-0.957950	-2.015407
C	2.325223	-1.062257	2.639934
H	1.286390	-0.752866	2.826672
H	3.004375	-0.361762	3.152723
H	2.447504	-2.035718	3.146257
C	0.934379	1.386159	-0.189720
C	2.992758	2.196731	-0.526781
C	2.710077	2.338138	0.801866
C	1.830087	1.316092	-2.547004
H	0.815129	1.020639	-2.823599
H	2.532021	0.495327	-2.759071
H	2.122738	2.209858	-3.114991
C	4.219630	2.502693	-1.295024
H	4.606014	1.601626	-1.800012
H	5.006893	2.874943	-0.626174
H	4.047672	3.271128	-2.066102
C	3.532998	2.870075	1.911588
H	3.045951	3.716807	2.421213
H	4.497231	3.228936	1.528222
H	3.746581	2.097087	2.669236
C	0.681777	1.908164	2.231147
H	0.055969	2.813934	2.261966
H	1.386047	1.920525	3.071769
H	0.043126	1.020814	2.339178
O	-1.017973	0.692090	-1.925767
H	-1.893583	1.026723	-2.177772

Zero-point correction= 0.613832 (Hartree/Particle)
Thermal correction to Energy= 0.651146
Thermal correction to Enthalpy= 0.652090
Thermal correction to Gibbs Free Energy= 0.546168
Sum of electronic and zero-point Energies= -1728.487277
Sum of electronic and thermal Energies= -1728.449962
Sum of electronic and thermal Enthalpies= -1728.449018
Sum of electronic and thermal Free Energies= -1728.554941

Table S33. Cartesian coordinates and energy values of [**9**]

P	0.543265	0.219535	-0.900486
O	0.397077	-0.394471	-2.272072
N	-2.034744	1.448010	-1.262288
C	-0.925782	1.298706	-0.520752
C	1.263733	-2.530407	2.717243
H	1.447736	-3.179498	3.576860
C	3.725453	-0.930032	-0.895546
C	-1.679849	-1.519613	0.579188
C	-2.212897	2.855242	0.438729
C	-2.666581	-0.769830	1.243749
N	-1.014640	2.162356	0.510216
C	0.787365	-0.870547	0.534580
C	3.898032	0.734135	0.887819
C	-3.964824	-0.745002	0.725235
H	-4.728706	-0.147373	1.237587
C	4.931229	1.350820	0.178970
H	5.409208	2.239168	0.607778
C	3.268566	-0.392368	0.327737
C	-3.337775	-2.278307	-1.002855
H	-3.607993	-2.900316	-1.864152
C	3.129424	-2.173686	-1.491852
H	2.232096	-1.944364	-2.092319
H	2.833685	-2.903204	-0.721136
H	3.851985	-2.663260	-2.160642
C	-0.289012	-1.578523	1.113911
C	-4.321731	-1.492612	-0.396154
C	4.769940	-0.286364	-1.557515
H	5.127155	-0.702236	-2.506250
C	5.378716	0.862000	-1.047628
C	2.109765	-1.035092	1.008491
C	2.322615	-1.861949	2.113873
H	3.344398	-1.988650	2.483318
C	-2.021454	-2.307566	-0.543102
C	-2.380652	-0.039857	2.524151
H	-2.558440	-0.695269	3.394794
H	-3.047123	0.829273	2.646581
H	-1.334873	0.293128	2.607376
C	-1.012642	-3.186096	-1.220007
H	-0.308597	-2.589038	-1.823703

H	-1.506072	-3.902828	-1.891509
H	-0.415179	-3.757855	-0.491482
C	-2.860263	2.393491	-0.677392
C	3.521037	1.285033	2.234099
H	4.245251	0.963155	3.002582
H	2.534243	0.946019	2.584073
H	3.537653	2.386977	2.235968
C	-0.027046	-2.397521	2.213747
H	-0.856598	-2.949671	2.665447
C	-4.180562	2.743092	-1.246818
H	-4.092406	3.153097	-2.265567
H	-4.679561	3.498188	-0.625747
H	-4.838815	1.860072	-1.298491
C	0.022417	2.405396	1.501518
H	0.606105	1.488618	1.660606
H	-0.444910	2.687188	2.453716
H	0.690865	3.216221	1.171667
C	-2.373167	0.755427	-2.506598
H	-2.587127	1.507410	-3.278754
H	-3.259125	0.127641	-2.336645
H	-1.520787	0.137358	-2.811553
C	6.505258	1.518274	-1.783396
H	6.695735	2.536975	-1.415756
H	6.302805	1.572786	-2.864154
H	7.439328	0.944293	-1.662789
C	-5.718332	-1.476112	-0.938519
H	-6.161862	-2.484818	-0.923033
H	-5.738886	-1.145388	-1.991355
H	-6.377343	-0.812654	-0.359375
C	-2.601537	3.882859	1.431447
H	-2.707584	3.459023	2.443903
H	-3.566368	4.329433	1.158090
H	-1.862555	4.698415	1.485226
H	1.566108	1.204206	-0.760924

Zero-point correction= 0.612923 (Hartree/Particle)
Thermal correction to Energy= 0.649846
Thermal correction to Enthalpy= 0.650790
Thermal correction to Gibbs Free Energy= 0.545986
Sum of electronic and zero-point Energies= -1728.478835
Sum of electronic and thermal Energies= -1728.441912
Sum of electronic and thermal Enthalpies= -1728.440968
Sum of electronic and thermal Free Energies= -1728.545772

Table S34. Cartesian coordinates and energy values of [**10**]

P	-0.613123	0.168417	-1.077276
N	1.947765	1.411356	-1.347345
N	0.876687	2.130900	0.389458
C	-0.753690	-0.827610	0.461582
C	0.341383	-1.475784	1.083858

C	0.095141	-2.271468	2.205168
H	0.937398	-2.783768	2.680257
C	-1.196907	-2.454204	2.690356
H	-1.366201	-3.089095	3.563366
C	-2.273474	-1.852529	2.047042
H	-3.294634	-2.008123	2.407905
C	-2.071772	-1.042852	0.928399
C	-3.240348	-0.423052	0.238607
C	-3.715208	-0.985949	-0.966695
C	-4.799229	-0.390308	-1.606584
H	-5.171806	-0.832331	-2.537562
C	-5.433698	0.742480	-1.091136
C	-4.969618	1.259031	0.116914
H	-5.472640	2.128691	0.554713
C	-3.894600	0.688116	0.802216
C	-3.516860	1.238976	2.147764
H	-4.131851	0.782213	2.942942
H	-3.693117	2.325001	2.199936
H	-2.469844	1.035705	2.418136
C	-3.084697	-2.210095	-1.563830
H	-2.171052	-1.964722	-2.137442
H	-3.773198	-2.701438	-2.266266
H	-2.794055	-2.946318	-0.797548
C	-6.582203	1.368502	-1.819035
H	-7.098560	2.117313	-1.201521
H	-7.320131	0.611272	-2.127239
H	-6.240990	1.872196	-2.738892
C	1.728645	-1.434376	0.537698
C	2.041607	-2.201229	-0.606852
C	3.352216	-2.198609	-1.083986
H	3.595886	-2.810114	-1.961130
C	4.364230	-1.452456	-0.474452
C	4.036993	-0.721899	0.666827
H	4.820531	-0.152030	1.180782
C	2.745026	-0.723566	1.201502
C	1.010150	-3.040173	-1.305124
H	0.318082	-3.523049	-0.597286
H	1.488231	-3.827219	-1.905968
H	0.387706	-2.441977	-1.996520
C	5.755246	-1.461214	-1.031353
H	6.182126	-2.477233	-1.017979
H	6.431210	-0.808616	-0.459479
H	5.772043	-1.131655	-2.084571
C	2.490026	0.003625	2.489091
H	1.511972	0.509436	2.504791
H	3.277448	0.746935	2.687430
H	2.485562	-0.691654	3.345994
C	0.813626	1.251763	-0.635030
C	2.764298	2.350740	-0.738350
C	2.084565	2.812771	0.356992
C	2.295168	0.711029	-2.573405

H	1.524361	-0.039195	-2.792000
H	3.259034	0.197565	-2.447367
H	2.353772	1.425633	-3.407430
C	4.110599	2.677918	-1.257987
H	4.767405	1.791119	-1.240670
H	4.581601	3.456179	-0.643375
H	4.073862	3.049204	-2.294596
C	2.446980	3.835585	1.364349
H	1.814225	4.735191	1.283510
H	3.488473	4.155117	1.226808
H	2.346053	3.449046	2.391175
C	-0.201115	2.405581	1.324872
H	-0.230108	3.482747	1.534755
H	-0.061265	1.855306	2.268578
H	-1.156732	2.108151	0.871597

Zero-point correction= 0.597653 (Hartree/Particle)
Thermal correction to Energy= 0.632885
Thermal correction to Enthalpy= 0.633829
Thermal correction to Gibbs Free Energy= 0.532445
Sum of electronic and zero-point Energies= -1652.667738
Sum of electronic and thermal Energies= -1652.632507
Sum of electronic and thermal Enthalpies= -1652.631563
Sum of electronic and thermal Free Energies= -1652.732947

Table S35. Cartesian coordinates and energy values of [**11**]

P	-0.353594	-0.078565	-1.212648
N	1.955162	1.566021	-1.280749
N	0.582204	2.278059	0.228450
C	-0.666932	-0.913205	0.419217
C	0.422842	-1.528966	1.069348
C	0.195756	-2.247327	2.246216
H	1.046982	-2.720979	2.745135
C	-1.088579	-2.387483	2.759337
H	-1.255321	-2.964551	3.671895
C	-2.162561	-1.811425	2.093037
H	-3.180175	-1.937750	2.474637
C	-1.979986	-1.072379	0.918515
C	-3.180837	-0.513300	0.235956
C	-3.620437	-1.079451	-0.981513
C	-4.730342	-0.533527	-1.620993
H	-5.072570	-0.981125	-2.561132
C	-5.426939	0.558423	-1.096126
C	-4.996059	1.080250	0.120230
H	-5.541873	1.920749	0.564206
C	-3.899963	0.551711	0.810214
C	-3.573517	1.123248	2.162070
H	-4.256427	0.717486	2.928516
H	-3.709361	2.217152	2.175527
H	-2.554470	0.888453	2.500858

C	-2.930181	-2.264195	-1.596129
H	-2.062269	-1.970091	-2.217170
H	-3.613629	-2.808240	-2.264191
H	-2.558095	-2.971657	-0.838477
C	-6.618466	1.115221	-1.811231
H	-6.962621	2.057525	-1.361446
H	-7.461679	0.405244	-1.782851
H	-6.397942	1.302249	-2.874109
C	1.815035	-1.479514	0.533707
C	2.197484	-2.365341	-0.494703
C	3.521875	-2.352836	-0.940058
H	3.818725	-3.050520	-1.731214
C	4.478639	-1.495553	-0.394739
C	4.078946	-0.634818	0.630561
H	4.820610	0.030422	1.089780
C	2.770768	-0.626175	1.118613
C	1.220428	-3.334324	-1.092209
H	0.651021	-3.869553	-0.315193
H	1.734767	-4.081242	-1.713218
H	0.478370	-2.827634	-1.734512
C	5.900604	-1.519951	-0.866320
H	6.515441	-2.176140	-0.227266
H	6.361257	-0.519930	-0.828073
H	5.984948	-1.901967	-1.894560
C	2.428214	0.248481	2.289745
H	1.428334	0.702544	2.200679
H	3.171695	1.050131	2.420903
H	2.412430	-0.333636	3.227137
C	0.750589	1.335935	-0.722551
C	2.572656	2.637540	-0.659206
C	1.703481	3.089484	0.298162
C	2.562562	0.823823	-2.376395
H	1.857483	0.065362	-2.736125
H	3.475040	0.324490	-2.018808
H	2.805091	1.515477	-3.195234
C	3.922393	3.104632	-1.048379
H	4.668111	2.297303	-0.960014
H	4.244028	3.932053	-0.402595
H	3.946350	3.467524	-2.088789
C	1.824210	4.191278	1.279374
H	1.078732	4.984305	1.104992
H	2.817603	4.654205	1.214893
H	1.689629	3.827143	2.311378
C	-0.592819	2.441473	1.066462
H	-1.442186	1.914562	0.614360
H	-0.836991	3.509194	1.145422
H	-0.408989	2.034660	2.073601
H	-1.542886	0.716309	-1.264401

Zero-point correction= 0.606985 (Hartree/Particle)
Thermal correction to Energy= 0.643516

Thermal correction to Enthalpy= 0.644461
Thermal correction to Gibbs Free Energy= 0.539464
Sum of electronic and zero-point Energies= -1653.283152
Sum of electronic and thermal Energies= -1653.246621
Sum of electronic and thermal Enthalpies= -1653.245677
Sum of electronic and thermal Free Energies= -1653.350674

Table S36. Cartesian coordinates and energy values of [**12**]

P	-0.522378	0.247019	-0.907240
N	2.092171	1.423947	-1.285583
N	1.055812	2.233133	0.432608
C	-0.682547	-0.864344	0.540825
C	0.347010	-1.609183	1.137434
C	0.031674	-2.433835	2.223968
H	0.833570	-3.009881	2.695899
C	-1.273315	-2.538030	2.692216
H	-1.500321	-3.192689	3.536872
C	-2.296825	-1.821072	2.078049
H	-3.330047	-1.924603	2.424567
C	-2.007322	-0.979171	1.001603
C	-3.136726	-0.322628	0.287037
C	-3.648470	-0.962598	-0.907213
C	-4.802696	-0.465781	-1.478383
H	-5.190518	-0.935625	-2.386955
C	-5.510126	0.606899	-0.912809
C	-5.046624	1.169543	0.297170
H	-5.620794	1.982744	0.752438
C	-3.898722	0.731000	0.912040
C	-3.418339	1.389262	2.160242
H	-4.233176	1.928100	2.663104
H	-2.643947	2.130326	1.901885
H	-2.969737	0.682299	2.873224
C	-2.959092	-2.138493	-1.509621
H	-2.047491	-1.815829	-2.047056
H	-3.615261	-2.645350	-2.229931
H	-2.639072	-2.865687	-0.746028
C	-6.730276	1.151275	-1.562833
H	-7.516201	1.368002	-0.822518
H	-7.131109	0.475966	-2.330576
H	-6.492518	2.112181	-2.053679
C	1.751547	-1.565627	0.636456
C	2.115737	-2.373704	-0.461411
C	3.439726	-2.349286	-0.898758
H	3.726740	-2.985656	-1.744012
C	4.408557	-1.545495	-0.292409
C	4.027072	-0.771225	0.802828
H	4.777770	-0.155565	1.313054
C	2.718999	-0.788880	1.296646
C	1.113921	-3.253113	-1.145508
H	0.528948	-3.845794	-0.422912

H	1.608401	-3.951660	-1.835327
H	0.403170	-2.642506	-1.728064
C	5.815391	-1.536302	-0.808528
H	6.261601	-2.543009	-0.764202
H	6.461440	-0.859090	-0.230538
H	5.854757	-1.225834	-1.866945
C	2.393494	-0.021979	2.545222
H	1.415379	0.482208	2.496040
H	3.167600	0.730096	2.762799
H	2.344311	-0.692632	3.420699
C	0.954803	1.340104	-0.572319
C	2.936479	2.357860	-0.711998
C	2.279948	2.878645	0.371849
C	2.447419	0.678774	-2.492599
H	1.597786	0.046658	-2.776136
H	3.333292	0.062703	-2.281436
H	2.672402	1.395680	-3.294838
C	4.282598	2.640398	-1.258147
H	4.913747	1.736177	-1.249013
H	4.788514	3.409245	-0.659840
H	4.235664	3.002458	-2.297620
C	2.692029	3.924382	1.336737
H	2.001663	4.783196	1.330651
H	3.689932	4.303205	1.079735
H	2.741221	3.540230	2.369008
C	0.009291	2.533388	1.396771
H	-0.743049	3.194845	0.943581
H	0.459512	3.015282	2.273065
H	-0.480550	1.603328	1.713839
O	-0.250754	-0.482886	-2.201975
O	-1.748187	1.187503	-0.726871

Zero-point correction= 0.606519 (Hartree/Particle)
Thermal correction to Energy= 0.644034
Thermal correction to Enthalpy= 0.644978
Thermal correction to Gibbs Free Energy= 0.538685
Sum of electronic and zero-point Energies= -1803.064308
Sum of electronic and thermal Energies= -1803.026792
Sum of electronic and thermal Enthalpies= -1803.025848
Sum of electronic and thermal Free Energies= -1803.132141

Table S37. Cartesian coordinates and energy values of [**13**]

. P	-0.483643	0.360542	-0.811620
N	2.158864	1.351156	-1.284856
N	1.320951	2.095625	0.571632
C	-0.782528	-0.788626	0.572638
C	0.279429	-1.541376	1.122550
C	0.005232	-2.405301	2.186196
H	0.828032	-2.987954	2.611244

C	-1.286573	-2.552314	2.677298
H	-1.482170	-3.238474	3.504753
C	-2.335391	-1.858144	2.086078
H	-3.363971	-2.012253	2.425635
C	-2.109622	-0.981277	1.022501
C	-3.294544	-0.377138	0.343777
C	-3.757043	-0.946788	-0.860430
C	-4.866962	-0.372808	-1.487424
H	-5.224491	-0.812369	-2.424791
C	-5.534776	0.728761	-0.956692
C	-5.073568	1.257074	0.253520
H	-5.592220	2.115438	0.694632
C	-3.977040	0.715767	0.923163
C	-3.522218	1.310594	2.223157
H	-4.151860	2.164339	2.510455
H	-2.480072	1.668075	2.164025
H	-3.556078	0.577499	3.045112
C	-3.096878	-2.143020	-1.480695
H	-2.210971	-1.846027	-2.067786
H	-3.789320	-2.656452	-2.162840
H	-2.761908	-2.870076	-0.723685
C	-6.734933	1.311212	-1.634974
H	-6.764612	2.406669	-1.533642
H	-7.664123	0.922196	-1.185441
H	-6.759730	1.060941	-2.705296
C	1.670086	-1.520533	0.579510
C	1.960485	-2.275503	-0.580435
C	3.271735	-2.292594	-1.054846
H	3.500161	-2.887203	-1.947288
C	4.302758	-1.590708	-0.423845
C	3.998038	-0.886890	0.739902
H	4.798192	-0.358495	1.272822
C	2.705124	-0.866834	1.272177
C	0.905263	-3.080236	-1.278804
H	0.309452	-3.673427	-0.565755
H	1.358160	-3.774192	-2.000939
H	0.202863	-2.431290	-1.828462
C	5.694189	-1.628550	-0.978708
H	6.105874	-2.650562	-0.945320
H	6.380026	-0.976976	-0.417126
H	5.716408	-1.321216	-2.038372
C	2.478481	-0.197956	2.596699
H	1.447729	0.161528	2.730883
H	3.175192	0.643048	2.746461
H	2.663231	-0.904833	3.424543
C	1.082769	1.290369	-0.482129
C	3.109712	2.180996	-0.719514
C	2.579009	2.661046	0.449184
C	2.355705	0.692103	-2.576603
H	1.449929	0.133132	-2.835529
H	3.217990	0.014543	-2.503158

H	2.545941	1.462373	-3.337204
C	4.431826	2.401032	-1.345689
H	4.998075	1.456323	-1.409761
H	5.025537	3.109488	-0.753696
H	4.342724	2.808576	-2.365036
C	3.138674	3.601752	1.446642
H	2.490806	4.481683	1.586959
H	4.120669	3.964170	1.115758
H	3.276581	3.125472	2.431678
C	0.387973	2.402395	1.648124
H	-0.259213	3.244269	1.362992
H	0.956921	2.656440	2.550678
H	-0.235463	1.524154	1.860149
O	-0.461124	-0.246025	-2.183979
O	-1.443197	1.655869	-0.596500
H	-2.390247	1.408071	-0.570901

Zero-point correction= 0.619392 (Hartree/Particle)
Thermal correction to Energy= 0.657020
Thermal correction to Enthalpy= 0.657965
Thermal correction to Gibbs Free Energy= 0.551974
Sum of electronic and zero-point Energies= -1803.714181
Sum of electronic and thermal Energies= -1803.676553
Sum of electronic and thermal Enthalpies= -1803.675609
Sum of electronic and thermal Free Energies= -1803.781599

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