

Supporting Information
for
Thermodynamics-Inspired Identification of Privileged
Organocatalysts for Hydrogen Evolution Reactions

Yu-Shan Zhang,^a Bing Zhong,^a Likun Dong,^a Jin-Dong Yang,^{*,a,c} and Jin-Pei Cheng^{a,b,c}

^a Center of Basic Molecular Science (CBMS), Department of Chemistry, Tsinghua University,
Beijing 100084.

^b State Key Laboratory of Elemento-organic Chemistry, Nankai University, Tianjin 300071, China.

^c Haihe Laboratory of Sustainable Chemical Transformations, Tianjin 300192, China.

*E-mail: jdyang@mail.tsinghua.edu.cn

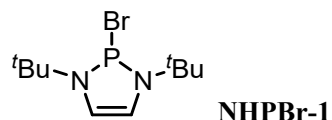
Content

1. General Information.....	1
2. Substrate and Reagent Synthesis	2
3. General Electrochemistry.....	11
4. Computational Details	15
5. NMR Spectra	46
6. References.....	61

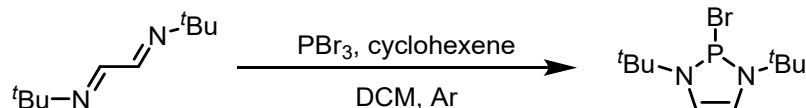
1. General Information

Unless noted, materials were purchased from commercial source and used without further purification. ¹H, ¹³C and ³¹P NMR spectra were recorded on a Bruker Ultra Shield 400 MHz spectrometers (¹H NMR frequency, corresponding ¹³C frequencies are 100 MHz) and spectra were referenced to the solvent (¹H NMR: CDCl₃ at 7.26 ppm; ¹³C NMR: CDCl₃ at 77.16 ppm). Data for ¹H NMR spectra are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, td = triplet of doublet, dt = doublet of triplet, dd = doublet of doublet), coupling constants (Hz), and integration. Coupling constants (*J* values) were calculated directly from the spectra.

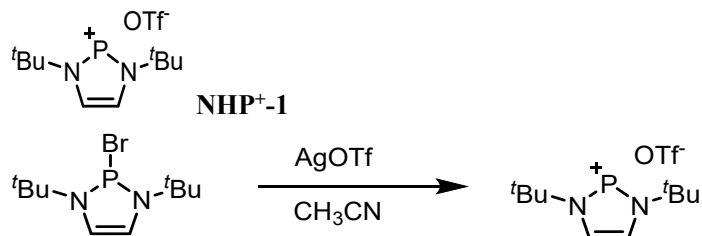
2. Substrate and Reagent Synthesis



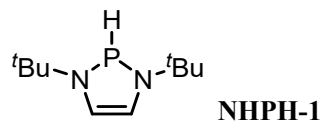
NHPBr-1 was prepared according to a modified literature.¹

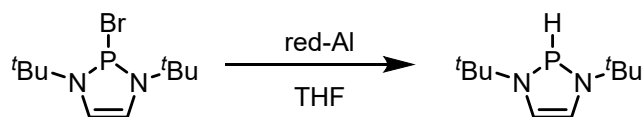


Cyclohexene (3.62 mL, 35.6 mmol, 3 equiv.) and 1,4-Diazabutadiene (2.00 g, 11.9 mmol, 1.0 equiv.) were dissolved in anhydrous dichloromethane (20 mL) in a Schlenk tube under argon atmosphere and cooled to 0 °C using an ice bath. PBr₃ (1.13 mL, 11.9 mmol, 1 equiv.) was added to the solution over 5 minutes. After 10 minutes, the cooling bath was removed, and the reaction was stirred for 48 hour. The solvent was then removed in vacuo. The Schlenk tube was taken into a glovebox, and 40 mL anhydrous n-Hexane was added. The mixture was then stirred for 10 minutes, and any solid stuck to the side was scraped off with a spatula. The mixture was filtered, and the solid was washed with 2 x 20 mL of n-Hexane to yield compound **NHPBr-1** (3.31 g, 11.9 mmol, >99%) as a pale yellow powder. ¹H NMR (400 MHz, CDCl₃) δ 7.31 (s, 2H), 1.75 (d, *J* = 2.0 Hz, 18H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 124.5, 124.4, 59.3, 59.2, 30.2, 30.1. ³¹P NMR (162 MHz, CDCl₃) δ 186.51.

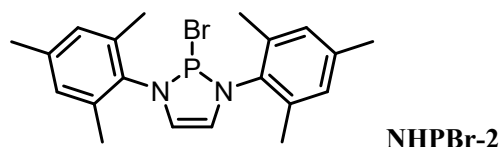


NHPBr-1 (0.28 g, 1 mmol, 1 equiv.) was placed in a Schlenk tube in the glovebox, and dry CH₃CN (5 mL) was added. Then AgOTf (0.26 g, 1 mmol, 1 equiv.) was added. The reaction was stirred for 1 hour, then the precipitation was filtered out. The volatiles were removed in vacuo to yield compound **NHP⁺-1** as an off-white solid (0.26 g, 0.75 mmol, 75% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.17 (s, 2H), 1.81 (d, *J* = 1.8 Hz, 18H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 132.8, 132.8, 62.7, 62.6, 31.3, 31.2. ³¹P NMR (162 MHz, CDCl₃) δ 202.34. ¹⁹F NMR (376 MHz, CDCl₃) δ -78.37.

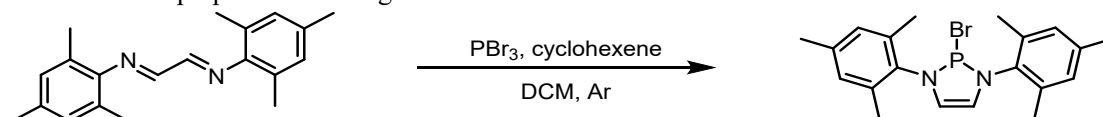




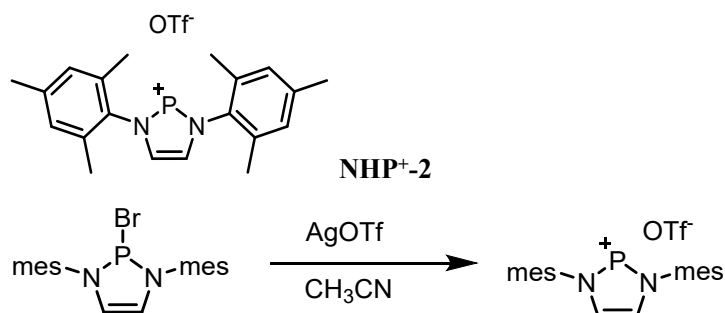
In a glovebox, compound **NHPBr-1** (2.79 g, 10.0 mmol, 1 equiv.) was placed in a tall Schlenk flask, with a stir bar. The flask was removed from the glovebox and attached to a nitrogen bubbler. Anhydrous THF (25 mL) was added, and the suspension was cooled with dry-ice/ acetone to -78 °C. Red-Al solution in toluene (1.64 mL, 5.0 mmol, 0.5 equiv.) was carefully added over 5 minutes, resulting in the suspension becoming paler. The reaction was stirred for 10 minutes, then the cooling bath was removed. After 2 hours, the solvent was removed in vacuo. The flask was taken into the glovebox, and 25 mL of hexane was added. The mixture was stirred and filtered, and the solids were extracted with a further 2 x 20 mL aliquots of hexane. The hexane was removed in vacuo to give an orange oil and was immediately purified by vacuum distillation under argon atmosphere. ¹H NMR (400 MHz, C₆D₆) δ 6.12 (d, *J* = 184 Hz, 1H), 5.99 (d, *J* = 3.9 Hz, 2H), 1.15 (d, *J* = 1.1 Hz, 18H). ³¹P NMR (162 MHz, C₆D₆) δ 57.45 (d, *J* = 184.8 Hz).



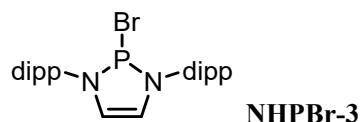
NHPBr-2 was prepared according to a modified literature.²



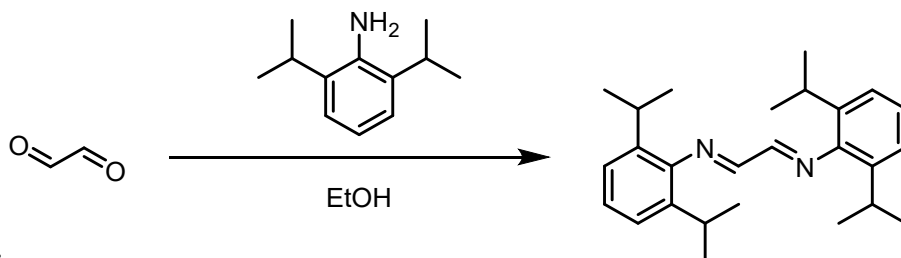
Cyclohexene (2.66 mL, 26.1 mmol, 3.0 equiv.) and N,N'-bis(2,4,6-trimethylphenyl)ethane-1,2-diimine (2.54 g, 8.7 mmol, 1.0 equiv.) were dissolved in anhydrous dichloromethane (20 mL) in a Schlenk tube under argon atmosphere and cooled to 0 °C using an ice bath. PBr₃ (0.83 mL, 8.7 mmol, 1.0 equiv.) was added to the solution over 5 minutes. After 10 minutes, the cooling bath was removed, and the reaction was stirred for 24 hours. The solvent was then removed in vacuo. The Schlenk tube was taken into a glovebox, and 40 mL anhydrous n-Hexane was added. The mixture was then stirred for 10 minutes, and any solid stuck to the side was scraped off with a spatula. The mixture was filtered, and the solid was washed with 2 x 20 mL of n-Hexane to yield compound **NHPBr-2** (3.15 g, 7.8 mmol, 90%) as a yellow powder. ¹H NMR (400 MHz, CDCl₃) δ 7.02 (s, 4H), 6.69 (s, 2H), 2.45 (s, 12H), 2.34 (s, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 138.7, 135.6, 135.6, 133.3, 130.0, 123.4, 123.3, 21.0, 19.3, 19.2. ³¹P NMR (162 MHz, CDCl₃) δ 174.49.



NHPBr-2 (201.3 mg, 0.5 mmol, 1 equiv.) was placed in a Schlenk tube in the glovebox, and dry CH_3CN (2 mL) was added. Then AgOTf (128.5 mg, 0.5 mmol, 1 equiv.) was added. The reaction was stirred for 1 hour, then the precipitation was filtered out. The volatiles were removed in vacuo to yield **NHP⁺-2** as an off-white solid (189.2 mg, 0.4 mmol, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.38 (s, 2H), 7.14 (s, 4H), 2.42 (s, 6H), 2.22 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.73, 139.38, 133.67, 133.63, 130.28, 21.16, 17.49, 17.33. ^{31}P NMR (162 MHz, CDCl_3) δ 204.18. ^{19}F NMR (376 MHz, CDCl_3) δ -78.40.

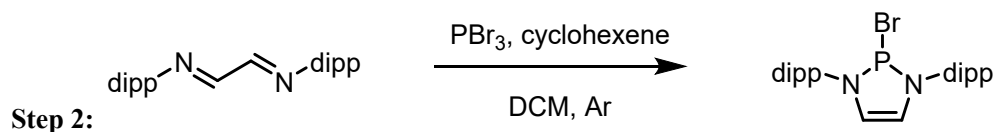


NHPBr-3 was prepared according to a modified literature.³



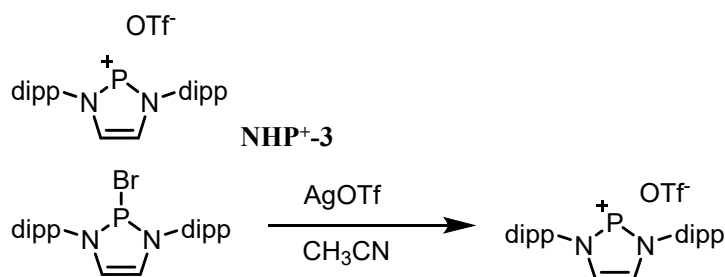
Step 1:

8.86 g (50 mmol, 2.0 equiv.) 2,6-Diisopropylaniline was dissolved in 40 mL ethanol. 2.87 mL (3.63 g, 25 mmol, 1.0 equiv.) of 40% glyoxal and 4 mL water were added under stirring. This reaction was stirred for 24 h. The resulting mixture was filtered. The precipitation was washed by ethanol and yield 6.12 g *N,N'*-Bis(adamantan-1-yl)-1,4-diazabutadiene as a yellow powder (65%). ^1H NMR (400 MHz, CDCl_3) δ 8.14 (s, 2H), 7.21 (m, 6H), 2.98 (sept, $J = 6.9$ Hz, 4H), 1.25 (d, $J = 6.9$ Hz, 24H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 163.1, 148.1, 136.7, 125.1, 123.2, 28.1, 23.4.

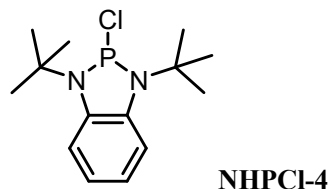


Cyclohexene (3.33 mL, 32.7 mmol, 3.0 equiv.) and) *N,N'*-Bis(2,6-diisopropylphenyl)-1,4-

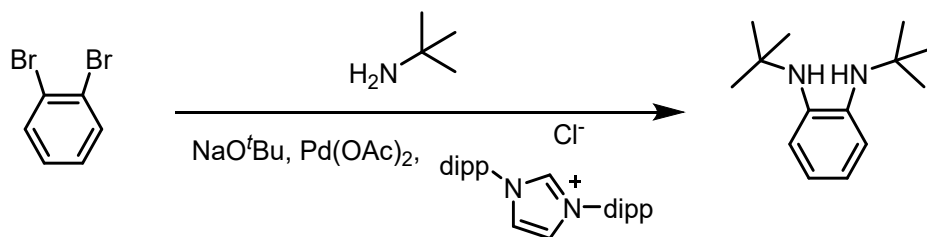
diazabutadiene (4.10 g, 10.9 mmol, 1.0 equiv.) were dissolved in anhydrous dichloromethane (20 mL) in a Schlenk tube under argon atmosphere and cooled to 0 °C using an ice bath. PBr₃ (1.04 mL, 10.9 mmol, 1.0 equiv.) was added to the solution over 5 minutes. After 10 minutes, the cooling bath was removed, and the reaction was stirred for 24 hour. The solvent was then removed in vacuo. The Schlenk tube was taken into a glovebox, and 40 mL anhydrous n-Hexane was added. The mixture was then stirred for 10 minutes, and any solid stuck to the side was scraped off with a spatula. The mixture was filtered, and the solid was washed with 2 x 20 mL of n-Hexane to yield compound **NHPBr-3** (4.42 g, 9.1 mmol, 83%) as an off-white powder. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (td, *J* = 7.6, 6.9, 1.2 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 4H), 6.60 (s, 2H), 3.37 (sept, *J* = 6.8 Hz, 4H), 1.38 (d, *J* = 6.8 Hz, 12H), 1.24 (d, *J* = 6.9 Hz, 12H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 147.2, 147.2, 132.9, 132.8, 129.5, 124.7, 123.6, 123.5, 28.9, 25.5, 24.5. ³¹P NMR (162 MHz, CDCl₃) δ 168.27.



NHPBr-3 (243.8 mg, 0.5 mmol, 1 equiv.) was placed in a Schlenk tube in the glovebox, and dry CH₃CN (2 mL) was added. Then AgOTf (128.5 mg, 0.5 mmol, 1 equiv.) was added. The reaction was stirred for 1 hour, then the precipitation was filtered out. The volatiles were removed in vacuo to yield compound **NHP⁺-3** as an off-white solid (199.7 g, 0.38 mmol, 76% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.59 (s, 2H), 7.62 (t, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 4H), 2.46 (hept, *J* = 6.8 Hz, 4H), 1.34 (d, *J* = 6.7 Hz, 12H), 1.25 (d, *J* = 6.9 Hz, 12H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 144.83, 144.79, 140.76, 140.74, 132.25, 129.81, 129.74, 124.95, 29.14, 25.54, 25.52, 23.78. ³¹P NMR (162 MHz, CDCl₃) δ 204.95. ¹⁹F NMR (376 MHz, CDCl₃) δ -78.41.

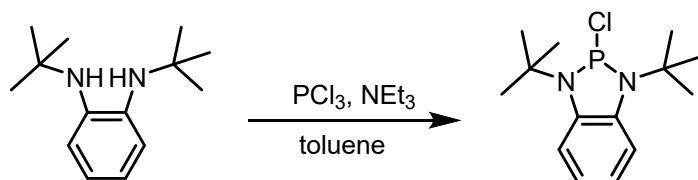


NHPCl-4 was prepared according to a modified literature.⁴



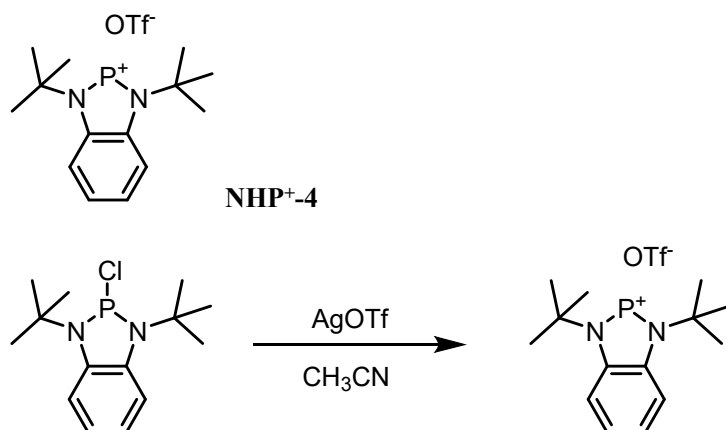
Step 1:

Sodium *tert*-butoxide (38 mg, 0.4 mmol, 0.08 equiv.), palladium(II) acetate (45 mg, 0.2 mmol, 0.04 equiv.), and 1*H*-Imidazolium, 1,3-bis[2,6-bis(1-methylethyl)phenyl]-, chloride (1:1) (170 mg, 0.4 mmol, 0.08 equiv.) were placed in a 250 mL pressure-resistant reaction flask. Then, 20 mL of toluene was added, and the mixture was heated to 135 °C and reacted for 15 minutes. After cooling to room temperature, sodium *tert*-butoxide (1.92 g, 20 mmol, 4.0 equiv.), *tert*-butylamine (1.83 g, 25 mmol, 5.0 equiv.), and 1,2-dibromobenzene (1.18 g, 5.0 mmol, 1.0 equiv.) were sequentially added, followed by the addition of 20 mL of anhydrous toluene. The reaction mixture was then purged with argon for 10 minutes, sealed, and heated at 135 °C for 20 hours. Upon cooling, the mixture was filtered with the aid of diatomaceous earth, washed with dichloromethane, and the organic phase was concentrated under reduced pressure. Column chromatography using a petroleum ether (PE) to ethyl acetate (EA) ratio of 8:1 yielded *N*¹,*N*²-di-*tert*-butylbenzene-1,2-diamine. ¹H NMR (400 MHz, CDCl₃) δ 6.92 (dd, *J* = 5.9, 3.5 Hz, 2H), 6.79 (dp, *J* = 7.3, 3.7 Hz, 2H), 3.70 (s, br., 2H), 1.31 (s, 18H).

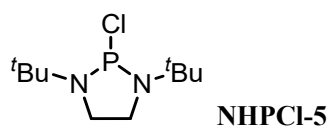


Step 2:

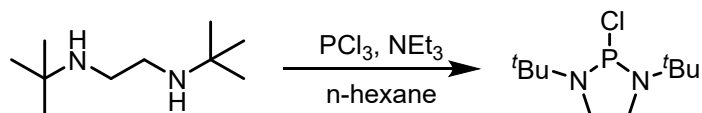
3.64 mL (2.63 g, 26.0 mmol, 2.6 equiv.) NEt₃ was treated dropwise with a solution of 2.20 g (10.0 mmol, 1.0 equiv.) *N*¹,*N*²-di-*tert*-butylbenzene-1,2-diamine and 1.06 mL (1.66 g, 12.0 mmol, 1.2 equiv.) of phosphorus trichloride in 60 mL of ultra-dry toluene under argon atmosphere and cooled to 0 °C using an ice bath. After 10 minutes, the cooling bath was removed. After stirring overnight, the reaction mixture was filtered under argon atmosphere. Toluene was removed from the filtrate in vacuum to yield compound **NHPCI-4** (2.65 g, 9.3 mmol, 93%) as a pale-yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.44 (dd, *J* = 6.4, 3.5 Hz, 2H), 7.08 (dd, *J* = 6.2, 3.3 Hz, 2H), 1.85 (d, *J* = 3.0 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 136.97, 136.86, 120.46, 115.16, 115.15, 56.79, 56.69, 29.43, 29.30. ³¹P NMR (162 MHz, CDCl₃) δ 153.27.



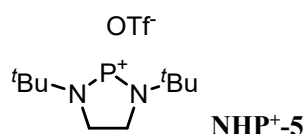
NHPCI-4 (284.7 mg, 1.0 mmol, 1 equiv.) was placed in a Schlenk tube in the glovebox, and dry CH_3CN (5 mL) was added. Then AgOTf (257.0 mg, 1.0 mmol, 1 equiv.) was added. The reaction was stirred for 1 hour, then the precipitation was filtered out. The volatiles were removed in vacuo to yield compound **NHP⁺-4** as a yellow solid (325.6 mg, 0.82 mmol, 82% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.95 (dt, $J = 7.1, 3.6$ Hz, 1H), 7.57 (dt, $J = 6.6, 3.6$ Hz, 1H), 2.03 (d, $J = 2.8$ Hz, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 138.64, 138.57, 125.44, 125.42, 117.09, 62.49, 62.39, 30.37, 30.25. ^{31}P NMR (162 MHz, CDCl_3) δ 216.26. ^{19}F NMR (376 MHz, CDCl_3) δ -78.41.

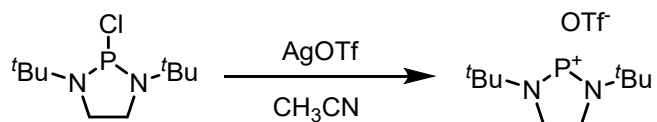


NHPCI-5 was prepared according to a modified literature.⁵

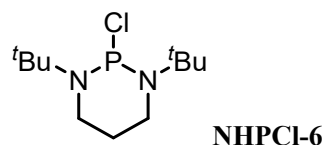


2.10 mL (3.30 g, 24.0 mmol, 1.2 equiv.) of phosphorus trichloride was treated dropwise with a solution of 4.31 mL (3.45 g (20.0 mmol, 1.0 equiv.) $(\text{CH}_2)_2(\text{NHtBu})_2$ and 7.23 mL (5.26 g, 52.0 mmol, 2.6 equiv.) NEt_3 in 150 mL of ultra-dry hexane under stirring at 0 °C. After stirring overnight, the reaction mixture was filtered under argon atmosphere. Hexane was removed from the filtrate in vacuum to yield 4.9 g compound **NHPCI-5** as a white to pale yellow crystal (87%). ^1H NMR (400 MHz, CDCl_3) δ 3.39 (d, $J = 6.6$ Hz, 4H), 1.40 (d, $J = 2.0$ Hz, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 54.0, 53.8, 45.5, 45.4, 28.9, 28.8. ^{31}P NMR (162 MHz, CDCl_3) δ 170.25.

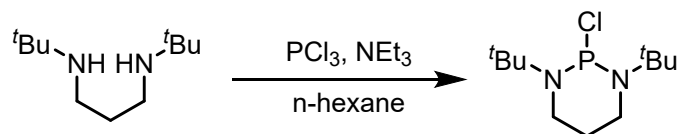




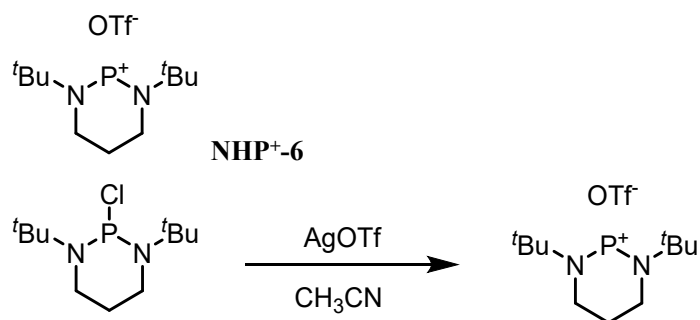
NHPCl-5 (236.7 mg, 1.0 mmol, 1 equiv.) was placed in a Schlenk tube in the glovebox, and dry CH_3CN (5 mL) was added. Then **AgOTf** (257.0 mg, 1.0 mmol, 1 equiv.) was added. The reaction was stirred for 1 hour, then the precipitation was filtered out. The volatiles were removed in vacuo to yield compound **NHP⁺-5** as a white solid (297.7 mg, 0.85 mmol, 85% yield). ^1H NMR (400 MHz, CDCl_3) δ 3.93 (d, J = 4.8 Hz, 4H), 1.52 (d, J = 2.0 Hz, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 57.66, 57.56, 48.36, 48.27, 29.23, 29.13. ^{31}P NMR (162 MHz, CDCl_3) δ 266.41. ^{19}F NMR (376 MHz, CDCl_3) δ -78.20.



NHPCl-6 was prepared according to a modified literature.⁵

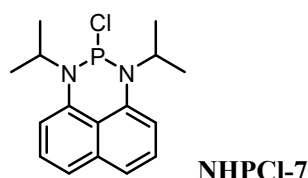


2.12 mL (3.33 g, 24.2 mmol, 1.2 equiv.) of phosphorus trichloride was treated dropwise with a solution of 3.74 g (20.1 mmol, 1 equiv.) $(\text{CH}_2)_3(\text{NH}^t\text{Bu})_2$ and 7.27 mL (5.29 g, 52.3 mmol, 2.6 equiv.) NEt_3 in 150 mL of ultra-dry hexane under stirring at 0 °C. After stirring overnight, the reaction mixture was filtered under argon atmosphere. Hexane was removed from the filtrate in vacuum to yield 5.5 g compound **NHPCl-6** white to pale yellow solid (91%). ^1H NMR (400 MHz, CDCl_3) δ 3.19 – 3.09 (m, 4H), 1.88 (p, J = 5.5 Hz, 2H), 1.37 (d, J = 3.5 Hz, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 57.8, 57.6, 40.3, 40.2, 28.4, 28.3, 25.9. ^{31}P NMR (162 MHz, CDCl_3) δ 165.59.

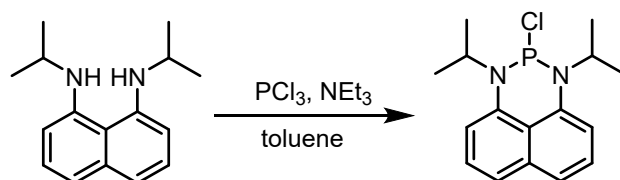


NHPCl-6 (250.8 mg, 1.0 mmol, 1 equiv.) was placed in a Schlenk tube in the glovebox, and dry CH_3CN (5 mL) was added. Then **AgOTf** (257.0 mg, 1.0 mmol, 1 equiv.) was added. The reaction

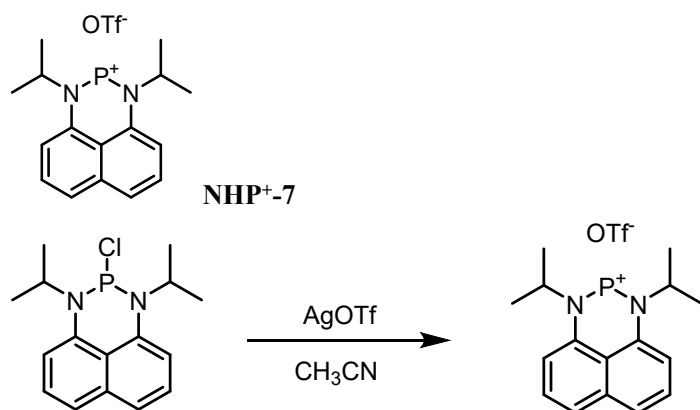
was stirred for 1 hour, then the precipitation was filtered out. The volatiles were removed in vacuo to yield compound **NHP⁺-6** as a white solid (305.5 mg, 0.84 mmol, 84% yield). ¹H NMR (400 MHz, CDCl₃) δ 3.52 (q, *J* = 5.8 Hz, 4H), 2.16 (ddt, *J* = 11.1, 7.7, 4.4 Hz, 2H), 1.56 (d, *J* = 3.0 Hz, 18H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 62.80, 62.62, 43.45, 43.37, 28.94, 28.79, 24.15. ³¹P NMR (162 MHz, CDCl₃) δ 256.76. ¹⁹F NMR (376 MHz, CDCl₃) δ -78.17.



NHPCl-7 was prepared according to a modified literature.⁶



1.06 mL (1.66 g, 12.0 mmol, 1.2 equiv.) of phosphorus trichloride was treated dropwise with a solution of 2.42 g (10.0 mmol, 1.0 equiv.) 1,8-Naphthalenediamine, *N*1, *N*8-bis(1-methylethyl)- and 3.36 mL (2.44 g, 24.0 mmol, 2.6 equiv.) NEt₃ in 60 mL of ultra-dry toluene under stirring at 0 °C. After stirring overnight, the reaction mixture was filtered under argon atmosphere. Hexane was removed from the filtrate in vacuum to yield 2.53 g orange solid **NHPCl-7** (82%). ¹H NMR (400 MHz, CDCl₃) δ 7.41 - 7.34 (m, 4H), 6.85 (p, *J* = 4.5 Hz, 2H), 4.33 (dp, *J* = 17.7, 6.7 Hz, 2H), 1.59 (dt, *J* = 6.8, 1.6 Hz, 12H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 138.1, 138.0, 135.8, 126.5, 120.9, 119.2, 108.2, 108.2, 50.6, 50.3, 23.5, 23.3, 21.0, 20.8. ³¹P NMR (162 MHz, CDCl₃) δ 103.20 (t, *J* = 18.2 Hz).



NHPCl-7 (306.8 mg, 1.0 mmol, 1 equiv.) was placed in a Schlenk tube in the glovebox, and dry CH₃CN (5 mL) was added. Then AgOTf (257.0 mg, 1.0 mmol, 1 equiv.) was added. The reaction

was stirred for 1 hour, then the precipitation was filtered out. The volatiles were removed in vacuo to yield compound **NHP⁺-7** as a brown solid (391.3 mg, 0.93 mmol, 93% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.39 (t, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 2H), 4.46 (dhept, *J* = 13.3, 6.6 Hz, 2H), 1.67 (dd, *J* = 6.7, 2.5 Hz, 12H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 135.79, 135.03, 134.97, 126.64, 122.94, 109.19, 109.16, 52.33, 52.06, 22.36, 22.18. ³¹P NMR (162 MHz, CDCl₃) δ 160.40. ¹⁹F NMR (376 MHz, CDCl₃) δ -77.57.

3. General Electrochemistry

Cyclic voltammogram (CV) of NHP⁺

Cyclic voltammetry (CV) experiments were performed using a CHI 660E electrochemical workstation. Cyclic voltammetry (CV) experiments were performed on three-electrode systems using glass carbon (GC, 3 mm²) as a working electrode, Pt wire as a counter electrode, and saturated calomel electrode (Ag/AgNO₃) as a reference electrode. As supporting electrolyte 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆, ≥99.0%, J&K Scientific) in ultra-dry MeCN was used. Before use, TBAPF₆ was recrystallized from ethanol three times and then dried under vacuum. The scan rate was 100 mV/s. The experiments were all under argon atmosphere.

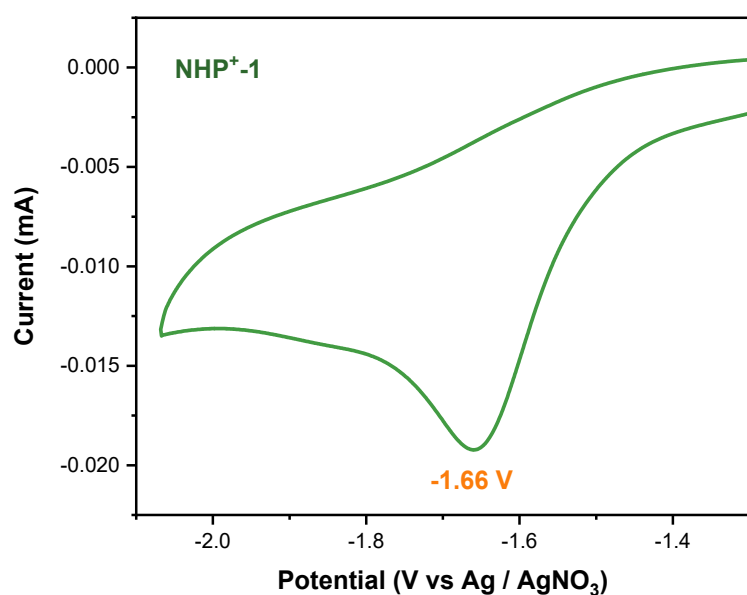


Figure S3-1. The CV of NHP⁺-1 in 0.1 M TBAPF₆

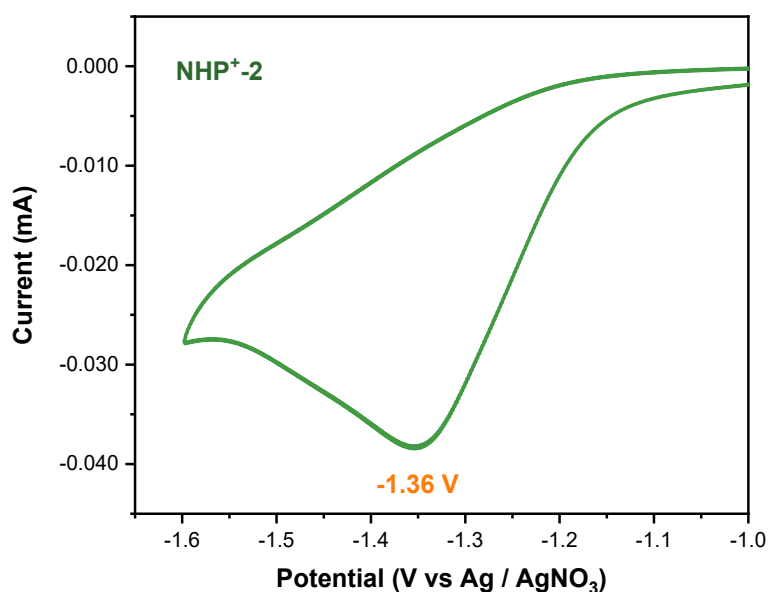


Figure S3-2. The CV of **NHP⁺-2** in 0.1 M TBAPF₆

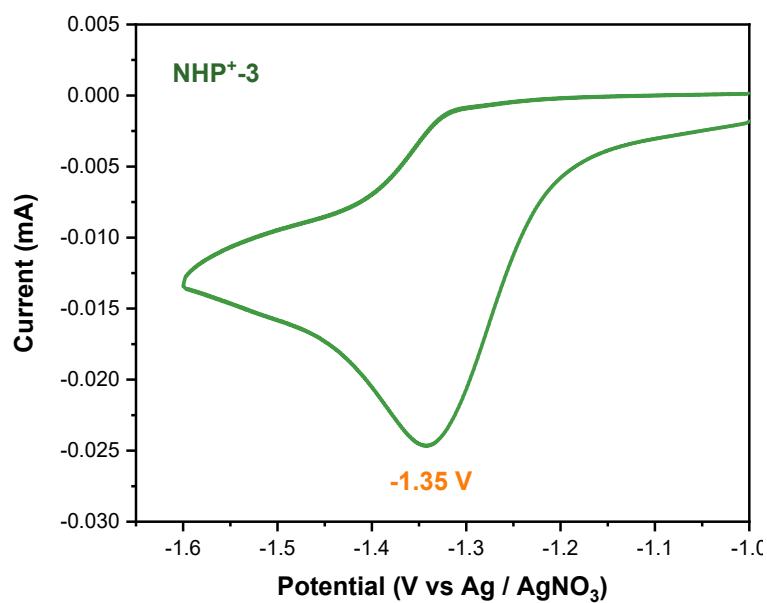


Figure S3-3. The CV of **NHP⁺-3** in 0.1 M TBAPF₆

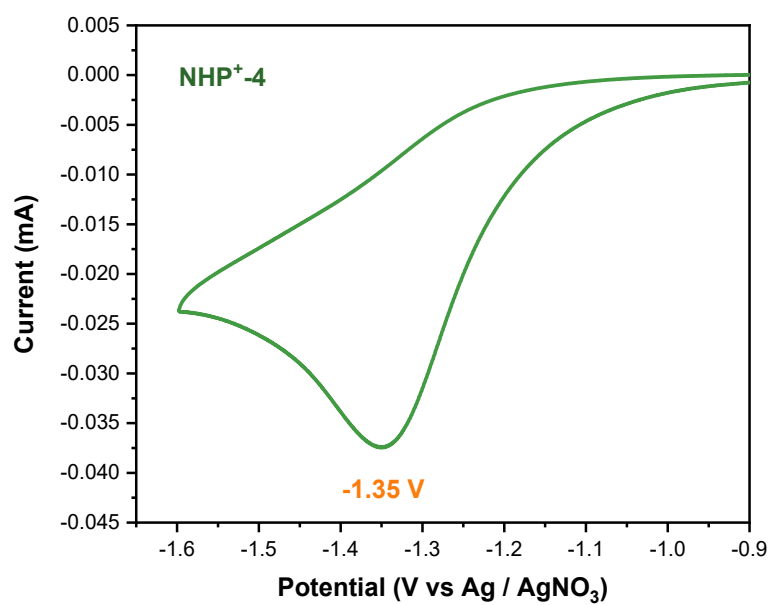


Figure S3-4. The CV of **NHP⁺-4** in 0.1 M TBAPF₆

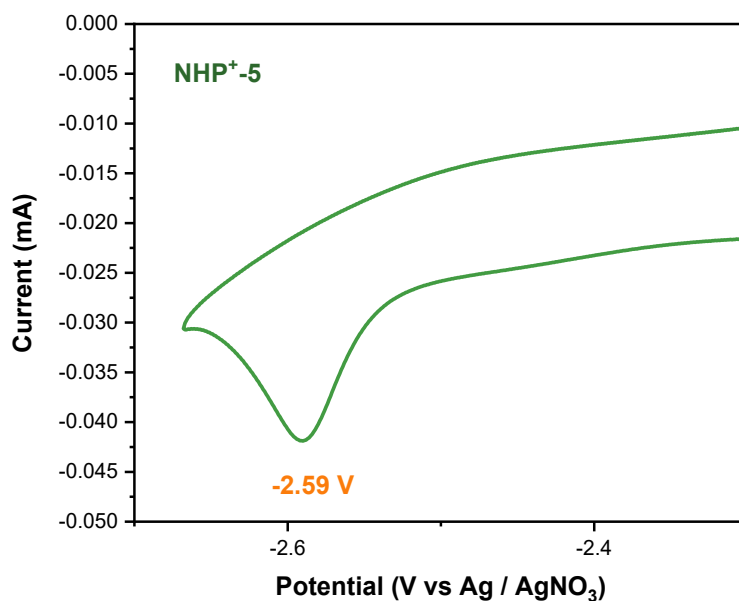
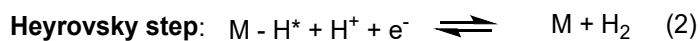
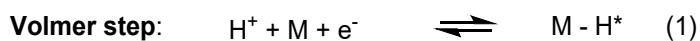


Figure S3-5. The CV of NHP⁺-5 in 0.1 M TBAPF₆

Mechanism of HER electrocatalysis in acidic condition⁷



There are two possible mechanisms: the Volmer-Heyrovsky and the Volmer-Tafel mechanism.

General Electrochemical Method for Hydrogen Evolution Reaction (HER)⁷

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) experiments were performed on three-electrode systems using carbon paper (CP, 1 cm²) as a working electrode, Pt plate as a counter electrode, and Ag/AgCl as a reference electrode. The experiment was performed in a cylindrical ø 4 cm x 4.8 cm glass cell (50 mL). Unless otherwise mentioned, the scan rate was kept constant at 10 mV/s for all the CV and LSV experiments.

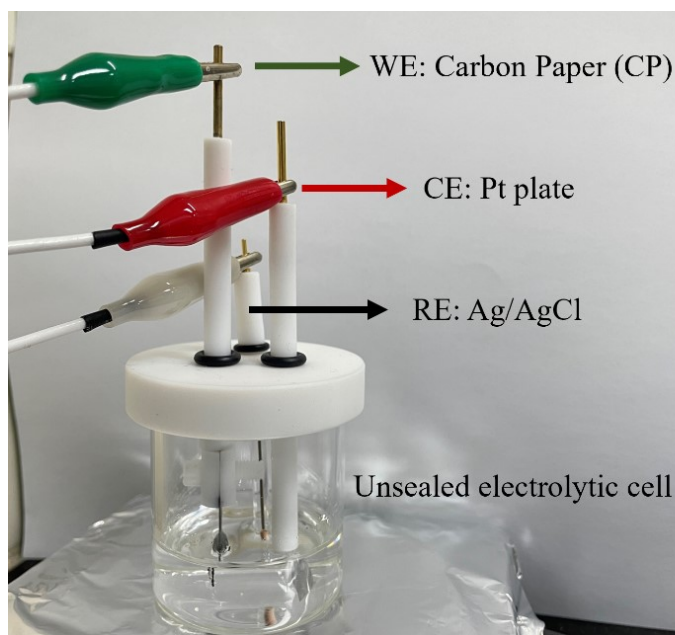


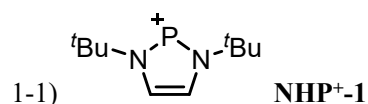
Figure S3-6. Unsealed hydrogen gas collection device for CV tests.

As supporting electrolyte 0.5 M H_2SO_4 was obtained by diluting concentrated sulfuric acid. To prepare the working electrode, 0.02 mmol catalyst and 20 μL Nafion (D520, 5%) were dispersed in 0.3 mL MeCN/EtOH, sonicate to obtain a homogeneous catalyst solution, and evenly load to 1 cm^2 clean carbon paper (the temperature should not be too high during this process). Using a platinum plate as the counter electrode and Ag/AgCl as the reference electrode. Activate 100 cycles of CV while stirring before conducting CV/LSV testing.

4. Computational Details

All of the calculations were performed using Gaussian 16 software.⁹ The M06 exchange correlation functional¹⁰ combined with the 6-31++G(d,p) basis set is utilized to optimize structures in acetonitrile. This level of theory describes the system accurately at a moderate computational cost because the M06 functional has been parameterized with experimental thermodynamic data for similar molecular systems.⁹ Previously, this theoretical methods have been used to study the thermodynamic and electrochemical properties of Diazaphospholenes.⁸ The NICS(1)_{av} were analyzed using the Multiwfn software.¹¹⁻¹³

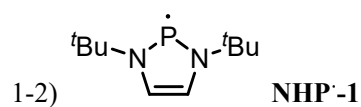
The Cartesian Coordinates for the key compounds (Bq means ghost atoms 1 Å above and below the NHP ring center) :



Charge = 1 Spin multiplicity = 1

P	-0.00000100	-0.99499000	-0.02064300
N	1.18522600	0.19522100	-0.01635400
N	-1.18522300	0.19522600	-0.01635200
C	0.68314900	1.46433400	-0.01448500
C	-0.68313900	1.46433800	-0.01447300
H	1.33341000	2.32815400	-0.01127400
H	-1.33339100	2.32816300	-0.01126500
C	2.66490800	-0.07382600	0.00419100
C	-2.66490700	-0.07382000	0.00419100
C	3.22553300	0.50803600	1.30232900
H	2.74694500	0.04058400	2.16831200
H	4.29995000	0.30868500	1.34450700
H	3.07567700	1.59012600	1.35374200
C	3.28360200	0.59112700	-1.22523800
H	4.35384200	0.36761700	-1.24455600
H	2.82739800	0.20280600	-2.14085600
H	3.16437500	1.67767200	-1.19940800
C	2.89641500	-1.58112100	-0.04108500
H	2.49226300	-2.02486400	-0.95735500
H	3.97406800	-1.76201900	-0.02876700

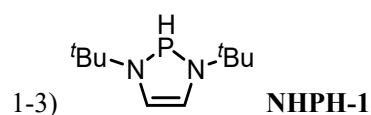
H	2.46404200	-2.08423700	0.83066300
C	-3.28361000	0.59116200	-1.22521400
H	-4.35384800	0.36764300	-1.24452900
H	-3.16439600	1.67770700	-1.19936000
H	-2.82740700	0.20286200	-2.14084200
C	-3.22553000	0.50799700	1.30235000
H	-2.74691700	0.04053500	2.16831500
H	-3.07570100	1.59008900	1.35379300
H	-4.29994100	0.30861500	1.34453700
C	-2.89641800	-1.58111300	-0.04113500
H	-3.97407100	-1.76201200	-0.02878700
H	-2.49229600	-2.02482200	-0.95743400
H	-2.46402000	-2.08426400	0.83058100
Bq	0.0000000000	0.1155511633	0.9827095867
Bq	-0.0000000000	0.1208376167	-1.0172834267



Charge = 0 Spin multiplicity = 2

P	-0.00003000	1.05430000	-0.18550000
N	-1.22359800	-0.19404500	-0.24228400
N	1.22358500	-0.19400200	-0.24227100
C	-0.67671700	-1.46497400	-0.15192600
C	0.67674600	-1.46494800	-0.15192600
H	-1.30898700	-2.34205500	-0.12002400
H	1.30905500	-2.34200500	-0.12003100
C	-2.65550900	0.05727800	0.04396300
C	2.65550500	0.05730200	0.04396200
C	-2.92116600	-0.17615600	1.53603400
H	-2.29583800	0.48838800	2.14242400
H	-3.97193000	0.02311300	1.77024600
H	-2.69698600	-1.21229600	1.81079100
C	-3.51620400	-0.88223200	-0.80598300
H	-4.57247600	-0.64242100	-0.65028800

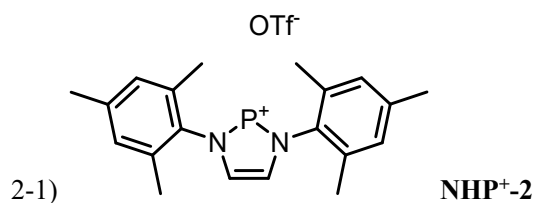
H	-3.28367000	-0.75862400	-1.86865100
H	-3.37107000	-1.93147000	-0.53414800
C	-2.98793400	1.50397300	-0.32547100
H	-2.77268500	1.69900900	-1.38115100
H	-4.05266900	1.68309300	-0.15103700
H	-2.42741700	2.21714200	0.28942800
C	3.51608100	-0.88263900	-0.80561800
H	4.57239100	-0.64300300	-0.64990500
H	3.37069100	-1.93176600	-0.53347100
H	3.28366200	-0.75930700	-1.86834300
C	2.92106000	-0.17569100	1.53611800
H	2.29579000	0.48913100	2.14226300
H	2.69673400	-1.21171400	1.81119900
H	3.97183900	0.02351500	1.77031000
C	2.98819600	1.50382600	-0.32593900
H	4.05295500	1.68282100	-0.15152600
H	2.77302600	1.69855400	-1.38169200
H	2.42778900	2.21729600	0.28870800
Bq	0.0000000000	-0.1181193132	-1.1948177800
Bq	0.0000000000	-0.0741428868	0.8046986800



Charge = 0 Spin multiplicity = 1

N	-1.22321100	-0.20811700	0.31053800
N	1.22321100	-0.20812000	0.31053800
C	-0.67198400	-1.47201500	-0.00095200
C	0.67198100	-1.47201700	-0.00095300
H	-1.30810000	-2.34082800	-0.10834600
H	1.30809500	-2.34083000	-0.10834800
C	-2.65431300	0.05731300	0.02627500
C	2.65431300	0.05731100	0.02627500
C	-3.50350400	-0.89778600	0.86997300
H	-3.28748200	-0.76003100	1.93446800

H	-4.56530500	-0.69421800	0.69910100
H	-3.31905400	-1.94423200	0.60944600
C	-2.95965700	-0.14114300	-1.46408600
H	-4.01183900	0.08459900	-1.66570800
H	-2.34235100	0.52055900	-2.08124100
H	-2.76720400	-1.17519700	-1.76892400
C	-2.97737900	1.49669200	0.43127600
H	-2.46683800	2.22429700	-0.21032200
H	-4.05334200	1.66741300	0.33237300
H	-2.68916100	1.68365400	1.47108900
C	2.95967200	-0.14120700	-1.46407400
H	4.01185500	0.08453500	-1.66569800
H	2.76723100	-1.17527700	-1.76886800
H	2.34236700	0.52046100	-2.08126500
C	3.50351000	-0.89773800	0.87002400
H	3.28747200	-0.75994100	1.93451100
H	3.31908400	-1.94419800	0.60953900
H	4.56530900	-0.69415700	0.69915700
C	2.97735700	1.49671200	0.43121400
H	4.05331900	1.66744300	0.33231300
H	2.46681200	2.22428200	-0.21042100
H	2.68912700	1.68371700	1.47101600
P	0.00000100	0.99460200	0.02144000
H	0.00000000	0.94583700	-1.44282700
Bq	-0.0000000000	-0.0777656143	-0.8863872148
Bq	0.0000000000	-0.1720277057	1.1113902148

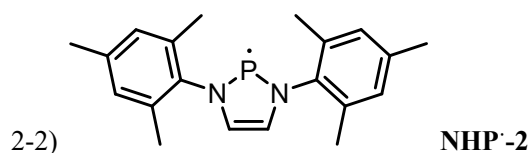


Charge = 1 Spin multiplicity = 1

N	-1.17489200	0.01802600	0.40790600
C	-0.68298500	0.10642900	1.68320200

C	0.68288800	0.10641100	1.68327500
N	1.17491100	0.01799200	0.40804700
P	0.00008400	-0.06354400	-0.78496400
C	-2.59373200	0.00227400	0.12083400
C	2.59374800	0.00226200	0.12096100
C	-3.23775200	-1.23342000	0.01153000
C	-4.60998800	-1.21725400	-0.25706000
C	-5.31385400	-0.02135700	-0.41215100
C	-4.62226700	1.18981500	-0.29132600
C	-3.25442100	1.22976300	-0.02321500
C	3.23776100	-1.23342600	0.01157800
C	4.60998700	-1.21724700	-0.25706400
C	5.31383800	-0.02134300	-0.41216300
C	4.62224500	1.18982700	-0.29129100
C	3.25441700	1.22976400	-0.02310700
C	-2.51675300	2.53518900	0.11031400
C	2.48751700	-2.52885500	0.17381100
C	-2.48752100	-2.52883100	0.17385500
C	2.51674000	2.53517800	0.11051800
C	-6.79244300	-0.02198800	-0.69931600
C	6.79240300	-0.02196600	-0.69944100
H	-1.35678000	0.16279100	2.52765100
H	1.35658500	0.16262400	2.52781400
H	-5.13667400	-2.16455200	-0.34430400
H	-5.16104200	2.12774900	-0.40784900
H	5.13667300	-2.16454200	-0.34434200
H	5.16101600	2.12776100	-0.40783600
H	-3.19932900	3.37198000	-0.04855500
H	-2.07079900	2.63925500	1.10507000
H	-1.70519000	2.61034700	-0.62168100
H	1.78801400	-2.68737000	-0.65465600
H	3.18459900	-3.36864700	0.19234100
H	1.90564600	-2.54010200	1.10108200
H	-1.90620000	-2.54030400	1.10146800

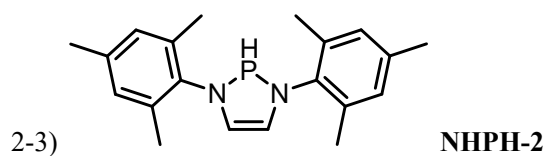
H	-3.18454600	-3.36868300	0.19173900
H	-1.78746200	-2.68707500	-0.65419200
H	3.19916600	3.37197700	-0.04894900
H	1.70471900	2.61011500	-0.62099300
H	2.07138600	2.63946000	1.10552200
H	-7.17686800	-1.04071300	-0.78681100
H	-7.34188200	0.48652400	0.09947500
H	-7.00655300	0.50960400	-1.63191100
H	7.17691500	-1.04069700	-0.78649100
H	7.00637500	0.50919500	-1.63231600
H	7.34186600	0.48698700	0.09905100
Bq	0.0000000000	1.0105030492	0.2630704264
Bq	0.0000000000	-0.9847660492	0.4005521536



Charge = 0 Spin multiplicity = 2

N	1.20720400	0.03153800	0.42281400
C	0.67622800	-0.34095800	1.65168600
C	-0.67622300	-0.34091400	1.65170200
N	-1.20720400	0.03162200	0.42284300
P	-0.00000200	0.32042200	-0.80086300
C	2.60645500	0.01871400	0.14416300
C	-2.60645100	0.01876500	0.14418600
C	3.30026500	1.23332700	0.04882600
C	4.66984700	1.19313200	-0.23596200
C	5.34644800	-0.01362400	-0.42198500
C	4.62371600	-1.20776800	-0.31783000
C	3.25657600	-1.21494500	-0.03938200
C	-3.30024400	1.23337000	0.04861600
C	-4.66982500	1.19314300	-0.23617200
C	-5.34644600	-0.01363600	-0.42197000
C	-4.62373300	-1.20777000	-0.31758400

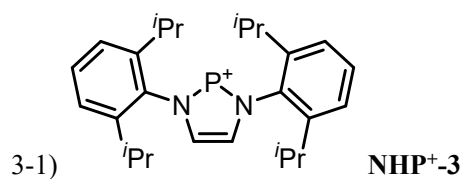
C	-3.25659300	-1.21491900	-0.03913700
C	2.49112300	-2.50787500	0.06518000
C	-2.59426900	2.54798900	0.25507000
C	2.59429700	2.54791000	0.25552300
C	-2.49117100	-2.50784900	0.06564900
C	6.82256800	-0.04191800	-0.72579600
C	-6.82255500	-0.04196200	-0.72583100
H	1.33472700	-0.56550700	2.48075000
H	-1.33471600	-0.56542600	2.48077900
H	5.21893500	2.12980800	-0.30683500
H	5.13619400	-2.15700000	-0.46412500
H	-5.21889700	2.12981600	-0.30722000
H	-5.13622600	-2.15702300	-0.46370300
H	3.09184300	-3.33911700	-0.31093600
H	2.22169700	-2.72663000	1.10450800
H	1.55827100	-2.46022500	-0.50666400
H	-1.96757200	2.80059200	-0.60757700
H	-3.31984600	3.35281300	0.39395500
H	-1.93700800	2.51039700	1.12938400
H	1.93717700	2.51021500	1.12994000
H	3.31987600	3.35273600	0.39437700
H	1.96745200	2.80058000	-0.60699600
H	-3.09184100	-3.33911100	-0.31050400
H	-1.55822500	-2.46025300	-0.50604500
H	-2.22192300	-2.72653500	1.10503800
H	7.23074500	0.96955100	-0.79193300
H	7.37098800	-0.58270000	0.05249900
H	7.01585900	-0.55269900	-1.67472500
H	-7.23081400	0.96949300	-0.79168200
H	-7.01576700	-0.55246400	-1.67493000
H	-7.37095800	-0.58303400	0.05227200
Bq	0.0000000000	-0.9328087321	0.0572369331
Bq	0.0000000000	0.9958554521	0.5866275869



Charge = 0 Spin multiplicity = 1

N	1.20828000	-0.38144300	0.26423200
C	0.67306300	-1.08937800	1.36211900
C	-0.67270100	-1.08835400	1.36275700
N	-1.20794600	-0.37954200	0.26547000
C	2.59216100	-0.09921100	0.09969500
C	-2.59200300	-0.09837400	0.10046100
C	3.02467200	1.23695300	0.12635400
C	4.38799900	1.50302100	-0.04123500
C	5.32050300	0.47924200	-0.21803300
C	4.86052900	-0.84205800	-0.23616100
C	3.50737000	-1.15176400	-0.09046600
C	-3.02521300	1.23760700	0.12560600
C	-4.38862900	1.50282800	-0.04253700
C	-5.32060200	0.47841500	-0.21846900
C	-4.85994700	-0.84265600	-0.23517200
C	-3.50666400	-1.15156600	-0.08890000
C	3.03543000	-2.58197300	-0.14234800
C	-2.04411100	2.36077800	0.33651400
C	2.04294300	2.35939400	0.33823700
C	-3.03419100	-2.58166200	-0.13940600
C	6.78820300	0.77889700	-0.38847800
C	-6.78840900	0.77716700	-0.38956800
H	1.32966300	-1.48764700	2.12475200
H	-1.32915700	-1.48578500	2.12595000
H	4.72747100	2.53663000	-0.02029500
H	5.57225700	-1.65270500	-0.38396200
H	-4.72859900	2.53629600	-0.02276400
H	-5.57122900	-1.65380700	-0.38236200
H	3.80117300	-3.22044800	-0.58952400
H	2.81942100	-2.96864900	0.86005000

H	2.11534100	-2.67182900	-0.72760200
H	-1.41208500	2.51101900	-0.54646100
H	-2.57109400	3.29691200	0.53612200
H	-1.37695300	2.14387700	1.17688900
H	1.37491500	2.14070700	1.17746100
H	2.56937200	3.29534900	0.54014200
H	1.41187400	2.51104300	-0.54518700
H	-3.79936400	-3.22064800	-0.58683200
H	-2.11358200	-2.67166600	-0.72380300
H	-2.81897900	-2.96762600	0.86343600
H	6.97726100	1.85477200	-0.35532600
H	7.37921500	0.30312800	0.40100600
H	7.15700500	0.39642800	-1.34596400
H	-6.97802900	1.85297300	-0.35739100
H	-7.15675400	0.39369300	-1.34682800
H	-7.37939600	0.30177300	0.40016100
P	-0.00019100	-0.15713600	-0.94885500
H	-0.00163600	-1.51369100	-1.47257400
Bq	0.0006600024	0.4135183880	0.5317433119
Bq	-0.0006600024	-1.4174946880	-0.2728617919

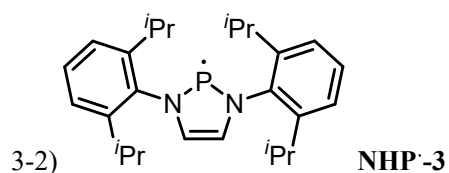


Charge = 1 Spin multiplicity = 1

N	1.17266600	0.00013400	-0.42316100
C	0.68364800	0.00012500	-1.70078600
C	-0.68364000	0.00008000	-1.70081000
N	-1.17269100	0.00009900	-0.42319600
P	-0.00002600	0.00007500	0.77490000
C	2.59161500	0.00010200	-0.12696400
C	-2.59157700	-0.00004100	-0.12699200
C	3.23731100	-1.23822700	0.01113100

C	4.59896000	-1.20890600	0.32760900
C	5.27087300	0.00001900	0.48737600
C	4.59894200	1.20898100	0.32802900
C	3.23727700	1.23838800	0.01157200
C	-3.23709800	-1.23842000	0.01162100
C	-4.59872800	-1.20917500	0.32815000
C	-5.27081600	-0.00028600	0.48750100
C	-4.59907500	1.20871000	0.32766800
C	-3.23743200	1.23818600	0.01111800
C	2.50314500	-2.56129600	-0.13145600
C	3.25992900	-3.54780600	-1.02648100
C	2.24124400	-3.17325300	1.25129400
C	2.50307400	2.56150400	-0.13047600
C	2.24149400	3.17308100	1.25250900
C	3.25962300	3.54824100	-1.02544600
C	-2.50340600	2.56134100	-0.13148700
C	-3.26025400	3.54773400	-1.02657400
C	-2.24161300	3.17333300	1.25126500
C	-2.50277700	-2.56146600	-0.13050000
C	-2.24137700	-3.17326400	1.25241500
C	-3.25919400	-3.54806700	-1.02573700
H	1.35819200	0.00021100	-2.54669000
H	-1.35820600	0.00003200	-2.54669300
H	5.13745100	-2.14332100	0.45502400
H	6.32776200	-0.00002300	0.73668500
H	5.13741500	2.14336200	0.45575700
H	-5.13707900	-2.14362100	0.45594100
H	-6.32769300	-0.00040400	0.73686700
H	-5.13765700	2.14307100	0.45509200
H	1.53403300	-2.37057100	-0.60401200
H	2.64990500	-4.44273500	-1.18371700
H	3.48334200	-3.10856800	-2.00377600
H	4.20202100	-3.86472800	-0.56783500
H	1.68115500	-4.10870700	1.15084700

H	1.66383400	-2.49372400	1.88791800
H	3.18772300	-3.39218200	1.75834100
H	1.53383600	2.37091400	-0.60282300
H	1.68147100	4.10861600	1.15243900
H	1.66413100	2.49341700	1.88902800
H	3.18807900	3.39178000	1.75945000
H	2.64954700	4.44319600	-1.18234100
H	3.48282500	3.10923300	-2.00289400
H	4.20180800	3.86508300	-0.56693600
H	-1.53426600	2.37069900	-0.60401600
H	-2.65031000	4.44270900	-1.18386300
H	-3.48363300	3.10841800	-2.00384500
H	-4.20237100	3.86461000	-0.56795000
H	-1.68180700	4.10895800	1.15081200
H	-1.66395600	2.49396100	1.88783100
H	-3.18811700	3.39197900	1.75838100
H	-1.53347800	-2.37076100	-0.60267500
H	-1.68131000	-4.10876300	1.15226200
H	-1.66412100	-2.49368500	1.88912400
H	-3.18801900	-3.39208000	1.75919900
H	-2.64919600	-4.44309300	-1.18252500
H	-3.48207400	-3.10895700	-2.00321300
H	-4.20155200	-3.86478500	-0.56749300
Bq	0.0000000000	1.0000000000	-0.3458137500
Bq	0.0000000000	-1.0000000000	-0.3458137500

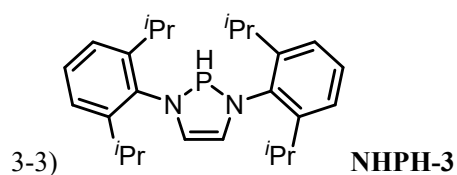


Charge = 0 Spin multiplicity = 2

N	-1.20152000	0.00008700	0.36381900
C	-0.67720800	0.00006200	1.64798200
C	0.67718600	0.00009100	1.64799000

N	1.20151300	0.00015800	0.36383400
P	0.00000500	0.00016800	-0.89289700
C	-2.60119300	0.00004200	0.08147000
C	2.60118900	0.00000700	0.08149900
C	-3.26674700	-1.23153200	-0.06446900
C	-4.63202200	-1.20726800	-0.36797800
C	-5.30967100	-0.00004100	-0.52023700
C	-4.63212400	1.20722700	-0.36784900
C	-3.26685100	1.23157400	-0.06434100
C	3.26666800	-1.23162400	-0.06429900
C	4.63194700	-1.20748000	-0.36779300
C	5.30967200	-0.00031200	-0.52018500
C	4.63219700	1.20701500	-0.36794300
C	3.26692400	1.23148300	-0.06444500
C	-2.54393400	-2.55854800	0.09614200
C	-3.17194800	-3.40374200	1.21039200
C	-2.51798500	-3.33273100	-1.22720100
C	-2.54414700	2.55863300	0.09640300
C	-2.51830000	3.33297300	-1.22685100
C	-3.17220500	3.40364000	1.21077100
C	2.54430700	2.55860600	0.09615500
C	3.17247300	3.40373800	1.21036600
C	2.51843700	3.33275800	-1.22720900
C	2.54377100	-2.55857600	0.09645600
C	2.51792300	-3.33299400	-1.22675100
C	3.17162900	-3.40359500	1.21092800
H	-1.33920400	0.00001700	2.50448600
H	1.33917200	0.00006500	2.50450200
H	-5.16914800	-2.14492600	-0.48802100
H	-6.36964100	-0.00007300	-0.75760800
H	-5.16933000	2.14485200	-0.48779100
H	5.16901600	-2.14518700	-0.48771800
H	6.36964500	-0.00043600	-0.75754500
H	5.16946400	2.14459300	-0.48798800

H	-1.50838700	-2.34727600	0.38000600
H	-2.59941600	-4.32657400	1.35023500
H	-3.18286400	-2.86009900	2.16092800
H	-4.20254200	-3.68162100	0.96361000
H	-1.95370000	-4.26409200	-1.10964500
H	-2.04488300	-2.74380300	-2.02041400
H	-3.53332100	-3.58946600	-1.55029100
H	-1.50857400	2.34741800	0.38021300
H	-1.95410000	4.26437300	-1.10919900
H	-2.04516100	2.74418200	-2.02014200
H	-3.53366700	3.58965200	-1.54989000
H	-2.59975700	4.32651100	1.35070100
H	-3.18303700	2.85988700	2.16124400
H	-4.20283400	3.68144800	0.96405400
H	1.50873800	2.34748900	0.38005200
H	2.60007300	4.32665300	1.35020400
H	3.18334100	2.86011600	2.16091400
H	4.20309800	3.68147000	0.96354700
H	1.95430400	4.26421100	-1.10966000
H	2.04521900	2.74388300	-2.02039100
H	3.53380400	3.58932300	-1.55033600
H	1.50820200	-2.34720600	0.38016900
H	1.95357200	-4.26430100	-1.10908700
H	2.04493700	-2.74418100	-2.02011800
H	3.53327600	-3.58984800	-1.54969100
H	2.59907000	-4.32639700	1.35085400
H	3.18243200	-2.85979200	2.16137300
H	4.20225200	-3.68152200	0.96431900
Bq	0.0000000000	-1.0000000000	0.2665348600
Bq	0.0000000000	1.0000000000	0.2665348600

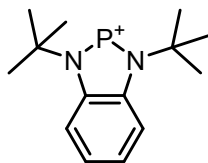


Charge = 0 Spin multiplicity = 1

N	1.27686800	-0.59371000	0.30555600
C	0.68764400	-0.64751300	1.59690300
C	-0.64393000	-0.45858700	1.57200400
N	-1.13813600	-0.19987600	0.27949300
C	2.57974500	-0.03240900	0.12128500
C	-2.52590500	-0.05842200	-0.02555800
C	2.77888300	1.35629500	0.22296900
C	4.07825200	1.85239800	0.05703000
C	5.14259500	0.99656100	-0.20612800
C	4.92740100	-0.37754900	-0.30904500
C	3.64806800	-0.91451200	-0.14452100
C	-2.99453300	1.20407800	-0.45429900
C	-4.34885000	1.33607200	-0.76768700
C	-5.22154700	0.25391100	-0.64807100
C	-4.74523200	-0.98035400	-0.22287800
C	-3.39005200	-1.16361700	0.08217900
C	1.63401400	2.32175500	0.48074800
C	1.83521600	3.08252900	1.79669700
C	1.46808200	3.29485700	-0.69337100
C	3.38613900	-2.40349200	-0.29461200
C	3.00114400	-2.72014000	-1.74715900
C	4.56270500	-3.27855700	0.14168800
C	-2.89878900	-2.53977900	0.50049900
C	-3.57784100	-3.00496400	1.79393300
C	-3.10766000	-3.56196000	-0.62331800
C	-2.05095700	2.39506200	-0.49797500
C	-2.50650400	3.51168800	-1.43753700
C	-1.85672100	2.94502600	0.92308200
H	1.31552000	-0.78961900	2.46754700
H	-1.31984000	-0.44551800	2.41894900
H	4.25440300	2.92281300	0.13113600
H	6.14374600	1.39858200	-0.33331100
H	5.76699800	-1.03425100	-0.51670700

H	-4.73473400	2.29411500	-1.10173000
H	-6.27313000	0.37702200	-0.89098500
H	-5.42836000	-1.82213400	-0.13990500
H	0.70873400	1.74279600	0.56742300
H	0.98520000	3.74653800	1.98584500
H	1.92523100	2.39217000	2.64222900
H	2.74127800	3.69788800	1.76024100
H	0.61281800	3.95737000	-0.52041800
H	1.30016000	2.75680700	-1.63307200
H	2.35919000	3.92132400	-0.81336100
H	2.52648300	-2.64637100	0.33950400
H	2.74457800	-3.77921600	-1.85658100
H	2.14340400	-2.12481800	-2.08101400
H	3.83952500	-2.49763900	-2.41783500
H	4.26091200	-4.33068900	0.13186800
H	4.89620300	-3.02895000	1.15422700
H	5.41727300	-3.17662300	-0.53563900
H	-1.82449700	-2.47759000	0.69208100
H	-3.17634900	-3.97538000	2.10415400
H	-3.41360600	-2.29054700	2.60752400
H	-4.65852200	-3.11718300	1.65254900
H	-2.69198900	-4.53263100	-0.33265400
H	-2.61412700	-3.24074600	-1.54681800
H	-4.17344500	-3.70090500	-0.83684600
H	-1.07817300	2.03767300	-0.85454000
H	-1.71773000	4.26721600	-1.51378200
H	-2.71476600	3.13491200	-2.44430600
H	-3.40636200	4.01374000	-1.06584400
H	-1.17335400	3.80130700	0.91471100
H	-1.44681600	2.18446200	1.59629300
H	-2.81774500	3.28190100	1.32989800
P	0.05107700	-0.64894000	-0.90559700
H	-0.18359100	-2.07887400	-0.87338500
Bq	-0.1075315014	-1.5239671177	0.2290410385

Bq 0.2052337614 0.4513274977 0.2093161015

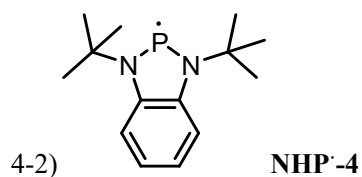


4-1) **NHP⁺-4**

Charge = 1 Spin multiplicity = 1

C	0.70731800	0.90980100	0.00004300
C	-0.70731100	0.90982600	0.00016800
C	-1.41794700	2.12562400	0.00020100
C	-0.70355900	3.30720300	-0.00001000
C	0.70367900	3.30717400	-0.00025700
C	1.41800800	2.12556100	-0.00022000
H	-2.49783000	2.15866800	0.00047700
H	-1.24138200	4.24939300	-0.00001000
H	1.24155000	4.24933700	-0.00048000
H	2.49788800	2.15853300	-0.00032600
C	-2.66201100	-0.77384600	0.00004500
C	2.66198200	-0.77389200	0.00009800
P	-0.00002700	-1.54145500	-0.00045900
N	-1.20190100	-0.38978400	-0.00007600
N	1.20187600	-0.38981900	-0.00018500
C	3.31349200	-0.24282100	1.27917600
H	4.35268600	-0.58238600	1.30340900
H	3.31416100	0.84572300	1.34118500
H	2.79646700	-0.64453700	2.15599300
C	3.31392900	-0.24328100	-1.27893000
H	3.31470000	0.84524400	-1.34128400
H	4.35314800	-0.58283800	-1.30261300
H	2.79725100	-0.64535500	-2.15577700
C	2.77032900	-2.30050800	0.00037200
H	2.32212300	-2.74505500	0.89553100
H	2.32209300	-2.74541100	-0.89458700
H	3.83240500	-2.55712300	0.00045500

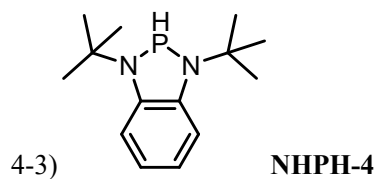
C	-3.31351400	-0.24323300	1.27930700
H	-3.31375700	0.84527600	1.34192700
H	-4.35284100	-0.58241600	1.30321900
H	-2.79675500	-0.64562000	2.15597000
C	-3.31392900	-0.24279000	-1.27881200
H	-4.35314500	-0.58235400	-1.30264600
H	-3.31470500	0.84575200	-1.34080200
H	-2.79721500	-0.64455400	-2.15577800
C	-2.77037600	-2.30045300	-0.00023500
H	-2.32224800	-2.74502300	-0.89541300
H	-2.32208600	-2.74534800	0.89470900
H	-3.83246100	-2.55704100	-0.00012000
Bq	0.0000000000	-0.4432822500	-1.0000000000
Bq	0.0000000000	-0.4432822500	1.0000000000



Charge = 0 Spin multiplicity = 2

C	0.71285200	0.88856300	-0.00001400
C	-0.71287400	0.88860300	0.00000300
C	-1.40548500	2.10636800	0.00002900
C	-0.69565900	3.31029300	0.00002700
C	0.69586700	3.31025000	0.00000100
C	1.40556800	2.10626200	-0.00001800
H	-2.48567400	2.13910800	0.00005400
H	-1.24468600	4.24681900	0.00004600
H	1.24496700	4.24673400	-0.00000200
H	2.48575400	2.13878800	-0.00003000
C	-2.67413600	-0.74468500	0.00000900
C	2.67408300	-0.74478600	-0.00001900
P	-0.00005800	-1.63264600	0.00000400
N	-1.22534000	-0.40118000	-0.00001200

N	1.22528500	-0.40122900	-0.00004000
C	3.33972500	-0.21255900	1.27612500
H	4.38908500	-0.52320300	1.29143100
H	3.31121600	0.87502000	1.35490000
H	2.84162900	-0.63493400	2.15518300
C	3.33972000	-0.21268000	-1.27621900
H	3.31118100	0.87489200	-1.35510700
H	4.38909000	-0.52329500	-1.29148400
H	2.84164300	-0.63516200	-2.15523300
C	2.83145400	-2.27057000	0.00005700
H	2.38898300	-2.72443800	0.89286900
H	2.38897700	-2.72451900	-0.89271000
H	3.89924600	-2.50547400	0.00006500
C	-3.33969100	-0.21257000	1.27624900
H	-3.31054000	0.87495400	1.35549400
H	-4.38922900	-0.52263200	1.29132300
H	-2.84192200	-0.63557600	2.15518800
C	-3.33974300	-0.21256600	-1.27620300
H	-4.38924000	-0.52276500	-1.29130100
H	-3.31074300	0.87496500	-1.35538600
H	-2.84191700	-0.63545600	-2.15516600
C	-2.83153000	-2.27045600	0.00000000
H	-2.38910100	-2.72436300	-0.89281200
H	-2.38902800	-2.72438600	0.89276400
H	-3.89933300	-2.50533000	0.00004400
Bq	0.0000000000	-0.4874003600	-1.0000000000
Bq	0.0000000000	-0.4874003600	1.0000000000

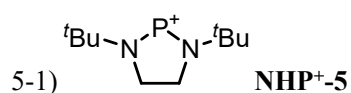


Charge = 0 Spin multiplicity = 1

C	0.71280500	0.90098700	0.03859500
---	------------	------------	------------

C	-0.71291300	0.90083600	0.03859900
C	-1.40317800	2.11107800	-0.01596100
C	-0.69407900	3.31949000	-0.06722800
C	0.69335000	3.31965700	-0.06722000
C	1.40275600	2.11142100	-0.01595300
H	-2.48383600	2.14191100	-0.02660500
H	-1.24520600	4.25356200	-0.11681500
H	1.24424400	4.25386600	-0.11679800
H	2.48339600	2.14256400	-0.02658400
C	-2.66748300	-0.74894600	0.08855400
C	2.66765000	-0.74863300	0.08855200
N	-1.22321100	-0.40467200	0.14574800
N	1.22334800	-0.40444600	0.14572500
C	3.39331700	-0.14337900	1.29731500
H	4.45151700	-0.42079400	1.25908100
H	3.33590900	0.94514800	1.33484100
H	2.96448000	-0.54073400	2.22297000
C	3.29105800	-0.29795400	-1.24055300
H	3.29441600	0.78713200	-1.36027300
H	4.32793100	-0.64500400	-1.29514300
H	2.73902600	-0.73421200	-2.08033600
C	2.81490600	-2.27171200	0.18675400
H	2.33138900	-2.66168100	1.08793100
H	2.39746400	-2.78227800	-0.68868600
H	3.87986200	-2.51616700	0.23350300
C	-3.39312500	-0.14358300	1.29726600
H	-3.33566400	0.94495100	1.33467700
H	-4.45133700	-0.42095600	1.25905100
H	-2.96429900	-0.54087300	2.22295300
C	-3.29083700	-0.29815100	-1.24052600
H	-4.32773900	-0.64510700	-1.29514700
H	-3.29409100	0.78695200	-1.36015300
H	-2.73882700	-0.73439700	-2.08033000
C	-2.81483500	-2.27202700	0.18675900

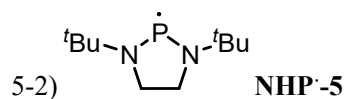
H	-2.39745700	-2.78262800	-0.68869100
H	-2.33132700	-2.66203200	1.08792500
H	-3.87980500	-2.51641200	0.23353300
P	0.00016700	-1.54273300	-0.32496400
H	0.00013600	-1.28248500	-1.75649100
Bq	0.0000342062	-0.5608220423	0.9332965953
Bq	-0.0000342062	-0.3422307377	-1.0547219753



Charge = 1 Spin multiplicity = 1

P	-0.00000100	0.93502200	-0.00003100
N	-1.20410100	-0.16687000	0.00071100
N	1.20410000	-0.16686600	-0.00076900
C	-2.66280300	0.13732500	-0.01245400
C	2.66280300	0.13732600	0.01246600
C	-0.72867800	-1.55165100	0.22144000
C	0.72868200	-1.55165200	-0.22147300
H	0.82494500	-1.78419700	-1.28749100
H	-1.32348600	-2.25904100	-0.35749300
H	-0.82493600	-1.78417700	1.28746300
H	1.32349200	-2.25903000	0.35747300
C	-3.26270800	-0.43135700	-1.30150300
H	-3.13363000	-1.51556500	-1.36257800
H	-4.33544400	-0.21752900	-1.32316900
H	-2.79481600	0.03186000	-2.17562400
C	-2.86575500	1.65054000	0.02516800
H	-3.93852200	1.85845700	0.00053300
H	-2.45618400	2.08889500	0.94189100
H	-2.41110200	2.14153500	-0.84275600
C	-3.30455400	-0.50620700	1.21882600
H	-4.36578900	-0.24321000	1.24406900
H	-3.22857600	-1.59705100	1.18924900
H	-2.83165200	-0.14068100	2.13603200

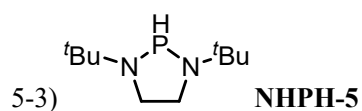
C	3.26261800	-0.43124600	1.30160600
H	3.13348800	-1.51544300	1.36278300
H	4.33536200	-0.21746000	1.32331000
H	2.79469500	0.03207900	2.17565400
C	2.86575600	1.65053600	-0.02527500
H	2.45615200	2.08881800	-0.94201700
H	2.41113600	2.14159900	0.84262700
H	3.93852500	1.85845400	-0.00068800
C	3.30464100	-0.50631100	-1.21871300
H	4.36587300	-0.24329300	-1.24391200
H	3.22868600	-1.59715300	-1.18903700
H	2.83179300	-0.14088000	-2.13598400
Bq	0.0831302936	-0.1565993100	0.9965386868
Bq	-0.0831302936	-0.1565993100	-0.9965386868



Charge = 0 Spin multiplicity = 2

P	0.00000000	0.98255400	-0.00000200
N	-1.21835700	-0.21895600	-0.24953100
N	1.21835700	-0.21895600	0.24953100
C	-2.64233100	0.11773200	-0.01116900
C	2.64233100	0.11773200	0.01116900
C	-0.73958200	-1.53870900	0.16979600
C	0.73958200	-1.53870900	-0.16979800
H	0.87488100	-1.68986100	-1.25271000
H	-1.26443500	-2.33418300	-0.36512400
H	-0.87488100	-1.68986200	1.25270800
H	1.26443400	-2.33418400	0.36512100
C	-3.52139100	-0.95437100	-0.66337400
H	-3.42560300	-1.92120200	-0.16029200
H	-4.57099500	-0.65058200	-0.60206200
H	-3.25686200	-1.08008500	-1.71887900
C	-2.93980200	1.46646000	-0.67328000

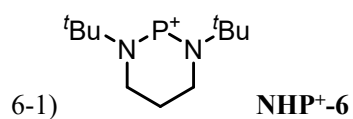
H	-4.00629700	1.69280000	-0.58103000
H	-2.38662200	2.28361500	-0.19690400
H	-2.67944100	1.44070800	-1.73683200
C	-2.95910500	0.20057700	1.48955900
H	-4.01062200	0.46873600	1.63635400
H	-2.78501500	-0.75857900	1.98740000
H	-2.33802700	0.96203700	1.97420500
C	3.52139100	-0.95436900	0.66337900
H	3.42560400	-1.92120100	0.16029900
H	4.57099500	-0.65057900	0.60206800
H	3.25686000	-1.08008100	1.71888300
C	2.93980000	1.46646100	0.67327800
H	2.38662100	2.28361500	0.19689900
H	2.67943700	1.44071300	1.73682900
H	4.00629600	1.69280200	0.58102900
C	2.95910700	0.20057400	-1.48955800
H	4.01062500	0.46873300	-1.63635200
H	2.78502100	-0.75858400	-1.98739700
H	2.33802900	0.96203100	-1.97420700
Bq	-0.0909787265	-0.1524753700	0.9958528362
Bq	0.0909787265	-0.1524753700	-0.9958528362



Charge = 0 Spin multiplicity = 1

N	1.21742600	-0.18193500	-0.27962500
N	-1.21679200	-0.21594400	-0.28107900
C	2.64913000	0.12586500	-0.07265100
C	-2.64990400	0.11997200	-0.08671000
C	0.77225200	-1.56225500	-0.01575100
C	-0.75338100	-1.52179200	0.20663900
H	-0.97643800	-1.64362600	1.27864400
H	1.26102300	-1.98646100	0.87179200
H	1.02578000	-2.19450500	-0.87353000

H	-1.24299800	-2.33252300	-0.33843800
C	3.02655800	0.13541000	1.41711800
H	2.78634100	-0.81900300	1.89706600
H	4.10153800	0.30943800	1.53501200
H	2.49451600	0.93222000	1.94894500
C	2.95337900	1.49831900	-0.68071800
H	4.02791600	1.69753200	-0.62062500
H	2.65016900	1.52769900	-1.73270600
H	2.43507700	2.30295400	-0.14898200
C	3.48250000	-0.92981800	-0.80756600
H	4.54256100	-0.66384000	-0.75080900
H	3.36305800	-1.92301900	-0.36364500
H	3.19332500	-0.98188200	-1.86295100
C	-3.50245600	-1.05515500	-0.57560100
H	-3.41348900	-1.92585000	0.08127900
H	-4.55480200	-0.75567500	-0.59111500
H	-3.21102600	-1.34917800	-1.58989700
C	-2.97404100	1.34689700	-0.94415400
H	-2.39863400	2.22326200	-0.62931600
H	-2.74970100	1.14608000	-1.99699400
H	-4.03682100	1.59287500	-0.85349300
C	-2.98567800	0.41660300	1.38322400
H	-4.06430800	0.56560100	1.50061400
H	-2.68694800	-0.41041900	2.03607200
H	-2.48197500	1.32767200	1.72630200
P	-0.00960200	0.93363100	0.18922900
H	-0.03472300	0.69706100	1.62028100
Bq	-0.0442324559	-0.1875537158	-0.9953092991
Bq	0.0422679959	-0.1422019242	1.0023044991

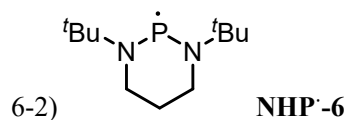


Charge = 1 Spin multiplicity = 1

C	1.25481400	1.67779100	0.22531400
---	------------	------------	------------

C	-1.25239100	1.67546500	0.23862600
C	-0.00255100	2.25406100	-0.39534800
H	1.30365600	1.91582800	1.29352200
H	-2.13820200	2.10488800	-0.22967600
H	-0.00229200	3.33594800	-0.24218000
N	-1.30753900	0.21030000	0.07080000
N	1.30738700	0.21132500	0.06744000
P	0.00007800	-0.75798800	-0.06459800
H	-1.28669600	1.90607400	1.30909300
H	-0.00866900	2.06155500	-1.47456500
H	2.13496300	2.10282500	-0.25777300
C	2.68628100	-0.40294800	0.00440000
C	-2.68648600	-0.40281500	0.00366200
C	-3.49088600	0.10651300	1.20288500
H	-3.64826300	1.18733000	1.16638000
H	-4.47284600	-0.37483600	1.19477600
H	-2.98566300	-0.14881000	2.13997200
C	-3.33947900	0.00523000	-1.32026400
H	-2.74334700	-0.35770400	-2.16345700
H	-4.33550400	-0.44359700	-1.37879500
H	-3.45742300	1.08822900	-1.40954100
C	-2.61566600	-1.92954600	0.07098500
H	-3.64078700	-2.30861000	0.06677900
H	-2.09995600	-2.36309500	-0.79153100
H	-2.13111000	-2.27513000	0.99047800
C	2.61561200	-1.92887400	0.08917900
H	3.64074900	-2.30792700	0.08864500
H	2.13161500	-2.26338500	1.01307500
H	2.09936200	-2.37282400	-0.76759300
C	3.49326500	0.11904100	1.19646900
H	4.47412000	-0.36458900	1.19255200
H	3.65304800	1.19896200	1.14700600
H	2.98902900	-0.12417900	2.13729700
C	3.33701300	-0.00920400	-1.32489300

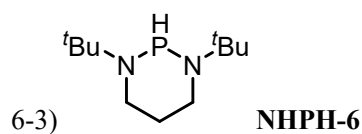
H	4.33343800	-0.45758900	-1.37988000
H	2.74004300	-0.38211800	-2.16313000
H	3.45347700	1.07291300	-1.42624300
Bq	-0.0034596128	0.4991541278	-0.9918169023
Bq	0.0031647928	0.5482723722	1.0075688823



Charge = 0 Spin multiplicity = 2

C	-1.22968200	1.66741500	-0.25485800
C	1.29212200	1.66076600	-0.16840600
C	0.01235300	2.21775300	0.42951500
H	-1.22873900	1.97411900	-1.31270900
H	2.14730700	2.06314000	0.39072500
H	0.02215400	3.30706900	0.32350900
N	1.32152800	0.19369900	-0.14270600
N	-1.31449400	0.19491000	-0.16030900
P	-0.00088300	-0.70991200	0.48722700
H	1.38891400	2.01165800	-1.20568400
H	-0.02876300	1.98777100	1.50208200
H	-2.10913100	2.11759700	0.21034600
C	-2.69318500	-0.39184500	-0.07966300
C	2.67666700	-0.40527000	-0.08702000
C	3.54716200	0.24800100	-1.16586200
H	3.71061500	1.31496800	-0.97765000
H	4.52612200	-0.24046500	-1.18302900
H	3.08540200	0.13306500	-2.15248500
C	3.31340800	-0.19847000	1.29411500
H	2.71352700	-0.69234400	2.06647700
H	4.32197500	-0.62508600	1.31534400
H	3.39436800	0.86445200	1.54525900
C	2.61242700	-1.90615600	-0.38367700
H	3.63265500	-2.29379600	-0.45965400
H	2.10297500	-2.46497400	0.40684300

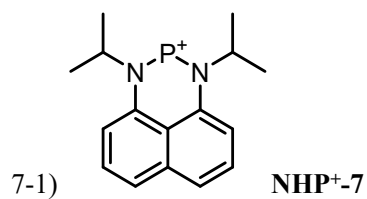
H	2.09685700	-2.09486300	-1.33105300
C	-2.64071500	-1.91474100	-0.27236800
H	-3.66430800	-2.29958100	-0.32605100
H	-2.12311600	-2.17442600	-1.20215900
H	-2.14012600	-2.42207900	0.55842800
C	-3.55150900	0.19367100	-1.21699800
H	-4.53784400	-0.28166800	-1.20887300
H	-3.70348400	1.26700200	-1.11326300
H	-3.08261600	0.00076600	-2.18840300
C	-3.34403800	-0.08495300	1.28379800
H	-4.35580100	-0.50281800	1.32611100
H	-2.75366900	-0.52871800	2.09346500
H	-3.42132700	0.99059200	1.46366800
Bq	0.0302282436	0.4728364673	-0.8833661822
Bq	-0.0098140036	0.5810281127	1.1133038422



Charge = 0 Spin multiplicity = 1

C	-1.28204200	1.67700900	-0.21062000
C	1.27691400	1.67381800	-0.22510700
C	0.00143000	2.30116800	0.33410200
H	-1.38950900	1.95033800	-1.26969500
H	2.13551100	2.12233600	0.29371000
H	0.00114100	3.36360200	0.07057600
N	1.29773800	0.20534000	-0.09192100
N	-1.29802200	0.20726300	-0.09173100
H	1.36824600	1.93779100	-1.28821300
H	0.00817400	2.25024800	1.42648500
H	-2.13359200	2.11948800	0.32513700
C	-2.63510900	-0.43708200	-0.13238500
C	2.63598300	-0.43611400	-0.13106100
C	3.44507300	0.16572800	-1.28829600

H	3.66384400	1.22595700	-1.13370000
H	4.40066300	-0.36080800	-1.37329600
H	2.90403000	0.05510200	-2.23467600
C	3.38701600	-0.22260800	1.19258300
H	2.84144900	-0.69423600	2.01827300
H	4.38848100	-0.66498500	1.14725400
H	3.49999200	0.84319500	1.41803900
C	2.49635600	-1.94013400	-0.39274100
H	3.49003400	-2.36954600	-0.55459900
H	2.03763900	-2.46581700	0.44864000
H	1.88896100	-2.12193300	-1.28645900
C	-2.49250400	-1.93724900	-0.41405800
H	-3.48568000	-2.36783100	-0.57596100
H	-1.88955400	-2.10541800	-1.31344200
H	-2.02736000	-2.47222200	0.41784400
C	-3.45164100	0.17715200	-1.27776300
H	-4.40548300	-0.35210100	-1.36532700
H	-3.67386600	1.23430700	-1.10782800
H	-2.91468200	0.08135600	-2.22808100
C	-3.38031300	-0.24208200	1.19738200
H	-4.38119800	-0.68564700	1.15102100
H	-2.83029300	-0.72330600	2.01457200
H	-3.49391100	0.82058200	1.43693800
P	-0.00043900	-0.55730100	0.73115900
H	-0.00143100	0.17319300	1.96874700
Bq	-0.0033697483	0.4505605873	-0.7914435266
Bq	0.0023585283	0.7366300327	1.1879835266

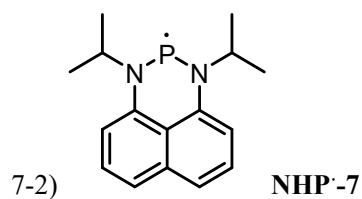


Charge = 1 Spin multiplicity = 1

C	2.75143700	0.15841600	-0.10493200
---	------------	------------	-------------

C	3.48993100	-1.04184300	-0.08644000
C	2.84800600	-2.25338300	-0.07433300
C	1.42961100	-2.30878100	-0.07804500
C	0.67000900	-1.10107900	-0.10071800
C	1.38569000	0.13688600	-0.11806500
C	0.77187800	-3.56671800	-0.05339100
C	-0.59376200	-3.63050800	-0.04505900
C	-1.36849500	-2.44922000	-0.06739900
C	-0.76215300	-1.20157100	-0.10327800
N	0.67279300	1.35543900	-0.15233400
P	-0.95301900	1.53081300	-0.17029700
N	-1.54015100	0.00291000	-0.15070700
C	-3.04512700	-0.09951300	-0.12154500
C	-3.50976900	-0.36739900	1.30716600
C	-3.73495200	1.13147800	-0.70074800
C	1.48405300	2.62485000	-0.10140500
C	0.73625600	3.83808400	-0.64647700
C	1.94990900	2.86444100	1.33001800
H	3.30178500	1.09262500	-0.10039500
H	4.57359700	-0.98656000	-0.07859900
H	3.40320200	-3.18640700	-0.05764600
H	1.37843400	-4.46709100	-0.03694200
H	-1.10376700	-4.58808700	-0.01951500
H	-2.44144500	-2.55566700	-0.04626000
H	-3.28353000	-0.93402900	-0.78027300
H	-4.58650900	-0.55796400	1.30665500
H	-3.00715800	-1.22617400	1.75653800
H	-3.31235500	0.51494100	1.92508500
H	-4.79752500	0.89074200	-0.78830600
H	-3.36086700	1.37817400	-1.69918700
H	-3.65092200	2.00923200	-0.05297000
H	2.32905100	2.44834100	-0.77197900
H	1.46019800	4.65411600	-0.71427300
H	0.33675700	3.65643300	-1.64914900

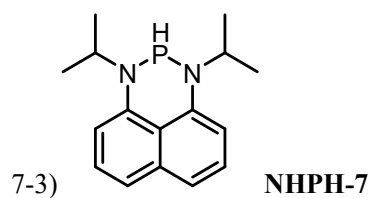
H	-0.07134600	4.17049200	0.01202000
H	2.63780200	3.71415200	1.34856700
H	2.46117300	1.99543400	1.75136300
H	1.08507200	3.10181900	1.95892700
Bq	-0.2647763178	0.4031801797	-1.1404827748
Bq	-0.2850044822	0.4477342403	0.8589185748



Charge = 0 Spin multiplicity = 2

C	-2.62979400	0.94236600	-0.09796300
C	-2.82992100	2.33718600	-0.09223500
C	-1.76523700	3.19846900	-0.06618900
C	-0.43957900	2.68739400	-0.05314600
C	-0.20875600	1.27587600	-0.05621100
C	-1.35217100	0.39385000	-0.08483400
C	0.65414100	3.59431000	-0.06249900
C	1.93786400	3.11746800	-0.08559500
C	2.19263100	1.73145300	-0.09121700
C	1.15624400	0.80465600	-0.08186700
N	-1.15640400	-0.99293400	-0.11768200
P	0.28072300	-1.71396900	0.49399200
N	1.41287400	-0.57236000	-0.11753100
C	2.81290800	-1.04750800	-0.24678800
C	3.53175200	-1.07039600	1.10359300
C	2.88539900	-2.41016800	-0.93414700
C	-2.33221400	-1.88959400	-0.24525900
C	-1.96581800	-3.20858900	-0.92370200
C	-3.00998700	-2.13167300	1.10470600
H	-3.50528400	0.30782200	-0.09402600
H	-3.84714900	2.71803200	-0.10030200
H	-1.90888800	4.27499500	-0.06034900

H	0.44664700	4.66038500	-0.05720300
H	2.78055400	3.80284300	-0.09101600
H	3.22429400	1.40764300	-0.08458500
H	3.30627600	-0.33672800	-0.91405200
H	4.59289200	-1.29855100	0.96246600
H	3.45025800	-0.11066100	1.62165400
H	3.09961300	-1.84566500	1.74671200
H	3.92952800	-2.61407000	-1.18975800
H	2.29496200	-2.41746300	-1.85541000
H	2.53606700	-3.22059000	-0.28747800
H	-3.02351900	-1.37760200	-0.91885900
H	-2.89031500	-3.73601700	-1.17707400
H	-1.40324100	-3.03293100	-1.84568100
H	-1.37724900	-3.86161300	-0.27269000
H	-3.94435900	-2.68439500	0.96525200
H	-3.23658500	-1.19256300	1.61744000
H	-2.35542700	-2.72687300	1.75168600
Bq	0.0999194354	-0.6049852108	-0.8934296437
Bq	0.0566591846	-0.3481455892	1.0895383237



Charge = 0 Spin multiplicity = 1

C	1.00940200	2.51037800	-0.04403800
C	2.40042400	2.68054100	0.11970600
C	3.24516500	1.60167100	0.13151100
C	2.71701200	0.28767800	0.00581900
C	1.31055500	0.08925200	-0.17457500
C	0.44585300	1.25293000	-0.21799000
C	3.58596300	-0.83059700	0.11379300
C	3.08663500	-2.10897000	0.07392700
C	1.70526900	-2.32388400	-0.09558600

C	0.82303900	-1.26405800	-0.22345600
N	-0.93219300	1.09006000	-0.41289900
N	-0.55249200	-1.53194800	-0.41655500
C	-1.24596200	-2.38602500	0.58210600
C	-1.78794200	-1.55557900	1.74596400
C	-2.34146200	-3.21681900	-0.07555000
C	-1.85180300	2.19168800	-0.05210700
C	-3.26905600	1.95617500	-0.56245900
C	-1.87214300	2.39909000	1.46334200
H	0.38304300	3.39338200	-0.04008900
H	2.79288300	3.68699500	0.23434600
H	4.31677600	1.72414900	0.25997400
H	4.64920700	-0.64854900	0.24356100
H	3.75193300	-2.96313900	0.15955000
H	1.32178500	-3.33803600	-0.15353800
H	-0.48802100	-3.07077500	0.96996400
H	-2.19555800	-2.20918800	2.52396500
H	-0.99682200	-0.94029000	2.18837900
H	-2.59262900	-0.89282600	1.40412200
H	-2.77560300	-3.90180500	0.65913500
H	-1.93772000	-3.80410400	-0.90579700
H	-3.14722000	-2.58119200	-0.45801300
H	-1.49198600	3.10595600	-0.53944500
H	-3.87411800	2.82865700	-0.29963900
H	-3.30087200	1.83508600	-1.64945700
H	-3.72478500	1.07501000	-0.09891000
H	-2.45224800	3.29322300	1.71295900
H	-0.86636200	2.52070300	1.87420800
H	-2.34106000	1.53596000	1.94833300
P	-1.45709500	-0.33412600	-1.24269200
H	-0.54710100	-0.24495000	-2.32949100
Bq	-0.0692529199	-0.1182862844	-1.5587590733
Bq	-0.6659028201	-0.2100543756	0.3479625933

5. NMR Spectra

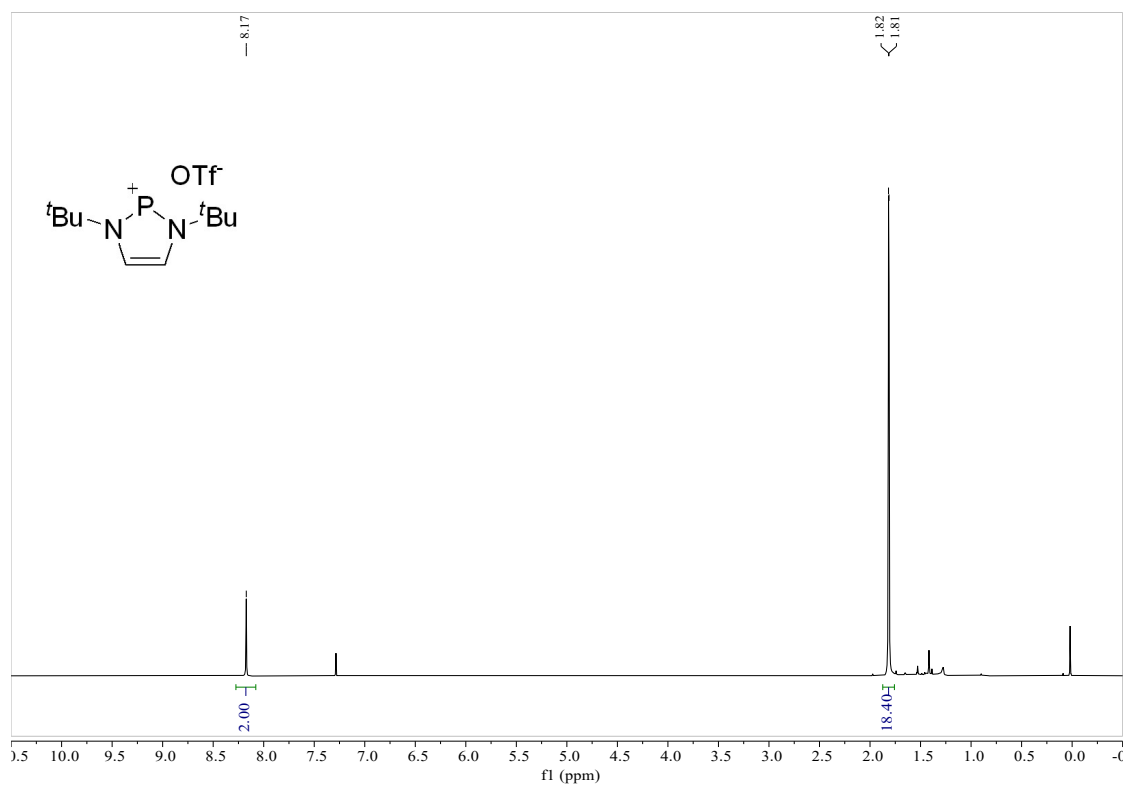


Figure S5-1 ¹H NMR (400 MHz, CDCl₃) of NHP⁺-1.

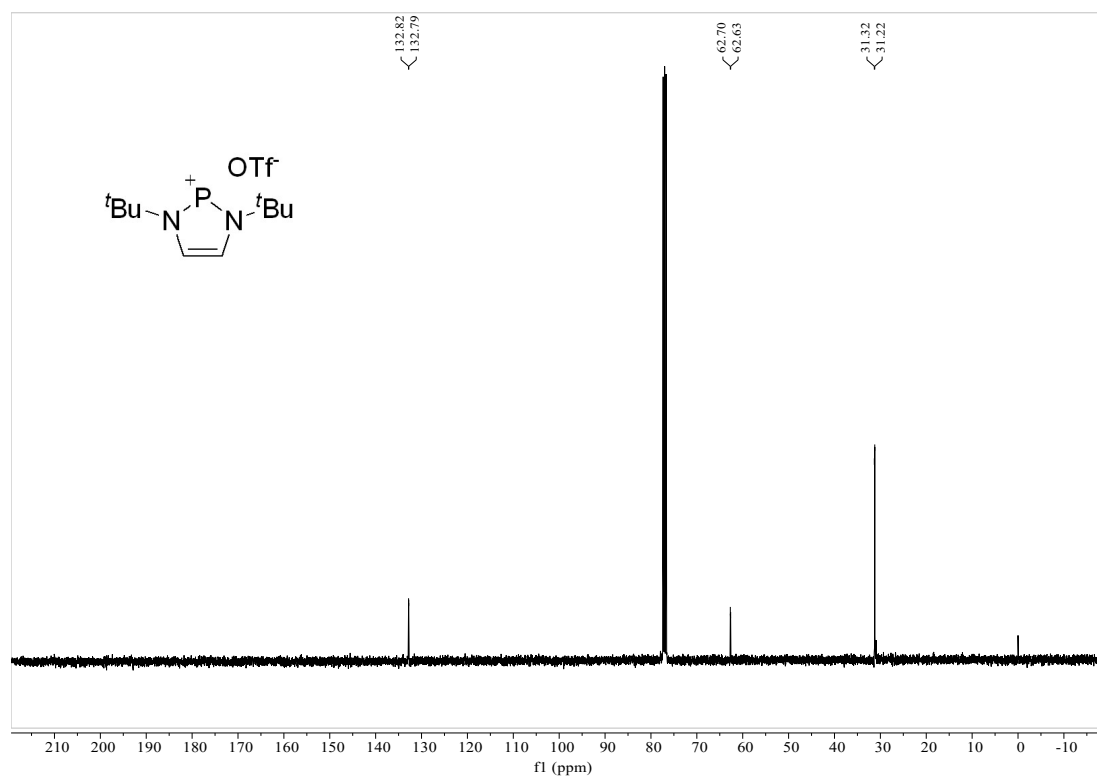


Figure S5-2. ^{13}C NMR (101 MHz, CDCl_3) of **NHP⁺-1**.

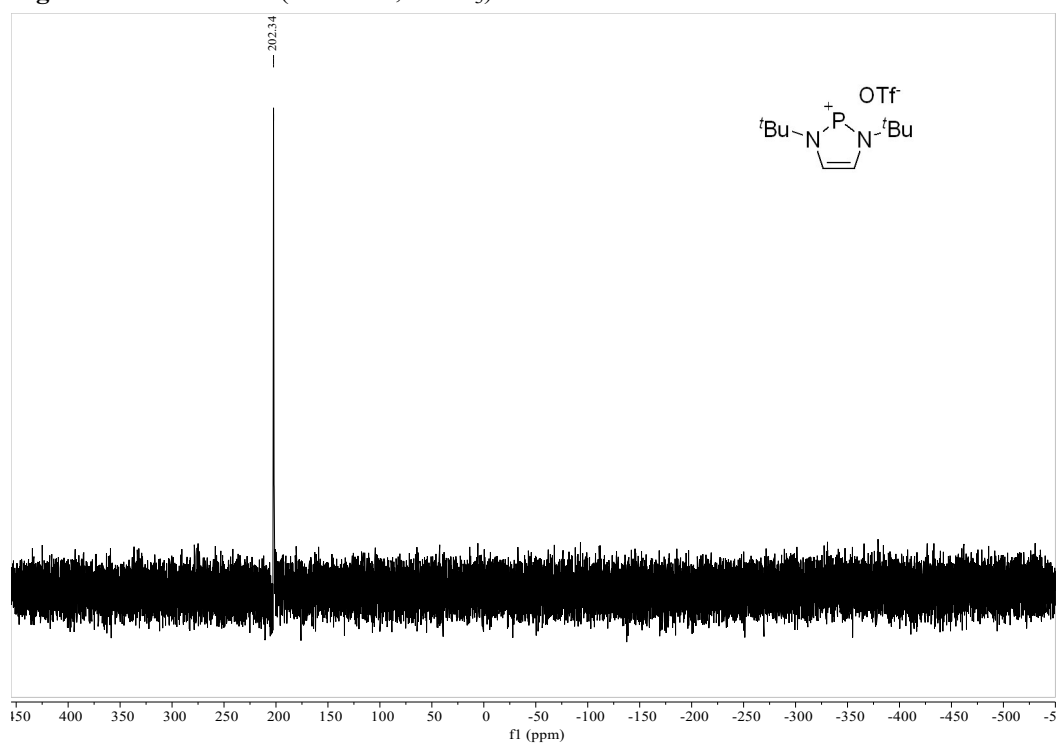


Figure S5-3. ^{31}P NMR (162 MHz, CDCl_3) of **NHP⁺-1**.

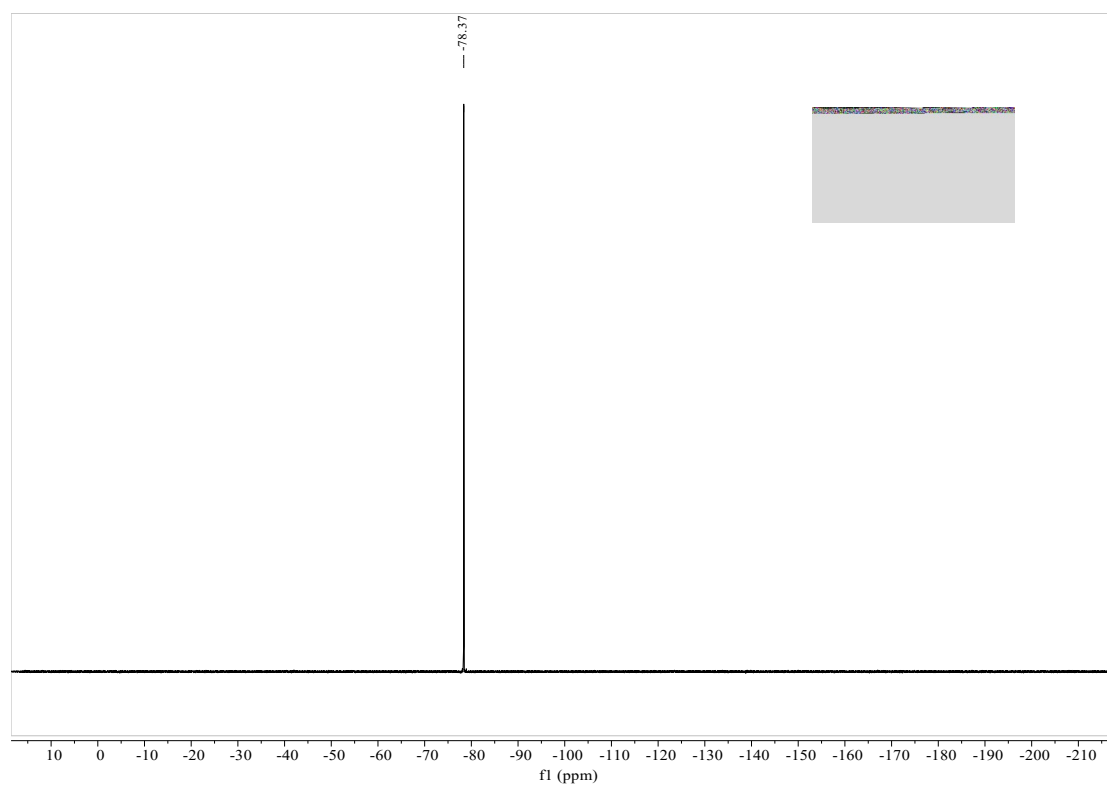


Figure S5-4. ^{19}F NMR (376 MHz, CDCl_3) of **NHP⁺-1**.

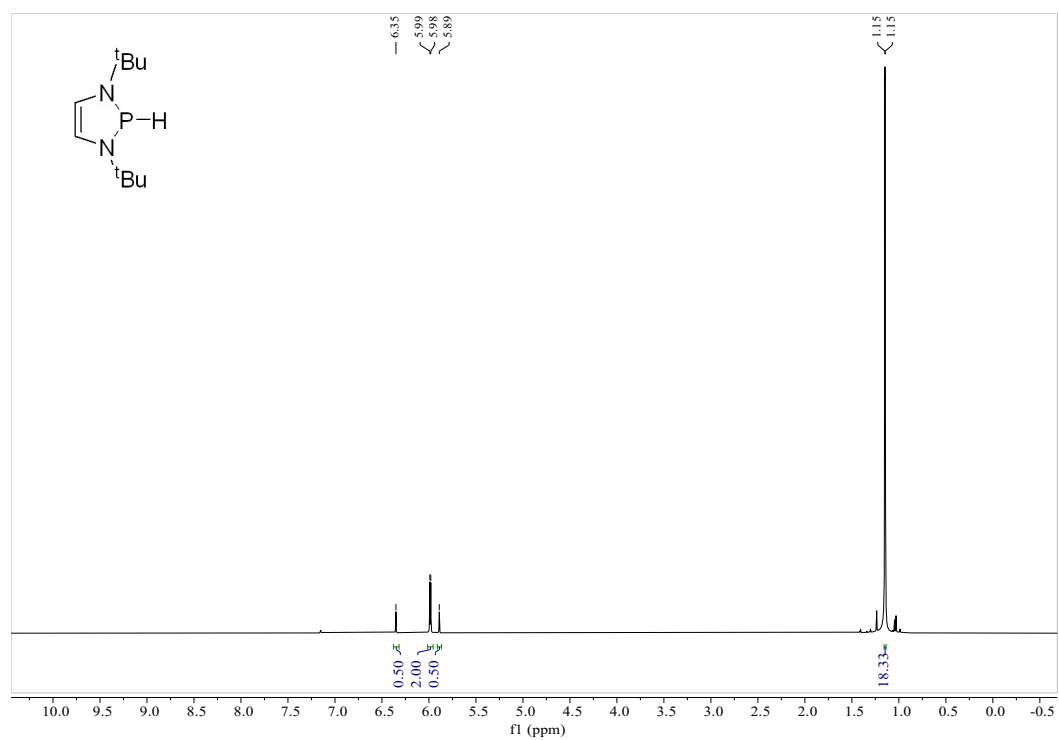


Figure S5-5. ¹H NMR (400 MHz, CDCl₃) of NHPH-1.

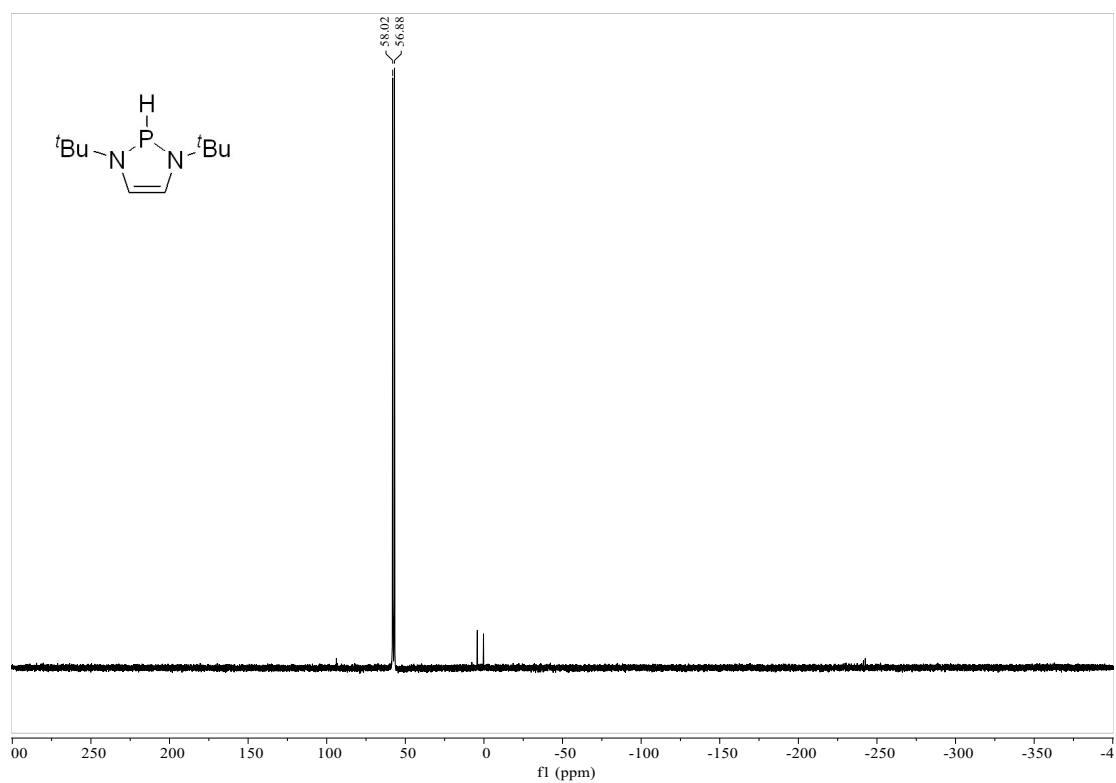


Figure S5-6. ³¹P NMR (162 MHz, CDCl₃) of NHPH-1.

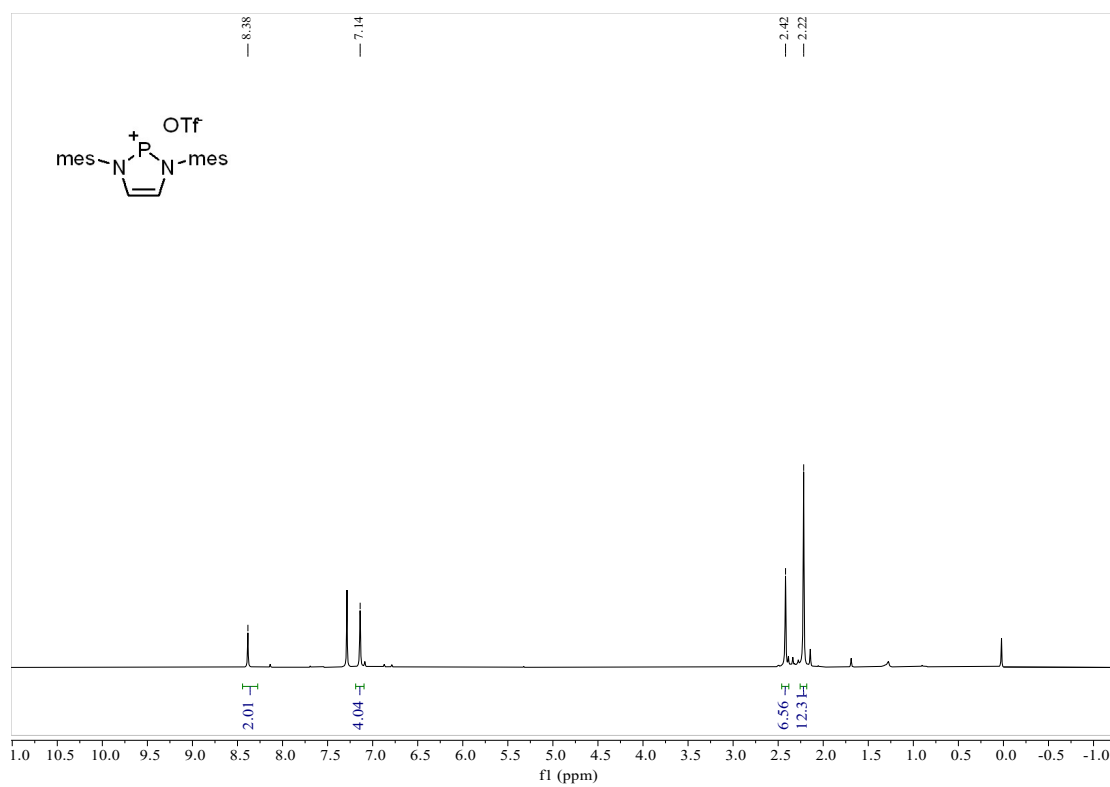


Figure S5-7. ¹H NMR (400 MHz, CDCl₃) of NHP⁺-2.

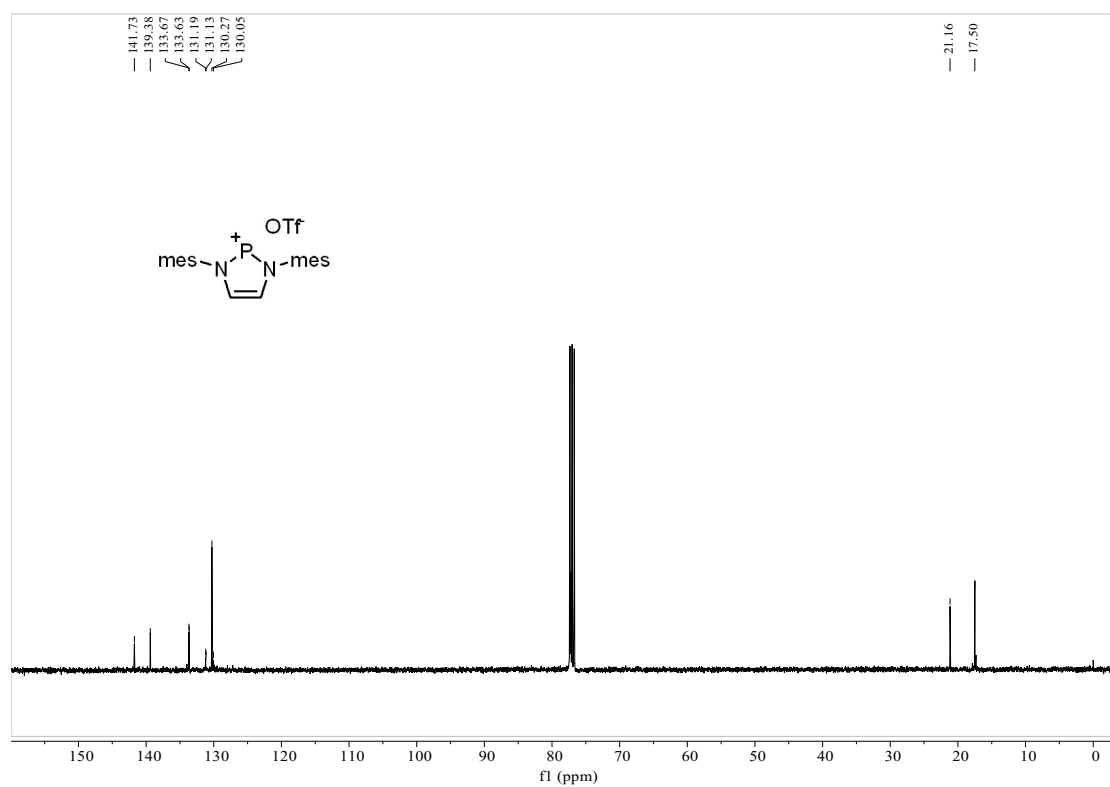


Figure S5-8. ¹³C NMR (101 MHz, CDCl₃) of NHP⁺-2.

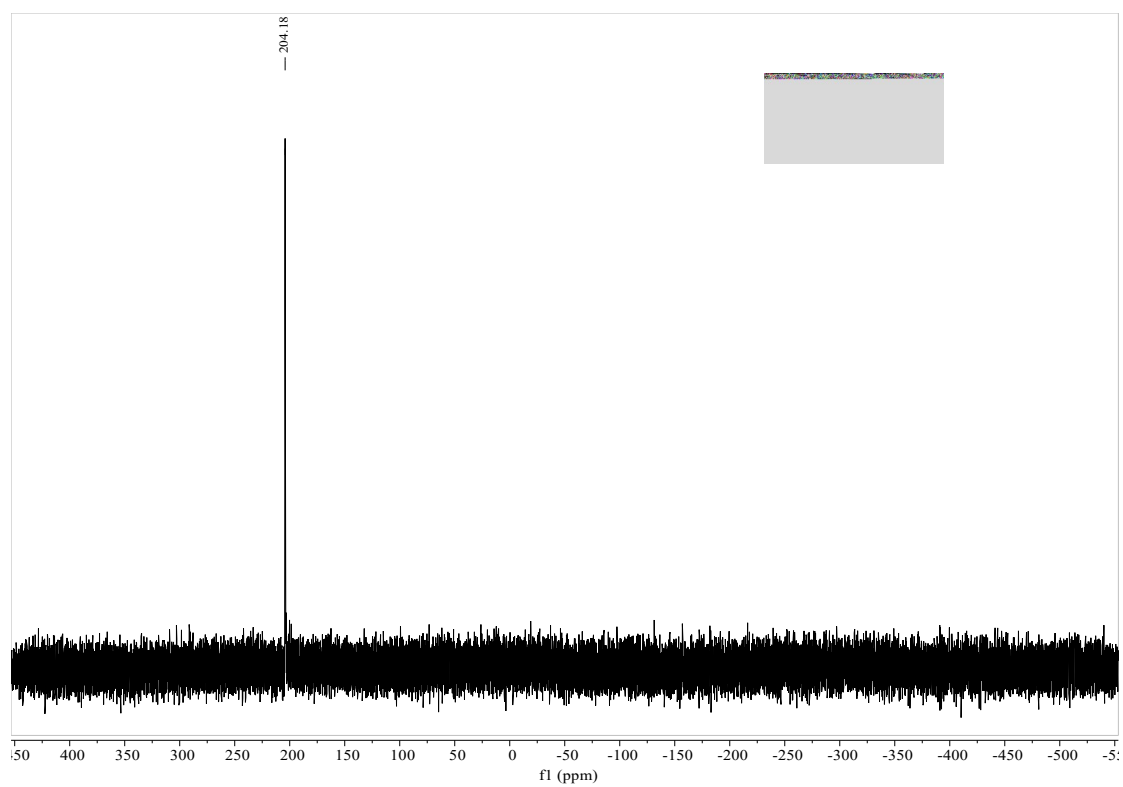


Figure S5-9. ^{31}P NMR (162 MHz, CDCl_3) of NHP^+-2 .

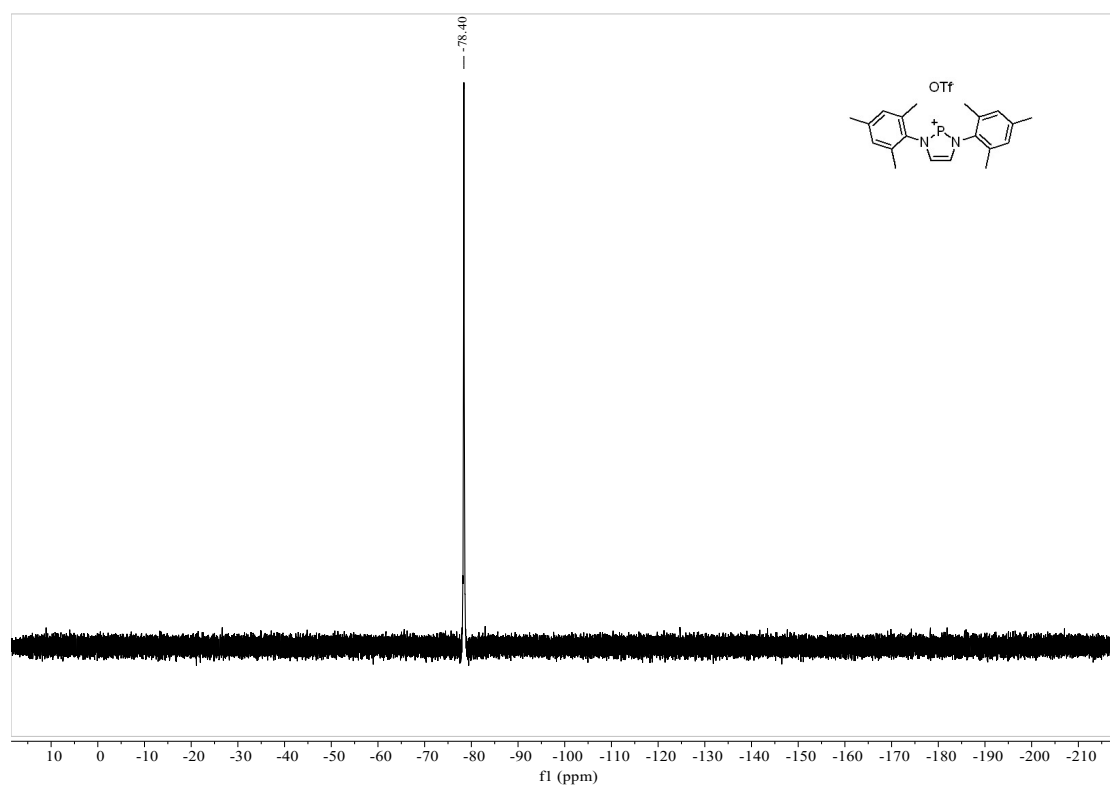


Figure S5-10. ^{19}F NMR (376 MHz, CDCl_3) of NHP^+-2 .

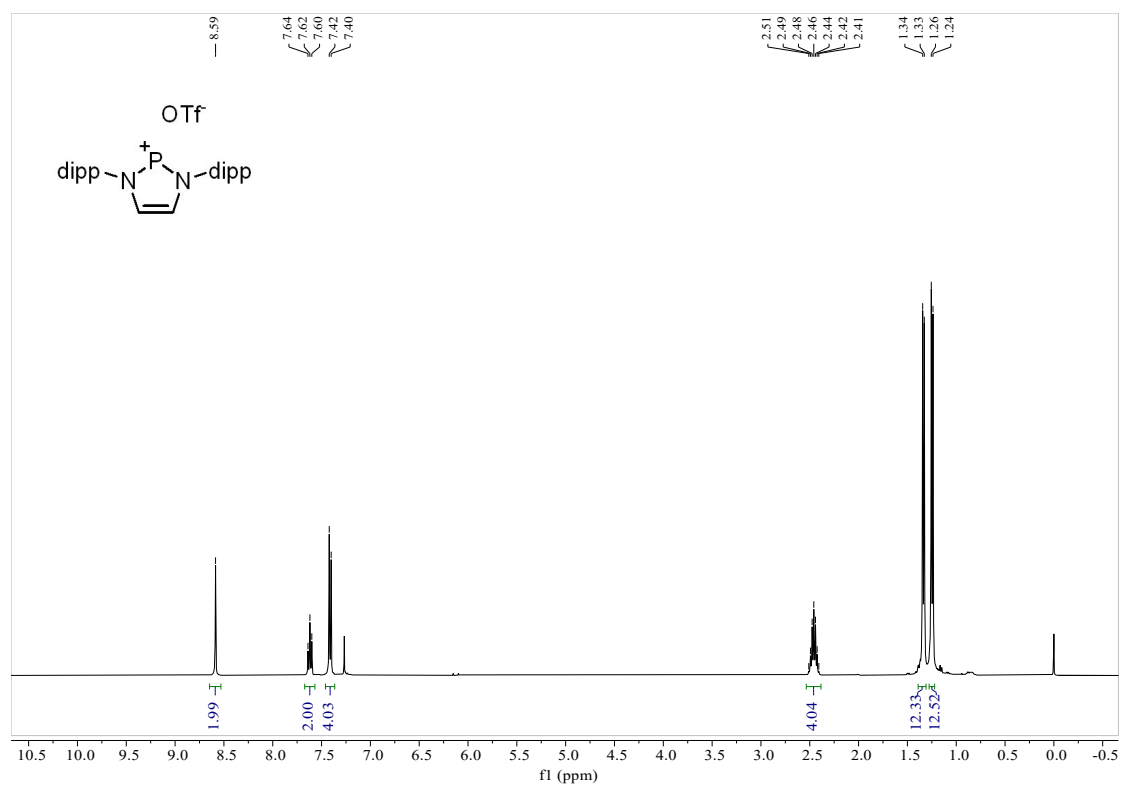


Figure S5-11. ¹H NMR (400 MHz, CDCl₃) of NHP⁺-3.

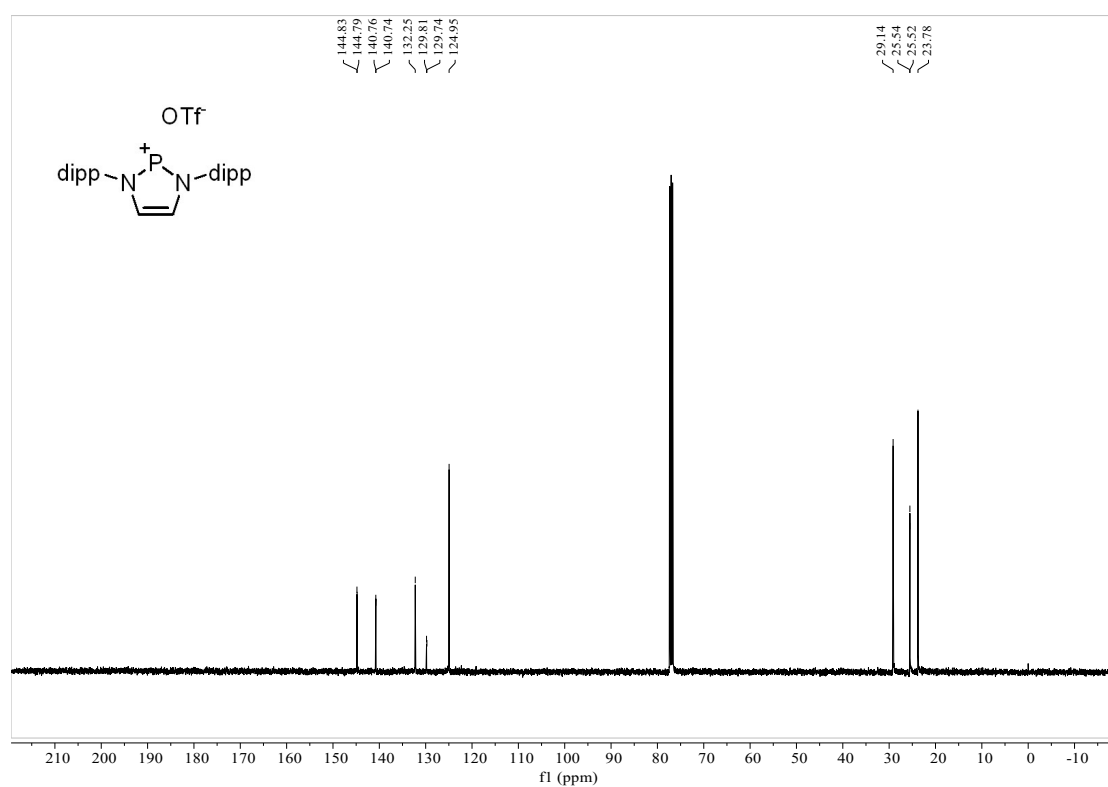


Figure S5-12. ¹³C NMR (101 MHz, CDCl₃) of NHP⁺-3.

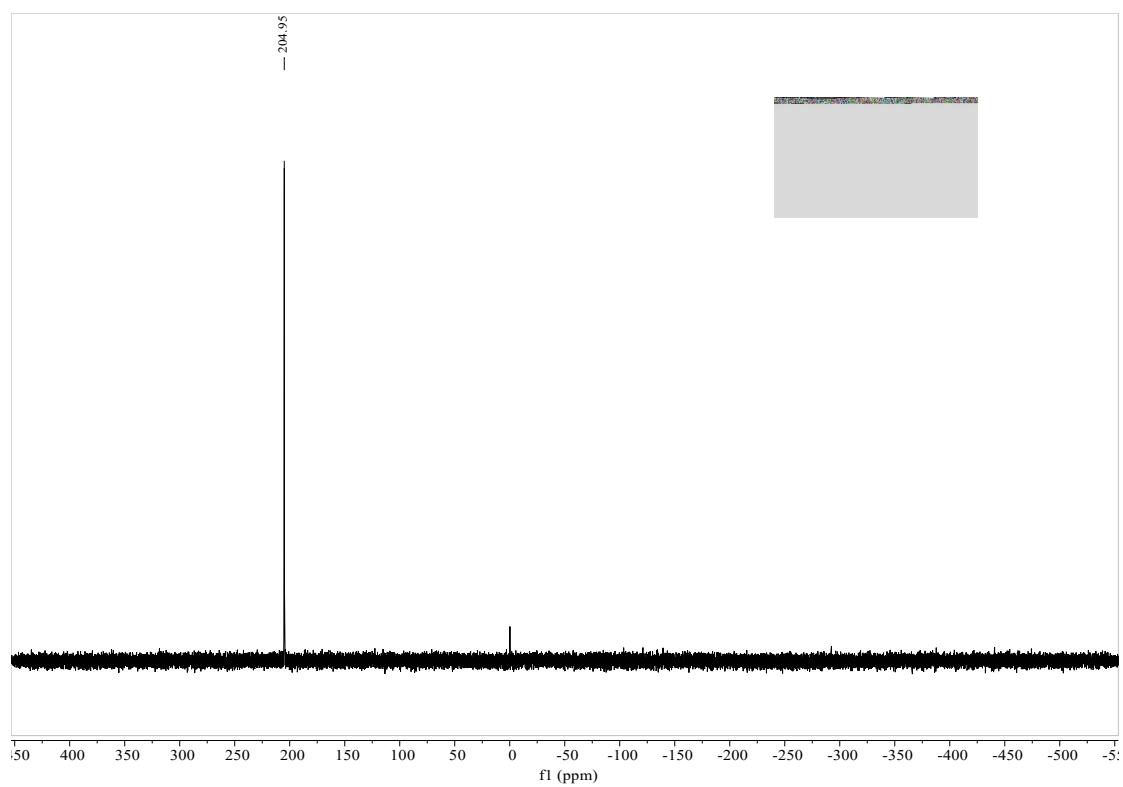


Figure S5-13. ³¹P NMR (162 MHz, CDCl₃) of NHP⁺-3.

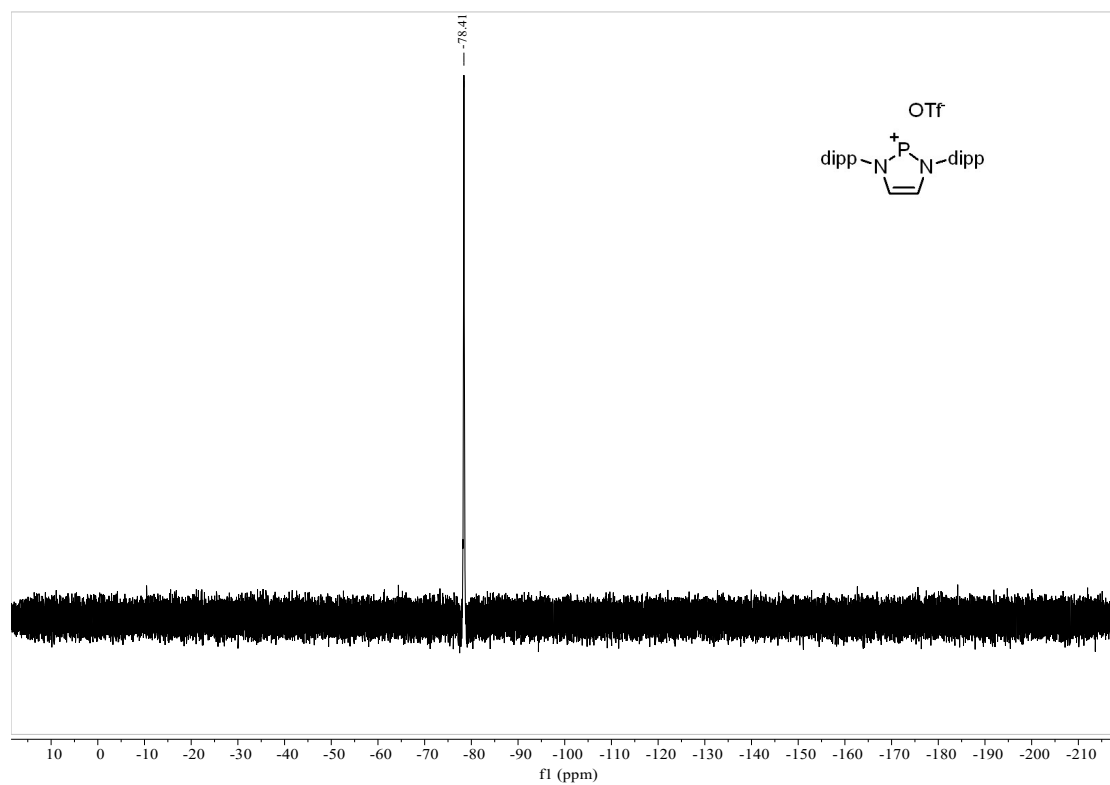


Figure S5-14. ¹⁹F NMR (376 MHz, CDCl₃) of NHP⁺-3.

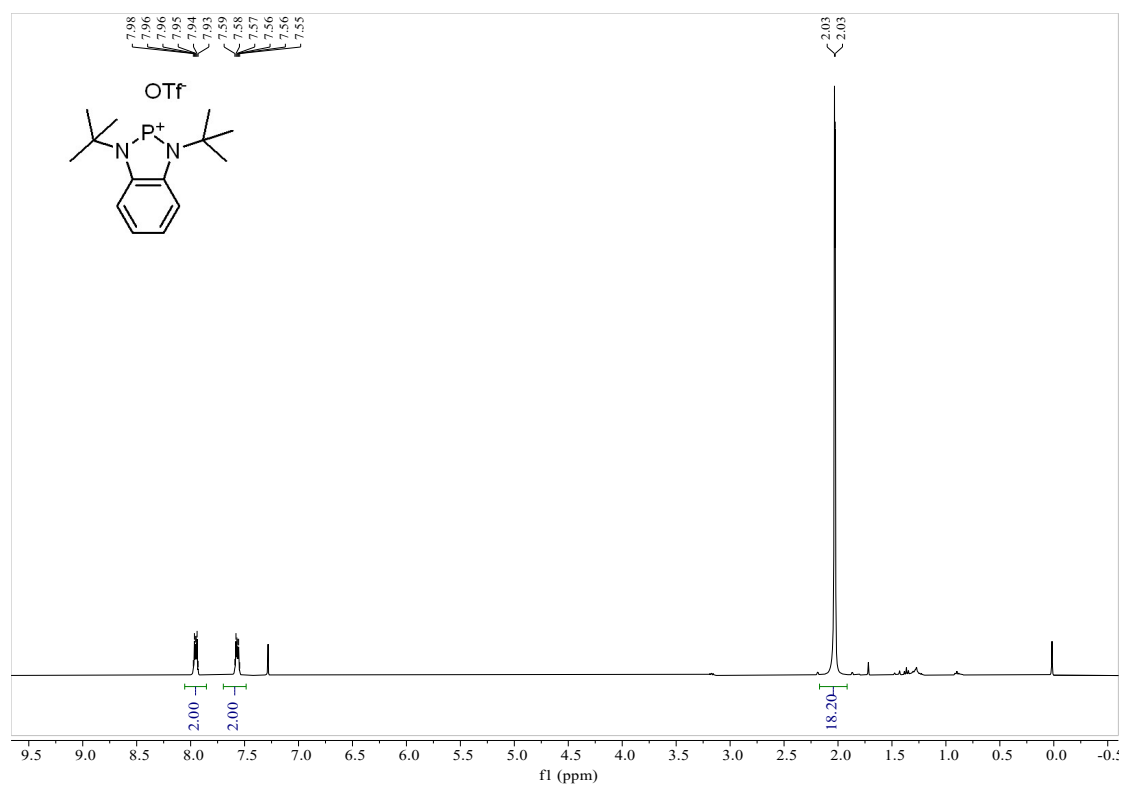


Figure S5-15. ¹H NMR (400 MHz, CDCl₃) of NHP⁺-4.

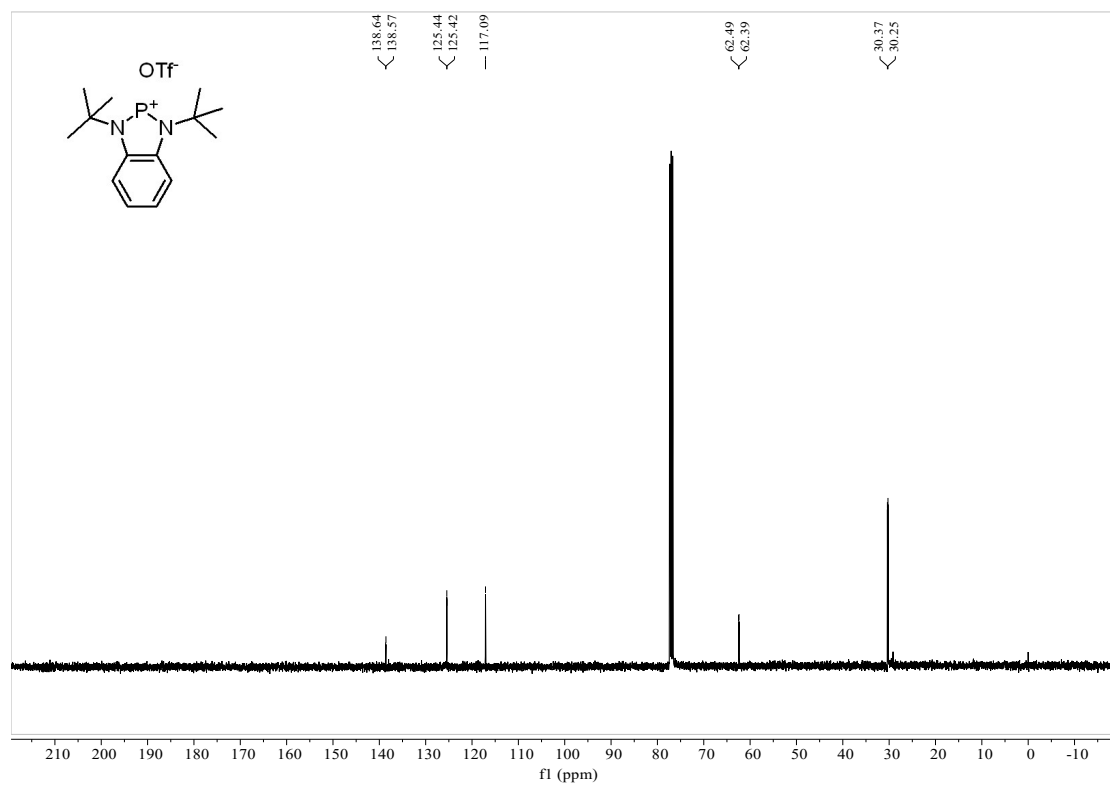


Figure S5-16. ¹³C NMR (101 MHz, CDCl₃) of NHP⁺-4.

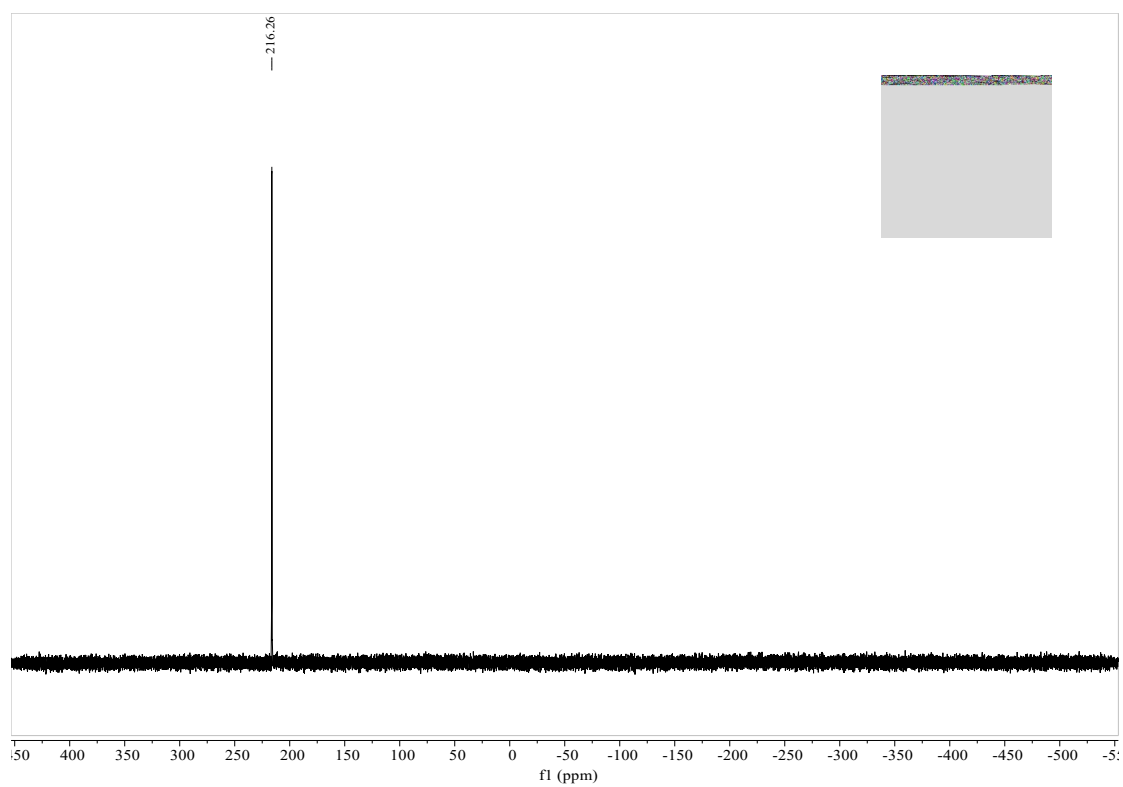


Figure S5-17. ³¹P NMR (162 MHz, CDCl₃) of NHP⁺-4.

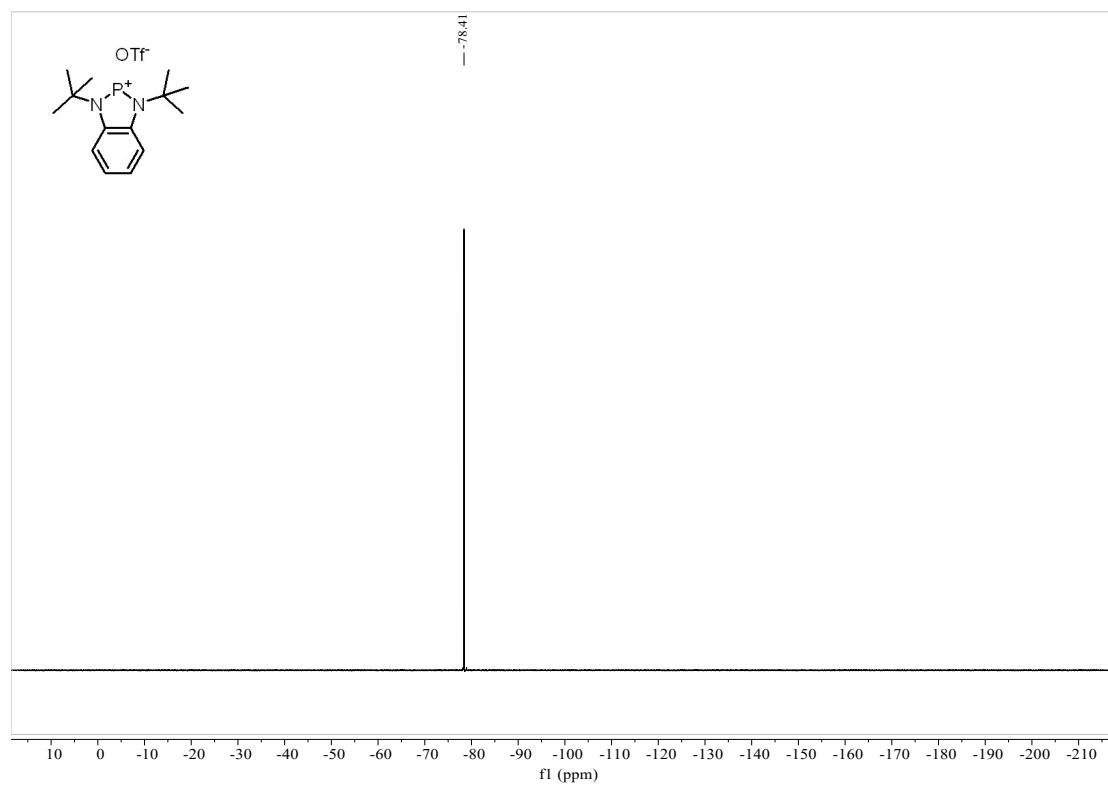


Figure S5-18. ¹⁹F NMR (376 MHz, CDCl₃) of NHP⁺-4.

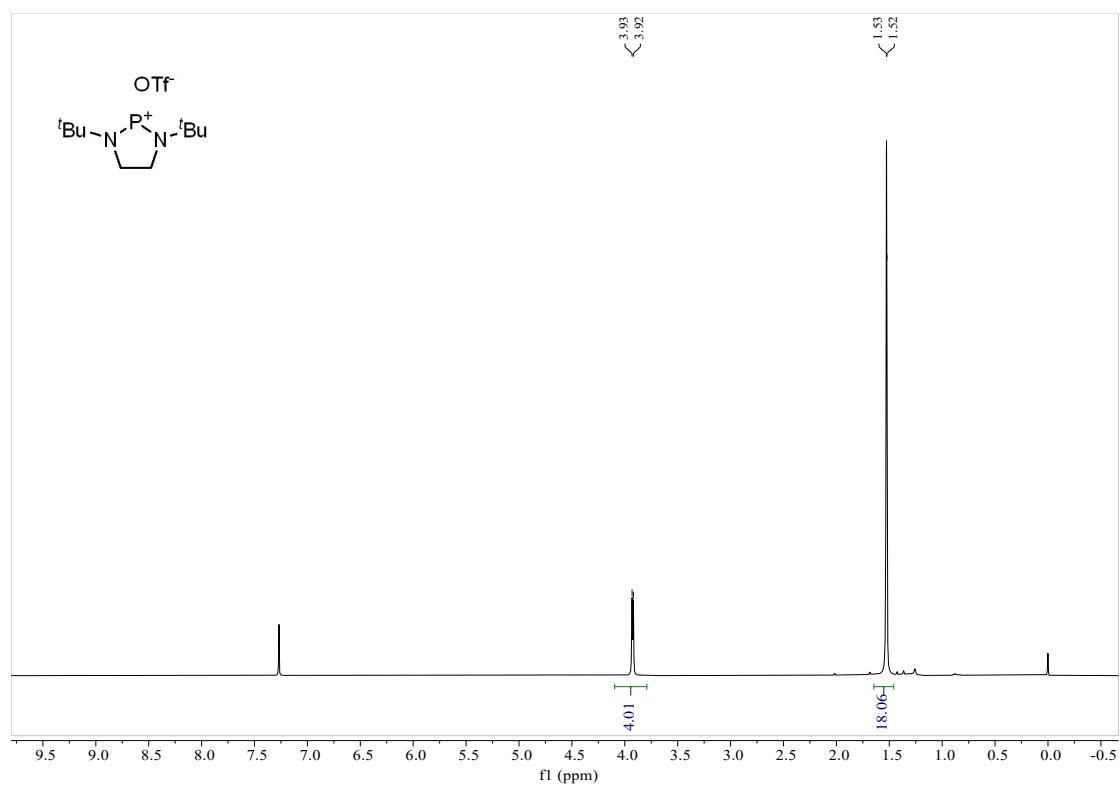


Figure S5-19. ¹H NMR (400 MHz, CDCl₃) of NHP⁺-5.

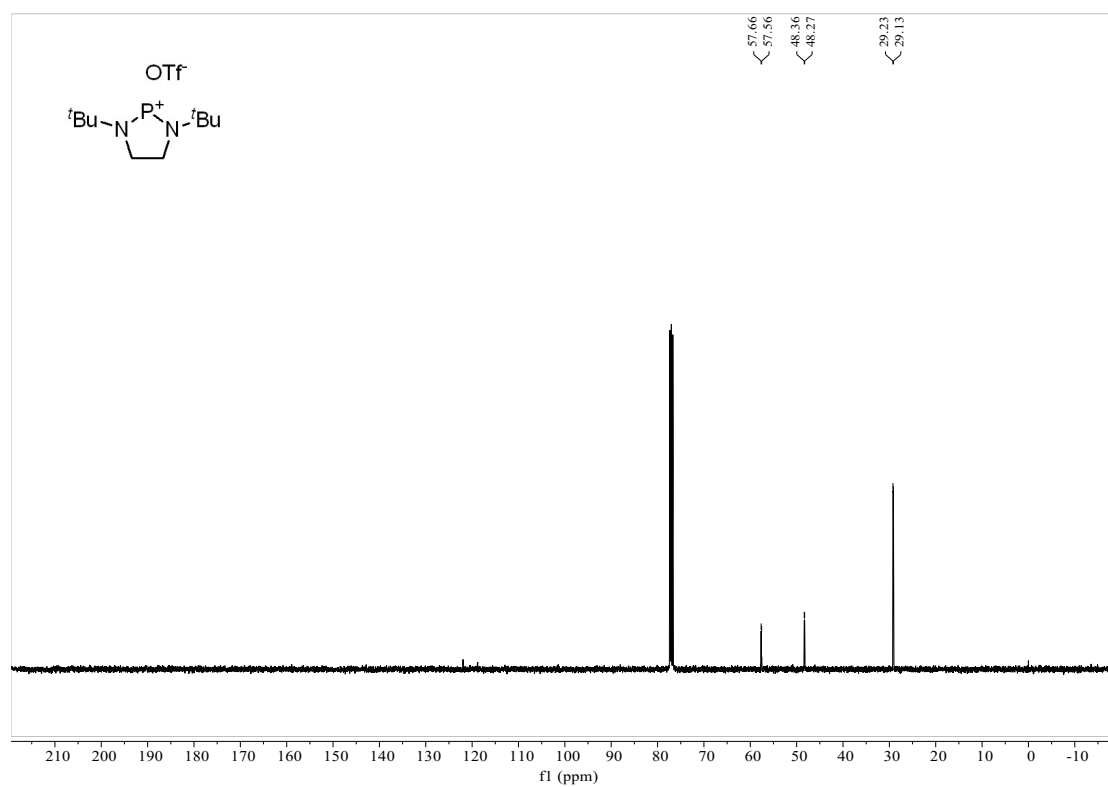


Figure S5-20. ¹³C NMR (101 MHz, CDCl₃) of NHP⁺-5.

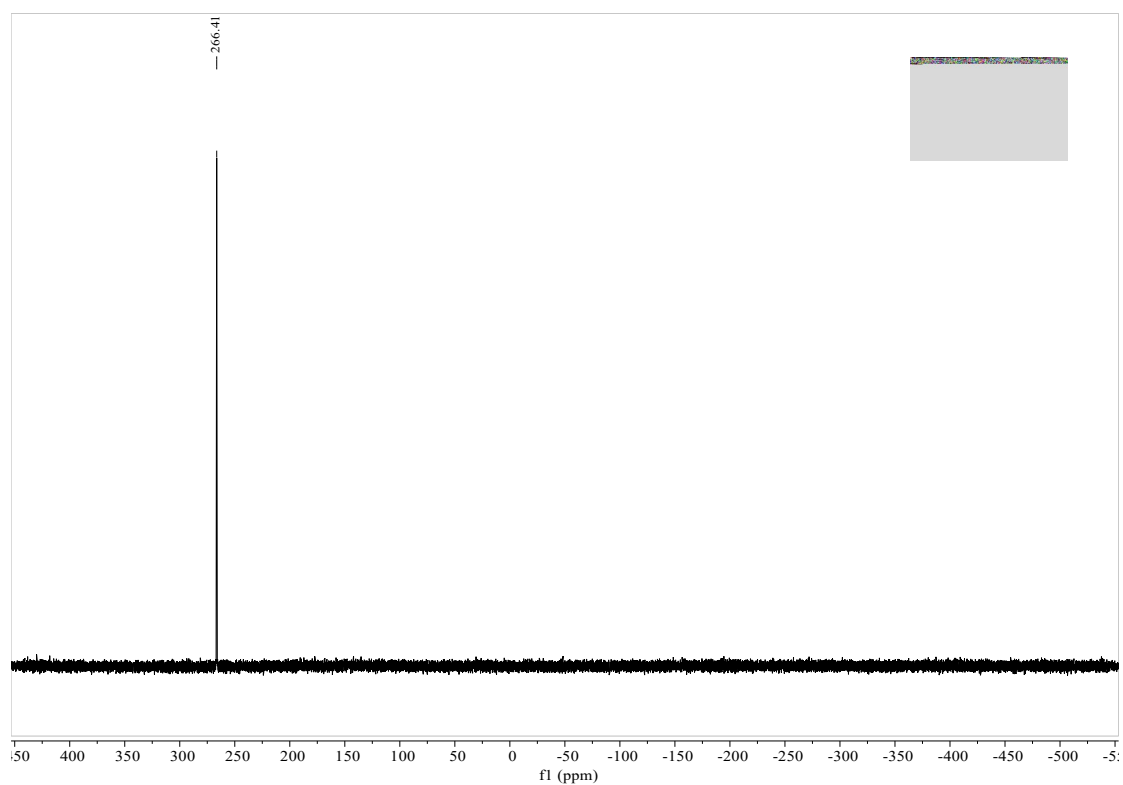


Figure S5-21. ^{31}P NMR (162 MHz, CDCl_3) of **NHP⁺-5**.

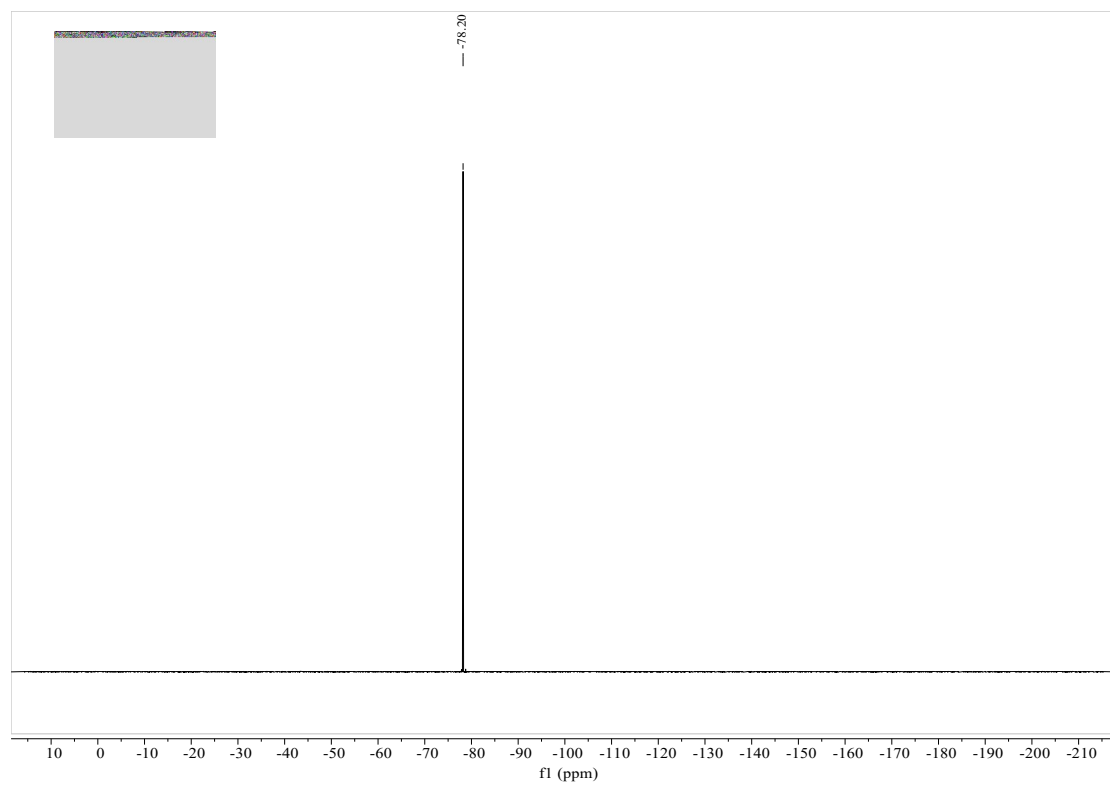


Figure S5-22. ^{19}F NMR (376 MHz, CDCl_3) of **NHP⁺-5**.

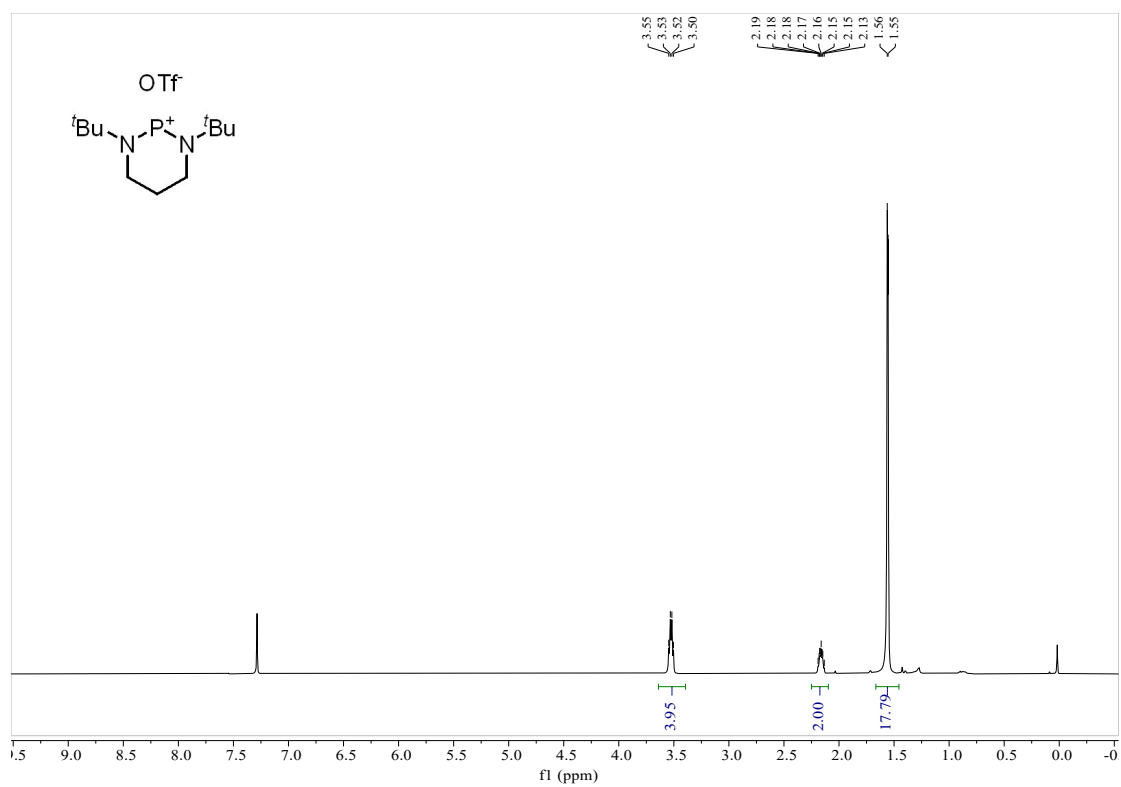


Figure S5-23. ¹H NMR (400 MHz, CDCl₃) of NHP⁺-6.

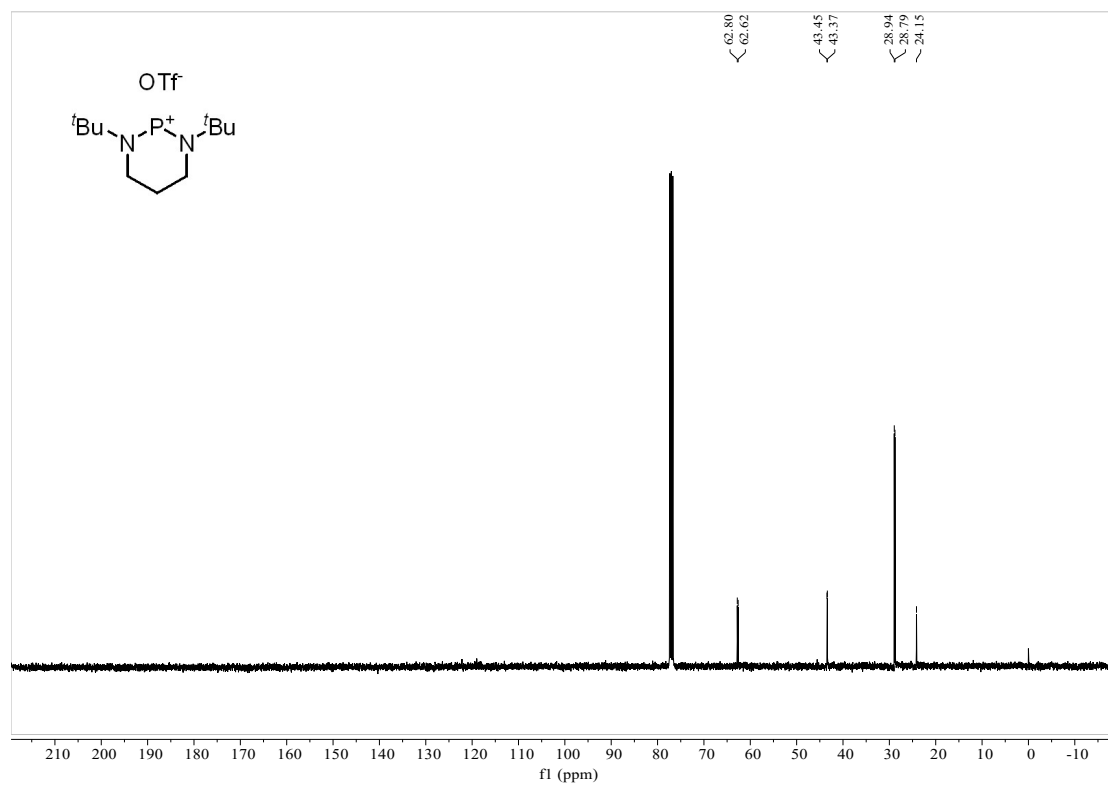


Figure S5-24. ¹³C NMR (101 MHz, CDCl₃) of NHP⁺-6.

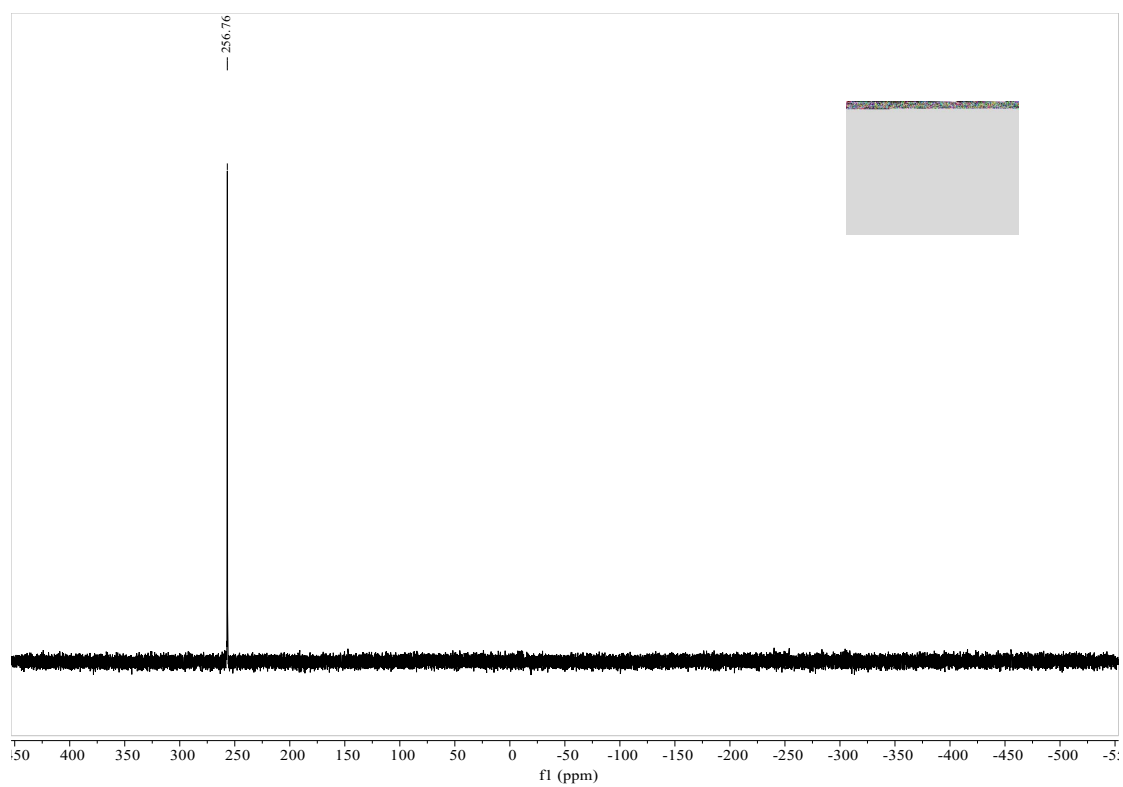


Figure S5-25. ^{31}P NMR (162 MHz, CDCl_3) of $\text{NHP}^+\text{-6}$.

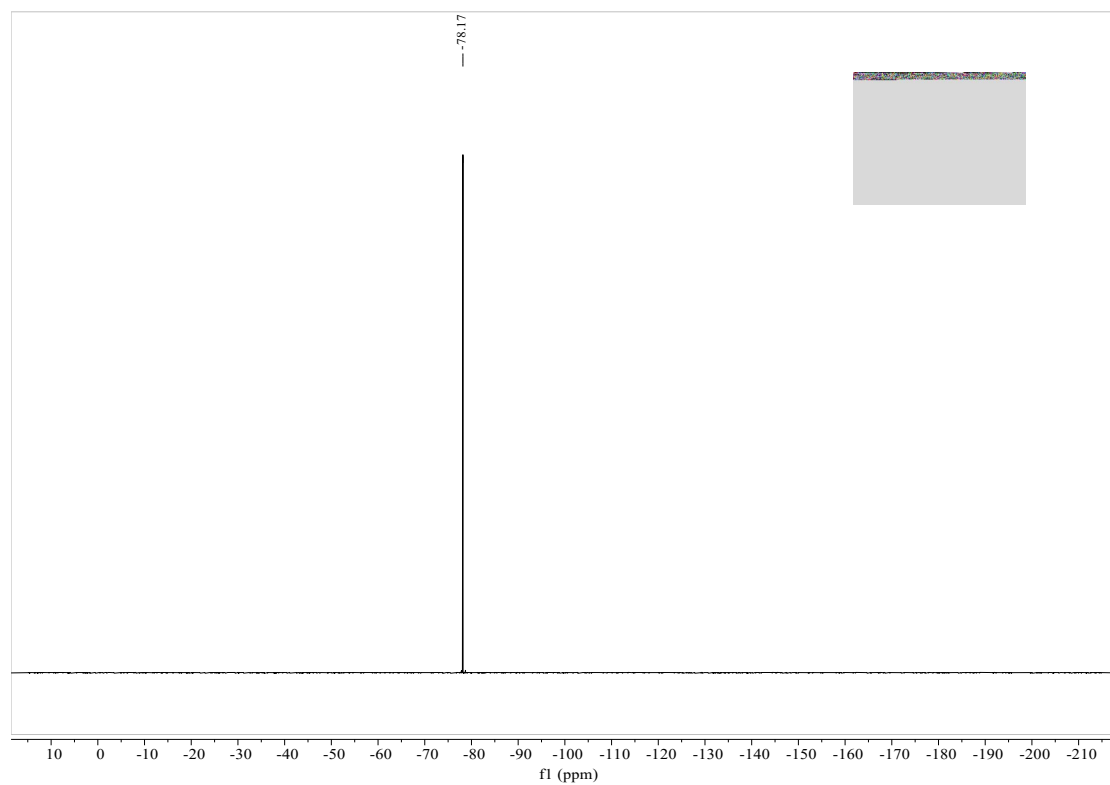


Figure S5-26. ^{19}F NMR (376 MHz, CDCl_3) of $\text{NHP}^+\text{-6}$.

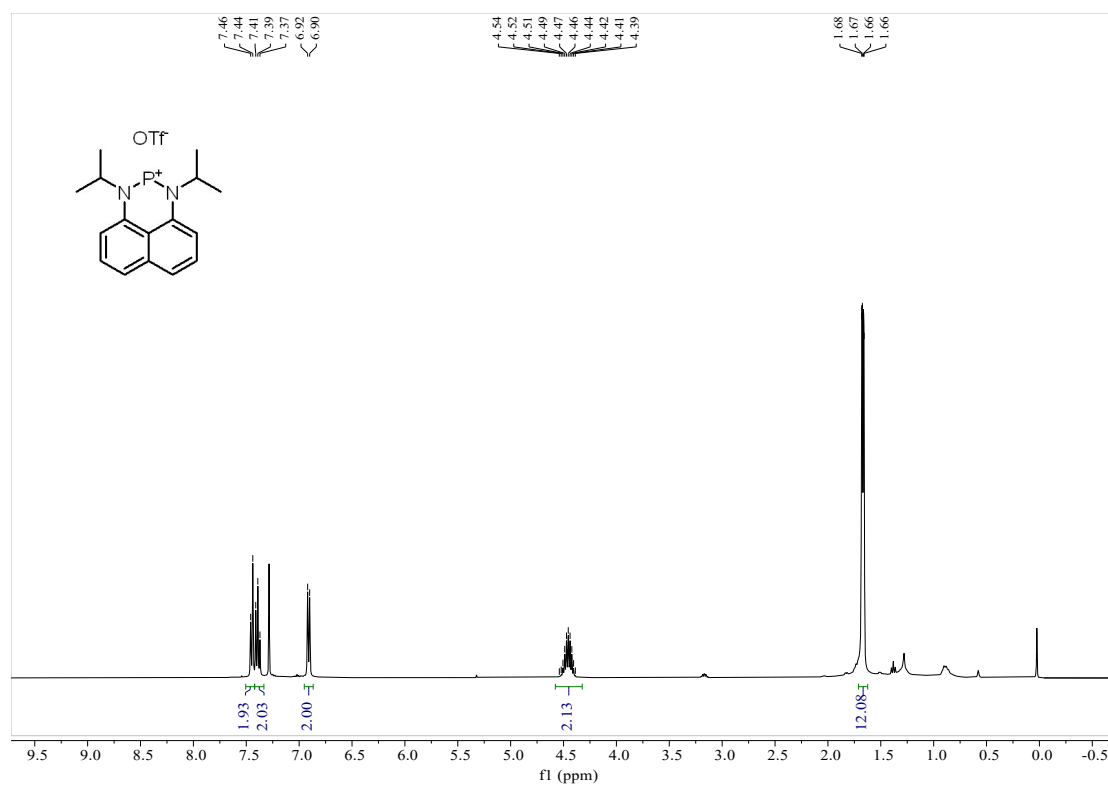


Figure S5-27. ¹H NMR (400 MHz, CDCl₃) of NHP⁺-7.

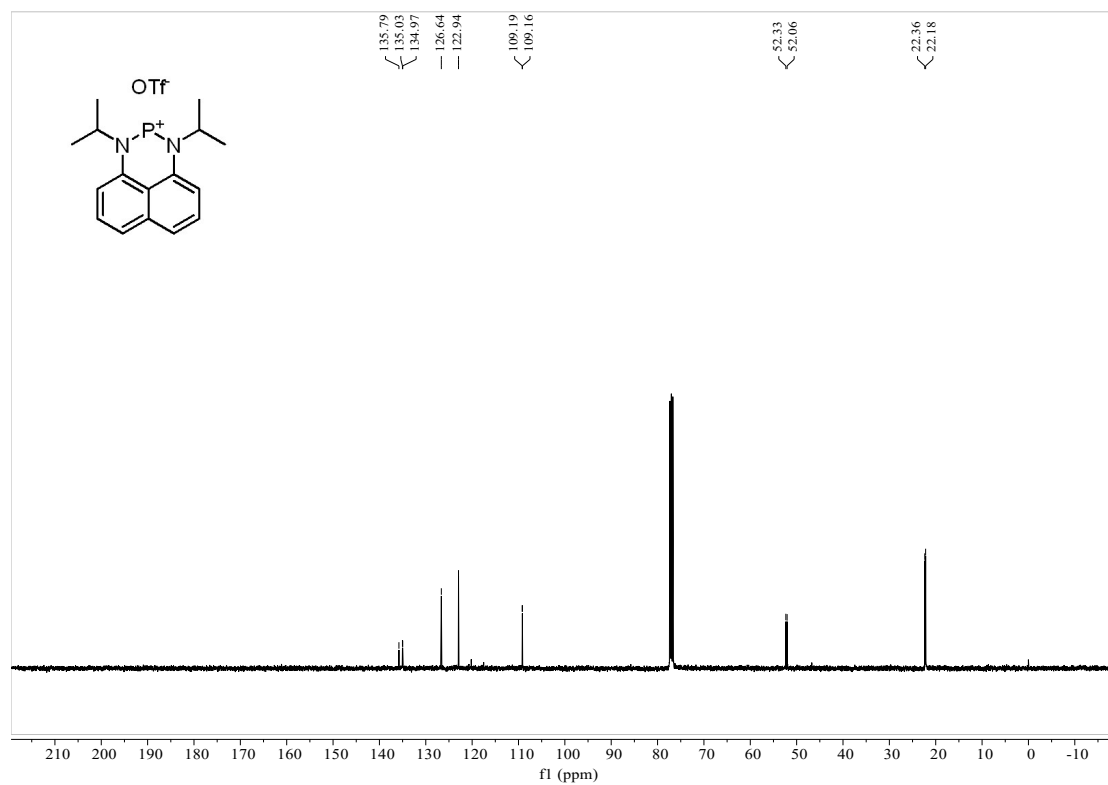


Figure S5-28. ¹³C NMR (101 MHz, CDCl₃) of NHP⁺-7.

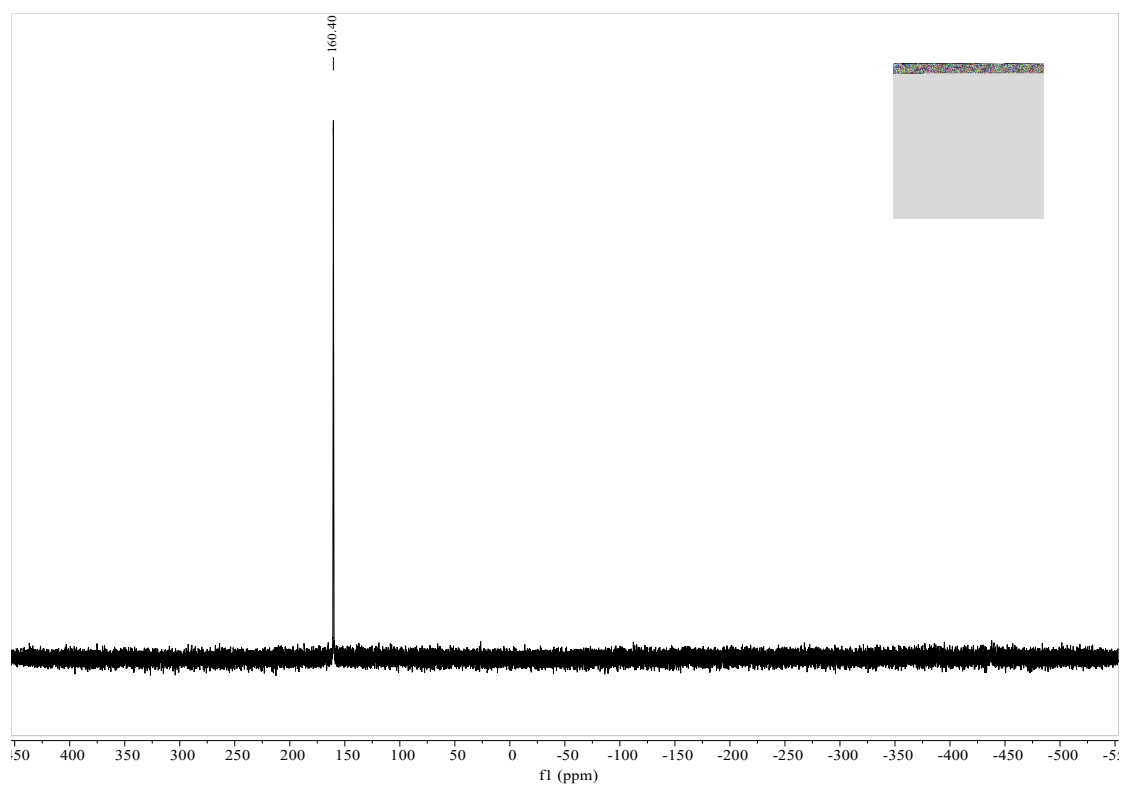


Figure S5-29. ^{31}P NMR (162 MHz, CDCl_3) of NHP^+-7 .

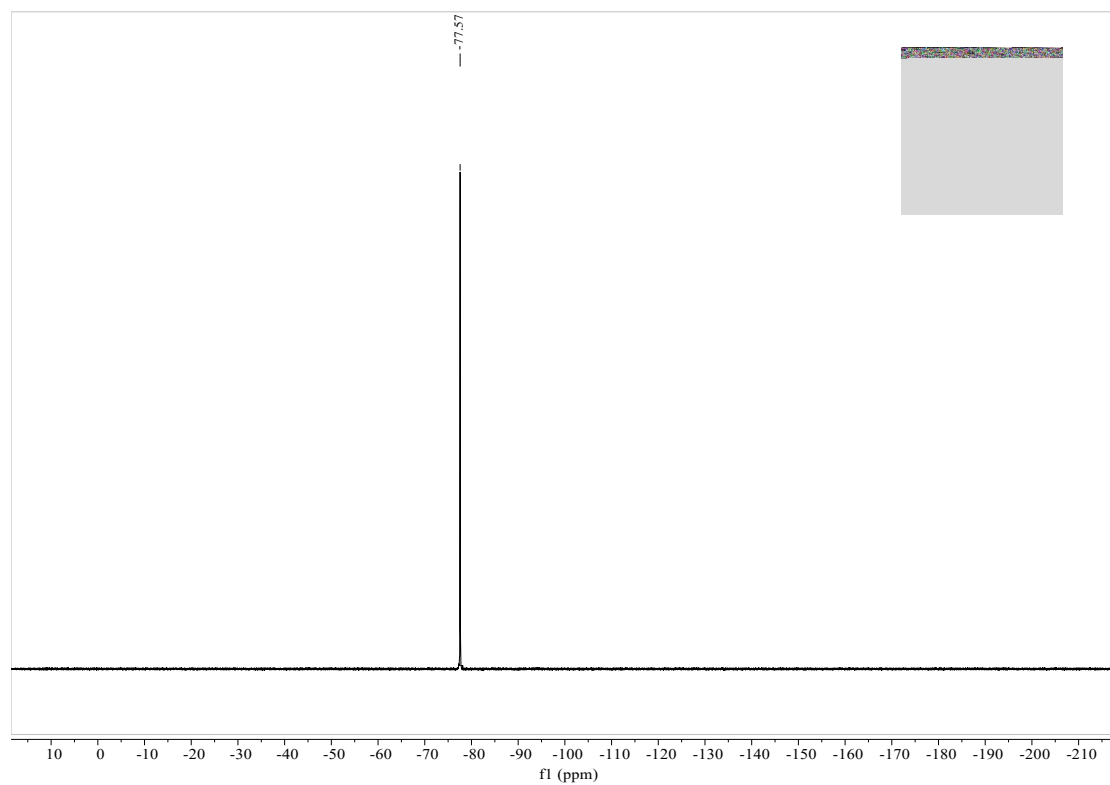


Figure S5-30. ^{19}F NMR (376 MHz, CDCl_3) of NHP^+-7 .

6. References

- (1) M. R. Adams, C.-H. Tien, B. S. N. Huchenski, M. J. Ferguson, A. W. H. Speed, *Angew. Chem. Int. Ed.* **2017**, *56*, 6268-6271.
- (2) D. Gudat, A. Haghverdi, M. Nieger, *Angew. Chem. Int. Ed.*, **2000**, *39*, 3084-3086.
- (3) S. Burck, D. Gudat, M. Nieger, W.-W. Du Mont, *J. Am. Chem. Soc.* **2006**, *128*, 3946-3955.
- (4) J. Zhang, J.-D. Yang and J.-P. Cheng, *Angew. Chem. Int. Ed.*, **2019**, *58*, 5983-5987.
- (5) R. B. King, P. M. Sundaram, *J. Org. Chem.* **1984**, *49*, 1784-1789.
- (6) H. A. Spinney, I. Korobkov, G. A. DiLabio, G. P. A. Yap, D. S. Richeson, *Organometallics* **2007**, *26*, 4972-4982.
- (7) K. Xu, Y.-S. Zhang, B. Zhong, L. Zhang, J.-D. Yang and S. Luo, *J. Am. Chem. Soc.*, 2024, **146**, 25956-25962.
- (8) a) M. F. Alkhater, A. W. Alherz, C. B. Musgrave, *Phys. Chem. Chem. Phys.* **2021**, *23*, 17794-17802. b) J. Zhang, J. -D. Yang and J. -P. Cheng, *Chem. Sci.*, **2020**, *11*, 3672-3679.
- (9) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, **2016**.
- (10) Y. Zhao, D. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.
- (11) T. Lu and F. Chen, *J. Comput. Chem.*, **2012**, *33*, 580-592.
- (12) T. Lu, *J. Chem. Phys.*, **2024**, *161*.
- (13) J. C. Dobrowolski and P. F. J. Lipiński, *RSC Adv.*, **2016**, *6*, 23900-23904.