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Electronic Supplementary Information

Ni Complexes of an Alane/Tris(phosphine) Ligand Built Around a Strongly Lewis Acidic Tris(N-pyrrolyl)aluminum

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Table of Contents

I. General Considerations

Unless otherwise specified, all reactions and manipulations were carried out inside an argon-filled glove box or using Schlenk line techniques. THF, diethylether, toluene, and pentane were dried and deoxygenated via the solvent purification system and stored over molecular sieves in the glove box filled with argon. C_6D_6 were dried over NaK /Ph_2CO/18-crown-6, distilled and stored over molecular sieves in an Ar-filled glove box. Fluorobenzene was dried over CaH_2, distilled and stored over molecular sieves in an Ar-filled glove box. NMR spectra were recorded on a Varian Inova 500 spectrometer (^{1}H NMR, 499.703 MHz, ^{13}C NMR 125.580 MHz), Varian Inova 400 (^{11}B NMR, 128.191 MHz, ^{27}Al NMR, 104.223 MHz) spectrometer. Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference (^{1}H NMR: δ 7.16 for C_6D_6, 5.32 for CD_2Cl_2, 2.08 for d_8-toluene; ^{13}C NMR: δ 128.06 for C_6D_6, 53.84 for CD_2Cl_2, 20.43 for CD_3CN). UV-Vis spectra were collected on a Hitachi U-4100 UV-Vis spectrophotometer. Elemental analyses were performed by CALI Labs, Inc. (Highland Park, NJ). 1H-pyrrole was purchased from Oakwood chemicals, then was dried with CaH_2 and distilled before use. Other chemicals were purchased from commercial vendors and used without further purification. N-tert-butoxycarbonyl-2-bromopyrrole[1] (**1**) and N-tert-butoxycarbonylpyrrole[2] (**6**) were synthesized according to the literature.

II. Synthesis of 1H-2-diisopropylphosphinopyrrole (4).

Method A:

Synthesis of N-tert-butoxycarbonyl-2-diisopropylphosphinopyrrole (3). To a 250 mL Schlenk flask, 19.4 g (78.8 mmol) **1** (prepared according to the previous procedure with 87% purity) was loaded with 100 mL THF. The resulting solution was cooled in an acetone/dry ice bath for 10 min, before 31.5 mL 2.5 M ^{n}BuLi (78.8 mmol, 1.0 equiv) was added drop wise via syringe over a course of 30 min. The colorless solution turned orange upon the addition of ^{n}BuLi solution. Then 13.8 mL $^{i}Pr_2PCl$ (86.6 mmol, 1.1 equiv) was added to the orange solution via a syringe over a course of 30 min. The resulting mixture was allowed to warm up to r.t., and then THF was removed under vacuum. 6.0 g silica gel and 40 mL pentane were added to the residue and stirred at r.t. for 10 min, then was filtered through a short pad of Celite. The colorless pentane filtrate was concentrated under vacuum to afford 21.2 g (85% yield with 87% purity) of **3** as colorless oil.^{1}H NMR (500 MHz, C_6D_6, **Figure S1**) δ 7.54 (dt, *J* = 3.2, 1.6 Hz, pyrrole-*H*, 1H), 6.38 (brs, pyrrole-*H*, 1H), 6.19 (t, *J* = 3.3 Hz, pyrrole-*H*, 1H), 2.13 – 2.06 (m, $(CH_3)_2CH$, 2H), 1.33 (s, $(CH_3)_3C$, 9H), 1.13 (dd, *J* = 14.5, 7.0 Hz, $(CH_3)_2CH$, 6H), 1.10 (dd, J_{C-P} = 14.0, 7.0 Hz, $(CH_3)_2CH$, 6H). $^{13}C\{^{1}H\}$ NMR (125.7 MHz, C_6D_6, **Figure S2**): δ 149.6 (s, C=O), 131.3 (d, J_{C-P} = 29.3 Hz, pyrrole-*C*), 125.1 (s, pyrrole-*C*), 121.2(brs, pyrrole-*C*), 111.4 (s, pyrrole-*C*), 83.5 (s, $(CH_3)_3C$), 27.9 (s, $(CH_3)_3C$), 24.6 (d, J_{C-P} = 14.6 Hz, $(CH_3)_2CH$), 20.4 (d, J_{C-P} = 14.1 Hz, $(CH_3)_2CH$), 19.93 (d, J_{C-P} = 17.0 Hz, $(CH_3)_2CH$). $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, **Figure S3**): δ -5.4 (brs).

Deprotection of N-tert-butoxycarbonyl-2-diisopropylphosphinopyrrole (3) to give crude 4. 21.2 g (74.8 mmol) of **3** with 87% purity was dissolved with 50 mL THF in 250

mL Schlenk flask, which was cooled in a ice/water bath. 40 mL methanol solution containing 20.0 g NaO^{t}Bu (205 mmol, 3 equiv) was degassed by bubbling Ar through for 30 min, then was cannula transferred to the precooled THF solution. The resulting mixture was stirred for 45 min before 40 mL degassed distilled water was added via cannula transferred. The suspension formed after water addition was further stirred at r.t. for 30 min. The desired product was extracted with degassed hexane (3×20 mL). The hexane solution was concentrated to afford 13.7 g (83% yield, 87% pure) of **4** as light yellow oil (**Figure S4** and **Figure S5** NMR spectra before purification).

Purification of 4 via deprotonation followed by reprotonation. 6.77 g (37.0 mmol) of the crude product **4** (87% pure) was loaded in a 100 mL Schlenk flask and dissolved with 30 mL diethyl ether. The solution was cooled in -35 °C for 30 min before the addition of 14.8 mL 2.5 M ^{n}BuLi (37.0 mmol, 1.0 equiv) via syringe. The resulting orange solution was stirred at r.t. for 30 min and then was concentrated under vacuum. The saturated diethyl ether solution was cooled in a -35 °C freezer overnight to yield 7.00 g (60%) of **5** as white crystals. The white crystals **5** was dissolved in 30 mL THF, and then 20 mL degassed water was added via cannula transfer. The resulting suspension was stirred at room temperature for 30 min and then extracted with degassed hexanes. The hexanes extraction was concentrated after passing through a short pad of silica gel to yield 4.6 g (47% based on phosphine) of desired product **4** as white solid. NMR data for **5** follow. ^{1}H NMR (500 MHz, C_6D_6, **Figure S6**) δ 7.53 (s, pyrrole-*H*, 1H), 6.82 (s, pyrrole-*H*, 1H), 6.77 (s, pyrrole-*H*, 1H), 2.11 (septd, J = 7.0, 3.4 Hz, $(CH_3)_2CH$, 2H), 1.19 (dd, J = 14.4, 7.1 Hz, $(CH_3)_2CH$, 6H), 1.15 (dd, J = 11.9, 6.9 Hz, $(CH_3)_2CH$, 6H). $^{13}C\{^1H\}$ (125.7 MHz, C_6D_6, **Figure S7**): δ. 132.15 (d, $J_{C\text{-}P}$ = 12.9 Hz, pyrrole-*C*), 131.64 (d, $J_{C\text{-}P}$ = 17.2 Hz, pyrrole-*C*), 115.72 (s,

pyrrole-*C*), 111.63 (s, pyrrole-*C*), 65.72 (s, *C*$H_2$$CH_3$), 24.49 (d, $J_{C\text{-}P}$ = 5.9 Hz, (CH_3)$_2$*C*H), 20.62 (d, $J_{C\text{-}P}$ = 15.4 Hz, (*C*H_3)$_2$CH), 20.08 (d, $J_{C\text{-}P}$ = 8.8 Hz, (*C*H_3)$_2$CH), 14.35 (s, CH_2*C*H_3). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, **Figure S8**): δ -6.6 (brs).

Method B:

A 300-mL round bottom flask was charged with TMP (7.6 g, 54 mmol) and THF (50 mL). The solution was cooled to -78 °C in a dry ice/acetone bath. To the TMP solution, n-BuLi (2.5 M, 21 mL, 52.5 mmol) was added slowly via syringe. The solution was stirred for 10 min in the dry ice/acetone bath before being placed in an ice water bath for 20 min. After the 20 min, the solution was placed back in the dry ice/acetone bath and allowed to cool for 5 min. N-Boc pyrrole[2] **6** (8.4 g, 50 mmol) in THF (12 mL) was added dropwise via an addition funnel. The solution began to turn orange before becoming opaque and brown. The resultant solution was stirred for 20 min then transferred via cannula to a flask containing diisopropylchlorophosphine (8.6 g, 56 mmol) cooled in a dry ice/acetone bath. The reaction was stirred for 1 h. After 1 h, a degassed solution of sodium methoxide (formed by stirring sodium *tert*-butoxide (28 g, 250 mmol) in degassed methanol (80 mL)) was cannula transferred into the phosphine solution and then stirred for 3 hours. Volatiles were removed under reduced pressure and the crude extracted with water (100 mL) and ethyl acetate (3 × 50 mL) and concentrated under vacuum to afford a black/brown oil. The final product **4** was isolated via vacuum distillation as an oil and then recrystallized from isooctane to afford a white solid (6.6 g, 75% yield) in above 95% purity. ^1H NMR (500 MHz, C_6D_6, **Figure S9**) δ 7.45 (brs, pyrrole-N*H*, 1H), 6.52 – 6.49 (m, pyrrole-*H*, 2H), 6.37 (dd, *J* = 5.3, 2.6 Hz, pyrrole-*H*, 1H), 1.91 – 1.78 (dsept, *J* = 7.0, 1.0 Hz, (CH_3)$_2$C*H*, 2H), 1.01 (dd, *J* = 15.8, 7.0 Hz, (C*H*$_3$)$_2$CH, 6H), 0.95 (dd, *J* = 11.1, 6.9 Hz, (C*H*$_3$)$_2$CH, 6H).

$^{13}C\{^{1}H\}$ (125.7 MHz, C_6D_6, **Figure S10**): δ 19.7 (d, $J_{C\text{-}P}$ = 7.5 Hz, (CH_3)$_2$CH), 20.8 (d, $J_{C\text{-}P}$ = 19.0 Hz, (CH_3)$_2$CH), 24.4 (d, $J_{C\text{-}P}$ = 7.9 Hz, (CH$_3$)$_2$*C*H), 110.3 (d, $J_{C\text{-}P}$ = 3.5 Hz, pyrrole-*C*), 117.6 (d, $J_{C\text{-}P}$ = 7.7 Hz, pyrrole-*C*), 121.5 (d, $J_{C\text{-}P}$ = 4.6 Hz, pyrrole-*C*), 124.3 (d, $J_{C\text{-}P}$ = 12.7 Hz, pyrrole-*C*). $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, **Figure S11**): δ -10.1 (s).

III. Synthesis of AlP_3 and its Ni complexes.

Synthesis of AlP_3 (7). To a 10 mL toluene solution dissolving 272 mg of **4** (1.5 mmol) in a culture tube, 250 µL $AlMe_3$ solution (0.50 mmol, 2.0 M in heptane) was added. The culture tube was then heated in a 80 °C oil bath for 2 h. All the volatile was removed under vacuum to afford 312 mg (98% yield) a light orange oil. The ligand was used without further purification (purity is greater than 95% according to $^{31}P\{^1H\}$ NMR). ^1H NMR (500 MHz, C_6D_6, **Figure S12**) δ 7.54 (d, *J* = 0.9 Hz, 3H, pyrrole-*H*), 6.79 – 6.74 (m, 3H, pyrrole-*H*), 6.60 (d, *J* = 3.0 Hz, 3H, pyrrole-*H*), 1.93 – 1.87 (m, 6H, $(CH_3)_2CH$), 0.96 – 0.92 (m, 36H, $(CH_3)_2CH$). $^{13}C\{^1H\}$ (125.7 MHz, C_6D_6, **Figure S13**): δ $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, **Figure S14**): δ -4.0 (s).

Synthesis of Ni(AlP_3) (8). To a top-screw cap culture tube, 340 mg (0.59 mmol) of **7** was loaded with 163 mg $Ni(COD)_2$ (0.59 mmol, 1.0 equiv) in 10 mL toluene. The resulting light green solution was heated in 100 °C oil bath for 4 h and turned deep green. The deep green solution was filtered through a short pad of Celite, then removed toluene under vacuum to afford green solid. The crude **8** was recrystallized by slow diffusion pentane into concentrated toluene solution in the freezer, and 280 mg (75%) dark green crystal was obtained. Single crystal was obtained via slow diffusion of vapor pentane into a concentrated toluene solution. ^1H NMR (500 MHz, C_6D_6, **Figure S15**): δ 7.05 (brs, 3H, pyrrole-*H*), 6.69 (d, J = 2.9 Hz, 3H pyrrole-*H*), 6.63 – 6.62 (m, 3H, pyrrole-*H*), 2.51 (m, 6H, $(CH_3)_2CH$), 1.10 (br, 18H, $(CH_3)_2CH$), 0.85 (bm, 18H, $(CH_3)_2CH$). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, **Figure S16**): δ 13.0 (s). $^{27}Al\{^1H\}$ NMR (104 MHz, C_6D_6, **Figure S17**): δ 104.4 (brs). UV-Vis (in toluene, **Figure S18**): nm (ε [$L \cdot mol^{-1} \cdot cm^{-1}$]) 342 (1900), 460 (2220),

616 (520). calcd for $C_{30}H_{51}NiAlP_3N_3$: C 56.98; H 8.13, N 6.65; found: C 56.81; H 8.07; N 6.46.

Reaction of 8 with 1 atm H_2 to form 8-H_2. To a J. Young tube, 12.6 mg of **3** (0.02 mmol) was loaded with 0.5 mL C_6D_6. The solution was degassed via freeze-pump-thaw 3 cycles and then back filled with 1 atm H_2. The dark green solution turned pale green (almost colorless) within 5 min. ^{1}H NMR (500 MHz, C_6D_6, 298K, **Figure S19**): δ 7.27 (s, 3H, pyrrole-*H*), 6.67 (d, *J* = 3.0, 2.4 Hz, 3H, pyrrole-*H*)), 6.57 (dd, *J* = 3.1, 0.6 Hz, 3H, pyrrole-*H*), 2.08 (m, 6H, $(CH_3)_2CH$), 0.96 (dd, *J* = 13.6, 6.8 Hz, 18H, $(CH_3)_2CH$), 0.52 (dd, *J* = 5.2 Hz, 18H, $(CH_3)_2CH$), -2.09 (brs, 2H). ^{1}H NMR (500 MHz, d_8-toluene, 193K, **Figure S20**) δ 7.30 (s, 3H, pyrrole-*H*), 6.78 (s, 3H, pyrrole-*H*)), 6.57 (s, 3H, pyrrole-*H*), 2.16 (m, 3H, $(CH_3)_2CH$), 1.73 (m, 3H, $(CH_3)_2CH$), 0.97 (brs, 9H, $(CH_3)_2CH$), 0.79 (brs, 18H, $(CH_3)_2CH$), 0.02 (brs, 9H, $(CH_3)_2CH$), -2.49 (brs, 2H). ^{31}P{^{1}H} NMR (202 MHz, d_8-toluene, **Figure S21**): δ 24.3 (s). ^{27}Al{^{1}H} NMR (104 MHz, C_6D_6, **Figure S22**): δ 138.0 (brs).

Variable-Temperature Spectroscopic Analysis of 8-H_2. To a J. Young tube, 12.6 mg of **8** (0.02 mmol) was loaded with 0.5 mL d_8-toluene. 3 cycles of freeze-pump-thaw were performed to evacuate the headspace of the J. Young tube before 1 atm H_2 was back filled. The resulting **8-H_2** pale green solution was cooled from 25 °C to -80 °C and monitored by ^{1}H NMR. Upon cooling, the bound H_2 resonance sharpens and free H_2 resonance appears as a broad signal at 253 K, which is not visible at r.t. T1 values for **8-H_2** above 253 K could not be reliably obtained due to the quick exchange of free and bounded H_2 at those temperatures. T_1 = 22 ms was observed at 228 K for **8-H_2**

Table S1. Variable temperature T1 inversion recovery data collected on hydride resonance at -2.1 ppm in toluene-d8 for **8-H$_2$** using a Varian iNova 500 MHz spectrometer.

T(temperature/K)	T1/ms
228	22.2(2)
223	24.2(1)
218	26.1(2)
213	28.6(2)
208	36.0(4)
203	43.9(8)
198	56.6(2)
193	98(3)

Variable-Temperature Spectroscopic Analysis of 8-HD. To a J. Young tube, 12.6 mg of **8** (0.02 mmol) was loaded with 0.5 mL d_8-toluene. 3 cycles of freeze-pump-thaw were performed to evacuate the headspace of the J. Young tube before 1 atm HD was back filled. HD gas was generated by treating D_2O with excess CaH_2 in a top-screw-cap Schlenk flask, where the head space was evacuated via freeze-pump-thaw cycle before mixing. The pale green solution containing mixture of **8-H$_2$** and **8-HD** was cooled from 25 to -80 °C and monitored by ^{1}H NMR. ^{1}H NMR (500 MHz, d_8-toluene, 203K, **Figure S24**): δ 7.31 (s, 3H, pyrrole-*H*), 6.80 (s, 3H, pyrrole-*H*)), 6.58 (s, 3H, pyrrole-*H*), 2.17 (m, 3H, $(CH_3)_2CH$), 1.73 (m, 3H, $(CH_3)_2CH$), 0.96 (br s, 9H, $(CH_3)_2CH$), 0.79 (br s, 18H, $(CH_3)_2CH$), 0.01 (br s, 9H, $(CH_3)_2CH$), -2.50 (t, J_{HD} = 35 Hz, *H*D).

Reaction of 8 with 1 atm CO to form 8-CO. To a J. Young tube, 12.6 mg of **3** (0.02 mmol) was loaded with 0.5 mL C_6D_6. The solution was degassed via freeze-pump-thaw 3 cycles and then back filled with 1 atm CO. The solution turned orange immediately upon refilling with CO. ^{1}H NMR (500 MHz, C_6D_6, **Figure S25**): δ 7.21 (br s, 3H, pyrrole-*H*),

6.65 (dd, *J* = 3.2, 2.2 Hz, 3H, pyrrole-*H*)), 6.55 (dd, *J* = 3.1, 0.6 Hz, 3H, pyrrole-*H*), 2.24 – 2.21 (m, 6H, $(CH_3)_2CH$), 1.05 (q, *J* = 6.6 Hz, 18H, $(CH_3)_2CH$), 0.63 (q, *J* = 7.2 Hz, 18H, $(CH_3)_2CH$. ^{1}H NMR (500 MHz, C_6D_6, **Figure S26**): δ 209.41 (br s, *C*O), 129.62 – 128.73 (m, pyrrole-*C*), 127.19 (dd, *J* = 10.2, 5.3 Hz, , pyrrole-*C*), 115.46 (s, pyrrole-*C*), 113.43 (s, pyrrole-*C*), 28.69 (ddd, *J* = 17.0, 10.1, 3.4 Hz, $(CH_3)_2CH$), 18.92 (s, $(CH_3)_2CH$), 17.84 (s, $(CH_3)_2CH$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, **Figure S27**): δ 25.9 (s). ^{27}Al{^{1}H} NMR (104 MHz, C_6D_6, **Figure S28**): δ 144.8 (br s). IR (ATR, cm^{-1}, **Figure S29**): 1972 cm^{-1}.

IV. NMR Spectra

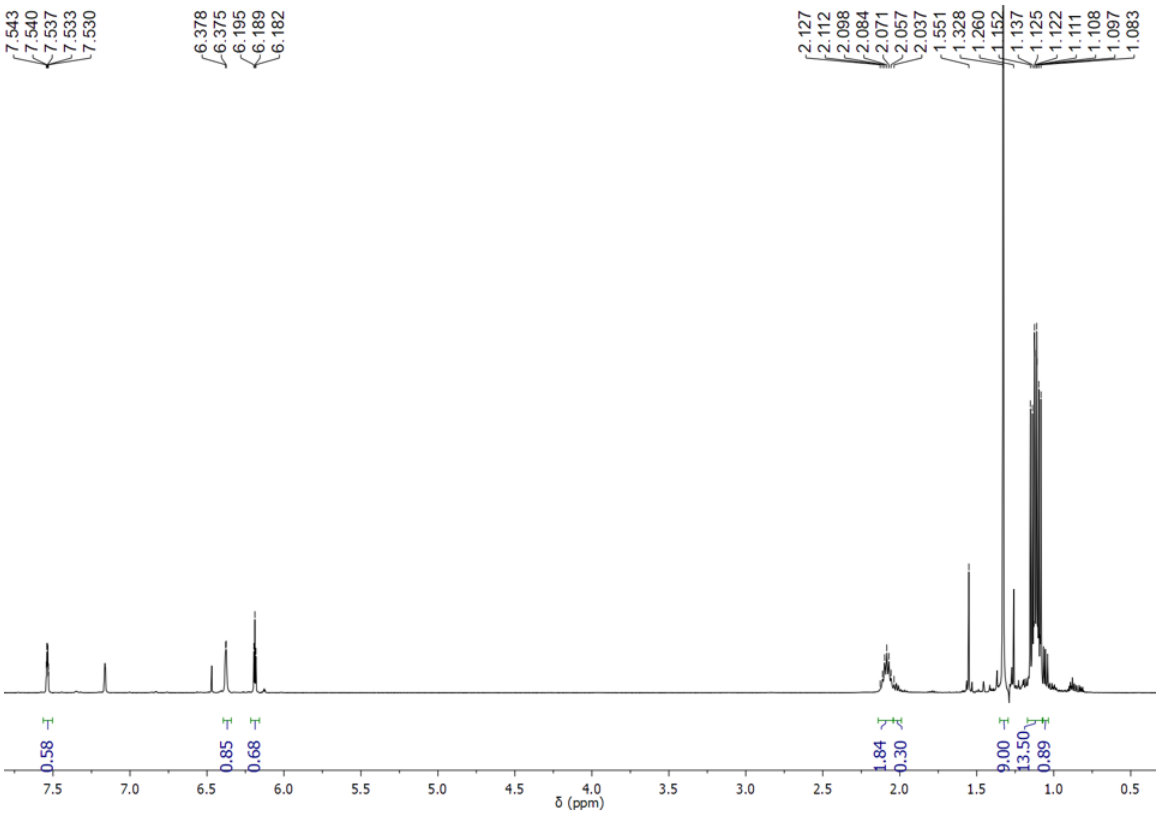

Figure S1. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **3**

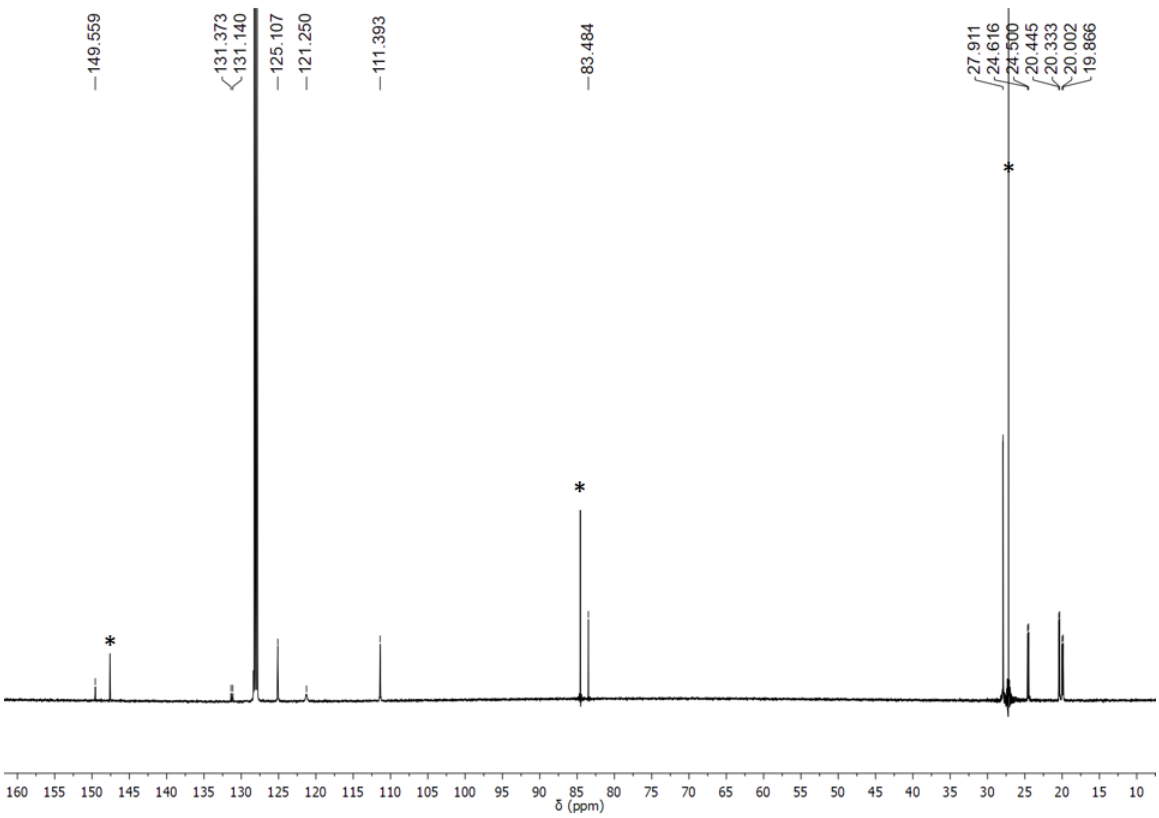

Figure S2. $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6) spectrum of **3** (the impurity BOC_2O was denoted by *). The spectrum was collected after treating the pure **4** with BOC_2O.

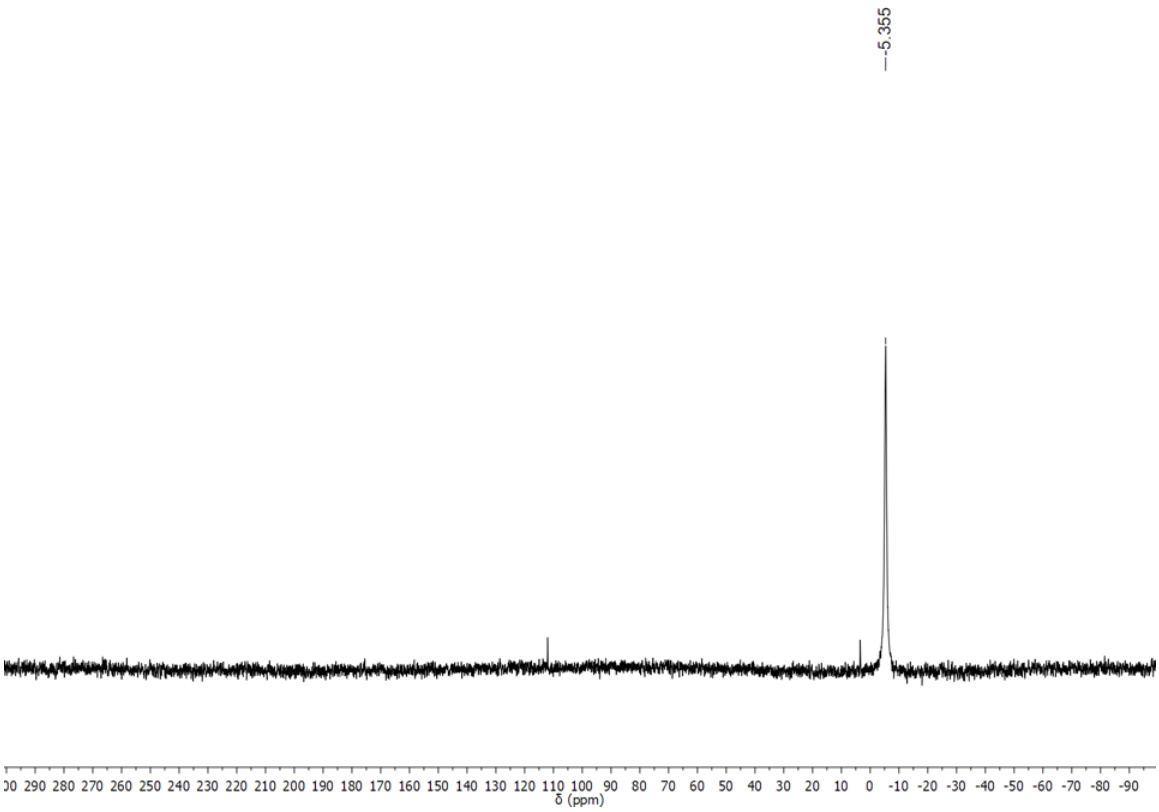

Figure S3. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6) spectrum of **3**.

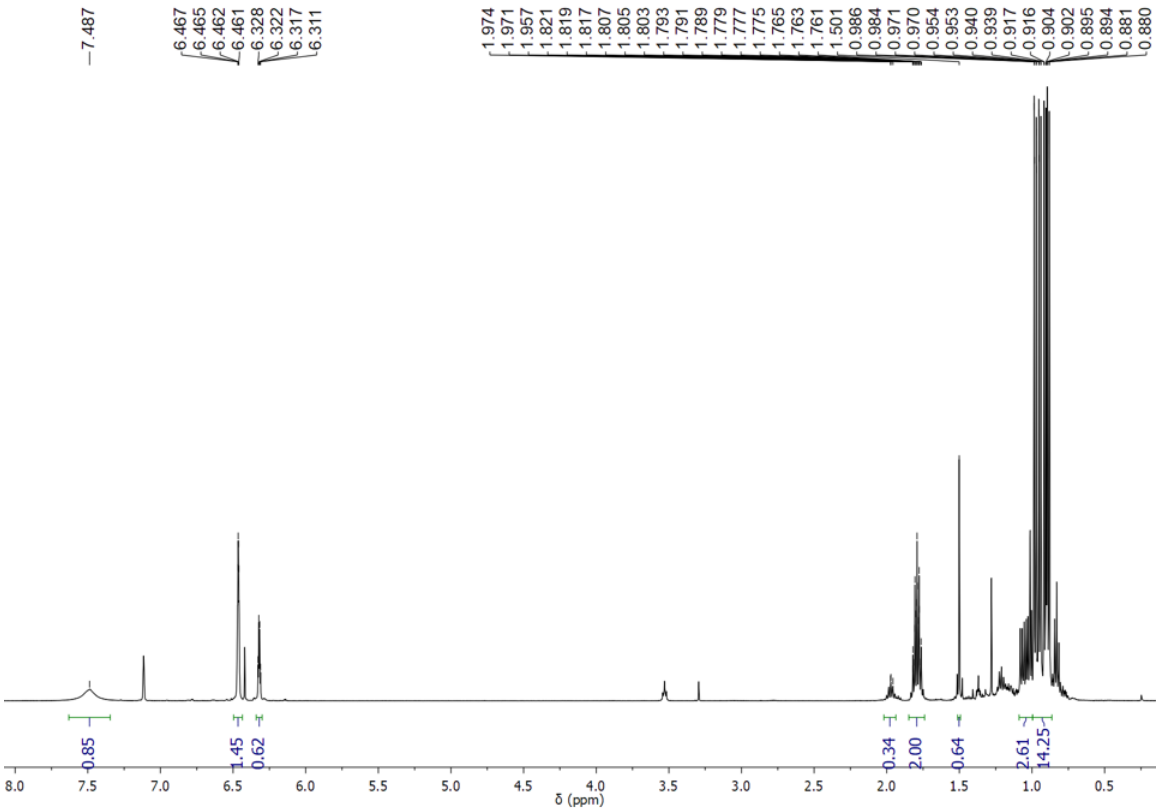

Figure S4. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **4** before purification.

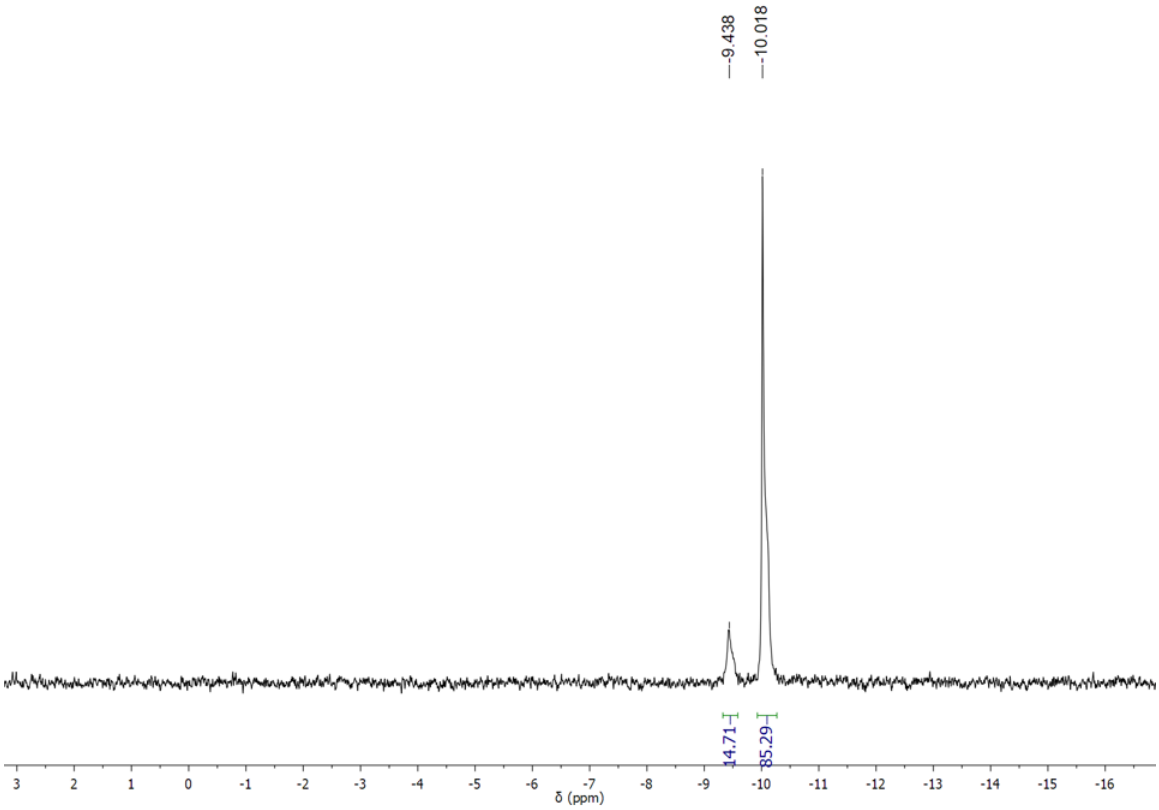

Figure S5. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6) spectrum of **4** before purification.

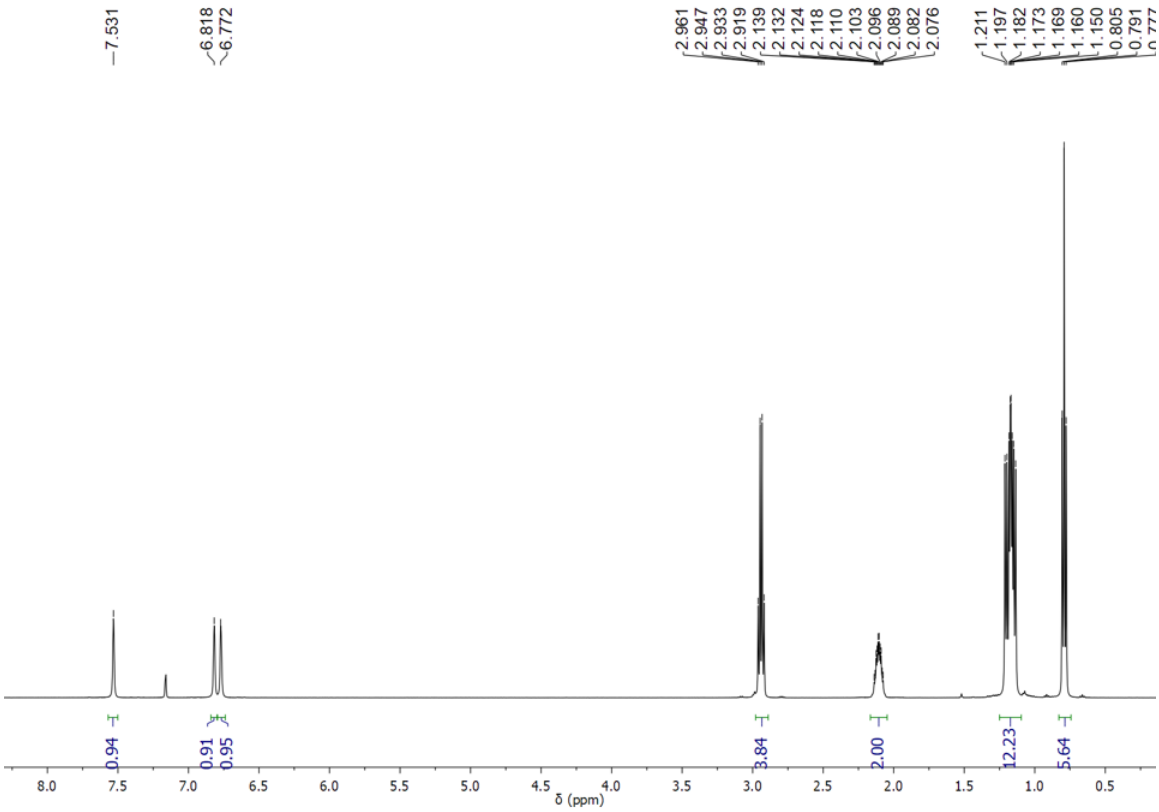

Figure S6. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **5**.

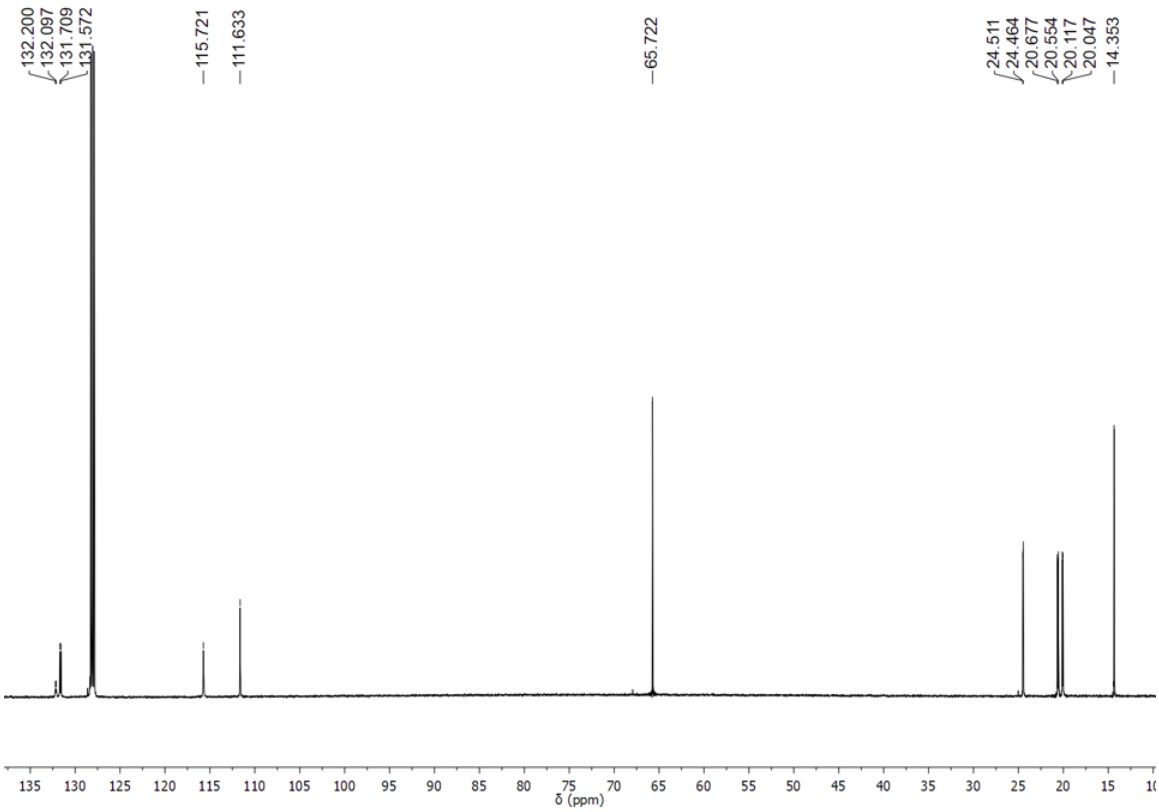

Figure S7. $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6) spectrum of **5.**

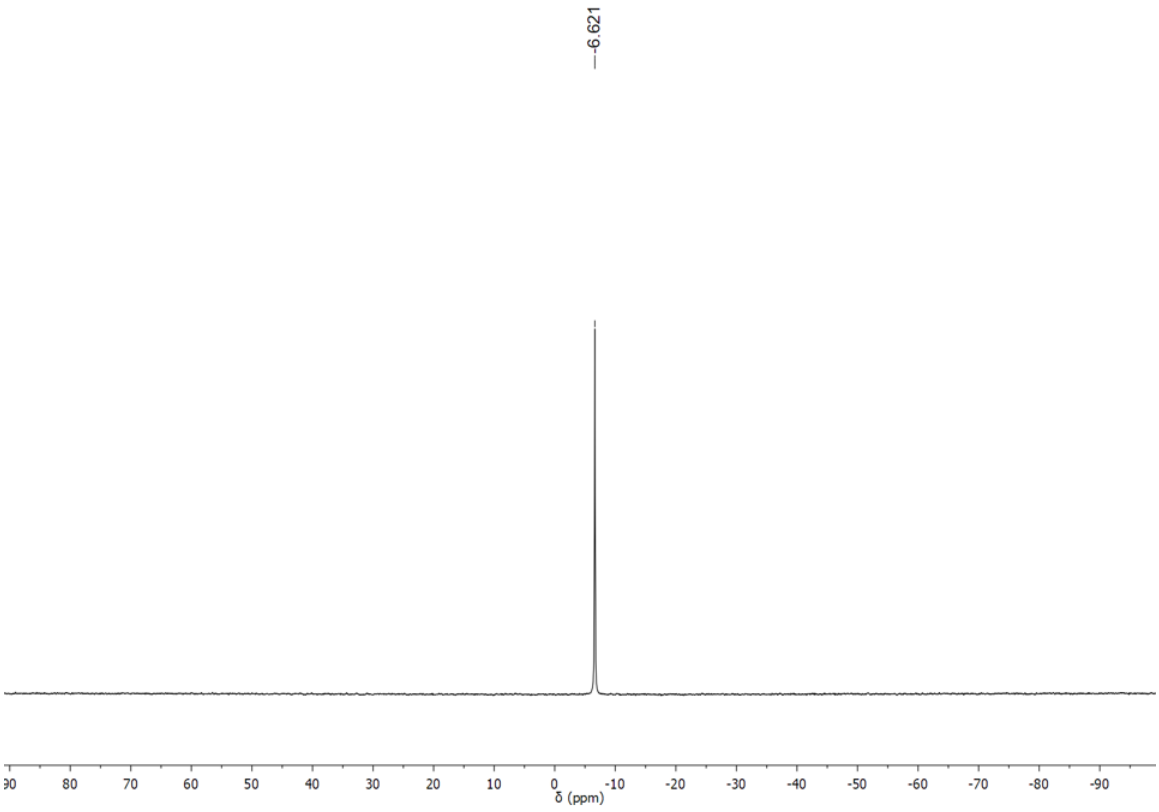

Figure S8. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6) spectrum of **5**.

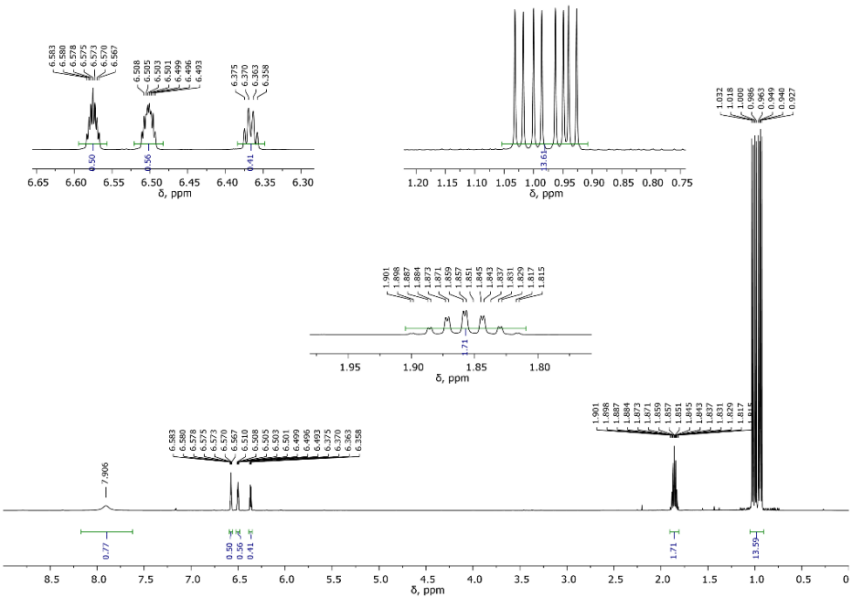

Figure S9. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **4**.

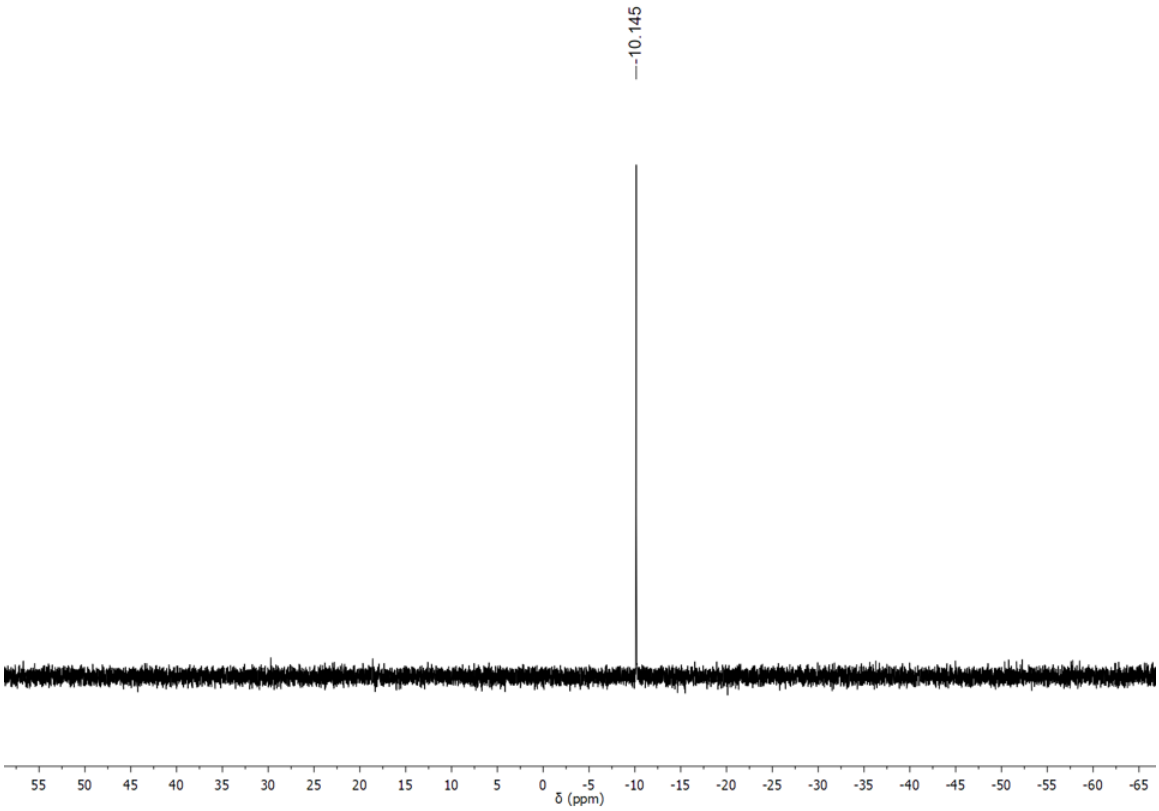

Figure S10. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6) spectrum of **4**.

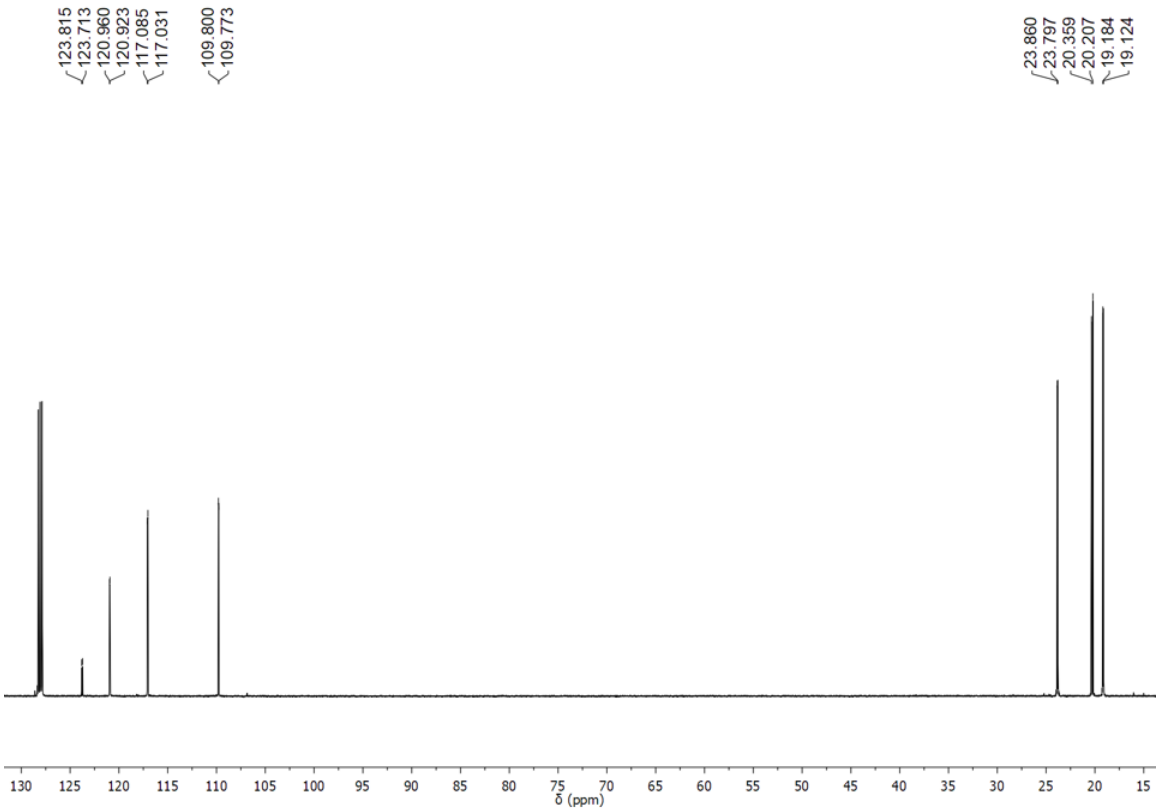

Figure S11. $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6) spectrum of **4**.

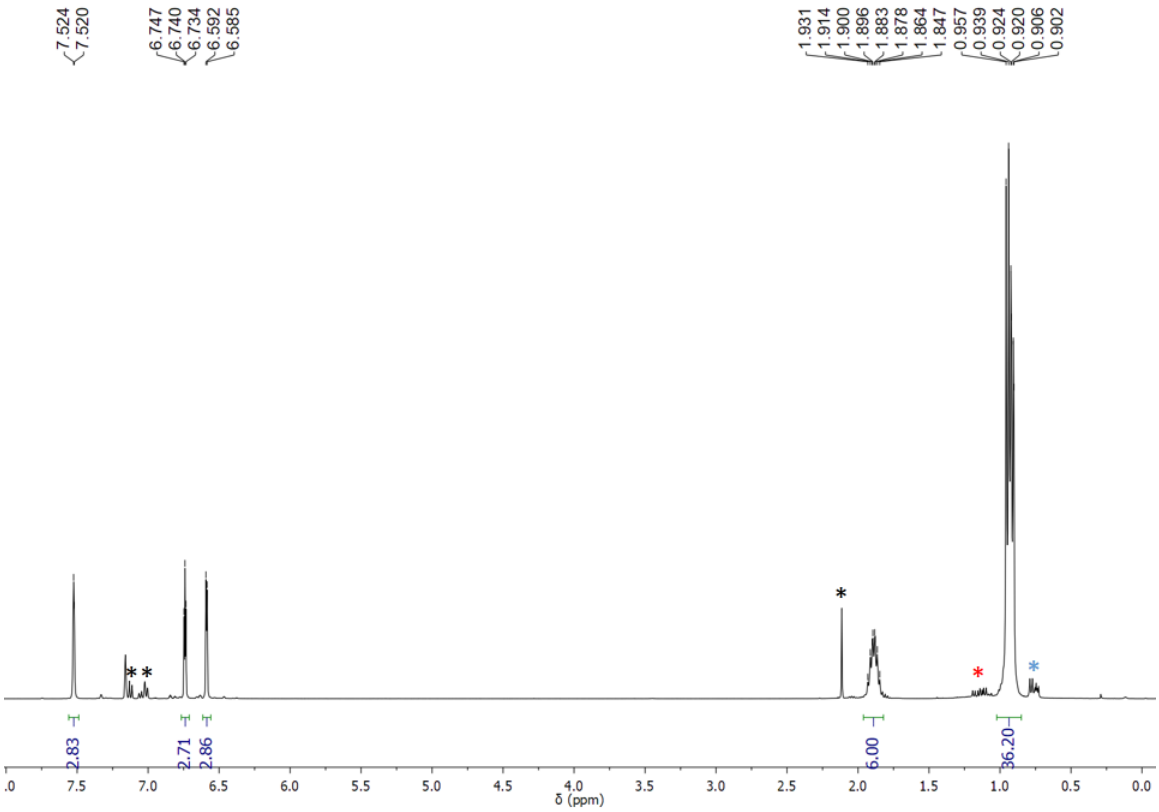

Figure S12. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **AlP$_3$** (toluene resonances are denoted *, other unknowns containing phosphine are denoted by * and *).

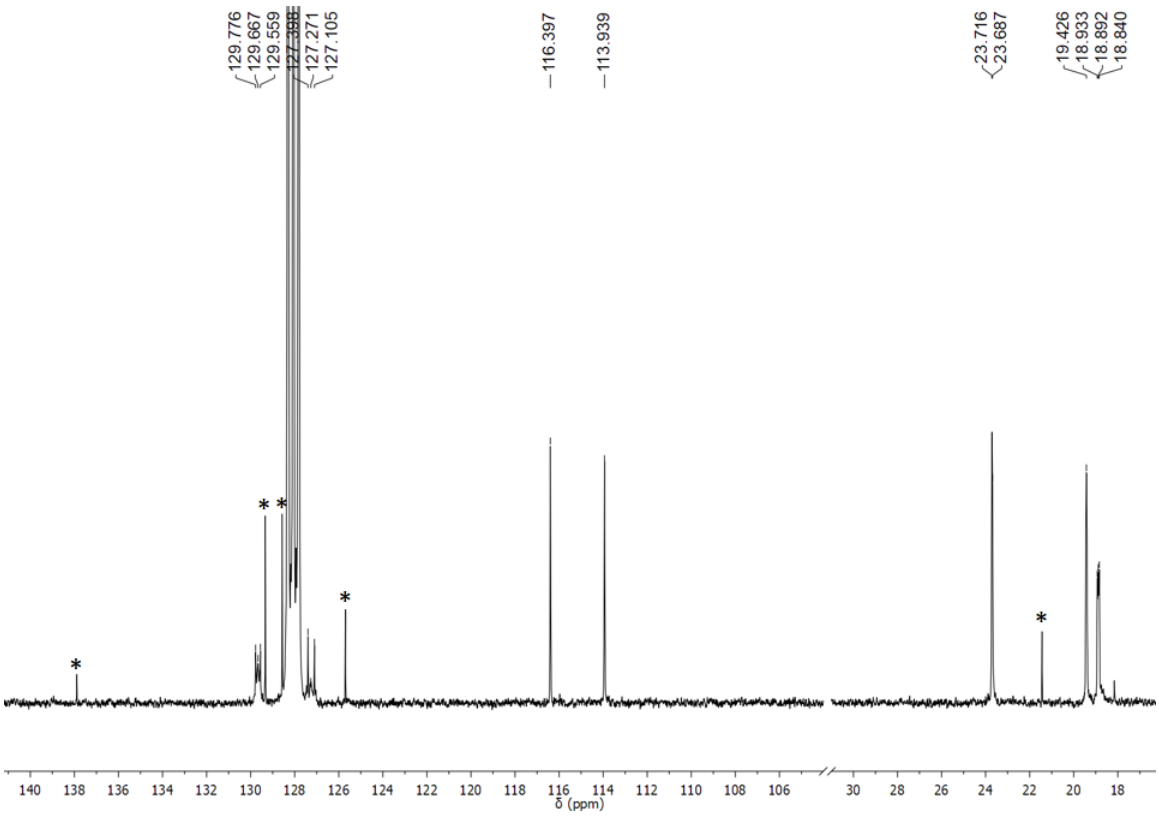

Figure S13. $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6) spectrum of **AlP_3** (toluene residual signals are denoted by*).

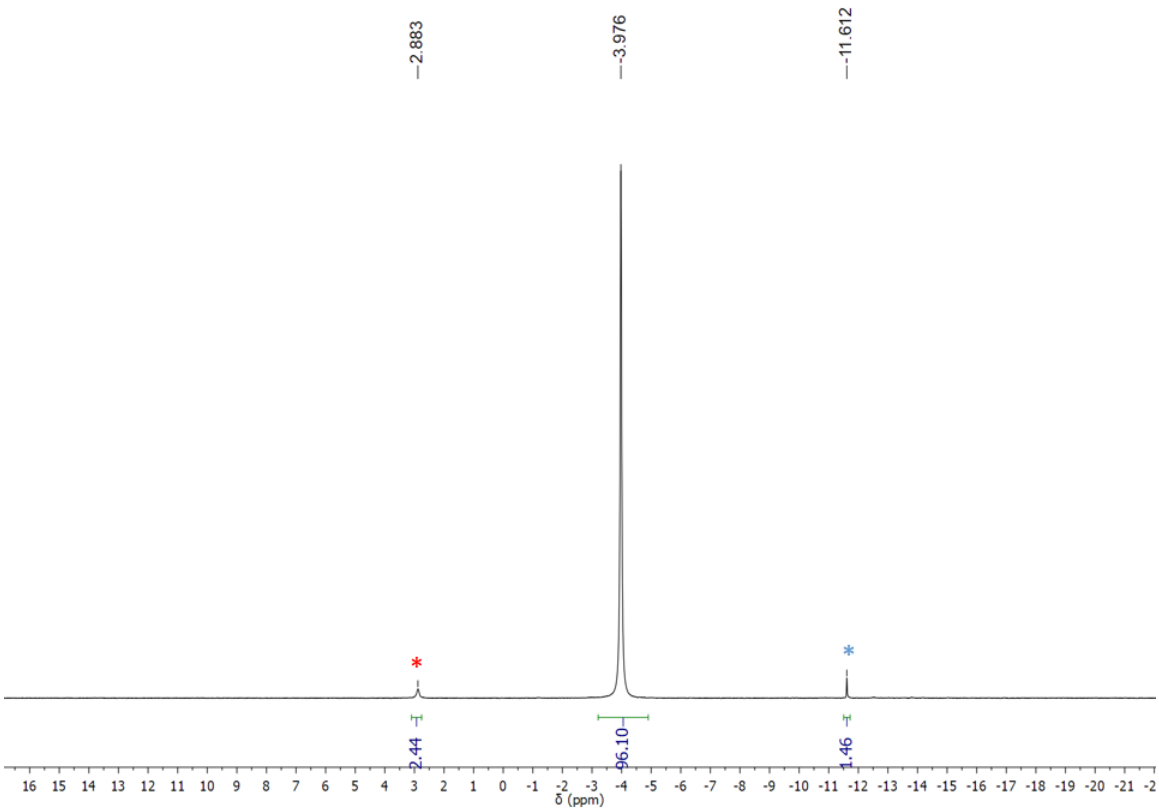

Figure S14. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6) spectrum of **AlP_3** (unknown phosphine resonance is denoted by * and *).

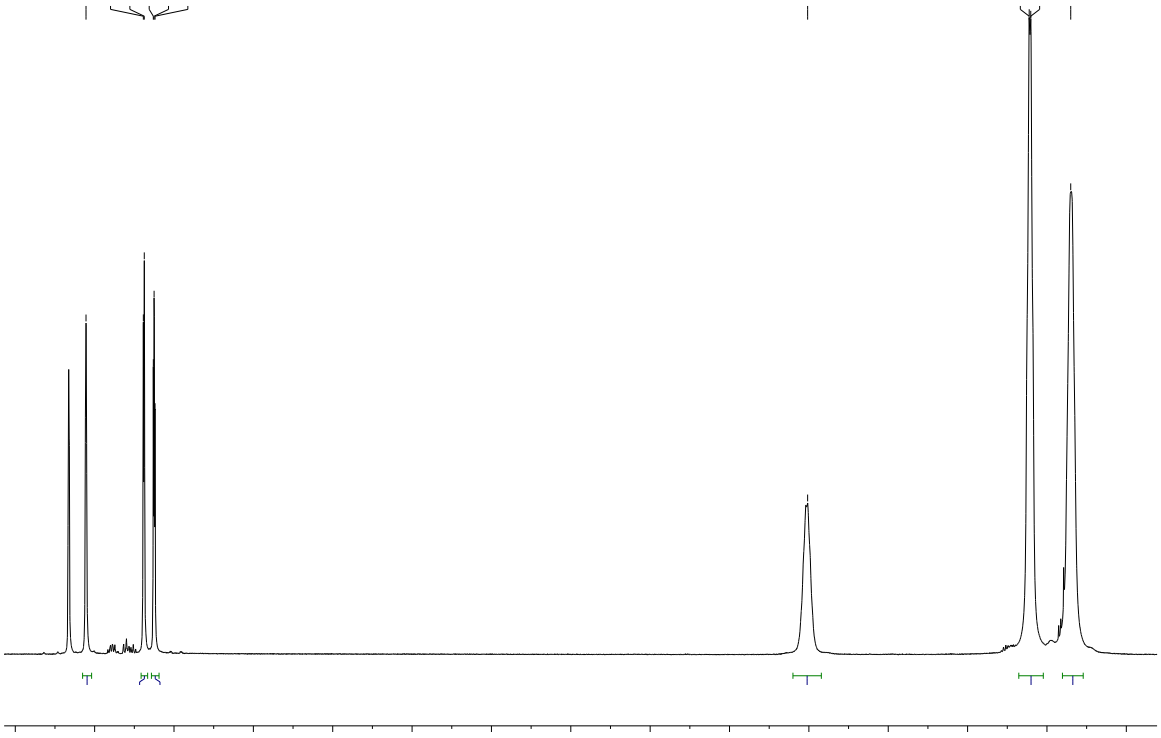

Figure S15. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **8** (fluorobenzene and pentane resonances are denoted by * and # respectively).

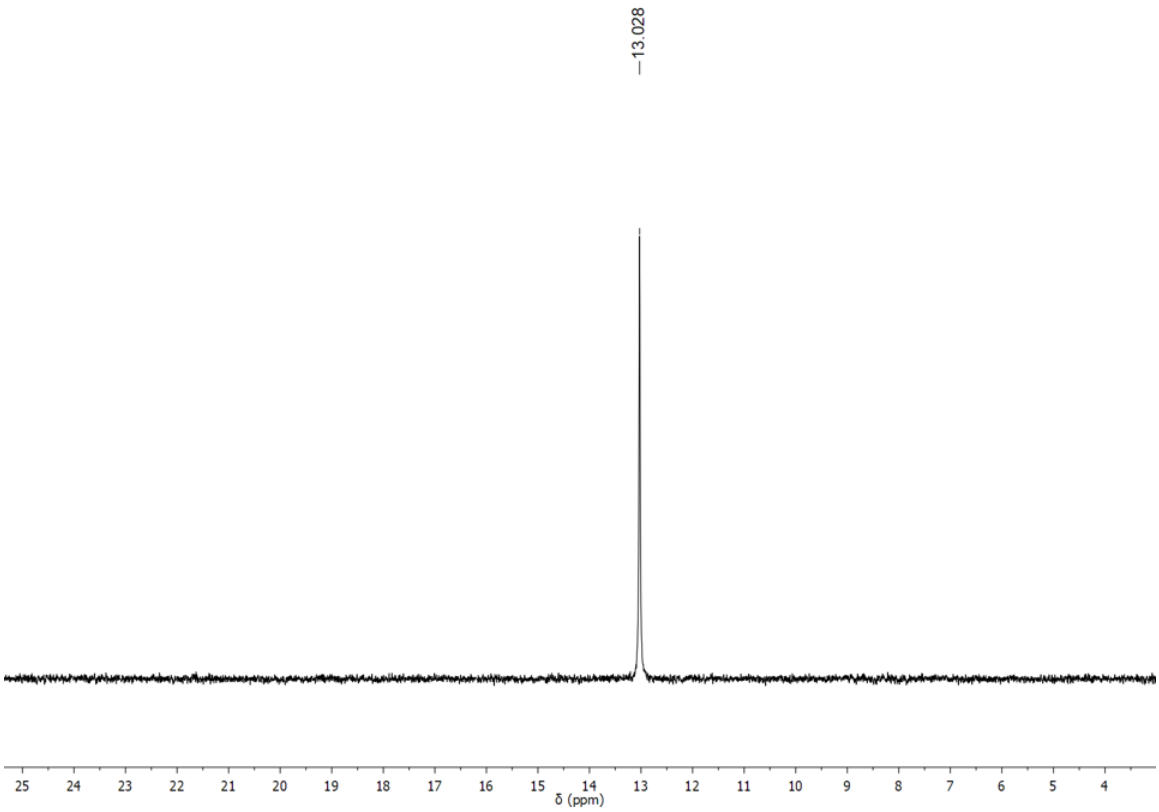

Figure S16. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6) spectrum of **8**.

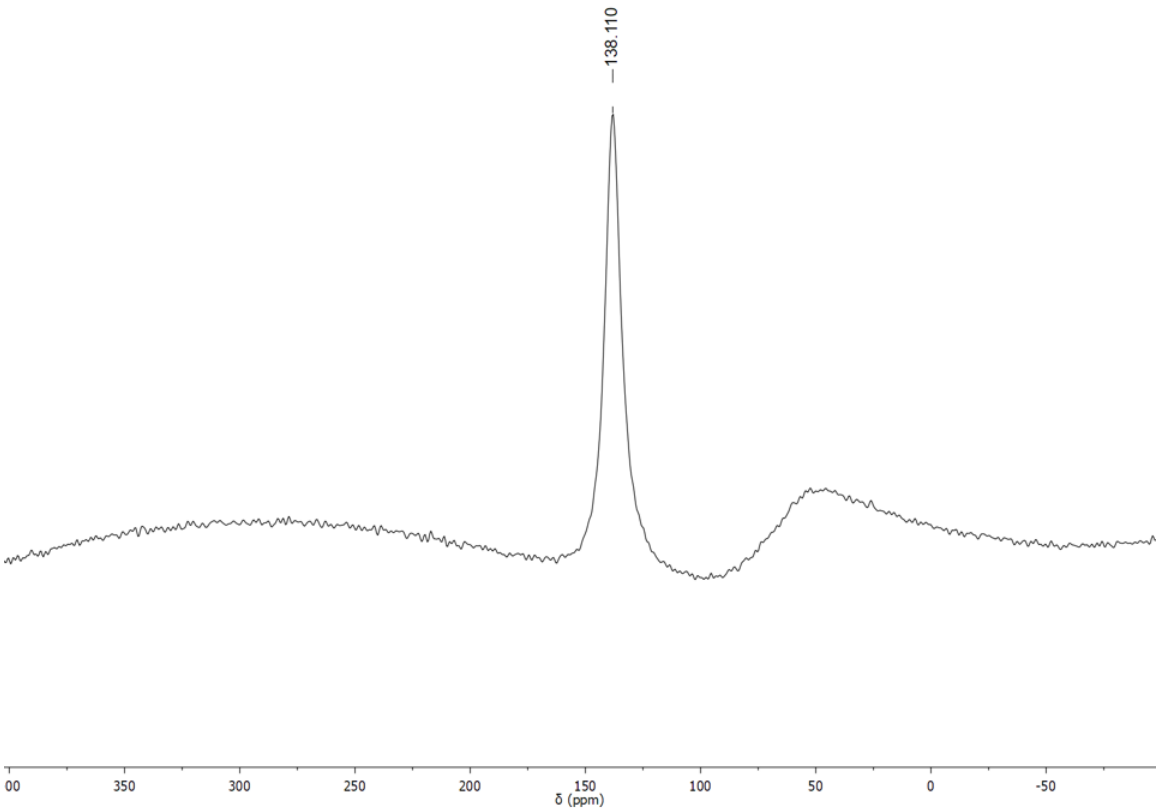

Figure S17. $^{27}Al\{^{1}H\}$ NMR (104 MHz, C_6D_6) spectrum of **8**.

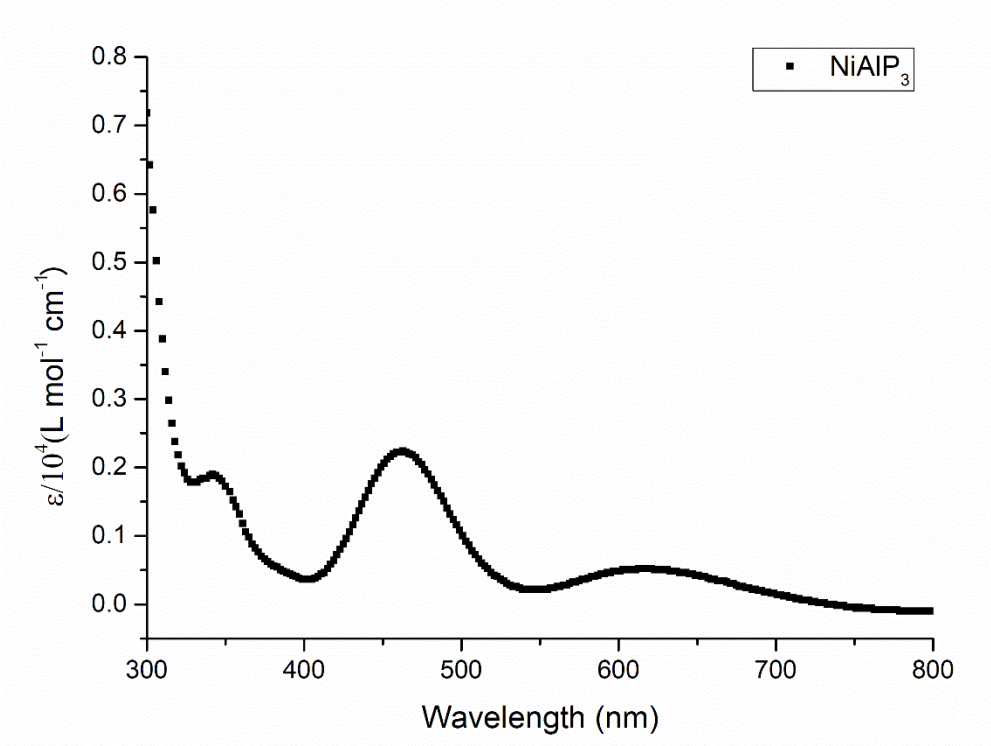

Figure S18. UV-Vis spectrum of **8** in toluene.

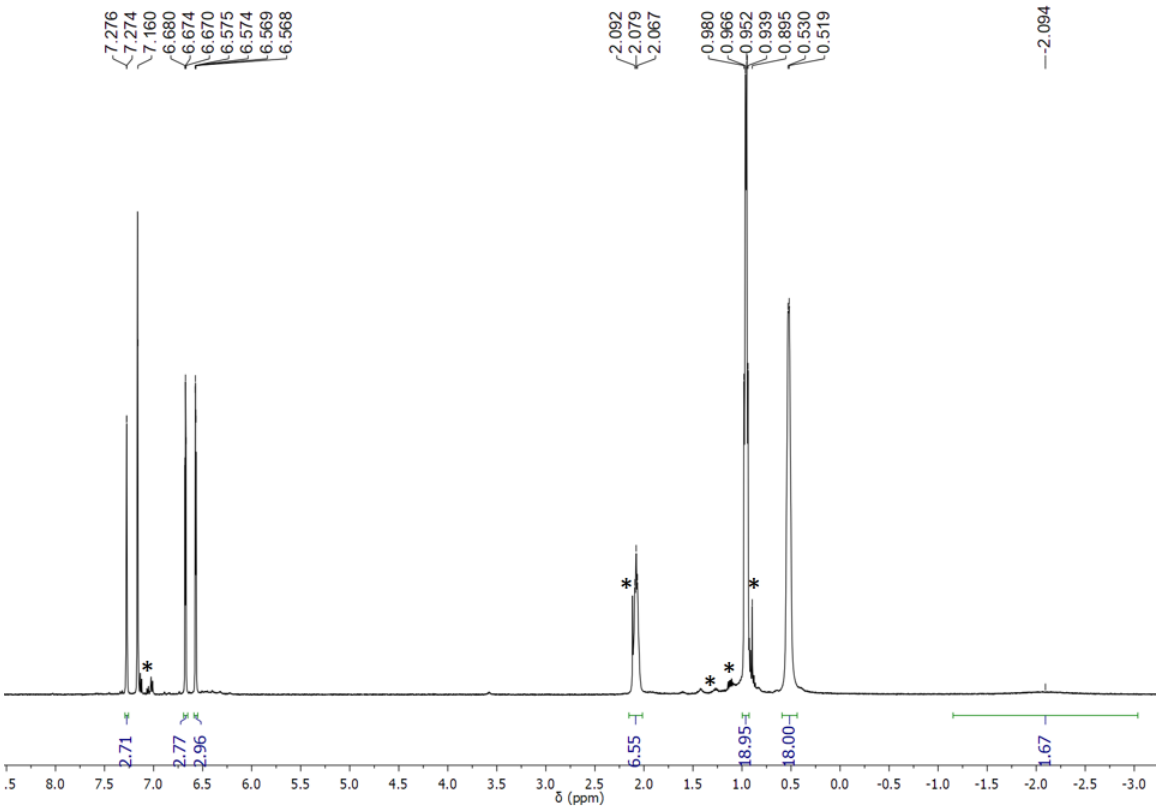

Figure S19. ^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of **8-H$_2$** (toluene and pentane resonances are denoted by *).

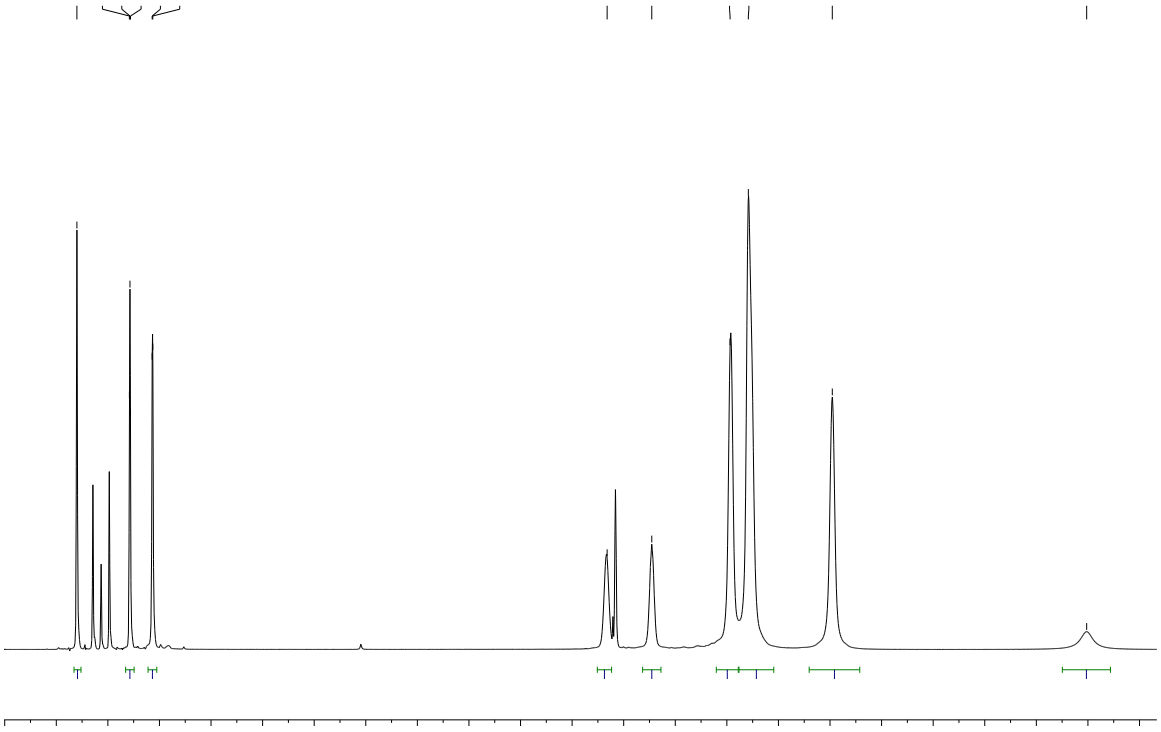

Figure S20. ^{1}H NMR (500 MHz, C_6D_6, 193 K) spectrum of **8-H$_2$**.

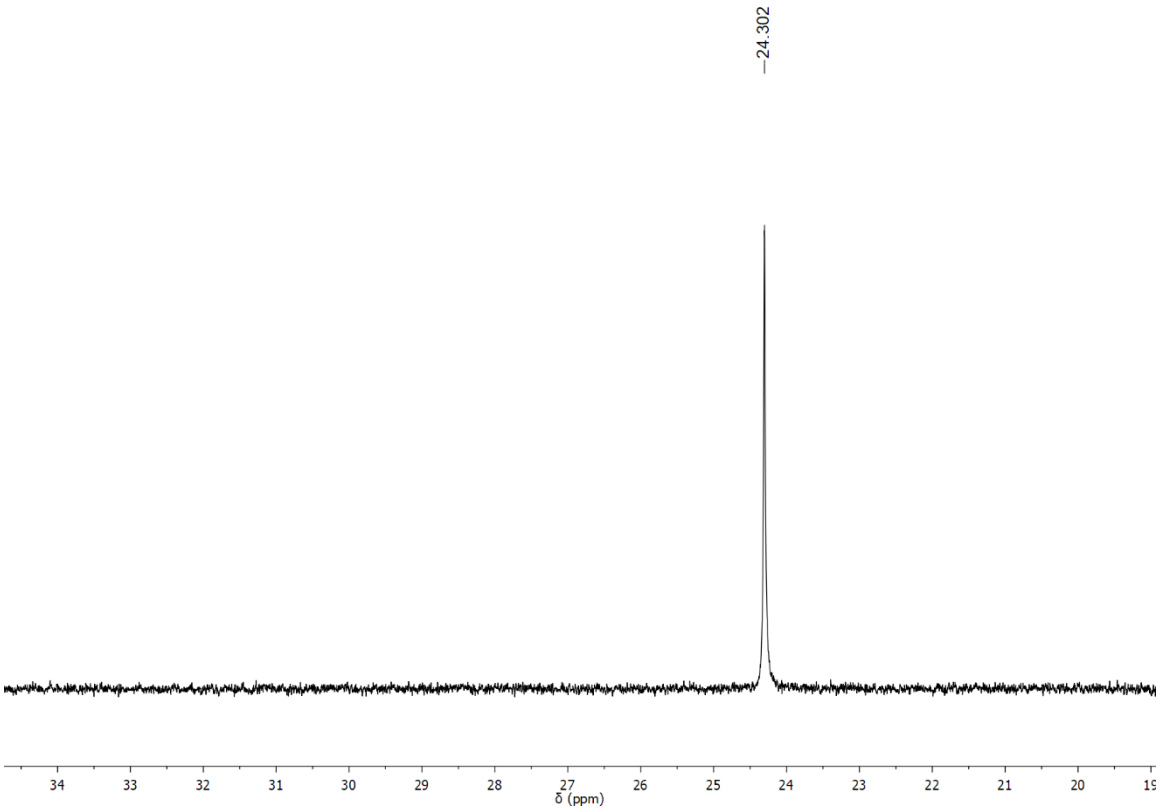

Figure S21. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6) spectrum of **8-H$_2$**.

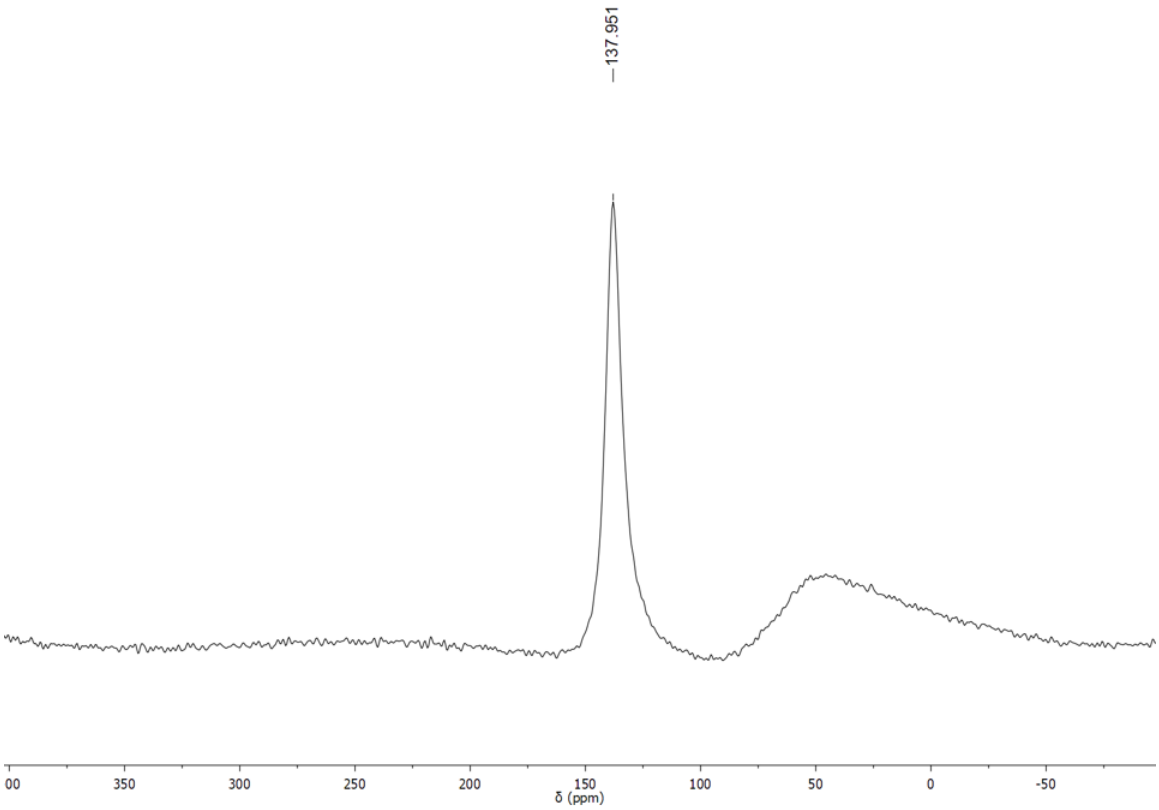

Figure S22. $^{27}Al\{^{1}H\}$ NMR (104 MHz, C_6D_6) spectrum of **8-H$_2$**.

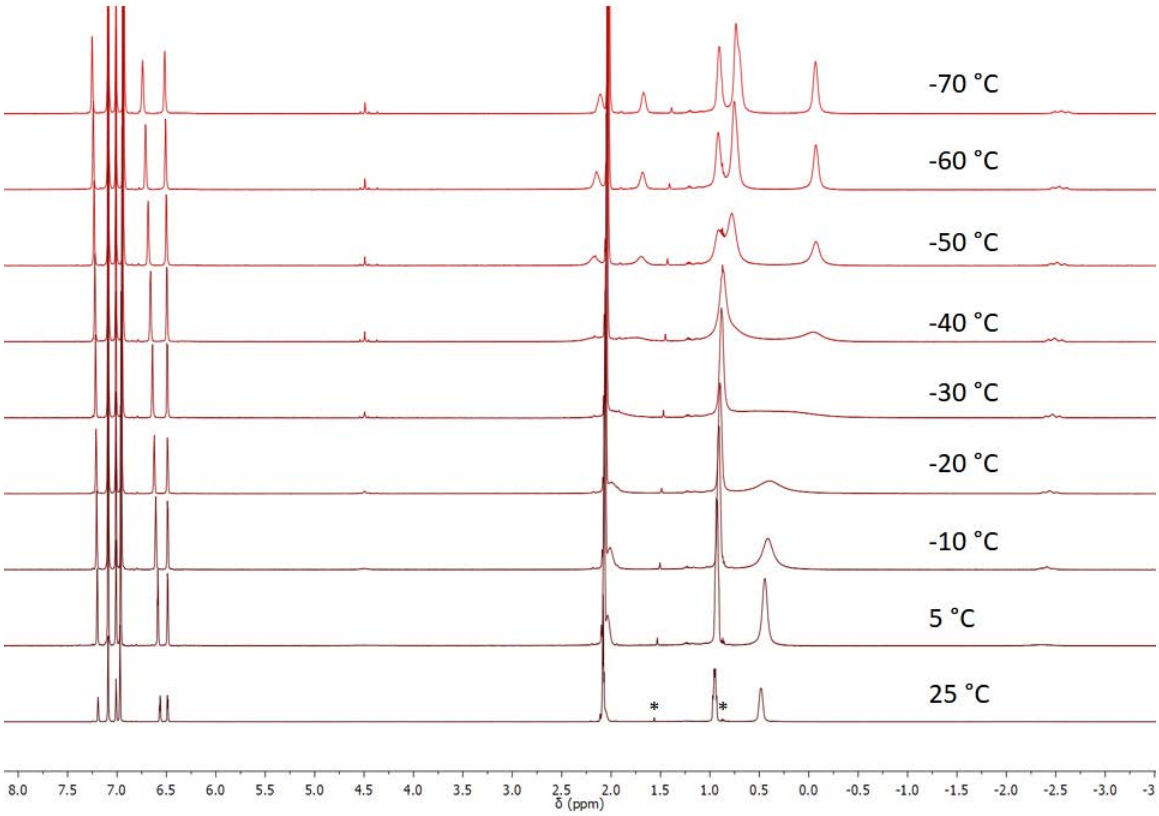

Figure S23. ^{1}H NMR (500 MHz, toluene-d_8) spectrum of **8-HD** at various temperatures from 298 K to 203 K (acetone and pentane peaks are denoted by *).

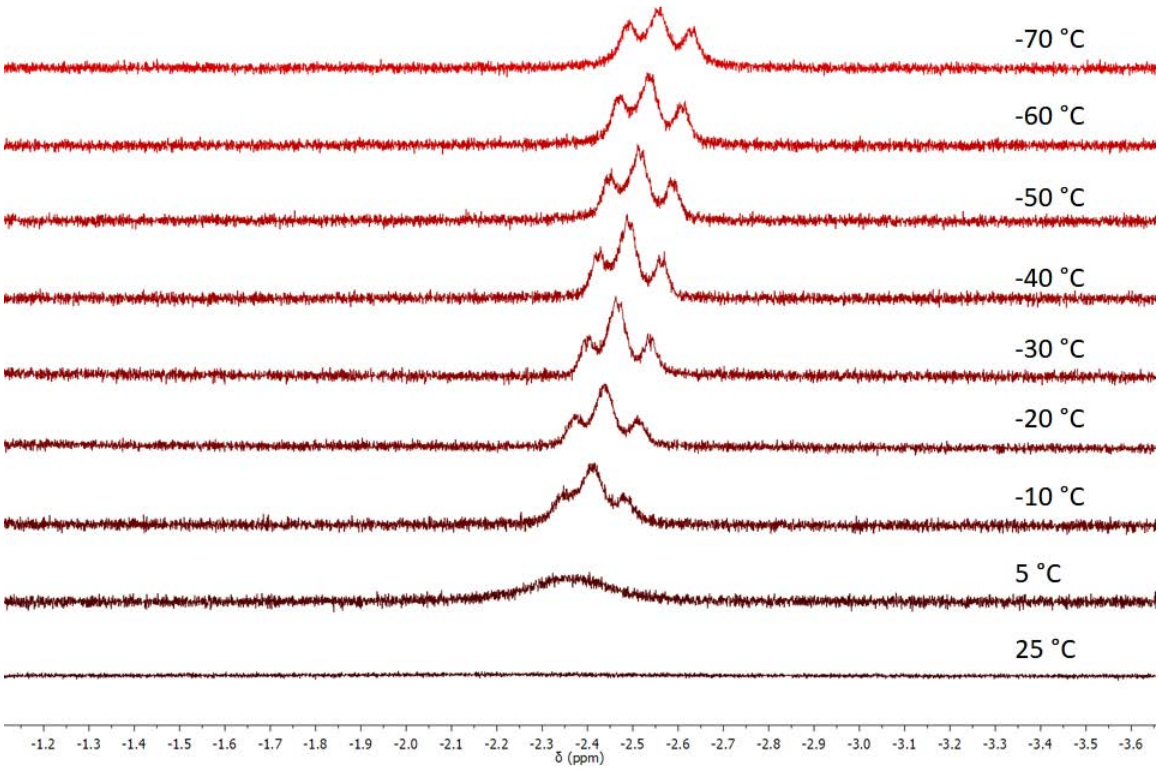

Figure S24. Hydride region of ^{1}H NMR (500 MHz, toluene-d_8) spectrum of **8-HD** at various temperatures from 298 K to 203 K. $^{2}J_{H\text{-}D}$ = 35 Hz.

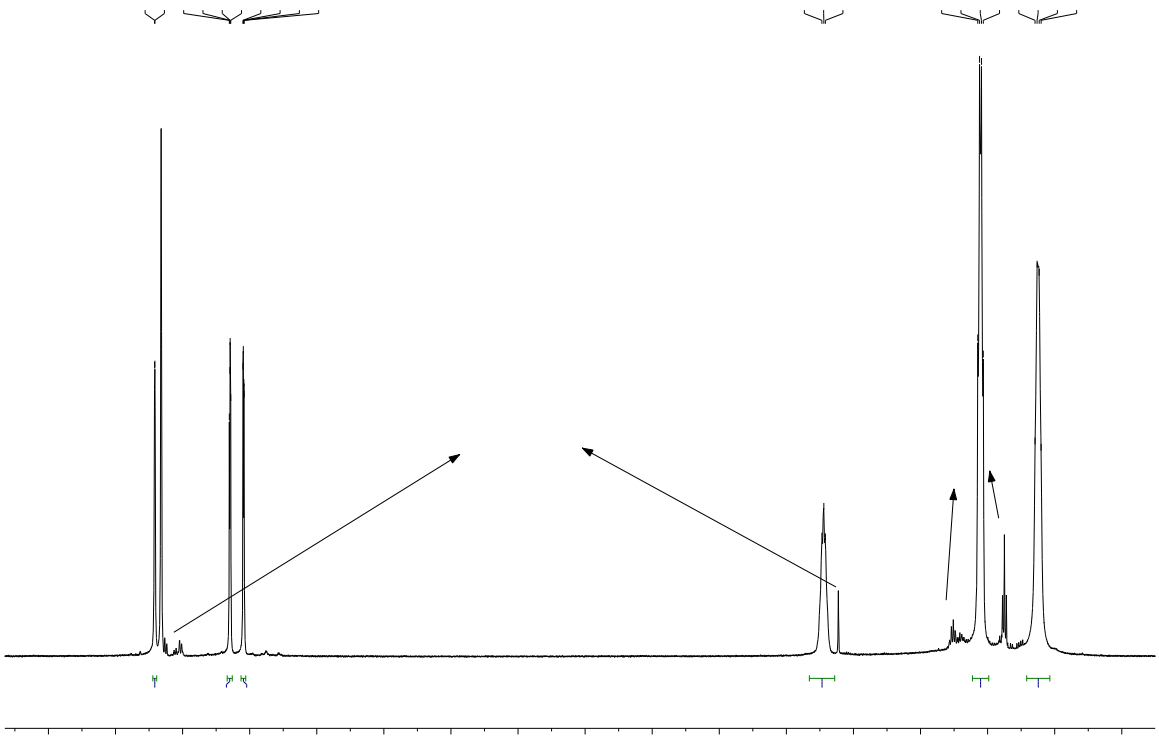

Figure S25. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **8-CO** obtained by from a solution of **8** under 1 atm CO.

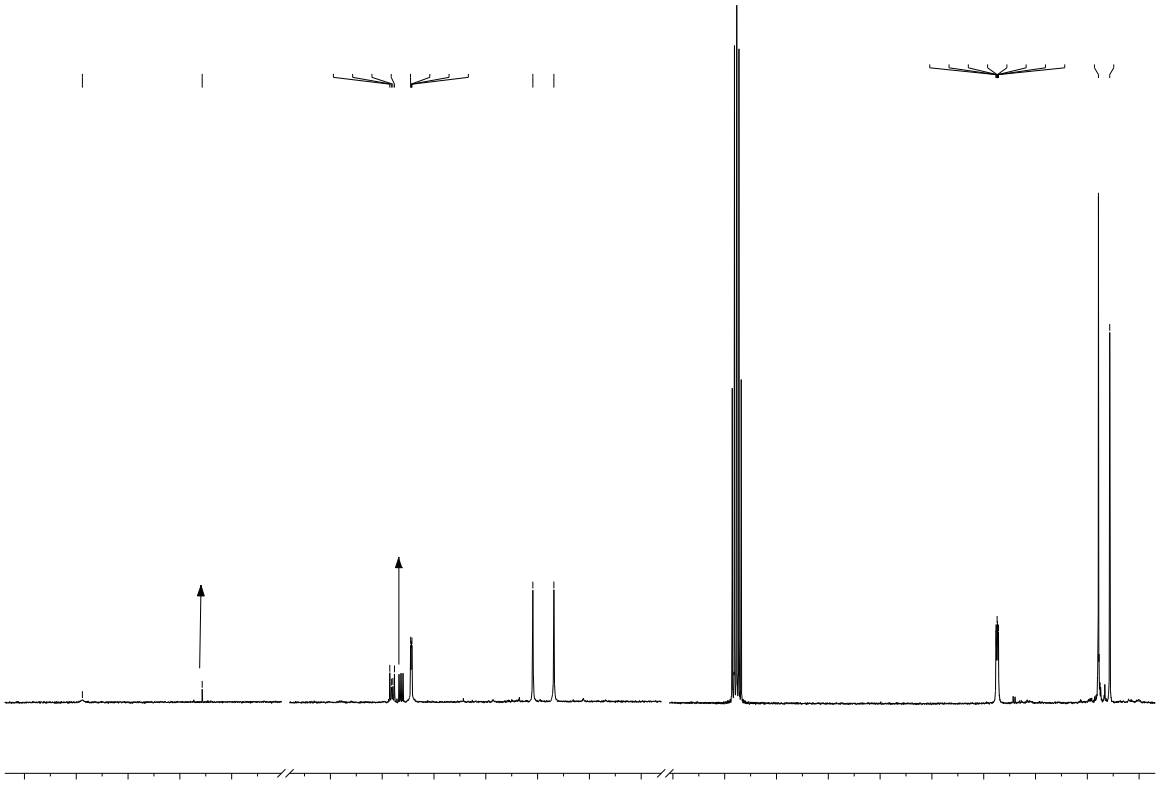

Figure S26. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) spectrum of **8-CO** obtained by from a solution of **8** under 1 atm CO.

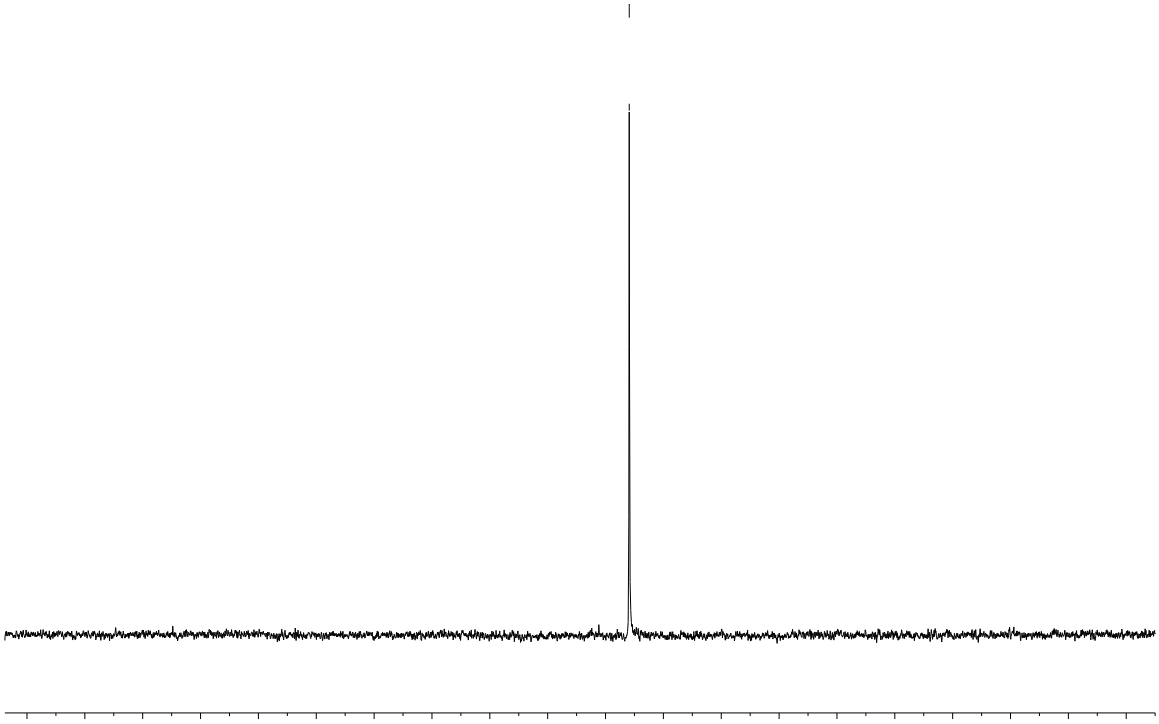

Figure S27. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6) spectrum of **8-CO** obtained by from a solution of **8** under 1 atm CO.

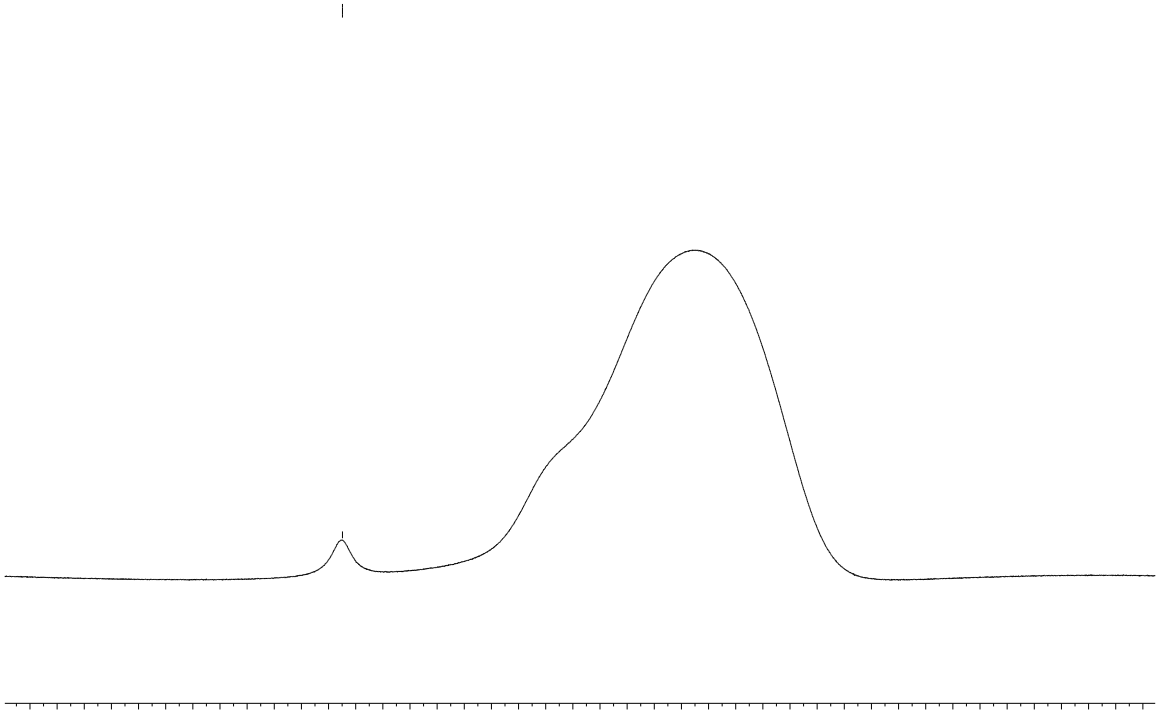

Figure S28. $^{27}Al\{^{1}H\}$ NMR (104 MHz, C_6D_6) spectrum of **8-CO** obtained by from a solution of **8** under 1 atm CO.

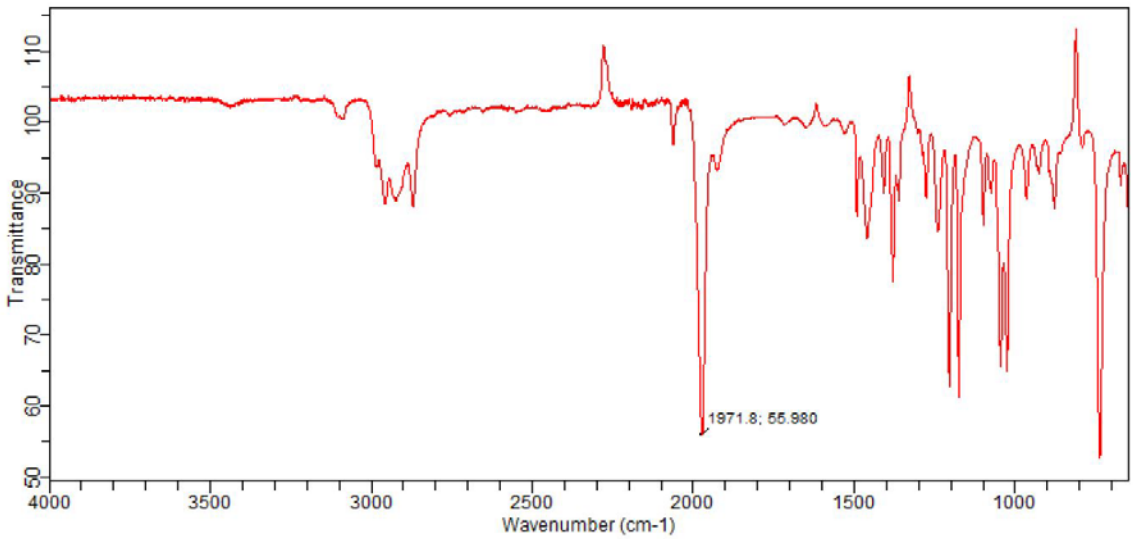

Figure S29. ATR-IR spectrum of **8-CO** in C_6D_6 solution.

V. X-Ray Structural Determination Details

A dark green block of **3 (CCDC 1915840)** was mounted onto a nylon loop and placed in a cold stream of nitrogen. Low temperature (110 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, Kα = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[3] An absorption correction was applied using SADABS.[4] The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2. The structure was solved in the monoclinic P21/n space group using XS[5] (incorporated in SHELXLE). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in idealized positions and refined using riding model. The structure was refined (weighted least squares refinement on F^2) and the final least-squares refinement converged. No additional symmetry was found using ADDSYM incorporated in PLATON program.[6]

VI. Electrochemical Analysis

Electrochemical studies were carried out using a CH Instruments Model 700 D Series. Electrochemical Analyzer and Workstation in conjunction with a three electrode cell. The working electrode was a CHI 104 glassy carbon disk with a 3.0 mm diameter and the auxiliary electrode was composed of platinum wire. The third electrode, the reference electrode, was a $Ag/AgNO_3$ electrode. This was prepared as a bulk solution composed of 0.01 M $AgNO_3$ and 0.2 M [*n*-Bu_4N][PF_6] in fluorobenzene. This was separated from solution by a fine porosity frit. CVs were conducted in fluorobenzene with 0.2 M [*n*-Bu_4N][PF_6] as supporting electrolyte and were reported with a scan rate of 100 mV/s. The concentration of the analyte solutions were approximately 1.00×10^{-3} M. CVs were referenced to $Fe(\eta\text{-}Cp)_2^+$/ $Fe(\eta\text{-}Cp)_2$ redox couple.

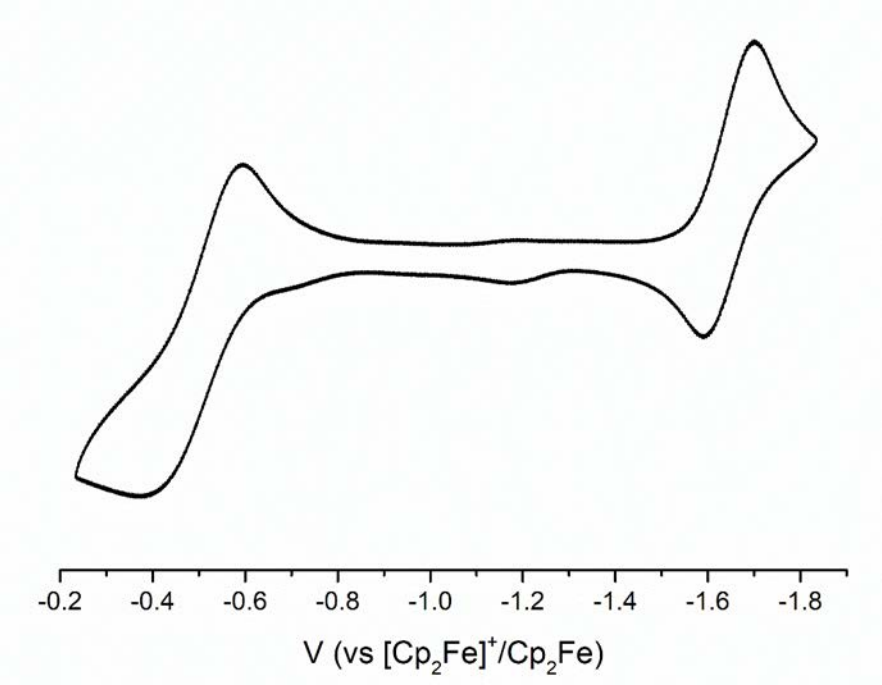

Figure S30. Cyclic voltammograms of $NiAlP_3$ scanned in 0.2 M [$^nBu_4N$][PF_6] in PhF at 100 mV/s.

VI. ESI References.

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[3] APEX2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Madison, WI, June **2006**

[4] G.M. Sheldrick, "SADABS (version 2008/1): Program for Absorption Correction for Data from Area Detector Frames", University of Göttingen, **2008**.

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